ARTIFICIAL OR NATURAL ORIGIN OF HEMATITE-BASED RED PIGMENTS IN ARCHAEOLOGICAL CONTEXTS: THE CASE OF RIPARO DALMERI (TRENTO, ITALY)*

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This study concerns those crystallographic and microstructural features that can provide indications on the actual origin of red pigments based on hematite (Fe_2O_3). The main features of natural and artificial hematite are recalled and used to discuss the results obtained from the characterization of red-ochre samples coming from the Palaeolithic site of Riparo Dalmeri, a rock-shelter located in northeastern Italy, dated to 13 000 cal. BP, and notorious for the presence, among the other finds, of red-painted calcareous stones. Painting and the treatment of leather and hides obtained from the intensive hunting activity were the main uses of the hematite-based red-ochres at Riparo Dalmeri. It turns out that hematite was mostly obtained from the thermal treatment of goethite, which, unlike hematite, was and still is widely available in the neighbourhood of the site.

KEYWORDS: PALAEOLITHIC, PREHISTORIC PAINTINGS, OCHRE, HEMATITE, GOETHITE, RED PIGMENTS, LEATHER, HIDE, RAMAN SPECTROSCOPY, TRANSMISSION ELECTRON MICROSCOPY, X-RAY DIFFRACTION

INTRODUCTION

Natural pigments have been used since prehistoric times for decorating objects, weapons, cave walls and vaults, human bodies, hides and so on. Early paintings also played an important role in the development of communication, information storage and cognition (Dowson 1998; Chalmin *et al*. 2004); body decoration, in view of the relevant symbolism, can even be taken as an indicator of the evolutionary level achieved by human cultures (Zilhão *et al*. 2010). Materials of natural origin were the first to be employed for these purposes. In their selection, two main criteria were most probably followed: one is the symbolic and ritual value of the colour, while the other is more related to the availability of the material itself. Black, white, yellow and red are regarded as the first base colours that were widely used for a variety of decorative purposes, as indicated by a number of archaeological surveys and finds (Marean *et al*. 2008). Actually, these same colours retained their importance over time (Colombo 2003), notwithstanding the widening of the available palette and related materials, eventually resulting in the recent development of synthetic colours, based on organic solvents and colorants (Ball 2003). Generally, white was obtained from calcite-based minerals and kaolin clay (Colombo 2003), black from wood com-

bustion products and manganese oxides (Chalmin *et al*. 2006), and yellow and red from soils containing iron oxides, possibly hydrated (Cornell and Schwertmann 1996). In this respect, goethite (FeOOH) and hematite (Fe_2O_3) were common choices, in view of their widespread diffusion on the Earth. Interestingly, the two minerals are correlated as concerns the colour issue. In fact, hematite can be obtained by heating goethite up to moderate temperatures (300–350°C), depending on the level of impurities present in the material (Ruan *et al*. 2002) and microstructural features, such as grain size and shape (Cornell and Schwertmann 1996). Correspondingly, a colour change from yellow (goethite) to red (hematite), associated with the loss of water molecules, is observed. Therefore, accidental heating of yellow-painted goethite surfaces has provoked the change of their colour into red. This is what happened to some wall paintings in Pompei, after the hot dust ejected by the Vesuvius volcano in AD 79 reached them (Ciaghi *et al*. 2009). Of course, this colour change has also been deliberately exploited in case only 'yellow earths' were available and red was needed. In some prehistoric contexts, this technology must have interacted with another important one, in this case related to stone flaking (Domanski and Webb 1992, 1994; Domanski *et al*. 2009). The practice of heating pieces of flint and other siliceous stones, in order to improve their flakeability and, thus, raising the efficiency of producing stone tools by chipping, has been demonstrated by several studies, some of which were based on experimental archaeology methods, starting from the pioneering work by Crabtree and Butler (1964). The reader is referred to the cited literature for more comprehensive information on the use of heat in lithic technologies (Odell 2000, 2001), whose application has been sometime inferred just from the colour change of the goethite-containing flints, which were originally yellow and then turned into red. Interestingly, in the case of uncontrolled overheating, the microstructural changes introduced by heating flint materials may even result in serious damage to the lithic samples. In this case, the term 'burnt flint' can be used in place of 'heated flint'. The process may lead to a complete crumbling of the initial piece of stone. Similarly, the disruption of a solid, compact and hard goethite lump can be more easily obtained when it is exposed to heat for a sufficiently long time to turn the goethite lump into a friable, much more easily pulverizable, piece of hematite. In view of its usage as a pigment, this is not to be taken as a deleterious practice, but rather as a deliberate procedure to obtain a high-quality fine-grained red pigment. This aspect will be considered here with reference to a possible approach to the production of red pigments at Riparo Dalmeri, the site from which the analysed samples come (Dalmeri *et al*. 2002).

Considering these technological implications, it is not surprising that a number of research efforts have been devoted to the search for a reliable method to tell natural hematite from artificial hematite—that is, hematite obtained by the heating of goethite (Pomies *et al*. 1998, 1999a–c; Frost *et al*. 2003; de Faria and Lopes 2007). The guidelines described in these references and the results obtained from a systematic (micro)structural investigation on the goethite-to-hematite thermally induced phase transition (Gialanella *et al*. 2010), have been applied to some lumps of red ochre found in the Epigravettian site of Riparo Dalmeri (Trentino, Italy: Dalmeri *et al*. 2002, 2004, 2005a,b). This rock-shelter has been frequented over two separate Palaeolithic time intervals: the older, from 13 410 to 13 210 cal. BP, and a more recent one, dated to 13 130/ 12 900 cal. BP (Montoya 2008). In this later period, traces of two very close subsequent occupations have been detected: this may be one of the reasons for the difficulty faced in setting a precise time scale for the relevant archaeological layers (Fiore and Tagliacozzo 2008). Numerous painted calcareous stones have been found in the oldest layer of the site, together with a large number of ochre lumps, with different shades of red colour used to decorate the stones, mainly with geometric and naturalistic subjects. These specimens of red ochres have been proved to be

Label	Stratigraphic unit	Chronology (years cal. BP)
43Mb	SU 14-26b	13 130–12 900
42Mb	SU 14-26b	13 130–12 900
42Mf	SU 14-26b	13 130–12 900
44Lf	SU 14-26b	13 130–12 900
51Mh	SU 14-26b	13 130–12 900
43Gc	SU 15a-65	13 410–13 210

compatible with the stone paintings (Belli *et al*. 2007), whose production was interrupted later on, so that painted stones were no longer found in the subsequent, more recent, layers. Therefore, a relatively sudden evolution in the activities based at Riparo Dalmeri can be inferred. In fact, one of the more significant archaeological aspects of this later occupation is the massive presence of bone and lithic findings, many of which are weapons for hunting and tools for dressing leather and tanning hides (Cristiani 2008; Gurioli 2008). Thus, hunting and related activities were the main features of the more recent occupations of Riparo Dalmeri. In this context, red ochres, still present in the relevant layers, were employed mostly in the processing of leather and hides, both as abrasives and colorants (Cristiani 2008), in agreement with the findings of other investigations that have also highlighted the effectiveness of hematite as an antibacterial agent (Wadley *et al*. 2004; Wadley 2005). On the other hand, as already noted, the activity of decorating stones, with all the well-known ritual and symbolic implications (Wreschner *et al*. 1980), was fully abandoned.

The massive exploitation of hematite may explain the remarkable number of red lumps found in the anthropic layers of the shelter. The lack of documented deposits of hematite in the neighbourhood, which, on the other hand, is comparatively rich with goethite nodules (Bertola 2008), raises the question of the actual origin of the hematite of Riparo Dalmeri, one of the main issues that is addressed by the present paper.

MATERIALS AND METHODS

Several red lumps from Riparo Dalmeri, that, according to the results of former investigations (Belli *et al*. 2007, 2008a,b, 2011) and those presented in the following, can be classified as ochres, have been considered in this study. The term 'ochre' is appropriate, as not only red pigments, mainly hematite, are present in the analysed specimens, but even the so-called *white pigments* or *mineral extenders*, such as calcite, dolomite, quartz and so on, have been found, being either naturally present in the specimens or deliberately added to tune the resulting colour and relevant hue of the mixture.

Samples have been selected, among a very large collection, after a thorough inspection by the naked eye, aimed at choosing those materials that might provide results that are profitably useable as reference data, in case more extensive analyses are carried out on many more samples from the site. As specified in Table 1, samples mostly came from the more recently inhabited layer of the shelter (SU 14-26b, SU = stratigraphic unit) and just one from the oldest anthropic layer (SU

15a-65), adjacent to the previous one. In the cited references on the site, detailed indications on the retrieval locations of the samples can be found.

In addition to these archaeological samples, artificial hematite specimens have also been prepared by annealing goethite materials of different provenance and grade. A goethite nodule coming from the same area of Riparo Dalmeri (sample GN) was kept in a furnace in air for 1 h at 1000°C. Such high-temperature treatment is capable of inducing not only the goethite-to-hematite transformation, according to the following reaction:

$$2\ FeOOH \rightarrow Fe_2O_3 + H_2O,$$
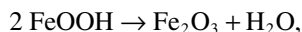
but even a complete recrystallization and partial sintering of the hematite grains, with a simultaneous reduction of structural and chemical defects. A similar treatment was applied to another two goethite materials: a natural one (GS), containing 10 wt% of quartz and coming from a site in Sardinia (Italy), and a commercial powder (SA), in which a larger overall amount of secondary phases were present, in addition to goethite, whose concentration in this case was equal to 61 wt% only, as described in detail in Gialanella *et al*. (2010).

X-ray diffraction (XRD) analyses were conducted on an IPD 3000 diffractometer with a Debye–Scherrer diffraction geometry and using Cu–K$_\alpha$ radiation, monochromatized on the incoming beam. Powder specimens were obtained from the corresponding lump, once the outer weathered layer was eliminated, through a moderate grinding operation, so as to get a homogeneous grain size of the powder, without introducing any additional microstructural change that might affect the analyses. All experimental data were analysed using the Material Analysis Using Diffraction (MAUD) program (Lutterotti *et al*. 1997)—some original software used to work out quantitative crystallographic and microstructural information using a Rietveld code, exploiting the entire diffraction pattern for quantitative phase analysis (QPA) and line profile analysis (Lonardelli *et al*. 2005). Scanning electron microscopy (SEM) observations were carried out with a field emission gun instrument equipped with an energy-dispersive X-ray spectrometer (EDXS), with a Si(Li) detector sensitive to elements from boron to uranium.

Selected powder specimens were prepared for transmission electron microscopy (TEM). A small amount of each sample was suspended in ethanol, using an ultrasonic bath to get rid of any agglomeration. A drop of this suspension was deposited on to a carbon-coated copper grid. Images of the microstructure and the relevant selected area electron diffraction (SAED) patterns were acquired using an analytical electron microscope, operated at 120 kV. The SAED patterns were indexed using the software package described in Labar (2005).

Raman spectroscopy measurements, upon 632.8 nm excitation, were carried out by means of a micro-Raman spectrometer with a single, 1800 lines per millimetre, grating. The polarization of the collected spectra was not defined. The measurements were performed with low excitation power (about 0.02 mW, on a 5 μm^2 region) in order to avoid a significant laser heating of the samples. The resolution, as obtained from the measure of Rayleigh line, was 2 cm^{-1}. The parameters of the spectra were extracted by fitting the Raman peaks to Lorentzian curves, after subtracting the background contribution due to luminescence.

RESULTS AND COMMENTS

Figure 1 shows, as an example, the XRD pattern of sample 43Gc. In this pattern, and similarly in the XRD patterns of the other samples too, hematite is present; that is, the pigment affording the typical reddish colour observed in all analysed specimens. Other phases are also present to different extents, as indicated in the data listed in Table 2. Where hematite is present as the
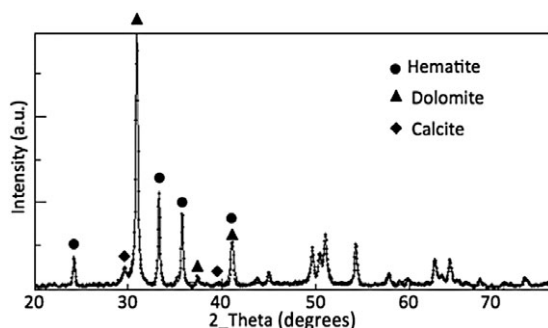
Figure 1 *The XRD pattern of one of the archaeological ochre samples from Riparo Dalmeri (sample 43Gc).*

Table 2 *The phase composition and microstructural features of the archaeological samples of ochres from Riparo Dalmeri, as evaluated from the LPA of the XRD patterns in Figure 1*

Sample	Fe_2O_3 Hematite (wt%)	FeOOH Goethite (wt%)	$CaCO_3$ Calcite (wt%)	$CaMg(CO_3)_2$ Dolomite (wt%)	SiO_2 Quartz (wt%)
43Mb	48	–	19	33	–
42Mb	37	–	22	36	5
42Mf	57	–	–	42	1
44Lf	10	–	54	22	10
51Mh	14	3	5	78	–
43Gc	26	–	3	71	–

majority phase, this is in agreement with the solid dark red colour of the relevant samples. On the other hand, even the 44Lf and the 51Mh materials, containing only 10 wt% and 14 wt% of hematite, still display quite an intense colour, confirming the effectiveness of this iron oxide as a pigment material.

Figure 2 shows the Raman spectra of the archaeological samples and of the heat-treated natural goethite, considered as reference samples. In all spectra, the visible peaks are attributed to the vibrational modes of hematite. No contribution from the white pigments (calcite, dolomite and quartz) detected by XRD are present. There are two different reasons for this. First, the Raman activity of the hematite phase is high due to the excitation at 633 nm, which is on the tail of the band-to-band electronic transition of Fe_2O_3, producing an intense pre-resonant condition for Raman scattering. Second, the region analysed by micro-Raman has a size of the order of few microns and this allows the selection of a region rich in hematite with stronger Raman scattering. However, this second effect is so important in the case of archaeological samples, indicating that the hematite crystallites are quite homogeneously distributed.

Figure 2 displays also spectra of hematite artificially obtained from heated goethite (materials GN, SA and GS). As specified earlier, the goethite nodule (GN) used for this experiment comes from the area surrounding Riparo Dalmeri (la Marcesina plateau). It is worth noticing that similar geological samples, partially heated and ground, were also found in the anthropic layer of the shelter from which the more recent ochre lumps had come (Bertola 2008). The data presented herewith not only confirm the proposed existence of natural goethite at Riparo Dalmeri, but even
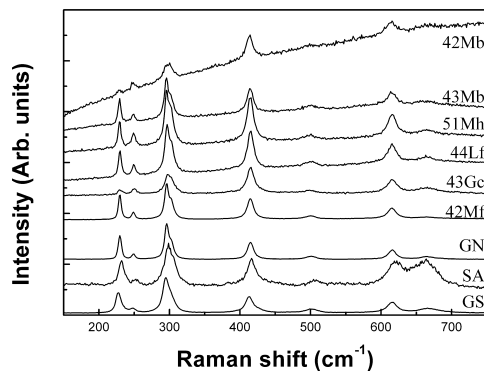
Figure 2 *A set of Raman spectra upon 633 nm excitation of the archaeological samples of ochres from Riparo Dalmeri. For comparative purposes, a set of spectra from hematite samples obtained from the thermally induced transformation (1 h at 1000°C) of goethite samples (GN, SA and GS—see the text for details) is also displayed. No luminescence correction has been applied to any of the spectra in the figure.*

show the affinities among the GN and the archaeological specimens: 42Mf, 43 Mb, 44Lf and 51Mh (Fig. 2). The spectra of the 42Mb and 43Gc archaeological materials look rather different. In particular, the intensities of the two Raman lines, which fall in the low-wavenumber range, are much lower than the same lines in the other archaeological materials. This can be generally regarded as due to impurities, which are present to a higher extent in these two materials.

For a better quantification of the microstructure-related aspects, a more accurate analysis of the spectra is required. A background due to luminescence is present in all spectra, with differing intensities relative to the Raman contribution. Furthermore, the intensities of the various spectra cannot be easily compared and the scale is arbitrary. However, we can compare the relative intensities of differing peaks in the same spectrum. All observed peaks are present in all spectra, but with different intensities, indicating that the crystalline structure of Fe_2O_3 is defective. In particular, the intensity of the highest frequency peak (660 cm^{-1}) is very sample dependent. The ratio of the intensity of this peak to the intensity of the 610 cm^{-1} peak has been used as a measure of the impurity content (Bersani *et al*. 1999; Gialanella *et al*. 2010). Another parameter used to measure the defect structures is the width of the Raman lines. Different microstructural defects affect these parameters in different ways (Gialanella *et al*. 2010). In order to reveal the similarities between the samples, Figure 3 shows the full width at half maximum (FWHM) of the 226 cm^{-1} Raman line, plotted as a function of the ratio of the integrated intensity of the hematite lines at 660 cm^{-1} and 610 cm^{-1}. All archaeological specimens, except for the already mentioned 42Mb and 43Gc, are concentrated in the same region of the plot (see Fig. 3), so that a similar, comparatively low, level of chemical impurities can be inferred. The heated GN sample also contains hematite. This datum confirms the proposed chemical composition, based on iron oxides, of nodules retrievable in the area near Riparo Dalmeri (Bertola 2008). The position in the plot in Figure 3 of the peak parameters provided by the RMS data for the geological GN material indicates its affinity, with regard to impurity and microstructural concentration, to the red lumps found in the rock-shelter. The other two 'artificial' hematite specimens display higher values of FWHM, owing to a higher concentration of chemical impurities, as explained elsewhere (Gialanella *et al*. 2010).

On the basis of the Raman and XRD results, including those already published on the microstructural features of the ochre materials (Belli *et al*. 2008a), samples were selected for
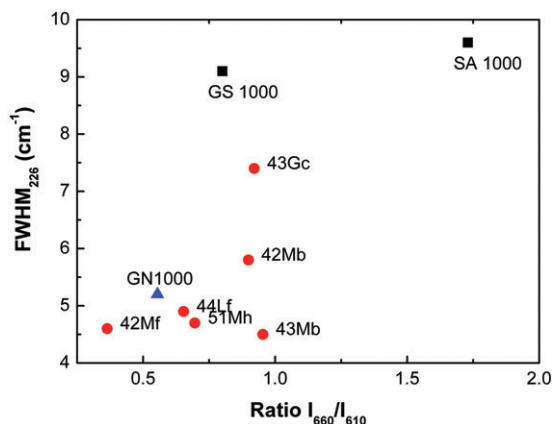
Figure 3 *The FWHM of the 226 cm⁻¹ peak as a function of the intensity ratio of the 660 and 610 cm⁻¹ peaks of the archaeological samples and of those obtained by annealing the goethite materials, GN, GS and SA, at 1000°C for 1 h.*

microscopy observations. The SEM micrographs of the samples with higher concentrations of hematite are shown in Figures 4 and 5. The first set of images (Fig. 4) shows similar grain morphology, with blocky-plate submicrometric particles. In the case of the 42Mb powder, rod-like grains are also visible on the surface of the lump. A secondary formation cannot be ruled out in this case, possibly resulting from the exposure to burial conditions. The morphology of sample 43Gc looks quite different, in general more irregular (Fig. 5). Several components can be inferred to be present in this sample (43Gc) from the different microstructure of the grains, although individual crystallites are difficult to spot, and the sample seems to have undergone some kind of densification process. As a general comment on these microscopy observations, it can be stated that, as expected, these natural ochres display heterogeneous microstructural features. However, some aspects, related to the grain morphology and shape, can be assumed as effective parameters for the identification of their formation processes.

TEM analyses were conducted on these same materials, as shown by the micrographs in Figure 6. In all cases, the hematite grains were shown to be mixed up with particles of other phases, the *white pigments* of the ochre, according to the findings of the XRD analyses (see Fig. 1 and Table 2). With regard to hematite grains, identified through electron diffraction and X-ray spectroscopy, the following features can be noticed from the micrographs. For sample 42Mb, the presence of elongated rod-like crystallites (Fig. 6 (c)), already documented in the SEM micrographs (Fig. 4 (b)), is confirmed. Even in other regions of the 42Mb TEM specimen, with a higher concentration of hematite, clusters of such crystallites have been observed, in this case also displaying their typical elongated shape, confirming the already proposed idea of a secondary crystallization of this component in the material of sample 42Mb.

A different situation has been observed in the other specimens in Figure 6 (a-43Mb, b-43Gc and d-42Mf). First of all, again in agreement with SEM data, hematite grains appear generally equiaxed or prismatic. Two microstructural features deserve some attention. Remnant porosity can be seen inside hematite grains of the samples 43Mb, 43Gc and 42Mf (see the white arrows in Fig. 6), although contributions from other microstructural defects, such as vacancy coalescence, cannot be ruled out. Moreover, in all these three samples evident signs of densification and
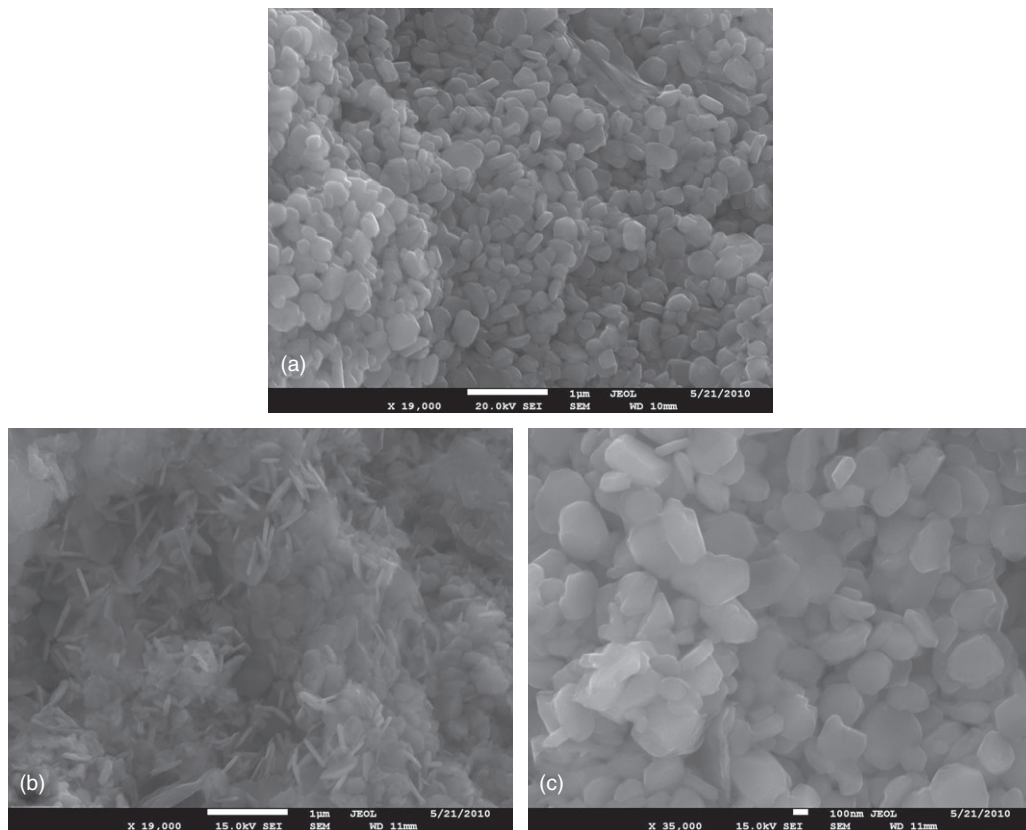
Figure 4   *SEM micrographs showing the micromorphology of the samples: (a) 42Mf; (b) 42Mb; (c) 43Mb.*

sintering are present. The 43Gc material features clusters of particles that not even the ultrasonic bath used for TEM sample preparation was capable of dissolving. Although not to the same extent as the 43Gc sample, some interconnections are also visible in the 42Mf sample (see the black-arrowed 'necks' in Fig. 6 (d)).

GENERAL DISCUSSION

The first documented proof of the early occupation of Riparo Dalmeri dates back to 13 400 cal. BP. In the first place, the shelter was mainly used for ritual purposes, as attested by the red-painted stones, the main archaeological features of the period. Subsequently, the site became a sort of base camp for intensive hunting activities, proved by the conspicuous amount of bone remains—mainly, but not only, alpine ibex—that can be found in different locations in the shelter. According to former literature investigations, the following points can be made:

• In the shelter, red ochres were used not only for the paintings of calcite–dolomite stones belonging to the early occupation. In fact, red traces were also found on lithic and bone tools, such as scrapers, blades and so on, mostly belonging to the late occupation (Dalmeri *et al*. 2001).

• This has been taken as an evidence of the use of hematite for treating leather and tanning hides,
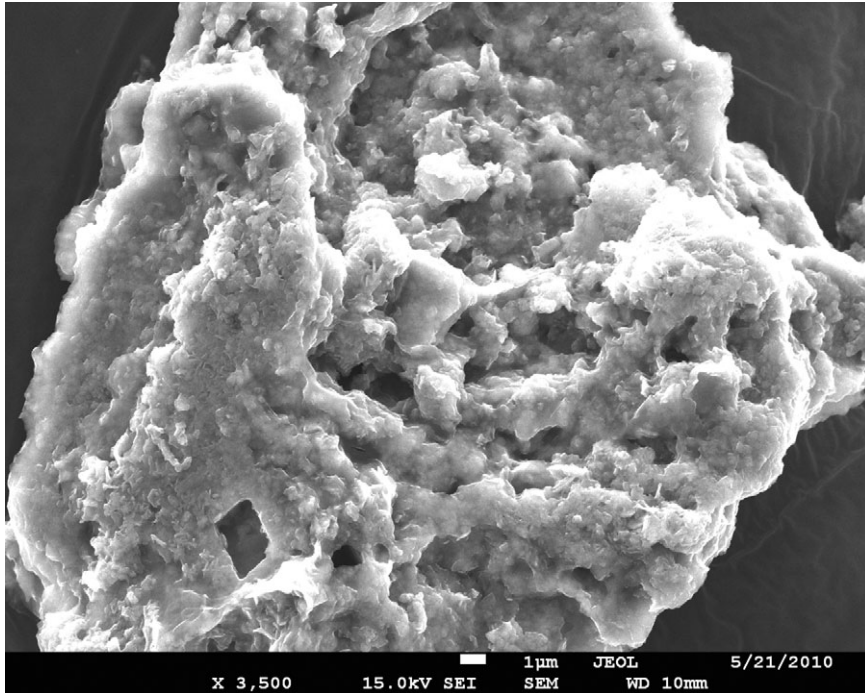
Figure 5   *An SEM micrograph of sample 43Gc.*

in agreement with similar archaeological findings and historical evidence referring to other prehistoric contexts (Cristiani 2008).

• In the area surrounding Riparo Dalmeri, no significant sources of hematite have been found or recorded, whereas goethite is ubiquitous and, most importantly, easily available (Bertola 2008).

All these aspects and the above experimental results can be gathered together and provide the following picture for a proposed *cycle of hematite* at Riparo Dalmeri. After the initial period, that of the red-painted stones, most of this mineral was primarily used for the processing of the hides of the hunted prey. For this purpose, comparatively large quantities were required, and this would be in agreement with the significant presence of reddish lumps on the ground of the late-inhabited layer of the shelter. This presumably high hematite consumption, in association with the reported lack of local natural hematite, suggests that this pigment tended to be obtained by heating goethite. The main archaeometric elements that would back this hypothesis are the affinity of the archaeological hematite to that obtained from the annealing experiment of a goethite nodule (sample GN; see the Raman data in Figs 2 and 3).

Some of the archaeological hematite specimens, 42Mf, 43Gc and 43Mb, that have been analysed using microscopy, display a crystallite shape, a compaction state and a porosity resembling those seen both in archaeological (Pomies *et al*. 1999a) and commercial (Gialanella *et al*. 2010) hematite samples, obtained from thermal transformation of goethite. In particular, the microstructural features in the archaeological samples are comparable to those of goethite treated at temperatures close to 800°C, and for times sufficiently long to guarantee the accomplishment of the involved structural and micromorphological transformations. In this regard, readers are referred to Gialanella *et al*. (2010) for a detailed description of the evolution occurring in goethite
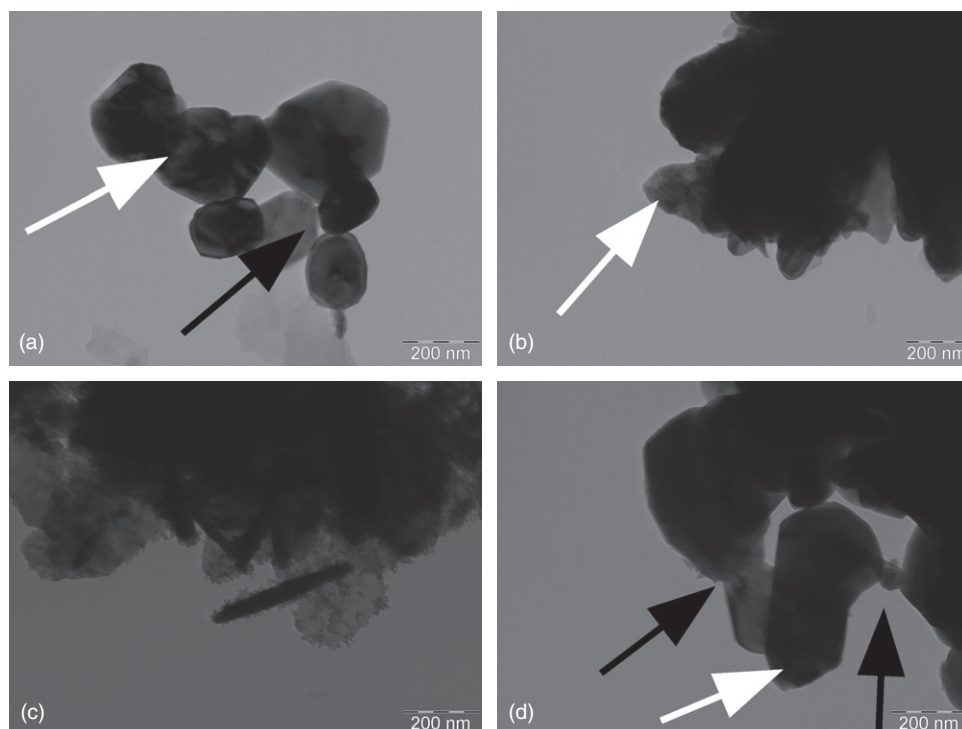
Figure 6   *TEM micrographs showing the microstructures of the (a) 43Mb, (b) 43Gc, (c) 42Mb and (d) 42Mf ochre samples. White arrows indicate pores and black arrows indicate necks.*

samples upon heating from room temperature up to 1000°C. Among the analysed samples, the 42Mb sample displays a peculiar grain morphology, that seems not to be obtained from an annealing process and, as such, can be assumed to be the result of a natural precipitation process. All these aspects are reliably confirmed by the multi-analytical approach adopted in the present study, which involves and integrates electron microscopy, a key technique that, as stated, had already been proposed for similar investigations (Pomies *et al*. 1999a).

Further indirect evidence of a sort of *goethite–hematite industry* at Riparo Dalmeri comes from a number of lithic and bone tools found at the site and clearly used for grinding, mixing and applying red ochres. In Figure 7, a bone fragment found in one of the analysed specimens (43Gc) is shown.

The proved skills in managing the transformation and processing of goethite and hematite materials were a common factor to all periods during which Riparo Dalmeri was inhabited. Originally, the red colour, possibly obtained by chance, was a fundamental raw material for the decoration of the calcareous stones. Subsequently, hematite-based materials were mainly used in the processing of hide and leather, exploiting the property of this pigment to prevent or reverse the decay process of the organic tissues (Wadley *et al*. 2004; Wadley 2005). Interestingly, in these studies, with reference to a former investigation based on an experimental archaeology approach (Audouin and Plisson 1982), the higher effectiveness of hematite in comparison to goethite with regard to the quality of the products was demonstrated. It can be argued that a similar conclusion
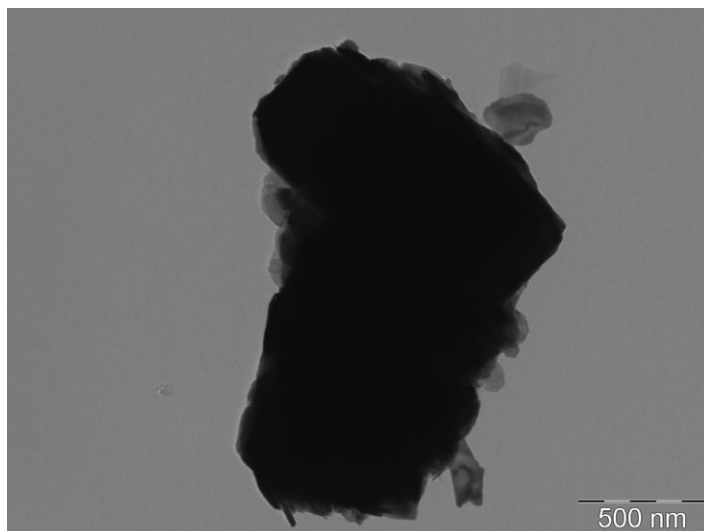
Figure 7   *A TEM micrograph of a bone fragment found in the 43Gc ochre. This fragment may come from the bone tool used to grind or apply hematite and mix it with the components of the white pigments.*

was achieved by the hunters operating at Riparo Dalmeri too, thus reinforcing the idea of a deliberate use of hematite obtained from goethite.

CONCLUSIONS AND FURTHER DEVELOPMENTS

The cross-checking of archaeometric results and archaeological proxies, regarding the site of Riparo Dalmeri, has been adopted to assess the technological contours of the use of red pigments, based on hematite and goethite, for different activities featuring different occupation periods of the rock-shelter, that started with a prevalent use of hematite for decoration purposes. The results indicate that for dressing and processing of leather and hides obtained from the hunting activities carried out in the area of Riparo Dalmeri, until late occupation, hematite was the mineral that was primarily used.

The results reported here provide a high level of support for the attainment of hematite by annealing goethite, a raw material that is widely available and easily accessible on the site. The artificial origin of the hematite is confirmed even by the compositional and microstructural features of the analysed materials, obtained by an experimental approach, set according to the guidelines proposed in Pomies *et al*. (1999a), that has been actually extended using further experimental techniques. It is important to remark that reliable conclusions could be drawn directly from such a multi-analytical approach, thus confirming the limits, which have already been shown in the past (see, e.g., de Faria and Lopes 2007), of studying this sort of question while just relying on one single experimental tool.

These results can be profitably used for extending the research to a wider range of ochre samples from Riparo Dalmeri.

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