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SIRACUSA | 26-29 FEBBRAIO 2008

a cura di:
Anna Gueli

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Raman characterization of prehistoric pigments

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Riassunto

Polveri di goethite con diversi gradi di purezza sono state riscaldate a temperature comprese tra 200 e 1000 °C. La spettroscopia Raman mostra che, dopo la transizione di fase in ematite, a circa 300 °C, c'è una evoluzione continua degli spettri con la temperatura. Questa è legata alla riduzione di ioni OH e all'aumento delle dimensioni dei cristalliti. Si è studiata la possibilità di separare questi contributi negli spettri Raman.

Parole chiave: Raman, ematite, goethite, ocre preistoriche.

Abstract

Goethite powders with different degrees of purity were annealed at temperatures ranging from 200 to 1000°C. Raman spectroscopy showed that, after the phase transition into hematite occurring at about 300°C, there is a continuous evolution of the spectra in temperature, related to the decrease of residual OH ions and to the increase of crystallite size. The possibility to discriminate their contributions in the Raman spectra was studied.

Keywords: Raman, hematite, goethite, prehistoric ochre.

Introduction

Ochre materials containing natural pigments have been used since pre-historic ages (Colombo, 2000). In the present study we refer to the anthropic layers of Riparo Dalmeri (RD, ca. 13.000 cal. BP, Trentino, Italy), where countless archaeological ochre fragments were found (Dalmeri et al., 2004; Belli et al., 2007).

A recurring archaeological issue about red ochres is whether hematite (Fe_2O_3), which constitutes the basis of the pigments, is natural or it is obtained from heated goethite (FeOOH). In fact, the transition from goethite to hematite occurs at a temperature low enough (about 300 °C) to be achieved by a wood fire, a technology certainly within reach of the hunter-gatherers who lived at RD.

In a previous work (Belli et al., 2008), a detailed XRD analysis of the goethite changes upon heat treatment at increasing temperatures up to 1000 °C showed a continuous growth of the hematite crystallites from 10 to 100 nm. Moreover, the hematite crystallites retained the same prismatic crystallographic habitus as goethite up to 800°C, whereas evident recrystallisation was observed in the hematite obtained by annealing goethite at 1000°C. As the habitus of natural hematite is reported to be platy or rhombohedral (Cornell and Schwertmann, 2003) the proposed approach may provide clue to answer the above question. However, this methodology is not always easily applicable when analyzing a thin painted layer on rough substrate like stone, wood, etc. In the present work, we characterize the goethite-hematite transition by Raman spectroscopy and study the possibility to discriminate between artificial and natural origin of the pigments even when dealing with paintings requiring in situ measurements.

Experimental

The transformation of goethite into hematite was studied by heating in air a commercial goethite powder (Sigma-Aldrich, Goethite - CAS No. 20344-49-4: ca. 35% Fe), at temperatures ranging from 200 to 1000°C. The powder was not pure, but it contained also significant concentrations of MgO , SiO_2 , CaO and Al_2O_3 (actually these impurities constitute about half of the total

powder weight, as for pure goethite Fe content would be 63 wt. %). The Sigma Aldrich (SA) samples were compared with natural hematite (NH) and natural goethite samples (NG) obtained from nearby locations. For SA and NG samples, the final number in the label denotes the temperature of heat treatment. The duration of treatment, carried on placing the powders in an alumina crucible and by means of an electric oven, was 1 hour or 12 hours (NG650 and NG1000 only). A commercial hematite (BDH Chemicals) with a 95% purity and fragments of red ochre found at RD (43Gc, 43Mb) were also characterized.

Raman spectra upon 632.8 nm excitation were collected by means of a Jobin Yvon HR800 LabRam microRaman single grating spectrometer. The polarization of the collected spectra was not defined (note that the scattering process with powders leads to the loss of the initial polarization). The measurements were performed with a low power of excitation (about 0.02 mW, on a 5 μm^2 region - 70 \times magnification) in order to avoid a significant heating of the samples induced by the laser absorption. The resolution, as measured from the Rayleigh line, was 2 cm^{-1} .

Results and discussion

Goethite and hematite have high optical absorption coefficients in the visible region. Therefore, the exposure to the laser light, needed for performing Raman spectroscopy, may considerably increase the temperature of the investigated region. This effect can be even more important in microRaman spectroscopy, where higher power density can easily lead to remarkable temperature increase if the material is a poor conductor of heat.

Permanent and temporary effects on the materials, and henceforth on the Raman spectra are expected, due to the temperature rise. In the present study, it may easily happen that, while analyzing goethite samples they irreversibly transform into hematite (at about 300 °C). Moreover, as we will discuss in the following, other less evident microstructural changes may occur during the transformation.

Eventually, even in the absence of permanent changes, the shape and the position of the characteristic Raman peaks are affected by temperature changes through the anharmonicity of the normal modes of vibration. These

effects are often neglected while using Raman spectroscopy as analytical tool for materials characterisation. However, as in this study it will be of interest considering the finer features of the spectra and we have to take into account the thermal effects also. In order to evaluate them, we measured Raman spectra of a natural hematite sample (NH), upon increasing power of the exciting laser, controlled by inserting neutral filters. Figure 1 shows the raw spectra, just normalized in order to have the same height for the peak at 293 cm^{-1} .

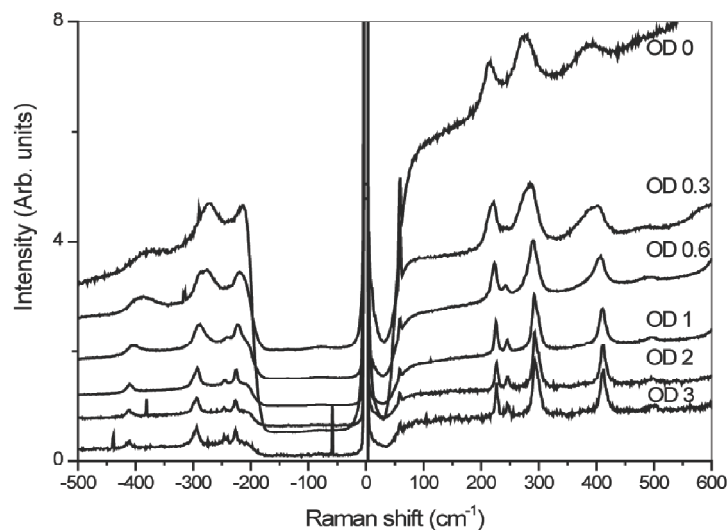


Figure 1 - Raman spectra of the natural hematite sample (NH) upon different excitation powers ($\lambda=632.8\text{ nm}$). OD is the optical density of the filter that has been used in order to adjust the incident power between 0.002 (OD=3) and 2 mW (OD=0) . The spectra were normalized in order to have the same height for the 293 cm^{-1} peak.

The intensity in the region between -200 and 100 cm^{-1} is strongly reduced because of the presence of the notch filter. It turns out that the use of different powers leads to: 1) a different ratio between Raman peaks and luminescence background, mostly due to electronic transition of Fe^{3+} ions, whose occurrence increases with the power; 2) an important broadening and red-shift of the Raman peaks, due to anharmonic effects. From a comparison between spectra acquired at low power at the beginning and at the end of the test, we observed no permanent change in the sample resulting from the temperature increase during the high power measurements. In order to quantify the actual test temperature, after subtracting the luminescence background, we compared the intensity of the Stokes (IS) and AntiStokes (IAS) Raman peaks.

Based on the thermal occupation of the states, their ratio is given by the well known expression:

$$\frac{I_S}{I_{AS}} = \frac{(\nu_0 - \nu_k)^4}{(\nu_0 + \nu_k)^4} \exp(hc\nu_k / k_B T)$$

where ν_0 is the laser wavenumber, ν_k is the Raman shift, h is the Planck constant, c is the speed of light, k_B is the Boltzmann constant and T is the absolute temperature. This allows to determine the temperature of the scattering region, even if with some incertitude (± 25 °C).

Figure 2 shows the spectra after the subtraction of the background: the broadening and the shift of the Raman peaks are still more evident.

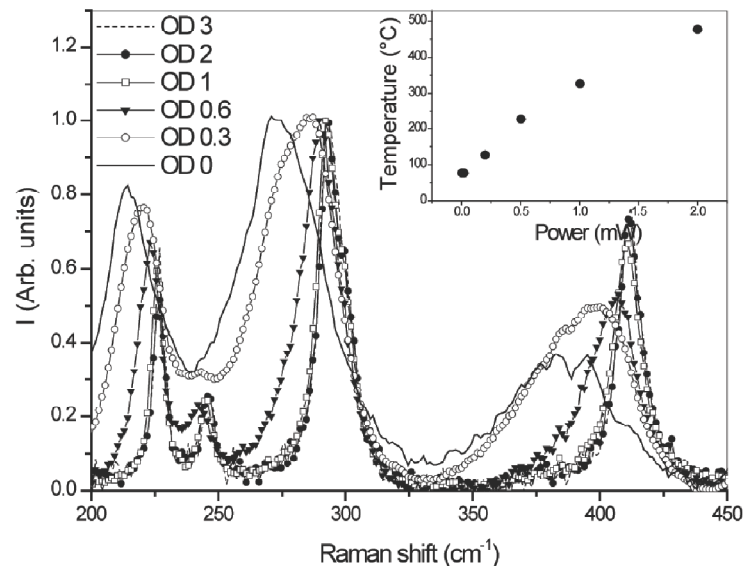


Figure 2 - Dependency of the shape of the Raman lines on the incident power. The corresponding temperatures, obtained from the ratio of Stokes to AntiStokes intensity, at different are indicated in the inset.

The estimated temperatures of the specimen during the measurements are reported in the inset. For a power below 0.02 mW, with a 50 \times objective, (filters with optical density 2 or 3) the increase of temperature is low and the effects on the Raman spectra are negligible.

On the basis of these results, for the following measurements we kept the filter with optical density 2 in order to reduce as much as possible the thermal effects, but still retaining reasonably low integration times (below 1000 s).

Figure 3 shows the raw Raman spectra of the samples of commercial goethite, heat treated at temperature ranging from 200 to 1000 °C.

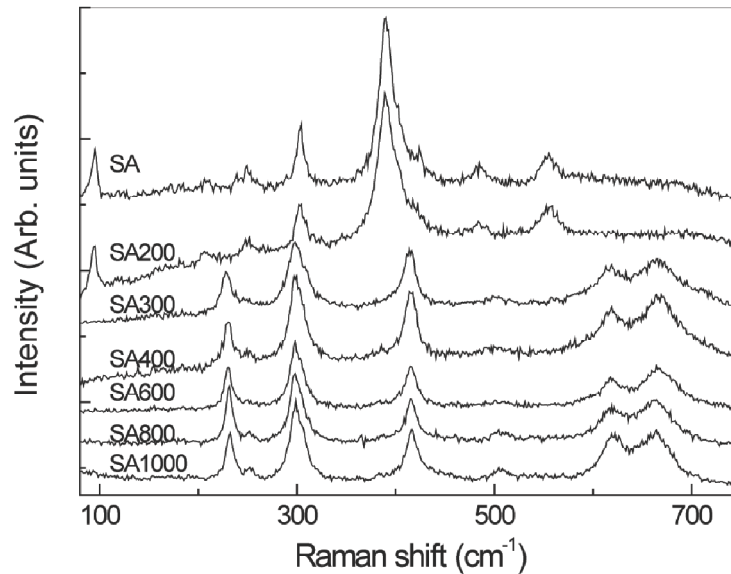


Figure 3 - Raman spectra upon 632.8 nm excitation of commercial goethite powders (SA) heat treated in air at temperatures ranging from 200 to 1000 °C for 1 hour.

The temperature induced phase transition from goethite to hematite is well apparent from the presence of well distinct peaks, corresponding to the typical features of goethite (SA0 and SA200) and hematite (in all the other spectra). Between 200 and 300 °C most of goethite transforms even if some shoulders due to hematite peaks are already present in SA200 while residual goethite still affects the SA300 spectrum. The evolution does not stop after the phase transition, but other changes, related to the microstructural modifications already evidenced by X-ray diffraction (Belli et al., 2008) are observed. In particular we would like to stress two aspects that are quite evident: 1) the behaviour of the peak at about 660 cm^{-1} and 2) the progressive narrowing of the Raman peaks with annealing temperature.

The peak at 660 cm^{-1} is not present in the Raman spectrum of pure hematite single crystals. In fact, it is due to the presence of defects, like cationic or anionic substitutional impurities, which break the central symmetry of the primitive Fe_2O_3 cell and render Raman active also an infrared active mode, otherwise absent. In natural hematite, the impurities are usually cationic often aluminium and titanium ions replace iron ions (Cornell and Schwertmann, 2003). In hematite obtained from the heat treatment of goethite also residual OH groups may be present, as far as the treatment temperatures are sufficiently low (de Faria and Lopes, 2007). Observing Figure 3, we note that in SA samples, the peak decreases as the temperature increases but it remains

always dominant with respect to the nearby 610 cm^{-1} peak. This is so even after the $1000\text{ }^{\circ}\text{C}$ treatment, when OH groups should be completely removed, as an indication that the above peak is mainly due to other not volatile impurities.

Although the width of the Raman peaks of perfect crystals is only due to the thermal broadening, in real crystals the presence of impurities, vacancies or other imperfections of the lattice leads to an additional broadening of the Raman lines. Moreover, as observed with XRD (Belli et al., 2008) the size of the crystallites is nanometric and the confinement of the vibrational modes provokes a relaxation of the selection rules for the exchanged wavevector, thus providing an additional contribution to the peaks width. Therefore, in SA samples the narrowing of the peaks as the temperature increases can be attributed both to the decrease of OH content and to the growing of the hematite crystallites. However, the former should be a minor term as the main part of the defects remains in the crystals also after the $1000\text{ }^{\circ}\text{C}$ treatment, as previously noted.

On the basis of these observations we can reconsider the initial question about the possibility of telling natural hematite from heated goethite by means of Raman spectroscopy. A recent work by De Faria and Lopes (2007) gives an utterly negative answer. In heated goethite samples, they ascribe both the broadened features of the Raman spectra and the 660 cm^{-1} peak to the residual OH groups. As they increase the heat treatment temperature, the linewidths decrease and the 660 cm^{-1} peak disappears, in agreement with a high purity of the analyzed material. Comparing the spectra with those obtained from natural, impurity-rich, hematite, they conclude that neither the broadening nor the presence of the 660 cm^{-1} peak are distinctive features of low temperature treatments, like those that can be made using a wood fire: in this regard, it would be impossible to discriminate reliably the artificial origin of archaeological pigments.

On the other hand, our XRD analyses on the same samples considered in this study (Belli et al., 2008) evidence characteristic microstructural features of heated goethite, namely the shape and sizes of the hematite crystallites. Moreover, we have just shown that Raman spectra are influenced in a different way by substitutional defects and by nanometric size of crystallites.

Even if the effects are correlated, they can be in principle separated. This can be better appreciated if we compare the previous spectra with the ones

of another heat treated goethite sample, found in a nearby location and with the archaeological ochre fragments. The spectra are shown in Figure 4, together with the spectrum of the BDH, which was adopted as a standard for pure hematite.

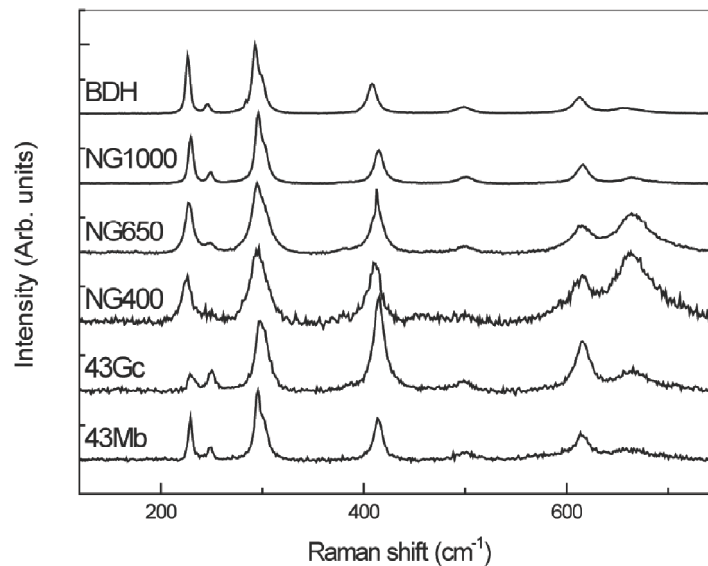


Figure 4 - Raman spectra upon 632.8 nm excitation of pure commercial hematite powders (BDH), powders of natural goethite (NG) heat treated at temperatures between 400 and 1000 °C and archaeological ochre fragments found in Riparo Dalmeri.

The features of the spectra were evaluated by fitting 8 peaks (those at about the following wave numbers: 226, 245, 293, 300, 413, 498, 610, 660 cm^{-1}) with lorentzian functions. Apart from the NG400 and NG650 samples, where OH groups are still present, the other samples show a very weak 660 cm^{-1} peak, indicating a higher purity of hematite as compared to the SA material. For a better comparison among all samples, Figure 5 shows the evolution of the ratio of the area of the 660 cm^{-1} and 610 cm^{-1} peaks, while in the inset the width the 226 cm^{-1} peaks is reported (but all the linewidths have similar behaviours).

Note that the 1000°C heat treatment of the purer goethite, the NG sample, produces hematite that presents very similar features to the BDH standard (indicated by the dashed lines in the figure).

In the evolution with temperature of the Raman spectra, it is difficult to separate the effects due to defects concentration and confinement, as both decrease when the temperature increases. This can be more easily accompli-

shed in the presented archeological samples. 43Gc and 43Mb present the same, low, value of ratio of the of the area of the 660 cm^{-1} and 610 cm^{-1} peaks, indicated by dotted lines in Figure 5, but 43Gc presents significantly broader linewidths. This discrepancy has to be attributed to the effect of confinement. As a matter of fact, the results of XRD analysis (Belli et al., 2008) show that the average size of crystallites in 43Gc is about 30-40 nm, while the crystallites size is about 100 nm in 43Mb.

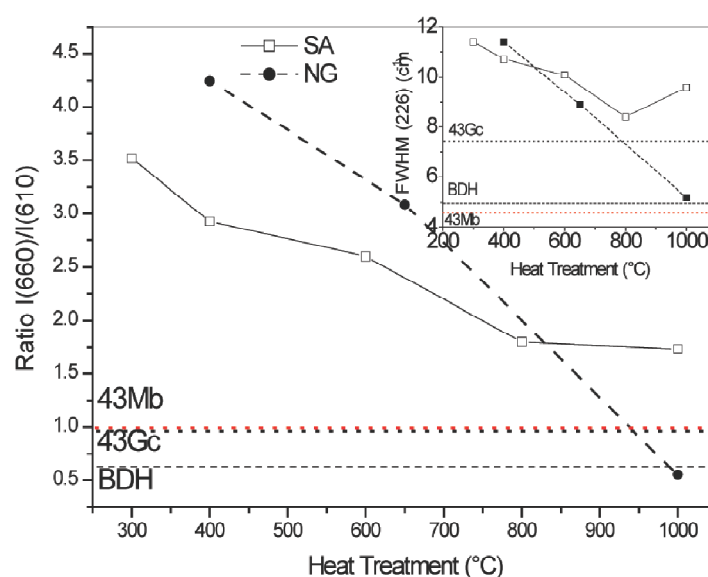


Figure 5 - Intensity ratio of the 660 cm^{-1} and 610 cm^{-1} peaks as a function of the heat treatment temperature. The dotted or dashed lines indicate the values of the hematite standard (BDH) and of the archeological ochre fragments (43Gc and 43Mb).

Conclusions and further developments

Goethite to hematite transition has been studied by Raman spectroscopy. Widths and intensity of the Raman lines are sensitive both to the size of the hematite crystallites and to substitutional impurities. However, from the comparison with XRD results, it has been shown that the two effects can be separated in the Raman spectra features. Getting an estimate of the crystallite size from Raman measurements only, requires in any case a more complete database of hematite samples with different degrees of purity and microstructural parameters. Such information should allow to substitute XRD with a non invasive technique in the evaluation of crystallite size, and hence-

forth firing temperatures, of hematite based pigments. Further investigations are required to understand if the Raman spectra are sensitive to the various habits of the natural and synthetic hematite.

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