CHAPTER FORTY ONE

FINDING CHEMICAL AND PHYSICAL EVIDENCE OF HEAT TREATMENT OF OCHRE BY USING NON-DESTRUCTIVE METHODS: A PRELIMINARY STUDY

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Abstract

Many Middle Stone Age (MSA) sites such as Rose Cottage and Sibudu Caves yield large quantities of ochre pieces (9000 pieces from Sibudu alone). Physico-chemical characterisation is required to add value to the prior studies of ochre use traces. This project involves a non-destructive and multi-analytical approach (including Raman spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and X-ray fluorescence) to characterise ochre pieces. The main goal of these analyses is to establish a method to identify heated ochre pieces. This is investigated here predominantly through experimental heat treatment of geological pieces to create a database of heated ochre. Heat treatment is an indicator of advanced technological

practices; this research will ultimately help to gain deeper understanding of behaviour and cognition of people living in the MSA.

Keywords: Ochre, Heat treatment, Middle Stone Age, Multi-analytical Approach

Introduction

Ochre can be described as natural earth rocks that contain iron oxides or oxyhydroxides and which leave a red or yellow streak. It is derived from various geological processes and it includes a range of rocks such as shales, sandstones, mudstones and specularite. The iron oxides and oxyhydroxides present in ochre are most commonly haematite, goethite, and magnetite and the secondary compounds are minerals associated with rocks such as quartz, clay, and mica.

Ochre was used worldwide from before the origin of our species. The use of ochre dates to the early MSA at sites such as Twin Rivers in Zambia and GnJh-15 in Kenya (McBrearty 2001), and the Middle Palaeolithic where Neanderthals used ochre more than 200 000 years ago at Maastricht-Belvédère in the Netherlands (Roebroeks et al. 2012). It can be used for its colouring properties, for example in rock paintings and body daubing. Ochre also has medicinal qualities: it has an astringent effect, arrests haemorrhages and has antiseptic and deodorizing properties. The preparation of hides can include the use of ochre: it colours and protects leather from bacterial action (Rifkin 2011). It can also be smeared on the body as protection against cold, sun and insects (Rifkin et al. 2015); and it can be eaten, presumably as an iron supplement (Hodgskiss 2012).

The colour of ochre is influenced by numerous factors such as mineralogy, crystal structure, particle and grain size. Colour changes are observed by heating ochre. For example, the heat treatment of ochre containing goethite, which is generally yellow, results in the formation of haematite with a red hue because of a dehydration process. The literature records several temperature ranges that change the composition and/or structure of goethite/haematite. These depend on the characteristics of the material such as average grain size, shape, crystallinity, porosity and excess water content and also whether natural or synthetic (Goss 1987) materials are used. Nevertheless, it is not straightforward to distinguish heated goethite from geological haematite (de Faria et al. 2007, Pomiès et al. 1999).

In South Africa, ochre was found in many MSA sites for example Blombos Cave (Henshilwood et al. 2012), Pinnacle Point (Watts 2010) and Diepkloof (Dayet et al. 2013). Rose Cottage and Sibudu Caves yielded

a large number of ochre pieces, many of which bear signs of use. Some attributes of the ochre have already been studied macroscopically (Hodgskiss 2013). The use traces were formed by grinding, rubbing and/or scoring actions. Sibudu is located in KwaZulu-Natal approximately 40 km north of Durban and about 15 km inland of the Indian Ocean. The long MSA cultural sequence at Sibudu has been dated, using single grain optically stimulated luminescence, between 77 000 and 38 000 years ago (Jacobs et al. 2008). Rose Cottage is a large cave located near the Caledon River, near Ladybrand in the eastern Free State. It appears to have been occupied, intermittently, between about 96 000 and 30 000 years ago (Pienaar et al. 2008).

In MSA contexts, ochre with a strong red hue predominates (Wadley 2009) which raises the question of whether people living in the MSA had sufficient understanding of ochre to know that by heating it to a particular temperature, it underwent certain transformations like colour change from yellow to bright-red. This research aims to use multi-analytical and non-destructive approaches; including Raman spectroscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR); to characterise experimental and archaeological ochre pieces. Physico-chemical investigations of the archaeological ochre will help us to gain a deeper understanding of changing patterns in ochre collection, preparation, and use through time. Part of the preparation phase may have involved heat treatment to alter the colour and mechanical properties of the ochre. Observations made during heating experiments will inform our understanding of the physical and physico-chemical changes that occur when ochre is heated. Investigating this is important because heat treatment has significant cognitive implications for the people who were practicing it.

Materials and Methods

The archaeological samples are ochre pieces from the MSA layers at Sibudu and Rose Cottage Caves. The levels we are dealing with are dated from 96 000 to 35 000 years ago. The samples include utilised and unutilised pieces (pieces with or without traces of use). They represent a variety of raw materials (iron oxide, mudstone, shale, siltstone, snuffbox shale and weathered dolerite), grain size (clayey, sandy, silty), colours (varying from yellow, red, purple to dark colours), traces of use (ground, rubbed, scored) and some of them are associated with combustion features.

The experimental material comprises 10 geological blocks, which were collected from a shale/slate quarry one km from Sibudu. They have the

same variation of attributes as the archaeological pieces. Each block was broken into 10 pieces and the experimental samples were labelled from 1.1 to 10.10. Thus, 100 experimental pieces were processed. Two experimental methods of heating were used with wood fires. Heating in an open fire, with each piece being heated to particular temperatures, at the soil surface (therefore directly below the fire) and also buried in the sand 5 cm underneath the fire. Wood logs, from an indigenous wood taxon named *Dichrostachys cinerea* (Sicklebush), were added or removed when necessary, in order to create and maintain the desired heat. Temperatures were difficult to control exactly, especially for prolonged periods. After reaching the desired temperature, it was maintained for six hours. Burnt wood and ash were then removed and ochre samples collected'. A third method involved heating samples in a muffle furnace to create 'control' samples that were heated to precise temperatures. Due to the fragmentary and fissile nature of ochre, pieces crack and sometimes 'explode' when heated. To avoid damaging the furnace, we heated the pieces in crucibles covered with sand. Experimental samples were heated at 250, 300, 350 and 450°C, each for six hours.

This multi-analytical study aims, in future, to compare the experimental pieces with the archaeological samples from Sibudu and Rose Cottage Caves. At this stage, only a few per cent of the samples have been analysed by all the methods listed below. In the case of the archaeological samples, only non-destructive methods should be used to establish evidence of heating in order the preserve the artifacts.

Several complementary analytical techniques were used to provide a complete approach to assess whether ochre was heated during the MSA. X-ray fluorescence (pXRF) was performed with a Thermo Scientific Niton XL3t 950 portable XRF Analyser. Measurements were acquired in the air with a constant working distance by using a lead receptacle to which the spectrometer is fixed. An area of 8 mm in diameter was analysed and semi-quantitative measurements were produced. The excitation source was a filament based X-ray tube of 50 kV and the data were collected with a Drift Detector (GOLDD+). Backscattering spectra were collected on a LabRam HR 800 spectrometer (Horiba Jobin Yvon) equipped with a charge-coupled device detector, using a 514.5 nm line focused with a x50 objective. The power at the samples was maintained below 0.8 mW. The 600 g/mm grating used provided a 2 cm^{-1} spectral resolution. Mid-infrared spectra (4000-375 cm^{-1}) were recorded with a Bruker Alpha equipped with an attenuated total reflectance (ATR) module and a DeutériumTriGlycine Sulfate (DTGS) detector. The instrument provided a 4 cm^{-1} spectral resolution and 64 scans were averaged for background and sample spectra.

SEM was performed with a JEOL JSM-5510LV. The accelerating voltage used to observe the ochre pieces ranged from 5 to 20 kV. The samples were observed (without metallisation) on a metal support. A PANalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-Kα radiation was used in bulk analysis to obtain the X-ray diffractograms.
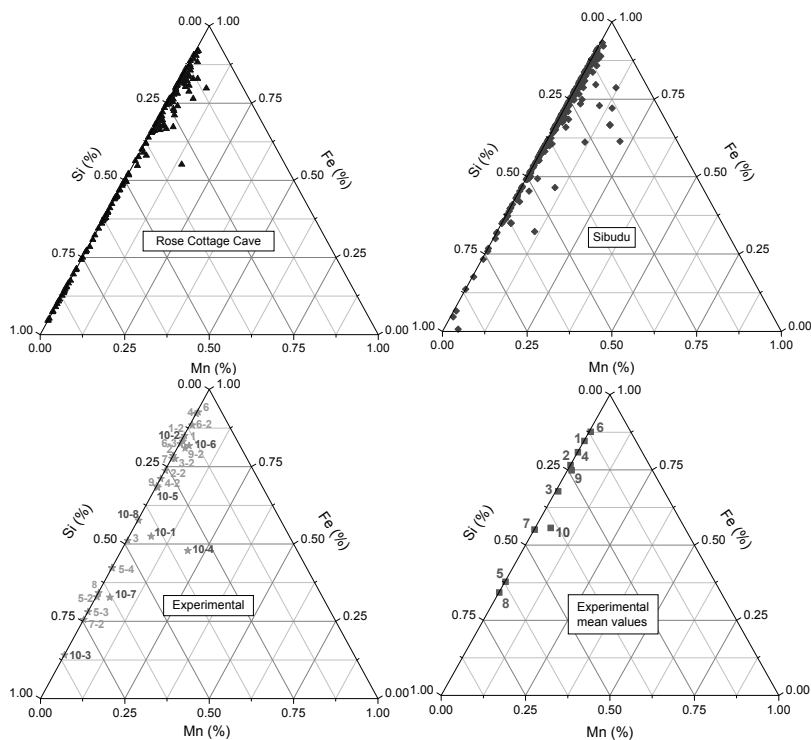

Fig. 41.1. Ternary diagrams as a function of Fe, Si and Mn content in ochre pieces from Rose Cottage (top left), Sibudu (top right), experimental selection (bottom left: all values and bottom right: mean values); data obtained by pXRF.

Results and discussion

pXRF was performed on archaeological and experimental samples for a semi-quantitative elemental analysis. The proportion of the different elements can help us to understand whether there was a selection of specific types of ochre through time and/or for the different type of uses.

To be analysed, the sample should have a flat area of at least 8 mm. Consequently, only 148 ochre pieces from Rose Cottage Cave and 294 from Sibudu could be analysed with pXRF. At least two measurements were performed on each sample and averaged. To classify ochre samples, we plotted some ternary diagrams as a function of three of the major elements (Fe, Si, Mn; Fig. 41.1). In both Sibudu and Rose Cottage Caves, the dispersion is quite similar and the most common major element is iron, which is consistent with the presence of iron oxides and oxyhydroxydes. The silicon content is associated with silica minerals such as quartz, clay or mica. Some of the samples, mostly from Sibudu, contain manganese which can give rise to manganese oxides or oxyhydroxides. For the experimental ochre selection, the dispersion of Fe, Si and Mn matches the one from the archaeological samples. pXRF measurements were performed on two areas of each experimental block except for the block 10 for which 8 measurements were carried out (for the pieces 10.1 to 10.8). For the latter, the manganese content ranges from about 0.1 to 10% depending on the broken piece analysed. The sample is quite heterogeneous and manganese oxides are localised on specific parts of the sample. For the next part of the paper, we will focus on this sample which contains manganese. Experimental block 10 is a snuff-box shale with a clayey/silty grain size and a colour ranging from yellow to dark red or brown colours (see photograph in Fig. 41.3).

Before heating, the pieces from experimental block 10 were subjected to Raman and XRD. These two methods complement the elemental analysis by providing clues on the molecular and crystallographic state of the matter. The results (data not shown) showed the presence of goethite, kaolinite, quartz, carbon and manganese oxide in the darker areas of the block. Since it is not possible to distinguish natural haematite from heated goethite by Raman spectroscopy, we chose to focus on manganese species (Fig. 41.2). Manganese oxides are strongly influenced by heating, as we explain shortly, and these oxides are often found in ochre. However, the Raman band attribution of manganese oxides is not straightforward because of the innumerable compounds that manganese may constitute and because of numerous discrepancies among published Raman spectra (Ospitali et al. 2006). Another problem for a clear identification of manganese compounds is that manganese occurs in several oxidation states (Mn II, Mn III, Mn IV) in the form of many completely distinct oxide and oxyhydroxide species. In the case of ochre samples, another difficulty is the overlapping of the manganese oxide bands with iron oxides bands since the atomic number of manganese and iron are very close. XRD analysis identified the presence of pyrochroite ($Mn(OH)_2$) in

sample 10 before heating, however, pyrochroite exhibits one strong Raman feature around 638 (Ramírez et al. 2015) to 647 cm^{-1} (Lafuente 2015) and this does not appear in our spectra. The local structure of manganese dioxides, especially for samples with a poor crystallinity, makes it difficult to apply the Rietveld refinement of the XRD data (Julien et al. 2003). Before heating, the two main bands of the broad feature appear at 580 and 620 cm^{-1}. Julien et al. (Julien et al. 2003) recognised three major features of birnessite-type MnO_2 at 500-510, 575-585 and 625-650 cm^{-1} which match with the signature of the unheated ochre samples labelled 10.

At 250°C on the wood fire subsurface, two different manganese oxide signatures were detected in sample 10.1. The first one shows three components at 500, 577 and 629 cm^{-1}; they correspond to the birnessite-type as for the unheated sample, but the intensity band ratio of the two strongest bands is reversed. The assignment of the band at 635 cm^{-1}, appearing in the second spectrum, is quite ambiguous because of disagreement about the Raman band attributions in the literature. Nevertheless, the attribution to pyrolusite seems to be the most reasonable assignment since Perseil et al. (Perseil 1974) observed the transformation through heating from birnessite to pyrolusite. At 250°C on the wood fire surface and at 300°C on the fire subsurface, an identical fingerprint was detected. The spectra obtained contain an amorphous carbon signal (not shown) with a high level of fluorescence; the signal to noise ratio is low. However, several components are detected. The component at 680 cm^{-1} can be assigned to bixbyite (M_2O_3 or natural $(Mn,Fe)_2O_3$) (Julien et al. 2004) which can come from the heat treatment of pyrolusite (Chalmin 2003). In the literature, no spectra have been recorded exhibiting a maximum intensity at 723 cm^{-1}. However, bands detected around 730-780 correspond to polymorphs of MnO_2 such as nsutite (γ-MnO_2), pyrolusite (β-MnO_2) or ramsdellite (R-MnO_2) (Julien et al. 2004, Ospitali et al. 2006). The Raman spectrum obtained at 350°C at the fire subsurface shows one strong Raman band at 648 cm^{-1}. The attribution to pyrolusite is most likely. The intense band around 650 cm^{-1} corresponds to Ag mode; the full width at half maximum is almost half the width (FWHM = 64 cm^{-1}) of the one obtained at 250°C (FWHM = 111 cm^{-1}). This suggests the presence of a better organised material.

The manganese oxide spectrum of the sample placed directly in the fire surface and heated to 450°C displays bands at 165, 266, 398, 475, 506, 534, 585 (shoulder), 611 (strong), 655 and 730 cm^{-1}. These features correspond to Mn_5O_8 (Azzoni et al. 1999). This manganoxide may be an intermediate in the transformation from pyrolusite to bixbyite (Chalmin 2008). The presence of Mn_5O_8 could be the result of heat treatment, but it

does not constitute sufficient evidence on its own. Even if Mn_5O_8 is not common in nature, it was found in a natural manganite-pyrolusite mixture (Rask 1986). To confirm those attributions and to find other evidence of heating, complementary methods such as X-ray diffraction or SEM analysis need to be used.
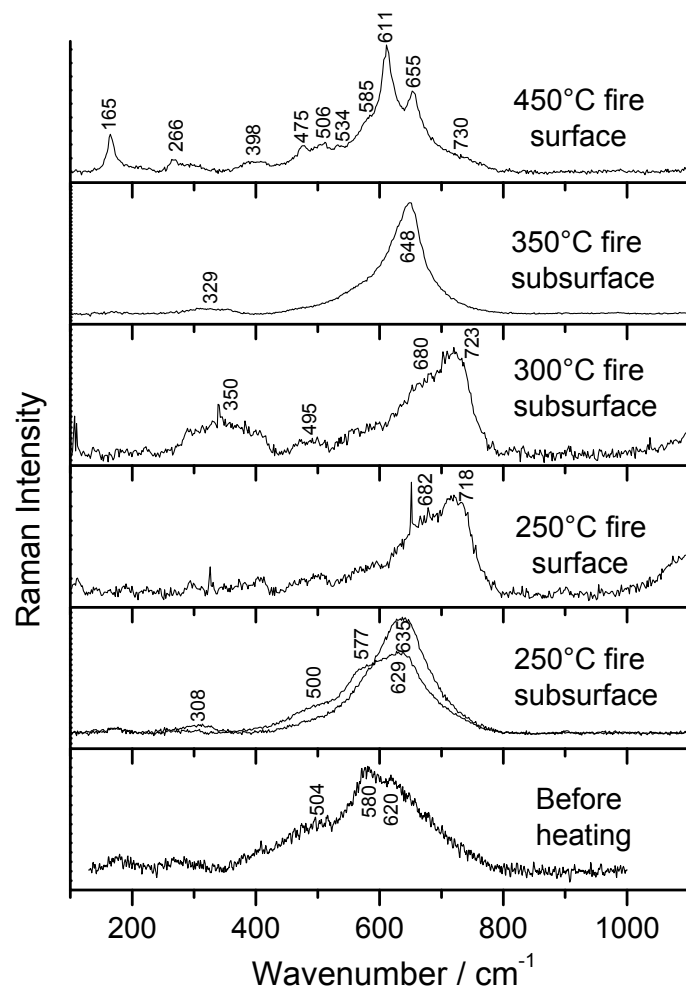

Fig. 41.2. Raman spectra of manganese oxides present in the experimental sample 10 at various fire temperatures and methods of heating the sample (fire surface and subsurface).

Mid-infrared spectra were recorded (Fig. 41.3) with an ATR module to enable micro-sampling. The method is thus invasive, but non-destructive. With FTIR, the selection rules are different from those in Raman, so we have access to complementary information. Between 400 and 500 cm^{-1}, the vibration of iron-oxygen bonds is observed (Hakeem et al. 1986, Ruan et al. 2002). From 700 to 800 and at 1163 cm^{-1}, we can observe the features of quartz (Moenke 1994) and of interest are the bands between 900 and 1200 cm^{-1} related to clay minerals. Before heating, we observe several components in that region attributed to H-O-Al and Si-O vibrations. Moreover, we can see the bending and stretching modes of O-H bonds mostly assigned to water. Especially at 3620 and 3700 cm^{-1}, two sharp bands are attributed to water in kaolinite (Prost 1989). After heating at 450°C at the fire surface, the quartz bands are identical to the ones before heating; the temperature is too low to cause changes in quartz crystals. The departure of water is observed with a shift of the O-H bending band from 1640 to 1630 cm^{-1} and the quasi-disappearance of O-H stretching vibrations. The H-O-Al absorption band at 911 cm^{-1} also disappeared. The area of clay exhibits a broad band around 1060 cm^{-1}. All those changes show the transformation from kaolinite to amorphous metakaolin (Ozer et al. 2015). This dehydroxylation reaction commonly occurs in the temperature range of 450°C to 700°C. The transformation is observable because the temperature at the fire surface was oscillating between 416 to 516°C during the experiment.

Other evidence of transformations that occur during heating is obtained by SEM-EDS. Fig. 41.4a shows the secondary electron micrograph of the experimental sample 6.9 heated in the furnace at 450°C. We can see a spongy structure which is characteristic of the clay sheets. Moreover, we can observe three crystals, which the EDS analysis shows to be quartz crystals because the two elements detected are silicon and oxygen (data not shown). If we zoom in on one of these crystals (Fig. 41.4a'), we observe a moat around it. This has formed as the matrix moves when heated while the quartz grain remains stable. The micrograph of a sample from Rose Cottage (found possibly in a hearth) highlights the same feature (Fig. 41.4c). Another structure showing heating can be seen on Fig. 41.4b where micro-fractures have formed due to dehydration. The fractures resemble mud-cracking.
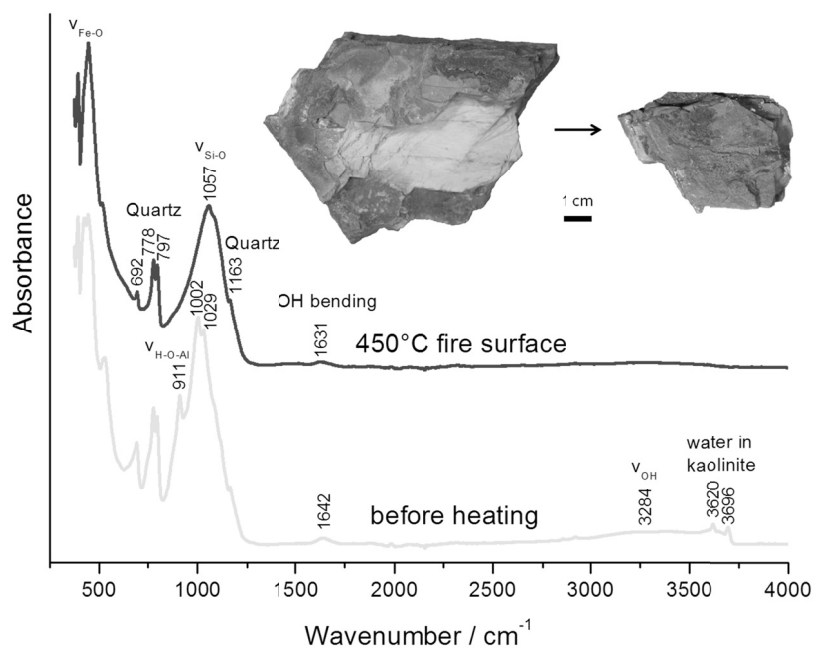
Fig. 41.3. Infrared spectra and photographs of the experimental sample 10 (entire piece) before, and after heating at the fire surface at 450°C (piece 10.4).

Conclusion

This contribution represents an initial attempt to recognise ochre heat treatment by using various non-destructive analytical techniques mostly on experimental, but also on some archaeological samples. In the Raman spectra, the presence of pyrolusite, bixbyite, nsutite, and more specifically Mn_5O_8, can be a clue for recognising heat treatment, but does not constitute sufficient evidence on its own. The attribution of the spectra still needs to be confirmed by performing XRD and SEM. When a sample is heated to more than 450°C, the infrared spectra show a low water content and the presence of metakaolin, which forms as a result of the heating of the kaolinite present in the ochre sample. SEM shows different features of heat treatment such as drying cracks and moat formation around quartz grains. These analytical methods are non-destructive and useful in assessing whether samples have been heated or not. The fire/furnace experiments create an experimental database of heated ochre. A systematic

analysis of experimental pieces and also ochre from Sibudu and Rose Cottage still needs to be done. Eventually we should be able to determine whether ochre was intentionally heated at these sites depending on the quantity of ochre showing evidence of heating, combined with spatial, surface and physical analyses of the pieces.
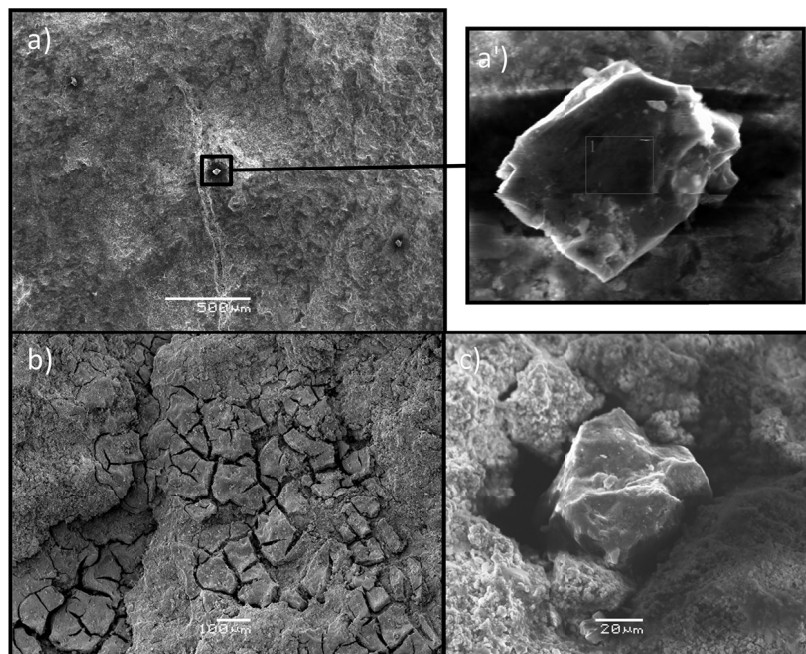

Fig. 41.4. SEM micrographs of a) experimental sample 6.9 heated at 450°C in the muffle furnace; a') zoomed view on a quartz grain; b) experimental sample 3.4 heated at 450°C at the fire surface and c) moat around a quartz grain for a sample from Rose Cottage found possibly near hearth.

Acknowledgements

References

Azzoni, C.B., Mozzati, M.C., Galinetto, P., Paleari, A., Massarotti, V., Capsoni, D., Bini, M., 1999. "Thermal Stability and Structural Transition of Metastable Mn_5O_8: in situ micro-Raman Study." *Solid State Communications* 112 (7): 375-378.

Chalmin, E., Menu, M., Vignaud, C., 2003. "Analysis of Rock Art Painting and Technology of Palaeolithic Painters." *Measurement Science and Technology* 14 (9): 1590.

Chalmin, E., Vignaud, C., Farges, F., Menu, M., 2008. "Heating Effect on Manganese Oxihydroxides Used as Black Palaeolithic Pigment." *Phase Transitions* 81 (2): 179-203.

Dayet, L., Texier, P.J., Daniel, F., Porraz G., 2013 "Ochre Resources from the Middle Stone Age Sequence of Diepkloof Rock Shelter, Western Cape, South Africa." *Journal of Archaeological Science* 40 (9): 3492-3505.

de Faria, D.L.A., Lopes, F.N., 2007. "Heated Goethite and Natural Hematite: Can Raman spectroscopy Be Used to Differentiate Them?" *Vibrational Spectroscopy* 45 (2):117-121.

Goss, C.J., 1987. "The Kinetics and Reaction Mechanism of the Goethite to Hematite Transformation." *Mineralogical Magazine* 51: 437-451.

Hakeem, N.A., Basily, A.B., Sagr, N., Moharram, M.A., 1986. "Study of the Thermal Transformation of Natural Goethite Using Infrared Spectroscopy." *Journal of Materials Science Letters* 5 (1): 4-6.

Henshilwood, C., van Niekerk, K., 2012. "Middle Stone Age Chemists A 100,000 Year Old Pigment Processing Workshop at Blombos Cave, South Africa." *The Digging Stick* 29: 1-5.

Hodgskiss, T. 2012"An Investigation into the Properties of the Ochre from Sibudu, KwaZulu-Natal, South Africa." *Southern African Humanities* 24: 99-120.

Hodgskiss, T. 2013. "Ochre Use in the Middle Stone Age at Sibudu, South Africa: Grinding, Rubbing, Scoring and Engraving." *Journal of African Archaeology* 11 (1): 75-95.

Jacobs, Z., Roberts, R.G., Galbraith, R.F., Deacon, H.J., Grün, R., Mackay, A., Mitchell, P., Vogelsang, R., Wadley, L., 2008. "Ages for the Middle Stone Age of Southern Africa: Implications for Human Behavior and Dispersal." *Science* 322 (5902): 733-735.

Julien, C.M., Massot, M., Poinsignon, C., 2004. "Lattice Vibrations of Manganese Oxides: Part I. Periodic Structures." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 60 (3): 689-700.

Julien, C., Massot, M., Baddour-Hadjean, R., Franger, S., Bach, S., Pereira-Ramos, J.P., 2003. "Raman Spectra of Birnessite Manganese Dioxides." *Solid State Ionics* 159 (3-4): 345-356.

Lafuente B., Downs, R.T., Yang, H., Stone, N., 2015. "The Power of Databases: the RRUFF Project." In Armbruster, T., Danisi, R.M. (ed.) *Highlights in Mineralogical Crystallography*, 1-30, Berlin: W. De Gruyter.

McBrearty, S., 2001. "The Middle Pleistocene of East Africa." In Barham L., Robson-Brown, K. (eds.) *Human roots: Africa and Asia in the Middle Pleistocene*, 81-98, Bristol: Western Academic & Specialist Press.

Moenke, H.H.W., 1994. *The Infrared Spectra of Minerals*. Farmer, V.C. (ed.) *Mineralogical Society*. London.

Ospitali, F., Smith, D.C., Lorblanchet, M., 2006. "Preliminary Investigations by Raman Microscopy of Prehistoric Pigments in the Wall-Painted Cave at Roucadour, Quercy, France." *Journal of Raman Spectroscopy* 37 (10): 1063-1071.

Ozer, I., Soyer-Uzun, S., 2015. "Relations Between the Structural Characteristics and Compressive Strength in Metakaolin Based Geopolymers With Different Molar Si/Al ratios." *Ceramics International* 41 (8): 10192-10198.

Perseil, E.A., Perinet, G., Picot, P., 1974. "La Birnessite dans les Gisements Manganésifères Pyrénéens. Sa Place dans la Paragénèse et son Origine." *Bulletin de la Société Française de Minéralogie et de Cristallographie* 97: 475-478.

Pienaar, M., Woodborne, S., Wadley, L., 2008. "Optically Stimulated Luminescence Dating at Rose Cottage Cave." *South African Journal of Science* 104 (1-2):65-70.

Pomiès, M.P., Menu, M., Vignaud, C. 1999. "Red Palaeolithic Pigments: Natural Hematite or Heated Goethite?" *Archaeometry* 41 (2): 275-285.

Prost, R., Dameme, A., Huard, E., Driard, J., Leydecker, J.P., 1989. "Infrared Study of Structural OH in Kaolinite, Dickite, Nacrite, and Poorly Crystalline Kaolinite at 5 to 600 K." *Clays and Clay Minerals* 37: 464-468.

Ramírez, P.B., de Balbín Behrmann, R., Laporte, L., Gouézin, P., Cousseau, F., Barroso Bermejo, R., Hernanz Gismero, A., Iriarte Cela, M., Quesnel, L., 2015. "Natural and Artificial Colours: The Megalithic Monuments of Brittany." *Antiquity* 89 (343): 55-71.

Rask, J.A., Buseck, P.R., 1986 "Topotactic Relations Among Pyrolusite, Manganite, and Mn_5O_8: A High-resolution Transmission Electron Microscopy Investigation." *American Mineralogist* 71 (5): 805-14.

Rifkin, R.F., 2011. "Assessing the Efficacy of Red Ochre as a Prehistoric Hide Tanning Ingredient." *Journal of African Archaeology* 9 (2): 131-158.

Rifkin, R.F., Dayet, L. Queffelec, A., Summers, B., Lategan, M., d'Errico, F., 2015. "Evaluating the Photoprotective Effects of Ochre on Human Skin by *In Vivo* SPF Assessment: Implications for Human Evolution, Adaptation and Dispersal." *PLoS ONE* 10 (9): e0136090.

Roebroeks, W., Sier, M.J., Kellberg Nielsen, T., De Loecker, D., Maria Parés, J., Arps, C.E.S., Mücher, H. J.. 2012. "Use of Red Ochre by Early Neandertals." *Proceedings of the National Academy of Sciences* 109 (6): 1889-1894. doi: 10.1073/pnas.1112261109.

Ruan, H.D., Frost, R.L., Kloprogge, J.T., Duong, L., 2002. "Infrared Spectroscopy of Goethite Dehydroxylation: III. FT-IR Microscopy of in situ Study of the Thermal Transformation of Goethite to Hematite." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 58 (5): 967-981.

Wadley, L., 2009. "Post-depositional Heating May Cause Over-Representation of Red-Coloured Ochre in Stone Age sites." *The South African Archaeological Bulletin* 64 (190):166-171.

Watts, I., 2010. "The Pigments from Pinnacle Point Cave 13B, Western Cape, South Africa." *Journal of Human Evolution* 59:392–411.