Complementary Raman and Mössbauer Archaeological Studies

John D. Cashion[a], Colin A. Hope[b] and William H. Jay[b,c]

[a] *School of Physics and Astronomy, Monash University, Victoria 3800, Australia.*
[b] *Centre for Archaeology and Ancient History, Monash University, Victoria 3800, Australia.*
[c] *Private Researcher, P.O. Box 34, Chelsea, 3196, Australia.*

Two Egyptian and two English archaeological artefacts were examined by Raman and Mössbauer spectroscopy to show how these enable more accurate description of their starting materials, manufacturing conditions and final state. The results enhance the use of scientifically-based reasons for the assignment of archaeological artefacts instead of the practice of connoisseurship.

1.   Introduction

Archaeological investigations often proceed by a mixture of extensive careful digging and searching followed by physical and scientific examination and comparisons with previous related samples. In common with all scientific investigations, they build on previous work. However, as with works of art, there is often reliance on connoisseurship to certify that a particular item can be attributed to a certain provenance. Proving, or disproving, such assertions can involve much detailed scientific analysis.

Archaeological investigations can provide much useful knowledge on the state of technological capability at that time and place, the development and transfer of technology, trade routes and so on. We have been carrying out investigations on Egyptian artefacts from the Dakhleh Oasis and River Nile from circa 18th dynasty (3300+ years ago) and 18th century Limehouse porcelain and Lancaster delftware as they developed their clays and glazes.

Using two different spectroscopies produces a much more detailed picture. For example, one item of particular interest is the firing temperature available at that time. Raman is able to identify the minerals in the body and the glazes and, from knowledge of the formation and transformation temperatures of the minerals, ascertain the minimum temperature reached and also deduce that other temperatures were not reached.

2.   Samples and Results

2.1   Ferric slag, Mut al-Kharab, Dakhleh Oasis, Western Desert, Egypt

The first sample selected is a slag sample from Mut al-Kharab in the Western Desert region of Egypt, found under a probable 25th dynasty (c 747-656 BCE) temple, but the site has been disturbed and the sample is tentatively dated at approximately 18th dynasty. The slag has been broken off the inside of a kiln and we examined both the outer surface and the fractured face [1]. The Mössbauer spectrum of the fractured face showed a magnetically split spectrum of goethite, α-FeOOH, with 68% of the area and a doublet due to a clay mineral accounting for the remainder [1]. The slag outer surface had grooves formed by being pressed against the Halfa grass biomass used as fuel and in scraping off material for Mössbauer spectroscopy it became apparent that some of the material was in the form of long needles up to 7 mm in length and which appeared to be single crystals. These needles (Fig. 1a) were allowed to lie flat in a perspex absorber holder for Mössbauer spectral examination. Considerable gaps were unavoidable in the holder, reducing the quality of the spectrum.

The spectrum (Fig. 1b) has been fitted with three sextets to cope with the spread of crystallinity and hence hyperfine fields, and a small doublet for the clay mineral impurity. It is

immediately apparent that the intensities of the lines do not follow the 3 : 2 : 1 ratio appropriate for powder samples, the two outer sextets having the weighted ratio of 3 : 3.2 : 1, compared to a perfectly oriented single crystal of 3 : 4 : 1. This shows that the needles are principally single crystals which have formed over 3500 years by the dissolution and recrystallization of the goethite on the surface of the slag, while the clay mineral has been covered over by this process. Raman spectra of the fractured surface identified principally goethite and diopside. SEM also showed a crystal of what would relate to bloomery iron. The purpose of the slag is not clear – was it an early experiment at the start of the iron age?
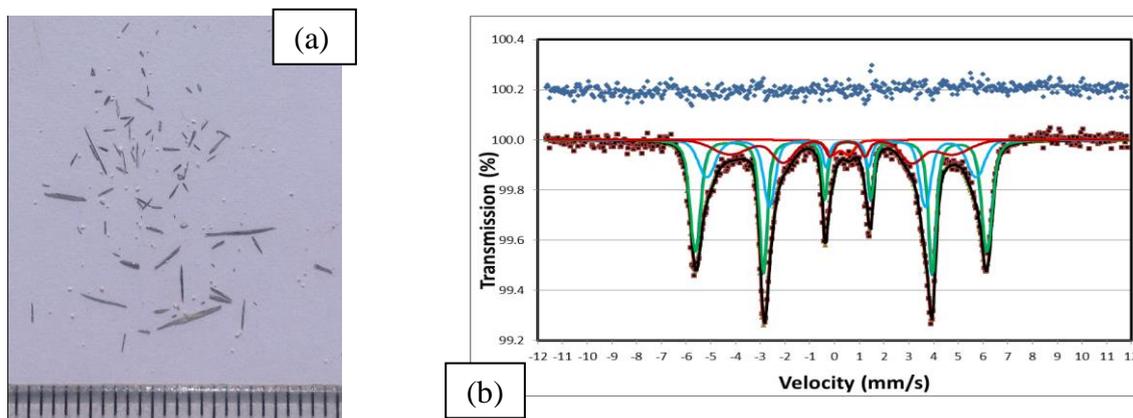

Fig. 1. (a) Single crystal needles of goethite with mm scale, (b) room temperature spectrum of the needles. Three sextets (green, blue, red) are all goethite, doublet (orange) is a clay mineral with octahedral Fe^{3+}.

2.2 Amarna pottery sherd, Nile River, Egypt

The second sample is a pottery sherd from Amarna, established in approximately year 5 of the reign of Amenhotep IV/Akhenaten (c. 1352-1336 BCE) in the 18th Dynasty as his capital, but abandoned only 20 years later by Tutankhamun. Material was scraped from the outside and the body centre of the sherd, Amarna A5, to investigate the temperature obtained and the uniformity of firing. The Mössbauer spectra of the two samples are shown in Fig. 2 and differences are immediately obvious.

The lower spectrum is of the centre of the sherd with prominent doublets and a much weaker magnetically split part. The dominant doublet (yellow) is from the pyroxene diopside, $Mg_{1-x}Fe_xCaSi_2O_6$, with 42% of the area. Both sextets are due to hematite with 14%. In the spectrum of the outer part, the hematite contribution has risen to 53%. The doublet contributions, apart from being reduced in proportion, have also become much more oxidized with the ferrous/ferric ratio changing from 1.46 to 0.57. The green doublet (octahedral Fe^{3+}) has doubled in area, while the red doublet (tetrahedral Fe^{2+}) has disappeared. Thus the artefact has been underfired, with the firing insufficient to achieve a uniform transformation throughout the body. We can, of course, sympathise with the artisans, who did not have the benefit of our modern measuring instruments! Raman spectra support underfiring with the observation of poorly formed diopside, metakaolin and anorthite suggesting a temperature approaching 900 °C

2.3 Pottery sherd, Limehouse pot works, London

The next two case studies investigate the development of English pottery in the 18th century. The first is from the Limehouse pot works, founded in London in 1745. It only operated until June 1748 and the sherds studied were collected over a 6-week excavation window in 1990 before the site became part of the Limehouse Link Road Tunnel. Why is such a short-lived pot works important? It produced many experimental compositions and

glazes and, on closure, one of the principals, probably Benjamin Lund, went to Bristol to found Lund's Bristol Pottery. It was bought three years later by the Worcester partners leading to two factories which contributed to porcelain manufacture for the next 260 years.
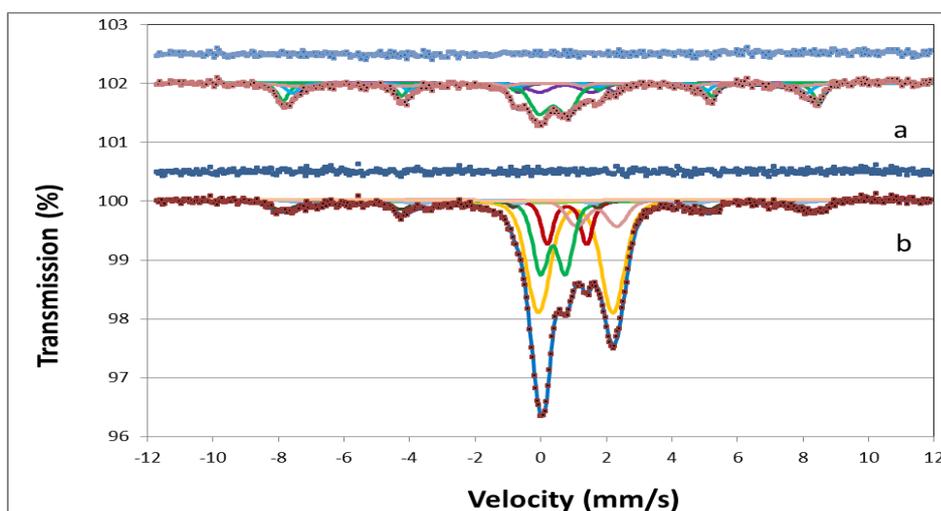

Fig. 2. Mössbauer spectrum of (a) the surface and (b) the inner body of the pottery sherd Amarna A5

The Raman spectroscopy [2] showed that three different body types were trialled – an experimental Si-Al, an experimental but intermediate Si-Al-Ca composition and a Si-Al-Ca porcellaneous body with progressively increasing K_2O and CaO fluxes and finally Na_2O as well. There was no MgO, which would indicate steatite (soapstone), nor P_2O_5, indicative of bone ash, although steatite and bone ash were used at Lund's Bristol shortly later. Firing led to the formation of cristobalite and mullite, indicating a temperature of ~1250 °C, while the Mössbauer spectrum [2] showed that 9% of the iron was ferrous, indicating that a slightly reducing atmosphere was used. A 2-step firing was used, but there were still hydroxylated minerals in the core which led to stresses and also bubbles under the mature glaze from continuing body chemical reactions. The presence of anatase indicated that Dorset ball clay was the basis of the body and which transformed to rutile at ~1000 °C. Cobalt ores from Schneeburg, Germany, were mixed into the body composition to whiten it, but at relatively small additions, difficulty was experienced in obtaining uniformity. Cassiterite, SnO_2, was also added to the body and glaze, probably by dissolving it in lead and then milling it.

2.4   Lancaster delftware

Delftware, or tin-glazed earthenware, came to England from Antwerp in the mid-16th century. The Lancaster pottery was founded in 1754, mainly to export to the Americas and West Indies. Its success was principally due to obtaining clay from Carrickfergus, near Belfast, which was mixed with local red clay and possibly some white pipe clay. The Carrickfergus clay could only be collected at low tide and is now covered by sea wall defences, preventing any current scientific assessment. An archaeological recovery on the Lancaster potworks site in 2008 [3] enabled the collection of biscuit and tin-glazed delftware sherds as well as unfired Carrickfergus clay and fired local clays. This has enabled the first scientific analysis of the Carrickfergus clay [4] and will greatly assist in the attribution, or re-attribution, of 18th century English delftware which frequently relies on the decoration, a fraught procedure when artisans moved between potteries.

Raman spectra of the Carrickfergus clay [4] showed it to be highly dolomitic, $(CaMg(CO_3)_2)$, which produced diopside and forsterite, Mg_2SiO_4 on firing. Until a recent SEM-EDS determination [4], Carrickfergus clay was thought to be Ca-rich [5] and, with this

knowledge of the chemical form, they provide an analysis reference to contrast other clays. Flint is commonly used as the silica raw material and Raman spectroscopy [4] was able to identify that the flint contained the silica polymorphs chalcedony intergrown with moganite, an identification which requires an accuracy of 1 cm^{-1}. When heated above 600 °C the material shatters, making it readily amenable to fine grinding. From other transformations, the firing temperature was deduced to be 800-900 °C, not 1050 °C as previously suggested [6].

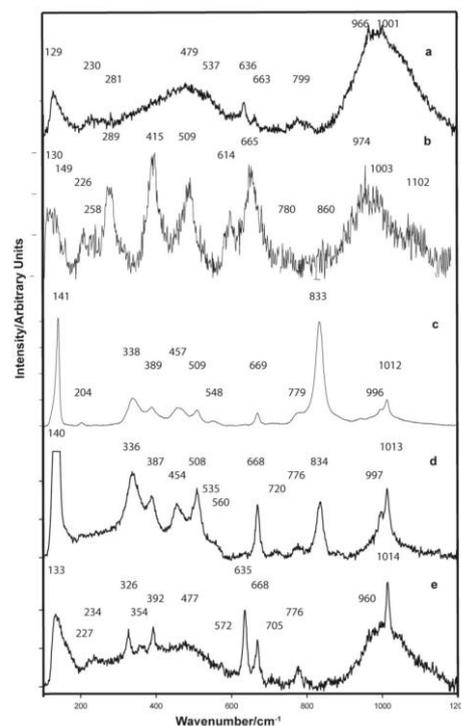Fig. 4. Two coloured glazed Lancaster sherds.

Fig. 3. Raman spectra of different glazes: (a) brown, (b) red, (c) yellow, (d) yellowish-green, (e) bluish-green. (Refer to RRUFF database for identification.)

The pigments are complex (Fig. 3) and were applied as dry powders or as a slurry with some non-uniformity noticeable (Fig. 4). One blue pigment was cobalt olivine or, sometimes, cobalt spinel, presumably formed in each case as silicates from cobalt-glass (smalt) and flint. Another blue is the 5-element Co pigment, (Mn, Fe, Co, Ni, Cu, Zn, As), also obtained as a glass from Schneeberg, while the bluish-green was a Cu-Ni mixture from dioptase and rammelsbergite. The yellow pigment was a synthetic triple-oxide Pb-Sb-Sn complex while the brown pigment was a mixture of the manganese minerals kanoite and donpeacorite which could be doped to form pinks, maroon, etc. The red is poorly crystalline or impure hematite.

4. Conclusion

Four examples have been presented showing the information about the manufacture and origin of particular components of archaeological artefacts obtainable from combined Raman and Mössbauer spectroscopy analyses.

Acknowledgments

References

[1] Jay W H, Cashion J D and Hope C A 2015 *Pottery of the Egyptian Western Desert*, in press.
[2] Jay W H and Cashion J D 2013 *J. Raman Spectroscopy* **44** 1718
[3] Blenkinship B 2008-2009 *J. Northern Ceramic Soc.* **25** 40
[4] Jay W H, Cashion J D and Blenkinship B 2015 submitted for publication
[5] Francis P 2000 *Irish Delftware*, Jonathan Horne Publications, London
[6] Britton F 1994 *English Ceramic Circle Trans.* **15(2)** 308