NEW IMAGING METHODS TO IMPROVE TEXT LEGIBILITY OF OSTRACA

Gregory Bearman, Mark S. Anderson[#] & Kenneth Aitchison[§]*

*ANE Image, Pasadena, CA. E-mail: gregb@snapshotspectra.com
[#]Jet Propulsion Laboratory, Pasadena, CA.
[§]Los Gatos, CA.

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ABSTRACT

We report on experiments on three new methods to improve text contrast for carbon ink ostraca. These are (1) Raman imaging, (2) Micro-focus XRF scanning and (3) exogenous contrast agents either to enhance the X-ray signal or create an optical fluorescence signal. We tested all three methods with modern 'stunt' ostraca, made using a variety of carbon-based inks. In each imaging modality, the inks are clearly differentiated from the clay background. The exogenous contrast enhancement, in particular, suggests a variety of approaches to improving text legibility.

Introduction

Sherds are a staple of archaeological excavations. Found by the thousands at digs in the Levant, when reassembled into pots, sherds are used extensively for dating levels and delineating trade routes. Ostraca are sherds (or stone flakes, but these will not be considered in the present work) with writing or pictorial images on them. Since fired clay is so durable, ostraca often serve as the only exemplars of writing on sites exposed to conditions that destroy organic writing substrates, such as parchment or papyrus. However, they are sometimes difficult to read and many times go unrecognized as ostraca. Standard practice is to wash sherds on site, as it makes text, if any, more visible, most likely due to changes in scattering from the higher index of refraction of water relative to air. Photographers of ostraca have employed infrared imaging above 720 nm to attempt to improve text legibility, reasoning by analogy with the known use of Near Infra-Red (NIR) photography of the Dead Sea Scrolls and other texts (Cross, 1962; Rosenbaum, 1986). Recent work on spectral imaging has helped us understand the science

behind NIR improvement with imaging (Bearman, 2010). We consider NIR imaging a useful but only intermittently successful technique for ostraca and so wish to explore other methods for reading the text; we report here on a variety of high-technology methods for doing so.

The problem with illegible texts of any sort is low contrast – the ink and substrate look about the same so they cannot be separated – the black cat at midnight problem. Using parchment as an analogy, many texts are hard or impossible to read in the visible, but not in the infrared. Spectral imaging showed that the reason is that the ink and parchment have about the same reflectance in the visible, producing little contrast (Chabries, 1997). However for the Dead Sea Scrolls and many papyri, the substrate becomes much brighter, more reflective in the NIR, increasing contrast so the text becomes more legible. For ostraca, we need to find a way to differentiate between the ink and pottery. It seems that some ostraca behave the same way optically as parchment texts, and spectral imaging can help improve contrast (Bearman, 2010). However, the improvement is in many cases marginal and other methods are needed. We explored several approaches to contrast improvement, taking advantage of what we know about the inks and the pottery. Specifically, we looked at three new modalities: (1) Raman imaging, (2) X-ray fluorescence (XRF) and (3) the application of exogenous contrast agents.

Raman Imaging

Ancient inks were typically made using carbon soot and binders, organic and otherwise (see http://www.djmcadam.com/ink-recipe.html). The inks of the Dead Sea Scrolls have been shown to be carbon based (Nir-El, 1996), not iron-gall, as in later texts. Since the shift to iron-gall inks began about the 3rd century CE, it is pretty safe to argue that the ink of ostraca excavated in the ancient Near East are carbon based. We can think of the ink in two distinct ways for this study, one as soot and the other as a highly adsorptive material, similar to activated charcoal. Raman spectroscopy of soot combustion products shows a strong double peak at 1302 and 1590 cm^{-1} (Escribano, 2001). With this in mind, we decided to look at Raman imaging to detect the ink carbon and improve the contrast; since the pottery does not have a spectral feature at these wavelengths, the carbon ink would show up with high contrast.

We made faux ostraca using modern clay pots and assorted carbon inks. Three different inks were used in this study: a commercial India ink and two homemade inks, one with lampblack and one with fullerene soot. The ink analogs were not an attempt to replicate ancient ink formulas. The only purpose of the ink is to create a thin-enough writing solution to deliver carbon soot to the pottery surface as writing. All of the methods explored here rely only on various physical properties of carbon, not the binder used. The lampblack ink (sold as paint pigment) and fullerene soot ink (Sigma-Aldrich 572497-5G) were made with canola oil and thinned with mineral spirits to a consistency to write letters with a brush. Since carbon soot usually contains some fullerenes, we wanted to use them to detect the fullerene Raman bands as another contrast mechanism. Raman spectroscopy of the three inks on clay clearly showed the soot peaks and also demonstrated that pottery itself does not provide a signal at the wavelength of the peaks; we did not see clearly any of the fullerene Raman peaks. Figure 1 shows spectra of the lampblack at two excitation wavelengths, 525 nm and 785 nm. The 785 nm excitation shows much less fluorescence. In this case, it seems that a single detection wavelength at one of the soot peaks would provide significant contrast improvement without the need for a lot of multi-wavelength imaging processing. We will present complete Raman images in a later publication, but this one demon-

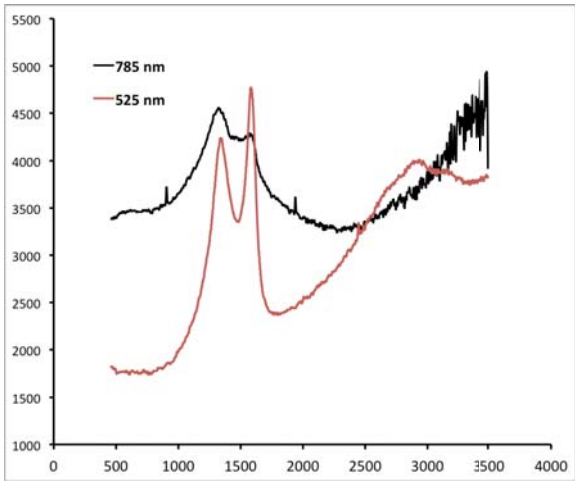

Figure 1. Raman spectra of the lampblack ink at two different excitation wavelengths. Source: NIST data at http://www.nist.gov/pml/data/index.cfm.

strates the concept. We are focused on imaging aspects rather than chemical analysis of the ink or corrosion products (from iron-gall inks). While this is not the first application of Raman spectroscopy to ink, it is noteworthy that nearly all of the Raman work on inks has been on medieval or later parchment texts that use iron-gall inks (Lee, 2006; Bioletti 2009), which have a very different manufacturing technology and whose chemical composition and spectra are also very different.

XRF

X-ray Fluorescence (XRF) has been used recently to unravel palimpsests; most notably the Archimedes Palimpsest, where there are at least two inks: erased carbon ink overwritten with iron-gall ink (Bergman, 2009). The SLAC National Accelerator Laboratory synchrotron light source used a micro-focused X-ray beam to raster-image the document and create elemental maps, which have helped to differentiate between iron-gall ink and other inks. In our case, one might think that the candidate element signal would be a carbon X-ray line from the ink, but this line is difficult to detect due to its low energy. Instead, we looked at the possibility of obtaining a negative of the text; the carbon ink would absorb low energy X-ray fluorescence from elemental lines of the pottery (Al, Si, Ca, for example) and thus reduce the signal where there is ink. We imaged our fake ostraca with a Horiba micro focus XRF with a scanning stage to obtain images. In fact, we do see negative images of the three inks. Figure 2 shows a montage of images from the XRF study with the Horiba instrument. The X-ray excitation beam spot size is 100 μ and provides plenty of resolution for typical text feature sizes of 1-2 mm. The rings around the text in the visible image are due to the ink solvent wetting a larger area around the brushstroke. We see a strong reverse image in the Al and Si lines, which are the major elemental components of clay. The signal for the inks is reduced relative to the clay from typically 55 DN to 38 DN, going as low as 20 in some spots to make a negative image. The homemade inks have a strong signal in spots, most likely, as they were not as thin as the commercial India ink and may contain more carbon or flocculated carbon particles. However, even the

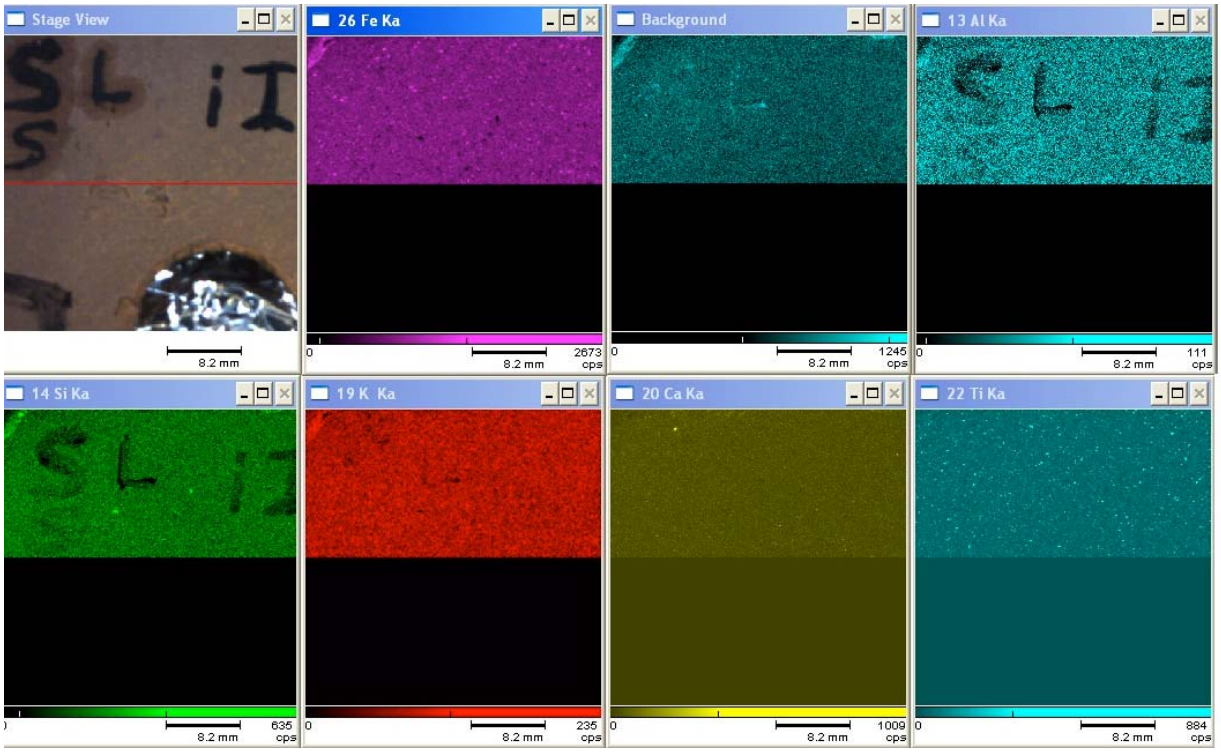

Figure 2. XRF elemental maps of three different types of carbon black inks. Two were homemade from fullerene soot (S in the image), lampblack (L in the image) and commercial India ink (I in the image). The first image in the top row is a video view of the sample. The elements are, left to right on the top, Fe, background, Al. On the bottom, left to right, are Si, K. Ca and Ti. Image by G. Bearman.

India ink 'i' shows up nicely in the elemental images. The Michelson contrast ratio for the three letters is about the same, ~0.2. (see http://en.wikipedia.org/wiki/Contrast_%28vision%29). Part of the contrast may be due to absorption by the ink carbon of the excitation beam, although since the carbon absorption at the excitation beam energy of 30 KeV is not very large this may not be a big effect.

XRF Contrast Agents

Since the soot contains carbon particles, we can think of the ink is as activated charcoal – it has a lot of surface area and internal volume and can adsorb gases and chemicals. We exposed the ostracon to I_2 vapor for 12 hours at 20 C and imaged again with the Horiba XRF. We choose I_2 since it binds easily with carbon and has a strong XRF signal. Figure 3 shows a montage of the results. There are two important results here. One is the strong I_2 XRF signal, showing that the ink carbon preferentially adsorbs the I_2 and we can observe the I_2 signal on all three inks. Despite the rather porous network nature of the unglazed clay surface, it does not take up the I_2 so there is no I_2 XRF background to reduce contrast; the I_2 XRF signal alone provides significant contrast for reading.

The second observation is that the contrast for the Al and Si lines is now stronger. For example, the Michelson ratio in the Si map has increased to ~0.6 from 0.2. Note that there is now a faint text signal for the Ti line. The increased contrast for the Si, Al and other lines after the I_2 exposure may be due to the I_2 absorbing the XRF lines from the underlying pottery. Figures 4 and 5 show the X-ray absorption coefficients of iodine and carbon respectively. The Kα lines for the elements we are looking at are from ~1.4-6.4 KeV, as in table 1. Over that range the X-ray absorption of iodine is typically 10 times that of carbon, so the extra contrast is due to increased absorption of the Si and Al lines by the iodine adsorbed onto the ink carbon. At the beam excitation energy of 30 KeV, iodine is also more than an order of magnitude more absorptive than carbon, so we may be seeing a double effect: attenuation of both the excitation and fluorescence. After exposure to iodine, the Ti line is now faintly visible, but it is brighter than the pottery substrate, so the contrast mechanism (unknown for now) is not the same as for the other elemental lines.

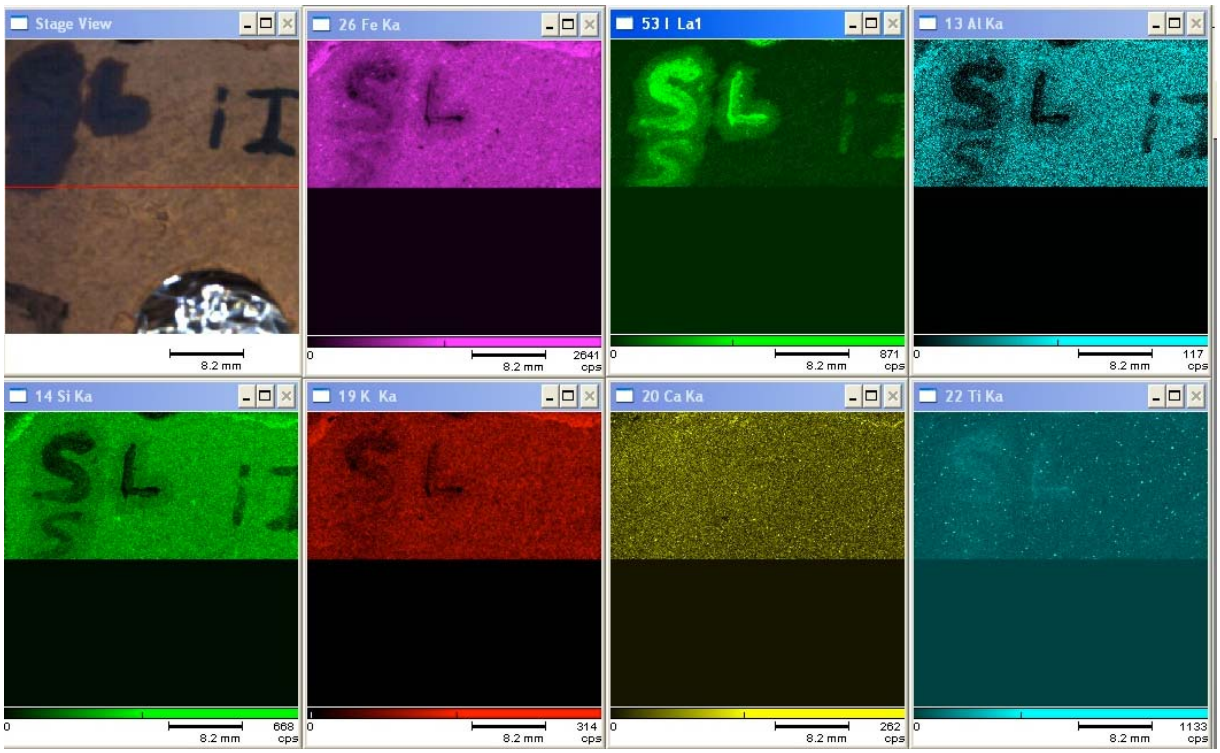

Figure 3. XRF elemental maps after exposing the ostracon to I_2 vapor for 12 hours at 20 C. The first image in the top row is a video view of the sample. The elements are, left to right on the top, Fe, I, Al. On the bottom, left to right, are Si, K. Ca and Ti. Image by G. Bearman.

Element	Kα line
Si	1.7
K	3.3
Fe	6.4
Al	1.48
Ca	3.6

Table 1. Energies of elemental lines in KeV.

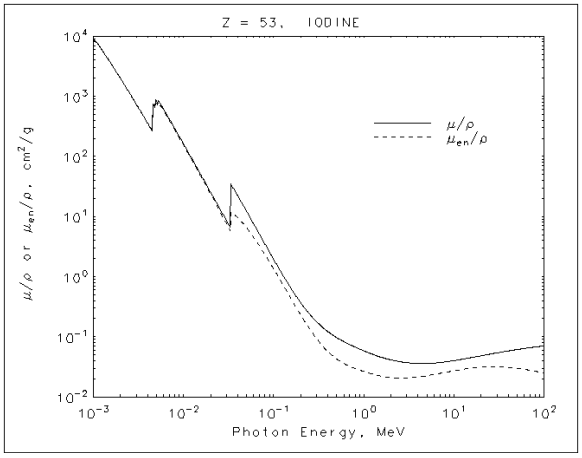

Figure 4. Absorption of iodine. Source: NIST data at http://www.nist.gov/pml/data/index.cfm.

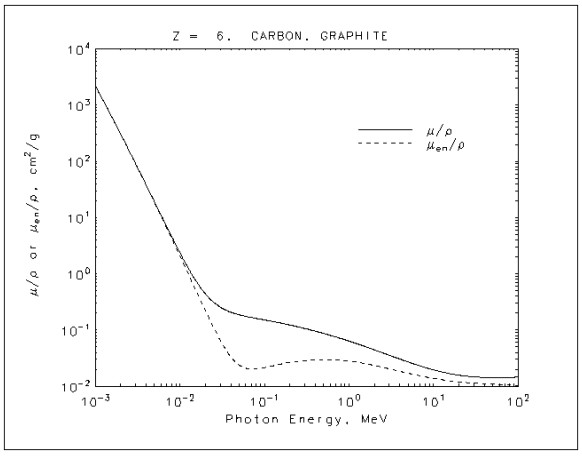

Figure 5. X-Ray absorption of Carbon. Source: NIST data at http://www.nist.gov/pml/data/index.cfm.

One concern is how well the contrast agent sticks to the carbon; *i.e.*, can we remove it after imaging and is there enough adsorbed to be of concern? Adsorption is the result of weak *Van der Waals* forces between the carbon and I_2; there are no high-energy chemical bonds to strongly bind the I_2. Adsorbed materials can be typically be removed (desorbed) by heating to a temperature on the order of the bond energy. A recent calculation (Rudenko, 2010) suggests that the sorption binding energy for I_2 on carbon is ~6-12 kcal/mole or ~0.3-0.5 eV. Heating to ~90-100 F should effectively desorb the I_2 (although this temperature is a bit lower than the sorption bond energy), especially if the object is in an oven with a flow of dry air, which continually drives the equilibrium to desorption. The ostraca have already spent plenty of time at ~80-100 F, typical surface air temperatures in the Near East, so this should not present a danger. There are other iodine containing chemicals such as iodobenze that may desorb at lower temperatures.

The use of I_2 vapor to improve contrast either as a tag itself or a secondary effect suggests a wide range of new approaches to exogenous contrast enhancers. We can borrow some ideas from biology and use fluorophores. There are a large number of biological assays that use a fluorphore linked to a molecule that in turn selectively binds to something else (ELISA assays, for example, see http://en.wikipedia.org/wiki/ELISA). This targeting liganded molecule attaches only to a specific target and then fluoresces to indicate binding as well as to provide localization through a fluorescence image. Similarly, a fluorphore linked to a molecule that binds selectively to carbon would generate an image of the carbon (ink) on an ostracon. We would have to engineer the chemistry to test this new method.

Bulk XRF has been used extensively for analysis of pottery for elemental, provenance and fabrication technology studies. There is synchrotron XRF work producing elemental maps of art (Krug, 2007) and ceramics (Mirguet, 2008), for pigment and mineralogical analysis, not content imaging, as reported here (Synchrotron beams produce a small enough spot size to obtain a rastered image). Our strategy of enhancing the text with contrast agents is novel; any previous work would have a difficult time detecting the carbon *directly*, although others could have seen the reverse elemental image if they had worked on ostraca. Not only did we use the ink carbon itself as a contrast agent, but using exogenous probes that take advantage of carbon's affinity for chemicals is a new twist on XRF imaging for content. The considerable body of literature on the application of synchrotron XRF to art and archaeological artefacts demonstrates that the beam excitation is not considered damaging by the conservation

community (see, for example, the special issue "Synchrotron Radiation in Art and Archeology" of the 'Journal of Analytical Atomic Spectroscopy' 2011 v. 26).

There are some reasons exogenous contrast enhancers may not work with real ostraca. Having been exposed to water, either through the water table or rain and all the active carbon sites may be full, and they will not adsorb the contrast agent. If the carbon sites are already full, one way to reactivate them would be to heat gently to desorb the water, as discussed with desorbing I_2. The lower temperatures we can use would simply either take longer or not drive the desorption to completion and leave some filled sites in the carbon. Another possibility for failure with genuine artefacts is that since the ostraca are unglazed, they may absorb soluble salts from the soil that physically cover the ink so the contrast agent cannot access it and the Raman excitation laser is also blocked. XRF should work in this case, though, since the excitation beam can penetrate the surface layers. There are methods for cleaning ostraca (Muros, 2005) to remove the encrusted salts without damaging the ink that could be used to prepare ostraca for either the Raman imaging or the application of XRF contrast agents. Recent work on using supercritical methods and plasmas (Steelman, 2004) to extract carbon for carbon dating from textiles and other archaeological objects suggests additional gentle ways to surface-clean ostraca for application of the methods presented here, particularly the XRF exogenous contrast agents. A third possible cleaning method is Focused Ion Beam Milling (FIB) that borrows a well-known technique from the micro-electro mechanical systems (MEMS) and semi-conductor industries and has been applied to archaeological ceramics (Sciaua, 2009).

Summary

In summary, we have proposed, tested and demonstrated three new imaging modalities for reading of carbon-ink ostraca. Our studies are experimental in that they demonstrate these methods are applicable – the true test will come with using genuine ostraca. The new contrast mechanisms demonstrated provide another example of the power of applying high-technology methods to archaeology.

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