X-RAY FLUORESCENCE RECOVERS WRITING FROM ANCIENT INSCRIPTIONS

1. Introduction

Although epigraphy has profited from modern technology in recent years, little has been done to significantly improve the legibility of heavily weathered and worn stone surfaces. In 1992, M. Chambers published successful results obtained by illuminating a marble Greek inscription with two red laser beams directed through the stone.1 In 2004, collaboration between the Physics and Classics Departments at Cornell University and the Cornell High-Energy Synchrotron Source (CHESS) led to the application of X-ray fluorescence (XRF) to measure and map the concentrations of trace elements in the surfaces of three marble inscriptions.2 The images created in this way correspond exactly to the published text of the inscription, both when traces of letters are visible with the naked eye and when they are barely detectable. This method is effective for naturally worn surfaces but not intentionally erased surfaces. XRF has the potential to become a general tool for recovering legible images from abraded lettering, and can be implemented using a portable device.

2. Experiment

2.1 X-ray fluorescence

In X-ray fluorescence (XRF), a sample is illuminated with high-energy X-ray radiation. Atoms near the sample surface absorb X-ray photons and become excited into higher energy states. After a very short time interval, these atoms decay to their ground states, emitting X-ray radiation.

In order to excite X-ray fluorescence from a given element, an incident X-ray photon must have sufficient energy to remove an electron from an inner shell. The energies of the fluorescent X-ray photons depend upon the element (e.g. Ca, Fe, Pb) and the state into which the incident photon excites the element. They depend only very weakly upon the chemical environment of the element. Thus, the spectrum of fluorescence photon energies allows the elements present in the illuminated volume to be determined. The emitted intensities at each energy provide information about elemental concentrations. By raster scanning a sample through the X-ray beam and recording the emitted radiation at each position, a map or image of the distribution of each element in the sample can be generated.

A significant fraction of the incident X-rays are scattered rather than absorbed by the sample and a fraction of these reach the detector. X-rays that undergo coherent (elastic) scattering reach the detector with their energy unchanged. X-rays that undergo incoherent (Compton inelastic) scattering, in which they lose some energy to electrons in the atoms without being absorbed, reach the detector with a slightly lower energy.

2.2 Experiment

Experiments were conducted at the Cornell High-Energy Synchrotron Source (CHESS). The synchrotron’s hard-bend magnets produce “white” (polychromatic) X-ray radiation with a maximum useful energy of about 30 keV. A 25.5 Å W:C multilayer monochromator with a 1.23% band pass selected out photons with an energy near 16 keV, corresponding to an X-ray wavelength of 0.8 Å. Two pairs of mechanical slits defined a beam size of 0.5 × 0.5 mm or 0.2 × 0.2 mm, depending on the size of the lettering to be examined.

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2 We wish to acknowledge with gratitude the help of Professor Roger Bagnall of Columbia University and the staff of the Butler Library.
Ion chambers measured the intensity of the incident X-ray beam both before and after the beam-defining slits, providing a reference intensity. The incident photon flux was roughly $7 \times 10^{11}$ photons/sec/mm$^2$.

The incident X-ray beam was directed perpendicular to the plane of the inscribed stone surface. Fluorescent and back-scattered X-rays were recorded by an energy dispersive X-ray detector, oriented at roughly a 160° angle from the X-ray beam. A multi-channel analyzer (MCA) counted the number of detected photons in each of 1024 energy bins spanning the energy range between 0 and 20 keV. The MCA provided a reference signal to account for detector dead time, and normalized the photon count to the incident X-ray beam strength using the ion chamber output.

Due to changes in local surface orientation in inscribed regions and to general surface roughness, the angle of the incident and scattered/fluorescent X-rays relative to the illuminated surface varied from point to point during a scan. In some places the path to the detector passed through marble in adjacent regions, producing attenuation. These effects combined to produce uncertainties in quantitative interpretation of the image data.

In order to detect X-ray fluorescence from a given element, the emitted photon must have sufficient energy to escape the sample and reach the detector. With our air-filled paths between sample and detector, this required a minimum photon energy of roughly 3 keV. Strong Ca fluorescence from CaCO$_3$, the primary constituent of marble, dominated the energy range from 3 to 4.5 keV. Consequently, with a 16 keV incident beam our experiment was sensitive to the K lines of elements 20 (calcium) to 38 (strontium) and to the L lines of elements 56 (barium) to 83 (bismuth). These elements include those common in ancient pigments and tools with the notable exception of tin, whose fluorescence energies for a 16 keV incident beam fell within the large Ca fluorescence peak.

The inscribed stones were clamped in a vertical orientation to a carriage mounted on a pair of motorized, computer-controlled translation stages. The x-axis stage scanned the stones horizontally, with a range of motion of more than 40 cm and a resolution of about 20 µm. The z-axis stage displaced the stones vertically after each horizontal scan, with a range of motion of about 5 cm and a resolution of about 1 µm. For the inscriptions examined, this x-z range was sufficient to scan one to two letters vertically and more than five letters horizontally. Although this range was small compared to the total inscribed area, scan sizes were more constrained by the time for data collection and by handling the large amount of data produced. Optical fluorescence from the marble induced by the incident X-ray beam was found to be very helpful in defining the region to be scanned. For coarse positioning of the inscribed stones, a manually adjustable table provided an additional 50 cm of range in x and z.

Translations and MCA data collection were automated using the SPEC software package.\textsuperscript{3} Data were analyzed using the MCASPEC package,\textsuperscript{4} which runs under MATLAB. MCASPEC plots the full spectrum (counts versus energy bin) for any position on a sample’s data collection grid, calibrates the energies of the spectra using multiple reference points, and performs corrections based on the MCA’s dead-time correction signal. It determines the fluorescence intensity for a particular element by summing (after background subtraction) the number of X-ray photons detected within the characteristic energy range of that element. The resulting intensities for each element at each position on a surface can be displayed as a color-mapped image.

2.3 Inscriptions
Three marble inscriptions were investigated: CIL VI 35066 (Butler Library Inv. No. L 13), IG II$^2$ 1969 (Butler Library Inv. No. G 475), and CIL VI 12139 (Butler Library Inv. No. L 407). Their specific post-inscription history and the physical conditions to which they were exposed are not known. Stones of this type were typically chiseled flat and then inscribed using flat-bladed and pointed iron chisels. The letters were often painted, but no remaining paint was visible to the eye on any of the three inscriptions. One

\textsuperscript{3} SPEC. Certified Scientific Software. <http://www.certif.com/>

\textsuperscript{4} MCASPEC. Dr. Rong Huang, Advanced Photon Source, Argonne Nat’l Lab.
inscription, *CIL* VI 12139, contained some residual material in the most deeply inscribed areas that appeared to be dirt. Paints used in antiquity included entirely organic pigments\(^5\) made up of carbon, oxygen, and hydrogen, which could not be detected with our present XRF equipment, and pigments containing metals, many of which should be readily detectable.

Figure 1: *CIL* VI 35066 (Butler Library Inv. No. L 13). H. 26.5 cm; W. 33 cm; Th. 3 cm. This Latin inscription shows few signs of weathering or wear and is clearly readable with the unaided eye under normal illumination. The last line was intentionally erased in antiquity and is illegible. The lighting used may cause the letters to appear raised; this is not the case.

Figure 2: *IG* II\(^2\) 1969 (Butler Library Inv. No. G 475). H. 30.5 cm; W. 24 cm; Th. 10 cm. This Greek inscription has smaller and shallower letters than the Latin inscriptions. The overall topography of the surface is quite rough but it appears to be evenly weathered. Aside from a damaged area in the bottom right, the inscription is fully legible.

Figure 3: *CIL* VI 12139 (Butler Library Inv. No. L 407). H. 63.5 cm; W. 40.5 cm; Th. 6.5 cm. The surface of this Latin inscription has been naturally eroded and is nearly completely worn in parts. Details in many of the letters are not readily visible to the unaided eye.

3. Results

3.1 *CIL* VI 35066

*CIL* VI 35066 was examined first, using a 0.5 mm beam, to see what XRF could reveal in a legible inscription. Although some characters are shallower in parts, this inscription shows few signs of weathering and is clearly readable with the naked eye under normal lighting. The only significant damage is in the last line, which was intentionally erased in antiquity.\(^6\)

A fluorescence spectrum taken on an inscribed region indicated the presence of iron, zinc, and lead, with smaller amounts of other trace elements (Fig. 4). Uninscribed regions showed much smaller but still significant concentrations of these elements. The strong calcium fluorescence signal associated with CaCO\(_3\) was reduced in inscribed regions. This may have resulted from surface roughness or from absorption by metal atoms at the surface of the inscribed areas.

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\(^5\) See V. Brinkmann, *Die Polychromie der archaischen und frühklassischen Skulptur*. ??? (????).

\(^6\) Cf. the *editio princeps*, G. Olcott, *AJA* 3 (1899) 235.
Figure 4: X-ray spectrum from an inscribed point (black line) and an uninscribed point (gray line) on CIL VI 35066. The elemental electronic transitions responsible for prominent fluorescence peaks are marked. Peaks I and C are incoherent (Compton inelastic) and coherent (elastic) scattering, respectively from the incident 16 keV X-ray beam.

Inscribed areas showing more wear yielded lower iron and zinc fluorescence and higher calcium fluorescence compared with less worn areas. This can be seen in Fig. 5, which shows the letter ‘D’ using iron and calcium fluorescence.

Figure 5: The letter ‘D’ on the third line of Fig. 1, CIL VI 35066. From left to right, an optical image, an iron fluorescence (Fe K$_a$) image, and a calcium fluorescence (Ca K$_a$ + K$_b$) image, respectively. The letter can easily be discerned with the unaided eye under normal lighting. Inscribed areas show higher iron and lower calcium levels, an effect that is reduced in more worn regions such as the upper right portion of the letter.

Figure 6 shows part of the erased area and its corresponding iron fluorescence image. The latter shows some marks, including those directly visible to the eye, but clear writing could not be discerned. The iron level in erased and inscribed regions is comparable, suggesting that the iron in both cases is derived from tool wear and that similar tools were used for inscribing and erasing.

Figure 6: An intentionally erased area on CIL VI 35066, imaged optically (top) and using iron (Fe K$_a$) fluorescence (bottom). Neither image shows discernible text, although the iron fluorescence level is comparable to that found in inscribed text.

3.2 IG II² 1969

IG II² 1969 is more weathered than the first sample examined but the weathering is relatively even. It has smaller and shallower letters, and so a 0.2 mm beam was used. Unlike the other two inscribed marble stones, this stone did not phosphoresce in the visible region of the spectrum under X-ray irradiation, suggesting a difference in marble composition.

X-ray fluorescence spectra (Fig. 7) from inscribed regions indicated the presence of several elements, including iron, zinc, lead, and copper. All of the trace elements except copper were clearly present in larger concentrations in the inscribed regions than in the uninscribed regions.
X-ray Fluorescence Recovers Writing from Ancient Inscriptions

Figure 7: X-ray spectrum from an inscribed point (black line) and an uninscribed point (gray line) on IG II² 1969. Prominent fluorescence peaks are marked. The peaks I and C are incoherent (Compton inelastic) and coherent (elastic) scattering, respectively.

However, iron fluorescence images of a letter Σ (Fig. 8) are not as clear as for CIL VI 35066. The source of this problem is that the variation in iron fluorescence levels among points is large compared to the difference between the average iron fluorescence levels for inscribed and uninscribed areas. These variations are, however, a factor of 10 larger than the expected statistical fluctuations in photon count and so reflect actual concentration differences. Similar intensity variations were observed for the other trace elements. This suggests that the elements present in the background may have been introduced by tools used in flattening the surface, but similar levels of variation were not observed in the other inscriptions.

Figure 8: A letter Σ on IG II² 1969. From left to right, an optical image (taken from Fig. 2), an iron fluorescence (Fe Kα) image, and a calcium fluorescence (Ca Kα + Kβ) image. Inscribed regions show somewhat higher iron fluorescence.

3.3 CIL VI 12139

The Latin inscription CIL VI 12139 is well-suited to XRF examination. The letters are large, so a 0.5 mm beam and a coarse scan could be used to increase measured fluorescent photon counts and decrease data collection time. The surface has been naturally eroded and is nearly completely worn in parts. Details in many of the letters are not readily visible to the unaided eye, as can be seen in Fig. 3.

Typical spectra from inscribed regions indicated the presence of iron, zinc, lead, and copper (Fig. 9) at much higher concentrations than in uninscribed regions. Lead contrast was particularly strong and, as in CIL VI 35066, calcium fluorescence was generally lower in inscribed regions.

Figure 9: X-ray spectrum from an inscribed point (black line) and an uninscribed point (gray line) on CIL VI 12139. Prominent fluorescence peaks are marked. The peaks I and C are incoherent (Compton inelastic) and coherent (elastic) scattering, respectively.

Three segments of text that contained heavily worn letters or letter fragments were scanned. Figure 10 shows the first scanned segment. In the optical image, the left and center strokes of the ‘A’ and right stroke of the ‘V’ are particularly faint. The iron fluorescence image is not a significant improvement, but the lead fluorescence image clearly shows the full original lettering. The
poorer contrast in the iron image is due to large background iron levels in the uninscribed areas, either due to iron impurities present in the marble or to iron residues from tool wear during initial surface flattening. The background lead levels in uninscribed regions are much smaller, producing much larger contrast between inscribed and uninscribed regions.

Figure 10: A worn region of text ("IVSAL", part of line 6: A · PopilliIVS · A · L · Chrestio) on CIL VI 12139. From top to bottom: an optical image, an iron fluorescence (Fe Kα) image, and a lead fluorescence (Pb Kα) image. The letters are legible with the unaided eye using oblique lightning, but more worn portions of some letters cannot be discerned. Inscribed regions show higher iron and lead fluorescence.

Lead fluorescence was again the most revealing in the two other regions scanned, shown in Fig. 11. Wear patterns are similar in all regions. The ‘A’, one leg of the ‘V’, and the ‘C’ are heavily worn but easily visible in the lead XRF image. Optical observation under high magnification shows no visible differences between inscribed and uninscribed regions that would indicate differences in composition.

Figure 11: Two worn regions of text from CIL VI 12139 and their corresponding lead fluorescence images. As in Fig. 9, the letters are decipherable with the unaided eye using oblique lightning, but more worn parts of letters cannot be discerned. The letters of the upper text are “VSALCH”, part of line 7: A · PopilliVS · A · L · CHresimus; the lower, “LLAC”, part of line 8: Popillia · A · L · LAChe. Strong lead fluorescence is visible even in the heavily worn inscribed regions.

4. Discussion

X-ray fluorescence data indicate that many elements are introduced into the stone by inscription and that the suitability of a particular element for recovering text varies among inscriptions.

The origins of the trace elements observed by XRF in inscribed regions are unclear, although they are most likely derived from the tools and paints used in the original inscription. Iron residues may be due to wear of iron/steel chisels. The large background iron levels seen in uninscribed regions suggests the use of iron tools for initial surface flattening. Iron ores and ancient steels can contain small amounts (roughly 1%) of copper, but negligible amounts of lead and zinc. Iron in inscribed regions may also be due to iron-containing red, yellow (massicot) and ochre pigments; the use of red pigments was especially common. Similarly, lead in inscribed regions may be due to lead-containing white, yellow, and red pigments, and copper may be due to green (malachite) or blue (azurite) pigments. However, since inscribed letters were typically painted with one or at most two pigments, the coincidence of all three elements at the same point in an inscription (as in Fig. 8) is a bit surprising. Even more surprising is the presence of large concentrations of zinc, an element not found in steels or in common pigments. The coincidence of copper, lead, and
zinc could indicate the use of tools made from bronze alloys. Bronze will cut marble, but not as well as iron or steel. It is more expensive and harder to make, and alloys with sufficient hardness are more brittle. Tin, the other major constituent of bronzes, could not be examined because the 16 keV X-rays used to illuminate the stones could not excite tin’s K X-ray fluorescence. Additional experiments to evaluate tin concentrations would help resolve the source of these elements.

Based on the present very limited data, lead – when present – may be particularly useful in recovering text. For CIL VI 12139, rough calculations indicate that the average lead fluorescence intensity in inscribed regions corresponds to a thickness of pure lead of 10 nm. The X-rays sampled a depth on the order of 100 µm. If the lead were evenly distributed over this depth, its concentration would be roughly 100 ppm. Extrapolating measured high-temperature diffusion rates of lead in single-crystal, crack-free calcite7 (a primary constituent of marble) to typical environmental temperatures gives diffusion distances of less than one unit cell. Thus, simple lattice diffusion cannot account for the presence of lead in regions eroded to depths on the order of a millimeter beneath the original contours of the inscribed stone. Diffusion or other means of transport (e.g., infiltration of acidic rain containing dissolved carbon dioxide) along cracks and grain boundaries is more likely responsible for the persistence of lead in the eroded marble surface.

5. Summary

The present experiments have established the potential of X-ray fluorescence to reveal traces of letters on abraded surfaces of ancient inscriptions, and to provide information about how the inscriptions were created. The small number of inscriptions examined here is not sufficient to establish this method’s overall effectiveness and the factors relevant to its successful application. A proof-of-concept study on an inscription with unrecovered text is required. This should employ a uniformly but modestly eroded stone and more advanced data collection and analysis protocols to maximize fluorescence signal-to-background and to extract character patterns from noisier data. Characterization of the composition of ancient marbles, tools and pigments by XRF or related techniques, together with an understanding of how tool and pigment residues weather, wear, and infiltrate marble would be valuable in interpreting observed trace element concentrations and distributions. With further development, X-ray fluorescence has the potential to become an essential tool in epigraphy. By revealing text that has long been hidden, it may shed new light on many ancient civilizations.

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