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The Relationship between Inherent Material Evidence in Cultural Heritage and Preservation Treatment Planning: Solving the Ptolemy Puzzle, Part II

ABSTRACT

The ongoing technical study and conservation of an important historic atlas, a 1513 hand-colored edition of Ptolemy's *Geographia* in the Library of Congress' Lessing J. Rosenwald Collection, is discussed from the point of view of how technical analysis, in particular elemental analysis by X-ray fluorescence, contributes to an understanding of the provenance, method of manufacture, treatment history, and present condition. Results strongly suggest that a subset of maps were treated with a potash alum-gelatin sizing or coating, which appears to have had a major role in the degradation of both the paper substrate and a green copper-based pigment.

INTRODUCTION

It is a given that curators, conservators and cultural heritage scientists are united in their endeavor to preserve and maintain access to cultural heritage. It is also a given that these experts tend to approach collection items with different sets of questions and viewpoints, variously placing value on aesthetics, historical evidence and condition. Amid the balancing act between intrinsic value, condition, and intended use that is part of preservation planning, the question arises as to whether there is inherent tension between preservation of both intangible material "evidence" and the tangible object. Conservation protocols include many physical treatments that are applied using current knowledge and materials. While interventions purposely alter chemical and/or physical properties of an object to enhance stability and handling, as conservators and scientists are keenly aware, treatments may also subtly alter material evidence. The advent of improved, non-invasive analytical tools, such as X-ray fluorescence (XRF) and spectral imaging, has raised our awareness of what this trade-off may entail. The body of analytical evidence these techniques gather without sampling and time consuming analysis can add valuable information regarding an artifact's provenance, history of manufacture and treatment history. Yet, the window of opportunity to collect this somewhat vulnerable evidence is most often before treatment. Are, then, scientific analysis and conservation protocols driven by conflicting values or mutually beneficial?

The ongoing technical study and conservation of an important historic atlas, a 1513 hand-colored edition of Ptolemy's *Geographia* in the Library of Congress' Lessing J. Rosenwald Collection, is a case in point (Albro et al. 2011). This paper highlights non-invasive elemental analysis by XRF that, in combination with other analyses, has made significant contributions to decipherment of the object's provenance, method of manufacture, treatment history, and present condition. These results assist, although they delay, the treatment planning and execution of this important volume.

EXPERIMENTAL

XRF was conducted using a Bruker Tracer TurboSD energy dispersive XRF spectrometer. The instrument has a miniature X-ray tube, Rhodium anode and silicon drift detector; it was operated on a tripod with vacuum pumping at either 15 kV and 55 μA or 40 kV and 20 μA, with or without a titanium filter; exposures were 180 seconds. The instrument beam spot has a size of approximately 3 x 4 mm. All XRF data are analyzed qualitatively as difference spectra from the average paper spectrum background; spectra shown below are not normalized, since scattering is essentially equivalent for comparison. XRF analysis was augmented by spectral imaging, conducted using an Artist® Multispectral Imaging System in the Conservation Division. Results obtained by these two non-invasive methods lead to further analysis of several microsamples. Fourier-transform infrared (FTIR) microscopy was conducted using a Thermo Nicolet Nexus 670 spectrometer equipped with a Smart DuraScope attenuated total reflectance (ATR) accessory with a diamond crystal and DTGS CsI detector. Spectra

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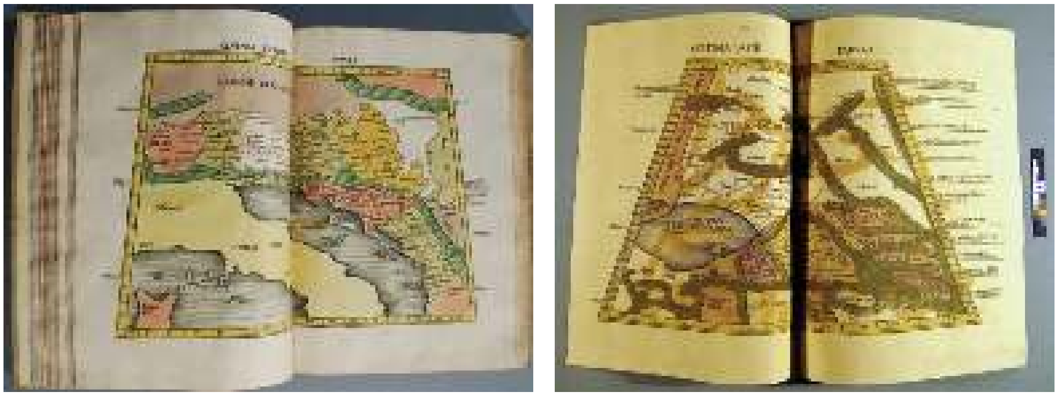

Fig. 1. Quinta Europa Tabula map (left) and Septima Asiae Tabula map (right) from Ptolemy *Geographia*, 1513, Rosenwald Collection, Library of Congress, showing a map in good condition compared to one in relatively poor condition with visible offset from green pigmented areas

were collected at 4 cm^{-1} for 128 to 1064 scans. In addition, micro-X-ray diffraction (μXRD) was carried out on a Rigaku D/Max Rapid instrument at The Smithsonian National Museum of Natural History. The equipment has an image plate area detector, and was run using monochromatic molybdenum Kα (λ = 1.42 Å) radiation at 200 kW. Samples were mounted on glass fibers in a collimated beam (0.3 or 0.1 mm); goniometer parameters were: *chi* fixed at 45°, *omega* fixed at 1°, 2°, or 3°, and *phi* spun through 360° rotation at 1° s^{-1}. Patterns were integrated with *AreaMax* software and qualitatively matched using *Jade* 7.5 software and the International Center for Diffraction Data database.

RESULTS AND DISCUSSION

Materials analysis of the 1513 Rosenwald Ptolemy atlas has been an integral part of its technical study. Analysis initially focused on solving why only seven out of the 47 maps are in poor condition. Figure 1 illustrates the difference in visual appearance of a map in relatively pristine condition, the Quinta Europa Tabula (left), and one in poor condition, the Septima Asiae Tabula (right). The images also show that an overly tight rebinding led the volume to be pinched in the gutter region and difficult to open without causing damage, which was why the volume was sent for conservation (Albro et al. 2011). As seen in figure 1, the Septima Asiae map exhibits yellow-brown and embrittled paper, with green pigment that has turned muddy or brown and caused both offset staining and strikethrough. These features are typically associated with verdigris syndrome, i.e., deteriorated copper acetate-based pigment that has induced cellulose degradation (Scott et al. 2001). While XRF analysis readily provided proof that the green pigment found throughout mountain details of the atlas is copper-based, XRD, FTIR and Raman analyses have yet to confirm that the pigment is actually verdigris. On the other hand, no evidence has been obtained that the pigment is another likely copper-based pigment, such as malachite or azurite plus an organic yellow colorant. Whether the green pigment is verdigris or not, however, does not explain

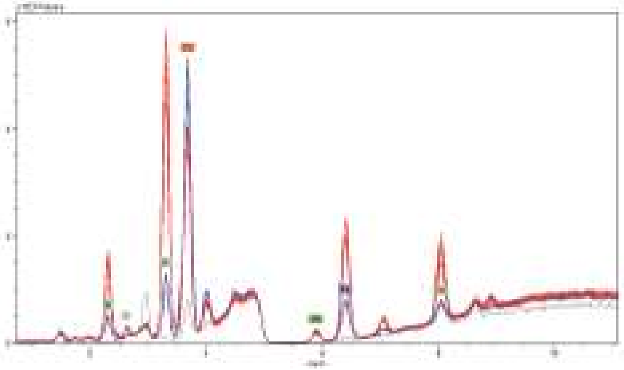

Fig. 2. XRF spectra of paper spots from Quinta Europa map (good condition, 5 spots) and Septima Asiae Tabula (poor condition, 10 spots); the grey line shows the air spectrum, which contains peaks that are artifacts from materials in the instrument. Peak labels are shown directly above peaks in the Quinta Europa map spectra

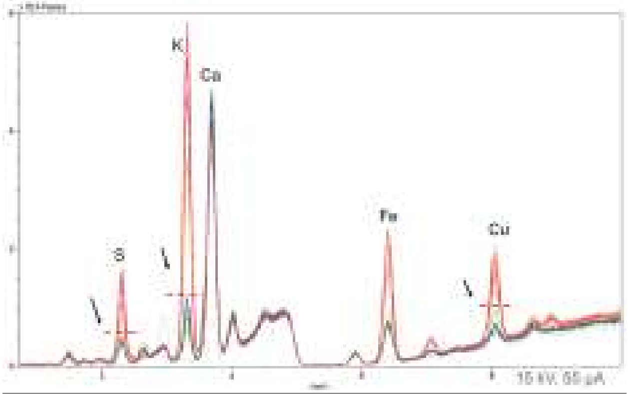

Fig 3. XRF spectra of paper spots from Quinta Europa (blue), Tabula Moderna Bossinae, Tabula Prima Africae, Tabula Prima Asiae, Nona Asiae Tabula, Tabula Secunda Africae, and air spectrum (grey); dotted lines and arrows indicate approximate demarcation of map groups in terms elements associated with good vs. poor condition by dotted lines

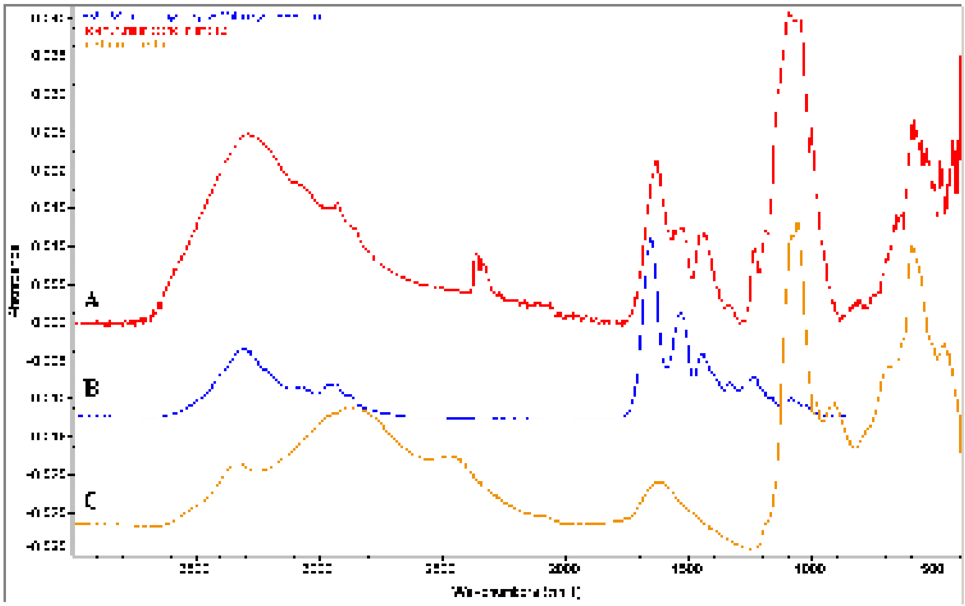

Fig. 4. FTIR analysis of the white accretion: A) ATR spectrum, after correction, of a sample of whitish accretion taken from Nona Asiae Tabula; B) transmission reference spectrum of gelatin (IRUG database); and C) ATR spectrum, after correction, of fresh potassium alum powder

why a select number of maps exhibit advanced degradation, including, in some cases, a whitish accretion over the surface.

XRF analysis was conducted on a group of maps and text pages in various conditions to further explore this question. Figure 2 compares spectra from uncolored and unstained areas of the paper substrates of the Quinta Europa and Septima Asiae maps (fig. 1). Results show that the paper in poor condition is associated with relatively higher concentrations of iron (Fe) and copper (Cu). These transition elements are well known to be catalysts for cellulose degradation and may provide at least partial explanation for the observed differences in condition (Shahani and Hengemihle 1986). In addition, it is noted that calcium (Ca), which is generally associated with a beneficial effect on paper longevity, appears somewhat higher in the Quinta Europa map. A better statistical sampling of Ca in the papers would, however, be required to make firm conclusions about whether this element plays a positive role in the condition of some maps. What is most noteworthy, however, is that the map paper in poor condition is also associated with relatively high amounts of potassium (K) and sulfur (S). This suggests the presence of potash alum, $KAl(SO_4)_2$. While relatively minor amounts of K and S, as detected in the Quinta Europa map, could reasonably be ascribed to an alum-hardened sizing on the paper, the finding of much higher detected levels of K and S in the Septima Asiae Tabula map requires more explanation.

Figure 3 shows XRF spectra of the paper substrates in five additional maps overlaid with that of the Quinta Europa. Together, these spectra reveal two distinct groups in terms of elemental composition, where Group I contains relatively lower levels of Cu, K and S, and Group II contains relatively higher levels of these elements. These two groups correspond fairly neatly, in fact, to maps in good or poor condition, the latter three (Tabula Prima Asiae, Nona Asiae Tabula, and Tabula Secunda Africae) having symptoms similar to those described in the Septima Asiae Tabula. These results lead to the hypothesis that the substance associated with K and S, presumably potash alum, has had a direct impact on the condition of the map paper and that this is not typical verdigris syndrome.

Figure 4 shows the FTIR spectrum of a sample of the whitish accretion from the Nona Asiae Tabula map. Comparison to reference spectra shows that the removed sample matches well with a combination of potash alum and gelatin. Additional XRF analysis of the in situ accretion without a Ti filter (not shown) reveal the presence of aluminum (Al), plus even higher detected levels of K and S than in other areas of the paper. These results confirm that the white surface accretion and paper substrates of maps in poor condition contain a highly concentrated potash alum-gelatin sizing or coating. This solution was evidently brushed onto the maps, as evidenced by brushstrokes that are clearly visible in UV imaging (Albro et al. 2011). This may correspond to a "strengthening treatment," which is known to have been popular until relatively recently in areas such as Eastern Europe (Khan 2011). Brushing of the solution over the face of the maps would explain the presence of elevated Cu in all of the treated map papers (figs. 2–3): in other words, the treatment most likely spread copper from the pigment throughout the

Fig. 5. Detail of Nona Asiae Tabula, showing preserved green pigment and paper in the gutter region, vs. altered green pigment and browned paper outside of the gutter region

paper, rendering these substrates much more prone to future degradation (Shahani and Hengemihle 1986). The solution was concentrated enough to cause precipitation of the potash alum over time in some cases.

The most striking evidence pertaining to this reconstructed treatment history was discovered after reinforcing strips over the original guards were removed from the gutter of most maps. At this time the maps could be fully opened and it was observed that, as shown in a detail of Nona Asiae Tabula (fig. 5), the gutter regions of treated maps appear preserved in terms of undeteriorated green pigment and brighter paper. In contrast, deterioration of the green pigment outside of the gutter region, where elevated potash alum is detected, is evident. Therefore, we may posit a direct cause and effect between the potash-alum treatment and the poor condition of the treated maps.

The answer to why the potash alum solution was applied to select maps in the first place may be related to the existence of several types of paper used in the production of the original atlas, as well as the overly tight binding. During initial examination, conservators noted that the volume contains three basic types of paper: 1) a crown watermarked paper of generally high quality manufacture in good condition (used for maps only); a minority of fleur-de-lys watermarked paper of intermediate quality (used for some maps and text); and a large number of unwatermarked, visibly poorer quality papers, that were used for both maps and a large portion of the text (Albro et al. 2011). As mentioned above, XRF analysis of the paper substrates suggests that papers in poorer condition have a relatively low ratio of Ca to Fe (figs. 2–3). This observation generally applies to maps and text on unwatermarked paper and suggests that these papers are inherently at risk for deterioration. Perhaps at the time of modern rebinding and treatment, maps on unwatermarked paper were beginning to show browning, weakening and copper staining. These maps would have been especially prone to tearing from handling in the restrictive binding. However, a few maps on good quality paper also experienced handling tears, which explains their removal for pulp repairs. These two conditions, deteriorated paper and handling tears, provide rationale for removal and overall treatment of a select group of maps, possibly at the same time as the twentieth century rebinding (Albro et al. 2011).

There are several important implications of this treatment history. First, XRF analysis of removed guards shows that the potash alum is easily removed by washing; this will directly impact the conservation treatment strategy for the maps. Second, the revelation of the potash alum treatment not only helps our understanding of the condition, but is part of the volume's history and provenance. Third, analysis reveals important potential causes of "verdigris" syndrome, which will impact its treatment and lead to a better understanding of this commonly observed phenomenon. The treatment plan, which is still evolving, will take into account this intangible material evidence, which is now documented. Results of this ongoing study will be elaborated in an upcoming publication.

CONCLUSION

Ongoing technical study and conservation of an important historic atlas, a 1513 hand-colored edition of Ptolemy's *Geographia* in the Library of Congress' Lessing J. Rosenwald Collection, has been analyzed non-invasively by XRF, in combination with some other techniques. Results show the presence of a potash alum-gelatin sizing or coating, which was likely to been applied during a later intervention, possibly a twentieth century rebinding. This treatment appears to have had direct and dramatic impact on the condition of seven maps, which are now in quite poor condition in terms of both the paper substrate and a green, copper-based pigment. Further study of the relationship between inherent paper quality, current condition and past treatment in the 1513 Ptolemy atlas is expected to lead to a better understanding of the substrates' condition and a reappraisal of what was at first thought to be typical "verdigris" syndrome. These results assist in the treatment planning and execution of this important volume, and also have made significant contributions to decipherment of the object's provenance, method of manufacture, treatment history, and present condition.

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