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# Pigment and Ink Analysis of University of Portland Library's Illuminated Manuscripts using Spectroscopic Techniques

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## Abstract

Raman and XRF spectroscopy were used to analyze pigments and inks of five illuminated manuscripts from the University of Portland's Clark Library Special Collections. The five manuscripts were acquired at different times. Some were collected by members at the university and have been in the Special Collections for years. Others were recently acquired from Marylhurst University after the school's closure in 2018. To address questions regarding their authenticity and possible origin, this study, which is the first of its kind on these manuscripts, was begun. Pigment analysis found the presence of phthalocyanine green dark, first made in the 1930s, in the first manuscript. Burnt sienna, not known as a pigment until the 18<sup>th</sup>-century, was also found in this same manuscript. In two sheets, analysis revealed the presence of vermilion, which is a common pigment for the time period that these manuscripts were thought to be from. Due to interrupted access to the manuscripts as a result of the pandemic, more information was unable to be collected, meaning few conclusions could be made about all five manuscripts. The work presented here aims to inform future analysis of these manuscripts, so that the authenticity and origin of these manuscripts can be better understood.

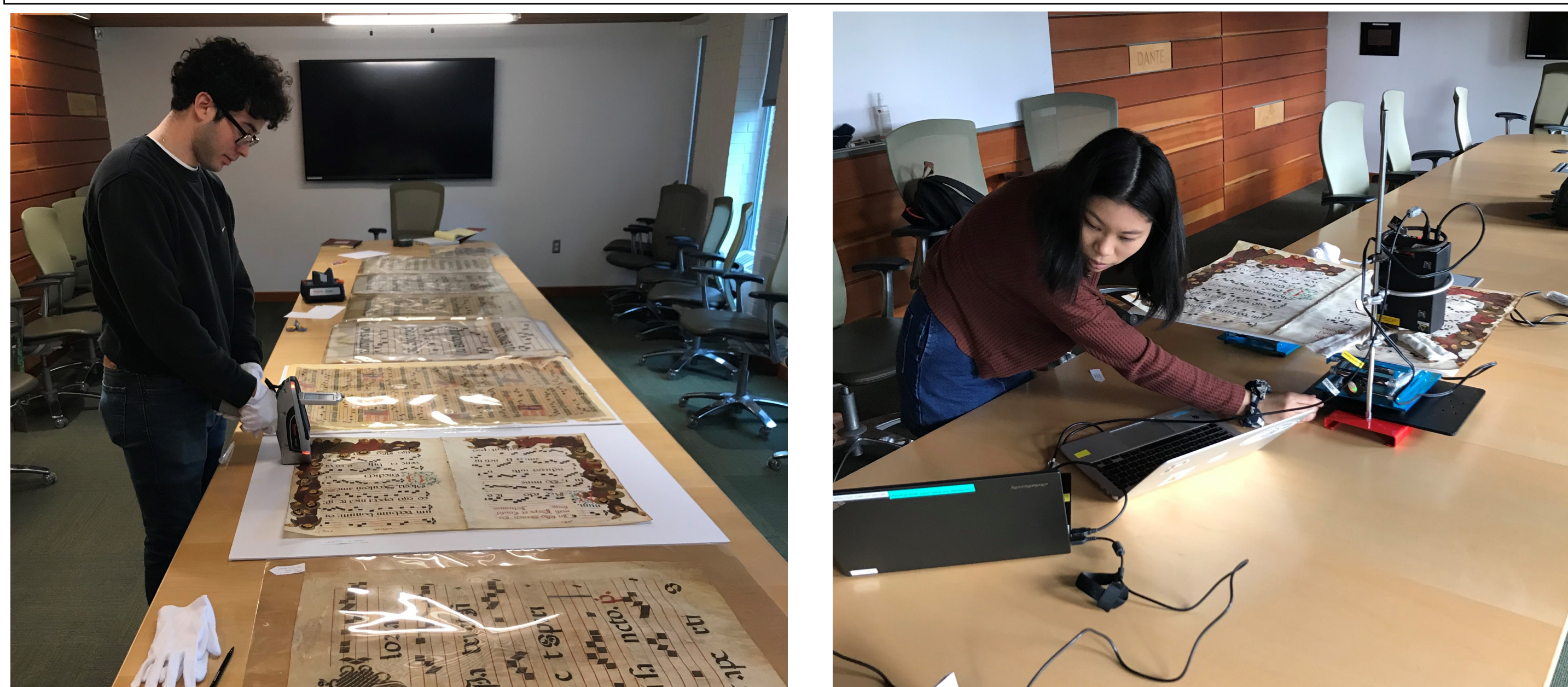


Figure 1. UP students using portable XRF and Raman spectrometers to examine medieval manuscripts in the UP Clark Library

## Experimental Methods

### XRF

Portable XRF measurements were performed *in situ* with a handheld Thermo Scientific Niton XL3t GOLDD+ analyzer equipped with an Ag anode (50 kV and 200  $\mu$ A) X-ray tube. Typically, measurements were made in two modes: Mining Cu/Zn (better for wt. % > 1%) and Soil modes (better for wt. % < 1%) for 120 s each. Found elements are listed in order of decreasing weight percentage.

### Raman

Raman data was collected using a portable Delta Nu Inspector Raman spectrometer with an excitation wavelength of 785 nm and maximum laser power of up to 13 mW. Spectral resolution was set to 15  $\text{cm}^{-1}$ . Total integration times (time per scan x number of scans) were up to 8 mins.

## References

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Figure 2. Graduale, 12<sup>th</sup> Century Medieval Manuscript, 55 cm x 39 cm.

## Graduale

The description in the [Clark Library Digital Collections](#): Six lines of chant music with black neumes on five-line staff. Border decoration in left and lower margins of nine Franciscan friars wearing brown habits with bands of gold on sleeves and in cowls. Additional information: It was cataloged by a nun who helped catalog the rare book room when UP still had a Library Science program. Catalog notes date back to about 1949. Calligraphic notes: S of Sacerdos, B of Benedicta; both red and gold with green leaves. The reverse side is much less decorated.

## Results and Discussion

### Phthalocyanine Green Dark

The Raman spectrum in Figure 3 shows bands at 682, 735, 770, 1209, 1279, 1337, and 1535  $\text{cm}^{-1}$  which match those for the known pigment phthalocyanine green dark (also known as pigment green 7 with formula  $\text{C}_{32}\text{Cl}_{16}\text{CuN}_8$ ). XRF analysis found a small amount of copper and chlorine in another spot with similar green decoration which further supports the identification of the pigment. The presence of this pigment suggests that the manuscript may have been modified because phthalocyanine green dark was not available commercially until 1938.

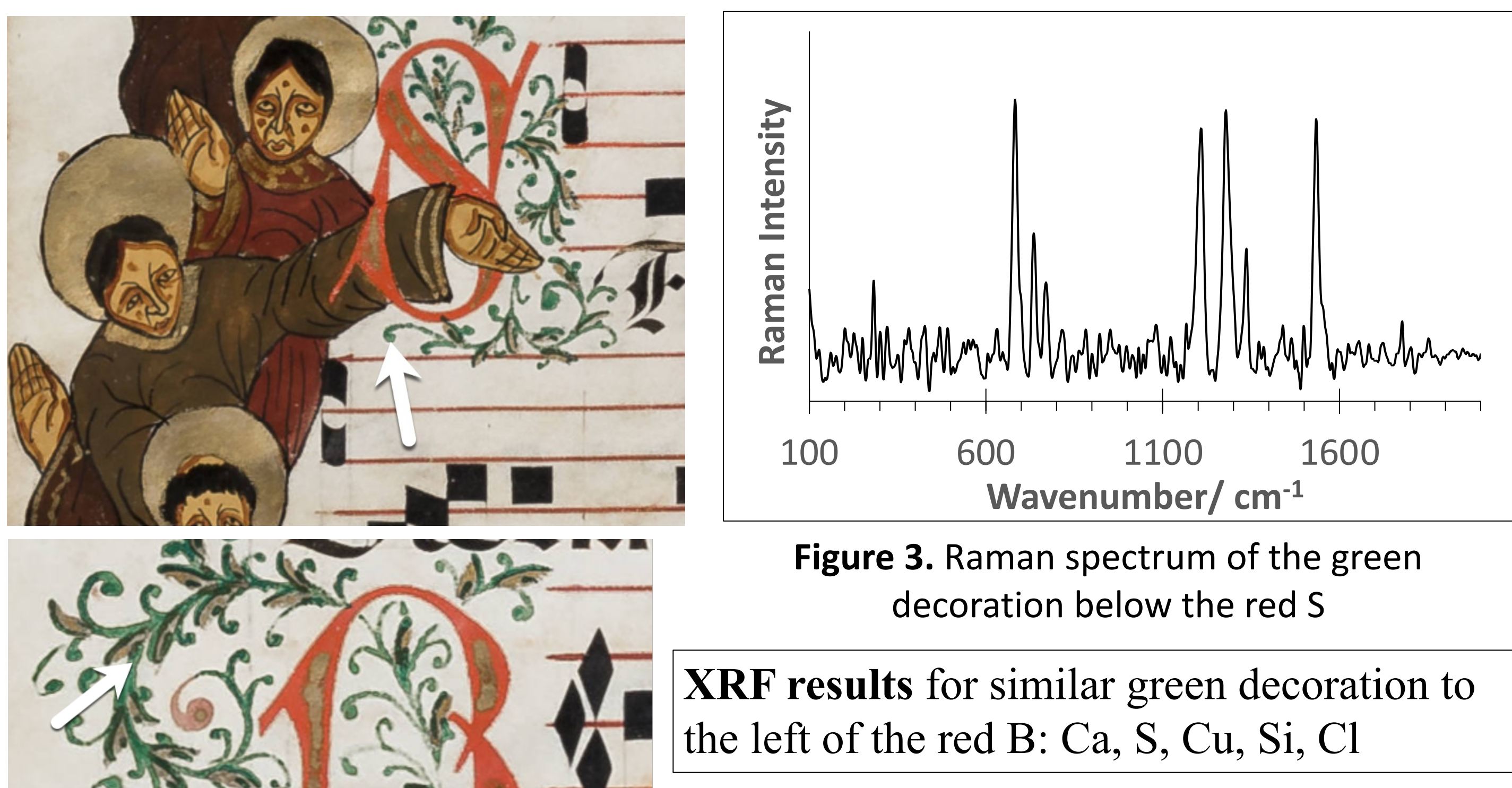


Figure 3. Raman spectrum of the green decoration below the red S

XRF results for similar green decoration to the left of the red B: Ca, S, Cu, Si, Cl

### Vellum and Black Ink

XRF results for vellum: Ca, S, Si, K

XRF results for black ink: S, Ca, K, P, Si, Fe (small)

Despite many attempts, no Raman bands were found for the ink.



Figure 4. Examined areas of vellum and black ink

## Burnt Sienna

The Raman spectrum in Figure 5 has bands at 219, 284, and 395  $\text{cm}^{-1}$  which are consistent with the literature spectrum for burnt sienna, an iron oxide with varying amounts of clay and quartz. The XRF data also showed that Fe is present in this area. Therefore, the pigment in this area was identified as burnt sienna. The peaks at 1124 and 1337  $\text{cm}^{-1}$  are possibly from clay, quartz, or another iron oxide mixed in. Burnt sienna was not known as a pigment until the 18<sup>th</sup>-century.

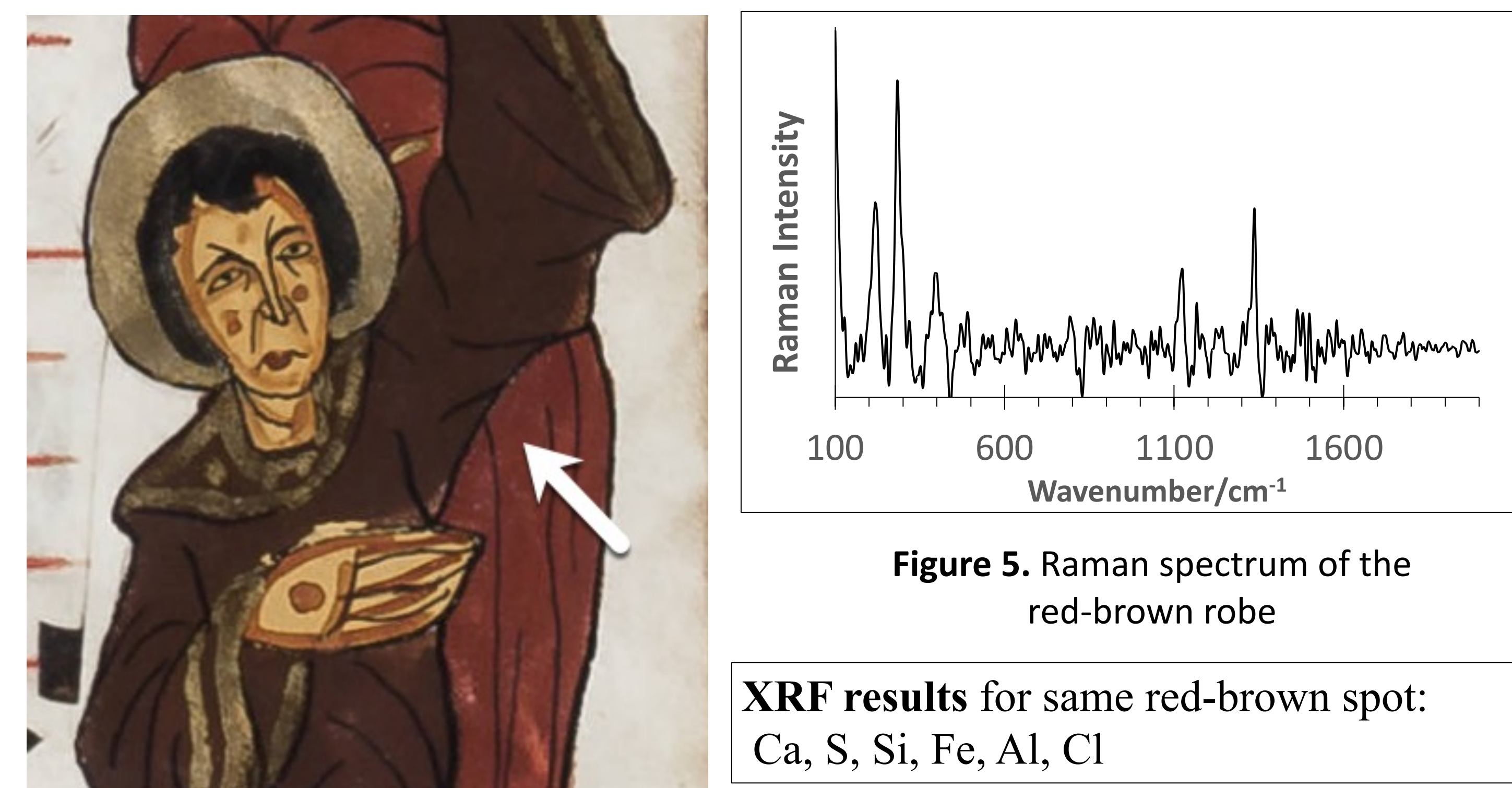


Figure 5. Raman spectrum of the red-brown robe

XRF results for same red-brown spot: Ca, S, Si, Fe, Al, Cl

## Vermilion

The Raman spectrum in Figure 6 has bands at 251, 282, and 342  $\text{cm}^{-1}$ , which are characteristic of vermilion ( $\text{HgS}$ ). Mercury and sulfur are present in the XRF data for another spot with similar red color confirming this assignment. Vermilion has been used as a pigment for millennia, so its identification is not helpful for dating purposes. Gold was also found by XRF in the red B area.

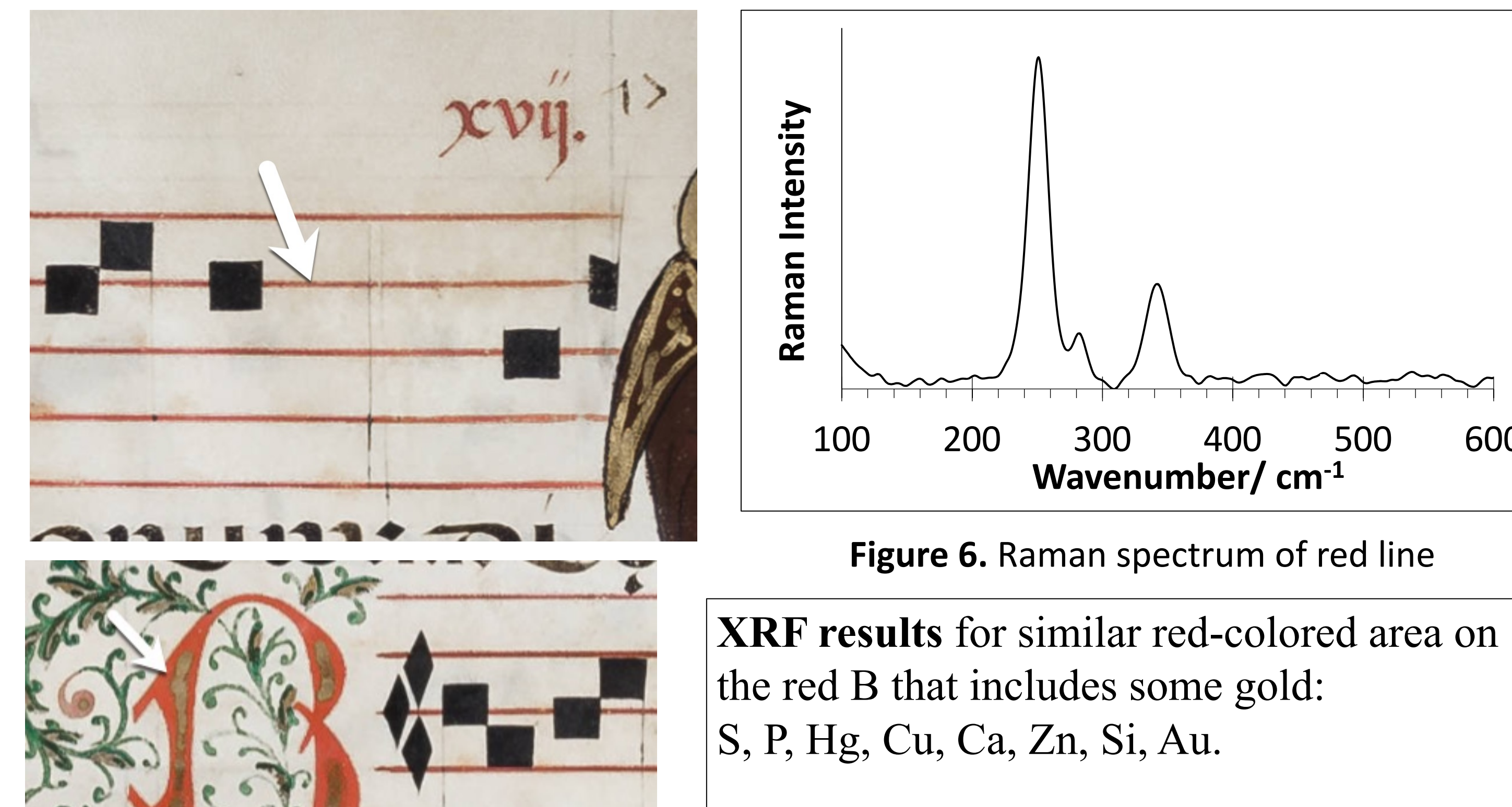


Figure 6. Raman spectrum of red line

XRF results for similar red-colored area on the red B that includes some gold: S, P, Hg, Cu, Ca, Zn, Si, Au.

## Conclusions

- 1) The identification of phthalocyanine green dark and burnt sienna suggests that the Graduale may not actually be a 12<sup>th</sup> century manuscript or that it was significantly modified later, most likely the latter. The anachronistic pigments appear only in the Franciscan friars and the green leaves, and the reverse side does not have these decorations.
- 2) Iron was found in the ink, so may be iron gall ink, commonly used in medieval manuscripts. Unfortunately, no identifying Raman bands have yet been found.
- 3) Gold, commonly used in medieval manuscripts, was found in the decorated B.
- 4) The historic pigment, vermilion, was found in the Graduale and in a second medieval manuscript (not shown here).
- 5) Future plans are to continue the analysis of the Graduale and the other four medieval manuscripts associated with this project.

## Acknowledgements

The chemists in the group greatly appreciate the opportunity to analyze medieval manuscripts in UP's Clark Library. Many thanks to all who helped make this possible!