Non-destructive Identification of Turquoise Inlay on Chinese Belt Hooks

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Introduction

- Dr. Paul Singer collection of the Sackler includes 44 inlaid belt hooks
- Burial conditions caused much original inlay to be lost or damaged
- Many belt hooks had some or all of lost inlay replaced
- Identification of the inlay materials can help determine authenticity
- Traditional methods of turquoise identification require sampling
- The small size of the inlay pieces makes sampling problematic: a non-invasive identification method is needed
- Scientific literature mentioning the distinctive reflectance spectrum of turquoise showed the potential of non-invasive fiber optic reflectance spectroscopy (FORS)
- Ten belt hooks with a variety of inlay materials were selected for intensive study

Belt Hooks

- Worn horizontally with the button attached to one end of the belt and the hook to the other
- First found in China in 6th century BC; by 2nd century AD largely replaced by belt buckles
- Earliest belt hooks were plain and small; later hooks were larger and more ornate, with inlay and gilding indicating luxury status
- Very common objects in burial sites, belt hooks are usually bronze, but also made of solid jade, iron, bone, gold or silver
- Many belt hooks made after the late 5th century BC were inlaid with precious materials such as gold, silver and turquoise

Turquoise

- Turquoise is a hydrated copper aluminum phosphate:
  $CuAl_6(PO_4)_4(OH)_8 \cdot 5\,H_2O$
- Iron can substitute for the aluminum in the turquoise structure
- Copper and iron give turquoise its characteristic blue-green color
- Mined in Asia, Europe, and both North and South America
- Turquoise was available in China from mines and trade along the silk route
- Many materials have been used to imitate turquoise, including:
  - Dyed bone and odontolite (copper colored fossilized bone)
  - Other blue-green minerals such as chrysocolla, lazulite, and wardite
  - Glass
  - Enamel
  - Stained minerals
  - Plastics
  - Fragmented, degraded or inferior turquoise dyed and/or impregnated with resin

Scientific Methods of Turquoise Identification

X-Ray Diffraction

- Unique turquoise spectrum
- Used for identification in jewelry industry
- ✗ Requires sample

Fourier Transform-Infrared Spectroscopy

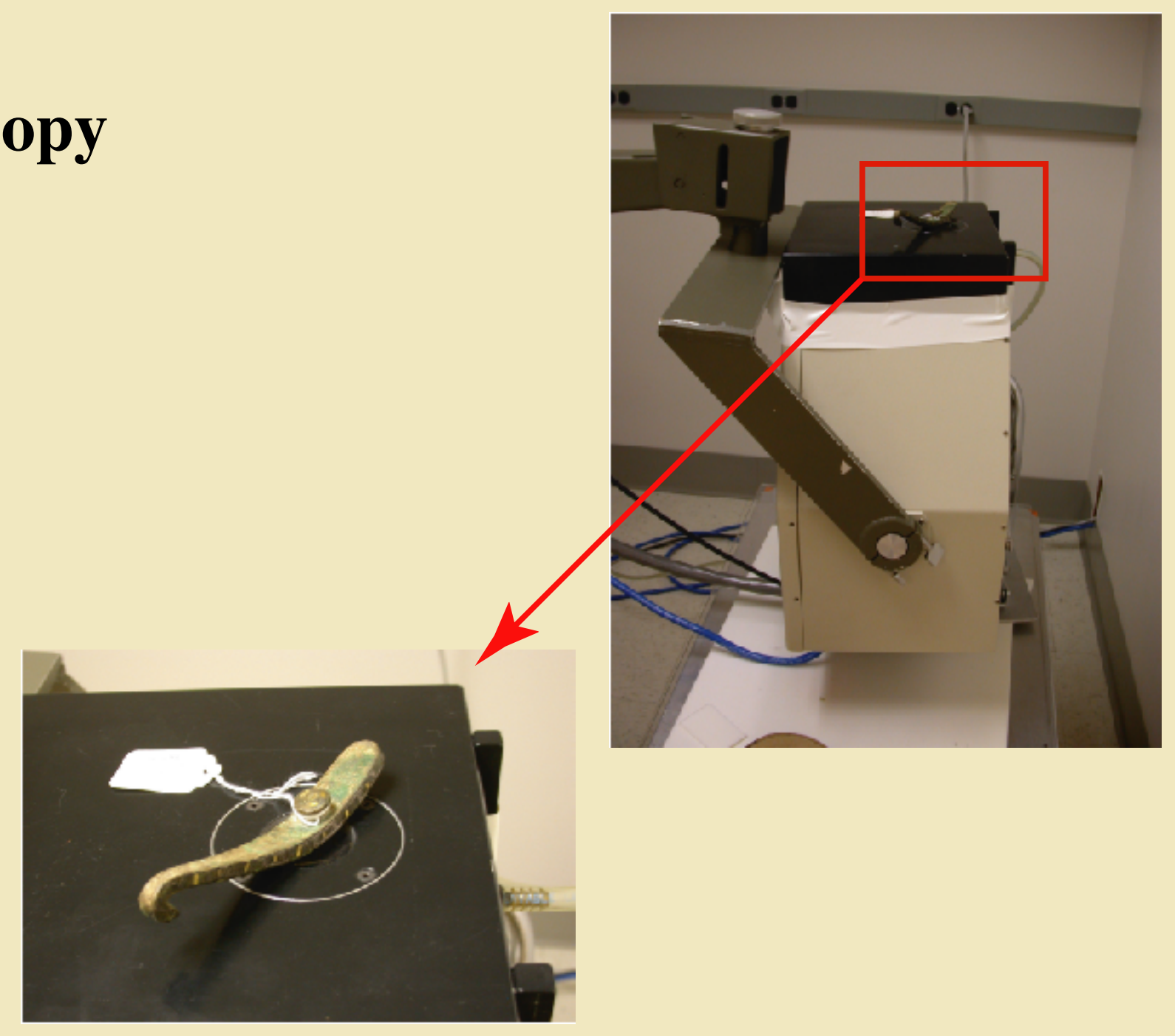
- Unique turquoise spectrum
- Used for identification in jewelry industry
- Can show organic additions
- ✗ Requires sample

Ultraviolet Examination

- No sampling
- No fluorescence under short wave UV light
- Variable fluorescence under long wave UV light
- ✗ Can't identify turquoise, only some substitutes

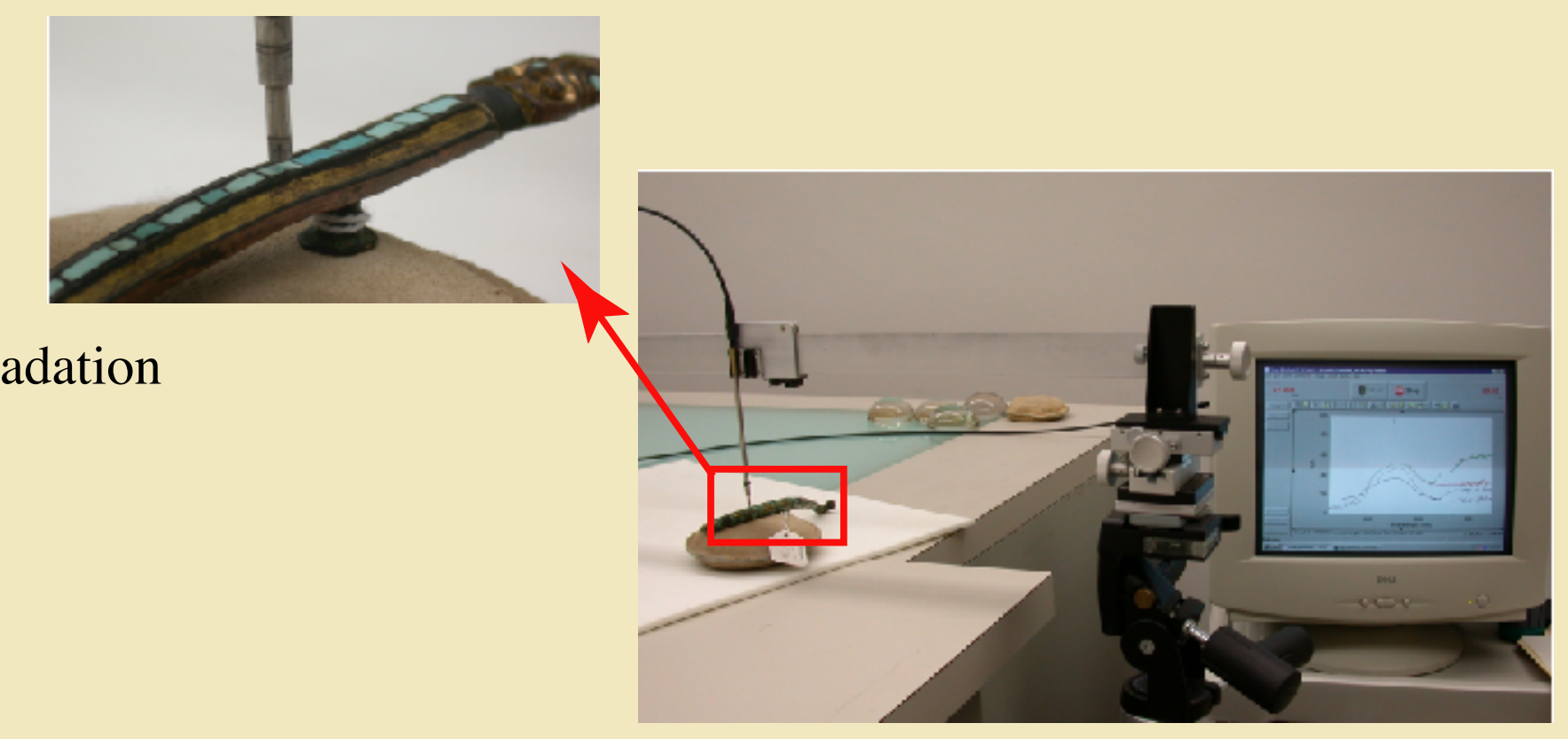
X-Ray Fluorescence Spectroscopy

- No sampling
- Identifies presence of aluminum and phosphorus
- ✗ Large spot size (~1 cm)
- ✗ Requires use of helium chamber to see phosphorus and aluminum
- ✗ Aluminum peak is often too small to observe, even using helium chamber
- ✗ Gilding interferes with phosphorus identification

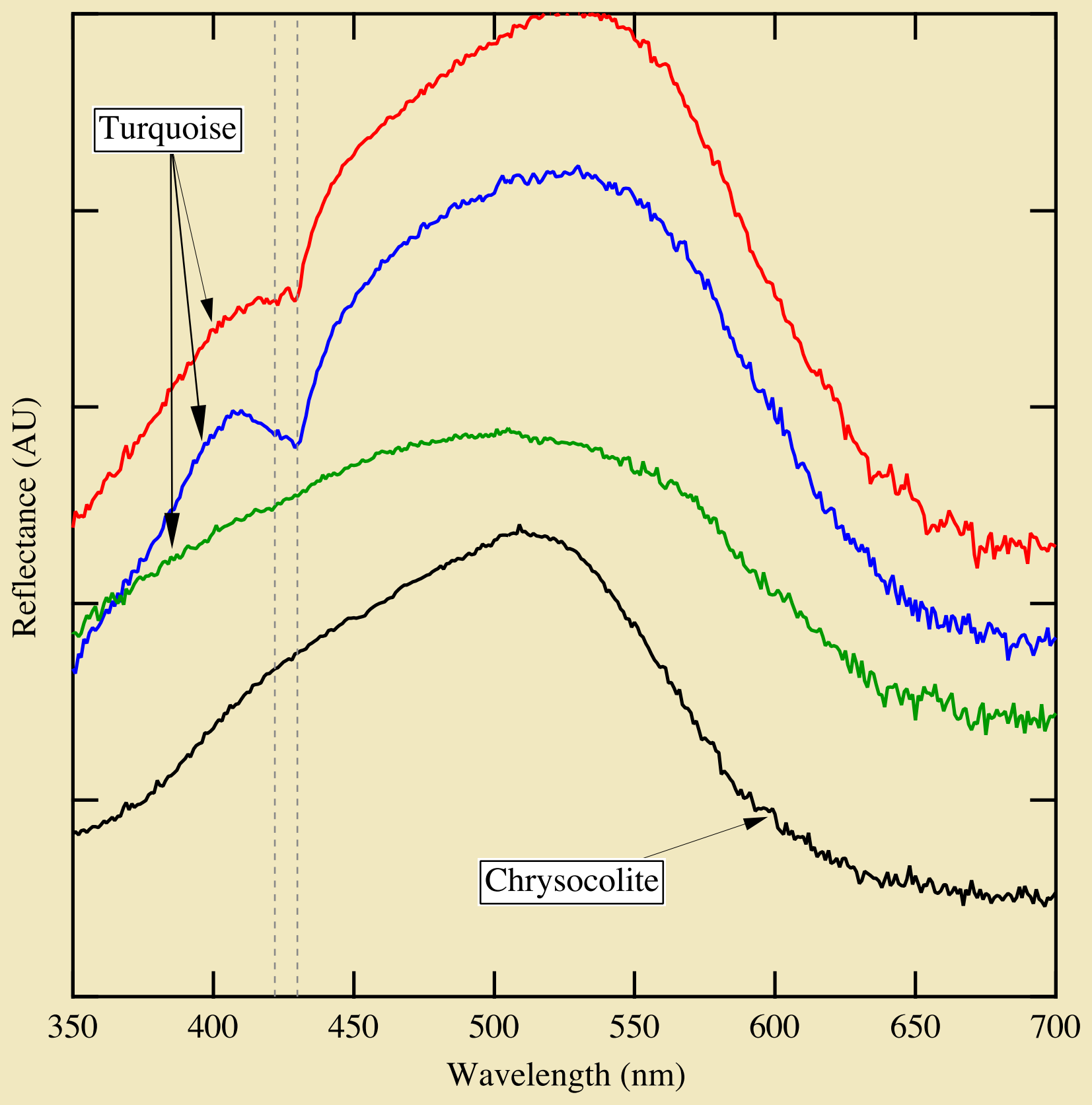


Fiber Optic Reflectance Spectroscopy

- No sampling
- Small spot size (~1 mm)
- Can help identify "enhanced" turquoise
- Identifies Fe^{3+} substitution in turquoise at 422 and 430 nm
- ✗ Peak visibility varies with Fe^{3+} content and turquoise degradation



Results

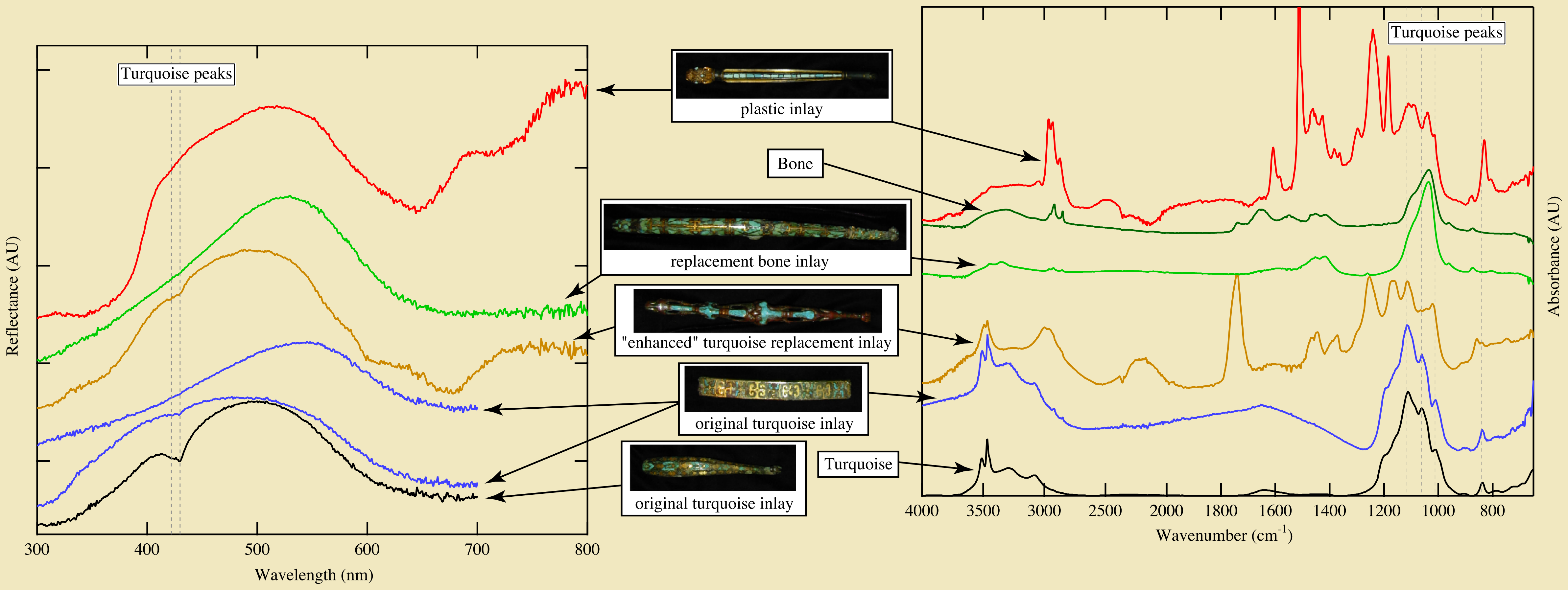


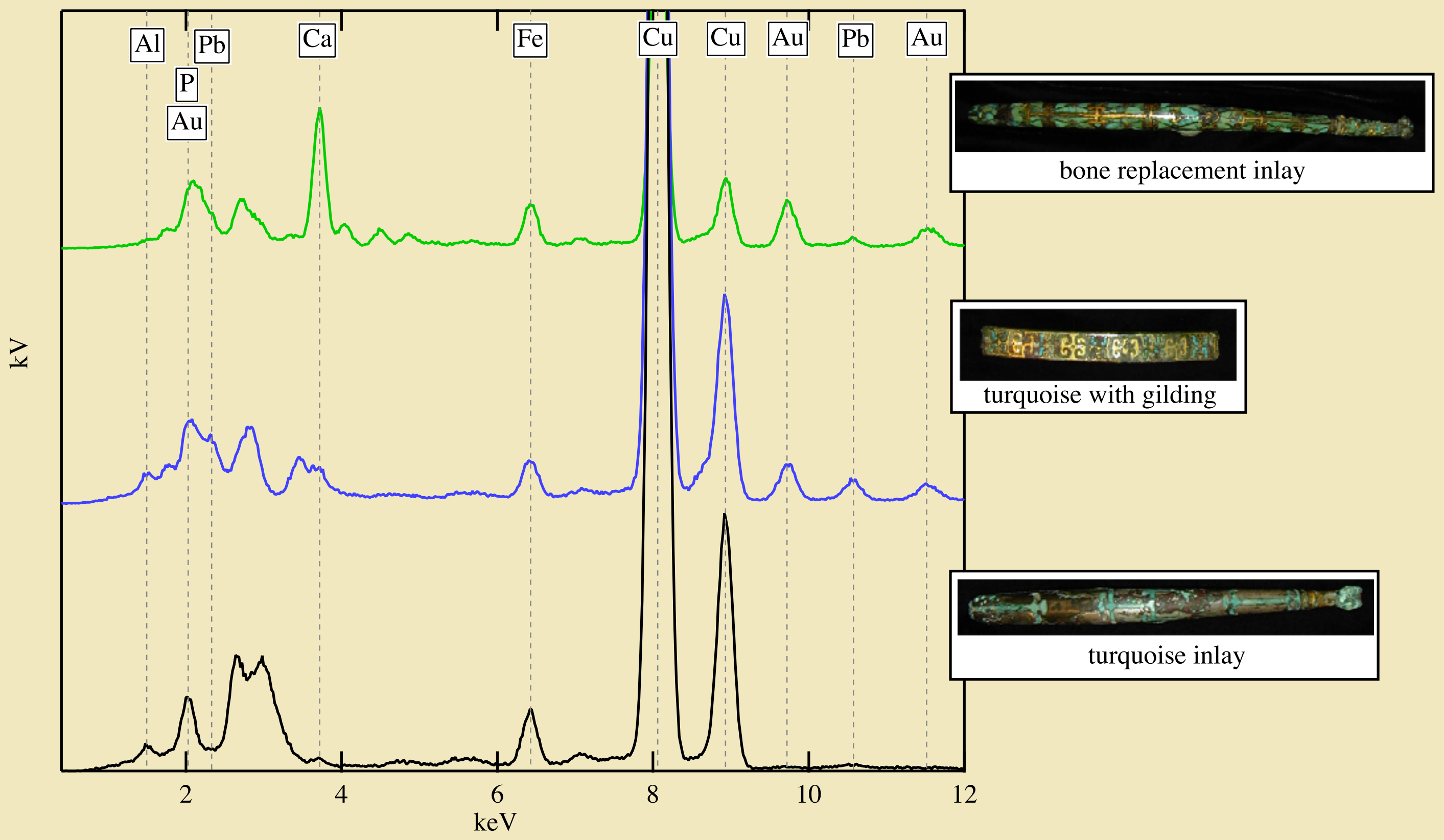
Fiber Optic Reflectance Spectroscopy

- The doublet at 422 and 430 nm varies with Fe^{3+} concentration and the state of degradation of the turquoise
- The doublet may appear as a single broad peak or may not be visible at all
- The non-uniformity of turquoise can lead to different spectra in the same sample of turquoise
- Peaks in the blue region (600+ nm) indicate the presence of organic dyes, either to enhance the blue color of poor quality turquoise or in a dyed substitute inlay material

Fourier Transform-Infrared Spectroscopy

- FT-IR was used in our study to independently confirm the presence (or absence) of turquoise
- IR was also helpful in giving more information about replacement inlay pieces containing plastics and dyes





X-Ray Fluorescence Spectroscopy

- The presence of a phosphorus and an aluminum peak indicate the presence of turquoise
- Gold peaks overlap the phosphorus peak: turquoise on gilded belt hooks could not be identified
- The aluminum peak is very small, and may not be visible
- The presence of a phosphorus and a large calcium peak can indicate the presence of bone
- The peaks of other elements can give additional information about the belt hook

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Conclusions

- Our investigation found that a combination of XRF, FORS and careful examination can usually identify turquoise inlay
- Although helpful, IR didn't provide any turquoise identifications that the combination of FORS, XRF and careful examination didn't previously identify
- If sampling is possible, IR or XRD can be used to confirm ambiguous identifications or give more information about replacement inlay
- Although FORS has been most commonly used in pigment analysis on paintings, this study shows that FORS can have a useful application in the study of objects

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