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ANALYSIS REPORT #088
Kiribati Archaeological Artifacts

DATE: 5/5/2008

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Object Description and Reason for Analysis

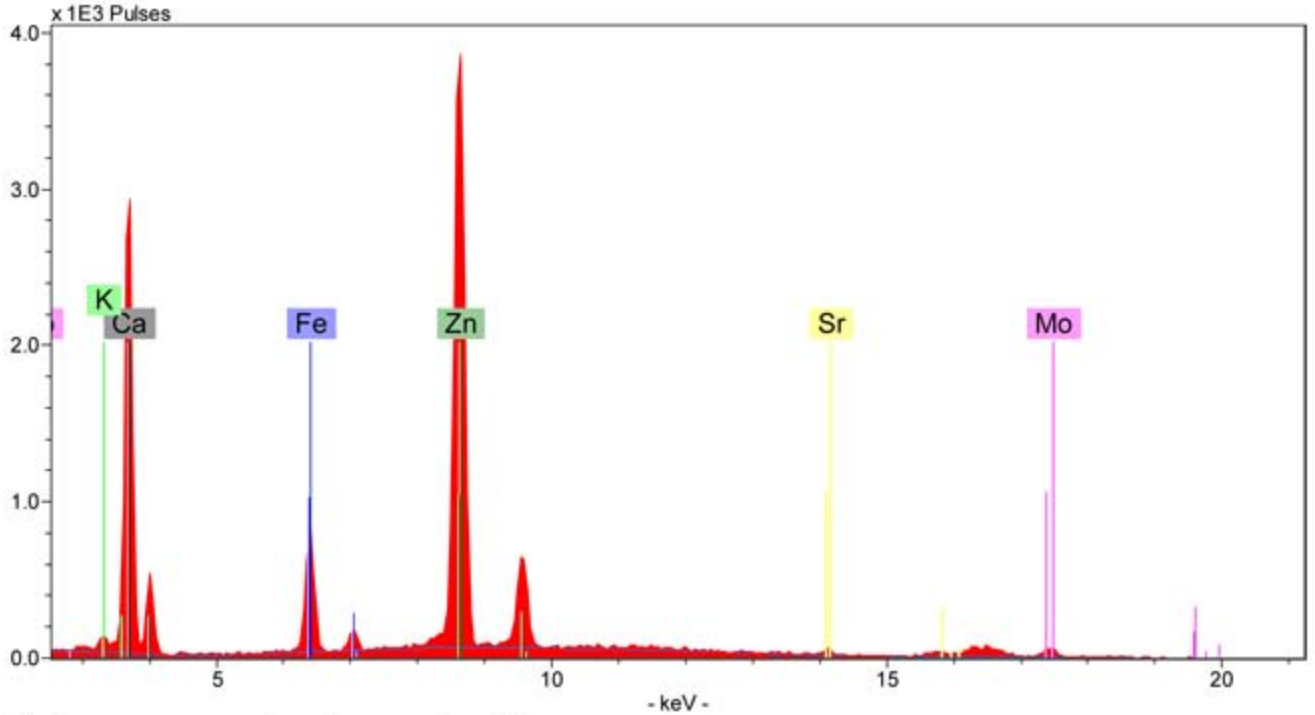
- **OBJECT DESCRIPTION (form, material, color, etc):** The objects submitted for analysis are archaeological material excavated from the Republic of Kiribati and reference material related to the Kiribati artifacts. They include: artifact 2-8-5-39 (a dark red flat cake with a black crust), artifact 2-8-5-40 (a ferrous artifact with a white concretion on its surface), 2-8-5-13 (a .22 casing with a bright red material on its surface), and a Mondaine cosmetic case containing two items, a dark pink rouge labeled 'Medium' and a very pale pink pressed foundation powder labeled 'flesh'.

- **REASON FOR ANALYSIS:** Could these objects have an early twentieth-century American provenance? Could they have been manufactured prior to 7/2/37? Specific questions include: Is the composition of the red concretion consistent with that of a cosmetic? If so, is its composition consistent with an early twentieth-century provenance? What is the composition of the two cosmetics in the Mondaine compact? How do they relate to the composition of the red cake-like material found on the Kiribati site? What is the alloy composition of the 0.22 shell casing? Is the red material on its surface a paint (containing a cadmium, mercury, or iron pigments) or is it cuprite, a red copper oxide corrosion product? What is the composition of the flat ferrous artifacts? What is the composition of the white encrustation on its surface?

- **SAMPLING:** Microgram sized samples were removed from the 'medium' and 'flesh' powders in the compact for FTIR and Raman analysis using a #11 steel scalpel blade. Samples were removed from the black concretion on the red cake for FTIR analysis also using a size 11 steel scalpel blade. All samples for chemical analysis were transferred to glass containers to prevent contamination prior to analysis. All other analyses were performed nondestructively.

- **ANALYSIS PROTOCOL:** X-ray fluorescence analysis was used to identify the elemental compositions of the 0.22 casing, the ferrous artifact and white concretion, the red cake, and the Mondaine compact contents. Fourier transform infrared spectroscopy (FTIR) was used to identify the molecular composition of the Mondaine compact contents, the black crust on the red cake, and the white concretion on the ferrous artifact. Raman spectroscopy was used to identify the molecular composition of the Mondaine compact contents and the red cake.

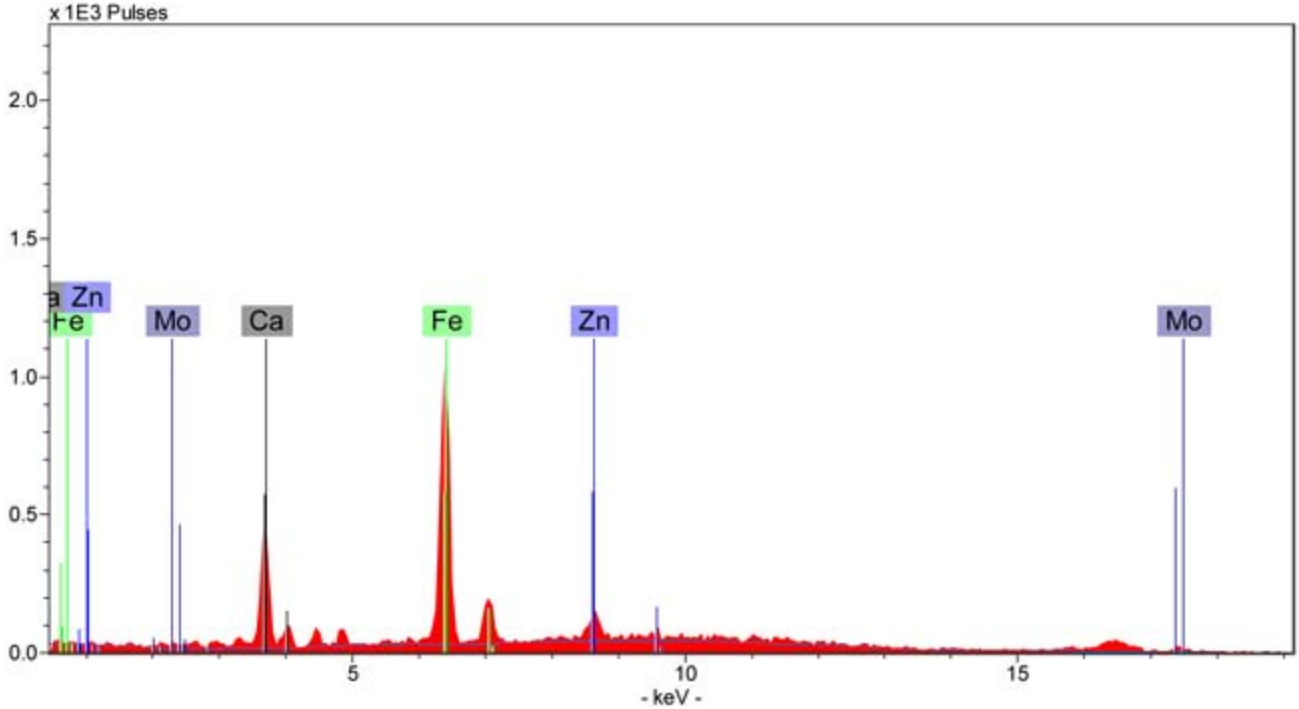
Mondaine Compact XRF Spectrum 1 – Pale Pink Cosmetic Labeled ‘Flesh’



Major components: zinc and calcium

Minor components: potassium, strontium, and iron

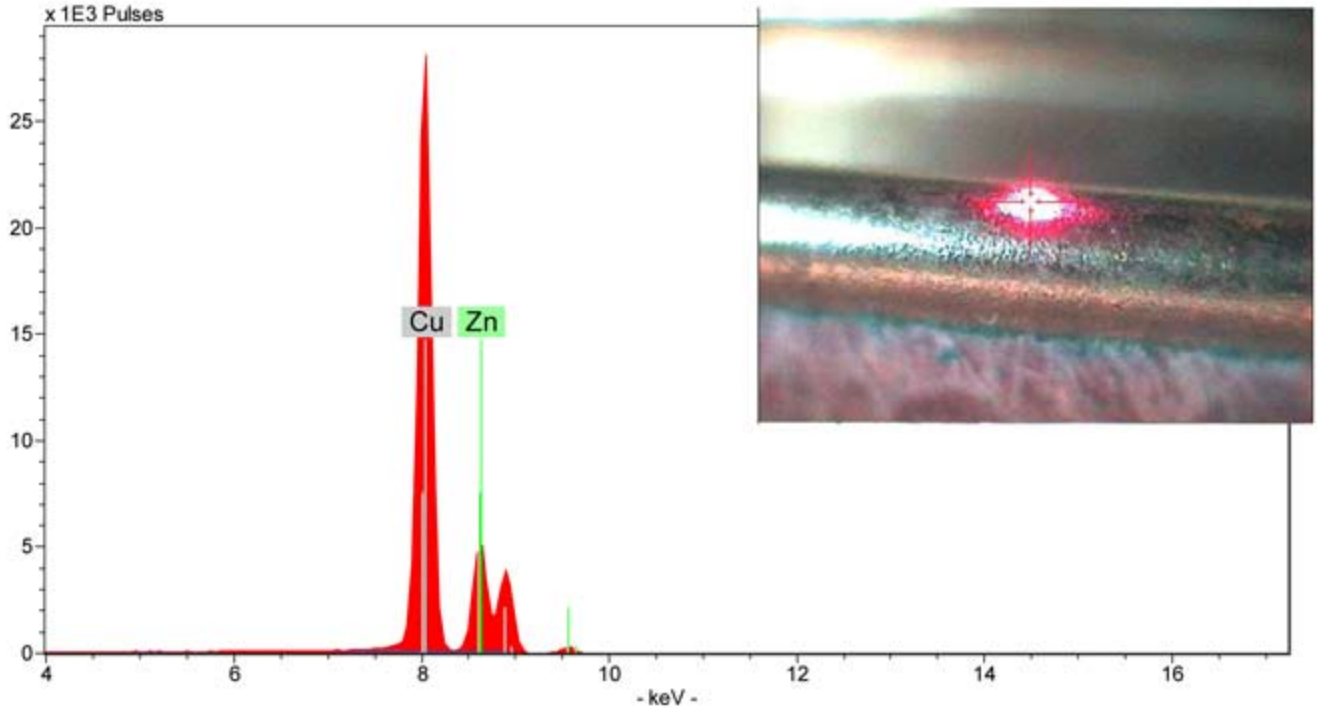
Mondaine Compact XRF Spectrum 2 – Dark Pink Cosmetic Labeled ‘Medium’



Major components: Calcium and iron

Minor component: zinc

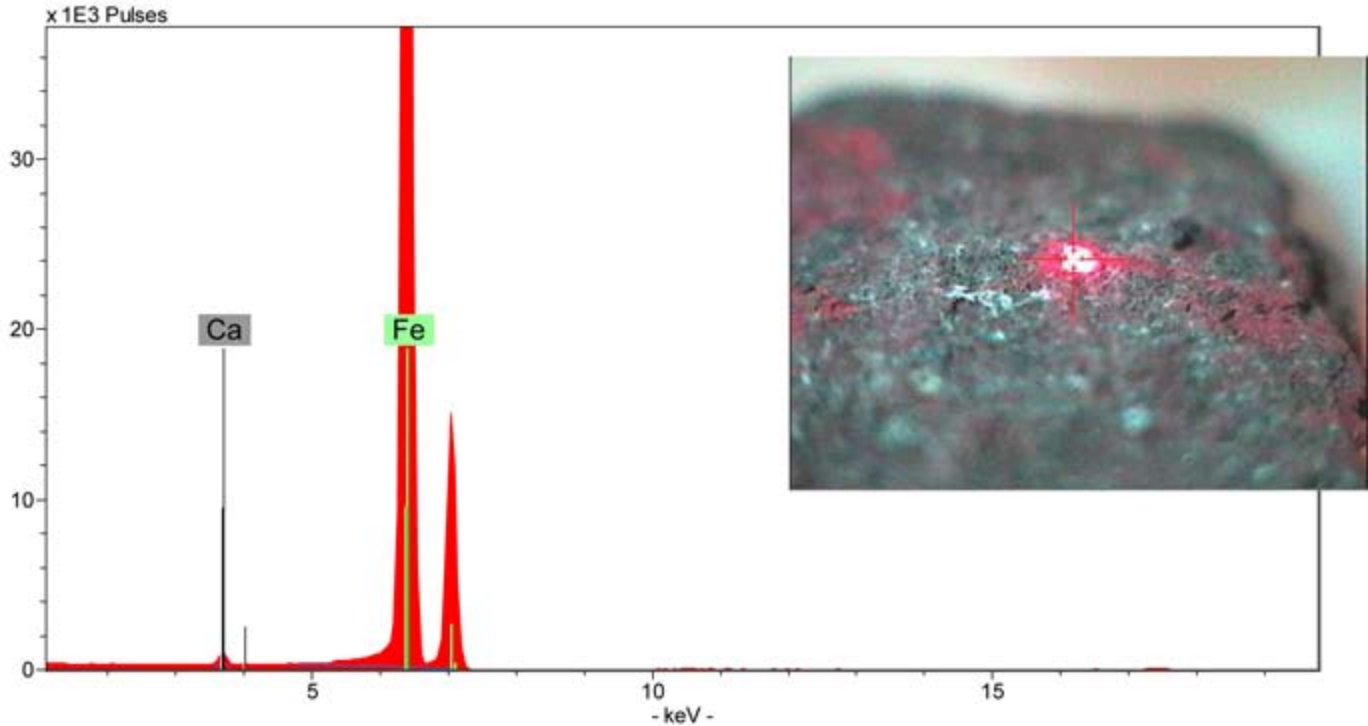
Mondaine Compact XRF Spectrum 3 – Alloy Comprising Case



Major components: Copper and zinc

Alloy = brass

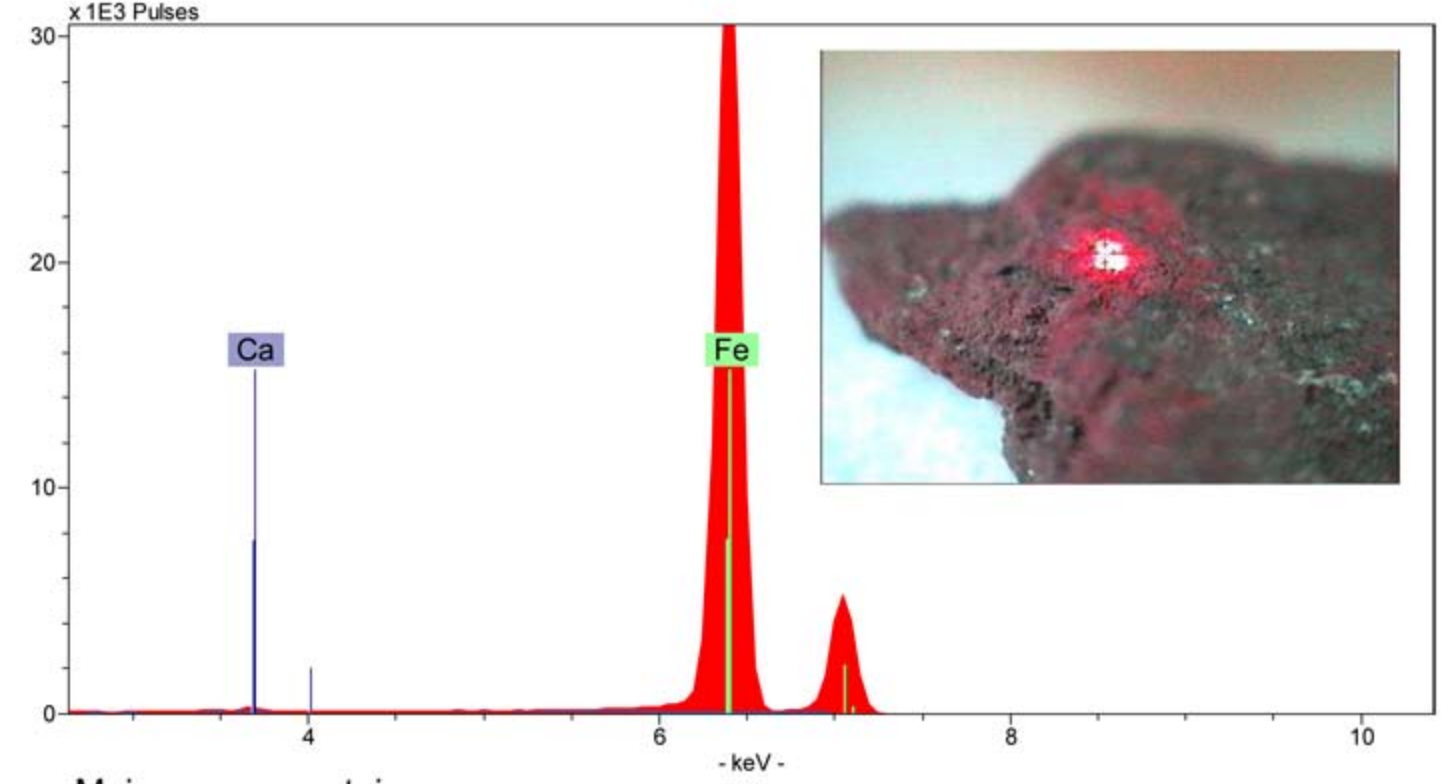
Red Cake-like Material: 2-8-S-39-Black Crust



Major component: iron

Minor component: calcium

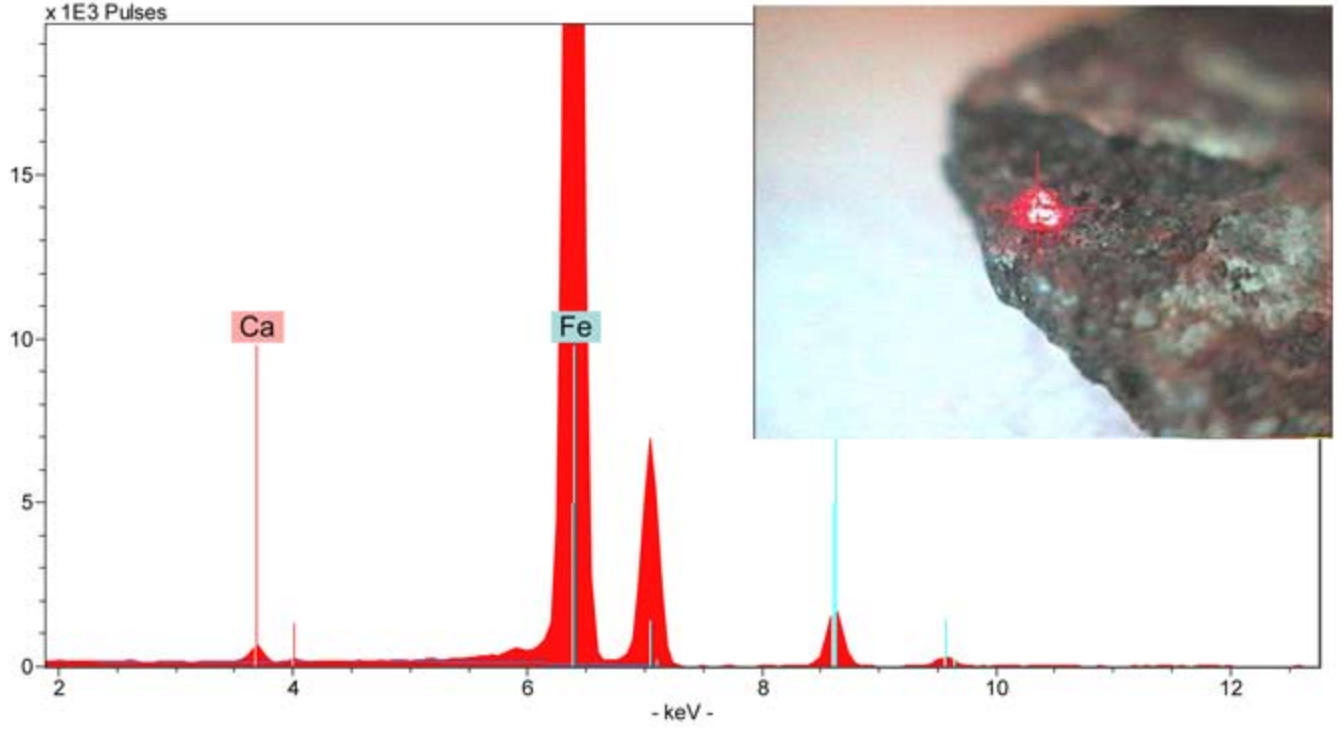
Red Cake XRF Spectrum: 2-8-S-39 Red



Major component: iron

Minor component: calcium

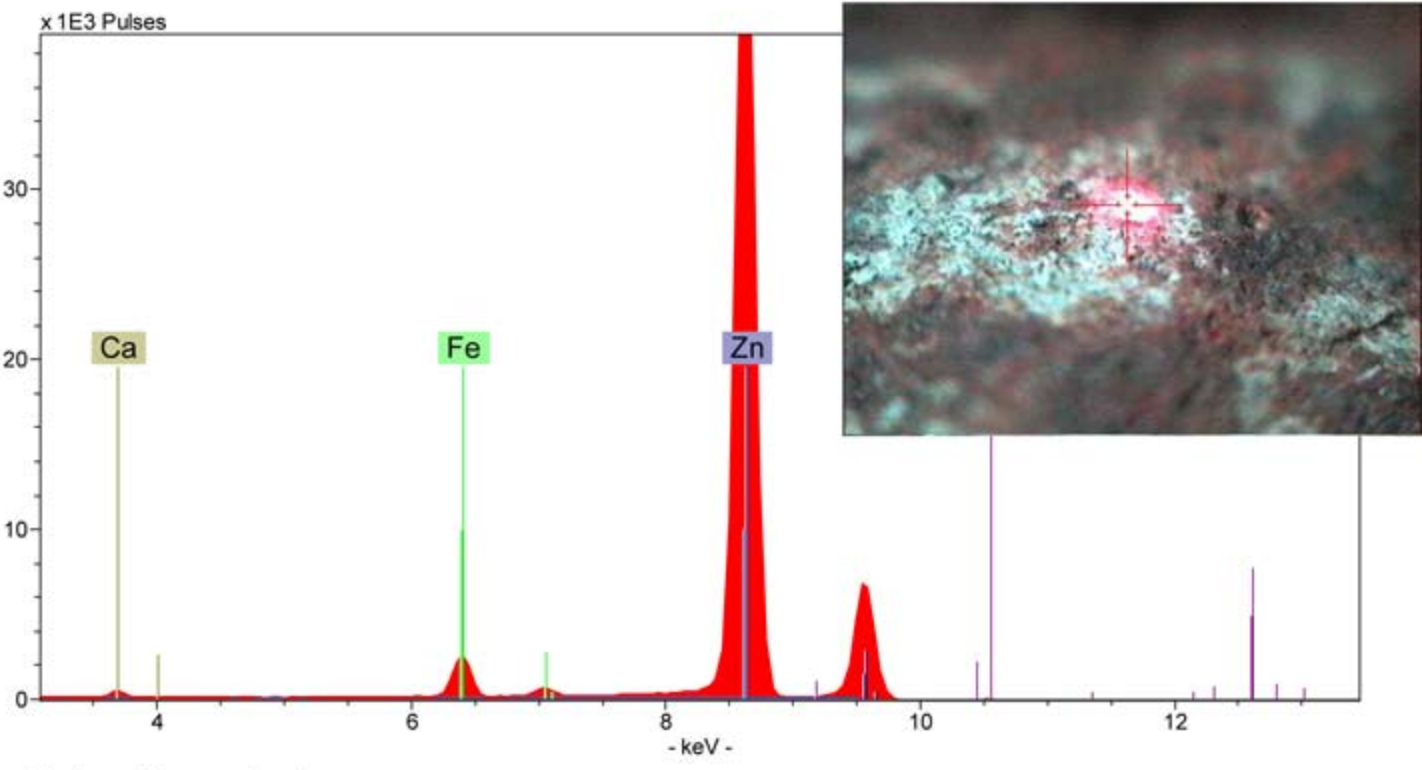
XRF Spectrum of 2-8-S-40: Ferrous Substrate



Major component: iron

Minor component: calcium

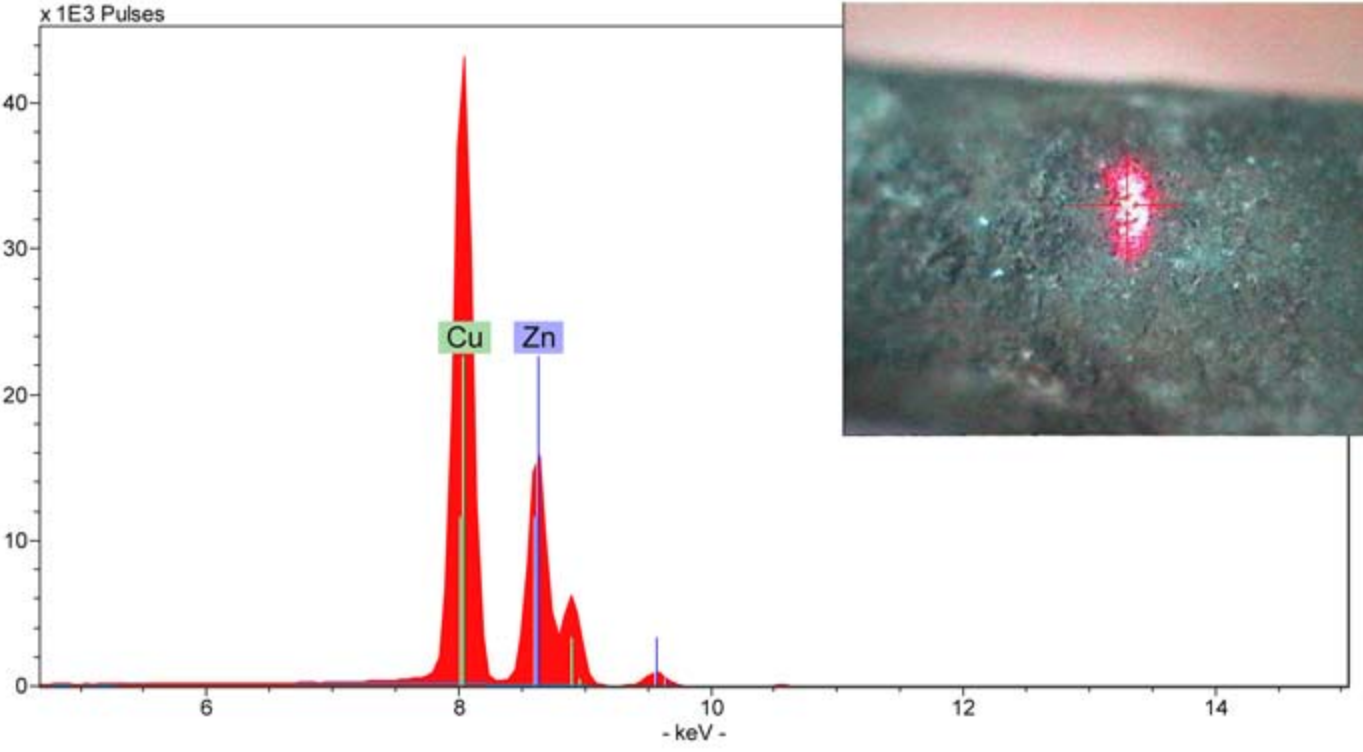
XRF Analysis of White Concretion on Ferrous Object 2-8-S-40



Major element: zinc

Minor elements: iron, calcium

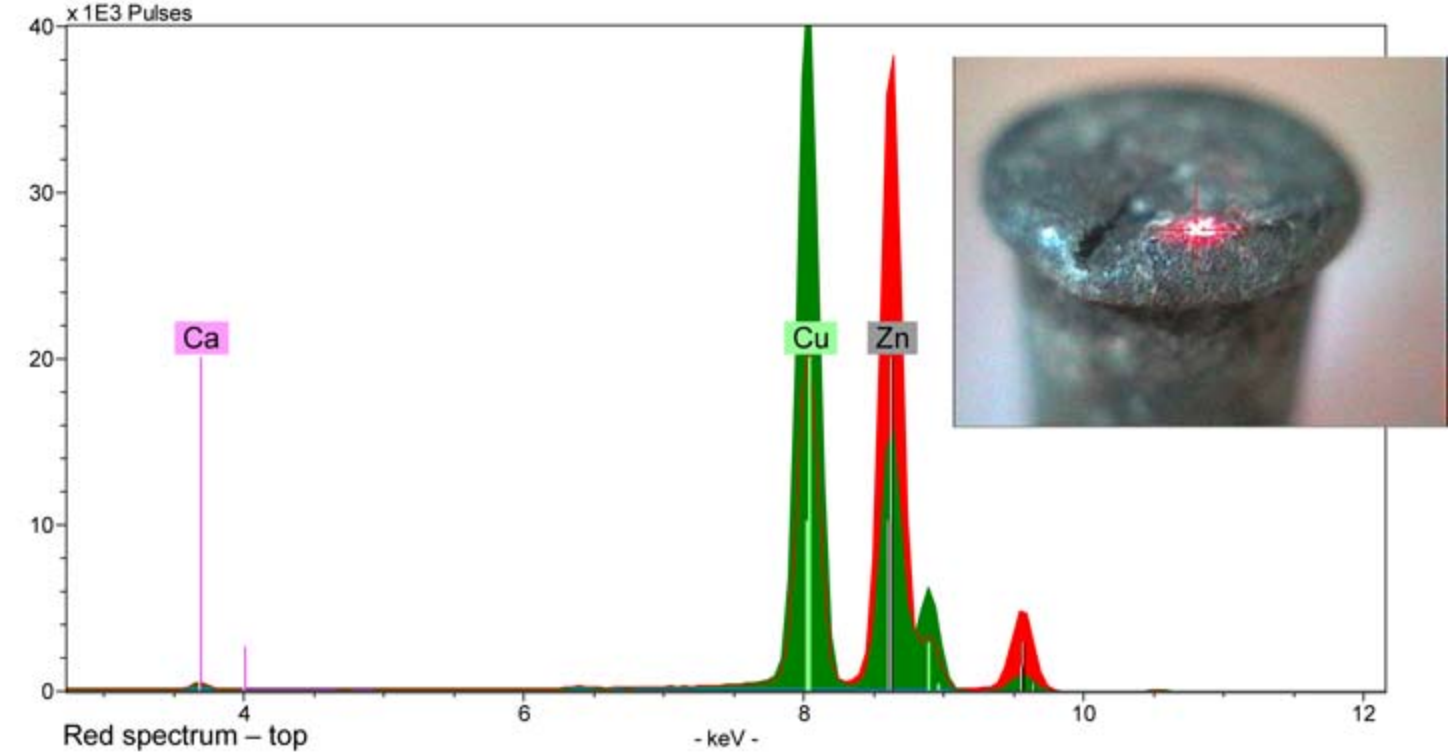
XRF Analysis of Artifact 2-8-S-13: .22 Casing - Casing Side



Major elements: Copper and zinc

Alloy: Brass

XRF Spectrum of 2-8-S-13 0.22 Casing - Red Material on Top



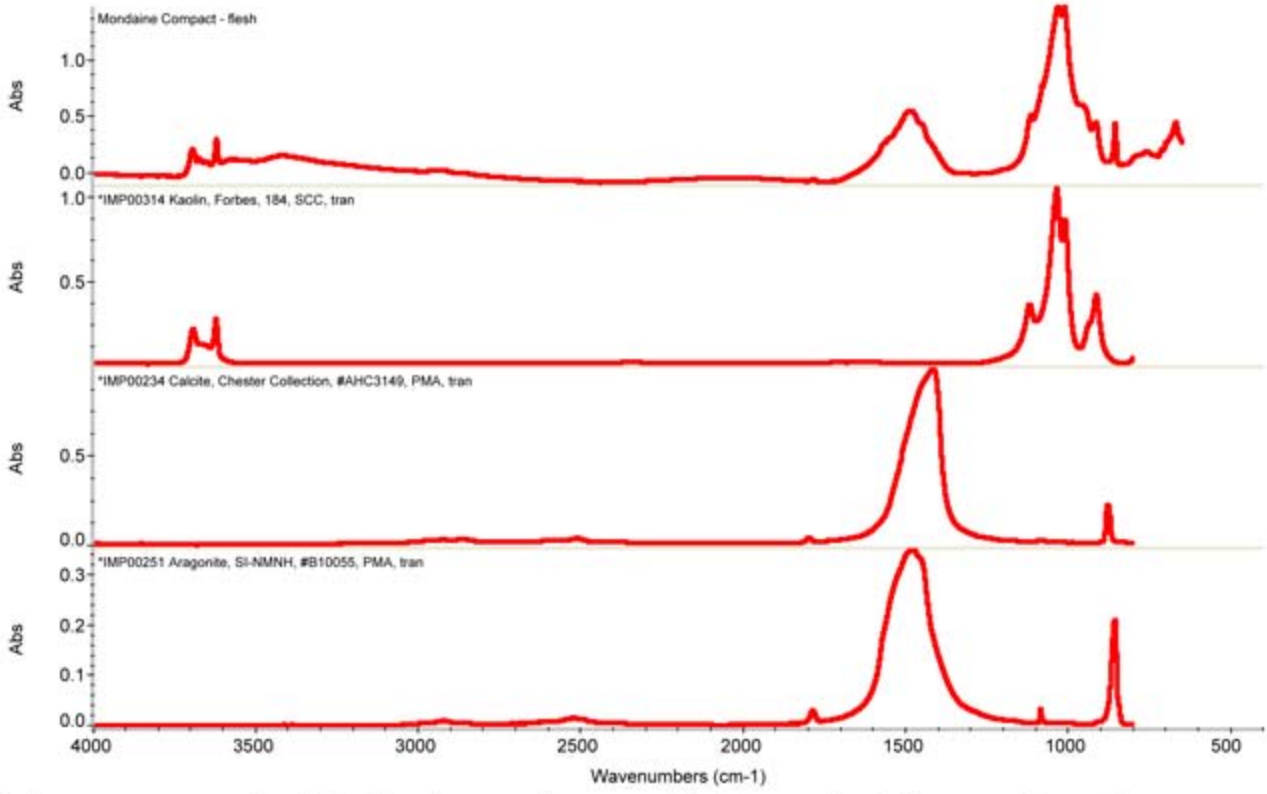
Red spectrum – top

Green spectrum – side

Major elements: zinc and copper

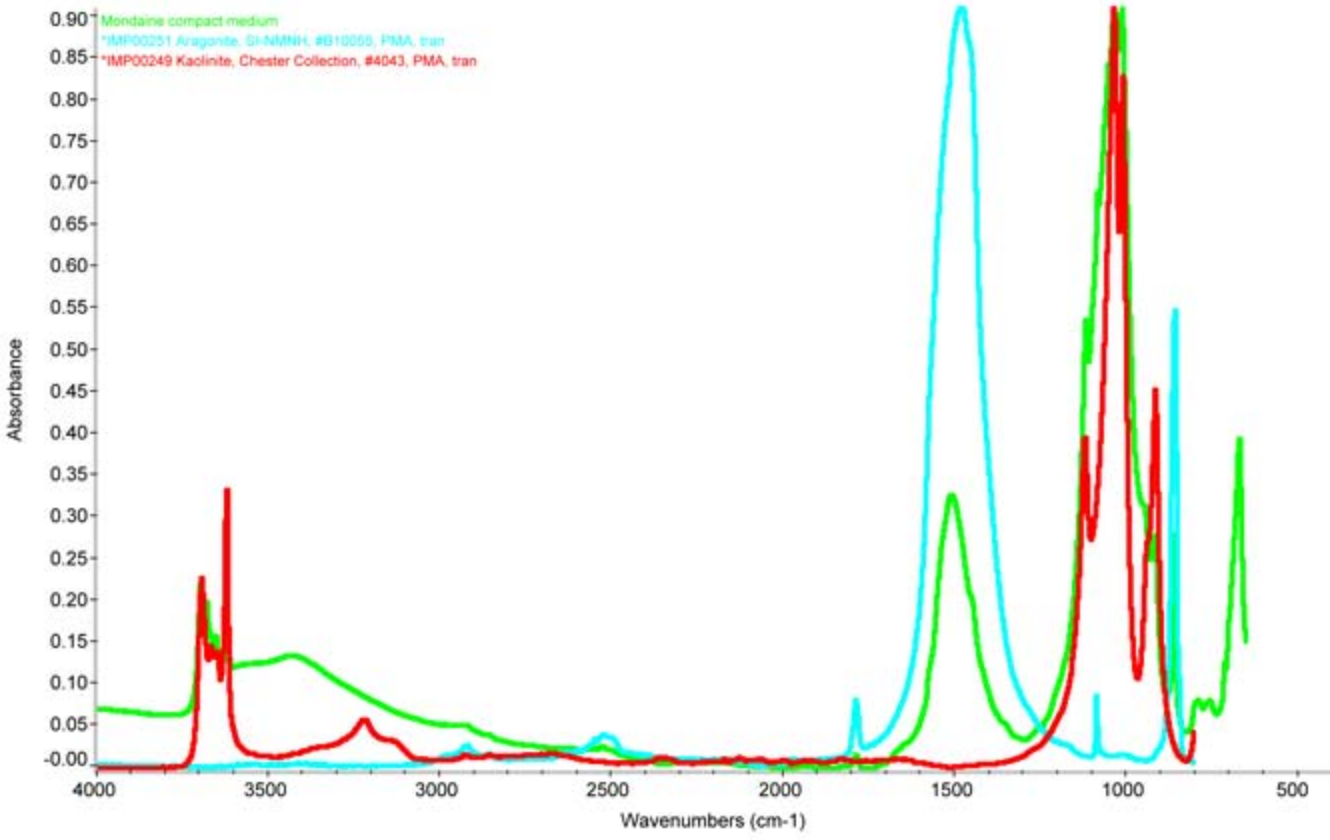
Minor elements: calcium

FTIR Spectrum of Mondaine Compact ‘Flesh’ Cosmetic



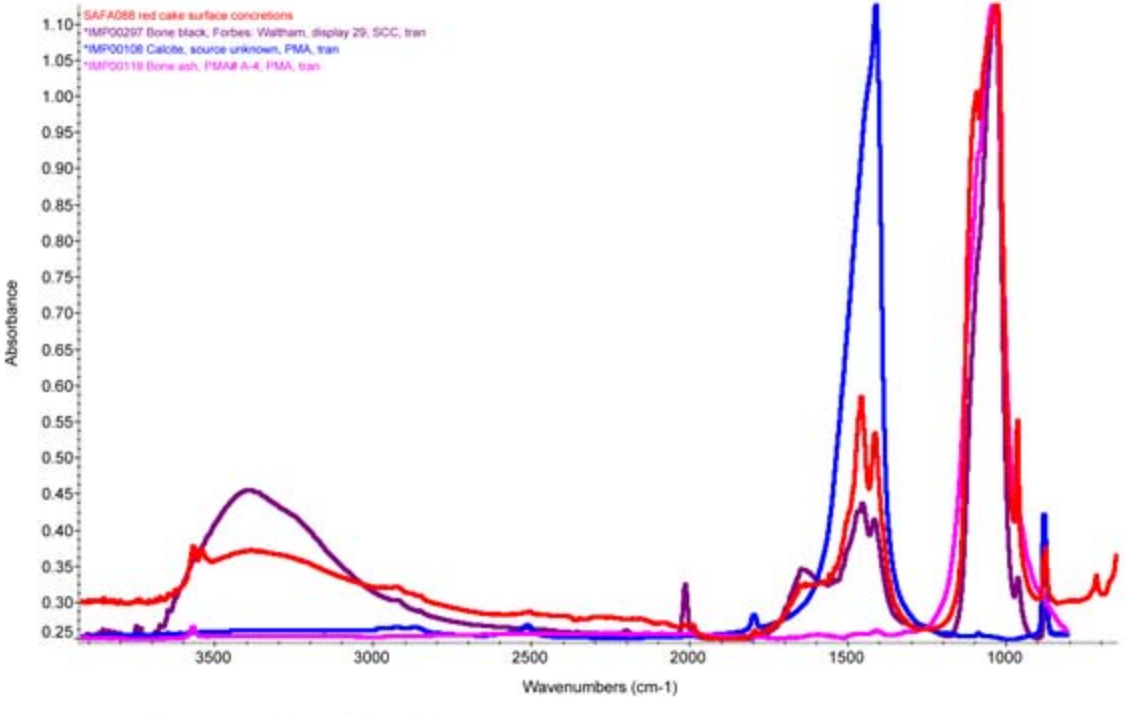
Major components: Kaolin clay and aragonite form of calcium carbonate

FTIR Spectrum of Mondaine Cosmetic 'Medium'



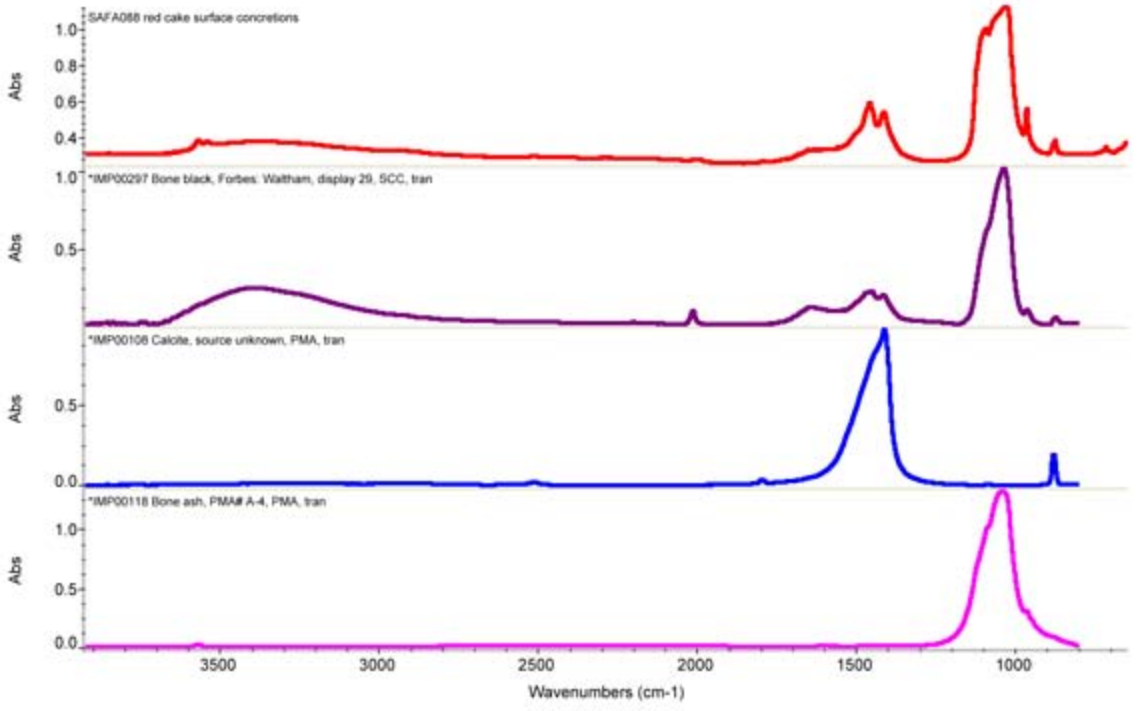
Major components: Kaolin and aragonite

FTIR Spectrum of Red Cake, Black Surface Concretion, 2-8-S-39



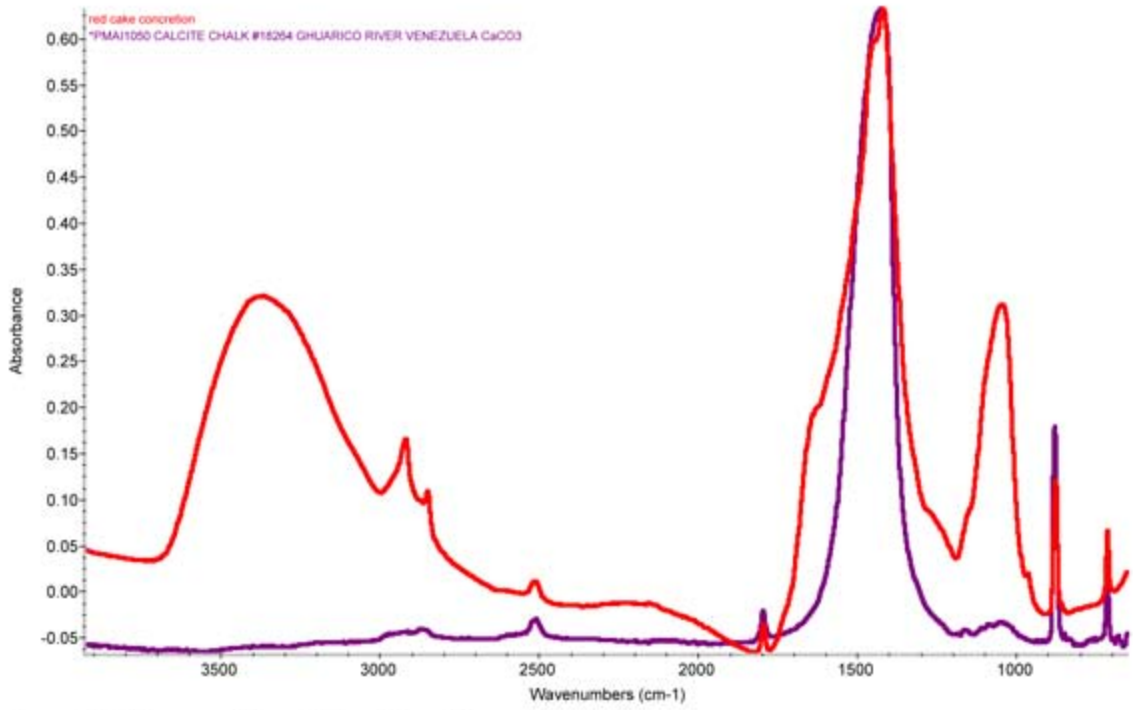
Major components: bone ash and calcite

FTIR Spectrum of Red Cake, Black Surface Concretion, 2-8-S-39



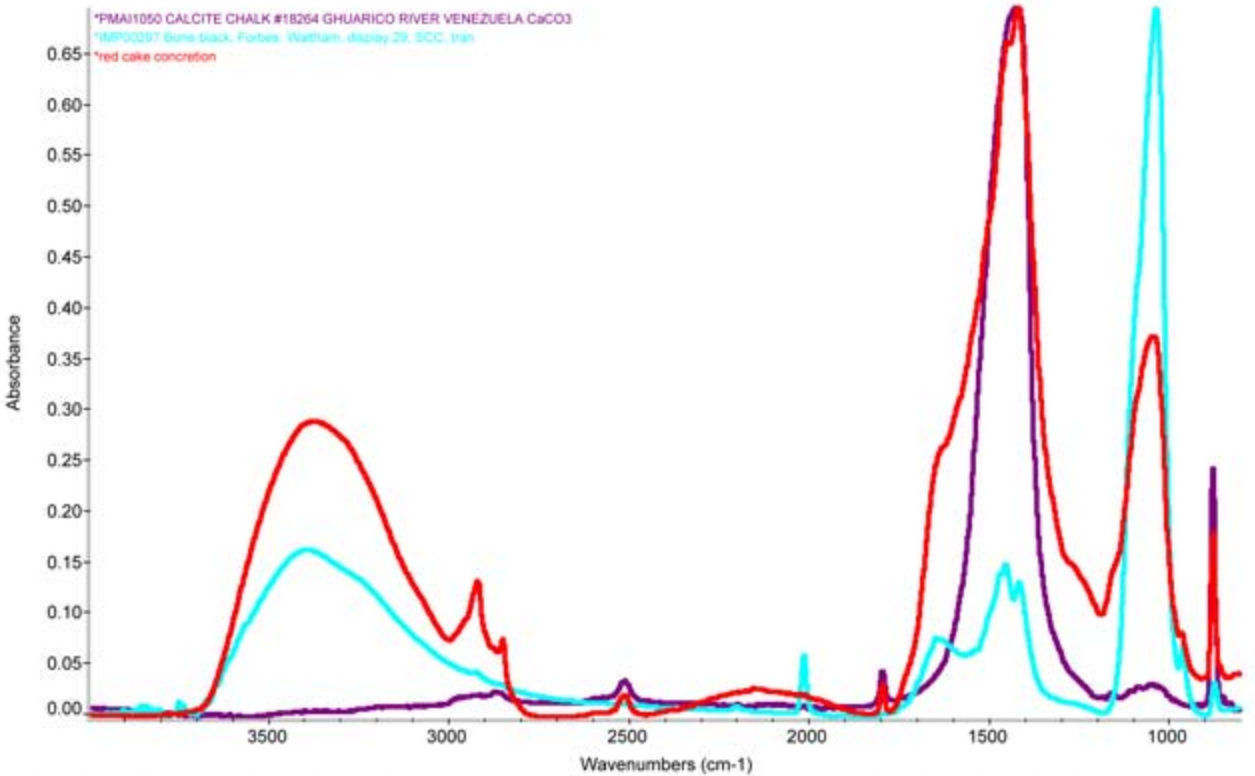
Major components: bone ash and calcite

FTIR Spectrum of Red Cake, Black Surface Concretion, 2-8-S-39



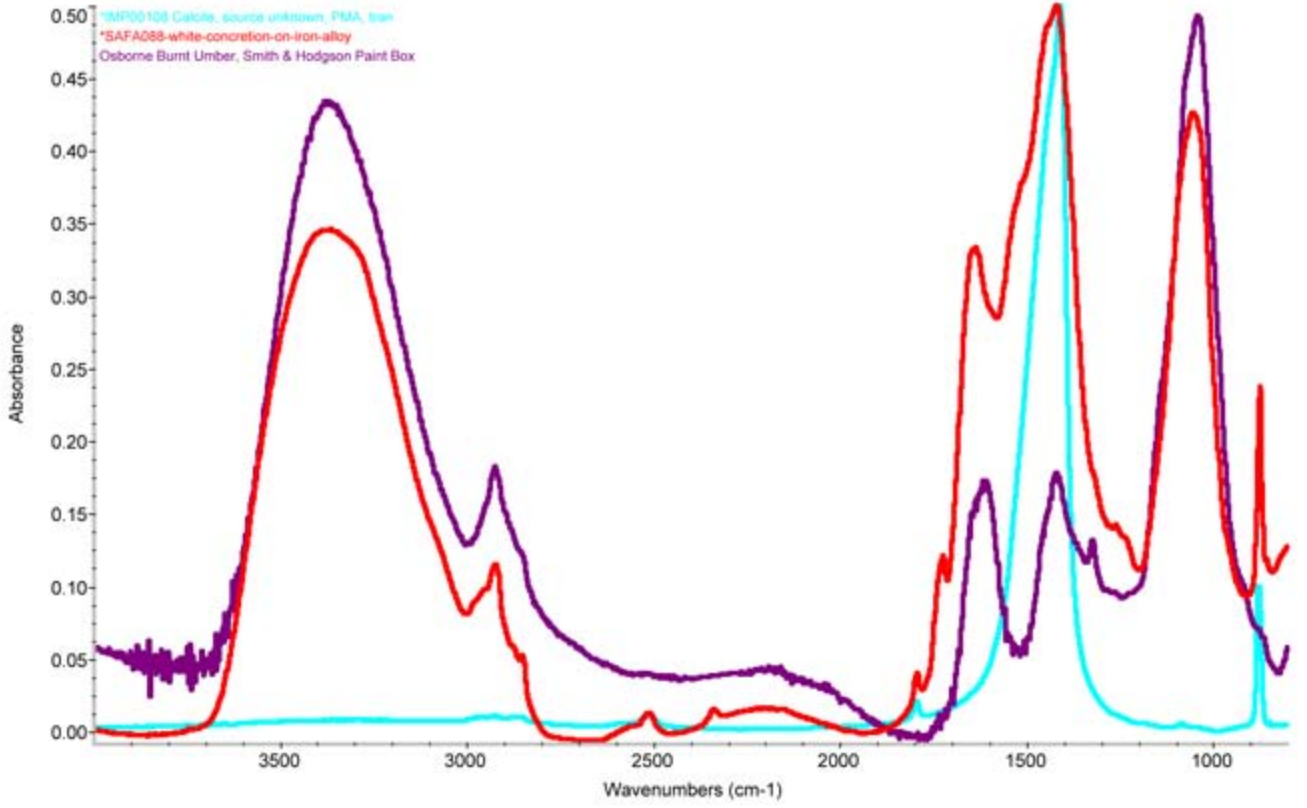
Best match for positive identification of calcite

FTIR Spectrum of Red Cake, Black Surface Concretion, 2-8-S-39

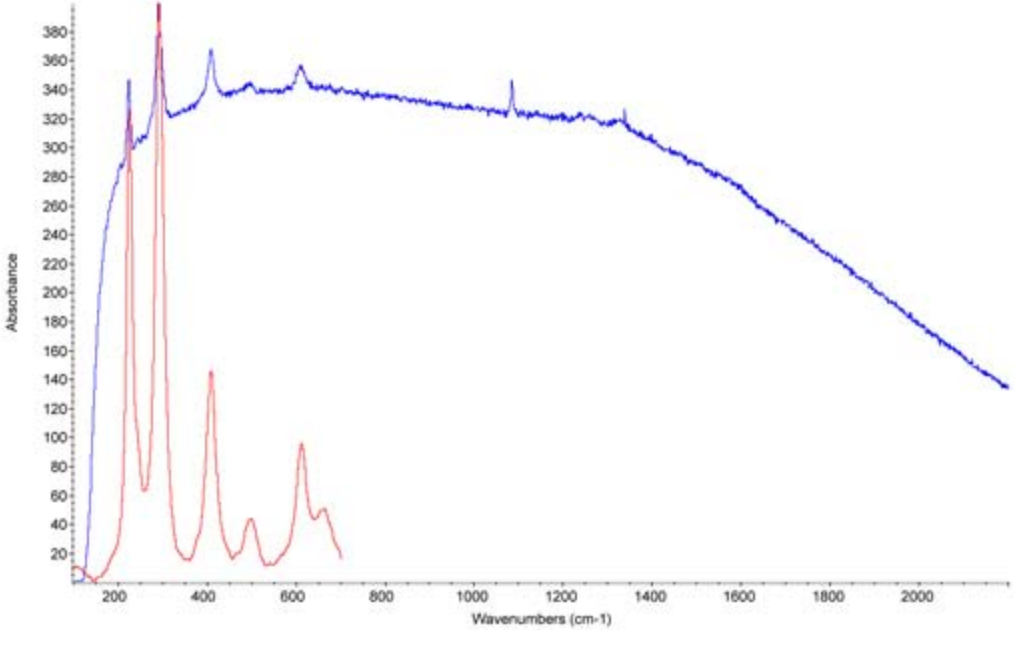


Best match for positive identification of bone ash and calcium carbonate

FTIR Analysis of White Concretion on Ferrous Object 2-8-S-40

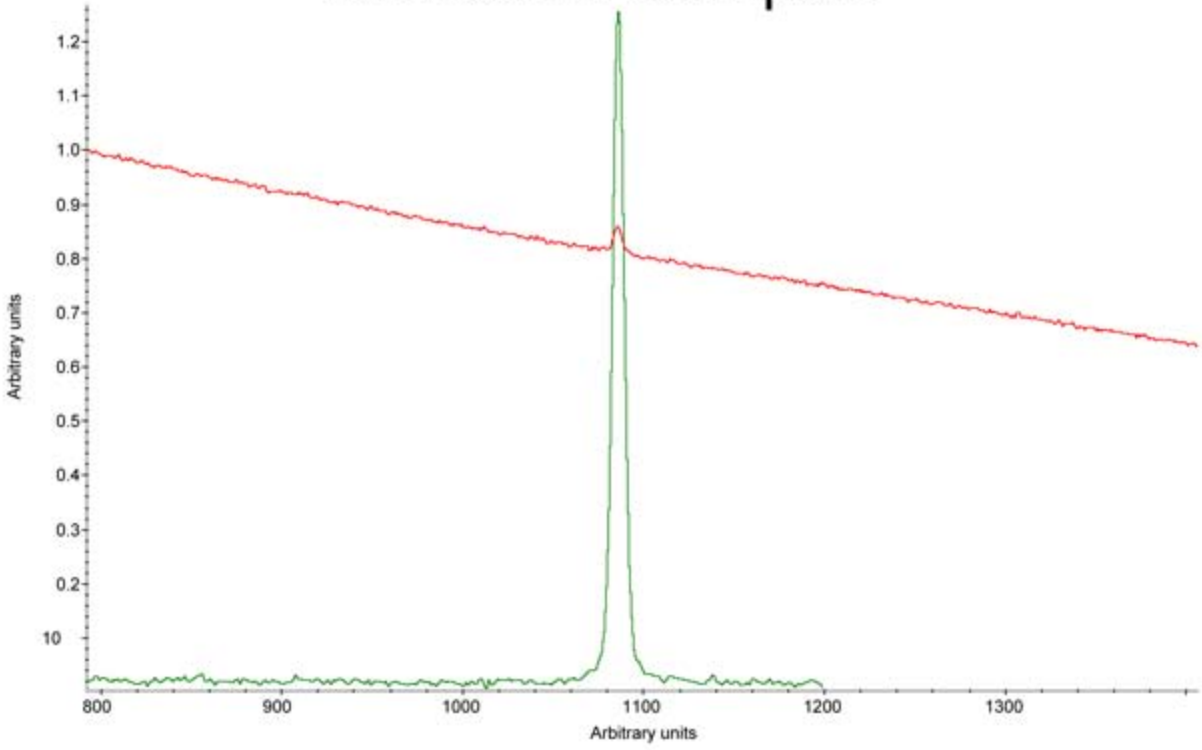


Raman Spectrum of 'Medium' Cosmetic from Mondaine Compact



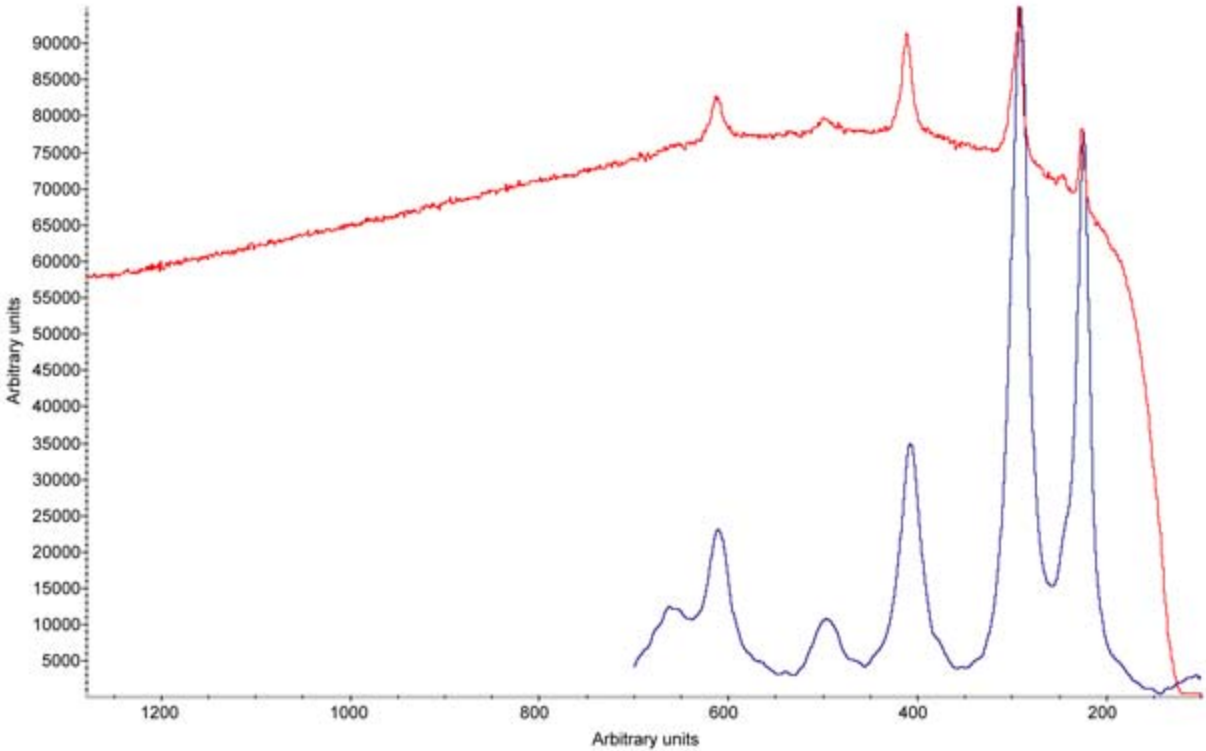
- Major component – iron oxide red (Fe_2O_3) minor component – calcite (reference spectrum not shown)

Raman Spectrum of Flesh Cosmetic from Mondaine Compact



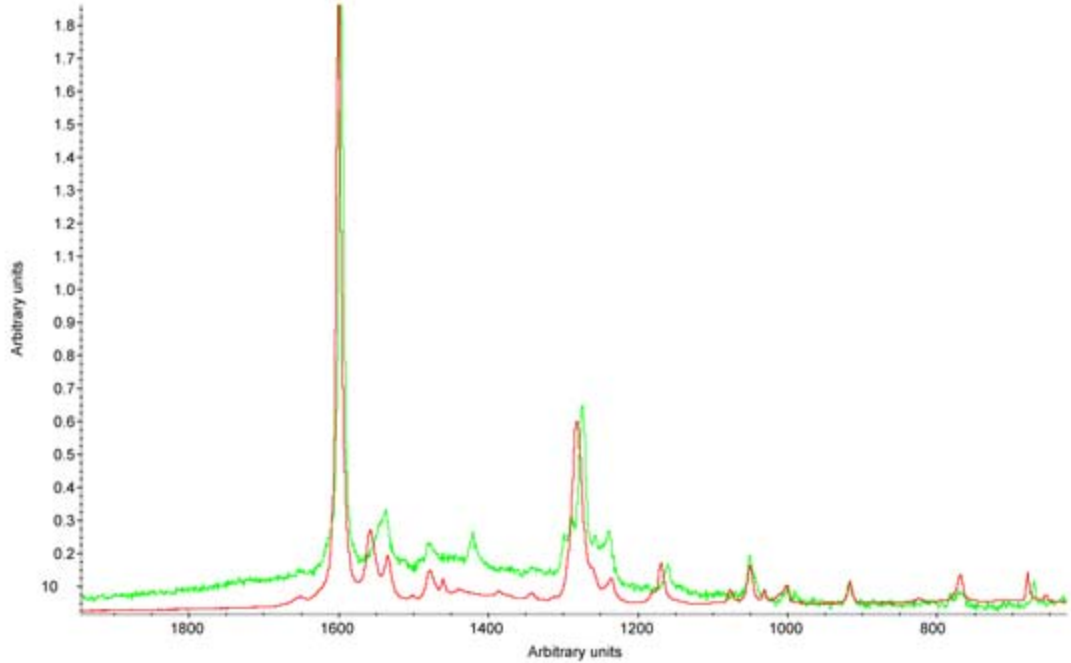
Major component: calcium carbonate (calcite or aragonite, not enough peaks to determine)

Raman Spectrum of Red Cake, 2-8-S-39



Major component: Iron oxide red (Fe_2O_3)

Raman Spectrum of Red/Orange Paint on 0.22 Bullet Casing (2-8-S-13)



- Red/orange paint on bullet casing (green spectrum) and reference spectrum for PO13 (synthetic orange azo dye disazopyrazolone, manufactured by CIBA, also known as Irgalite, Orange P, Permanent Orange G, and CI#21110, see *Industrial Organic Pigments: Production, Properties, Applications*, by Willy Herbst, Klaus Hunger, p. 266, 2006, Wiley, VCH Press, for chemical structure.

High Magnification Image of Concretion 2-8-S-18, Unknown Beige Material

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High Magnification Image of Concretion 2-8-S-18, Unknown Beige Material

Results and Conclusions

1. Mondaine Cosmetics Compact:

1. The pale pink 'flesh' cosmetic is composed of zinc, calcium, potassium, and iron-containing compounds. The main molecular constituents include kaolin clay ($Al_2Si_2O_5(OH_4)$), aragonite (a form of calcium carbonate, $CaCO_3$). The zinc-containing component was identified by the fine structure of the carbonate band in the FTIR, which suggests that a zinc carboxylate compound such as zinc stearate or zinc octanoate is present. This type of compound, formed from the reaction of zinc with animal fats, is a common early 20^{th} century cosmetic component and has recently been identified in a late 19^{th} c. cosmetic at Winterthur.
2. The dark pink 'medium' cosmetic is composed primarily of iron, calcium, and zinc. The main molecular constituents of this cosmetic are kaolin clay, the aragonite form of calcium carbonate, and iron oxide red, which is in part responsible for its pink color. There also appears to be a red organic dye present in this cosmetic, and liquid chromatography would be required for a positive identification of this material.
3. The metal housing of the cosmetic case is made from brass, a copper and zinc alloy.

Results and Conclusions

1. red cake-like material (2-8-S-39)
    1. The red interior of this material is comprised of an iron-containing compound, and the black crust on the exterior is comprised of a calcium-containing compound. Raman analysis reveals that the red compound is iron oxide red, Fe_2O_3. FTIR analysis reveals that the calcium-containing compound in the black crust is bone ash, calcium hydroxyapatite or $Ca_{10}(PO_4)_6(OH)_2$. Calcium carbonate is also present. This suggests the presence of burned human or animal remains at this archaeological site.

2. Ferrous material with white concretion (2-8-S-40)
    1. The presumably ferrous substrate is indeed an iron-containing compound. The white concretion is a zinc-containing compound. FTIR reveals that the white concretion contains calcite as well as compounds due to surface dirt such as silicates and iron oxides. The zinc compound that comprises the majority of this sample was not FTIR active, which suggests that it is white zinc oxide. Raman spectroscopy of the concretion could not confirm this due to the strong fluorescence of the sample The identification of an oxidized iron-containing material that has an oxidized zinc encrustation suggests that the sample is a piece of highly degraded galvanized steel. The galvanization process of coating steel with zinc to retard the iron alloy corrosion was invented in the eighteenth-century and patented in the second quarter of the nineteenth-century.

3. 0.22 bullet casing
    1. 1. Analysis of the side of the casing, which shows a green copper alloy corrosion product characteristic of a copper alloy, revealed the presence of copper and zinc, suggesting that the casing is a brass. The analysis of the top of the casing, which contains the red material, also reveals both copper and zinc, although the zinc is present in a higher concentration than on the side of the case. Raman spectroscopy revealed that the red material is a synthetic organic orange dye of the disazopyrazolone class of azo dyes. The red color is therefore due to the presence of a red paint rather than cuprite corrosion product. Azo dyes were invented in the late nineteenth century.

Results and Conclusions

1. **Concretion 2-8-S-18, Unknown Beige Material**

   The calcium carbonate (calcite) beige concretion from SAFA0710 was found to be composed of microtubules which suggests some type of fossilized marine life. However, a marine origin for the calcium carbonate would predict an aragonite form for this mineral. As such, this concretion may be an example of psuedomorphism, in which crystals of aragonite are slowly recrystallized to calcite *in situ*, without changing their crystal habits. This type of calcite/aragonite pseudomorphism is sometimes observed in shells in natural history collections, and is known as 'Byne's Disease'.

Experimental Details

- **FTIR analysis:**
- For FTIR (Fourier transform infrared) analysis, samples were transferred directly to a diamond compression cell half. The samples were rolled flat to transparency with a steel roller and then analyzed using the Thermo-Nicolet Magna 560 infrared bench with the Nic-Plan infrared microscope with MCT-A detector (range 4000-650 cm-1, 120 scans, 4 cm-1 resolution). Resulting spectra were interpreted with the aid of commercial and art conservation infrared reference spectral libraries.

- **ED-XRF (Energy-dispersive x-ray fluorescence) analysis:**
- Non-destructive qualitative energy-dispersive x-ray fluorescence analysis (ArtTAX μ-XRF spectrometer, molybdenum or tungsten tube, 50 kV, 600 μamps, 100 sec, 20) was performed on each metal and glass artifact to determine its elemental composition.

- **Raman microspectroscopy analysis:**
- A Renishaw InVia Raman spectrometer was used to conduct dispersive Raman spectroscopy using a 50 mW 785 nm (red) laser , 1200 line/mm diffraction grating, and a spectral resolution of 3 cm-1. Spectra were collected over a 100 cm-1 to 3200 cm-1 range for 20s collection times with a laser power of 1%.