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What is the Red Plaster in the Mastodon Tusk?

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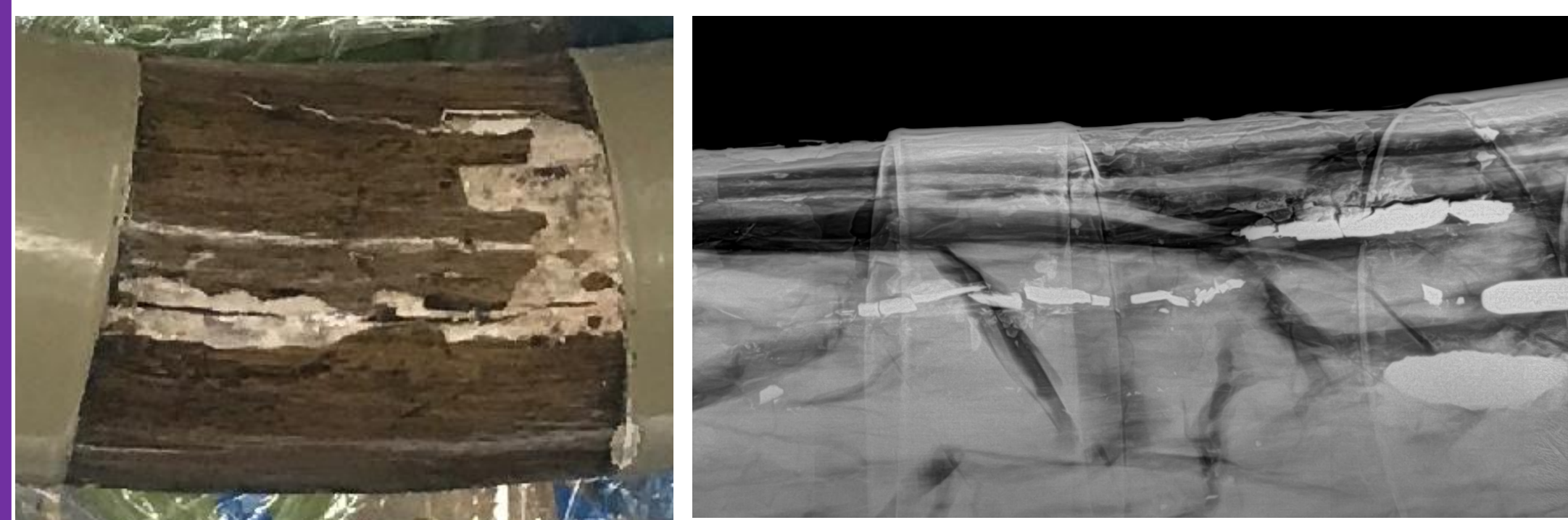
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What is the Red Plaster in the Mastodon Tusk?

Tray Hickie

Background

- During the first visit to the tusk, Dr. Sebree found the crack that had been filled with a strange plaster that was not known at the time.
- After seeing the plaster glow from the small flashlight Dr. Sebree had with him, identifying this material seemed like an interesting project.
- Due to the fact that the plaster's makeup is unknown, but identifying the material it was made of, future attempts to restore and preserve the fossil can be done more safely in the event that the material is harmful
- Initial x-ray analysis of the mastodon tusk revealed many unexpected surprises.
- In section 4 of the tusk, a series of cracks had been packed with a red-ish plaster that was opaque to x-rays indicating a high concentration of possible heavy metals.



- If the material is a heavy metal, extra precautions would need to be taken to stay safe while working with the tusk.
- Popular methods of preserving fossils in the past use harmful materials.^[2]
- Lead oxides blood affect bone marrow, central nervous system, peripheral nervous system and kidneys and may be a carcinogen.
- This includes plasters that use heavy metals such as lead.
- The tusk has also never been tested for a radiation, so there is a chance of the material being radioactive.

- The sample was unable to be tested for radioactivity, however.

Possible Makeup

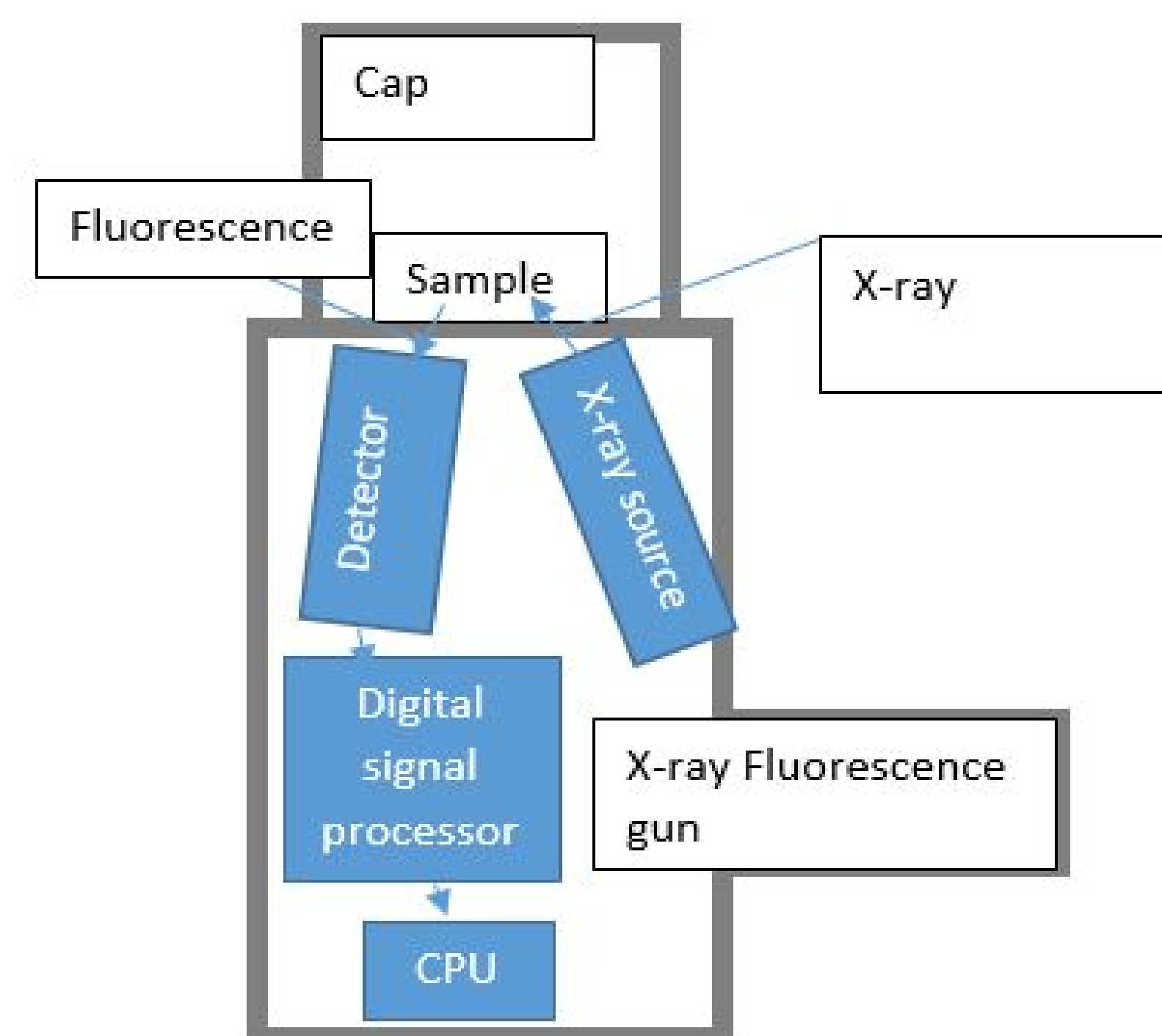
Prior to beginning to use the instruments to determine the material, there were several guesses.

- Lead, as we knew from the Home Depot test that there is lead paint in the tusk
- Arsenic, due to the coloring
- Uranium red, due to coloring and the tusk never having been tested for radioactivity.

Technical Approach

- X-Ray Fluorescence Spectroscopy (XRF)
 - XRF shows the elements within a sample. This allows the user to quickly narrow down the chemicals present in a sample by knowing what elements are present.
- X-Ray Diffraction (XRD)
 - XRD identifies compounds based off of how x-rays are diffracted at certain angles. The intensities and angles are used to find what is in a sample
- Raman
 - Raman uses the polarizability of a molecule to help identify what it is. It was used to double check the results of the XRD.

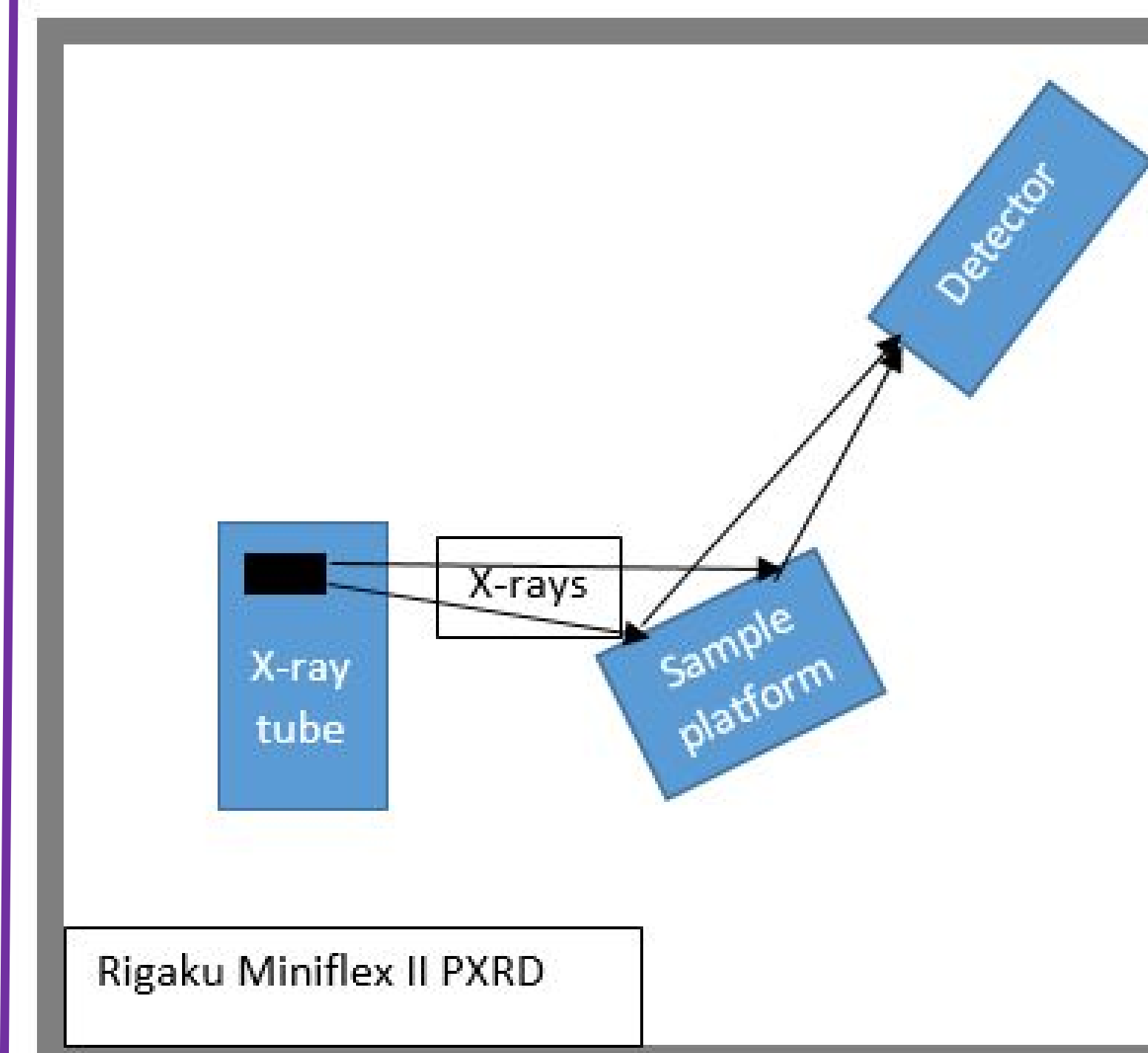
Instrument Diagrams



Parameters for XRF

- Atmosphere: Air
- Voltage: 40 kV
- Current: 7 μ A
- Assay time: 30 s
- Collimator: 8 mm
- Filter Wheel: Ti 25um; Al 300um
- Manual Filter: Blank

An x-ray beam is released from the source, which interacts with the sample by displacing electrons from the inner shells of the atom. This results in a difference in energy between the x-ray beam emitted and the energy that holds electrons into the proper orbits. When the x-ray's energy is higher than the binding energy of the electron, they are displaced. Because all atoms have different spacing for their orbits, XRF allows the user to identify the elements in the sample.

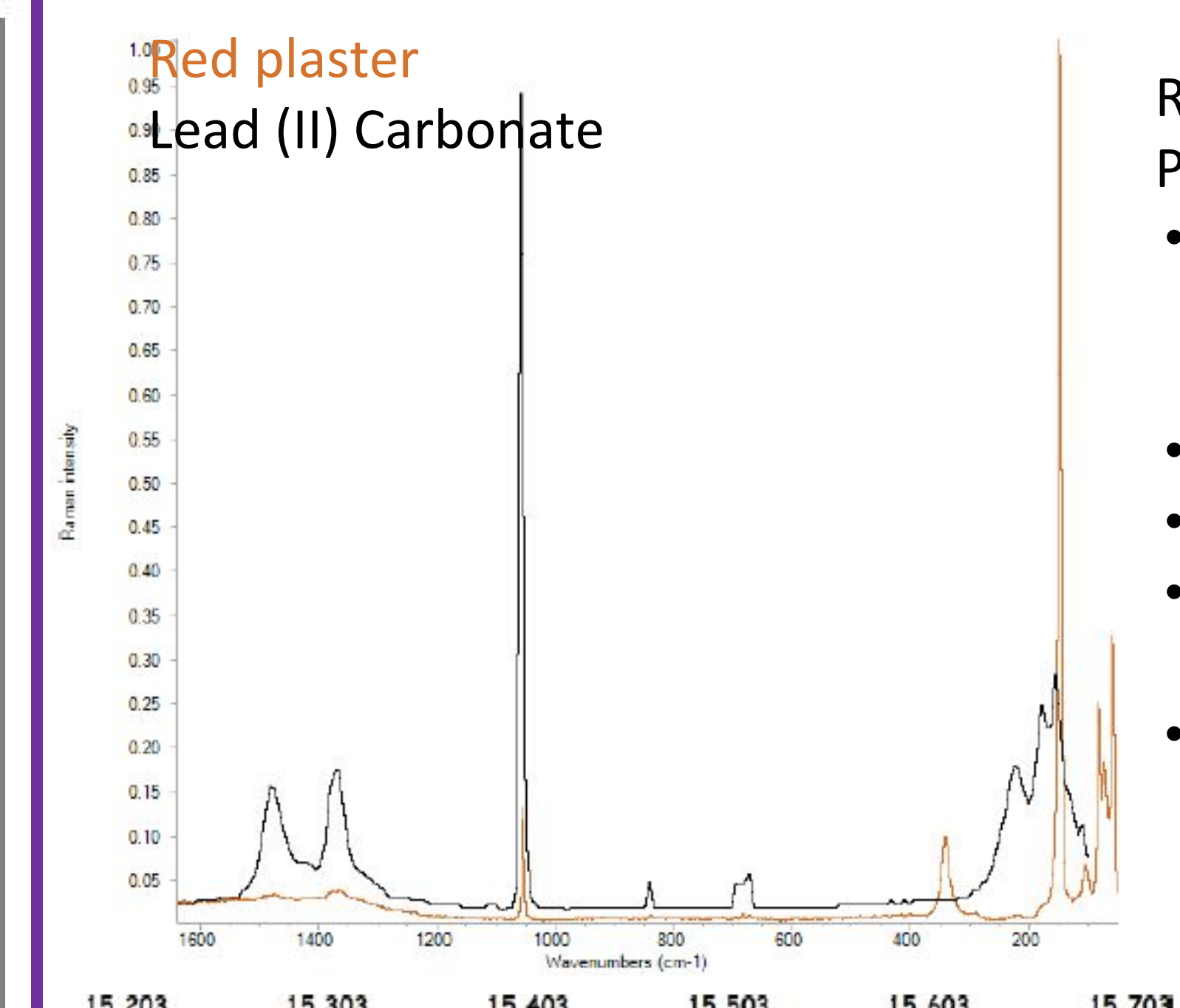


Parameters for PXRD

- No spinning of sample
- Sampled from 5 to 85°
- Sampled every 0.02°
- Scan speed of 2° per minute
- Electron tube voltage of 30 kV
- Current of 15 mA

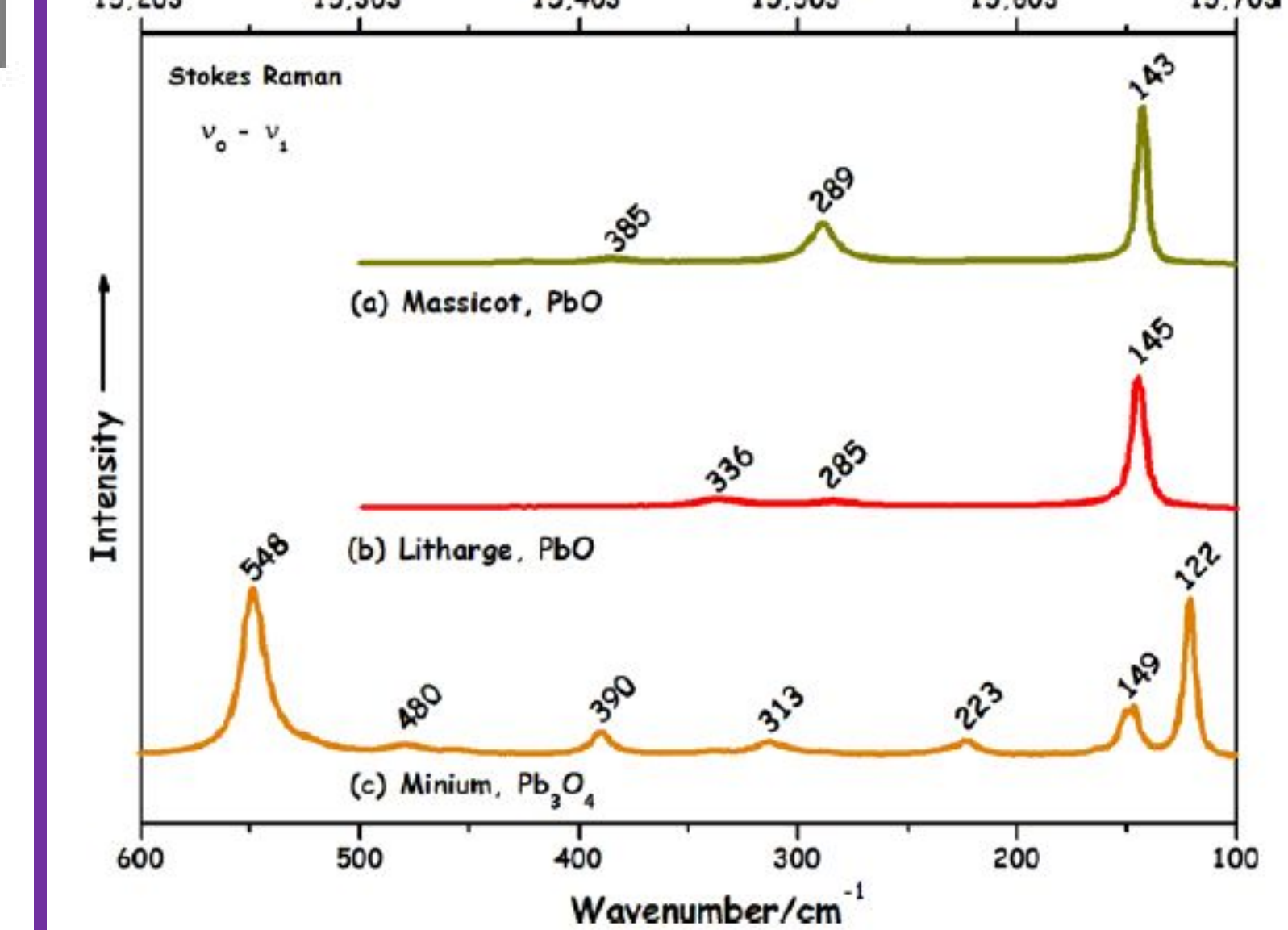
When light from a single source is scattered by two or more points in a space, the light waves will propagate until they interfere with each other. This is known as diffraction. Because the repeating units within a crystal are ordered, the scatter of x-rays works similar to the scattering to optical gratings. In a crystal, however, the scattering occurs in three dimensions and contains information about the atoms within the crystal.

Data (continued)



Raman Spectroscopy Parameters

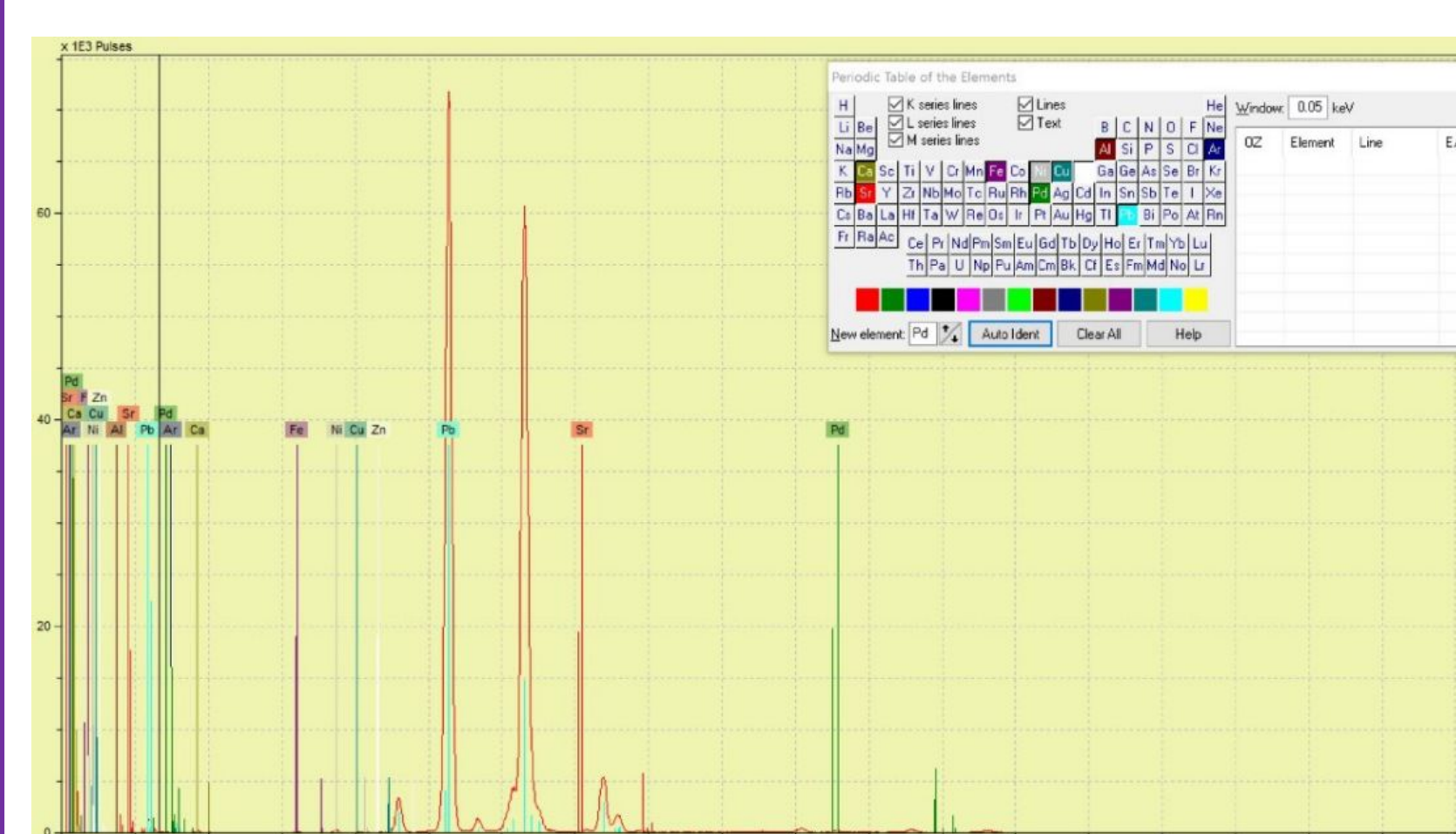
- Data from 50 to 3300 wavenumbers
- 785 nm laser
- Resolution 1.9285
- Grating 400 lines/mm
- Slit width 25 μ m



Spectra of massicot, litharge, and minium from Smith and Clark ^[3]

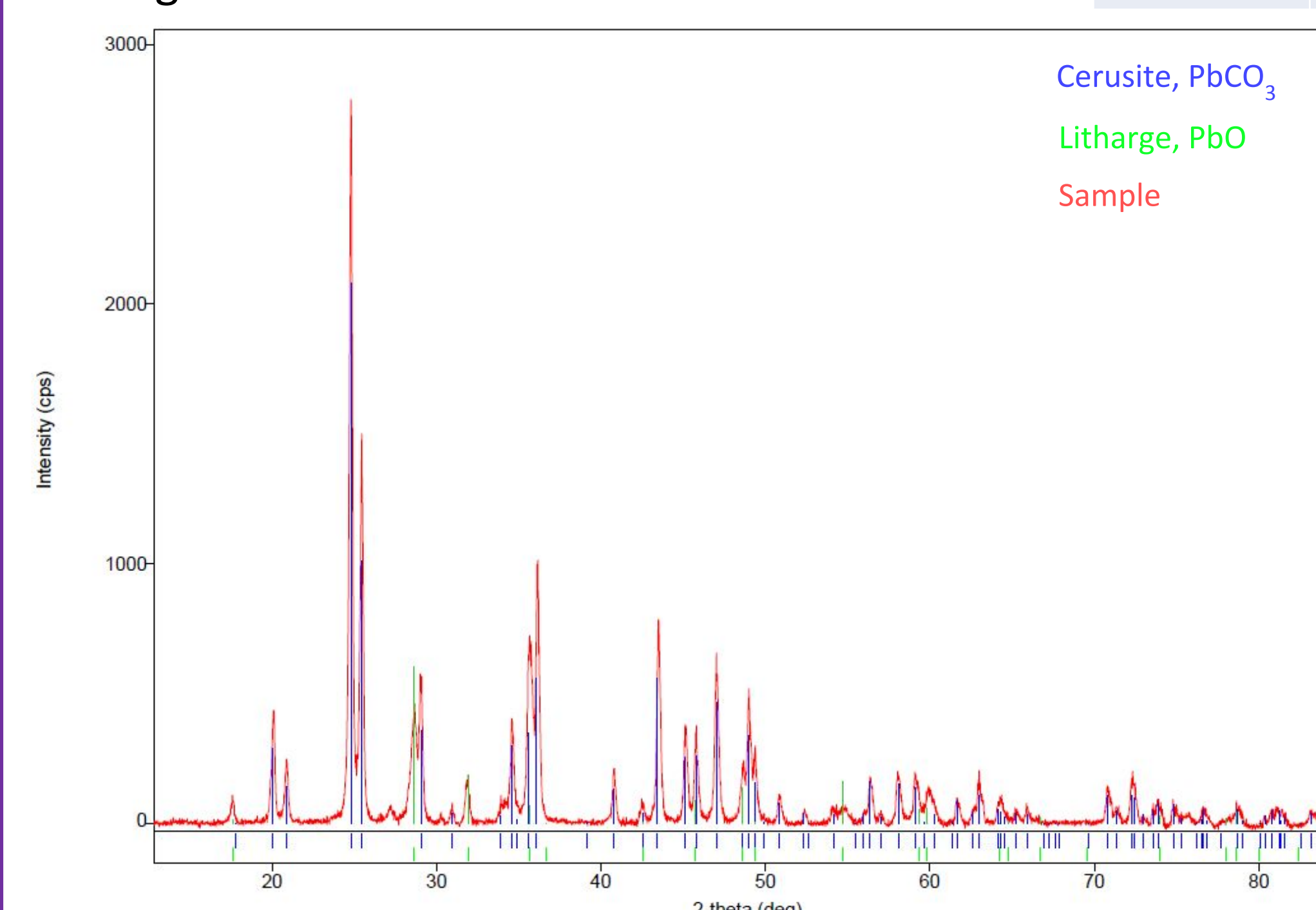
- The chemicals identified in PXRD were looked for using Raman to confirm that they are present.
- The lead (II) carbonate cerusite was within the database in the program and added to the spectrum
- When ignoring the difference in scale, the lead (II) carbonate overlaps the red stuff's spectrum.
- Because litharge was not in the database, it and a similar chemical were found to be compared
- Minium was not in the PXRD's database, but is used in lead paints, so it was compared as well.
- When ignoring the scale, the litharge spectrum fits over the red plaster spectrum, showing that it is present
- For detailed information of Raman of the tusk itself, see Nina's poster

Data



The XRF data shows the sample contains lead, an expected element. Other elements found are consistent with the instrument's background.

Element	Net	Background	Percent Composition
Al	215	395	2.95x10 ⁻⁴
Ar	319	514	4.37x10 ⁻⁴
Ca	1623	342	2.23x10 ⁻³
Fe	1464	292	2.01x10 ⁻³
Ni	2309	373	3.17x10 ⁻³
Cu	366	535	5.02x10 ⁻⁴
Zn	238	783	3.26x10 ⁻⁴
Sr	2162	2481	2.96x10 ⁻³
Pd	2551	2296	3.50x10 ⁻³
Pb	729178	3759	1



After running the PXRD, the spectrum was compared to those within the program's database to find the chemicals that were within the sample.

Conclusions

The red plaster that was studied using x-ray fluorescence, powdered x-ray diffraction, and Raman spectroscopy has been determined to be primarily cerusite and litharge. The amounts appear to be in about a 2:1 ratio of cerusite to litharge.

Acknowledgments

- Roy J. Carver Charitable Trust for making the project possible and allowing the purchase of the Raman spectrometer that was used.
- The UNI museum for allowing the project to be possible and allowing the usage of their x-ray fluorescence gun.
- Dr. Colin Weeks for assisting with the use of powder x-ray diffraction.

References

1. Spencer, J. *Preserving The Past: Scientific Study, Conservation, And Interpretation of The Mammut Americanum*, 2016
2. Howie, F. Materials Used for Conserving Fossil Specimens Since 1930, *Studies in Conservation* 29:sup, 92-97
3. Smith, G., Clark, R. Raman Microscopy in Archaeological Science, 2003, *Journal of Archaeological Science* volume 31, issue 8