XRD Analysis of the Corrosion Products from a Tlingit Copper Rattle
MCI#6241

Object: Tlingit Stikine Rattle

Owner/Custodian: National Museum of the American Indian

Artist/Manufacturer: Unknown

Geographic/Cultural Provenience: Tlingit

Material/Techniques of Manufacture: Copper, abalone, human hair, wood, sinew

Date: n/a

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Executive Summary

As part of the SI loan (NMNH and NMAI) to the Anchorage Museum History and Art, a Tlingit copper rattle was selected for analysis by XRD to look for evidence of “bronze disease” in the corrosion product. Bronze disease is caused by chloride contamination and is indicated by the following products: atacamite Cu_2Cl(OH)_3, paratacamite Cu_2Cl(OH)_3, or nantokite CuCl. Because this object will be housed in a new facility with a new HVAC system, the chlorine contamination will likely worsen as a result of the unstable environmental conditions. Therefore XRD analysis was used to determine if bronze disease is present, thereby informing upon further treatment decisions.

Materials and Methods

X-ray diffraction (XRD) is ideally suited for probing the structure of atoms and molecules in a wide range of materials, including pigments, ceramics, salts and corrosion. XRD has traditionally been conducted on materials in the form of ground powders that randomize the orientation of crystallites in the X-ray beam so that the diffracted X-rays are emitted in sets of three-dimensional cones, known as Debye cones. The cross-section of these cones is then detected as a series of concentric circles on film or a two-dimensional plate. The Rigaku D/Max Rapid at MCI utilizes the collimation of monochromatic X-rays to a microbeam, which can be focused on samples as small as 100 microns. The instrument’s goniometer is set by the operator to appropriately move the sample through two different axes, omega (Ω) and phi (Φ), during X-ray exposure in order to randomize orientation of the crystallites with respect to the beam as much as possible. In this way, the characteristic angles of diffraction appear as whole or partial Debye cones.

The detector on the Rapid diffractometer contains an extremely sensitive, curved image plate (IP) coated with phosphors, which are sensitized to the diffracted X-rays and then “developed” by a laser that causes the storage phosphors to release the energy they have captured. This energy is converted into a digital image, which is integrated with Rigaku AreaMax 2.0 software, so that the pattern may be read as a series of peaks or “lines” of varying intensity that radiate along an axis corresponding to the scattering angle (denoted in two-theta or d-spacing). The experimental patterns thus produced, after background subtraction, are qualitatively matched using Jade 8.0 software to reference patterns of known materials in the International Center for Diffraction Data (ICDD) libraries and/or user libraries developed from reference materials. These libraries contain diffraction patterns, descriptive information, and individual powder diffraction file (PDF) numbers. Because there may exist polymorphs and multiple compounds may share similar crystalline structures, several may be reported.

The experimental XRD patterns are produced from small areas of a sample, as determined by collimator size and the angle of the incident beam. The depth of penetration into a sample is typically on the order of 20-100 micrometers, depending on the density and mass of elements, as well as the angle of incidence. Most XRD patterns obtained from samples taken from historic artifacts and works of art represent a complex mixture of phases, often with overlapping peaks. Difficulty in reading patterns due to
high background noise may be produced by several sources, such as amorphous, or disordered, material in the sample, as well as fluorescence from iron-containing materials when analyzed with Cu Kα radiation. Changes in peak width and position can arise from differences in crystal size, purity, and texture, as well as hydration state. In addition, some materials, especially those with well-formed crystals, may be better scatterers than others (resulting in higher peak intensity), while other materials have different mass absorption coefficients with respect to the X-rays. Therefore, diffraction intensities do not accurately reflect the proportions of different phases in an inhomogeneous material. Thus, XRD results are qualitative and major/minor phases are only estimated. Difficulty in the interpretation of obtained diffraction patterns may be due to the following: differences in structure and chemical composition between samples and standards, preferred orientation in the sample, overlapping peaks, fluorescence, counting statistics, peak versus background statistics, and displacement of the sample from the focusing center. Depending on the signal/noise ratio and degree of overlapping of peaks in multi-phased material, trace phases may not be detected by this method.

**Experimental Conditions**

A. Sampling: corrosion product mounted on glass fiber with Elmer’s glue

B. Instrumental Parameters

   Instrument: Rigaku D/Max Rapid Micro X-ray Diffractometer

   Power: 46 kV; 39 mA; 1.79 kW (50 kV; 40 mA; 2.00 kW for sample 1C)

   Radiation: Chromium Kα (Copper Kα for sample 1c)

   Goniometer:

   a) chi: fixed at 45º

   b) phi: speed 1º/sec
Results
Tlingit_1c_3-24-09
Major phases: **Paratacamite (?), Copper Chloride Hydroxide (?)**
Minor phases: **Copper Hydroxide Hydrate, Silicon Dioxide**
(Cu tube)
Exposure time: 10 min
Collimator (mm): 0.3
Omega: 0°
Phi: spin

Figure 1: Sample 1C experimental pattern and ICCD reference patterns for Copper Hydroxide Hydrate, Paratacamite, Copper Chloride Hydroxide and Silicon Dioxide.

The experimental patterns of the samples, shown in Figure 1, match very well with the silicon dioxide and copper hydroxide hydrate reference patterns. However, because this sample matches very well with both paratacamite and copper chloride hydroxide it is impossible to determine which is present in the sample. There appears to be no additional crystalline phases present in the sample.
Tlingit_2_2-24-09
Major phases: **Paratacamite**
*(Cr tube)*
**Exposure time:** 30 min  
**Collimator (mm):** 0.8  
**Omega:** 0°  
**Phi:** 60 - 100°

**Figure 2:** Sample 2 experimental pattern, overlaid with ICCD reference patterns for several forms of paratacamite denoted with their ICDD powder diffraction file numbers.

The experimental pattern of sample 2 matches very well with several paratacamite reference patterns. Because these reference patterns are nearly identical, it is impossible to distinguish which form of paratacamite is present in the sample. The wide secondary peaks also suggest that more than one form of paratacamite may be present in the sample. Additionally, because paratacamite has a similar crystalline structure to copper chloride hydroxide (as shown in the previous sample), we were unable to rule out the presence of this compound in sample 2.
The third and final sample analyzed from the copper rattle was primarily amorphous. However, a second/longer analysis of the sample resulted in an excellent match for silicon dioxide, which is ubiquitous in nature. No chloride contamination was present in this sample.

**Conclusion**

Although analysis of the first two sampling areas on the copper rattle did not allow us to differentiate which chlorine contaminant was present, it was able to demonstrate that the object likely contains several forms of copper chloride residue. Because several forms of paratacamite share similar crystalline structures to copper chloride hydroxide, we were unable to determine which chlorine contaminant is present in the samples.