Japanese *Sugito* in the Philadelphia Museum of Art: Investigation of Painted Decorations and Soluble Nylon Coatings

Philadelphia Museum of Art

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Introduction

Twenty Japanese cedar wood sliding doors (*sugito*) are in the East Asian Art Collection of the Philadelphia Museum of Art (PMA). *Sugito* were commissioned [16th century through the Edo Period (1615-1868)] for architectural spaces, such as castles & estates of military & civilian elite. Panel sizes varied with intended site. The PMA *sugito* are painted masterfully in polychrome w/ figures & flora/fauna carrying seasonal and symbolic meanings. Comparable *sugito* are in Nagoya and Nijo Castles, Japan.

The PMA *sugito* can be divided into four groups by size, subject matter & artist's hand. Three *sugito* are highlighted here: *Hollyhocks & Butterflies* (Figure 1), *Courtier on Horseback* (Figure 4) and *Deer Under Maple Leaves* (Figure 2).

Figure 1. *Hollyhocks and Butterflies*

In the 1960's, the painted decorations were treated with soluble nylon (N-methoxymethyl nylon) of unknown origin to stabilize the flaking & friable paint. Several soluble nylon products were manufactured using different copolymers (DuPont, BASF, ICI).[1] Plenderleith (1974) mentions for conservation use Calaton CB™ (ICI), made by treating Nylon 6,6 with formaldehyde.[2] Soluble nylon products fell out of favor later due to their intractable nature & alteration on aging.[3]

Our *sugito* study is interinstitutional & ongoing to 1) elucidate painting materials & techniques, which have not been studied extensively & 2) confirm that the polymeric consolidant is nylon-based & determine composition. Because the PMA *sugito* fall outside the Cultural Properties Designation of Japan, we were able to undertake micro-sampling & analysis. We report here our initial findings.

Instrumental Methods

Samples were analyzed by selective use of MFTIR, Raman, XRF, SEM-EDS, & XRD; in-situ analyses via portable Raman & XRF (point analysis, mapping); & consolidant w/ MFTIR & Py-GCMS. Calaton CB™ was obtained & analyzed by MFTIR & Py-GCMS (also by TGA-IR, DSC & EGA not shown).[4] Cross-sections were viewed by VLM & FLM. *MFTIR*: 1) Thermo-Nicolet Continuum (MCT-A), Nexus 670 spectrometer, HG apodization, trans. mode, 4000-600 cm^{-1}, 4 cm^{-1} res., 200 scans, & Omnic 8.3a. 2) Bruker Hyperion (FPA), 4000-800 cm^{-1}, 8 cm^{-1} res., 64x64, & OPUS 7.2. *Raman*: 1) Bruker Senterra (CCD), 785 & 532 nm lasers & OPUS 8.1. 2) Bruker Bravo Raman Analyzer (CCD), 785 & 852 nm lasers, 3200-300 cm^{-1}, 10-12 cm^{-1} res., & OPUS 7.5. VLM, FLM, XRF, XRD, Py-GCMS details on request.

Results

The color palette for all *sugito* groups is red, blue, white, green, orange, black, & gold, except for one group with this same palette but no blue. The pigment palette is limited. (Table 1) (Figure 2) No modern colorants were detected. The simple palette belies the skill of the painter & complexity of compositions. The binder is proteinaceous (probably animal glue), implying use of glue bound paints (distemper). Ca oxalate (weddellite, $CaC_2O_4{\cdot}2H_2O$) was found in association with the binder, likely formed via oxidative degradation of organic material & reaction with calcite pigment or other particulate (Figure 3).

Table 1: *Sugito* Pigments

Color	Pigment name	Chemical name & ideal formula	Japanese pigment name	Raman bands (cm^{-1})
Red	Vermilion[4,5]	Mercury(II) sulfide [HgS]	*Shu* (朱)	342, 280, 253**
	Hematite[1,4,5]	Iron(III) oxide [Fe_2O_3]	*Shudo* (朱土)	280 br**
	Organic red	(Not analyzed)	—	—
Orange-red	Red lead[4,5]	Lead(II, IV) oxide [Pb_3O_4]	*Entan* (鉛丹)	549, 390**
Green	Malachite (M) +/- philipsburgite (P)[1,2,3,4,5]	Basic copper(II) carbonate [$Cu_2(CO_3)(OH)_2$] (M); [$(Cu,Zn)_6(AsO_4,PO_4)_2(OH)_6{\cdot}H_2O$] (P)	*Rokushō* (緑青)	433, 268, 217, 178, 155 (M)*
	Brochantite (B), antlerite (A), posnjakite (P)[1,2,3,4,5]	Basic copper(II) sulfate [$Cu_4(SO_4)(OH)_6$] (B), [$Cu_3(SO_4)(OH)_4$] (A); Hydrated basic copper(II) sulfate [$Cu_4(SO_4)(OH)_6{\cdot}H_2O$] (P)	***	985-972 br (SO_4 sym. str.)*
Blue	Azurite[1,2,4,5]	Basic copper(II) carbonate [$Cu_3(CO_3)_2(OH)_2$]	*Gunjō* (群青)	1096, 401, 281, 248, 179, 171*
White	Calcite[1,4,5]	Calcium carbonate [$CaCO_3$]	*Hōkaimatsu* (方解朱)	1086, 280, 157**
Black	Carbon black[4,5]	Carbon [C]	*Sumi* (墨)	1581,1361 br**
Gold	Gold (powder, leaf)[2,5]	Gold [Au] w/ minor silver [Ag], copper [Cu], nickel [Ni]	*Kin* 金 *(Kindei* 金泥, *Kim-paku* 金箔*)*	—
Off-white to none	Accessory minerals[1,5]	Quartz, montmorillonite, aluminosilicate clay, kaolinite	—	—

Key: 1=MFTIR, 2=SEM 3=XRD, 4=Raman, 5=XRF,*=532 nm laser, **=785/852 nm lasers, ***=not translated

Figure 2. Left: *Deer Under Maple Leaves.* Right top: Detail of painted leaves in visible light. Right bottom: XRF false color map, revealing the selection & distribution of elements in colors of the autumn maple leaves: Hg (pink), Cu (green), Pb (blue), & Ca (purple).

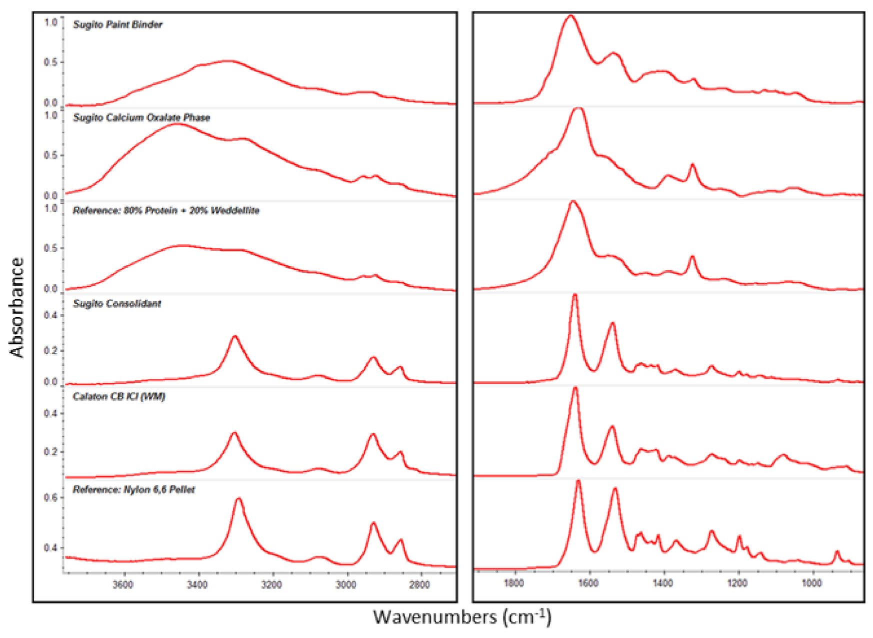


Figure 3. FTIR spectra of *sugito* binder, oxalate & consolidant with reference spectra of Calaton CB & Nylon 6,6.

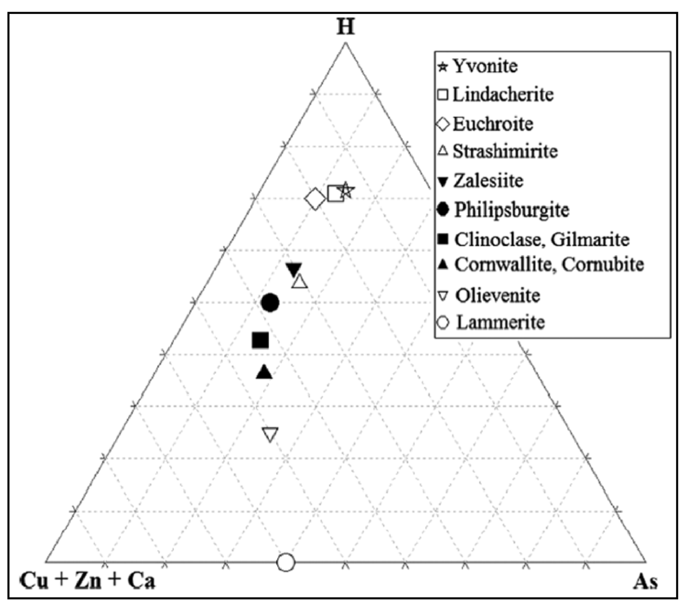


Figure 5. Copper(II) arsenate minerals ternary diagram. Black markers indicate Yamato mine minerals: philipsburgite, cornwallite & zalesiite.[5] Philipsburgite was detected on the *sugito*.

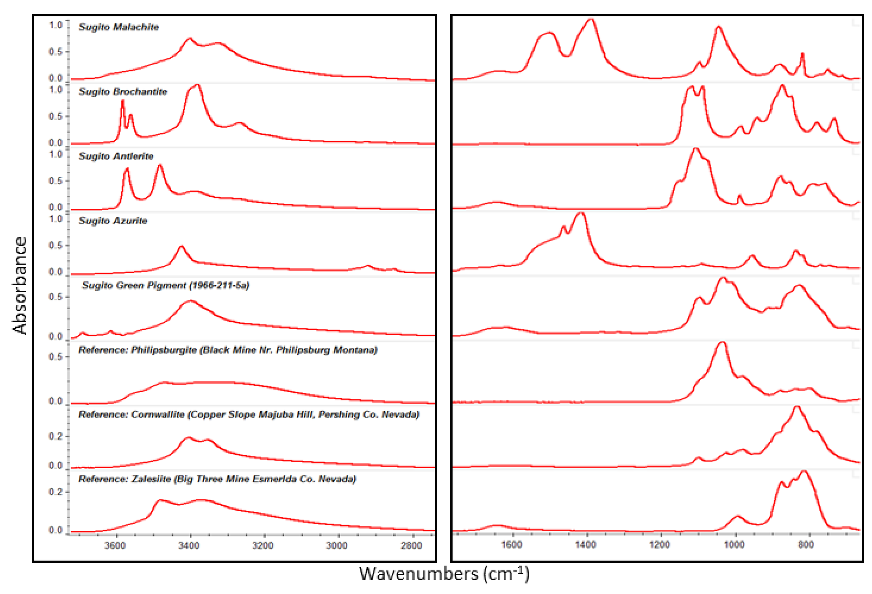


Figure 6. FTIR spectra of *sugito* green & blue pigments and related reference minerals.

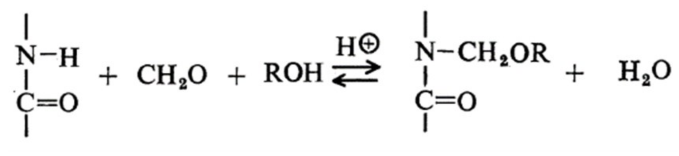


Figure 7. Formation of N-methoxymethyl nylon

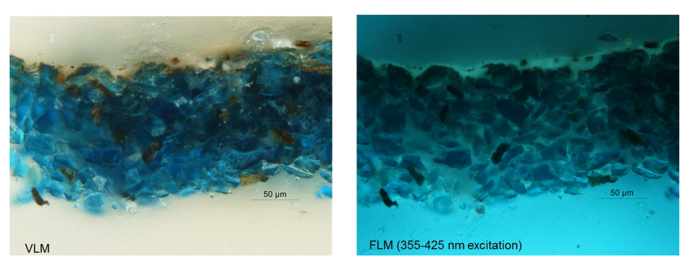


Figure 8. VLM & FLM images of blue paint cross-section containing azurite. FLM image shows nylon consolidant layer on top of & infused into paint layer.

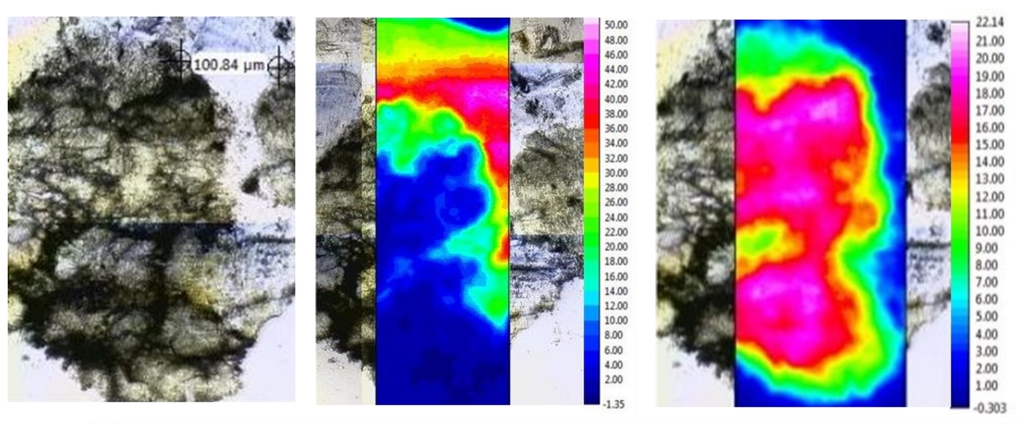
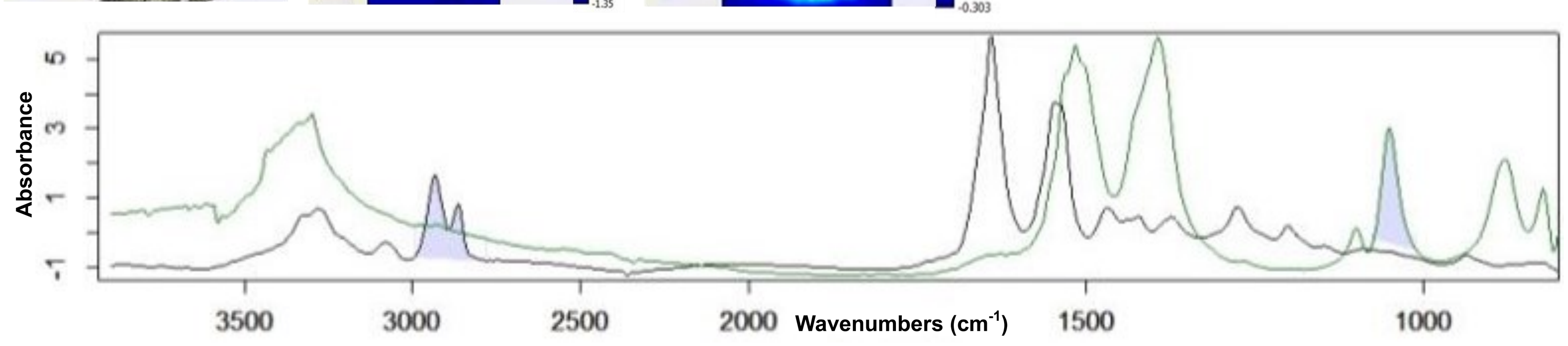


Figure 9. Left: VL image of *sugito* nylon consolidant adhered to malachite (light=consolidant, dark=malachite). Middle: IR FPA chemical maps of consolidant & malachite (integrated bands shaded in spectrum below), left & right respectively, where red=high concentration, blue=low. Below: extracted IR spectra (green=malachite & black=nylon consolidant).



A Focus on the Green Pigments

Two greens were identified by FTIR & Raman as malachite & a mixture of basic copper sulfates (brochantite, antlerite & posnjakite). On *Hollyhocks & Butterflies* (Figure 1), malachite is dark green & coarsely ground (131-147 µm avg. across), thus imparting texture to the upper surfaces of leaves. Black tenorite (CuO), occurring with the malachite, likely contributes to the dark shade. A lighter shade of green (underside of leaves) was made with finely ground brochantite rather than the addition of white pigment.

On some *sugito*, in-situ XRF analysis detected **Cu**, **As**, and **Zn** in green areas. XRF element maps show the distribution of these elements in foliage on *Courtier on Horseback*. (Figure 4)

Figure 4. Left: *Courtier on Horseback.* Right top: Detail of pine tree in visible light. Right bottom: XRF false color map showing distribution of Cu (red), As (blue) & Zn (green) in green paint containing philipsburgite.

Further investigation of green paint by XRD (not shown), revealed the mineral philipsburgite [$(\mathbf{Cu},\mathbf{Zn})_6(\mathbf{As}O_4,PO_4)_2(OH)_6{\cdot}(H_2O)$] in conjunction w/ the malachite pigment. Philipsburgite is known to occur in zones near malachite & its detection may provide a clue to local sources. One possibility is the "old Yamato copper mine," Shimo, Ofuku, Mine City, Yamaguchi Prefecture; in 2011, it was the only confirmed locality with philipsburgite in Japan.[5] (Figure 5) To our knowledge, this is the first report of philipsburgite on *sugito*.[6] Cornwallite [$\mathbf{Cu}_5(\mathbf{As}O_4)_2(OH)_4$] another mineral known to occur with malachite & brochantite, was suggested by MFTIR data but requires confirmation. (Figure 6)

Soluble nylon consolidant

Soluble nylon is made by partial methoxymethylation of nitrogen on nylon. (Figure 7) In Calaton CB™, 30-35% is so modified. On aging, cross-linking & loss of methoxylmethyl groups is thought to occur, making the polymer harder & less flexible. This appears to have happened on the PMA *sugito* and is suggested by FTIR.[7] (Figure 3) Paint cross-sections show the consolidant infused into the paint and entrapped particulate. (Figure 8) This is apparent in IR focal plane array (FPA) chemical maps of a consolidant sample found to be nylon-based (adhered to malachite). (Figure 9) Preliminary Py-GCMS data (not shown) for the consolidant suggest Nylon 6,6; Nylon 6,10; & Nylon 6,12; copolymer products (Dupont, BASF) may have been applied, in addition to a product like Calaton CB™ (modified Nylon 6,6).

Future work

We have characterized the color palette, major pigments & proteinaceous binder of the PMA *sugito* by FTIR & Raman. Notably, the uncommon mineral philipsburgite was identified by XRD. We will explore other mineral occurrences to group the *sugito*. Of particular interest is the chemical nature of the soluble nylon and its interaction with the metal cations of the various pigments & binder now characterized. Using Gaussian 16, we plan to model vibrational modes for N-methoxymethyl nylon.

References

1. See, for example, Cairns. Process for Obtaining N-alkoxymethyl Polyamides. DuPont, assignee. US Patent 2430908A. 1947.
2. For conservation preparation methods, see Plenderleith, H. J. The Conservation of Antiquities and Works of Art: Treatment, Repair, and Restoration. 2nd ed. London: Oxford UP, 1988.
3. Sease, Catherine. "The Case against Using Soluble Nylon in Conservation Work." Studies in Conservation 26.3 (1981): 102-10.
4. Calaton CB reference samples were kindly provided by Ken Sutherland, Art Institute of Chicago; Catherine Matsen, Winterthur Museum; and Arlen Heginbotham, The J. Paul Getty Museum.
5. Shirose, Yohei, and Seiichiro Uehara. "Philipsburgite from the Yamato Mine, Yamaguchi Prefecture, Japan." Journal of Mineralogical and Petrological Sciences 106.3 (2011): 153–157.
6. Philipsburgite was identified on a 17th century Japanese folding screen. See, Hayakawa, Yasuhiro, et al., "Analysis of Pigments Used in a Japanese Painting." Advances in X-ray Analysis 51 (2008): 263-268.
7. For IR reference spectra of methoxymethyl modified Nylon 6,6 (Spectrum 5.11) & other nylons published by ICI in 1965, see Haslam, John, et al. Identification and Analysis of Plastics. 2nd ed. London: Iliffe, 1972.

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