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Tracing the Alteration of Verdigris Pigment through Combined Raman Spectroscopy and X-ray Diffraction, Part I

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Abstract: This research investigates chemical alteration in the important historical pigment called verdigris, both in the form of neutral verdigris ($\text{Cu(II)} (\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) and basic verdigris ($\text{Cu(II)}_x(\text{CH}_3\text{COO})_y(\text{OH})_z \cdot n\text{H}_2\text{O}$), using reference pigment powders and historically relevant “mock-up” samples exposed to artificial aging. Analytical study of model samples by combined Raman spectroscopy, X-ray diffraction and visible spectroscopy provides new evidence that clarifies and builds on the often conflicting body of literature, first in terms of analytical identification of different forms of verdigris pigment, and second by tracing the alteration of neutral verdigris in systems that link to its behavior in aqueous media on historical types of paper. Results further suggest that the historical importance of neutral verdigris as a pigment is underestimated, since commercially available verdigris throughout its heyday – from before the Renaissance through the eighteenth century – was likely to have been dominated by the more easily manufactured neutral salt. This misunderstanding may arise from pigment alteration, whereby the neutral verdigris converts to basic copper salts, or forms organo-copper complexes.

Keywords: verdigris, Raman spectroscopy, X-ray diffraction, visible reflectance spectroscopy

1 Introduction

Alchemical endeavors in the ancient and medieval world led to many synthetic products, including the artists’ pigment called verdigris, which was the most important alternative to natural green colorants or blue-yellow mixtures until the nineteenth century. Despite its well-known instability, the pigment remained popular,

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especially among print, map, and book colorists, who desired a green colorant that would not obscure the printed lines. Historical recipes for verdigris developed empirically over centuries, and commonly involved the corrosion of copper sheets with acetic acid derived from wine or other fermented substances (Benhamou 1984; Clarke 2011; Gettens and Stout 1942; Kühn 1993; Merrifield 1849; Theophilus 1963). Previous attempts to reconstruct historical recipes for copper-based green pigments have demonstrated that natural variations in the starting materials, inclusion of additives like honey or salt, and varying production methods produce an array of blue to green copper compounds (Banik and Ponahlo 1982/1983; Banik et al. 1981, Bette et al. 2018, 2017; Chaplin et al. 2006; De la Roja et al. 2007a, 2007b; Fuchs and Oltrogge 1990; Gauthier 1959; Mairinger et al. 1980; Rahn-Koltermann et al. 1991; San Andres et al. 2010; Schweizer and Mühlethaler 1968; Scott 2002; Scott et al. 2001a, 2001b). Similar efforts by the present authors also expose the capricious nature of verdigris synthesis, and confirm the fact that there are two types of verdigris. The first is the neutral copper acetate monohydrate (Cu(II) $(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$). The second type is a series of basic copper acetate hydroxide salts that are extremely sensitive to synthesis conditions, resulting in variable (xyz) stoichiometry $(\text{Cu(II)}_x(\text{CH}_3\text{COO})_y(\text{OH})_z \cdot n\text{H}_2\text{O})$. For clarity, these compounds are summarized in Table 1 with common alternative designations and chemical formats.

Table 1: Verdigris compounds and nomenclature.

	Compound Alternative Names	Chemical Compound Name	Chemical Formula***	Source/Reference
NV	Neutral Verdigris	Copper(II) Acetate Monohydrate	(a) $\text{Cu} (\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (b) $[\text{Cu} (\text{CH}_3\text{OO})_2] \cdot \text{H}_2\text{O}$	Commercial Verdigris; ICDD PDF 27-1126
BV1	Basic Verdigris 1; Basic Verdigris D*; Basic Verdigris (132)**	Basic Copper (II) Acetate	(a) $\text{Cu}_2 (\text{CH}_3\text{COO}) (\text{OH})_3 \cdot \text{H}_2\text{O}$ (b) $[\text{Cu} (\text{CH}_3\text{OO})_2] [\text{Cu} (\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$	Recipe 11 in Scott*; ICDD PDF 50-0407, 58-0183
BV2	Basic Verdigris 2; Basic Verdigris A*; Basic Verdigris (215)**	Basic Copper (II) Acetate	(a) $\text{Cu}_3 (\text{CH}_3\text{COO})_4 (\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (b) $[\text{Cu} (\text{CH}_3\text{COO})_2]_2 [\text{Cu}(\text{OH})_2] \cdot 5\text{H}_2\text{O}$	Recipe 8 in Scott*
BV3	Basic Verdigris 3; Basic Verdigris B*; Basic Verdigris (115)**	Basic Copper (II) Acetate	(a) $\text{Cu}_2 (\text{CH}_3\text{COO})_2 (\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (b) $[\text{Cu} (\text{CH}_3\text{COO})_2] [\text{Cu}(\text{OH})_2] \cdot 5\text{H}_2\text{O}$	Recipe 9 in Scott*

* Scott (2002). ** Rahn-Koltermann et al. (1991), *** two common variations of identical (xyz) stoichiometric formulas.

When freshly prepared, both types of copper acetate salts are crystalline and quite amenable to analytical characterization. It is known that neutral verdigris (NV) and basic verdigris (BV) are structurally quite distinct. Neutral verdigris monohydrate, the mineral hoganite, has an unusual cage-like structure that contains two copper centers and four bridging acetates, resulting in a Cu to acetate (Cu:Ac) ratio of 1:2 (Gregson et al. 1971; Musumeci and Frost 2007). In contrast, the most commonly encountered form of basic verdigris, $\text{Cu}_2(\text{CH}_3\text{COO})(\text{OH})_3 \cdot \text{H}_2\text{O}$, which is found in the International Center for Diffraction Data (ICDD) database and is here designated as basic verdigris 1 (BV1), is a layered hydroxide salt, where the Cu(II) and hydroxyl ions are connected in extended sheets; acetate groups lie between the sheets, where they engage in hydrogen bonding (Švarcová et al. 2011). The extent of acetate grafting can vary in BV, leading to stoichiometric variations with Cu:Ac ratios of approximately 2:1 (Kozai et al. 2005; Masciocchi et al. 1997; Newman and Jones 1999; Pereira et al. 2006; Yamanaka et al. 1989). The difference in these two types of crystal structures has apparent implications for their reactivity, where BV is initially more stable. However, the relatively large acetate anions tend to cause disorder in the BV lattice and can exchange with other anions such as chloride, sulfate or nitrate (Masciocchi et al. 1997). The latter reactions can lead to mixtures containing other mineral phases, including, respectively, atacamite, brochantite, or gerhardite and their polymorphs (Newman and Jones 1999). This suggests that the latter phases may form naturally as alteration products of verdigris in paint layers over time and under appropriate conditions.

Identification of verdigris pigment in historical art, which may be an essential aspect of a technical study, is another matter altogether, since its alteration products may have little in common with verdigris reference materials. This problem is exemplified in the case of a green copper-based pigment found in hand-colored maps of a 1513 edition of Ptolemy's *Geographia* (Figure 1a). As previously reported, in some maps in this volume the pigment appears brown-green and chalky and is associated with copper-induced paper deterioration, while in other maps the paint films are a clear green color and have not caused any apparent alteration to the support. The paint films are thickly applied in many areas, allowing microsampling of pigment particles. Optical microscopy of the pigment from clear green areas is similar to, but does not match, reference verdigris, and samples from both types of greens exhibit Raman spectra with highly fluorescent backgrounds and only very broad, weak peaks with maxima near 1580, 1440, and 1350 cm^{-1} (Figure 1b) (Albro et al. 2011, 2012; Brostoff et al. 2011, 2013). Due to the well-known behavior of copper salts to combine with proteinaceous and resinous media (Scott 2002; Gunn et al. 2002; Aceto et al. 2010; Santoro et al. 2014), such copper-containing green pigments without other

Figure 1: (Left) hand-colored maps in (A) good and (B) poor condition from the 1513 edition of the Ptolemy *Geographia* (Library of Congress, Rosenwald Collection). (Right) *in situ* Raman spectra (514 nm excitation) of a green copper pigment from same maps (C) in good condition, and (D) in poor condition, showing typical lack of distinct peaks and fluorescent background (280 second exposure, 50x objective).

identifying characteristics are often described as organo-copper complexes and presumed to be altered verdigris (Kühn 1993; Scott 2002; Mairinger et al. 1980; Banik et al. 1981; Banik and Ponahlo 1982/1983; Chaplin et al. 2006; Nastova et al. 2012; Chaplin et al. 2005; Groen 1975). However, it is also known that in some cases artists made amorphous copper-based green colorants or glazes intentionally (Conti e.g. 2014; De la Roja et al. 2007a; Gettens and Stout 1942; Gunn et al. 2002; Kühn 1993; Woudhuysen-Keller 1995).

Previous investigations of verdigris primarily focus on characterization of the unaged reference salts, or on verdigris alteration in oil, resin, or proteinaceous media (e.g. Cartechini et al. 2018; Gunn et al. 2002; Mendes et al. 2008; Richardin et al. 2011; Santoro et al. 2014; Švarcová et al. 2014; Zoleo et al. 2014). Studies of verdigris in aqueous media are fewer in number, and often focus on the deleterious effects of copper ions on cellulose deterioration (Ahn et al. 2015; Banik and Ponahlo 1982/1983; Bhowmik 1970; Henniges et al. 2006; Kühn 1993; Shahani and Hengemihle 1986) or the evaluation of stabilization treatments (Henniges et al. 2006; Maitland 2009; Kolar et al. 2008; Ahn et al. 2014; Hofmann et al. 2015; Malešič et al. 2015; Hofmann et al. 2016). A carbohydrate-based watercolor medium is quite different from oils, waxes, and resins, and the well-established formation of amorphous organo-copper complexes has not been demonstrated in thinly applied gum and glair media. Additionally, studies of alteration of the pigment in isolation from a binding medium are unknown to the authors. Given the common use of verdigris in watercolor painting and

tinting of prints, chemical alteration of verdigris pigment itself and its behavior in aqueous media thus invite further study and clarification.

In order to better identify and understand verdigris as found in historical works on paper, and as the basis for ongoing work into verdigris treatment strategies (not reported here), this paper focuses on identification of verdigris in different states of alteration, both in the form of individual pigment particles and in historically relevant, artificially aged “mock-up” paint films on paper, through complementary Raman spectroscopic and X-ray diffraction (XRD) analysis. Because verdigris is sparingly soluble in aqueous media, grinding the pigment in water or a dilute aqueous medium results in partial dissolution with settled green particles and a vivid green supernatant. While some historical recipes specify use of the clear green liquid, the complete paint mixture was commonly employed. In this study, NV was ground in dilute acetic acid before adding to the binding medium to obtain evenly-toned paint films, following historical practice and to mimic the relatively thick paint films found on the Ptolemy atlas (described above). Paint films of NV in gum Arabic or glair (beaten egg white) were deposited and artificially aged on four paper substrates: (1) Whatman No. 1 filter paper, and (2, 3, 4) handmade, gelatine-sized, rag paper either buffered, with low Ca content, or with low Ca and high Fe content, as described in Appendix 1. Corresponding samples were made from lab-synthesized, pre-characterized BV, but without dissolution in acetic acid. By linking the aging behavior of the pigments in powder form to paint films on different substrates, the study aims first to facilitate better informed analytical identification of verdigris alteration products in historical works on paper, and second to better understand the relative stability of verdigris paint films in such preparations.

2 Results and Discussion

2.1 Pigment powder reference samples

XRD and Raman analysis of several commercial verdigris pigment powders are in excellent agreement with the ICDD database and published Raman spectra (Bell et al. 1997; De la Roja et al. 2007a, 2007b; San Andres et al. 2010; Scott 2002; Scott et al. 2001a; Yamanaka et al. 1989) for neutral copper acetate monohydrate. Elemental analysis of the verdigris purchased from Kremer Pigments, Inc. confirms stoichiometry consistent with the neutral verdigris monohydrate (Table 2). These results definitively show that Kremer, Sinopia and Cornelissen commercial

Table 2: Experimental elemental compositions* of verdigris pigment compared to theoretical stoichiometry.

Sample	Commercial neutral verdigris	Neutral verdigris mono- hydride	Synthetic BV1,** trial 1	Synthetic BV1,** trial 2	Oven- converted BV	BV1
Stoichiometry	Experimental	Theoretical	Experimental		Theoretical	
Cu	1.0	1.0	1.0	1.0	1.0	1.0
C	4.2	4.0	1.0	1.0	1.1	1.0
H	8.2	8.0	3.3	3.8	3.9	4.0
O	5.3	5.0	2.9	2.7	2.9	3.0

BV = basic verdigris; *determined by CHNO analysis or ICP-OES; **Schweizer and Mühlethaler recipe #4.

pigments are NV, contrary to some information on their websites (Figures 2, 3c–e). This is not a minor point, since many studies utilize these reference materials and identify them as the basic variety, and thus have based interpretations on this erroneous information (e.g. Maitland 2009; Ohlídalová et al. 2015).

Figure 2: XRD pattern of commercial verdigris pigment purchased from Kremer Pigments, Inc. with overlaid reference lines (blue) for neutral verdigris (hoganite or copper acetate monohydrate, ICDD 056–0009); the result was identical for verdigris purchased from L. Cornelissen & Son and Sinopia Pigments.

Simple laboratory syntheses of verdigris on a copper sheet at room temperature or at 85 °C from exposure to vinegar fumes, the most common methods found in historical texts, form an analytically identical product to commonly available NV

(Appendix 1, Figure 3b). Some variation is noted in peak intensities between 3200–3500 cm^{-1} in the Raman spectra of different grains (Figure 3), suggesting minor modifications in hydration water or crystal orientation that could contribute small color differences (De la Roja et al. 2007a; Frost et al. 2004). When any of the neutral or basic verdigris products are mixed with acetic acid, they readily dissolve and re-precipitate to form pure, teal-blue NV. The Raman spectrum of re-precipitated NV is shown in Figure 3a, and the product is pictured in Figure 4a. This procedure appears to have in fact been adopted throughout the pigment's heyday to produce a high quality commercial pigment, sometimes known as French, distilled or refined verdigris, as was recommended as workshop practice by Cennino Cennini in the fifteenth century and other historical sources (Cennini 1960; De la Roja et al. 2007b; Gettens and Stout 1942; Kühn 1993; Merrifield 1849; Neven 2016; Van Eikema Hommes 2001).

Figure 3: Raman (514 nm excitation) spectra of pure neutral verdigris pigments obtained from different sources: (A) product from dissolution and recrystallization in acetic acid of basic verdigris 1 (see Figure 3a); (B) homemade verdigris from copper exposed to acetic acid fumes (room temperature and humidity); (C) Cornelissen verdigris; (D) Sinopia verdigris; and (E) Kremer verdigris. Power at the samples was 0.05–0.6 mW. The slight variations $>3000 \text{ cm}^{-1}$ are most likely due to differences in hydration water.

BV synthesized by the authors from any one published recipe was variable from batch to batch in terms of color, particle shape and purity, as detailed in Appendix 1. In all cases, Raman spectra (Figure 5) and XRD patterns (not shown) of the BV products are distinct from NV, but exhibit minor differences

Figure 4: Neutral and basic verdigris pigments, (A) crystals of neutral verdigris precipitated from dissolution of basic verdigris in acetic acid, and (B) crystalline “balls” of basic verdigris 1 synthesized according Scott recipe #11. The white scale bars are each equal to 1 mm.

Figure 5: Raman spectra (514 nm excitation) of pigment powder references of basic verdigris: (A) clear-pale green particle in BV1 (Scott recipe #11); (B) green particle and (C) blue particle in basic verdigris 2 (BV2, Scott recipe #8); (D, E) different particles in basic verdigris 3 (BV3, Scott recipe #9). Power at the samples was 0.05–0.6 mW.

between them, as has been previously noted (Chaplin et al. 2006; De la Roja et al. 2007a; Kühn 1993; San Andres et al. 2010; Scott 2002). For example, repeated trials of Schweizer and Mühlethaler’s (1968) procedure for BV1 resulted in either deep green crystalline balls (Figure 4b) or powdered medium bluish-green products, which in both cases analytically match the predicted BV1 product. Light element analysis of the lab-synthesized BV1 (Table 2) confirms that the stoichiometry is approximately $\text{Cu}_2(\text{CH}_3\text{COO})(\text{OH})_3 \cdot \text{H}_2\text{O}$.

Reproduction of Rahn-Koltermann's (1991) procedure for BV2 ($\text{Cu(II)}_3 (\text{CH}_3\text{COO})_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) resulted in a very fine, pale green precipitate, which under magnification is seen to contain light blue and medium green particles in the mixture. While XRD and Raman analysis show good matches to BV1, Raman spectra of some particles show possible matches to BV2 and BV3 varieties reported by Chaplin et al. (2006), plus an alternative BV1 in the blue grains (Figure 5b, 5c). A second filtering from this recipe resulted in a product that has additional peak in the XRD pattern at $d = 11.75 \text{ \AA}$; this peak may correspond to a peak at $d = 11.9 \text{ \AA}$ reported for BV2 by Kühn (1993) and Scott (2002). When heat is not well controlled during synthesis, black tenorite (CuO) with some spertinite (Cu(OH)_2) is formed, as confirmed by XRD (data not shown, ICDD 41-0254 and 035-0505, respectively).

Reproduction of the Schweizer and Mühlethaler (1968) procedure for BV3 ($\text{Cu(II)}_2(\text{CH}_3\text{COO})_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) resulted in an array of light blue to green to purple layered products, similar to that reported by both Scott et al. (2001a) and Chaplin et al. (2006). Raman spectra of different grains show variations from BV1, but are difficult to identify as any one type of BV (Figure 5d, 5e). These inconsistent and sometimes unsuccessful results to make pure reference compounds of the BV salts, especially BV3, have been noted by others (Bette et al. 2017, 2018; Chaplin et al. 2006; Rahn-Koltermann 1991; Scott 2002; Švarcová et al. 2011). The multiple products resulting from BV3 synthesis proved to be unstable at ambient conditions, altering visibly over a few weeks.

Overall, Raman and XRD spectra of BV samples illustrate the difficulty in using freshly synthesized compounds as references, since BV compounds have varying stoichiometry (Table 1) and overlapping spectral features, and mixtures are easily produced. It is noted, for example, that the Raman spectrum reported by Chaplin et al. (2006) for BV1 reasonably matches that produced in this study, while variants of BV2 and BV3 in Chaplin et al. (2006) show what appear to be residual NV peaks (Mathey et al. 1982; San Andres et al. 2010; Van Eikema Hommes 2001). Detailed data obtained from these samples are the subject of a future publication. That said, reference samples for NV and BV1 are well characterized by these methods.

2.2 Artificially aged pigment powders

Exposure of a thin layer of ground teal-blue NV in an oven set at 45°C and 65 % RH for 14 days produced a green product, which elemental analysis shows is in excellent agreement with the theoretical stoichiometry for BV1 (Table 2). NV pigment particles exposed to a saturated humid environment

overnight at ambient temperature also convert to BV1 (data not shown). These results imply that BV1 may be expected to form naturally from NV. This is also the form of BV most readily obtained in the synthesis experiments discussed above.

While reproduction of historical recipes does not clarify whether controlled manufacture of BV was ever achieved on a commercial level, it is well established that a market for NV existed since the Renaissance and that artists tended to re-distill commercial verdigris in any case, thus obtaining the neutral monohydrate form. This gives rise to the notion that artists were commonly using NV in their paints, for example to color foliage, despite its blueish hue. Analytical studies of surviving art works (Kirby and Saunders 1998; Salvado et al. 2013; Ricciardi et al. 2013) and review of artists' technical treatises reveal that painters often admixed yellow colorants with verdigris to achieve warmer green tones (Merrifield 1849; Thompson 1936; Kühn 1993; Clarke 2011; Neven 2016). Therefore, one should not assume, as has been remarked (Gettens and Stout 1942; Mairinger et al. 1980; Scott 2002; Salvado et al. 2013; Ohlídalová et al. 2015), that BV is the historically more relevant variety of this artists' pigment.

2.3 Model verdigris paint films

2.3.1 Verdigris paint films in gum Arabic on Whatman No. 1 paper

Reactivity of verdigris in paint films on various substrates should be established separately from study of pigment powders in order to better understand the condition of verdigris in historical materials. As a first step, a series of model paint films in gum Arabic on Whatman No. 1 filter paper were produced from both NV (Kremer Pigments, Inc.) and the lab-synthesized BV1 (Appendix 1). Model samples were artificially aged according to a new protocol that the authors developed using 50 °C and 65 % RH in order to delay as much as possible alteration of the pigment to the historically non-relevant form of black tenorite (CuO), as described in Appendix 1.

Visible reflectance spectra confirm that all NV paint films examined in this study initially have a maximum reflectance about 490–495 nm before aging (Figure 6), which corresponds visually to a bright teal-blue color; this terminology and result differ from that reported by, among others, Kühn (1993), but agree with more recent studies (De la Roja et al. 2007a, 2007b; San Andres et al. 2010). BV1 paint films, on the other hand, initially have a distinctly different, broad maximum reflectance from about 500–530 nm (data not shown).

Figure 6: (Left, A) UV-Vis data for neutral verdigris (Kremer) in gum Arabic on white Whatman No. 1 filter paper, showing a consistent shift in the reflectance maximum from ~490 to ~510 nm and broadening when aged 0–42 hr. as it converts to basic verdigris; black tenorite forms overall by 116 hours. NB: small sharp peaks are artifacts from subtraction of reference. (Right, B-F) neutral verdigris (Kremer) in gum Arabic on Whatman No. 1 drawn-down paint film samples after different intervals of artificial aging at 50 °C and 65 % RH, showing the measured color shifts.

It is known empirically that relative humidity is a major factor in the color change of verdigris (Kühn 1993). As shown in Figure 6, after exposure of NV in gum Arabic on Whatman to the new artificial aging protocol (50 °C and 65 % RH), color alteration from teal-blue to green takes place in most particles during the first 4–24 hours; this is measured as a shift in the visible reflectance spectra from ~490 nm to ~510 nm or higher. Visual signs of alteration include development of a pale green precipitate on top of, and eventually consuming, larger crystals of NV, as well as transparent green areas. In contrast, BV1 paint films show no noticeable color change with artificial aging, although after 286.5 hours of aging the reflectance curve narrows somewhat and shows a maximum close to 525 nm (data not shown).

Raman spectroscopy and XRD analysis of the samples firmly establish that the color shift in NV paint films corresponds to chemical alteration to BV1; this is unclear in the literature (e.g. Kühn 1993), although numerous sources note that a color shift of verdigris is expected. Analytical evidence thus supports the historical importance of NV as a pigment. Detailed analysis of the Raman spectra (Figures 7, 8) allows us to trace the chemical path of NV conversion in paint films in gum Arabic in terms of hydroxyl and acetate group vibrations. Following assignments in the literature (Colthup et al. 1990; De la Roja et al.

Figure 7: Raman spectra (514 nm excitation) of various particles in paint films of neutral verdigris in gum Arabic on Whatman No. 1 filter paper, with artificial aging at 50 °C and 65 %RH for: (A) 0 hours, (B), (C) and (D) 4 hours, and (E) 16 hours, showing changes in spectra with transformation of neutral to BV1. Power at the samples was 0.05–0.6 mW.

Figure 8: Detail of Figure 7 showing the shift from ~948 to ~937 cm⁻¹ that indicates transformation from neutral to basic verdigris. Power at the samples was 0.05–0.6 mW.

2007a, 2007b; Frost and Klopogge 2000; Mathey et al. 1982; Newman and Jones 1999; Trentelman et al. 2002) distinctive spectral characteristics include: 1) shift in the strong doublet near 949 cm^{-1} to a singlet near 936 cm^{-1} (C-CH₃ stretch); 2) disappearance of peaks near 703 cm^{-1} (bidentate O-C-O symmetric deformation) and 321 cm^{-1} (bidentate Cu-Cu-O); 3) appearance of new peaks near 400 and $485\text{--}500\text{ cm}^{-1}$, tentatively assigned to Cu-OH deformation; and 4) appearance of free OH stretching peaks between $3500\text{--}3700\text{ cm}^{-1}$. In particular, shift of the 949 cm^{-1} peak to about 938 cm^{-1} alone appears to be a reliable indicator of the presence of BV (Figure 8). Raman spectra in some cases suggest that additional alteration products, possibly BV2 and BV3, and/or alternate forms of BV1, may be present in the artificially aged samples, but all particles from which spectra were obtained generally match BV1.

XRD analysis also suggests the development of intermediate phases other than BV1 during artificial aging of the NV model samples. The presence of a somewhat broad peak in XRD patterns near $d = 11.2\text{--}11.7\text{ \AA}$ around 4 hours is noted in most samples. This peak subsequently diminishes as aging proceeds, suggesting formation of an alternate, unstable phase under these aging conditions. A similar peak is found in six XRD patterns reported by Scott (2002) for BV products and one historical sample. This was also seen in two historical samples examined in this laboratory, although the patterns have incomplete correspondence to any one of those reported by Scott.

Experimental work shows that above 50°C NV model samples convert rapidly to tenorite, CuO, a black product (ICDD 041-0254, data not shown), which is not known on historical paint samples. This key observation was used to design artificial aging parameters in this study at mild conditions, in contrast to other studies in the literature. Despite these mild conditions, NV samples convert mainly to black-brown tenorite by 116–287 hours of artificial aging (data not shown). This transformation occurs at temperatures well below that reported for the mineral hoganite by thermogravimetric analysis in the absence of oxygen (Frost et al. 2004; Gao 1996) and raises questions about the interpretation of results of conservation treatment studies that have employed artificial aging temperatures over 70°C . Tenorite also forms during Raman analysis if the power from a 785 nm laser is too high. In sharp contrast, paint films of lab-synthesized BV1 in gum Arabic on Whatman show no discernable change, either visually, by Raman spectroscopy or by XRD, at least through 1390 hours of artificial aging (Figure 9). The difference in reactivity between BV formed as an alteration product, and the directly synthesized BV1 is noteworthy; possibly this arises from an increase in crystal defects in the *in situ* alteration product.

Figure 9: XRD patterns (without baseline subtraction) of (A) lab-synthesized BV1 paint film in gum Arabic on Whatman No. 1 paper, no artificial aging; (B) lab-synthesized BV1 paint film in gum Arabic on Whatman No. 1 paper artificially aged at 50 °C and 65 %RH for 287 hr.; and (C), BV1 product from NV alteration in gum Arabic paint film on Whatman No. 1 paper after artificial aging at 50 °C and 65 %RH for 16.5 hr. Results show no significant change in the lab-synthesized BV1 paint film, even up to 1390 hours of aging (not shown), and that the oven-aged, altered verdigris paint film also matches BV1 (copper acetate hydroxide hydrate, ICDD 058–0183, shown with green lines).

2.3.2 Model verdigris paint films on historically relevant paper

NV and BV1 paint films were also deposited on a series of paper substrates in order to gauge the possible effects of historically relevant substrates on verdigris alteration. These substrates include: (1) University of Iowa (UI) handmade, gelatine-sized, buffered rag paper (~15,000–18,000 ppm Ca); (2) custom-made, gelatine-sized, low Ca UI rag (~7000 ppm Ca); and (3) gelatine-sized, low Ca UI rag doped with FeSO_4 (~400–600 ppm Fe and ~5000 ppm Ca). The papers were selected to echo the fibre furnish, pH, thickness and trace element ratios typical of paper found in historical maps and prints. Results are compared to those on Whatman No. 1, and summarized in Table 3.

While the effect of additional variables introduced by these samples, including pH and metal content, are the subject of further study, results consistently show (1) no detectable change in the BV1 samples through 1360 hours of artificial aging, and (2) somewhat faster alteration of neutral to basic verdigris on

Table 3: Compilation of XRD and Raman results from artificially aged neutral verdigris paint films on four substrates.

0–16.5 hours	4 hours		16.5 hours	
Sample*	XRD	Raman	XRD	Raman
Kremer/gum Arabic, Whatman No. 1 (pH 6.4) 	NV and BV; unknown peak at $d \sim 11.3 \text{ \AA}$	NV + some BV on top of neutral crystals	BV1	BV1 + isolated particles of NV
Kremer/gum Arabic, UI rag (pH 9.4) 	NV + some BV; weak unknown peak at $d \sim 11.3 \text{ \AA}$	NV, crystalline and amorphous-looking; some BV with unknown peaks ~ 1603 , 1319 , 1296 cm^{-1}	NV, crystalline and amorphous-looking, + BV1	Mixed NV and BV, both crystalline and amorphous-looking; BV with unknown peaks ~ 1606 , 836 cm^{-1}
Kremer/glair, UI rag (pH 9.4) 	NV + some BV; medium unknown peak at $d \sim 11.3 \text{ \AA}$	NV + tentative BV and unknown peaks ~ 1603 and 830 cm^{-1}	BV, somewhat amorphous-looking, with diminished peak at $d \sim 11.3 \text{ \AA}$	BV1, crystalline and amorphous-looking, with unknown peaks ~ 1606 , 1247 cm^{-1} ; isolated NV
Kremer/gum Arabic, Fe-doped, low Ca UI rag (pH 9.4) 	NV + some BV; medium unknown peak at $d \sim 11.3 \text{ \AA}$	NV and BV, crystalline and amorphous-looking; unknown peaks ~ 1602 , 1249 cm^{-1}	BV1, with diminished peak at $d \sim 11.3 \text{ \AA}$	BV1, crystalline and amorphous-looking, with unknown peaks ~ 1602 , 1303 cm^{-1} ; isolated NV

*white scale bar equal to 1mm for all microphotographs.

Whatman filter paper than on the gelatine-sized rag papers, where particles of neutral verdigris remain up to about 42 hours of aging. In the sized rag paper samples, the transient XRD peak near $d = 11.2\text{--}11.7 \text{ \AA}$ also persists longer than

on Whatman paper. Visual observation of the model paint films by light microscopy suggests that this effect is largely due to the sizing of the rag paper, which renders it much less absorbent and allows pigment particles to be encapsulated in the medium. This provides some degree of protection from the environment and is consistent with observations, both historical and modern, of the barrier protection afforded by an organic medium on verdigris (Gettens and Stout 1942; Gunn et al. 2002).

In addition, results suggest that more complex alteration pathways of NV alteration may occur on the historically relevant model samples, including the formation of thus far unidentified products, as shown in Table 3. This could be the result of increased interaction between the pigment and medium, as well as the pH of the substrate and other constituents in the paper. For example, both Raman and XRD analyses suggest the formation of amorphous material in the model samples. As shown in Figure 10, Raman spectra of some remaining green areas in model samples of verdigris in glair artificially aged 116 hours (Figure 10a, 10b) are dominated by fluorescent backgrounds with broad, overlapping peaks between $2800\text{--}3020\text{ cm}^{-1}$ and $1600\text{--}1200\text{ cm}^{-1}$ (plus peaks associated with tenorite). These features are strikingly similar to the amorphous-looking spectra of copper greens obtained from the Ptolemy maps (Figure 10c).

Figure 10: Raman spectra (514 nm excitation) of Kremer neutral verdigris pigment in glair on (A) Whatman No. 1 and (B) UI rag artificially aged for 116 hr. @ 50 °C and 65% RH, compared to (C) verdigris particle on 1513 Rosenwald Collection Ptolemy *Geographia* and (D) Kremer pigment in gum Arabic on Fe-doped rag paper, artificially aged for 16.5 hr. @ 50 °C and 65% RH. Power at the samples was ~0.05 – 0.6 mW.

In the artificially aged samples in gum Arabic, similar alterations begin to appear in some particles after 16.5 hours of aging (Figure 10d).

Overall, these changes in NV model samples suggest aging pathways in historical works on paper that give rise to the development of structural disorder that leads to loss of crystallinity, and new molecular species associated with methylene group vibrations. These results also lend new support to the proposed reaction of NV over time with its medium, including gum Arabic. Such reactions theoretically may involve loss of acetate anions, as well as reaction through the enol tautomer intermediate of the acetate anion, which would be stabilized under acidic conditions (Caballol et al. 1988; Gao 1996). Evidence for similar reactions in BV paint films has yet to be obtained, but may be possible. Such alterations render the pigment no longer strictly verdigris, but an unspecified organo-copper complex. These complex interactions are the subject of a future publication.

3 Conclusions

Preparation of model samples through laboratory synthesis of verdigris according to historical recipes further demonstrates the difficulty of controlling the manufacture of BV, and highlights the simplicity of producing extremely pure NV. This suggests that the historical importance of NV is generally underestimated, since it is more viable as a controlled commercial and a studio product. Our results also clarify that commercial verdigris obtained from Kremer, Sinopia, and L. Cornelissen & Son are NV (not BV).

Study of artificially aged, verdigris reference pigment powders and model paint films in aqueous media by XRD, visible spectroscopy, and Raman spectroscopy clarifies several issues surrounding the chemistry and behavior of verdigris, as follows: (1) neutral verdigris (NV) pigment is originally bright teal-blue in color; (2) NV readily alters to the bluish-green basic verdigris 1 (BV1) upon exposure to humidity, with or without heat; (3) alteration behavior of NV in gum Arabic on Whatman No. 1 filter paper mimics that of the pure pigment; and (4) lab-synthesized BV1 is more resistant to heat and other alterations in mild artificial aging conditions than BV1 formed as an alteration product, suggesting the latter is less stable, possibly due to increased defects in the crystal structure.

Detailed study of the Raman spectra of NV samples supports several hypothetical pathways for NV alteration to BV, involving (1) reconfiguration of the bridging acetate of NV into a group that is singly bound to Cu and capable of hydroxyl bonding in BV, and (2) increasing loss of acetate groups. The resulting

molecular reorganization allows potential exchange of acetate groups with anions in the local environment and may also lead to amorphous forms of verdigris; this evidence provides new support to the supposition that ill-defined organo-copper compounds often encountered in historical paint films are altered verdigris.

Comparative study of “mock-up” samples fashioned to represent historical materials and artificially aged according to a new protocol that delays alteration to tenorite (CuO) allows some preliminary observations. Notably, alteration behavior of NV paint films in gum Arabic or glair on sized cellulosic substrates is afforded some protection by the medium and therefore alters more slowly than on unsized paper. In addition, the alteration of NV to BV may take some unexpected routes in the former systems. Factors that promote or delay the dramatic chemical and crystallographic alteration of NV may include: the amount of surface area in pigment grains exposed to atmospheric moisture; the chemical nature of the medium; and pH of the immediate environment. This is part of ongoing investigation.

By linking the aging behavior of the pigments in powder form to ground verdigris paint films, our results clarify key aspects of verdigris aging and alteration in the context of cultural heritage preservation. This understanding is critical first to facilitate better informed analytical identification of verdigris alteration products in historical works on paper, and second to better understand the relative stability of verdigris paint films in aqueous media. More specifically, comparison of dry reference pigments with model paint films on Whatman No. 1 and historically relevant paper allows a clearer understanding of the importance of NV, its instability, and its alteration pathways. Analogous study of BV1 paint films shows that this form of verdigris has surprising relative stability, by contrast. Analysis of these chemically distinct variants of verdigris and their alteration products, as well as their propensity to alter under different conditions, as reported here, clarifies some issues in the analytical identification of the pigment and ultimately affects aesthetic interpretation of a work's original appearance. Results also impact the design of treatment studies and development of preservation strategies, the latter of which is an area of ongoing study for this historically important pigment.

4 Material sources

Paper substrates were: (1) Whatman No. 1 filter paper, purchased from Fisher Scientific, USA; (2) University of Iowa (UI) handmade, gelatine-sized, buffered

rag paper (~15,000–18,000 ppm Ca); (3) custom-made, gelatine-sized, low Ca UI rag (~7000 ppm Ca); and (4) gelatine-sized, low Ca UI rag (paper 3) doped with FeSO_4 (~400–600 ppm Fe and ~5000 ppm Ca), as determined by X-ray fluorescence spectroscopy.

Reference verdigris pigments were purchased or synthesized. Neutral verdigris was purchased from Kremer Pigments, Inc. (2 batches), L. Cornelissen & Son, Ltd, and Sinopia Pigments. Neutral verdigris was also synthesized by suspending a copper sheet over white wine vinegar in a closed container for 15–29 days at room temperature and at 85 °C. Basic verdigris reference pigments were synthesized according to three recipes in Scott (2002), clarified by reference to the original publications of Schweizer and Mühlethaler (1968) and Rahn-Koltermann et al. (1991), as detailed in the appendix. All syntheses were repeated to confirm reproducibility of results.

Gum Arabic powder was purchased from Acros Organics and prepared as a stock solution in deionized water at 2 g/10 ml. Glair was prepared in the traditional manner from egg whites whipped to a foam, using the runoff liquid collected after standing overnight.

XRD reference spectra were obtained from the International Center for Diffraction Data (ICDD) Powder Diffraction File (PDF)-2, 2011 Release, ICDD, Joint Committee on Powder Diffraction Standards, Newton Square.

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Appendix 1: Sample preparation

A1.1 Reference verdigris pigments were purchased from Kremer Pigments, Inc. (New York, USA), L. Cornelissen & Son (London, UK), and Sinopia (San Francisco, USA). NV was also synthesized by placing a copper sheet in a closed container with white wine vinegar for 15–29 days (1) at room temperature and (2) in an oven at 85 °C.

Basic verdigris salts were synthesized according to the procedures in Schweizer and Mühlethaler (1968) or Rahn-Koltermann et al. (1991), as also followed by Scott (2002).

Basic verdigris 1 (1–3-2, BV1) from Schweizer & Mühlethaler #4: 12.77 g of NV (Kremer) was dissolved in 200 ml DI water. To half this solution, concentrated ammonia (Fisher, 29.8 %) was added dropwise while stirring, forming a thick sediment. Addition continued until this precipitate re-dissolved. The second portion of neutral verdigris solution was then added, with vigorous stirring to homogenize; the resulting thick solution was left to settle over several days, leaving vibrant green crystals on the bottom of the beaker.

Basic verdigris 2 (2-1-5, BV2) from Rahn-Koltermann: 5.85 g NV (Kremer) was dissolved in 50 ml DI water, giving an 11.7 % wt.:vol. solution. Concentrated ammonia (Fisher, 29.8 %) was added in slow increments with ~30 seconds of stirring between additions until the solution and precipitate hue shifted from sky blue to deep blue. The solution (about 4 ml) was then filtered, a light blue portion was collected. The remaining solution was left to settle and subsequently yielded a greener precipitate.

Basic verdigris 3 (1-1-5, BV3) was attempted several times following Schweizer and Mühlethaler #2: 5.6 g of NV (Kremer) was dissolved in 75 ml DI water. Sodium hydroxide solution (0.56 g/10 ml) was added with constant stirring, resulting in a thick rubbery cerulean blue gel. Like Scott, we found that several days are required for the gel to settle and evaporate; this procedure yields multiple salts in shades of purple, dark blue, light blue, and green. Unlike Scott, the products did not separate cleanly into homogenous layers or regions. Stir speed, addition rate, and stirring time after addition were varied over several trials with no meaningful change in results.

A1.2 Model paint samples were made as draw-down films of NV (Kremer Pigments, Inc.) or lab-synthesized BV1 in gum Arabic or glair on various paper substrates. Artificial aging was conducted in a Parameter Generation and Control model 9131-3110 environmental chamber according to a new protocol using 50 °C and 65 % RH, with testing at time periods from 0–1390 hours. These

mild conditions are necessary to delay alteration of the pigment to black tenorite (CuO), which is not known to form naturally in historical works.

Appendix 2: Analytical Instrumentation and Methods

A2.1 pH measurement. The pH of all paper substrates was determined using TAPPI Method T509.

A2.2 Ca and Fe content in papers was determined using a Bruker Tracer III-SD X-ray fluorescence spectrometer with a Rh anode, 15 kV and 55 μ A, a 0.001 mm Ti filter, according to partial least squares regression line calibration from a series of lab-made metal-doped Whatman No. 1 and historical reference papers for which S, Cl, K, Ca and Fe content was determined by inductively coupled plasma mass spectrometry (ICP-MS) conducted at the University of Missouri using a PerkinElmer NexION DRC quadrupole ICP-MS instrument. Samples were digested by microwave-assisted nitric acid dissolution for ICP-MS.

A2.3 The stoichiometry of purchased and synthesized verdigris samples was determined by elemental analysis of Cu, C and H conducted by Galbraith Laboratories, Inc. (Knoxville, TN). Light element analysis was performed with a PerkinElmer 24500 Series II CHNS/O Analyzer for steady state thermal conductivity analysis using a 1–5 mg sample in a tin capsule and combustion at $>950^\circ\text{C}$. Cu was analyzed by ICP optical emission spectrometry (ICP-OES) using an ICP-OES Optima 5300 on an acid-digested sample.

A2.4 X-ray diffraction (XRD). XRD patterns were recorded with a Rigaku D-Max Rapid μ Diffraction using Cu $K\alpha$ radiation, a large area image plate detector, 40 kV and 30 mA power, a 0.3 mm collimator, 0° ω geometry, and 360° ϕ rotation.

A2.5 Raman spectroscopy. Raman spectra of multiple grains in each sample were obtained using a Renishaw inVia Raman system outfitted with a Leica DM2500 microscope, 514 nm Ar^+ laser, 2400 l/mm grating, Rayleigh notch filters, and a CCD detector. Calibration was performed using the 520.5 cm^{-1} line of silicon. Spectra were collected using 20x, 50x or 50x LWD objectives and neutral density filters to keep power at sample $\leq 0.6\text{ mW}$, typically for 60–300 second exposures.

A2.6 Visible reflectance spectroscopy. Visible spectra were collected with an Ocean Optics Jaz Spectrometer outfitted with a pulsed Xenon light source, silicon CCD array detector, and $450\text{ }\mu\text{m}$ XSR bifurcated fibre optic cable using a 90° geometry, D65 illuminant and 2° observer reflection.

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Zusammenfassung

Untersuchung der Veränderungen von Grünspan durch kombinierte Raman-Spektroskopie und Röntgenbeugung, Teil I

Diese Studie untersucht die chemische Veränderung von neutralem Grünspan ($\text{Cu}(\text{II})_x(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) und basischem Grünspan ($\text{Cu}(\text{II})(\text{CH}_3\text{COO})_y(\text{OH})_z \cdot n \text{H}_2\text{O}$) mit Referenzpigmenten und historisch relevanten Modellproben, die einer künstlichen Alterung ausgesetzt wurden. Analytische Untersuchungen von Modellproben durch kombinierte Raman-Spektroskopie, Röntgenbeugung und sichtbare Spektroskopie liefern neue Beweise, die den oft widersprüchlichen Literaturbestand klären, und zwar erstens im Hinblick auf die analytische Identifikation von verschiedenen Formen von Grünspanpigmenten, und zweitens durch Verfolgung der Veränderung von neutralem Grünspan in wässrigen Bindemitteln, deren Verhalten historischen Typen von Grünspan in Verbindung mit Papier reflektieren. Die Ergebnisse legen ferner nahe, dass die historische Bedeutung von neutralem Grünspan als Pigment unterschätzt wird, da im Handel erhältliches Grünspan in seiner gesamten Blütezeit – von vor der Renaissance bis ins 18. Jahrhundert – wahrscheinlich von dem leichter herzustellenden neutralen Salz dominiert wurde. Dieses Missverständnis kann durch Pigmentveränderung entstehen, bei der sich neutraler Grünspan in basische Kupfersalze umwandelt oder Organokupferkomplexe bildet.

Resumé

Tracer l'altération du pigment vert-de-gris au moyen des techniques combinées de spectroscopie Raman et de diffraction de rayons X, partie 1

Cette recherche étudie l'altération chimique de l'important pigment historique appelé vert-de-gris, à la fois sous son état de vert-de-gris neutre ($\text{Cu(II)} (\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) et de vert-de-gris basique ($\text{Cu(II)}_x(\text{CH}_3\text{COO})_y(\text{OH})_z \cdot n\text{H}_2\text{O}$), en utilisant des poudres de pigments de référence et des échantillons historiques maquettes vieillis artificiellement.

L'étude analytique des échantillons en combinant la spectroscopie Raman, la diffraction de rayons X et la spectroscopie visible a donné de nouveaux indices qui clarifient le corps de littérature souvent contradictoire, premièrement à la fois en termes d'identification analytique des différentes formes du pigment vert-de-gris et deuxièmement en traçant les altérations du vert-de-gris neutre sous forme de système en lien avec son comportement en médium aqueux sur des papiers historiques. Les résultats suggèrent que l'importance historique du vert-de-gris neutre comme pigment est sous-évaluée, étant donné que le vert-de-gris disponible sur le marché depuis son apogée — d'avant la Renaissance jusqu'au 18ème siècle — a probablement été dominé par le sel neutre fabriqué plus facilement. Ce malentendu peut surgir de l'altération du pigment, selon laquelle le vert-de-gris neutre se convertit en sels de cuivre basiques ou forme des complexes organiques de cuivre.

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