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Large-scale assessment of light-induced color change in air and anoxic environments

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A wide-ranging sample set consisting of dry pigments, dyed textiles, organic and aniline-based dyes, gouaches and watercolors, fluorescent inks, and natural history specimens was exposed to light in air (20.9% oxygen) and near-anoxic environments. After a light dosage of approximately 17.5 Mlux-hours under controlled temperature and humidity conditions, 113 of 125 samples (90% of the sample set) were shown to exhibit less color change in a low-oxygen environment compared with its behavior in air. Thirty-nine percent of this subset displayed color change in anoxia that was between two and four times lower than that observed in air, whereas 47% showed color change in anoxia reduced by a factor of four or more. In contrast, six samples exhibited greater color change in anoxia than in air – these samples included Prussian blue watercolor (three samples), Antwerp blue watercolor, Verdigris dry pigment, and Fluorescent Yellow Winsor & Newton Gouache. Although the results from this small sample subset may cause concern when considering the use of anoxia in the conservation of cultural heritage, particularly for colorant systems whose behavior in anoxia has not yet been identified, this study demonstrates the overwhelming benefits of anoxic light exposure for the vast majority of samples investigated here.

Keywords: Anoxia, Color change, Light exposure, Pigment, Textile, Dye, Gouache, Natural history

Introduction

Object damage from excessive light exposure is a major conservation issue that must be managed for each collection and, ever more frequently, for each significant object. The most common means of reducing light damage has been to (1) maintain light levels between 50 and 200 lux depending on the presumed sensitivity of an object; (2) eliminate or severely reduce illumination during periods when the galleries are not open to the public; (3) filter ultraviolet and infrared wavelengths from the light source; and (4) curtail periods when the object is on exhibition (Thomson, 1986). In doing so, one can reduce the light dosage an object receives, prolonging an artwork's lifetime. However, these measures limit the public's interaction with an art piece and low light levels have drawn criticism as a difficult viewing environment. Michalski (1997) recommended a series of conditions whereby light levels may be raised for older visitors, assuming low contrast and/or dark compositions and for objects that are visually complex – these recommendations, while frequently discussed, are seldom used.

Since 2002, the Getty Conservation Institute (GCI) has sought to examine this lighting and viewing

dilemma by researching alternative techniques by which cultural institutions can better manage light damage. One component of this research focus has been the development of multi-coating filters to reduce the total energy reaching the paper surface while maintaining good color rendering of an object (Delgado *et al.*, 2011). Through modifications in the spectra of the light source itself, a minimum reduction of 50% in the radiant energy received by an object can be achieved.

The GCI has also examined how changes in the gaseous environment to which an object is exposed can affect light-induced color change. When the energy of an individual molecule of an object is elevated by the absorption of light and that energy is not dissipated as heat or emitted as fluorescence or phosphorescence, the excited molecule has the potential to undergo irreversible photochemical reactions, which may affect the object's appearance (Geuskens, 1975). The probability of a photochemical reaction occurring is dependent on a number of factors, including the chemical characteristics of the molecule, a reaction's quantum yield (number of times a defined event occurs per photon absorbed), and the composition of its surrounding environment (Schaeffer, 2001).

Photooxidation represents a major category of complex photochemical reactions that may affect

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color (Scott, 1965). This process is typically initiated by the absorption of a photon by a dye, pigment, binder, or support to create a free radical. This initial radical reacts with atmospheric oxygen to produce a secondary alkylperoxy radical, which can react further (e.g. hydrogen abstraction, addition to a double bond) with other molecules and potentially lead to a change in color. Although there are many paths by which a colorant could undergo color change on exposure to light and oxygen, restricting exposure to oxygen can eliminate a broad range of potentially harmful reactions. In the absence of oxygen, other photochemical reactions may still occur, including inter- and intra-molecular rearrangements (such as *cis-trans* isomerizations), the splitting of molecules into smaller components with or without the formation of free radicals (photocleavage and photodecomposition), addition of a proton to an excited molecule (proton provided by a photo-reduced molecule), and the linking of two like molecules (photodimerization) (Schaeffer, 2001).

The idea of replacing the typical air environment (20.9% oxygen) surrounding an artifact with one lacking in oxygen has remained a promising means of limiting light-induced color change for colorants. Studies by Chevreul (1837) and Russell & Abney (in 1888, see Bromelle, 1964) were among the earliest to examine the effects of a near-anoxic environment on the color change of textiles and watercolors, respectively. Color change in low-oxygen conditions has been further investigated for a variety of colorants (e.g. Giles *et al.*, 1972; Arney *et al.*, 1979; Buss & Crews, 2000; Korenberg, 2008; Casella, 2009). Although demonstrating reduced color change for many samples exposed to light in anoxia, these studies have also revealed for some materials the potential for accelerated color change in low-oxygen environments. First noted by Chevreul (1837) and examined further by Kirby (1993), Kirby & Saunders (2004), and Rowe (2004), Prussian blue has become a prominent example of increased color change in low-oxygen environments. Townsend *et al.* (2008) also conducted a literature review to assess the effect of low oxygen on colorants and summarized additional materials potentially at risk in near-anoxic conditions.

Despite the effort put forth in investigating color change in anoxic environments, the use of low-oxygen conditions for long-term storage and display has been limited. This is due in part to the relatively small sample set whose color change behavior has been characterized in anoxic conditions, highlighting the fear of accelerating color change for materials yet to be studied. The widespread use of fumigation treatments using inert gases, however, has exposed affected objects to brief periods of near-anoxic conditions

(Gilberg, 1988; Valentin & Preusser, 1990; Selwitz & Maekawa, 1998). Many studies on colorant behavior in anoxia also did not report the oxygen concentrations conditions to which samples were exposed (Townsend *et al.*, 2008). This lack of information on specific exposure conditions, including temperature and relative humidity, of previous work makes the comparison to current results difficult.

As pressure mounts to extend exhibition times and ultimately implement more flexible light levels for visually challenging artifacts, potentially increasing light exposure, it is important to better define the advantages and limitations of anoxia by widening the scope of materials subjected to examination. As a result of the large number of samples examined, the focus of this study will be on the color change behavior of each sample rather than the chemical mechanisms by which the color change occurs.

Experimental method

Samples

Over 170 samples were selected for examination of the effects of light-induced color change in air and anoxic environments. Among the sample types included were dry pigments, dyed textiles, organic and aniline-based dyes, gouaches and watercolors, fluorescent inks, paper, and natural history specimens such as leaves, grasses, and butterfly wings. Although some sample sets provided a wide range of easily accessible materials (e.g. Forbes Pigment Collection, GCI's Asian Organic Colorants Project), several sample sets were selected because they included materials known to exhibit moderate-to-poor lightfastness (e.g. Winsor & Newton Designers' Gouache and Artists' Water Colour, Dr Ph. Martin's Radiant Concentrated Watercolors). Owing to the large number of materials and the restricted dimensions of the exposure cases, samples were separated into two exposure trials, during which they were securely fastened to a perforated platform positioned inside each case approximately equidistant between the top and bottom panels. Tables 1 and 2 list 125 samples exposed during the first and second exposure trials, respectively, whose color change in air and/or anoxia was considered statistically significant, the criteria of which will be discussed later.

The samples exposed in this experiment comprised both commercially manufactured materials and materials specifically prepared for study or use as a reference. The primary distinction between the two sample sets was the availability of compositional information. Typically lacking detail on its chemical makeup, commercially produced materials included in the study were aniline dyes from Dr Ph. Martin (Radiant Concentrated Watercolors), fluorescent ink from Sanford (Sharpie Accent Highlighters), and pigments

Table 1 Samples exposed during the first exposure trial

Collection	Sample	Type	Collection no. – source	
Canadian Museum of Nature (CMN)	<i>Acer</i>	Leaf		
	<i>Aster</i>	Leaf		
	<i>Dryopteris</i>	Leaf		
	<i>Scirpus</i>	Grass		
	<i>Trifolium</i>	Leaf		
	<i>Zinzania</i>	Grass		
Druzik Forbes Pigment	<i>Papilio phorcas</i> (green regions)	Butterfly wing		
	Bitumen	Dry pigment	4.04.5 – Weber	
	Brazilwood	Dry pigment	6.03.1 – F. Weber	
	Carmine Lake	Dry pigment	6.03.19 – F. Weber	
	Dragon's Blood	Dry pigment	6.03.3 – C. Roberson & Co. 1914	
	Emerald Green	Dry pigment	9.06.7 – F. Weber Co.	
	Eosine	Dry pigment	6.04.1 – Imperial Paper & Color	
	Indian Lake	Dry pigment	6.03.4 – C. Roberson & Co. 1928	
	Indian Lake	Dry pigment	6.03.5 – W&N	
	Indigo	Dry pigment	8.08.1 – Weber Co.	
	Lithol Red	Dry pigment	6.04.5 – Imperial Chemical & Paper	
	Madder/Lake	Dry pigment	6.03.10 – Fezandie/Sperrle	
	Magenta	Dry pigment	6.04.6 – F. Weber Co.	
	Mauve	Dry pigment	7.01.3 – F. Weber	
	Orpiment	Dry pigment	3.02.4 – Ferandie/Sperrle	
	Powdered Kermes	Dry pigment	6.03.21 – Dimroth/Wruzburg	
	Purple Madder	Dry pigment	6.03.7 – Newman/London	
	Realgar Powder	Dry pigment	5.01.2 – Hamilton/London	
	Saffron	Dry pigment	3.07.6 – EWF	
	Sepia	Dry pigment	2.06.2 – F. Weber Co.	
	Verdigris	Dry pigment	9.03.4 – Buckner/Munich/1914	
	Yellow Lake	Dry pigment	3.09.2 – Fezandie & Sperrle	
	GCI Reference	Carmine	Dry pigment	Dye 12498 – Kremer Pigment
		Cochineal	Dry pigment	Dye 17655/Cat #: 0106E – Zecchi
	Library of Congress (LC)	Brazilwood*/Alum	Organic dye	
		Brazilwood*/Lake	Organic dye	
		Brazilwood*/No Mordant	Organic dye	
Brazilwood*/Potash		Organic dye		
Lac/Alum		Organic dye		
Lac/Lake		Organic dye		
Lac/No Mordant		Organic dye		
Lac/Potash		Organic dye		
Madder**/Alum		Organic dye		
Madder**/Lake		Organic dye		
Madder***/No Mordant		Organic dye		
Madder***/Potash		Organic dye		

Source: * Sappanwood; ** CI Natural Red 8; *** Tucson.

from a variety of manufacturers. Pigments from the Forbes Collection were of particular concern as white pigment samples (not included in this study) had previously been shown to be misidentified (Carriveau & Omecinsky, 1983). An exception to the lack of technical information for commercially produced materials was the Winsor & Newton Designers' Gouaches and Artists' Water Colours, for which chemical composition data were provided and shown in Table 2. Although chemical information was not available for the majority of commercial samples, it was thought that their inclusion to the sample set would broaden the scope of the experimental study.

The remaining samples included in this experiment were purposely prepared for scientific examination and, as a consequence, had known chemical compositions – among these well-characterized subsets were material from the GCI's Asian Organic Colorants Project (Grzywacz & Wouters, 2008), the Library

of Congress (Ryan & Baker, 2008), and the Canadian Museum of Nature.

The substrate for the majority of samples tested was an acid-free off-white paper (Strathmore Drawing Medium, 400 Series). Although colorants have been previously applied to Whatman filter paper due to its color stability (Korenberg, 2008), Strathmore paper was considered a better representation of the substrate used by artwork on paper. Dry pigment samples were evenly rubbed as best as possible onto the paper with a cotton swab through a 7 mm diameter hole in a 5 mm thick Mylar sheet, with each sample card containing at least two medium density swatches. Aniline-based dyes, gouaches, watercolors, and fluorescent inks were evenly painted or marked onto the paper substrate, of which two 7 mm diameter swatches were adhered with gum arabic to a separate paper card. Four watercolor samples – Prussian blue (Kremer and Schminke), Antwerp blue (L. Cornelissen & Son), and

Table 2 Samples exposed during the second exposure trial

Collection	Sample (permanence rating)	Type	Collection no./CI name
Asian organic colorants (AOC, GCI project)	<i>Caesalpinia sappan</i>	Silk A, Wool A, Pigment A	
	<i>Carthamus tinctorius</i>	Silk A, Wool A, Prepigment on paper	
	<i>Curcuma longa</i>	Silk N/A, Wool A, Pigment A	
	<i>Gardenia augusta</i>	Silk N/A, Wool A, Pigment A	
	<i>Laccifer lacca</i>	Wool A, Pigment A	
	<i>Lithospermum erythrorhizon</i>	Silk N/A, Pigment A	
	<i>Phellodendron amurense</i>	Silk N, Pigment A	
	<i>Rhamnus catharticus</i> , immature berries	Silk A, Pigment A	
	<i>R. catharticus</i> , ripe berries	Silk A, Wool A	
	<i>Rubia tinctorum</i>	Silk A, Wool A, Pigment A	
EU-Artech	<i>Sophora japonica</i>	Silk A, Wool A, Pigment A	
	<i>Reseda luteola</i>	Wool A, Pigment AC/AL/AP	
	<i>Rocella tinctoria</i>	Wool A	647
Schweppe	ISOBW 1	Wool	CI Acid Blue 104
	ISOBW 2	Wool	CI Acid Blue 109
	ISOBW 3	Wool	CI Acid Blue 83
Dr Ph. Martin's Radiant Concentrated Watercolor	Alpine Rose	Aniline dye	4A
	Amber Yellow	Aniline dye	16B
	Cherry Red	Aniline dye	6A
	Crimson	Aniline dye	18B
	Daffodil Yellow	Aniline dye	15B
	Grass Green	Aniline dye	11A
	Juniper Green	Aniline dye	12A
	Mahogany	Aniline dye	27B
	Moss Green	Aniline dye	24B
	Moss Rose	Aniline dye	7A
	Persimmon	Aniline dye	3A
	Scarlet	Aniline dye	5A
	Slate Blue	Aniline dye	22B
	True Blue	Aniline dye	9A
	Turquoise Blue	Aniline dye	8A
	Wild Rose	Aniline dye	19B
	Sharpie accent highlighters	Green	Fluorescent ink
Magenta		Fluorescent ink	
Orange		Fluorescent ink	
Yellow		Fluorescent ink	
Winsor & Newton Designers' Gouaches and Artists' Water Colours (W&N)	Alizarin Crimson, tint (B)	Gouache	4 / PR12, PR83
	Bengal Rose (C)	Gouache	28 / PR173
	Flesh Tint (B)	Gouache	257 / PW6, PR4, PY42
	Fluorescent Yellow (B)	Gouache	260 / Fluorescent dye/resin based pigment*
	Havannah Lake (B)	Gouache	309 / PBk6, PR83, PY42
	Madder Carmine (B)	Gouache	378 / PR83
	Magenta (C)	Gouache	380 / PR173, PV2
	Orange Lake Light (B)	Gouache	453 / P013
	Parma Violet (C)	Gouache	463 / PV3, PV2
	Periwinkle Blue (B)	Gouache	471 / PB1, PB15
	Permanent Green Light (B)	Gouache	483 / PY3, PG7
	Primary Red (B)	Gouache	524 / PR48:3
	Prussian Blue, (A**)	Watercolor	538 / PB27
	Rose Malmaison (C)	Gouache	591 / PR173, PR48:3
Rose Tyrien (C)	Gouache	593 / PR173	
Spectrum Violet (C)	Gouache	625 / PV3	
Forbes	Verdigris (replicate of Trial 1 sample)	Dry pigment	9.03.4 – Buckner/Munich /1914
Kremer	Orpiment, Genuine	Dry pigment	
	Realgar	Dry pigment	
	Prussian Blue	Watercolor	
Cornelissen	Antwerp Blue	Watercolor	
	Prussian Blue	Watercolor	
Schminke	Prussian Blue	Watercolor	
Sigma Aldrich	Crystal Violet (ACS reagent)	Watercolor	
Strathmore Drawing Medium 400 Series	Paper Blank	Paper	

* Chemical description. CI name not available; ** Fluctuating color, fades in light, recovers in dark.

Letter designations under type refer to mordant: A, alum; N, no mordant; C, chalk; P, potash; L, lime water.

Permanence ratings are as follows: A, permanent; B, moderately durable; C, fugitive.

Crystal Violet (Sigma Aldrich, ACS Reagent) – were prepared at the GCI by mixing dry pigment with a solution of gum arabic and water. The mordanted organic dyes from the Library of Congress were received painted on sheets of BHG 2000 hemp (100% gelatine/alum sized 1–2%) – two 7 mm diameter swatches of each sample were attached to a paper card with gum arabic. Single samples of natural history specimens and colored textiles (except for ISO Blue Wools which were pre-mounted on a paper substrate) were mounted on to paper cards with gum arabic and staples, respectively.

Exposure cases

Colorants were exposed to air and near-anoxic environments using GCI-designed hermetically sealed cases (Maekawa, 1998) (Fig. 1). The exposure cases consisted of aluminum plates slotted into six sides of an aluminum frame with a top panel of Starfire (low-iron) glass facing the light source. The hermetic seal was created by applying pressure via spring strips through the glass and metal plates onto Viton O-rings positioned in a groove in the frame.

Environmental monitoring and temperature regulation were also incorporated into the case design. Calibrated before each exposure trial, air temperature and relative humidity sensors (Vaisala HMT338 Transmitter) were installed in both cases and an oxygen sensor (Teledyne Analytical Instruments Micro Fuel Cell Class B-2C attached to a Model 317 Solid State Trace Oxygen Analyzer) installed only in the anoxic case (Fig. 1). Heat exchanger plates were also mounted onto the side plates of both cases and positioned around the interior perimeter, with each set piped to a temperature-controlled water bath. By flowing cold water through the heat exchanger plates, heat introduced by the light source above could be removed from the case and a stable interior temperature maintained (approximately 22 and 24°C during the first and second exposure trials, respectively).

Although the oxygen leak rate of the two cases was measured at less than 10 ppm per day, moisture-neutral oxygen absorbers (Mitsubishi RP System – K Type) were inserted into the anoxia case to assure a near-anoxic condition. The interior environments of each case were established by purging with compressed air or nitrogen humidified to similar relative humidity levels (approximately 35 and 30% during the first and second exposure trials, respectively). The oxygen concentration inside the anoxia case stabilized at less than 10 ppm during the first and second exposure trials, respectively. Therefore, the ‘anoxic’ environment referred to in this study contains a small residual of oxygen in the exposure case. The relatively low humidity levels established within the exposure cases suggest that the color change observed in this study may be

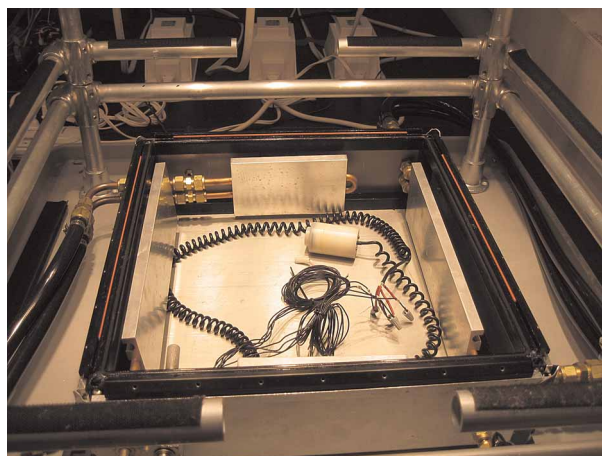


Figure 1 Interior of anoxic exposure case showing perimeter heat exchanger plates and sensors for oxygen (white cylinder) and air temperature/relative humidity (silver probe in lower left of case). Tubing from case connects interior heat exchanger plates to temperature-controlled water bath.



Figure 2 Lighting scaffold positioned above exposure case with diffuser plate and three of four side panels mounted.

somewhat less than what would be expected at higher humidity values (Giles *et al.*, 1976; Saito *et al.*, 1988). However, the humidity conditions during the two exposure trials are not uncommon, even in modern air-conditioned museums in arid climates such as the Southwestern United States.

Lighting

Situated above each exposure case was a lighting scaffold housing nine 50 W halogen MR16 lamps (with no

cover glass) arrayed in a three-by-three grid, with adjacent lamps positioned approximately 180 mm apart (Fig. 2). A pane of frosted glass was placed between the lamps and the case to improve light diffusion, and white panels were attached to the perimeter of the scaffolding to limit light loss and reflect light inwards. Approximate distances between the lamps and various components were as follows: 470 mm from lamps to diffuser glass, 560 mm from lamps to top glass panel of case, and 620 mm from lamps to sample stand.

Before the start of each exposure trial, light levels within the air and anoxia cases were assessed with photometric sensors (Licor LI210), and light dosage for the first and second exposure trials was estimated at 17.4 and 17.7 Mlux-hours, respectively. Although exhibiting a difference of 1.7%, the light dosages for the two exposure trials were considered roughly equivalent (~17.5 Mlux-hours). Extrapolation of these elevated light levels to normal gallery lighting is applicable as the levels did not significantly exceed the light exposure (8000 lux) at which reciprocity over two orders of magnitude was shown to be valid (Saunders & Kirby, 1996). The ultraviolet component of light was also assessed with an Elsec 764 Environmental Monitor and measured at 43 uw/lumen, an acceptable value for museum lighting.

Color measurement

Before and after each exposure trial, the air and anoxia sample sets were analyzed with a spectrophotometer (Varian Cary 50 Bio UV–Vis) connected to a diffuse reflectance sampling probe (Harrick Video Barreliino) to examine reflectance in the visible region. The Video Barreliino had a spatial resolution of less than 1 mm and used a normal/diffuse measurement geometry (Milosevic, 2004). At the start of each analytical session, an Ocean Optics WS-1 diffuse reflectance standard was used to determine full reflectance.

Owing to the instrument's small illumination spot and potential color variation of the sample, particularly for dry pigments, natural history specimens, and dyed textiles, at least five locations on each sample were analyzed based on standard illuminant D65 (daylight) and a 2° observer angle, generating a minimum of five sets of Commission Internationale de l'Éclairage 1976 L*, a*, b* (CIELAB) coordinates. Although areas of relatively uniform color were examined for all samples, analysis of dyed textiles also focused on the top areas of the fiber. Mean pre-exposure and post-exposure CIELAB values were then calculated and an average color difference, or ΔE , was quantified. For samples with multiple swatches, the ΔE reported for the sample was the mean of the ΔE values calculated for each swatch.

ΔE values presented here are based on a calculation derived from the 2000 color difference equation (Luo *et al.*, 2001; Sharma *et al.*, 2004).

To distinguish the environment in which a sample's color change was quantified, color change as result of exposure in air will be referred to as ΔE_{Air} , whereas color change due to exposure in anoxia will be termed ΔE_{Anox} . Used as a means of comparing color change behavior in air and anoxia, the ratio between ΔE_{Air} and ΔE_{Anox} was calculated for each sample and will be referred to as ΔE_{R} .

Statistical analysis

A statistical technique called the 'mean color difference to the mean' (MCDM) was used to assess uncertainty associated with the experimental process (Berns, 2000). The MCDM for a sample is calculated by determining the average color difference between individual CIELAB results and the mean CIELAB value, giving this method the advantage of expressing variability in a number directly comparable with the color change of the sample. The MCDM was quantified for pre-exposure and post-exposure data and used to calculate ratios between the MCDM and the sample's color change, with the maximum MCDM: ΔE ratio of each sample in air and anoxia reported. For samples with multiple swatches, the maximum MCDM: ΔE ratio for each set of swatches exposed in air and anoxia was reported.

The threshold chosen to reflect acceptable uncertainty in measurement was an MCDM: ΔE ratio of 0.5 or lower, indicating that the MCDM was less than its associated color change by at least a factor of two. Fifty-nine samples exhibited maximum MCDM: ΔE ratios below 0.5 in both air and anoxia, indicating statistically significant color changes in both environments. An additional five samples were included with maximum MCDM: ΔE ratios in air and/or anoxia slightly exceeding 0.5 (up to 0.55).

Sixty-one samples with maximum MCDM: ΔE ratios less than 0.5 for only one of its samples exposed in air and anoxia were also included for discussion, although the comparison between color change in the two environments was highly approximate. In many cases, the sample exhibiting a maximum MCDM: ΔE ratio above 0.5 corresponded with a small color change. For example, the anoxic exposure of a *Trifolium* leaf exhibited a mean color change of 0.9 and a maximum MCDM value of 1.3, resulting in a maximum MCDM: ΔE ratio above one. In contrast, the average color change and maximum MCDM for the *Trifolium* sample exposed in air were 17.1 and 1.5, respectively, resulting in a maximum MCDM: ΔE ratio below 0.1. Although the color change for one sample may not be statistically significant (MCDM: ΔE >0.5), the comparative color

change in air and anoxia merits discussion due to the disparity in behavior. To provide the most conservative comparison of color change for this subset, samples with maximum MCDM: ΔE ratios exceeding one replaced color change with the maximum MCDM to calculate ΔE_R . In the case of the *Trifolium* leaf sample, the use of the maximum MCDM (1.3) in place of color change (0.9) for the sample exposed in anoxia resulted in a more moderate assessment of relative color change in air and anoxia (ΔE_R reduced from 19.3 to 13.2).

Results

Tables 3 and 4 show color change results for samples exposed to light in air and anoxic environments. Table 3 lists results for samples with known chemical compositions, and Table 4 focuses on commercial samples lacking chemical information. Although this study will largely concentrate on ΔE values, CIELAB and ΔE (1976, 1994, and 2000 calculations) data for all colorants listed are available as supplementary data (see Supplementary Material 1 <http://dx.doi.org/10.1179/204705812X13255179622341.S1>).

Color change in air and anoxia

The comparison of color change for 125 samples exposed to light in air and anoxia illustrated the effect that low-oxygen conditions can have on colorants. Color change for samples exposed in air ranged from 0.6 to 54.9 with a mean value of 12.9 (SD = 10.2) (Tables 3 and 4). In comparison, samples exposed in low-oxygen conditions exhibited a smaller range of color change (0.3–30.3) with a lower average value of 3.8 (SD = 4.1). A paired-samples *t*-test comparing color change in the two environments showed a significant difference in the scores for air and anoxic conditions ($t(124) = 11.3$, $P = 3.7 \times 10^{-21}$).

As shown in Fig. 3, the majority of ΔE_{Air} values (34% or 42 samples) were between 5 and 10, whereas the majority of ΔE_{Anox} values (49% or 61 samples) were between 1.5 and 5. Using a ΔE of 1.5 to estimate the threshold for a just noticeable difference (JND) in color (Ashley-Smith *et al.*, 2002), 30% (37 samples) of ΔE_{Anox} values were below the JND threshold, whereas only 2% (three samples) of ΔE_{Air} values met this criterion. It should be noted that a ΔE of 1.5 represents a mean JND across a non-uniform CIELAB color space and a population's perception of JND follows a normal distribution. On the other end of the spectrum, 45% (56 samples) of ΔE_{Air} values exceeded 10, whereas only 6% (8 samples) of ΔE_{Anox} values were above this level.

Used to quantify light exposure, ISO Blue Wool standard cards consisting of eight dyed textile samples with progressive degrees of lightfastness (ranging from the highly fugitive BW1 to the durable

BW8) were included in the second exposure trial (CIE 157, 2004). Blue Wool samples exposed in air exhibited statistically significant (maximum MCDM: $\Delta E_{Air} < 0.5$) color change for BW1 (ΔE_{Air} : 30.5), BW2 (24.9), and BW3 (6.6). The color change observed in air for the remaining Blue Wool samples was less than a JND. To distinguish its level of lightfastness, every sample exposed to light in air was identified by its approximate ISO Blue Wool equivalent, including intermediate BW designations (i.e. BW1.5, BW2.5, and BW3.5) (Tables 3 and 4). Similar use of ISO Blue Wool as a lightfastness index in anoxia was not possible due to the narrow spread of ΔE_{Anox} – only BW1 (7.0) and BW2 (5.9) exhibited color change in anoxia above a JND – and the fact that they have not been calibrated for environments other than air.

Color change ratio (ΔE_R)

To facilitate a comparison of light-induced color change behavior in air and anoxia for each sample, the ratio between ΔE_{Air} and ΔE_{Anox} was calculated. This color change ratio, or ΔE_R , combines a sample's color change in both air and anoxia into a single number that expresses relative color change in the two environments. As previously stated, if the maximum MCDM: ΔE (uncertainty in color change measurement) in either air or anoxia exceeded 1, the maximum MCDM measured in the same environment was used in place of color change to calculate ΔE_R , allowing for a more conservative estimate of relative color change.

Although ΔE_R values above and below 1 theoretically represent more and less color change in air than in anoxia, respectively, a more conservative interpretation of ΔE_R was necessary to account for error introduced during sample preparation, handling, and analysis. The following are the ΔE_R thresholds used in the remainder of this paper:

- $\Delta E_R < 0.8$: Less light-induced color change in air than in anoxia.
- $0.8 \leq \Delta E_R \leq 1.2$: Similar light-induced color change in air and anoxia.
- $\Delta E_R > 1.2$: More light-induced color change in air than in anoxia.

In addition to determining a sample's relative color change behavior when exposed to light in air and anoxia, ΔE_R also provides a quantitative assessment of the benefit or harm of exposing a sample in a low-oxygen environment. For example, a ΔE_R value of 2 indicates that exposure of a sample in an anoxic environment reduced color change by a factor of approximately two compared with exposure in air. Samples with higher ΔE_R values may show even more benefit from exposure to low-oxygen conditions with respect to color change. In contrast, a sample with a ΔE_R value of 0.5 indicates that exposure in

Table 3 Color change data for samples with known chemical compositions

Source	Sample	Trial	Type	ΔE_{Air}			$MCDM_{Air}:\Delta E_{Air}$ Max	$MCDM_{Air}$ Max	ΔE_{Anoxia}		$MCDM_{Anox}:\Delta E_{Anox}$ Max	$MCDM_{Anox}$ Max	ΔE_R
				Mean	SD	BW			Mean	SD			
AOC	Caesalpinia sappan	2	Dyed silk A	8.0		3	0.12		2.1		0.61		3.8
		2	Dyed wool A	9.8		3	0.16		2.0		0.46		4.9
		2	Pigment A	19.6	0.8	2.5	0.14		5.4	0.1	0.46		3.6
	Carthamus tinctorius	2	Dyed silk A	19.3		2.5	0.06		2.9		0.44		6.6
		2	Dyed wool A	12.2		2.5	0.11		2.8		0.73		4.3
		2	Prepigment on paper	19.7	0.4	2.5	0.05		3.2	0.1	0.40		6.2
	Curcuma longa	2	Dyed silk A	8.7		3	0.12		6.6		0.18		1.3
		2	Dyed silk N	8.5		3	0.18		3.8		0.61		2.2
		2	Dyed wool A	12.3		2.5	0.09		7.7		0.09		1.6
	Gardenia augusta	2	Pigment A	8.6	0.4	3	0.20		4.2	0.9	0.37		2.1
		2	Dyed silk A	6.4		3	0.18		1.1		0.80		5.6
		2	Dyed silk N	9.2		3	0.30		2.8		0.42		3.3
	Laccifer lacca	2	Dyed wool A	7.2		3	0.26		3.1		0.43		2.3
		2	Pigment A	16.3	0.4	2.5	0.10		11.4	0.3	0.16		1.4
		2	Dyed wool A	5.1		3	0.29		0.9		1.24	1.1	4.5*
	Lithospermum erythrorhizon	2	Pigment A	6.1	0.3	3	0.32		0.8	0.6	9.99	3.0	2.0*
		2	Dyed silk A	6.5		3	0.29		5.4		0.40		1.2
		2	Dyed silk N	8.6		3	0.18		4.0		0.40		2.2
	Philodendron amurense	2	Pigment A	16.9	1.6	2.5	0.17		4.3	0.3	0.49		4.0
		2	Dyed silk N	4.7		3.5	0.34		3.7		0.39		1.3
		2	Pigment A	7.2	0.1	3	0.18		0.7	0.4	1.72	1.0	7.0*
	Rhamnus catharticus, immature	2	Dyed silk A	5.2		3	0.31		0.7		1.83	1.2	4.4*
		2	Pigment A	11.2	0.1	2.5	0.15		1.7	0.4	1.06	1.5	6.5
		2	Dyed silk A	10.7		3	0.09		4.2		0.60		2.5
	R. catharticus, ripe	2	Dyed wool A	7.2		3	0.18		2.9		0.57		2.5
		2	Dyed silk A	3.9		3.5	0.37		2.7		0.72		1.5
		2	Dyed wool A	5.1		3	0.19		2.7		0.45		1.9
Rubia tinctorum	2	Pigment A	6.8	0.8	3	0.31		1.3	1.2	5.56	2.3	3.0*	
	2	Dyed silk A	3.4		3.5	0.54		2.3		0.52		1.5	
	2	Dyed wool A	5.0		3.5	0.32		2.2		0.51		2.2	
EU-Artech	Reseda luteola	2	Pigment A	9.6	1.6	3	0.25		1.2	0.1	1.52	2.0	4.9*
		2	Dyed wool A	2.0		4	0.51		2.1		0.55		0.9
		2	Pigment AC	7.8	0.6	3	0.15		0.9	0.1	1.08	1.0	8.3*
Schweppe	ISOBW	2	Pigment AL	7.5	0.7	3	0.08		0.8	0.1	1.37	1.0	7.4*
		2	Pigment AP	5.5	0.5	3	0.28		1.2	1.1	5.67	2.6	2.2*
		2	Dyed wool A	12.1		2.5	0.28		3.0		0.72		4.1
CMN	Acer	2	Dyed wool	30.5		—	0.02		7.0		0.11		4.3
		2	Dyed wool	24.9		—	0.03		5.9		0.17		4.2
		2	Dyed wool	6.6		—	0.19		0.6		1.45	0.8	8.2*
CMN	Aster	1	Leaf	16.4		2.5	0.10		2.3		1.03	2.4	6.9*
		1	Leaf	23.3		2	0.04		1.6		0.76		14.2
		1	Leaf	26.4		1.5	0.05		1.3		0.98		20.8
		1	Grass	9.2		3	0.27		0.4		2.48	1.0	9.6*
CMN	Trifolium	1	Leaf	17.1		2.5	0.09		0.9		1.46	1.3	13.2*

Continued

Table 3 Continued

Source	Sample	Trial	Type	ΔE_{Air}			$MCDM_{Air}:\Delta E_{Air}$	$MCDM_{Air}$	ΔE_{Anoxia}		$MCDM_{Anox}:\Delta E_{Anox}$	$MCDM_{Anox}$	ΔE_R
				Mean	SD	BW			Max	Max			
Druzik LC	Zinzania	1	Grass	20.9		2	0.05		0.9		1.15	1.1	19.9*
	Papilio phorcas (green regions)	1	Butterfly wing	17.4		2.5	0.11		6.8		0.40		2.6
	Brazilwood/Alum	1	Organic dye	24.9	1.8	2	0.06		4.3	0.1	0.38		5.8
	Brazilwood/Lake	1	Organic dye	30.9	0.4	>1	0.03		10.4	0.3	0.19		3.0
	Brazilwood/No Mordant	1	Organic dye	24.4	1.8	2	0.09		4.2	0.0	0.47		5.8
	Brazilwood/Potash	1	Organic dye	37.4	0.3	>1	0.02		14.5	0.5	0.07		2.6
	Lac/Alum	1	Organic dye	5.7	0.6	3	0.23		0.3	0.0	4.05	1.3	4.4*
	Lac/Lake	1	Organic dye	10.0	0.0	3	0.08		4.7	0.1	0.25		2.1
	Lac/No Mordant	1	Organic dye	2.5	0.1	3.5	0.20		0.8	0.1	1.00		3.3
	Lac/Potash	1	Organic dye	20.1	0.3	2.5	0.03		7.2	0.3	0.12		2.8
	Madder/Alum	1	Organic dye	3.2	0.2	3.5	0.25		0.7	0.3	1.83	0.9	3.5*
	Madder/Lake	1	Organic dye	7.7	0.1	3	0.18		1.0	0.2	1.01	0.9	8.0
	Madder/No Mordant	1	Organic dye	12.2	0.2	2.5	0.07		2.2	0.5	0.37		5.6
	Madder/Potash	1	Organic dye	12.0	0.3	2.5	0.10		1.9	0.8	0.81		6.4
W&N	Alizarin Crimson, tint	2	Gouache	4.8	0.2	3.5	0.29		1.6	0.3	0.63		3.0
	Bengal Rose	2	Gouache	13.0	0.2	2.5	0.07		2.8	0.1	0.15		4.6
	Flesh Tint	2	Gouache	3.3	0.6	3.5	0.08		3.1	0.3	0.35		1.1
	Fluorescent Yellow	2	Gouache	5.6	0.0	3	0.09		8.4	0.1	0.04		0.7
	Havannah Lake	2	Gouache	3.5	0.1	3.5	0.34		1.6	0.2	0.71		2.3
	Madder Carmine	2	Gouache	1.6	0.1	4	0.39		1.1	0.1	0.57		1.5
	Magenta	2	Gouache	7.5	0.0	3	0.08		1.8	0.0	0.32		4.2
	Orange Lake Light	2	Gouache	1.0	0.1	4	0.51		1.1	0.0	0.46		0.9
	Parma Violet	2	Gouache	3.5	0.1	3.5	0.31		1.4	0.0	0.75		2.4
	Periwinkle Elue	2	Gouache	4.5	0.2	3.5	0.20		0.7	0.1	1.03	0.8	5.5*
	Perm Green Light	2	Gouache	1.8	0.0	4	0.38		1.0	0.2	0.71		1.8
	Primary Red	2	Gouache	9.4	0.0	3	0.08		3.4	0.0	0.28		2.8
	Prussian Blue	2	Watercolor	0.6	0.2	4	1.84	1.3	3.2	0.1	0.40		0.4**
	Rose Malmaison	2	Gouache	19.3	0.0	2.5	0.05		7.5	0.0	0.13		2.6
Rose Tyrien	2	Gouache	36.1	0.4	>1	0.01		12.2	1.0	0.06		3.0	
Sigma Aldrich Strathmore	Spectrum Violet	2	Gouache	7.8	0.1	3	0.10		1.5	0.7	2.06	2.1	3.7*
	Crystal Violet	2	Watercolor	54.9	1.0	>1	0.03		8.1	0.4	0.12		6.8
	Paper Blank	2	Paper	2.7	0.0	3.5	0.06		1.0	0.1	0.24		2.6

Standard deviation (SD) shown for samples with multiple swatches. BW indicates approximate ISO Blue Wool equivalent with respect to color change in air. Maximum MCDM shown for samples with maximum $MCDM:\Delta E$ ratios >1. * ΔE_{Anox} replaced with Max $MCDM_{Anox}$ to calculate ΔE_R ; ** ΔE_{Air} replaced with Max $MCDM_{Air}$ to calculate ΔE_R .

Table 4 Color change data for samples lacking information on chemical composition

Source	Sample	Trial	Type	ΔE_{Air}			$MCDM_{Air}:\Delta E_{Air}$	$MCDM_{Air}$	ΔE_{Anoxia}		$MCDM_{Anox}:\Delta E_{Anox}$	$MCDM_{Anox}$	ΔE_R
				Mean	SD	BW			Max	Max			
Dr Ph. Martin	Alpine Rose	2	Aniline dye	27.2	2.0	1.5	0.07		1.8	0.5	0.53		14.9
	Amber Yellow	2	Aniline dye	9.1	0.5	3	0.11		1.8	0.5	0.48		5.0
	Cherry Red	2	Aniline dye	31.9	0.5	>1	0.03		3.0	0.5	0.23		10.6

	Crimson	2	Aniline dye	7.3	0.1	3	0.11		3.0	0.2	0.26		2.4
	Daffodil Yellow	2	Aniline dye	4.5	0.1	3.5	0.11		0.9	0.1	0.61		5.1
	Grass Green	2	Aniline dye	22.6	0.9	2	0.04		4.5	0.2	0.41		5.1
	Juniper Green	2	Aniline dye	12.2	0.5	2.5	0.14		7.1	0.4	0.30		1.7
	Mahogany	2	Aniline dye	21.9	0.4	2	0.04		8.4	1.1	0.13		2.6
	Moss Green	2	Aniline dye	22.5	0.5	2	0.07		2.1	0.8	0.86		10.9
	Moss Rose	2	Aniline dye	37.6	1.1	>1	0.05		2.9	0.2	0.18		13.0
	Persimmon	2	Aniline dye	31.4	0.6	>1	0.11		2.7	0.1	0.20		11.6
	Scarlet	2	Aniline dye	4.5	0.2	3.5	0.17		2.0	0.3	0.44		2.3
	Slate Blue	2	Aniline dye	13.4	0.5	2.5	0.12		1.8	0.3	0.76		7.5
	True Blue	2	Aniline dye	35.4	0.8	>1	0.06		4.5	0.4	0.26		7.8
	Turquoise Blue	2	Aniline dye	10.0	0.2	3	0.19		3.4	0.1	0.28		2.9
	Wild Rose	2	Aniline dye	36.6	1.4	>1	0.03		2.6	0.0	0.42		14.0
Sharpie	Green	2	Fluorescent ink	21.4	0.5	2	0.04		20.7	0.1	0.04		1.0
	Magenta	2	Fluorescent ink	32.0	0.5	>1	0.02		30.3	0.0	0.03		1.1
	Orange	2	Fluorescent ink	28.2	0.3	1.5	0.03		16.4	0.3	0.07		1.7
	Yellow	2	Fluorescent ink	5.8	0.1	3	0.08		1.7	0.2	0.19		3.5
GCI Reference	Carmine	1	Dry pigment	15.5	0.2	2.5	0.12		1.0	0.2	2.14	1.6	9.7*
	Cochineal	1	Dry pigment	16.5	0.4	2.5	0.22		0.8	0.1	2.46	1.8	9.4*
Kremer	Orpiment, Genuine**	2	Dry pigment	9.9	0.1	3	0.15		1.1	0.3	0.87		8.8
	Realgar	2	Dry pigment	12.9	0.9	2.5	0.08		7.0	0.3	0.21		1.8
Schminke	Prussian Blue	2	Watercolor	1.8	0.1	4	0.79		3.4	0.1	0.37		0.5
	Prussian Blue	2	Watercolor	1.2	0.0	4	1.01	1.3	4.8	1.1	0.30		0.3
Cornelissen	Antwerp Blue	2	Watercolor	2.6	0.2	3.5	0.94		5.4	0.5	0.42		0.5
Forbes	Bitumen	1	Dry pigment	9.2	0.2	3	0.32		0.5	0.0	6.21	3.1	3.0*
	Brazilwood	1	Dry pigment	7.9	1.6	3	0.22		3.9	1.1	0.41		2.0
	Carmine Lake	1	Dry pigment	12.1	3.0	2.5	0.38		1.2	0.7	3.41	2.1	5.8*
	Dragon's Blood	1	Dry pigment	22.2	1.4	2	0.13		1.3	0.3	2.13	3.5	6.4*
	Emerald Green	1	Dry pigment	2.4	0.2	3.5	0.47		1.2	0.2	0.91		1.9
	Eosine	1	Dry pigment	17.9	5.0	2.5	0.38		1.4	0.3	2.08	2.2	8.2*
	Indian Lake (Roberson)	1	Dry pigment	9.2	0.3	3	0.18		1.6	1.2	2.45	1.9	4.9*
	Indian Lake (W&N)	1	Dry pigment	10.4	0.6	3	0.17		3.6	0.4	0.49		2.9
	Indigo	1	Dry pigment	8.2	0.6	3	0.30		4.4	0.3	0.60		1.9
	Lithol Red	1	Dry pigment	17.0	1.8	2.5	0.33		3.7	0.2	0.59		4.6
	Madder/Lake	1	Dry pigment	13.2	0.2	2.5	0.08		4.1	1.0	0.33		3.2
	Magenta	1	Dry pigment	31.1	1.7	>1	0.06		10.6	0.6	0.18		2.9
	Mauve	1	Dry pigment	33.7	3.3	>1	0.07		7.2	0.2	0.56		4.7
	Orpiment	1	Dry pigment	7.5	0.9	3	0.14		1.5	0.1	0.20		5.0
	Powdered Kermes	1	Dry pigment	4.2	0.0	3.5	0.34		1.2	0.6	2.15	2.2	1.9*
	Purple Madder	1	Dry pigment	7.7	0.9	3	0.23		2.6	1.0	0.95		3.0
	Realgar Powder	1	Dry pigment	5.1	0.4	3	0.27		1.8	0.1	0.79		2.8
	Saffron	1	Dry pigment	13.3	1.1	2.5	0.09		5.6	0.4	0.21		2.4
	Sepia	1	Dry pigment	3.6	0.1	3.5	0.26		0.8	0.2	1.57	1.6	2.3*
	Verdigris	1	Dry pigment	3.5	1.3	3.5	0.25		7.7	0.0	0.11		0.5
	Verdigris, replicate	2	Dry pigment	7.9	0.3	3	0.09		9.8	0.4	0.10		0.8
	Yellow Lake	1	Dry pigment	3.8	0.6	3.5	0.46		0.6	0.5	4.53	1.3	3.0*

Standard deviation (SD) shown for samples with multiple swatches.

BW indicates approximate ISO Blue Wool equivalent with respect to color change in air. Maximum MCDM shown for samples with maximum MCDM:ΔE ratios above 1.

*ΔE_{Anox} replaced with Max MCDM_{Anox} to calculate ΔE_R.

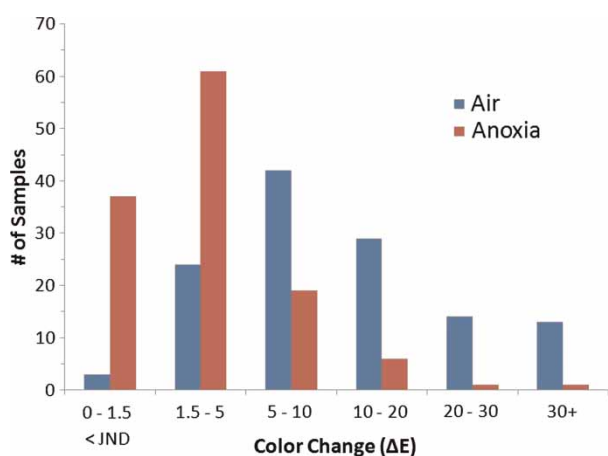


Figure 3 Histogram of color change in air (ΔE_{Air}) and in anoxic (ΔE_{Anox}) environments. The left pair of bars indicates samples exhibiting color change less than $\Delta E = 1.5$ or one JND.

anoxia increased its color change by a factor of approximately two compared with exposure in air, suggesting a cautious perspective when considering the use of anoxic environments for this colorant system. ΔE_R provides only a rough estimation of the degree of benefit or harm provided by an anoxic environment, particularly for those samples in which either its air or anoxia component exhibited a maximum MCDM: ΔE ratio above 0.5. (ΔE_R examines the ratio between color change measurements, MCDM: ΔE represents the uncertainty associated with these measurements and with MCDM: ΔE values above 0.5 indicating a high level of uncertainty.)

ΔE_R values for each of the 125 samples tested are shown in the right column of Tables 3 and 4, whereas Fig. 4 provides a graphical summary of its distribution. Ninety percent (113 samples) of the samples examined displayed ΔE_R values above 1.2, indicating more color change in air than in anoxia. Within this subset, 39% (44 samples) of the samples had ΔE_R values between 2 and 4, whereas 47% (53 samples) of the samples had ΔE_R values above 4. In contrast, six samples exhibited ΔE_R values below 0.8, denoting more color change in low-oxygen conditions than in air. Six samples also had ΔE_R values between 0.8 and 1.2, indicating similar color change in both environments.

Discussion

This study has demonstrated the capacity of near-anoxic environments to influence light-induced color change for a vast majority of the 125 samples examined. A paired-samples *t*-test comparing color change when exposed to light in air and anoxia indicated that the presence of oxygen or lack thereof had a statistically significant effect on color change. Specifically, the results suggest that exposure to light in an anoxic environment will generally reduce color change compared with samples exposed to light in air.

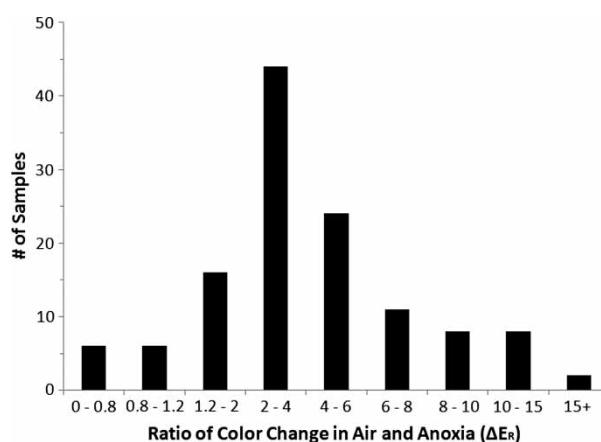


Figure 4 Histogram of ratios of color change in air and anoxic environments (ΔE_R). Samples with ratios below 0.8 indicate less color change in air than in anoxia, whereas those with ratios above 1.2 indicate more color change in air than in anoxia.

The vast majority of samples (113 of 125 samples) investigated here exhibited less color change when exposed to light in anoxia than in air ($\Delta E_R > 1.2$) (Fig. 4). Within this subset, 39% (44 samples) indicated that exposure to light in a low-oxygen environment would reduce color change by a factor of two to four compared with exposure to light in air. Furthermore, 47% (57 samples) exhibited color change in anoxia that was reduced by a factor of four or more compared with color change in air. This decrease in color change when exposed to a near-anoxic environment suggests that photooxidation may be the dominant photochemical reaction for these samples. However, color change in anoxia exceeded a JND (ΔE : ~ 1.5) for 70% (88 samples) of these samples, indicating that photochemical reactions not requiring oxygen also affected color change for most colorant systems.

Of the 125 samples examined, only six samples exhibited more color change in anoxia than in air ($\Delta E_R < 0.8$) (Fig. 4). In each case, exposure to light in a low-oxygen environment resulted in a color change that was greater by a factor of two or more than that observed in air, suggesting that a photochemical reaction not needing oxygen (e.g. photoreduction) may be affecting color change for these samples. In addition, the color change for these samples exposed in air was above a JND for four of the six samples, implying that additional photochemical reactions played a role in color change. The samples for which color change was accelerated by exposure to light in anoxia were three watercolor samples of Prussian blue (Kremer, Schminke, and Winsor & Newton), one watercolor sample of Antwerp blue (Kremer), one gouache sample of Fluorescent Yellow (Winsor & Newton), and a dry pigment sample of Verdigris (Forbes).

Six samples also exhibited similar color change in air and anoxia when exposed to light ($0.8 \leq \Delta E_R \leq 1.2$) (Fig. 4). The comparable color change of these samples irrespective of the oxygen concentration in the surrounding environment suggests that color change may be due to a non-oxidative photochemical reaction. The samples for which color change was roughly equal in air and anoxia were two samples of Sharpie Accent Highlighter fluorescent ink (green and magenta), two samples of Winsor & Newton Designers' Gouaches (Orange Lake Light and Flesh Tint), and samples of Verdigris dry pigment (Forbes) and *Reseda luteola* dyed wool (EU-Artech).

Paper blank

The paper substrate for the majority of samples examined in this study was Strathmore Drawing Medium (400 Series), a sample of which was included in the exposure trial. Samples not applied to this paper substrate were natural history specimens, dyed textiles, and those from the Library of Congress. The paper blank had a lightfastness in air roughly equivalent to BW3.5 and the sample exhibited reduced color change in anoxia compared with in air (ΔE_R : 2.6). Although the potential color change of the paper substrate influences the color change observed for a colorant sample, it is difficult to determine the extent to which each component contributes to the sample's overall color change. Therefore, color changes observed in this study are attributed to a specific colorant system, which includes the colorant, the binder, and the substrate as they would interact on an artifact.

Dyed textiles and associated pigments

This sample set included well-characterized samples of dyed silk, dyed wool, and associated pigments from the GCI's Asian Organic Colorants Project, with additional material from EU-Artech (Kirby *et al.*, 2006; www.organic-colorants.org) and the Schwebpe Collection (early synthetic dyes and dyed fabric swatches assembled by the late Helmut Schwebpe). Lightfastness in air for most samples in this subset was roughly equivalent to BW2.5 to BW3.5 (Table 3). Twelve of 13 samples of dyed wool and all samples of dyed silk and associated pigments exhibited less color change when exposed to light in anoxia than in air. ΔE_R values exceeded 2 for eight silk samples, ten wool samples, and 12 pigment samples, indicating that their color change in anoxia was reduced by a factor of two or more. A wool sample dyed with *R. luteola* (alum mordant) was the only sample that did not benefit from anoxia, exhibiting similar color change in the two environments.

A previous study by Hoyo-Meléndez & Mecklenburg (2011) described a silk sample dyed with turmeric (*Curcuma longa*) that displayed similar

color change in air and anoxic environments. Although this study included one silk sample dyed with *C. longa* (alum mordant) that also exhibited color change roughly similar in both environments (ΔE_R : 1.3), a second silk sample (no mordant, ΔE_R : 2.2) and a wool sample (alum mordant, ΔE_R : 1.6) dyed with *C. longa* displayed reduced color change when exposed to light in anoxia compared with in air.

Natural history specimens

Six leaf and grass samples from the Canadian Museum of Nature and one butterfly wing from the personal collection of one of the authors were included in the study. These samples exhibited lightfastness in air ranging from BW1.5 to BW3 (Table 3). All leaf and grass samples exhibited color change in anoxia that was reduced by at least a factor of seven compared with that in air. Although color was only quantified at the beginning and end of each trial, a rapid transition from green to brown was observed during the exposure of leaf and grass samples in air, indicating the bleaching of chlorophyll (Aronoff & Mackinney, 1943). The green regions of the *Phorcas* butterfly wing also exhibited a decrease in color change in anoxia compared with in air (ΔE_R : 2.6). The bicolorant phorbacilin, first extracted from *Papilo phorcas*, has been known to undergo partially reversible photochemical transitions (Kayser, 1985).

Organic dyes

Twelve organic dye samples with known chemical compositions were received from the Library of Congress for examination. Consisting of four variations (no mordant, alum, potash, lake) of three organic dyes (Brazilwood, Madder, and Lac), these samples typically exhibited lightfastness in air between BW2 and BW3.5, although two samples of Brazilwood (Potash and Lake) had light sensitivities exceeding BW1 (Table 3). All organic dye samples exhibited color change in anoxia that was decreased by a factor of two or more compared with in air, with half of the samples exhibiting ΔE_R values above 4. The reduced color change of Brazilwood in a low-oxygen environment was consistent with behavior reported by Lerwill (2012). (Brazilwood examined in this study used sappanwood from Japan.) However, the darkening of Madder during reduction bleaching treatments as reported by Norville-Day *et al.* (1997) was not observed for Madder samples exposed in anoxia.

Gouaches and watercolors

This sample set consisted of 20 samples, 17 of which had known chemical compositions – these included 15 samples of Winsor & Newton Designers' Gouaches, one sample of Winsor & Newton Artists' Water Colours (Prussian blue), and one watercolor

sample of Crystal Violet (Sigma Aldrich). The Winsor & Newton Gouache samples were listed by the manufacturer as having permanence ratings of either B (moderately durable) or C (fugitive) (www.winsornewton.com). In addition, samples of Winsor & Newton Designers' Gouaches were described as achieving opacity due to exceptionally high levels of pigmentation rather than by the addition of chalk or other such materials. The chemical compositions of the three remaining watercolor samples – two samples of Prussian blue (Kremer and Schminke) and one sample of Antwerp blue (Kremer) – were not verified. This sample set exhibited varying degrees of lightfastness in air, ranging from light sensitivities exceeding BW1 to BW4.

Thirteen of the 20 gouache and watercolor samples displayed reduced color change when exposed to light in anoxia than in air, with 11 samples exhibiting ΔE_R values of 2 or more. (Tables 3 and 4) The lower color change in anoxia of the Winsor & Newton Alizarin Crimson and Bengal Rose Gouaches and Sigma Aldrich Crystal Violet watercolor corroborated results from Korenberg (2008) and Casella (2009). Two Winsor & Newton Gouache samples (Orange Lake Light and Flesh Tint) exhibited similar color change in both environments and three samples of Prussian blue watercolor (Kremer, Schminke, and Winsor & Newton), one sample of Antwerp blue watercolor (Kremer), and one sample of Fluorescent Yellow Gouache (Winsor & Newton) displayed more color change in anoxia than in air.

The color change behavior of the three Prussian blue samples was consistent with the accelerated color change in anoxia observed in the literature (Chevreul, 1837; Rowe, 2004; Korenberg, 2008; Hoyo-Meléndez & Mecklenburg, 2011). Described as a variation of Prussian blue with translucent extender added to reduce color intensity and modify its working properties (Kirby & Saunders, 2004), the color change behavior of Antwerp blue in air and anoxia was also similar to that measured by Korenberg (2008). Although color reversion had been observed for Prussian blue after subsequent storage in the dark (Ware, 1999), analysis of Prussian blue and Antwerp blue samples was conducted shortly after the end of the exposure trial, limiting the potential for phototropic behavior. Despite the lack of compositional information for two of the three Prussian blue samples (Kremer and Schminke) and the Antwerp blue sample (Kremer), the parallel color change behavior of these samples with that observed by other studies suggests that these specific samples were properly identified.

Winsor & Newton's Fluorescent Yellow Designer Gouache was described by the manufacturer as a fluorescent dye/resin-based pigment. Although its

accelerated color change in anoxia was similar to the color change behavior described by Buss & Crews (2000) for a cotton fabric dyed with an unverified pink fluorescent dye, the same study observed similar color change in both air and anoxia for cotton dyed with an unverified yellow fluorescent dye. In addition, a study by Ellis *et al.* (2002) indicated that the color change for five daylight fluorescent colors was similar in both air and anoxic environments.

Aniline dyes

Primarily formulated for graphic artwork on paper surfaces intended for reproduction, 16 samples of Dr Ph. Martin's Radiant Concentrated Watercolors were included in the study. Although chemical compositions were not available, the sample set was generally described as aniline-based dyes, as opposed to traditional watercolors or pigment suspensions. The lightfastness in air for these samples ranged from color change exceeding that of BW1 to BW3.5 (Table 4). All samples of Dr Ph. Martin's Radiant Concentrated Watercolors exhibited reduced color change when exposed to light in anoxia compared with exposure to light in air. Fifteen of 16 samples displayed ΔE_R values exceeding 2 and 11 samples exhibited color change in a low-oxygen environment that was reduced by a factor of 5 or more compared with in air.

Fluorescent inks

Four samples of Sharpie Accent Highlighter (green, yellow, magenta, and orange) were exposed to light in air and anoxia. Lacking information on specific chemical compositions, the samples were assumed to be fluorescent inks. Lightfastness for these samples ranged from exceeding BW1 to BW3 (Table 4). Although two samples (orange and yellow) had less color change in anoxia compared with in air, samples of green and magenta exhibited similar color change in both environments. As discussed previously, the literature has shown varying color change behavior for fluorescent samples (Buss & Crews, 2000; Ellis *et al.*, 2002).

Dry pigments

Lacking verification of chemical composition, this sample set included 26 dry pigment samples, the bulk of which were taken from the Forbes Pigment Collection. Also examined were dry pigments from Kremer (Realgar; Orpiment; and Carmine, GCI Reference) and Zecchi (Cochineal, GCI Reference). Although pigments are rarely used without binder, the idea was to examine a simple two-component system consisting of only the colorant and the paper substrate. The lightfastness of these samples ranged from color change exceeding BW1 to BW3.5 (Table 4). Twenty-four of 26 dry pigment samples

displayed reduced color change in anoxia compared with in air, with 20 samples exhibiting ΔE_R exceeding 2. The remaining two dry pigment samples were replicates of Verdigris, with one sample exhibiting more color change in anoxia (ΔE_R : 0.5) and the other roughly similar color change in both environments (ΔE_R : 0.8). Although shown to exhibit poor lightfastness (Allen & Edge, 1992), these results suggest that basic copper acetate samples may be at risk in low-oxygen conditions.

A study by Korenberg (2008) investigated color change for two colorants, Orpiment and Realgar, also examined here. The reduced color change in anoxia of two dry pigment samples of Orpiment (Forbes and Kremer) was similar to that observed by Korenberg for a watercolor sample of Orpiment (Kremer), suggesting that the Orpiment samples included in this study were correctly identified. The same study also reported similar color change in air and in anoxia for a watercolor sample of Realgar (Kremer), contrasting with the reduced color change in anoxia observed for two dry pigment samples of Realgar (Forbes and Kremer) examined here. This result suggests that a colorant's color change behavior might be dependent on its application (watercolor or dry pigment). Although the Kremer Realgar sample was chemically verified using a Renishaw inVia Raman microscope system (785 or 633 nm laser excitation using a L50X microscope objective), analysis of the Forbes Realgar sample suggested the presence of an amorphous arsenic-sulfide species, implying that the Forbes sample had undergone substantial light-induced transformation before inclusion in this study. Exposure of the original Kremer Realgar sample to successive shots of low wavelength visible light from a 488 nm laser source was able to induce a transformation somewhat similar to that seen for the Forbes sample. Furthermore, ΔE values for the Forbes Realgar sample in both air (5.1) and anoxia (1.8) were lower than those seen for the Kremer Realgar sample in the two environments (ΔE_{Air} : 12.9, ΔE_{Anox} : 7.0), supporting the theory that the Forbes sample had been previously exposed to light (Table 4).

Conclusion

When exposed to light, anoxic conditions were shown to reduce color change for the vast majority of samples included in this study. Of the 125 samples examined, 90% (113 samples) of the samples exhibited reduced color change when exposed in anoxia. Compared with its color change in air, 39% of this sample subset displayed color change in anoxia that was reduced by a factor of 2 to 4, whereas 47% exhibited color change in anoxia reduced by a factor of 4 or more. This divergent color change behavior in air

and anoxic environments suggests that photooxidation may play a major role in the color change of these samples. An obvious implication of these results is the potential for anoxic environments to dramatically extend the viewing lifetime or expand the exhibition parameters of colored artwork.

Six samples also displayed more color change when exposed to light in anoxia compared with in air – these samples included Prussian blue watercolor (three samples), Antwerp blue watercolor, Verdigris dry pigment, and Fluorescent Yellow Winsor & Newton Gouache. (Six samples also showed similar color change in air and anoxia.) The color change behavior of Prussian blue and Antwerp blue in a low-oxygen environment was consistent with the results described by previous studies. Although these samples represented only 5% of the sample set investigated here, they represent some concern to the more widespread use of anoxia in the conservation of cultural heritage, particularly from the risk of accelerating color change for colorant systems whose behavior in anoxia has yet to be identified. However, one must also consider the growing evidence for the overwhelming benefits of anoxic light exposure generally when applying this strategy. No protective measure is without risk leaving the traditional question to be answered by the conservator, 'Do the risks outweigh the benefits?'

Although the protocol described in this study was capable of assessing color change behavior in air and anoxia for a large sample set, the experimental setup required extended time periods to achieve a sizeable light dosage and did not easily permit intermediate measurements of color change. In contrast, the micro-fading tester, first developed by Paul Whitmore at Carnegie Mellon University (Whitmore *et al.*, 1999), allows for short exposure times due to its high-intensity light source and simultaneous and continuous color measurement and has been used previously by Hoyo-Meléndez & Mecklenburg (2011) and Lerwill (2012) to assess anoxic color change. The combination of microfadeometry with the environmental control and monitoring provided by the exposure cases used in this study will provide a practical tool for making rapid assessments of lightfastness and examining color change kinetics in air and anoxic environments.

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Manufacturers

Dr Ph. Martin Radiant Concentrated Watercolor: www.docmartins.com

Elsec 764 Environmental Monitor: www.elsec.com

Harrick Video Barrelineo: www.harricksci.com

Kremer pigments: www.kremerpigments.com

L. Cornelissen & Son pigments: www.cornelissen.com

Licor LI210 Photometric Sensor: www.licor.com/env

Mitsubishi RP System K-Type: www.mgc-a.com/AGELESS

Ocean Optics WS-1 Diffuse Reflectance Standard: www.oceanoptics.com

Schminke pigments: www.schmincke.de

Sharpie Accent Highlighter: www.sharpie.com

Sigma Aldrich Crystal Violet ACS Reagent: www.sigmaaldrich.com

Strathmore Drawing Medium, 400 Series: www.strathmoreartist.com

Teledyne Analytical Instruments Micro Fuel Cell Class B-2C and Model 317 Solid State Trace Oxygen Analyzer: www.teledyne-ai.com

Vaisala HMT338 Humidity and Temperature Transmitter: www.vaisala.com

Varian Cary 50 Bio UV-Vis Spectrophotometer: www.chem.agilent.com

Winsor & Newton Designers' Gouache and Artists' Water Colour: www.winsornewton.com

References

Allen N.S., Edge M. 1992. Lightfastness of Dyes and Pigments. In: *Fundamentals of Polymer Degradation and Stabilisation*. London: Elsevier Applied Science, pp. 176–93.

Arney J., Jacobs A., Newman R. 1979. The Influence of Oxygen on the Fading of Organic Colorants. *Journal of the American Institute for Conservation*, 18: 108–17.

Aronoff S., Mackinney G. 1943. The Photo-oxidation of Chlorophyll. *Journal of the American Chemical Society*, 65(5): 956–8.

Ashley-Smith J., Derbyshire A., Pretzel B. 2002. The Continuing Development of a Practical Lighting Policy for Works of Art on Paper and Other Object Types at the Victoria and Albert Museum. In: Vontobel R. ed. *ICOM Committee for Conservation, 13th Triennial Meeting, Preprints*. James & James, vol. 1, pp. 3–8.

Berns R.S. 2000. *Billmeyer and Saltzman's Principles of Color Technology*, 3rd ed. New York: Wiley-Interscience, pp. 97–99.

Bromelle N.S. 1964. The Russell and Abney Report on the Action of Light on Watercolors. *Studies in Conservation*, 9: 140–52.

Buss J.J.B., Crews P.C. 2000. Influence of Nitrogen Gas and Oxygen Scavengers on Fading and Color Change in Dyed Textiles. *AIC Textile Specialty Group Postprints*, 10: 55–67.

Carrievau G.W., Omecinsky D. 1983. Identification of the Forbes Collection Pigments: I. Whites. *Journal of the American Institute for Conservation*, 22(2): 68–81.

Casella L. 2009. Autochrome Research at the Metropolitan Museum of Art: Testing Methodology and Preliminary Results for Anoxia Light-Fading. *Topics in Photographic Preservation*, 13: 128–36.

Chevreul M. 1837. Recherches Chimiques sur la Teinture. *Mémoires de l'Académie Royale des Sciences de l'Institut de France*, 16: 41–116.

CIE 157. 2004. *Control of Damage to Museum Objects by Optical Radiation*. Vienna: Commission Internationale de L'Eclairage.

Delgado M.F., Dirk C.W., Druzik J., Westfall N. 2011. Lighting the World's Treasures: Approaches to Safer Museum Lighting. *Color Research Application*, 36(4): 238–54.

del Hoyo-Meléndez J.M., Mecklenburg M.F. 2011. The Use of Micro-fading Spectrometry to Evaluate the Light fastness of Materials in Oxygen-free Environments. *Spectroscopy Letters*, 44(2): 113–21.

Ellis M.H., McGlinchey C.W., Chao E. 2002. Daylight Fluorescent Colors as Artistic Media. In: Stratis H.K., Salvesen B. eds. *The Broad Spectrum*. London: Archetype, pp. 160–6.

Geuskens G. 1975. Photodegradation of Polymers. In: Bamford C.H. ed. *Chemical Kinetics, Volume 14*. Amsterdam: Elsevier, pp. 333–424.

Gilberg M. 1988. Inert Atmosphere Fumigation of Museum Objects. *Studies in Conservation*, 34: 80–4.

Giles C.H., Haslam R., Duff D.G. 1976. An Examination of the Cause of the Humidity Sensitivity of the Lightfastness of Dyed Materials. *Textile Research Journal*, 46: 51–4.

Giles C.H., Shah C.D., Watts W.E. 1972. Oxidation and Reduction in Light Fading of Dyes. *Journal of the Society of Dyers and Colourists*, 88(12): 433–5.

Grzywacz C., Wouters J. 2008. A Contribution to the Characterization of Ancient Chinese Colorants, Appendix 3: Table of Productions and Lab Recipes. Internal Report, Getty Conservation Institute.

Kayser H. 1985. Pigments. In: Kerkut G.A., Gilbert L.I. eds. *Comprehensive Insect Physiology, Biochemistry, and Pharmacology*. New York: Pergamon Press.

Kirby J. 1993. Fading and Colour Change of Prussian Blue: Occurrences and Early Reports. *National Gallery Technical Bulletin*, 14: 62–71.

Kirby J., Saunders D. 2004. Fading and Colour Change of Prussian Blue: Methods of Manufacture and Influence of Extenders. *National Gallery Technical Bulletin*, 25: 73–99.

Kirby J., van Bommel M., Higgitt C., Wassink M.G., van den Berghe I., Wouters J., Sotiropoulou S., Karapanagiotis I., Valianou L., Qye A., Peggie D., McNab H., Hulme A., Grzywacz C., Miliani C., Clementi C., Petrovicu I. 2006. Dyeing and Dyestuffs Revealed: The EU-ARTECH Collaborative Study of Reference Materials. Paper presented at Dyes in History and Archaeology (DHA) 25, Suceava, Romania, 21–22 September.

Korenberg C. 2008. The Photo-ageing Behavior of Selected Watercolour Paints Under Anoxic Conditions. *The British Museum Technical Research Bulletin*, 2: 49–57.

Lerwill A. 2012. Micro-fading Spectrometry: An Investigation into the Display of Traditional Watercolour Pigments in Anoxia. PhD Thesis, Nottingham Trent University.

Luo M.R., Cui G., Rigg B. 2001. The Development of the CIE 2000 Colour-difference Formula: CIEDE2000. *Color Research and Application*, 26: 340–50.

Maekawa S. 1998. *Oxygen-Free Museum Cases*. Los Angeles: The Getty Conservation Institute.

Michalski S. 1997. The Lighting Decision. In: *Fabric of an Exhibition: An Interdisciplinary Approach, Preprints of Textile Symposium 97*. Ottawa: Canadian Conservation Institute, pp. 97–104.

Milosevic M. 2004. The Video Barrelineo. Paper presented at Infrared and Raman Users' Group (IRUG) 6 Conference, Florence, 29 March–1 April.

Norville-Day H., Townsend J.H., Johnston F. 1997. A Study of the Effects of Bleaching Treatments on C19 Pigments, With Special Reference to Turner's Watercolour Palette. In: Eagan J. ed. *IPC Conference Papers*. Leigh, UK: Institute of Paper Conservation, pp. 137–49.

Rowe S. 2004. The Effect of Insect Fumigation by Anoxia on Textiles Dyed with Prussian Blue. *Studies in Conservation*, 49: 259–70.

Ryan C.C., Baker M. 2008. Lightfastness Testing in an Anoxic Environment. Paper presented at the American Institute of Conservation Annual Meeting: *Creative Collaborations*, Denver, 21–25 April.

Saito M., Minemura C., Nanashima N., Kashiwagi M. 1988. Colour Fading Behavior of Anthraquinone Dyes Due to Environmental Conditions. *Textile Research Journal*, 58: 450–4.

Saunders D., Kirby J. 1996. Light-induced Damage: Investigating the Reciprocity Principle. In: Bridgland J. ed. *ICOM Committee for Conservation, 11th Triennial Meeting, Preprints*. James & James, pp. 187–90.

- Schaeffer T.T. 2001. *Effects of Light on Materials in Collections: Data on Photoflash and Related Sources*. Los Angeles: Getty Conservation Institute.
- Scott G. 1965. *Atmospheric Oxidation and Antioxidants*. Amsterdam: Elsevier.
- Selwitz C., Maekawa S. 1998. *Inert Gases in the Control of Museum Pests*. Los Angeles: Getty Conservation Institute.
- Sharma G., Wencheng W., Dalal E.N. 2004. The CIEDE2000 Color-difference Formula: Implementation Notes, Supplementary Test Data, and Mathematical Observations. *Color Research and Application*, 30: 21–30.
- Thomson G. 1986. *The Museum Environment*, 2nd ed. Oxford: Butterworth-Heinemann.
- Townsend J.H., Thomas J., Hackney S., Lerwill A. 2008. The Benefits and Risks of Anoxic Display for Colorants. In: Saunders D., Townsend J.H., Woodcock S. eds. *Conservation and Access*. London: IIC, pp. 76–81.
- Valentin N., Preusser F. 1990. Insect Control by Inert Gases in Museums, Archives and Libraries. *Restaurator*, 11: 22–33.
- Ware M. 1999. *Cyanotype: The History, Science, and Art of Photographic Printing in Prussian Blue*. London: Science Museum and National Museum of Photography, Film, and Television.
- Whitmore P.M., Pan X., Bailie C. 1999. Predicting the Fading of Objects: Identification of Fugitive Colorants Through Direct Nondestructive Lightfastness Measurements. *Journal of the American Institute of Conservation*, 38: 395–409.