

Preliminary study of a Georgia O'Keeffe pastel drawing using XRF and μ XRD

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X-ray fluorescence spectrometry (XRF) and micro-X-ray diffraction (μ XRD) were used to analyze the composition of pigments on a pastel drawing, *Special No. 32*, by Georgia O'Keeffe. XRF analyses showed that, among other pigments present in the drawing, the red, orange, and yellow pigments may possibly be identified with lead- and chromium-based pigments: lead chromates, red and yellow lead oxides, and/or lead carbonates, plus calcium-based pastel fillers, such as whiting or gypsum. XRD examination of a sample removed from a dark mottled area of coral red pastel confirmed that this pigment layer, which is associated with a darkened appearance and high Pb:Cr ratios, matches the red lead oxide, minium ($2\text{PbO}\cdot\text{PbO}_2$). © 2009 International Centre for Diffraction Data. [DOI: 10.1154/1.3133137]

Key words: XRF, XRD, pastel, pigment, red lead, O'Keeffe

I. INTRODUCTION

As part of a conservation assessment of *Special No. 32*, a Georgia O'Keeffe 1915 pastel drawing on black paper (mounted to paperboard) in the collection of the Smithsonian American Art Museum (SAAM) (Figure 1), a pigment survey analysis using non-invasive X-ray fluorescence (XRF) spectrometry was coupled with minimally invasive micro-X-ray diffraction (μ XRD) analysis of a single sample. The analyses were undertaken by the Smithsonian's Museum Conservation Institute (MCI) in order to assist in developing an approach for the conservation and treatment of the work, as well as to lay the groundwork for a planned technical study of O'Keeffe pastels. Non-invasive XRF was chosen as a survey tool that enabled *in situ* analysis of the delicate drawing. XRF allowed rapid preliminary investigation of the range of possible pigments present and provided a better understanding of the condition of the piece with regard to select pigments in red and orange areas that appear to have a dark brownish surface mottling. The uneven quality of this mottling, and the observation that it appears to be isolated to the uppermost surfaces of some areas of coral red pastel, suggested that these areas may consist of an altered red pigment, rather than an intentional application of a darker pastel. XRF data guided decisions with regard to microsampling for further analysis of the dark mottling by μ XRD. Overall, the goals of the XRF and μ XRD analyses were to identify possible materials present in the piece and to explore whether the pastel's current appearance is a significant departure from the artist's original intent.

Natural and synthetic red lead pigments have been in use since antiquity and their susceptibility to darkening has been recognized at least since the Renaissance (Gettens and Stout, 1942). It also has been observed that red lead pigments are relatively stable when protected from air by a rich organic

medium such as glue or linseed oil (Gettens and Stout, 1942). However, the mechanisms and products of red lead pigment alteration are incompletely understood. Fitzhugh (1986) remarks that the darkening of lead tetroxide (Pb_3O_4 or $2\text{PbO}\cdot\text{PbO}_2$) may be more complex than simple oxidation to the lead dioxide (PbO_2). While environmental factors such as light, humidity, pollution, hydrogen sulfide, and also microbial contamination clearly have potential mechanistic roles, recent investigations also show that composition and microstructural features of the red lead grains, which result from the manufacturing process, may be determining factors in the pigment alteration process (Gettens and Stout, 1942; Fitzhugh, 1986; Kuchitsu, 1997; Saunders *et al.*, 2002; Aze *et al.*, 2002). Therefore, the incorporation of red lead into pastels, which are by nature large amounts of dry pigment bound by a minimal amount of organic medium, would be expected to yield an artist's material that is vulnerable to alteration and color conversion (Gettens and Stout, 1942; Fitzhugh, 1986).

In O'Keeffe's writings, the artist conveyed that meaning in her art resides in color and shape itself. This was true particularly after the pivotal year of 1915, when, in her own words, "I first had the idea that what I had been taught was of little value to me except for the use of my materials as a language—charcoal, pencil, pen and ink, watercolor, pastel, and oil" (O'Keeffe, 1976). O'Keeffe used a variety of commercial pastel sticks and appears to have also made pastels herself, as indicated by materials left in her studio (Walsh, 2000). Several studies and the record of her working practices by Caroline Keck (Walsh, 2000; Barilleaux and Whitaker Peters, 2006) provide information about O'Keeffe's materials and techniques. However, further investigation, especially technical study, is warranted. As stressed by Keck and Walsh (Walsh, 2000), it was imperative to O'Keeffe that



Figure 1. (Color online) *Special No. 32*, 1915, pastel on paper, by Georgia O'Keeffe (credit: the Smithsonian American Art Museum, Acc. No. 1995.3.2, 14 × 19 1/2 in.).

her works remain in pristine condition, especially in terms of color. Therefore, information about the artist's materials and possible changes in color resulting from interaction with the environment are of great significance to the understanding of her *oeuvre*.

II. EXPERIMENTAL

A. XRF analysis

The instrumentation used was an Innov-X Systems Alpha Series XT-440 handheld energy dispersive X-ray fluorescence spectrometer (ED-XRF) that incorporates a miniature X-ray tube with a silver anode, a Si-PIN diode detector, and a primary beam aluminum filter. The XRF will operate between 10 to 40 kV and 10 to 100 μA ; detector resolution is less than 200 eV. The beam diameter of analysis is approximately 14 mm. For this research, the instrument was operated in the "soil mode," at 35 kV and 13 μA . The purpose of utilizing these beam settings was to optimize sensitivity to a broad range of elements, i.e., those found from potassium (K) to bismuth (Bi). The depth of penetration in the area of examination is dependent on the beam settings, as well as the elements present, the density of the material, and the loss of photons from scattering in the air and through the material matrix itself. Without available purging or vacuum capability in this analysis, elements lighter than sulfur (S) were not detectable and elements lighter than calcium (Ca) were expected to show decreased sensitivity.

The portable XRF unit was used in a stationary mode by attachment to a specially designed tripod and arm that extended out over the object, which lay flat on a polymer-composite laboratory benchtop. The benchtop did not contribute an elemental signature to the analysis, nor did it contribute significantly to the spectral backgrounds. Furthermore, this horizontal support system, including the backmat, allowed for the safest handling of the object during analysis. In this configuration, the XRF instrument was held flush with the front mat, about 2.0 mm above the surface of the object, in order not to damage any of the extremely friable media (Figure 2). This precise working distance was maintained throughout each exposure by keeping the XRF instrument stationary and manually repositioning the drawing under-

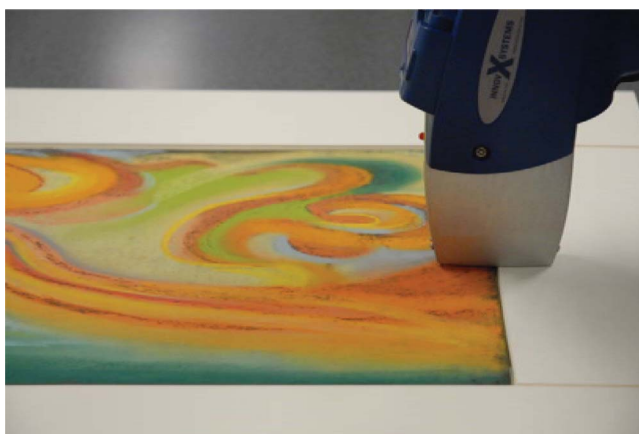


Figure 2. (Color online) XRF positioned ~ 2 mm above artwork.

neath the nose of the instrument to the area of interest. Several areas also were examined using a faceplate that limited the analysis to a maximum of 5.0 mm in diameter, and, as expected, greatly decreased the intensity of the X-ray beam. Due to the thickness of the faceplate, these spectra were obtained at an added distance above the object of about 1.0 mm, further limiting detection of X-ray intensity. The window did not significantly contribute to detection of elements of interest (see Results section). Exposures were 180 s for good peak to background ratio.

The Innov-X software incorporates built-in peak deconvolution and factory calibration for the beam settings. Based on an assumption of infinite thickness, empirically-derived, linear calibration factors are used to calculate the concentrations of detected elements based on the measured intensities and normalization to the Compton backscattering peak between 20 to 24 keV. These calculation methods make use of several assumptions that were not met in practice, and therefore do not accurately express elemental quantities. Deviations from ideal sampling geometries that are expected to cause quantification errors include sample thickness much less than an infinite thickness, inhomogeneity of materials, and scattering from separation between the instrument window and the object. Another problem in interpretation of software-generated results is spectral interference of peaks that are poorly resolved and depend on software deconvolution. For example, there is poor resolution between titanium (Ti) K and barium (Ba) L lines, and spectral overlap of lead (Pb) $L\alpha$ and arsenic (As) $K\alpha$ peaks, as well as Pb M lines and sulfur (S) K lines. Other potential sources of error arise from matrix effects, including overestimation or underestimation of concentrations due to absorption-enhancement effects from the particular mix of elements in the sample matrix, especially as these phenomena relate to the presence of heavy metals like Pb. However, due to the nature of pastels, which are essentially a thin layer of pigment(s) ground with a minimum of gum binder and differing quantities of chalk or gypsum, it is reasonable to assume that matrix effects from the pigment layer or paper are negligible.

B. XRD analysis

XRD analyses were performed on a Rigaku D/Max Rapid diffractometer with an image plate detector using cop-

TABLE I. XRF results.

Reading	Description of area of analysis	Cr	Fe	Cu	Zn	As ^a	Pb	Other ^b	Pb:Cr range ^c	Proposed identification based on color and elemental composition
Large window										
4	Benchtop	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD			
7	12 ply rag matboard	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	Ca, Ti, Fe		
10, 11, 29	Average black paper+other support materials	530	1200	51	21		290	Ca, Ti, Sr	0.55	
	RSD black paper+other support materials	21%	20%	18%	13%		29%		±12%	
17	Coral-red area w/black paper showing through	600	1400	<i>120</i>	<i>83</i>		6400		9.4 to 12	Red lead (Pb) (+Pb white/litharge or talc +ZnO?)
18	Nearby in coral-red	720	1600	69	40		5400		6.6 to 8.4	Red lead (+Pb white or talc ?)
19	Orange area with no visible mottling	6200	1000	51	34		7900	Ca	1.1 to 1.4	Chrome orange (Pb,Cr)+gypsum/whiting (Ca)
20	Dark mottling in coral-red stripe over orange	5400	1100	<i>120</i>	35		13000	Ca	2.1 to 2.7	Chrome orange+gypsum/whiting+red lead
21	Coral-red, little or no dark mottling	600	1200	58	42		12000		18 to 22	Red lead (+Pb white or talc?)
22	Coral-red with more dark mottling	560	1300	70	39		11000		17 to 22	Red lead (+Pb white or talc?)
23	Dark mottling in coral-red stripe over orange	930	1200	76	33		14000	Ca	13 to 17	Red lead (+Pb white or talc ? +nearby orange)
28	Brighter red, bottom right	750	1400	83	38		2400	Ca, Ba, Ti	2.8 to 3.6	Red lead+gypsum/whiting+barite (Ba)+ ? (+TiO ₂ ?)
24	Dark green at top	2900	2700	420	20	800	1900	Ca	0.58 to 0.73	Emerald green (Cu,As)+chrome green (Pb, Cr, Fe) (and/or viridian?) +gypsum/whiting
25	Light blue	710	1500	<i>110</i>	36		460	Ca	0.57 to 0.73	Organic blue or synthetic ultramarine (?)
26	Yellow	1700	1300	66	24		2000	Ca, Ba	1.0 to 1.3	Chrome yellow+gypsum/whiting
27	Yellow-green	7500	1600	71	46		8300	Sr, Ba	1.0 to 1.2	Chrome yellow+Sr yellow (Sr,Cr)+barite or Ba yellow+blue
Small window										
5	Benchtop (faceplate background)	<LOD	100	40	<LOD		<LOD			
13, 30	Average black paper+other support materials	200	500	80	5		100		0.5	
	RSD black paper+other support materials	4%	1%	4%	141%		27%		±24%	
31	Orange (same as 19)	2000	400	60	10		2000	Ca	0.8 to 1.2	Chrome orange
32	Dark mottling/coral-red stripe over orange (20)	1000	400	90	<LOD		3000		2.3 to 3.7	Chrome orange+red lead (+Pb white or talc?)
33	Dark mottling/coral-red stripe over orange	900	400	80	<LOD		3000	Ca	2.5 to 4.1	Chrome orange+red lead (+Pb white or talc?)
34	Dark mottling in coral-red stripe over orange (23)	<LOD	400	70	<LOD		4000	Ca	Pb only	Red lead (+Pb white or talc (?)+stray whiting/gypsum?)

KEY: LOD=limit of detection, RSD=relative standard deviation, bold=greater than LOD ($3 \times \max \text{RSD} + \text{ave. background}$), and italics=questionable (near LOD).

^aArsenic not confirmed in spectra other than yellow-green.

^bNo values available for Ca; other elements detected in raw spectra as relatively trace peaks.

^cPb:Cr ratio ranges reported based on 12% variation (large window) or 24% variation (small window) RSD for background paper.

per $K\alpha$ radiation, 50 kV acceleration voltage, and 40 mA current. For these analyses, one tiny sample was mounted onto a glass fiber using an amorphous cyanoacrylate-based adhesive and exposed to a microbeam for 15 min using a 0.3 mm collimator, and 5 h using a 0.1 mm collimator. The goniometer parameters were chi axis fixed at 45° , omega axis fixed at 0° , and phi axis spun 360° at $1^\circ/\text{sec}$. Experimental patterns were integrated over a large 2 theta region to minimize preferred orientation effects. After background subtraction, the patterns were qualitatively matched using JADE 7.5 software to known materials in the International Center for Diffraction Data (ICDD) database.

III. RESULTS AND DISCUSSION

XRF results are provided in Table I according to the analyses and areas of examination, which are marked as reading numbers and shown in Figure 3. The table includes software-determined values only for elements that were verified by the analyst to be present in the raw spectra; therefore, only one value for arsenic (As) is reported. Additional peak identifications are shown in the column marked "other;" here elements are reported only if they appear above levels detected in the paper and support materials. Note that the Innov-X system was not set up in this study to determine values for elements below titanium (Ti) or for strontium (Sr); additionally, lack of vacuum in the instrument (or a helium purge) precluded qualitative detection of light elements, below about sulfur (S). It must be stressed that the numeric values listed in Table I for each analyte cannot be interpreted in a quantitative manner because of non-ideal examination conditions, as discussed above. However, the software-generated values, which are normalized to the Compton scattering and scaled according to predetermined sensitivity factors, may be used for purposes of internal comparison, and are therefore presented without units, although the software reports these values as parts per million (ppm).

The relative standard deviations (RSDs) of elements detected in the paper (Table I) provide a baseline reference with which to compare levels of elements detected in the pastel layers. Values determined from a relatively small available area of unpigmented paper show quite high relative standard

deviations (RSD); this is most likely due to the typical inhomogeneous distribution of trace elements in the paper, as well as the presence of stray pigment in this area. Although this raises the limits of detection, elements may still be detected at levels significantly above the background, here shown in bold when greater than three times the maximum RSD (29%), plus the average value detected in the composite of supporting materials, i.e., the black paper, its paperboard mount, rag matboard and benchtop; questionable elements detected at approximately two times the background levels or less are shown in italics. The RSDs of trace elements detected in the background are a product of the analytical method and the paper itself, which, as mentioned, is contaminated with stray pigment. On the other hand, the RSD of Pb:Cr ratios in the paper is more indicative of Pb:Cr variation in the pastel layer, as measured with this method, and is more consistent. However this range remains an estimate. Reflecting this uncertainty, the elemental values are rounded to two significant figures for the large window and one significant figure for the small window. Based on elemental composition and color, Table I proposes possible pigments for the pastel colorants in different areas of examination with varying certainty.

Results indicate the presence of one or more of the following elements in most areas of interest: calcium (Ca), titanium (Ti), barium (Ba), chromium (Cr), iron (Fe), copper (Cu), strontium (Sr) and lead (Pb); zinc (Zn) detection appeared variable and inconsistent. By selecting slightly different spots in the one sufficiently large area of black paper without visible pastel (readings 10, 11, 13, 29, Figure 3), it was determined that elements associated with the various support materials are as follows: (1) no significant quantity of elements is detected in the benchtop; (2) the matboard has a measurable trace quantity of Ti (presumably from TiO_2), as well as variable trace Ca and Fe; (3) trace Ca, Cu, Sr and zinc (Zn) are found in the paper/paperboard; (4) Cr and Pb, detected in the black paper areas, are possibly associated with the nearby yellow pastel; and (5) somewhat higher, variable levels of Fe are detected in the black paper/paperboard.

Measurements obtained from the drawing's red, orange (Figure 4), and yellow (not shown) areas indicate that the pastel colorants are primarily associated with the elements Pb, Cr, and Ca. As shown in Tables I and II, this evidence suggests that O'Keeffe's pastels may contain pigments made from lead chromates (chrome orange, chrome yellow, and chrome red), lead oxides (red lead with or without litharge or massicot), lead carbonates and/or sulfates (lead whites), and white calcium-containing pigments such as whiting (CaCO_3) and/or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). This assessment is based on the color, known formulas of pigments available to O'Keeffe (Table II), and the lack of evidence for significant levels of potassium (K), Fe, molybdenum (Mo), As, cadmium (Cd), or mercury (Hg), elements that would indicate other possible pigments. Along with clay, both whiting and gypsum are common ingredients and fillers in pastels. The presence of Ba may indicate either a pigment or barite, which is a common extender; the less common extender, calcium chromate, also could be present, as well as trace amounts of zinc white (ZnO) in some cases. It is notable that neither Ca nor Ba is detected in the coral-red areas. This implies that these pastels

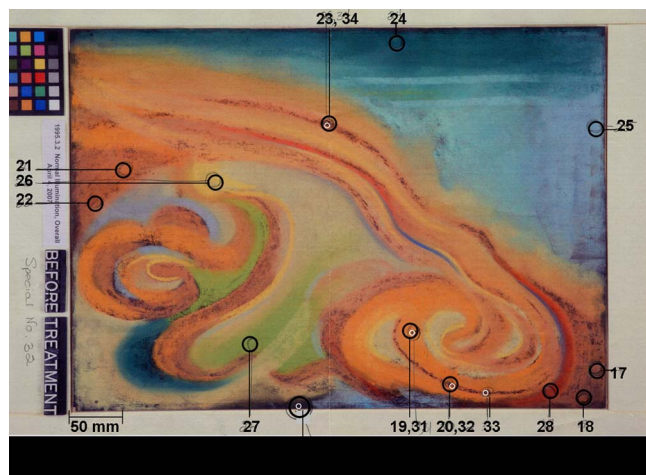


Figure 3. (Color online) Areas of analysis.

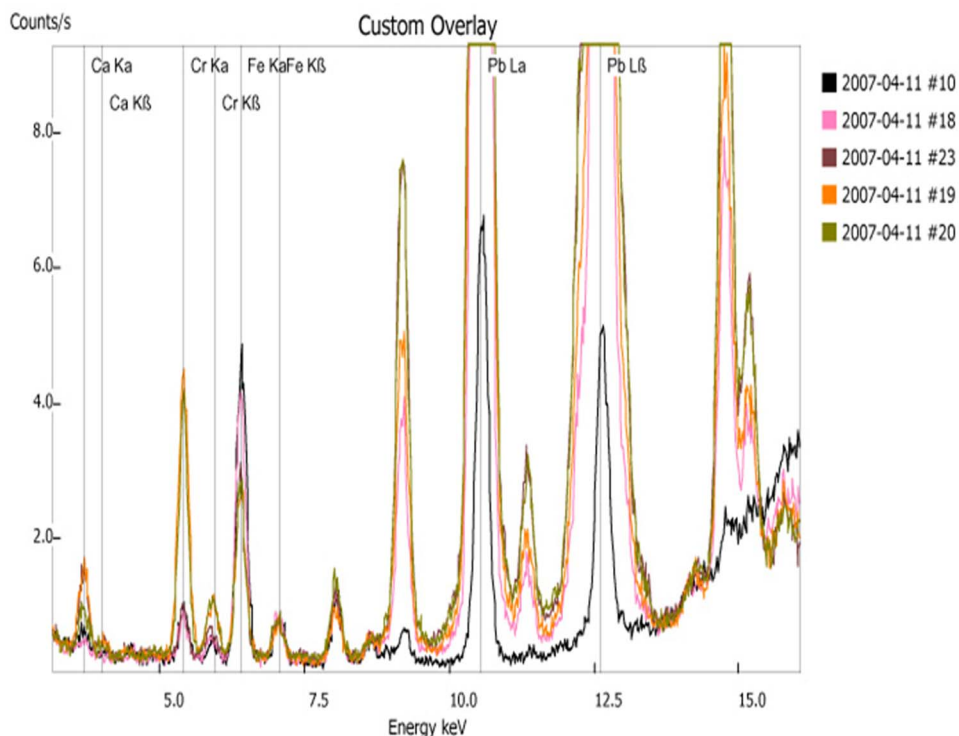


Figure 4. (Color online) Details of XRF spectra of various orange and red areas (colored readings 18, 19, 20, and 23) overlaid with spectrum of an area of mostly unpigmented black paper and support (black, reading 10).

may consist of a clay base plus pigments and fillers, including red lead, lead monoxide, lead whites and/or talc (hydrated magnesium silicate).

Analysis of the darker blue-green pastel (Table I) clearly demonstrates the presence of Ca, Cr, Cu, As, and Pb, as well as somewhat higher levels of Fe. These results tentatively suggest a mixture of chrome green (Pb, Cr, Fe) and emerald green (Cu, As), plus a calcium-based filler such as whiting or gypsum. It also is possible that viridian (hydrated chromium oxide) is present in this pastel color. Results for the yellow-green area are interesting. In addition to Cr and Pb, trace amounts of Sr and Ba are indicated. These results suggest

that the yellow-green pastel contains a mixture of chrome yellow, strontium yellow (SrCrO_4), barium sulfate (barite) and/or barium yellow (BaCrO_4), and an undetected blue pigment.

Analysis of the light blue pastel (Table I) does not reveal notable levels of any element that can be ascribed to the pastel layer except for Ca. Because the presence of both Fe and Cu are variable in the background materials, they have a fairly high limit of detection; the detection of Fe and Cu at comparable levels in the blue pigment may therefore be assigned to the paper itself. Detection of Pb and Cr is also

TABLE II. Possible lead-, chromium-, and Ca-based pigments (Gettens and Stout, 1942).

Color	Common name	Composition
White or grey	Lead white (hydrocerussite)	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$
White	Lead carbonate (lead white)	PbCO_3
White	Basic lead sulfate	$\text{PbSO}_4 \cdot \text{PbO}$, typically used with ZnO
White	Lead sulfates	PbSO_4 (and variants)
Yellow	Massicot	PbO
Yellow-orange	Litharge	PbO
Red	Red lead (minium)	Pb_3O_4
Orange	Chrome orange	$\text{PbCrO}_4 \cdot \text{Pb}(\text{OH})_2$ or $\text{PbCrO}_4 \cdot \text{PbO}$
Yellow	Chrome yellow	PbCrO_4 and $\text{PbCrO}_4 \cdot \text{PbSO}_4$, usually with extenders
Yellow	Barium yellow	BaCrO_4
Yellow	Strontium yellow	SrCrO_4
Green	Chromium oxide	Cr_2O_3
Blue-green	Viridian	$\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
Green	Chrome green	Chrome yellow + Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$)
White	Chalk or whiting	CaCO_3
White	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

comparable to that detected in the bare paper. Certain pigments can be eliminated from consideration, including cobalt, manganese and cerulean blues, so that the blue pastel colorants may possibly be synthetic ultramarine ($\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$) or an organic (carbon-based) blue, plus whiting or gypsum. As mentioned above, with the described analytical setup light elements such as those found in a carbon-based pigment or ultramarine either would not be detected or would have poor sensitivity, such as in the case of sulfur. Prussian blue (ferric ferrocyanide) cannot be ruled out as a component of the blue pigment or as an additive in the yellow-green pastel, although it is expected that the pastel layers are thick enough in most areas of the drawing that iron- or copper-based pigments should show clear differentiation from trace levels of these elements in the backing materials.

Results in Table I further indicate that inter-elemental ratios, e.g., those taken from the simple mathematical quotient of XRF values for Pb and Cr (marked Pb:Cr), may be used to locate areas that possibly contain red lead, as distinct from lead chromate pigments. The Pb:Cr ratios in Table I are shown as a range, the latter of which is determined from the experimental RSD of Pb:Cr ratios in the black paper and support materials. Note that the RSD of this ratio is less than the RSD of values for individual elements. Validity of numerical elemental ratios is based on several assumptions, including (1) linearity of calibration factors for each element; (2) homogeneity of the area of examination; and (3) fair uniformity in the matrix across the surface of the drawing. While homogeneity may be compromised by layering and/or blending of pigments in the pastels, the measured ratios of Pb:Cr, which are particular to the instrumentation and setup, appear to differentiate red or orange lead-based pastels from the lead chromate-based pastels. This is significant due to the increased stability, in the absence of sulfur in the environment, of basic orange and red lead chromates (Gettens and Stout, 1942; Kühn and Curran, 1986). As discussed above, the orange area (reading 19) contains Ca as well as Cr and Pb, suggesting identification with whiting or gypsum and chrome orange (lead chromate). Here the measured Pb:Cr ratio is 1.1 to 1.4. Because this technique is not quantitative, the elemental ratio cannot be correlated with the known stoichiometry of pure chrome orange, which is $\text{PbCrO}_4 \cdot \text{Pb(OH)}_2$. In other words, the ratio more likely reflects a characteristic orange pastel composition in this analysis. Results for the yellow and yellow-green areas (readings 26, 27) suggest that the pastels contain chrome yellow (PbCrO_4); here the Pb:Cr ratio is similar to that in the orange area. While the analysis of reference pigments could clarify this relationship somewhat, elemental ratios found in the artwork may also reflect the presence of common contaminants or additives, such other lead-rich pigments or a PbSO_4 component, since different shades of chrome pigments are achieved by varying this additive (Kühn and Curran, 1986).

Despite limitations in interpretation of the XRF-derived Pb:Cr ratios, there appears to be consistent separation of the measured Pb:Cr ratios in differently colored areas. For example, compared to the orange areas (reading 19), spots with uneven, dark mottling (readings 17 and 18, 21 and 22) show dramatically increased Pb:Cr ratios, between 6.6 and 22. The

breadth of this range is likely to arise from differences in application thickness and detection of Cr at background levels in thinly applied coral-red pastel. The Pb:Cr ratios in this case support the appearance that the same lead-based pastel is used in coral-red areas of the drawing, all of which exhibit the uneven, dark mottling. Pb:Cr ratios also appear revealing in blended or layered coral-red and orange areas. For example, in dark, mottled, coral red stripes over orange areas (readings 20, 23), the Pb:Cr ratios are somewhat lower than coral-red areas (readings 17, 18, 21,22), which appear to be a single layer of color. Perhaps more significantly, the Pb:Cr ratios in dark, mottled areas, particularly the stripe in reading 23, suggest the presence of red lead, possibly mixed with other lead oxides, carbonates and/or sulfates.

Pb:Cr ratios obtained using the small-spot window plate on the XRF instrument further suggest red lead in the dark, mottled stripes and areas of the drawing. As shown in Table I, peak intensities are about 1/3 of those measured without the faceplate. Comparison of Pb:Cr ratios in orange and coral-red areas with and without the small aperture confirms that the ratios are similar (readings 19 vs. 31, and readings 32 to 33 vs. 20). This indicates that use of the small window, and the additional distance to the detector, does not compromise detection of the pigment elements. In reading 34, i.e., an area limited to a heavily mottled stripe, only Pb is detected in significant quantities. Although not definitive, the Pb:Cr ratios thus suggest a link between the dark mottling and high amounts of Pb, and thus converted red lead oxide pigment.

One red area appears different both in color and in Pb:Cr characterization. This is the brighter, more intense red area examined in reading 28, which does not exhibit dark mottling. Here the ratio is 2.8 to 3.6, with overall lower intensity of Pb, Cr at background levels, plus a small amount of Ba (and possibly Ti). While this evidence might suggest a thin application of red lead, the appearance of this red and its different elemental signature suggest rather that it is an admixture of red lead with an undetected red colorant and/or other additive. This points out that Pb:Cr ratios by themselves are not indicative of composition.

Following XRF analysis, one tiny sample was removed from the dark surface in a coral-red area for μXRD analysis. Sampling was considered warranted based on the interpretation of the XRF results and necessary, at this point, to further understand the condition of the artwork. The sample, about 30 microns in diameter, is shown in Figure 5 mounted on a glass fiber (~ 0.1 mm diameter) in the instrument. The resulting XRD pattern, obtained with a 0.1 mm collimator, is shown in Figure 6. The large hump in the raw pattern (above) is produced mainly by amorphous scattering from the glass fiber and adhesive and may be responsible for obscuring small peaks in this region. The background-corrected pattern (below) provides an excellent match with minium, the natural version of red lead (Pb_3O_4 , PDF #01-071-0561); in fact, the experimental pattern accounts for all the peaks in the reference pattern for this mineral, shown by the vertical bars. Thus, μXRD results confirm XRF results, indicating that the dark pigment particles in the non-uniformly mottled areas are associated with red lead (Pb_3O_4 , properly written as $2\text{Pb}_2\text{PbO}_4$).

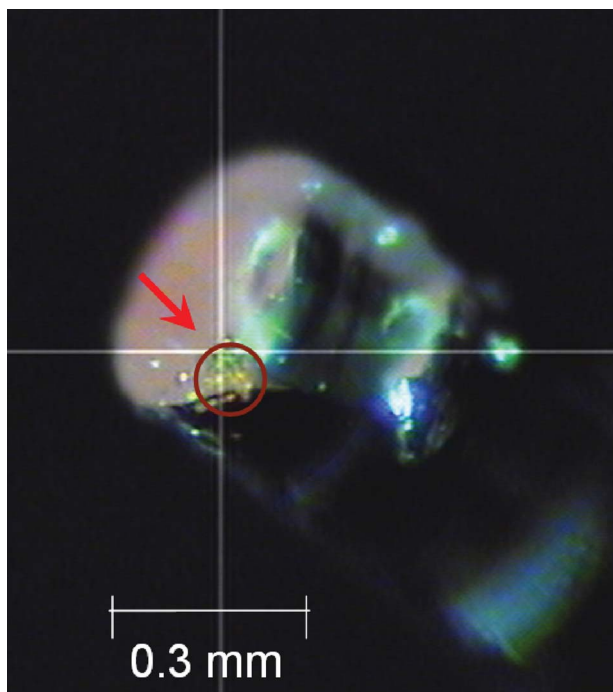


Figure 5. (Color online) Particle from mottled area mounted onto a glass fiber.

Red lead is well known to be subject to darkening as mentioned above. The brown or black products that may form from the pigment depend on environmental conditions, including exposure to nitric acid, acetic acid, hydrogen sulfide, or simply to air, humidity and light (Gettens and Stout, 1942; Fitzhugh, 1986). Except for the sulfide product, darkening is thought to arise primarily from the formation of brown-black lead dioxide (Gettens and Stout, 1942;

Fitzhugh, 1986). Darkening has also been ascribed to formation of a mixture of lead monoxide and metallic lead, and the tendency of a red lead pigment to darken has been related to the amount of free PbO (lead monoxide) that is naturally present in the pigment, as well as the composition and microstructural features of the red lead grains (Kuchitsu, 1997; Saunders *et al.*, 2002; Aze *et al.*, 2002). In this context, it is worth noting that the experimental XRD pattern also is consistent with identification of the minor or poorly crystallized phase scrutinyite (PbO_2 , PDF #01-072-2440 or 00-045-1416), which is closely associated with plattnerite, a more commonly referenced lead dioxide alteration product of red lead (Fitzhugh, 1986). However, because the most intense peak in the XRD pattern of scrutinyite is coincident with a peak in the pattern of minium, and because plattnerite is not identified, it is difficult to ascertain the presence of the lead dioxide. In addition, it is noted that the presence of some PbO in the form of litharge (PDF #00-005-0561) is consistent as a trace phase in the experimental pattern (Gettens and Stout, 1942; Fitzhugh, 1986); no lead sulfide, lead carbonate or lead sulfates are identified in the pattern.

Despite the lack of evidence for the presence of lead dioxide, which is a well-known analytical problem, the virtually non-invasive, rapid XRF and μXRD analysis of the Georgia O'Keeffe pastel supports visual observations that the uneven, dark brown mottling on the surface of coral-red areas is likely to be converted red lead. Most importantly, analysis supports suspicions gathered from visual observations that the drawing has changed from its original appearance. The detection of red lead in unmottled areas therefore has implications for the future care of the drawing, including protection from environments in which red lead is known to be unstable, including light, high humidity, and atmospheres containing sulfur and other pollutants. The preliminary XRF

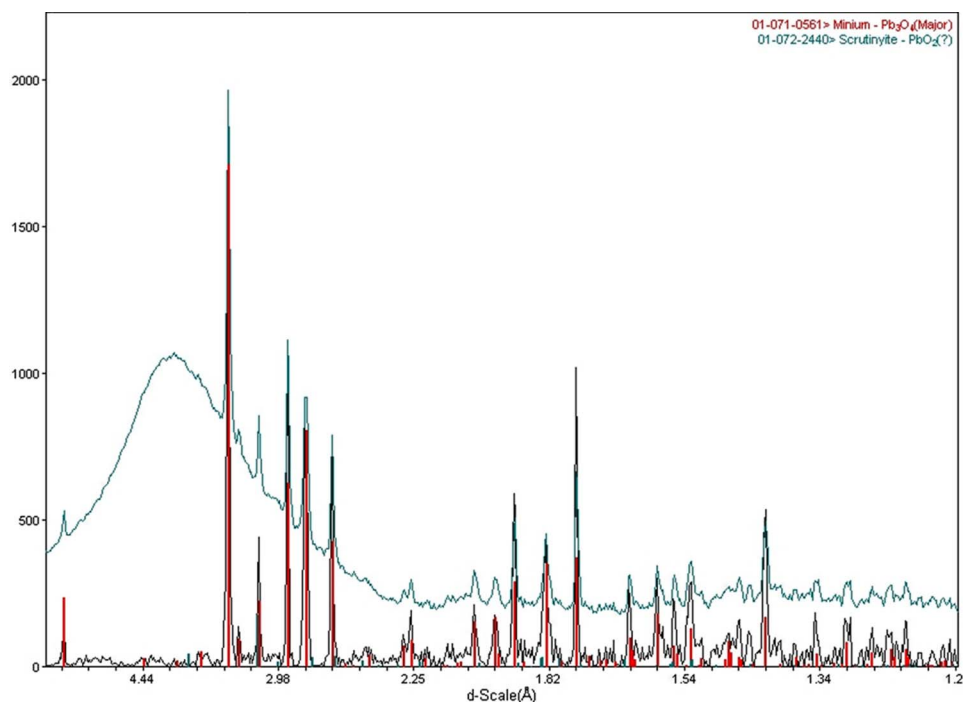


Figure 6. (Color online) μXRD pattern, with and without background subtraction, obtained with 0.1 mm collimator from brownish particle in dark mottling.

survey of representative areas of other pastel pigments in the drawing suggests numerous pastel compositions and invites further study of O’Keeffe’s materials.

IV. CONCLUSIONS

Preliminary XRF and μ XRD analyses of the Georgia O’Keeffe pastel, *Special No. 32*, provide evidence for the existence of red lead, an unstable pigment, in coral-red areas of the drawing. This supports conservators’ suspicions that dark brown, uneven mottling in these areas may be associated with red lead pigment, which is well known to be prone to alteration and darkening. Conversion of red lead pigments may occur over time in a nonuniform manner from exposure to air, humidity and light, as is consistent with the appearance of this pastel drawing. The evidence consists firstly of XRF analysis of relative Pb:Cr ratios, which allows lead-based pigment composition in red areas to be differentiated from more stable lead chromate-based pigments in orange and yellow areas of the drawing. Secondly, XRD analysis of one microsample removed from a dark mottled area provides definitive evidence for the presence of red lead oxide, which is identical to the mineral minium. Neither the expected alteration product, lead dioxide, nor lead monoxide is positively identified, although they could be present as trace phases in the XRD experimental results. On the other hand, lead sulfide, lead carbonate, and lead sulphates do not appear consistent with the XRD patterns. Therefore, results of the preliminary analysis suggest that the brown mottling may be converted red lead, although discoloration from an unknown mold or undetected pollutant products cannot be ruled out. The detection of red lead in perceived unchanged areas has further implications for the future care and protection of the drawing from harmful environments.

Additional pigments and fillers indicated by XRF analysis based on color and elemental composition include calcium-based pigments such as whiting or gypsum, stron-

tium yellow, and chromium-based greens such as chrome green and probably emerald green. Blue pigments cannot be proposed with confidence due to limitations of this instrument in detecting light elements, but some blue pigments can be eliminated, including cobalt, manganese, and cerulean blues. Due to fairly high levels of Fe and varying trace levels of Cu in the paper support materials, iron- or copper-containing pigments cannot be ruled out in some cases; however, results suggest that the blue pigments, used either alone or as admixtures in other pigments, are likely to be synthetic ultramarine or carbon-based. The findings of this preliminary study of O’Keeffe’s early pastel drawing warrant and invite further investigation of materials used by this important artist.

- Aze, S., Vallet, J.-M., and Grauby, O. (2002). “Chromatic degradation processes of red lead pigment,” *ICOM Committee for Conservation preprints, 13th Triennial Meeting, Rio de Janeiro* (ICOM, London), pp. 455–463.
- Barilleaux, R. P. and Whitaker Peters, S. (2006). *Georgia O’Keeffe, Color and Conservation* (Mississippi Museum of Art/Penn State University Press, Jackson, Mississippi).
- Fitzhugh, E. W. (1986). *Artists’ Pigments: A Handbook of their History and Characteristics*, edited by Feller, R. L. (National Gallery of Art, Washington, D.C.), pp. 109–140.
- Gettens, R. J. and Stout, G. L. (1942). *Painting Materials: A Short Encyclopedia* (Dover Publications, New York, NY).
- Kuchitsu, N. (1997). “Mineralogical consideration on discoloration of red lead,” *Hozon-kagaku* **36**, 58–66.
- Kühn, H. and Curran, M. (1986). *Artists’ Pigments. A Handbook of their History and Characteristics*, edited by Feller, R. L. (National Gallery of Art, Washington, D.C.), pp. 187–200.
- O’Keeffe, G. (1976). *A Studio Book* (Viking Press, New York).
- Saunders, D., Spring, M., and Higgitt, C. (2002). “Colour change in red lead-containing paint films,” *ICOM Committee for Conservation preprints, 13th Triennial Meeting, Rio de Janeiro* (ICOM, London), pp. 455–463.
- Walsh, J. C. (2000). *O’Keeffe on Paper*, edited by Fine, R. E., Lynes, B. B., Glassman, E., and Walsh, J. C. (National Gallery of Art, Washington, D.C.), pp. 57–80.