Conservation Studies of Heritage Materials Focus Topic
Room: 313 - Session CS-ThM

Conservation Studies of Heritage Materials
Moderator: David S. McPhail, Imperial College London, UK, Naoko Sano, NEXUS, Newcastle University, UK

8:00am **CS-ThM1 Complementary Ion and Electron Microscopy Studies for Heritage Conservation**, ***Barbara Shollock***, Imperial College, London **INVITED**

Heritage conservation is an ever-growing discipline, fuelled by factors such as environmental pollution, and the issues surrounding conservation are not always clear. Defining the conservator's needs and the information required to address them can stimulate scientists to apply analytical techniques to new and unconventional challenges.

In this presentation, we will review some of the key issues faced in heritage conservation and the boundaries imposed by the ethics of conservation. Understanding these ethical considerations can guide the dialogue between conservator and analytical scientist to form a research approach that can satisfy both the scientific questions and the ethics of conservation. The application of electron and ion beam techniques will be considered in terms of conservation studies, and case studies will be used to illustrate the advantages and limitations of these techniques.

8:40am **CS-ThM3 Conservation Science at the National Archives: Science in Support of the Preservation of the Records of the Federal Government**, ***Jennifer Herrmann***, National Archives and Records Administration **INVITED**

The National Archives and Records Administration (NARA) is the repository of the permanently valuable records of the United States Government, including the Charters of Freedom, and a wide range of records that document the working of federal agencies and the rights and privileges of citizens. These materials range from Civil War-era pension files to immigration records and from homestead records to logs of Navy ships. NARA has the mission of preserving all of these records for future generations to access. Conservators and conservation scientists work together at NARA to support this dual mission of preservation and access. The Research and Testing Lab (R&T) works closely with the exhibits program and facilities across NARA to ensure that the products and materials used to display and store records will not contribute to their deterioration. In order to answer these questions as well as help preserve individual NARA holdings, R&T uses many standard analytical techniques. FTIR is the first non-destructive analytical technique we use to identify unknowns in the laboratory, including deteriorating films which could be cellulose nitrate or acetate. If FTIR cannot give us enough information, we often rely on the non-destructive XRF and also SPME-GC-MS, which is useful for monitoring off-gassing of records or materials used around records. For example, XRF has been useful in determining if a forgery of a date on a Lincoln Pardon could be reversed safely. This technique has also been used to study platinum photographs of different known recipes and processing conditions to see if the ghost image phenomenon that often occurs with historic platinum images could be better understood. DART MS, XPS, SEM, and FTIR have all been attempted for this photographic research project, as well as accelerated aging tests, microfading experiments, and fiber and paper analysis. The most visible R&T project that supports the dual mission has been the re-encasement and monitoring of the Charters of Freedom (the Declaration of Independence, Constitution, and Bill of Rights) and the Rubenstein Magna Carta. Instrumentation to monitor leaks and oxygen content, as well as air tight connections and plumbing are required in order to determine the conditions within these high tech encasements. As can be seen, the field of conservation science has many great tools from analytical chemistry to help preserve our important records and art.

9:20am **CS-ThM5 Advanced Spectroscopy for Traditional and Modern Heritage Materials**, ***Fenella France***, Library of Congress **INVITED**

The conservation of art and cultural heritage objects requires advances in non-invasive, non-destructive analytical techniques to characterize cultural heritage materials, including substrates (paper, parchment) and media (inks, pigments, colorants). Spectral imaging systems developed for astronomical imaging and remote sensing have been adapted and customized for libraries and museums. T he Library of Congress LC) is using hyperspectral imaging to support preservation of cultural heritage materials with a range of capabilities. With an integrated 39 MegaPixel camera and LED illumination panels to capture high-resolution images in ultraviolet, visible and near infrared spectrum, researchers can create a spectral map of a manuscript or object that can be linked with other non-invasive analyses. Hyperspectral imaging captures non-visible and visible information in registered high resolution digital images, with further capabilities including identification of materials through spectral response, and monitoring of degradation or changes due to environmental conditions and conservation treatments.

The Library utilizes this system to address challenges associated with characterizing manuscript materials, including: early Portolan (nautical) Charts, L'Enfant Plan of Washington D.C., Jefferson's handwritten draft of the Declaration of Independence, and Herblock political cartoons. It has been used to illustrate non-invasive characterization of materials, deterioration, and detection of non-visible changes due to exhibition and storage. Assessing the long-term effects of treatments on collection materials is a growing area of research at LC. The conservation of a 1513 hand-colored Ptolemy Geographia posed interesting challenges in terms of the treatment of select maps in poor condition, due to the presence of verdigris, and a later restoration treatment. Analysis for treatment to stabilize these seven maps included a combination of quantitative X-ray fluorescence, spectral imaging, and Raman spectroscopy. Development of reference databases and integration of data from other analytical techniques allows a more complete mapping of collection materials. Linking this mapping data with other spectroscopic techniques allows for more data from single-point analyses, and provides a greater depth of information. Scriptospatial mapping of data enables direct sharing and visualization of data, with capture of standardized instrumentation parameters and object metadata. The scriptospatial interface enhances interaction between a range of professions, allowing multidisciplinary collaboration for integration of preservation, scientific and cultural information.

11:00am **CS-ThM10 Building a Case for the Future: Design and Construction of an Encasement and Monitoring System to Protect the US Bill of Rights for the Next 100 Years**, ***Jacob Ricker***, *J.H. Hendricks, N.J. Brandenberg, G.F. Strouse*, NIST

NIST has been working to revolutionize the way we monitor and protect our historical documents by designing and constructing the next generation of document encasement. While the encasement "operates" at atmospheric pressure, to protect important documents it must perform like an ultra-high vacuum (UHV) system in terms of purity requirements, outgassing rate, permeation and leak rates. It has long been known that documents degrade overtime, but archivists and historians have been working to slow this process down through limiting exposure to damaging agents (oxygen, dust, excess humidity, mold, etc.) while still allowing visibility of the document for the public. NIST's design is innovative due to its ability to seal the document in a humidified Argon environment using a custom designed chamber with a double o-ring seal to reduce oxygen permeation through the second viton o-ring seal. This system required several innovative solutions to reduce differential pressure on the display glass and to improve and leak test the o-ring sealing.

The Encasement also features a custom designed sensor suite to monitor the status of the internal environment. The NIST design monitors and wirelessly transmits differential pressure, barometric pressure, temperature, humidity, oxygen content, and GPS location. All of the sensors were designed to be vacuum compatible with metal seals to ensure integrity of the encasement. The talk will feature discussions on oxygen permeation rates and measurement along with monitoring sensor performance.

11:20am **CS-ThM11 Parylene Coating for Paper/Book Strengthening**, ***Lei Pei***, *M. Pollei, S. Jordan-Mowery, J. Baty*, Johns Hopkins University

Parylene, the generic name for a class of polymers with the base monomer para-xylylene, has been used to strengthen papers via chemical vapor deposition. The deposited monomers polymerize *in situ*, forming a thin conformal coating that adds strength. Compared to other paper strengthening techniques, such as lining and paper splitting, which are mostly based on individual sheet treatment, parylene coating has the unique ability to treat all the pages of a book simultaneously. Parylene as a paper strengthening technique, however, has had limited recognition within the conservation community since the pioneering research was completed in the 1990s. The major conservation concerns centered at that time on how well Parylene coatings improve the durability of brittle papers and how well the treatment would enable future conservation intervention. One of the earliest criticisms revolved around reversibility of the treatment. No one would reasonably argue that it is desirable to return an embrittled book back to a state of embrittlement, which prevents its being used and/or its ability to accept other traditional repair techniques. Given that we cannot readily correct depolymerization of cellulose at this stage, the real value in parylene is the extent to which it will impart adequate material strength and be receptive to the range of traditional repair techniques as would be used on a non-embrittled book, and all other things being equal, how long the strength will last.

To answer these concerns and highlight the potential of this paper strengthening technique, we present the results obtained from mechanical testing and the behavior of parylene coated paper in standard paper conservation treatments. These results show that Parylene-treated groundwood pulp book papers from 1951 reveal many of the characteristics of a new wood pulp paper, in term of rattle, turn radius, and general tactile experience. The treated paper has over 30% improvement in tear resistance and more than three times higher folding endurance (based on a log scale of the number of double folds via an MIT folding endurance tester). Additionally, parylene treated paper is receptive to conventional paper conservation treatments such as traditional wheat starch paste and Japanese paper tear mending, guarding, washing and resizing. We will also discuss moisture content measurements to clarify concerns about the vacuum treatment involved in the Parylene coating process and its effect upon the treated paper.

11:40am **CS-ThM12 Iron Gall Ink Chemistry and Corrosion of Historical Documents Probed by XPS and Raman**, ***Karen Gaskell**, A.A. Ponce, S. Gibbons, P. Zavalij,* University of Maryland, College Park*, L. Brostoff,* Library of Congress*, B. Eichhorn*, University of Maryland, College Park

Iron gall inks were the major writing medium from the middle ages through the 19th Century in the Middle East and Europe, and are present in hundreds of thousands of important cultural heritage objects worldwide, including books, manuscripts and artistic drawings. Iron gall ink depending on its preparation is well known for its potentially corrosive effect on paper or other writing medium, over time, changes in temperature and humidity can accelerate this degradation resulting in the worst case, complete loss of documents. The major ingredients of ion gall ink are iron salts, most often iron sulfate, tannic acids derived from vegetable sources such as gall nuts and gum arabic used as a binder. In this study, X- Ray Photoelectron Spectroscopy (XPS), is used to probe the chemistry of iron gall ink and to study the effect of common preservation techniques such as deacidification and phytate treatment. Despite much research in this area the chemistry of iron gall ink is still poorly understood, including the structure of the complex itself, resulting from the reaction between iron sulfate and gallic acid. The two most widely accepted structures in literature have been proposed by Krekel and Wunderlich, these structures will be discussed and compared to XPS, Raman, FTIR and X-ray crystallography data obtained from model compounds.

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Conservation Studies of Heritage Materials 2
Moderator: H. Frederick Dylla, American Institute of Physics, Robert Opila, University of Delaware

2:20pm **CS-ThA1 A Conservator's Perspective of Technical Studies and Scientific Analysis**, ***Patricia Favero***, The Phillips Collection **INVITED**

The nature of technical studies is necessarily interdisciplinary as they address various questions about works of art and artifacts: What materials did the artist use ; how did he use his materials; and most importantly, what is the significance of this information for a greater understanding of the artist and his work? What is learned in technical studies often both augments art historical research and informs conservation treatment decisions.Collaboration between conservators, scientists, and art scholars is becoming ever more common in the study of works of art. Results of in-depth studies are now featured in exhibitions and scholarly publications, and their importance is increasingly recognized within larger art historical studies of an artist's oeuvre.

In this light, this presentation will consider two recent technical studies carried out at The Phillips Collection in Washington, D.C. The first, a study of a group of Georges Braque's mid-career paintings, was conducted in collaboration with conservation scientists from Harvard Art Museums and curators at the Phillips and the Kemper Art Museum in St. Louis. The results of the study were featured in the exhibition *Georges Braque and the Cubist Still Life, 1928-1945* and in the related publication. The second study focuses on one painting, *The Blue Room* (1901), an early Blue Period picture by Pablo Picasso in the collection at the Phillips. Ongoing research of this picture is being conducted in collaboration with independent Picasso scholars and scientists from the Winterthur Museum in Delaware, Cornell University, and the National Gallery of Art.

Both studies began in the conservation studio with the conservator carefully examining each painting in good light and under magnification, considering each artist's technique and how it may have influenced their material choices. Other examination techniques, such as UV-induced fluorescence, infrared imaging, and x-radiography were also employed.

In both studies, paint samples were taken and analyzed to positively identify the artists' materials and understand them in context. In the Braque study, the increasingly wide-spread use by conservators of portable x-ray fluorescence (pXRF) spectroscopy allowed for comparative pigment analysis of eight paintings from five different collections. For the Picasso, three non-invasive techniques—reflectance imaging spectroscopy, fiber optic reflectance spectroscopy (FORS), and XRF intensity mapping—were used.

The presentation will consider the collaborative nature of both studies and evaluate what made them successful in addition to discussing the process and outcome of each project from the conservator's perspective.

3:00pm **CS-ThA3 State of the Art: Probing Complexity in Paint**, ***Francesca Casadio***, *F. Pozzi, L. Chang,* The Art Institute of Chicago, *D. Kurouski, S. Zaleski, N.C. Shah, R.P. Van Duyne,* Northwestern University, *V. Rose*, Argonne National Laboratory **INVITED**

In recent years, the scientific analysis of painted surfaces has made a giant leap forward. At the same time as innovative standoff macro-scale imaging modalities have been developed to deliver elemental mapping (using macro X-ray fluorescence spectroscopy) and molecular imaging (with Ultra-Violet/ Visible, Near Infrared, Mid-Infrared reflectance, fluorescence, and Raman imaging), our ability to probe local paint chemistries and mechanical properties at the nanoscale has grown exponentially. These recent developments have fundamentally changed the way conservators, curators and conservation scientists approach the study of works of art, leading to cutting-edge research on pigment degradation phenomena and enabling us to retrieve otherwise lost information on altered colors or hidden compositions that make up the original aspect of masterpieces.

This talk will present recent research employing high resolution nanoprobe synchrotron X-ray fluorescence (XRF) mapping of metallic impurities with 30 nm resolution in single grains of zinc oxide pigments used in early 20th century paints formulated for artists and other commercial uses and widely employed by Pablo Picasso (1881-1973). Such highly detailed chemical characterization of paints at the nanoscale opens the path to a better understanding of their historical fabrication and chemical reactivity.

For the characterization of organic molecules used in paintings Surface-Enhanced Raman Spectroscopy (SERS) has recently been developed into a robust, reliable and highly sensitive technique to detect and unambiguously identify minute quantities of organic colorants. SERS has seen the field of cultural heritage become one of its foremost research and application areas, resulting in improved analytical protocols applicable to several other fields such as pharmaceuticals and forensic analysis. In particular, our efforts to develop methods to identify more than one colorant on a single sample using combined Thin Layer Chromatography / SERS and microfluidics SERS approaches will be discussed. Pushing the envelope of in-situ SERS analysis, first results on the use of Tip-Enhanced Raman spectroscopy (TERS) for the high spatially resolved, highly sensitive and non-invasive investigation of dyes used on paper supports will be discussed and preliminary results presented. This first demonstration of TERS spectral acquisition directly on a paper substrate confirms the analytical potential of TERS to identify organic colorants in artworks with high sensitivity, high spatial resolution, and minimal invasiveness opening the way to future developments for the nano-scale mapping of organic constituents of works of art.

4:00pm **CS-ThA6 The Degradation Mechanisms of Cadmium Pigments in Works by Henri Matisse, Edward Munch, and Their Contemporaries**, ***Jennifer Mass***, Winterthur Museum, *E. Pouyet,* ESRF, France, *F. Meirer,* Utrecht University, Netherlands, *M. Cotte,* ESRF, France, *A. Mehta*, Stanford Synchrotron Radiation Lightsource **INVITED**

Cadmium carbonate ($CdCO_3$) has for several years been identified in the altered cadmium yellow (CdS) paints found Impressionist, early modernist, and post-Impressionist works. When it is concentrated at the surface of the painting, $CdCO_3$ appears to be a result of the photo-alteration of CdS, likely through a $CdSO_4$-containing phase. However, in other cases $CdCO_3$ is distributed throughout the paint layer. This is significant because $CdCO_3$ is highly insoluble (K_{sp} of 1.0×10^{-12}), and if it were formed solely as a result of photo-alteration it would not be expected to migrate away from the painting's surface. In cadmium yellow paints in works such as Edvard Munch's c. 1910 *The Scream* (The Munch Museum, Oslo), Plahter et al. have recently proposed that $CdCO_3$ is present because this compound was used in the indirect wet process synthesis of CdS (through, for example, the reaction of $CdCO_3$ and Na_2S). This would mean that the $CdCO_3$ is a residual starting reagent rather than a photo-alteration product. Such an interpretation is supported by the identification of $CdCO_3$ in the unaltered cadmium yellow paints of early modernist works such as Pablo Picasso's *The Blue Room* (The Phillips Collection, 1901) and Henri Matisse's *Flower Piece* (The Barnes Foundation, 1906).

To address this question of $CdCO_3$'s role, a flake of apparently nondegraded cadmium yellow paint was removed from Henri Matisse's *Flower Piece* so that the distribution of $CdCO_3$ could be studied, both as a function of depth in the paint layer and in individual pigment particles.

X-Ray microspectroscopy and microdiffraction were respectively carried out at ESRF ID21 and Petra III, supplemented by light microscopy, backscattered electron microscopy with X-ray microanalysis, and Fourier transform infrared spectroscopy. This presentation will focus on results from X-ray microspectroscopy: μ-X-ray fluorescence (XRF scanning) allowed precise mapping of local elemental distribution, and Full Field X-ray Near-Edge Absorption Structure (FF-XANES) for mapping the chemical speciation using the Cd-L_3 and S-K edges.

FF-XANES imaging of a 15 micrometer thin section at CdL3-edge revealed the presence of three Cd-based phases: CdS, $CdSO_4$, and $CdCO_3$. The $CdSO_4$ was concentrated on only one surface of the sample, suggesting its role as a photo-alteration product. Cadmium carbonate was found to comprise the bulk of the individual pigment particles, suggesting that it is a synthesis starting reagent. CdS was found to be concentrated on the surface of these $CdCO_3$ particles. $CdSO_4$ could also be observed to surround some of the $CdCO_3$ particles, suggesting the beginnings of photo-oxidation of the thin CdS coating.

4:40pm **CS-ThA8 Characterisation of Modern Watercolour Paints using XPS, HIM, ToF-SIMS and Principal Component Analysis Techniques**, ***Naoko Sano***, *P.J. Cumpson,* NEXUS, Newcastle University, UK, *E. Cwiertnia, B.W. Singer*, Northumbria University, UK

To conserve old masterpieces is, of course, critical but modern fine/contemporary arts also need preservation as future cultural heritage. Therefore, nowadays many modern artistic works have been studied using scientific techniques to preserve their condition. As with easel oil paintings, modern watercolour paintings represent some of our great cultural heritage from artists such as J.M.W. Turner, Paul Klee or Georgia O'Keeffe. For conservation scientists, the characterization of the binder and pigments in modern paintings is especially important yet problematic in terms of conservation treatments and environmental conditions for display or storage.

In investigation of modern paintings it is often critical to identify the origin of organic molecules in the paintings, since modern paintings have commonly used artists' paints containing synthetic organic pigments due to their greater selection of colours. In addition, in terms of watercolour paints, commonly used binders such as gum arabic, gum tragacanth or honey are not straight forward to identify due to their organic content.

To contribute to a better understanding of modern artists' paints for conservation, this study presents a scientific investigation into commercially prepared watercolour cakes and binders from the 20th century. Analysis focuses on the characterisation of commercial watercolour paints (red colour) that may contain quinacridone and/or saccharide materials, and shows different surface chemistries of the paint between powder and cake types. Moreover, we attempt the identification of the synthetic organic pigments and the plant gum binder from the watercolour paint using surface analysis techniques and principal component analysis (PCA). Especially, we feel surface analysis techniques such as x-ray photoelectron spectroscopy (XPS), helium ion microscopy (HIM) and time of flight secondary ion mass spectrometer (ToF-SIMS) are powerful techniques for cultural heritage preservation.

5:00pm **CS-ThA9 The Analysis of Egg-Oil Binding Media by Time-of-Flight Secondary Ion Mass Spectrometry**, ***Zachary Voras***, *K. DeGhetaldi, D. Clark,* University of Delaware, *J.L. Mass,* Winterthur Museum, *T.P. Beebe, Jr.*, University of Delaware

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is quickly becoming a critical tool in the field of art conservation. This technique provides high-resolution spatial maps of both inorganic and organic components located across and below the surface of a paint cross-section or other art object. With recent advancements in surface analysis, ToF-SIMS can now be used to identify specific amino acids present in protein-containing materials as well as fatty acids present in drying oils. For example, the detection of the ion fragment associated with the amino acid hydroxyproline can be used to confirm the use of animal glue in a paint sample. As an analytical technique, ToF-SIMS avoids the need for derivatization/silylation reagents, with no interference by the presence of reactive or unreactive pigments. Furthermore, the layered systems that are often encountered in historical paint samples remain intact throughout the analytical procedure. This allows for the co-localization of organic and inorganic species in specific layers (e.g., eggyolk paint atop a glue ground). Because of this ability to localize the analytical signal to approximately 1µm or less, the mass spectral information can be used to produce mass-resolved and spatially resolved images which can be correlated to previous studies of the same preserved samples. In this study, ToF-SIMS was used to analyze paint cross-sections obtained from various time periods. A focus will be on works by Italian artists such as Raphael (from the Walters Art Museum) with additional mentions of a painting by Matisse (from the Barnes Foundation) and Henry Ossawa Tanner (from the Smithsonian American Art Museum).

5:20pm **CS-ThA10 The Right Snuff? A Technical Study of Two Snuff Boxes from the Winterthur Museum Collection**, ***Marlene Yandrisevits***, Winterthur/ University of Delaware Program in Art Conservation, *J.L. Mass, C. O'Grady, C. Matsen,* Winterthur Museum Scientific Research and Analysis Laboratory, *E. Torok*, Winterthur/ University of Delaware Program in Art Conservation

The nasal inhalation of snuff tobacco stored in vanity boxes was a fashionable custom among the colonial European elite. From the late 18th to the early 19th century, small decorative enameled boxes were manufactured in England to supply a bourgeois demand for stylish, but less expensive, imitative snuff boxes. The utilization of traditional materials and techniques for later 19th/ early 20th century repair and revival fabrication of enameled boxes introduces a serious challenge in distinguishing the original from the copy or the heavily restored. This study examines two enameled boxes at the Winterthur Museum with the goal to contribute technical data to provenance and dating discussions. Ultraviolet-induced visible fluorescence surface examination, x-radiography, energy dispersive x-ray fluorescence spectroscopy, microRaman spectroscopy, cross-sectional microscopy with visible and UV illumination, scanning electron microscopy – energy dispersive x-ray spectroscopy/ back-scattered electron imaging, Fourier transform infrared spectroscopy, and gas chromatography – mass spectrometry were used to characterize the composition and stratigraphy of the materials comprising the boxes, followed by comparison to period materials and techniques reported in historical sources and to the findings of previous research. As characterized in this study, aluminosilicates were inferred as the enamel network forming agent combined with lead arsenate and tin oxide opacifiers and potash flux on both boxes, with soda flux additionally on one box. Enamel colorants were metal-based (including iron oxides in red, pink and purple overglazes; colloidal gold in pink and purple overglazes; cobalt oxides/ glass in blue and green overglazes; and Pb-Sb-Sn oxides in yellow and green overglazes). Findings suggest that, while significant titanium-containing restoration overpaint and synthetic coatings are present on both boxes, the enamel and mount materials of one box are consistent with the early production. The majority of materials on the other are also consistent with the early stage of enameled snuff box production in England, with the possible exceptions of chromium-based green enamels, iron oxide pink and purple enamels, and brass-based imitation gilding in localized areas which may represent an early restoration campaign. The materials identified on both boxes are consistent with the findings of previous analyses, excluding a yellow colorant identified in previous research as Naples yellow ($Pb(SbO_3)_2$/ $Pb_3(Sb_3O_4)_2$) now detected in this study and recharacterized as a related Pb-Sn-Sb triple oxide ($Pb_2(SnSb)O_6$), which may suggest further research towards a reliable dating scheme.

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Conservation Studies of Modern Heritage Materials 3
Moderator: Karen Gaskell, University of Maryland, College Park

9:00am **CS-FrM3 Faces from the Past: Microbeam Imaging and Analysis of Artifacts from ancient Mesoamerica**, ***Timothy Rose**, J.M. Walsh*, Smithsonian Institution **INVITED**

Working in the analytical laboratories in the Department of Mineral Sciences in the National Museum of Natural History provides plenty of challenging problems just involving geologic materials. Requests from other departments within the museum and elsewhere are growing as the understanding spreads to other disciplines of how our tools can be applied to an even wider variety of materials. Here we provide details about two recent and ongoing studies of cultural artifacts from ancient Mesoamerica. These studies were performed using a variable pressure field emission FEI NovaNanoSEM 600 outfitted with a ThermoFisher silicon drift detector energy dispersive x-ray spectrographic (EDS) analysis system. They were conducted on uncoated whole specimens or fragments and tiny samples removed from the surface or from deep recesses of the objects.

A large collection of spectacular artifacts was delivered to the museum with a request to provide information as to their authenticity. The collection included carved stone figurines and masks and ceramic pieces with various surface coatings. The objects were photographed, measured and placed into groups based on their apparent cultural affinity. Initial observations were made using optical microscopy with particular attention paid to tool marks. In the SEM, some whole artifacts stretched the limits of sample chamber size and geometry. Very few objects showed evidence of modern tools at either the optical or SEM scale. Chemical compositions of minerals in, and surface coatings on, stone artifacts were determined in order to characterize the rock type and other materials. Rock types included jadeitite, serpentinite and syenite. One group of several syenite masks were partially coated with a probable modern tan gypsum plaster. Several ceramic artifacts of unique design have complex surface decorations. A small cross-sectional multi-colored fragment of the coating on one object was studied in detail revealing five chemically distinct layers. We interpret this as original Olmec fresco paint. The results of the ongoing research indicate that the large majority of the artifacts are authentic pre-Columbian objects belonging to the Olmec, Maya, Teotihuacan and Mezcala civilizations which date from 1500BC to 600AD.

In the first comprehensive study of the iconic stone “masks” from Teotihuacan (100 BC to 600AD), we examined nearly 200 masks. Sampling of the artifacts was prohibited however silicone molds taken austensibly to study tool marks and carving methods also removed tiny grains from deep in drill holes. Study of these grains reveal that some are very likely residue from the original carving and polishing of the stone.

9:40am **CS-FrM5 Atomic Layer Deposited Diffusion Barriers on Non-ideal Silver and Bronze Cultural Heritage Objects**, ***Amy Marquardt***, University of Maryland, College Park, *E. Breitung*, E-Squared Art Conservation, *G. Gates, T. Drayman-Weisser*, The Walters Art Museum, *G.W. Rubloff, R.J. Phaneuf*, University of Maryland, College Park

Atomic layer deposited metal oxide diffusion barriers are investigated to better preserve cultural heritage metal objects in museum collections. Recently, the effectiveness and reversibility of ALD films to create diffusion barriers for non-ideal silver and copper alloy (bronze) cultural heritage objects has been studied. Previous results demonstrate the ability of ALD films to protect clean, uniform silver substrates at laest an order of magnitude longer than current silver protection methods. The capability of ALD films to protect surfaces representative of “real” museum metal objects was investigated. These objects included silver surfaces with pre-existing surface treatments, including polishing abrasives, chemical dips or organic lacquers, and patinated copper alloys surfaces with changing chemical composition and topography. The ability of ALD films to uniformly wet non-ideal, chemically varying metal surfaces was investigated under accelerated aging in corrosive gas and acidic aqueous environments. ALD films were structurally engineered through thin film modeling and reflectance spectroscopy measurements to minimize object appearance and color change on patinated or tarnished substrates. Film reversibility was also examined to determine an acceptable technique to remove the ALD films without significantly altering the underlying metal substrate, an important requirement for art conservation practices.

*Work supported by the NSF under SCIART collaborative research grant #DMR1041809

10:00am **CS-FrM6 Studies of the Effects of Cleaning Protocols on Museum-based Plastics using Advanced Surface Analysis Techniques**, ***Anna Fricker**, D.S. McPhail*, Imperial College London, UK, *B. Keneghan*, Victoria and Albert Museum, UK

The conservation of plastic artefacts is an area of interest for curators and conservators of cultural heritage. Many museums contain artefacts that are made wholly or partly from plastic and these objects may be present in collections ranging from jewellery to spacesuits. The stability of these polymeric materials is a concern for conservators, particularly as plastic objects can exhibit severe degradation which can occur suddenly and without warning.

The natural soiling of objects in museum collections results in a need to clean plastic artefacts for aesthetic reasons and to maintain artistic integrity. The contamination of plastics with particulate matter may also facilitate degradation. However, the act of cleaning may itself result in damage to an artefact, either immediately after treatment or at a later date. The issue is compounded by the many different types of plastics present in collections: a treatment for one object may be unsuitable for another.

This work examines the physical and chemical changes to the surface of poly (methyl methacrylate) (PMMA) that has been treated with a range of cleaning techniques commonly used in conservation. Methods include the application of solvents and surfactants to the substrate surface. Physical changes to the surface have been examined using microscopy techniques while secondary ion mass spectrometry (SIMS) has been used to characterise the chemical changes to the substrate. The efficacy of these cleaning methods to remove an artificial soil from the polymeric substrate is also discussed.

10:40am **CS-FrM8 Microchemical Characterization of 19th Century Nanotechnology-Daguerreotype Photographs**, ***Edward Vicenzi***, Smithsonian Institution **INVITED**

The daguerreotype photographic process represents the first practical form of photography and was presented to the scientific community in France in 1839. The technology spread rapidly and was widely used for roughly two decades. Image formation can be generalized in four steps: 1) sensitizing a silver-coated copper plate to halogen vapors, 2) exposing the sensitized plate to visible light within a camera, 3) development of an image after the plate is treated with heated mercury vapor, and finally 4) deposition of a gold gilding layer [1,2]. A effort is underway to evaluate several aspects of daguerreotypes including obtaining the composition of the nanoparticles that give rise to image contrast, the protective gilding layer, and corrosion products formed from exposure to atmospheric and other contaminants. A range of scanning and transmission electron- and X-ray-induced spectroscopies have been utilized to characterize these plates on the nano- and submicron- length scales in an effort to inform the long term preservation of these precious objects.

Re fe rence s:

[1] Barger MS and White WB. The daguerreotype: nineteenth-century technology and modern science The Johns Hopkins University Press, ISBN-13: 978-0801864582, 280 pgs (2000).

[2] Swan A, Fiori CE, and Heinrich KFJ. *Scanning electron microscopy* **1**, 411-423 (1979).

11:20am **CS-FrM10 The Application of Advanced Surface Analysis Techniques to the Study of Museum-Based Problems**, ***David S. McPhail***, Imperial College London, UK

Museum materials are often (but not always) relatively stable and inert and the changes that take place to their appearance over time can be so slow as to be essentially imperceptible. For example a materials surface decaying at the rate of 1 nm per day requires approximately three millennia to form a 1 mm crust (assuming linear kinetics). It follows that extremely sensitive analytical instruments with very high sensitivity and resolution are required to measure these ultra-slow surface processes. It is interesting, therefore, that the very latest analytical tools developed primarily to characterise the very latest generation of modern materials such as nanomaterials and semiconductor quantum wells, are also very well suited for the study of the surfaces of historic and pre-historic materials.

In this talk I will show how techniques such as Secondary Ion Mass Spectrometry (SIMS), Focused-Ion Beam SIMS (FIB-SIMS) and Low Energy Ion Scattering (LEIS) can be used to determine the mechanisms and kinetics of processes such as oxidation, diffusion, corrosion and ion exchange at and near the surfaces of a variety of materials from museum collections. The materials will include glass, metals and ceramics. These analytical techniques can also be used to look at the changes that occur to surfaces as a result of cleaning interventions and can be used to look at how the surfaces becomes re-contaminated over time after cleaning interventions. Being ion-beam based UHV techniques they form the latter parts of any analytical hierarchy. These ion-beam based techniques can exploit stable isotope exchange protocols using ions such as D and O18 to aid the analysis.

There is of course a tension between conservation science and surface analysis as surface analysts like to sample objects and use techniques that consume the object – this is not very welcome by the museum community for obvious reasons. I will discuss this issue and introduce approaches to sampling that might be tolerable.

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