

# SYMPOSIUM OO

## Materials Issues in Art and Archaeology VII

November 30 - December 3, 2004

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### Symposium Support

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Proceedings to be published in both  
book form and online  
(see *ONLINE PUBLICATIONS* at [www.mrs.org](http://www.mrs.org))  
as volume 852  
of the Materials Research Society  
Symposium Proceedings Series.

\* Invited paper

## 8:30 AM INTRODUCTORY REMARKS

### 8:45 AM OO1.1

#### **Prehispanic Metallurgy in Michoacan, Mexico.**

Blanca Estela Maldonado<sup>1</sup>, Paul R. Howell<sup>2</sup> and Thilo Rehren<sup>3</sup>;

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Mesoamerican copper metallurgy emerged in West Mexico sometime between A.D. 600-800. Over a period of approximately 900 years a wide variety of artifacts, typically decorations and other valuable non-utilitarian goods were produced. By 1450 A.D., the Tarascan kingdom in the state of Michoacan had become the most important center of Pre-Hispanic metalworking. Metallurgy played a significant role in the structure of political and economic power in the Tarascan Empire. Metal adornments used as an insignia of social status and public ritual became even more associated with political power. While metal was used for an array of goods, virtually nothing is known about the manufacture and the organization of production of this craft. Archaeological research at the site of Itziparátzico, near the modern Tarascan community of Santa Clara del Cobre, has recently located potential production areas where concentrations of manufacturing slag were recorded. The smelting of ores is almost invariably related to the formation of slags, because slags act as collectors for impurities introduced into the smelting process. Slag analysis thus has the potential for revealing important information about metallurgical technology. Copper smelting slag recovered from the excavations at Itziparátzico has been analyzed for microstructure and compositional properties using optical microscopy, X-ray fluorescence spectroscopy (XRF), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS). Preliminary results indicate a smelting technology that used sulfidic ores and highly efficient furnaces. While further archaeological investigations are required to precisely date these activities, this technological information is important for establishing the context and scale of production of metal goods in ancient Mesoamerica.

### 9:00 AM OO1.2

#### **The Application of Modern Metallurgical Principles and Knowledge to the Manufacture of Mokume Gane**

**(Wood-Grain Metal) Decorative Alloy.** Ian Ferguson and Brian Derby; Materials Science Centre, University of Manchester Institute of Science & Technology, Manchester, United Kingdom.

Mokume Gane layered metal is a 300 year old decorative layered metal technique peculiar to the isolated culture of the Japanese Shogunate. Like many craft practices handed down through individual experience, the manufacture and development of Mokume Gane has changed minimally over time. The application of contemporary metallurgical knowledge and solid state bonding techniques such as Hot Isostatic Pressing and Hot Roll-Bonding provide advantages over the traditional procedures for further development of Mokume Gane: bonding success rates are improved, manufacturing times are reduced. The range of possible metal combinations is substantially increased; 42 different combinations to date have been successfully bonded, including a new type of Mokume Gane employing aluminium alloys. This research has allowed for a very large increase in the variety of colours and patterns available to contemporary metalsmiths and jewellers.

### 9:15 AM OO1.3

#### **The Development and Manufacture of Aluminium Mokume Gane (Wood-Grain Metal) Decorative Alloy.**

**Ian Ferguson and Brian Derby;** Materials Science Centre, University of Manchester Institute of Science & Technology, Manchester, United Kingdom.

The application of contemporary metallurgical knowledge and solid state bonding techniques provide for development of entirely new Mokume Gane combinations. A multi-layered aluminium alloy is manufactured by the successive hot roll-bonding of two different aluminium alloys. The surface is then embossed with a selected pattern and machined back, exposing the various alloys. A range of suitable alloy combinations has been identified. When anodised, the surface presents the pattern as a strong contrast due to the differing anodising properties of the constituent alloy layers. The anodic coating can then be dyed with a wide range of colours to develop the true decorative potentials of the technique.

### 9:30 AM OO1.4

#### **Optical Profilometry as a Non-Destructive Technique to Quantify Engraving on an Arsenius Astrolabe.**

**Brian Dale Newbury, M. R. Notis and G. S. Cargill III;** Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania.

Optical profilometry has been performed on an astrolabe dated 1556 AD and attributed to the famous maker Gualterus Arsenius of Louvain, Belgium. The astrolabe represents the most sophisticated tool in pre-telescopic astronomy, and was used for a variety of tasks including: telling the time, calculating star positions, and surveying. This astrolabe, constructed for and bearing the coats of arms for Mary Tudor and husband Philip II of Spain, represents an interesting mix of both world politics at the time of construction and the pinnacle of scientific instrument construction. In this non-destructive technique, a beam of white light is impinged on the sample and combined with the chromatic aberration technique to accurately measure surface features. With machine parameters set to a vertical resolution of 0.1 microns, lateral resolution to 6 microns and a 3 millimeter depth of field, various engraving features on the astrolabe were studied. Both hand-scribed and stamped markings are present on the astrolabe face. Inspection of the hand-scribed date on the instrument's mater allows one to quantify the shape and dimensions of the tool used, as well as the direction and inclination of the engraving tool during inscription. Optical profilometry was also used to study very faint guide markings on the reverse side of the astrolabe rete used by the instrument maker during construction. These markings were used to label the star position and name, as well as define the geometry of the rete itself during the metalworking prior to decorating the front of the instrument. The results of this analysis give information about how the astrolabe was constructed in one of the Renaissance's greatest scientific instrument workshops. The results are compared to similar engravings on a later period, undated and unsigned, Islamic astrolabe tympan; and modern brass engravings performed by the investigators.

### 10:15 AM OO1.5

#### **Low-Temperature Diffusion Data Measured from Historical**

**Artifacts.** R. J. Kremer, M. A. Dayananda and Alex King; School of Materials Engineering, Purdue University, West Lafayette, Indiana.

Diffusion processes in typical metals are considered to be slow at room temperature but there are many applications for which very long-term use is envisaged and stability needs to be assured over a timescale of 10,000 years, where even slow processes can be important. It is clearly impractical to make diffusion measurements under controlled conditions for this length of time, so it is common to perform accelerated tests at higher temperatures and extrapolate the necessary information from the measurements so obtained. We have tested the validity of this type of extrapolation for room-temperature, grain boundary diffusion in the copper-silver system, by measuring low-temperature diffusion profiles in antique samples of Sheffield plate. This is a form of silver-clad copper that was manufactured as a lower-cost alternative to solid silver, between 1740 and 1840, so it provides samples that represent room temperature behavior over times on the order of 200 years. We will present our compositional measurements and analysis, along with a comparison to diffusivity data extrapolated in the usual manner. Acknowledgment: this work is supported by the US Department of Energy, under contract number DE-FG01-01ER45940.

### 10:30 AM OO1.6

#### **The Role of $\beta\text{FeOOH}$ in the Corrosion of Archaeological Iron.**

**David Edward Watkinson** and Mark Tudor Lewis; School of History and Archaeology: Conservation Section, Cardiff University, Cardiff, United Kingdom.

Archaeological iron from non-waterlogged burial environments normally contains dissolved chlorides, which are held as counter ions at anodes. The ability of the chloride ion to act as an electrolyte and the post-excavation oxidation of ferrous ions accelerates corrosion of the archaeological iron. Attempts to preserve such iron have focussed on the removal of chlorides and on inhibitive techniques. Chloride extraction techniques have proved both unpredictable and inconsistent. Inhibitive systems are hampered by the presence of chloride and the ethical and aesthetic demands of conservation, which require the retention of the mineralised iron layer that contains the original shape of the object. While desiccation has been employed to prevent archaeological iron from corroding, neither the corrosion processes occurring at low humidity nor optimum storage parameters have been adequately researched. It is necessary to examine the influence of relative humidity on the corrosion mechanisms occurring during the drying process, in order to establish the degree of desiccation required to prevent corrosion of chloride infested archaeological iron. Several corrosion processes occur as the iron dries and this paper examines one of these; the occurrence of akaganite ( $\beta\text{FeOOH}$ ) and its role in the corrosion of archaeological iron. As iron corrodes in chloride rich environments  $\beta\text{FeOOH}$  may form as a

corrosion product. Using a climatic chamber the hygroscopic properties of  $\beta\text{FeOOH}$  are examined and its contribution to the corrosion of iron over a wide range of relative humidities is tested. Results offer information on the 'no-corrosion' relative humidity for mixtures of  $\beta\text{FeOOH}$  and iron powder, as well as corrosion rates of iron at various relative humidities above this value.  $\beta\text{FeOOH}$  is washed in aqueous solutions to remove adsorbed chloride from its structure and then its effect on iron powder is noted for various relative humidities. Results reveal that washed  $\beta\text{FeOOH}$  causes less corrosion than unwashed  $\beta\text{FeOOH}$ . An assay of 25 year old  $\beta\text{FeOOH}$  enabled comment on the reported metastability of this compound with respect to  $\alpha\text{FeOOH}$ . Collation of these results provides an overview of the role of  $\beta\text{FeOOH}$  in the corrosion of archaeological iron and establishes it as a dangerous corrosion product. Links between the effect of aqueous wash treatments on archaeological iron and the success of desiccated storage are discussed. This work has implications for other chloride infested ferrous metals.

#### 10:45 AM OO1.7

##### **Electrochemical Techniques Applied to Metals Conservation.** Virginia Costa, IRRAP, Meudon, France.

Since its earliest application by Rathgen at the end of the 19th century, electrochemistry has only begun to be used more widely in the field of conservation in the last decades, attaining nowadays a well recognised place in this area. This paper shows through selected examples the role played by the advances in scientific instrumentation in the evolution of approach for conservation. Regarding several applications, electrochemistry has been used in two different ways: as a method of treatment and as a technique of investigation. In the first case electrochemistry was mostly applied as a cleaning procedure, to treat silver, copper, lead iron and tin and their alloys by reducing the corrosion products at the surface. The earlier use was simply performed by galvanic coupling with a less noble metal and / or by using a reducing agent in the solution. On this way all surface products were removed indiscriminately. Later, current or voltage suppliers have been integrated to the conservation instrumentation and also another form of treatment developed: the stabilisation of severely corroded archaeological alloys, by electrochemical removal of retained chlorides, for example. Since the last decade electrochemistry finally began to be used as a technique of investigation to study the behaviour of materials concerning conservation. This includes identification of the nature of surface products, evaluation of the corrosivity of case materials, evaluation of the protection given by inhibitors. The advent of the potentiostat enabled a better knowledge of the reactions occurring at the surface, allowing a more precise choice of what material should be removed, with no attack of the base metal.

SESSION OO2: Paintings: Technical Studies, New  
Diagnostics and Conservation Treatments  
Chairs: Johanna Bernstein and Karen Trentelman  
Tuesday Afternoon, November 30, 2004  
Room 301 (Hynes)

#### 1:30 PM \*OO2.1

##### **New Materials on the Palette of Sixteenth Century Venetian Painters.** Barbara H. Berrie, Scientific Research Dept, National Gallery of Art, Washington, District of Columbia.

In the early 1500s Venetian painters, including Titian and Giovanni Bellini, were noted for their brilliant palette of colors that made their work look different from their contemporaries' paintings. The 1534 inventory of a shop in Venice belonging to a colorseller revealed a stock of raw materials, tools of the trades, and finished products for artists and artisans. Materials for glass-making, dyeing, and painting are noted on the list. The materials on the 1534 inventory provided a fresh starting point for re-examination of the Venetian palette. Scanning electron microscopy with energy dispersive spectrometry and x-ray powder diffraction were used to characterize some of the materials used by Venetian artists to formulate their paint. Cross sections from paintings by the Venetian artists Lorenzo Lotto, Giovanni Bellini, and Titian and artists from other areas were examined. Materials usually thought of as supplies for dyeing or glass-making were found as colorants and extenders in paint. Combinations of red lake pigments, mixed together or applied as alternating glazes were found using fluorescence microscopy. The unexpected use of finely ground silica as an extender in these paints was determined using SEM-EDS. Additionally, other glassy materials—either true glasses or frits—were identified in the paint films. The results show that in addition to mineral pigments, inorganic compounds, and organic molecules, artists of the Italian Renaissance increased the range of their palette through the addition of glasses. Written evidence suggests these glasses were known as "smalti" and were employed by artists as pigments. It seems likely that the use of

these materials on the artists' palette would not only have increased the color range but improved the handling properties of their paint.

#### 2:00 PM OO2.2

##### **A Study of the Materials of Pontormo's "Portrait of Alessandro de' Medici".** Ken Sutherland, Beth A. Price, Irma Passeri and Mark Tucker; Conservation department, Philadelphia Museum of Art, Philadelphia, Pennsylvania.

In studies of the materials of old master paintings, the characterization of thin and degraded layers often presents unusual challenges for routinely used methods of analysis. This paper will discuss analyses performed as part of a study of the techniques and materials of Pontormo's "Portrait of Alessandro de' Medici", dating from c. 1534-5, carried out during a recent cleaning and restoration of the painting. The portrait was found to be built up using a complex sequence of preparation, drawing and paint layers, the analysis of which was complicated further in some areas by the presence of degraded materials on the paint surface. Gas chromatography/mass spectrometry (GCMS), Fourier transform infrared microspectroscopy (FTIR) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) were used to characterize the materials used for the various stages of preparation and painting; the focus of this paper will be the particular approaches taken to the characterization of the multiple preparation layers, and of the degraded surface materials. Examination of cross-section samples from the painting, using visible and fluorescence light microscopy in addition to SEM, and in conjunction with visual examination of local areas of damage and abrasion in the painting where underlying layers had been exposed, allowed the discernment of separate stages of surface preparation, drawing and underpainting used in the construction of the image. GCMS analysis of the protein component of samples from the preparatory layers indicated the presence of an animal glue "sealing layer" applied to the surface of the gesso ground, and, unusually, the use of an egg-based medium for extensive brown undermodeling of the composition, prior to the final painting in oil. The individual layers could not be separated for analysis; the presence of these materials was deduced from statistical analysis of the amino acid composition of samples comprising several layers. Analysis of a degraded brown surface layer present in local areas of the painting using FTIR and SEM-EDS indicated the presence of a number of components typical of airborne particulate dirt. The detection of copper in the layer by EDS suggested that the layer might represent residues of a pigmented toning or glaze layer, in which the surface dirt had become embedded. However, because of the resolution limits for elemental mapping on such a small scale, and the degradation of the organic components of the layer, its identity as an intentional paint layer could not be confirmed with confidence.

#### 2:15 PM OO2.3

##### **The Technological Study of Icons Originating from South-Eastern Poland from the 15-17-th Century.** Ewa Panczyk and Lech Walis; Materials Research, Institute of Nuclear Chemistry and Technology, Warsaw, Poland.

The aim of this examination is the implementation of a complex research method to be used in the studies over icons from 15-17-th century. The results might constitute the basis for conservation and further studies in the field of the history of art conducted following the principles of the "new connoisseurship". These methods go far beyond traditional attributive studies, usually limited to the comparisons of compositional, iconographic and stylistic nature. Being enlarged with a through technological analysis of a painting they also allow us to follow the creation process. The study includes all elements of the multilayer structure of a painting important for the final artistic expression. It is possible due to the application of research methods such as: X-ray radiographic, infrared analysis, which enable us to see the preliminary drawing, the underpainting, the author's corrections and restoration works. As material for the examination a group of 20 icons from Poland and Ukraine Schools are owned by the Museum Palace in Lancut near Rzeszow was chosen. In term of paintings techniques the studies were divided into two stages. Stage I include basic research using X, UV and IR rays, the analysis of the structure of layers based on stratigraphy and identification of pigments (LMA-AES). Detailed comparative analysis of the results of research works and the degree of the preservation of painting together with the information on previous works allowed us to identify the initial schedule of conservation works. The following research works were foreseen in stage II: SEM-EDS, XRD, instrumental neutron activation analysis (INAA) -trace elements analysis in lead white and dendrochronological dating. All the methods selected for both stages are highly sensitive, complementary physicochemical analyses which supply us with information based on the microsamples (ca. 1mg) or non-destructive examination. The results of technological and materials research works are confronted with the knowledge on various artistic workshops, helped to attribute the icons, to locate them in time and the reconstruct their history. The development of

technological research together with more thorough studies of the achieves could explain the so far unknown stages of the history of the icons and their restorations.

### 3:00 PM OO2.4

**Fiber Optics Reflectance Spectroscopy in the Entire UV-VIS-IR Range: A Powerful Tool for the Non-Invasive Characterization of Paintings.** Mauro Bacci<sup>1</sup>, Roberto Bellucci<sup>2</sup>, Costanza Cucci<sup>1</sup>, Cecilia Frosinini<sup>2</sup>, Marcello Piccolo<sup>1</sup>, Simone Porcinai<sup>2,1</sup> and Bruno Radicati<sup>1</sup>; <sup>1</sup>Structure of Matter & Spectroscopy, Institute of Applied Physics - CNR, Florence, Italy; <sup>2</sup>Opificio delle Pietre Dure, Florence, Italy.

Fiber optics reflectance spectroscopy (FORS) in the ultraviolet and visible ranges is a technique that by now is well accepted by the scientific and restoration communities for the identification of pigments and the monitoring of color alterations. Since the first applications in the 1980s, the improvement in detector technology and in the materials constituting fiber optics have made it possible to extend the spectroscopic analysis up to the mid-infrared region (900  $\text{cm}^{-1}$ ). Consequently, the entire range of interest for electronic spectroscopy and most of the region involved in vibrational spectroscopy have been made accessible by means of completely non-invasive measurements. In this communication, a case study, the Madonna of the yarn winder by Leonardo da Vinci, is reported. Several tens of areas (about 0.3  $\text{cm}^2$ ) were examined throughout the painting. The following particularly relevant results were obtained. The blue areas were painted using lapis lazuli. However, there are some blue areas in which the spectra are significantly different from the former ones and can be confidently attributed to cobalt aluminate. Since this latter pigment was unknown before the 19th century, however, the corresponding areas were obviously retouched in relatively recent times. In the near infrared region, an intense absorption band around 1415 nm is evident, plus an inflexion at 1390-1400 nm, which suggests the existence of clay materials. Since these features are present in all the investigated areas, it is reasonable to suppose that clay was used as a preparatory layer together with gypsum and/or lead white, as has also been shown in another painting of the same period [1]. In the mid infrared region, interpretation of the spectra is not straightforward, owing to band distortions due to the reflection mode, in which the spectra are recorded. However, preliminary results show the presence of oil as a binding medium. In fact, the presence of a carbonyl band at  $1740 \div 1750 \text{ cm}^{-1}$  plus an additional band at  $1770 \div 1780 \text{ cm}^{-1}$  is typical of aged oils [2]. 1. Barbara H. Berrie, JAIC, 33, 307 (1994). 2. Raymond J. Meilunas, James G. Bentsen and Arthur Steinberg, Studies in Conservation, 35, 33 (1990).

### 3:15 PM OO2.5

**Confocal X-ray Fluorescence (XRF) Microscopy: A New Technique for the Nondestructive Compositional Depth Profiling of Paintings.** Jennifer Mass<sup>1,6</sup>, Arthur R. Woll<sup>5</sup>, Sol M. Gruner<sup>5,3</sup>, Christina Bisulca<sup>6</sup>, Donald H. Bilderback<sup>5,2</sup>, Rong Huang<sup>5</sup> and Ning Gao<sup>4</sup>; <sup>1</sup>Conservation, Winterthur Museum, Winterthur, Delaware; <sup>2</sup>Applied and Engineering Physics, Cornell University, Ithaca, New York; <sup>3</sup>Physics, Cornell University, Ithaca, New York; <sup>4</sup>X-ray Optical Systems, Albany, New York; <sup>5</sup>Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York; <sup>6</sup>Art Conservation, University of Delaware, Newark, Delaware.

A confocal x-ray fluorescence microscope was built at the Cornell High Energy Synchrotron Source (CHESS) to determine the composition of buried paint layers, 10-80 microns in thickness, in paintings as a function of depth. The microscope consists of a borosilicate monocalcapillary optic to focus the incident beam onto the sample and a commercial borosilicate polycapillary lens to collect the fluorescent x-rays. The overlap of the two focal regions is several tens of microns in extent, and defines the active, or confocal volume of the microscope. The resolution of the microscope was measured by scanning a variety of thin metal films through this confocal volume while monitoring the fluorescence signal. The capabilities of the technique were then tested using paint films with up to four distinct pigment layers. Results from confocal XRF were compared with those from stand-alone XRF and visible light microscopy of the paint cross-sections. We find that, since the fluorescence signals from different layers are separated in energy, the effective resolution of the instrument is typically 5-10 microns, far smaller than the size of the confocal volume. The position and thickness of individual layers were extracted from their fluorescence profiles by fitting to a simple, four parameter model convolved with an approximation to the measured resolution profile. The CHESS confocal XRF system was then used to investigate the composition of a twentieth century oil painting on canvas. Scans were directed inward from both the painting surface and from the canvas to successfully determine the materials and techniques used by the artist. The depth profiles obtained by this method provide paint layer positions, compositions, and thicknesses, and so serve as virtual cross-sections that are obtained in a totally

nondestructive manner.

### 3:30 PM OO2.6

**Atomic Oxygen Treatment and Its Effects on a Variety of Artist's Media.** Sharon Miller<sup>1</sup>, Bruce Banks<sup>1</sup> and Deborah Waters<sup>2</sup>; <sup>1</sup>Electro-Physics, NASA Glenn Research Center, Cleveland, Ohio; <sup>2</sup>QSS Corporation, Cleveland, Ohio.

Atomic oxygen treatment has been investigated as an unconventional option for art restoration where conventional methods have not been effective. Exposure of surfaces to atomic oxygen was first performed to investigate the durability of materials in the low Earth orbit environment of space. The use of the ground based environmental simulation chambers, developed for atomic oxygen exposure testing, has been investigated in collaboration with conservators at a variety of institutions, as a method to clean the surfaces of works of art. The atomic oxygen treatment technique has been evaluated as a method to remove soot and char from the surface of oil paint (both varnished and unvarnished), watercolors, acrylic paint, and fabric as well as the removal of graffiti and other marks from surfaces which are too porous to lend themselves to conventional solvent removal techniques. This paper will discuss the treatment of these surfaces giving examples of each, and a discussion of the treatment results.

### 3:45 PM OO2.7

**Laser Cleaning of 15th Century A.D. Wax Votive Images from St. Peter's Cathedral, Exeter, England.** Teresa Moreno, Arizona State Museum, University of Arizona, Tucson, Arizona.

A rare collection of cast votive images (ex-votos) made of beeswax were found in the 1940s behind the cresting of a screen above the tomb of Bishop Edmund Lacey in the Cathedral Church of St. Peter in Exeter, England. Some of these fragmentary, aged and brittle waxes, dating to the late 15th to early 16th centuries A.D., served as the basis to further test the cleaning of dirt and accretions using a Q-switched Nd:YAG laser. Observations also were made of the effects on the wax substrates due to heat emitted from the laser. Preliminary optical microscopy was used to establish a typology of the waxes based on their condition and nature of the weathering phenomena. Several techniques were used to characterize the waxes and the surface deposits, including gas chromatography-mass spectroscopy (GC-MS), energy-dispersive x-ray fluorescence (EDXRF) and scanning electron microscopy (SEM-EDS), in addition to simple tests of melting point and hardness that served to help understand the nature, condition and treatment of the waxes.

### 4:00 PM OO2.8

**Parametric Analysis of Relative Humidity Effects on Traditional Panel Paintings.** Eric Hagan<sup>2,1</sup>, Evan Quasney<sup>2</sup> and Marion Mecklenburg<sup>2</sup>; <sup>1</sup>Art Conservation, Queen's University, Kingston, Ontario, Canada; <sup>2</sup>SCMRE, Smithsonian Institution, Suitland, Maryland.

A finite element analysis was performed on panel painting structures subjected to changes in relative humidity. Measured Young's modulus values and humidity expansion coefficients were used to define material properties for characteristic northern and southern European panels. Models of northern panels simulated white oak with two layers of oil paint, while models of southern panels simulated cottonwood with gesso and two oil paint layers. In both cases, the properties of the oil paints were input for lead white and Naples yellow respectively. Influence of radial/tangential grain orientation, panel thickness, and structural support were investigated through various humidity changes. Results are presented in the form of stress in the wood, gesso, and paint layers as well as curvature of the painted surfaces. Verification of the model was performed with a derivation of general stress equations for a cradled painting with no friction between the battens and the panel. Comparison of derived and parametric results confirmed accurate behavior of the model. The parametric study emphasized the role of gesso stiffness, wood grain orientation, and cradling on the structural response of panel paintings. Tangential end grain and the presence of gesso both contributed to increased warping; however, stress levels were negligible for unhindered panels under moderate humidity fluctuations. Analyses of cradled panels with and without friction were performed by adding appropriate boundary conditions to the models. An ideal, frictionless, cradle produced a flat surface profile, although stress was further increased in the gesso layer. Locking battens in the cradle caused severe warping and increased stresses to magnitudes that induce cracking. The characteristic waviness of a locked cradle matched well with deformation shown by the parametric model.

### 4:15 PM OO2.9

**Effects of Water Exposure on the Mechanical Properties of Early Artists' Acrylic Paints.** Eric Hagan and Alison Murray; Art Conservation, Queen's University, Kingston, Ontario, Canada.

The mechanical properties of artists' acrylic paints were investigated under controlled amounts of aqueous additive leaching in order to identify changes caused by cleaning acrylic paintings with water. Paint samples studied in this work were custom-manufactured by Golden Artist Colors according to published Rohm & Haas formulations. Bone black and naphthol red colours were provided using Rhoplex AC-234 as a binder ingredient to duplicate artists' acrylic paints from the 1960's to the 1990's. Strength and stiffness values were obtained through uni-axial tensile testing and were compared with the results of similar experiments in which paint films were tested under various ages, temperatures, and relative humidities (RH). Analysis of acrylic paint properties across a range of conditions puts the effects of water exposure in context with effects induced by other factors. Changes in mechanical properties were recorded after carefully altering individual test variables from a control condition of seven months age, 21°C, 50%RH, and no water exposure. Naturally aged paint specimens were studied at values ranging from one day to 13 months, while temperature and RH experiments were conducted in conditions ranging from 1.5°C to 31°C, and 20% to 80% respectively. Controlled removal of water-soluble additives was accomplished by immersing specimens in distilled water for selected time intervals followed by 72 hours of drying. Mechanical properties of the leached specimens were compared with results from samples modified by age, temperature or relative humidity. Strength and stiffness were both shown to increase with decreased temperature, decreased RH, increased age, and increased additive removal. By far the largest impact on mechanical properties was caused when temperature was lowered to the  $T_g$  region around 5°C. Significant changes were caused by RH fluctuations; however, these were much less dramatic than changes caused by variations in temperature. Quantifying the effects of additive leaching required strict environmental control as the increased strength and stiffness resulting from extreme immersion was equivalent to the results obtained by decreasing relative humidity from 50% to 35%. Paints from which the water-soluble additives were removed were as responsive to RH as the control samples.

SESSION OO3: Paintings: Technical Studies, New  
Diagnostics and Conservation Treatment II  
Chair: Alison Murray  
Wednesday Morning, December 1, 2004  
Room 301 (Hynes)

#### 8:30 AM \*OO3.1

##### **The Changing Mechanical Properties of Ageing Oil Paints.**

Marion F. Mecklenburg and Charles S. Tumosa; SCMRE, Smithsonian Institution, Suitland, Maryland.

The mechanical properties of unsupported oil paint films were measured over a period of 20 years. This systematic study used paints that were commercially available and some that were manufactured to rigorous specifications by the authors. The specially manufactured paints contained a selection of different drying oils and pigments traditionally used over the centuries. The results of this testing established that there is a significant difference between paint that is "dry to the touch" and those that are those that are dry throughout the paint film. Most oil paints take a very long time to dry. Testing suggests that there are active processes continuing for decades, possibly centuries. The research also shows that a pigment's ability to partially dissolve in the oil plays a significant role in the drying behavior of the film. While paints made with most traditional pigments remain fairly flexible, certain pigments such as zinc oxide can cause the paint to become extremely brittle in less than three years.

#### 9:00 AM OO3.2

**Artists' Oil Paints as Ionomers.** Charles S. Tumosa, Marion F. Mecklenburg and David Erhardt; SCMRE, Smithsonian Institution, Suitland, Maryland.

Artists' oil paints are made from oils containing unsaturated fatty acid esters of glycerin. The long term fate of the paint film involves oxidation and hydrolysis. After polymerization on drying, the covalent oil film can oxidize at the C9 double bond to give the diacid azelaic acid, leaving a pendant carboxylic acid group. Sequential hydrolysis of the three ester linkages can yield up to three more carboxylic acid groups. Each of these groups is attached to the chain making an ionomer. Pigments within the film can react with these acid groups altering the properties of the original paint film. A series of paints was synthesized to mimic this long term behavior and create model ionomers to determine their physical and chemical behavior. The results of this research lead to a better understanding of the behavior of old paint films and the effects of conservation treatments on old paintings.

#### 9:15 AM OO3.3

##### **Chemical and Physical Stability of Artists' Acrylic Emulsion Paints.** Dominique Scalapone<sup>1</sup>, Oscar Chiantore<sup>1</sup> and Tom Learner<sup>2</sup>;

<sup>1</sup>IPM Chemistry, University of Torino, Torino, Italy; <sup>2</sup>Tate, Millbank, London, United Kingdom.

Acrylic latexes have been used in paint formulations since the 1950s, but detailed studies on the stability of these materials have only recently been reported. Most artists' acrylic emulsion paints are based on poly (EA-co-MMA) or poly (nBA-co-MMA) copolymer binders, with the latter being generally preferred in more recent paint formulations. In this contribution, the chemical and physical properties and performances of several brands of artists' acrylic emulsion paints are discussed and compared. As properties of waterborne coatings and pigmented paints largely depend on the presence of many different additives (surfactants, thickeners, stabilizers, antifoam agents, etc.), an initial part of the study was aimed at the identification of relevant components. Compositional information on acrylic binders and surfactants was obtained by 1H-NMR, Py-GC-MS and SEC-FTIR, extenders and inorganic pigments were quantified by thermogravimetric analysis and most were identified by infrared spectroscopy. As a second step similar investigations were performed on samples aged under natural indoor and accelerated laboratory conditions, revealing two main phenomena. First, a general trend was observed pointing to a tendency for acrylic emulsion paints to become less soluble in solvents with increasing light exposure. However in some cases a different behaviour was observed and it is not clear yet if these changes are related to the development of chain entanglements or to cross-linking reactions. And second, the surfactant that migrates to the surface of each paint film was observed to degrade with subsequent light exposure. Another aspect is the stability of the acrylic component, which is largely controlled by the reactivity of the alkyl side group. The photostability of aliphatic acrylic polymers is generally very high, but under accelerated photo-oxidative conditions they undergo both scissions on the side ester groups, with formation of volatile molecules, and cross-linking of the polymer backbone. Further, acrylates are much more reactive towards photo-oxidation than methacrylates. In both types of monomeric units when the ester side group is short, scission reactions prevail over cross-linking, while when there is a butyl ester group the polymer samples undergo fast and extensive cross-linking. At longer irradiation times radical fragmentation reactions compete with cross-linking leading to the loss of ester groups and to the formation of tertiary macroradicals, of new carbonyl compounds and hydroxyl groups. At present the experimental work is still in progress, but the final purpose will be to compare the results obtained for the different types of artists' emulsion paints and, if possible, to correlate features such as photo-oxidative stability, solubility, colour changes, surfactant phase separation, etc. with the paint composition, looking in particular at the nature of the acrylic binder and at the effects of different pigments and surfactants.

#### 9:30 AM OO3.4

##### **An Investigation of the Chemical Changes of Artist Acrylic Paint Films When Exposed to Water.** Rebecca Ploeger<sup>1</sup>, Alison

Murray<sup>2</sup>, Simon Hesp<sup>3</sup> and Oscar Chiantore<sup>4</sup>; <sup>1</sup>Engineering Chemistry / Art Conservation, Queen's University, Kingston, Ontario, Canada; <sup>2</sup>Art Conservation, Queen's University, Kingston, Ontario, Canada; <sup>3</sup>Chemistry, Queen's University, Kingston, Ontario, Canada; <sup>4</sup>Dipartimento di Chimica IFM, Università di Torino, Torino, Italy.

During the past 50 years, acrylic polymer coatings have become popular and are now widely used in a number of industrial and artist applications. This new artist medium has a host of major conservation concerns with respect to the sensitivity to leaching of paint components during aqueous cleaning. This paper addresses some of those concerns by investigating the chemical changes of artist acrylic paint films caused by exposure to water and the rate at which some of the changes occur. One-hour immersion experiments were performed on the acrylic films; from a conservation perspective, this process appears to be drastic, however, it provides some important insight into the leaching processes. Three different acrylic paint films were investigated: a synthetic organic pigment film (light naphthol red), a natural inorganic pigment film (bone black) and a raw polymer film with no paint manufacture additives (Rhoplex AC-234). All acrylic films were cast on Mylar sheets and naturally aged in a laboratory environment. Analytical techniques used to identify changes included Fourier transform infrared - attenuated total reflectance (FTIR-ATR), thermo-gravimetric analysis (TGA), pyrolysis gas chromatography mass spectrometry (py-GC-MS) and atomic force microscopy (AFM). Real-time capillary rise and conductivity measurements gave an indication of the rate at which these changes occur. Much of the measurable leaching occurred within the first 20 minutes of the paint film being exposed to water, while the most rapid leaching occurred within the first five minutes, before approaching an equilibrium state. Accompanying the leaching process were observable changes in the physical properties and chemical composition. These physical changes

were in colour, dimension, mass and morphology. A decrease in size and mass indicated that material had been permanently removed from the paint films. AFM images and colour measurements also showed evidence of changes caused by the exposure to water. The leached material and the original paint films were analyzed to identify the chemical species that had been leached out. Thus far, the major additive identified in the leached material was a surfactant of the alkylphenol (poly)ethoxylate type. Leaching of the surfactants may dramatically affect the chemical and mechanical stability of the paint films, since they act not only as emulsion stabilizers, but also as plasticizers. Even a limited exposure time to water immersion causes some irreversible leaching and damage to the paint film surface; analogous studies need to be performed using typical conservation treatments to determine if there are similar leaching effects and the rate that they occur.

SESSION OO4: New Materials and Techniques for  
Conservation  
Chair: Alison Murray  
Wednesday Morning, December 1, 2004  
Room 301 (Hynes)

#### 10:15 AM OO4.1

**Using ICP-MS to detect inorganic elements in organic materials: a new tool to identify mordants or dyes on ancient textiles.** Laure Dussubieux, Dan Naedel, Roland Cunningham, Harry Alden, Joe Koles and Mary Ballard; Smithsonian Center For Materials Research and Education, Suitland, Maryland.

Many natural dyes contain inorganic components either as mordants or substituent groups on the dye molecule. Mordants have been identified by the analysis of ashed sample using microchemical testing and by scanning electron microscopy electron dispersive spectrometry (SEM/EDS). A new method, with lower limits of detection is now available. This paper focuses on the comparison of inductive coupled plasma mass spectrometry with these other two methods, using undyed mordanted wool, standard reference dyed samples, known dyed antique textile samples, and archaeological material from the Gordion tomb associated with King Midas'tomb. The color a textile is dependent not only on the dyestuff but also its method of application-the mordant or metal ligand that complexes the dye and holds it to the fiber or substrate. Different cultures and different periods used different mordant systems and different procedures to produce certain hues. This paper explores the possibility of using ICP-MS to establish the mordant or inorganic component of the dyed textile, and provides comparison to other established methods. Different kinds of modern or ancient textiles were investigated. Few milligrams were ashed at 600°C for 18 hours and then dissolved in ultra-pure nitric acid. Samples were run without external or internal calibration to produce qualitative results. Aluminum, copper, iron, and tin based mordants were successfully detected with ICP-MS. These results match those of comparative mordanting tests espoused by Dr. Helmut Schweppe, as well as results found using ashing/microchemical tests, and SEM/EDS. However, there are important advantages and disadvantages to the use of ICP-MS. Due to the great sensitivity of the method, impurities and contaminants that were original to the mordanting system can be detected. Thus, the iron-mordanting may indeed have a significant portion of copper-from a copper kettle?-or copper mordanting may show high levels of aluminum-from subsequent soiling or a mixed mordant system. In this way, ICP-MS can help explain Max Saltzman's dictum "You can't judge a dye by its color" and clarify some aspects of pre-industrial dyeing technology. At the same time, ICP-MS may provide too much precision, leading to some confusion as to which metal ligand is the major mordanting constituent, while comparative mordanting, microchemical spot testing, and even SEM/EDS have the advantage of self-limiting detectable limits. For SEM/EDS this has produced problems with the detection of chromium mordants. For comparative mordanting, the sample and references may be problematic. In approaching archaeological material where the fiber or dye may already be deteriorated, ICP-MS can be helpful, especially when a comparative sample of adjacent soil is available, but the sample size must be quite small. Textile fabric residues found in the tomb mound at Gordion, perhaps the tomb of King Midas, exemplify the benefits and limitations of this method.

#### 10:30 AM \*OO4.2

**The Development of Ultra-cool Melt Adhesives for Mounting Resin Coated (RC) Photographic Papers.** Chris McGlinchey<sup>1</sup> and Bing Yuan<sup>2</sup>; <sup>1</sup>The Museum of Modern Art, NY, New York; <sup>2</sup>Polymer Research Institute, Polytechnic University, Brooklyn, New York.

The development of an adhesive that is a hybrid between a pressure sensitive adhesive and a heat seal adhesive is described. The need for such a material arises from the fact that pressure sensitive materials

may stain the photograph and cool-melt adhesives are activated at temperatures (65°C) that are too high and can cause changes in surface appearance. The goal of this project, which is a joint collaboration between the Museum of Modern Art and the Polymer Research Institute, is to develop a preservation quality adhesive for application to RC print photographs that minimizes or eliminates negative aspects of pressure sensitive and heat seal adhesives. In arriving at a formula for an adhesive to be used by conservation professionals certain properties that go into the formulation of commercial adhesives can be eliminated. The main features of commercial PSAs are quick and aggressive tack that enables adequate adhesion by a wide range of users under a broad range of temperatures. The term ultra-cool is used to describe a formulation that is activated at 40°C. This does not mean that at temperatures above 40°C the adhesive will fail, rather the bond may be more susceptible to creep- a property that is present in PSAs under shearing load. In the museum environment temperatures are typically 22°C and the threat of long term creep from an adhesive activated at 40°C is minimized. To establish consistent activation temperatures a heated water bath is used to insure that the steel blocks used to apply pressure do not exceed the prescribed temperature limit. In studies it was found that the blocks (2.5 cm square) cut to the length of the adhesive joint cooled to room temperature in 15 to 20 minutes, depending upon room temperature. This is not the quick tack of a commercial pressure sensitive adhesive but it produces bonds that appear uniform across the entire surface area. It was determined that steel blocks cut to the above dimensions produced what might be considered light finger pressure and did not produce any harmful impressions in the RC paper. The use of such steel blocks establishes a consistent pressure and will help verify that conditions are standardized across a variety of users.

SESSION OO5: In-Room Poster Session  
Chairs: Jennifer Mass and Alison Murray  
Wednesday Morning, December 1, 2004  
11:00 AM  
Room 301 (Hynes)

#### OO5.1

**The Role of SnO<sub>2</sub> and of Lies/Vinegar in Lustre Formation.** Philippe L. Colomban, LADIR UMR7075 UPMC, CNRS, Thiais, France.

The oldest known nanotechnology dates back to the fabrication of the first lustre potteries. A lustre is a thin film formed just below the surface of medieval Islamic glazed potteries which contains silver and/or copper in the metallic and ionic form. Raman study of the lustre films of different ceramics excavated from Fustat (near Cairo, Egypt, 11-12th) or from the Silk Road (Termez, 13-14th centuries) shows they associate many layers of different compositions (with or without cassiterite). EDS analysis shows all studied glazes are Ca (and K)-rich, nearly free of Al silicates, with some addition of lead. Distribution of Ag and Cu element is very heterogeneous in the lustre decor. The main Raman signatures of the lustre film is assigned to Ag<sup>+</sup> and Cu<sup>+</sup> ions (50-100 cm<sup>-1</sup> peaks). The additional low wavenumber features could be due to the Ag (or (Ag<sub>n</sub>)<sup>m+</sup>) nanoclusters modes. It is clear that the lustre colour arises from the combination of iridescence (diffraction) and absorption/diffusion. Raman criteria are proposed for a sample classification as a function of processing (cassiterite content, processing temperature). The glazing technique is discussed on the basis of experimental evidences and ancient potters reports. Exothermic burning of acetate residues is proposed as the key-step for the preparation of polychrome lustre. Tin oxide play a key role in displacing the Ag, Ag<sup>+</sup> and Cu, Cu<sup>+</sup>, Cu<sup>++</sup> redox equilibrium toward metal side. Controlled combustion of carbonised acetate residues appears as a possible explanation for lustre polychrome. Ph. Colomban Applied Physics A: Materials Science & Processing 79 (2004) 167-170. Ph. Colomban, C. Truong J. Raman Spectrosc. 35 [3] (2004) 195-207.

#### OO5.2

**Electron Microscopy Investigations of Ancient Coins from The Brazilian Colonial Period.** Guadalupe Nascimento Campos<sup>1</sup> and Guillermo Solorzano<sup>1</sup>; <sup>1</sup>Department of Materials Science and Metallurgy, PUC-Rio, Rio de Janeiro, RJ, Brazil; <sup>2</sup>Department of Materials Science and Metallurgy, PUC-Rio, Rio de Janeiro, RJ, Brazil.

The present work has as its objective a microanalytical study of metallic archaeological artifacts using methods of optical microscopy (MO), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The object of the study corresponds to coins from the Brazilian colonial period, dating from the late XVIII century, removed from an archaeological site ( Site Rochedo), in excavations conducted by researchers of the Brazilian Archaeological Institute.

Sample preparation required a meticulous procedure in view of the fragility of the objects. The coins have been suffering the action of oxidation-corrosion over the years, thereby making the impregnation of mineral sediments possible. A detailed metallographic analysis, coupled with spectroscopic SEM and TEM measurements, allows one to conclude that the coin was made of copper from European origin. The equi-axial microstructure of Cu matrix strongly suggest a metal forming and annealing procedure was conducted on the alloy containing Bi, As and Pb. Current studies using non-destructive methods such as ICP-MS and XPS, aiming at determining trace elements and, thereby, assess the origin of the raw material, are in progress.

#### OO5.3

##### Non-Destructive X-ray Diffraction of Museum Artefacts.

Nicola Meller<sup>1</sup>, Katherine Eremin<sup>2</sup> and Christopher Hall<sup>1</sup>; <sup>1</sup>Centre for Materials Science and Engineering, The University of Edinburgh, Edinburgh, United Kingdom; <sup>2</sup>Conservation and Analytical Research, National Museums of Scotland, Edinburgh, United Kingdom.

X-ray diffraction (XRD) is widely used for the identification of the crystalline component of artefacts and art works. However such analysis is traditionally destructive, involving the removal of a sample from the artefact. On polychrome or multi-component artefacts several samples may be required. These samples are normally presented to the X-ray beam as a powder or solid material with a flat upper surface. A flat upper surface is required in order to prevent peak shift when using Bragg-Brentano geometry with a focussed beam (typically used in theta-two theta configuration with a primary monochromator). Modern XRD techniques now allow non-destructive in-situ analysis of polycrystalline artefacts with irregular surfaces. These are, however, rarely applied to museum artefacts. A preliminary study between the University of Edinburgh and the National Museums of Scotland is investigating the application of such X-ray diffraction techniques for the non-destructive analysis of art works and artefacts. The replacement of the monochromator with a Göbel Mirror produces a parallel beam. This eliminates the need to present a flat surface to the X-ray beam. Hence, sample height is no longer an issue and diffraction patterns can be obtained from samples with variable height. This allows in-situ analysis of the surface layers of any object containing crystalline material, e.g. rocks, metals, ceramics, glass or glazes and plastics. Parallel beam technology also allows the use of grazing incidence diffraction (GID). This technique can be used to provide information from different layers within the surface. Hence we can determine the phase composition of coatings (for example on ceramics, coins and painted artefacts) or alteration layers as well as of the underlying substrate. As the technique is non-destructive the substrate can be analysed without exposure, which would normally involve removing the outer layers. Hence there is no alteration of the artefacts surface. The strength of these non-destructive X-ray techniques for artefact studies within the museum field is being investigated on a range of artefact types, including Islamic tiles, Scottish Medieval coins, glass manufacturing debris and degrading early plastics, for which conventional non-destructive techniques can only provide chemical information. The phase and structural information obtained from parallel beam XRD techniques hence complement and extend other analytical techniques currently used within the museum.

#### OO5.4

##### <sup>27</sup>Al, <sup>29</sup>Si and <sup>23</sup>Na Solid-State NMR Studies of Ultramarine Pigments and their Degradation Products.

Eleonora Del Federico<sup>1</sup>, Wolfgang Schofberger<sup>2</sup>, Sally Pusede<sup>1</sup> and Alexej Jerschow<sup>2</sup>; <sup>1</sup>Mathematics and Science, Pratt Institute, Brooklyn, New York; <sup>2</sup>Chemistry, New York University, New York, New York.

Lazurite, the natural ultramarine pigment and the source of "royal blue", has been a popular choice for painters since the late 13th century when it was introduced to Europe by Marco Polo. Because it was even more precious than gold those who commissioned its use were primarily those who wanted to convey their high status. In addition, Lazurite was "fresco-compatible", as opposed to other blue pigments available at the time, and therefore feasible for usage in lime-mortar environments. From a conservation standpoint, it is important to note that some instances of the pigment fading in alkaline mediums have been reported. Lazurite's synthetic counterpart was first synthesized in 1828 by furnacing kaolin, sodium carbonate and sulfur in an oxygen-free atmosphere. By controlling the furnacing temperature and mixture composition, different colors of the pigment (blue, turquoise, green, violet, pink) became available. Ultramarine pigments are aluminosilicates characterized by a sodalite framework with the generic formula  $[Al_3Si_3O_{12}]^{3-}$  (also known as the "b-cage"). Strong paramagnetic ( $S_3^-$ ,  $S_2^-$ ) and diamagnetic ( $S_4$  or  $S_3Cl$ ) guests are enclathrated inside the cages and are responsible for the color of these pigments. Negative charges are generally balanced by Na cations, which are also inside the cages. Although many studies

have been published about the aluminosilicate framework structure, scarce information is available on the chromophore concentration and occupancy. To better understand the structure, color and fading mechanisms of these pigments, it is necessary to gain insight into the concentration and occupancy of these chromophore species. Solid-state NMR is an ideal technique for the study of these systems as it provides detailed information on the local structure around the observed nuclei. This allows the study of the interaction between guests and their host framework. Good observation of quadrupolar nuclei relevant for these studies (<sup>27</sup>Al and <sup>23</sup>Na) has recently become accessible. This is due to the availability of high-field NMR spectrometers in combination with averaging techniques such as Magic Angle Spinning (MAS) and Multiple Quantum Magic Angle Spinning (MQMAS). In this work, we have applied <sup>27</sup>Al, <sup>29</sup>Si and <sup>23</sup>Na MAS and MQMAS NMR to study several ultramarine pigments and their degradation products under the action of lime mortar. Preliminary data suggests that paramagnetic and diamagnetic guests appear clustered in the sodalite cages. We observe an increase in the number of diamagnetic cages as pigments become violet and pink. NMR studies on the faded pigments suggest the existence of non-chromophore paramagnetic species encapsulated in the b-cages. The identity and relevance of these species to the chromophore degradation mechanisms is discussed.

#### OO5.5

##### Laser Removal of Conservation Treatments.

Kelly Simmons-Potter<sup>1</sup>, Boris Glebov<sup>1</sup>, Pamela Vandiver<sup>2</sup>, Teresa Moreno<sup>3</sup> and Alix Deymier<sup>2</sup>; <sup>1</sup>Electrical and Computer Engineering, University of Arizona, Tucson, Arizona; <sup>2</sup>Materials Science and Engineering, University of Arizona, Tucson, Arizona; <sup>3</sup>Arizona State Museum, University of Arizona, Tucson, Arizona; <sup>4</sup>Optical Sciences Center, University of Arizona, Tucson, Arizona.

It is important that materials, such as adhesives and coatings used in the restoration or conservation treatment of art and artifacts be removable and/or reversible should the need arise. In addition, this removal process must be accomplished without causing surface damage. Laser removal of aged and degraded adhesives and coatings from objects offers the advantage of a non-contact, non-solvent method of cleaning. We have studied laser cleaning by a model system consisting of two common conservation materials, polyvinyl acetate, and acryloid B-17 acrylic resin, that were applied by spin coating onto glass substrates. We will discuss the relationship among optical absorption in PVA and B-17, the laser wavelength, the laser pulse energy and cleaning efficiency. Moreover, we will discuss the impact of our results as we extend our efforts to study the removal of conservation treatments from actual art and artifact surfaces.

SESSION OO6: Architectural Materials: Materials Identification, Technological Studies, and Conservation  
Chair: Robert Tykot  
Wednesday Afternoon, December 1, 2004  
Room 301 (Hynes)

#### 1:30 PM OO6.1

##### Analysis of the Stucco Floors from The Citadel of the

Archaeological Zone of Teotihuacan, Mexico. Luis M. Torres<sup>1</sup>, Manuel Reyes Garcia<sup>1</sup>, Julie Gazzola<sup>2</sup> and Sergio GomezCh.<sup>2</sup>; <sup>1</sup>Instituto de Investigaciones Antropológicas, Universidad Nacional Autónoma de México, México, D. F., México; <sup>2</sup>Zona Arqueológica de Teotihuacan, INAH, México, Edo. de México, México.

Due to the losses of large areas of the "Citadel" stucco floors on the Archaeological Zone of Teotihuacan in the State of Mexico, large amounts of water percolates to the ground during the rainy season. The water impregnates the structures causing severe damages to the temple of "Quetzacoatl" one of the more important buildings of the site, due to the fact that when the water evaporates through the facade, salt efflorescence appears over it, promoting a fast deterioration of the sculptures of the Feather Serpent. The pre-Columbian draining system was rehabilitated and in order to prevent further infiltration of water, and to make even lower the infiltration of water, a possible solution was to complete the floors. To know the composition of the ancient floors, three different samples were taken from the stucco to make a chemical analysis. The stucco is composed of a nucleus made of coarse sand of Tezontle, (a red volcanic slag) and clay, covered by thin layer, some 3 mm thick, made of lime and fine sand. The particles of sand, clay and lime in both layers are joined by an organic adhesive identified by infrared spectroscopy as the sap of nopal, and to help to give more strength to the floors, cotton fibers, identified by its characteristic structure by optical microscopy. The floors are a composite material whose properties were adjusted with selection of the particle size of the aggregates according to the needs of several particular uses. It is the first time that such composite materials and floors have been analyzed and characterized.

### 1:45 PM OO6.2

**Estimation of Elastic Constants of Restoration Mortars, used in on Historic Masonries Restoration Interventions, via Ultrasonic Technique and Correlation to their Mechanical and Microstructure Parameters.** Eleni Aggelakopoulou, Antonia Moropoulou, Asterios Bakolas and Anastasia Odatzidou; Chemical Engineering, Section of Materials Science and Engineering, National Technical University of Athens, Athens, Greece.

Several types of restoration mortars, addressed to restoration interventions of historic masonries were produced, using traditional materials (aerial and hydraulic lime, natural and artificial pozzolanic additives). These mortars are tested by the time of chemical and mechanical stabilization using the following techniques: Ultrasonic technique for the determination of the ultrasonic velocity propagation and the mortars elastic constants (dynamic modulus of elasticity, Poisson ratio) Mercury Intrusion Porosimetry for the microstructure characteristics evaluation (percentage open porosity, bulk density, average pore radius, total cumulative volume, specific surface area). Water immersion tests, Water capillary rising tests for the determination of mortars total cumulative volume accessible to water and their capillary rising coefficient. Conventional mechanical tests for the determination of mortars flexural and compressive strength. The obtained data result to a correlation between the mortars microstructure characteristics and their mechanical strength and furthermore these are correlated to the mortars initial mix design and their chemical composition.

### 2:00 PM OO6.3

**Protection Efficacy and Durability of Fluorinated Acrylic Copolymers Applied on Historical Italian Marbles.** Tommaso Poli and Lucia Toniolo; Sezione di Milano "Gino Bozza", CNR ICVBC, Milan, Italy.

Committing stone protection to polymeric materials started in the sixties but the study and knowledge of the complex and multiple interactions between stone and polymers has been carried out only recently. It is important to note that, together with the factors related to the polymeric system itself, intrinsic properties of the stone substrate, like composition, porosity and crystalline structure, play a relevant role. In the first part of this study (1) we faced the problems related to the efficacy of a stone treatment (film formation, penetration and coating behavior); in this paper the behavior of the applied polymers after thermal and solar simulated UV ageing has been studied and compared. In particular the issues related to stability and durability of two fluorinated acrylic protectives applied on three different Italian marbles, have been investigated. The considered marbles are: Candoglia marble, employed in the building of the Milan Cathedral, Carrara marble, widely used in sculpture and historical architecture and S. Giuliano marble, used in the building of Pisa Cathedral and its famous leaning tower. Specimens of the three quarried stones have been characterized, treated with two new partially fluorinated acrylic copolymers, 2,2,2-trifluoroethyl methacrylate/methyl acrylate (TFEMA/MA) and trifluoromethyl-2,2,2-trifluoroethyl methacrylate/methyl acrylate (HFIMA/MA), and tested according to UNI-Normal Italian protocol. All the measurements including capillary water absorption, static contact angles, colour variation, water vapour permeability and SEM morphological analysis have been carried out before and after a long solar simulated UV ageing of 1500 hours and after thermal ageing. The latter has been carried out at the temperature (50°C) usually reached in the UV chamber, in order to separate and compare the two ageing contributions (photochemical and thermal). The aim of the work is to evaluate the durability of protective effect of the fluorinated copolymers. (1) Appl. Phys. (2004) A 79, 347-351

### 2:15 PM OO6.4

**Producing new stone consolidants for the conservation of monumental stones.** Maria Jesus Mosquera, Physical Chemistry, University of Cadiz, Puerto Real, Cadiz, Spain.

A customary procedure in monumental conservation is the consolidation of decaying stone by the application of commercial products containing tetraethoxysilane (TEOS). These products polymerize within the porous structure of the decaying stone significantly increasing the cohesion of the material. However, TEOS-based consolidants suffer some drawbacks, such as cracking of the network during the drying phase, and significant blocking of the rock pores. These limitations are related to the growth of a dense microporous network of the xerogel inside the stone material, which is typical from TEOS sols. Therefore, the purpose of this paper is to increase porosity of the product by including colloidal particles in the starting sol. I prepared a hybrid colloid-polymer gel using TEOS and a commercial silica colloid. The percentage by weight of silica colloid particles to total silica was 54%. Ethanol and dibutyltindilaurate (DBLT) were chosen as solvent and catalyst, respectively. This

catalyst promotes the gelation at a neutral pH. This catalyst, which promotes the gelation at a neutral pH, prevents stone decay related to acid or basic catalysis. Water was not added because of the environmental moisture is enough to achieve the hydrolysis step. We characterised the properties playing a key role in consolidation. Data were compared with those obtained using several popular commercial products: Wacker OH (Wacker), Tegovakon V (Goldsmith) and Tegovakon V100 (Goldsmith). In spite of the colloidal particles addition, sols exhibited viscosity values close to those of the commercial products, as consequence of their dispersion in ethanol. A gelation time similar to that of commercial consolidants was maintained whereas the sol into closed container was stable over a period of time up to several months. Concerning textural parameters, the addition of colloid permitted to obtain a mesoporous material structure. Moreover, the incorporation of colloid reduced the gel shrinkage. We also evaluated penetration depth and textural and mechanical changes in several consolidated stones. Notably, improving properties were obtained on samples treated with our gel than on commercial consolidants-treated samples.

SESSION OO7: Ceramics, Glass, and Glazes: Materials Characterization, Conservation, and Mechanisms of Degradation

Chairs: Katherine Eremin and Jennifer Mass  
Wednesday Afternoon, December 1, 2004  
Room 301 (Hynes)

### 3:00 PM OO7.1

**Bamiyan Buddhas, Samarkand Tiles and Angkorian Kilns: Craft Knowledge as an Intangible Cultural Property.** Pamela B. Vandiver, Materials Science and Engrg, University of Arizona, Tucson, Arizona.

Reverse engineering past craft technologies involves using the basics of materials science and engineering to a new end: their preservation and continuation. Examples are presented of the tile glaze technology of Samarkand, Uzbekistan, the plaster technology of Bamiyan, Afghanistan and the kiln and firing from Tani, the imperial kiln complex near Angkor Wat in Cambodia.

### 3:15 PM OO7.2

**Understanding Bronze Age Faience in Britain & Ireland.** Alison Sheridan<sup>1</sup>, Andrew Shortland<sup>2</sup> and Katherine Eremin<sup>3</sup>; <sup>1</sup>Archaeology, National Museums of Scotland, Edinburgh, United Kingdom; <sup>2</sup>Research Laboratory for Archaeology and the History of Art, University of Oxford, Oxford, United Kingdom; <sup>3</sup>Conservation & Analytical Research, National Museums of Scotland, Edinburgh, United Kingdom.

Faience beads have been found on around 120 Bronze Age sites in Britain and Ireland, some from burials of cremated bone. Their relationship with Near Eastern and Mediterranean faience has long been debated, and various previous compositional analyses undertaken. Their composition and manufacturing techniques provide vital clues to their origin and use. However their relative scarcity necessitates predominantly non-destructive techniques. A National Museums of Scotland-led international research project is investigating these and other aspects for a Corpus of faience from Britain, Ireland and adjacent parts of mainland Europe. Non-destructive controlled-pressure scanning electron microscopy with energy dispersive microanalysis (CP-SEM-EDS), x-ray fluorescence (XRF) and binocular microscopy provides compositional and textural information without sampling or coating. Examination and wavelength-dispersive electron microprobe analysis of a small number of polished samples provides more accurate compositional and technological information, for comparison with data from non-destructive techniques. Non-destructive CP-SEM-EDS examination and analysis indicates extensive surface alteration, particularly on examples cremated with their owners, with extensive, but patchy, loss of alkalis. In better preserved areas, significant sodium, potassium, magnesium and aluminium indicates a mixed alkali glaze from plant ash, consistent with the use of certain inland plants or seaweed. Most British beads have a blue glaze, sometimes only as remnants, with high levels of copper. In many of these beads, tin is concentrated in discrete areas throughout the glaze. The overall tin content greatly exceeds that likely from using bronze metal as the source of copper, suggesting tin or its oxide was deliberately added. The beads were manufactured on a small-scale, sometimes on a single-bead basis. Various glazing techniques were used, including direct application of a glaze slurry to one or both sides. The beads were fired at 800-1000C. Calcium phosphate particles (some with a spongy, porous appearance resembling bone fragments) were identified on some of the cremated beads. Non-destructive x-ray diffraction is planned to identify the calcium phosphate phase. The calcium phosphate particles were dispersed throughout the surface, often



lodged in cracks or pores. Some beads display obvious signs of heat damage while others, from the same necklace, may not. To investigate this phenomenon further, an experimental cremation of a pig will take place in September 2004. Replica beads, made using local materials, will be placed on a clothed pig carcass and examined by CP-SEM-EDX before and after cremation.

### 3:30 PM OO7.3

**The Analysis of Glazed Stone Sculpture from Kerma, Capital of Ancient Kush (Sudan).** Lisa Ellis and Richard Newman; Conservation and Collections Management, Museum of Fine Arts, Boston, Massachusetts.

This paper summarizes research on a collection of blue glazed, white stone sculpture, excavated from 1913-1916 by a Harvard University/Museum of Fine Arts Expedition. Now in the collection of the Museum of Fine Arts, Boston, the sculptures were unearthed from funeral tumuli at the site of the ancient city of Kerma, the capital of the kingdom of Kush, in today's Sudan. They date from the mid third to mid second millennia B. C., a time during which Kerma was flourishing. Carved from white, opaque quartzite onto which a glaze was then fired, this unparalleled collection of sculpture portrays exclusively animals. There are fragments of two lions, a ram's head, a scorpion and a hawk. The stone substrate varies from friable and dull in appearance to extremely hard and glassy. The surfaces of some of the fragments are covered with sizeable spans of well-adhered glaze, while others exhibit only traces of what were poorly bound glazes. The glazes range in color from dark to light blue to light green. Most of the stones exhibit significant cracks into some of which the glaze has melted during firing. Polished cross sections of glaze and stone substrates were analyzed by scanning electron microscopy/energy-dispersive X-ray spectrometry (SEM/EDS), and estimates of glaze melting points carried out by thermal analysis. The compositions of the glazes then were compared with those of applied glazes found on faience objects also excavated at Kerma, and now found in the collection of the Museum of Fine Arts, Boston. While it has been assumed that the glazing of stone was connected to the manufacture of faience, the exact relationship is not clear. One specific question addressed by the research is whether the stone glazes could have been made from scrapings taken off of glazed faience objects that had been manufactured by the efflorescence method. The research described in this paper aims both to answer specific questions about the glazed stone objects excavated at the site, which have never before been subjected to scientific inquiry, and also attempts to resolve larger issues concerning local technologies and manufacturing practices. Although Kerma has been extensively excavated by both the Harvard University/Museum of Fine Arts Expedition and more recently by the Swiss Archaeological Mission in Nubia, many aspects of life in the ancient city remain mysterious. Its population does not appear to have had a written language and there are many lacunae in the archaeological record. All evidence to date suggesting Kerma as the place of manufacture of the glazed stone sculptures is circumstantial, and some dispute their local origin. The scientific identification of materials, determination of methods of manufacture, and comparison with locally made wares carried out in this paper should help resolve the matter.

### 3:45 PM OO7.4

#### **Prehistoric Obsidian Trade in Corsica (France).**

Robert Howard Tykot, Michael Glascock, Robert J. Speakman, Michel Claude Weiss and Francois Lorenzi; Anthropology, University of South Florida, Tampa, Florida.

Glassy obsidian was widely used in the central Mediterranean during the Neolithic period (ca. 6000-3000 BC). The large island of Corsica has numerous archaeological sites where obsidian artifacts have been recovered, and several hundred were tested to determine their source. Previous studies have identified the Monte Arci region of Sardinia as the most likely source, but in general have not focused on the specific source location and how their usage may have changed over time. Published data for Sardinia now indicate that at least five chemically different Monte Arci sources were available, and that their respective use varied over time and space. More recent use-wear studies specifically correlate this variation with differences in physical characteristics between the sources, i.e. color, transparency, brittleness, and crystallinity. Another factor is the quantity and accessibility of the obsidian sources, which in some cases changes over time. The known distribution of Sardinian obsidian not only to Corsica but to mainland Italy and France makes our knowledge of the actual routes and circumstances of ancient trade in this region of particular significance. In this study, a large number of obsidian artifacts from many different archaeological sites in Corsica were selected for specific source analysis. Laser ablation ICP mass spectrometry was used to minimize destructivity on the artifacts, with the results compared directly to the geological database created using the same method. Along with visual, physical, and density analyses, precise source attributions are made for all of the tested artifacts. The

results obtained are presented here and the geographic and chronological patterns compared with data available from other sites and regions.

### 4:00 PM OO7.5

#### **Technical Study of Pigments and Paintings in Archaeological Ceramics from Northwestern Argentine Region: An Archaeometrical Approach and Implications for Their Conservation Through SEM-EDS.**

Guillermo Adrian De La Fuente, School of Archaeology, National University of Catamarca, Catamarca, Province of Catamarca, Argentina.

The ancient technology involved in the applications of pigments and paintings used by potters to decorate ceramic vessels is one of the most interesting aspects of the ceramic technology in the past. Potters have used in the past several sources (eg. inorganic and organic) to decorate the vessels in order to achieve the colours desired and fix them in the vessels throughout the firing process. In this paper, we present the results of a technological and chemical characterisation of pigments and paintings through the application of Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) analytical technique to ceramics from the Middle Period (ca. 650 AD - 900 AD) at Northwestern Argentine region. The Aguada Portezuelo Ceramic Style The Aguada Portezuelo ceramic style (ca. 650 AD - 900 AD) from Northwestern Argentine region presents a great variation and complexity in the manufactures techniques employed by the ancient potters concerning the surface treatments and the decoration applied to the ceramic vessels. The main aspects related to the manufacture processes involving the shaping and the decoration of these vessels have not been fully investigated at the present. The macroscopic and microscopic (polarizing microscope, 40X-100X) observations done until now allow us to preliminary establish that these ceramic sherds present a very fine-grained and compact ceramic fabric, mainly characterised by the presence of rounded quartz sands, biotite and muscovite as the principal mineralogical constituents. Concerning the decoration one of the highlight characteristics of these ceramics is their marked polychromy, the motifs are elaborated in negative and positive designs, and the colours used range from purple red, reddish, black, white, and yellow, being this latter colour almost unique in the archaeological ceramics from the Northwestern Argentine. Materials and Methods Thirty samples have been selected to perform analyses throughout the application of SEM-EDS. The samples have been selected from several archaeological sites investigated in the Catamarca valley, and they represent the whole variation currently present in the Aguada Portezuelo ceramic type. Samples were analysed after polishing the cross sections of the sherds and coating them with gold. Several spectra and chemical profiles were obtained for each the pigments and slips analysed, as well as for the matrix of the fabric of each sherd. We used a Phillips 500 Scanning Electron Microscope coupled with an EDS (EDAX- system of microanalysis) detector to perform the analyses at the Constituyentes Atomic Centre, Argentine. Additionally, all the samples were analysed by using a polarizing microscope, which give us the opportunity to study the technology involved in the manufacture of these vessels.

SESSION O08: Ceramics, Glass and Glazes: Materials Characterization, Conservation, and Mechanisms of Degradation II

Chairs: Jennifer Mass and Robert Tykot  
Thursday Morning, December 2, 2004  
Room 301 (Hynes)

### 8:30 AM \*O08.1

**The Provenance of Ancient Glass through Compositional Analysis.** Ian Charles Freestone, School of History and Archaeology, Cardiff University, Cardiff, United Kingdom.

In the past, determination of the provenance of ancient glass through materials analysis has been hampered by the absence of a suitable framework within which to interpret the data. Recently archaeological and analytical developments have converged to provide such a framework, the key component of which is the appreciation that glass production was divided between a relatively limited number of primary production sites, making the raw glass from sand and alkali, and a larger number of secondary production sites, where vessels, windows, beads and so on were fabricated. Thus, while we may be unable to source glass vessels to the workshop that made them, we are able to determine the probable source of the raw glass. Focusing upon the Roman glassmaking traditions of the first millennium A.D., the relationship between technology, raw materials and composition is outlined using major element, trace element and isotopic data. Major elements may be used to form characteristic compositional groups. Strontium isotopes indicate the environmental origins of the lime source. Trace elements provide a fingerprint of the geological origins

of the glassmaking sand. Isotopic and elemental data can indicate mixing of materials from different sources, while transition metal colorants, incidentally incorporated through the use of cullet, indicate glass recycling. This approach is used to illustrate the probable origins of glass used in assemblages from several sites dating to between the fourth and ninth centuries A.D. and located from the eastern Mediterranean to northwestern Europe.

#### 9:00 AM OOS.2

**Spectroscopic and Microscopic Investigations on the Decorative Technique and Conservative State of Italian Renaissance Majolica Masterpieces.** Michela Ombelli<sup>1</sup>, Costanza Miliani<sup>2</sup> and Assunta Morresi<sup>3</sup>, <sup>1</sup>Department of Anesthesia, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>2</sup>CNR Institute of Molecular Sciences and Technologies (ISTM), Department of Chemistry, University of Perugia, Perugia, Italy; <sup>3</sup>Department of Chemistry, University of Perugia, Perugia, Italy.

The results of a systematic characterization of the constituents of glazes and pigments used in the manufacture of ceramic objects from the Renaissance period and an evaluation of their states of conservation will be presented. Standard techniques such as SEM-EDX, X-ray fluorescence and optical microscopy, have been employed in the study of the structure and composition of sherds of historical artifacts. In addition to these commonly used archaeometric techniques, non-destructive or micro-destructive spectroscopic techniques including FT-IR, UV-Vis, fluorescence and micro Raman, were developed and applied. We found that the use of spectroscopic techniques can yield valuable information regarding the composition of the samples, especially if coupled with microscopic sampling. The research efforts were mainly directed to the analysis of two ceramic masterpieces: the flooring of the Church of St. Francis in Deruta (Perugia, Italy), dated 1524, one of the most important examples of ceramic floorings in Italy due to the originality of its iconography, with respect to the local coeval pottery production and a majolica altar manufactured by Andrea della Robbia, dated 1490 and conserved at St. Mary of the Angels in Assisi (Perugia, Italy). The yellow decorations, in particular, have been examined using a number of spectroscopic techniques along optical and scanning electron microscopy. The yellow pigment has been identified as lead antimonate, the well-known Naples Yellow. Its use in the course of history seems to be strongly discontinuous, but the diagnostic techniques used previously may not have been adequate. Samples from original masterpieces have been compared with a yellow pigment synthesized in our laboratory, following a Renaissance-era ancient recipe for Naples Yellow. Concordant results have been obtained with FT-IR, UV-Vis reflectance, Raman microscopy, optical microscopy and SEM. It is demonstrated, for the first time, that the micro-Raman technique is very efficacious for an unambiguous identification of the pigment and its firing temperature.

#### 9:15 AM OOS.3

**Raman Spectrometry, a Unique Tool for On-Site Analysis and Identification of Ancient Ceramics and Glasses.** Philippe L. Colomban, LADIR UMR7075 UPMC, CNRS, Thiais, France.

Raman micro-spectroscopy allows remote non-destructive analysis of materials. Our laboratory was one of the first to apply this technique to pigments. Recently we focused our efforts on ancient ceramics and glasses: body and glaze, crystalline and amorphous phases can be identified, including the glaze/glass-colouring nanosized pigments (e.g. in lustre ware, the 1st nano-optic device). Last generation instruments are portable, which allows examination at the museum. In nanostructured, nanocrystalline/amorphous materials (e.g. silicate glass, glaze and most of their pigments), Raman parameters and their multivariable analysis are used to recognize ancient compositions as well as to classify them as a function of their processing temperatures. This overview addresses the procedure (choice of the exciting radiation, control of the Raman resonance, data processing and extraction of pertinent parameters such as the index of polymerization, the different signatures characteristic of lead-based glazes, etc.). Selected glasses from the Punic/Roman empires as well as glazes of various porcelains, celadon, faïences and potteries, representative of the different production technologies used in the Antique, European, Mediterranean, Islamic and Asian worlds were considered. 1. Colomban Ph., Polymerisation Degree and Raman Identification of Ancient Glasses used for Jewellery, Ceramics Enamels and Mosaics, *J. Non-Crystalline Solids*, 323, 180-187, 2003. 2. Liem N.Q., Thanh N.T. & Colomban Ph., Reliability of Raman Microspectrometry in Analysis of Ancient Ceramics: The case of Ancient Vietnamese Porcelains and Celadon Glazes, *J. Raman Spectr.* 33, 287-294, 2002. 3. Colomban Ph., Milande V. & Lucas H., On-site Raman Analysis of Medici Porcelain, *J. Raman Spectr.* 35, 68-72, 2004. 4. Colomban Ph., Sagon G. & Faurel X., Differentiation of Antique Ceramics from the Raman Spectra of their Colored Glazes and Paintings, *J. Raman Spectr.* 32, 351-360, 2001. 5. Colomban Ph.

& Treppoz F., Identification and Differentiation of Ancient and Modern European Porcelains by Raman Macro- and Microspectroscopy, *J. Raman Spectr.* 32, 93-102, 2001. 6. Colomban Ph., Milande V. & Le Bihan L., On-site Raman Analysis of Iznik Pottery Glazes and Pigments, *J. Raman Spectr.* 35, in press, 2004. 7. Colomban Ph. & Truong C., A Non-destructive Raman Study of the Glazing Technique in Lustre Potteries and Faïences (9th-14th centuries): Silver ions, Nanoclusters, Microstructure and Processing, *J. Raman Spectr.* 35, 195-207, 2004. 8. Colomban Ph., Lapis Lazuli as unexpected blue pigment in Lajvardina ceramics, *J. Raman Spectr.* 34, 420-425, 2003. 9. Faurel X., Vandepierre A. & Colomban Ph., Pink Pigment optimization by resonance Raman Spectroscopy, *J. Raman Spectr.* 34, 290-294, 2003.

#### 9:30 AM OOS.4

**Raman Analysis of Ancient Ceramics. Recent Case Studies: Opacification of Medici and of French Soft-Paste Porcelains Glazes; Lapis Lazuli Pigment in Lajvardina Wares; Differentiation Between Iznik and Kutayha Wares; Where was Cassiterite First Used as Opacifier and Cassiterite Key Role in Lustre Preparation?** Philippe L. Colomban, LADIR UMR7075 UPMC, CNRS, Thiais, France.

We demonstrate the potential of Raman spectroscopy as a non-destructive on-site technique for the characterization of ceramics and glasses. Different technologies will often give products of very similar outward appearances (from the visual and sensory points of view), but completely different in their micro/nanostructure. Much information on the process remains written in the sample and the non-destructive Raman analysis of the micro-structure (for ceramics) and nano-structure (for glasses and enamels) offers a way to identify it and, sometimes, to date ancient artefacts. Different Raman signatures are obtained if different technologies were applied to the same starting batch or if a given technology was applied to raw materials processed differently. In this review we address key developments in the course of ceramic history: i) the use of cassiterite for opacification and the invention of the polychrome lustre by Abbasid potters, ii) the invention of the hybrid-paste porcelain by the Duke of Medici and the soft-paste porcelain by the French Manufactures in the eighteenth century, iii) the development of polychrome Iznik fritware and Kutayha wares by Ottoman potters; iii) the use of Lapis Lazuli pigment. We found unexpected results and discuss their consequence. 1. Colomban Ph., Milande V., Lucas H., On-site Raman Analysis of Medici Porcelain, *J. Raman Spectr.* 35, 68-72, 2004. 2. Colomban Ph., Milande V., Le Bihan L., On-site Raman Analysis of Iznik Pottery Glazes and Pigments, *J. Raman Spectr.* 35, in press, 2004. 3. Colomban Ph., Truong C., A Non-destructive Raman Study of the Glazing Technique in Lustre Potteries and Faïences (9th-14th centuries): Silver ions, Nanoclusters, Microstructure and Processing, *J. Raman Spectr.* 35, 195-207, 2004. 4. Colomban Ph., Lapis Lazuli as unexpected blue pigment in Lajvardina ceramics, *J. Raman Spectr.* 34, 420-425, 2003. 5. Colomban Ph., Robert I., Roche C., Sagon G., Milande V., Identification des porcelains tendres du 18 siècle par spectroscopie Raman: Saint-Cloud, Chantilly, Mennecey et Vincennes-Sevres, *Rev. Archeometrie*, 2004, in press.

#### 10:15 AM OOS.5

**Nanosparticles in Lustre Reconstructions.** Peggy Fredrickx<sup>1</sup>, Jo Verbeeck<sup>1</sup>, Dominique Schryvers<sup>1</sup>, Dorian Helary<sup>2</sup> and Evelyne Darque-Ceretti<sup>2</sup>, <sup>1</sup>Physics, University of Antwerp, Antwerp, Belgium; <sup>2</sup>CEMEF, Ecole des Mines de Paris, Sophia-Antipolis cedex, France.

Lustre glazes have a remarkable appearance: the name is derived from their display of a (golden) metallic lustre or sheen, applied to a white substrate glaze made opaque by SnO<sub>2</sub> crystals. They appear for the first time in Persia in the 9th century. Following the expansion of Arabic culture they were also fabricated in Spain from the 12th century on. The lustrous effect is due to the surface plasmon resonance of metallic nanoparticles in the glaze. More specifically, it becomes ever more clear that the displayed colour cannot be described only by the quantitative composition of elements or element ratios, but that it also depends on the micro- and nanostructure of the lustre layer. Therefore, Transmission Electron Microscopy (TEM) is crucial to the understanding of these materials. The materials investigated here are samples of two objects, slightly different in colour and made by a contemporary potter in Granada, Spain, working in the ancient style in an attempt to recreate the ancient manufacturing procedures and lustres. The first object has a design with a brownish golden colour while the second one yields a classic golden lustre. These are two of the wide range of colours and hues that appear in ancient lustre glazes found in several sites around the Mediterranean. Both materials were the subject of different investigations with a variety of techniques in order to get a profound materials characterisation of both samples. In the present contribution, the nanoscale distribution of copper and silver particles is clarified by recording EDX maps with the JEOL 3000F TEM-STEM apparatus, operated at 300kV. A 0.5nm analytical probe was used in combination with the HAADF detector. These

maps confirm the earlier assumptions that samples of the first object display a nanolayered structure: under the transparent particle-free top layer, there is a very dense layer of silver nanoparticles, mostly smaller than 15 nm in diameter. Under this layer, there is an increase in copper particles. These particles are larger, mostly around 20 nm in diameter. Most particles consist only of silver or copper, although some give the impression to be at least partially mixed. The EDX maps also show that there is less sodium in the top of the glaze layer, as expected because of the ion exchange mechanism with which the ions finally forming the particles are brought into the material. The resulting colour of this sample is brownish gold. The golden colour is caused by the upper layer of silver particles. Since the layer is very dense most of the incident light is reflected off this top layer, and this is the main contribution to the overall colour. However, the copper will contribute an undertone of red, which is finally seen as the brown. The second material contains a similar silver layer as the first one but less copper and no special copper spatial distribution, which confirms the more classic golden colour.

#### 10:30 AM OOS.6

##### Use of Differential Scanning Calorimetry for Estimating the Firing Temperature of Archeological Pottery.

Adriana Giordana<sup>1</sup>, Claude Evan Peacock<sup>2</sup>, Michael J. McCarthy<sup>1</sup>, Konstantin Guilbeau<sup>3</sup>, William Gene Ramsey<sup>4</sup>, Paul F. Jacobs<sup>2</sup> and Joe D. Seger<sup>2</sup>; <sup>1</sup>DIAL, Mississippi State University, Starkville, Mississippi; <sup>2</sup>Cobb Institute of Archaeology, Mississippi State University, Starkville, Mississippi; <sup>3</sup>College of Veterinary Medicine, Mississippi State University, Starkville, Mississippi; <sup>4</sup>Earthstone, LTD, Plano, Texas.

Digital Scanning Calorimetry (DSC), a thermal characterization technique, can be used to rapidly obtain a rough upper estimate of the firing temperature of archeological pottery as well as some indication of its composition. The theory is based on the fact that some phase changes and decomposition of compounds that occur when a material is heated at a specific temperature are irreversible processes. Thus, when pottery is fired, some changes occurring at or below the firing temperature will occur, while other changes occurring at higher temperature will not. If the pottery is reheated, only reversible changes will occur below the firing temperature, while irreversible changes will be observed above the firing temperature. In our technique, a sample of archeological pottery is heated at 1400 °C, cooled down, and reheated again. The two curves are then compared. Since the response of a sample is depending also on its composition, the curves during the two heating cycles allow to point out differences in process and composition between different sherds, potentially separating local and imported pottery. The validity of the technique was evaluated by a blind test in which 35 tiles fired at different temperatures were analyzed without knowing their firing point, and by analysis of known local and import samples.

#### 10:45 AM OOS.7

##### Morphological and Chemical Analyses of Manganese Dioxide Accretions on Archaeological Mexican Ceramics.

Caitlin Rose O'Grady, Materials Science and Engineering, University of Arizona, Tucson, Arizona.

Analysis of West Mexican ceramics in the collection of the Department of the Arts of Africa, Oceania and the Americas at the Metropolitan Museum of Art has preliminarily established five different morphological types of manganese dioxide (MnO<sub>2</sub>) accretions resulting from a combination of bacterial and weathering activity in a post-depositional context, as well as other processes. Microchemical spot tests, x-ray diffraction (XRD) and Raman spectroscopy proved inconclusive in the identification and differentiation of the five morphologies; whereas, optical microscopy, scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDS) and x-ray fluorescence (ND-XRF) were successful. Accretion morphology and substrate characteristics, together, suggest scenarios for the mechanism of formation and offer a qualitative tool for authentication. More extensive research and analysis of accretions has been conducted on the Casas Grandes collection at the Arizona State Museum, University of Arizona, as part of the comprehensive conservation survey conducted through the Save America's Treasures Pottery Project. Initial results from the survey have helped to confirm and modify preliminary research, as well as identify previously undocumented surface phenomena including preferential development of MnO<sub>2</sub> accretions on manganese based paints and accretion development along surface tide lines.

#### 11:00 AM OOS.8

##### Understanding Glass Deterioration in Museum Collections through Raman and SIMS analysis.

Laurianne Robinet<sup>1,4</sup>, Sarah Fearn<sup>2</sup> and Katherine Eremin<sup>3</sup>; <sup>1</sup>Centre for Materials Science and Engineering, School of Engineering and Electronics, University of Edinburgh, Edinburgh, United Kingdom; <sup>2</sup>Department of Materials, Imperial College, London, United Kingdom; <sup>3</sup>Conservation &

Analytical Research, National Museums of Scotland, Edinburgh, United Kingdom; <sup>4</sup>Laboratoire de Dynamique Interactions et Reactivite, CNRS, Thiais, France.

A significant percentage of 19th century glass within the National Museums of Scotland is compositionally unstable. Analysis of the glass, corrosion products and environment indicates deterioration results from inherently unstable glass compositions, fluctuations in relative humidity (RH) and high levels of organic pollutants. However, the mechanisms remain poorly understood. Detailed investigation is required to understand the chemical and physical changes, the phase transformations and the best preservation strategies. The current project involves simulation experiments on replica glass to elucidate the corrosion mechanisms and transformations between corrosion phases. The effects of different pollutant gases (formic acid, acetic acid, formaldehyde and carbon dioxide) and the influence of RH and light on selected glass compositions, close to those of unstable museum glass, are investigated. Raman spectroscopy and low energy secondary ion mass spectrometry (LE-SIMS) are used to investigate the chemical and physical changes within the glass surface as corrosion proceeds. The two techniques are complementary, with LE-SIMS identifying nanoscale chemical changes in the surface, while Raman spectroscopy identifies micron-scale structural changes. Raman spectroscopy is also used to identify the corrosion products and investigate phase transformations with time and changing relative humidity. A combination of LE-SIMS, electron microprobe analysis and scanning electron microscopy is used to quantify the glass composition and examine chemical zoning of the altered surface. Two series of artificial corrosion experiments were undertaken. The first series was exposed to different pollutants at ambient conditions for 4 weeks. The glass surface was analysed by LE-SIMS, with Na, Al, Si, K and Ca followed as a function of depth to measure the depletion region, defined as the distance from the surface to where the SIMS signals become constant and represent the bulk glass composition. The depletion depths varied from 93 to 550 nm. Depletion depths were greater with light than without light for the same pollutant and greater with CO<sub>2</sub> and organic acids than H<sub>2</sub>O. In the second series, the same glass composition was exposed to identical pollutants (except for CO<sub>2</sub>) in the dark for 4 weeks at 100% RH and 60 °C. Micro-Raman spectroscopy was used in-situ to measure the depletion depth, defined as the minimum depth at which the spectrum of unaltered glass was measured. Depletion depths ranged from 3 to 17 μm and followed the same trend as measured on the ambient samples by LE-SIMS. These preliminary results show the effects of environment on depletion depths and help indicate which atmospheres are most detrimental to unstable glass. Work is continuing with longer ageing times and additional conditions to increase understanding of glass corrosion. This is essential for museums to understand the optimum environment for storage and display of vulnerable glass artefacts.

Thursday, December 2, 2004  
1:30 PM - 5:00 PM

#### LABORATORY VISITS

Museum of Fine Arts,  
Boston Scientific Research Laboratory,  
Harvard University Art Museum Straus  
Center for Conservation

Friday, December 3, 2004  
8:30 AM - 5:00 PM

#### ONE DAY WORKSHOP "COLOR FROM STRUCTURE"

MIT Glass Lab in the  
Materials Science Department

This workshop will present neriage ceramic, mokume metal and millefiori glass processes in which color is imparted by compositional and microstructural manipulation rather through various coating or surface treatment technologies.