SYMPOSIUM OO
Materials Issues in Art and Archaeology VII

November 30 - December 3, 2004

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* Invited paper
SESSION 001: Metals: Archaeometallurgy, Degradation, and Conservation
Chair: Pamela Van Dyke
Tuesday Morning, November 30, 2004
Room 301 (Hynes)

8:30 AM INTRODUCTORY REMARKS

8:45 AM 001.1
Prehispanic Metallurgy in Michoacan, Mexico.
Blanca Estela Maldonado1, Paul R. Howell2 and Thilo Rehren3;
1Anthropology, Penn State University, University Park, Pennsylvania;
2Materials Science and Engineering, Penn State University, University Park, Pennsylvania;
3Institute of Archaeology, University College London, London, United Kingdom.

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 Itziparatzico, 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 excavation at Itziparatzico 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 important technology that used sulfuric 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 001.2
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 expertise, 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 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 001.3
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 provides 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 001.4
Optical Profilometry as a Non-Destructive Technique to Quantify Engraving on an Aztec Astrolabe, Brian Dale Newbury, M. R. Norris 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 Arsenus 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 predicting eclipses. 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 micron, 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 scientific instrument workshops. The results are compared to similar engravings on a later period, undated and unsigned, Islamic astrolabe tymanum; and modern brass engravings performed by the investigators.

10:15 AM 001.5
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 timescales of the order of 200 years. We will present our experimental 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 001.6
The Role of /FeOOH in the Corrosion of Archaeological Iron, David Edward Watkinson and Mark Tudor Lovis; 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-extraction 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 ineffective. Inhibitive systems, such as 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 desalination has been employed to preserve 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 akaganeite (FeOOH) and its role in the corrosion of archaeological iron. As iron corrodes in chloride rich environments FeOOH may form as a...
corrosion product. Using a climatic chamber the hygroscopic properties of FeOOH are examined and its contribution to the corrosion of iron in a wide range of humidities is studied. Results offer information on the "no-corrosion" relative humidity for mixtures of FeOOH and iron powder, as well as corrosion rates of iron at various relative humidities above this value. 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 FeOOH causes less corrosion than unwashed FeOOH. An essay of 25 years old FeOOH enabled comparison of its corroded morphology with that of this compound with respect to FeOOH. Collation of these results provides an overview of the role of 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 O01.7 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 recognized 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, electrochemical treatments have been used 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 treatments. The results of these investigations allowed the discernment of separate stages of surface corrosion. The portrait was found to be built up using a complex sequence of preparation, drawing and painting 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.

2:15 PM O02.3 The Technological Study of Icons Originating from South-Eastern Poland from the 15-17th Century. Ewa Pancezk 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 15-17th centuries. 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 comparison of compositional, iconographic and stylistic features. 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 multi-layer 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 enabled 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 Roszow 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 (LMAAES). 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. Since some icon 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, complementing a chemical and physical supply of information on the microsamples (ca. 1mg). The results of technological and materials research works are confronted with the knowledge on various artistic workshops, helping to attribute them in time and the reconstruct their history. The development of
Fiber optics reflectance spectroscopy (FORS) in the ultraviolet and visible range enable 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 cm²) 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 blue, or ultramarine.

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 intersection at 1300-1400 nm. Although the combination of these two bands makes it difficult to identify the clay minerals, these features are present in all the investigated areas, it is reasonable to suppose that clay was used as a preparatory layer together with gesso and/or lead white, as has 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 characteristic carboxyl band was identified at 1700-1780 cm⁻¹ typical of aged oils [2].


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 borsilicate monochromatic optic to focus the incident beam onto the sample and a commercial borsilicate polycapillary lens to collect the fluorescence light. This technique provides spatial and compositional maps of the few 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. A second set of experiments, since the two 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 performed both from the paint 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.

Atomic Oxygen Treatment and Its Effects on a Variety of Artist’s Media. Sharon Miller1, Bruce Banks1 and Deborah Waters2; 1Electro-Physics, NASA Glenn Research Center, Cleveland, Ohio; 2QSS 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 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.

Laser Cleaning of 15th Century A.D. Wax Votive Images from St. Peter’s Cathedral, Exeter, England. Teresa Moreno,2,3; Costanza Cucci1, Cecilia Frosinini2, Marcello Picollo1, Simone Pocquin1 and Bruno Radianti1. 1Structure of Matter & Spectroscopy, CNR, Florence, Italy; 2Opificio delle Pietre Dure, Florence, Italy.

A rare collection of cast votive images (ex-votos) made of beeswax was found during the creation of a screen above the tomb of Bishop Edmund Lacy in the Cathedral of St. Peter in Exeter, England. Some of these fragmentary, aged, and blette waxes, dating to the late 15th to early 16th centuries A.D., served as the basis for further test and analysis of the effects of atomic oxygen treatment has been investigated as an unconventional technique to clean the surfaces of works of art. 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.
The mechanical properties of artists’ acrylic paints were investigated under controlled amounts of aqueous additive leaching in order to identify changes caused by cleaning techniques. 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 CC34 as a binder and duplicate artists’ acrylic paints from the 1960’s to the 1990’s. Strength and stiffness values were obtained through uniaxial 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 aged, 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 water content. The temperature was lowered to the Tg 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 additional leaching and the 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 0%. Paints from which the water-soluble additives were removed were as responsive to RH as the control samples.

 SESSION 03: Paintings: Technical Studies, New Diagnostics and Conservation Treatment II  
 Chair: Alison Murray  
 Wednesday Morning, December 1, 2004  
 Room 301 (Hynes)

8:30 AM 003.1  
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 study the effects of conservation treatments on old paintings. 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 CC34 as a binder and duplicate artists’ acrylic paints from the 1960’s to the 1990’s. Strength and stiffness values were obtained through uniaxial 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 aged, 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 water content. The temperature was lowered to the Tg 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 additional leaching and the 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 0%. Paints from which the water-soluble additives were removed were as responsive to RH as the control samples.

9:15 AM 003.3  
Chemical and Physical Stability of Artists’ Acrylic Emulsion Paints, Marion F. Mecklenburg and Charles S. Tumosa; SCMRE, Smithsonian Institution, Suitland, Maryland.

Acrylic latexes have been used in paint formulations since the 1950s, but relatively few studies on the stability of these materials have 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 paints and pigmented paints largely depend on the presence of many different additives (surfactants, thickeners, stabilizers, anti-foam 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 FTIR-ATR, Py-GC-MS and 1H NMR, and acrylate units and pigments were quantified by thermogravimetric analysis and mass 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 behavior 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 over time. Another aspect is the stability of the acrylic component, which is largely controlled by the reactivity of the alkyl side group. The photosensitivity of aliphatic acrylic polymers is generally very high, but under accelerated photo-oxidative conditions they undergo both cross-linking 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 both cross-linking leading to the loss of ester groups and formation of tertiary microcradicals, 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 003.4  
An Investigation of the Chemical Changes of Artists’ Acrylic Emulsion Paints When Exposed to Water, Rebecca Plesiger1, Alison Murray2, Simon Hesp3 and Oscar Chiantore4; 1Engineering Chemistry / Art Conservation, Queen’s University, Kingston, Ontario, Canada; 2Art Conservation, Queen’s University, Kingston, Ontario, Canada; 3Chemistry, Queen’s University, Kingston, Ontario, Canada; 4Dipartimento di Chimica IFM, Universita 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. The different acrylic binders 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 (Rhophex AC-294). 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), thermal-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 water-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
films, since they act not only as emulsion stabilizers, but also as sample size must be quite small. Textile fabric residues found in the system. In this way, ICP-MS can help explain Max Saltzman's dictum that were original to the mordanting system can be detected. Thus, to the great sensitivity of the method, impurities and contaminants provide too much precision, leading to some confusion as to which problematic. In approaching archaeological material where the fiber or substrate. Different cultures and different produced problems with the detection of chromium mordants. For production (cassiterite content, processing temperature). The main Raman signatures of the lustre film is assigned to oxide playa key role in displacing the Ag,Ag+ and Cu+,Cu++,Cu+++ ions (50-100 cm⁻¹ peaks). The additional low wavenumber features could be due to the Ag (or (Agₙ)m⁺ ) nanoclusters mentioned above. The lustre colour arises from the combination of iridescence (diffraction) and absorption/diffusion. Raman study of the lustre films of different ceramics excavated from Fustat (near Cairo, Egypt, 11-12th) or from the Silk Road (Termes, 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 AI 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⁺ and Cu⁺ ions (50-100 cm⁻¹ peaks). The additional low wavenumber features could be due to the Ag (or (Agₙ)m⁺ ) nanoclusters mentioned above. 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⁺ and Cu⁺,Cu++,Cu+++ 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) 157-170. Ph. Colomban, C. Truong J. Raman Spectrosc. 35 [5] (2004) 155-207.

O05.2 Electron Microscopy Investigations of Ancient Coins from The Brazilian Colonial Period. Guadalupe Nascimento Campos1, and Guilermo Solozanno1, 1Department of Materials Science and Metallurgy, PUC-Rio, Rio de Janeiro, RJ, Brazil; 2Department 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 cover 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 non-conservation years. To better understand the structure of mineral sediments possible. A detailed microanalytical analysis, coupled with spectroscopic SEM and TEM measurements, allows one to conclude that how was made of copper from European origin. The equi-axial microstructure of Cu matrix. This suggests 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.

**OOO-3**
Non-Destructive X-ray Diffraction of Museum Artefacts.
Nicola Molitor, 1 Katherine Eremiya 2 and Christopher Hall 2; 1 Centre for Materials Science and Engineering, The University of Edinburgh, Edinburgh, United Kingdom; 2 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). XRD techniques allow non-destructive in-situ analysis of polycrystalline artefacts with irregular surfaces. These are, however, rarely applied to museum artefacts. A preliminary study of 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 glasses 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, metal and paint layers) 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, Egyptian pots, glass vessels and pendants. For conventional XRD methods only, 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 in the museum.

**OOO-4**

27Al, 29Si and 23Na Solid-State NMR Studies of Ultramarine Pigments and their Degradation Products.
Eleonora Del Federico, 1 Wolfgang Schöberger, 2 Sally Pueschel 1 and Alejandra Jeschke 2; 1Mathematics and Science, Pratt Institute, Brooklyn, New York; 2Chemistry, 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. 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 damage to the temple of “Quetzalcoatl” one of the most 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 drainage 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 cover the floors. To know the composition of the stucco 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 Tzontle, (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 are affected with variation of the particle size of the aggregates according to the needs of particular uses. It is the first time that such composite materials have been analyzed and characterized.
1:45 PM 006.2  
Estimation of Elastic Constants of Restoration Mortars, used in on Historical Masonries Restoration Interventions, via Ultrasonic Technique and Correlation to their Mechanical and Microstructure Parameters. Eleni Aggelakopoulou, Antonios Marios Kossackou, Vassilios Katsarou, Giorgos Balidakis;  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 characterization (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 were carried out 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.

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 crystallographic 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 polymeric systems 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 trifluoromethylethyl-methacrylate/methyl acrylate (HFIMA/MA), and tested according to UNI-Normal Italian protocol. All the mortars were characterized with x-ray absorption, contact angles colours, light absorption and contact possibility analysis. Mercury Intrusion Porosimetry for the microstructure characterization (percentage open porosity, bulk density, average pore radius, total cumulative volume, specific surface area) and their capillary rising coefficient. Conventional mechanical tests were carried out 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 006.3  
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.

Producing new stone consolidants for the conservation of monumental stones. Maria Jesus Moquin, 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-based consolidants. Therefore, the purpose of this paper was 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 TEOS (DBLT) was 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. TEOS 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 containing tetraethoxysilane (Wacker OH V, Tegovak V, Tegovak V100 and Tegovak 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 gellation 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.

3:15 PM 007.1  

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 Tain, the imperial kiln complex near Angkor Wat in Cambodia.

3:15 PM 007.2  
Understanding Bronze Age Faience in Britain & Ireland. Alison Sheridan. 1 Andrew Shortland 2 and Katherine Eremia 3.

1 Archaeology, National Museums of Scotland, Edinburgh, United Kingdom; 2 Research Laboratory for Archaeology and the History of Art, University of Oxford, Oxford, United Kingdom; 3 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 burial of cremated bone. Their relationship with Near Eastern and Mediterranean faience has long been debated, and various previous compositional analyses undertaken. Their composition and glazing 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 alunites. In better preserved areas, significant sodium, potassium, magnesium and aluminium indicate a mixed alunite 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. These 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 800-1000°C. 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, an experimental cremation of a pig took 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 007.3

This paper summarizes research on a collection of blue-glazed, white stone sculptures from 1935-1936 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 Middle Period (ca. 650 AD - 900 AD) to the Kingdom of Kush, in today's Sudan. They date from the 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 glossy. The surfaces of some of the fragments are covered with sizeable spans of well-adhered glazed, 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 examined by scanning electron microscopy/energy-dispersive X-ray spectrometry (SEM/EDS), and estimates of glaze melting points carried out by thermal analysis. The composition of the glaze has been then compared with the composition of specific 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 the 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 007.4
Prehistoric Obsidian Trade in Corsica (France). Robert Howard Tykot, Michael Glascoc, 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 the material 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 comparing this variation with differences in physical characteristics between the sources, i.e. color, transparency, brittleness, and crystallinity. Another factor is the quality and accessibility of the obsidian sources, which in some cases changes over time. The knowledge of Sardinian not only by 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 were excavated from 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. New elemental and density values were determined. Moreover, the source attribution is based on a database that was only recently developed. The results obtained are presented here and the geographic and chronological patterns compared with data available from other sites and regions.

4:00 PM 007.5
Technical Study of Pigments and Paintings in Archaeological Ceramics from Northwestern Argentina: 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 Argentina 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 manufacturing techniques employed by the ancient potters concerning the surface treatments and the decoration applied to the ceramic vessels. The main aspects related to the manufacturing processes involving the shaping and the decoration of these vessels has not been fully investigated at the present. The microscopic and microscopic (polarizing microscope, 40X-100X) observations done until now allow us to preliminary establish that these ceramic sherds present a very fine-ground texture 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 polychromy of the fabrics 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 variety currently present in the ceramic type of the Aguada Portezuelo Ceramic style. The selected 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. The primary object of this study was to study the technology involved in the manufacture of these vessels.

SESSION 008: 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 008.1
The Provenance of Ancient Glass through Compositional Analysis. 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 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.
Transmission Electron Microscopy (TEM) is crucial to the identification and characterization of ceramic artifacts. Since the turn of the twentieth century, advancements in TEM technology have facilitated the study of the structure and composition of sherds (fragments) of antique ceramics. This is particularly true for those from the eastern Mediterranean to northwestern Europe.

The results of a systematic characterization of the constituents of glasses and pigments used in the manufacture of ceramic objects from the Renaissance period and beyond, or in other contexts such as Mediterranean, Islamic, and Asian worlds, have been compared with a yellow pigment identified with the aid of SEM-EDX, X-ray fluorescence, and optical microscopy. We have employed in the study of the structure and composition of sherds of antique ceramics from the Raman Spectra of their Colored Glazes and Pigments.

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 described directly addressed the specific questions of interest: the dating of the eastern Mediterranean to northwestern Europe.

We present the results of a systematic characterization of the constituents of glasses and pigments used in the manufacture of ceramic objects from the Renaissance period and beyond, or in other contexts such as Mediterranean, Islamic, and Asian worlds. The yellow pigment has been identified as lead azurite, confirming historical art documents.

The results of a systematic characterization of the constituents of glasses and pigments used in the manufacture of ceramic objects from the Renaissance period and beyond, or in other contexts such as Mediterranean, Islamic, and Asian worlds, have been compared with a yellow pigment identified with the aid of SEM-EDX, X-ray fluorescence, and optical microscopy. We have employed in the study of the structure and composition of sherds of antique ceramics from the Raman Spectra of their Colored Glazes and Pigments.
maps confirm the earlier assumptions that samples of the first object display a layered structure: under the transparent particle-free top layer, there is a very dense layer of silver nanoparticles, mostly smaller than 15nm in diameter. Under this layer, there is an increase in copper particles. These particles are larger, mostly around 20nm in diameter. Most particles consist only of silver or copper, although some grains are unusually large and 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 that sample is brownish gold. The glaze 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 underlying red or reddish brown or brownish orange. 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 Q08.6
Use of Differential Scanning Calorimetry for Estimating the Firing Temperature of Archeological Pottery

Afrinna Giordan3, Claude Evan Peacock2, Michael J. McCarthy1, Konstantin Guibbeau3, William Gene Ramsey4, Paul F. Jacobs2 and Joe D. Sager4, 1DIAL, Mississippi State University, Starkville, Mississippi; 2Cobb Institute of Archaeology, Mississippi State University, Starkville, Mississippi; 3College of Veterinary Medicine, Mississippi State University, Starkville, Mississippi; 4Earthstone, 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 temperatures will not. If the pot is cooled down and 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 Q08.7
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 (MnO2) 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 effort conducted through the Smithsonian’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 MnO2 accretions on manganese based paints and accretion development along surface tide lines.

11:00 AM Q08.8
Understanding Glass Deterioration in Museum Collections through Raman and SIMS analysis

Laurianne Robinet1,4, Sarah Fearn2 and Katherine Eremia3; 1Centre for Materials Science and Engineering, School of Engineering and Electronics, University of Edinburgh, Edinburgh, United Kingdom; 2Department of Materials, Imperial College, London, United Kingdom; 3Conservation & Analytical Research, National Museums of Scotland, Edinburgh, United Kingdom; 4Laboratoire 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 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 glass 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 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 550nm. Depletion depths were greater with light than without light for the same pollutant and greater with CO2 and acidic ionic than H2O. In the second series, the same glass composition was exposed to identical pollutants (except for CO2) 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 between 9 to 17um 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, 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 than through various coating or surface treatment technologies.