EUROPEAN
MATERIALS RESEARCH SOCIETY

Strasbourg (France)

E-MRS Spring Meeting 2003
June 10 - 13, 2003

SYMPOSIUM O

Materials aspects of art characterization, conservation & restoration

Symposium Organizers:

Giuseppina Padeletti, CNR Monterotondo (Roma), Italy

Michel Menu, C2RMF, LOUVRE, Paris, France

Pamela Vandiver, Smithsonian Center, Suitland, USA

Michael Stuke, MPI, Goettingen, Germany

Symposium Support:

CNR Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate II"
CNR Istituto per lo Studio dei Materiali Nanostrutturati

Papers will be published in Applied Physics A

E-MRS 2003 SPRING MEETING

SYMPOSIUM O

Tuesday, June 10, 2003 — Morning
Mardi 10 juin 2003 — Matin

08:45 WELCOME
G. Padeletti

Session I: Ceramics/glazes 1
Session chair: M. Menu

O-I.1 9:15 -Invited HEAVEN AND EARTH, MADONNE COL BAMBINO AND RUSTIQUES FIGULINES: RENAISSANCE MASTERPIECES IN GLAZED TERRACOTTA

Anne Bouquillon, Centre de Recherche et de Restauration des Musées de France – UMR CNRS 171, 6 rue des Pyramides, 75041 Paris cedex 01, France

Two main artists influenced the art of the ceramic during the Renaissance : Luca della Robbia in Italy (dates) and Bernard Palissy in France (dates).
Through the study of their productions we aimed to enlighten their improvement to the terracotta techniques as well as the possible influence of della Robbia to Palissy's researches. Most of the della Robbia glazed sculptures we studied are exhibited in different French museums, especially in the Louvre. Some are well attested pieces kept inside Italian collections. Luca della Robbia, originally sculptor on marble, invented again glazing on terracotta sculptures. He transmitted his knowledge to his disciples ; they mainly used one kind of paste, very calcareous, which physical and chemical characteristics are perfectly in accordance with tin-lead glazes. Those glazes were coloured in bulk with traditional metallic oxides : cobalt, manganese, copper, lead antimoniate... Palissy is reported fascinated by della Robbia works, he tried all along his life to bring to light the secrets. Nevertheless, the study of his artefacts discovered in the Louvre excavations during the 1980's proves that Palissy was a real inventor. Not only for the renewal of the themes but also for the working of the matter : mixed earths, use of coloured slips. During his experimentation, he probably found new properties of some chemical elements, for example tin, and he was successful in reproducing transparent, as well as opaque and opalescent glazes

O-I.2 9:55 -Invited- CHEMICAL AND MINERO-PETROGRAPHIC CHARACTERISAT ION OF A COLLECTION OF DIFFERENT TYPOLOGIES OF GLAZED POTTERY FOUND IN SICILY (ITALY)

Ignazio L. Fragalà, Dipartimento di Scienze Chimiche, Università degli Studi di Catania, V.le A. Doria 6, 95125 Catania, Italy

A large amount of ceramic’s fragments with painted surfaces and manufactured from tenth to nineteenth century AD, have been analysed using Scanning Electron Microscopy-Energy Dispersive Spectrometry, Optical Microscopy and X-Ray Diffraction. All the handicrafts, attributed to Italian and Spanish workshops, have been excavated in different Sicilian sites including Siracusa, Caltagirone, Sciacca, Piazza Armerina.
Based on different stylistic typologies a selected number of ceramic bodies and glaze coatings of these shreds have been characterised mineralogically and chemically. Microstructures and morphologies have been studied as well. The perspective of this wide body of activities has been the identification of ceramic reference groups for each typology of medieval and post-medieval Sicilian pottery. There is clear evidence that the attribution of these ceramics to specific production sites or workshops often remains ambiguous when based either on stylistic considerations or on macroscopical observations of painting techniques, shapes of ceramic bodies and stilema. Chemico-physical supports are, therefore, required to identify production centres or manufacturing techniques. The present results show remarkable differences between the various examined pottery productions depending on typologies and locus of excavation. The comparison of minero-petrographic features, manufacturing techniques, firing conditions have been successfully used for provenance studies.

O-I.3 10:35

RAMAN SPECTROMETRY, AN UNIQUE TOOL TO ANALYZE AND CLASSIFY ANCIENT CERAMICS AND GLASSES

Ph. Colomban, LADIR-UMR 7075 CNRS & University Pierre-et-Marie-Curie, 2 rue Henry-Dunant, 94320 Thiais, France

Raman scattering is a unique tool providing information on the composition, structure and short-range order of matter. Last generation of instruments is portable which allows examination in museum, on site, etc. This paper gives an overview of the effective and potential advantages of the Raman spectrometry technique to analyse ancient ceramics and glasses. Selected glasses as well as porcelains, celadons, faiences and potteries with various glazes, enamels and paintings, representative to the different production technologies used in the European, Mediterranean, Islamic and Asian worlds were studied by non-destructive macro- and micro-Raman spectroscopy. Their identification is based on the study of the Raman fingerprint of crystalline and glassy phases. Extracting some parameters from the Raman spectra of glass/glaze allows their classification as a function of composition and/or temperature processing. Special attention is given to the spectra of amorphous and colouring phases (pigment) that enable the easy discrimination between e.g. soft- and hard-paste porcelains of different productions, as well as between original and copies, etc.

10:55 **BREAK**

Session II: Ceramics/glazes 2

Session chair: J. Mass

O-II.1 11:15 -Invited-

SOME ASPECTS OF THE CHARACTERIZATION OF DECORATIONS ON CERAMIC GLAZES

J.P. Pérez-Arantegui, Dep. Analytical Chemistry, University of Zaragoza, 50009 Zaragoza, Spain

>From the Antiquity, glazes have been one of the techniques used for decorating ceramics. Potters took advantage of the physical properties of these materials to improve the quality of the pot, but they especially used optical properties of glazes to obtain an appearance or some characteristic effects that had commercial success. This is why it is important to know the reasons of the visual appearance of glazes in their characterization.

Some aspects of the characteristics of glazes, as composition (alkaline, high-lead or lead-alkaline glazes), transparency and opacity, colour, in-glaze and on-glaze decorations (pigments and metallic lustre), have been studied in order to understand the final appearance, and consequently to know also the materials used in glaze production, the processes followed and its technological evolution.

O-II.2 11:55

PRODUCTION OF GOLD AND RUBY-RED LUSTRES IN GUBBIO (UMBRIA-ITALY) DURING THE RENAISSANCE PERIOD

G. Padeletti, CNR-ISMN, cp 10, 00016 Monterotondo Staz., Roma, Italy, P. Fermo, Dip. Chim. Inorg. Met. e An., University of Milan, Via Venezian 21, 20133 Milano, Italy

Aim of this work is to gain a further insight into the knowledge of the production process of lustre decorated ancient majolicas. Lustre is a sophisticated technique employed in the decoration of majolicas, used in Central Italy during Renaissance period. It consists of a beautiful iridescent gold or ruby-red like thin metallic film, containing silver, copper and other substances and obtained in a reducing atmosphere on a previously glazed ceramic. Nowadays it is not possible to replicate the outstanding results obtained by the ancient ceramists, since the original recipes were lost. It seems quite interesting to study the lustre production technology by means of the analytical techniques now employed for advanced research on materials (XRD, ICP-OES, TEM-EDX-SAED and UV-Vis). In this work, we have focused our attention on ceramic fragments decorated with both gold and ruby-red lustre, which was difficult to obtain due to complex reduction conditions required and which was a prerogative of Gubbio production. The two lustre colours differ for the nanostructure as well as for the chemical composition. The presence of bismuth was disclosed and it was ascertained to be a distinctive feature of the Italian production.

O-II.3 12:15

HOW THE HYPOTHESIS OF THE BISMUTH KNOWLEDGE DURING RENAISSANCE IS STRENGTHENED BY THE EMPLOYMENT OF THIS ELEMENT IN ITALIAN LUSTRES PRODUCTION

G. Padeletti, CNR-ISMN, cp 10, 00016 Monterotondo Staz., Roma, Italy, P. Fermo, Dip. Chim. Inorg. Met. e An., University of Milan, Via Venezian 21, 20133 Milano, Italy

The knowledge of bismuth during XV and XVI centuries is an open question since, according to some authors, this element was confused with lead, tin and silver. On the contrary, G. Agricola (1494-1555), the pioneer of mineralogical science in Europe, in his two works (De Natura Fossilium, Lib. X,1546 and Bermannus Sive De Re Metallica Dialogus,1528) asserts that bismuth was considered as an element distinct from the other metals known at that time. This question gave rise to some interest, and Von Lippmann in 1930, wrote a treatise dealing with the history of bismuth between 1400 and 1800.

In this work we present the results obtained on Italian and Hispano-Moresque shards studied by means of XRD, ETAAS, ICP-OES and SEM. It seems that our work could provide a new and important contribution to this debate, because we found bismuth in lustre composition of Renaissance shards produced in Central Italy. Furthermore, we found that it could be considered also a discriminating element between Italian and Hispano-Moresque productions.

O-II.4 12:35 A TEM-STUDY OF NANOPARTICLES IN GLAZES

P. Fredrickx(a), D. Hélary(b), D. Schryvers(a), E. Darque-Ceretti(b), (a)EMAT, Groenenborgerlaan 171, 2020 Antwerp, Belgium, (b)Ecole des Mines de Paris, CEMEF (CNRS UMR 7635), BP 207, 06904 Sophia-Antipolis cedex, France

Because of its high magnifications with high resolution, a transmission electron microscope (TEM) can easily be applied in the study of nanocrystalline particles. These particles have a determining influence on the appearance of the object, for they induce colour. The exact resulting colour is dependent on the shape, size, number and composition of the particles present, and these characteristics are in their turn determined by the way the material was formed. Thus, studying the particles can give information about the manufacturing processes involved. In this contribution, examples will be given based on the study of contemporary Spanish luster glazes. They were created to verify ancient production methods. Lustre-ware consists of a ceramic body glazed with an opaque tin-rich layer, which is topped by a thin layer containing Ag/Cu nanocrystals that give rise to the golden appearance. The sizes, shapes and penetration profiles were studied in image mode, and the morphology was evidenced with High Resolution TEM. The nature of the particles was determined by EDX-analyses, as well as with EELS, which also supplies electronic information so that possible oxides could be identified in individual particles. Furthermore EFTEM has been used to create mappings of the nanoparticles to visualise the depth distribution for each class of particles.

12:55 **LUNCH**

Session II: Ceramics/glazes 2 (continued)
Session chair: J. Mass

O-II.5 14:00

THE ROLE OF SILVER AND COPPER NANOCLUSTERS IN THE LUSTRE DECORATION OF ITALIAN RENAISSANCE POTTERY: AN EXAFS STUDY

S. Padovani, C. Sada, P. Mazzoldi, INFM, Dipartimento di Fisica, Università di Padova, via Marzolo 8, 35131 Padova, Italy, B.G. Brunetti, A. Sgamellotti, I. Borgia, A.Giulivi, INSTM, Dipartimento di Chimica, Università di Perugia, via Elce di Sotto 8, 06123 Perugia, Italy, F. D'Acapito, INFM, GILDA CRG c/o ESRF, BP 200, 38043 Grenoble, France, G. Battaglin, INFM, Dipartimento di Chimica Fisica, Università di Venezia, Dorsoduro 2137, 30123 Venezia, Italy

Lustre is one of the most important decorative techniques of the Medieval and Renaissance pottery of the Mediterranean basin. The lustre was obtained by putting a mixture of copper, silver and iron salts and oxides, together with vinegar, ochre and clay, on the surface of a previously glazed pottery. Then, the whole system was heated to about 600 °C in a reductive atmosphere, produced by the introduction of smoking substances in the kiln.

Following the recent finding that the colour of lustre decorations is mainly determined by copper and silver nanoclusters dispersed in the more external layer of the glaze, the local environment of copper and silver atoms has been studied by Extended X-ray Absorption Fine Structure spectroscopy, using synchrotron radiation, in original samples of gold and red lustre. The study was performed on fragments of Italian Renaissance pottery, belonging to the Museo Regionale della Ceramica di Deruta. EXAFS spectroscopy is one of the most suitable techniques for studying the local order around dopant atoms in glass, for its sensitivity to diluted samples and the possibility to characterise both cluster structures and oxide phases. It has been found that the chromatic properties of gold and red lustre can be mainly attributed to the silver and copper nanoclusters, respectively. However in both gold and red lustre, copper is mostly the oxidized form (Cu+ and Cu2+) with a large prevalence of Cu+. In the gold lustre, silver also is partly in the oxidized form.

O-II.6 14:20

LUMINESCENCE PROPERTIES OF LUSTRE DECORATED MAJOLICAS

A. Galli, M. Martini, E. Sibilia, INFM and Dip. di Scienza dei Mat.,Univ. di Milano-Bicocca, via R. Cozzi 53, 20125 Milano, Italy, G. Padeletti, CNR-ISMN, cp 10, 00016 Monterotondo Staz., Roma, Italy, P. Fermo, Dip. Chim. Inorg. Met. e An., Via Venezian 21, University of Milan, 20133 Milano, Italy

In the frame of the characterisation of the raw materials used to manufacture lustre decorated majolicas, we have performed luminescence measurements on several majolicas shards, coming from the two Italian major centres of production of this ware (Gubbio and Deruta, Umbria, Central Italy) and from Spain. First at all, the majolicas have been dated by Thermoluminescence (TL), to distinguish the former Spanish artefacts from those produced in Italy. For all the Italian samples, photoluminescence, TL and wavelenght-resolved TL measurements, have also been performed on the samples surfaces (lustre plus glaze) to characterise their defects and recombination centres. The associated physical parameters (main peak temperature, emission wavelenght, order of kinetics) together with the elemental composition, determined by atomic emission spectrometry, have been used in a statistical analysis to possibly discriminate the majolicas produced in Gubbio from those coming from Deruta. In fact, just on the base of the shards chemical composition, discriminating between the two kinds of production may be difficult due to the geographical closeness of the two centres. The preliminary results obtained are presented and discussed.

Session III: Dating
Session chair: D. Erharth

O-III.1 14:40 -Invited- THERMOLUMINESCENCE DATING: RECENT RESULTS AND NEW PERSPECTIVES IN THE STUDY OF GLASS MOSAICS

Marco Martini, Istituto Nazionale di Fisica della Materia (INFM), Università degli Studi di Milano-Bicocca, Dipartimento di Scienza dei Materiali, Via Cozzi, 53, 20125 Milano, Italy

Crystalline inclusions contained in ceramics act as thermoluminescence (TL) dosimeters, the irradiation source being the natural radiation environment. On this grounds various ceramic materials (pottery, bricks, cooked clays, bronze clay-cores) have been dated by thermoluminescence (TL).

In principle, TL Dating should apply also to glass materials. The lack of crystallization and the transparency which causes TL bleaching are the main drawbacks to the application of TL Dating to glasses. Recently we have studied the feasibility of TL Dating to a particular case of glasses, i.e. mosaic glass tesserae: various samples have been analysed through their TL glow-curves and emission spectra. TL protocols have been developed to test the sensitivity and the sensitivity changes, the optical bleaching and the signal regeneration by sunlight. The data obtained have been handled by exploratory multivariate method (HCA and PCA). The TL sensitivity and the temperature and wavelength of the main TL peak have been chosen as parameters describing the TL characteristics of the samples From the principal components obtained it can be observed that TL sensitivity and antimony oxide content are correlated. Sb_2O_5, used as opacifier by the glassmakers, forms, with the CaO contained in the glass, micro-crystals of $CaSb_2O_6$. Their presence in our samples has been confirmed by X-ray diffraction measurements. It is concluded that an important role is played by these crystals in the TL of mosaic glasses, promisingly datable by TL.

O-III.2 15:20 HIGH RESOLUTION RADIOCARBON DATING OF PREHISTORIC SITES IN SOUTHERN ITALY

L. Calcagnile, G.Quarta, M.D'Elia, Department of Engineering of Innovation, University of Lecce, 73100 Lecce, Italy

The University of Lecce, Lecce, Italy has completed the installation of a new facility dedicated to the development and the application of advanced nuclear spectroscopic techniques to the study on cultural heritage. The facility is based on a 3 MV high current HVEE TandetronTM accelerator equipped with three experimental lines for accelerator mass spectrometry (AMS) radiocarbon dating, high energy ion implantation and ion beam analysis.

In this paper we describe the new AMS beam line consisting of a sputter ion source and a low energy and an high energy mass spectrometer. The system, which supports unattended operation, has a throughput of 2000 samples per year. It has been designed to have an high ion beam acceptance and to reduce, by a proper tuning, the machine induced mass fractionation. Precision measurements performed on modern Oxalic Acid II and on “blank” samples supplied by the International Atomic Energy Agency (IAEA) have shown that the 13C/12C and 14C/12C ratios can be measured with a precision of 0.03 % and 0.3 % respectively and that sample preparation background is better than 50’000 years. Many different kind of samples (bones, wood, charcoal) have been analysed and the results have given a fundamental contribution to the solution of several problems both in archaeology and in the history of art. Among them the dating of a prehistoric cave and the authentication of a medieval painting are the most relevant cases. In the near future already founded research projects are planned to expand the system capabilities by the design and the installation of new dedicated ion beam lines.

15:40 **BREAK**

16:00 POSTER SESSION

Ceramics

O/P.01 CHARACTERISATION OF IRANIAN (X-XIII CENTURY) AND ITALIAN (XV-XVI CENTURY) LUSTREWARE

I. Borgia, B. Brunetti, A. Giulivi, F. Presciutti, C. Ricci, A. Sgamellotti, INSTM, Department of Chemistry, University of Perugia, Perugia, Italy, F. Shokouhi, P. Oliaiy, J. Rahighi, M. Lamehi-Rachti, Van de Graaff Laboratory, AEOI, P.O. Box 14155-1339, Tehran, Iran, M. Mellini, C. Viti, Dipartimento di Scienze della Terra, Università di Siena, Siena, Italy

The production of Persian lustreware is believed to have begun around 10th century, although the major developments of Persian lustre pottery have taken place under Seljuks around the middle of the 12th century. The Persian lustre production was not lost with the Mongol invasions between 1224 and about 1250. In fact, lustre indebted to Seljuk traditions, gradually changing in style and idea, was also produced under the Mongol dynasty of the Il-Khanid, mostly between 1260 and 1340[1]. After its first developments in Middle-East, the lustre technique diffused all along the Mediterranean basin together with the spread of Islamic culture and arrived in Italy, through Spain, during XV-XVI century. This work consists of the parallel characterisation of Persian (X-XIII century) and Italian (XV-XVI century) lustreware, carried out by several experimental techniques such as PIXE, XRF, SEM-EDS, UV-VIS, and TEM-EDS with electron diffraction. The nanostructural nature of lustre, already characterised in a previous work [2],has been confirmed. In both cases the optical properties of the decoration mainly depend on the dispersion of metallic silver and copper nanoclusters within the glassy matrix of the glaze. The results have been analysed in the effort to identify analogies and differencies between decorations of the same type produced in different countries and in different times.

[1]. F. Shokouhi, P. Oliaiy , J. Rahighi, M. Lamehi-Rachti, Z. Roohfar and S. Durali, Int. J. PIXE (2002), in the press.
[2]. J. Perez-Arantegui, J. Molera, A.Larrea, T. Pradell, M. Vendrell-Saz, I. Borgia, B. G. Brunetti, F. Cariati, P. Fermo, M. Mellini, A. Sgamellotti and C. Viti , J. Am. Ceram. Soc., 84 (2) 442-46 (2001).

O/P.02 CLASSIFICATION OF ANCIENT ETRUSCAN CERAMICS USING STATISTICAL MULTIVARIATE ANALYSIS OF DATA

P. Fermo, S. Gilardoni, F. Cariati, Dip. Chim. Inorg. Met. e An., Via Venezian 21, University of Milan, 20133 Milano, Italy, D. Ballabio, V. Consonni, Dip. di Scienze dell'Ambiente e del Territorio, Univ. Milano Bicocca, Piazza della Scienza 1, 20216 Milano, Italy, G. Bagnasco Gianni, Dip. di Scienze dell'Antichità, Via Festa del Perdono 7, 20100 Milano

Pottery provenance determination by element analysis is one of the oldest field in archaeometry. In the present work Etruscan ceramic shards dating from the VIII to the IV century BC and coming from the archaeological excavation at Pian di Civita in Tarquinia (central Italy) have been chemically analyzed by ICP-OES and AES with flame atomization in order to settle their provenance and to acquire knowledge about the ceramic production technology. The examined shards belong to the class of the depurata pottery, a fine craem ware characterized by a highly homogeneous ceramic body and produced in Tarquinia over a long period. Fifteen elements have been determined. The analytical results acquired have been treated by multivariate analysis techniques such as principal components analysis (PCA) and Kohonen neural networks (K-ANN). The results obtained have provided two type of information: from one hand it has been demonstrated that the most part of the analyzed shards has been locally produced while from the other hand it has been possible to get information concerning the production technology used in Tarquinia over a long period.

O/P.03 STUDY OF THE METALS DISTRIBUTION IN LUSTRE DECORATED MAJOLICAS

G. Padeletti, CNR-ISMN , cp 10, 00016 Monterotondo Staz. (Roma), Italy, P. Fermo, Dip. Chim. Inorg. Met. e An., Via Venezian 21, University of Milan, 20133 Milano, Italy, L. Toniolo, C. Colombo, CNR Istituto per la conservazione e la valorizzazione dei Beni Culturali - Sezione di Milano 'Gino Bozza', P.zza L. da Vinci 32, 20133 Milano, Italy

Lustre technique is as old as the early ninth century AD and started in Iraq from where it spread all over the Mediterranean basin, first in Spain and then in Italy. Lustre consists of a thin metallic film used for the decoration of ancient majolicas containing silver, copper and other substances applied in a reducing atmosphere on a previously glazed ceramic. According to the kind of lustre (Arabian, Hispano-Moresque or Italian), the recipe used for the impasto preparation was quite different. Furthermore, the recipes used were kept secret and nowadays it is not possible to obtain the outstanding results of the past. In the present work some lustred decorated shards of different provenance have been investigated by emission atomic spectrometry (ICP-OES) in order to put in evidence the main differences as concerns the chemical composition. A detailed study of the metal distribution on the lustre surface within the glaze layer underlying the lustre film has been also carried out by means of a scanning electron microscope (SEM) operating in low vacuum mode and equipped by a X-ray spectrometer to measure the backscattered map of the different layers. A preliminary optical microscopy study of the stratigraphy of the lustred shards has been carried out to try the interpretation of the SEM results.

O/P.04 TECHNOLOGICAL STUDY ON ANCIENT CERAMICS PRODUCED IN CASTELDURANTE DURING THE REINASSANCE PERIOD

G. Padeletti, M.G. Ingo , G. Chiozzini, CNR-ISMN , cp 10, 00016 Monterotondo Staz. (Roma), Italy, P. Fermo, Dip. Chim. Inorg. Met. e An., Via Venezian 21, University of Milan, 20133 Milano, Italy, A. Galli, INFM and Dip. di Scienza dei Mat., Univ. di Milano-Bicocca, via R. Cozzi 53, 20125 Milano, Italy

In order to recover the ancient tradition for what concerns the materials used for decoration, ceramic shards produced during the Renaissance in Casteldurante, a famous centre for ceramic production in Central Italy, have been studied. The ceramic body, the glaze and the pigments applied on the ceramic surface have been investigated to acquire information concerning the production technology. In particular, the ceramic body has been studied with optical microscopy, DTA-TG, ICP-OES, XRD, FT-IR and SEM-EDS. The identification of the pigments employed has been carried out by means of UV-Vis diffuse reflectance spectroscopy, total X-ray fluorescence analysis (TXRF) and by SEM-EDS technique. Thermoluminescence (TL) measurements have been also performed on the examined ceramics in order to identify the production period. The results obtained are presented and discussed.

O/P.05 MICROCHEMICAL AND MICROSTRUCTURAL CHARACTERISATION OF MEDIEVAL AND POST-MEDIEVAL CERAMIC GLAZE COATINGS

R. Alaimo, CEPA s.r.l., Palermo, G. Bultrini, Dipartimento di Scienze Chimiche, Università di Catania, Italy, I. Fragalà, Dipartimento di Scienze Chimiche, Università di Catania, Italy, R. Giarrusso, CEPA s.r.l., Palermo, Italy, G. Montana, Dipartimento di Chimica e Fisica della Terra, Università di Palermo, Italy

A large number of ceramic samples (from 10th to 19th century) , discovered in several Sicilian archaeological sites (Siracusa, Caltagirone, Sciacca and Piazza Armerina), have been studied by the combination of Scanning Electron Microscopy (SEM), Energy Dispersive X-ray fluorescence Spectrometry (EDS) and Optical Microscopy (OM). Attention has been focused on the microchemical and microstructural physico-chemical properties of painted surfaces to investigate the nature of enamels and pigments of decoration layers. The purpose of the study has been the identification of self-consistent archeometric criteria, beside classical stylistic considerations, suited for a safe attribution of production sites.

Thus, the different glaze coatings have been characterized in terms of microstructural and microchemical composition of enamels of each ceramic typology. The breadth of results represent a suited data base for identification of ceramic reference groups enabling discrimination of provenance of artifacts. In addition, present data allow the identification of the raw materials used for pigments and highlight relevant differences with existing documentation about old recipes. Finally, attention has been also devoted to manufacturing techniques and firing operational conditions adopted for each typology of glaze coatings depending on the different discovery sites.

O/P.06 ARCHAEOMETRY OF SICILIAN GLAZED POTTERY

R. Alaimo,CEPA s.r.l., Palermo,Italy, G. Bultrini, Dipartimento di Scienze Chimiche, Università di Catania, Italy, I. Fragalà, Dipartimento di Scienze Chimiche, Università di Catania, Italy, =R. Giarrusso, CEPA s.r.l., Palermo, Italy, G. Montana, Dipartimento di Chimica e Fisica della Terra , Università di Palermo, Italy

Unambiguous identification of fabrication sites of majolica handicrafts still remains open to question when relies only upon stylistic considerations. In this perspective 90 samples discovered in Sicily and 60 samples of uncertain provenance but attributed to Sicilian workshops due to stylistic features, have been studied by X-ray diffraction (XRD), optical microscopy (OM) and X-ray fluorescence (XRF). All the samples, dated back from XVI to XIX century, are part of the collection of the “Museo della Ceramica” (Caltagirone, Italy).

This paper presents mineralogical, petrographical and chemical studies, including compositional and textural data, of biscuits of these handicrafts. The data, including minor and trace elements analysis, have been submitted to computer assisted multivariate statistical techniques. The obtained results represent a suited data base for identification of ceramic reference groups enabling discrimination of provenance of artifacts. Finally, present results have been compared/contrasted with attribution assessed on the simpler basis of historical/stylistic considerations.

Pigments

O/P.07 ADVANTAGES OF A PORTABLE X-RAY FLUORESCENCE DEVICE IN THE ANALYSIS OF ART OBJECTS

V. Desnica, Institute of Sciences and Technology in Art, Academy of Fine Arts, Schillerplatz 3, 1010 Vienna, Austria and Manfred Schreiner, Institute of Sciences and Technology in Art, Academy of Fine Arts, Schillerplatz 3, 1010 Vienna, Austria

A field-portable x-ray fluorescence (XRF) analyzer using a silicon drift detector (SDD) was developed and assembled at the Academy of Fine Arts in Vienna. SDD circumvents the need for a bulky liquid N2 detector cooling system. Combined with the overall miniaturization of the device it is possible to carry out in-situ examinations and studies of art objects e.g. mural paintings in churches and cathedrals. Its analytical capabilities were judged against the results obtained by a laboratory XRF and a comparative evaluation of the systems has been established. The potential of the hand-held XRF has been demonstrated in circumstances where a conventional instrument was inapplicable. Both the portable and lab device are compared and the advantages and disadvantages of the two respective XRF types are discussed. The importance of a combined utilization of both systems is presented.

O/P.08 IMPORTANCE OF USING DIFFERENT ANALYTICAL TECHNIQUES FOR PIGMENT CHARACTERIZATION

V. Desnica, Institute of Sciences and Technology in Art, Academy of Fine Arts, Schillerplatz 3, 1010 Vienna, Austria, K. Furic, R. Boskovic Institute, Bijenicka c. 54, 10000 Zagreb, Croatia and Manfred Schreiner, Institute of Sciences and Technology in Art, Academy of Fine Arts, Schillerplatz 3, 1010 Vienna, Austria

A number of analytical techniques was applied in a study of 30 distinct ultramarine pigments from the pigment collection of the Academy of Fine Arts. In order to determine their structural and visual dissimilarity a thorough and complete investigation was done by X-ray fluorescence analysis, X-ray diffractometry, Raman and infrared spectroscopy as well as by colorimetry. It could be shown that only the combination of all these techniques enables to achieve enough information for full differentiation of the samples, and to obtain the complete characterization of each pigment.

O/P.09 DETERIORATION PROCESSES OF SMALT PAINT LAYERS

Enrico Ciliberto and Claudia Altavilla, Dipartimento di Scienze Chimiche dell'Università di Catania, viale A.Doria 6, 95125 Catania, Italy

Smalt is a moderately, finely to coarsely, ground blue coloured potassium glass. The colour blue is due to small but variable amounts of cobalt added as cobalt oxide during manufacturing. In this work we studied smalt as a pure pigment and in proteic binders by using XPS (X-ray photoelectron spectroscopy) to characterize the surfaces of pure pigment grains and the surfaces of paint layers prepared according to early recipes. Samples were also exposed to humidity and UV radiation in the presence of SO2 and NOx. To obtain the artificial aging it was employed a Heraeus Votsch HC 4030 system. The XPS spectra of the aged paint layers show in addiction the signals of sulphur.In particular, in the high resolution S2p spectra, B.E value is typical of the sulphate group (Fig.7,8).The proteic paint layer appears diaphanous to reactive vapours because we observed the SO4-- species on internal and external surfaces of sample layers, being the internal surface the interface preparation-paint layer, and the external surface the interface paint layer-air. Furthermore we observed that, after aging, the surface atomic concentration of cobalt decreased in respect to the silicon one. This loss of cobalt may be the reason why this pigment partially or completely discolours with time and the simultaneous presence of SO2 and NOx seems to have no synergic effect on the degradation.

References -E.Ciliberto, I. Fragalà, G. Pennisi, G. Spoto Science and Technology for Cultural Heritage, 3.1994:163-168 - Bruno Mòhlethaler and Jean Thissen, "Smalt" , Studies in Conservation, 14 (1969), 47-61 -Baldini F. , Botticelli G., Danti C.,Matteini M. and Moles A., "Case Studies in the Conservation of Stone and Wall Paintings, IIC, London (1986) 186-189

O/P.10 ANALYSIS OF PIGMENTS FROM THE FRENCH PALEOLITHIC CAVE OF MARSOULAS

Pamela B. Vandiver, Smithsonian Center for Materials Research and Education, Suitland MD 20746, USA and Richard Potts and Michael Petraglia, National Museum of Natural History, Smithsonian Institution, Washington D.C., USA

Joint French and Smithsonian excavations of a small floor area in the French cave of Marsoulas led to collection of artifacts and pigments that have been characterized and analyzed with reference to other studies of pigments from the Pyrenees. The minute size of samples, many as small as 20 microns, circumscribed the techniques of sampling and analysis.

Metallurgy

O/P.11 MICROSTUCTURAL ANALYSIS OF AN ARCHAEOLOGICAL TOOL RESCUE FROM A HISTORICAL SITE IN BRAZIL

G.N. Campos and I.G. Solórzano, Department of Materials Science and Metallurgy, PUC-Rio, Rio de Janeiro, Brazil

The present work has as objective a microanalytical analysis of a metallic archaeological artifact using metals of optical microscopy (MO), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The object of study correspond to an agricultural tool, a hoe, from the Brazilian colonial period, dating beginning of XVII century, removed from an archaeological site Rochedo, in excavations conducted by researches of the Brazilian Archaeological Institute. Sample preparation require a meticulous procedure in view of the fragility of the object. The hoe has been suffering the action of oxidation-corrosion for over 300 years, thereby making possible the impregnation of mineral sediments. A detailed metallographic analysis, couple with spectroscopic SEM and TEM measurements allowed to conclude that the hoe was made of puddle iron, retaining significant slag, probably by African slaves, who had metallurgical knowledge from their ancestors, under a Portuguese control. The equi-axial microstructure of ferrite grains, together with the alignment of slag inclusions, strongly suggest a metal working procedure follow by heat treatment and slow cooling rate conducted on a 0,2% carbon containing puddle iron. The similarity with other agricultural tools found in the Americas dated from the same period is also discussed.

O/P.12 MICROCHEMICAL STUDY OF THE CORROSION PRODUCTS ON ARCHAEOLOGICAL BRONZES BY MEANS OF THE COMBINED USE OF SEM+EDS, XRD, GDOES AND OM

Gabriel Maria Ingo (a), Emma Angelini(b), Tilde de Caro(a) and Giuseppe Bultrini(c), (a)Istituto per lo Studio dei Materiali Nanostrutturatidel Consiglio Nazionale delle Ricerche, CP10, 00016 Monterotondo Scalo, Roma, Italy, (b)Dipartimento SCIMAT, Politecnico di Torino, c.so Duca degli Abbruzzi, Torino, Italy, (c)Dipartimento di Chimica, Università di Catania, v.le A. Doria 6, 95125 Catania, Italy

Glow discharge optical emission spectrometry (GDOES), scanning electron microscopy + energy dispersive spectrometry (SEM+EDS), optical microscopy (OM) and X-ray diffraction (XRD) are used for studying the microchemistry of the long term corrosion products, i.e. the patina, on archaeological bronzes found during the excavation of Tharros (nort-western Sardinia). The results evidence that via GDOES it is possible to obtain reliable and detailed elemental composition depth profiles for the corrosion products of the patina and for the bulk chemical composition of the bronzes that are in good agreement with the microchemical features obtained via SEM+EDS. The results provide good insight into the corrosion layers evidencing copper and lead selective corrosion and depletion phenomena, leading to the formation of a complex microchemical structure and further, show clearly the interaction between the inorganic constituents of the soil such as iron, silicon and phosphorus in contact with the corrosion products grown on bronzes. Finally, the results show that GDOES, with its ability of routine and rapid analysis of layers of thickness up to 150 microns, in combination with SEM+EDS, XRD and OM, has significant potential in studies of the corrosion products for the restoration and conservation of archaeological bronzes.

O/P.13 MICROCHEMICAL INVESTIGATION ON RENAISSANCE COINS MINTED AT GUBBIO (CENTRAL ITALY) FINALISED TO DEFINE THE MANUFACTURING PROCESS

G.M. Ingo, G. Padeletti, G. Chiozzini, A. Cavicchi* CNR-ISMN, c.p.10 Monterotondo Staz., 00016 Monterotondo (Roma), Italy *Euguvium Studio Numismatico,Corso Garibaldi 88/a, Gubbio (PG), Italy

By means of the combined use of scanning electron microscopy + energy dispersive spectrometry (SEM+EDS) and optical microscopy (OM) the bulk composition and the microchemical structure of the external layers of coins minted at Gubbio (Central Italy) and dated between XV and XVI centuries a.C., are studied in order to identify their manufacturing process.
Only for some series the results evidence a complex manufacturing technique involving oxidation and etching processes for obtaining a surface silver finishing. This technique was based first on the production of a coin blank characterised by a silver content of about 2 wt% and then on the use of thermal and chemical treatments carried out for removing copper and enriching the surface silver content. These microchemical results combined with historical and economical information provide good insight into the economy of Central Italy in the Renaissance age.

O/P.14 COPPER METALLURGY AT THE ETRUSCAN SITE OF POPULONIA-BARATTI (SOUTHERN TUSCANY, ITALY)

M. Benvenuti(a), L. Chiarantini(a), P. Costagliola(a), I. Mascaro(a), G. Tanelli(a), I.M. Villa(b), (a)Dip.to Scienze della Terra, Univ. Firenze, Italy, (b)Isotopengeologie, Erlachstrasse 9a, 3012 Bern, Switzerland

Significant production of iron, copper, bronze, lead and silver was achieved in Etruscan and Roman times (7th century BC - 2th century AD) at Populonia-Baratti (Tuscany, Italy), leaving behind huge heaps of metallurgical slags, large part of which (referable to iron production) were actively exploited for re-smelting in blast furnaces in the fist half of past century. As part of an extensive archaeometallurgical project on the Baratti site, we present here the results obtained from analysis of copper slags, aimed to define (a) their chronological position with respect to (dominant) iron metallurgy, (b) the metallurgical process, and (c) the provenance of smelted metals The research has been mainly carried out on a relatively undisturbed slag deposit, about 3 meters thick, extending along the Baratti beach for about 200 m in length. Remarkable quantities of copper slags were found only at the bottom of the slag beach deposit. They can be temptatively dated (upon archaeological findings) at the V century BC or earlier. Two different types of copper slags have been identified, each showing peculiar mineralogical and textural features. We suggest that the two slag types can represent the waste products of a two-stage smelting process of copper production. The high lead and zinc contents of both types of copper slag, and their Pb isotope signature are in agreement with inferred provenance of smelted copper from Cu (±Pb,Zn) ores occurring in the nearby Campiglia Marittima mining district.

O/P.15 ARCHAEOLOGY OF LISBON OLD-CITY: CERAMIC CRUCIBLES FROM PRE-XVIIIth CENTURY METALLURGICAL FOUNDRIES

M.O. Figueiredo, T. Pereira da Silva and J.P. Veiga, CENIMAT, Dept. Mat. Sci., New Univ. Lisbon, Caparica, Portugal and Cryst. & Miner. C., IICT, Alameda Afonso Henriques, 41-4º, 1000-123 Lisbon, Portugal, A.M. Dias Diogo and L. Trindade, Cultural Heritage Dept., Lisbon City-Hall, Palácio dos Coruchéus, 1700-019 Lisboa, Portugal

During an emergency archaeological intervention conducted downtown Lisbon (old city centre), ceramic foundry crucibles were collected in a layer of embankment debris used after the earthquake that destroyed the city in 1755. A chemical and phase constitution study was undertaken to complement the dating and to ascertain the kind of foundries (metallurgical or glass-working) concerning two intact cup-shaped crucibles and a fragment displaying glassy outflows.
Non-destructive methodologies were preferably used, namely, laboratory techniques - X-ray fluorescence spectrometry (XRF-WDS) and X-ray diffraction (XRD), either using a Bragg-Brentano diffractometer to irradiate the entire object or by the photographic Debye-Scherrer method for minute surface-collected slag and corrosion samples - combined with synchrotron radiation-induced X-ray micro-fluorescence (µ-SRXRF). Analytical results are presented and discussed. A possible Islamic origin (ante-XVIIIth century) was disclosed for the small crucible as tin was detected in the external metal outflow and further confirmed by minute cassiterite (SnO2) grains. Significant contents of copper and zinc found in the glassy material over the internal surface of the isolated fragment point towards a metallurgical use for the original crucible. SRXRF analysis of the glassy outflow on the larger crucible revealed the presence of mercury and gold traces, along with copper, suggesting that it could had been used to manipulate gold amalgams.

Conservation/Restoration

O/P.16 APPLICATION OF NEW TECHNOLOGIES FOR THE CONSERVATION AND PRESERVATION OF BONE MATERIALS FROM UNDERWATER EXCAVATIONSAPPLICATION

A. Aliboni(a), A. D'Andrea(a), G.F. Guidi(a), S. Mariani(a), P. Negri(a), S. Omarini(a), F. Pierdominici(a), A. Tagliacozzo(b), E.Cerilli(c), (a)ENEA C.R. Casaccia, Via Anguillarese 301, 00060-S Maria di Galeria (Rome), Italy, (b)Soprintendenza Speciale al Museo Nazionale Preistorico ed Etnografico "Luigi Pigorini", Piazza Guglielmo Marconi 14, 00144 Roma, Italy, (c)Società Cooperativa ARX a. r. l. , Via di San Giovanni in Laterano 210, 00184 Roma, Italy

The aim of this poster is to show the results of a project dealing with new methodologies and technologies applied to faunal osteological remains from underwater excavations.
During the project the technologies will be tested on the specimens collected during the excavation campaigns in the Neolithic village of "La Marmotta" (Anguillara Sabazia, Rome), carried out by the Soprintendenza Speciale al Museo Nazionale Preistorico Etnografico "Luigi Pigorini", under the direction of M.A. Fugazzola Delpino from 1992 to 1999. The need to study a perfectly preserved osteological assemblage that can be handled without damage, is of vital importance for the formulation of a correct paleoeconomic model, that defines correctly the subsistence strategies and the sequences regarding both the distribution of animal resources and the production of bone tools and ornaments. Two are the technologies will be tested, because two different approaches can offer a wider range of solution to the problem of the conservation of osteological remains from underwater excavations. New conservation methodology A: drying with acetone and consolidation with Paraloid B72(r) in acetone. This process seems to produce, in most cases, satisfying results both for the structural stabilization of the skeletal elements and for the legibility of the surfaces also by optical microscopy. New conservation technology B: supercritical drying process. This process seems is to choose in the case the methodology A failed. The observation of the conservation and legibility of the morphological characteristics of the traces by means of optical and electronic (SEM) microscopy on the specimens themselves and on resin replicas is trained out to verify the results of both methodologies.

O/P.17 LIBS AS A DIAGNOSTIC TOOL DURING THE LASER CLEANING OF ANCIENT MARBLES FROM MEDITERRANEAN AREAS

F. Colao(a), R. Fantoni(a), V. Lazic(a), A. Santagata(b), A. Morone(b),A. Giardini(c), (a)ENEA, FIS-LAS, Frascati (RM), Italy, (b)CNR, IMIP - Sezione di Potenza, Tito Scalo (PZ), Italy, (c)Università “La Sapienza”, Dipartimento di Chimica, P.le Aldo Moro 5, Roma, Italy

Laser ablation for stone cleaning is nowadays rather well assessed in the preservation of outdoor artwork surfaces exposed to environmental stresses. In particular, problems related to the laser treatment of marble surfaces in monuments have been already studied, leading to phenomenological models of the process for samples exposed to different aging factors, including chemical pollution. However, it is of interest to characterize spectroscopically the sample surface before and during the laser ablation in order to implement automatic control of the cleaning process. To this aim we have undertaken systematic LIBS analysis on different clean and dirty surfaces of marble fragments collected from ancient quarries in Greece, Turkey and Italy. Since the LIBS technique is able to supply information on the atomic composition of the surface layers, it has been monitored the effectiveness of the cleaning process by following the disappearance on LIBS spectra of the encrustation elements. The LIBS analysis of clean surfaces of the examined samples confirmed that bulk main composition is based on Calcium and Magnesium Carbonates, with the addition of Strontium and, to a minor extend of Manganese substituents. On the contrary, the samples’ encrustation resulted rich in Sodium, Aluminium, Iron, Silicon and for the Greek ones even in Titanium, Lithium and Manganese. In this work, the on line LIBS diagnostics during the laser ablation process will be presented through significant elements’ ratios, where the fast disappearance of light components (Al, Na) is the most evident feature of cleaning effectiveness. Furthermore, in order to assess the LIBS data obtained, Energy Dispersion X-Ray Spectra acquired before and after the laser interaction will be reported.

O/P.18 THE EFESTUS PROJECT "TAILORED STRATEGIES FOR CONSERVATION, RESTORATION AND VALORISATION OF HISTORICAL AND ARCHAEOLOGICAL COPPER BASED ARTEFACTS FROM MEDITERRANEAN COUNTRIES"

G.M. Ingo(a), E. Angelini(b) and T. de Caro(a), (a)CNR - ISMN, CP 10, 00016 Monterotondo Stazione Roma, Italy, (b)Dipartimento SCIMAT, Politecnico di Torino, c.so Duca degli Abbruzzi, Torino, Italy

The general objectives, the scientific activities and the first results obtained in the frame of the EFESTUS project financially supported by the European Commission are presented.

The aim of the project is to identify the degradation causes of Cu-based archaeological value artefacts selected as a function of the archaeological context and of the chemical composition and structure. Starting from this knowledge, innovative or traditional methods, anchored in local actions, are used for the restoration and conservation of the artefacts after validation tests carried out on Cu-based reference alloys with a microchemical structure similar to the one of ancient alloys. The project intends to develop, validate and disseminate tailored approaches for stopping degradation of these artefacts and for preventing further damage in Museum show boxes and deposits. The first results of the project EFESTUS are presented by summarising the activities of the twelve participating Research Centers and Institutions from Algeria, Egypt, Greece, Italy, Jordan, Spain, Tunisia and Turkey. Well-defined groups of Cu-based archaeological artefacts, as coins, weapons and small artistic objects are considered. They are characterized by means of traditional and innovative analytical techniques (XPS, GDOES, SEM+EDS, XRD, OM, XRF, ICP-MS, DTA-TG, electrochemical techniques); particular attention is devoted to the corroded areas of the artefacts and to the archaeological context, such as soil nature, previous restoration and conservation treatments, storage history, current environmental conditions.The development of an integrated information system for exchange of data and restoration procedures between the Mediterranean Institutions is the ultimate goal.

Other materials in cultural heritage

O/P.19 USING SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE SPECTROSCOPY TO ANALYSE A TEXTILE PIECE COATED WITH SILVER AND GOLD

R. Belli and A. Miotello, INFM and Dipartimento di Fisica, Università di Trento, 38050 Povo (TN) Italy

A textile piece discovered during excavation in the church of S. Maria Assunta in Civezzano, near Trento city (Italy), was carefully examined by using scanning electron microscopy equipped with energy dispersive spectroscopy. The piece comes approximately from Early Middle Ages. The analytical techniques permitted to establish that the piece is made by a silk core coated with a sheet having a non homogeneous composition. More precisely, the external portion of the sheet is essentially a thin gold film while the internal layers are made by silver and copper. We established this configuration by systematically changing the primary electron energy, and so the sampled volume, to investigate the sheet. Because both of the archaeological place where the piece was discovered and the quality of the manufactured piece we suppose that the dress belonged to sacred tissues.

O/P.20 CHARACTERISATION OF WAXES AND WAX MIXTURES IN CONSERVATION SAMPLES BY DSC AND DRIFTS

U. Knuutinen, EVTEK Institute of Art and Design, Conservation Department, Lummetie 2, Vantaa 01300, Finland, J. Lehtonen and A. Norrman, EVTEK Institute of Technology, Leiritie 1, 01600 Vantaa, Finland

This paper reports on the observations made on samples from waxes and wax mixtures including reference samples and samples from conservation objects using Differential Scanning Calorimetry (DSC) and DRIFTS (Diffusion Reflectance Method in Fourier Transform Infrared Spectroscopy). Our earlier studies had shown that the use of melting point area in DSC can give detailed information about the composition of a wax. This has led to further studies of behaviour of wax mixtures in this endothermic area. DSC provided information of changes in melting enthalpies by varying the portions in wax mixtures. DSC–curves could also reveal if temperatures in exothermic area had been used in melting.

To find characteristic absorptions of waxes, silicon carbide paper as a sampling tool was used for DRIFT spectroscopy and wax containing surfaces were analysed without any sample preparation. Also mixtures of waxes gave characteristic absorptions in IR spectra if endothermic area had been used in melting. Combining DSC and DRIFTS results, information about chemical classification of wax samples and the changes in composition caused by the melting/heating process was received.

O/P.21 VERSO LASER CLEANING OF TEXTILES

A. Barone, F. Bloisi, L. Vicari, INFM - Istituto Nazionale per la Fisica della Materia, Dipartimento di Scienze Fisiche, Universita Federico II di Napoli, Italy, E. Martuscelli, G. Gentile,Polcaro, CAMPEC s.c.r.l., Italy

High intensity short duration laser pulses have been, in recent years, widely used for “laser cleaning” of different materials since a laser generated acoustic shock wave removes extraneous particles from sample surface. Laser cleaning has been found especially effective in removing sub micron particles or organic films and has found applications to several materials in the field of conservation and restoration. To achieve good results the fluence (pulse energy per unit surface) and the repetition rate (pulses per unit time) must be between cleaning threshold and damage threshold. Even if substrate damage threshold is generally high enough, on delicate surfaces (e.g. written paper or painted tiles) colour alteration may occur. In a recent paper [A. Barone, F. Bloisi, L. Vicari. Verso laser cleaning of mechanically thin films, Appl. Surf. Sci., in press] we have presented the "verso laser cleaning" technique: in some conditions the higher penetration depth of thermoelastic wave with respect to the temperature profile propagation allows efficient removing of extraneous particles from one surface of a "mechanically thin" film by applying laser pulses to rear surface. Here we present the encouraging results obtained applying this technique to several textile samples.

O/P.22 STUDY OF ANCIENT MORTARS FROM THE ROMAN VILLA OF POLLIO FELICE IN SORRENTO (NAPLES)

D. Benedetti(a), S. Valetti(a), E. Bontempi(a), C. Piccioli(b), L.E. Depero(a), (a)Structural Chemistry Laboratory, University of Brescia and Consorzio Interuniversitario Nazionale di Scienza e Tecnologia dei Materiali (INSTM), Italy, (b)Ufficio Restauro della Sovraintendenza Archeologica di Napoli e Sorrento, Italy

The study of ancient mortars is an important aspect of building conservation: the choice of their structural elements has varied according to historical period, regional habits, and the specific function in the structure.

Ancient mortars are composites, comprised of hydraulic or aerial binding materials, aggregates and additive, passive of active, which react with the binding material. Moreover, they were modified during their setting, hardening and ageing, according to processes not yet well known. Even if Italy is very reach on historical centres, in the literature only few works have been devoted on the enormous scientific potential of these virtually untouched sites. For this study, an interdisciplinary research is mandatory as well as the development of new analysis methods based on advanced techniques.

In this communication, in the frame of a collaboration between the INSTM Consortium and the restoration office of the "Sovraintendenza Archeologica" of Naples and Salerno, we present a study of ancient mortars from the villa of Pollio Felice of Sorrento (Naples). The analysis has been performed by traditional techniques (grain size and lime-percentage analysis, optical and electron microscopies, X-ray diffraction, and microRaman spectroscopy) and by means of a laboratory X-ray microdiffractometer equipped with the image plate detector. This system, applied for the first time to archaeological studies, can reach a spatial resolution of 10 microns and it allows to obtain the phase identification of binder and filler particles.

O/P.23 THE PROTECTION OF DIFFERENT ITALIAN MARBLES WITH TWO PARTIALLY FLUORINATED ACRYLIC COPOLYMERS

Tommaso Poli, Lucia Toniolo, CNR – ICVBC Sezione Milano “Gino Bozza”, Politecnico di Milano, P.za L. da Vinci 32, 20133 Milano, Italy, Oscar Chiantore, Dipartimento di Chimica IFM, Università di Torino, Via Giuria 7, 10125 Torino, 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's 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 characteristics, play a relevant role.

In this paper the issues related to protection of three different Italian marbles have been investigated: 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 tower. Samples coming from 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-trifluorethyl 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 the polymeric treatment. The aim of the work is to evaluate the protective efficacy of these two new partially fluorinated acrylic copolymers on the three different marbles and correlate the different behaviours with the polymeric systems properties and with the stone substrates characteristics.

Session IV: Metallurgy 1
Session chair: P. Vandiver

O-IV.1 14:00 -Invited- ANCIENT METAL OBJECTS - MATERIAL SCIENCE METHODS TO DETERMINE THEIR PROVENANCE AND THEIR AUTHENTICITY

E. Pernicka, Institut für Archäometrie, TU Bergakademie Freiberg, Gustav-Zeuner-Str. 5, 09596 Freiberg, Germany

The trace element fingerprint to relate artefacts with ore deposits is difficult to read and and conclusions derived from it have always been in dispute. Isotope analysis has introduced a new dimension in provenance studies of metals. The present status of this field will be reviewed with a recently discovered sensational metal hoard as example. It contains among other objects a bronze disc with gold inlays dated to around 1600 BC. On the disc one can identify 32 stars and two complete celestial forms which probably represent the sun and moon. The find is so exceptional, because it is the earliest astronomically identifiable representation of the night sky.

The scientific investigations initially centered around the question of authenticity, which has been confirmed by investigations of the metal working technology, the chemical composition of the metals, the composition and structure of the corrosion layer and by measuring the radioactivity of 210Pb in the bronze. It is also highly desirable to determine the provenance of the metal(s), because the find exhibits unusual technical features that so far have been known only in the eastern Mediterranean. Several methods of analysis including XRF, PIXE, LA-ICP-MS, neutron activation, and optical microscopy have been used. The results will be compared with ore samples from the Erzgebirge and the Harz mountains that have become available only recently.

O-IV.2 14:40 SURFACE TOPOLOGY INVESTIGATION FOR ANCIENT COINAGE ASSESSMENT USING OPTICAL INTERFEROMETRY

R.I. Grynszpan, J.L. Pastol, E. Leroy, Institut des Sciences Chimiques Seine-Amont, (LCMTR & CECM), IFR-CNRS-1780, 8 rue H. Dunant, Thiais, France, S. Lesko, E. Paris, Veeco Metrology, BP 43, Dourdan, France, C. Raepsaet, LPS, CEA-Saclay, France

Authentication of ancient coinage commonly relies on visual expertise, which is a clear limitation to objective assessment of specimens, owing to the variety of wearing states possibly encountered for a given series of coins. Even Scanning Electron Microscopy (SEM) observation at the sub-millimeter scale may lead to ambiguous allegations. On the other hand, chemical analysis, which might provide quantitative and often definite prove, cannot always be carried out in a non-destructive way or with sufficient high precision. In this work we consider the possibility to use 3-D optical interferometry as a versatile mean to examine coin surface topology with sub-micron precision and to define objective criteria for ancient specimen comparison. As an example, we performed isoclinal profiling analyses to tentatively ascertain the stamping process and possible provenance of a series of famous gold coins bearing Louis XVI's "horned" effigy, presumedly minted in Strasbourg in 1786 [1]. Conclusions seem compatible with SEM observations and both e - and p + microprobe elemental analyses.

[1] Montbrison (Oberkirch), Memoirs, H. Colburn edit., London (1845).

O-IV.3 15:00 THE ANALYSIS OF PLATINUM GROUP ELEMENTS AND OTHER ELEMENTS OF INTEREST IN ANCIENT GOLD USING LA-ICP-MS

Laure Dussubieux, Lambertus van Zelst, Smithsonian Center for Materials Research and Education, 4210 Silver Hill Road, Suitland MD 20746, USA

Questions regarding trade and exchange of ancient gold artifacts may be addressed by compositional characterization of source material, through determination of minor and trace element concentrations. Since refining and alloying operations can be expected to affect the concentrations of some trace impurities, especially the Platinum group elements should be of interest.

The analytical method used for this kind of study has to be sensitive enough for a wide range of elements and be as non-destructive as possible due to the value and uniqueness of the objects. One of the most promising analytical methods for ancient gold study is laser ablation - inductively coupled plasma mass spectrometry (LA-ICP-MS). It is a multi-elemental analytical method with detection limits in the range of ppm or below, depending on the element. The laser ablation sampling allows analyses while leaving only 100 microns wide craters, almost invisible to the naked eye. The quantitative analysis of some trace elements in gold using LA-ICP-MS is complicated by the lack of suitable matrix matched standard. To overcome that problem we consider ancient gold coins as standards, their trace element contents having been determined by ICP-MS after acid digestion, and their major elements with X-ray fluorescence measurements. The repeatability and the accuracy of the results obtained with such standards will be discussed in the presentation.

O-IV.4 15:20

IN-SITU TM-AFM AND IRRAS INVESTIGATIONS OF THE INITIAL ATMOSPHERIC CORROSION BEHAVIOUR OF VARIOUS METALS/ALLOYS USED IN WORKS OF ART

Ch. Kleber, Institute of Sciences and Technologies in Art, Academy of Fine Arts, Schillerplatz 3, 1010 Vienna, Austria, M. Schreiner, Institute of Sciences and Technologies in Art, Academy of Fine Arts, Schillerplatz 3, 1010 Vienna, Austria

In-situ Tapping Mode Atomic Force Microscopy (TM-AFM), a powerful high resolution imaging technique, and in-situ Infrared Reflection Absorption Spectroscopy (IRRAS), a highly sensitive method for the chemical characterisation of surfaces, were used to determine the influence of different contents of humidity with or without addition of acidifying gases such as SO2 or NO2 to the early stages of corrosion. The information obtained are the change of the topography of the sample surfaces with emphasis on the shape and lateral distribution of the corrosion products grown within the first 1300 min of weathering as well as a tracking of the surface reactions taking place during interactions of the investigated materials with the ambient atmosphere or under synthetic conditions. A complete different mechanism of the early stages of corrosion of pure copper and pure iron could be determined as well as a corrosion accelerating effect of zinc as alloy constituent in brass. Furthermore an increased corrosion rate with increasing humidity in the surrounding atmosphere could be observed during weathering of pure copper, pure zinc and different brass samples. The formed corrosion products could be identified by the aim of IRRAS.

15:40 **BREAK**

Session V: Metallurgy 2
Session chair: E. Pernicka

O-V.1 16:00 -Invited-

COMBINED USE OF SURFACE AND MICROCHEMICAL ANALITICAL TECHNIQUES FOR THE STUDY OF ANCIENT COINS

Emma Angelini, Dept. Materials Science and Chemical Engineering, Politecnico di Torino, Torino, Italy, Gabriel Maria Ingo and Tilde de Caro, ISMN-CNR, Roma, Italy

Ancient coins are interesting artefacts from historical, archaeological and technological point of view. The knowledge of their chemical composition and microstruture may be employed for obtaining information on the metal ores and on the technological competency of ancient civilizations in carrying out the pyrometallurgical processes as well as for investigating the alloying and minting processes.

An integrated analytical approach on a series of Pre-Roman and Roman coins of silver and copper based alloys is presented. The characterizations have been carried out by using bulk and advanced surface analytical techniques such as OM (optical microscopy), SEM+EDS (scanning electron microscopy+energy dispersive spectrometry, XRD (X-ray diffraction), SA-XPS (selected area X-ray photoelectron spectroscopy), GDOES (glow discharge optical emission spectrometry, EIS (Electrochemical impedance spectroscopy). The results allow to identify the causes of degradation phenomena such as corrosion and brittleness, as well as the chemical composition and the manufacturing techniques. Particular attention has been paid to the microchemical characterization of the patina and of the noble metal thin films used to produce suberatae coins. The results disclose on the surface of these latter coins the presence, in few cases, of mercury, thus demonstrating the use of gilding and silvering techniques in Ancient Rome.

O-V.2 16:40

TECHNOLOGIES FOR FORGERIES OF GREEK SILVER DRACHMS ANALYSED BY XRF AND PIXE

B. Constantinescu, Institute of Atomic Physics, POB MG-6, 76900 Bucharest, Romania

For coins, chemical differences that occur during preparation of alloys could be used for the identification of technologies and workshops and to distinguish between originals and counterfeits. We illustrate with the case of Greek Apollonia and Dyrrhachium silver drachms emitted for Pompejus. The important presence of these coins in Romania can be explained by the hypothesis that they were probably used as bursaries to pay the Dacian mercenaries. We used two methods: Am-241 gamma source based X-Ray Fluorescence (XRF) and in vacuum 3 MeV protons Particle Induced X-ray Emission (PIXE), for approx. 300 drachms. Five main categories were found: - original coins with 97-99% silver, low (1-2%) copper content, -debased coins with silver content down to 70% and copper content from 5 to 25%, -official (original dies) counterfeits from bronze (70% copper and 30% tin) covered by a very thin layer of argentarium (tin-lead alloy imitating the silver), -official counterfeits from tin, -plated coins consisting in a bronze core covered by 0.2-0.5 mm silver plates, using argentarium or lead as intermediate layer between bronze and silver. In our case, the method of attaching a thin silver foil by soldering (e.g. with argentarium mentioned by Elder Pliny in his "Historia Naturalis") is used in the majority of plated drachms.

O-V.3 17:00

"GOLD CORROSION": RED STAINS ON A GOLD AUSTRIAN DUCAT

G. Gusmano, Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma-Tor Vergata, Italy, R. Montanari, Dipartimento di Ingegneria Meccanica, Università di Roma-Tor Vergata, Italy, S. Kaciulis, ISMN- CNR-Montelibretti, Roma , Italy, G. Montesperelli, Dipartimento di Ingegneria dei Materiali e del Territorio, Università di Ancona, Italy, R. Denk, Kunsthistorisches Museum Wien, Austria

Surface defects (stains or spots of different colours) have been observed from time to time on historic and modern gold coins in several countries. An Austrian Ducat of the Kunst Historische Museum in Wien developed in the years some red spots on its surface. The same defects have been observed also in modern coins of higher gold purity. The spots have been examined by OM, SEM, EDS microanalysis, XPS and AES.

Optical microscopy observations showed that the "red" defects exhibit in fact a nuance of colors. The surface analysis put in evidence the presence, in addition to gold, of silver and sulphur in the stains. The peak of silver clearly appears in EDS, AES and XPS measurements.

Auger electron spectra and maps showed that sulphur is present in the same area of silver. XPS showed that sulphur is present as sulphide thus it can be assumed that the stains are made of silver sulphide (Ag2S).

It was not possible to determine the origin of the silver (segregation towards the surface of silver present in the alloy or external particles of silver embedded in the matrix) and the thickness of stains because XPS depth profiling have been not performed to avoid to alter the coin surface.

Depth profiling performed on modern coins suffering the same problem allowed to demonstrate that the nuance of colors is due to the inhomogeneous thickness of the spot present on the gold surface. Moreover, it was demonstrated that the spots are formed by two layers: an outer layer made of silver sulphide and an inner layer made of of silver.

Session VI: Conservation/restoration 1
Session chair: M. Stuke

O-VI.1 8:40 -Invited-

LASER PHOTONS FOR ART'S SAKE

C. Fotakis and D. Anglos, Foundation for Research and Technology-Hellas (FORTH), Institute of Electronic Structure and Laser (IESL), P.O. Box 1527, Vassilika Vouton, 711 10 Heraklion, Crete, Greece

There is a number of laser material processing, spectroscopic and interferometric techniques, which have been adapted to the requirements of a variety of demanding conservation applications. Nowdays, there is a number of successful examples of laser cleaning and diagnostic applications of artworks and antiquities, which rely on the use of different types of lasers. Laser based diagnostic techniques are largely non-intrusive and appropriate for the in situ analysis of composition and structural diagnosis of objects. In contrast, the intrusive character of laser cleaning is raising several challenging questions for its safe applications. Laser spectroscopic techniques, for the on line monitoring of the laser cleaning process together with fundamental studies for parameter optimization are critical in this respect. Selected examples will be given and the prospects and limitations of laser technology in art conservation will be discussed.

O-VI.2 9:20 -Invited-

EFFECTS OF CHEMICAL AND BIOLOGICAL WARFARE REMEDIATION AGENTS ON THE MATERIALS OF MUSEUM OBJECTS

Caroline Solazzo, David Erhardt, David von Endt, and Charles Tumosa, Smithsonian Center for Materials Research and Education, Smithsonian Institution, Museum Support Center, 4210 Silver Hill Road, Suitland MD 20746-2863, USA

In the fall of 2001, anthrax contaminated letters were sent to public figures in the United States. Chemical and radiation treatments were employed to decontaminate exposed buildings, objects, and materials. These treatments are effective, but potentially damaging to exposed objects and materials. The recommended surface chemical treatments include solutions, gels, and foams of oxidizing agents such as peroxides or chlorine bleaching agents. Such oxidizing agents are effective against a wide range of hazardous chemical and biological agents. Knowing how these reagents affect various substrates would help to anticipate and to minimize any potential damage. We are examining the effects on typical museum materials of reagents likely to be used, including hydrogen peroxide, sodium hypochlorite, and potassium peroxymonosulfate. Results so far show significant changes in a number of materials. Surface corrosion was observed on metals such as copper, silver, iron, and brass. Color changes occurred with at least one reagent in about one fourth of the dyed fabric swatches tested, and about half of the inks. Samples of aged yellowed paper are bleached. Effects varied with both the substrate and the tested reagent. The observed changes were generally less drastic than might have been expected. Enough materials were affected, though, to preclude the use of these reagents on museum objects unless no less drastic alternative is available. It appears that many objects of lesser intrinsic value can be treated without severe loss of properties or usefulness. For example, most documents should remain legible if the appropriate reagent is used. This work will provide a basis for determining which treatment is most appropriate for a specific situation.

O-VI.3 10:00

UNIDIRECTIONAL NMR SPECTROSCOPY APPLIED TO THE CULTURAL HERITAGE

D. Capitani, A.L. Segre, N. Proietti, S.Viel, Istitute of Chemical Methodologies, CNR Research Area of Rome M.B. 10, 00016 Monterotondo Staz (Rome), Italy, B. Blumich, Institute of Makrom. Chemie, Aachen, Germany, F. Tedoldi, Bruker Biospin, Via G. Pascoli 70, Milano, Italy

NMR spectroscopy is a bulk technique able of measuring several parameters related to the structure of fully different materials such a stones, ceramics, wood and paper. Some of the measurable parameters is strongly sensitive to the state of conservation of the material constituting a manufactured object. Paper is mostly made by cellulose and water. Using different solid state NMR techniques it was possible to measure the water contained in pores embedded in the cellulose matrix. The dimension of the pores and its distribution was obtained. Moreover we observed that degradation, both chemical and enzymatic, is always accompanied by a reduction of the transversal relaxation time of the water component. This is a very important parameter because it is one of the few which can be measured even in strongly inhomogeneous magnetic field. Therefore we propose a new instrument based on the concepts of “unidirectional NMR”. The new NMR instrumentation is rather inexpensive and transportable. It can be applied near to the surface of most manufactured objects which cannot be moved either because too large or too precious. The depth of penetration is still not very large. However with suitable coils presently we can measure at a maximum depth of about 7-8mm. The methods works well not only on organic solids, wood, textiles, paper, but also on porous stones and ceramics. In porous stones, porosity, measured with conventional mercury porosimeters, compares well with data obtained using unidirectional NMR.

O-VI.4 10:20

CORROSION OF 85-5-5-5 BRONZE IN NATURAL AND SYNTHETIC ACID RAIN

Luciano Morselli, Elena Bernardi, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy, Giancarlo Brunoro, Cristina Chiavari, Alessandra Colledan, Corrosion Study Centre "A.Daccò", University of Ferrara, Via L.Borsari 46, 44100 Ferrara, Italy

Nowadays, air pollution and acid depositions strongly contribute to the decay of open-air materials and works of art. So, multidisciplinary studies, inclusive of environmental chemistry, are necessary to investigate cause and effect correlation and to evaluate decay evolution in order to develop suitable strategy of safeguard.

Up to now, the artificial weathering experiments were carried out on bronze exposed to an environment simulating urban-industrial depositions, but a synthetic solution can hardly reproduce the complexity of the real composition. To this regard, a research project is started with the aim to investigate the decay of bronzes exposed to real acid wet depositions. Specifically, comparative studies have being performed by following the corrosion behaviour of different sets of bronze specimens exposed either to the natural rain or to the artificial solution similar in composition, except for the lack of organic components, in order to evaluate their influence. The real rain consists in a mixture of natural rain samples, with pH < 4.5, collected in the monitoring station located in Bologna urban site. As cast G85 bronze specimens were exposed to the aggressive solutions for two periods of 15 and 77 days through a wet-dry technique. The pH trend of solutions and the amount of metals transferred in the solutions were periodically monitored. MO, SEM, XRD, RAMAN analyses and ac electrochemical measurements were performed on artificially weathered specimens. Preliminary results, showing the difference between the ageing in natural and synthetic rain, are here reported.

10:40 **BREAK**

Session VII: Conservation/restoration 2
Session chair: C. Fotakis

O-VII.1 11:00 -Invited-

EIGHTEENTH CENTURY PENNSYLVANIA GERMAN SULFUR INLAID FURNITURE: CHARACTERIZATION, REPRODUCTION, AND AGING PHENOMENA

J.L. Mass and M.J. Anderson, Conservation Department, Winterthur Museum, Garden, and Library, Winterthur DE 19735, USA

The Pennsylvania Germans employed sulfur inlay as an alternative to wood inlay for the decoration of furniture in the late 18th and early 19th centuries. There has been substantial confusion about the composition of these ivory-colored inlays and their manufacture. In 1977, several inlays were identified as an unspecified sulfur allotrope, and in 1995 a method of reproducing them was demonstrated by pouring molten sulfur into an incised decoration. The reproductions were structurally successful, containing air bubble inclusions observed in the 18th century inlays, but they are the yellow color characteristic of alpha-S8, the sulfur allotrope stable at ambient temperatures. 18th century Pennsylvania German ivory-colored furniture inlays were characterized by XRD, FTIR, SEM-EDS, XRF, and GC-MS. The majority of the inlays contained only pure alpha-S8. Artificial aging of a reproduction successfully produced the ivory color of the 18th century inlays. The aged inlay and the 18th century inlays were studied by colorimetry and XRD to identify the source of the ivory color. The results of these experiments suggest that the ivory color is caused by pulverization of the inlay during climactic cycling. The thermal expansion properties of sulfur and black walnut (the wood into which sulfur was typically inlaid) and the walnut's volume changes with relative humidity will be examined as potential causes. Sulfur inlay antecedents, restoration, and contexts will also be discussed.

O-VII.2 11:40

A PERCOLATION CONTEXT EVIDENCED BY THERMOSTIMULATED CURRENTS IN OIL-RESIN ART MEDIA

O. Pagès(a), M. Ajjoun(a), T. Tite(a), J.P. Laurenti(a), J. Townsend(b), (a)Institut de Physique, 1 Bd. Arago, 57078 Metz, France, (b)Tate Gallery Museum, London, U.K.

Due to their thixotropic character natural oil-resin mixtures were used as media by the art painter W. Turner to free from the canvas and create three-dimensional effects. However, local degradations of Turner's paintings occur in the long term, for no valid reason. In naturally-aged home-made oil-resin mixtures, phase separation and color change are observed at low- (R<R1=30%) and large- (R>R2=60%) resin contents (R), respectively. Such thresholds encourage a discussion of the time-behavior in terms of percolation1, i.e. long-range topological effects, rather than by using an approach involving the molecular entities, which are of a forbidding complexity. Such discussion requires to identify one physical property with sharp contrast between the oil and the resin. Precisely the dipolar responses obtained by thermostimulated currents (TSC) differ by three orders of magnitude, to the advantage of the oil. Therefore TSC spectra from the mixtures yield information upon the oil only. At R>R1 the TSC signal suddenly complies with a so-called compensation behavior, which is attributed to a change in the spatial organization of the oil from a continuum (R<R1) into a dispersion of bounded clusters (R>R1). The surveillance of the compensation indicates that the oil clusters tend to coalesce so as to form bigger clusters with aging. The coalescence process is more efficient when the resin forms a continuum (R>R2) than a dispersion (R<R2).

[1] O. Pagès et Al., J. Mater. Res. 14, 606 (1999)

O-VII.3 12:00

RESEARCH ON COATING MATERIALS FOR CONSERVATION OF LIMOGES PAINTED ENAMELS

Blythe McCarthy, Smithsonian Institution, Freer Gallery of Art/Arthur M. Sackler Gallery, Washington D.C.,USA, Monika Pilz and Hannelore Roemich, Fraunhofer Institute for Silicate Science, Wuerzburg, Germany

This paper will describe a project that tested the suitability of several materials as protective coatings for Limoges painted enamels of the early Renaissance. These enamels (alkali-lead-silicate glasses applied to a copper support) are subject to severe degradation. Model enamels of glass composition similar to that found in the Limoges enamels were made. A series of both fresh and weathered enamels were coated and subjected to artificial weathering. Fourier transform infrared spectroscopy (FTIR) was used in reflectance mode along with optical microscopy to obtain a measure of the effectiveness of the coatings.

O-VII.4 12:20

ION BEAM AND INFRARED ANALYSIS OF MEDIEVAL STAINED GLASS

M. Vilarigues(a), P. Redol(b), L.C. Alves(c) and R.C. da Silva(c), (a)Dep. Conservação e Restauro, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal, (b)Mosteiro de Santa Maria da Vitória, 2440 Batalha, Portugal, (c)Dep. Física, ITN, E.N.10, 2686-953 Sacavém, Portugal

Ion beam analysis (IBA) and Fourier Transform Infrared (FTIR) spectroscopy were used to characterize 15th century stained glass fragments from Batalha Monastery. This information is being used to help establishing the origins, art schools and artistic trends involved in the manufacture of these panels.

Being the preservation of the art objects and artifacts a major issue, the combined use of the ion beam based analytical techniques Rutherford Backscattering Spectrometry (RBS) and Particle Induced X-ray Emission (PIXE), in broad beam and focused microbeam modes, with FTIR spectroscopy, aims at achieving non-destructively a clear cut characterisation of elemental compositions of the bulk glass and painted layers, as well as identifying corrosion products. Elemental maps were obtained with a nuclear microprobe, and compared with the results of micro-FTIR. Although the bulk composition found is consistent with the glass manufacturing practices of the middle ages, the grisailles were found to be based on lead oxides and silicates with a very high Fe content, and also with significant Zn and Cu contents, at variance with the reports of those practices, in particular the uncommon association of Zn with Fe and Cu. The analysis also revealed a surface layer impoverished in Si and K and enriched in Ca. This may be due to the movement of Ca ions to the surface, a process known common to glass corrosion and consistent with the finding of $CaCO_3$ by micro-FTIR.

12:40 **LUNCH**

Session VIII: Paper/ink
Session chair: E. Angelini

O-VIII.1 14:00

NANOMETRIC SIZE CONTROL AND TREATMENT OF HISTORIC PAPER MANUSCRIPTS AND PRINTS WITH LASER LIGHT AT 157 NM

Z. Kollia, E. Sarantopoulou, A.C. Cefalas, National Hellenic Research Foundation, TPCI, 48 Vassileos Constantinou Avenue, Athens 11635, Greece, S. Kobe, Z. Samardlija, Jozef Stefan Institute, 1000 Ljubljana, Jamova 39 Slovenija

In this communication we report on evaluating the results of foxing removal from different historic paper prints following laser treatment at 157nm by mass spectroscopy X-ray microanalysis. AFM and SEM imaging of treated surfaces indicate only localized effects following laser treatment. Laser treatment [1] of old paper at 157nm [2] is an effective method of removing foxing and organic stains from old paper because: a) at 157nm photo-dissociation of organic matter is taking place b) absorption at this wavelength is at least one order of magnitude higher in comparison to 193 and 248nm, allowing therefore high resolution depth control, and c) the limit of the spatial resolution control over exposed areas could be extended down to 100 nm. d) heating of the substrate is avoided due to the fact that the dissociation of fungus is a purely photochemical process.

[1] J. Kolar, M. Strlic, S. Pentzien, W. Kautek, Appl. Phys. A71, 87 (2000).
[2].A.C. Cefalas, E. Sarantopoulou, Z. Kollia, Appl. Phys. A 73, 571 (2001).

O-VIII.2 14:20

SURFACE ANALYSIS OF PAPER DOCUMENTS DAMAGED BY “FOXING”

R. Buzio(a), P. Calvini(b), A. Ferroni(c) and U. Valbusa(a), (a)INFM and Dipartimento di Fisica, Via Dodecaneso 33, 16146 Genova, Italy, (b)Soprintendenza Beni Architettonici della Liguria, Via Balbi 10, 16126 Genova, Italy, (c)Laboratorio di Restauro e Conservazione di Opere su Carta, Via Ravasco 4/1, 16128 Genova, Italy

The causes of foxing, a rust-red spotting of engravings, books and archive documents, are not yet completely understood, but they are usually ascribed to mould growth and/or heavy-metals induced degradation of cellulose and sizing materials[1].

In the present work we report the use of ATR-FTIR, AFM and Image Analysis as non-destructive tools for the surface analysis of foxing stains in respect to their chemical and physical characteristics. It is known from the literature that most foxing stains fluoresce pale-yellow to white in near-UV, and some preliminary results of the deconvolution of FTIR spectra indicate that both the fluorescence and the brownish visible discoloration are due to increasing amount of conjugated chemical groups(beta diketones and beta,alphaunsaturated carbonyls). In some cases of very brown and not fluorescent stains the overall FTIR spectrum, together with an anomalous high absorbance at 1552 cm-1, reveals a beta diketone-metal complex. The AFM results show that the foxing stains have a self-affine [2] nature over 6 orders of magnitude. The sample shows in fact the same fractal dimensionality from the real dimension of a few millimetres, down to 10 nm.

[1]. Bertalan, S. (1994) Foxing. Paper Conservation Catalog, 9th edn., American Institute for Conservation, chapter 13, 1-39.
[2]. Barabasi, A.L. and Stanley, H.E. (1995) Fractal Concepts in Surface Science. Cambridge University Press 1995.

O-VIII.3 14:40

CHARACTERIZATION OF LASER-TREATED PAPER

Pascale Rudolph(a), Frank J. Ligterink(b), Jose L. Pedersoli Jr.(b), Hadeel Abdul Aziz(c), John B.G.A. Havermans(c), Hans Scholten(d), Dennis Schipper(d), Wolfgang Kautek(a), (a)Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany, (b)Netherlands Institute for Cultural Heritage, Postbus 76709, 1070 KA Amsterdam, The Netherlands, (c)Netherlands Organisation for Applied Scientific Research, PO.Box 49, 2600 AA Delft, The Netherlands, (d)Art Innovation, Westermaatsweg 11, 7556 BW Hengelo, The Netherlands

Paper represents one of the most important materials in cultural heritage. For both aesthetic and conservation reasons, cleaning of these materials is often wanted. Conventional methods (wet or mechanical) are not always successful. Dirt penetrated into the fibre structure cannot be removed without chemical or mechanical damage.

In contrast to these traditional methods, a ns-pulse laser provides promising cleaning results in many difficult cases [1-4]. The influence of various laser wavelengths (355nm, 532nm, and 1064nm) and the aging status of modern paper test systems were studied. Colorimetric measurements and the determination of the degree of polymerisation proved to be most useful for the characterization of the laser-treated paper.

[1]. W. Kautek, S. Pentzien, P. Rudolph, J. Krüger, and E. König, Appl. Surf. Sci 127-129 (1998) 746.
[2]. W. Kautek, S. Pentzien, J. Krüger, and E. König, in "Lasers in the Conservation of Artworks I", Restauratorenblätter (Special Issue), (Eds.) W. Kautek and E. König, Mayer & Comp., Wien, 1997, S. 69.
[3]. P. Rudolph, S. Pentzien, J. Krüger, W. Kautek, and E. König, "Lasertechnik in der Restaurierung", Restauro 104 (6), (1998) 396.
[4]. J. Kolar, M. Strlic, S. Pentzien, W. Kautek, Appl. Phys. A 71 (2000) 87-90.

O-VIII.4 15:00

THE IMPACT OF GALLIC ACID ON IRON GALL INK CORROSION

V. Quillet, C. Rémazeilles, J. Bernard, Laboratoire d'Etude des Matériaux en Milieux Agressifs, Université de La Rochelle, 25 rue Enrico Fermi, 17000 La Rochelle Cedex, France, A. Wattiaux, L. Fournes, Institut de Chimie de la Matière Condensée de Bordeaux, Chateau Brivazac, 87 avenue du Docteur Schweitzer, 33608 Pessac Cedex, France

Iron-gall ink corrosion is a threat for our graphic patrimony since it concerns a large amount of old manuscripts. Corroded papers turn brown and brittle. The chemical reactions involved in this corrosion are relatively well known : they include both acidic hydrolysis and oxidation catalysed by free iron II.

Yet, a great variety of iron-gall ink recipes including a wide range of ingredients can be found in the literature and the visual aspect of old inks can be very different from one inscription to another, even if those have been written on the same sheet of paper. This suggest that even if the free iron II plays a dominant role in the paper alteration, the contribution of other ingredients should not be neglected. For this reason, we explored the impact gallic acid may have on the corrosion mechanisms and in particular on the oxidation reactions. These investigation were carried out on laboratory probes prepared with 100% linters paper sheets immerged in different solutions, all containing the same amount of iron sulphate, and different gallic acid concentrations. These probes were then artificially aged and their degradation state was evaluated by bursting strength measurements, FTIR spectrometry and Mössbauer spectrometry. All these analysis lead to a better understanding of the impact of gallic acid on the oxidation mechanisms, and gives some tracks for the interpretation of the visual feature observed on old manuscripts.

15:20 **BREAK**

Session IX: Pigments
Session chair: A. Bouquillon

O-IX.1 16:00

IDENTIFICATION OF PIGMENTS ON AN AZTEC RELIEF IN THE SMITHSONIAN COLLECTIONS

Pamela Vandiver, Smithsonian Center for Materials Research, Suitland MD, USA and Jane Walsh, National Museum of Natural History, Washington D.C., USA

Optical microscopy was used to identify the original coloration on an Aztec stone relief re-used in recent times as a stair step. Minute traces of pigment were sampled and analyzed by a variety of techniques (SEM-EDS, XRD, FTIR and micro-DTA) in order to identify colorants, binder and the use of plaster in some of the colors.

O-IX.2 16:20

CADMIUM COLOURS, COMPOSITION AND PROPERTIES

J. Paulus and U. Knuutinen, EVTEK Institute of Art and Design, Conservation Department, Lummetie 2, 01300 Vantaa, Finland

This research investigates the composition and the properties of the cadmium colours. The examined colours were 24 different aquarelle cadmium colours from six different manufacturers. The colours ranged from light, bright yellows to the dark, deep red tones. The aim of this research was to find out if the pigments contain cadmium salts: sulphides or selenides. This information would help in choosing colours in the conservation process. Today water colours not containing cadmium pigments are being sold as cadmium colours, thus their properties might be different from actual colours.

The goal of the research was to verify that the colour samples chosen contained cadmium pigments and to estimate their composition and ageing properties. Element analyses were detected from colour samples using micro chemical tests and X-Ray fluorescence measurements. Thin layer chromatography was used for detecting gum arabic that possibly had been used as a binding media in the colour samples chosen. Through ageing tests, the resistance of colour samples to the exposure to light, heat and humidity was investigated. ICS (Instrumental Colour System) spectrophotometer was used in determining the hues and hue changes of the water colour samples. The apparatus used CIE Lab tone colour measuring system. From the colour measurements the changes in the lightness/ darkness, redness, yellowness and saturity of the samples were examined.

O-IX.3 16:40

PALAEOLITHICAL PAINTING MATTER: NATURAL OR HEAT-TREATED MANGANESE OXIDES?

E. Chalmin(a,b), C. Vignaud(a,c), M. Menu(a), (a)Centre de Recherche et de Restauration des Musées de France, UMR 171 du CNRS, 6 rue des Pyramides, 75041 Paris, France, (b)Laboratoire des Géomatériaux, Université de Marne la Vallée, 5 boulevard Descartes, Champs sur Marne, 77454 Marne la Vallée cedex, France, (c)Laboratoire Interfaces et Systèmes Electrochimiques, UPR 15 du CNRS, Université P et M Curie, 4 place Jussieu, 75252 Paris Cedex 05, France

Since the recognition of rock art in 1902 by Cartailhac, painting media used by Palaeolithic man has been the subject of numerous physico-chemical studies. The first analyses performed were elemental and scanning electron microscopy (SEM). Methods such as X-ray diffraction (XRD) or Raman spectroscopy allow determination of the structure. Nevertheless, these techniques can not provide evidence of the thermal history of an object. Using transmission electron microscopy (TEM), it has been demonstrated that red hematite can be obtained by the dehydration of goethite via the detection of pores. This method is now applied to study the more complex phase transformations in manganese oxides.

The different phases of manganese oxide can be distinguished using their elemental composition, their structure and the oxidation state of Mn ion (II, III, IV). TEM also allows distinguishing the morphology and crystallinity of the various Mn oxides. This method was used as a substitute for XRD when the sample size is small or the specimen is poorly crystallized. Moreover, presence of longitudinal channels or larger pores coming from dehydration of manganite (MnOOH) can be visualized. At 360°C the monoclinic manganite (MnOOH) phase transform to tetragonal pyrolusite (MnO_2) by oxidation. At 560°C this pyrolusite can then be reduced to cubic bixbyite (Mn_2O_3). Finally bixbyite transforms to tetragonal hausmannite (Mn_3O_4) at 950°C. TEM observations at different temperatures show the typical porous microstructure accompanying the phase transformation.

Less is known about the complex process of transformation in ternary barium manganese oxides. XRD coupled with differential thermal analysis (DTA) sheds light on the progressive evolution from the monoclinic (b.c.) barium manganese oxide hydrate (romanechite $BaMn_5O_{10}$, xH_2O, channel 3x2) to monoclinic (b.c.) hollandite $BaMn_8O_{16}$, xH_2O (channel 2x2) up to 500°C. But nowadays no characteristic defect of this processing has been detected.

To better understand the mechanisms of these transformations, in situ TEM observations were performed using a heating stage. The appearance of pores, morphological evolution and recrystallization are observed directly.

This technique of TEM was applied on painting samples from the cave of Lascaux (Dordogne, France) and more precisely from black "crayons", from the famous "Scène du Puits", "blazons", and "Grand Taureau" representations. These studies are evidence of the use of raw or mixed black pigments, however there is no evidence of heat treatment of these materials.

O-IX.4 17:00

DARKENING OF PAINTED SURFACES BY COPPER BASED PIGMENTS IN ORGANIC MEDIA

B. Brunetti, C. Miliani, L. Cartechini, I. Borgia, A. Sgamellotti, INSTM, Department of Chemistry, University of Perugia, Perugia, Italy, S. Padovani, P. Mazzoldi, INFM, Department of Physics, University of Padova, Padova, Italy, F. D'Acapito, INFM, ESRF, GILDA-CRG, Grenoble, France, A. Casoli, Dipartimento di Chimica, Universita' di Parma, Parma, Italy

Browning of painted surfaces, characterised by copper based pigments in organic media, has been reported. The characterisation of such phenomenon is fundamental in conservation of paintings and also relevant in restoration. Indeed, in the presence of darkening of painted surfaces, a question arise whether to remove the darkened layer away, to reveal the bright underlying pigment, or not. The choice may be different if the dark layer is made by a direct alteration of the pigment or only by a non-original superficial upper layer [1]. In a recent study of a panel painting of Niccolo' Alunno (dated 1499), currently under restoration, we have found the singular case where two different copper based pigments, such as malachite (green) and azurite (blue), in a proteinaceous medium turned to a brown-black alteration. Using several experimental techniques, blackened layers have been characterised. They are composed by organic materials, containing only a small amount of copper. The original crystals of the underlying pigments appear unaltered. In order to better characterise the composition of the organic phase which cover for about 1 micron the underlying pigment, EXAFS measurements have been carried out using synchrotron radiation at Cu K-edge (8979 eV. State and chemical environment of copper have been determined. 1. M.Gunn, G. Chottard, E. Riviere, J.J. Girerd, and J.C. Chottard, Studies in Conservation 47 (2002) 12-23.

Session X: Other materials in cultural heritage
Session chair: G. Padeletti

O-X.1 8:40 -Invited-

CHEMICAL INVESTIGATION ON FRENCH WAX SCULPTURES FROM THE 19th CENTURY
S. Colinart(a), M. Regert(a), M. Proust(a), J. Vatelot(b),(a)Centre de Recherche et de Restauration des Musées de France (C2RMF) UMR 171 CNRS, 6 rue des Pyramides, 75041 Paris cedex 01, France, (b)14 chemin des Côtes Bizières, 95520 Osny, France
Wax sculptures are currently considered as minor art even though they represent the different stages of an artist's creation.
These artifacts are fragile and they often show alterations which can be observed on their surface as bleaching and weeping. The waxy material of some models, medals, preparatory study or finished pieces from French museum collection have been studied by the means of infrared spectrometry (IRTF), gas chromatography (GC, GC-MS) and scanning electron microscope (SEM-EDS) in order to identify their composition and the physico-chemical alteration processes of their surface. Thanks to chemical investigations performed on different materials such as the ones used by Degas,Fremiet,Rodin, several inventive waxy recipes were enlightened. Beeswax, the traditional wax for modeling and molting since antiquity, is still mainly employed during the 19th century, mixed with organic additives (fats, natural resins) and coloring materials (pigments, dyes). The use of starch, coming from wheat or potato flour, has been encountered in some modeling pastes, giving evidence for the evolution of sculpture techniques through time since this material was not used in waxy pastes before the 19th century. The development of chemistry during the 19th century is also perceptible in the composition of some pastes. The identification of stearin and of some other waxy by-products shows the rapid diffusion of Chevreul’s work within the industrial and artistic worlds The aging of the various organic substances in the waxy pastes can lead to modifications of the initial composition. The chemical investigations indicate that surface alterations may be the result of hydrolysis, vaporization, salt crystallization or mechanical alterations.

O-X.2 9:20

ANALYSIS AND TECHNOLOGY OF PLASTERS FROM THE BAMIYAM BUDDHAS IN AFGHANISTAN
Pamela B. Vandiver, Smithsonian Center for Materials Research and Education, 4210 Silver Hill Road, Suitland MD 20746, USA and Paul Bucherer, Afghanistan Museum in Exile, Hauptstrasse 34, 4416 Bubendorf, Switzerland
Results are presented of analyses of composition, microstructure and properties of the fiber-reinforced gypsum plaster technologies of the two Bamiyan Buddhas that were destroyed by the Taliban in Afghanistan. Replicative studies were conducted in order to aid in conservation of the monuments and in the hope that the technology will be revived and continue to be practiced.

O-X.3 9:40

LEACHING PHENOMENA ON LEAD SILICATE GLASSES
Laura Milanese, Renzo Bertoncello, Dept. C.I.M.A. (unità I.N.S.T.M.), University of Padova, via Loredan 4, 35131 Padova, Italy and Anne Bouquillon, Jean Claude Dran, Joseph Salomon, Benoit Mille, C2RMF-UMR CNRS, 6 rue des Pyramides, 75041 Paris, France
Lead silicate glasses (45.3 weight % of lead oxide) were leached in aqueous static solutions of HNO3 at pH=2 and T=90°C for different leaching times, to study the weathering mechanism of lead glasses, that simulate archaeological materials, in acidic environment.
The leached surface was analysed by different analytical techniques like RBS (Rutherford Backscattering Spectrometry), XPS (X-ray Photoelectron Spectroscopy) and SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectrometry). Even the leaching solutions were analysed by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) to measure the amount of lead and other ions that migrate from the glass to the solution. The results obtained show that the leached layer, depleted of lead and alkaline ions, is some hundreds of nanometres thick. It is about ten times thinner than the one obtained on lead-rich glasses (66 weight % of lead oxide), but the kinetics of the leaching process is exactly the same: a stabilisation takes place after 2 leaching days and a Pb-enriched surface thin layer (a few nanometres thick) is formed.

O-X.4 10:00

INVESTIGATION OF CHINESE ARCHAIC JADE BY PIXE AND µRAMAN SPECTROSCOPY

T.-H. Chen, T. Calligaro, S. Pagès-Camagna, M. Menu, Centre de Recherche et de Restauration des Musées de France, CNRS-UMR 171, Palais du Louvre, Paris, France

Manufactured as tools and particularly as ritual objects, jade was much employed in China since the Neolithic (6000 -2500 B.C.). It is therefore an important witness of ancient Chinese history. In this work, we studied Chinese jade objects from Guimet Asian Museum in Paris by means of non-destructive techniques. Major, minor and trace elements are determined with external beam PIXE (Particle Induced X-ray Emission) and PIGE (Particle Induced Gamma-ray Emission). The structure of jade is characterised by µRaman spectrometry using two laser sources (532nm, 632nm). The studied jades, dated from the Neolithic to Han Dynasty (about 3,000 BC to 9 AD), having diverse colour including white, green yellow, green, dark green and brown, are mainly nephrite, the so-called " true jade".

The aim of the present research is to investigate the distribution of cations in nephrite structure, which is often linked to deposits, and plays an important role in the mechanism of coloration of nephrite.

Nephrite, a variety of tremolite-actinolite of the amphibole group, presents variable Fe and Mg concentrations. Fe/(Fe + Mg) ratio is used to distinguish tremolite from actinolite. Moreover, this value is an indicator of the type of nephrite deposit. With the elemental concentration obtained by PIXE/PIGE and according to electroneutrality, we can also evaluate the ratio of Fe^{3+} / Fe^{2+} which is crucial for the colour of nephrite.

The OH stretching vibration band of nephrite (3620 - 3680 cm^{-1}) by µRaman spectrometry (532nm laser), depending on the electronegativity of the bonded Fe and Mg cations, presents one to four peaks which, together with the results of PIXE/PIGE, allow us to estimate cation occupancies in the nephrite structure. Fe^{2+}, Fe^{3+}, Mg^{2+} and Mn^{2+} occupancies in the three octahedral sites M1, M2 and M3 of nephrite are not randomly distributed. We will discuss the possible dominant factors influencing this distribution .

lastly study of cation distributions, linked with geological conditions of nephrite formation or alteration, might reveal jade provenance.

O-X.5 10:20

TRANSMISSION ELECTRON MICROSCOPY INVESTIGATIONS OF ANCIENT EGYPTIAN COSMETIC POWDERS

C. Deeb, P. Walter and J. Castaing, Centre de Recherche et de Restauration des Musées de France, CNRS UMR 171, 6 Rue des Pyramides, 75041 Paris Cedex 01, France, P. Penhoud and P. Veyssière Laboratoire d'etude des microstructures, CNRS UMR 104, ONERA, BP 72, 92322 Chatillon Cedex, France

The processing technologies available during the times of ancient Egypt are of present concern to the field of Archaeology and Egyptology. Materials characterization is the most promising tool for establishing the processing history of archaeological specimens. In this study, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are used for phase identification and to study the microstructure and characteristic defect structures in ancient Egyptian cosmetic powders. These powders generally consist of a mix of Pb-containing mineral phases: galena (PbS), cerusite ($PbCO_3$), phosgenite ($Pb_2Cl_2CO_3$), etc. Modern materials are fabricated according to recipes found in ancient texts to mimic the processing in ancient times and to compare with the archaeological specimens. In particular, the dislocation structure of PbS crystals deformed in the laborator

10:40 **BREAK**

11:00 CLOSING REMARKS & DISCUSSION