

*Biotechnology, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Yokohama 226-8501, Japan. E-mail: mgr@indiana.bio.purdue.edu*

The contractile tail of bacteriophage T4 undergoes major structural transitions when the virus attaches to the host cell surface. The baseplate at the distal end of the tail changes from a hexagonal to a star shape. This causes the sheath around the tail tube to contract and the tail tube to protrude from the baseplate and pierce the outer cell membrane and the cell wall, before reaching the inner cell membrane for subsequent viral DNA injection. Analogously, the T4 tail can be contracted by treatment with 3 M urea. The structure of the T4 contracted tail, including the head-tail joining region, has been determined by cryo-electron microscopy to 17 Å resolution. This 1200 Å-long, 20 MDa structure has been interpreted in terms of multiple copies of its approximately 20 component proteins. A comparison with the metastable hexagonal baseplate of the mature virus shows that the baseplate proteins move as rigid bodies relative to each other during the structural change.

**Keywords:** bacteriophage T4, infection, conformational changes

#### MS58 CRYSTALLOGRAPHY AND UNDERSTANDING OF CULTURAL HERITAGE

**Chairpersons:** Salvatore Siano, Henk Schenk

##### MS58.28.1

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#### An Archaeometric Study of Lead-White Pigment and its Production using Neutron Diffraction

Dirk Visser<sup>a</sup>, Winfried Kockelmann<sup>b</sup>, Leslie Carlile<sup>c</sup>, <sup>a</sup>*NWO-Physics, ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK.* <sup>b</sup>*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK.* <sup>c</sup>*Netherlands Institute for Cultural Heritage (ICN), Department of Conservation Science, Gabriël Metsustraat 8, 1071 EA Amsterdam, NL.* E-mail: d.visser@rl.ac.uk

In antiquity up to very recent times lead-white pigment was widely used. However the structures of its phases as well as the interaction of the lead-white pigment with oil are not well known. In this paper we look at the different production processes of the lead-white through the ages by means of historically based reconstructions (the Dutch stack method, the German and French production processes). The products involved in the different stages of the lead white production process are characterised by means of Rietveld phase analysis of neutron diffraction data. The interaction of linseed oil, produced according to historical recipes, with the lead-white pigment as well as with the hardener materials is studied using paint reconstructions under varying external conditions. Neutron diffraction can also be used in this case to obtain information on the reacted products.

**Keywords:** archaeometry, phase analysis, neutron diffraction

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#### Powder Diffraction in Art and Archaeology

Eric Dooryhée<sup>a</sup>, Pauline Martinetto<sup>a</sup>, Michel Anne<sup>a</sup>, Jean-Louis Hodeau<sup>a</sup>, Manuel Sanchez del Rio<sup>b</sup>, Philippe Walter<sup>c</sup>; <sup>a</sup>*Laboratoire Cristallographie CNRS, 25, avenue des Martyrs, BP 166, 38042 Grenoble Cedex 9, France,* <sup>b</sup>*ESRF, BP 220, 38043 Grenoble Cedex c* <sup>c</sup>*C2RMF CNRS, 6, rue des Pyramides, 75041 Paris Cedex 1, France,* E-mail: pauline.martinetto@grenoble.cnrs.fr

Powder diffraction is one of the most common techniques used as a tool for non-destructive investigations of archaeological objects. It enables both the study of small specimen (extracted from easel paintings, cosmetics recipients, walls of prehistoric caves...) and the direct analysis of painted fragments. Part of our activity is to apply relevant crystallographic techniques on ancient powdered materials, particularly using synchrotron X-ray and neutron radiation, supplemented by spectroscopic and microscopic methods: identification of the crystalline phases, quantitative and microstructural analysis, structure determination... Some difficulties, due to the specificity of the samples (rare, precious, multiphased,

poorly crystallised, spread on a support...) have to be controlled. We will give some relevant examples showing the applicability of powder diffraction to the study of ancient pigments[1-3]. Recent developments about data analysis routines will be presented.

[1] Walter P., et al., *Nature*, 1999, **397**, 483-484. [2] Martinetto P., et al., *Acta Crystallographica*, 2002, **C58**, i82-i84. [3] Sanchez del Rio M., et al., *Archaeometry*, in press.

**Keywords:** powder diffraction, archaeology, non-destructive analysis

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#### X-ray Powder Microdiffraction: Useful Tool in Investigation of Wall Painting Layers

Veronika Simova, Petr Bezdicka, Janka Hradilova, David Hradil, Eva Kotulanova, Tomas Grygar, *Academic Laboratory of Materials Research of Paintings (ALMA) - joint workplace of the Institute of Inorganic Chemistry AS CR in Rez and Academy of Fine Arts in Prague, Czech Republic.* E-mail: veronika@iic.cas.cz

Identification of inorganic and organic compounds in colour layers helps in dating and restoring of historical paintings. X-ray powder microdiffraction (micro-XPRD) extends the possibilities of traditional optical microscopy and SEM/EDX used in microanalysis of mineral pigments in fragments of paints. Laboratory diffractometers with monocapillary primary optics and x,y,z-stage are now available for a routine analysis of 0.1 mm large samples, heterogeneities in fragments and colour layers in cross-sections with a roughly flat surface. Resulting diffractograms usually need no pre-treatment before their search-match analysis.

As an example, measurements of the top green layer in a sequence of colour layers in wall paints from the Plasy Monastery, Czech Republic, are shown. The sample was measured both in Bragg-Brentano geometry and micro-XPRD, and quartz, albite, celadonite, chlorite, calcite, and gypsum were found. Micro-XPRD showed that chlorite and quartz are a contamination from the sand used in plaster. Micro-XPRD also revealed that gypsum is a part of the salt efflorescence on the outer surface. Micro-XPRD identified celadonite as a green pigment in colour layer that would not be possible using spectral methods.

**Keywords:** micro-XPRD, mineral pigments, paintings

##### MS58.28.4

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#### Colouring and Opacifying Agents in Roman Glass: a Multi-technique Analytical Approach

Rossella Arletti<sup>a</sup>, Simona Quartieri<sup>b</sup>, Giuseppe Sabatino<sup>b</sup>, Maurizio Triscari<sup>b</sup>, Giovanna Vezzalini<sup>a</sup>, <sup>a</sup>*Department of Earth Science, University of Modena and Reggio Emilia, Italy.* <sup>b</sup>*Department of Earth Science, University of Messina, Italy.* E-mail: rarletti@unimore.it

Many samples of opaque Roman glass of different typology (mosaic tesserae, game counters, vessels and artefacts) and colours (red, green, yellow, white and blue) coming from different Italian archaeological sites have been analysed to identify and characterize the colouring and opacifying agents.

The chemical analyses were carried out using wavelength dispersive electron microprobe (WDS-EMPA), the crystalline phases used as opacifiers were identified using both an automatic powder diffractometer (XRPD) and a Gandolfi camera. Secondary electron (SEM) and backscattered electron (BSE) images were performed to study the distribution and morphology of the opacifier particles, whereas their qualitative chemical analysis was obtained with an energy dispersive system (EDS). Moreover X-ray absorption spectroscopy (XAFS) and XPS studies have been performed on green and red samples to investigate the influence of coordination and oxidation state of copper atoms on colour and opacity of the glass. These analyses allowed to conclude that, in the most of the red opaque samples, copper is mainly present as metallic nano-clusters, accompanied by monovalent copper coordinated to the oxygen atoms of the glass framework, whereas in few ones, it is present as less stable cuprite crystals, leading to a more weathered glass. In green

samples, both Cu<sup>+</sup> and Cu<sup>2+</sup> were detected, both incorporated in the glass matrix, the second one being responsible for the colour of the artefacts.

**Keywords:** archaeometry, glass, EXAFS

#### MS58.28.5

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##### Maya Blue: a Long Lasting Mystery Revealed

Giacomo Chiari<sup>a</sup>, Roberto Giustetto<sup>b</sup>, <sup>a</sup>*Getty Conservation Institute, Los Angeles, California.* <sup>b</sup>*Dip. Scienze Mineralogiche e Petrologiche, Università di Torino, Italy.* E-mail: gchiari@getty.edu

The composition of Maya Blue, one of the most important pigments in antiquity, has puzzled scientists for decades. Recent studies using different analytical techniques including synchrotron and neutron powder diffraction, proved that the pigment is a combination of palygorskite (characterized by large channels), and the organic dye indigo.

Pigment preparation was repeated successfully and is easy (mix clay and dye and heat at ~100°C for a few hours). Chemical modelling showed indigo fitting the channels without impediment, thus it was assumed that indigo would fully or partially occupy the channels. However, energy calculations and thermal analyses showed indigo cannot penetrate into channels, since the water present does not leave the channels at synthesis temperature and strong H-bonds formed by the first molecule in the channels need to be broken.

A new concept of Maya Blue structure is presented, based on the fact that indigo only fill the grooves present at the crystal's surface. These grooves, which can be thought of as half channels split along cleavage planes, can equally well accommodate the dye molecule, forming one or two H-bonds explaining the stability and colour of the complex. A possible line of study to determine the provenance of Maya Blue is based on mutual abundance of the monoclinic and orthorhombic polymorph of palygorskite, determined via Rietveld refinement. . On the basis of the new theory all the facts previously hard to explain, become comprehensible.

**Keywords:** maya blue structure, palygorskite, synchrotron and neutron powder diffraction

#### MS59 APPLICATIONS OF SYNCHROTRON AND NEUTRON FACILITIES IN STRUCTURAL CHEMISTRY

**Chairpersons:** Paul Raithby, Trevor Forsyth

#### MS59.28.1

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##### Microcrystal X-ray Diffraction and MAS NMR Studies of Zeolites

Russell E. Morris, *School of Chemistry, University of St Andrews, Purdie Building St Andrews KY16 9ST UK.* E-mail: rem1@st-and.ac.uk

Zeolites are notoriously difficult to prepare as large single crystals. Until the last decade we have had to rely on powder diffraction as our major tool for determining their structure. With the advent of single crystal X-ray diffraction as a standard tool at synchrotron sources this limitation has been somewhat reduced. In this presentation I will discuss some of our recent work on studying the structure and properties of zeolites using the single crystal X-ray diffraction station at the Synchrotron Radiation Source, Daresbury, UK.

Not only have new structures been solved using this facility, but we have also shown how the details of previous powder X-ray diffraction work have sometimes been incorrect. In addition, the facility has also allowed us to crystallographically study the thermal properties of zeolites, such as negative thermal expansion, in more detail than was previously possible.

I will also explain how solid state MAS NMR studies can be used to improve the accuracy of our crystallographic models, and I will discuss the possibilities for solving structures from NMR data.

**Keywords:** zeolites, microcrystal diffraction, NMR

#### MS59.28.2

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##### Combined X-ray and Neutron Charge Density Studies on C-H activation catalysts

Wolfgang Scherer<sup>a</sup>, Bjørn Pedersen<sup>b</sup>, G. Sean McGrady<sup>c</sup>, <sup>a</sup>*Institute of Physics, University of Augsburg.* <sup>b</sup>*FRM-II, TU Munich, Germany.* <sup>c</sup>*Department of Chemistry, University of New Brunswick, Canada.* E-mail: wolfgang.scherer@physic.uni-augsburg.de

The new single crystal diffractometer RESI (*RE*ciprocal Space *I*nvestigat*o*r) at the new high-flux neutron source FRM-II (www.frm2.tum.de) has been optimized for the demands of combined X-ray and neutron charge density studies (high resolution data at low backgrounds) by employing an X-ray and neutron sensitive imaging plate detector, a flexible  $\kappa$ -goniometer geometry and a focusing neutron guide for thermal neutrons. The new diffractometer concept will be outlined, and the advantage of combined X-ray and neutron charge density studies illustrated by first applications in the field of catalyzed C-H activation. We will demonstrate that so-called 'ligand-induced charge concentrations' in the valence shell of main group and transition metal complexes (*i*) can be identified by experimental charge density studies; and (*ii*) act as controlling parameters in C-H activation processes.[1,2] Systematic experimental studies of molecular charge distributions will thus lead to significant advances in the design and chemical control of catalysts for C-H activation and other processes, with central relevance to many reactions of academic and commercial importance.

[1] Scherer W., McGrady G.S., *Angew. Chem. Int. Ed.*, 2004, **43**, 1782. [2] Scherer W., Sirsch P., Shorokhov D., Tafipolsky M., McGrady G.S., Gullo E., *Chem. Eur. J.*, 2003, **9**, 6057.

**Keywords:** electron density, neutron diffraction, agostic interactions

#### MS59.28.3

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##### Structure and Dynamics of Co-ordination Compounds by Neutron Scattering

Alberto Albinati, *Department of Structural Chemistry, University of Milan, Milan, Italy.* E-mail: alberto.albinati@unimi.it

The importance of transition metal hydrido-complexes, both classical and non-classical (i.e. compounds containing the M-H or M-H<sub>2</sub> moieties) in catalytic reactions, in particular hydrogenations, is well known, and much work has been carried out in recent years to obtain a detailed understanding of the nature and reactivity of the M-H and M-H<sub>2</sub> moieties.

Single crystal neutron diffraction, at low temperature, has been instrumental in establishing the correct co-ordination geometry in non-classical hydrides. It has been established that the H-H separation can cover a wide range of distances, from ~ 0.8 Å (strong H-H bond) to ~ 1.4 Å (weak H-H bond), corresponding to various degree of the H-H activation, thus neatly spanning the oxidative addition pathway and giving support to the mechanistic studies.

However, it is worth noting that a complete description of the reactivity in hydrido-compounds can only be achieved by combining the diffraction results with the knowledge of their dynamics that can be obtained from neutron incoherent inelastic scattering (INS) experiments.

I will discuss some recent structural results on transition metal poly-hydrides and show how, by combining neutron diffraction, INS and DFT calculations, the H<sub>2</sub> dynamics can be explained.

**Keywords:** transition metal hydrides, molecular hydrogen complexes, neutron scattering

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##### Location of a 4-coordinate H Atom via Neutron Diffraction

Robert Bau<sup>a</sup>, Muhammed Yousufuddin<sup>a</sup>, Zhaomin Hou<sup>b</sup>, Olivier Tardif<sup>b</sup>, Jens Baldamus<sup>b</sup>, Sax A. Mason<sup>c</sup>, Garry J. McIntyre<sup>c</sup>, <sup>a</sup>*Dept. of Chemistry, University of Southern California, Los Angeles, CA 90089, USA.* <sup>b</sup>*RIKEN (Institute of Physical and Chemical Research), Saitama*