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Science and art

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A marriage between science and art. The X-rays at the ESRF have become a tool sto study art and archaeology. See pp2–15.

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The ESRF and Institute of Physics Publishing have formed a partnership to produce *ESRF Newsletter*. Institute of Physics Publishing produces *ESRF Newsletter* under contract. The ESRF provides editorial content and retains editorial control, while production, advertising sales, printing and distribution are handled by Institute of Physics Publishing. Institute of Physics Publishing is an experienced STM publisher and produces a portfolio of magazines, including *Physics World* and *CERN Courier*.

Erratum: In the May issue of the *ESRF Newsletter*, in the feature entitled "Stardust may hold secrets of solar system" (pp10–11), the caption to the picture at top left should have read: "Beam teams. The team from University of Frankfurt, Ghent University and the University of Antwerp (left) did experiments using ID13.

Editorial

Guest editors: Marine Cotte, postdoctoral researcher, and Jean Susini, scientist in charge of ID21 and ID22

ESRF SUPPORTS ART AND ARCHAEOLOGY

This issue is dedicated to the chemical and physical analysis of museum objects at the ESRF. Whatever the technical and methodological approach, questions commonly tackled by archaeologists can be separated into two main concerns: a better understanding of the past and an intelligent prediction of the future.

Regarding the past, analyses are intended to reveal as much as possible about the secrets of artefacts. What are the objects made of? Which ingredients were used in their fabrication? How were they made (the extraction of the materials, purification, synthesis, and so on)? Where do the ingredients and the objects come from? When and by whom were they made (with the particular purpose of authentication)?

Regarding the future, a great deal of research is being carried out to improve methods of restoration and conservation to preserve objects for as long as possible. Furthermore, deeper knowledge of ancient techniques can sometimes provide new ideas for the development of future technologies.

Much information can be obtained without the use of synchrotron radiation, such as from macroscopic observations (the shape of an object, the place where it was discovered, etc). However, synchrotron radiation can be used to provide an insight into the chemical and/or structural compositions of samples.

Such analyses present a number of difficulties. First, the artefacts are precious, so sampling is usually forbidden or must remain limited in number and size. Second, they are often made of complex mixtures of organic and mineral materials, so a single method is generally not enough to identify all of the ingredients. In addition, they are rather heterogeneous at the micrometre scale, which requires discriminative techniques, such as high-resolution imaging.

The benefits of SR

The use of synchrotron radiation in this field of research has a number of advantages:

- the relatively non-invasive methods don't require sample destruction because they are based on light–matter interactions (from infrared to X-rays);
- the abundance of information that can be gathered (from the atomic to the structural level);
- the quality of data, thanks to the high beam brightness, allowing researchers to obtain data rapidly and from a small amount of matter;
- the beam-spot size, in particular for micro-imaging, which enables selective analysis.

All of these attributes explain the growing interest in using the ESRF in this field, as exemplified by the creation of a dedicated review committee, Environmental and Cultural Heritage Matters (EC), in 2005, and by the increasing number of proposals in this area.

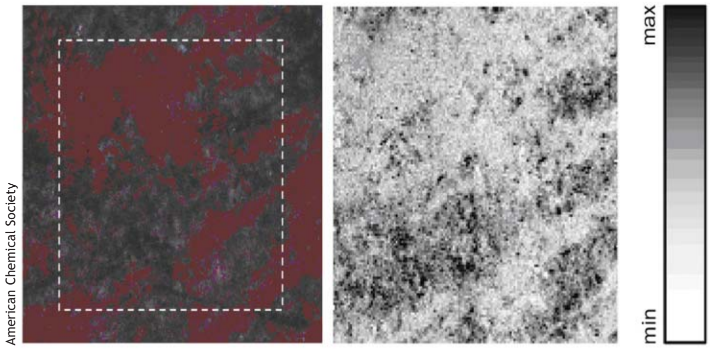
The ESRF and some users are carrying out various studies on "hard matter" – ancient metals, and the decoration of jades or bronzes – and "soft matter" – paper, textiles and wood (*ESRF Newsletter* **42**, December 2005) and paint, for which questions relative to past and future are tackled. The ESRF is also involved in analysing the remains of historical figures like Napoleon and Agnès Sorel (*ESRF Newsletter* **41**, July 2005).

In this issue, recent results are presented in various related fields. Some of them involve improving our understanding of the past (e.g. ancient techniques of painting on pp6, 9, 11 and 14 and glass manufacturing on p13); others are intended to give insight into the future by improving our knowledge of degradation and restoration (e.g. the blackening of pigment on p4, the interaction between lead pigments and binders in oil paintings on p9, and the degradation of fibres in ancient Chinese silk on p8). The common aim here is to see the invisible. ●

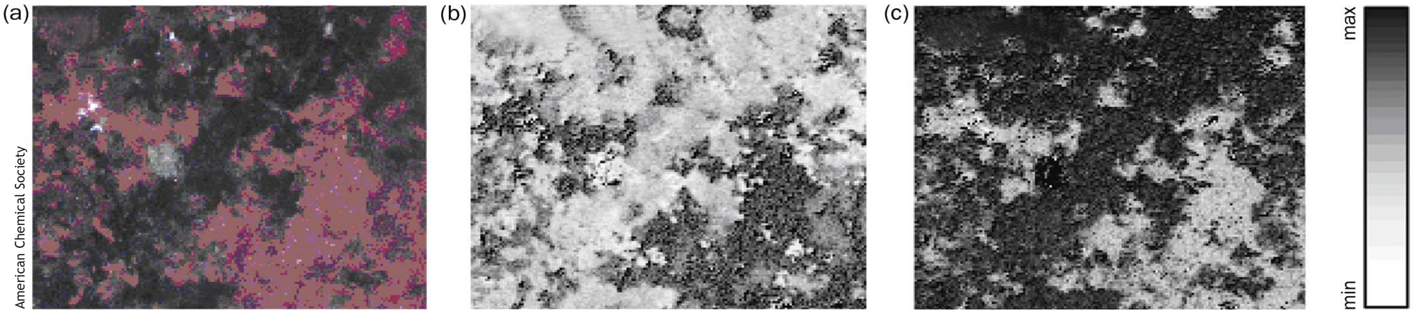
WHY DO THE RED WALLS OF POMPEII GO BLACK?

Why have the characteristic red walls of Pompeii, revealed by excavations of the city buried by the eruption of Vesuvius, turned black over the last two decades? ESRF's synchrotron offers new insight into this process.

Turning black. A wall painted red in the remains of Pompeii.



A new approach. A visible light microscopy image (left) and the atomic distribution of chlorine (right) in one of the samples with moderate alterations (obtained using μ-XRF with an exciting beam of 3.9 keV).



Visible light image (a) and the distribution of reduced (b) and oxidized (c) sulphurs on the most degraded wall sample (8 × 7 mm).

On 24 August AD 79, Vesuvius erupted, burying nearby towns under pumice and ash. The Villa Sora in Torre del Greco remained entombed until 20 years ago, when excavation works revealed its hidden secrets. In the remains of the house the frescoes featured the distinctive red often found in Pompeii and Herculaneum. However, this has since turned black in many places in a rapid degradation that's not well understood scientifically.

Scientists have wondered for many years why the red in Pompeii's walls, a dye that is made from cinnabar (HgS), turns black. In 1 BC, Vitruvius, in his treatise *De Architectura*, mentioned the problem, which, at the time, could be prevented by applying a type of varnish based on "punic wax". The causes and mechanisms that are responsible for cinnabar discoloration still remain a mystery. Consequently, conservators are unable to avoid the deterioration. The most common explanation of the phenomenon is that exposure to sunlight transforms it into metacinnabar, which is black. A Franco-Italian team of researchers has now used the ESRF synchrotron light to study four samples to test this theory.

No longer seeing red

The scientists found that the chemical composition in the affected samples was different from that of metacinnabar, which indicated that some important chemical reactions had taken place. On the one hand, cinnabar had reacted with chlorine, which led to the formation of grey chlorine mercury compounds. The chlorine came from the sea and possibly punic wax (the wax that was used in the frescoes). On the other hand, the sulphation of calcite resulted in the black coating on the paintings' surface.

The scientists investigated a cross-section of one of the samples to map the depth of alteration in the painting.

They realized that this layer was only around 5 µm thick and that beneath it the cinnabar remained intact.

So what makes the red turn black so quickly? "The chemical distribution of the samples is not stable, which means that atmospheric conditions probably play a role in this change of colour," explains Marine Cotte, the first author of the team's paper. "The sun surely influences this process, but the rain may possibly do so too." Atmospheric contamination or bacterial activities can also contribute to sulphation mechanisms.

Important research

"The research carried out at the ESRF has an extraordinary importance not only for the conservation of wall paintings in the Villa Sora but in general for the preservation of Roman wall paintings discovered in the most important Roman archeological sites (e.g. Pompeii and Herculaneum)," says Corrado Gratziu, who is professor emeritus in geology with a specialization in petrology of sedimentary rocks at the University of Pisa, and part of the team.

The experiments carried out at the ESRF needed high chemical sensitivity, low detection limits and high lateral resolution of synchrotron X-ray microspectroscopy. The researchers did the experiments on the X-ray microscopy beamline ID21 by combining micro-X-ray fluorescence mapping and micro-X-ray absorption spectroscopy. The former detected the chlorine and sulphur presence while the latter identified their speciation (i.e. the way they are bonded to other atoms).

The research is still far from complete: "The next step is to examine more samples – not only from frescoes in the archaeological site but also from those in museums. In this way we will be able to compare the results and better establish the causes for their degradation," explains Cotte.

UNESCO made Pompeii a World Heritage Site in 1997, and it is the most visited archaeological site in Europe, according to the Italian ministry of foreign affairs. ●

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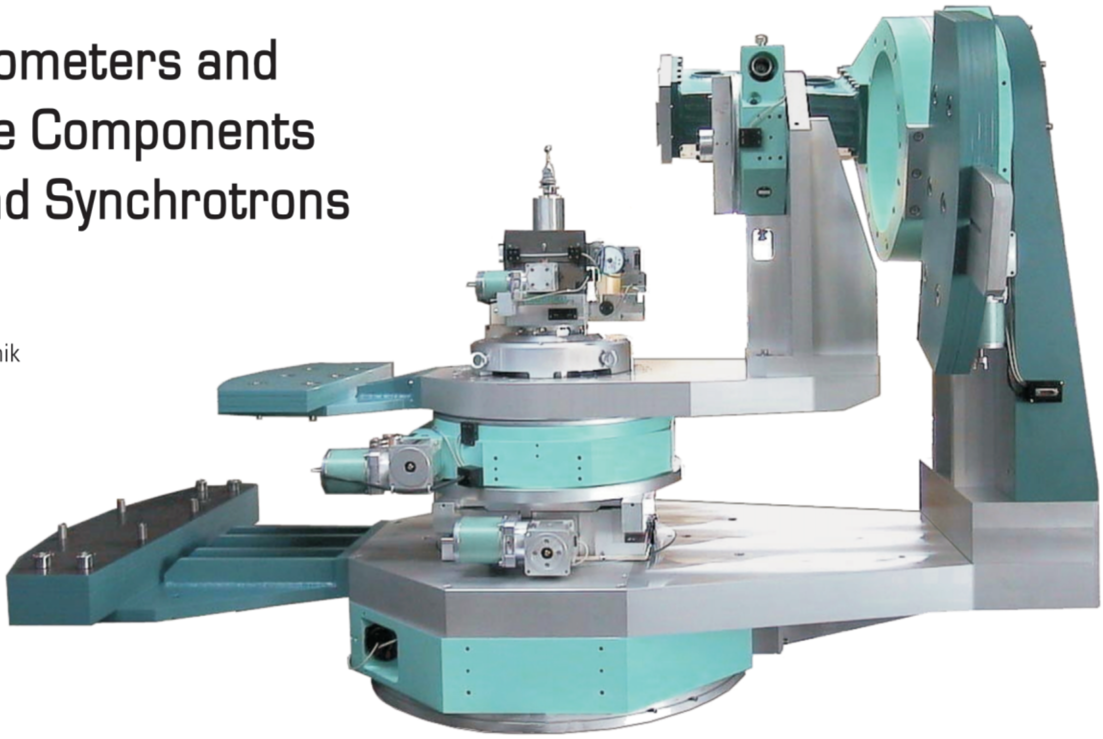

X-RAYS HELP TO UNRAVEL BRUSH STROKES

Scientists and conservators combine forces to apply imaging techniques to study a Manet picture in depth.

The setting is Berck-sur-Mer in the north of France in the year 1873. Edouard Manet is in the dunes near the seaside. In front of him a woman is riding a horse. He paints the horse in a detailed, realistic style while the woman is depicted with a more impressionistic touch.

Today, more than 130 years later, scientists want to know more about the impressionist parts of the painting. Using traditional X-ray film they have confirmed that there is a strongly impressionistic air painted around the woman. However, under the top layers, the first strokes should be revealed to tell researchers more about Manet's painting process.


Chantal Argoud

Joris Dik (left), Milko Den Leeuw and Wijnand Dalmijn examine the painting.

Milko den Leeuw, painting conservator at the Atelier for Restoration and Research of Paintings (see www.arrs.nl) in the Netherlands, explained that "several elements bring us closer to Manet's personal brushstroke or, maybe better, his painted handwriting".

The monogram "M" in the corner of the canvas is an obvious sign. Although Manet usually signed only his drawings with a monogram, there are at least two other examples of a monogrammed painting, which were given as presents. In addition, horsewomen are a recurring motif throughout his work. However, "we want to know every detail of this painting," explains den Leeuw, who added: "One way to find it out is to see if there are any painted layers underneath the painting." He has combined his knowledge with that of Joris Dik, a physicist from the Technical University of Delft (the Netherlands). The conservator and the scientist, together with their other collaborators, have embraced science as a way of gaining an insight into art.

Museums all over the world use many different techniques to study paintings. However, "conventional laboratory-based techniques sometimes have limitations", says Dik. The elemental composition of paint covers virtually the entire periodic table of elements and, since a traditional X-ray radiograph is only sensitive to the heavy metals, it doesn't show light pigments. Light element pigments are thus easily overshadowed by heavier ones.

Yet these light element pigments can still potentially reveal very valuable information about the creation of a painting. In the past four decades, element-specific imaging techniques have been developed for paintings. While these spot a number of elements, they also have their drawbacks. One of them is that collecting the data takes up to three months, which is very inconvenient for museums. Another disadvantage is that the lead historically used in white paint serves to shield any underlying layers, making the information inaccessible.

To address these issues, Dik and den Leeuw turned to more sophisticated methods to find out what the brush strokes say. Over the last three years the team has brought about eight canvases to the ESRF for research on beamline ID17.

The works of art are not harmed by this process. ESRF researcher Alberto Bravin explains: "We limit the exposure time of the X-rays so that we don't cause any damage to the paintings."

The new research on paintings at the ESRF is based on the K-edge imaging technique. This involves taking two images at two different energies and bracketing the threshold (K-edge) energy of the element to be investigated. This energy is element-specific. The pair of images – acquired using a monochromatic X-ray beam – are logarithmically subtracted to yield two complementary images: one maps the specific element while the other maps the background.

With the painting facing the invisible X-rays, researchers take scans of the canvas in strips of 150 mm and assemble them. Each scan takes a minute.

In the Manet painting the researchers examined the distribution of lead, mercury and barium, a pigment lengthener of 19th- and 20th-century paint. Thanks to the imaging technique, the researchers identified an underlayer in the painting where barium allowed them to see a modified version of the scene. In this hidden sketch the shadow of the horse is situated at a higher level and facing in a different direction from that in the final image. In addition, several other barium stripes indicate a history of undocumented restorations.

The researchers also noticed in the barium underlayer the presence of a first sketch that was linked to a watercolour by Manet that is part of the collection at the Brooklyn Museum of Art in New York.

"Manet apparently used the more nebulous relationships of the colours of the underpainting to help to establish the tonalities that he sought for the final effect. It makes sense that below the top layer one could find a thin and freely painted underlayer," says Anne Coffin Hanson, a Manet expert at the University of Yale, in her book *Manet and the Modern Tradition*.

The ESRF's X-rays gave the scientists new clues about the painting. Milko den Leeuw will include the conclusions of the investigations in an upcoming publication about the painting in 2007. "The unravelled brushstrokes from totally different pigments could only be seen by synchrotron radiation," says den Leeuw. •

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UNRAVELLING THE THREAD OF FIBRES' DECAY

ID13 has helped scientists to investigate the decay of ancient Chinese silk found in a Buddhist sanctuary.

Scientists from Germany, the UK and the ID13 beamline have recently studied ancient Chinese silk fabrics found in the Famen Si (Doorway Temple), one of the most important Buddhist sanctuaries. Their results reveal for the first time how fabric degradation is related to the structure of the individual fibres. This may open new doors for the preservation of ancient silk artefacts.

Some 1300 years ago the emperors of the T'ang dynasty (AD 618–907) offered silk fabrics as part of a gift to the Famen Si. Today these fabrics, along with many others, continue their slow decay. Their preservation and restoration is the aim of a bilateral German-Chinese project. Many factors have contributed to their decay throughout the centuries, including light, humidity and microbes. However, not much was known about how this occurs and how to prevent it, until now.

The researchers from the ESRF, the Fachhochschule Köln (Germany), the Römisch-Germanisches Zentralmuseum in Mainz (Germany) and the Textile Conservation Centre in Southampton (UK) used scanning synchrotron radiation microdiffraction, with a 1 µm beam, to investigate three pieces of fabric at different stages of decay. As the beam is only one-tenth the diameter of a silkworm's thread, the internal structure of individual fibres could be probed.

The results show that the onset of fabric degradation can be related to the loss of an amorphous fraction of protein chains in the fibres. This breakdown in the silk's hierarchical structure makes it fragile and prone to becoming disordered. Consequently, cleavage can occur in the remaining nanofibrils, leading to fibre- and fabric-scale disintegration.

The key to preserving fabric may thus be to protect the fibres' nanofibrillar morphology. The team suggests using an artificial polymer matrix to replace the missing protein and retard degradation. This molecular-scale scaffolding may ensure that artefacts from our cultural heritage can be appreciated centuries from now. •

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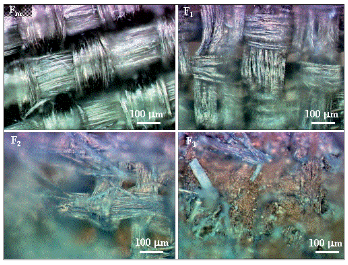
Famen Temple Museum (China)



American Chemical Society

Top left: The pagoda of the Famen Si, which was heavily affected by rain then pulled down in 1987. During its dismantling a vault was discovered that contained rich treasures, including the silk garments that have been studied at the ESRF. Centre: Optical microscopy images of a current plain-weave silk fabric (F_m) and three archaeological plain-weave silk fabrics (F_1–F_3) from the Famen Si site, classified according to the increasing visibility of their decay. Bottom: A very well preserved silk gown from the Famen Si site.

Famen Temple Museum (China)

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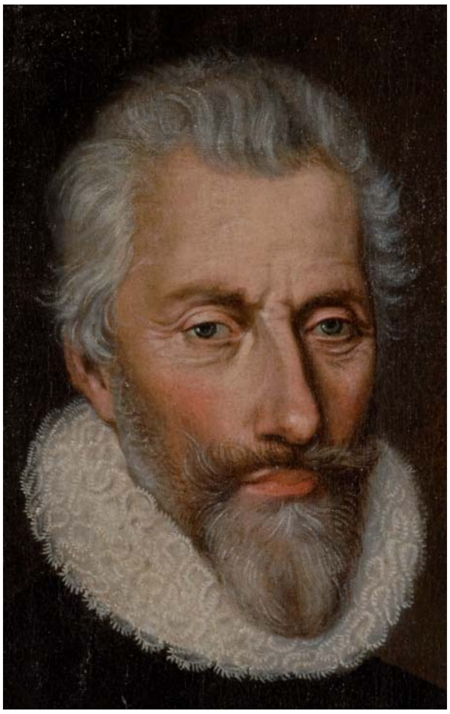
INP/Ghyslain Vanneste, thanks to J.L Coudrot, head conservator, musée du Châtillonnais



INP/Ghyslain Vanneste

INP/Ghyslain Vanneste

Far left: a portion of the anonymous painting from 1610 prior to restoration. Left: the same portion after restoration. Above: One of the protrusions.

COSMETICS AND PAINTS SHARE THE SAME RECIPES

Scientists have recreated lead salt mixtures of similar composition used in medical remedies, make-up and oil paints to unearth some of the secrets of the past and help them to preserve artefacts well into the future.

Ancient pharmaceutical recipes, as well as archaeological findings from Egyptian burial sites, show that lead salts were used in cosmetics and medicines in a mixture that included fat, which stuck them together in lead soap. These soaps are also present in some oil canvases and sometimes produce protrusions that damage the painting. Two teams of French scientists (one team with pharmacologists; the other with painting curators) have reproduced these mixtures, following ancient recipes, and have monitored their kinetics.

In the Musée du Chatillonais in the Bourgogne region of France, an anonymous portrait of 1610 shows some protrusions that have appeared over the years. These spots, which can be white or orange, measure from around tens of micrometres to millimetres and can damage the painting by causing it to crack. A team of French researchers is studying the reasons for this phenomenon and the best way to prevent it. Emilie Checroun, a restorer in the team, explained that the main aim is to “define a treatment for the conservation of the painting”.

Why these protuberances appear is not fully understood. The main reason for this reaction is the combination of lead salts and oil that results in oil saponification (i.e. the formation of a lead soap). The best way to understand this process is to reproduce the formula for paints used in the past. A recipe from the 16th-century chemist and physician Sir Theodore Turquet de Mayerne was chosen as a model for the preparation of lead medium. Painters such as Leonardo da Vinci, Titian, Tintoretto and Rubens used similar preparations with their own variations.

Recipe for success

The blend is made from a combination of walnut oil, water and lead oxide, mixed and heated to get a ductile paste instead of liquid oil. This was used to create a replica for study alongside the original painting.

Using infrared spectroscopy and microfluorescence at beamline ID21, scientist Marine Cotte and Checroun identified and localized the organic components of the paintings and some minerals. They found that the lead involved in a protrusion does not necessarily come from

FOCUSING ON LEAD WHITE

A similar case-study on cosmetics and paintings focused on lead white. This is one of the eldest man-made pigments among the white pigments used commonly for artistic and cosmetic purposes, with a history dating back to ancient Greece. Pauline Martinetto (CNRS Grenoble) and Eléonore Welcomme (C2RMF) examined Greek foundation creams well preserved in small ceramic boxes dating from the 4 BC using beamlines ID31 and ID22. The creams consisted of mixtures of two lead carbonates: hydrocerussite and cerussite. Although cerussite is found in natural ores, hydrocerussite is synthesized by the action of vinegar on metallic lead. The different recipes were described by several ancient authorities, such as Theophrastus and Pliny the Elder.

The structure of hydrocerussite was resolved using X-ray diffraction. The composition and microstructure of the pigments vary from one sample to another.The next step is to find out why the proportions change, so as to unravel the manufacturing process behind this kind of recipe.

This approach is also being applied to the white lead pigments used in easel painting during the beginning of the German Renaissance, starting with Matthias Grünewald's masterpieces of the 16th century). Microbeam X-ray fluorescence and diffraction enable us to scan this material through the different chromatic layers, providing new insights into the artist's palette and techniques.

pigment but more likely from the siccative agent added to oil to accelerate its drying. In their modern reconstruction they observed that crystallized lead soap aggregates can be formed after only one month and that, contrary to what is sometimes found, protrusion formation doesn't necessarily require centuries.

As far as preservation is concerned, the researchers found that water and heating accelerate saponification, so cold and dry conditions are best to keep this process to a minimum.

This study has changed scientists' attitude to the protrusions. "They have always been considered a mechanical problem more than a chemical one. We thought that they were coming from bad-quality white lead coming up to the surface of the painting because of the age and the settling of the oil," says Checroun. The English and Dutch carried out research into these protuberances and showed that lead soap created this effect. "We confirm that the French phenomenon of protrusion has the same explanation," she adds.

Studying make-up

Lead substances are also abundant in make-up powders from ancient Egypt. In 2001 Philippe Walter at the Centre de Recherche et de Restauration des Musées de France (C2RMF) and colleagues at CNRS Grenoble and ESRF, in collaboration with l'Oréal, studied some recipes for Egyptian cosmetics. They noticed the presence of two lead ingredients (laurionite and phosgenite), which are both very rare in nature.

This led scientists to conclude that Egyptians manufactured artificial lead-based compounds and added them to the cosmetic product. This revealed that wet chemistry was already being practised in around 2000 BC. In addition, some cosmetics were found to be a mixture of these complex minerals, sometimes including fat.

Amazingly, recipes for the treatment of skin and eye diseases written on papyrus from 1500 BC describe preparations based on heated mixtures of oil and lead salts. These formulations are equivalent to lead plasters, and pastes often used from Antiquity up to the 20th century.

Researching historical cosmetics and pigments in parallel can prove interesting and fruitful because these compounds have many similarities – after all, applying make-up is essentially face-painting! •

MC

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C Reyes-Valerio

Pottery figurine from the Great Temple, Mexico City, representing Tláloc, the Aztec god of rain. Images of Tláloc are commonly decorated in blue.

C Reyes-Valerio

The west wall, room 1 of the Mayan site Bonampak, from 8 AD, exhibiting different blue and green hues.

AZTEC PIGMENT PROVES TO BE AHEAD OF ITS TIME

How did the Maya civilization create a beautiful, long-lasting turquoise-blue pigment when no-one else could?

Mineral blue pigments were very expensive in ancient times. The alternatives to mineral pigments were organic colorants, which were altered by external conditions. As a consequence there isn't much blue in frescoes from the Middle Ages and the Renaissance. However, the Maya civilization achieved what contemporary and previous civilizations couldn't: they synthesized a long-lasting blue pigment from an organic colorant. The pigment's amazing stability has led researchers to study it thoroughly, especially with regard to the creation of new materials.

The colorants used in antiquity were organic molecules extracted from plants and animals. They were not suitable for use in artworks because they are not stable for many years. They fade with light, age and exposure to pollutants, and some of them even react with other chemicals that are used in artwork.

By contrast, pigments that are made from minerals are very stable, which makes them preferable for many artistic works such as murals, oil paintings and polychromatic pottery.

A pigment with longevity

The Maya succeeded in "mineralizing" indigo – the most common blue colorant known to many ancient civilizations. They embedded it in a particular clay mineral called palygorskite. This combination results in a beautiful turquoise-blue with an amazing resistance to acids and biodegradation through the centuries. The pigment is present mostly in Mexico, but it has also been found in Guatemala, Belize and Cuba.

Researchers at the ESRF, the CNRS (Grenoble) and the

Instituto Nacional de Antropología e Historia (Mexico) have studied this pigment in some depth. Their research has three aims: “We want to study its composition in archaeological samples, since it can enlighten us about the origin of the materials used, trade routes and manufacturing technology,” explains Manuel Sanchez del Río, a physicist at ESRF. “Second, the chemical interaction between indigo and clay, which is responsible for its resistance, is still not fully understood. Finally, their research is also looking to develop new composites that incorporate organic molecules in inorganic materials.”

The team has synthesized several Maya blue samples using palygorskite clay, known by the Mayas as “white earth”, and also sepiolite, a clay with a similar channel-like structure. Much more resistant pigments are obtained from the palygorskite substrate than from the sepiolite. The scientists have studied archaeological samples using microdiffraction and microfluorescence at ID18F and ID22. Also, XAFS experiments were carried out at ID26 and powder diffraction at BM25A.

The research into the Maya blue will answer questions about the past, and may also be useful for the future. Eric Dooryhée and co-workers (CNRS Grenoble) have been trying to mimic the properties of this pigment using other classes of nanoporous material, in the search for new organomineral composites with potential uses in optics and optotronics. They recently succeeded in incorporating and stabilizing the indigo dye in ordered aluminosilicates. By controlling and changing the synthesis parameters, the scientists expect to obtain stable and non-toxic Maya-like hybrid colorants.

It is hoped that this work will enable researchers to unravel the secrets of the Maya blue in order to understand its history better and to use this knowledge in future applications. •

MC

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DIFFERENT MINERALS DICTATE COLOUR OF GLASS

Scientists from Italy and the ESRF are studying how the elements in glass can determine its colour.

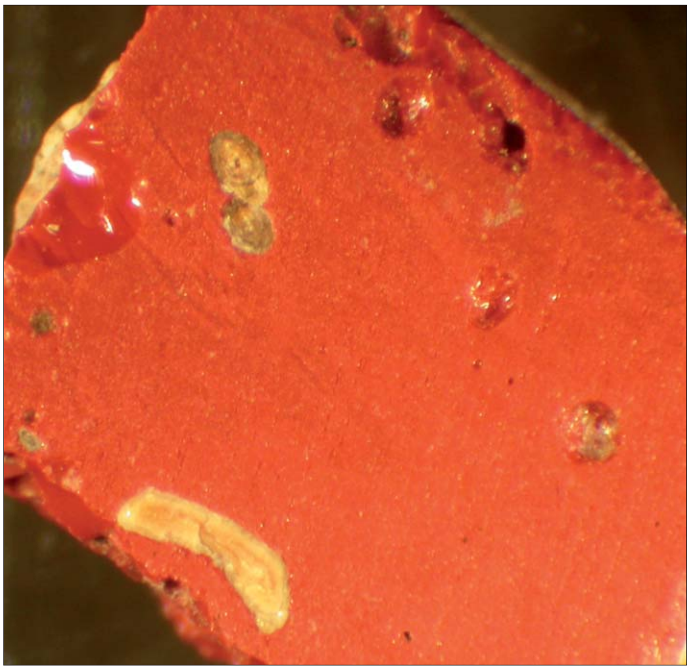
Glassy matrices can exhibit different colours depending on the oxidation state and the electronic configuration of the metal ions that are contained in them. For example, iron at high concentration can produce a green coloration.

To minimize this problem in transparent artefacts, artisans from around the first millennium BC added substances to neutralize the colorant effects of the iron. Before the Roman period, antimony was the main bleaching agent, while from the 2 BC manganese was more frequently used. As far as opaque vitreous materials are concerned, the colour and opaque effects were obtained by means of many different substances, depending on the age of the material and the desired effects. The colour and opacity of red glass, in particular, are frequently due to the presence of tiny metallic copper particles.

Over the last four years, to improve our understanding of how ancient glasses were manufactured and the origin of their colours, scientists from Italy and the ESRF have been studying different artwork from Sicily and Pompeii. They use X-ray absorption spectroscopy (XAS) to find out the oxidation state of iron and manganese in a number of transparent glass samples of archaeological interest, characterized by different colours (from green to pale brown to uncoloured), and of copper in a series of opaque red tesserae. "The advantages of using XAS are that it is non-destructive, it allows virtually any size and type of sample, and it is applicable to most of the elements of interest," explains Francesco D'Acapito, scientist in charge of the Collaborating Research Group (CRG) beamline GILDA (BM08).

Thanks to XAS, scientists can track the presence of monovalent copper cations incorporated into the glass matrix of two opaque red artefacts, accompanied by copper nanoclusters. In other examples, the results show that the final artwork underwent intentional discoloration during production.

In another part of this research the team focused on



Assessorato Regionale Al Beni Culturali, Ambientali E Alla Pubblica Istruzione Della Regione Siciliana

A sample of ancient mosaic tesserae from the Museo Archeologico Regionale Eoliano.

the formation of the lustre on ceramics. In several glazes of shards belonging to 10th- and 13th-century pottery from Iran, researchers noticed that the presence of copper and silver ions in the glaze confirms that lustre formation results from a copper- and silver-alkali ion exchange, followed by nucleation and growth of metal nanoparticles. Previous research into Renaissance pottery gave very similar results (*ESRF Newsletter* 38, December 2003).

MC

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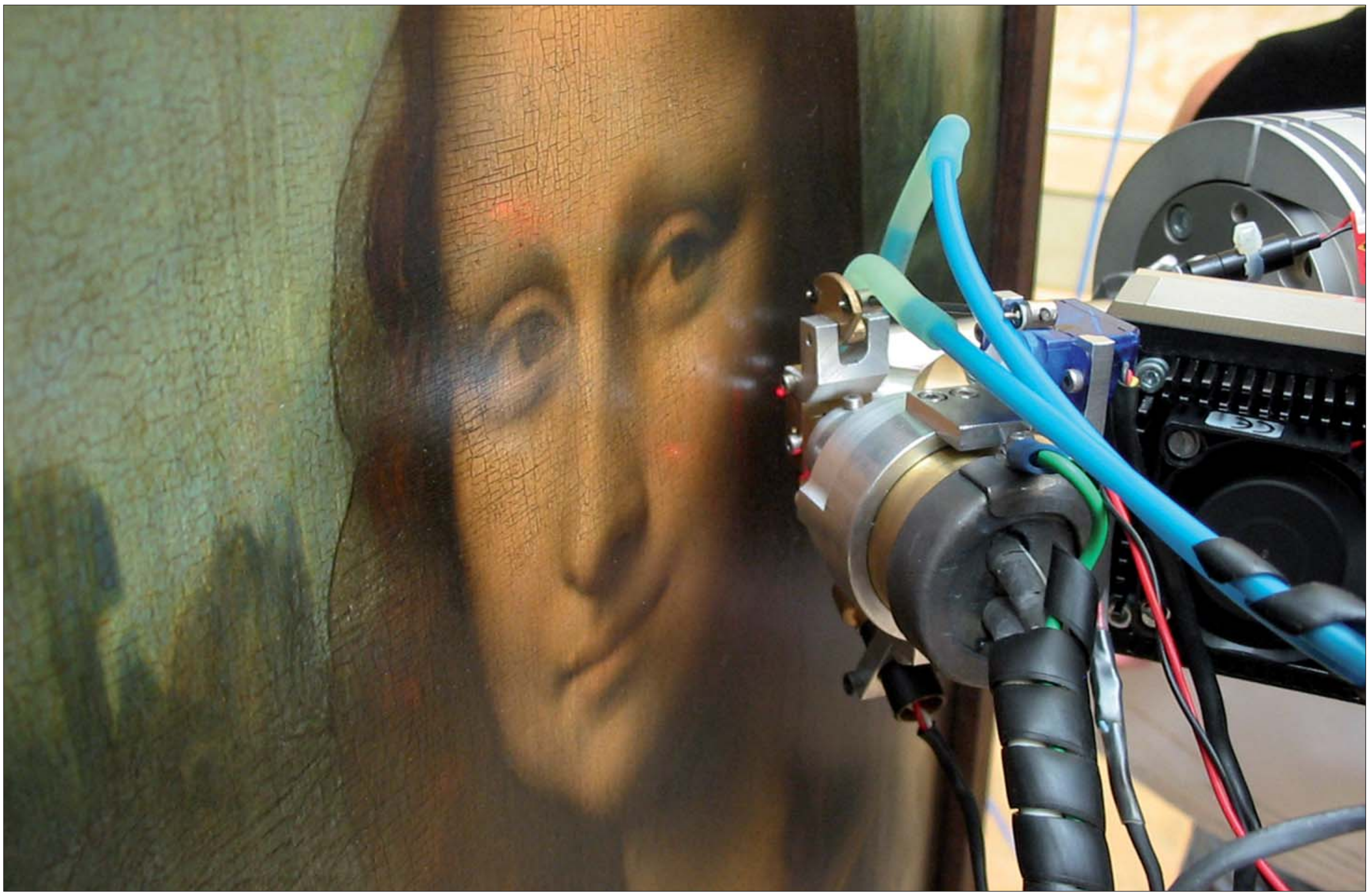

V Armando Solé

Line by line. The ESRF's PyMCA software created an elemental pigment map of Leonardo da Vinci's mysterious *Mona Lisa*.

BLISS GROUP HELPS TO CRACK DA VINCI'S CODE

The ESRF mainly contributes to research via scientific results. However, tools such as precise software can become essential in the quest for the unknown. PyMCA is a programme for online and offline X-ray spectrum analysis that was developed by the ESRF for its beamlines, but it is also being used in art research.

When V Armando Solé from the Beamline Instrument Software Support (BLISS) group developed the PyMCA software, he didn't think that it would take him to the *Mona Lisa*. However, that's just what happened, and he was able to study the painting without the glass box that normally surrounds it. He was invited to an X-ray experiment in the Louvre to use his software to decipher the data.

The main asset of the software is its ability to model the lines that come out in X-ray fluorescence experiments. These indicate certain energies and are important when defining the chemical composition of a painting, for example. "Until PyMCA there wasn't any programme implementing a full description of all of the M lines, and that was capable of resolving the superimposition that occurs with the K lines of sulphur and the M lines of lead and mercury," explains Solé.

In the case of the *Mona Lisa*, the aim was to study the *sfumato* technique that was created by Leonardo da Vinci by estimating the thickness of the different layers of the painting. This method overlays translucent layers of colour to create perceptions of depth, volume and form. In particular, it refers to the blending of colours or tones – so subtly that there is no perceptible transition.

The scientists also used the software to produce an elemental pigment map. "Apart from a large amount of lead, which is not too surprising because the support of the *Mona Lisa* is actually a piece of poplar having a lot of lead white as a priming layer to cover the wood, there are unusual ratios of Mn and Fe," explains Solé.

The *Mona Lisa* is only taken out once a year for

BLISSFUL SOFTWARE

Encyclopaedia Britannica defines software as "instructions that tell a computer what to do. Software comprises the entire set of programs, procedures, and routines associated with the operation of a computer system." The ESRF's Beamline Instrument Software Support (BLISS), comprising 17 computer engineers and physicists, is developing this essential tool for computerized experiments. It created the software to control experiments remotely. Data visualization and scientific analysis tools complete the control by allowing scientists to evaluate the quality of the experiment immediately afterwards. "Our mission is to assist researchers with their experiments; we are at their service," explains Vicente Rey, head of BLISS.

The programs don't have a commercial use and scientists can request or download them for free. They are flexible, easy to configure and versatile, so they can adapt to different beamlines.

conservation studies. The team from the Centre de Recherche et de Restauration des Musées de France (C2RMF) used an X-ray tube that was optimized at low energies and they had only three hours to experiment.

The same team from C2RMF, led by Philippe Walter, had already used the software to study techniques used by Matthias Grünewald, a painter in the 15th and 16th centuries. Thanks to the experiments at the ESRF beamlines ID21 and ID22, and to PyMCA, the team created an elemental map of the painting's cross-section. Characterization of the pigments pointed out various minerals for green and black. Results showed small particles of antimony correlated with sulphur, which led to the identification of stibnite – an extremely rare black pigment.

Despite being created only in late 2004, PyMCA has already crossed borders. It is used not only by the C2RMF researchers but also at other synchrotron sources, such as DESY (Germany), CHESS and SSRL (US), Elettra (Italy) and X-ray tube-based laboratories elsewhere in the world.

MC

FOSSILIZED EMBRYO STRUCTURE GETS CLEARER

A team of researchers has used ID19 to explore the structure of fossilized embryos from south-west China.

The evidence of the first animals on Earth goes back some 700 million years. However, the origin of complex animals that have symmetry in a central plane (bilateria) has remained a point of speculation until now. Researchers from China, the US and France have found that complex embryonic development equivalent to that of some modern bilateria existed 40 million years earlier than thought (i.e. 580 million years ago).

In addition to the scientists' studies with a scanning electron microscope, they came to the ESRF to use the powerful X-rays of ID19 to investigate non-destructively the internal structures of fossilized embryos from south-west China. They demonstrated that the cellular cleavage pattern in the fossil embryos bears a striking resemblance to the pattern of modern polar lobe-forming embryos.

The polar lobe is a structure observed in many molluscs, such as the mud snail, and in a few annelids. It is a symmetry-breaking process that occurs at the early stage of embryonic development and leads to blastomeres (embryonic cells) of unequal sizes. This process leads to particular embryonic structures (trefoil, J-shaped and five-lobed) that are unique to the early development of polar lobe-forming embryos. The researchers have identified typical structures from phosphate deposits that are 580 million years old.

Important evidence

These findings provide new evidence pushing the arrival of the first bilaterian animals back to as early as 40 million years before the Cambrian period. The beginning of the Cambrian (540 million years ago) is known as the Cambrian explosion because that's when most of the major groups of animals appear in the fossil record. This breakthrough implies that a complex embryonic development comparable to that of modern molluscs existed much earlier than scientists thought.

The team examined the samples taken from the Precambrian rocks in Weng'an, China, using synchrotron radiation microtomography at the ESRF and the National Synchrotron Radiation Research Centre in Taiwan. Thanks to the 3D data collected on the ID19 beamline, they revealed the typical internal structures linked to the polar-lobe formation process, which validated their interpretation of these fossils. "Taking into account the size of the samples [250–500 µm] and their mineralization pattern, only microtomography with submicrometric resolution and phase contrast could have revealed the internal structures in detail with their 3D organization," says Paul Tafforeau, a paleontologist at the ESRF and an author of the paper.

The team is continuing its investigation into the history of living beings by studying other fossils from the Precambrian rocks.

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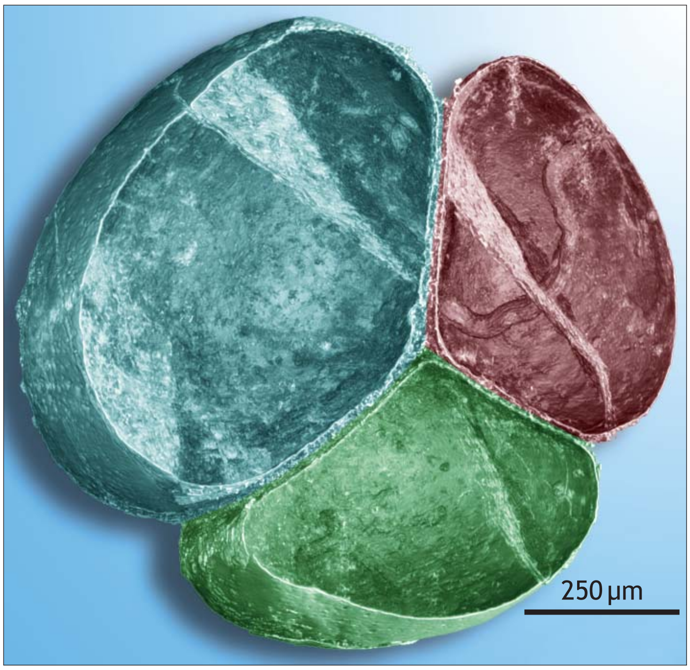

Li Gang and Paul Tafforeau

Embryonic exploration. Virtual cross-section of a fossilized embryo around 580 million years old. Different colours correspond to each of the three embryonic cells (blastomeres). The blue blastomere is twice the volume of the others, which strengthens the polar-lobe formation interpretation.

Reference

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WE HAVE BEEN LISTENING TO OUR READERS

Earlier this year survey of our readers revealed that there's still some way to go to serve their needs better.

Chantal Argoud

Reader satisfaction. Most of the feedback from the newsletter's readers is very positive, but there are lessons to be learned.

The editor of the *ESRF Newsletter* and Institute of Physics Publishing carried out a survey of its readers last July to find out what they thought of the publication. Overall the feedback was very positive, but there is always room for improvement and the suggestions that readers had were very welcome.

The newsletter is read primarily by the scientific community, especially users and potential users of the synchrotron facility. At present each issue is read by more than 10 000 people from all over the world. There were 331 respondents to the survey (3.3% of the total readership). The profile of these individuals reflects that of a typical ESRF user: male, aged 35–54, holding a PhD, and working as a scientist or a lecturer in a university or research-council laboratory.

Most of the survey results relating to the profile of the readers were unsurprising. Nevertheless, some aspects where there is still potential to improve did stand out. For example, only 16% of readers are younger than 35, while only 13.8% are PhD students or postdoctoral researchers. This suggests that more effort should be made to attract younger scientists. Targeting this group more aggressively will also make them more aware of how the ESRF can benefit their research.

Good news is that the newsletter's readership has increased by 22% during the last two years. This is partly owing to a collaborative effort by Institute of Physics Publishing and the ESRF to enlarge the distribution list. This includes sending copies of the magazine to relevant conferences and new synchrotron sources. In this way new users can be targeted directly while existing users can be kept abreast of the latest developments at the ESRF.

The survey also revealed which of the newsletter's contents are most popular with the readership. The three favourite sections (in order) are the Scientific Highlights, the Feature News and the Scientific Articles. The popularity of the Scientific Highlights section probably reflects its diversity, because it covers a variety of scientific interests.

Two of the sections that are read the most have a style and structure that is typical of a scientific publication in a specialized journal. The exception to this is the Feature News, which is written in a more journalistic style and is enjoyed by most of the readers.

The survey also revealed that the least-read articles in the newsletter include the Machine section, the Gallery of Events and the Interviews (both of ESRF staff and users). Around 30% of the readers who responded to the survey never (or rarely) read these items.

All respondents were entered into a draw for a $200 Amazon voucher. The lucky winner was Geert Silversmit from Ghent University.

MC


Chantal Argoud

"There are a lot of very competent people around you and they are always available. In a small group in a university it would probably be far more difficult to find scientists who could help you."

Three in one. Montserrat Capellas Espuny interviews students Guillaume Potdevin, Yvonne Gruender and Roberta Poloni.

WHAT'S IT LIKE BEING A PHD STUDENT AT THE ESRF?

They arrive at the ESRF straight from university and are faced with the challenge of working in a scientific institute. They take the first steps of their career at the ESRF and the synchrotron offers them the chance to carry out a PhD surrounded by researchers from different disciplines who can help them with their work. They also learn about the science being done by other students, thanks to the annual Students' Day. This is an excellent springboard to promote their work here. There are 33 full-time PhD students as well as many others who carry out part of their research at the facility. Three of them – Yvonne Gründer, Roberta Poloni and Guillaume Potdevin – talk freely about their experiences at the ESRF.

How much have you learned about your subject since starting your PhD?

Roberta Poloni The learning process for me has been a curve that goes up all of the time. At the beginning I had to do a lot of studying about the subject of my thesis, which is not something that I was familiar with. Later I could focus on the techniques.

Yvonne Gründer I have learned a lot about the beamline and my subject. I just had my first results, but we have to repeat the experiment to confirm them.

Guillaume Potdevin This is our first job, one could say. Therefore the number of different concepts that you learn in the first years is very important. The international nature of the ESRF has made it very easy for me to adapt to the system, because I like meeting and mixing with people from new cultures a great deal.

How much have you learned about the science at the ESRF in general?

RP I think it's difficult to understand everything that goes on at the ESRF. Seminars are a good source of information, but if it is not in my field I don't understand the details of the research.

GP In most of the seminars and talks that I attend, I probably understand 50% of the content having been at the ESRF for two years. Even if I've studied the subject, I can't always understand everything. In a lot of cases you actually need to be a specialist in the particular topic to understand it properly

Interviewee	Age	Nationality	Year	Thesis	Group
Guillaume Potdevin	25	French	Third and last year of PhD	Development of photocathodes for a new generation of detectors.	Special Detectors Group
Yvonne Gruender	26	German	Second year of PhD	Electrochemical metal desposition on semiconductors. This could be used to improve transistors.	Surface and Interface Science Group
Roberta Poloni	27	Italian	Third and last year of PhD	Study of heavy alkaline metal-doped fullerenes under high pressure and temperature. The aim is to form high-order polymers with predicted properties.	X-ray Absorption and Magnetic Scattering Group

YG There should be specialized seminars and more general presentations that we could follow more easily.

What are the benefits of doing a PhD at the ESRF rather than somewhere else?

YG The ESRF is a great place to meet a lot of people. For starters the people on my beamline (ID32) are very helpful. Then you get to know a lot of users by going for lunch and having informal discussions when they are on the beamline. This can be an opportunity for future collaborations.
RP There are a lot of very competent people around you and they are always available. In a small group in a university it would probably be far more difficult to find scientists who could help you. An important benefit of being at the ESRF is that you can get beamtime more easily, such as when there are buffer days.
GP Additionally, the ESRF provides a lot of material and expertise in many domains. This makes it easier to get both information and help when your subject deals with a wide variety of technical aspects.

Do you feel that you're well supported by your supervisor?

YG I really appreciate the level of freedom at the ESRF that allows me to work at my own pace. I like to be independent and not have someone looking over my shoulder at what I'm doing all of the time. At the same time we have group meetings every week, so I really feel integrated into the group.
GP There are quite a few PhD students who claim that they are not supported enough. Supervisors at the ESRF are always available, but they are not very proactive. You often have to learn things the hard way. However, there is always someone to give you a hand when you really need it.
RP: When I carry out experiments I get help from colleagues from my university and also my beamlines (BM29 and ID24). On a day-to-day basis they are also able to help if I have any questions.

What do you envisage for your career following the ESRF?

GP I wouldn't mind working in industry or even changing my subject. I like what I do, but I think it's dangerous to stay in the same place for a long time.
RP I would definitely like to stay in academia because I enjoy studying and handling data more than working on the beamline constantly. I definitely envisage a postdoctoral position but I don't know where.
YG I still don't know what I'll do after my thesis but for the moment I like working in academia.

As well as adjusting to a work environment you're living far from home. Do you enjoy life in Grenoble?

YG I come from Berlin and for me it is amazing that it only takes me 10 minutes by bike to get to work. I only miss German bread and beer!
GP Grenoble is great because it is close to the mountains and has many cultural activities.
RP The lifestyle is definitely different from the Italian lifestyle. Moreover, with the mountains surrounding us and the little nightlife of the town, I think I've learned to live more for the days than for the nights. •

MC

The machine

FILLING PATTERNS START WITH A FINE COMPROMISE

The ESRF has developed new filling patterns for its beamlines by taking account of the parameters of the experiments as well as the limits of the hardware.

The ESRF has the specificity to deliver various filling patterns from one week to another, following a mode schedule that is determined for a period of six months. In fact the injector complex allows a variety of filling patterns in the storage ring (1—992 bunches of electrons) with the possibility of filling one or more bunches with a greater number of electrons. The maximum number of bunches is 992 because the radio frequency (RF) cavities of the storage ring make particles cross the accelerating gap when the voltage compensates exactly for the average energy loss per turn owing to synchrotron radiation. Consequently, the 352.2 MHz RF, which corresponds to a multiple h = 992 of the particle revolution frequency (ring circumference 844 m), groups electrons with a periodicity of 2.8 ns.

The choice of filling pattern results from a fine compromise between user requirements and the hardware and tuning capabilities of the accelerator. To understand it better, let's first look more closely at the different requirements of the users, which vary depending on the type of experiment. Most experiments require a stable high-brightness beam, with a filling pattern that is compatible with the saturation of the detector. The time-structure user community can be divided into two groups: those who need a pure pulsed beam at a high repetition rate and those who use the short pulses at a low repetition rate.

On the machine side, user requirements can be translated into stability, brightness, bunch length, energy spread, peak brightness and purity.

The stability of the beamline optics during an experiment is essentially determined by the current variation between two refills. The longer the beam lifetime, the more stable the beam. The contribution of filling pattern to the beam lifetime is mainly governed by the higher probability of a collision between particles when electron density increases in a bunch. This contribution to the lifetime, called the Touschek

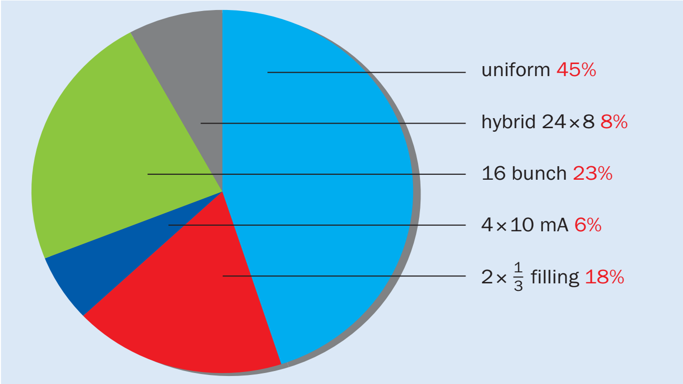


Figure 1. Repartition of filling modes at the ESRF in 2006.

effect, is dominant in single bunch but also has a significant impact in all other modes of operation.

The brightness in terms of filling pattern is limited by the heat load capacity of some machine components. Front-end absorbers and dipole crotch absorbers limit the current to 300 mA with the present machine configuration. Nevertheless, the beam power deposited in the RF fingers (which are used to connect various pieces of the vacuum chamber) restrains the current to a much lower value with few high-current bunches. The vertical emittance, which is also a key parameter governing the brightness, is strongly affected by transverse instabilities caused by ion trapping when all bunches are filled. This effect, which improves with vacuum conditioning of the ring, is always present in uniform filling. This beam blow-up disappears as soon as there is a gap of more than 10% in the multibunch filling pattern. One should also note that, in a few bunch modes, the vertical emittance is voluntarily increased from 20 pm rad up to 60 pm rad to increase the lifetime. The energy spread, which is constant at less than 4.5 mA per bunch, starts to increase to more than this value. This effect makes the increase of the undulator spectral brightness less than linear versus current. One should also note that, with proper calibration of beam-position monitors, positional stability should not depend on the filling pattern.

Regarding the bunch length, increasing the number of electrons in a bunch induces a stronger interaction with the impedance of the surrounding vacuum chamber, which leads to bunch lengthening. The bunch length, which is 20 ps rms at 0.2 mA per bunch (200 mA uniform

Current, lifetime, bunch length and energy spread in various representative filling modes used at the ESRF

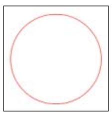
	uniform	2×1/3	7/8			hybrid			16 bunch	4 bunch
					single			single		
Repartition of (%)	45	18	–	0	–	–	8	–	23	6
Modes (2006) (h)	2365	946	–	0	–	–	420	–	1209	315
Refill current (mA)	200	200	200	–	2	196	–	4	90	40
Number of bunches	992	704	868	–	1	24×8	–	1	16	4
Number of refills a day	2	2	–	2	–	–	2	–	4	6
Current decay between refills (mA)	25	35	–	–	–	60	–	2	40	20
Average current (mA)	185	180	–	–	–	160	–	3.7	70	30
Lifetime at refill current (h)	80	65	72	–	15	30	–	7	12	6
H emittance (nm rad)	4	4	4.2	–	–	4.2	–	–	4.5	4.5
V remittance (pm rad)	30	25	22	–	–	60	–	–	60	60
Energy spread ($\times 10^{-3}$)	1	1	1	–	1	1	–	1	1.2	1.5
Bunch length (ps)	20	20	20	–	35	25	–	40	50	60

filling), reaches 60 ps at 10 mA per bunch.

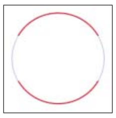
It has previously been possible to deliver intensities of up to 20 mA in single bunch. However, this is now limited to a peak brightness of 10 mA in operation owing to the increasing number of low gap chambers that are installed in the insertion device straight sections, which increases the impedance of the ring.

The purity and extreme contrast requested in pulsed modes between filled and unfilled buckets ($<10^{-9}$) is obtained after the cleaning process done in the storage ring at each refill.

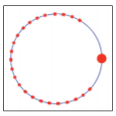
Given the machine potential and limitations, five filling patterns are delivered routinely to users (as shown in figure 1 and with the parameters given in the table):



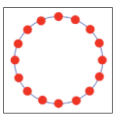
Uniform (200 mA) With a maximum of 992 bunches, this filling pattern, which has the lowest current per bunch (0.2 mA), gives the longest lifetime of 80 h at 200 mA. However, owing to ion-trapping instabilities, the lowest vertical emittance is limited to 30 pm rad in this mode. The maximum current, at present limited to 200 mA owing to longitudinal beam instabilities that are induced by the RF cavities (HOM), is routinely raised to 250 mA during machine-dedicated time. This will be increased to 300 mA by using the longitudinal multibunch feedback, which is being developed. Ion instabilities could possibly be limited using a transverse multibunch feedback, which is also being developed.



2×⅓ (200 mA) With approximately 2×352 bunches, the current per bunch is slightly more than in uniform, reducing the lifetime to 65 h at 200 mA. The presence of two empty gaps totally removes the beam-ion instabilities and consequently gives a minimum vertical emittance of around 25 pm. The two-bunch train is used by the pulsed-beam community, besides being useful for tuning the time parameters of the beamlines.



Hybrid (200 mA) This filling pattern is organized into 24 groups of eight consecutive bunches at 1 mA per bunch with a single bunch of 4 mA in a gap. The maximum current is 200 mA owing to the heat load that is induced in the RF fingers. Cleaning allows the pulsed-beam community to use this filling pattern. A fast chopper can isolate the single bunch and use it in pump and probe experiments with a time resolution given by the X-ray pulse length.



16 bunch (90 mA) With 16 equidistant bunches the maximum current is limited to 100 mA owing to the heat load induced in the RF fingers. The high current per bunch (5.6 mA) reduces the lifetime to 12 h, even with a blow-up of the vertical emittance. This pattern is ideal for the pure pulsed-beam users (e.g. nuclear resonance scattering).

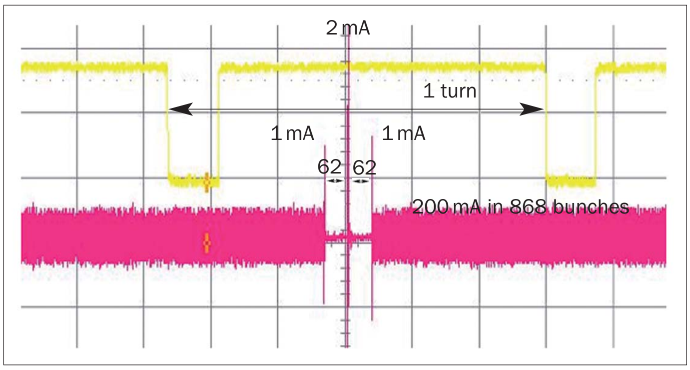
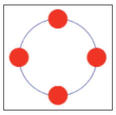


Figure 2. A high-brightness filling pattern with time structure.

In addition the time spacing of 176 ns is long enough for a chopper to isolate a single X-ray pulse.



4 bunch (40 mA) With four equidistant bunches the maximum current is limited to 45 mA by transverse beam instabilities. Owing to the very high current per bunch (10 mA), the lifetime is reduced to 6 h, even with an artificial blow-up of the vertical emittance. This pattern is targeted at Laue experiments on proteins that require an intense flash of X-rays in a single shot. The pulse spacing is as long as 705 ns and single pulses of X-rays are readily isolated by a chopper.

The simultaneous demand for time structure and high intensity has led to the design of a new multibunch filling pattern (figure 2). With chromaticities identical to present multibunch modes, the lifetime is around 72 h at 200 mA. The presence of a gap, one-eighth of the circumference, excludes beam-ion instabilities, thus maintaining the vertical emittance at a value as low as 22 pm rad. The width of the gap is reduced to the minimum value required by the most demanding beamline to minimize the current by bunch and maximize the lifetime. A single bunch of 2 mA, placed in the middle of the gap, is delivered with a contrast ratio of 10^{-9} between filled and unfilled bunches. To optimize the use of this mode the first and last bunch of the train are filled at 1 mA. This new mode, which has been tested by a few beamlines during machine-dedicated time, is ready for operation. With improvement, the multibunch feedback could be operational in this configuration and consequently the maximum current could be increased to 300 mA.

Topping up: a way to improve stability?

Implementing particle injection with front ends open in 2003 has greatly improved the stability of the beamline optics, with continuous availability of the X-ray beam. Thanks to the long lifetime in multibunch (close to 80 h), only two short refills are done each day. Between each refill the beam is delivered for 12 h without any stability perturbation and with a smooth current variation of 15%. By contrast the larger current variation during decay makes topping-up (or more frequent injection) the most interesting in time-structure modes.

The cleaning process done in the storage ring currently blows up the beam for 30 s at each refill, making it incompatible with more frequent injections. A process to clean the injected beam in the booster is under development. The extreme purity required by the most demanding beamline makes this process very challenging for routine operation. With a refill every 5 min, the stability will improve immediately. However, with the present configuration of the lattice, beam-position deviation induced in the storage ring by the injection magnets, such as kickers, makes the beam unusable during injection, imposing gating in the data acquisition on beamlines. Some work is required to minimize this. Topping-up in time-structure modes will be implemented when the cleaning process in the injector becomes operational.

J-L REVOL AND L HARDY
ESRF OPERATION MANAGERS.

The appliance of science to art. Joris Dik (centre) surrounded by his colleagues during a visit to carry out an experiment at the ESRF.

"In the research department of the Getty Museum...I learned a lot about examining art. Then I went back to Holland, where I met a chemistry professor, Henk Schenk, who was crazy enough to hire me as a PhD student."

ART HISTORIAN CROSSES OVER INTO SCIENCE

Joris Dik is possibly the most "artistic" user of the ESRF. He holds an MA in art history and it wasn't until his PhD that he came into contact with science. He then started focusing on the authentication and conservation of paintings, teaming up with the restorer Milko den Leeuw. He has worked for auction houses such as Christie's, but he now devotes his time to his students at the Technical University of Delft, where he teaches materials science in art and archaeology. He is proof that science and art are not incompatible, and he and Den Leeuw use the ESRF regularly for their investigations.

Why did you change your career path so drastically?

It wasn't really a change in career. In my family there are some painting restorers: my grandfather and my uncle both made a living out of it. When I left school I was determined to become one, but then I realized that I had "two left hands". You need manual dexterity to carry out restorations yourself and I didn't have any. I then became interested in the materials and the techniques of painting.

How did you get into the scientific aspects of art?

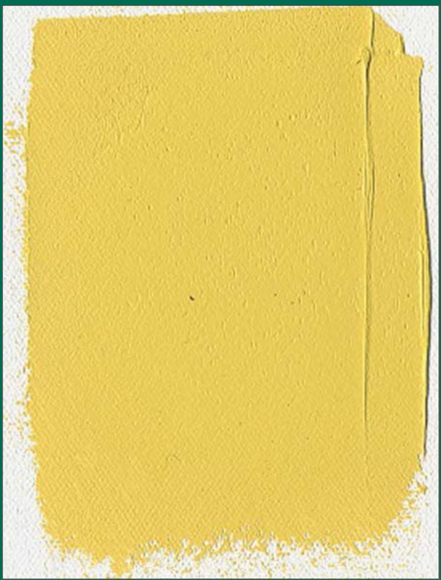
I was given the chance of a one-year traineeship in the research department of the Getty Museum in Los Angeles. It was a fantastic year when I learned a lot about examining art. Then I went back to Holland, where I met a chemistry professor, Henk Schenk, who was crazy enough to hire me as a PhD student.

How difficult was it to do a PhD in chemistry?

It was hard. I didn't have any knowledge of the theory so I had to study a lot. I found out that there is a nice interface between science and arts. During my PhD I used the ESRF several times. In the end, everything turned out well – after five years I got my PhD.

NAPLES YELLOW FOR DATING

Joris Dik did his thesis on Naples yellow, a pigment that has existed for thousands of years. Ancient Egyptians used it, but it fell into obscurity until it reappeared in AD 1000. Slowly its use spread to western Europe from the Middle East in the 16th through to the 18th century. The pigment's complex phase composition changed throughout the years, and Dik's aim was to determine these different compositions. His research could prove useful for dating purposes. When he came to the ESRF for the first time, Dik carried out X-ray diffraction experiments on ID11 and BM01. He says that, as a result of his work, "the early type of pigment, in the 16th century, was very pure and contained lead and antimonite. However, as it spread north, it was adulterated." The pigment was commonly called Naples yellow because people believed that it came from a volcanic mineral from Vesuvius, although this was eventually proved to be a misconception.



What is the main aim of your research?

I focus on conservation studies. Specifically, I work on cadmium pigments and how they lose their colour through the centuries. The aim is to understand the degradation mechanism so that we can stop the damage before it is too late. I am working in collaboration with museums on paintings from Van Gogh at the moment.

How important is the use of synchrotron light in artistic research?

Synchrotron radiation is very useful for certain experiments, but you should only use it when it is necessary. There are two different paths of analytical possibilities at the ESRF that can be of interest for art researchers: the analysis of microsamples, and the non-destructive analysis of entire objects, such as bones and paintings. At the moment my team has a research project for visualization studies on ID17. In general there's a lot of research on art going on at the ESRF and there is even a review committee focused only on proposals for experiments about art. However, there are still things to be done.

How could research into art develop at the ESRF?

Personally, I would be in favour of further measures to help with the transportation of objects for non-destructive analysis. Obviously the safe acclimatization of objects is important, but perhaps the community could also think about setting up a sort of travel and insurance fund, because these are costs that usually cannot be paid for from running budgets. It might be an idea to request European funding for this with the help of the ESRF. After all, in the EU we share not only the synchrotron facility but also our cultural heritage.

Could you develop new techniques for your research at the ESRF?

Not really. I think we are too small a community to demand instrumental developments. Nevertheless, we should be opportunistic and make the most of the new possibilities that come up.

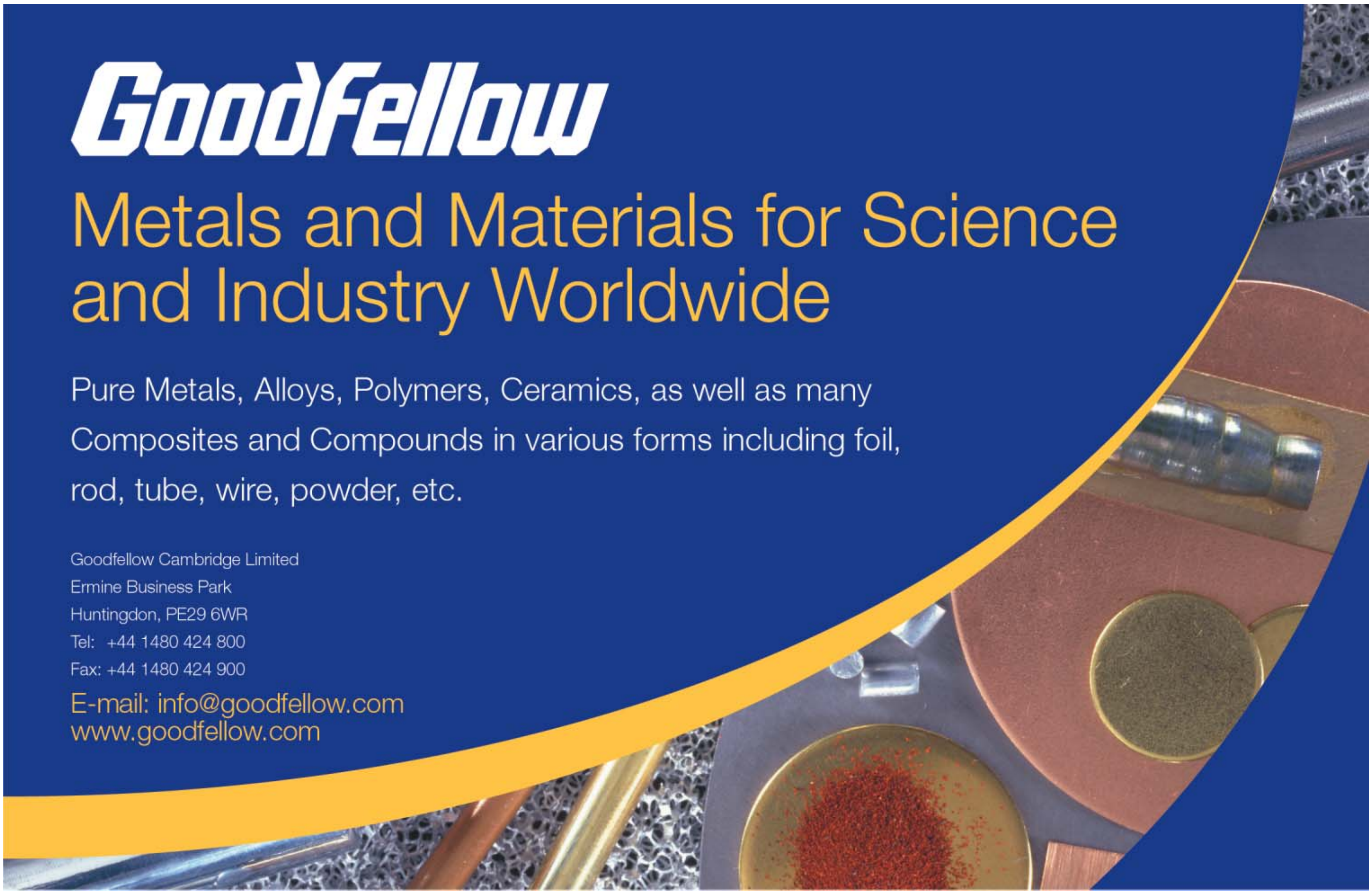
What is the state of the research into art carried out at other synchrotrons?

The ESRF is one of the leaders in this field. SRS, BESSY, SOLEIL and CHESS at Cornell are also quite active in this field. However, it's worth pointing out that neutron sources are also a good way to study art and are complementary to synchrotron sources.

Do you feel closer to science or to art today?

I definitely feel closer to science, but I would like to be nearer to art. I am very happy with what I am doing, but I can't help missing art.

MC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Scientific highlights

NEW DEVELOPMENTS AT ID20

Resonant X-ray scattering under extreme conditions: investigating the physics of multiple-ordered states

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Combining resonant X-ray scattering (RXS) techniques and extreme experimental conditions, such as low temperatures, high pressures and high magnetic fields, opens new possibilities of investigating structural, magnetic and anomalous scattering properties of strongly correlated electron systems. Careful variation of the experimental environment conditions in which a material is placed while making observations helps to unravel the ground-state properties of these complex materials and their enigmatic modifications. Of particular importance in this regard are low temperatures, high magnetic fields and high pressures, which are pioneered at the ID20 Magnetic Scattering Beamline at the ESRF.

Electronic degrees of freedom promote structural modifications, transport effects and magnetic phenomena such as spontaneous long-range magnetic order, magnetoresistivity and magnetoelectricity. Many transition metal oxides exhibit interesting long-range ordered electronic states, such as ferroelectrics, colossal magnetoresistive manganites and cuprate superconductors. Even though magnetic ordering is common, it is rare to find the coexistence of multiple long-range orderings. Materials possessing more than one "ferroic" order (which include long-range magnetism, ferroelectricity and elastic distortion) are called multiferroics, and this class of compound comprises exceptional materials, for which the electric polarization can be controlled by a magnetic field, or for which the magnetic polarization can be controlled by an electric field. As well as being of fundamental scientific interest, such materials have great potential as an alternative route to spintronic devices, and they open the possibility of a number of technological applications (Fiebig 2005).

RXS is a site-, element- and shell-selective technique that allows the exploration of the anisotropic properties of atomic scattering tensors. It represents a unique method of characterizing the microscopic atomic interactions in solids from the electronic point of view. RXS is based on enhancing the X-ray scattering cross-section close to an absorption edge, such as the K edges of transition metals, the $L_{2,3}$ edges of rare earths and the $M_{4,5}$ edges of actinides. The resonant process involves promoting core electrons to empty intermediate states in the vicinity of the Fermi level, and their subsequent decay accompanied by the emission of an elastic photon, which reflects the

Figure 1. Superconducting 10 T split-pair magnet (Oxford Instruments) on the a-magnetic six-circle diffractometer (Huber GmbH) in the ID20 second experimental hutch.

electronic state of the magnetically ordered species. Moreover, the resonant cross-section has a characteristic polarization dependence, which can be exploited to obtain further information about the magnetic-moment direction and the space group of the ordered state.

The recently commissioned high-field magnet facility on ID20 opens new avenues of research in materials with complex and competing order parameters, including multiferroics.

A superconducting split-pair 10 T magnet, which can reach the basic temperature of 1.8 K and is accommodated on a dedicated six-circle diffractometer, is designed to support heavy loads and built from non-magnetic materials (figure 1). An in-vacuum polarization analyser assembly is mounted on the detector arm and can rotate about the X-ray beam that is scattered by the sample to make the full linear polarization analysis. The custom design of the magnet allows RXS at low energy (down to 3.5 keV) with wide scattering angles and low absorbing beryllium windows.

In one of the first experiments, this facility investigated the phase diagram of the multiferroic compound $TbMnO_3$. Previous bulk measurements established that in zero applied magnetic field the ferroelectric polarization, P, aligns along the c-axis, as in the phase labelled FE (P ∥ c) in figure 2. Meanwhile above a critical threshold of applied magnetic field, P flops to be along the a-axis, FE (P ∥ a) (Kimura *et al.* 2003). However, these measurements obviously don't provide a microscopic atomic-scale description of changes to the structural and magnetic correlations.

Scattering data, particularly RXS with its element and electron shell sensitivities, provides such information. The experiment performed at both the Tb L edges and Mn K edge with the new magnet facility allowed us to study the phase diagram in great detail (Mannix *et al.*). For example, for all of the phases identified by the bulk studies, we studied the underlying chemical and magnetic structures.

As a result the different commensurate (C) and incommensurate (IC) phases can be studied in detail, and the contribution to the X-ray diffraction signals from Tb of Mn electrons can be distinguished, as well as the corresponding magnetic and electronic modulations in each phase. This allowed us to establish, among other things, that an IC to C (lock-in) transition drives the flop of the polarization along the a-axis.

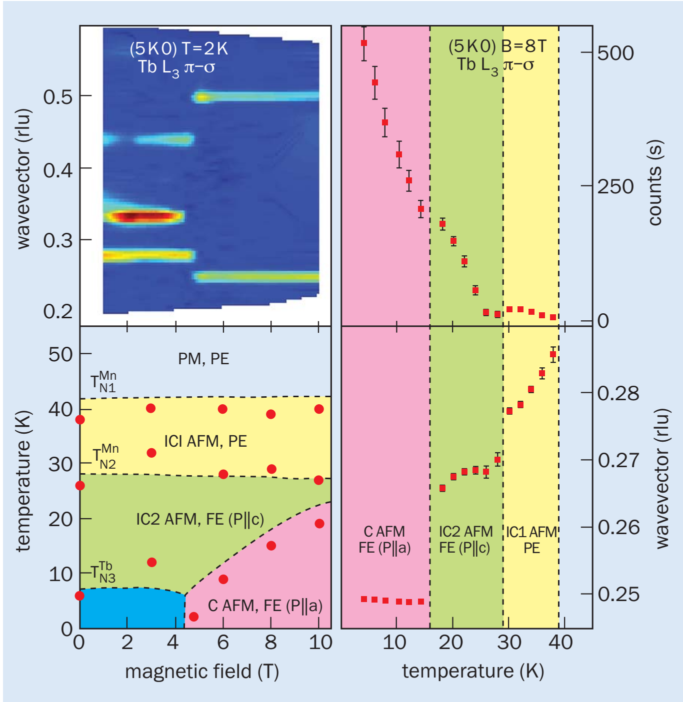

Figure 2. Left: magnetic field dependence of RXS at Tb L_3 edge of satellite reflections (5 k 0) at 2 K (top) and the corresponding H–T phase diagram (bottom). Right: Evolution of the intensity (top) and the wavevector (bottom), measured in reciprocal lattice units (rlu), of the satellite reflection (5 k 0) as a function of the temperature, under an applied magnetic field of 8T.

Conclusions

Combining extreme conditions, such as high pressures, low temperatures and high magnetic fields, with the RXS technique opens new possibilities to investigate and single out structural, magnetic and anomalous scattering. New and exciting fields of research, such as orbitally ordered systems, multiferroics, actinides and charge-ordered systems, can benefit from these unique sample environment conditions.

Planned improvements to the focusing properties and stability of the beamline optics will allow extensive use of these combined techniques in the future.

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SOFT CONDENSED MATTER GROUP

Simultaneous μRaman and μXRD: probing the deformation of a single high-performance fibre

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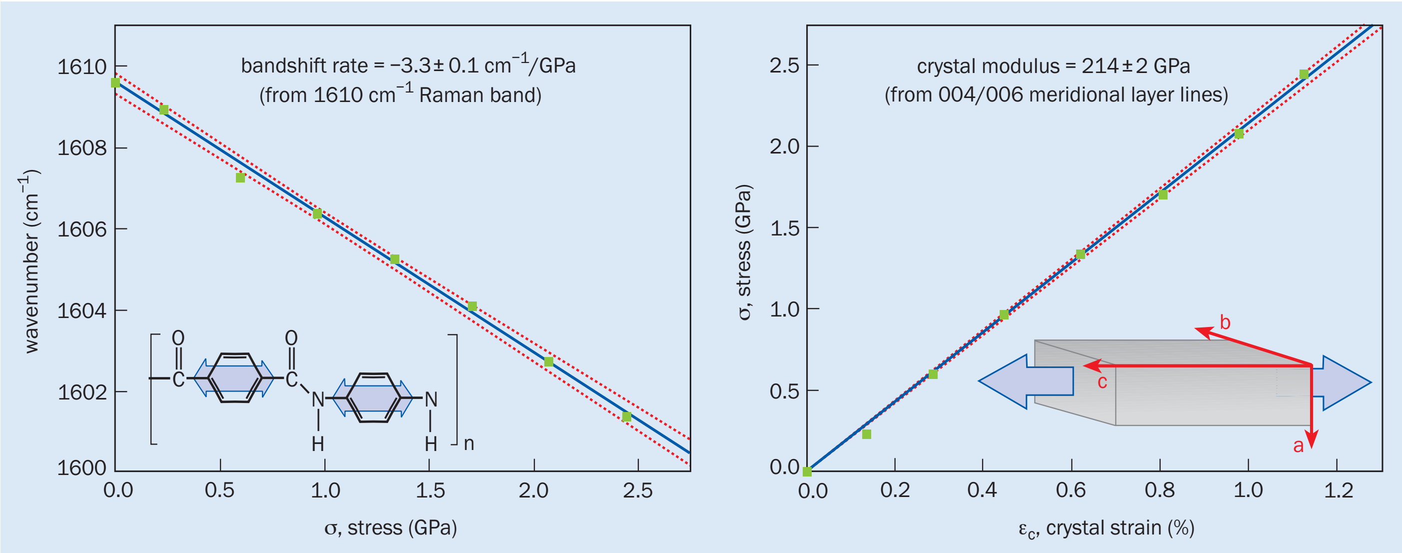

Figure 1: (a) Variation of the 1610 cm^{-1} Raman band with increasing stress. The bandshift corresponds to direct deformation of the PPTA molecule, as shown in the schematic. (b) Stress versus crystal strain, calculated from a change in the c-spacing of the crystal lattice. Lattice distortion is also shown schematically.

Raman spectroscopy and X-ray scattering are complementary techniques on many levels (Davies *et al.* 2005). For this reason they are both used extensively in many scientific fields. These range from mineralogy, archaeology and materials science to studying biological systems, such as proteins. The ID13 μRaman set-up allows both techniques to be performed simultaneously, with the X-ray and laser beams being delivered coaxially to a single point on the sample. With both beams measuring 1 μm in diameter, the ID13 system is the first of its kind and provides unique access to confined sample volumes.

In a recent application (Davies, Burghammer and Riekel 2006), μRaman and μXRD have been combined to probe structural changes within a single poly(p-phenylene terephthalamide), PPTA or Kevlar[49] fibre. The results show that during deformation both the 1610 cm^{-1} Raman band and crystal strain (along the fibre axis direction) change linearly with macroscopic stress (figure 1). This indicates that stress is being transferred directly between crystalline domains and individual molecular bonds. The resulting Raman band shift rate and crystal modulus are −3.3 cm^{-1}/GPa and 214 GPa respectively. Deformation also causes a stress-induced increase in crystalline domain orientation consistent with the non-reversible rotation of chains.

Combining the information provided by both techniques has provided a new insight into deformation micromechanics within single PPTA fibres. In particular, it reveals how molecular- and crystallographic-scale contributions influence a material's mechanical properties. This has enabled a completely new bicomponent mechanical model to be developed for PPTA. It also explains for the first time how heterogeneous stiffening can occur within the fibre during macroscopic deformation.

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Visiting a beamline

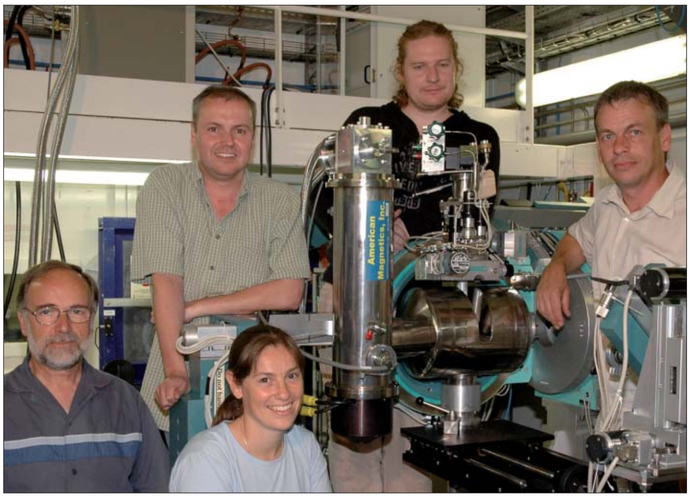
BM28: A BRITISH XMAS CREATES AN INTERNATIONAL MAGNETIC ATTRACTION

For more than eight years the British beamline BM28, X-ray Magnetic Scattering (XMaS), has been welcoming users, who mainly study magnetism in materials. Today its scientists continue to enhance the beamline's experimental facilities.

Many of the CRG beamlines at the ESRF are multipurpose, so they can fulfil the whole range of possible experiments by their international users. However, the British beamline XMaS functions differently. It has always been focused on magnetism and magnetic scattering and its original design was optimized for this line of research.

There is a healthy demand in this field among the UK scientific community and, indeed, throughout the world. However, despite its specificity, this beamline is not restricted to a single technique. "A little more than 40% of our research is magnetism related; the rest is very diversified, including research on polymers, multilayers, surface nanoarrays, electrochemistry and biotissue – even corrosion in museum artefacts and the crystallinity of teeth have been studied. Although we have a core group of regular users from about a dozen universities and research establishments in the UK, we continue to attract new interest in the beamline from both the UK and elsewhere in Europe," explains David Paul, beamline coordinator. He notes that the beamline is "well subscribed, both in the UK proposals round and also in the ESRF public round". It is funded on five-year grants by EPSRC and it is managed jointly by the universities of Liverpool and Warwick.

A novel feature of the beamline has been the team's continual efforts to enhance the experimental facilities. A new 4 T magnet that has recently been installed follows an impressive list of hardware innovations – polarization analyser; motorized x, y, z cryostat/sample stage; in-vacuum low-angular profile slits; 1 T electromagnet; low-temperature cryostats; etc. "For the moment we are the only beamline at the ESRF able to study a sample at 1 K, while retaining the same



Chantal Argoud

The BM28 team. Standing around the new 4T superconducting magnet, clockwise from the right: Simon Brown, Laurence Bouchenoire, David Paul, Paul Thompson and Danny Mannix.

angular access on the diffractometer as for a standard 10 K displex," explains one of the staff, Paul Thompson. A number of these developments have been commercialized and some can be found at synchrotrons worldwide. Currently the team is developing a phase plate flipper facility, based on phase-locking techniques, where the helicity of the X-ray beam polarization is flipped rapidly between opposite states, principally to investigate ferromagnetic materials. The beamline team works together in close collaboration in all of the in-house research projects, which often lead to spin-off instrumentation.

XMaS is probably one of the few places at the ESRF where English is spoken nearly all of the time and mostly without foreign accents. This is because almost the entire staff are British (David Paul, Paul Thompson, Simon Brown and Danny Mannix), except for Laurence Bouchenoire. The secretariat of the beamline as well as the directors – Malcolm Cooper and Chris Lucas – are based in the UK. The British nature of the beamline is also reflected in the group meetings, so it's not surprising that some of them take place in the pub around a beer. It couldn't get much more British.

MC

Gallery of events

ESRF RESEARCHERS SHARE THEIR SCIENCE

The biannual Science Days take on a slightly different format and prove to be just as successful as before.

Montserrat Capellas

Lively discussions. Coffee breaks were a good opportunity to discuss recent scientific achievements with colleagues.

The science at the ESRF covers such a range of disciplines that it can be difficult for individual scientists to know what goes on there outside their own field. This is the reason why the ESRF Experiments Division organizes biannual Science Days. These events are also intended to stimulate discussions between scientists. This year the Science Day took place in Autrans on 7 and 8 June and had a very young atmosphere and, out of the 145 participants, 43% were PhD students or postdoctoral researchers.

This year the structure of the event was slightly modified: the chairs of the different sessions were scientists from different groups than the speakers. "We wanted to remind speakers that they should address everybody and to make the audience feel free to ask questions, even if they are basic," explains Andy Fitch, one of the organizers. In this way the audience could see Nick Brookes, head of the X-ray Absorption and Magnetic Scattering Group, introducing biology talks, which are far away from his field. The new formula "was quite successful, and worked in some talks better than in others", says Fitch. According to Blanca Detlefs from ID20, "since the event is only two days long, the oral presentations should be more general so that everybody can follow them".

Four students were awarded a poster prize: Guillaume Potdevin, Adeline Buffet, Guillaume Morard and Filippo Bencivenga. Their efforts won them a bottle of champagne. "We decided on four prizes in recognition of the very high general standard of the students' work and its presentation in the posters; it's important that students know that their efforts are appreciated," explains Fitch.

MC

ESRF HOSTS THE LATEST THREE-WAY MEETING

Last summer the ESRF opened its doors to staff from the three biggest synchrotron facilities in the world.

Every 18 months the ESRF, the APS or SPring8 hosts a meeting to discuss scientific and technical issues of common interest. This year the ESRF welcomed 31 participants in the Three-Way Meeting on 19 and 21 June. The event started with the 4th X-ray Optics Workshop. The agenda included talks on the aging of accelerator components; micro- and nanofocusing; high-energy insertion devices; extreme conditions; the accelerator complex; and recent highlights and future developments of X-ray imaging and synchrotron-radiation instrumentation.

MC

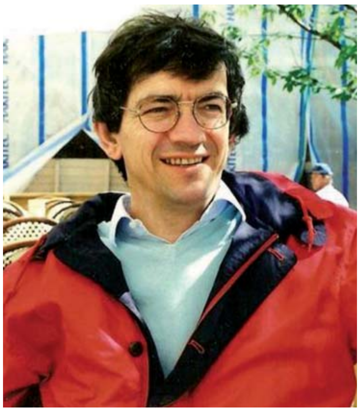
Chantal Argoud

All together. The Three-Way Meeting held this year brought together more than 30 people from three different continents.

EVENT REMEMBERS THE WORK OF PAOLO CARRA

Paolo Carra's work was celebrated at a popular and successful symposium on magnetism in solids in September.

The event entitled Theoretical Concepts on Magnetism in Solids: Symposium In Memoriam Of Paolo Carra was held at the ESRF on 14 and 15 September. Organized by the ESRF and the ILL, it highlighted the solid-state physics field of magnetism in solids, addressing both theoretical and experimental aspects.



Doon Gibbs

The presentations put into perspective scientific concepts of magnetism together with the challenges for the future in this research area, and they also gave a special emphasis to the important contributions made by the work of Paolo Carra.

The symposium attracted many international speakers and about 70 participants from all over the world. Although the emphasis was on theory, the two-day event was an opportunity for experimentalists and theorists to get together and there were lively discussions throughout this very successful meeting.

It was also a great opportunity to highlight and honour the contributions that Paolo Carra made in this field of research and how they are still influencing the new challenges in the properties of advanced magnetic materials.

Paolo Carra's pioneering work in magnetic X-ray dichroism was recognized by the Agilent Technologies Europhysics Prize, which he was awarded in 2000. The award was shared with Gerrit van der Laan and Gisela Schütz-Gmeineder.

THE ORGANIZING COMMITTEE

HERCULES GOES FROM STRENGTH TO STRENGTH

Chantal Argoud

The first ones. The group of researchers who benefited from the first Hercules specialized course on synchrotron radiation.

Hercules now offers a new set of one-week courses that are already proving popular with delegates.

Hercules is stronger than ever. This spring the Higher European Research Course for Users of Large Experimental Systems, organized by the Institut National de Polytechnique de Grenoble (INPG) and Joseph Fourier University (UJF), started a series of one-week specialized courses on synchrotron radiation. These are composed of lectures and practicals aimed at PhD students and postdoctoral scientists. They are supported by the European Commission. The Hercules programme's main feature is a five-week European course in March on large instruments, which focuses on both synchrotron and neutron radiation.

The first Hercules specialized course in 2006, on 21–26 May, covered X-ray imaging techniques based on absorption, phase contrast, diffraction and fluorescence. One of the participants said: "[The course] enables us to broaden our knowledge – we get to learn different techniques that we didn't know about before coming."

Even though the programme is limited to 20 participants, the lectures are open to anyone who is interested in the subject. For instance, Paul Tafforeau, a palaeontologist working at the ESRF, listens to the lecture courses to learn more about the techniques that allow him to scan his findings everyday. "I like to know the theoretical part of my practice," he says.

From the 77 applications to attend the course, the organizers selected the candidates who would profit the most from this experience and who showed definite motivation. The students came from all over Europe. One of the organizers and speakers, José Baruchel, commented: "Participants get together and can create for themselves a network of acquaintances for the future." However, the delegates are not the only ones to benefit from the course. "Hercules also represents an enrichment for the speakers, who learn from their colleagues," adds Baruchel.

Montserrat Capellas

Poster session. Participants had the opportunity to explain some of their research to lecturers and other delegates.

At the time of going to press there were two new specialized courses planned for the end of the year: one on structural genomics and the other on surfaces, interfaces and nanostructures. Registration for the courses for 2007 is now open.

For more information, visit www.esrf.fr/NewsAndEvents/Conferences/HSC/.

ANNE BENHAMOU