Australian Synchrotron
Research Highlights 2010 - 2012

Australian Synchrotron

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Contents

Foreword

It is my pleasure to introduce the Australian Synchrotron Research Highlights Report for the period 2010-12. This selection of research showcases only the tip of the iceberg of the efforts by a remarkable and large community of visiting researchers and expert scientific and support staff at the Australian Synchrotron, who have worked tirelessly to support researcher outcomes.

With 9000 researcher visits and 750 peer-reviewed journal articles during the period covered by this report, the Australian Synchrotron demonstrated its status as a world-class national landmark research facility. For a facility with less than five years of operations behind it this achievement, which contributes to the social, economic and physical well being of all Australians, is exceptional.

The initial suite of nine beamlines has enabled researchers to make outstanding contributions across the breadth of the research spectrum. The quality of this research is evidenced by the number of papers published in the very highest impact journals. And, the number of research projects with industrial outcomes is continuing to rise, with over 130 commercial companies having benefited from Synchrotron research, either directly or via research providers.

Such research efforts are not possible without ongoing development of support capabilities. The top-up mode of accelerator operation was completed in May 2012, improving photon beam stability. The upgraded imaging and medical beamline now delivers high-dose micro-beam radiotherapy and fast computed tomography and, in the satellite building, phase-contrast imaging using the world's widest synchrotron beam. The MASSIVE high-performance computing cluster came online in 2011 facilitating data reduction, real-time visualisation and data storage. This capability has been enhanced by scientific computing initiatives, supported by the federally funded National eResearch Collaboration Tools and Resources project. Federal funding under the Education Investment Funds scheme has also seen a much-needed expansion in Australian Synchrotron infrastructure with the addition of a 50-room guesthouse, engineering and computing offices, and the National Centre for Synchrotron Science.

Facility operations were funded to 30 June 2012 by the State of Victoria, the Australian Federal Government and the New Zealand Government. In 2012, a new funding package was secured to June 2016 with contributions from the previous funders, most Australian and New Zealand universities, the Australian Research Council, the National Health and Medical Research Council, the Science Industry Endowment Fund and the Australian Nuclear Science and Technology Organisation (ANSTO), which assumed responsibility for Synchrotron operations from 1 January 2013.

As well as stabilising operational funding, the 2010-12 period also saw the consolidation of planning for new beamlines and other capabilities through the Australian Synchrotron Development Plan. International synchrotron best practice would normally see a significant increase, after the first few years of operations, in the number of beamlines available to researchers. Obtaining broad support for continued development in capability at the Australian Synchrotron is now essential if the facility is to continue to deliver exceptional scientific and industrial outcomes for Australia.

The case studies and materials in this Research Highlights report demonstrate the wonderful achievements of the facility in years 3 – 5 of operation. We hope you are as impressed and excited by them as we are, and we look forward presenting the next update in the series as the facility continues to evolve.

Professor Andrew Peele

Head of Science 2011 – 2012

About the Australian Synchrotron

The Australian Synchrotron is a world-class research facility that uses accelerator technology to produce a powerful source of light – x-rays and infrared radiation, many times brighter than the sun.

The facility has nine different experimental stations, or beamlines, which harness that light so researchers can see the fundamental structure and composition of materials, on scales ranging from the atomic to the macroscopic – with a level of detail, speed and accuracy not possible in conventional laboratories.

The Australian Synchrotron supports a broad range of high quality research, with applications in sectors from medicine and nanotechnology to manufacturing and mineral exploration. Our highly advanced techniques and passionate staff are contributing directly and demonstrably to scientific advances and industrial innovations with medical, social and economic benefits for all Australians.

Vision

The Australian Synchrotron's vision is to be the catalyst for the best research and innovation in Australia and New Zealand. The focus for the facility is to provide a thriving environment that is conducive to creating, inspiring and nurturing the best outcomes, enabled by scientific excellence, for users and staff of the facility.

Mission

The Australian Synchrotron's mission is to enable science for the benefit of the community, by providing world-class synchrotron expertise and facilities.

Core values

The facility is driven by the core values of passion, respect, innovation, collaboration, and excellence.

Our research capabilities

The Australian Synchrotron's sophisticated scientific techniques provide benefits for diverse scientific and industrial fields and purposes, including:

- **Biomedicine:** offering new world-class diagnostic, imaging and therapeutic techniques and high-throughput structural biology capabilities.
- **Defence:** enabling study of the sub-atomic nature of materials, sensors and heavy metals.
- **Environmental technologies and services:** supporting environmental remediation work and analysing soil samples, the quality and composition of fresh and salt water, air and atmospheric samples, pollutants, toxins and contaminants.
- **Food technology:** analysing the composition of ingredients, assessing the effectiveness of food processes and determining the nutritional impact of foods in the body.
- **Forensics:** refining or developing new forensic processes, techniques and applications.
- **Manufacturing:** investigating the structure and characterisation of alloys, catalysts, fibres, textiles, adhesives, polymers, plastics, surfaces, interfaces and coatings; and analysing stresses in engineered components.
- **Minerals:** supporting all aspects of mineral exploration and mineral processing.
- **Natural resources:** supporting the development of exploration and fuel processes, the reduction of pipeline scale formation, and fuel cell innovations.
- **Pharmaceuticals:** analysing proteins, nucleic acids, viruses and biomimetic materials (such as artificial skin and organs) as well as conducting cell imaging, quality control monitoring, identification and assessment of the effectiveness of drug targets.
- **Scientific instruments:** developing detector technologies, measurement techniques, medical implants and delivery systems.

Beamline Capabilities

Imaging and Medical Beamline (IMBL)

The upgraded imaging and medical beamline (IMBL) began limited operations in November 2012. It caters for very high dose micro-beam radiotherapy (MRT) research, and fast, medium-resolution computed tomography imaging. High-resolution phase-contrast imaging (PCI) and slower computed tomography with PCI are available in a satellite building that accommodates preclinical research.

A new superconducting multipole wiggler system supplies very high energy x-rays to the beamline, either in the form of a wide energy 'white beam', or as a monochromatic beam after reflecting from a high-stability double crystal monochromator. Delivering this very large x-ray beam (500mm x 40mm) to the satellite building 136 metres from the wiggler, involved designing and installing a large vacuum transfer pipeline.

Bone, cardiovascular, heart, lung and radiotherapy research streams have been formed in consultation with clinicians, biomedical and clinical researchers. Bone research concentrates on in-vivo high-resolution imaging and MRT for musculoskeletal diseases.

Infrared Microspectroscopy Beamline (IRM)

The infrared microspectroscopy beamline (IRM) is a mature facility with a strong user base. Regular workshops introduce users to data analysis tools such as advanced multivariate statistical methods.

Using the MASSIVE high-performance computing cluster, researchers can correct data from biological samples 100 times faster than by personal computer. Data analysis software is available through the remote access to Infrared Data Analysis Resource (RAIDAR).

Integrating a focal plane array imaging detector with the synchrotron beam will further improve spatial resolution and reduce collection times.

Terahertz/Far-Infrared Beamline (THz/Far-IR)

The terahertz/far-infrared beamline (THz/Far-IR) users have diverse interests that include biological, atmospheric, astrophysical, renewable energy, and materials research and applications. For example, users are studying protein-water interactions, water ice particles – which play important roles in interstellar and atmospheric photochemical processes, catalytic properties of ligand-stabilised gold clusters, hydrogen release from new hydrogen storage materials, and new cathode materials for non-aqueous lithium ion batteries.

New instrumentation is increasing the scientific capabilities at the beamline and offering more techniques to condensed-phase and gas-phase users.

Macromolecular and Micro-crystallography Beamlines (MX1 and MX2)

The macromolecular crystallography beamline (MX1) performs standard experiments with high throughput. The micro-crystallography beamline (MX2) has a micro-focussed beam for tackling more challenging problems. These mature and productive facilities have a large user base.

Addressing the needs of chemical and macromolecular crystallographers is challenging but enriching. The beamlines also service the needs of commercial users.

Automated data processing gives users near real time feedback on data quality. AutoRickshaw can automatically solve structures where data have sufficient information content. Beamline development is ongoing.

The Australian structural biology community regularly produces internationally significant research using Australian Synchrotron MX data and crystal structures. Recent highlights include insights into the regulation of blood clotting and cancer cell metastasis, and discoveries that could lead to more effective treatments for some cancers and neurodegenerative diseases.

Powder Diffraction Beamline (PD)

Powder diffraction beamline (PD) staff are extending the beamline's sample environments and supporting users to more effectively process their data for publication.

A high-pressure diamond anvil cell exposes samples to pressures found in the Earth's deep mantle or on other planetary bodies. A high-temperature furnace enables data collection up to 1500°C.

New user support features include in-house data visualisation, processing and reporting software (PDViPeR). Web-based tutorials are available to help new users refine synchrotron powder diffraction data.

Current projects will enhance beamline capabilities for experiments on polycrystalline solids and films, and improve operation of the Mythen microstrip detector. Forward plans include a faster auto-alignment spinner for sample capillaries and a sample-loading robot to improve throughput.

Small and Wide Angle X-ray Scattering Beamline (SAXS/WAXS)

The small and wide angle x-ray scattering beamline (SAXS/WAXS) is a world-class facility for protein solution scattering, which accounts for almost half of beamline use. The beamline is fully automated for running solution samples and *in situ* size exclusion chromatography, and caters for exceptionally dilute samples. Users have full control of optics performance. Automatic data processing outputs include an initial 3D shape reconstruction.

High-performance software includes: AreaVision for high-speed sample alignment; and ScatterBrain for data acquisition, processing, and analysis. Beamline staff have developed a comprehensive wiki of beamline documentation and troubleshooting.

Recent user highlights include new structural insights into the body's cellular defences against viral pathogens, discovered by examining protein conformational changes in solution, which are not accessible to crystallography.

Soft X-ray Spectroscopy and Imaging Beamline (SXR)

The soft x-ray spectroscopy beamline (SXR) has a new branchline and imaging endstation. Internationally-recognised experts in coherent diffraction imaging from the Centre of Excellence for Coherent X-ray Science recommissioned an instrument they designed and operated at Chicago's Advanced Photon Source.

The original beamline supports diverse users, mainly for soft x-ray spectroscopy and surface preparation under ultra-high vacuum. The beamline offers sample heating to 1000 °C, cooling to -130 °C, argon ion beam etching, and limited reactive ion etching. Thermal sources for *in situ* sample preparation allow evaporation from 50 to 1400 °C.

The past year has seen notable scientific outcomes in diamond-based electronics, organic solar cells and semiconductors.

X-ray Absorption Spectroscopy Beamline (XAS)

The x-ray absorption spectroscopy beamline (XAS) supports diverse users from biology to materials science, specialising in ultra-dilute, *in situ* and extreme environment investigations. XAS is facing increasing demand following closure of the Australian National Beamline Facility (ANBF).

XAS beamline refurbishments will enhance delivery of the highest quality data from transmission and fluorescence measurements at room and low temperatures. Synchrotron staff are overhauling the second experimental station to accommodate large roll-in, roll-out equipment for extreme chemistry, high temperature and high pressure measurements.

X-ray Fluorescence Microscopy Beamline (XFM)

The x-ray fluorescence microscopy beamline (XFM) accommodates users from biological, geological and environmental sciences, with significant cultural heritage and materials science program. It offers elemental mapping, spectroscopy and tomography with 120 nm to 200 µm resolution.

The beamline's popularity is largely due to the Maia detector system, being further developed in collaboration with CSIRO and Brookhaven National Laboratory. Maia offers an order-of-magnitude improvement in experimental efficiency, with extremely short dwells for high definition investigations. Users can inspect images during acquisition: high quality analysis is supplied within minutes of scan completion using the GeoPIXE software on MASSIVE.

Staff are implementing cryogenic capabilities to improve microprobe mapping, spectroscopy and tomography through reduced radiation damage. Maia upgrades will improve energy resolution, extend low energy detection and enhance transmission imaging quality.

Highlights

The early efforts of the Australian Synchrotron user community have produced a bounty of scientific outcomes. The period 2010-2012 saw peer-reviewed journal publications from in-house Synchrotron instruments increase 10-fold to 753, up from 80 in 2007-2009. Around 200 additional journal papers resulted from Australian researchers using the Australian National Beamline Facility and other overseas facilities through the International Synchrotron Access Program.

One in 10 papers was published in outstanding journals such as *Nature* and its affiliate journals, *Cell*, *Immunity*, *Angewandte Chemie*, *ACS Nano*, *Advanced Materials*, *Energy and Environmental Science*, *Physical Review Letters*, and *Proceedings of the National Academy of Science USA*.

Here are some highlights of the breadth and quality of Australian Synchrotron-supported research:

Award-winning detector

The Maia x-ray detector system developed by CSIRO, Brookhaven and Australian Synchrotron staff has facilitated important new research findings in earth, environmental, forensic and life sciences. The Maia team received a 2011 R&D 100 Award and the 2012 CSIRO Research Achievement Medal.

Excellent health outcomes

Excellent health and medical research outcomes have come from studies of heart disease, cancer, HIV/AIDS, trace element deficiencies and toxicity, drug development and delivery, and the immune system. A major highlight was the discovery of how a protein called perforin punches holes in cancer cells, enabling toxic enzymes to enter and destroy the rogue cells.

Better ways to deliver drugs

Researchers are developing nanoscale drug-delivery systems based around lyotropic liquid crystalline systems formed by molecular assembly of surfactant or lipid molecules. Similar systems can support the stabilisation of membrane proteins for structural studies.

Alternative energy systems

A major research effort focuses on catalysts and new energy materials for organic solar cells, lithium-ion batteries, hydrogen storage and carbon sequestration. For example, powder diffraction studies demonstrated hydrogen storage and release from borohydride compounds that exceed the US Department of Energy storage target for 2015 by up to 50%.

New radiotherapy technique

Infrared microspectroscopy studies have suggested a mechanism by which microbeam radiotherapy, a promising experimental radiotherapy technique, kills the whole tumour despite only a small percentage receiving peak irradiation.

Upgraded x-ray imaging

The upgraded imaging and medical beamline delivers a very large (500mm x 40mm) x-ray beam to a satellite building outside the main ring building. In November 2012, the beamline began accepting user experiments in all three modes of operation.

Preserving our heritage

A promising new area of work involves synchrotron studies of cultural and heritage items such as historic paintings, providing vital information for galleries, restorers and conservators.

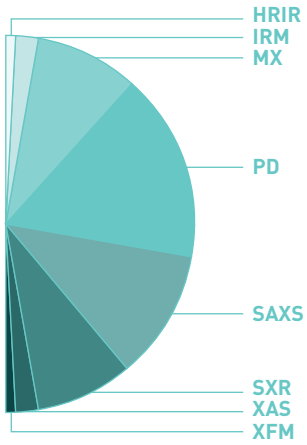
The heart of the Synchrotron

After demonstrating a world record low vertical emittance for the Australian Synchrotron electron beam in 2011, accelerator science staff have continued their strong work in vertical emittance tuning.

Advanced Materials and Engineering Science

353 papers

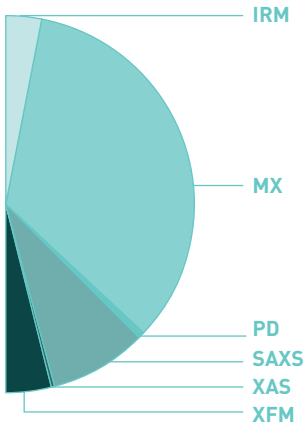
45 papers appeared in high-impact journals	12.7%
93 papers had one or more AS co-authors	26.3%
PD accounted for 114 papers in this area	32.3%
SAXS accounted for 78 papers	22.1%
52 papers had 10 or more citations	14.2%
7 papers had 30 or more citations	2.0%



Medical and Life Sciences

250 papers

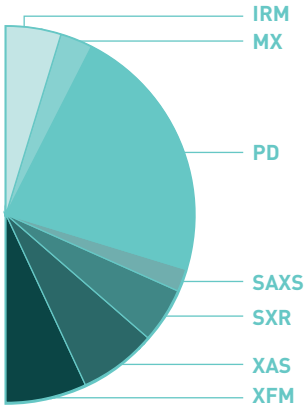
57 papers appeared in high-impact journals	22.8%
45 papers had one or more AS co-authors	18%
MX1 & 2 accounted for 170 papers in this area	68%
65 papers had 10 or more citations	26%
10 papers had 30 or more citations	4.0%



Earth and Environmental Sciences

52 papers

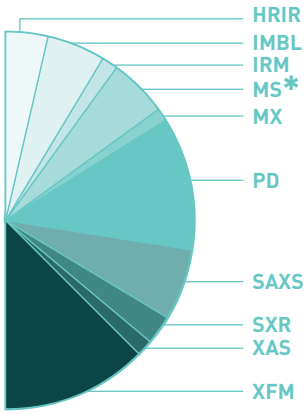
15 papers had one or more AS co-authors	28.8%
PD accounted for 23 papers in this area	44.2%
4 papers had 10 or more citations	7.8%



Accelerator and Beamline Development

40 papers

4 papers appeared in high-impact journals	10%
24 papers had one or more AS co-authors	60%
XFM accounted for 10 papers in this area	25%
PD accounted for 9 papers in this area	22.5%
9 papers had 10 or more citations	22.5%



High-impact journals (which published 14.9% of AS-related papers) are defined here as having an impact factor of 6.6 or above for 2011. High-impact papers (2.3% of total) are defined as having 30 or more citations as of June 2013 (date of this analysis). Middle to high impact papers (18.0% of total) are defined as having 10 or more citations as of June 2013.

** Machine studies involving accelerator science team.*

The User Office

The User Office is the first point of contact for all current and prospective users, and central to the experiences associated with working at the Australian Synchrotron and producing research outcomes.

In addition to ensuring that more than 700 proposals a year are properly reviewed, ranked by scientific merit and awarded beamtime, the User Office services the practical requirements of the hundreds of users who come to the Australian Synchrotron annually.

The User Office oversees the review of all merit-based proposals to use the facility, the scheduling of beamtime, the provision of travel support and accommodation for users visiting the facility and the flow of information and advice to the user community. Post-beamtime, the User Office manages the collation of publications containing scientific outcomes resulting from work conducted on the Australian Synchrotron beamlines.

The User Office also runs the International Synchrotron Access Program, which funds Australian research groups travelling to overseas synchrotron facilities.

Aside from the successful management of over 4000 safe user visits to the Synchrotron, the main achievement of 2010-2012 was the grand opening in April 2012 of a two-storey onsite guesthouse. The guesthouse comprises 50 ensuite rooms, and provides users with a fully-equipped communal kitchen and spacious dining and lounge areas, just metres from the main Synchrotron building. The guesthouse facility has been very well received by users and continues to exceed user expectations. The User Office's efforts to provide exceptional customer service to the user community are reflected in the positive feedback received via the ongoing user exit survey. During 2010-2012, most users rated their experience with the User Office as "excellent".

The User Office Team

Dr Cathy Harland, Group Leader – User Office

Dr Glyn Devlin, Associate Group Leader – User Office

Ms Amanda Costanzo, User Office Administrator

Mr Scott Kendall, User Office Administrator

Ms Donna Popov, User Office Administrator

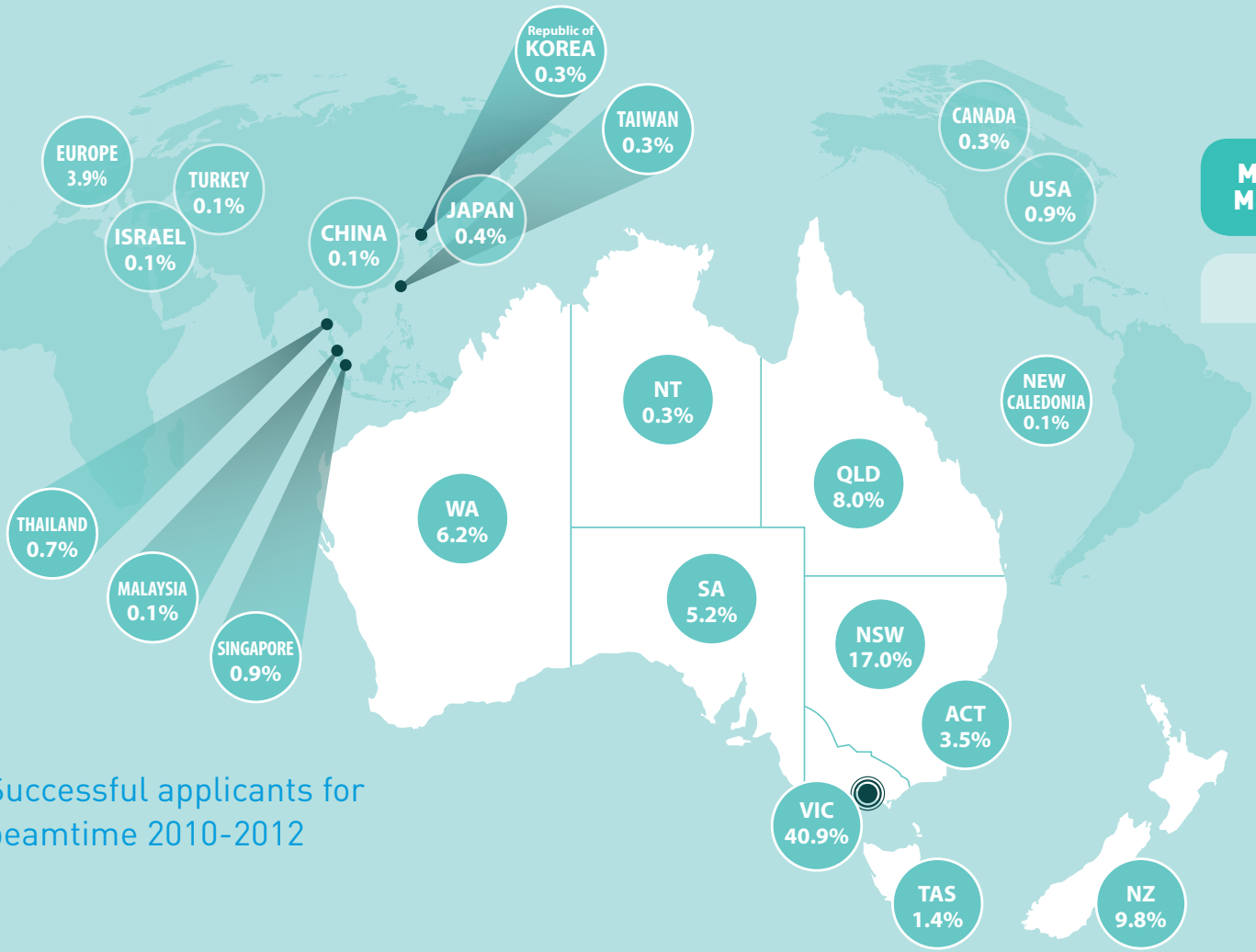
Mrs Amanda Kirby, Publications & Admin Support

Applying for beamtime

To apply to use the facility's beamlines, or receive funding to access overseas synchrotron facilities, users submit their proposals via the Australian Synchrotron's online proposal system. http://portal.synchrotron.org.au/

Our user community

The diverse Australian Synchrotron user community continues to expand, and currently encompasses more than 6000 individuals. It includes government, academic and industrial scientists from across Australia, New Zealand and the world. Many users are students and early-career researchers, indicating the Australian Synchrotron's important contribution to developing further the national and international synchrotron science communities.



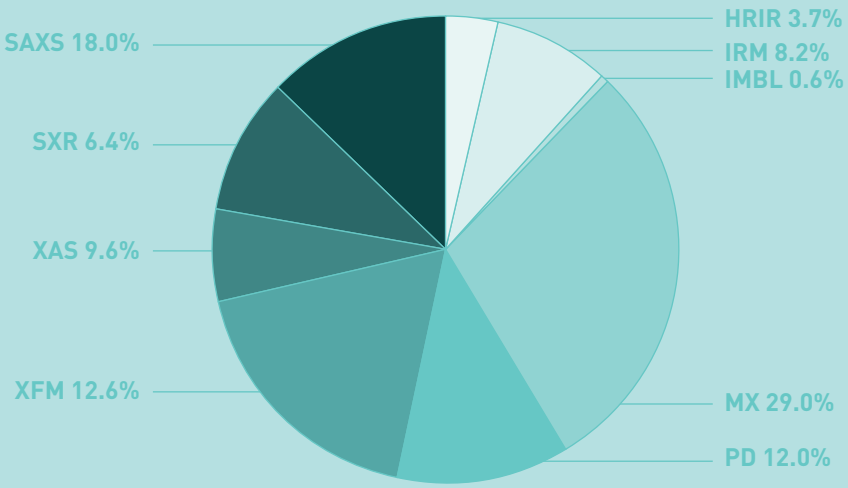
Successful applicants for beamtime 2010-2012

BREAKDOWN OF EUROPEAN USERS	
Belgium	0.2%
Croatia	0.2%
Demark	0.9%
France	0.5%
Great Britain	1.4%
Italy	0.4%
Poland	0.1%
Spain	0.1%
Switzerland	0.1%

REGISTERED USERS BY REGION	
Australia	1246
New Zealand	148
Europe	53
International	65

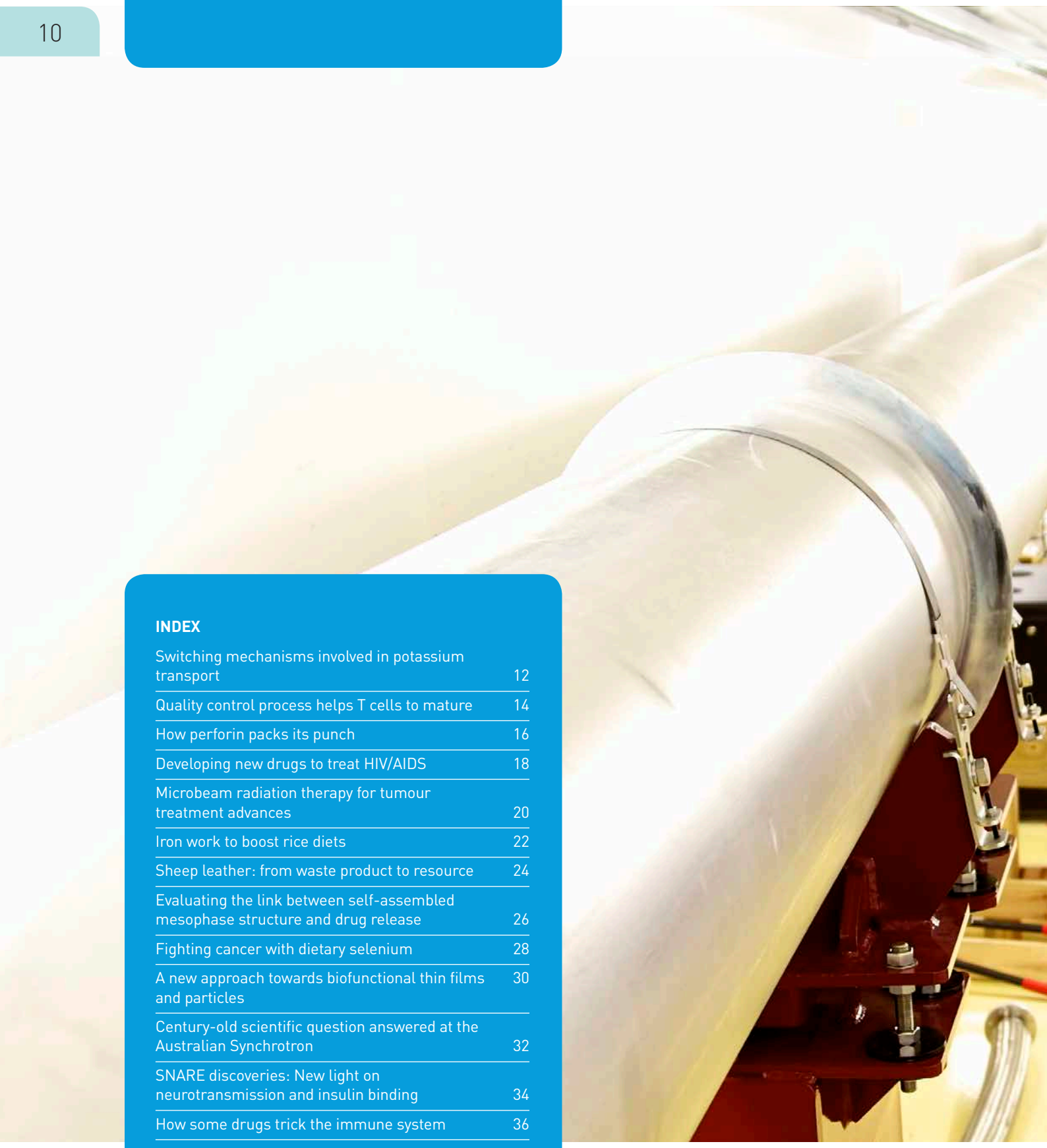
AUSTRALIA ACTUAL NUMBERS	
Australian Captial Territory	53
New South Wales	257
Northern Territory	4
Queensland	121
South Australia	79
Tasmania	20
Victoria	619
Western Australia	93

Beamtime proposals submitted by beamline 2010-2012



The imaging and medical beamline (IMBL) was only available to general users for one of the nine beamtime cycles in 2010-12.

Medical and life sciences



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Switching mechanisms involved in potassium transport

Australian researchers have made a significant discovery about the biological mechanisms controlling the electrical currents that underpin sensory perception and nervous system function in humans. They revealed new information about the mechanisms that control the flow of potassium ions across cell membranes.

Context

Electrical currents within the human body are a consequence of the coordinated interplay of different types of ion channels. Ions carry electrical charge, and the flow of potassium ions through channels in cell membranes can be precisely measured in the form of an electrical current.

Potassium currents are important in many cellular processes, particularly those involving communication between cells. They play an essential role in the electrical signalling underlying organ function, sensory perception and neurotransmission. In the heart, for example, contractions occur in response to the rhythmic ebb-and-flow of potassium. Specialised pores responsible for these currents, known as potassium channels, are highly selective for potassium over other ions.

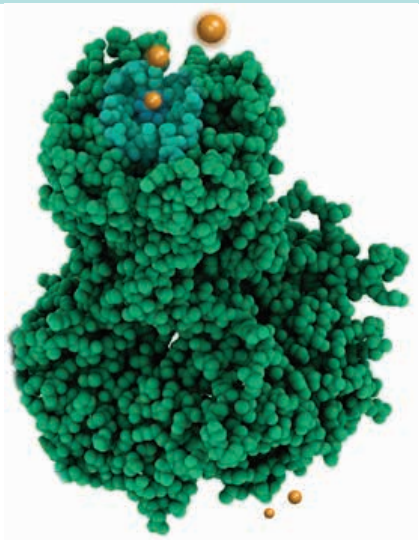
All potassium channels have a common pore structure with a signature region known as the ion selectivity filter. This filter selectively enables potassium to permeate the membrane, while blocking the passage of sodium.

Research question & Synchrotron technique

Medical researchers from Melbourne and Sydney used micro-crystallography (MX2) to obtain a new perspective on the molecular mechanisms that switch conduction off and on in response to regulatory signals, controlling the flow of potassium currents across cell membranes.

Publication

Oliver B. Clarke, Alessandro T. Caputo, Adam P. Hill, Jamie I. Vandenberg, Brian J. Smith, Jacqueline M. Gulbis, Domain Reorientation and Rotation of an Intracellular Assembly Regulate Conduction in Kir Potassium Channels, Cell, 141, 6, 1018-1029, (2010) 03 June 2010.



Potassium ions (orange) shown entering a Kir potassium channel. In living systems the upper lobe representing the pore would be embedded in a cell membrane, while the lower lobe is suspended within the cell. (Figure: Jacqui Gulbis)

Beamline
Micro-crystallography (MX2)

Technique:
Single crystal x-ray diffraction

Tweak:
We required microfocus x-rays both for the high intensity and so that we could test different regions of the crystal for optimal diffraction

Sample

Type:
Single crystals containing solubilised ion channels

Of note:
Some are crystallised in bicelles (bilayer long-chain/short-chain phospholipid aggregates used for crystallising membrane proteins in a lipidic environment)

Environment:
Low temperature

Synchrotron benefits
Our crystals typically diffract too poorly to be screened for diffraction in-house. They diffract well under the intense beam of MX2. Before it was built we required the intense focussed beamlines at SLS or EMBL. Although we were able to gain competitive time on those beamlines, the cost of travelling and shipping more than once per year proved prohibitive – which adversely affected our productivity. We need regular access to make progress. Using the Australian Synchrotron also enabled us to optimise stabilisation and cryoprotection protocols on the fly, which we couldn't easily do when shipping frozen crystals overseas.

Findings

The researchers showed that changes in remote regions of the channel assembly enable the selectivity filter to act as an on/off switch that is independent of other conformational changes in the protein, alternately curbing or permitting the flow of potassium ions. The research revealed a previously unsuspected role for the selectivity filter as an auxiliary gate, suggesting that dual interdependent gates work together to control K+ flux.

Different families of channels are distinguishable on the basis of domains that regulate their activity. The study revealed how a regulatory assembly specific to Kir potassium channels controls the direction of potassium flow. In the same manner as a one-way valve promotes unidirectional flow, polyamine block preferentially enables K+ ion flow into the cell. Comparison of multiple crystal structures revealed the mechanistic basis of inward current rectification - a two-stage process of polyamine binding and release.

Impact

Kir channels have many essential roles, such as in cardiac activity and the secretion of insulin from pancreatic beta cells. They play a major role in setting the resting potential of cells at or near the reversal potential of potassium. This underpins phenomena such as modulation of action potentials in the central nervous system. They were employed in the study as a model system for studying general principles of potassium channel gating.

Quality control process helps T cells to mature

Australian researchers made a breakthrough in the field of cellular immunity, revealing details of the 'quality control' process that immature T cells, a kind of white blood cell important in the body's immune system, must undergo before they can mature.

Context

T cells are a population of cells that play a key role in cell-mediated immunity. On the surface of each T cell is a T cell receptor (TCR) composed of two polypeptide chains that bind together when an antigen is present, leading to T cell activation and an immune response. Random recombination or shuffling within the TCR genes gives rise to variations in the receptor from T cell to T cell, that allow populations of T cells to recognise a wide range of pathogenic organisms.

While gene shuffling and variation are key features associated with TCRs, the process also inevitably gives rise to variations that are no longer able to perform the dimerisation and signalling functions of the TCR. For this reason T cells go through a quality checkpoint during their maturation. In this process, an invariant pre-T cell TCR chain binds to the variant T cell receptor chains in the absence of an antigen and in this context the binding and signalling allow the immature cells to become mature T cells.

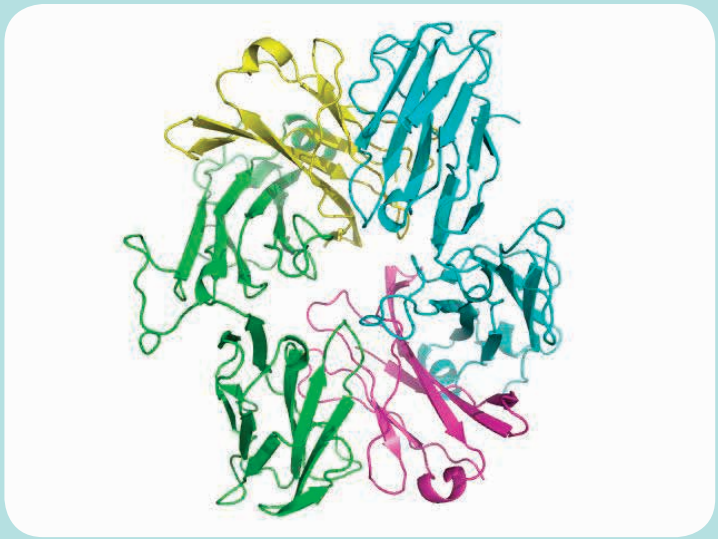
Research question & Synchrotron technique

Victorian and Queensland researchers used x-ray crystallography to determine the atomic resolution structure of a pre-T cell dimeric complex.

The structure reveals the molecular mechanism by which these proteins dimerise and how the pre-T cell chain 'samples' the variant chain to test for integrity.

Publication

Siew Siew Pang, Richard Berry, Zhenjun Chen, Lars Kjer-Nielsen, Matthew A. Perugini, Glenn F. King, Christina Wang, Sock Hui Chew, Nicole L. La Gruta, Neal K. Williams, Travis Beddoe, Tony Tiganis, Nathan P. Cowieson, Dale I. Godfrey, Anthony W. Purcell, Matthew C. J. Wilce, James McCluskey and Jamie Rossjohn, The structural basis for autonomous dimerization of the pre-T-cell antigen receptor, Nature 467 (7317), 844-8 (14 October 2010).



Dimerization is mediated mainly between the pre-Tα and the unpaired Vβ domains.

Findings

The mode of dimerisation seen in the crystal structure was validated in solution by small angle x-ray scattering (SAXS) experiments.

The researchers commented that the dimerisation process represented a unique mechanism in nature in which developmental quality control regulated the expression and signalling of an integral membrane receptor complex.

Impact

By working out the structure and function of a protein called pre-T alpha the researchers showed that the pre-T alpha molecule not only assists in the expression of functional T cell receptors, but it also allows two molecules to bind together, which alerts the T cell that this receptor is constructed properly. This allows the T cell to move to the next step in its development. Additionally, there is some evidence that pre-T alpha may also be involved in some childhood leukaemias, so this new knowledge of how it functions may be important in diagnosis and treatment of acute lymphoblastic leukaemia.

How perforin packs its punch

An international research collaboration has revealed how a protein called perforin, punches holes in cancer cells and cells hijacked by viruses, enabling toxic enzymes to enter and destroy the rogue cells.

Context

Inside our bodies, the critically important work of killing virus-infected and neoplastic cells (cells showing abnormal growth or division) is carried out by natural killer (NK) cells and cytotoxic T lymphocytes. The NK cells and T lymphocytes do their job by releasing the pore-forming protein perforin and granzyme proteases (enzymes that break down other proteins) into the cleft formed when a killer cell docks alongside a target cell.

Dubbed the 'assassin protein', perforin is a key part of the body's defence mechanisms. If perforin isn't working properly, the body cannot fight infected cells. Defective perforin activity can also cause problems, such as when the wrong cells are marked for elimination, notably in autoimmune disease conditions such as early onset diabetes, or in tissue rejection following bone marrow transplantation.

Perforin is a thin, key-shaped molecule that works by joining forces with other perforin molecules to penetrate cell membranes and form pores in the cell surface that allow granzyme proteases to enter the target cells.

Research question & Synchrotron technique

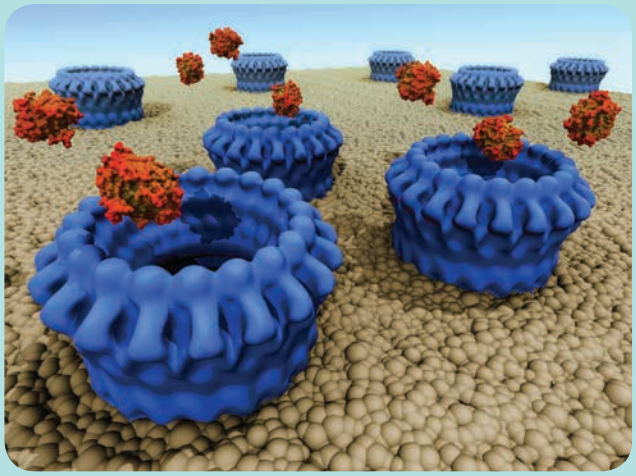
The 10-year perforin study drew on structural information from the Australian Synchrotron's macro-crystallography (MX1) beamline and high-powered electron microscopy images from the United Kingdom.

Crystallisation of perforin has been pursued for a number of years by a number of groups. There were two main hurdles:

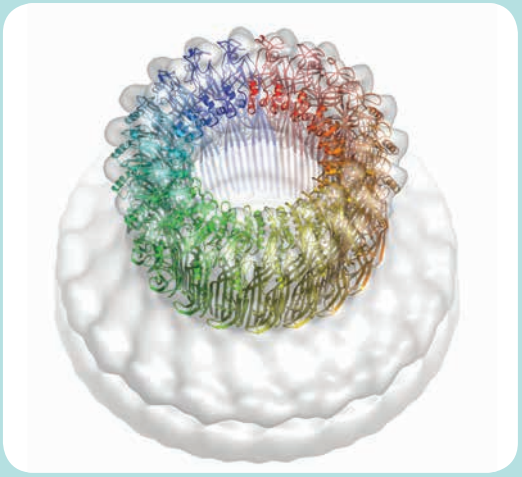
1. Expression of recombinant perforin was technical and the yield was poor. Researchers have refined the expression strategies and are now able to produce recombinant perforin successfully.
2. At high concentrations, purified proteins aggregate uncontrollably. To overcome this issue, a polymerisation deficient mutant was used. This mutant carries a surface charged residue arginine mutated to glutamate and has a slower polymerisation rate. As a result, it forms polymers on the surface of the cell a lot slow than the wild-type and has a slower tendency to polymerise in solution.

Publication

Ruby H. P. Law, Natalya Lukoyanova, Ilia Voskoboinik, Tom T. Caradoc-Davies, Katherine Baran, Michelle A. Dunstone, Michael E. D'Angelo, Elena V. Orlova, Fasséli Coulibaly, Sandra Verschoor, Kylie A. Browne, Annette Ciccone, Michael J. Kuiper, Phillip I. Bird, Joseph A. Trapani, Helen R. Saibil and James C. Whisstock, The structural basis for membrane binding and pore formation by lymphocyte perforin, Nature 468, 447–451 (18 November 2010) doi:10.1038/nature09518.



Perforin molecules (blue) create pores in a cell membrane, allowing granzyme toxins to enter and destroy the cell. Image: Mike Kuiper, VPAC



Perforin molecules (rainbow) create pores in a cell membrane, allowing granzyme toxins to enter and destroy the cell. Image: Mike Kuiper, VPAC

Beamline
Macro-mollecular crystallography (MX1)

Technique:
Single crystal x-ray diffraction

Sample
Perforin - a protein molecule which is recombinantly expressed in insect cells

Environment:
Low temperature

Tweak:
In order to collect high-resolution data, we used very high radiation energy. As this can lead to intense radiation damage, we used more than 80 crystals to collect sufficient data. We ran repeated experiments with the 'attenuation' setting, used the 'collimator' and made use of the many useful tools developed by the beamline's software developers, to find right balance between resolution and completeness of data, required when working with such difficult samples.

Synchrotron benefits:
Both synchrotron radiation and the staff of the Australian Synchrotron facility are indispensible for this work. Without them, our work would have been much more difficult – expensive and time-consuming – as experiments would have to be performed overseas at APS (USA) or SLS (Switzerland). Staff from the MX beamline have been actively involved in this project: in the development of strategies, data collection and structural analysis. Our collaboration with Australian Synchrotron staff has been a very productive operation.

Findings

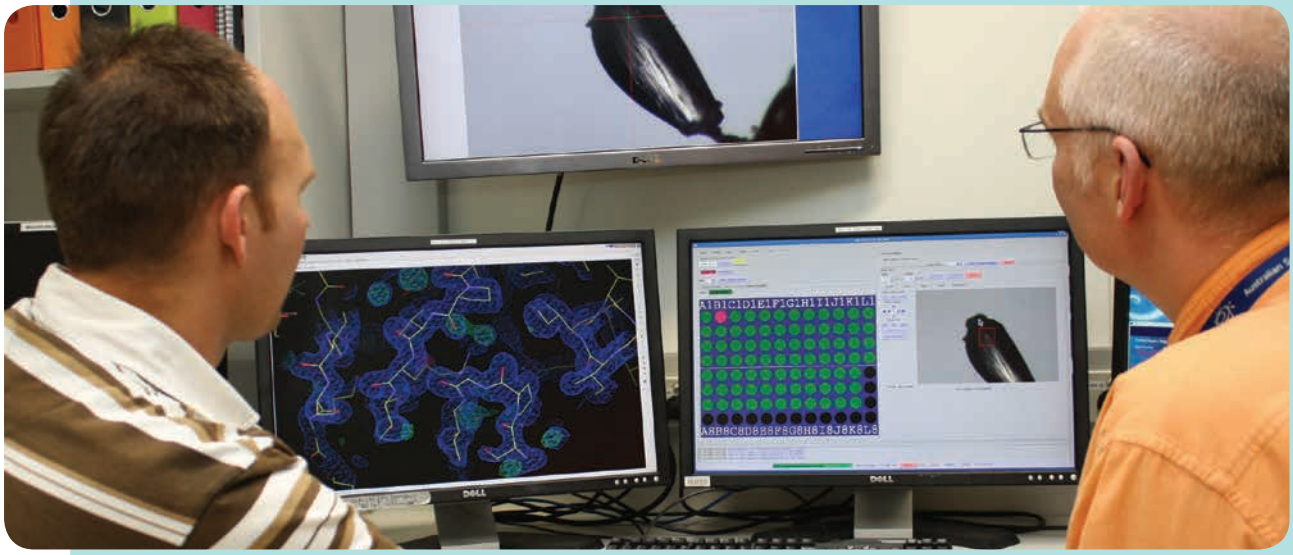
The research showed that the important parts of the perforin molecule are quite similar to those in toxins deployed by bacteria such as anthrax, listeria and streptococcus, demonstrating their common ancestry.

An unexpected finding was that the perforin docks with the rogue cell surface in the opposite orientation to its bacterial counterparts, suggesting that the two groups of proteins must have undergone some extraordinary structural adaptations.

Impact

Perforin was the first x-ray crystal structure published on the mammalian membrane attack complex and perforin like protein (MACPF) family. These data reveal that although the overall structure of mammalian MACPF protein and bacterial cytolysin are very similar, the mechanisms of pore formation can be quite different. These results, provide new insights into how related immune defence molecules such as complement proteins assemble into pores.

Developing new drugs to treat HIV/AIDS



Designing drugs that could help over 30 million people living with HIV is an ongoing battle made worse by the virus' ability to develop resistance to existing drugs. Melbourne researchers have used x-ray crystallography to help identify potential new drugs.

Context

Infection with human immunodeficiency virus (HIV) leads to acquired immunodeficiency syndrome (AIDS). Although the death rate has been reduced, AIDS still accounts for about 1.8 million deaths a year. Existing treatments reduce viral loads and slow the progression of AIDS but don't eradicate the virus or prevent the spread of infection. Many patients are also being compromised by the emergence of drug-resistant HIV strains. New drugs are desperately needed.

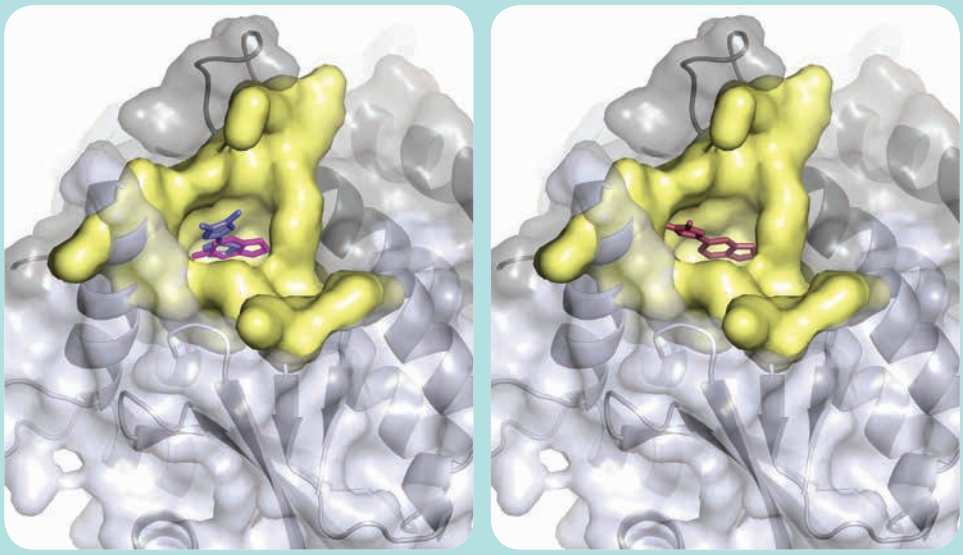
Drugs that block the action of a HIV protein called integrase and prevent the insertion of the viral DNA genome into the host DNA will stop the virus replicating and halt the progression to AIDS.

Research question & Synchrotron technique

A group of Melbourne-based researchers have used a technique called fragment-based drug discovery to identify small chemical compounds that bind to HIV integrase. They grow tiny crystals of these compound-protein complexes, which are smaller than a grain of sand. The crystals are then frozen in liquid nitrogen (-190˚C) and exposed to powerful x-rays generated at the Australian Synchrotron. The data collected are used to build three-dimensional models of the compound-protein complexes at atomic resolution (see over page). Using the models they can study the interactions between the compound and the protein and design more effective drugs against HIV. Chemists then synthesise new compounds guided by the models so that they can be tested in assays to measure their anti-HIV potency and put back into crystallography for further refinement.

Publication

Jerome Wielens, Stephen J. Headey, John J. Deadman, David I. Rhodes, Giang T Le, Michael W. Parker, David K. Chalmers, Martin J. Scanlon, Fragment-based design of ligands targeting a novel site on the integrase enzyme of human immunodeficiency virus 1, ChemMedChem., 2011 Feb 7;6(2):258-61. doi: 10.1002/cmdc.201000483. Epub 2010 Dec 16.



Examples of fragments bound in a pocket on HIV-1 integrase. (A) A superimposition of two crystal structures of fragments (purple and magenta sticks) bound to HIV-1 integrase. Chemists used features from the two overlapping fragments to design a new compound (brown sticks) (B) which is shown on the right. This new compound had a greater binding affinity for integrase compared to the two initial fragments.

Beamline
Macro-mollecular crystallography (MX1)

Technique:
Single crystal x-ray diffraction

Tweak:
We had a lot of samples to test. To improve efficiency at the beamline, our samples were mounted in a cassette and loaded into the x-ray beam using a robot. Our cassettes held 96 samples and we could store up to three cassettes in the liquid nitrogen bath.

Sample

Type:
Crystals of the integrase core domain were individually soaked with small compounds before being frozen and exposed to x-rays.

Of note:
Protein crystals typically contain about 50 per cent water, and compounds soaked into preformed crystals can reach the binding site by flowing through solvent channels. Soaking is more straightforward than co-crystallisation (forming a protein-ligand complex first and then crystallising) but it assumes that the binding site on the protein is accessible in the crystal.

Environment:
Low temperature

Tweak:
We grew crystals of the integrase core domain that were very small: ~ 200 x 100 x 50 µm. For this project several hundred crystals were tested with various compounds.

Findings

Wielens and co-workers first identified a series of fragment compounds that bind to integrase using Nuclear Magnetic Resonance (NMR) spectroscopy. With the help of x-ray diffraction data collected from the Australian Synchrotron they have been able to visualise where they bind on HIV integrase and improve the potency of these compounds and progress their development to new anti-HIV drugs.

Impact

As well as providing a useful basis for designing more potent compounds, the Synchrotron data enabled the researchers to identify a previously unknown binding pocket on integrase that has the potential to be a valuable drug target.

Synchrotron benefits
Before the Australian Synchrotron, we travelled overseas several times per year to Chicago or Japan to use their synchrotrons. Protein crystals are fragile and shipped frozen at -190˚C; we had to trust airlines, couriers and customs to deliver our precious samples safely and efficiently. With local access we can test samples more easily and more often. Synchrotron x-rays are more intense and focussed than those generated in house, so datasets are collected in minutes rather than hours and we can process our results quicker and fast-track the drug development process.

Microbeam radiation therapy for tumour treatment advances

Microbeam radiation therapy (MRT) is a promising experimental radiotherapy technique that uses finely divided synchrotron x-rays to destroy tumours without seriously affecting normal tissue. Infrared analysis provides evidence for a mechanism by which MRT kills the whole tumour despite only a small percentage receiving peak irradiation.

Context

Around half of all cancer patients receive radiotherapy. However, the radiation dose delivered to a tumour can't exceed the dose that can be tolerated by normal tissues surrounding the tumour.

MRT challenges pre-conceived ideas about radiotherapy for two main reasons. Firstly, normal tissue seems to tolerate peak MRT doses 100 times greater than the doses used in conventional radiotherapy. Secondly, entire tumours may be destroyed under MRT even though only one-tenth of their volume has been irradiated at peak doses.

Jeff Crosbie and his colleagues have been developing and assessing MRT for several years, using x-ray imaging at synchrotron facilities in France (ESRF) and Japan (SPring-8) and increasingly now at the Australian Synchrotron.

Research question & Synchrotron technique

The researchers are investigating how MRT 'works' on a cellular and molecular level – and how it compares with conventional radiotherapy in terms of controlling tumour growth and minimising damage to normal, healthy tissue.

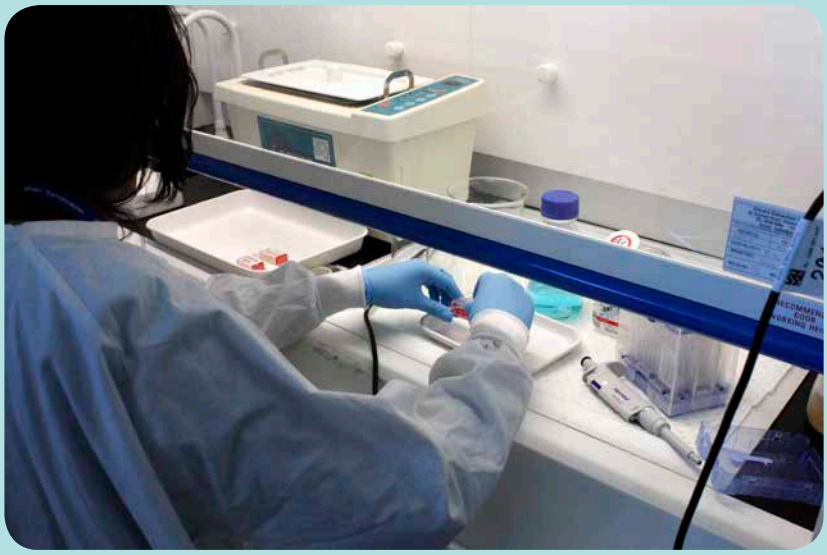
To complement their x-ray imaging studies, Crosbie and his colleagues recently used Fourier-transform infrared microspectroscopy at the Australian Synchrotron to investigate biochemical changes in rodent tumour tissue following MRT and broad beam radiation.

Findings

The MRT and broad-band irradiated tumour sections showed clear chemical shifts corresponding to differences in functional group vibrations in proteins, lipids and nucleic acids. The MRT peak and valley regions showed chemical shifts in the nucleic acid region but virtually identical absorbance patterns for proteins and lipids.

Impact

The researchers concluded that the lack of difference between MRT peak and valley irradiated areas suggested a holistic tissue response to MRT occurring within four hours. This might be the first evidence for a mechanism by which MRT kills the whole tumour despite only a small percentage receiving peak irradiation.



Left: Jeff Crosbie from The University of Melbourne places a tumour sample on the IMBL beamline for x-ray irradiation.

Right: Monica Sharma, a 2011 honours student at The University of Melbourne, processes an irradiated tumour sample.

Jeff and his colleagues previously examined the impact of different microbeam widths and separations, using a controlled cell culture system and monoenergetic (5.35 keV) synchrotron x-rays to gain further insight into the underlying cellular response to MRT [Sprung et al. 2011]. They demonstrated proof of concept for a modified reference image topography optical calorimetry method that measures the peak-to-valley dose ratio for synchrotron MRT [Ackerly et al. 2011].

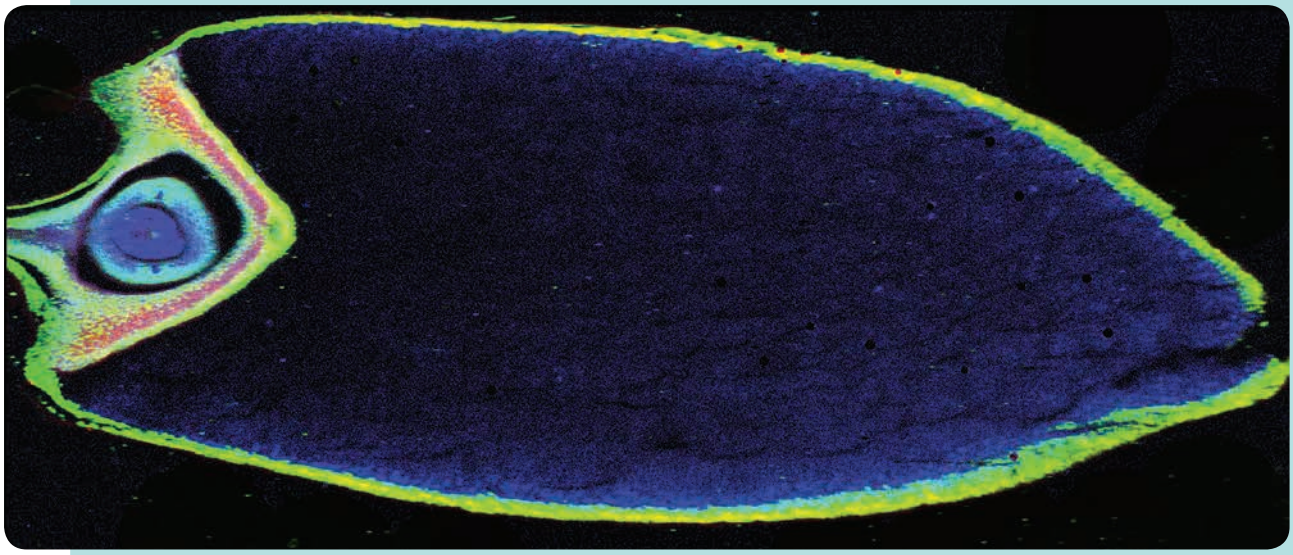
Publications

Monica Sharma, Jeffrey C Crosbie, Ljiljana Puskar, Peter A W Rogers, Microbeam-irradiated tumour tissue possesses a different infrared absorbance profile compared to broad beam and sham-irradiated tissue, Int J Radiat Biol. 2013 Feb;89(2):79-87. doi: 10.3109/09553002.2012.721052. Epub 2012 Sep 10. http://lib.bioinfo.pl/paper:22892032

Beamline: IRM
Carl N. Sprung, Marian Cholewa, Noriko Usami, Katsumi Kobayashi and Jeffrey C. Crosbie, DNA damage and repair kinetics after microbeam radiation therapy emulation in living cells using monoenergetic synchrotron x-ray microbeams, J. Synchrotron Radiat., 18, 630-636 (2011) Received 5 August 2010, Accepted
30 March 2011; Vol 18 part 4, July 2011

External facility (AS funded trip)
carl.sprung@monash.edu T. Ackerly, J.C. Crosbie, A. Fouras, G.J.Sheard, Simon Higgins and Robert A. Lewis, High resolution optical calorimetry for synchrotron microbeam radiation therapy, J. Inst., 6, P03003-1 to P03003-11 (2011) External facility (not AS funded) plus Imaging and Medical. jcrosbie@unimelb.edu.au

Iron work to boost rice diets



A new iron-enriched rice variety developed by Melbourne and Adelaide researchers could help solve iron deficiency problems that currently affect more than two billion people. According to the World Health Organisation, iron is the world's most common nutritional deficiency.

Context

Despite being a major food source for billions of people in developing countries, particularly in Asia, polished or white rice does not contain enough iron, zinc or pro-vitamin A to meet daily nutritional requirements. In fact, rice has the lowest iron content of the cultivated cereal crops. These vital nutrients are more prevalent in the outside husk of rice, which is lost in the milling process designed to cater to the taste of consumers, prolong shelf life and reduce cooking times.

Research question & Synchrotron technique

Rice doesn't exhibit a lot of genetic variation for iron accumulation in the grain, which has hindered conventional breeding programs trying to increase iron levels in rice.

Researchers from Melbourne and Adelaide resolved this issue by developing a new iron-enriched rice using gene technology to increase the amount of iron transported into the endosperm – the central part of the rice grain that most people eat. The mineral-enriched rice has an additional copy of a rice gene involved in the biosynthesis of nicotianamine, a molecule involved in transporting metal cations throughout the rice plant.

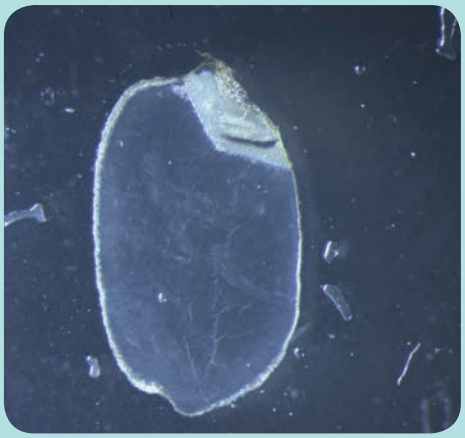
The researchers used x-ray fluorescence microscopy (XFM) techniques to map the distribution of iron, zinc and other minerals in the enriched rice grain and compare that to standard rice.

Publication

Alexander A. T. Johnson, Bianca Kyriacou, Damien L. Callahan, Lorraine Carruthers, James Stangoulis, Enzo Lombi, Mark Tester, Constitutive Overexpression of the OsNAS Gene Family Reveals Single-Gene Strategies for Effective Iron- and Zinc-Biofortification of Rice Endosperm, PLoS ONE 6(9): e24476. doi:10.1371/journal.pone.0024476 [6 September 2011].

(L-R) Alex Johnson, Enzo Lombi and Bianca Kyriacou.

Opposite: XFM image of potassium, iron and copper distribution in a rice grain. Image: Alex Johnson (University of Melbourne) and Enzo Lombi (University of South Australia)



Longitudinal sections of rice grain (70 microns thick) were cut using a vibrating blade microtome and placed onto Kapton tape for XFM analysis.

Beamline
X-ray fluorescence microscopy (XFM)

Technique:
Spectroscopic mapping

Sample

Type:
Rice grains. We were investigating the spatial distribution of elements, particularly those relevant to human nutrition, within rice grain.

Of note:
Our investigation focused on 'biofortified' rice grain with four-fold more iron and two-fold more zinc relative to commercial rice varieties.

Environment:
Open to air

Tweak:
Grains were glued to a plastic support and then sliced using a vibrating blade microtome in order to obtain a flat surface (Leica VT1000 S). A piece of Kapton polyimide film was then pressed on the surface of the sample with the blade of the microtome cutting underneath. In this way, longitudinal sections, 70 µm thick, were placed directly onto Kapton tape without the need for embedding.

Synchrotron benefits
Synchrotron x-ray fluorescence spectroscopy allowed us to finely map the distribution of iron and zinc in rice grain at elemental concentrations that are far too low to be detected by traditional histochemical stains such as Perl's Prussian Blue (PPB) and Dithizone (DTZ). Furthermore, the ability to overlap the distribution profiles of iron and zinc with those of elements that often bind to these metals, such as phosphorus, yielded important clues about the bioavailability of these metals within the grain.

Findings

The XFM beamline provided detailed maps of elemental distribution of the mineral-enriched rice, revealing that it had significantly more iron and zinc in the subaleurone and endosperm tissues, relative to wild-type rice, than remain in the milled grain. Relatively low phosphorus levels in iron-rich areas of the endosperm suggest that the additional iron is also likely to be available in human diets.

Impact

The newly-developed iron-enriched rich rice variety is the world's first 'biofortified' rice plant to exhibit such high levels of grain iron and zinc in a greenhouse environment, with the milled grain containing up to four times the iron and twice the zinc concentration of standard rice.

Sheep leather: from waste product to resource

Australia may once have ridden on the sheep's back, but it was a New Zealand researcher who discovered the secret of making sheep leather as strong as cowhide, and a new resource for the footwear industry.

Context

Sheep skin leather is only half as strong as cow hide leather, lowering its value and making it unsuitable for footwear. Until work with the Australian Synchrotron, the structure and arrangement of fibrous collagen in leather and the relationship between collagen structure and leather strength were poorly understood.

Research question & Synchrotron technique

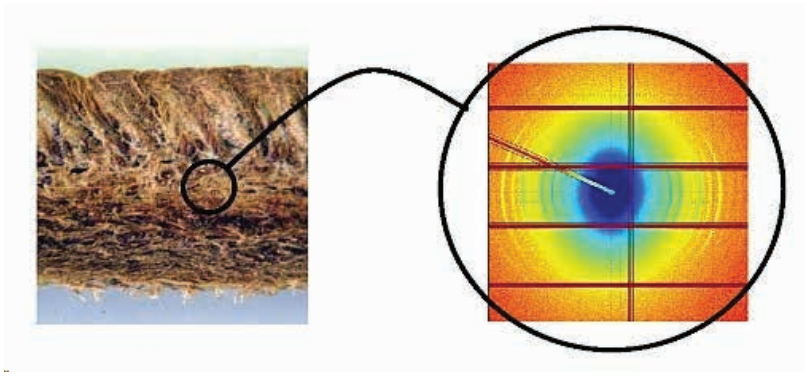
Richard Haverkamp from Massey University in New Zealand used the Australian Synchrotron to investigate the nanoscale basis for the difference in strength between cow and sheep leather and relate this to how easily the leather can tear. He used small angle x-ray scattering (SAXS), a technique that can reveal the three-dimensional shape of proteins – such as the cross-linked collagen fibres that make up the bulk of leather and determine its physical properties. Techniques on the SAXS beamline provided quantitative information on the amount of fibrous collagen, the orientation (direction and spread) of the collagen microfibrils, and the spacing between collagen layers in areas where the collagen are arranged in a more regular structure.

Findings

The work provided a clear understanding of a nanostructural characteristic of sheep skin and cow hide leather that leads to differences in their respective strengths. Stronger leather has the collagen fibrils arranged mostly parallel to the plane of the leather surface, while weaker leather has more fibrils that are less parallel.

Publication

Melissa M. Basil-Jones, Richard L. Edmonds, Sue M. Cooper, Richard G. Haverkamp, Collagen fibril orientation in ovine and bovine leather affects strength: a small angle x-ray scattering (SAXS) study, J Agric Food Chem. 2011 Sep 28;59(18):9972-9. Epub 2011 Sep 2. (2011).



(L-R) Optical image of sheep leather in cross-section (approx. 2.2 mm thick), with SAXS diffraction pattern from grain-corium boundary region.

Beamline
Small and wide angle x-ray scattering (SAXS/WAXS)

Technique:
Small angle x-ray scattering (SAXS)

Sample

Type:
Leather, which is a solid fibrous protein material consisting of collagen with other proteins and containing fat.

Of note:
The solid material is anisotropic therefore taking full advantage of the 2D detector. Collagen is a hierarchical material and there are several levels of structure we are interested in learning about using SAXS. The very good signal to noise obtained from the SAXS beamline with a huge dynamic range enables these different levels of structure to be investigated with a single diffraction pattern.

Environment:
Open to air

Tweak:
We designed, built and used a device to apply stress to our samples during diffraction pattern collection so that we could learn about the response of the structure to stress. For some samples we protected the samples from drying by sealing it kapton.

Synchrotron benefits
Without the equipment at the synchrotron, expertise and assistance of the beam line staff, and the stimulating environment that alerted me to the possibilities of applying this technique, these research outcomes would have not happened.

Impact

Richard and his colleagues used their findings to develop a processing strategy for making stronger sheep leather.

If this process were used to convert just half of Australia's annual lamb-skin production to leather suitable for footwear, it could potentially add $118 million a year to the value of Australian sheep products. A similar calculation applied to the New Zealand case puts the potential value for the NZ sheep industry at NZ$159 million a year.

Richard says New Zealand's preferred access to the Australian Synchrotron – as one of the facility's foundation investor groups – is what made the discovery possible. Using conventional laboratory equipment costs hundreds of thousands of dollars and still would not have given the high-resolution details needed for this discovery.

The beamline produces outstanding results – adequate diffraction patterns on microscopic areas could not have been achieved on a laboratory source.

However, of at least or greater importance has been the expertise available and the stimulating environment. This includes the beamline scientists who assisted and encouraged the work. It also includes the other scientists working at the facility and the interaction with this scientific community while at the synchrotron (on beamlines other than the one you are currently working on mostly) and at meetings arranged by the synchrotron (the User Meeting and various committees).

Evaluating the link between self-assembled mesophase structure and drug release

Researchers are exploiting advanced nanostructured self-assembly materials to encapsulate bioactive molecules – including proteins, peptides and drug molecules – for applications such as drug delivery and crystallisation of membrane proteins.

Context

The unique structure of nanostructured lipidic materials makes them ideal for encapsulating both water-soluble and hydrophobic drugs. Researchers have investigated the use of nanoparticles of these materials, called cubosomes, for drug delivery. Cubosomes offer numerous advantages over the better-known liposome particles for nanomedicine, including increased drug loading, a partially controllable release rate, and the potential for targeting the drug to the disease site, moderating adverse side-effects.

Research question & Synchrotron technique

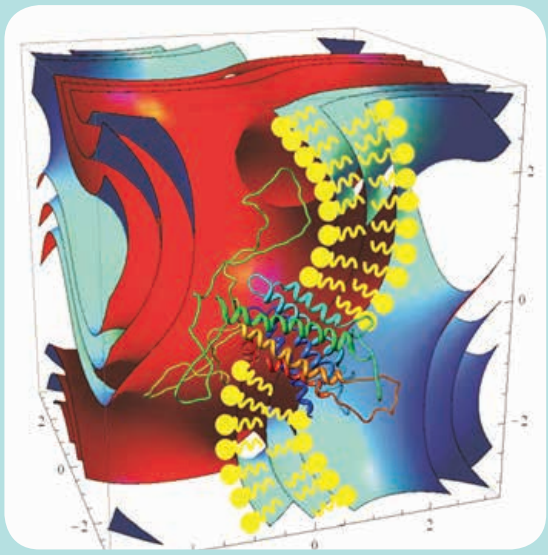
Researchers investigated how the cubosome structure changes when a drug is loaded inside the cubosome.

To cope with the extremely large number of samples and conditions that must be investigated, researchers developed a high-throughput set-up that can analyse the structure of thousands of samples in a 24-hour shift at the Australian Synchrotron's small angle x-ray scattering (SAXS) beamline. The high-throughput set-up and analysis of the resulting extremely large data sets was done in collaboration with the beamline's scientific staff.

Publication

Xavier Mulet, Danielle F. Kennedy, Charlotte E. Conn, Adrian Hawley, Calum. J. Drummond, High throughput preparation and characterisation of amphiphilic nanostructured nanoparticulate drug delivery vehicles. International Journal of Pharmaceutics 395, 290-297 (2010).

Charlotte E. Conn, Connie Darmanin, Xavier Mulet, Adrian Hawley, Calum. J. Drummond, Effect of lipid architecture on cubic phase susceptibility to crystallisation screens, Soft Matter 8 (26), 6884 – 6896 (2012)



An integral membrane protein and important drug target, the dopamine D2 receptor, is shown encapsulated within a cubic lipidic material.

Opposite: Stephen Mudie (Australian Synchrotron) checks a high-throughput sample holder on the SAXS beamline, which can analyse thousands of solution phase samples in a 24-hour shift.

Findings

The research team were able to identify how the nanostructure of the cubic phase changed on addition of a wide range of commercially available drugs, from pain-killers to chemotherapeutics.

They used similar high-throughput techniques to determine the structure of membrane proteins, which are the target of more than half of all commercially available drugs. These biomimetic materials offer a unique stabilising environment for fragile membrane proteins, facilitating the crystal growth process. However, not a lot is understood about how crystallisation occurs, and the structures of many important drug targets remain unsolved. This is reflected in the non-specific nature of many commercially available drugs, and the adverse side-effects associated with them. Using the SAXS and macro-molecular crystallography (MX1) beamlines, the researchers investigated the effect of a large number of variable crystallisation parameters on crystal growth, allowing the design of more effective crystallisation trials.

Impact

The use of lipidic materials for nanobiotechnology applications remains at a relatively early stage of development. However, the enormous human and commercial rewards from improved drug design and delivery, combined with high-throughput research studies that allow researchers to design and control the nanostructure of the material for particular applications, should ensure continued rapid growth in this area.

Fighting cancer with dietary selenium

A South Australian-led international research team revealed important details about how a particular form of selenium impacts human lung cancer cells. Selenium is a naturally occurring element – toxic in high levels, but vital in smaller amounts for fundamental cellular function.

Context

A deficiency of selenium in your diet means you're more likely to suffer some forms of cancer. If there's too much, you may suffer a range of other adverse effects. Even the chemical form of selenium influences its impact on the body.

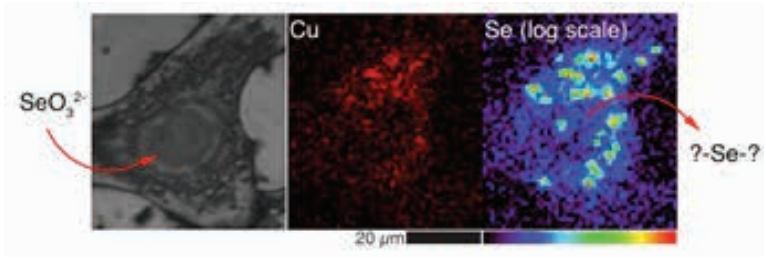
This study is part of a broad, long-term investigation of selenium metabolism, storage, accumulation and general biology, and how it interacts with other metals such as copper in the body. It is examining how the chemical form of selenium changes over time in human lung cancer cells, to assist the development of better ways to use selenium to treat human cancers while reducing the risk of adverse health effects.

Research question & Synchrotron technique

Researchers used micro x-ray absorption near edge structure (micro-XANES), x-ray fluorescence microscopy (XFM) and x-ray absorption spectroscopy (XAS) techniques to identify the chemical forms of selenium in lung cancer cells and where in the cells they were located.

Publication

Claire M. Weekley, Jade B. Aitken, Stefan Vogt, Lydia A. Finney, David J. Paterson, Martin D. de Jonge, Daryl L. Howard, Paul K. Witting, Ian F. Musgrave, and Hugh H. Harris, Metabolism of selenite in human lung cancer cells: x-ray absorption and fluorescence studies, J. Am. Chem. Soc., 133 (45), 18272–18279 (2011).



XRF elemental maps of human cancer cells treated with selenite show that selenium and copper are stored together in small compartments. Images: Hugh Harris, University of Adelaide.

Beamline
X-ray fluorescence microscopy (XFM)

Technique:
Microscopy – Mapping (Spectroscopy)

Sample

Type:
Human lung cancer cells treated with selenium compounds. Bulk cell pellets (~10^6 cells) were collected and freeze-dried for XAS. Cells were grown on silicon nitride windows, then fixed with methanol for XFM studies.

The XAS studies were conducted at the Stanford Synchrotron Radiation Laboratory (SSRL), but we can now conduct the same studies at the Australian Synchrotron.

Environment:
Low temperature

Synchrotron benefits
The assistance of the beamline staff in setting up the beamline to collect the best possible data was essential. Discussion of developments at the beamline and how they can be applied to our research are invaluable. Using the Australian Synchrotron saves us a significant amount of time and money on trips that would otherwise be made to international synchrotrons.

Findings

Using the Australian Synchrotron, the researchers found that when selenium enters human lung cancer cells in inorganic selenite form, the selenite is quickly taken up by cancer cells but then takes a day or more to start killing them.

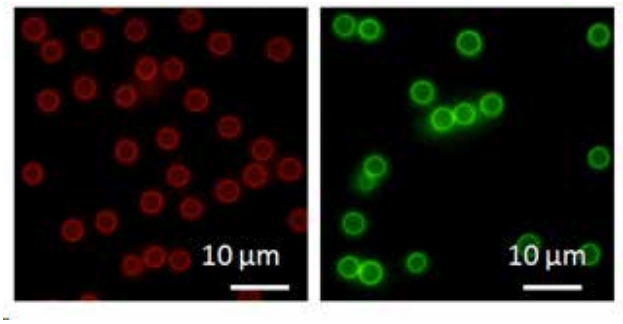
During the first 24-48 hours, the inorganic selenite is transformed through several intermediate forms into a different chemical form of selenium (selenocystine) that indicates oxidative stress in the cancer cells. Oxidative stress is a major area of research into a number of diseases.

The synchrotron results also showed that lung cancer cells store selenium in specific areas that contain raised copper levels, which may indicate a link between the effects of dietary selenium and copper.

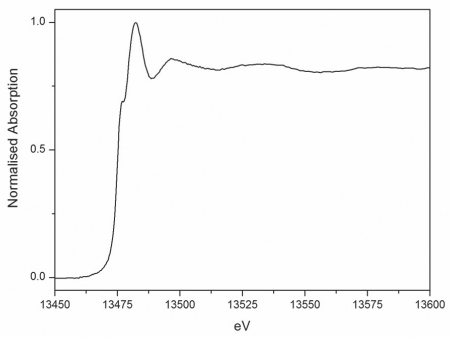
Impact

The findings have led to further investigations of the mechanisms by which selenite kills cancer cells and the intriguing relationship between selenium and copper. The researchers are now investigating the form and location of selenium in rat tissues using the same techniques

A new approach towards biofunctional thin films and particles



Fluorescence microscopy images of microcapsules made of a protein (human serum albumin (HSA) in red fluorescence) and of a polysaccharide (dextran in green fluorescence) made via the new approach developed by Mertz et al.



X-ray absorption spectrum of a frozen suspension of HSA replica biopolymer particles.

Biofunctional polymer thin films and particles have great potential in nanomedicine applications. However, their design and fabrication continues to encounter important challenges, mainly resulting from complicated processing parameters. Therefore, researchers have investigated a novel method to create versatile and stable biopolymer nanostructures through a highly simplified procedure.

Context

Nanoscale biofunctional thin films (ca. 10-50 nm thickness) usually consist of polymeric assemblies, and can be used as coatings for biomaterials or as self-supported capsules capable of delivering therapeutics or acting as imaging agents. They are attractive candidates for a range of applications, including targeted drug delivery to cancer cells and enhancing the contrast of lesions in tissue. However, methods for generating such nanostructures composed of biological macromolecules are limited, and an important challenge in this field is the formation of tunable, self-supported assemblies through simplified procedures.

Researchers from The University of Melbourne have pioneered an approach based upon the properties of bromo-isobutyramide (BrIBAM) and isobutyramide (IBAM) grafts to assemble stable non-covalent films and particles composed of biopolymers (for example proteins, oligonucleotides or polysaccharides) without the need of additional covalent cross-linking. BrIBAM-functionalised silica templates were initially used to facilitate the formation of biofunctional thin films from these biopolymers.

Following removal of the silica template, non-covalent free-standing biopolymeric assemblies (for example, hollow capsules or replicated spheres and fibres) can be obtained.

Research question & Synchrotron technique

Researchers used extended x-ray absorption fine structure (EXAFS) spectroscopy at the Australian Synchrotron with the aim of elucidating the driving force behind the non-covalent biopolymer assembly, and in particular the role of the grafted-BrIBAM bromine atoms. Previous studies have demonstrated that non-covalent intermolecular 'halogen bonding' can be a powerful interaction and it was the aim of EXAFS experiment to analyse the bromine environment in the biopolymer assemblies to identify the occurrence of such non-covalent bonding.

Halogen bonding is traditionally studied using x-ray crystallography of crystallized protein-molecule complexes. For the biopolymer assemblies in frozen matrices, EXAFS spectroscopy was used as a powerful alternative approach to extend halogen bond detection to polymers and soft matter.

Publication

Damien Mertz, Pramudana Tan, Yajun Wang, Tor Kit Goh, Anton Blencowe, Frank Caruso, Bromoisobutyramide as an Intermolecular Surface Binder for the Preparation of Free-standing Biopolymer Assemblies, Adv. Mater., 23, 5668-5673, (2011).

Damien Mertz, The University of Melbourne

Beamline
X-ray absorption spectroscopy

Technique:
Soft and hard x-ray spectroscopy; extended x-ray absorption fine structure (EXAFS) spectroscopy measurements

Tweak:
The Br K-edge was measured in fluorescence mode with a 100-element solid-state Ge detector at 90° to the incident beam. Energy was scanned using a Si 311 double crystal monochromator. The sample was moved in-between scans, in order to minimise radiation damage. Spectral averaging, background subtraction and analysis were carried out.

Sample

Type:
Protein-based microspheres (5 µm diameter) composed of human serum albumin (HSA) and BrIBAM linkers, dispersed in pure water at a concentration of 10 mg/mL.

Of Note:
The stable microspheres are held together solely through non-covalent interactions, one of which was hypothesised to be the unusual 'halogen bond' interaction.

Environment:
Low temperature

Tweak:
The microspheres were obtained through adsorption of HSA protein onto bromo-amide modified silica templates in water. The silica templates were removed by dissolution using aqueous hydrofluoric acid, yielding free-standing protein microspheres that were intensively washed with water. The protein microspheres were suspended in water containing 30 wt% glycerol, loaded into a Teflon liquid cell with a Kapton window, and flash frozen in liquid nitrogen prior to examination at 11 K.

Findings

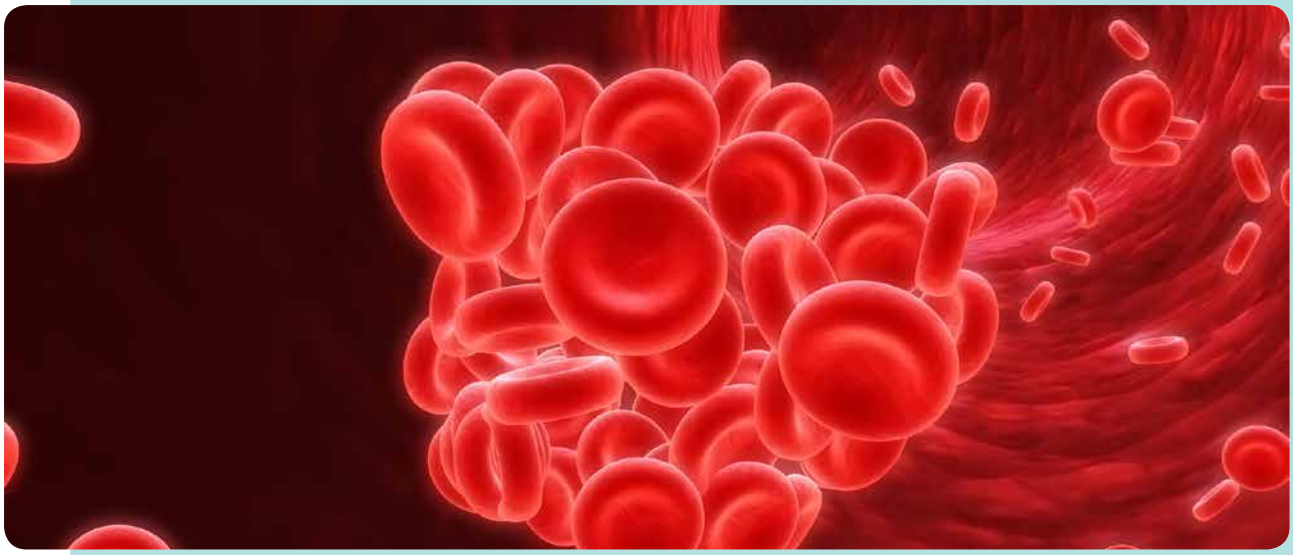
Analysis of the EXAFS bromine spectrum of the biopolymer assemblies suggested that the bromine atoms may interact favourably with the biopolymers by establishing non-covalent interactions. The data obtained revealed that the bond lengths with bromine atoms were close to three angstroms, which typically corresponds to the length of non-covalent halogen bonds. However, the fitting models employed could not precisely determine the nature of the atoms involved in interacting with the bromine atoms. Future studies are aimed at elucidating such interactions in detail.

Impact

This approach is expected to overcome limitations of traditional macromolecular assembly and allow the fabrication of novel particles and capsules with improved properties, including low-toxicity, biodegradability and good processability.

Synchrotron benefits
The work we performed at the Australian Synchrotron allowed us to characterise our materials with EXAFS. However, elucidation of the driving force of our assemblies will require additional experiment, especially to deeply understand the role of bromine atoms. The main benefit is experience and knowledge acquired at the Australian Synchrotron. This will be decisive for future works.

Century-old scientific question answered at the Australian Synchrotron



Melbourne researchers and Australian Synchrotron staff rivalled international efforts, publishing just three months before others in a century-long journey, to discover how enzymes work to dissolve blood clots and clean up damaged tissue in the body. Their findings could help reduce the number of heart disease-related deaths occurring each year as a result of blood clots.

Context

Plasminogen is a blood protein and the enzyme precursor to plasmin, the body's main enzyme for dissolving blood clots. Blood clots mainly consist of specialised cell fragments called platelets bound together by strands of fibrin protein, and may also include trapped blood cells.

Conversion of plasminogen to plasmin is essential for tissue remodelling and blood clot removal after injury. Patients with severe plasminogen deficiency may suffer difficult-to-treat inflammatory conditions such as ligneous conjunctivitis and gingivitis, and neural disorders.

Plasmin is also important in tumour metastasis, and plasmin inhibitors have an emerging role in treating some cancers. Plasminogen activators and inhibitors are used to treat clotting and bleeding disorders respectively, and the plasminogen system is an important drug target as a result of plasmin's potent ability to degrade fibrin blood clots. Some disease-causing bacteria hijack the plasminogen/plasmin system to enhance their ability to destroy tissue and invade the body.

The structure of plasminogen has evolved to guard against the risk of undesirable activation by proteases, which prompt the conversion of plasminogen to plasmin by attacking specific parts of plasminogen.

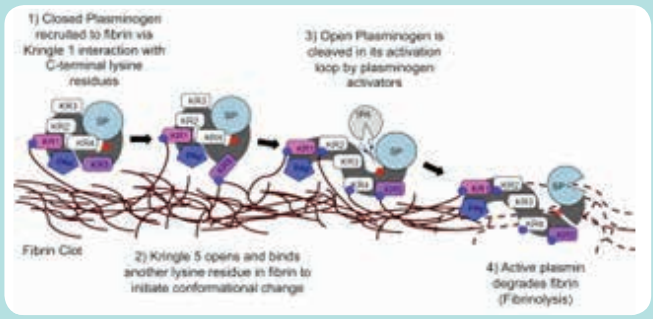
Research question & Synchrotron technique

Although the structure of plasminogen has been known for some time, science has had to wait almost a century for an answer to the question of how plasminogen is activated in the body.

In its activation-resistant 'closed' conformation, plasminogen consists of seven components or domains: a Pan-apple (PAp) domain, five kringle domains (KR1-5), and a serine protease (SP) domain. The researchers used Australian Synchrotron micromolecular crystallography (MX2) and small-angle x-ray scattering (SAXs) beamlines to determine the crystal structures and the solution models of the two forms of plasminogen. Together, these studies revealed the role of each domain in keeping the protease in its 'harmless' inactive form in the circulation.

Publication

Ruby H.P. Law, Tom Caradoc-Davies, Nathan Cowieson, Anita J. Horvath, Adam J. Quek, Joanna Amarante Encarnacao, David Steer, Angus Cowan, Qingwei Zhang, Bernadine G.C. Lu, Robert N. Pike, A. Ian Smith, Paul B. Coughlin , James C. Whisstock, The X-ray Crystal Structure of Full-Length Human Plasminogen, Cell Reports, 1, 185-190, (2012).



Beamline
Micromolecular crystallography (MX2)
Small-angle x-ray scattering (SAXS)

Technique:
Diffraction: single crystallisation

Tweak:
We used the collimator to reduce radiation damage whilst collecting data. To get the right balance between resolution and completeness of data before the crystals were destroyed by radiation damage requires time and repeated experiments. One way to optimise data collection is to make use of the best strategies for data collection. The software developers from the beamline have generated many useful tools that are extremely valuable when working with difficult samples.

Sample

Type:
Plasminogen, which was isolated from human plasma.

Environment:
Low temperature

Of note:
The active plasmin is an extremely potent protease; not only does it have a very broad spectra and low substrate specificity, it is also very difficult to terminate its activity.

Interestingly, pathogens such as Streptococcus pyogenes, secrete their own plasminogen activator, which activates plasminogen in a conformation independent manner to enhance its virulence.

Tweak:
The samples were very difficult to work with. In order to collect high-resolution data, we had to use very high radiation energy during data collection. However, this also leads to intense radiation damage to the samples. To collect sufficient data for our publications, we collected data on more than 80 crystals. We also had to run many experiments, with lots of help from the beamline scientists, in particular, Tom Caradoc-Davies.

Synchrotron benefits
Both synchrotron radiation and the staff of the facility are indispensible for this work. Without the Australian Synchrotron, our work would have been very difficult, as experiments would have to be performed overseas using synchrotron source from APS (USA) or SLS (Switzerland). This would make it very expensive and time consuming. Staff from the beamline have been actively involved in this project: in the development of strategies, data collecting and structural analysis. Our collaboration with the Australian Synchrotron staff has been a very productive operation.

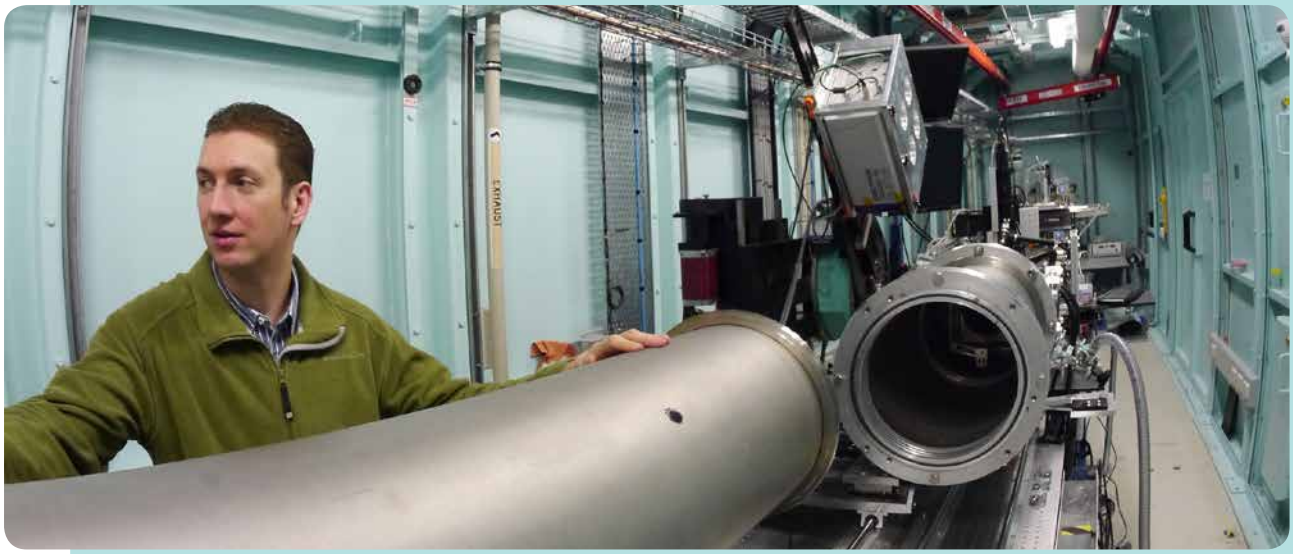
Findings

The closed conformation of plasminogen is maintained by PAp and SP, together with two stabilising chloride ions, through interactions with the kringle array. The kringle domains mediate the interactions with fibrin clots and cell-surface receptors: the precise positioning of the relatively mobile KR3 may be important for attracting closed plasminogen to the cell surface. KR5 appears to be the trigger for plasminogen to open. Once open, the plasminogen is cleaved and converted to plasmin by activator enzymes.

Impact

These findings will help drug companies to fine-tune their development of next-generation anti-clotting or 'clot busting' drugs and cancer treatments.

SNARE discoveries: New light on neurotransmission and insulin binding



Queensland researchers revealed details of the molecular mechanisms that govern fundamentally important biological processes, such as neurotransmitter release in nerve cells, and the uptake of glucose from blood in response to insulin signalling.

Context

When nerve cells communicate, cargo-carrying packages (known as vesicles) from one neuron, fuse with the presynaptic membrane, releasing chemicals that signal to the next neuron. When insulin binds to fat cells (adipocytes) or muscle cells, proteins required to transport glucose into the cell are delivered to the cell surface through vesicle fusion. This insulin-regulated system is essential for maintaining normal blood glucose levels.

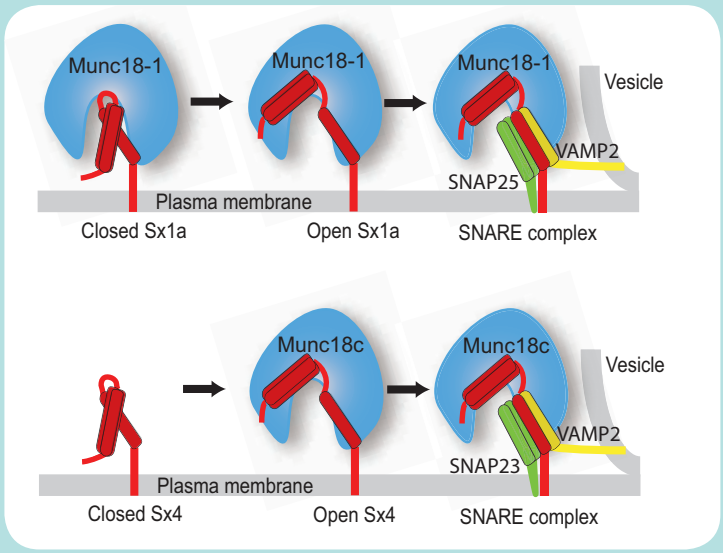
Both neuro-transmission and insulin-regulated glucose uptake involve members of the SNARE protein superfamily. SNARE proteins on vesicles bind to SNAREs on cell membranes to mediate the fusion process between transport vesicles and cell membranes or compartments inside cells, allowing the vesicles to deliver their cargo.

Research question & Synchrotron technique

Australian Synchrotron data from small angle x-ray scattering (SAXS) helped researchers determine that the SNARE protein Sx1a in neurons can interact with a regulatory protein Munc18-1 in an open binding mode as well as a closed binding mode. The equivalent SNARE protein in fat cells (Sx4) appears to bind its regulatory partner Munc18c only in an open binding mode. Open Sx bound to Munc18 can also bind SNARE partners in an interaction that underpins membrane fusion.

Publication

Michelle P. Christie, Andrew E. Whitten, Gordon J. King, Shu-Hong Hu, Russell J. Jarrott, Kai-En Chen, Anthony P. Duff, Philip Callow, Brett M. Collins, David E. James, and Jennifer L. Martin, Low-resolution solution structures of Munc18:Syntaxin protein complexes indicate an open binding mode driven by the Syntaxin N-peptide, PNAS June 19, 2012, 109, 25, 9816-9821. Published online before print June 5, 2012.



Synchrotron data helped researchers determine that membrane fusion protein Sx1a can interact with regulatory protein Munc18-1 in an open binding mode as well as a closed binding mode. The equivalent membrane fusion protein in fat cells (Sx4) appears to bind its Munc18c partner only in an open binding mode. Open Sx bound to Munc18 can also bind SNARE partners in an interaction that underpins membrane fusion. The finding that Munc18 binds open Sx indicates that the Munc18:Sx complex does not inhibit membrane fusion as had been thought previously.

Findings

Even though Munc18-1 and Munc18c belong to the same family they play different regulatory roles by binding to their Sx partners differently.

Impact

Synchrotron data helped to explain the different functional roles reported for Munc18 proteins by scientists previously.

Beamline
Small and wide angle x-ray scattering (SAXS/WAXS)

Technique:
Small and wide angle x-ray diffraction.

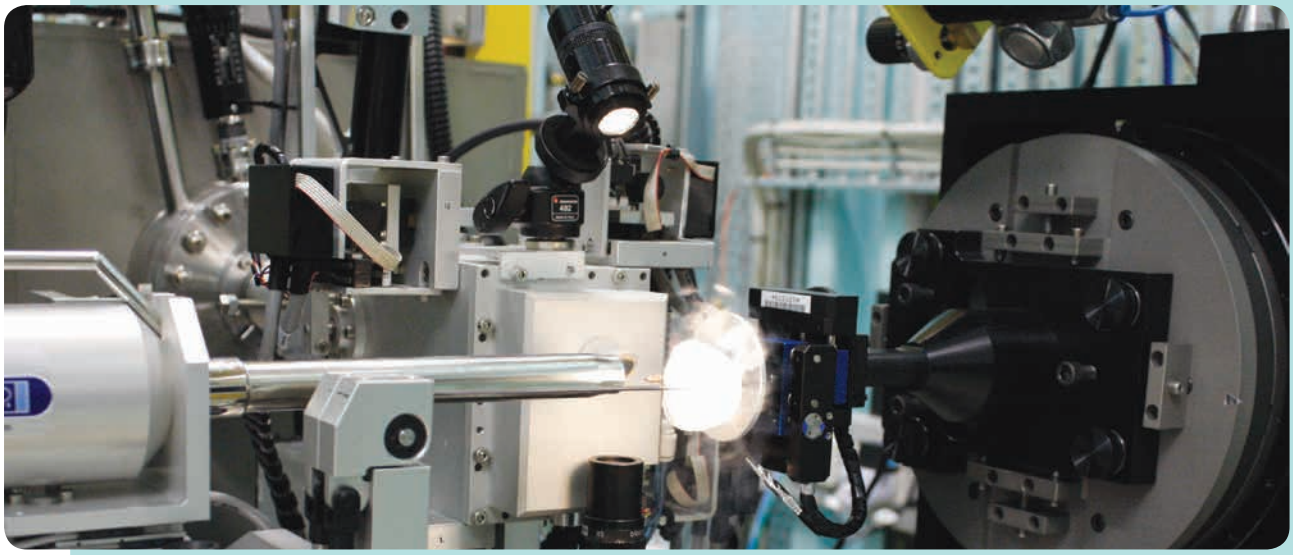
Sample

Type:
Proteins in solution.

Environment:
Liquid flow cell

Synchrotron benefits
Compared to conventional measurements in a lab, the synchrotron provides superb quality data using less sample in a matter of seconds (not hours). This allows us to rapidly perform multiple measurements in different conditions to gain additional insight into protein-protein interactions.

How some drugs trick the immune system



New research showing how some drugs cause side-effects by activating the immune system to attack the body's own tissues may lead to new drugs designed to avoid these side-effects.

Context

Human leukocyte antigen (HLA) molecules are an important part of our immune defences. They start the immune response by presenting peptides derived from the degradation of invading pathogens to T-cells, which then secrete small proteins that actively assist or regulate the immune response. Different HLAs vary considerably in the structure of the antigen-binding cleft, enabling them to deal with many different peptide antigens.

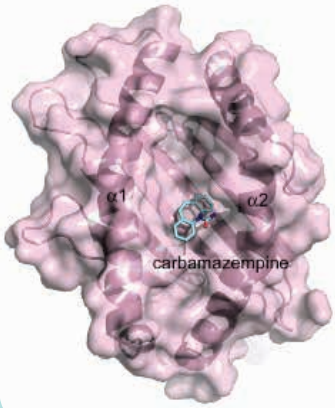
The drugs abacavir (for treating HIV and AIDS) and carbamazepine (mainly used to treat epilepsy and bipolar disorder) can cause immunologically-based drug reactions that are associated with specific HLA molecules: abacavir and carbamazepine give rise to hypersensitivity syndromes in individuals expressing the specific HLA alleles HLA B*57:01 and HLA B*15:02. In severe cases this leads to life threatening skin reactions such as Stevens–Johnson syndrome and toxic epidermal necrolysis. Until recently, however, little was known about the underlying mechanisms.

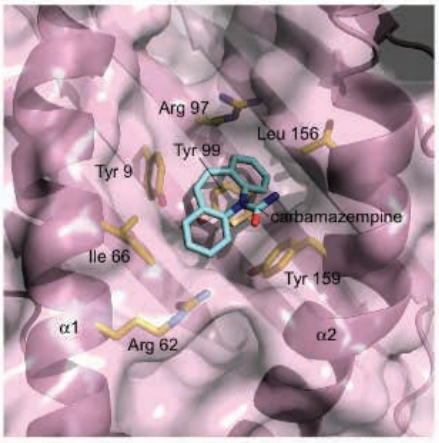
Research question & Synchrotron technique

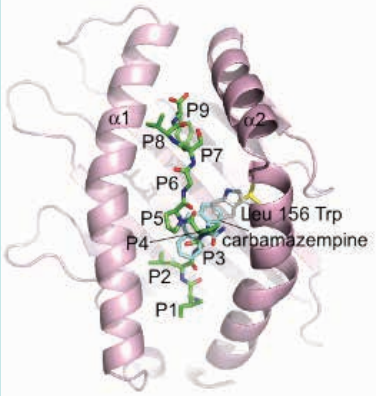
A team of researchers from Victoria, Queensland and Wales (UK) used the Australian Synchrotron micro-crystallography (MX2) beamline to solve crystal structures that show exactly how abacavir binds to a HLA B*57:01.

Publication

Patricia T. Illing, Julian P. Vivian, Nadine L. Dudek, Lyudmila Kostenko, Zhenjun Chen, Mandvi Bharadwaj, John J. Miles, Lars Kjer-Nielsen, Stephanie Gras, Nicholas A. Williamson, Scott R. Burrows, Anthony W. Purcell, Jamie Rossjohn & James McCluskey, Immune self-reactivity triggered by drug-modified HLA-peptide repertoire, Nature 486, 554–558 (28 June 2012).







(Opposite) Crystal sample mounted on the MX2 micro-crystallography beamline, which caters for difficult crystals and small molecules.

Findings

On binding, the abacavir molecule changes the shape and chemistry of the antigen-binding cleft, which then enables a range of the body's own endogenous (self) peptides to activate T cells, potentially leading to hypersensitivity syndrome.

Once the self-peptides bound to HLA B*57:01 are recognised by T cells, the body is triggered to start attacking its own tissues – leading to immune-mediated side effects.

Impact

This groundbreaking work will enable the development of new drugs that are specifically designed not to bind to HLAs. It also provides a general mechanism to explain some of the growing number of HLA-linked hypersensitivities that involve small-molecule drugs.

Advanced materials & engineering science

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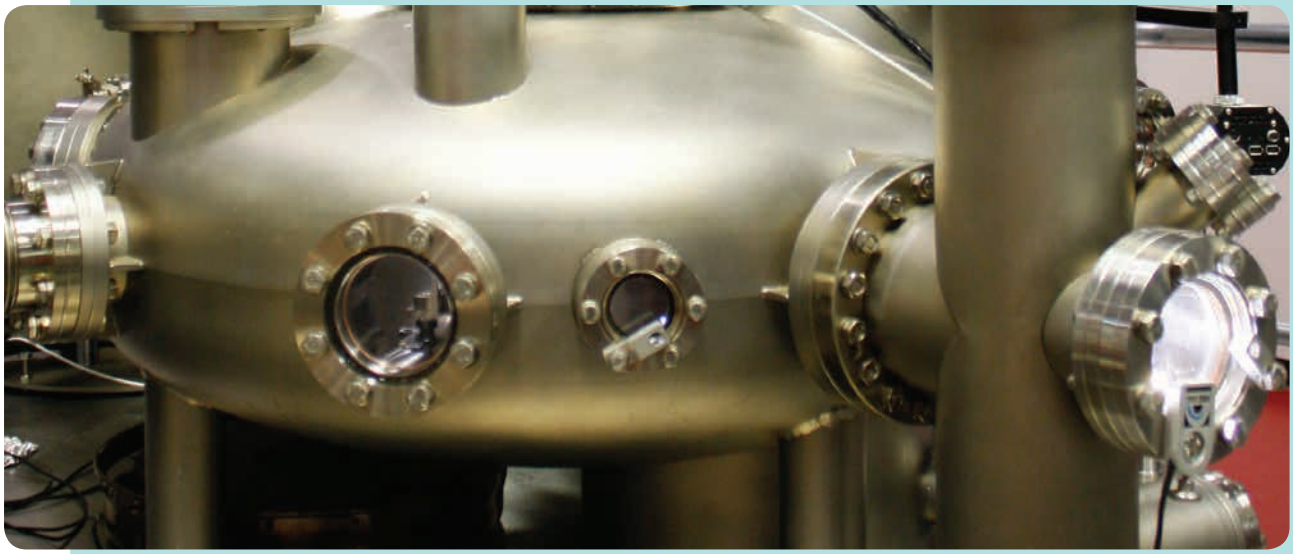
How annealing influences organic solar cell performance



The performance of organic solar cells is governed by the orientation, structure and morphology of polymer molecules in the cells. Researchers investigating vertical and interfacial molecular alignment in organic solar cells found that slower cooling of the polymers after heating (annealing) enhances cell efficiency.

Context

Global access to low-cost energy is a key challenge of our time. However, if climate change is to be addressed this low-cost energy production must also be sustainable.

Since their discovery in the mid-1980s, organic photo-voltaics (OPVs) based on semiconducting polymers have generated considerable excitement as a potentially inexpensive means of generating electricity directly from sunlight. The key advantage is that OPVs can be printed at high speeds using roll-to-roll processing techniques. This capability has created the tantalising vision of coating every roof and any other suitable building surface with photo-voltaic materials at extremely low cost.

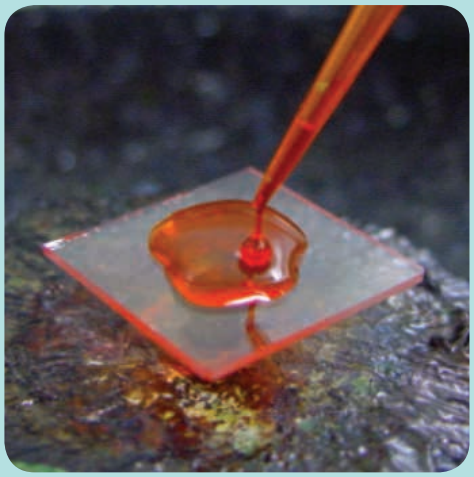
However, to date the performance of these devices has been hindered by the lack of understanding of how the polymer materials reorganise themselves after annealing, which is the process of heating the materials and then cooling them to achieve the right composition and molecular structure.

Research question & Synchrotron technique

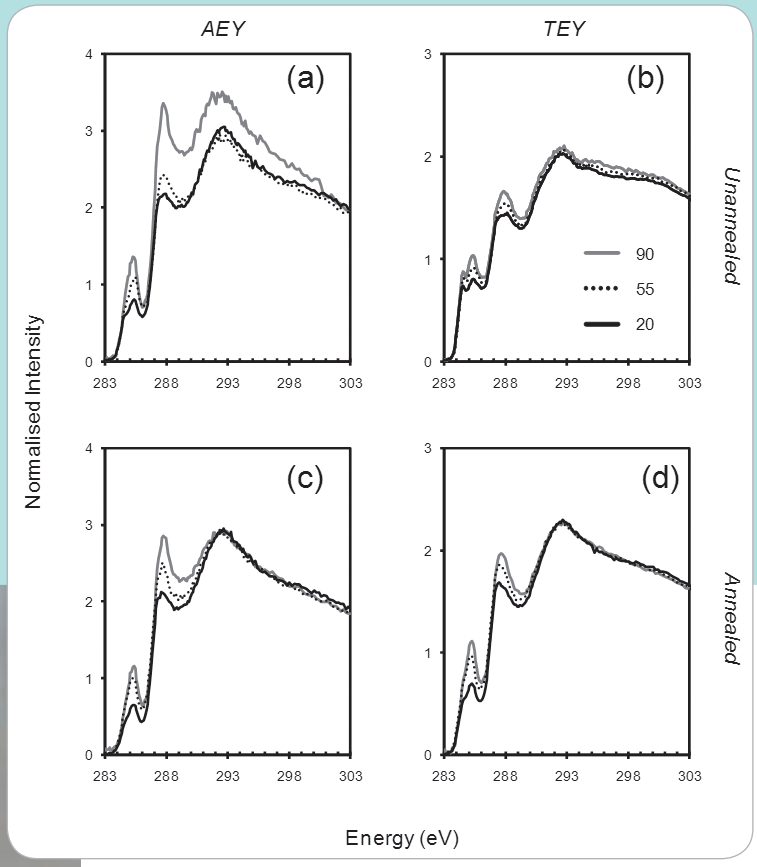
Researchers used soft x-ray (SXR) techniques at the Australian Synchrotron, and at overseas facilities through the Synchrotron's international access program, to probe the vertical structure of P3HT:PCBM (poly(3-hexylthiophene) and phenyl-C61-butyric acid methyl ester) polymer solar cells when they are cooled at different rates.

Publication

Bofei Xue, Ben Vaughan, Chung-How Poh, Kerry B. Burke, Lars Thomsen, Andrew Stapleton, Xiaojing Zhou, Glenn W. Bryant, Warwick Belcher and Paul C. Dastoor, Vertical Stratification and Interfacial Structure in P3HT:PCBM Organic Solar Cells, J. Phys. Chem. C, 114 (37), pp 15797–15805 (2010), 23 September 2010 (online 30 Aug).



Spin coating a typical polymer blend solution



(R) Carbon K-edge AEY and TEY NEXAFS spectra (20, 55 and 90° incidence) of the active layer/air interface for annealed and post-annealed P3HT:PCBM films: (a) Unannealed AEY, (b) Unannealed TEY, (c) Annealed AEY, (d) Annealed TEY.

Beamline
Soft x-ray (SXR)

Technique:
Soft x-ray NEXAFS spectroscopy

Tweak:
We used soft x-ray near edge x-ray absorption fine structure (NEXAFS) spectroscopy to characterise the alignment of the polymer chains at the different interfaces in the device.

Sample

Type:
Thin conducting polymer blend films.

Environment
Under vacuum

Tweak:
Measurements were of carbon edge NEXAFS.

Synchrotron benefits
Synchrotron radiation is the only technique that can provide information on the orientation of the polymer chains in these devices.

Findings

X-ray studies revealed a distinct and changing vertical stratification and interfacial structure in the P3HT:PCBM organic solar cells throughout the annealing process, with both composition and crystallinity (the extent of any regularly-ordered domains) varying through the active layer.

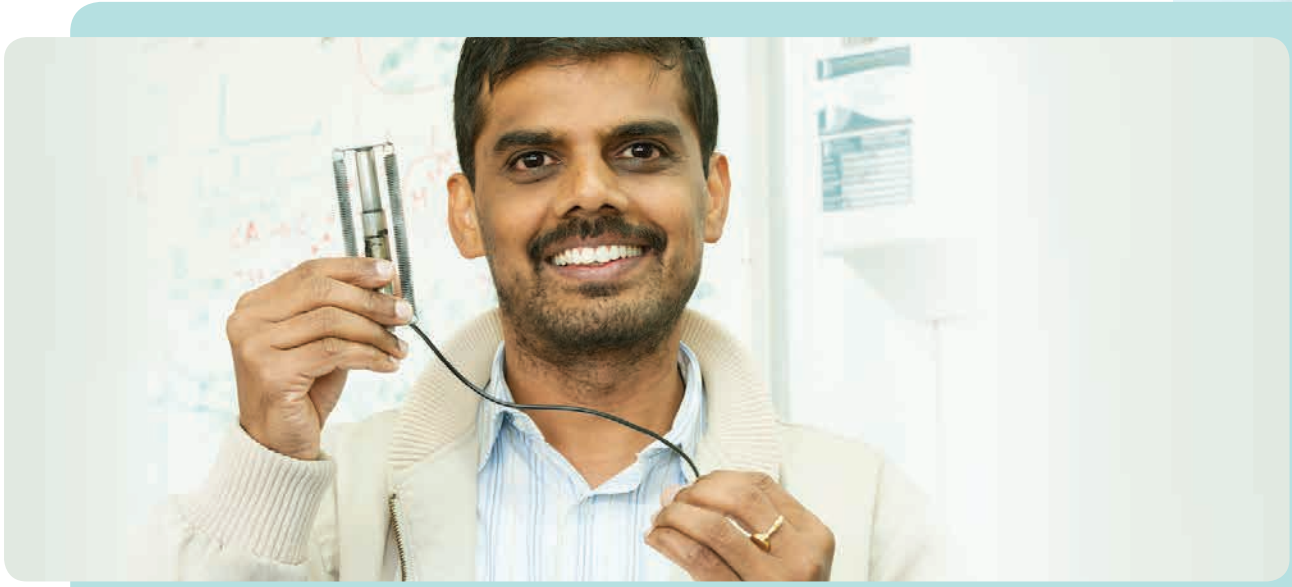
This data was then used to create a series of 'snapshots' of the reorganisation processes that occur upon annealing. In particular, they showed that annealing results in the formation of three distinct vertical layers in these polymer solar cell devices and that slowing the cooling rate increases the efficiency of power conversion.

This improvement in device performance is correlated with the observed increased crystallinity, polymer alignment and phase segregation both at the interfaces and in the bulk film. In particular, slow cooling results in an aligned interfacial structure that is beneficial for transporting the electrical charges across the solar cell.

Impact

The results of this work have demonstrated that vertical reorganisation in these devices plays an important role in determining device efficiency. As such, this work demonstrates a new pathway for optimising device performance.

Aqueous rechargeable lithium battery



Olivine-type lithium nickel phosphate ($LiNiPO_4$) is a potential cathode material that could improve the efficiency and safety, and reduce the cost and environmental impact, of aqueous rechargeable lithium batteries for large-scale energy storage.

Context

The availability of safe, low-cost rechargeable batteries is a critical bottleneck in the development of affordable large-scale energy storage. Rechargeable lithium ion batteries using non-aqueous electrolytes power today's portable electronics. However, scaling up this technology for large-scale applications is challenging, due to the reactivity of the electrode materials with the non-aqueous electrolytes.

Research question & Synchrotron technique

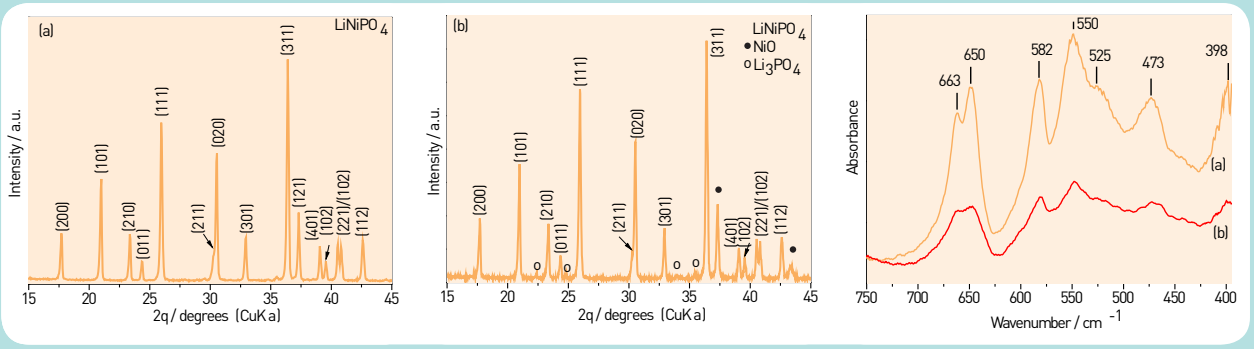
Dr Manickam Minakshi of Murdoch University, his collaborators at ANSTO and the Australian Synchrotron aimed to demonstrate that a rechargeable cell could be produced using aqueous electrolytes, which are inherently much safer. They used a prototype battery with an olivine phosphate cathode, a zinc (or) activated carbon anode and an aqueous LiOH electrolyte.

The researchers synthesised an olivine-type phosphate compound, $LiNiPO_4$, and used this as a cathode in an aqueous LiOH-electrolyte secondary battery system with a zinc anode. They developed a simple synthesis for $LiNiPO_4$ carried out in 'plain air' conditions through conventional (non-annealed) and annealed at modest temperatures yielding products of high purity compound in a single phase.

Publication

Manickam Minakshi, Pritam Singh, Dominique Appadoo, Danielle E. Martin, Synthesis and characterization of olivine $LiNiPO_4$ for aqueous rechargeable battery, *Electrochimica Acta*, 56, 4356-4360 (2011).

Manickam Minakshi, Neeraj Sharma, David Ralph, Dominique Appadoo and Kalaiselvi Nallathamby, Synthesis and Characterization of $Li(Co_{0.5}Ni_{0.5})PO_4$ Cathode for Li-Ion Aqueous Battery Applications, *Electrochemical and Solid-State Lett.* 14 (2011) A86-A89.



X-ray diffraction (XRD) patterns of prepared $LiNiPO_4$ olivine (a) annealed and (b) non-annealed samples (conventional cooling). Lines are indexed in the orthorhombic system.

The Far-IR spectra of the synthesised $LiNiPO_4$ (a) annealed and (b) non-annealed samples.

(Opposite) Dr Manickam Minakshi holding an aqueous rechargeable lithium battery.

Beamline
Terahertz/Far-infared (THz/Far-IR)

Technique:
Infrared (IR) spectroscopy

Sample

Type:
Oxides and phosphate powder samples for battery applications.

Environment:
Open to air

Tweak:
The sample was synthesised in two different conditions i.e. conventional (rapid- 2.5 degree celsius /min) cooling and annealed (slow cooling - 0.5 degree celsius /min) both were performed in air; bright yellow and green powders were achieved respectively.

Synchrotron benefits
IR spectroscopy is a complementary tool that helped us to correlate the colour of the nickel samples and its fundamental vibrations. Using synchrotron radiation gave us superior results with publishable quality. Sampling time was very quick. The IR studies helped us to resolve the cation substitution in the olivine structure. Consequently, we developed some of its analogues.

Findings

Minakshi worked with Drs Dominique Appadoo and Danielle Martin at the Australian Synchrotron to perform infrared spectroscopy analyses on annealed and non-annealed samples of $LiNiPO_4$. The synthesised powders ranged from bright yellow to green for annealed and non-annealed samples respectively. The green comes from Ni^{2+} ions in the NiO_6 octahedra. The yellow is due to Ni^{2+} present in NiO_6 sites distorted from octahedral symmetry – the pre-requisite for an olivine structure.

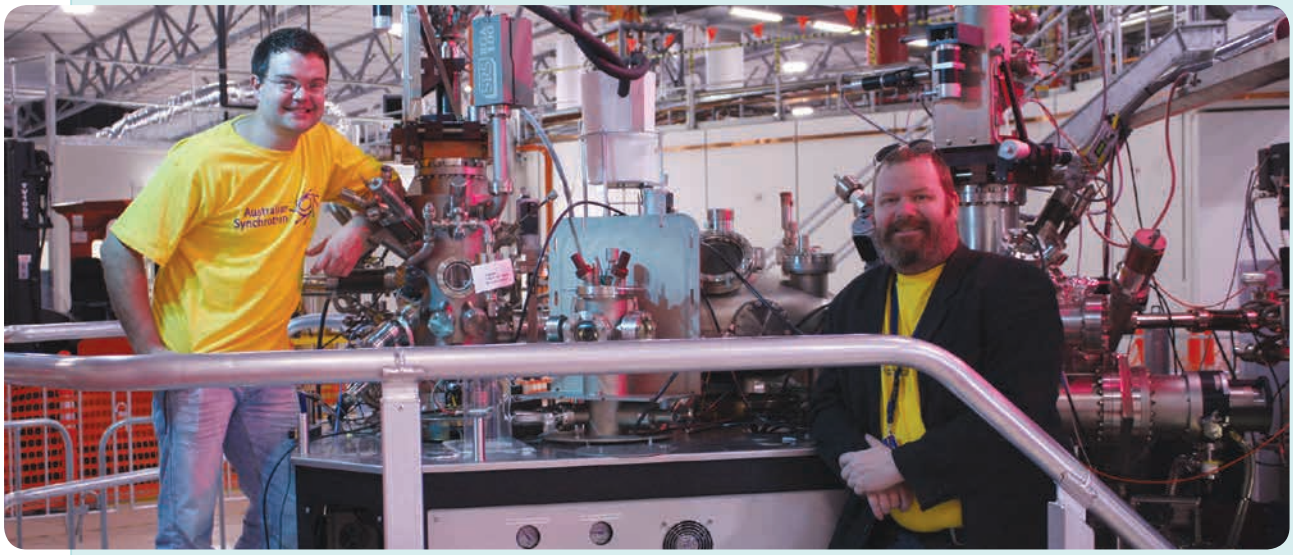
X-ray diffraction studies on these samples indicated that only annealed samples with a bright yellow colour exhibit a single phase of olivine-type $LiNiPO_4$. Correlations between the colour of the nickel compounds and their fundamental vibrations were studied through IR spectroscopy. Charging the annealed cathode $LiNiPO_4$ electrode showed that the lithium is extracted from the olivine structure. The lithium extraction/insertion into $LiNiPO_4$ was found to be reversible (rechargeable) over many tens of cycles. With further optimisation, this technology could be used for storing renewable energy.

The group concluded that annealing is critical for obtaining pure $LiNiPO_4$ and avoiding the formation of Li_3PO_4 and NiO.

Impact

The powder patterns of the $LiNiPO_4$ samples were recently chosen to include in the International Centre for Diffraction Data (ICDD) database. ICDD is considered one of the most authentic databases of crystal structures.

Improving chiral separation methods for effective pharmaceuticals



Drug synthesis often produces a mixture of left and right-handed mirror images of the drug molecule. Typically only one form is effective; the other even may be harmful, as with thalidomide. Improved separation methods could lead to more-effective pharmaceutical drugs.

Context

Any two objects which are non-superimposable mirror images of each other are referred to as chiral pairs, such as sea shells or our own pair of hands. In the natural world, chirality even extends to the molecular level where important biological molecules exist in pairs known as chiral enantiomers. One example is aspartame, an artificial sweetener; one of the enantiomers is sweet, the other is bitter.

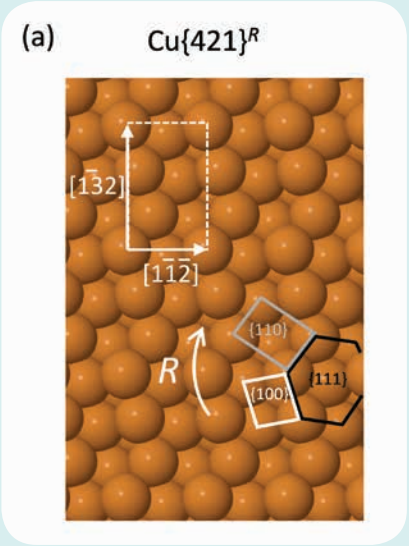
Research question & Synchrotron technique

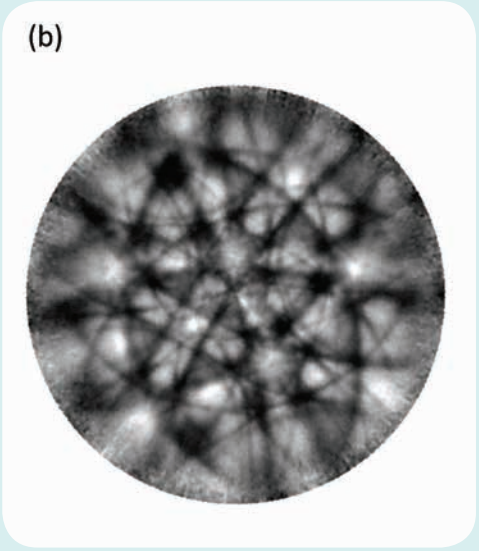
Each year many new synthetic drugs are developed which are chiral, however often one of the enantiomers is harmful to living matter, thus the importance of producing single-enantiomer products cannot be understated. Separating these chiral molecules from each other in a pure form is not an easy task.

Currently there is a significant level of interest in using special crystalline surfaces which can exist in two chiral forms as media for preferentially adsorbing one enantiomer over another, in a 'lock and key' type scenario. In such studies, it is vital to know the absolute chiral symmetry of the surface in order to understand its enantioselective properties.

Publication

Anton Tadich, J. Riley, Lars Thomsen, Bruce C.C. Cowie and M.J. Gladys, Determining the Orientation of a Chiral Substrate Using Full-Hemisphere Angle-Resolved Photoelectron Spectroscopy, Phys. Rev. Lett. 107, 175501 [4 pages] (2011), 21 October 2011 (online 17 Oct).





(b) emission distribution of photoelectrons excited from a chiral copper surface, Cu{421} (shown in (a)). The pattern allows researchers to identify the precise chiral orientation of the copper surface, which is important for understanding how the surface reacts with chiral molecules.

(Opposite) Anton Tadich and Lars Thomsen at the soft x-ray beamline.

Beamline
BESSY (Berlin), soft x-ray spectroscopy (conducted by Australian Synchrotron scientist, Anton Tadich)

Technique:
Complete emission distribution of electrons was measured using a unique electron spectrometer - a toroidal angle resolving analyser.

Sample

Type:
A low index surface of copper – a 'chiral' surface exhibiting no rotational symmetry.

Of note:
Copper is useful as a prototypical face-centred-cubic material that exhibits chiral surface terminations, and may be able to preferentially absorb one form of a chiral molecule over its mirror image sibling. The reverse face of the crystal exhibited the opposite chiral orientation.

Environment:
Ultra high vacuum

Tweak:
The sample was prepared to an atomically perfect, contaminant-free surface so that the symmetry of the crystal could be studied using angle resolved photoemission. This was achieved using argon ion bombardment and annealing in ultra high vacuum (UHV). Under these conditions, the crystal remains clean for several hours.

Synchrotron benefits
The entire electron emission pattern could be measured rapidly, in less than an hour, compared with several hours in conventional photoelectron spectrometer designs. This was important, as over time the crystal becomes 'dirty' under vacuum, degrading the signal.

Findings

In this work Australian Synchrotron researchers demonstrated that by exciting electrons from a chiral surface using either x-ray or ultraviolet radiation, and measuring the intensity of the emitted electrons from all emission directions, that the absolute chiral symmetry of the surface can be deduced.

Impact

In comparison to other techniques which facilitate chiral identification, this method can be applied on novel chiral surfaces prepared *in-situ*, such as chiral sculpting of an achiral surface using organic molecules.

Understanding lithium-ion battery materials

The same rechargeable batteries that are used in mobile phones and laptops, based on lithium-ion technology, have potential applications in electric vehicles. Researchers have contributed another step toward the advances required before this battery technology can be used effectively in these broader applications.

Context

A number of advances are required in lithium-ion technology before their potential can be realised in applications such as electric vehicles. The advances are tied in with the need for batteries to have safer operation, greater capacity (more energy) and faster rates of recharge.

Another barrier to their wider uses, is that the majority of lithium-ion batteries use carbon-based negative electrodes (anodes), which present safety issues due to the possible deposition of lithium metal on the electrode surface during operation. The possibility of lithium metal deposition can be exaggerated when batteries are charged and discharged (cycled) at faster rates.

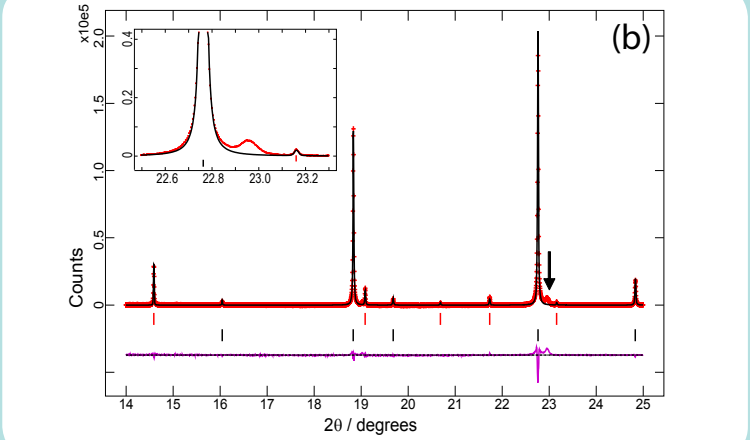
This work investigated an alternative anode material: Lithium Titanium Oxide ($Li_4Ti_5O_{12}$). This compound, which has excellent high-rate cycling performance, also avoids the deposition of lithium during cycling. Additionally, very small volume changes of this anode are found during conventional cycling (<1%) making it a potentially robust alternative for operation over longer periods, such as would be the demand for electric vehicles (pictured above).

Research question & Synchrotron technique

A research team actively studying lithium-ion batteries, concentrated their efforts on this anode material, to investigate the origin of any improvements in electrochemical properties. The team analysed a previous finding that small substitutions of bromine for oxygen in the compound of $Li_4Ti_5O_{12}$ led to an improvement in the performance of the battery. They were also curious as to why there was a particular bromine concentration that gave the best properties.

Publication

Guodong Du, Neeraj Sharma, Vanessa K. Peterson, Justin A. Kimpton, Dianzeng Jia and Zaiping Guo, Br-Doped Li4Ti5O12 and Composite TiO2 Anodes for Li-ion Batteries: Synchrotron X-Ray and in situ Neutron Diffraction Studies, Adv. Funct. Mater., 21, 3990-3997 (2011), 21 October 2011 (online 1 Sep).



(L) Typical research scale coin cells used to test the electrochemical performance of these batteries. (R) The model of the major compound $Li_4Ti_5O_{12-x}Br_x$ (black line) fitted to synchrotron x-ray diffraction data (red crosses). The arrows and inset indicate the presence of extra un-matched reflections which illustrate that there are other compounds in this electrode material.

Beamline
Powder diffraction (PD)

Technique:
Powder diffraction

Tweak:
A simple room temperature capillary experiment – routine.

Sample

Type:
A series of polycrystalline powders of composition $Li_4Ti_5O_{12-x}Br_x$.

Of note:
There was an ideal composition where this sample showed optimal electrochemical performance in a battery. However, there was no reason given in previous work, why this composition led to the best performance.

Environment:
Open to air

Tweak:
This was actually a routine room temperature capillary experiment on the powder diffraction beamline. Subsequently we have developed cells (batteries) and methods for performing and analysing materials like this in a real-life research cell while the cell is functioning (in situ).

Synchrotron benefits
Without the use of synchrotron x-ray diffraction facilities we would not know that this material is a composite of multiple phases. Laboratory x-ray diffraction cannot resolve these phases.

Findings

The Australian Synchrotron's x-ray powder diffraction (PD) beamline was critical in revealing that the materials were not pure compounds with composition $Li_4Ti_5O_{12-x}Br_x$ but a mixture of 2 to 3 compounds. Only the major compound was resolvable using laboratory-based experiments, while the others were too weak to observe.

The researchers found that it was the optimal ratio of these compounds that lead to the best battery performance as a composite electrode.
The composite nature was subsequently explored using neutron diffraction at ANSTO. This work showed that multiple compounds in the composite electrode are electrochemically active, that is, multiple compounds participate in battery function.

Impact

Findings such as these, will allow researchers to explore new materials and to understand how the composition and atomic arrangements within the materials influence battery performance. Such advances in new electrode materials, will likely lead to the next generation of batteries.

We would not have come up with a reasonable explanation for the observed performance enhancement. With the information from the synchrotron we were able to determine why the electrode shows better performance and describe how the different components function.

So the synchrotron experiments saved us time and money and gave better and arguably unique results which helped to answer our questions.

Self-assembly of huge ML spheres

Predicting the self-assembled structures of giant coordination polyhedra from metal ions and bridging ligands is almost impossible. Japanese researchers recently made successful empirical predictions of the critical structural switch from $M_{12}L_{24}$ to $M_{24}L_{48}$ based on the small difference in the ligand angles.

Context

Self-assembly is a powerful method for synthesising huge polyhedral molecules with diameters greater than several nanometres. In theory, the product structure can be predicted from the chemical structures and physical properties of starting materials. However, prediction is quite difficult when dealing with self-assembly of more than 50 components.

In previous work, Japanese and Finnish researchers synthesised M_nL_{2n} polyhedra from bridging ligands (L) and transition metal ions (M). Ligand 1 (bend angle $\theta = 127°$) and Pd^{2+} ions assembled into $M_{12}L_{24}$ cuboctahedra; ligand 5 ($\theta = 149°$) and Pd^{2+} ions assembled into $M_{24}L_{48}$ rhombicuboctahedra. When the researchers mixed ligands 1 and 5, the product structures critically switched from $M_{12}L_{24}$ to $M_{24}L_{48}$ at the threshold of a small initial difference in average $\theta = 131$-$134°$, showing molecular-level emergent behaviour. The ligand bend angle dominantly controls the resultant structures, and $M_{24}L_{48}$ polyhedra were prepared from a single ligand with designed θ and Pd^{2+} ions using the empirical prediction.

Ligands 2, 3, and 4 were designed with bend angles of 135°, 143° and 147° respectively, that is within the empirically predicted range (134-149°) required for $M_{24}L_{48}$ polyhedra. The researchers used nuclear magnetic resonance (NMR) and mass spectrometry (MS) to analyse the self-assembled products from ligand 2, 3, or 4 and Pd^{2+} ions in organic solvent, showing the formation of targeted $M_{24}L_{48}$ polyhedra.

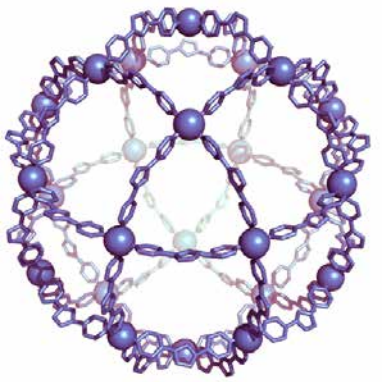
The mixture of $M_{12}L_{24}$ and $M_{24}L_{48}$ polyhedra was not observed, even with the bending angle of ligand 2 being only one degree larger than the empirically predicted value (134°).

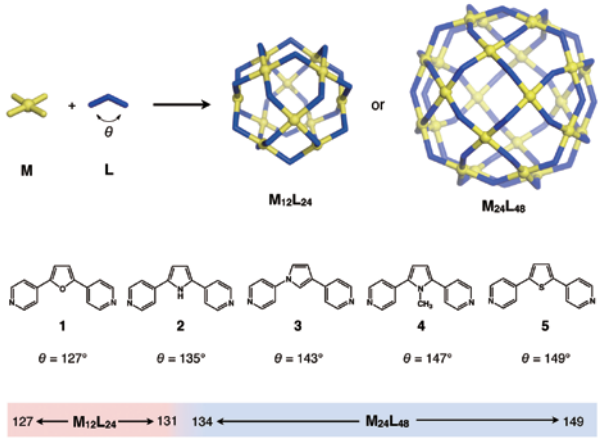
Research question & Synchrotron technique

The three-dimensional structures of the M_nL_{2n} polyhedra self-assembled from ligands 2, 3, or 4 and Pd^{2+} ions were only accessible by crystallographic analysis. However, laboratory diffractometers could not deal with the large unit cell of around 70 Å and large numbers of severely disordered solvent molecules. The researchers then used single crystal diffraction studies with the strong, small angle x-ray beam at the Australian Synchrotron's MX2 beamline.

Publication

Bunzen, J., Iwasa, J., Bonakdarzadeh, P., Numata, E., Kari Rissanen, Sota Sato, and Makoto Fujita, Self-Assembly of M24L48 Polyhedra Based on Empirical Prediction, Angew. Chem. Int. Ed., 51:3161–3163. doi:10.1002/anie.201108731 (2012), 26 March 2012 (online 10 Feb).





*(L) Crystal structure of $M_{24}L_{48}$ rhombicuboctahedron self-assembled from ligand **3** and Pd^{2+} ion. (R) Self-assembled M_nL_{2n} (n = 12 or 24) polyhedra and the structures of ligands.*

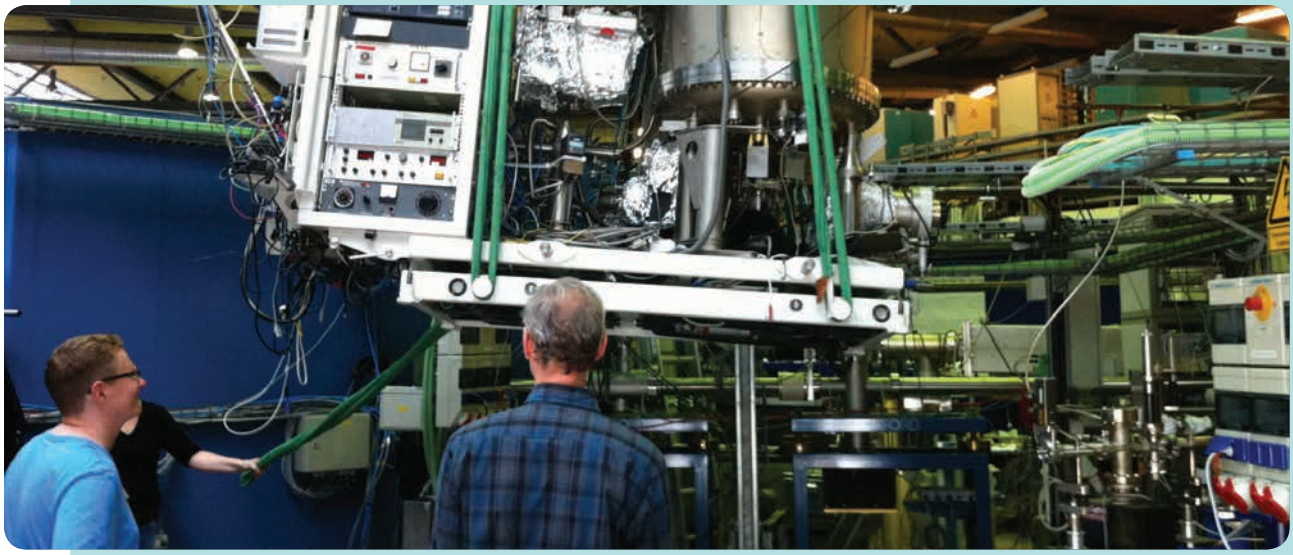
Findings

The structure of the highly symmetrical rhombicuboctahedron was finally determined at the MX2 beamline. This proved that the team had succeeded in the self-assembly of $M_{24}L_{48}$ rhombicuboctahedral complexes, producing the world's largest coordination molecules designed by empirical prediction and obtained by simple ligand-mixing experiments.

Impact

The successful demonstration of a simple rule for predicting a large, complicated, self-assembled system will help researchers to synthesise larger molecules with many more components.

Electrically-conductive diamond surfaces for use in electronic devices



Diamond is an excellent electrical insulator, but may behave quite differently at the material's surface. Diamond surfaces, with covalently-bonded hydrogen, can become electrically conductive if molecules with enough electron affinity (attractiveness) are adsorbed onto the surface.

Context

Diamond has been used since ancient times as a popular stone in jewellery — well known to be a girl's best friend. However recently, it has been attracting the attention of scientific researchers, given its promise in electronic devices for bio-sensing and drug delivery due to its biocompatibility.

In its natural form, diamond is an insulating material. However when hydrogen atoms are bonded to the diamond surface, and then exposed to molecules with high enough electron affinity, it becomes electrically conducting. This occurs right at the diamond surface and is as a result of charge transfer from the diamond into the molecules.

The molecules that can induce this type of conductivity include fullerenes (soccer ball shaped molecules made up of 60 carbon atoms), or fluoro-fullerenes (fullerene molecules with 48 fluorine atoms bonded to the outside of the soccer ball). Having the ability to transform only the surface of diamond into an electrical conductor, whilst the bulk of the material remains insulating, is an exciting possibility for new electronic devices to be created on a carbon-based platform.

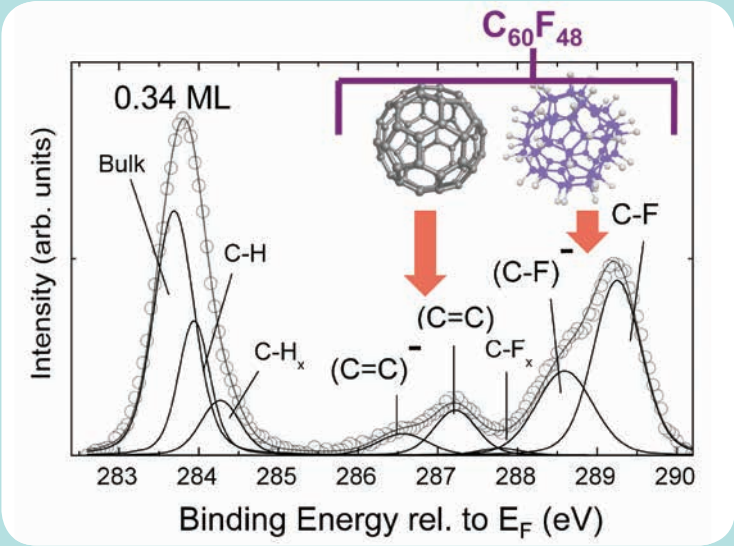
Research question & Synchrotron technique

An international team, along with Australian Synchrotron researchers, revealed important new details of how hydrogen-terminated diamond becomes surface conducting when exposed to fluoro-fullerene molecules. The team used soft x-ray (SXR) spectroscopy techniques at the Australian Synchrotron to reveal what happens to the fluoro-fullerene molecules when deposited onto the diamond surface in vacuum.

The aim was to understand the factors that govern how diamond becomes conducting at the surface when exposed to these molecules. This was investigated by utilising a specific energy of synchrotron light that probes less than a nanometer below the diamond surface.

Publication

Mark T. Edmonds, Martina Wanke, Anton Tadich, HM Vulling, Kevin J. Rietwyk, Peter L. Sharp, CB Stark, Y. Smets, Alex Schenk, Qi-Hui Wu, L. Ley, Chris I. Pakes, Surface transfer doping of hydrogen-terminated diamond by C60F48: Energy level scheme and doping efficiency, J. Chem. Phys. 136, Issue: 12 Article Number: 124701 (2012), 28 March 2012 (online 23 Mar) doi:10.1063/1.3695643.



(Opposite) Edmonds and collaborators at the BESSY II Synchrotron, Berlin on a trip funded by the Australian Synchrotron.

(L) Photoemission spectra of the hydrogen-terminated diamond surface with 0.34 of a monolayer of C60F48 molecules on the surface. The peaks corresponding to the molecules are denoted C=C and C-F represent the carbon-carbon and carbon-fluorine bonds respectively. The key feature of this graph is that two components exist denoted (C=C)- and C=C or (C-F)- and C-F which represents the molecules that have participated in charge transfer with diamond and those that have not.

Beamline
Soft x-ray spectroscopy (SXR)

Technique Tweak:
The photon energy was tuned in order to be extremely sensitive to the molecular overlayer. The high energy resolution of the beamline and spectrometer allowed the charged and uncharged components of the fluoro-fullerenes to be resolved. This was the key innovation in the paper that allowed a quantitative analysis of the transfer doping process. We have since applied this technique to other technologically relevant materials such as the graphene/fluoro-fullerene interface and organic-organic heterostructures.

Sample

Type:
A single crystal diamond composed of sp^3 bonded carbon. The diamond had been hydrogen-terminated in a microwave plasma prior to arriving at the Synchrotron.

Of note:
The hydrogen-terminated diamond sample becomes p-type surface conducting when fluorinated fullerenes are deposited onto the surface. This is due to electrons being transferred from the diamond valence band into the molecular overlayer, leaving holes behind in the diamond.

Environment:
Under vacuum

Tweak:
Sub-monolayer coverages of fluoro-fullerene were deposited in-situ and photoemission spectroscopy was performed at each deposition step.

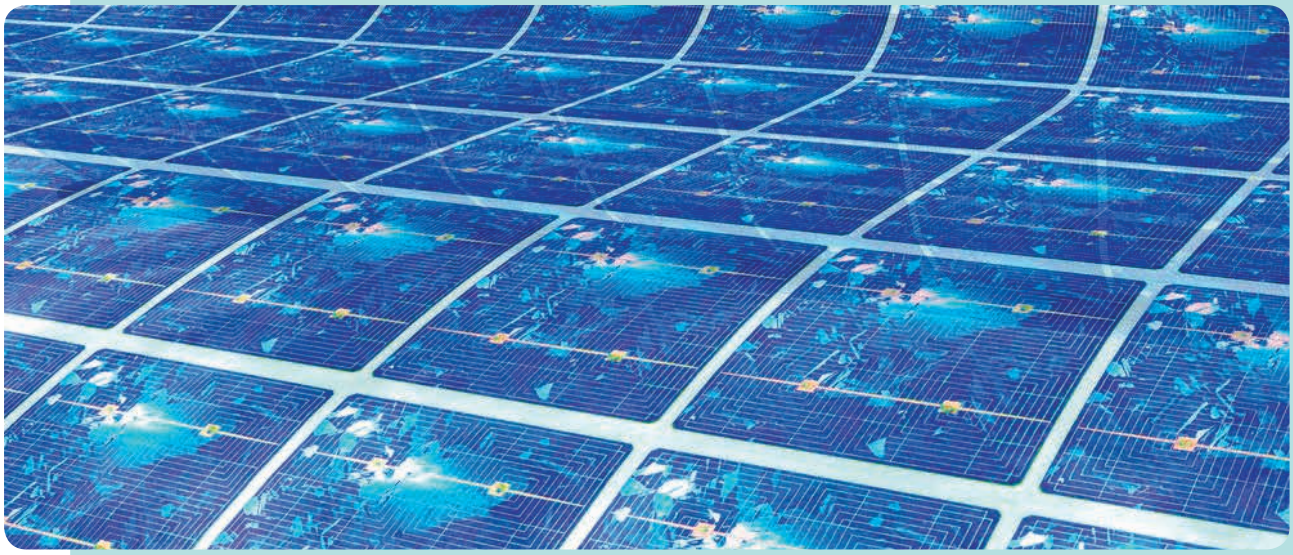
Findings

The high surface-sensitivity of this technique enabled the team to show that only some of the molecules on the diamond surface accept charge from the diamond while others remain neutral. By measuring the relative number of charged to unchanged molecules as the coverage changed the team was able to develop a model to understand in detail how the charge transfer process works.

Impact

The group have since applied this finding to a variety of other technologically relevant samples including fluoro-fullerene molecules on graphene. This research provides a fundamental understanding of how charge transfer occurs, and will be vital in the development of future electronic devices that utilise molecular dopants.

Molecular alignment, measured by resonant scattering, improves organic electronics



The possibility of printing electronic devices like newspaper could revolutionize how we use technology. Researchers have revealed how alignment of the molecules within such devices is key to how they work – and could lead to their wide-spread use.

Context

Roll-to-roll or ink-jet printing of electronic devices has recently been made possible by the development of solution-processable organic materials, with optical and electronic properties. Organic light-emitting diodes (OLEDS) are already being produced commercially and other Organic Solar Cells (OSCs), such as sensors and transistors, are under intense study.
Yet, fundamental understanding on how these materials organise at the nanoscale, and how that affects their operation is lacking, limiting progress.

Research question & Synchrotron technique

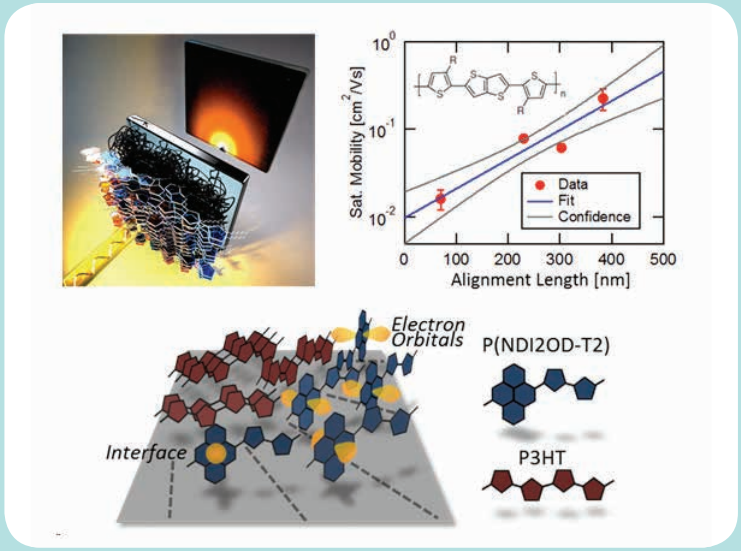
The experiment involved taking advantage of highly directional resonances in organic molecules that provide a marker for their orientation. Traditional hard x-rays are only sensitive to material density or crystallinity, but these materials are all made of light elements and exhibit low crystallinity. Resonant x-rays, however, can measure this orientation because they interact more strongly when their electric field is aligned with these markers.

Researchers used this interaction in both microscopy and scattering experiments to reveal molecular alignments in the devices. Key to the success was the ability to essentially measure the multi-component devices themselves, as the resonant x-rays can also be tuned to preferentially interact with only the device component of interest.

Please note, key aspects of this work were performed at the Advanced Light Source in Berkeley using a facility not available in Australia. However researchers used the Australian Synchrotron's soft x-ray (SXR) for reference spectroscopy, which was used for interpretation of Berkeley results.

Publication

B. A. Collins, J. E. Cochran, H. Yan, E. Gann, C. Hub, R. Fink, C. Wang, Torben Schuettfort, Chris R. McNeill, Michael L. Chabinyc & Harald Ade, Polarized x-ray scattering reveals non-crystalline orientational ordering in organic films, Nature Materials 11, 536–543 (2012), Vol 11 number 6, June 2012 (online 15 Apr). doi:10.1038/nmat3310.



(Top Left) The scattering setup where the x-ray passes through the film on to a CCD camera.

(Top Right) Charge carrier mobility as a function of molecular alignment.

(Bottom) The alignment of two different polymers at an interface in an OSC device.

Findings

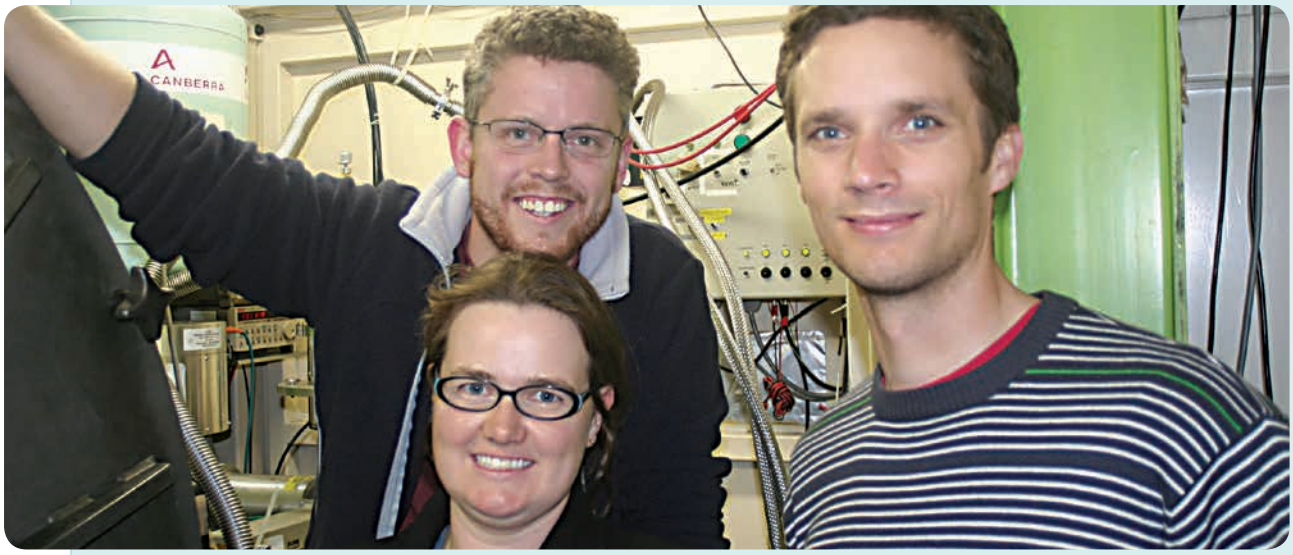
An international team of researchers revealed how alignment between adjacent molecules in these devices can result in a big impact on device performance. They found that increasing the average alignment of molecules, directly enhances the transport of charges through the device. Additionally they discovered that molecular alignment can occur at bulk interfaces within a device, and potentially be used to control the electronic behaviour in interface-critical devices like OLEDs and OSCs.

The researchers found that certain simple device-processing steps could maximize this alignment which tracked with charge mobility in a transistor. Additionally the scattering experiment on OSCs showed anisotropic scattering resulting in alignment of the molecules at the interfaces within the device.

Impact

OSCs are made up of a blend of two phase-separated materials creating a 3D network of interfaces. However, the two materials must interact electronically to separate charges and provide power. Tailoring the alignment of the molecules at these interfaces may affect how efficiently they can turn light into electricity.

Catalysts to make hydrogen: Towards affordable renewable energy sources



Hydrogen has enormous potential as a source of affordable and renewable energy. Researchers investigated its production using new catalysts derived from common earth materials, which would greatly increase production efficiency. They used Australian Synchrotron techniques to investigate precisely how the catalysts work by studying their molecular reactivity and functional components.

Context

One of the most promising approaches to the energy challenge of the 21st century is to design catalysts from earth-abundant materials, capable of catalysing key chemical reactions. This includes the key chemical reactions of splitting water into hydrogen and oxygen ($H_2O \rightarrow 2H^+ + O_2$); and both the oxidation ($H_2 \rightarrow 2H^+$) and reduction ($2H^+ \rightarrow H_2$) of hydrogen.

Promising catalyst materials for these reactions include commonly-occurring metal oxides and sulfides. Critical to developing robust catalysts, is an intimate understanding how these catalysts work in a catalytic state.

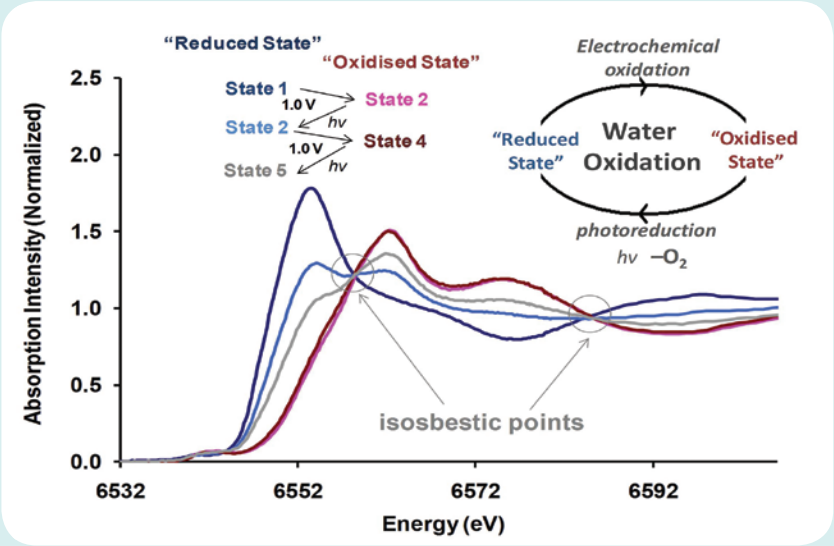
Research question & Synchrotron technique

Researchers tested newly developed catalysts in their functional active states to provide insight into structure and function. Tests involved correlations between advanced synchrotron based spectroscopic probes and electron microscopy based methods.

Publication

Rosalie K. Hocking, Shery L. Y. Chang, Douglas R. MacFarlane and Leone Spiccia, Preparation and Characterization of Catalysts for Clean Energy: A Challenge for x-rays and Electrons, Australian Journal of Chemistry 65(6) 608-614 (2012); 18 May 2012.

Rosalie K. Hocking, Robin Brimblecombe, Lan-Yun Chang, Archana Singh, Mun Hon Cheah, Chris Glover, William H. Casey & Leone Spiccia, Water-oxidation catalysis by manganese in a geochemical-like cycle, Nature Chemistry 3, 461–466 (2011), June 2011 (online 15 May).



The XAS spectra taken from a single electrode. Synchrotron-based x-ray absorption spectroscopy enabled precise observation of the Mn in the system – the data showed the interconversion between an MnOx oxidised state and the Mn2+ reduced state.

Beamline
Australian National Beamline Facility (ANBF)
X-ray absorption spectroscopy (XAS)

Technique:
Hard x-ray spectroscopy

Tweak:
We had to find ways to analyse our electrodes both in electrolyte and in air.

Sample

Type:
Catalyst material capable of splitting water into hydrogen and oxygen.

Of note:
Catalysts dramatically increase the rate of chemical reactions without themselves being changed. This means much less energy is needed to convert water into hydrogen and oxygen. We try to keep our samples as close as possible to their catalytically active state, and study them in situ.

Environment:
Open to air, as close to catalytic conditions as possible.

Synchrotron benefits
It would not be possible to study our material using any other technique at this time. Catalysts are often amorphous materials which are difficult to study by traditional analytical approaches. The tenability of the x-rays on the x-ray absorption beamline meant we could 'home in' on the catalytically active centres of our materials.

Findings

Using these techniques, the researchers were able to successfully elucidate the functional material in an active catalyst. They found that a water oxidation system that had previously been thought to be 'molecular' in origin, was actually a common earth material birnessite – an oxide mineral of manganese. They have since successfully developed a range of new deposition techniques to make integrated birnessite-based electrocatalysts.

In addition to characterising the newly identified birnessite catalyst, the studies also enabled the researchers to understand its likely mechanisms. The Synchrotron's XAS beamline techniques were key to this, as they could 'home in' on the manganese, isolate it from other components of the system, and follow it through a catalytic cycle.

Such a significant understanding of the true origin of the catalyst species, has since informed the design of new electrodes for water oxidation.

Impact

The correlations between the common earth material birnessite, MnOx and the active site of photosystem II. New research will investigate similar mineral based correlations in catalyst active sites.

Solid hydrogen storage material: toward hydrogen batteries

Researchers have developed a new ammine metal borohydride, with potential as a solid hydrogen storage material – in essence, as a hydrogen battery. Their work demonstrated that the storage material can release high purity hydrogen (>99.9%) below 115°C.

Context

Hydrogen is increasingly being considered an excellent source of renewable energy due to its abundance, high chemical energy, and pollution-free combustion.

Since 2003 there has been about 1.2 billion government dollars of research funding allocated to hydrogen-related research in the US. Similar amounts of funding also have been dedicated in EU and Asia. There are also large numbers of industry partners involved – for example, at the 2012 World Hydrogen Energy Conference, Daimler AG, Honda, Hyundai and Toyota all confirmed plans to produce commercial hydrogen fuel cell vehicles available from 2015.

However, an enormous challenge for the application of hydrogen as a renewable energy resource is the development of safe and efficient hydrogen storage materials.

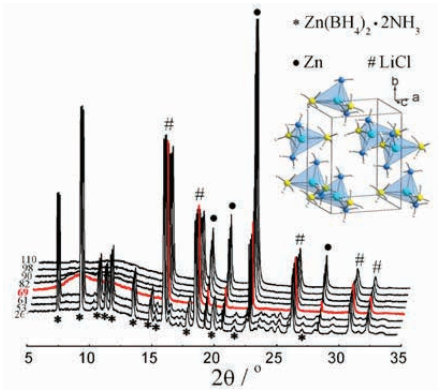
Research question & Synchrotron technique

Researchers from Australia and China aimed to enable novel materials, such as a newly discovered ammine metal borohydride ($Zn(BH_4)_2 \cdot 2NH_3$), to be considered as potential candidates as hydrogen storage materials. This would help provide a simple and viable strategy for the synthesis and modification of various systems, with tuneable hydrogen storage performances.

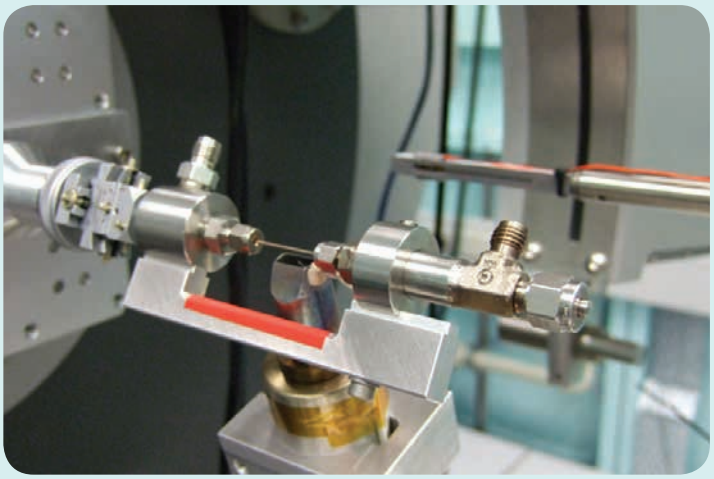
The powder diffraction (PD) beamline at the Australian Synchrotron was used to find new phases, and their structures, to investigate how much hydrogen they can release.

Publication

Qinfen Gu, Liang Gao, Yanhui Guo, Yingbin Tan, Ziwei Tang, Kia S. Wallwork, Feiwu Zhang, Xuebin Yu, Structure and decomposition of zinc borohydride ammonia adduct: towards a pure hydrogen release, Energy Environ. Sci., 5, 7590-7600 (2012), part 6, 1 June 2012 (online 20 April).



In-situ powder XRD patterns and crystal structure of $Zn(BH_4)_2 \bullet 2NH_3$.



Sample measured in a flow cell at PD beamline.

Beamline
Powder diffraction (PD)

Technique:
Powder diffraction

Technique tweak:
The Powder Diffraction beamline's specially designed flow cell, with a temperature control system, is most suitable for this kind of in-situ study.

Sample

Type:
A type of metallic borohydride material, that can release a high weight-percentage of pure hydrogen at a moderate temperature.

Environment:
Flow cell, gas.

Synchrotron benefits
Such in-situ experiments, are only possible with high flex and high resolution beam, as is provided by the Australian Synchrotron.

Findings

Researchers successfully revealed the structure of the new synthesized hydrogen storage material. The new synthesized phase, when compared to original material, had improved retention of H_2 which is a crucial quality for a good hydrogen storage material.

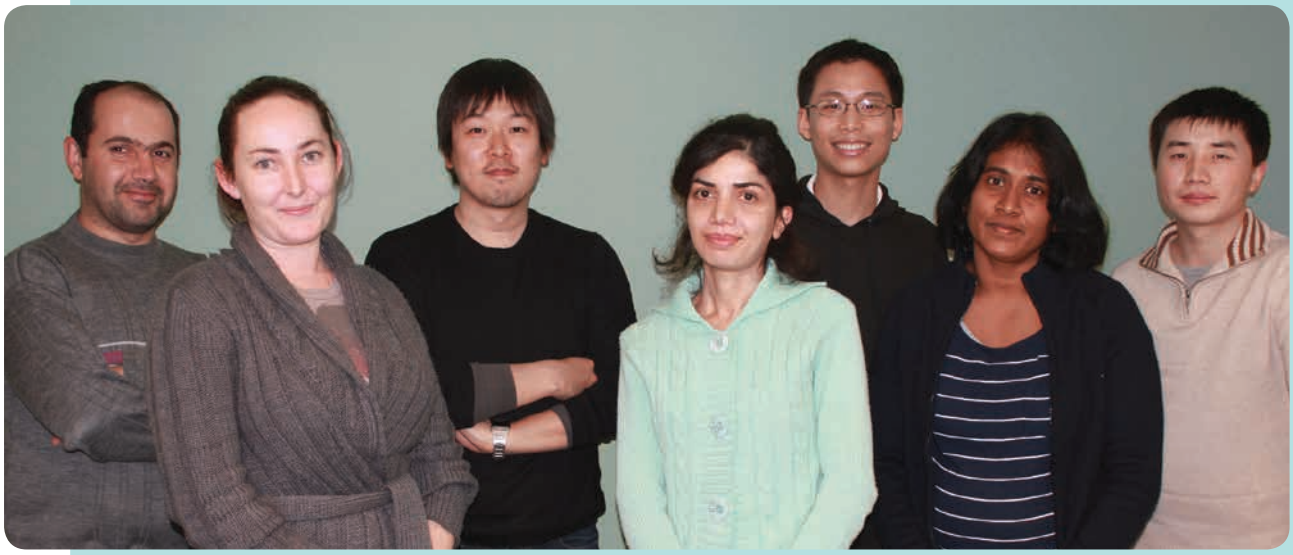
Furthermore, by comparing the crystal structures of metal borohydrides, $Me(BH_4)_2 \bullet 2NH_3$(Me=Zn,Ca,Mg), it has been shown that Zn-H bonding is remarkably shorter in the Zn analogue, thus leading to increased ionic character of H. A correlation between the decreasing of Me-H distance and the enhanced dehydrogenation performance has been observed.

This work demonstrated the potential of ammine metal borohydride for 'on-board' hydrogen storage, such as for laptops and even vehicles.

Impact

The outcome of this research, will enable the design of a hydrogen application chain, to produce hydrogen by electrolysis for the production of renewable electricity. That is, to store hydrogen in solid form and then reuse it to create electricity via a fuel cell, or to supply the hydrogen market.

Novel 'green chemistry' polymer recycling system



Researchers are developing a plastic recycling system in which the plastic is made from components that can later be decomposed by light. The system includes the first demonstration of a complete light-based plastic breakdown process, with the components able to be reused to make new plastic products.

Context

Plastics are complex networks of long molecules (polymers) produced by bonding together a long line of much-shorter, repeating components called monomers, with some links between different molecules as well. Plastics are used in virtually all areas of everyday life – from plastic bags and bottles to office equipment and components of electronic devices and cars. The high demand for plastics, is largely due to their low cost and ease of manufacture.

However, these materials don't break down easily. Predictions indicate that complete degradation of a plastic bottle, for example, could take as long as 30 years. As the fate of most consumable plastic items is as rubbish in landfill, lengthy degradation times present the obvious problem: 'What do we do with all that waste plastic?'

One answer to this question comes from researchers who have developed a novel polymer recycling system.

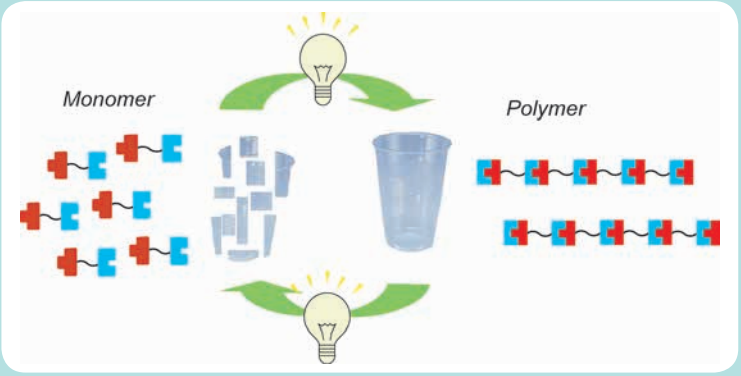
Research question & Synchrotron technique

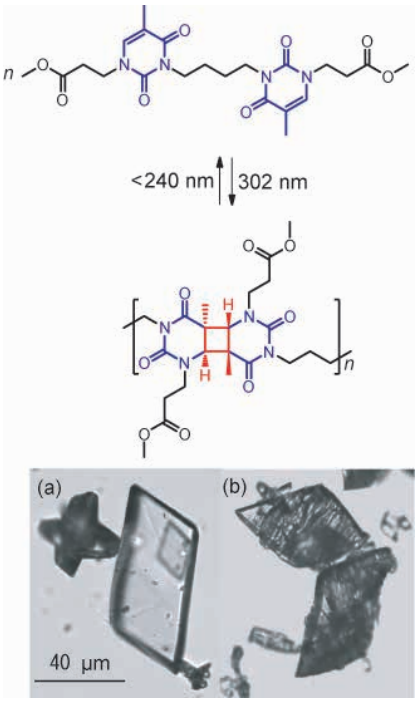
Solid state crystalline reactions are attractive 'green' synthetic pathways in material design, since they occur in solvent-free conditions, and in response to external stimuli such as heat and light. However, only a limited number of chemicals have been shown to undergo solid state crystalline reactions.

As only small or weakly diffracting crystals of monomer for the solid state crystalline reaction were obtained, the data were collected using the micro-crystallography (MX2) beamline at the Australian Synchrotron. This specialised beamline caters for 'difficult' crystals.

Publication

Priscilla Johnston, Carl Braybrook and Kei Saito, Topochemical photo-reversible polymerization of a bioinspired monomer and its recovery and repolymerization after photo-depolymerization, Chem. Sci., 3, 2301-2306 (2012), 1 July 2012 (online 18 Apr).





(L) Photo-reversible polymer recycling system

(R) Topochemical polymerization example. Optical micrographs (400x) of monomer crystals (a) before and (b) after irradiation with 302 nm UV (calc 0.5 kJ.cm-2).

Opposite: Dr. Kei Saito's research group

Beamline
Micro-crystallography (MX2)

Technique:
Single crystal diffraction

Sample

Type:
Solid crystals. The crystals were too small to be analysed by standard x-ray diffraction techniques.

Of note:
Polymerisation can take place in solid crystals.

Environment:
Open to air

Synchrotron benefits
As we could only obtain small or weakly diffracting crystals of monomer for the topochemical reaction, the data were collected using the micro-crystallography beamline at the Australian Synchrotron. This saved time and money and, most importantly, gave us a particular result that I could not get from other instruments.

Findings

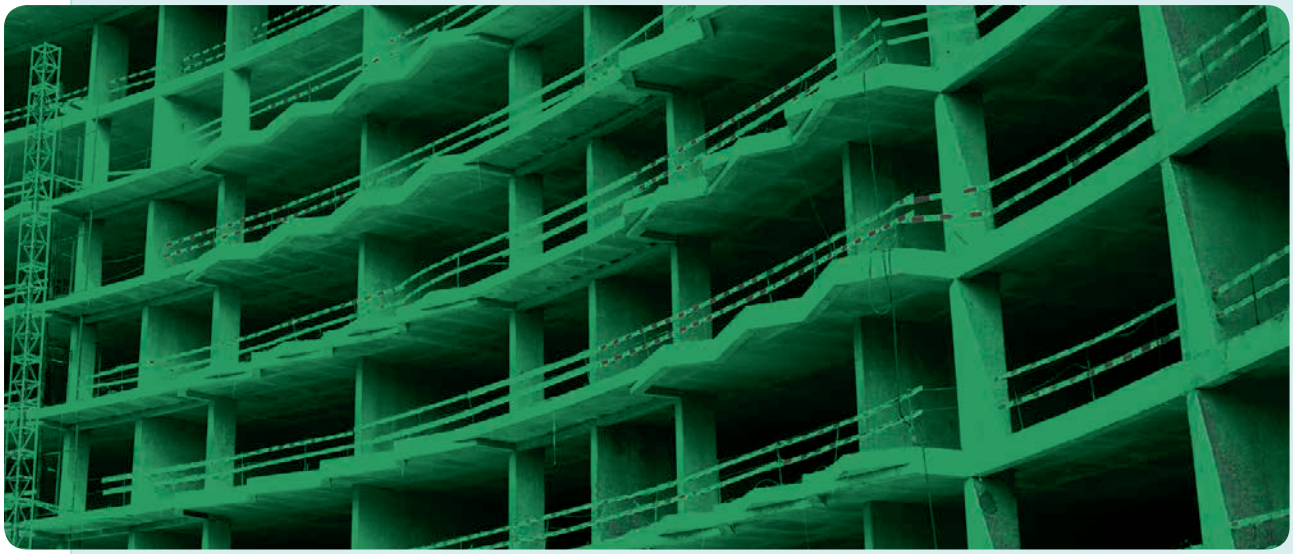
Researchers used the solid state crystalline reversible [2ϖ + 2ϖ] cyclo-addition of a bio-inspired bis-thymine monomer to develop a new polymer recycling system. The starting material, monomer crystal, forms a polymer on exposure to a particular wavelength of UV light.

The resulting polymer can be fully degraded by exposure to a different wavelength of UV light, back to the monomer starting materials, which can be chemically recycled to make new plastics.

Impact

This new technology produces a recyclable plastic that can be broken down into its original monomer components by UV light, and the monomer components then reused to create another polymer of similar structural integrity.

Constructing a lower carbon footprint



Melbourne company Zeobond, has produced a 'green' cement from fly ash – a by-product of coal production. They used the Australian Synchrotron to investigate its molecular structure, and demonstrate its strength for use in footpaths, buildings and major road construction projects. The product produces 80 per cent less CO_2 than other methods, and is now used on a commercial scale in Victoria.

Context

Concrete is the single most used material by humans on the planet. Its production is also the world's third largest contributor to CO_2 emissions.

Traditional concrete consists of gravel, sand, water and a binder such as Portland cement, a mineral mixture that includes tricalcium silicate ($3CaO.SiO_2$) and aluminate ($3CaO.Al_2O_3$). The cement hydrates when mixed with water and then hardens to bind the gravel and sand particles. Geopolymer alternatives replace the high-calcium binder with industrial wastes such as fly ash, considerably reducing CO_2 emissions during production, and solving a major waste management problem.

Melbourne company Zeobond produces 'green' geopolymer cement product, called e-crete, on a commercial scale for use in footpaths, buildings and major road construction projects.

Research question & Synchrotron technique

Researchers John Provis (formerly at the University of Melbourne) and Jannie van Deventer (the founder of Zeobond) and their colleagues used the Australian Synchrotron's x-ray flouresence microscopy (XFM) and infra-red radiation (IR) beamlines, to investigate the basic chemistry of geopolymer formation. This pairing of synchrotron techniques is rapidly increasing knowledge of binder structure across all the length scales that influence strength, permeability and durability.

Publication

John L. Provis, A. Hajimohammadi, C.E. White, S.A. Bernal, R.J. Myers, R.P. Winarski, V. Rose, T.E. Proffen, A. Llobet, Jannie S.J. van Deventer, Nanostructural characterization of geopolymers by advanced beamline techniques, *Cem. Concr. Compos.*, (2012). 36, February 2013, 56–64.

E-Crete used for new work on the Swan Street Bridge, Melbourne (Photo: Zeobond)

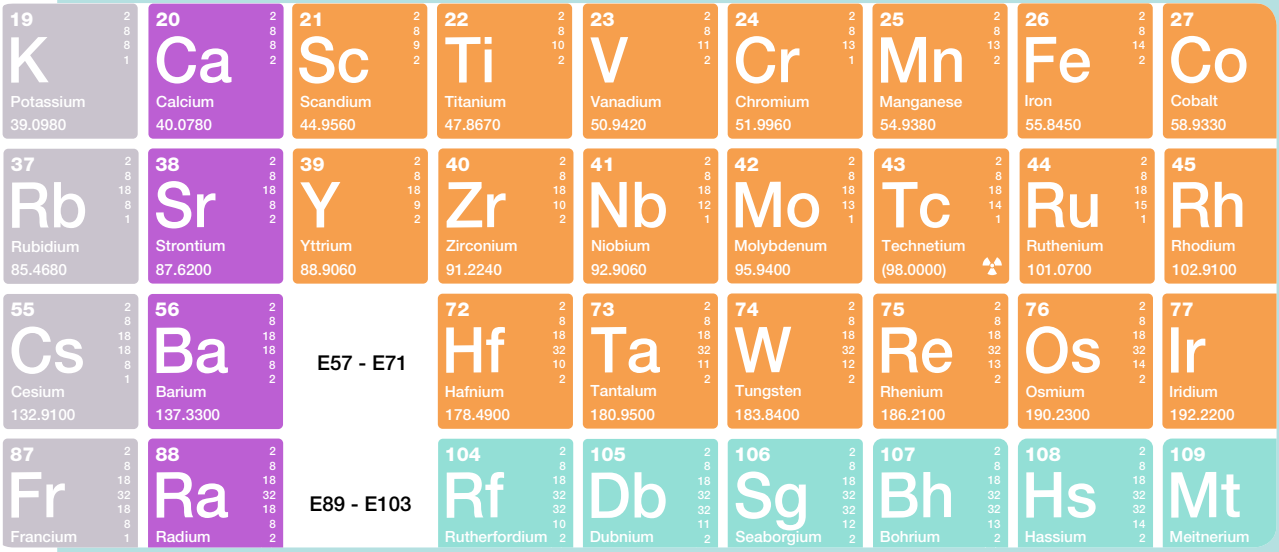
Findings

The researchers combined their synchrotron findings with other advanced techniques to develop a good understanding of geopolymer gel chemistry, nano- and microstructure in two and three dimensions, and the influences of seeded nucleation and precursor chemistry.

Impact

The availability of synchrotron techniques has helped bring about major improvements in the understanding of detailed geopolymer chemistry, previously considered intractable due to the disordered nature of the aluminosilicate binder gel. Researchers now understand how key compositional parameters influence nanostructure, and can manipulate both gel structure and reaction kinetics using methods such as seeding, temperature variation, and careful mix design.

An extraordinary magnetoelastic effect in a third-row transition metal oxide



The barium bismuth iridium oxide $Ba_3BiIr_2O_9$, a perovskite-type metal oxide, has been found to exhibit the largest magnetoelastic effect of any known third-row (5d) transition metal compound.

Context

Perovskite-type minerals have numerous commercial applications such as medical sensors for measuring blood pressure, microphones, mobile phones, hydrogen fuel cells, and sonar transducers for tracking fish and submarines. Japan alone fabricates an estimated four billion devices containing perovskites each year.

The reason for the widespread usage of perovskites is the enormous structural and compositional flexibility of their structure. Perovskite-type oxides can be fine-tuned to take advantage of an appropriate structural, electronic, or magnetic 'instability', which confers a particular functional capability such as that required for switches in computer memories.

The unusual phenomenon of negative thermal expansion (NTE), where the volume of a material expands on cooling, can arise through various mechanisms. Some are essentially mechanical, based on the thermal motion of coupled rigid units, as in zirconium tungstate, ZrW_2O_8, for example. Others involve a redistribution of electron density, often associated with changes in magnetic properties, as in the nickel-iron alloy Invar.

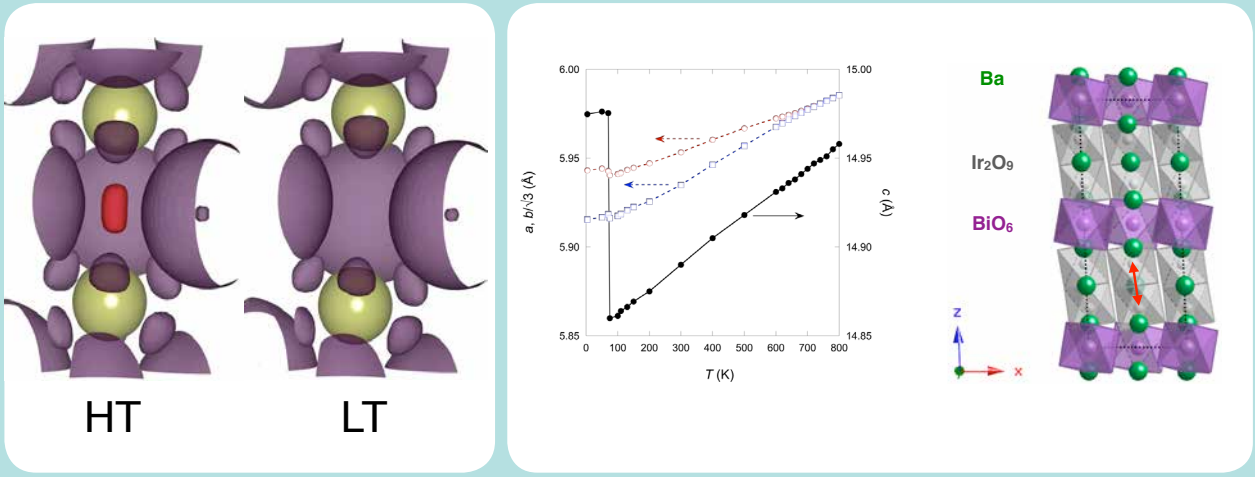
Second (4d) and third-row (5d) transition metals rarely exhibit quantum cooperative phenomena such as magnetoelasticity because their valence orbitals are much more diffuse than in their first-row counterparts.

Research question & Synchrotron technique

The researchers used Australian Synchrotron x-ray powder diffraction (PD) to investigate thermal expansion behaviour down to the temperature (T* = 74 K) at which the 6H-type hexagonal perovskite compound $Ba_3BiIr_2O_9$ undergoes a large negative thermal expansion due to the opening of a spin-gap. They used x-ray absorption spectroscopy (XAS) to assess the validity of an obvious (and less interesting) alternative explanation that valance transfer between bismuth and iridium might account for the observed behaviour at T*.

Publication

Wojciech Miiller, Maxim Avdeev, Qingdi Zhou, Brendan J. Kennedy, Neeraj Sharma, Ramzi Kutteh, Gordon J. Kearley, Siegber Schmid, Kevin S. Knight, Peter E. R. Blanchard and Chris D. Ling, Giant Magnetoelastic Effect at the Opening of a Spin-Gap in Ba3BiIr2O9, J. Am. Chem. Soc., 134 (6), 3265–3270 (2012), 15 February 2012 (online 26 Jan).



Electron localisation function (ELF) from ab initio calculations of the electronic structure for the high-temperature (HT) and low-temperature (LT) states. Isosurfaces are drawn for ELF = 0.38. The red localisation domain encloses a single ELF maximum of the Ir–Ir bond (ELF = 0.43) at HT, which vanishes at LT.

Findings

The results show that $Ba_3BiIr_2O_9$ is an entirely new example of negative thermal expansion involving a redistribution of electron density associated with magnetoelastic changes. As this compound is cooled through its transition temperature, a sudden four per cent increase in Ir-Ir bond length produces a giant 1.0 per cent volume NTE, accompanied by a sharp drop in magnetic susceptibility.

Impact

More-recent high-pressure, powder diffraction experiments using diamond anvil cells have revealed even more interesting behaviour in these and related compounds. The researchers believe that many more fascinating new compounds and phenomena remain to be discovered.

Beamline
Powder diffraction (PD)
X-ray absorption spectroscopy (XAS)

Technique:
Powder diffraction and hard x-ray spectroscopy

Sample

Type:
6H-type hexagonal perovskite-type $Ba_3BiIr_2O_9$

Of note:
This shows the largest magnetoelastic effect ever observed in a 5d (or 4d) oxide.

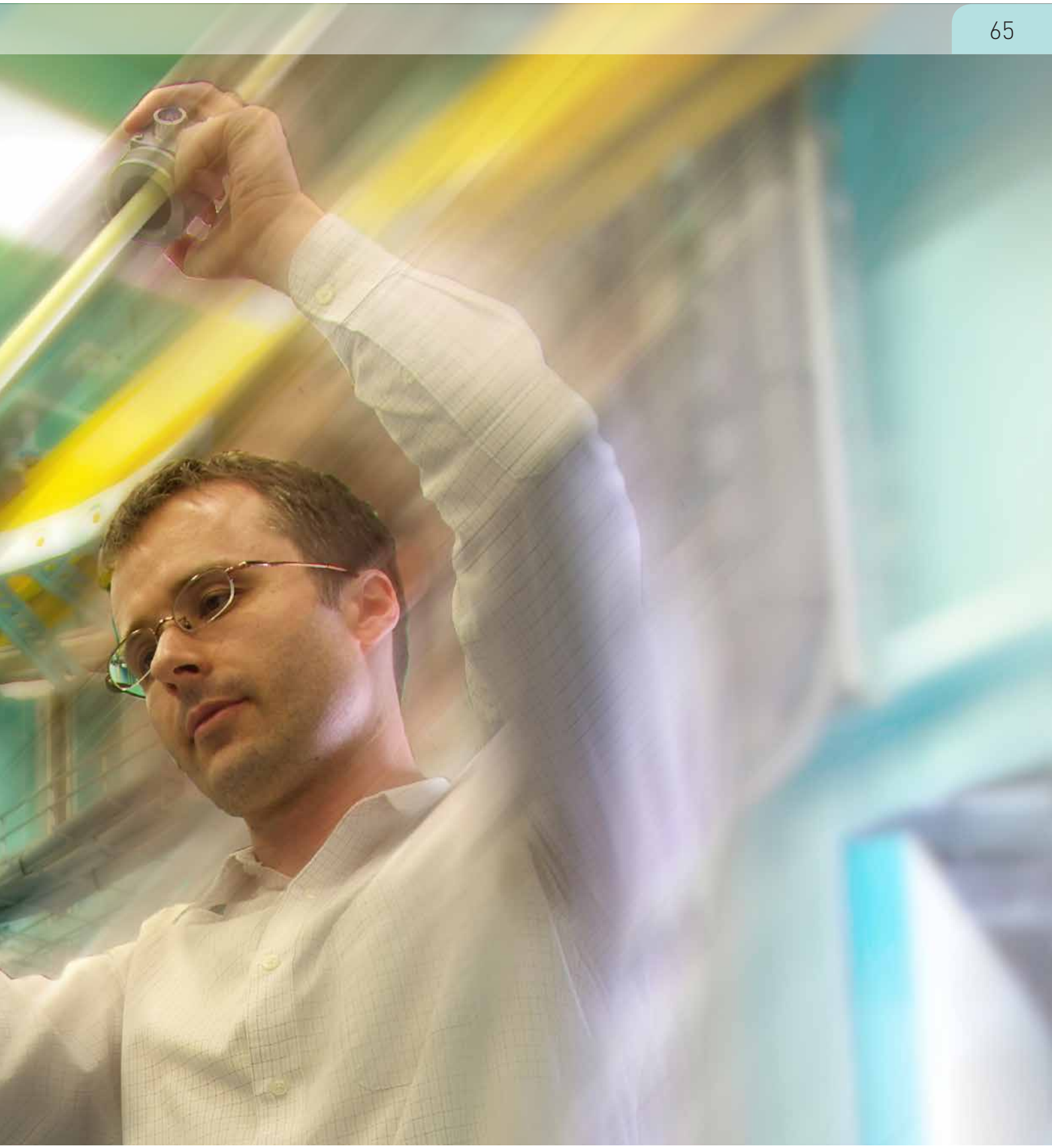
Environment:
Open to air, low temperature

Tweak:
The sample had to be deposited on high-grade filter paper, rather than pressed into a KBr pellet, due to its extremely high x-ray absorption cross-section.

Synchrotron benefits
The Australian Synchrotron provided unique information that allowed us to rule out a relatively trivial alternate explanation for the physical properties of our sample.

Earth & environmental sciences

INDEX



Preventing scale formation in alumina production – Bayer process

Uncontrolled nucleation and growth of scale material in processing lines causes substantial process losses for the alumina industry. This investigation into aluminium hydroxide crystallisation will assist in developing strategies to control scale formation and, therefore, more efficient processing.

Context

The Bayer process is used to refine bauxite ore - a mixture of various aluminium-bearing minerals, iron oxides and quartz - into alumina. Significant process losses are encountered through the build-up of insoluble scale material on the mild steel process equipment.

Research question & Synchrotron technique

In April 2010 a research team used the powder diffraction (PD) beamline at the Australian Synchrotron to investigate the effect of a number of different mild steel corrosion products on nucleation and growth of aluminium hydroxide under simulated Bayer process conditions. These in situ synchrotron experiments complemented larger scale crystallisation experiments performed by colleagues, where the kinetics of a number of different reactions were determined by monitoring the conductivity of Bayer liquors over time.

The rationale behind the PD experiments was to identify any variations in the mineralogy of the aluminium hydroxide throughout the crystallisation process, information not available using any other technique.

Findings

The results showed that goethite, one of the mild steel corrosion products - or 'seeds' - tested, was the most effective in promoting aluminium hydroxide crystallisation, followed by hematite and magnetite. In addition, for each seed the crystallisation proceeded via a two-stage mechanism. The early stages (that is, the first 5 minutes) were characterised by the nucleation of the gibbsite form of aluminium hydroxide on the seed material. As time increased, further gibbsite formation was accompanied by the formation of minor amounts of the bayerite and nordstrandite forms of aluminium hydroxide, both of which were previously unknown in the context of Bayer scale formation mechanisms.

Researchers have commented that the expertise provided by the beamline scientists before and during the experiment was crucial to achieving the desired outcomes. In addition, the very high resolution and signal-to-noise ratio of the PD data were essential to fully characterise the aluminium hydroxide nucleation and growth mechanisms, resolution and signal-to-noise ratio that are simply not attainable using laboratory-based PD instruments.

Publication

Nathan A.S. Webster, Melissa J. Loan, Ian C. Madsen, Robert B. Knott, Justin A. Kimpton, An investigation of the mechanisms of goethite, hematite and magnetite-seeded Al(OH)3 precipitation from synthetic Bayer liquor, Hydrometallurgy, 109, 72-79, (2011), September 2011.

Dr Nathan Webster setting-up a sample stage for in situ studies on the PD beamline.

Beamline
Powder diffraction (PD)

Technique:
Powder diffraction

Tweak:
Something which was fairly new to the beamline at the time (but which is routine now) was the connection of a gas pressure line to the capillary reaction vessel so as to apply an overpressure of N_2 to the capillary. The presence of the pressure line meant that the capillary was only oscillated through 270° to avoid tangling of the line. Oscillation was essential to ensure uniformity of heating and accurate observed relative peak intensities through sufficient particle statistics.

Sample

Type:
$Al(OH)_3$ polymorphs crystallising from mixtures of $FeOOH$, Fe_2O_3 or Fe_3O_4 seed materials and supersaturated $Al(OH)_4^-$ liquor at 70°C.

The known concentration of seed material in the starting mixture was used as a standard to determine the concentration of crystallising material, as a function of time, on an absolute basis.

Environment:
Capillary reaction vessel, mild heating

Tweak:
The choice of solid loading in the starting seed/liquor mixture (~14 wt%). This was a balance between achieving high peak-to-background ratios of both the seed and the crystallised $Al(OH)_3$ material, and achieving a mixture of appropriate viscosity to enable it to be injected into the capillary reaction vessel using a syringe.

Impact

The development of strategies to combat scale formation will create a more efficient process, saving the $12 billion dollar alumina industry in Australia, millions of dollars per year.

Synchrotron benefits

The excellent counting statistics and very high resolution of the data collected on the powder diffraction beamline were crucial for the observation of weak bayerite and nordstrandite (both polymorphs of Al(OH)3) reflections, in addition to those of the gibbsite polymorph (the major phase). The observation of these minor phases, which was not detected in parallel in situ experiments performed on a laboratory-based INEL diffractometer, was crucial for full characterisation of the mechanisms in the early stages of crystallisation, and the effects of the different iron oxide/oxyhydroxide seed materials on these mechanisms.

The question then asked was, "Why did these minor phases form?" Given that they were not observed in gibbsite-seeded and unseeded experiments also performed on the powder diffraction beamline, it was suggested that chemical interactions between the iron oxide/oxyhydroxide seeds and $Al(OH)^{4-}$ species in the liquor alters the arrangement of $Al(OH)_4^-$ adjacent to the seed particles. This then affects the network of hydrogen bonds holding layers of edge-shared Al-O octahedra together and, therefore, the ordering of the layers which distinguishes the bayerite and nordstrandite crystal structures from that of gibbsite.

Finding gold in semi-arid regions

Researchers investigating new gold exploration methods for semi-arid regions have found that near-surface laminated calcrete is a useful material to analyse. Gold, silver and calcium are mobile throughout soils in semi-arid environments and their presence in the calcrete may provide an indication of distant gold deposits.

Context

Calcrete sampling is the near-surface exploration method of choice for gold in many drier parts of the world, particularly southern Australia. Calcrete is mostly comprised of calcium carbonate and accumulates in the soil as a result of dust, aerosol and rainfall derived originally from the ocean.

Edoldeh Tank is a weakly mineralised gold prospect in calcreted terrain at the eastern edge of the Great Victoria Desert dunefield (South Australia). The dominant form of calcrete at Edoldeh Tank is a laminated form.

Research question & Synchrotron technique

The researchers used a variety of techniques, including scanning electron microscopy, laser ablation inductively coupled mass spectroscopy and x-ray fluorescence microscopy (XFM) at the Australian Synchrotron – to determine the distribution and nature of the gold in Edoldeh Tank calcrete at the microscale. The team also dated sediments to understand calcrete genesis.

Findings

In a series of 30 excavated soil pits, calcium and gold concentrations increased with depth, with a marked change at the laminated calcrete horizon at about 40cm. The team used multiple lines of evidence to identify a general association between gold and calcrete, but not as strong a correlation as seen with soil profiles elsewhere that contain younger powdery calcrete. This suggests that the gold is not as mobile in the calcrete once it is locked in there.

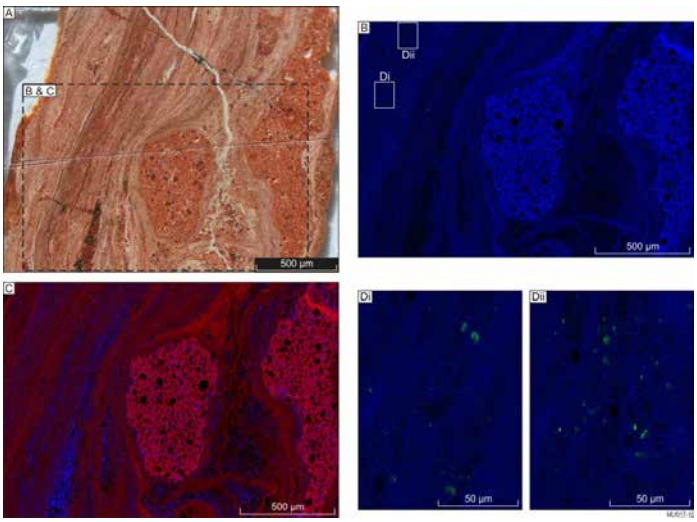
Using the Synchrotron we were able to locate, identify and characterise grains of gold within the calcrete. We found relatively large and small grains of gold throughout different regions of the calcrete. The studies complemented earlier work undertaken at the Synchrotron that showed gold associated with plant roots. Together these observations enabled us to make interpretations on how the gold may have been emplaced and specifically what geochemical processes may have been operating.

In summary:

1. Gold and silver are currently mobile in this environment despite the low rainfall and that gold occurs in two forms: gold (possibly ionic) occurs throughout the sample with some regions having higher concentrations than others; particulate gold occurs randomly but is more common where the general level of gold is higher.

Publication

Melvyn Lintern, Rob Hough and Chris Ryan, Experimental studies on the gold-in-calcrete anomaly at Edoldeh Tank Gold Prospect, Gawler Craton, South Australia, J. Geochem. Explor., 112, 189–205 (2012), January 2012.



Element mapping using SXRF for sample ETP08. (A) Thin section with outline showing SXRF analysis area. (B) Sr (blue) and Au (green) distribution. (C) Fe (red) and Sr (blue) distribution. (D) Detailed parts of image B showing presence of Au particles (green).

2. The laminated nature of the calcrete suggests it has formed episodically.
3. An association of silver with gold in calcrete suggests a means to distinguish anomalies that have developed in residual regolith from those that have dispersed into adjacent sediments.
4. Laminated calcrete is just as effective an exploration sample medium as powdery calcrete. Mobilised calcium, gold and silver in calcrete can extend the lateral extent and distance from the source of the geochemical anomaly thus providing an effective vector to target for sampling.

Impact

The study provides researchers and mineral explorers with a greater understanding of the behaviour of gold in a semi-arid environment. The work is expected to assist future efforts to discover new ore deposits in these difficult exploration environments.

Beamline
X-ray fluorescence microscopy (XFM)

Technique:
Spectroscopic mapping (SXRF)

Tweak:
We used a Maia 384 detector array with x-rays focussed into a beam spot of ~1.5 µm using the Kirkpatrick-Baez mirror-based lens system. This system enables rapid analysis (8 hours) of a large area (~2 cm^2) at about 1-2 µm spatial resolution; i.e. an order of magnitude more efficient compared with conventional x-ray detectors for identifying Au in soil samples.

Sample

Type:
A lump of calcrete rock excavated from the soil.

Of note:
The sample was taken from near a mineral deposit and was likely to contain gold.

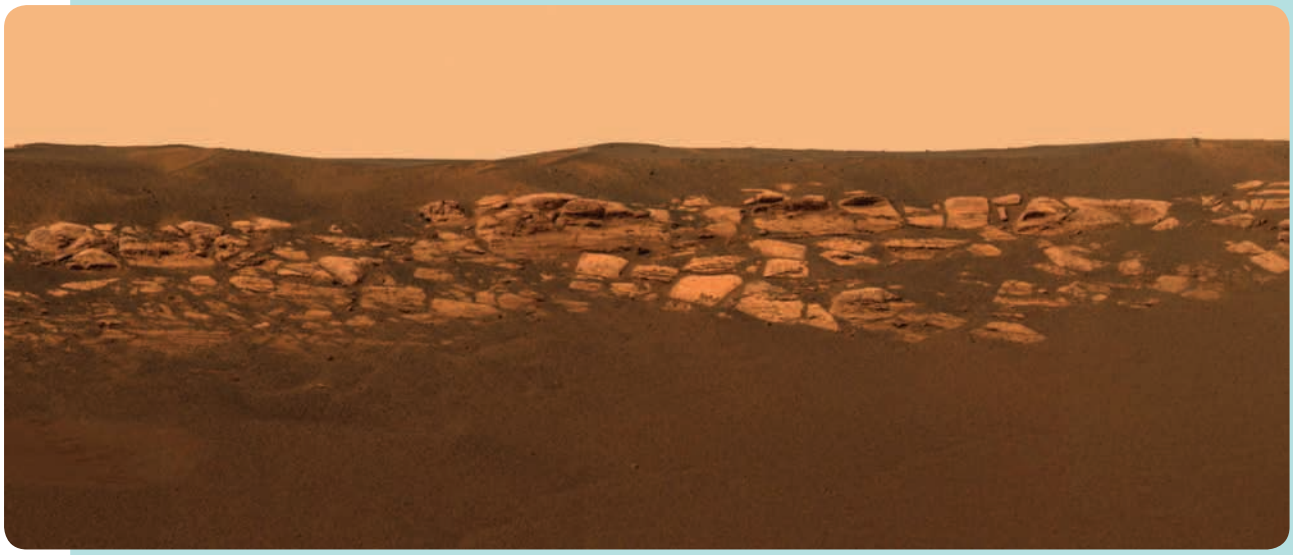
Environment:
Open to air

Tweak:
We prepared a 'thin section that was 'thick' enough to present a greater volume, because normal thin sections are easily penetrated by the synchrotron beam and much analysing power is 'wasted'. Trying to find gold in a calcrete sample is like trying to find a needle in a haystack! The Maia detector increases the odds in our favour!

Synchrotron benefits
Large area mapping at fine scale and real time processing increases the probability of being able to correlate petrological features in specimens, enables products of weathering and associated geochemical dispersion to be investigated and placed in a better context, and permits many more samples to be analysed, increasing the probability that observations are truly representative of the interpreted processes.

The Australian Synchrotron has been a boon to researchers such as ourselves. We would never have been able to identify and analyse gold in this way before.

Learning to control jarosite formation



Jarosites are important industrial minerals; they are formed deliberately to remove iron from hydrometallurgical circuits but form detrimental kinetic barriers in bioleaching systems. On Mars, jarosites may be the key to unlocking the geological history and environmental context of water.

Context

Jarosite minerals are naturally occurring hydrous sulphates of potassium and iron, and are widespread in a number of industrial and environmental settings. Understanding their formation, mineralogy and stability is of the highest priority in order to streamline industrial processes where jarosites are involved and understand the geological evolution of environments where they abound.

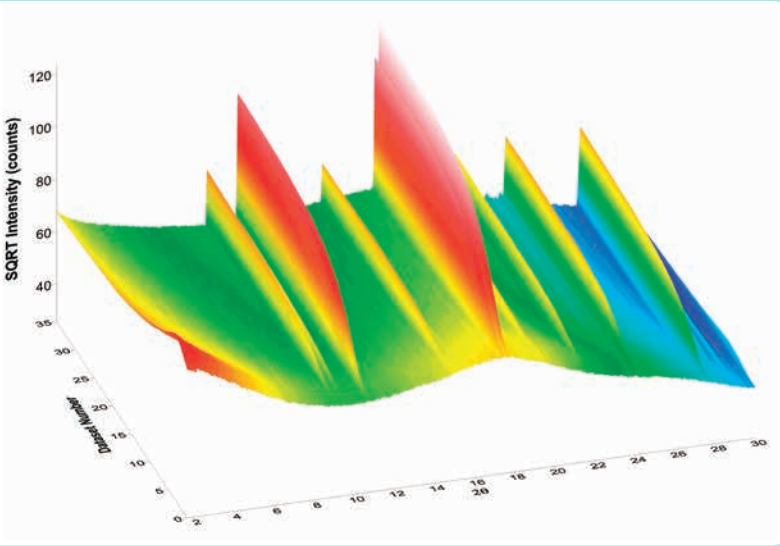
Research question & Synchrotron technique

As part of a larger suite of experiments designed to map the nucleation and crystallisation of jarosite, data was collected from both the small-angle scattering (SAXS) and powder diffraction (PD) beamlines at the Australian Synchrotron.

SAXS is sensitive to scattering from whole particles while powder diffraction results from the crystalline structure of the material. This means that SAXS can be used to probe the earliest stages of formation when the first nucleation of jarosite particles occurs. The powder diffraction measurements are then used to characterise the crystallisation process.

Publication

Helen E. A. Brand, Nicola V. Y. Scarlett and Ian E. Grey, In situ studies into the formation kinetics of potassium jarosite, J. Appl. Cryst. 45, 535–545 (2012), Vol 45 part 3, June 2012.



Accumulated synchrotron powder x-ray diffraction patterns showing the formation of jarosite from solution over time. Three-dimensional plot with diffraction angle (2theta) on the x-axis, dataset number (which relates to elapsed time) on the y-axis and intensity on the z-axis. The figure views the patterns from an angle that clearly shows the growth of the jarosite peaks.

(Opposite) Eagle crater PIA05163, Mars, where jarosite was first found on the ground (NASA/JPL/Caltech).

Findings

Jarosite was formed by coprecipitation from a solution of iron and potassium sulphates. Scattering data were collected continuously as the solutions were heated at different temperatures. Using this setup it was possible to observe the jarosite forming in real time. This in situ approach ensures that no information is lost or misrepresented through artefacts which may be introduced by cooling and sampling in a more traditional way.

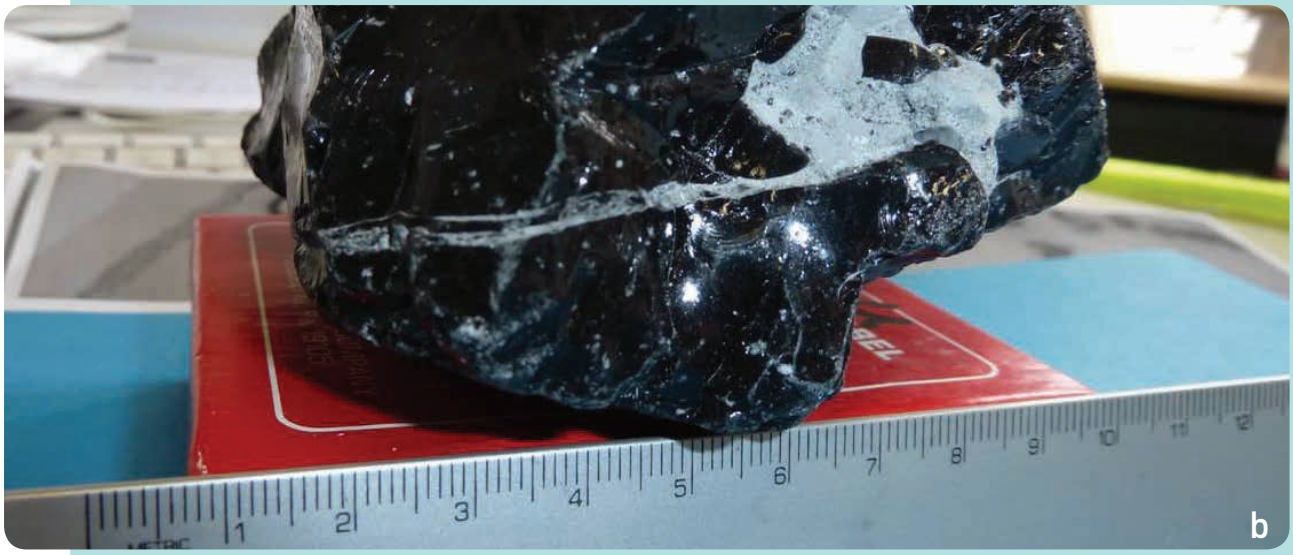
The small angle scattering results suggest that particles form via a single nucleation event: that is similar sized elliptical discs form at the same time and then grow. This happens very rapidly. From this observation, it is clear that controlling this nucleation event is the key to controlling jarosite formation in environments where its prevention is required.

The powder diffraction results show that the later crystallisation of the jarosites is mainly reliant on the availability of material in the solution. This is of great importance to areas where jarosite formation is actively encouraged, for example Zinc processing solutions. In these cases prolonged jarosite formation may be improved by paying particular attention to factors such as stirring and reagent supply rate.

Impact

For environments containing jarosite minerals, such as the equatorial regions of Mars, these results help to constrain the environmental conditions which must have been present for these minerals to form. And so, they provide another crucial data point in this planet's complicated geological evolution.

Understanding non-explosive volcanic emissions



Explosive volcanic eruptions of silicic magma often evolve towards non-explosive lava emissions, but the mechanisms driving this transition are unclear. Previously thought a critical influence, melt fracturing may instead provide gas-escape pathways for more efficient degassing of permeable vesicular magma in the conduit interior.

Context

Explosive eruptions occur when dissolved volatile components in magma, such as H_2O, CO_2, SO_2, and HCL, come out of solution, fuelling the growth of bubbles that later fragment the magma apart. Lava eruptions, which are mostly non-explosive, are believed to result from a fundamentally different degassing process that allows more efficient gas separation while the magma rises and extrudes at the surface.

Magma fragmentation, or melt fracturing, is a mechanism by which gas is widely thought to quiescently separate during lava eruptions. Degassing of tiny fragmented particles along with the permeable flow of liberated gas has been suggested to be critical in defusing explosive eruptions and making lava.

Research question & Synchrotron technique

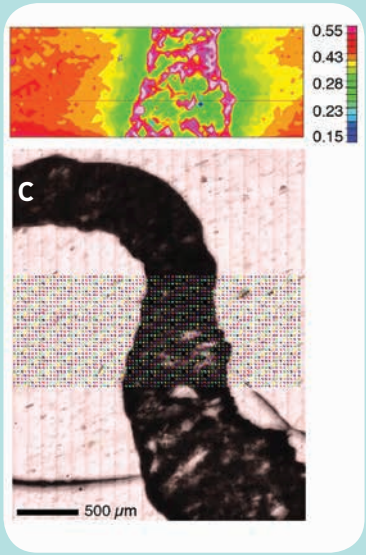
Led by Dr Jon Castro, a research team examined the degassing signatures of several fragmented lava samples from an active volcano in Chile to assess the feasibility of the melt fracturing hypothesis. The work demonstrated, for the first time, that the amount of time gas needs to escape effectively through fractured magma is significantly greater than the observed transition from energetic explosive to effusive volcanic eruptions.

Using highly sensitive measurements of H_2O at the Australian Synchrotron Fourier transform infrared spectroscopy (FTIR) data collection, at the microspectroscopy, the team were able to map the spatial distribution of magmatic 'water' around cracks.

Molecular H_2O and hydroxyl groups (OH-) are the most abundant volatile species in magma. These are not liquid species like surface waters but rather 'locked' into the melt structure via chemical bonds. Therefore, when magma explodes, it is due to the removal of this so-called magmatic 'water' from a dissolved state to one that is liberated as a gas in the atmosphere. Hydrous (water-based) species are also very resolvable with established FTIR techniques, meaning we can map their distribution with great precision and from these patterns learn about the modes and rates of magmatic degassing.

Publication

Jonathan M. Castro, Benoit Cordonnier, Hugh Tuffen, Mark J. Tobin, Ljiljana Puskar, Michael C. Martin, Hans A. Bechtel, The role of melt-fracture degassing in defusing explosive rhyolite eruptions at volcan Chaiten, Earth Planet. Sci. Lett. , 333-334, 63-69, (2012). 1 June 2012.



(a) The 2008 eruption of Chaitén volcano. Samples for this study come from the crater seen in this image (photo credit Jeff Marso, USGS). (b) Typical obsidian bomb containing fragmental lava (grey). We measure d the H_2O distribution at the contacts between the black glassy and lighter ashy infillings. (c) Thin wafter of glass-ashy (black) contacts and several analysis points defining the colourful map of H_2O concentration, overhead. The decrease of H_2O near the boundaries (degassing) is evident as a systematic shift of colour next to the ashy vein.

Beamline
Infrared microspectroscopy (IR)

Technique:
Microscopy - infrared spectroscopy and mapping

Technique tweak:

Our research benefited from collecting very large maps (>2000 analysis points) although, this took a very long time to acquire the data.

Sample

Type:
Natural volcanic glass of high silica content, from an active volcano. Magmatic 'water' can be imaged at high resolution and be shown to have migrated into cracked and fragmented lava.

Environment:
Open to dry air

Tweak:
We had to doubly polish our samples and thin them down to little over the thickness of a piece of paper (~50 μm).

Synchrotron benefits
The Australian Synchrotron is a 'top shelf' facility - it brought me much honour and excitement to be able to work there. The IR beamline is particularly well set-up for mapping and quantifying H_2O and CO_2 in glasses. This, along with the very low detection limits mean I can see geochemical patterns in my samples that I could not elsewhere.

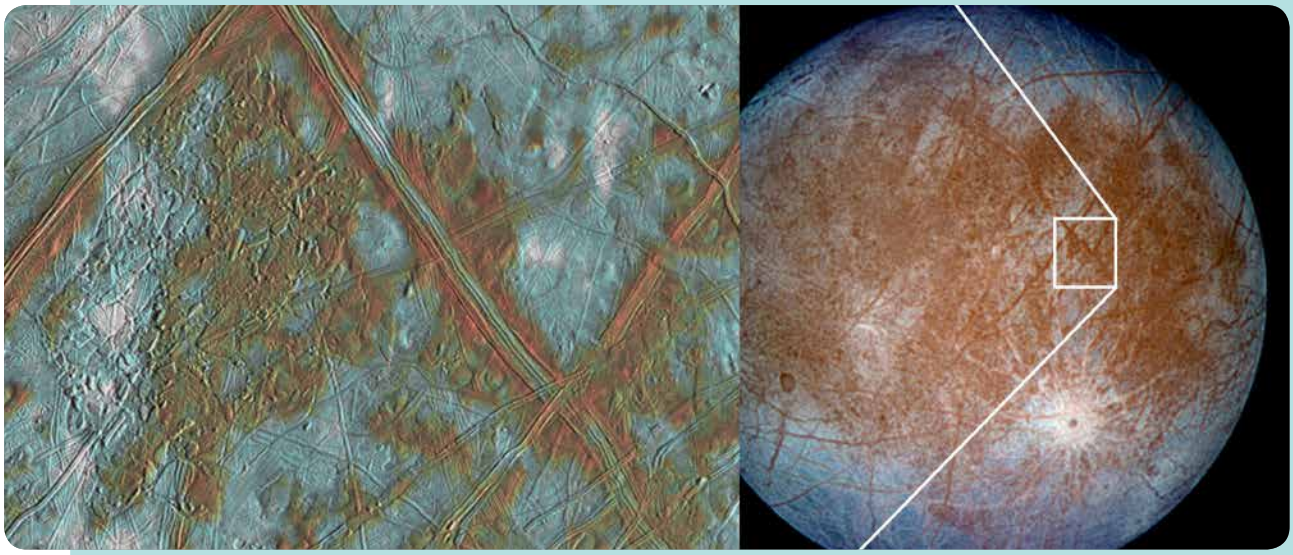
Findings

The geochemical patterns indicated by the Synchrotron technique, suggest that degassing into fractures is a very sluggish process and may take several days longer than expected to effectively degas lava. It was determined that the main role of fracturing during volcanic eruptions is to provide efficient gas escape paths for volatiles coming from deeper in the system. Importantly, those deeper, far-travelled volatiles must have been liberated by means other than melt-fracture degassing.

Impact

These findings paved the way for future studies seeking to identify important mechanisms of gas loss during volcanic eruptions, especially those that can be revealed utilizing synchrotron-source FTIR.

Powder diffraction goes to the planets



Recreating the environmental conditions of Jupiter and Saturn's icy moons sounds like an impossible task, but Australian Synchrotron's research staff are successfully investigating some of the simple materials behind the moons' extraordinarily complex geological features.

Context

Unlike Earth, which is made of silicate rocks, the moons in orbit around Jupiter and its sister planets Saturn, Uranus and Neptune are made of icy materials: mixtures of water, salts, methane and ammonia.

Despite their relatively simple makeup, these planetary bodies exhibit some extraordinarily complex geological features. From the Chaos Terrain on Europa (a moon of Jupiter) to the Tiger Stripes of Enceladus (one of Saturn's companions) it seems that these simple molecules can produce just as diverse features as their terrestrial silicate counterparts.

Researchers are still some way from discovering how these features form, mainly because all the physical parameters of the materials that make up these moons are not yet understood. For example, there's evidence to support the fact that crystalline sulphuric acid hydrates make up some of Europa's surface, but some fundamental questions about these materials, such as their crystal structures, remain unanswered.

Research question & Synchrotron technique

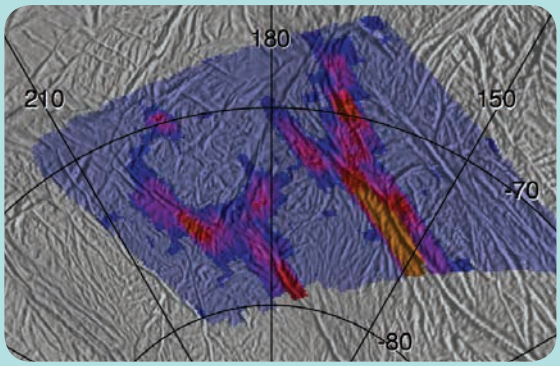
How do these materials respond to heat, and what crystal structures do they favour?

Australian Synchrotron researchers are recreating moon-like conditions at the powder diffraction (PD) beamline, and using the beamline's high-resolution diffraction capacity to probe these materials from the inside.

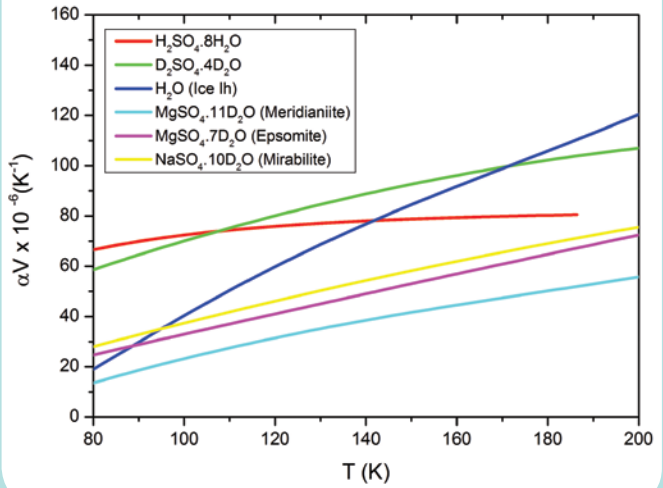
They have re-evaluated the structure of the most water-rich sulphuric acid hydrate (an octahydrate) and measured its thermal expansion.

Publication

Helen E. Maynard-Casely, Helen E. A. Brand and Kia S. Wallwork, Structure and thermal expansion of sulfuric acid octahydrate, J. Appl. Cryst. 45, 1198-1207 (2012), Vol 45 part 6, December 2012



Some of the rich surface features found on the icy moons of the outer solar system. (Opposite) The Chaos terrain on Europa, where rafted blocks of ice have been re-frozen into new positions. (Above) A heat intensity map of Enceladus's Tiger Stripe features, which actively spray water and volatiles from the moon's interior. Both images are from the Jet Propulsion Laboratory's photo journal site http://photojournal.jpl.nasa.gov



(Above) Comparison of the volume thermal expansion coefficient, for SAO (red line this work) as calculated via the Einstein model (circular points) compared with Ice Ih (blue line (Rottger et al., 2012)) and perdeuterated sulfuric acid tetrahydrate (green line, (Fortes, Wood, Vocadlo, et al., 2008)), Meridianiite (light blue line, (Fortes, Wood & Knight, 2008)), Epsomite (pink line (Fortes, Wood, Alfredsson, et al., 2006)) and Mirabilite (yellow line (Brand et al., 2009)).

Findings

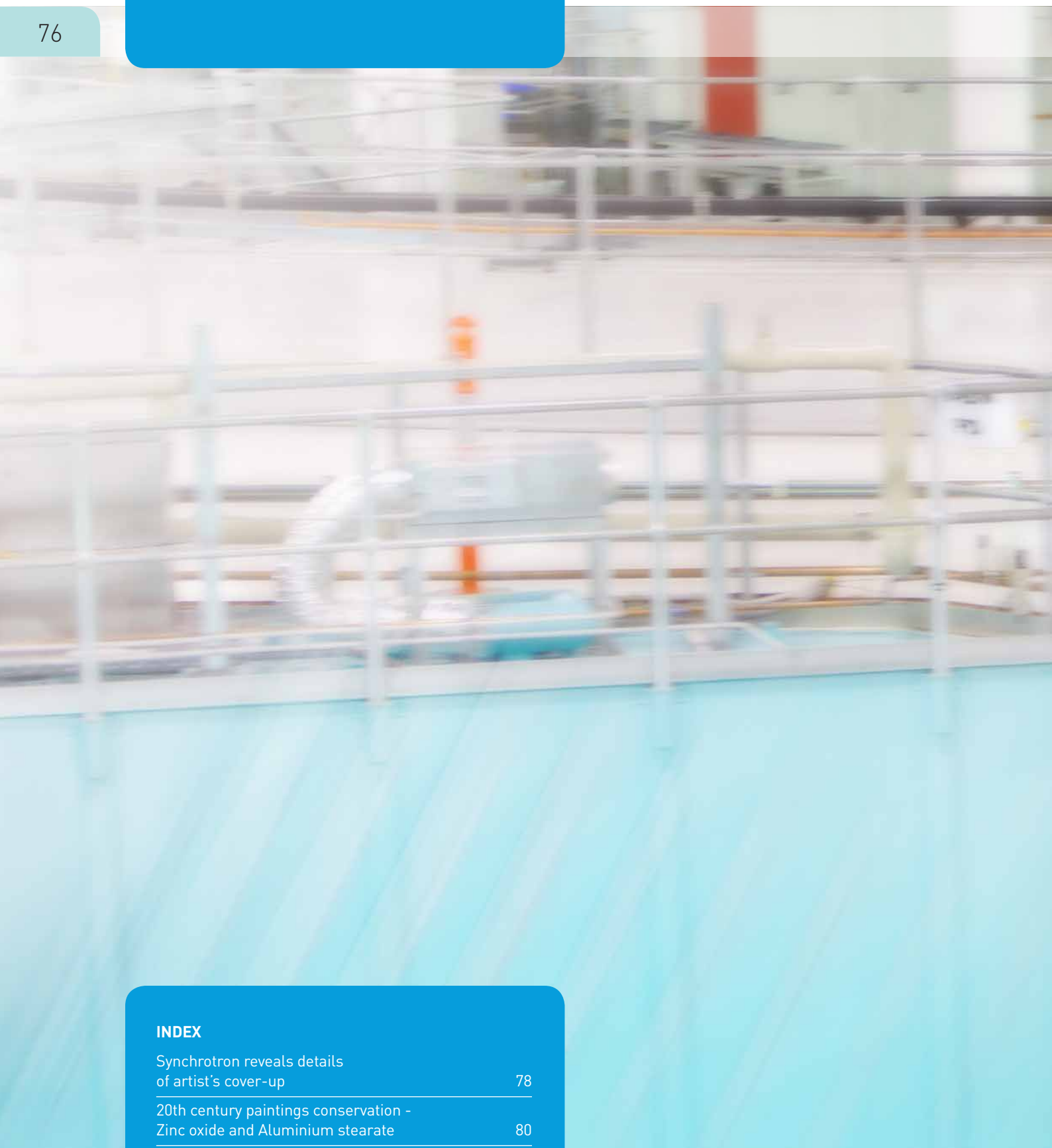
The results show that sulphuric acid octahydrate's response to heat is highly influenced by how the water molecules are coupled together throughout the structure. The relatively strong bonding of the water molecules restricts the structure from expanding in two directions, so that practically all the thermal expansion happens in only one crystallographic direction.

Sulphuric acid octahydrate also has high overall thermal expansion, exceeding that of water ice below 140 K (below minus 133°C). Since typical daily temperatures on Europa peak at 125 K or -148°C, models that only account for water ice would underestimate the material expansions that could occur in this temperature range.

Impact

The next step is to utilise the new high-pressure capabilities of the PD beamline to take a journey to the centre of the planets.

Culture & heritage



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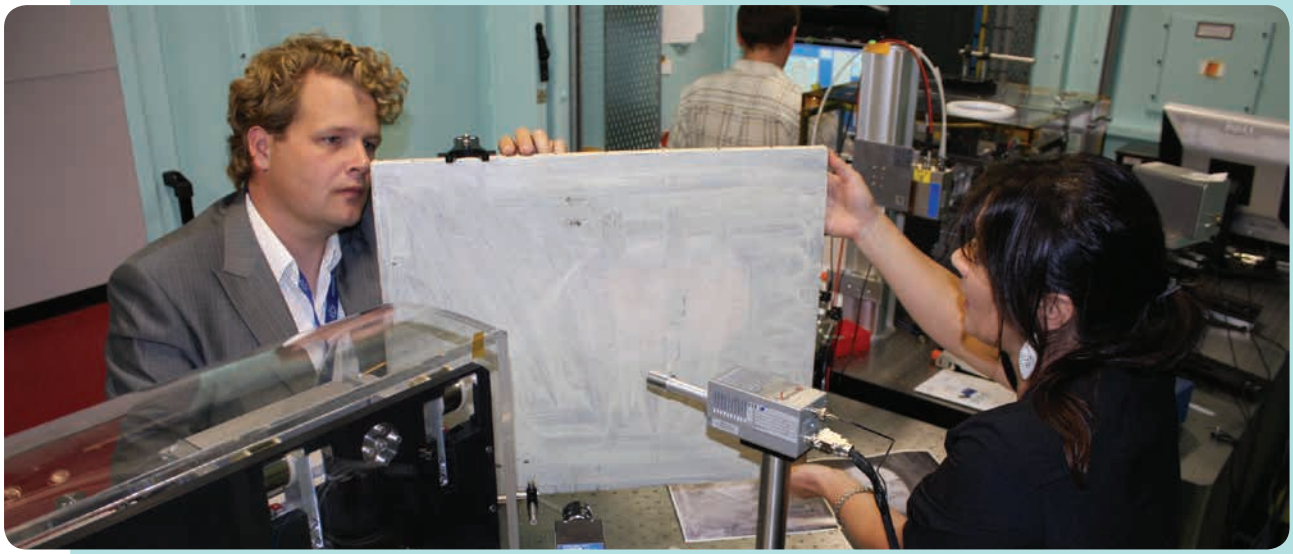
Synchrotron reveals details of artist's cover-up



Conservators from the National Gallery of Victoria are working with CSIRO and Australian Synchrotron researchers to develop new, non-destructive techniques for analysing precious artworks. Synchrotron techniques can identify metal distributions in pigments, reveal hidden layers and help answer questions of provenance and authenticity.

Context

When celebrated Australian painter Sir Arthur Streeton (1867–1943) decided that he wanted to reuse the canvas on which he had painted a rare self-portrait, he applied a heavy layer of white lead paint.

Eventually passed on to the artist's grandson, Oliver Streeton, the overpainted self-portrait may have been a practice run for another Streeton self-portrait, which now belongs to the Art Gallery of New South Wales.

Research question & Synchrotron technique

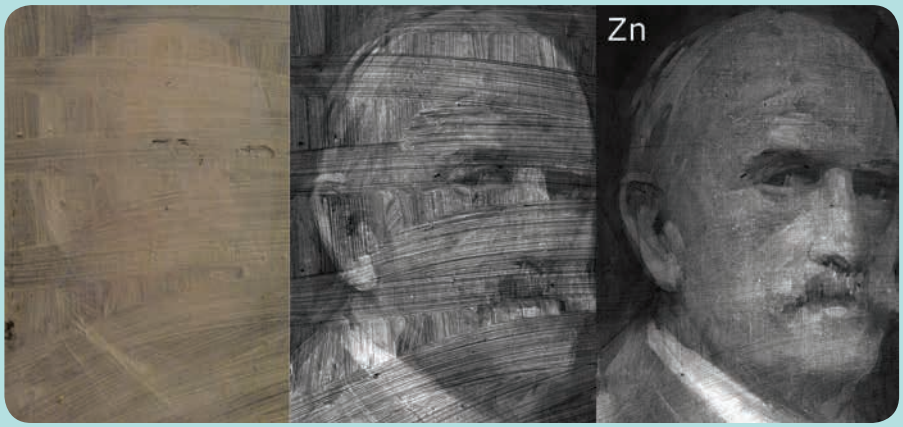
The layer of white lead paint posed a major challenge for National Gallery of Victoria conservators keen to obtain details of the image underneath.

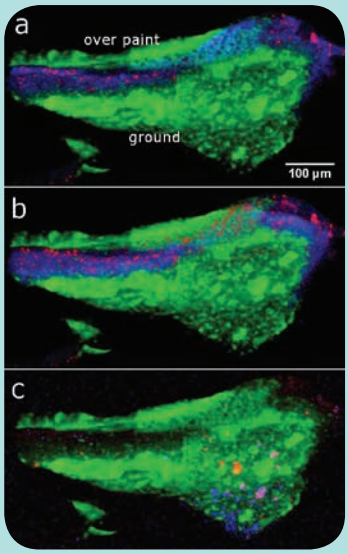
Most current examination methods involve taking small cross-sections, which damages the artwork. Laboratory x-ray techniques don't require cross-sections but may not reveal sufficient detail, or may be unsuitable for other reasons, for example if lead or other metals that strongly absorb x-rays are present, this could swamp the signals from other, lighter elements. The Streeton self-portrait had been studied using x-radiography and infrared reflectance techniques, but these only revealed limited details.

The conservators turned to the Australian Synchrotron's x-ray fluorescence microscopy (XFM) beamline, which offered much higher spatial resolution.

Publication

Daryl L. Howard, Martin D. de Jonge, Deborah Lau, David Hay, Michael Varcoe-Cocks, Chris G. Ryan, Robin Kirkham, Gareth Moorhead, David Paterson, and David Thurrowgood, High-Definition X-ray Fluorescence Elemental Mapping of Paintings, Anal. Chem., 84 (7), pp 3278–3286 (2012), 3 April 2012 (online 7 March 2012).





(L-R) Photograph of the covered Streeton self-portrait, the zinc map, and the zinc map corrected for the absorbance of the white lead overpaint.

False colour red, green, and blue (RGB) elemental maps of a paint sample cross-section measured from XFM: (a) arsenic, lead, and cobalt; (b) mercury, lead, and zinc; (c) barium, lead, and strontium.

Opposite: David Thurrowgood (NGV) and Deborah Lau (CSIRO) position a painted-over Streeton self-portrait for analysis.

Beamline
X-ray fluorescence microscopy (XFM)

Technique:
Microscopy – Imaging & Mapping (Spectroscopy)

Tweak:
We were able to scan the painting without exciting lead fluorescence, which would have severely limited detection sensitivity to the remaining elements.

Sample

Type:
A historic oil painting on canvas

It was a covered up self-portrait by Sir Arthur Streeton, and thus one of a kind.

Environment:
Open to air

Tweak:
Large motorised scanning stages were implemented and a custom sample support was designed to scan the painting.

Synchrotron benefits

This work simply would not have happened without the Australian Synchrotron staff.

Findings

Working with scientists from CSIRO and the Australian Synchrotron, the conservators were able to capture the world's highest-definition elemental maps of the surfaces of historic paintings, using XFM to study the Streeton self-portrait.

The Synchrotron technique and associated computer analysis of the data enabled the collaborators to virtually 'remove' the heavy layer of white lead paint, and reveal full details of the portrait below. Among other findings, the technique identified metal distributions in the pigments of underlying brushstrokes, which is valuable information for art experts charged with interpreting a painting.

Impact

Knowing which elements are present and where in a work of art provides valuable information on pigment usage, assisting scholars, curators and restorers – and potentially helps to answer questions of provenance and authenticity. It can also assist the NGV in assessing their collection's overall value, and thus contribution to the community.

The collaborators expect the technique to become widely used for analysing culturally significant and delicate artworks where conventional analytical methods are inadequate.

20th century paintings conservation - zinc oxide and aluminium stearate

Paintings conservators are studying the saponification, or soaping of zinc oxide – an industrial-age pigment that readily reacts with fatty acids in oil-based paints and may affect the stability of 20th century paintings. Aluminium stearate, a common paint additive, can make matters worse.

Context

Zinc oxide has been widely used as a white pigment for painting since industrial-scale production commenced in the mid 1800s. Its popularity peaked in the twentieth century and it is found in many paintings created during this period. Some are now showing a distinctive form of deterioration linked to the reaction of zinc oxide with fatty acids from the oils in paint. This reaction produces zinc soaps, such as zinc stearate.

In some paintings the zinc stearate separates from the main paint in the form of disfiguring lumps, while in other cases it accumulates between layers in the painting, causing flaking and instability. The deterioration is partly dependent on fatty acids in the oil paint, such as stearic acid. One source of stearic acid is aluminium stearate, a frequent additive in twentieth century paint formulations.

Research question & Synchrotron technique

A paintings conservator and PhD student from Queensland has been working with international collaborators to investigate the mechanism of zinc stearate formation and its distribution in affected paint samples through an ARC Industry Linkage Project, The Twentieth Century in Paint.

Findings

Research conducted on the infrared microspectroscopy (IR) beamline at the Australian Synchrotron has shown that the presence of aluminium stearate in a paint formulation can significantly increase the formation of zinc stearate, and contribute to its tendency to form a separate and potentially damaging phase within the paint.

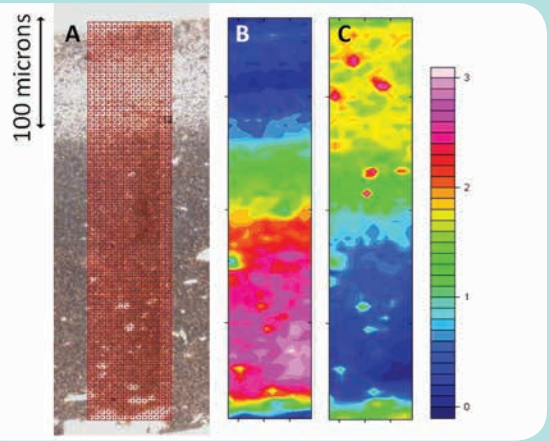
The researchers used aged paint samples to compare zinc stearate formation and behaviour within paints of specific pigment, oil and paint additive combinations. Imaging techniques were critical to distinguishing the different distribution patterns of the zinc stearate phase within each paint film. The high spatial resolution of the synchrotron-source infrared microscope enabled detailed correlation of chemical data with physical features observed using optical and scanning electron microscopic techniques.

Publication

Gillian Osmond, J.J. Boon, Ljiljana Puskar, J. Drennan, Metal Stearate Distributions in Modern Artists' Oil Paints: Surface and Cross Sectional Investigation of Reference Paint Films Using Conventional and Synchrotron Infrared Microspectroscopy, Appl. Spectrosc., 66, 1136-1144, (2012). 1 October 2012.

Surface appearance of zinc oxide paint samples formulated with different oils and aluminium stearate.

Opposite: Paintings Conservator and PhD candidate, Gillian Osmond at the Queensland Art Gallery.



Zinc oxide oil paint with aluminium stearate shown as optical image with grid area analysed (A) and synchrotron FTIR maps showing zinc stearate concentrated at the bottom of the paint film (B) and small areas of Al stearate towards the top (C).

Beamline

Infrared microspectroscopy (IRM)

Technique:
Fourier transform infrared spectroscopy (FTIR)

Tweak:
2D infrared map files were collected using 5x5 µm apertures and 5 µm steps following custom-defined grid points.

Sample

Type:
Artists' oil paint samples cast as films onto PET and naturally aged for up to 32 years. Samples include commercial and custom control paints containing zinc oxide in combination with different oils, pigments and additives.

Of note:
Paint samples were generously made available from the Smithsonian Museum Conservation Institute reference collection.

Environment:
Open to air

Tweak:
Samples from each paint were embedded in polyester or epoxy resin and microtomed to obtain a cross section normal to the paint surface. 5 µm thin sections were cut from each sample and positioned on a diamond window to enable transmission mode measurements.

Impact

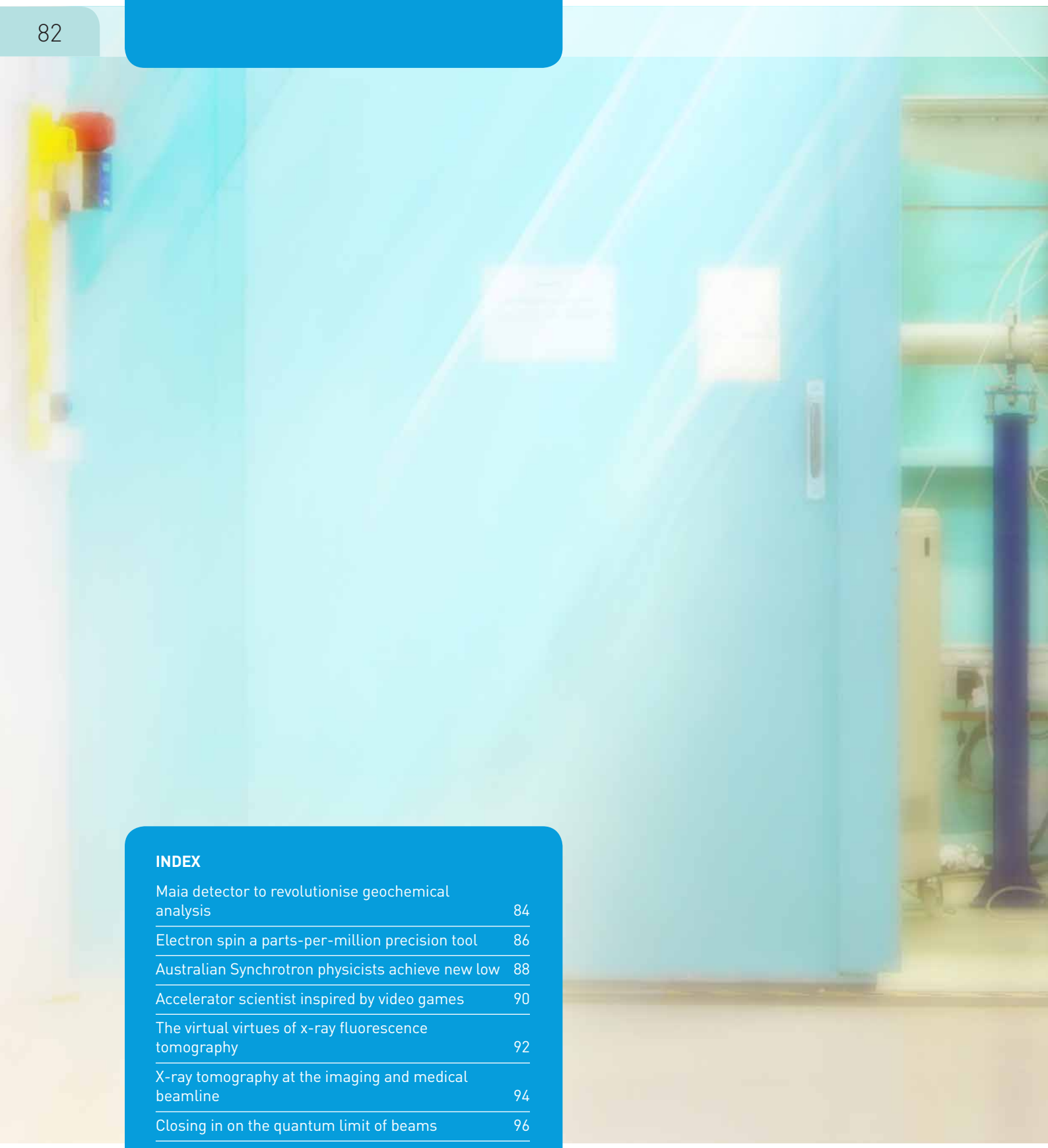
The finding that aluminium stearate significantly influences the formation and distribution of zinc stearate phases in the paint, is valuable information to help conservators better understand why deterioration can occur.

More broadly, the research will assist identification of at-risk paintings and help inform strategies to minimise associated deterioration.

Synchrotron benefits

Obtaining spatially-resolved data at high resolution was critical, and enabled correlation with complementary techniques including optical microscopy and scanning electron microscopy with energy dispersive x-ray (elemental) analysis. Individual spectra extracted from maps derive from a small aperture and allow compositional differences to be distinguished from micron sized features - which would not be possible using conventional FTIR techniques.

Accelerator & beamline development



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Maia detector to revolutionise geochemical analysis

Introduced in 2009, the Maia detector system on the x-ray fluorescence microscopy (XFM) beamline had an immediate impact, dramatically reducing Australian Synchrotron XFM data collection times and opening up new horizons in the study of trace and major element distribution and speciation in earth materials.

Context

Imaging at µm-scale the distribution and speciation (for example, oxidation state; bonding and crystallographic arrangement) of elements in natural samples is key to understanding key geochemical issues, such as the formation of ore deposits or heavy metal contamination in soils.

Prior to the development of the Maia detector system, synchrotron-based x-ray microspectroscopy was already a standard method in geochemistry. This was thanks to its ability to quantify concurrently the concentrations (x-ray fluorescence; SXRF) and speciation (x-ray absorption near-edge structure; XANES) of trace and major elements at high spatial resolution (~200 nm).

Research question & Synchrotron technique

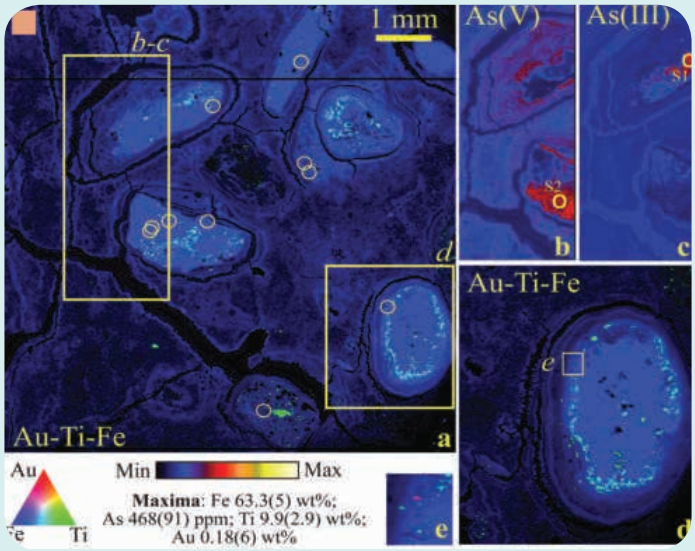
However, the use of synchrotron-based x-ray microspectroscopy for geochemical samples was affected by the long data collection time necessitated by the slow readout and limited count rate of conventional energy dispersive x-ray detectors. This placed severe limitations on sample size and the range of applications of the techniques.

To address these limitations, researchers from CSIRO and Brookhaven National Laboratory (US) jointly developed the Maia detector system.

Using a 96-element prototype Maia detector at the XFM beamline, Australian researchers then examined arsenic distribution in an environmental sample (an oxidised pisolitic regolith) and a metamorphosed, sedimentary exhalative manganese-iron ore.

Publication

Barbara E. Etschmann, Christopher G. Ryan, Joël Brugger, Robin Kirkham, Robert M. Hough, Gareth Moorhead, D. Peter Siddons, Gianluigi De Geronimo, Anthony Kuczewski, Paul Dunn, David Paterson, Martin D. de Jonge, David L. Howard, Peter Davey and Murray Jensen, Reduced As components in highly oxidized environments: evidence from full spectral XANES imaging using the Maia massively parallel detector, American Mineralogist, Volume 95, pages 884–887, 2010; May-June 2010.



Imaging of regolith sample. (a) 10.24 million pixel (8 × 8 mm2; 2.5 × 2.5 µm resolution; 17.5 keV) RgB image (published as CMYK) built from the Fe, Ti, and Au quantitative elemental maps, and showing in exquisite detail the relationship among the three elements. The salmon-colored square on the top left-hand corner illustrates the relative size of a 200 × 200 µm2 image. (b and c) XANES images, smoothed with a boxcar filter over (20,15) pixels from SXRF images 2 × 4.5 mm2 at 2.5 × 2.5 µm2). (d and e) Enlargement of areas indicated in c and d, respectively.

Beamline
X-ray flourescence microscopy (XFM)

Technique:
Microspectroscopic mapping

Tweak:
This was the first published study illustrating the capability of the Maia detector to perform XANES imaging.

Sample

Type:
A pisolitic ferruginous soil found near a gold prospect in Western Australia (and containing ~1 µg/g Au), and a metamorphosed manganese ore from a exhalative deposit in the Swiss Alps.

Environment:
Open to air

Tweak:
The remarkable thing is that we were able to work with standard petrographic mounts. In many beamlines, because only a small (µm size) area can be mapped, samples need to be prepared in special ways.

Synchrotron benefits
The Maia detector revolutionises elemental and speciation imaging for complex, inhomogenous natural samples. The success of this experiment reflects the amazing commitment of the staff at the XFM beamline to commission such a new technology.

Findings

The Maia detector system is designed for rapid collection (two orders of magnitude faster) of fully quantitative maps of the distribution of major and trace elements at micrometre spatial resolution over areas covering several cm^2. Spectroscopic and speciation information is available at each pixel in the map and can quickly be extracted and processed.

For both the geochemical samples analysed with the prototype Maia detector, arsenic *K*-edge XANES imaging revealed the localised occurrence of reduced arsenic in parts of these oxidised samples, which would have been difficult to recognise using traditional approaches. The maps also revealed that gold in the regolith sample was present as µm-size grains associated with detrital minerals.

Impact

The two samples analysed with the prototype system illustrated the quality and volume of information that could be extracted. Both samples also showed that the study of large areas was necessary to identify rare but highly significant objects such as buried gold-rich inclusions or regions containing toxic As(III) in samples otherwise dominated by the less toxic As(V). This information is critical in aiding mineral explorers to interpret the significance and origin of geochemical soil anomalies.

The work demonstrated that the combination of large area (mm^2 – cm^2), high-resolution (pixel size ~1 μm^2), quantitative elemental maps and XANES imaging had produced a paradigm change in geochemistry.

Electron spin a parts-per-million precision tool

Particle accelerators are built with many magnets, but the careful arrangement of these magnets is what makes the brightest light. Measurements at parts-per-million accuracy at the Australian Synchrotron confirm that novel magnet choices make brighter light.

Context

The most brilliant synchrotron light is produced by the smallest electron beams. One of the ways that the Australian Synchrotron gets a performance boost is to use bending magnets with a shaped magnetic field. These unconventional magnets have unique fields that influence the path the electrons take through the accelerator.

Such magnets are designed to efficiently bend and focus the electron beam to a smaller size. This well-known strategy will be employed at new synchrotron light sources in Armenia, Brazil, South Korea, Poland and Sweden.

Electrons produce synchrotron light because they have electric charge, but they also behave like small magnets. This magnetic behaviour produces high-energy quantum spin-flip light, which aligns the electron spins together. Historically, electron spin measurements originated from laboratories such as SLAC National Accelerator Laboratory in the USA, but over time that expertise has been lost.

Research question & Synchrotron technique

When Australian Synchrotron staff developed a new technique to model their unconventional magnets, they needed a very precise measurement to confirm the new technique. The best way to achieve this is to measure how much the beam energy changes for different orbits.

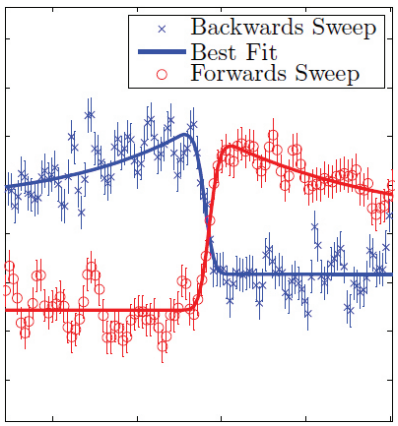
In 2010, a research team that included a postgraduate student, used resonant spin depolarisation to measure the electron beam energy with a precision of three parts per million by measuring an intrinsic property of the electron: its spin. The student developed apparatus to excite and measure the magnetic spins of the electron beam as part of his Masters thesis.

Publication

H.P. Panopoulos, K.P. Wootton, M.J. Boland, R.P. Rassool, Electron Beam Energy Measurement at the Australian Synchrotron Storage Ring, Proceedings of Int. Particle Accelerator Conference 2011, San Sebastian, Spain, p. 1138-40 (2011).

The Australian Synchrotron storage ring was calibrated with a precision of three parts-per-million by Harris Panopoulos. (Images: Harris Panopoulos)

Opposite: Harris Panopoulos, Austin Hospital.



Measuring the electron spin with a precision of three parts per million.

Beamline
Australian Synchrotron (AS)
Storage ring

Technique:
Using the method of resonant spin depolarisation we were able to perform one of the most accurate storage ring energy measurements in the world.

Establishing a means to measure the storage ring energy also allowed for the measurement of other aspects of the beam, such as the momentum compaction factor.

Sample

Type:
The energy of the storage ring electron beam.

Environment:
Under vacuum

Tweak:
A strip line kicker was used to excite the electron beam with a variable frequency signal to induce spin depolarisation, increasing the rate of Touschek scattering. NaI crystal detectors where placed in high loss areas of the storage ring lattice to monitor beam losses.

Synchrotron benefits
The facilities and personnel at the Australian Synchrotron are truly world class. It provides a great opportunity for students to be exposed to cutting edge research both locally and internationally.

Working with such a knowledgeable and passionate team at the Australian Synchrotron was a great experience. Their expertise and assistance ensured the success of this experiment.

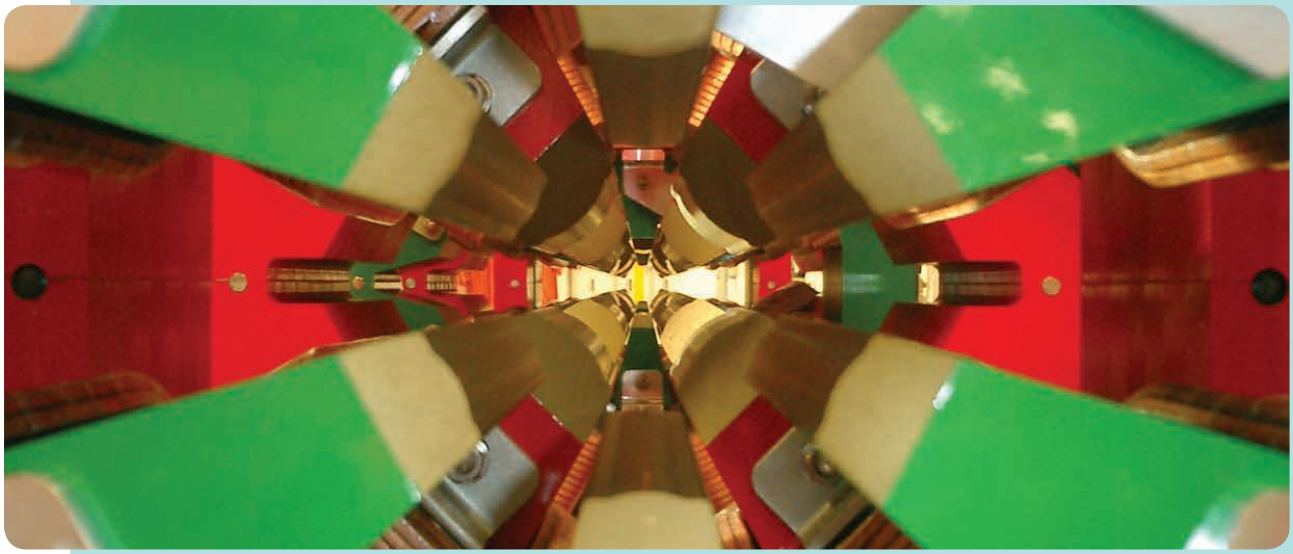
Impact

The team successfully developed and demonstrated a strategy for modelling advanced synchrotron rings that leverage unconventional magnets. The accuracy of their results showed that numerical simulations of accelerator magnets were a better description of the machine than traditional analytical equations.

Following the Australian success, the apparatus and Australian experience were exported to SLAC, where the beam was successfully measured in 2011, also with a precision of three parts per million.

Since completing his thesis, Harris has gone on to operate other Australian accelerators. At the Austin Hospital Centre for PET, he maintains and operates two proton cyclotrons to produce medical radioisotopes for use in hospitals across Australia.

Australian Synchrotron physicists achieve new low



The Australian Synchrotron accelerator science team set a new world record in 2010 for synchrotron beams: 'lowest vertical emittance' – meaning it was the world's 'flattest' beam.

Context

Hidden away under thick white concrete walls, the electron storage ring of the Australian Synchrotron might easily be taken for granted as a device for 'simply' generating experimental light. To the accelerator science team however, it is a highly advanced experimental apparatus that is rich in both physics and fascination.

While the team's first responsibility is to ensure the delivery of high quality photon beams to the experimental beamlines, the smooth operation of the accelerator systems allows the team to conduct research that will improve current accelerators as well as paving the way for future apparatus.

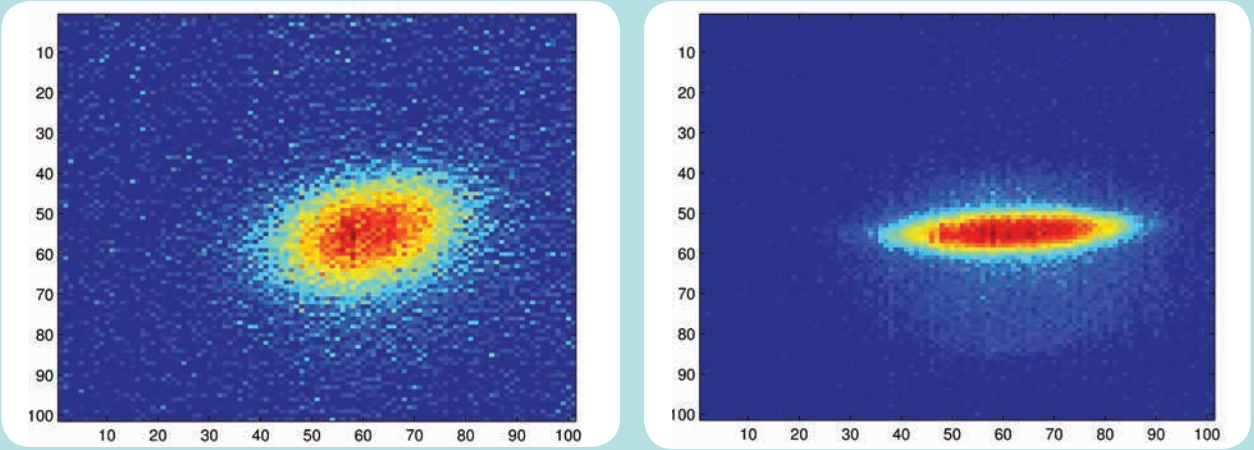
Research question & Synchrotron technique

Australian Synchrotron accelerator physicists achieved a world-record low vertical emittance of only 1.2 picometre radians, significantly lower than the previous record for an electron beam. While the record has since been surpassed, the Australian Synchrotron team is confident of regaining the record in current work.

Emittance is a quantity that describes the spread of position and angle of the individual electrons in the beam. A beam with a small emittance is small in size and well collimated. The magnitude of the beam's emittance in an electron storage ring is influenced by processes that cause it to 'grow', such as passage through bending magnets (pictured above), and processes that 'damp' it, such as emission of synchrotron radiation. The vertical emittance in a storage ring is largely determined by magnet misalignments that lead to coupling of beam motion between the horizontal and vertical planes.

Publication

Rohan Dowd, Mark Boland, Greg LeBlanc, and Y-R. Eugene Tan, Achievement of ultralow emittance coupling in the Australian Synchrotron storage ring, Phys. Rev. ST Accel. Beams 14, 012804 (2011). 29 January 2011



(Above) X-ray pinhole camera images of the storage ring electron beam from the x-ray diagnostic beamline of the Australian Synchrotron. (L) Normal operating conditions with 1% coupling. (R) The 'flattened' beam at minimised coupling of just 0.01%, or 1.2 pm vertical emittance – at the limit of the Synchrotron's measurement tools. The actual minimised vertical beam size is significantly smaller and could only be inferred by an extensive series of indirect measurements.

Findings

The record low vertical emittance was achieved by employing a novel beam analysis technique to determine the best configuration of magnet settings to minimise coupling in the storage ring.

Because of the extremely low vertical beam size, only a few micrometres high in places, it was not possible to directly measure the beam emittance. Instead, Australian Synchrotron staff used indirect measurements, inferring emittance by measuring other characteristics such as beam lifetime and cross-checking these against each other.

Impact

Researchers involved in the proposed International Linear Collider (ILC) and Compact Linear Collider (CLIC) projects are keenly interested because this is the first demonstration of a vertical emittance of the magnitude that they require in the damping rings of these colliders. The Australian Collaboration for Accelerator Science, of which the Synchrotron is a part, is contributing to design work for the CLIC project. Emittance tuning techniques will be a key area, drawing on experience gained on the Australian Synchrotron storage ring.

Accelerator scientist inspired by video games

The uncanny ability of advanced video games to mimic human movement has inspired the development of a new tool to boost the quality of the electron beams used in high-tech research experiments in Australia and Italy.

Context

The Australian Synchrotron is part of a major international collaboration involving the Elettra synchrotron in Italy and the Linac Coherent Light Source at the SLAC National Accelerator Laboratory in the US. This collaboration focuses on the development of the next generation of synchrotron light sources, which will use free-electron laser (FEL) sources to produce synchrotron light of even greater brilliance than current (third-generation) sources like the Australian Synchrotron.

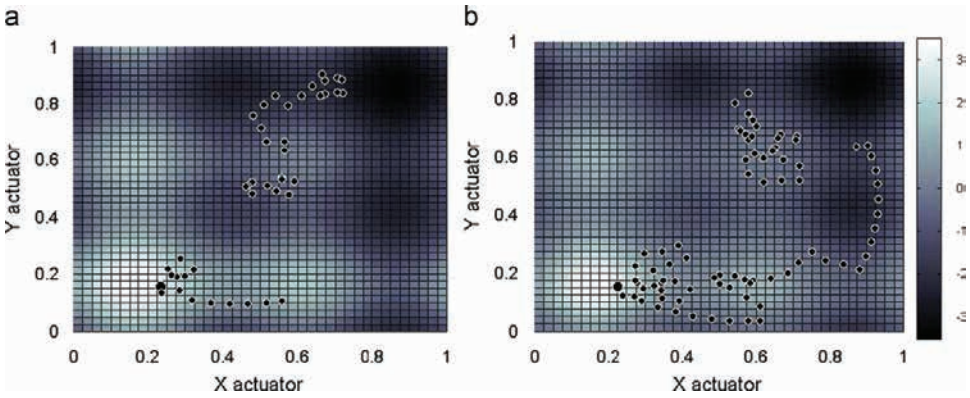
The Synchrotron's first PhD student was a key contributor to this collaboration, conducting research and developing new techniques as part of her PhD studies under joint supervision from FERMI@Elettra in Italy, the Australian Synchrotron, and the School of Physics at Monash University.

Research question & Synchrotron technique

An important achievement in this work was the development of a new tool to boost the quality of the electron beams used in high-tech research experiments in Australia and Italy – inspired by the ability of modern video games to precisely mimic human movement.

Publication

Evelyne Meier, Sandra G. Biedron, Greg LeBlanc, M.J. Morgan, Development of a novel optimization tool for electron linacs inspired by artificial intelligence techniques in video games, Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 632, Issue 1, 11 March 2011, 1–6



(Above) Examples of search with the local maxima avoidance structure. The search starts from (0.5,0.5) and (0.6,0.6) on the left and right plot, respectively. In both cases the network is able to find its way towards the global maximum, using the three substructures to direct its navigation.

Opposite: The gaming agent used was similar to the control mechanisms used in vintage video games, such as Age of Empires, by the opposing team to the player – essentially the strategic 'intelligence' of the game.

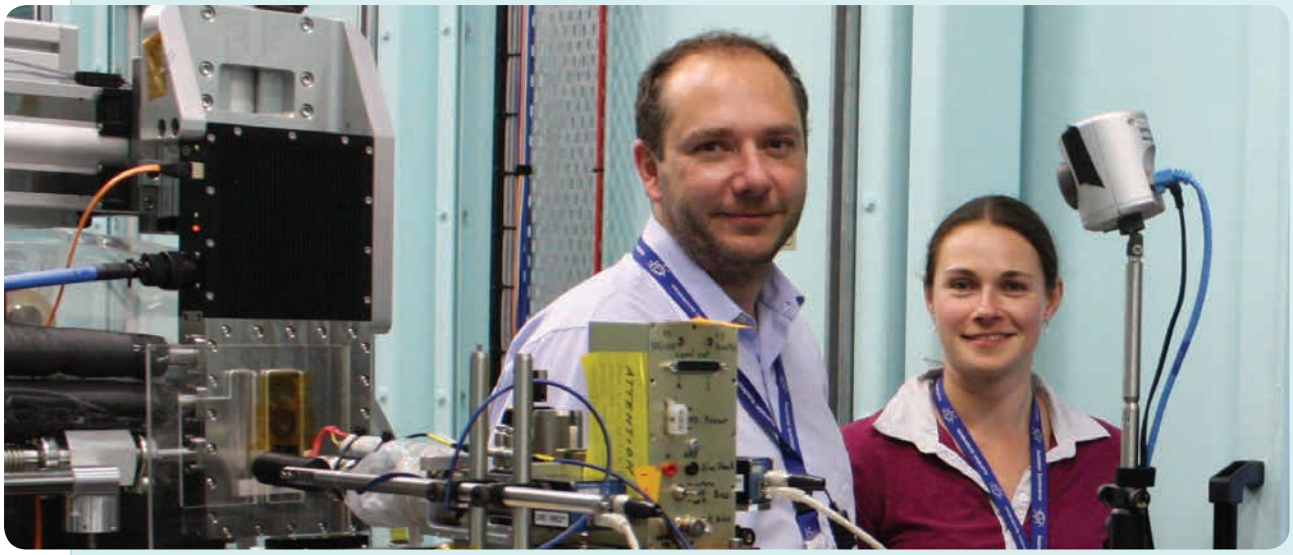
Findings

The new tool uses the same artificial intelligence methods that enable video game 'agents' to learn from their interactions with the human players who control them. This involves the use of artificial neural networks, whose structure evolves over time.

Impact

This work is contributing to the development of a precise and robust control system that will stabilise electron beam energy and energy spread for the FERMI@Elettra free electron laser at the Elettra Sincrotrone Trieste. This is in combination with other initiatives, including the development of a promising new approach, to stabilising electron beams, that combines feedback control with neural network feed-forward techniques.

The virtual virtues of x-ray fluorescence tomography



Intensive beamline development at the Australian Synchrotron combined with the powerful Maia detector system, enabled researchers to obtain the first 'virtual' images of small, delicate samples such as freshly hydrated plant roots at the x-ray fluorescence microscopy (XFM) beamline.

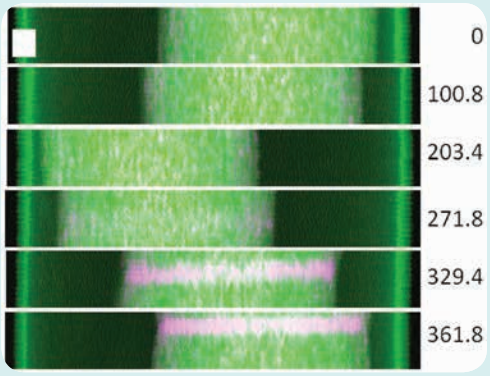
Elements such as zinc and selenium are required at trace concentrations for basic cellular functions in the body, but are toxic when present at high concentrations. Other elements such as arsenic or cadmium are toxic at even low concentrations. Each of these elements can potentially enter the food chain through the uptake from soils by plants.

Knowing where metals are distributed in plants is essential for understanding how trace elements are taken up by plant roots, transported to the edible shoots, and their toxic effects exerted. As trace elements are present at very low concentrations however, routine techniques such as scanning electron microscopy are not sufficiently sensitive to detect them. A further complication is presented by the need to dehydrate and chemically fix root samples for elemental mapping via conventional approaches, as these introduce the possibility of unwanted elemental redistribution that compromise the fidelity of the measurement.

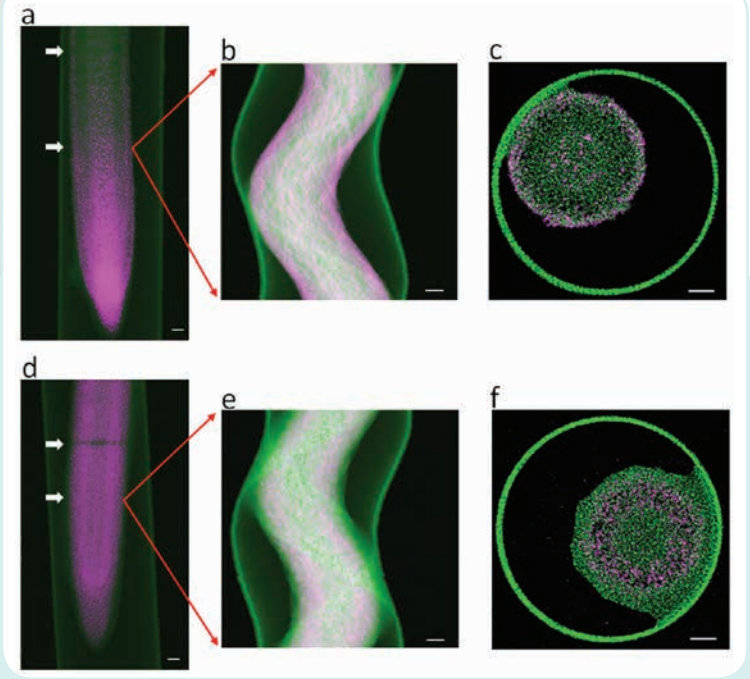
A powerful detector system known as Maia - developed by CSIRO, Brookhaven National Laboratory and the Australian Synchrotron - dramatically increased the speed of elemental imaging at the Australian Synchrotron's x-ray fluorescence microscopy (XFM) beamline. To obtain virtual 2D or 3D information, x-ray fluorescence microtomography acquires elemental maps at a number of angles, and uses standard computerised tomography algorithms to reconstruct a virtual model of the specimen. Measurement time is greatly reduced, overcoming the need to dehydrate and chemically fix specimens. The XFM technique had previously not been used for such delicate specimens due to the extended measurement times that would usually result in a combination of sample shrinkage and x-ray beam damage.

Using x-ray fluorescence microtomography, researchers were thus able, for the very first time, to obtain elemental distribution across virtual slices of fully hydrated plant roots. This initial proof-of-concept work has been followed by several other studies investigating the mechanism of trace element toxicity in plants.

This new capability has tremendous potential for investigating the mechanisms responsible for nutrient and contaminant uptake under physiologically relevant conditions, i.e. in fresh hydrated tissues, not only in plants but in



Zinc (magenta) x-ray fluorescence maps of the same V. unguiculata root volume collected at 6 orientations. The Compton signal is in green. The scale box is 50 µm wide by 20 µm tall. The onset of beam-induced damage can be seen from the maps collected at 271.8° onwards (all 100 frames available as Supplementary Movie 1 online).



(c) and (f) adapted from extended 'beamtime' caption in Chem. Aust., Aug 2012> 2D tomograms of nickel (left) and zinc (right) distribution in hydrated plant roots, demonstrating XFM's potential for investigating metals in radiation-sensitive, biological samples. Image by Enzo Lombi, Martin de Jonge, Erica Donner et al. first published in PLoS ONE 6(6), e20626. doi:10.1371/journal.pone.0020626

Opposite: (L–R) Prof Enzo Lombi, Dr Erica Donner, University of South Australia

Beamline
X-ray fluorescence microscopy (XFM)

Technique:
Microscopy – Mapping (Spectroscopy) & Tomography

Tweak:
X-ray fluorescence tomography is itself only recently feasible; this work capitalised on local capabilities and took data on one of the most delicate of samples known to the field – a freshly growing plant root. This work cannot yet be performed anywhere else in the world.

Sample

Type:
Here we were looking at (metal) micronutrient uptake and transport mechanisms in plants by investigating freshly harvested plant roots.

Freshly harvested plant roots can grow while they are being scanned! So it pays to scan the tip first otherwise it can grow out of the scan region.

Environment:
Open to air & environmental cell (humid atmosphere)

Tweak:
The root pieces were placed inside little straws with a tiny drop of water and sealed up with wax to keep them moist.

Synchrotron benefits
There is no question that this work cannot be performed anywhere else in the world, due to the unique combination of the Maia detector system and the spatial resolution of the XFM microprobe.

biological tissues in general.

For example, combining x-ray fluorescence microtomography with approaches that can visualise the distribution of molecules, such as trace element transporters, should enable researchers to functionally characterise targeted genes in living plants.

Publication

[1] Enzo Lombi, Martin D. de Jonge, Erica Donner, Peter M. Kopittke, Daryl L. Howard, Robin Kirkham, Chris G. Ryan, David Paterson, Fast X-Ray Fluorescence Microtomography of Hydrated Biological Samples. Plos One 6 (2011)

[2] Peter M. Kopittke, Neal W. Menzies, Martin D. de Jonge, Brigid A. McKenna, Erica Donner, Richard I. Webb, David J. Paterson, Daryl L. Howard, Chris G. Ryan, Chris J. Glover, Kirk G. Scheckel and Enzo Lombi, In Situ Distribution and Speciation of Toxic Copper, Nickel, and Zinc in Hydrated Roots of Cowpea. Plant Physiology 156 663 (2011)

[3] Kopittke, Peter M.; de Jonge, Martin D.; Menzies, Neal W.; et al.Examination of the Distribution of Arsenic in Hydrated and Fresh Cowpea Roots Using Two- and Three-Dimensional Techniques. PLANT PHYSIOLOGY Volume: 159 Issue: 3 Pages: 1149-1158 DOI: 10.1104/pp.112.197277 Published: JUL 2012

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X-ray tomography at the imaging and medical beamline

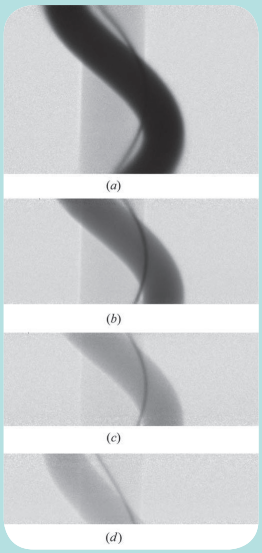
The first monochromatic x-ray tomography experiments at the imaging and medical beamline (IMBL) focused on a 'phantom' of nylon line, aluminium wire and finer copper wire. The findings are important for extracting quantitative information from x-ray tomography data across many disciplines, including materials and life sciences.

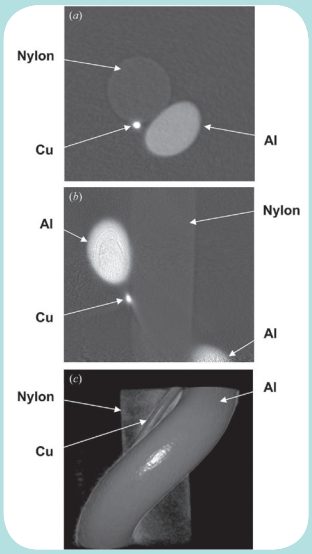
Context

The first peer-reviewed publication associated with the imaging and medical beamline (IMBL) reported the very first experiments performed following 'first light' on the beamline in December 2008. They involved both qualitative and quantitative imaging and tomography studies employing a (filtered) white beam. This second paper from IMBL provides a much more extensive study involving quantitative analysis of monochromatic tomography data collected for a simple 'phantom', and utilizing four x-ray energies.

Research question & Synchrotron technique

As the sample comprised three well-characterized materials of significantly different densities and thicknesses, the data provided a most valuable opportunity to compare theoretical and experimental values of Hounsfield (or CT) number. The factors considered, in establishing reasonable agreement between theory and experiment, included: the role of the point-spread function (PSF); the contributions from harmonic contamination; the response and efficiency of the charge-coupled device (CCD) imaging detector; the role of phase-contrast effects; the performance of the double-crystal Si monochromator; and a comparison of the performance of parallel-beam versus cone-beam tomographic reconstruction algorithms.





(L) Three-component phantom (nylon line, aluminium wire and copper wire) used for x-ray tomography experiments at the imaging and medical beamline.

(M) Examples of pre-processed x-ray images obtained for the three-component phantom at x-ray energies of: (a) 12.66 keV; (b) 18.00 keV; (c) 25.52 keV; (d) 30.49 keV. The field-of-view is 7.0 mm horizontally.

(R) (a) A typical reconstructed xz (horizontal) slice for the 25.52 keV data set; (b) a typical yz (vertical) slice for the 12.66 keV data set; (c) a view of the volume-rendered 12.66 keV data set. Rendering software used for (c): Drishti (Limaye, 2006).

Publication

Andrew W. Stevenson, Christopher J. Hall, Sheridan C. Mayo, Daniel Hausermann, Anton Maksimenko, Timur E. Gureyev, Yakov I. Nesterets, Stephen W. Wilkins and Robert A. Lewis, Analysis and interpretation of the first monochromatic x-ray tomography data collected at the Australian Synchrotron Imaging and Medical beamline, J. Synchrotron Radiat., 19, 728-750 (2012), September 2012 (online 11 July).

Beamline
Imaging and medical (IMBL)

Technique:
X-ray imaging and micro-tomography

Sample

Type:
A 'phantom' comprising three well-known materials (of known composition and density) twisted around each other.

Of note:
Using a phantom sample enabled us to quantitatively characterise the properties and capabilities of the IMBL and investigate how accurately it could determine the properties of the different materials.

Environment:
Open to air

Synchrotron benefits
This was the first monochromatic x-ray tomography study conducted on the IMBL. It used the DEI (monochromator) system obtained by Monash University from the Daresbury (UK) synchrotron.

The second paper produced by IMBL, this was a great help in establishing certain performance measures. It also served as a valuable demonstration of some of the beamline's unique capabilities.

Findings

After detailed consideration of the various factors mentioned above, and especially the role of the PSF, good agreement was obtained between theoretical and experimental values of Hounsfield number, for the different sample materials and x-ray energies. The experiments and analysis conducted also provide insights into, for example, the role of beam 'roll off' as a function of x-ray energy.

This study also provided an important opportunity to characterize the IMBL x-ray beam produced by the insertion device, an interim APS A permanent-magnet wiggler, which has recently been replaced by a dedicated super-conducting multipole wiggler (SCMPW).

Impact

The IMBL will be used to study a wide range of materials and samples spanning a variety of disciplines, including materials and life sciences. Detailed imaging and tomography studies will greatly benefit from the understanding gained in the present study. The knowledge gained will also be of importance in planned radiotherapy studies where x-ray beam quality and characteristics are important for dose and dose-rate considerations.

Some of the results will be compared with those obtained from the new SCMPW.

Closing in on the quantum limit of beams

Advanced synchrotron techniques, medical micro-beam radiation therapy (MRT) and high-energy collider requirements, demand that the host high-energy particle accelerator, produce beams of the highest energy and smallest width. At the Australian Synchrotron, scientists and engineers are leading the world by squeezing the facility's accelerator beam down to the limit of the most minute quantum fluctuations.

Context

The Australian Synchrotron produces a brilliant experimental light source, which spans the electromagnetic spectrum and is a million times brighter than the sun's rays. The resulting collimated – or narrowly focussed – beam of intense light can be used to examine matter at the size of individual atoms.

A light of such intensity makes experiments significantly faster than conventional methods, and can reveal entirely new answers to a range of scientific questions.

Research question & Synchrotron technique

Over the period 2010-2012, the Australian Synchrotron led the world by minimising the width, and therefore intensifying the focus of, the electron beam in the accelerator's storage ring, by 'squeezing' the beam width down to measurements in picometres – the limit of quantum fluctuations.

The approach was the interest of an Australian Synchrotron student who worked in collaboration with physicists from CERN in Switzerland, KEK Photon Factory in Japan, and the SLAC National Accelerator Laboratory in the US.

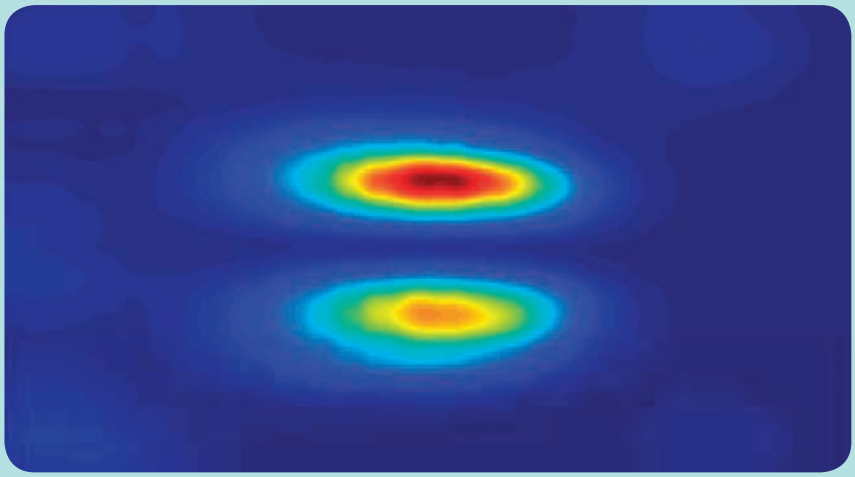
Findings

The unique capabilities of the soft x-ray (SXR) beamline at the Australian Synchrotron were used in this experiment. The SXR beamline boasts the capability of being a user-customised light source. The research team configured the beamline in a counter-intuitive fashion to develop this technique which can be applied at almost every storage ring-based light source in the world. Almost every undulator wiggles the electron beam left and right, but here the trick was to wiggle the beam up and down to measure the size of the electron beam.

The collaboration of accelerator and beamline scientists also developed a new diagnostic technique called vertical undulator emittance measurement, appropriately phasing the elliptically polarising undulator of the soft x-ray beamline.

Publication

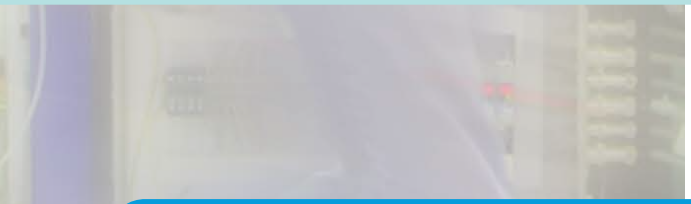
K.P. Wootton, M.J. Boland, R. Dowd, Y.-R.E. Tan, B.C.C. Cowie, Y. Papaphilippou, G.N. Taylor, R.P. Rassool (2012) Observation of Picometer Vertical Emittance with a Vertical Undulator, Physical Review Letters, 109 (19), 194801. doi: 10.1103/PhysRevLett.109.194801.



Coherent undulator x-rays measured with the SXR undulator the result of wiggling the electron beam up and down, rather than the usual left and right.

Kent Wootton, University of Melbourne.

Opposite: The SXR undulator (blue component) in the storage ring.



Beamline
Soft x-ray (SXR)

Technique:
Soft x-ray spectroscopy

Tweak:
The APPLE-II elliptically polarising undulator was phased to wiggle the electron beam in the vertical direction. Almost every undulator wiggles the beam in the horizontal direction.

Sample

Type:
The electron beam in the Storage Ring of the Australian Synchrotron

Of note:
Our storage ring held the world record for vertical emittance in 2011 – it was the flattest beam in any accelerator at 1 picometre radian emittance, and less than 1 micron size.

Environment:
Under vacuum

Tweak:
The skew quadrupole magnets of the storage ring were configured to minimise the vertical emittance of the electron beam. The heights of sextupoles were raised individually with thin shims to align their heights to within 50 micron of the electron beam orbit.

Impact

This work was of particular interest to CERN and other high-energy physics laboratories, as a world-wide strategy is developed for new accelerators to measure the Higgs boson. It is equally important for x-ray free electron lasers, to quantify the coherence of ultrabright, ultrashort x-ray pulses.

These results have demonstrated that the Australian Synchrotron storage ring is capable of producing world-leading electron beams. A direct benefit to the beamline has been the characterisation and modelling of the insertion device light source, demonstrating its performance with smallest beams.

Synchrotron benefits
One cannot sweet-talk electrons to an energy of 3 GeV – and they certainly don't want to stay there. It takes a special team of scientists, engineers and technicians to make brilliant photon beams, but it takes a dedicated team to keep the machine running reliably 24/7.

Ultimately, it is the passion and curiosity of the staff of the Australian Synchrotron that made this counter-intuitive experiment fruitful for us all.

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Melissa M. Basil-Jones, Richard L. Edmonds, Sue M. Cooper, Richard G. Haverkamp, Collagen fibril orientation in ovine and bovine leather affects strength: a small angle x-ray scattering (SAXS) study, J Agric Food Chem. 2011 Sep 28;59(18):9972-9. Epub 2011 Sep 2. (2011). *(Page 25)*

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Claire M. Weekley, Jade B. Aitken, Stefan Vogt, Lydia A. Finney, David J. Paterson, Martin D. de Jonge, Daryl L. Howard, Paul K. Witting, Ian F. Musgrave, and Hugh H. Harris, Metabolism of selenite in human lung cancer cells: x-ray absorption and fluorescence studies, J. Am. Chem. Soc., 133 (45), 18272–18279 (2011). *(Page 29)*

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