Beamline 11: Microdiffraction and fluorescence probe

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Potential Research Fields

Physical sciences

- Advanced materials
  - Ceramics
  - Biomaterials
  - Nanomaterials and composites
  - Metals and alloys
- Mineral exploration and beneficiation
- Earth sciences
- Oil and gas production and distribution
- Chemical reactions and catalysts

Advanced manufacturing

- Production and testing of microdevices

Introduction

The microdiffraction and fluorescence probe will provide rapid, simultaneous mapping of diffraction and fluorescence data. The incident x-ray beam size will be readily adjustable from several mm to 1–2 microns. With the smallest beam size the diffraction patterns measured will, in most scenarios, be indicative of single-crystal diffraction rather than powder diffraction. The innovative use of a broad bandpass incident x-ray beam will ensure that sufficient diffraction data will be obtained per incident beam position, regardless of crystalline grain size, to enable crystalline phase identification. The depth penetration of the high energy, high flux, broad bandpass incident x-ray beam will enable three-dimensional mapping of phase. In addition the provision of monochromatic radiation will enable XAS and fluorescence measurements at wavelengths selected to highlight a specific element. The definition of three-dimensional stress tensors on a grain by grain basis will be possible by the application of both broadband and monochromatic radiation.

Advantages of a Synchrotron Source

Only synchrotron light offers the possibility of simultaneous x-ray fluorescence (XRF) and x-ray diffraction (XRD) mapping at a micron scale.

In a laboratory setting a powder diffraction pattern is carried out using a monochromatic source as a function of diffraction angle but, with synchrotron radiation, diffraction data may be collected as a function of x-ray energy. In the microdiffraction and fluorescence probe, broadband Laue diffraction will be used in order to maximise the diffraction data collectable by an area detector without needing sample or detector rotation. This is not possible using a conventional x-ray source.

Because x-rays are efficient at causing excitation of inner-shell electrons, they produce low backgrounds and the samples require a minimum of preparation.

As synchrotron radiation provides white radiation, the incident x-ray energy can be selected to create maximum excitation for the element of interest. This, in addition to the high flux provided by a synchrotron x-ray source, can give rise to sensitivities in the order of parts per million. As very short wavelength x-rays are available that have a high sample depth penetration, analysis can be undertaken of melt and fluid inclusions without the necessity for destroying them.

User Community

The simultaneous XRD-XRF facility (with selected area XAS) is required for numerous scientific and industrial applications. These cover a wide range of fields and thus this instrument would serve as a basic infrastructure resource.

The beamline is likely to be used by researchers who are not expert in synchrotron techniques and so it will be designed to be simple to use and adjust. It will be supported by the necessary analytical algorithms to ensure rapid online crystalline phase identification, rapid strain mapping and calculation of stress and quantitative elemental analysis.

A significant number of industry sectors have been approached regarding their interest in using the facilities described. Letters of support have been received from the Australian Minerals Industry Research Association (AMIRA), Environmental Geochemistry International, Research Laboratories of Australia, TGR Biosciences and Rio Tinto. Mr Dick Davies, Chief Executive Officer of AMIRA, wrote:

> *… we view the possibility of being able to simultaneous map structure and composition via the VESPERS [Very sensitive Elemental and Structural Probe Employing Radiation from a Synchrotron] microprobe as highly exciting. As far as we are aware the provision of this form of rapid turn-around, on-line controlled microprobe specifically designed for industrial applications has not been attempted elsewhere. We foresee the extensive employment of this microprobe via AMIRA's member companies.*

Research Applications

Geochemical

The capacity for simultaneous XRF and XRD and complementary XAS will enable the relationship between trace elements and host phases to be established. It will also be possible to measure the diffusion and migration of elements as a function of mantle and sub-mantle conditions. Applications will include industrial mineral exploration, determination of elemental-mineral phase relationships (e.g. platinum group metals, the location of P, Si and Al in goethitic Fe-ores, and deportment of trace metals in high temperature melts and slags), process control during mineral processing, mineralogical, petrological, petrogenesis, environmental and whole-earth geochemistry research. The provision of XAS will enable the identification of elemental oxidation states as a function of crystalline phase.

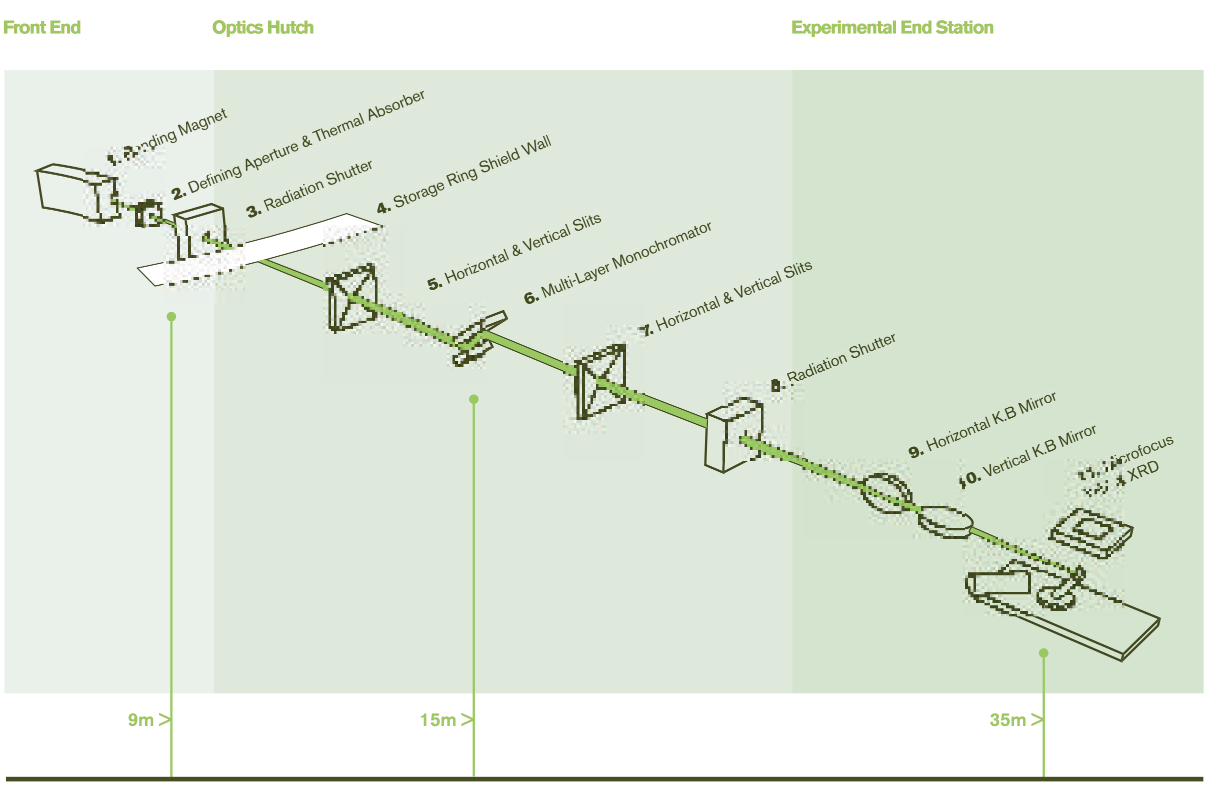
Environmental

Mineral weathering resulting in the release of acid mine drainage (AMD) is now of considerable environmental concern. It is estimated that in Australia remediation costs will be in the order of $900 million over the next fifteen years.

The dual XRF-XRD mapping facility, with XAS, will enable the identification of reaction and reprecipitation layering on mineral surfaces as a functioning of weathering. Understanding the evolution of these layers in terms of both their elemental composition and crystalline phase is important to the prediction and control of AMD. This combination of analyses will enable significant contributions to be made to the understanding of the release of toxic elements, which often accompanies AMD, and their bioavailability. The simultaneous XRF-XRD facility will also be of considerable application to other environmental concerns, for instance the identification of sources of industrial pollution.

Manufacturing

The XRF-XRD combination has many applications to the manufacturing and engineering industries. Aging of plastics and alloys to form microcrystalline domains, sometimes accompanied by elemental diffusion, is an area that could benefit from this combination of analyses.



BEAMLINE 11 Microdiffraction and Fluorescence Probe

Figure BL11.1. *Schematic of the microdiffraction and fluorescence probe*

Elemental partitioning is an area of particular importance to the microelectronics industry. The measurement of stress/strain as a function of diffusion processes that occur on corrosion, welding and annealing are also areas of application that require the combination of XRF and XRD.

The ability to map strain in metal fabrication products on a grain by grain basis at the surface will be valuable in many industrial applications, for example where surface compressive residual stress is introduced to improve fatigue performance.

Biotechnology

The combination of XRF and XRD also has biotechnological applications, for instance in the forensic sciences, for the production of bioceramics for bone implants and in the study of unwanted crystalline growths such as kidney stones.

Forensics

Typical forensic samples are small and complex matrices. Due to legal implications, the samples must be kept intact as far as possible. Non-destructive XRD-XRF mapping is an ideal analytical methodology and can be applied to materials such as metals, gunshot residues, paint, glass, soil, fibres, plastic and general polymers.

Beamline Design

The technical aims are to establish a microdiffraction and fluorescence probe that will:

- enable rapid simultaneous XRF and XRD high resolution mapping with three-dimensional resolution
- enable XAS and element-specific XRF
- be capable of mapping strain on a grain by grain basis
- require neither sample nor detector movement for collection of diffraction data
- be able to swap between white, pink and monochromatic incident x-ray modes without shifting the position of the x-ray beam incident on the samples so that XRF, XRD and XAS can all be carried out at the same point on a sample.

Beamline source

The beamline and end-station will be positioned on a bending magnet. A beam divergence of less than 2 mrad is required.

Beam focus

Grazing incidence Kirkpatrick-Baez mirrors will be used, providing a high degree of beam stability and ease of adjustment of beam size at the sample. They are applicable to broad bandpass radiation and will be insensitive to changes in wavelength, which is important when swapping the incident beam mode between white, pink or monochromatic incident radiation. Additionally the long focal length of these mirrors will enable flexibility in sample shape and alignment, and the use of robotics for sample changing.

Wavelength range and adjustment

A monochromator consisting of two graded multilayer mirrors will be required to enable the collection of sufficient data from a typical small unit cell mineral or alloy structure for single crystal diffraction analysis. Such multilayer crystals have now been designed.

To carry out XAS, strain mapping and selected element fluorescence there is also a requirement for monochromatic radiation. A Si (111) double crystal monochromator will be provided to enable these measurement modes.

Application of the Si (111) monochromator will enable the fluorescence of light elements down to approximately Na to be accessed with reasonable efficiency by using an incident x-ray energy in the region of 4 keV.

The monochromator housing will be based on a design by Ice et al[1]. This will enable rapid switching between broad bandpass, monochromatic and white beams while maintaining a static incident beam position on the sample. A spatial displacement on translation from white beam to monochromatic beam of less than 0.5 μm has been achieved.

Detectors

The optimum geometry for measurement of diffraction data is perpendicular to the plane of the storage ring. Hence it is proposed to mount a CCD camera vertically above the sample with the sample oriented at 45° to both the incident beam and the detector (i.e. 2θ of 90°). The CCD detector position will be easily changeable to enable glancing angle measurements and access to other 2θ diffraction angles.

The fluorescence spectra will be measured using an energy dispersive multi-element solid state detector. This detector will be in the plane of the synchrotron at 90° to the incident beam and 45° to the sample. Thus the footprint of the beam (when using the standard geometry) will be the same for the XRD and XRF measurement and the sample will simultaneously be tilted 45° off vertical and rotated 45° around a vertical axis. However, this will increase the footprint of the incident beam on the sample, for example a 1 μm incident x-ray beam would have a 1.4 μm footprint.

1 G.E. Ice, J.S. Chung, W. Lowe, E. Williams and J. Edelman, "Small-displacement monochromator for microdiffraction experiments", Rev. Sci. Inst., 71, 2001-2006 (2000)

Sample stage

The sample stage will be designed to be as compatible as possible with other instruments at the synchrotron and in the Clayton precinct. This will be important for ease of sample change between analytical facilities. Additionally, for mapping analyses a careful sample stage design will greatly facilitate the relocation of areas of interest on transferral of samples between facilities.

For detection of light elements (Ca and below) by XRF the sample and solid state detector will be enclosed by a glove bag-type arrangement with an internal positive pressure of He. Alternatively the latter section of the beamline, sample stage and detector system may be enclosed in a chamber under a moderate vacuum (0.1^{-1} torr).

Development of the concept

The microdiffraction and fluorescence probe is a new concept in beamline design. Considerable development work will be needed to prove the capability of simultaneously performing these two high precision techniques. In addition extensive research and calibration must be undertaken to derive the algorithms for interpretation of the results.

A similar beamline (VESPERS) is proposed to be commissioned on the Canadian synchrotron as part of its second suite of beamlines. A strong collaboration exists between the University of Western Ontario, the Canadian Light Source Inc. and researchers at the University of South Australia on the development and application of this beamline. This collaboration will provide a proven technical design and an experienced user base to support the establishment of the microdiffraction and fluorescence probe on the Australian Synchrotron.

Beamline 11 – Microdiffraction and Fluorescence Probe	
Source	Bending magnet
Energy range	4–37 keV
Resolution $\Delta E/E$	10^{-4}
Minimum beam size at sample (horizontal × vertical)	2 × 2 microns