Australian Synchrotron Development Plan
Project Submission Form

Section A: Summary and Proponent Details

Project Title

Integrated Development of new XAS Capabilities - Enhanced Capabilities for Beamline 12-ID & a Medium-Energy Bending Magnet XAS Beamline

Spokesperson

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Executive Summary (approx. 100 words)

This project will deliver an integrated suite of diverse cutting-edge XAS capabilities for the AS. These capabilities will be built around the existing high-energy, high-flux wiggler XAS beamline, 12-ID, together with a proposed bending-magnet beamline optimized for cutting-edge applications in biological and environmental science. The high photon flux provided by 12-ID will allow the development and implementation of the next level of state-of-the-art capabilities including: (i) resonant inelastic X-ray scattering and X-ray Raman spectroscopy; (ii) quick XAS; (iii) high-energy-resolution emission spectroscopy; and (iv) ultra-dilute XAS. It will also provide: (v) low-resolution microprobe capabilities and (vi) infrastructure support for radioactive sample handling and other specialist sampling for controlled environments of technological and environmental importance. This suite of enhanced capabilities will enable 12-ID to be dedicated to the photon-intensive experiments for which it was designed and intended. The complementary medium-energy bending-magnet XAS beamline will cover an extended energy range from the K-edge of Si through to the K-edge of Se, which covers most of the elements of interest for biological and environmental samples and also extends the range of XAFS that are possible for minerals and materials under conditions where a high vacuum is not required.

Other proponents (add more rows if necessary)

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XAS community as represented at a range of User Meetings over the years	Diverse range of institutions in Australasia	

Section B: Detailed Description

B1: Description of Proposed Beamline/Development Project

This is a merged proposal of two preliminary proposals submitted to the ASDP from XAS PAC spokespersons, Peter Lay and Mark Ridgway. It is designed to meet the XAS user community's short-term requirements that have been discussed at Users' Meetings and have included extensive input from the international and local XAS community about modern developments that are emerging at other synchrotrons and new capabilities built around local expertise. This has led to a coherent plan by the XAS PAC for an XAS development program that will take us through the next decade (with appropriate adjustments to take into account new technologies). The current proposal was also developed in consultation with the X-ray microprobe community to provide complementary capabilities to those of the current XFM beamline and new X-ray microprobe proposals. While the XAS development plan concentrates on the most pressing needs, the fact that the two XAS beamlines currently available to the AS are already heavily oversubscribed necessitates that a third XAS beamline be built before the end of the decade and a fourth be either planned or built within the same timeframe. The third could include new capabilities, as outlined in the preliminary ASDP project on High Accuracy XAS, for whom A/Prof. Chris Chantler was the spokesperson and is discussed briefly in Section 1.3.

Synchrotron-Radiation XAS Facilities and Australia

The Australian XAS community grew rapidly after the Australian National Beamline Facility (ANBF), (BM beamline at the Photon Factory, was opened in 1993 and access was afforded under the Major National Research Facilities Scheme to other state-of-the-art synchrotrons. This established a broad XAS community before the AS began operations.

Current and Future Status

The AS wiggler beamline (12-ID) began transmission experiments in 2008, and some fluorescence experiments were performed in 2009 with a single element Si drift detector. During 2010, it will reach its full fluorescence capabilities with a 100-pixel Ge detector being commissioned and the second hutch being fitted out for specialist experiments that will be able to use a 10-element Ge and Maia detectors for a diverse range of experiments.

An ARC LIEF grant extended the operation of the ANBF for the two years (2009-2010) and now the ANBF is solely dedicated to XAS studies. This has enabled:

(i) uninterrupted access to an established beamline dedicated to Australian users until such time as the ID AS beamline has become fully functional; and
(ii) has provided the additional capacity to accommodate some of the high over-subscription at the AS XAS beamline that already exists.

The highest priority for XAS beamline development is to replace the ANBF capability with a more advanced BM beamline as soon as possible to:

(iii) provide complementary science-driven specialist capacity (over the region 1.8-5 keV), such that the insertion-device XAS beamline of the AS can be most efficiently used for the true cutting-edge, high-intensity experiments for energies above 5 keV for which it was designed; and
(iv) provide optimal capability for high-quality transmission and fluorescence experiments that are better conducted with a bending magnetic beamline.

Even if such construction was to commence in 2010, interim arrangements will be need to be made to accommodate the XAS community at other synchrotrons, in order that high ranked projects funded by the ARC and other funding sources are not seriously compromised. The developments of ID-12 can occur during shutdowns (for optics upgrades) and during normal beamtime operations as installations can occur in Hutch 2 while Hutch 1 is used for routine XAS experiments on dilute solutions. Each point will now be addressed in greater detail.

(i) Uninterrupted Access

The outstanding track records of the XAS community have relied heavily on ANBF/AS for sustained success in securing ARC funding with an expectation of continuous access to XAS facilities. The successful completion of these ARC-funded grants, and those under review, required the short-term extension of operations at the ANBF, in addition to the new XAS beamline, to meet the scientific demands of these projects.

(ii) Additional capacity and over-subscription at the AS

Over recent years, the Australian XAS community has exceeded 100 research groups (many comprised of multiple users) and XAS experiments are one of the largest fractions of Australian synchrotron-science measurements. This matches experience at other synchrotrons where XAS beamlines are often the most heavily used (even though most mature facilities have multiple XAS beamlines), hence, a second XAS bending-magnet beamline was always projected as a high priority by the XAS PAC and included in the Decadal plan.

(iii) Complementary capacity for the most efficient use of AS beamlines

The cutting-edge experiments that will absolutely necessitate the high flux of the current AS beamline include: (i) resonant inelastic X-ray scattering and X-ray Raman spectroscopy; (ii) quick XAS; (iii) high-energy-resolution emission spectroscopy; and (iv) ultra-dilute XAS; but these experiments will be limited to energies above ~5 keV. The BM beamline would thus allow the current XAS beamline at the AS to give priority to those experiments. The proposed BM XAS beamline is an essential component of the plan as it will allow high-level XAS capabilities at energies down to 1.8 keV. This includes the K edges of Si and above; these being crucial in applications in biological and environmental science, as well as minerals processing. KB mirrors at both beamlines will provide low-resolution microprobe capabilities over this extended energy range to complement the heavily oversubscribed XFM beamline.

(iv) *Superior capability for certain experiments.*

A medium-intensity BM beamline will often yield superior data compared to a high-intensity ID beamline for certain experiments. Superior data result from the reduced thermal load on optical components (hence greater stability) and reduced photon-beam-induced degradation of sensitive samples during measurement. The less focused bending magnet beamline also provides superior transmission data, as it is less sensitive to sample inhomogeneity. Thus the BM beamline will often produce superior quality transmission and fluorescence data (for photosensitive and less dilute samples of absorbers with $Z<34$) than would ID-12.

Capabilities of the Beamlines

1.1 Advanced Capabilities for ID-12

Advanced X-ray Fluorescence Capabilities

XAS derived fluorescence measurements conventionally employ solid-state energy-dispersive detectors with moderate energy resolution (100s eV); this allows resolution of the X-ray emission signals from different elements. However, very high-energy-resolution X-ray fluorescence detection (of the order < 1 eV) allows resolution of the signals due to the same element in different environments [1]. Such high energy resolution can be achieved optically based on spherically bent crystals diffracting in a Rowland-circle geometry [2]. As a fixed energy range is accessible for a given crystal set, a number of crystal sets need to be obtained to cover edges of interest (first-row transition metals from V to Cu).

For the photon detector/counter of the spectrometer, we plan to use a position-sensitive X-ray camera, such as a Pilatus 300W, to optimise the resolution function due to any non-Rowland circle effects, as is typically employed in soft X-ray grating RIXS spectrometers. This would significantly simplify the process of aligning and optimising the spectrometer. XAS can become challenging due to the large fluorescence background for highly dilute systems (eg, dopant levels in semiconductors). For many systems, the high-resolution Rowland spectrometer can circumvent the count rate limitations of a solid-state detector; however, for very dilute systems, the resolution is too high to enable experimentally useful signal count rates. For such systems, a bent crystal Laue analyser (BCLA) based spectrometer using fixed bent crystals in Laue geometry exist that offer ~ 20-40 eV-type resolution but potentially unlimited throughput [3]. Such spectrometers are quite compact; however, they also require a range of crystal analysers to cover different energy ranges of interest. We propose a modular BCLA system with six analyser crystals.

These capabilities will enable:

(i) High-energy-resolution fluorescent detected XAS (HERFD): site-selective XAS (i.e., by collecting a narrow emission energy range, the fluorescence XAS from one site) can be probed selectively where more than one chemical form of an element is present.

(ii) X-ray Raman spectroscopy (XRS) refers to the inelastic scattering of hard X-rays by excitation of an inner-shell electron into an unoccupied state. It enables soft X-ray XAS information to be obtained with hard X-rays, and allows the study dipole-forbidden transitions that are not accessible with conventional XAS selection rules.

(iii) High-resolution X-ray emission spectroscopy (XES), where the intensity and energy of peaks are sensitive to the coordination environments from which the fluorescent electron is derived. This can enable an independent measure of the donor groups in an unknown sample when elements have similar XAS scattering (e.g., O/N donors).

(iv) Resonant inelastic X-ray scattering (RIXS), where tuning the incident energy to an absorption edge results in spectral changes in XES as a function of the incident energy. This allows fine details of the electronic structure of the system, as well as dynamics.

‘Quick’ EXAFS

The ability to monitor reactions and processes on short timescales is limited in a standard XAFS experiment by the step-settle-count-repeat measurement methodology. This typically limits the lowest attainable scan time to several minutes for a full EXAFS scan. By continuously slewing the monochromator and rapidly acquiring data (“on-the-fly”), a total scan time of ~10 s has been achieved on ID-12’s standard monochromator. However, to reduce further this time, a commercially available Q-EXAFS monochromator based on an eccentric CAM system is required [4,5]. A similar system exists at the Super XAS beamline at the Swiss Light Source and operates at a 40 Hz repetition rate (complete EXAFS spectra in ~ 13 ms). From the outset, this capability was integrated into the design for ID-12 and, hence, the optics of the XAS beamline was designed to enable its retrofit.

For transmission experiments, fast sampling of ion chambers is required; however, for fluorescence experiments, special fast detector readout methodologies must be used. The Maia detector, developed via a collaboration with BNL and AS/CSIRO, is uniquely matched for such experiments: it is a Si-based detector so the detectable energy range is well-matched to the Si(111) energy range, and the massive data rates with zero deadtime are fully compatible with the fast scanning rates. A 20 ms XANES scan with 500 data points limits data acquisition to 40 μs per data point. A Si-drift version of the 384-channel Maia detector offers a total count rate of ~ 100 Mcps, equating to a maximum of ~ 5000 cts/40 μs point.

Microprobe Capabilities

A set of KB mirrors would facilitate microbeam mapping, imaging and EXAFS studies with a spatial resolution of 2-100 μm with significant flux. Such control over spot size is often necessary for small sample environment experiments. This capability is complementary to those available at the XFM beamline – a large spot size, high quality spectroscopy measurements due to the wiggler source, and a source of microfocus X-rays up to 37 keV.

Other Infrastructure Upgrades.

Currently available at the beamline is a closed cycle He cryostat and specialised sampling equipment (eg, hydrothermal cell / XERT goiniometer). Additional general sample environments that are standard at XAS beamlines include: inert atmosphere 30–1000 °C furnace, diamond-anvil high-pressure cell for inert systems (20 GPa – modified for XAS), and solution cells for flow or in situ electrochemistry. In the minerals and radiopharmaceuticals area there is a demand for radioactive sample handling facilities, including sample holders and mounts, glove box / load lock for sample transfer and a containment tent with separate air handling facilities, which can be temporarily installed into ID12 Hutch B.

1.2 Bending Magnet Beamline

Energy Range.

This beamline will span an energy range of approximately 1.8-14 keV (K-edges Si-Se), which covers most of the elements of interest to biological and environmental samples (except for H, C, N, O, Na, Mg and Al) and also extends the range of XAFS that are possible for minerals and materials without the requirement of a high vacuum used in soft X-ray beamlines. It will also enable access to a range of L and M edges of the heavier elements, such that XAFS data can be obtained from most elements. It will be a BM beamline to minimize photodamage, e.g., photodamage associated with compounds containing S with insertion-device beamlines.

This energy range will require a water-cooled monochromator with two different crystal sets (InSb 111, 1750 to 3750 keV and Si 111, up to Se edge). A range of modern beamlines have these monochromator capabilities, including the Lucia beamline at Soleil 0.8-8 keV (incorporating InSb and Si and three other crystal sets on an undulator beamline) and BL16A, which is a bending magnetic beamline at NRSSC, Taiwan. Many other beamlines cover the energy range from 2 keV to much higher energies, so there are no technical impediments for rapid implementation. Consideration was given for a third monochromator material to reach the Al K edge, but it was generally felt that this would involve too many compromises, in addition to the extra cost of a third monochromator, since such an energy range extension of the beamline will require compromise of the higher energy performance.

Microprobe Capability

The microprobe capability will be provided by KB mirrors, which will provide complementary energy-range to those available on the XFM and ID-12 beamlines.

Detectors

Ion chambers will be available for transmission experiments and energy calibration. A four-element Si-drift detector (optimized for ~2-5 keV), will be the initial detector, but a Si-drift Maia detector, optimized for this energy range, is the next stage of development of this detector system and this should be available towards the end of the nominal three-year timescale for these projects. Such detectors would enable XRF maps down to Na for high Na^+ content and XAS data from the edges above Si. A multi-pixel Ge detector, or a Miai detector with the current capabilities, will be the preferred detector for higher energies. The choice will be made depending on the comparative performances of these two technologies that will be ascertained from studies on the current beamlines. An electron-yield vacuum cell will also be available for measurements conducted under moderate vacuum conditions.

Sample Environments and Hutches

Like ID-12, this beamline will have two hutches, with the first being set up for routine fluorescence and transmission experiments, while the second hutch will allow specialist experiments to be set up using environmental cells, etc., while other experiments are being performed in the first hutch. Different sampling environments will include a liquid He cryostat and the controlled atmosphere cells discussed for ID-12, which will be designed to enable transfer between the two beamlines. Particularly for the low energy experiments, the hutches will need to be designed for maximum beam intensity, which would include the incorporation of He flow or vacuum tubes before the sample and a capability for enclosing samples in a He atmosphere as used on standard XFM beamlines.

General Optics

The beamline design will rely on ray tracing and experience gained from similar beamlines that have been constructed recently or are in construction phases, but will include:
* collimating mirror (probably Si and Rh coated) at fixed angle of incidence.
* DCM (described above)
* Rh (Si may also be necessary) coated cylindrical mirror (not bendable)
* flat mirror (probably Si and Rh coated - bendable for vertical focusing).

Using the bender on the latter will produce superior vertically focused/defocused beams for a range of beamsizes. Also in this arrangement, the pitch of the second and third mirrors would move in a correlated such that one can adjust the horizontal focus size without the beam position changing at the sample, which will make the beamline much more user friendly. This would also allow for strong control over harmonic content. The mirrors will be used at ~ 4.5 mrad angle of incidence. As the angles will be large, the mirrors do not need to be 1.4 m long, so they will be less expensive.

Staffing

In order for the extensive upgrades to occur to ID-12 in Hutch B, while the BM is being constructed, at least two new beamline staff are required, which should build up to three asap.

1.3 High Accuracy XAS

High Accuracy XAS is driven towards improved theoretical models, the key constraint to information content and insight in experimental work is due to insufficient treatment of experimental systematics. Future developments could provide the AS with another leading-edge capability, but the lead time for consultation within the XAS community for the requirements of a third beamline in terms of appropriate optics and measurement components, and deciding on the appropriate beamline (super bend or insertion device), is beyond the current proposal. However, a third beamline is of sufficient importance that detailed planning and design should commence as soon as possible for medium-term implementation.

High accuracy XAS measurements allow measurement of thermal dependencies, dynamic ellipsoids, measurement of nano-roughness, single crystal XAS, absorption detection for dilute systems, improved accuracy of fluorescence studies, and investigations of accurate bonding and inelastic mean free paths [6]. While the primary focus of the BM beamline will be for general users, with careful attention to the design of the beamline, it could be possible to make provision for significant high accuracy XAS capabilities. In particular, this would include: (i) length of hutch to allow routine advanced diagnostics; (ii) interferometric encoding and feedback on process variables of optical elements including shutter, DCM, offset, and mirror settings; (iii) IDL control of routines for data collection and separately analysis; (iv) measurement of scattering, harmonic and linearity contributions to attenuation and fluorescence noise and correlation signals (using the equivalent of 'Daisy Wheels'); (v) filter bank to control and adjust saturation and non-linearity problems for sample or detectors; and (vi) a method across much of the energy range for quantifying energy non-linearities.

Some of these high-accuracy techniques that provide accuracies some 100 times better than the international standard [7] will not be able to be implemented (especially below 2 keV) – perhaps the key issue being vacuum sample diagnostics and standard samples. Moreover, high flux applications (i.e. high precision, ultra-dilute systems, enhanced sensitivity, transient catalytic or biological intermediates, short times or ultrafast dynamics, QuickXAFS, RIXS) argue for a wiggler/undulator or at least a superbend. The methodologies and equipment required for enhanced bonding distances, local structures and thermal (dynamic) ellipsoids using advanced techniques, are proven for systems between 5 keV and 60 keV, but can be extended in most aspects in a straightforward manner down to approximately 2 – 2.5 keV, hence potentially covering much of the energy range of this proposal. However, the enhanced components for more specialized capabilities are not included in this proposal.

B2: Applications and Potential Outcomes to Australasian Scientific Community

The research performed as a result of these new capabilities impinges on a diverse range of ARC Priorities

Frontier Technologies for Building and Transforming Australian Industries:
Breakthrough Science: Cutting edge science in Biological Sciences, Chemistry, Engineering, Environmental Sciences, Material Science, Medical Sciences, Physics and Soil Science.
Frontier technologies: beamline and sampling capabilities at the international cutting edge.
Advanced materials: advanced new materials in polymers, electronics and solar energy.

An Environmentally Sustainable Australia:
Transforming existing industries: improved mineral processing, improved crops.
Overcoming soil loss, salinity and acidity: detailed investigations of acidity in soil science.

Promoting and Maintaining Good Health:
Ageing well, ageing productively **and** *A healthy start to life:* drug design and metal toxicity.
Preventative healthcare: development of preventative treatments of diseases.

2.1. Advanced Fluorescence Capabilities

2.1.1. High-energy-resolution fluorescent detected XAS (HERFD).

Typically, the ~1-eV energy resolution leads to extremely high background rejection, which is independent of the count-rate. The narrow region of the fluorescence spectrum that can be sampled enables XAS measurements from a specific coordination environment in a sample containing more than one chemical environment of the same element. The resultant site-selective XAS can be used to provide speciation in complex biological, environmental and mineral systems, e.g., Ni speciation in Fe based minerals (A. Gerson, Uni SA); Mn and Fe oxides on Co soil chemistry (R. Collins, UNSW); the chemical state of Fe states in clays (W. Gates, Monash); Cu species during in-situ catalytic reaction (M. Stockenhuber, U. Newcastle); and EXAFS analysis of polynuclear metalloproteins and speciation in complex bioinorganic complexes (H. Harris, U. Adelaide; P. Lay, USyd, S. Best, UMelb).

This principle can also be extended to, eg, the case of mixed-valence compounds, where it is possible to exploit the chemical shift in the emission channel to perform direct site-selective measurements. There are also other advantages in the use of such systems such that the lifetime broadening of spectra can be removed so that spectral resolution of K-edge XANES could be similar to that of the L edges [8], eg, L-edge like spectra can be measured using hard X-rays at the K edge in 3d transition metals with sensitivity to record spectra even on dilute samples such as metalloproteins. This offers significant advantages to distinguish eg mixed-valence systems of V, Mn, Cr and Fe (A Berry, ANU/Imperial College).

2.1.2. X-ray Raman spectroscopy (XRS).

X-ray Raman spectroscopy refers to the inelastic scattering of hard X-rays by excitation of an inner-shell electron into an unoccupied state but has an extremely small cross-section (10^{-5} – 10^{-4} of that from conventional XAS). However, it is possible to obtain soft X-ray XAS information with hard X-rays, and allows the study dipole-forbidden transitions not accessible with conventional XAS selection rules. Typically C and O XAS measurements are performed under vacuum conditions and result in serious complications due to windows and self-absorption; however, the use of hard X-rays to obtain soft X-ray spectra enables samples to be studied under chemically relevant *in-situ* or extreme conditions, which is simply not feasible with soft X-rays. The power of the technique is illustrated in two prototypical examples – the study of the electronic and geometric structure of liquid water at the oxygen K edge [9] (the most cited *Science* paper in 2004), and the study of graphite under high pressures [10].

Applications to the Australian XAS community are numerous. Polymer and organic electronic materials may be measured in their natural environments, and the penetration depth of hard x-rays (compared to soft x-rays) ensures true bulk sensitive measurements (L Thompsen, AS); C in minerals can be studied in their natural state, without concerns of surface contaminants, or under extreme conditions with *in situ* cells. For many hard X-ray studies on natural or in-situ systems, it is of great interest to establish the organic ligand bonding to, eg, a metal site. By combining both hard X-ray XAS on the metal site and XRS for the low Z elements, it is possible to completely characterise the chemical bonding in the system. This is extremely useful for eg coordination chemistry and metal speciation in geological fluids (J Brugger, SAM; W Lui CSIRO) and the study of coal pyroloysis and liquidification reactions over inorganic catalysts at high temperatures (Li, Zhang, Curtin). It can also be used to study the C, N and O content of biological samples and how they change under different conditions (P Lay, USyd).

2.1.3. High-resolution X-ray emission spectroscopy (XES)

X-ray emission is a second-order process: a core hole is created and when this core hole is filled X-ray emission or fluorescence results. XES thus has chemical sensitivity via the chemical shift, which can be due to two mechanisms. If the core hole is replaced by another core hole, the final state core hole interacts with the valence electrons and this interaction shapes the emission line. The K_β lines, for example, are sensitive to the valence-shell spin-state. It is also possible to probe the valence shell directly. In this case, the energy of the emission spectrometer is tuned close to the Fermi level. These emission lines are very sensitive to the ligand orbitals of 3d transition metals and thus the type of ligand can be identified such as the coordination environment of Zn proteins with N/O donors [11].

2.1.4. Resonant inelastic X-ray scattering (RIXS)

The spectral shape of fluorescence lines depends on the way the core hole is created. Tuning the incident energy to an absorption edge results in spectral changes in XES as a function of the incident energy. Here, the absorbing atom is not ionized for resonant excitations, as the photoexcited electron stays within a bound state. The spectral features become sharper, as described above, and the lifetime of the final state now determines the broadening. This allows fine details of the electronic structure of the system, as well as dynamics to be determined. For examples, RIXS spectroscopy can be applied to understand the oxidation state of V in silicate glasses, which can be used as an indicator of the redox conditions under which the material is formed. This can provide insight into, eg., how the geological processes in the Earth have evolved in time (H. O'Neill, ANU). Mn 1s RIXS spectroscopy can be used to study Ru and Mn water oxidation catalysts (L. Spiccia, R. Hocking, Monash). The potential of this technique in the chemical sciences is considerable because valence shell excitations are observed by means of an element selective, hard X-ray technique.

2.1.5. Ultra dilute XAS

Trace levels of elements play a vital role in geology, environmental science, biology, chemistry, and material science and sometimes only small samples are available. The microprobe capability will enable XAFS to be obtained from very small ultra-dilute samples (i.e. below 1 mM, ~ 50 ppm). For instance, XAS studies of metalloproteins are often limited by solubility, or by the formation of oligomers or homodimers (Cu metallochaperone, Atx1), which are circumvented at μM concentrations (L. Giachini, AS). A detailed study and understanding of the role of dopants and defects sites in semiconductor systems has been sometimes elusive, and could be applied to many technology relevant systems (C. Jagadish, M. Ridgway ANU, C. Glover AS). In addition, such sensitive detection is essential for obtaining XAS from small biological samples, such as cell pellets (P. Lay, USyd).

2.2. 'Quick' EXAFS

Measurement of XANES or even full EXAFS with up to ~ 13 ms time resolution allows the dynamical chemical and geometrical structure of processes and chemical reactions to be monitored in realtime. Q-EXAFS has found significant applications in catalysis research [12] but also has wide applications to, eg, chemical decomposition reactions, thin film growth, solid-state reactions, phase transformations, and laser excited reactions. A Q-EXAFS facility coupled with *in-situ* capabilities and fast fluorescence detection capability (Maia) would further open significant opportunities for a wide range of research.

Active sites in heterogeneous catalysts are often dilute and, hence, require fluorescence detection and transient measurements, which are a crucial tool in the understanding and development of new catalytic processes and materials. This will enable, for example, the mechanisms of the deactivation mechanisms of zeolite catalysts to be determined (M. Stockenhuber, U. Newcastle). The rapid collection of XAS would open the possibility of in-situ studies of electrosynthesis reactions. The metal-specificity of Q-EXAFS XANES results would greatly assist in the analysis of results obtained using conventional spectro-electrochemical techniques (IR, UV-Vis) in the study of metallocatalysts (S. Best, U. Melb).

Q-EXAFS can monitor the reduction of U(VI) to U(IV) by Fe(II) sorbed onto Fe(III) oxides and subsequent incorporation into stable Fe(III) oxides to mimic natural phenomena - with the aim to reduce the environmental U mobility (R. Collins, UNSW).

When coupled with KB microfocusing capabilities, Q-EXAFS offers a novel and extremely fast method of XANES stack imaging. This is pertinent to photosensitive species in biological systems, which are elusive targets with intense x-ray beams; ie, rapid XANES spectra at each spatial point in a scan would allow much faster imaging, limiting dose and a more accurate representation of the distribution of photosensitive species. Mapping the distribution of different chemical forms of particular elements within intact tissue samples is an important goal of research aimed at understanding processes that occur in healthy cells and those challenged by disease or disease treatment (H. Harris, U. Adelaide; P. Lay, USyd).

2.3. Experimental infrastructure upgrades.

In situ cells (pressure, temperature, electrolysis, solution etc) offer real-life sample environments for much of the processes we observe in the world. *In situ* capabilities, coupled with Q-EXAFS and advanced fluorescence offer the possibility for a unique facility in the world. A high-temperature general purpose furnace will enable in-situ studies of formation and relaxation of material systems on either beamline, such as: clustering kinetics of metals in metallic alloys (of relevance to the CSIRO Light Metals National Research flagship); structural relaxation in amorphous semiconductor systems (M. Ridgway, ANU); formation/ properties of chalcogenide glasses for ultrahigh-bandwidth optical devices (D. Bulla, ANU). Many other opportunities exist to apply XAS to obtain element specific structural information from systems studied at high pressures with high fluxes, where past experiments efforts have been limited by the significant proportion of X-rays absorbed by the diamond anvils, eg, pressure-induced polyamorphism in glasses and liquid-liquid transitions in high P-T melts. Pressure can readily tune various magnetic and electronic properties providing opportunities to discover new novel materials [13] an anisotropic vibrational properties in semiconductors can be studied as a function of pressure and phase transformations (L. Araujo, ANU).

Radioactive sample handling will enable both natural and artificial radioactive studies. Australia holds the largest U deposits in the world, and studies performed under typical *in-situ* conditions can shed insight to highly relevant issues specific to Australia: including geothermal energy, U exploration and mining (J. Brugger, SAM). A more fundamental example is temperature-dependent charge ordering that can have a dramatic effect on the physical, magnetic and electronic properties of metal oxides. Charge ordering occurs where a metal cation has two accessible oxidation states and a small change in environment favours one state over another. Charge ordering is being studied in systems containing a 3d transition metal such as Mn or Cu together with a heavier metal – including Tc and U (B. Kennedy, USyd). Tc is also very important in the development of new radiopharmaceuticals for nuclear medicine and is formed during fission of U, hence, it is also important for the development of suitable ceramic waste forms to immobilise Tc wastes (Z. Zhang, ANSTO).

2.4 Extended Energy Range Capabilities

Biological Samples. The distribution of the lighter elements (S, P, Cl, Ca, K) and their chemical forms are crucial to understanding many biological processes, including diseases and their treatment. For example: the redox status of cells, which is defined by the RSH/RSSR ratio and their distributions are crucial in many biological samples; thiolates are also used in cellular resistance responses to anti-cancer drugs; the degree protein phosphorylation and the ratio of free phosphate compared to organic phosphate are important in many physiological functions; and the release of Cl^- ligands from metal-containing anti-cancer drugs can also be monitored as a function of time, space and environment, which is very important in understanding their biological activities. XAS on these elements are also of interest in studying biomolecules (Harris, Adel; Lay, Witting, USyd). Finally, the Si K-edge is important in certain biological samples, since Si is commonly incorporated into biominerals.

Environmental Samples. Similar issues as those mentioned above can be addressed in environmental samples, i.e., redox status and speciation from S K-edge, distributions and speciation of inorganic and organophosphate pollutants and their breakdown; speciation of organochlorine pollutants and their breakdown to inorganic Cl^-, etc. An example is the use of

Cl K-edge XAS to study the fate of NaCl in coal (Dr. R. Hocking, Monash, with Professor C. Z. Li, Dr M. Adadullah, Curtin Centre for Advanced Energy Science and Engineering). In particular, Cl K-edge XAS will be used to study the fate of NaCl in coal in order to determine temperature thresholds for the formation of organochlorine species.

Soils and Minerals. Silicates, phosphates, sulfur anions, (S^{2-}, S_2^{2-}, SO_4^{2-}, etc.), chloride, etc. are found in many minerals and the XANES from these anions are sensitive to the nature of the metal to which they are bound and the unit cell (environment). When combined with the metal XANES on the same samples (that will be possible with the beamline), superior speciation and spatial distributions will be possible than relying on a metal K-edge alone (Dr. W. Liu, CSIRO). With controlled environment cells, information can also be obtained on speciation of complexes under hydrothermal conditions leading to precipitation of certain minerals and studies of the crystallization processes. An example of a project is the use of S K-edge XAS characterization of acid sulfate soils (Dr R. Hocking, Monash; Dr E. Burton, and Prof L. Sullivan, Southern Cross University; and R. W. Fitzpatrick and M. R. Raven CSIRO). The S K-edge XAS will be used to identify reactive intermediates in reduced S sediments in order to characterize biotic vesus abiotic reaction chemistry, as well as key chemical differences between different acid sulfate soil environments.

Materials. There are many examples in which XAS of these elements are used for important scientific and technical problems; e.g., understanding amorphous Si phases (including structurally relaxed) and Si oxides of importance to mass produced solar cells (Dr. C. Glover).

Ionic Liquids. The chemistry of ionic liquids, which are finding their way into many areas of advanced science, including their interfacial characteristics as effective coatings on Mg alloys can be studied with P, Cl and S XANES (P. Howlett, CSIRO, D. McFarlane, Monash).

Bonding. The S, P and Cl XANES are very sensitive to the degree of covalency in bonding of a whole range of ligands with these donors bound to metal ions. A combination of such XANES spectroscopy, together with complementary information on the metal XANES and DFT calculations, is revolutionizing our understanding of bonding in metal complexes.

2.5 Fluorescence XAS Studies on Photosensitive Samples

BioXAS and Environmetal XAS. The BM beamline is preferred to ID-12 in terms of the quality of the XAS data that can be obtained due to both beamline stability and a reduction in photodamage. Thus it is expected to be the preferred beamline for fluorescence measurements involving the medium to higher concentration ranges appropriate for fluorescence experiments, or for much of the XAS of metalloproteins in high oxidation states, e.g., Fe(III) and Cu(II) metalloproteins are rapidly reduced by the beams available from insertion devices on third generation sources and, hence, more reliable XANES and XAFS data are obtained on bending magnetic beamlines [14]. As such, this beamline will be used for much of the high-quality science for which it is more appropriate than ID-12.

2.6 Transmission XAS

Nearly all transmission XAS will be moved from ID-12 to the new BM beamline because of the superior data that it will produce compared to ID-12 (due to greater beam stability, sample inhomogeneity distortions with a focused beam and, in some cases, photodamage). The following are examples of the types of experiments that will be undertaken.

Biological and Drug Samples. For a range of systems, including drugs in biological samples or the rapid precipitation of amorphous or microcrystalline intermediates high quality transmission data are required for three-dimensional structure determination about a metal centre (eg, reactive Cr(VI), Cr(V) and Cr(IV) intermediates involved in the biochemistry of Cr cancers and Cr dietary supplements [14].

Materials and Minerals. There are many materials, such as amorphous materials, microcrystalline materials and composite materials in which transmission XAS is the best method for characterization of metal and anion sites and speciation of mixtures.

Coordination Complexes. Studies on covalency in metal-ligand bonds are normally conducted in transmission mode. It is essential in calculating the bonding parameters that high quality data are obtained, free from any distortions caused by inhomogeneity.

2.7 Microprobe Capabilities

Microfocus capabilities on the ID-12 and BM beamlines will complement the capabilities of the highly oversubscribed AS XFM beamline and to some extent, the proposed new X-ray microprobe beamlines, in three main areas:

- 1.8-5 (Si to K K-edges) and additionally 20-37 keV since the focussed beam for Tc-I K edges at XFM suffers reduced performance above 20 keV).
- 2 – 100 µm spot size (being larger than XFM)
- Spectroscopy quality XAFS data on a microscopy spatial scale (XFM is undulator based)

Many opportunities exist in large area imaging, where smallest resolutions are not required, in archaeology, cultural heritage and forensics. Large scale X-ray imaging of the Archimedes Palimpsest [15] had made this field high profile, and the National Gallery of Australia is undertaking XRF imaging of artworks. In biology, gel electrophoresis is a technique used for the separation of DNA, RNA, or protein molecules using an electric current applied to a large area gel matrix. Large area XRF mapping and associated micro-XANES of post incubated and stained gels offers great possibilities to understand the in vivo mechanisms of the interaction of drugs and their target cells. Current studies include investigations of the biotransformations of metal pro-drugs, such as Ru- and Ga-based anti-cancer drugs and Cr- and V-anti-diabetic drugs on blood serum and cells is being studied by a combination of XRF mapping and XAS (P. Lay USyd). There are also many biological, environmental, mineral and materials samples where spectroscopic imaging over the elements Si-K are important and presently are not possible at the AS XFM.

Interest in Tc and Cd imaging has been expressed from the biological and environmental communities, and the geological communities are specifically interested in Ag, Sn and I [16]. For instance micro-XAS will be used for the investigation of metal speciation in soil, rock and fluid inclusions (W. Liu, CSIRO).

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B3: Match to Selection Criteria

☐ Meet the demands of an identified group of researchers for new techniques

The Australian XAS community is mature and well-developed after 15 years of experience at the ANBF plus many international facilities. This proposal provides a diverse array of state-of-the-art capabilities that will cover most of the needs of the Australasian XAS community. Specifically, the energy region of the K-edges of Si-Ca is extremely important for biological and environmental samples, minerals and materials and ambient and controlled atmospheric conditions, but it is underrepresented internationally in synchrotrons because of early challenges faced with energy range. It is a similar situation with the advanced spectroscopic capabilities of ID-12. In various User Meeting breakout sessions, there has been unanimous support amongst the large XAS community for these developments.

☐ Take advantage of the existing third generation light source

The upgrades of ID-12 require very high beam intensities at the sample that third generation light sources deliver. A BM beamline was chosen for the second beamline because chemical information is easily lost by photo-damage in these intermediate energy ranges (e.g. for S). However, a third-generation source is also required for the BM beamline in order to gain sufficient photon flux at the sample to be useful for the diverse range of studies.

☐ Will position Australasian scientists at the leading edge of their field

Australian researchers are at the leading edge of many areas of Biological, Chemical, Environmental, Materials and Minerals research but, in order to maintain this edge, they need to have access to a range of cutting-edge synchrotron tools. With the current capabilities at the AS and those proposed for new micro-XAS and XAS, this proposal will complete a capability for XAS that is difficult to access internationally because of the relatively few XAS beamlines with these capabilities.

☐ Can be demonstrated to be feasibly constructed within a 3 year timeframe

The proposed upgrades to ID-12 can be achieved within the 3-year timeframe, as much of the installation and development can go on in hutch B while hutch A is being used for experiments. For the BM beamline, all of the main components sought in this proposal leverage proven existing technologies, are low risk, and will be purchased from commercial suppliers. The Si-drift Maia detector required for the medium-energy range will be fabricated by local contractors (CSIRO), as the next phase of development and should be available towards the end of the 3-year timeframe. Significantly less than a three-year time frame will be readily achievable for the basic beamline and hutch capabilities.

B4: Potential Users

While only a small number of representative examples of projects from the Australasian XAS community can be detailed, this community is large in number, geographical spread and diversity of science, which cover most research areas of the international XAFS community.

The beamline proposal has created a wide range of interest from over 100 users from over 30 Australasian and international institutions. These users span Biological Sciences, Chemistry, Engineering, Environmental Sciences, Material Science, Medical Sciences, Physics and Soil Science. Given these are only people who have expressed an interest through the formal processes, the beamlines are of interest to many more users.