Maia Mapper: high definition XRF imaging in the lab

C.G. Ryan, R. Kirkham, G.F. Moorhead, D. Parry, M. Jensen, A. Faulks, S. Hogan, P.A. Dunn, R. Dodanwela, L.A. Fisher, M. Pearce, D.P. Siddons, A. Kuczewski, U. Lundström, A. Trolliet and N. Gao

Commonwealth Scientific and Industrial Research Organisation, Normanby Road, Clayton VIC 3168, Australia

National Synchrotron Light Source II, Brookhaven National Laboratory, Upton NY 11973, U.S.A.

Excillum AB, Torshamnsgatan 35, 164 40 Kista, Sweden

XOS, 15 Tech Valley Drive, East Greenbush, U.S.A.

E-mail: Chris.Ryan@csiro.au

Abstract: Maia Mapper is a laboratory μXRF mapping system for efficient elemental imaging of drill core sections serving minerals research and industrial applications. It targets intermediate spatial scales, with imaging of up to ∼ 80 M pixels over a 500 × 150 mm² sample area. It brings together (i) the Maia detector and imaging system, with its large solid-angle, event-mode operation, millisecond pixel transit times in fly-scan mode and real-time spectral deconvolution and imaging, (ii) the high brightness MetalJet D2 liquid metal micro-focus X-ray source from Excillum, and (iii) an efficient XOS polycapillary lens with a flux gain ∼ 15,900 at 21 keV into a ∼ 32 μm focus, and (iv) a sample scanning stage engineered for standard drill-core sections. Count-rates up to ∼ 3 M/s are observed on drill core samples with low dead-time up to ∼ 1.5%. Automated scans are executed in sequence with display of deconvoluted element component images accumulated in real-time in the Maia detector. Application images on drill core and polished rock slabs illustrate Maia Mapper capabilities as part of the analytical workflow of the Advanced Resource Characterisation Facility, which spans spatial dimensions from ore deposit to atomic scales.

Keywords: X-ray fluorescence (XRF) systems; X-ray detectors

Corresponding author.
1 Introduction

The goal of Maia Mapper is to capture fine details, such as trace element indicators and rare precious metal phases at micron dimensions, set in the broad spatial context of mineralized veins, bedding and alteration zones visible in hand specimens or drill core that span ~ 0.5 m collected in mineral exploration or ore body delineation campaigns. This combination of spatial and analytical resolution over such large length-scale bridges the gap in scale between the research environment examining micro-scale controls on mineralisation and metre-scale average values, which is the finest scale of granularity commonly used by mining companies. Datasets allow geologists to characterise the variability at the cm-scale and ensure that the sub-samples used for more detailed work are representative of the larger rock mass and that the micro-scale results can be meaningfully put back into this context.

Detecting small features requires small beam size and small image pixel. Large area mapping then demands a huge number of image pixels, and hence a small time allocated to each. This demands an intense focussed X-ray beam in order to excite adequate fluorescence yields and an efficient detector system capable of high count-rates in order to achieve useful counting statistics and detection limits in each pixel.

A further goal is to develop an enclosed laboratory-based system, which complements both synchrotron based systems, by providing greater accessibility, and portable macro-XRF (MA-XRF) systems (e.g. [1–3]), by permitting higher power sources with more intense X-ray beams combined with larger detector arrays for enhanced total count-rates and data throughput.

The Maia detector array has transformed X-ray fluorescence microscopy (XFM) at synchrotron laboratories [4–6]. XFM beamlines at the Australian Synchrotron in Melbourne [7], the Petra III synchrotron in Hamburg [8], the NSLS-II synchrotron at Brookhaven and the CHESS synchrotron at Cornell [9] use a Maia detector array interfaced to sample stage and beamline control to achieve high definition element imaging to beyond 100 M pixels with collection times of a few hours and
times per pixel as low as 50 µs. The main advantages it brings to the Maia Mapper project are its large collection solid angle (1.3 sr), to make the most of available fluorescence, its annular back-scatter geometry, to permit large sample movement despite close detection geometry, and its capability for ~ 100 M pixel images. The latter enables detail at 10’s of µm to be captured in images spanning up to 500 mm. Maia requires only a connection to the position encoders of the sample scanning stage to implement a complete XRF imaging system, including real-time elemental deconvolution and pixel dwell time normalization. This simplifies this project significantly.

The intensity of fluorescence lines is proportional to the ionization cross-sections, which vary as $\sim 1/E^3$ for exciting beam energies $E$ above the absorption edge. This favours using source energies (e.g. anode lines and filtered bremsstrahlung) immediately above the edges of elements of interest. However, elastic and inelastic scattering of the source spectrum can produce significant interference. In addition, for hardening filters to be effective in combining high source intensity with adequate suppression of the background under lines of interest, the useful parts of the filtered source spectrum must also be somewhat above the lines of interest to avoid excessive attenuation. For the detection of trace elements up to Zr K, this suggests filtered source energies $\sim$ 19–20 keV or more and significant hardening filters to suppress background.

For a given focussing optic, the focussed beam intensity is proportional to the source brightness, reflecting the phase space flux density, and the fraction of phase space sampled by the optic and spatial filters. Source options include the microfocus X-ray source, with recent innovations, such as the liquid metal jet anode [10] and the linear anode array [11], the rotating anode X-ray source and a range of emerging novel X-ray source concepts, which include the so-called benchtop synchrotron sources [12, 13] and laser induced X-ray sources [14–16]. Encouraging as these developments are, at the time of making design and purchase decisions for Maia Mapper, these novel source options were deemed to be experimental and not routine, of insufficient pulse repetition rate, or lacked indicative brightness data. Hence, selection and modelling were confined to the microfocus and rotating anode sources.

Targeting beam energies in the vicinity of 20 keV means that the critical angle for total external reflection for mirror surfaces shrinks to $\sim$ 1.5 mrad for glass and 4 mrad with a Pt coating. This limits the acceptance solid-angle of optical systems based on Kirkpatrick-Baez or nested Montel mirrors. Graded multilayer coatings can increase reflection angles with the added benefit of selecting a variable energy bandwidth. However, such multilayer thickness periods become very demanding at these energies and the total beam flux is reduced. In the Maia Mapper development, the target spatial detail of 10’s µm permits the use of polycapillary X-ray lenses, which provide hundreds of thousands of curved capillary channels working in parallel to offset the reduction in critical angle. The result is higher flux but with a focal spot size limited by the product of critical angle and working distance.

In summary, the design concept for the Maia Mapper converged towards a laboratory system capable of imaging details at 10’s µm set within a broad spatial context of up to 500 mm, based on the Maia detector array, a high brightness microfocus X-ray source, filtered to select energies of 19–20 keV and above, a polycapillary lens and a large format sample scanning stage. This paper describes the Maia Mapper in detail and illustrates its performance using drill core and polished rock samples from mineral exploration and processing applications.
2 Modelling and source selection

X-ray tube bremsstrahlung and characteristic lines spectra were modelled building on the paper by Ebel [17]. Ebel’s approach assumes pure element targets, so some work was needed to accommodate alloy anodes, such as the liquid Ga-In-Sn alloys used in the Excillum D2 source. Bremsstrahlung depends on an estimation of the mean electron depth distribution $\rho_z$, which is only weakly dependent on $Z$ between Ga, In and Sn. Hence, in analogy to using the Bragg rule for combining stopping power in a compound, the mean electron depth distribution was estimated using mass fraction weighting of inverse $\rho_z$ calculated for the component elements. The backscattering factor and self-absorption were also adapted to the alloy. The resulting model bremsstrahlung continuum plus characteristic lines spectrum agrees well with source spectra obtained from Excillum for the D2 at 70 kV.

Alternative sources schemes were evaluated for different source anode materials and voltage and hardening filters by considering the anticipated detection limits for the $\alpha$ line of a set of elements that sample potential trace elements of interest. The excitation of fluorescence for each element is proportional to the product of brightness and the ionization cross-section integrated over the filtered source spectrum. The expected background under fluorescence lines is related to the filtered source spectrum scattered from the sample and proportional to detector incomplete charge collection, which can produce background under the lines of interest. This approach was used to develop a figure of merit that allowed consideration of not only brightness, but simultaneously the influence of different anode materials and hardening filters on the model spectrum and resulting detection limits for the selected trace elements. This analysis showed that the high brightness of the Excillum D2 X-ray source more than offset the deficit in fluorescence that comes from using anode lines (e.g. In K lines) at higher energy compared to some solid anode sources. Thus the D2 was selected for Maia Mapper.

3 Instrument design

The Maia Mapper uses the Excillum MetalJet D2 microfocus X-ray source with liquid metal jet anode [10], which provides a 200 W, 70 kV electron beam focussed into a $80 \times 20 \mu m^2$ spot on the $\sim 175 \mu m$ metal stream for an effective $20 \mu m$ source size as viewed from each of two exit port axes orthogonal to the e-beam. The I2 alloy (Ga 47%, In 37% and Sn 16%) anode was selected for enhanced bremsstrahlung and In K line yields. Finer focussing options can be selected for a 50 W or 100 W beam into an effective source spot size of 5 or 10 $\mu m$, respectively. The Excillum source provides tight regulation of the e-beam current, which is well suited to routine applications and scans that can take from hours to days.

The polycapillary lens was supplied by XOS, designed to sit as close as possible to the Excillum source with some room for the addition of hardening filters. This set the input focal length of the polycapillary to 29 mm. An output focal distance of 14 mm permitted the polycapillary lens to be located just upstream of the Maia annular X-ray sensor. With these constraints, XOS produced a polycapillary lens with a high flux gain of 21,000 at Mo $K\alpha$ and an acceptance at the source of $\sim 43 \mu m$ (at 24 keV). The transmission measured by XOS means that this gain becomes 15,900 at 21 keV and 12,700 at 24.1 keV (In $K\alpha$). For a source size of $\sim 20 \mu m$, the measured focus spot size reported by XOS is 31.3 $\mu m$ at Mo $K\alpha$. For a source power of 200 W, and a 1.0 mm Al filter, the anticipated focussed flux becomes $1.6 \times 10^9$ ph/s.
The polycapillary, mounted on a pair of Micronix piezo XY stages, was built into a modified Maia detector vacuum housing. The stages enable the ends of the polycapillary to be moved ±2 mm in order to align it both with the X-ray source and the molybdenum collimator through Maia (figure 1), which also acts to suppress remnant high energy unfocussed beam. Maia is mounted on linear bearing tracks with stepper motor drive to provide about 5 mm of travel along the beam direction (Z). Used together with the piezo stages, this enables alignment of the polycapillary lens for maximum transmitted flux.

The Maia system is described in detail elsewhere [18, 19]. The sensor is a silicon monolithic array of 384 $1 \times 1$ mm$^2$ elements, each with its own charge amplification and pulse capture electronics, implemented by Application Specific Integrated Circuits (ASICs). Charge-sharing effects within the monolithic sensor, which may compromise the peak-to-background ratio, are suppressed by a molybdenum mask, which is optimized for the 10 mm distance between sample plane and sensor [20]. This sample plane is also the focal plane of the X-ray optic. ASIC readout, photon-by-photon correction, and real-time spectral deconvolution are performed in Field Programmable Gate Arrays (FPGAs). The latter uses a Dynamic Analysis (DA) transform matrix [21] constructed using the GeoPIXE software [22].

![Figure 1](image)

**Figure 1.** Perspective view of the Maia Mapper 3D model showing a section through the Maia detector and polycapillary lens with its two miniature Piezo XY adjustment stages used to align polycapillary acceptance with the source spot and thread beam through the Maia collimator.

Samples are supported on reconfigurable frames using various mounts tailored for standard drill core diameters, flat samples, and irregular shapes. The frame is positioned on the sample stage using a kinematic mount. Sample configurations can weigh up to 10 kg. The frame also supports fiducial markers and XRF standards.

The 3-axis, 4-motor sample stage comprises a pair of Parker ball-screw stages, operated in coordinated gantry mode, to provide 155 mm of vertical travel (Y), supporting a Parker linear motor.
stage with a 0.1 \( \mu \text{m} \) pitch linear encoder, providing about 700 mm of horizontal travel (X). Finally a low-profile Z stage supports the sample frame. This scheme provides a scanning volume of \( 520 \times 155 \times 5 \) mm\(^3\). The X stage is scanned as the fast raster axis. The Z stage is used to adjust the sample to the focal plane of the X-ray beam and Maia detector.

A camera, with telecentric lens and lighting located next to the Maia housing, is used to construct a tiled visual image of the entire sample frame, and a nearby parallax laser depth probe is used to construct a map of Z profile with \( \mu \text{m} \) precision. This map can be used to drive the Z stage to keep non-flat samples within the focal depth of the X-ray beam.

Future development of the Maia Mapper system will exploit the second output port of the Excillum source with a second Maia and explore an alternate optic for higher spatial resolution using a Sigray twin paraboloidal cylindrical mirror lens [11], which has an expected point spread function of 5 \( \mu \text{m} \) for an anticipated spatial resolution approaching 7 \( \mu \text{m} \).

The Excillum source and up to two Maia detectors and sample stages are mounted on an optical table inside a radiation shielded enclosure. Access is controlled for both radiation and motion safety purposes using a PLC based control system, which monitors the state of door and removable panel coded magnetic switches, the state and health of source shutters and high voltage and controls user access door locks.

![Maia scan of a polished sample from the ore zone of the Jundee gold mine](image)

**Figure 2.** Maia scan of a polished sample from the ore zone of the Jundee gold mine, (370 \( \times \) 149 mm\(^2\), 12333 \( \times \) 4967 pixels, 61 M pixel count, 30 \( \mu \text{m} \) pixel size, 2.7 ms dwell time) showing a) Ca distribution, and histograms of pixel b) count-rate and c) dwell time (ms).

Software is organized using cloud services with daemons providing dedicated control of the safety system, sample stages, Maia detectors, Piezo stages, cameras and Z profilers together with services such as detector cooling, using communication based on ZMQ protocols [23]. Global variables and daemon configuration parameters are stored in a Redis key-value store (KVS) accessed through ZMQ. Areas to be scanned are added to a scan list, stored in the KVS, which holds scan
parameters and sample metadata. Selected scans in the list are run in an automated sequence with Maia event data and metadata logged to cloud storage. DA images, detector spectra and a count-rate map are displayed in real-time using a graphical client.

4 Performance

The system performs automated, unattended mapping on ground drill core and polished rock slabs with scan areas typically 200–500 mm in length by 40–100 mm width for one or more drill cores and up to 150 mm for large slabs (e.g. figure 2). Typical transit time per 30 µm pixel is 2–10 ms with a distribution reflecting speed variations in the Galil stage controller (e.g. figure 2c). Count-rates per pixel up to 3 M/s are encountered (figure 2b), with detection from 2 to beyond 32 keV (Ba K), and dead-time per pixel per detector is small, typically only rising to ~ 1.5%.

The images (e.g. figure 2a), normalized to pixel transit time, show no evidence for uncorrected stage speed variations or source intensity fluctuations, which is consistent with accurate time per pixel determination (20 ns precision) and Excillum emission current monitoring that exhibits regulation at ~ 0.1% RMS. Linear traverse data extracted from images, across sharp euhedral grain boundaries, indicate an estimated beam FWHM of 32 µm.

5 Applications

Large area mapping of rock samples at super high definition can reveal informative trace element distributions and the locations of rare precious metal phases in the broad spatial context of the large slab or drill core section. Even low bulk concentrations of elements such as Au and Pt at tens of ppb may be concentrated in rare micron-scale particles, which can be detected using Maia Mapper. Their location can provide insight useful for understanding ore formation and for extracting Au or Pt during processing (e.g. figure 3).

Figure 3. Maia Mapper scan of a drill core distal to ore from the Jundee gold mine (231×46 mm², 7700×1533 pixels, 30 µm pixel size, 6.0 ms dwell time) showing RGB images of a) Ca-Fe-Mn, b) Rb-Sr-Mn, and insets showing c) Au-Fe-Ca image for a detail region (6.4 × 6.4 mm²) with a rare gold grain, and d) the spectrum extracted from the grain in (c) showing Au L lines.
The detail image in figure 3c shows a small gold grain detected in the large scan area of figure 3a,b. The changing signal for this particle across the detector array, reflecting self-absorption of Au L X-rays with changing take-off angles which span $13.9^\circ$ to $52.6^\circ$ across Maia, reveal that it is close to the surface of the sample (see method in [24]). The detected signal is consistent with a spherical model gold grain $\sim 8 \mu m$ in diameter. The detection limit corresponds to $\sim 3 \mu m$ particles under these conditions. Hence, it is possible with Maia Mapper to detect single gold particles down to $3 \mu m$ in diameter in an area of $\sim 100 \text{ cm}^2$ at a rate of $\sim 10$ minutes per cm$^2$.

6 Conclusions

The Maia Mapper achieves high definition XRF mapping of mineral samples at scales up to 500 mm with spatial resolution of $\sim 32 \mu m$ and sensitivity sufficient for trace element and rare particle detection. Count-rates up to 3 M/s indicate a good match between the high brightness of the Excillum microfocus source, the high gain of the XOS polycapillary lens and the large solid-angle of the Maia detector array, making good use of its count-rate capacity, and so provide XRF mapping performance approaching synchrotron pixel rates.

One Mapper is operational in CSIRO Melbourne and a second one is under construction for CSIRO Perth (using an Excillum D2+ source with 250 W power) that will ultimately support two end-stations for parallel mapping on both Excillum exit ports as part of the analytical workflow of the Advanced Resource Characterisation Facility, which spans spatial dimensions from ore deposit to atomic scales.

Acknowledgments

The development and construction of the Maia Mapper is supported by the Science and Industry Endowment Fund. The Jundee samples were generously provided by Northern Star Resources and Mark Creasy as part of an ongoing collaborative research project. The Advanced Resource Characterisation Facility (ARCF), under the auspices of the National Resource Sciences Precinct (NRSP) — a collaboration between CSIRO, Curtin University, and the University of Western Australia — is supported by the Science and Industry Endowment Fund.

References

[1] F.-P. Hocquet, H.-P. Garnir, A. Marchal, M. Clar, C. Oger and D. Strivay, A remote controlled XRF system for field analysis of cultural heritage objects, X-Ray Spectrom. 37 (2008) 304.
[2] M. Alfled, K. Janssens, J. Dik, W. de Nolf and G. van der Snickt, Optimization of mobile scanning macro-XRF systems for the in situ investigation of historical paintings, J. Anal. At. Spectrom. 26 (2011) 899.
[3] F.P. Romano, C. Caliri, P. Nicotra, S.D. Martino, L. Pappalardo, F. Rizzo et al., Real-time elemental imaging of large dimension paintings with a novel mobile macro X-ray fluorescence (MA-XRF) scanning technique, J. Anal. At. Spectrom. 32 (2017) 773.
[4] L.A. Fisher, D. Fougerouse, J.S. Cleverley, C.G. Ryan, S. Micklethwaite, A. Halfpenny et al., Quantified, multi-scale X-ray fluorescence element mapping using the Maia detector array: application to mineral deposit studies, Mineral. Deposita 50 (2014) 665.
[5] E. Lombi, M.D. de Jonge, E. Donner, C.G. Ryan and D. Paterson, Trends in hard X-ray fluorescence mapping: environmental applications in the age of fast detectors, Anal. Bioanal. Chem. 400 (2011) 1637.

[6] C.G. Ryan, D.P. Siddons, R. Kirkham, Z.Y. Li, M.D. de Jonge, D.J. Paterson et al., Maia X-ray fluorescence imaging: Capturing detail in complex natural samples, J. Phys. Conf. Ser. 499 (2014) 012002.

[7] D. Paterson, M.D. de Jonge, D. L. Howard, W. Lewis, J. McKinlay, A. Starritt et al., The X-ray fluorescence microscopy beamline at the australian synchrotron, AIP Conf. Proc. 1365 (2011) 219.

[8] U. Boesenberg, C.G. Ryan, R. Kirkham, D.P. Siddons, M. Allfield, J. Garrevoet et al., Fast X-ray microfluorescence imaging with submicrometer-resolution integrating a maia detector at beamline p06 at PETRA III, J. Synchrotron Rad. 23 (2016) 1550.

[9] L.M. Smieska, R. Mullett, L. Ferri and A.R. Woll, Trace elements in natural azurite pigments found in illuminated manuscript leaves investigated by synchrotron x-ray fluorescence and diffraction mapping, Appl. Phys. A 123 (2017) 484.

[10] D.H. Larsson, P.A.C. Takman, U. Lundström, A. Burvall and H.M. Hertz, A 24 keV liquid-metal-jet x-ray source for biomedical applications, Rev. Sci. Instrum. 82 (2011) 123701.

[11] W. Yun, S. Lau, B. Stripe, A. Lyon, D. Reynolds, S.J. Lewis et al., Novel, high brightness x-ray source and high efficiency x-ray optic for development of x-ray instrumentation, Microsc. Microanal. 22 (2016) 118.

[12] H. Yamada, S. Maeo, D. Hasegawa, M. Yamada, T. Yamada and T. Hayashi, MIRRORCLE type tabletop synchrotron light source realizing micron-order focus point, X-Ray Spectrom. 41 (2012) 201.

[13] E. Eggl, M. Dierolf, K. Aechterhold, C. Jud, B. Günther, E. Braig et al., The munich compact light source: initial performance measures, J. Synchrotron Rad. 23 (2016) 1137.

[14] T. Popmintchev, M.-C. Chen, D. Popmintchev, P. Arpin, S. Brown, S. Alisauskas et al., Bright coherent ultrahigh harmonics in the keV X-ray regime from mid-infrared femtosecond lasers, Science 336 (2012) 1287.

[15] T. Guo, C. Spielmann, B.C. Walker and C.P.J. Barty, Generation of hard x rays by ultrafast terawatt lasers, Rev. Sci. Instrum. 72 (2001) 41.

[16] S. Kneip, C. McGuffey, J.L. Martins, S.F. Martins, C. Bellei, V. Chvykov et al., Bright spatially coherent synchrotron X-rays from a table-top source, Nature Phys. 6 (2010) 980.

[17] H. Ebel, X-ray tube spectra, X-ray Spectrom. 28 (1999) 255.

[18] R. Kirkham, P.A. Dunn, A.J. Kuczowski, D.P. Siddons, R. Dodanwela, G.F. Moorhead et al., The Maia spectroscopy detector system: Engineering for integrated pulse capture, low-latency scanning and real-time processing, AIP Conf. Proc. 1234 (2010) 240.

[19] D.P. Siddons, R. Kirkham, C.G. Ryan, G.D. Geronimo, A. Dragone, A.J. Kuczowski et al., Maia X-ray microprobe detector array system, J. Phys. Conf. Ser. 499 (2014) 012001.

[20] C.G. Ryan, R. Kirkham, R.M. Hough, G. Moorhead, D.P. Siddons, M.D. de Jonge et al., Elemental x-ray imaging using the maia detector array: The benefits and challenges of large solid-angle, Nucl. Instrum. Meth. A 619 (2010) 37.

[21] C.G. Ryan, Quantitative trace element imaging using PIXE and the nuclear microprobe, Int. J. Imag. Syst. Tech. 11 (2000) 219.

[22] C.G. Ryan, D.P. Siddons, R. Kirkham, P.A. Dunn, A. Kuczowski, G. Moorhead et al., The new maia detector system: Methods for high definition trace element imaging of natural material, AIP Conf. Proc. 1221 (2010) 9.

[23] ZeroMQ, http://zeromq.org/.

[24] C.G. Ryan, D.P. Siddons, R. Kirkham, Z.Y. Li, M.D. de Jonge, D. Paterson et al., The Maia detector array and X-ray fluorescence imaging system: locating rare precious metal phases in complex samples, Proc. SPIE 8851 (2014) 88510Q.