MINSA
Mineralogical Association of South Africa
A division of the GSSA

Novel, interesting, and under-utilized techniques for applications in process mineralogy

RAMAN
SIMS
3D XRM
Micro XCT
LA-ICP-MS
XRD
Micro XRF

The GEODE

Newsletter
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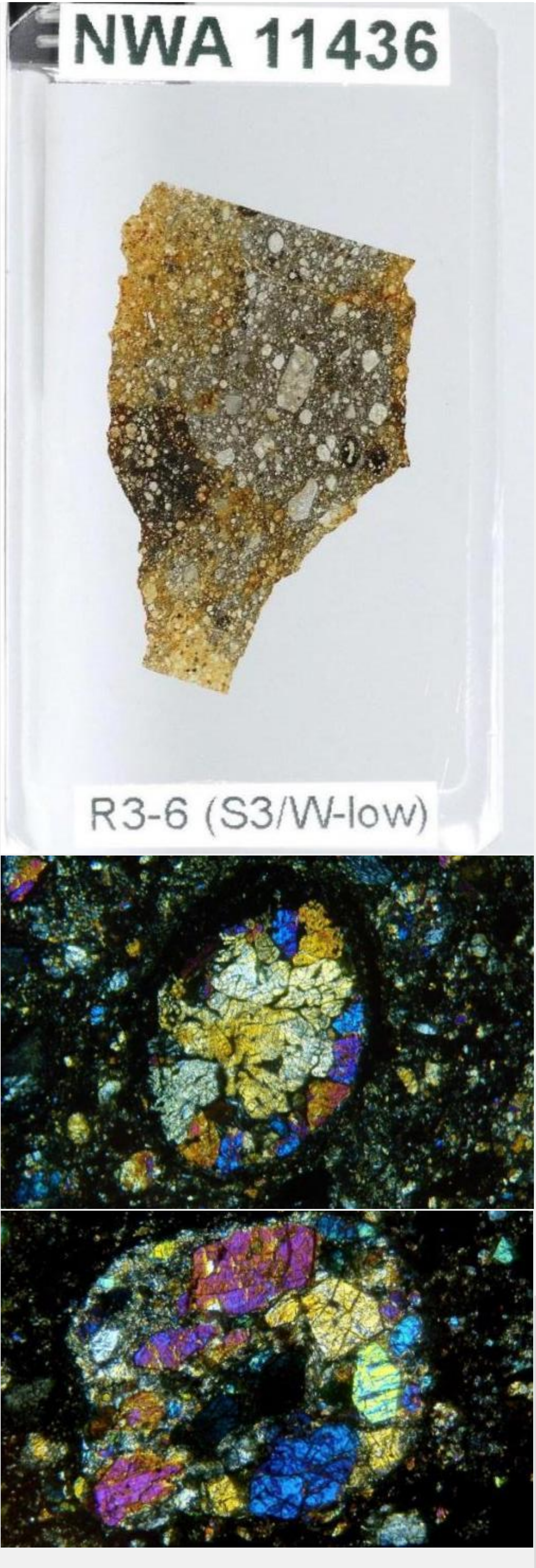


NWA 11436 Thin Section Rumuruti Chondrite R3 – 6 (S3/W-low). Found in Sahara, Northwest – Africa. All XPL photos seen are from the thin section

From the Chair

Welcome all current (and future) Minsa members to the second Geode of 2020! Although up to now the year has been quiet, at least mineralogically speaking, some interesting things lie ahead! The members of the Minsa committee are committed to providing activities and reading despite the lockdown restrictions.

Passing of Roger Dixon

Unfortunately, I have to start my column with sad news. We learned with great sadness of the sudden passing of Roger Dixon in early June. Roger was well-known in the geological and mineralogical communities of South Africa and spent many years working in forensics for the SAPS before he moved to the University of Pretoria, where he worked in the analytical facility for geosciences. Roger was also a long-time Minsa member, where he most recently served on the Executive Committee for the 2018/2019 period and was always involved through activities and contributions. One of his written pieces even features in this issue. He will be missed. Our thoughts go out to the family and friends he leaves behind. An obituary for Roger will feature in the next issue of Geode.

First Themed Geode

This is the first edition of the Geode with a special scientific theme, where experts in their field contribute short written pieces covering topics falling under that theme. Our first theme is **novel, interesting, and under-utilized techniques for applications in process mineralogy**. The contributions will include topics such as 3D X-ray microscopy (XRM), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), micro-focus X-ray computed tomography (µXCT), micro X-ray fluorescence (micro XRF), Raman spectroscopy, secondary ion mass spectrometry (SIMS), synchrotron-based techniques and X-ray diffraction (XRD). The contributors include Alan Butcher (Geological Survey of Finland), Candice Carelse (Mintek), Desh Chetty (Mintek), Johan de Villiers (University of Pretoria), Roger Dixon (University of Pretoria), Guy Freemantle (Mintek), Sarah Glynn (University of Witwatersrand), Axel Hofmann (University of Johannesburg), Andrew Menzies (Bruker), Roald Tagle (Bruker), Igor Tonžetić (University of Pretoria), Sabine Verryn (XRD Analytical and Consulting), Bjorn Von der Heyden (University of Stellenbosch) as well as myself (University of Johannesburg).

The next theme for the September 2020 Geode will be: **Sampling and sample management: how to avoid rubbish in and rubbish out**. We want to invite any contributions on anything related to the importance of sampling and samples, including, but not limited to, sampling strategies, sampling techniques, sample types, sample numbers and statistics, sample transport and sample receiving, as well as sample management and storage. This is a topic that is so critical to conducting good science and is very often either overlooked or not given the attention it deserves. Please e-mail us at minsa@gssa.org.za if you want to find out more or contribute.

COVID 19 Update

With the world still in the grip of the global COVID 19 pandemic, people are moving towards remote forms of work and communication for the foreseeable future. We are also investigating moving some of our activities online, and we will communicate these activities in due course. Please stay safe and take care of yourselves!

Mineralogist Feature coming to the Geode in September

For the September 2020 edition of the Geode, we will be introducing a new feature in the Geode. Here we will profile some experienced as well as young and upcoming mineralogists working in South Africa. We envision this as an informative yet fun piece that will help to remind us of the interesting and diverse community of mineralogists we have, as well as celebrate achievements and encourage a new generation of scientists. Please be on the lookout for that!

Bertus Smith
Minsa Chair

Minsa Book Prize

I want to remind people of the Minsa book prize, which is awarded to Masters dissertations at southern African universities. The main criterion is that the dissertation comprises at least 50% mineralogy. This book prize is advertised and administered through the Geological Society of South Africa's annual post-graduate student awards. This means the Minsa book prize will join the likes of the Best Fourth Year Geology Student Prize, the John Handley Award and the Corstorphine Medal and be awarded at the GSSA's annual general meeting. The call for nominations for the Minsa book prize is handled and should be submitted to the GSSA. The prize will still be adjudicated by Minsa. If you believe there is a completed dissertation that fits the criteria and is of merit, please submit a nomination by 30 June 2020.

Nominations for Minsa Executive Committee for 2020-2021 now open

And last but not least, the nomination process for people who want to serve on the Minsa Executive Committee for the 2020-2021 term is now open. To nominate someone or yourself, please contact us on minsa@gssa.org.za to get a nomination form and then fill it in and send it back to us by no later than 8 July 2020. Remember to indicate the portfolio the nominee would be interested in (you can pick more than one) and there must also be a proposer. The nominee and proposer need to be paid up Minsa members.

As always, please keep an eye on the Geode and our Minsa e-mail notifications for further activities coming this year and thank you again to Steve Prevec for his hard work in preparing the Geode every quarter. See you for the next column!

Kind regards,

Bertus Smith

Chair – Minsa Executive Committee 2019/2020

Forthcoming Events & Attractions

Due to the advent of the COVID-19 coronavirus global pandemic into South Africa, all of the scheduled interactive social-professional events up to the middle of 2020 have been postponed, cancelled, or gone virtual.

This includes the June-July GSSA Geocongress (Stellenbosch) and all scheduled Minsa talks. The talks will be rescheduled as it becomes appropriate to do so.

Online activities include:

- GSSA "Foundations for a Geological Career - Geoskills 2020" online workshop; Tuesdays (08:00-13:00) from July 7 to August 11. Contact GSSA for info.

And still on the cards if isolation restrictions are lifted in time:

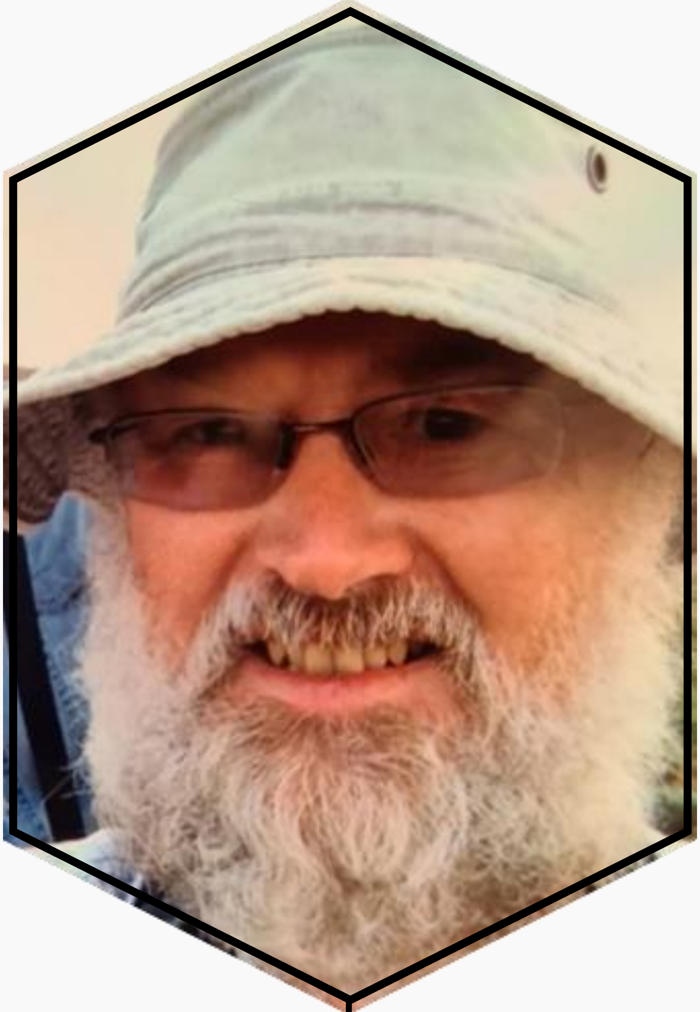
- Combined MINSA/Micromount Symposium – November 2020

The June Geode Theme:

Novel, interesting, and under-utilized techniques for applications in process mineralogy

Methods championed here:

- Micro X-ray fluorescence
- Micro-focus X-ray computed tomography MicroXCT and 3-D XRM
- X-ray diffraction
- SIMS & LA-ICP-MS
- Raman- & Synchrotron-based techniques



REMEMBERING DR ROGER DAVID DIXON

It was with shock that we heard of the untimely death of Roger on Friday June 5th 2020. Roger was a MINSA stalwart – he served on our committee on many occasions and helped organise several of the unique field trips that MINSA undertook over the years. Apparently, he even took his folks along on the Rèunion Island trip in 2000! He organised super interesting MINSA excursions to the SAPS Forensic Laboratory which he headed for a time. One of his favourite anecdotes of his international travels while involved with forensic boards all over the world, was when, on a trip to St. Petersburg, the Hermitage Museum was closed to the public so that the two South African visitors could have a private tour. Roger was an incredibly knowledgeable individual, and by all accounts, had a very interesting life. He was a legendary character; the roughest diamond I knew. He projected a gruff manner and certainly did not suffer fools gladly – often speaking his mind. However, under this stern, taciturn exterior he was one of the most entertaining and loyal of people I know. A real 'Mensch'.

We will certainly miss his sardonic sense of humour at MINSA meetings. Roger started a practise of alternating MINSA meetings north and south of the Jukskei - on some occasions I would arrive extra early in his Stoneman office to 'shoot the breeze'. During these visits, I obtained some insights into the myriad interests Roger pursued. We took a tour of the plinths he organised around the building which he designed for huge geological specimens and, while looking through his bookshelf, I found copies of the 2014 Clivia Society Yearbook which he co-edited. He regaled me with the latest developments in getting seemingly 'dead' instruments back into action in the revamped facilities.

Roger's enthusiasm was evident in his promotional work with the Selfrag and the Tornado – many of us in the mineral processing industry tested all manner of samples with him using these techniques. He proved that the Selfrag provides an impressive advancement in the technique of mineral separation and has been a huge benefit to geochronologists for both increased yield and better quality minerals to work with.

Roger will be sorely missed in the international and local mineralogical and geological fraternity. Many of us have special memories of him.

We extend our heartfelt condolences to his beloved children David and Cathy.

As Roger would have said:

'Do not shed tears when I have gone, but smile instead because I have lived.'
(From the poem 'Remember Me, by David Harkins).

Petra Dinham

Roger in the centre with Mine Surveyor (left) and Horst Windisch (right). This image was submitted by Professor Bruce Cairncross. He took the photo underground at the Messina copper mine in 1993 when he and Roger visited there on a recce for their "Minerals of South Africa" book.

Roger (right) with his signature glass of red wine at the MINSA anniversary Dinner in August 2019.
(Jaco Delport is also in the picture).

Micro-XRF: Another Automated Mineralogical Analysis Paradigm

Igor Z. Tonžetić
University of Pretoria

1 INTRODUCTION

Micro-XRF is an emerging technology that negates the problems of deciding on the stage-detector-chamber geometries traditionally associated with Auto-SEM-EDS instrumentation (Tonžetić, 2017) since the X-ray detector essentially performs the functions of both “imaging” and chemical EDS analysis (the analytical distance is the same as the “imaging” distance).

The de Broglie wavelength equation (Equation 1) suggests that ANY discrete package of energy (“quanta”) can be used to image any given material that is not transparent to it, that is, can be reflected, refracted, absorbed and/or transmitted in connection with it. It is the equation that allows for the utilization of electrons as a beam in the Scanning Electron Microscope (SEM) and, by extension, the creation of the minerals analysis industry standard Auto-SEM-EDS instruments, such as QEMSCAN, MLA, TIMA and Mineralogic®.

Equation 1: $\boldsymbol{\lambda = h/p}$

where **λ** represents wavelength; **h** represents Planck’s constant; and **p** is the momentum (mass x velocity) of the travelling body or quanta.

It is also the equation that in principle allows for the use of X-rays in imaging and analysis. As such, all these Auto-SEM-EDS instruments, utilize characteristic X-ray detection in addition to electron detection (used mostly for imaging) to further define and delineate the rule sets used for mineral identification. Unfortunately, because a single detector cannot be used to detect both X-rays and electrons at the same time, a unique X-ray detector and a unique electron detector must be used at the same time (at different spatial configurations) to detect the respective signals. This results in a disconnect between the “imaging focus” and the “analytical focus” of any given SEM-EDS instrument. This means that a compromise must be sought in the way that stage-detector-chamber geometries are implemented based on whether X-ray collection or electron imaging are to be emphasized. Which is to say, a conscious decision needs to be made for whether X-ray analysis is to be emphasized by lowering the sample mount or stage and bringing X-ray detectors closer to the surface of the sample (which is a typical QEMSCAN approach). Or whether electron (typically back-scatter electron or “BSE”) imaging is to be emphasized by raising the sample mount or stage and retracting X-ray detectors away from the surface of the sample (this is a typical MLA approach which in its turn facilitates “bright phase searching” of high average atomic number phases but also typically necessitates a centroid mode of X-ray analysis because of generally lower X-ray count rates).

These are not value statements and thus constitute the two end-member “paradigms” of these instruments. Some analyses require precision imaging with compensatory X-raying. Other analyses require superior X-raying with adequate imaging. As such, any given stage-detector-chamber geometry can essentially be configured just like any other, depending on whether a stage is lowered with X-ray detectors protracted for X-ray collection or raised with X-ray detectors retracted for enhanced imaging (Tonžetić, 2015).

In theory, it is possible to eliminate this compromise by having an imaging detector be the same as an analytical detector (as suggested by the de Broglie equation). In this instance, it would mean having the X-ray detector perform the function of X-ray imaging (as when doctors take X-ray images of broken bones or X-ray tomography) and X-ray analysis of characteristic X-ray spectra (as it currently does in Auto-SEM-EDS spectra).

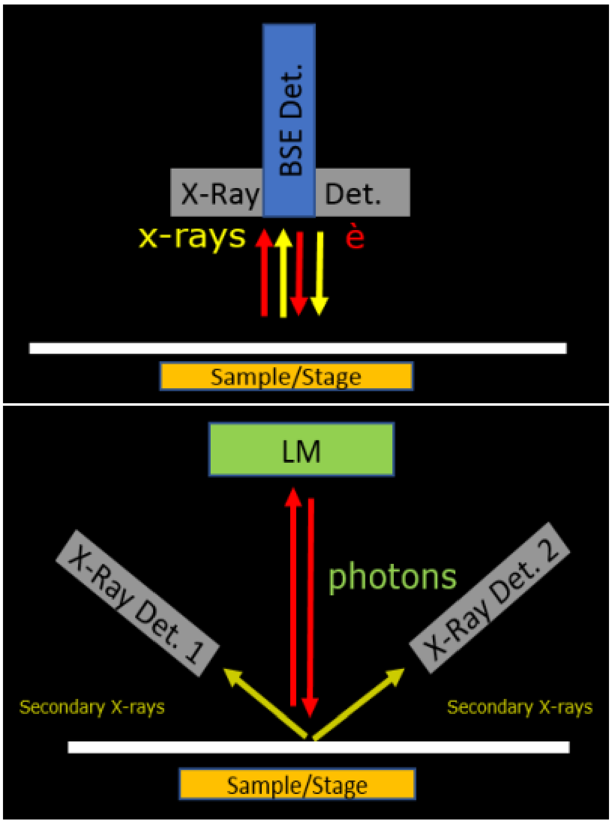


Figure 1: Comparison of Flat Quadrant X-ray detection with contemporary Micro-XRF chamber geometries. Top: Flat Quadrant detectors allow for BSE detectors to receive electron signals through the X-ray detector. Imaging distance and analytical distance are the same. Bottom: Micro-XRF uses a light microscope for rudimentary sample detection and placement before X-ray detectors proceed with the mapping of a sample.

For characteristic X-ray collection, it is possible to place a flat quadrant EDS X-ray detector directly above a sample where the imaging detector would be. This would make the analytical distance and focus distance be one in the same, such that both imaging and X-ray collection would be optimized. Unfortunately, since X-rays are highly penetrative and have no magnetic properties they cannot be directly focused through electromagnetic lenses (as used in SEM instruments). There is no known "lens" mechanism to focus them and there is no known material that could act as a lens to do such. The flat quadrant detector thus does not perform imaging of any kind and instead has an open aperture through which traditional BSE detectors (amongst others) can be placed (Frunzio et al., 2001). This means that the analytical focus and the imaging focus can still be the same. Unfortunately, flat quadrant detectors are on the order of 4x as expensive as regular SDD detectors.

Micro-XRF analysis seeks to solve this problem by not placing a premium on imaging (using a light microscope to roughly gauge analytical distance and area of interest to measure) whilst performing all analysis through the assistance of 1 or 2 EDS detectors reading excited sample/specimen X-rays generated from an X-ray tube. The interpreted data hence becomes the "imaging" of the instrument (Figure 1).

2 DISCUSSION

2.1 Case Study 1: Lithotyping

Figure 2 demonstrates that Micro-XRF is able to differentiate between mineral species in mineral groups. For instance, it can differentiate between albite, anorthite and K-feldspar as well as actinolite and tremolite. It appears to positively identify minor to trace amounts of minerals (in this case illite and kaolinite). The textural information supplied seems to be on par with Auto-SEM-EDS instruments, as seen by the clear de-lineation of an actinolite vein and micro-structural features (bearing in mind that these features are comparatively macroscopic and that Micro-XRF can have a beam-volume interaction of 50 microns).

The presence of low average atomic number epoxy resin is also not erroneously assigned mineral values. The "epoxy resin" is a relic of "plucking" from the sample preparation of the polished section and is identified primarily through the identification of Cl in type-spectra. Interestingly, this plucking may proxy for the "friability" of a rock type or ore since the more friable an ore or rock type, the more likely it is to experience “plucking” in sample preparation. By extension, this may have application in future studies of the “grind-ability” of an ore type.

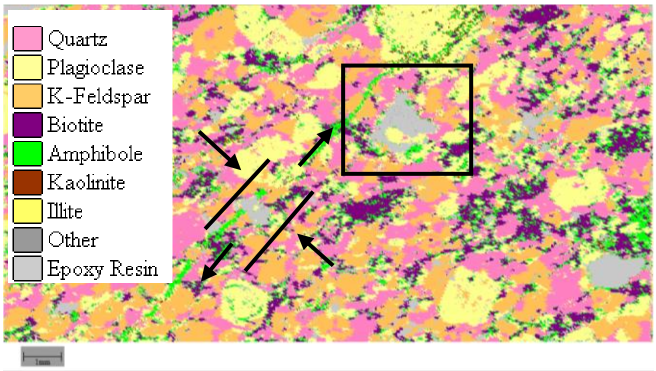


Figure 2: Micro-XRF mineral map of granitic pediment. Black arrows give an indication of possible compressive and expansive forces around ferroactinolite vein.

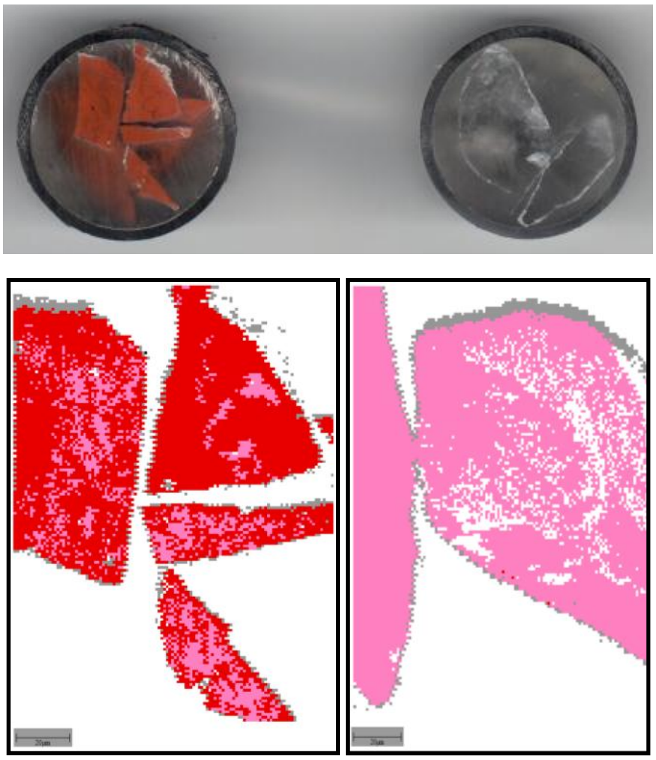


Figure 3: Top: Image of jasper (left) and quartz (right) mineral standards used for the study. Left: AMICS measured jasper standard. Right: AMICS measured quartz standard. Red: Jasper, Pink: Quartz, Grey: Other.

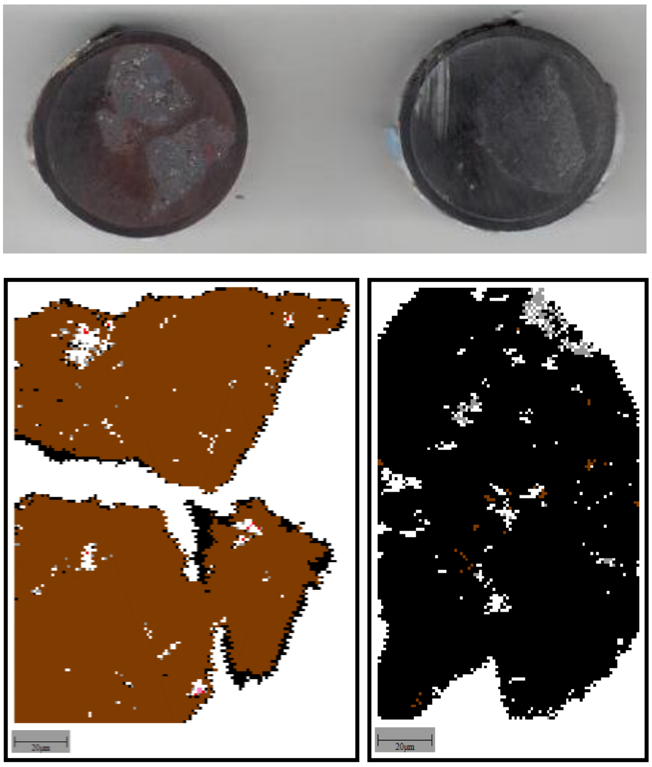


Figure 4: Top: Image of hematite (left) and magnetite (right) mineral standards used for the study. Left: AMICS measured hematite standard. Right: AMICS measured magnetite standard. Brown: Hematite, Black: Magnetite, Grey: Other.

2.2 Case Study 2: Iron Ore

Figures 3 and 4 demonstrate the ability of Micro-XRF to differentiate magnetite from hematite, but also (arguably more impressively) jasper from crystal quartz. Upon closer inspection of the sample standards, the “Jasper Std” clearly seems to have brown micro-veins which are being identified as quartz. Spot analysis of these points, presented no visible Fe peaks. Also, the quartz standard has a large scratch being identified as unknown.

Figure 5 demonstrates the emphatic resolution of mid periodic table elements at low concentrations at the 50 kV and 200 μA settings of the instrument. Even though the Fe peak is clearly visible with a high amplitude, it represents only a 0.6 mass percent total of Fe in the jasper being analyzed. The manipulation of the voltage and amperage settings for the Micro-XRF to emphasize or de-emphasize certain X-ray peaks provides for the possibility of analyzing various ore types through tailored methods of X-ray analysis (perhaps more so than is currently practiced with Auto-SEM-EDS instruments which, whilst they can run at different voltages, routinely do not do so).

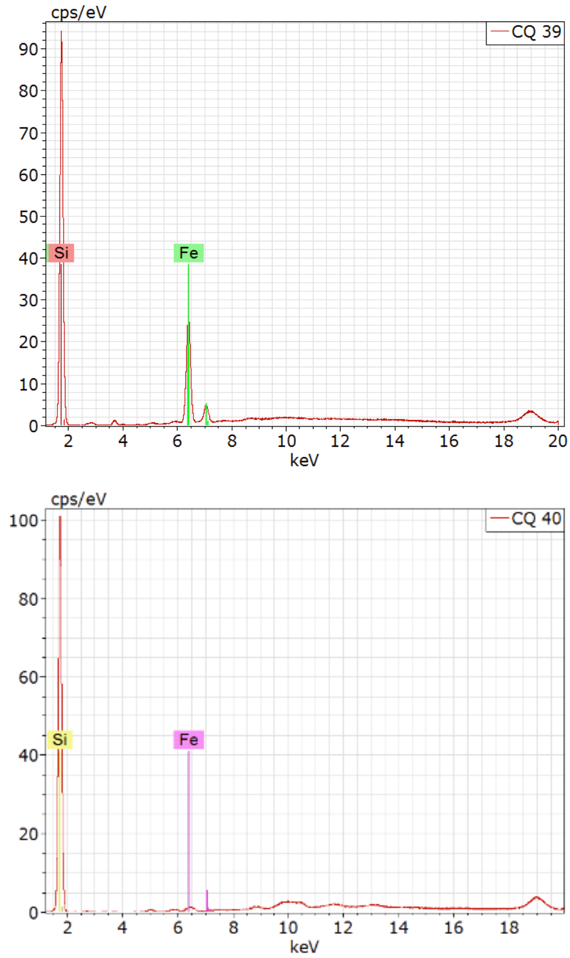


Figure 5: Type spectra used for jasper-quartz discrimination rule sets in the AMICS software. Left: Jasper. Right: Quartz.

The spectral matching approach, inherited from MLA, appears to perform very well for hematite-magnetite distinction. The occurrence of trace elements, most probably facilitates this (for instance V and Cr for magnetite; Al for hematite). Holes (plucking), and mineral boundaries appear to be the most problematic for identifications.

3 CONCLUSIONS

Micro-XRF seems to be a competent technology with regards to mineral analysis and offers some distinct advantages, namely:

1. Large samples can be accommodated for measurement which has applicability in, for instance, drill core analysis (Figure 6).
2. There is less of a reliance on perfect sample preparation (and carbon coating) which has applicability in faster measurement turnaround times.
3. It can operate at low or even no vacuum parameters which has applicability in the analysis of coal rich, clay rich or even theoretically moist samples.
4. It is considerably cheaper than fully equipped Auto-SEM-EDS instruments.
5. It seems to be better at differentiating mineral species or even mineral varieties that have minor elemental differences.

A conceivable disadvantage would be the analysis of minerals that have the same cations but different anions that are nevertheless X-ray invisible and share the same excitation potentials. The type example in this instance would probably be the discrimination of calcite and fluorite, which both have Ca^{2+} as their cations and the X-ray invisible (in a Micro-XRF system) anions $(CO_3)^{2-}$ and F^- which appear to have similar excitation potentials. Furthermore, the size of beam-volume interactions can be on the order of 50 microns with normal capillary tube “lenses”.

*For the full paper (not peer-reviewed) which includes complete sections on the methodologies of the case studies, instrumentation specifications, sample preparation, results, an extra case study, acknowledgments and references, please visit the author’s ResearchGate page.

Figure 6: Oblique chamber view of Bruker M4 Tornado. A "Ferrero Rocher" chocolate box is present in the chamber with 24 30mm diameter sample standards. The box represents an area of approximately 18 by 24 cm, all of which can be accessed with the stage movement and as such all of which can be measured and seen by the detectors.

Introduction to the Micro-XRF analytical technique and its application to Exploration, Mining and Metallurgy

Andrew H. Menzies[1*], **Roald Tagle**[1], **and Alan R Butcher**[2]

1. *Bruker Nano GmbH, Berlin; Germany*
2. *Geological Survey of Finland, Espoo, Finland*

Micro-X-ray fluorescence (micro-XRF) or X-ray fluorescence microanalysis, as it was termed initially, is a spatially-resolved version of traditional X-ray fluorescence analysis (XRF). The micro-XRF analytical technique was first described more than 50 years ago and since then it has remained mostly a niche technique, albeit quite common in several industrial application fields (e.g. coating analysis), but without becoming part of standard geo-analytical techniques used in universities, mining laboratories, and other higher education or research facilities.

In recent years, however, a series of technological developments, from excitation sources, to enhanced detection possibilities and signal processing capabilities and algorithms, have allowed improvement in the performance of the technique, consequently making micro-XRF (Figure 1) useful as a standard analytical tool. Specifically, these technological developments include improving (minimizing) beam size, improving X-ray source options and capabilities, applying numerous types of filters, and next generation SD detectors with high signal throughput and energy resolution. All of these changes, as well as other consideration about micro-XRF, are discussed in detail in Tagle et al. (2019).

The main difference with conventional X-ray fluorescence analysis is that micro-XRF uses a small spot to excite a predefined sample location. In conventional XRF, large sample areas of several millimeters are usually analyzed with the purpose of quantification, and thus samples are commonly prepared by sample crushing and homogenization. However, inhomogeneity of the sample can be an important aspect of the analytical question and thus spatially-resolved micro-XRF analysis can be extremely important. Quantification with the micro-XRF is still feasible but requires more caution and evaluation by the user.

Figure 1. Desktop Bruker micro-XRF M4 Tornado^{AMICS}.

The use of a focused beam, similar in principle to an electron beam but larger in diameter, allows studies of the compositional variations of inhomogeneous samples. This small X-ray beam can be produced by using collimators, or reflective optics such as mono- or polycapillary lenses. Polycapillary lenses are currently a good compromise between intensity, spot size and working distance, yielding a 15 µm to 25 µm spot size, with a working distance of approximately 8 mm. The small beam and localized measurement position can be used in single point mode, or in scanning mode as for a line scan or area map. In the latter, the full spectrum is saved for each measured location (pixel). This position-tagged style of spectroscopy then allows for the creation of element distribution maps, as well as for other complex post-processing procedures, including mineralogical analysis.

In a SEM, it is relatively easy (and very fast) to deflect the focused electron beam in order to “scan” over the sample. However, in a micro-XRF the movement of excitation relative to the sample calls for mechanical movement of either the excitation unit, or the sample itself. For closed instruments, moving the sample is the common approach, whereas open-beam instruments usually move the excitation unit. A detailed description is given in Haschke and Boehm (2017) regarding the difference in sample interaction between an electron beam source (for example on a SEM and EPMA) and X-ray beam source (micro-XRF).

Some of the main advantages of micro-XRF analysis can be summarized as follows:

- ability to perform large area maps on a variety of samples: including cut rock samples, drill core, briquettes, and polished sections;
- non-destructive, non-invasive, sample analysis
- little to no sample preparation (no carbon coating or polishing required);
- small spot analysis: and thus, ability to study well-defined small sample areas, or non-homogenous materials;
- fast measurements with major, minor and trace element sensitivity;
- elemental information on a point-by-point basis;
- information from within the sample, not just the immediate surface;
- identification of high energy X-Ray lines;
- meso-scale to micro-scale information: tens of centimetres-scale sample analysed at tens of micron-scale resolution;
- ability to process results for quantification and/or mineralogy.

The micro-XRF is also capable of generating hyperspectral maps that can be processed using the AMICS Automated Mineralogy software. Automated Mineralogy has been successfully used in the mining industry since the 1970s, with one common aspect in that they are all based on an electron beam (e-beam) system (*e.g.* scanning electron microscope (SEM) with Energy Dispersive Spectrometers (EDS)). However, a micro-XRF system can be operated using similar parameters as an e-beam system, and thus yield results compatible with traditional Automated Mineralogical analysis, but on samples or scales that would not normally be possible with a SEM. As with traditional Automated Mineralogical systems, there are fundamental parameters that impact on the mineralogical classification and analytical time; this includes (but is not limited too) X-ray beam excitation (kV and µA), detector active areas (mm^2), pixel spacing (µm), and dwell time (ms).

The aforementioned advantages of the microXRF makes it a suitable technique to include in the geological, exploration and mining, and metallurgical workflows, as indicated in Figure 2, which summarizes the different scales of observation and information and the various analytical techniques used over to bridge these scales. The micro-XRF is placed in what is termed a meso-scale analytical tool, that is the meter-centimeter-millimeter scale, however as discussed, it can also measure down to the micrometer scale. This makes it an ideal tool for the transition of samples from the field to the laboratory, whilst maintaining spatial relationships and integrity. This also helps with the flow of analytical information in the up-scaling or down-scaling of results.

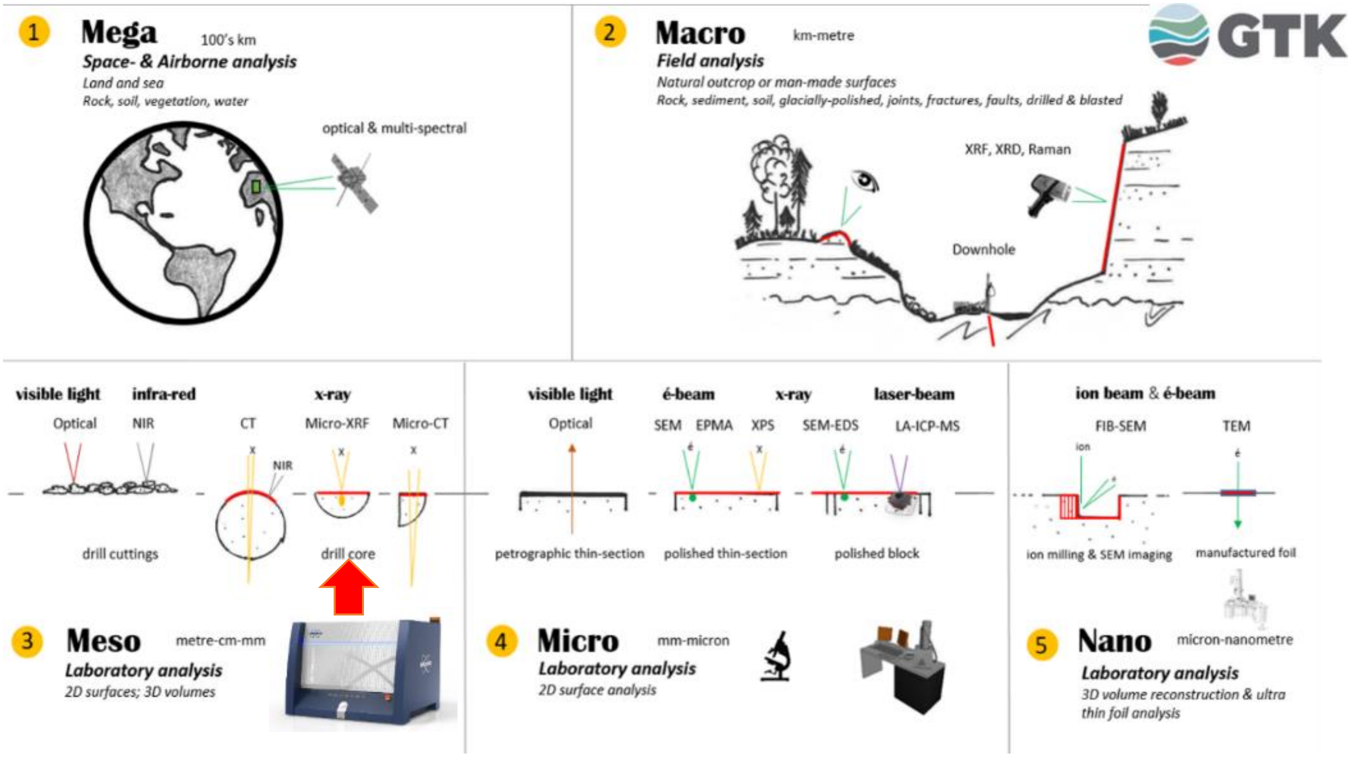


Figure 2. Summary diagram of information that is relevant on various scales to an exploration program (modified from Butcher, 2019). The Bruker micro-XRF M4 Tornado^{AMICS} *classifies as a meso-scale tool, however, in addition it is possible to measure on the micrometer scale.*

A recent webinar presented on May 19th, 2020 titled: "*Multi-scale in-situ non-destructive micro-XRF scanning analysis: Implications for ore mineralogy, petrogenesis and micro-metallurgical assessments*" uses the capabilities of the micro-XRF applied to current exploration projects in Finland, specifically relevant for the search for battery-related minerals, in this case cobalt-bearing.

The microanalysis of geological samples is common practice and provides valuable information on a variety of levels. This is particularly true for mineral exploration and process mineralogy studies (geometallurgy). The exploration process and subsequent metallurgical understanding occurs on scales that vary by numerous orders of magnitude (see Figure 2, modified from Butcher, 2019). The capabilities can then be shown at a more specific level related to drill cores and thin sections in Figure 3 (Butcher, 2019), which shows a sequential downscaling and upscaling of information and interpretation to aid an exploration program.

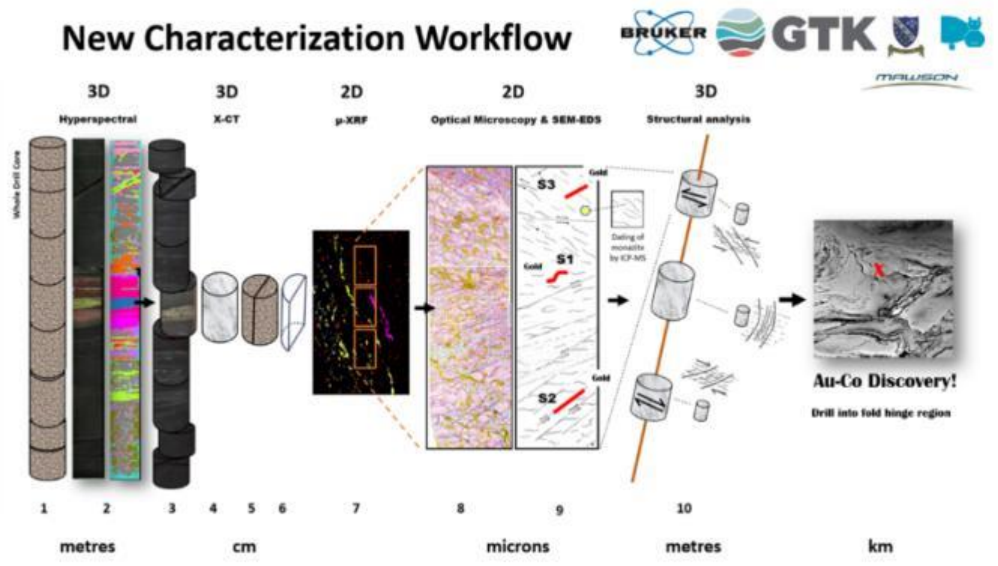


Figure 3. Analytical characterization workflow from the meter to micron scale and back again, highlighting where the micro-XRF fits into the sequence (from Butcher, 2019).

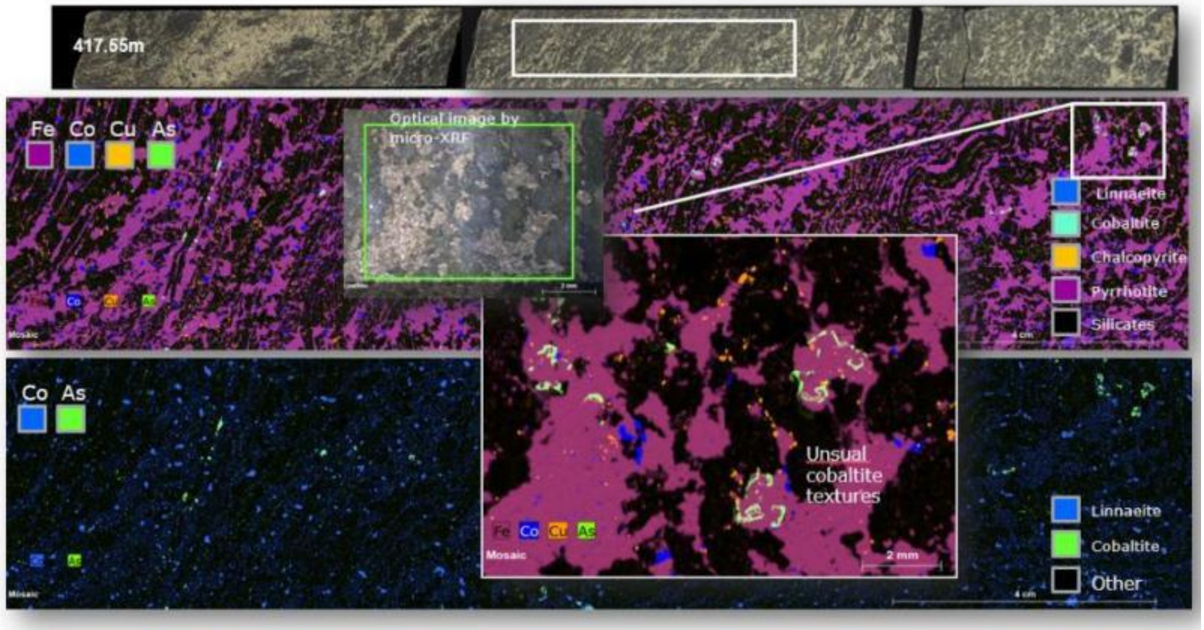
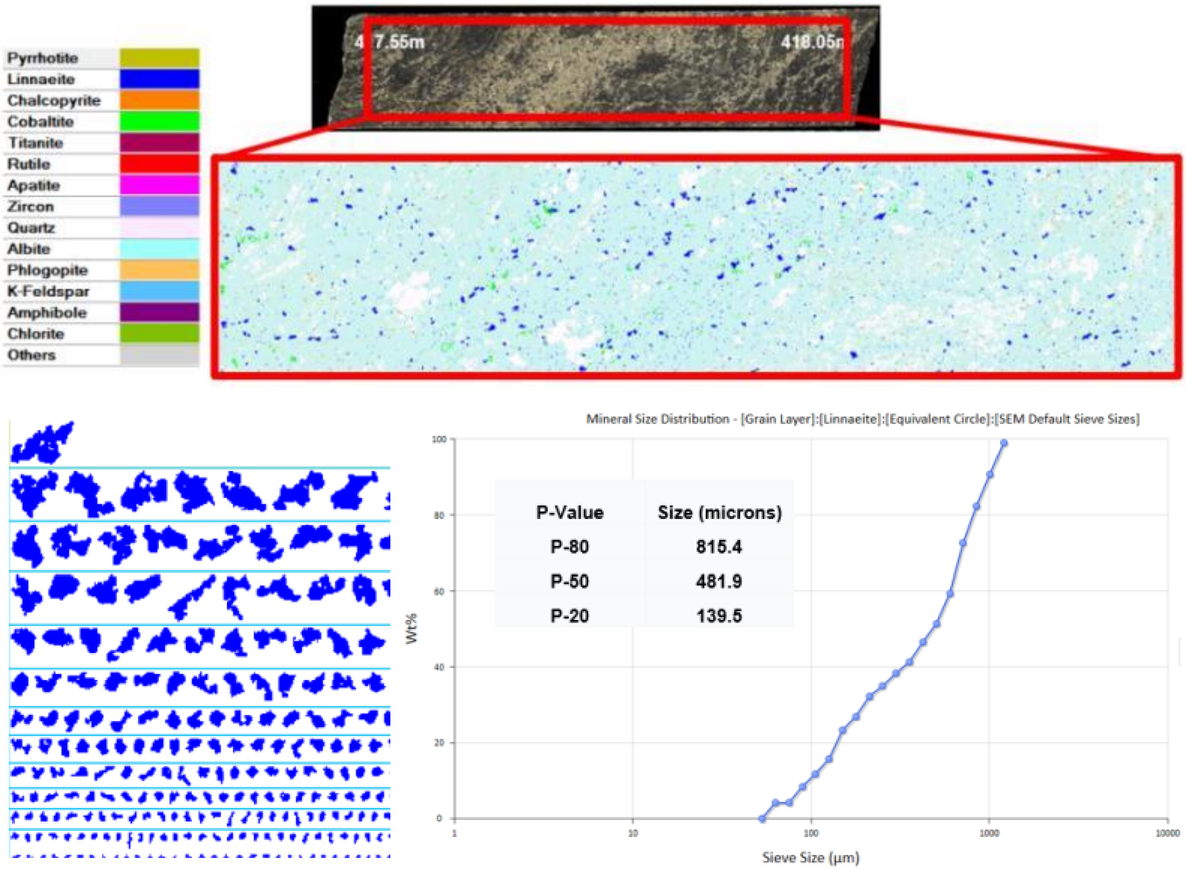


Figure 4. Large area micro-XRF scan shown spatial maps of elements of interest (and implied mineralogy) and zoomed in detailed areas to highlight the presence of unusual textural relationships.

The relevance of the micro-XRF is that it provides an important link in this chain from the transition from samples collected in the field to analysis in the laboratory. The micro-XRF is an enabling technology that bridges these challenging scales of observations allowing micro-analytical interpretations to be easily related to field samples (i.e. visually), as well as enabling the ability to select the appropriate samples for more detailed micro-analysis, which is often costly and time-consuming. The focus of this case-study is on the analysis of drill core sections and their interpretation, from both an up-scaling and down-scaling viewpoint using micro-XRF as a key component of the overall workflow. This includes characterization of mineralogy and distribution of element(s) of interest(s) and associated metals/elements, key mineralogical/geo-metallurgical ore properties, mineral associations, and micro-structural relationships.

Various examples were shown in the webinar related to the characterisation of cobalt-rich samples and using a geometallurgical approach that employs geoanalytical techniques to achieve multi-scale, multi-modal, and multi-dimensional information (involving the integration of 2D, 3D and 4D imaging and analysis of rock samples). For example, the micro-XRF can determine the mineral phases in a 2D mineralogical hypermap which can be used in turn to calibrate the 3D micro-CT scan which is based on mineral density changes. In the case study presented, Co-bearing samples were analysed to understand various mineralogical constraints.



P-Value	Size (microns)
P-80	815.4
P-50	481.9
P-20	139.5

Figure 5. AMICS Mineralogical map (top) of mineralized drill-core accentuating the minerals of interest. These minerals can then extracted individually in the software and various geometallurgical parameters can be determined, such as grain size distribution (bottom), shape factor, and mineral associations.

Figure 4 and Figure 5 show some of these data as elemental maps and mineralogical data sets from the same datasets of hyperspectral scans, highlighting how the data can be visualised and interpreted. Figure 4 is a large area micro-XRF scan showing spatial maps of elements of interest (and implied mineralogy), along with zoomed in detailed areas of interest to highlight the presence of unusual textural relationships.

Figure 5 is an AMICS Mineralogical map over the drill core surface accentuating the minerals of interest. These minerals are then extracted and various geometallurgical parameters can be determined, such as grain size distribution, liberation, shape factor, and mineral associations.

The change in resolution and dwell time impacts the total analytical time. Thus, it is important to define what is the goal of analysis prior to measurement. For example, in Figure 6, the same area is analysed under different analytical conditions. However, the usefulness of the data will be dependent on the requirements of how the data will be used. That is, low resolution high speed analyses will yield robust results for modal mineralogy, total element assays and identifying areas of interest. However, to determine mineral grain size distributions, fine scale textures, and mineral associations, a slower, high-resolution analysis would be required.

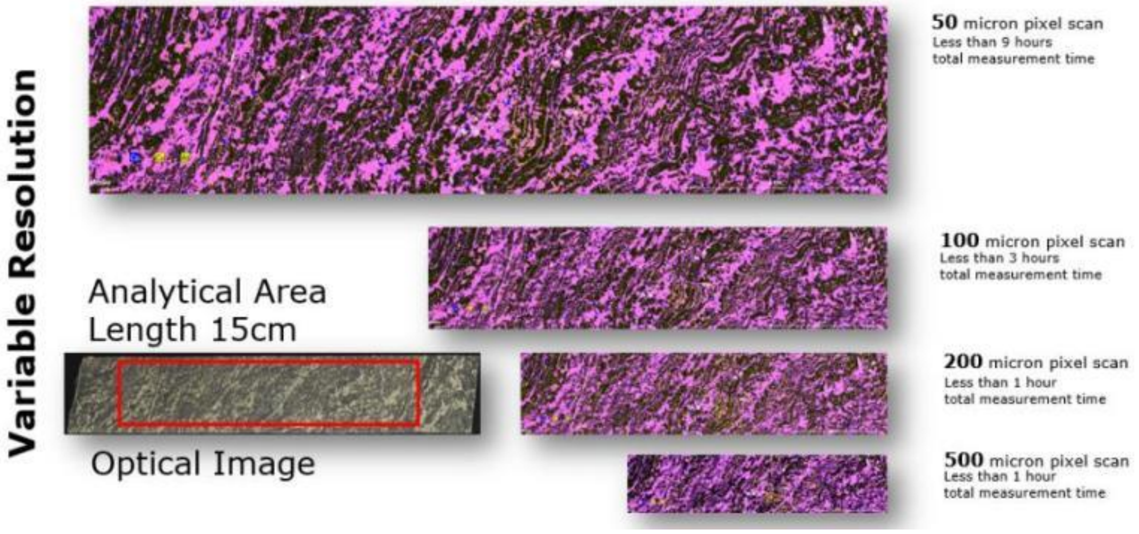


Figure 6. The change in resolution and dwell time impact total analytical time. Thus, it is important to define what is the goal of analysis prior to measurement. See text for discussion.

In addition, such analyses over this scale highlights the importance of representativity. Figure 7 shows a drill core section divided into numerous digitally generated "thin-section" sized areas. In this case, the elements and minerals of interest vary by more than a factor of two over the drill core section. However, the value for Co for the total section, either calculated from the total spectrum (i.e. whole rock calculation) is 10,400 ppm or back calculated from the mineralogy is 9,340 ppm, both of which are consistent with the corresponding whole-rock chemical assay for that section (417.6 – 418.6 m) of 9,769 ppm.

The ability to incorporate both elemental and mineralogical perspectives is vitally important in understanding the requirements for the geometallurgical process. As can be seen from Figure 8 (Dehaine et al., 2020), this information is relevant in all the stages of the geometallurgical process. The end result is a new perspective on commercial mineralogy incorporating details about liberation of both ore and gangue minerals at the early stages of any given project.

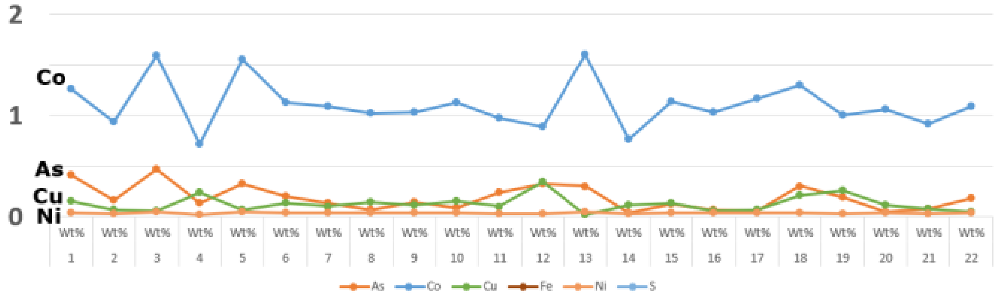
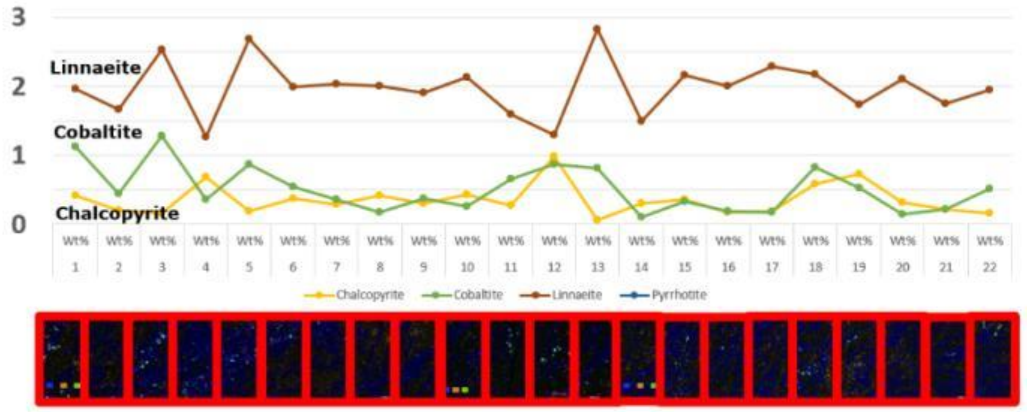


Figure 7. Variation in elemental concentrations (top) and mineralogy (bottom) based on thin-section sized areas (30 x 20 mm) over a drill-core section. As can be seen, both the elements of

interest and minerals of interest vary at least by a factor of two, and sometimes significantly more.



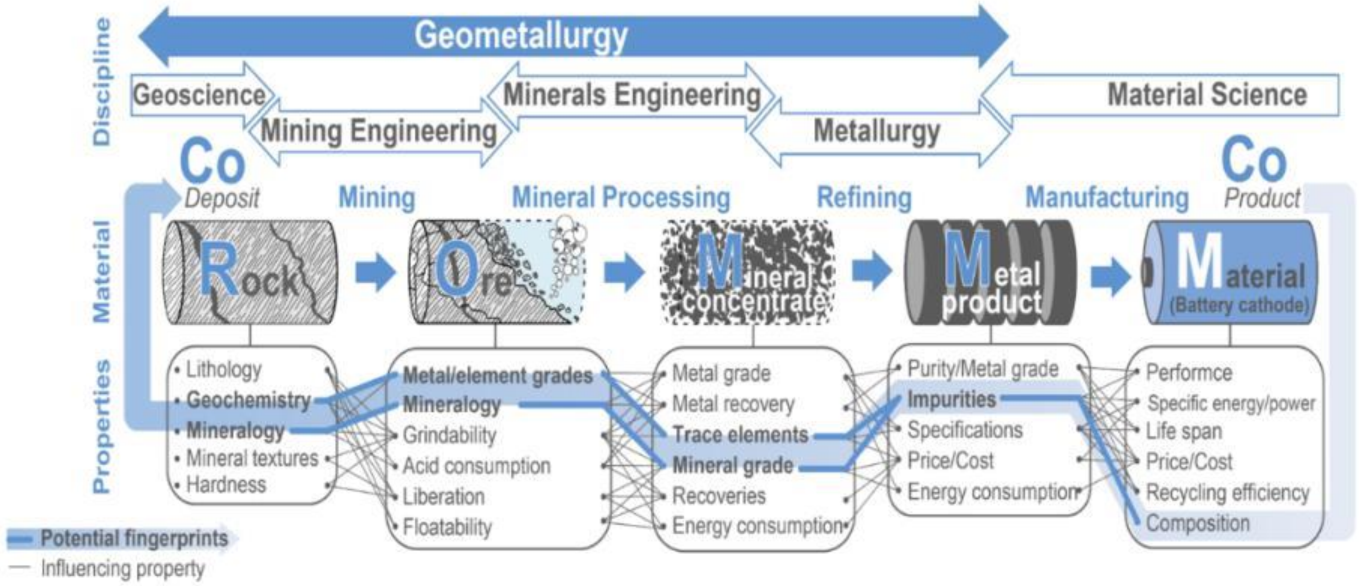


Figure 8. Geometallurgy: an integrated approach for optimisation and traceability along the battery materials value chain, highlighting, but no limited to, areas where micro-XRF analysis could yield relevant information (from Dehaine et al., 2020).

References:

Butcher, A. R. (2019). Upscaling of 2D mineralogical information to 3D volumes for geoscience applications using a multi-scale, multi-modal and multi-dimensional approach. in: EMAS 2019 Workshop, Book of Tutorials and Abstracts, Trondheim, Norway; 19-23 May 2019. ISBN 978 90 8227 695 4.

Butcher, A. R. (2019). Upscaling of 2D mineralogical information to 3D volumes for geoscience applications using a multi-scale, multi-modal and multi-dimensional approach. *EMAS 2019, Conference Proceedings Volume, Trondheim*, 19-23 May 2019.

Dehaine, D., Michaux, S., Pokki, J., Kivinen, M., and Butcher, A.R. (2020). Battery minerals from Finland: Improving the supply chain for the EU battery industry using a geometallurgical approach, *European Geologist 49*.

Haschke, M., and Böhm, S. (2017). Micro-XRF in scanning electron microscopy: in Hawkes, P. ed., *Advances in Imaging and Electron Physics, vol. 199*, p. 1-51, Academic Press.

Tagle, R. A., Reinhardt, F., Waldschläger, U., Hill, T., and Wolff, T. (2019). A deeper insight into materials: potentials and limitations of µ-XRF, EMAS, in: EMAS 2019 Workshop, Book of Tutorials and Abstracts, Trondheim, Norway; 19-23 May 2019. ISBN 978 90 8227 695 4.

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The authors would like to thank Dr Nick Cook (President of Mawson Resources) and his team in Finland for their continued support with regards to sample access and use of results. This work also forms part of the BATCircle project, funded by Business Finland.

Where is the gold in the scrap yard? – Using micro-XRF to help recycle precious metals for the circular economy

Deshenthree Chetty
Mineralogy Division, Mintek

Micro-XRF is an exciting technique for mapping a wide range of samples. It has become popular amongst geologists for large scale petrography that provides insights beyond traditional thin section microscopy. At Mintek, micro-XRF is used to map a variety of samples, from drill cores, to rock slabs, to sections of particles, to pyrometallurgical furnace products. The sample possibilities are vast. The theory behind micro-XRF and its comparison with e-beam techniques have been covered elsewhere in this newsletter. A key attribute of the technique is the ability to analyse unpolished, but relatively flat surfaces. This contribution cites an application in which the sample surface is rather uneven.

The circular economy is one that needs to be fully embraced, as more and more recycling of materials becomes necessary. As part of its eWasteSmelt initiative, Mintek has extracted precious metals from electronic waste, in this case, printed circuit boards (PCB). As is the norm in process mineralogy, the feed sample required characterisation to find gold, and to determine in what form it occurred. The feed sample in this case was shredded PCB, at a size of -3mm screened pieces.

In order to present the sample to Mintek's Bruker M4 Tornado micro-XRF mapping system, a suitable substrate was fixed with double-sided tape, onto which the pieces of shredded PCB were sprinkled in a layer and pressed down to adhere to the tape. This presented a suitable 'flat' surface for mapping (Figure 1). Focusing was carefully done at the highest point on the surface, to ensure that no piece sticking out too much would touch the housing to the detectors in the micro-XRF instrument. A mosaic image was collected for reference purposes, and to define the area for mapping. The instrument was run using a rhodium tube, at 50 kV voltage, and 600 µA current. A pixel size of 40 µm was chosen, along with a counting time of 15 ms per pixel, over an area of ~6x6 cm. The instrument generates a spectrum at each pixel of spacing, before the stage moves to the next spot. At the instrument settings used, almost 2.5 million spectra were collected in a time of 12 hours. This may seem long, but it is important to note that the time could have been shortened considerably by increasing the pixel spacing (to say, 100 µm) and decreasing the X-ray counting time (to say, 5 ms). A vacuum of 20 mbar was used, as lighter elements were of potential interest, but vacuum is not always necessary to run a sample.

Figure 1 further shows the gold map of the sample, which provided the location of gold-bearing pieces in the 'scrap yard'. Using an object function, the average X-ray spectrum of the chosen spot or area could be called up to check for the Au peaks. Inspection of the X-ray spectrum showed the consistent presence of Cu and Ni peaks, indicating that the Au occurs as an alloy with Cu and Ni (Figure 1). A deconvolution application ensured that peak overlaps were addressed, and that Au was definitely present.

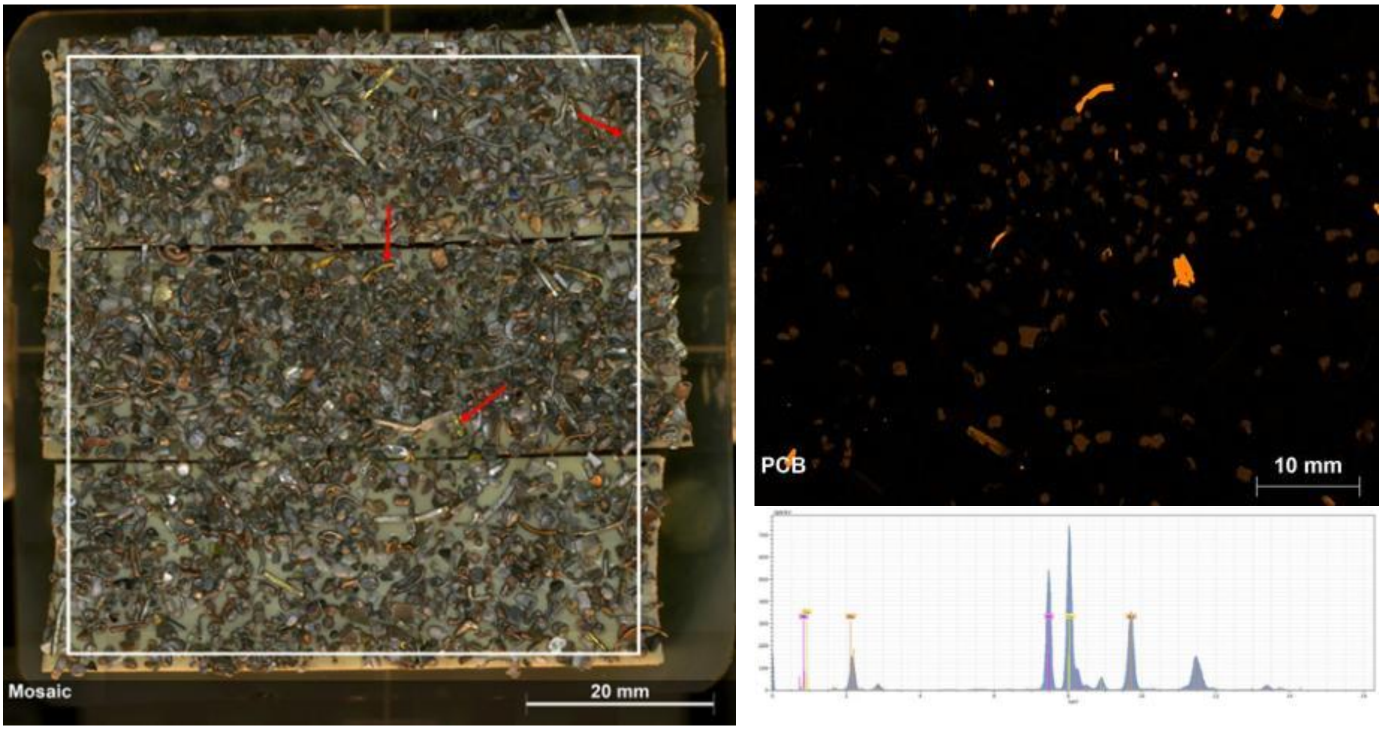


Figure 1: Top: a mosaic image of the 'junk yard' sample created by the Bruker M4 Tornado software. The white boundary delineates the area mapped. The red arrows point to the Au-containing shredded PCB pieces. Middle: The gold X-ray map showing bright portions enriched in gold. Bottom: A spectrum taken from a bright portion of the gold map, revealing the presence of Cu and Ni peaks in identifying the Au-Cu-Ni alloy pieces in the sample.

The elemental maps are slightly offset from the mosaic image of the sample, owing to imperfect focusing from the uneven surface, but still provides valuable information in seeking out the element of interest, which can be investigated in more detail. As all the spectral points are saved upon completion, all further investigation can be done offline, which is advantageous. As spectral information saves all detected elements, any number of elemental maps may be extracted. Only the gold map is shown here. Considering that Au occurs at ppm levels in the bulk sample analysis, micro-XRF proved successful in showing how and where this gold occurred. This provides the process engineers with options for gold recovery through possible sorting methods and in the smelting process itself.

Of course, the sample could have been made into a polished section, and a gold search could have been performed on an automated scanning electron microscope, but that would have involved consumable use (resin, carbon coating), and would have been somewhat more time-consuming. Micro-XRF is comparatively simple, efficient, and overall cheaper for analysis of larger scale samples that do not readily fit into a SEM. The resolution (highest resolution is around 20 µm) does not match that of a SEM (around 1 µm or less), but the two techniques are used in a complementary fashion to attain different scales of observation in samples.

Any micro-XRF-related queries for sample imaging may be directed to Dr Desh Chetty (deshc@mintek.co.za).

Applications of Micro X-ray Fluorescence Analysis

Roger D. Dixon[1] & Johan de Villiers[2]
1. *Dept of Geology, University of Pretoria*
2. *Dept of Materials Science and Metallurgical Engineering*

Micro x-ray fluorescence (µXRF) enables elemental analysis with a spatial resolution much smaller than conventional XRF, with focal spots of a few micrometres in diameter. The high intensity irradiation of the polycapillary X-ray optics on small sample areas (~25 µm) enables better trace element analysis and resolution of smaller features than conventional XRF methods. µXRF has been used in a diverse range of applications in fields including mineralogy, geology, materials science, art provenance and conservation, metallurgy, botany, environmental pollution, archaeology and forensic science. The instrument of choice is from Bruker, the M4 Tornado. This instrument is perfectly suited to a range of multidisciplinary applications. There are other µXRF instruments on the market, but they have different specifications and lack the versatility and functionality of the Bruker. Horiba offers the XGT-7200 (maximum scanning area 10 cm x 10 cm) and Edax the Orbis PC (maximum scanning area 12.4 cm x 12.4 cm). In addition to their more limited scanning areas, which limits the size of samples that can be analysed, they are restricted in the range of elements they can analyse and detection limits. This might have changed with time.

A µXRF is an energy dispersive X-ray spectrometer designed to analyse large areas with small analytical spot sizes, enabling the analysis of single spots or the creation of maps of large areas. It has similar capabilities to a scanning electron microscope (SEM/EDS), with point analysis, line scans and area analysis, but unlike SEMs can scan large areas, quickly. The instrument uses silicon-drift detectors for elements from C to Am. The SDD technology enables data acquisition at < 1 ms per pixel. At a step size of 25 µm, a standard geological thin section (~24 x 38 mm) can be mapped in about two hours, with greater resolution obtained by using a smaller step size.

Although the magnification of the µXRF is not that of an SEM, its strengths lie in sample visualisation. Elemental distribution maps of a large area enable easy identification of phases, whether it be minerals in rocks, pigments in a painting, synthetic phases in experimental work, organs in plants, in fact anything where the distribution of elements into specific associations is indicative of a particular process or product. The images thus produced are valuable as they can be processed further by specialised software for shape, size, texture and modal abundance, etc. The instrument is capable of analysing and mapping flat or rough surfaces, eliminating the need for much sample preparation, and so enabling totally non-destructive analysis. The M4 can scan an area of up to 190 x 160 mm at spot sizes of 25 µm, which can then be subdivided into smaller pieces for detailed analysis without the need to re-analyse.

This technique opens up many avenues of research by enabling a new look to be taken at old problems. Areas of research which have been looked at with great success at the University of Pretoria have come from all the disciplines listed above. The application of an elemental visualisation technique on a macro scale with micro scale analyses enables the distribution of various elements to be followed through natural, industrial and artificial processes. We have looked at the distribution of lead in vulture feathers, heavy metals in polluted waters in plants (Fig 1), pigments in paintings to determine provenance and authenticity, migration of elements during sintering, behaviour of ores during beneficiation by looking at surface coatings, mineral relationships and zonation for petrological information, and many more.

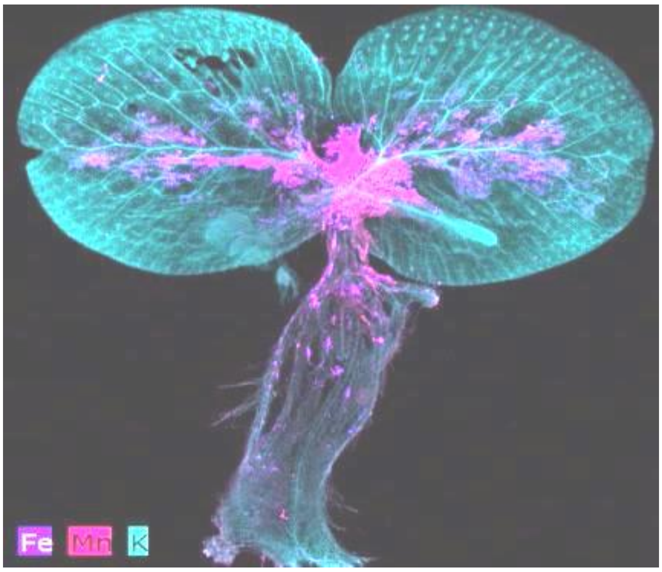


Figure 1. Salvinia – a floating water plant. Different elements are taken up by different parts of the plant, depending on the metabolic requirements of the different organs and cells.

As an example of how visualisation can help understand processes, an example is given here of Fe-ore sinter. Iron ore sinters are produced to agglomerate fine-grained ore particles that are unsuitable for use in blast furnaces. The furnace feed must be +6mm to facilitate reducing gas movement upwards through the blast furnace. During sintering a ~30-40 cm bed of a mixture of fine iron ore, limestone and char is ignited from the top and the flame front is sucked through the bed, resulting in partial fusion of the charge. The fused material crystallises on cooling and the resultant crystallised slag acts as a binding material to produce a strong, lumpy furnace feed.

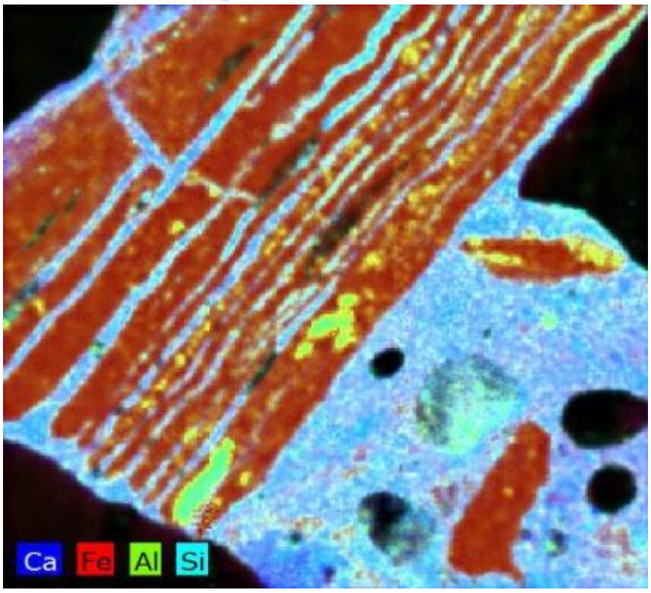


Figure 2. Crystallised slag adhering to and reacting with the silica layers of a banded ironstone particle. The distribution of the four elements is shown in different colours.

Figure 2 shows the binding material adhering to a banded ironstone ore particle. The crystallised slag contains a limestone particle at the bottom and calcium silicate inclusions. The ore particle contains predominant Fe as hematite, and layers of Si (SiO_2) as well as inclusions of an Al-containing phase. The black areas are pores. The importance of this image is that it shows the adherence and ingress of the slag phase into the iron ore particle to form a strong bond. Also apparent is the reaction of the silica layers with the slag. The distribution of the Ca from the slag phase is shown in blue. Also apparent is the fact that the hematite in the ore particle does not react appreciably with the slag. This is contrary to the expectation that a Si containing calcium ferrite (SFCA) binding phase will form.

The value of micro-focus X-ray computed tomography in mineralogy – breaching the two dimensional bias gap

Albertus J.B. Smith

DSI-NRF Centre for Excellence for Integrated Mineral and Energy Resource Analysis, Department of Geology, University of Johannesburg

What is micro-focus X-ray computed tomography?

Micro-focus X-ray computed tomography (µXCT) is a non-destructive technique that uses X-rays to create closely spaced cross sections of a physical object, with the cross sections then reconstructed in a computer to create three dimensional models of the object. Traditionally used in medicine, the applications of µXCT has branched out into other fields as well, such as engineering, archaeology, paleontology, geology and mineralogy, to name a few.

When can micro-focus X-ray computed tomography be used?

µXCT should be used in any instance where the user requires a three-dimensional model to be created in a non-destructive manner of an object or in internal feature within a larger sample as long as: the sample size is suited to the instrument; the sample can be penetrated by X-rays; and there is a density contrast between the feature of interest and its surroundings within the sample. µXCT is primarily used to investigate 3D morphology and not composition, unless another technique is used in conjunction with µXCT that can fix an observed density to a composition. It should also be noted that the resolution is controlled by the distance of the sample to the X-ray detector which, in turn, can be determined by the sample size.

Why use micro-focus X-ray computed tomography in geosciences and mineralogy?

In applied mineralogy, µXCT can provide two major advantages to other, more traditional techniques, namely quantification and elimination of two dimensional biases. µXCT has already been shown to work in creating 3D images of ore minerals within a host rock, such as the base metal sulphide aggregates in the Merensky and J-M Reefs (e.g. Godel et al. 2006). These 3D reconstructions can then also be used to quantify the volume of the minerals of interest as well as other particle shape and association parameters. However, as mentioned earlier, other mineralogical techniques such as optical and scanning electron microscopy are required to identify the minerals of interest and then link them to the observed densities in the µXCT scans. Skeptics might then point out that mineral quantification has already been addressed by automated scanning electron microscope techniques. With these techniques, polished blocks or thin sections are scanned in their entirety and energy dispersive X-Ray spectroscopy is used to identify the minerals, after which surface area is used to approximate for volume so that quantitative data such as mineral abundances and associations may be extracted. However, these techniques are done on flat, two dimensional surfaces, which introduce biases, grain size underreporting and statistical errors that can only be decreased by increasing sample numbers. µXCT completely removes this bias, reporting true, three dimensional mineral grain sizes and associations. Removing this two dimensional bias also has great value in assessing textures and structures within rock for other purposes as well, such as interpreting the genetic history of a rock.

Where can I conduct micro-focus X-ray computed tomography?

Two examples of laboratories in South Africa that allow outside researchers to utilize their µXCT facilities for mineralogical applications are the µXCT facility (MIXRAD) at the South African Nuclear Energy Corporation (Necsa) in Pelindaba, and the Central Analytical Facility (CAF) at the University of Stellenbosch. Other µXCT facilities also exist in South Africa. However, their accessibility for mineralogical applications might be more limited due to intense usage, different focus areas or exclusivity to the company owning the instrument.

How has micro-focus X-ray computed tomography assisted research? A brief case study from the assessment of early life on Earth

An example of where µXCT assisted in improving research outcomes, comes from the almost three-billion-year-old (Archean) Pongola Supergroup of southern Africa, where the world's oldest granular iron formation occurs (Smith et al., 2017; 2020). Iron formations have been a big source of debate with regards to early life on Earth, with mostly indirect evidence and other deductive arguments used to suggest that microbes played a role in their deposition (Konhauser et al., 2002; Smith, 2015). Granular iron formations are common in the Precambrian rock record. However, the example from the Pongola Supergroup is older than and markedly different from other Precambrian occurrences. From initial two dimensional petrography and geochemical studies it appeared as though the granules in this rock might be preserving evidence for ancient microbial life in a shallow ocean (Smith et al., 2017). The coatings had a strange and variable shape under the microscope, which made two dimensional assessment problematic (Figure 1). Luckily, the coatings of the granules are composed of magnetite, that has a much higher density than the surrounding quartz and calcite matrix. It was then decided these samples are ideal for µXCT assessment at the µXCT facility (MIXRAD) at Necsa (Hoffman and De Beer, 2012). The scans and reconstructions were successful, and opened up a microscopic world never before seen of microbial structures in the form of small domes (microstromatolites) that were grown by iron-oxidizing microbes around wave-agitated granules in an ancient shallow ocean along a southern African paleo-coastline (Figure 2; Smith et al., 2020). Furthermore, the resolution was so high that damage caused by original transportation by waves could be seen on the granule surfaces (Figure 2). This was the first time such microstromatolites were successfully imaged in three dimensions in an Archean iron formation.

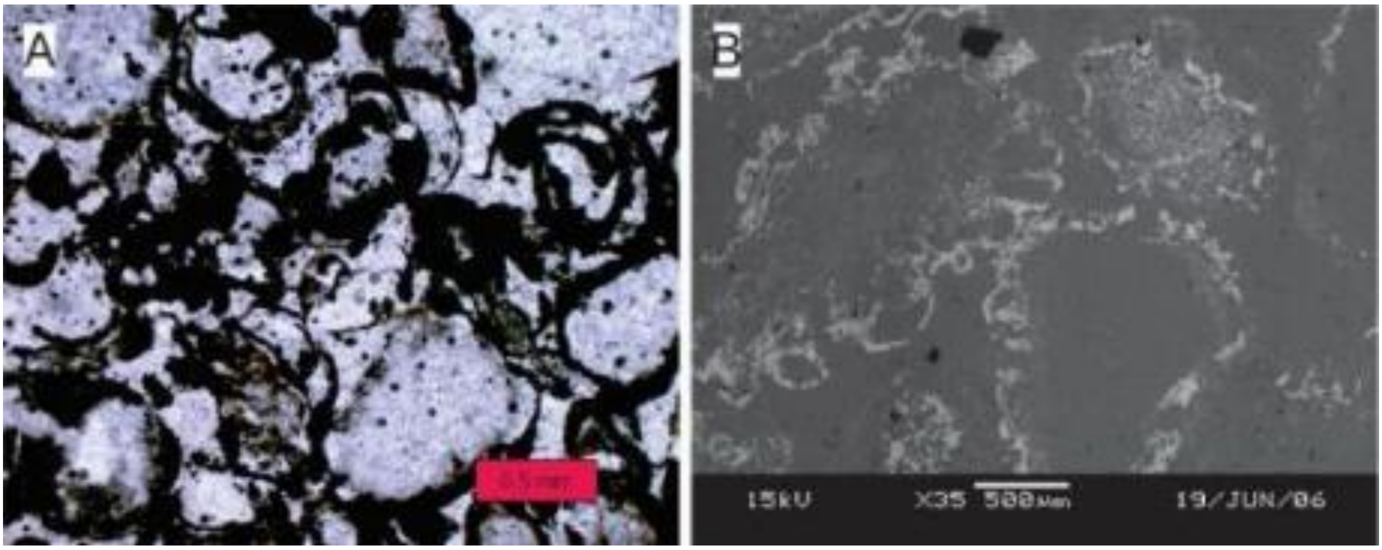


Figure 1:. Transmitted light optical photomicrograph (A) and a false colour backscatter electron image of the Pongola Supergroup granular iron formation (adapted from Smith, 2007).

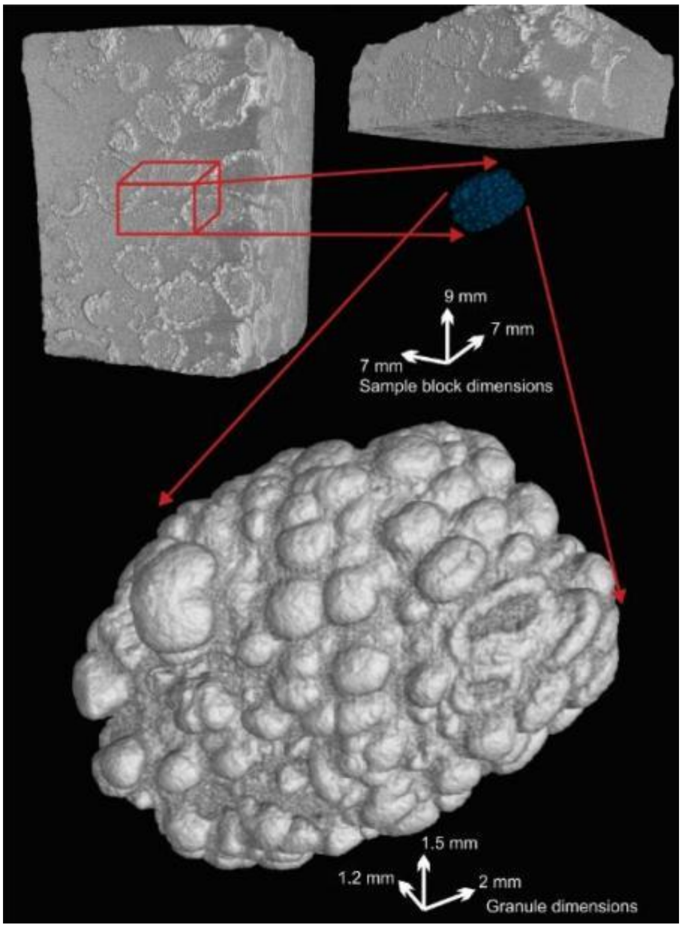


Figure 7: Three dimensional μXCT reconstructions of a sample block as well as one of the granules in the sample block from the Pongola Supergroup granular iron formation illustrating microstromatolites as well as sedimentary transport damage on the coating of the granule (adapted from Smith et al., 2020).

Acknowledgements

Thank you to my collaborators on this project: Stan Awramik, Nic Beukes, Andy Czaja, Frikkie de Beer, Jens Gutzmer, Kobus Hoffman, Clark Johnson and Noah Nhleko. A special thank you to the Department of Geology at the University of Johannesburg, the Palaeoproterozoic Mineralization Research Group (PPM), and the Department of Science and Technology (DST) and National Research Foundation (NRF) funded Centre of Excellence for Integrated Mineral and Energy Resource Analysis (CIMERA) for funding and support. AngloGold-Ashanti provided the samples for the study and are thanked for that.

References

Godel, B., Barnes, S. and Maier, W.D. (2006). 3D Distribution of Sulphide Minerals in the Merensky Reef (Bushveld Complex, South Africa) and the J-M Reef (Stillwater Complex, USA) and their Relationship to Microstructures Using X-Ray Computed Tomography. Journal of Petrology, v. 47, 1853-1872.

Hoffman, J.W. and De Beer, F.C. (2012). Characteristics of the Micro-focus X-Ray Tomography Facility (MIXRAD) at Necsa in South Africa. 18th World Conference on Non-destructive Testing, 16-20 April 2012, Durban, South Africa.

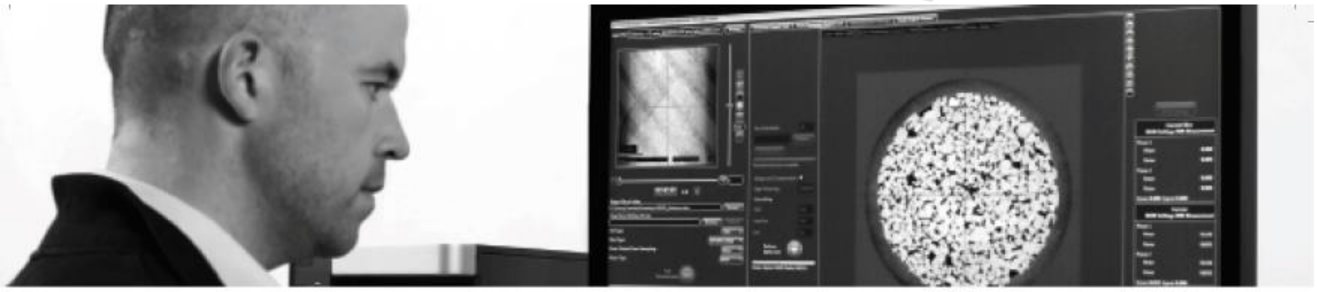
Konhauser, K.O. *et al.* (2002). Could bacteria have formed the Precambrian banded iron formations? Geology, v. 30, 1079-1082.

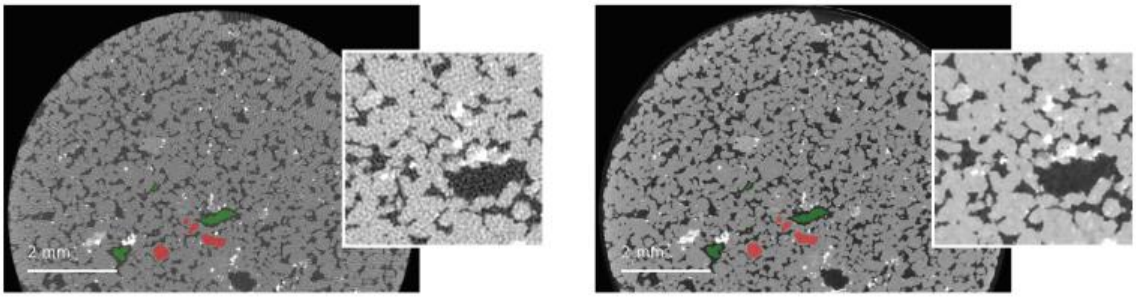
Smith, A.J.B. (2007). The paleo-environmental significance of the iron-formations and iron-rich mudstones of the Mesoarchean Witwatersrand-Mozaan Basin, South Africa. Unpublished MSc dissertation, University of Johannesburg, Johannesburg, South Africa, 208p.

Smith, A.J.B. (2015). The life and times of banded iron formations. Geology, v. 43, 1111-1112.

Smith, A.J.B. *et al.* (2017). Oncoidal granular iron formation in the Mesoarchean Pongola Supergroup, southern Africa: Textural and geochemical evidence for biological activity during iron deposition. Geobiology, v. 15, 731-749.

Smith, A.J.B. *et al.* (2020). Life on a Mesoarchean marine shelf – insights from the world's oldest known granular iron formation. Scientific Reports, in press.

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3D X-ray microscopy (XRM)

Deshenthree Chetty and Guy Freemantle
Mineralogy Division, Mintek

With roots in the medical sciences, 3D computed tomography has gained traction in various spheres of research in which 3D imaging has provided insights sorely lacking in conventional 2D imaging. The geosciences, specifically mineralogy, has keenly adopted the technology for the ability to image minerals in-situ, as well as in mineral processing products.

The key point about 3D computed tomography is that it is non-destructive. This is why (at low radiation) humans can be scanned (*e.g.* the CAT-SCAN) to detect problems in the body without our health being compromised in the process.

In the geosciences, we are familiar with the thin section. A sample could be sliced into successive cross sections. Each of these cross sections, however, could be imaged with X-rays, and the sections superimposed to provide a projection, much like a chest X-ray in medical imaging. Taking this concept into 3D, the sample is made to rotate relative to the imaging device, so that multiple projections can be taken (say every 2 degrees in a 360 degree rotation). These projections are then combined in a process called reconstruction, to produce the projected volume of the sample. Thus, X-ray imaging in 3D allows us to 'see what's inside' without physically destroying the sample (Figure 1).

In conventional laboratory-based X-ray computed tomography (XCT), an X-ray beam source is supplied (typically with maximum voltage ranging from 160 to 320 kV or more) at a given spot size (typically a few microns), in a cone beam fashion (Figure 1). The sample is rotated within this cone beam. During the rotation, the sample interacts with the X-rays passing through it, attenuating them. The attenuated X-rays then reach a detector, from which the X-rays excite a scintillator that generates a light signal that is imaged with a CCD camera. These images are then collated and a virtual volume of the sample (and whatever was inside it) is reconstructed.

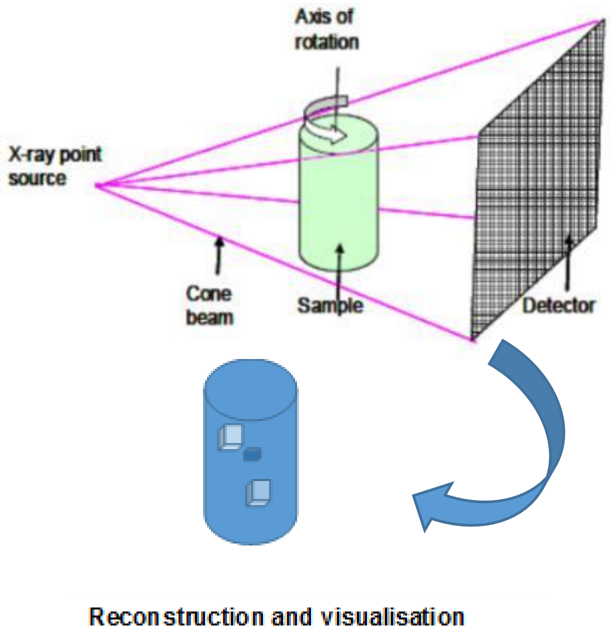


Figure 1: Schematic diagram showing conventional XCT configuration to produce a digital volume of a sample.

Classical XCT uses geometric magnification to project the image onto the detector. However, this is impeded by the focal spot size of the source, and often the sample must be small and placed close to the source to obtain the best resolution. In X-ray microscopy (XRM), a combination of geometric and optical magnification is used to produce a high resolution image of the sample at large working distances (Figure 2). The Zeiss Xradia system, for example, uses a two-stage magnification: images are initially enlarged through geometric magnification as they are in conventional micro-CTs. The projected image impinges on a scintillator, which converts X-rays to visible light. The system has the option of scintillators of different magnifications, much like the objective options on a light microscope. The image is subsequently magnified by an optical objective before reaching the detector. Pixel resolution as high as 0.7 µm within a 4 megapixel square image is possible with this configuration.

Once the volume is reconstructed, one can digitally 'slice' through it to decipher what occurs where, and information relating to the components can be gleaned. Such information can allude to the size of the components, their morphology, what they are associated with, where in the volume they occur, and surface characteristics, amongst others.

For geological materials, and especially in the analysis of ores, differentiation of minerals is necessary. Theoretically, differentiation is based on their linear attenuation coefficients, which, in turn, are related to their density and atomic number, as well as the energy of the X-ray beam passing through them. The quality of the 3D image, particularly optimal contrast and reduction in artefacts, is therefore important. Dual energy scanning is a method used to address such overlaps in attenuation between minerals. Additionally, minerals or phase calibration may be done through registering of 2D and 3D image information, e.g. SEM-based imaging with 3D imaging.

Another key aspect for consideration is the spatial resolution, which is determined by the voxel (*i.e.* 3D pixel) size of the image. This should be smaller than the minimum size sought for a specific feature in the sample. Resolutions of up to sub-micron, even nano-scale, can be obtained with modern laboratory scanners, but this is often at the cost of sample size scanned.

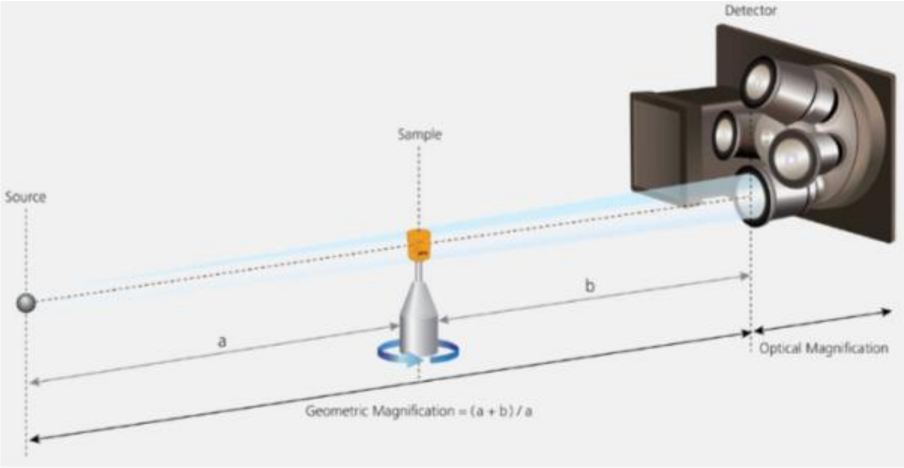
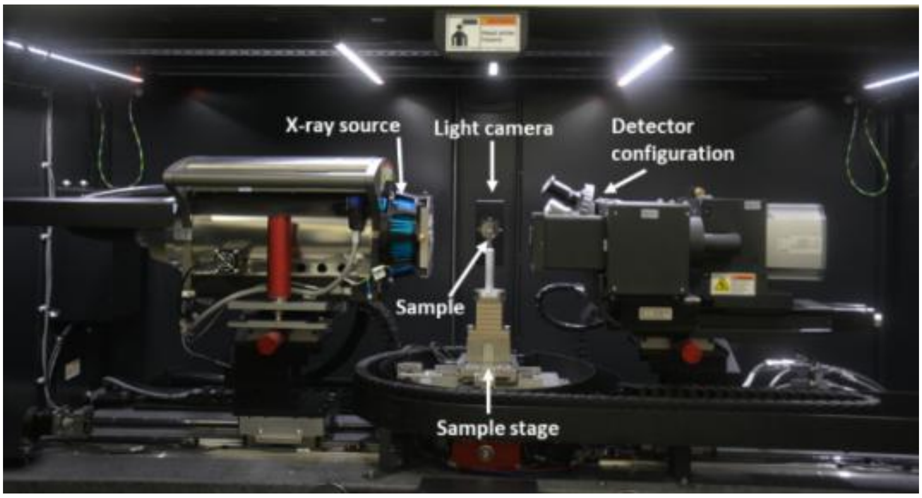


Figure 2: High Resolution 3D X-ray Microscopy:

Schematic configuration of XRM to enhance geometric magnification with optical magnification for optimal resolution. (https://www.zeiss.com/microscopy/int/products/x-ray-microscopy.html).



Configuration of the Mintek-Unisa XRM instrument.

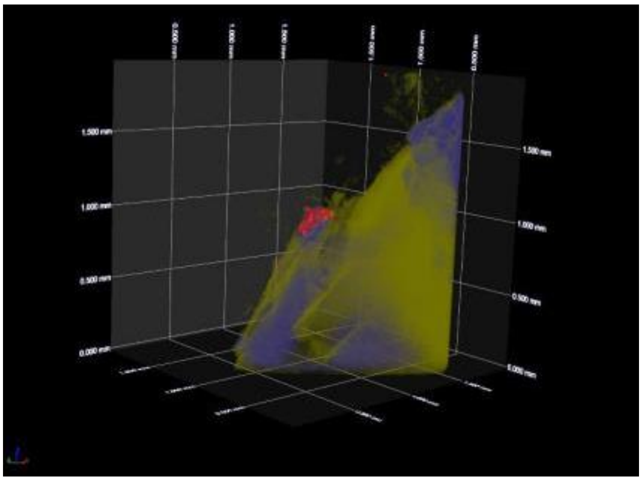
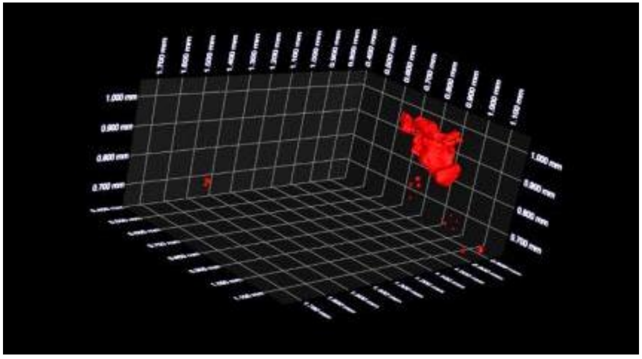


Figure 3: 3D volume rendering of a platinum group mineral (PGM – moncheite, red) associated with chalcopyrite (yellow) and pentlandite (blue) in Platreef ore. Note that chalcopyrite and pentlandite are distinguishable in attenuation contrast, whereas these minerals are difficult to distinguish in a standard back-scattered electron image from a scanning electron microscope.



The morphology of the PGM cluster, as well as grain size distribution of PGM may be gleaned from stripping away the other minerals to count the red voxels.

Amongst a plethora of applications outside medicine, in mineralogy, XRM finds application in ore research, e.g. how a mineral of interest occurs in ore (Figure 3) or how minerals occur in crushed and milled particles of an ore for processing (Figure 4).

The advantages range from its non-destructive nature, overcoming issues of stereology in 2D microscopy, to a reduction in sample preparation (sections, coating, etc.), to potentially shorter analysis times (e.g. finding the needle-in-the-haystack trace minerals in a sample) and direct visualisation and quantification of 3D attributes. Disadvantages lie in the cost of equipment (>R 10 Million), maintenance (source replacements, detector damage), and in very high computing power currently necessary for image analysis. Data processing can also be time-consuming in crunching through volumetric information with various algorithms. This has led to much attention being given to AI for data processing efficiency. Given attenuation contrast and potential resolution limitations compared with synchrotron-based systems (see elsewhere in this newsletter), laboratory-based XRM is best integrated with other mineralogical characterisation methods (XRD, SEM, autoSEM) to obtain optimal information about minerals in samples.

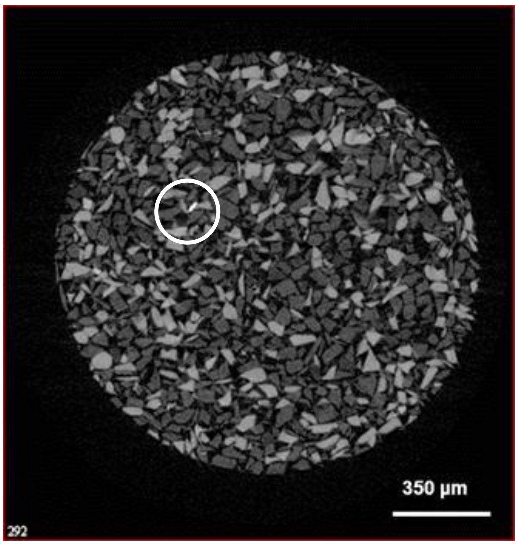


Figure 4: A digital 'slice' from a packed particle bed of particles in the -75+38 µm fraction of a flotation feed of chromitite ore. A bright PGM phase is shown, encircled. Darkest particles are silicates, whereas intermediate-shaded particles are chromite.

Any XRM-related enquiries may be directed to Dr Desh Chetty (deshc@mintek.co.za) or Dr Guy Freemantle (guyf@mintek.co.za).

X-ray Powder Diffraction and Rietveld Analysis

Sabine Verryn
XRD Analytical & Consulting cc

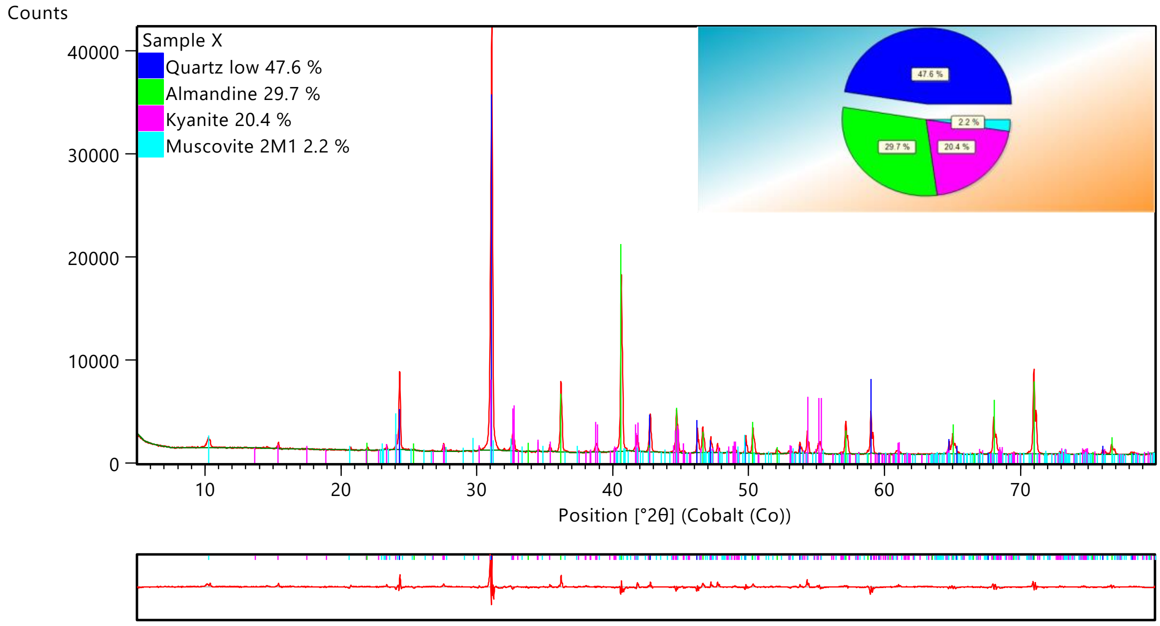
Diffraction of X-rays by matter has been used for more than 80 years, initially to elucidate the structure of crystalline matter, and to investigate the bonding between atoms. Each crystalline phase has a unique powder diffraction pattern. Therefore, it is possible to distinguish between compounds as the diffraction method is sensitive to structure and not just composition. The powder diffraction pattern for the spinel $MgAl_2O_4$ looks different from the powder pattern of a MgO and Al_2O_3 mixture. It is also possible to distinguish between different polymorphic forms of the same compound. So, X-Ray Powder Diffraction (XRPD – or here XRD) is a primary and rapid tool for identifying and quantifying the minerals and phases composing rocks, soils, particulates, cements, industrial products and processes.

Every mineral or compound has a characteristic X-ray diffraction pattern whose ‘fingerprint’ can be matched against a database of recorded phases. Modern computer-controlled diffraction systems can help interpret the diffraction traces produced for individual constituents and highly complex mixtures. By addition of a standard the amount of non-crystalline (amorphous) phases can be quantified – the quantification of amorphous phases can also be calibrated for samples of similar compositions without addition of a standard (e.g. amorphous slag content in cement). Quantification is achieved by the Rietveld method which is incorporated in modern XRD software. As the Rietveld method compares calculated vs. experimentally derived X-ray powder diffraction patterns for a phase, adjusting a wide variety of parameters until the two are in agreement the following data is needed:

- An XRD pattern with as low a background as possible. This should have good resolution and high diffraction peak intensities. With modern X-ray detectors, this can be achieved in minutes rather than hours
- Instrumental parameters such as goniometer radii and slit sizes are needed. These are the so-called ‘fundamental parameters’. They are used to calculate the shapes of the resultant diffraction peak profiles that are caused by the instrument. The parameters are used to correctly separate the instrumental effects on the diffraction pattern from the sample effects
- Phase specific parameters are needed for every phase that is present in the sample. These are the unit cell and space group, atomic parameters and, preferably, the compositions of solid solution phases (spinels, silicates, etc.).

Considering background, peak shape functions, integrated intensity, and non-linear least squares minimization – the groups of independent least squares parameters used in the Rietveld refinement are shown below.

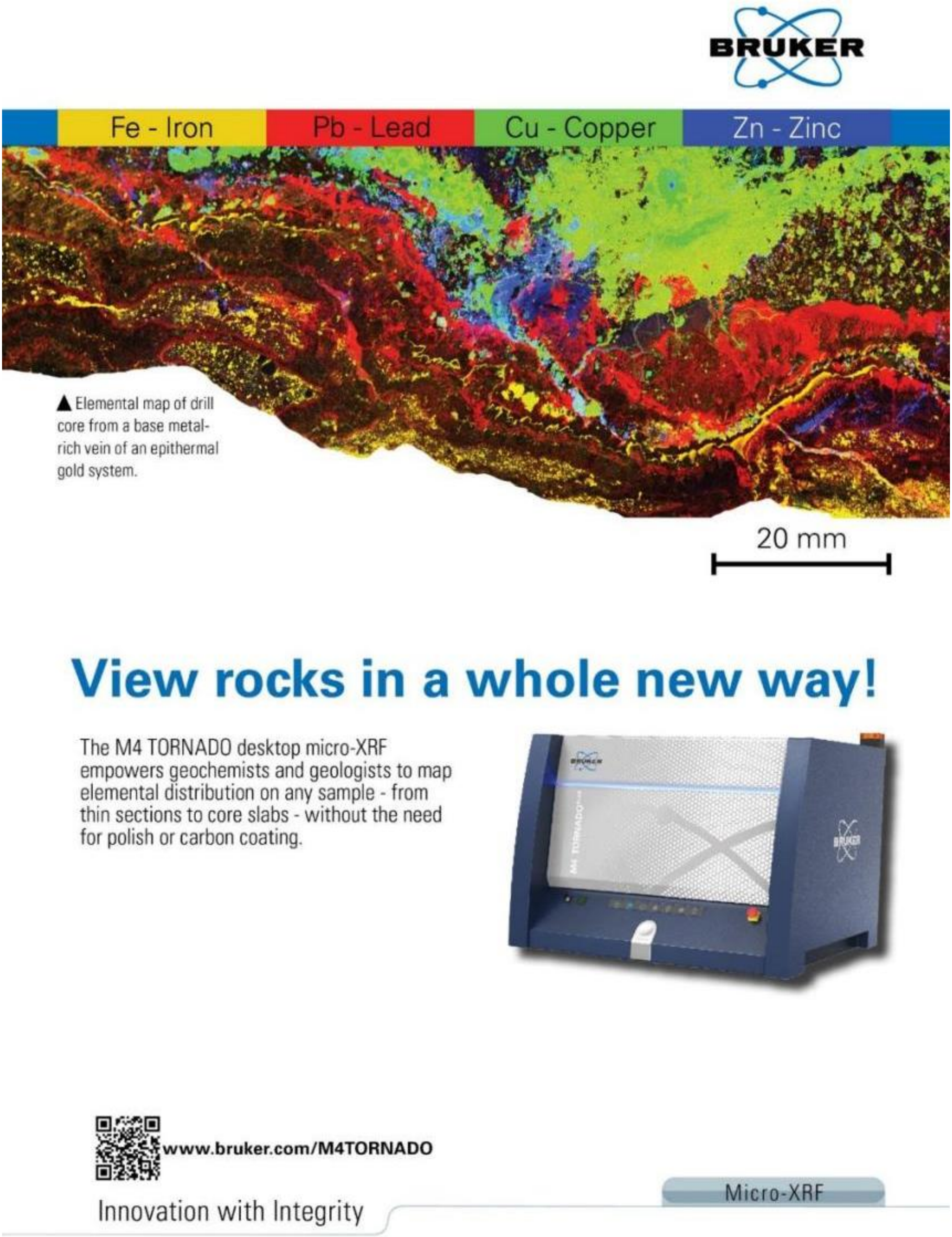
- Background parameters: usually 1 to 12 parameters.
- Sample displacement: sample transparency, and zero shift corrections
- Multiple peak shape parameters.
    - FWHM parameters
    - Asymmetry parameters
- Unit cell dimensions
    - one to six parameters (a, b, c, α, β, γ), depending on the crystal family/system, for each present phase.
- Preferred orientation, and sometimes absorption, porosity, and extinction coefficients, which can be independent for each phase.
- Scale factors (for each phase)
- Population parameters
    - Occupation of site positions by atoms.
- Atomic displacement parameters
    - Isotropic and anisotropic displacement parameters.



Using the above parameters, the Rietveld method fits the experimental data to a calculated pattern in which all the known phases are included. Overlapping of diffraction peaks of different phases is handled without difficulty and reliable results can be obtained in spite of this occurrence.

The modern software has greatly improved the stability and the peak profiles calculated from first principles, giving much better descriptions of the measured peak profiles than older software. This method has progressed from an unstable method that required constant operator intervention to a stable and robust method suited even for routine analysis, provided it is checked against known compositions of materials. Best results are obtained when there is an understanding of mineralogy, crystallography and both the overall philosophy and approach to a successful Rietveld analysis. Above an example of a successful Rietveld refinement with a difference plot at the bottom. Various agreement indices are automatically calculated.

Refinement control files can be developed and installed for samples with similar compositions to automatically perform a Rietveld refinement and report quantities. This is particularly beneficial in an industrial environment such as the cement industry and other processing plants and results can be obtained in minutes and no knowledge by the operator about Rietveld refinement is needed



Secondary Ion Mass Spectrometry (SIMS): an under-utilised tool for cutting-edge isotopic and trace element work on a micron-scale

Sarah Glynn
University of the Witwatersrand

SIMS is a technique that uses a finely-focused ion beam to sputter a micron-sized crater into the surface of a solid sample. The secondary ions produced by this process are then directed into a mass spectrometer - where they are separated according to their mass-over-charge ratio - allowing for precise isotopic measurements to be carried out with measurement uncertainties as small as 1 part in 10,000.

Ion probe instruments capable of performing such isotopic analyses unfortunately carry high investment and running costs, and it is therefore commonly unfeasible for researchers to obtain access to such instrumentation. In order to help overcome this problem for researchers within the southern African scientific community, a research co-operation agreement between the Helmholtz Zentrum Potsdam (GFZ, Germany) and the University of the Witwatersrand (Wits), has been established. This agreement provides users with approximately 20 days per annum of free access to the SIMS 1280-HR instrument in Potsdam via internet-based remote access.

The Potsdam Cameca 1280-HR.

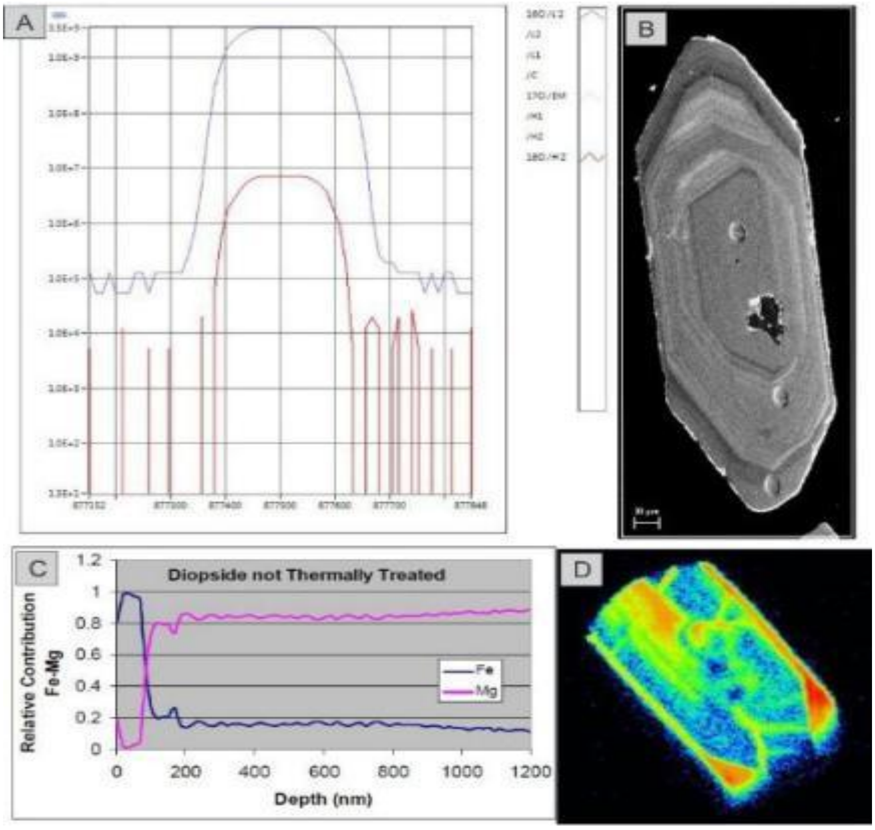
The Potsdam SIMS instrument has five modes of operation which have applications not only within the geosciences but within the realm of palaeoscience (and to a lesser extent materials science) as well.

- The most commonly utilised mode of operation is conducting isotopic analyses, which can be carried out on many major elements in a variety of crystalline matrices with high precision. Some routine examples include: δ^{18}O in silicates, δ^{34}S in pyrite and δ^{35}Cl in foraminifera.
- Trace element analysis: where most elements can be detected at or below 100 ng/g.
- U-Pb geochronology on zircon and other suitable minerals for dating. The typical spot size is ~20 µm.
- Depth profiling: the 1280-HR can quantify diffusion profiles (the depth resolution is ultimately dictated by the surface roughness) and for longer distances point profiles can be set up.
- The 1280-HR also has imaging capabilities with a spatial resolution of a few microns which allows for the production of semi-quantitative elemental distribution maps.

SIMS is a virtually non-destructive technique coupled with a small beam size. All combined SIMS is well suited to a large number of projects.

If you have any queries related to projects that may be carried out via the virtual SIMS, or would like to know more about how SIMS may be useful to you, please contact Sarah.Glynn@wits.ac.za.

Please note that a half-day SIMS workshop is being offered as part of the upcoming Geocongress meeting, so feel free to sign up for that once activity does resume on the conference website



Mass scan of the ^{16}O and ^{18}O peaks in multi collector mode (A), Cathodoluminescence image of a zircon grain dated using the Potsdam instrument (B), An example of a depth profile, the point at which the profile passes from the Fe-rich top layer into the diopside substrate is clearly visible (C), Semi-quantitative ^{178}Hf distribution map within a zircon grain, the field of view is 150 µm (D)..

Laser ablation ICP-MS for trace element analysis

Candice Carelse
Mineralogy Division, Mintek

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a micro-analytical technique used for, amongst others, the detection of trace elements in a variety of solid materials, as well as element mapping and isotope analysis. The technique comprises a laser ablation system, which is coupled to an ICP-MS system. It therefore combines the micrometer-scale resolution of a laser with the sensitivity, speed and multi-element capability of ICP-MS. It differs from standard ICP-MS in that solid materials can be analysed directly. The sample is placed into a sample holder or cell, which forms part of the LA (laser ablation) system, whereby the laser ablates the solid material and turns the ablated material into an aerosol. A crater is produced (Figure 1). Different ablation modes (spots, rasters, lines) and spot sizes (1 µm to 300 µm) can be used based on the application and concentrations required.

The aerosol is then transported by a flow of helium gas into the argon plasma of the ICP (inductively coupled plasma) where it is vaporised, atomised and finally ionised. The next part, the MS (mass spectrometer), separates these ions based on their mass to charge ratio, simply referred to as mass. The ions per second (intensity) of the ion beam is then converted to an electric signal which is measured and recorded (Sylvester, 2008). Various commercial configurations for mass analysers include the Time of Flight (TOF), quadrupole and magnetic sector field analysers. The latter is available as a single collector or multiple collectors and contains a magnet. The quadrupole systems are generally used for isotopic and elemental analysis due to their fast speed. The single collector ICP-MS system is also generally used for isotopic and elemental analysis, but has a slower analysing speed due to peak jumping times where the magnetic field must be changed (Sylvester, 2008). The multi collector ICP-MS system is used for high precision isotope determinations and is the slowest due to even slower peak jumping times between masses.

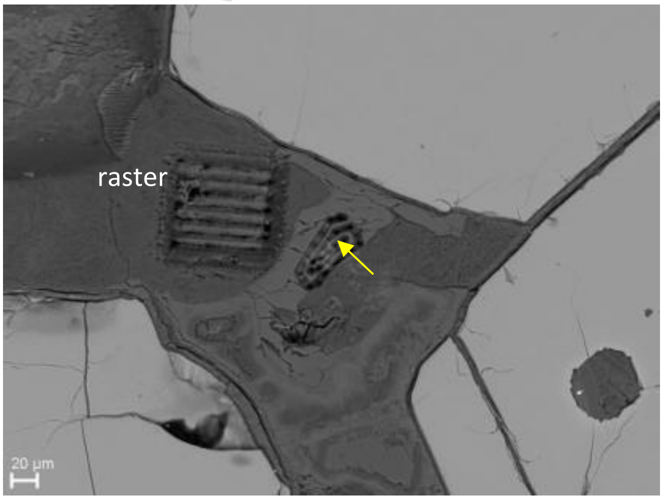


Figure 8. Laser image showing different ablation modes used for ablation of silicates.

In the field of mineralogy, laser ablation-ICP-MS finds practice in a range of applications and, at Mintek, is used for the determination of trace elements (TE's) in a variety of mineral matrices. Trace elements may be detected at much lower detection limits than afforded by electron probe microanalysis, and LA-ICP-MS therefore finds favour in applications where expected analyte concentrations are low (low parts per million levels). Examples of such applications include the detection and quantification of Platinum Group Elements (PGEs) in unconventional mineral matrices such as alteration silicates from oxidised Platinum Group Minerals (PGM) ores. This is necessary to understand PGE distribution, or deportment, in the ore to account for losses in recovery when the ore is processed. Results from oxidised chromitite ores show that chlorite, talc, amphibole and serpentine can host Rh in low ppm levels, with chlorite a prime host of highest Rh contents (up to 2.15 ppm). Palladium, on the other hand, appears to concentrate in talc, whereas highest Pt contents were found in amphibole in oxidised chromitite ores. Overall, chlorite shows the highest propensity for PGE uptake. Calculation of the PGE (Rh, Pd, Pt) deportment gives an indication as to how much PGE is likely to be lost to froth flotation tailings as these alteration silicates are not targeted in flotation (Chetty et al., 2018).

Another useful application is in the field of urban mining and recycling of electronic waste. Laser ablation ICP-MS was used in conjunction with scanning electron microscopy - energy dispersive spectrometry (SEM-EDS) and electron probe microanalysis to quantify gold and silver distribution in alloys produced from the smelting of printed circuit boards (Carelse et al., 2020). Gold (Au) and silver (Ag) were successfully detected and quantified in all phases identified by scanning electron microscopy, due to the much lower detection limits of LA-ICP-MS compared to the electron microprobe. These two precious metals were found to partition mostly into copper and lead alloy phases ranging in concentrations of a minimum of average 4 ppm Au to over 9%, on average, of Ag.

Other applications include provenance studies for the determination of TE in diamonds to fingerprint diamonds from different regions, i.e. are diamonds geochemically distinct. It is also used in provenance studies for the determination of columbite-tantalite ores to determine its pegmatitic source (Melcher et al., 2008).

Laser ablation–ICP-MS is similar to electron probe microanalysis, but with the added advantage of much lower detection limits down to the parts per billion (ppb) level. In a single analysis, concentrations ranging from the percent level down to ppb level can be detected with the aid of a Faraday detector. Precision and accuracy of between 1 and 10% can be achieved for most elements and minimal sample preparation is required. Solid materials can be analysed as is without the need for polished section preparation as long as a flat surface is available. Analysis time is also quick and can range from a few seconds to a couple of minutes depending on the number of analytes being measured and the type of MS used.

A disadvantage of this technique is the non-availability of matrix-matched standards. Most matrix-matched standards are produced in-house and are not available commercially. Non-matrix matched standardization has been used over the past few years, however, with reliable results. Standards also need to be homogeneous on the fine micron scale and well characterised. Interferences from isobaric, molecular and doubly-charged ion interferences also occur, which can lead to erroneous results, but can be eliminated or reduced by careful choice of analytes and optimisation of instrument parameters. Lastly it is a destructive technique as opposed to electron-beam techniques, but ablation holes are on the micron scale and thus cause minimal damage to a sample and can simply be polished away.

Enquiries on LA-ICP-MS may be directed to Ms Candice Carelse: candicec@mintek.co.za

References

Carelse, C., Manuel. M., Chetty, D. and Corfield, A. (2020). Au and Ag distribution in alloys produced from the smelting of printed circuit boards-an assessment using SEM-EDS, EPMA and LA-ICP-MS analysis. *Journal of the Southern African Institute of Mining and Metallurgy*, **120**, 203-210.

Chetty, D., Mogoru, J., Carelse, C., Bergmann, C. and Selepe, K. (2018). The impact of mineralogy on platinum group element recovery from oxidised ores of the Middle Group chromitite, western Bushveld Complex. In: Proceedings of the Process Mineralogy '18 conference, MEI, Vineyard Hotel, Cape Town.

Melcher, F., T Graupner, T., Henjes-Kunst, F., Oberthür, T., Sitnikova, M., Gäbler, E., Gerdes, A., Brätz,H., Davis, D. and Dewaele, S. (2008). Analytical Fingerprint of Columbite-Tantalite (Coltan) Mineralisation in Pegmatites – Focus on Africa. *Ninth International Congress for Applied Mineralogy Brisbane, QLD*, 615-624.

Sylvester, P. e.d. (2008). Laser ablation-ICP-MS in the Earth Sciences. CURRENT PRACTICES AND OUTSTANDING ISSUES. *Mineralogical Association of Canada Short Course Series*, **v. 40**.

Raman spectroscopy and applications in the Earth Sciences

Axel Hofmann
Department of Geology, University of Johannesburg

Raman spectroscopy is a very versatile tool in the Earth Sciences, as it allows for the identification and characterization of minerals and mineral inclusions, mineral phase transitions under varying temperatures and pressures, geological fluids enclosed in minerals and geobiological materials, specifically permineralized organic matter.

When a monochromatic beam of light illuminates a medium (e.g., gas, liquid or solid), a very small proportion of the incident intensity is scattered inelastically by interaction with vibrations of the material. Shifts in the frequency of Raman-scattered light is characteristic of the vibrational species that gives rise to the scattering. Raman measurements are frequently concerned with shifts in the frequencies of vibrations due to changes in bond lengths and interatomic and inter-and intramolecular interactions. Raman spectroscopy is thus an important method in elucidating crystal structures, but can also be used as a method of qualitative analysis (fingerprinting), e.g., in determining the phases of very small areas in petrographic thin sections of geological materials without destroying them.

Recent developments in instrumentation now allow Confocal Raman Imaging (CRI), whereby the spatial distribution and association of components or mineral phases, or chemical variation can be observed. CRI can be applied to large-scale scans in the centimetre range to much smaller areas with nanometre-scale resolution. As many geo-materials are transparent to some degree, CRI can be done three-dimensionally due to the confocal set-up of the microscope.

CRI allows for a large number of research applications in the field of the Earth Sciences alone. These include the identification of mineral phases and their distribution, high resolution spectral and spatial mapping of the chemical variation of minerals and organic materials, and 3D mapping of fluid and mineral inclusions in non-opaque samples. Samples can include hand specimens, petrographic thin sections and single mineral mounts. Compositional information can be obtained even in the smallest sample volumes, such as aerosol particles and interstellar dust. CRI is for the most part a non-destructive technique and provides complementary information to data obtained by other techniques, such as electron microprobe or secondary ion mass spectrometry.

The Department of Geology at University of Johannesburg houses a WITec alpha300R Confocal Laser Raman Microscope. The instrument combines a 532nm laser with an automated sample stage that allows 2D microraman mapping of sample specimens and a piezostage that allows 3D microraman mapping with a resolution down to 200 nm. The instrument is available for academic and industry research and can be booked via email to Axel Hofmann (ahofmann@uj.ac.za).

What is a synchrotron and how can we use one to advance mineralogy?

An interview with Dr Bjorn von der Heyden
Dept of Geology, University of Stellenbosch

In this edition of your favourite mineralogical bulletin, we find out more about how synchrotron X-ray radiation can be used to advance the science of mineralogy, particularly here on the African continent. Our ½-sycophant, ½-blatantly-obnoxious reporter finds novel and effective ways to evade lock-down personal-distancing regulations to get up-close and personal with Dr Bjorn von der Heyden, a researcher at Stellenbosch University, who has been convinced by his own mother that he is handsome, and who has used synchrotron X-rays to study nanoparticulate iron oxides.

Figure 0: Bjorn von der Heyden gets interviewed by a staff reporter in his back yard.

Reporter: Good day Dr von der Heyden. You are looking frightfully fit and happy despite being locked in a two bedroom house with a one year-old and a one month old.

BvdH: Thank you sir. I could say the same for you. No one would guess that you are even a day over thirty years old.

Reporter: Tell me Bjorn, what is a synchrotron light source?

BvdH: A synchrotron light source is a particle accelerator that is designed specifically to emit high brilliance light for scientific investigations.

Reporter: You mean like a giant light bulb, or more like an X-ray machine?

BvdH: A bit of both really. The light emitted from a synchrotron is much 'brighter' than a standard light bulb. Its brightness (measured in number of photons/second/0.1%BW/mm^2/mrad^2) is comparable to one million suns shining through a 1 mm x 1 mm gap in your shade netting. Our eyes would perceive the component of this sunlight that exists in the visible spectrum (1.6 – 3.3 eV), whereas the energy of the synchrotron X-rays are orders of magnitude larger (up to 117 000 eV). The advantages of the synchroton X-rays relative to a standard X-ray machine are 1) the much higher brightness (enabling molecular level studies at nanometer size scales), 2) a high degree of energy tuneability (enabling that specific metals can be targeted for detailed study at their respective X-ray absorption edges).

Reporter: Nice, you really have a knack for explaining these things. You must be really clever. Do you have to be really clever to access to a synchrotron?

Figure 1: An inside view of the circular trajectory that the storage ring of a synchrotron. Inset shows Prof S. Myneni, a specialist in soft X-ray spectroscopy, taking notes whilst running experiments at the end-station (experimental hutch) of the Environmental Sciences beamline (11.0.2.) at the Lawrence Berkeley National Laboratory (CA, USA).

BvdH: Not at all. And nor do you have to be really rich. In fact, most synchrotron facilities allow free access to scientists to use the beam time (i.e., time at the synchrotron facility making use of the synchrotron X-ray beam). However, you need to remember that because there are a finite number of synchrotron facilities (~60 world-wide, with none currently in Africa), a finite number of 'end-stations' or experimental hutches attached to the synchrotron storage ring (Fig. 1), a finite number of days in the year, and an infinite number of synchrotron experimental possibilities; the demand for this beam time is very high.

Reporter: OK great. So even I can go to the synchrotron to do experiments. I'm a mineralogist and I want to shine synchrotron light on the some minerals to see if they glow. Maybe as soon as this travel ban ends we can head across to a synchrotron together?

BvdH: *(laughing)* It's not quite that simple. As I mentioned, the demand for the beam time is very high. It is therefore imperative that you put together a strong proposal supported by sufficient preliminary work using other more common technologies (e.g., optical microscopies, SEM, etc.), in order to stand a good chance of being allocated synchrotron beam time. An alternative approach is to contact established synchrotron scientists to access beam time through collaboration.

Reporter: Ah, that ubiquitous term 'collaboration'. I am always being told I should collaborate on this, or collaborate on that. I'm from the old school train of thought, I much prefer the comfort of my ivory tower. There I can write whatever I want without everyone else trying to get their names onto my paper. Take this article for example, see your name already stands there in the very second line.

BvdH: Umm, surely that's because you're interviewing me?

Reporter: Indeed, yes. We digress. Let's get back to the interview. So you said no synchrotrons on the African continent? Why is that? Surely we need an African synchrotron to help us decolonize science?

BvdH: Well that is a multi-part question and I'll do my best to respond. There are multiple arguments for having a synchrotron on the African continent. For example, it would better enable African researchers to compete within the global scientific arena (the so-called African science renaissance); it would encourage the African scientists currently working and living abroad (the so-called African Diaspora) to return to contribute within their home countries; it would attract 'scientific tourism' to a world-class facility hosted in Africa; and it would promote the development of up-stream and down-stream enterprises, the latter especially important given the host of innovative solutions that can arise through synchrotron science and related industry-academia interactions. Some of the arguments against having a synchrotron here include issues with consistent and dependable supplies of electricity; political risk factors in many potential host countries in Africa; and of course the cost. A small synchrotron costs on the order of ½ to 1 million Euros (R9.5 – R20 million) to construct and a similar amount to maintain each decade thereafter (Connell et al. 2019). To put that into perspective, the Green Point stadium build for the 2010 Soccer World Cup cost R4.4 billion (M&G, 2011), and let's be honest, Science is way cooler and way more important than Soccer. For the decolonization part, I really can't comment…

Reporter: Ok enough of that, if there's no decolonization then it's really no use to me. I need to use the word 'decolonization' to get my grants funded. Let's talk about minerals instead. Will synchrotron light make my minerals glow?

BvdH: Sure, if you select the right mineral and the right energy range for the synchrotron light. This really is one of the advantages of synchrotron light. It's highly tuneable and it covers an extensive energy range, from Infrared and UV-vis all the way up to the hard energy range (generally ~ 40 keV, but as high as 117 keV). So I guess if you interrogated scheelite using low energy synchrotron UV-vis spectroscopy, you would end up with a glowing mineral.

Reporter: OK, you previously mentioned the tuneability and energy range stuff. Why are you repeating yourself. I thought you said you are really clever?

BvdH: *(cutting in)* Actually, it was you who said I must be really clever. And I only repeat it because it is really important. These (and the brightness, and small spot size of the light beam) are what set synchrotron techniques apart from other, more conventional techniques.

Reporter: Alright then, I forgive you for thinking yourself clever, and for the repetition, and for only caring about glowing minerals. What can you do with synchrotron light and those other boring minerals.

BvdH: (*getting exasperated, but trying to hold it together*) Are you not reporting for a mineralogical society? Surely there are no boring minerals for you?

Reporter: Listen Doc, I'm asking the questions here. But, yes, quartz bores me. Now get back to the question I asked.

BvdH: (*shaking his head whilst rolling his eyeballs- actually quite a skill, and super disorientating for the observer*) I think you should change you would change your mind about quartz if you knew that its piezoelectric properties were what is keeping your wrist watch ticking away accurately. But to get back to your question, there are multiple techniques that employ synchrotron light to advance the field of mineralogy, geology and the general earth sciences. I list them briefly here:

1. **Synchrotron X-ray Diffraction (sXRD):** single-crystal is a preferred approach (over bulk powder diffraction) used to characterize or describe the crystallography of a mineral (e.g., unit cell parameters, etc.). The two main advantages of sXRD are that it has a very small spot size which enables micro-characterizations, and that the high intensity beam results in a good signal-to-noise ratio (Reynolds et al. 2010). A recent example of a new mineral that has been described using sXRD is Zincoberaunite [$ZnFe^{3+}_5(PO_4)_4(OH)_5 \cdot 6H_2O$], which occurs as 3 µm thick elongate fibers in a pegmatite in Germany (Chukanov et al. 2017).
2. **Synchrotron X-ray Fluorescence (sXRF):** this arises as a result of the photoelectron effect and provides quantitative measure of elemental concentrations within a specific mineral or within a rock sample. It is especially useful for mapping trace-element distributions within geological samples since it has a better spatial resolution than LA-ICP-MS mapping, and a better detection limit than the electron microprobe (or SEM-WDS mapping).
3. **X-ray Absorption Spectroscopy (XAS):** This comprises a set of spectroscopies that exploit the interactions of the synchrotron beam with the core and outer electrons around the atoms of a specific element. It includes X-ray Absorption Near-Edge Spectroscopy (XANES) which provides spectral information pertaining to the redox state and coordination number associated with metal centers in mineral structures. In Figure 2, an example is shown of how XANES spectra helped to determine the Fe valence state (and to an extent) mineralogy of some marine iron-rich nanoparticles (von der Heyden et al., 2019). The Extended X-ray Absorption Fine Structure (EXAFS) is the spectral region beyond the main absorption edge and provides information related to the coordination number, the degree of disorder in the local coordination environment, the bond distances and the chemical identity of the surrounding atoms (Newville, 2015). Both of these techniques are especially useful for studying the characteristics of poorly-crystalline material (e.g., precipitates from Acid Mine Drainage).
4. **Synchrotron X-ray Computed Tomography (sXCT):** This synchrotron-based XCT technique is similar to standard bench-scale XCT with the

advantage that samples can be imaged over much faster acquisition time-scales. Achievable spatial resolutions are on the order of 50 nm voxel size. An exciting development in the field of sXCT is its coupling with other high-level and spectroscopies. For example, sXCT can be coupled with sXRF, XANES, and sXRD detectors to respectively provide the 3D distributions of elemental concentration, valence state, and mineralogy within a studied sample. This has been demonstrated quite exceptionally by Suuronen and Sayab (2018) who evaluated the micropetrography (inclusion speciation, zonation patterns, lattice parameters, and trace element distributions) within individual 100 µm zircon crystals at a spatial resolution of ~100 nm.

Reporter: Thanks for that overview, that's about all I have space for. I promised the editor two pages of writing and we're already on three. And besides, I have to get back to doing absolutely nothing- since this is what I've done throughout the rest of lockdown.

BvdH: Thanks reporter, it's been somewhat great chatting to you. Do you mind if I ask the favour of conducting some shameless self-promotion?

Reporter: Sure, I'm not surprised at your request. You've been grandstanding throughout the interview.

BvdH: Great, thanks! Should anyone be interested in more information related to the African Light Source Initiative, please see:
https://www.africanlightsource.org/.

For more information on how synchrotron techniques are applied in the field of Ore Geology, please see the paper by von der Heyden (2020) "*Shedding light on ore deposits: A review of synchrotron X-ray radiation use in ore geology research*".

For insights into the use of synchrotron light in the broad field of Earth Sciences (geology, geochemistry, paleontology) specifically within the African context, please look out for the submitted paper: von der Heyden et al. "*Synchrotron X-ray radiation and the African earth sciences: a critical review*". It will hopefully be out later in the year in the Journal of African Earth Sciences- if the paper reviewers do not think our writing is too bad!

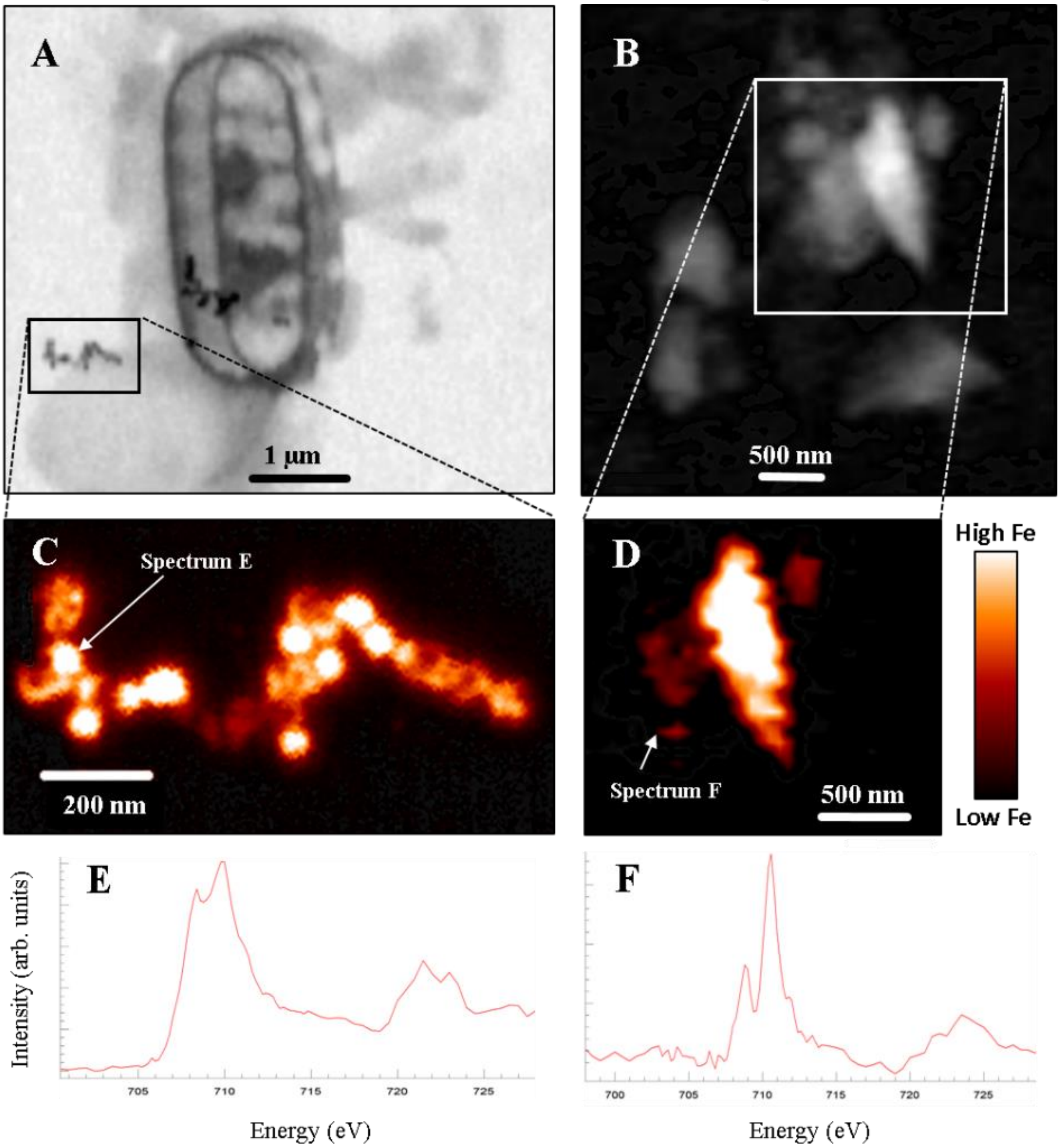


Figure 2: *The soft X-ray beamline (11.0.2.) was used to investigate the nanomineralogy of iron oxides collected from the Southern Ocean (where they play a crucial role potentially supplying iron as a trace nutrient for phytoplankton growth, with further implications for marine biogeochemistry and global climate feedback loops).* ***A, B:*** *Fe-rich suspended colloids and nanoparticles identified.* ***C, D:*** *false colour zoomed-in images of the Fe-rich particles.* ***E, F:*** *Fe L-edge XANES spectra of the Fe-rich particles. The spectral shape and the relative intensity of the two main peaks was used to identify a magnetite mineralogy in the nanoparticles in (**E**), and a poorly-crystalline Fe^{3+}-bearing colloid in (**F**). Figure taken from von der Heyden et al. (2019).*

References:

Chukanov, N.V., Pekov, I.V., Grey, I.E., Price, J.R., Britvin, S.N., Krzhizhanovskaya, M.G., Kampf, A.R., Dünkel, B., Keck, E., Belakovskiy, D.I. and MacRae, C.M., 2017. Zincoberaunite, ZnFe3+5(PO4)4(OH)5·6H2O, a new mineral from the Hagendorf South pegmatite, Germany. Mineralogy and Petrology, 111(3), pp.351-361.

Connell, S.H., Mtingwa, S.K., Dobbins, T., Khumbah, N., Masara, B., Mitchell, E.P., Norris, L., Ngabonziza, P., Ntsoane, T. and Winick, H., 2019. Towards an African light source. Biophysical reviews, 11(4), pp.499-507.

Mail and Guardian (M&G) web resource. https://mg.co.za/article/2011-06-10-stadiums-score-costly-own-goals/ Accessed 22/05/2020.

Newville, M., 2015. Fundamentals of XAFS. In: Henderson, G.S., Neuville, D.R., Downs, R.T. (Eds.), Spectroscopic Methods in Mineralogy and Materials Sciences. Mineralogical Society of America, Chantilly, VA, pp. 33–74.

Suuronen, J., Sayab, M., 2018. 3D nanopetrography and chemical imaging of datable zircons by synchrotron multimodal X-ray tomography. Sci. Rep. 4747. https://doi.org/10.1038/s41598-018-22891-9.

Von Der Heyden, B., Roychoudhury, A. and Myneni, S., 2019. Iron-rich nanoparticles in natural aquatic environments. Minerals, 9(5), p.287.

Minsa invites any submissions to do with **"Samples, Sampling and Sample Preparation"** for our next special issue of the Geode. Submissions close August 31st 2020.

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The editor's desk

Mineralogical Association of South Africa
A division of the GSSA

NOMINATIONS FOR EXECUTIVE COMMITTEE: 2020-2021

Nominations are hereby invited for the Minsa executive committee to hold office for 2020-2021. A nomination from is attached. All nominations must be sent to:-

minsa@gssa.org.za

The closing date for nominations is **8th July 2020**. Each nominee must have a proposer (to be filled in above nomination table). The proposer must be a Minsa member. The proposer must ensure that the nominee is willing to serve, is able to attend at least 50% of committee meetings (as per GSSA Council guidelines), whether in person or through a conference call facility (such as Skype). Executive members must be BOTH a Minsa and a GSSA member.

Please list as many nominees as you wish (no maximum), bearing the nominee criteria in mind. Outgoing members of the executive are listed below for your information. Please mark (tick) which portfolios the nominated member is willing to run for (they may run for all the portfolios).

Outgoing members of the Executive Committee are:-

Dr Bertus Smith (Chair)	bertuss@uj.ac.za
Dr Sabine Verryn (Treasurer)	sabine.verryn@xrd.co.za
Ms Sara Turnbull (Communications)	sara.sjt.turnbull@gmail.com
Mrs Petra Dinham (Secretary)	pea.dinham@gmail.com

As Vice Chair for 2019–2020, Igor Tonzetic automatically becomes the Minsa Chair for 2020-2021 (as per Constitution).

See next page for nomination form:

MINSA
Mineralogical Association of South Africa
A division of the GSSA

MINERALOGICAL ASSOCIATION OF SOUTH AFRICA

NOMINATIONS FOR THE EXECUTIVE COMMITTEE
2020-2021

Proposer: ______________________________

Nominee	Vice Chair	Treasurer	Secretary	Communications

Please complete the form and email to Igor Tonzetic at:

minsa@gssa.org.za

by 8th July, 2020

Bridge The Gap Geosciences Guidance Program (BTG) celebrated three years of mentorship during the month of May!

BTG is a student run organization based at the University of the Witwatersrand, which focuses on mentorship between undergraduate and postgraduate students, as well as students and industry professionals. In addition to the mentorship program, BTG hosts a number of informative talks, workshops and field trips to expose prospective students and graduates to opportunities and expectations in the work environment.

BTG thanks all postgraduate students and industry professionals who volunteer as mentors and those who have presented talks to motivate students and act as positive role models. We are most grateful to all our sponsors and partners including the GSSA and MINSA who have generously donated funds and for freely availing opportunities for students beyond the classroom, such as access to mine visits, CDP courses and training on top industry computer software programs.

In the spirit of the three year celebration, BTG invites all geosciences/mining related companies and industry professionals to "bridge the gap" between students and industry, and to act as positive role models by joining the BTG program as a mentor, sponsor or motivational speaker, which are much needed during these uncertain times of COVID19. If you are interested in getting involved please complete the Google form by clicking on the following link: https://forms.gle/Sf5tMciuSStAQuFL8

Or email bridgethegap.wits@gmail.com for more information.

Your influence can go a long way in encouraging and shaping aspiring geologists to become future leaders. We believe that each of us can inspire and empower students by being "the mentor you wish you had”. We remain committed to inspiring and empowering young geologists to become the best versions of themselves. Here's to many more years of meaningful mentorship and partnership.

Bruce's Beauties: Amethyst Geodes

I thought that as the Minsa newsletter is titled "The Geode", it might be appropriate to feature some photos of geodes, and with amethyst being one of the most well know, these are the preferred species.

Although not a geode as such, the specimen below has been trimmed from a Brazilian geode. Apart from amethyst, calcite is a common mineral within the cavities and is always a later stage mineral. This is a 25-cm sceptered calcite on a base of amethyst. The photo was taken in a dealer's booth at the 2012 Munich Mineral show.

Bruce Cairncross photo ©.

The picture above is of a10.5 cm quartz-amethyst geode from the Jozini area in northern KwaZulu-Natal. These are collected by locals from the Drakensberg volcanics that outcrop in the region and are sometimes sold along the roadside. *Bruce Cairncross sample and photo ©.*

Arguably, or perhaps not, the most famous amethyst geodes come from Ametista do Sul, Rio Grande do Sul, in Brazil. These are seen at most international shows around the world and range from fist-sized to larger than an average bathtub. They are invariably sawn in half and then each half is polished. Sometimes yellow citrine is present in place of purple amethyst, but in the case of this picture, the "citrine" is produced by heating the purple amethyst. This picture was taken at the 2017 Tucson Gem & Mineral show in a Brazilian dealer's stall. The vertical tube amethyst on the right is approximately one and half metres tall. *Bruce Cairncross photo ©.*

Minsa Crossword for June 2020

This puzzle's theme is 'alteration minerals' (or rocks) (for no particular reason);

1	▨	▨	▨	▨	▨	▨	▨	2	▨	▨	▨
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	▨	▨	2								▨
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4							5		▨	▨	
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	▨	5								▨	
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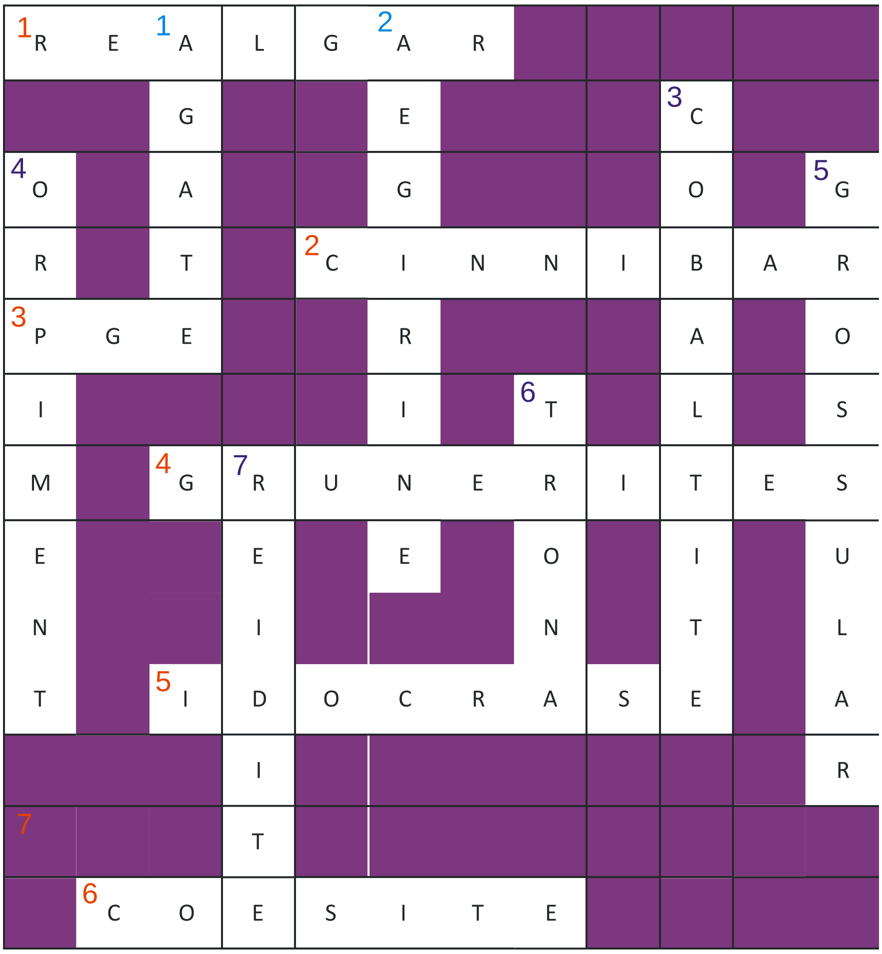
ACROSS:

1. A now–discarded (as of 2006) European name for the hydrated subspecies of kaolinite synonymous with hallyosite-10Å; $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$.
2. A rock, of any type, which can be best described as "f&^%ed up beyond all recognition"; an informal descriptive term beloved of field geologists.
3. The clay mineral $Al_2Si_2O_5(OH)_4$, for which the largest economic deposits in South Africa are found (and mined) in the Makhanda area (Grahamstown).
4. The informal term for a generic rock sample that, for whatever reason, your preference is to "rock name"-there, meaning 'not take it with you'.
5. The oxidised iron hydroxide mineral named for the (German) author of the evolutionary precursor, "*The Metamorphosis of Plants*" in 1790, and, later, *Faust*. The mineral provides the basis for the colouring pigment known as "brown ochre".
6. The serpentine mineral forming as a high temperature alteration of olivine, which is particularly effective as a fibrous insulator, and as a carcinogen-inducer, formerly ('til 2012!) most prominently mined near the town of Asbestos, Québec (Canada).

DOWN:

1. The phyllosilicate formed from the hydrothermal alteration of biotite or phlogopite, and characterised by (and named for) the distinctive wormy exfoliation texture when heated.
2. The mineral name for the fine grained aggregate of white micas and clays associated with hydrothermal alteration of feldspars, commonly found as phyllites and schists, and named for its silky textural appearance.
3. A brown granular hydrothermal (or weathering) alteration product of ilmenite, perovsite or titanite, mostly consisting of microcrystalline rutile.
4. A species of nickeliferous serpentine whose name derives from the National Institute of Metallurgy of South Africa, and which was found in the Barberton area, South Africa, associated with the Scotia talc mine.
5. The name of the moon of Neptune which consists largely of solid (frozen) nitrogen. OK, not exactly an alteration mineral, but only a small logical leap.

Minsa Crossword Solution for March 2020



1 R	E	1 A	L	G	2 A	R	■	■	■	■	■
■	■	G	■	■	E	■	■	■	3 C	■	■
4 O	■	A	■	■	G	■	■	■	O	■	5 G
R	■	T	■	2 C	I	N	N	I	B	A	R
3 P	G	E	■	■	R	■	■	■	A	■	O
I	■	■	■	■	I	■	6 T	■	L	■	S
M	■	4 G	7 R	U	N	E	R	I	T	E	S
E	■	■	E	■	E	■	O	■	I	■	U
N	■	■	I	■	■	■	N	■	T	■	L
T	■	5 I	D	O	C	R	A	S	E	■	A
■	■	■	I	■	■	■	■	■	■	■	R
7 ■	■	■	T	■	■	■	■	■	■	■	■
■	6 C	O	E	S	I	T	E	■	■	■	■

ACROSS:

1. An arsenic sulphide mineral also known as “ruby sulphur”, on the street. Also, when I was an undergraduate, we thought this would be an excellent name for a child. Now, as a parent, not so much.
2. A hydrothermal mercury sulphide mineral, HgS, constituting the only important mercury ore. Its bright red colour made it attractive as a colouring pigment for thousands of years, mined from volcanic precipitates, although its toxicity to humans has been recognised as early as ancient Roman times.
3. The three letter acronym for the six elements chemically associated with rhodium, for which the Critical Zone of the Bushveld Complex hosts much of the global economic reserves to date.
4. The plural form (yes, it’s a bit of a cheat) of the Ca-Fe garnet subgroup found in contact metamorphosed skarns associated with heating of impure limestones.
5. Another mineral found in impure limestone-hosted skarns, this Ca-Mg-Fe sorosilicate is also known as vesuvianite, but the gem version is often known as this.
6. The high pressure polymorph of quartz first synthesized in 1953 by Loring Coes Jr, a chemist at an American commercial abrasives-making company, it is associated in nature with meteorite impact craters.

DOWN:

1. A variant of cryptocrystalline silica consisting of a mixture of chalcedony and microgranular quartz, associated with precipitation from volcano-genically-heated fluids.
2. A pyroxene found in alkaline igneous rocks, or high pressure metamorphic rocks, in which sodic minerals feature prominently. This mineral also features elsewhere in this issue of the Geode.
3. A cobalt arsenic sulphide mineral, found in high temperature hydrothermal deposits. The primary element is named from the German, Kobold, meaning “underground spirit”, with reference to its refusal to smelt as expected.
4. An arsenic sulphide mineral found in low-temperature hydrothermal deposits and in hot springs and volcanic fumaroles. Its name derives from its golden colour.
5. The Ca-Al garnet subgroup also found in skarns, the unintended theme of this crossword. A green gem variety, Tsavorite, named for the Tsavo region of Kenya, occurs in Kenya and Tanzania.
6. This hydrated carbonate mineral is the primary source for sodium carbonate in the U.S.A. (but not elsewhere), and forms in non-marine evaporates. It also occurs in salt pans in Namibia and the Kenyan rift valley.
7. This mineral is the recently recognized high-pressure polymorph of zircon, diagnostic of the conditions unique to large impact craters. It also features elsewhere in this issue of the Geode.

Note: The recommended deadline for submissions for the next issue of the Geode is August 31, 2020.