the Geode
the Geode

MINSA
Mineralogical Association of South Africa
A division of the GSSA

Methods for determining the modal mineralogy of rocks

petrographic microscopy

XRD

EDS hyperspectral imaging

obituary notice: Morris Viljoen

QEMSCAN

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anthropo-morphic minerals

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Next issue theme:
Family-friendly geoscience activities

The Editor's Site

Welcome to the penultimate issue of the Minsa Geode for 2021. In this issue, we welcome the start of the next term as Minsa Chair by Bertus Smith, and we feature five articles on various approaches to the determination of the actual (modal) mineralogy of rocks, ranging from the troglodytic techniques involving actually looking at rocks to the use of various x-ray scanning techniques to do it for you. Which save a lot of time and are more accurate and precise, but will lead inevitably to Skynet, time-travelling Terminators, and the end of the world as we know it. Just sayin'. The theme for the final issue of 2021 is "family-friendly geoscience"; please tell us your favourite places to combine social gatherings and geoscience, which as our readership would doubtless attest, go together like iridium into a monosulphide solid solution. For more explanation of this thematic concept, see also the infomercial for it on page 14 of this issue.

The Editor, with lockdown moustache, in a core yard.

Preceding our thematic section, we offer a short tribute to the late Morris Viljoen, whom we sadly lost in August. From komatiites to Kruger Park, and from

student to stalwart, his contributions have been enormous.

To finish, Bruce Cairncross introduces us to a whimsical pass at minerals from his collection that are reminiscent of living things, loosely characterised as anthropomorphic. Our crossword for this issue is on the theme of biblical geology; gems, metals and rocks mentioned in the Bible. In "Other Gems", we explain why, note some new publications of mineralogical interest, and also provide a possible answer to the age-old question: what do Sodom and Siberia have in common? (no suggestions, please).

And that's the perspective from the Editor's site.

Steve Prevec

From the Chair

Welcome to the first Geode for the 2021/22 term of Minsa! It is with great excitement that I get to serve a second, non-consecutive term as the Chair of Minsa's Executive Committee, my previous chair term taking place during 2019/20. We have been able to secure consistency on the Minsa Executive Committee, with the same members from the 2020/21 term staying on, albeit slightly reshuffled. Therefore, other than me, the Executive Committee comprises Igor Tonžetić (University of Pretoria, Vice-Chair), Petra Dinham (Wits University, Secretary), Sabine Verryn (XRD Analytical and Consulting, Treasurer), Sara Turnbull (Independent, Communications and Marketing) and Sarah Glynn (University of the Witwatersrand, Without Portfolio). I am very thankful to them for their willingness to stay on, as their experience and abilities will remain of great value to Minsa.

I also want to thank all Minsa Co-opted Committee members, past, present and future, for accepting our

invitation to add value and take active part in Minsa's plans.

Covid still has a negative impact on our ability to plan events and move as freely as we would like, but with vaccine rollout picking up steam there is always hope for some normality to return sooner rather than later. For the rest of 2021, there are still two Minsa activities taking place: A visit to Palabora Mine (6 October 2021); and Night at the Museum (Ditsong Museum, 26 November 2021). If you are not yet planning to, but want to attend any of these activities, please contact us (minsa@gssa.org.za) for more information. Please also be on the lookout for Minsa activities to take place during 2022, which will include public lectures, field trips, training opportunities and seminars. Important to note, is that the Geological Society of South Africa's Geocongress, originally planned to take place in 2020, is likely to take place during 2022 in Stellenbosch, and we will aim to maximize Minsa's fingerprint at this event.

Going into 2022, my aim is to continue growing Minsa, especially the student membership, as they will be our mineralogists of tomorrow. Furthermore, as Executive and Co-opted Committee, we will remain committed to serving the mineralogy community in southern Africa to the best of our abilities. Please keep your eyes on the Minsa activity calendar and the Geode, which we will regularly circulate, and join in so that we can make this a memorable term!

Kind regards,

Bertus Smith

Forthcoming Events & Attractions

Many of these events are still missing dates, as a consequence of lockdown logistics: Minsa will let you know! Watch for e-mailed announcements.

- Palabora Mine visit –Wednesday 6th October – joint Minsa / SAMS excursion
- Excursion to tile factory
- Joint Minsa-SAMS excursion to the Leeuwpoort Tin mine
- Wirsam Visit
- Night @ the Museum VI – 26th November at R150 per person
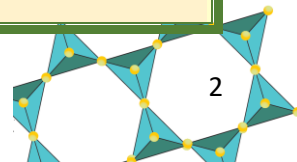
Obituary notice for Morris Viljoen

On August 19th, many of those in the geological community received a notification of the passing of Morris Viljoen earlier that day. Morris's impact on the South African geoscience community would be hard to overstate. Accordingly, a substantive memorial is being prepared for the Geological Society of South Africa in the near future, to which we would direct interested readers. However, in lieu of the well-informed version, presumptuous or not, we offer a personal perspective on Morris's contributions from an 'outside' perspective, as a demonstration of his impact. Among his many other contributions, some of which are highlighted below, he also served as the Chair of Minsa in 1997.

Morris James Viljoen (1940-2021).

Photo courtesy of the School of Geosciences, University of the Witwatersrand.

Carl Anhauesser has noted that he, Morris and Richard Viljoen go back 63 years, to when Carl first encountered the Viljoen brothers when registering for geology at the University of the Witwatersrand in 1958. All three of them mapped components of the Barberton Greenstone Belt for their Ph.D. research projects, conducted through Wits, in the 1960s. This work led to the recognition that the ultramafic lavas exposed there represented previously unrecognized and distinctive magmas in terms of composition and texture: the komatiite, which Morris and Richard named after the river and its tributaries which had exposed these rocks.

The komatiite, subsequently recognized in Australia and Canada shortly thereafter, became a cause célèbre in our understanding of mantle melts, with studies on the nature of mantle melting, on the physical behaviour of magmas, and as a potential source for

PGE- and Cr-ore deposits hosted in chemically primitive rocks pivoting on the komatiite ever since (to this day).

4. THE GEOLOGY AND GEOCHEMISTRY OF THE LOWER ULTRAMAFIC UNIT OF THE ONVERWACHT GROUP AND A PROPOSED NEW CLASS OF IGNEOUS ROCKS

by

M. J. Viljoen and R. P. Viljoen

I. INTRODUCTION

As noted in an accompanying paper, tholeiitic successions of the calc-alkaline type constitute the main rock types of the lowermost volcanic assemblages of most early Precambrian greenstone belts. In the Barberton belt, however, a substantial succession of highly distinctive and as yet undescribed or undefined rock types has been encountered below a normal tholeiitic succession of the calc-alkaline type. The tholeiitic succession constitutes the upper three formations of the Onver-
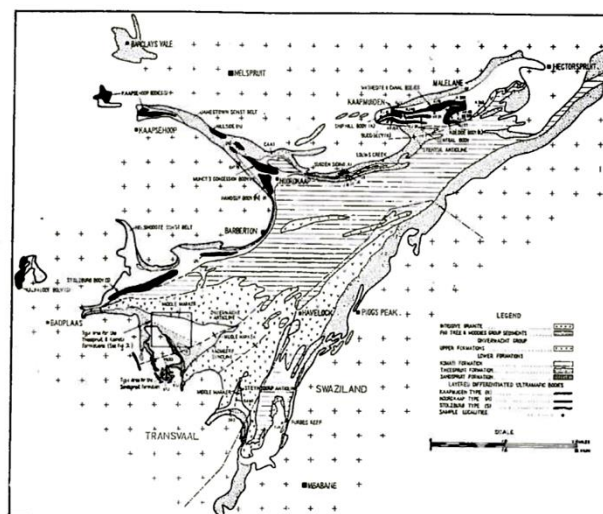
Fig. 1. Distribution of the three lower formations of the Onverwacht Group around the Barberton Mountain Land showing the type area and localities of the chemical analyses quoted.

The landmark publication on komatiites, published in 1969 in Special Publication number 2 of the Geological Society of South Africa (pages 55–86). For more on the significance of komatiites, interested readers are directed to the 2019 short review paper by Morris and Richard Viljoen, "Discovery and significance of komatiite: 50th Anniversary" in the South African Journal of Science, News and Views, volume 115 *(2 pages).*

Morris was part of the generation of geologists who were educated prior to the development of plate tectonics theory, began their research careers as this theory was developing, and became practicing geologists in a era defined by the mixture of old and new paradigms, a time therefore of great challenge and of opportunity, depending on your perspective. In Morris' case, this time period was occupied by about twenty years in the minerals exploration industry following his Ph.D., prior to his appointment at Wits in 1990, which is as true a test of putting theories into practice as a geologist can hope for.
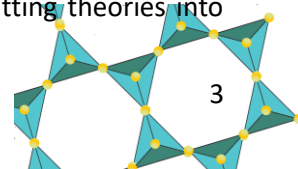
In those subsequent decades, Morris made pioneering contributions in the study of the Bushveld Complex, with emphasis on the origins of the platinum ore-bearing Upper Critical Zone rocks, particularly the Merensky Reef, and to the origins of the phenomena that vertically displace and disrupt the ore horizons, including the iron-rich ultramafic pegmatoids (IRUPs), and the pothole structures, models which continue to inspire new theories for layered intrusion emplacement mechanics today. He was the first author on several papers on these topics in the *Mineral Deposits of Southern Africa* volume published in 1986. I have fond memories of the first time I met Morris, who spent a good thirty to forty minutes very enthusiastically introducing me to the Bushveld Complex and explaining the principles of the pothole and IRUP models to me in his office, when I visited Wits in 1997 for a job interview in the Bernard Price Institute of Geophysical Research. His research postgraduate students that I knew in the late 1990s and early 2000s were very appreciative of his supervision and of the insights and awareness of the links between mineralization processes and host rock genesis and the exploration criteria for those metals, a perspective that few academically-based geoscientists can offer, and that Morris excelled at. In my experience of interacting with Morris sporadically over only the past twenty years or so, Morris stood out as someone always supportive and generous with his time and his expertise, assisting with field trips and research project collaborations, in spite of being conspicuously industrious and active, and always seemingly with a smile and a twinkle in the eye lurking.

A quick search of research platforms online shows that there were few prominent aspects of South African geoscience that escaped Morris' attentions. In addition to the topics already mentioned here, he authored or coauthored publications on the Wits Goldfields, including the reclamation and sustainability of the gold tailings, on the geomorphology of the Kruger Park and landforms of the northeast and on South African geoheritage more generally, and on the northern limb of the Bushveld, in which area Morris was also active in the context of mineral exploration and extraction relating to the mafic and granitic rocks, over the past two decades.

Morris leading an excursion through Johannesburg geology to an SEG student group from Canada in 2015. Photo S. Prevec.

Among his many accolades, Morris received the GSSA's highest honour, the Draper Memorial Award for the advancement of South African geosciences, in 1984, after which award he continued advancing it for another three and a half decades. He also served as President of the Geological Society of South Africa in 1988, in addition to his subsequent services to Minsa, noted earlier.

Obituaries for Morris have also appeared in Mining Weekly and on the Wits University website, and a link to his memorial service video (1 hour) can be found here.

Contributed by Steve Prevec
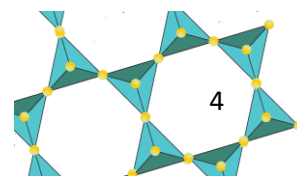
Articles

September issue theme: Determining the modal mineralogy of rocks.

The theme invited thoughts on the determination of the actual mineral content of rocks. Five articles are presented, starting with an overview of the traditional approach based on petrographic microscopy, followed by introductions to a range of analytical tools for mineral compositional and proportion assessment in rocks.

➢ Determining modal mineralogy by optical petrography (Steve Prevec).
➢ Modal composition analysis by chemical modelling and EDS hyperspectral imaging (Tobias Salge).
➢ The use of modern technologies to determine the modal abundance of minerals in rocks (Deshenthree Chetty & Susan Brill).
➢ The use of QEMSCAN as an all-round mineral characterisation tool (Keshree Pillay & Megan Becker).
➢ Strategies for dealing with mixed spectra in Auto-SEM-EDS instruments (Igor Željko Tonžetić).

Determining modal mineralogy by optical petrography

Stephen A. Prevec

Dept of Geology, Rhodes University, Makhanda, R.S.A., 6140.

Modal mineralogy, or the mode of a rock, refers to the proportions of the actual minerals present in the rock (as distinct from hypothetical mineralogies calculated from the rock composition, or normative mineralogy). Until the last decade or two, this mainly consisted of studying the actual rock in thin section using a petrographic microscope. This has the drawback that it requires training and petrographic skills, and so requires skilled analysts, sometimes (in the more distant past) equipped with refractive index oils, and

takes considerable time to perform, especially for large numbers of samples.
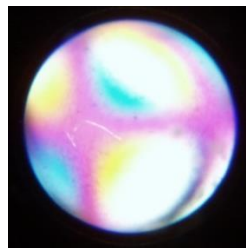
Can you tell your SiO₂ from your elbow?: an off-center uniaxial positive indicatrix (quartz!), photographed using the Bertrand Lens. If this means nothing to you, then analytical scanning technology is your best bet!

This process requires first establishing the identity of all of the major phases in a rock, based on thin section examination. In some rocks, such as bulk of the mafic rocks of the Bushveld Complex, this is a can of corn, as there are basically two major minerals constituting most of the rock (plagioclase feldspar and orthopyroxene), with other minerals (clinopyroxenes, olivine, apatite, biotite ± phlogopite, and "opaques" constituting the remainder). Opaques can be a nuisance if you have more than one flavour of opaque phase, such as oxides (spinels, for example) and sulphides, in the same rock. Assessing the modes for these minerals is complicated, as you would require a combination of transmitted light assessment for the non-opaque silicates, phosphates, & carbonates, and then reflected light for the opaque mineral evaluation. More problematic is the fact that typically the opaque minerals are accessory minerals, present in small volume proportions in average rocks, so the statistical validity of assessments of their modal proportions could be problematic.

The method of quantitatively determining the mode of a rock from a thin section involved the process of point counting. This requires the addition of a mechanical stage that screws onto the rotating stage on the microscope, effectively locking the thin section into position. The mechanical point counting stage could be adjusted in either X or Y dimensions, effectively moving the crosshairs of the ocular by fixed increments across the thin section, thus traversing it without bias. The operator would then record the identity of each grain appearing directly under the cross hairs. In the zootier point counting arrangements, the stage was directly connected by cables to a counter, so each time you pressed a key on the counter for the appropriate mineral, the stage would automatically advance to the next point. If not, you were advancing the stage
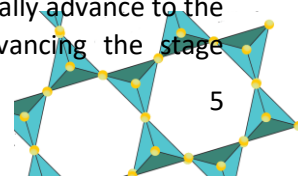
manually and recording your findings. The limitation implicit in the use of this stage is that once your slide is locked in, you no longer have the liberty of "fiddling" with it to determine mineral identification; you need to pretty much know already. You can cross and uncross the polarizers, and maybe rotate the stage (but only if you're not physically wired to the counter). Rocks with numerous low relief minerals, such as granitoids or paragneisses, where quartz, orthoclase, cordierite, and untwinned metamorphic plagioclase can coexist in equilibrium and all look very similar when they appear under the cross-hairs, can be problematic.
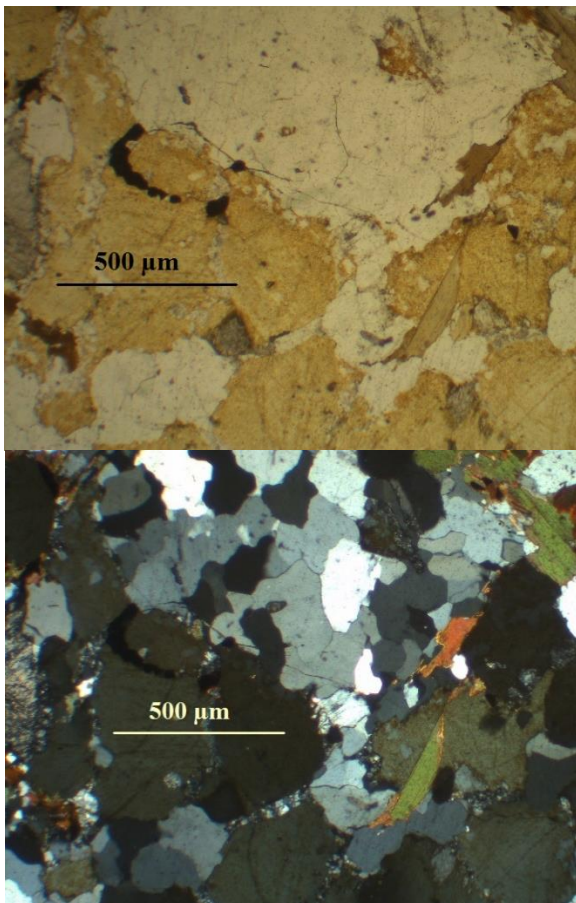
A thin section stained for K, showing the yellow alkali feldspars contrasting with colourless quartz (and coloured biotites and iron oxides) in plane polarised light (top), and in crossed-nicols below.

During my M.Sc. and Ph.D. studies, when I was young and enthusiastic, I therefore stained my thin sections using a sodium cobaltinitrite solution (for K) and a combination of $BaCl_2$ (to first replace the Ca with Ba) and rhodizonate solution (to then stain the Ba) to distinguish calcic, potassic, and 'neither' (i.e., quartz) tectosilicate minerals at a glance. This required the

construction of an HF acid bath (yes, yes, in a fume hood, and with all the proper precautions) to etch the section surfaces with HF vapour, followed by two staining stages. It was quite a lot of trouble, but greatly facilitated the point counting and rock evaluation process for 50-100 thin sections. Definitely worth the long-term health risks. Staining can even reveal delicate fine-scale optical features, as illustrated in the following images.
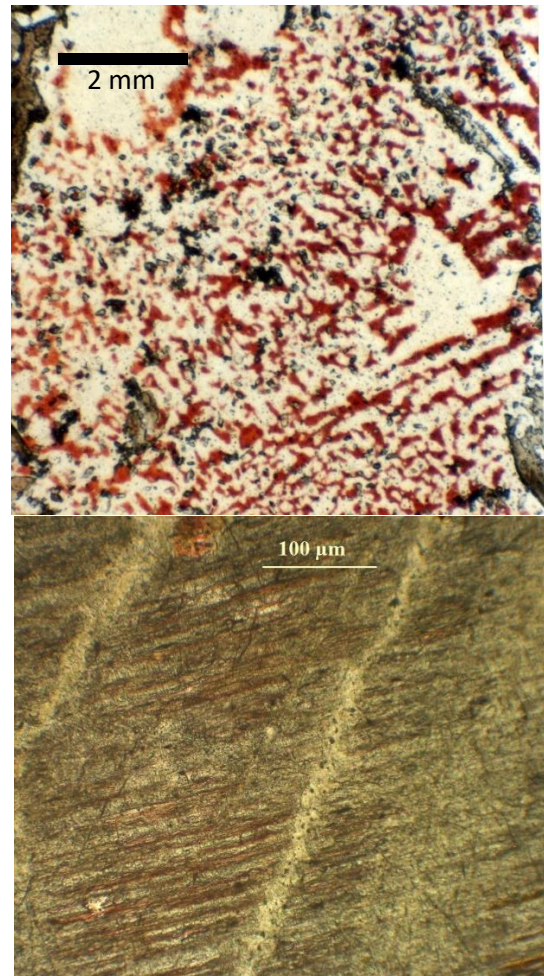

Thin sections stained for Ca, showing a symplectic intergrowth of plagioclase (red) with quartz (white) in amphibolitised gabbro, above. Below, high-Ca pyroxene exsolution lamellae show as red/pink, contrasting with the host low-Ca pyroxene grain. The colour of the red stain has faded in the 30+ years since the slide was stained (whereas the upper image was obtained soon after staining, so the red colour is still vivid).

For a relatively fine-grained, homogeneous rock such as a massive sedimentary rock, or hypabyssal (that's shallow-crustal, relatively rapidly cooled rocks, folks,
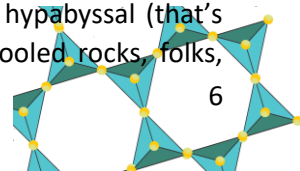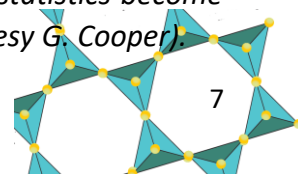
such as dolerites), as few as 100-200 counts could provide a reliable modal analysis, say to ± 1 vol.%. How do we know? First, we assume that area % can be equated to volume %. If you are looking at strongly foliated and/or lineated rocks, you would need to get thin sections cut both parallel to and perpendicular to the fabric, measure them both, and average them to correct for this. (Another good reason to avoid metamorphic rocks. They also tend to have more than three or four main minerals, unlike igneous or sedimentary rocks.) Check the mineral proportions after each 100 point counts, and if your mineral abundance totals stop changing by more than 1%, you can probably stop counting. For coarse-grained or heterogeneous rocks, anywhere from 500 to 1000 counts could be needed.

Some early efforts to digitize point counting were made using photomicrographs, specifically targeting mineralogically simple systems, such as chromite-plagioclase-orthopyroxene rocks, such as are found in the Lower Critical Zone and the bottom half of the Upper Critical Zone in the Bushveld Complex. In these types of rocks, plane-polarised or even unpolarized images of thin sections could be scanned, and then analysed by optical-recognition software available twenty years ago to derive area proportion information. However, these were not easily able to discriminate phases of similar relief or colour, and the stage was set, as it were, for the scanning microanalytical tools that have come in the following decades. Some of these are described in the articles to follow.
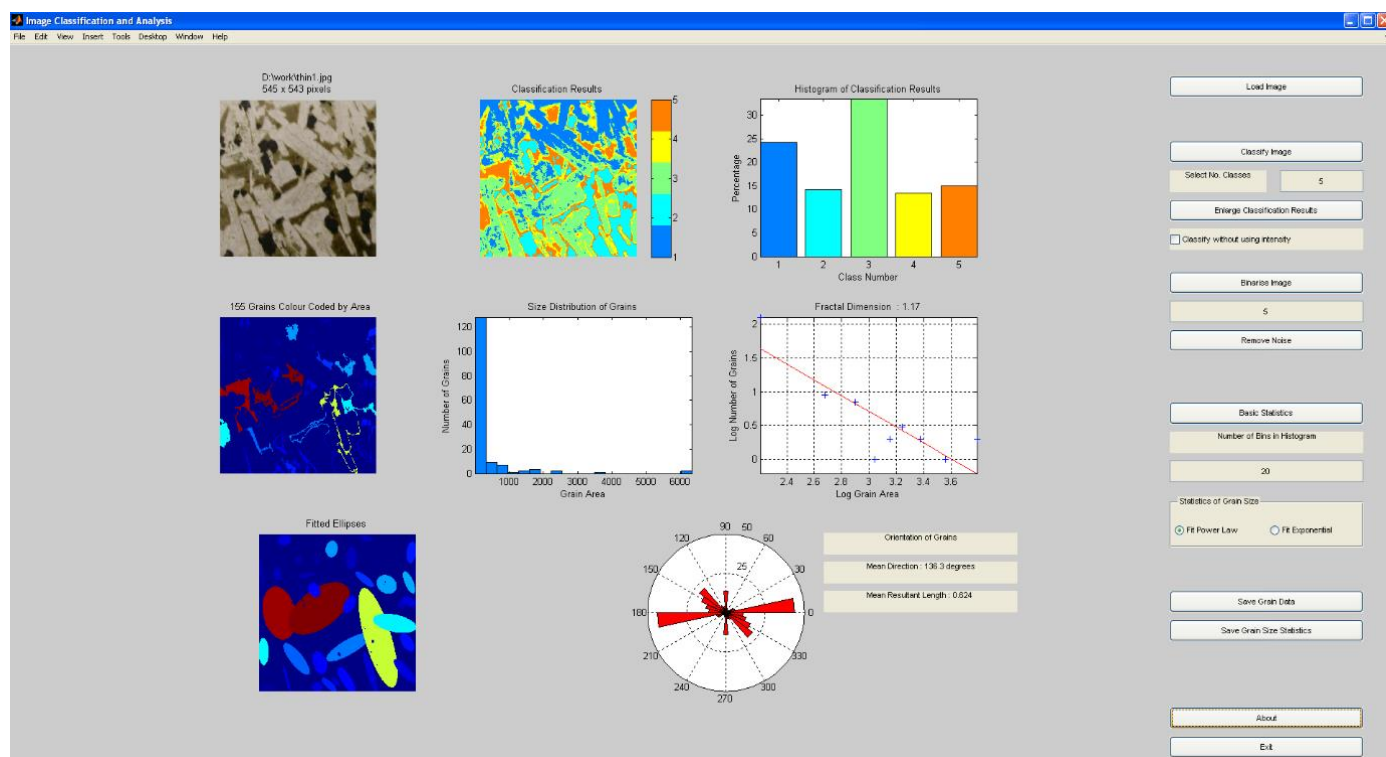
An example of optical recognition software, developed by Prof. Gordon Cooper in the School of Geosciences at the University of the Witwatersrand. This takes the colour plane-polarised light photomicrograph and converts this into dimensional and area proportion data. The interpretation process starts with a colour image which is first classified using the k-means method. The classification results are used to determine the grain boundaries, from which their areas can be calculated and analysed statistically in different ways. Ellipses are fitted to the grain boundaries to obtain information on their orientation, and again the results can be analysed statistically. The main problem with this automated approach is when grains of the same mineral are in contact with each other, since they appear as false larger grains and the statistics become distorted. Analysis of images takes less than 1s on a modern computer. (Explanation courtesy G. Cooper).

Do you have an analytical service relating to mineral analysis, mineral extraction, or mineral identification?

Can you make polished thin sections competently and efficiently? Fire x-rays at polished surfaces and measure what comes out?

Do you have capacity to conduct additional services and to get paid for it?

If your answer to any of these questions is "yes, I guess so", then you could be advertising in this space at very reasonable rates, making some revenue, and contributing to the geoscience economy of the nation. What are you waiting for?

Modal composition analysis by chemical modelling and EDS hyperspectral imaging

Tobias Salge

Imaging and Analysis Centre, Core Research Laboratories, Cromwell Road, SW7 5BD, United Kingdom. t.salge@nhm.ac.uk

The estimation of modal mineralogy is commonly obtained by point counting of thin sections, image analysis, quantitative X-ray diffraction, or automated mineralogy analysers. This article focusses on alternative approaches to estimate modal mineralogy based on chemical modelling. The first example presented demonstrates that the modal content can be calculated from mineral and bulk rock compositions. The second utilises hyperspectral imaging techniques for scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) to quantify the area fraction of mineral phases.

Chemical modelling from mineral and bulk compositions

The method of chemical modelling from mineral and bulk compositions utilises the PetMix spreadsheet (www.geologynet.com/programs/petmix410.xls), which is based on the constrained mixing model of Le Maitre (1979) and the least square fit. This approach has been used to calculate the modal content for 13 samples from the K-Pg boundary sequence of El Guayal, Tabasco, Mexico (Salge et al. 2021).

Table 1. *Mineral phase and bulk compositions that were used to calculate the modal content. The two right hand side columns represent the bulk composition results for two calculations.*

Method	EPMA	EPMA				XRF / IR	Petmix1	Petmix2
Phase	Clay1	Clay2	Calcite	Quartz	Haematite	Bulk	Calc.	Calc.
SiO_2	35.5	53.4		100.0		42.40	42.33	42.21
TiO_2	0.08	0.10				0.34	0.07	0.07
Al_2O_3	15.1	17.7	0.07			11.60	11.59	11.31
Fe_2O_3	7.97	3.48	0.09		100.0	4.82	2.83	4.63
MnO	0.02	0.01	0.06			0.07	0.02	0.02
MgO	24.2	9.27	0.49			7.42	7.92	7.17
CaO	0.77	2.21	55.2			15.23	14.87	14.73
K_2O	0.08	1.90				0.96	1.08	1.11
Na_2O	0.05	0.27				0.04	0.16	0.16
CO_2			44.1			10.50	10.80	10.69
Total	83.7	88.3	100.0	100.0	100.0	93.39	91.67	92.08

Here, the calculation is presented for one sample. On the left-hand side of Table 1, two average clay mineral compositions, obtained by electron microprobe, as well as assumed or documented values for calcite, quartz, and haematite are presented. Additionally, the bulk composition shown has been measured by X-ray fluorescence analysis and the CO_2 concentration has been analysed by infrared spectrometry.

For the first calculation (Petmix1) both clay mineral compositions, quartz and calcite were considered (Table 2). The data shows that the calculated modal content has a cumulative error of 2.1 vol.%. Comparison of the calculated bulk rock composition at the right-hand side of Table 1 alongside the measured bulk rock composition reveals that this error mainly derives from Fe_2O_3; the calculated concentration (2.83 wt.%) is significantly lower than the analysed concentration (4.82 wt.%). By including haematite in a second calculation (Petmix2) results are a better match for the calculated Fe_2O_3 bulk composition (4.63 wt.%, Table 1), produce a modal haematite content of 2.0 vol.% (Table 2), and have a lower cumulative error of 0.8 vol.%.

Table 2. *Results of the modal content (vol.%) calculations.*

	Clay1	Clay2	Calcite	Quartz	Haematite	s
PETMIX1	10.6	56.5	24.5	8.4	-	2.1
PETMIX2	6.9	58.0	24.3	8.8	2.0	0.8

Chemical phase analysis by advanced SEM-EDS

Modern EDS systems acquire a hyperspectral database that contains a four-dimensional data cube (position X and Y, spectrum channel and number of counts in each energy channel). Saving complete spectra for each pixel of the SEM image allows a range of advanced analysis options. These are presented for a sulphate–carbonate-dominated breccia matrix of a sample from the UNAM-7 borehole near the crater rim of the Chicxulub impact structure (Salge et al. 2019). Figure 1a shows a back-scattered electron (BSE) image of the microcrystalline breccia matrix. Some minerals, e.g., dolomite and sodium feldspar, cannot be distinguished due to their similar BSE contrast. However, the elemental maps (Figs. 1b-d) provide a clearer view enabling identification of the different minerals. The
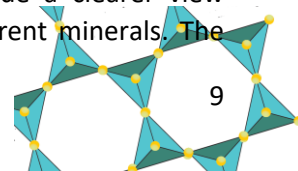
composite map of carbon and sulphur (Fig. 1b) allows for the detection of carbonates and sulphates. Calcite and dolomite can also be distinguished from each other by the composite map showing the distribution of calcium and magnesium (Fig. 1c). The distribution of the minor components sodium feldspar, potassium feldspar and celestine (strontium) is shown in Fig. 1d.

An advanced analysis routine, chemical phase analysis (Friel et al. 2017), can be used to enhance the display of mineral distributions and quantify the modal proportions. This analysis option can detect similarly composed spectra with the help of mathematical methods, e. g. principal component analysis or cluster analysis. The phase maps (Figs. 1e and 1f) were obtained under consideration of the X-ray line intensities (C, O, Na, Mg, Al, Si, Sr, S , K , Ca) of the areas shown in Fig. 1a. The modal proportions of mineral phases are presented in Table 3.

Table 3. *Results from chemical phase analysis by SEM-EDS hyperspectral imaging (Figs. 1e and 1f). The modal proportion of mineral phases is represented as area % and µm² fractions.*

| Phase	Area (%)	Area (µm²)
Calcium sulphate	51.8	69,859
Calcium magnesium carbonate	30.6	41,266
Calcium carbonate	14.9	20,119
Potassium feldspar	1.0	1,289
Strontium sulphate	0.7	985
Sodium feldspar	0.5	625
Unassigned	0.5	712
Total	100	134,855

Summary

The calculation of the modal content by PetMix includes a relatively large rock volume. The data shows this approach may provide a more reliable result when compared to point counting of thin sections, specifically for samples that are heterogenous on a thin section scale. Chemical phase analysis by hyperspectral EDS imaging allows quantification of mineral proportions at a resolution beyond light microscopy. Moreover, this methodology can further discriminate minerals that are difficult to distinguish by BSE image analysis.
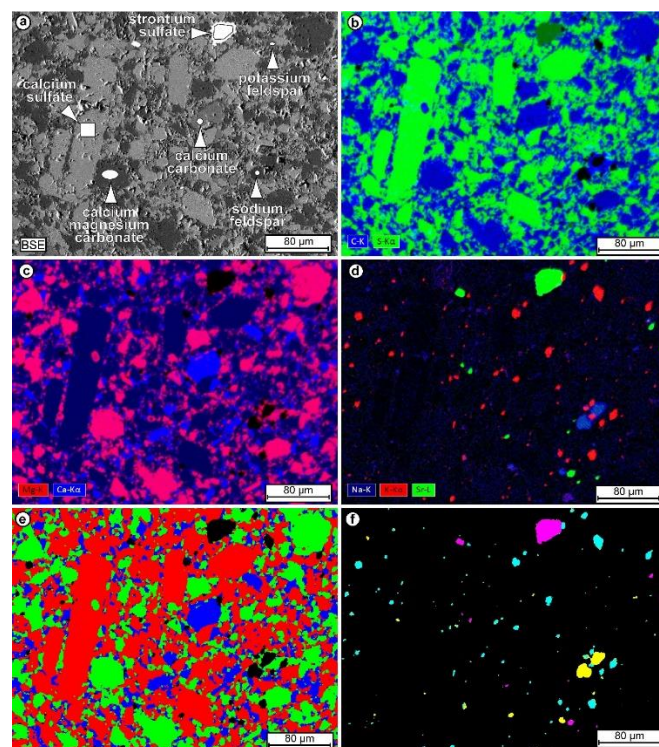
Figure 1. *The sulphate–carbonate-dominated microcrystalline breccia matrix from the UNAM-7 borehole at 381.40 m depth (Salge et al. 2019). (a) Backscattered electron (BSE) image of an area that was analysed by hyperspectral energy-dispersive spectrometry imaging (15 kV, 244 kcps, 800 x 600 pixels, 1.89 µm pixel size). White, black outlined areas show regions that were used to detect similar spectra and obtain the modal abundance by chemical phase analysis (Table 3). (b-d) Composite net intensity maps. (e, f) Result of chemical phase analysis showing the distribution of calcium sulphate (red), calcium magnesium carbonate (green), calcium carbonate (blue), potassium feldspar (turquoise), strontium sulphate (magenta), and sodium feldspar (yellow). © The Trustees of the Natural History Museum, London.*

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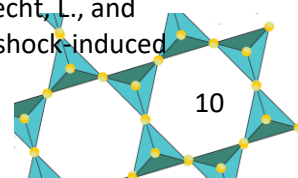
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A note on hyperspectral imaging

What is hyperspectral imaging? For some readers, hyperspectral imaging is imaging specifically using only the electromagnetic spectrum. For others, it might call to mind to the following:

(The Editor, patronising the Green Man)

However, as an aid to the well-informed, Dr Salge has provided us with the following context:

Hyperspectral imaging is commonly used for EDS and other techniques or remote sensing. See its Google Scholar entry here, for example.

Synonyms for hyperspectral imaging include *spectrum imaging* and *hyperspectral datasets*. A complete spectrum is saved for each pixel of the SEM image in the context of SEM-EDS. The electromagnetic spectrum also includes X-rays.

A link to another presentation that explains hyperspectral Images for microanalysis can be found here. We also used this term for the 3rd edition of Friel: Friel, J. J., Terborg, R., Langner, S., Salge, T., Rohde, M., and Berlin, J., 2017, X-ray and image analysis in electron microscopy, Pro BUSINESS, 118 p.

One of the more recent significant developments in the field of EDS was reported by Mott *et al.* (1995, 1999), and it involves the ability to store an entire spectrum at every pixel in an image. From the 3-dimensional data structure it is possible to extract maps for any element and spectra from any region. This is commonly referred to as position tagged spectrometry (PTS), Hyperspectral x-ray imaging, or in the Bruker QUANTAX EDS system, HyperMap.

The use of modern technologies to determine the modal abundance of minerals in rocks

Susan Brill and Deshenthree Chetty

Mineralogy Division, Mintek

Ores and their related mineralogy have become increasingly complex, especially as we strive to dig deeper and uncover low grade, more intricate ore bodies. The study of these is made possible with instruments such as scanning electron microscopes, electron microprobes and X-ray diffractometers. One of the first steps in a mineralogical assessment is to determine the bulk compositions of one or a group of samples. Bulk modal mineralogy gives the mineralogist a broad overarching understanding of an ore body and its mineralogical variability. This helps further to pinpoint where valuable minerals might be targeted for processing to separate and recover them from gangue in the rock.

Many instruments are useful to determine the compositions of rocks (and processed) samples. The "go-to" instrument in this instance is the X-ray diffractometer, which can assess both the semi-quantitative and quantitative composition of various crystalline samples in a relatively short time period. X-ray diffraction focuses an X-ray beam generated from a cathode tube from set incident angles. These X-rays are diffracted by the crystals in the samples to produce a diffraction pattern. The peaks from the pattern are identified based on their d spacing derived from Bragg's law:

$$2d\sin\theta = n\lambda$$

where d is the spacing between diffracting planes, θ is the incident angle, n is an integer and λ is the beam
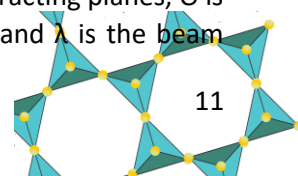
wavelength. Depending on the needs of the user, semi-quantitative (categorical) results or quantitative results may be obtained with the assistance of various software programs and databases. This is also dependant on the acceptable detection limit of the user, as 1 to 3 mass % is generally the lowest limit of detection achieved. X-ray diffraction analysis is used to not only identify crystalline phases but also to quantify them, specifically with the use of Rietveld Refinement. Rietveld Refinement makes use of whole pattern fitting by comparing lattice parameters, peak shape and width and preferred orientations to derive a calculated pattern. This pattern (correctly fitted and refined) is compared to that achieved from a sample to determine quantities of crystalline phases present, as per the formula:

$$W_r = S_r(ZMV)_r / \Sigma_t S_t(ZMV)_t$$

where W_r is the relative fraction of phase r in a sample that contains t phases; S is the scale factor derived from the refinement; Z is the number of formula units per cell; M is the mass of the formula unit and V is the volume of the unit cell (Hill, 1991).

An example of the refinement achieved through the use of two software programmes (Bruker EVA and TOPAS) to determine the composition of a cement sample is shown in **Figure _1_** and **Table _1_**.
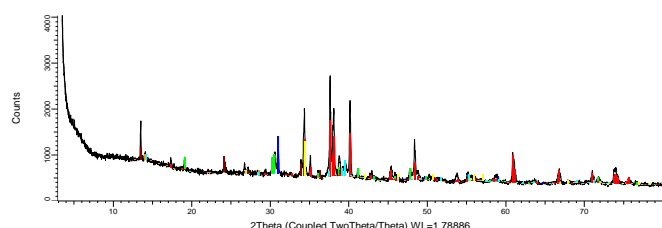
Figure 1. *X-ray diffractogram of a cement sample.*

Table 1. *Bulk modal mineral composition of a cement sample.*

| Legend	Mineral Phase	Abundance (mass %)
	Antigorite	2.6
	Brownmillerite	14.4
	Calcite	7.5
	Gypsum	5.0
	Hatrurite	44.2
	Mullite	14.1
	Quartz	12.3
Mineral total		100

Where a lower detection limit is required, for example on a low-grade Cu ore, automated scanning electron microscopy (AutoSEM) analysis is a more suitable technique for determining the bulk modal compositions of samples. The limit of detection of AutoSEM is 0.1 mass % and this is best used for deportment of Cu in Cu-bearing minerals towards heap leach assessments, as an example, and where the total amount of Cu in the ore body is less than 1 wt. %. Whereas XRD analysis uses pulverised and micronised powders with particle sizes smaller than ~20 micron, AutoSEM analysis makes use of mounted resin blocks of crushed and screened sample, with particles up to a few mm in diameter. Automated SEM technology (e.g. QEMSCAN, MLA) utilise back-scattered electron (BSE) signal intensities and energy dispersive X-ray signals (EDS) at specified measurement points to assign mineral identities compared to a predetermined database. These minerals are represented as false colour image grids (*Figure 2*).


Figure 2. *False-colour particle map from a sample from the Bushveld Complex UG2 Reef.*

Bulk modal mineralogy is determined by counting up the area of each mineral in the images, and applying the mineral density to calculate its mass fraction. This is based on the assumption that area% is equivalent to volume%, which holds true as long as a sufficient number of grains has been measured on randomly orientated sections through the sample. The bulk modal mineral composition (*Figure 3*) of each fraction is recombined according to a weighted average and may be presented together with liberation, grain size distributions and mineral associations of selected minerals.

Bulk modal compositions from both XRD and autoSEM should be compared to the bulk chemical composition in a mineral-chemical reconciliation exercise. This is done routinely against calculated and actual assays determined for quality control purposes.
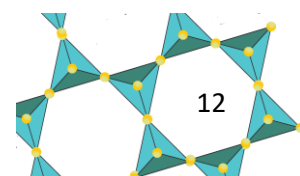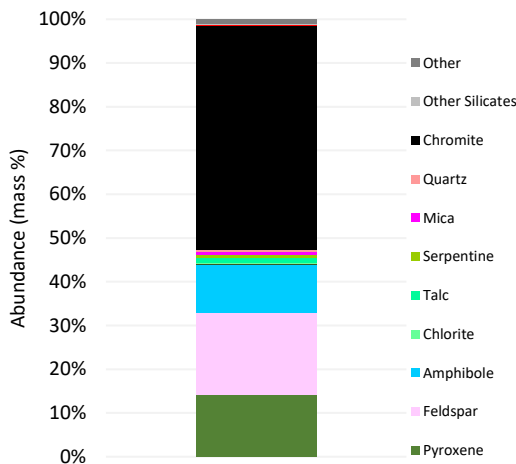
Figure 3. *Bulk modal composition of a sample from the Bushveld Complex UG2 Reef.*

To overcome the limitations with large samples that may not fit into SEM chambers, modal mineralogy may be achieved using micro-XRF technology. Instead of an electron beam typical of SEM methods, X-rays are focused on the sample at a minimum spot size of 20 microns, and energy dispersive X-ray spectrometry is used to collect elemental spectra that may be assigned to different minerals. In this way, similarly to a point count, mineral proportions may be determined by quantitatively assessing all of the mineral spectra collected. This is done through such systems as the Bruker M4 Tornado micro-XRF with associated AMICS (Advanced Mineral Identification and Classification System) software. Elemental maps may be converted to mineral maps in this way (Figure 4). A further advantage of this technique is that samples can be run with a reasonably flat surface, with no polishing or carbon coating required. Detection limits can be sub-percentage, depending on the nature of the mineral, as heavier elements fluoresce better than lighter elements. Consequently, gold may be better detected than quartz at very low concentrations, for example.

From small-scale (micron to mm) to larger-scale (cm) measurement, autoSEM and micro-XRF technologies, respectively, afford 2D methods for measuring the mineral abundance. It must be noted, however, that stereological bias can affect results. For this reason, mineral-bulk chemical quality checks are important in achieving correct results, and random cuts through as many particles as possible, along with proper particle sizing, facilitates quality results.
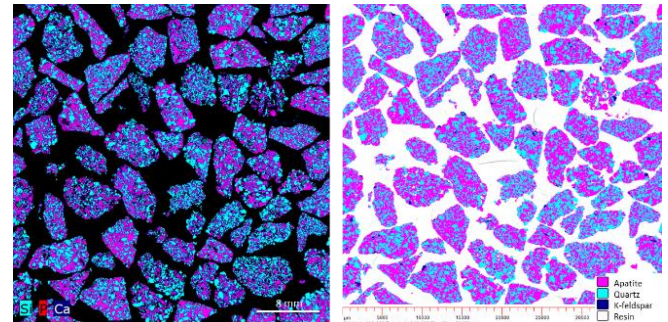

Figure 4. *Elemental (left) and mineral (right) maps of particles of phosphate scanned by micro-XRF. The minerals proportions are apatite (~64%), quartz (~34%) and K-feldspar (~1%).*

Modal mineralogy can be done in 3D, thus removing the need to address stereological bias. Tomography scanning may be used for the purpose. The method makes use of a cone beam of X-rays that pass through a sample rotating in their path. The components in the sample will attenuate the X-rays to different degrees, dependent on their density, atomic mass and the energy of the X-ray beam. An image is projected onto a detector system, much like an X-ray is taken of a broken bone in hospital. However, because the sample is rotating in the X-ray beam, multiple projections are taken, then reconstructed into a tomogram. The tomogram is a 3D rendering of the volume, and is made up of voxels (3D pixels). The Zeiss Versa system contains optical magnification to enhance resolution and provides good attenuation contrast. Spatial resolution can be obtained to sub-micron level (on smaller samples), whereas attenuation contrast is important to differentiate minerals, which are shown by grey level differences amongst the voxels in the tomogram. Using image registration techniques, virtual 'slices' from the tomogram can be correlated with backscattered electron images on a SEM to differentiate and identify minerals. The resulting information is transferred to the full volume of the tomogram in assigning the different grey levels to minerals (Figure 5). Counting up all the voxels of the different grey levels therefore provides the modal abundance of the grey level intervals, and therefore, of the minerals. Applying the mineral densities, the mass distribution of minerals may be determined.
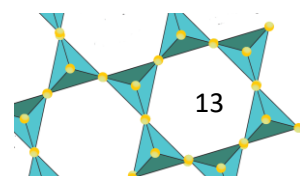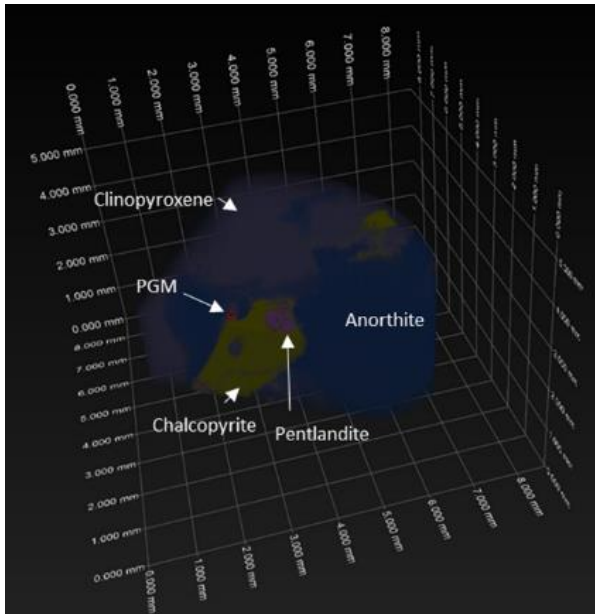
Figure 5. *3D rendered image showing classified minerals derived from grey level thresholding and image registration of a piece of Platreef ore.*

The full suite of options, from optical microscopy (traditionally used, older method) to XRD, autoSEM, microXRF and now 3D tomography, may be used for the determination of mineral modal abundance in a variety of rocks and other processed materials. For the purposes of mineral processing at Mintek, these techniques provide important information on valuable minerals vs. gangue mineral abundance and mode of occurrence, and consequent approaches for optimal separation and recovery of this value.

Reference:

Hill, R.J. (1991) Expanded use of the Rietveld method in studies of phase abundance in multiphase mixtures. *Powder Diffr.*, 6, 74-77.

Minsa Affairs

Please note that the 5th Annual Southern African Mineral Symposium, originally scheduled for Saturday 20 November 2021, has been postponed for a year ('til Nov. 2022). For more information, please contact Igor Tonžetić at the Minsa address provided.

For more info: minsa@gssa.org.za

INVITATION FOR SUBMISSIONS TO THE NEXT THEMED ISSUE OF THE GEODE

Minsa invites its members to contribute submissions for our next issue of the Geode, on the theme of "*Family-friendly Geosciences*" (see below), for December 2021.

Submissions can be sent to minsa@gssa.org.za and should reach us by 30st November 2021.

Where can you take your family and friends, or a class of school children, to interest them in the marvels of the natural world, specifically rocks and minerals? From mineral collections at museums to stunning views of incised landscapes, where are the destinations that turn your crank, geologically-speaking, and why?
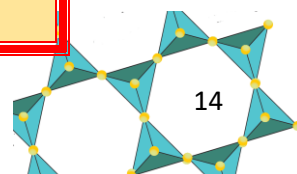
Earn CPD points through mentoring!

Be "the mentor you wish you had" and assist in giving some guidance to geology students by signing up to be a mentor through the Bridge the Gap Geosciences Guidance Program (BTG).

BTG is a student run organisation that focuses primarily on mentorship between undergraduate and postgraduate students. However, all interested individuals are invited to "bridge the gap" between students and industry by joining the BTG program. This could take the form of mentorship, giving a talk, leading an excursion or simply providing sponsorship.

To get involved please complete the Google form via this link:
https://forms.gle/Sf5tMciuSStAQuFL8 or email bridgethegap.wits@gmail.com for more information.

# The use of QEMSCAN as an all-round mineral characterisation tool

Keshree Pillay *(Chief Scientific Officer, Dept of Chemical Engineering, UCT)* **& Megan Becker (Assoc. Prof., Dept of Chemical Engineering, UCT).**

Since the first official QEMSCAN (Quantitative Evaluation of Minerals by SCANnning Electron Microscopy) prototype was released in the 1990s, built on an earlier foundation of QEM*SEM technology, the QEMSCAN has been a major contributor to the characterisation of rocks, minerals and products of the metallurgical industry. The advantage of automated mineralogy technology such as QEMSCAN is the production of rapid, repeatable, statistically representative mineralogical data. The ability to accurately quantify mineral proportions and valuable metal deportment, as well as textural characteristics such as grain sizes and shapes, mineral liberation, mineral associations and porosity, enables mineralogy to be used more effectively as a tool for predicting the performance of metallurgical processes as well as for troubleshooting.

**Figure 1.** *High resolution FEG QEMSCAN at the Centre for Minerals Research, University of Cape Town (left), standard sample holder containing 30 mm polished sections (top right), rough rock holder with ~70x70 mm polished rock slab (bottom right)*

The QEMSCAN is based on a scanning electron microscope (SEM) platform with energy-dispersive X-ray spectrometry (EDS) detectors (up to four in some

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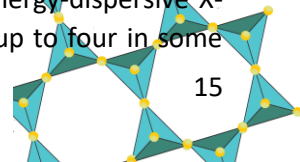
machines). Together with information from backscattered electron (BSE) images, the X-ray analyses are classified into mineral categories by a user-defined reference list known as a species identification protocol (SIP). By this process, false-colour mineral maps of 2D surfaces are produced, with resolutions ranging from less than one micron to tens of microns. Samples are mostly scanned in the form of resin-mounted polished sections, however thin sections or polished rock surfaces can also be analysed.

A variety of measurement modes are used, which include line scans to measure modal mineralogy, and particle and field mapping for generating images from which textural information is derived. One of the most important functions of the instrument is the ability to perform automated searches for trace minerals, which is most useful for precious metal ores, where the ore minerals are often very fine-grained and low in abundance. A major strength of QEMSCAN is its built-in data processing capabilities that allow for flexibility in how mineral and particle properties are described and reported. Since mineralogy techniques are often not used in isolation, the QEMSCAN software also allows the input of supporting data such as mineral chemistry from electron microprobe analysis, which helps with the accurate calculation of elemental deportment, or bulk chemistry data that can be used to validate the bulk mineralogy results.
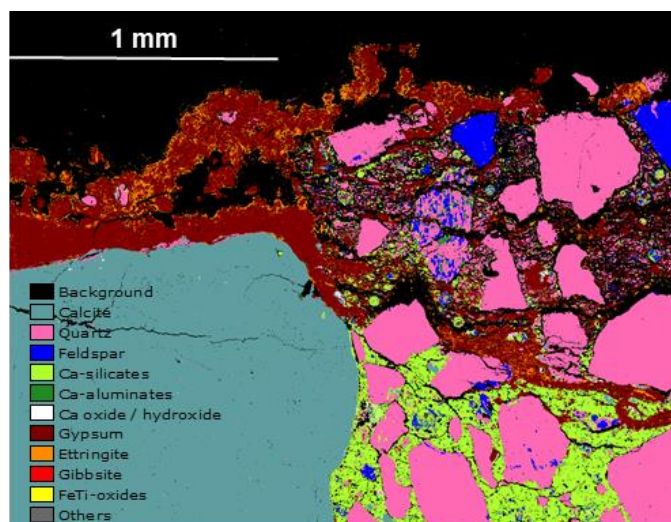
Figure 2. *QEMSCAN false-colour image of a concrete surface corroded by sewer sulfuric acid attack.*

Traditional QEMSCAN projects commonly focus on producing information on representative, milled

samples for geometallurgical studies or the prediction and monitoring of concentrator performance. Geology users make use of the technique for the mapping of microstructures or to search for and map accessory minerals such as zircons for dating, or apatite for isotope studies. In the Centre for Minerals Research at the University of Cape Town, in addition to such analyses, the different university departments make use of the QEMSCAN for a variety of interesting projects, such as the evaluation of mine tailings to assess suitability for reaction to form stable geopolymers, the monitoring of concrete corrosion in sewers, and the mapping of archaeological ceramics to determine provenance sediments and ancient pottery techniques.

Although the QEMSCAN product line has now been discontinued and software development has ceased, QEMSCAN still plays a vital role in many process mineralogy labs around the world and remains one of the most advanced technologies available for automated mineral characterisation.

Strategies for dealing with mixed spectra in Auto-SEM-EDS instruments

Igor Željko Tonžetić

University of Pretoria

<u>Introduction</u>

Mixed spectra, often referred to as "boundary phases" in Auto-SEM-EDS instruments (QEMSCAN, MLA, Mineralogic®, TIMA, AMICS, INCAMineral, NanoMin) are notoriously problematic in ensuring accurate mineral abundance (bulk mineralogy) measurements. QEMSCAN operators, for instance, commonly associate these occurrences with entries like "Al??Si??" (an entry that signifies that we are possibly seeing Al and Si – by extension, some kind of aluminosilicate boundary phase?) or "NaDSiLCaH" (Na – Definite; Si – Low; Ca – High...an anorthite boundary phase maybe?) in their "Species Identification Protocol" (SIP) lists. Importantly though, not all mixed spectral occurrences are manifest by allocation to these entries (commonly falling into "unknown" or "unclassified" entries). And perhaps even more
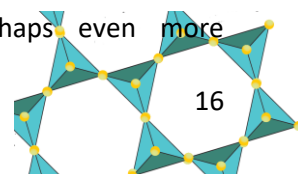
importantly, not all mixed spectra are as a result of "boundary phases" (sensu stricto, the occurrence where an instrument beam intersects a grain boundary - this is surprisingly common and even a cursory attempt at point counting by way of a light microscope with a coarse grid spacing of 40 identification points can see an operator quite easily intersect 4 grain boundaries – with Auto-SEM-EDS instruments, one is typically dealing with millions of analysis points per sample). Figure 1 shows three scenarios where mixed spectra can be expected to occur in any given analysis (briefly: 1. True grain boundaries; 2. Finely intergrown lamellae or textural intergrowths smaller than beam-volume interaction; 3. Shallow exposures of mineral being analysed). The explicit reason for the abundance of these mixed spectra is as a result of scanning electron microscopy (SEM) physics…namely that the beam volume interaction (diaphaneity) of x-ray generation is far larger than the image produced from back-scattered electrons. In other words, what the SEM operator measures is far larger than what the SEM operator actually sees (Figure 2).
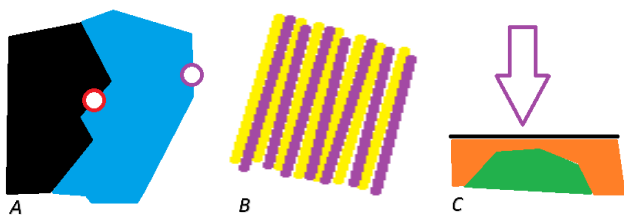
Figure 1: Causes of mixed spectra. A) True grain boundaries (red spot: true grain boundary within a particle is intersected; purple spot: grain boundary with epoxy resin mounting media is intersected). B) Finely intergrown lamellae or textural intergrowths smaller than beam-volume interaction. C) Shallow exposures of mineral being analysed (cross-section).

This article attempts to highlight all strategies currently being employed in dealing with mixed spectra in Auto-SEM-EDS instruments. They are presented (quite debatably) from "least sophisticated" to "most sophisticated" (which is to very generally say from most easily implemented to least easily implemented by an operator/mineralogist but also bearing in mind the degree of difficulty in coding for the applications or implementation of the strategy). This ranking is not intended to be a value statement.
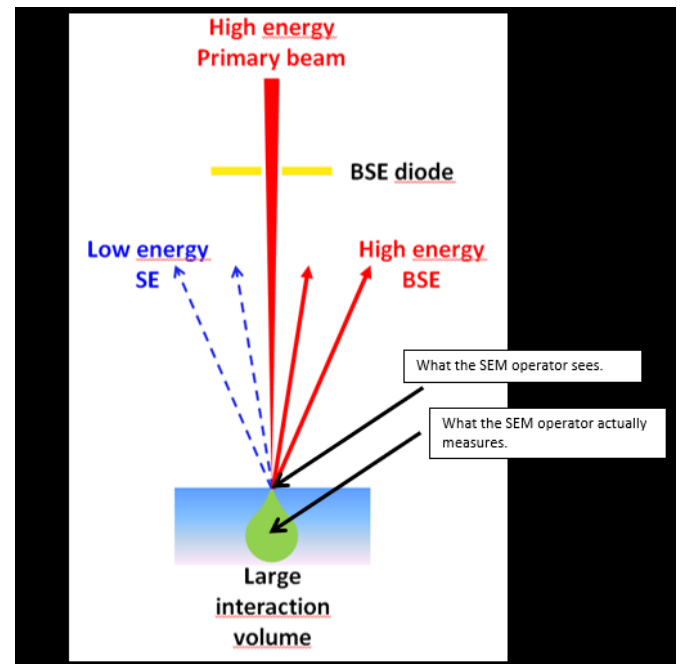

Figure 2: SEM physics resulting in abundance of mixed spectra (cross-section).

Mass Normalisation

In principle, if all entries in a mineral identification protocol (SIP List, Standards File, Mineral Recipe, Mineral Classification etc.) were equally rigorous and equally well constrained, then a simple normalisation of "unknown" or "unclassified" identifications out of the mineral abundance measurements would result in accurate bulk mineralogy. That is to say, that one could simply ignore and filter out "unknowns" and "unclassifieds" from the mineral abundance measurements since every entry in the mineral identification protocol would have an equal chance of falling into an "unknown" or "unclassified" entry. This might hold true for some adequately experienced operators with (more likely than not) simple mineralogy ore bodies. However, Figure 3 shows an example of where it might not hold true. Here we have a zircon concentrate from a heavy mineral sands deposit that has well constrained mineral identification definitions for quartz and rutile (relatively few unknown pixel classifications in the particles) but poorly constrained definitions for zircon (abundant unknown pixels in zircon particles). In this instance, the multitudinous unknown classifications in the zircon have nothing to do with the rigour of mineral identification rules in the identification protocol but rather the abundance of metamict zircon in the
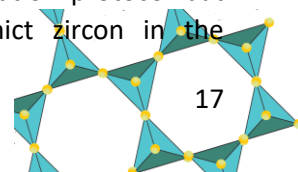
deposit. In other words, the ubiquitous radioactive decay in the zircons is not considered in the mineral identification and is resulting in many spectra not falling into a strict zircon identification protocol. Applying a mass normalisation to this sample is going to result in an underestimation of total zircon content (because most unknowns in this sample are zircon). This informs (as a general rule for all mixed spectra strategies) how we should, in principle, go about organising our mineral identification rule sets. That is to say, that poorly constrained ("boundary phase") entries should be at the bottom of our rule sets (if our spectral matching is based on the "First Match" principle) or they should be given low priority (if our spectral matching is based on the "Best Fit" principle).
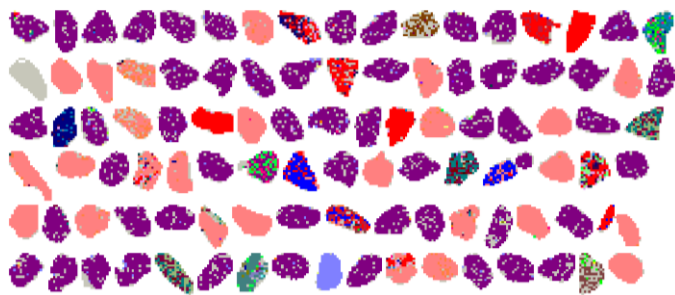
Figure 3: *Zircon concentrate from a heavy mineral sands deposit. Purple = zircon; pink = quartz; red = rutile; grey = unknown. Note that the 1st particle in the 2nd row is wholly unclassified. In a well-constrained, well-defined mineral identification ruleset this might be indicative of a mineral never before seen in the deposit (or even a new mineral species unknown to science).*

The following sections (expanding mineral definitions, boundary phase definitions) deal with how the manipulation of mineral identification rulesets can be used in dealing with mixed spectra.

Expanding Mineral Definitions

Fear of the "unknown" is largely what informs this strategy for dealing with mixed spectra (though it certainly informs most if not all strategies to a lesser extent). That is to say that most operators would rather have all mineral identifications fall into a "something" category rather than an "unknown" category, even if that something category is all wrong! For example, Figure 4A has a rigorous, well-defined entry for catching kyanite spectra which admittedly (and by definition) will not catch all kyanite boundary phases or mixed spectra with kyanite. An operator might be

inclined to increase the allowable limits for Al, Si and O to account or compensate for this. Unfortunately, if the operator is not paying attention, the new expanded elemental definitions of kyanite might start misidentifying kaolinite as kyanite in the analysis (this could be more or less catastrophic depending on whether the operator is going to group all of these entries as "gangue" at a later point and whether it actually makes a difference in the mineralogical/metallurgical processing downstream).

Admittedly if one expands an already rigorous mineral identification rule set equally then this strategy performs as well as mass normalisation or "boundary phase processing" (see below), though we might actually be filtering out some really useful information (minerals undiscovered to science?).
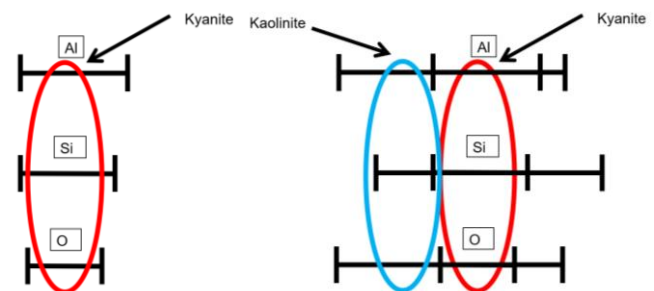
Figure 4: *Example of how expanding the parameters of a mineral in a mineral identification list can lead to erroneous classifications (an expanded kyanite definition might accidentally classify kaolinite spectra as kyanite).*

Boundary Phase/Mixed Spectra Entries

At the expense of keeping mineral identification entries explicitly rigorous and well-defined, one might opt to create mineral entries dealing exclusively with boundary phases or mixed spectra (grouping them with legitimate mineral entries later and during image processing once the data has been interrogated – for example by looking at assay reconciliations). Once again (for the QEMSCAN operators amongst us) this harkens back to those Al??Si??/NaDSiLCaH type entries. Unfortunately, if we are to be exhaustive in defining the number of mixed spectra that can occur in a suite of minerals, we quickly come to realise that there will be more mixed spectra than legitimate mineral entries by an order of magnitude. For example, in a simple suite of 10 minerals (nature is never this
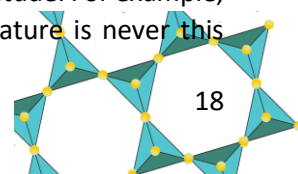
simple) we have to account for 45! mixed spectra as seen by the equation below (not factorial since we only consider grain boundaries by definition to consist of 2 minerals in contact with one another and we assign the same value to reverse entries…for instance a kaolinite-quartz boundary phase is of the same value as a quartz-kaolinite boundary phase).

$$\sum_{i=n}^{n} = (n-1) + (n-2) + (n-3) \dots (n-n)$$

Unfortunately, this only accounts for entries where both minerals contribute approximately 50% to the mixed spectra (otherwise the mixed spectra would be infinite) and doesn't even consider triple junctions (though to be fair, to encounter these would be extremely rare though not impossible).

This strategy though is not without utility. Take for instance the case of "leucoxene". Whilst not a recognised and legitimate "mineral" classification, it is a recognised and legitimate "particle" classification in heavy mineral sands processing and the heavy mineral sands industry as a whole (which is to say that a "leucoxene" particle will return to you a defined amount of Ti once processed – definitions vary but can be specified according to the needs of the processing operation). That means that we can create a "leucoxene" mixed spectra/boundary phase entry (being a mixture of clays, quartz, ilmenite, rutile etc.) according to the amount of Ti present within the analysis point which theoretically will be indicative of the amount of Ti that could be extracted from that point (and cumulatively from the particle)…remembering that we are using essentially chemical information derived from energy dispersive spectroscopy analyses to proxy for the minerals we are identifying in the first place. A similar approach can be used for instance in creating multiple "Mn-Wad" entries (and other "wads" occurring in super-/hypogene enriched ores) which, whilst not explicitly mineral entries (and perhaps explicitly mixed spectral entries), will return metallurgical information to a processing plant with great utility (and would certainly make assay reconciliation easier). Perhaps, an appropriate strategy with regards to this kind of naming convention might just be the "repurposing" of obsolete mineral names, mineral varieties, microtextural/intergrowth/microlithotypical terms as

conceptualised in Table 1 (see Glossary of obsolete mineral names, Bayliss, 2011). Of course, this is to be used with extreme caution (especially with regards to accidentally creating an entry that is explicitly a mixed spectra but that actually corresponds to a legitimate mineral phase…for instance a "wollastonite" entry might be catching quartz-calcite boundary phases and vica versa) but a leucoxene mixed spectra entry would provide far more utility than an entry like "Fe??Ti??Si??". And an operator can always buffer the value of creating such entries by assigning them low priorities in the mineral identification rulesets. This is a somewhat "creative" approach to managing boundary phases/mixed spectra.

The following sections (x-ray centroiding, x-ray average spectrum, x-ray sum spectrum, border delineation, automatic measurement parameter optimisation) deal with how beam scanning techniques can be used in dealing with mixed spectra.

X-ray Centroid (Spot Centroiding)

This is a favourite paradigm of the MLA analysis technique where a BSE image is used to segment each particle on the basis of its BSE variation, with a single x-ray and a single BSE value subsequently being collected from each phase (from the geometric/co-ordinate mean of the particle, Figure 5A). Typically, this ensures that spectra are collected far away from any grain boundaries thus minimising the opportunity for mixed spectra to be collected in the first place. This goes some way towards explaining why MLA standards files are much smaller in size than QEMSCAN SIP files where the measurement paradigm is usually full x-ray mapping on a grid basis (boundary phases are seldom encountered with x-ray centroiding so there is no need to create boundary phase entries). However, caution must be exercised if mineral grains are thin or of a peculiar shape (molybdenite, phyllosilicates etc.), or if minerals share similar BSE brightness's and are likely to be touching (chalcopyrite, pentlandite and pyrrhotite for instance), or finely intergrown lamellae are ubiquitous in a sample. In all instances, the geometric co-ordinate mean of a grain within a particle is likely to often occur at its extremities and thus attract the possibility that a mixed spectra will result (Figure 5B).
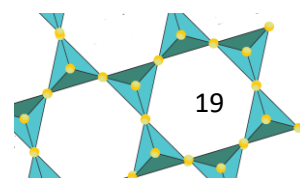
Table 1: *Examples of borrowed terms being used qualitatively for mixed spectra (Ms).*

| Boundary Phases	Description	Qualifier	Source
Jasper (Ms)	Quartz+Hematite	Essentially quartz with no more than 5% Fe	Borrowed varietal name
Prase (Ms)	Quartz+Chlorite	Essentially quartz with no more than 5% Al, Fe, Mg, Ca	Borrowed varietal name
Chrysoprase (Ms)	Quartz+Kerolite/Bunsenite	Essentially quartz with no more than 5% Ni, Mg	Borrowed varietal name
Micrographite (Ms)	Quartz+K-Feldspar	50-50 weighted average for quartz and k-feldspar	Borrowed textural name
Myrmekite (Ms)	Quartz+Plagioclase	50-50 weighted average for quartz and plagioclase	Borrowed textural name
Pseudoleucite (Ms)	K-Feldspar+ Analcime +Nepheline	Elemental averages with buffer	Association/pseudomorphological term
Micrite (Ms)	Calcite+Quartz+Kaolinite	Elemental averages with buffer	Borrowed rock term
Ophicalcite (Ms)	Calcite+Serpentine	50-50 weighted average for calcite and serpentine	Borrowed dimension stone term
Ophite (Ms)	Dolomite+Serpentine	50-50 weighted average for dolomite and serpentine	Borrowed dimension stone term
Plessite (Ms)	Kamacite+Taenite	50-50 weighted average for kamacite and taenite	Borrowed textural association
Leucoxene (Ms)	Rutile+Hematite +Kaolinite etc.	Intermediate Fe-Ti product between rutile and ilmenite	Borrowed particle classification
Psilomelane (Ms)	Romanechite+Todorokite +Hollandite	Elemental averages with buffer	Borrowed "bucket" term
Pimelite (Ms)	Kerolite+Willemseite	50-50 weighted average for kerolite and willemseite	Discredited mineral name
Garnierite (Ms)	Mg-Silicate+Chlorite+Ni-Silicate	Elemental averages with buffer	Discredited mineral name
Kochelite (Ms)	Zircon+Fergusonite (Y)	50-50 weighted average for zircon and fergusonite (Y)	Borrowed textural association
Bustite (Ms)	Enstatite+Serpentine	50-50 weighted average for enstatite and serpentine	Borrowed textural association

X-ray Average Spectrum

If full x-ray mapping is used (Figure 5C) as a scanning technique (typically with QEMSCANs) then one way of minimising mixed spectral signals is to average the spectra collected for a given BSE grayscale (used to delineate grains within a particle). This will minimise or "average out" the mixed spectra that are bound to occur on the edge of a grain. However, the effectiveness of this strategy is going to be proportional to the size of grains being measured. The larger the grain, the easier it is going to be to average out the effects of grain boundaries because boundary phases are going to be proportionately less when compared to the area of the grain. The smaller the grain, the higher the boundary phase occurrences are
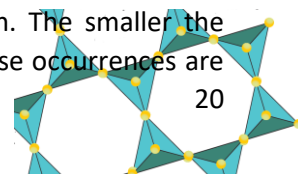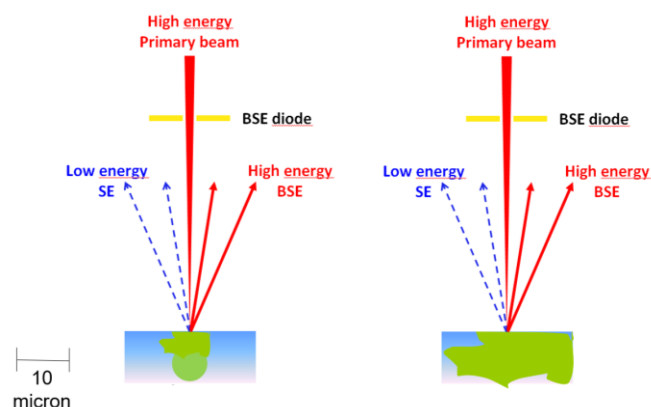
going to be relative to the area of the grain being measured (Figure 6).
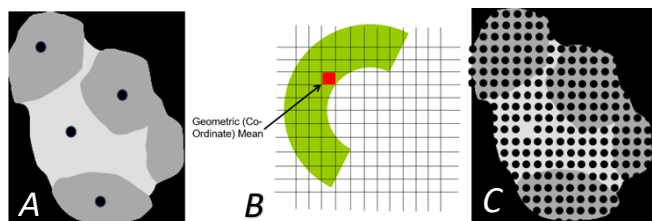
Figure 5: *Scanning techniques used in Auto-SEM-EDS bulk mineralogy measurements. A) Spot centroiding. B) Peculiarly shaped particle having a geometric mean spot centroid fall close to its periphery. C) X-ray mapping.*

Figure 6: *Cross section showing the relative influence of grain size on the expected amounts of boundary phase/mixed spectra occurrence.*

X-ray Sum Spectrum

Another approach to use, when full x-ray mapping is being implemented, is to sum all spectra within a common grayscale area rather than average all spectra. The results of this, minimise the impact of the boundary phases within that grain but additionally it means that the spectral identification of that grain somewhat approaches the quality of a spot EDS analysis (we move away from taking a 1000 count spectrum per spot to getting 1 million counts in a grain that has 1000 analysis points – though obviously that grain would have to be pretty large and therefore the same caveats in x-ray averaging apply here). Thus, we have a twofold improvement in minimising spectral interferences: 1.) less noise therefore less artefacts therefore less mixed spectra; 2.) effectively mixed

spectra are normalised out akin to the manner used in x-ray averaging. This strategy is currently mostly being employed in TIMA instruments.

Feature Scanning Border Delineation

The scanning methodologies so far mentioned beg the question…if we are applying full x-ray mapping in conjunction with the summing or averaging of the spectra to minimize the effects of boundary phases on the periphery of the grains, why not just avoid measuring the peripheries of those grains? Why not just delineate a border around the grain which doesn't get measured whilst still applying x-ray averaging or x-ray summing to still obtain cleaner spectra? "Feature Scanning" allows for this by asking the operator to specify a "Feature Scan Border" dimension within which the instrument will not take any spot analyses. The function is typically used in Mineralogic® systems (Figure 7).
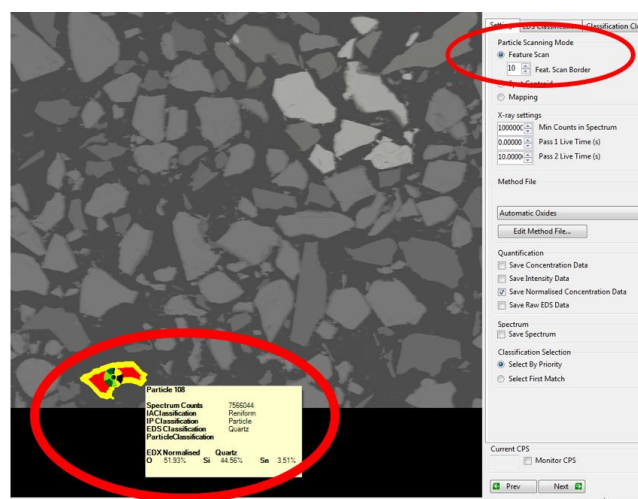
Figure 7: *Screenshot of "Feature Scan" functionality within a Mineralogic® system.*

Automatic Measurement Parameter Optimisation

A "smart systems" approach might involve an Auto-SEM-EDS instrument deciding on the best beam stepping interval (commonly known as "point spacing" and sometimes, though incorrectly known as "pixel size" – pixel size is a function of the point spacing but they are not the same thing) based on parameters set by the operator (the most appropriate of which would be the grain size of the mineral of interest). Operators have a tendency (once again driven by fear of the unknown and simply because they can) to implement ridiculously small beam stepping intervals (on the
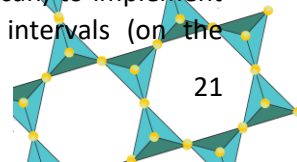
order of 1 micron point spacings – especially redundant when one considers that beam volume interactions are often on the order of 10 microns depending on the mineral being interacted with). Figure 8 shows why applying the smallest beam stepping interval imaginable might not always be a good idea. If a coarse beam stepping interval encounters an irregularly shaped grain boundary, then (in this case Figure 8A) there will be relatively few mixed spectra occurrences. If a fine beam stepping interval encounters the same irregularly shaped grain boundary (Figure 8B) then comparatively more mixed spectra occurrences occur and the problem of mixed spectra is compounded (we now have more mixed spectra occurrences that we have to deal with, not less). Mineralogic® and QEMSCAN currently have versions of this approach, though since time to analysis ("time is money") is the primary determinant in the application of measurement protocols, these are seldom used.
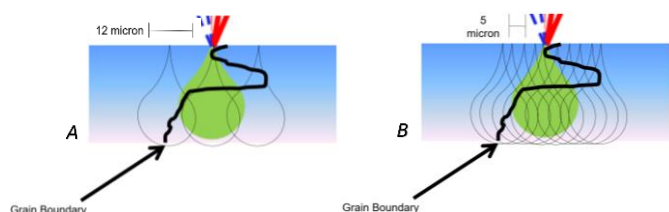
Figure 8: *Cross section showing implications of coarse and fine beam stepping intervals. A) A coarse beam stepping interval of 12 microns results in 3 intersections of a grain boundary and hence 3 pixels being assigned "unknown". B) A fine beam stepping interval of 5 microns intersects the same grain boundary 10 times with 10 pixels now being classified as "unknown".*

 "Unclassified" Boundary Phase Processing (Nearest Neighbour Analysis)

An "image processing" approach (post-measurement) can also be utilised to attempt to clean-up the results of mixed spectral interferences. This is a form of "nearest neighbour analysis" and is commonly referred to as "Boundary Phase Processing" in the QEMSCAN world. In short, if a pixel of "unknown" or "unclassified" is bounded on two to four sides by a legitimate mineral entry and there is no "conflict of interest" (for instance if the pixel of interest is bound equally by two legitimate mineral entries) in resolving that pixel into said legitimate mineral phase then the "unknown" or "unclassified" pixel can be successfully converted into the appropriate mineral phase (Figure 9).
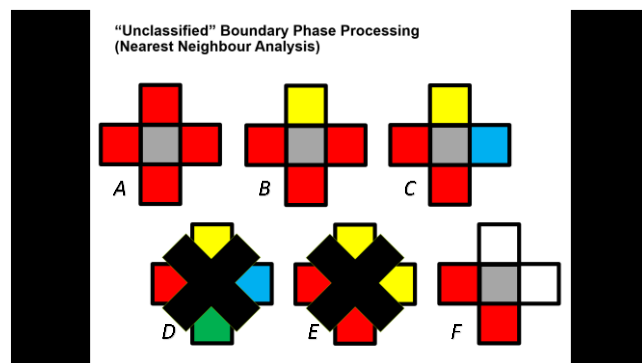
Figure 9: *Where "boundary phase processing" (nearest neighbour image processing) can and can't be applied to clean-up a dataset (colours proxy for minerals; grey = unknown; white = epoxy resin mounting media). A) Unknown is bound on 4 sides by red (100% association) therefore unknown can be justifiably converted into red. B) Unknown is bound on 3 sides by red (75% association) therefore unknown can be justifiably converted into red. C) Unknown is bound on 2 sides by red (50% association), on 1 side by yellow (25% association) and 1 side by blue (25% association). Since there is no conflict of interest (red association outweighs yellow and blue contribution to mixed spectrum) unknown can be justifiably converted into red. D) Unknown is bound on 1 side by red (25% association), on 1 side by yellow (25% association), on 1 side by blue (25% association) and on 1 side by green (25% association). Since there IS a conflict of interest (all colours contribute equally to the mixed spectrum) unknown CANNOT be justifiably converted into red. E) Unknown is bound on 2 sides by red (50% association) and 2 sides by yellow (50% association). Since there IS a conflict of interest (red and yellow contribute equally to the mixed spectrum) unknown CANNOT be justifiably converted into red (or yellow). F) Unknown is bound on 2 sides by red (50% association) and 2 sides by epoxy resin (50% association). But since epoxy resin is not a mineral and simply the mounting media, there is no conflict of interest (white is moot) and unknown CAN be justifiably converted into red. In principle, the Auto-SEM-EDS will not see the epoxy resin in the first place (exclude it) and the association is 100% red. Note: Some platforms give the option of "up-down" and "left-right" boundary phase processing options (in which case "C" would constitute a conflict of interest), the utility of which escapes the author.*

If this image processing is applied wholesale, systematically and equally ("unknown" is allowed to be converted into all legitimate mineral entries within a mineral identification ruleset – and this is quite

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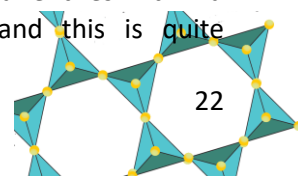
reasonable because the algorithms will not allow "unknowns" to convert unless there is a proximal association) till most "unknowns" are converted (within a well-defined, well-constrained mineral identification ruleset) then this method somewhat approaches the results of what otherwise might be achieved through mass normalisation (although of course the images will look better and more cohesive). Remembering, of course that any unclassified pixels with a "conflict of interest" will not be converted and the operator is then going to have to group these into an appropriate category.

"Unclassified" Boundary Phase Processing (Spectral Deconvolution)

The most sophisticated way of resolving mixed spectra (probably by far) would be to mathematically determine what mineral is contributing most to any given mixed spectra. Unfortunately, whilst it has been regularly spoken of in the Auto-SEM-EDS community, it is also the one technique that has never been satisfactorily implemented. Spectral deconvolution is often used in the background of EDS spot analyses to "deconvolute" or separate the contributions made to specific energy peaks (especially with regards to peak overlaps) but it is not used to separate mathematically the contributions made to an EDS analysis by separate minerals. But simplistically put…given an "unclassified" pixel of a specific, measured, chemical composition below:

"Unclassified"   = SiO_2 +   MgO

31% Mg 13% Si 54% O   47% Si 53%O   42% Mg 55% O

And assuming ideal compositions for the minerals, quartz and periclase, it is quite easy mathematically (and even intuitively) to see that periclase is contributing most to the "unclassified" spectrum (periclase, in this instance is contributing ~74% to the chemistry of the spectrum). Therefore the "unclassified" pixel can be quite confidently and justifiably allocated to the mineral periclase (assuming there's not another legitimate mineral in existence with the unclassified's composition, that it doesn't occur in one's ore deposit or that if you do have a mineral like that in your ore deposit that it is being caught in another legitimate mineral entry and that is why it is here "unclassified").

Conclusion

Not all of these applications are available across all Auto-SEM-EDS platforms. That is not to say that they will never be. However, it may just require some operator coding experience. Strides have already started being made in the Picksal app created by Dr Pieter Botha of Hippo Geoscience that uses the python coding language to extract pixel-by-pixel information from all Auto-SEM-EDS platforms. In principle, pixel reclassifications based on a deconvolution approach could thus be performed or ways of dealing with mixed spectra that are unique or exclusive to one platform might be applied to others.

Table 2: *Summary of strategies for dealing with mixed spectra in Auto-SEM-EDS instruments.*

Level of Sophistication	Mixed Spectra Handling	Grouping
Least	Mass Normalisation	
	Expanding Mineral Definitions	Mineral Identification Ruleset Manipulation
	Boundary Phase/Mixed Spectra Entries	
	Spot Centroiding	
	X-Ray Averaging	
	X-Ray Summing	Scanning Techniques
	Feature Scanning (Border Delineation)	
	Automatic Measurement Parameter Optimisation	
	Nearest Neighbour Analysis	Boundary Phase Processing
Most	Spectral Deconvolution	

As a final word on the subject… "Fear of the unknown" has led to some arbitrary heuristics being applied in dealing with mixed spectra. For instance, the idea that 10% "unknowns" (regularly encountered if not sometimes being implicitly hidden behind a plethora of strategies dealing with mixed spectra) is "bad" and must be reduced to less than 1% (who decided that anyway?). It may be the one explicit reason why Auto-SEM-EDS instrumentation has NEVER discovered new mineral phases from first principles (though they have been used in a complimentary fashion to confirm such…at least once to my knowledge). This is despite, millions of spot analyses per sample being performed,
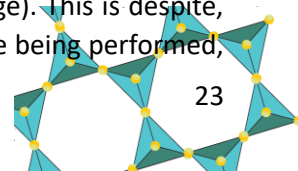
and I would imagine at least 50 million samples having been measured since the <u>commercial</u> advent of the technology (I think this is very conservative…~400 machines in the world running at 65% efficiency for the past 20 years). At 1500 particles per sample (another arbitrary heuristic) that means at least 75 billion particles have been measured with this technology. It is entirely conceivable, that if mineral identification rulesets were kept aggressively well-constrained and well-defined that entire grains would be classified as "unknown" (as seen in Figure 3). And if we systematically went back and re-investigated these grains, we would find new mineral species quite often and quite easily (or so I believe). So, use these strategies as a tool to improve your data…not as an end in themselves.

Other Gems

Gold in pyrite

A recent paper in *Geology* by Denis Fougerouse, Steven Reddy, Mark Aylmore, Lin Yang, Paul Guagliardo, David Saxey, William Rickard and Nicholas Timms (authors from universities and research institutes in Western Australia and Beijing) suggests that gold in pyrite need not be present only as sulphide alloys or as nanoparticles. Entitled *[A new kind of invisible gold in pyrite hosted in deformation-related dislocations](#)*, they use NanoSIMS to resolve dislocation-hosted gold in concentrations on the order of hundreds of ppm (atomic), representing a third host type for invisible gold in pyritic gold ores.

Contributed by S. Prevec

Rocks and Minerals in the Bible

The crossword puzzle for this issue is based around the theme of minerals and rocks found in the Bible. This perhaps unlikely theme is what you get when your editor is travelling to and from field areas involving multiple-day drives, and ends up at a Bed & Breakfast (in Bloemfontein) featuring inadequate WiFi (the kind that reaches to the limits of the main office) and limited TV channel selection, but two bedside bibles, courtesy of the Gideons. I got to browsing Revelations, which is what you get when your editor is out of liquor, after four days of driving out of five, in the eighteenth month of COVID semi-lockdown. So it transpires that rocks,

metals and minerals, or euphemisms thereof (brimstone, etc.), feature over 1700 times in the Bible[1] (I didn't count them). Many of these appear to be variants of microcrystalline silica, either different styles of occurrence, or similar mineralogical occurrences by different names, especially in the description of the foundation stones and walls of what Revelations calls "the New Jerusalem" (or celestial, or heavenly Jerusalem, elsewhere).

Interestingly, and depending on the specific translation (which is influenced by the mineral conventions of the age at which the translations occurred, as well as the languages involved on either end; from Hebrew, Greek, Latin, English, German, etc.), diamond, which was not so prominent at that time in the Middle East, is evidently not mentioned explicitly. There are minerals named specifically in the context of their extreme hardness, such as emery and adamant, which are assumed to be synonyms for diamond in some translations, but are also alternatively believed more likely to be varieties of corundum. A lot of the gemstones mentioned were not local to the Middle East, but would have been well known there as a result of trade from the Indian subcontinent in particular. This also leads us to this 'Dad Joke': Which (ca. 1980) New Wave music star is mentioned in the Bible? Adam Ant. Go ahead, impress people at parties with that one (but not at parties with Bible scholars, as the original Hebrew word for adamant is *shmyr*, pronounced 'shamir').

On the subject of biblical geoscience, a very recent publication (September 20, in the journal *Nature*) by a group of twenty one U.S.-based researchers has suggested that the account of the obliteration of the unworthy in Sodom (and presumably Gomorrah, although this wasn't mentioned) recounted in the Old Testament and in the Qur'an may have been based on the outcome of a [Tunguska-like explosion](#) of a meteorite in the low atmosphere around 3600 years ago.

1. Voynick, S. (2021) Minerals & Metals of the Bible (Part I). Rock 'n' Gem website: https://www.rockngem.com/minerals-metals-of-the-bible-part-i/.

Contributed by S. Prevec

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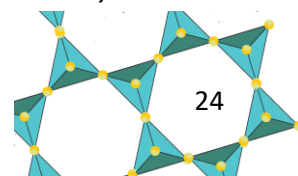
IMA 2022
## MINERALOGY AND SPACE
Lyon, 18-22 July

Following the tradition of quadri-annual general meetings of the International Mineralogical Association organized by national societies, the French Society for Mineralogy and Crystallography will host the 23rd general meeting of the IMA in Lyon, France during 18-22 July 2022.

2022 is the year to celebrate mineralogy. It marks the bicentennial of the death of René Just Haüy (born 1743) who is a father of modern mineralogy and crystallography. Two centuries ago is also when Haüy's Traité de mineralogy and Traité de cristallographie were published. Back to our days, in 2022, the last two main Mars exploration programs, Perseverance (Mars2020) and Huoxing 1, will just have had enough time for science return and post-processing. With the return of Hayabusa 2, for the first time, fragments of a primitive carbonaceous asteroid will be analysed.

The 23rd meeting of the IMA will mark these celebrations. In Lyon, we want to paint IMA 2022 with the colours of space exploration. Alongside the more traditional mineralogist we want to inspire the new generation and make a step closer toward the final frontier. The meeting will bring together all the new facets of modern mineralogy; it will be the playground where mineralogy as we know it will meet exploratory planetology, and it will be the place to celebrate two centuries of mineralogy.

The overarching themes of the IMA2022 are:

* Mineral Systematics
* Physics and Chemistry of Minerals
* Ores and Ore Mineralogy
* Mineralogy and Petrology
* Planetary Mineralogy
* Planetary Interiors
* The Dynamical World Of Minerals
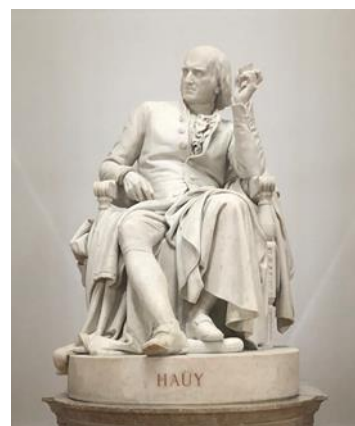
To stay updated visit regularly the official conference website: https://ima2022.fr and follow us on Facebook and twitter. The venue is the Lyon Convention Centre, a state-of-the-art, impressive convention centre featuring 25,000m² of innovative architecture and situated between the Rhône river and the Tête d'Or Park.

On behalf of the French Society for Mineralogy and Crystallography, the leading committee is formed of Razvan Caracas, Herve Cardon, and Cathy Quantin-Nataf.

We are looking forward to seeing you in Lyon in 2022!

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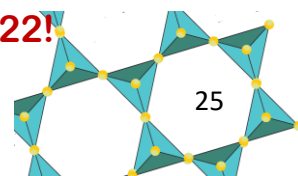
Bruce's Beauties: Anthropomorphic mineral specimens

Definition: anthropomorphic – having human characteristics. In the world of minerals and mineral collecting, specimen sometimes take on the appearance of human traits, whether they are rocks or minerals. Assigning "names" to such specimens, or seeing such features in minerals, is the theme for this issue.
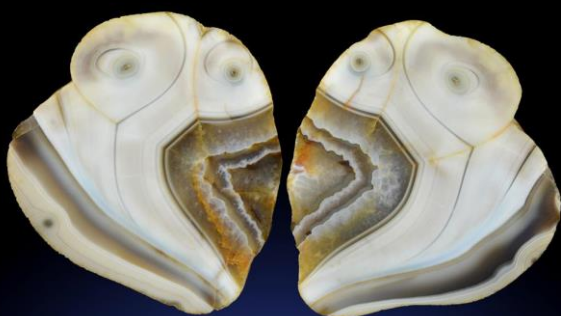
"The Agate-Eaters"; this 3.5 cm agate was collected from the alluvial diamond digging dumps on the Vaal River at Windsorton. The outside of the agate gave very little hint of the internal structure, but when it was cut and polished, the two halves revealed this internal structure.

"The Turtle"; not human, but interesting nonetheless. This 6.1 cm doubly-terminated quartz-amethyst-smoky quartz specimen was acquired from a local digger in the Goboboseb Mountains west of the Brandberg, in Namibia. Backlit to show the internal structure.


"The Angel"; this small 1.8 cm specimen is from the Tsumeb mine in Namibia. The "wings" and "head" are yellow adamite, a zinc arsenate, while the "body" is smithsonite, a zinc carbonate.

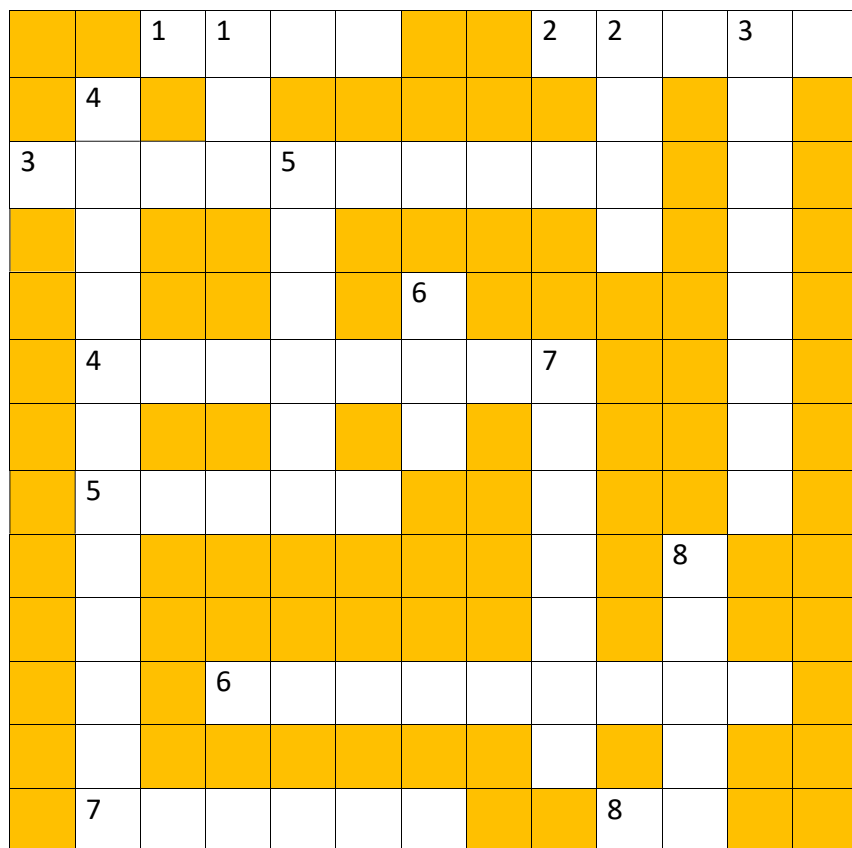"The Alien"; not a mineral, but a sandstone pebble, 7.7 cm. Self-collected from the beach at Cannon Rocks, Eastern Cape. The sandstone contains inclusions of varying hardness, usually softer than the host sandstone. Continual reworking in the nearshore surf zone causes preferential weathering of the inclusions producing different stages and shaped the facial features.

All specimens and photos © Bruce Cairncross.
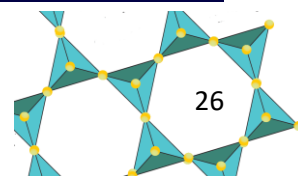
Minsa Crossword for September 2021

This issue's crossword theme is "minerals and rocks mentioned in the Bible".
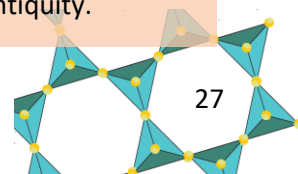
ACROSS:

1. This metal is mentioned more than 400 times in the Bible (the most frequently cited).
2. A yellow gemstone mentioned in the King James translations of the Bible, likely a misattribution; up to the Middle Ages, any yellow gemstone was referred to as this mineral, now restricted to use for a specific Al- and F-bearing nesosilicate.
3. A cryptocrystalline aggregate of two polymorphs of silica; namely quartz (triclinic) and moganite (monoclinic), named for the city in westernmost Asia, across the straits from what is now Istanbul.
4. The blue gemstone variant of corundum, famously derived from Sri Lanka in antiquity. The world's main producer is Madagascar.
5. The singular of the aragonitic spheres formed by molluscs, and harvested along the Indian Ocean coastline in antiquity.
6. The brownish-red semiprecious variant of 3-across, its name derives from the similarly-coloured cornel cherry, found in southwestern Asia.
7. The metal used as the primary medium for coinage in the Holy Land during the Roman occupation, mined in southern Greece (very near Athens) in antiquity.
8. The most common base metal, mined in antiquity between India and the eastern Middle East, the earliest use of it was from meteoritic finds.

DOWN:

1. An organic liquid deployed in the Bible for anointing. This is a bit of a liberty in this context, as the Biblical variant is likely derived from fruits or plants, rather than minerals.
2. The banded, typically (but not necessarily) black variant of 3-across, and/or 8-down. The red variant is known as sard, or sometimes sard____ (this mineral), prominent in the Holy Land and in India.
3. The violet gemstone, the occidental version of which is a coloured variant of quartz (mined in Greece and Egypt in antiquity), while the oriental version is a variety of corundum.
4. The green variant of 8-across, resulting from high Ni content, this stone is described as the tenth foundation stone of the celestial Jerusalem in Revelations.
5. The metal that provides the main constituent for Bronze, the Age of which preceded the Age of 8-across around the second millennium B.C.
6. The second most prominent metal in bronze, and strongly preferred to the other naturally occurring bronze alloy component, arsenic, this metal was mined in southern Turkey in antiquity.
7. The green (Cr-contaminated) gemstone variant of beryl, constituting the fourth foundation stone of celestial Jerusalem (Revelations); also the colour of Oz's capital city (as in "The Wizard of").
8. Continued at bottom of right-hand column:

8. A rock (rather than a mineral) consisting of a mixture of quartz and 3-across, typically grey and laminated, named for its discovery site near the mouth of the Achates River in Sicily, in antiquity.

Minsa Crossword Solution for June 2021

The crossword theme was mineral oxides and minerals containing transition metals in multiple crystallographic sites.

¹U	L	¹V	O	S	P	I	N	E	²L			³S
		A							I			H
⁴S		N			²C	H	R	O	M	I	T	E
C		A							O			L
³H	Y	D	R	O	X	Y	L		N			L
O		I							I			
R		N		⁴M	⁵A	G	N	E	T	I	⁶T	E
L		I			N				E		A	
		T			A		⁷F		⁵N	N	O	
	⁶H	E	M	A	T	I	T	E			T	
					A						I	
		⁷H	A	U	S	M	A	N	N	I	T	E
					E						E	

ACROSS:

1. An Fe^{+2}-Ti-oxide mineral, it breaks down to magnetite plus ilmenite during cooling, commonly found with primary magnetite in magmatic rocks.
2. The primary magmatic ore of chromium, different valence states of V can replace both Cr and Fe in its structure, serving as a proxy for oxidation conditions (see article pg. 12-13 this issue)
3. The anionic molecular species of H oxide, commonly found incorporated into oxidised mineral structures.
4. The common Fe oxide mineral containing both ferric and ferrous iron in its structure.
5. The abbreviation for the oxygen reaction buffer that is the next one more oxidised than QFM, the buffer most relevant to magmatic rocks.
6. The common Fe oxide mineral containing only ferric iron. It has the same crystal structure as corundum and ilmenite, and takes its name from the Greek word for blood.
7. A Mn oxide ore mineral containing both divalent and trivalent Mn, and featuring in the article on pg. 13-14 of this issue).

DOWN:

1. A chlorinated lead vanadate mineral, it forms from oxidation of galena, and is an important ore mineral of V.
2. A hydrated iron oxide, also containing 3-across, it is a characteristically yellow Fe ore mineral, named for the Greek for a "wet meadow".
3. The term used to describe the residence of electrons in any particular orbital configuration around an atomic nucleus.
4. The Fe-bearing subspecies of tourmaline, it is named for the village in Saxony (Germany) near which it was found at a local tin mine, associated with tin oxide ores.
5. The metastable polymorph of rutile, it is typically the first oxide of Ti to form, before reverting to a more stable cousin.
6. A rare tantalum (+5) oxide mineral, found in granite pegmatites, first described in 1983 from the Kola Peninsula (Russia).
7. The transition metal which is the heaviest element produced during the normal operations of a sun (i.e., preceding supernova stage). See also pg. 3).

Note: The recommended deadline for submissions for the next issue of the Geode is November 30, 2021.