the Geode
the Geode

MINSA
Mineralogical Association of South Africa
A division of the GSSA

Analytical methods for determining the oxidation state of rocks & minerals

titration

X-ray photoelectron spectroscopy

Illinois fluorites

Cr/V in chromite

Mössbauer spectroscopy

the KZN ‘diamond’ rush

Fe_2O_3*

mineral stoichio-metrics

The GEODE

Minsa Newsletter
Volume 8
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MINSA
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website: www.gssa.org.za/Minsa
e-mail: Minsa@gssa.org.za

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NEWSLETTER
Volume 8 No. 2
June 2021

"the magazine you can share, virus-free"

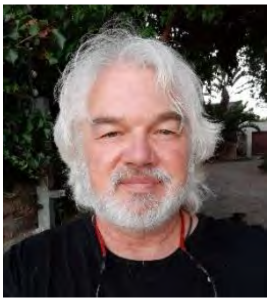
Contents

Next issue theme:

Determining the modal mineralogy of a rock (i.e., the mineral contents)

The Editor's Site

In this issue, we endeavour to keep you informed and entertained as we here in South Africa re-enter a more restrictive lockdown to combat the 3rd wave of the COVID virus pandemic. Our feature section is on the determination of the oxidation state of minerals and rocks, that is, effectively, determining the valence state of elements in those minerals.



We feature six articles, beginning with an introduction into the concept and to the chemical titration method, followed by an introduction to two direct spectroscopic approaches, x-ray photo-electron spectroscopy and Mössbauer spectroscopy.

These are complemented by three applied techniques involving the use of mineral chemistry to infer stoichiometric site occupancies and thus extrapolate oxidation conditions, using Cr/V in chromite, Mn in manganese ores, and a generalised programme designed for all common minerals. Preceding all that, our outgoing President waxes sentimental at the close of his third term.

Following the thematic section, amongst the other gems, we offer some thoughts on the recent KZN 'diamond' rush, Bruce Cairncross introduces us to fluorites from the Pb-Zn mines of Illinois, and our crossword for this issue is aligned with our theme of mineral oxidation.

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

Steve Prevec

From the Chair

Well… what a year this has been… an entire chairmanship run from behind a computer (which is not my custom).

In my first outing as Chair of the association things were obviously tough 'cause it was my first time in the magma chamber.

My second outing as Chair wasn't any easier, 'cause it was the 40th anniversary of the association and that necessitated the running of multitudinous extra activities in celebration of the event (I had really hoped it would've been easier).

And in my third outing, I had to attempt to chair one of the most active voluntary scientific associations in the GSSA (I can only think of one that is perhaps a bit more active) in the midst of a global pandemic. Go figure. When the volcano rains…it pyroclastically pours…

Igor Željko Tonžetić

But I got through all of this because of the people I was fortunate enough to be surrounded by. People who asked no favour…and gave everything in return. There are too many of you to mention in this short column and I wouldn't want to run the risk of leaving anyone out (I have tried over all these years to explicitly mention you all in my Chair's reports) …but to all of you… thank you… thank you from the plutonic depths of my shadow to the Himalayan heights of my soul. I don't know what I would've done without you all. It has never in any given femtosecond gone without notice.

Thank you… and goodnight. May we rise in a new epoch filled with hope and diamonds on the souls of our shoes.

Yours truly

Igor

Forthcoming Events & Attractions

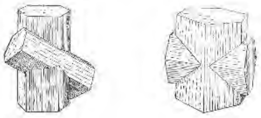
Many of these events are still missing dates, as a consequence of lockdown logistics: Minsa will let you know! Watch for e-mailed announcements.

- Note that the GSSA's online "**Geocongress Appetiser Series**" planned for mid-year (July) has been cancelled, due to Zoom-burnout and competition from other online international conferences at this time. The GSSA lunchtime talks will continue unabated, however, so you can still see your favourite GSSA presenters in action. Ask for them by name!
- **MINSA Annual General Meeting** (Online)
  Date: Wednesday 11 August 2021
  Keynote Speaker: **Dr Neville Plint** (Director Sustainable Minerals Institute, University of Queensland). Topic: The topic will be in celebration of the UN's "**International Year of Creative Economy for Sustainable Development**"
- Excursion to tile factory
- Joint Minsa-SAMS excursion to the Leeuwpoort Tin mine
- Wirsam Visit
- Phalaborwa visit – proposed for the end of winter or spring 2021.
- 5th Annual Southern African Mineral Symposium – Saturday 20 November 2021.
- Night @ the Museum VI (Nov. 26, tentatively).

5TH SOUTHERN AFRICAN MINERAL SYMPOSIUM 2021

FIRST CIRCULAR

A one-day symposium highlighting minerals and mineral and gemstone deposits of southern Africa hosted jointly by the Mineralogical Association of South Africa and the South African Micromount Society



Important Information

Date: Saturday 20th November 2021
Venue: University of the Witwatersrand, Johannesburg
Cost: R200.00
Enquiries: Symposium Chairman – Igor Željko Tonžetić: minsa@gssa.org.za

Abstracts Due Date: 5 August 2021

The Mineralogical Association of South Africa (MINSA) in conjunction with the South African Micromount Society (SAMS) would like to invite you and all interested parties to submit abstracts/extended abstracts/short communications (for presentation) at the 5th Southern African Minerals Symposium 2021. Please try to keep your abstracts/extended abstracts/short communications down to 2 pages (Calibri 11, Single Line Spacing). Abstracts/extended abstracts/short communications longer than 4 pages will not be accepted. You are welcome to include images/figures/pictures/photos/diagrams etc in your abstract. You are also welcome to include references. Be sure to include a title, author name, and affiliation/address in your abstract. Accepted abstracts will be published with short biographies.

A poster programme will run concurrently. As such you are also welcome to submit posters for display.

Background to the symposium…

This symposium will be the fifth 'mineral symposium' that has been held in South Africa, albeit not on a very regular basis. The '*1st International Gem & Minerals Symposium*' was organised in September 1975 by the Pretoria Gem & Mineral Club in Pretoria on behalf of the Federation of South African Gem and Mineralogical Societies. Four overseas and three local mineralogists and gemmologists delivered a series of talks over three days and one day was taken up by field trips. The themes of the lectures were focused primarily on overseas minerals, mineral localities and on gemstones.

Seventeen years later! Bruce Cairncross organized and convened the '*First SA Mineral Collectors Symposium*' at the Rand Afrikaans University in Johannesburg in September 1992. This concentrated more on local content than the first symposium held in Pretoria, which had a distinct international flavour. This took place over a week-end with thirteen local experts presenting talks on various aspects of minerals, mineral localities, mineral identification, analytical techniques and gemstones. After a day and a half of talks, delegates then visited some of the local collectors in the Johannesburg-Pretoria area to view their collections.

Eighteen years later, in 2010 the '*3rd Southern African Mineral Symposium*' was held at the Council for Geoscience in Pretoria. Jointly organised by some members of the Witwatersrand Gem and Mineral Club and the South African Micromount Society, this one-day event showcased local experts and specialists (both amateur and professional) in mineralogy, gemmology, mineral collecting and related topics presenting a wide ranging series of talks and poster displays on the region's minerals and gemstones. The symposium was a tremendous success, with over 100 participants, 14 speakers along with 9 poster presentations.

Similarly, and heralding on from the success of the previous symposium the 2012 symposium was held at the Council for Geoscience in Pretoria and attracted 12 speakers with over 100 delegates in attendance. Topics included: the Phalaborwa Complex, Okiep Copper District, the industrial archaeology of silver in the Pretoria region, microminerals of the Bushveld Complex, FOSAGAMS mineral excursions, the Museum Africa minerals collection, mineral connoisseurship, detrital rutile, diamond morphology, tanzanite, meteorites, the Kalahari Manganese Field and the Rosh Pinah Pb-Zn Mine.

The purpose of the 2021 symposium (as with previous symposiums), is twofold. Firstly, to get together the 'professionals' and the 'amateurs' who are experts in their respective fields and to have stimulating discussions on minerals, gems and related topics. Secondly, the symposium acts as a vehicle for promoting and highlighting minerals, mineral heritage, mineral collecting and mineral preservation in our region. It is therefore envisaged to use the success of the current symposium, and the previous ones, to have these on a more regular basis.

Day's Programme

08:00 – 09:00 Arrival, registration and tea
09:00 – 09:10 Welcome and announcements
09:10 – 10:50 Presentations – Session 1
10:50 – 11:20
Morning tea, posters and dealer sales
11:20 – 12:35 Presentations – Session 2
12:35 – 13:45 Lunch and dealer sales
13:45 – 15:25 Presentations – Session 3
15:25 – 15:55
Afternoon tea, posters and dealer sales
15:55 – 17:10 Presentations – Session 4
17:10 – 17:20 Closing remarks
17:20 – 19:30 Posters and dealer sales

Minsa Affairs *(no, not that kind)*

IMA Representatives from Minsa invited

The IMA hosts six commissions on specific themes within mineralogy. Four of these do not have a MINSA representative. We therefore seek volunteers to act as MINSA representatives on these IMA commissions:

- The IMA commission on Gem Materials: IMA-CGM
- The IMA commission on Museums: IMA-CM
- The IMA commission on Ore Mineralogy: IMA-COM
- The IMA commission on the Physics of Minerals: IMA-CPM

Please contact us at minsa@gssa.org.za if you would be interested in representing MINSA on an IMA Commission. More information on the work of the commissions may be found at

https://www.ima-mineralogy.org/

Articles

June issue theme: Determining the oxidation state of rocks and minerals.

The theme invited thoughts on the determination of the oxidation, or valence states of elements in minerals and rocks. Five articles are presented in terms of increasing indirectness of oxidation state determination, more or less, with the first two articles including direct quantitative measurements, and the latter articles deducing valences based on inferred crystallographic site occupancies in minerals.

- Determining Fe^{+3}/Fe^{+2} in rocks; titrations and educated estimates (S. Prevec).
- Measuring valence states using XPS (D. Craig); XPS analysis (L. Mostert).
- Measuring valence states using Mössbauer (F. Waanders)
- Using Cr/V ratios in chromite to infer oxidation state (S. Dyan).
- Using XRD & bulk rock chemistry to derive Mn valences in Mn ore minerals (D. Chetty).
- Using bulk rock chemistry ± EPMA to derive site occupancies in minerals (S. Büttner).

On the determination of Fe^{+2}/Fe^{+3} ratios in rocks

Stephen A. Prevec

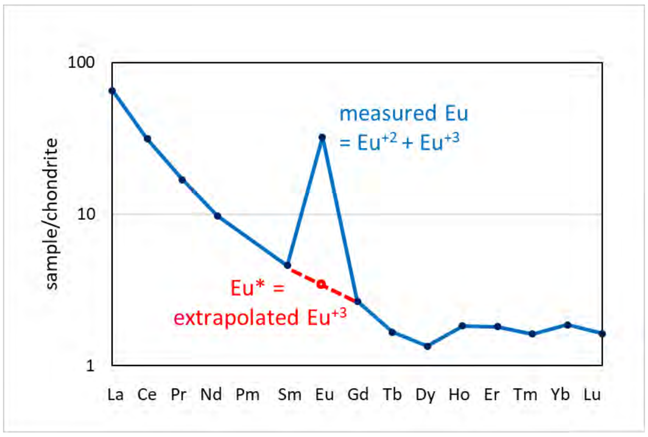
Dept of Geology, Rhodes University, Makhanda, R.S.A., 6140.

Iron, the heaviest element produced by nuclear processes taking place within our star (the Sun), is near and dear to our hearts, and makes up between about 3-16 wt.% of common rocks[1], as well as most of the Earth, by weight (mostly in the core). It's abundance can be much higher in rocks in which iron is specifically enriched, such as in Banded Iron Formations (*vis* the Northern Cape), or the thick magnetitite layers in the Bushveld and in the PanXi intrusions of southwestern China (see image on next page), or even as iron-rich lava flows (as found in Mexico), many of which comprise significant ore resources for iron, principally as the main ingredient in steel. Iron is unique on our planet (Earth) inasmuch as it is the only element that is both a major element (i.e., occurs in >1 wt.% in virtually all rock types) and occurs naturally in geological environments (i.e., underground, in the relatively reducing environment of the inner Earth, away from regular interaction with the atmosphere) as either of two oxidation (valence) states, either +2 (ferrous iron) or +3 (ferric iron).

Red mudstones underlying grey-green mudstones at a Permian-Triassic boundary site in the Eastern Cape, South Africa. The change from red (oxidised) to green (reduced) corresponds to probable variations in depositional settings. (Photo Rose Prevec.)

For practical purposes, the two valence states represent two distinct major elements, where both commonly occur in concentrations >1 wt.%, with ferrous iron having a charge of +2, an ionic radius of 0.076 nm, while ferric iron has a charge of +3, an atomic radius of 0.064 nm, and a different electronegativity.

There are other geologically and mineralogically important elements with multiple valence states expressed in geological environments. Transition elements are particularly prone to this, and Mn, V and Cr are prominent ore elements for which their polyvalence is relevant in studies of their provenance. Of the rare earth elements, Eu is the only one which is commonly both trivalent (in common with the rest of the REE in most rocks) and bivalent, resulting in the diagnostic Eu anomaly featuring in the standard chondrite-normalised abundance histograms. The proportion of +2/+3 in this case can be calculated by comparing the measured Eu concentration with that extrapolated between its nearest neighbours, Sm and Gd, which is assumed to therefore represent the abundance of Eu^{+3} (this is known as Eu*, as illustrated below).



A standard chondrite-normalised REE plot, in which the valence (oxidation) state relationship between Eu^{+2} and Eu^{+3} is illustrated, for a plagioclase-rich granitoid from Namaqualand. (S. Prevec).

The most routine analytical technique for whole rock major element geochemical analysis is by XRF (x-ray fluorescence), which typically does not discriminate between Fe^{+2} and Fe^{+3}. As a result, Fe is then typically reported as either Fe_2O_3 (i.e., ferric iron oxide) or FeO (ferrous iron oxide) as a matter of convention, but independent of the actual oxidation state of Fe in the analysed rock. This, then, is (or should be, but often is not) reported in publications as either Fe_2O_3* or FeO*, where the star denotes “total iron reported as”. In fact, sample preparation for XRF on major elements, which involves crushing the rock to a fine powder (in air), and then melting it in air in combination with a Li-metaborate (B-oxide, or some variant thereof) flux to produce a glass disc for XRF analysis has probably converted much of the original Fe^{+2} into Fe^{+3}, so that what is being analysed is no longer representative of the actual original rock. Similarly, electron probe microanalysis (EPMA) of major elements in minerals, which uses the same principles of electron excitation and subsequent discrimination of the secondary x-rays, does not discriminate between the oxidation states of Fe, as the primary electrons being displaced are inner shell electrons, whereas the electrons involved in the valence state are (typically) outer shell electrons. (Having said that, in researching this article, I encountered a paper from 2010[2] suggesting that XRF can in fact resolve the oxidation states to varying precisions, depending on the degree of oxidation of the rock, although I have not seen this ever applied or offered in the XRF analyses which I routinely obtain.)

The other common geochemical analytical tools, inductively-coupled plasma spectroscopy (ICP-OES) or mass spectrometry (ICP-MS), are superficially similarly oblivious to oxidation state, as both valence states have the same atomic mass. The high temperature (around 6000 °C) of the argon plasma that ionizes and vapourizes the elements (in air) does not produce a reliable stream of Fe oxides and/or argides to allow molecular compounds of the different oxidation states to be measured.

There are a number of analytical techniques which can actually measure ionic valence states. Some of these will be discussed ‘properly’ in other contributions to this issue. The most commonly cited historical method, and the one that does not require a specialized spectrometer, involves dissolution and so-called ‘wet chemical’ titration (are there dry chemical techniques, I wonder?). This is typically referred to as a ‘simple’ titration method by people who have mentioned it to me, but seems to be rarely done. This method will briefly be summarized here.

The principles are as follows[3]: The powdered sample is dissolved using HF (hydrofluoric acid) at room temperature in a non-glass container (otherwise, the HF dissolves your container, so usually in geoscience labs a Teflon variant is used). Dissolution occurs in the presence of excess V^{5+}, which is provided by adding a solution of NH_4VO_3 (ammonium vanadate). The V^{5+} oxidizes the Fe^{2+} to Fe^{3+} as it is released from the minerals (by stealing electrons from it, in effect), while the vanadium is thus reduced to V^{4+}. The V^{5+} remaining after dissolution is titrated against a Fe^{2+} solution (of $Fe(NH_4)_2(SO_4)_2{\bullet}6H_2O$) (or iron (II) ammonium sulphate) that has been calibrated against a $K_2Cr_2O_7$ (potassium dichromate) standard, using sulphuric acid (H_2SO_4) as the solvent. So, then, the initial moles of V^{5+} minus the final moles V^{5+} = moles Fe^{2+} in the sample. This is known as the potassium dichromate titration technique, after the standard cited in the previous sentence.

If you really want to avoid sample oxidation during analysis, and also to dissolve tricky refractory oxide phases such as chromite (which are resistant to HF, which only attacks the silicates), then you may need to go the extra mile (1.6 km) and dissolve the sample powder in an HF-HSO_4 mixture in a CO_2 atmosphere[1]. If you don't like playing with H_2SO_4, you can, alternatively, dissolve spinels (such as chromite) in aqua regia (an exothermic mixture of concentrated HCl-HNO_3, which is no picnic either), but if you're already going to be opening the H_2SO_4 bottle for your dichromate standard, then why not throw away the cork, figuratively? So, suddenly it's not such a mystery why this is not so common for routine geological analysis.

There are techniques advocated in the biological sciences (i.e., for organically-bound Fe) involving the separation of Fe^{+2} from Fe^{+3} using "strong cation exchange chromatography" (SCX), followed by regular elemental analysis by ICP-MS[4]. The difference between "strong cation exchange chromatography" and 'regular' cation exchange is that certain elements, strong ion-exchangers, are able to retain their valence state during chromatography in the cation exchange resin columns over a wide range of pH, whereas other elements cannot. Superficially, this sounds to me like a lot less trouble and chemical expertise than the titration above. However, this is "not your father's" old cation exchange resin columns as traditionally used for separating Sr and the REE from Fe and the other elements for isotopic analysis, for example, in modestly diluted HCl or HNO_3, but rather requires specialized resins at specific pH values, equilibrated in specialized buffer solutions (such as ammonium citrate and pyridine-2,6-dicarboxylic acid[4]). Enough said.

In the Panzhihua intrusion, in southwestern China, oxidation of the iron-rich parent magma caused by assimilation of footwall marbles (the white rocks on the left) is thought (by some workers) to have resulted in the precipitation and accumulation of massive Fe-Ti-V oxide (magnetite) ore bodies in the overlying ferrogabbroic intrusions. This model has also been suggested for parts of the Bushveld Complex. (Photo S. Prevec.)

The preferred approach for geologists involves building on the data provided by others and thus benefitting from their hard work without having to spend valuable time and money, and risk the routine acid burns to skin and clothing that featured through my postgraduate years. Neil Irvine and Bob Baragar, both then of the Geological Survey of Canada, compiled such a dataset and determined that for volcanic igneous rocks, where most of the Fe^{+3} is assumed to be associated with Ti within minerals such as (titano)magnetite, the expression $Fe_2O_3 = TiO_2 + 1.5$ (all in wt.%) was proposed. The surplus Fe is then assumed to be present as FeO, occupying +2 sites in mafic silicate minerals (such as olivines and pyroxenes) or oxides (ilmenite, chromite). This is suitably convenient, as long as the rocks are not overly oxidized (it cannot be usefully applied to metasedimentary rocks, for example, as the expression was derived from observations of igneous volcanic rocks), or for compositionally extreme rocks such as anorthosites, which consist of >90% plagioclase feldspar and thus have anomalously low abundances of mafic minerals, and hence also Fe.

In anorthosites, where $Fe_2O_3^* < (1.5 + TiO_2)$, negative values of FeO will result from Irvine & Baragar's approximation. An alternative has been provided by Eric Middlemost[6], who, based on similar but updated database analysis designed to facilitate the calculation of normative mineralogy from the chemical composition of the rock, suggested that the ratio of Fe_2O_3/FeO ranges from around 0.2 in basaltic melts up to 0.5 in granitic melts, with recommended specific values for this ratio offered for a range of volcanic rock types. This offering is an update of a Fe_2O_3/FeO value of 0.15 proposed specifically for basalts, suggested earlier[7].

These approaches are probably reasonably reliable, and at least provide a basis for comparative study, in the case of igneous rocks. However, these approximations would be irrelevant in the study of sedimentary and metamorphic rocks and minerals. Chemical sedimentary rocks are precipitated in a potentially chemically homogeneous equilibrium at low temperatures (<100 °C) and relatively oxidizing conditions (compared to magmas). Metamorphic rocks are similarly equilibrated at higher temperatures and over a range of oxidation states within the crust, but for which Fe_2O_3/FeO values can be calculated based on thermodynamic principles once the equilibrating conditions have been set, and then the predicted mineral assemblage can be matched to the observed one. Clastic sedimentary rocks, which represent a mixture of rocks and minerals formed in a range of environments, and then cemented together, are probably beyond guessing at, and actual measurements are the only practical approach to a reliable estimation of Fe_2O_3/FeO proportions.

References:

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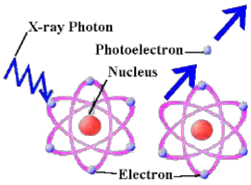
XPS Analysis for establishing elemental valencies in minerals / compounds.

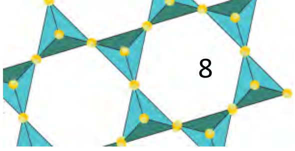
Deborah Craig

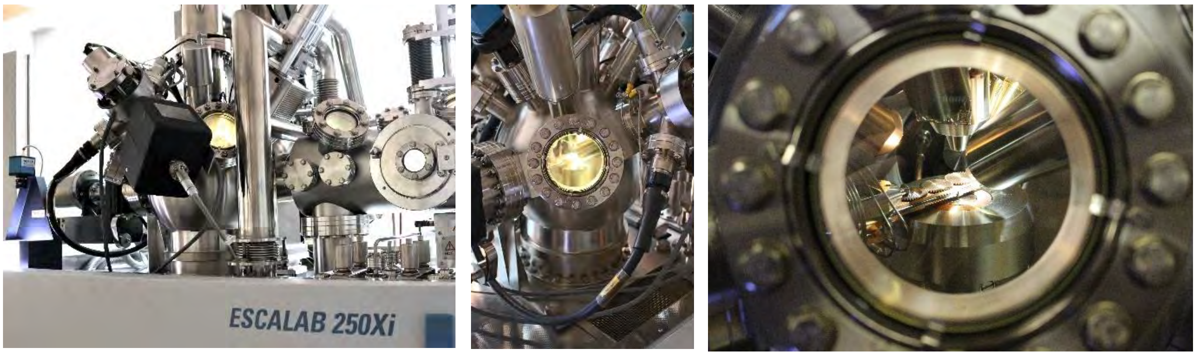
Metallurgist, Anglo American Technical Solutions – Research (RSA)



What is XPS?

XPS, or **X-ray photo-electron spectroscopy**, involves the quantitative spectroscopic analysis of the photoelectric effect induced by x-ray bombard-ment of a sample surface. It can identify the element, its chemical state, and the overall electronic structure and density of the electronic states in the material. For more info, why not try Wikipedia (*just like I did, here. The Editor.*)?





NMISA XPS

The National Metrology Institute of South Africa (NMISA) would like to bring to your attention one of our specialised services which could offer significant benefits to your Research and Development programmes. X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a powerful method for studying the surfaces of solid materials and is a vital tool for understanding surface chemistry. XPS is used to overcome challenges in materials manufacturing, failure analysis and research and covers a wide range of industries and applications such as semiconductors, polymers, catalysts, sensor technology, pharmaceuticals, and the automotive sector to mention but a few.

XPS is commonly used to explore surface chemistry and the data obtained provides a quantified composition of the outer few nanometres of a material. It details both the elements present (except for H and He) and the chemical states or functional groups of those elements. Knowing this information is crucial for understanding and improving the performance of a material. The surface sensitivity of XPS means that it reveals the surface chemistry at a level that other routinely used analytical techniques cannot. The types of materials that can be analysed are typically inorganic solids like metallic alloys, glass, fibres, ceramics, catalysts, and nanomaterials. The technique offers limited support for organic materials, mostly limited to functional group identification. Samples may take the form of fine powders, of which at least 0,1 g is needed, or whole solids that should be less than 10 mm x 10 mm with a maximum thickness of 5 mm.

XPS analysis can be applied in such a way that the technique penetrates the material through a process known as depth profiling, where layers is slowly removed from the surface of the material using an ion beam, collecting data after each etching cycle. With depth profiling the composition changes from surface to bulk or interface-to-interface can be observed and changes due to adhesion, corrosion, oxidation and contamination of the surfaces or interface layers can be readily studied.

For more information, please contact mat@nmisa.org.

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National Metrology Institute of South Africa

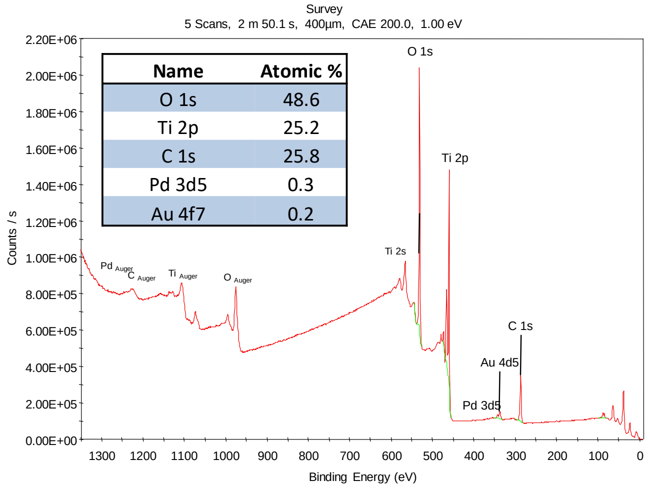
The surface of a solid is the point where it interacts with the environment that it is being exposed to, and information pertaining to the electronic, chemical and physical properties can all depend on the first few atomic layers of the material. Modern laboratories need to have a range of equipment to deliver a complete answer to any material problem. The XPS provides information about the surface of materials that other techniques cannot achieve, this perfectly complements more bulk sensitive analytical tools such as microanalysis, XRF, FTIR, and Raman. During a chemical process, the modified layer of a solid at the reaction interface is often far too thin to be characterized with most techniques. The extreme surface sensitivity of XPS ensures that only the top few nanometers of the sample are analyzed.

The capabilities of XPS includes the identification of which elements are present at the surface, except for hydrogen, the quantification of each element detected and the determination of stoichiometry. The detection limit for most elements is ~0.05 %. The application of XPS is broad and can traverse across many different material types such as metals, oxides, powders, glass, plastics, polymers, carbon, ceramics, fibres, biomaterials and nanomaterials.

The whole system needs to be under an ultra-high vacuum (< 10^{-8} Torr) to ensure surfaces are kept clean and allow longer photoelectron path length. Samples are usually in the form of solid substrates or powders and the technique assumes a homogenous surface, if this is not the case, further data processing is required. If surfaces are insulating, this is a limitation and the insulation layer would need to be sputtered off the surface (using an ion gun – Argon ions, usually takes a few minutes) prior to analysis. The samples are secured to a sample block either with a clip or by means of carbon tape to ensure that they are grounded. The height of the sample cannot exceed 3mm for the standard sample block, if higher, then a specialised sample block would need to be used.

Case Study of a titanium catalyst

An XPS analysis of a TiO_2 catalyst sample (below) containing small levels of gold and palladium was required to determine the chemical state of all the elements, as well as the atomic concentration of each element and their respective chemical states.

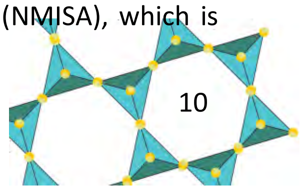


Name	Atomic %
O 1s	48.6
Ti 2p	25.2
C 1s	25.8
Pd 3d5	0.3
Au 4f7	0.2

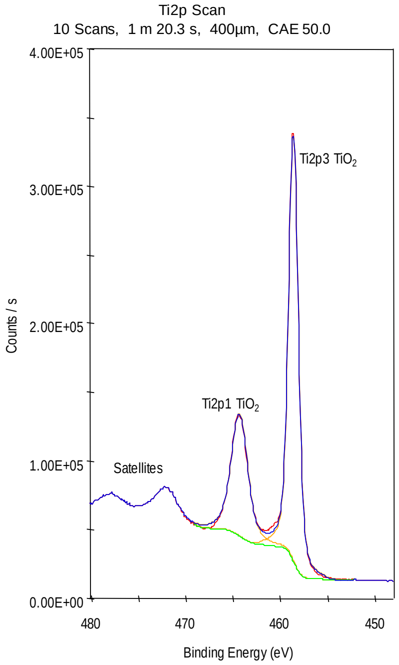
A survey scan indicated the presence of titanium, oxygen, palladium, gold and some carbon contamination on the surface. The survey scan provided quantitative information indicating that majority of the surface is composed of titanium and oxygen (with the exclusion of the carbon contamination), while containing very small amounts of palladium and gold.

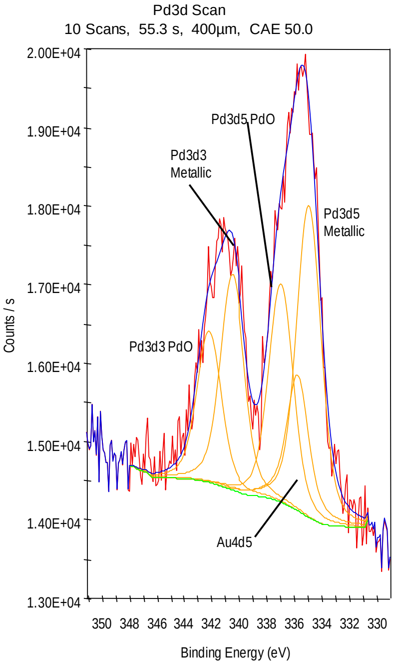
Region scans (above) provide more accurate analyses, more specifically concerning the chemical states of each element present at the surface. The results show that the surface is contaminated with an organic carbon, carbonyl and carboxyl species which together constitute 15 atomic % of the surface coverage. The titanium is present as titanium oxide (TiO_2) at a value of 64.4 % coverage whilst the remaining oxygen that is not associated with the organic contamination, is in the form of palladium oxide (PdO), the only species present for palladium. The gold is found to form 0.2 atomic %, a very small component of the surface and present as metallic gold.

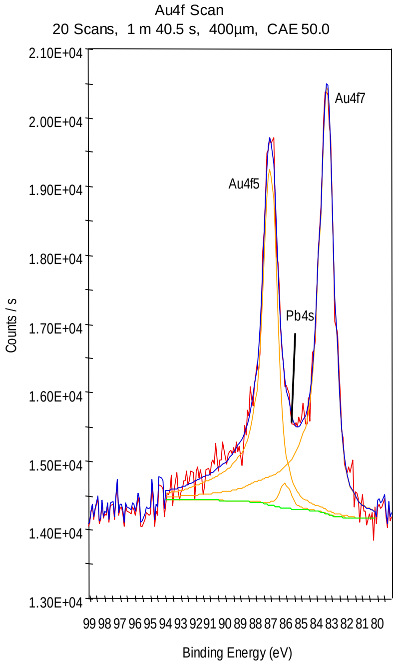
The technique of surface characterization using XPS can be very powerful since the reactions and chemical processes occur at the surface of a solid, the information that one can obtain may provide valuable detail in determining the mechanisms and reactions occurring at any given time. There are two such instruments in South Africa; the one at Anglo American Technical Solutions is used for specialized research applications within the organization to determine the speciation and surface composition after certain chemical interactions. The other instrument is at the National Metrology Institute of SA (NMISA), which is

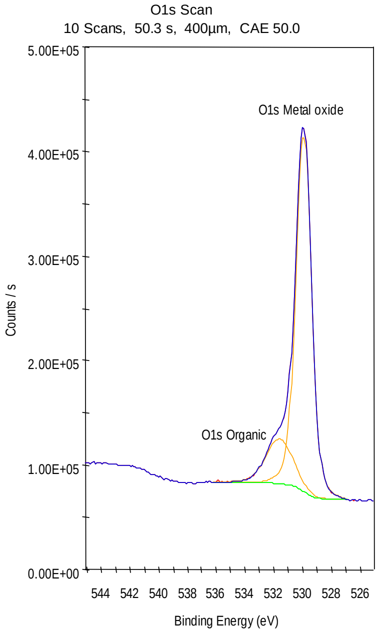


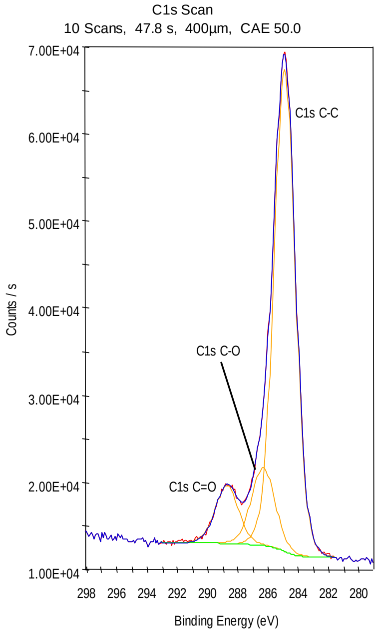
available to undertake sample analyses for any organisation (see accompanying infotisement).











Name	Atomic %
O1s Metal oxide	41.0
Ti2p3 TiO_2	23.4
C1s C-C	20.2
O1s Organic	8.6
C1s C-O	3.7
C1s C=O	2.7
Au4f7	0.2
Pd3d5 Metallic	0.2
Pd3d5 PdO	0.1

THE USE OF MÖSSBAUER SPECTROSCOPY IN OPERATIONAL RESEARCH

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Acting DVC Research and Innovation
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Introduction:

South Africa's total mineral reserves remain some of the world's most valuable, having the world's fifth-largest mining sector in terms of GDP value and even during the COVID-19 pandemic and resulting lockdown periods it was one of the best performers in South Africa.

South Africa has the world's largest reserves of manganese and platinum group metals (PGMs) and among the largest reserves of gold, diamonds, chromite ore and vanadium [1]. Most of these reserves consist of ores that are complex in character and research is necessary before effective processes for their beneficiation can be put into operation. The use of Mössbauer spectroscopy in South Africa to solve operational industrial problems, is however very limited, although Mössbauer spectroscopy was first used by Rudolf L. Mössbauer in 1958 and is defined as a technique of studying the absorption of γ–rays by the nuclei of the different atoms. A more detailed definition entails the recoilless absorption and emission of γ –rays by specific nuclei within a solid, and it provides an opportunity to study the local atomic environment around the nuclei, thus providing information about mineral transformation on a microscopic level [2]. The type of solid, in which the nuclei are found, affects the nuclear emission and absorption energies and the events that occur in Mössbauer spectroscopy is illustrated in Figure 1.

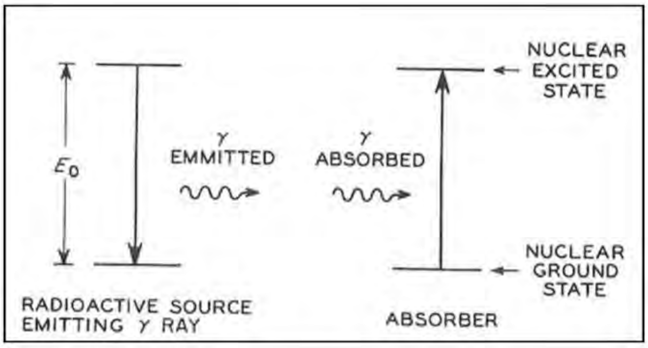

Figure 1*: In the left-hand side of the figure the nuclear state of the radioactive source is shown, and changes from an excited state to a ground state with the result that a γ –ray is emitted. The emitted γ –ray is absorbed by the absorber on the right-hand side of the figure, resulting in an increase in the nuclear state of the absorber, i.e. from ground state to excited state [2].*

The Mössbauer spectrum that is studied and analyzed is produced by varying the γ –ray energy of the source and then measuring the resonance absorption as a function of the γ -ray energy. The γ –ray energies that equal the possible excitation energy of the nuclei in the absorber, resulting in nuclear resonance which leads to an increase in absorption and an absorption line will emerge [2]. The spectrum is usually displayed as a % transmission *versus* γ –ray energy shift spectrum. Analysis of this data is carried out by means of a least square fitting programme. The Mössbauer spectrum can effectively provide two types of information, the first being the relative and absolute line energies that are determined by electronic effects. The second type of information is the nuclear energy levels. These effects are grouped together and termed hyperfine parameters which can be subdivided into the so-called isomer shift, quadrupole interaction and dipole hf interaction [2].

Due to the presence of iron in a large percentage of mineral matter, Mössbauer spectroscopy is a useful, and to a certain degree unique, analytical tool in the identification of iron-bearing minerals [3] and provides quantitative information about the distribution of iron among its oxidation states, the identification of iron-bearing phases, and the distribution of iron among those phases [4]. There are other Mössbauer sources such as tin, gold etc., but these need special experimental set-ups, whilst that of iron can be done at room temperature and is easy to operate.

Experimental procedures

Representative samples for various industry related investigations can be used and prepared according to standard procedures – samples must only be finely ground and placed between two Perspex sheets of roughly 1 cm^2 area. All Mössbauer spectra are obtained with the aid of a Halder Mössbauer spectrometer, capable of operating in conventional constant acceleration mode using a proportional counter filled with Xe-gas to 2 atm. The samples are placed between Perspex plates and irradiated with γ-rays from a 50 mCi 57Co(Rh) radioactive source to obtain a room-temperature Mössbauer spectrum.

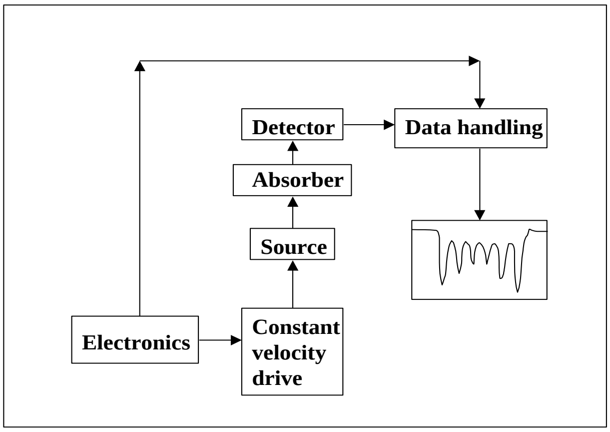

Figure 2A: *Schematic representation of the experimental set-up for Mössbauer spectroscopy.*

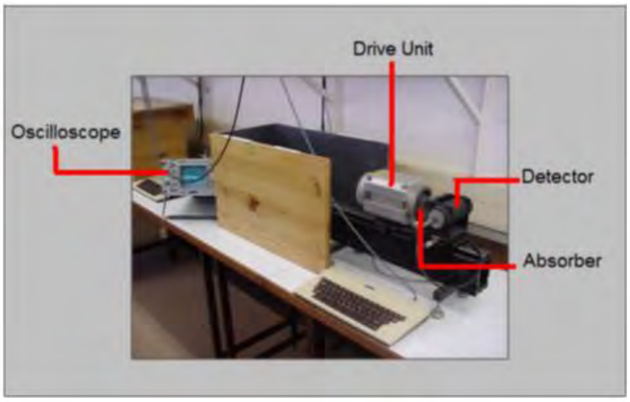

Figure 2B: A*ctual photograph of the apparatus used at the NWU.*

The data are collected in a multi-channel analyser (MCA) to obtain a spectrum of count rate against source velocity. A least-squares fitting program is used and, by superimposing Lorentzian line shapes, the isomer shifts, quadrupole splitting, and/or hyperfine magnetic field of each constituent can be determined with reference to the centroid of the spectrum of a standard α-Fe foil at room temperature. The amount of each constituent present is then deduced by the areas under the relevant peaks. The schematic representation of the experimental set-up used, is shown in Figure 2.

Example results

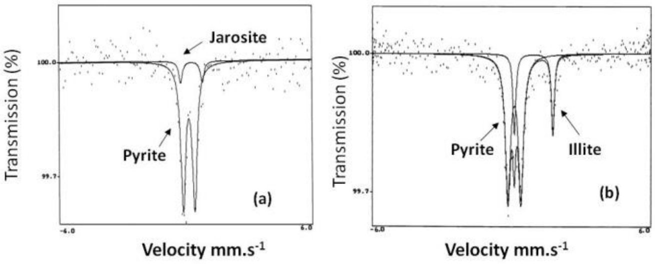

Figure 3: *A typical Mössbauer spectrum of an as-received coal sample containing pyrite and jarosite where the non-isometric form of the doublet indicates that jarosite was present in the sample and (b) a spectrum of another coal sample that contained pyrite and illite with clearly different Mössbauer parameters. [5]*

Dumping of coal ash, waste and discards from gold mining, result in the formation of acid mine drainage (AMD) due to the high sulphur content of the coal and the waste products. The main Fe-S-bearing minerals in most of the dumping sites are pyrite, jarosite and ferrous sulphate, a weathering product of pyrite.

A typical Mössbauer spectrum of two different coal samples is shown in Figure 3 and resulting Mössbauer parameters are shown in Table 1.

In the ash, produced due to gasification of the coal, the main Fe-constituents are $Fe^{2+,3+}$ glass (≈ 30%) and hematite (70%) and an example of a Mössbauer spectrum of the transformation the iron in the coal undergoes, is shown in Figure 4.

Since South Africa is the largest producer of platinum and smelting of the ore, magnetite formation in the 2-stage furnace process can be used as an indicator of the effectiveness of the reduction and the Fe^{2+} and Fe^{3+} ratio is used to monitor the process. In the flash furnace the ratio is 2-6, whilst in the electric furnace it is ≤ 0.02. If not monitored closely a large amount of nickel loss will occur if sent to the waste dump.

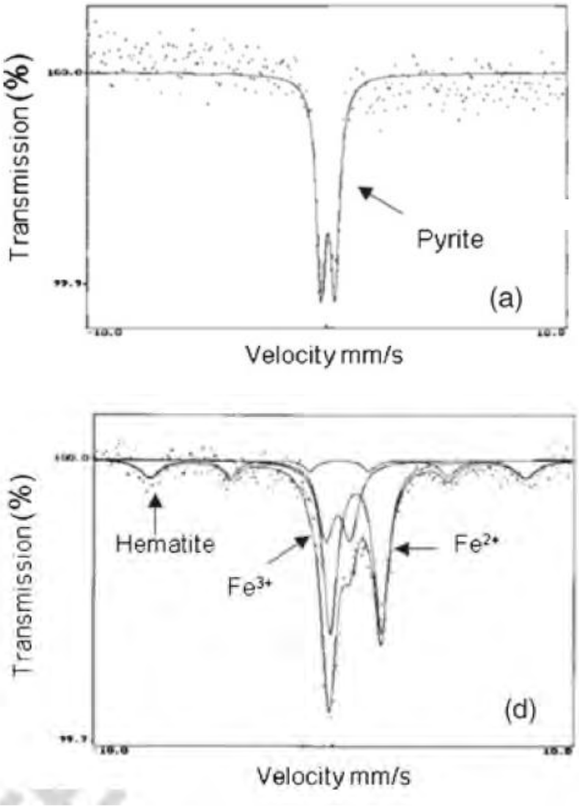

Figure 4. *Mössbauer spectra of the pyrite occurring in the coal (top) and the spectrum of the ash sample after gasification (bottom). [6]*

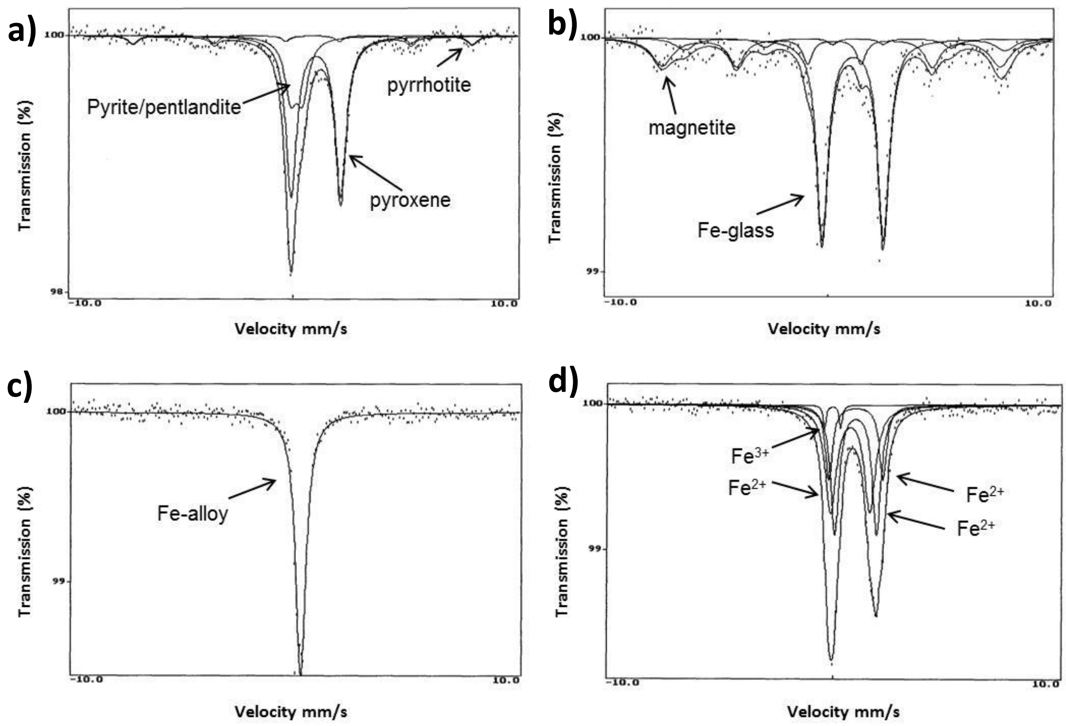

Figure 5. *A Mössbauer spectrum of (a) PGM ore concentrate, (b) slag formed in the flash furnace and sent to the electric cleaning furnace, (c) the spectrum obtained for the matte formed in the flash furnace and (d) the spectrum for the electric cleaning furnace slag. [7]*

Table 1: Room temperature Mössbauer parameters of various coal samples [5-7].

Sample	Mineral	δ (mm.s^{-1}) ± 0.01	Δ (mm.s^{-1}) ±0.01	H (T)	Relative area (%)
Figure 3a	Pyrite	0.33	0.58	-	58
	Ankerite	1.17	1.59	-	42
Figure 3b	Pyrite	0.30	0.62	-	75
	Illite	1.04	2.52	-	25
Figure 4a	Pyrite	0.30	0.61	-	77
Figure 4b	Fe^{2+}	0.93	2.11	-	27
	Fe^{3+}	0.38	1.01	-	38
	Hematite	0.34	-0.08	49.3	35
Figure 5a	Doublet 1 Fe^{2+} pyroxene	1.13	2.21		67±1
	Doublet 2 Fe^{3+} pyrite/pentlandite	0.28	0.53		25±1
	Sextet 1 pyrrhotite	0.77	-0.35	46.6	8±2
Figure 5b	Doublet 1 Fe^{2+} Fe-glass	1.11	2.73		66±1
	Sextet 1 magnetite	1.14	-0.61	44.4	12±1
	Sextet 2 magnetite	0.23	-0.15	46.9	22±2
Figure 5c	Singlet (Fe-alloy)	0.41	0.00		100
Figure 5d	Doublet 1 Fe^{2+}	1.30	2.35		26±3
	Doublet 2 Fe^{2+} {Fe-glass}	1.13	2.04		32±4
	Doublet 3 Fe^{2+}	0.88	1.82		39±4
	Doublet 4 Fe^{3+}	0.06	0.61		3±1

δ = Isomer shift relative to α-iron, Δ = Quadrupole splitting, H = magnetic hyperfine field

Conclusion

One of the main drivers in the economies around the world still remains the exploitation of their vast ore reserves. Mössbauer spectroscopy is unfortunately not used often as a tool to monitor the processes and with the addition of special characterising techniques such as SEM, SEM-EDS, HR-TEM, help to broaden the information gained in the industrial processes discussed and for the industry to better understand the mineral changes and recovery processes. This ensures that the industry obtains an optimum recovery condition and ensuring minimum pollution effects to occur. In this short summary paper two examples are shown of the use of Mössbauer spectroscopy, but many more examples exist in literature.

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Estimating oxidation state using the vanadium-partitioning in Cr-spinel oxybarometer

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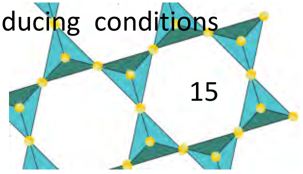
Introduction

Oxygen fugacity (fO_2) estimates are significant in deciphering the stability conditions of oxide and sulphide minerals in mafic magmas. In addition, oxygen fugacity influences speciation of multivalent elements in planetary materials and their distribution between phases, which can be used to constrain fO_2. In geological environments, vanadium exists as V^{3+}, V^{4+}, and V^{5+}, including V^{2+} in highly reduced systems, and previous studies have indicated that redox conditions control V partitioning between minerals and melt (Canil 1999; Papike et al. 2005, 2013; Sutton et al. 2005; Mallmann and O'Neill 2009). Because V is immobile during post-cumulus processes, redox conditions recorded at equilibration remain preserved even in older rocks (Canil 2002). Thus, the partitioning of V in chromite has an excellent potential to serve as an oxygen barometer (oxybarometer) for early-forming oxides. Vanadium oxybarometers have been experimentally calibrated for a wide variety of mineral-melt systems to investigate how V partitioning shifts as a function of fO_2 (e.g. Canil 2002; Sutton et al. 2005; Mallmann and O'Neill 2009; Papike et al. 2013). In chromite, V^{3+} substitutes for Cr^{3+}; therefore, the partition coefficient ($D_V^{Chr/Melt}$) decreases with increasing oxygen fugacity. Thus, V may indicate the overall changes in redox conditions during crystallization. The V-partitioning oxybarometer was tested on chromian spinels from the extensively carbonate-contaminated northern limb of the Bushveld Complex.

Redox dependence of partitioning

The partitioning of 'bulk' vanadium between chromite and melt is strongly dependent on the valence state of V in the melt. Thermodynamic calibrations of Mallmann & O'Neill (2009) use partition coefficients of individual V species, $D_{V^{2+}}^{min/melt}$,$D_{V^{3+}}^{min/melt}$, $D_{V^{4+}}^{min/melt}$, and $D_{V^{5+}}^{min/melt}$, and the equilibrium constants K_a and K_b, to calculate the bulk partition coefficient ($D_V^{min/melt}$). Because V^{2+} exists under highly reducing conditions



(less than QFM-2; Sutton et al. 2005), only V^{3+}, V^{4+} and V^{5+} were included in the calculations. I used the parameters developed by Mallmann & O'Neill (2009) to constrain the relationship between $D_V^{Chr/melt}$ and the oxygen fugacity for the northern limb chromites utilising the following equation:

$$D_{\Sigma V}^{spinel/melt} = \frac{(D_{V^{3+}}^{sp/m} \times (K'_{(a)})^{-1} \times (f_{O2})^{-1/2}) + (D_{V^{4+}}^{sp/m} \times (K'_{(b)})^{-1} \times (f_{O2})^{-1/4}) + D_{V^{5+}}^{c/m}}{((K'_{(a)})^{-1} \times (f_{O2})^{-1/2}) + ((K'_{(b)})^{-1} \times (f_{O2})^{-1/4}) + 1}$$

Assessing the V-in-spinel oxybarometer

Oxygen fugacity values from the V oxybarometer reveal values ranging between -8.78 and -5.76 log units (NNO-0.2 to NNO+1.8). These results suggest that the chromites crystallised under oxidising conditions. Because these chromites are associated with carbonate-contaminated units, oxidising fluids (CO_2, H_2O) mobilised during crystallisation may have increased the overall redox conditions of the magma. Furthermore, in concurrence with high fO_2, the high $Fe^{3+}/\sum Fe$ ratio of these chromites suggest oxidising conditions.

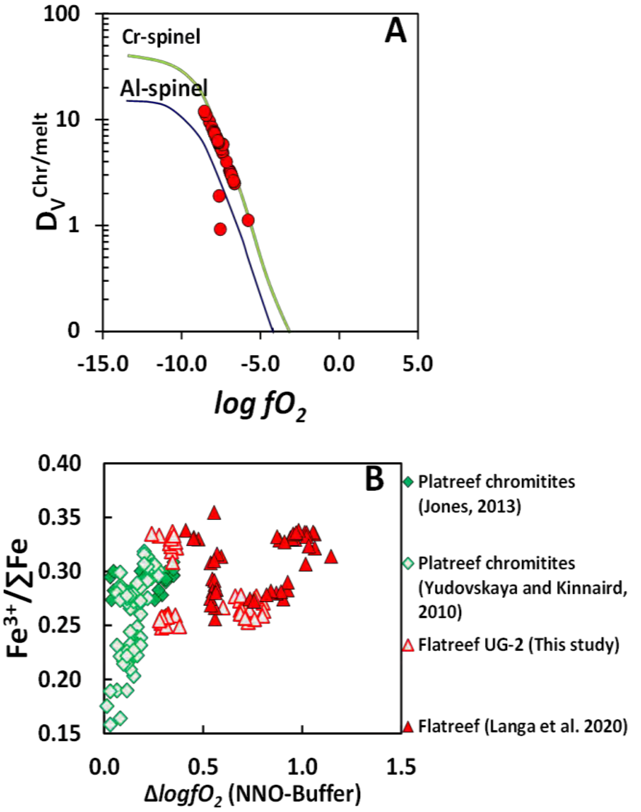


Fig. 1: A) shows the relationship between the constrained $logfO_2$ and the partition coefficient. The overlapped Cr-spinel and Al-spinel compositional lines are extracted from Mallmann and O'Neill (2009). B) shows an increasing Fe3+/∑Fe with increasing fO_2 in northern limb chromites.

It is worth noting that this oxybarometer needs to be used with caution as it requires known V concentrations of the parental melt, which are independent of fO_2.

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Determining the bulk oxidation state of manganese in ores from the Kalahari Manganese Field: implications for processes and processing

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When obtaining standard bulk chemical assays of major elements in manganese ores, the oxidation state of the Mn is often difficult to properly assign, as Mn can

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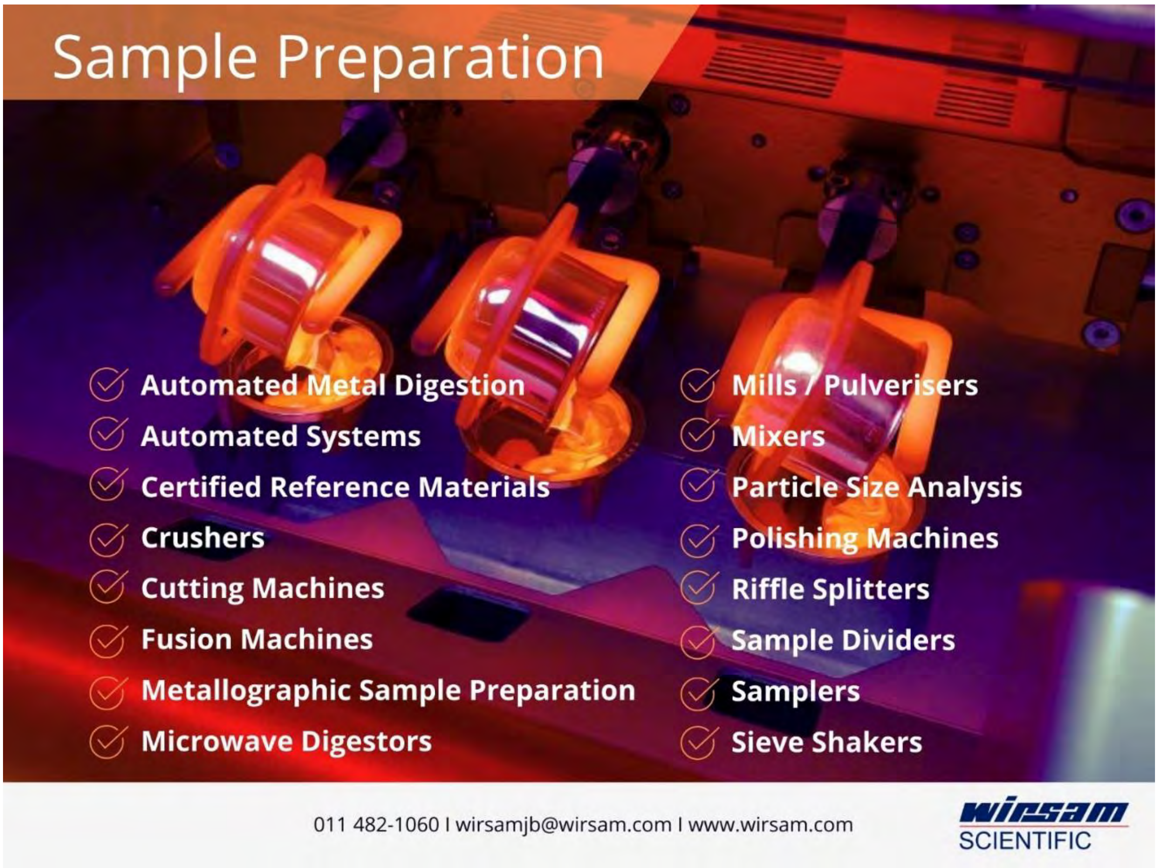

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occur in multiple oxidation states (di-, tri- and tetravalent), all in significant proportions in the ore. Expressing the Mn as Mn_3O_4 may provide good totals in bulk chemical analysis, but still does not fully account for the different Mn oxidation states that may be present in an ore.

Wet chemical methods have been used to determine the amount of oxygen associated with the Mn. However, Mn_2O_3 disproportionates in solution to produce MnO_2 and MnO. Whilst the associated oxygen does not change, the exact species that was originally in the ore cannot be determined. Thus, it is not known whether there are MnO_2 minerals (e.g. pyrolusite) in the original ore, or whether this MnO_2 could have formed from the disproportionation of trivalent Mn, as found, for example, in bixbyite, $(Mn,Fe)_2O_3$.

Methodology

In a similar vein to standard element deportment calculations done in process mineralogical investigations, Mn valence deportment can be calculated (Chetty, 2008). This relies on 1). Electron probe microanalysis (EPMA) to obtain the exact mineral chemical compositions in the ore; 2). A modal analysis of the minerals present in the ore; 3). Good bulk chemical analysis of the ore (expressing Mn as is, with no associated oxygen).

With EPMA, the standard protocol of Deer et al. (1992) is applied to assign anions and cations in the Mn minerals. Additionally, partitioning of the Mn into different valencies appropriate for the given Mn mineral may be determined (e.g., hausmannite, $(Mn,Fe)_3O_4$, contains both divalent and trivalent Mn). In this way, a comprehensive mineral chemical database has been established for ores from the world's largest land-based manganese repository – the Kalahari Manganese Field (KMF) in the Northern Cape Province of South Africa.

To conduct a bulk mineralogical modal analysis, quantitative X-ray diffraction offers a rapid method. Using Rietveld refinement, mineral proportions down to ~1 mass% may be quantified (Figure 1). As Mn is a major element, this detection limit is more than adequate to find the minerals contributing to the Mn budget of the ore.

Major element composition can be obtained using XRF or ICP-OES methods, which are standard in most analytical laboratories. In this instance, there is no need to express the Mn in any given oxidation state.

Using the bulk modal mineral abundance, as well as the mineral chemistry of the identified minerals, a total Mn concentration can be calculated by simple cross-multiplication methods. So, if pure hausmannite contains 69% Mn, and there is 10% pure hausmannite in the sample, then hausmannite contributes 6.9% Mn to the bulk ore assay. Adding up all of the contributions of Mn from the different minerals, we get the mineralogically-derived Mn assay for the sample, which can be compared with the assay measured by bulk analytical methods like ICP-OES or XRF (Figure 2). Where the two assays (measured and calculated) are in acceptable agreement (typically <5% relative difference in concentrations), individual mineral contributions to the total Mn^{2+}, Mn^{3+} and Mn^{4+} content in the sample may be determined in much the same way as for the total Mn content. The different valencies may be expressed as the respective oxides, or a ratio may be calculated to compare different ores.

From processes to processing

In a genetic sense, primary, carbonate-rich, chemical sedimentary ores of the northern KMF are deemed to have been hydrothermally altered to produce high grade ores. This happened through the leaching of the carbonates by acidic solutions that were introduced through normal faults in this part of the orebody (Gutzmer and Beukes, 1995). Within the highly variable hydrothermal alteration regime, different ore types have been identified, and the modal mineralogy quantified. Applying the valence calculations, it was found that the least altered, carbonate-rich ores display very similar Mn^{3+}/Mn^{2+} ratios to the highest grade, hydrothermally altered ore (Figure 3). This led to the theory that the different ore types were formed through a series of acid-base reactions dependent on different fluid/rock interaction ratios, not through redox reactions, as might be assumed from some rather 'oxidised' assemblages (Chetty, 2008). This further enabled the prediction of their distribution relative to major faulting in this part of the ore deposit.

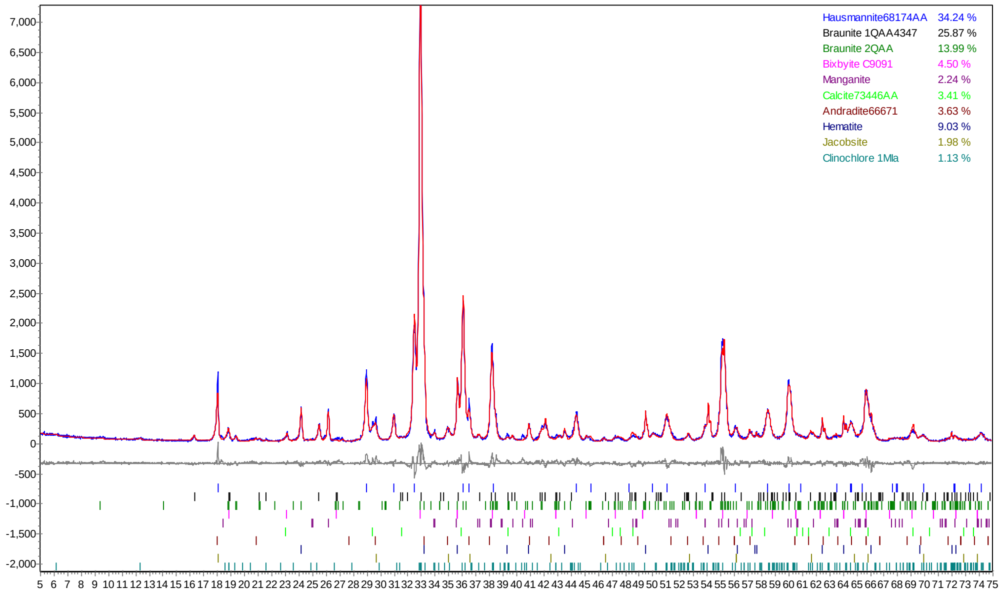

Figure 1: *Measured (blue) and calculated (red) profile for QXRD by Rietveld refinement of a high grade Mn ore.*

(Editor's note: the blue and red curves strongly overlap, so it looks like one curve with occasional colour changes. They are both in there, though.)

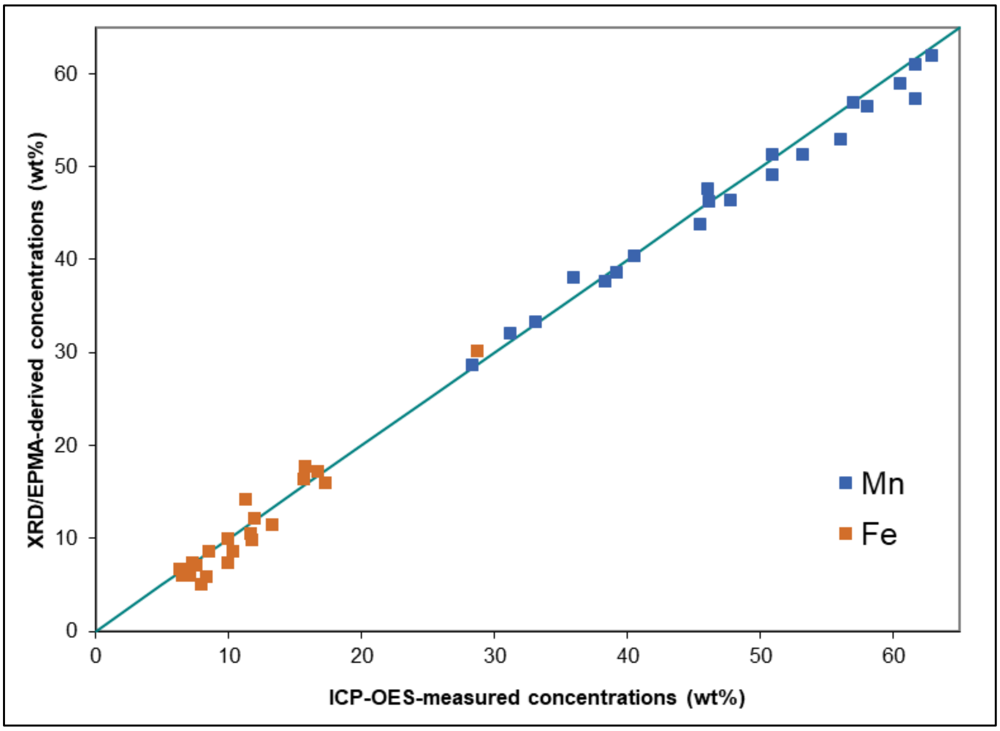

Figure 2: *Measured vs. mineralogically calculated assays for Mn and Fe in ores of different grade.*

When smelting Mn ores to produce ferromanganese (important for the steel industry), the initial bulk ore oxidation state will influence energy consumption in pre-reduction in the furnace. From a processing point of view, starting with a higher oxidation state for the Mn (i.e. a higher oxygen content associated with the Mn, e.g. pyrolusite-rich ore) results in first reduction reactions being highly exothermic, thus releasing energy that can be consumed in further, endothermic reactions. Starting with a lower oxidation state (e.g., hausmannite-rich ore), the reactions are chiefly endothermic, thereby requiring higher inputs of energy into the furnace, which of course, is costly. Figure 1 clearly shows that different ore grades produce similar Mn^{3+}/Mn^{2+} valence ratios, and that ores of similar grades may produce very different ratios. This is primarily a function of the mineralogical make-up of these ores, and brings home the importance of understanding the mineralogy and its effect on furnace operations. After all, we do not process grades, we process minerals.

Thus a novel method was devised using a mineralogical approach to calculate bulk Mn oxidation state of ores from the KMF. This has led to insights into the genesis of hydrothermal ores and a prediction of their distribution in the northern KMF, as well as energy requirements for their smelting.

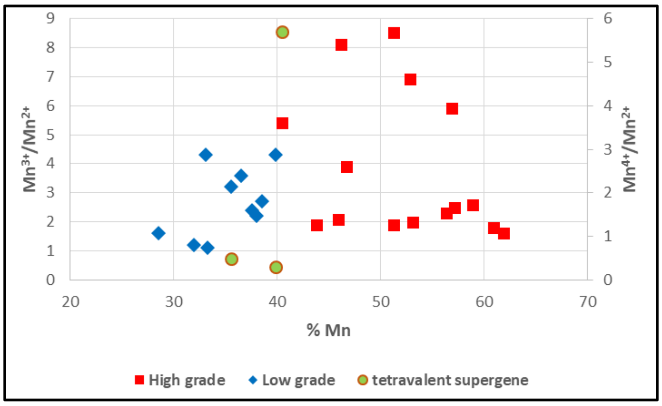

Figure 3: Plot of bulk Mn valence ratios against Mn grade of ore samples (Chetty and Gutzmer, 2018). Note, only the tetravalent supergene data points should be read against the right hand axis of Mn^{4+}/Mn^{2+} ratio.

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Rock Maker 4: The Excel tool for mineral and whole rock chemistry calculations and estimations of ferric and ferrous iron proportions

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The Rock Maker software was initially published in 2012 as a basic Excel worksheet tool for calculations that simulate either the blending of whole rock chemistries, or the extraction of phases or components from bulk rock compositions (Büttner, 2012). Since then, a number of new features and worksheets have been added, and the software is currently available in its fourth edition Rock Maker 4.3.

The publication from 2012 in Mineralogy and Petrology describes the basic functions of the software and presents several worked examples, such as magma mixing, the effect of extracting cumulate phases from parent magmas, or the calculation of whole rock compositions from their mineral modes. These types of calculations are conducted in the worksheet *Whole Rock Maker*. The source data for such calculations may be obtained from XRF, EPMA or ICP-MS analysis or from literature data. The software considers major and minor element oxide contents, trace elements and REE for bulk chemistry calculations. A requirement for correct calculations are appropriate estimations of rock or mineral densities.

The separate worksheet *Phase Rock Maker* may be particularly useful for teaching purposes. This worksheet offers to choose modal compositions from about 100 common rock forming minerals and solid solutions in order to calculate the resulting whole rock composition. The *Phase Rock Maker* is connected to a data base in the worksheet *Mineral Data Set*, which allows to generate mineral compositions in oxide weight percent from relative element oxide proportions or structural formulas. New phases can be added easily.

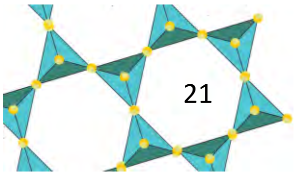
These worksheets may be used for a wide variety of student exercises that aim to explain the relationships between minerals, mineral chemistry, whole rock compositions and rock classification. One possible exercise may be students obtaining modal mineral proportions in igneous rocks from point counting, convert the structural formulas of the ideal mineral compositions into molar oxide proportions and oxide weight proportions, and calculate the whole rock composition from these data. The results can be tabulated and plotted in rock classification diagrams, connecting observations from optical microscopy to mineral chemistry, rock chemistry, and rock identification.

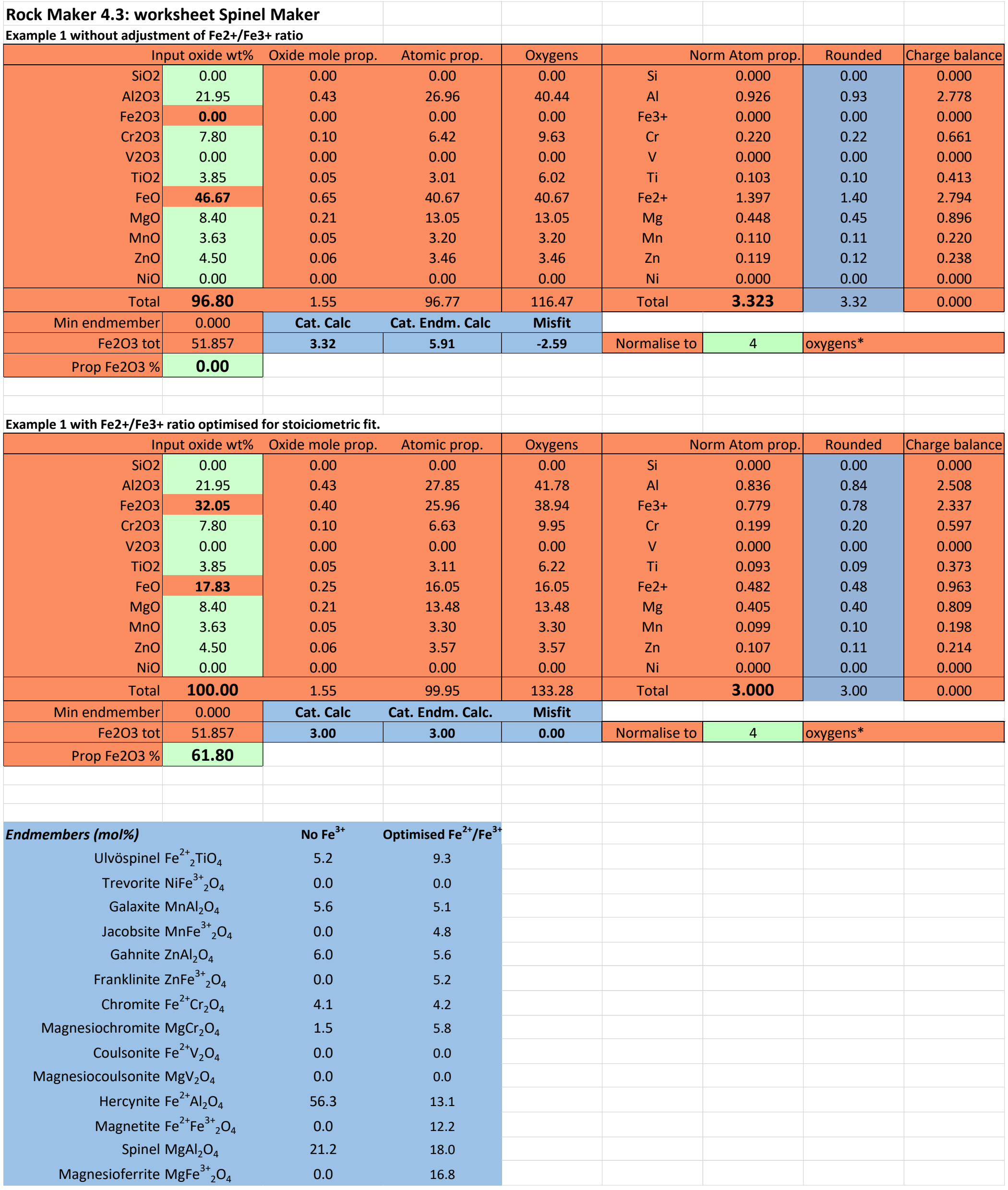
The main additions to the original Rock Maker from 2012 are worksheets calculating cation proportions and endmembers for common minerals and solid solutions, with particular consideration of the oxidation state of iron in solid solutions. These worksheets are mainly based on the original *Mineral Maker* sheet, a one-size-fits all basic calculation of cation proportions from oxide wt. %, with a choice of the number of allocated oxygens and of the FeO/Fe_2O_3 ratio. Many alternatives may be available for such calculations, but Rock Maker 4.3 shows features that are not commonly found. Most worksheets have some form of quality control feature, comparing the cation distribution in the analysis with the ideal mineral stoichiometry as a quantified stoichiometrical error. This may be particularly beneficial to the inexperienced user.

One mineral group for which the oxidation state of iron is particularly relevant is spinel. Rock Maker 4.3 presents three separate spinel worksheets. Two of those are dedicated to the simulation of spinel compositions from specific endmember proportions (*Spinel Data Set, Spinel Simulator*), and one (*Spinel Calculator*) calculates cation proportions and endmembers from simulated or measured oxide compositions. The challenge in calculating spinel endmembers is that, beyond the problem of an unknown Fe^{2+}/Fe^{3+} ratio, each bivalent cation species on the A position may be paired with up to five different trivalent cation species on the B position, or with Ti^{4+} (ulvöspinel), which requires a change in cation numbers on A and B positions. The *Spinel Calculator* overcomes this difficulty by first optimizing the cation total to a value as close to 3 cations by iterative change of the Fe^{2+}/Fe^{3+} ratio, followed by a stepwise distribution of cations to endmembers, considering the Fe/Mg ratio of the remaining composition after each step.

Figure 1 illustrates the importance of adjusting the proportions of FeO and Fe_2O_3. The unprocessed EPMA analysis of Example 1 appears oxide deficient and shows a cation total significantly exceeding 3.00. These cations cannot be distributed in a meaningful way to the spinel endmembers because of a shortfall of trivalent element species that can be allocated to the B position. Adjusting the Fe_2O_3 proportion to 61.8 %, either by manual iteration or application of the Excel Solver tool, delivers an oxide total of 100 %, a cation total of 3.00, and it reduces the misfit in the end-member distribution to 0.00. The calculated end-member proportions shift from a hercynite/spinel dominated composition to a solid solution with significant magnetite, magnesioferrite, jacobsite and franclinite components.

The *Pyroxene* worksheet shows an elaborate distribution of cations to 14 different endmembers, using a similar procedure as the *Spinel Maker*. The rationale of the step-by-step distribution procedure is evident from a labelled section within the worksheet. In addition to these 14 endmembers, the software normalizes the cation proportions to the three endmembers of the pyroxene quadrilateral, enstatite, ferrosilite and wollastonite. Optimizing the oxidation state of iron is critical to the correct allocation of cations to the aegirine/aegirine-augite and essenite endmembers. Excel-Solver based iterations optimize the proportion of ferric/ferrous iron in order to minimize the stoichiometric misfit.





Rock Maker 4.3: worksheet Spinel Maker

Example 1 without adjustment of Fe2+/Fe3+ ratio

	Input oxide wt%	Oxide mole prop.	Atomic prop.	Oxygens		Norm Atom prop.	Rounded	Charge balance
SiO2	0.00	0.00	0.00	0.00	Si	0.000	0.00	0.000
Al2O3	21.95	0.43	26.96	40.44	Al	0.926	0.93	2.778
Fe2O3	**0.00**	0.00	0.00	0.00	Fe3+	0.000	0.00	0.000
Cr2O3	7.80	0.10	6.42	9.63	Cr	0.220	0.22	0.661
V2O3	0.00	0.00	0.00	0.00	V	0.000	0.00	0.000
TiO2	3.85	0.05	3.01	6.02	Ti	0.103	0.10	0.413
FeO	**46.67**	0.65	40.67	40.67	Fe2+	1.397	1.40	2.794
MgO	8.40	0.21	13.05	13.05	Mg	0.448	0.45	0.896
MnO	3.63	0.05	3.20	3.20	Mn	0.110	0.11	0.220
ZnO	4.50	0.06	3.46	3.46	Zn	0.119	0.12	0.238
NiO	0.00	0.00	0.00	0.00	Ni	0.000	0.00	0.000
Total	**96.80**	1.55	96.77	116.47	Total	**3.323**	3.32	0.000
Min endmember	0.000	**Cat. Calc**	**Cat. Endm. Calc**	**Misfit**				
Fe2O3 tot	51.857	**3.32**	**5.91**	**-2.59**	Normalise to	4	oxygens*	
Prop Fe2O3 %	**0.00**							

Example 1 with Fe2+/Fe3+ ratio optimised for stoiciometric fit.

	Input oxide wt%	Oxide mole prop.	Atomic prop.	Oxygens		Norm Atom prop.	Rounded	Charge balance
SiO2	0.00	0.00	0.00	0.00	Si	0.000	0.00	0.000
Al2O3	21.95	0.43	27.85	41.78	Al	0.836	0.84	2.508
Fe2O3	**32.05**	0.40	25.96	38.94	Fe3+	0.779	0.78	2.337
Cr2O3	7.80	0.10	6.63	9.95	Cr	0.199	0.20	0.597
V2O3	0.00	0.00	0.00	0.00	V	0.000	0.00	0.000
TiO2	3.85	0.05	3.11	6.22	Ti	0.093	0.09	0.373
FeO	**17.83**	0.25	16.05	16.05	Fe2+	0.482	0.48	0.963
MgO	8.40	0.21	13.48	13.48	Mg	0.405	0.40	0.809
MnO	3.63	0.05	3.30	3.30	Mn	0.099	0.10	0.198
ZnO	4.50	0.06	3.57	3.57	Zn	0.107	0.11	0.214
NiO	0.00	0.00	0.00	0.00	Ni	0.000	0.00	0.000
Total	**100.00**	1.55	99.95	133.28	Total	**3.000**	3.00	0.000
Min endmember	0.000	**Cat. Calc**	**Cat. Endm. Calc.**	**Misfit**				
Fe2O3 tot	51.857	**3.00**	**3.00**	**0.00**	Normalise to	4	oxygens*	
Prop Fe2O3 %	**61.80**							

Endmembers (mol%)	**No Fe^{3+}**	**Optimised Fe^{2+}/Fe^{3+}**
Ulvöspinel $Fe^{2+}{}_2TiO_4$	5.2	9.3
Trevorite $NiFe^{3+}{}_2O_4$	0.0	0.0
Galaxite $MnAl_2O_4$	5.6	5.1
Jacobsite $MnFe^{3+}{}_2O_4$	0.0	4.8
Gahnite $ZnAl_2O_4$	6.0	5.6
Franklinite $ZnFe^{3+}{}_2O_4$	0.0	5.2
Chromite $Fe^{2+}Cr_2O_4$	4.1	4.2
Magnesiochromite $MgCr_2O_4$	1.5	5.8
Coulsonite $Fe^{2+}V_2O_4$	0.0	0.0
Magnesiocoulsonite MgV_2O_4	0.0	0.0
Hercynite $Fe^{2+}Al_2O_4$	56.3	13.1
Magnetite $Fe^{2+}Fe^{3+}{}_2O_4$	0.0	12.2
Spinel $MgAl_2O_4$	21.2	18.0
Magnesioferrite $MgFe^{3+}{}_2O_4$	0.0	16.8

Figure 1. *The effect of adjusting the iron oxidation state on stoichiometry and end-member calculations in spinel.*

Two worksheets are available for garnet, one for anhydrous and one for hydrous compositions. In anhydrous garnet, the main stoichiometric variable is the ratio of ferric and ferrous iron, which can be adjusted manually or via the Excel Solver tool in order to maximize stoichiometric fit. The distribution of cations to 11 common garnet endmembers in the worksheet *Garnet* follows a similar rationale as the *Pyroxene* sheet, starting with element species that are restricted to single or few endmembers (Ti, Cr), and distributing the remaining elements according to element availability and element proportions.

Few, if any, other worksheets exist for the calculation of hydrous garnet endmembers. Typically, the water content of garnet can be estimated from either the oxide deficiency from 100 wt. %, the silica deficiency, or direct OH quantification. The latter is not routinely done. The former two methods are hampered by several factors that often cannot be easily quantified. The oxide deficiency to 100 wt. % can either result from the presence of OH or from a high proportion of ferric iron in the total iron content. Low Si contents may indicate either the presence of OH or a high schorlomite content, which may be indicated by the presence of significant Ti (and Fe^{3+}). Furthermore, the overall quality of the EPM analysis needs to be carefully considered. However, high oxide deficiencies in combination with low Si and high Ca contents may suggest the presence of hydrous garnet endmembers, and in this case the use of the *Hydrous Garnet* worksheet is recommended. Its use is more complicated, because an iterative approach is required to identify the reasons for low Si on the tetrahedral position (Ti related to schorlomite, or OH related to hydrogrossular or katoite), and the ferric iron content that maximizes stoichiometric fit. The stepwise procedure is explained on the worksheet.

Further worksheets include software for the calculation of micas, serpentine, perovskite, tourmaline, kassite, hydrous amorphous calcium phosphate, olivine and chlorite. Worksheets for sulphides (Sulphide Maker and Sulphide Simulator) operate according to similar principles but use element weight percentages rather than oxide proportions. Future versions of the Rock Maker will be extended and improved, and the author is grateful for suggestions and the indication of errors. The Rock Maker 4.3 software or newer versions are available (click preceding link), and the original publication can be obtained from Springer here, or from the author on request.

Reference:

Büttner, S.H. (2012) Rock Maker: an MS Excel™ spreadsheet for the calculation of rock compositions from proportional whole rock analyses, mineral compositions, and modal abundance. Mineralogy and Petrology 104 (1), 129-135.

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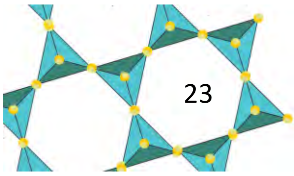
INVITATION FOR SUBMISSIONS TO THE NEXT THEMED ISSUE OF THE GEODE

Minsa invites its members to contribute submissions for our next issue of the Geode, on the theme of “*Determining the modal mineralogy of a rock*” (see below), for September 2021.

Submissions can be sent to minsa@gssa.org.za and should reach us by 31st August 2021.

Submissions dealing with methods for determining the actual (modal) mineralogy of rocks are solicited. From traditional petrographic microscopy (including the even-more traditional use of refractive index oils) we now also have access to modern innovations, from computerised thin section evaluation to QEMSCAN and SEM-based imaging of thin sections and/or rocks. How do YOU do petrography, and why that method?



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!

Be the mentor you wish you had!

Bridge the Gap Geosciences Guidance Program (BTG), is a student run organization that focuses on mentorship between undergraduate and postgraduate students as well as students and industry professionals. In addition BTG hosts a number of informative talks, workshops and field trips to expose students and graduates to opportunities and expectations in the work environment.

Earn CPD points through mentoring!

Be the mentor you wish you had and assist in giving some guidance to geology undergraduate and postgraduate students by signing up to be a mentor through BTG. We invite all geosciences/ mining related companies, industry professionals and academics to 'bridge the gap' between university and industry, and to act as positive role models by joining the BTG program as a mentor, sponsor or motivational speaker.

If you are interested in getting involved please complete the Google form by clicking on the following link: https://forms.gle/Sf5tMciuSStAQuFL8

BridgeTheGap
GeosciencesGuidanceProgram
EMPOWER || INSPIRE

Your influence can go a long way in encouraging and shaping aspiring geologists to become future leaders. We believe that each of us can inspire and empower students by being 'the mentor you wish you had'

The program will start in February/March 2021

Other Gems

Great moments in Geological Education: the KZN diamond field

In June 2021 the apparent discovery of a prospective new diamond field was announced near the village of KwaHlathi, south of Dundee, in KwaZulu-Natal, featuring abundant crystals accessible near the surface, in a manner strongly reminiscent of the Kimberley diamond rush of 1871. From the perspective of the geological community, this was always going to be a long shot, as photos of locals holding handfuls of multi-centimetre-sized angular euhedral to subhedral crystals flooded the internet and the news.

KwaHlathi, east of Ladysmith

from SABC News

It behooves us to address this through the following elements:

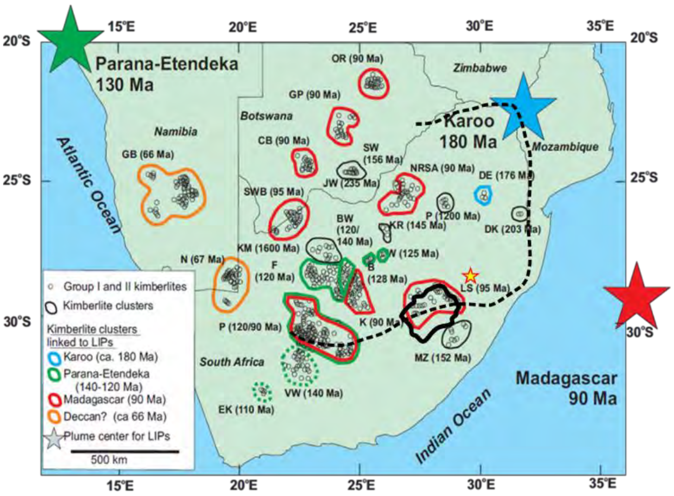
1. 100+ years of mineral exploration by 'experts' has failed to reveal this resource, therefore these cannot be anything valuable (insert patronizing noises here).
2. Is this the right area to find diamonds anyway?
3. How can anyone confuse diamonds with some other, more common mineral (quartz, specifically)?
4. What economic value is there in quartz, then?

How is it that locals could find what has eluded the experts for so long?

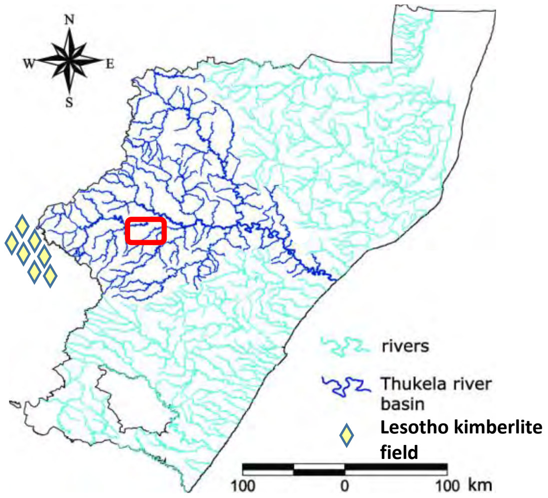
While yes, on the surface (so to speak), it seems unlikely that nobody would have discovered a virtually at-surface trove of non-lithified mineral grains, there are factors that allow for this to be considered. First, there is a long history of world-class ore deposits being discovered by accident, even after having been mapped in detail by geologists, never mind lay-persons. It is true that pyrite acquired the nickname of "Fool's Gold" because of the confusion of over-stimulated potential prospectors confusing it for gold (with which it is commonly associated). However, in Canada in my adult lifetime two major ore deposits have been discovered "by accident" (i.e., by persistence in the face of uncertainty). These include the discovery of gold in the early 1980s within less than a kilometre of the trans-Canada highway (constructed in the late 1950s) near Wawa, Ontario, which became the Hemlo gold mining camp, one of the richest gold discoveries in the last century in Canada (>6 million ounces of gold over 20+ years). The Voisey's Bay Ni-PGE ore deposit was discovered in Labrador in the 1990s, where a gossan that had been repeatedly noted, sampled and tested by geological survey geologists over the years finally gave an anomalous (but as it turned out, representative) high metal content that led to the discovery of the biggest economically viable Ni-PGE sulphide ore deposit in recent history, and subsequently to a bidding war that arguably led to the demise (as in takeovers) of both Inco and Falconbridge, the Canadian nickel giants, as a consequence. So just because it seems too good to be true, doesn't mean it still can't be!

Is northwestern KZN right for diamonds?

This region lies within the boundaries of the Kaapvaal Craton, which means that, in theory, kimberlites passing through the craton on their way from the mantle to the surface could access a potentially diamondiferous cratonic root. There is a kimberlite field located not too far away, to the west, in northern Lesotho, associated with 90-95 million year old mantle plume (hotspot) activity beneath the continent. The diagram below, from Rao & Ernst (2018), has been modified to show the locations of the boundaries of Lesotho (solid black line), the edge of the Kaapvaal Craton (dashed black line), and the KwaHlathi area (yellow star), for reference.



A diamondiferous kimberlite, when exposed to the elements, would rapidly decompose and be suitable for excavation by pick and shovel, as demonstrated in the early Kimberley workings. However, a kimberlite would provide a distinctly different matrix than soil. Is it possible that the KwaHlathi area could host placer diamonds? It is not out of the question, as the drainage in the upper Thukela (Tugela) is very broadly consistent with transport from the west into the area (and although the current position of the Thukela is unlikely to be quite the same as it has been over the past tens of millions of years, the Drakensberg volcanic highlands have been there providing a high altitude water source over that entire time).

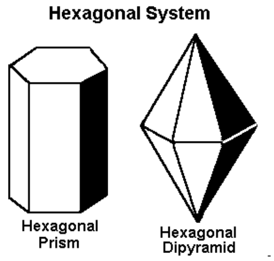


Modern drainage patterns in KwaZulu-Natal, modified after Bertuzzo et al. (2008), showing the location of the KwaHlathi area (red square) and the area of diamondiferous kimberlites in Lesotho to the west.

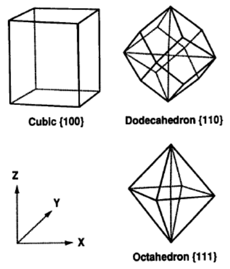
Another factor is that enhanced land degradation over recent times could have accelerated erosion, exposing previously land surfaces buried under late Palaeozoic or Palaeogene sediments. So the possibility of diamondiferous deposits in this area is not entirely far-fetched, on this basis.

How could diamonds be confused with quartz?

Diamonds, composed of C, and quartz (alpha-quartz, specifically), composed of SiO_2, have some fundamental similarities, particularly in the field. In terms of hardness, both are "harder than steel" (around 6 or so on the Mohs scale), which is our normal high-hardness reference material. Both can be translucent and white, grey, colourless, or coloured. Diamond is indeed denser (has a higher Specific Gravity) than quartz, averaging around 3.3 g/cm^3 (similar to an ultramafic rock composed of pyroxenes and olivines, for example) compared to around 2.6 g/cm^3 for quartz. These differences are, however, relatively subtle when dealing with small crystals, and especially for the inexperienced. Quartz also does not have a natural cleavage, but can grow as euhedral crystals when precipitating out of fluids, such as in volcanically-heated geothermal areas (also prevalent in the regions upstream to our site). Diamonds are typically euhedral, and have a characteristically greasy lustre, contrasting to the vitreous lustre of quartz, but quartz can also have a waxy look in some crystals. In terms of crystal symmetry, diamonds possess a cubic crystal lattice, forming octahedra, while quartz belong to the hexagonal crystal *family*, characterized by six-fold (hexagonal) and three-fold (trigonal) symmetry axes.



Hexagonal symmetry, characteristic of quartz.



Cubic symmetry of diamond.

Diamonds are also hydrophobic, in contrast to most silicate minerals, so while quartz will just "get wet" in water, diamonds will not, and will become greasy and oily with handling. (This enables diamonds to be separated from silicate minerals using a greased table with water running across it, which the diamonds stick to but not the silicates).

For a more subtle distinguishing characteristic, the ability of these minerals to conduct heat is very different. Quartz has a thermal conductivity k, in units of $Wm^{-1}K^{-1}$, of around 1-10. It is an insulator, like all silicate minerals. Pure copper, the element we use as out preferred electrical conductor (so far), has a value of around 400, similar to steel (think about how quickly your spoon heats up when you leave one end in your cup of tea or coffee). Diamonds have a k value of 1000-2000, making them more efficient conductors than most metals. So pop those crystals into your tea for a minute, and Bob's your uncle; if it's diamonds, you'll burn your tongue on the hot, greasy crystals, whereas quartz will be wet and cool. Don't rub them on your teeth; that's for pearls, and it will wear out your tooth enamel. Even worse, don't try to bite it: that's for (pure, 24-carat) gold; both quartz and diamonds are harder than your tooth enamel!

What economic value is there in quartz, then?

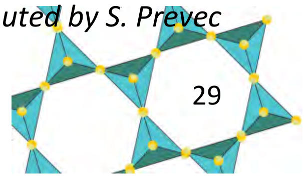
OK, so unlike diamonds, quartz is not "forever", nor is it "a girl's best friend", in general. (That would be dogs or cats, in my experience). As gemstones, both diamonds and quartz variants are assessed in terms of carats (1 carat = 200 mg = 0.2 g), and much of the final value of a stone comes from how it is cut and prepared, in addition to its size, colour, purity, etc. Clear gem quality quartz is on the order of $0.01/carat as raw ore, but can run up to nearly $10/carat for cut gems. Rose quartz and smoky quartz are more valuable, with amethyst (purple-tinted quartz) topping the list at $10-15/carat. Quartz has other, industrial economic value based mainly on its piezoelectric properties. In addition, pure quartz sand is valuable as the raw ingredient for making glass, but for this, beach sand is preferred to crystalline quartz, as it is closer to "process-ready". So of these options, if the KZN quartz field is laden with volcanogenic quartz crystals, which would be consistent with their apparent habit and size population (as distinct from, for example, vein quartz), then raw ore for gemstones might be the best bet, at ca. 5 cents/gram = $50/kg = R714 per kg, at today's exchange rate, assuming all prices in U.S. dollars.

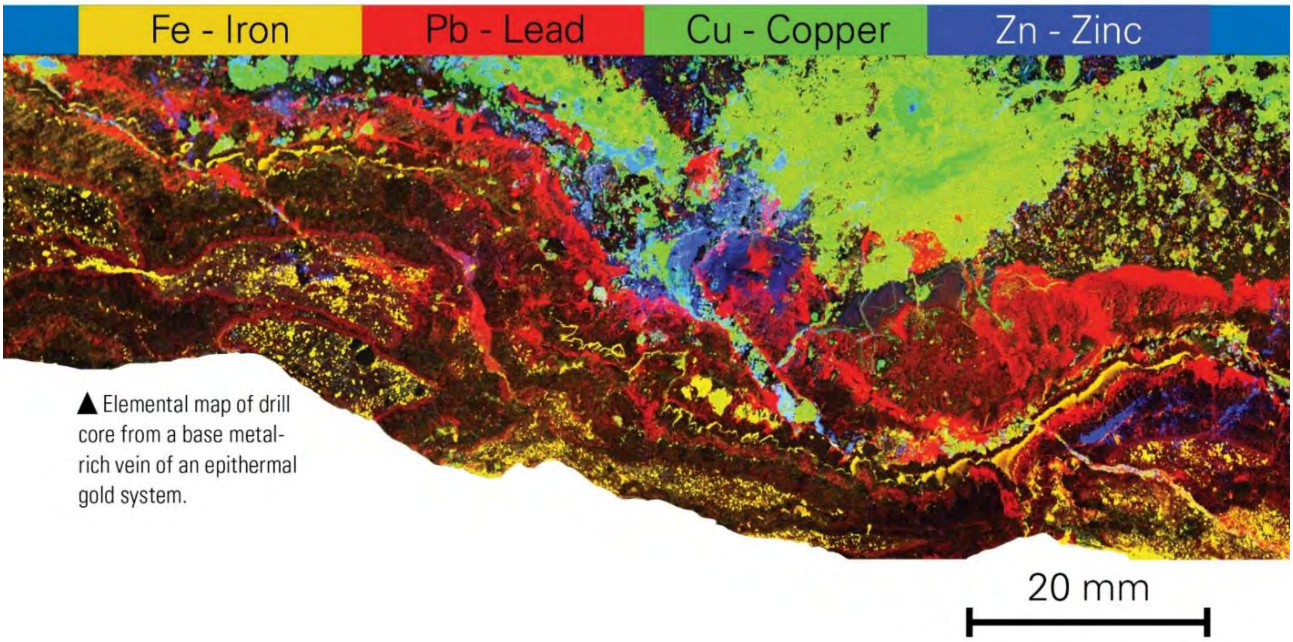
References:

Bertuzzo et al. (2008) Water Resources Research, Vol. 44, W01424.

Rao & Ernst (2018) http://www.largeigneous provinces.org/18sep.

Contributed by S. Prevec




Fe - Iron
Pb - Lead
Cu - Copper
Zn - Zinc
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BRUKER
M4 TORNADO
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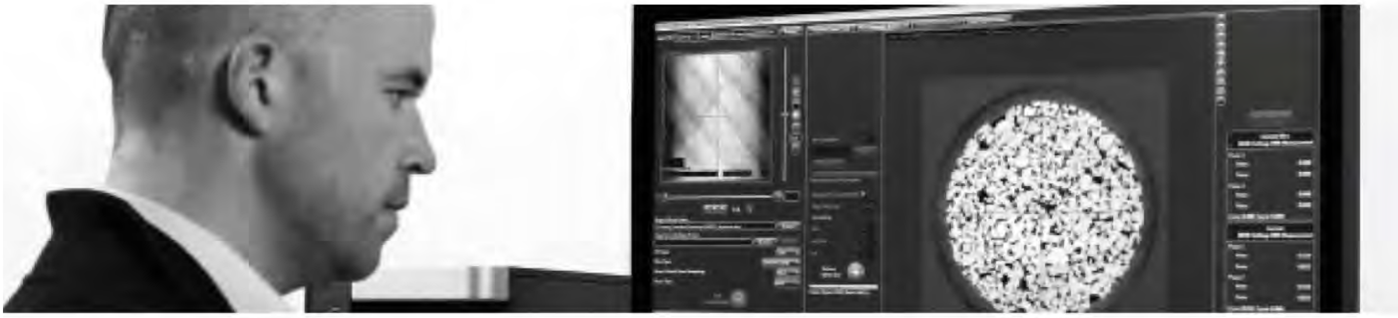
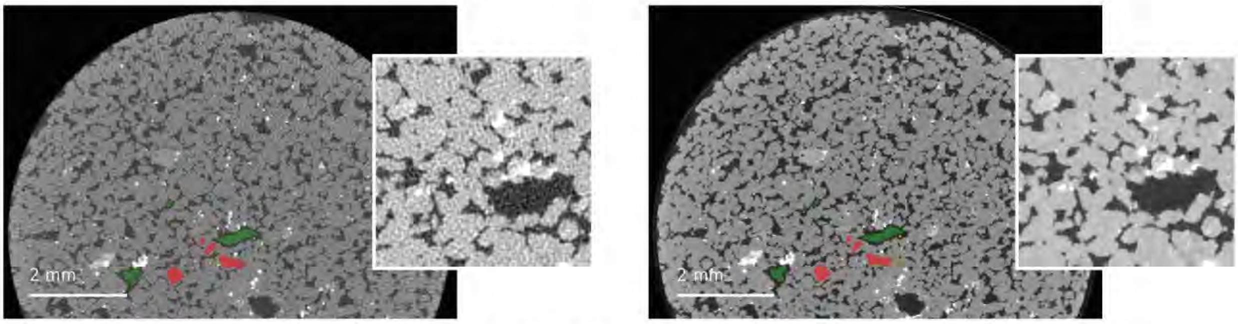


ZEISS OptiRecon for Your Xradia Versa 3D X-ray Microscope

Optimize Tomographic Output for Natural Resources Imaging



Conventional filtered back projection (left) compared to ZEISS OptiRecon (right) at 400 projections each. A typical 1600-projection scan can be reduced by a factor of four, retaining image quality.

The application of X-ray microscopy to industrial workflows is often limited by the acquisition time of the microscope. One of the fundamental components of the 3D X-ray microscopy workflow is tomographic reconstruction, where a set of 2D projections, captured usually at equally spaced angular increments, is transformed into a 3D volume. ZEISS OptiRecon is an implementation of iterative reconstruction that greatly increases acquisition throughput, while optimizing image quality.

Same Results, 4x Faster

ZEISS OptiRecon for the Versa X-ray microscope (XRM) allows you to achieve the same image quality with about one quarter of the data acquisition time for many samples typically found in the oil and gas, mining and metals industries.

Similarly, for many applications where it is currently difficult to achieve good image quality in a typical data acquisition time, ZEISS OptiRecon can greatly improve results. An example is strong interior tomography, where a small region inside a larger sample is imaged at high resolution.

Fast and Efficient

Iterative reconstruction is much more computationally intensive than standard filtered back projection and usually requires very long reconstruction times.

ZEISS OptiRecon features a proprietary, efficient implementation that allows reconstruction of a standard dataset of 1024 x 1024 x 1024 voxels in about three minutes, substantially faster than typical filtered back projection.

Compatible with ZEISS Xradia 500 and 600 series Versa 3D XRM, ZEISS OptiRecon is implemented on a dedicated high-end workstation and does not require a cluster configuration as typically required in other iterative reconstruction offerings.

User-friendly

Normally, iterative reconstruction requires a skilled user and the expertise to fine-tune processing parameters for each dataset. ZEISS OptiRecon has a workflow-based user interface with easy-to-use parameter tuning that does not require specific expertise in tomographic reconstruction. Typical new users find they are able to set up full reconstructions of a standard data-set in fewer than 10 minutes.

Use ZEISS OptiRecon for your digital rock or mineral liberation analyses based on your priority of speed or image quality. ZEISS OptiRecon opens new opportunities for your dynamic *in situ* experimentation at a previously inaccessible temporal resolution.

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ZEISS
Seeing beyond

Bruce's Beauties: Fluorite (International)

Several issues back, 'Geode' featured three fluorite specimens from southern Africa. This time around, the specimens are from the lead-zinc mines in Illinois. The characteristic fluorite-sphalerite-galena assemblage of Illinois specimens are well known amongst collectors worldwide, and especially those in North America.

Fluorite with scattered chalcopyrite crystals on the surface and as inclusions, 7 cm. South-End Rosiclare Horizon, Denton mine, Southern Illinois. Collected in 1986. Bruce Cairncross specimen and © photo.

Fluorite with scalenohedral calcite, 8 cm. Denton mine, Southern Illinois. Bruce Cairncross specimen and © photo..

Fluorite with translucent sphalerite, 7.2 cm. Denton mine, Southern Illinois, collected in 1988. Bruce Cairncross specimen and © photo.

For those readers who are interested in mineral collecting, gemmology, and how it is that Prof. Bruce Cairncross came to find himself embedded in this career/hobby, Bruce was interviewed earlier this year by Mineral Talks Live, hosted by Blue Cap Productions out of Hawaii. The interview, available on YouTube, is ca. 1.3 hours, but the time flies by (yes, I have watched it), and features a look at selected samples, the story of Bruce, and even a brief musical interlude at the end. Click the link on Mineral Talks live, above, to view it.

Minsa Crossword for June 2021

This issue's crossword theme, consistent with the theme of the actual issue, for a change, is mineral oxides and minerals containing transition metals in multiple crystallographic sites.

1		1							2	■	■	3
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4	■		■	■	2							
	■		■	■	■	■	■	■		■	■	
3								■		■	■	
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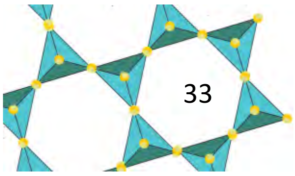
■	■		■	■		■	■	7	■	5		
■	6								■	■		■
■	■	■	■	■		■	■	■	■	■		■
■	■	7										
■	■	■	■	■		■	■	■	■	■		■

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. 5).

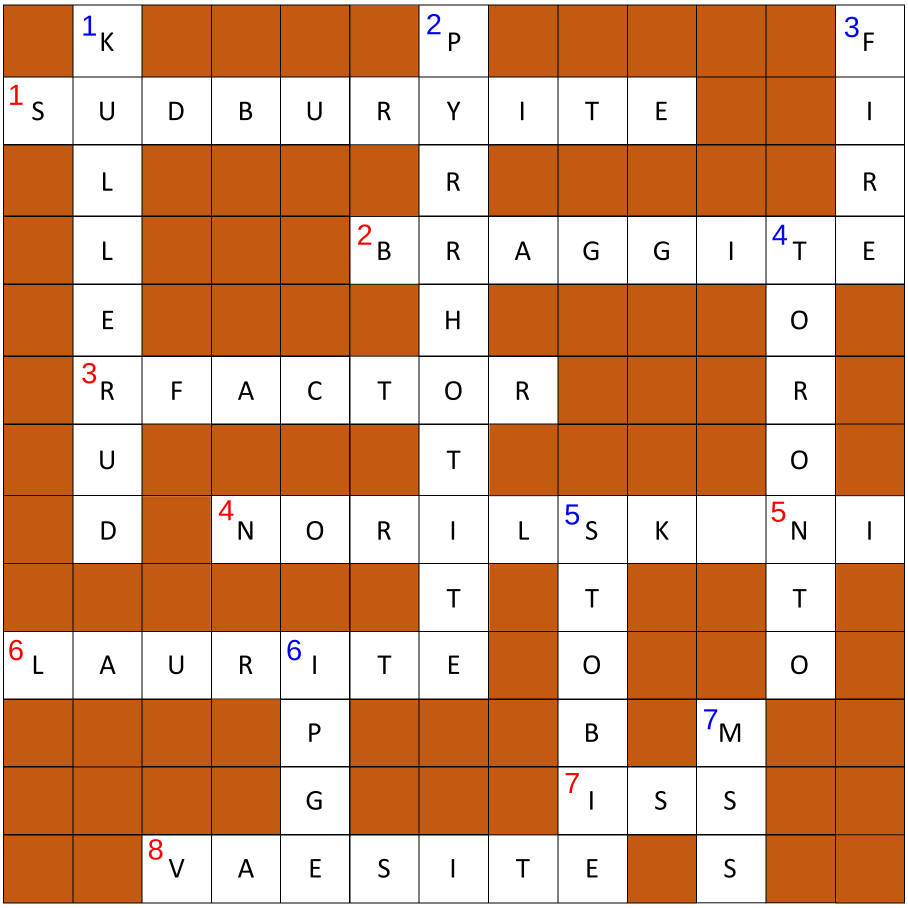
ACROSS:

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. 15-16 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. 18-19 of this issue).



Minsa Crossword Solution for March 2021

This puzzle's theme honoured the late Anthony (Tony) J. Naldrett (1933-June 2020).



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

ACROSS:

1. Naldrett's post-doc employer at the Geophysical Lab, from whence all those wonderfully complex ternary Ni-Fe-S and Cu-Fe-S phase diagrams originated; NiSe$_2$ is named for him.
2. The dominant mineral phase that proceeds from crystallization of immiscible sulphide liquid. Also, non-stoichiometric troilite.
3. ______-assay; The essential preconcentration stage for PGE+Au analysis, usually involving an oven, some powdered Pb or Ni, and S.
4. The city hosting Naldrett's academic home base for more than 30 years.
5. Frood-______ mine; During World War II, this mine accounted for a full 40 per cent of all the nickel used in Allied artillery production; the headframe was finally demolished in December 2020, after >100 years of mining.
6. The acronym for the Ir-associated PGE, compatible in sulphide solids (relative to sulphide liquids).
7. The acronym for the first solids to appear from cooling sulphide liquid, prior to ordering themselves into stoichiometric minerals.

DOWN:

1. The mineral (Pd,Ni)Sb, named for the mining camp at which Naldrett's career was linked for nearly half a century.
2. A sulphide of Pt, Pd and Ni discovered in the Bushveld Complex and named for the father & son who developed the x-ray techniques by which it was characterised.
3. The subject of Campbell & Naldrett's (1979) iconic paper in Economic Geology, providing a key to understanding partitioning behaviour of siderophile metals into sulphides in real magmatic systems. Normally written with a hyphen after the first letter (but not here).
4. The mining camp in Russia prominent in Naldrett's career, host to the largest known Ni-Cu-Pd ore deposit on Earth.
5. The chemical symbol for the main commodity mined at Sudbury (Canada).
6. The main Ru sulphide mineral, prominent as chromite-hosted grains in ophiolites and podiform chromitites.
7. A Cu-rich solid sulphide phase, exsolving at late magmatic temperatures from solids in 7 Down, forming mainly chalcopyrite.
8. NiS$_2$; the high temperature Ni phase associated with pentlandite ores.