

**THE MINERALOGY AND CRYSTALLOGRAPHY OF PYRRHOTITE**  
**FROM SELECTED NICKEL AND PGE ORE DEPOSITS**  
**AND ITS EFFECT ON FLOTATION PERFORMANCE**

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## SYNOPSIS

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Pyrrhotite ( $\text{Fe}_{(1-x)}\text{S}$ ) is one of the most commonly occurring metal sulfide minerals and is recognised in a variety of types of ore deposits. Since the principal nickel ore mineral, pentlandite, almost ubiquitously occurs with pyrrhotite, the understanding of the behaviour of pyrrhotite during flotation is of fundamental interest. For many nickel processing operations, pyrrhotite is rejected to the tailings in order to control circuit throughput and concentrate grade and thereby reduce excess sulfur dioxide smelter emissions. For the platinum group element processing operations however, pyrrhotite recovery is targeted due to its association with the platinum group elements and minerals. Therefore, the ability to be able to manipulate pyrrhotite flotation performance is of importance. It can be best achieved if the mineralogical characteristics of the pyrrhotite being processed are known and their relationship to flotation performance is understood.

Pyrrhotite is known to naturally occur in different forms that have varying physical and chemical attributes. These different pyrrhotite forms are commonly known as magnetic ( $\text{Fe}_7\text{S}_8$ ) and non-magnetic pyrrhotite ( $\text{Fe}_9\text{S}_{10}$ ,  $\text{Fe}_{10}\text{S}_{11}$ ,  $\text{Fe}_{11}\text{S}_{12}$ ) and as a result of their varying properties are expected to show some difference in their reactivity towards oxidation and flotation performance. Yet the accounts in the literature are inconsistent as to which of the pyrrhotite types is more reactive. Similarly, there appears to be little agreement in the literature as to which of the pyrrhotite types is more floatable. It is probable that this lack of agreement arises from the fact that previous studies have not given due consideration to the effect of the mineralogy of the samples examined. The success of the discipline of process mineralogy as a whole however, has been to gain an understanding of how the mineralogy of an ore affects its processing properties.

The objective of this process mineralogy study was to develop the relationship between pyrrhotite mineralogy and flotation performance based on a thorough characterisation of pyrrhotite from selected nickel and platinum group element ore deposits in terms of their crystallography, mineral association, mineral chemistry and mineral reactivity. This was

achieved through the characterisation of the mineralogy and mineral reactivity of pyrrhotite samples obtained from the Sudbury ore in Canada, Phoenix ore in Botswana and the Merensky Reef and Nkomati ores in South Africa. Based on the linkage of these characteristics to flotation performance, an understanding of the relationship and mechanisms that cause pyrrhotite mineralogy to influence pyrrhotite flotation performance has been gained.

Mineralogical characterisation of the pyrrhotite samples in this study was performed using ore petrography, x-ray diffraction and mineral chemistry analysis. On the basis of these results pyrrhotite samples were classified as: single phase magnetic 4C Fe<sub>7</sub>S<sub>8</sub> pyrrhotite, single phase non-magnetic 5C Fe<sub>9</sub>S<sub>10</sub> pyrrhotite; two phase magnetic 4C Fe<sub>7</sub>S<sub>8</sub> pyrrhotite intergrown with non-magnetic 5C Fe<sub>9</sub>S<sub>10</sub> pyrrhotite and as two phase non-magnetic 6C Fe<sub>11</sub>S<sub>12</sub> pyrrhotite intergrown with 2C FeS troilite. Nickel was identified as the main trace element impurity in the pyrrhotite structure and the amount of solid solution nickel in the pyrrhotite structure was correlated with whether the pyrrhotite was magnetic or non-magnetic, and whether it coexisted with another pyrrhotite phase. All pyrrhotite samples investigated showed a strong association to pentlandite that occurred in both granular and flame pentlandite forms. These key features of pyrrhotite mineralogy were in turn shown to be controlled by the bulk composition and cooling history of the monosulfide solid solution (MSS) from which pyrrhotite is derived.

The reactivity of the different pyrrhotite samples towards oxidation was determined using open circuit potential, cyclic voltammetry and oxygen uptake measurements at both pH 7 and 10. Non-magnetic Sudbury Copper Cliff North pyrrhotite was the most unreactive of the samples examined, whereas magnetic Sudbury Gertrude West pyrrhotite was the most reactive. The magnetic Sudbury Gertrude West pyrrhotite was so reactive that open circuit potential and oxygen uptake measurements showed it was already passivated and likely covered with hydrophilic ferric hydroxides. The magnetic Phoenix pyrrhotite was slightly less reactive than the magnetic Sudbury Gertrude West pyrrhotite. The reactivity of the Nkomati Massive Sulfide Body (MSB) mixed pyrrhotite was in between that of the non-magnetic Sudbury Copper Cliff North and magnetic Phoenix pyrrhotite, due to the combined contribution of intergrown magnetic and non-magnetic pyrrhotite to its reactivity.

The flotation performance of the different pyrrhotite samples was investigated at both pH 7 and 10 using microflotation tests. A variety of different reagent conditions was also investigated that included the use of different chain length xanthate collectors (sodium isobutyl xanthate (SIBX), sodium normal propyl xanthate (SNPX)) and the use of copper activation. The collectorless flotation of the non-magnetic Sudbury Copper Cliff North pyrrhotite was the greatest of the samples investigated. Only with the addition of flotation reagents were differences in the floatability of the other pyrrhotite samples identified. Magnetic Phoenix pyrrhotite showed good flotation performance whereas the flotation performance of the magnetic Sudbury Gertrude and Gertrude West pyrrhotite was very poor. The Nkomati MSB mixed pyrrhotite only showed good flotation performance at pH 7. All pyrrhotite samples generally showed improved flotation performance with the use of the longer chain length SIBX collector than the shorter chain length SNPX, whereas the efficiency of copper activation was influenced by pyrrhotite mineralogy, pH and collector chain length.

Differences in the flotation performance of the pyrrhotite samples investigated were linked to their reactivity towards oxidation. Although not directly measured, the formation of hydrophilic ferric hydroxides on pyrrhotite surfaces due to oxidation was inferred as the reason for the poor flotation performance of some of the pyrrhotite samples. Key features interpreted to influence both pyrrhotite reactivity and flotation performance were pyrrhotite crystallography, mineral chemistry and mineral association. It has been proposed that differences in the amount of vacancies in the pyrrhotite crystal structure influence the oxidation rate and similarly the greater proportion of ferric iron in the magnetic pyrrhotite structure was argued to account for its greater reactivity relative to non-magnetic pyrrhotite. Differences in the solid solution nickel content and trace oxygen in the pyrrhotite structure were also proposed as additional characteristics influencing pyrrhotite oxidation rate and flotation performance. Depending on the degree of association of pyrrhotite to pentlandite, its flotation performance could be affected by the liberation characteristics and flotation of composite particles containing abundant locked flame pentlandite, although this could be manipulated by changing the grind size. The presence of nickel ions derived from the flame pentlandite in these composite particles could also assist in the activation of pyrrhotite and further improvement of its flotation performance.

Some guidelines are also presented as to which simple mineralogical and mineral reactivity measurements have been of the most use in developing the relationship between mineralogy and flotation performance.



## DECLARATION

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This thesis has not been submitted in part, or in whole for another degree at any other institution.

Signed: \_\_\_\_\_

## STATEMENT OF ORIGINALITY

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The following outcomes listed below are considered as original contributions from this research:

The creation of a unique pyrrhotite mineral chemistry database consisting of over 1000 EMP analyses from well-known nickel and platinum group element ore deposits derived from Southern Africa and Canada. The inclusion of crystallographic information and details of mineral associations between pyrrhotite types and associated sulfide minerals contributes to the uniqueness of the database. This database also provides a framework upon which to evaluate pre-existing datasets examining pyrrhotite reactivity and flotation performance.

The first complete crystal structure solution of natural 5C non-magnetic pyrrhotite based on the solution of the Sudbury CCN  $\text{Fe}_9\text{S}_{10}$  pyrrhotite (De Villiers *et al.*, Submitted). This includes the establishment that natural non-magnetic 5C pyrrhotite of composition  $\text{Fe}_9\text{S}_{10}$  is actually orthorhombic and not hexagonal as conventionally accepted, and that the crystal structure contains partially occupied iron sites instead of vacant sites as conventionally known for the 4C monoclinic pyrrhotite. This study has also demonstrated that natural 4C  $\text{Fe}_7\text{S}_8$  pyrrhotite does not always fall into the monoclinic  $C2/c$  space group, but can show  $C2$  symmetry based on the crystal structure solution of the Impala Merensky pyrrhotite sample *IMP-1* (De Villiers *et al.*, In Prep).

The refinement of analytical methodology for magnetic and non-magnetic pyrrhotite analysis and quantification using quantitative powder x-ray diffraction (QXRD) with Rietveld refinement and automated SEM techniques.

An understanding of the relationship between pyrrhotite mineralogy, reactivity and flotation performance based on the interpretation of pyrrhotite crystallography, mineral chemistry and



mineral association. Several mechanisms have also been proposed to account for differences in the oxidation rate and flotation response of magnetic and non-magnetic pyrrhotite.

## LIST OF PUBLICATIONS AND PRESENTATIONS

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Becker M., Bradshaw, D.J., De Villiers, J.P.R., Bradshaw D.J. The mineralogy of pyrrhotite from the Sudbury CCN and Phoenix nickel deposits and its effect on flotation performance. Submitted for presentation at the *5th Southern African Base Metals Conference*, Kasane.

Becker M. 2008. Process Mineralogy: Multidisciplinary research to intrigue the curious and challenge the problem solvers. Keynote paper presented at *Africa Uncovered: Mineral Resources for the Future, SEG-GSSA Student Conference*, Misty Hills, Johannesburg.

Becker M., De Villiers J.P.R., Bradshaw D.J. 2008. Evaluation of pyrrhotite from selected Ni and PGE ore deposits and the influence of its mineralogy on flotation performance. In: *9th International Congress for Applied Mineralogy*. pp. 401-409. (AusIMM: Brisbane).

Becker M., Butcher A.R., Botha P.W.S.K., Cropp A.F.R., De Villiers J.P.R., Bradshaw D.J. 2007. Development of a measurement technique for the quantitative determination of hexagonal and monoclinic pyrrhotite: Evaluation using examples from the Bushveld Complex using QEMSCAN®. Presented at *MEI Automated Mineralogy*, Brisbane.

De Villiers J.P.R., Liles D., Becker M. In Press. The crystal structure of a naturally occurring 5C pyrrhotite from Sudbury, its chemistry and vacancy distribution. *American Mineralogist*.

De Villiers J.P.R., Liles D., Becker M. In Prep. The crystal structure of a naturally occurring 4C pyrrhotite from the Merensky Reef, its chemistry and vacancy distribution.

Ekmekci Z., Becker M., Bagki Tekes E., Bradshaw D.J. The relationship between pyrrhotite mineralogy and electrochemistry. Submitted for presentation at the *83<sup>rd</sup> ACS Colloid and Surface Science Symposium*, New York.

Wiese J.G., Becker M., Bradshaw D.J., Harris P.J. 2007. Interpreting the role of reagents in the flotation of platinum-bearing Merensky ores. *South African Institute of Mining and Metallurgy* 107: 29-36.

Wiese J.G., Becker M., Bradshaw D.J., Harris P.J. 2006. Interpreting the role of reagents in the flotation of platinum-bearing Merensky ores. In: *Platinum Surges Ahead*. pp. 175-180. (SAIMM: Sun City).

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## LIST OF ABBREVIATIONS

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AA	Atomic absorption spectroscopy
AMD	Acid mine drainage
AES	Auger electron spectroscopy
ARXPS	Angle resolved x-ray photoelectron spectroscopy
BET	Brunauer, Emmett, Teller
BIC	Bushveld Igneous Complex
BMS	Base metal sulfide
BSE	Back scattered electron
CCN	Copper Cliff North
Ccp	Chalcopyrite
CMC	Carboxymethylcellulose
DETA	Diethylenetriamine
EBSD	Electron back scattered diffraction
EDTA	Ethylenediaminetetraacetic acid
EMP	Electron microprobe
FTIR	Fourier transform infrared spectroscopy
Hex	Hexagonal
HRTEM	High resolution transmission electron microscopy
LA ICP-MS	Laser ablation inductively coupled plasma mass spectrometry
LIMS	Laser ion mass spectrometry
M	Metal
Mag	Magnetite
Mag Po	Magnetic pyrrhotite
Mon	Monoclinic
MSB	Massive Sulfide Body (Nkomati)
MLA	Mineral Liberation Analyser
MMZ	Main Mineralized Zone (Nkomati)
MSS	Monosulfide solid solution

Non-mag Po	Non-magnetic Pyrrhotite
ORP	Oxidation reduction potential
Ortho	Orthorhombic
PDA	Personal digital assistant
Pent	Pentlandite
PGE	Platinum group elements
PGM	Platinum group minerals
PIXE	Particle induced x-ray emission
Po	Pyrrhotite
Py	Pyrite
QEMSCAN	Quantitative evaluation of minerals by scanning electron microscopy
QXRD	Quantitative powder x-ray diffraction
RPL	Reflected polarised light
SEM	Scanning electron microscope
SCE	Standard calomel electrode
SHE	Standard hydrogen electrode
SIBX	Sodium isobutyl xanthate
SIC	Sudbury Igneous Complex
SNPX	Sodium normal propyl xanthate
TETA	Triethylenetriamine
ToF SIMS	Time of flight secondary ion mass spectroscopy
Tr	Troilite
Wt	Weight
X	Xanthate
X <sub>2</sub>	Dixanthogen
XANES	X-ray absorption near-edge structure spectroscopy
XMCD	X-ray magnetic circular dichroism
XPRL	Cross polarised reflected light
XPS	X-ray photoelectron spectroscopy
X-ray CT	X-ray computed tomography
XRD	X-ray diffraction

## GLOSSARY

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The following definitions are given within the context of this study:

Anhedral	Textural term to describe a mineral grain that does not show a well developed crystal form
Antiferromagnetic	Magnetic state of a material where opposing magnetic moments are equal and result in no net magnetic character
Archean	Geological time period 2.5 billion years before present
Disseminated	Textural description of an ore consisting of fine grains of valuable minerals dispersed throughout the bulk of the rock
<i>En echelon</i>	Textural term to describe very closely spaced, overlapping and parallel to sub-parallel structural features
Euhedral	Textural term to describe a mineral grain that shows well developed crystal form
Exsolution	Unmixing of two phases from a solid solution
Ferrimagnetic	Magnetic state of a material where opposing magnetic moments are unequal and result in a net magnetic character
Greenstone belt	Ancient geological structure comprised of metamorphosed volcanic rocks with associated sedimentary rocks
“Hexagonal” pyrrhotite	Common reference to non-magnetic NC pyrrhotite used in the literature. When quoted here, it is in reference to the terminology used by the authors of a particular study, even though 5C pyrrhotite is shown to be orthorhombic.
Liberated	A particle with greater than 95% surface area exposed
Liberation	Proportion of the surface area of a particle which is exposed
Locked	Mineral grain that is entirely enclosed by other grains and has no exposed surface area
Middlings	Mineral grain that is partially liberated

Orogenic	Mountain building
Paramagnetic	Magnetic state of a material where the orientation of magnetic moments is completely random
Petrogenesis	Origin of rocks
Petrography	Description of rock textures
Proterozoic	Geological time period from 1.5 billion to 542 million years before present
Subhedral	Textural term to describe a mineral grain that shows partially developed crystal form
Superstructure	Pyrrhotite structure based upon multiple repeats of the smaller NiAs unit cell