

Chapter 7

DISCUSSION

7.1 Introduction

This chapter develops the relationship between the mineralogy of pyrrhotite from selected nickel and platinum group element ore deposits, and flotation performance based on the mineralogical characterisation of pyrrhotite (Chapter 4), measurement of its reactivity towards oxidation (Chapter 5) and measurement of its flotation performance (Chapter 6). The chapter is subdivided into sections, each of which address one of the key questions proposed in Section 1.3. Once the relationship between pyrrhotite mineralogy and flotation performance has been investigated, some final implications of this relationship are given.

7.2 Variation in Pyrrhotite Mineralogy

The aim of this section is to answer the first key question; "How does the mineral association, mineral chemistry and crystallography vary between magnetic and non-magnetic pyrrhotite."

Based on the variation observed in composition, crystallography and mineral association of magnetic and non-magnetic pyrrhotite samples examined in this study, some generalisations regarding pyrrhotite as a mineral can be made. In order to do this, it is easiest to use a classification system for the different pyrrhotite types which accounts for the composition of pyrrhotite in terms of its mineral association. The classification system proposed is based on several other systems given by Zapletal (1972) and Arnold (1967), but the one used in this work integrates detailed pyrrhotite mineral compositional and crystallographic information and is shown in table 7.1

The basis of this classification system is the division of pyrrhotite occurrences on their mineral association. Pyrrhotite occurrences can be subdivided as either *single phase* pyrrhotite with no association to troilite or another pyrrhotite phase, or as *two phase* pyrrhotite which shares an association to an additional pyrrhotite phase. The degree of nickel association is only shown as solid solution nickel in pyrrhotite in table 7.1, even though the association to pentlandite is of importance in all the pyrrhotite samples examined in this study (e.g. Section 4.2, Figure 6.3, 6.4).

Using the classification given in table 7.1, the first group of pyrrhotite occurrences corresponds to the very iron rich non-magnetic 6C pyrrhotite of composition $\text{Fe}_{11}\text{S}_{12}$ and which coexisted with stoichiometric FeS or 2C troilite. This occurrence corresponds to the Impala Merensky Reef pyrrhotite sample *IMP-2* examined that had an average atomic metal content of 47.9 ± 0.47 %, and average sulfur content of 52.1 ± 0.47 %. This pyrrhotite occurrence showed the least enrichment in solid solution nickel.

The next pyrrhotite occurrence in the proposed classification system shown in table 7.1 is comprised of single phase non-magnetic or single phase magnetic pyrrhotite. The Sudbury CCN pyrrhotite was the only example of single phase non-magnetic pyrrhotite examined in this study (47.2 ± 0.38 atomic metal %, 52.8 ± 0.38 atomic sulfur %), whereas several occurrences of single phase magnetic pyrrhotite were recognised. These included the Sudbury

Table 7. 1: Summary table of the mineralogy and crystallography of the pyrrhotite occurrences in this study. xC represents the pyrrhotite superstructure determined on the basis of the cell parameters or interpreted from mineral chemistry. The average atomic metal, atomic metal / sulfur ratio and weight % nickel contents of magnetic and non-magnetic pyrrhotite with their associated number of analyses (No) and 2σ standard deviation are also given.

PYRRHOTITE SAMPLE	Ideal comp.	xC	No.	At. Metal % Ave	2σ	At. Metal / S % Ave	2σ	Wt Nickel % Ave	2σ
2 PHASE									
Troilite and Non-magnetic Po									
Merensky: Impala (<i>IMP-2</i>) Troilite	FeS	2C - Hex	21	49.4	(0.67)	0.976	(0.026)	0.12	(0.18)
Merensky: Impala (<i>IMP-2</i>) Non-mag Po	Fe ₁₁ S ₁₂	6C - ?	101	47.9	(0.46)	0.918	(0.017)	0.22	(0.07)
1 PHASE									
1 Phase: Non-magnetic Pyrrhotite									
Sudbury: CCN Non-mag Po	Fe ₉ S ₁₀	5C - Ortho	201	47.2	(0.38)	0.894	(0.014)	0.75	(0.19)
1 PHASE									
Magnetic Pyrrhotite									
Sudbury: Gertrude Magnetic Po	Fe ₇ S ₈	4C - Mon	194	46.4	(0.32)	0.867	(0.011)	0.82	(0.19)
Sudbury: Gertrude West Magnetic Po	Fe ₇ S ₈	4C - Mon	68	46.4	(0.37)	0.865	(0.013)	0.78	(0.12)
Merensky: Impala (<i>IMP-1</i>) Magnetic Po	Fe ₇ S ₈	4C - Mon	103	46.5	(0.40)	0.870	(0.014)	0.67	(0.27)
Nkomati: MMZ (<i>MMZ-4</i>) Magnetic Po	Fe ₇ S ₈	4C - Mon	42	46.5	(0.32)	0.870	(0.011)	1.10	(0.18)
Tati: Phoenix Magnetic Po	Fe ₇ S ₈	4C - Mon	203	46.5	(0.33)	0.869	(0.011)	1.06	(0.67)
2 PHASE									
Non-magnetic and Mag Po									
Nkomati: MSB & <i>MMZ-1</i> Non-mag Po	Fe ₉ S ₁₀	5C - Ortho	115	47.2	(0.33)	0.895	(0.012)	0.75	(0.10)
Nkomati: MSB & <i>MMZ-1</i> Magnetic Po	Fe ₇ S ₈	4C - Mon	72	46.6	(0.35)	0.873	(0.012)	0.43	(0.18)
Non-magnetic pyrrhotite	Fe ₁₁ S ₁₂	6C	101	47.9	(0.46)	0.918	(0.017)	0.22	(0.07)
Non-magnetic pyrrhotite	Fe ₉ S ₁₀	5C	316	47.2	(0.36)	0.895	(0.013)	0.75	(0.16)
Magnetic pyrrhotite	Fe ₇ S ₈	4C	699	46.5	(0.36)	0.869	(0.013)	0.84	(0.57)

Gertrude, Gertrude West, Impala Merensky Reef (sample *IMP-1*), Nkomati MMZ (sample *MMZ-4*) and Phoenix pyrrhotite samples. The average atomic metal and sulfur contents of these single phase 4C magnetic pyrrhotite occurrences of ideal composition close to Fe₇S₈ fell within the standard deviation of one another (~ 46.5 atomic metal %, ~ 53.5 atomic sulfur %). Single phase magnetic pyrrhotite occurrences were more nickel rich (0.67 – 1.10 wt % Ni) than single phase non-magnetic pyrrhotite (0.75 ± 0.19 wt % Ni).

The final type of pyrrhotite occurrence proposed here consists of intergrown magnetic and non-magnetic pyrrhotite as observed in the Nkomati MSB and MMZ sample *MMZ-1*. Ideal pyrrhotite compositions of the 4C magnetic phase were close to Fe₇S₈ and showed little compositional difference in terms of atomic metal (46.6 ± 0.35 %) and atomic sulfur (53.4 ±

0.35 %) contents to single phase magnetic pyrrhotite. Coexisting non-magnetic $5C$ Fe_9S_{10} pyrrhotite also showed little compositional difference in terms of atomic metal and sulfur contents (47.2 ± 0.33 ; and 52.8 ± 0.33 %, respectively) to single phase non-magnetic pyrrhotite. The most notable difference however, was in terms of the solid solution nickel content. Magnetic pyrrhotite that coexisted with non-magnetic pyrrhotite was less enriched in nickel than the non-magnetic phase (0.43 and 0.75 wt % Ni, respectively for Nkomati pyrrhotite). Two phase magnetic pyrrhotite intergrown with non-magnetic pyrrhotite was also significantly less enriched in nickel than single phase magnetic pyrrhotite.

In the study of Arnold (1967) which examined the mineralogy of 82 different natural pyrrhotite samples from around the world, 73 % of the samples were mixtures of intergrown magnetic (monoclinic) and non-magnetic (“hexagonal”) pyrrhotite. The remaining pyrrhotite samples were either single phase magnetic (9 % monoclinic), single phase non-magnetic (13 % “hexagonal”) or two phase non-magnetic pyrrhotite (“hexagonal”) intergrown with troilite (5 %). Since the focus of this study is on the detailed examination of pyrrhotite mineralogy from several locations as opposed to a simple examination of the mineralogy of pyrrhotite from multiple locations, comparison cannot be made as to whether the results of this study are consistent with those of Arnold (1967) with respect to the frequency of the different pyrrhotite occurrences.

However, it is possible to compare the range in atomic metal compositions of the different pyrrhotite types with the compilations published by Carpenter and Desborough (1964) and Arnold (1967). The majority of the compositions given in these compilations were based on either bulk chemical measurements or using the x-ray spacing method of Arnold and Reichen (1962). No distinction was provided by these compilations between the composition of magnetic and non-magnetic pyrrhotite, but rather a bulk pyrrhotite composition for the two intergrown phases is given. Therefore, the importance of the data from this study is that it has been obtained using microbeam x-ray analysis methods (EMP; Section 3.2.4), that allowed for spot analysis of the different pyrrhotite phases.

Comparison of the atomic metal content between pyrrhotite examined in this study with that of Carpenter and Desborough (1964) shows that there is good overlap for non-magnetic pyrrhotite, although non-magnetic pyrrhotite in this study extends beyond 47.8 atomic metal % (Figure 7.1a). This can be accounted by the fact that no $6C$ $Fe_{11}S_{12}$ pyrrhotite was

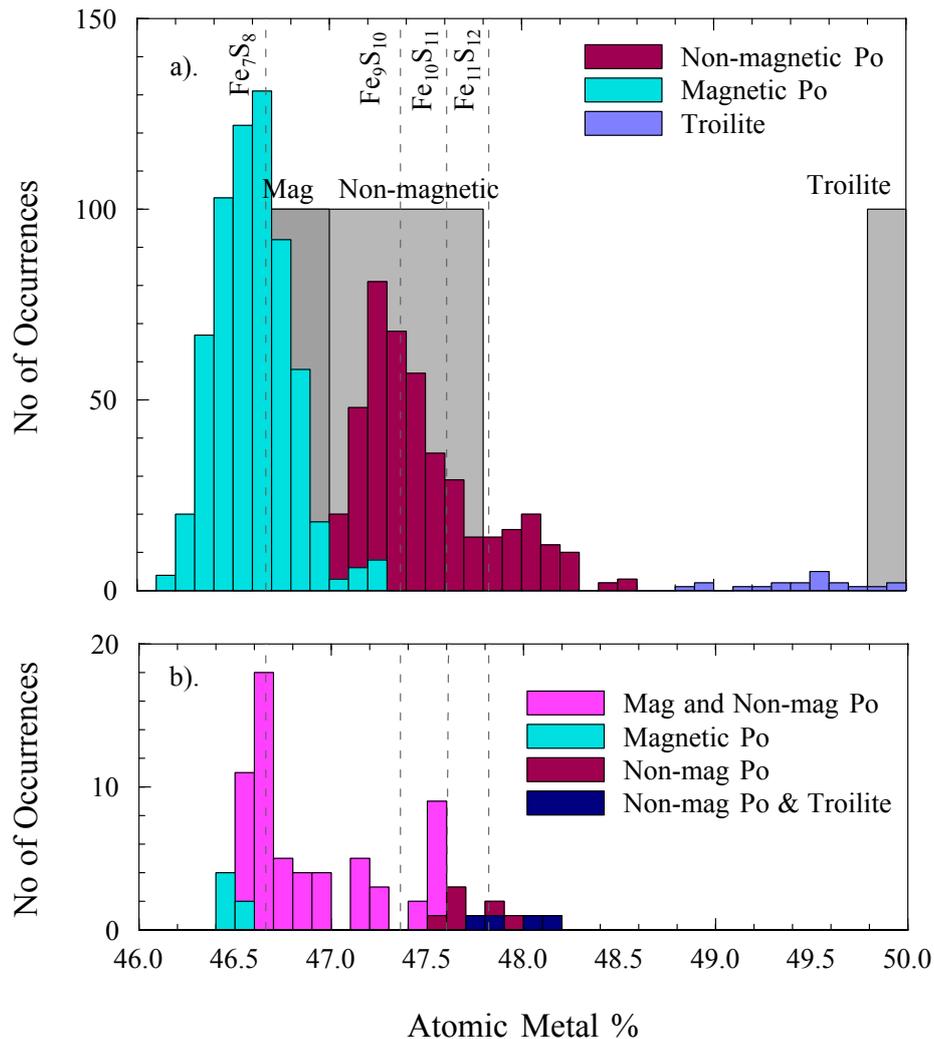


Figure 7. 1: (a) Comparison of the atomic metal content for all magnetic and non-magnetic pyrrhotite occurrences examined in this study. Grey bars illustrate atomic metal contents for pyrrhotite as given in Carpenter and Desborough (1964). (b) Comparison of the atomic metal contents given in Arnold (1967) as determined by the x-ray spacing method. Compositions given for “magnetic and non-magnetic pyrrhotite” and “non-magnetic pyrrhotite and troilite” pyrrhotite represent the bulk chemical composition of the two intergrown pyrrhotite phases. Note the change in scale on the y-axis between (a) and (b).

examined in the study of Carpenter and Desborough (1964). The poor overlap between the troilite compositions is due to the analytical difficulties experienced in analysing Merensky Reef troilite (Section 4.4). The composition of magnetic pyrrhotite in this study was also broader than that given by Carpenter and Desborough (1964) in terms of some of the more atomic metal poor compositions (< 46.5 atomic metal %). This is most likely accounted for by the fact that the detailed variation in pyrrhotite compositions within an ore deposit have been examined in this study (i.e. the intra pyrrhotite compositional variation) as opposed to the

variation between pyrrhotite deposits (i.e. the inter pyrrhotite compositional variation) as studied by Carpenter and Desborough (1964). As such, the compositional variation in magnetic pyrrhotite from any particular location is expected to show a close to Gaussian distribution (Figure 7.1a)

Comparison of the atomic metal compositions of the pyrrhotite in this study with those given by Arnold (1967) as illustrated in figure 7.1b broadly shows a similar range in composition. However, the comparison is limited by the size of the data set of Arnold (1967) and that there was no discrimination between the compositions of intergrown magnetic and nonmagnetic pyrrhotite that represents 73 % of the pyrrhotite examined in the study.

The complete dataset of mineral compositions from the pyrrhotite samples in this study are shown as a histogram of their metal / sulfur ratios in figure 7.2 in order to examine the variation in composition of the mineral pyrrhotite. Metal / sulfur ratios of Merensky Reef troilite are also shown for comparison but due to the small size of the dataset, they are only shown for reference. The three pyrrhotite compositions recognised in this study comprising 4C Fe_7S_8 , 5C Fe_9S_{10} and 6C $\text{Fe}_{11}\text{S}_{12}$, where the 5C and 6C pyrrhotites are part of the NC group of pyrrhotites are shown as distinct groups. A Gaussian distribution function has been fitted to each of the pyrrhotite compositions based on the mean composition and standard deviation of the pyrrhotite analyses (Table 7.1). Based on figure 7.2, three important observations with respect to the mineralogy of pyrrhotite can be made.

Firstly, it is evident from figure 7.2 and table 7.1 that the most frequently occurring metal / sulfur ratio for magnetic Fe_7S_8 pyrrhotite is 0.869, and the ratio for non-magnetic Fe_9S_{10} pyrrhotite is 0.895, both of which are slightly more deficient in iron than the theoretical ratio (metal / sulfur = 0.875 for Fe_7S_8 , 0.900 for Fe_9S_{10}). Therefore it is necessary to determine whether this is statistically relevant or is an analytical artefact due to the precision of the measurement. During the EMP analysis, a synthetic troilite standard was prepared to check the calibration of the pyrrhotite analysis routine (Section 3.2.4). On the basis that the synthetic troilite standard was homogenous, the error in the metal / sulfur ratio associated with repeat analyses of the standard can be used to determine the precision of the technique. Since the 2σ standard deviation calculated for the metal / sulfur ratio obtained from repeat analyses of the troilite standard was 0.01 (Section 3.2.4), this means that the most frequently occurring metal

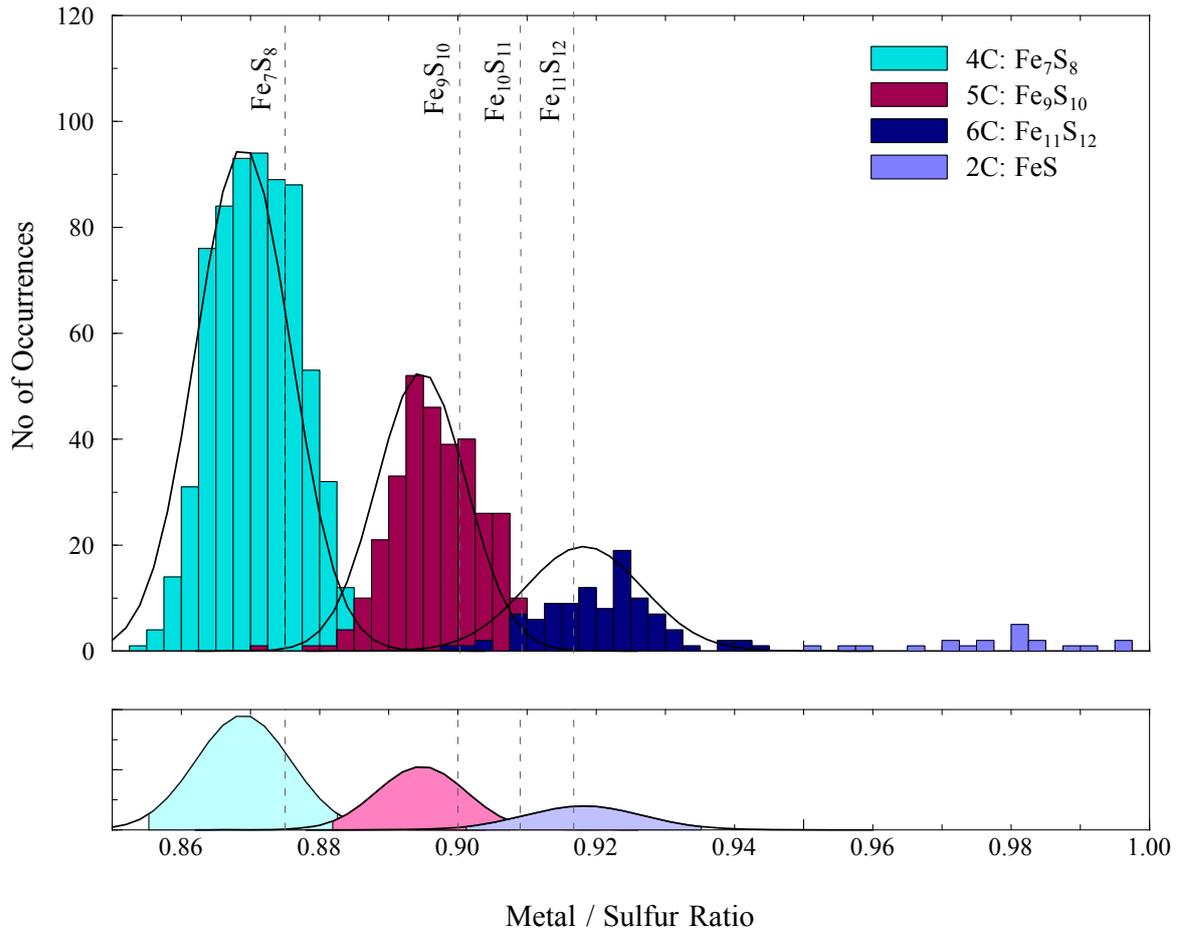


Figure 7.2: Comparison of the atomic metal to sulfur ratios for all 4C magnetic (Fe₇S₈) and NC non-magnetic pyrrhotite (Fe₉S₁₀, Fe₁₁S₁₂) occurrences examined in this study. The normal or Gaussian distribution function corresponding to the mean metal / sulfur ratios given in table 7.1 is also shown. The area under the Gaussian function which represents metal / sulfur ratios within 2σ of the mean are shown in colour in the bottom inset.

/ sulfur ratios for magnetic and non-magnetic pyrrhotite fall within the precision which the EMP allows. Therefore the observation that the most frequently occurring metal / sulfur ratio for magnetic and non-magnetic pyrrhotite in this study is slightly more depleted in iron than the ideal is not significant.

Secondly, it is evident from figure 7.2, that the naturally occurring magnetic 4C Fe₇S₈ pyrrhotite analysed in this study shows a range of atomic metal to sulfur ratios that approaches a Gaussian distribution. Similarly, it is evident that the naturally occurring magnetic 5C Fe₉S₁₀ pyrrhotite analysed in this study shows a range of atomic metal to sulfur ratios that approaches a Gaussian distribution. Even though the distribution of metal to sulfur

ratios for 6C $\text{Fe}_{11}\text{S}_{12}$ pyrrhotite were slightly skewed to more positive values due to troilite contamination, the histogram approaches a Gaussian distribution. This implies that a degree of non-stoichiometry is present in naturally occurring pyrrhotite.

Thirdly, it is evident from figure 4.24 that there is some overlap in the distribution of the metal to sulfur ratios between naturally occurring 4C Fe_7S_8 , 5C Fe_9S_{10} and 6C $\text{Fe}_{11}\text{S}_{12}$ pyrrhotite. In particular, the distribution functions for the Fe_9S_{10} and $\text{Fe}_{11}\text{S}_{12}$ pyrrhotite are noted to show some overlap that encompasses the field of $\text{Fe}_{10}\text{S}_{11}$ pyrrhotite. However, no 11C $\text{Fe}_{10}\text{S}_{11}$ pyrrhotite was encountered in this study even though it has been previously described by others (e.g. Morimoto *et al.*, 1970). The absence of $\text{Fe}_{10}\text{S}_{11}$ pyrrhotite in this study is attributed to the analytical precision of the EMP. Since the calculated two sigma standard deviation in the metal to sulfur ratio of troilite was 0.01 (Section 3.2.4), it indicates that the EMP is unable to distinguish between Fe_9S_{10} (metal / sulfur = 0.900) and $\text{Fe}_{10}\text{S}_{11}$ (metal / sulfur = 0.909). Similarly, the EMP is unable to distinguish between $\text{Fe}_{10}\text{S}_{11}$ (metal / sulfur = 0.909) and $\text{Fe}_{11}\text{S}_{12}$ (metal / sulfur = 0.917). In theory though, discrimination between Fe_9S_{10} and $\text{Fe}_{11}\text{S}_{12}$ is possible. On the basis that both the mineral chemistry and crystallographic studies showed that non-magnetic Sudbury CCN pyrrhotite was 5C Fe_9S_{10} pyrrhotite some confidence can be placed in the results of this study.

However, in order to determine whether the degree of overlap between 4C magnetic and NC non-magnetic pyrrhotite (5C, 6C, and 11C) is real, the field that encompasses the 2σ standard deviation (95% confidence interval) for the composition of naturally occurring 4C, 5C and 6C pyrrhotite samples is shown in the bottom inset of figure 7.2. Since these calculated fields overlap one another, it suggests that the coincidence in metal / sulfur ratios between some 4C and NC pyrrhotite is real. The implication of this is that certain metal / sulfur ratios exist in nature where there is a probability that either 4C or NC pyrrhotite can. Similarly, there must be a probability that for certain metal / sulfur ratios, 5C, 6C or 11C pyrrhotite can form (even if they cannot be distinguished analytically from one another with ease).

Therefore, the mechanism by which the pyrrhotite structure is able to accommodate non-stoichiometry is of interest. Two potential options exist that allow the pyrrhotite structure to accommodate non-stoichiometry. The first of which is based upon the presence of partially occupied iron sites. The crystal structure solutions proposed for stoichiometric magnetic 4C Fe_7S_8 pyrrhotite consist of alternating fully occupied layers with vacancy containing layers

(Tokonami *et al.*, 1972; Powell *et al.*, 2004). Within the 4C pyrrhotite crystal structure, the vacancy layers consist of either fully occupied or completely vacant iron sites (Figure 4.10a). In contrast, the crystal structure proposed for naturally occurring 5C pyrrhotite from Sudbury CCN by De Villiers *et al.* (Submitted), consisted of no fully occupied layers. Instead each layer contained a series of fully occupied and partially occupied iron sites. Several different partial occupancies were also proposed for the 5C Sudbury CCN pyrrhotite structure. On this basis, it is possible that natural pyrrhotite is able to accommodate non-stoichiometry. Therefore, it would be anticipated that the exact partial occupancy of iron sites is variable between individual pyrrhotite crystals.

An additional mechanism to account for the non-stoichiometry present in pyrrhotite is by the presence of non-integral or incommensurate pyrrhotite types. Morimoto *et al.* (1975b) described pyrrhotite crystals from Kishu mine in Japan that were mixtures of 4C, 4.88C and 5C pyrrhotite types. Morimoto *et al.* (1975b) also described pyrrhotite crystals from the Kohmori mine that were mixtures of NC and 2C pyrrhotite with N varying between 5.36 and 5.80. Therefore, the possibility also exists that the non-stoichiometry observed in pyrrhotite samples from this study could be accounted for by the presence of some non-integral pyrrhotite types intergrown with the stoichiometric 4C or 5C pyrrhotite superstructures. However, since pyrrhotite mineral chemistry was used to interpret pyrrhotite superstructure based on the relationship of Morimoto *et al.* (1970), should there have been any non-integral pyrrhotite types present within the samples analysed, they would not have been identified. This does not apply to the pyrrhotite samples analysed by single crystal x-ray diffraction by which it would be possible to recognise non-integral pyrrhotite types.

7.3 Effect of Ore Deposit Formation on Pyrrhotite Mineralogy

The aim of this section is to answer the second key question; "How does ore deposit formation affect the mineralogy of pyrrhotite." Based on the results of Chapter 4; the following are considered important attributes of the mineralogy of the pyrrhotite ore samples examined:

- (i) The magnetic properties, crystallography and mineral chemistry of pyrrhotite.
- (ii) The identity of the minerals and relative proportions of the individual sulfide, oxide and silicate minerals present.
- (iii) The textural properties of the minerals present (grain size, shape) as well as their association to the other minerals present. This would include different types of intergrowth textures between the minerals.

Since the focus of this study is on pyrrhotite, only the mineralogy of the sulfide contingent and how it is affected by ore deposit formation will be concentrated upon. Pyrrhotite samples in this study were selected from magmatic nickel and platinum group element ore deposits (Section 2.1) which are commonly accepted to have formed from the crystallisation of a monosulfide solid solution (MSS; Naldrett *et al*, 1967; Naldrett and Kullerud, 1967; Kelly and Vaughan, 1983). The two main parameters that control the key attributes of the pyrrhotite mineralogy noted above are the bulk composition and cooling history of the MSS, each of which will be further evaluated.

The phase diagram for the FeS to FeS₂ system given in figure 2.8 (Kissin and Scott, 1982; Wang and Salveson, 2005) in section 2.2 shows that the type and composition of pyrrhotite formed is controlled by the bulk composition of the MSS. It is noted that the bulk composition in turn is heavily influenced by sulfur fugacity (f_{S_2}). According to Toulmin and Barton (1964), the mole fraction of FeS in the system FeS-S₂ was determined by both sulfur fugacity and temperature. Figure 2.8 shows that for equilibrium crystallisation of pyrrhotite from the MSS with a bulk composition of 48.5 atomic % iron, the formation of non-magnetic NC pyrrhotite coexisting with troilite is likely. For a slightly lower bulk composition of 47.5 atomic % iron, the formation of non-magnetic NC pyrrhotite is likely. For an even lower bulk composition of 47.0 atomic % iron, the formation of non-magnetic NC pyrrhotite coexisting

with magnetic 4C pyrrhotite is expected. For the lowest atomic % iron contents, the formation of 4C magnetic pyrrhotite coexisting with pyrite is expected.

Since the intergrowth textures between magnetic 4C and non-magnetic NC pyrrhotite types described in this study (Section 2.7, 4.2) were generally lamellae-like features and not irregular intergrowths, they are primary textures indicative of the cooling history of the MSS. These textures are related to the sub-solidus exsolution of magnetic pyrrhotite from a non-magnetic pyrrhotite host. Similarly, the formation of troilite coexisting with non-magnetic NC pyrrhotite is through exsolution. Since the intergrowth textures were noted in Section 4.2 to be crystallographically controlled, it further confirms that they formed through sub-solidus exsolution from the MSS. Exsolution lamellae of magnetic 4C pyrrhotite hosted by non-magnetic NC pyrrhotite could be further developed by lamellae coarsening due to annealing as a result of slow cooling (Brady, 1987). Examples of this type of lamellae coarsening were readily noticeable in the mixed pyrrhotite samples such as the Nkomati MSB or MMZ pyrrhotite. Box work textures were also observed in the Nkomati MSB and Phoenix pyrrhotite samples (Section 4.2), and which Lianxing and Vokes (1996) argued to represent the more advanced stages of lamellae coarsening. Crystal defects such as the twinning noted for some of the pyrrhotite samples examined in Section 4.2 are also a function of the cooling history of the pyrrhotite.

This shows that both the bulk composition and cooling history of the MSS influence the magnetic properties, composition and crystallography of each pyrrhotite phase. Similarly, these factors also influence the nature of the intergrowth patterns between pyrrhotite types and determine whether two phase non-magnetic NC pyrrhotite coexisting with troilite, single phase non-magnetic NC pyrrhotite, two phase non-magnetic NC pyrrhotite coexisting with magnetic 4C pyrrhotite or single phase magnetic 4C pyrrhotite according to the classification scheme given in table 7.1 is formed.

The MSS can be further extended to account for the contribution of nickel to the iron-sulfur system. It is well known from both petrographic and experimental evidence that pentlandite formation occurs via exsolution from the MSS (e.g. Naldrett *et al.*, 1967; Ramdohr, 1969; Kelly and Vaughan, 1983; Fleet, 2006), and the exsolution of pentlandite from pyrrhotite in the samples examined in this study would be no exception. The experimental studies of Kelly and Vaughan (1983) showed the dependency of pentlandite exsolution on the metal / sulfur

ratio and cooling time (Figure 2.13). It is evident from figure 2.13 that the formation of flame pentlandite lamellae was preceded in time by the exsolution of pentlandite blebs and blades on grain boundaries and fractures. Flame pentlandite formation was however, restricted to those experimental studies which had the highest metal / sulfur ratio (metal / sulfur = 0.981).

The composition of pyrrhotite samples used in microflotation tests was shown to contain differing proportions of pentlandite that varied between 6.61 wt % (Nkomati MSB mixed pyrrhotite) and 16.9 wt % (Phoenix magnetic pyrrhotite; Table 3.1, 3.3). However, of greater importance to pyrrhotite flotation performance was the difference in pentlandite liberation. Petrographic examination of the pyrrhotite samples in Section 4.2 showed that the Phoenix magnetic pyrrhotite hosted abundant flame pentlandite, Nkomati MSB contained slightly less flame pentlandite whereas only minor flame pentlandite was noted for the Sudbury pyrrhotite samples. MLA analysis of the flotation feed samples confirmed this difference in the amount of flame pentlandite between the pyrrhotite samples. Pentlandite in the Phoenix magnetic pyrrhotite samples was only 48.5 % liberated, was 53.6 % liberated in the Nkomati MSB pyrrhotite and was over 75 % liberated for the Sudbury pyrrhotite samples. Using pentlandite liberation as a proxy for the proportion of flame pentlandite, it can be concluded that the MSS from which the Phoenix pyrrhotite formed, had a sufficiently high metal / sulfur ratio and a long, slow cooling history that allowed the formation of abundant flame pentlandite. In contrast, it can be concluded the initial metal / sulfur ratios of the Sudbury pyrrhotite samples was possibly not as high, or that the cooling time was slightly more rapid and did not allow for the formation of abundant flame pentlandite.

Localised exsolution of flame pentlandite was also sometimes associated with the formation of monoclinic pyrrhotite. Kelly and Vaughan (1983) described how the localised removal of a metal rich component (pentlandite) from the MSS caused the zone surrounding the area of flame pentlandite exsolution to be more sulfur rich, with the consequent formation of rims of the more sulfur rich pyrrhotite phase (magnetic pyrrhotite) surrounding the pentlandite flames. This was observed in both the Nkomati and Sudbury pyrrhotite samples examined in this study (Section 4.2) and has previously been described by authors such as Naldrett and Kullerud (1967).

In the experimental studies of Naldrett *et al.* (1967) on the MSS, it was similarly shown that pentlandite exsolution was dependent on the initial metal to sulfur ratio of the MSS. In

addition, Naldrett *et al.*, (1967) showed that pentlandite exsolution was dependent on the nickel content of the MSS which in turn affects the composition of pyrrhotite. During the cooling of the MSS, the composition of the MSS continually changes with pentlandite exsolution. The residual nickel content of the MSS however, represents the amount of solid solution nickel substituting for iron and hosted by pyrrhotite (Naldrett *et al.*, 1967; Kelly and Vaughan, 1983). As part of the mineralogical characterisation of pyrrhotite, it was shown that the solid solution nickel content varied between pyrrhotite type, although some correlation existed between nickel content and pyrrhotite association (Table 7.1). For single phase pyrrhotite occurrences, non-magnetic pyrrhotite was less nickel rich than magnetic pyrrhotite. For two phase pyrrhotite occurrences, the host phase was generally more nickel rich than the exsolved phase, i.e. the nickel content of non-magnetic pyrrhotite from which magnetic pyrrhotite lamellae had exsolved was more nickel rich than the magnetic pyrrhotite exsolution lamellae (e.g. Nkomati MSB, MMZ sample *MMZ-4* pyrrhotite).

Other impurity minerals or elements that may be associated with the bulk composition of the MSS include pyrite, chalcopyrite, magnetite and the platinum group elements. If the bulk composition of the MSS was enriched in sulfur and had a sufficiently high fS_2 , the formation of pyrite coexisting with magnetic 4C pyrrhotite would be expected. This was observed for the magnetic pyrrhotite samples in this study (Merensky Reef sample *IMP-1*, Nkomati MSB and MMZ, Phoenix and Sudbury Gertrude and Gertrude West pyrrhotite). No pyrite was noted in the non-magnetic NC pyrrhotite samples examined (Merensky sample *IMP-2*; Sudbury CCN). Given the compatibility of the platinum group elements in a sulfide liquid compared to the silicate fraction, the MSS could also have some association to the platinum group elements (Crockett *et al.*, 1997). If the bulk composition of the MSS was enriched in the platinum group elements then the cooling history would determine whether the platinum group elements occurred in solid solution with pyrrhotite or pentlandite. The formation of discrete platinum group minerals would be a consequence of a fractional crystallisation cooling history.

The effect of the bulk composition and cooling history of the MSS are considered to be the most important features controlling the primary mineralogy of pyrrhotite. Although not necessarily a very significant feature in the samples analysed in this study, the role of secondary processes and their effect on the mineralogy of pyrrhotite should be mentioned. This includes oxidation, hydrothermal alteration and weathering. Depending on the partial

pressure of oxygen during the cooling of the MSS, oxidation may also be relevant during primary ore formation.

Pyrrhotite is known to be associated with magnetite and which can be related to the oxygen fugacity (fO_2) in the Fe-S-O system and hence the bulk composition of the system. The experimental studies of Kullerud (1957) showed that below $675^{\circ}C$, ferrous iron in pyrrhotite could be oxidised to ferric iron with the resultant formation of magnetite if oxygen was introduced to the system. This reaction could be followed by the subsequent formation of pyrite from the excess sulfur (Kullerud, 1957; Naldrett and Kullerud, 1967). It was also shown by Kullerud (1957) and Desborough and Carpenter (1965) that “hexagonal” pyrrhotite could be converted to monoclinic pyrrhotite and magnetite at relatively high fO_2 . Magnetite was noted to occur in association for all of the pyrrhotite samples examined in this study other than the Merensky Reef pyrrhotite, where the oxide phase was chromite. For the Nkomati MMZ pyrrhotite, magnetite occurred as discrete grains as well as very fine-grained rod like inclusions (Section 4.2). It has also previously been shown that the crystal structures of monoclinic and “hexagonal” pyrrhotite may contain some oxygen (Graham and Mc Kenzie, 1987). This provides further evidence to suggest that fO_2 may be an important influence on the bulk composition of the system from which pyrrhotite forms.

Alternatively, “hexagonal” pyrrhotite can be converted to monoclinic pyrrhotite by hydrothermal alteration processes (Desborough and Carpenter, 1965). Lianxing and Vokes (1996) attributed the development of irregular intergrowth textures between magnetic and non-magnetic pyrrhotite due to this type of alteration. Although the formation of magnetic pyrrhotite rims surrounding non-magnetic pyrrhotite was not observed for the samples examined in this study, it does not preclude that this may be an important mechanism controlling the mineralogy of pyrrhotite for some ore deposits. Liebenberg (1970) noted the formation of monoclinic pyrrhotite along cracks and grain boundaries of “hexagonal” pyrrhotite in samples examined from the Bushveld Complex. Mackinawite ($Fe_{(1+X)}S$) has also been known to form during the secondary alteration of pyrrhotite (Ramdohr, 1969; Liebenberg, 1970).

Silicate minerals were not focussed upon here since the majority of the pyrrhotite samples studied were massive in nature. However, the silicate minerals may well influence the flotation performance of pyrrhotite. Two hydrous ferromagnesian silicate minerals in

particular that commonly form through alteration of magmatic sulfide deposits are known to have a detrimental effect on flotation performance of these ores. Talc is a naturally hydrophobic mineral and although only present in small quantities in the Merensky Reef, is known to have a disproportionately detrimental effect on flotation performance, particularly due to its froth stabilising properties (Shortridge, 2002; Wiese *et al.*, 2005). Talc has previously been shown to form through the alteration of orthopyroxene (Hemley *et al.*, 1977; Nesbitt and Bricker, 1978; Viti *et al.*, 2005) which is the major gangue mineral in the Merensky Reef ore. Talc was also reported as a problematic mineral in the processing of the Sudbury ores (Lotter *et al.*, 2008). Serpentine on the other hand, forms through the alteration of olivine (Hemley *et al.*, 1977). The presence of serpentine in the processing of nickel ores may cause severe rheological problems due to its fibrous nature and effect on the yield stress of the ore slurry (Senior and Thomas, 2005; Burdukova *et al.*, 2008).

7.4 Effect of Mineralogy on Pyrrhotite Reactivity

The aim of this section is to answer the third key question, “*How does the reactivity of magnetic and non-magnetic pyrrhotite differ and can these differences be accounted for by the crystallography, mineral chemistry and mineral association of pyrrhotite?*” In order to do this, the results from the open circuit potential, cyclic voltammetry and oxygen uptake experiments in Chapter 5 are first reviewed and discussed in order to understand the nature of the pyrrhotite surface in the different experiments. These results need to be interpreted with care since if the reaction rates are so rapid, an apparently “unreactive” surface which has already been passivated may be detected upon measurement. Only once these results have been interpreted, can any attempt be made to develop the relationship between pyrrhotite mineralogy and reactivity.

Based on the literature review the reaction product of pyrrhotite that most commonly forms under standard oxidising conditions is ferric hydroxide. Since the measurement conditions of the open circuit potential and cyclic voltammetry studies did not include any interaction with flotation reagents, the results can be directly interpreted to give an indication of the difference in reactivity of the pyrrhotite samples due to their mineralogy. Since the differences between the various electrodes were more significant at pH 10 than pH 7 due to the increase in electrochemical reaction rates at the higher hydroxide ion concentrations (Janzen, 1996; Chirita *et al.*, 2008), differences in pyrrhotite reactivity due to mineralogy are best interpreted using the results of the tests at pH 10 (Section 5.2, 5.3).

On this basis, non-magnetic Sudbury CCN pyrrhotite was the most unreactive of the pyrrhotite samples examined in this study. Non-magnetic Sudbury CCN pyrrhotite showed the lowest open circuit potential of the samples examined which suggests the surface of the pyrrhotite electrode was covered with the lowest amount of ferric hydroxide species (Section 5.2.1). Non-magnetic Sudbury CCN pyrrhotite also showed the smallest changes in current density associated with the REDOX reactions in the cyclic voltammetry studies that indicate that the pyrrhotite was not very reactive.

Magnetic Sudbury Gertrude West pyrrhotite was the most reactive of the pyrrhotite samples examined. Since the open circuit potential measurements obtained at pH 10 for the magnetic Sudbury Gertrude West pyrrhotite electrode were by far the highest (Section 5.2.1), it can be

concluded that the surface of the electrode was covered with the greatest proportion of ferric hydroxide species. This was likely due to the very reactive nature of the Gertrude West magnetic pyrrhotite and the consequent formation of ferric hydroxides following rapid oxidation. The cyclic voltammetry studies confirmed the very reactive nature of the Sudbury Gertrude West magnetic pyrrhotite due to the fact that it was the pyrrhotite sample that showed the greatest changes in current density (Section 5.3.5).

The magnetic Phoenix pyrrhotite sample was also relatively reactive towards oxidation although the reaction rates were not as rapid as for the magnetic Sudbury Gertrude West pyrrhotite sample. Open circuit potential measurements obtained for the Phoenix magnetic pyrrhotite were somewhere in between the unreactive non-magnetic Sudbury CCN and very reactive Sudbury Gertrude West pyrrhotite (Section 5.2.1). Similarly, the current density obtained in the cyclic voltammetry studies of the Phoenix magnetic pyrrhotite electrode was significantly greater than the unreactive non-magnetic Sudbury CCN and less reactive than the magnetic Sudbury Gertrude West pyrrhotite (Section 5.3.5).

The reactivity of the Nkomati MSB mixed magnetic and non-magnetic pyrrhotite sample is considered to be in between that of the reactive magnetic Phoenix pyrrhotite and the unreactive non-magnetic Sudbury CCN pyrrhotite samples. Although little difference was observed in open circuit potential between the mixed Nkomati and magnetic Phoenix pyrrhotite electrodes at pH 10 (Section 5.2.1), significantly lower current densities were measured for the REDOX reactions of the Nkomati pyrrhotite in comparison to the Phoenix magnetic pyrrhotite. Significantly higher current densities were obtained in the cyclic voltammetry studies of the Nkomati pyrrhotite relative to the non-magnetic Sudbury CCN pyrrhotite. This indicates that the Nkomati mixed pyrrhotite was less reactive than the Phoenix magnetic pyrrhotite and more reactive than the non-magnetic Sudbury CCN pyrrhotite.

Similarly to the interpretation of the open circuit potential and cyclic voltammetry studies, the results of the oxygen uptake studies are best interpreted at pH 10 in the absence of flotation reagents in order to identify differences in reactivity due to mineralogy. The relatively unreactive character of the non-magnetic Sudbury CCN pyrrhotite was confirmed by the oxygen uptake studies where the lowest oxygen uptake factor was obtained for the Sudbury CCN pyrrhotite relative to the other pyrrhotite samples examined (Section 5.4.5). Next to the

non-magnetic Sudbury CCN pyrrhotite, the lowest oxygen uptake factor was obtained at pH 10 for the slurry of the magnetic Sudbury Gertrude West pyrrhotite (Section 5.4.5). The low oxygen uptake factor obtained for the magnetic Sudbury Gertrude West pyrrhotite slurry is interpreted to be due to the fact that it was already covered by ferric hydroxide species and passivated at the time of measurement due to its very reactive character as evidenced by the open circuit potential and cyclic voltammetry studies. It is probable that despite careful sample preparation for the oxygen uptake tests, sufficient opportunity was available for the oxidation of the very reactive Sudbury Gertrude West pyrrhotite. In contrast, the sample preparation procedure used in manufacturing pyrrhotite electrodes for the cyclic voltammetry studies was able to expose a fresh layer of Gertrude West pyrrhotite at the start of each measurement such that its very reactive nature was recorded by the cyclic voltammetry studies. The very reactive nature of the Sudbury Gertrude West and Gertrude pyrrhotite was also noted during the preparation of the cut pyrrhotite surfaces used for the photomicrographs of the pyrrhotite samples shown in figure 3.3. With the period of a week, the Gertrude and Gertrude West pyrrhotite sample surfaces showed considerable tarnishing whereas, those of the other pyrrhotite surfaces remained relatively fresh.

The highest oxygen uptake factor was obtained for the slurry of the Phoenix magnetic pyrrhotite sample and which confirms its reactive nature. It is also of interest to note, that the slurry containing the Phoenix magnetic pyrrhotite had the lowest dissolved oxygen content of the samples investigated prior to sparging the slurry with oxygen (Section 5.4.5). This indicates that prior to sparging the solution with oxygen, the pyrrhotite had already depleted the available oxygen in solution during oxidation. No indication was obtained from the reactivity studies to suggest that the Phoenix magnetic pyrrhotite surface was already passivated.

Similarly to the open circuit potential and cyclic voltammetry studies, the oxygen uptake factor of the Nkomati MSB mixed pyrrhotite was greater than the non-magnetic Sudbury CCN pyrrhotite and lower than the magnetic Phoenix pyrrhotite. This indicates that the reactivity of the intergrown magnetic and non-magnetic pyrrhotite was in between that of magnetic and non-magnetic pyrrhotite.

The relative differences in reactivity between the pyrrhotite samples were generally conserved with the addition of flotation reagents. The results from Section 5.4 showed that the pulp

oxygen content was generally higher and the dissolved oxygen uptake factor lower for a pyrrhotite slurry conditioned with xanthate collector relative to a slurry with no collector. Previous studies that have examined the change in pulp dissolved oxygen content on an operating plant at the point of reagent addition have showed little change in dissolved oxygen content. Buswell *et al.* (2002) showed little difference in dissolved oxygen content of the pulp with xanthate addition on a platinum plant, but this was attributed to the very low sulfide content (1 %) of the Merensky Reef ore. Ekmekci *et al.* (2003) also showed little difference in dissolved oxygen content at the point of xanthate addition for a Turkish pyrite ore. However, since dissolved oxygen measurements from this work corresponded with the point of the initiation of flotation following conditioning (Section 3.4.4; 4.5.1), the results are not entirely comparable to previous research. Results in this study are interpreted to represent the state of the pulp subsequent to the electrochemical interactions between the pyrrhotite samples with collector.

The decreased reactivity of the pyrrhotite slurry conditioned with xanthate was attributed to the formation of a surface coating most likely corresponding to several monolayers that would have protected the pyrrhotite surface from further oxidation. Sparging of the pulp with oxygen therefore caused an increase in pulp dissolved oxygen content and decrease in the oxygen uptake factor since the amount of oxygen consumption through pyrrhotite oxidation was limited. This is consistent with the interpretation of Spira and Rosenblum (1974), although the decrease noted in oxygen demand for the pyrrhotite ore in their study was due to sodium cyanide addition that was similarly argued to restrict the access of oxygen to the pyrrhotite surface.

The dissolved oxygen content was also generally lower and the oxygen uptake factors higher, when the shorter chain length SNPX was used as a collector (Table 5.1). In addition to the difference in solubility product between xanthate collectors of varying chain lengths (M.C. Fuerstenau, 1982), it would be expected that they would show differences in oxidation rate. Harris and Finkelstein (1977) investigated the amount of oxygen consumed with the addition of xanthate to chalcocite. They showed a consistent change in the rate of oxygen consumption corresponding with xanthate chain length. The rate of oxygen consumption was far greater for the longer chain length hexyl, amyl and butyl xanthate relative to the propyl and ethyl xanthate. Since the time required for the oxidation of SIBX to its dixanthogen species would be less than that required for SNPX, it is expected that the time required to form a surface

layer of dixanthogen on pyrrhotite would be longer for the latter. Prior to complete dixanthogen surface coverage, the pyrrhotite surface would still be able to interact with oxygen and prone to oxidation. This scenario is proposed to account for the difference in oxygen uptake factor between SNPX and SIBX addition to the pyrrhotite slurry. During the additional time required for dixanthogen formation from SNPX, the pyrrhotite would still have been reactive and prone to oxidation which is evidenced by the slightly higher oxygen uptake factor.

Similarly to the reduction in pyrrhotite reactivity with collector addition, the addition of copper caused a further decrease in oxygen uptake factor. This effect was only manifested for the magnetic Phoenix and Sudbury Gertrude West pyrrhotite samples where the oxygen uptake factor was approximately halved due to copper addition. Using ToF-SIMS, Gerson and Jasieniak (2008) showed that following copper addition, the surface of pyrrhotite was covered with an adsorbed layer of copper. Comparison of the degree of surface oxidation using ToF-SIMS also showed that pyrrhotite samples that had been exposed to copper showed significantly lower proportions of oxidation products (e.g. lower O/S ratio) relative to pyrrhotite with no copper activation. The reduction in oxygen uptake factor due to copper addition in conjunction with collector is therefore attributed to the formation of an adsorbed layer of copper, and formation of a hydrophobic copper collector species that protected the pyrrhotite surface from further oxidation.

On the whole, the mineral reactivity studies have shown that non-magnetic pyrrhotite is relatively unreactive whereas magnetic pyrrhotite is reactive. The studies have also shown that definite differences exist in the reactivity of magnetic pyrrhotites derived from different ores. The reactivity of mixed magnetic and non-magnetic pyrrhotite was in between that of pure magnetic and non-magnetic pyrrhotite most likely due to the combined contribution of the reactive magnetic pyrrhotite intergrown with the unreactive non-magnetic pyrrhotite. Therefore, it is now of interest to explore possible mechanisms that could allow for the crystallography, mineral chemistry and mineral association of pyrrhotite to influence its reactivity.

Crystallography

Pyrrhotite is known to oxidise rapidly and therefore it is of relevance to review the oxidation mechanism. As described in Chapter 2, Pratt *et al.* (1994) proposed a mechanism for pyrrhotite oxidation by which the only movement of species during the reaction was the transfer of electrons from the crystal lattice and the diffusion of iron towards the surface ferric oxyhydroxide layer. Pratt *et al.* (1994) argued that the most reactive sites for oxygen reduction were associated with the ferric iron sulfur bonds and the vacancies in the pyrrhotite crystal lattice. The presence of vacancies would likely facilitate electron transfer as well as the diffusion of iron through the crystal lattice to the surface, thereby assisting the oxidation reaction. Since the magnetic pyrrhotite structure has more vacancies relative to the non-magnetic pyrrhotite, it is hypothesised that the greater abundance of vacancies accelerates the oxidation process for magnetic pyrrhotite relative to non-magnetic pyrrhotite. For the samples examined in this study, this would theoretically relate to 1 vacancy for every 8 iron sites for the magnetic 4C Fe₇S₈ Phoenix and Sudbury Gertrude West pyrrhotite samples, whereas only 1 in 10 iron sites would be vacant for the non-magnetic 5C Fe₉S₁₀ Sudbury CCN pyrrhotite.

The presence of vacancies and their role in facilitating more rapid oxidation and greater reactivity for magnetic pyrrhotite relative to non-magnetic pyrrhotite is in agreement with the results of the oxidation studies of Gerson and Jasieniak (2008) and Lehmann *et al.* (2000). Gerson and Jasieniak (2008) observed more rapid oxidation of monoclinic pyrrhotite relative to “hexagonal” pyrrhotite with ToF-SIMS. Lehmann *et al.* (2000) measured both larger rate constants and lower activation energy for the oxidation of monoclinic relative to “hexagonal” pyrrhotite. The results from this study are not in disagreement with Janzen (1996) where no correlation was found between oxidation rate and crystallography. However, since the experiments of Janzen (1996) were performed on pyrrhotite derived from multiple provenances, it is likely that the dataset was not sensitive enough in order to isolate these differences. The oxygen demand tests of Spira and Rosenblum (1974) also showed a greater oxygen demand for non-magnetic pyrrhotite relative to magnetic Noranda pyrrhotite. Spira and Rosenblum (1974) did however comment that the non-magnetic pyrrhotite sample was most likely troilite and so direct comparison with the results of this study is not necessarily possible.

Mineral Chemistry

Both oxygen and ferric iron are known to be oxidising agents of pyrrhotite (Hamilton and Woods, 1981; Janzen, 1996; Belzile *et al.*, 2004) and so the presence of both these species within the pyrrhotite structure needs to be evaluated. Ferric iron was also noted by Janzen (1996) to be a much stronger oxidising agent than oxygen. The ideal formula for magnetic and non-magnetic pyrrhotite has been argued to contain both ferrous and ferric iron. The presence of both these iron species would then maintain the charge balance due to the variation of the relative proportions of these two cations (Bertaut, 1953; Pratt *et al.*, 1994; Mikhlin and Tomashevich, 2005). Therefore, magnetic pyrrhotite of formula $\text{Fe}^{3+}_2\text{Fe}^{2+}_5\text{S}^{2-}_8$ (Fe_7S_8) contains proportionally more ferric iron in its structure than non-magnetic pyrrhotite of formula $\text{Fe}^{3+}_2\text{Fe}^{2+}_7\text{S}^{2-}_{10}$ (Fe_9S_{10}). Consequently, it could be expected that magnetic pyrrhotite is more prone to oxidation than non-magnetic pyrrhotite because of the greater proportion of ferric iron acting as an oxidising agent within its structure.

In the case of oxygen as an oxidising agent, the results of the mineralogical characterisation of pyrrhotite in Chapter 4 provide more than sufficient evidence to suggest that oxygen in the form of magnetite is often associated with pyrrhotite. The most well developed example of this was the presence of very fine grained elongate rod-like inclusions of magnetite hosted by pyrrhotite in the Nkomati MMZ samples (Section 4.2.2). On the basis of this observation, it can be concluded that oxygen is present during the crystallisation of the MSS and formation of pyrrhotite. Therefore, it is not implausible that some minor proportion of oxygen could have been accommodated within the pyrrhotite crystal structure. The results of the nuclear microprobe analyses of Graham and Mc Kenzie (1987) showed the presence of detectable amounts of oxygen of ~ 0.05 wt % within both monoclinic and “hexagonal” pyrrhotite. The presence of trace amounts of dissolved oxygen in the pyrrhotite crystal structure is proposed here as a possible mechanism to account for the differences in reactivity between magnetic pyrrhotite samples derived from different ore deposits. Therefore, if the Sudbury Gertrude West magnetic pyrrhotite sample contained a greater concentration of oxygen within its structure than the Phoenix magnetic pyrrhotite sample, it could be expected that the greater oxygen content would facilitate the oxidation reaction thereby increasing the reactivity of the magnetic Sudbury Gertrude West pyrrhotite. This is clearly an area for further investigation (see Chapter 8).

It is recognised that the concentration of trace oxygen within the pyrrhotite crystal structure is not necessarily correlated with the actual proportion of magnetite present in the sample. The MLA results of the microflotation feed and oxygen uptake samples (Table 3.3) showed only minor differences in magnetite concentration between the magnetic Sudbury Gertrude West (0.61 wt % magnetite) and Phoenix pyrrhotite (0.19 wt %). It is noted that the Nkomati MSB pyrrhotite had the highest proportion of magnetite (5.49 wt %), yet this pyrrhotite was noted to be less reactive than the magnetic Sudbury Gertrude West and Phoenix pyrrhotite samples.

The mineralogical characterisation also showed that the solid solution nickel content in pyrrhotite was variable (Table 7.1). In the study of Kwong (1993), a semi-quantitative correlation was found between nickel and cobalt content and oxidation rate for monoclinic pyrrhotite. Pyrrhotite samples enriched in nickel and cobalt were found to oxidise slightly slower. This was most likely due to the positive effective charge as a result of the donor defects caused by the substitution of cobalt and nickel for iron (Janzen, 1996). Since cobalt concentrations were relatively negligible for the pyrrhotite samples analysed in this study, the focus is on nickel. The implication of a positive effective charge within the vicinity of nickel substitution sites would be to retard the movement of electrons, thereby inhibiting the oxidation process. This is another additional mechanism to potentially account for the difference in reactivity observed between magnetic pyrrhotite samples derived from different ore bodies. The average solid solution nickel content of Phoenix pyrrhotite (1.06 ± 0.67 wt % Ni) was found to be slightly greater than for the magnetic Sudbury Gertrude West (0.82 ± 0.19 wt % Ni). It is possible that the resultant positive effective charge was greater in the Phoenix pyrrhotite and helped to stabilise the pyrrhotite structure. In contrast, the positive effective charge was not as significant in the magnetic Sudbury Gertrude West pyrrhotite and therefore it would have been prone to more severe oxidation as observed.

Mineral Association

In this study, only the Nkomati MSB and MMZ (sample *MMZ-4*) pyrrhotite consisted of intergrown magnetic and non-magnetic pyrrhotite. In the study of Arnold (1967) on the range in composition and structure of naturally occurring terrestrial pyrrhotites however, 73 % of the samples examined were mixtures of monoclinic and “hexagonal” pyrrhotite. Therefore, the association between magnetic and non-magnetic pyrrhotite is relatively important when evaluating the effect of mineral association on the reactivity of pyrrhotite in general. Due to the conductive or semi-conductive nature of the sulfide minerals, they may facilitate electron

transfer when they come into contact with one another, thereby creating a galvanic cell. The presence of a galvanic interaction could cause more severe oxidation than expected for the anodic mineral compared to that expected if the mineral occurred on its own. Since magnetic and non-magnetic pyrrhotite are commonly intergrown with one another, they could be considered prime candidates for the creation of a galvanic cell. Middlings or locked particles are known to suffer from galvanic effects more so than liberated particles (Almeida and Giannetti, 2003). A galvanic interaction between two minerals however, is dependent on the difference in rest potential of the two sulfide minerals and only when the difference is sufficiently high enough between the anodic and cathodic minerals, will there be a galvanic current. Even though differences have been noted here between the reactivity of magnetic and non-magnetic pyrrhotite, these are by no means comparable to the scale of the differences that are experienced during the operation of a true galvanic cell (Ekmekci and Demirel, 1997). Therefore, it is considered unlikely that galvanic interactions are effective between magnetic and non-magnetic pyrrhotite.

The reactivity of the mixed magnetic and non-magnetic Nkomati MSB pyrrhotite was observed to be in between that of the reactive Phoenix magnetic pyrrhotite and unreactive non-magnetic Sudbury CCN pyrrhotite. Therefore, even though a galvanic interaction is unlikely between intergrown magnetic and non-magnetic pyrrhotite, the effect of intergrown pyrrhotite does influence pyrrhotite reactivity. The effect of intergrown pyrrhotite appears to cause the resultant reactivity to be in between that of the reactive magnetic and unreactive non-magnetic pyrrhotite components.

Pyrrhotite samples in this study were observed to occur in association with other sulfide minerals of which the association to pentlandite was the strongest. Minor associations to chalcopyrite and pyrite were also noted. Therefore, the importance of galvanic effects between pyrrhotite and these minerals does need consideration, especially since the abovementioned minerals are more noble than pyrrhotite (Rand, 1977). In the weathering experiments conducted on real ores samples by Kwong (1993), rapid alteration due to oxidation of pyrrhotite was most noticeable for the monoclinic pyrrhotite sample that contained the greatest amount of pyrite (15 %). Similarly, results of flotation studies that have investigated the effect of galvanic interactions on floatability have only shown galvanic interactions to be effective when the proportion of the cathodic mineral is relatively high (e.g. Cheng and Iwasaki, 1992; Nakazawa and Iwasaki, 1995; Ekmekci and Demirel, 1997). Since

pentlandite is the only volumetrically significant sulfide in the pyrrhotite samples investigated, galvanic interactions between pyrrhotite and pentlandite need to be evaluated.

SEM images of the pyrrhotite electrodes used for the mineral reactivity tests showed some pentlandite contamination of the electrodes (Figure 3.7) and similarly, so did the MLA and QXRD analyses of the pyrrhotite samples (Tables 3.1, 3.3). MLA analyses of the Phoenix magnetic pyrrhotite sample showed that it contained the greatest amount of pentlandite contamination (16.9 wt % pent) relative to the other pyrrhotite samples investigated (6.61 – 8.21 wt % pent). Since galvanic interactions are most effective when the anodic and cathodic minerals are in contact with one another, the pyrrhotite samples with the lowest degree of pentlandite liberation would be expected to experience the strongest galvanic interaction. Phoenix magnetic pyrrhotite showed the lowest pentlandite liberation (48.5 % liberated particles) relative to the other pyrrhotite samples examined (53.6 -89.3 % liberated particles) due to the abundant locked flame pentlandite. However, the results of the pyrrhotite reactivity tests did not give any conclusive indication that the reactivity of the Phoenix pyrrhotite was significantly increased due to galvanic interactions with pentlandite. The most reactive pyrrhotite sample was the Sudbury Gertrude West pyrrhotite for which the pentlandite was 77.1 % liberated. Therefore, these results are argued to show negligible influence of galvanic effects on the reactivity of pyrrhotite. This does not necessarily mean that the flotation performance could not be adversely affected by a galvanic interaction between pentlandite and pyrrhotite. This will be further investigated in Section 7.5.

7.5 Effect of Mineralogy on Pyrrhotite Flotation Performance

The aim of this section is to answer the fourth key question, “*How does the flotation performance of magnetic and non-magnetic pyrrhotite differ and can these differences be accounted for by the crystallography, mineral chemistry and mineral association of pyrrhotite?*” In order to do this, the results from the microflotation tests in Chapter 6 are first reviewed and discussed in order to understand the interactions of the pyrrhotite surface with the flotation reagents. Only once these results have been interpreted, can any attempt be made to develop the relationship between pyrrhotite mineralogy and flotation performance.

As described in Section 2.4.2, some mild oxidation is required for the collectorless flotation of pyrrhotite. A variety of species varying between elemental sulfur, polysulfides, metal deficient sulfides to a stable $\text{Fe}(\text{OH})\text{S}_2$ intermediate species have all been proposed to provide the necessary hydrophobicity for the collectorless flotation of pyrrhotite (Hamilton and Woods, 1981; Heyes and Trahar, 1984; Hodgson and Agar, 1984; Buckley and Woods, 1985; Legrand *et al.*, 2005a). However, extensive oxidation is well known to be detrimental to the flotation performance of pyrrhotite due to the formation of hydrophilic ferric hydroxide species (e.g. Rao and Finch, 1991; Kelebek, 1993). Although ferric hydroxide species were not actively identified on the surface of pyrrhotite during the flotation tests in this study, their presence is inferred as the reason for poor pyrrhotite flotation. Therefore, the interpretation of the flotation results needs to account for the balance between mild and severe oxidation that causes differences in pyrrhotite floatability with the propensity of the different pyrrhotite samples for oxidation i.e. their reactivity.

The degree of collectorless flotation was generally very low for all the pyrrhotite samples in this study other than the non-magnetic Sudbury CCN pyrrhotite sample. This suggests that the degree of oxidation experienced by the Sudbury CCN pyrrhotite was just mild enough to cause the production of hydrophobic species such as elemental sulfur or polysulfides. This agrees with the results of the mineral reactivity tests that showed the non-magnetic Sudbury CCN pyrrhotite was the most unreactive of the samples examined. In contrast, more extensive oxidation probably occurred for the magnetic and non-magnetic pyrrhotite due to their increased reactivity (Section 7.4), resulting in the formation of hydrophilic ferric hydroxides species that prevented the particles from being recovered during flotation. Since the

collectorless flotation of the magnetic and mixed pyrrhotite samples was so poor, no significant differences were observed between the samples that were related to their mineralogy. Similarly, since the collectorless flotation was so poor for the magnetic and mixed pyrrhotite samples, no significant differences were observed that were related to pH. Only the non-magnetic Sudbury CCN pyrrhotite showed a decrease in its collectorless floatability that could be attributed to the increase in electrochemical reaction rates and increase in the amount of hydrophilic ferric hydroxides at the greater hydroxide ion concentration (pH 10).

The floatability of all the pyrrhotite samples was significantly improved with the addition of xanthate collector. This is attributed to collector adsorption on the pyrrhotite surface followed by oxidation and formation of the dixanthogen species (MX_2) which is known to render pyrrhotite its hydrophobicity during flotation (Allison *et al.*, 1972; Fornasiero *et al.*, 1995; Bozkurt *et al.*, 1998). Kelebek (1993) suggested that mild oxidation of the pyrrhotite surface promoted the amount of surface sites available for xanthate adsorption, the production of elemental sulfur and the oxidation of xanthate to dixanthogen. Extensive oxidation however, would have shifted the balance so that the layer of hydrophilic ferric hydroxides covering the surface of the pyrrhotite would have been too thick to allow for sufficient xanthate adsorption. Therefore differences in the floatability of the different pyrrhotite samples with collector addition are interpreted to be influenced by the reactivity of pyrrhotite for oxidation.

With the addition of collector, non-magnetic Sudbury CCN pyrrhotite was still one of the most floatable pyrrhotites of the samples investigated at both pH 7 and 10, although a reduction in floatability was observed at the higher pH. This is once again attributed to the increase in concentration of ferric hydroxides at pH 10 and is in agreement with the Barsky relationship where $[\text{X}^-]/[\text{OH}^-] = K$ (Kelebek *et al.*, 2007). Differences in the floatability of the magnetic and mixed magnetic and non-magnetic pyrrhotite samples also became more evident. The magnetic Sudbury Gertrude and Gertrude West pyrrhotite samples showed the poorest flotation recovery of all the pyrrhotite samples. This was interpreted to be the result of severe oxidation of the Gertrude and Gertrude West pyrrhotite samples due to their very reactive nature (Section 7.4). It suggests that the surface of the pyrrhotite was already passivated and covered with hydrophilic ferric hydroxides prior to the addition of collector so that no interaction between the reagent and the pyrrhotite surface was possible.

The microflotation studies showed that the floatability of the Phoenix magnetic pyrrhotite was considerably better than the magnetic Sudbury Gertrude and Gertrude West pyrrhotite samples in the presence of a collector. This suggests that oxidation of the magnetic Phoenix pyrrhotite samples was less intense than the Gertrude and Gertrude West pyrrhotite so that some interaction between the pyrrhotite surface with xanthate was possible. At pH 7, the microflotation recovery of the Phoenix magnetic pyrrhotite in the presence of collector was virtually equal to the non-magnetic Sudbury CCN pyrrhotite. At pH 10, however the reactive nature of the Phoenix pyrrhotite was significantly increased due to the increase in pH, so that interaction with the collector was inhibited and its flotation performance was poor. A similar argument is able to account for the good flotation performance of the Nkomati MSB mixed pyrrhotite at pH 7 and the poor flotation performance at pH 10 in the presence of a collector.

The microflotation recovery of the different pyrrhotite samples was also greater for the longer chain length SIBX collector than the shorter chain length SNPX collector. Longer chain length xanthate collectors are known to have lower solubility products in water and therefore are more hydrophobic (M.C. Fuerstenau, 1982). This increase in hydrophobicity with the longer chain length SIBX collector was therefore attributed for the improved flotation performance of pyrrhotite with SIBX. An additional mechanism that could account for the lower recovery of pyrrhotite using the shorter chain length SNPX collector is related to the xanthate oxidation rate. The lower oxidation rate of the shorter chain length SNPX relative to SIBX (Section 5.5; Harris and Finkelstein, 1977) could also allow for more extensive oxidation of pyrrhotite thereby increasing the concentration of ferric hydroxides and impairing its floatability.

The effect of copper activation on the flotation recovery of the different pyrrhotite samples was mixed and showed a dependence on pyrrhotite mineralogy, pH and collector chain length. The inherent mechanism behind the improvement in pyrrhotite flotation performance with copper activation is through the adsorption of cupric copper onto the pyrrhotite surface and its rapid reduction to cuprous copper (Section 2.4.4). Following xanthate addition to the system, a hydrophobic copper - xanthate - hydroxide species most likely formed which rendered the pyrrhotite hydrophobic. The exact nature of this species is unknown and remains the subject of debate in the literature (e.g. Chandra and Gerson, 2009). It has also been shown that oxidation of the pyrrhotite surface prior to copper addition negatively interferes with the copper activation mechanism (Gerson and Jasieniak, 2008).

At pH 7, all of the pyrrhotite samples other than the Nkomati MSB mixed pyrrhotite showed some improvement in flotation performance due to copper activation. Even the magnetic Sudbury Gertrude and Gertrude West pyrrhotite samples showed some improvement in flotation performance even though they are considered to have been the most oxidised. Only the Nkomati MSB mixed pyrrhotite showed negligible improvement in flotation performance with copper addition, which was probably due to the fact that its flotation performance with collector at pH 7 was already excellent.

At pH 10 however, only the non-magnetic Sudbury CCN and Phoenix magnetic pyrrhotite samples showed a distinct improvement in flotation performance at pH 10 due to copper activation in conjunction with SIBX or SNPX collector addition. The magnetic Sudbury Gertrude and Gertrude West and Nkomati MSB pyrrhotite samples showed a very minor improvement in flotation performance at pH 10 due to copper activation and only when in conjunction with the addition of the stronger SIBX collector. This suggests that at pH 10, the Gertrude, Gertrude West and Nkomati pyrrhotite samples were much more reactive due to the increase in pH, and the effect of prior surface oxidation was detrimental to copper activation.

The microflotation results for the tests with copper activation at pH 10 of the Phoenix magnetic and Nkomati mixed pyrrhotite however, were not consistent with what was expected based on the relative reactivity of these pyrrhotite samples. It was expected that the Phoenix magnetic pyrrhotite would have been negatively affected by oxidation and therefore copper activation during flotation would not have occurred. It is also unclear why copper activation was not significant in the flotation performance of the mixed Nkomati MSB pyrrhotite at pH 10. Given its excellent flotation performance at pH 7 and its relatively unreactive character towards oxidation, it was anticipated that the Nkomati pyrrhotite would have shown a significant improvement in flotation performance due to copper activation. This suggests that understanding copper activation on the different pyrrhotite samples is relatively complex.

The microflotation results are generally consistent with those from the mineral reactivity studies and show that pyrrhotite floatability is primarily controlled by the degree of oxidation of the pyrrhotite surface. In general, the unreactive non-magnetic pyrrhotite showed the best floatability. The flotation performance of magnetic pyrrhotite was variable according to its origin but in general, showed poorer flotation performance than non-magnetic pyrrhotite. The

flotation performance of mixed magnetic and non-magnetic pyrrhotite was in between magnetic and non-magnetic pyrrhotite. Therefore, the same factors that influence the propensity of the different pyrrhotite types for oxidation, must affect their flotation performance although not necessarily in the same manner. Consequently, the effect of crystallography, mineral chemistry and mineral association are reviewed again.

Crystallography

In Section 7.4, it was argued that magnetic pyrrhotite is more reactive towards oxidation than non-magnetic pyrrhotite due to the greater proportion of vacancies in its crystal structure that facilitate the oxidation reaction. Consequently, the increased oxidation of magnetic pyrrhotite and formation of hydrophilic ferric hydroxides is proposed to account for its poorer flotation performance relative to non-magnetic pyrrhotite. The results from this study are in agreement with the account of Iwasaki (1988) from Harada (1967; In Japanese), that “hexagonal” pyrrhotite was more floatable than monoclinic pyrrhotite when the sample was oxidised. Harada (1967) also noted that freshly ground monoclinic pyrrhotite was more floatable. Given the sample preparation procedure used in this study whereby microflotation studies were performed on a selected pyrrhotite size fraction which had been prepared in advance (Section 3.5), flotation of a freshly ground sample was not possible. The results from this study are in partial agreement with Kalahdoozan (1996), where it was found that “hexagonal” pyrrhotite was more floatable than monoclinic pyrrhotite at pH 10. At pH 7, however, monoclinic pyrrhotite was more floatable. In the study of M.F. He *et al.* (2008), it was shown that monoclinic pyrrhotite was more floatable through a range of pH conditions in the presence of xanthate collector. However, since M.F. He *et al.* (2008) used pyrrhotite derived from lead zinc ores in their flotation experiments, the influence of pyrrhotite origin may account for the differences in flotation performance.

Both the results of this study and the literature suggest that a relationship exists between pyrrhotite crystallography, degree of oxidation and copper activation during flotation (Kalahdoozan, 1996; Wiese *et al.*, 2005; Gerson and Jasieniak, 2008; M.F. He *et al.*, 2008). Gerson and Jasieniak (2008) clearly showed that preoxidation is detrimental to the efficiency of copper activation and that copper activation stabilised the surface of pyrrhotite from further oxidation. On the basis that magnetic pyrrhotite is more reactive to oxidation, it is expected to be more sensitive to copper activation. Yet, the results of this study have shown that any pyrrhotite sample with a magnetic pyrrhotite component (including mixed pyrrhotite) does

not necessarily behave according to what would be expected from its reactivity towards oxidation. For some pyrrhotite samples, such as the magnetic monoclinic Phoenix pyrrhotite, the effect of copper activation is very significant in improving its flotation performance. Results of flotation studies from the literature have suggested that monoclinic pyrrhotite is more “sensitive” to copper activation. Kalahdoozan (1996) showed that the effect of changes in collector concentration with copper activation were more significant to the flotation performance of monoclinic pyrrhotite than “hexagonal” pyrrhotite. M.F. He *et al.* (2008) showed greater improvement in the flotation performance of monoclinic pyrrhotite with copper activation at pH 10 than “hexagonal” pyrrhotite. Wiese *et al.* (2007) also showed the effect of copper activation on pyrrhotite flotation differed according to whether the pyrrhotite was derived from the Impala or Lonmin Merensky Reef mine. Figure 7.3 shows that copper activation caused minor improvement in the flotation performance of pyrrhotite derived from the Impala Platinum mine, whereas the improvement in flotation performance with copper activation on the Lonmin pyrrhotite was significant.

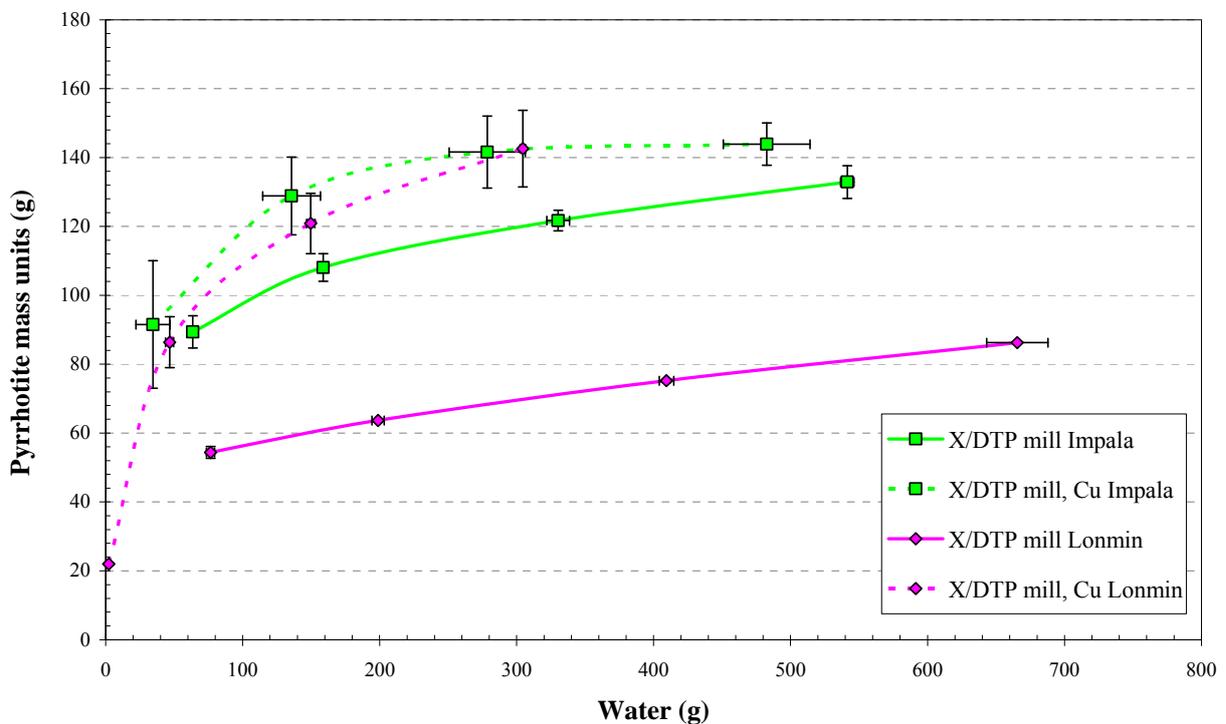


Figure 7.3: Comparison of the difference in calculated mass units of pyrrhotite recovered in batch flotation tests of Impala and Lonmin Merensky Reef ore for tests with and without copper activation. X represents xanthate and DTP, dithiophosphate. Adapted from Wiese *et al.* (2005) and Wiese (Unpublished data).

In order to determine whether there were significant mineralogical differences between the pyrrhotite from the two Merensky Reef ores, pyrrhotite concentrates from the flotation test results shown in figure 7.3 were prepared for mineralogical characterisation (J. Wiese, Pers. Comm. 2005). Mineral chemistry results of the different pyrrhotite samples analysed by Bushell (2005) have been reworked here, and are now presented in figure 7.4 as a histogram of metal to sulfur ratios. The entire pyrrhotite data set from this study is shown for reference in figure 7.4.

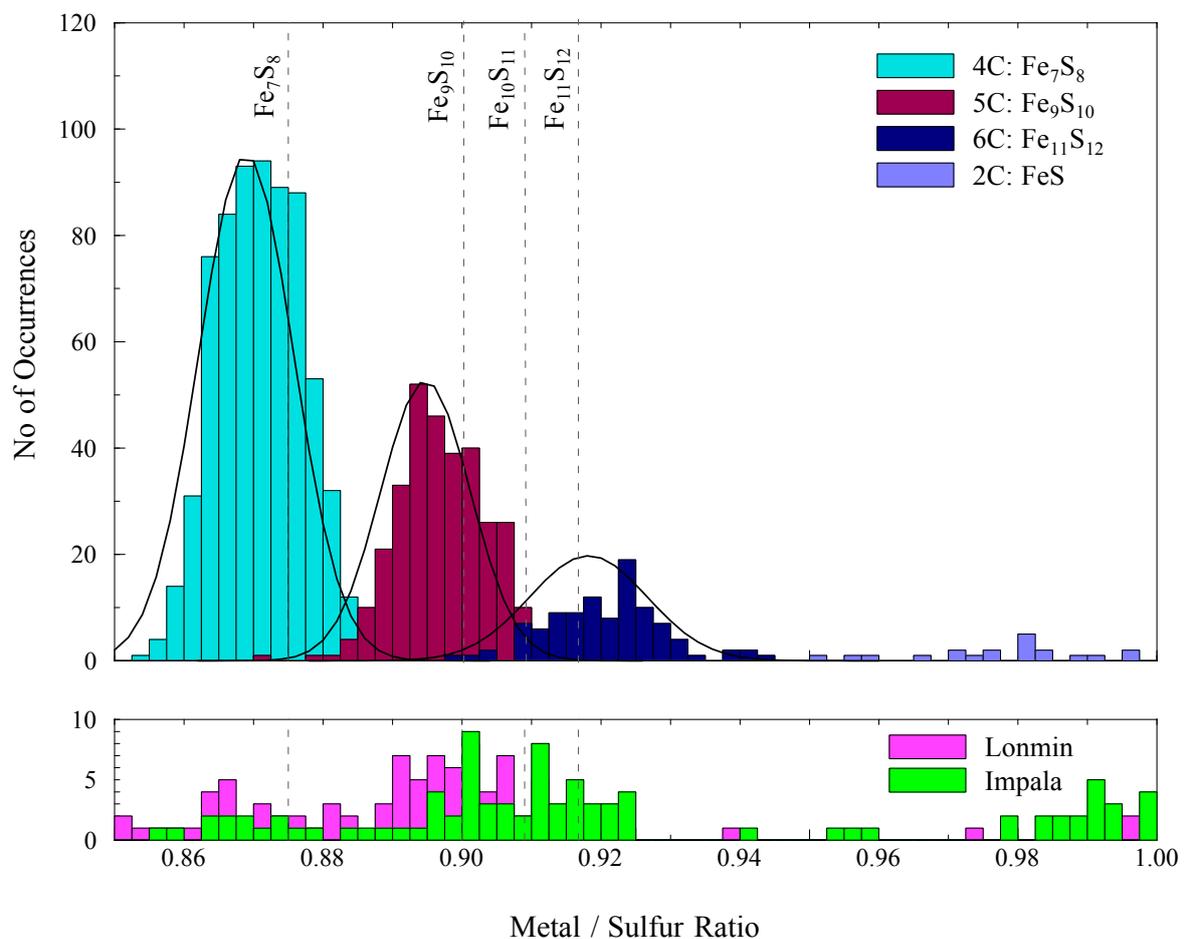


Figure 7.4: Comparison of the metal to sulfur ratio of pyrrhotite from batch flotation tests of Lonmin and Impala Merensky Reef pyrrhotite with pyrrhotite analyses from this study. Impala and Lonmin pyrrhotite metal to sulfur ratios were recalculated from Bushell (2005) based on pyrrhotite samples derived from batch flotation tests by Wiese *et al.* (2005) and Wiese (Unpublished data).

It is evident from figure 7.4 that the pyrrhotite population from both the Impala and Lonmin Merensky Reef mines is comprised of magnetic pyrrhotite (Fe_7S_8), non-magnetic pyrrhotite

(most likely Fe_9S_{10}) and troilite (FeS), although the abundance of each of these phases varies. Even though the pyrrhotite populations are relatively small, it is evident that a greater proportion of the pyrrhotite samples analysed from the Lonmin Merensky ore contained slightly lower metal / sulfur ratios than the Impala Merensky pyrrhotite. This suggests that there may be more magnetic pyrrhotite present in the Lonmin Merensky ore. The presence of a greater proportion of magnetic pyrrhotite in the Lonmin ore may account for its significant improvement in flotation performance with copper activation if magnetic pyrrhotite is more sensitive to copper activation. This effect could be enhanced if the magnetic pyrrhotite was secondary in origin and occurred as magnetic pyrrhotite rims surrounding non-magnetic pyrrhotite with which the copper could interact. If the magnetic pyrrhotite formed through hydrothermal alteration of “hexagonal pyrrhotite” (Desborough and Carpenter, 1965), the formation of magnetic pyrrhotite rims surrounding non-magnetic pyrrhotite may have occurred and which was previously described for Bushveld pyrrhotite by Liebenberg (1970).

These results suggest that magnetic pyrrhotite is more sensitive to copper activation but the underlying mechanism is considered to be complex. Some correlation to surface preoxidation probably does exist (Gerson and Jasieniak, 2008), but other mechanisms such as the role of pulp oxidation potential (He *et al.*, 2005), surface defect properties (e.g. Harris and Richter, 1985) or preferential copper adsorption on to particular crystallographic sites may well be important factors that need further investigation

Mineral Chemistry

As argued in Section 7.4, the presence of a greater proportion of ferric iron in the magnetic pyrrhotite structure likely increases the reactivity of magnetic pyrrhotite and particularly so since ferric iron is a stronger oxidising agent than oxygen. Consequently, the increased reactivity of magnetic pyrrhotite relative to non-magnetic pyrrhotite results in the increased formation of hydrophilic iron hydroxides that impair its floatability. Similarly, the presence of oxygen within the pyrrhotite structure could also be an oxidising agent to pyrrhotite. This might account for the differences in the reactivity and flotation performance between the different magnetic pyrrhotite samples (Phoenix, Sudbury Gertrude and Gertrude West). An additional mechanism that could account for the differences in the flotation response of the magnetic Phoenix and magnetic Sudbury Gertrude and Gertrude West pyrrhotite samples is the concentration of solid solution nickel. The creation of a positive effective charge in the vicinity of these sites of substitution would likely retard the oxidation (Section 7.4) and

formation of ferric hydroxide species on the pyrrhotite surface, thereby reducing its floatability. This is consistent with the flotation results obtained by Chanturia *et al.* (2004) where the floatability of iron rich, cobalt rich and nickel rich pentlandite was investigated. Chanturia *et al.* (2004) found that nickel rich and cobalt rich pentlandite were more floatable than iron rich pentlandite, which they suggested was due to differences in open circuit potential and the preferential formation of hydrophobic species on the nickel rich pentlandite.

Mineral Association

Given the importance of the association between magnetic and non-magnetic pyrrhotite occurring as intergrowths with one another in terms of the general occurrence of pyrrhotite (Arnold, 1967), so their effect on flotation performance is of interest. The microflotation results of the Nkomati MSB mixed magnetic and non-magnetic pyrrhotite was similar to the non-magnetic Sudbury CCN and magnetic Phoenix pyrrhotite samples at pH 7 in the presence of collector and copper activation. This suggests that similarly to its mineral reactivity, the floatability of the Nkomati mixed pyrrhotite was governed by the floatability of the intergrown magnetic and non-magnetic pyrrhotite phases. At pH 10 however, the decrease in the flotation performance of the Nkomati pyrrhotite was most likely due the stronger influence of the floatability of the magnetic pyrrhotite component that was adversely affected by the increase in hydroxide concentration.

The mineral association between pyrrhotite and pentlandite may also be important with respect to the possibility of galvanic interactions and particularly so for composite particles. The results from the reactivity studies however, gave no conclusive indication that the reactivity of pyrrhotite was adversely affected by a galvanic interaction with pentlandite (Chapter 5, Section 7.4). Galvanic interaction between pyrrhotite and pentlandite is expected to be detrimental to pyrrhotite flotation since pentlandite is the more noble of the two minerals. The addition of xanthate to the system may be of further detriment to pyrrhotite flotation since the anodic oxidation of xanthate to dixanthogen preferentially occurs on pentlandite (Bozkurt *et al.*, 1998). S.H. He *et al.* (2008) proposed a galvanic interaction as one of the mechanisms to account for the difference in pentlandite flotation between the magnetic and non-magnetic streams at the Clarabelle Mill in Sudbury. Due to the greater concentration of pyrrhotite in the magnetic stream, it was proposed that a galvanic interaction would cause the preferential oxidation of pyrrhotite relative to pentlandite, causing the improved pentlandite recovery noted. In this study, it is only really applicable to investigate the effect of

galvanic interactions between pyrrhotite samples which are similar in magnetic character. Due to the greater proportion of flame pentlandite and lower pentlandite liberation in the Phoenix magnetic pyrrhotite sample relative to the Sudbury Gertrude and Gertrude West pyrrhotite samples, it would be expected that if a galvanic interaction was significant, the floatability of the Phoenix magnetic pyrrhotite would be more adversely affected. However, the results of the microflotation studies showed that the presence of pentlandite enhanced the floatability of the Phoenix pyrrhotite sample. Consequently an additional mechanism needs to be investigated.

Various studies have described how the flotation rate of pyrrhotite is slower than pentlandite (e.g. Buswell and Nicol, 2002; Miller *et al.*, 2005). On the basis that pentlandite is more floatable than pyrrhotite, a mechanism for the flotation of composite pyrrhotite and pentlandite particles is proposed. This mechanism would be directly applicable to account for the improved floatability of pyrrhotite samples containing abundant locked flame pentlandite. It is proposed that preferential collector adsorption and bubble – particle attachment occurs at sites where unliberated pentlandite is partially exposed on the surface of the composite particle. Therefore, the recovery of pyrrhotite during flotation would be by virtue of its association to pentlandite. This mechanism of composite particle flotation would be relevant to the Phoenix magnetic pyrrhotite and the Nkomati MSB mixed pyrrhotite. It provides an additional mechanism to account for the differences in floatability between the magnetic Phoenix and Sudbury Gertrude and Gertrude West pyrrhotite samples. It may be an additional explanation to account for the difference in flotation performance of the Phoenix magnetic pyrrhotite relative to the Nkomati MSB mixed pyrrhotite at pH 10. Given that the liberation of pentlandite in the Nkomati mixed pyrrhotite sample is slightly greater than the Phoenix magnetic pyrrhotite, the composite particle flotation would not be as strong for the Nkomati pyrrhotite and therefore its flotation recovery with collector addition was poor. Since copper activation is known not to have any influence on pentlandite flotation (Senior *et al.*, 1995; Wiese *et al.*, 2007), the effect of pentlandite activation by copper in improving the flotation of pyrrhotite can be ruled out as a mechanism influencing the success of copper activation of pyrrhotite.

Another mechanism related to the presence of pentlandite associated with pyrrhotite is that caused by the release of nickel ions from pentlandite and inadvertent activation of pyrrhotite. The inadvertent activation of pyrrhotite from nickel ions has previously been described for the

Sudbury ores by Yoon *et al.* (1995) and Xu and Wilson (2000). It is possible that the flotation performance of those pyrrhotite samples containing significant locked flame pentlandite would be improved due to inadvertent activation by nickel ions associated with the flame pentlandite. This provides yet another mechanism that may account for the differences in the flotation performance of the Phoenix magnetic pyrrhotite to the Sudbury Gertrude and Gertrude West pyrrhotite samples.

7.6 Implications of this Study

As described in Chapter 1, the aim of this study was to develop the relationship between pyrrhotite mineralogy and flotation performance. The motivation behind this research was that mineral processing operations treating pyrrhotite need to manipulate pyrrhotite flotation performance. This is in accordance to whether pyrrhotite needs to be actively recovered due to its association with the platinum group elements and minerals (e.g. Merensky Reef, South Africa) or rejected in order to control circuit throughput and concentrate grade and thereby reduce excess sulfur dioxide smelter emissions (e.g. Sudbury, Canada).

The results of this study have shown that good flotation performance was achieved by the non-magnetic pyrrhotite and suggests that the recovery of this type of pyrrhotite should not be problematic for processing operations targeting pyrrhotite flotation recovery. In contrast, the recovery of the reactive magnetic pyrrhotite is likely to be more problematic. In order to optimise the recovery of magnetic pyrrhotite, the effect of surface oxidation and copper activation need to be more clearly understood. Investigation of mechanisms to prevent the extensive oxidation and formation of hydrophilic ferric hydroxide species on the surface of magnetic pyrrhotite that impair its floatability is needed. Similarly, investigation of the properties that influence the success of copper activation on magnetic pyrrhotite is needed in order to optimise the flotation of this pyrrhotite phase.

The results of this study have shown that the poorest flotation performance was achieved by the most reactive pyrrhotite sample towards oxidation. Therefore, for processing operations targeting pyrrhotite rejection during flotation, the role of oxidation is of particular interest. Although the use of oxygen as a pyrrhotite depressant has previously been evaluated (e.g. Kelebek, 1993), it does not appear to have been implemented in flotation operations where DETA or TETA in conjunction with sodium metabisulfite is the favoured pyrrhotite depressant (Lawson *et al.*, 2005). This is probably due to the large amount of space required to actively oxidise pyrrhotite in terms of conditioning tanks, and that too much oxidation would be detrimental to pentlandite recovery. Given the unreactive nature of non-magnetic pyrrhotite this would not be advised. The results from this study suggest that it should not be too difficult to actively oxidise very reactive magnetic pyrrhotite, and perhaps the use of oxidation should be reevaluated as a depressant for these reactive pyrrhotite types. An additional benefit of using oxygen as a pyrrhotite depressant is that it is not only relatively

inexpensive but is also environmentally friendly. Since pyrrhotite flotation performance was also heavily influenced by the presence of locked flame pentlandite, a change in the grind size and liberation characteristics of pyrrhotite and pentlandite should also be evaluated as a mechanism to assist in manipulating pyrrhotite flotation performance.

Finally, the importance of process mineralogy as a whole is to be able to better understand and optimise flotation performance. Although prediction of flotation performance is not necessarily possible from the results of this study, the results do provide a means to understand and optimise pyrrhotite flotation performance. Simple measurements of well controlled experiments that have been of the most use in this study and that can be readily repeated are those which determine pyrrhotite identity, the identity and relative proportions of minerals in the sample and the oxygen uptake of the mineral slurry. Pyrrhotite identity can easily be determined with the use of hand magnet (magnetic versus non-magnetic), optical microscopy with the magnetic colloid method (magnetic versus non-magnetic) or powder XRD (monoclinic versus orthorhombic). Depending on the nature of the sample and the analyst, the identity and relative proportions of the minerals in the sample can similarly be determined with the use of optical microscopy, powder XRD or automated SEM techniques (QEMSCAN, MLA). Oxygen uptake measurements have also been of benefit and are simple to carry out given that only a dissolved oxygen probe and TPS meter are required. However, these measurements need to be interpreted with care, especially if the pyrrhotite is so reactive that it is readily passivated.

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The aim of this thesis 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 deposit in terms of their mineralogy and mineral reactivity. It is considered that the aim of this thesis has been addressed since a clearer understanding of this relationship now exists. This thesis has shown what the critical parameters are that influence pyrrhotite reactivity and hence flotation performance. Various mechanisms to account for the differences in pyrrhotite reactivity and flotation performance have been proposed.

Based upon the examination of the mineral association, crystallography and mineral chemistry of pyrrhotite, the variation in mineralogy between magnetic and non-magnetic pyrrhotite was described by the proposed classification scheme:

- i). *Two phase pyrrhotite*: Non-magnetic $6C$ $Fe_{11}S_{12}$ pyrrhotite intergrown with $2C$ FeS troilite (Impala Merensky sample *IMP-2*).
- (ii). *Single phase pyrrhotite*: Non-magnetic $5C$ Fe_9S_{10} pyrrhotite (Sudbury CCN).
- (iii). *Two phase pyrrhotite*: Magnetic $4C$ Fe_7S_8 intergrown with non-magnetic pyrrhotite $5C$ Fe_9S_{10} (Nkomati MSB, Nkomati MMZ sample *MMZ-4*)
- (iv). *Single phase pyrrhotite*: Magnetic $4C$ Fe_7S_8 pyrrhotite (Impala Merensky sample *IMP-1*, Nkomati MMZ sample *MMZ-1*, Phoenix, Sudbury Gertrude and Gertrude West).

Single crystal analysis of the magnetic Impala Merensky sample *IMP-1* and Phoenix pyrrhotite samples confirmed they were monoclinic. Single crystal analysis of the non-magnetic Sudbury CCN pyrrhotite proved that $5C$ Fe_9S_{10} pyrrhotite was actually



orthorhombic in contrast to its commonly accepted crystallography as “hexagonal” pyrrhotite. Using the unique mineral chemistry dataset derived in this research, it was shown that the average atomic metal / sulfur ratios obtained for magnetic 4C Fe_7S_8 was 0.869 ± 0.013 ($n = 699$), for non-magnetic 5C Fe_9S_{10} was 0.895 ± 0.013 ($n = 316$) and for non-magnetic 6C $\text{Fe}_{11}\text{S}_{12}$ was 0.918 ± 0.017 ($n = 101$). The histogram comparing metal / sulfur ratios of all the pyrrhotite samples analysed showed a continuum of metal / sulfur ratios for each of the pyrrhotite superstructures. Some minor overlap in composition between pyrrhotite superstructures was observed and determined to be statistically significant. These features were interpreted to be representative of non-stoichiometry in the pyrrhotite mineral structure.

Based upon the examination of the mineral association, crystallography and mineral chemistry of pyrrhotite, it was argued that these features were primarily controlled by ore deposit formation. It was argued that the pyrrhotite superstructure and composition; intergrowth textures between magnetic and non-magnetic pyrrhotite, non-magnetic pyrrhotite and troilite, pyrrhotite and pentlandite; and the relative abundance of each sulfide phase, were influenced by the bulk composition and cooling history of the monosulfide solid solution (MSS) from which the pyrrhotite crystallised. Additional attributes of pyrrhotite mineralogy that were inferred to be important were the presence of oxygen during the crystallisation of the MSS (as evidenced by the presence of magnetite) and hydrothermal alteration of non-magnetic pyrrhotite to magnetic pyrrhotite (as evidenced by descriptions of magnetic pyrrhotite rims surrounding non-magnetic pyrrhotite in the literature).

Using open circuit potential, cyclic voltammetry and oxygen uptake measurements the reactivity of magnetic and non-magnetic pyrrhotite was investigated at pH 7 and 10. Non-magnetic Sudbury CCN pyrrhotite was the most unreactive of the pyrrhotite samples investigated, whereas magnetic pyrrhotite was considerably more reactive. Magnetic Sudbury Gertrude West was interpreted to be so reactive that the surfaces were already oxidised and passivated at the time of the oxygen uptake measurement, whereas the reactivity of Phoenix magnetic pyrrhotite was not as extreme. The reactivity of the Nkomati MSB pyrrhotite was in between non-magnetic Sudbury CCN and magnetic Phoenix due to the combined contribution of intergrown magnetic and non-magnetic pyrrhotite. Addition of flotation reagents to the pyrrhotite slurry caused a decrease in the reactivity of the pyrrhotite samples that was attributed to the formation of an adsorbed surface layer that protected the pyrrhotite from further oxidation.

Based upon carefully controlled microflotation studies of pyrrhotite under selected conditions, the flotation performance of magnetic and non-magnetic pyrrhotite was investigated at pH 7 and 10. Differences in the flotation performance of the different pyrrhotite samples were primarily attributed to their relative reactivity towards oxidation and formation of hydrophilic ferric hydroxides on the surface of pyrrhotite particles. Where pyrrhotite oxidation was more severe, it appeared that any interaction of the flotation reagents (SIBX, SNPX or copper sulfate) with the pyrrhotite surface was not possible as evidenced by the poor flotation performance of these pyrrhotite samples, especially at the higher pH. The non-magnetic Sudbury CCN pyrrhotite was the most floatable of the samples examined, whereas the magnetic Sudbury Gertrude and Gertrude West pyrrhotite samples showed the poorest flotation performance. Phoenix magnetic pyrrhotite also showed good flotation performance, whereas the flotation performance of the Nkomati MSB mixed pyrrhotite was only good at pH 7.

The key mineralogical characteristics of pyrrhotite that were interpreted to affect its reactivity and flotation performance were crystallography, mineral chemistry and mineral association. On the basis that magnetic pyrrhotite has more vacancies in its crystal structure than non-magnetic pyrrhotite (1 in 8 iron sites versus 1 in 10 iron sites), it was proposed that the presence of these vacancies facilitates the oxidation reaction and accounts for the increased reactivity of magnetic pyrrhotite. The greater proportion of ferric iron in the magnetic pyrrhotite structure relative to the non-magnetic pyrrhotite (2Fe^{3+} out of 7 cations versus 2Fe^{3+} out of 9 cations) was also argued to act as a stronger oxidising agent for magnetic pyrrhotite and accounts for its increased reactivity. Differences in the reactivity and flotation performance between magnetic pyrrhotite samples were postulated to be linked to the solid solution nickel content and its effect on positive effective charge that would likely retard pyrrhotite oxidation. Although not measured in this study, the influence of trace amounts of oxygen in the pyrrhotite structure could also influence the reactivity of magnetic pyrrhotite. Given the association of pyrrhotite with magnetite, it is known that $f\text{O}_2$ is important during crystallisation and cooling of the MSS and therefore it is not unlikely that some trace amount of oxygen may have been accommodated in the pyrrhotite crystal structure. The association of pyrrhotite with pentlandite was very important since pyrrhotite flotation could be positively influenced by the flotation of composite particles comprised of abundant locked flame pentlandite. Nickel ions derived from the locked flame pentlandite could also assist in the activation of pyrrhotite and further improve its flotation performance. The mineral association



between pyrrhotite types was noted to be important since the reactivity and flotation performance of mixed pyrrhotite was likely controlled by the contribution of the intergrown magnetic and non-magnetic pyrrhotite components.

This study has also shown the usefulness of process mineralogy as a field of research in aiding the understanding of pyrrhotite flotation performance. Although the process mineralogy measurements performed here cannot necessarily predict flotation performance, they can assist in the understanding and potential optimisation of pyrrhotite flotation performance according to whether the recovery or rejection of pyrrhotite is targeted. Simple mineralogical and mineral reactivity measurements which have been of the most use in developing this relationship between mineralogy and flotation performance include the identification of pyrrhotite type (magnetic versus non-magnetic), determination of the relative proportions of minerals in a sample and investigation of the oxygen uptake.

8.2 Recommendations

In light of the findings of this thesis, several recommendations for future research are made below:

- Quantitative analysis of platinum group elements in pyrrhotite with laser ablation ICP-MS or PIXE methods using synthetic sulfide standards doped with the platinum group elements in order to determine whether there is a relationship between pyrrhotite type and PGE content.
- Further sampling of pyrrhotite from the Merensky Reef to comprehensively explore the compositional variation of pyrrhotite in this ore deposit, and confirm the presence of intergrown magnetic and non-magnetic pyrrhotite phases that was not encountered in the samples examined in this study.
- Single crystal analysis of a 6C $\text{Fe}_{11}\text{S}_{12}$ pyrrhotite crystal in order to determine and solve its crystal structure. With the addition of the 6C crystal structure to the pyrrhotite crystal structure database, naturally occurring 4C, 5C and 6C pyrrhotite structures would be available for quantitative powder XRD using Rietveld refinement.
- Validation of the pyrrhotite mapping procedure using EBSD and further QEMSCAN or MLA analysis methods to establish a procedure which can routinely be used for mineralogical analysis of metallurgical samples.
- The use of nuclear microprobe techniques to measure oxygen in magnetic and non-magnetic pyrrhotite samples and determine whether a correlation between oxygen content and reactivity exists.
- The use of EDTA, pH and Eh measurements in conjunction with oxygen uptake studies on pyrrhotite samples may provide further insight into pyrrhotite oxidation. The use of ToF-SIMS would also be of interest to confirm differences in the extent of oxidation of pyrrhotite samples examined in this study.



- Further electrochemical measurements such as cyclic voltammetry or electrical impedance spectroscopy to evaluate the interactions of the different pyrrhotite samples with flotation reagents. The assignment of the appropriate equations to the various REDOX reaction is also necessary.
- Further electrochemical and flotation studies to examine the effect of the galvanic interaction on pentlandite flotation performance.
- Further investigation into the mechanism of copper activation on pyrrhotite and the factors that influence its success, particularly for magnetic pyrrhotite.
- Laboratory scale batch flotation tests on pyrrhotite samples in order confirm the results of this study and determine the influence of additional variables such as the effect of grinding media, silicate mineralogy and presence of a froth phase on pyrrhotite flotation. Subsequent MLA or QEMSCAN analysis of metallurgical samples would also be beneficial.
- Key ideas from this research should be extended to the application of pyrrhotite flotation in other nickel deposits (e.g. Noris'lk Talnakh, Russia) and lead zinc type ore deposits in order to determine whether the same mineralogical factors also influence pyrrhotite flotation.
- Key ideas from this research should be extended into the field of acid mine drainage research in order to determine whether pyrrhotite mineralogy is a controlling factor in acid producing potential.