The Composition and Crystal Structures of Pyrrhotite: A Common but Poorly Understood Mineral

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Pyrrhotite Characterization

- Pyrrhotite \((\text{Fe}_{1-x}\text{S})\) is a common sulfide mineral in nickel and platinum group metal (PGM) deposits
- It is an unwanted phase in nickel processing because it dilutes the nickel concentrate and is expensive to remove
- It is recovered in PGM processing because many platinum group minerals are associated with it. It also contributes to matte-fall in UG-2 matte smelting
- Pyrrhotite occurs in several forms with different symmetry and usually slightly different compositions
- In Nature two major forms exist:
  - Magnetic \text{Fe}_7\text{S}_8 and can in principle be separated from…..
  - Non-magnetic \text{Fe}_9\text{S}_{10} and \text{Fe}_{11}\text{S}_{12}
- We are investigating the flotation behaviour of the two pyrrhotite types – hence the need to characterise and quantify them
Pyrrhotite Removal - Clarabelle Mill Sudbury

- Magnetic separation can only separate the magnetic pyrrhotite from the pentlandite concentrate.
- Flotation is used to remove pyrrhotite from the pentlandite concentrate.
Microflotation Recovery of Pyrrhotite – pH 7
Microflotation Recovery of Pyrrhotite – pH 10
Merensky Pyrrhotite

Electron Backscatter Images
Known Pyrrhotites

- **Troilite FeS (Evans, 1970)**
  - Stoichiometric with a 2C superstructure (C is the c-axis of the NiAs subcell)
  - Distorted NiAs structure

- **Monoclinic Pyrrhotite (Tokonami et al, 1972)**
  - Stoichiometric Fe$_7$S$_8$ with 4C superstructure
  - The structure does not explain the non-stoichiometry

- **Other natural varieties** – **structures unknown**
  - Fe$_9$S$_{10}$ - 5C
  - Fe$_{10}$S$_{11}$ – incommensurate
  - Fe$_{11}$S$_{12}$ - 6C

- **Synthetic varieties**
  - Fe$_7$S$_8$ - Hexagonal 3C

- **All varieties thought to be derived from the ordering of vacancies**
- **Natural varieties have not been synthesized**
Pyrrhotite Phase relations

- Transition of troilite (315°C)
- Phase relations unknown
- Transition of troilite (140°C)

Temperature (°C):
- 325
- 275
- 225
- 175
- 125
- 75
- 25

FeS:
- 50
- 49.5
- 49
- 48.5
- 48
- 47.5
- 47
- 46.5

Fe atomic percent (%):
- 33.33
- 25

Phase compositions:
- 1C + pyrite
- MC + pyrite
- NA + pyrite
- 4C + pyrite
- 2C + 1C
- 2C + NC
- MC
Compositional Variation – 1106 Analyses
New Pyrrhotite structures

• 5C Pyrrhotite from Sudbury, Canada
  – Described as Hexagonal
  – Hexagonal structure determination not successful
  – Structure determined with SHELX and refined to $R = 0.060$
  – Orthorhombic: Cmce
  – $a = 6.893(3)$ Å, $b = 11.939(3)$ Å and $c = 28.63(1)$ Å

• 6C Pyrrhotite from Mponeng Mine, South Africa
  – Structure correctly predicted by Koto et al. (1975)
  – No atomic coordinates given by them
  – Structure refined with SHELX and refined to $R = 0.029$
  – Non-standard Space Group Fd (to preserve orthogonality)
  – $a = 6.897(2)$ Å, $b = 11.954(3)$ Å, $c = 34.521(7)$, $\beta = 90.003^\circ$
  – Structure can be transformed to Cc space group setting
New Pyrrhotite structures

• 4C Pyrrhotite from Bushveld Complex
  – Cell similar to published F-centered cell
  – Cell is C-centered
  – Structure determined with SHELX and refined to $R = 0.052$
  – Monoclinic: C2
  – Cell: $a = 11.890(4) \, \text{Å}$, $b = 6.872(2) \, \text{Å}$, $c = 22.786(8) \, \text{Å}$
  – F2/d: $a = 11.902(8) \, \text{Å}$, $b = 6.859(5) \, \text{Å}$, $c = 22.787(10) \, \text{Å}$
    (Tokonami et al.)

• The crystal structures are needed:
  – to understand the compositional variation
  – to quantify the different pyrrhotites
  – to calculate their bonding and oxidation properties
  – to model the docking of reagents on mineral surfaces
NiAs Structure
Troilite – FeS (stoichiometric)
5C Pyrrhotite - Layer-0
5C Pyrrhotite - Layer-1
Adjacent Fe-octahedra
New Pyrrhotite Superstructures

“Fe\textsubscript{7}S\textsubscript{8}”

“Fe\textsubscript{9}S\textsubscript{10}”

“Fe\textsubscript{11}S\textsubscript{12}”
Refinement of 5C pyrrhotite - TOPAS

\[ R_{wp} = 1.76\% \]

Pyrrhotite-4C  3.07 %
Pentlandite  3.29 %
Po-5C-Cmca  93.65 %
Accuracy of quantification - Pyrrhotites

Simultaneous refinement of all samples in a set seems to give the best results.
Non-stoichiometry

• From the compositional data it seems likely that Fe$^{3+}$ is substituting for Fe$^{2+}$, i.e. $\text{Fe}^{2+}_5\text{Fe}^{3+}_2\text{S}_8$
• The presence of ferric iron seems to stabilise non-stoichiometric pyrrhotites
• A neutron diffraction study of $\text{Fe}_7\text{S}_8$ supports a fast charge transfer with iron valency of $\text{Fe}^{2.29+}$
• No evidence for Fe$^{3+}$ from Mössbauer spectroscopy
• There are probably many more pyrrhotite structures
• The proportion of ferric iron will influence the tendency of pyrrhotite to oxidise:
  – Affecting flotation behaviour
  – Affecting the production of acid mine drainage
  – Affecting combustion in flash furnaces
  – Affecting their magnetic properties
Unresolved questions:..................

• The perceived absence of ferric iron in Mössbauer and XMCD studies of pyrrhotites needs to be resolved
• The crystallographic information of the samples needs to be carefully characterised
• Materials modelling on the structural stability of the superstructures is in progress at UP and Curtin University
• Spectroscopic and neutron diffraction work needs to be done on natural pyrrhotites to resolve their magnetic character
• Powder XRD is not sufficient to characterise natural pyrrhotites – neither are SEM based methods
• Perhaps high-resolution synchrotron and neutron powder data can help
• Flotation behaviour is still unexplained !!!!!!
• There is still a lot of work to be done!
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