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

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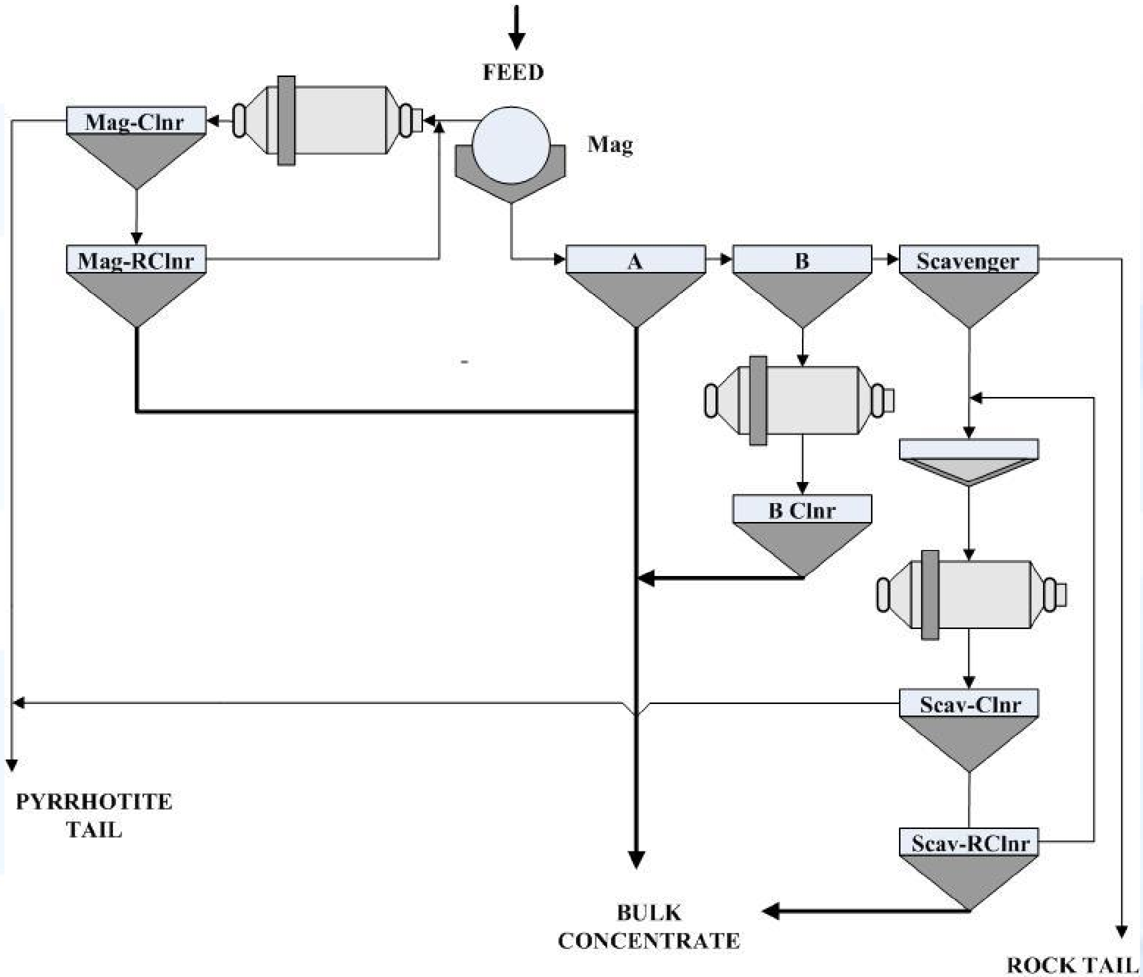
Pyrrhotite Characterization

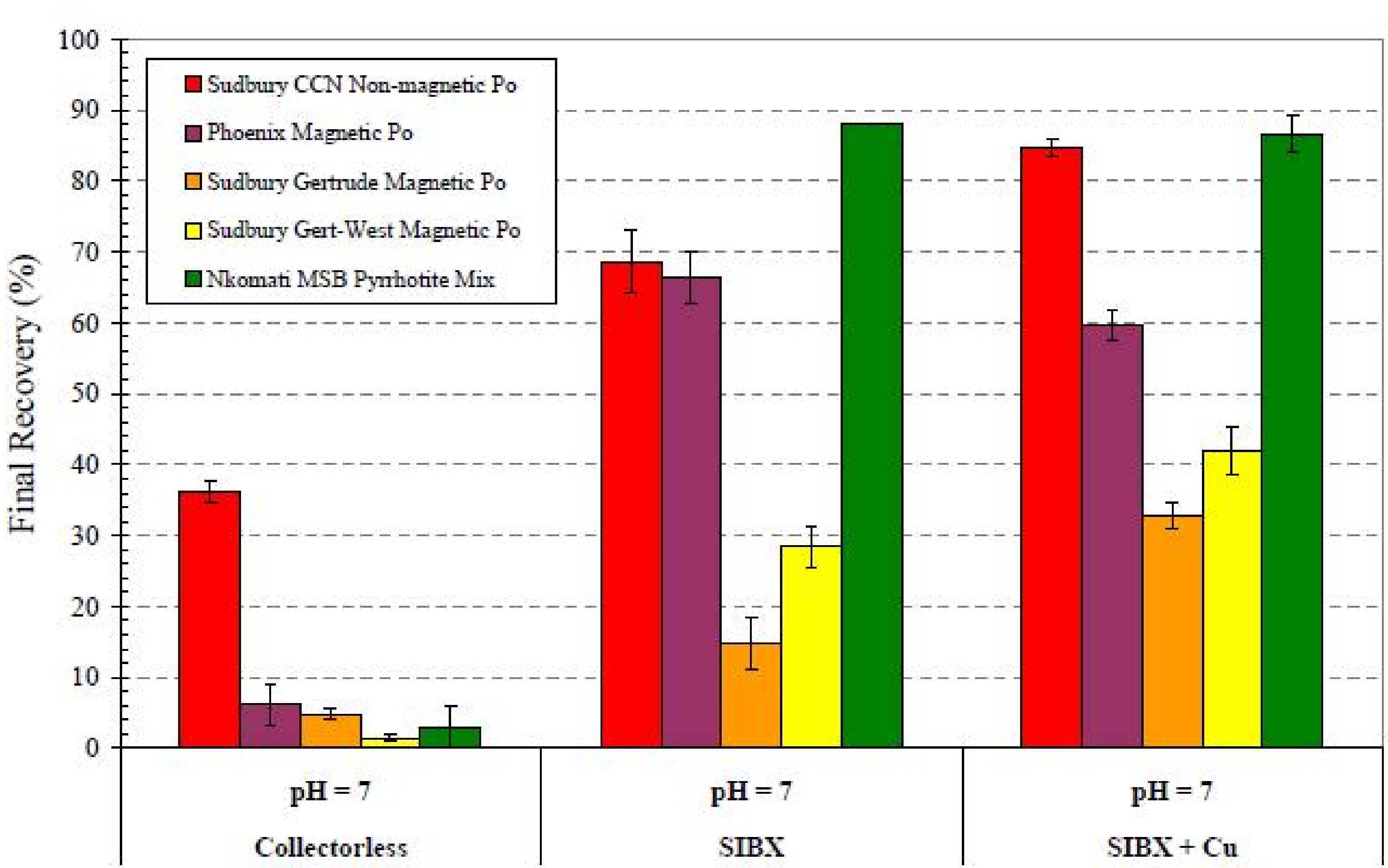
- Pyrrhotite ($Fe_{1-x}S$) is a common sulfide mineral in nickel and platinum group metal (PGM) deposits
- It is an unwanted phase in nickel processing because it dilutes the nickel concentrate and is expensive to remove
- It is recovered in PGM processing because many platinum group minerals are associated 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 Fe_7S_8 and can in principle be separated from…..
  - Non-magnetic Fe_9S_{10} and $Fe_{11}S_{12}$
- We are investigating the flotation behaviour of the two pyrrhotite tipes – hence the need to characterise and quantify them

Pyrrhotite Removal - Clarabelle Mill Sudbury

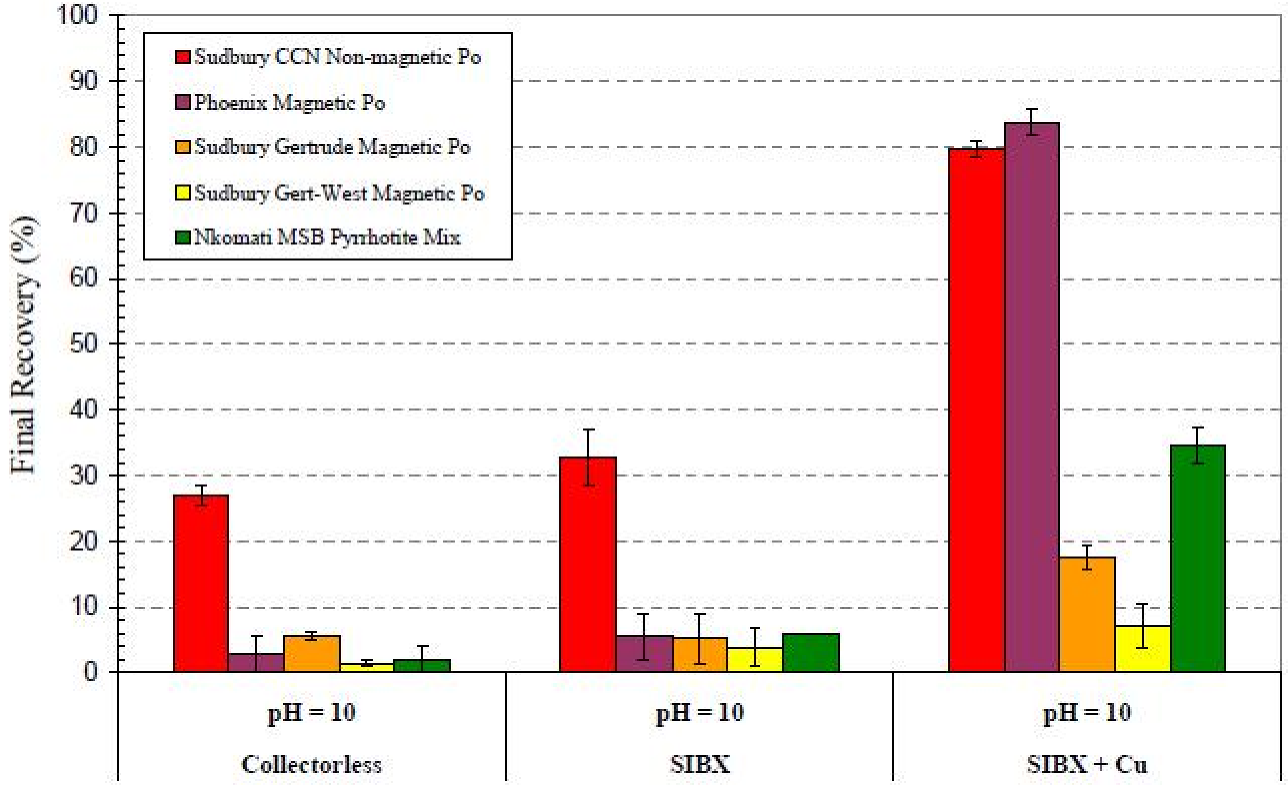


- Magnetic separation can only separate the magnetic pyrrhotite from the pentlandite concentrate
- Flotation is used to remove pyrrhotite from the pentlandite concentrate

Microflotation Recovery of Pyrrhotite – pH 7



Microflotation Recovery of Pyrrhotite – pH 10



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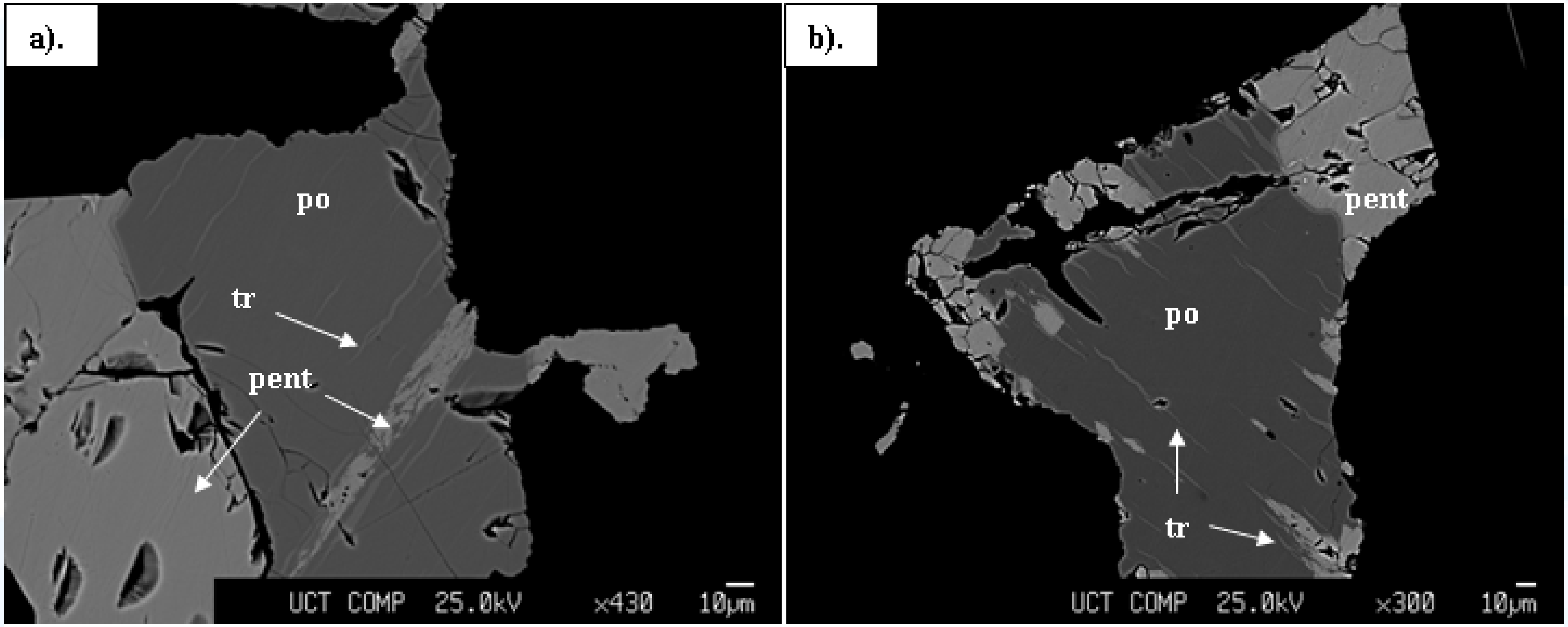
Merensky Pyrrhotite

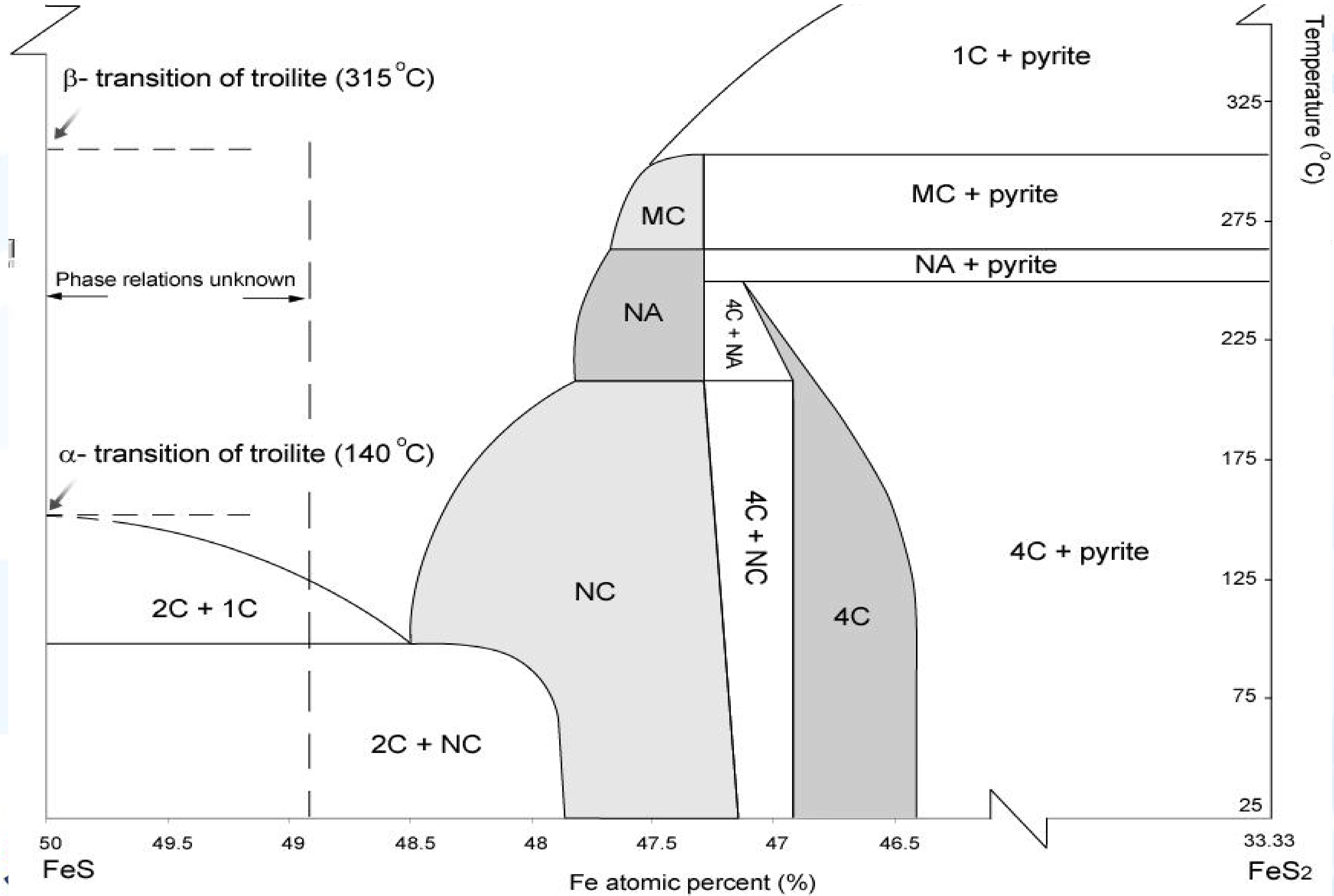


Electron Backscatter Images

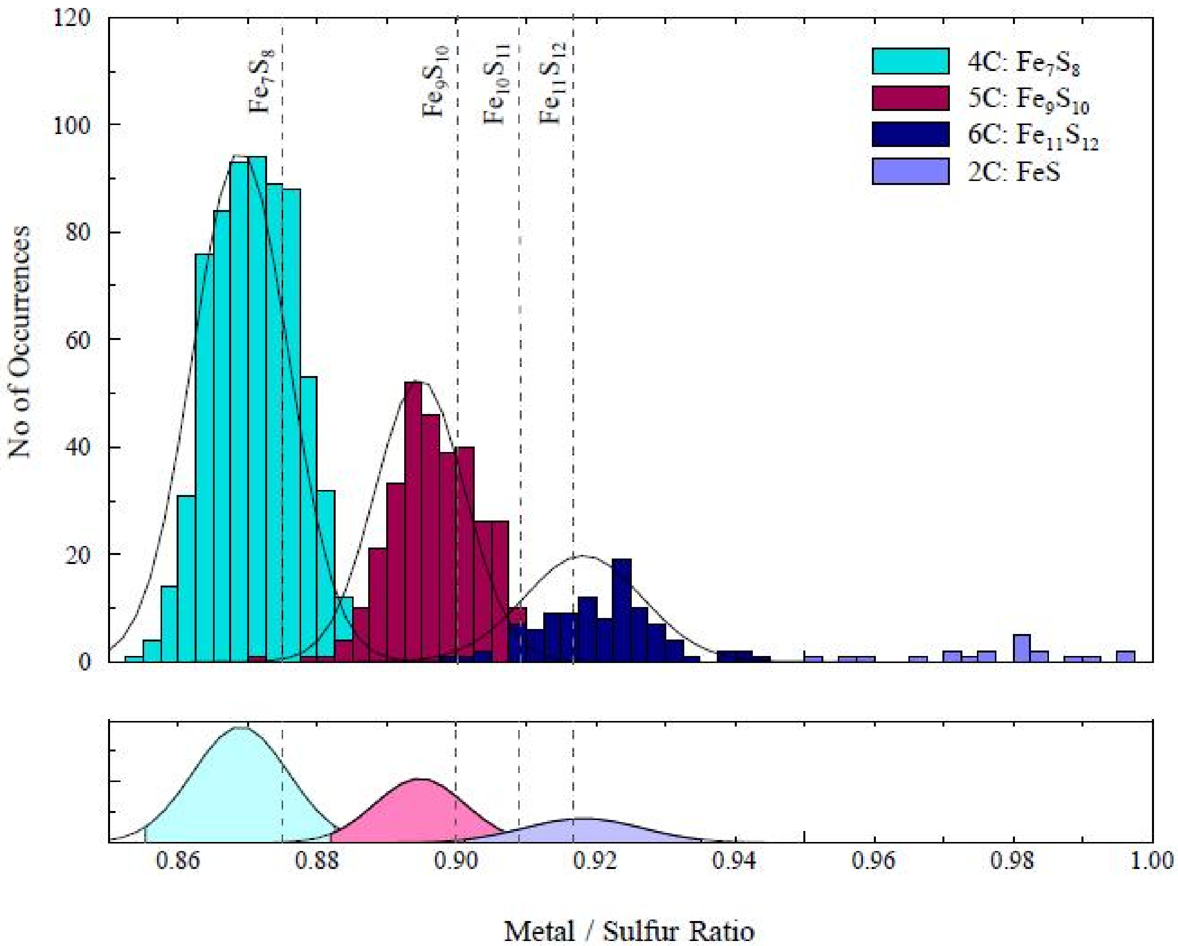
Known Pyrrhotites

- 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_7S_8 with 4C superstructure
  - The structure does not explain the non-stoichiometry
- Other natural varieties – structures unknown
  - Fe_9S_{10} - 5C
  - $Fe_{10}S_{11}$ – incommensurate
  - $Fe_{11}S_{12}$ -6C
- Synthetic varieties
  - Fe_7S_8 -Hexagonal 3C
- All varieties thought to be derived from the ordering of vacancies
- Natural varieties have not been synthesized

Pyrrhotite Phase relations



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

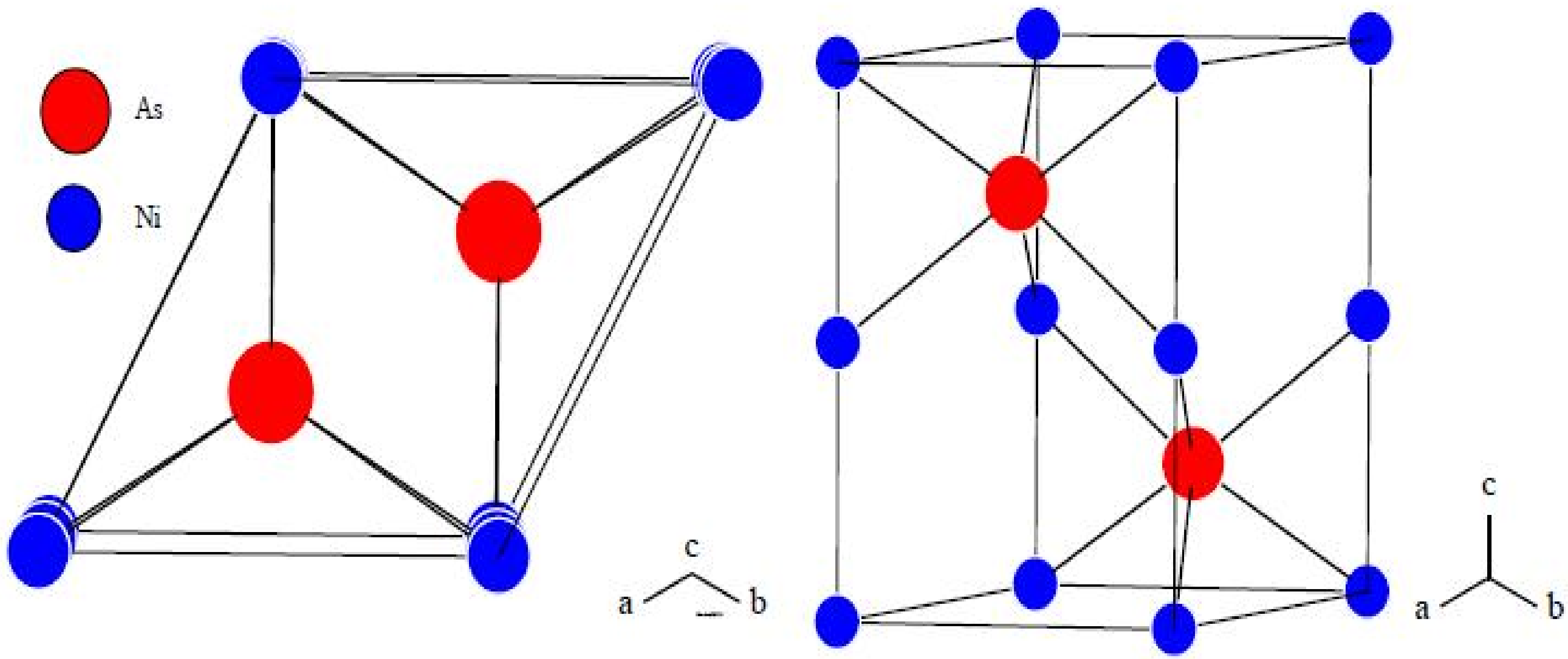
- 6C Pyrrhotite from Mponeng Mine, South Africa
  - Structure correctly predicted by Koto et al. (1975)
  - No atomic coordinates given by them
  - Structure refined with SHELX and refined to R=0.029
  - Non-standard Space Group Fd (to preserve orthogonality)
  - a = 6.897(2) Å, b = 11.954(3) Å, c =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

New Pyrrhotite structures

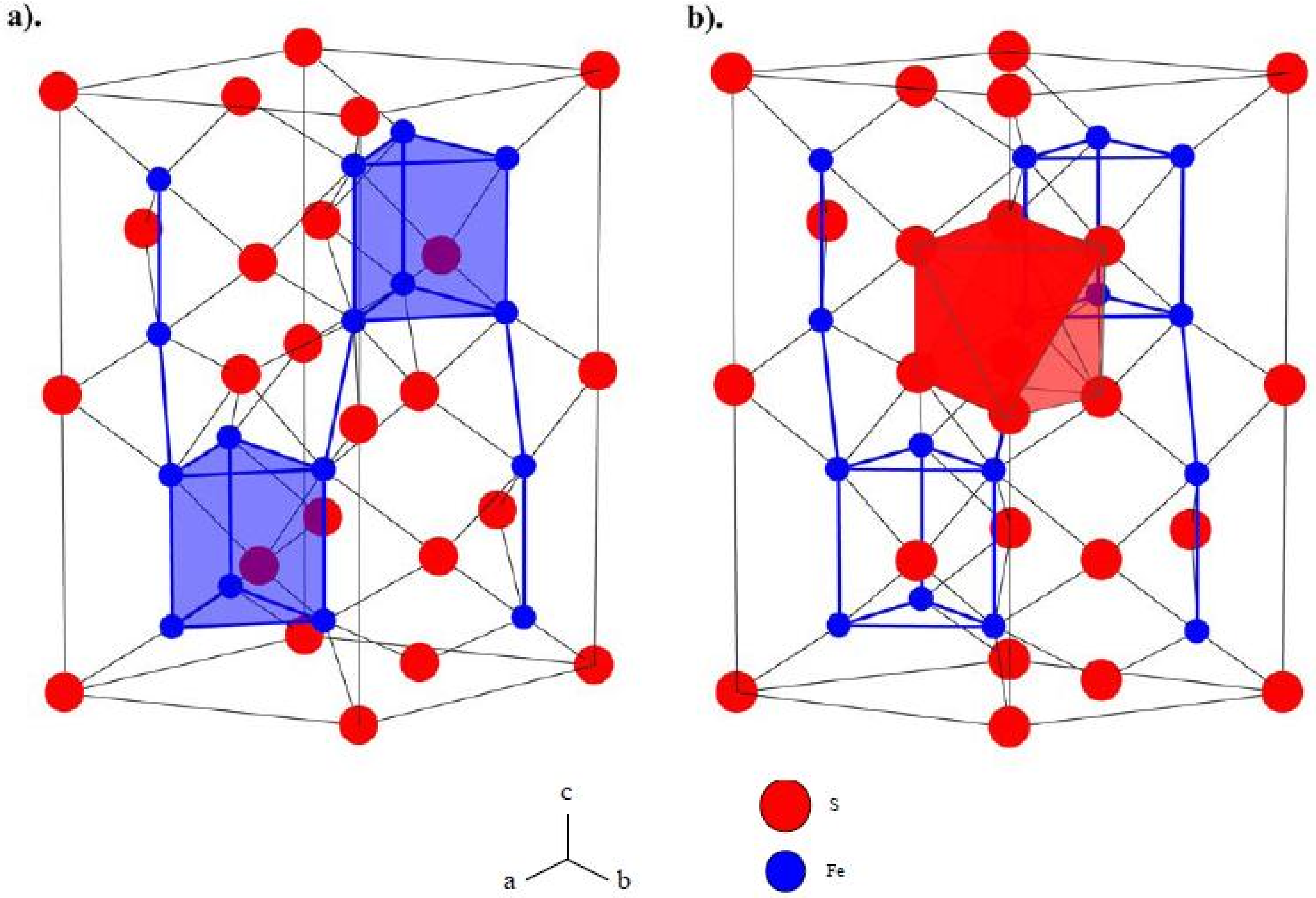
- 4C Pyrrhotite from Bushveld Complex
  - Cell similar to published F-centered cell
  - Cell is C-centered
  - Structure determined with SHELX and refined to R = 0.052
  - Monoclinic: C2
  - Cell: a = 11.890(4) Å, b = 6.872(2) Å, c = 22.786(8) Å
  - F2/d: a = 11.902(8) Å, b = 6.859(5) Å, c = 22.787(10)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

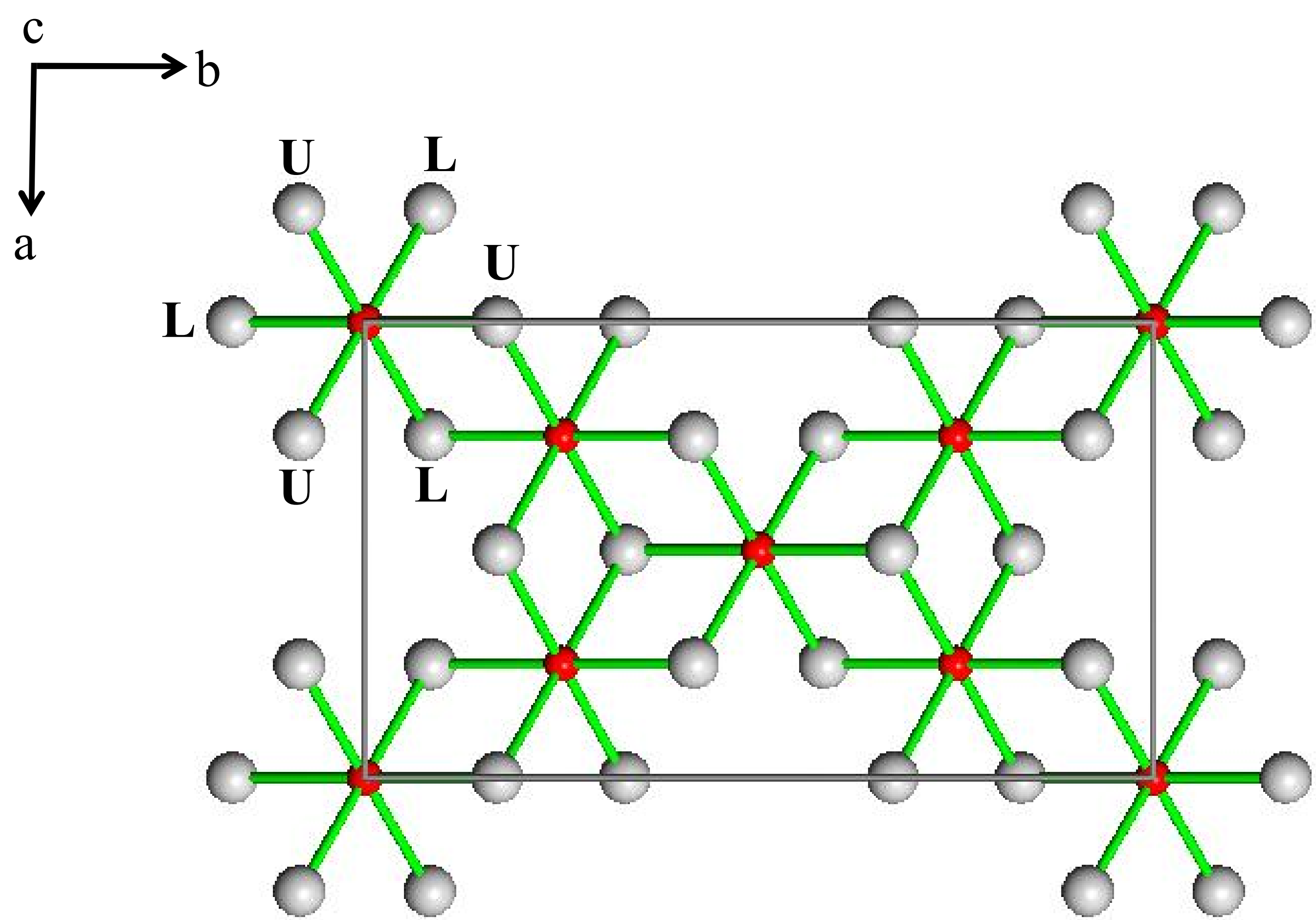
NiAs Structure



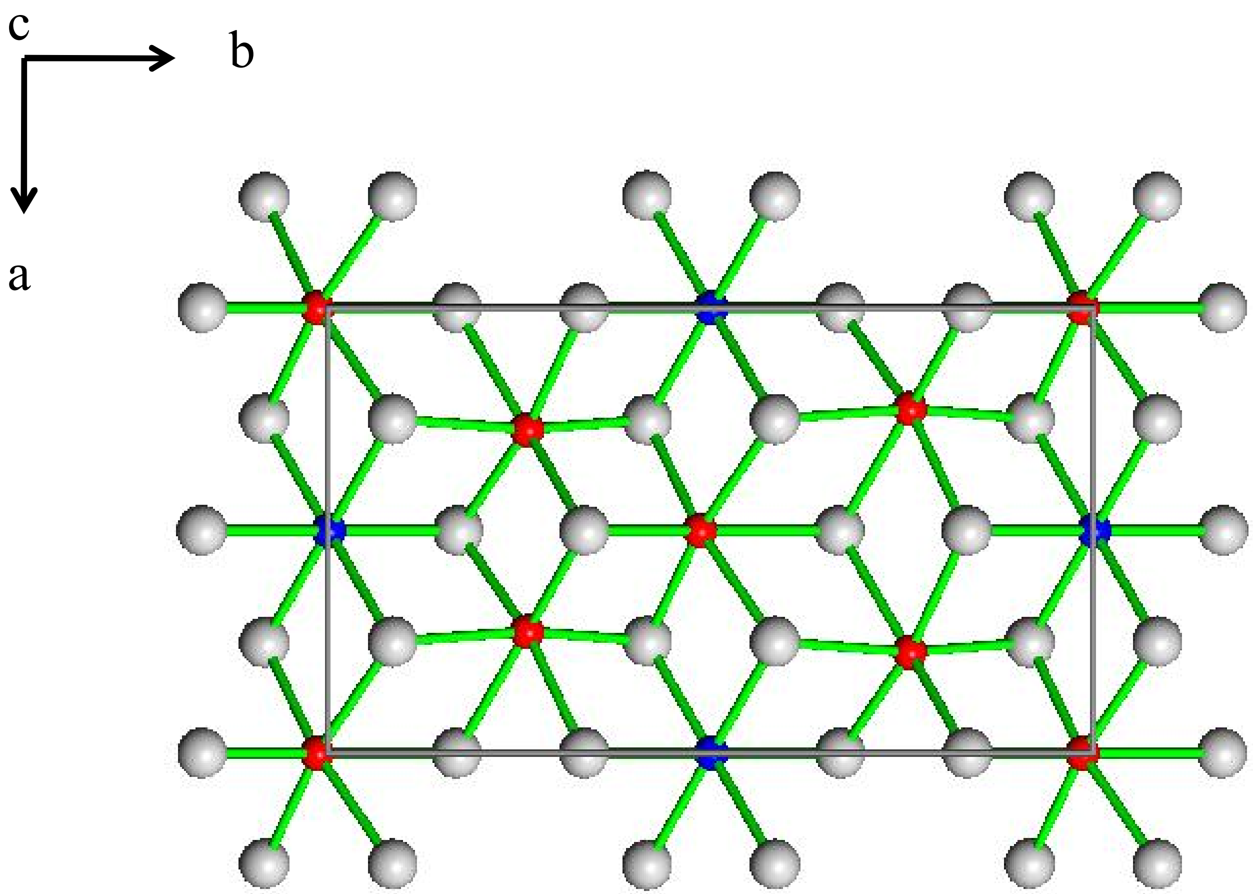
Troilite – FeS (stoichiometric)



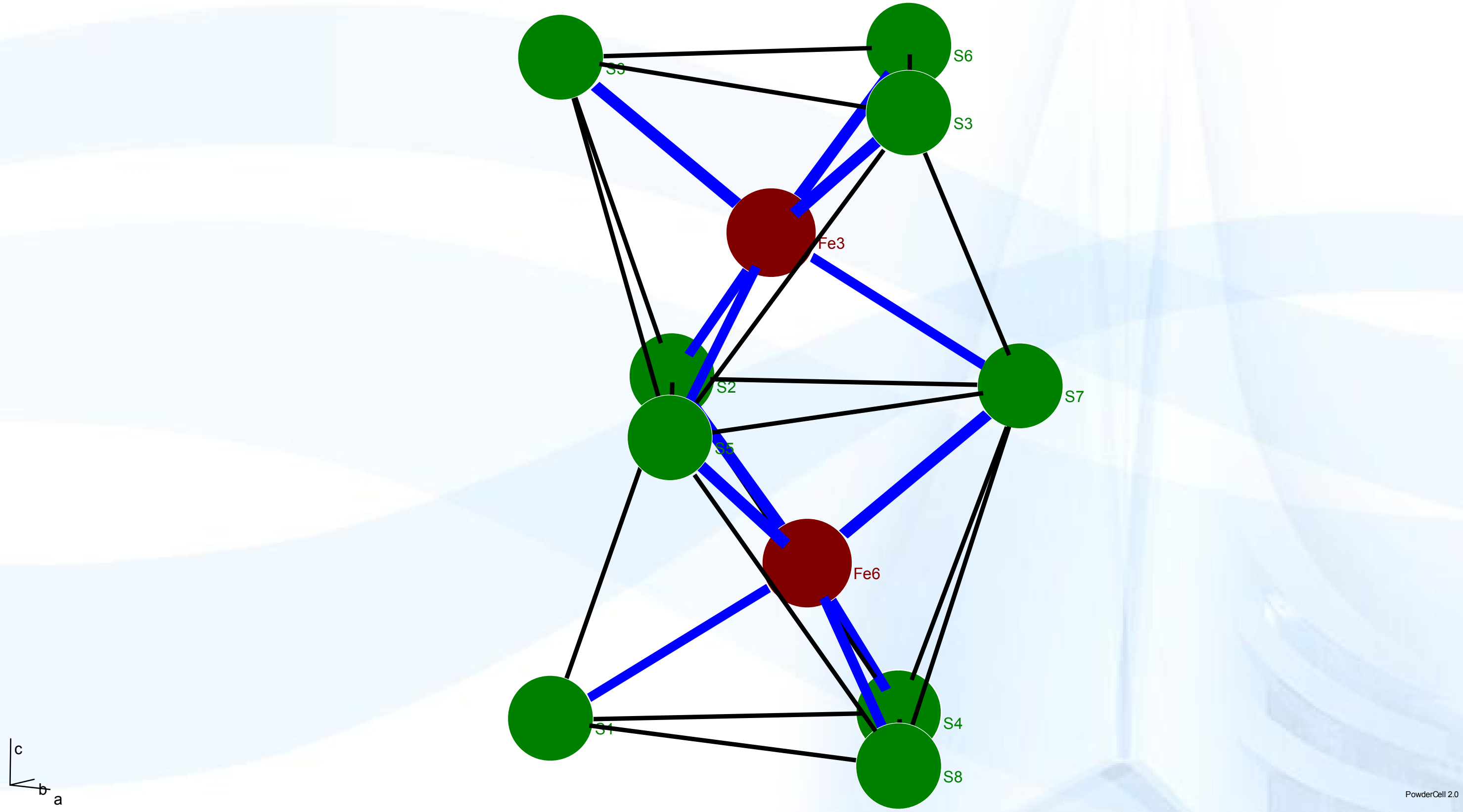
5C Pyrrhotite - Layer-0



5C Pyrrhotite - Layer-1

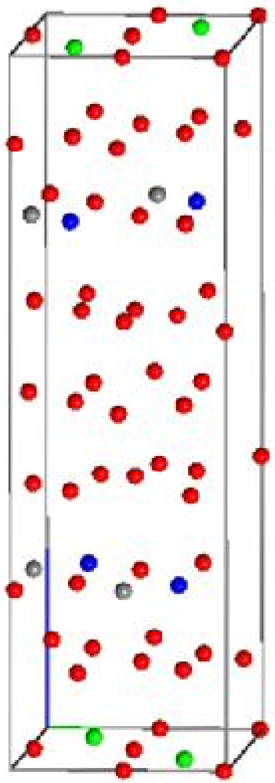


Adjacent Fe- octahedra



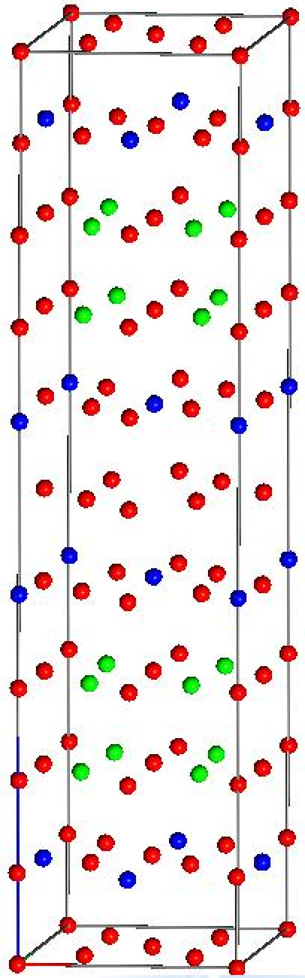
New Pyrrhotite Superstructures

"Fe_7S_8"



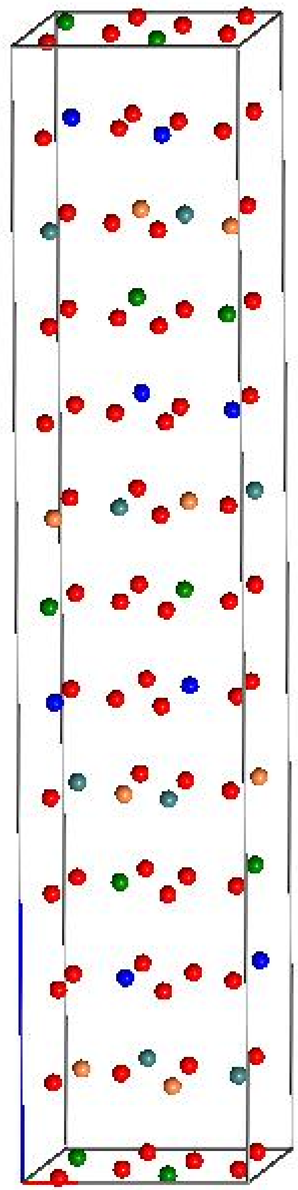
4C

"Fe_9S_{10}"



5C

"$Fe_{11}S_{12}$"



6C

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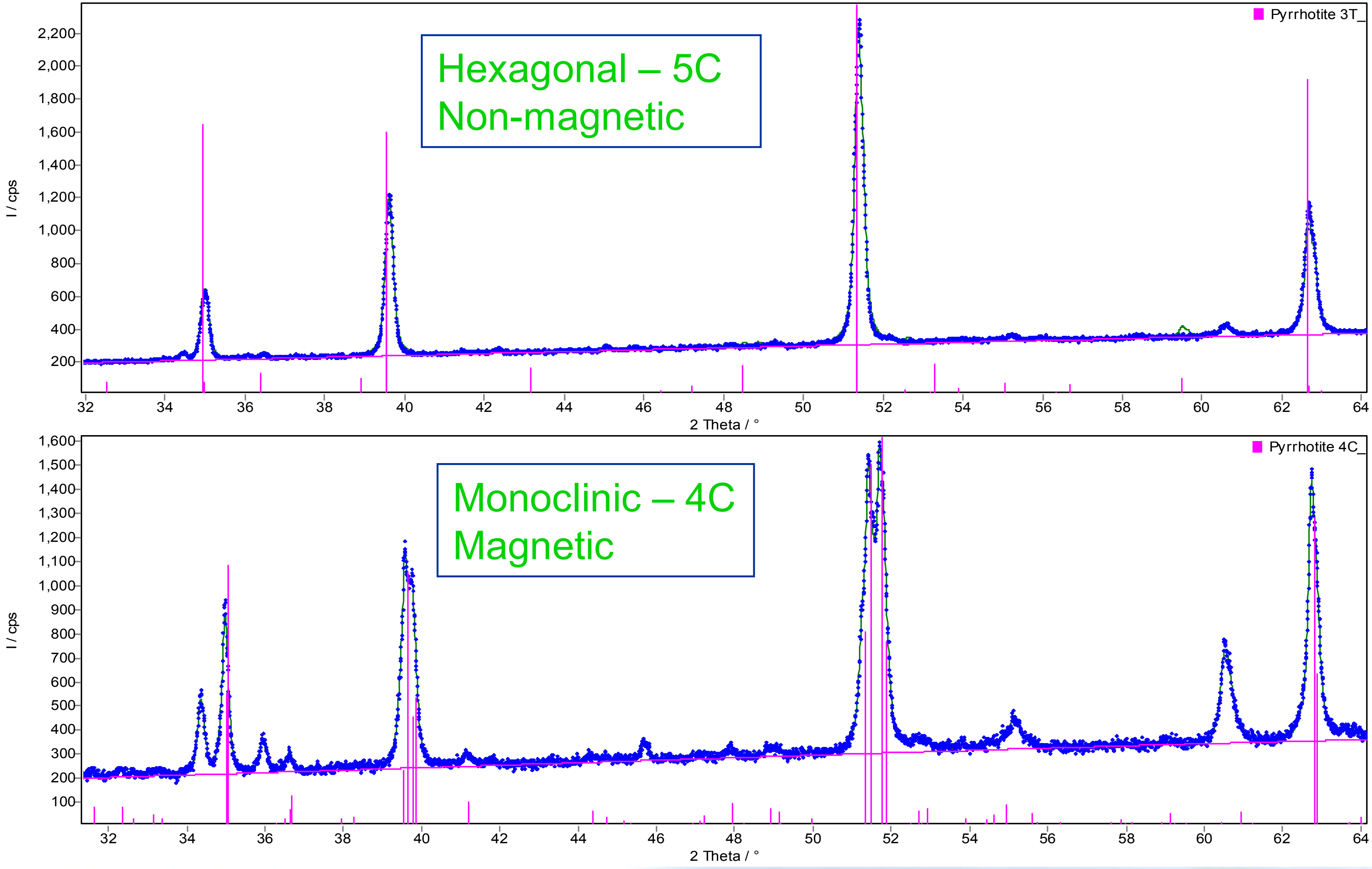
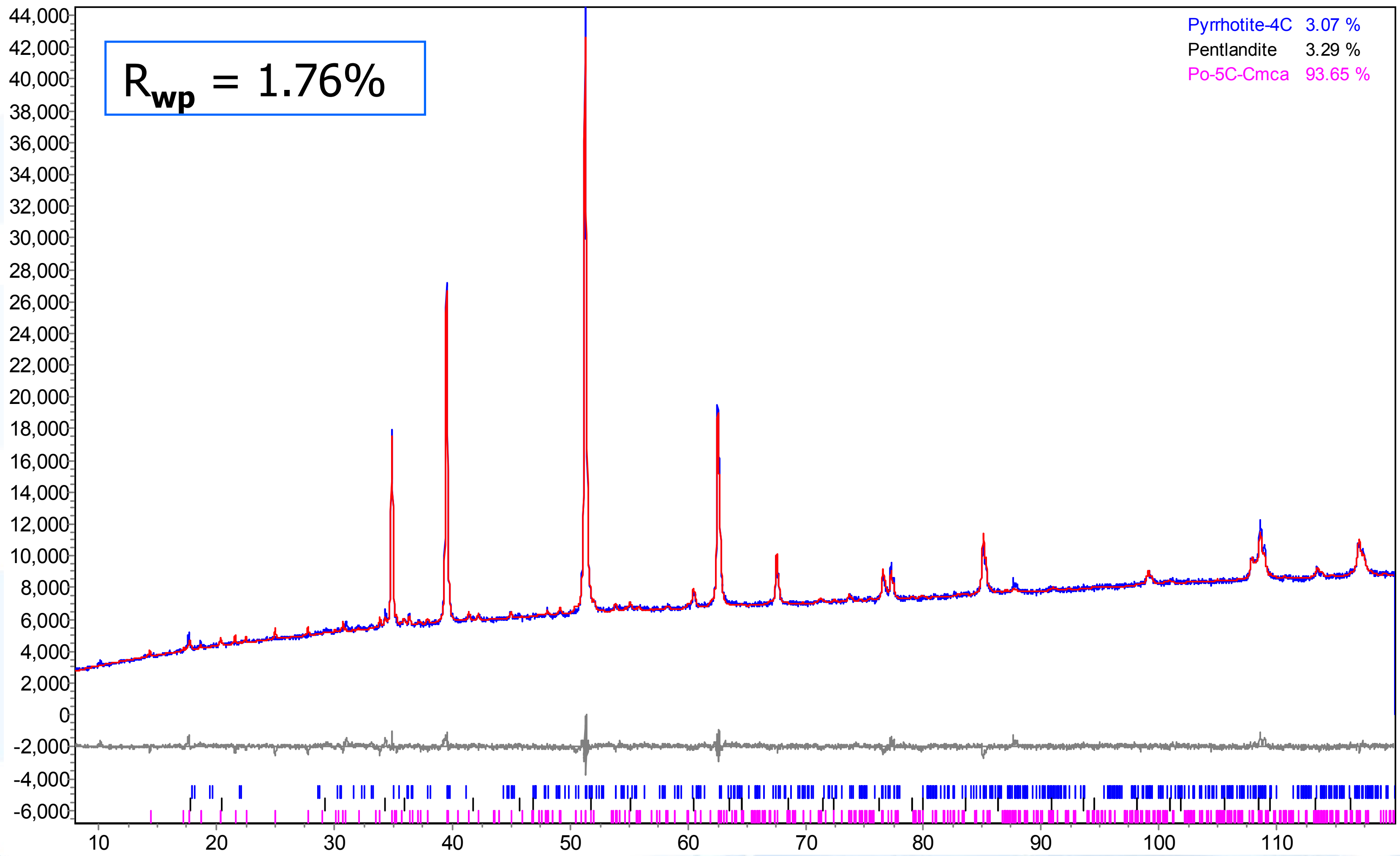
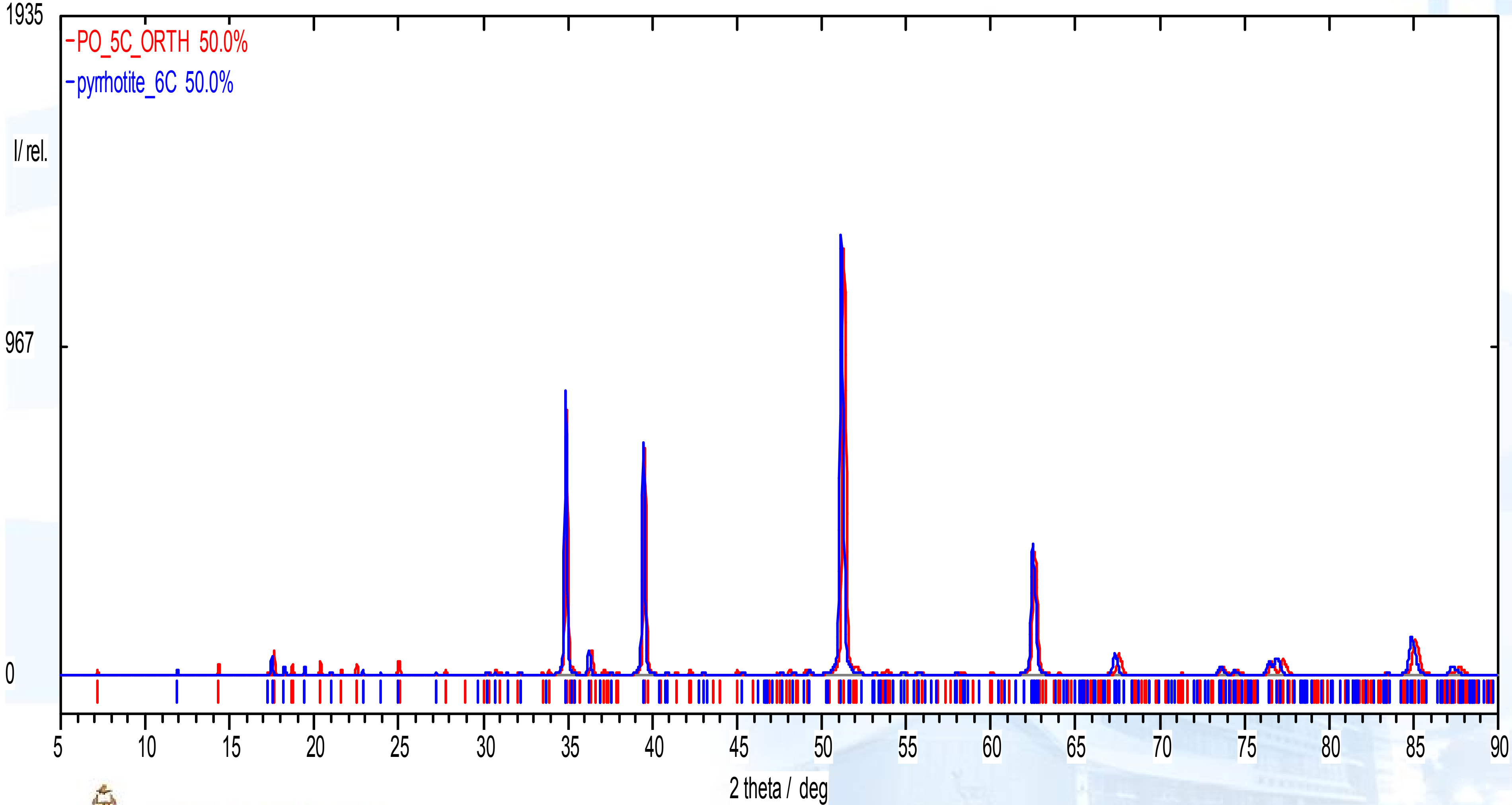
Pyrrhotite - Quantification



Refinement of 5C pyrrhotite - TOPAS



Calculated XRD Powder Patterns – 5C vs 6C



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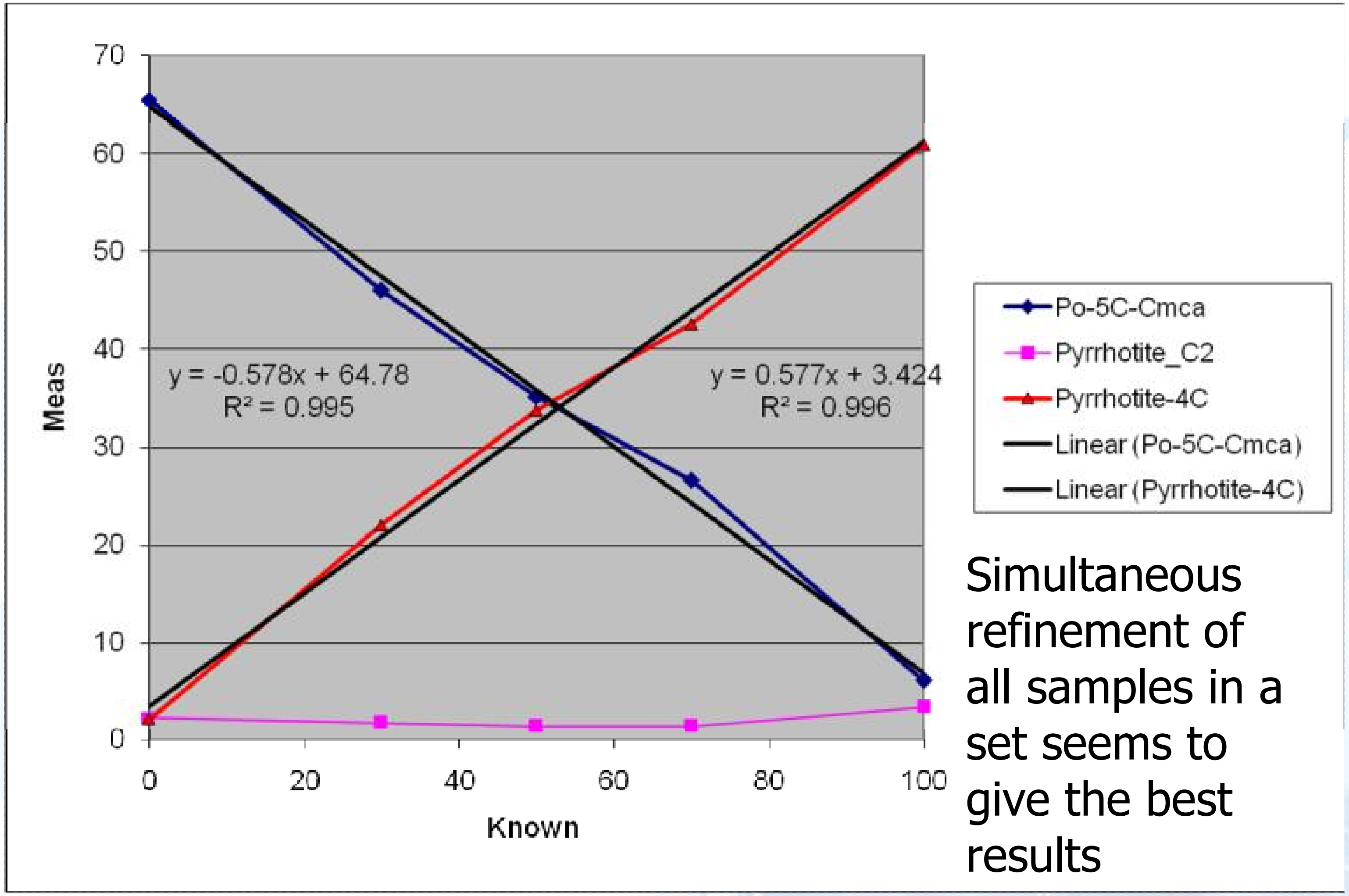
Accuracy of quantification - Pyrrhotites



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 $Fe^{2+}_5Fe^{3+}_2S_8$
- The presence of ferric iron seems to stabilise non-stoichiometric pyrrhotites
- A neutron diffraction study of Fe_7S_8 supports a fast charge transfer with iron valency of $Fe^{2.29+}$
- 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!

Acknowledgments

- Megan Becker for compositional data, for flotation data, and for samples, also for stimulating my interest in pyrrhotites
- Sabine Verryn for precise XRD data
- Peter Gräser for microprobe data of single crystals
- Dave Liles for single crystal data
- Alison Tuling for help with microscopy
- Ian Madsen and Nicola Scarlett of CSIRO Minerals for help with simultaneous refinements using TOPAS

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