The impact of powder X-ray diffraction on mineral science, mineral processing and process optimization

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The Mining Industry

It is the source of the major commodities and an important source of revenue for many countries

Contribution to the GDP of producing countries:

Chile	19.2%
Russia	13.8%
Australia	8.8%
South Africa	8.6%
Brazil	3.6%
India	2.3%

http://minerals.usgs.gov/minerals/pubs

Research in this field is a priority

Resource sustainability is also important

XRD in the Minerals Industry

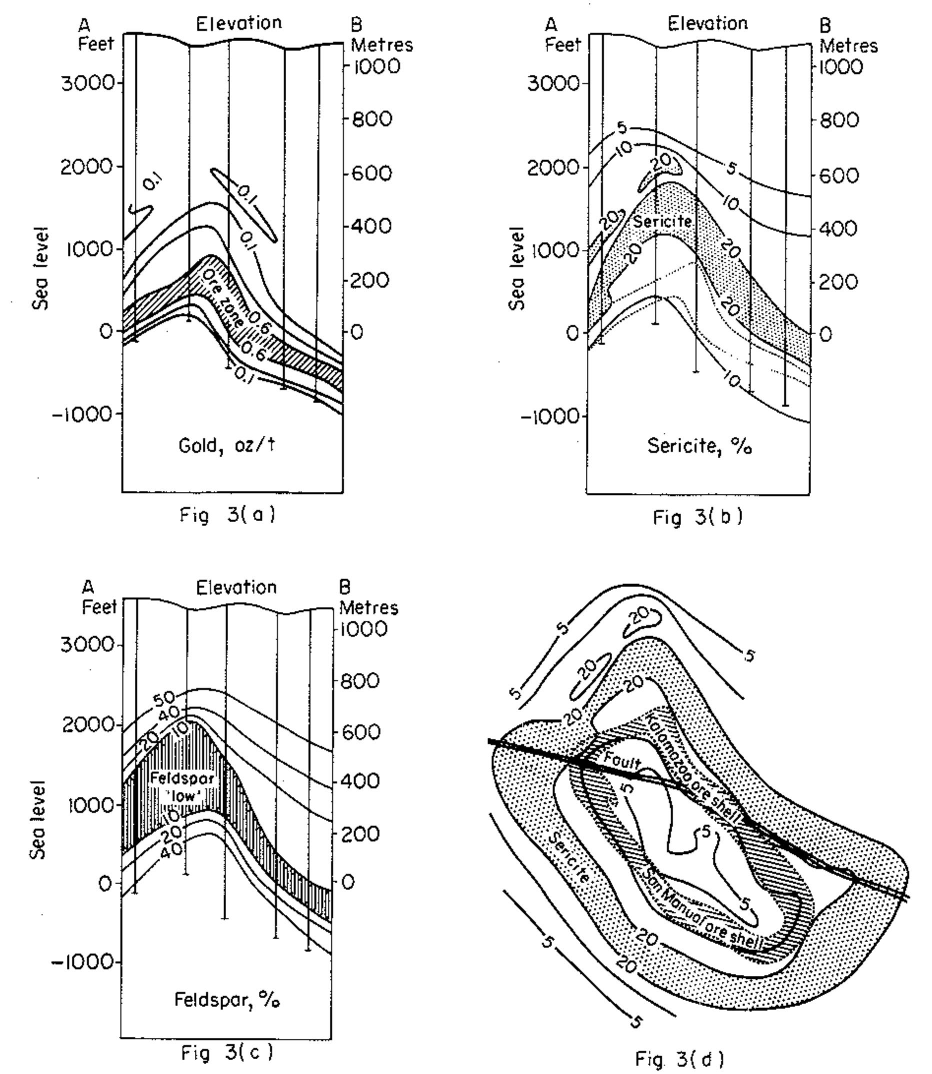
- Research and process evaluation are needs driven and often dictated by industry
- They usually have important financial implications
- They rely heavily on methods developed by academia and instrument developers
- Accuracy is as relevant here as elsewhere
- Examples
- Exploration and orebody evaluation
- Minerals processing
- High-temperature processing
- Materials characterization

XRD Use in the Minerals Industry

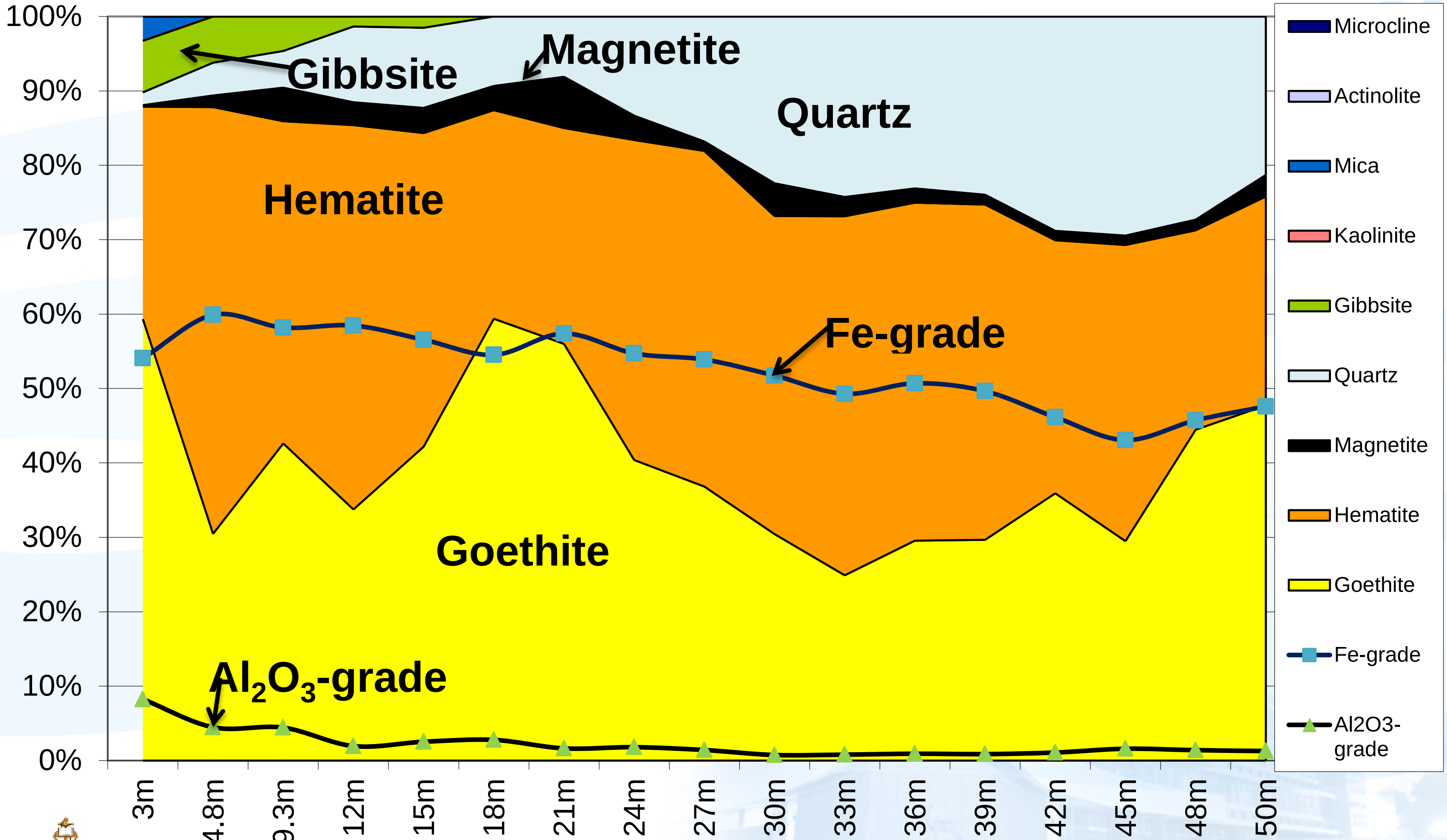
- Exploration and Orebody Evaluation
  - Mineralization is often associated with alteration features
    - Porphyry copper mineralization
    - Carlin gold exploration
  - Mineral speciation determines process options
    - Sulfide vs silicate or oxide mineralogy
    - Presence of problematic gangue (accessory) minerals
    - Presence of environmentally harmful minerals (AMD)
  - Ore variability to be determined – resource evaluation
    - Mineralogical variation across the orebody
    - Extent of alteration in the orebody affects processing

Wall Rock Alteration as an Exploration Tool – Don Hausen, 1981

At Kalamazoo, San Manuel District, Nevada, copper mineralization is enclosed by a sericite mica alteration zone, as determined by quantitative XRD



Congolese Fe-ore: XRD vs Chemistry



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Proper Ore Characterization: Its Importance

- Beenup Heavy Minerals Mine, Western Australia
  - "The mine operated for two years before being closed prematurely due to high operating costs." (Closure in 1999)
  - Environmental Problems:
    - More clay was found among the titanium minerals than planned, and the tailings proved to be very fine and rich in pyrite
    - groundwater acidity and metal concentrations remained substantial
    - Arsenic concentrations in the trial pit area ranged from 210 to 4300 ppb
  - ***Clearly the impact of pyrite and clay on the viability of the mine has been underestimated.*** (a A$1 billion tax claim plus commissioning (A$260 million) and ongoing remediation costs)

Applicability of QPA for Ore Evaluation

- XRD is most used for the quantification of ores with major amounts of valuable minerals
  - Iron/Mn ores 55% Fe(Sishen)
    20% Fe(Labrador trough)
  - Fluorspar 9-10% (USGS)
  - Ilmenite/rutile 8% (Hard Rock)
    2-3% (Heavy minerals
- Gangue minerals can be quantified
  - Effects of gangue minerals on processing
  - Zoning of mineralization defined by silicate minerals
  - Fine-grained ores are easily quantified (<5 µm sizes are below the resolution limit of micro-analysis)
- Relatively easy and representative sample preparation compared to sampling and polishing for SEM analysis

Limitations of QPA for Ore Evaluation

- Most valuable minerals in ores occur in quantities at or below the detection limit of XRD
  - Sulfide Ni 0.1% (Tati/Selkirk)
  - Copper 0.22 – 0.92% (Anglo Mines)
  - Platinum 1-2 ppm

  (This severely limits the applicability of the method)
- Only concentrates or pre-concentrated feed and tailing samples can be quantified
- SEM-based quantification is superior and phases at ppm levels can be determined
- SEM-based methods can give valuable information on mineral liberation and textural features

XRD Use in the Minerals Industry

- Mineral processing
  - Minerals and not chemical species are processed
  - Gangue minerals affect recovery of valuable minerals
  - Mass balance calculation to assess the extent of upgrading possible

- Pyrometallurgical processing
  - Evaluation of reaction mechanisms
  - Kinetics of metallurgical reactions
  - Troubleshooting of processes
  - Assessment of suitability of slag reprocessing/reuse

The need for Materials Characterization in Process Optimization: Example PGM

- Worldwide platinum-group metals production (2009)
  (Prices at 30 Sept 2010, Johnson Matthey Group)

PG Metal	'000 oz	US$ Million
Platinum	5,920	9768
Palladium	7,175	4104
Rhodium	719	1654
Total Supply	**13 474**	**15 526**

- Recovery from the ore is usually 75-85%
- Huge efforts are expended to increase this figure
- A 1% increase in recovery translates into increased revenue of ~$150 million per year!
- At very little extra expenditure

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PGM Processing – Revenue and Costs

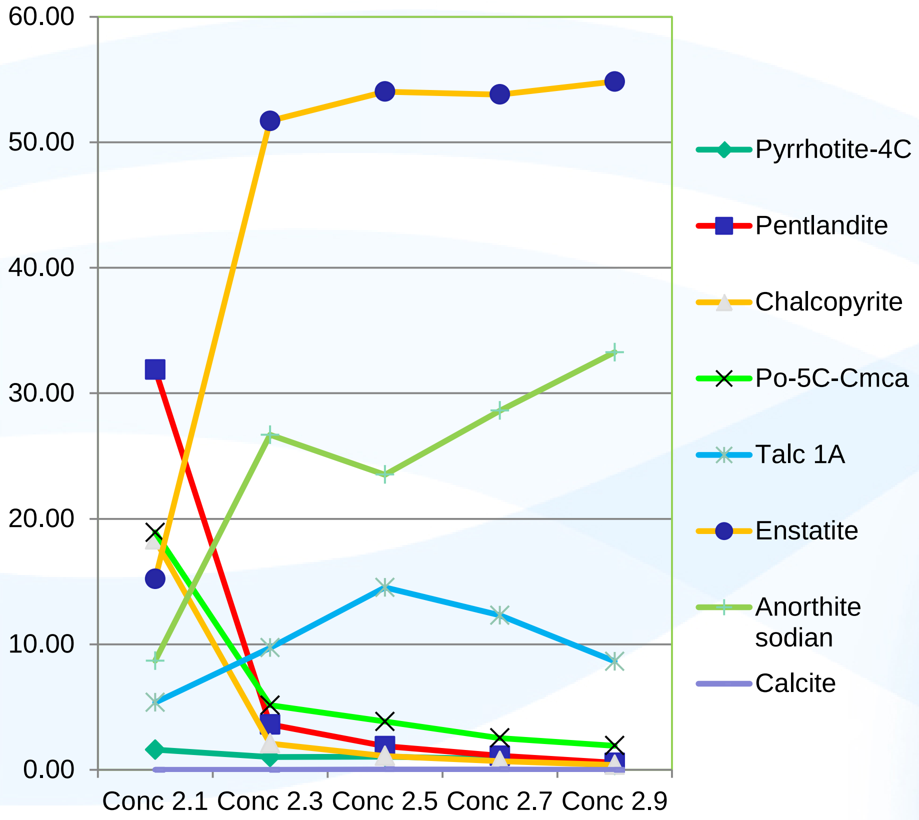
Key Features of PGE Extraction – Lonmin

Parameter	Mining	Milling & Flotation	Smelting & Converting	Base Metal Refining	Precious Metal Refining	Total
Percent of Total Cost	65 - 75	9 - 12	6	7	4 - 5	100
PGE Grade	4 - 6 g/ton	100 - 600 g/ton	640 - 6000 g/ton	30 - 65 %	>99.8%	-
PGE Recovery (%)	-	80 - 90	95 - 98	>99	98 - 99	75 - 85
Concentration Ratio	-	30 - 80	20	75	2	200 000
Processing Time (days)	-	2	7	14	30 - 150	Up to 170

"Underground and overall concentrator recoveries increased from 80.5% and 79.0% to 85.1% and 85.0% respectively year on year. "

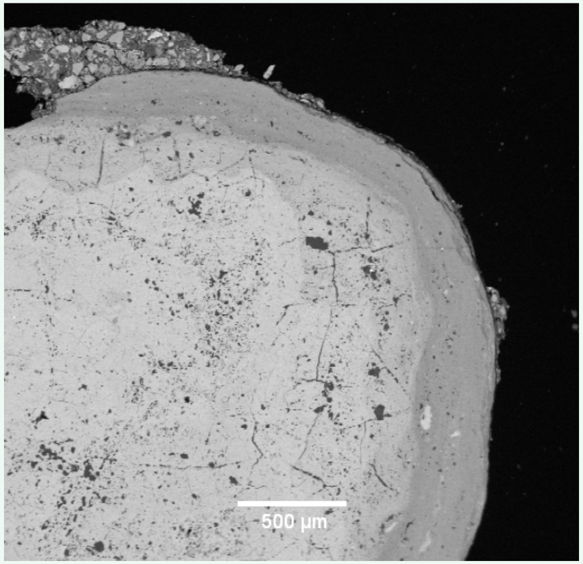
Lonmin 3rd Quarter 2010 Production Report

PGE Process Design

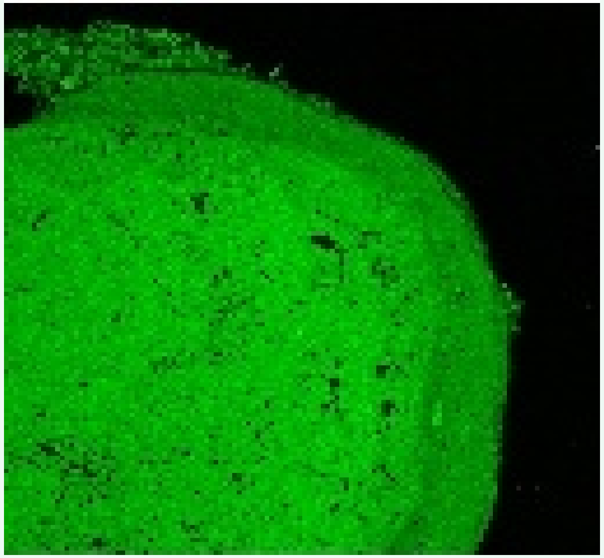


Element Distribution in Iron Ores

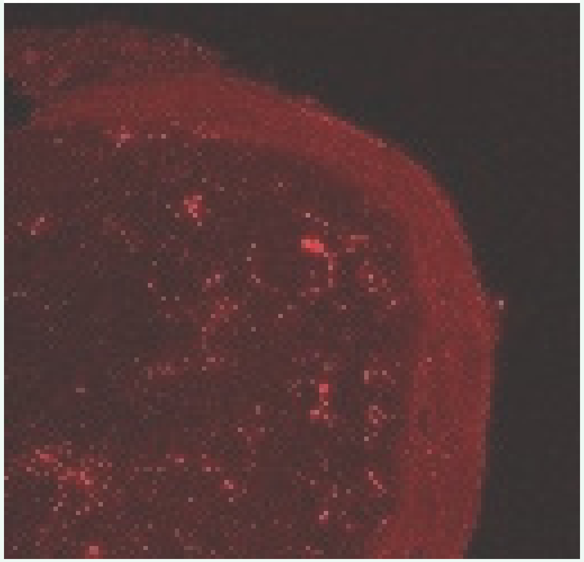
BSE



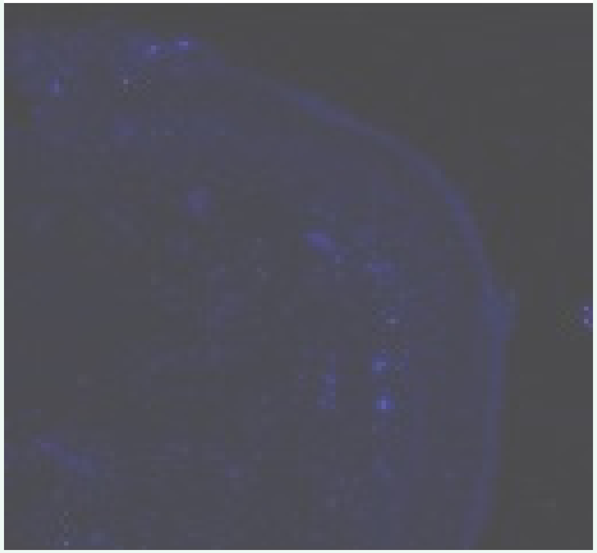
Fe



Al



Si



Mass Balance: Combination of XRD and XRF

Mass Balance Calculation - Fe ore FCF11-A

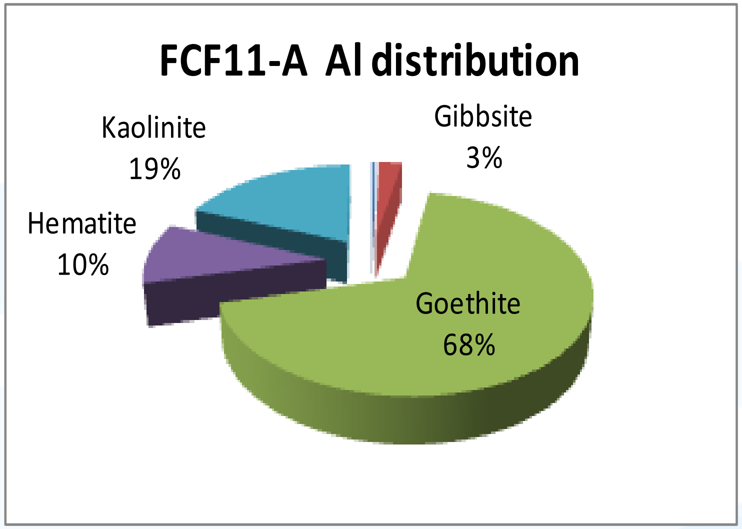
Mass Balance	Fraction(XRD)	SiO2	Al2O3	TiO2	Fe2O3	LOI	P2O5	K2O		
Annite	0.21	0.06	0.02	0.00	0.09	0.00	0.00	0.03		
Gibbsite	0.17	0.00	0.11	0.00	0.00	0.06	0.00	0.00		
Goethite	60.48	2.49	3.09	0.81	47.80	6.29	0.00	0.00		
Hematite	32.78	0.33	0.46	0.00	31.99	0.00	0.00	0.00		
Kaolinite	2.17	1.00	0.85	0.00	0.00	0.30	0.00	0.00		
Magnetite_	3.82	0.00	0.01	0.00	3.94	0.00	0.00	0.00		
Quartz	0.38	0.38	0.00	0.00	0.00	0.00	0.00	0.00		
Total	100.01	4.27	4.54	0.81	83.83	6.64	0.00	0.04	100.12	**R(%)**
Analysis		3.59	4.54	0.69	82.58	7.44	0.11	0.00	98.95	**3.03**

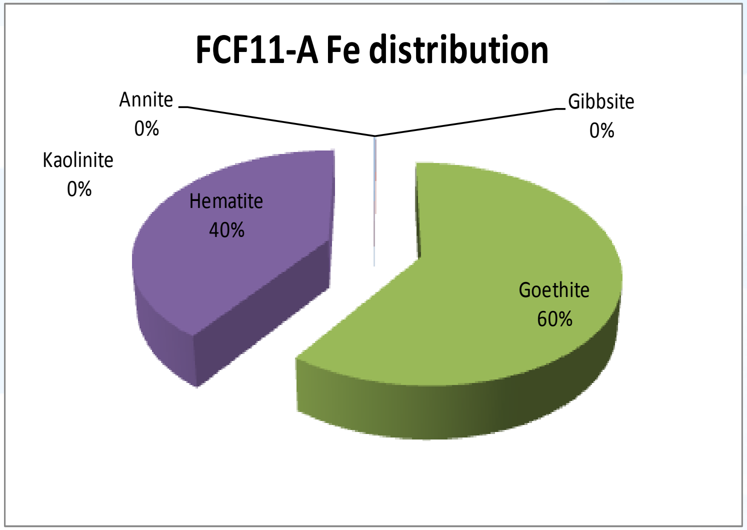
QPA can be seriously in error because of:

- the presence of undetected phases or minerals
- the presence of amorphous material
- preferred orientation and micro-absorption effects

Mass balance can alert the analyst of serious discrepancies

Al and Fe Distribution in Iron Ore Minerals

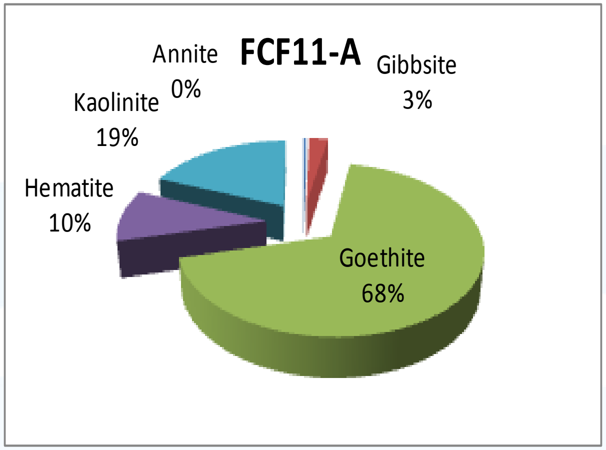


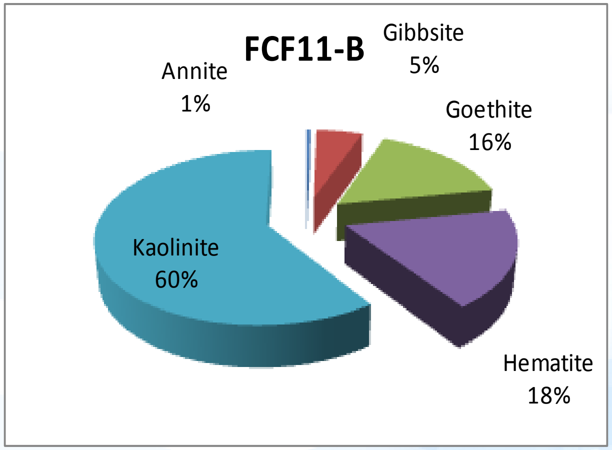


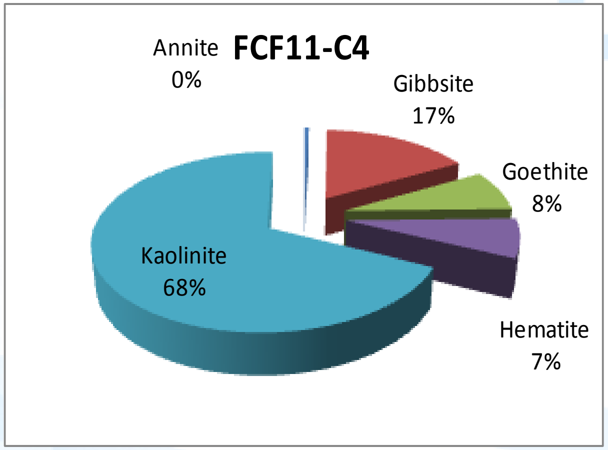
COMMENTS

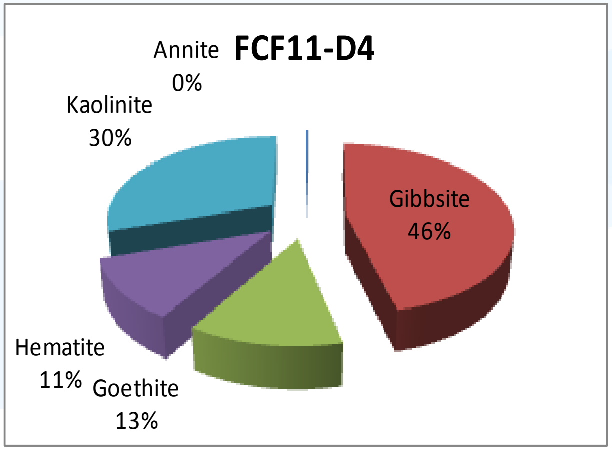
- The percentage deviation (3%) in the mass balance calculation is acceptable to draw conclusions
- 68% of the Al in the sample is due to the presence of goethite
- The goethite also contains 60% of the iron in the sample and cannot be removed
- Therefore, if Al is to be removed, only kaolinite and gibbsite can be eliminated without major iron loss
- Only 22% of the Al can be removed by flotation or other methods

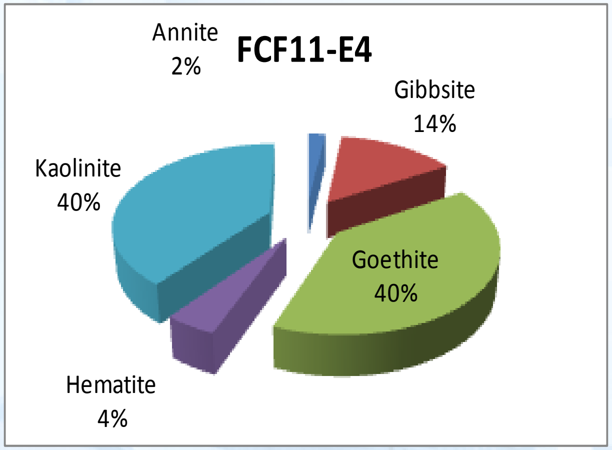
Al Distribution in Minerals in Goethite Ores



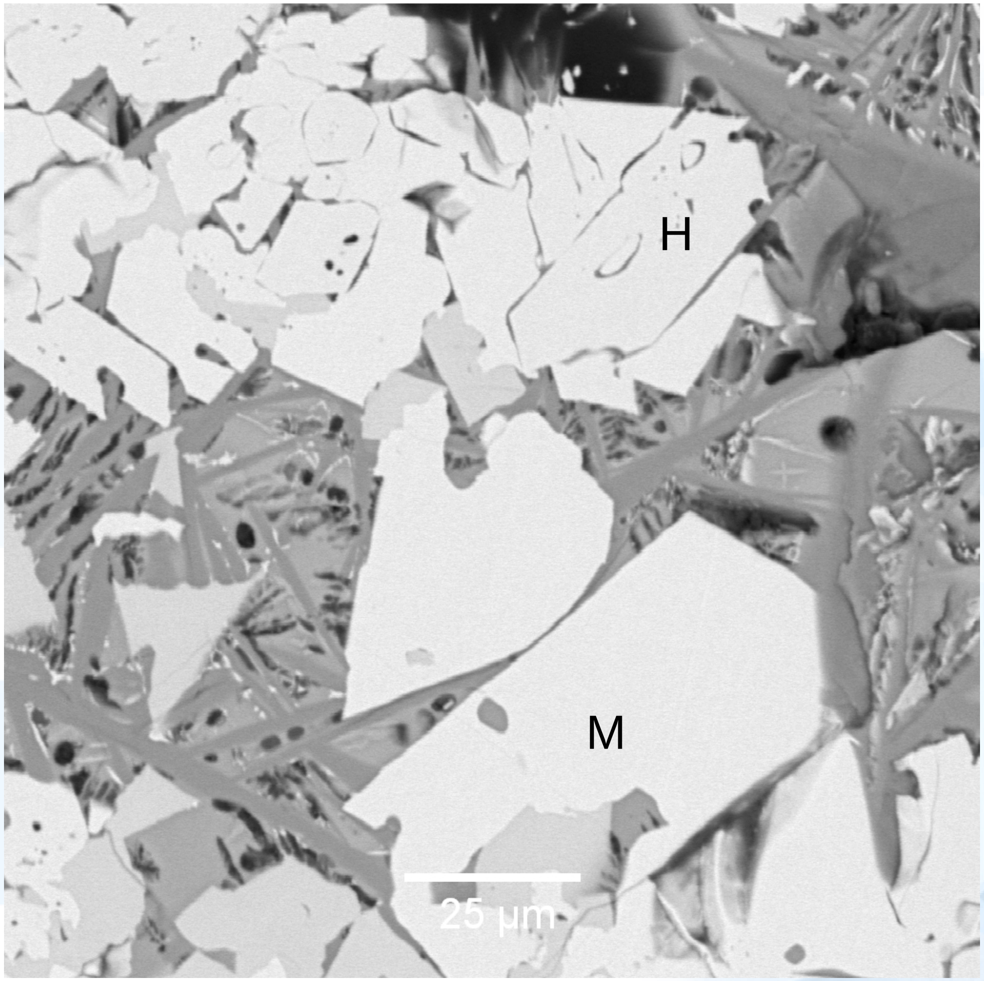








Contrasting Hematite and Magnetite

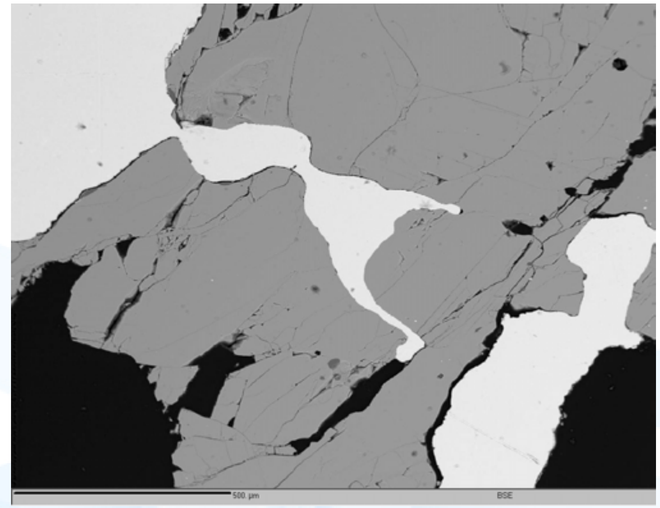


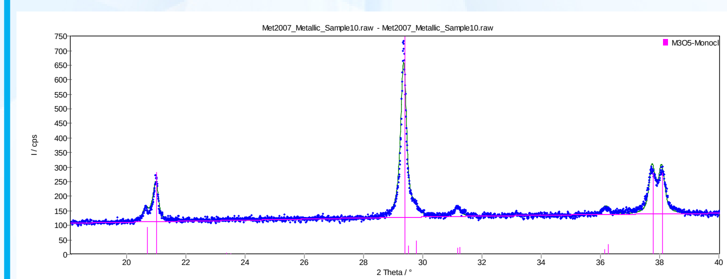
To distinguish Hematite and Magnetite in sinters using SEM methods is problematic

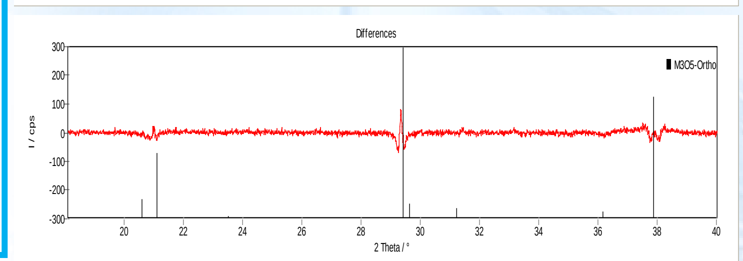
With XRD it is easy!

Accretion layers in Titania slag furnaces

- Accretion layers form in titania slag furnaces
- The layers prevent the accumulation of molten pig iron in the furnace hearth
- Accretion layers also reduce the furnace volume leading to lower throughput
- The accretion layers consist of anosovite (Almost pure Ti_3O_5) with a very high solidus temperature (1775°C)
- The metal phase is a mixture of iron and cementite (Fe_3C)
- Removal of the accretion layer without furnace shutdown ? Ilmenite addition





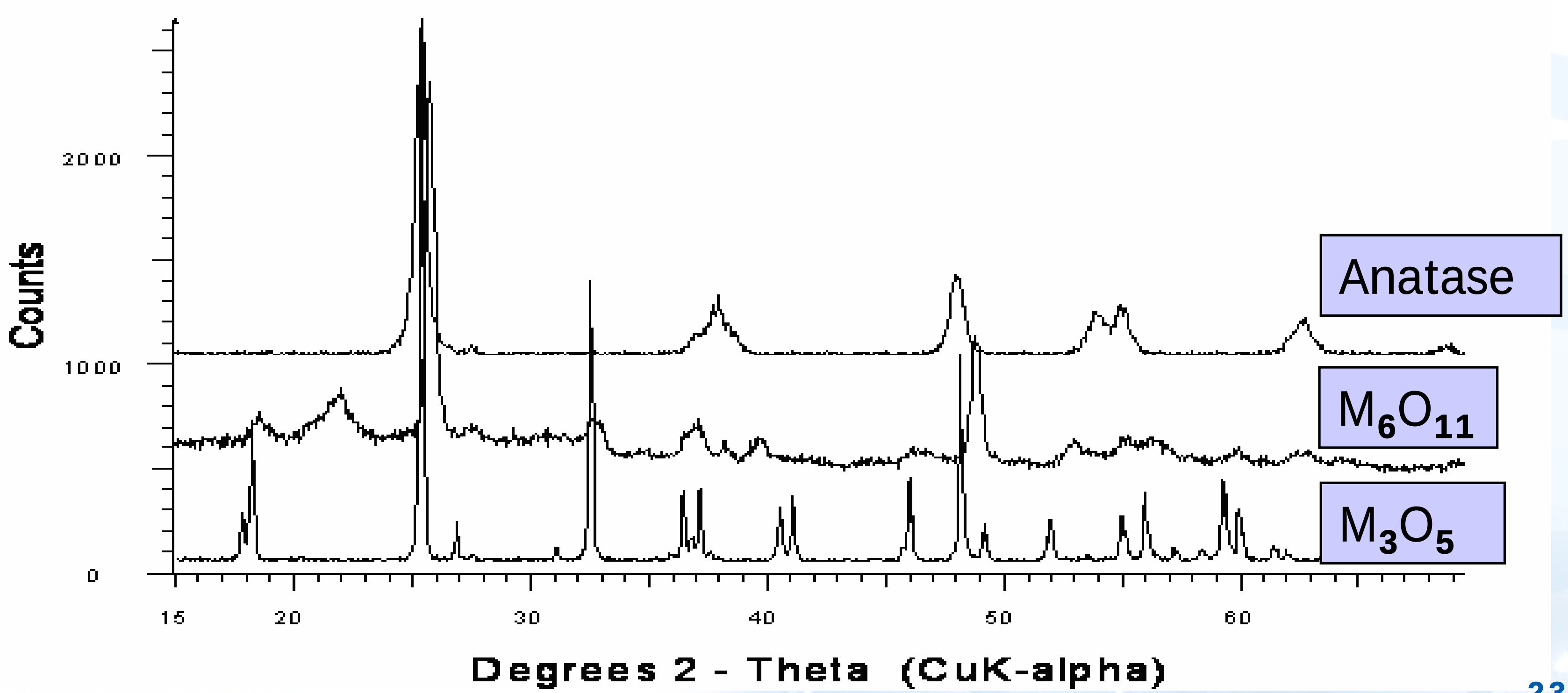


Titania Slag Disintegration:

- Disintegration of slag blocks collected from 1.5 MW pilot furnace
- Excessive fine material is generated – Causes problems in fluid bed chlorination reactors
- Mechanism?

Titania Slag Disintegration: Oxidation of pseudobrookite

- The structure of a M_6O_{11} phase was determined by Ian Grey at CSIRO using powder XRD and TEM methods (+ ingenuity)
- It is related to pseudobrookite, and anatase



Titania slag disintegration:

Oxidation (M_6O_{11})is associated with cracking and segmentation of very small fragments – generation of fines in slag blocks

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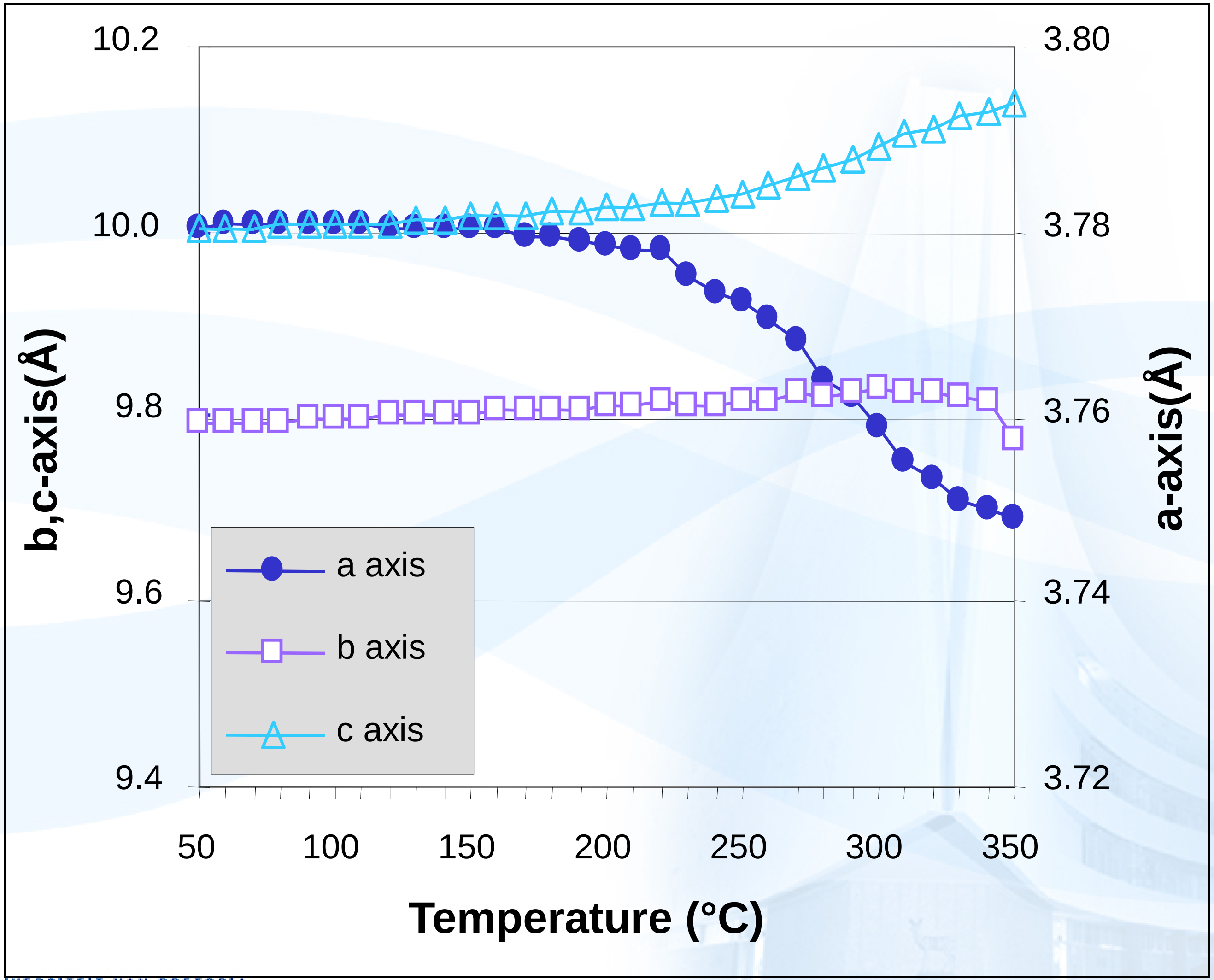
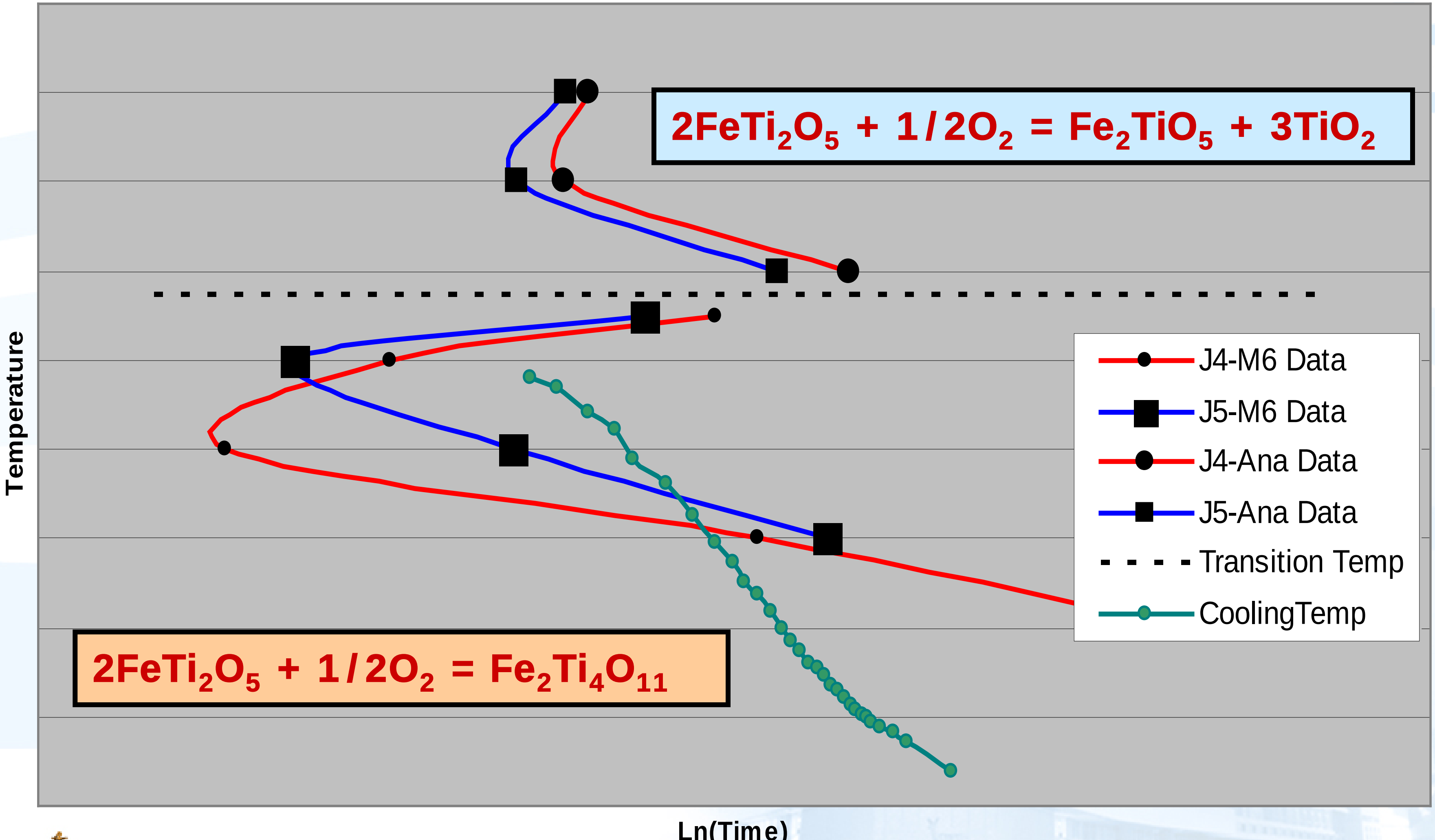
Dimensional Changes: Lattice Constants



Oxidation Kinetics: Titania Slags (20% Reaction)



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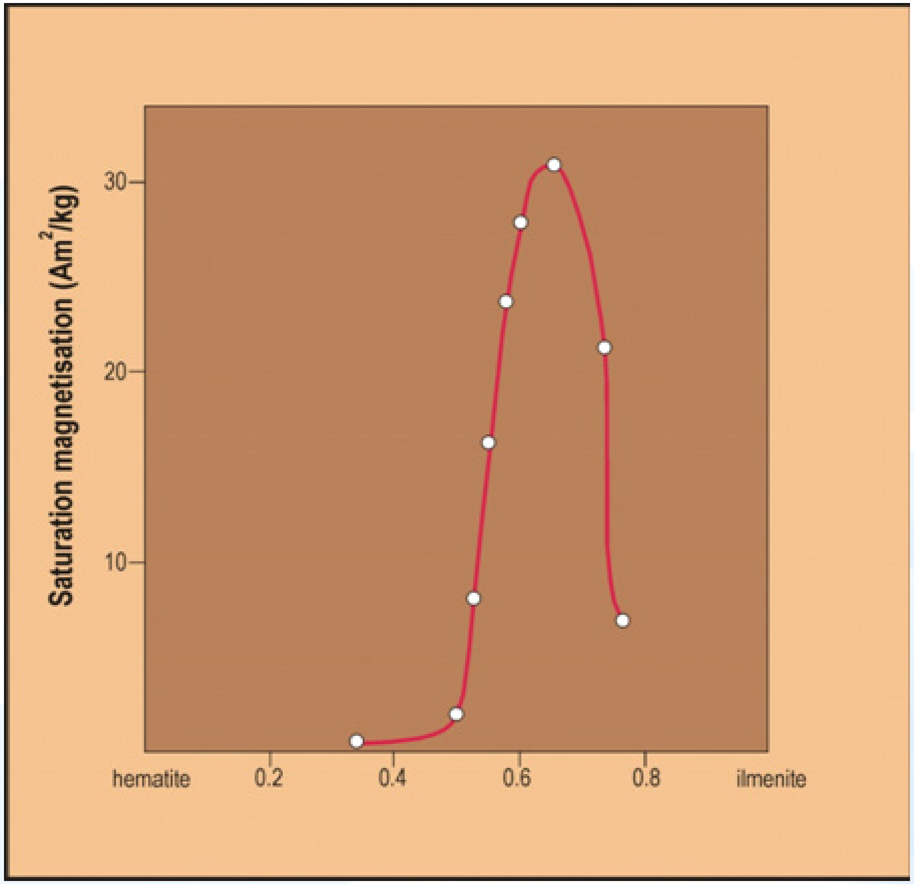
Lattice Constant Refinement
Example: Ilmenite Purification

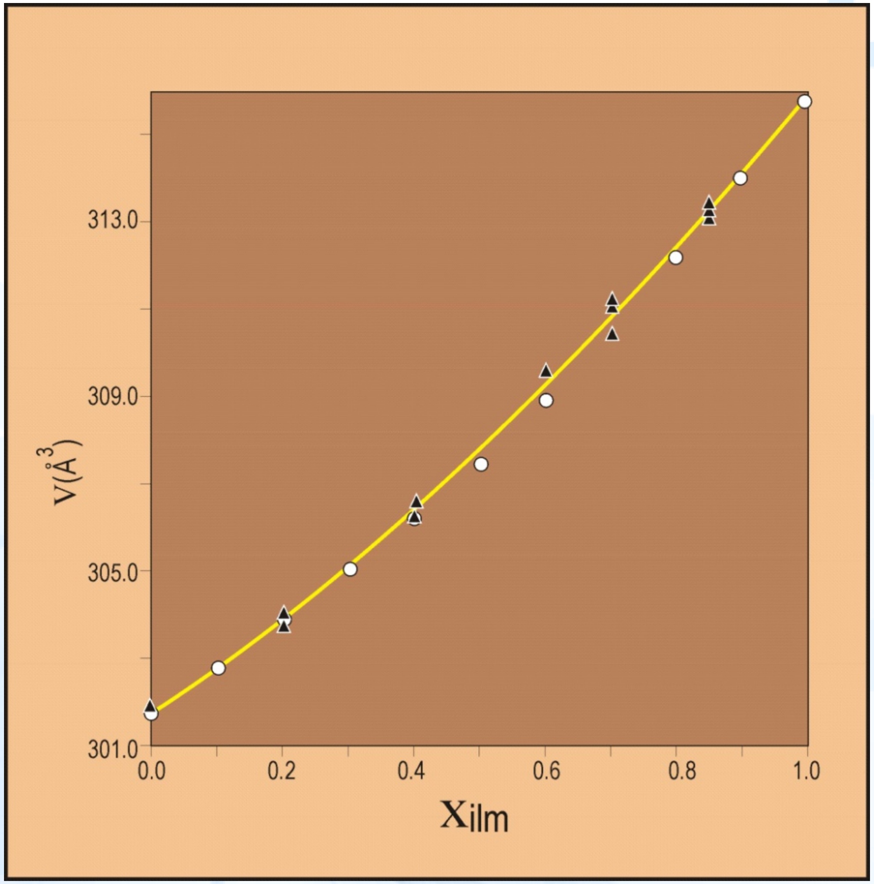
- Ilmenite is used as a feedstock for rutile pigment production
- Impurities such as Cr and V are undesirable as they colour the white pigment
- Other impurities such as Ca and Mg cause problems in the fluid bed chlorination of ilmenite or titania slag, produced from ilmenite
- Most plants use oxidative roasting to modify the magnetic properties of ilmenite, so that it can easily be purified
- The Fe^{2+} is oxidised to Fe^{3+} with the formation of anatase or rutile:

$$FeTiO_3 + O_2 \Rightarrow TiO_2 + (Fe_2O_3\text{-}FeTiO_3)ss$$

- The longer the oxidation – the more Fe-rich the solid solution

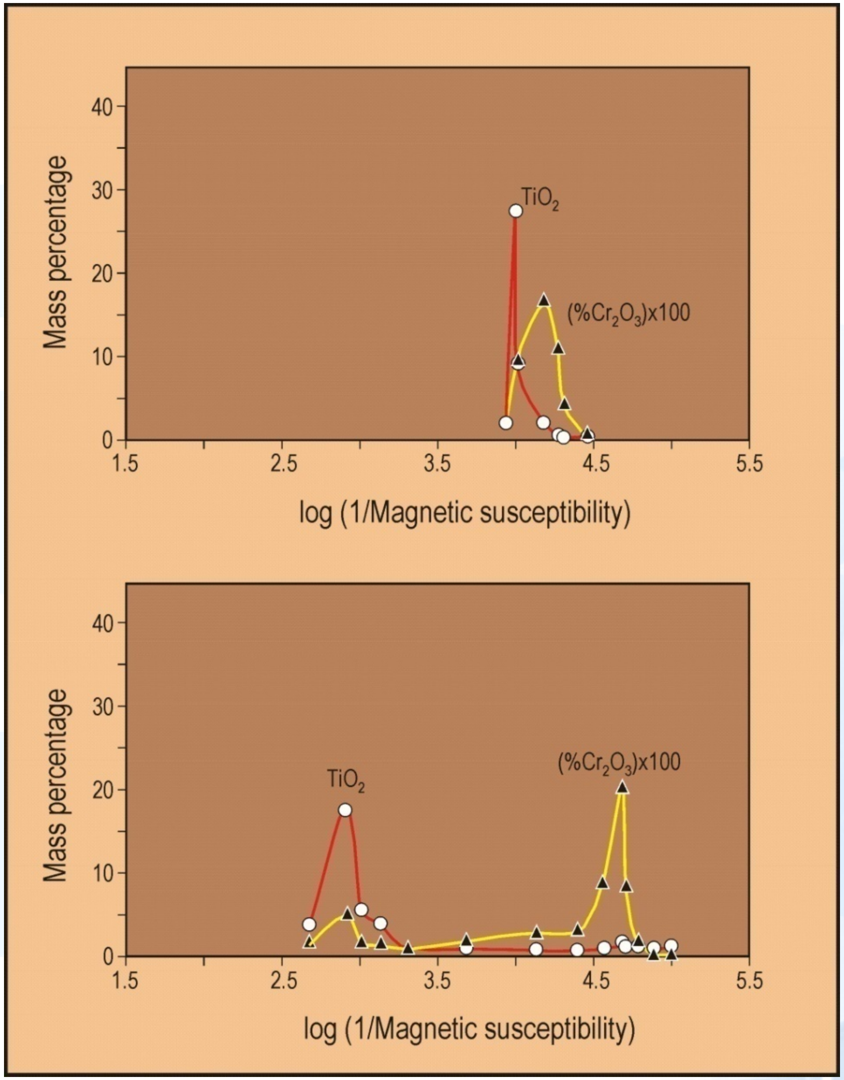
Tracking Ilmenite Magnetization – Unit Cell Volume





This is the most reliable way to track the extent of oxidation

Differences in Ilmenite magnetic susceptibilty



Before Roasting:

Ilmenite and chromite cannot be separated using magnetic separation

After Roasting:

Ilmenite and chromite can be easily separated

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Lattice Constant Refinement Example: Hydrohematite

- Hematites worldwide have been shown to contain (OH) replacing O, with a concomitant cation vacancy, with formula $(Fe_{1-x}Al_x)_{2-z/3}(OH)_zO_{3-z}$ (Neumann & Avelar, 2012)
- This replacement affects mainly the c-lattice constant and has been comprehensively studied by Stanjek and Schwertmann (1992)
- Many iron ores originate from a tropical laterite environment and contain significant goethite (and possible (OH) in hematite)
- This (OH) substitution can affect the surface properties of the hematite
- As a result the widely used flotation processes can be affected and needs to be related to the (OH) content or loss on ignition

Determination of X_{Fe}, X_{Al} and $X_{(OH)}$ in Hematite and X_{Al} in Goethite

$X_{OH^-} = (c - 13.7454)/0.24222105$

$X_{Al} = (6019.83338 - 1518.37137 * a + 4.66753 * a^2 * c)/100$

$X_{Fe} = (1-(c-13.7454)/0.72666315)-(6019.83338-1518.37137 * a + 4.66753 * a^2 * c)/100$

(These occupancies are included in the refinement)

Hematite - Neumann & Avelar (2012)

Sample		Hematite				Goethite		
	X(Fe)	X(Al)	X(OH)	LOI(%)	c	Mole % Al	X(Al)	Rwp
FCF11-A	0.953	0.035	0.036	0.67	3.0154	5.22	0.052	2.07
FCF11-B	0.96	0.021	0.059	1.10	3.0188	3.25	0.033	1.62
FCF11-C4	0.941	0.031	0.083	1.54	3.0202	2.43	0.024	1.93
FCF11-D4	0.958	0.025	0.053	0.98	3.0180	3.71	0.037	1.64
FCF11-D4	0.872	0.084	0.133	2.47	3.0188	3.24	0.032	2.31

X_{Al} (Goethite) – Knorr & Neumann (2011)

Challenges for Powder XRD and its Wider Application in Mineral Science

- Decrease the detection limits of the various phases
- More reliable quantification of minor and trace phases
- Need better formalisms for preferred orientation and micro-absorption
- Increased use of cluster analysis for ore characterization
- Choice of appropriate crystal structures for the minerals present in the samples (39 chromites, 95 diopsides, etc. in the Topas database)
- Better and faster sample grinding and micronising to reduce particle size without overmilling
- Spray drying and micro-agglomeration to reduce preferred orientation must be given serious consideration

Summary – Research Opportunities

- Research is driven mostly by industry needs
  - Use in exploration
  - Proper ore characterization
  - Process optimization is as important as before
- Materials characterization
  - Some common minerals and phases need better characterization
- Materials behaviour in metallurgical processes
  - Can evaluate the kinetics of the reactions
  - Can assist in the thermodynamic analysis
- Troubleshooting of processes
  - Examination of side reactions
  - Possible elimination of problematic situations

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