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Three current issues in production of clean steel:
dephosphorisation,
ladle desulphurisation, and
inclusion imaging

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Overall theme:
Production of clean steel
by liquid-steel processing

≡ control of impurities (dissolved and second-phase):

- Amounts: parts per million (ppm) to tens of ppm
- Second-phase particles (inclusions):
size, shape, and composition are important

Removal / remediation approaches:

Dissolved elements:

- remove **chemically** to other phase(s)
 - To gas (as molecules)
examples: [C] removed as $(\text{CO})_g$;
[H] removed as $(\text{H}_2)_g$
 - To slag (as ions)
examples: [P] removed as (PO_4^{3-})
[S] removed as (S^{2-})
[Si] removed as (SiO_4^{4-})

Removal / remediation approaches:

Inclusions:

- remove **physically** (flotation)
 - little or no effect on inclusions $< 2 \mu\text{m}$
- modify **chemically**
 - example: Ca injected to modify spinels & Al_2O_3

Phosphorus removal in steelmaking

Basic reaction (strongly exothermic):



dissolved P
in metal

dissolved
oxygen
in metal

oxygen
anions
in slag

dissolved P
in slag

⇒ Dephosphorisation requires:

oxidising conditions
high slag basicity
relatively low temperature

⇒ every processing step in
ironmaking & steelmaking
is a compromise as far as
dephosphorisation is concerned

Processing steps and dephosphorisation

⇒ Dephosphorisation requires:

oxidising conditions (higher [O] or higher p_{O_2})

high slag basicity

relatively low temperature

	p_{O_2}	(O^{2-})	T
Blast furnace hearth	↓ ↓ (10^{-16} atm)	↑	lower
Oxygen steelmaking / EAF	↑ (10^{-9} atm)	↑	higher
Ladle (deoxidised steel)	↓ (10^{-14} atm)	↑	higher

Dephosphorisation options

Oxygen steelmaking:

- limit tapping temperature
- control slag volume
- maximise basicity (ensure CaO dissolves)
- enhance kinetics (e.g. bottom stirring)

*Note: steelmaking involves oxidising
C (~4%), Si (~0.5-1%) and P (~0.1%)
out of hot metal*

Dephosphorise before decarburising

- inject oxidant (e.g. iron oxide) + fluxes into hot metal
- two-slag approach to steelmaking

Current projects at Carnegie Mellon

Oxygen steelmaking:

improved correlation for equilibrium P distribution

Electric furnace steelmaking:

effect of (Al_2O_3) on equilibrium P distribution

Hot metal dephosphorisation:

optimal slag composition for two-slag practice

Oxygen steelmaking:

improved correlation for equilibrium P distribution

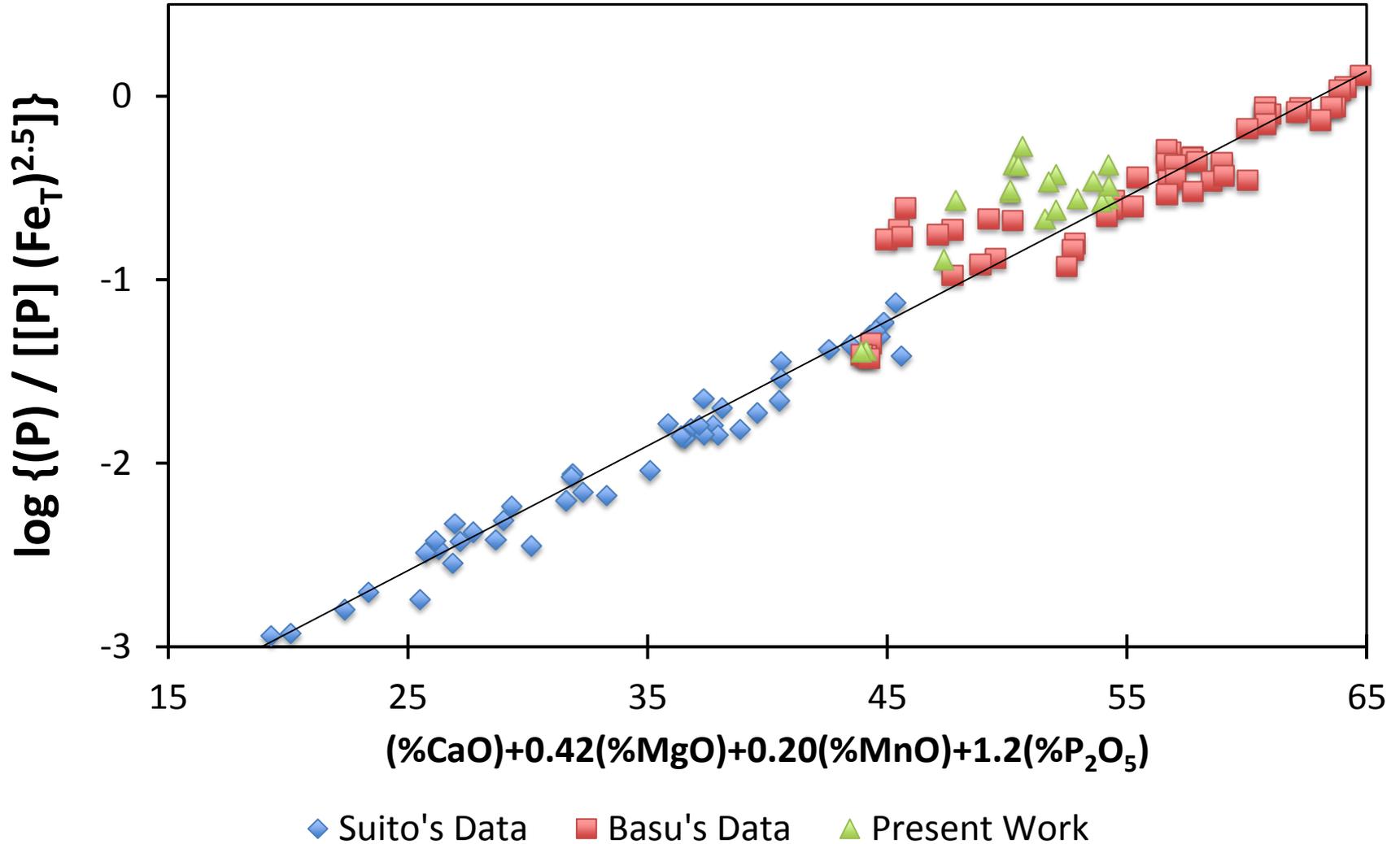
- Equilibrium experiments

(MgO-saturated slag, 1600° C)

- Literature data

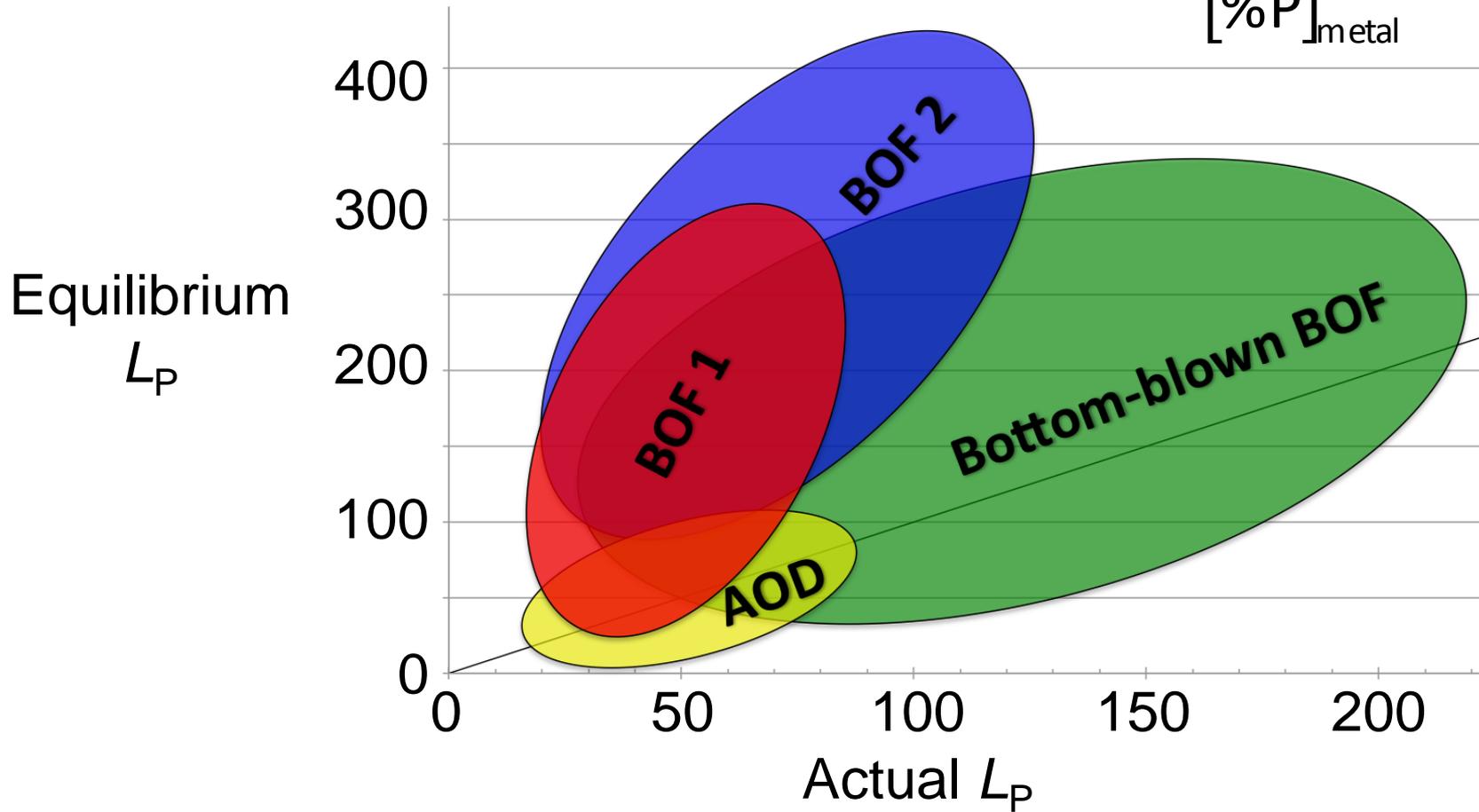
$$\log \left(\frac{(P)}{[P]} \frac{1}{(\text{Fe})_{\text{total}}^{2.5}} \right) = 0.068 [(\%CaO) + 0.42(\%MgO) + 1.16(\%P_2O_5) + 0.2(\%MnO)] + \frac{11570}{T} - 10.52$$

Improved correlation and equilibrium data



Departure from equilibrium: plant data

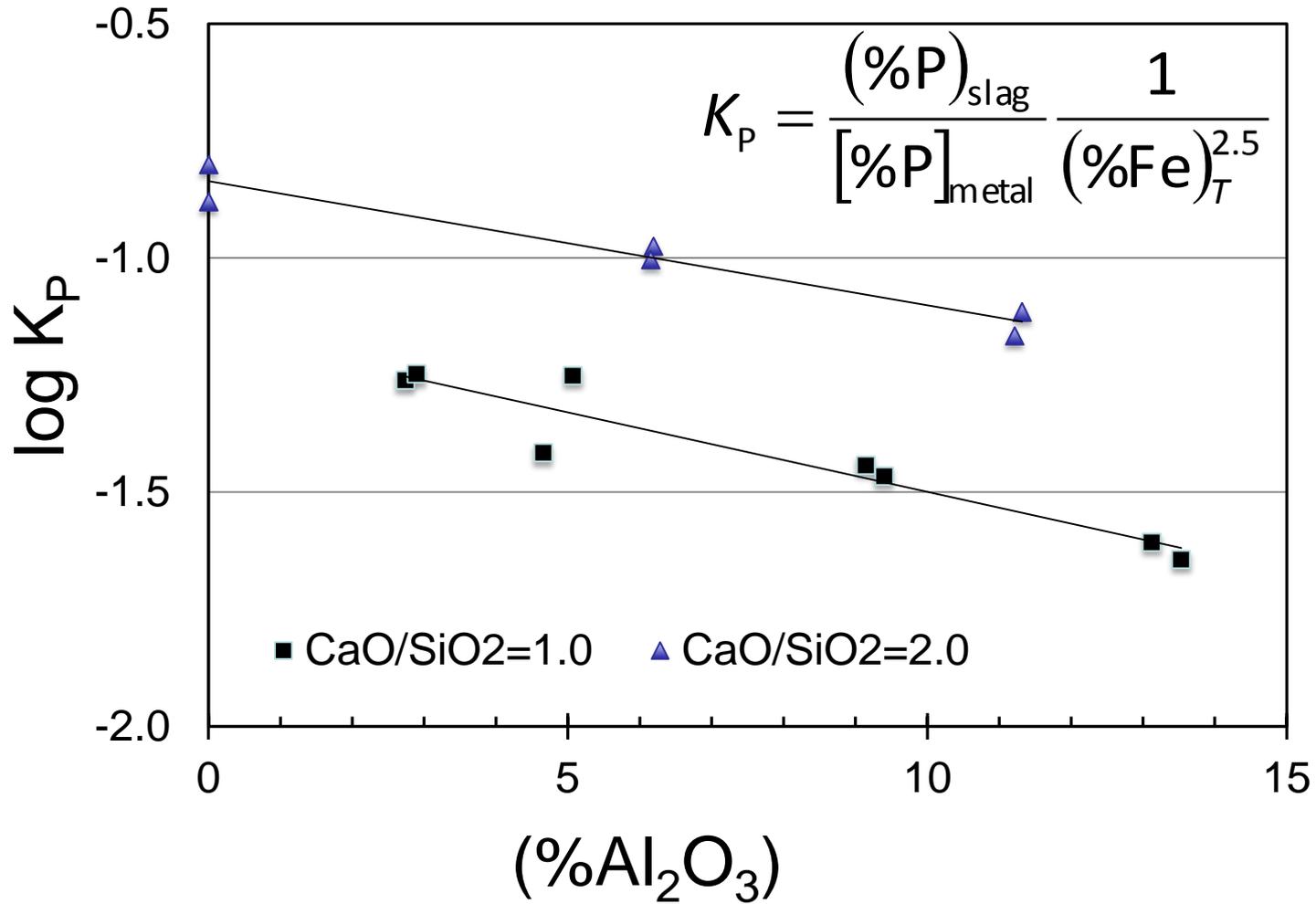
$$L_p = \frac{(\%P)_{\text{slag}}}{[\%P]_{\text{metal}}}$$



Electric furnace steelmaking:

Correlation extended to include (Al_2O_3) effect

- Equilibrium experiments
(MgO-saturated slag, 1600°C)
- **Main result: Al_2O_3 decreases L_p**
- Important for plants that charge a high proportion of direct-reduced iron



Hot metal dephosphorisation:

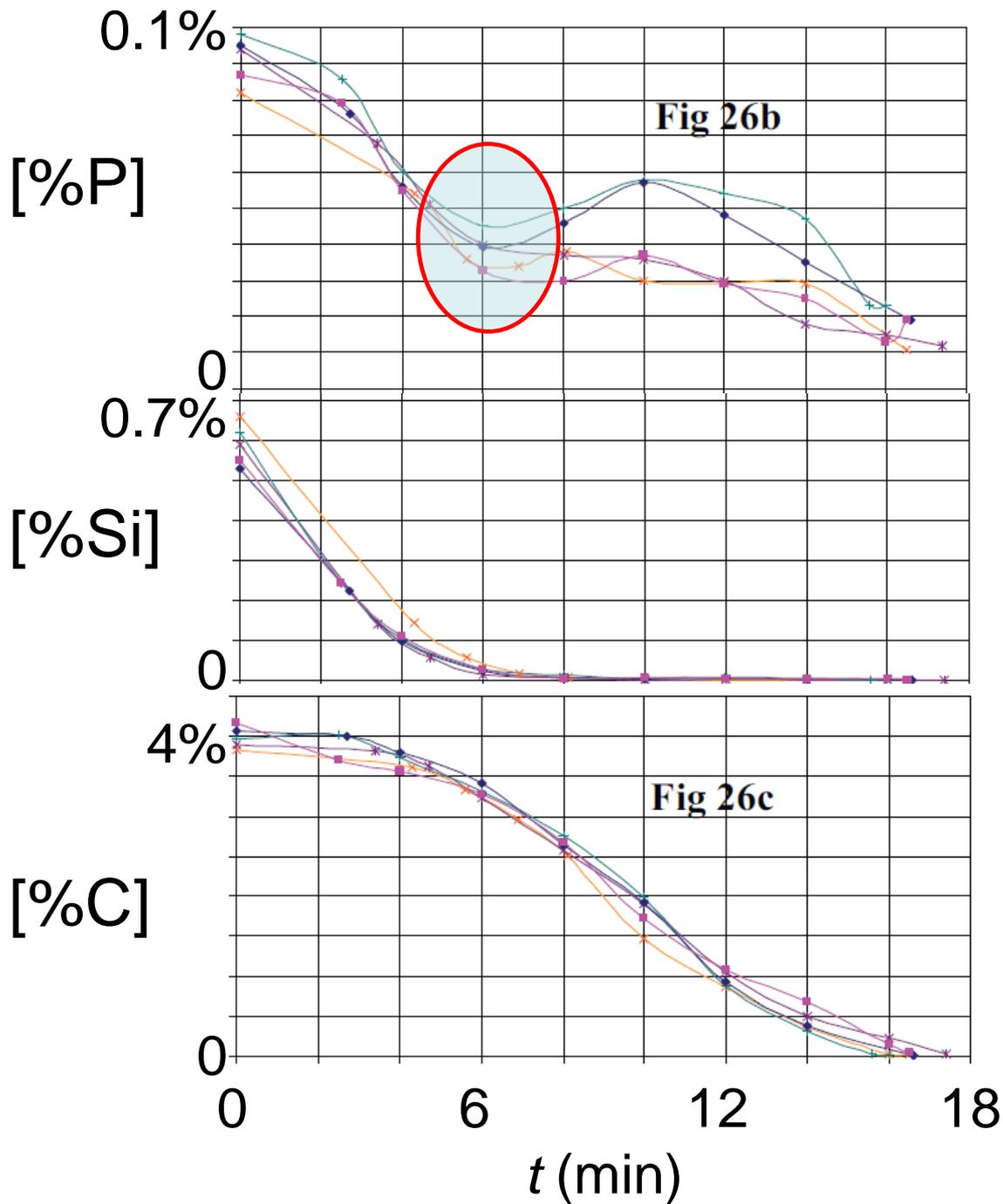
optimal slag composition for two-slag practice

- Equilibrium experiments

 - MgO-saturated slag, 1400° C

 - metal phase: Cu-%Fe alloy; solid Fe

- Liquid slag ranges predicted with FactSage



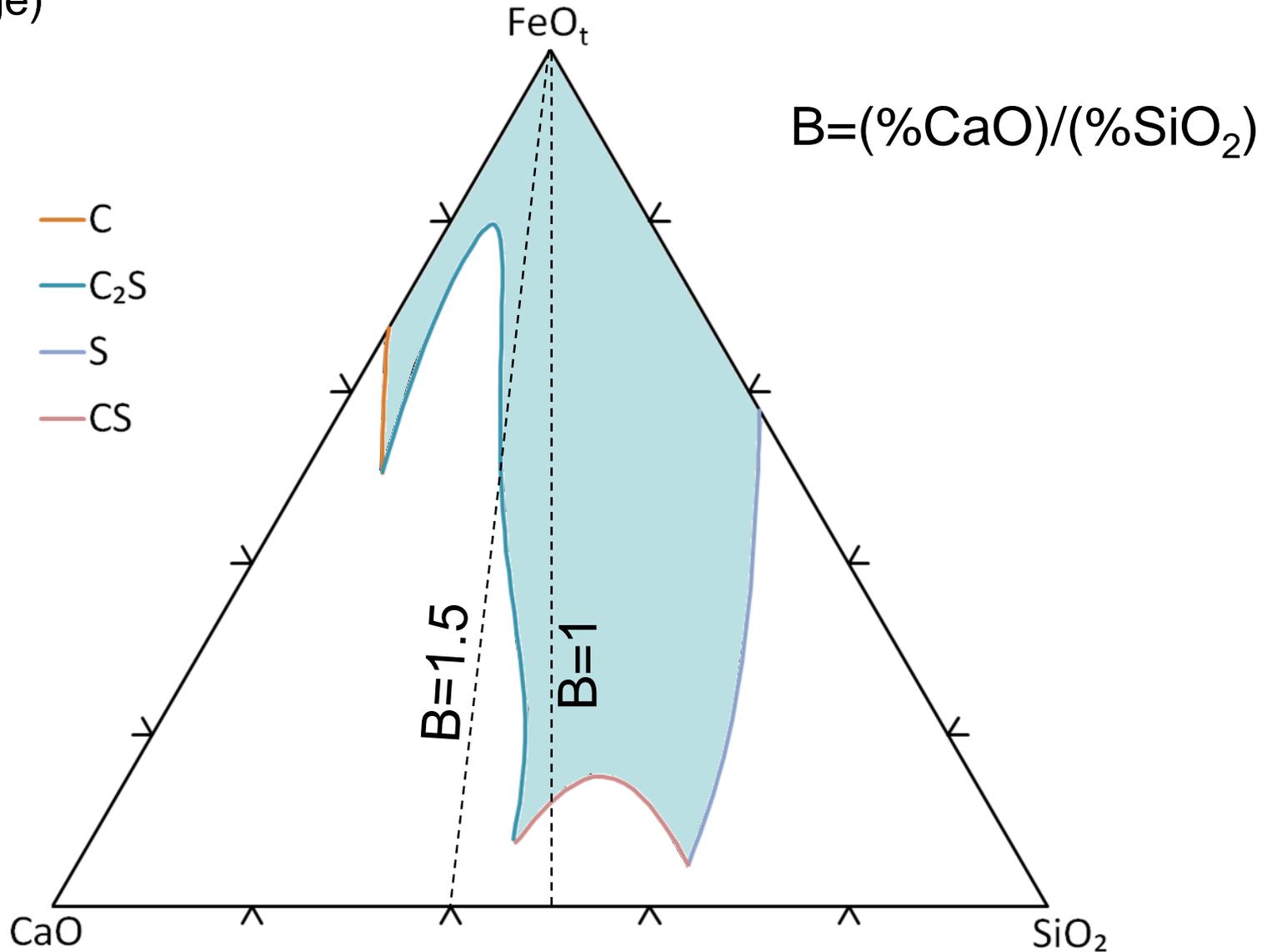
Metal composition change during oxygen steelmaking:
Possible to achieve early P and Si removal, while removing little C

(Millman *et al.*,
IMPHOS report, 2011)

Limited range of fully liquid slags

CaO-FeO-SiO₂ system, 1400° C (plotted as mass fractions)

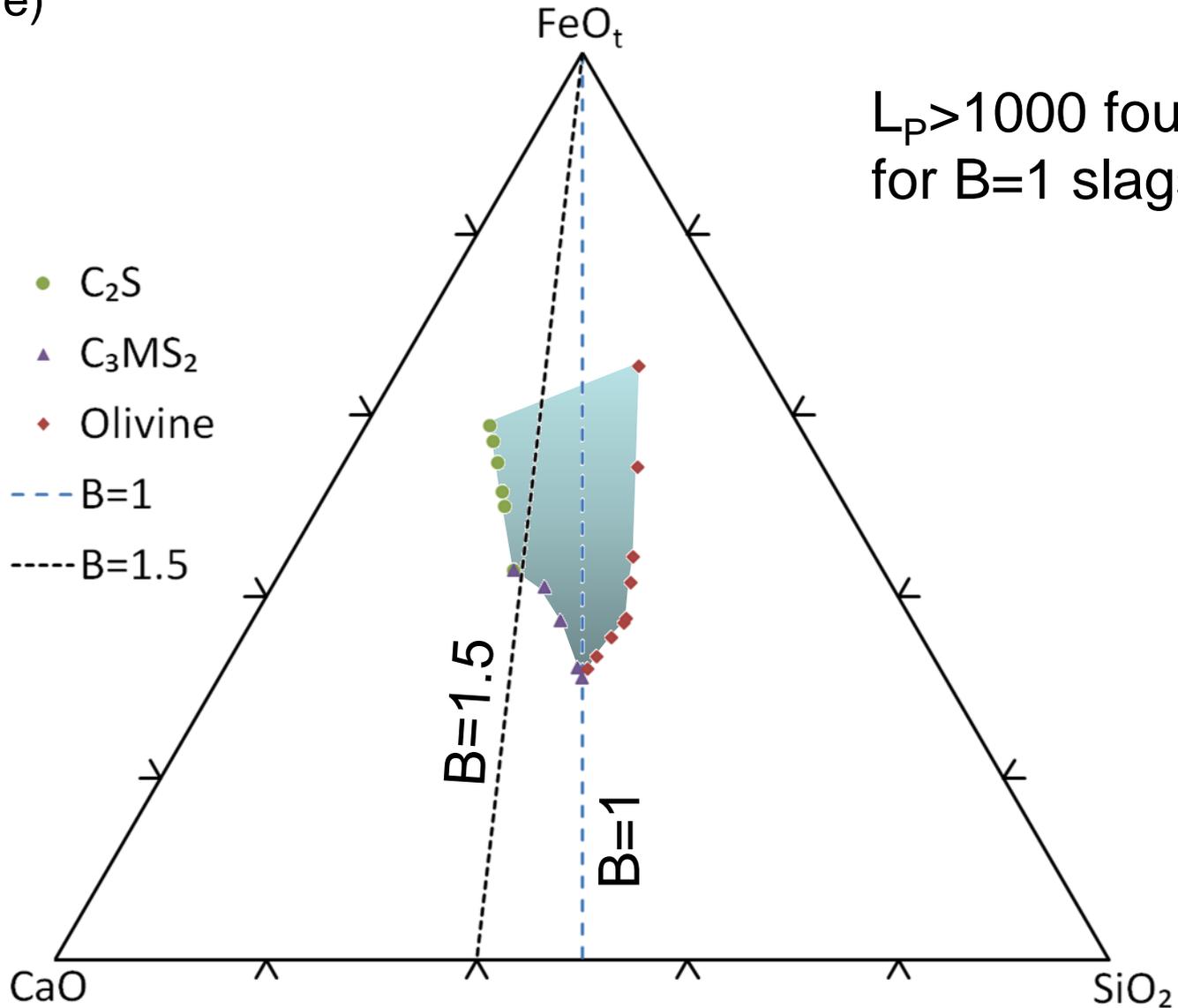
(FactSage)



Limited range of fully liquid slags

CaO-FeO-SiO₂-MgO_{sat}-Fe_{sat} system, 1400° C

(FactSage)

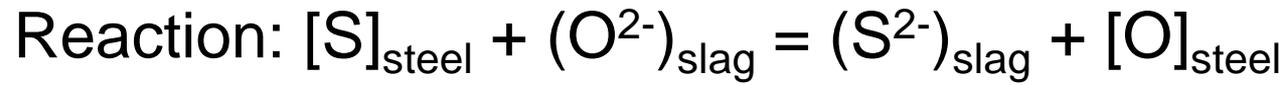


Ladle desulphurisation

What do we need for good desulphurisation?

Basic slag, reducing conditions

⇒ Ladle desulphurisation uses CaO-rich slag, with Al deoxidation (low h_O)



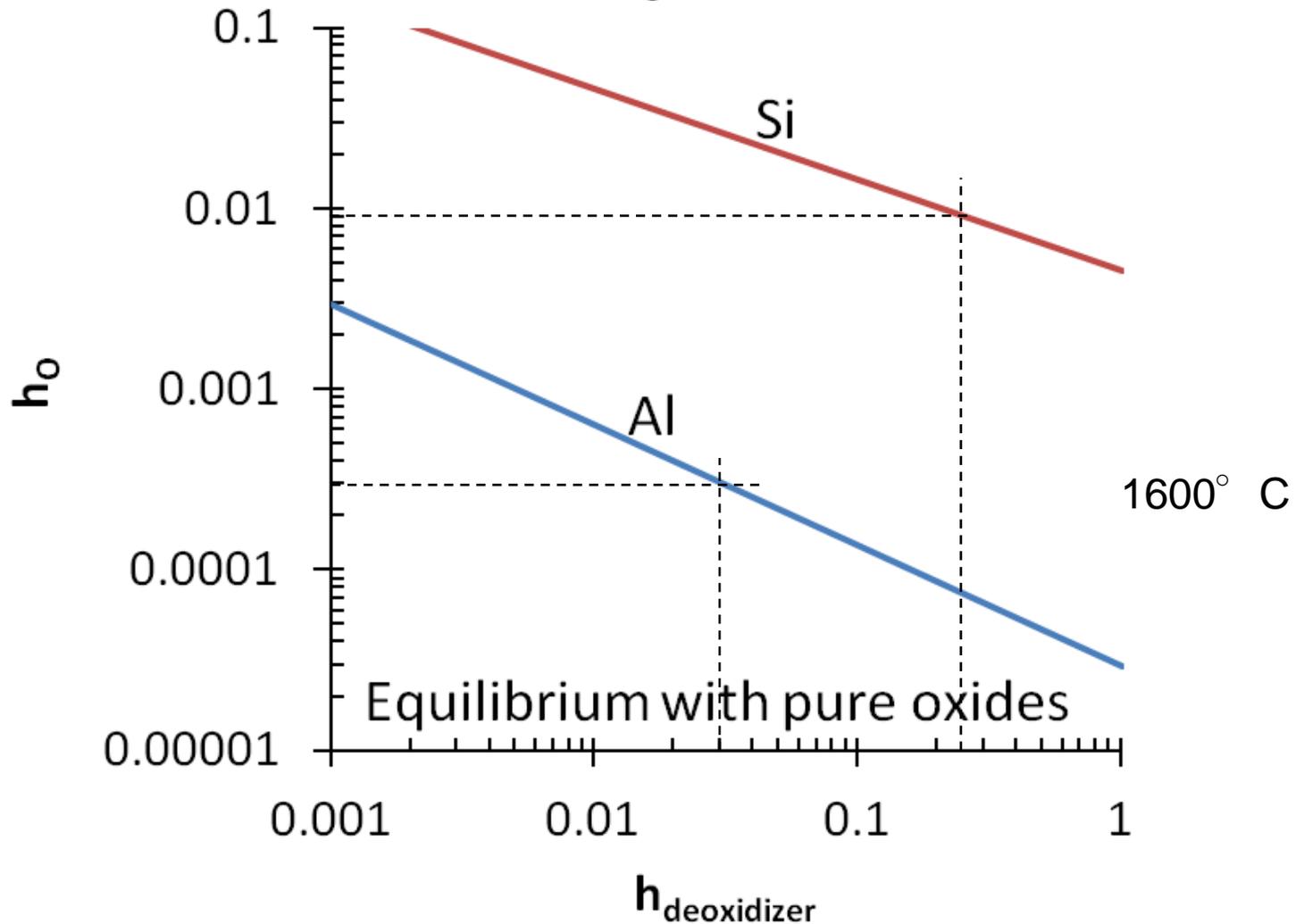
How can [Si] affect desulphurisation?

[Si] can control the oxygen potential in **Al**-killed steel if

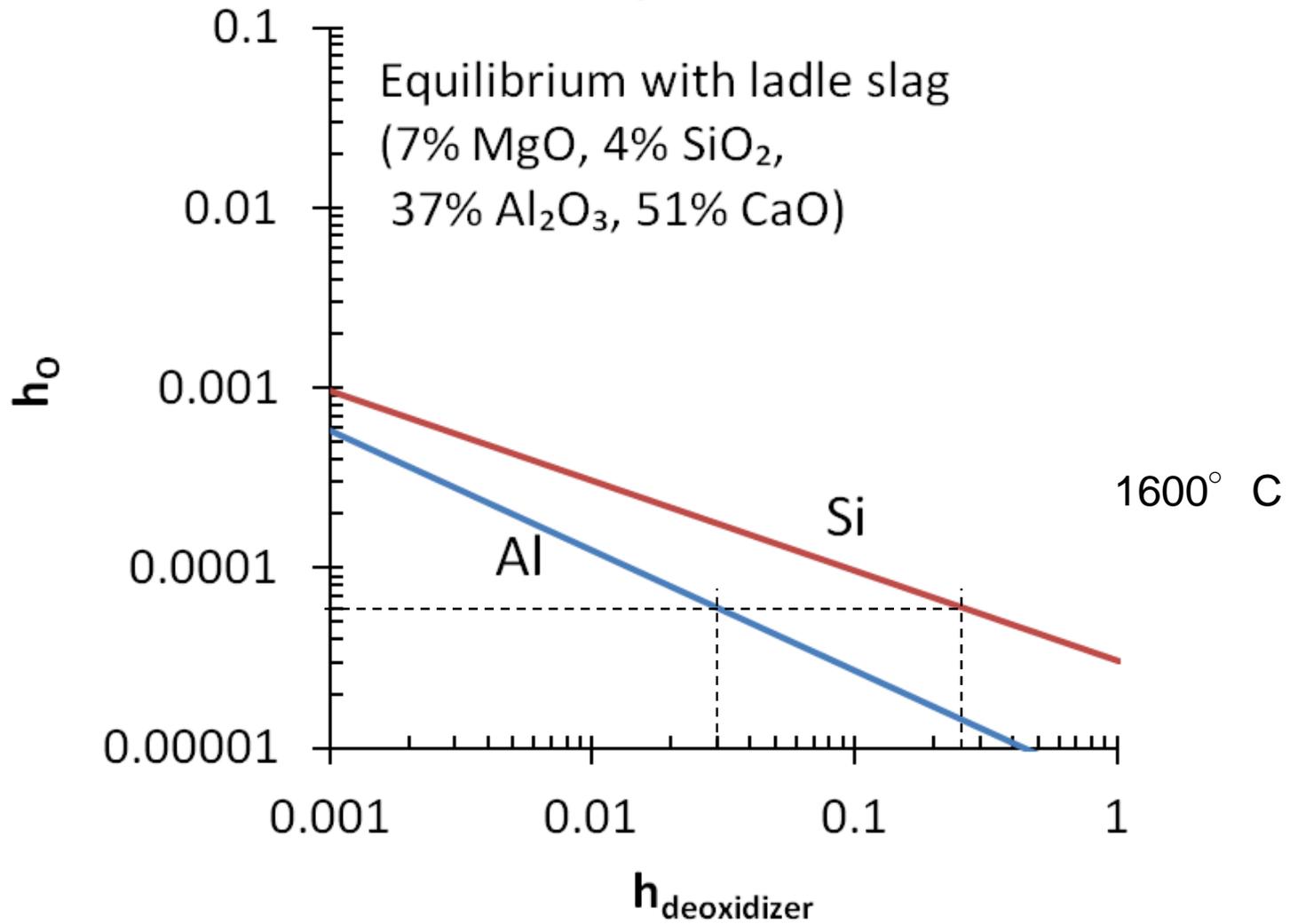
- steel equilibrates with the slag
- low SiO_2 activity in slag (relative to Al_2O_3 activity)

Conventional idea:

Al is a much stronger deoxidiser than **Si**



Difference between Al and Si is much smaller if steel equilibrated with ladle slag



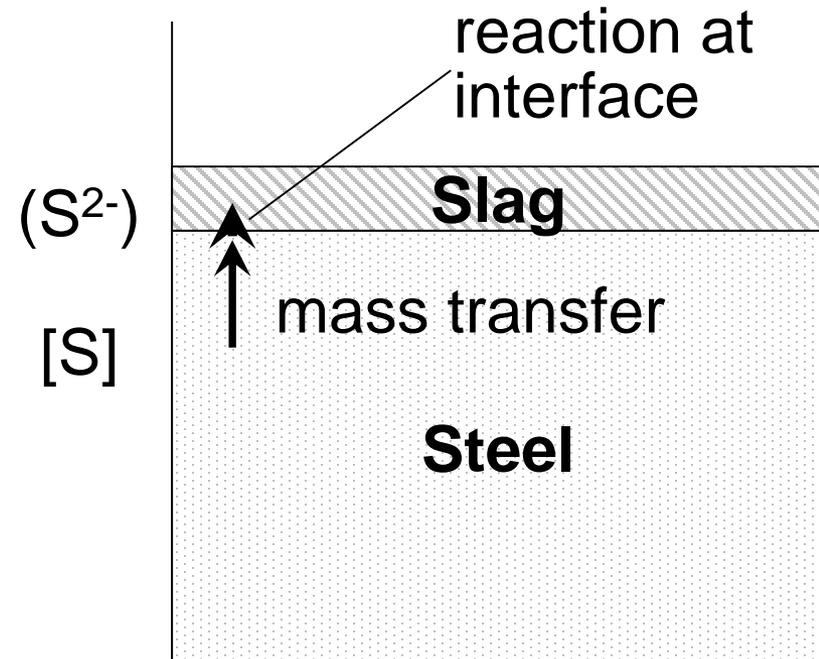
Expected effect of [Si]:

(SiO_2) can oxidise [Al] if [Si] low \rightarrow poor desulphurisation

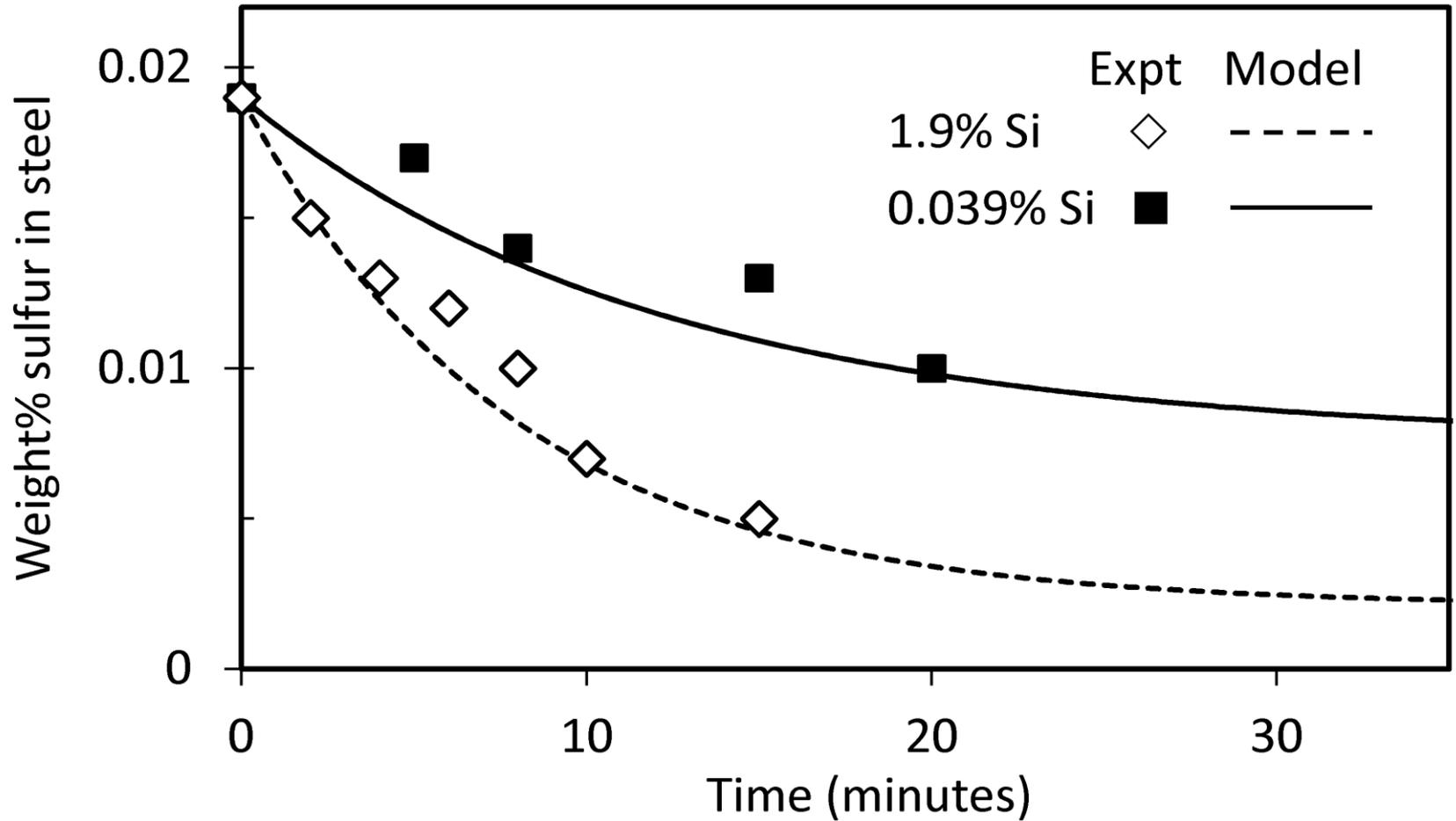
If [Si] high: [Al] pick-up and better desulphurisation expected

Prediction tested:

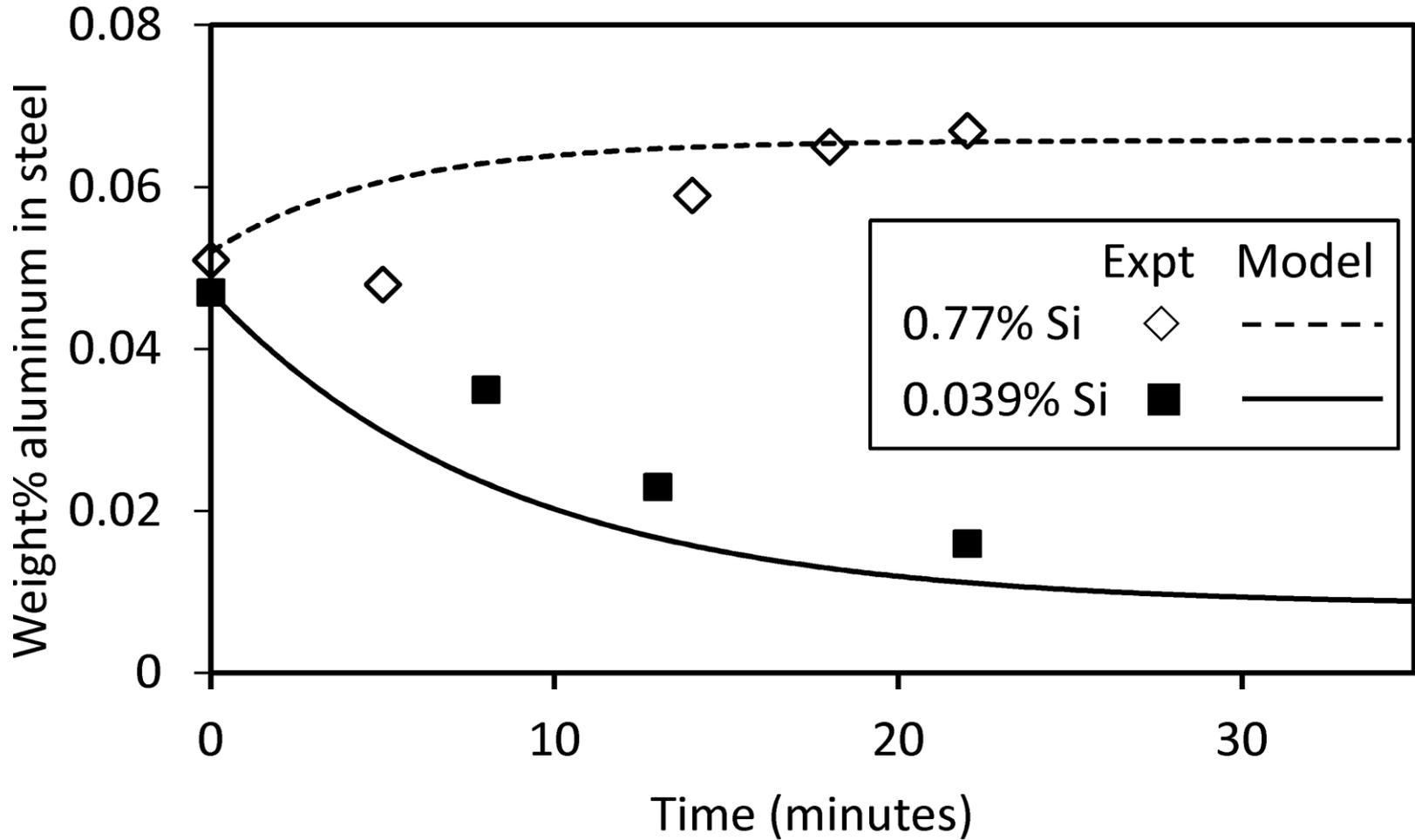
- Kinetic model
- Laboratory testing
- Plant trials



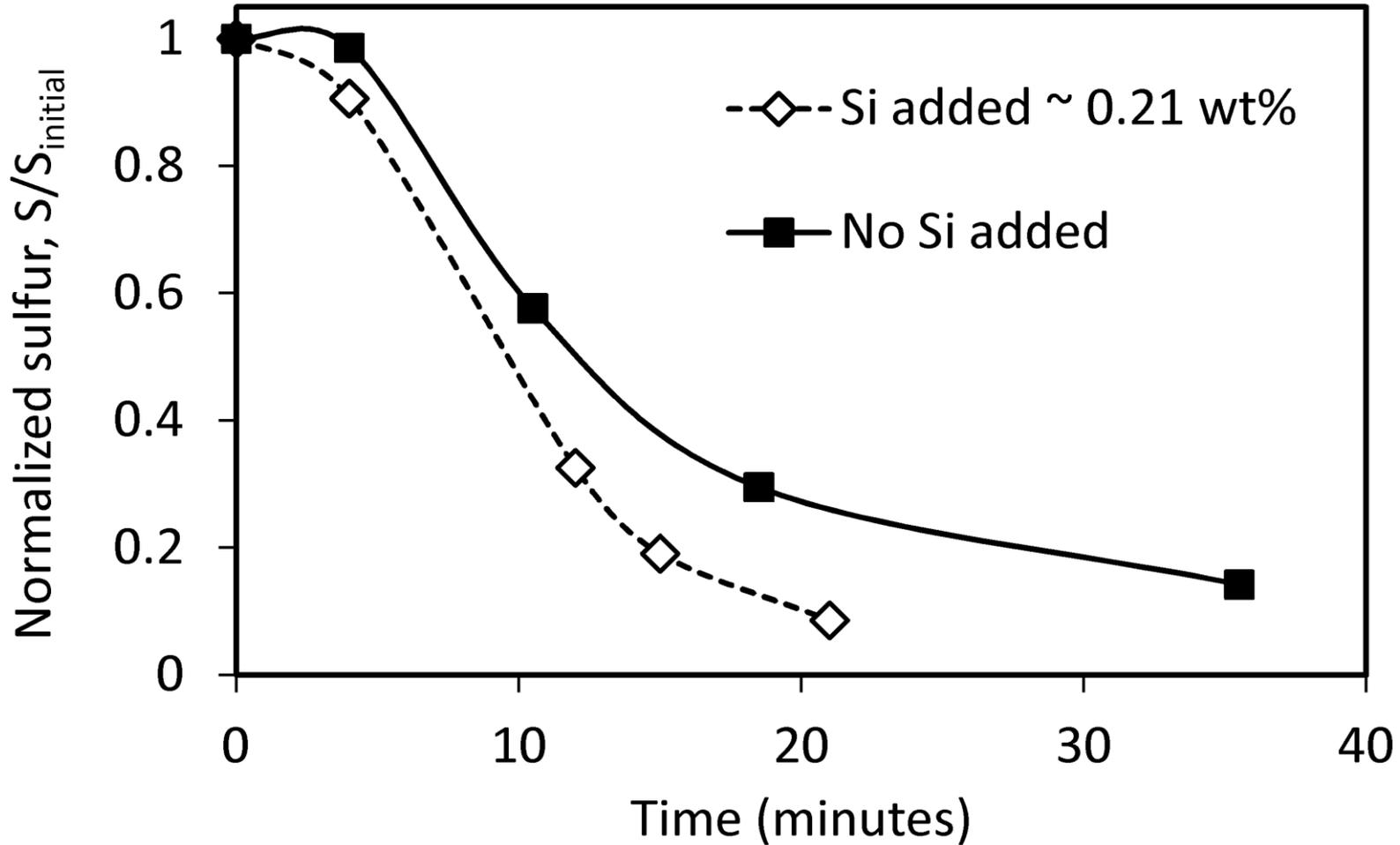
Laboratory results: High Si contents improve desulphurisation
(slag: 40% CaO, 40% Al₂O₃, 9% SiO₂, 11% MgO)



Laboratory results: High Si contents cause Al pick-up
(slag: 49% CaO, 33% Al₂O₃, 10% SiO₂, 8% MgO)



Example of plant trial result:
Less desulphurisation of Si-restricted heats



Practical implications of [Si] effect:

- $[\text{Si}]/(\text{SiO}_2)$ affect Al pick-up / fade
- Add Si early for faster desulphurisation

Microscopy of inclusions in solid steel

Typical inclusion size: microns

Inclusions are rare,
typically 100 ppm or less by volume

What is the best way to prepare samples for scanning electron microscopy?

Two main sample preparation methods:

- polishing of cross-sections
- inclusion extraction (steel matrix dissolved)
 - ❖ bromine-methanol chemical method
 - ❖ electrolytic etching

Advantages:

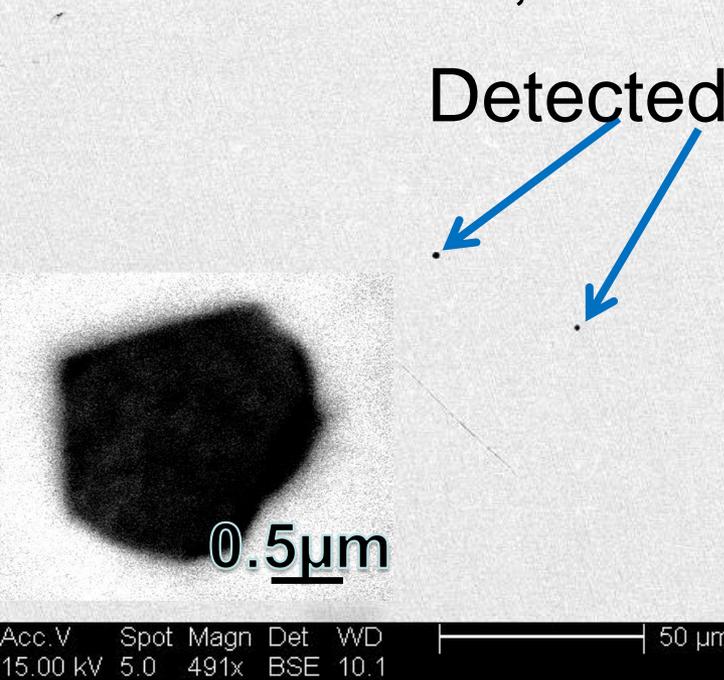
- *polished cross-sections*: analysis readily automated
- *extracted inclusions*: reveal three-dimensional morphology

Possible sources of contamination / artifacts:

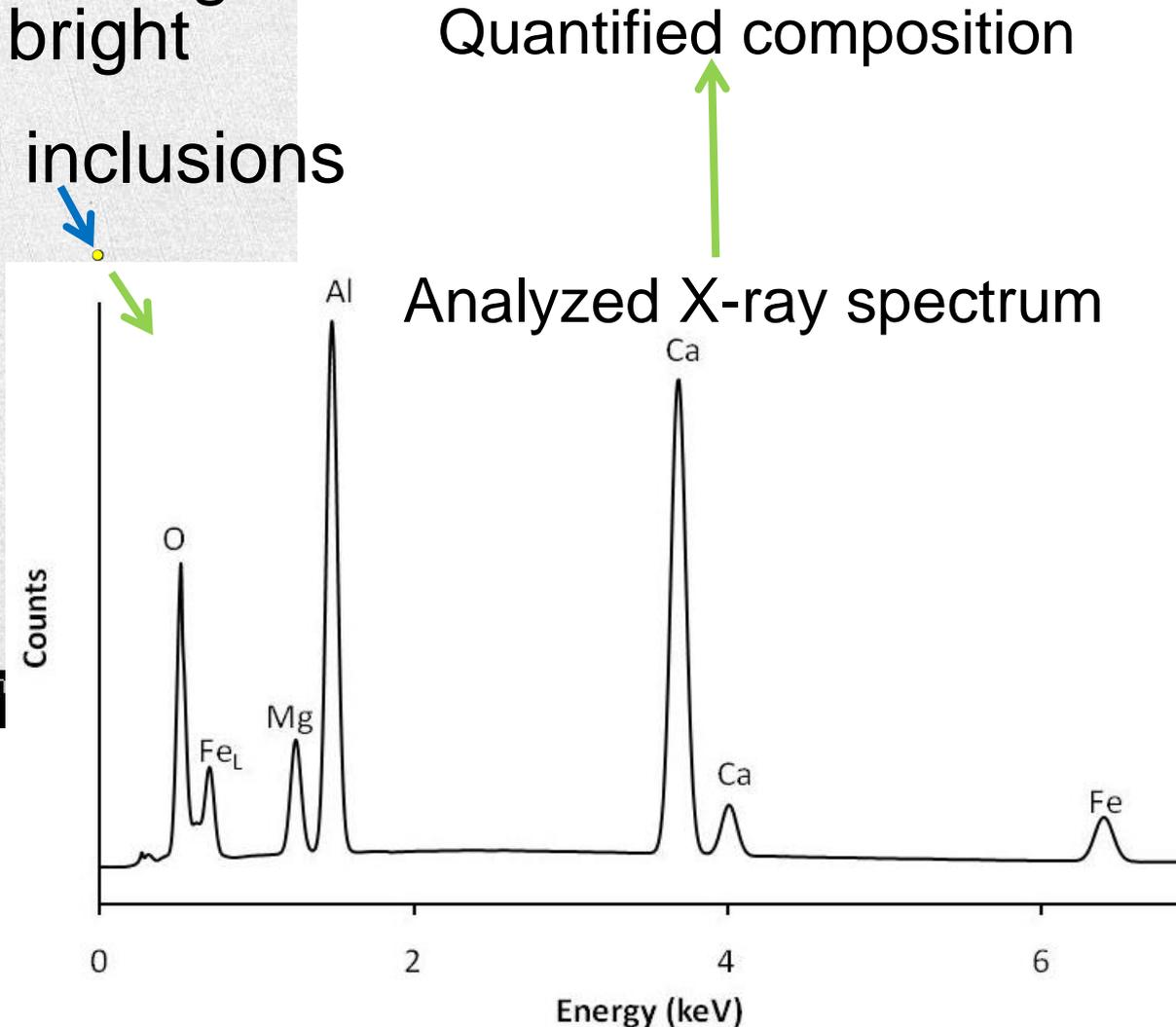
- *polished cross-sections*:
polishing medium particles may remain
embedded in sample surface
- *extracted inclusions*:
inclusion compositions can be altered during extraction

Inclusion detection and analysis: polished sections

Backscattered electron image:
inclusions dark; steel bright



*Hundreds of
inclusions analyzed
in tens of minutes*

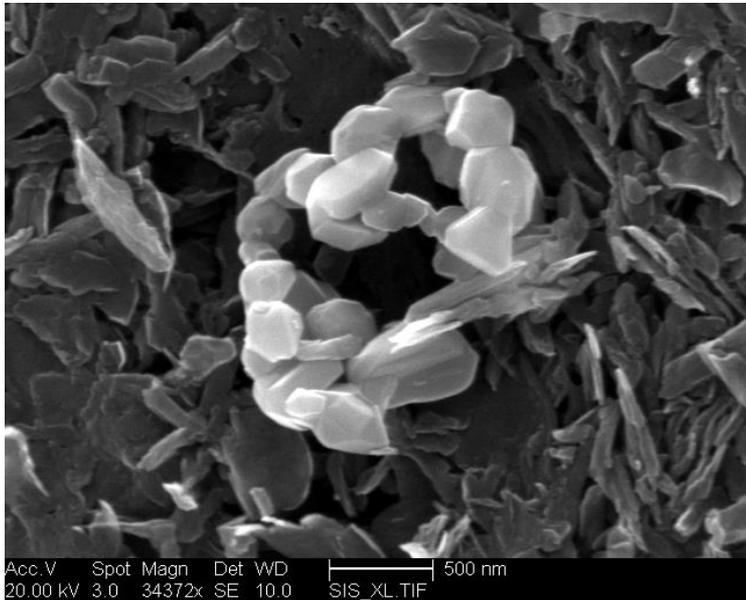
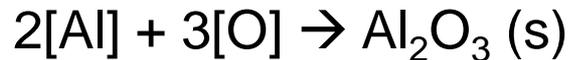


Solid oxide inclusions in Al-killed steel

- exclusions extracted with bromine-methanol

Alumina

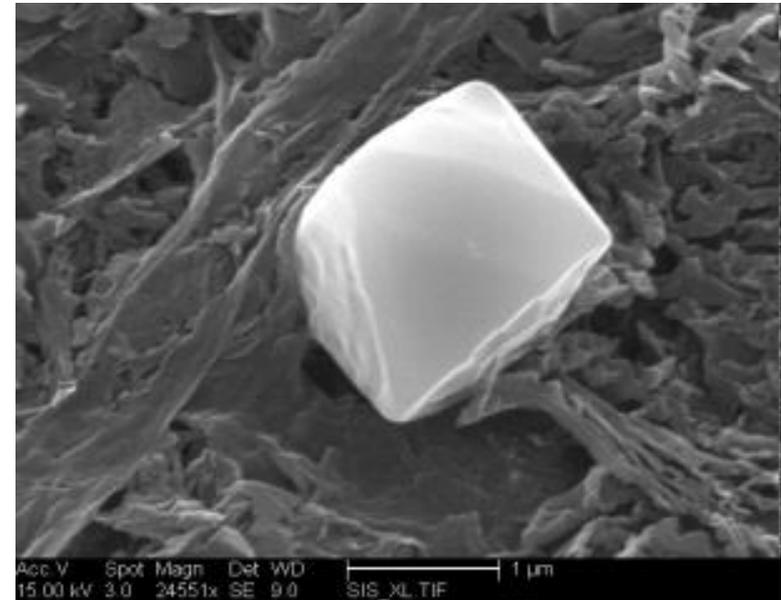
From Al deoxidation



Clustered alumina

Spinel

- Solid solution of MgAl_2O_4 and Al_2O_3
- Mg source: mainly slag



Spinel

Experimental conditions: electrolytic dissolution

Non-aqueous electrolyte:

10wt% **acetylacetone** - 10wt% **sodium perchlorate** - **methanol**

chelating reagent
to dissolve Fe^{n+}

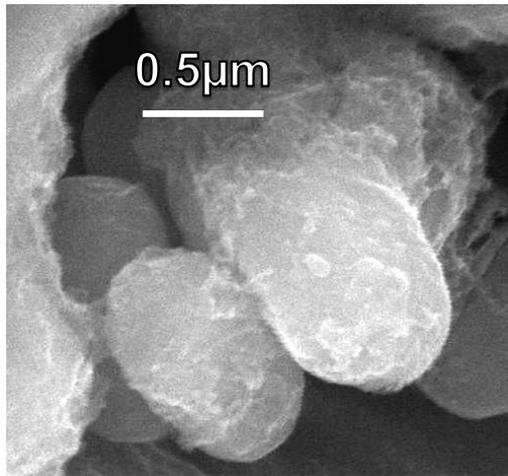
provides
conductivity

solvent

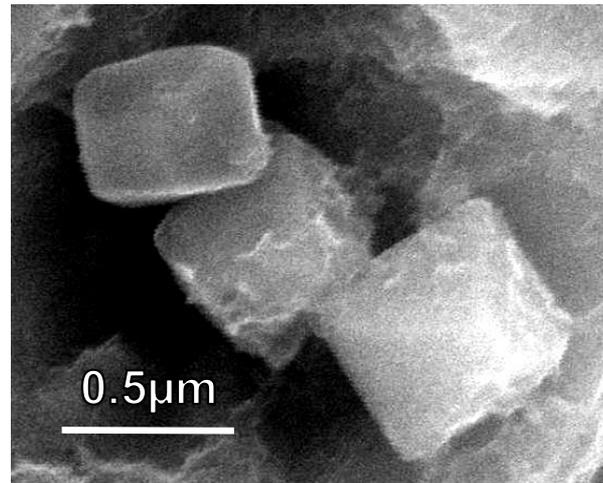
anodic current density $\sim 1 \text{ A/cm}^2$; graphite cathode

Examples of inclusions:

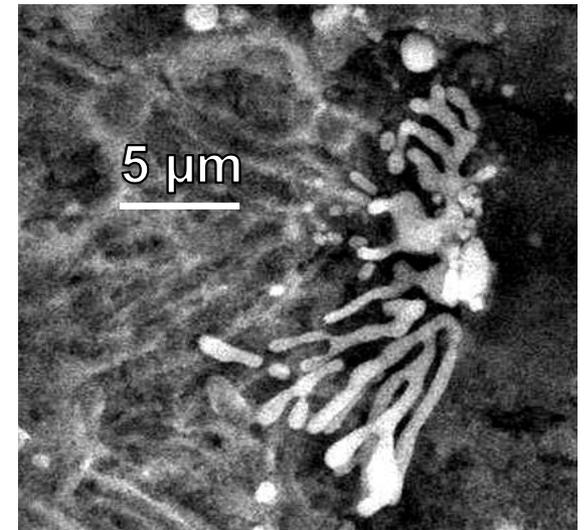
Al-killed steel containing ~100 ppm S, 1% Mn, 0.1% Cu;
surface etched electrolytically



Al_2O_3 covered by
(Mn, Cu)S



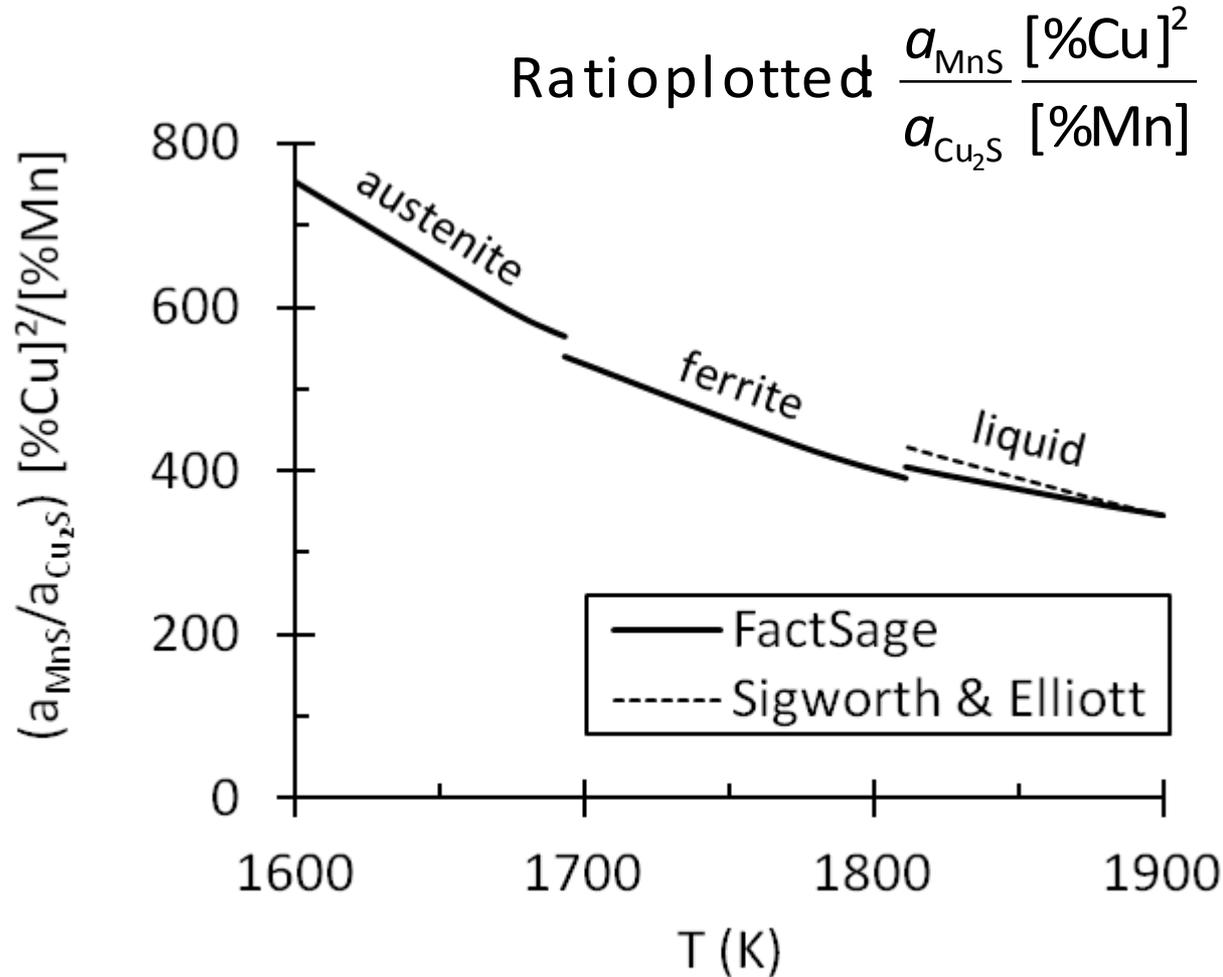
(Mn, Cu)S



(Mn, Cu)S

secondary electron images

But: Copper sulphide is not stable in steel that contains manganese



The observed copper sulphide is an artifact that forms during electrolytic dissolution of the steel

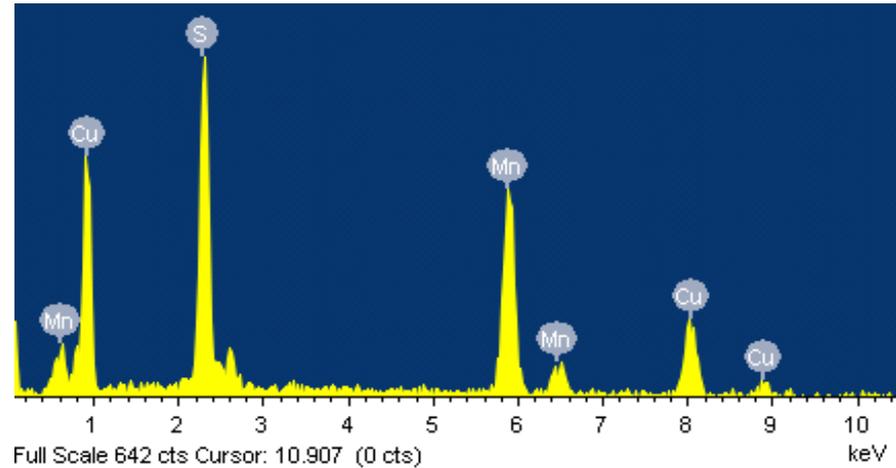
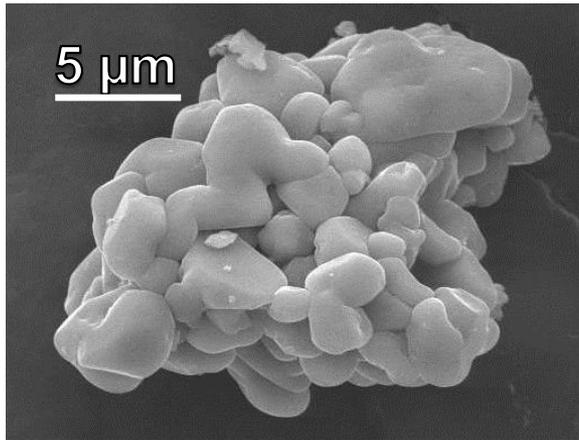
Large driving force for Cu ions to be precipitated from **electrolyte solution** by other sulfides, at room temperature

reaction	equilibrium constant
$\text{Cu}^{2+} + \text{MnS} \rightarrow \text{CuS} + \text{Mn}^{2+}$	5.7×10^{21}
$\text{Cu}^{2+} + \text{CaS} \rightarrow \text{CuS} + \text{Ca}^{2+}$	1.0×10^{35}
$\text{Cu}^{2+} + \text{FeS} \rightarrow \text{CuS} + \text{Fe}^{2+}$	3.2×10^{15}

CuS_x artifact formation: experimental test

Electrolytic dissolution as for steel sample,
but using copper anode, and 0.2g MnS powder added to the
electrolyte before dissolution:

⇒ Copper sulfide forms on MnS



(Mn, Cu)-S particle after electrolysis,
with EDX spectrum

Conclusions

- Required impurity levels in steel are steadily decreasing
- General principles of clean-steel production are well established
- Improvement in quantitative information:
 - dephosphorisation: see also FactSage study; IMPHOS project in Europe
 - slag-based deoxidation: affects ladle desulphurisation
- Inclusions: improved imaging and analysis; beware artifacts