advancing through insight

Thermochemistry Measurements and Models in Pyrometallurgy

How (un)sure are we?

GTT Users Meeting, Aachen

27 June 2019

Content

- Ex Mente
- Global trends
- The pyrometallurgical industry
- Mass and energy balances
- Case studies
- Uncertainty
- Conclusions

Overview of Ex Mente

Ex Mente
Who are we?

From Pretoria, South Africa.

Specialist process engineering consulting company.

Focused on non-ferrous pyrometallurgy.

Ex Mente
Purpose

We help our clients
to better understand
their materials, processes, and equipment
to make them more successful.

Ex Mente
Activities

Operational analysis

Advanced process control

Process improvement

Failure analysis

Process design

New process development

Ex Mente
Methods

Computational thermochemistry studies

Process modelling

(steady-state mass and energy balances, dynamic process models)

Multiphysics modelling

(fluid flow, heat transfer, electromagnetics, multi-phase, granular, chemistry)

Mostly computational work

Very reliant on **material property data**,

especially thermochemistry.

Ex Mente

Approach

Credible computational modelling work is **not easy**

We use:

Strong theoretical basis

Formal and reliable methods

Focused on developing understanding and insight

To reduce uncertainty and risk for our clients

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Ex Mente
Approach – Delivering to Clients

Integrate intelligence into the plant

Integration with plant systems

Make it usable for non-experts (like Sedi's black box)

Distributed software, no more isolated "islands"

(e.g. EMSIM)

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Global Trends

Global Trends
Raw Materials

Lower quality ores

Necessity of recycling

More complex raw materials

Global Trends
Processes and Projects

More challenging process conditions

Bigger process units

(economy of scale, improved efficiency)

Shorter project time lines

Greater speed, greater uncertainty, greater risk

Pyrometallurgical Industry

Pyrometallurgical Industry
A necessary “evil”?

A necessary and valuable part of society

It’s not going away … soon

Significant environmental impact

Image in the eyes of the public?

Not great.

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Pyrometallurgical Industry

Recent Bad Experiences

Koniambo Ferronickle, New Caledonia

Kazchrome Aktobe Smelter, Kazakhstan

AMIC Ilmenite Smelter, Saudi Arabia

Pyrometallurgical Industry
Consequences

Financial losses

Safety risks

Poor efficiency

Environmental impact

Can we afford such mistakes in future?

Pyrometallurgical Industry
Causes of Problems – Several Possible Reasons

Design

Engineering practices

Poor understanding

Bad design basis data

Bad thermochemical data

Bad application

Operation

Poor understanding

Bad plant data

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Mass and **Energy** Balances

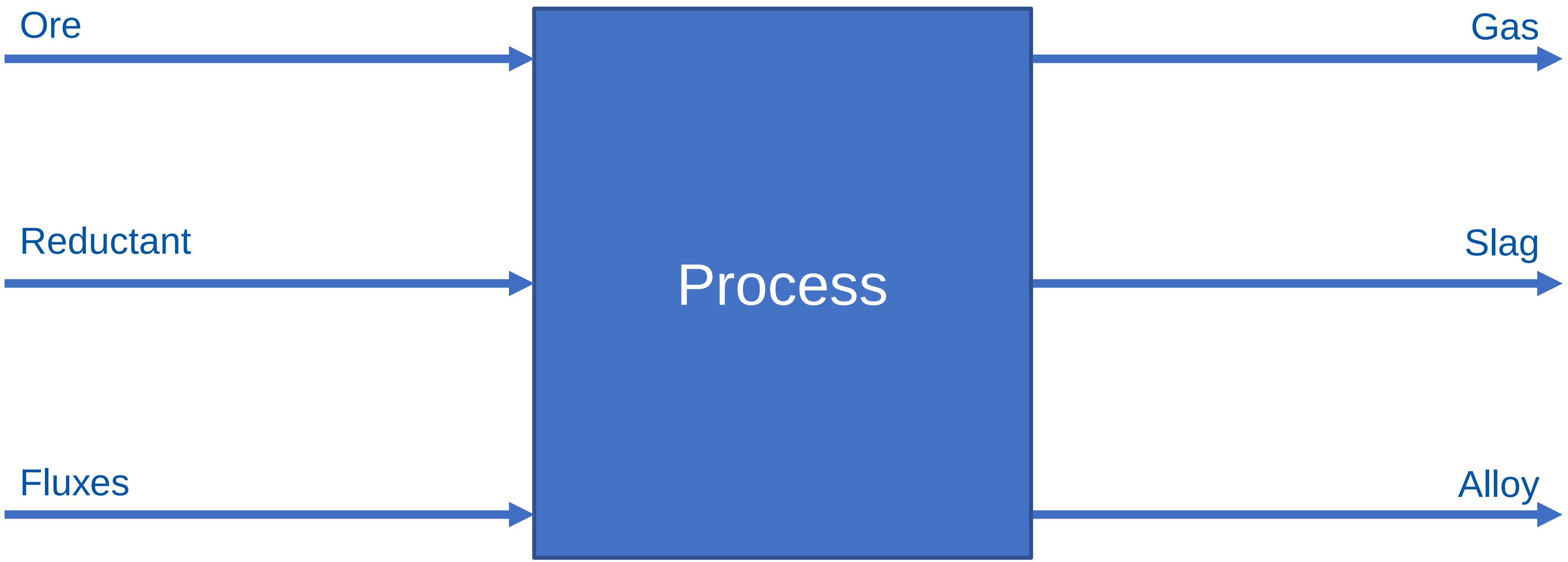
Mass and Energy Balances
Our Most Basic Tool

Most widely used type of model in pyrometallurgy

Of fundamental importance
to **design** and **operation**

Mass and Energy Balances
Basic Concept

Hess's Law for Enthalpy



Simple, right?

Mass and Energy Balances

Required Data

Raw Materials (low temperature)

Enthalpies of formation ($\Delta H_{f,298}$)

Heat capacities

Products

Liquidus temperatures

Enthalpies of fusion

Heat capacity

Enthalpies

Case Studies

Chromite Melting
Low-carbon Ferrochrome

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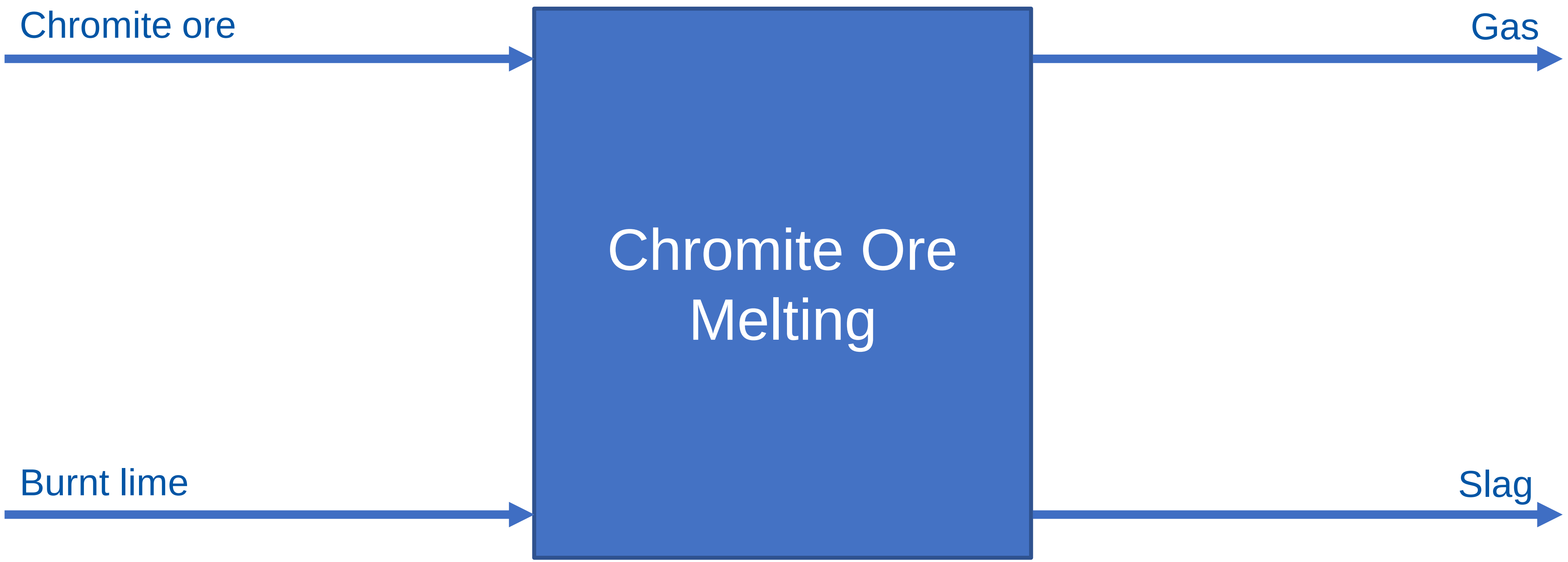
Case Studies
Chromite Melting (low-carbon ferrochrome)



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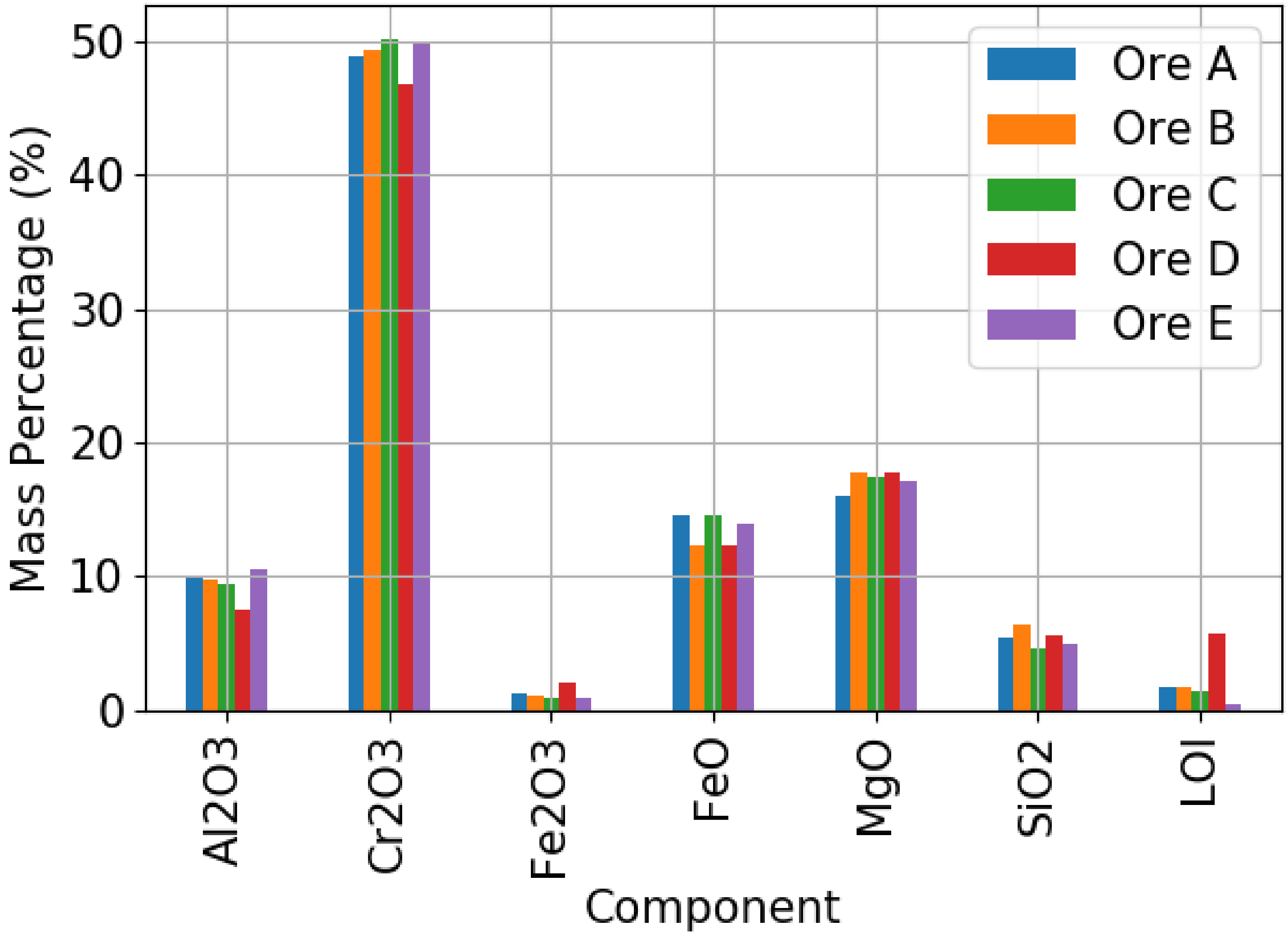
Case Studies
Chromite Melting – 5 Chromite Ores (chemical)



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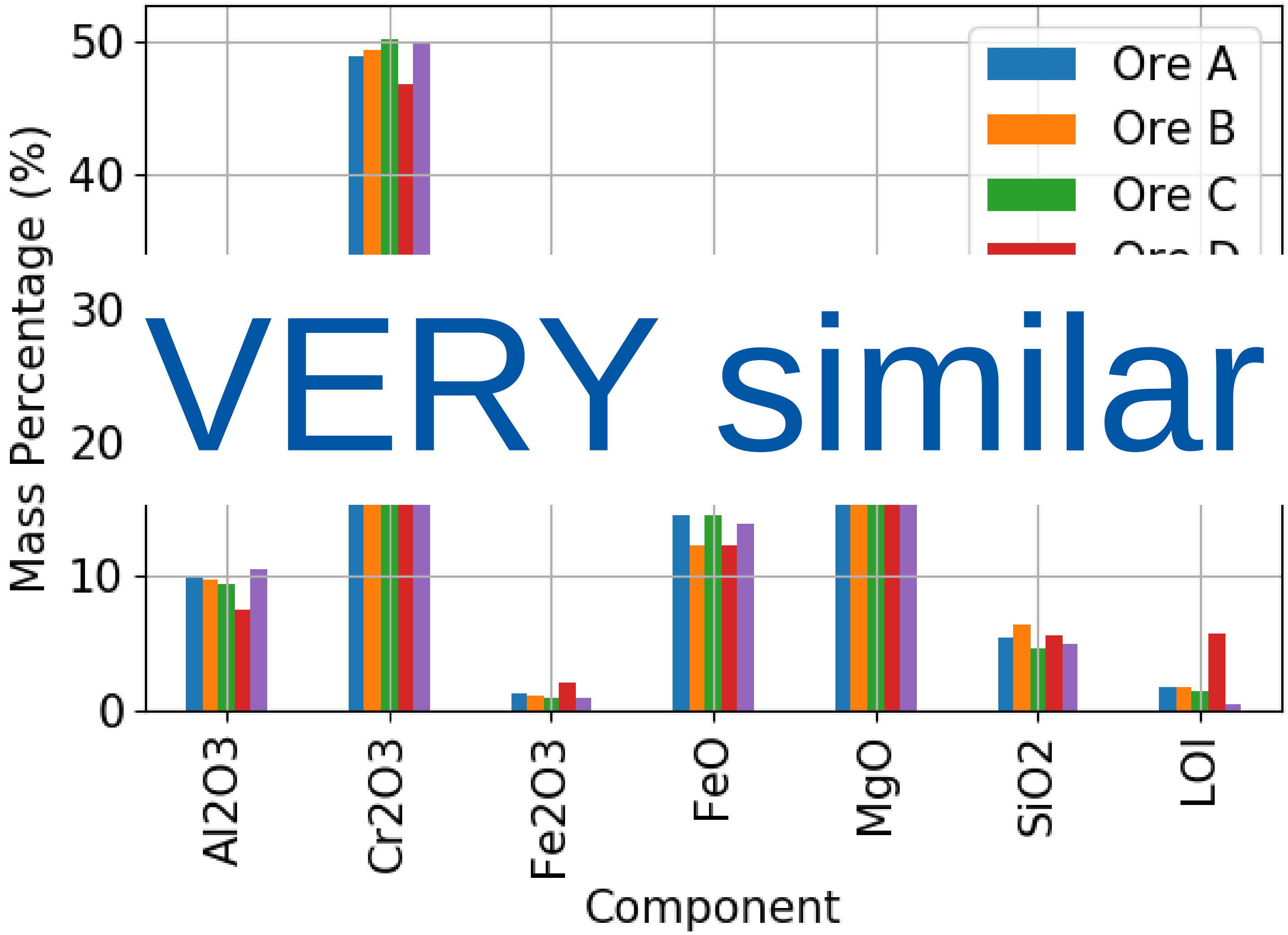
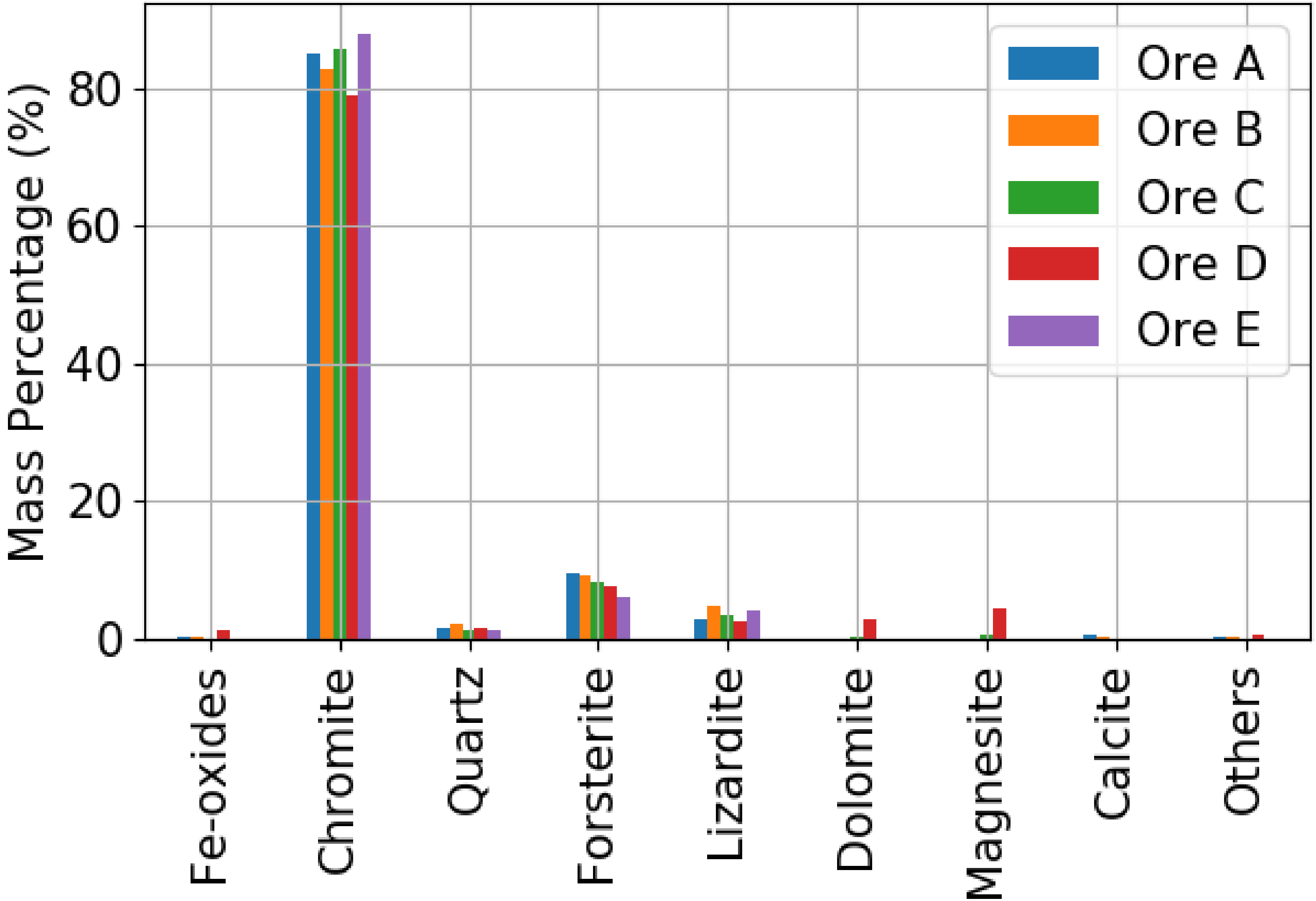
Case Studies
Chromite Melting – 5 Chromite Ores (chemical)



VERY similar

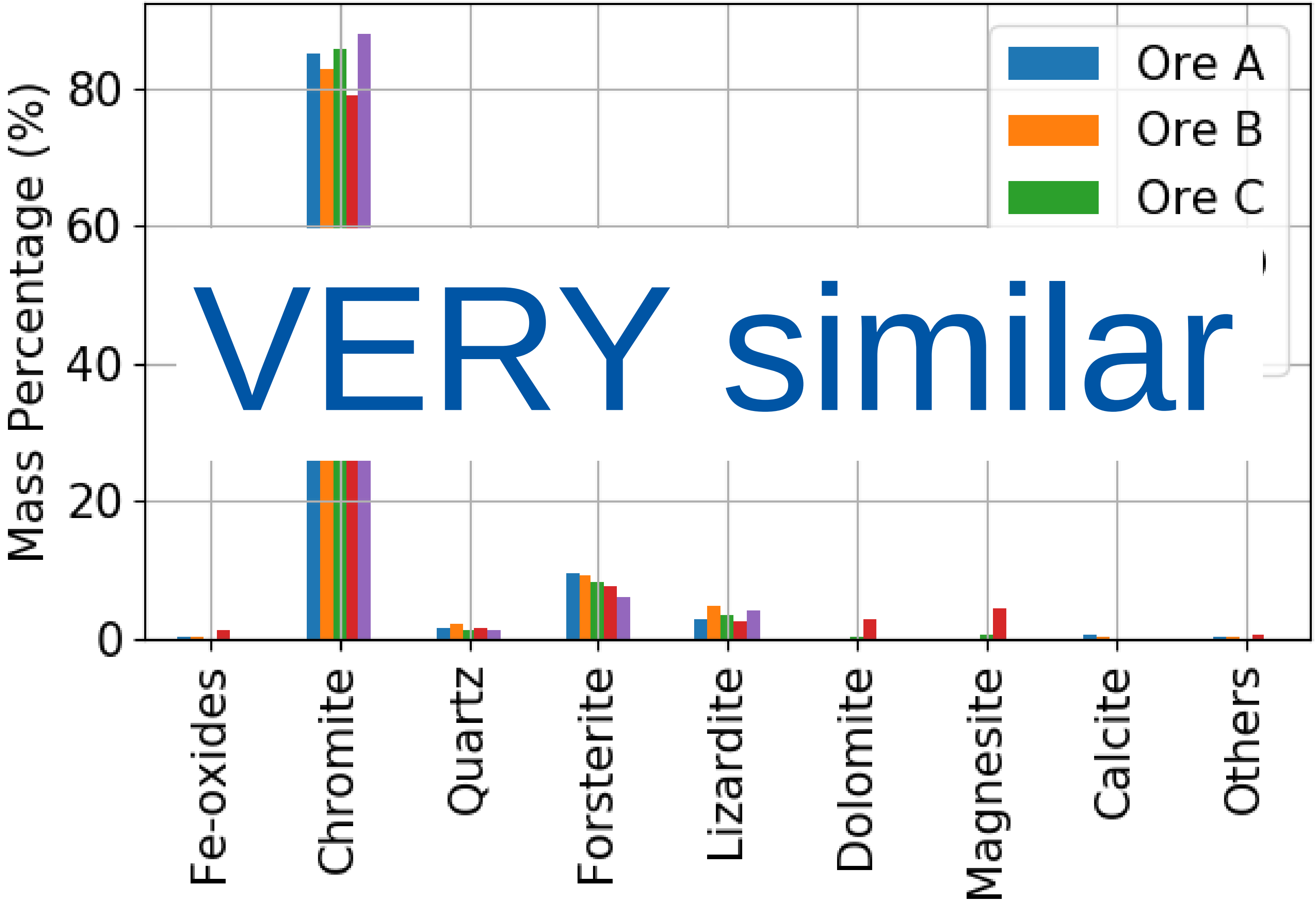
EXMENTE

Case Studies
Chromite Melting – 5 Chromite Ores (mineralogical)



EXMENTE

Case Studies
Chromite Melting – 5 Chromite Ores (mineralogical)



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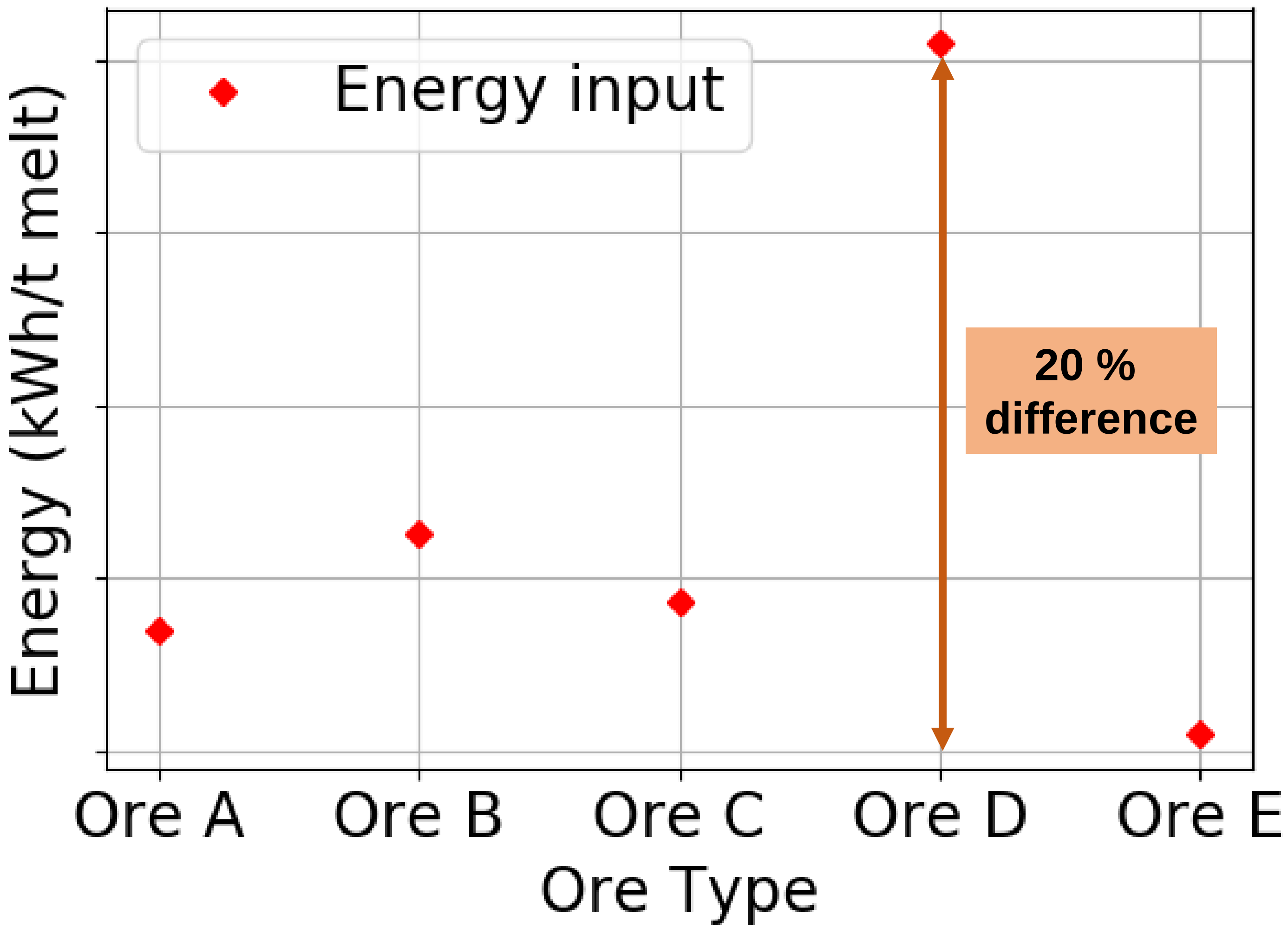
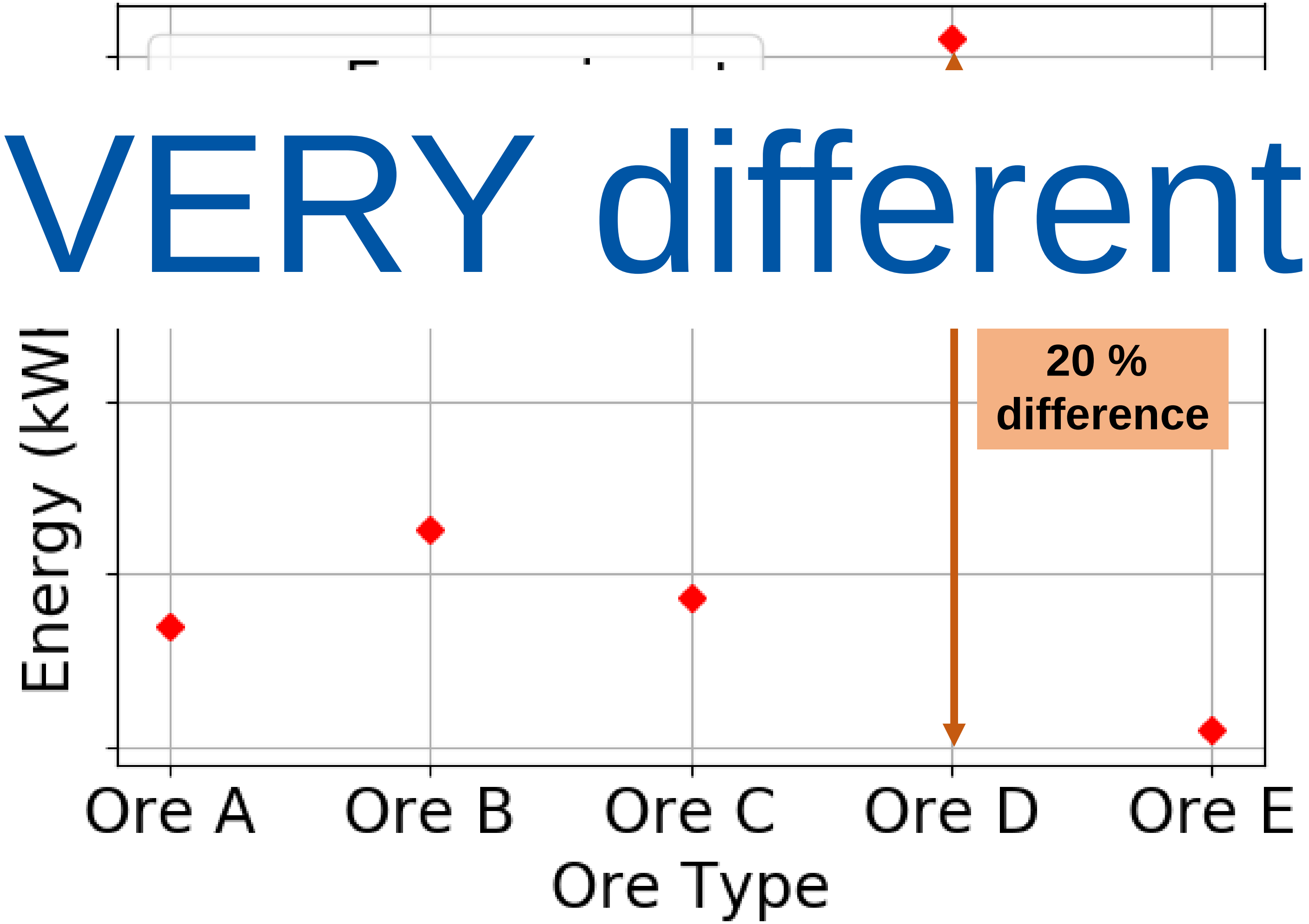
Case Studies
Chromite Melting – Different Energy Consumptions



Case Studies

Chromite Melting – Different Energy Consumptions



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Case Studies

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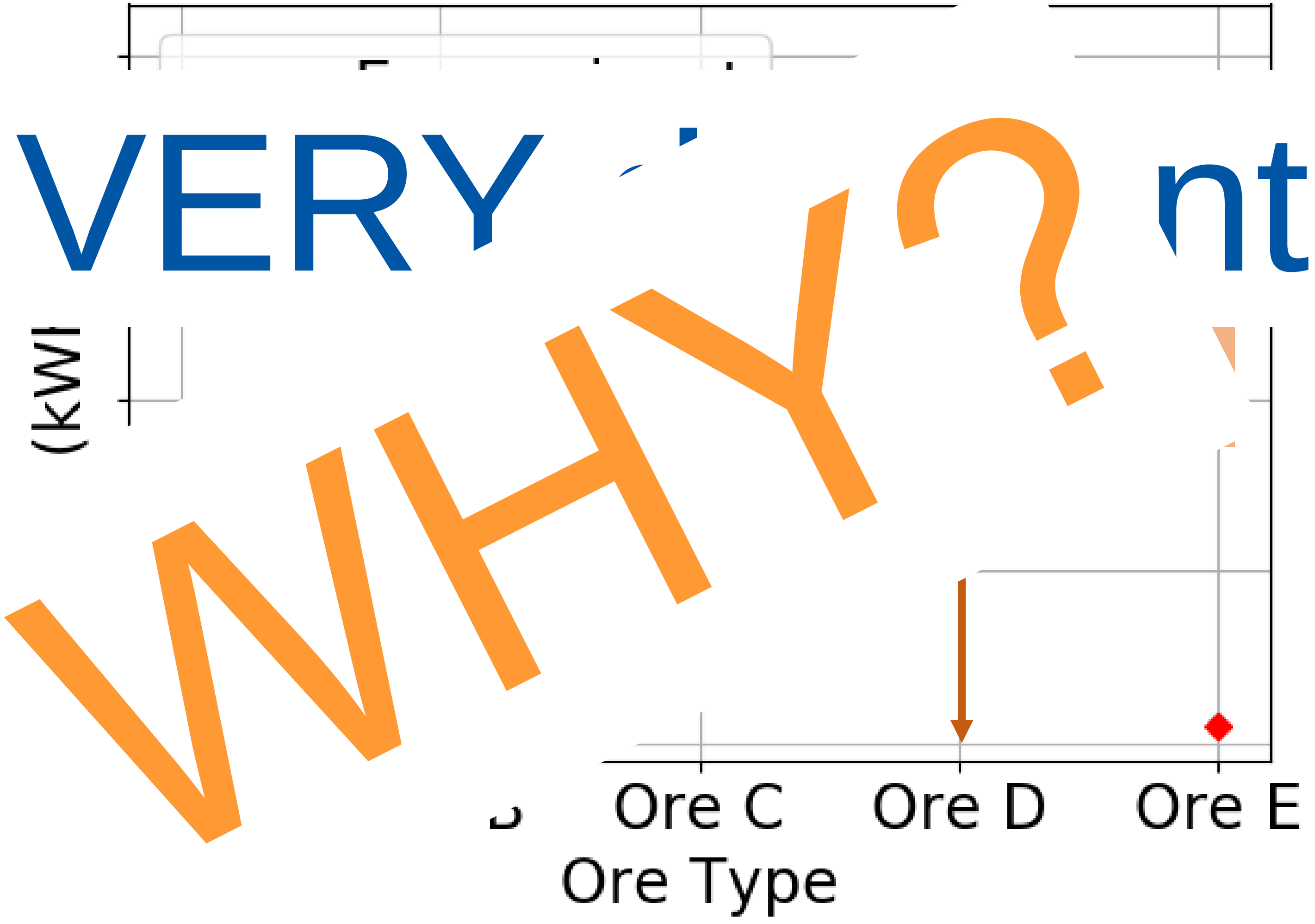

Case Studies
Chromite Melting

Consistent Operation for All Ores

Electrical power is constant

Tap-to-tap time is constant

Operating time is constant

Tap mass is constant

(slightly suspicious)

What should we consider?

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Case Studies

Chromite Melting – What can cause this?

Ore and Burnt Lime (25 °C)

Enthalpies of formation ($\Delta H_{f,298}$)

Products

Liquidus temperatures

Enthalpies of fusion

Heat capacity

Enthalpies

i.e. **melting behaviour**.

Case Studies

Chromite Melting – Chromite $\Delta H_{f,298}$

Calculate with ChemAppPy + FToxid

Based on EDS mineral assays

Spinel solid solution model

Temperature: 25 °C

How valid is this?

Spinel data probably determined at high temperature

Case Studies

Chromite Melting – Chromite $\Delta H_{f,298}$

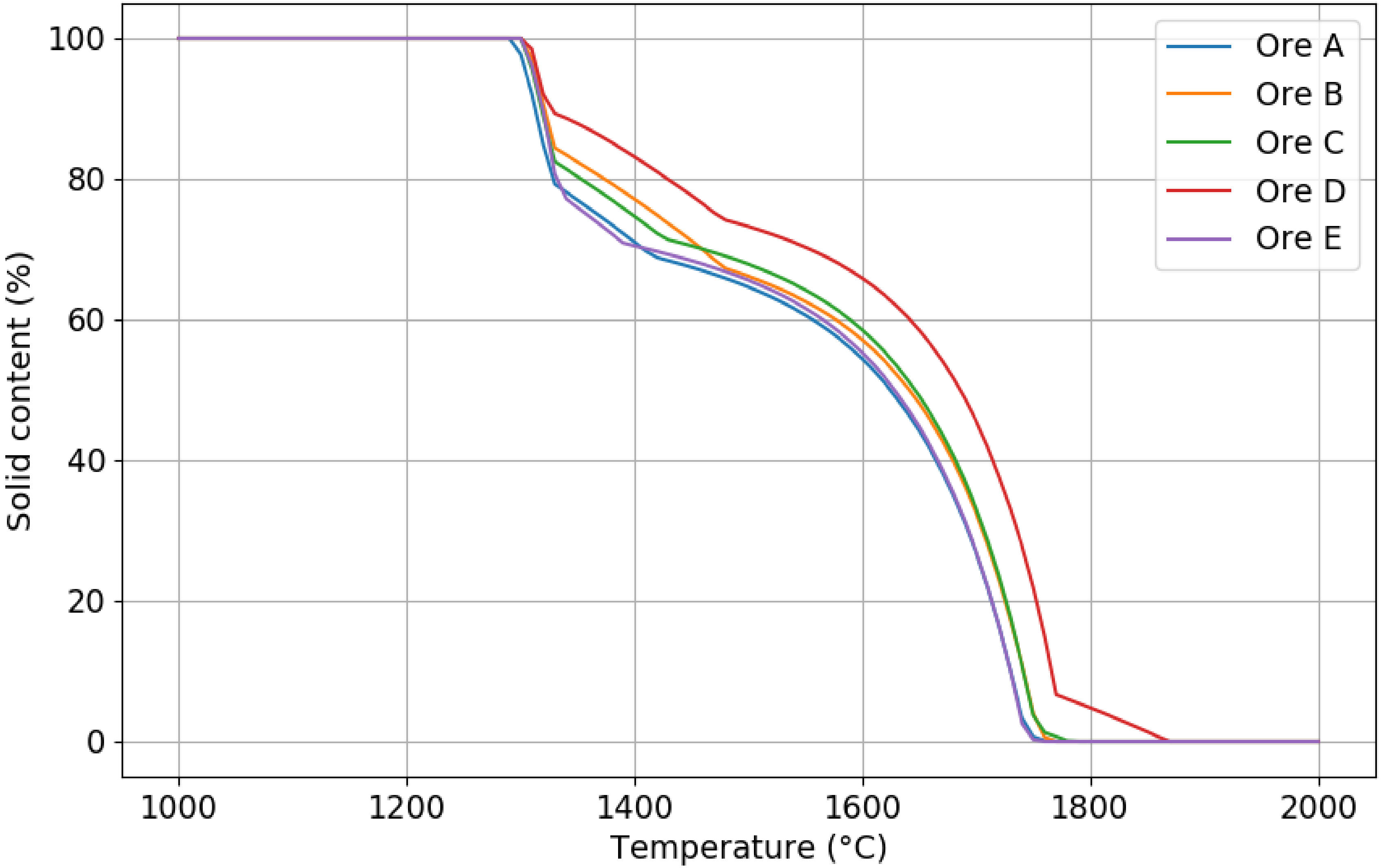
How large are the calculation errors?

How much can we trust it?

How can we measure it?

We attempted it with FZ Jülich, no success yet.

Case Studies
Chromite Melting – Melting Behaviour



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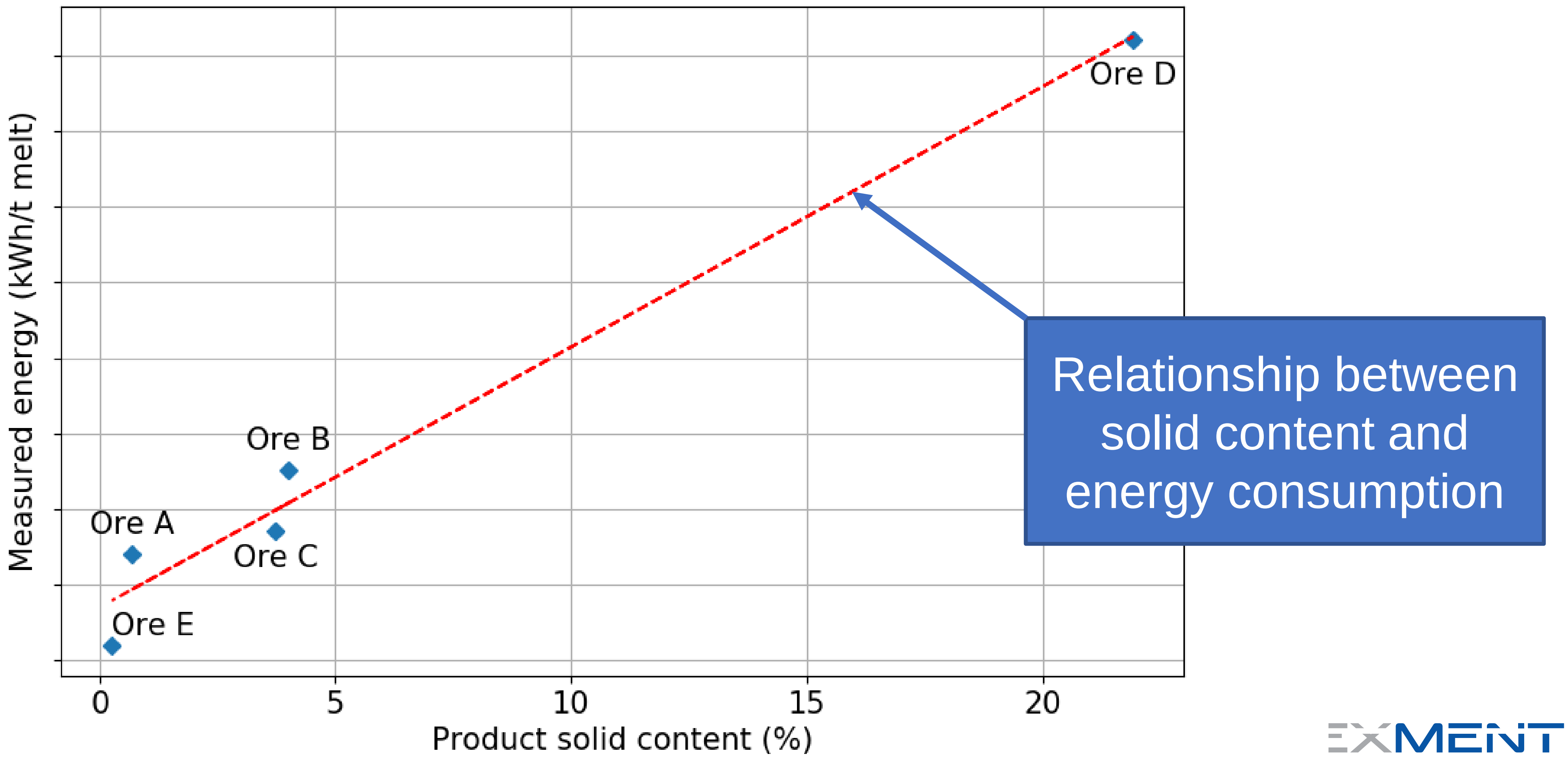
Case Studies
Chromite Melting – Melting Behaviour



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Case Studies

Chromite Melting – Melting Behaviour

Results look convincing

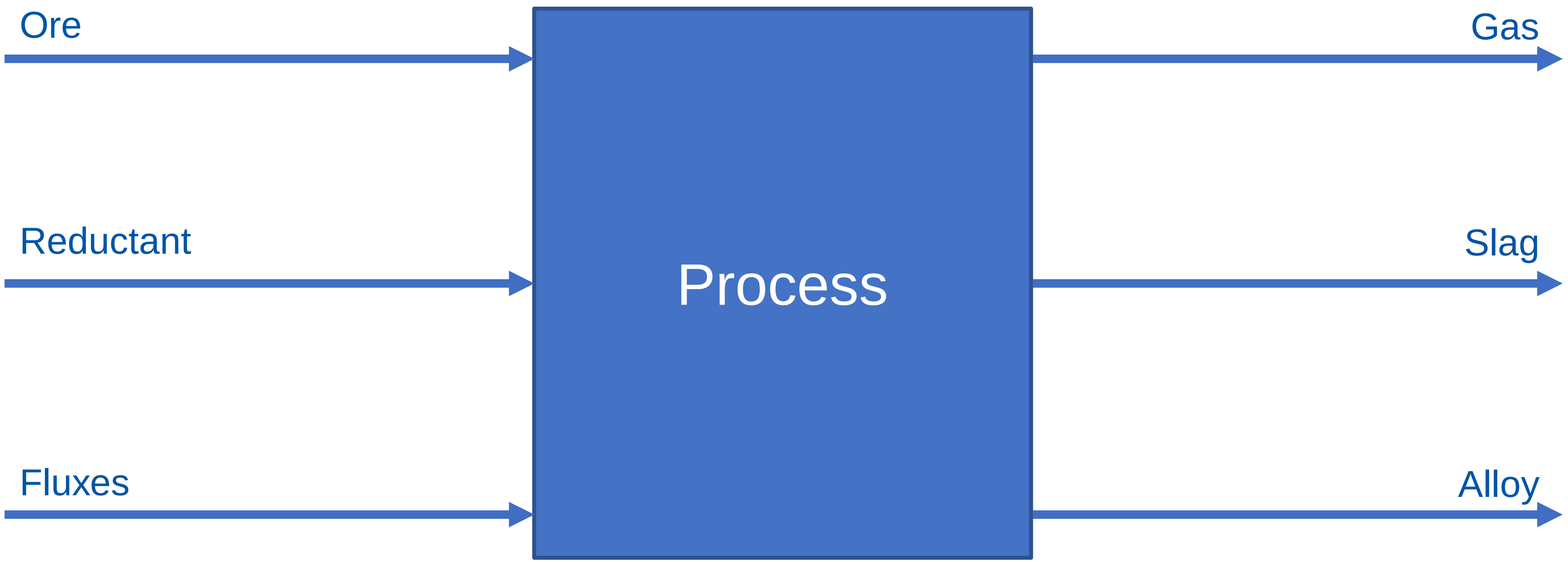
How large are the calculation errors?

How much can we trust it?

Case Studies

Chromite Smelting
High-carbon Ferrochrome

Case Studies
Chromite Smelting



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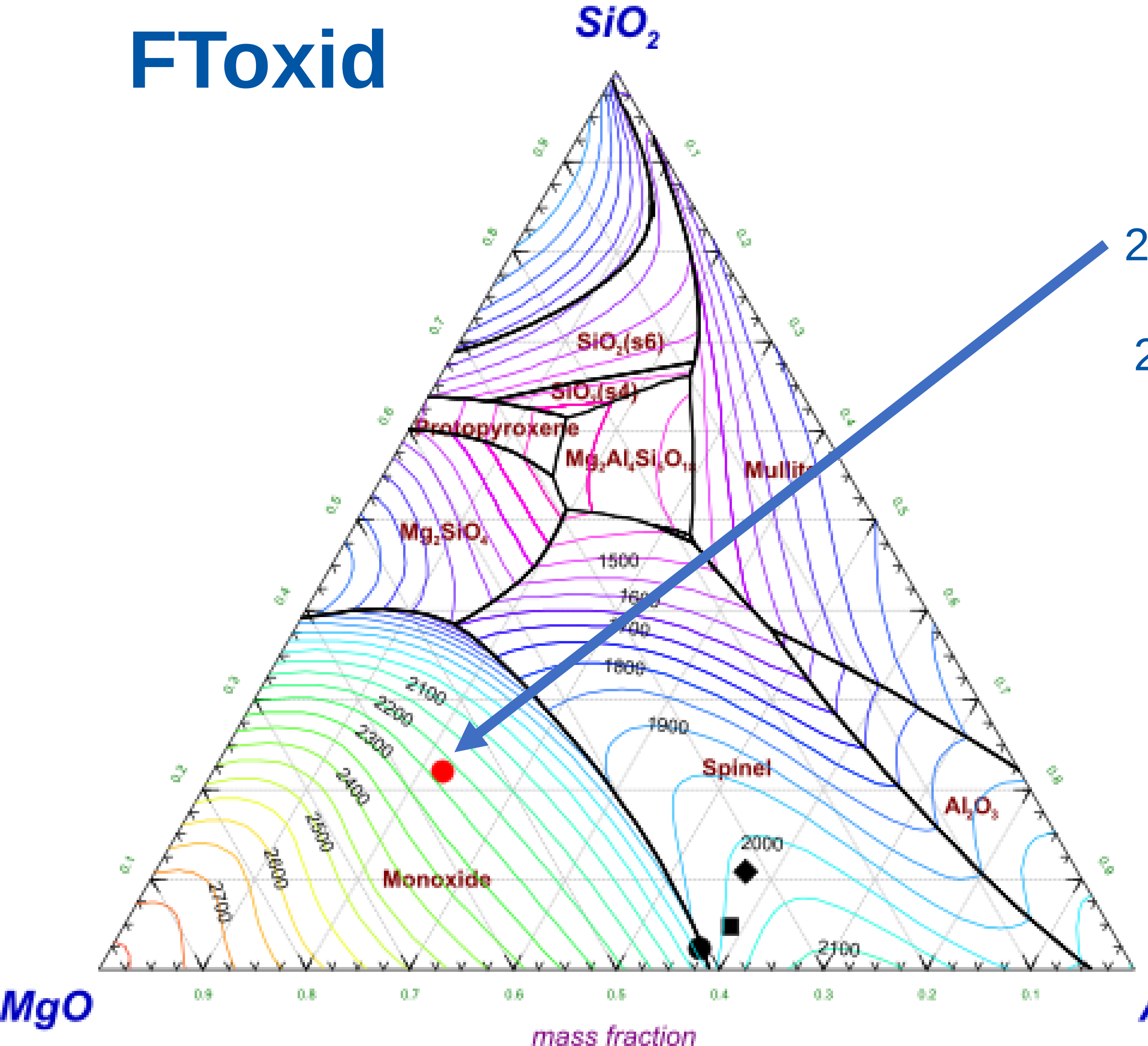
Case Studies
Chromite Smelting – Slag Behaviour

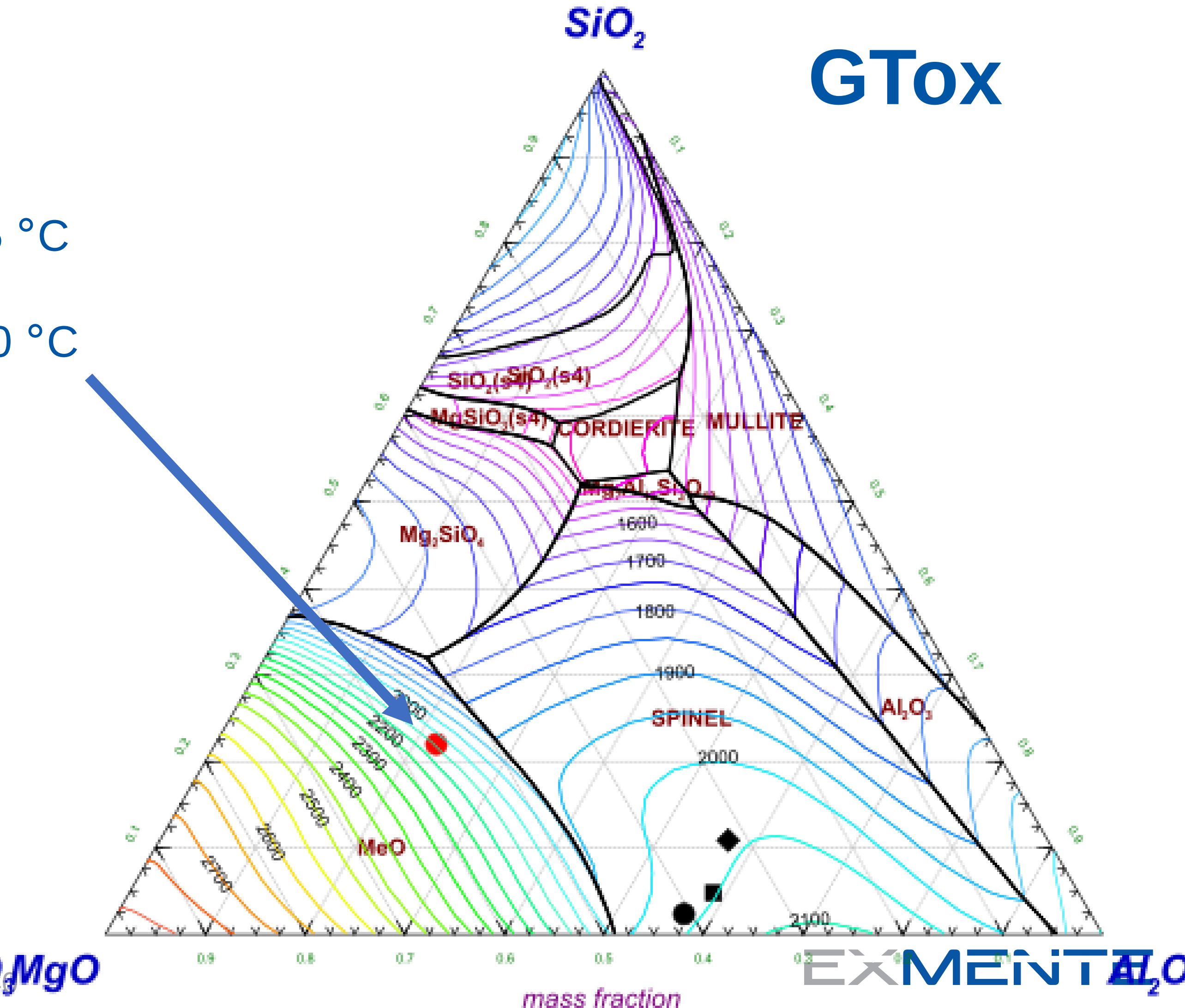
FToxid



2225 °C

2100 °C

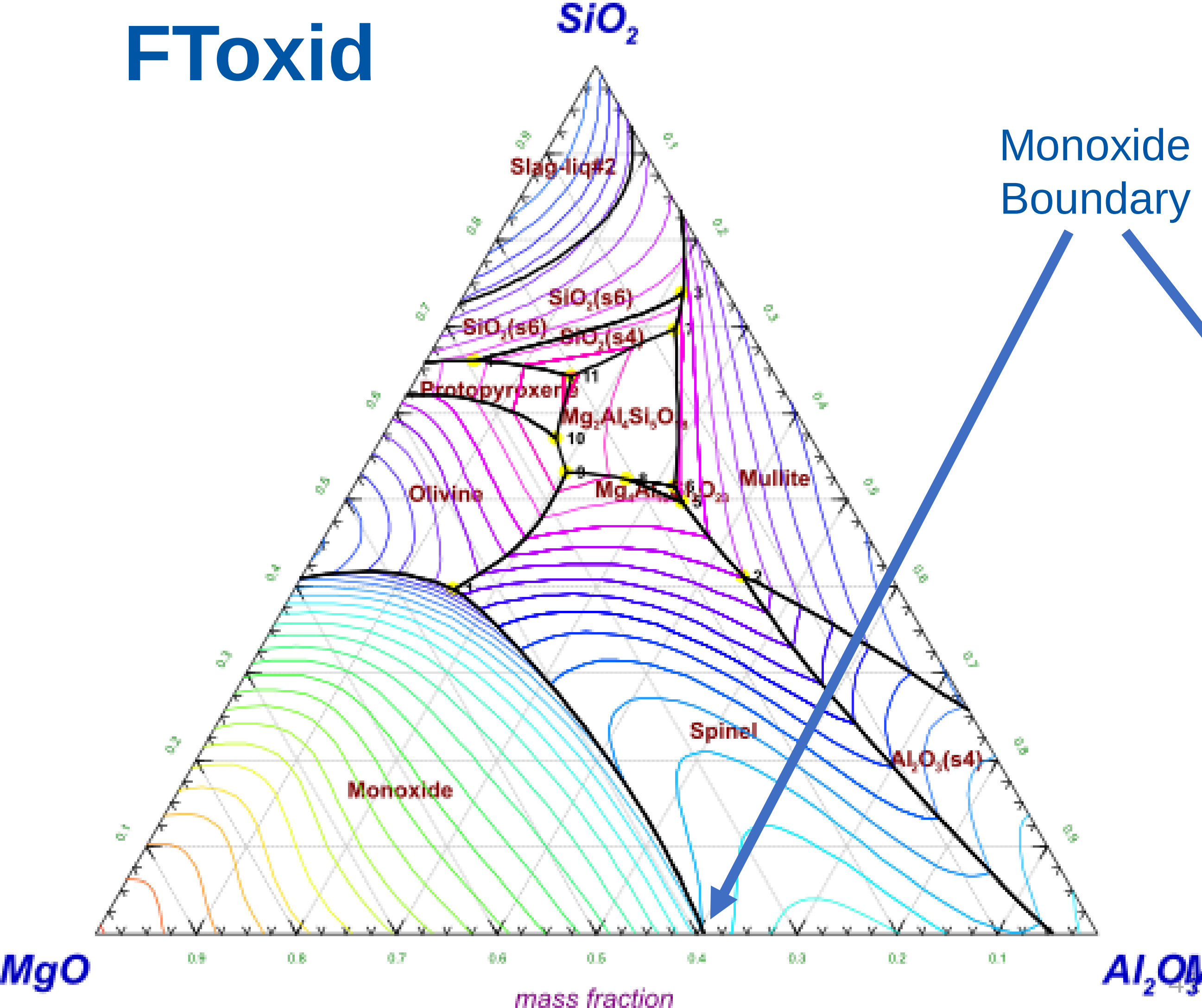
GTox



Case Studies

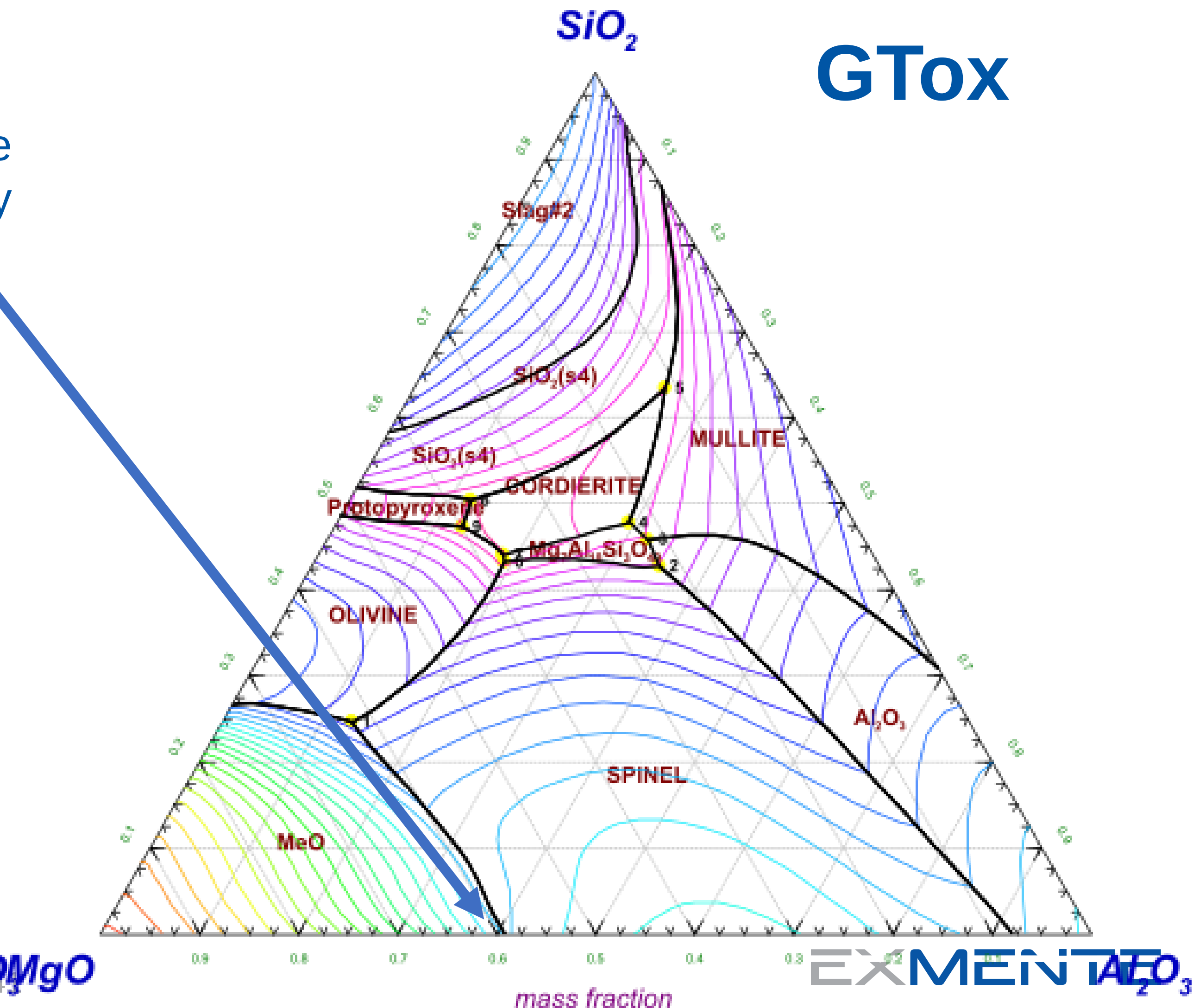
Chromite Smelting – Slag Behaviour + 3.5% CaO

FToxid



Monoxide Boundary

GTox



Case Studies

Chromite Smelting – Slag Behaviour + 3.5% CaO

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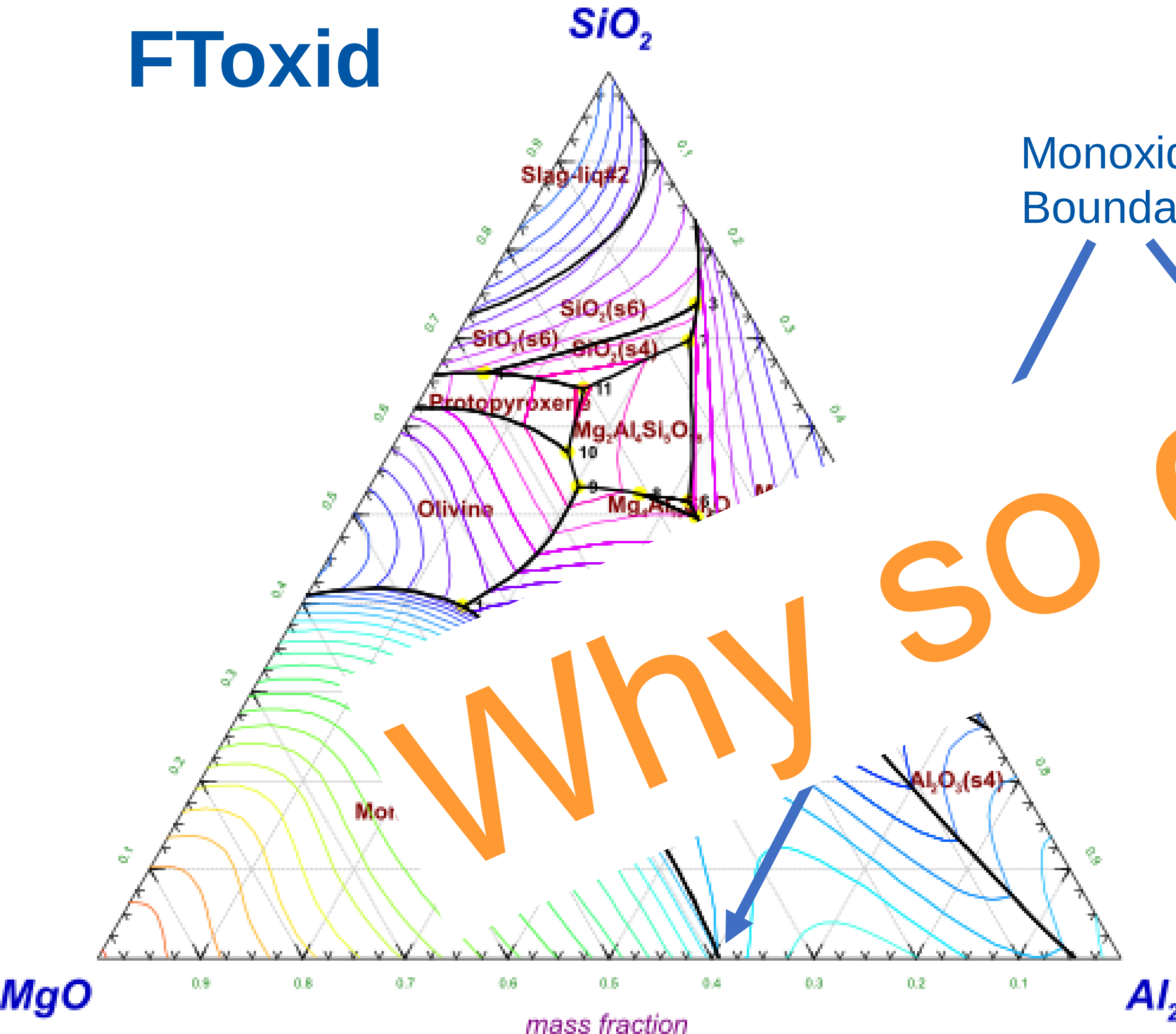
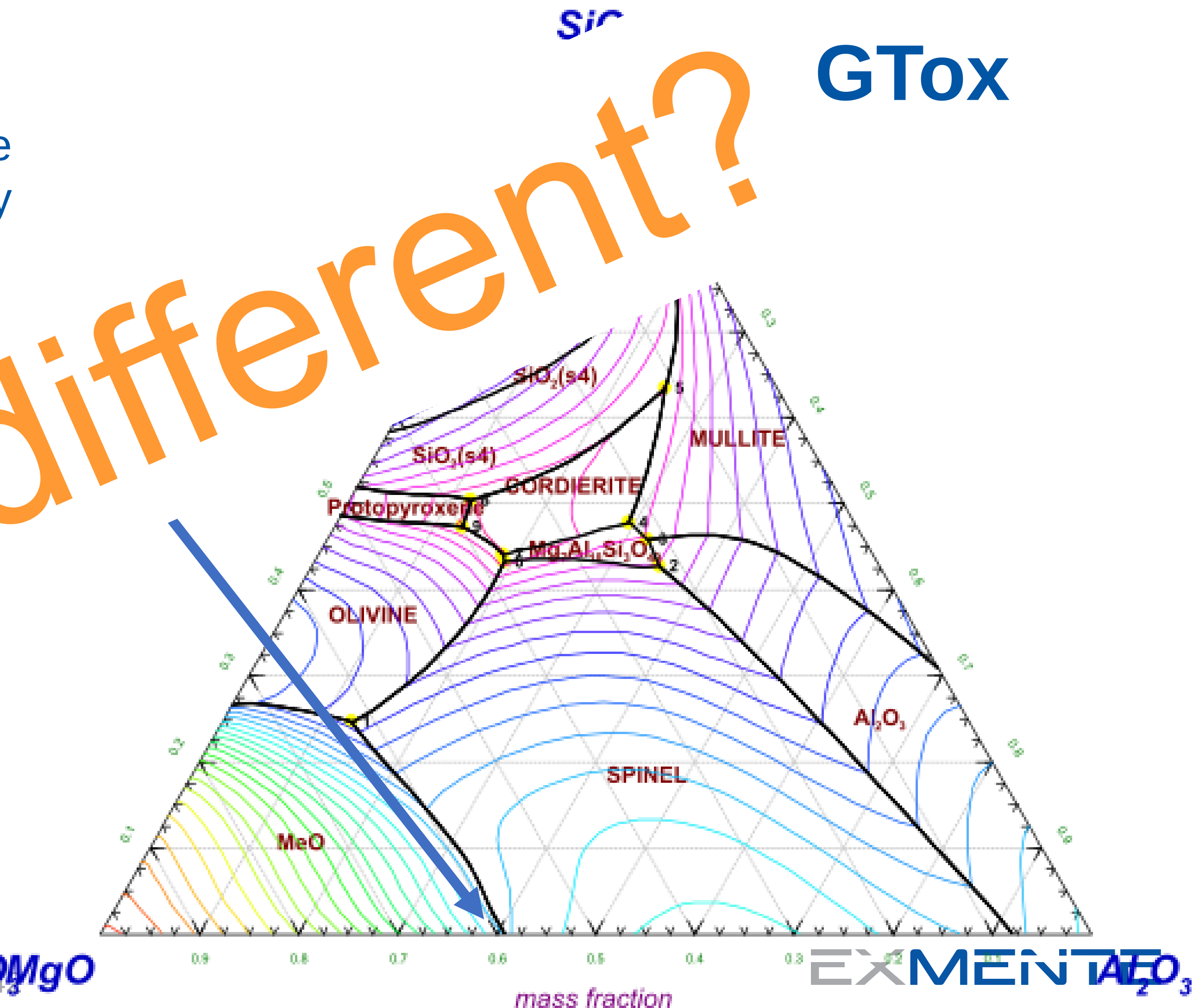


Monoxide Boundary

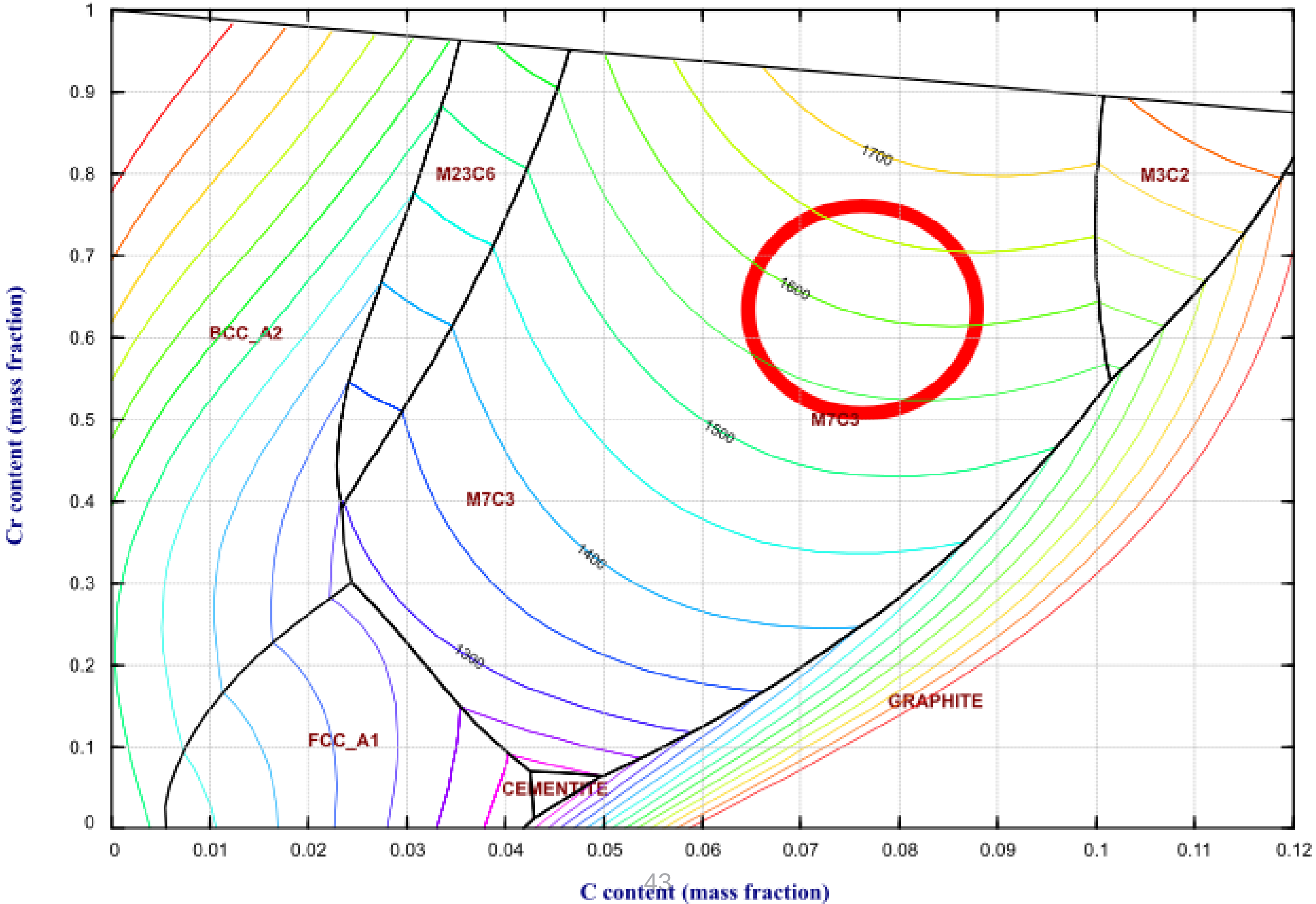
Why so different?

GTox



Case Studies
Chromite Smelting – Alloy Behaviour (T_{liq})

SGTE



Case Studies
Chromite Smelting – Process Conditions

Operating Temperature

1900 – 2000 °C

Alloy Tapping Temperatures

1800 – 1900 °C

Slag Tapping Temperature

1900 – 2000 °C

Case Studies
Chromite Smelting – Process Conditions

Operating Temperature

1900 – 2000 °C

How good is the data at these temperatures?

Slag Tapping Temperature

1900 – 2000 °C

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Case Studies

Chromite Smelting – Theoretical Energy Requirement

Initial estimates for plant design:

~ 5 000 kWh/t alloy*

Calculated with EMSIM, and FactSage data:

4 170 kWh/t alloy*

Difference of **roughly 20%**,
which is **significant for design**.

* Figures were adjusted to hide confidential information.

Uncertainty in Computational Thermochemistry

Uncertainty in Thermochemistry
Importance

We need to estimate and report uncertainty,

to apply calculation results with confidence in design and operation of large industrial furnaces.

Uncertainty in Thermochemistry
Can we estimate it?

It appears so

A number of presentations addressed this at CALPHAD 2019 in Singapore

Tools are starting to appear

Uncertainty in Thermochemistry

Our Tools – FactSage and ChemApp

Pure substances

Warns when outside valid temperature range

No uncertainty information

Solutions

No warnings regarding valid ranges

No uncertainty information

This results in uncertainty and risk.

Conclusions

Conclusions

The importance of computational thermochemistry
will only increase in future.

We need to consider incorporating uncertainty
as an integral part of
experimental work, assessment, and application.

We can support the design and operation
of efficient, environmentally responsible operations.

Thank you