Phase Relations in Stainless Steel Slags

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Promoters: Bart Blanpain and Patrick Wollants
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- Our mission:

  "InsPyro improves metallurgical processes by research-based industrial projects

  and develops new sustainable high-temperature processes in cooperation with its customers"

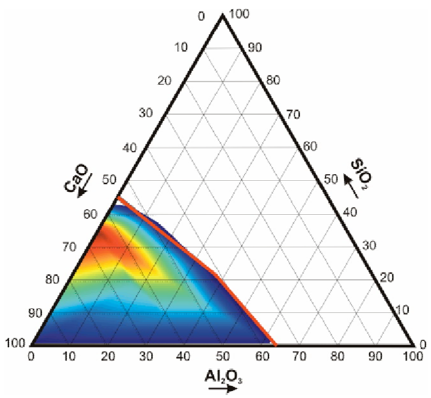
Tools

High temperature experimentation

Tube furnaces
Induction furnace
CSLM
DSC
...

Materials characterization

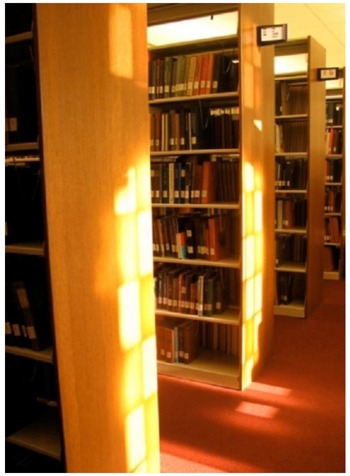
SEM
EPMA
XRD
ICP
...



Thermodynamic Modelling

Liquidus
Solidification
Reactions
Equilibrium

FactSage™



Scientific Literature

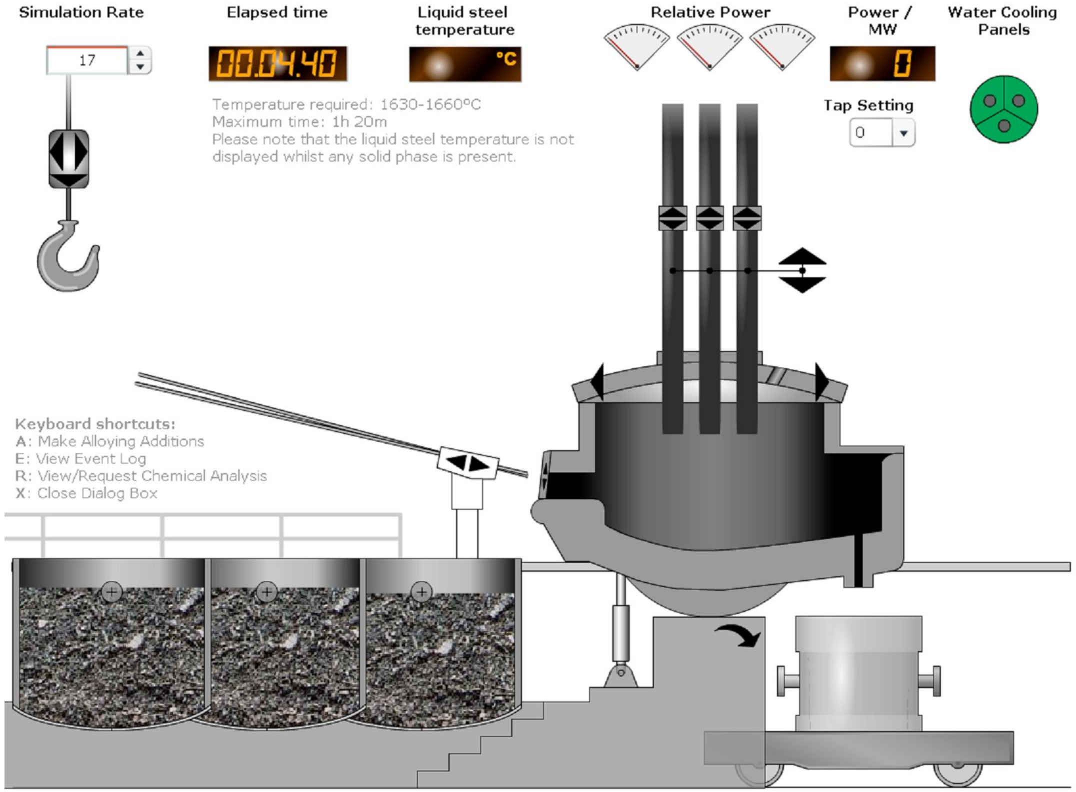
Journals
Proceeding
Reports
...

Overview

- Background
- Experimental method
- Results on the multicomponent system $CaO\text{-}CrO_x\text{-}MgO\text{-}SiO_2 + Al_2O_3$
- Results + optimisation on the ternary system $CrO_x\text{-}MgO\text{-}SiO_2$
- Back to the multicomponent system
- Conclusions

Background

- Recycling stainless steel

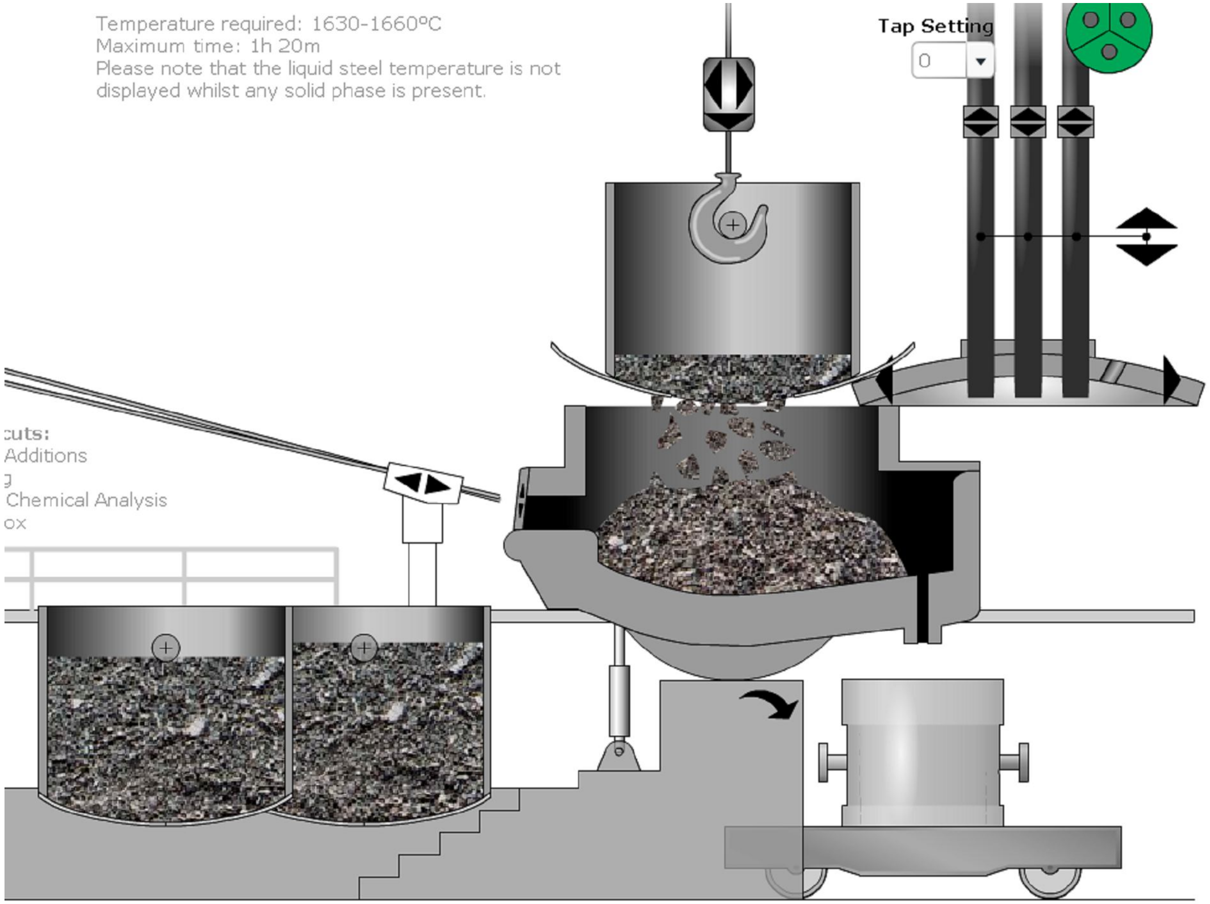


Try to recycle carbon steel yourself on www.steeluniversity.org

steeluniversity.org

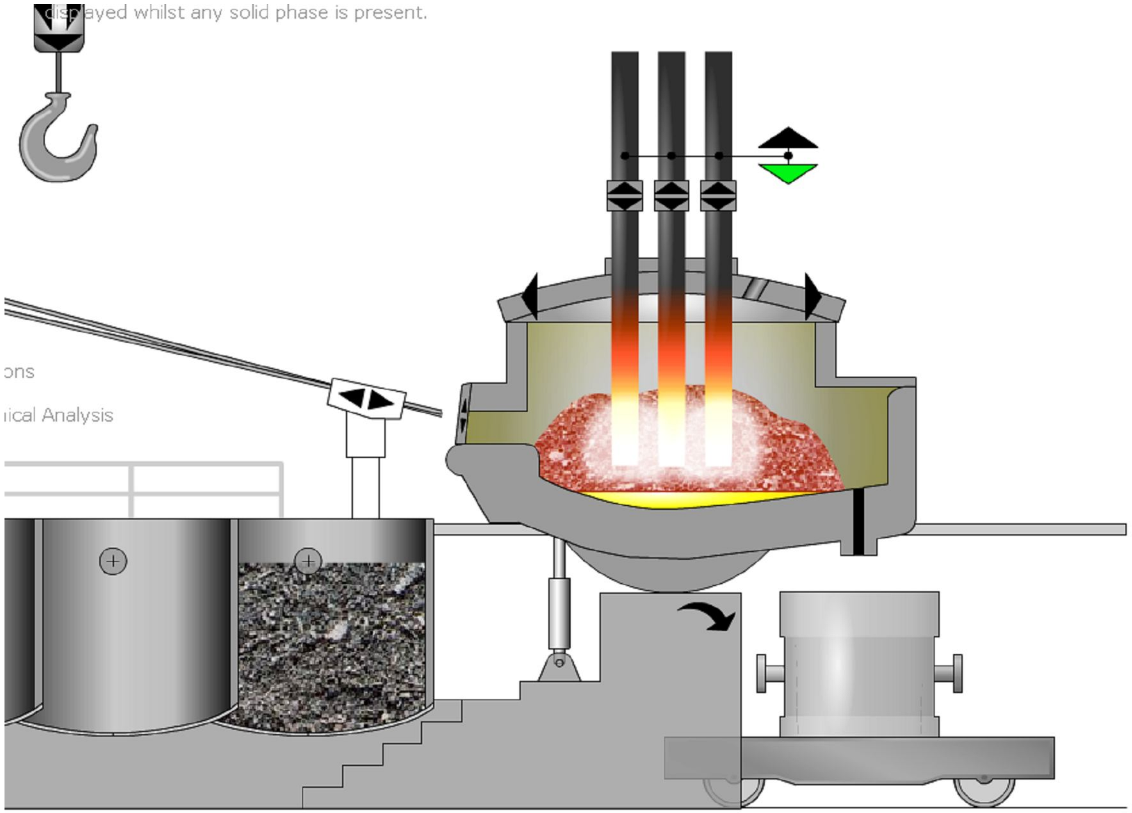
Background

- Scrap is the main raw material



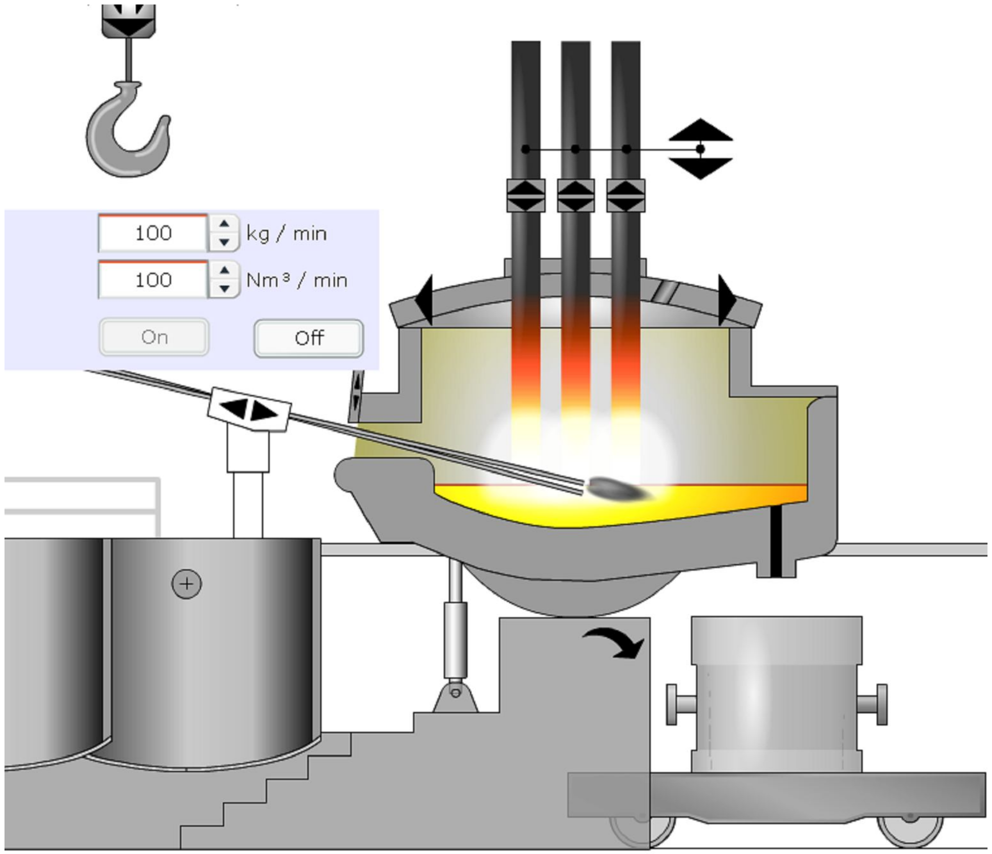
Background

- Electrical energy melts the feed materials



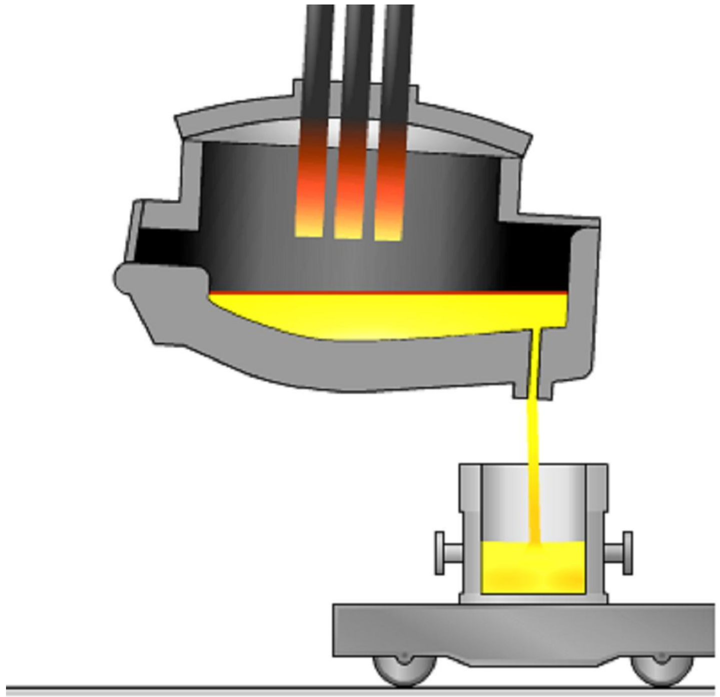
Background

- Liquid steel and slag are formed



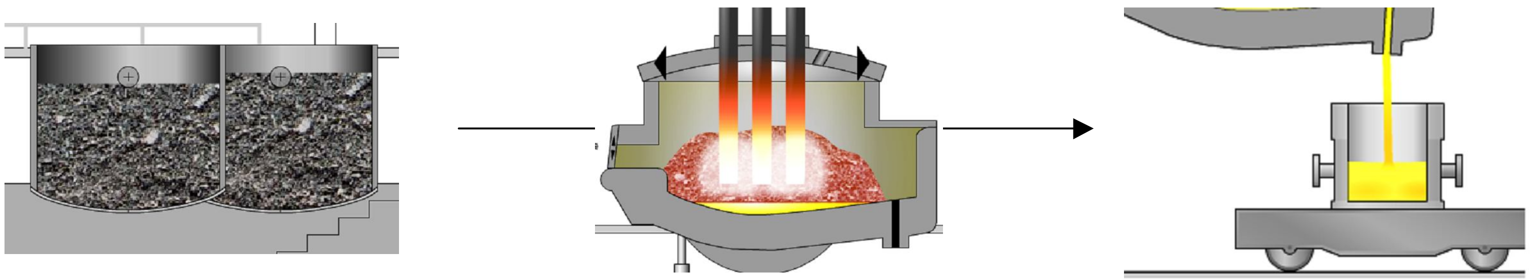
Background

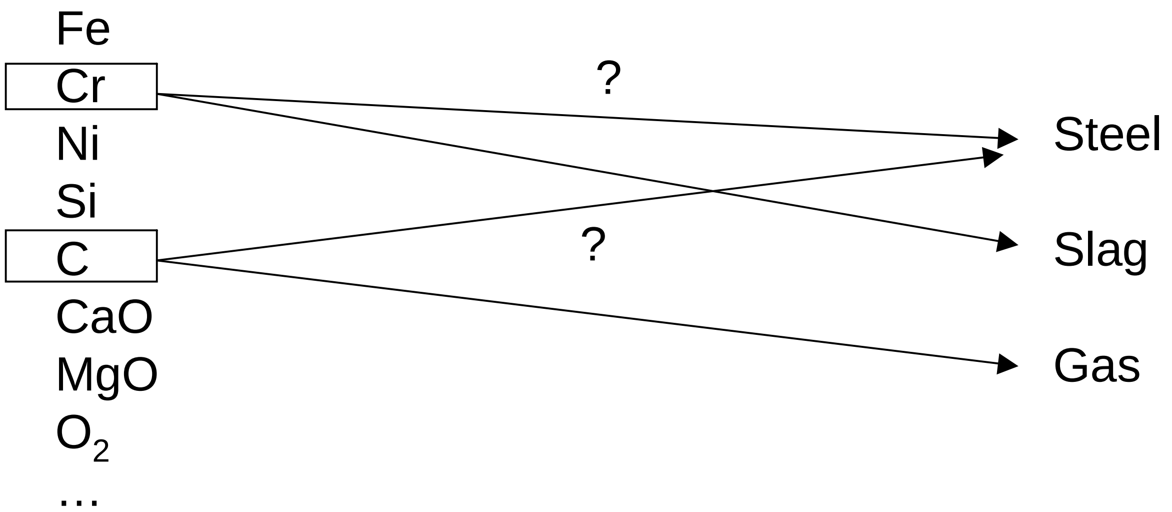
- The molten material is tapped



Thermodynamic questions

- Where does everything end up?

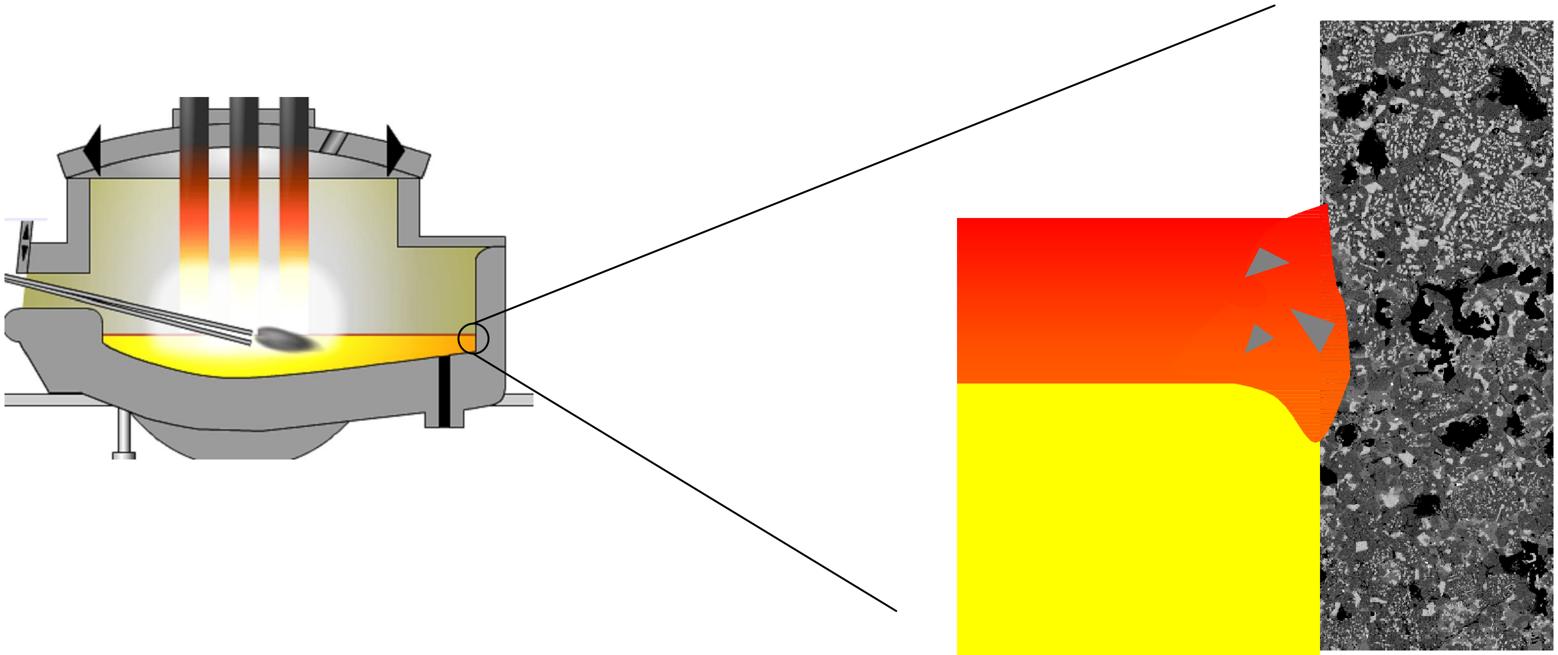




More information on the thermodynamics of the EAF process: S. Arnout et al., Steel Res Int

Thermodynamic questions

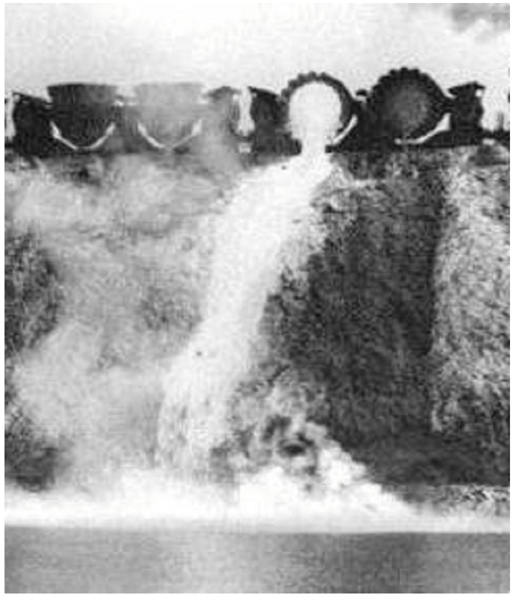
- What happens to the refractory?

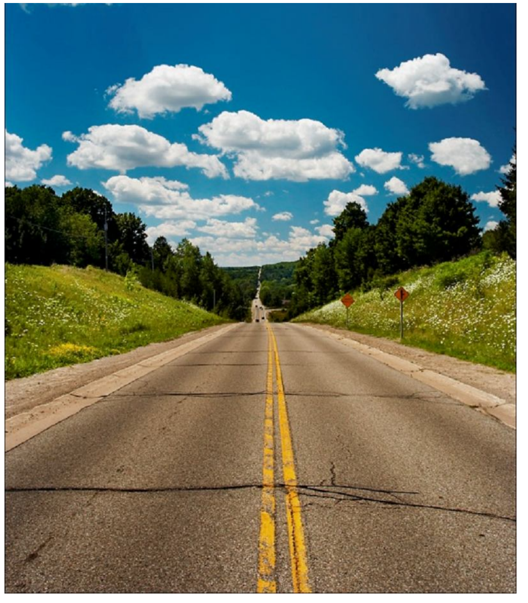


More information on the refractory degradation in stainless steel: P.T. Jones et al., J Eur Ceram Soc

Thermodynamic questions

- What will become of the slag when it is cooled?
  ? waste or useful side product?





Thermodynamic questions

- What will become of the slag when it is cooled?
  - ? Depends on the macroscopic properties
  - ? Properties depend on microstructure
    - C_2S phase: destructive transformation leads to powder slag
    - Spinel phase: is believed to bind Cr well, less leaching
    - CS phase: has some solubility for Cr, as opposed to C_2AS
    - [Glass phase: not so strong…]
  - ? Microstructure depends mostly on composition
- Link composition – stable phases/microstructure

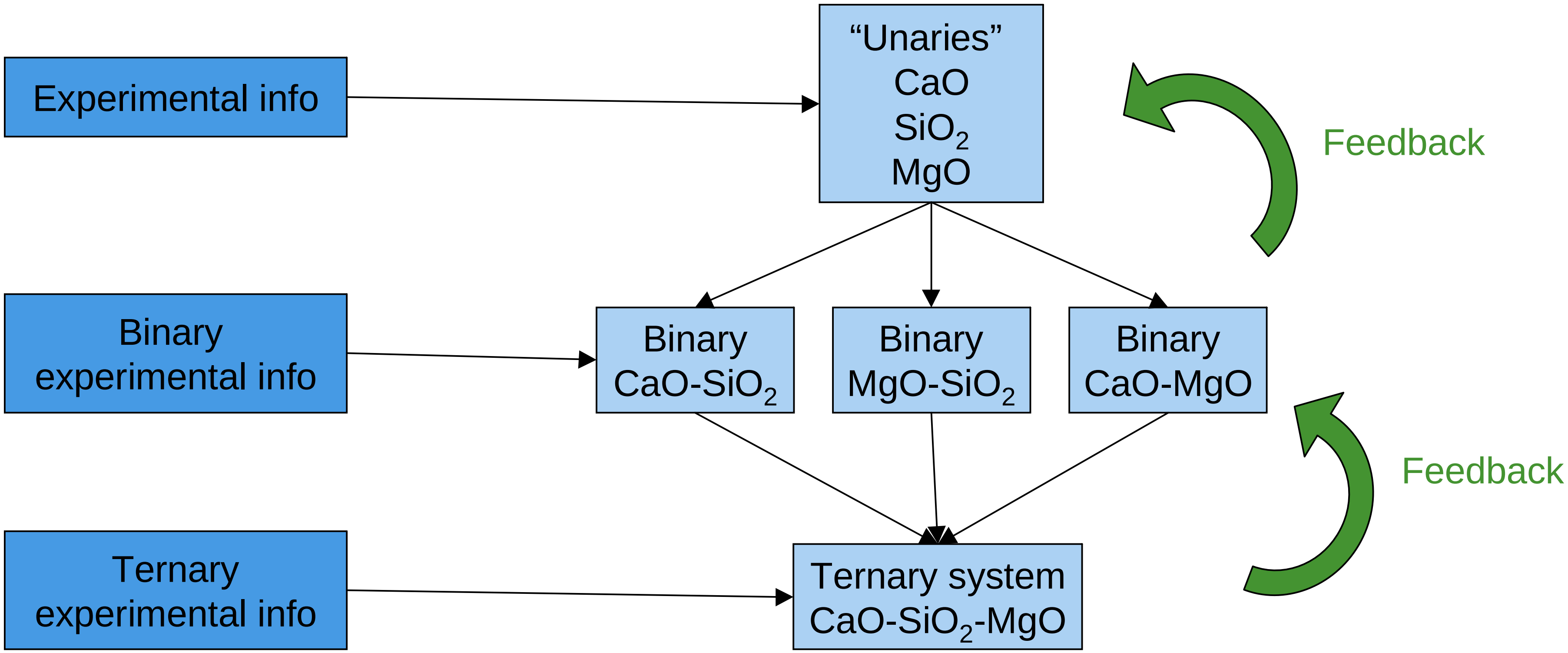
  = Thermodynamics

**More info on process-properties-microstructure for slag: D. Durinck et al., J Am Ceram Soc*

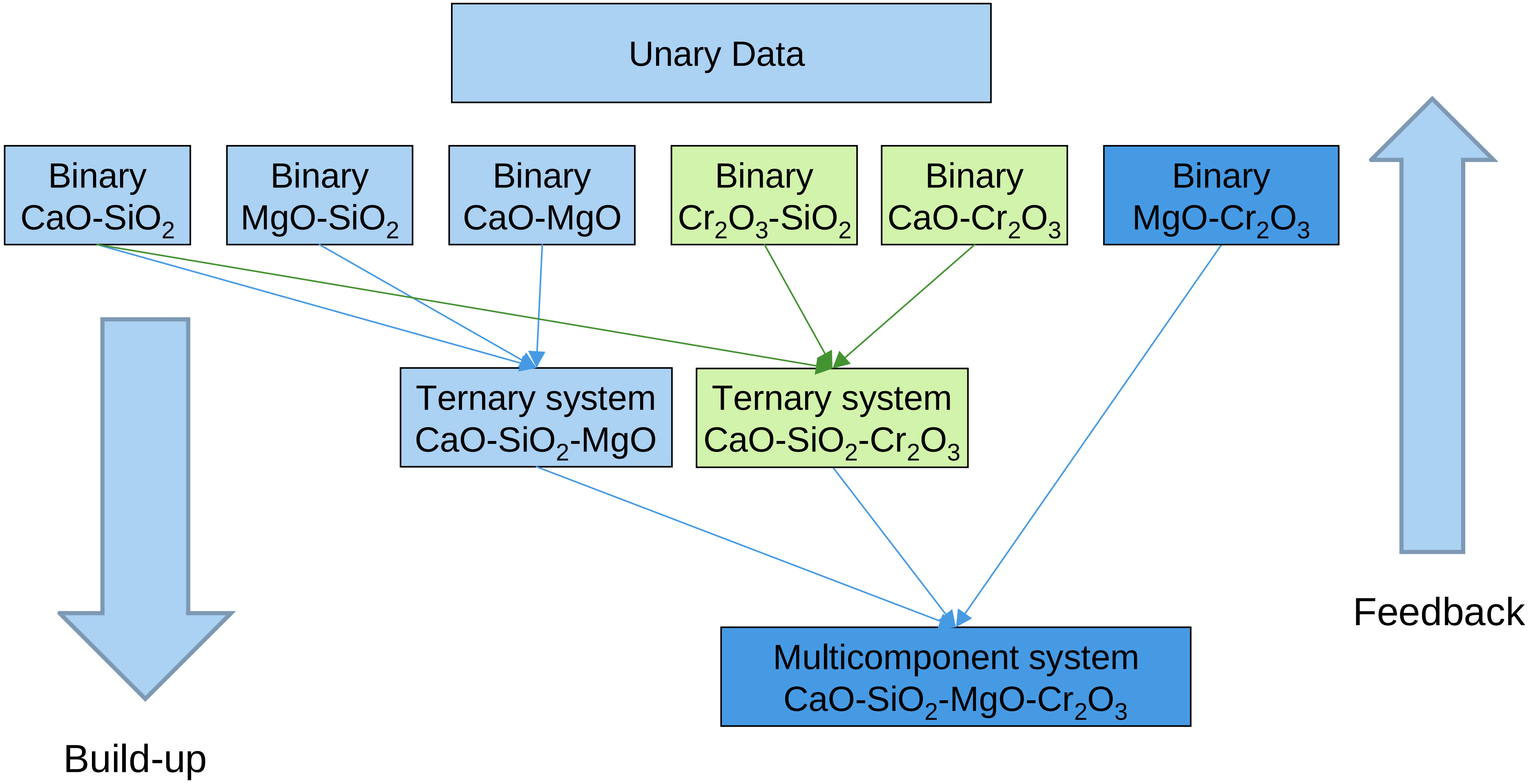
Goal of this thesis

- Improve the description of stainless steel slags
- 5 component system
  - CaO
  - SiO_2
  - MgO
  - CrO_x (CrO and Cr_2O_3)
  - Al_2O_3
- Experimental liquidus determination
- Comparison with FactSage
- Evaluation and improvement of the database

Database construction (Calphad)



Database construction (Calphad)



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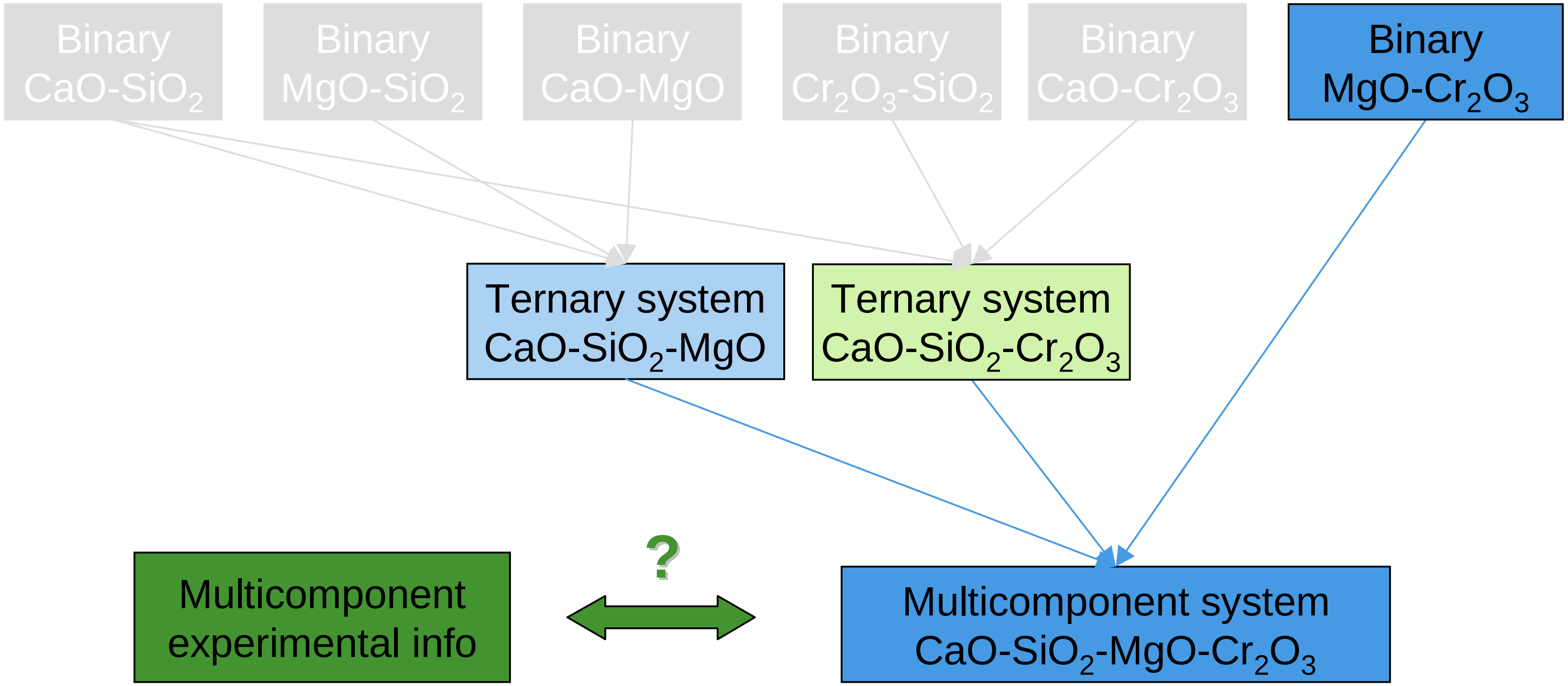
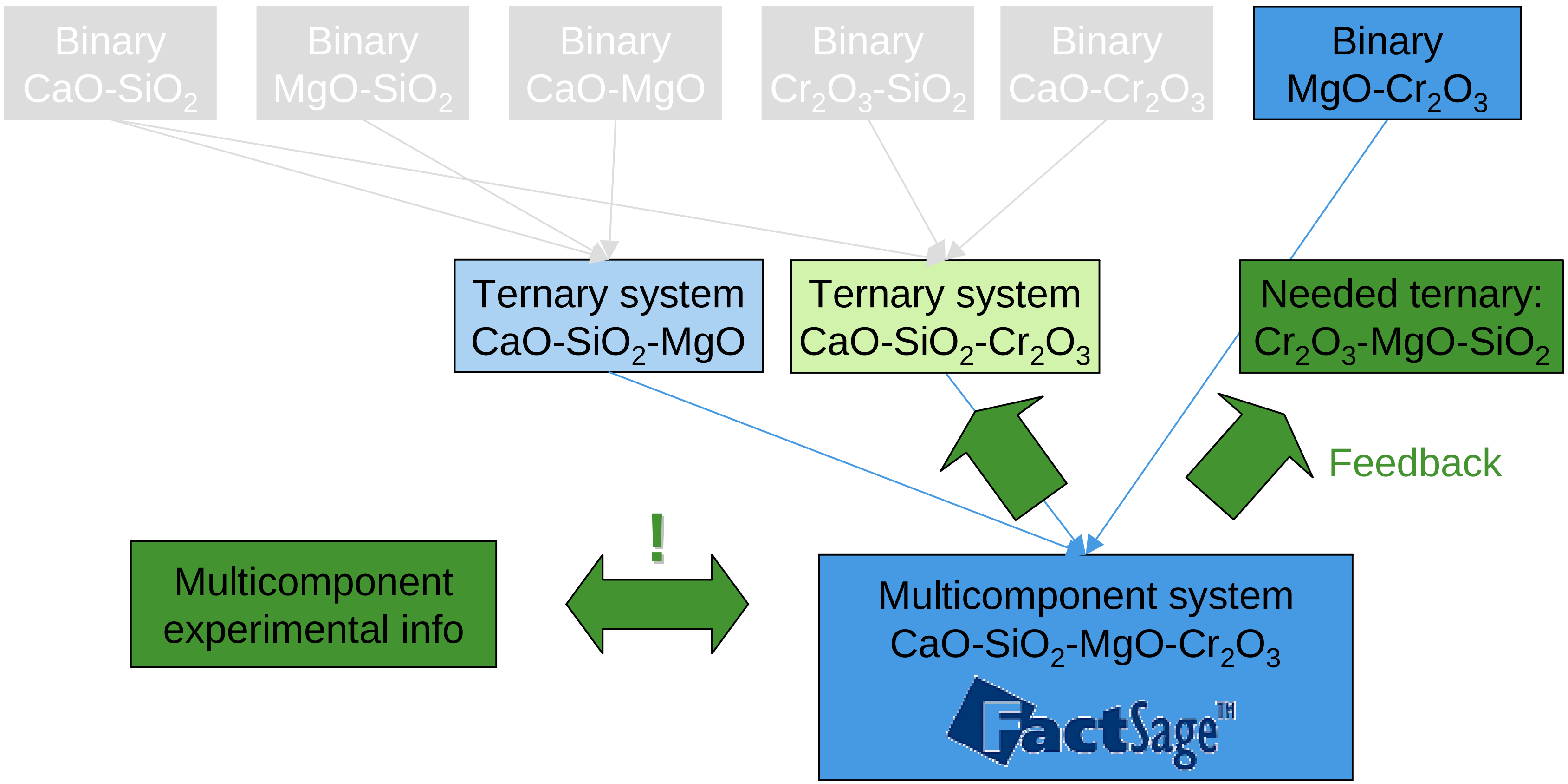


Strategy of this work



Experimental method

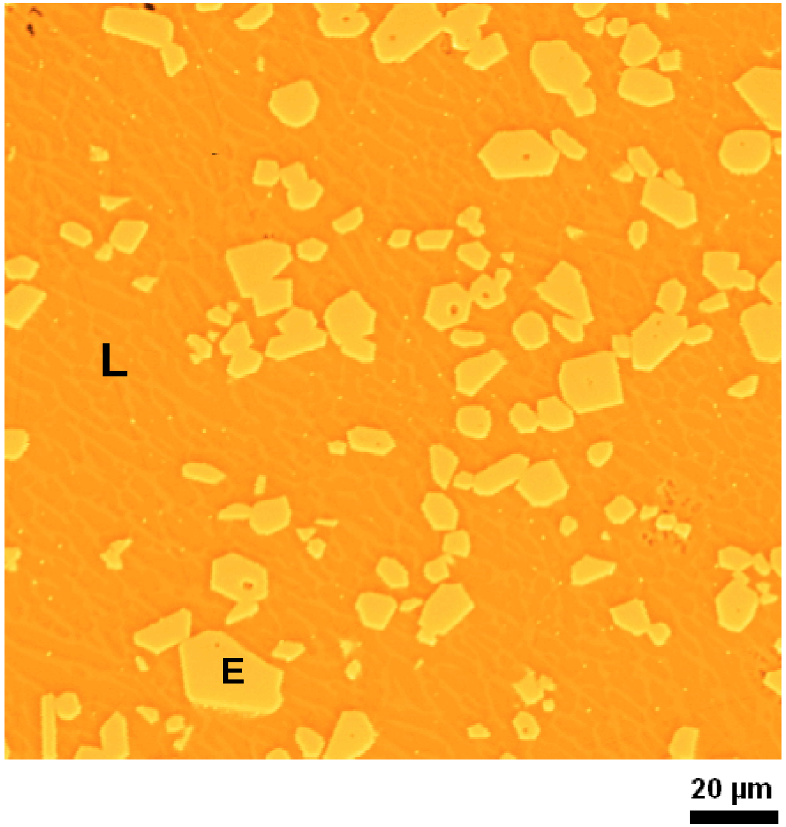
- Mixing powders from pure oxides
- Equilibration in tube furnace
  - Mo crucibles (reuseable)
  - Control p_{O2} by CO/CO_2 mass flow ($CO + ½ O_2 = CO_2$)
- Sampling
  - Gas tight sampling with Al_2O_3 bars
- EPMA-WDS with standards

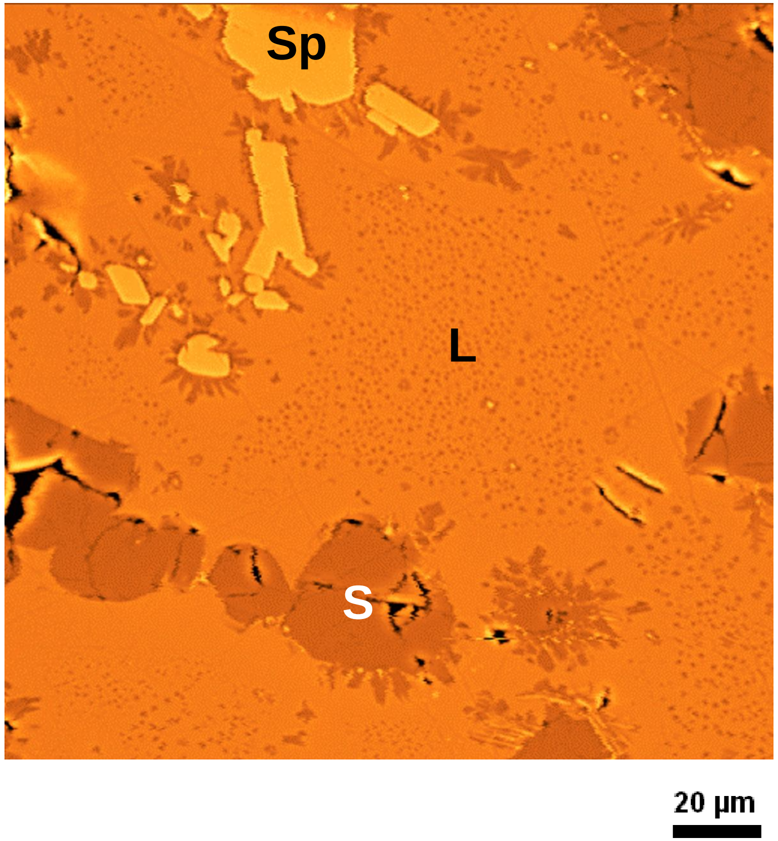
Observed phases

- L = liquid
- E = eskolaite (Cr_2O_3 with Al_2O_3 solubility)
- Sp = spinel ($MgO.Cr_2O_3$ with Al_2O_3 solubility)
- P = periclase (MgO with $CrO_{1.5}$ solubility)
- S = SiO_2
- C_2S = $2CaO.SiO_2$
- M_2S = $2MgO.SiO_2$ (with CrO solubility)
- MS = $MgO.SiO_2$ (with CrO solubility)

Resulting microstructures

- Sedimentation makes amount of precipitates vary strongly
- Cooling effects: precipitation in matrix, growth of solids





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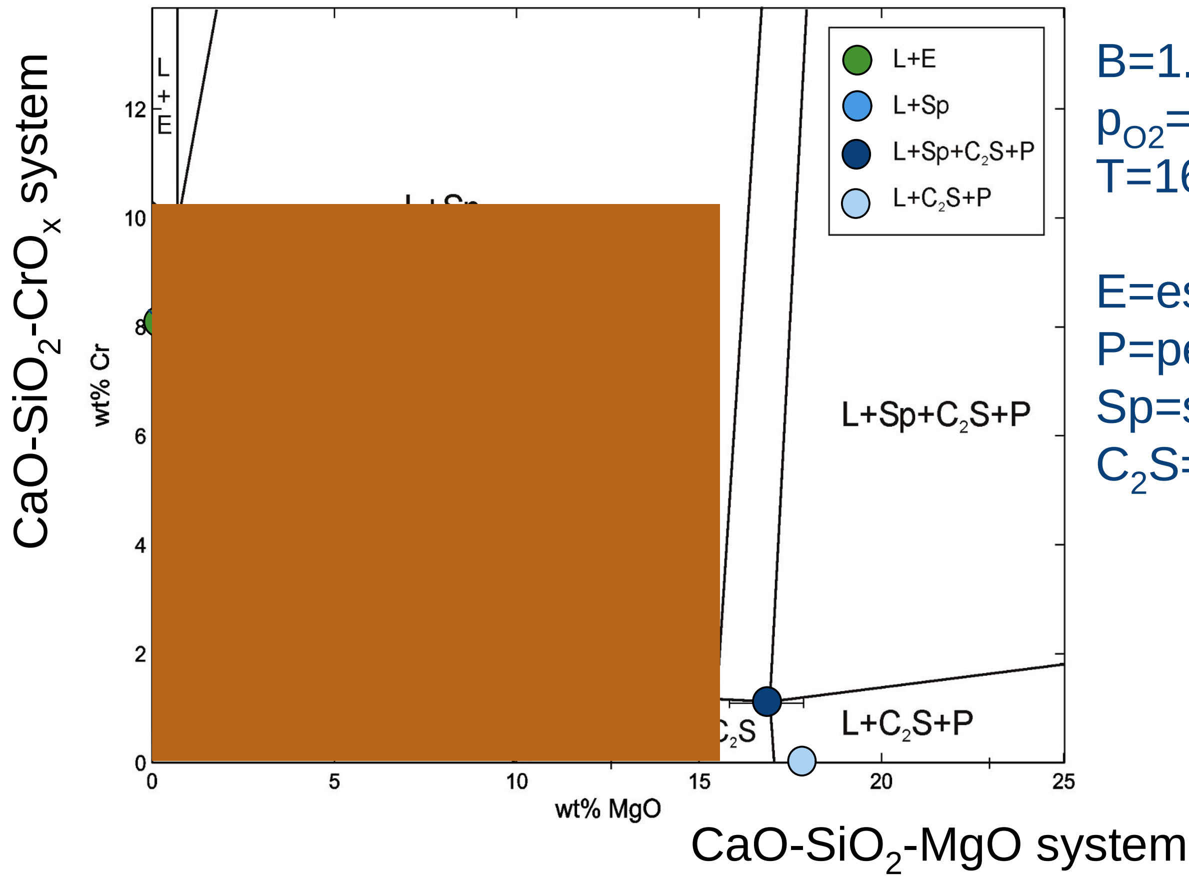
Results: $B=CaO/SiO_2=1.2$



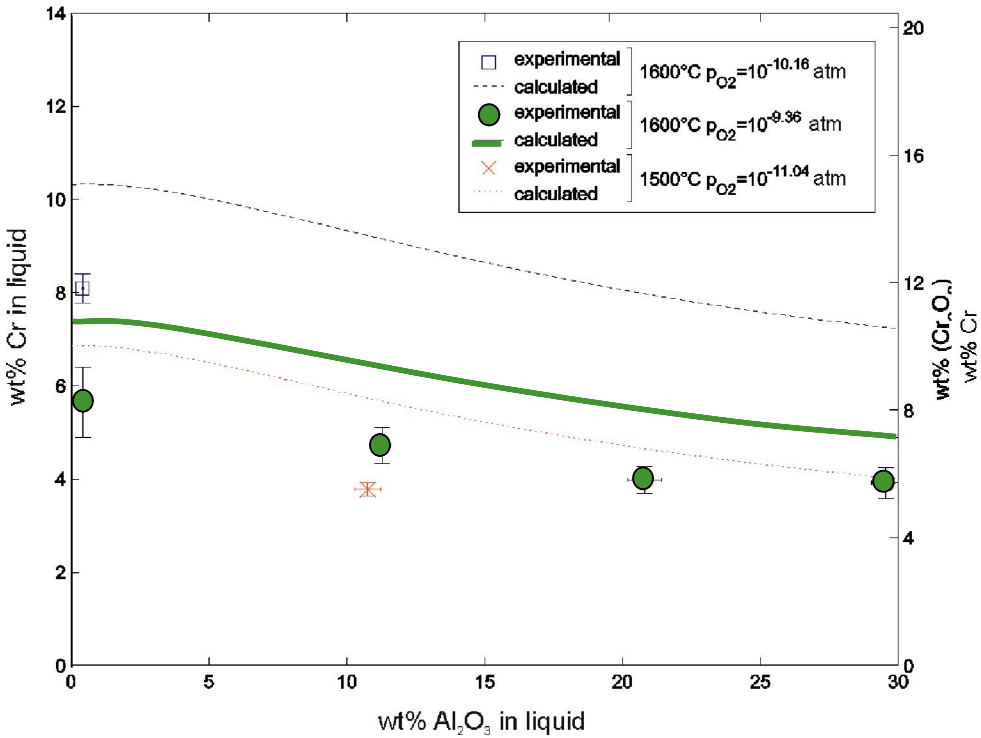
$B=1.2$
$p_{O2}=10^{-10.16}$
$T=1600°C$

E=eskolaite Cr_2O_3
P=periclase MgO
Sp=spinel $MgO.Cr_2O_3$
$C_2S=2CaO.SiO_2$

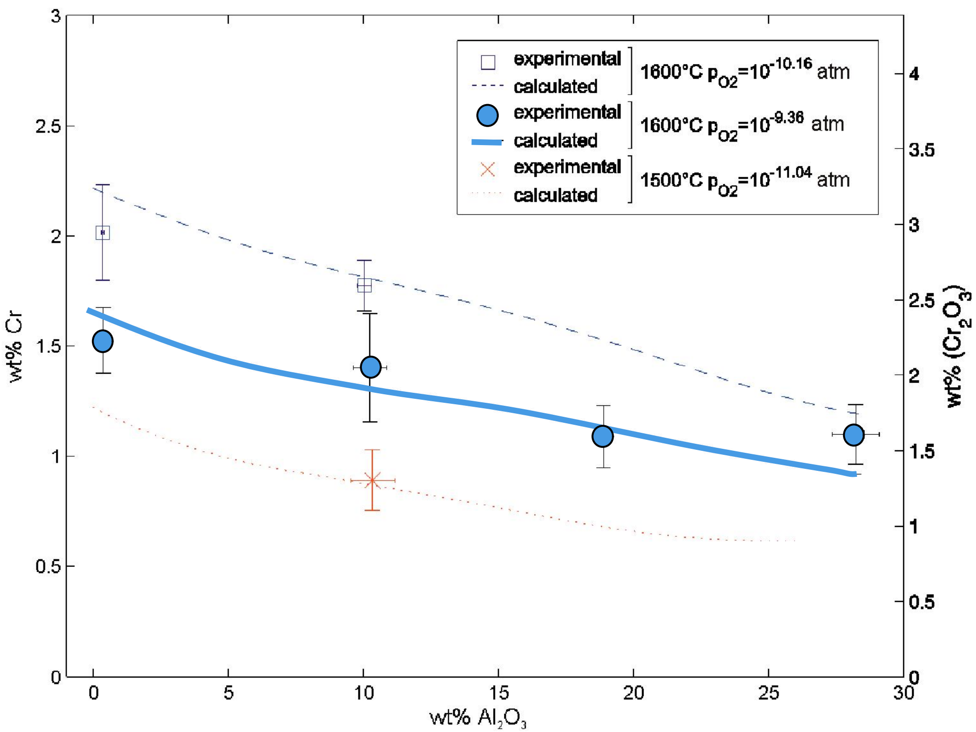
- Similar results at different p_{O2}, T, and Al_2O_3 level

Addition of Al_2O_3: Liquidus

- Eskolaite liquidus

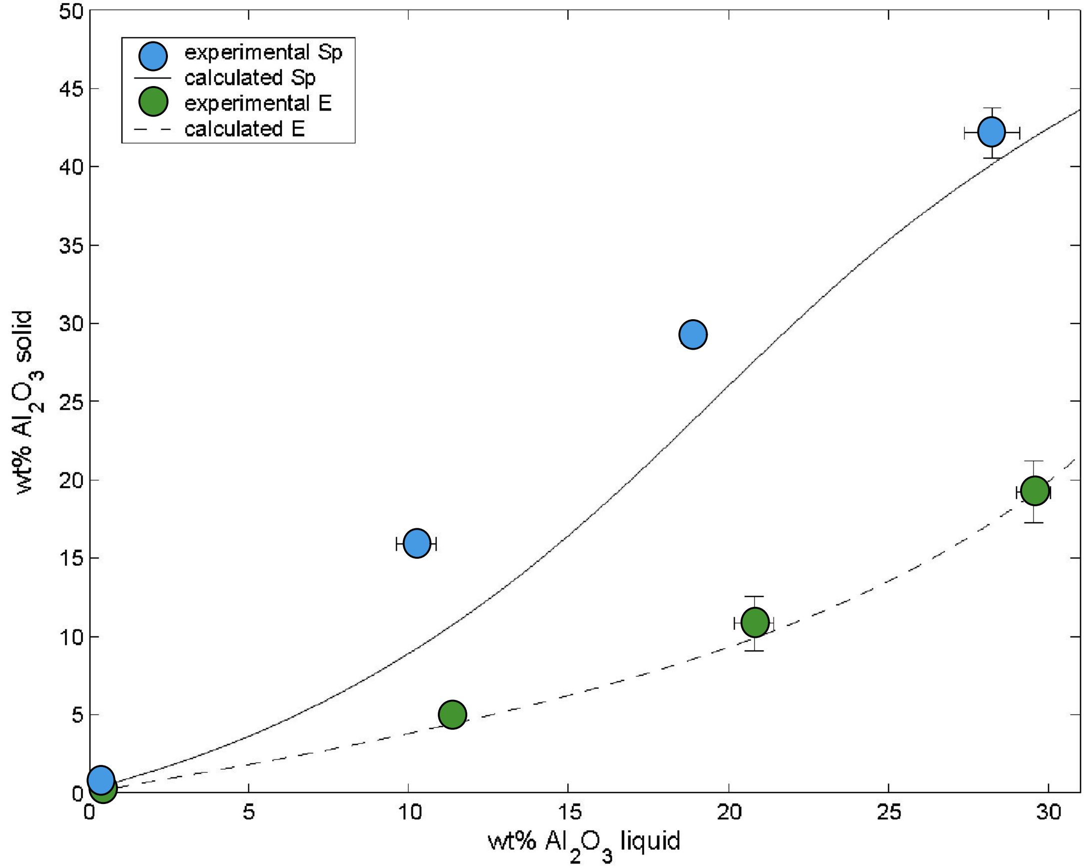


- Spinel liquidus



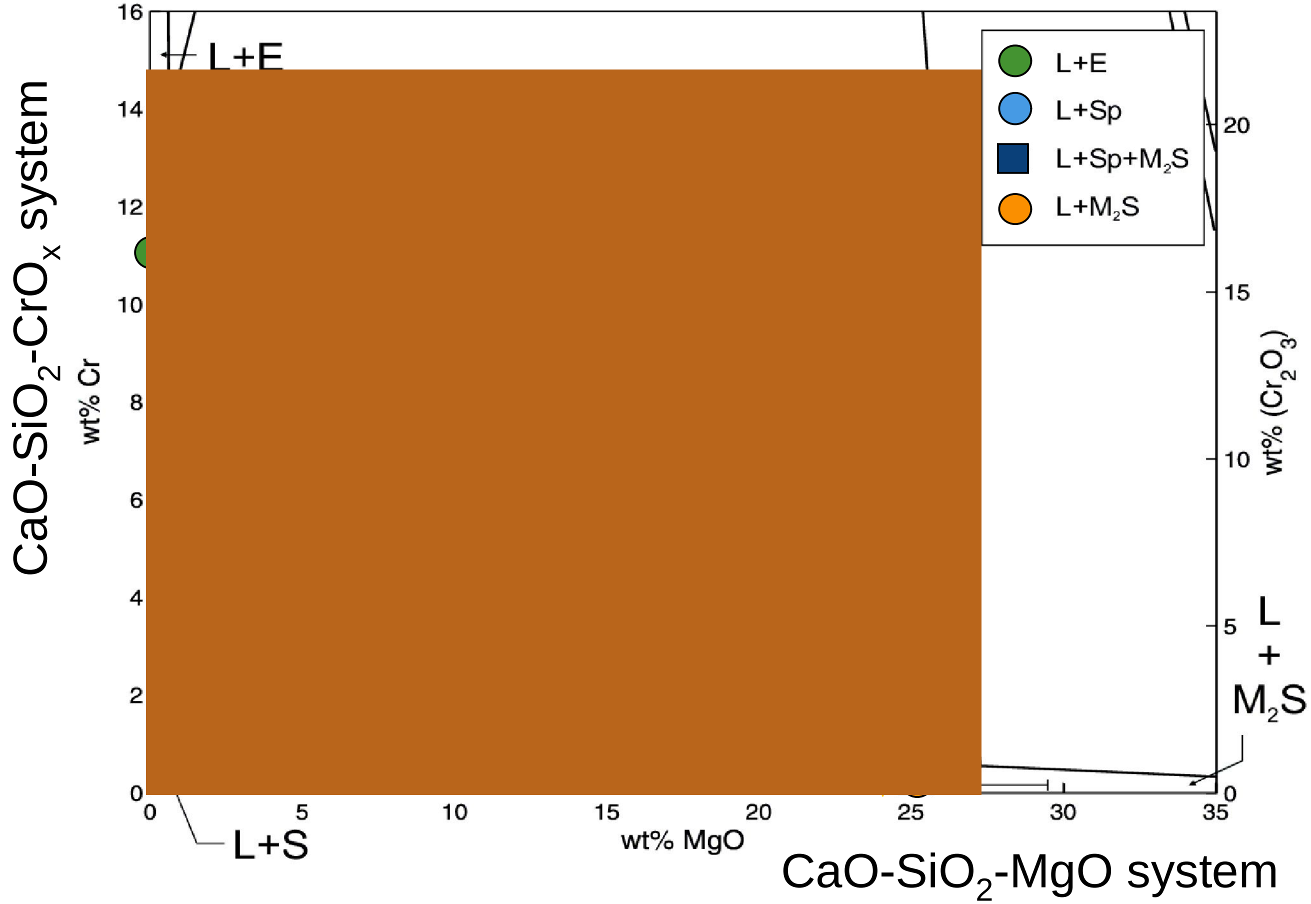
Addition of Al_2O_3: Solidus

- Alumina content in spinel and eskolaite



B=1.2
$p_{O2}=10^{-9.36}$
T=1600°C

Results: B=CaO/SiO$_2$=0.5



B=0.5
$p_{O2}=10^{-11.04}$
T=1500°C

- Similar results at different T

Origin of differences

- On Y-axis: $CaO-CrO_x-SiO_2$ system
- Centrally at low basicity:
  - Only at high SiO_2 content
  - When both MgO and CrO_x present
  - $CrO_x-MgO-SiO_2$ system!
- Experiments + new model for $CrO_x-MgO-SiO_2$

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CrO_x-MgO-SiO_2 system

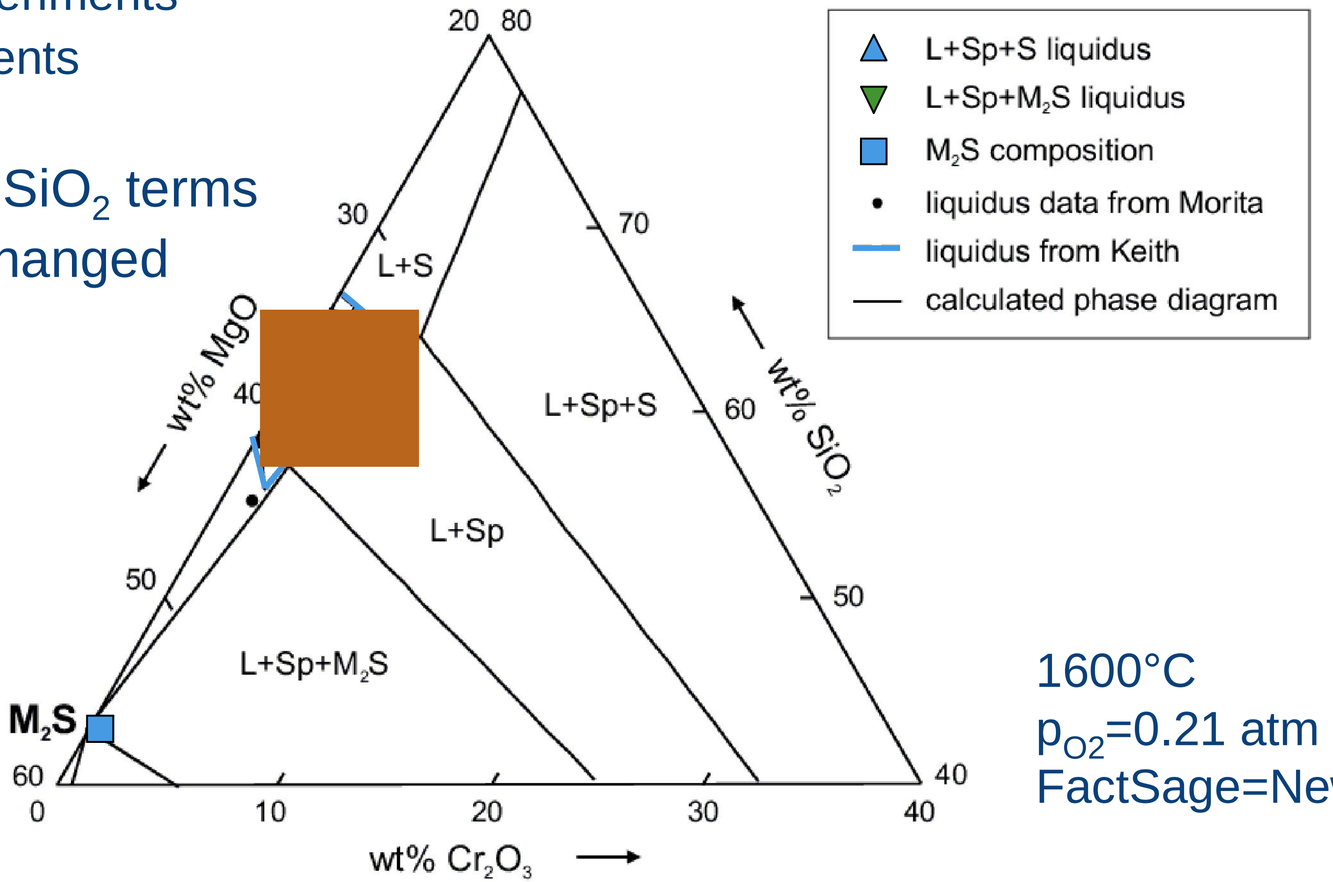
- Different p_{O2}, at T=1600°C:

- Air p_{O2} = 0.21 atm (all Cr = Cr^{3+})
- CO/CO_2=25 p_{O2} = $10^{-9.56}$ atm
- CO/CO_2=50 p_{O2} = $10^{-10.16}$ atm
- Metallic Cr p_{O2} ~ 10^{-13} atm (all Cr = Cr^{2+})

- Solubility of Cr^{3+} in liquid very limited (stable solids)
- Solubility of Cr^{2+} in liquid extensive

CrO_x-MgO-SiO_2 system in air

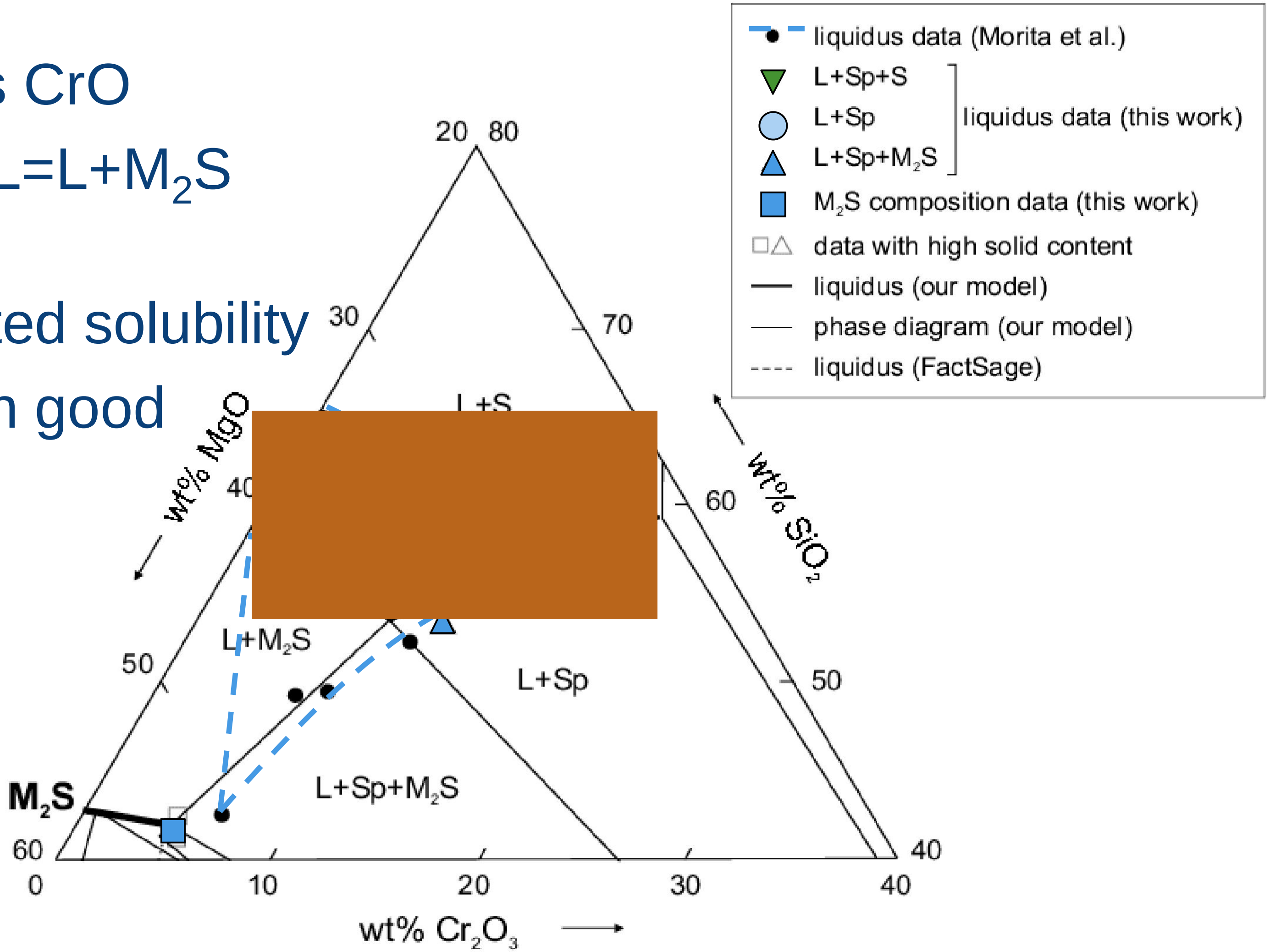
- Good agreement
  - literature experiments
  - new experiments
  - model
- No Cr_2O_3-MgO-SiO_2 terms
- FactSage not changed



1600°C
p_{O2}=0.21 atm
FactSage=New

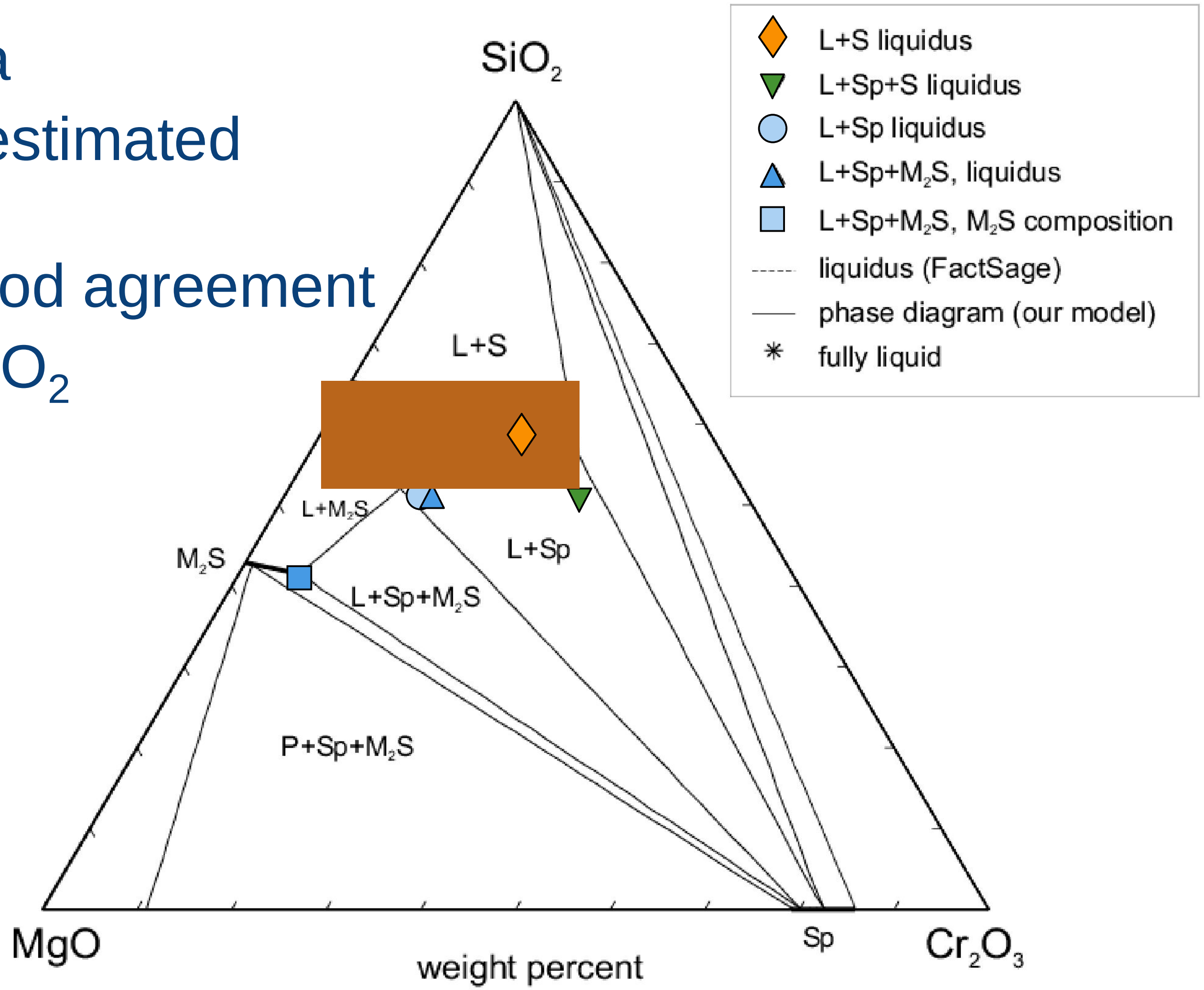
CrO_x-MgO-SiO_2 system at $10^{-9.56}$ atm O_2

- M_2S contains CrO
- Morita data: $L=L+M_2S$
- FactSage underestimated solubility
- New model in good agreement



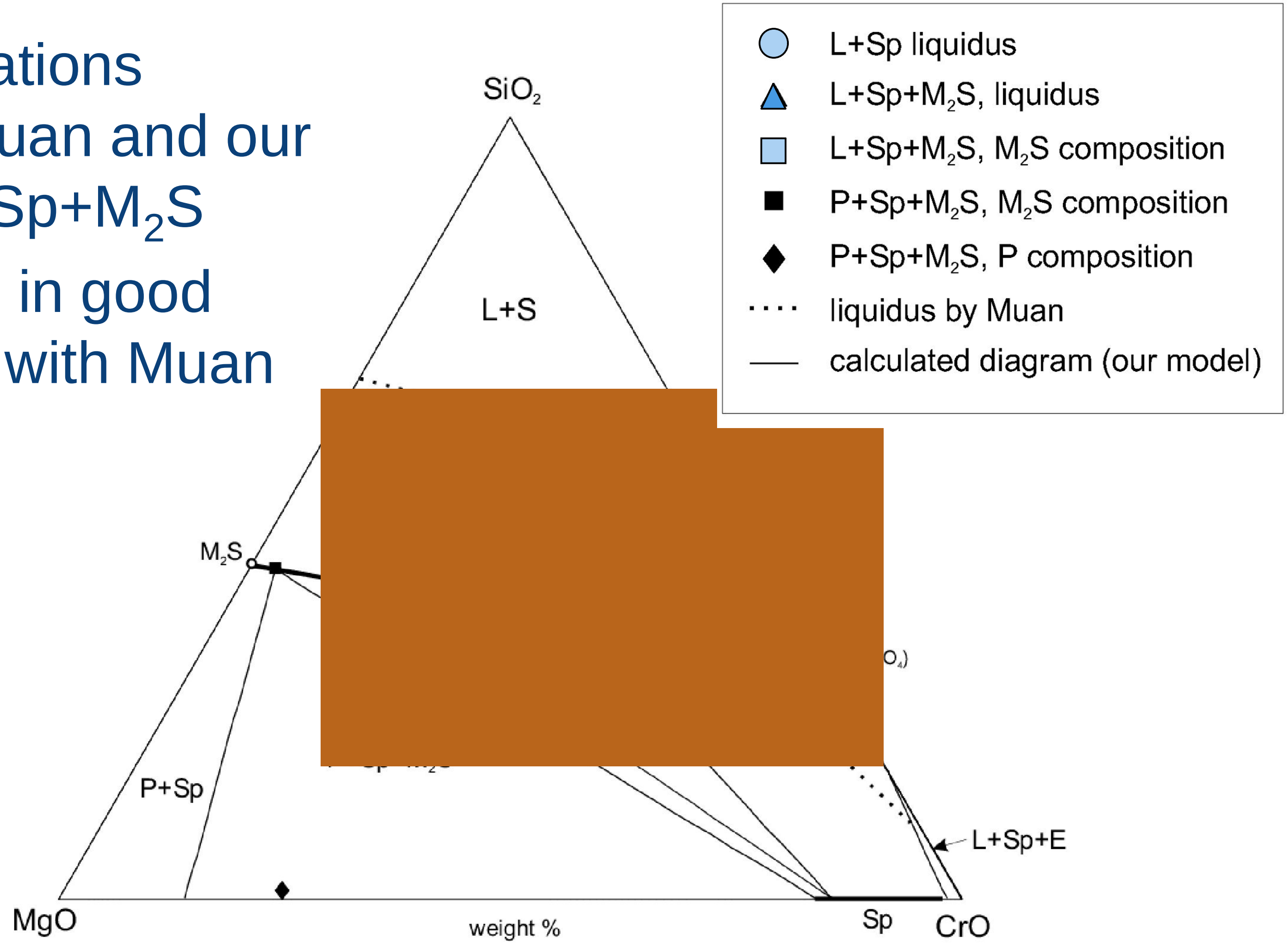
CrO_x-MgO-SiO_2 system at $10^{-10.16}$ atm O_2

- No literature data
- FactSage underestimated solubility
- New model in good agreement
- L+Sp+S point: SiO_2 precipitation

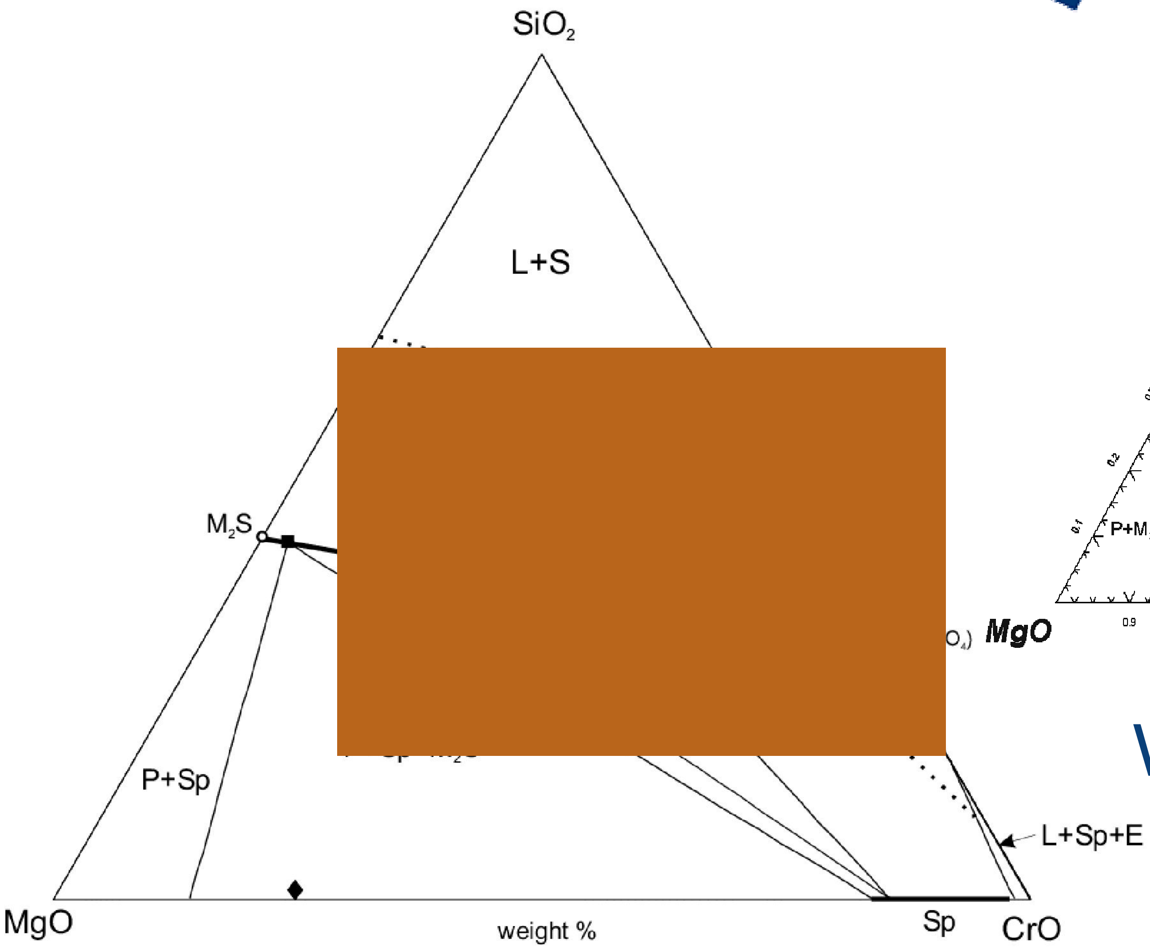


CrO_x-MgO-SiO_2 system with Cr metal

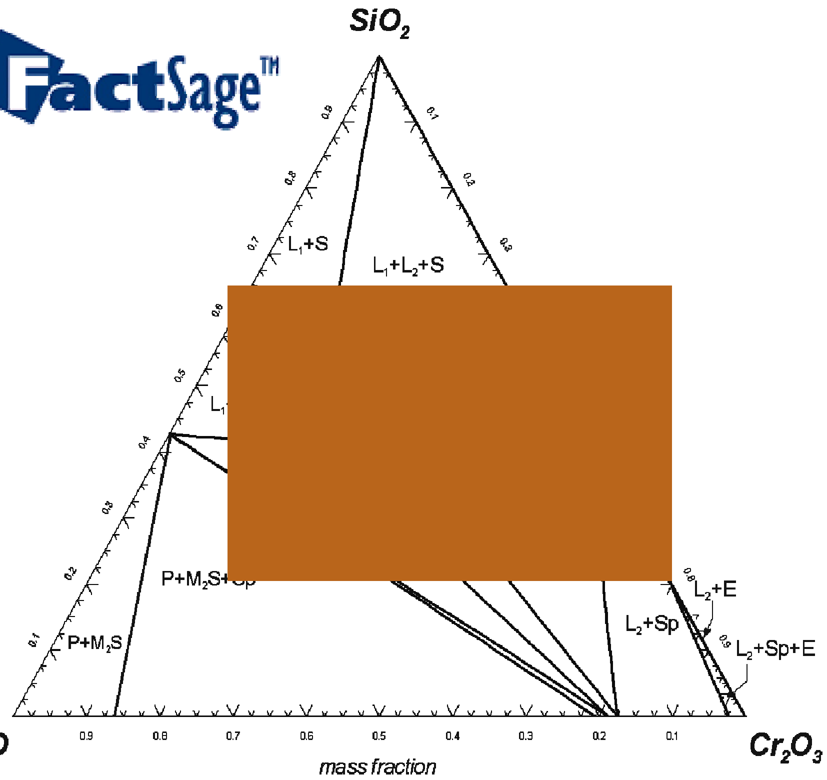
- Some deviations between Muan and our data on L+Sp+M_2S
- New model in good agreement with Muan



CrO_x-MgO-SiO_2 system with Cr metal



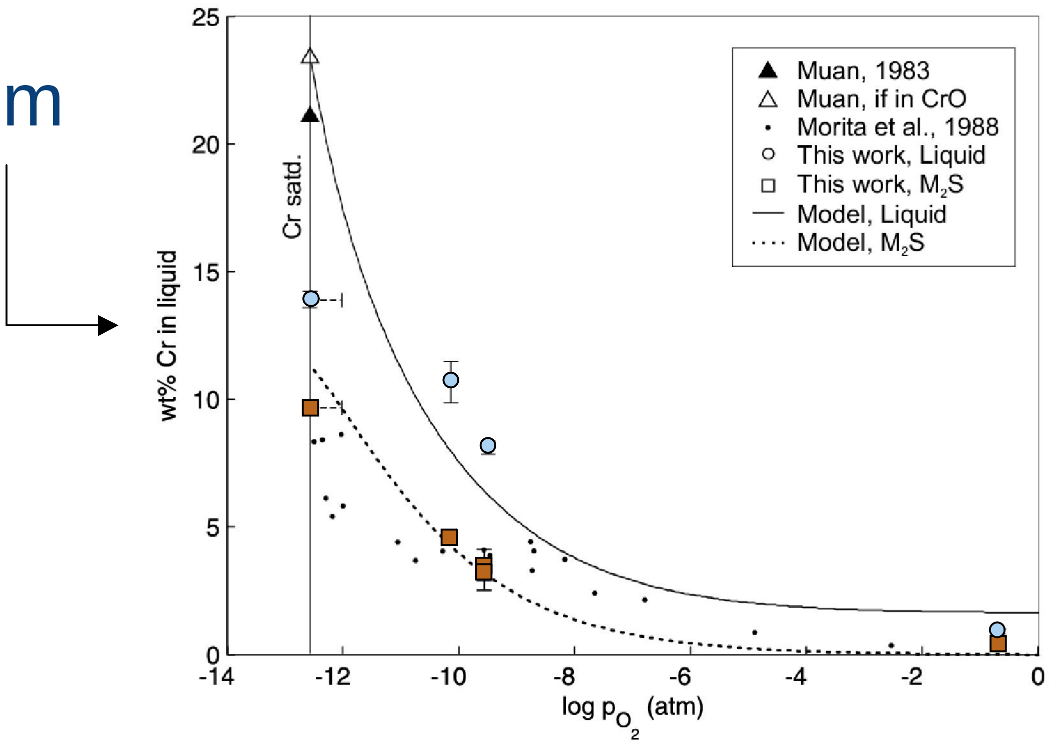
FactSage™



Wrong miscibility gap!

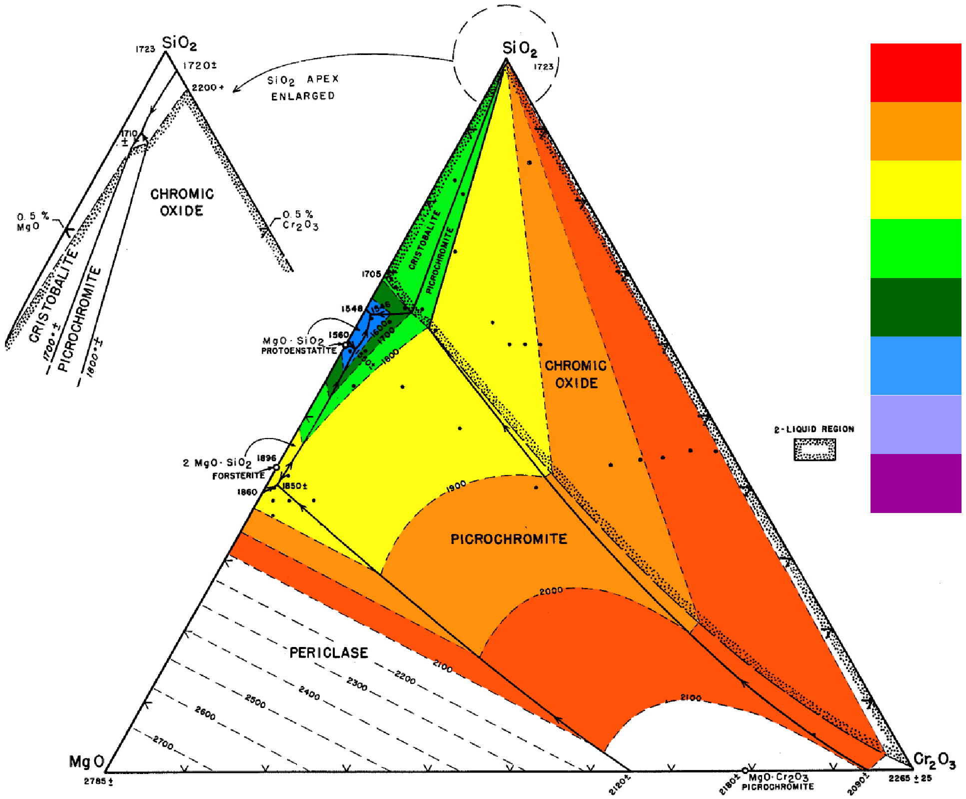
Challenges in optimisation

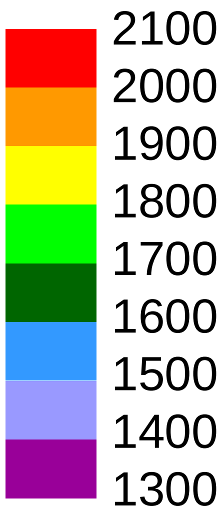
- SiO_2 liquidus location
- Spinel liquidus slope
- $L+Sp+M_2S$ equilibrium

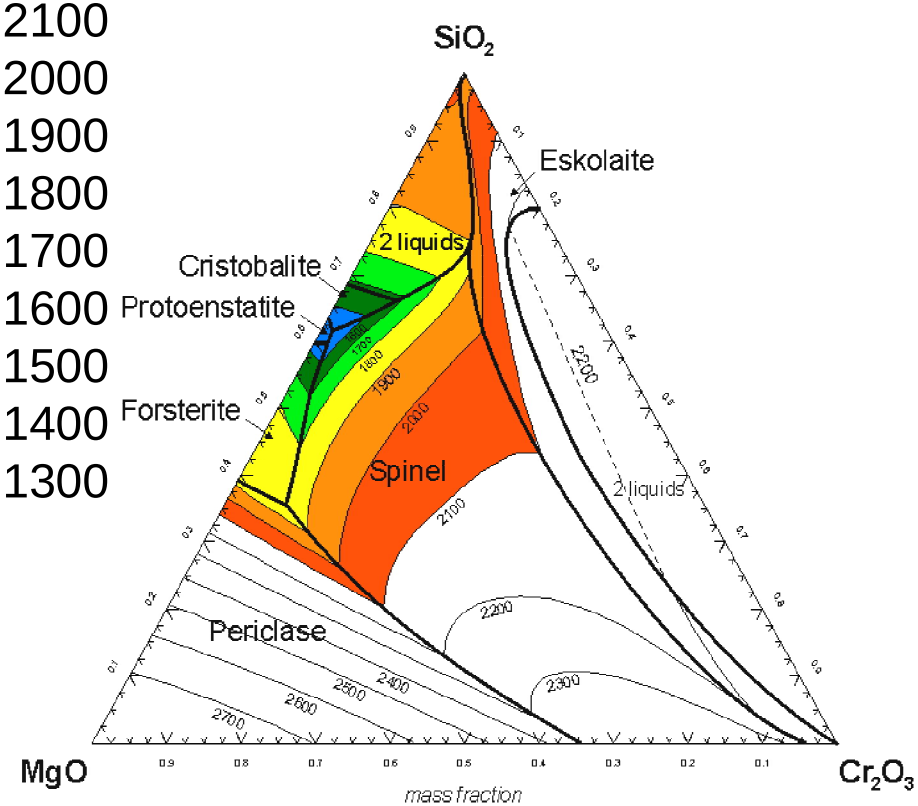


Liquidus projection

- In air:
  - experimental data < 1850°C

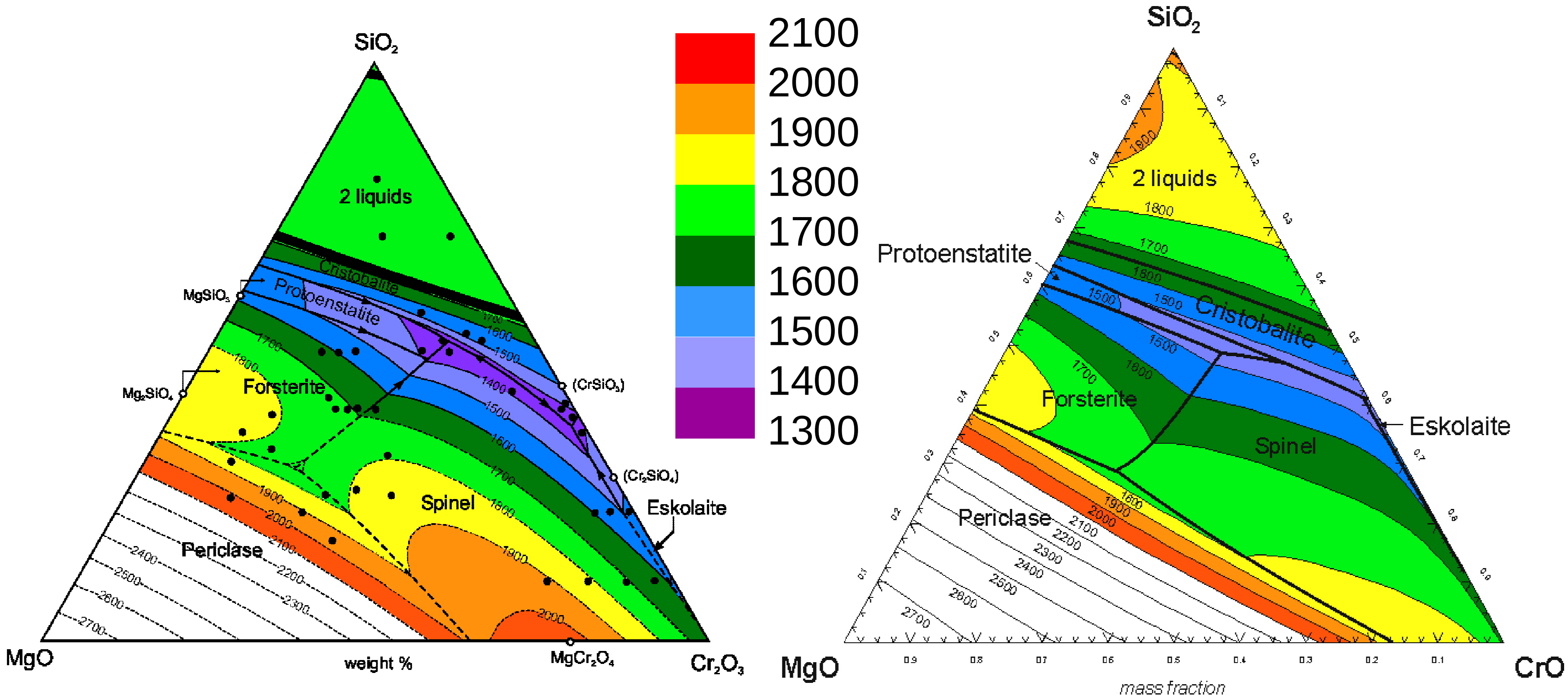






Liquidus projection

- With metallic Cr



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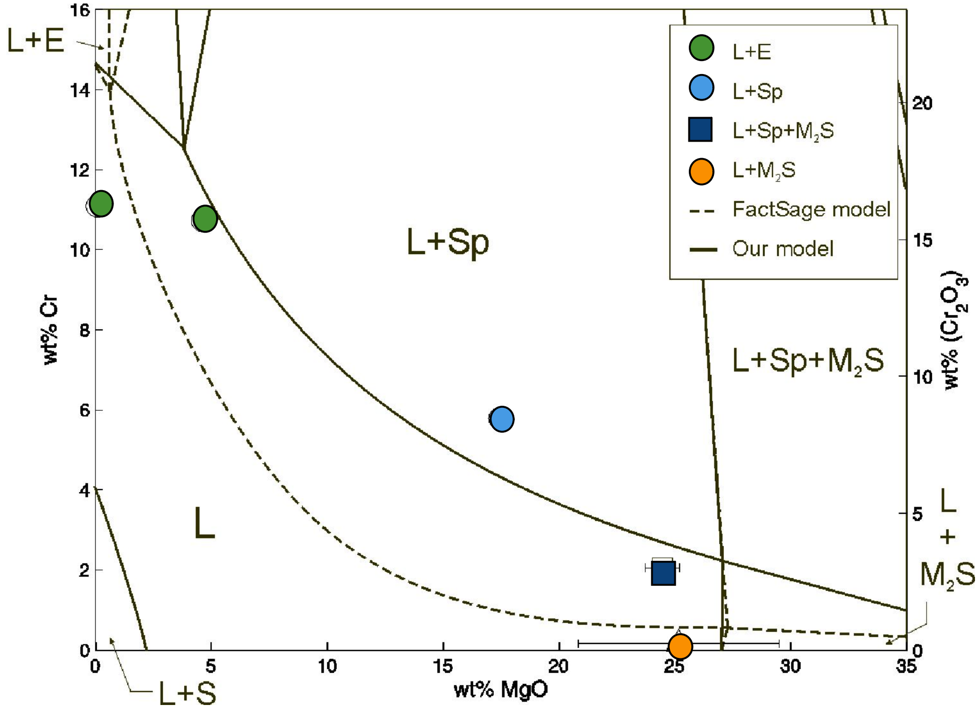
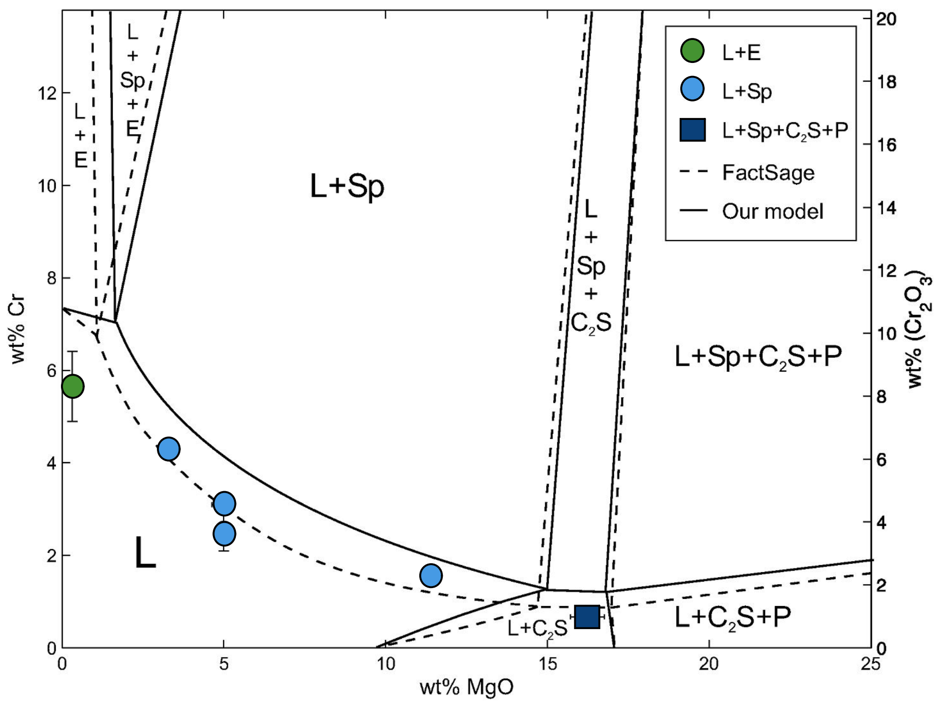
Quaternary system

- B=0.5



- B=1.2



Conclusions

- Experiments in the multicomponent system
  - Difference on eskolaite liquidus in $CaO\text{-}CrO_x\text{-}SiO_2$
  - Large differences originating in $CrO_x\text{-}MgO\text{-}SiO_2$
- Experiments in ternary system $CrO_x\text{-}MgO\text{-}SiO_2$
  - Most literature confirmed
  - M_2S liquidus clarified
  - Solubility of Cr in M_2S
- Modelling of the ternary system
  - Improved description
  - Also in the quaternary ? FactSage 6.0
- Full text on http://hdl.handle.net/1979/2076