PHASE FIELD MODELING OF ISOTHERMAL SLAG CRYSTALLIZATION

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GTT - TECHNOLOGIES

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Outline

- Introduction
  - Research framework and organization
- Concepts of phase field modeling
- Slag specific properties in the model
  - Thermodynamic data
  - Stoichiometric phases
  - Facet interfaces
  - Redox equilibria
- Case studies (simulation results)
- Conclusions

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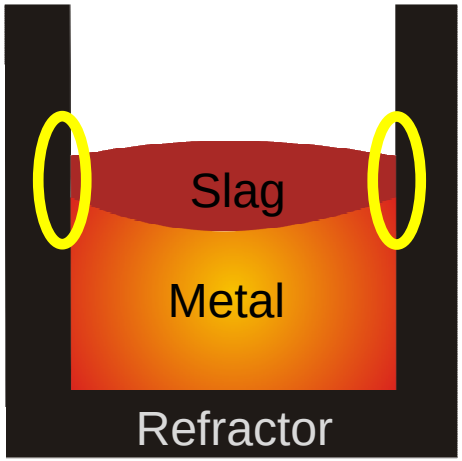
Goal and framework of this research

- **Problem statement**
  - Microstructure evolution of metallurgical slags controls many aspects of pyrometallurgical processes
    - e.g. freeze lining, refractory wear, tapping and cooling
- **Goals**
  - Develop a multiphase and multicomponent model to simulate microstructure evolution in slags
  - Perform necessary high temperature experiments
    - … to compare with the model
    - … to supply data for the model

Microstructure evolution in slags

- Process slag in contact with furnace refractories
- Freeze lining formed by solidification of process slag
- Tapping slag at high temperature and cooling down



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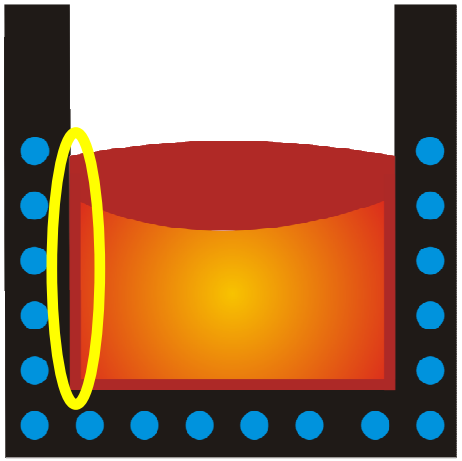

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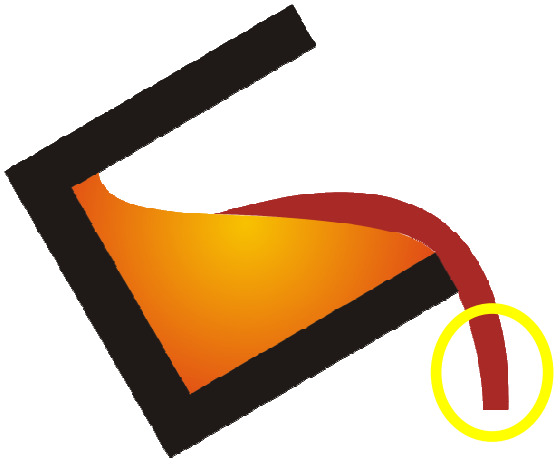
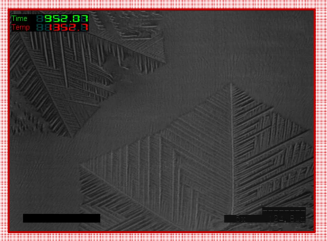


Organization of the research



... to compare with the model

... to supply data to the model

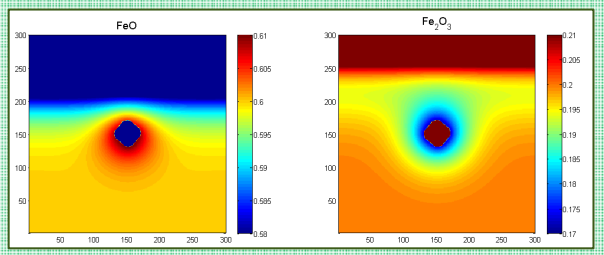
HIGHT T EXPERIMENTS

CSLM

Phase field modeling of isothermal slag crystallization

HPC

SIMULATIONS

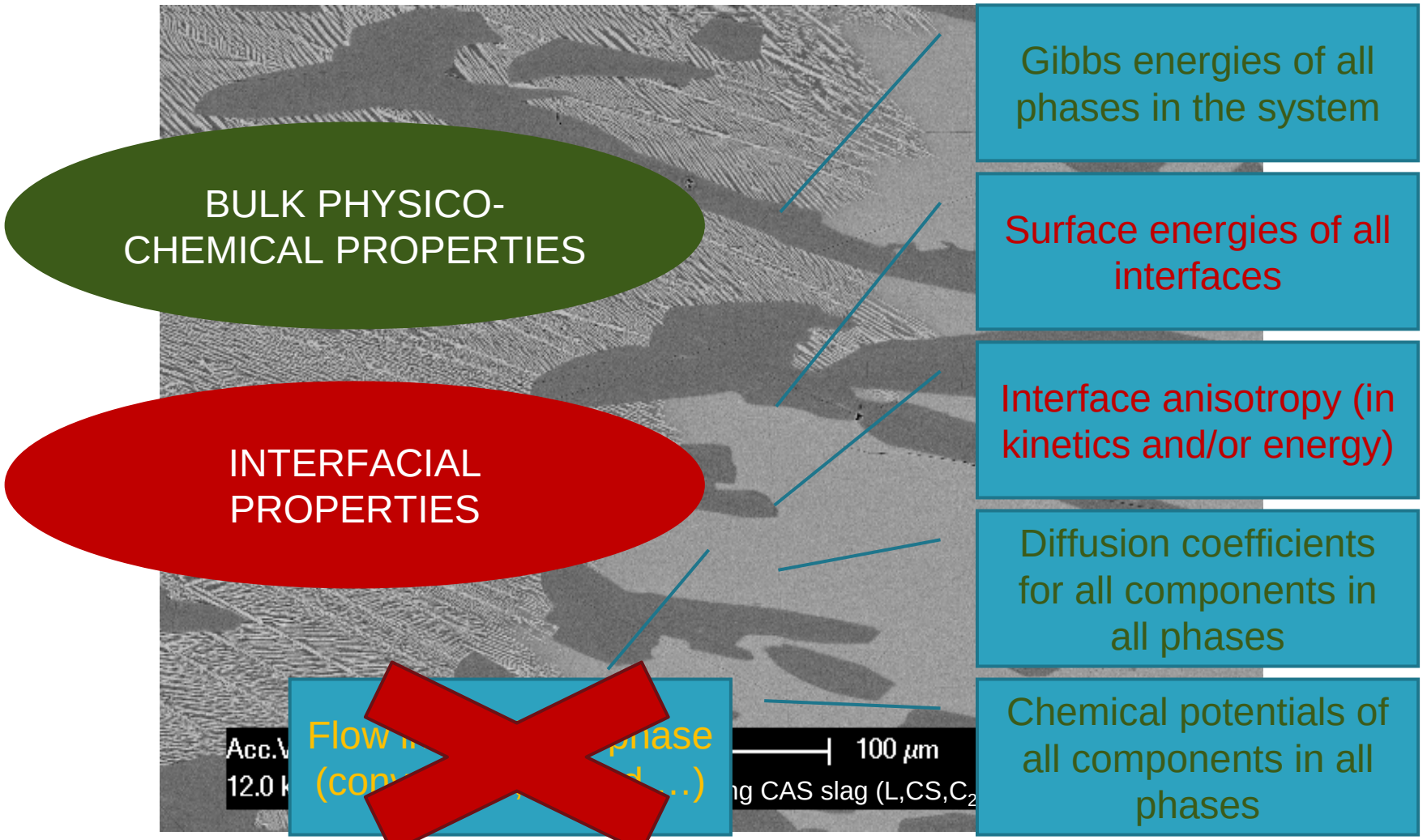


... develop model

... interpret results

- Phases
- Interfaces
- Phase field model
- Numerics

Modeled physical phenomena



Investigated slag systems

$CaO-Al_2O_3-SiO_2$

- 4-component system
  - Ca-Al-Si-O
- 3-component if oxides are assumed to diffuse
  - CaO
  - Al_2O_3
  - SiO_2
- p_{O_2} independent

$FeO-Fe_2O_3-SiO_2$

- 3-component system
  - Fe-Si-O
- Transition to FeO and Fe_2O_3 to study redox
  - FeO (Fe^{2+})
  - Fe_2O_3 (Fe^{3+})
  - SiO_2
- p_{O_2} ~ FeO/Fe_2O_3

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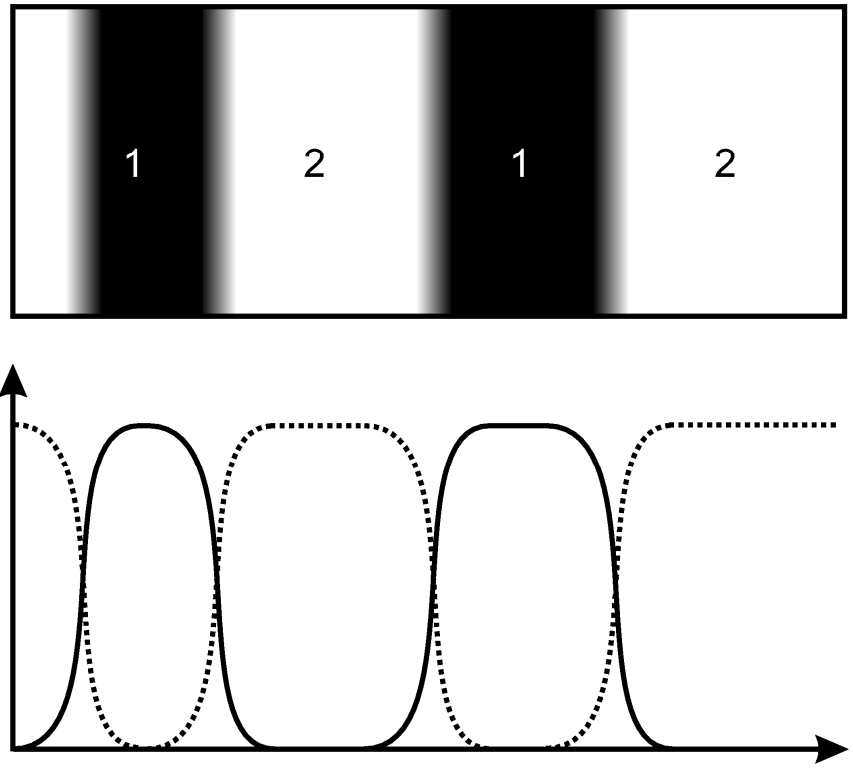
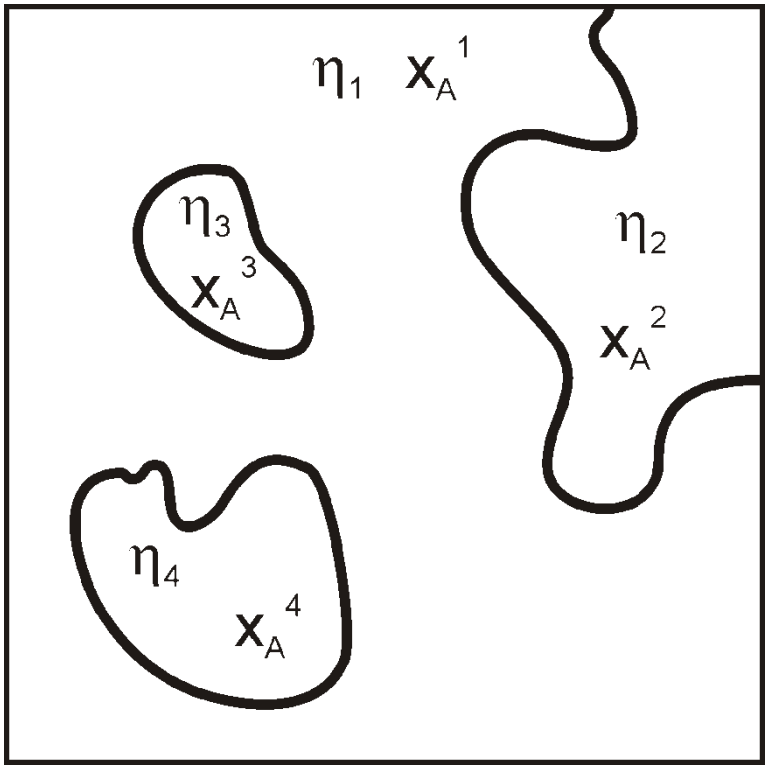
Concepts of phase field modeling

- Diffuse interfaces between different phases can treat arbitrary interface shapes





Microstructural evolution

- System of *p* phases and *c* components
- Phase fields evolve by energy minimization:

$$\frac{\partial \eta_i}{\partial t} = -L \frac{\delta}{\delta \eta_i} \left(\int_V \left(mf_0 + \frac{\kappa}{2} \sum_{r=1}^{p} |\nabla \eta_r|^2 + f_{chem} \right) dV \right)$$

  - **Interfacial energy** (Double well and gradient term)
  - **Chemical energy** (Gibbs energies of phases)
- Diffusion equation for every component:

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left(\sum_{i=1}^{p} \phi_i \sum_{r=1}^{c-1} M^i_{rk} \nabla \tilde{\mu}^i_r \right) \qquad \tilde{\mu}^i_r = \mu^i_r - \mu^i_{SiO_2}$$

Thermodynamic equilibrium

- Local (volumetric) chemical energy is calculated as:

$$f_{chem} = \sum_{i=1}^{p} \phi_i f^i$$

- Equality of diffusion potentials of c-1 components in p phases:

$$\tilde{\mu}_1^i = \ldots = \tilde{\mu}_k^i = \ldots = \tilde{\mu}_{c-1}^i \qquad i = 1..p$$

- Mass balance to link phase concentrations to x_k:

$$x_k = \sum_{i=1}^{p} \phi_i x_k^i \qquad k = 1..c-1$$

- Set of equations is solved for phase concentrations x_k^i

Kim SG, Kim WT, Suzuki T, Physical Review E 60(6), 1999
Eiken J, Bottger B, Steinbach I, Physical Review E 73(6), 2006

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Thermodynamic data of slags

- The phase field model uses:
  - Gibbs energies of all phases (solid and liquid)
    - $f_i(x_k,T)$ depends on local composition and temperature
    - 2nd order Taylor expansion for local approximation
  - Diffusion potentials of all components
    - $\mu_k(x_k,T)$ depends on local composition and temperature
  - Second derivative of Gibbs energies
- This data can be calculated using ChemApp
  - Converting *c* chemical potentials into *c-1* diffusion potentials
  - Carefully assess and use reference states for $\mu_k(x_k,T)$

2nd order Taylor approximation

- Gibbs energy of phase *i* is approximated by:

$$\hat{f}^i = \sum_{k=1}^{c-1}\left(\frac{A_{kk}^i}{2}\left(x_k^i - \hat{x}_k^i\right) + \sum_{l\neq k}^{c-1} A_{kl}^i\left(x_k^i - \hat{x}_k^i\right)\left(x_l^i - \hat{x}_l^i\right) + B_k^i\left(x_k^i - \hat{x}_k^i\right)\right) + C^i$$

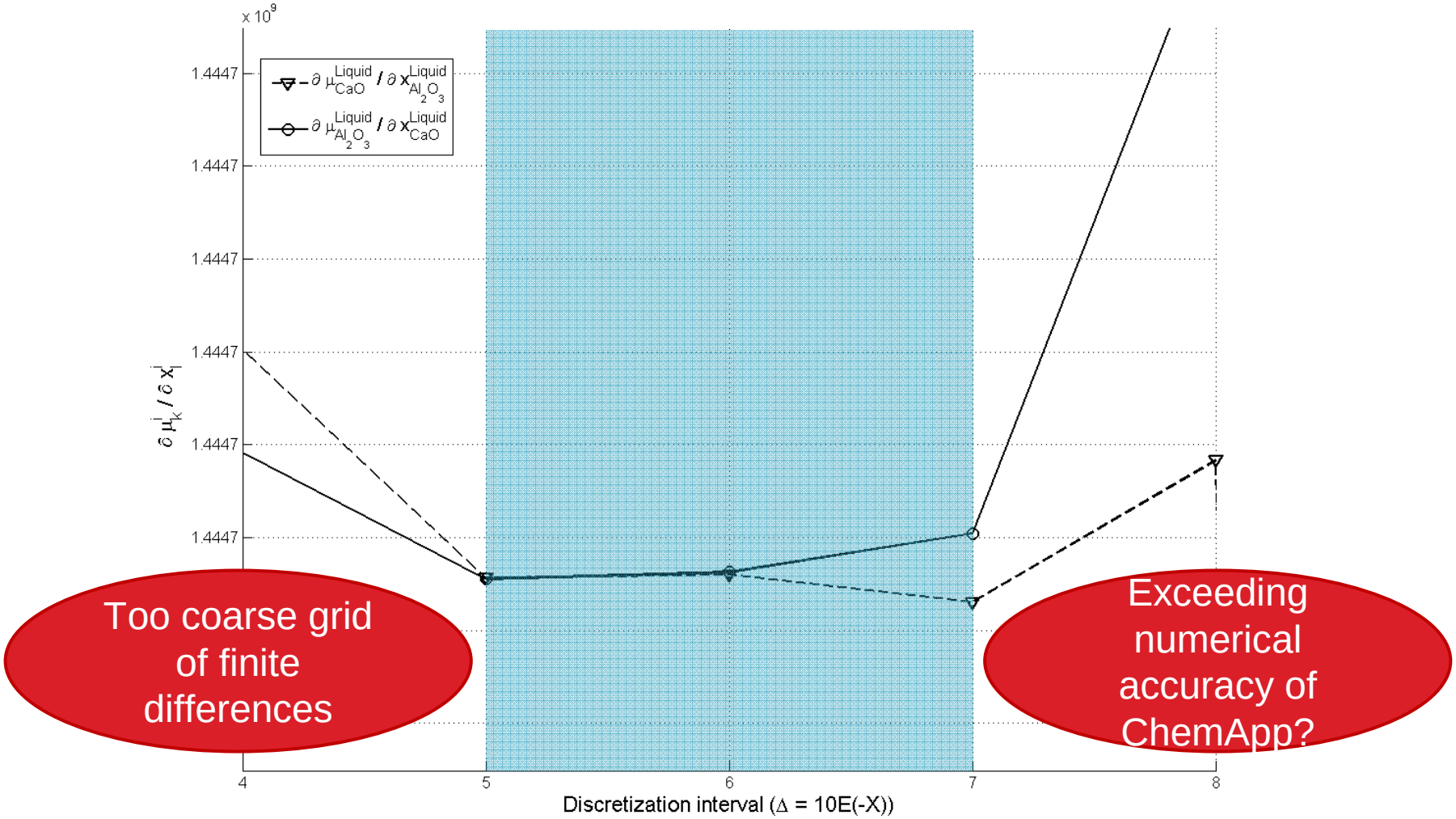
$$A_{kl}^i = \frac{\partial^2 f^i}{\partial x_k^i \partial x_l^i} \qquad B_k^i = \frac{\partial f^i}{\partial x_k^i} = \tilde{\mu}_k^i \qquad C^i = f^i$$

  - **A**, **B** and **C** are retrieved by ChemApp and stored in an array to load in the phase field code
- Diffusion potentials are linear in concentrations, which greatly reduces computational effort

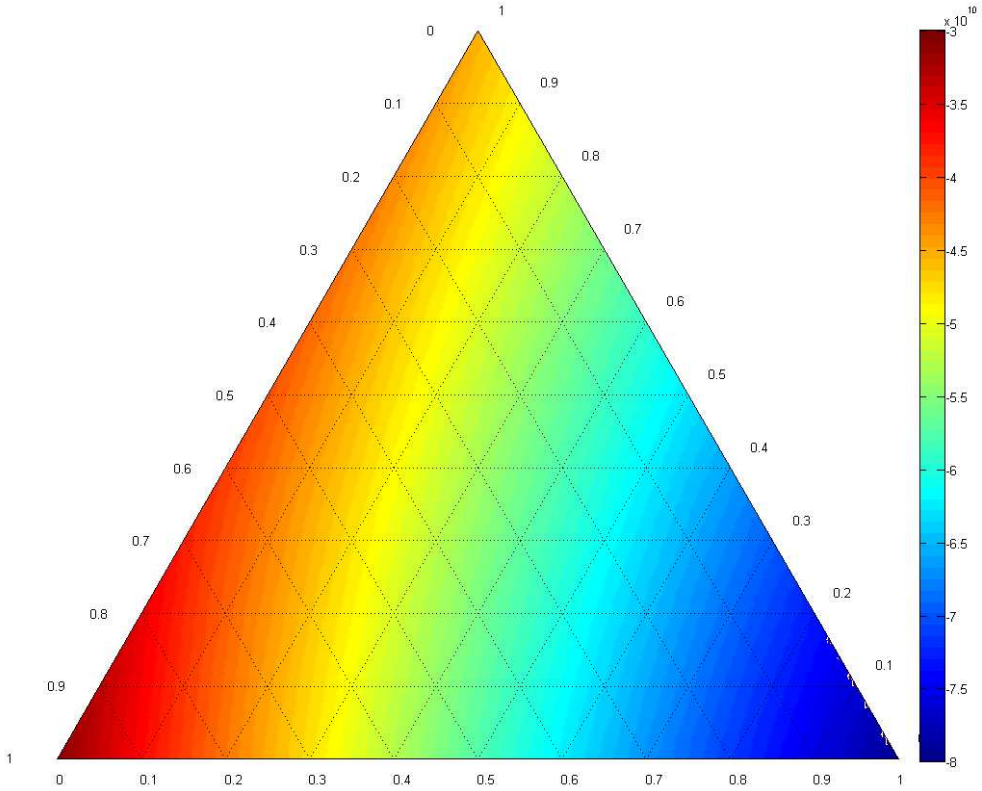
ChemApp calls (liquid phase)

- Gibbs energy
  - `call tqgetr('GM', 0, 0, F, noerr)`
- Diffusion potential of CaO
  - `G_SiO2_0` and `G_CaO_0` *(standard states in liquid at certain T)*
  - `call tqgetr('MU', i_liquid, i_SiO2, mu_SiO2, noerr)`
    `mu_SiO2 = G_SiO2_0 + mu_SiO2`
  - `call tqgetr('MU', i_liquid, i_CaO, mu_CaO, noerr)`
    `mu_CaO = ((G_CaO_0 + mu_CaO) - mu_SiO2)/Vm`
- Second derivative of Gibbs energy
  - `call tqsetc('IA ', i_liquid, i_CaO, x_CaO±dr, numcon, noerr)`
  - **`dmu_dCaO = (mu2-mu1)/(2.d0*dr)/Vm`**

Numerical determination of $d\mu/dx$



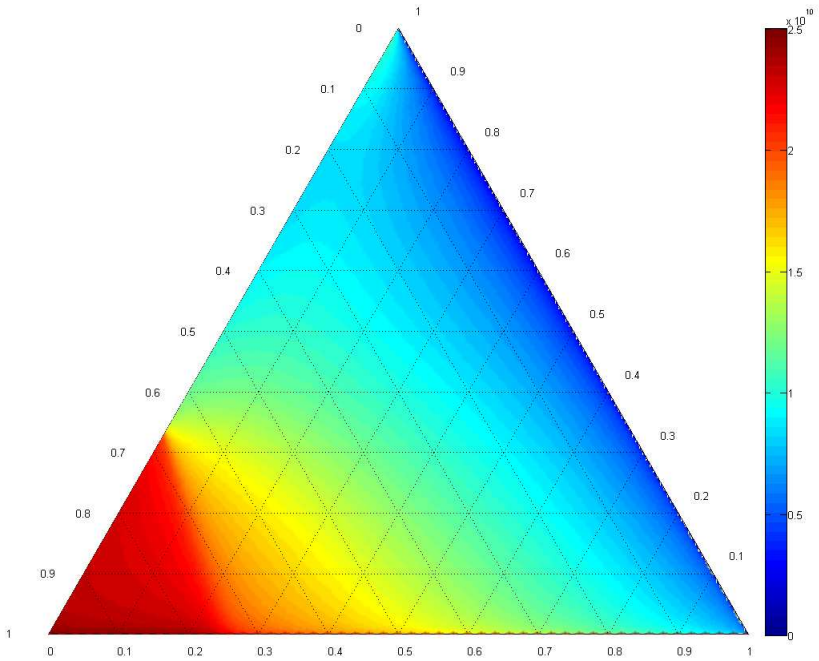
Gibbs energy of liquid



- All phases suspended
- Liquid phase is entered
- Stored in an array with $\Delta = 0.001$ spacing
- Locally approximated with 2nd order Taylor expansion
  - First derivatives
  - *Second derivatives*

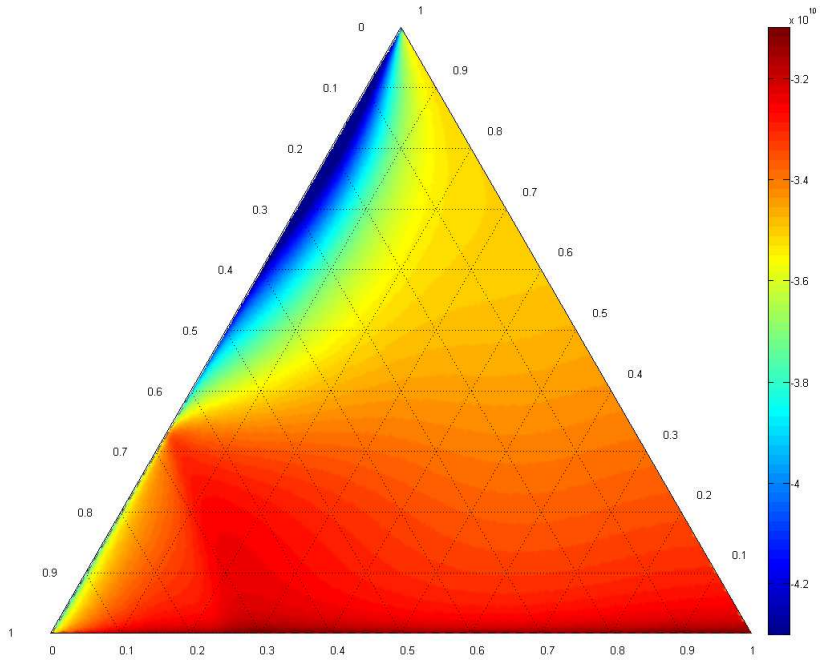
Diffusion potentials in liquid

$$\tilde{\mu}_{CaO}^{liquid} = \mu_{CaO}^{liquid} - \mu_{SiO_2}^{liquid}$$



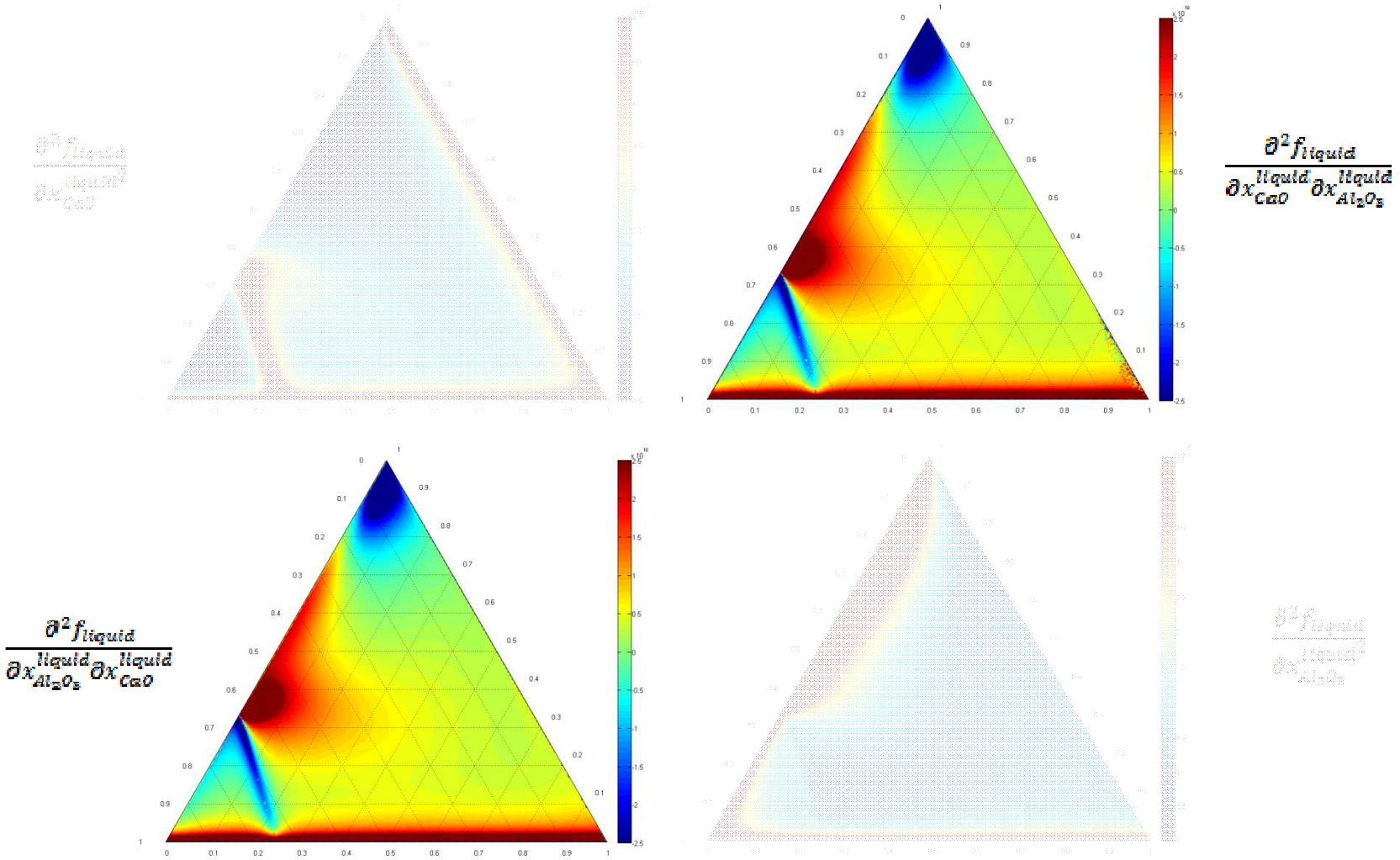
$$\frac{\partial f_{liquid}}{\partial x_{CaO}^{liquid}}$$

$$\tilde{\mu}_{Al_2O_3}^{liquid} = \mu_{Al_2O_3}^{liquid} - \mu_{Al_2O_3}^{liquid}$$

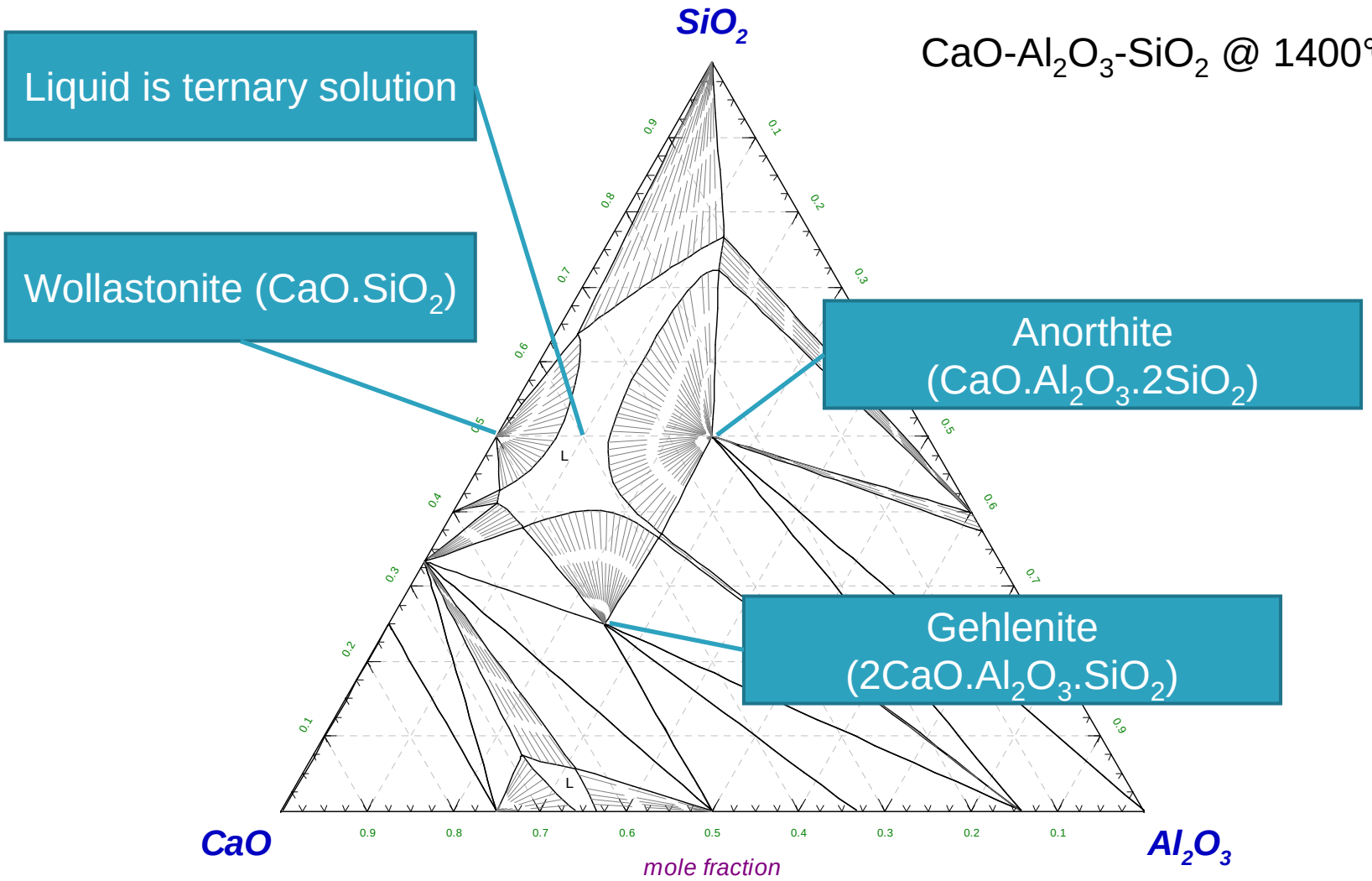


$$\frac{\partial f_{liquid}}{\partial x_{Al_2O_3}^{liquid}}$$

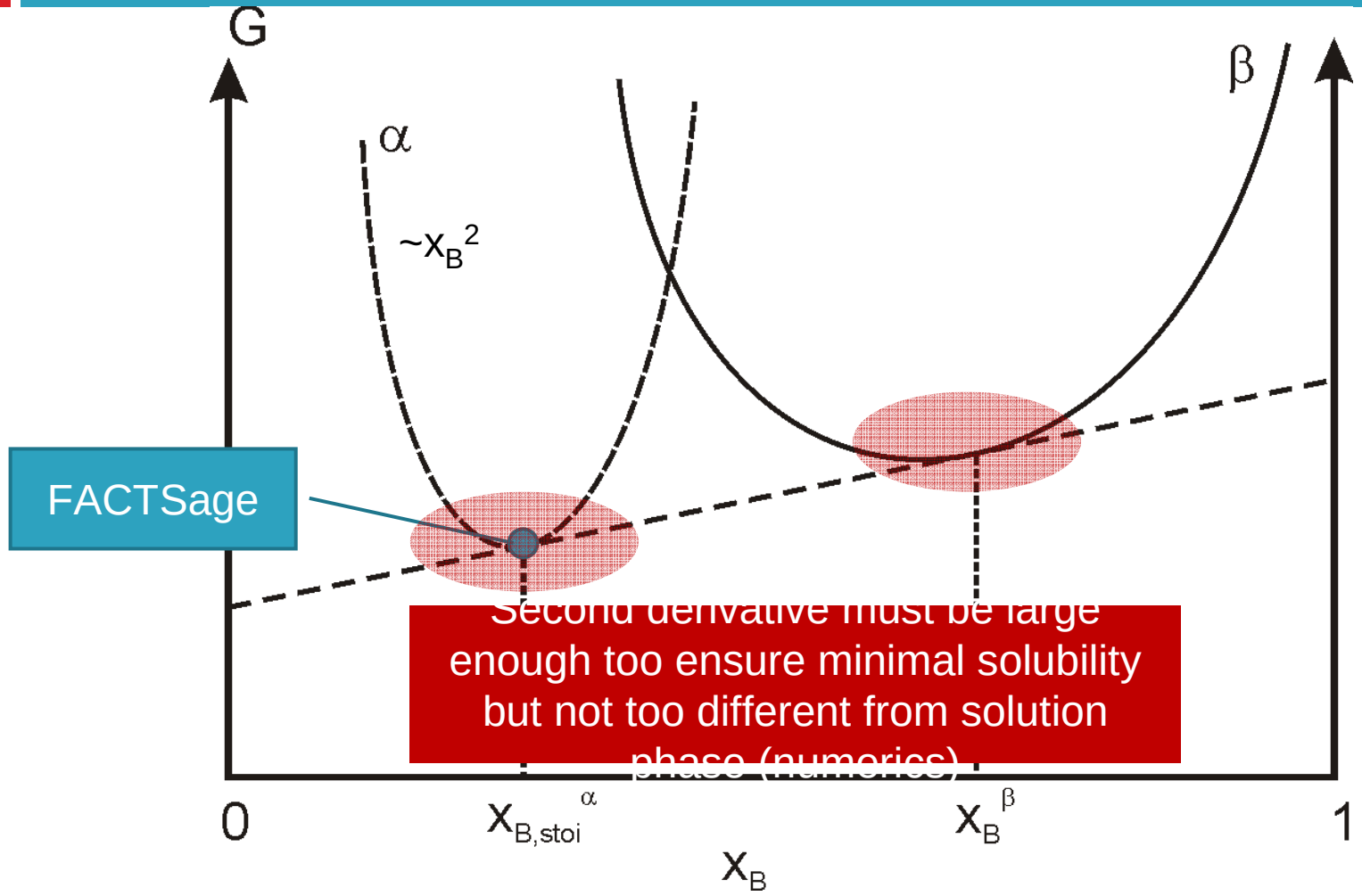
Second derivative of Gibbs energy



Stoichiometric phases in slags



Stoichiometric phases (binary version)



Hu SY, Murray J, Weiland H, Liu ZK, Chen LQ, CALPHAD 31(2), 2007

Diffusion matrix of $_{42}CaO$-$_{10}Al_2O_3$-$_{48}SiO_2$

- Kinetic coefficients in diffusion equations can be determined by literature data and ChemApp
- Diffusion equation for component *k*:

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left(\sum_{i=1}^{p} \phi_i \sum_{r=1}^{k-1} M^{i}_{rk} \nabla \tilde{\mu}^{i}_{r} \right)$$

- **M** matrix relates to interdiffusion matrix **D**:

$$\begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} = \begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} \cdot \begin{bmatrix} \frac{\partial \tilde{\mu}_1}{\partial x_1} & \frac{\partial \tilde{\mu}_1}{\partial x_2} \\ \frac{\partial \tilde{\mu}_2}{\partial x_1} & \frac{\partial \tilde{\mu}_2}{\partial x_2} \end{bmatrix}^{-1}$$

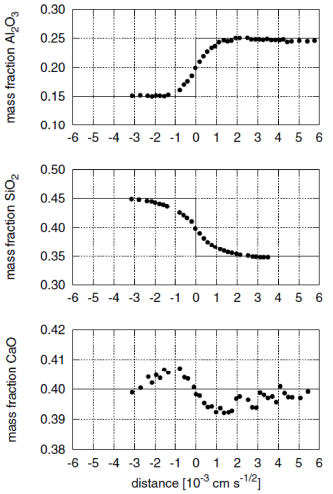
MODEL | LITERATURE | CHEMAPP

Diffusion matrix of $42CaO$-$10Al_2O_3$-$48SiO_2$

- Interdiffusion matrix **D** at 1350℃
  Sugawara et al., Met. Trans. 8B, 1977, 605

Uphill diffusion!

$$\begin{bmatrix} D_{CaO-CaO} & D_{CaO-Al_2O_3} \\ D_{CaO-Al_2O_3} & D_{Al_2O_3-Al_2O_3} \end{bmatrix} = \begin{bmatrix} 8.734 & -2.464 \\ -3.948 & 5.977 \end{bmatrix} \cdot 10^{-11}$$

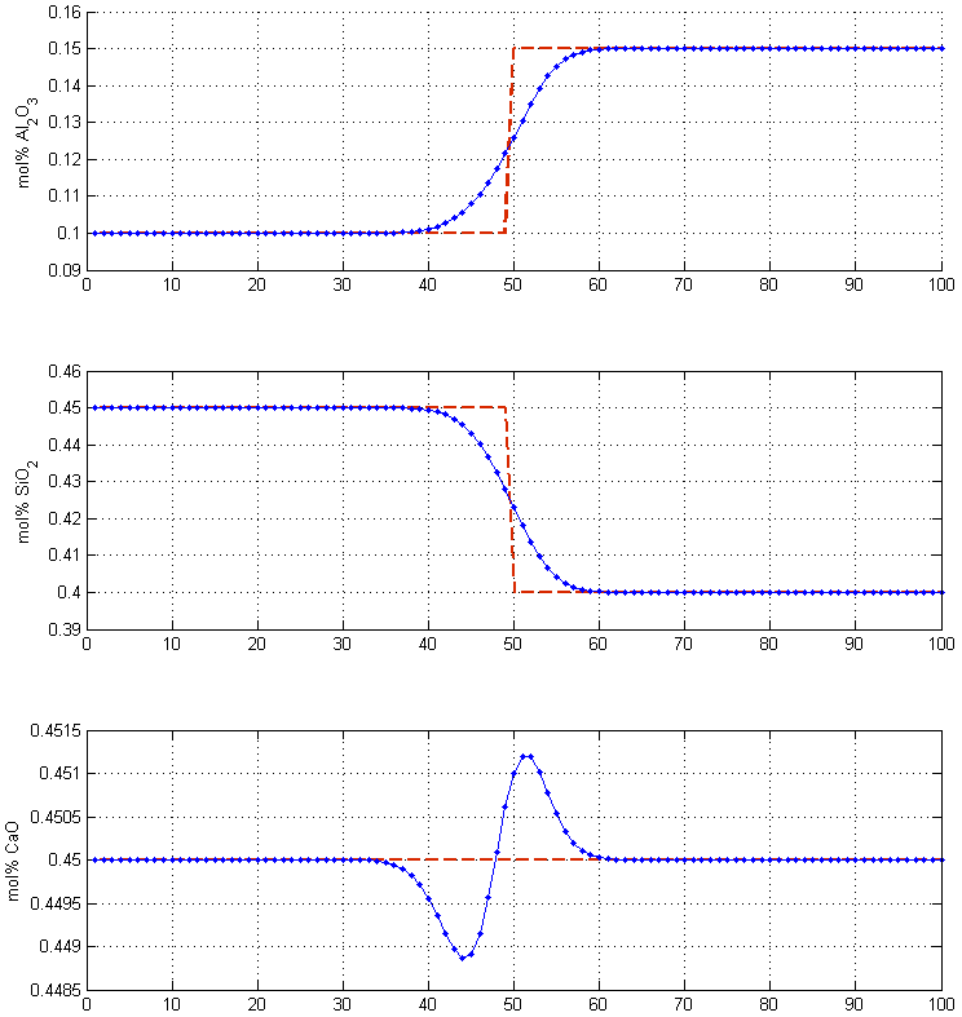


- Thermodynamic factors matrix **G** at 1350
  ChemApp

$$\begin{bmatrix} \frac{\partial \tilde{\mu}_1}{\partial x_1} & \frac{\partial \tilde{\mu}_1}{\partial x_2} \\ \frac{\partial \tilde{\mu}_2}{\partial x_1} & \frac{\partial \tilde{\mu}_2}{\partial x_2} \end{bmatrix} = \begin{bmatrix} 1.375 & 1.420 \\ 1.420 & 4.307 \end{bmatrix} \cdot 10^{10}$$

- Resulting **M** matrix for the model can now be calculated

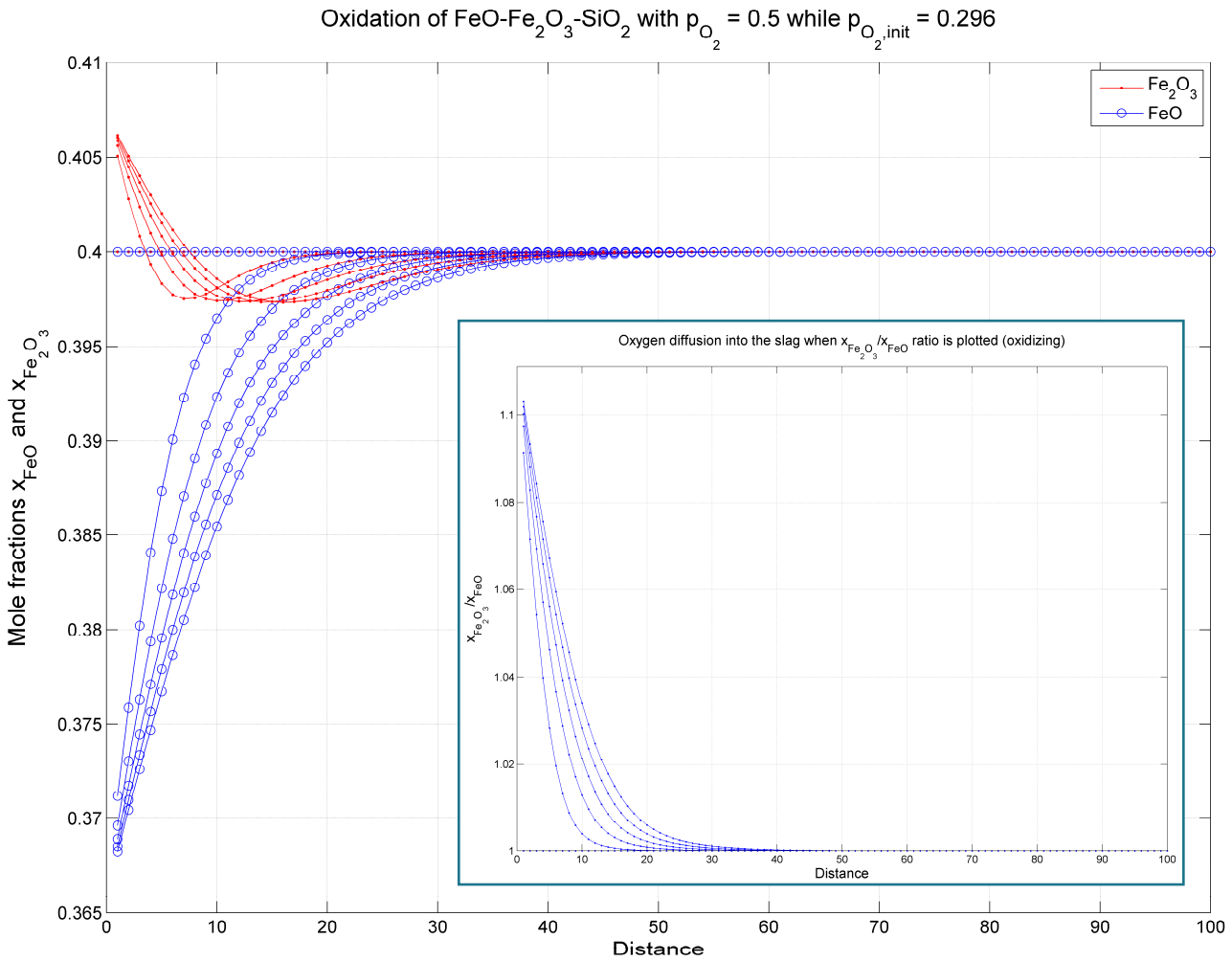
Op 'rim' diffusion in CaO Al_2O_3 SiO_2



Redox equilibria of multivalent cations

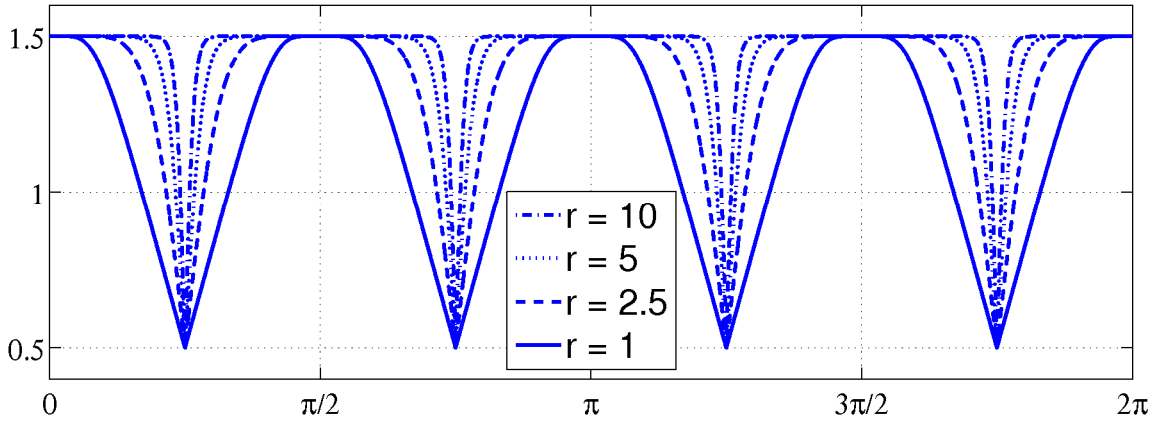
- Oxygen dependent system
  - $FeO-Fe_2O_3-SiO_2$
- Open systems with at least one boundary in contact with O_2 atmosphere (with fixed p_{O2})
- Assumptions made regarding to redox reactions
  - Redox equilibria are locally always in equilibrium
    - Fe^{3+} / Fe^{2+} is a direct measure for local oxygen potential
    - O_2 can only diffuse into the slag by changing the local multivalent composition
- Special boundary condition to preserve Fe but not O

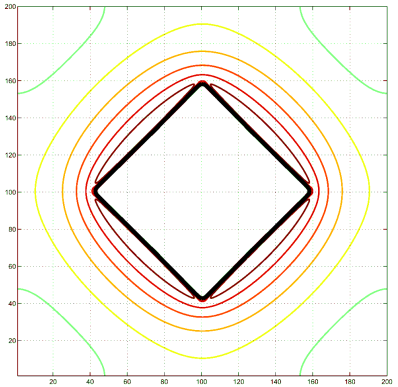
Diffusion of Fe_2O_3 and FeO (1500℃)



Faceted growth of minerals

- Conditions for a faceted interface:
  - Interface controlled growth (diffusion is faster)
  - Interface mobility is heavily dependent on orientation





- *Tanh* type function has physical meaning (Burton-Carbrera-Frank)

Uehara T, Sekerka RF, Journal of Crystal Growth 254, 2003

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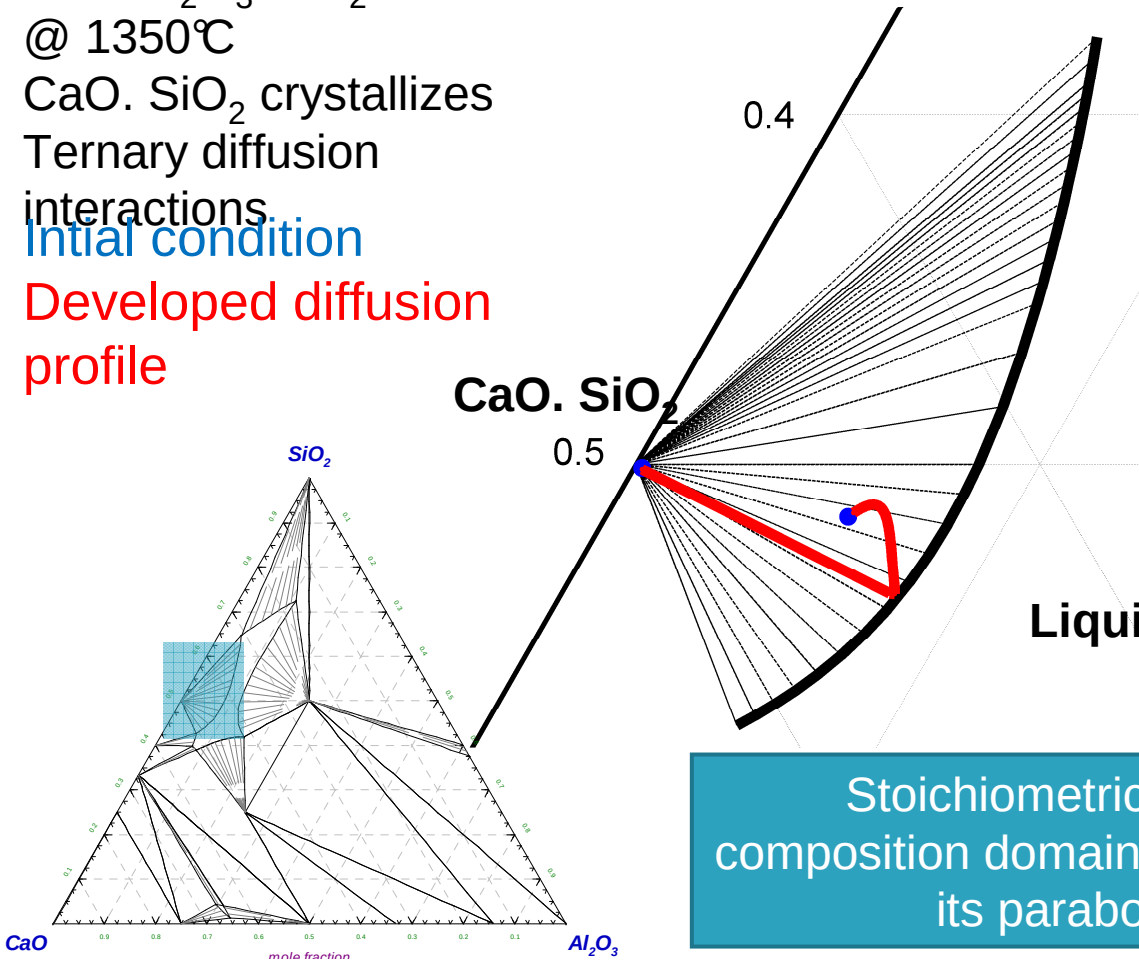
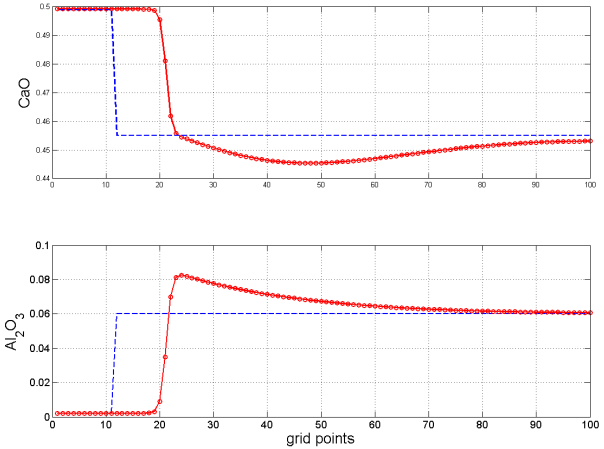
Isothermal mineral crystallization

$CaO\text{-}Al_2O_3\text{-}SiO_2$
@ 1350℃
$CaO.\ SiO_2$ crystallizes
Ternary diffusion interactions.

Intial condition

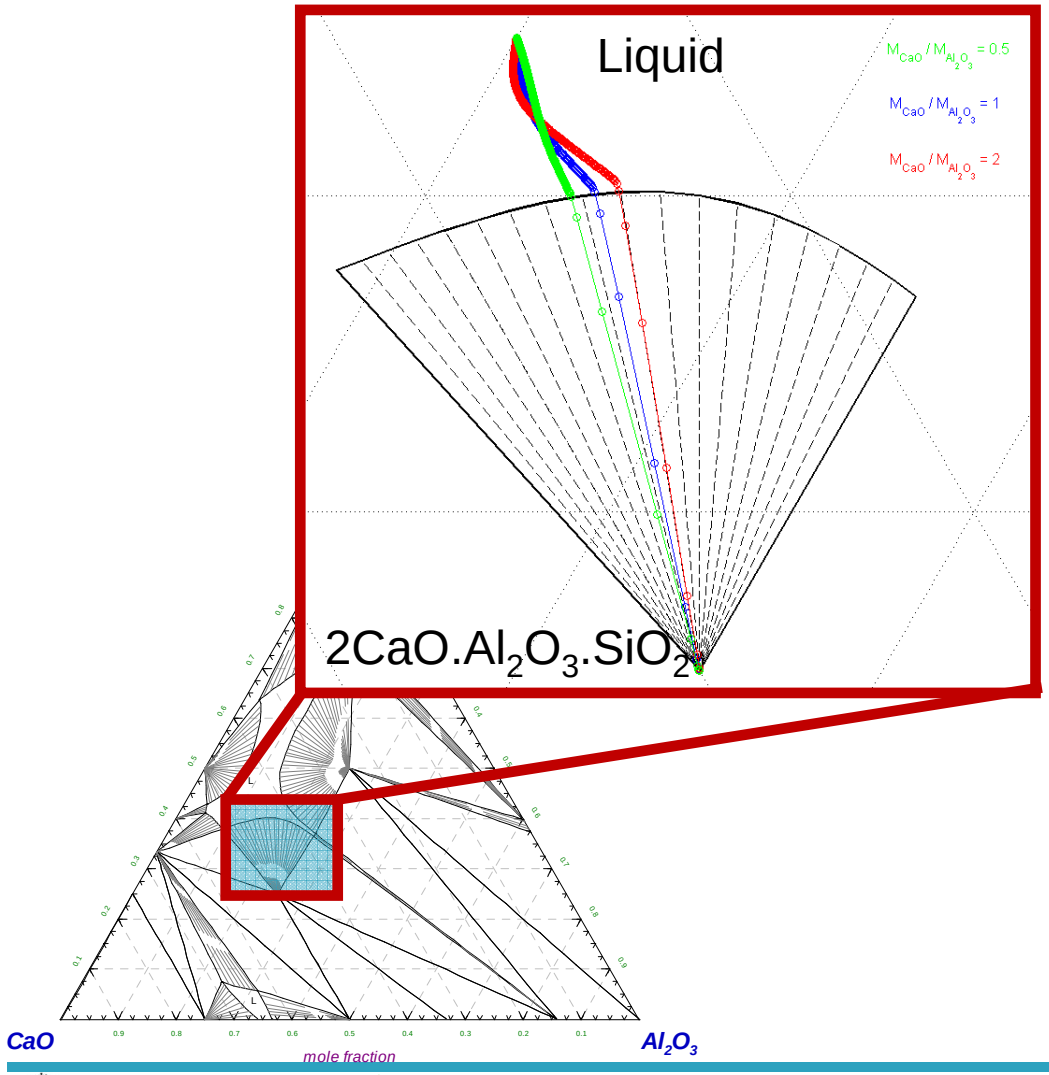
Developed diffusion profile



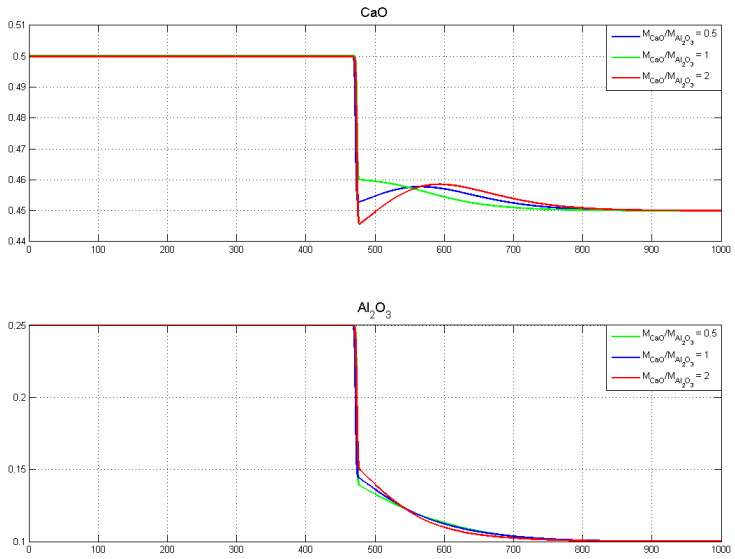


Stoichiometric phase at boundary of composition domain requires careful selection of its parabolic approximation.

Ternary diffusion paths in slags



CaO-Al_2O_3-SiO_2
@ 1400℃
Liquid and
$2CaO.Al_2O_3.SiO_2$
Different tie-line selection



thermo research group

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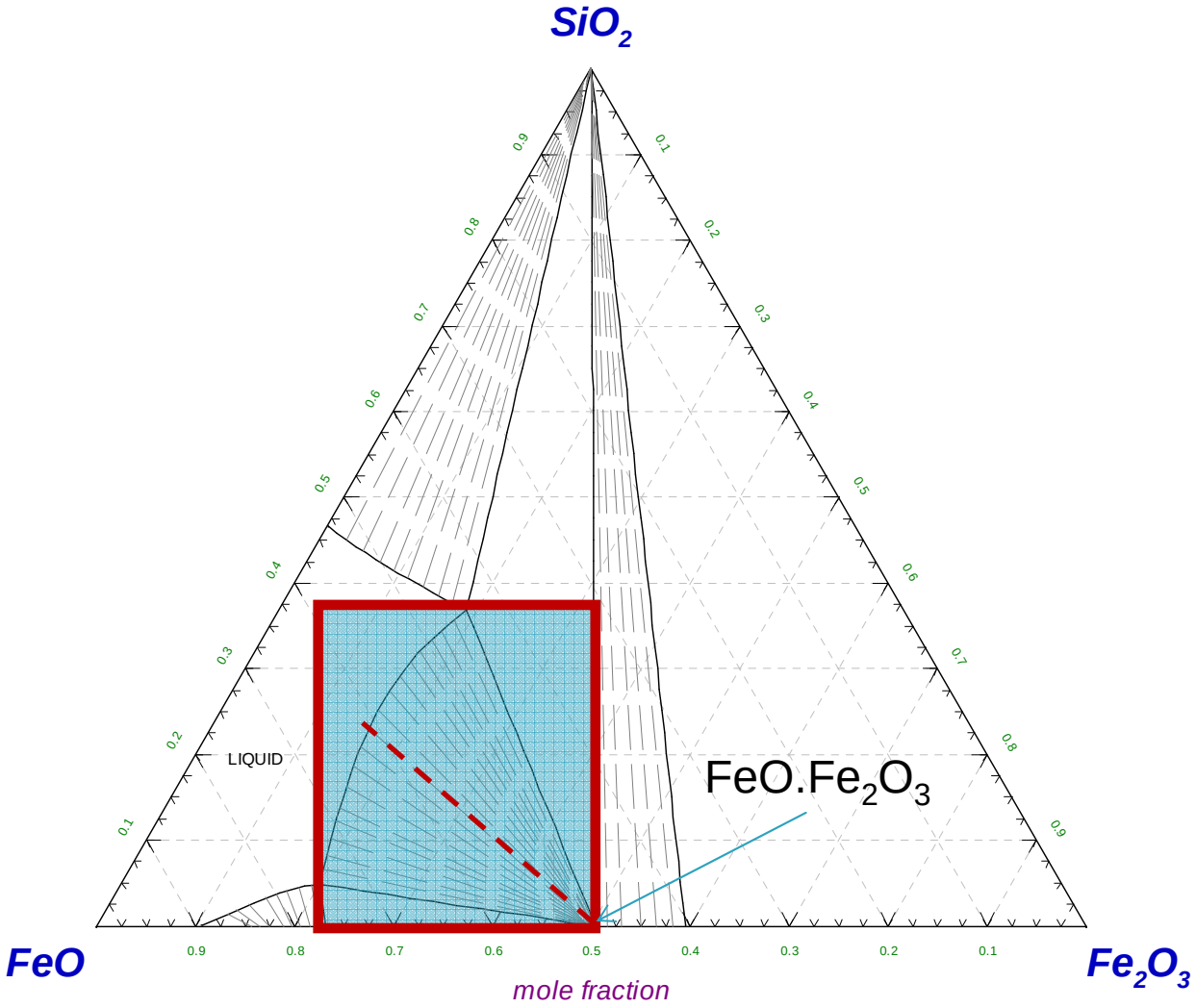
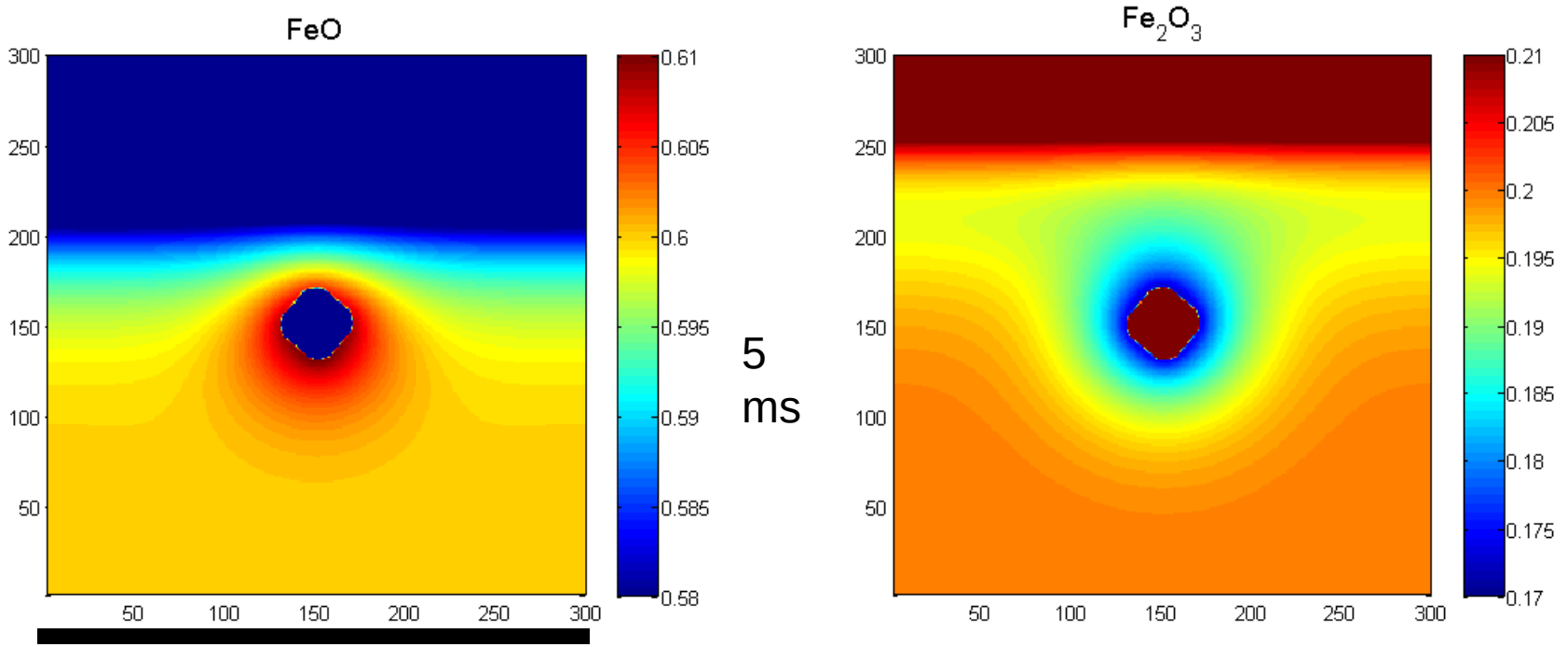
FeO Fe_2O_3 SiO_2 system at 1400℃



Open boundary in FeO-Fe_2O_3-SiO_2

- Initial slag is in equilibrium with p_{O2} = 2.4E-5
- Upper boundary has p_{O2} = 1.5E-3



Conclusions

- Phase field model linked with FACT database
  - Gibbs energies and diffusion potentials are retrieved
  - Stoichiometric phases → parabolic Gibbs energies
  - Faceted growth with cusp function in mobility
- Case studies of simulations
  - Mineral growth and diffusion path calculations
    - Stoichiometric phase in contact with liquid
  - Mineral growing with varying oxygen potential
    - Two competing diffusion fields

Isothermal mineral crystallization in liquid is