

Oxidation and diffusion in oxides – a progress report



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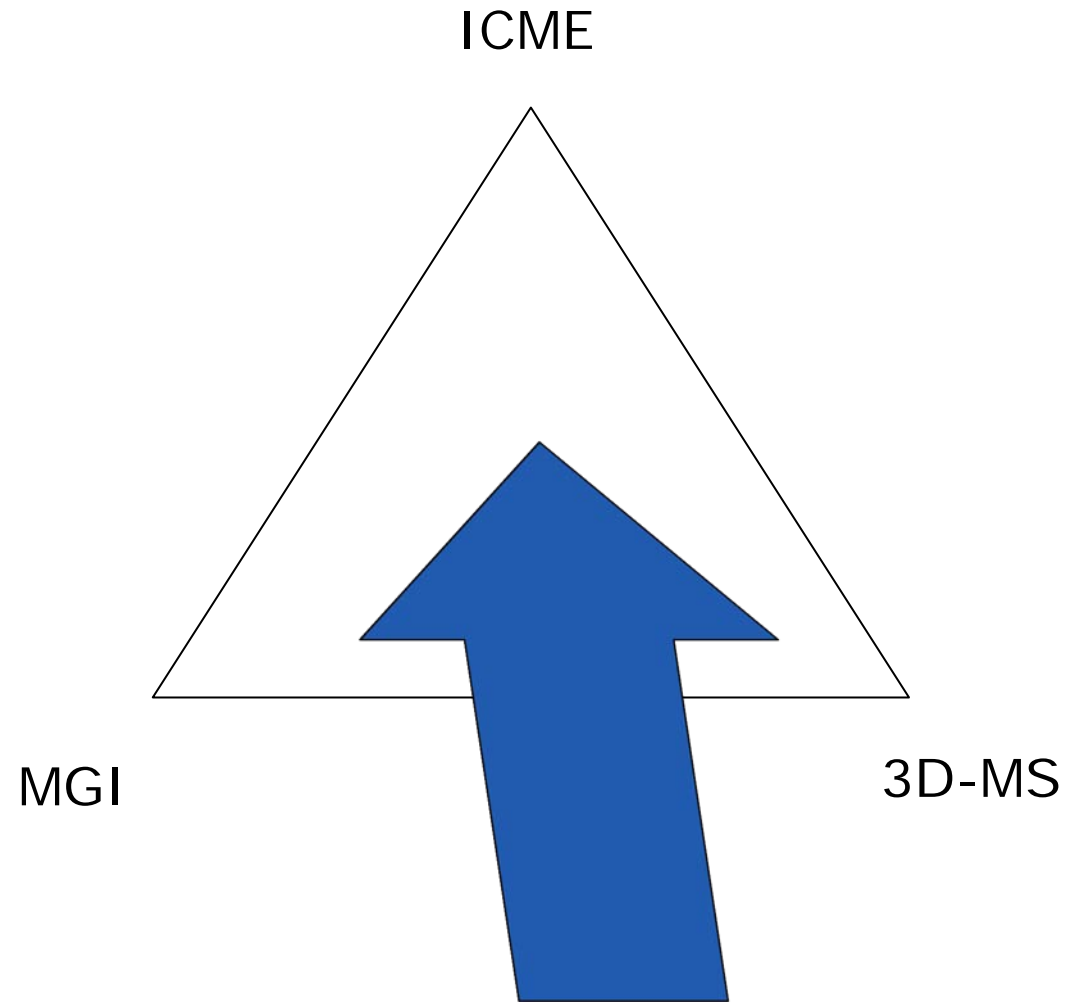
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Malin Selleby



New Research directions in Materials science **and** Engineering:



Content

1. Aim of work
2. Issues in modelling of oxidation
3. Bulk diffusion in oxides
 - a) Summary and present stage
 - b) Some issues in the diffusion modelling
 - c) Defect structures for oxygen diffusion and results
4. Grain boundary diffusion
5. Kirkendall porosity

1. Aim of work

Predict oxidation:

- Sharp-interface methods – DICTRA
- Diffuse-interface methods – phase-field

For example:

- Oxidation of steels
- Degradation of superalloy coatings

We need:

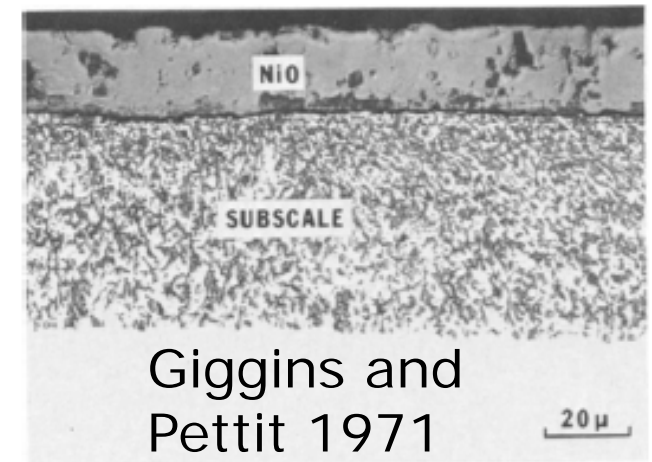
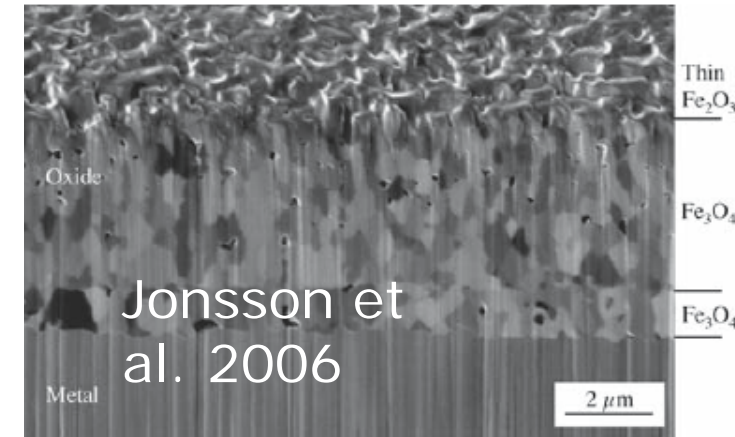
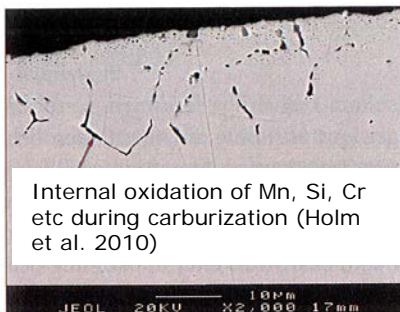
- Mathematical expressions for oxidation rate in terms of diffusional flux as function of gradients in composition or chemical potentials.
- Parameters that characterize a given material



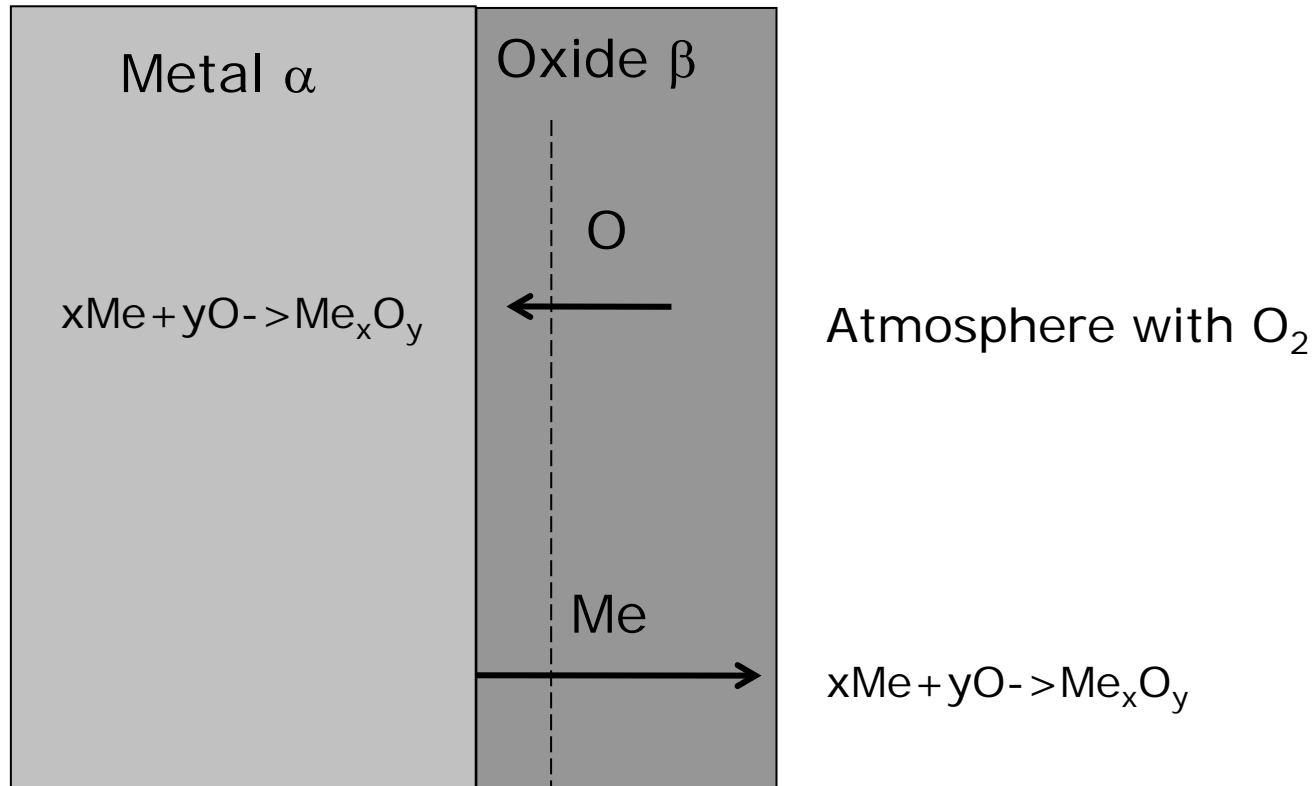
2. Issues in modelling of oxidation

Predict:

- Rate of oxidation
 - External (growth of external layers)
 - Internal (internal oxide particles)
 - Grain boundaries in metal and in oxides
- What oxides form?
- Porosity
 - Kirkendall effect

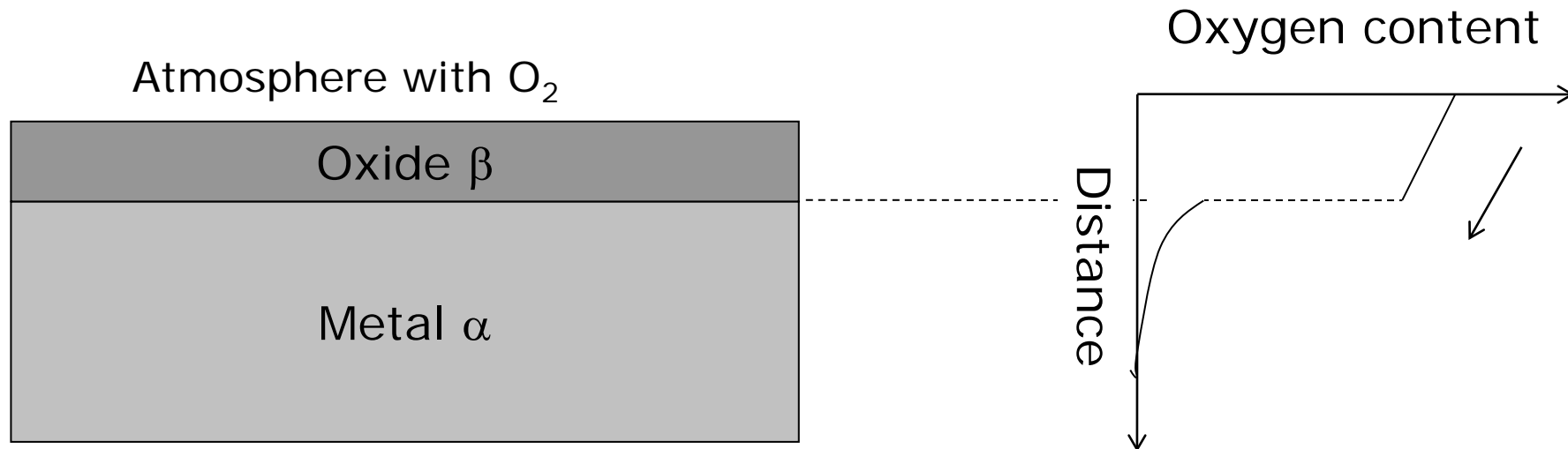


External oxidation - general Inward and outward growth



- Oxygen diffusion in the oxide layer gives inward growth
- Metal diffusion in the oxide layer gives outward growth

Growth of external layers



Diffusion and flux balances in sharp-interface modelling!

Growth of internal oxide particles

- Oxygen must diffuse through external oxide layers and dissolve in the metallic matrix.
- Rate may be controlled by oxygen diffusion, alloy element diffusion or both.

3. Bulk diffusion in oxides

3.a) Summary and present stage

Flux:

$$J = -L \frac{\partial \mu}{\partial x} = -L \frac{\partial \mu}{\partial c} \frac{\partial c}{\partial x} = -D \frac{\partial c}{\partial x}$$

$$D = L \frac{\partial \mu}{\partial c}$$

Kinetic parameters
from model.

Darken's thermodynamic factor,
e.g. from Calphad analysis.

Base models on a vacancy mechanism!

Present stage

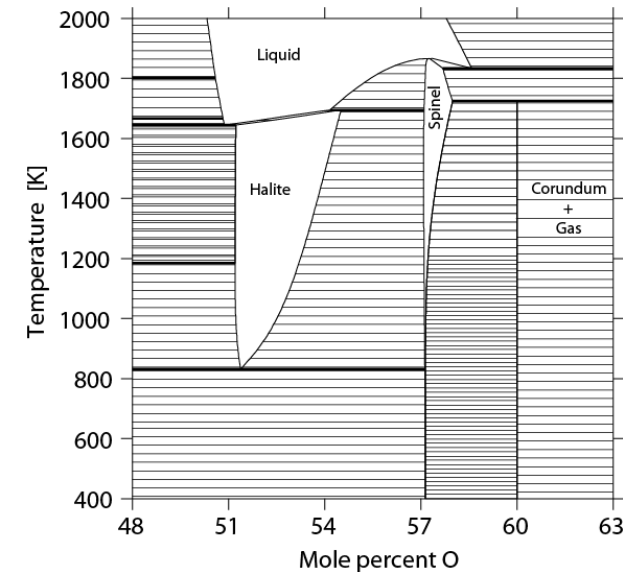
The models have been implemented in DICTRA.

Data base now contains diffusional mobilities of

- Wüstite (Halite)
 - Fe and O
- Magnetite (Spinel)
 - Fe Cr O
- Hematite (Corundum)
 - Fe, Cr, O

3.b) Some issues in the diffusion modelling

- Phase equilibria and driving forces – Calphad thermodynamics
- Defect structures
 - Vacancies and interstitials
 - Oxygen substitutional
 - Fe, Cr etc interstitial
- Diffusing species
 - Ions
 - Neutral atoms
 - Positive holes
- Rate equations



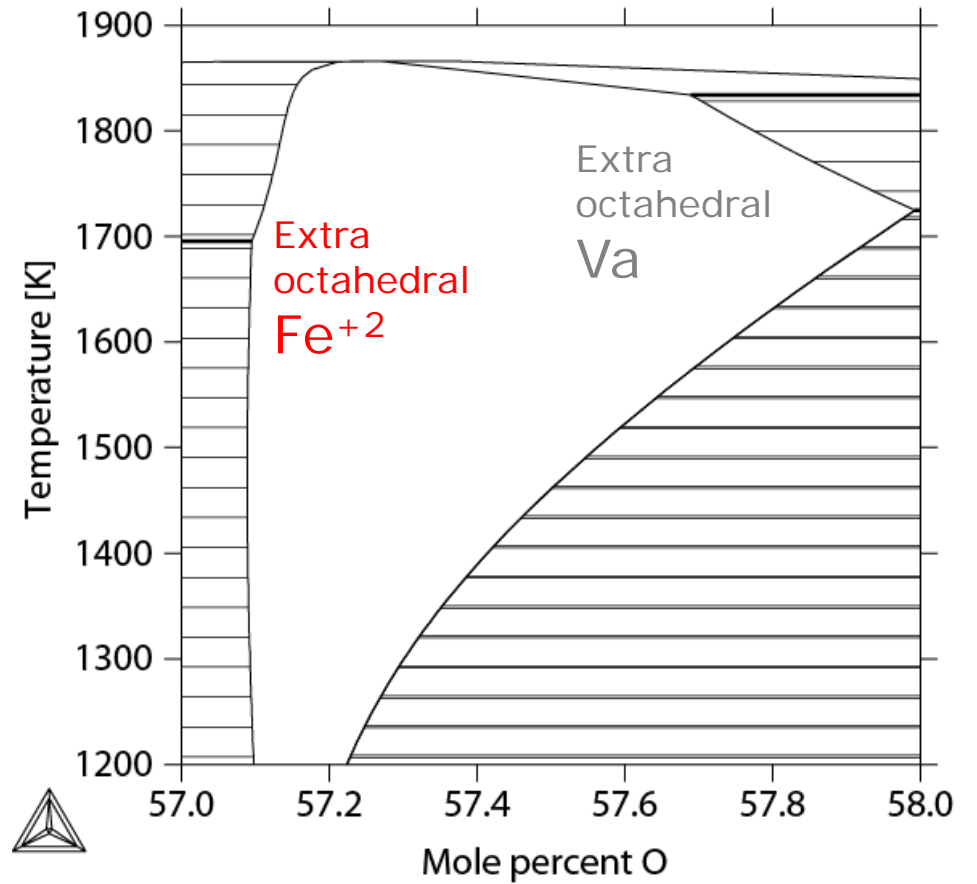
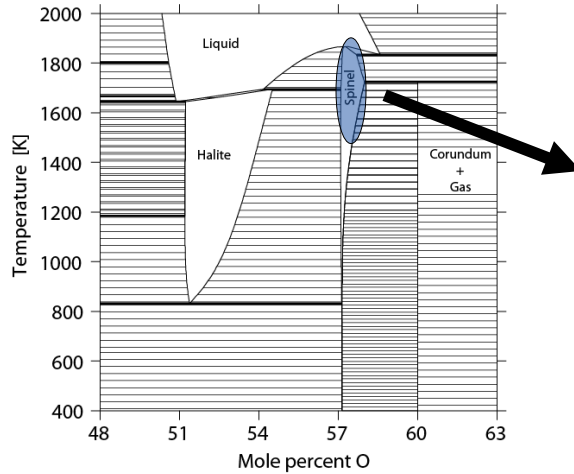
Fe-O Calculated from Sundman 1991.

Diffusing species: in ionic systems – two extremes

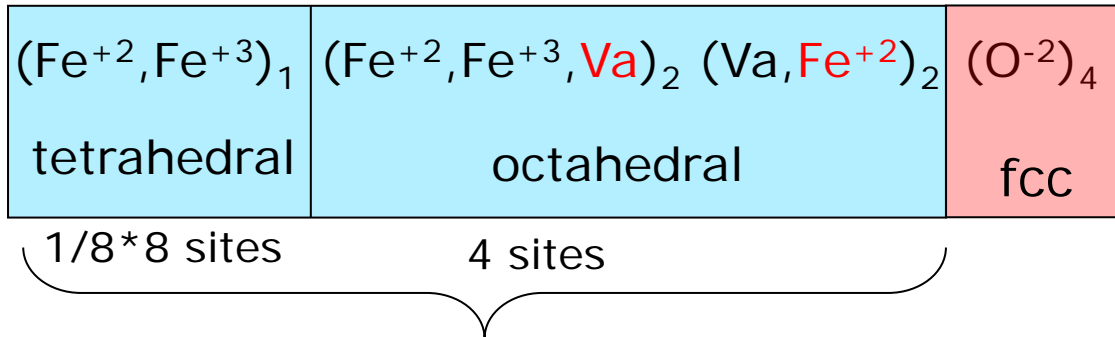
- Electronic conduction compared to diffusion:
 - Much faster (charge does not need to be included)
 - Much slower (ions diffuse as species)

If electronic conduction and diffusion are about the same rate (electronic conduction needs to be accounted for)

Fe diffusion in spinel (lattice-fixed frame of reference, Hallström et al. 2011)



Thermodynamic model (Sundman 1991):



Interstitial sites

Absolute reaction rate arguments:

$$J_{Fe}' = -\frac{1}{2} \left[y_{Va}'' y_{Fe}'' M_{FeVa}'' + y_{Fe}''' y_{Va}''' M_{FeVa}''' \right] \frac{1}{V_s} \frac{\partial \mu_{Fe}}{\partial z}$$

Normal octahedral sites

extra octahedral sites

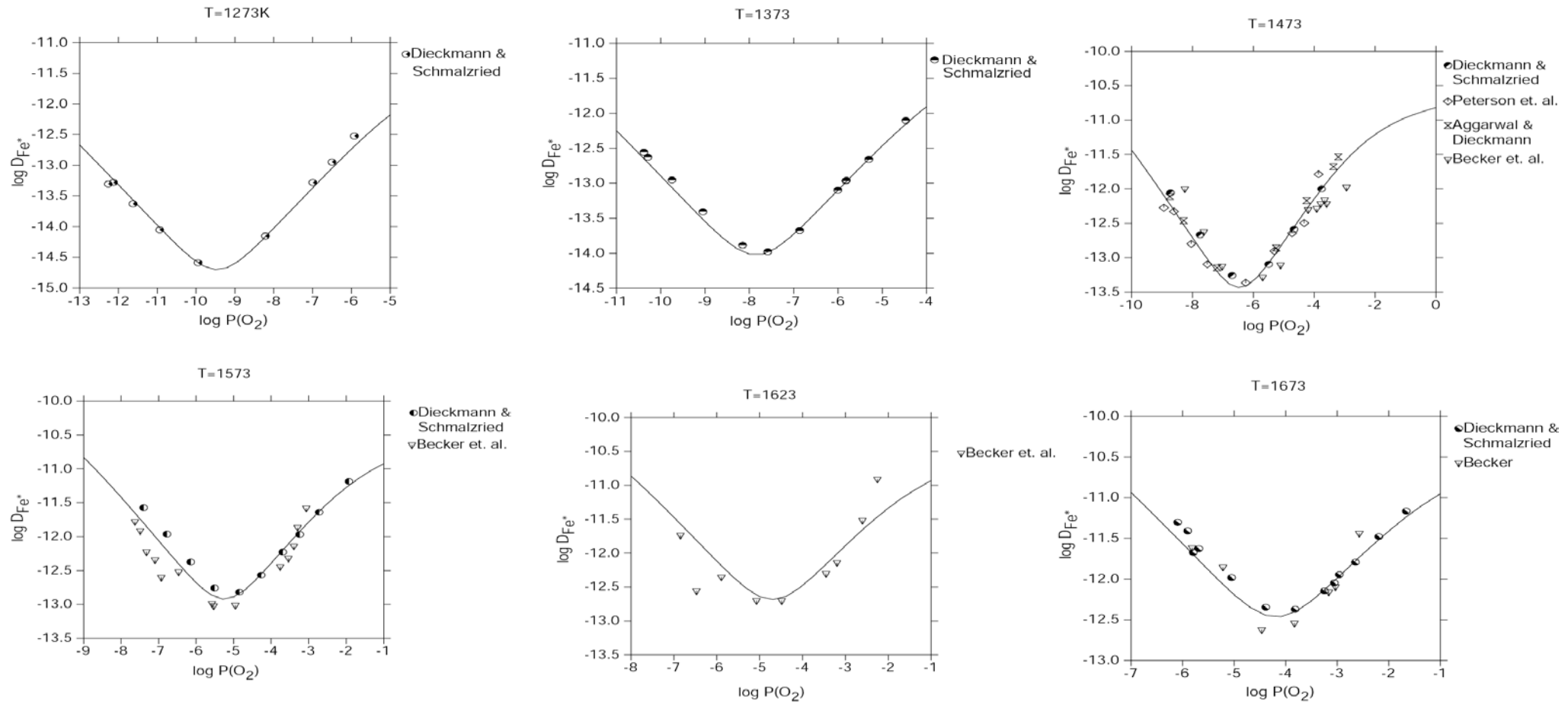
L_{Fe}

$$RTM_k = \delta^2 v \exp(-\Delta G_k / RT)$$

$$D_{Fe^*} \cong RT \frac{1}{2} \left[y_{Va}'' y_{Fe}'' M_{FeVa}'' + y_{Fe}''' y_{Va}''' M_{FeVa}''' \right] \frac{1}{u_{Fe}}$$

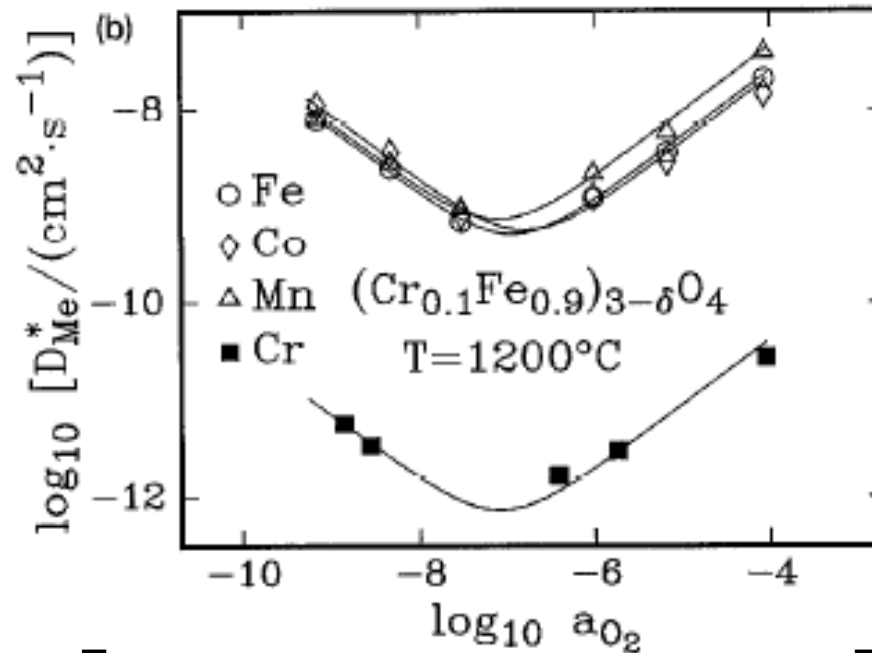
Experimental data on Fe tracer diffusion in spinel - Optimization of Fe mobilities

(Hallström et al. 2011)



Alloy elements in spinel (lattice fixed frame of reference)

Töpfer et.al. 1995



Cr content of inward growing spinel will inherit Cr content of alloy.

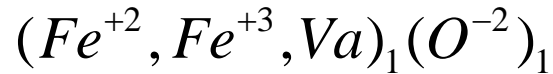
$$J_{Cr} = - \left[y_{Va}'' y_{Cr}'' M_{CrVa}'' + y_{Cr}''' y_{Va}''' M_{CrVa}''' \right] \frac{1}{V_s} \frac{\partial \mu_{Cr}}{\partial z}$$

$$D_{Cr}^* = RT \left[y_{Va}'' y_{Cr}'' M_{CrVa}'' + y_{Cr}''' y_{Va}''' M_{CrVa}''' \right] / u_{Cr}$$

3.c) Defect structures for oxygen diffusion and results

Wüstite (Halite)

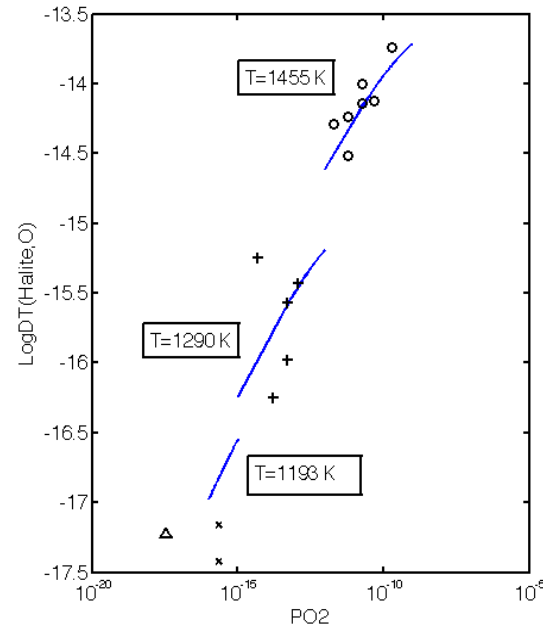
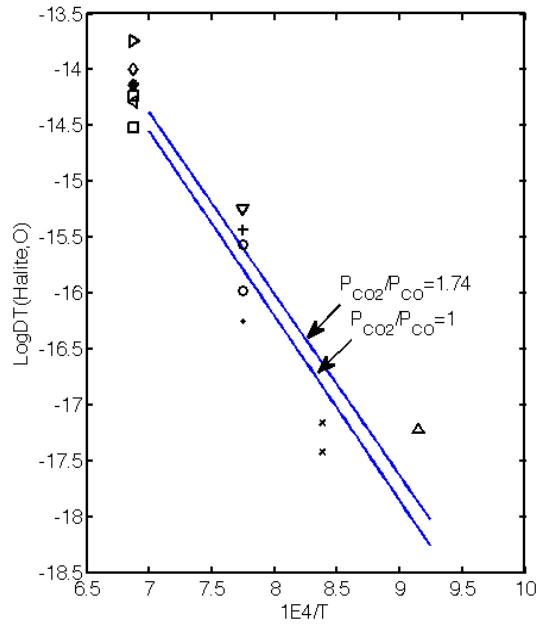
Sundman's model:



Yamagochi et al. 1982 found that oxygen diffusion rate increases with oxygen potential. Thus oxygen vacancies cannot be the dominating mechanism. We thus postulate that oxygen diffuses on interstitial (cation) sites:

$$J_O = - \left[y'_{Va} y''_O M^i_{OVa} \right] \frac{1}{V_m} \frac{\partial \mu_O}{\partial z}$$

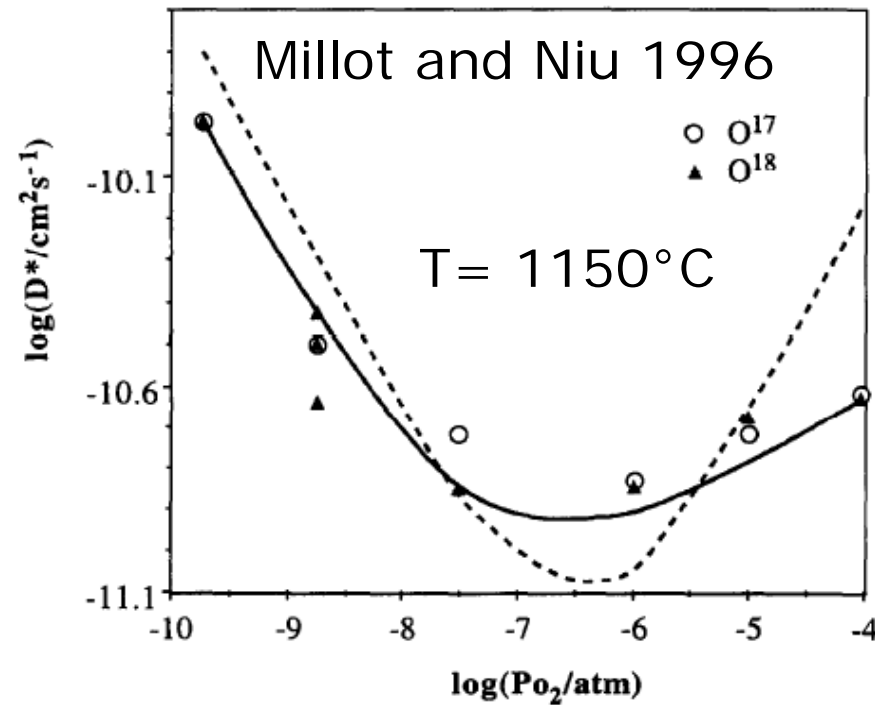
$$D_O^* = \left[y'_{Va} y''_O M^i_{OVa} \right] \frac{1}{n_O}$$



Experiments from Yamaguchi et al 1982

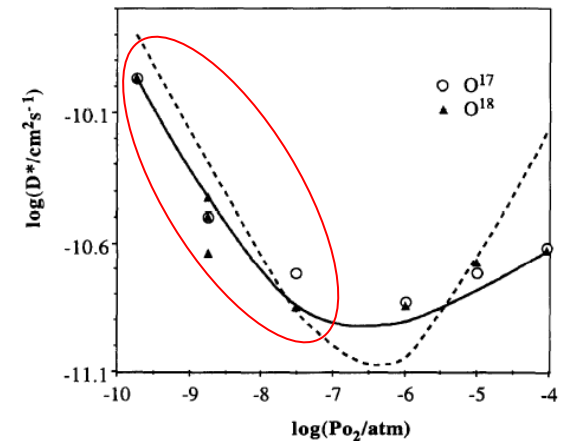
Oxygen tracer diffusion in Wüstite.

3.c) Defect structures for oxygen diffusion and results Magnetite (Spinel)

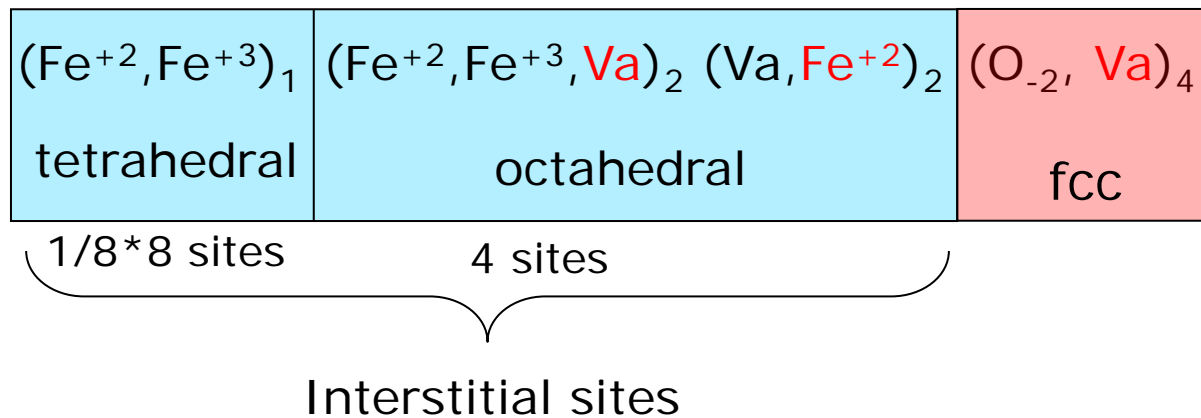


O tracer diffusion in spinel (lattice-fixed frame of reference)

At low oxygen potentials it seems reasonable that oxygen diffusion is assisted by anion vacancies. The lower the oxygen potential, the higher fraction of vacancies and rate of diffusion.



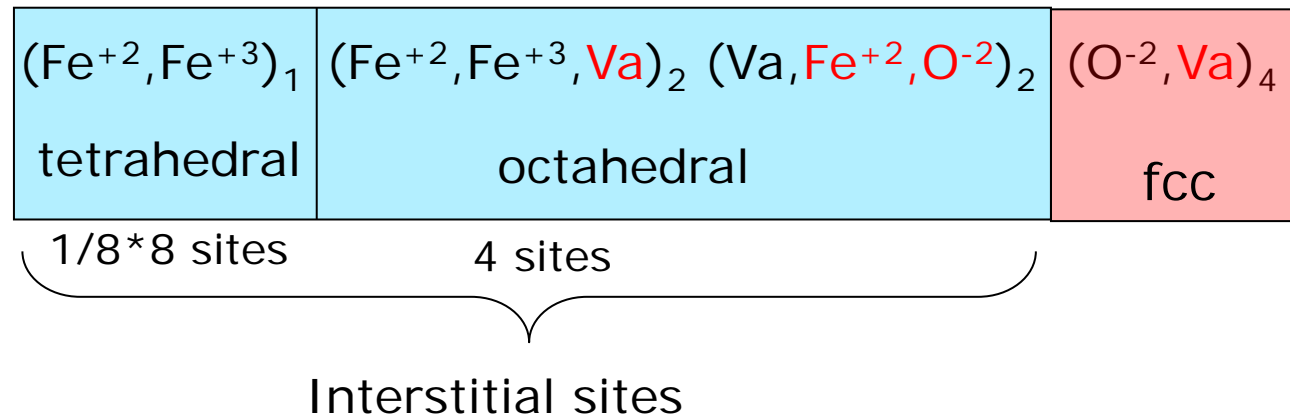
Modification of Sundman's thermodynamic model:



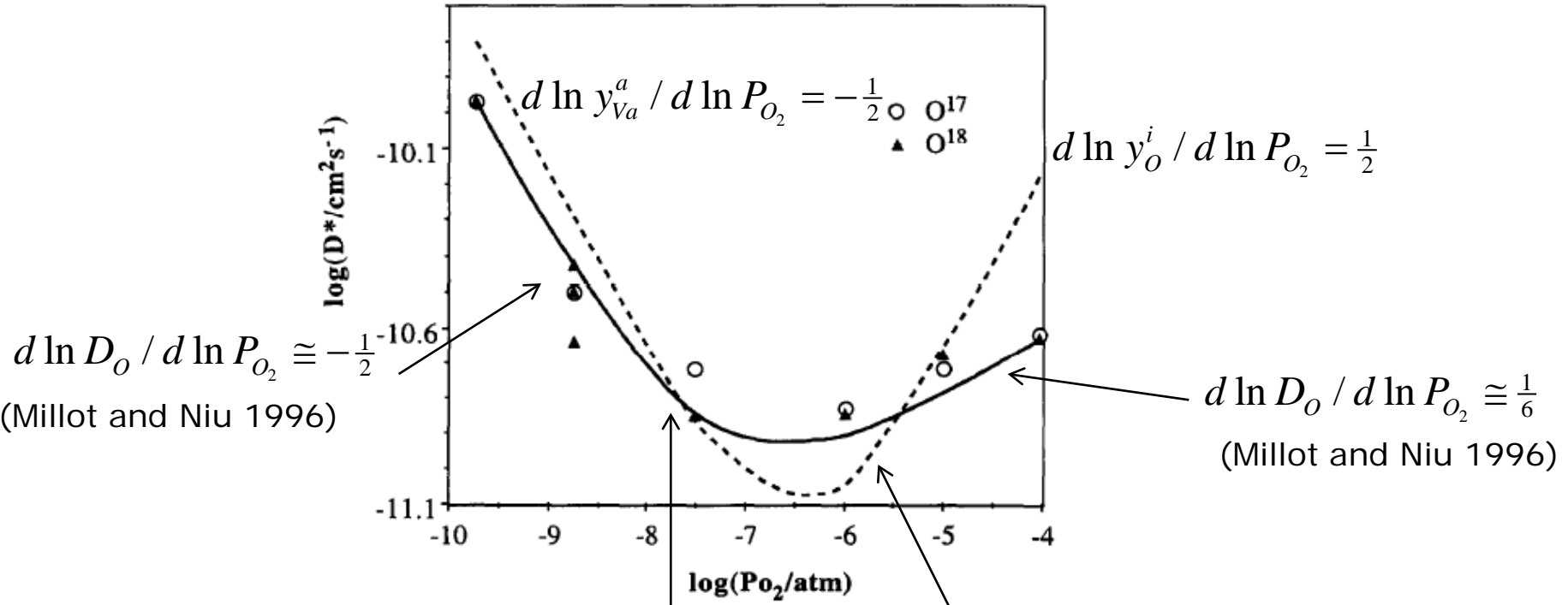
At high oxygen potentials this model predicts very low vacancy fractions . The lower the oxygen potential, the higher fraction of vacancies and rate of diffusion. This is not in agreement with experiments!

Modification of Sundman's thermodynamic model:

Alternativ 1



This may work but gives too a strong increase in vacancy content at high oxygen potentials. It also requires a complete re-assessment of Fe-O!

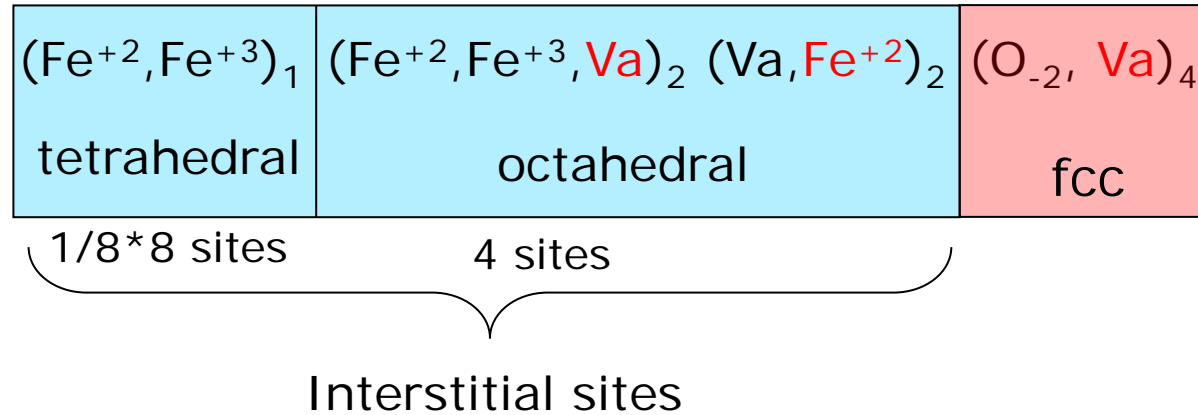


Schematic diagram

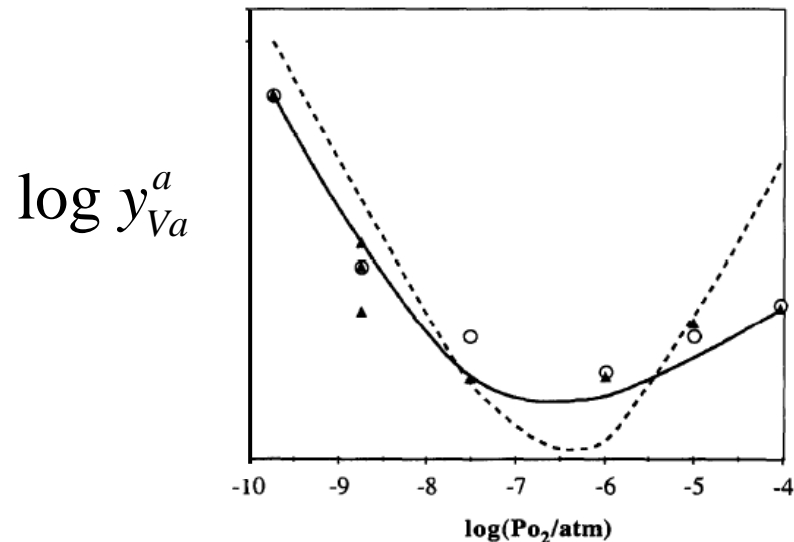
$$J_O = - \left[y_{Va}^a y_O^a M_{OVa}^a + y_O^i y_{Va}^i M_{OVa}^i \right] \frac{1}{V_m} \frac{\partial \mu_O}{\partial z}$$

Modification of Sundman's thermodynamic model:

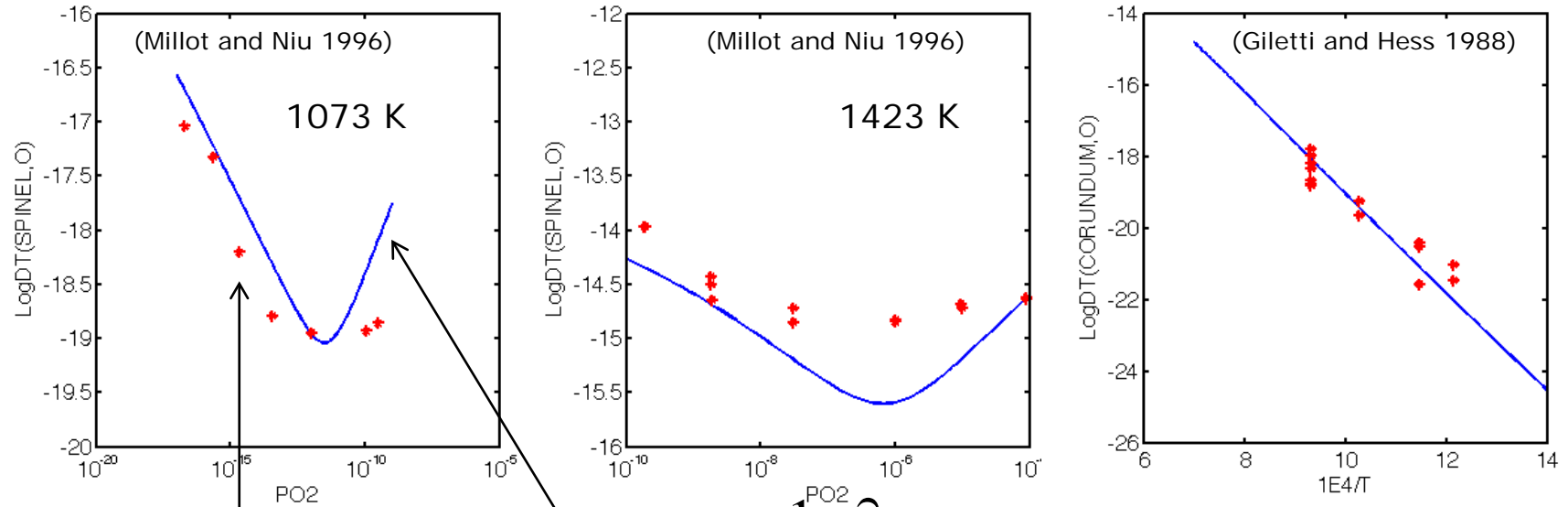
Alternativ 2



Could the vacancy formation energy be chosen such that:



At present we have



$$J_O = -y_O^a \left[y_{Va}^a M_{OVa}^a + y_{Va}^i M_{OVa}^i \right] \frac{1}{V_m} \frac{\partial \mu_O}{\partial z}$$

$$D_O^* = -y_O^a RT \left[y_{Va}^a M_{OVa}^a + y_{Va}^i M_{OVa}^i \right] \frac{1}{n_O}$$

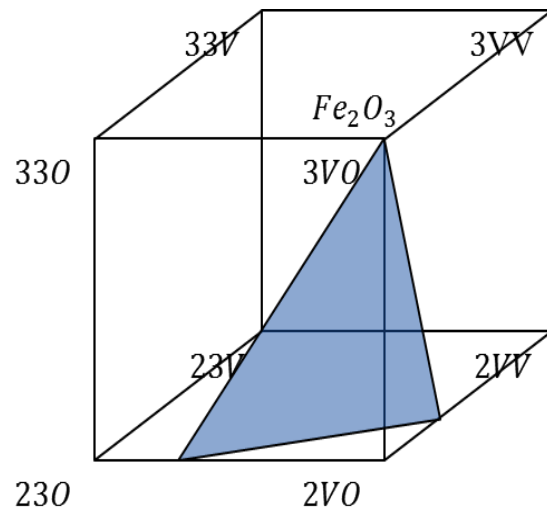
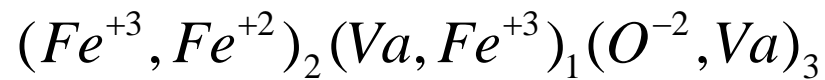
$$M_{OVa}^a = 6.995057e - 10. \exp(-9.774850e4/RT)/RT$$

$$M_{OVa}^i = 2.218464e - 5. \exp(-2.151230e5/RT)/RT$$

3.c) Defect structures for oxygen diffusion and results

Hematite (Corundum)

Kjellqvist et al. 2008



$$G_{2VV}^{\circ} + G_{23O}^{\circ} = G_{2VO}^{\circ} + G_{23V}^{\circ}$$

$$G_{3VO}^{\circ} + G_{2VV}^{\circ} = G_{3VV}^{\circ} + G_{2VO}^{\circ}$$

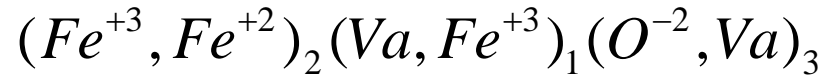
$$G_{2VV}^{\circ} = G_{3VV}^{\circ}$$

$$\frac{2}{3} G_{2VO}^{\circ} + \frac{1}{3} G_{2VV}^{\circ} = G_{3VO}^{\circ} + a' + b'T$$

$$a' = 1200000, \quad b' = 0$$

where 2 denotes Fe^{+2} , 3 Fe^{+3} , V vacancies, and finally O denotes O^{-2} .

"End members" and
plane of electro neutrality

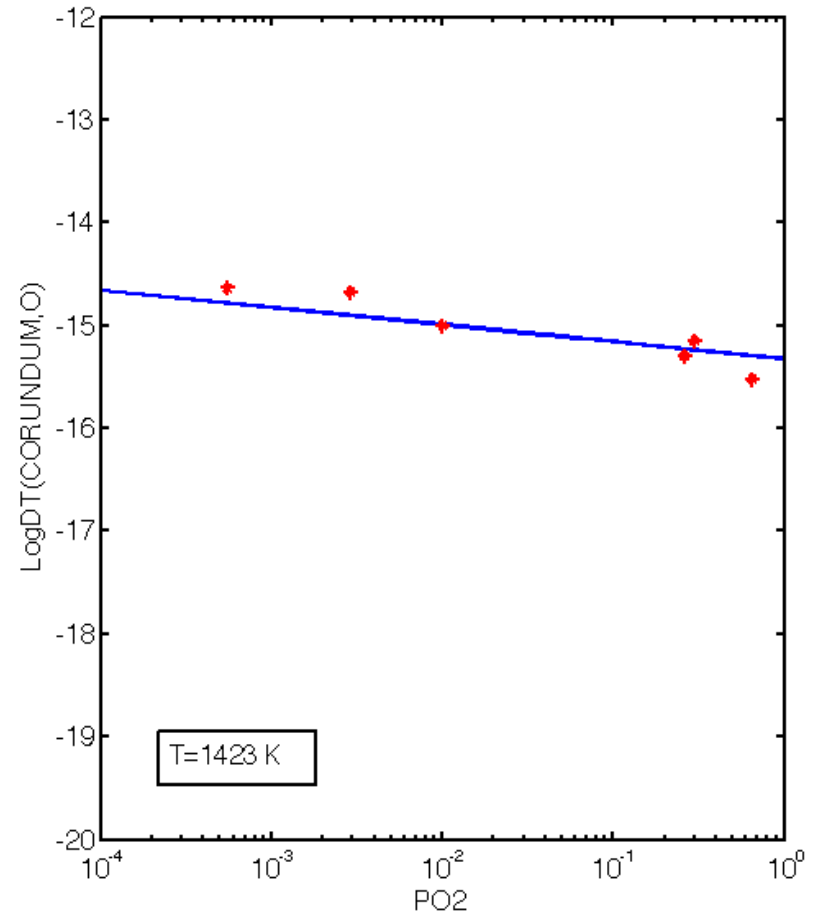
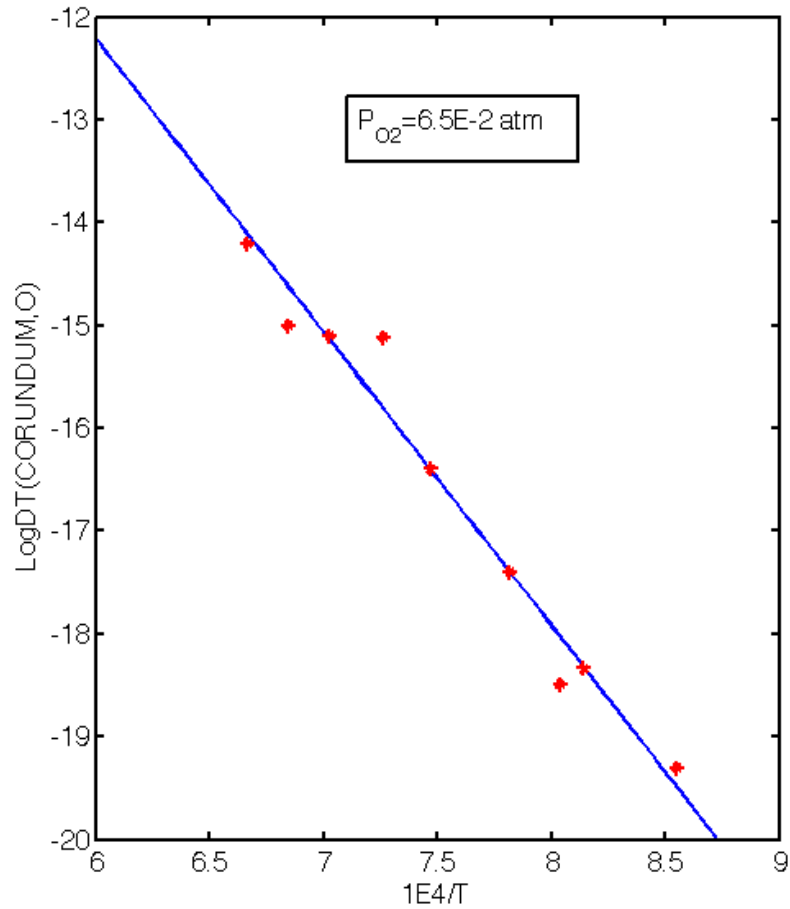


We postulate

$$J_O = - \left[y_{Va}^a y_O^a M_{OVa}^a \right] \frac{1}{V_m} \frac{\partial \mu_O}{\partial z}$$

$$D_O^* = \left[y_{Va}^a y_O^a M_{OVa}^a \right] \frac{1}{n_O}$$

Experiments: Amami et al. 1999

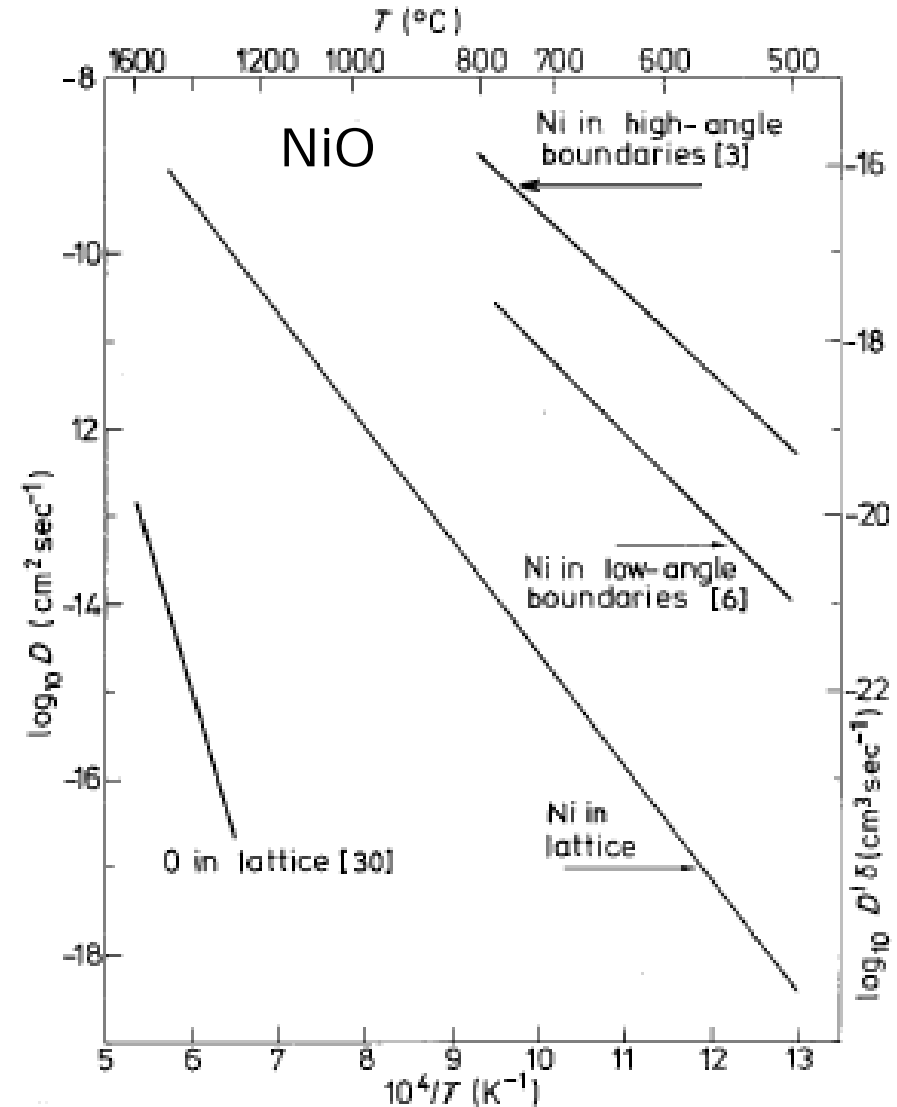


4. Grain boundary diffusion

Simplified approach:

$$D_{eff} = (1 - \delta / d) D_{bulk} + \delta / d D_{gb}$$

$$Q_{gb} \cong \alpha Q_{bulk} \quad 0.3 < \alpha < 0.5$$



5. Kirkendall porosity

Oxygen is substitutional, divergence of oxygen flux gives Kirkendall effect:

$$\frac{v}{V_m} = -J = -J'_{O^{-2}} / x_{O^{-2}} \quad V_m = \text{molar volume/mole of atoms}$$

Rate of density ($\rho = 1/V_m$) change:

$$\frac{1}{V_m^2} \dot{V}_m = \mathbf{div}(J)$$

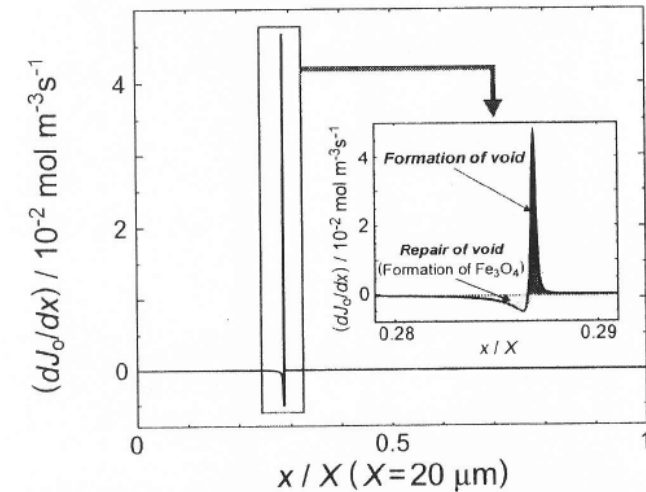
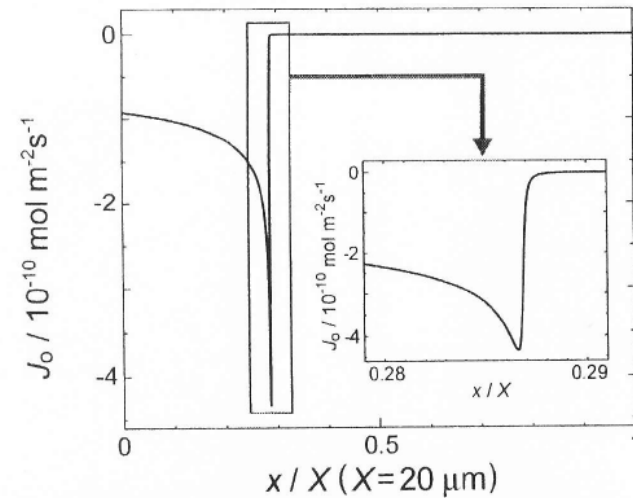
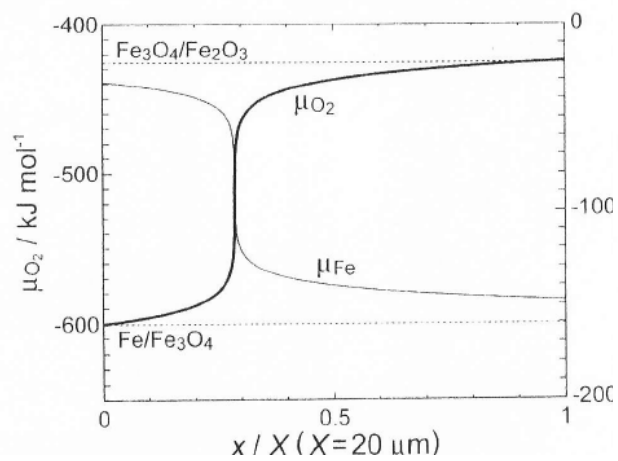
No porosity \Rightarrow Strain rate:

$$\dot{\epsilon}_{11} + \dot{\epsilon}_{22} + \dot{\epsilon}_{33} = \frac{1}{V_m} \dot{V}_m = V_m \mathbf{div}(J)$$

Only porosity (volume fraction f_p):

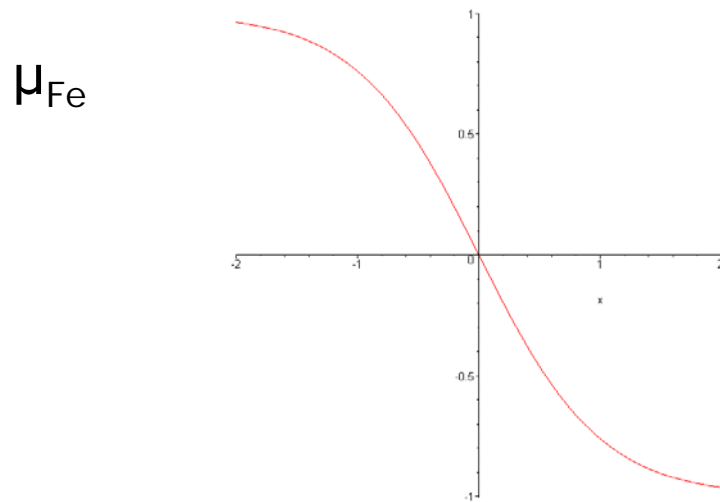
$$\frac{\dot{f}_p}{(1-f_p)^2} = -V_m \mathbf{div}(J)$$

Maruyama et al. 2004



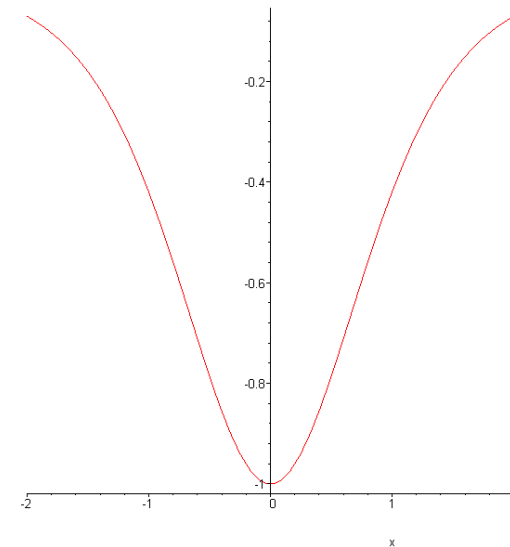
Voids form as a consequence of a divergence in the oxygen flux.

Schematics of Kirkendall effect in magnetite



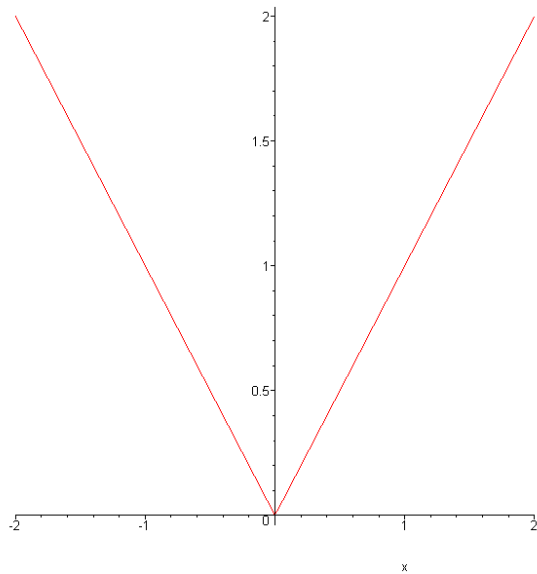
Distance

$$\frac{\partial \mu_{Fe}}{\partial z}$$



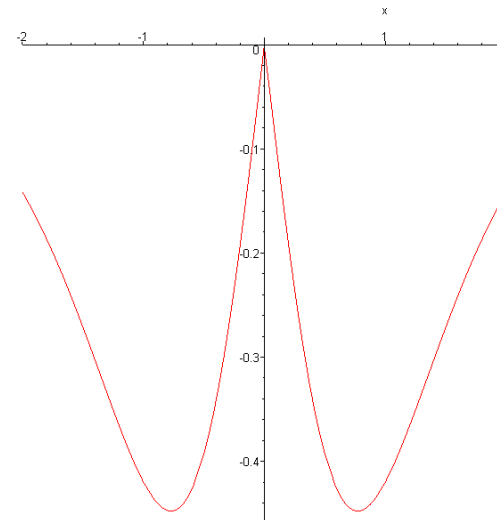
Distance

Oxygen mobility



Distance

Oxygen flux

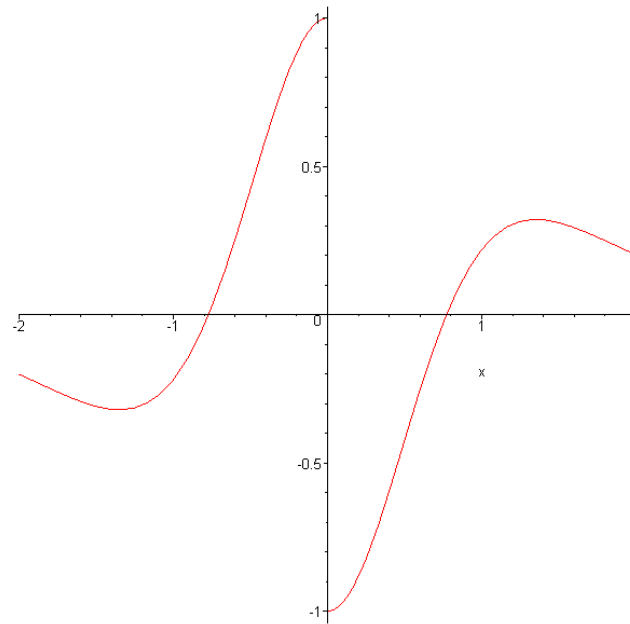


Distance

$$\partial y_{va} / \partial t = \partial J_o / \partial z$$

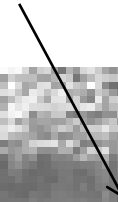
Pores

Pores



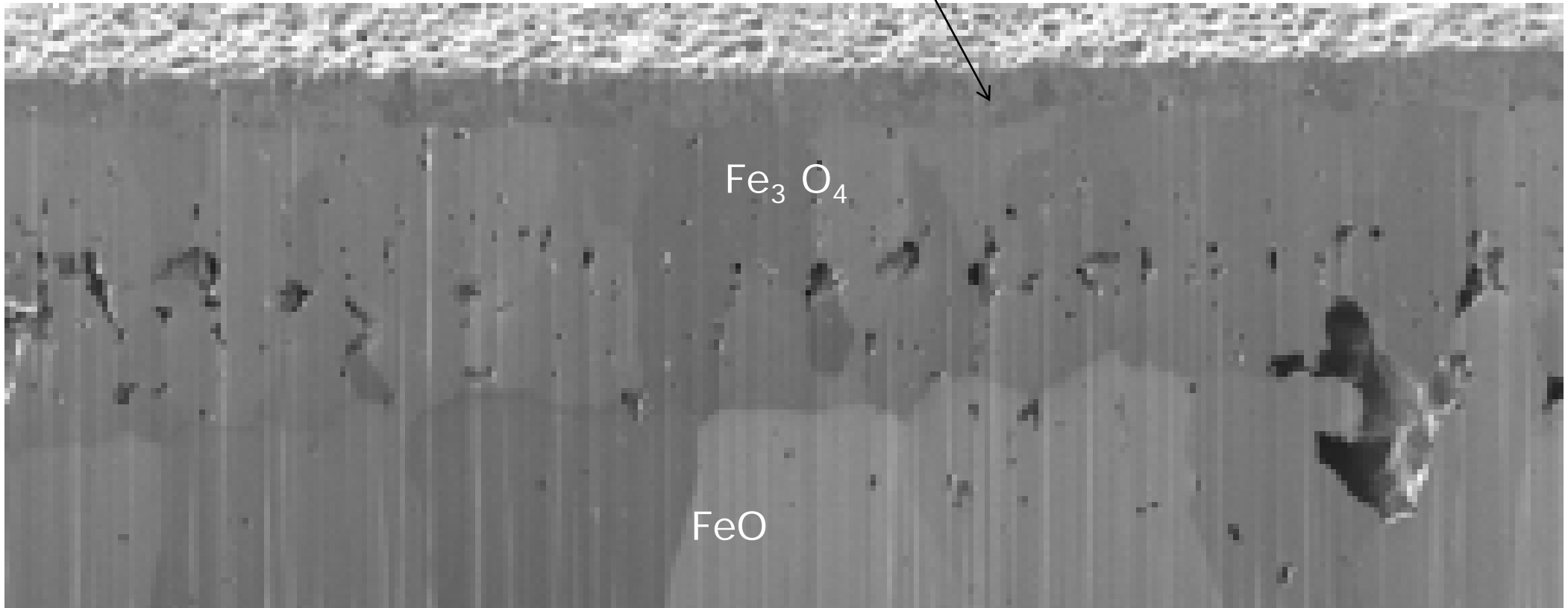
Distance

Fe_2O_3



Fe_3O_4

FeO



T. Jonsson et al. 2008

Summary

- DICTRA can now handle diffusion in oxides allowing prediction of oxidation.
- Data base now contains diffusional mobilities of
 - Wüstite (Halite): Fe and O
 - Magnetite (spinel): Fe Cr O
 - Hematite (Corundum): Fe, Cr, O
- Grain boundary diffusion is taken into account in a simplified manner.
- Oxygen diffusion may cause Kirkendall effect and porosity.