ORP-42447-VA
Revision 0

Crystallization in High-Level Waste Glasses

U.S. Department of Energy - Office of River Protection, WTP Engineering Division

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Office of River Protection

P.O. Box 450
Richland, Washington 99352

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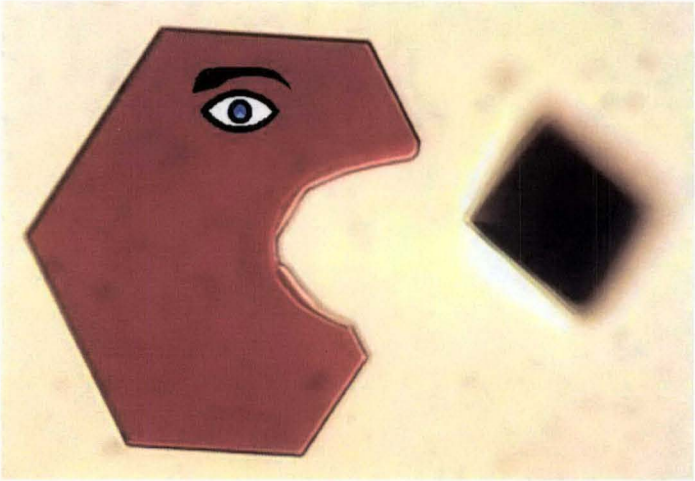
Crystallization in High-Level Waste Glasses



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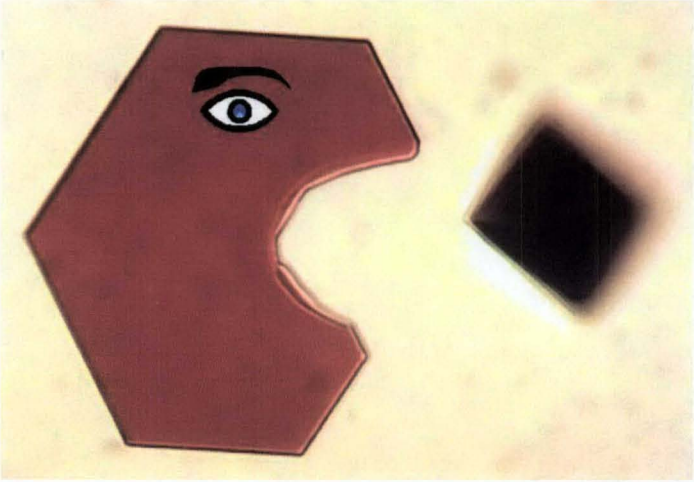
Crystallization in High-Level Waste Glasses



Pavel Hrma

Pacific Northwest National Laboratory

Richland, Washington

Crystallization in a Multicomponent Glass under General Conditions

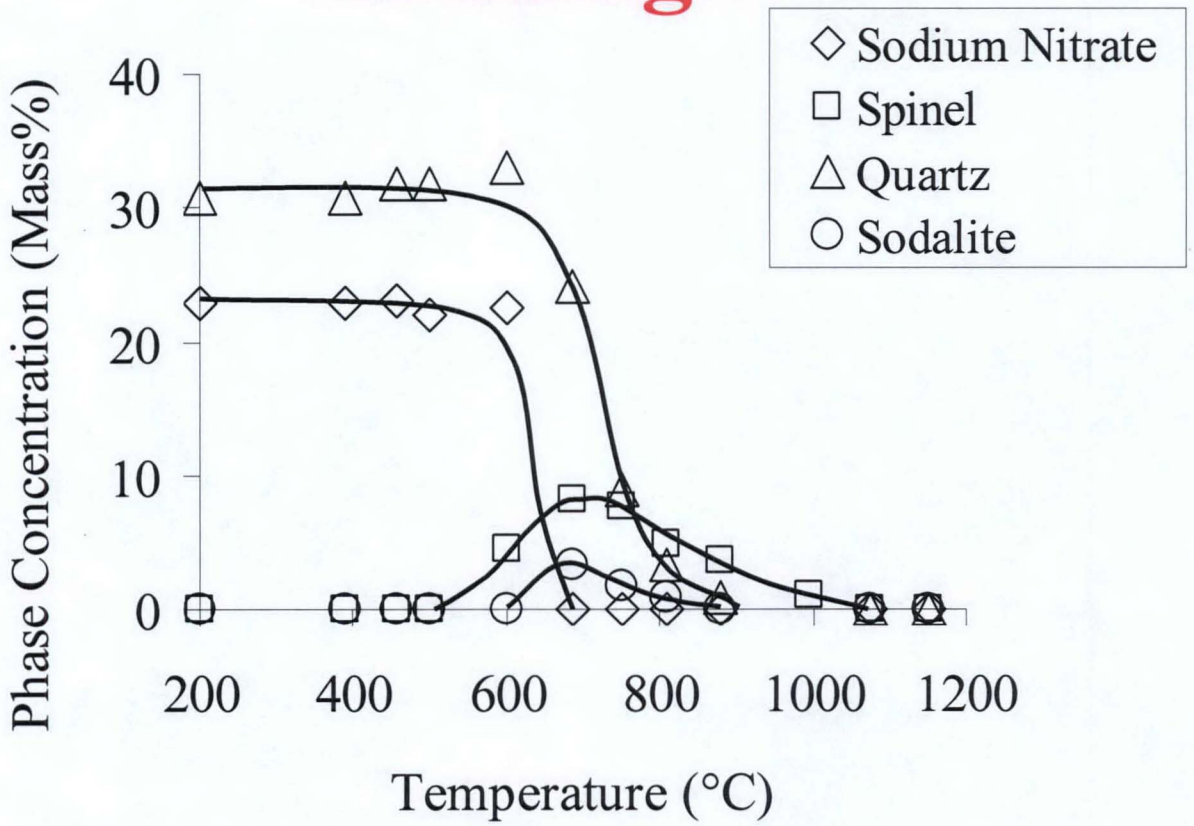
Various circumstances influence crystallization in glassmaking, for example

- Crystals nucleate and grow before the glass-forming melt occurs
- Crystals grow or dissolve in flowing melt and during changing temperature
- Crystals move under the influence of gravity
- Crystals agglomerate and interact with gas bubbles

Crystallization in HLW Glass

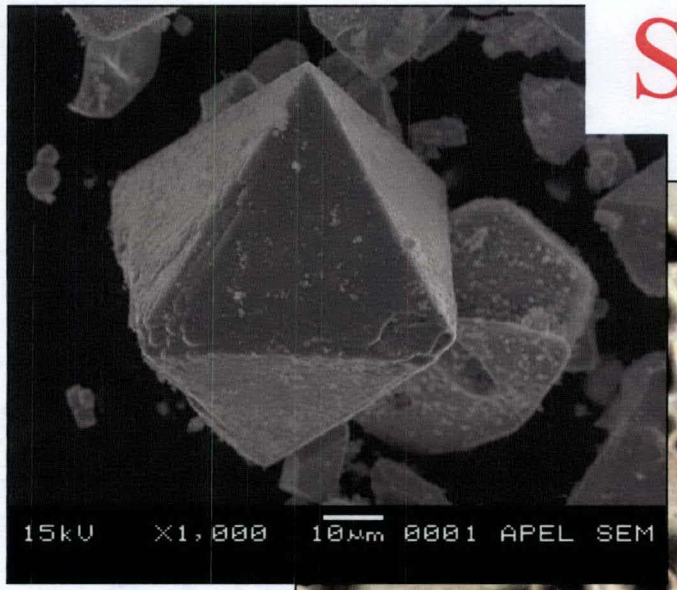
- High-level wastes (HLW) are mixtures of a large number of components in unusual proportions
- Melter processing of HLW and the slow cooling of HLW glass in canisters provides an opportunity for a variety of crystalline forms to precipitate
- Settling of crystals in a HLW glass melter may produce undesirable sludge at the melter bottom
- Crystallization of the glass product may increase, but also ruin chemical durability

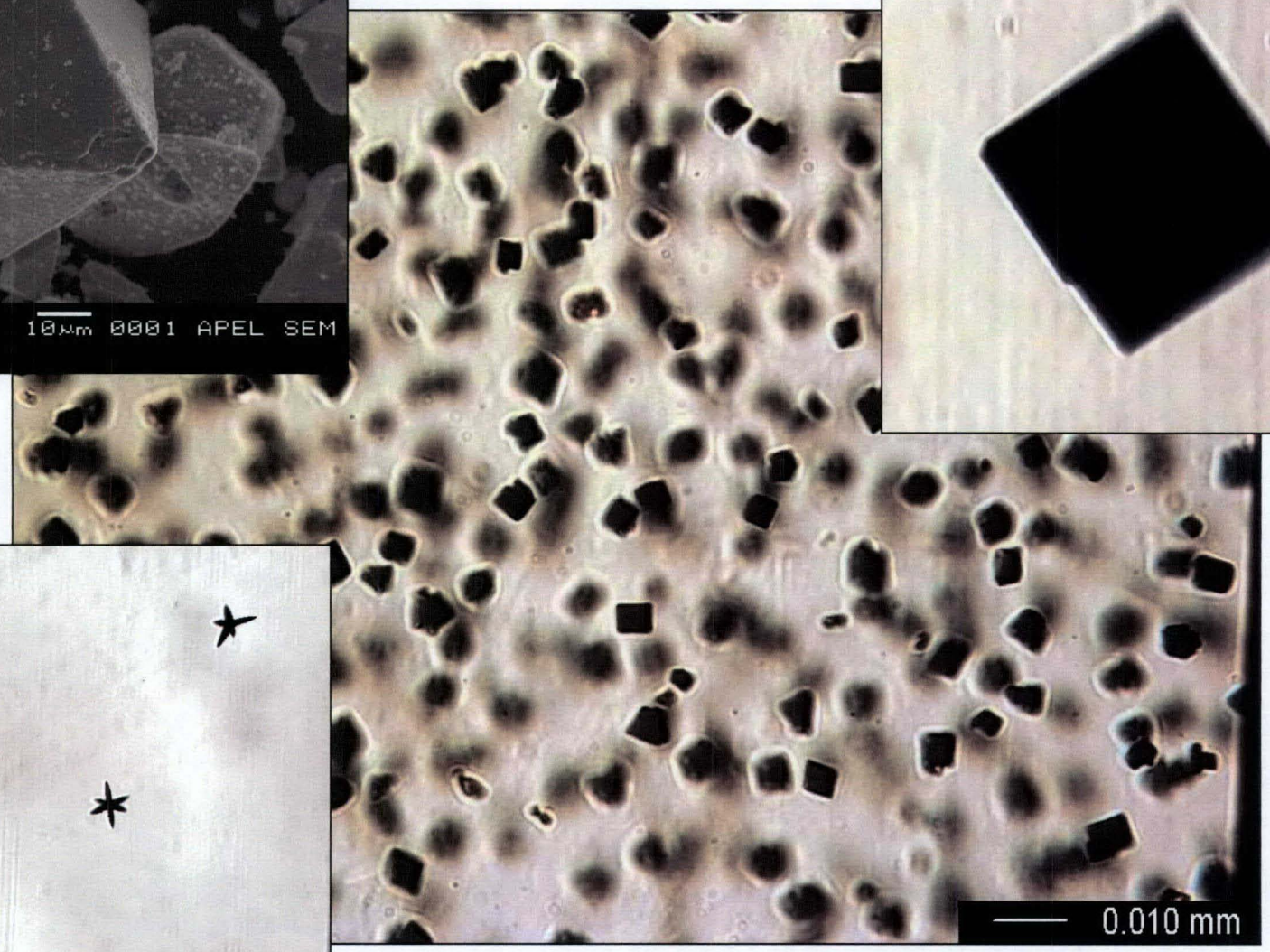
Crystalline Phases that Form in Nuclear Waste Glass during Melting

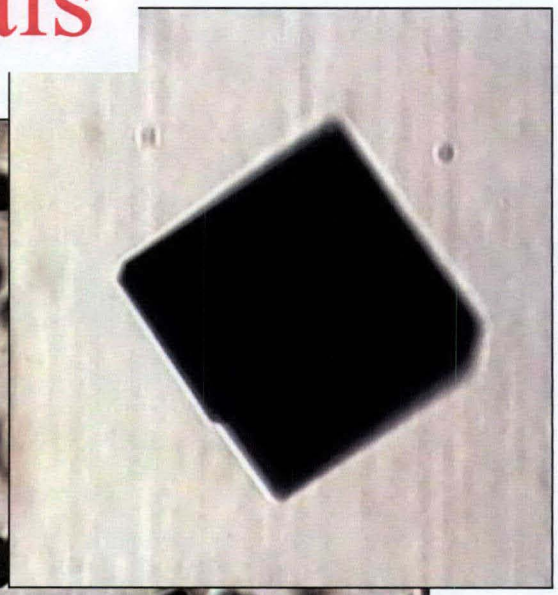


4°C/min

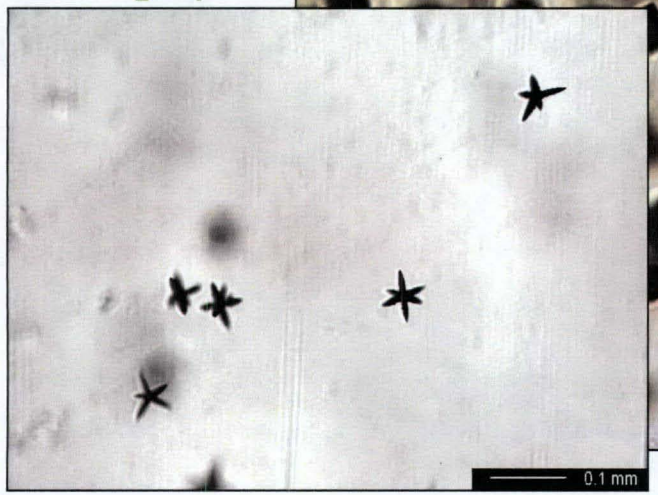
Spinel Crystals



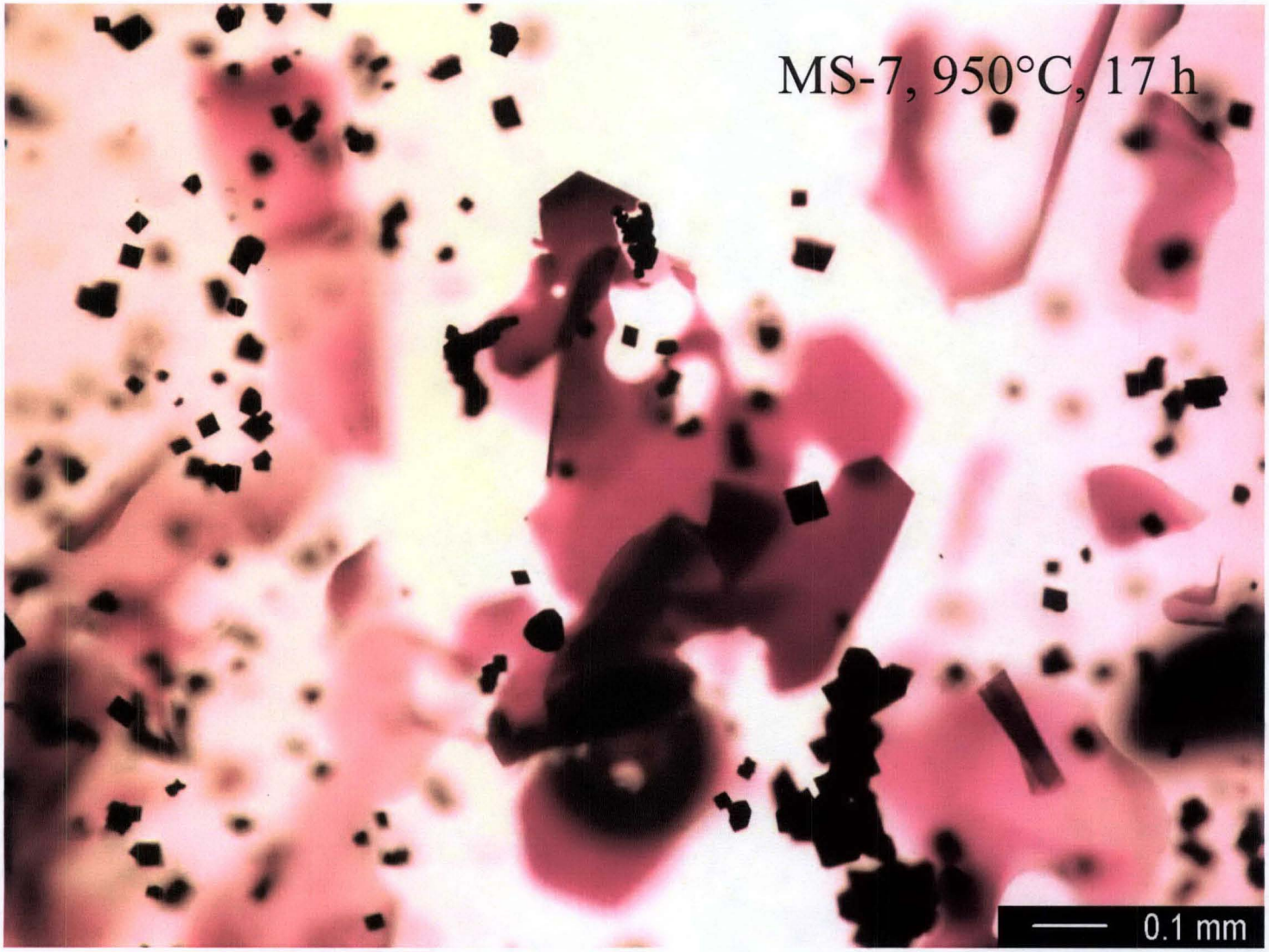




Fe_3O_4
$NiFe_2O_4$
$FeCr_2O_4$

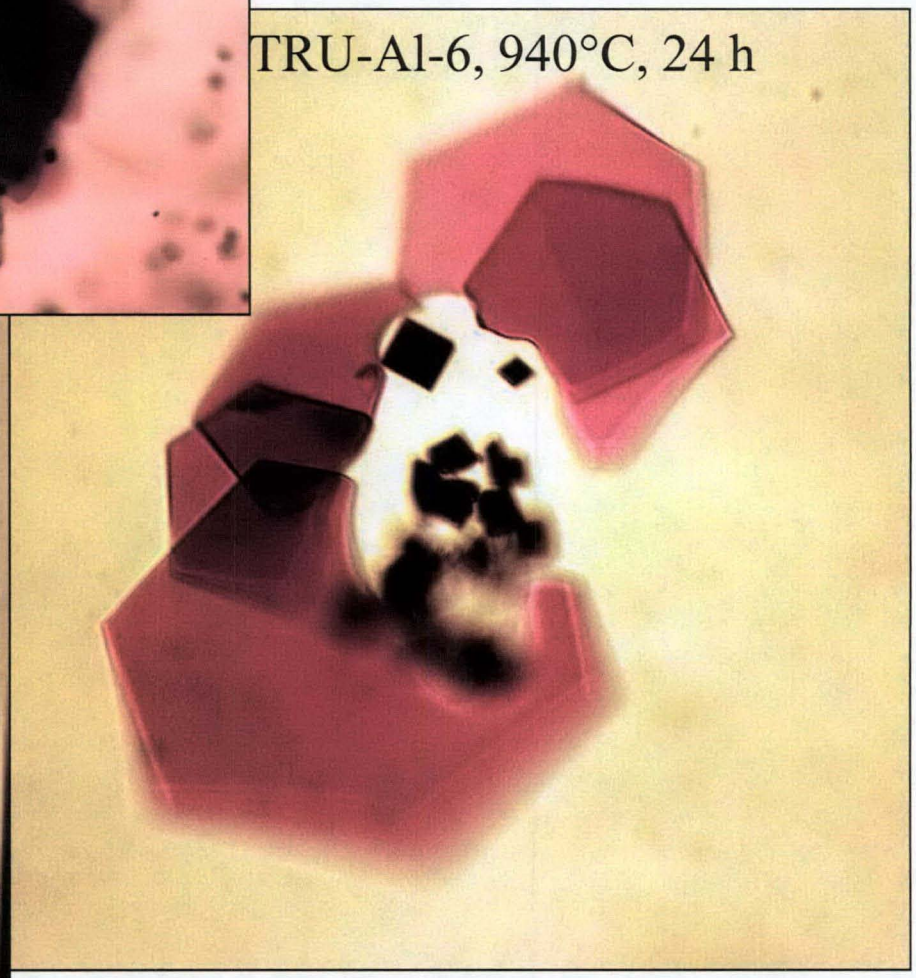


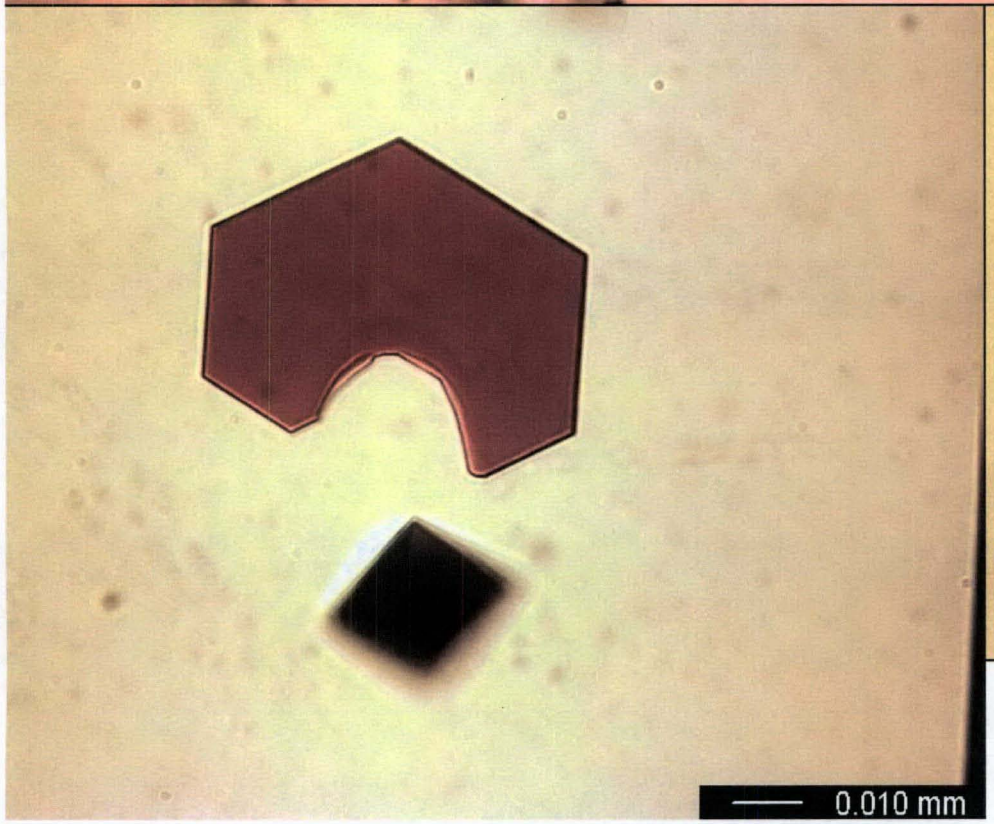
Hematite and Spinel



← **Zircon, hematite and spinel**

TRU-Al-6, 940°C, 24 h





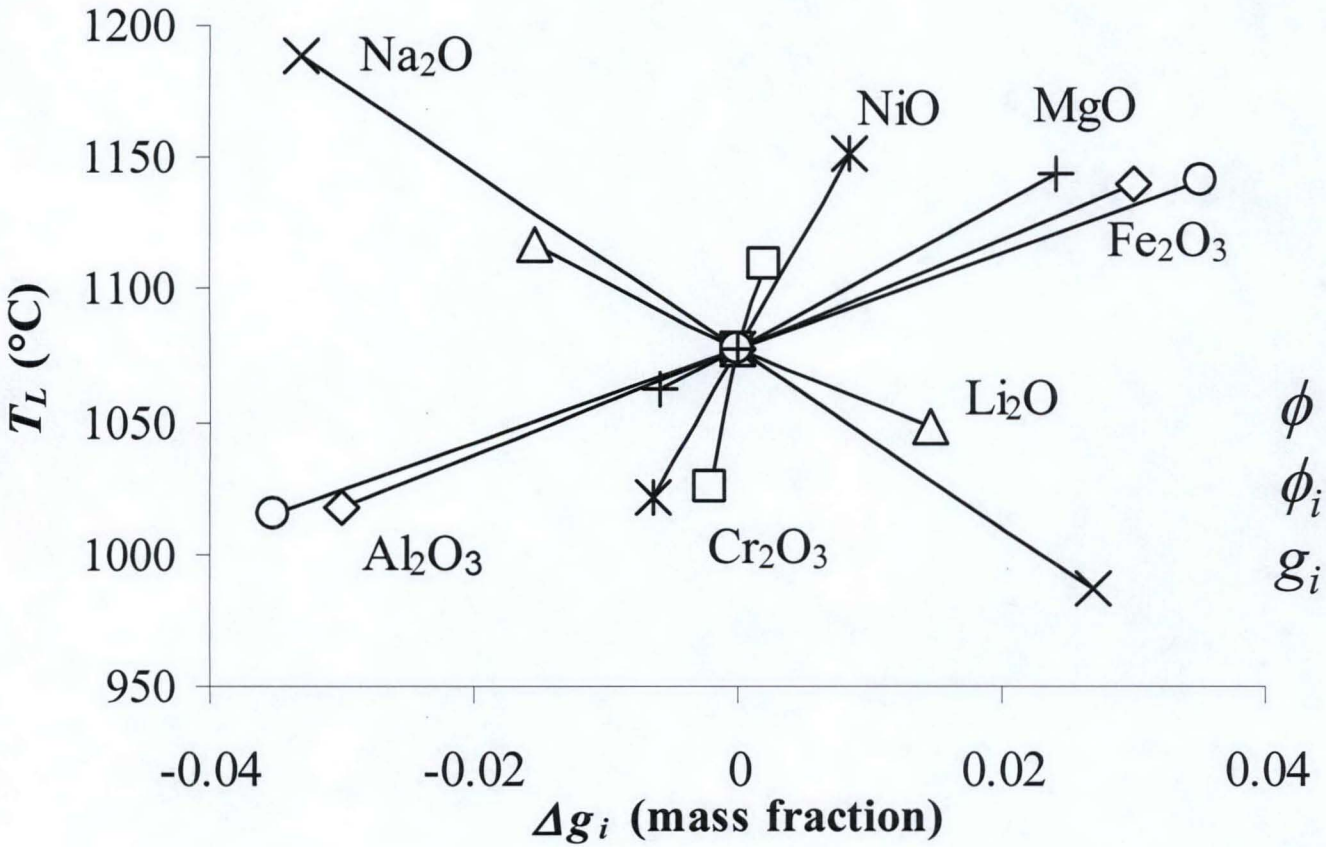
←↑**Hematite and spinel**

MS-7, 950°C, 5 h

Phase Equilibria

Liquidus Temperature (T_L)

Spinel primary phase



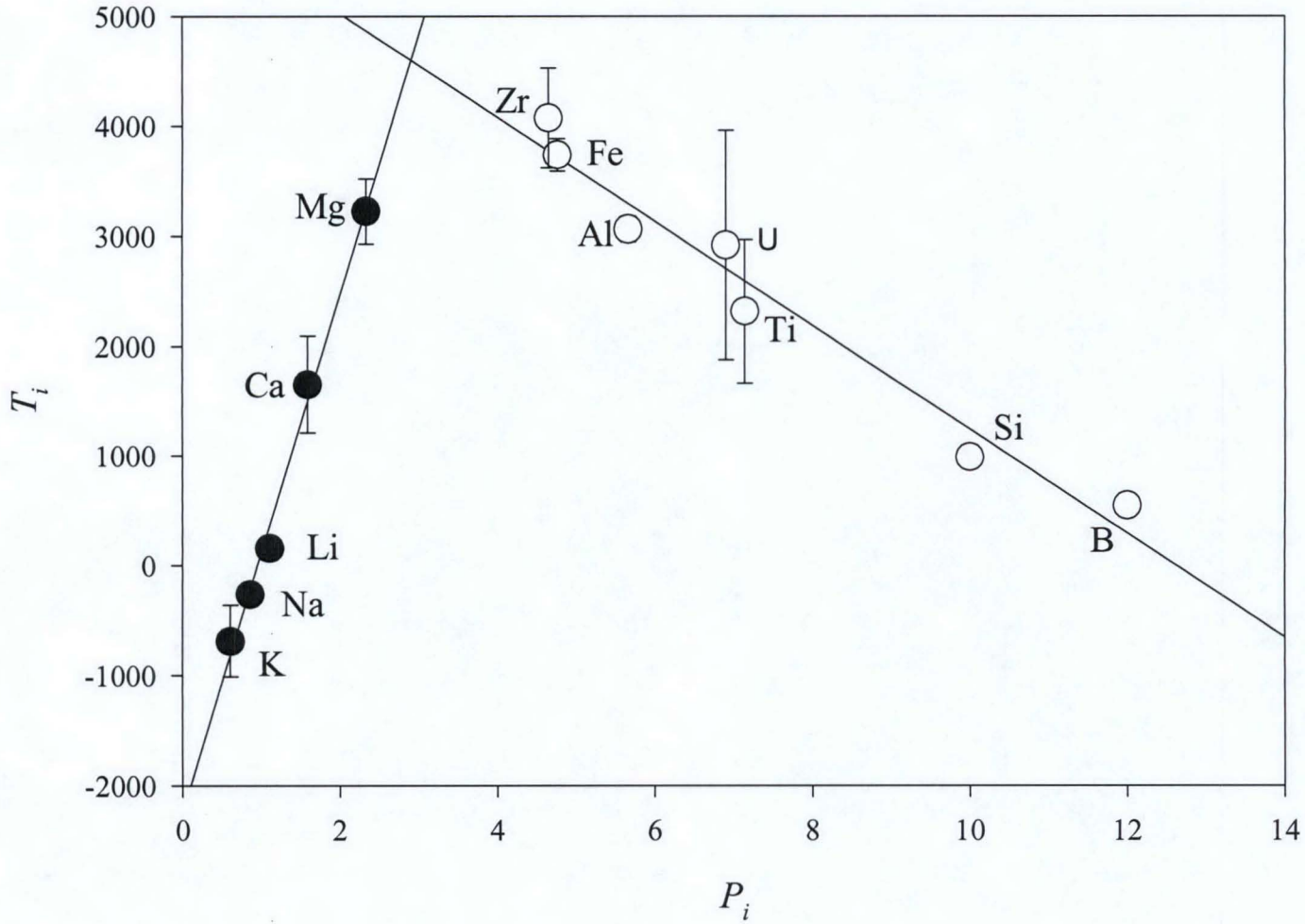
$$\phi = \sum_{i=1}^{N} \phi_i g_i$$

ϕ glass property

ϕ_i partial property

g_i mass/mol fraction

Spinel T_L versus Ionic Potential (P_i)



Spinel T_L vs. P_i

$$T_L = \sum_{Ni,Cr,Mn} T_i x_i + \sum_{Alk,AlkE} (t_{ion} + \Theta_{ion} P_i) x_i + \sum_{remaining} (t_{cov} + \Theta_{cov} P_i) x_i$$

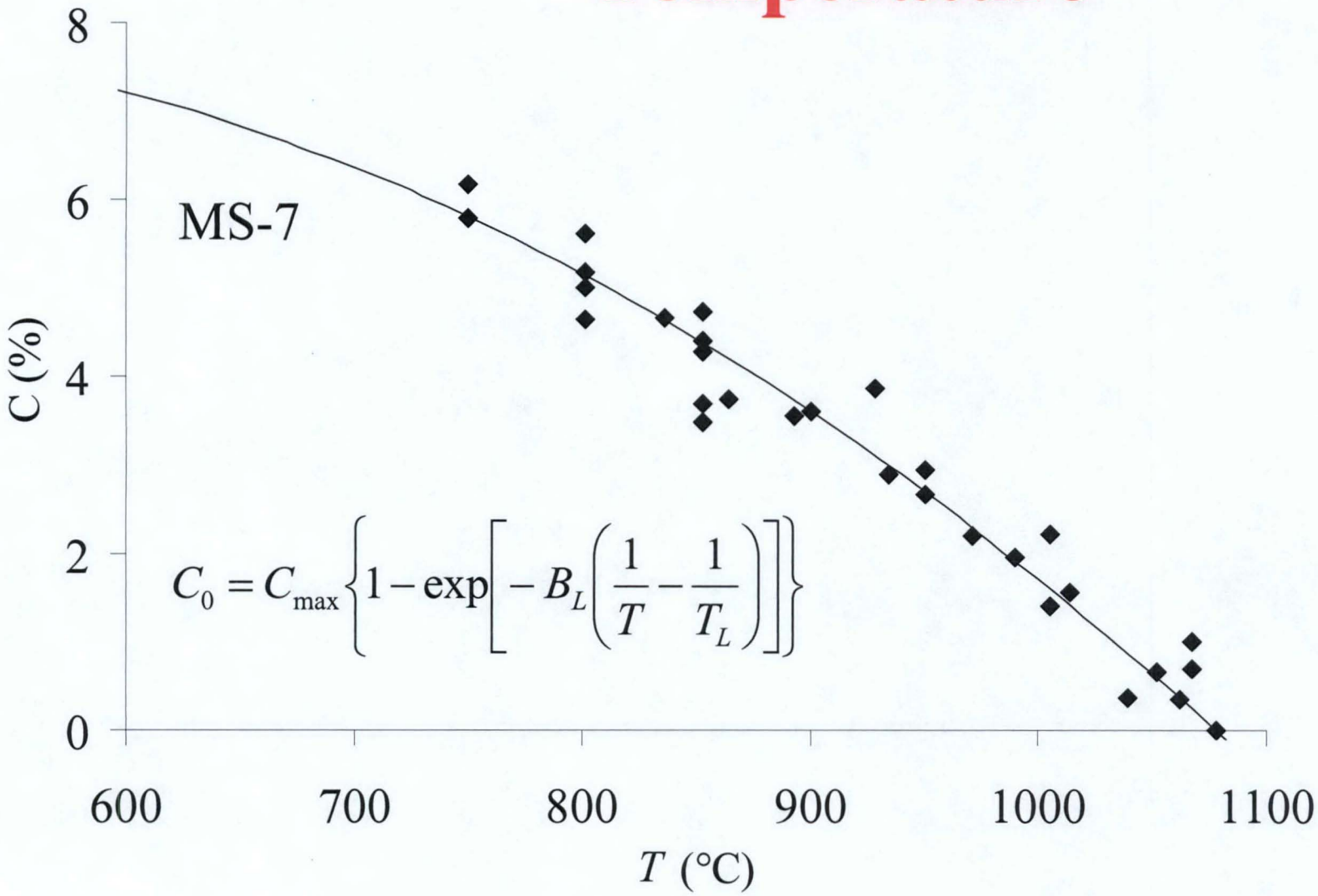
T_i coefficients for Ni, Mn, and Cr

t_{ion}, t_{cov}, Θ_{ion}, Θ_{cov} coefficients for ionic and remaining components

x_i mole fraction of the i-th electropositive element

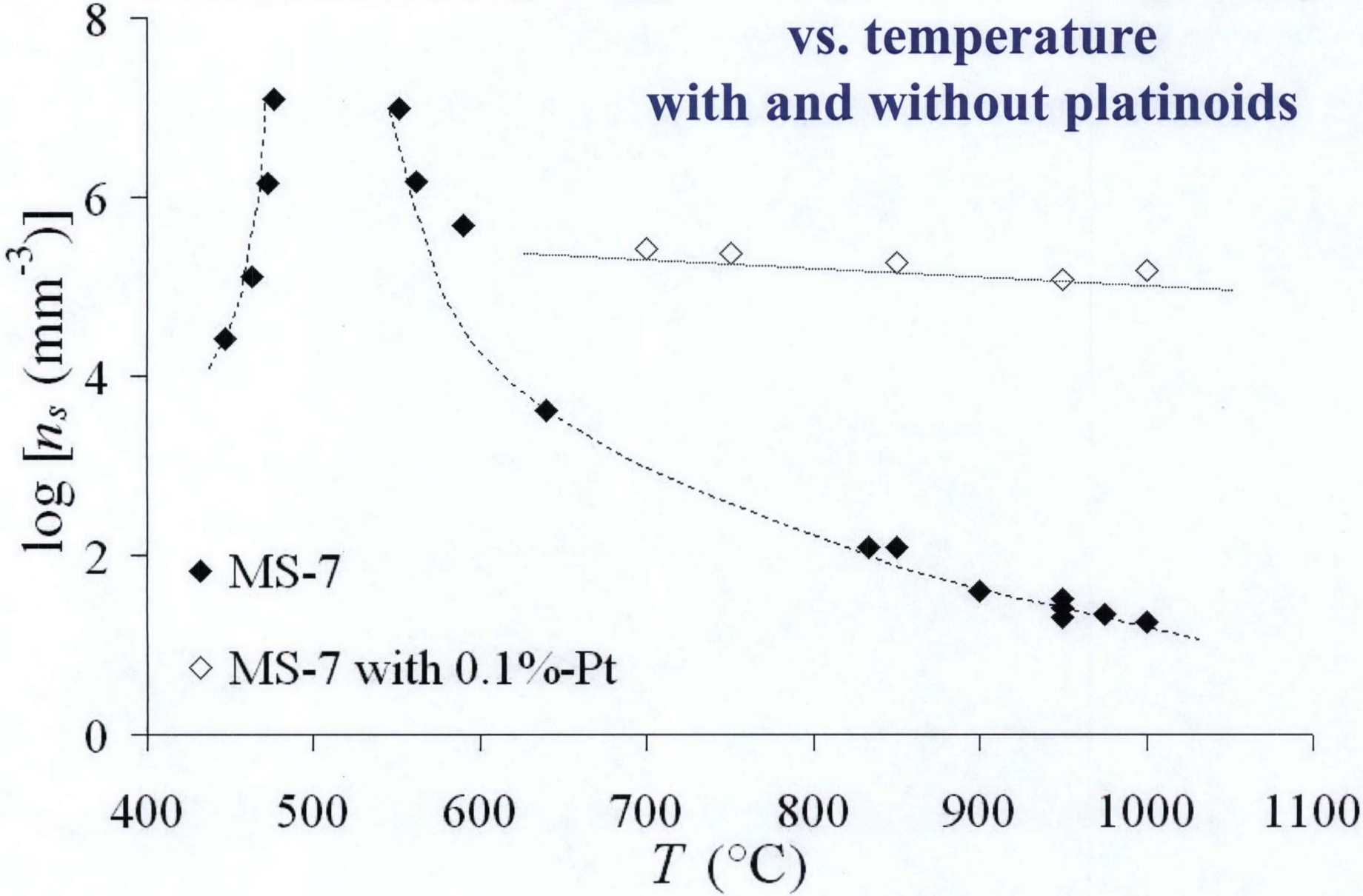
Coefficients for ionic and remaining components can be estimated also for components for which no data exist

Equilibrium Concentration vs. Temperature



Nucleation

Spinel crystal number density vs. temperature with and without platinoids



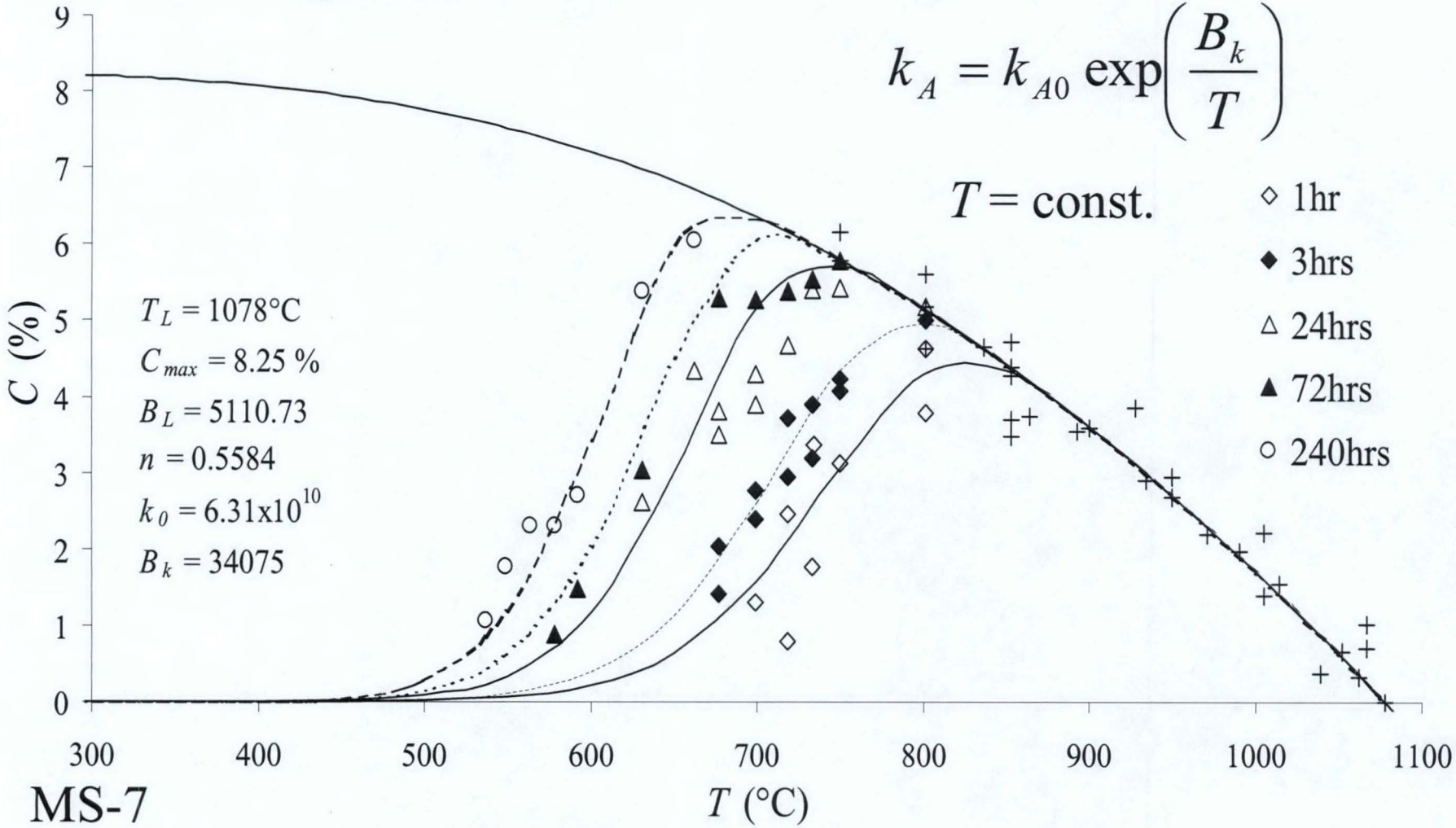
Crystal Growth

Kolmogorov-Mehl-Johnson-Avrami Equation

$$\frac{C_0 - C}{C_0 - C_i} = \exp\left[-(k_A t)^n\right]$$

$$k_A = k_{A0} \exp\left(\frac{B_k}{T}\right)$$

$T = \text{const.}$

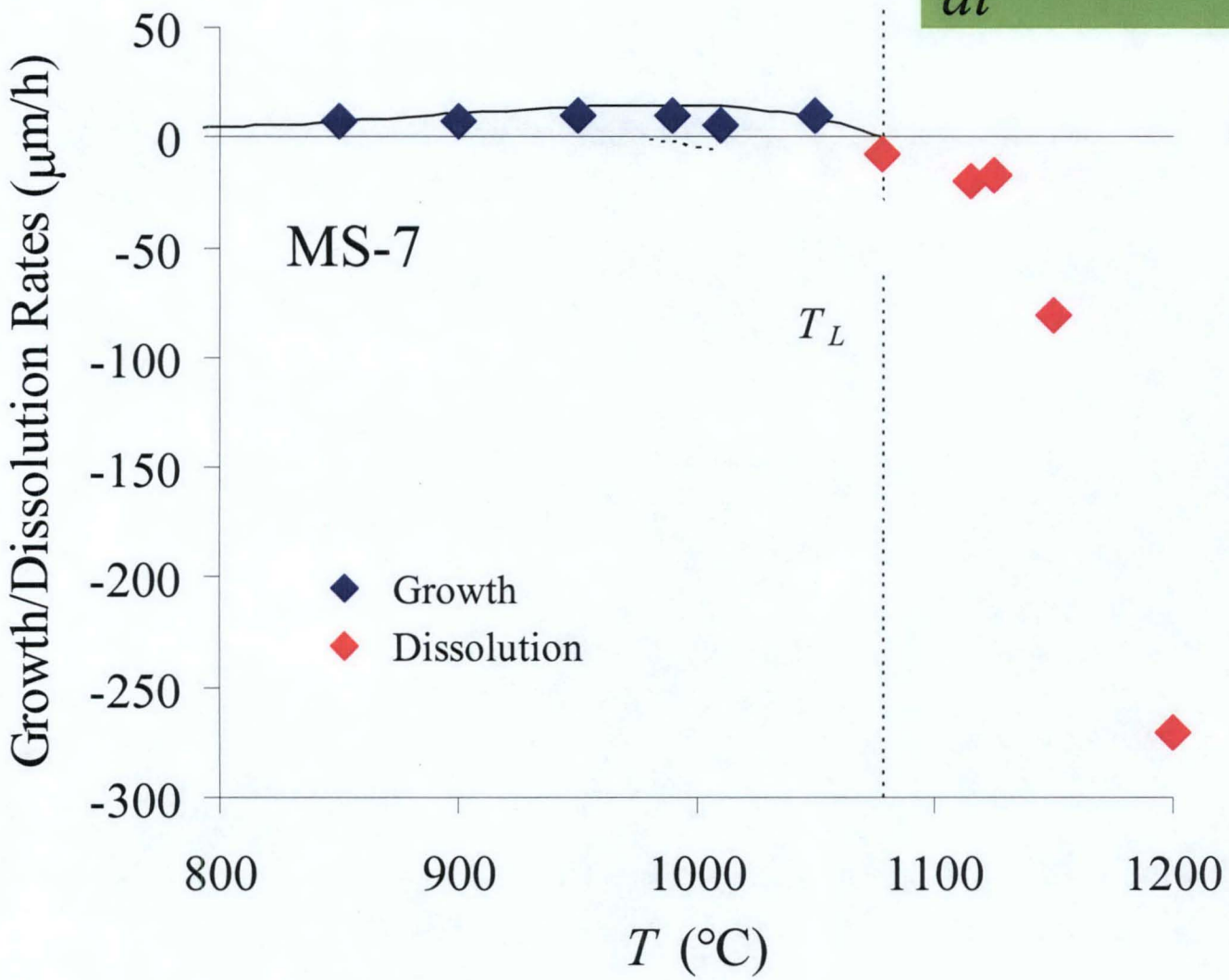


MS-7

Crystal Growth and Dissolution

Hixson-Crowell Equation

$$\frac{da}{dt} = 2n_S k_H \left(a_0^3 - a^3\right)$$



$$k_H = k_{H0} \exp\left(\frac{B_H}{T}\right)$$

a	crystal size
t	time
k	mass transfer coefficient
C	concentration
C_0	equilibrium concentration

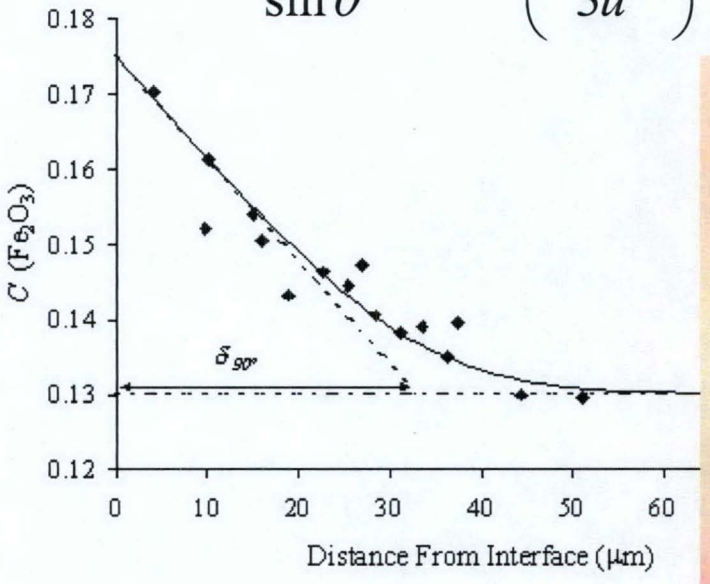
Diffusion-Controlled Dissolution of Falling Particle

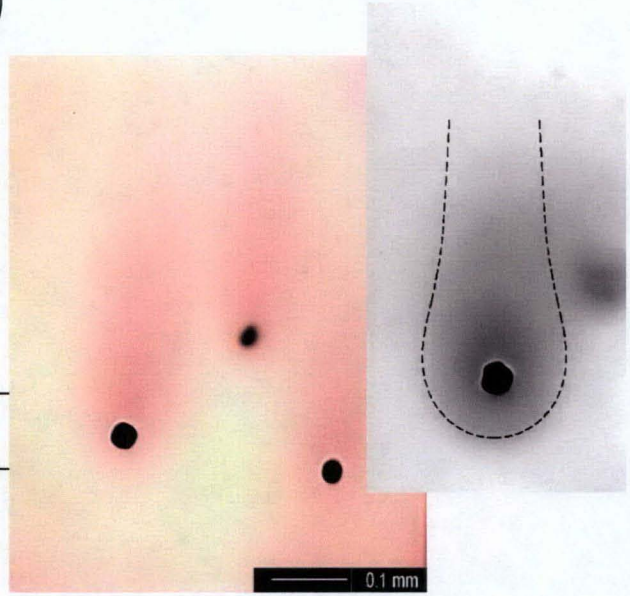
Concentration-boundary-layer thickness around a dissolving or growing spherical particle (Levich)

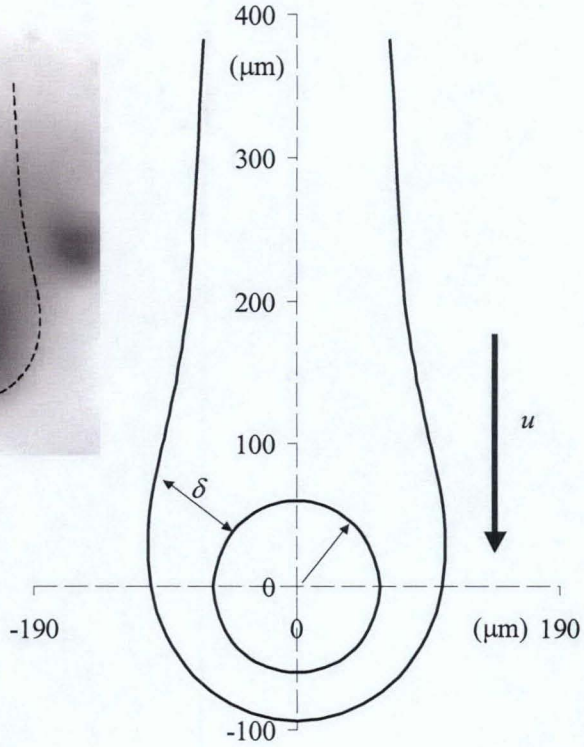
$$\delta = \frac{1.15\left(\theta - \frac{\sin 2\theta}{2}\right)^{1/3}}{\sin\theta}\left(\frac{4Dr^2}{3u}\right)^{1/3}$$

D diffusion coefficient,
r particle radius
u particle velocity

$$\dot{r} = \frac{\rho_g}{\rho_s}\frac{D}{\delta}(C_0 - C)$$



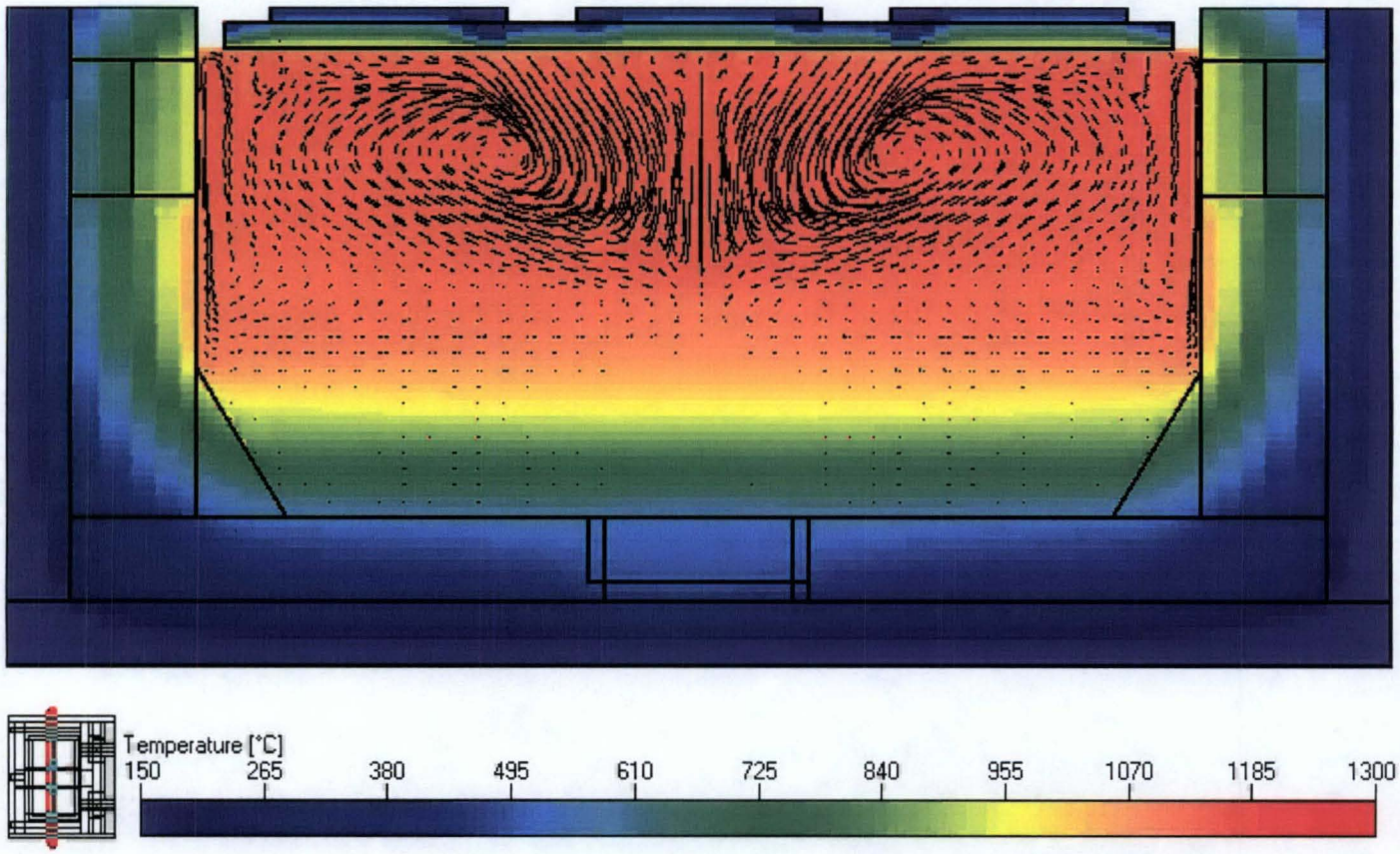




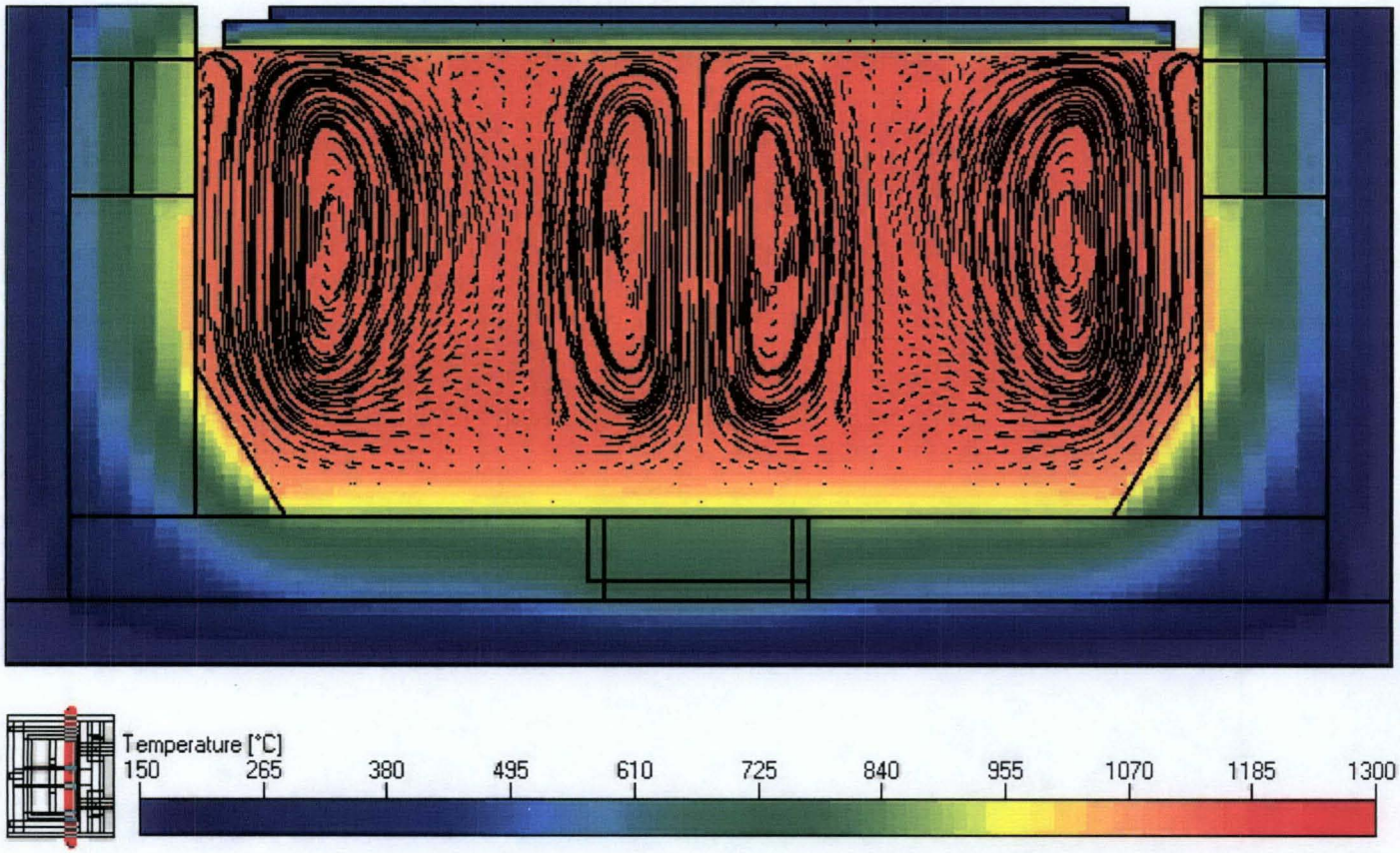
Horizontal distribution of Fe_2O_3 concentration of falling crystal a spinel in molten glass

Temperature and Velocity Fields in a Melter for Nuclear Waste Glass

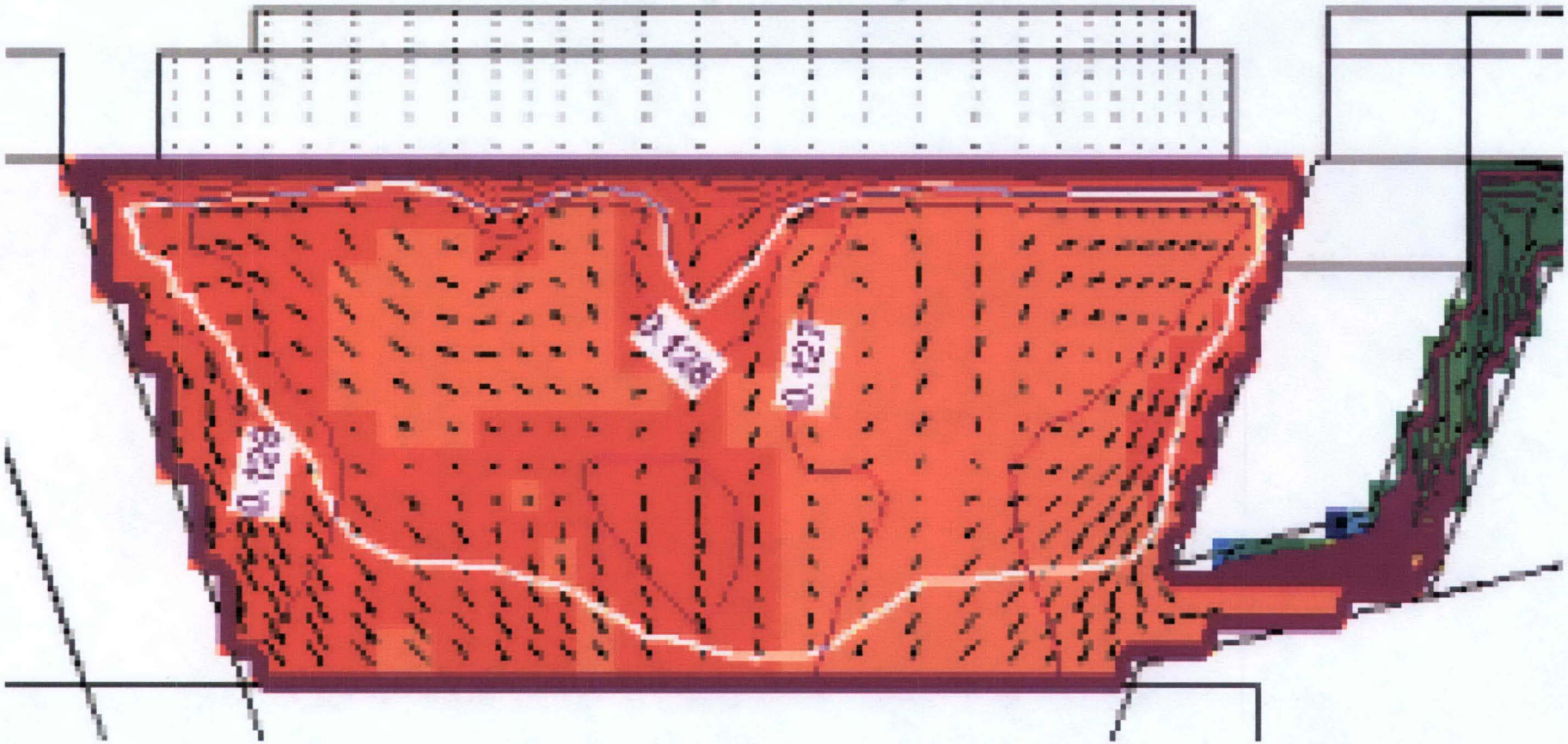
Duratek HLW model, Case 2A: Feed, 2el
Front View (YZ)



Duratek HLW model, Case 5A: Feed, 2el, bubl
Front View (YZ)



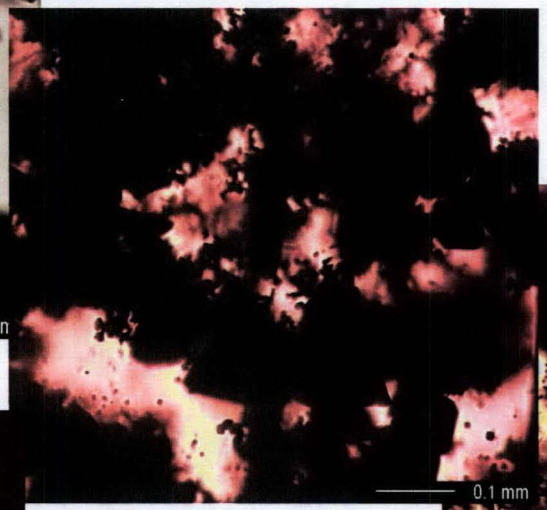
Impact of Crystals on Melters



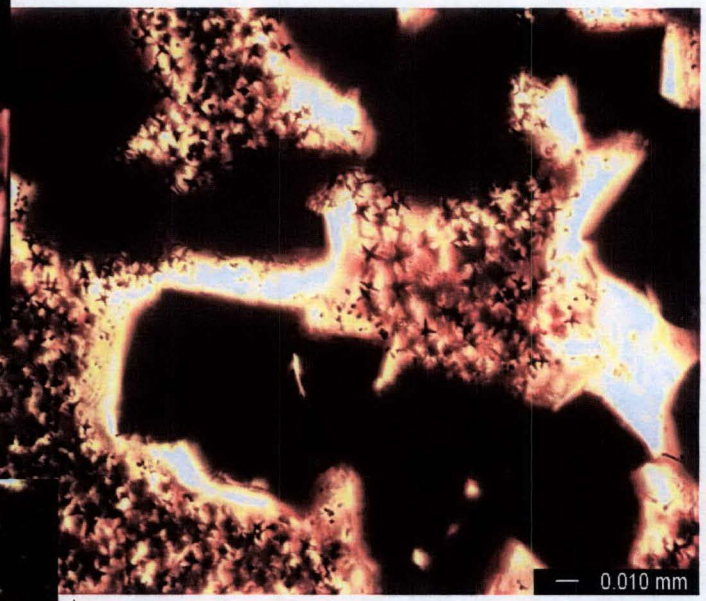
White contour line: T_L isotherm in a HLW glass melter

Spinel Sludge

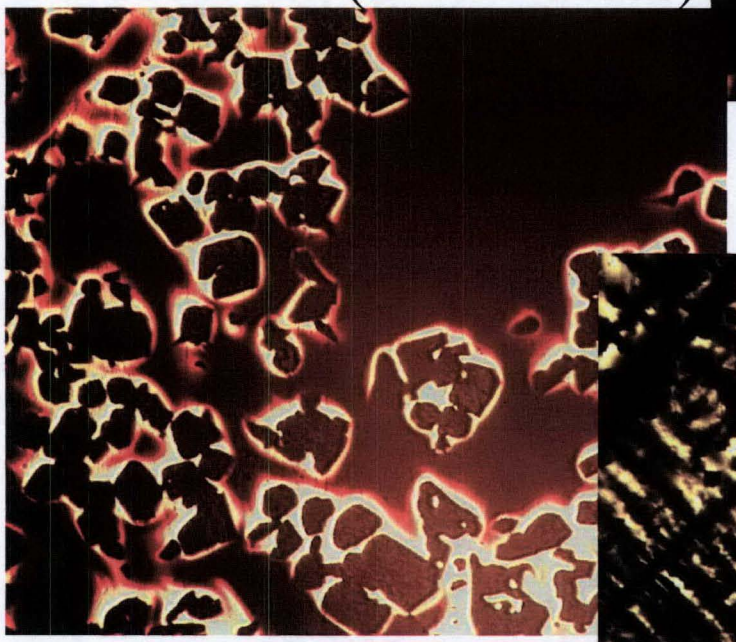
As received (27.6 mass%)



←Heat treated at 1035°C
(25.8 mass%)



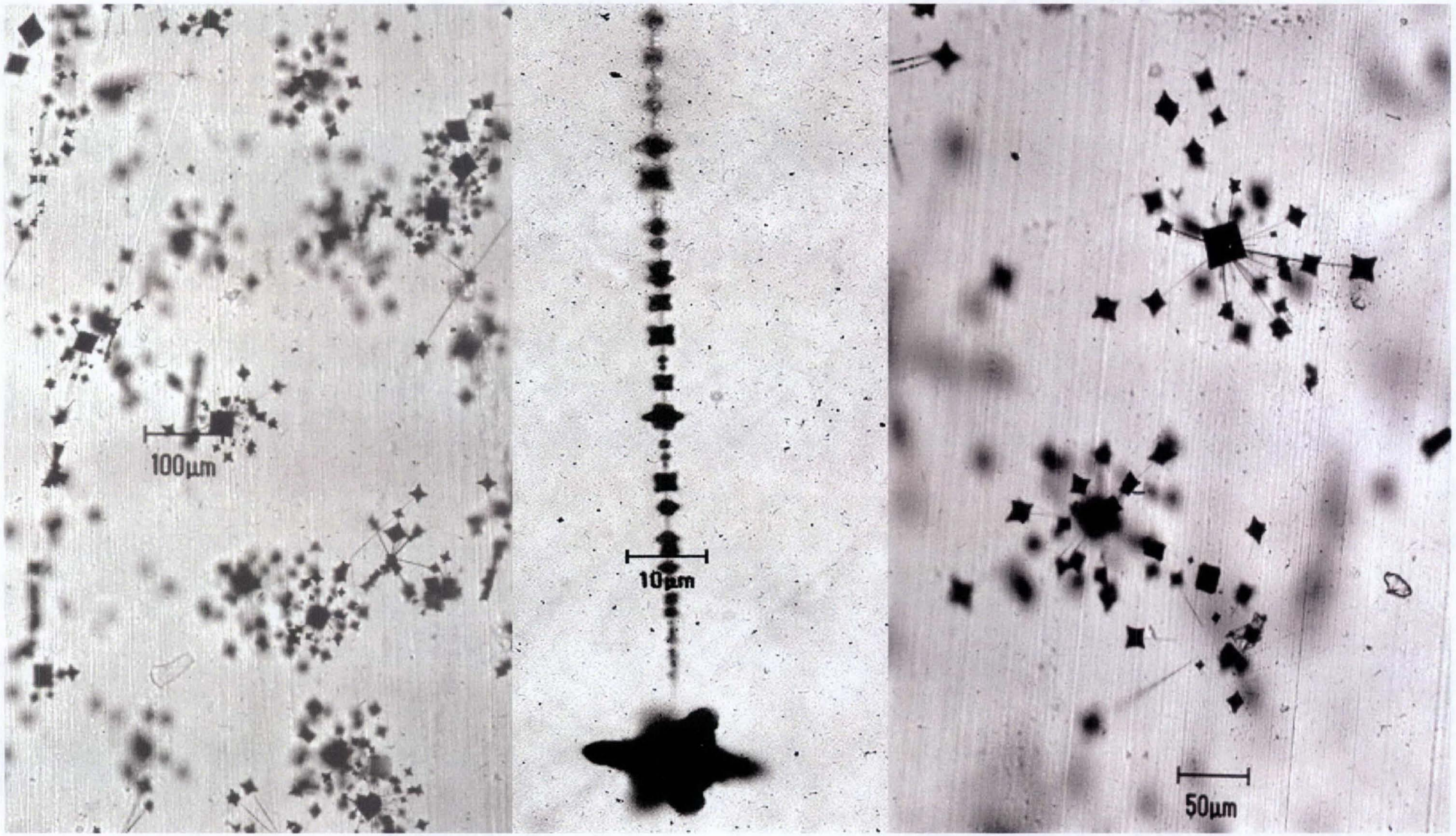
↑Heat treated at 1250°C
(16.4 mass%)



Heat treated at 1303°C
(15.3 mass%)

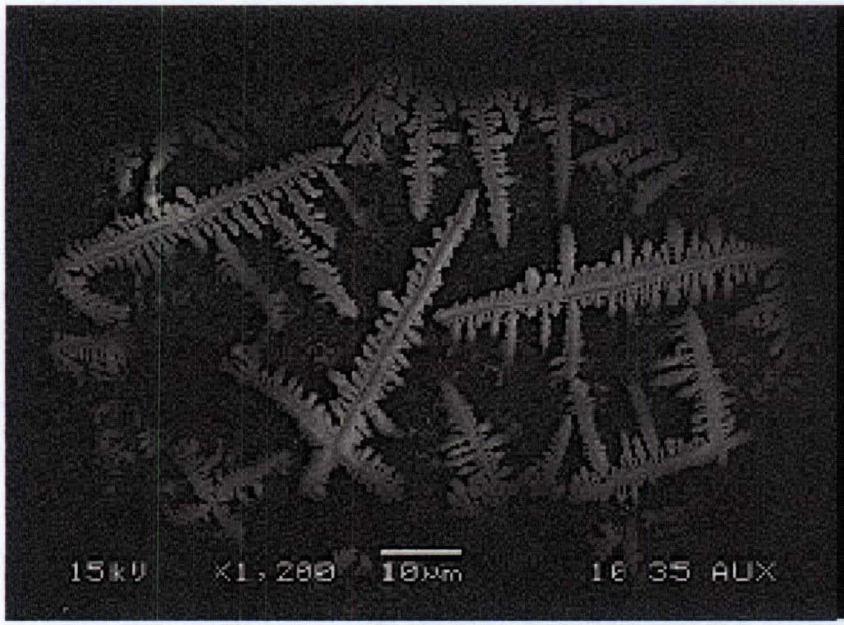
←Heat treated at 1400°C
(28.6 mass%)

Spinel and RuO_2

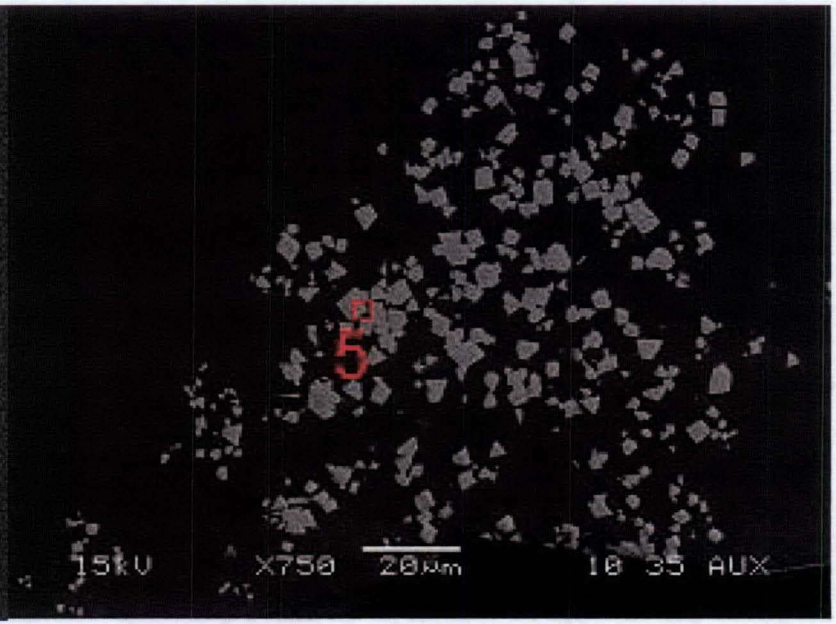


Cooling rate 9.25×10^{-3} K/s

Agglomeration

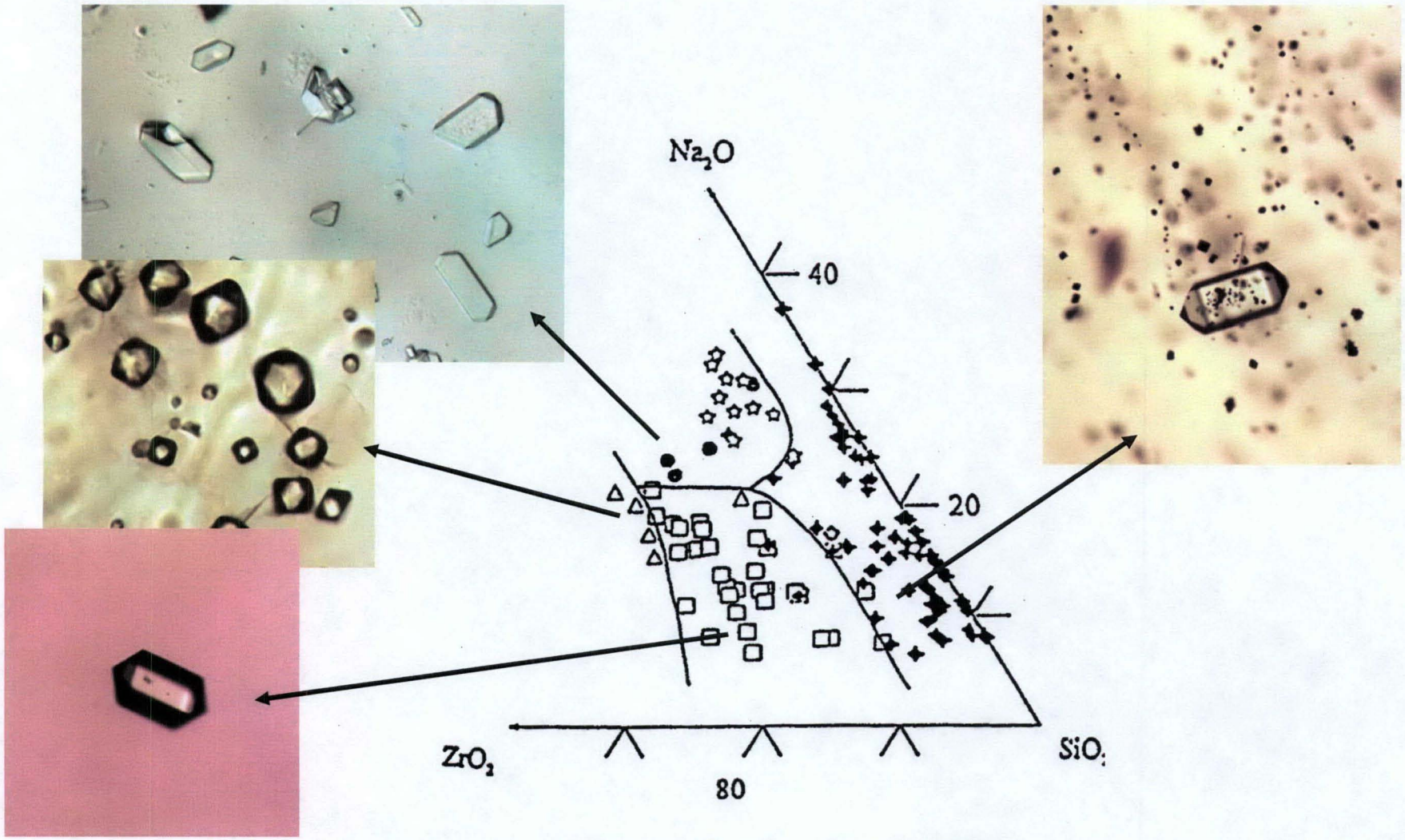


Nepheline



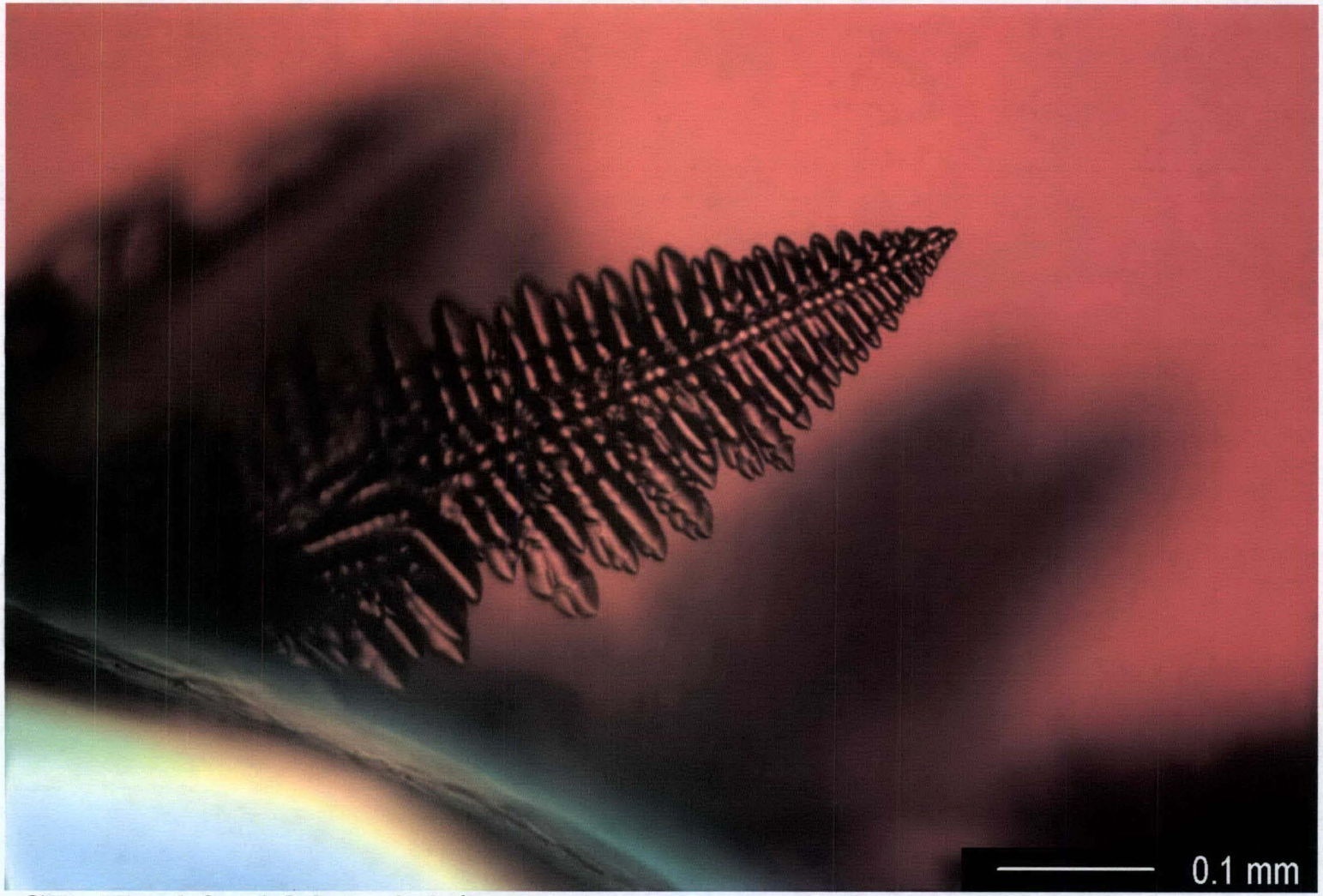
Spinel

Zr-Containing Phases



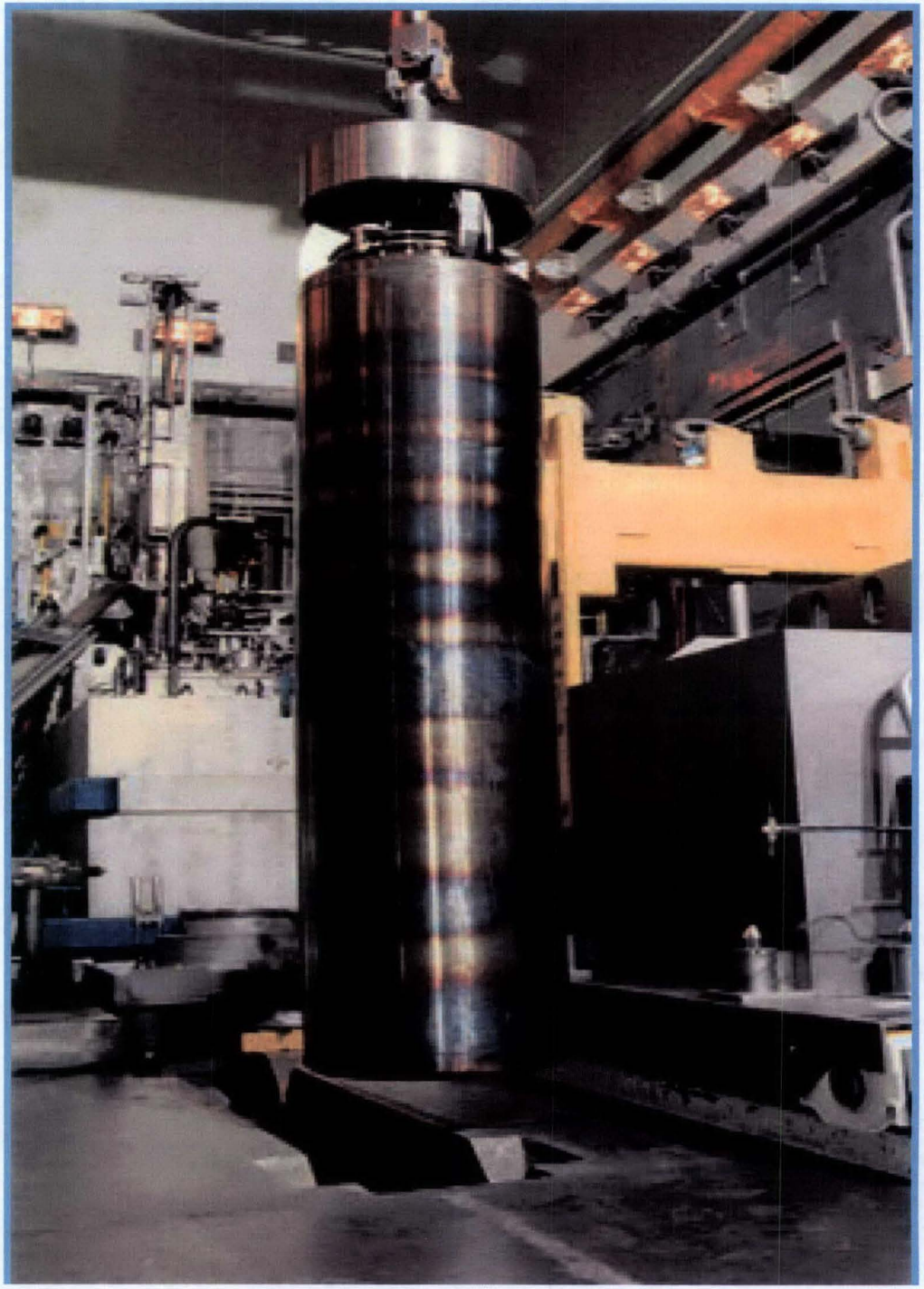
□ Zircon, Δ Baddeleyite, ● Sodium-Zirconium Silicate,
☆ Rare Earth Zirconate, ◆ Non-Zirconium Phases

Dendrite of Baddeleyite (ZrO_2)



SP-Zr-10, 1225, 24 h

HLW Glass Canister



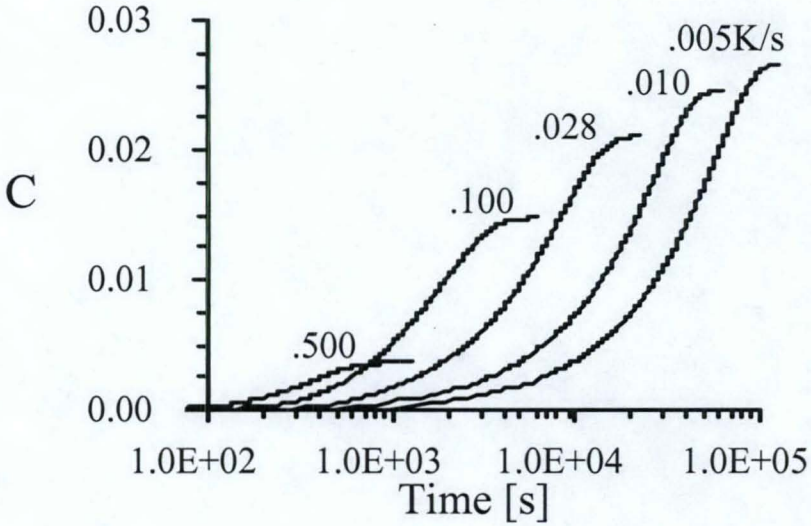
Avrami Equation in Differential Form

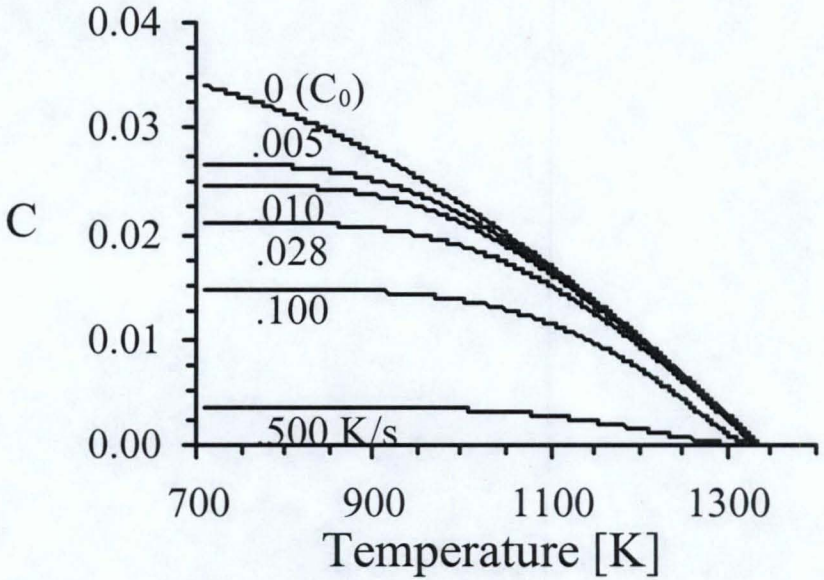
$$\dot{C} = nk_A(C_0 - C)\left[-\ln\left(\frac{C_0 - C}{C_0 - C_i}\right)\right]^{(n-1)/n}$$

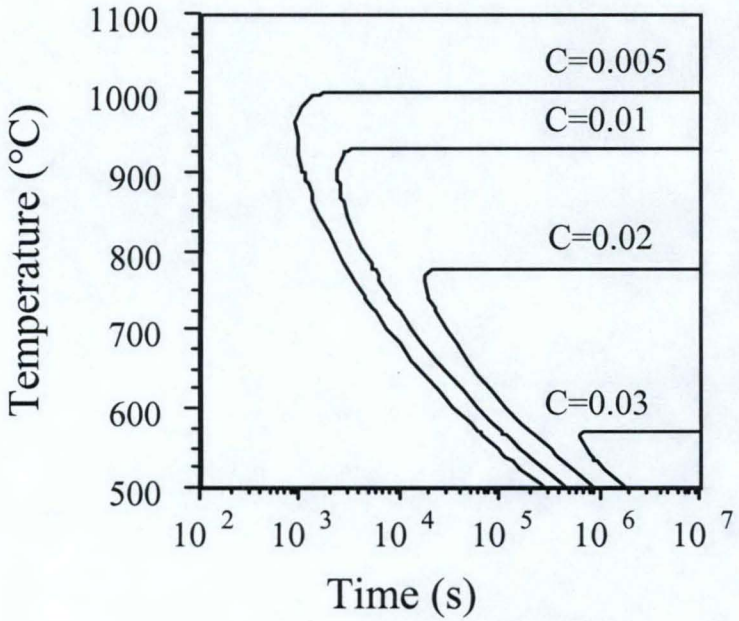
n is Avrami exponent

The differential form is necessary to obtain the evolution of crystallinity during changing temperature.

Crystallization at d*T*/d*t* = const.







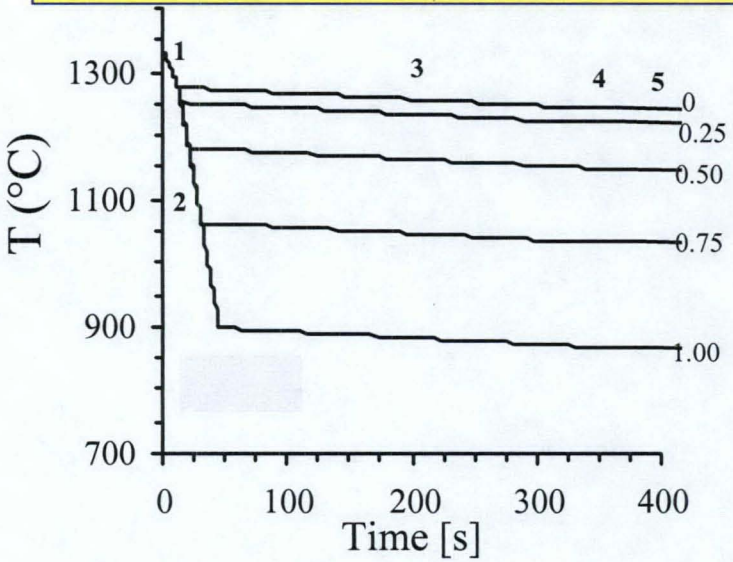
↑ **Spinel volume fraction versus time and temperature during constant-rate cooling**

← **Time-temperature transformation diagram**

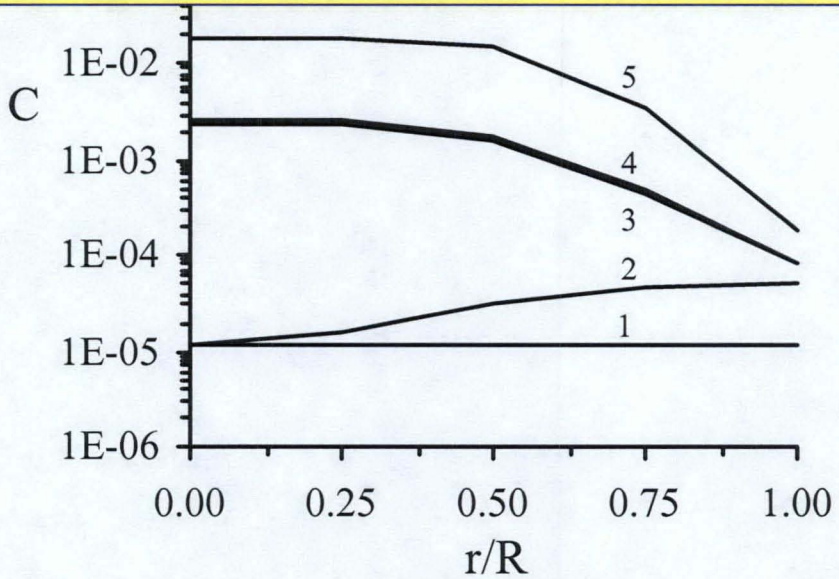
Crystallization in Canister

Process stages

1) Stream of melt from melter spout to canister
2) Melt flows from the point of impact towards canister wall
3) Melt rests on the top surface of glass in canister
4) Top melt is covered by the subsequent layer
5) Glass cools down



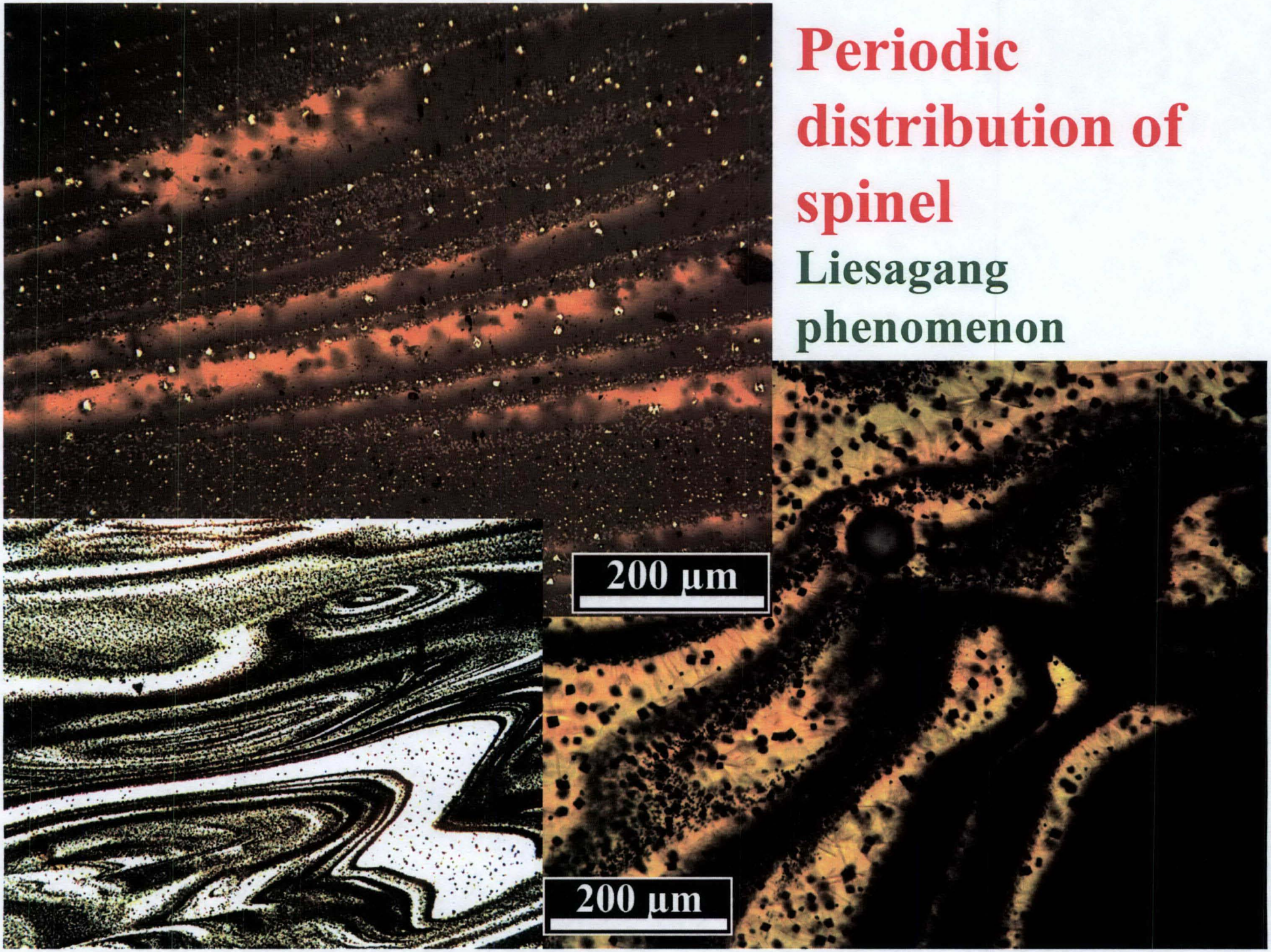
Temperature vs. time



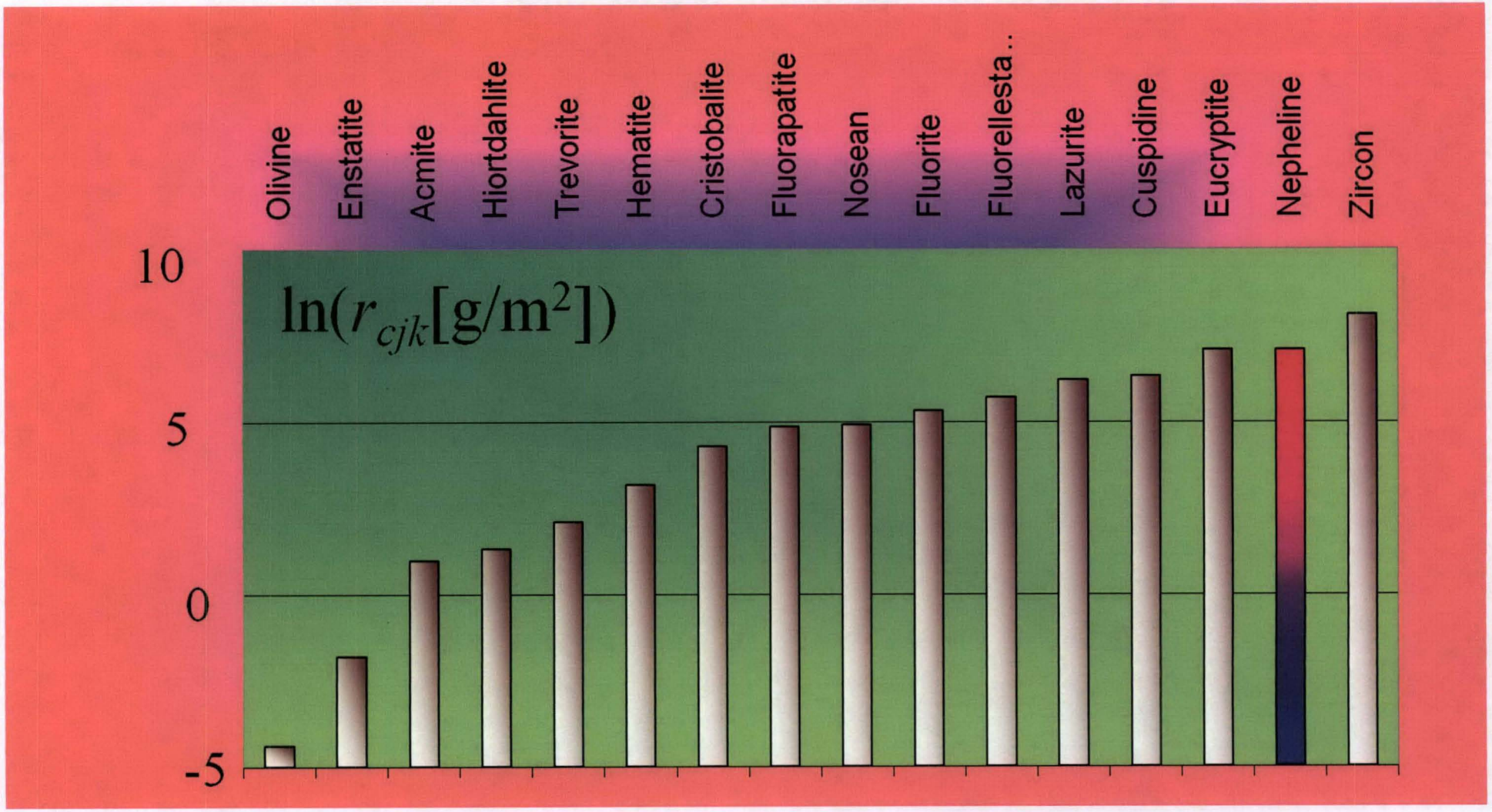
Spinel volume fraction vs. radius

Periodic distribution of spinel

Liesagang phenomenon

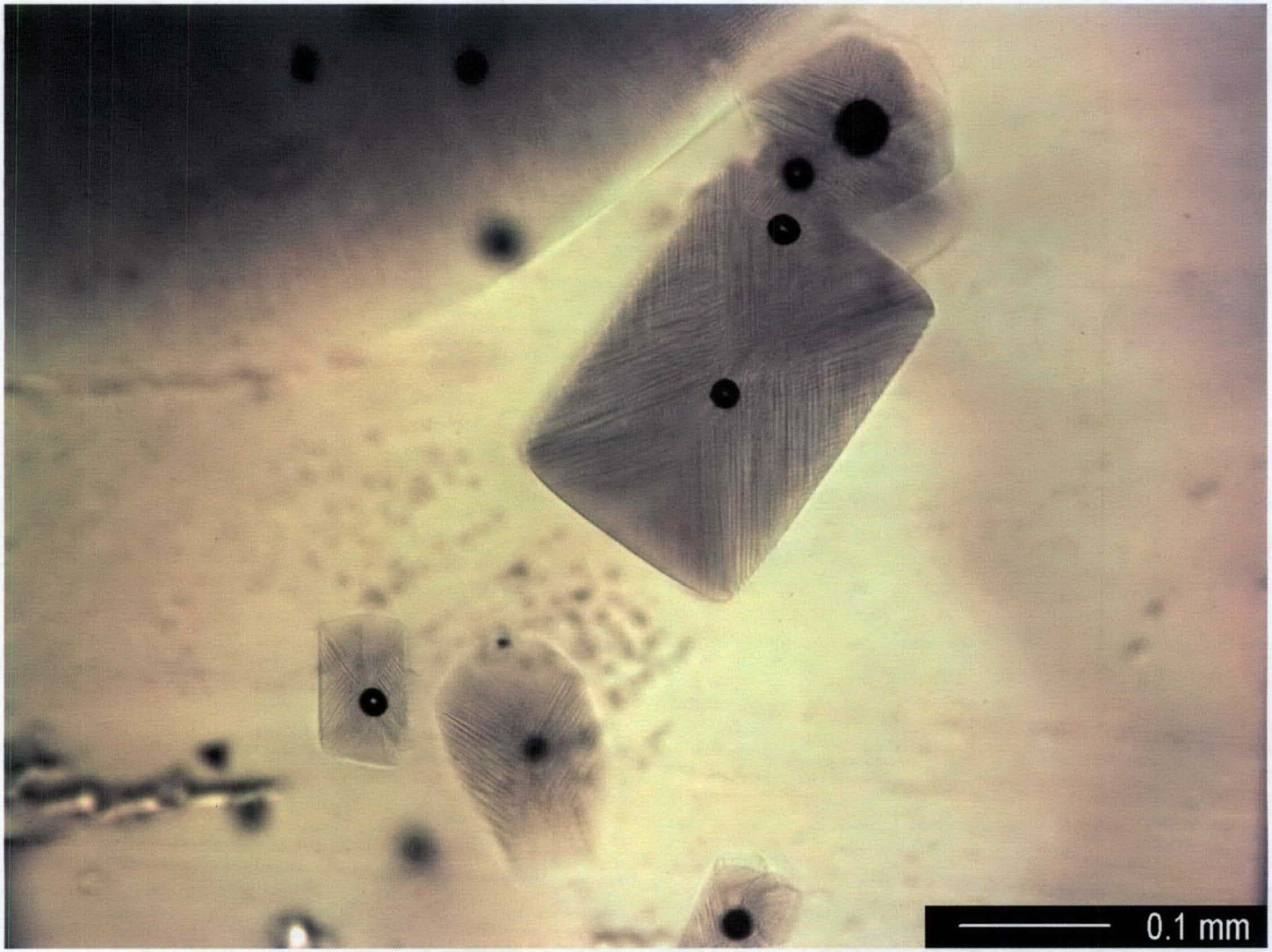


Effect of Minerals on Chemical Durability of HLW Glass



Only a few minerals (nepheline) reach a high enough fraction in glass to affect chemical durability.

Nepheline Crystals



NP-Al-1, 1150°C

Conclusions

- Crystal growth and dissolution typically proceed in a convective medium at changing temperature
- To represent crystallization or dissolution
  - the kinetics <u>must</u> be expressed in the form of rate equations, such as

$$\frac{dC}{dt} = f(C,T)$$

  - The temperature dependence of kinetic coefficients and equilibrium concentrations <u>must</u> be accounted for
- Non-equilibrium phenomena commonly occur:
  - metastable crystallization
  - periodic distribution of crystals
  - dendritic crystal growth

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