GTT-Technologies' Annual Workshop,
Herzogenrath, Germany, June 20 - 22 2007

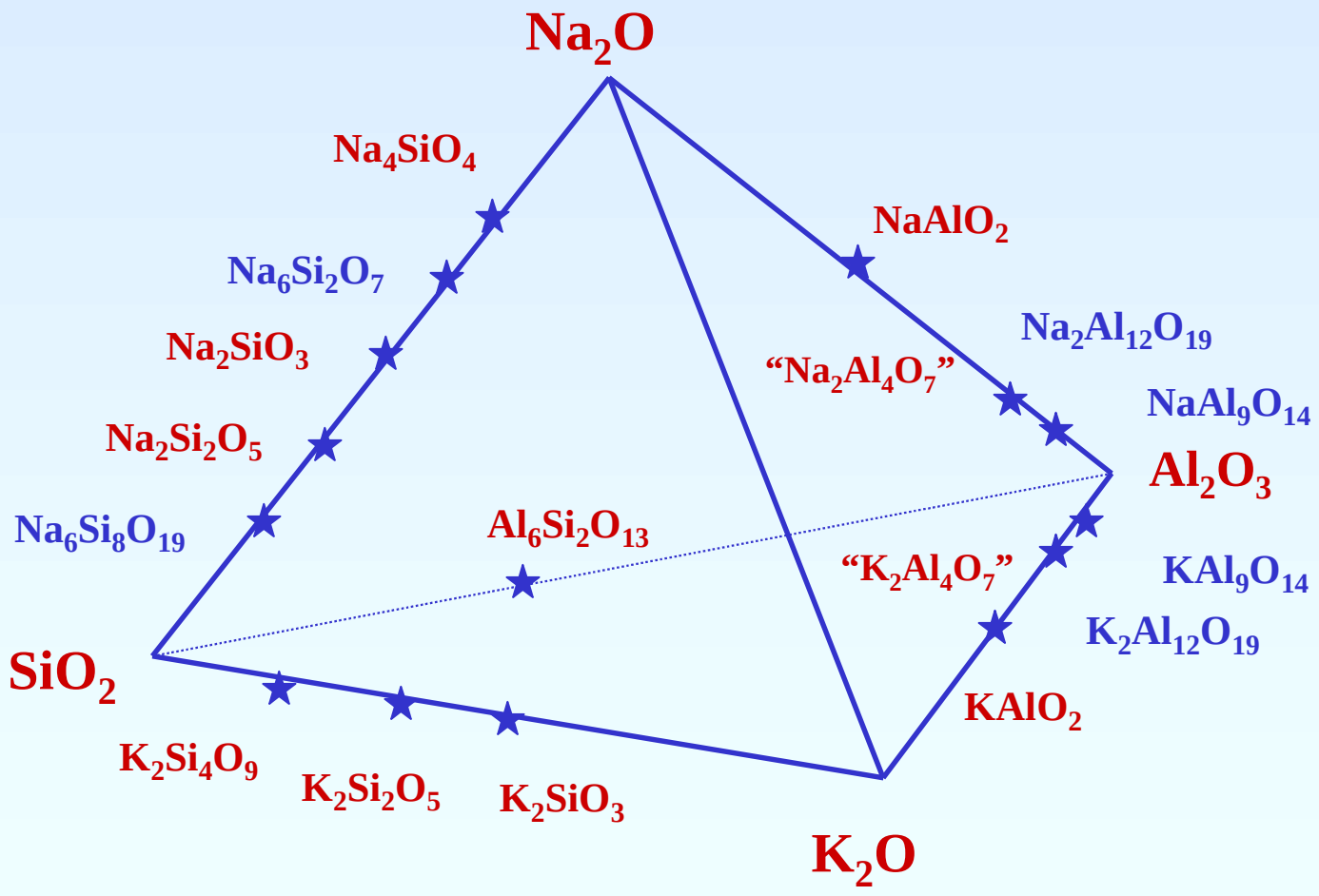
# Thermochemical assessments

# of alkali oxide - $Al_2O_3$ - $SiO_2$ systems

E.Yazhenskikh, K. Hack*, M. Mueller

Forschungszentrum Jülich, IEF-2, *GTT-Technologies

# $Na_2O$-$K_2O$-$Al_2O_3$-$SiO_2$



# Contents

- ✓ Model and optimisation
- ✓ Application of a new data base for binary subsystems
- ✓ Application of a new data base for ternary subsystems
- ✓ Conclusions and outlook

# Associate species model

**Liquid (slag)**, solid solutions, mullite

**Binary liquid**

Pure liquid oxide:
$Na_2O$, $K_2O$, $Al_2O_3$, $SiO_2 \cdot 2/5$

+

| Congruent melting compounds | Associate species |
|---|---|
| $Na_4SiO_4$ | $Na_4SiO_4 \cdot 2/5$ |
| $Na_2SiO_3$ | $Na_2SiO3 \cdot 2/3$ |
| $Na_2Si_2O_5$ | $Na2Si2O5 \cdot 1/2$ |
| $K_2SiO_3$ | $K_2SiO_3 \cdot 2/3$ |
| $K_2Si_2O_5$ | $K_2Si_2O_5 \cdot 1/2$ |
| K2Si4O9 | $K_2Si_4O_9 \cdot 1/3$ |
| $NaAlO_2$ | $NaAlO_2$ |
| | $Na_2Al_4O_7 \cdot 1/3$ |
| $KAlO_2$ | $KAlO_2$ |
| | $Na_2Al_4O_7 \cdot 1/3$ |
| $Al_6Si_2O_{13}$ | $Al_6Si_2O_{13} \cdot 1/4$ |

+

**Interaction parameters between species**

**Solution components**
**(Spear et al.)**

# Associate species model

Liquid (slag), **solid solutions, mullite**

**Solid solutions:**

**Solution components:**
**Solid "boundary" compounds**

**Nepheline**
$NaAlSiO_4$ (nepheline)
$NaAlSi_2O_6$ (jadeite)

**Carnegieite**
$NaAlSiO_4$ (carnegieite)
$NaAlSi_2O_6$ (jadeite)

**$KAl_{1-x}Si_xO_4$**
$KAlO_2$
$KAlSiO_4$

\+ **Interaction parameters between species (by request)**

**Mullite**

**Associate species model**
**$Al_6Si_2O_{13}\cdot 1/4$, $Al_2O_3$, $SiO_2\cdot 2$**

**four-sublattice model**
**(Hillert, Mao et al.)**

Experimental data: phase diagram data, activity data (for binary systems)

Pure solid and liquid substances from the FACT database

Some solution species from database of Spear et al.

## Optimisation

**Adjustable parameters: $?H_f^{298}$ and $S^{298}$ for the liquid and solid solution species, $\Delta H_f^{298}$ and $S^{298}$ for the pure solid compounds (part.), interaction parameters between species**

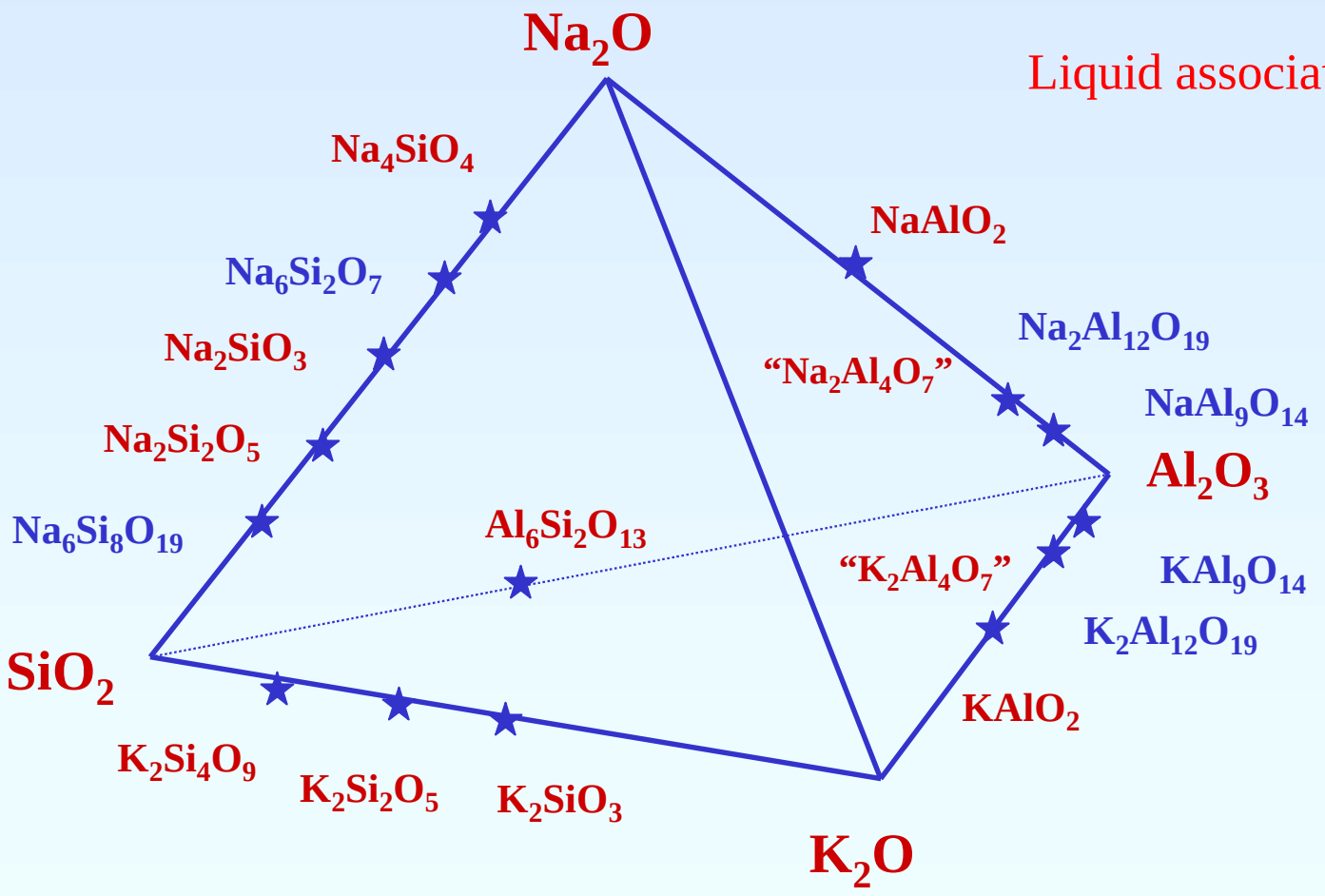
$$G_m = \sum x_i G_i^0 + RT \sum x_i \ln x_i + \sum_{i<j} \sum x_i x_j \sum_v L_{ij}^{(v)} (x_i - x_j)^v$$

$$L_{ij}^{(v)} = A_{ij}^{(v)} + B_{ij}^{(v)} \cdot T + C_{ij}^{(v)} \cdot T \cdot \ln T + D_{ij}^{(v)} \cdot T^2 + \ldots$$

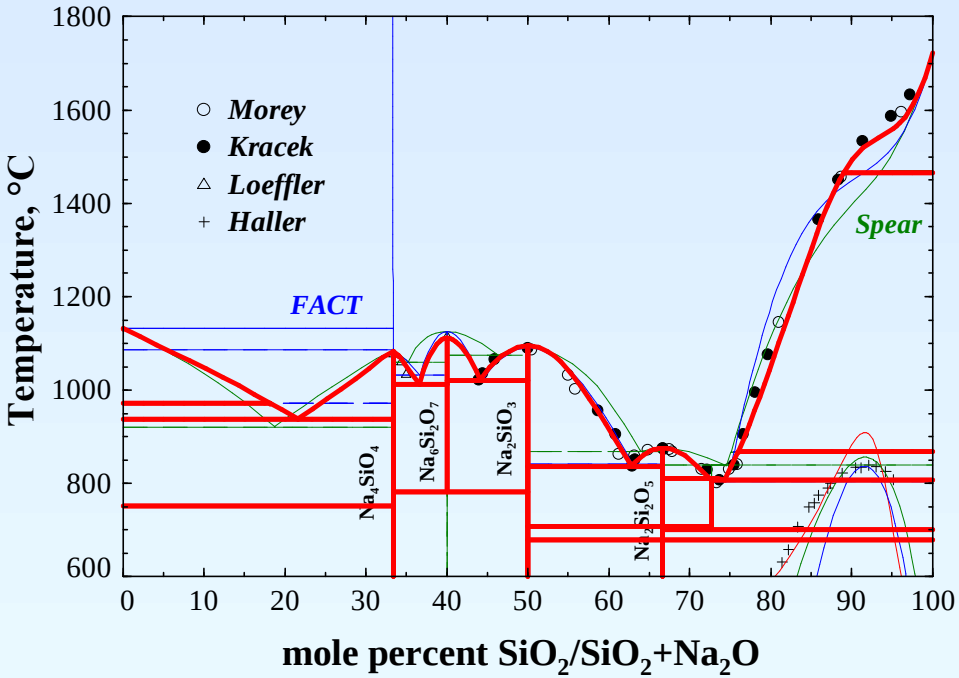
**New database**

# $Na_2O$-$K_2O$-$Al_2O_3$-$SiO_2$ system

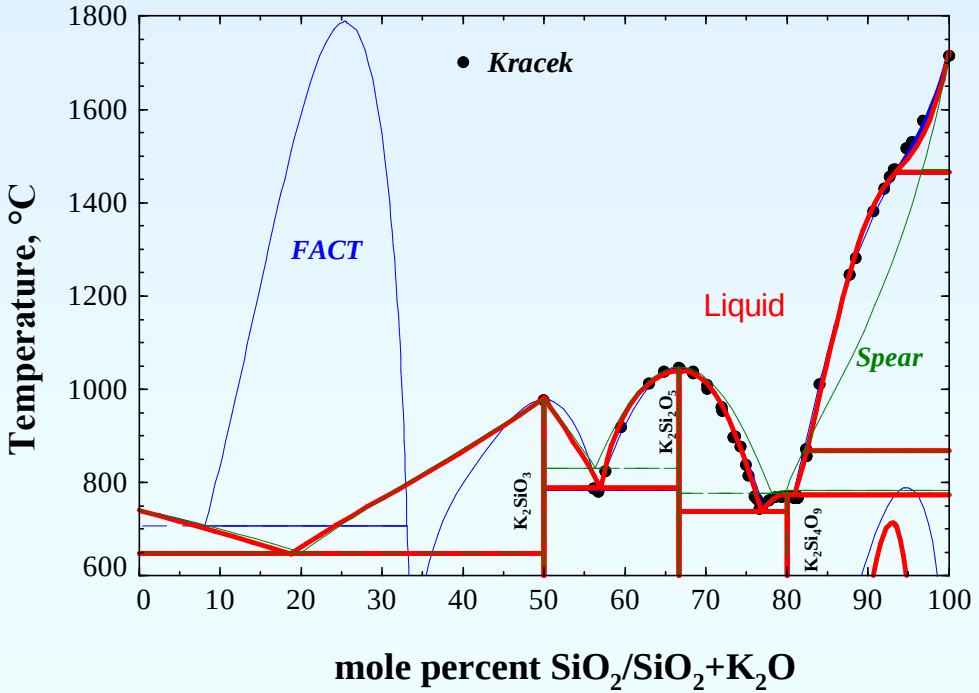
Liquid associate species



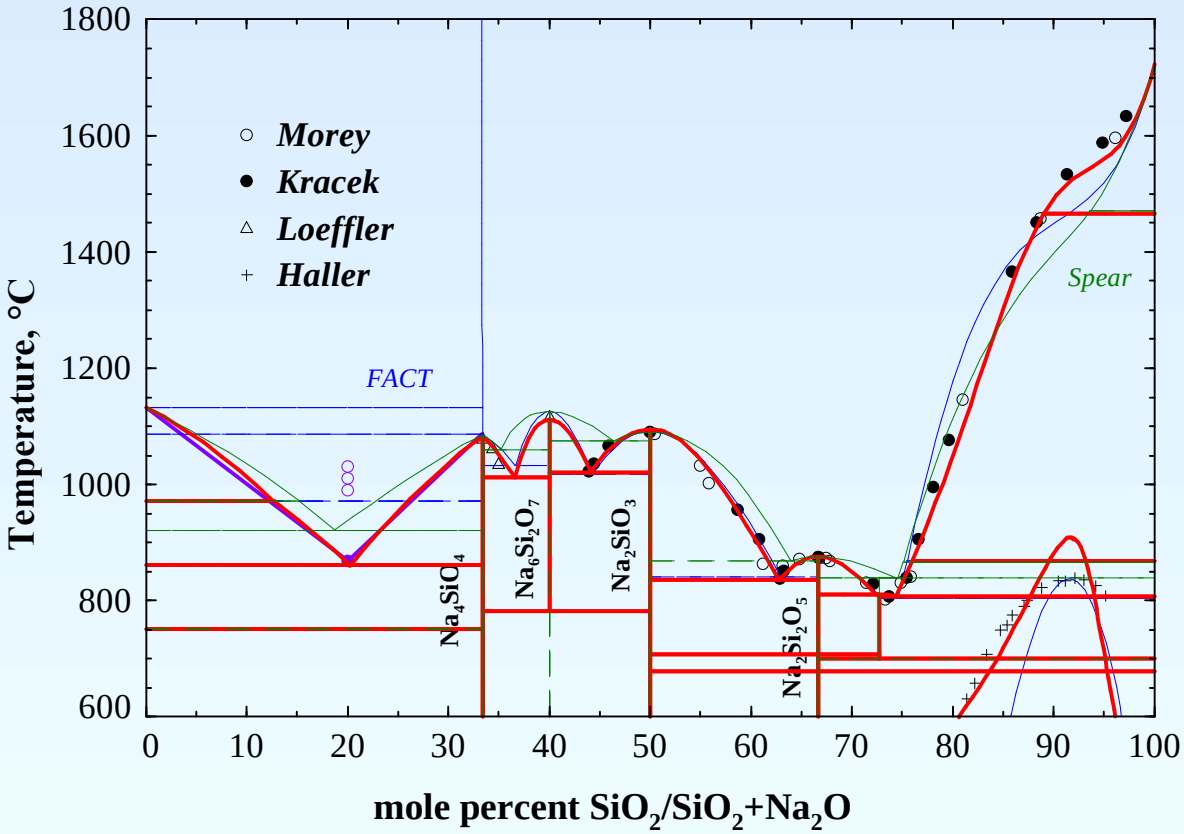
# New database for the $Me_2O$-$SiO_2$ systems (Me=Na, K)




No solution using the FACT database in the $Me_2O$-rich region

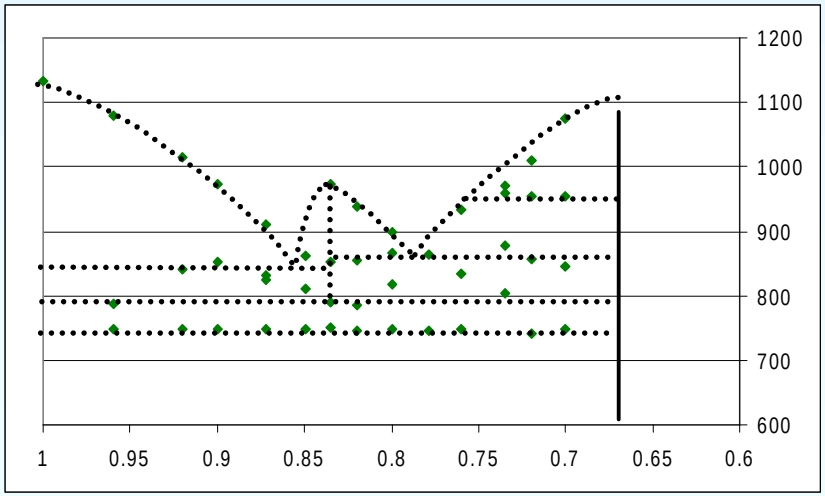


# DTA measurements in the $Na_2O$-$SiO_2$ system



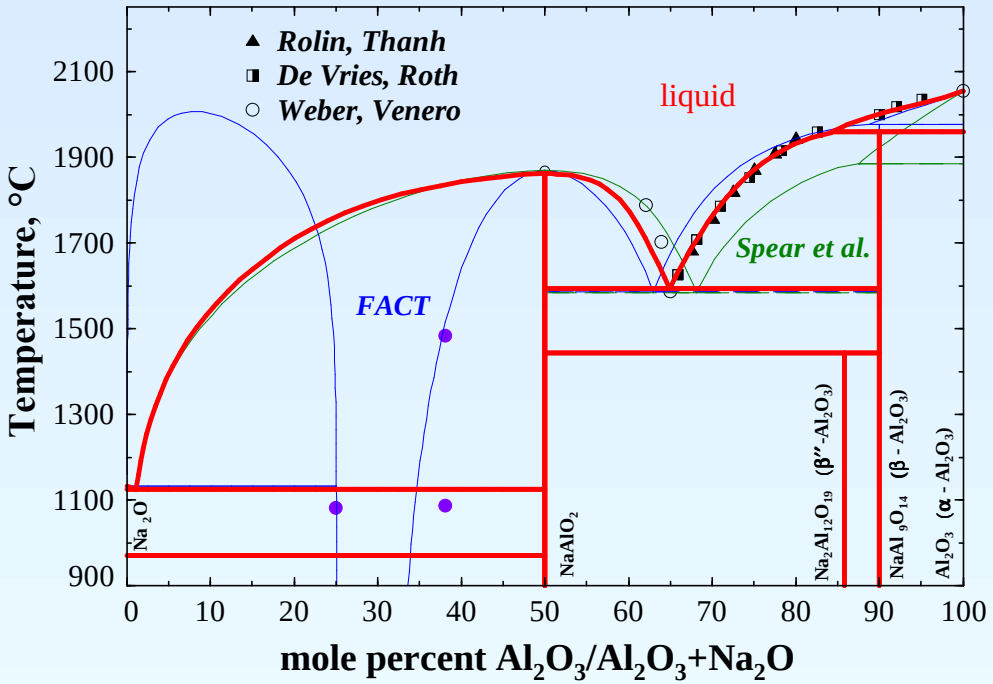

*Experimental data*

*of M. Rys, IEF-2*

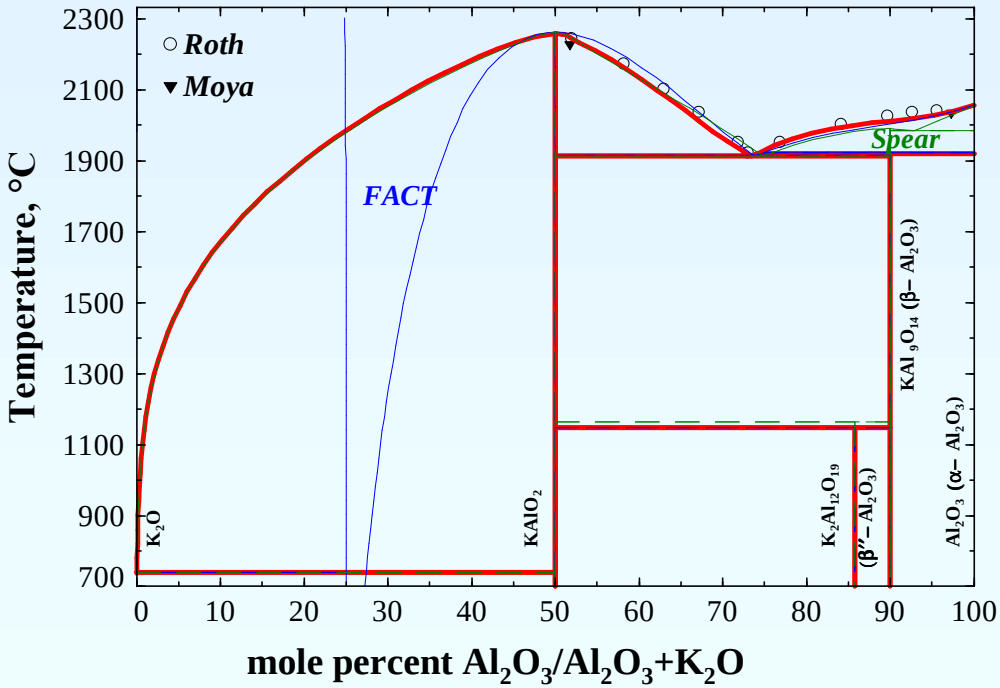


**New eutectic point at 867 °C**

# New database for the $Me_2O$-$Al_2O_3$ systems (Me=Na, K)



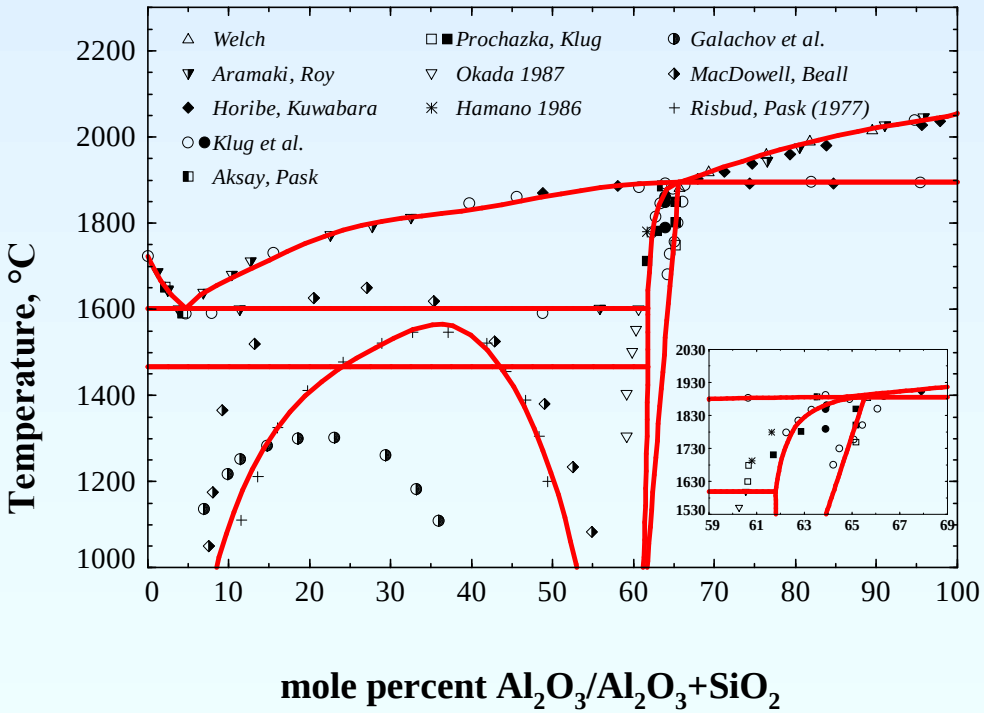

Thermodynamic data for the Na aluminates ($Na_2Al_{12}O_{19}$, $NaAl_9O_{14}$) were re-optimised



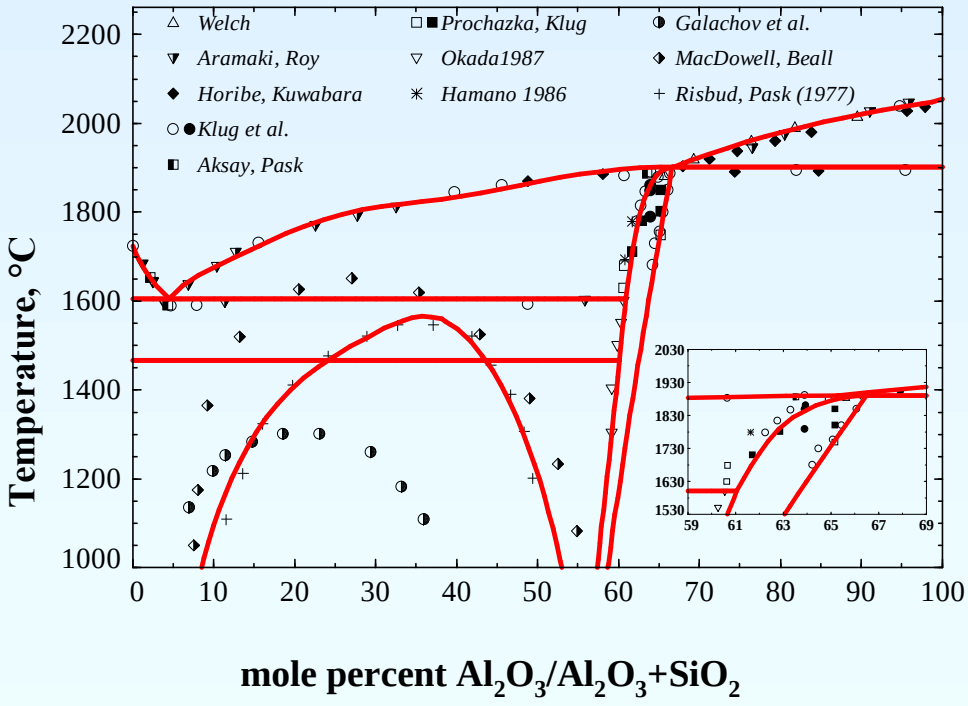

No solution using the FACT database in the $Me_2O$-rich region

# Thermodynamic assessment of the $Al_2O_3$-$SiO_2$ system

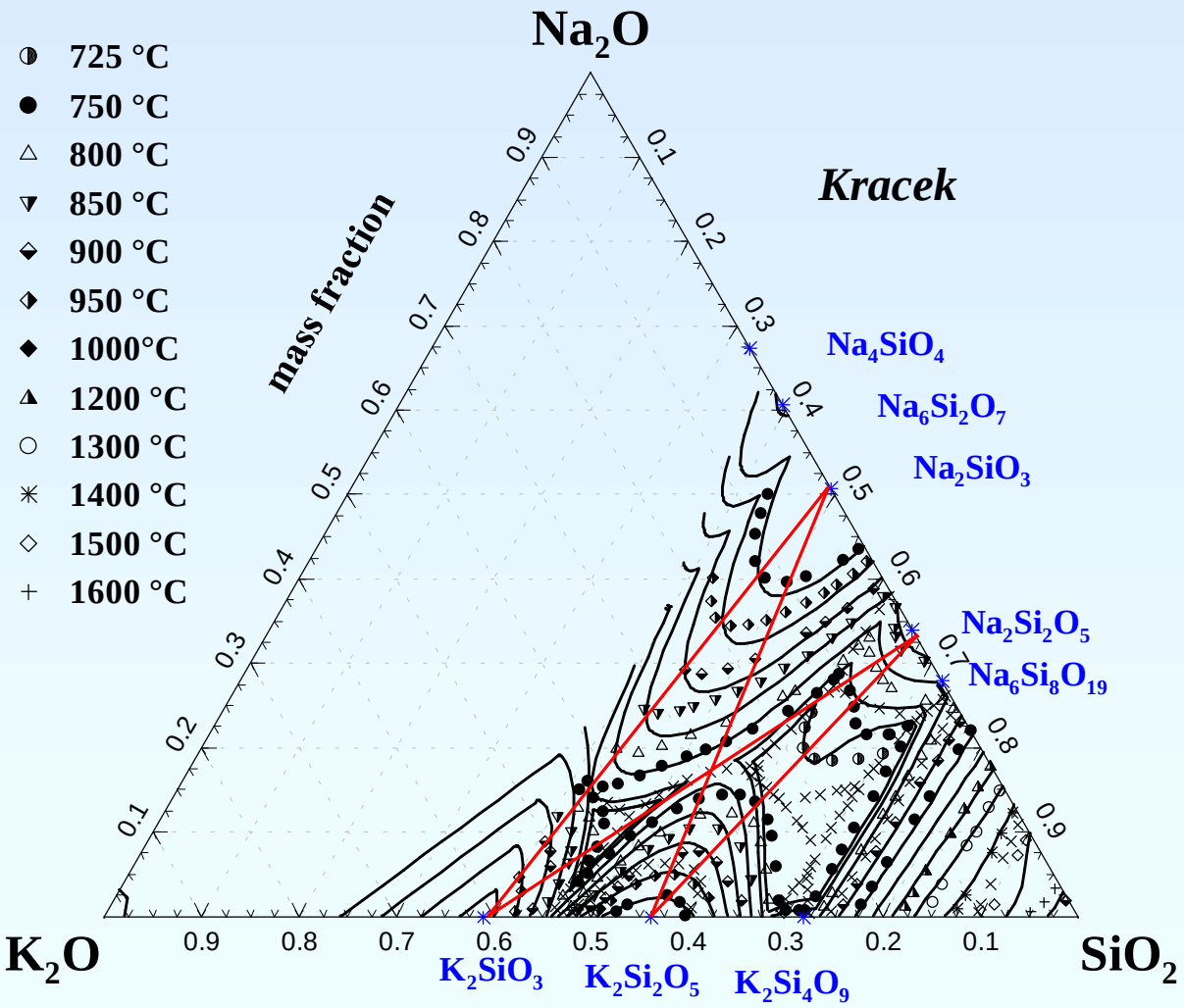
## Associate model for mullite




## Four-sublattice model for mullite



# $K_2O$-$Na_2O$-$SiO_2$ system: comparison of the calculated isotherms with the experimental points



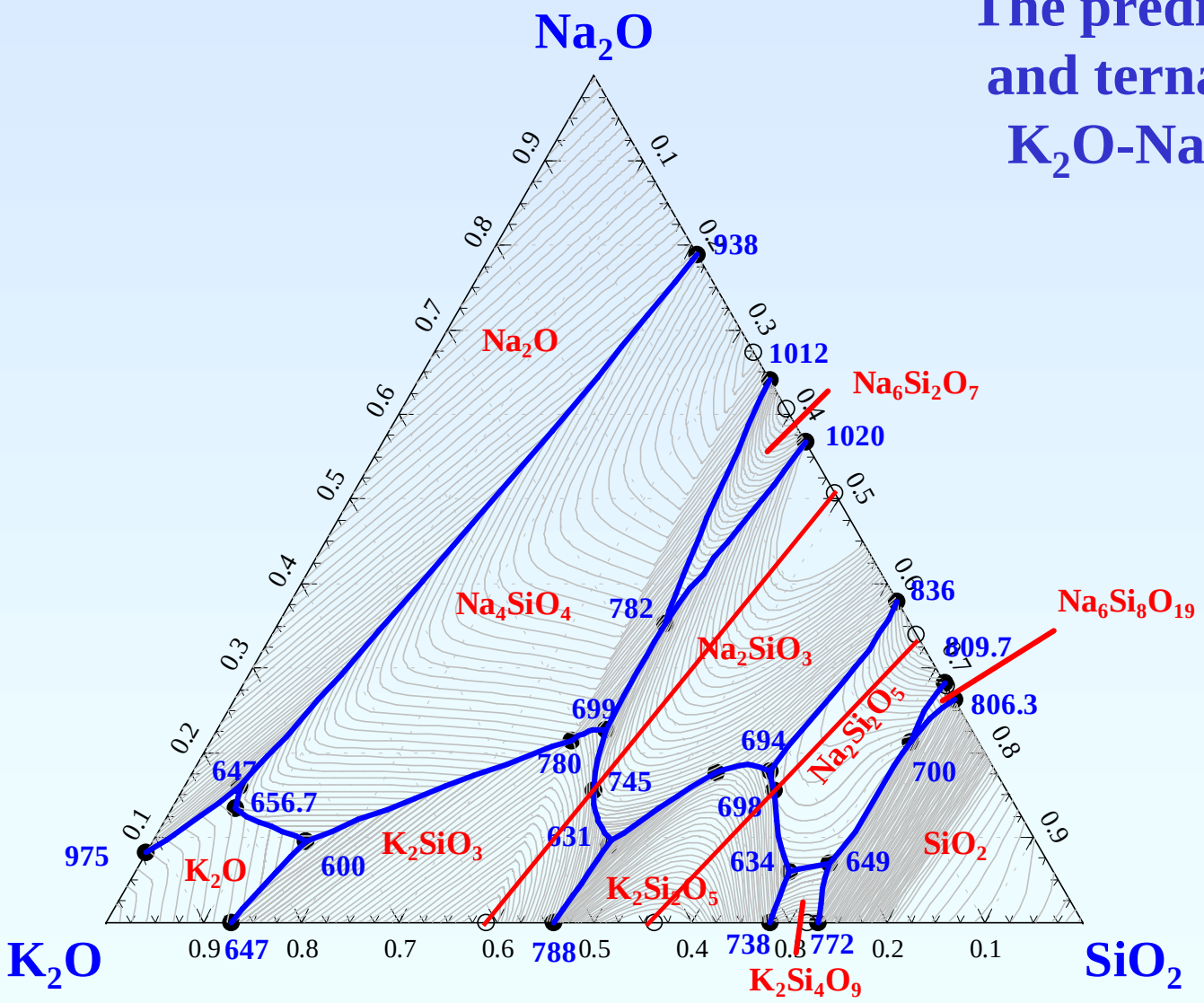

## Solution species:

| | |
|---|---|
| N414 | $Na_4SiO_4$*2/5 |
| N213 | $Na_2SiO_3$*2/3 |
| N225 | $Na_2Si_2O_5$*1/2 |
| K213 | $K_2SiO_3$*2/3 |
| K225 | $K_2Si_2O_5$*1/2 |
| K249 | $K_2Si_4O_9$*1/3 |

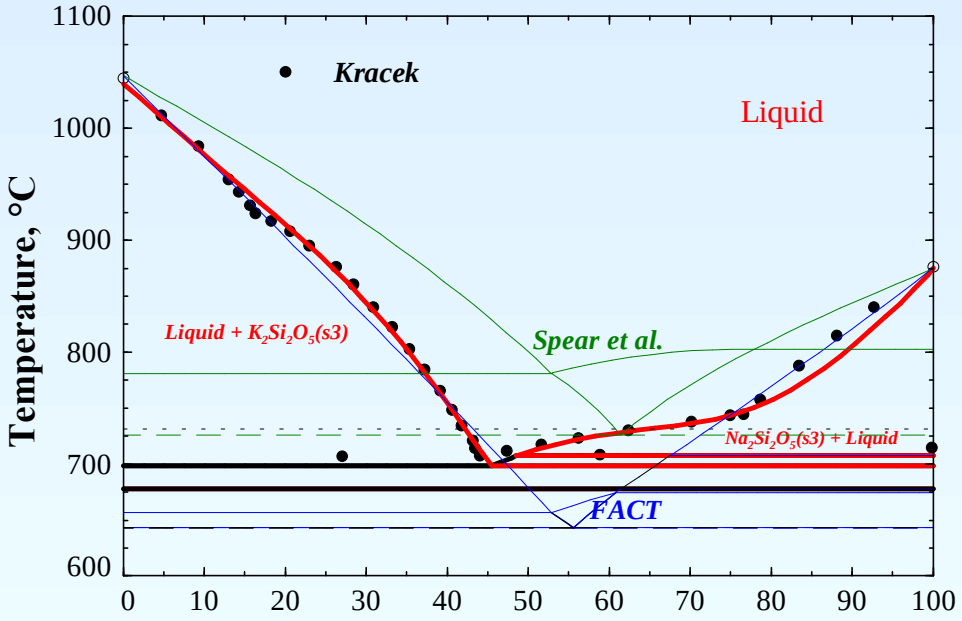
## Interaction parameters:

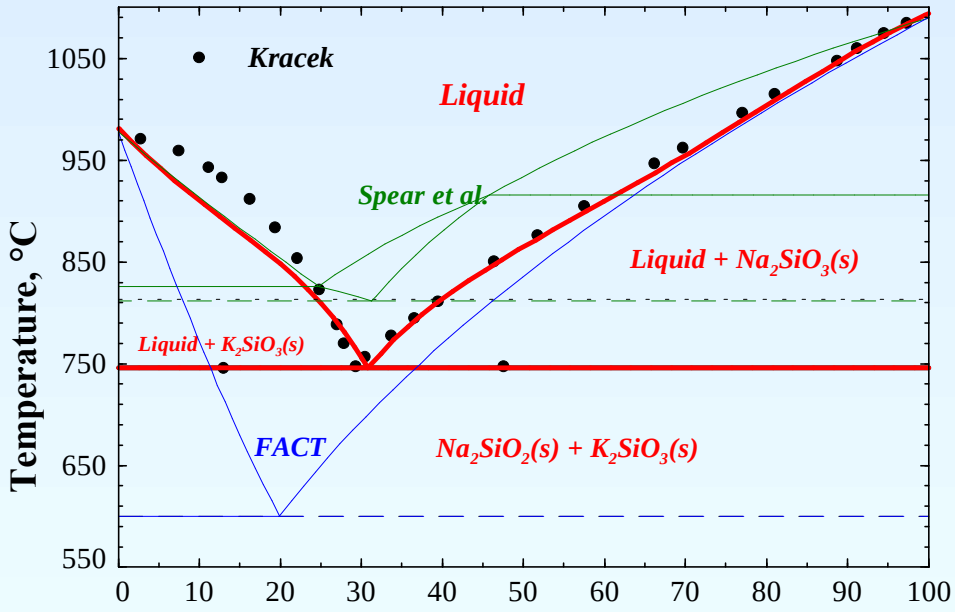
N213-K213
N225-K225
N213-K225
N225-K213

# The predicted phase fields and ternary points in the $K_2O$-$Na_2O$-$SiO_2$ system

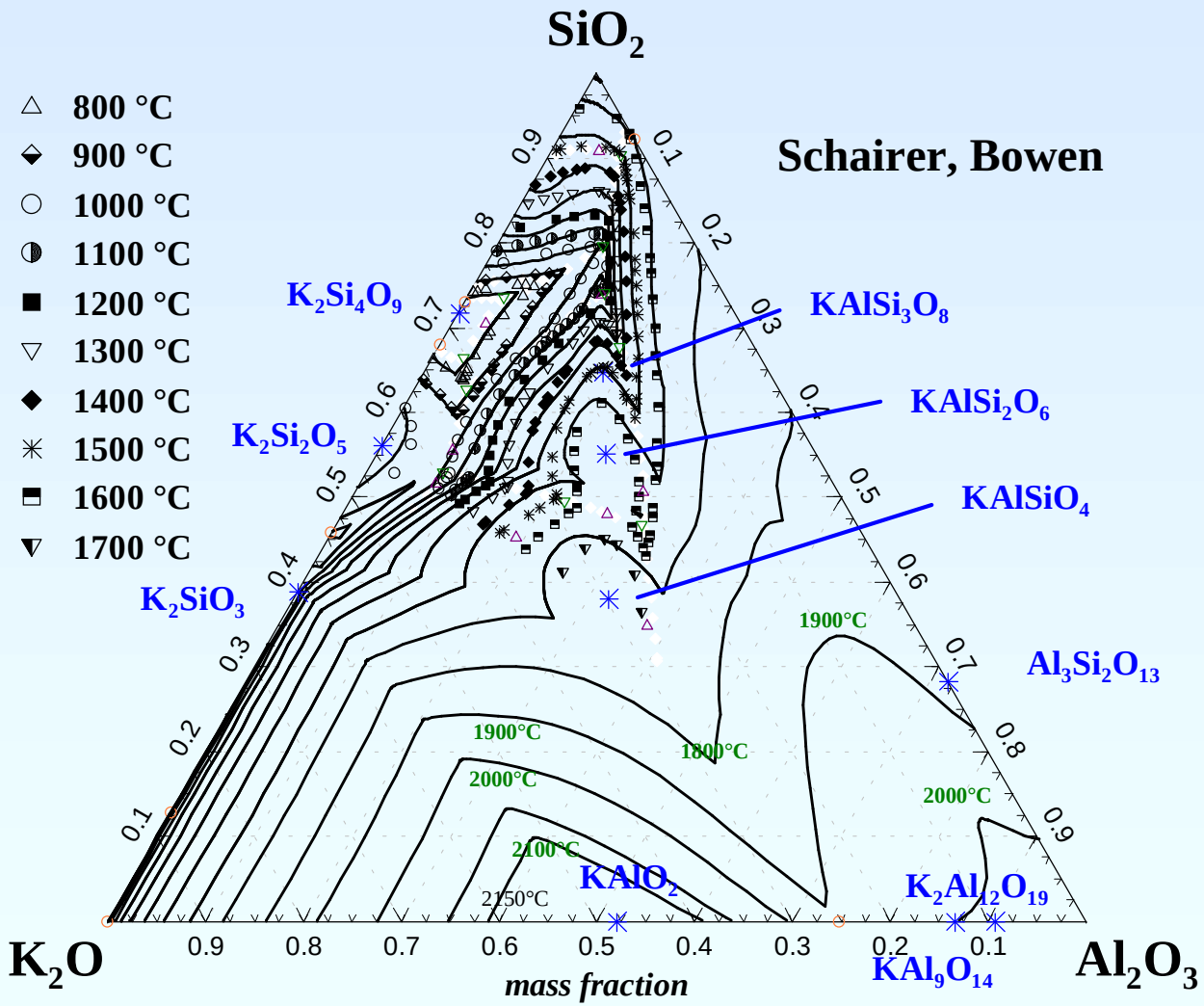


# Quasi-binary section $Me_2Si_2O_5$ and $Me_2SiO_3$ (Me=Na, K)



# $K_2O$-$Al_2O_3$-$SiO_2$ system: comparison of the calculated equlibria with the experimental points

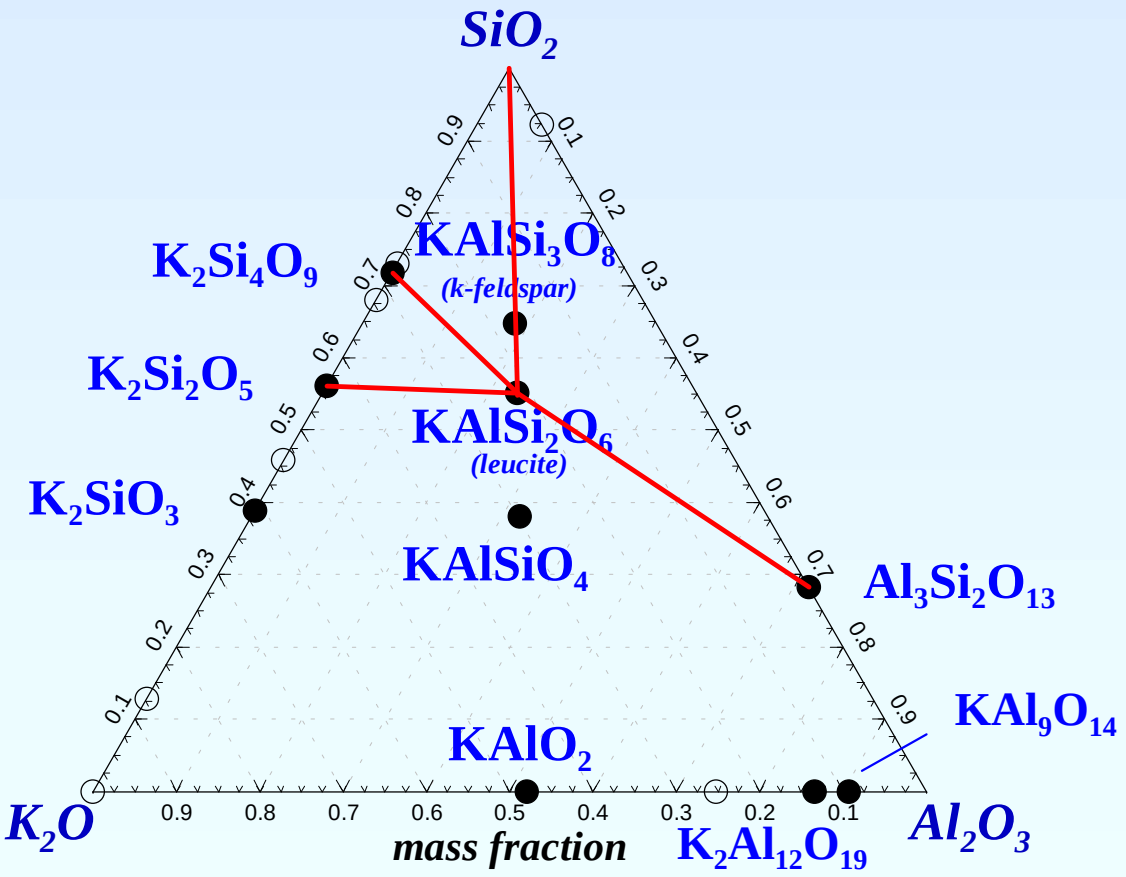



**Liquid**

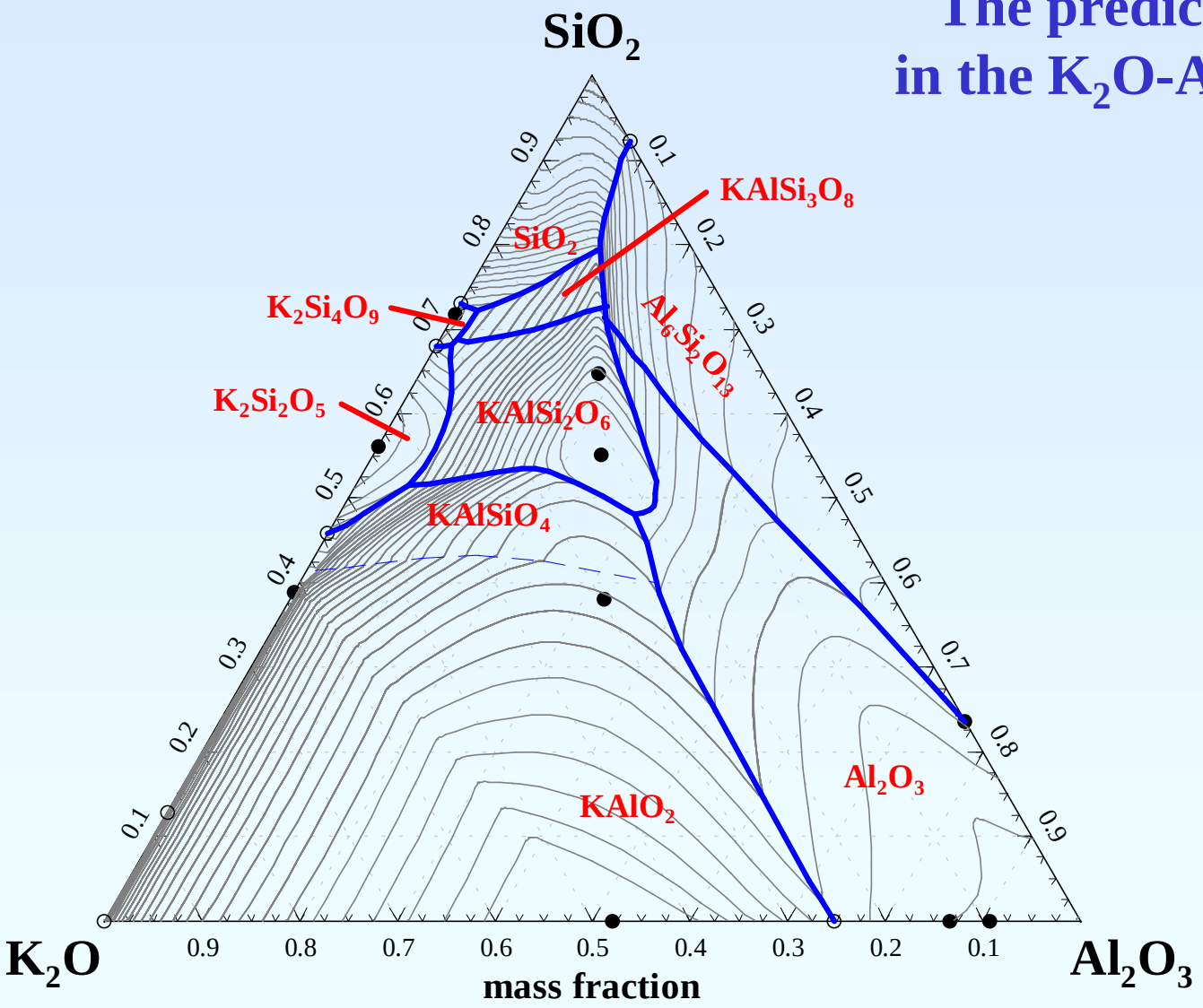
- **binary associate species**
- **ternary species: $KAlSi_2O_6 \cdot 1/2$ and $KAlSiO_4 \cdot 2/3$**

# Solution species in the ternary liquid in the $K_2O$-$Al_2O_3$-$SiO_2$ system

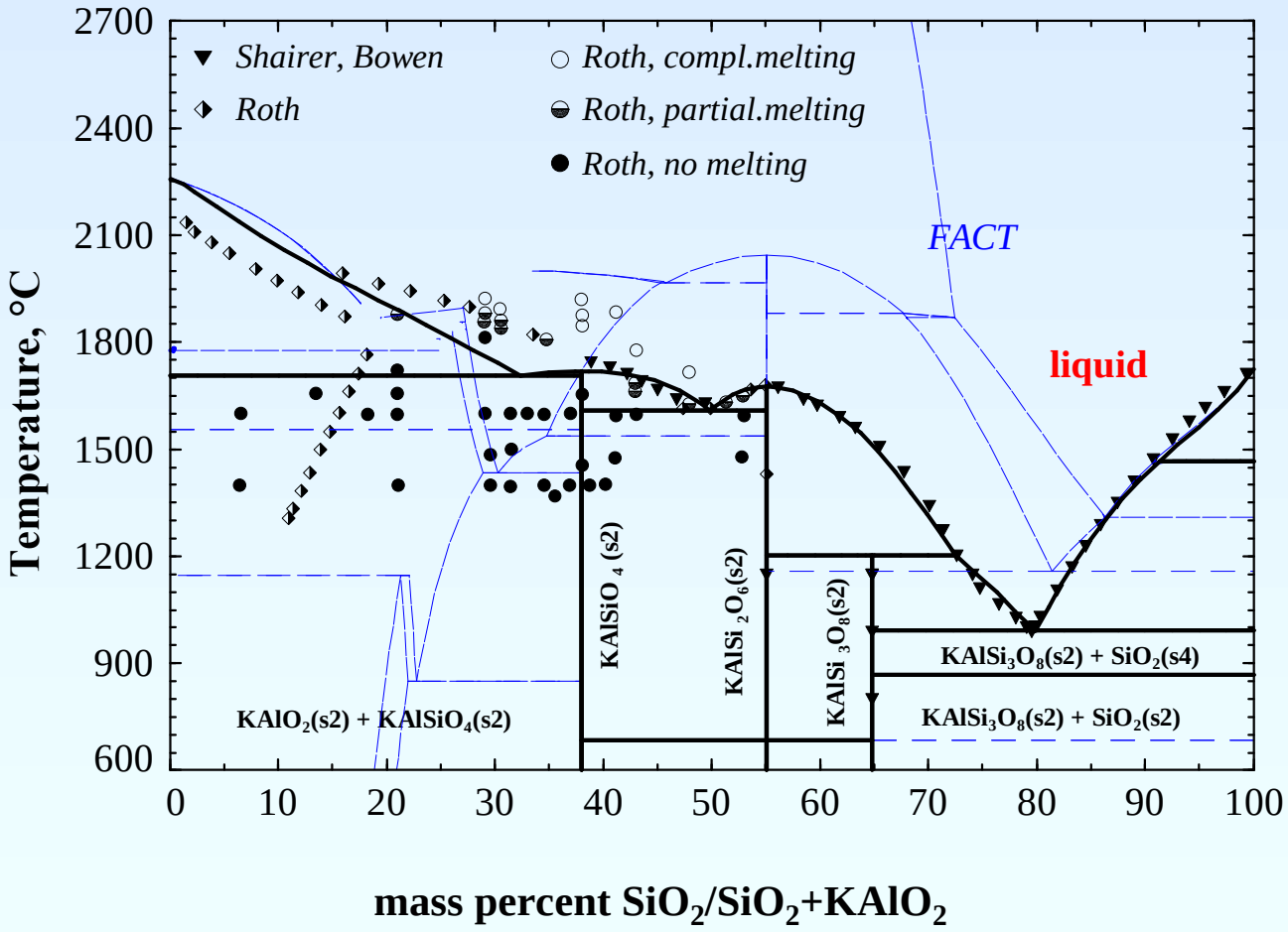
| Interaction parameter between: | |
|---|---|
| Binary species | Ternary species |
| $K_2Si_4O_9$ | $KAlSi_2O_6 \cdot 1/2$ |
| $SiO_2 \cdot 1/2$ | $KAlSi_2O_6 \cdot 1/2$ |
| $K_2Si_2O_5$ | $KAlSi_2O_6 \cdot 1/2$ |
| $Al_6Si_2O_{13} \cdot 1/4$ | $KAlSi_2O_6 \cdot 1/2$ |

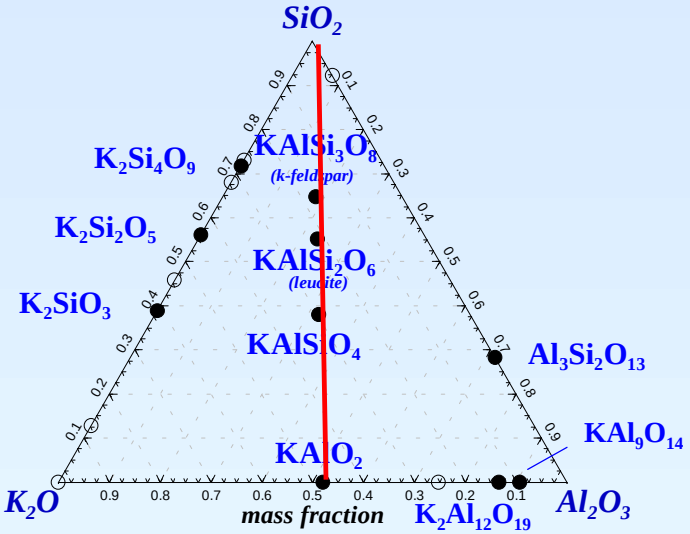


# The predicted phase fields in the $K_2O$-$Al_2O_3$-$SiO_2$ system



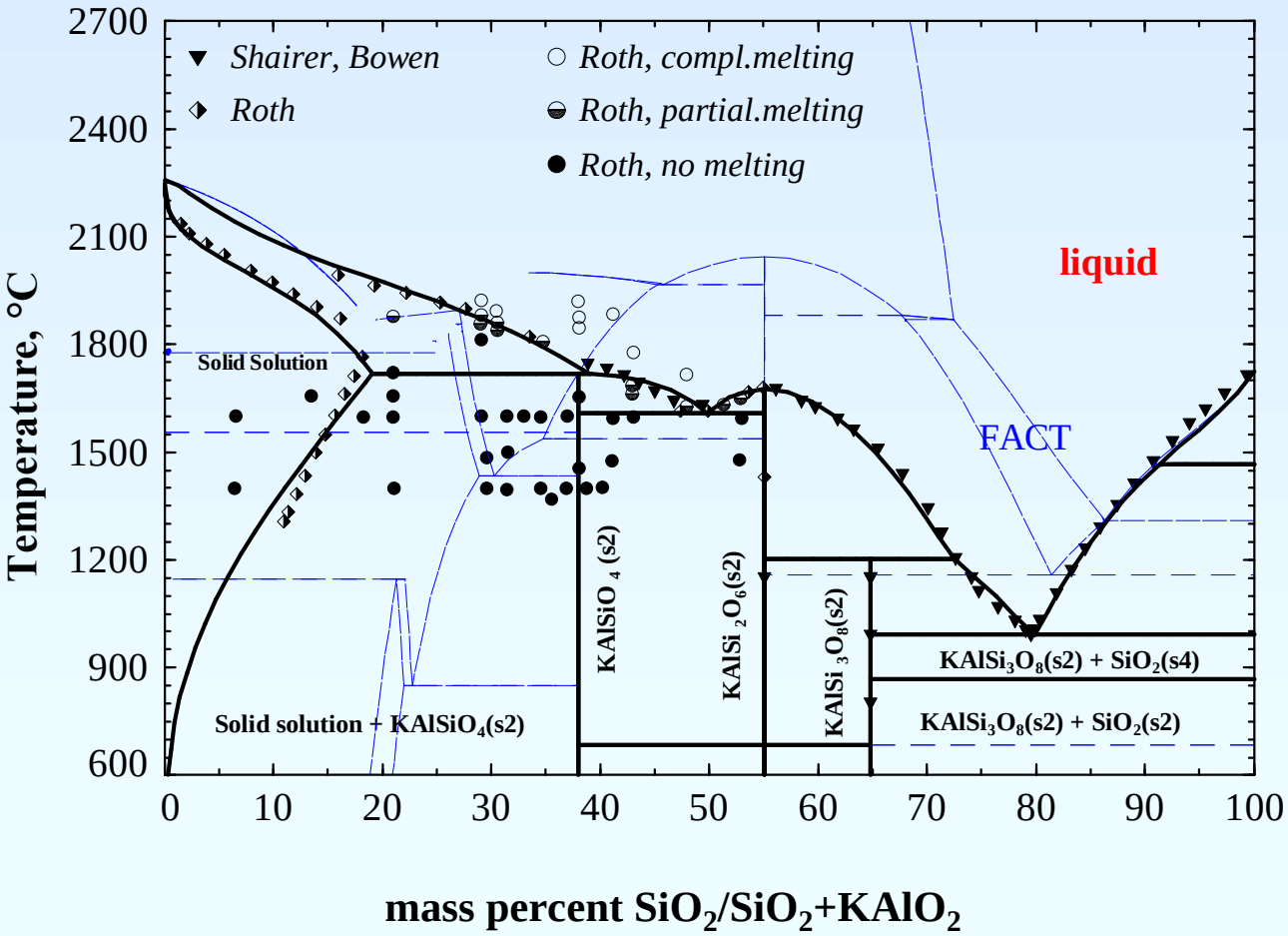
# Quasi-binary section $KAlO_2$-$SiO_2$/ version I

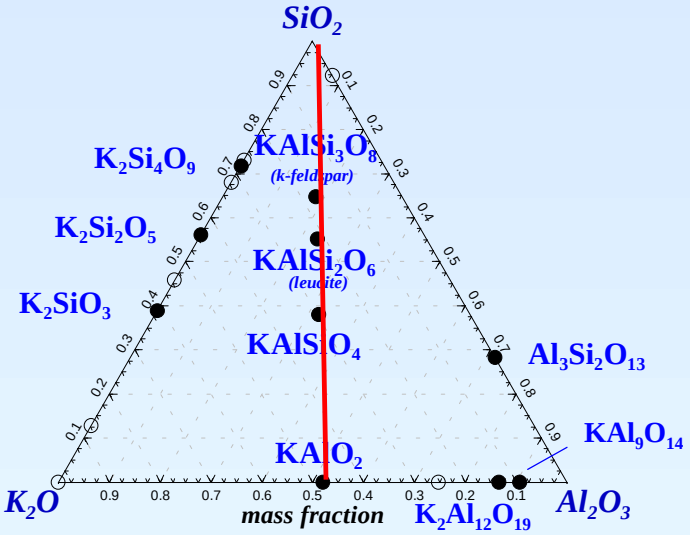



Thermodynamic data for $KAlSi_3O_8$ (K-feldspar) were re-optimised

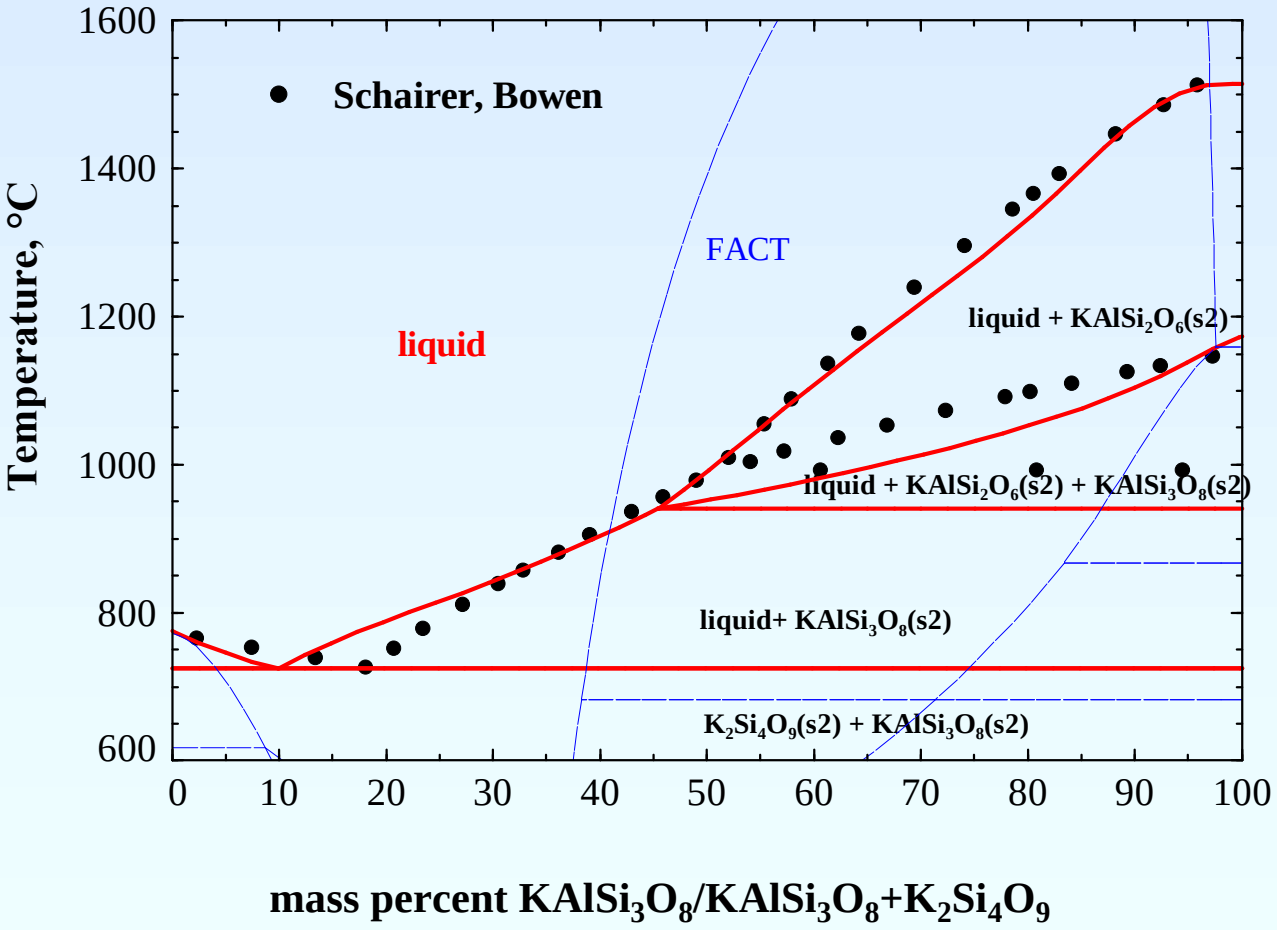
# Quasi-binary section $KAlO_2$-$SiO_2$ / version II

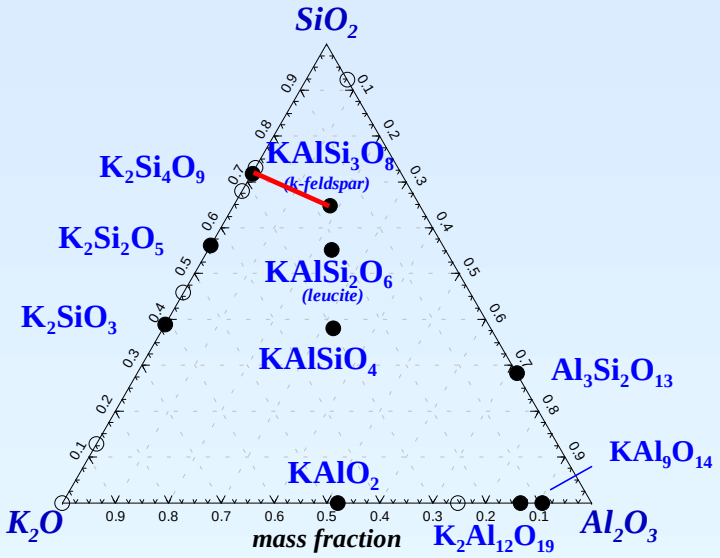


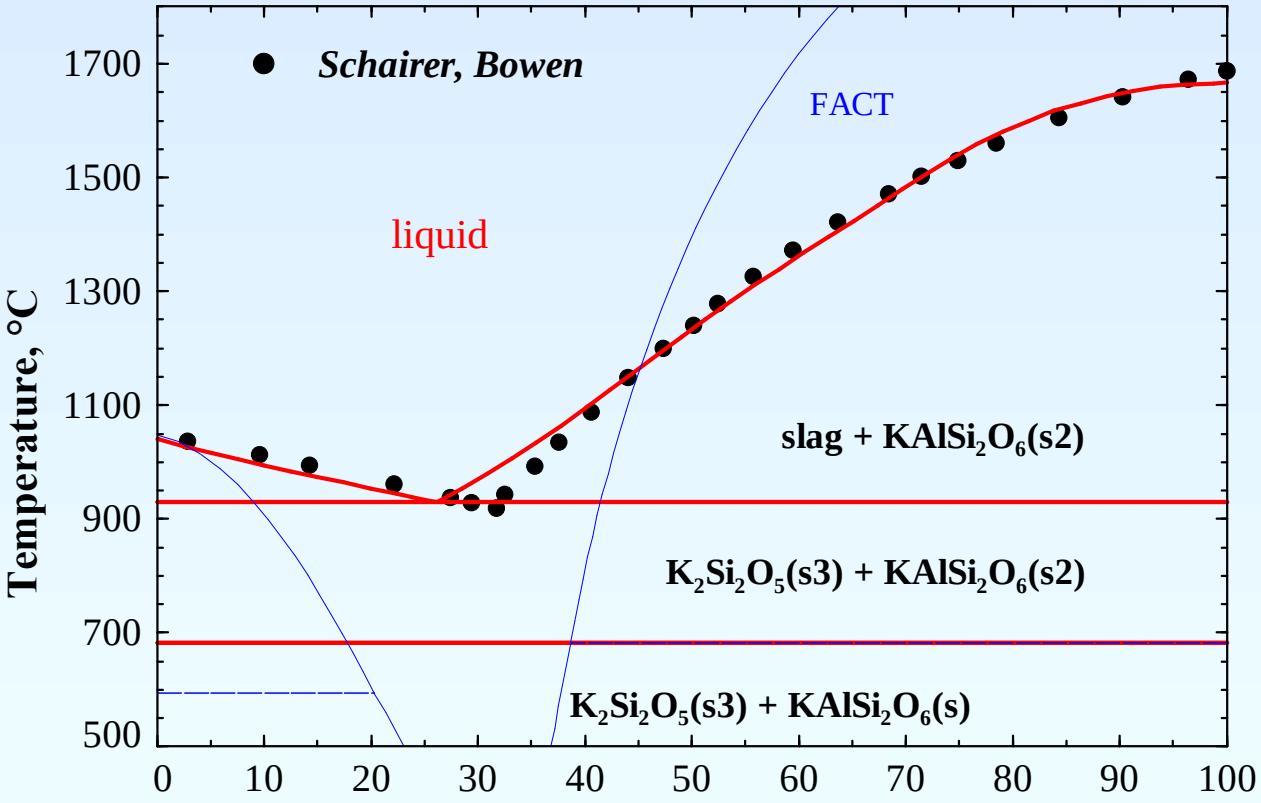

**Solid solution components:**
**Associate species:**
**$KAlO_2$**
**$KAlSiO_4$**

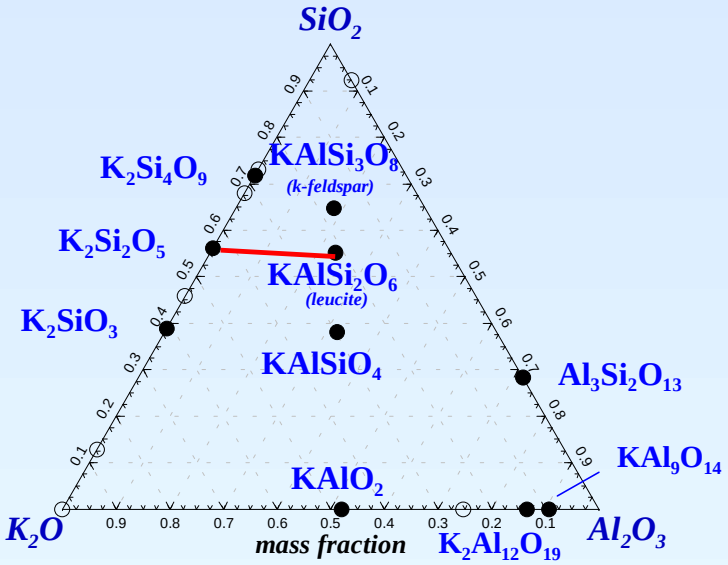
# Quasi-binary section $K_2Si_4O_9$-$KAlSi_3O_8$ (k-feldspar)



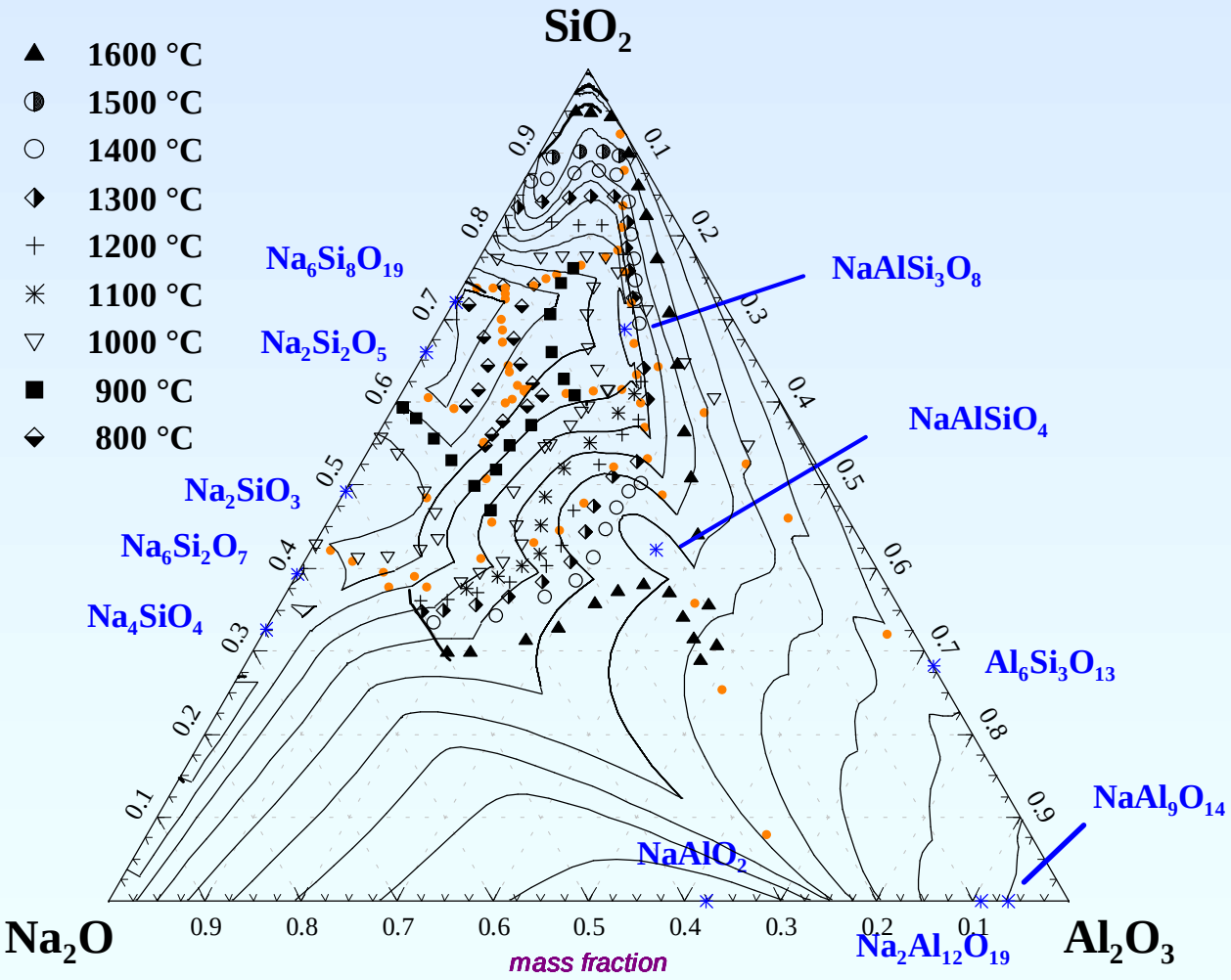



# Quasi-binary section $K_2Si_2O_5$-$KAlSi_3O_8$ (leucite)



# Current results: predicted phase equlibria in the $Na_2O$-$Al_2O_3$-$SiO_2$ system

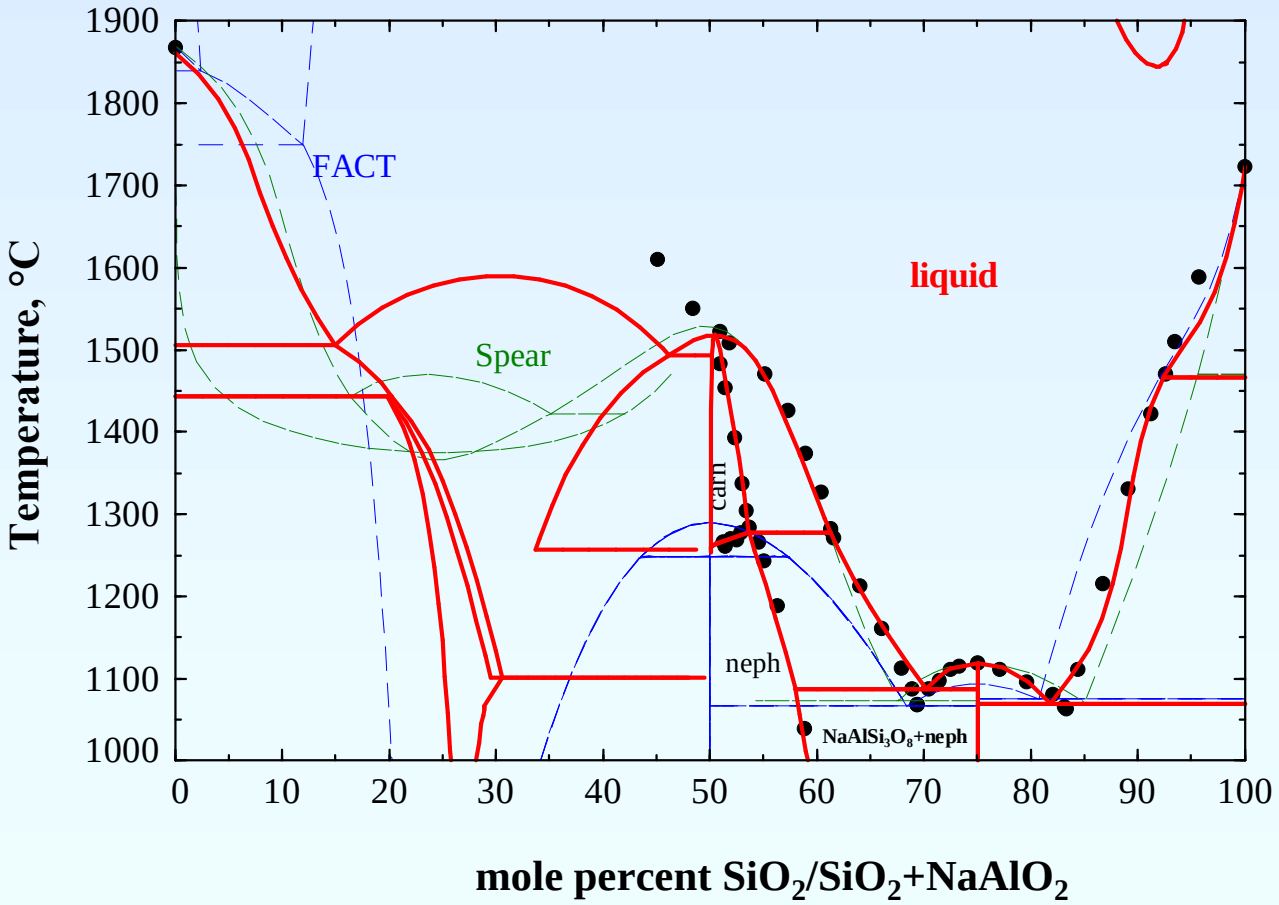


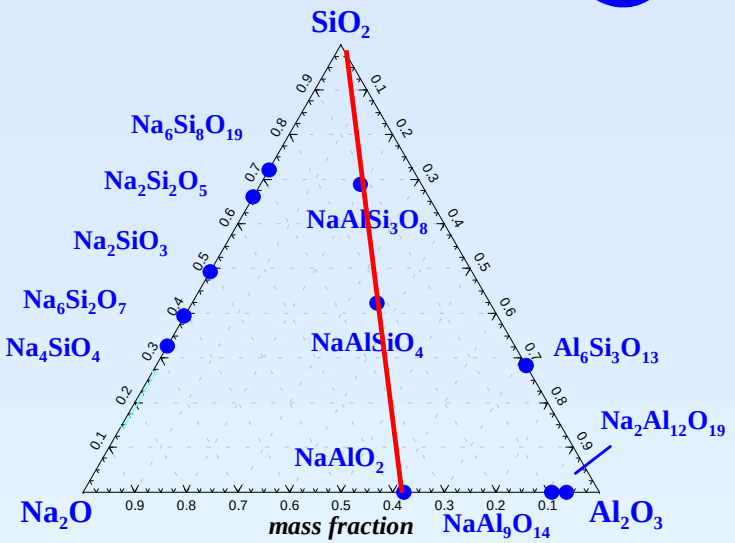

Thermodynamic data for $NaAlSi_3O_8$ (albite) were re-optimised

**Liquid**

- **binary associate species**
- **ternary species: $KAlSi_3O_8 \cdot 2/5$ and $KAlSiO_4 \cdot 2/3$**

# Current results: quasi-binary section $NaAlO_2$-$SiO_2$




## Solid solutions

**Nepheline**

$NaAlSiO4$ (neph, s3)

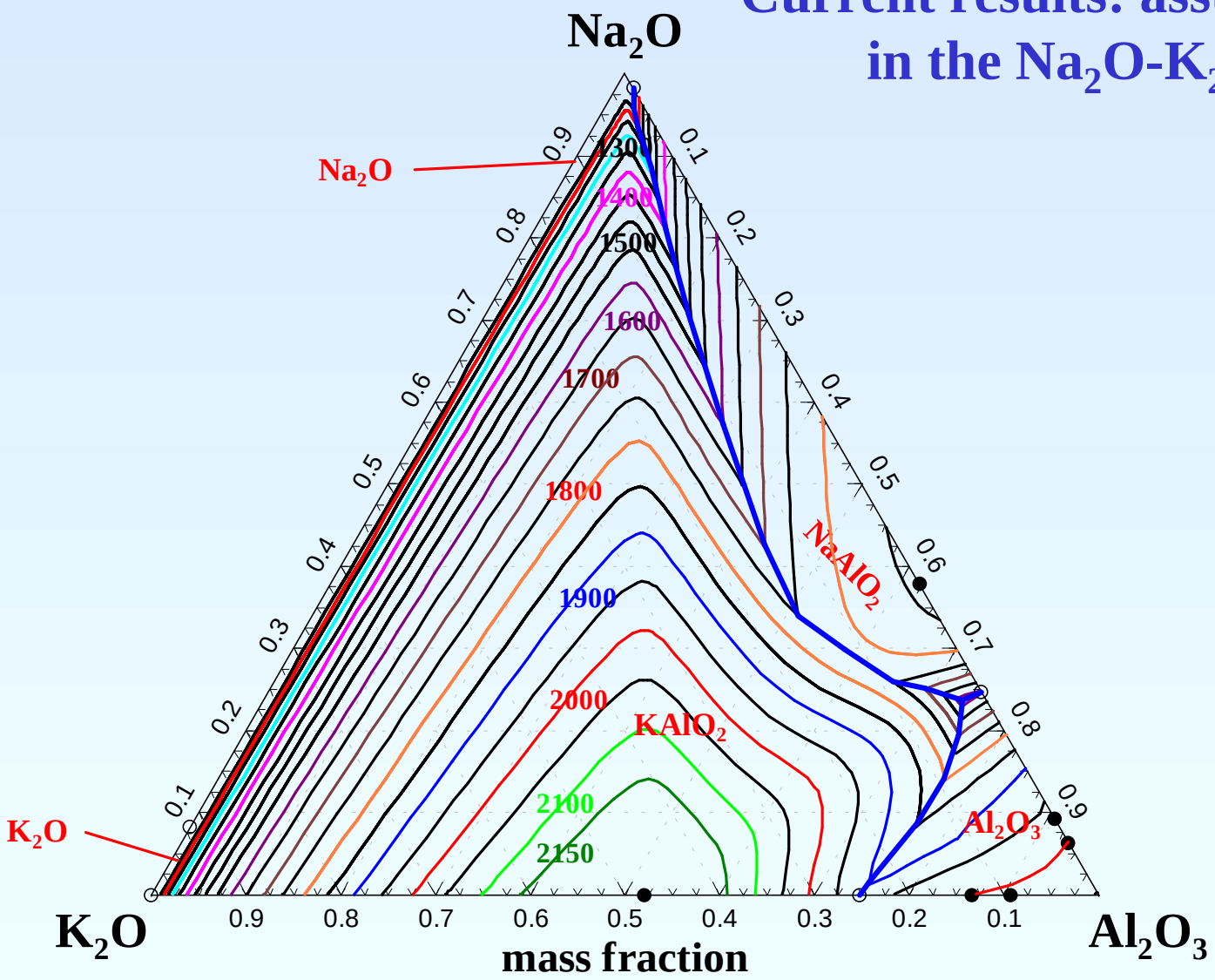
$NaAlSi_2O_6$ (jadeite)

**Carnegieite**

$NaAlSiO_4$ (carn, s4)

$NaAlSi_2O_6$ (jadeite)

# Current results: assumed phase equlibria in the $Na_2O$-$K_2O$-$Al_2O_3$ system



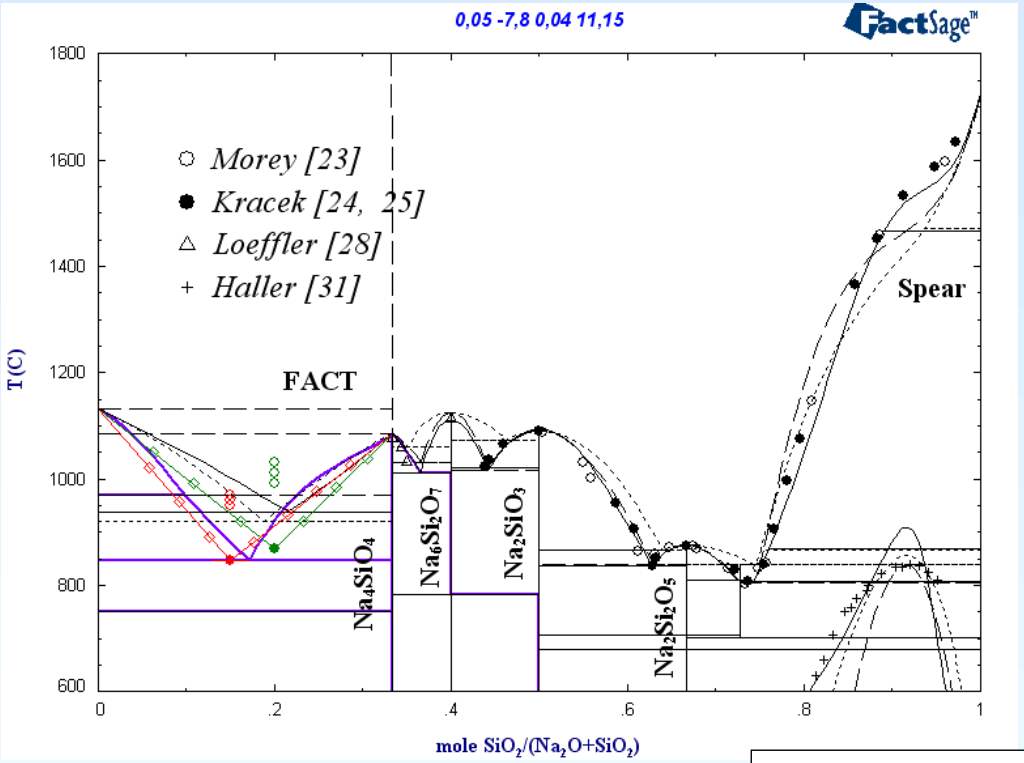
# Conclusions

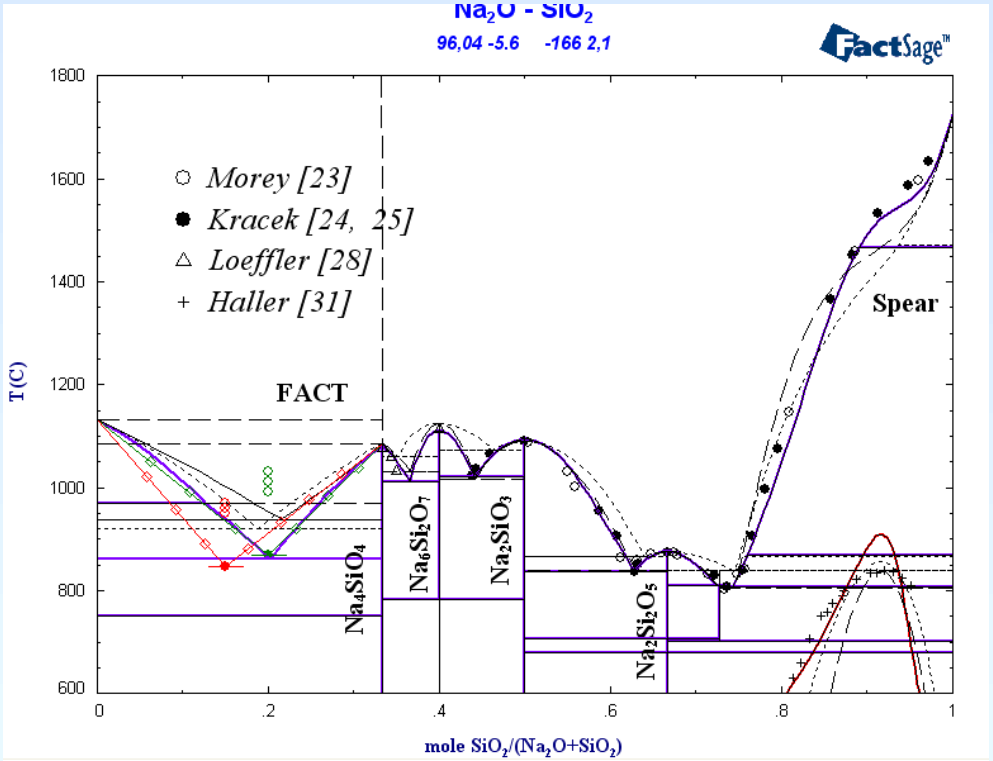
- **The solution data for the binary systems $Me_2O$-$SiO_2$, $Me_2O$-$Al_2O_3$ (Me=Na, K) and $Al_2O_3$-$SiO_2$ were improved to accurate description of the phase diagrams of the slag system**
- **Solid and liquid solutions in the ternary systems $Na_2O$-$K_2O$-$SiO_2$, $K_2O$-$Al_2O_3$-$SiO_2$ and $Na_2O$-$Al_2O_3$-$SiO_2$ (partly) were described using the new database**

# In the future:

- **Assessment the further solution parameters in the $Na_2O$-$Al_2O_3$-$SiO_2$ system**
- **Consideration of the oxide systems containing CaO and MgO**

# Thank you for your attention




**New eutectic point at 845 °C**

**New eutectic point at 867 °C**

***Experimental data***

***of M. Rys, IEF-2***