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Thermochemical assessments for alkali-containing oxide systems with silica and alumina

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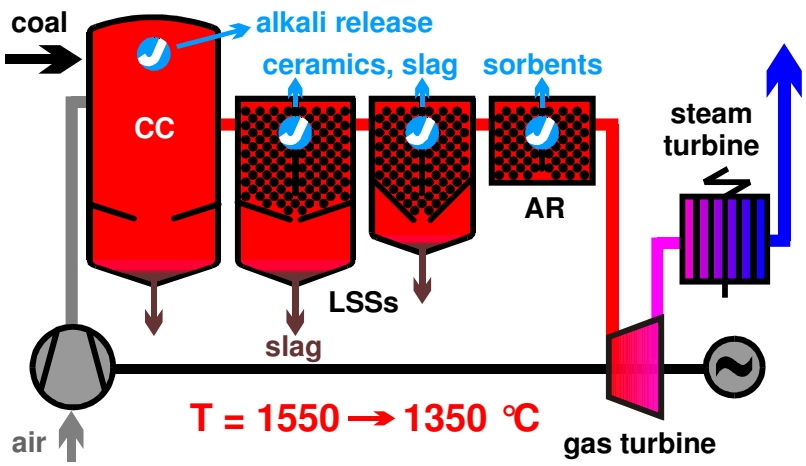
- Model and optimisation
- Application of a new data base for binary subsystems
- Application of a new data base for ternary subsystems
- Conclusions and outlook

Introduction and aim



Pressurized Pulverized Coal Combustion – as potential concept of power plant with reduced CO_2-emission and increased efficiency

Hot gas cleaning: alkali removing by slags with high potential of alkali retention (SiO_2, Al_2O_3, Fe_2O_3) or by getter materials (kaolin, bauxite)

Available databases are not sufficient to model the complete coal ash (slag) system

Aim – development of a new data base for the slag relevant system containing alumina, silica, alkali oxides

Associate species model

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

Liquid (slag)

Ternary components	
Compounds	**Associate species**
$KAlSiO_4$	$KAlSiO_4 \cdot 2/3$
$KAlSi_2O_6$	$KAlSi_2O_6 \cdot 1/2$

Binary components	
Compounds	**Associate species**
Na_4SiO_4	$Na_4SiO_4 \cdot 2/5$
Na_2SiO_3	$Na_2SiO_3 \cdot 2/3$
$Na_2Si_2O_5$	$Na_2Si_2O_5 \cdot 1/2$
K_2SiO_3	$K_2SiO_3 \cdot 2/3$
$K_2Si_2O_5$	$K_2Si_2O_5 \cdot 1/2$
$K_2Si_4O_9$	$K_2Si_4O_9 \cdot 1/3$
$NaAlO_2$	$NaAlO_2$
	$Na_2Al_4O_7 \cdot 1/3$
$KAlO_2$	$KAlO_2$
	$Na_2Al_4O_7 \cdot 1/3$
$Al_6Si_2O_{13}$	$Al_6Si_2O_{13} \cdot 1/4$

Mullite:
$Al_6Si_2O_{13} \cdot 1/4$, Al_2O_3, $SiO_2 \cdot 2$

$KAl_{1-x}Si_xO_4$ solid solution:
$KAlO_2$, $KAlSiO_4$

Optimisation

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.

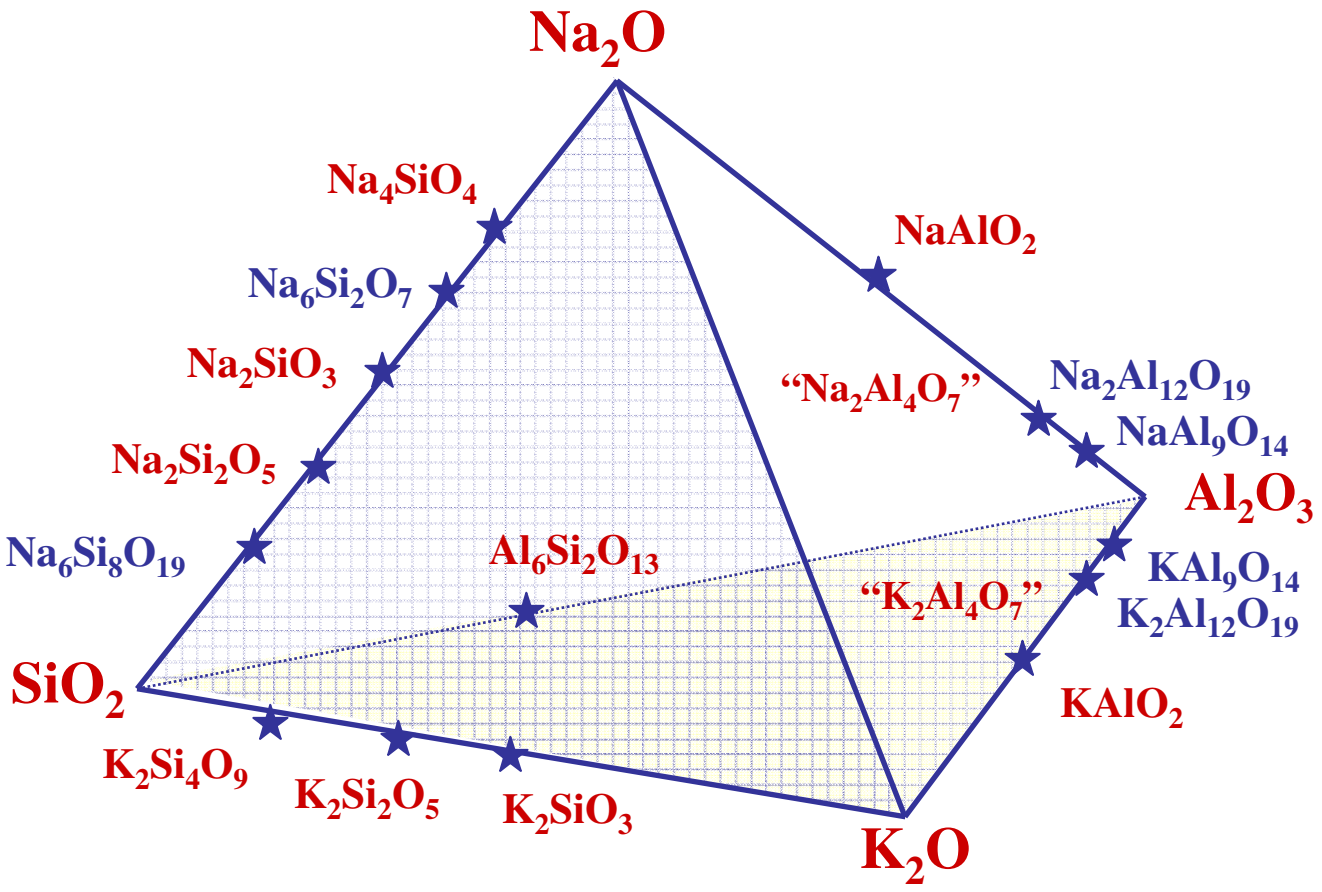
Adjustable parameters: ΔH_f^{298} and S^{298} for the liquid and solid solution species, ΔH_f^{298} and S^{298} for the pure solid compounds (part.), interaction parameters between species

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

$$L_{ij}^{(v)} = A_{ij}^{(v)} + B_{ij}^{(v)} \cdot T + C_{ij}^{(v)} \cdot T \cdot \ln T + D_{ij}^{(v)} \cdot T^2 + \ldots, v = 0,1$$

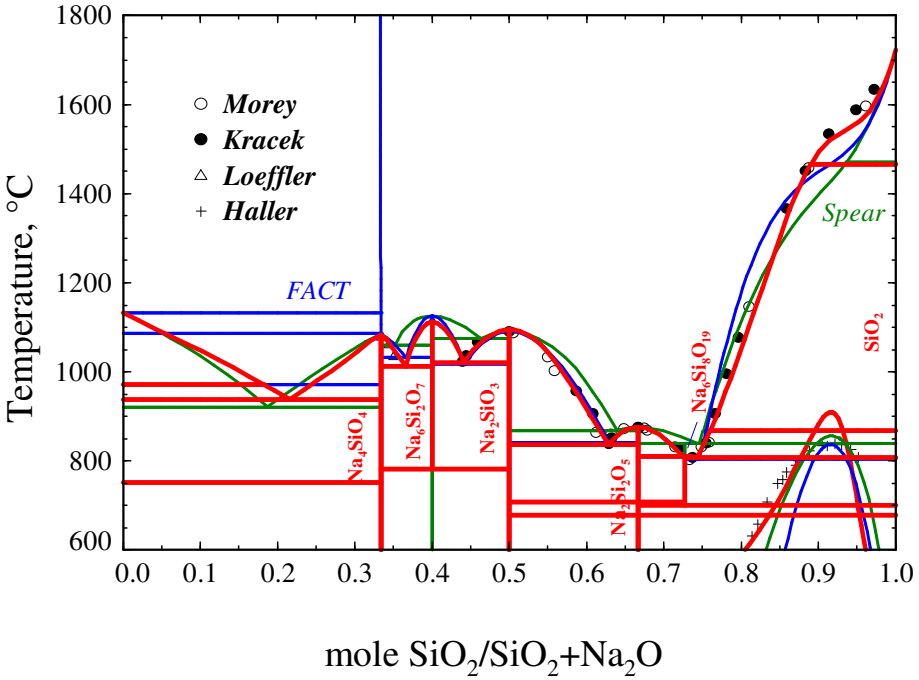
New database for the oxide systems

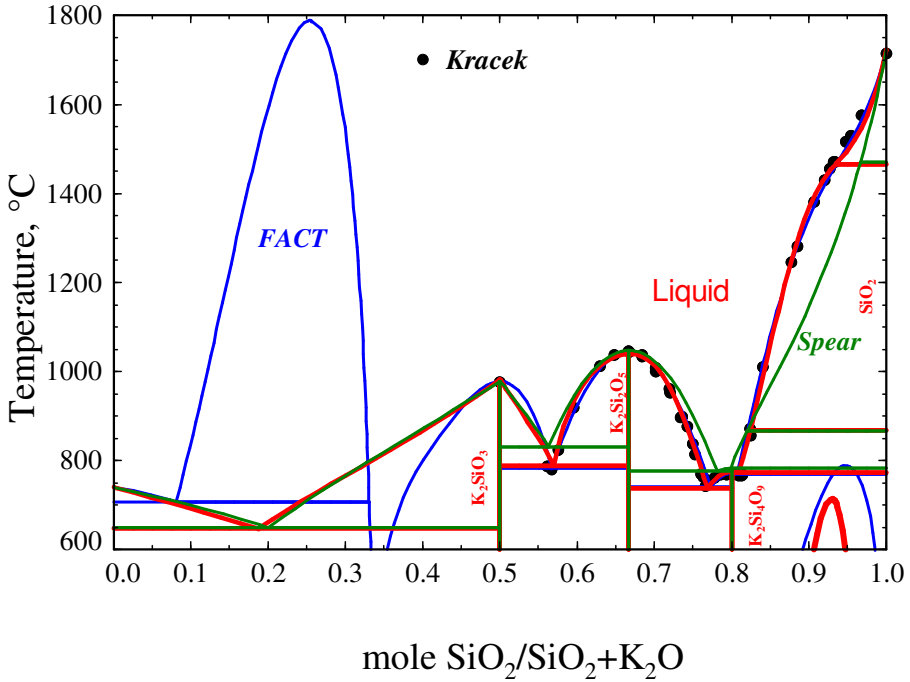
Oxide system



Results of assessment for the binary systems

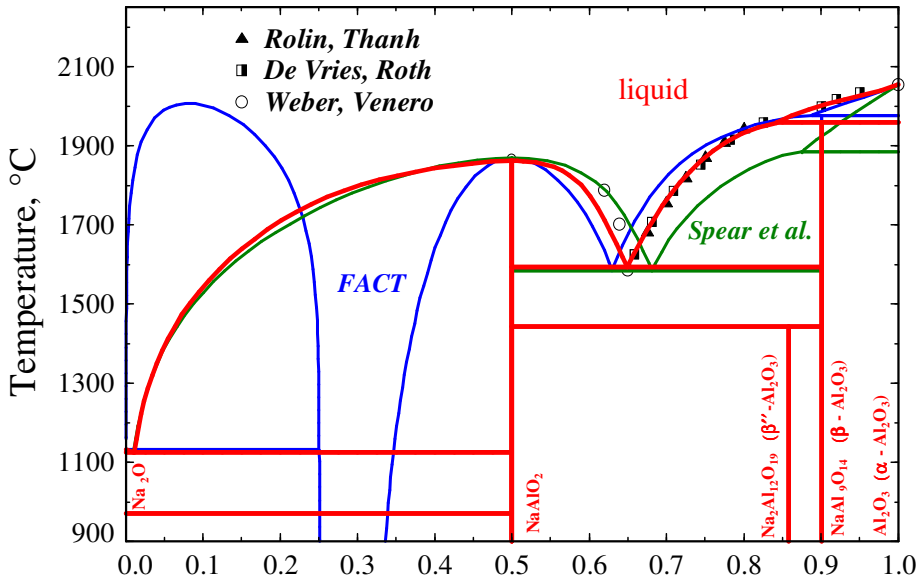
Me_2O-SiO_2, Me=Na, K

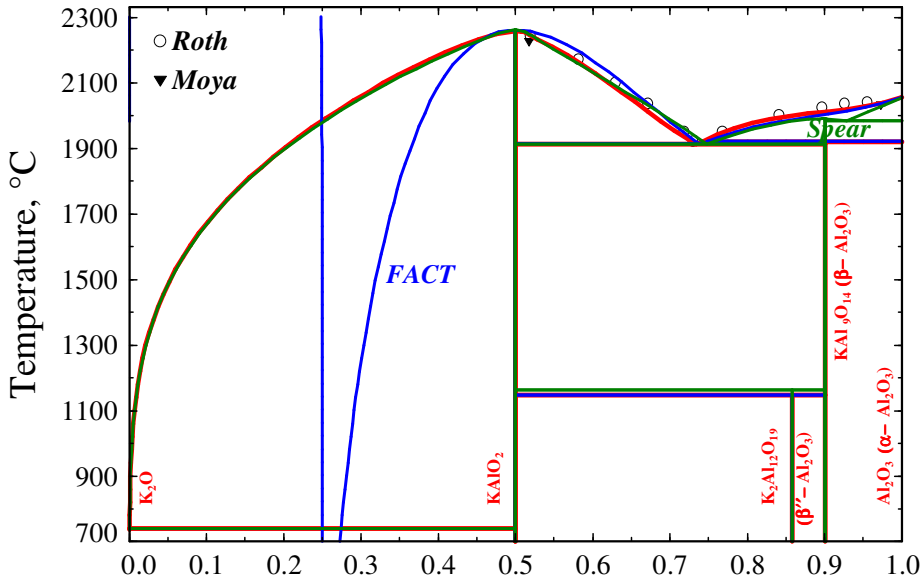




Results of assessment for the binary systems

Me_2O-Al_2O_3, Me=Na, K

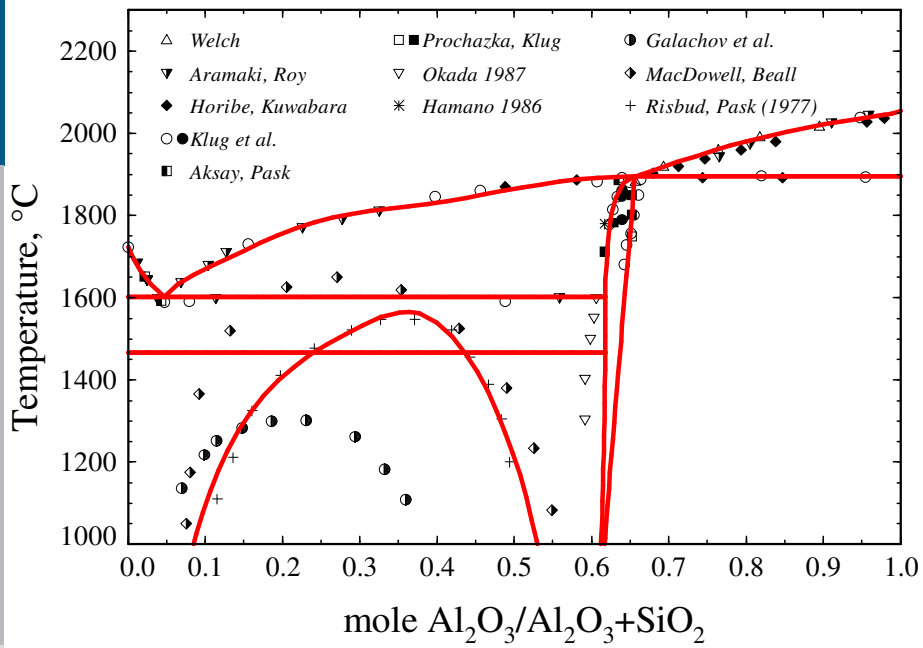




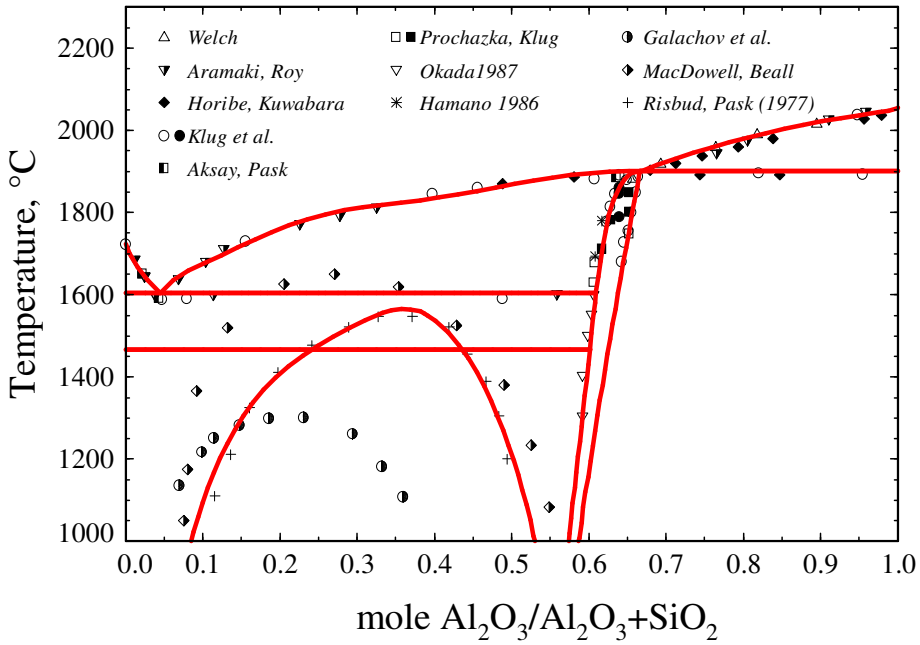
Thermodynamic data on $NaAl_9O_{14}$ (β-alumina) and $Na_2Al_{12}O_{19}$ (β``-alumina) were optimised.

Results of assessment for the binary systems

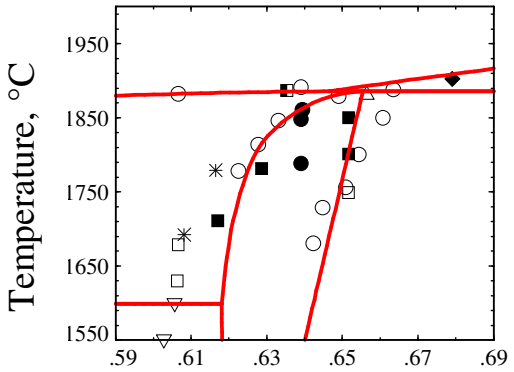
Associate model for mullite

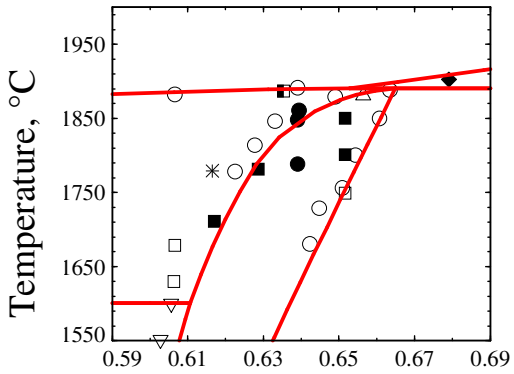


Four-sublattice model for mullite



Congruent

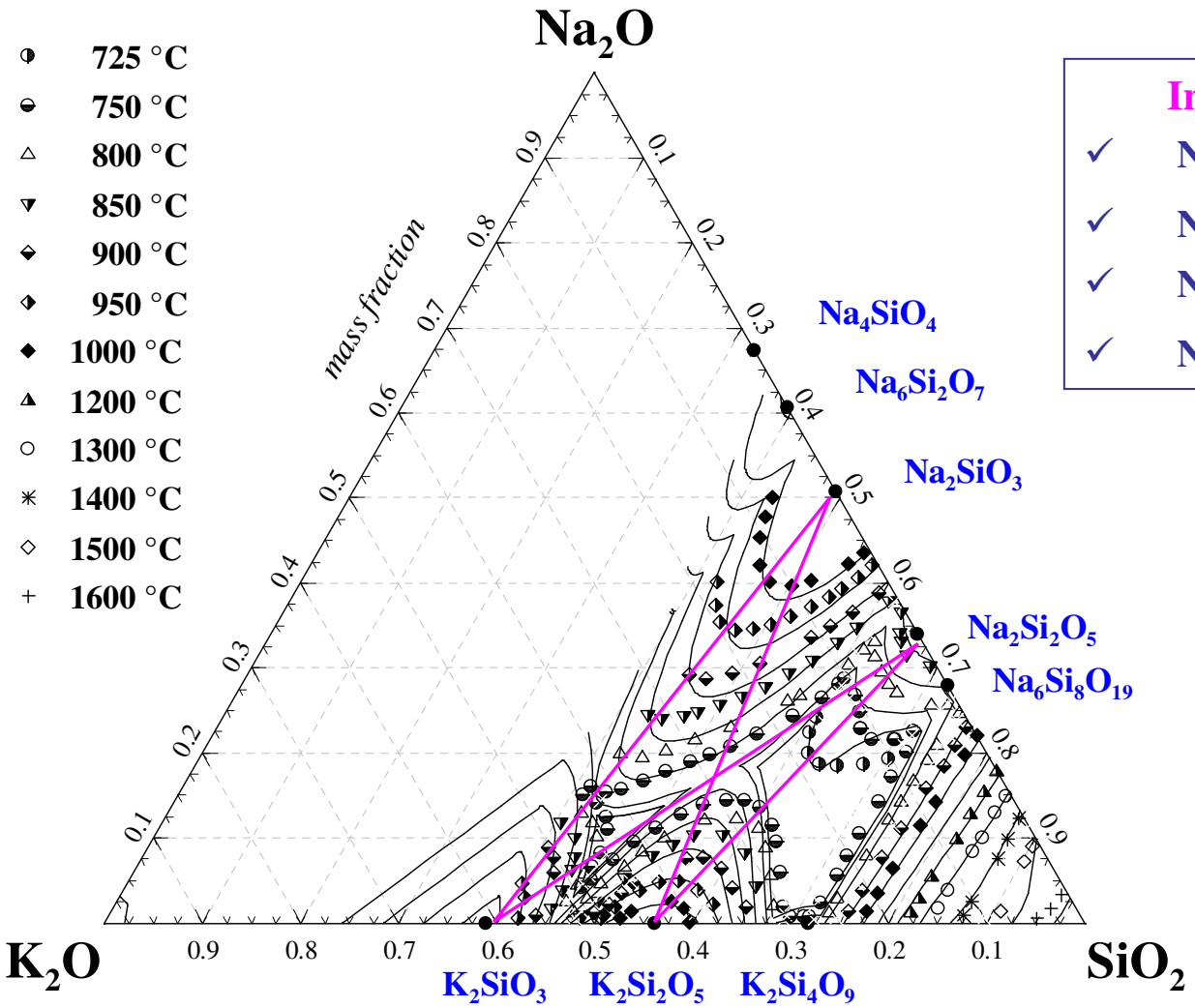




Incongruent

Ternary K_2O-Na_2O-SiO_2 system

Comparison of the calculated isotherms with the experimental points

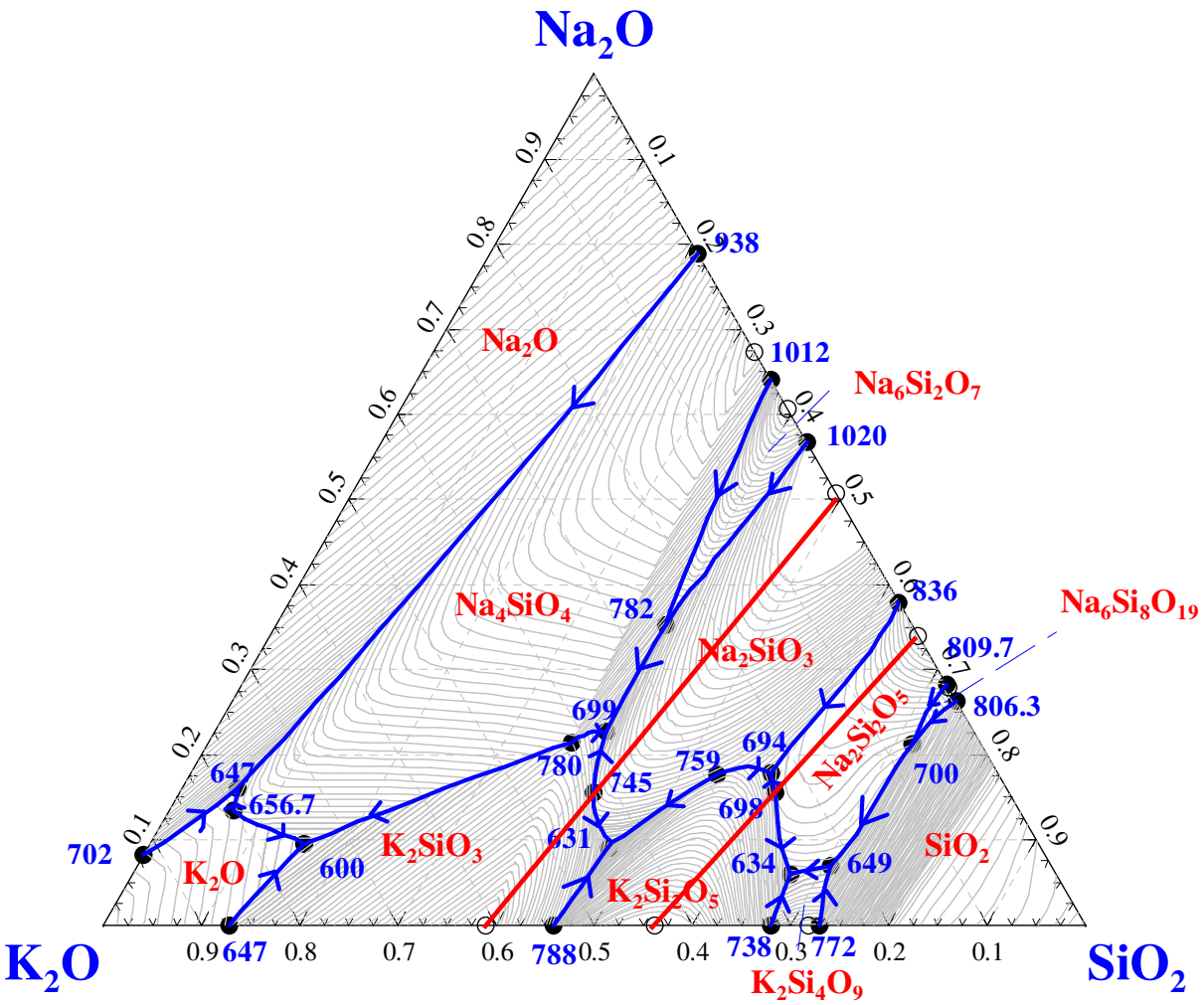


Interaction parameters:

- ✓ Na_2SiO_3*2/3 - K_2SiO_3*2/3
- ✓ $Na_2Si_2O_5$*1/2 - $K_2Si_2O_5$*1/2
- ✓ Na_2SiO_3*2/3 - $K_2Si_2O_5$*1/2
- ✓ $Na_2Si_2O_5$*1/2 - K_2SiO_3*2/3

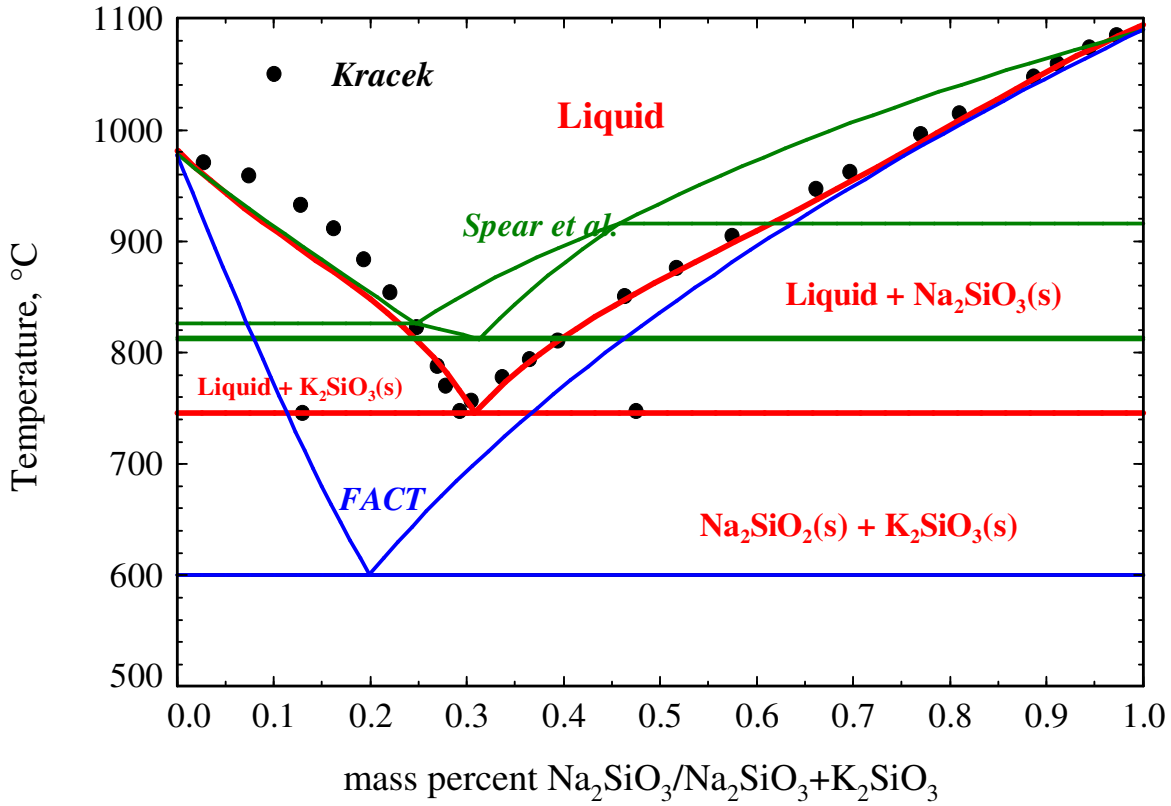
Ternary K_2O-Na_2O-SiO_2 system

Predicted phase fields and ternary points



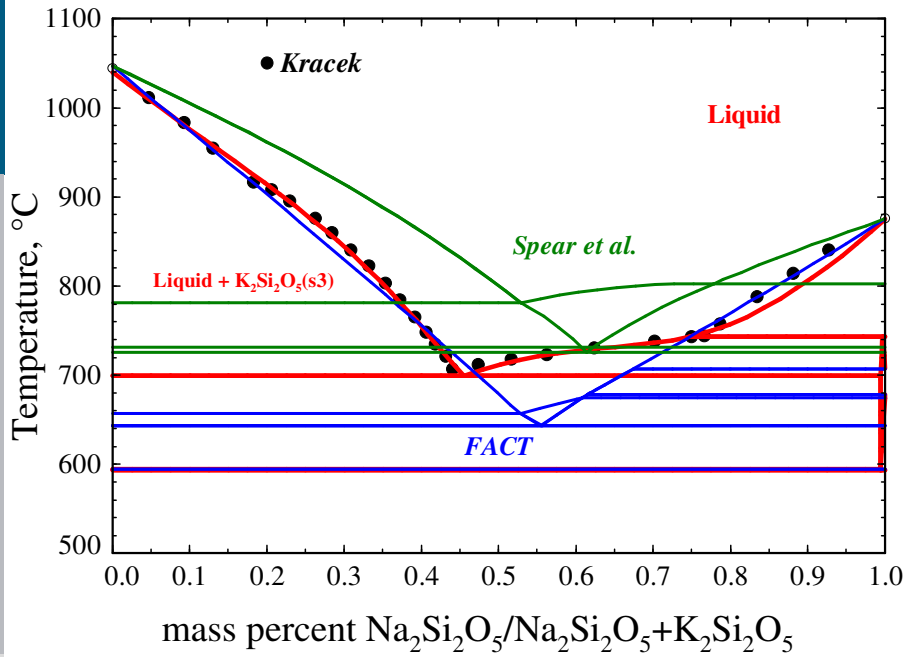
Quasi-binary sections in the K_2O-Na_2O-SiO_2 system

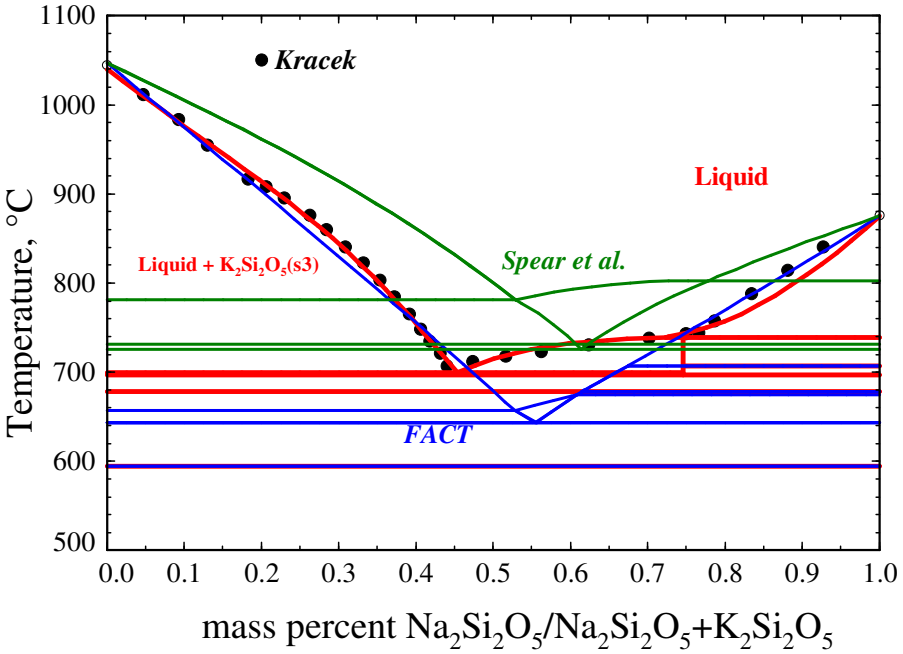
K_2SiO_3-Na_2SiO_3

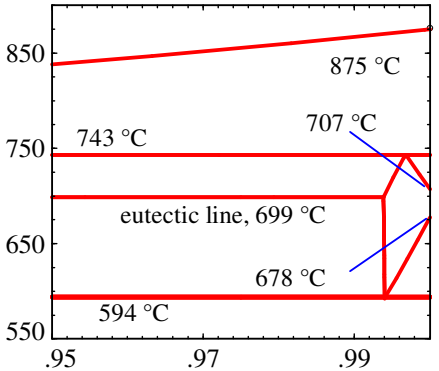


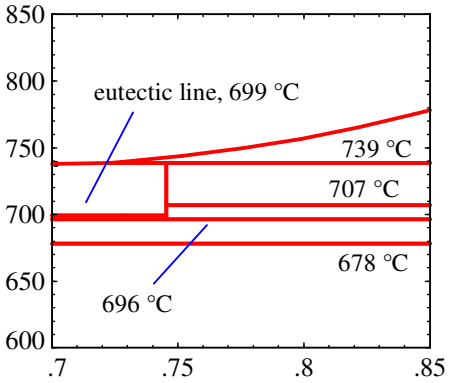
Quasi-binary sections in the K_2O-Na_2O-SiO_2 system

$K_2Si_2O_5$-$Na_2Si_2O_5$



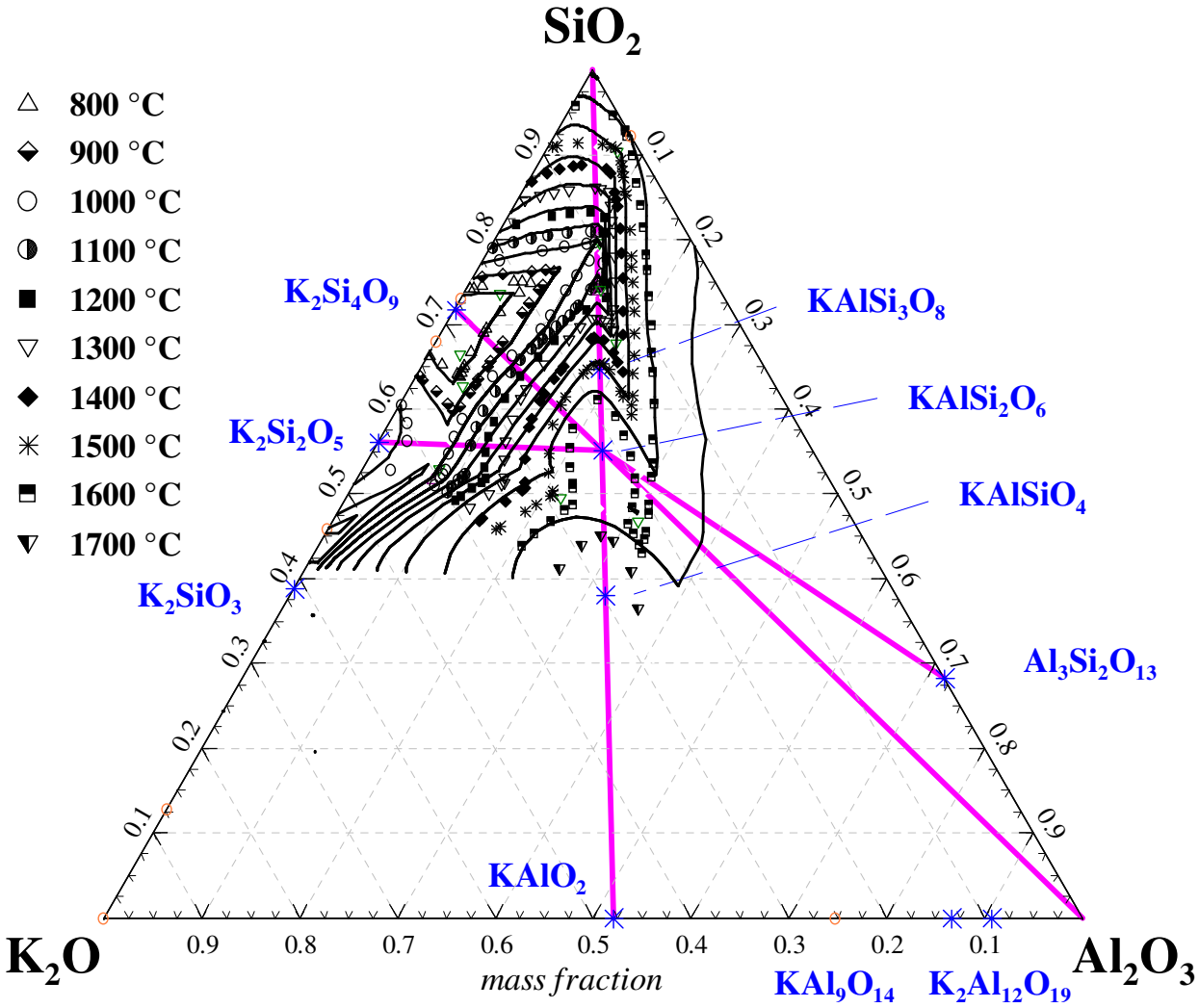






K_2O-Al_2O_3-SiO_2 system

Comparison of the calculated equlibria with the experimental points

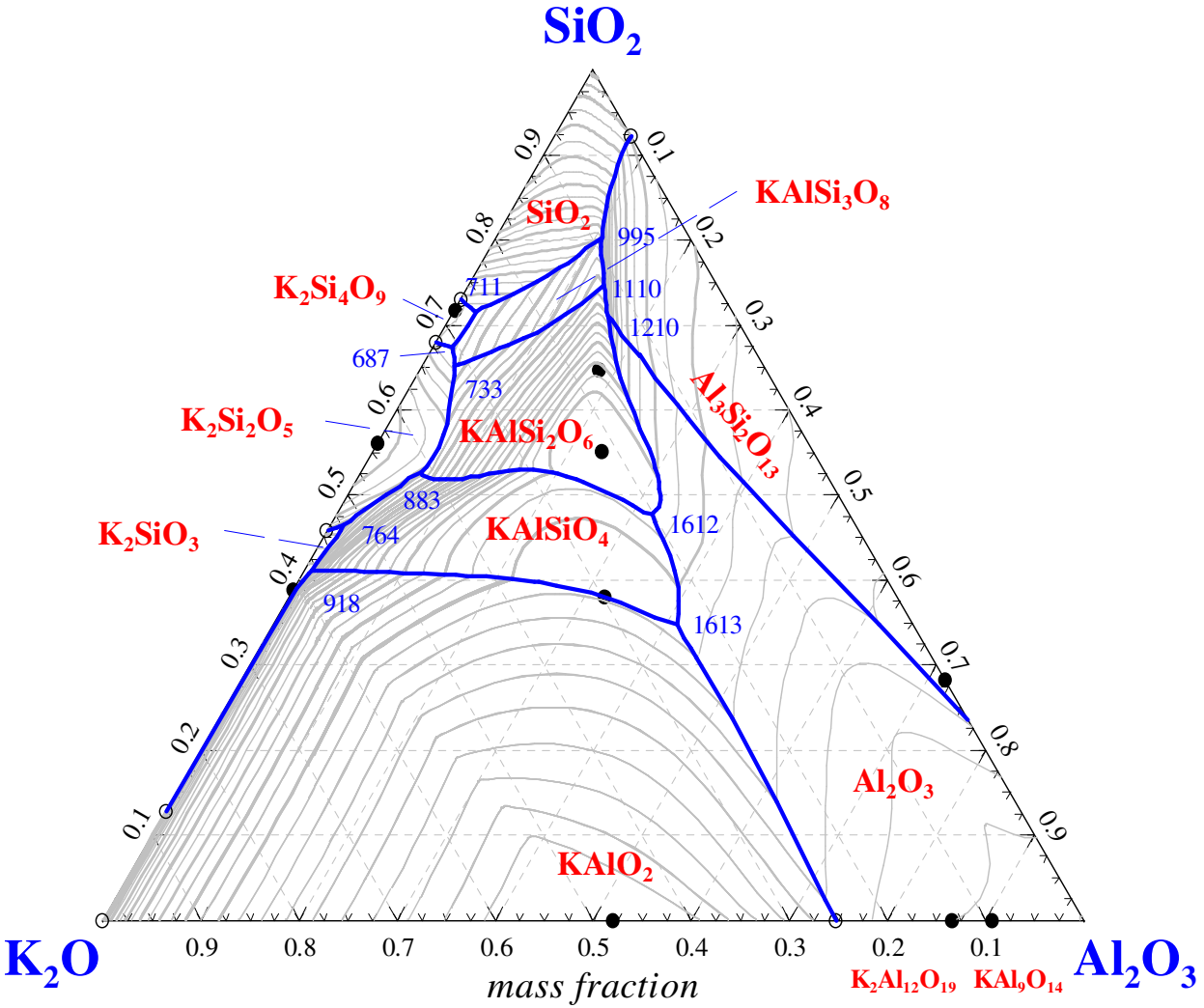


Liquid

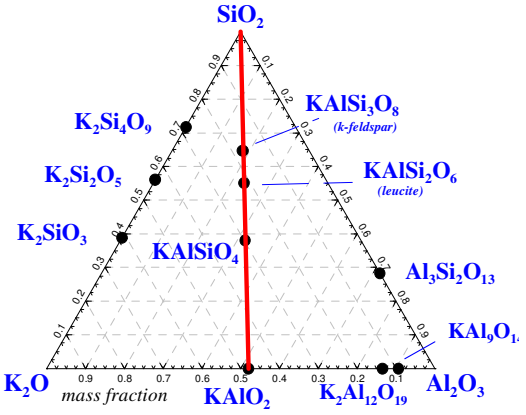
- binary associate species
- ternary species: $KAlSi_2O_6 \cdot 1/2$ and $KAlSiO_4 \cdot 2/3$
- interaction parameters between binary and ternary species

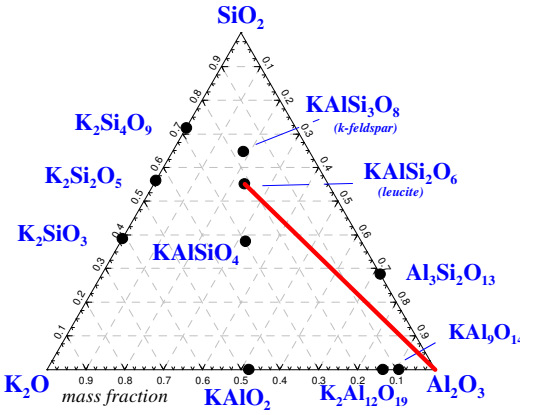
K_2O-Al_2O_3-SiO_2 system

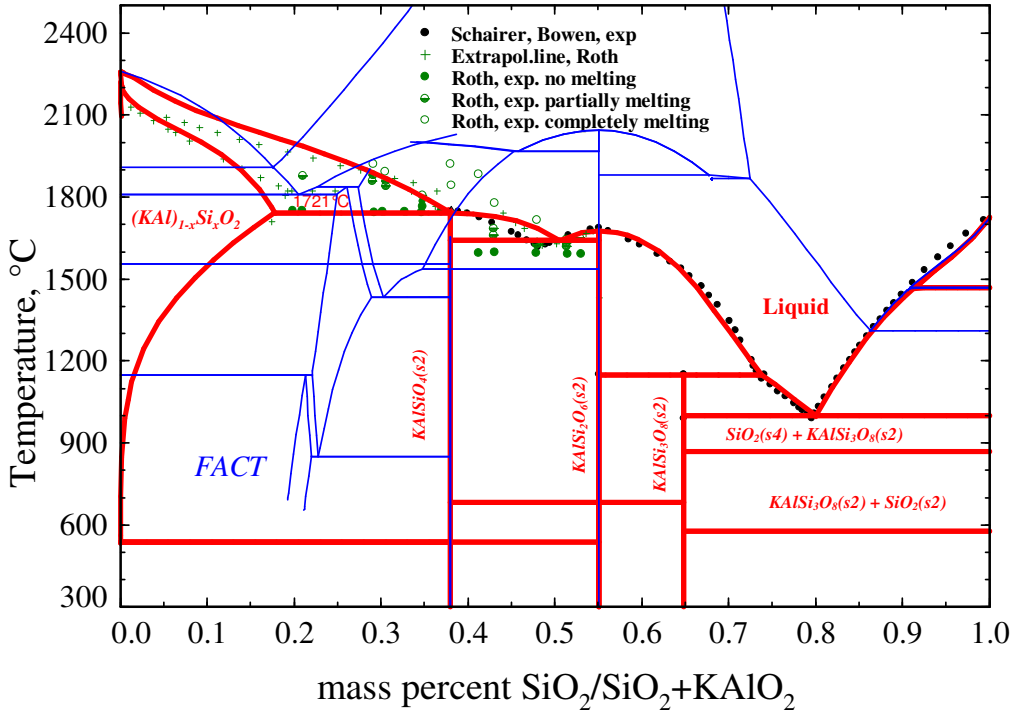
Predicted phase fields boundaries

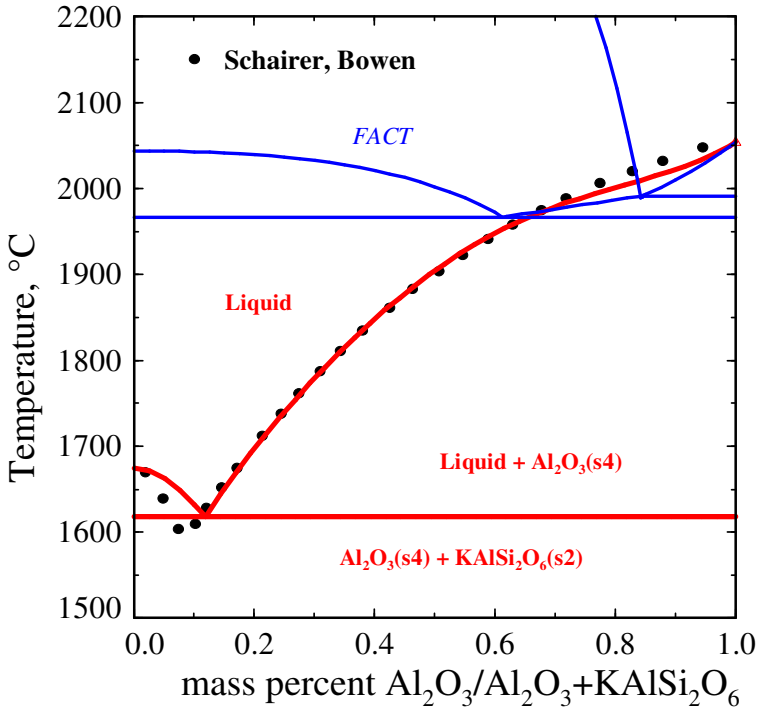


Quasi-binary section in the K_2O-Al_2O_3-SiO_2 system-1

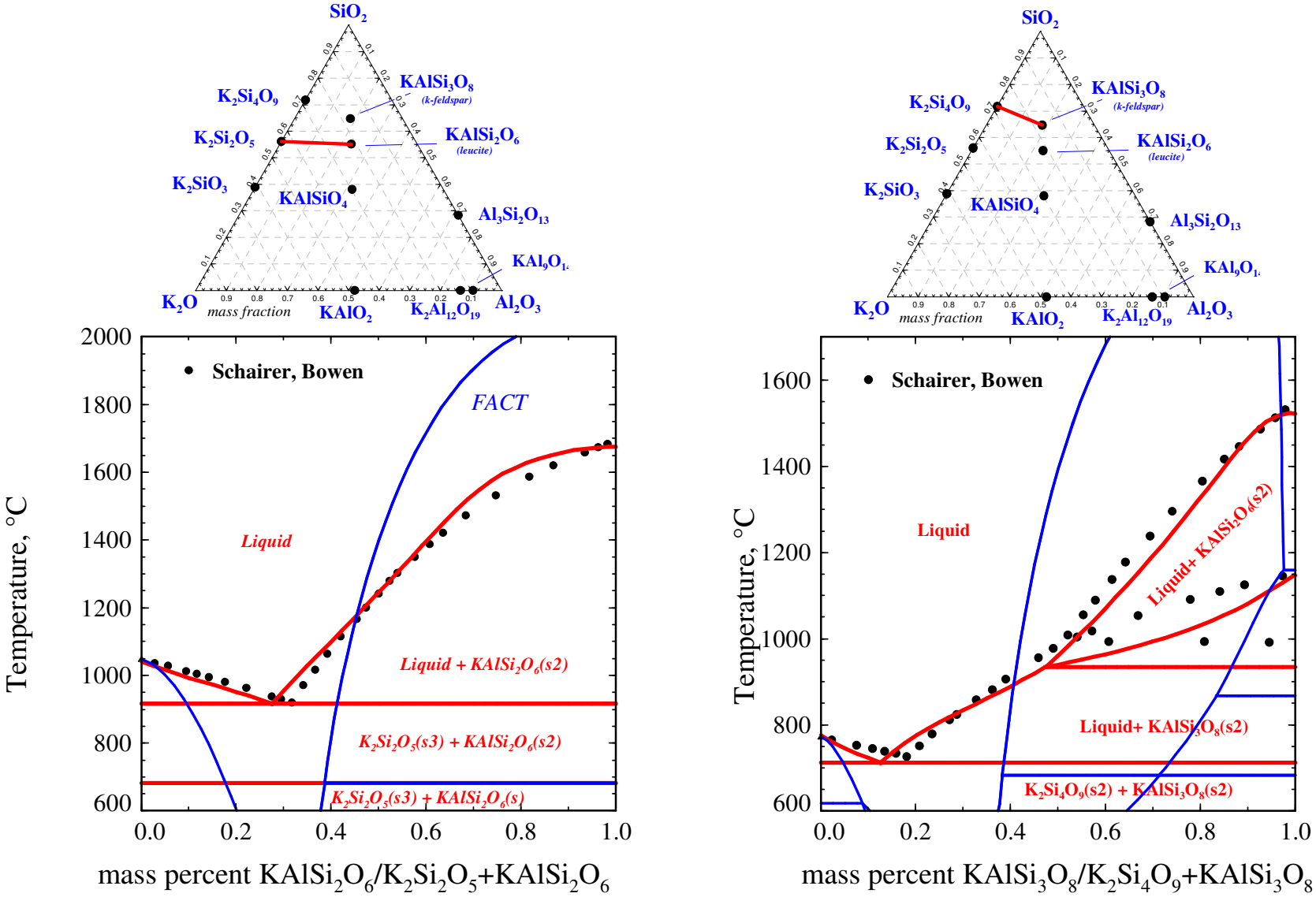








Quasi-binary section in the K_2O-Al_2O_3-SiO_2 system-2



Thermodynamic data on $KAlSi_3O_8$ (s2, feldspar) and $KAlSiO_4$ (kaliophilite) were optimised.

Conclusions and outlook

- 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 generated to accurate description of the phase diagrams
- Solid and liquid solutions in the ternary systems Na_2O-K_2O-SiO_2 and K_2O-Al_2O_3-SiO_2 were described using the new database

- **Future goals:**
- Assessment the further solution parameters in the Na_2O-Al_2O_3-SiO_2 system
- Addition of magnesium and calcium oxides to the database

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Thank you for your attention