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JÜLICH FORSCHUNGSZENTRUM

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Thermodynamic optimisation of the systems K_2O-Al_2O_3-SiO_2 and Na_2O-Al_2O_3-SiO_2

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Content

Motivation and aims

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)

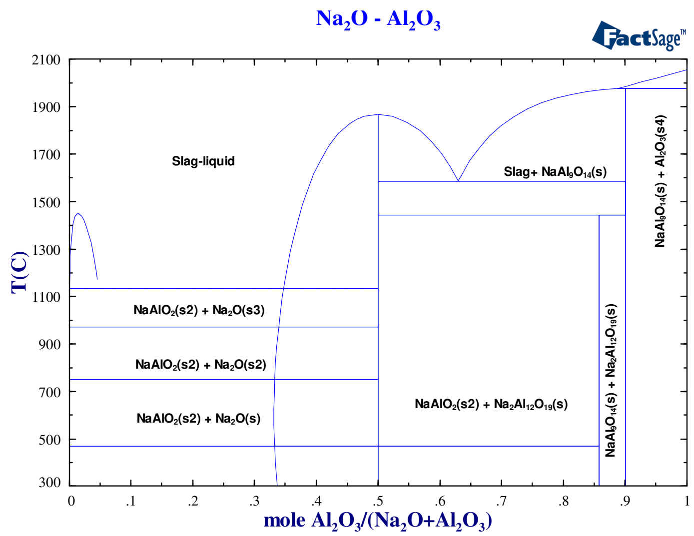
Thermodynamic calculation/prediction for slag relevant oxide systems, which are different from the point of view of experimental measurements

Calculation requires:

- Reliable database, based on the experimental data
- Software

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

No solution



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

Modelling of liquid and solid solutions

Composition of the liquid slag – silica, alumina, Alk_2O (Alk=Na, K)

Chosen model – associate species approach (introduced for slag by Spear, Allendorf, Besmann, 2002):

- suitable for this system
- relatively simple for using and modification

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

+

Ternary components	
Compounds	**Associate species**
$KAlSiO_4$	$KAlSiO_4 \cdot 2/3$
$KAlSi_2O_6$	$KAlSi_2O_6 \cdot 1/2$
$NaAlSiO_4$	$NaAlSiO_4 \cdot 2/3$
$NaAlSi_3O_8$	$NaAlSi_3O_8 \cdot 2/5$

+

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	$K_2SiO_3 \cdot 2/3$
$K_2Si_2O_5$	$K_2Si_2O_5 \cdot 1/2$
$K_2Si_4O_9$	$K_2Si_4O_9 \cdot 1/3$
$NaAlO_2$	$NaAlO_2$
-	$Na_2Al_4O_7 \cdot 1/3$
$KAlO_2$	$KAlO_2$
-	$Na_2Al_4O_7 \cdot 1/3$
$Al_6Si_2O_{13}$	$Al_6Si_2O_{13} \cdot 1/4$

Interaction between solution components

Mullite

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

4 sublattice model:
$(Al^{3+})_1(Al^{3+})_1(Al^{3+}, Si^{4+})_1(O^{2-}, Va)_5$

$(KAl)_{1-x}Si_xO_2$ solid solution:
Associate species $KAlO_2$, $KAlSiO_4$

Optimisation procedure

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

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

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

↓

New database for the oxide systems

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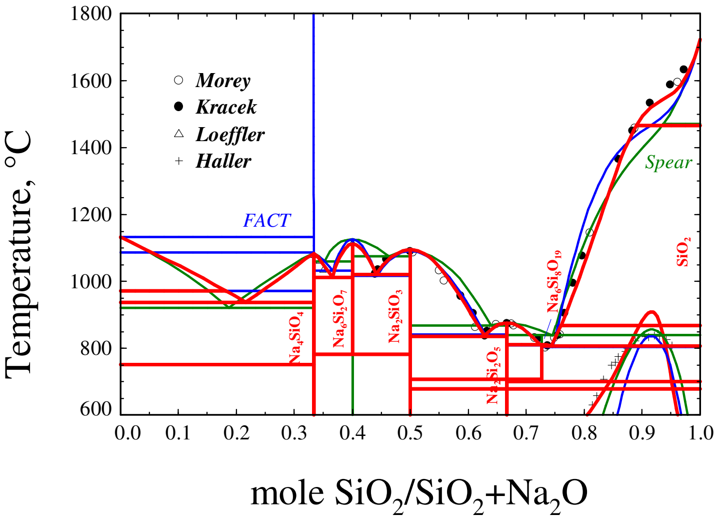
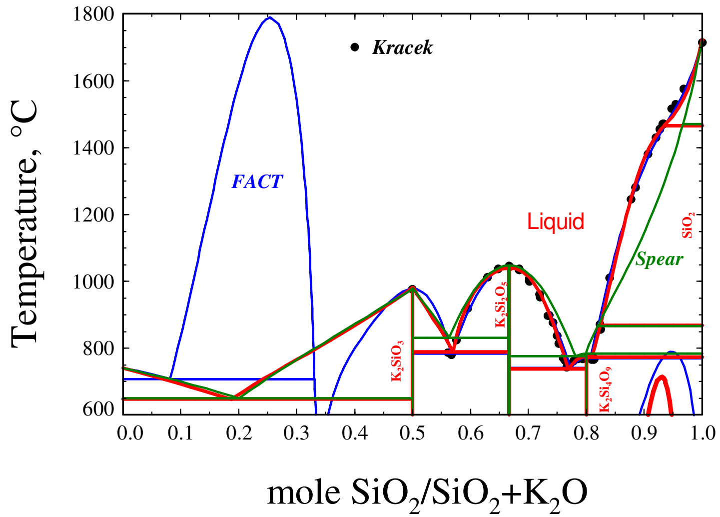
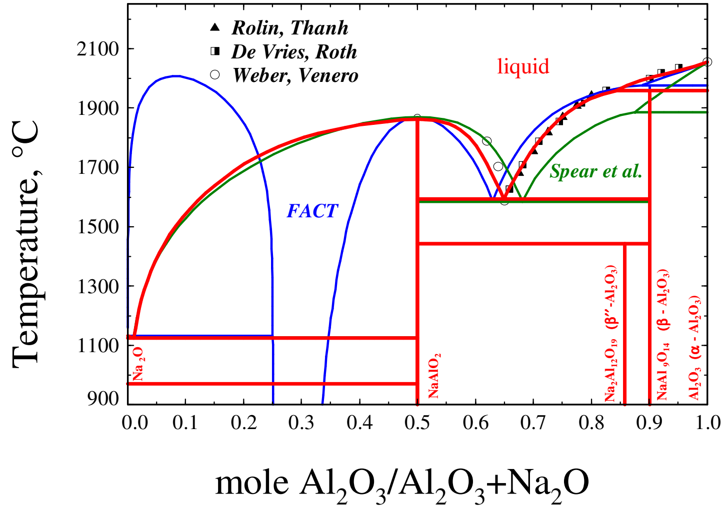
Results of assessment for binary systems

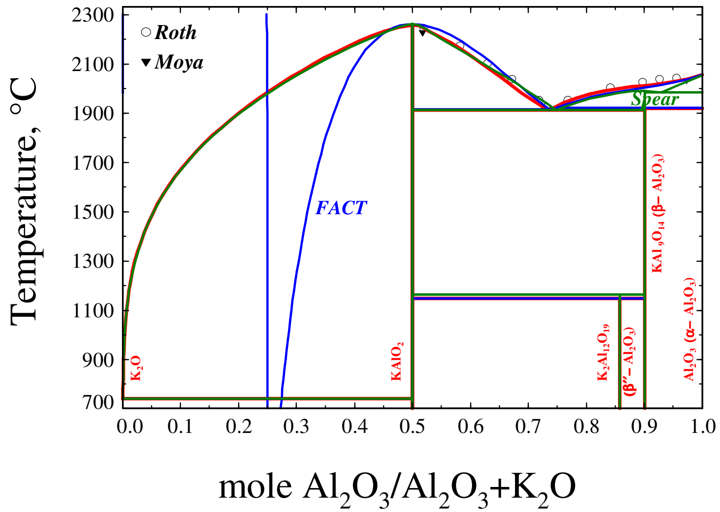
Alk_2O-SiO_2, Alk=Na, K





Alk_2O-Al_2O_3, Alk=Na, K





Results of assessment for binary systems

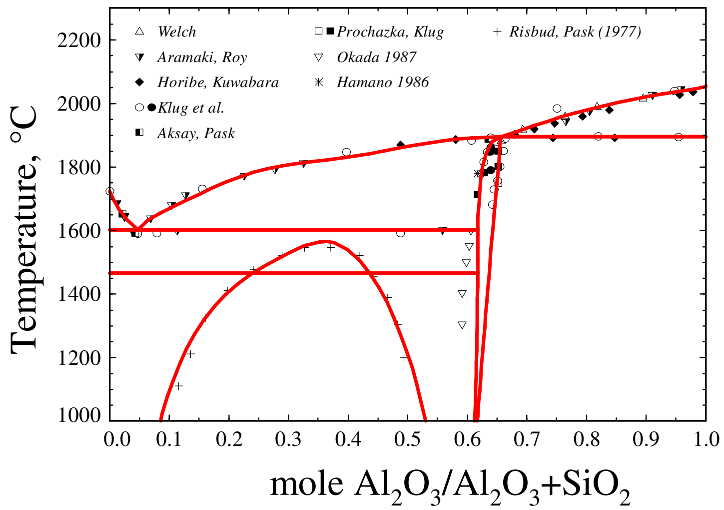
Associate model for mullite

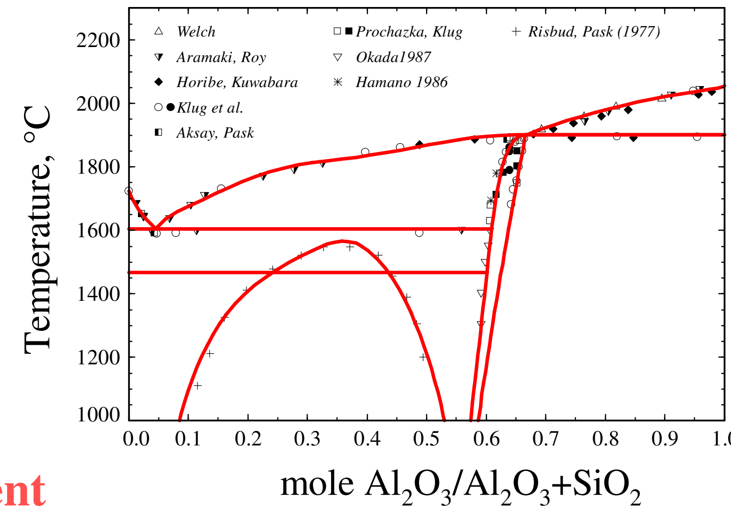
[Spear at al. in 2002]

Four-sublattice model for mullite

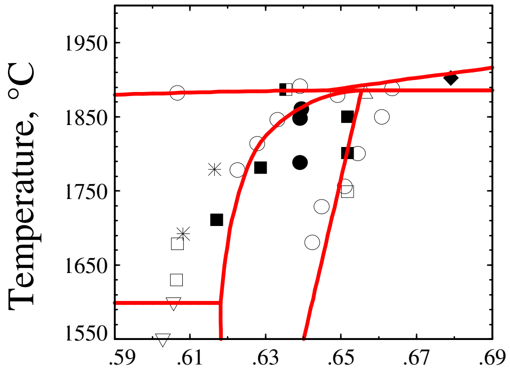
[Mao et al. in 2005]

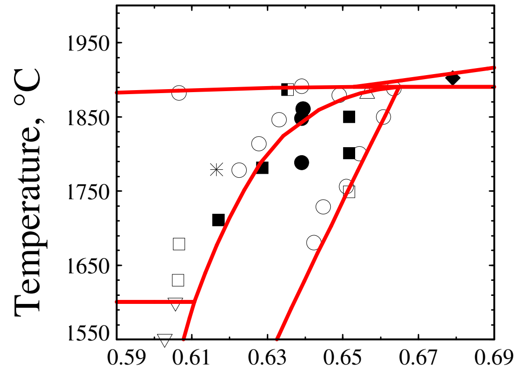
Model parameters are optimised for both melting behaviour of mullite





Congruent



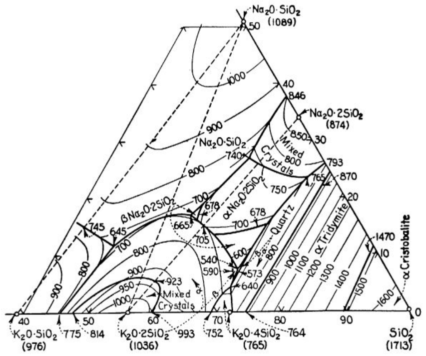


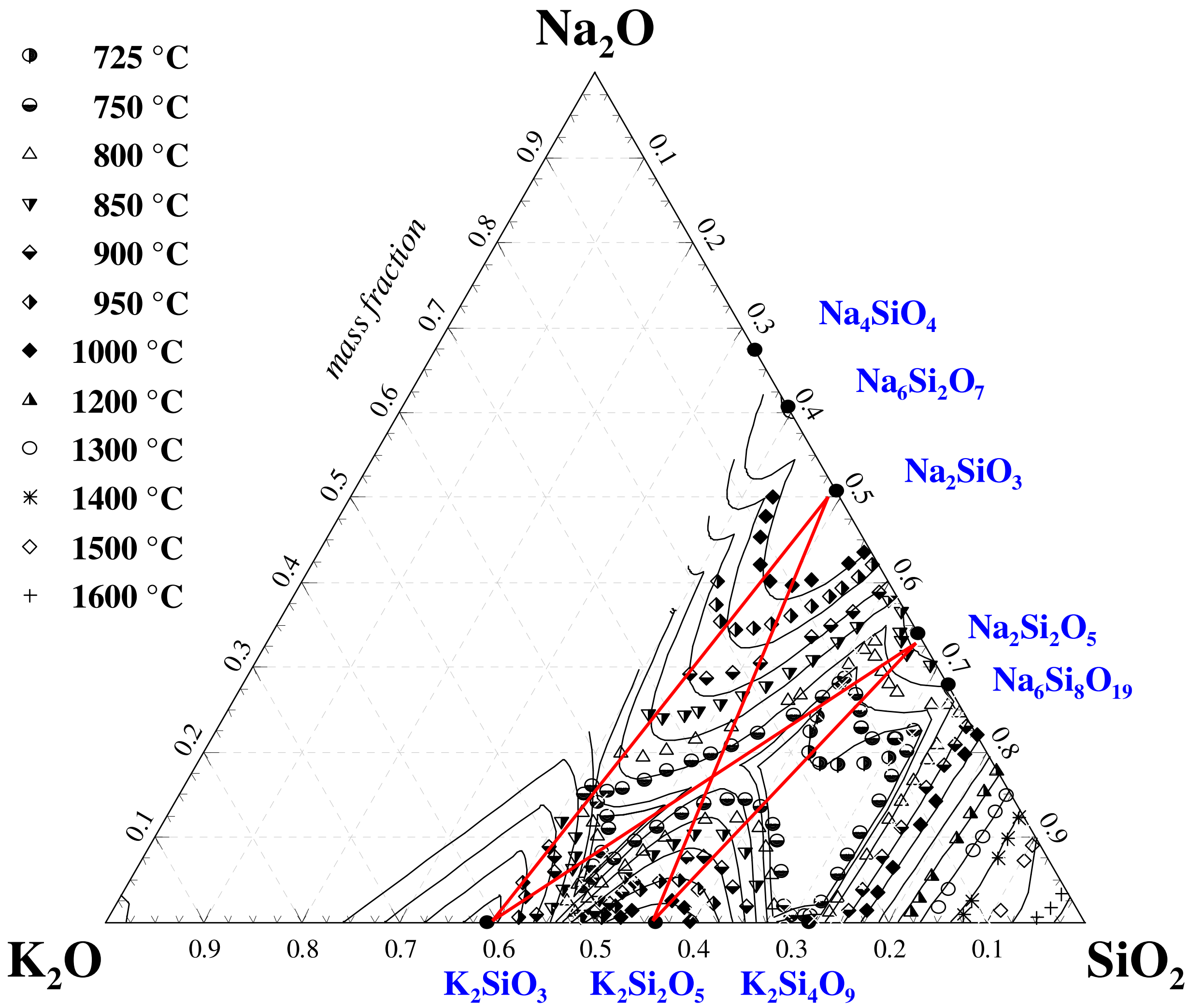
Incongruent

Results of assessment for ternary systems

Comparison of the calculated isotherms with the experimental points

Na_2O-K_2O-SiO_2





The same binary species in ternary liquid

Interacting components:

Na_2SiO_3*2/3 - K_2SiO_3*2/3

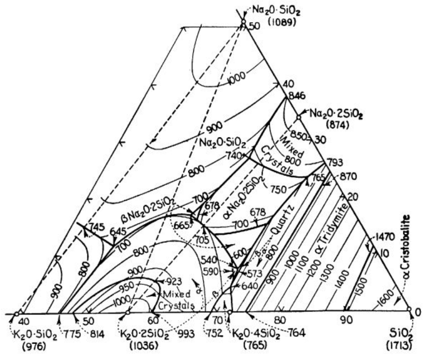
$Na_2Si_2O_5$*1/2 - $K_2Si_2O_5$*1/2

Na_2SiO_3*2/3 - $K_2Si_2O_5$*1/2

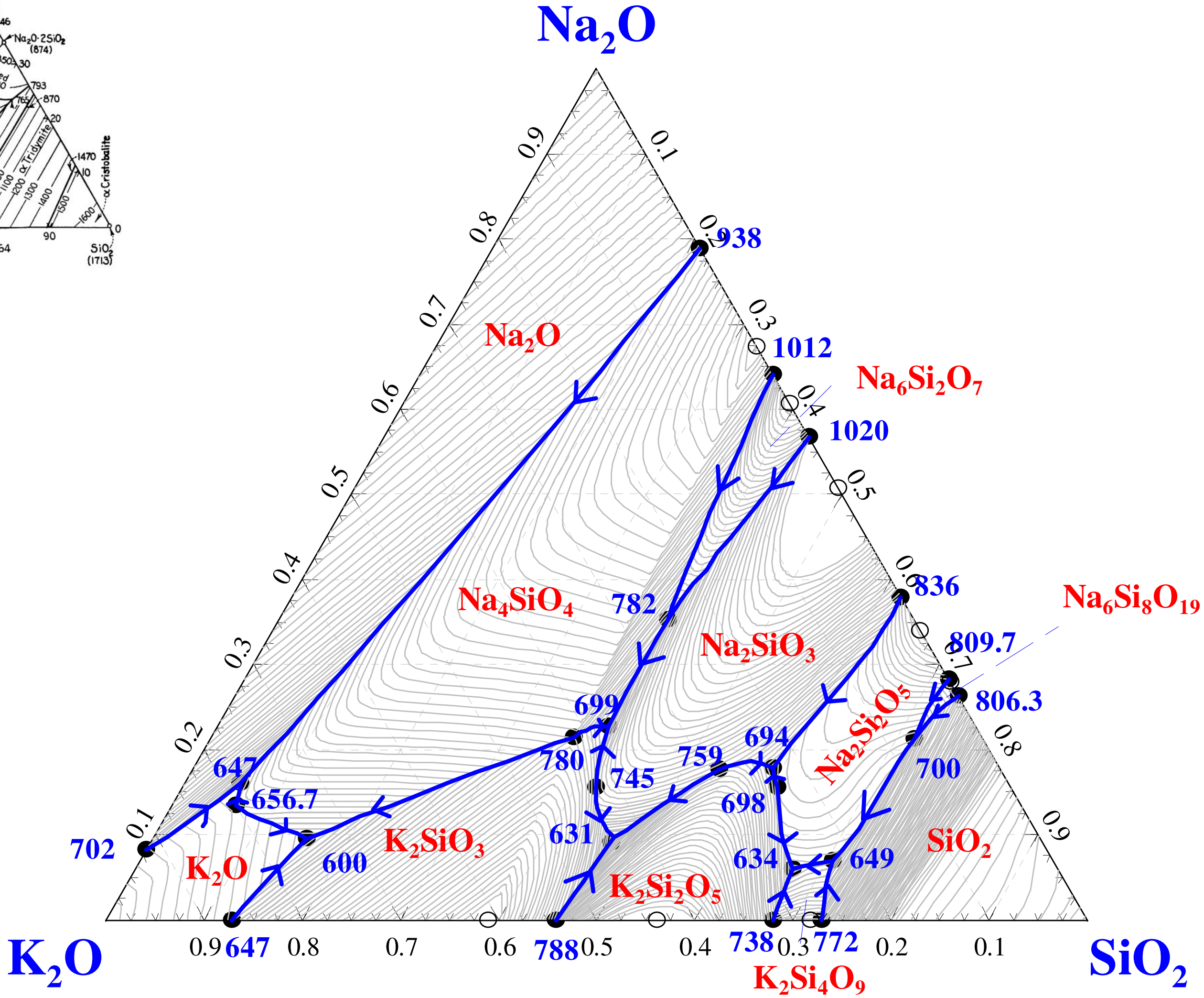
$Na_2Si_2O_5$*1/2 - K_2SiO_3*2/3

Results of assessment for ternary systems

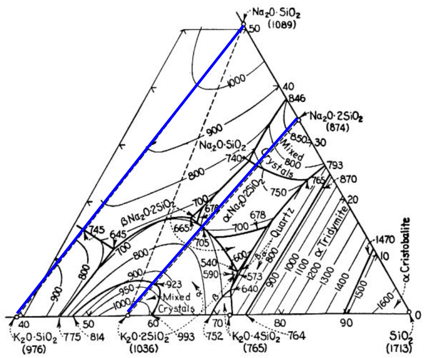
Predicted phase fields and ternary points

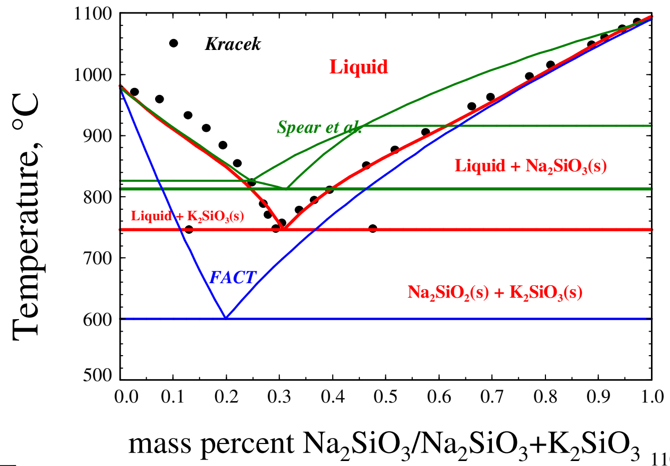


Na_2O-K_2O-SiO_2

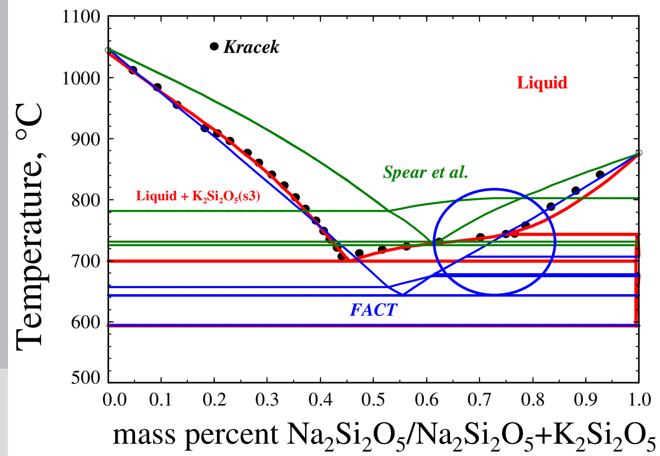


Quasi binary section in the Na_2O-K_2O-SiO_2 system

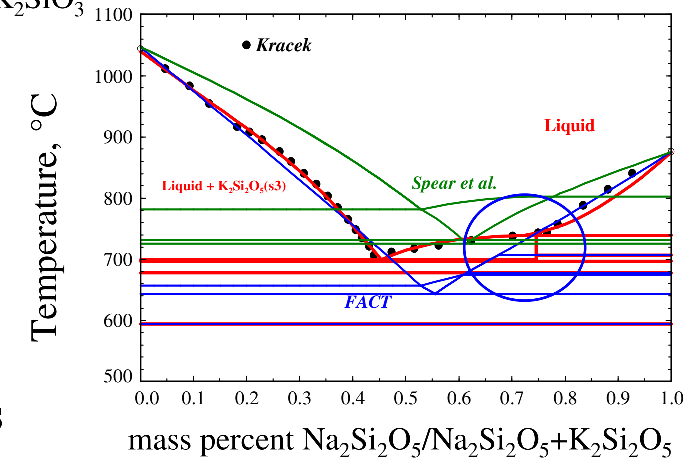




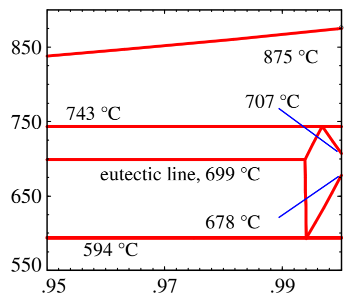
K_2SiO_3-Na_2SiO_3



$K_2Si_2O_5$-$Na_2Si_2O_5$

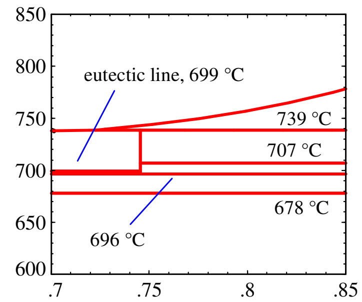


Possible interpretations



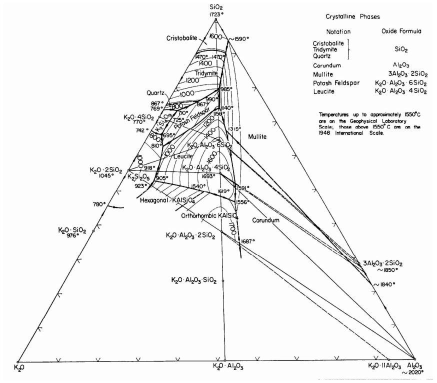
Solubility region

Additional "ternary" compound



Results of assessment for ternary systems

Predicted phase fields and ternary points



K_2O-Al_2O_3-SiO_2

The same binary + ternary species

Interacting components:

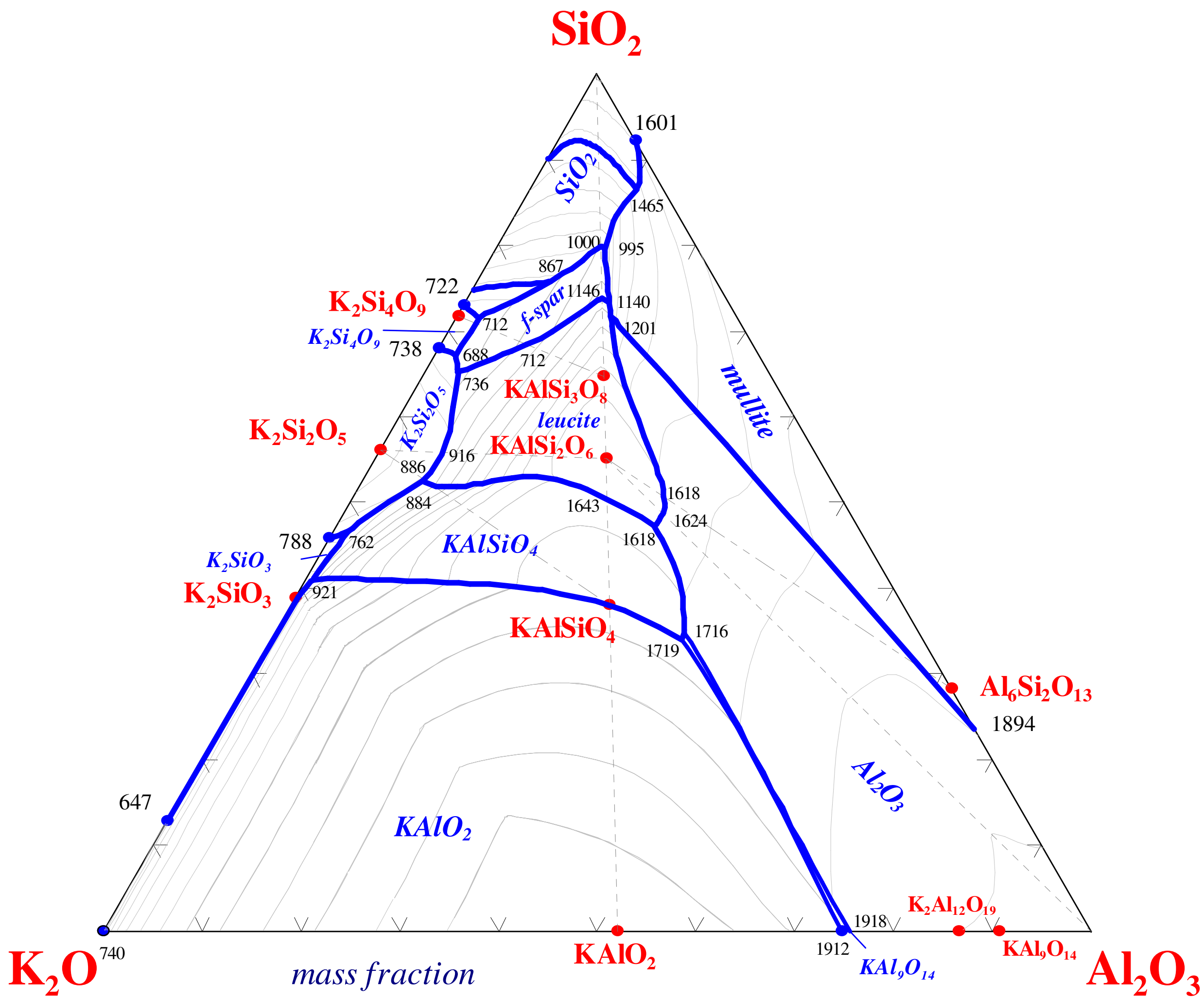
Al_2O_3 – $KAlSi_2O_6$*1/2

$K_2Si_2O_5$*1/2 - $KAlSi_2O_6$*1/2

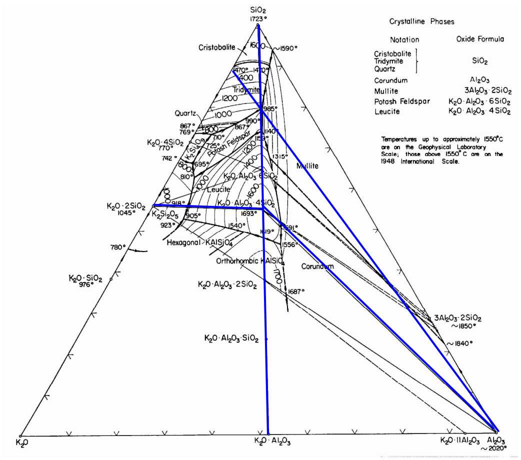
$K_2Si_4O_9$*1/3 - $KAlSi_2O_6$*1/2

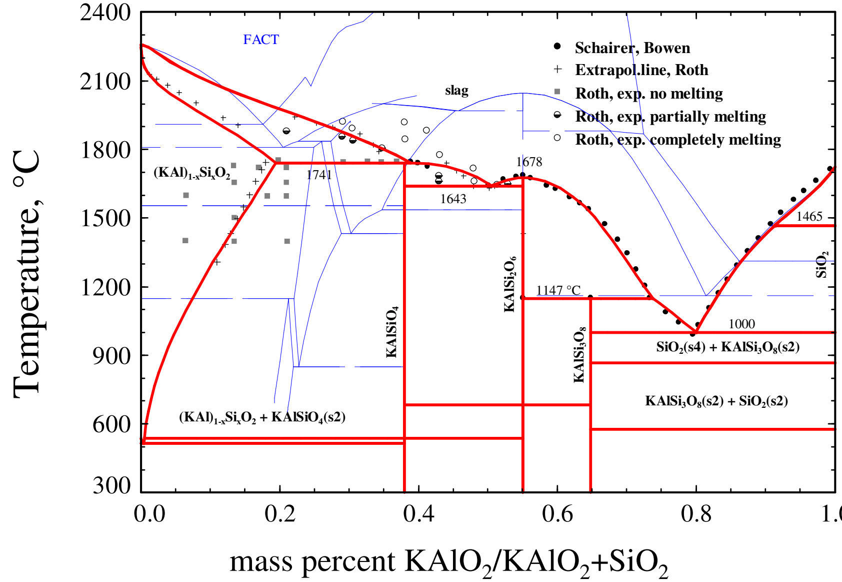
Si_2O_4 - $KAlSi_2O_6$*1/2

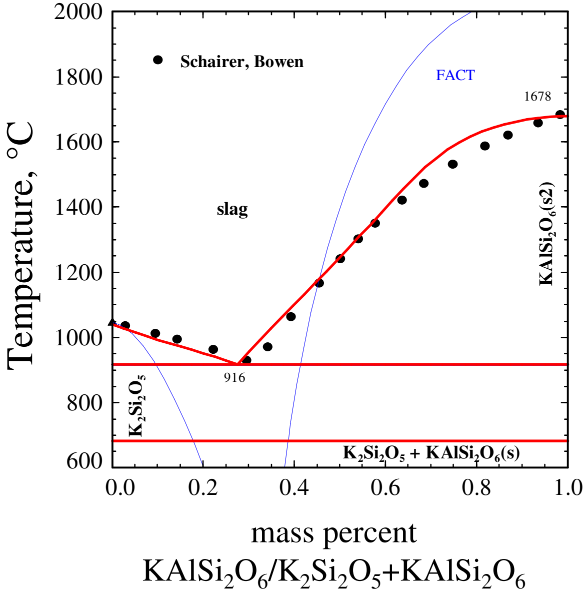
$Al_6Si_2O_{13}$*1/4 - $KAlSi_2O_6$*1/2

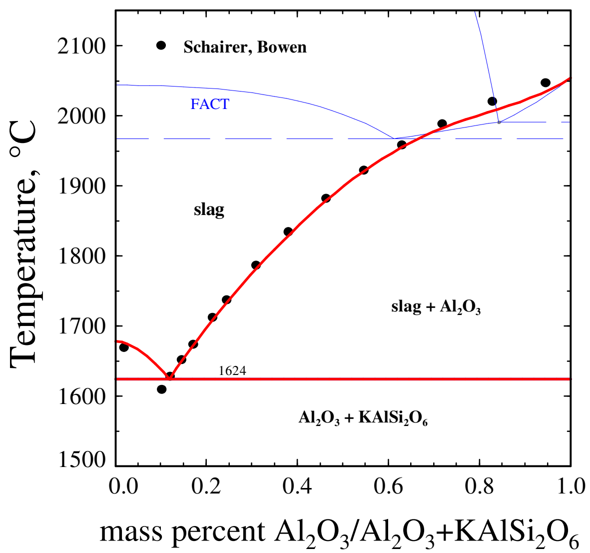


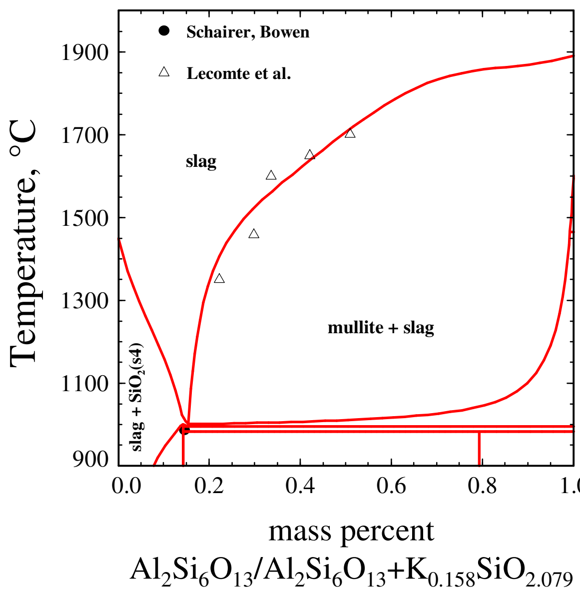
Quasi binary section in the K_2O-Al_2O_3-SiO_2 system











Available experimental phase diagram

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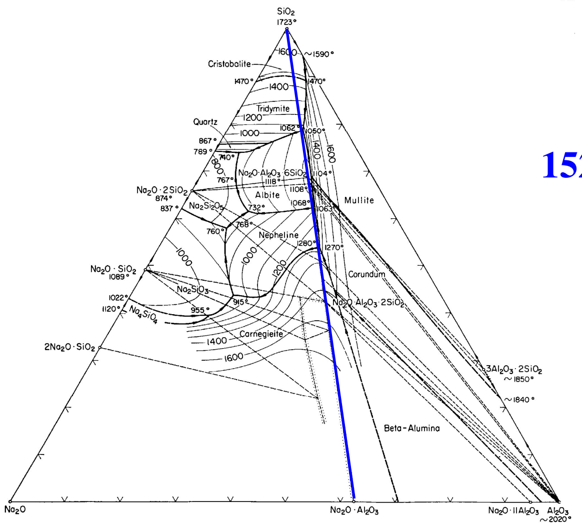
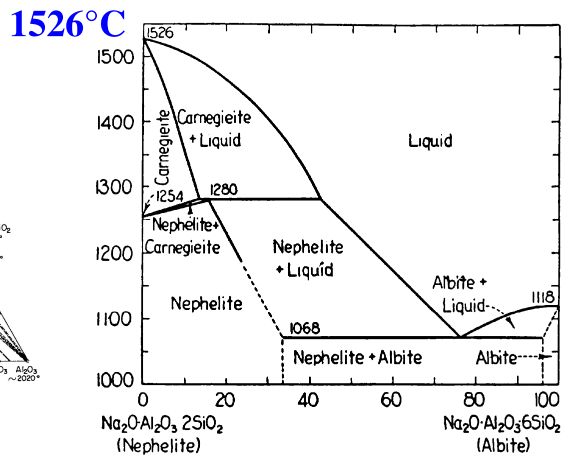
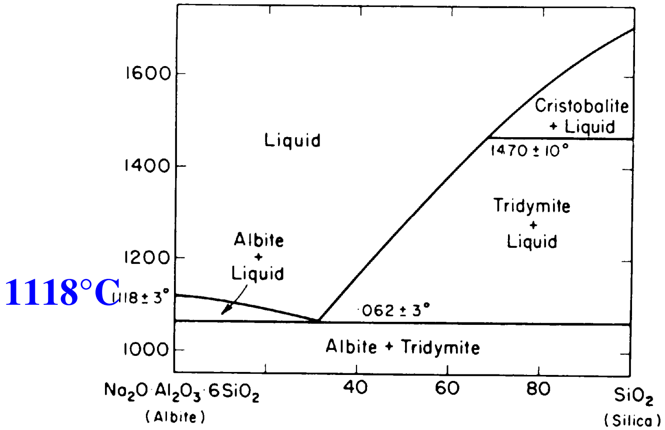
Na_2O-Al_2O_3-SiO_2





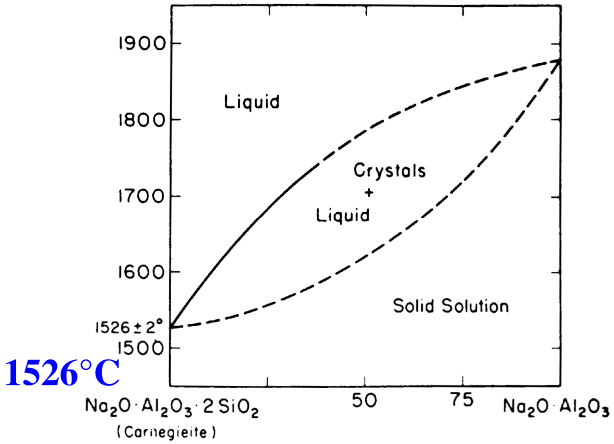
$NaAlSiO_4$ (Neph/Carn) –$NaAlSi_3O_8$

Greig and Barth (1938)



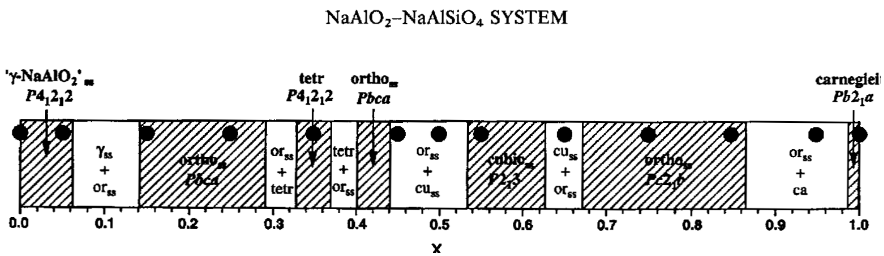
$NaAlSi_3O_8$ (Albite) - SiO_2

Schairer and Bowen (1956)



$NaAlSiO_4$ - $NaAlO_2$

Schairer and Bowen (1956)



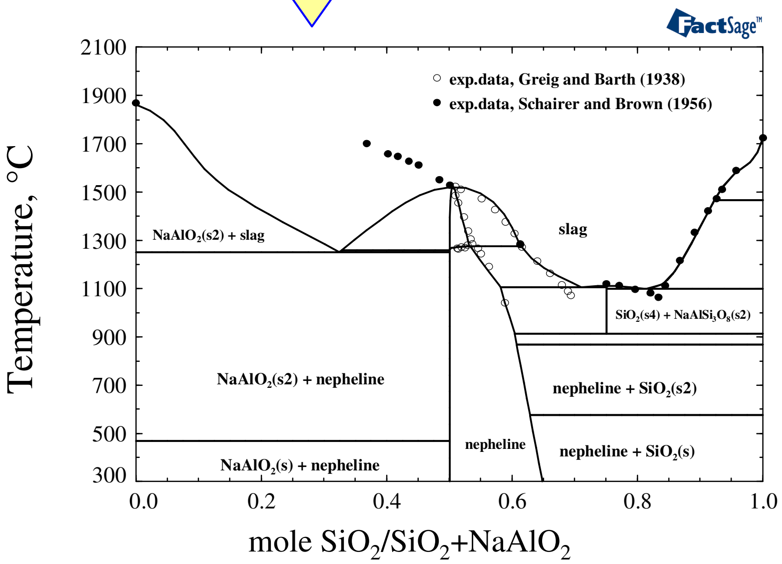
$NaAlO_2$ - $NaAlSiO_4$

Thompson (1997), Proposed compositional phase diagram at 1300 °C for the system $Na_{2-x}Al_{2-x}Si_xO_4$, $0 \le x \le 1$

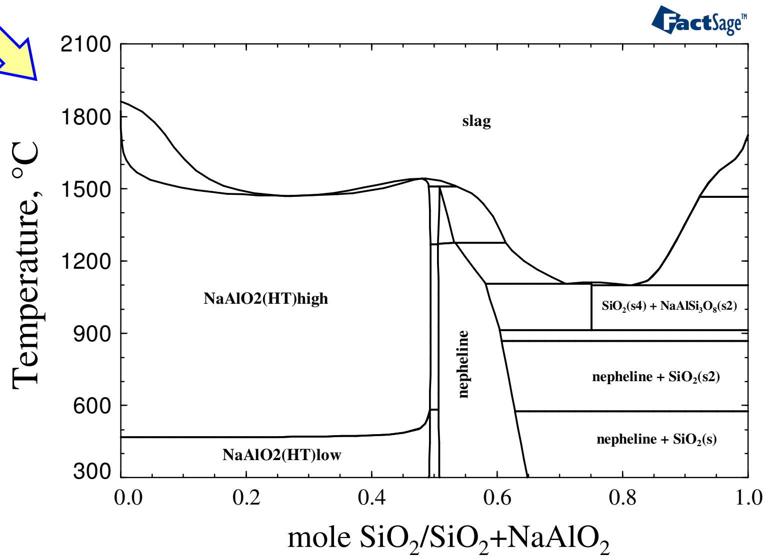
Modelling of solid phases

Associate Species

Name	Solid solution components	remark
Mullite	$Al_6Si_2O_{13}$: $Al_6Si_2O_{13}\cdot 1/4$, Al_2O_3, $SiO_2\cdot 2$	OK
Natrium disilicate	$(Na_{1-x}K_x)_2Si_2O_5$: $Na_2Si_2O_5$, $K_2Si_2O_5$	OK
Potassium aluminate	$(KAl)_{1-x}Si_xO_2$: $KAlO_2$, $KAlSiO_4$	OK
Nepheline, carnegieite	$NaAlSiO_4$: $NaAlSiO_4$, $NaAlSi_2O_6$	OK
Natrium aluminate	$(NaAl)_{1-x}Si_xO_2$: $NaAlO_2$, $NaAlSiO_4$	?



NaAlSiO$_4$ (neph, carn) as associate solutions
NaAlO$_2$ (low, high) as stoichiometric compounds

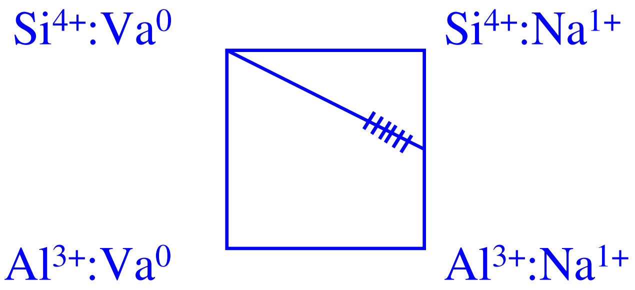


NaAlSiO$_4$ (low, high) and NaAlO$_2$(low, high)
- as associate solutions

Modelling of solid phases

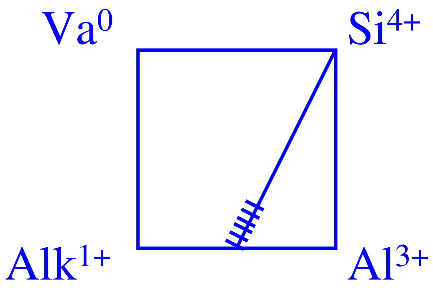
Sublattice approach

Name	Formula	remark
Mullite	$(Al^{3+})_1(Al^{3+})_1(Al^{3+}, Si^{4+})_1(O^{2-}, Va)_5$	**OK**
$NaAlSiO_4$	Nepheline (low T), carnegieite (high T) 4 sublattices: $(Al^{3+}, Si^{4+})_2 Va^0{}_1 (Na^{1+}, Va^0)_1 (O^{2-})_4$	**new**
Potassium aluminate	$KAlO_2$ - low T, high T 3 sublattices: $(Al^{3+}, Si^{4+})_1(K^{1+}, Va^0)_1(O^{2-})_2$	**new**
Natrium aluminate	$NaAlO_2$ - low T, high T 3 sublattices: $(Al^{3+}, Si^{4+})_1(Na^{1+}, Va^0)_1(O^{2-})_2$	**new**



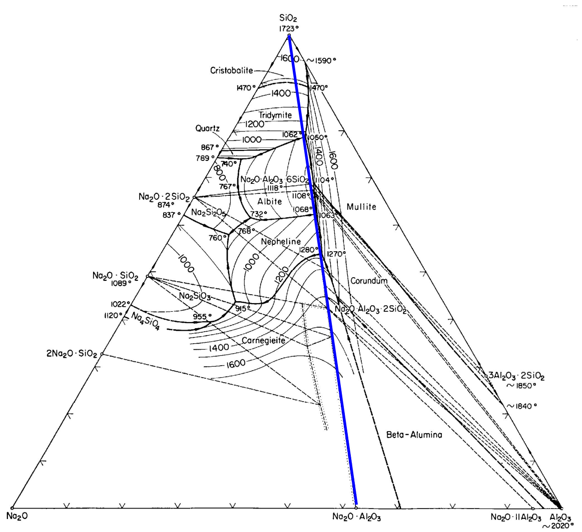
from $NaAlSiO_4$ to SiO_2

Composition scheme



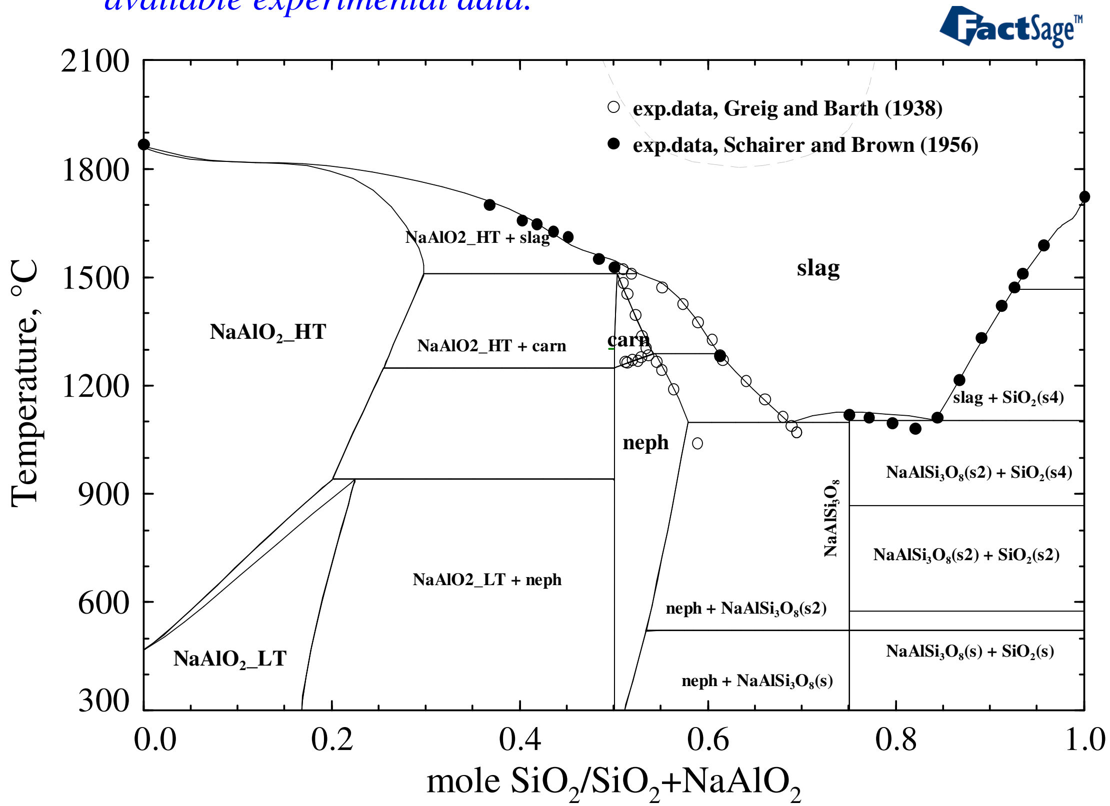
from $NaAlO_2$ to SiO_2

Preliminary results for the quasi binary section $NaAlO_2 - SiO_2$



Na_2O-Al_2O_3-SiO_2

$NaAlO_2$ (low T, high T), Nepheline, Carnegieite are represented by sublattice approach. The parameters of the solutions are optimised to obtain good description of the available experimental data.

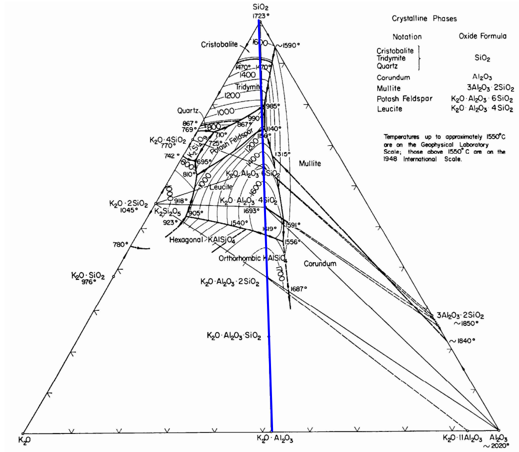


Problems:

✓Unknown solubility boundaries for $NaAlO_2$ (low T, high T) solutions

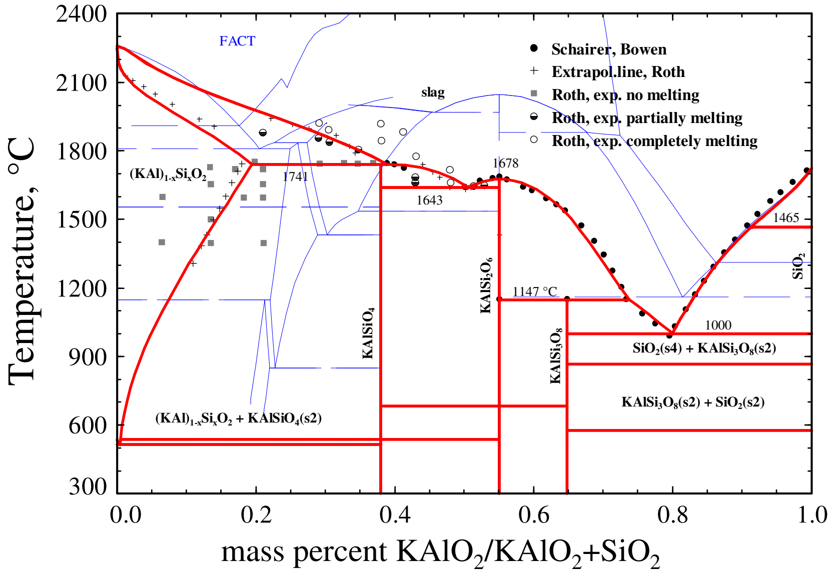
✓Possible presence of a series of solid solutions with different crystallographic structure between $NaAlO_2$ and $NaAlSiO_4$

Comparison between 2 models for the solid solution based on $KAlO_2$

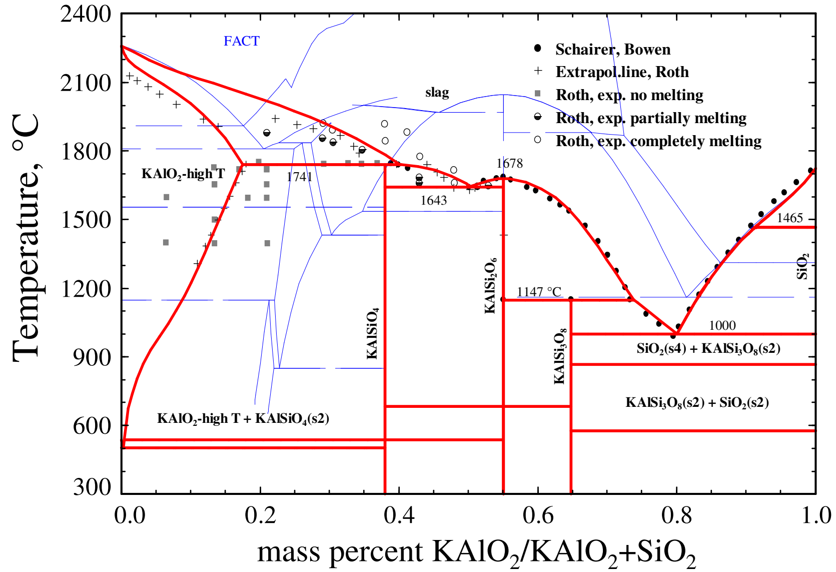


$K_2O-Al_2O_3-SiO_2$

Slag, solid solution – Associate species



Slag– Associate species model solid solution - sublattice



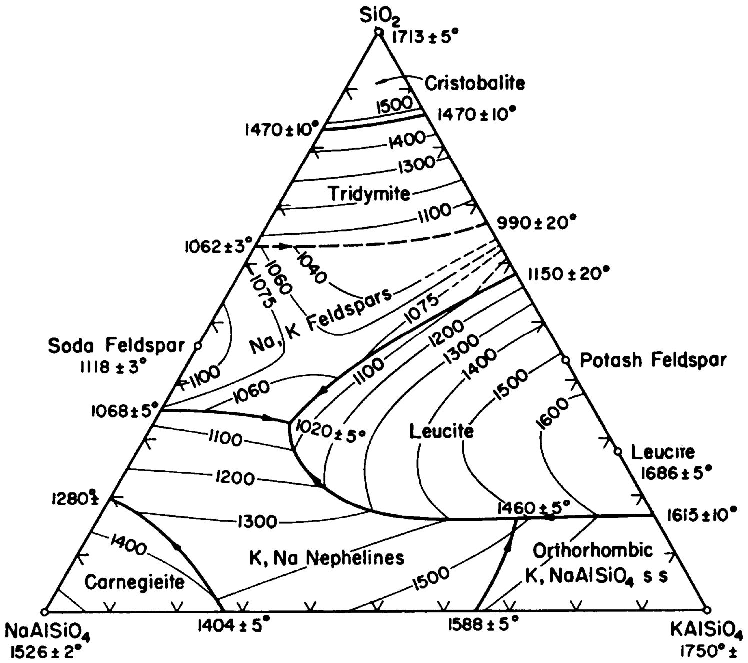
Sublattice model should be used for the purpose of „uniformity“ for both aluminates, $NaAlO_2$ and $KAlO_2$, and further for quaternary solution (Na, K)AlO_2

Summary and outlook

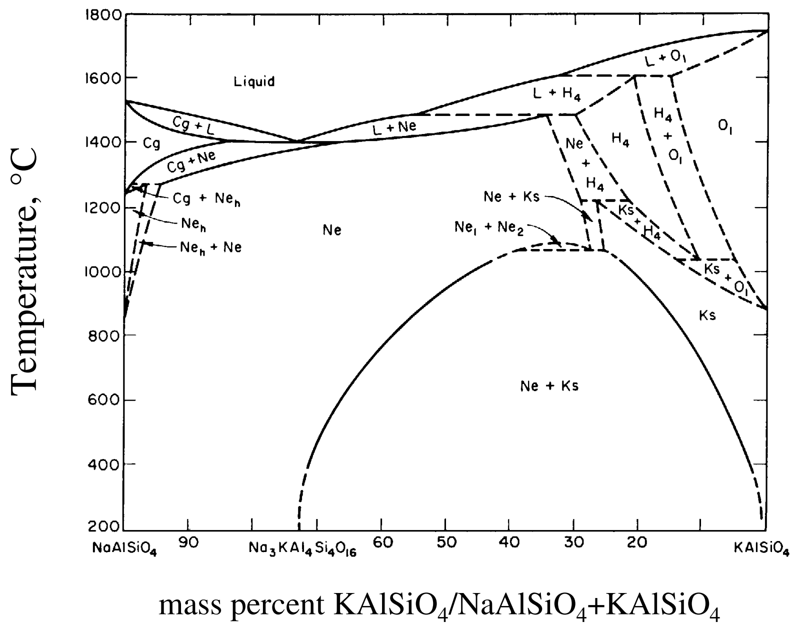
- The solution data for the binary systems Alk_2O-SiO_2, Alk_2O-Al_2O_3 (Alk=Na, K) and Al_2O_3-SiO_2 were generated to accurate description of the phase diagrams
- Solid and liquid solutions in the ternary systems Na_2O-K_2O-SiO_2 and K_2O-Al_2O_3-SiO_2 were described using the new database
- Sublattice model was successfully applied for the solid solutions in the Na_2O-Al_2O_3-SiO_2 and K_2O-Al_2O_3-SiO_2 systems

In future:

- Optimisation of the solution parameters in the Na_2O-Al_2O_3-SiO_2 system
- Creation of the database for possible quaternary solutions, e.g. (Na, K)AlO_2 and (Na, K)(Al, Si)O_4



SiO_2 – $KAlSiO_4$ - $NaAlSiO_4$
Schairer (1950)



$NaAlSiO_4$ – $KAlSiO_4$
Tuttle, Smith (1958)

Thank you for your attention