GTT-Technologies, 12th Annual Workshop, June 16-18, 2010

Thermodynamic optimisation of the system Al_2O_3-K_2O-Na_2O-SiO_2

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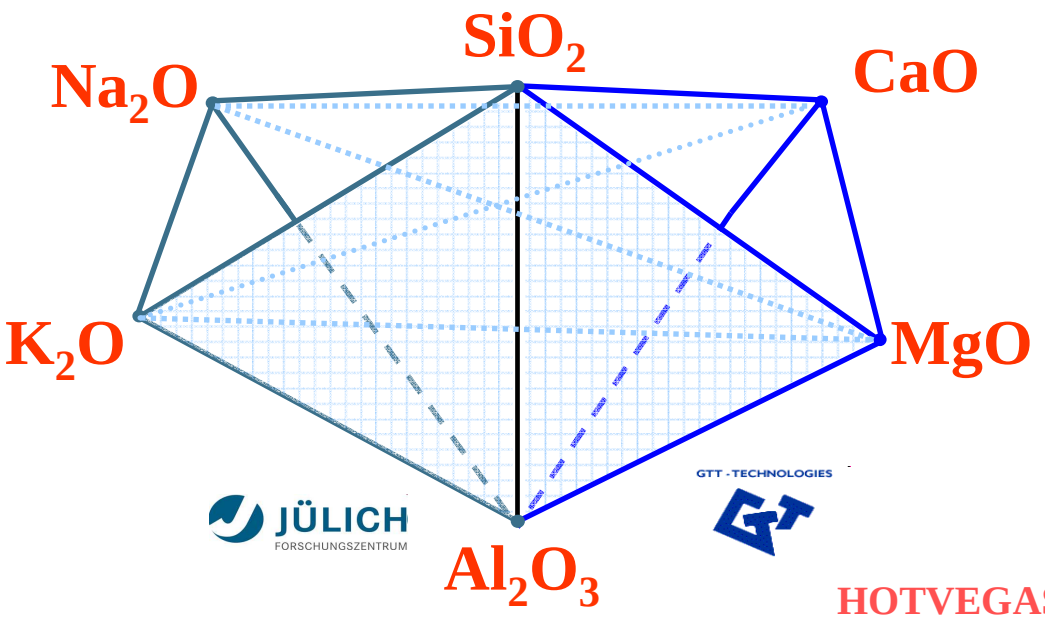
- Motivation and aim of the work
- Models and optimisation procedure
- Results of re-assessment for binary systems
- Assessment for ternary systems
- Conclusions and outlook

Motivation and aims

Thermodynamic calculation/prediction for slag relevant oxide systems, which are difficult 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

Purpose of out work - development of a new data base, which is:

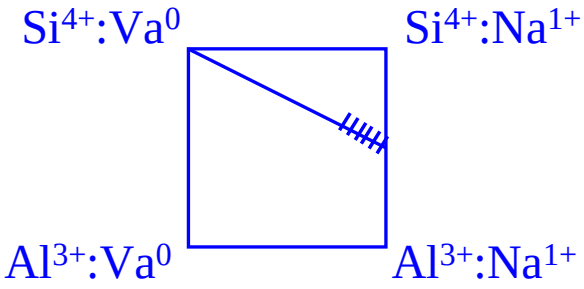
✓ applicable for the slag relevant system containing alumina, silica, alkali, alkali-earth oxides

✓ suitable for the calculations and/or predictions of the phase equilibria and other thermodynamic properties by variation of temperature and composition

Modelling of liquid and solid solutions

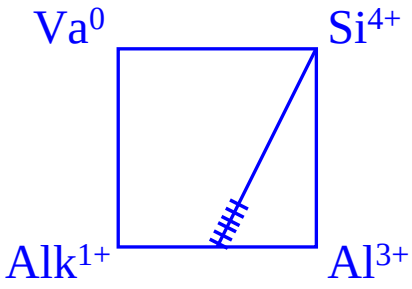
*Applied and **chosen** model for the phases under consideration*

Phase name	**Associate species model**	**Multi-sublattice model**
Liquid	**Liquid pure oxides, binary and ternary liquid species**	**-**
Mullite	$Al_6Si_2O_{13}$: $Al_6Si_2O_{13}\cdot 1/4$, Al_2O_3, $SiO_2\cdot 2$	**$(Al^{3+})_1(Al^{3+})_1(Al^{3+}, Si^{4+})_1(O^{2-}, Va)_5$ (Mao et al., 2005)**
Natrium disilicate	**$(Na_{1-x}K_x)_2Si_2O_5$: $Na_2Si_2O_5$, $K_2Si_2O_5$**	**-**
Potassium aluminate	$(KAl)_{1-x}Si_xO_2$: $KAlO_2$, $KAlSiO_4$	**$KAlO_2$ - low T, high T** **3 sublattices: $(Al^{3+}, Si^{4+})_1(K^{1+}, Va^0)_1(O^{2-})_2$**
Nepheline, carnegieite	$NaAlSiO_4$: $NaAlSiO_4$, $NaAlSi_2O_6$	**Nepheline (low T), carnegieite (high T)** **4 sublattices: $(Al^{3+}, Si^{4+})_2Va^0{}_1(Na^{1+}, Va^0)_1(O^{2-})_4$**
Natrium aluminate	$(NaAl)_{1-x}Si_xO_2$: $NaAlO_2$, $NaAlSiO_4$	**$NaAlO_2$ - low T, high T** **3 sublattices: $(Al^{3+}, Si^{4+})_1(Na^{1+}, Va^0)_1(O^{2-})_2$**



from $NaAlSiO_4$ to SiO_2

Composition scheme



from $AlkAlO_2$ to SiO_2

Modelling of liquid – Associate species approach

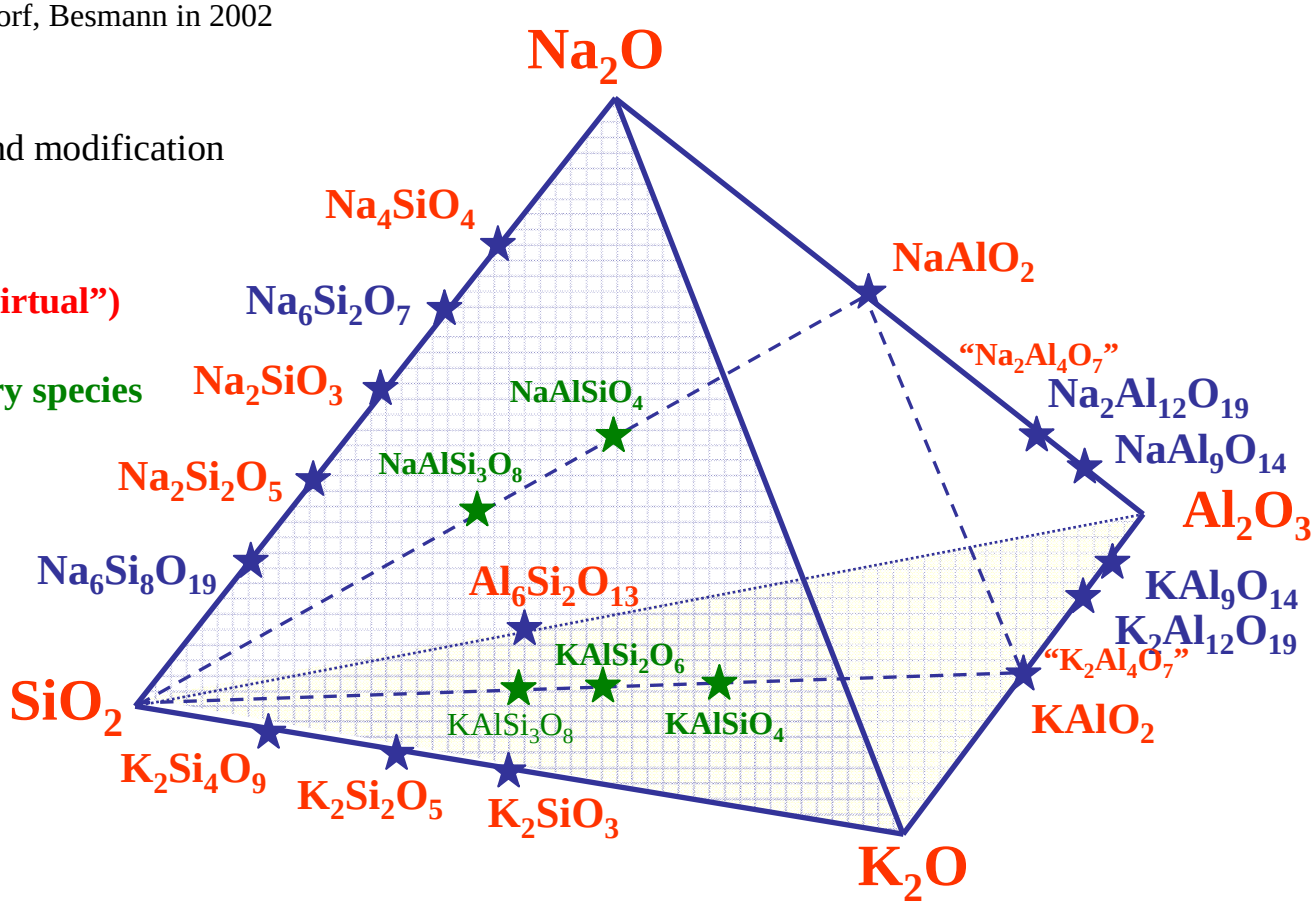
introduced for slag by Spear, Allendorf, Besmann in 2002

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

✓**pure liquid oxide**
✓**binary liquid species (incl. "virtual")**
✓**binary compounds (rest)**
✓ternary compounds **and ternary species**

+

Interaction between solution components



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

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

Database development

Experimental data:
phase diagram data,
activity data (if they are available)

Choice of the suitable model

Initial data for pure solid and liquid substances, liquid and solid solutions

OptiSage in FactSage™

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

optimisation

Comparison of the results with exp. data

disagreement

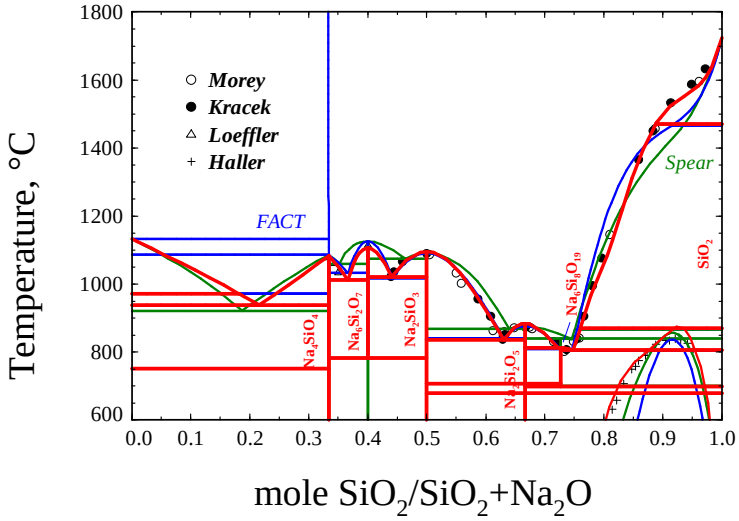
agreement

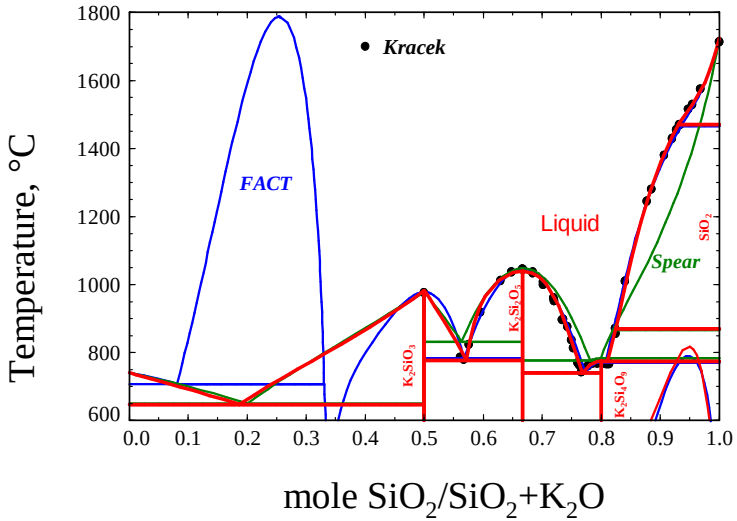
New dataset

✓Re-assessment:
Gibbs energy for pure oxides were changed from FACT to SGTE Pure Substance database

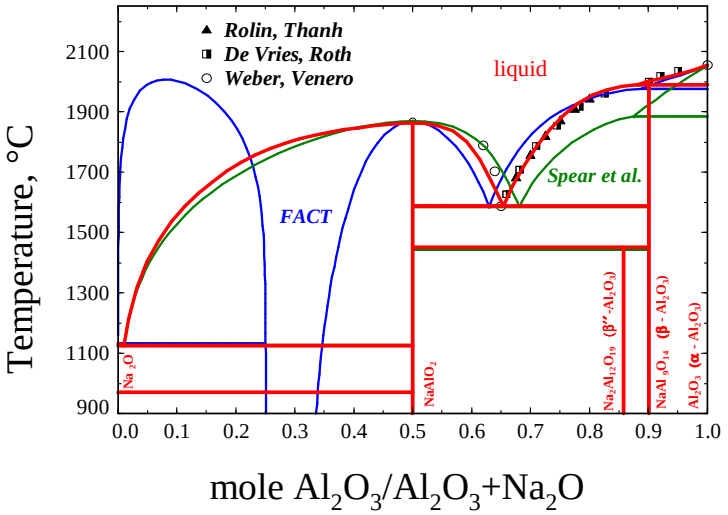
Results of re-assessment for binary systems-1

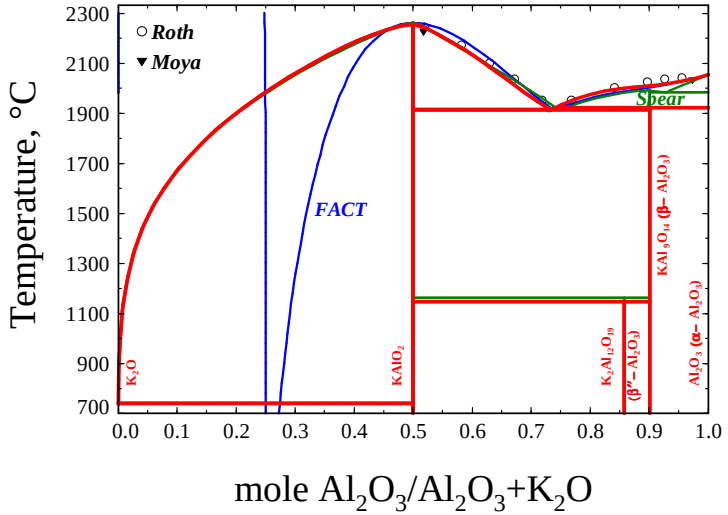
Alk_2O-SiO_2, Alk=Na, K





Alk_2O-Al_2O_3, Alk=Na, K



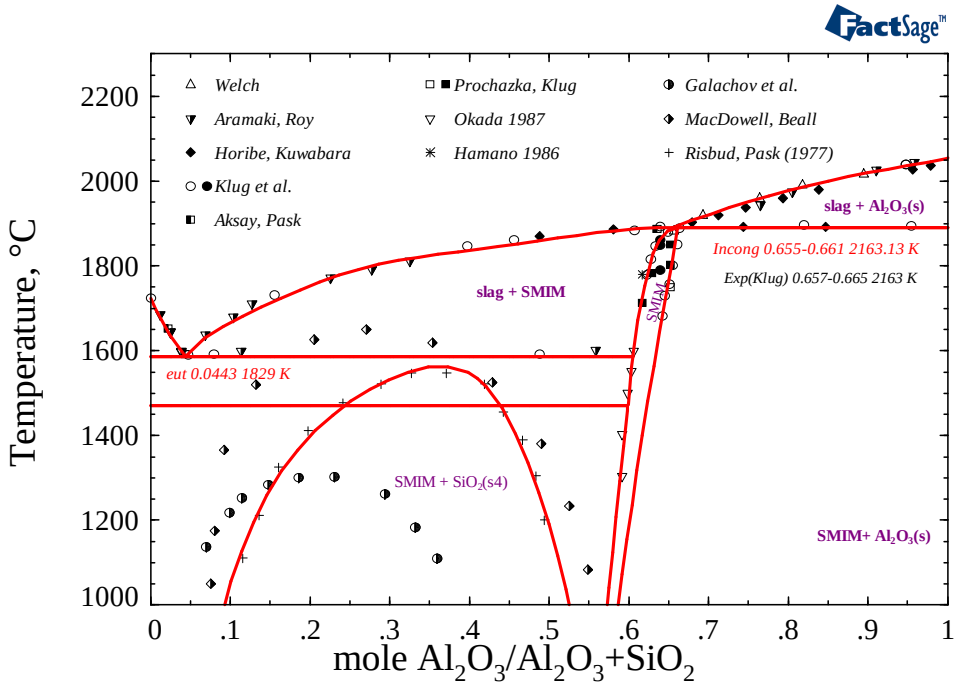


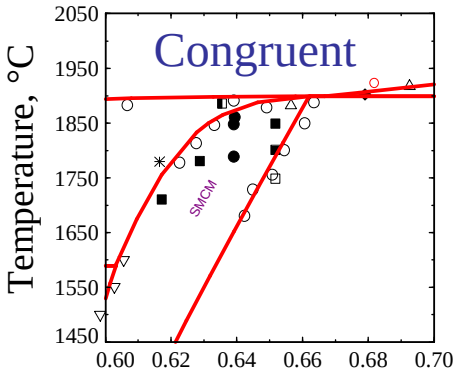
Results of re-assessment for binary systems-2

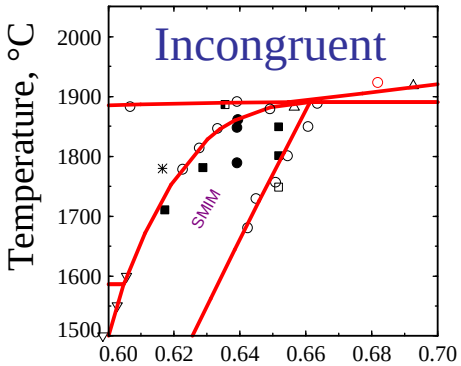
Mullite

Associate species model (introduced by Spear at al. in 2002):
$Al_6Si_2O_{13}\cdot 1/4$, Al_2O_3, $SiO_2\cdot 2$

4 sublattice model (introduced by Mao et al. in 2005):
$(Al^{3+})_1(Al^{3+})_1(Al^{3+}, Si^{4+})_1(O^{2-}, Va)_5$



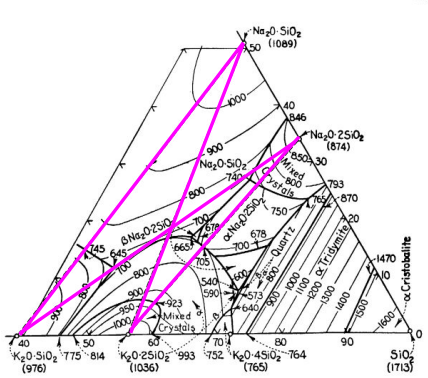




✓*Model parameters are optimised for both melting behaviour of mullite*

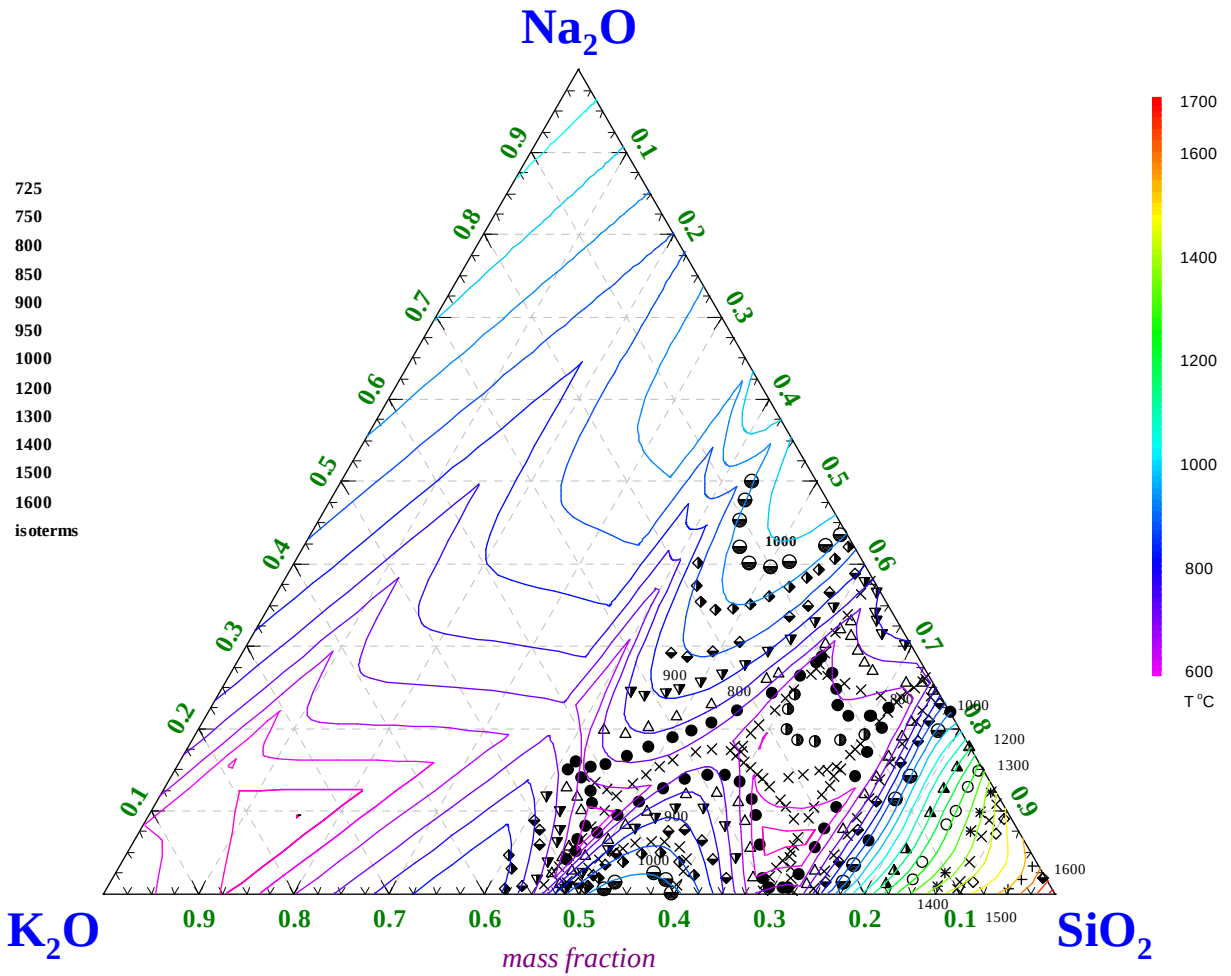
Re-assessment for ternary system Na_2O-K_2O-SiO_2

Comparison of the calculated isotherms with the experimental points



F.C. Kracek,
*The ternary system K_2SiO_3-Na_2SiO_3-SiO_2, J. Phys. Chem., **36** [10], (1932), 2529-2542*

- 725
- 750
- 800
- 850
- 900
- 950
- 1000
- 1200
- 1300
- 1400
- 1500
- 1600
- isoterms



Interacting components:

Na_2SiO_3*2/3 - K_2SiO_3*2/3

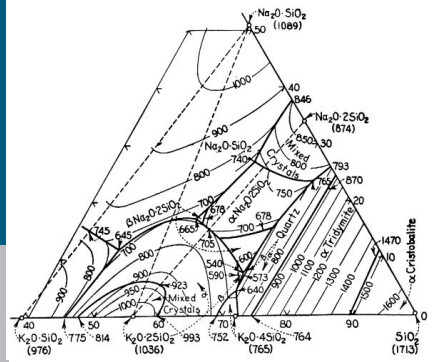
$Na_2Si_2O_5$*1/2 - $K_2Si_2O_5$*1/2

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

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

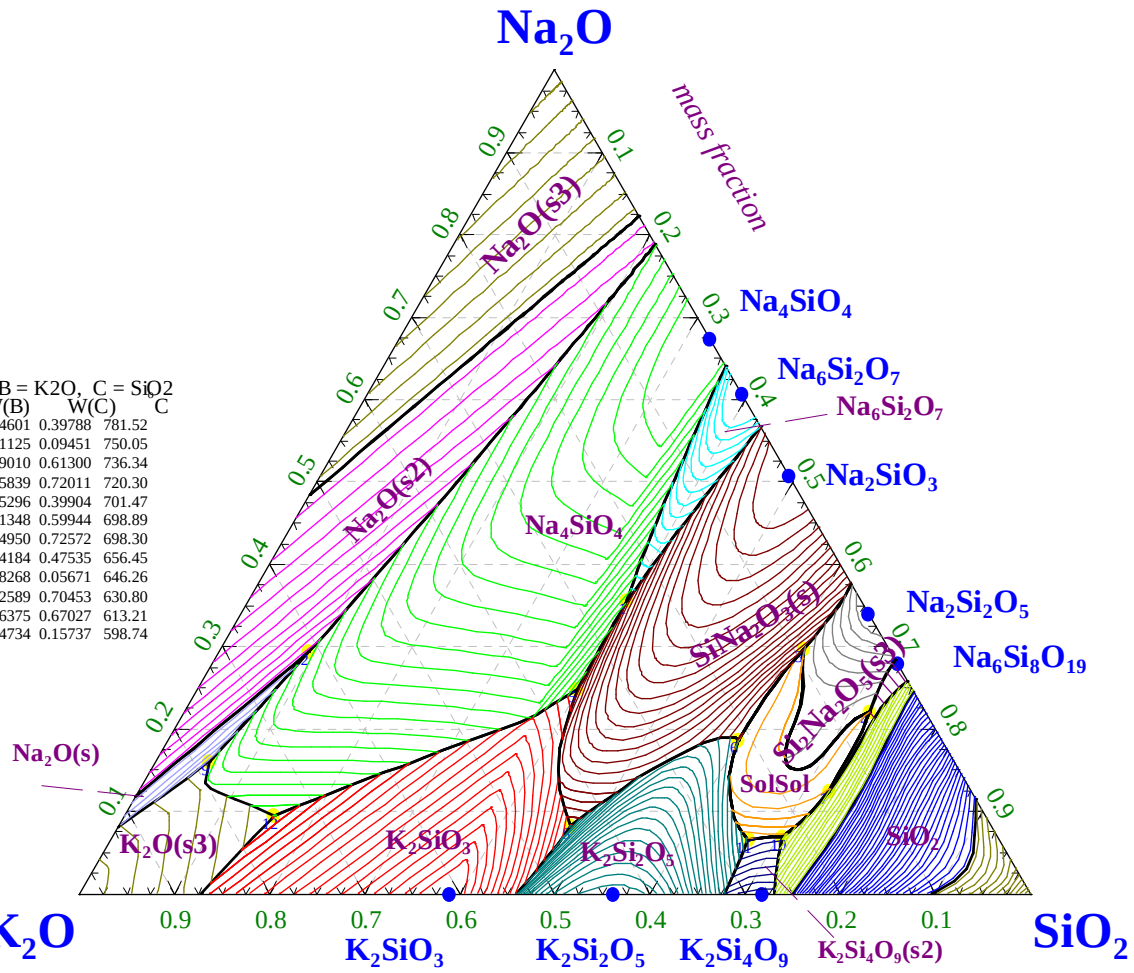
Re-assessment for ternary system Na_2O-K_2O-SiO_2

Predicted phase fields and ternary points



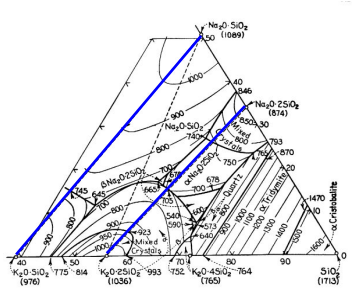
A = Na2O, B = K2O, C = SiO2

	W(A)	W(B)	W(C)	C
1:	0.35611	0.24601	0.39788	781.52
2:	0.29424	0.61125	0.09451	750.05
3:	0.29690	0.09010	0.61300	736.34
4:	0.22150	0.05839	0.72011	720.30
5:	0.24800	0.35296	0.39904	701.47
6:	0.18708	0.21348	0.59944	698.89
7:	0.12477	0.14950	0.72572	698.30
8:	0.08281	0.44184	0.47535	656.45
9:	0.16061	0.78268	0.05671	646.26
10:	0.06958	0.22589	0.70453	630.80
11:	0.06598	0.26375	0.67027	613.21
12:	0.09529	0.74734	0.15737	598.74

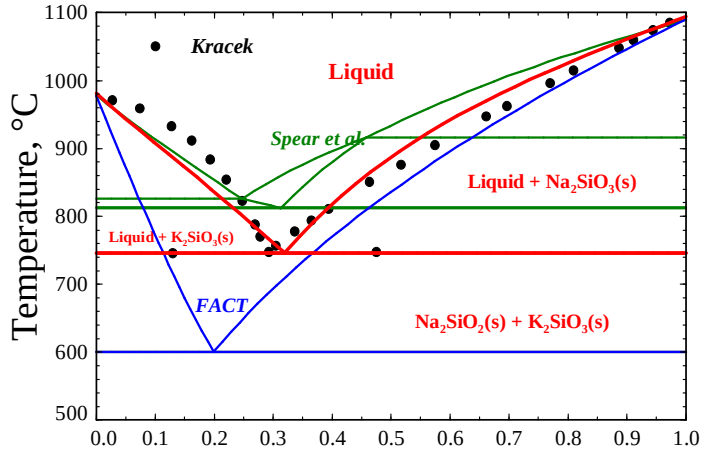


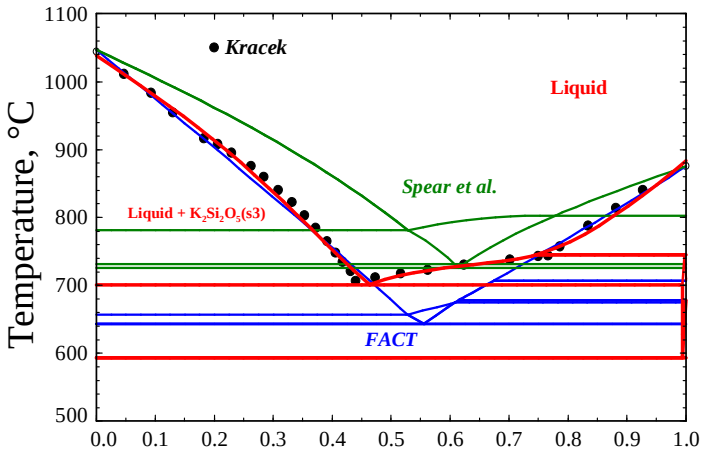
Quasi binary section in the Na_2O-K_2O-SiO_2 system

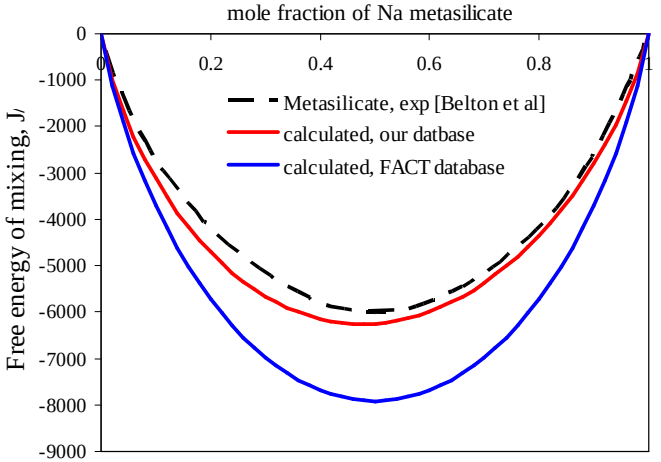
K_2SiO_3-Na_2SiO_3

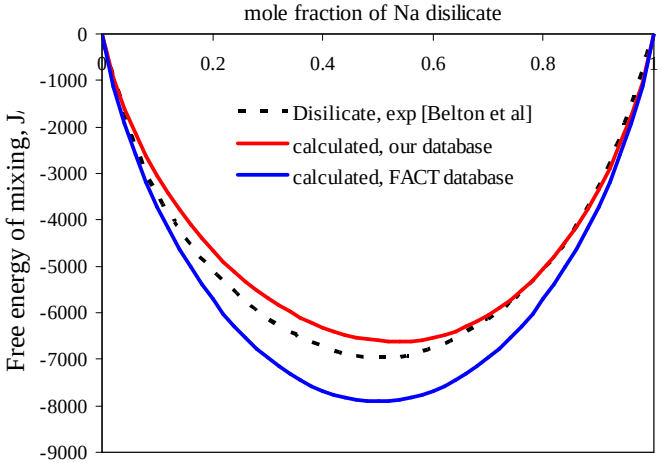


$K_2Si_2O_5$-$Na_2Si_2O_5$





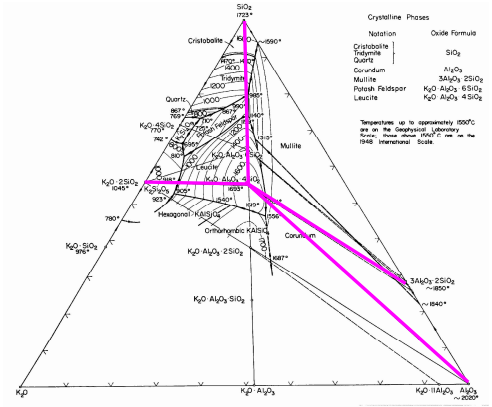




[Belton et al.] *G.R. Belton, U.V. Choudary, D.R. Gaskell, Thermodynamics of mixing in molten sodium-potassium silicates, Phys. Chem.Process. Metall., Richardson Conf., (1974), 247-253*

Assessment for ternary system K_2O-Al_2O_3-SiO_2

Predicted phase fields and ternary points



J.F. Schairer, N.L. Bowen, The system K_2O-Al_2O_3-SiO_2, Am. J. Sci. ***253*** *(1955) 681-746.*

A = SiO2, B = K2O, C = Al2O3

	W(A)	W(B)	W(C)	°C
1:	0.01311	0.24418	0.74270	1912.52
2:	0.36226	0.23314	0.40460	1708.40
3:	0.47085	0.21014	0.31901	1613.97
4:	0.87363	0.02233	0.10404	1470.06
5:	0.69778	0.13377	0.16845	1284.86
6:	0.73362	0.12110	0.14528	1139.03
7:	0.79763	0.09283	0.10953	995.02
8:	0.41262	0.57991	0.00747	914.33
9:	0.52169	0.42185	0.05645	882.60
10:	0.76447	0.16216	0.07337	869.84
11:	0.46682	0.52131	0.01186	751.92
12:	0.65432	0.31411	0.03157	745.84
13:	0.72414	0.24992	0.02594	706.01
14:	0.67671	0.30211	0.02118	691.63
15:	0.12761	0.87231	0.00007	648.02

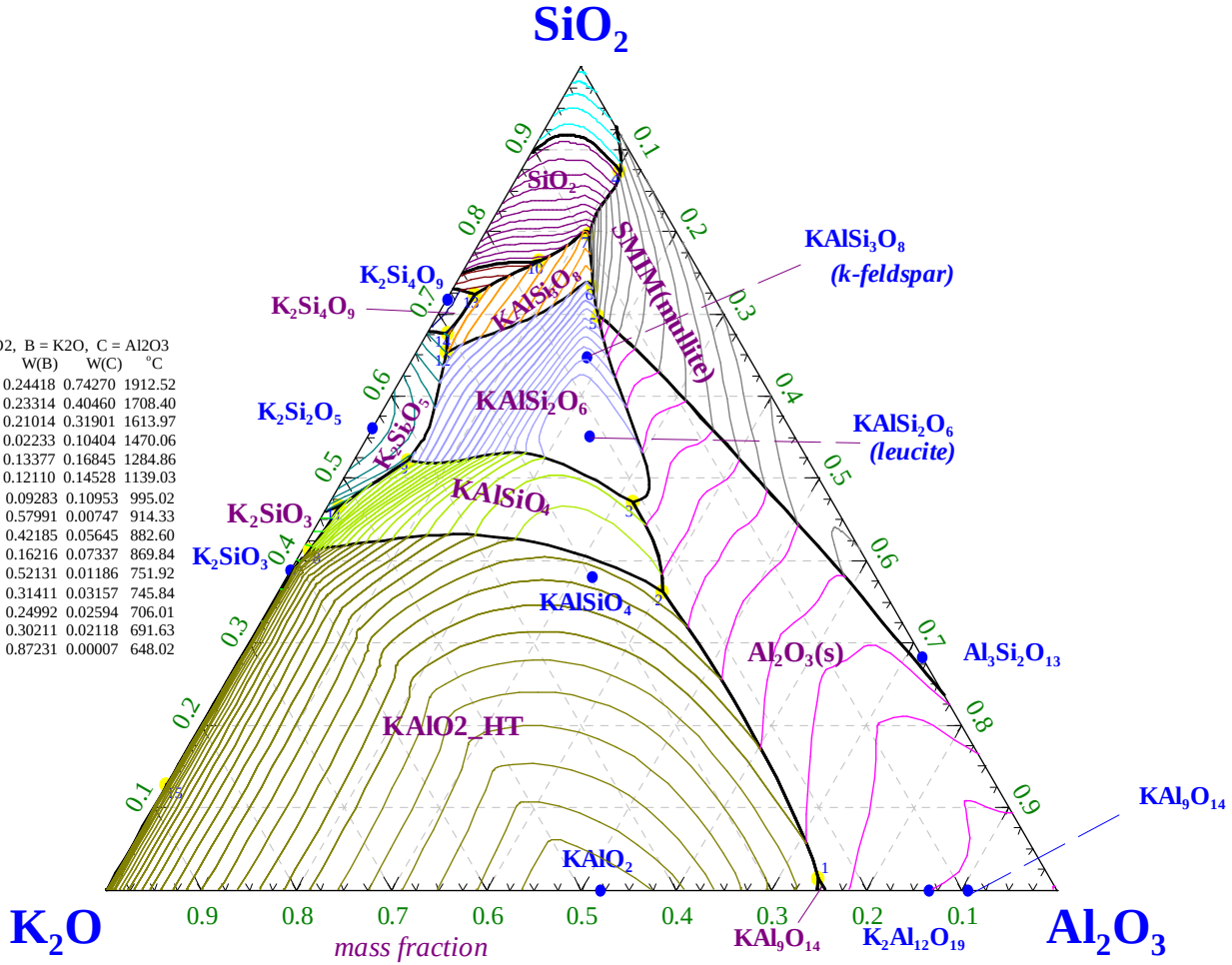
Interacting components

Al_2O_3 – $KAlSi_2O_6$*1/2

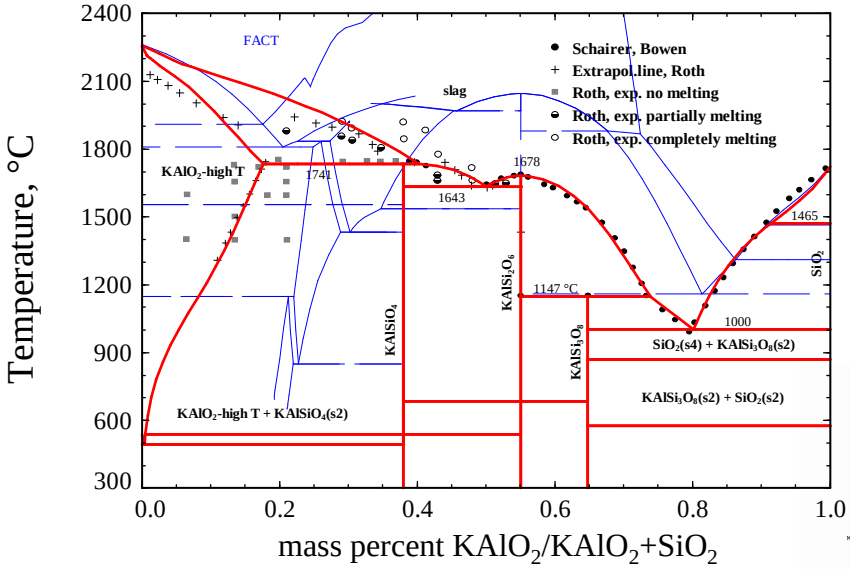
$K_2Si_2O_5$*1/2 - $KAlSi_2O_6$*1/2

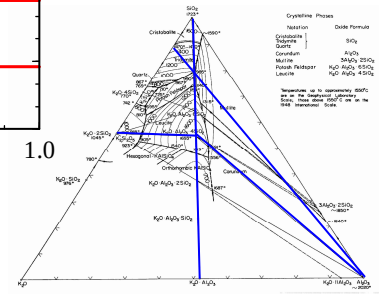
Si_2O_4 - $KAlSi_2O_6$*1/2

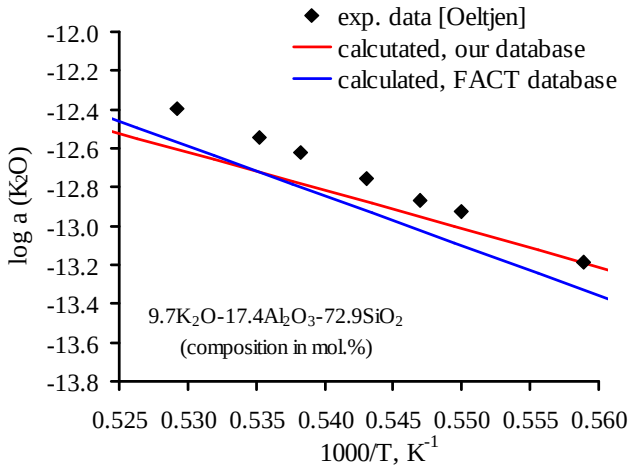
$Al_6Si_2O_{13}$*1/4 - $KAlSi_2O_6$*1/2



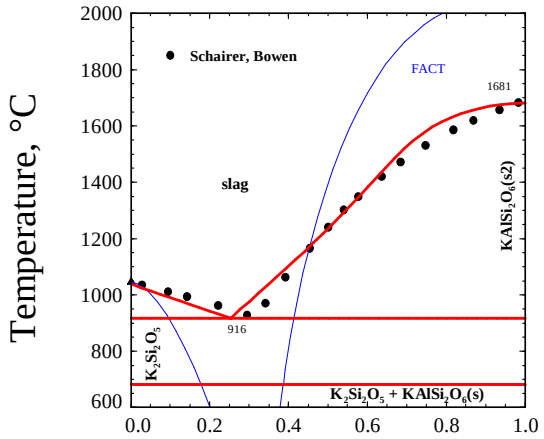
Quasi binary sections in the K_2O-Al_2O_3-SiO_2 system

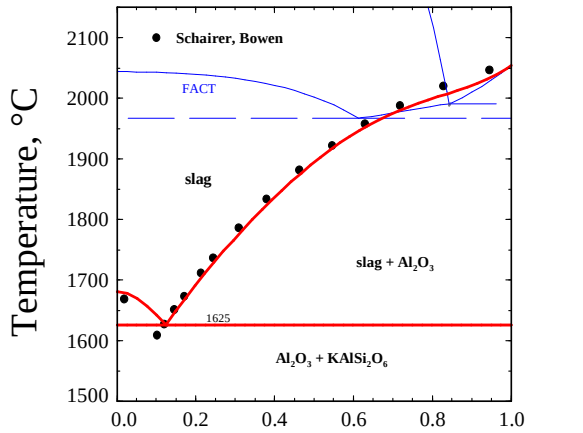


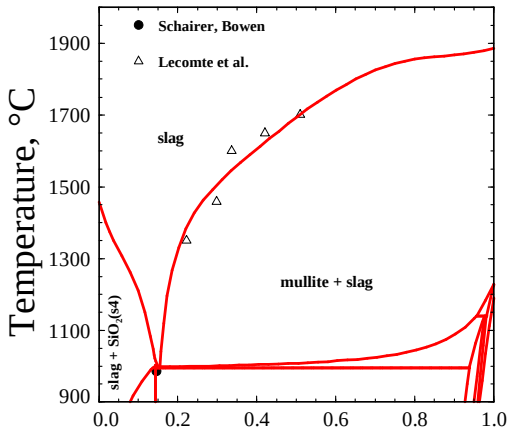




[Oeltjen] *L.Oeltjen, Diss. RWTH Aachen,1999*
[Lecomte et al.] *G. Lecomte, B. Pateyron, P. Blanchart, Mater. Res. Bull.* ***39*** *(2004) 1469-1478.*

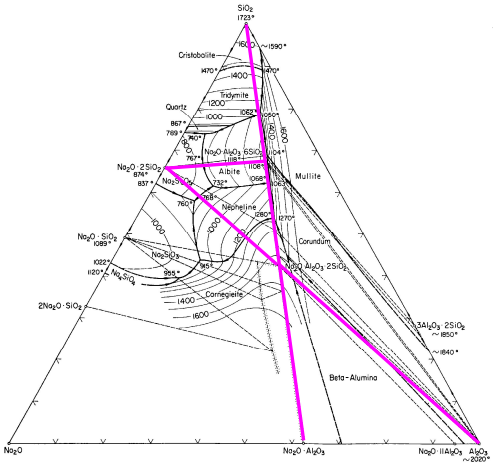






Assessment for ternary system Na_2O-Al_2O_3-SiO_2

Predicted phase fields and ternary points



J.F. Schairer, N.L. Bowen, The system Na_2O-Al_2O_3-SiO_2, Am. J. Sci. 254(2) (1956) 129-195.

A = SiO2, B = Na2O, C = Al2O3

	W(A)	W(B)	W(C)	°C
1:	0.40792	0.21201	0.38007	1519.42
2:	0.42251	0.19540	0.38209	1505.51
3:	0.88518	0.01816	0.09666	1470.06
4:	0.54021	0.16640	0.29338	1275.75
5:	0.44654	0.39125	0.16221	1254.26
6:	0.44174	0.43333	0.12493	1177.65
7:	0.67037	0.12095	0.20868	1112.21
8:	0.61689	0.14329	0.23982	1066.45
9:	0.77440	0.08320	0.14240	1048.17
10:	0.35263	0.62645	0.02092	991.55
11:	0.41326	0.54413	0.04261	982.16
12:	0.17265	0.81468	0.01267	970.05
13:	0.42828	0.51801	0.05371	962.79
14:	0.42218	0.53200	0.04583	952.36
15:	0.20999	0.77849	0.01153	933.58
16:	0.73407	0.18613	0.07980	869.85
17:	0.71991	0.24417	0.03593	736.29
18:	0.70900	0.24848	0.04252	736.29
19:	0.62044	0.23136	0.14821	706.87
20:	0.59874	0.24282	0.15844	706.86
21:	0.60031	0.23540	0.16429	677.83
22:	0.60155	0.23193	0.16653	659.73

Interacting components

Al_2O_3 – $NaAlSi_3O_8$*2/5

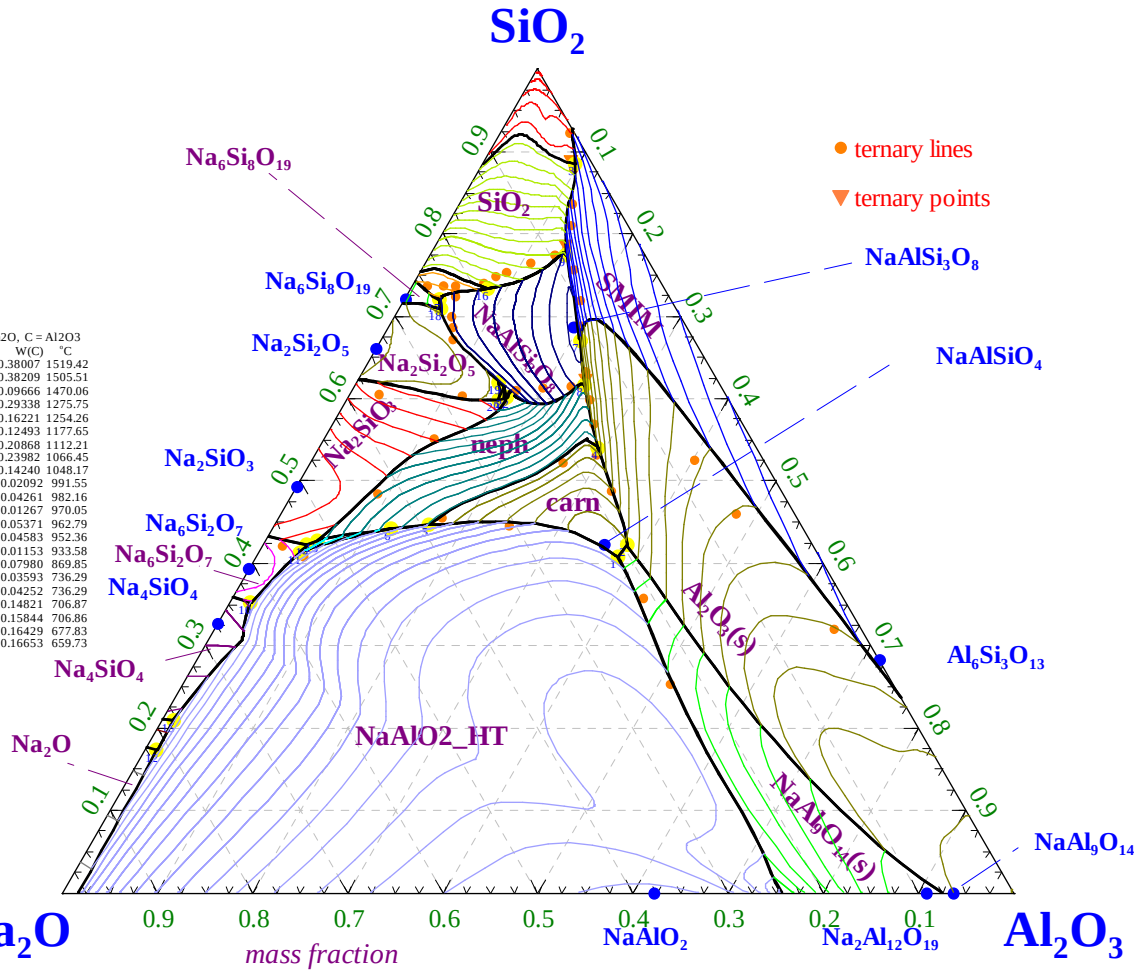
$Na_2Si_2O_5$*1/2 – $NaAlSi_3O_8$*2/5

$Na_2Si_2O_5$*1/2 – $NaAlSiO_4$*2/3

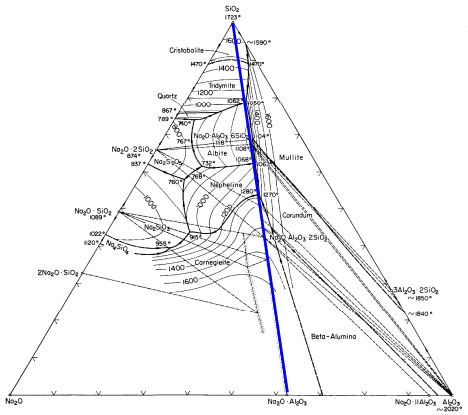
Si_2O_4 – $NaAlSi_3O_8$*2/5

$NaAlSi_3O_8$*2/5-$NaAlSiO_4$*2/3

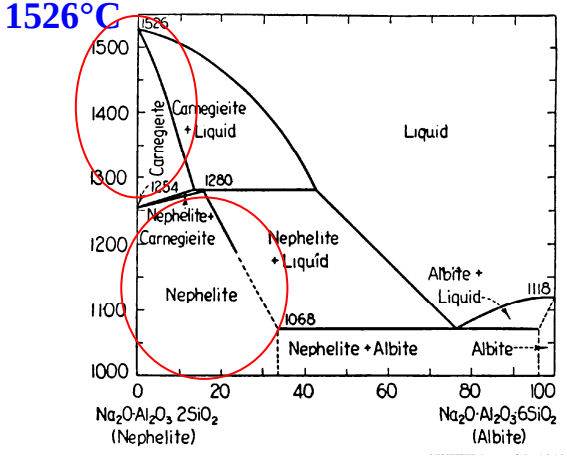
$NaAlO_2$ - $NaAlSiO_4$*2/3



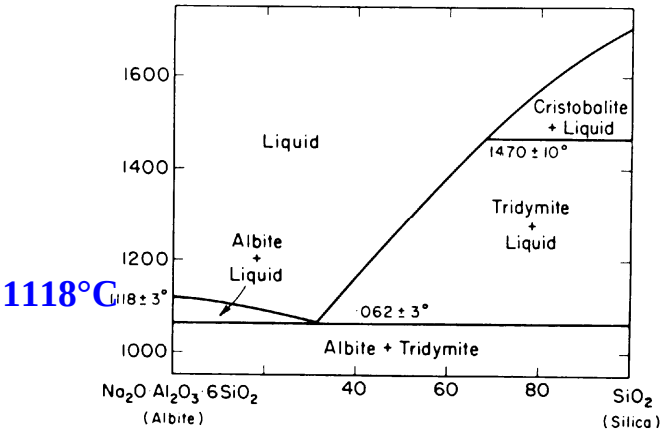
Available experimental phase diagram $NaAlO_2$-SiO_2

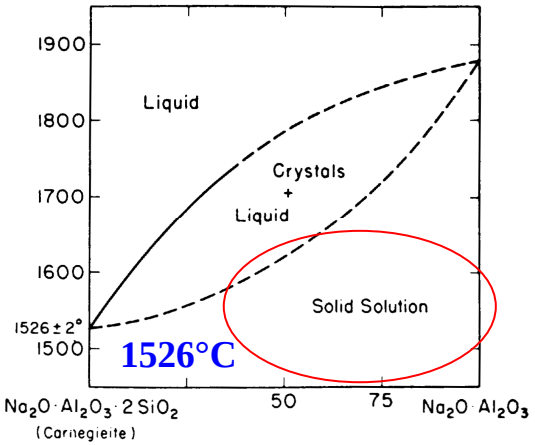


$NaAlSiO_4$ –$NaAlSi_3O_8$
Greig, Barth(1938)

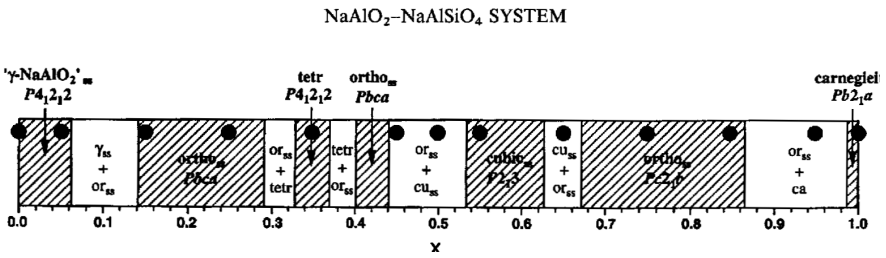


$NaAlSi_3O_8$ (Albite) - SiO_2
Schairer and Bowen (1956)





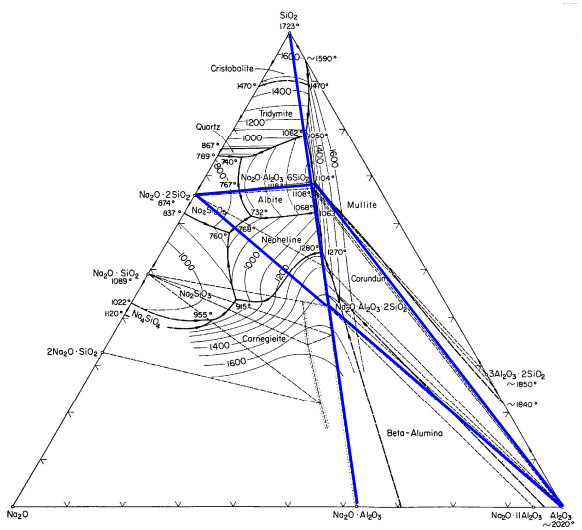
$NaAlSiO_4$ - $NaAlO_2$
Schairer and Bowen (1956)



$NaAlO_2$ - $NaAlSiO_4$
Thompson (1997), Proposed compositional phase diagram at 1300 °C for the system $Na_{2-x}Al_{2-x}Si_xO_4$, $0 \le x \le 1$

J.F. Schairer, N.L. Bowen, The system Na_2O-Al_2O_3-SiO_2, Am. J. Sci. ***254(2)*** *(1956) 129-195.*
Greig J.W., Barth T.F.W., Am.Jour.Sci., 5th ser., ***35A****, p.93-112 (1938)*
Thompson J.G., Melnitchenko A., Palethorpe S.R., Withers R.L., J.Solid State Chem., ***131****, p.24-37 (1997)*
Thompson J.G., Withers R.L., Melnitchenko A., Palethorpe S.R., Acta Cryst., ***B54****, p.531-546 (1998)*

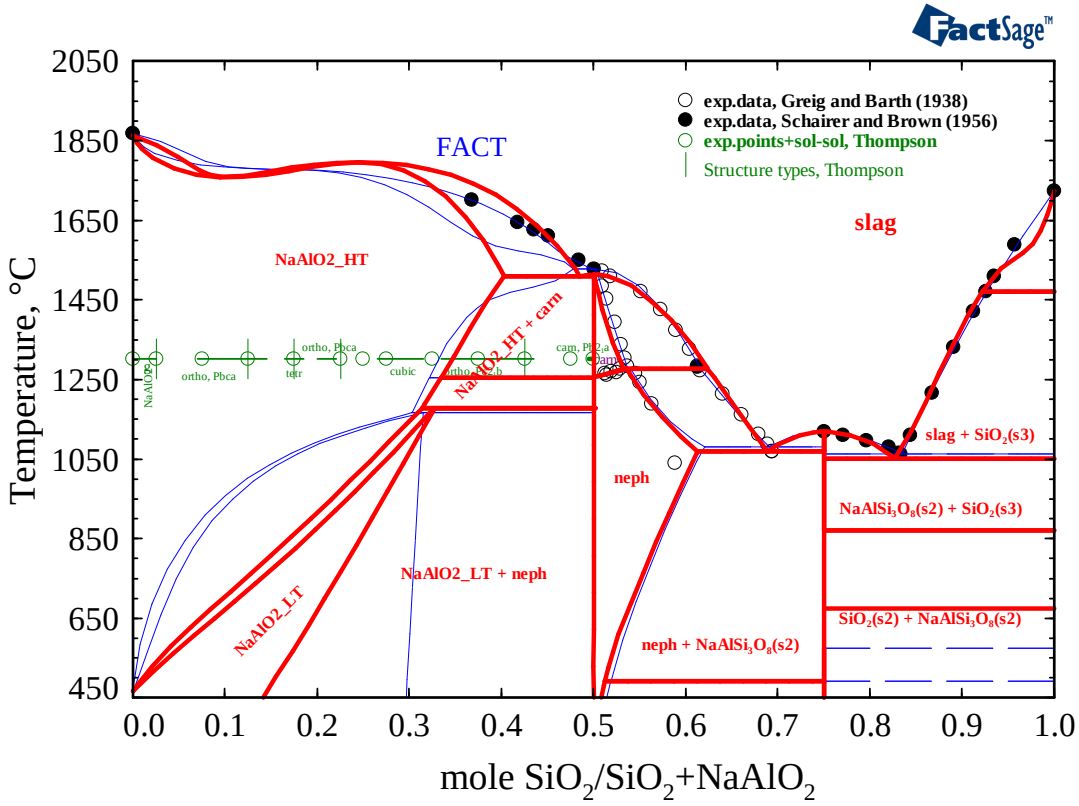
Current results of the assessment for the system $NaAlO_2$-SiO_2



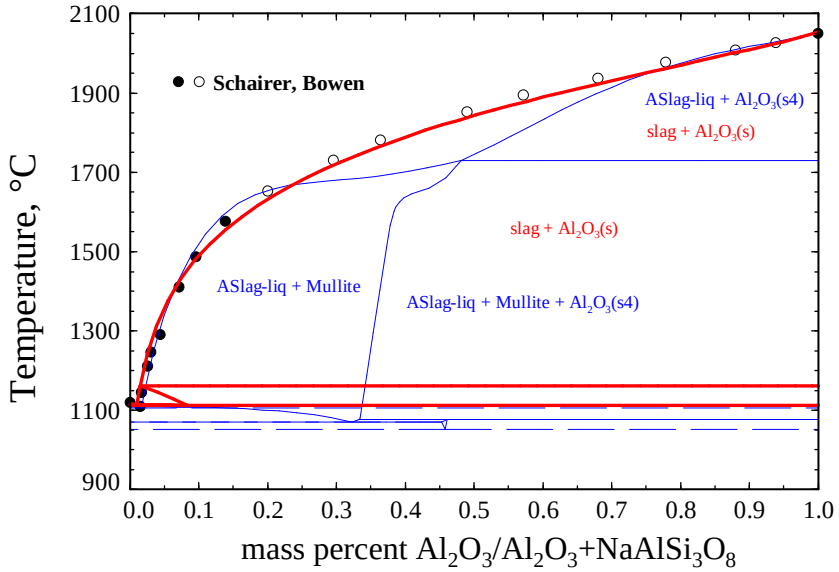
$NaAlO_2$ (low T, high T), Nepheline, Carnegieite are represented by sublattice approach. The parameters of the solutions are optimised to obtain good description of the available experimental data.

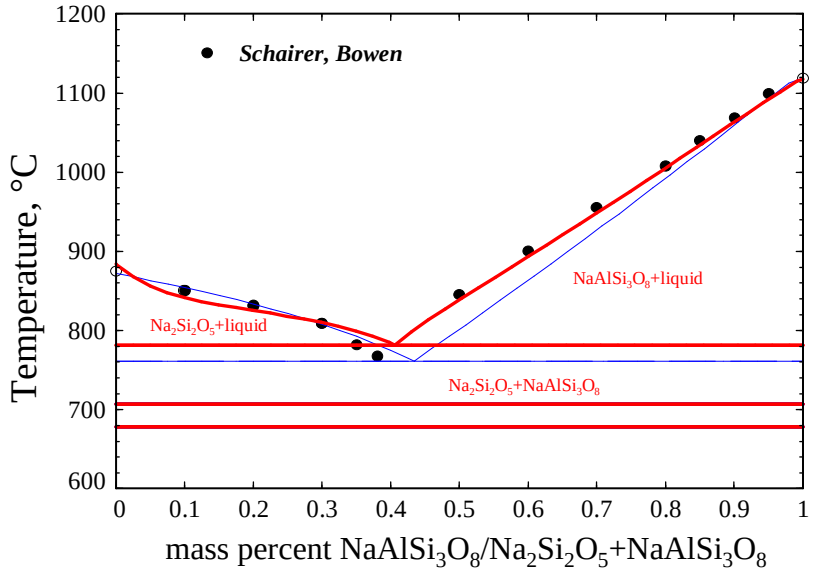
Problems:

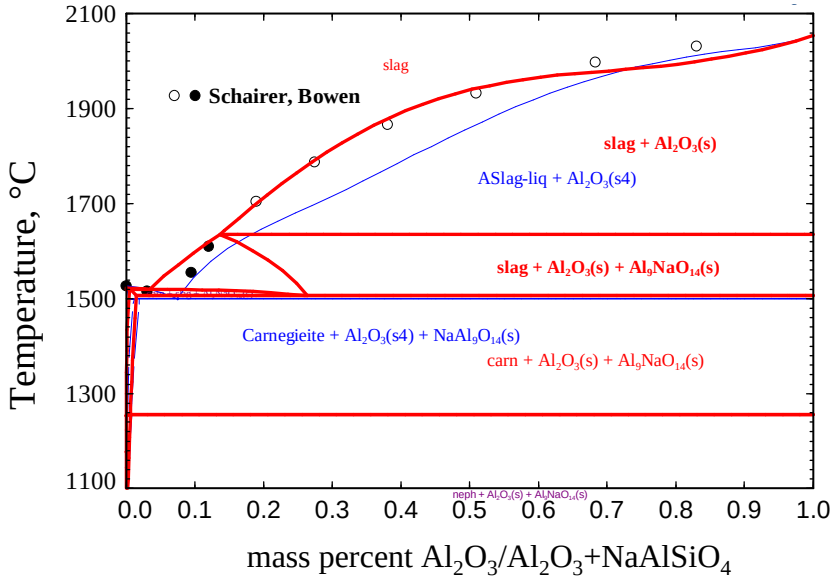
- ✓*Unknown solubility boundaries for $NaAlO_2$ (low T, high T) solutions*
- ✓*Possible presence of a series of solid solutions with different crystallographic structure between $NaAlO_2$ and $NaAlSiO_4$*

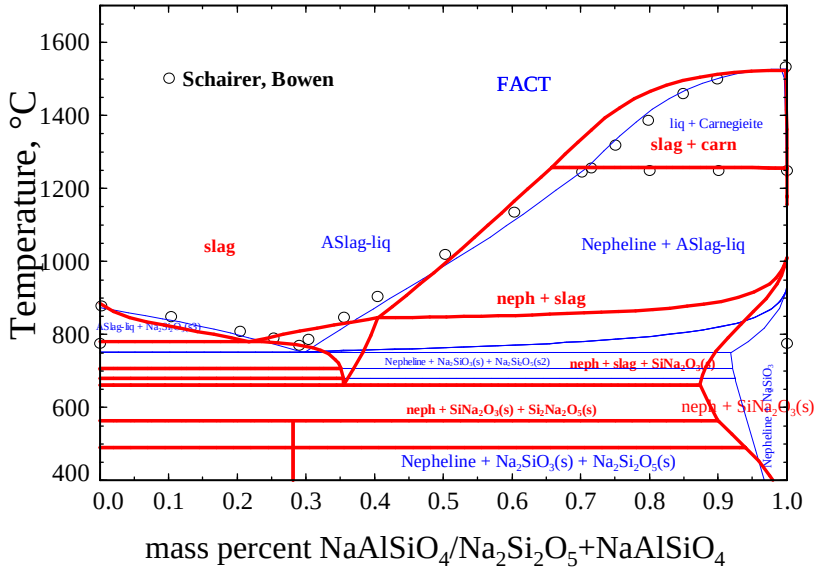


Quasi binary sections in the Na_2O-Al_2O_3-SiO_2 system









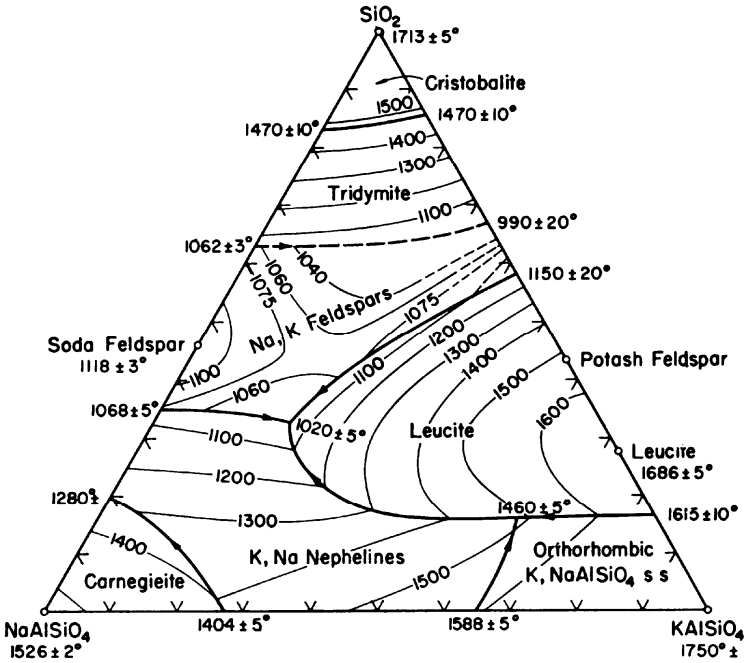
Conclusions

- 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 re-optimised to accurate description of the phase diagrams taking into account the changes concerning the data on the pure liquid oxides
- Solid and liquid solutions in the ternary systems Na_2O-K_2O-SiO_2 and Alk_2O-Al_2O_3-SiO_2 (Alk=Na, K) 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

Outlook

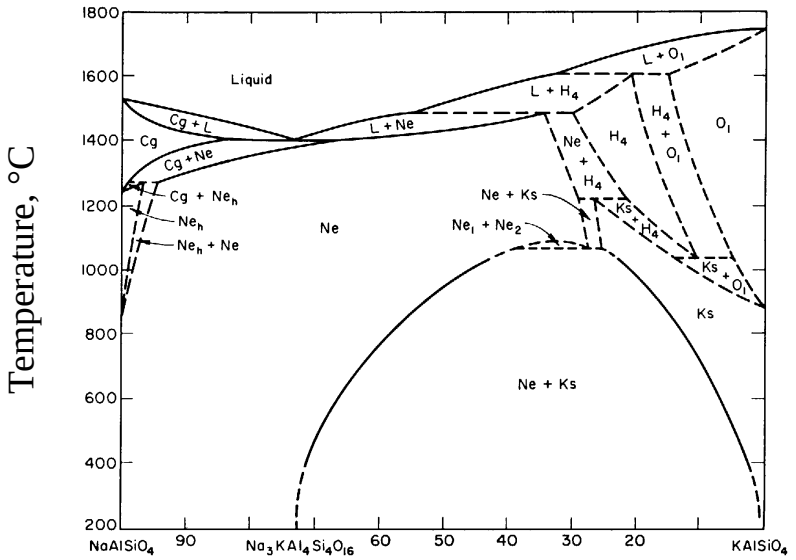
- Assessment of the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2 system
- Creation of the database for possible quaternary solutions, e.g. (Na, K)AlO_2 and (Na, K)(Al, Si)O_4

SiO_2 – $KAlSiO_4$ - $NaAlSiO_4$



*Schairer, J.F., The alkali-feldspar join in the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2, J. Geol. **58** (5) 512-517*

$NaAlSiO_4$ – $KAlSiO_4$



mass percent $KAlSiO_4/NaAlSiO_4+KAlSiO_4$

O.F. Tuttle, J.V. Smith, The nepheline-kalsilite system II. Phase relations Am. J. Sci. 256 (1958) 571-589

Thank you for your attention