JÜLICH FORSCHUNGSZENTRUM

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Incorporation of P_2O_5 into the oxide core database with Al, Si, Ca and Mg

4. Juli 2013 | Elena Yazhenskikh[1], Klaus Hack[2], Tatjana Jantzen[2], Michael Müller[1]

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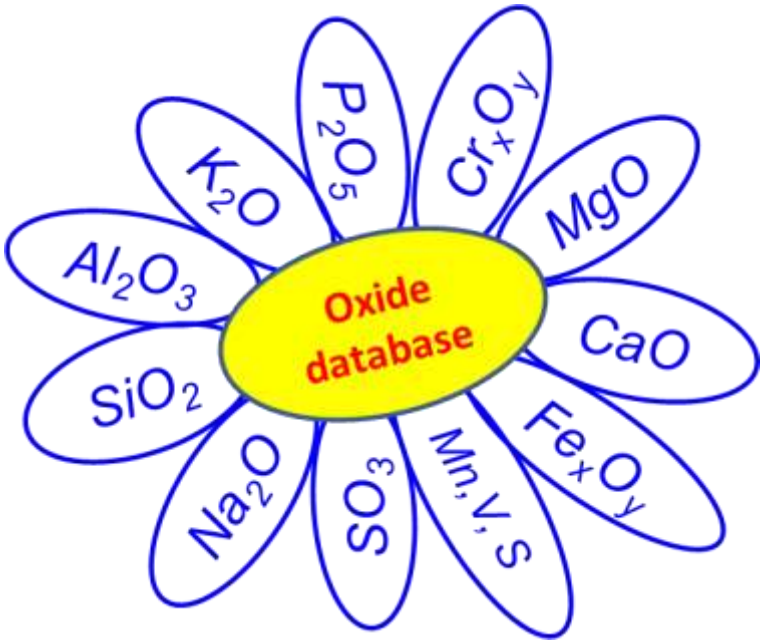
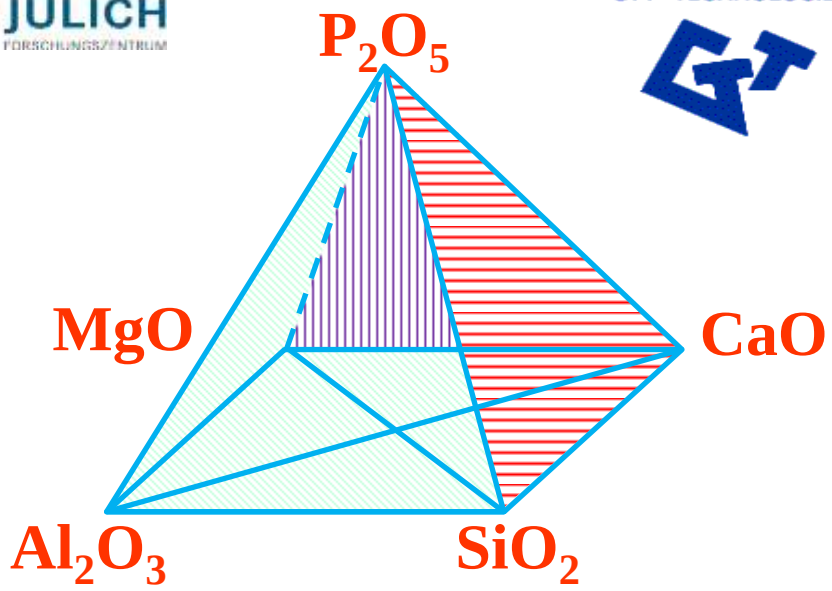
Motivation and aim of work



- ✓ *P_2O_5 is an essential component for the co-gasification of phytogenic and zoogenic biomass.*
- ✓ *The addition of P_2O_5 improves the fluidity of molten slags.*
- ✓ *The phosphates are of interest in connection with soil-fertilizer relationships.*
- ✓ *The dephosphorization is important in the iron and steel industry.*

State of the art:

- ✓ 2-, 3- and multicomponent systems have been thermodynamically assessed using all available experimental data
- ✓ phase diagrams and other thermodynamic properties can be calculated with the obtained self-consistent datasets



Aim of our work:

development of a new data base, which is applicable for the slag relevant system containing oxides of Si, Al, Na, K, Ca, Mg, Fe, P, S, Cr etc. and suitable for the calculations and/or predictions of the phase equilibria and other thermodynamic properties by variation of T and composition

Database development

Experimental data from literature source and from our measurements: phase diagram data, activity data etc.

Choice of the suitable model

Initial data for pure substances, liquid and solid solution components

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
- ✓ Interaction parameters between species

optimisation

Comparison of the results with exp. data

disagreement

agreement

New dataset

✓ **Liquid: non-ideal associate solution using Redlich-Kister-Muggianu equation**

$$G_m = \sum x_i G_i^0 + RT\sum x_i \ln x_i + \sum\sum x_i x_j \sum L_{ij}^{(v)}(x_i - x_j)^v \ldots +$$

✓ **Solids: stoichiometric compounds**

$$G^\circ = A + B*T + C\,T*\ln(T) + D*T^2 + E*T^3 + F/T$$

✓ **Solid solutions: sublattice approach (CEF)**

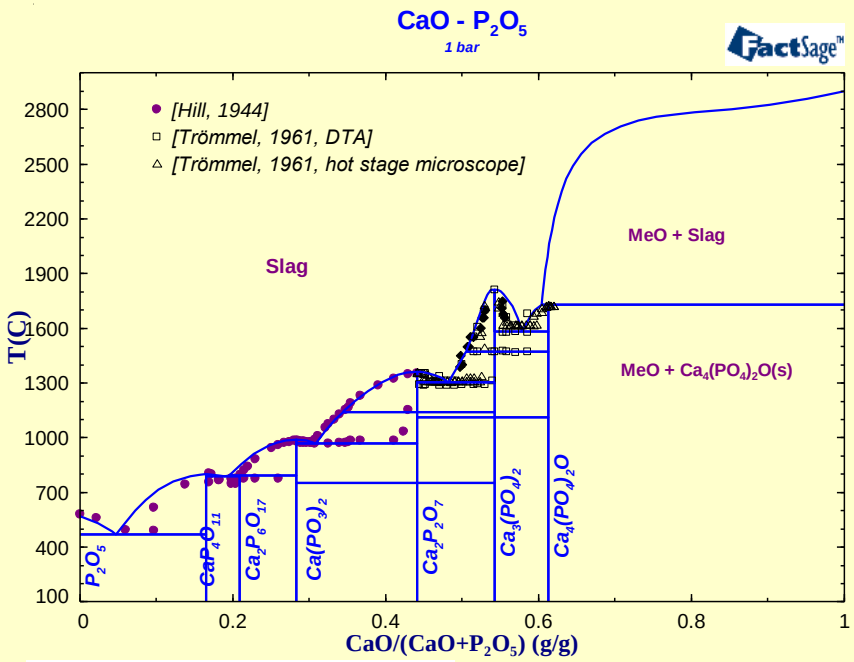
$$G_m = \sum_{I_0} P_{I_0}(Y)\,{}^0G_{I_0} + \sum_{s=1}^{n} a_s RT \sum_{i=1}^{n_s} y_i^s \ln(y_i^s) + \sum_{I_1} P_{I_1}(Y)\,L_{I_1} + \sum_{I_2} P_{I_2}(Y)\,L_{I_2} + \ldots$$

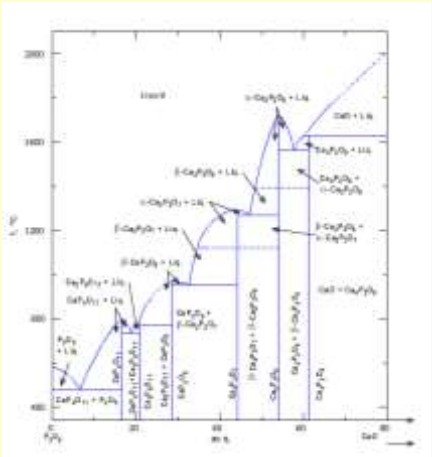
Modelling of binary P_2O_5-containing phases

The species in the non-ideal associate solution containing P_2O_5 were added in order to describe the liquid phase. Binary solid phases were considered as stoichiometric compounds

System	*Associate species in liquid Me_xO_y:P_2O_5*	*Solid phase*	*Description of solid phase*
CaO-P_2O_5	3:1, 2:1, 1:1 $Ca_3P_2O_8$, $Ca_2P_2O_7$, CaP_2O_8 [Serena 2011]	$CaO{\cdot}2P_2O_5$ $2CaO{\cdot}3P_2O_5$ $CaO{\cdot}P_2O_5$ $2CaO{\cdot}P_2O_5$(s1,s2,s3) $3CaO{\cdot}P_2O_5$(s1,s2,s3) $4CaO{\cdot}P_2O_5$	stoichiometric stoichiometric stoichiometric stoichiometric stoichiometric stoichiometric
MgO - P_2O_5	3:1, 2:1, 1:1 $Mg_3P_2O_8$ (SGPS), $Mg_2P_2O_7$, MgP_2O_8	$MgO{\cdot}P_2O_5$ $2MgO{\cdot}P_2O_5$ $3MgO{\cdot}P_2O_5$	stoichiometric stoichiometric stoichiometric
Al_2O_3-P_2O_5	1:1 $AlPO_4$(SGPS)	$3Al_2O_3{\cdot}P_2O_5$ $AlPO_4$(s3,s2,s1) $Al_2O_3{\cdot}3P_2O_5$	stoichiometric stoichiometric stoichiometric
SiO_2-P_2O_5	1:1 SiP_2O_7	$SiO_2{\cdot}P_2O_5$ $5SiO_2{\cdot}3P_2O_5$	stoichiometric stoichiometric

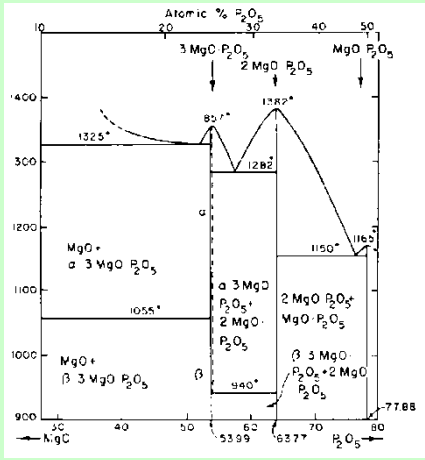
$CaO-P_2O_5$ and $MgO-P_2O_5$

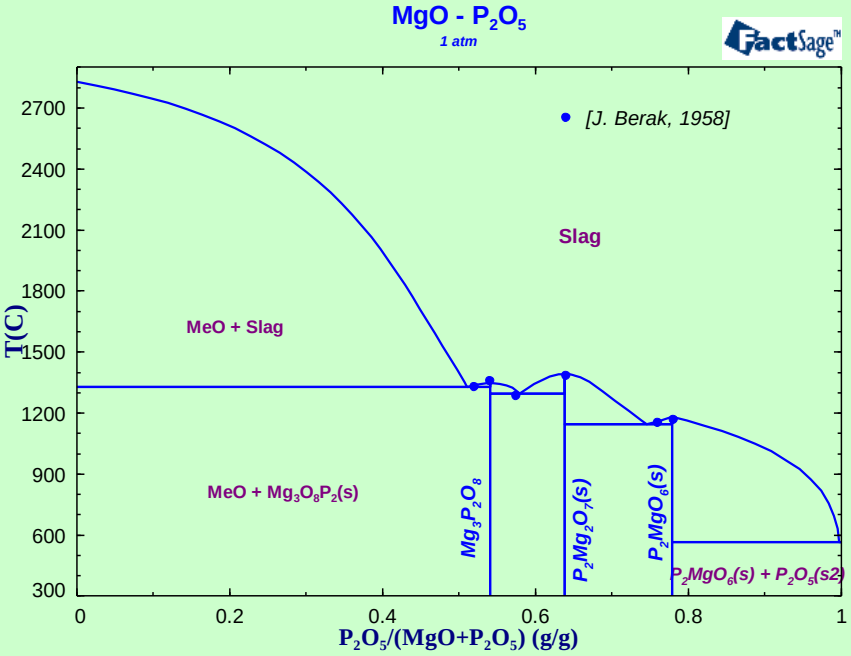




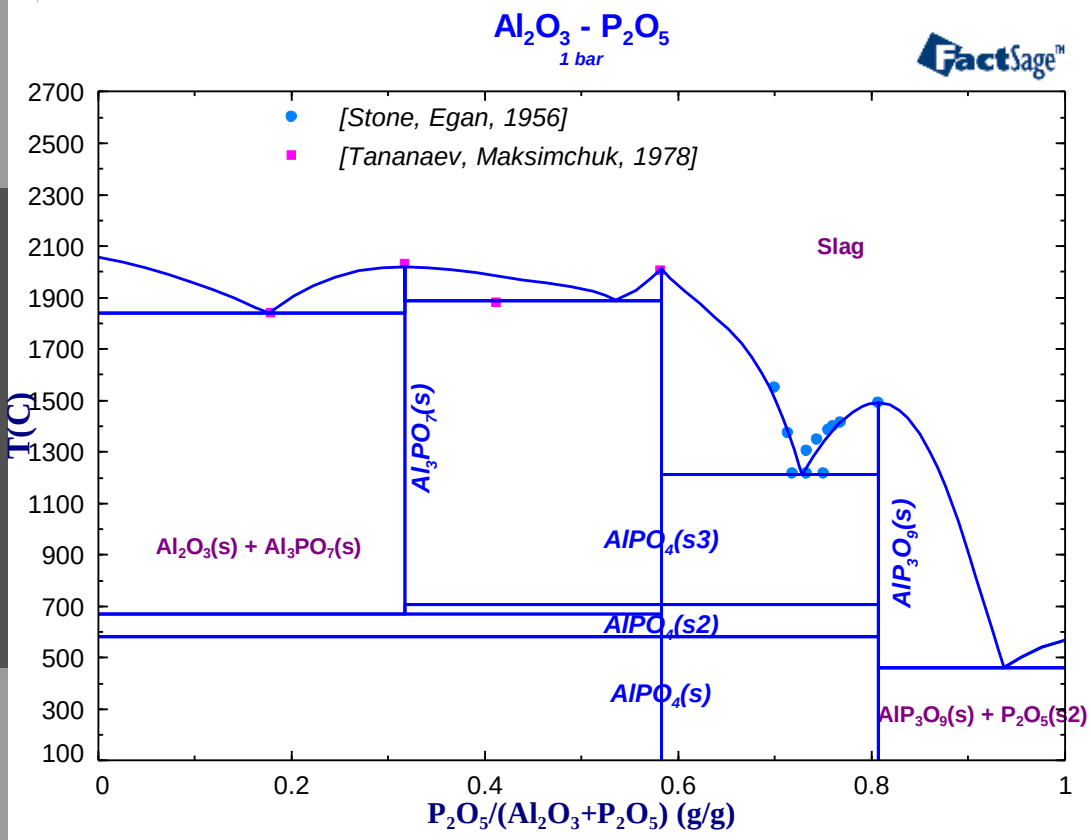
*W. L. Hill, G. T. Faust, and D. S. Reynolds, Am. J. Sci., **242** [9] 457-477 (1944); G. Troemel, Stahl Eisen, **63** [2] 21-30 (1943).*

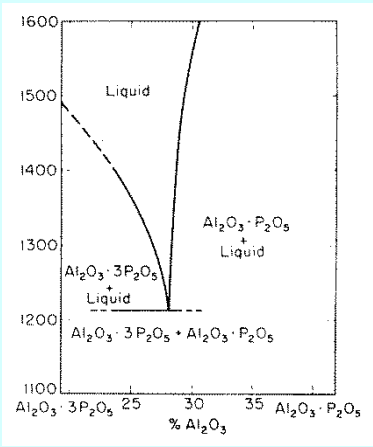
J. Berak, Rocz. Chem., 32 [1], (1958), pp.17-22.



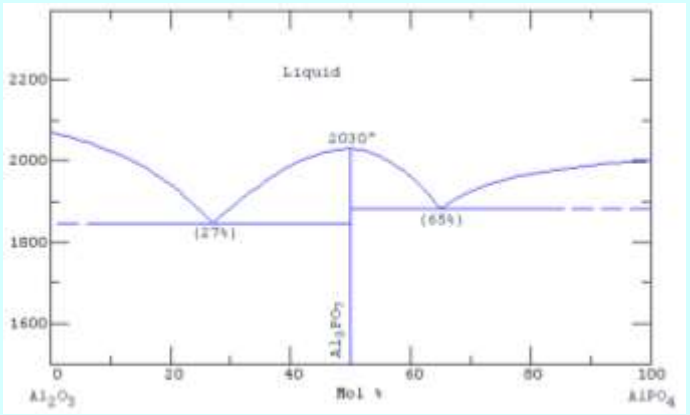


Al_2O_3-P_2O_5



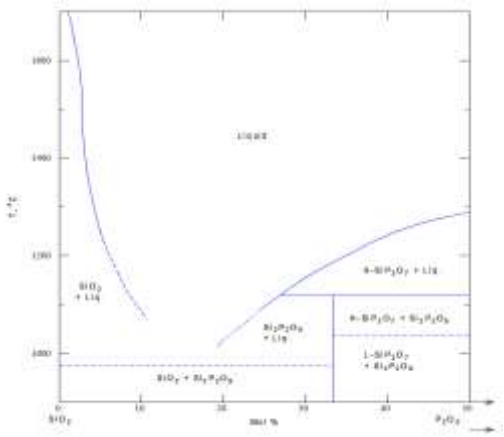


P.E. Stone, E.P. Egan, J.R. Lehr, J. Am, Ceram. Soc., 39 [3], (1956), pp.89-98.



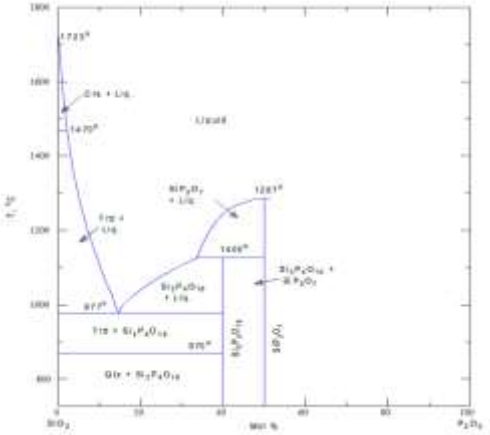
I.V. Tananaev, E.V. Maksimchuk,Y. G. Bushuev, S.A. Shestov, Izv. Akad. Nauk SSSR, Neorg. Mater., 14 [4], (1978), pp.719-722.

SiO_2-P_2O_5: experimental data

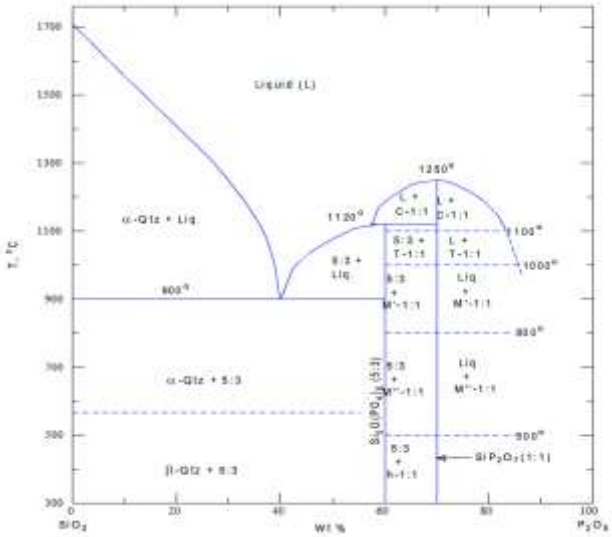


T. Y. Tien and F. A. Hummel, J. Am. Ceram. Soc., ***45*** *[9] 422-424 (1962).*

There is not enough experimental data on phase diagrams and compounds. The few data available is contradictory. Hence, experimental studies are needed.

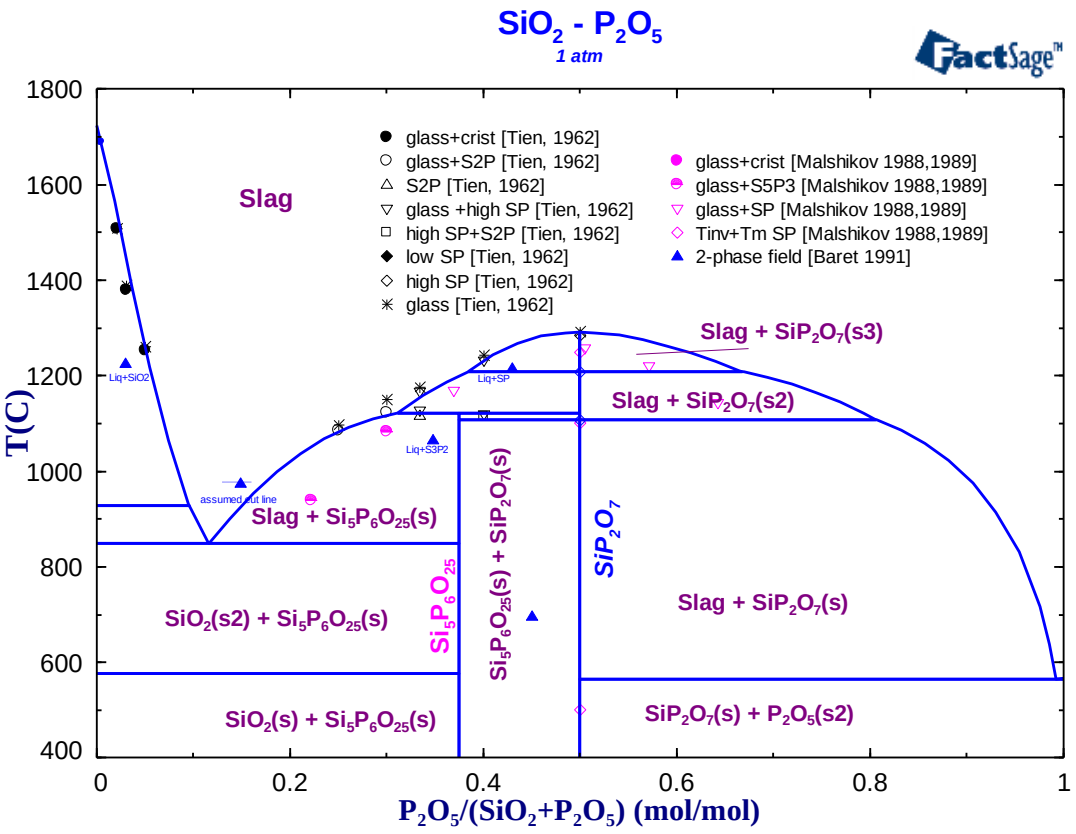


G. Baret, R. Madar, and C. Bernard, J. Electrochem. Soc., ***138*** *[9] 2830-2835 (1991).*

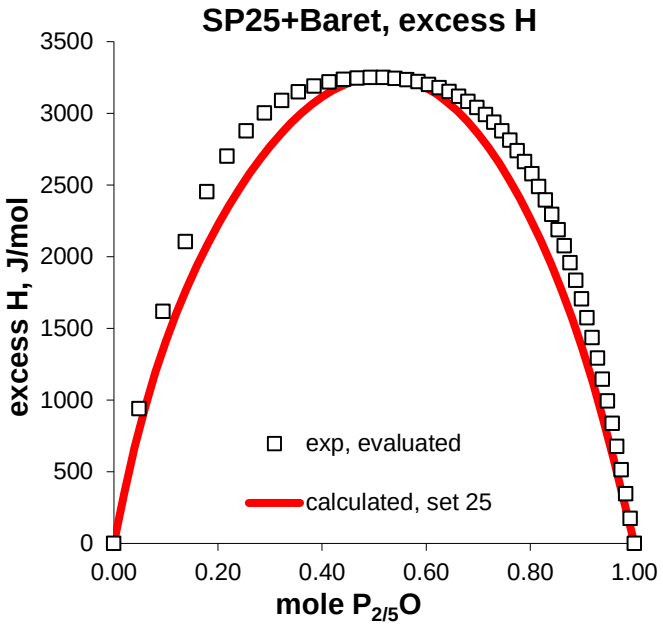


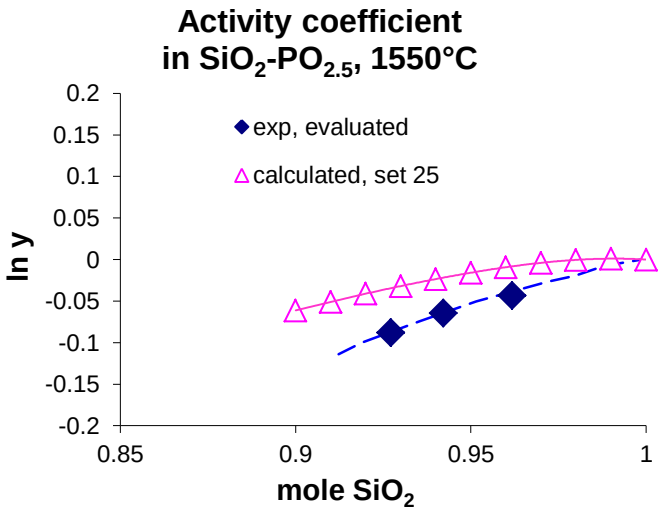
A. E. Mal'shikov and I. A. Bondar, Russ. J. Inorg. Chem. (Engl. Transl.), ***33****[1] 109-112 (1988).*

SiO_2-P_2O_5: calculation



In the present work, the compound $5SiO_2{\cdot}3P_2O_5$ (Tm, XRD data) has been taken into account





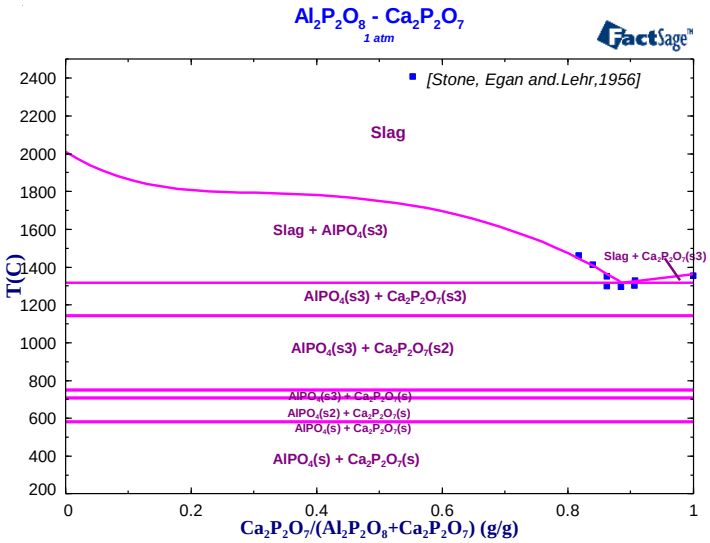
Modelling of ternary P_2O_5-containing phases

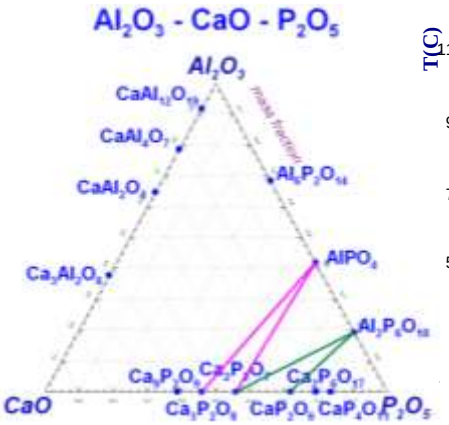
In all ternary systems there are **no** ternary species, with the exception of the system **Al_2O_3-MgO-P_2O_5**, where one ternary species **$Al_2O_3 \cdot 3MgO \cdot P_2O_5$** was incorporated

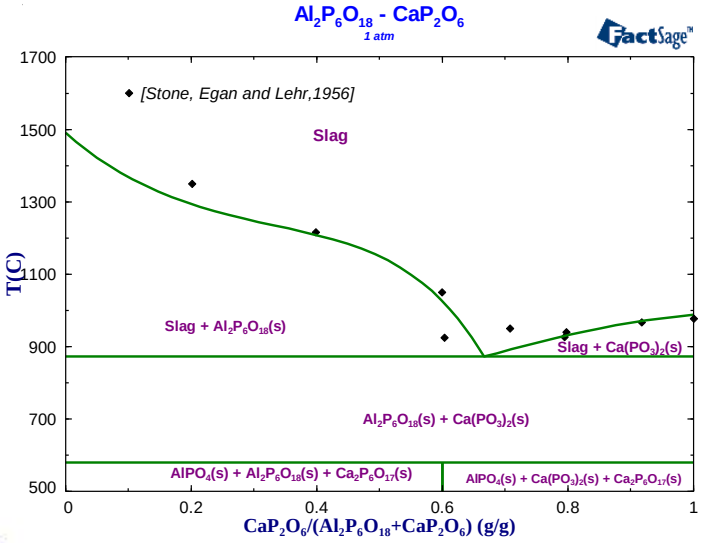
*System**	*Solid phase*	*Description of solid phase*
Al_2O_3-SiO_2-P_2O_5	$AlPO_4$_MT	$(Al^{3+}, Si^{4+})(P^{5+}, Si^{4+})(O^{2-})_4$
	$AlPO_4$_HT	$(Al^{3+}, Si^{4+})(P^{5+}, Si^{4+})(O^{2-})_4$
	SiO_2_HT	$(Al^{3+}, Si^{4+})(P^{5+}, Si^{4+})(O^{2-})_4$
	SiO_2_MT	$(Al^{3+}, Si^{4+})(P^{5+}, Si^{4+})(O^{2-})_4$
	$Al_2O_3 \cdot 4SiO_2 \cdot 3P_2O_5$ (no data)	Stoichiometric
CaO-SiO_2-P_2O_5	Ca_2SiO_4-alpha =$Ca_3P_2O_8$-alpha prime	$(Ca^{2+})_3(Ca^{2+},Va)_1(P^{5+},Si^{+4})_2(O^{2-})_8$
	Ca_2SiO_4-alpha-prime	$(Ca^{2+})_3(Ca^{2+},Va)_1(P^{5+},Si^{+4})_2(O^{2-})_8$
	$7CaO \cdot P_2O_5 \cdot 2SiO_2$	Stoichiometric
	$5CaO \cdot P_2O_5 \cdot SiO_2$	Stoichiometric
CaO-MgO-P_2O_5	C3P- beta	$(\underline{Ca}^{2+},Mg^{2+})_3(P^{5+})_2(O^{2-})_8$
	C3P-alpha	$(\underline{Ca}^{2+},Mg^{2+})_3(P^{5+})_2(O^{2-})_8$
	C3P-alpha-prime	$(\underline{Ca}^{2+},Mg^{2+})_3(P^{5+})_2(O^{2-})_8$
	M3P	$(Ca^{2+},\underline{Mg}^{2+})_3(P^{5+})_2(O^{2-})_8$
	C2P-MT	$(\underline{Ca}^{2+},Mg^{2+})_2(P^{5+})_2(O^{2-})_7$
	M2P	$(Ca^{2+},\underline{Mg}^{2+})_2(P^{5+})_2(O^{2-})_7$
	C3M3P2	**$(\underline{Ca}^{2+},Mg^{2+})_3(Mg^{2+})_3(P^{5+})_4(O^{2-})_{16}$**
	CMP	**$(Ca^{2+},\underline{Mg}^{2+})_1(Ca^{2+})_1(P^{5+})_2(O^{2-})_7$**

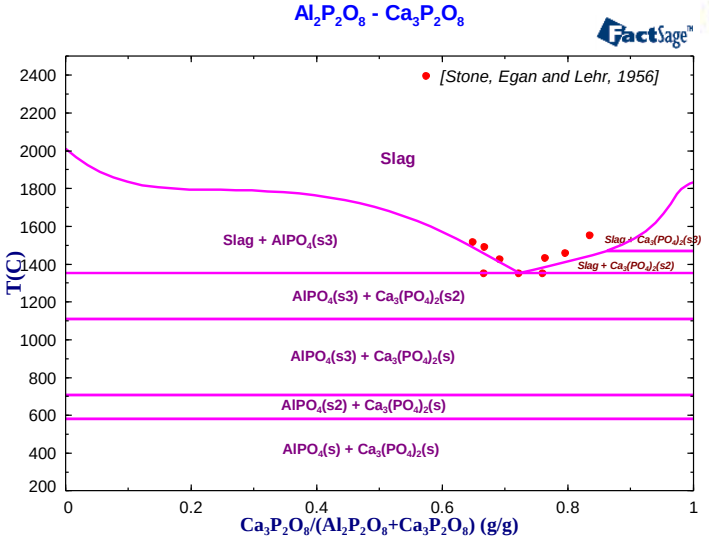
*All other systems do not have ternary compound or phases

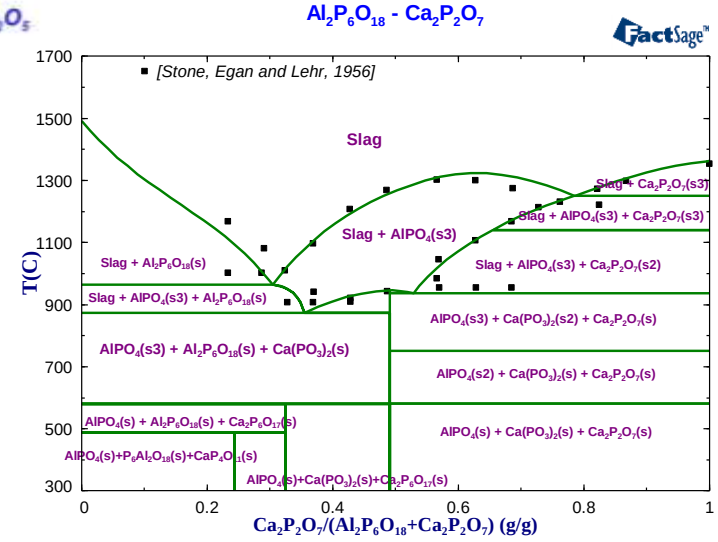
$CaO-Al_2O_3-P_2O_5$: isoplethal sections



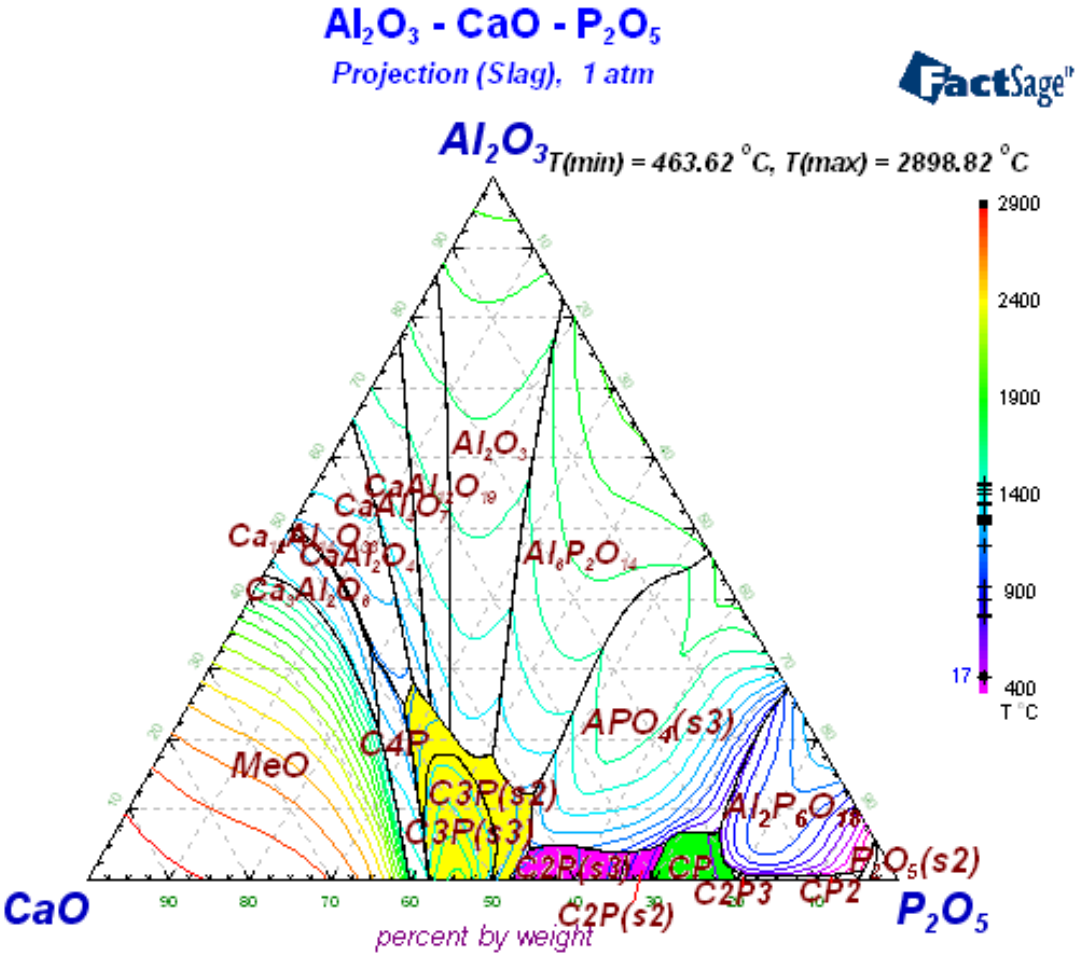


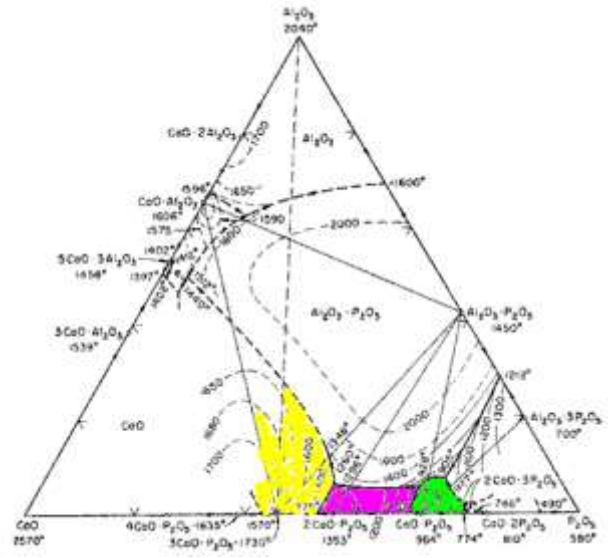






$CaO\text{-}Al_2O_3\text{-}P_2O_5$: liquidus surface



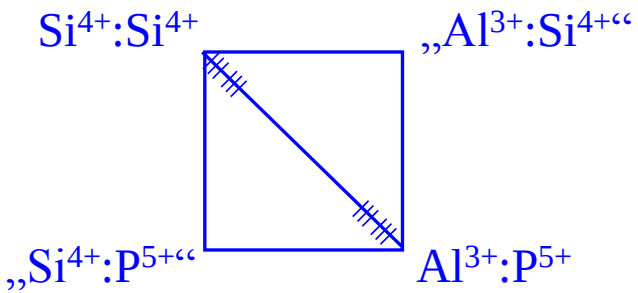


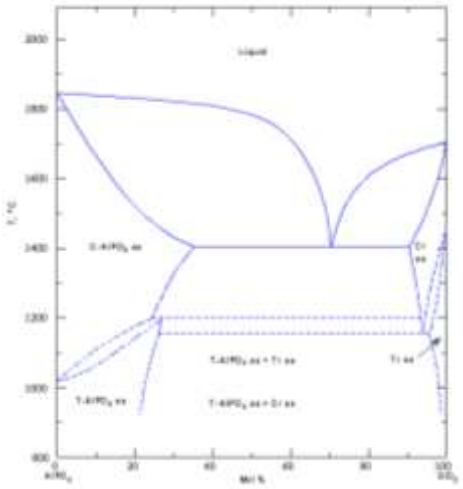
P. E. Stone, E. P. Egan, Jr., and J. R. Lehr, J. Am. Ceram. Soc., 39 [10] , (1956), pp. 361-362 .

Modelling of $AlPO_4$-SiO_2 phases

Solid solubility of $AlPO_4$ in SiO_2 and SiO_2 in $AlPO_4$ for 2 crystalline modifications on the each side is described using the formula

$$(Al^{3+}, Si^{4+})(P^{5+}, Si^{4+})(O^{2-})_4$$





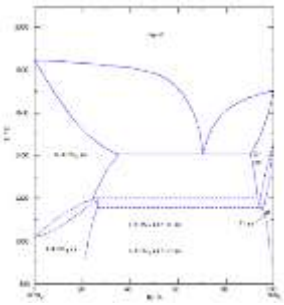
W. F. Horn and F. A. Hummel, Cent. Glass Ceram. Res. Inst. Bull., 26 [1-4] 47-59 (1979).

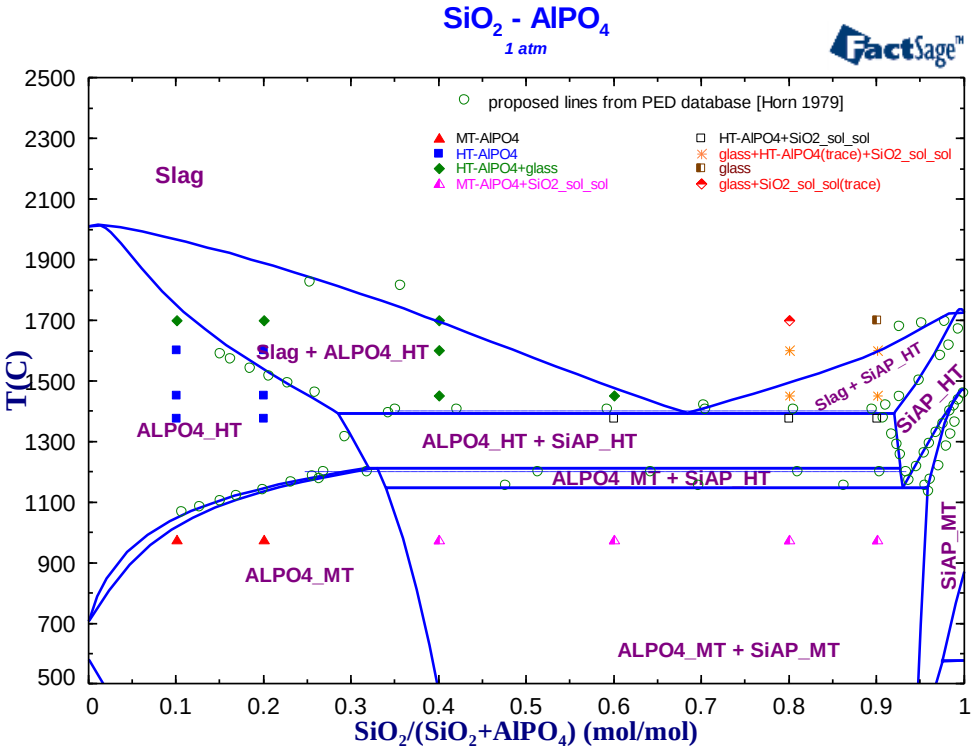
For each phase, the following reciprocal equation was applied:

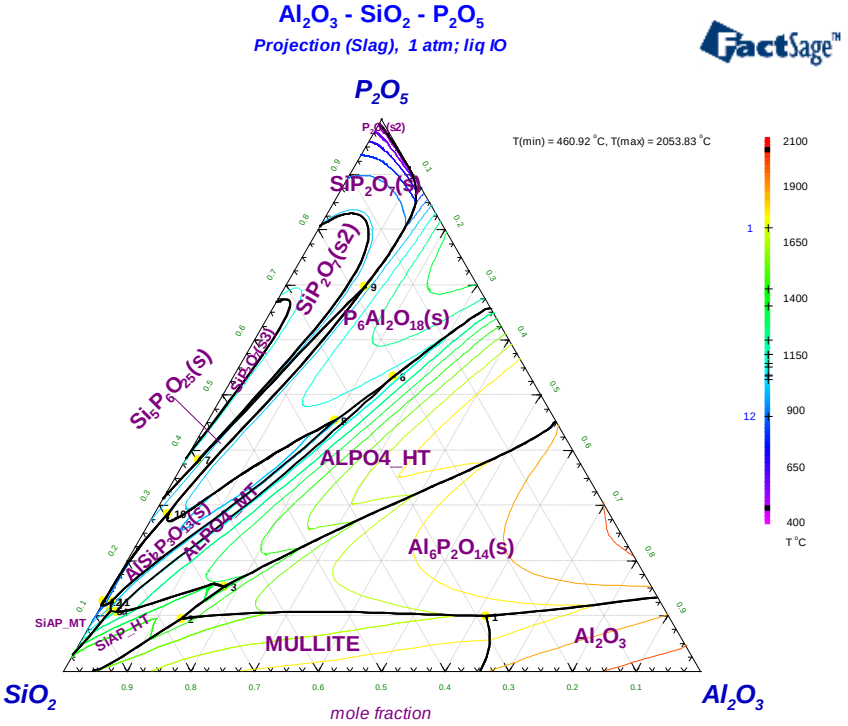
G(Si:Si:O) + G(Al:P:O) - G(Al:Si:O) – G(Si:P:O) = 0

System	Solid phase	Description of solid phase
Al_2O_3-SiO_2-P_2O_5	$AlPO_4$_MT	$(Al^{3+}, Si^{4+})(P^{5+}, Si^{4+})(O^{2-})_4$
	$AlPO_4$_HT	$(Al^{3+}, Si^{4+})(P^{5+}, Si^{4+})(O^{2-})_4$
	SiO_2_HT	$(Al^{3+}, Si^{4+})(P^{5+}, Si^{4+})(O^{2-})_4$
	SiO_2_MT	$(Al^{3+}, Si^{4+})(P^{5+}, Si^{4+})(O^{2-})_4$
	$Al_2O_3 \cdot 4SiO_2 \cdot 3P_2O_5$ (*no experimental data*)	Stoichiometric

Al_2O_3-SiO_2-P_2O_5: calculation

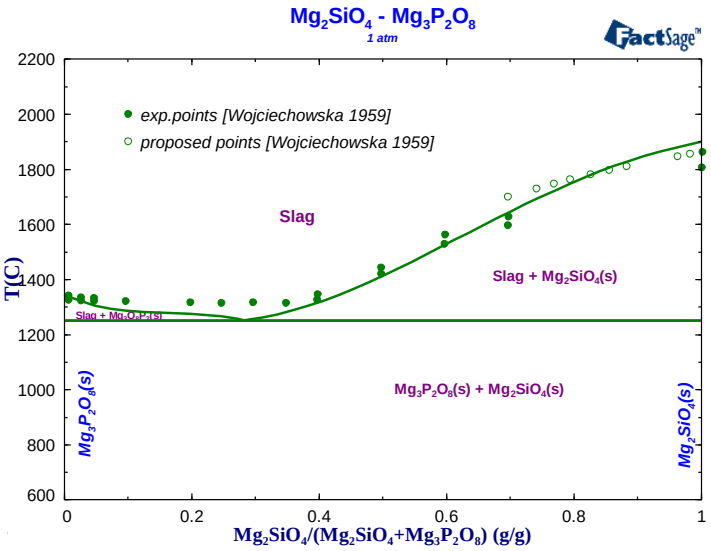


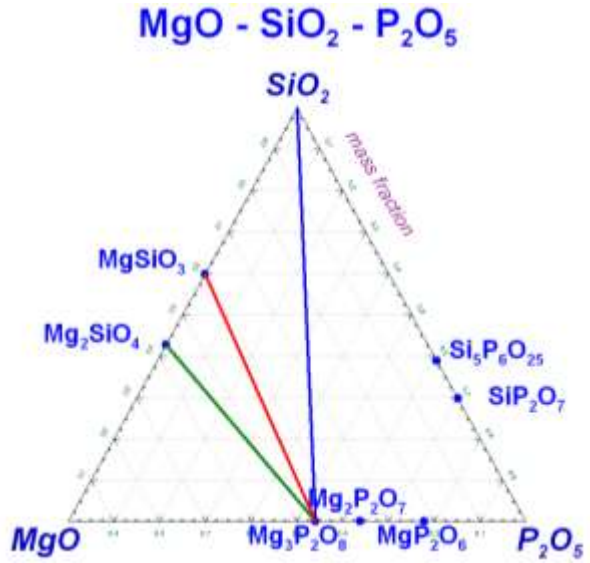


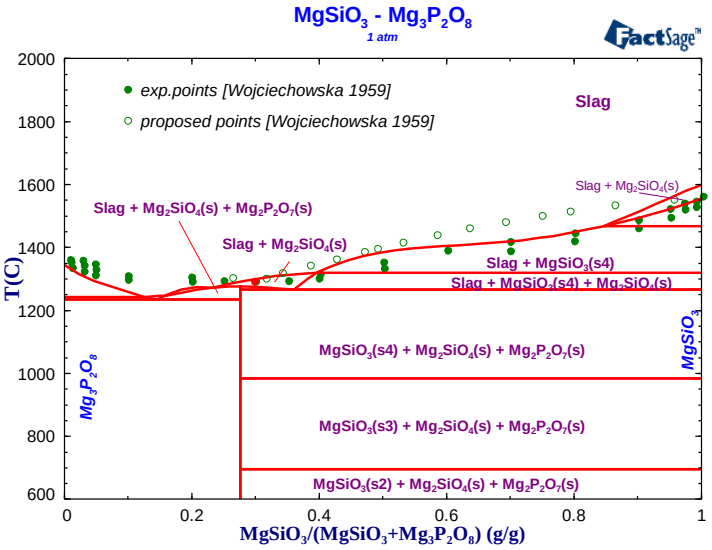


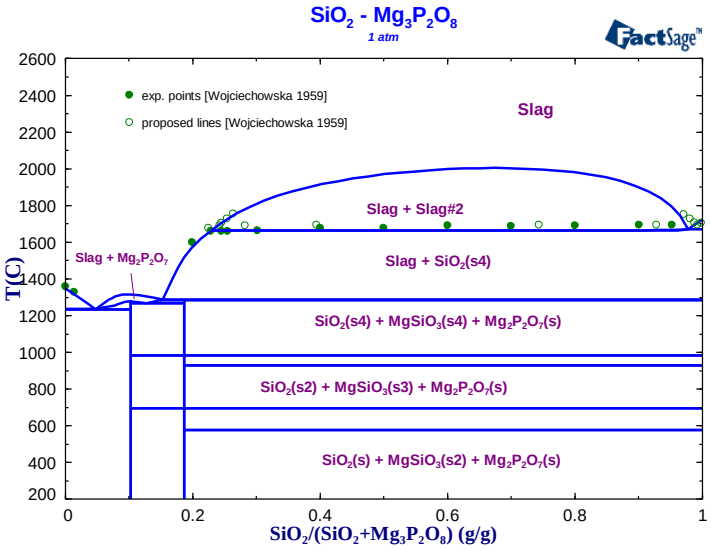
There is not enough experimental data on phase diagrams and compounds. The few data available is contradictory. Hence, experimental studies are needed.

$MgO\text{-}SiO_2\text{-}P_2O_5$: isoplethal sections

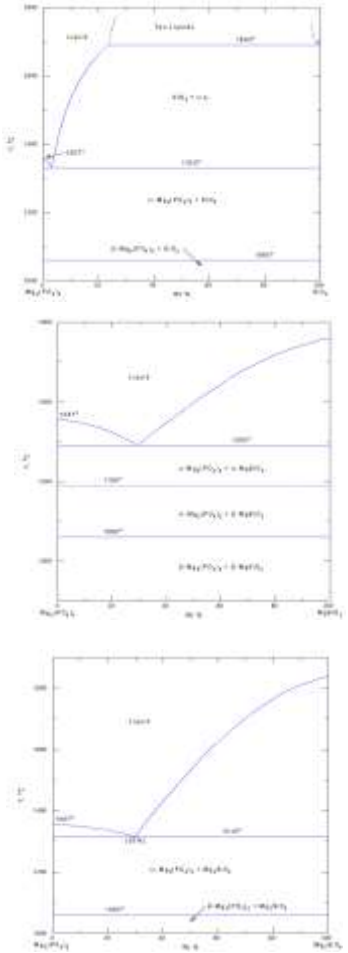






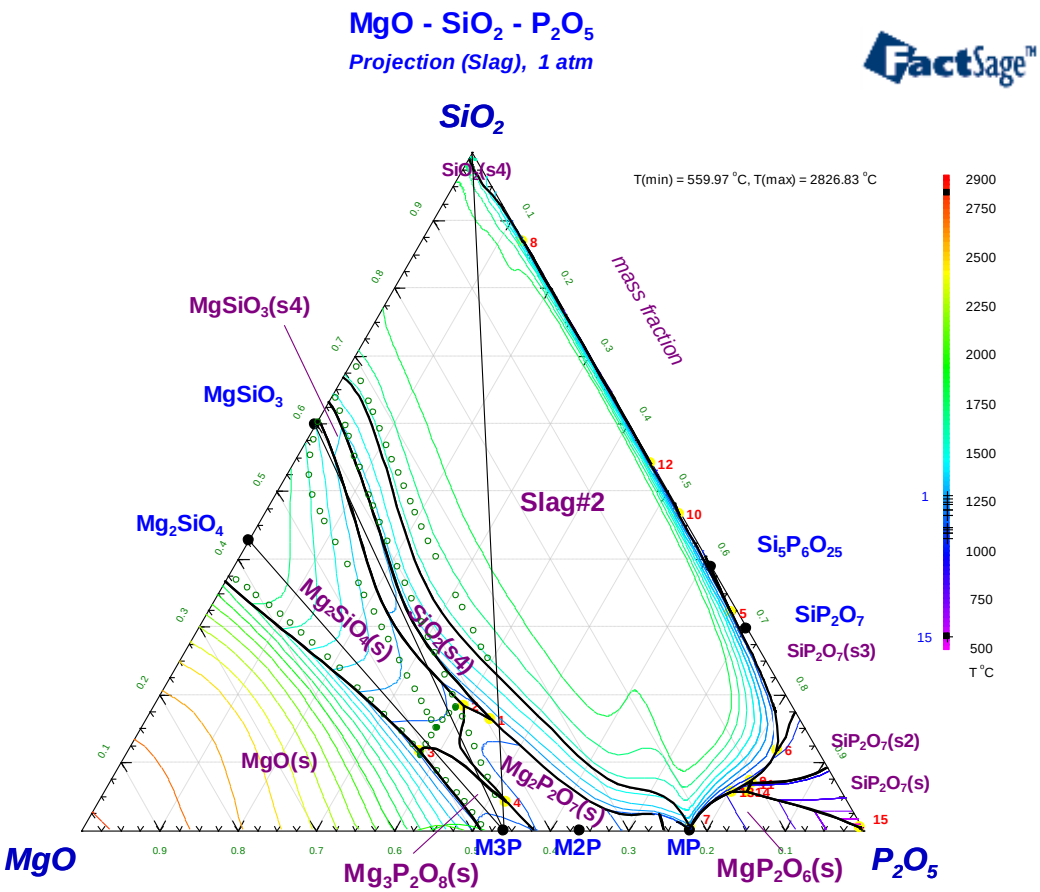


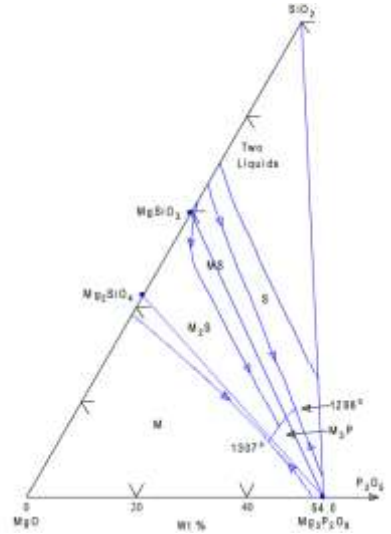
experiment



*J. Wojciechowska, J. Berak, Rocz. Chem., **33**[1] 21-31 (1959).*

MgO-SiO_2-P_2O_5: liquidus surface



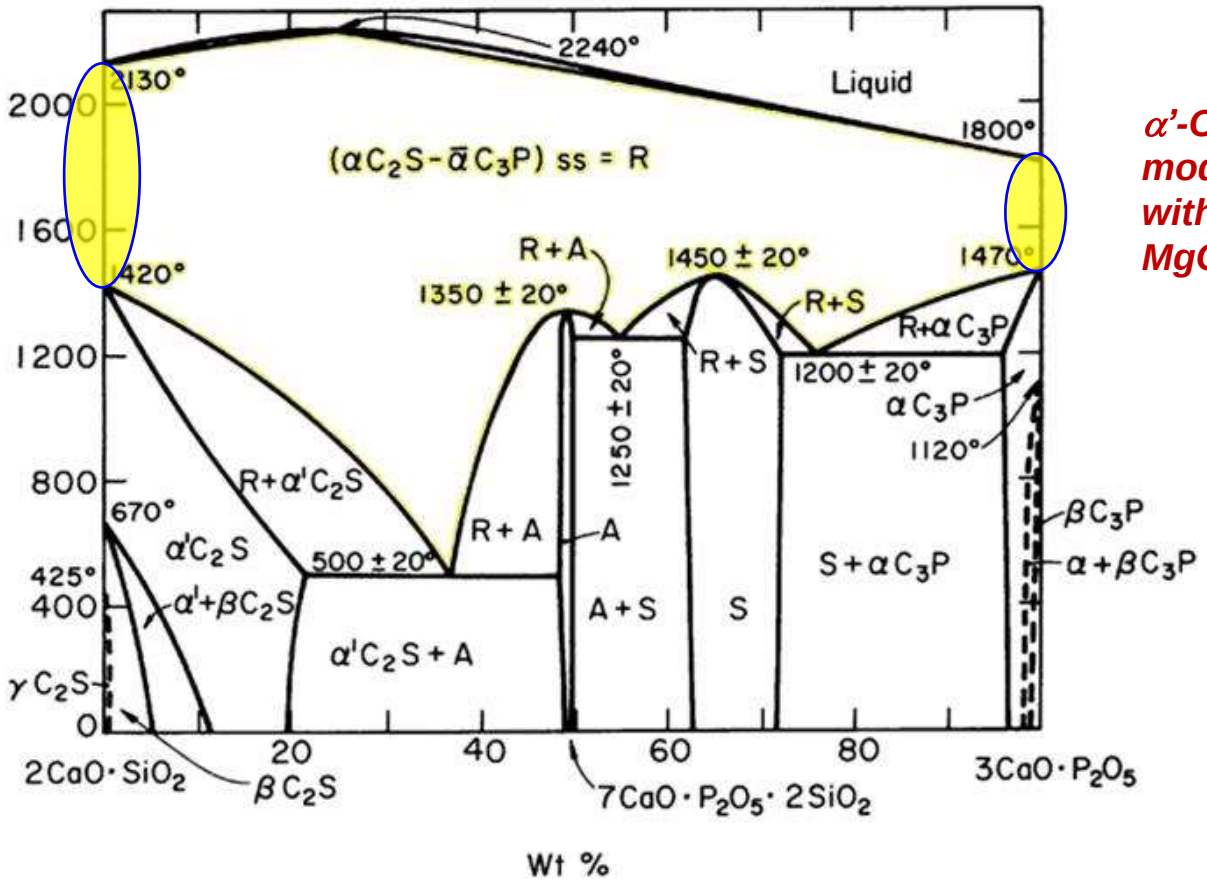


*J. Wojciechowska, J. Berak, Rocz. Chem., **33**[1] 21-31 (1959).*

There is not enough experimental data on phase diagrams, especially in the P_2O_5-rich area. The few data available is contradictory. Hence, experimental studies are needed.

$CaO\text{-}SiO_2\text{-}P_2O_5$: section $Ca_2SiO_4\text{-}Ca_3P_2O_8$

α-Ca_2SiO_4, modelled before with solubility for CrO and MgO



α'-$Ca_3P_2O_8$ modelled before with solubility for MgO

W. Fix, H. Heymann, and R. Heinke, J. Am. Ceram. Soc., 52 [6] 346-347 (1969).

$CaO\text{-}SiO_2\text{-}P_2O_5$: modelling of $\alpha\text{-}Ca_2SiO_4$

Previous description:

$\alpha\text{-}\ Ca_2SiO_4$: $(Ca^{2+},Cr^{2+},Mg^{2+})_2\,(Si^{4+})\,(O^{2-})_4$

$\alpha'\text{-}\ Ca_3P_2O_8$: $(Ca^{2+},Mg^{2+})_3\,(P^{5+})_2(O^{2-})_8$

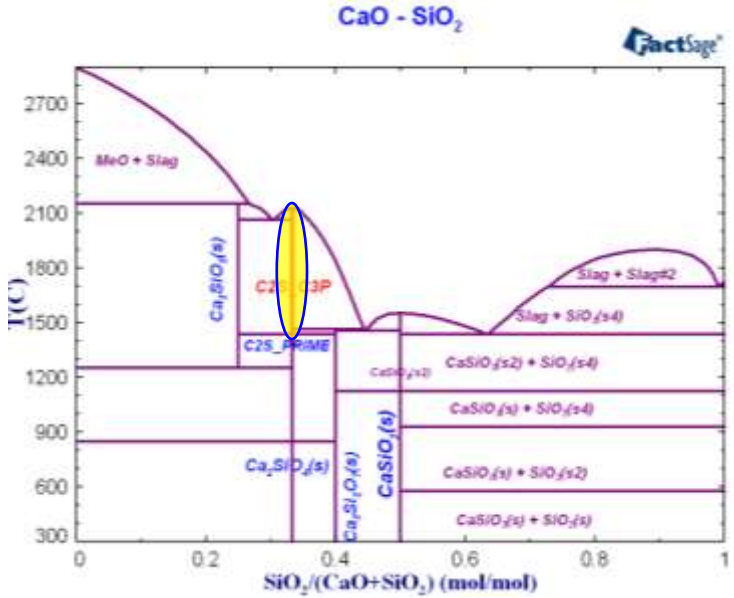
The following description was suggested for the phase C2S-C3P:

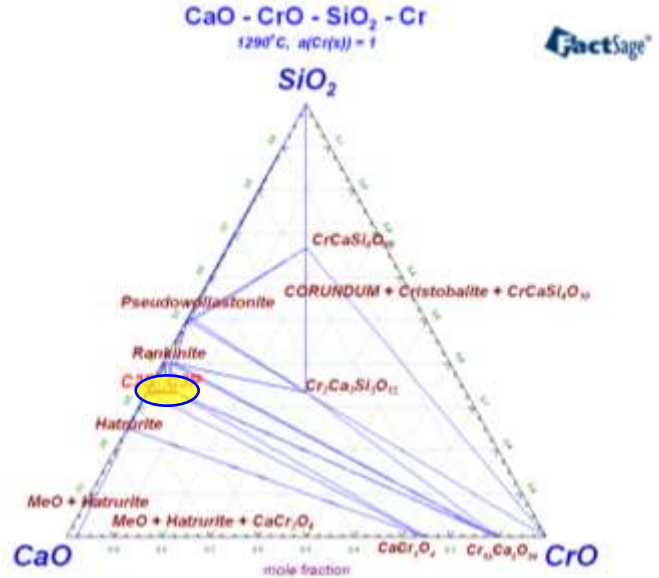
$$(Ca^{2+},Cr^{2+},Mg^{2+})_3(Ca^{2+},Va^{0})_1(P^{5+},Si^{4+})_2\,(O^{2-})_8$$

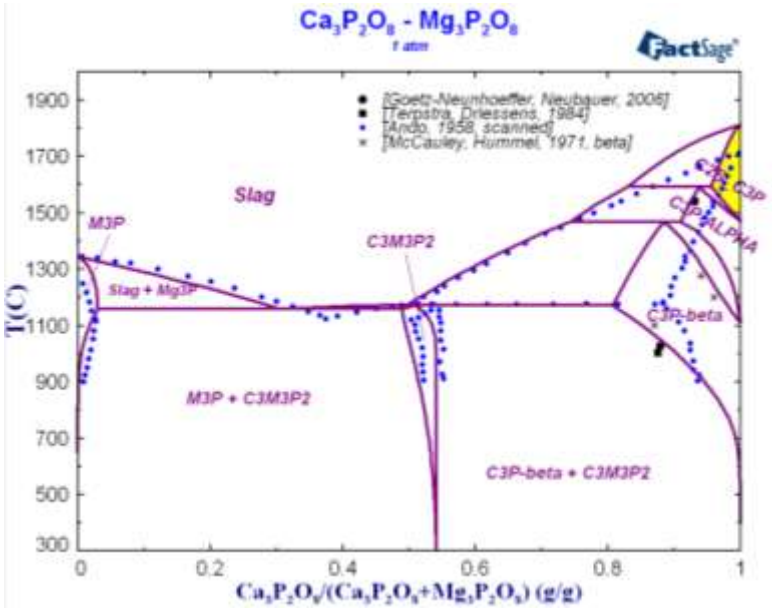
For the description of C2S-C3P the following reciprocal equation has been applied:
G(Ca:Ca:Si:O) + G(Ca:Va:P:O) - G(Ca:Ca:P:O) - G(Ca:Va:Si:O) = 0

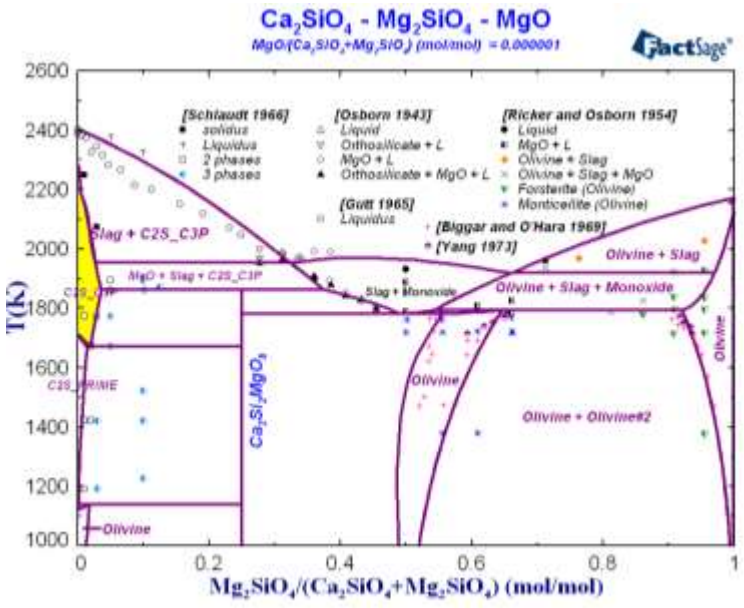
System	*Solid phase*	*Description of solid phase*
$CaO\text{-}SiO_2\text{-}P_2O_5$	**Ca_2SiO_4-alpha =$Ca_3P_2O_8$-alpha prime**	**$(Ca^{2+})_3(Ca^{2+},Va)_1(P^{5+},Si^{+4})_2(O^{2-})_8$**
	Ca_2SiO_4-alpha-prime	$(Ca^{2+})_3(Ca^{2+},Va)_1(P^{5+},Si^{+4})_2(O^{2-})_8$
	$7CaO\ P_2O_5\ 2SiO_2$	Stoichiometric
	$5CaO\ P_2O_5\ SiO_2$	Stoichiometric

The phase α–Ca_2SiO_4 in different systems



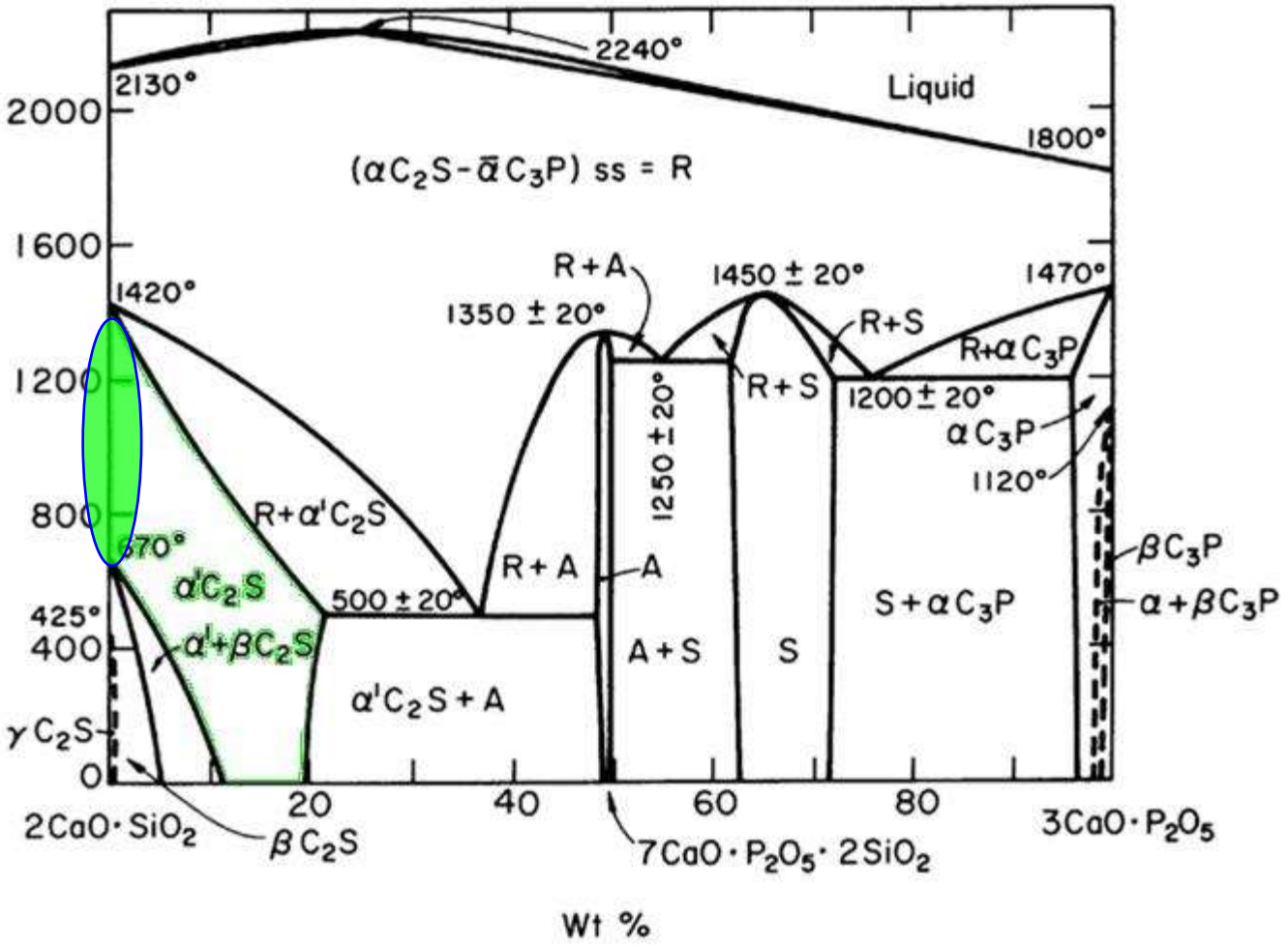






$CaO\text{-}SiO_2\text{-}P_2O_5$: section $Ca_2SiO_4\text{-}Ca_3P_2O_8$

α'-Ca_2SiO_4, modelled before with solubility for FeO and MgO



W. Fix, H. Heymann, and R. Heinke, J. Am. Ceram. Soc., 52 [6] 346-347 (1969).

$CaO\text{-}SiO_2\text{-}P_2O_5$: modelling of α`-$Ca_2SiO_4$

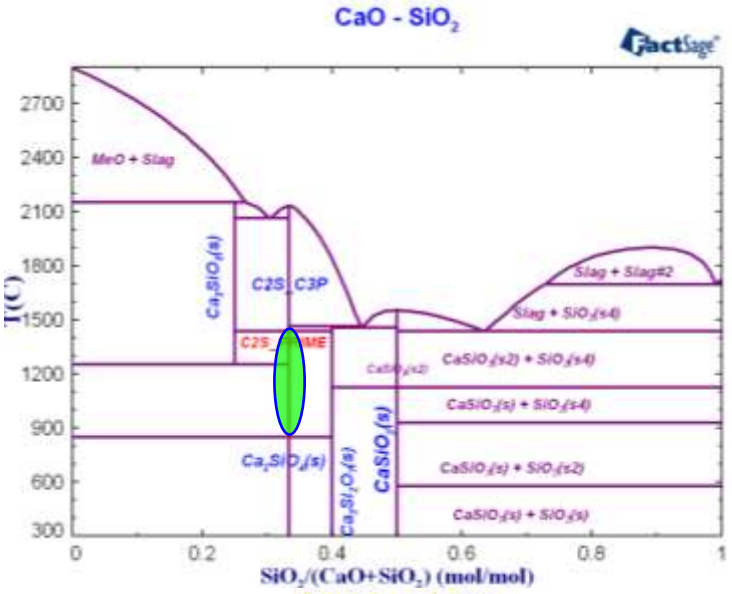
The following description characterises the solubility for MgO, FeO and P_2O_5 in the phase α′-Ca_2SiO_4

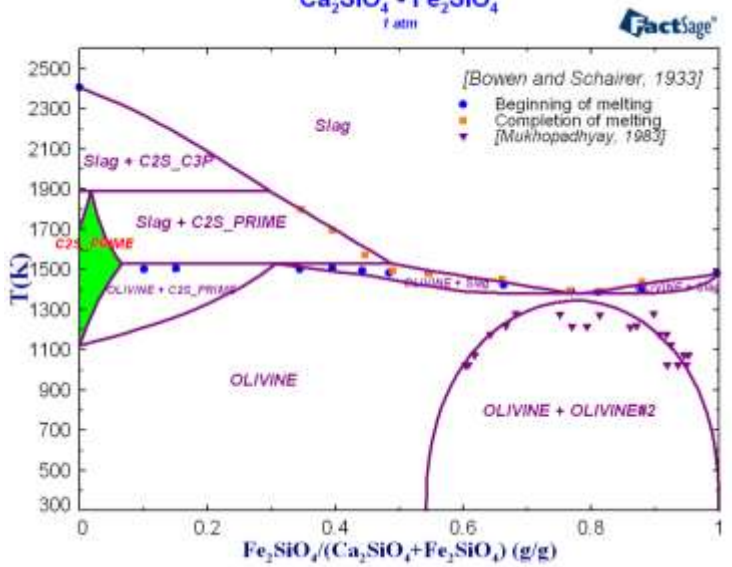
C2S-PRIME :

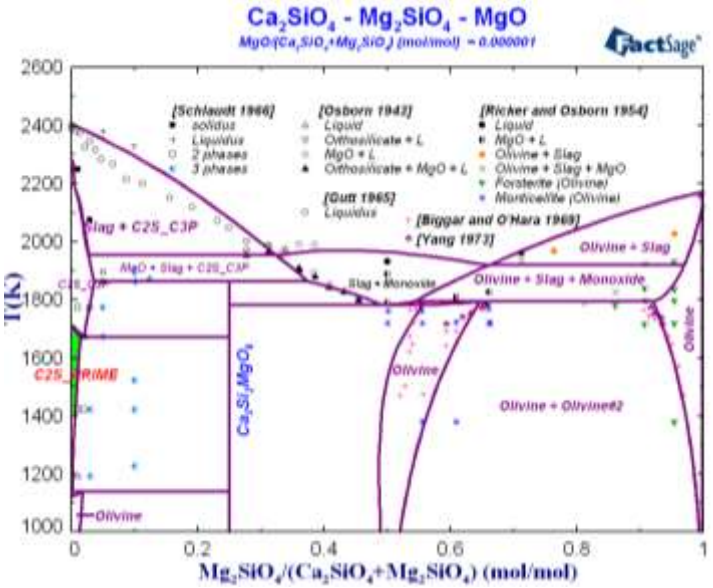
$$(\underline{Ca}^{2+},Fe^{2+},Mg^{2+})_3(\underline{Ca}^{2+},Va^0)_1(P^{5+},\underline{Si}^{4+})_2\,(O^{2-})_8$$

System	*Solid phase*	*Description of solid phase*
$CaO\text{-}SiO_2\text{-}P_2O_5$	Ca_2SiO_4-alpha =$Ca_3P_2O_8$-alpha prime **Ca_2SiO_4-alpha-prime** $7CaO\ P_2O_5\ 2SiO_2$ $5CaO\ P_2O_5\ SiO_2$	$(Ca^{2+})_3(Ca^{2+},Va)_1(P^{5+},Si^{+4})_2(O^{2-})_8$ **$(Ca^{2+})_3(Ca^{2+},Va)_1(P^{5+},Si^{+4})_2(O^{2-})_8$** Stoichiometric Stoichiometric

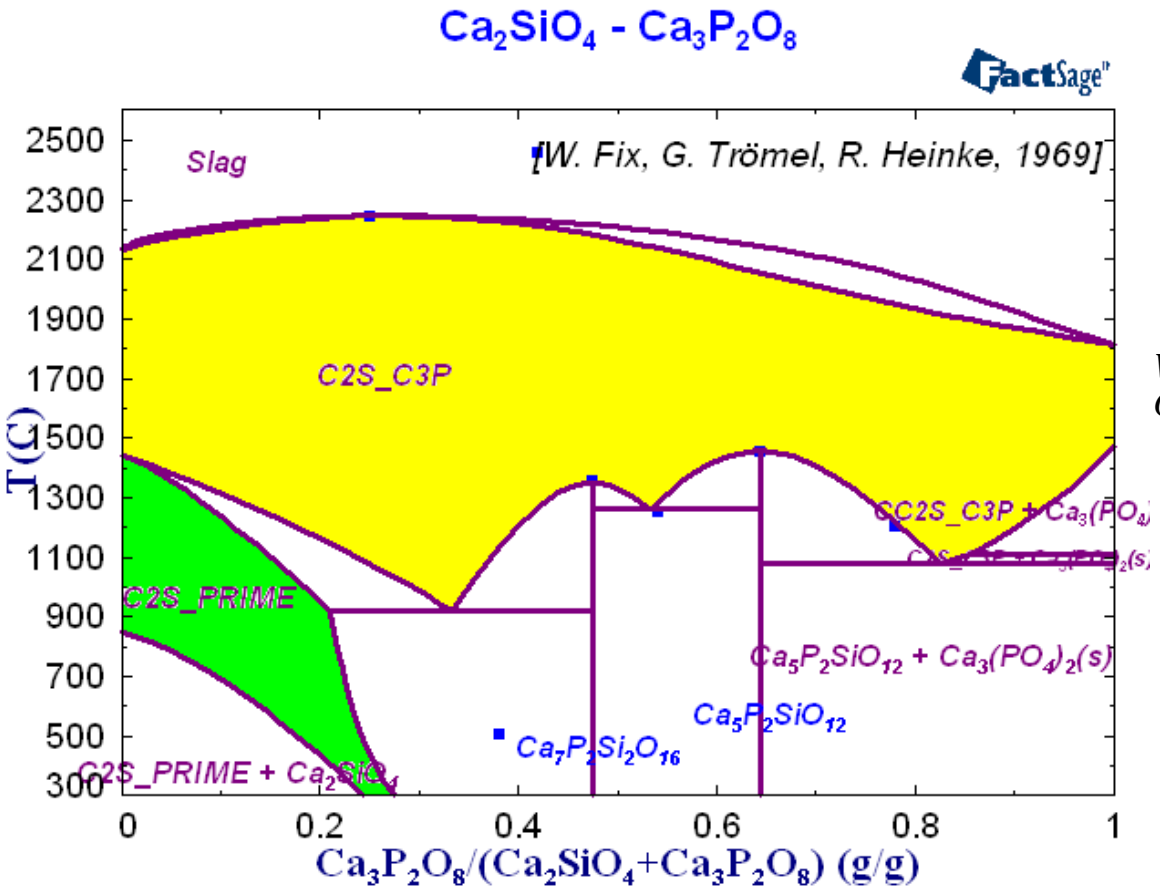
The phase α'–Ca_2SiO_4 in different systems



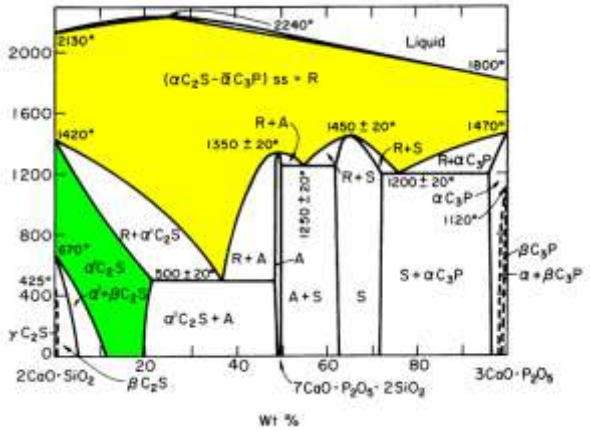




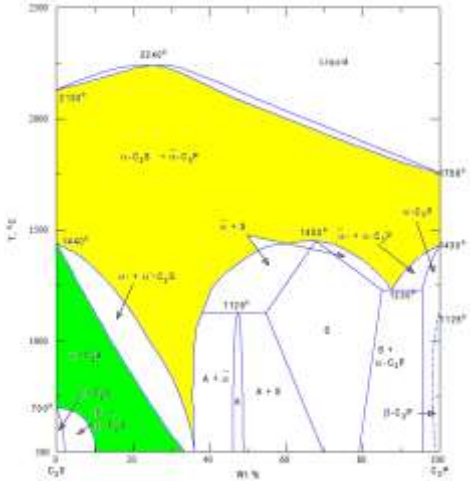
$CaO\text{-}SiO_2\text{-}P_2O_5$: section $Ca_2SiO_4\text{-}Ca_3P_2O_8$



Both phases, α and α´,based on Ca_2SiO_4, are included into the dataset to describe the phase diagram



W. Fix, H. Heymann, and R. Heinke, J. Am. Ceram. Soc., 52 [6] 346-347 (1969).



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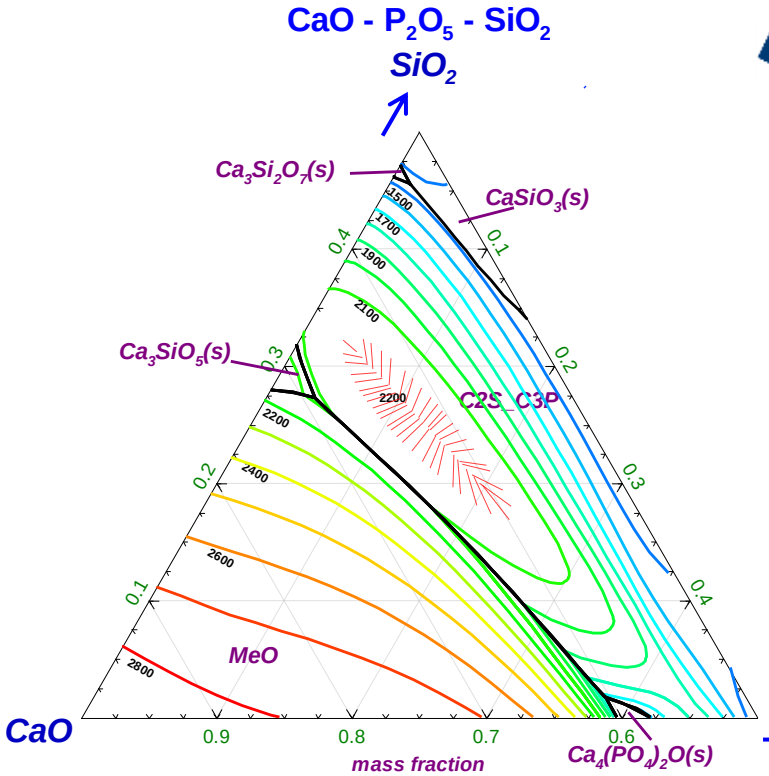
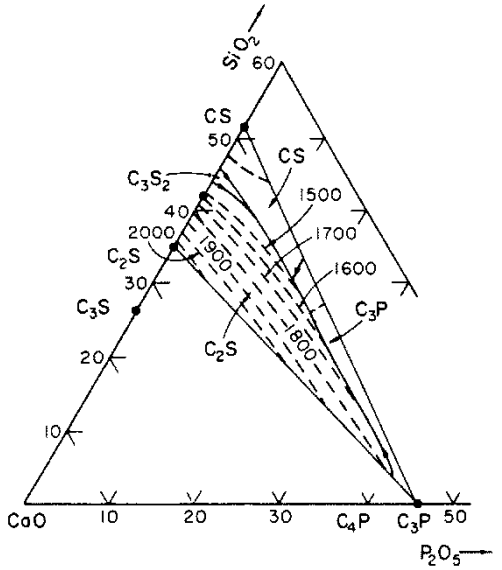
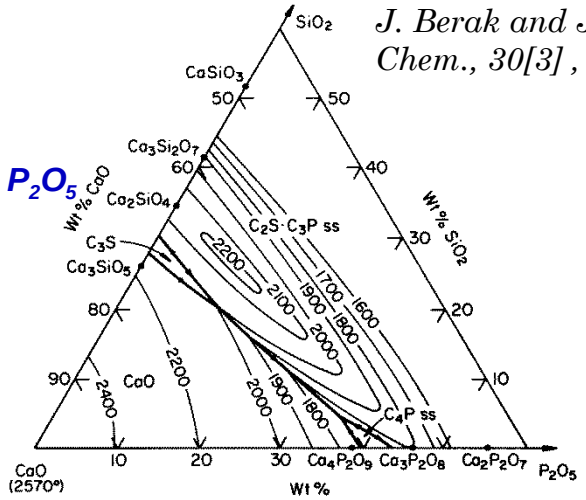
CaO-SiO_2-P_2O_5: liquidus surface





J. Berak and J.Wojciechowska, Rocz. Chem., 30[3] , (1956), pp.757-769 .



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Conclusions

- ✓ The liquid phase in all subsystems was evaluated using non-ideal associate species model (two cations per species).
- ✓ All systems were assessed using experimental phase diagram information.
- ✓ Solid solubility SiO_2 in $AlPO_4$, and vice versa, was considered.
- ✓ The new models of α–Ca_2SiO_4 and α'-Ca_2SiO_4 were introduced within the transition from α–Ca_2SiO_4 to α'–$Ca_3P_2O_8$ as well as the solubility of corresponding oxides have been described.

Outlook

- ✓ Addition of alkalis in the Al_2O_3-CaO-MgO-SiO_2-P_2O_5 system
- ✓ Thermodynamic assessment of all combination of 2,3 etc. oxides

On behalf of all co-authors:

Thank you for your attention!

Vielen Dank für Ihre Aufmerksamkeit!

Благодарю за внимание!