JÜLICH FORSCHUNGSZENTRUM

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HotVeGas database development: Ternary systems Alk_2O-MeO-P_2O_5 (Alk=Na,K; Me=Ca, Mg)

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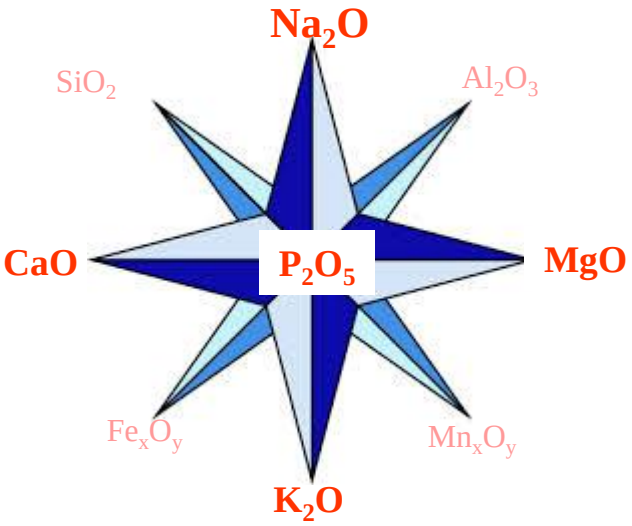


HOTVEGAS

- Motivation and aim of the work
- Solid solubilities in the ternary systems
- Assessment of the systems Alk_2O-MeO-P_2O_5:
  - K_2O-CaO-P_2O_5
  - K_2O-MgO-P_2O_5
  - Na_2O-CaO-P_2O_5
  - Na_2O-MgO-P_2O_5
- Conclusions and outlook

Motivation and aim of work

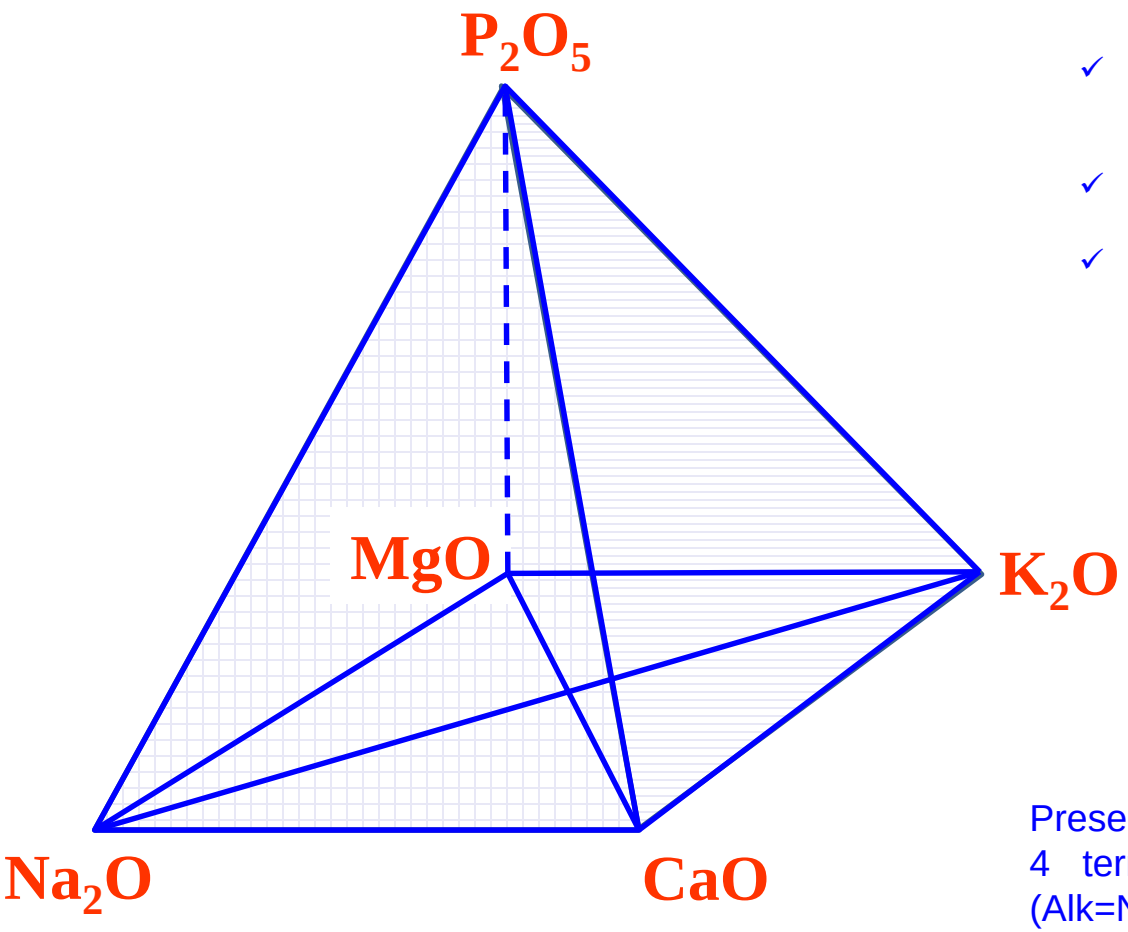
State of the art:

- ✓ 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

HOTVEGAS
Hochtemperaturvergasung und Gasreinigung

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

Including P_2O_5

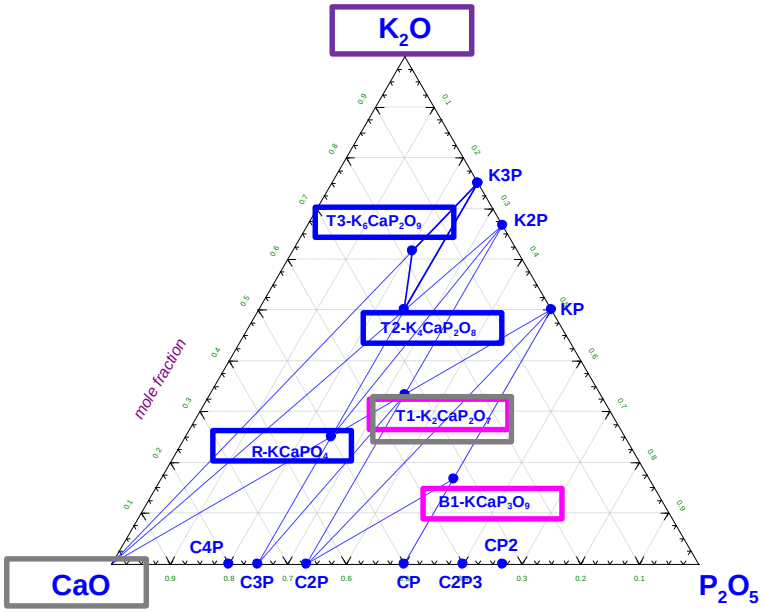


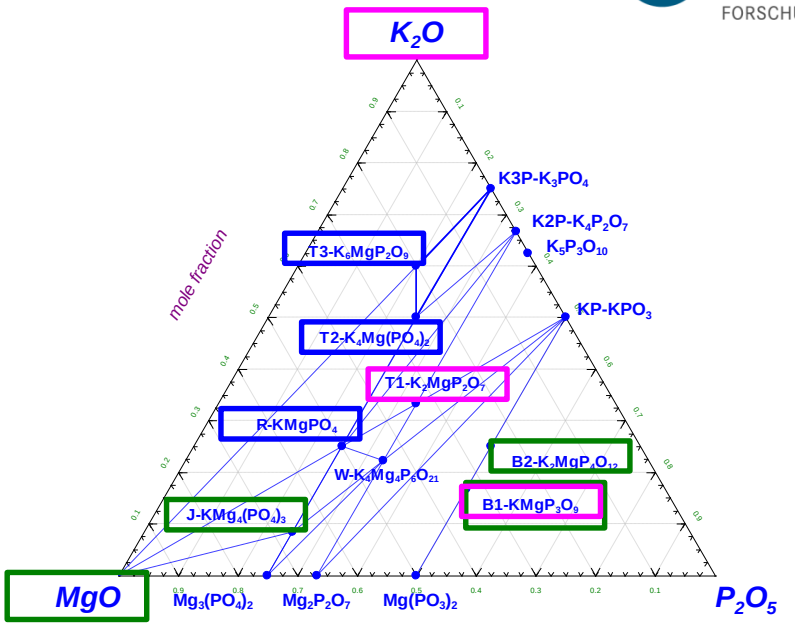
- ✓ P_2O_5 is a next important slag component to be added into the database
- ✓ P_2O_5 occurs in biomass ashes and metallurgical slags
- ✓ All binary systems with P_2O_5 have been already evaluated and added to the database

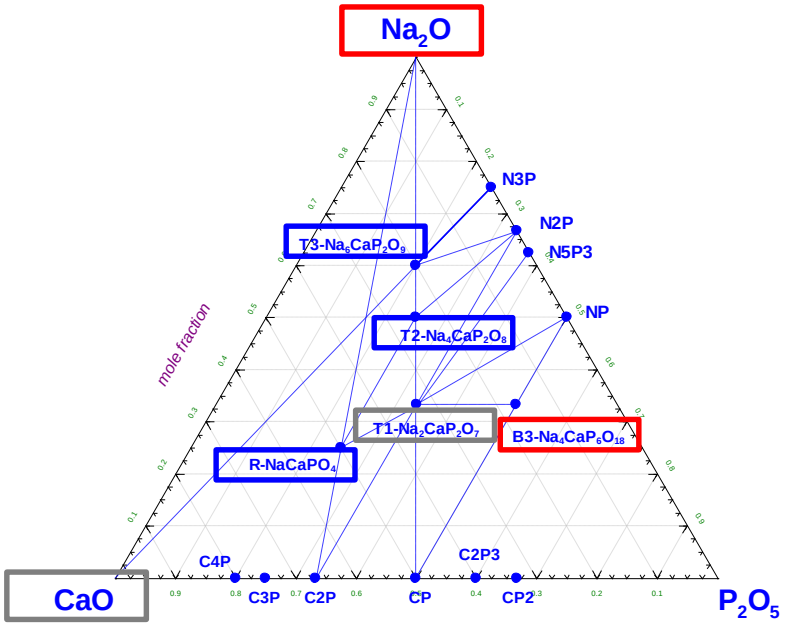
⇩

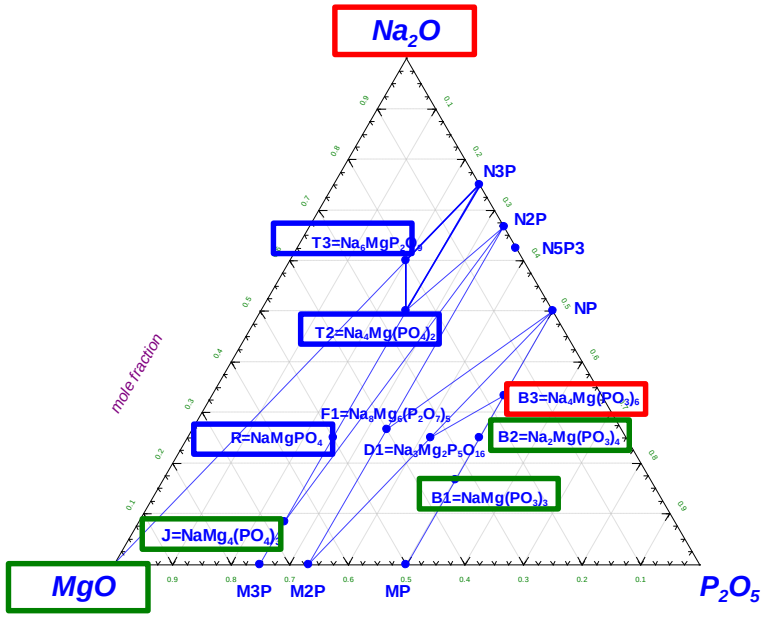
Present task:
4 ternary systems Alk_2O-MeO-P_2O_5 (Alk=Na,K; Me=Ca,Mg) are considered including the solid solubilities regarding complex phosphates

The system Na_2O-K_2O-CaO-MgO-P_2O_5

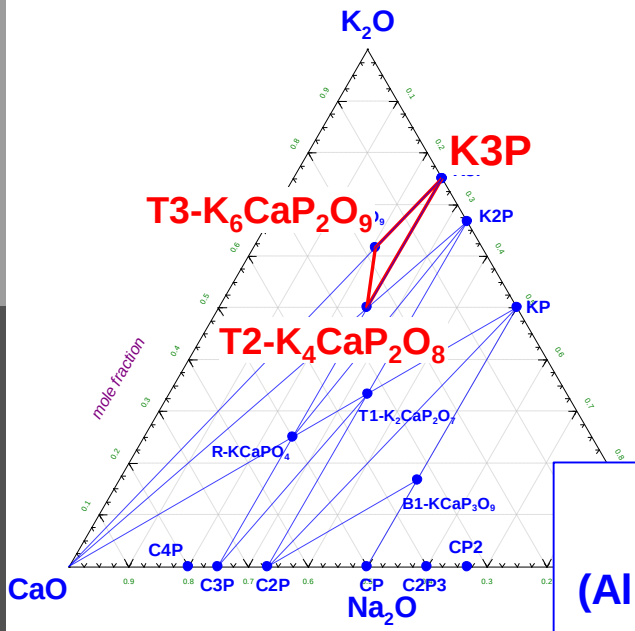


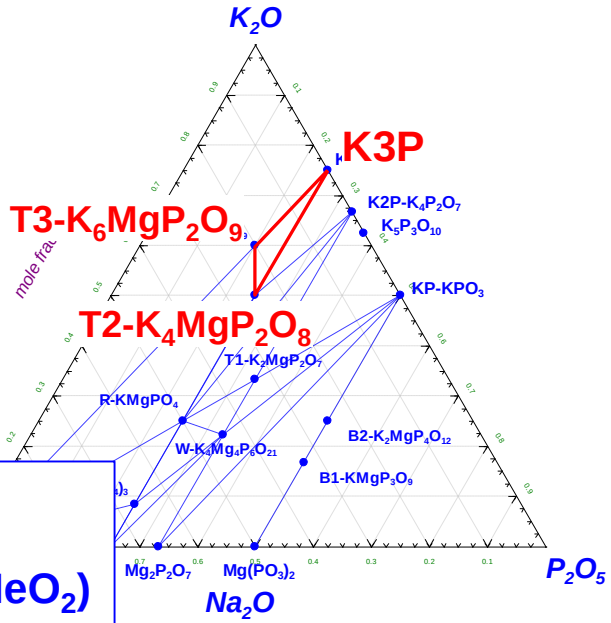






Solid solutions

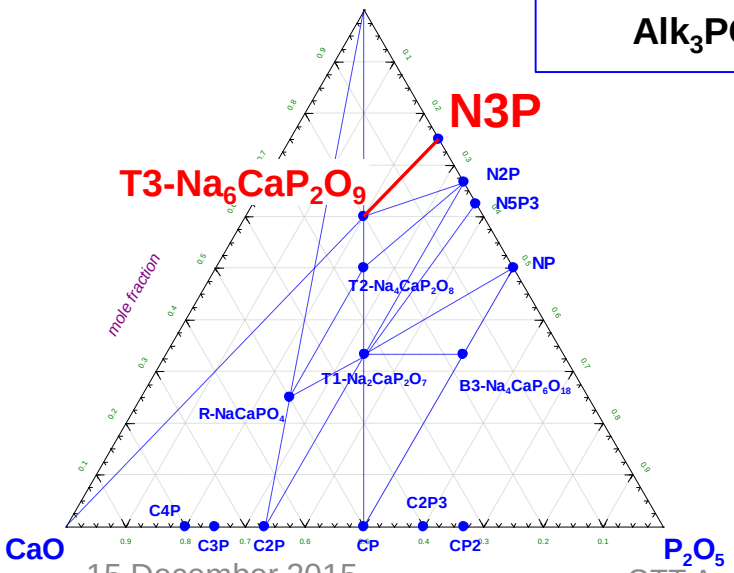


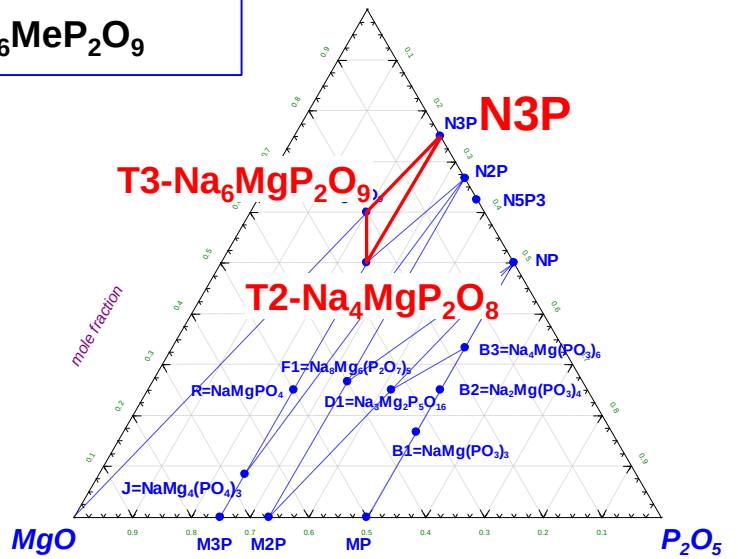


Alk3P-T2-T3 solid solutions
for HT,(MT),LT modifications

$(Alk_2O)_2(P_2O_5)_2(Alk_2O,MeO,Alk_2MeO_2)$

Alk_3PO_4-$Alk_4Me(PO_4)_2$-$Alk_6MeP_2O_9$





Description of the solid solutions

Phase	Description	Used data	
N3P-LT	$(Na_2O)_2(P_2O_5)(Na_2O, Na_2CaO_2, MgO, K_2MgO_2)$	N3P-Na_3PO_4(s1)- FZJ	
		-	T2-$Na_4MgP_2O_8$(s1)-FZJ
		T3-$Na_6CaP_2O_9$(s1)-GTT	T3-$Na_6MgP_2O_9$(s1)-FZJ
N3P-HT	$(Na_2O)_2(P_2O_5)(Na_2O, Na_2CaO_2, MgO, K_2MgO_2)$	N3P-Na_3PO_4(s2)- FZJ	
		-	T2-$Na_4MgP_2O_8$(s1)-FZJ
		T3-$Na_6CaP_2O_9$(s2)-GTT	T3-$Na_6MgP_2O_9$(s1)-FZJ
K3P-LT	$(K_2O)_2(P_2O_5)(K_2O, CaO, K_2CaO_2, MgO, K_2MgO_2)$	K3P-K_3PO_4(s1)- FZJ	
		T2-$K_4CaP_2O_8$(s1)-GTT	T2-$K_4MgP_2O_8$(s1)-FZJ
		T3-$K_6CaP_2O_9$(s1)-GTT	T3-$K_6MgP_2O_9$(s1)-FZJ
K3P-MT	$(K_2O)_2(P_2O_5)(K_2O, CaO, K_2CaO_2, MgO, K_2MgO_2)$	K3P-K_3PO_4(s2)-FZJ	
		T2-$K_4CaP_2O_8$(s2)-GTT	T2-$K_4MgP_2O_8$(s2)-FZJ
		T3-$K_6CaP_2O_9$(s2)-GTT	T3-$K_6MgP_2O_9$(s2)-FZJ
	H_{tr} (s1→s2) is proposed to be equal to K_3PO_4 or Na_3PO_4		
K3P-HT	$(K_2O)_2(P_2O_5)(K_2O, CaO, K_2CaO_2, MgO, K_2MgO_2)$	K3P-K_3PO_4(s3)-FZJ	
		T2-$K_4CaP_2O_8$(s3)-GTT	T2-$K_4MgP_2O_8$(s3)-FZJ
		T3-$K_6CaP_2O_9$(s3)-GTT	T3-$K_6MgP_2O_9$(s3)-FZJ
	H_{tr} (s2→s3) is proposed to be equal to K_3PO_4 or Na_3PO_4		

Description of the system

The species with compositions R and B_1 in the non-ideal associate solution were added in order to describe the liquid phase

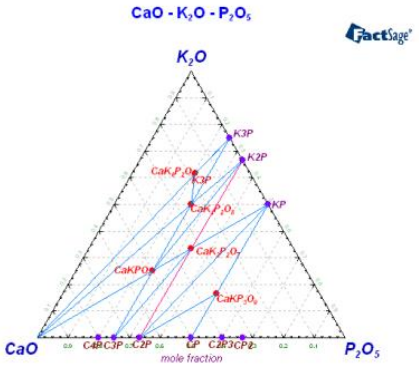
Name	***Composition***	***Melting, °C***	***Liquid species***	***Description*** (modelled by GTT)
R	$KCaPO_4$	1580, congruent	$KCaPO_4 \cdot 2/3$	stoichiometric
T1	$K_2CaP_2O_7$	1143, congruent		stoichiometric
T2	$K_4Ca(PO_4)_2$	1645, congruent		K3P-T2-T3 solution
T3	$K_6CaP_2O_9$	1750, incongruent		K3P-T2-T3 solution
B1	$KCa(PO_3)_3$	845, congruent	$KCa(PO_3)_3 \cdot 2/5$	stoichiometric

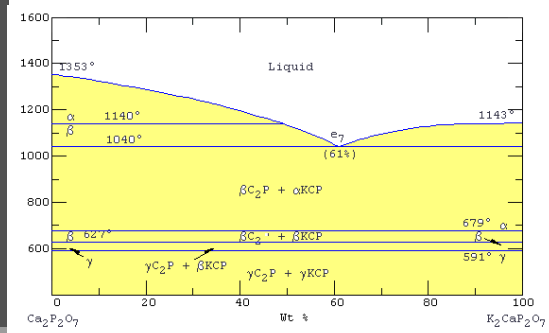
K3P-T2-T3 solid solutions for HT, MT, LT modifications

$(K_2O)_2(P_2O_5)_2(K_2O, CaO, K_2CaO_2)$

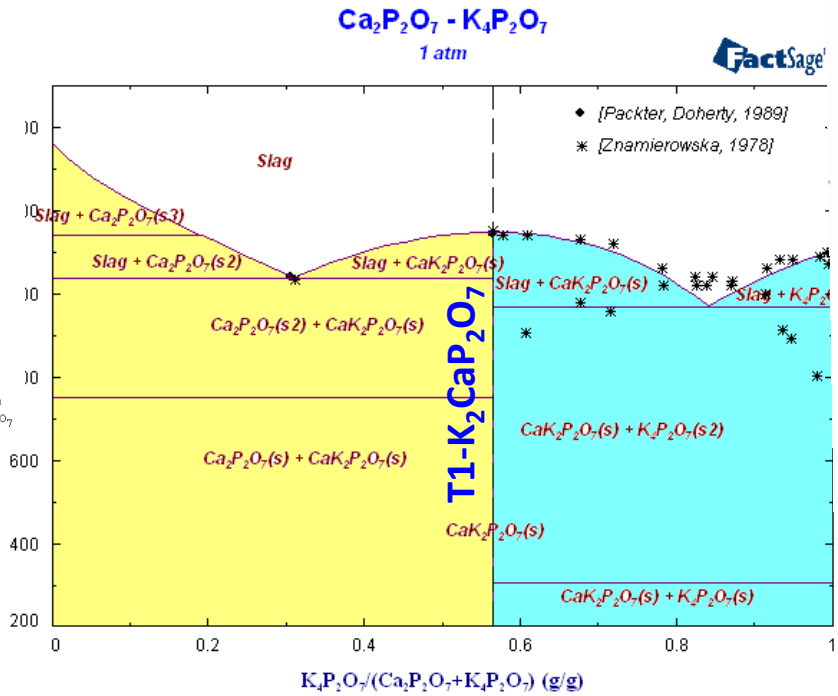
K_3PO_4-$K_4Ca(PO_4)_2$-$K_6CaP_2O_9$

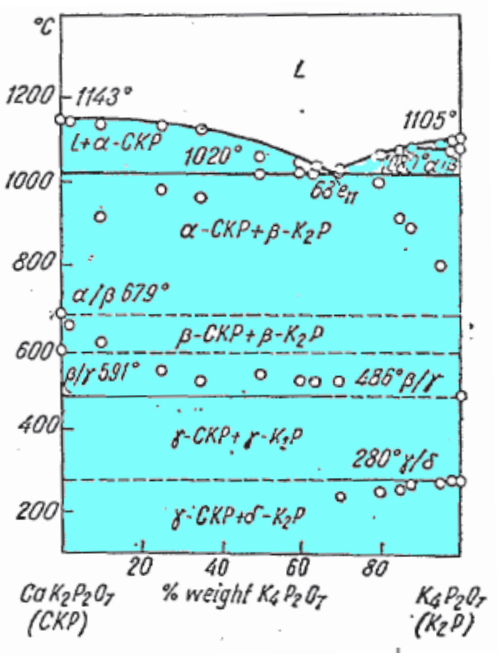
Quasi-binary section $Ca_2P_2O_7$-$K_4P_2O_7$





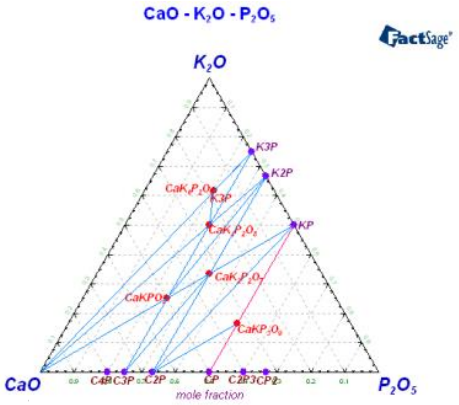
T. Znamierowska, Pol. J. Chem., 52 [6] 1127-1134 (1978).



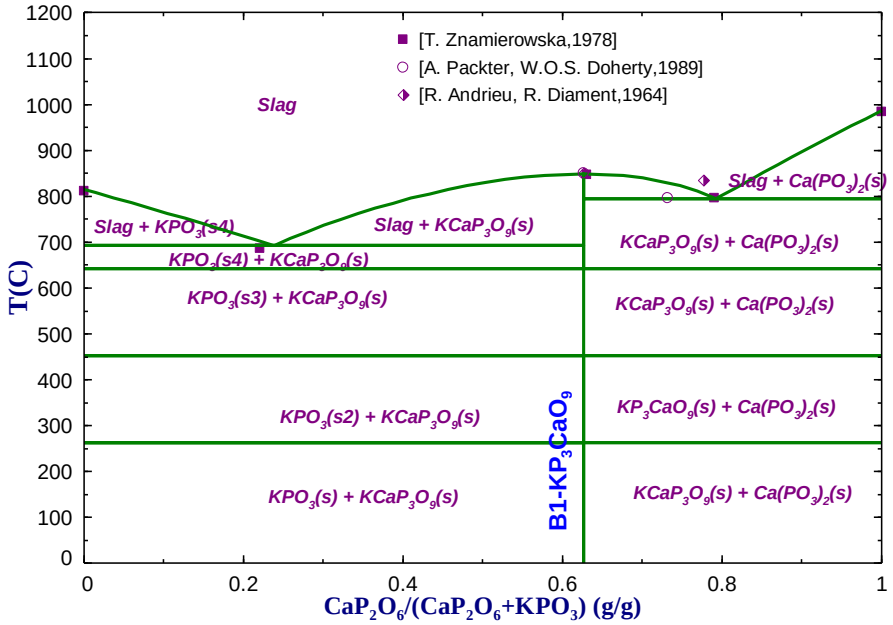


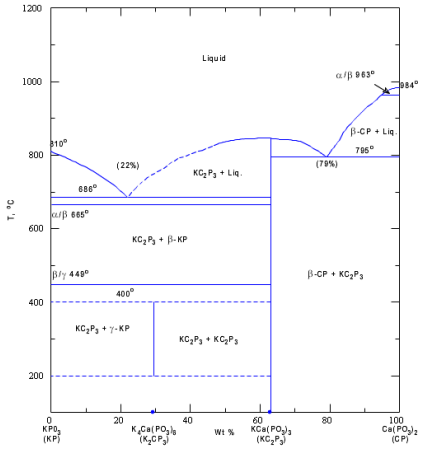
T. Znamierowska, Pol. J. Chem., 52 [10] 1889-1895 (1978).

Quasi-binary section KPO_3 - CaP_2O_6

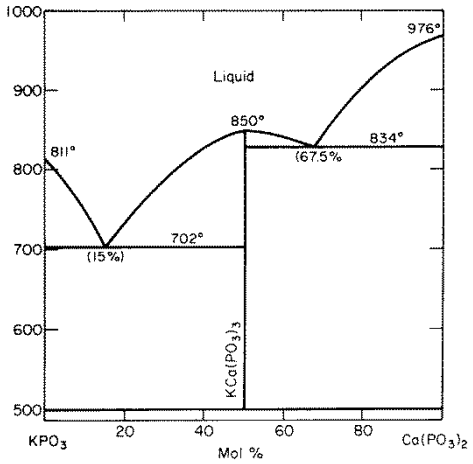


KPO_3 - CaP_2O_6



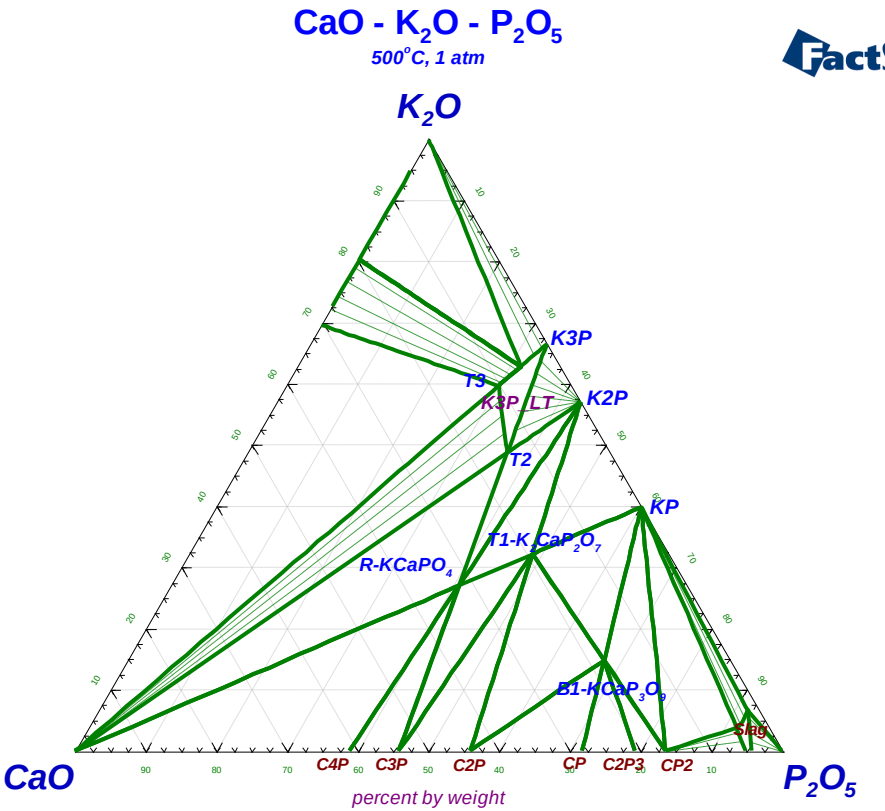


T. Znamierowska-Kubicka, Rocz. Chem., 51 [11] 2089-2098 (1977).



R. Andrieu and R. Diament, C. R. Hebd. Seances Acad. Sci., 259 [25] 4708-4711 (1964).

Isothermal section at 500°C



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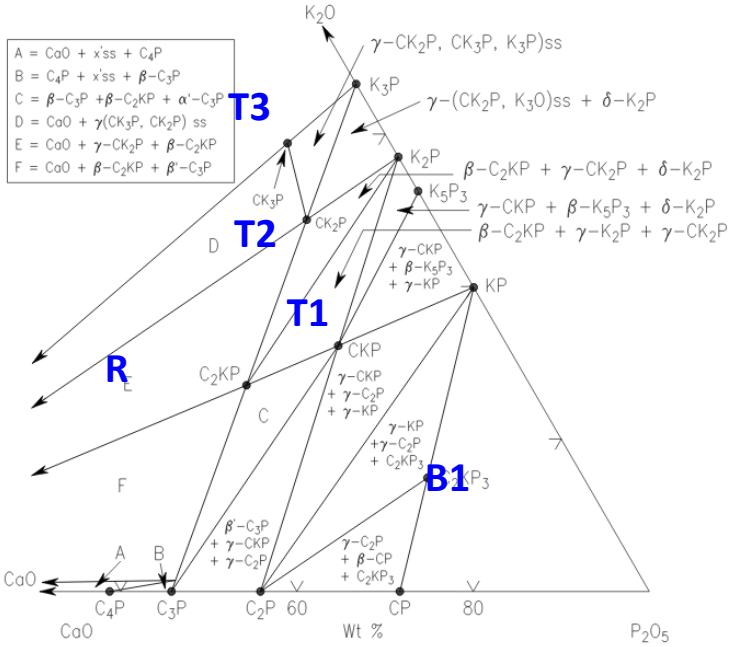
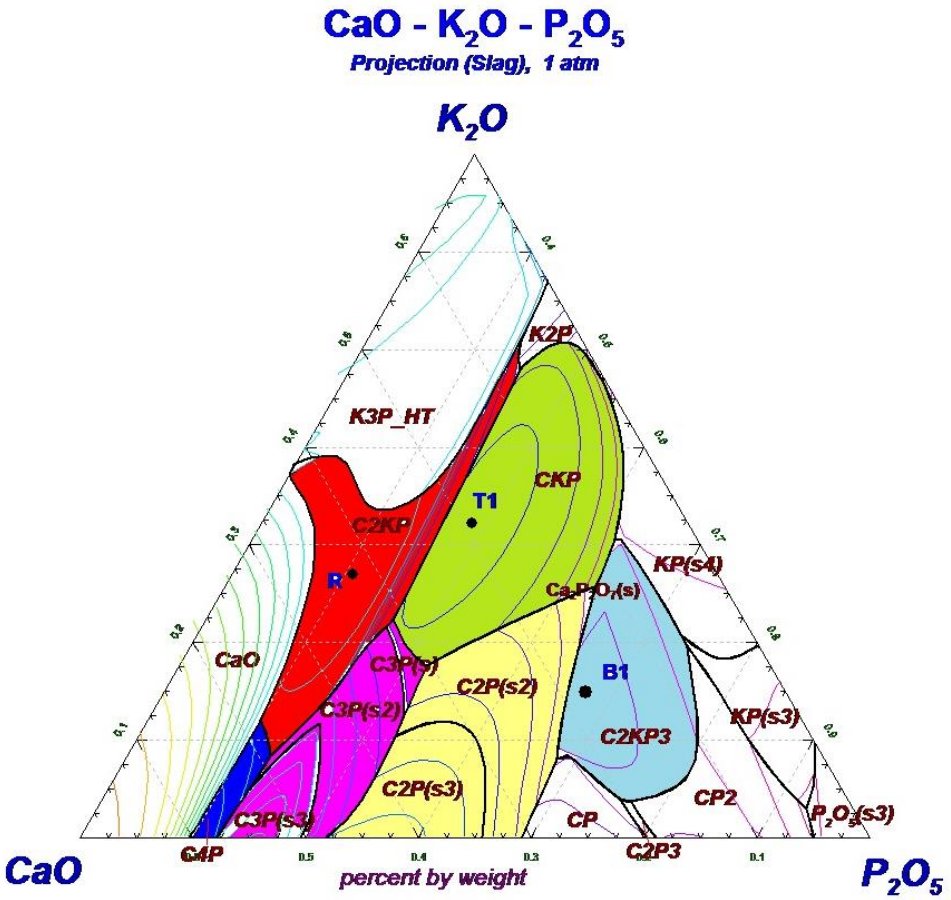
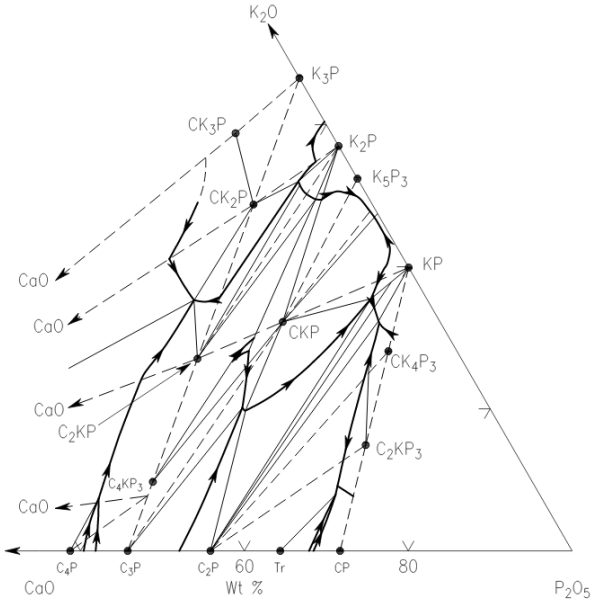


T. Znamierowska, Zesz. Nauk. Politech. Slask., Chem., 709 [100] , p.23-32 (1982).

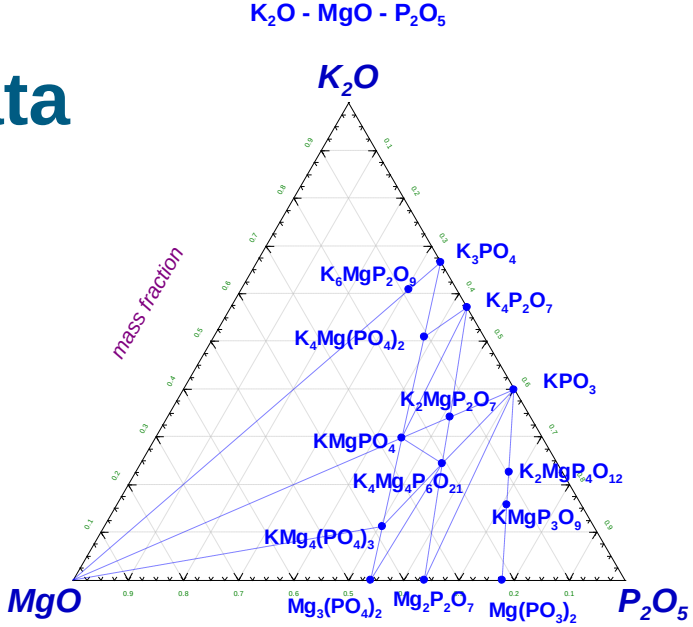
Liquidus surface



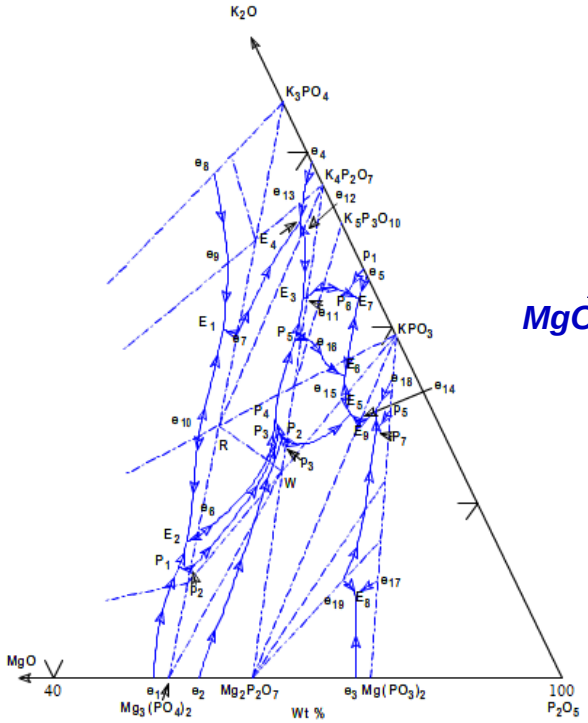


T. Znamierowska, Zesz. Nauk. Politech. Slask., Chem., 709 [100] , p.23-32 (1982).

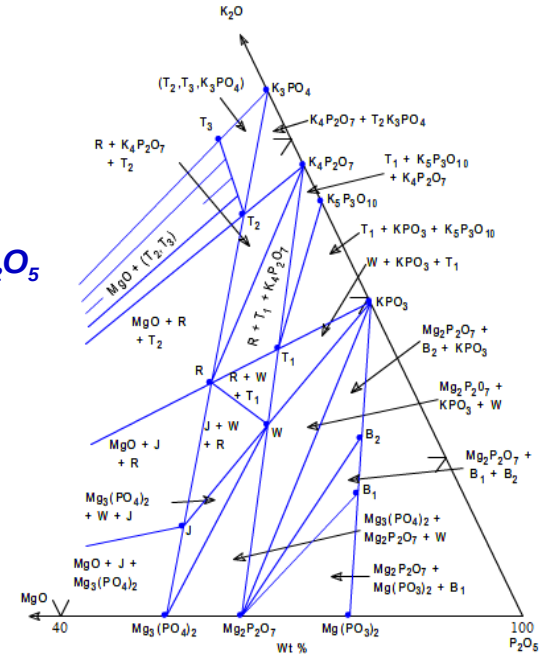
Experimental data



8 ternary compounds including the solid solubility are found in the system, the quasi-binary sections are studies by thermal, microscopic, dilatometric and X-ray analysis



Partial liquidus projection with invariant points labeled



Solid state compatibility observed at room temperature

J. Berak and T. Podhajska-Kazmierczak, Pol. J. Chem., 65 [7-8] 1137-1149, 1151-1163, 1165-1172, 1173-1184 (1991)

Description of the system

The species with compositions R and B_1 in the non-ideal associate solution were added in order to describe the liquid phase

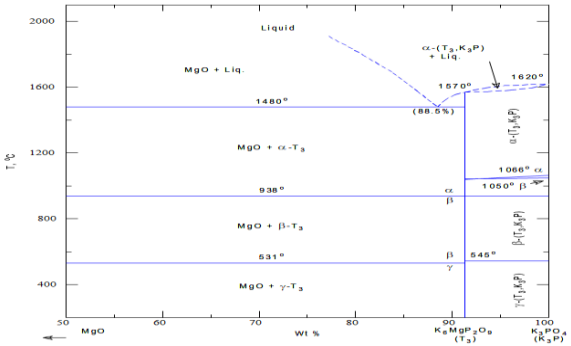
Name	***Composition***	***Melting, °C***	***Liquid species***	***Description*** (modelled by FZJ)
R	$KMgPO_4$	1520, congruent	$KMgPO_4 \cdot 2/3$	stoichiometric
J	$KMg_4(PO_4)_3$	1175, incongruent		stoichiometric
W	$K_4Mg_4P_6O_{21}$	792, incongruent		stoichiometric
T1	$K_2MgP_2O_7$	736, incongruent		stoichiometric
T2	$K_4Mg(PO_4)_2$	1374, congruent		K3P-T2-T3 solution
T3	$K_6MgP_2O_9$	1570, incongruent		K3P-T2-T3 solution
B1	$KMg(PO_3)_3$	906, congruent	$KMg(PO_3)_3 \cdot 2/5$	stoichiometric
B2	$K_2Mg(PO_3)_4$	730, incongruent		stoichiometric

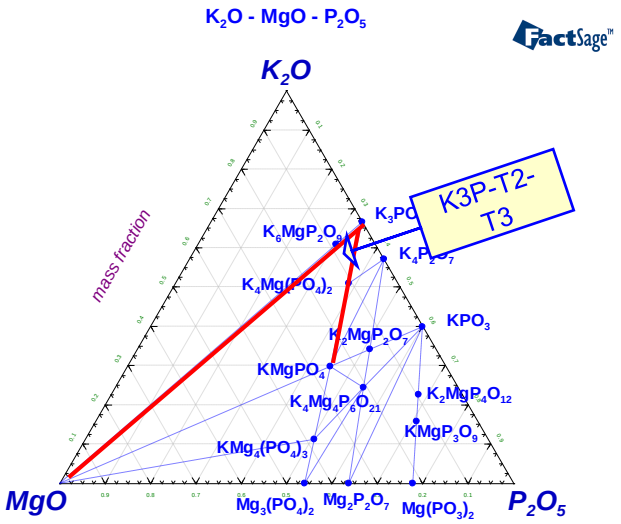
K3P-T2-T3 solid solutions for HT, MT, LT modifications

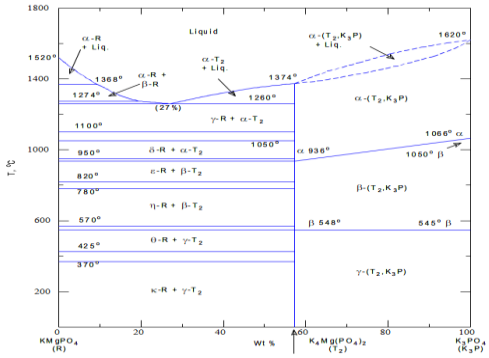
$(K_2O)_2(P_2O_5)_2(K_2O, MgO, K_2MgO_2)$

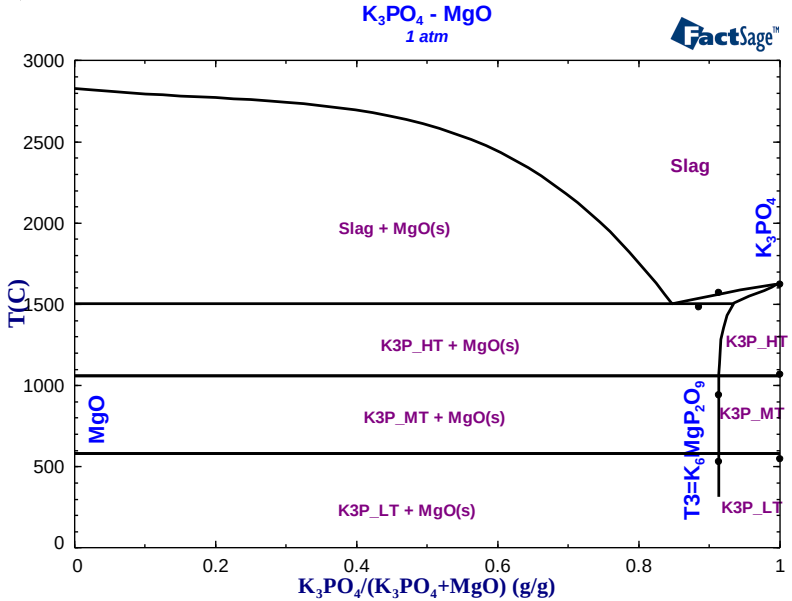
K_3PO_4-$K_4Mg(PO_4)_2$-$K_6MgP_2O_9$

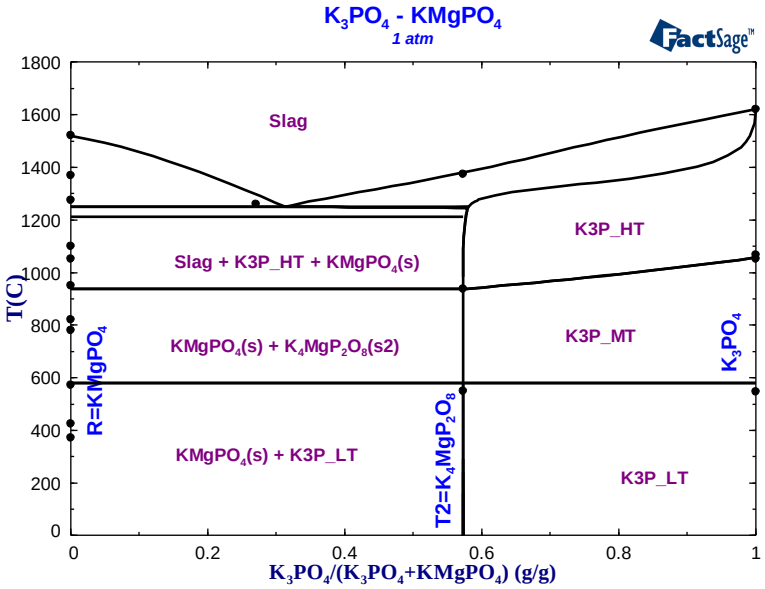
Sections MgO-K_3PO_4 and K_3PO_4-$KMgPO_4$



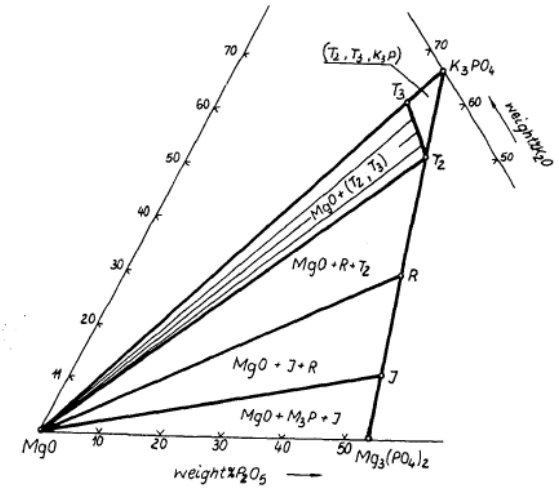






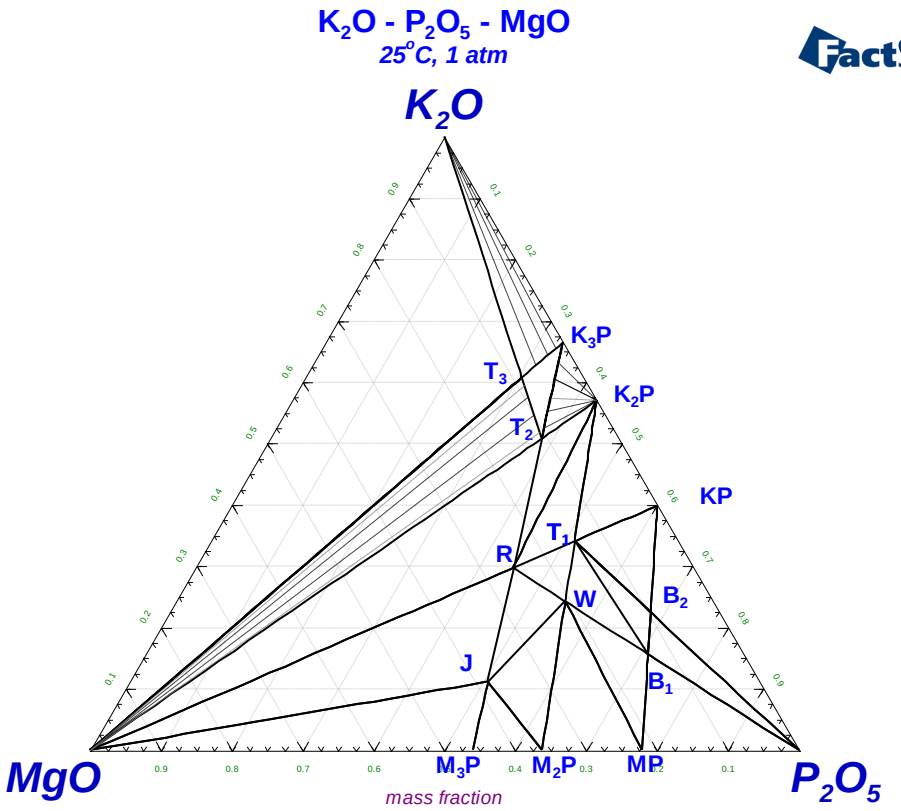


Preliminary isothermal section at 25°C

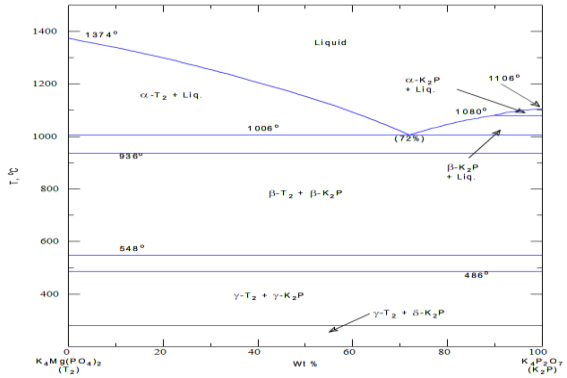


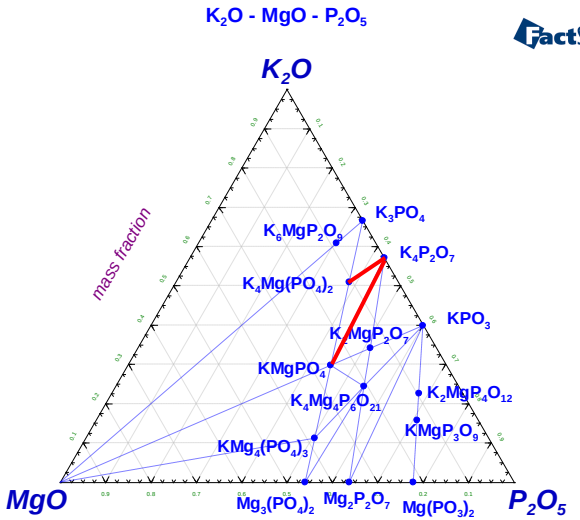
J. Berak and T. Podhajska-Kazmierczak, Pol. J. Chem., 65 [7-8] 1137-1149 (1991).

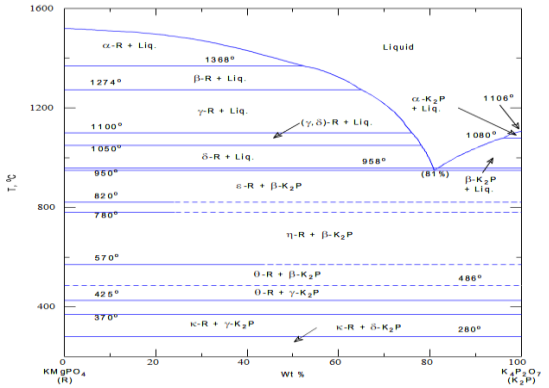
The solid solubilities based on K_3PO_4-$K_4Mg(PO_4)_2$-$K_6MgP_2O_9$ are included into the database.

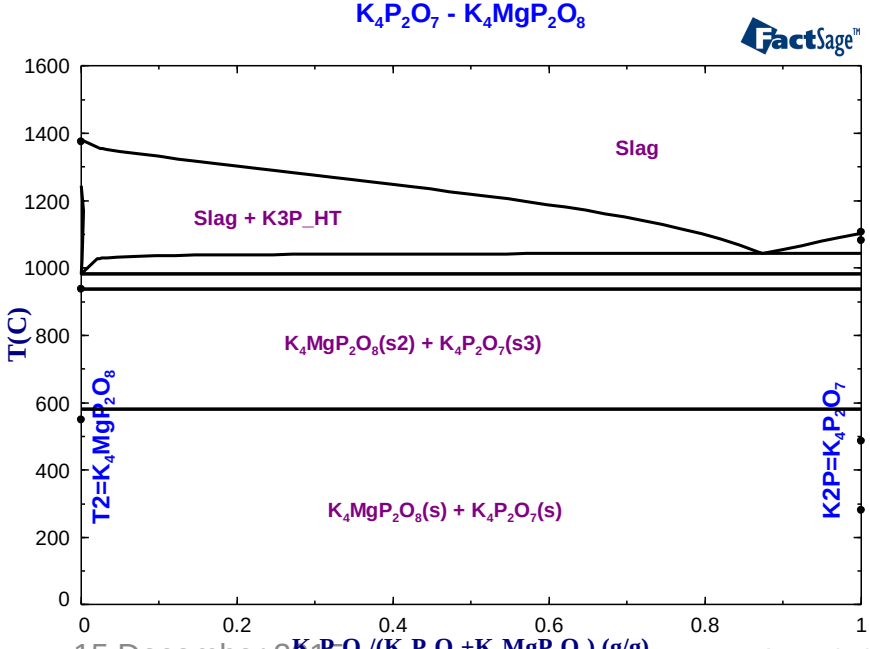


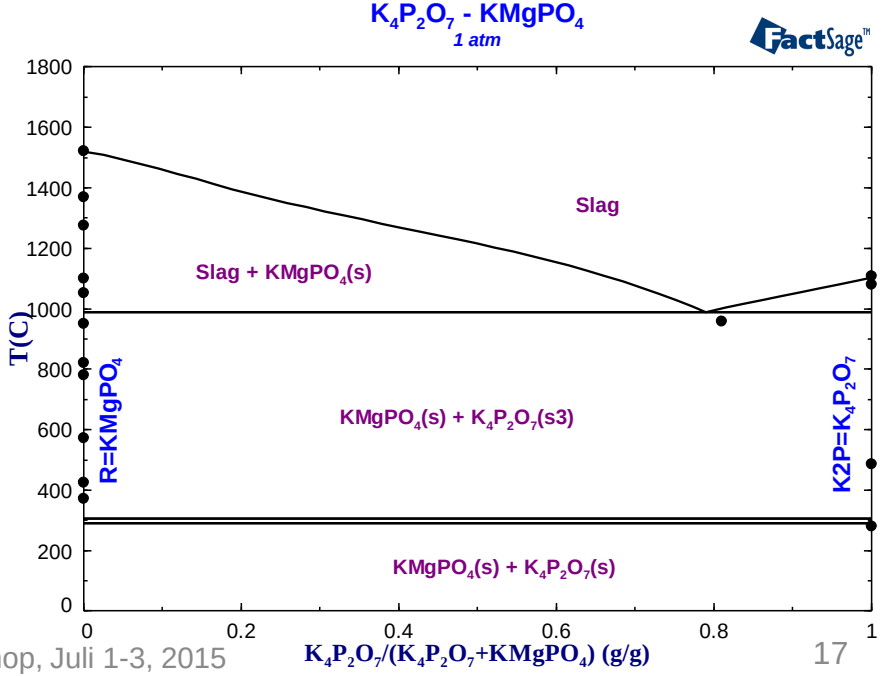
Sections $K_4P_2O_7$-$KMgPO_4$ and $K_4P_2O_7$-$K_4MgP_2O_8$



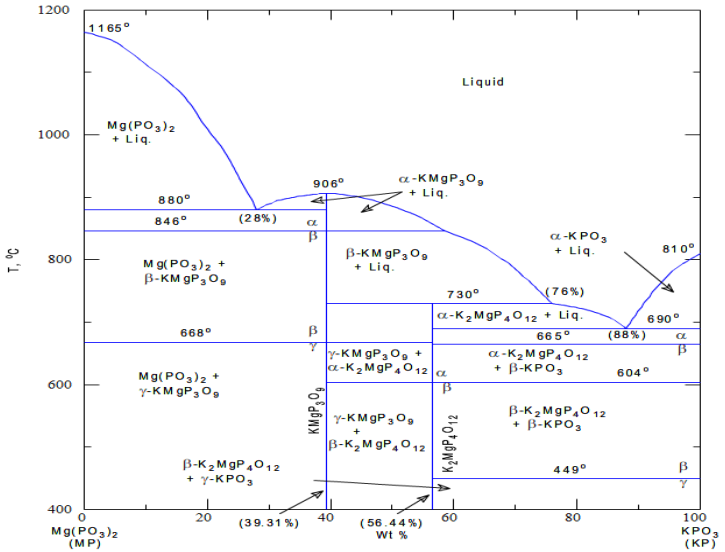


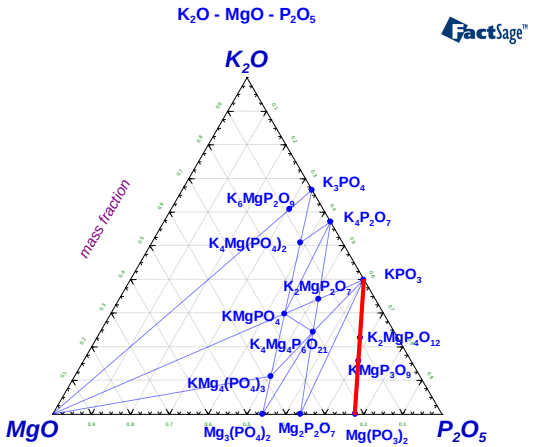


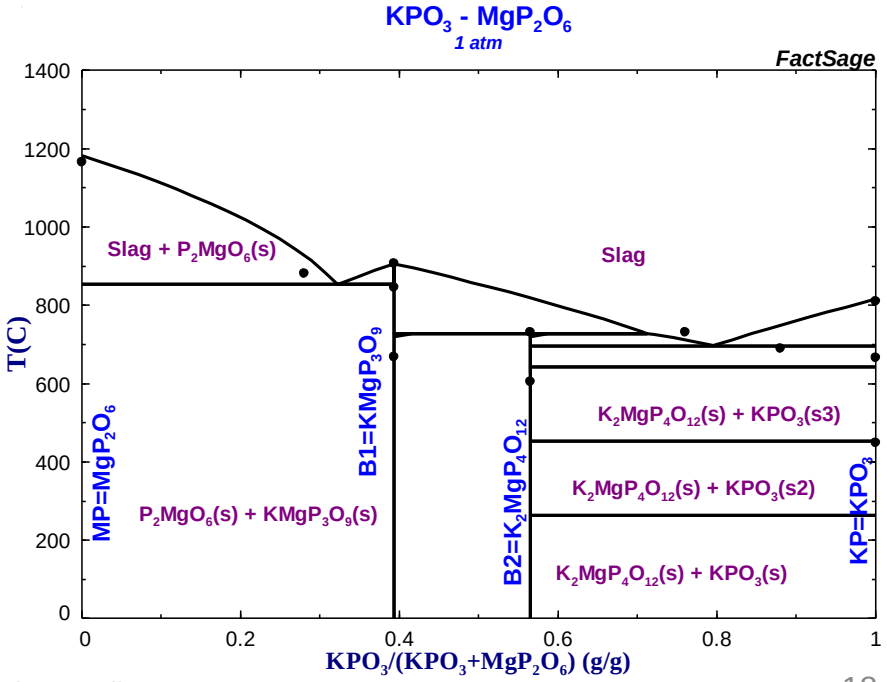




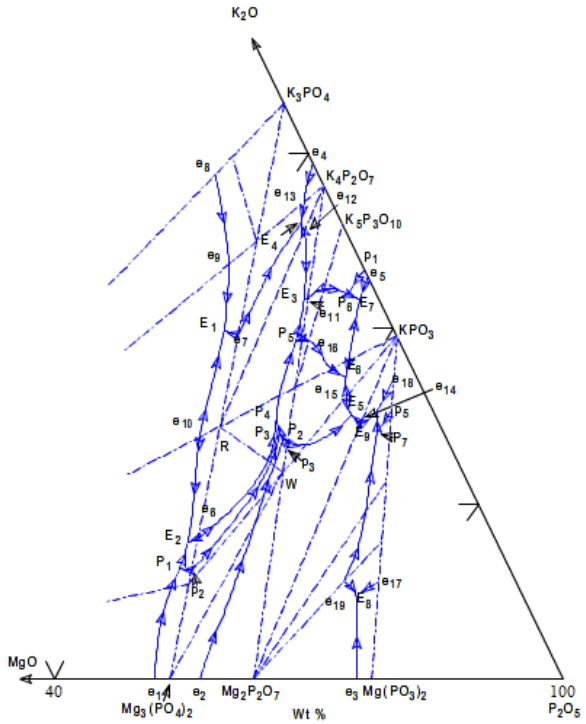
Pseudo-binary section MgP_2O_6-KPO_3



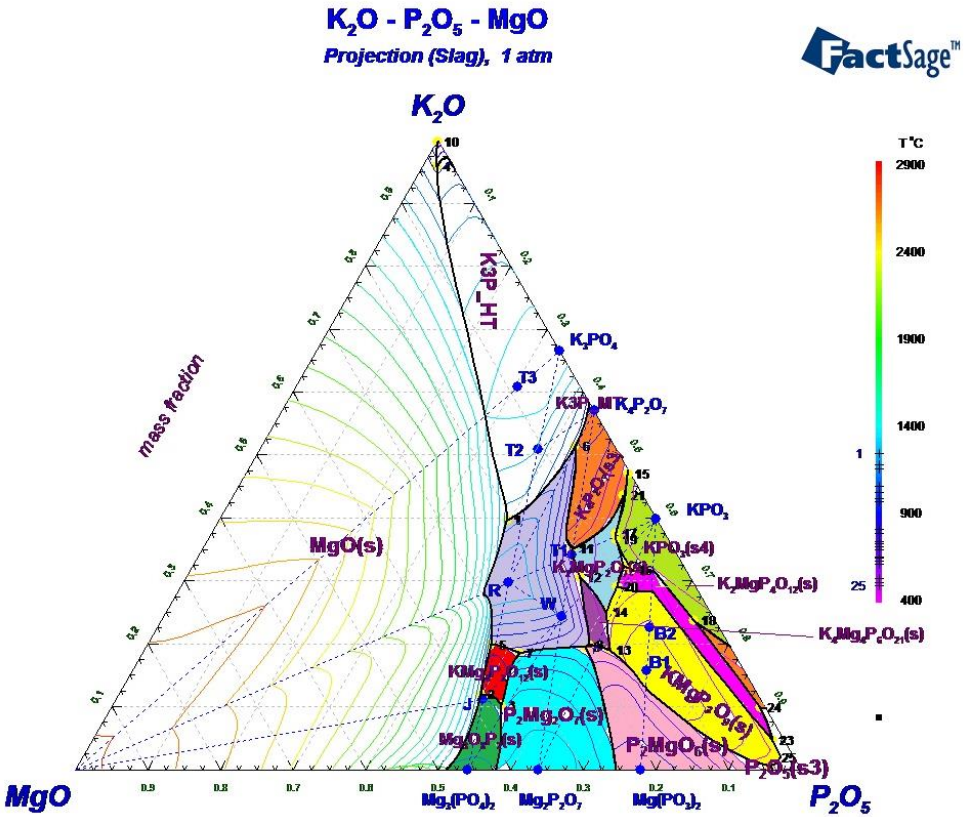




Liquidus surface



J. Berak and T. Podhajska-Kazmierczak, Pol. J. Chem., 65 [7-8] 1137-1149, 1151-1163, 1165-1172, 1173-1184 (1991)



Description of the system

The species with compositions R and T2 in the non-ideal associate solution were added in order to describe the liquid phase

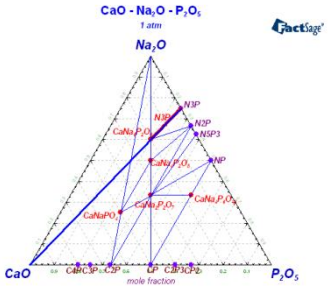
Name	***Composition***	***Melting, °C***	***Liquid species***	***Description*** (modelled by GTT)
R	$NaCaPO_4$	1830, congruent	$NaCaPO_4 \cdot 2/3$	Stoichiometric
T1	$Na_2CaP_2O_7$	814, incongruent		Stoichiometric
T2	$Na_4Ca(PO_4)_2$	1750, congruent	$Na_4Mg(PO_4)_2 \cdot 2/7$	Stoichiometric
T3	$Na_6CaP_2O_9$	1800, congruent		N3P-T3 solution
B3	$Na_4Ca(PO_3)_6$	733, congruent		stoichiometric

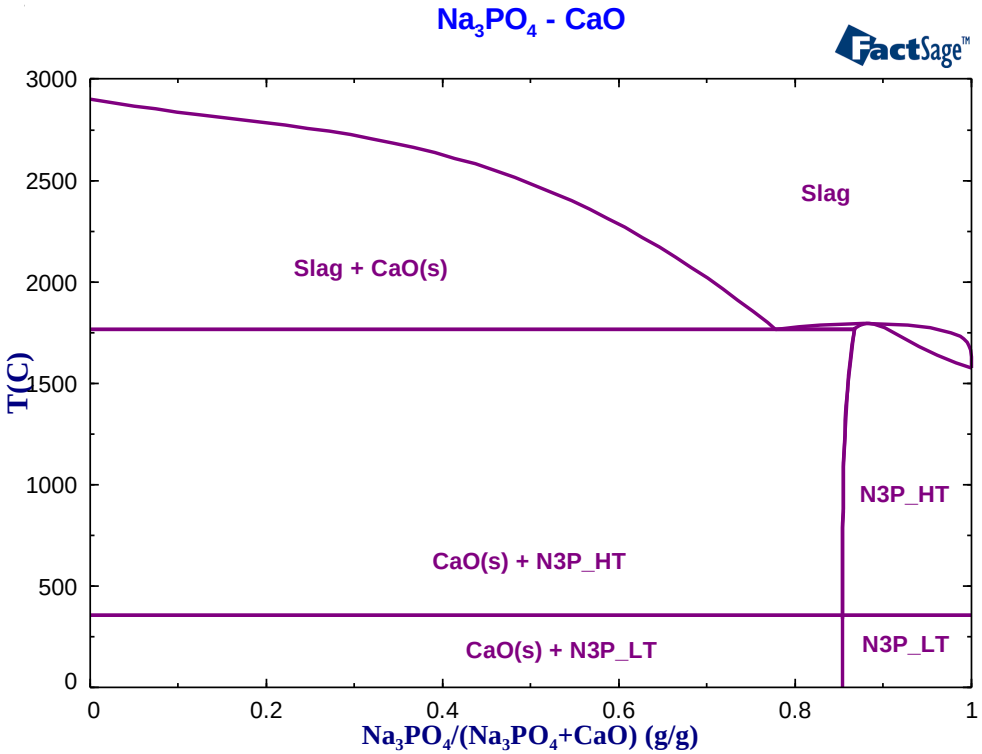
N3P-T3 solid solutions for HT, LT modifications

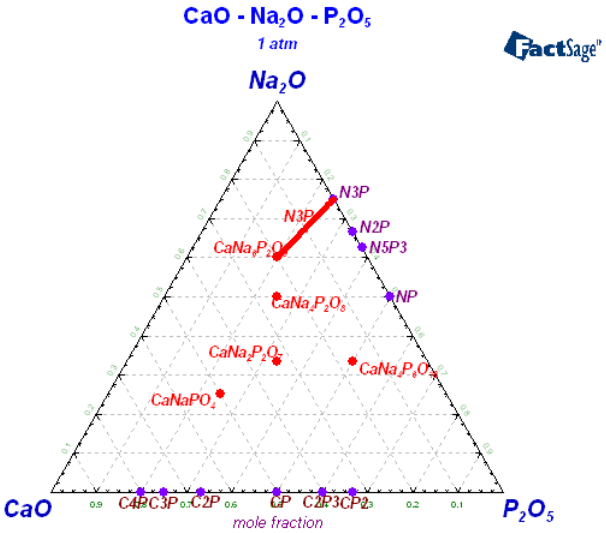
$(Na_2O)_2(P_2O_5)_2(Na_2O, Na_2CaO_2)$

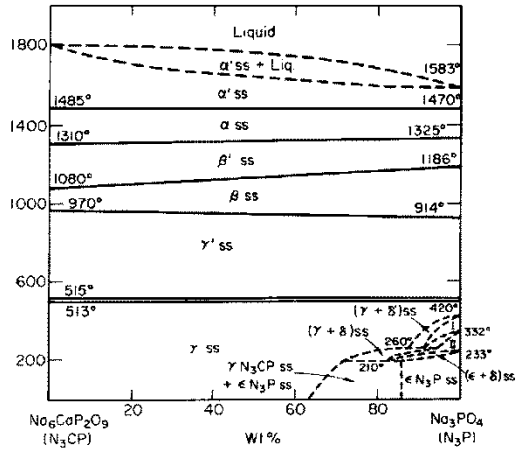
Na_3PO_4-$Na_6CaP_2O_9$

Solubility between Na_3PO_4 and $Na_6CaP_2O_9$



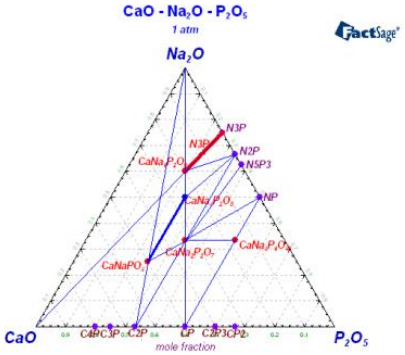


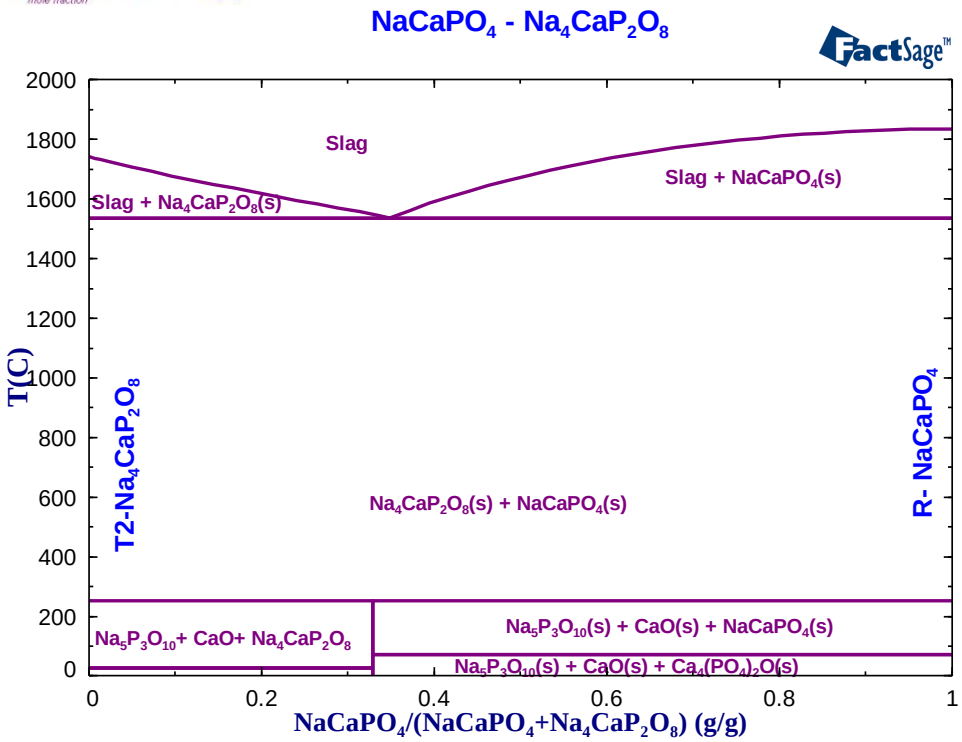


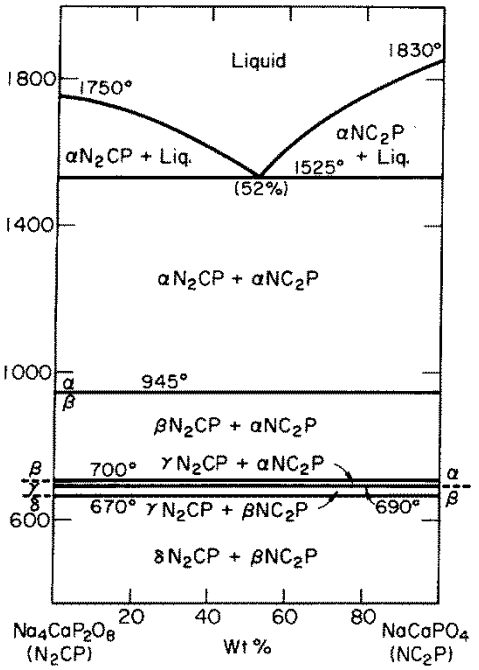


J. Berak and T. Znamierowska, Rocz. Chem., 46 [10] 1697-1708 (1972).

Section $NaCaPO_4$-$Na_4CaP_2O_8$

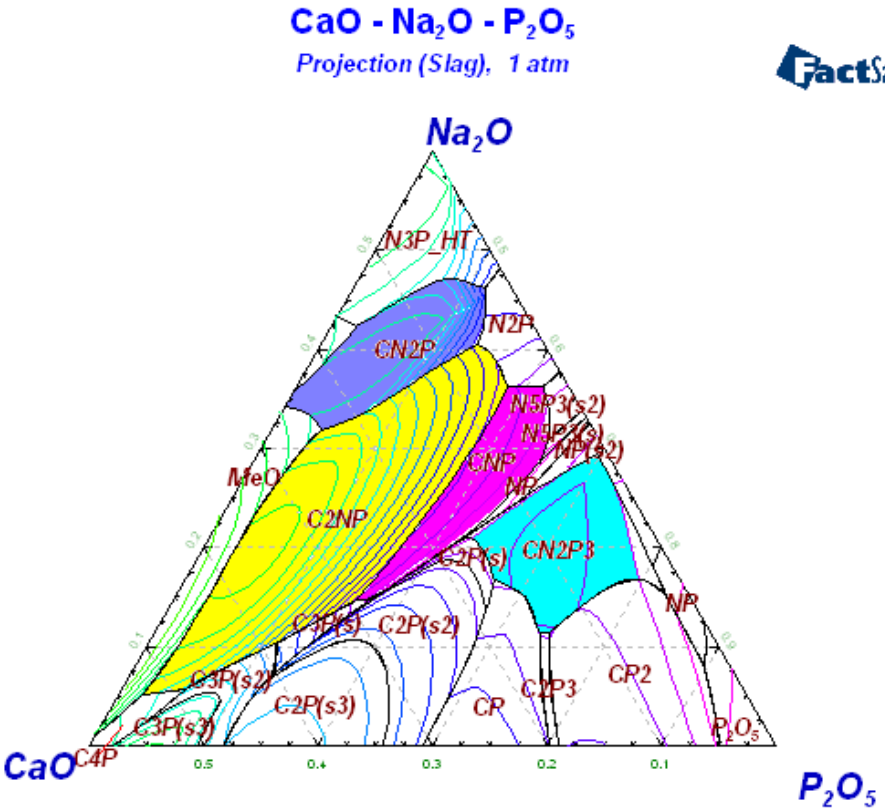


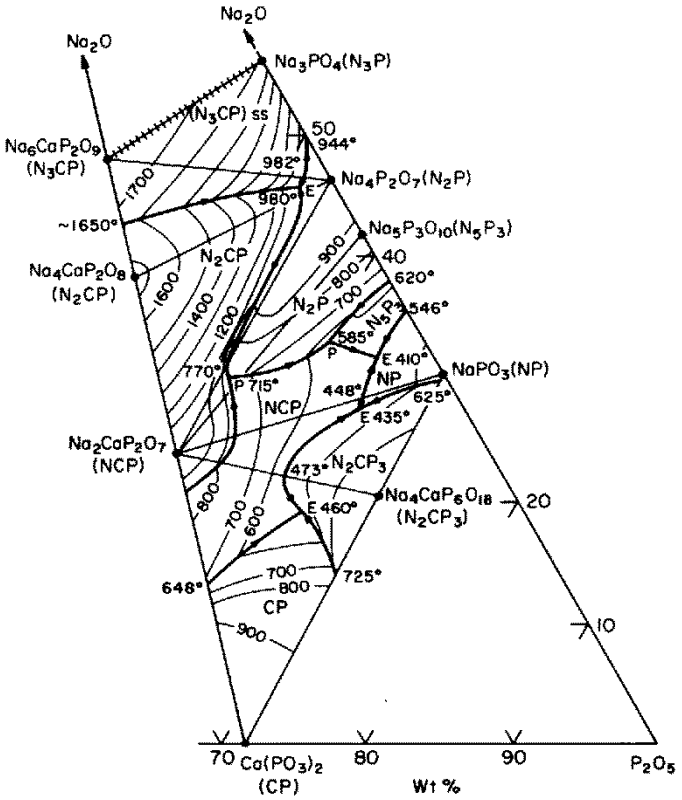




J. Berak and T. Znamierowska, Rocz. Chem., 46 [11] 1921-1929 (1972).

Liquidus surface





J. Berak, T. Znamierowska, Rocz. Chem. Ann. Soc. Chim. Polonorum, 46(1972), 1697-1708.

Description of the system

The species with compositions F1 and T2 in the non-ideal associate solution were added in order to describe the liquid phase

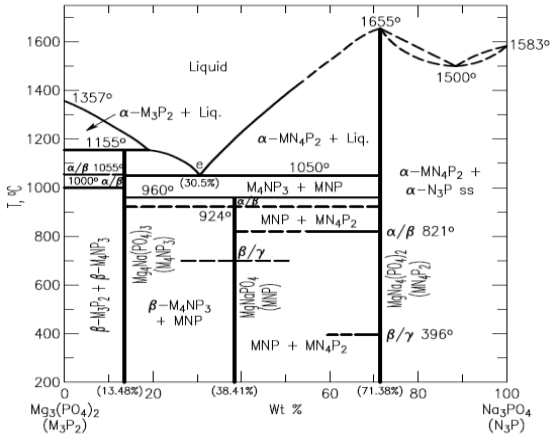
Name	***Composition***	***Melting, °C***	***Liquid species***	***Description*** (modelled by FZJ)
R	$NaMgPO_4$	960, incongruent		stoichiometric
T2	$Na_4Mg(PO_4)_2$	1655, congruent	$Na_4Mg(PO_4)_2 \cdot 2/7$	N3P-T2-T3 solution
T3	$Na_6MgP_2O_9$	1665, congruent		N3P-T2-T3 solution
B1	$NaMg(PO_3)_3$	942, incongruent		stoichiometric
B2	$Na_2Mg(PO_3)_4$	916, congruent		stoichiometric
B3	$Na_4Mg(PO_3)_6$	784, incongruent		stoichiometric
F1	$Na_8Mg_6(P_2O_7)_5$	808, congruent	$Na_8Mg_6(P_2O_7)_5 \cdot 1/12$	stoichiometric
D1	$Na_3Mg_2P_5O_{16}$	675, incongruent		stoichiometric

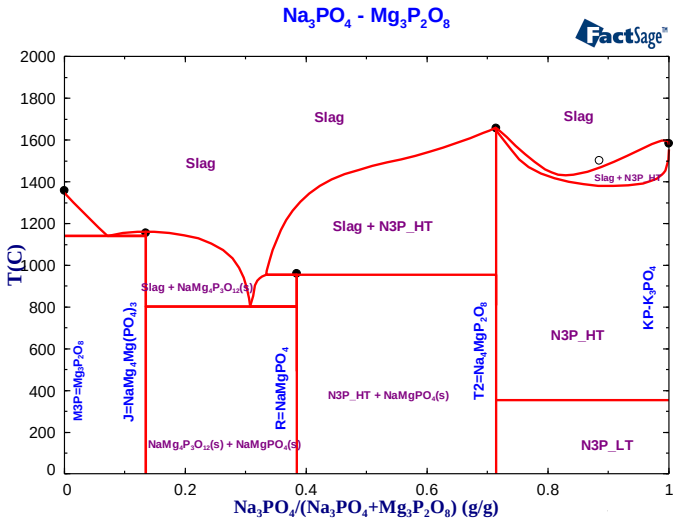
N3P-T2-T3 solid solutions for HT, LT modifications

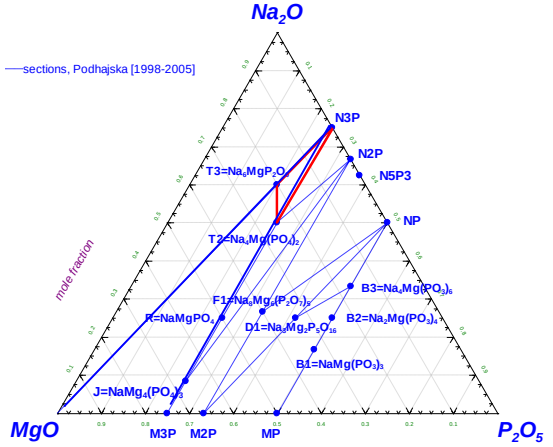
$(Na_2O)_2(P_2O_5)_2(Na_2O, MgO, Na_2MgO_2)$

Na_3PO_4-$Na_4Mg(PO_4)_2$-$Na_6MgP_2O_9$

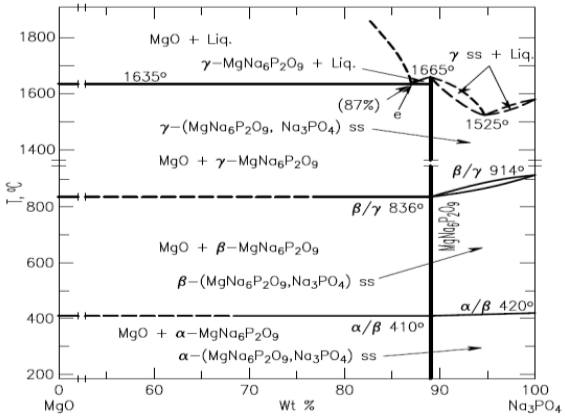
Sections Na_3PO_4-$Mg_3P_2O_8$ and Na_3PO_4-MgO

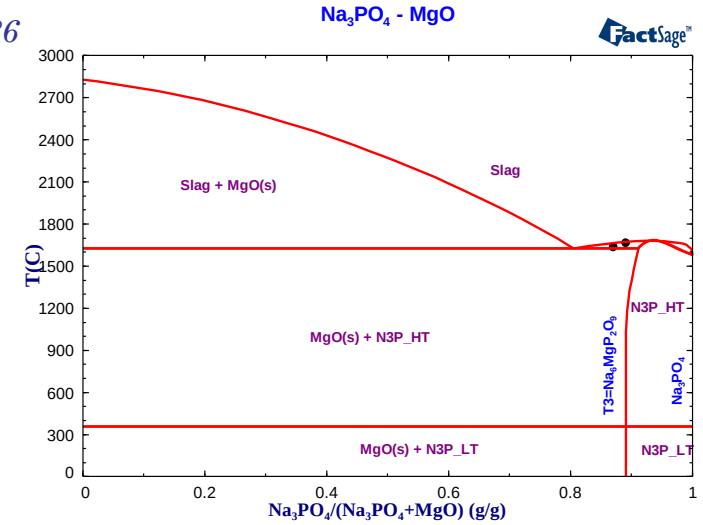






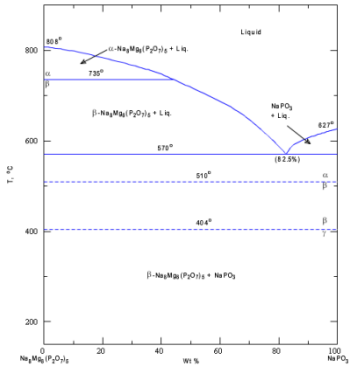
*T.Podhajska-Kazmierczak, T.Znamierowska, Pol. J. Chem., **73** [2] 279-286 (1999).*

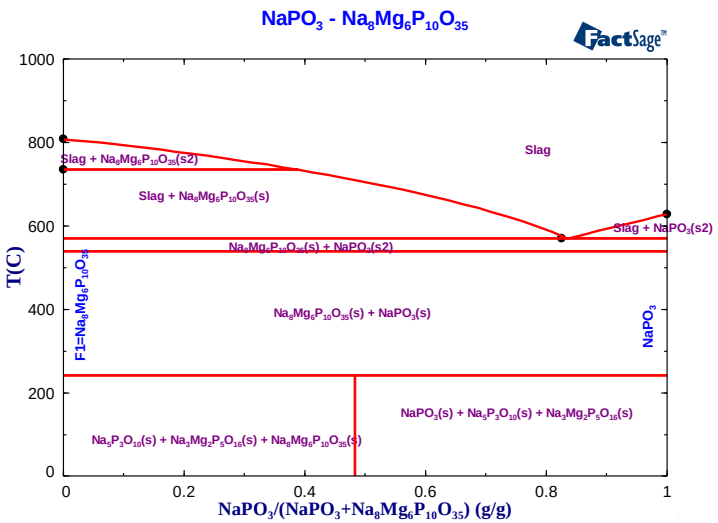


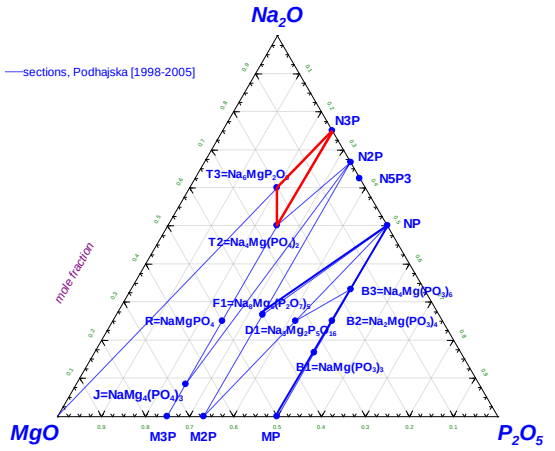


T. Podhajska-Kazmierczak, Pol. J. Chem., 77 [3] 295-301 (2003).

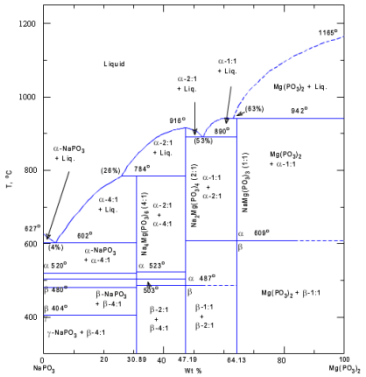
Sections $NaPO_3$-$Na_8Mg_6P_{10}O_{35}$ and $NaPO_3$-MgP_2O_6

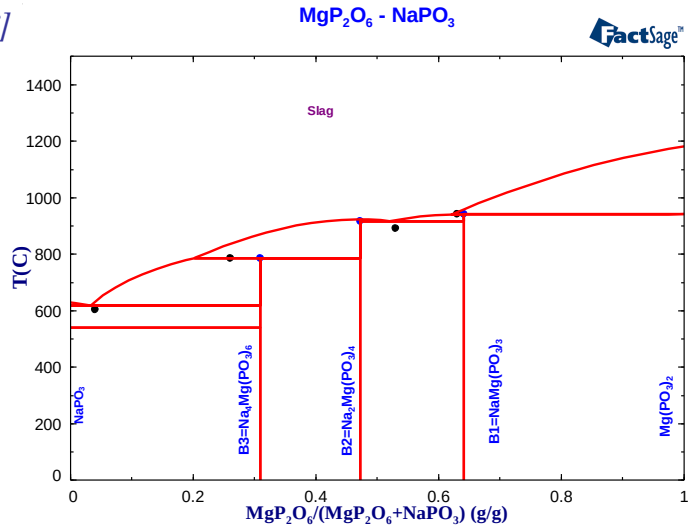






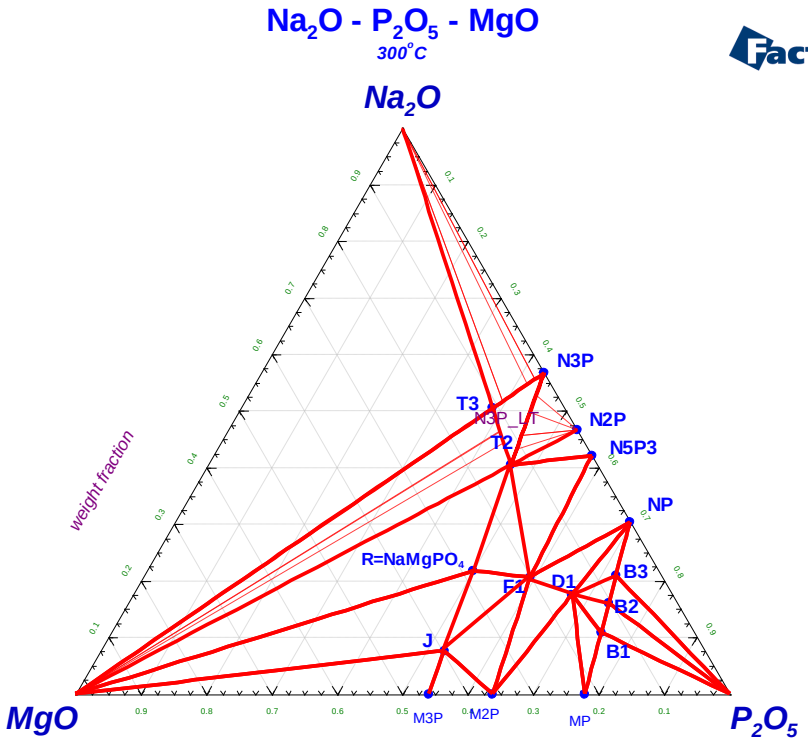
T. Podhajska-Kazmierczak and T. Znamierowska, J. Therm. Anal., 45 [6] 1541-1546 (1995)

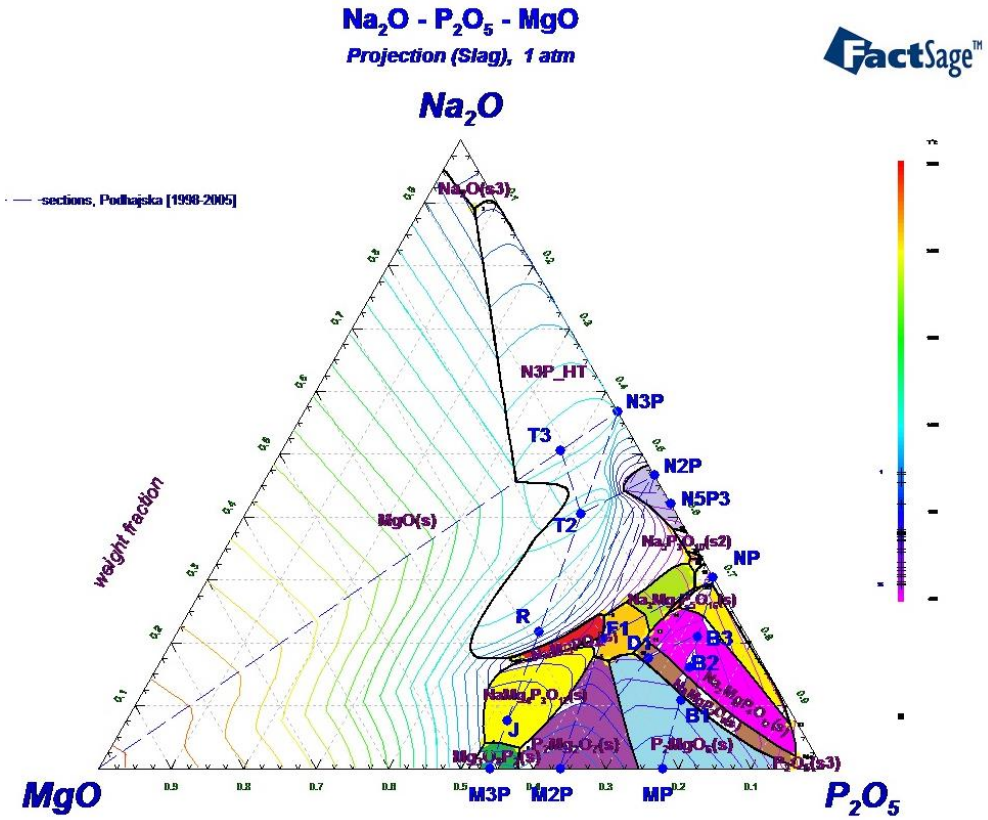




T. Podhajska-Kazmierczak and T. Znamierowska, Pol. J. Chem., 65 [7-8] 1121-1125 (1991).

Isothermal section and liqiudus surface



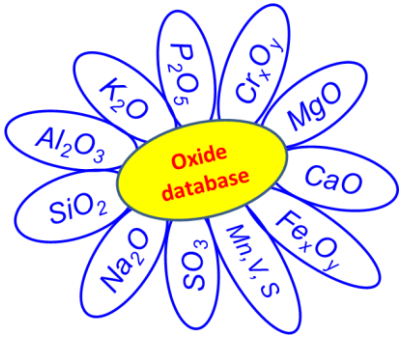


Conclusions

- ✓ All ternary compounds in the ternary systems Alk_2O-MeO-P_2O_5 (Alk=Na, K; Me=Ca, Mg) have been included into the oxide database. The preliminary thermodynamic dataset including solubilities between Alk_3PO_4-$Alk_4Me(PO_4)_2$-$Alk_6MeP_2O_9$ allows the description the phase equilibria in the different sections
- ✓ The corresponding ternary species have been included into the slag of the system Na_2O-K_2O-CaO-MgO-P_2O_5. 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.
- ✓ The quasi-binary sections and liquidus surfaces in the systems Alk_2O-MeO-P_2O_5 have been calculated using the corresponding data

Outlook

- ✓ Thermodynamic assessment of further P_2O_5-containing systems
- ✓ Extension of the database by addition of further oxides



On behalf of all co-authors:

Thank you for your attention!

Vielen Dank für Ihre Aufmerksamkeit!

Благодарю за внимание!

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