Addition of TiO_2 to the HotVeGas Oxide database

GTT-Technologies, Herzogenrath

GTT Users Meeting, 28.06-30.06.2017 Herzogenrath

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Contents of presentation

- Introduction
- Binary systems
- Solid solution phases in ternary systems
  - *Cubic Spinel*
  - *Titania Spinel*
  - *Pseudobrookite*
  - *Corundum*
- Conclusions

Addition of TiO_2 to GTOX database

GTT-Technologies

- **Binary systems**
  - *Al-O*
  - *Ti-O*
  - *Al-Ti*
  - *Al_2O_3-TiO_2*
  - *Al_2O_3-Ti_2O_3-O_2*
  - *MgO-TiO_2*
  - *CaO-TiO_2*
  - *FeO-TiO_2-Fe*
  - *Fe_2O_3-TiO_2-O_2*
  - *MnO-TiO_2-Fe*
  - *Mn_2O_3-TiO_2-O_2*
  - *SiO_2-TiO_2*
- **Ternary systems**
  - *Al-O-Ti*
  - *Al_2O_3-MgO-TiO_2*
  - *MnO-Mn_2O_3-TiO_2*
  - *FeO-Fe_2O_3-TiO_2*
  - *SiO_2-TiO_2-Ti_2O_3*
  - *Al_2O_3-SiO_2-TiO_2*
  - *Al_2O_3-TiO_2-Ti_2O_3*
  - *MnO-Ti_2O_3-TiO_2*
  - *MgO-SiO_2-TiO_2*
  - *MgO-TiO_2-Ti_2O_3*

Introduction

The associate species were added in order to describe the liquid phase in TiO_x-containing systems. The composition of the liquid oxide species are as introduced by Spear taking two moles of cations per associate. Species for similar systems are modelled in the same way, i.e. using the same stoichiometry.

System	Associate species	Used data for Gibbs energy
Ti-O	*Ti (SGPS), Ti_2O_2*, Ti_2O_3*, Ti_2O_4*	*SGPS database, [99Waldner]*
Me_2O_3-TiO_2	*Al_2TiO_5*	*This work*
	Fe_2TiO_5	*This work*
MeO-TiO_2	*$CaTiO_3$*	*This work*
	$FeTiO_3$	*SGPS*
	$MgTiO_3$, Mg_2TiO_4**	*SGPS*
	$MnTiO_3$, Mn_2TiO_4	*This work*
MeO-Ti_2O_3	*$MgTi_2O_4$, $MnTi_2O_4$*	*This work*

** H_f changed in this work.*

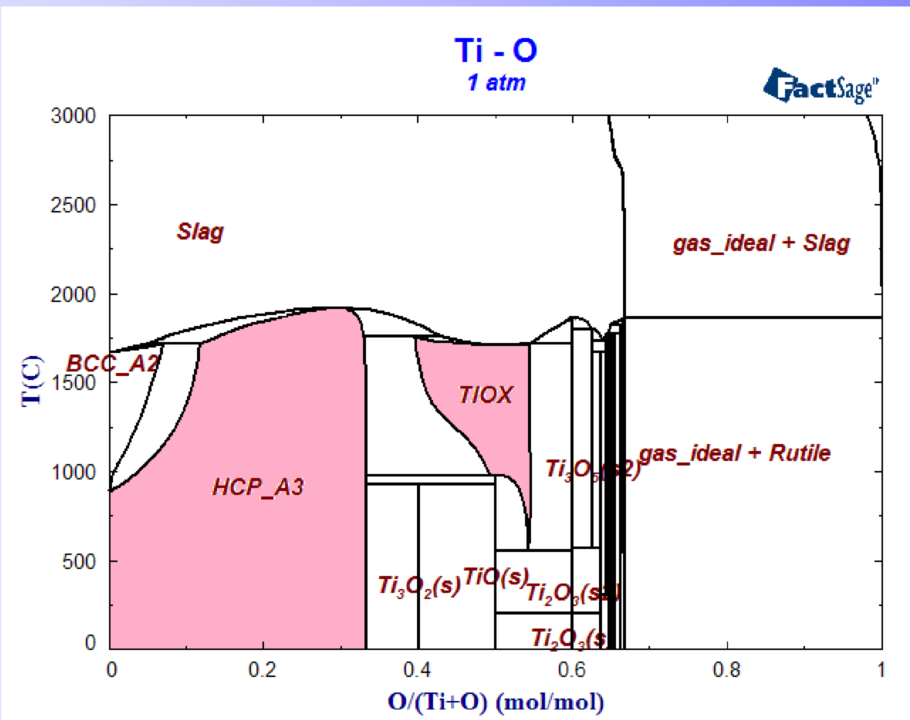
Modelling of ternary systems

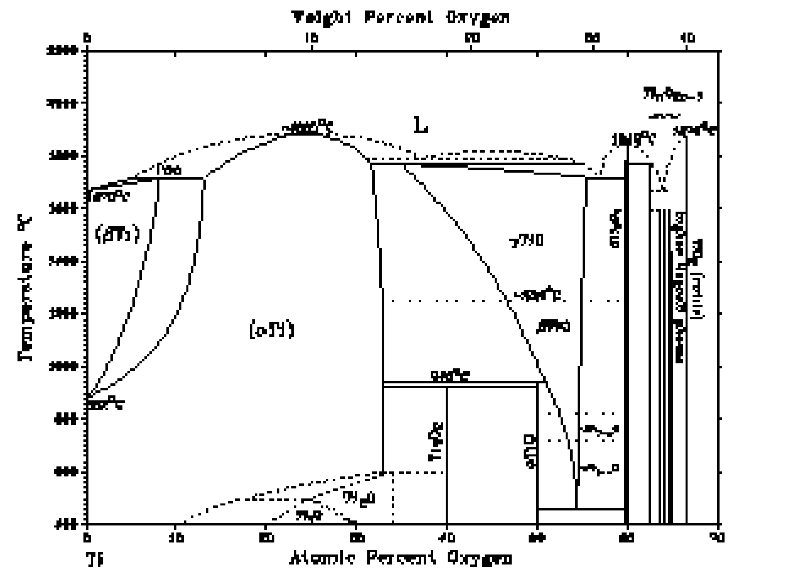
System	*Phase*	*Description*	*Used data*
Al_2O_3-MgO-TiO_2	Spinel	$(Al^{+3},Mg^{+2},Ti^{+4})_1(Al^{+3},Mg^{+2},Va)_2$ $(Mg^{+2},$ <u>Va</u>$)_2(O^{-2})_4$	This work
	Pseudobrookite	$(Al, Mg,Ti)_1(Al, Ti)_1(Ti)_1(O)_5$	This work
Al_2O_3-SiO_2-TiO_2	Pseudobrookite	$(Al, Ti)_1(Al, Ti)_1(Ti)_1(O)_5$	This work
FeO-Fe_2O_3-TiO_2	Spinel	$(Fe^{+2},Fe^{+3},Ti^{+4})_1(Fe^{+3},Va)_2$ $(Fe^{+2},Va)_2(O^{-2})_4$	This work
	Pseudobrookite	$(Fe, Ti)_1(Ti, Fe)_1(Ti)_1(O)_5$	This work
	Corundum	$(Fe^{+3}, Ti^{+3}, Fe_{0.5}Ti_{0.5}{}^{+3})_2(Va)_1(O^{-2})_3$	This work
MgO-TiO_2-Ti_2O_3	Titania-Spinel	$(Mg^{+2},Ti^{+4})_1(Ti^{+3},Mg^{+2},Va)_2(O^{-2})_4$	This work
	Pseudobrookite	$(Mg, Ti)_1(Ti)_1(Ti)_1(O)_5$	This work
	Corundum	$(\mathit{Ti}^{+3},Mg_{0.5}Ti_{0.5}{}^{+3})_2(Va)_1(O^{-2})_3$	This work
MnO-Mn_2O_3-TiO_2-Ti_2O_3	Spinel	$(Mn^{+2},Ti^{+4})_1(Mn^{+2}, Mn^{+3},Mn^{+4},Va)_2$ $(Va)_2(O^{-2})_4$	This work
	Titania-Spinel	$(Mn^{+2},Ti^{+4})(Mn^{+2}, Mn^{+3}, Ti^{+3},Va)_2(O^{-2})_4$	This work
	Pseudobrookite	$(Mn, Ti)_1(Ti)_1(Ti)_1(O)_5$	This work
	Corundum	$(Mn^{+3}, Ti^{+3},Mn_{0.5}Ti_{0.5}{}^{+3})_2(Va)_1(O^{-2})_3$	This work

Modelling of Ti-containing phases

Phase	Description
fcc-A1	(Al, Ca, Fe, Cr, P, Mg, Mn, S, Si, Zn, Ti, O) (Va)
bcc-A2	(Al, Ca, Fe, Cr, P, Mn, S, Zn, Ti, O, TiO_3) $(Va)_3$
hcp-A3	$(Al, Ti)_2$ (O, Va)
Cubic Spinel	$(Al^{+3},Cr^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Zn^{+2},Ti^{+4})(Al^{+3},Ca^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Mn^{+3},Mn^{+4},Va)_2$ $(Cr^{+2}, Fe^{+2}, Mg^{+2},Va)_2(O^{-2})_4$
Titania Spinel	$(Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Ti^{+4})(Al^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Mn^{+3},Va, Ti^{+3})_2$ $(O^{-2})_4$
PSbrookite-Ti_3O_5	$(Al, Mg, Fe, Mn, Ti)_1(Al,Ti, Fe)_1(Ti)_1(O)_5$
TIOX	$(Ti^{+3}, Ti^{+2}, Va)_1(Ti, Va)_1(O^{-2})_1$
Rutile	$(Ti^{+3}, Ti^{+2}, Va)_1(Ti, Va)_1(O^{-2})_1$
Al3M_D022	$(Al,Ti)_3(Ti)$
TI3AL	$(Al, Ti)_3(Al, Ti)(O,Va)_2$
TIAL	$(Al, Ti)(Al, Ti)(O,Va)_2$
Corundum	$(Al^{+3},Cr^{+2},Cr^{+3},Fe^{+3},Mn^{+3}, Ti^{+3},Fe_{0.5}Ti_{0.5}{}^{+3},Mg_{0.5}Ti_{0.5}{}^{+3}, Mn_{0.5}Ti_{0.5}{}^{+3})_2$ $(Cr^{+3},Va)_1(O^{-2})_3$
SiO_2-HT	$(Si^{+4},Ti^{+4})(Si^{+4}, Ti^{+4})$ $(O^{-2})_4$
MeO	$(Al^{+3},Ca^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Mn^{+3},Ti^{+4},Ti^{+3},Zn^{+2})(O^{-2})$

Ti-O phase diagram

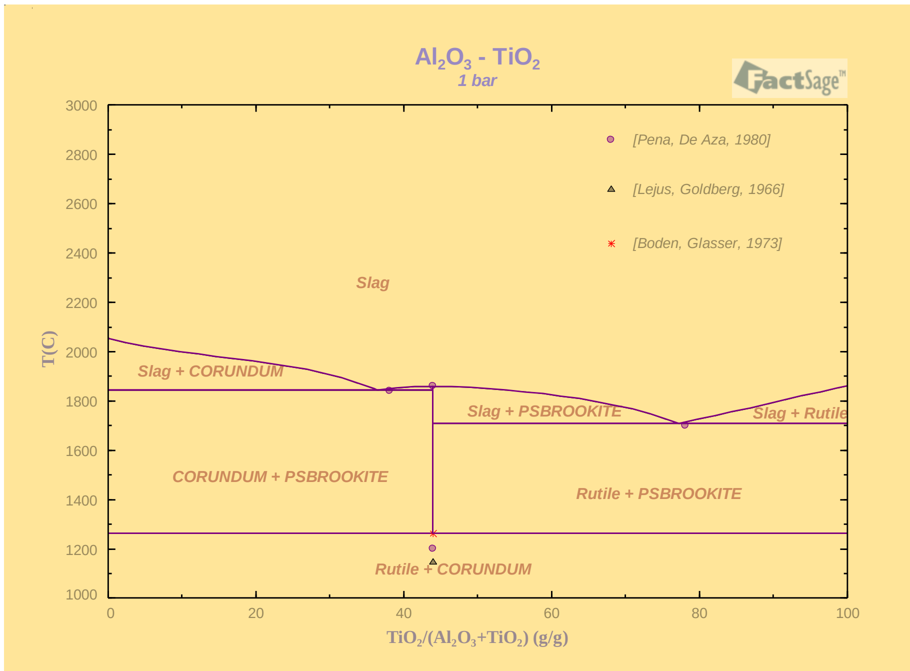


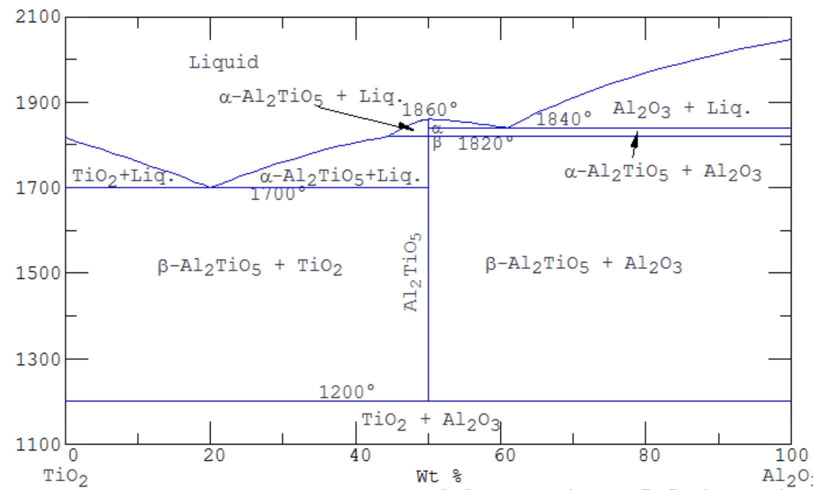


T.B. Massalski (ed), Binary Alloy Phase Diagrams, Second Edition, ASM International, Metals Park, OH 1990.

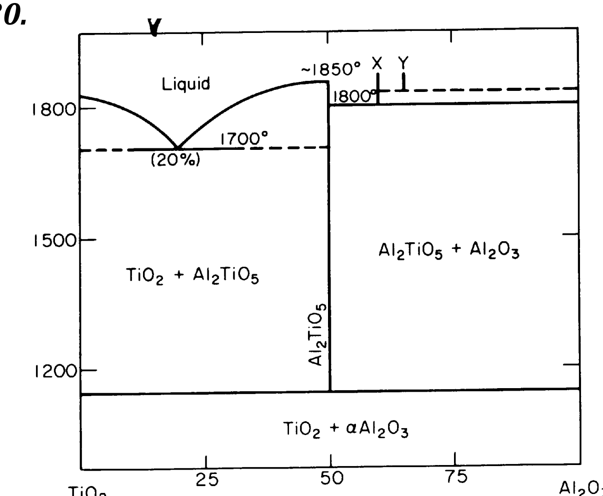
Phase	Description	Used data
Slag	(Ti, Ti_2O_2, Ti_2O_3, Ti_2O_4)	This work
bcc-A2	($\underline{Ti}$, O, TiO_3) $(Va)_3$	This work
hcp-A3	$(\underline{Ti})_2$(O, Va)	[07Cancarevic]
TIOX	$(Ti^{+3}, Ti^{+2}, Va)_1(\underline{Ti}, Va)_1(O^{-2})_1$	[07Cancarevic]
Rutile	$(Ti)_1(O, Va)_2$	[99Waldner]
Ti_3O_2, TiO, Ti_2O_3, Ti_3O_5, Ti_4O_7, Ti_5O_9, Ti_6O_{11}, Ti_7O_{13},	stoichiometric	[99Waldner]
Ti_8O_{15}, Ti_9O_{17}, $Ti_{10}O_{19}$, $Ti_{20}O_{39}$	stoichiometric	[99Waldner]

Al_2O_3-TiO_2 phase diagram



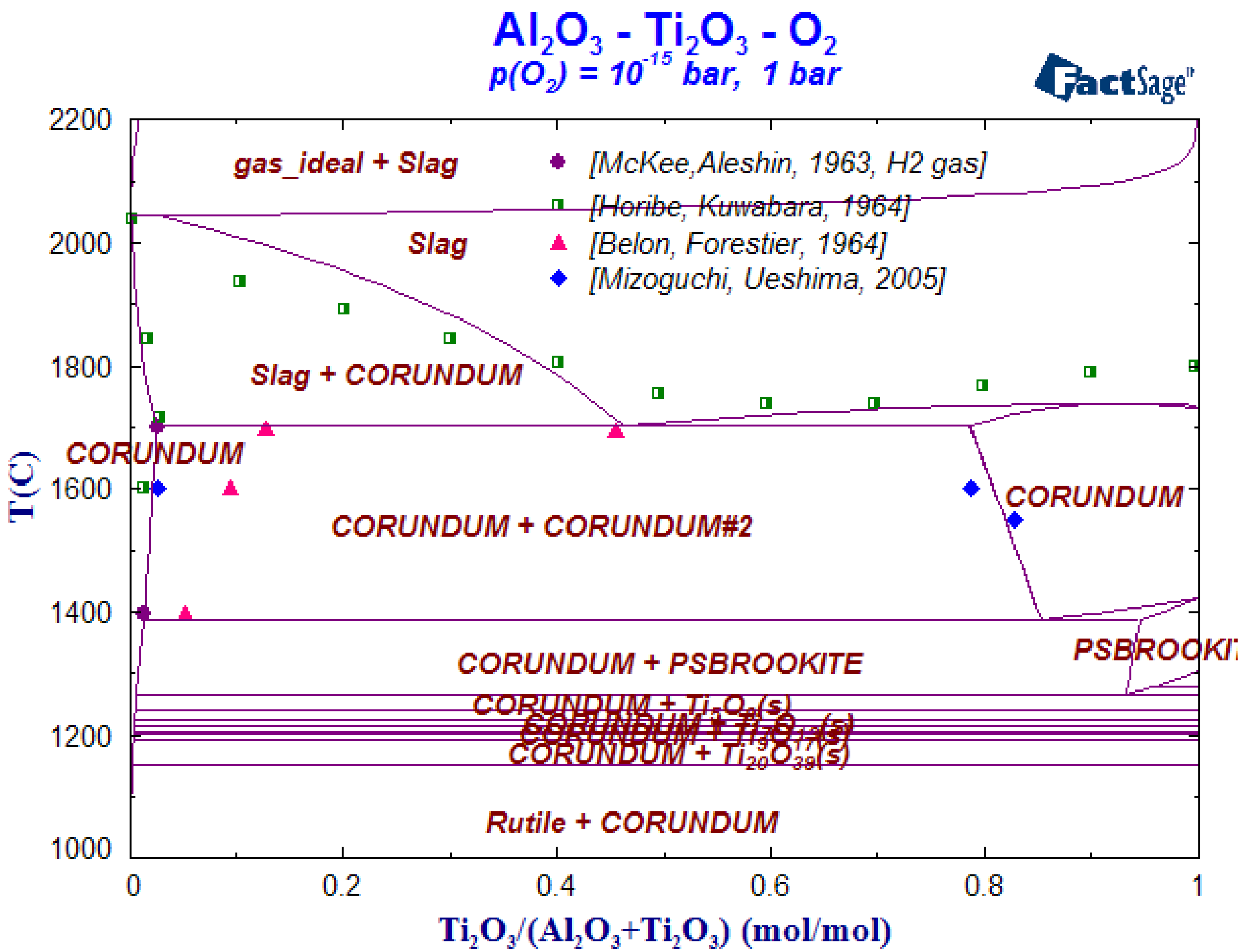


P. Pena, S. DeAza, Ceramica (Florence), 33 [3], (1980), pp. 23-30.

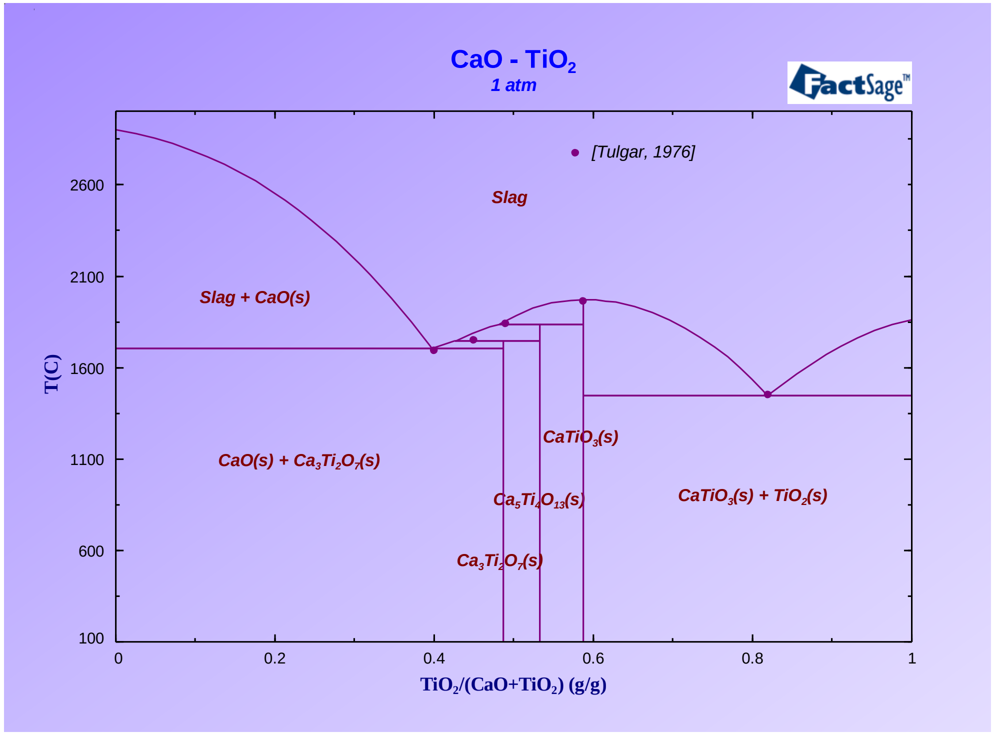


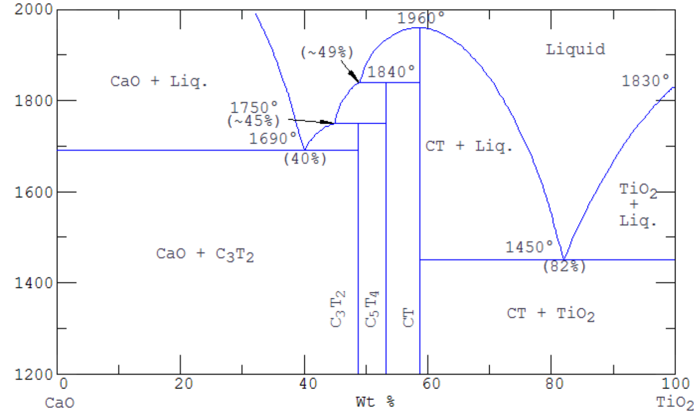
A.M. Lejus, D. Goldberg, A. Revcolevschi, C.R. Seances Acad. Sci., Ser. C, 263 [20], (1966), pp.1223-1226.

Calculated Al_2O_3-Ti_2O_3 phase diagram

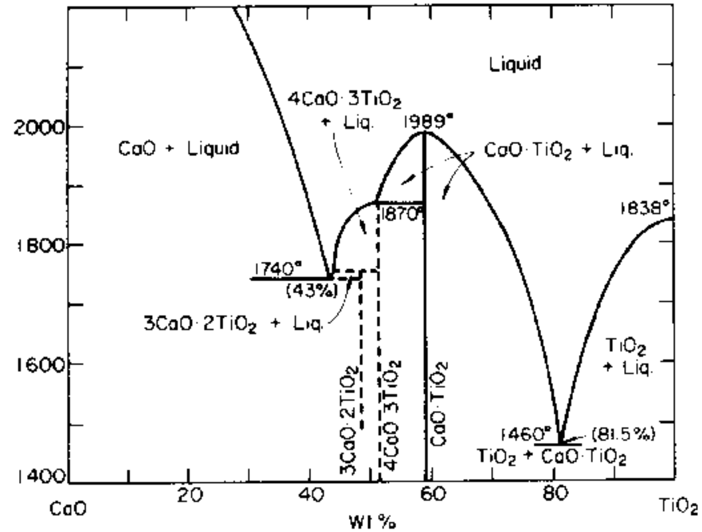


CaO-TiO$_2$ phase diagram



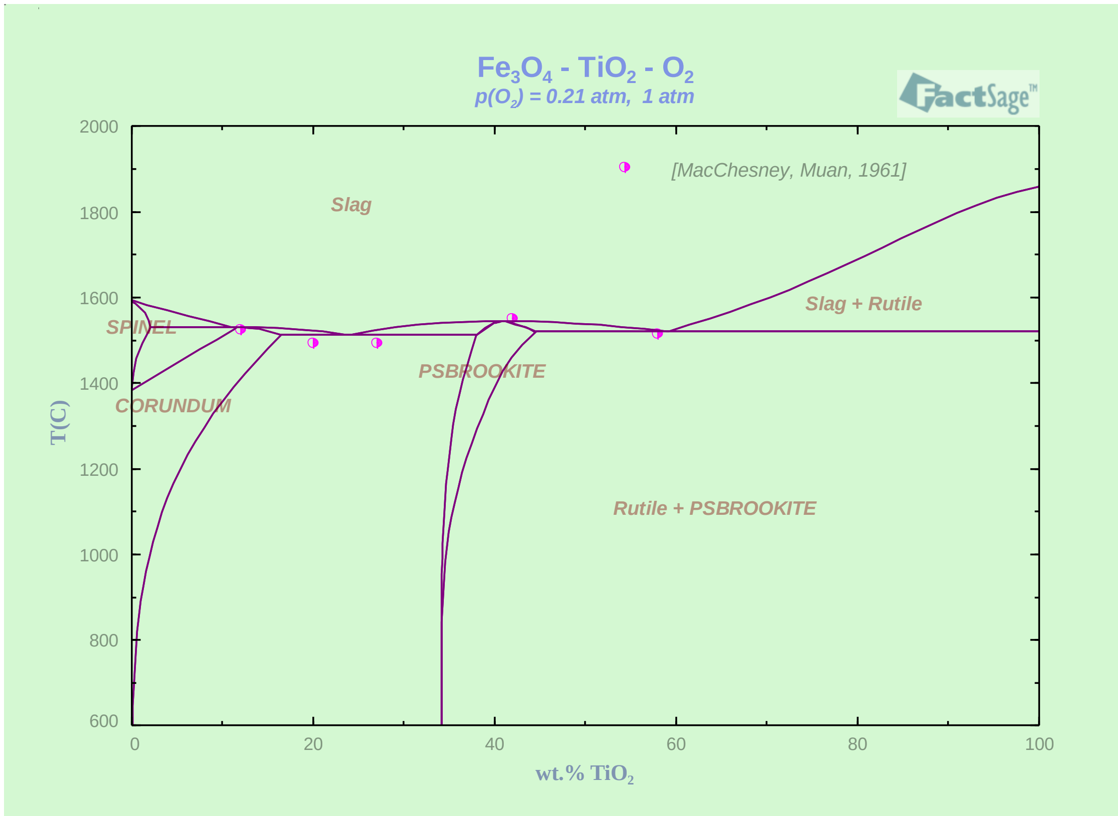


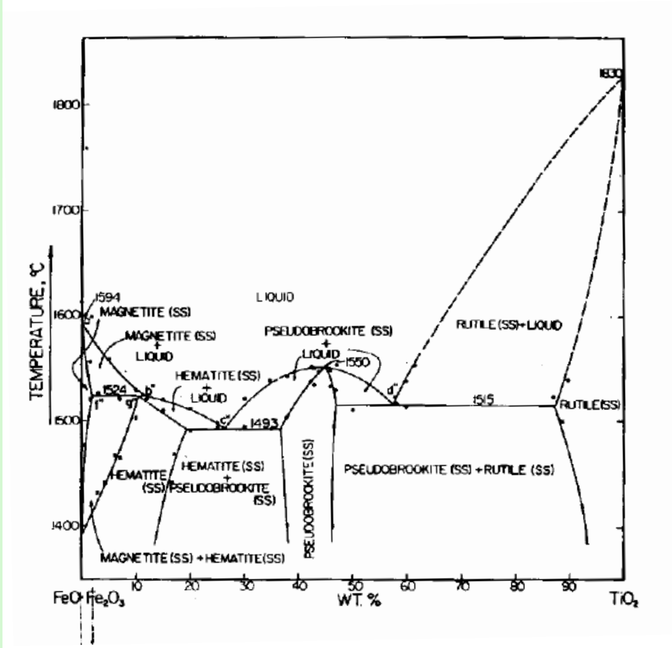
H.E. Tulgar, Istanbul Tek. Univ. Bul., 29 [1], (1976), pp. 111-129.



A. Jongejan, A.L. Wilkins, J. Less-Comon Met., 20 [4], (1970), pp. 273-279.

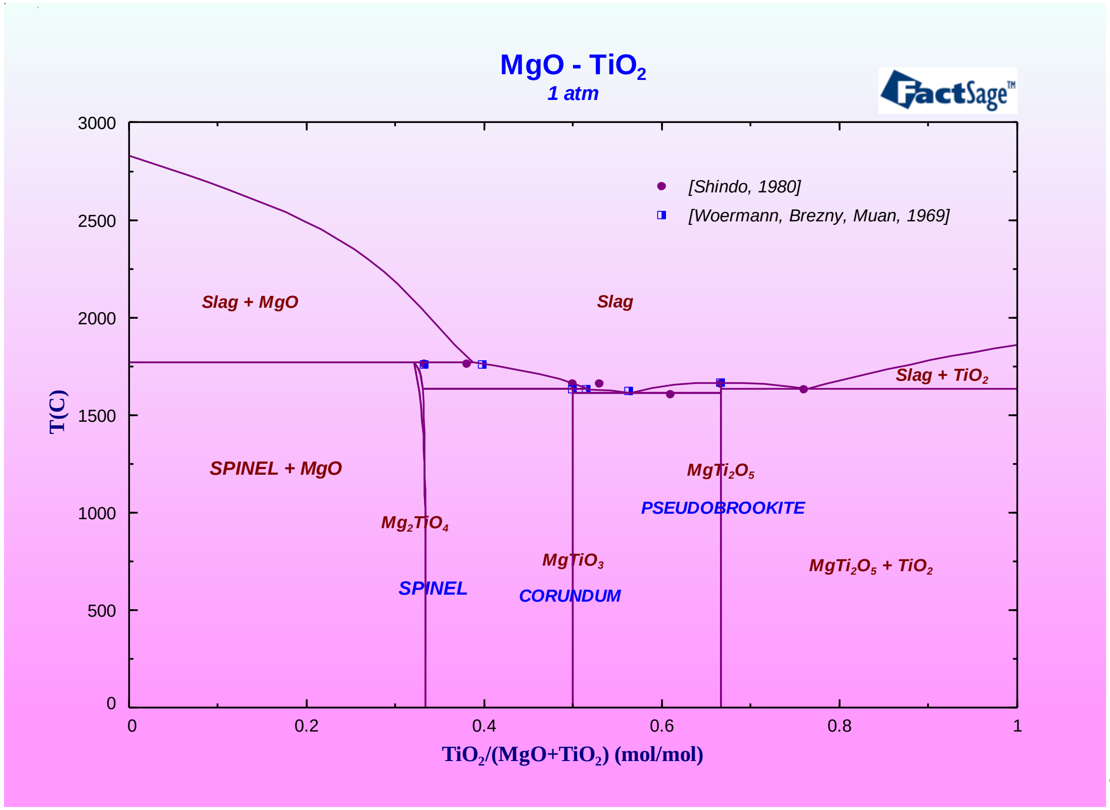
Fe_3O_4-TiO_2 phase diagram in air

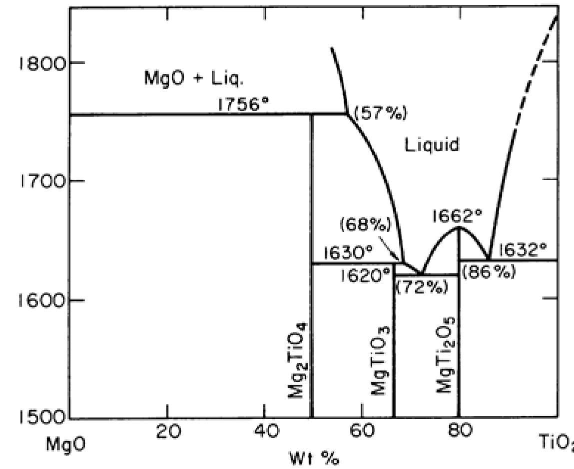




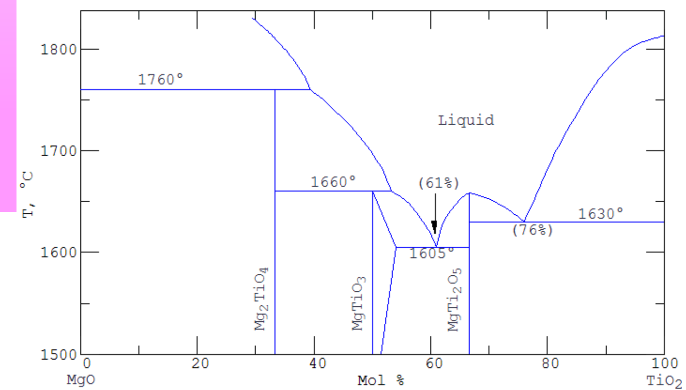
J.B. MacChesney, A. Muan, Am. Mineral, 44 [9-10], (1959), pp. 926-945.

MgO-TiO_2 phase diagram





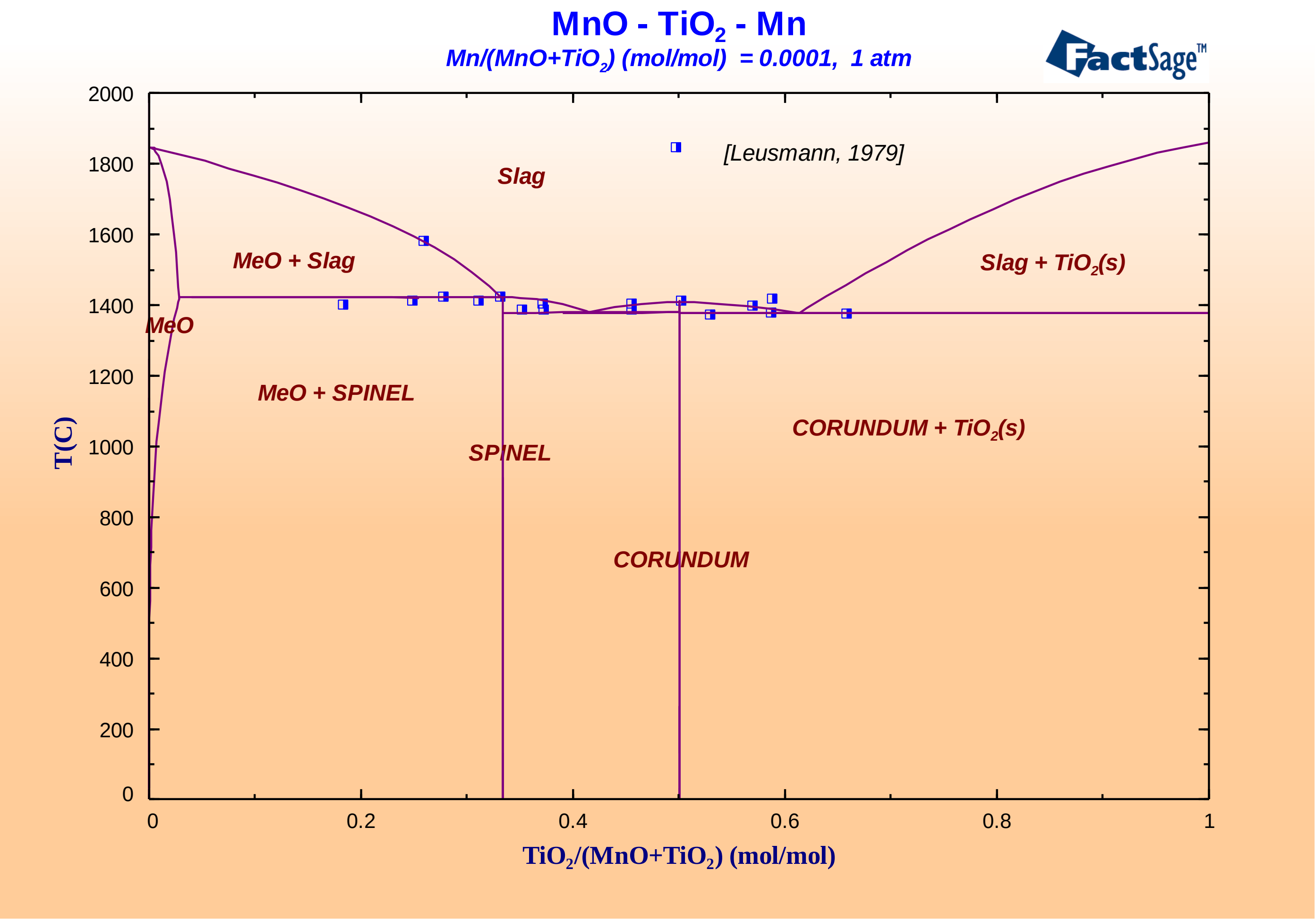
E. Woermann, B. Brezny, A. Muan, Am. J. Sci., 267A, (1969), pp.463-479.



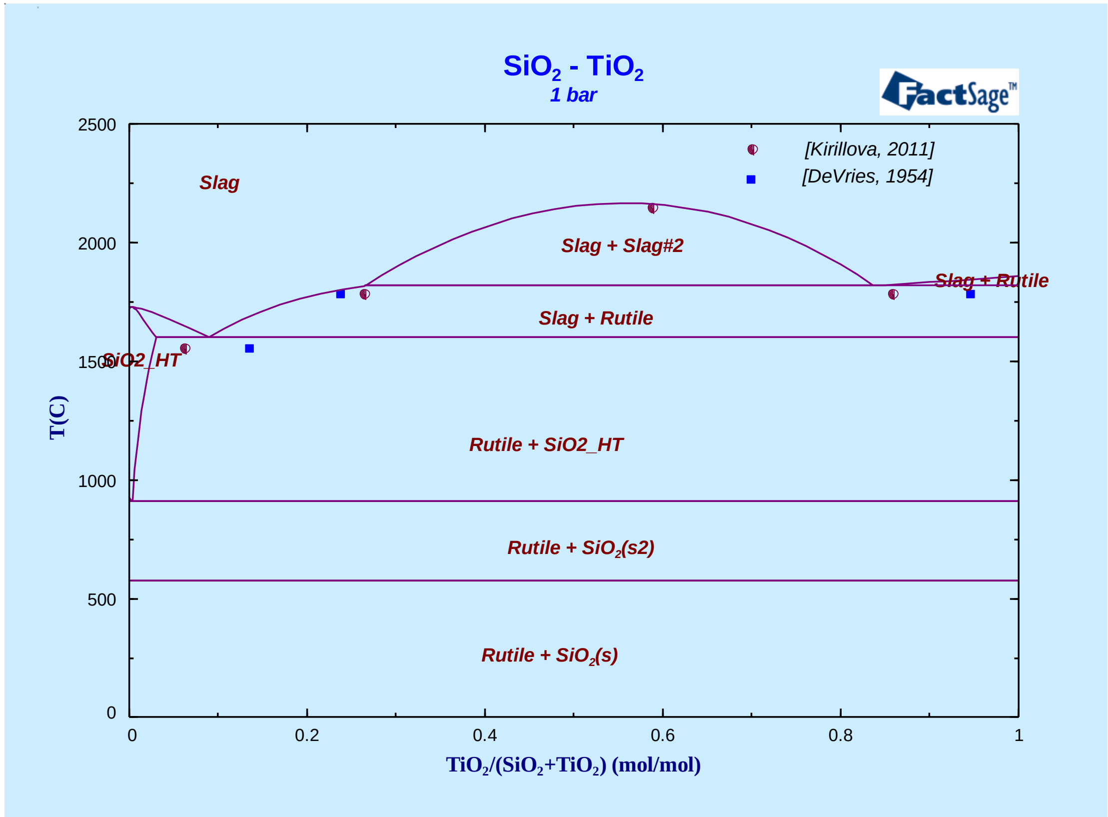
J. Shindo, J. Chryst. Growth, 50 [4], (1980), pp.839-851.

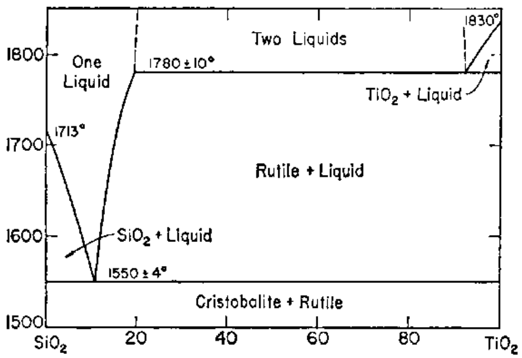
Phase	Description
Spinel	$(Mg^{+2},Ti^{+4})(Mg^{+2}, Va)_2(Mg^{+2}, Va)_2(O^{-2})_4$
PSbrookite	$(Mg, Ti)_1(Ti)_1(Ti)_1(O)_5$
Corundum	$(Ti^{+3}, Mg_{0.5}Ti_{0.5}^{+3})_2(Va)_1(O^{-2})_3$

MnO-TiO_2 phase diagram

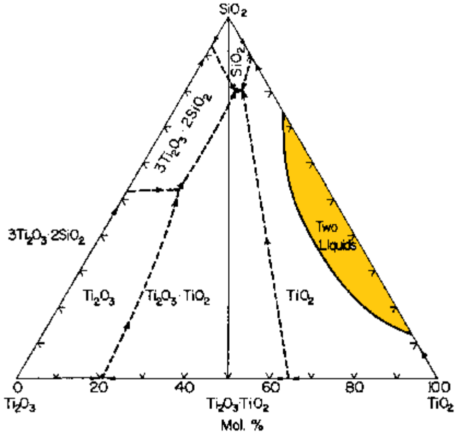


SiO_2-TiO_2 phase diagram





R.C. DeVries, R. Roy, E.F. Osborn, Trans. J. Br. Ceram. Soc., 53 [9], (1954), pp. 525-540.

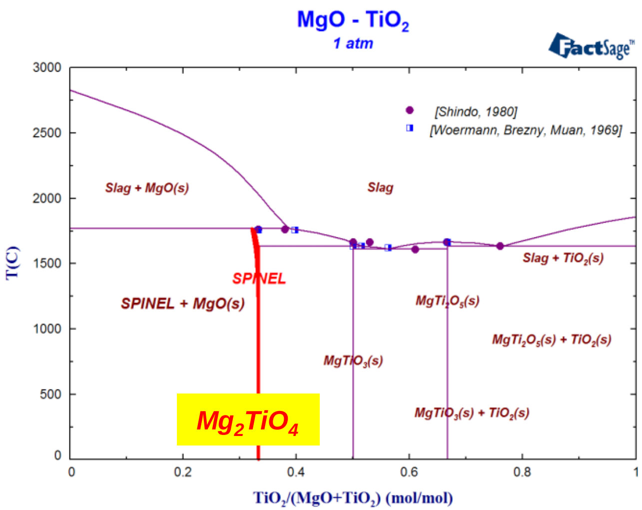


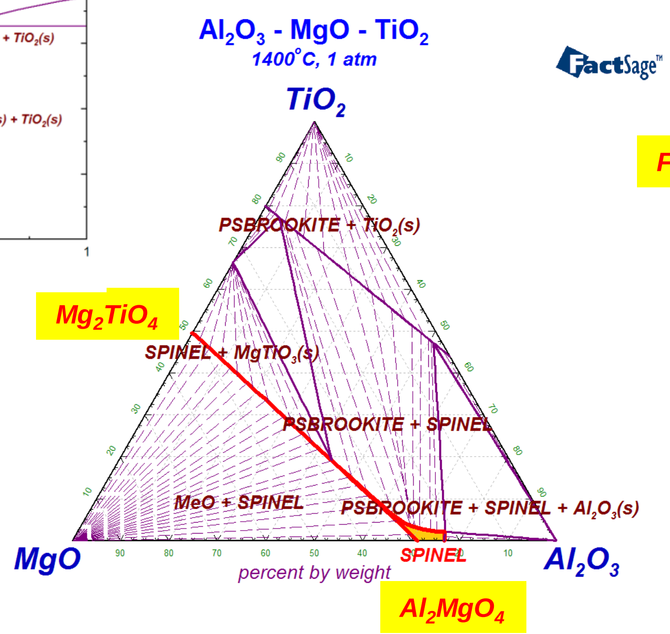
R. Roy, R.C. DeVries, D.E. Rase, M.W. Shafer, E.F. Osborn, 1952.

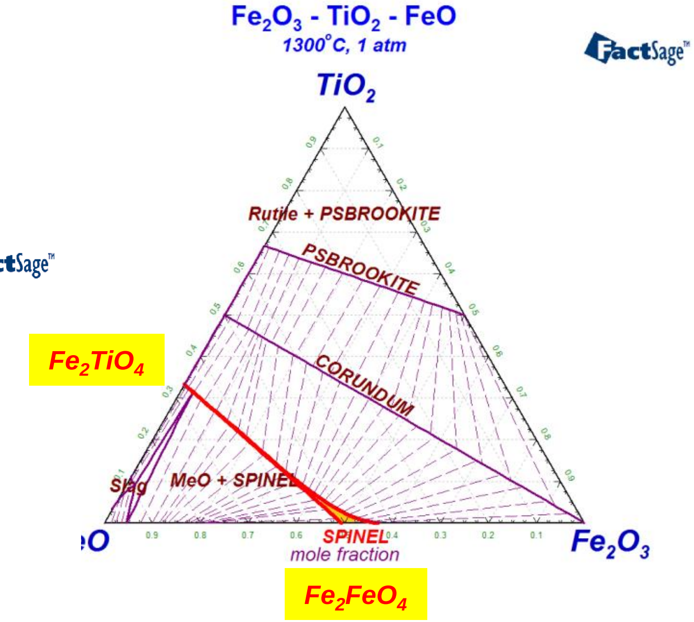
Description of the phase Spinel

Spinel ***(Al^{+3},Cr^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Zn^{+2}, Ti^{+4})***
(Al^{+3},Ca^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2}, Mn^{+2},Mn^{+3},Mn^{+4},Va)$_2$ (Cr^{+2}, Fe^{+2}, Mg^{+2},Va)$_2$(O^{-2})$_4$

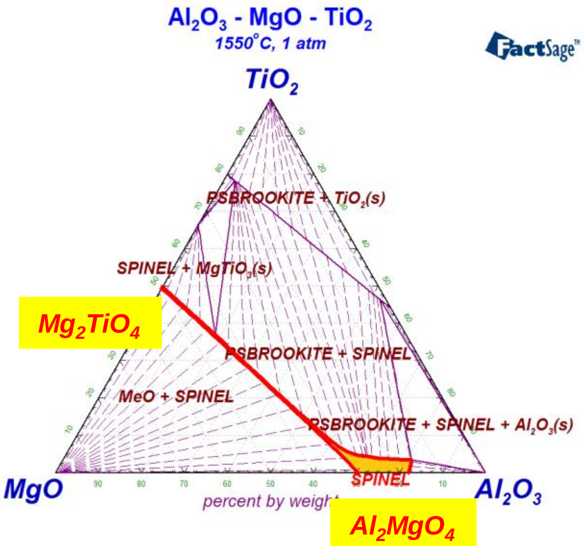
Gibbs energies of real Spinels are taken from SGPS database and G of fictive compounds are estimated using reciprocal equations.





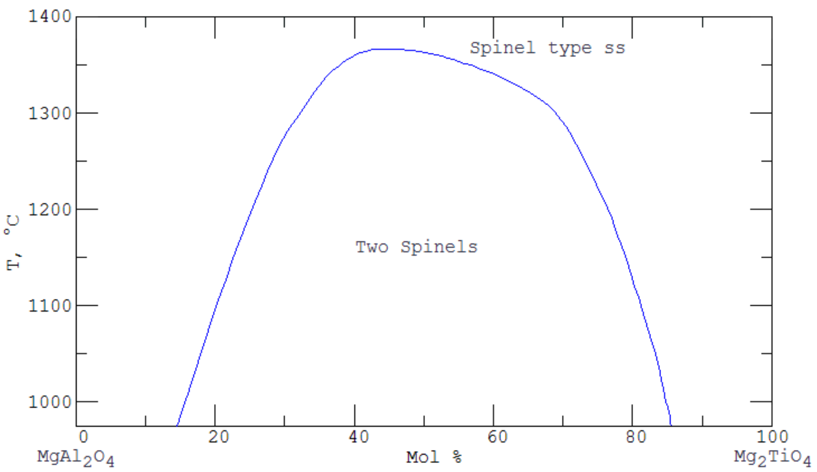


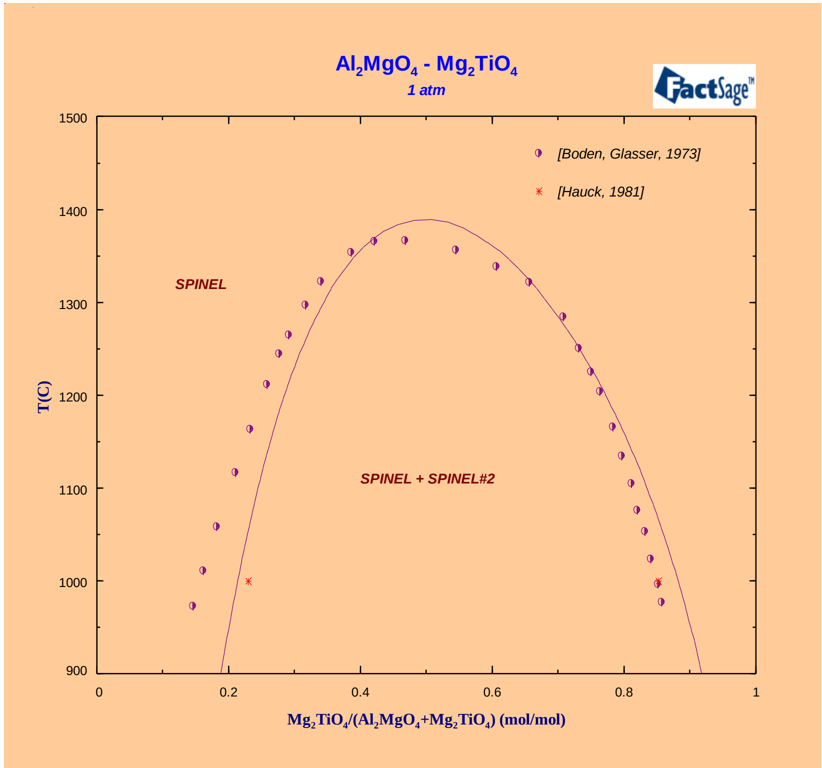
Spinel in Al_2O_3-MgO-TiO_2



Spinel – solid solution phase with end-members Al_2MgO_4 and Mg_2TiO_4

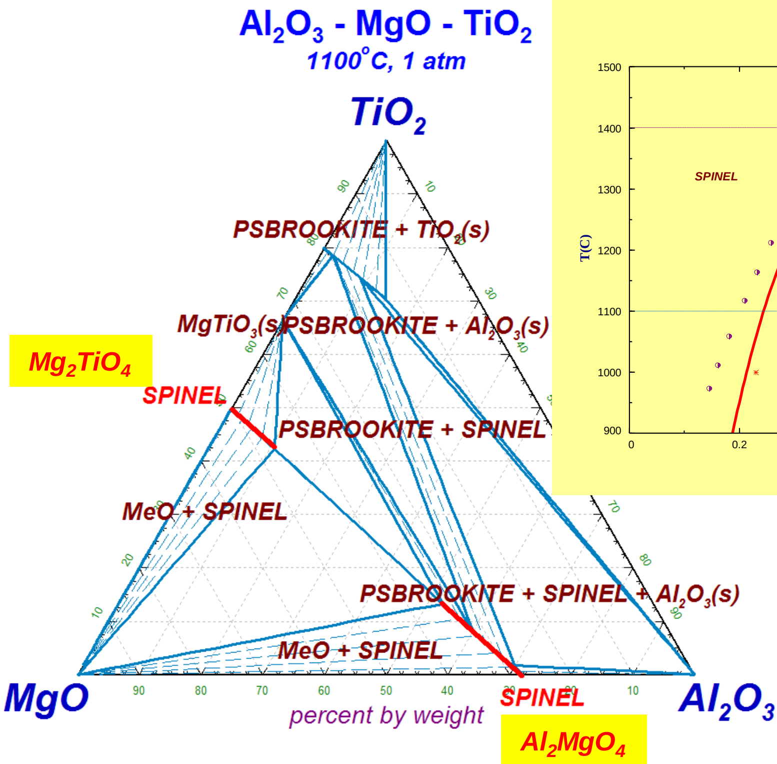
$(Al^{+3},Mg^{+2},Ti^{+4})_1(Al^{+3},Mg^{+2},Va)_2(Mg^{+2},\underline{Va})_2(O^{-2})_4$

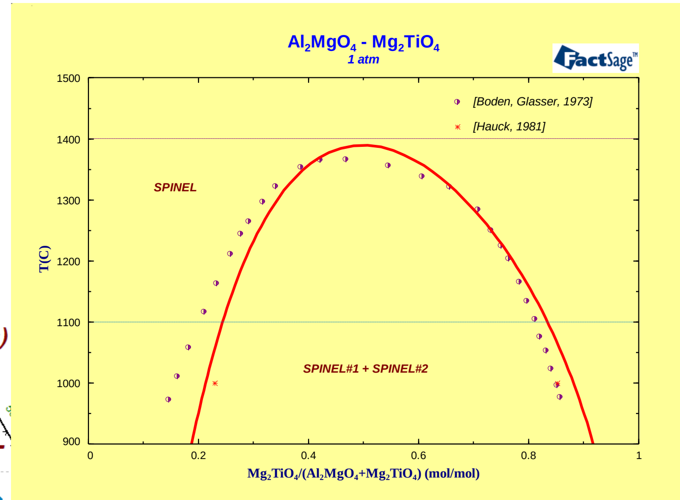


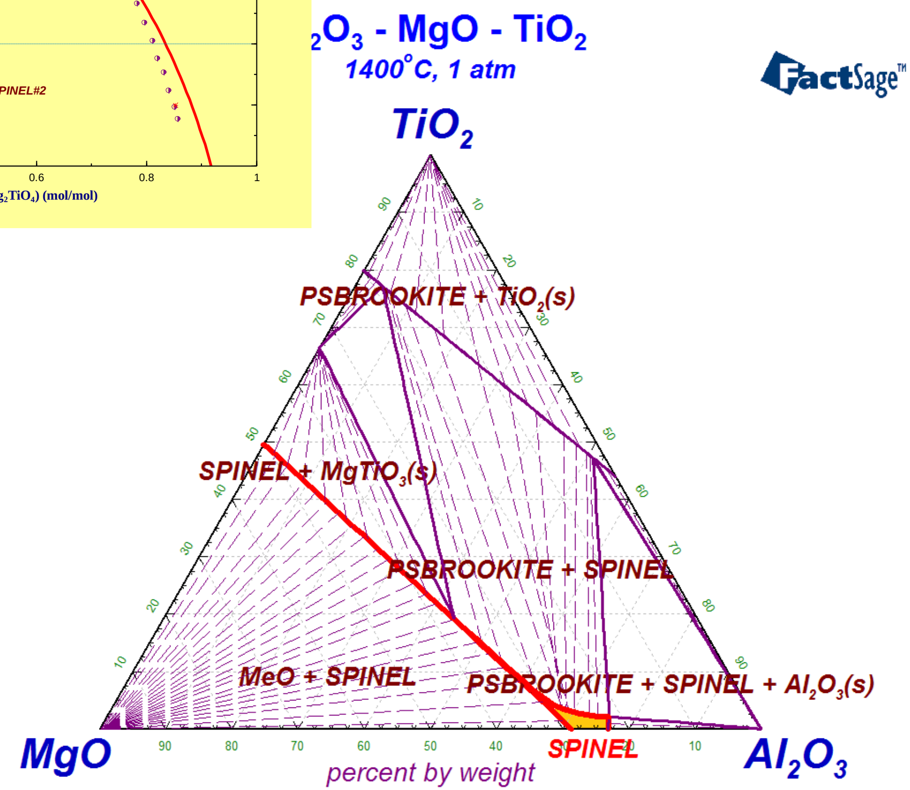


P. Boden, F.P. Glasser, Trans. J. Br. Ceram. Soc., 72[5], (1973), pp. 215-220.

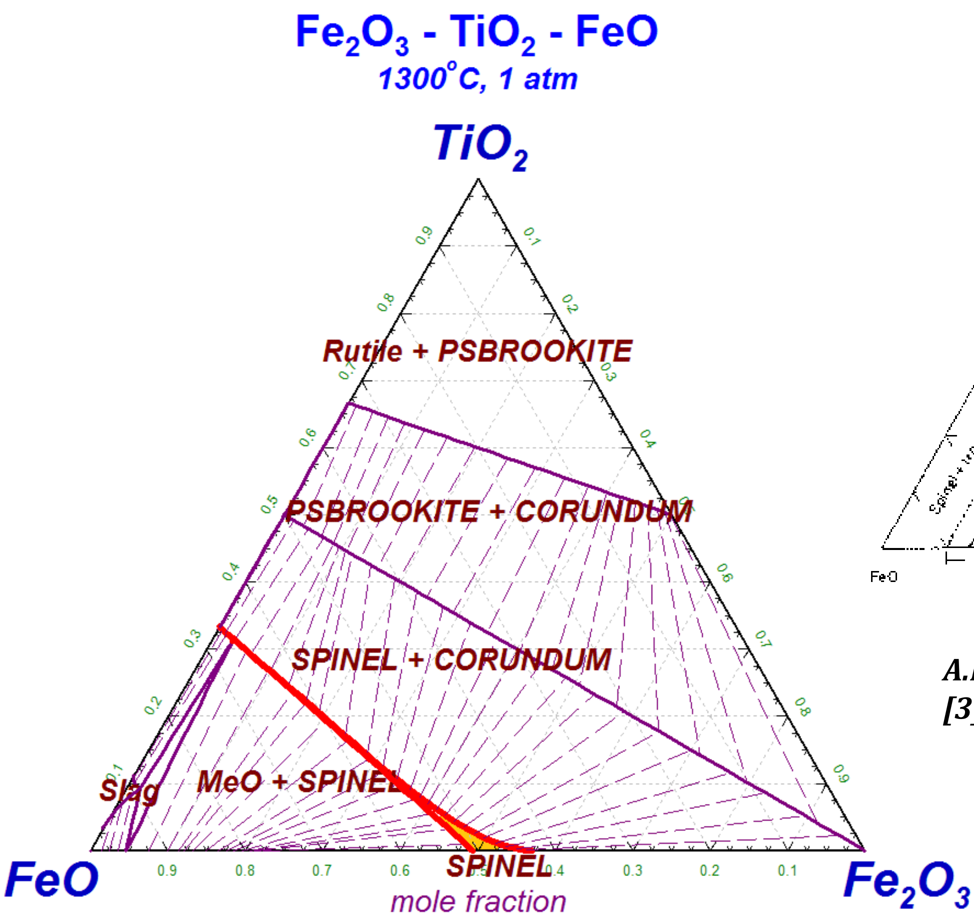
Spinel in Al_2O_3-MgO-TiO_2

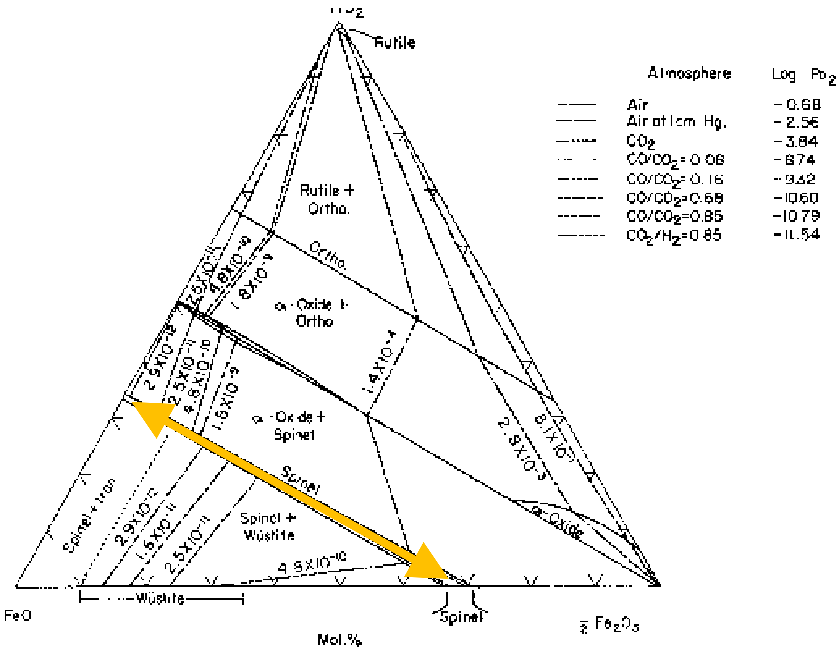






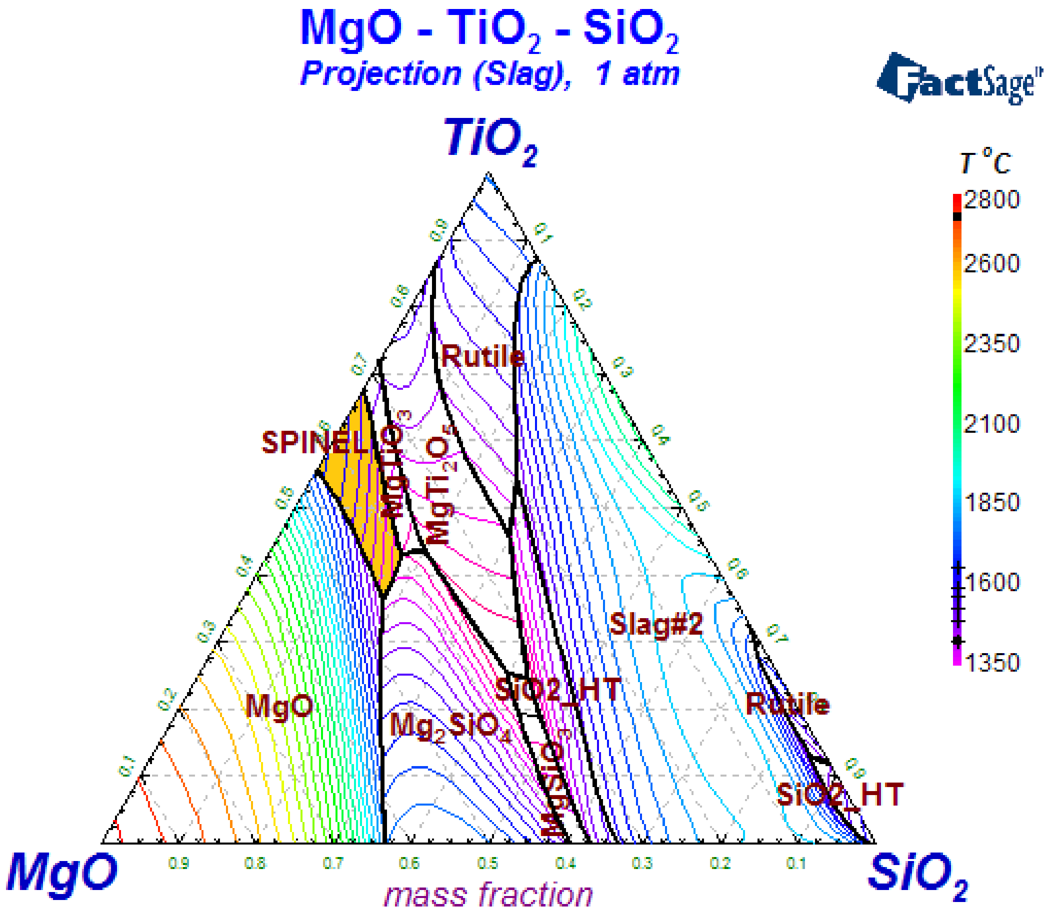
Isothermal section at 1300°C in $FeO-Fe_2O_3-TiO_2$

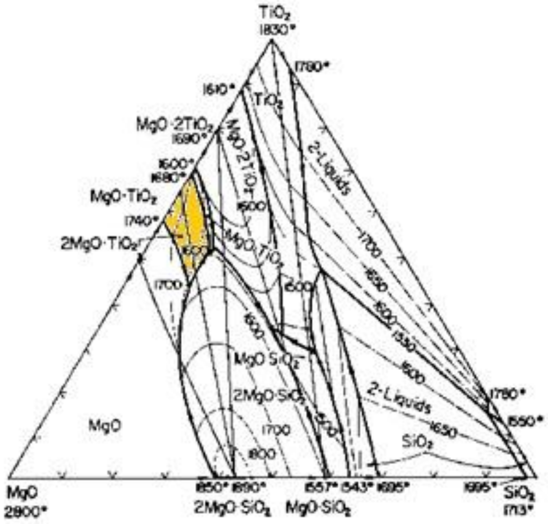




A.H. Webster, N.F.H. Bright, J. Am. Ceram. Soc., 44 [3], (1961), pp.110-116.

Liquidus surface in MgO-SiO_2-TiO_2





F. Massazza, E. Sirchia, Chim. Ind. (Milan), 40 [6], (1958), pp. 460-467.

Modelling of Titania Spinel

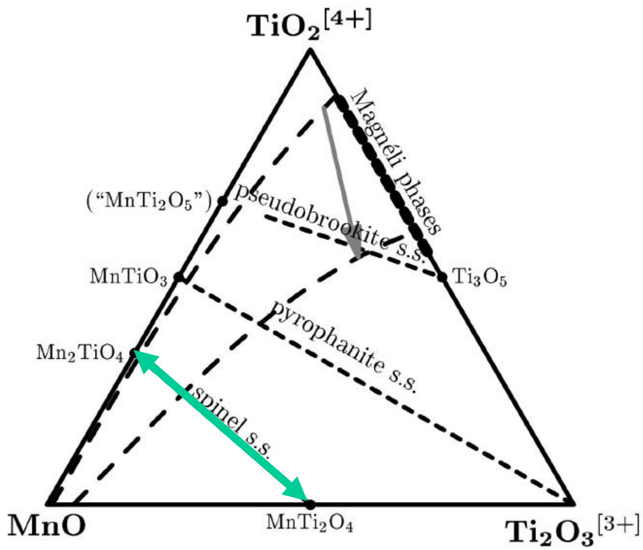
Titania Spinel

Ti^{+3}

(Fe^{+2},Fe^{+3},Mg^{+2}, Mn^{+2}, Ti^{+4})

(Al^{+3},Fe^{+2},Fe^{+3},Mg^{+2}, Mn^{+2},Mn^{+3},Ti^{+3},Va)$_2$ (O^{-2})$_4$ 40 Gibbs energies

Mg_2TiO_4, $MgTi_2O_4$, Mn_2TiO_4, $MnTi_2O_4$, Fe_2TiO_4



J.-B. Kang, H.-B. Lee, ISIJ Intern., 45 (2005), pp. 1543-1551.

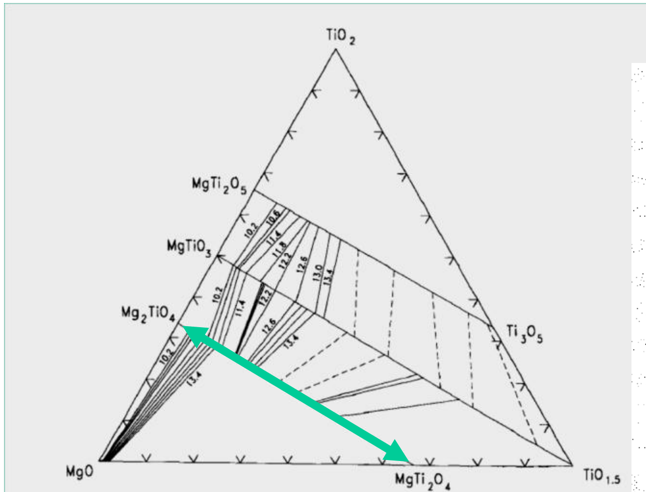
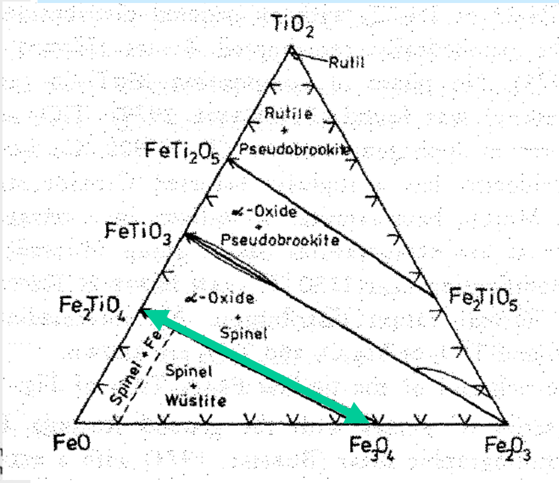


Fig. 1. Equilibrium tie-lines in the MgO-TiO$_2$-TiO$_{1.5}$ system at 1500°C. (Composition in mole%). Solid lines experimental. Dashed lines calculated. Numbers written on th tie-lines are [$-\log f_{O_2}$ (bar)].

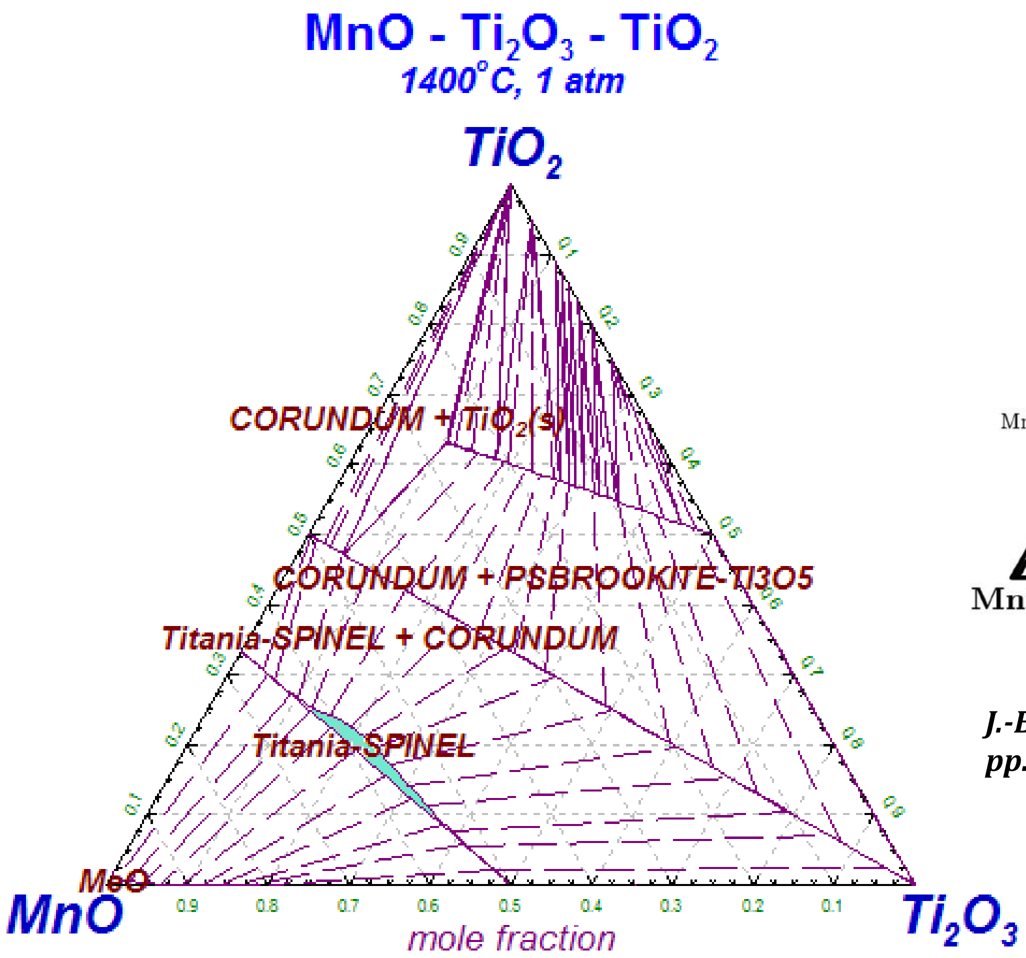
A.D. Pelton, G. Eriksson, D. Krajewski, M.Göbbels, E. Woermann, Z. Phys. Chem., 207 (1998), pp. 163-180.

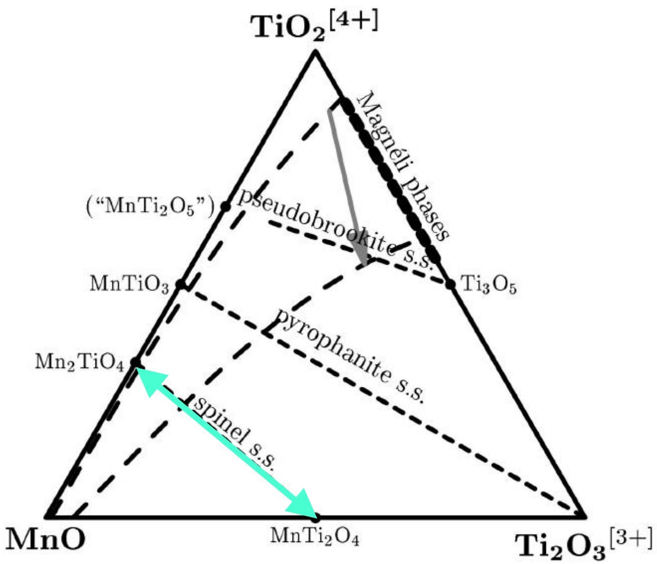
$FeTi_2O_4$ does not exist



B. Leusmann, N. Jb. Miner. Mh., 12 (1979), pp. 556-559.

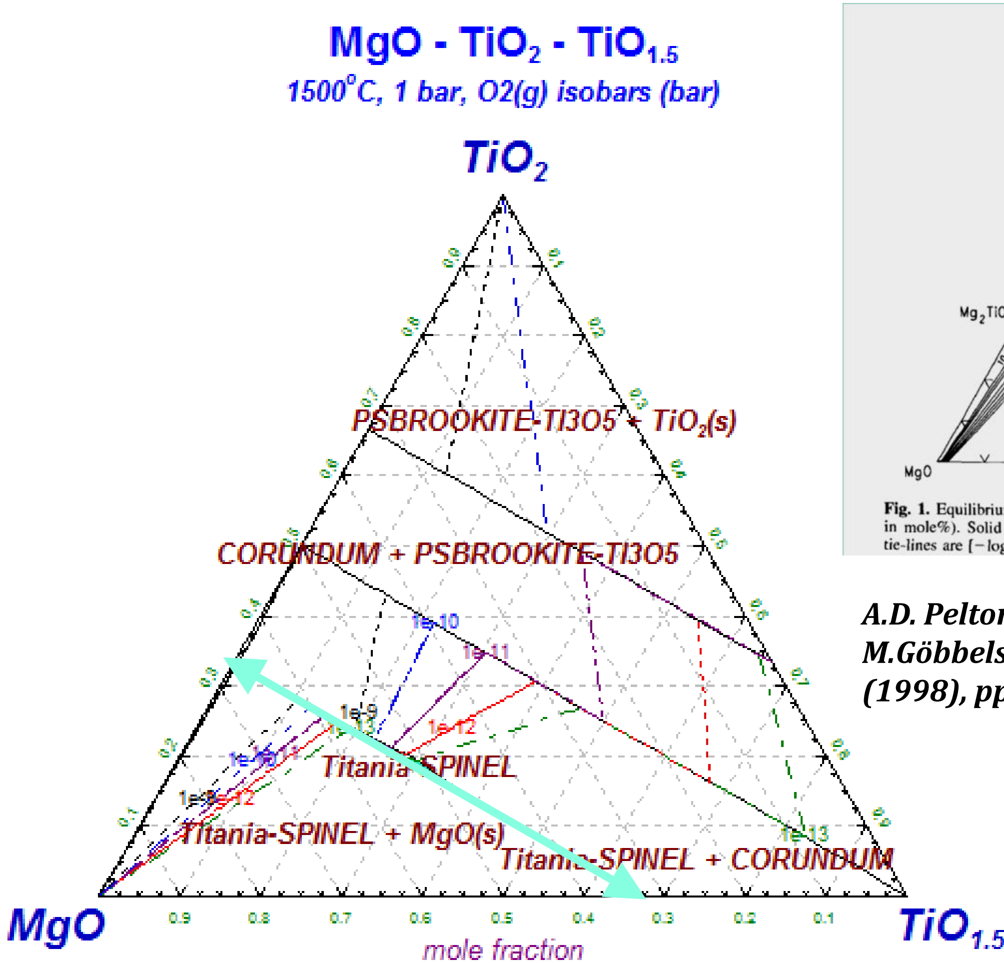
Isothermal section at 1400ºC in $MnO-TiO_2-Ti_2O_3$





J.-B. Kang, H.-B. Lee, ISIJ Intern., 45 (2005), pp. 1543-1551.

Isothermal section at 1500°C in MgO-TiO_2-Ti_2O_3



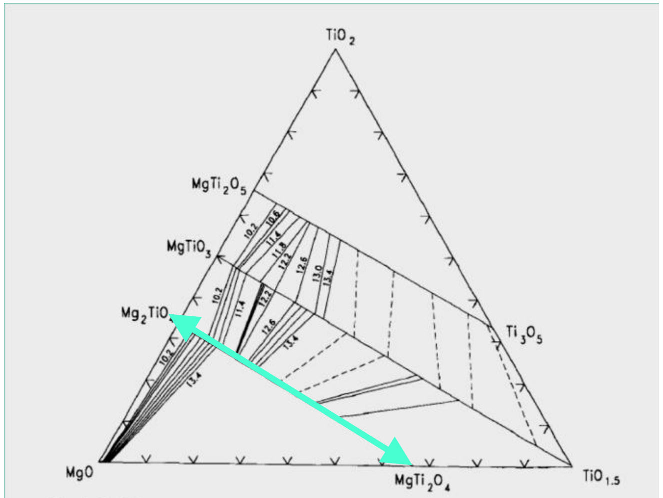
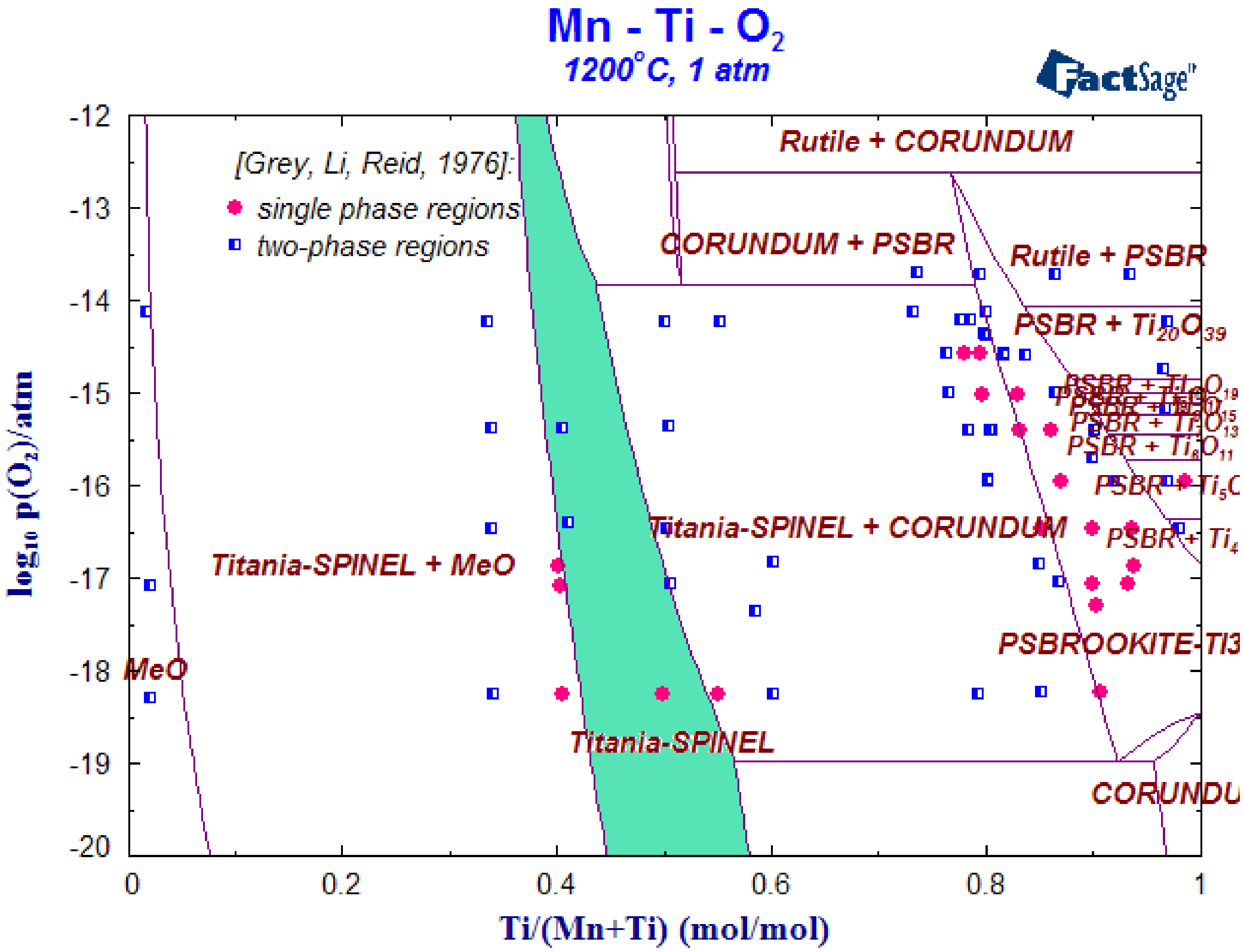


Fig. 1. Equilibrium tie-lines in the MgO-TiO_2-$TiO_{1.5}$ system at 1500°C. (Compositions in mole%). Solid lines experimental. Dashed lines calculated. Numbers written on the tie-lines are $[-\log f_{O_2}$ (bar)].

A.D. Pelton, G. Eriksson, D. Krajewski, M.Göbbels, E. Woermann, Z. Phys. Chem., 207 (1998), pp. 163-180.

Isothermal section at 1200ºC in MnO-TiO_2-Ti_2O_3

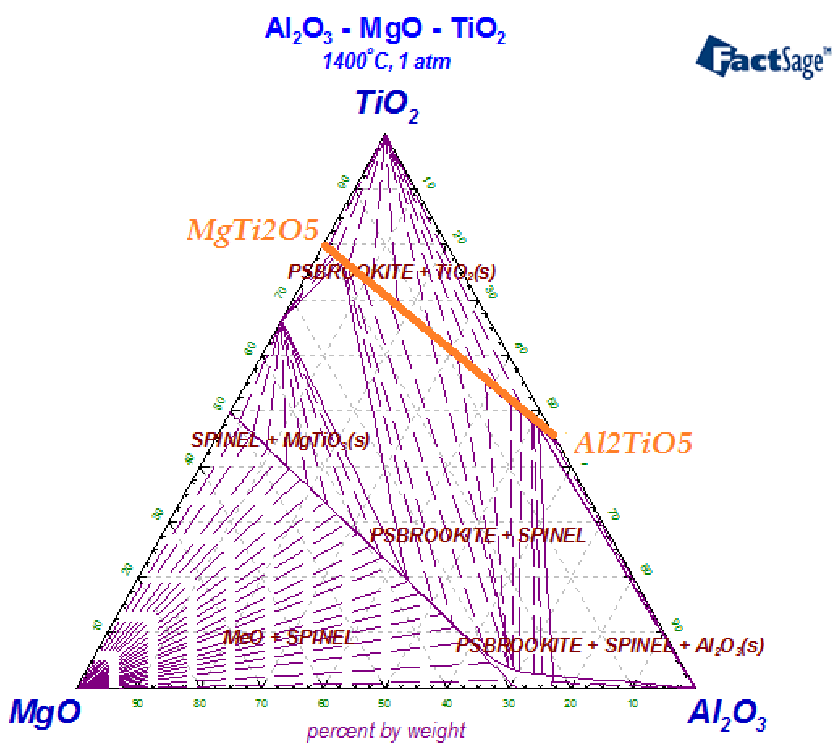


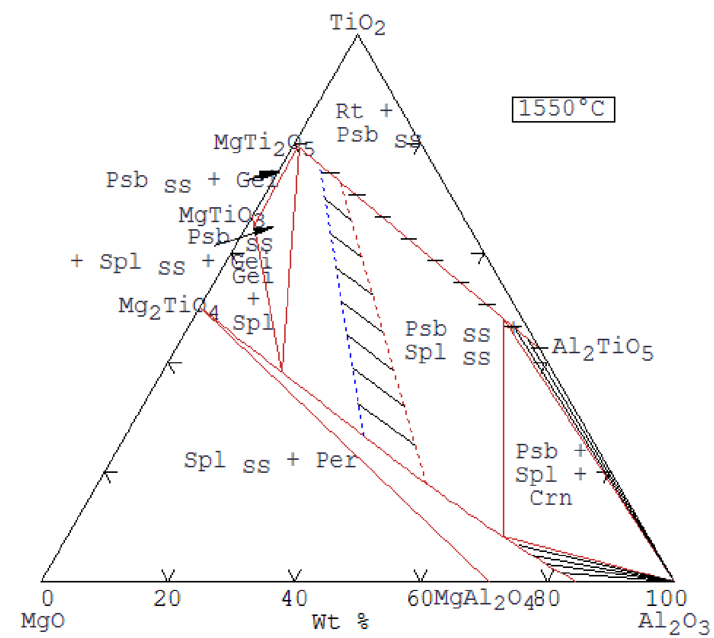
Pseudobrookite in Al_2O_3-MgO-TiO_2

***Pseudobrookite** – solid solution phase*

$(Al,Mg,Mn,Fe,Ti)_1(Al,Fe,Ti)_1(Ti)_1(O)_5$ with end-members:

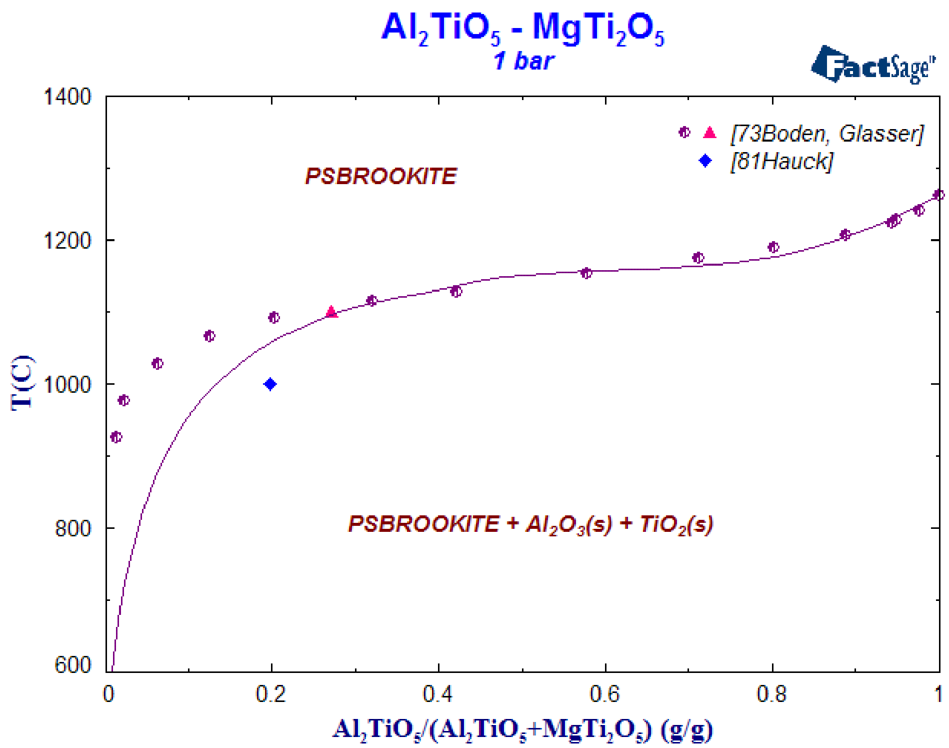
Ti_3O_5	Al_2TiO_5	$MgTi_2O_5$	$FeTi_2O_5$	Fe_2TiO_5

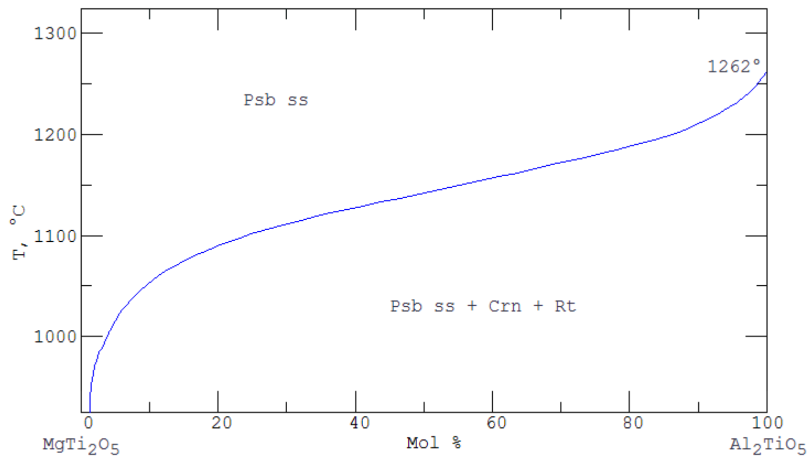




P. Boden, F.P. Glasser, Trans. J. Br. Ceram. Soc., 72[5], (1973), pp. 215-220.

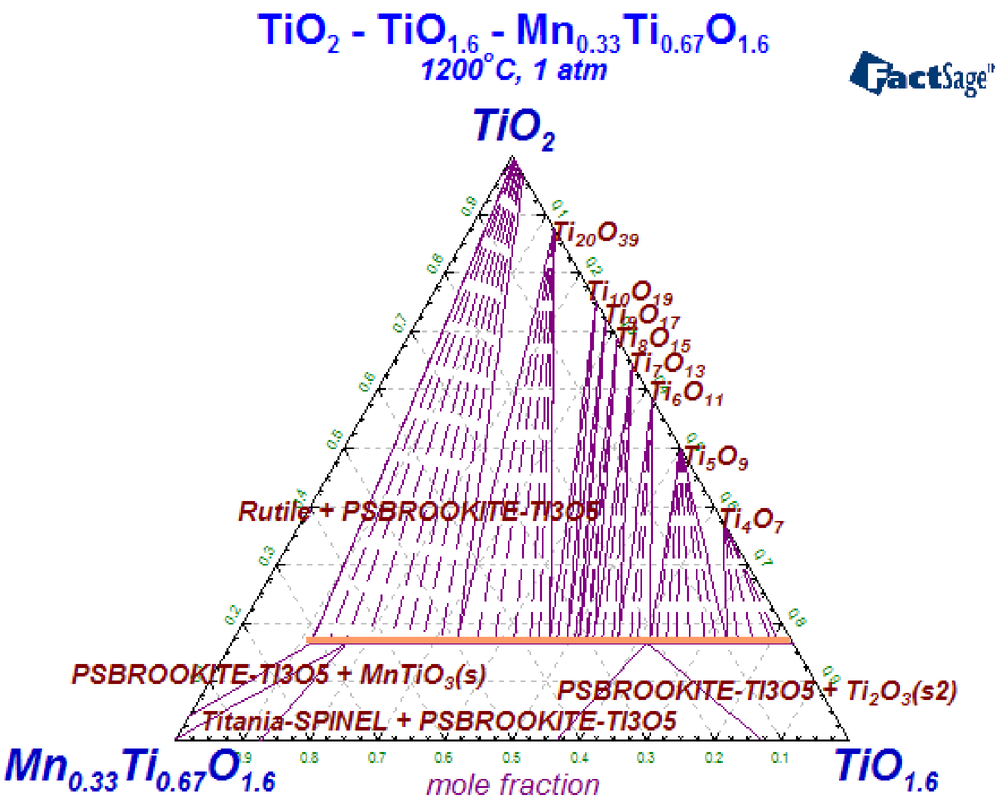
Isopleth Al_2TiO_5-$MgTi_2O_5$ in Al_2O_3-MgO-TiO_2

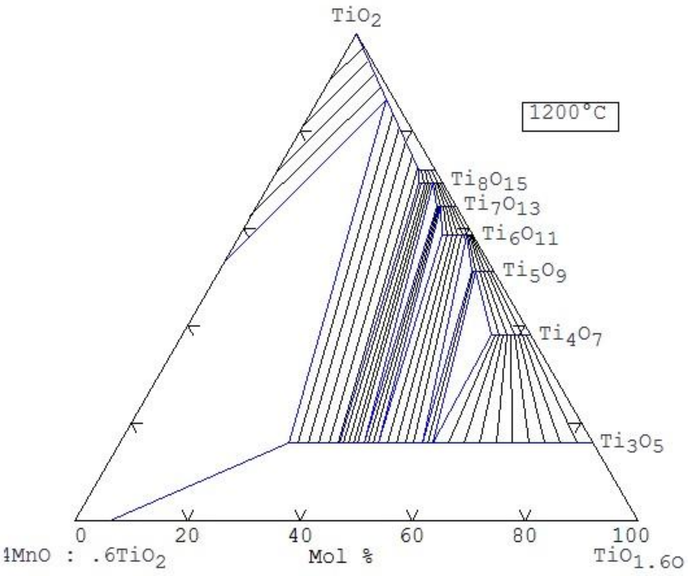




P. Boden, F.P. Glasser, Trans. J. Br. Ceram. Soc., 72[5], (1973), pp. 215-220.

Isothermal section at 1200ºC in $MnO\text{-}Ti_2O_3\text{-}TiO_2$

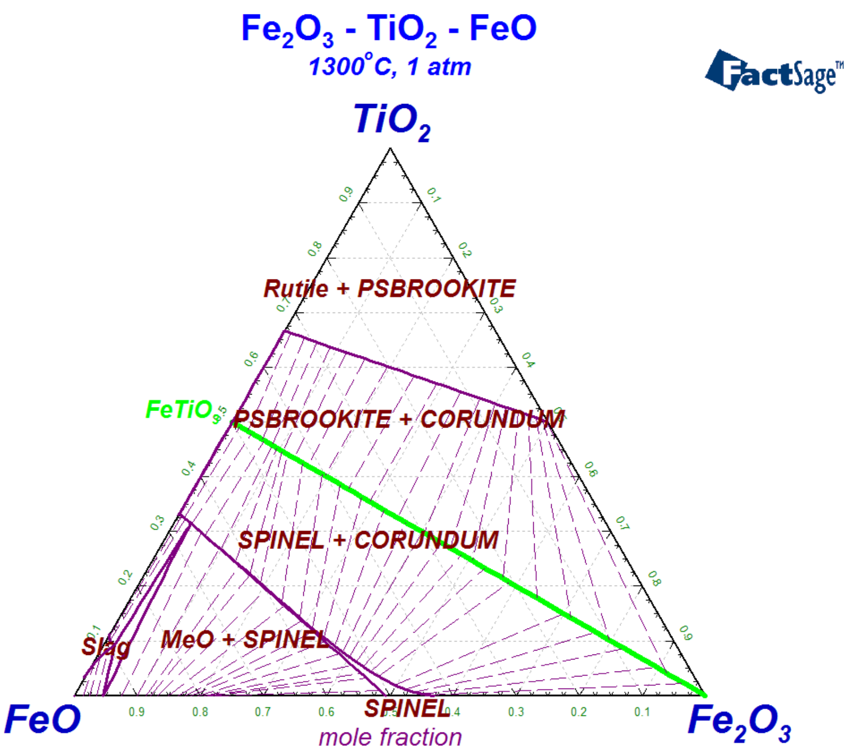


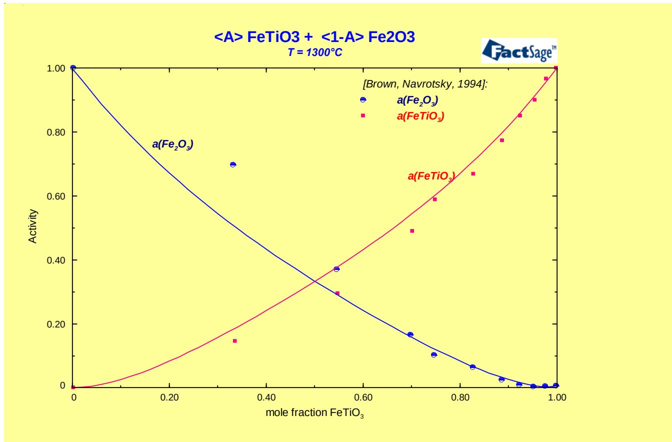


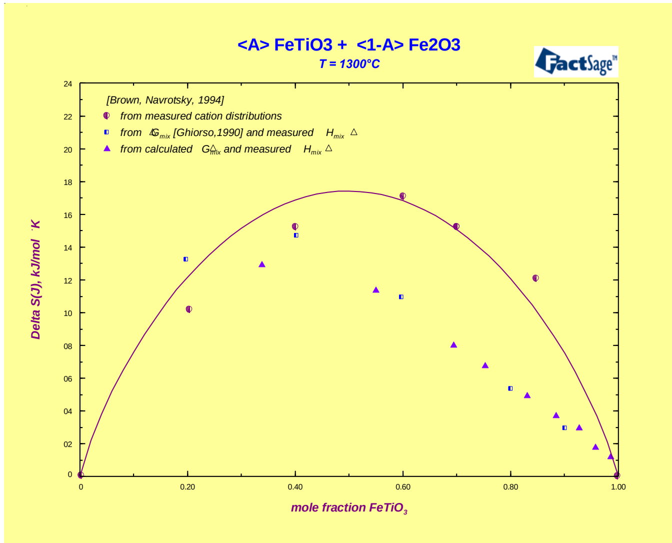
I.E. Grey, C. Li, A.F. Reid, J. Solid State Chem., 17 [4], (1976), pp. 343-352.

Corundum in $FeO-TiO_2-Fe_2O_3$

Corundum ($\underline{Al^{+3}}$, Cr^{+2}, $\underline{Cr^{+3}}$, $\underline{Fe^{+3}}$, $\underline{Mn^{+3}}$, $\underline{Ti^{+3}}$, $\underline{Fe_{0.5}Ti_{0.5}}^{+3}$, $\underline{Mg_{0.5}Ti_{0.5}}^{+3}$, $\underline{Mn_{0.5}Ti_{0.5}}^{+3}$)$_2$($Cr^{+3}$, Va)$_1$($O^{-2}$)$_3$

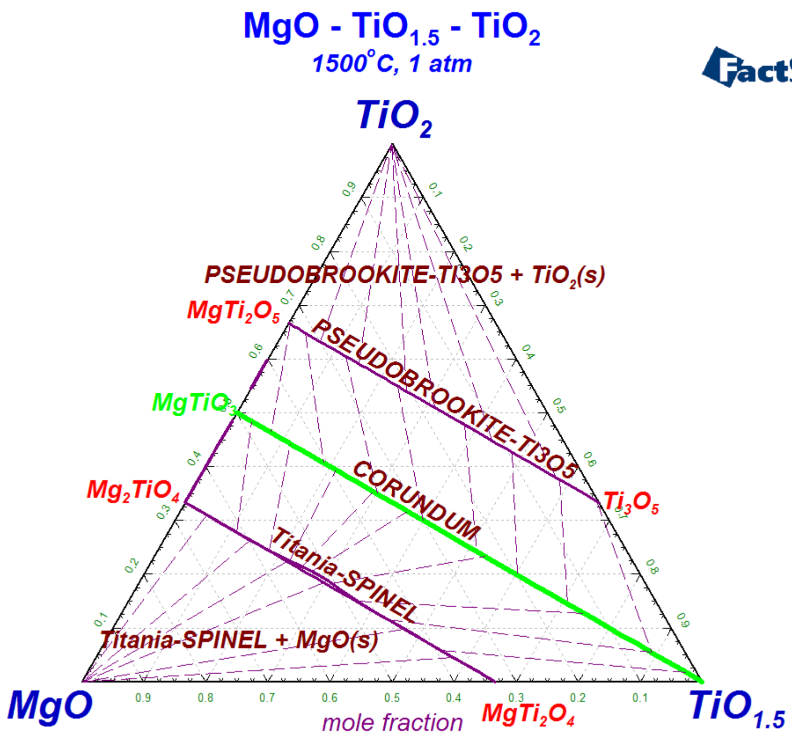


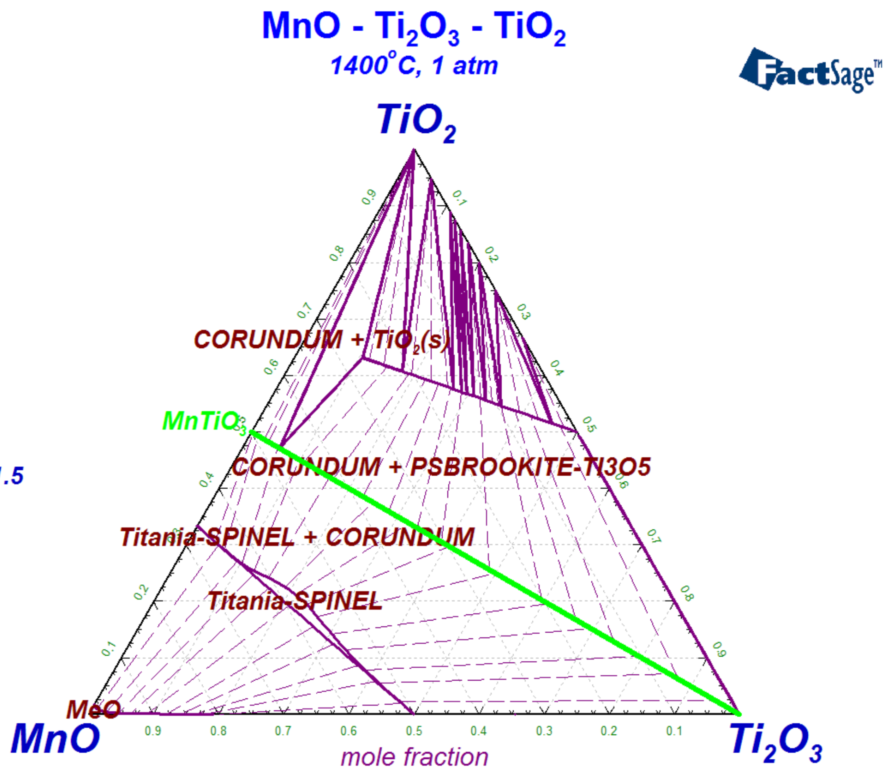




Corundum in MgO-TiO_2-Ti_2O_3 and MnO-TiO_2-Ti_2O_3

GTT-Technologies





Conclusions

- The liquid phase in all subsystems was evaluated using associate species model (two cations per species).
- All systems were assessed using experimental phase diagram information.
- 12 binaries and 10 ternary systems were described.
- The 39 stoichiometric phases containing Ti were incorporated.
- The solubility ranges of 14 solid solution phases containing Titanium were described using available experimental data.

Thanks for your attention