Addition of MeS and MnO_x to the GTT Oxide database

GTT-Technologies

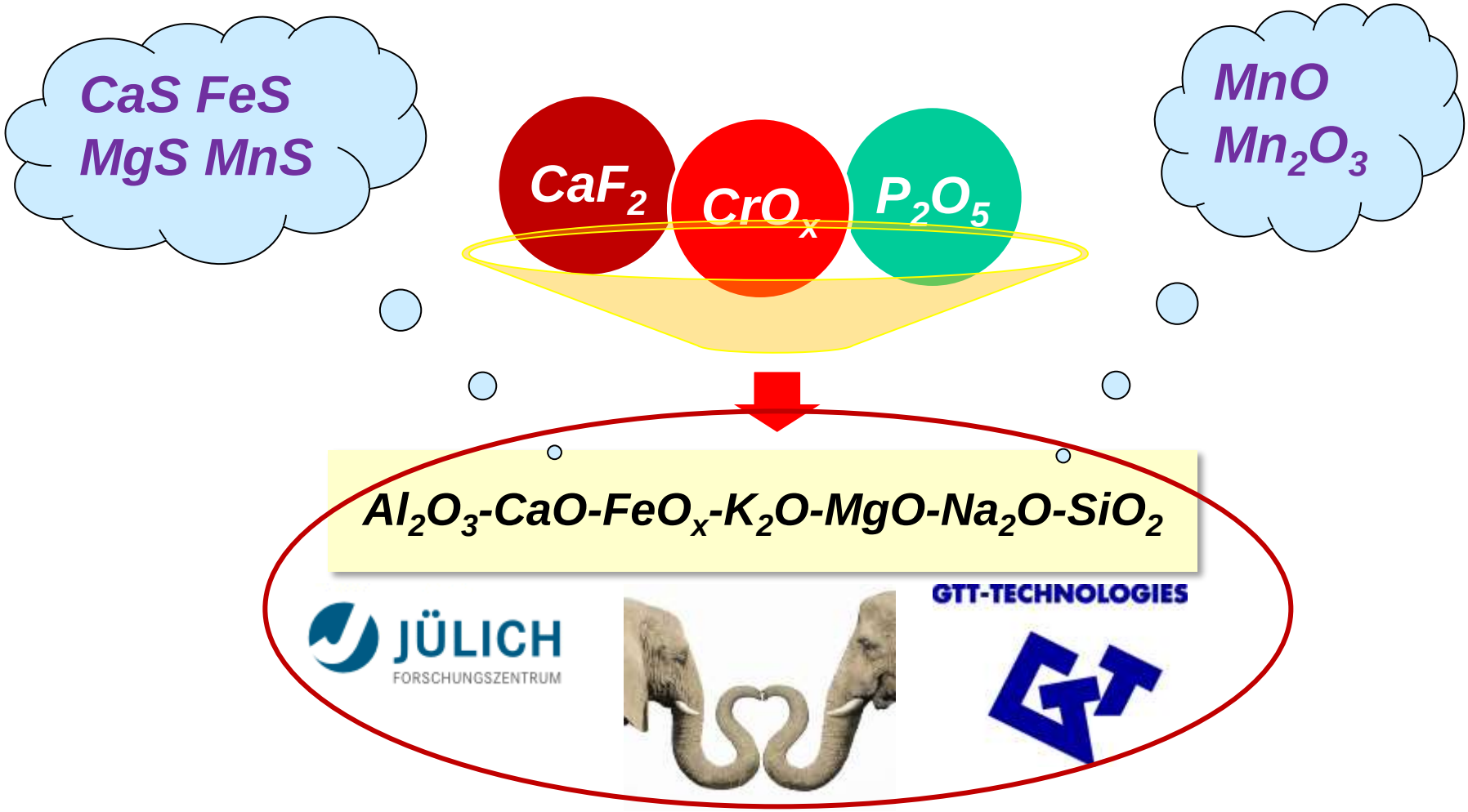
GTT-Workshop, 3-5. Juli 2013, Herzogenrath

Klaus Hack, Tatjana Jantzen

Contents of presentation

- Introduction
- Addition of MeS
- Addition of MnO_x
- Conclusions
- Future developments

GTT oxide database



Sulphur in oxide glasses

Sulphur

Natural minerals may contain substantial quantities of sulphur.

Sulphide glasses can be used for high refractory index materials.

Sulphur species are present in radioactive and toxic wastes.

Sulphur added to glasses as sulphate can be used as refining agent, as sulphide gives amber colour.

Addition of MeS

- Introduction

- The Me-S phase diagrams (Me= Ca, Fe, Mg, Mn)
- The Me_1O-Me_2S systems
- The Me_1S-Me_2S phase diagram

- The ternary Fe-O-S system
- The ternary Al_2O_3 – CaO - CaS system
- The ternary CaO - CaS - SiO_2 system
- The ternary CaS – FeS - MgS system

Modelling of binary S-containing phases

System	Phase	Description	Used data
Ca-S	Liquid	(Ca, CaS, S)	proposed by GTT
Fe-S	Liquid	(Fe, FeS, S)	Fe-FeS - Steel database, FeS-S - optimized by GTT
Mg-S	Liquid	(Mg, MgS, S)	proposed by GTT
Mn-S	Liquid	(Mn, MnS, S)	Steel database
CaS-FeS	Oldhamite	(Ca, Fe)(S)	modelled by GTT
CaS-MgS	Oldhamite Niningerite	(Ca, Mg)(S) (Ca, Mg)(S)	modelled by GTT
FeS-MgS	Troilite-HT Niningerite	(Fe, Mg)(S) (Fe, Mg)(S)	modelled by GTT

Metal oxide - Metal sulphide phase diagram

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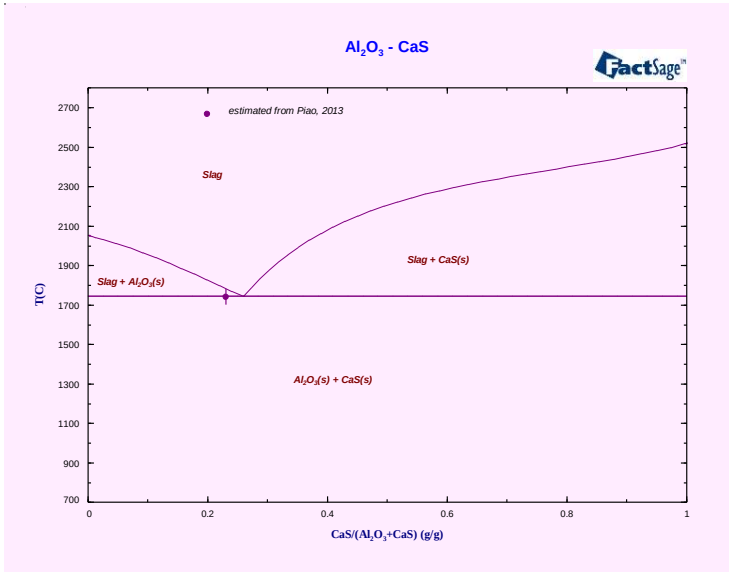
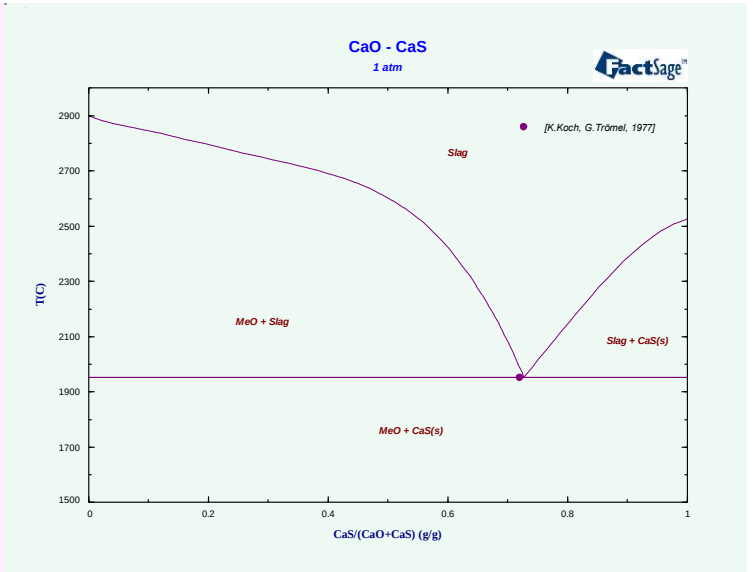
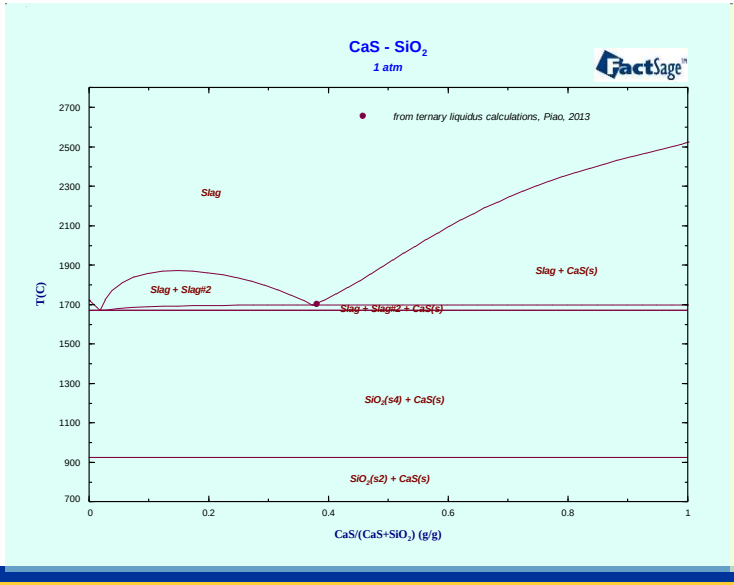
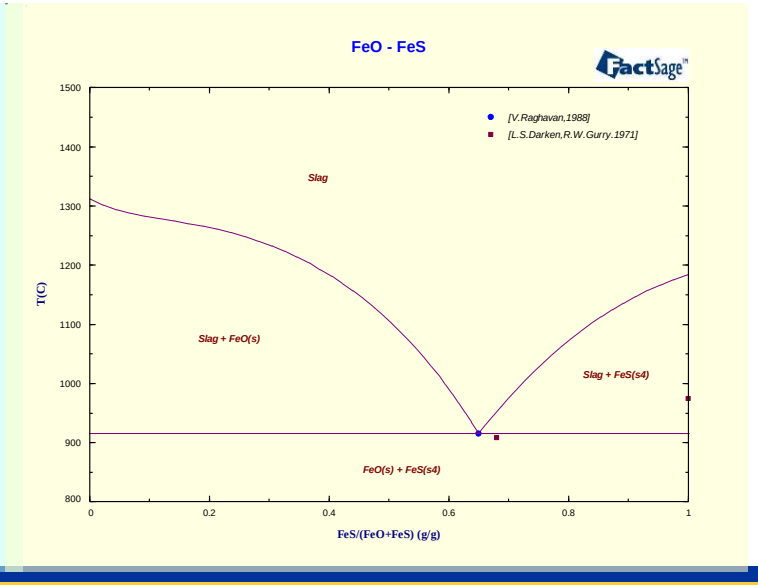
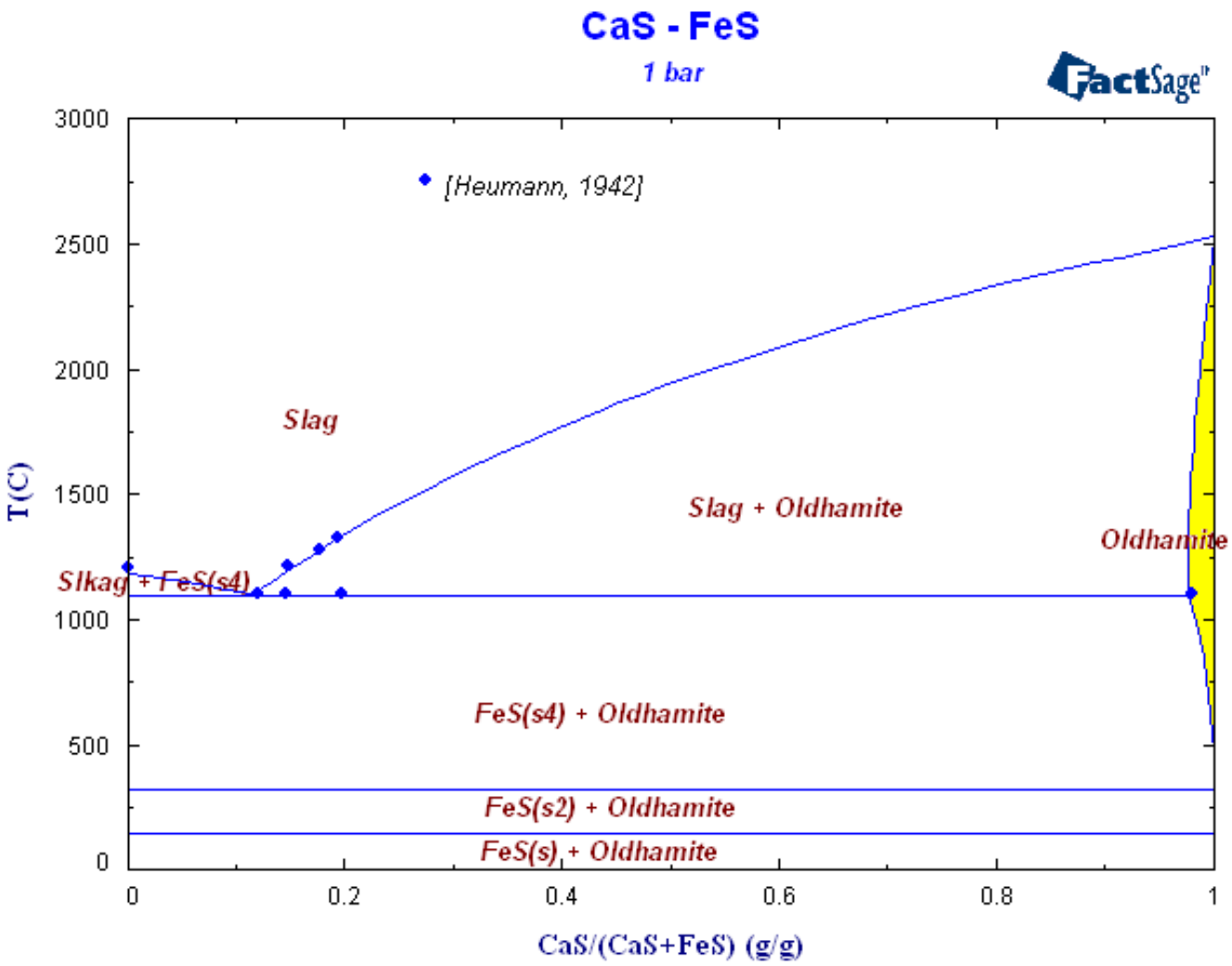




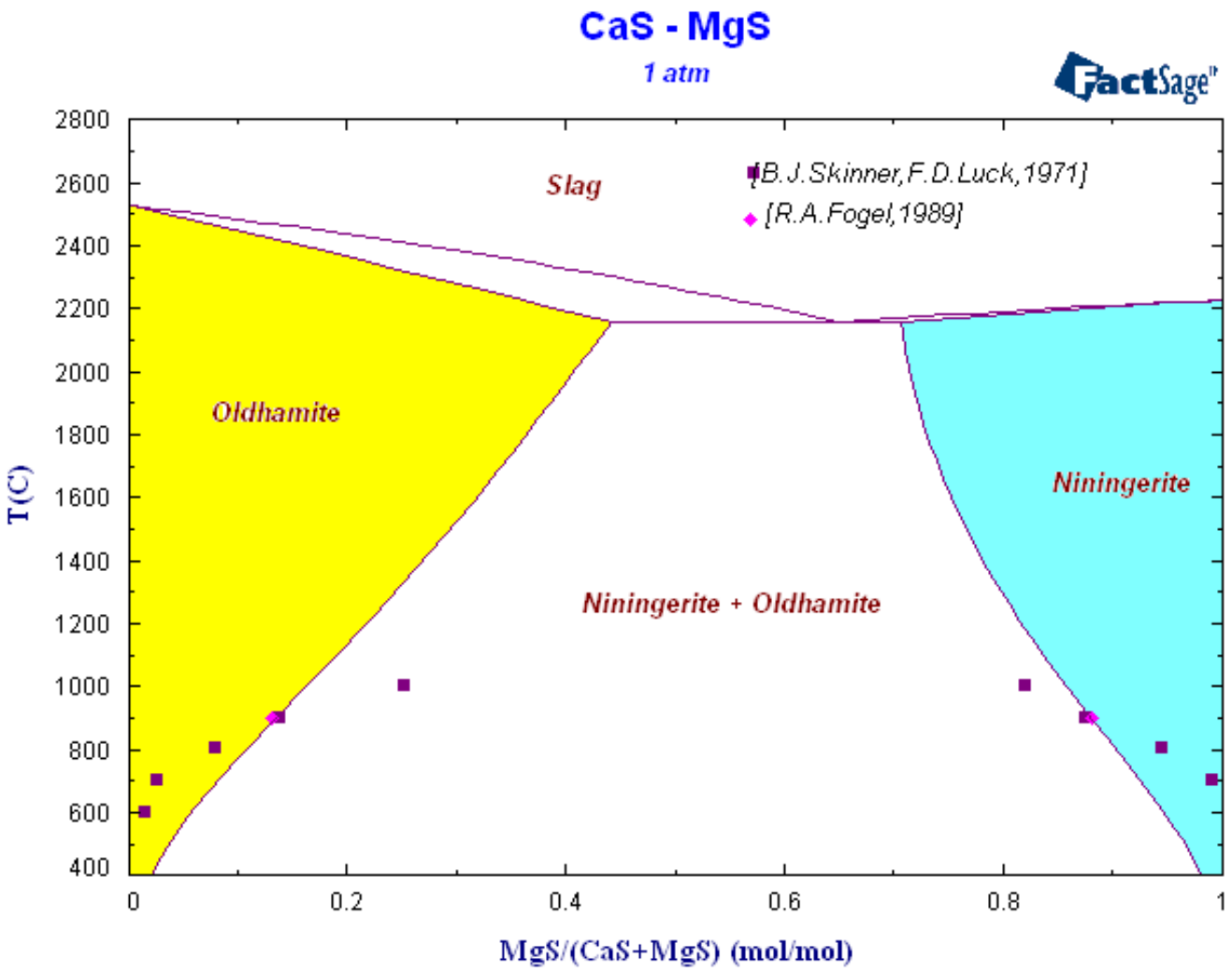




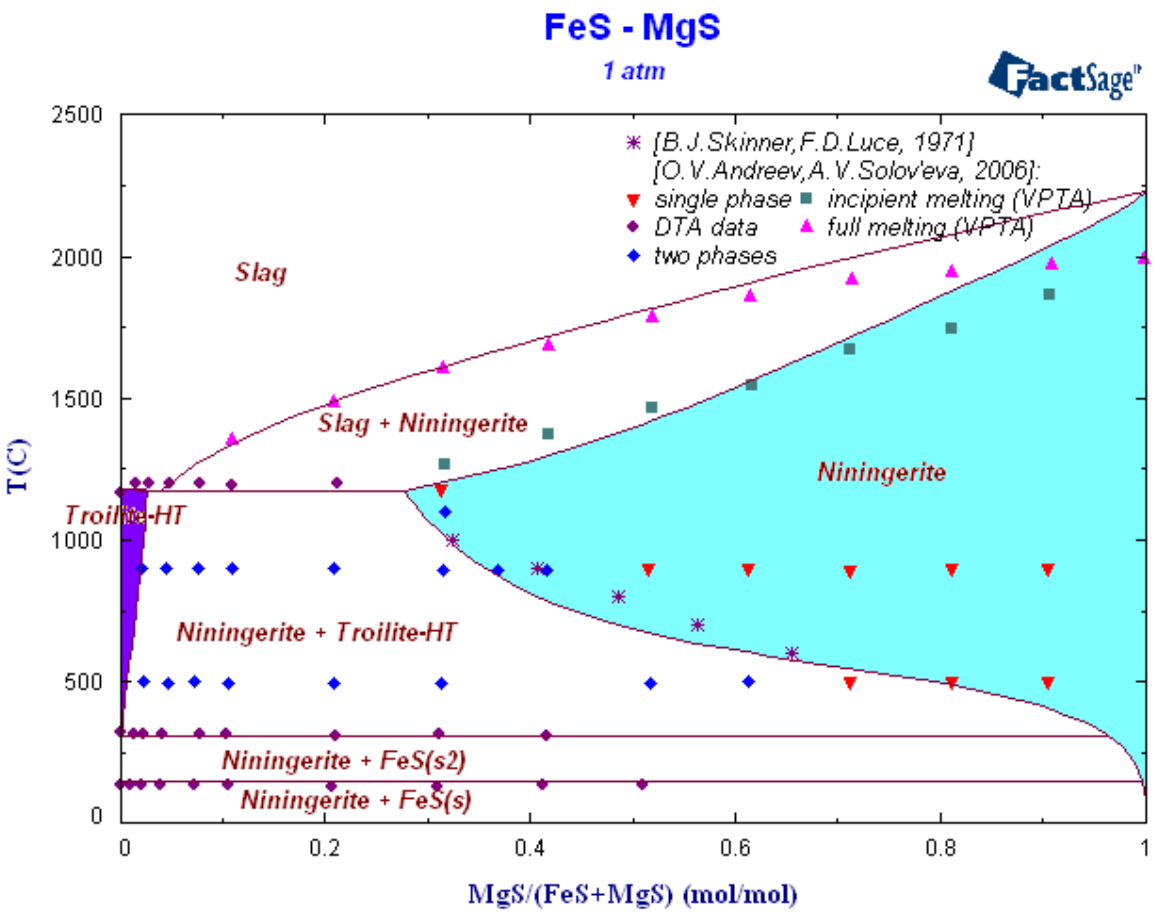
CaS-FeS phase diagram

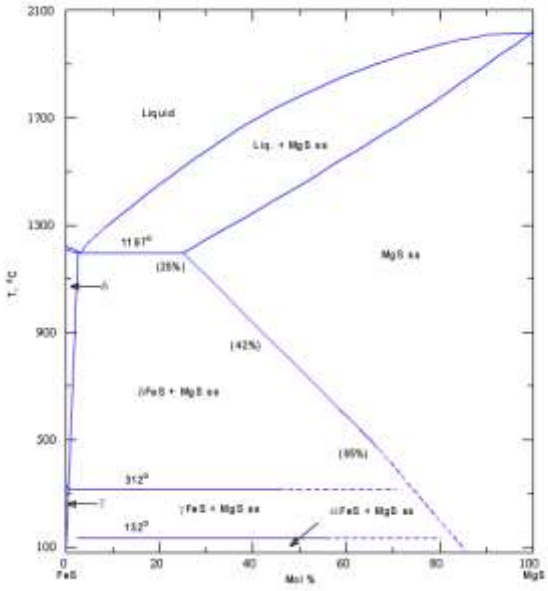


CaS-MgS phase diagram



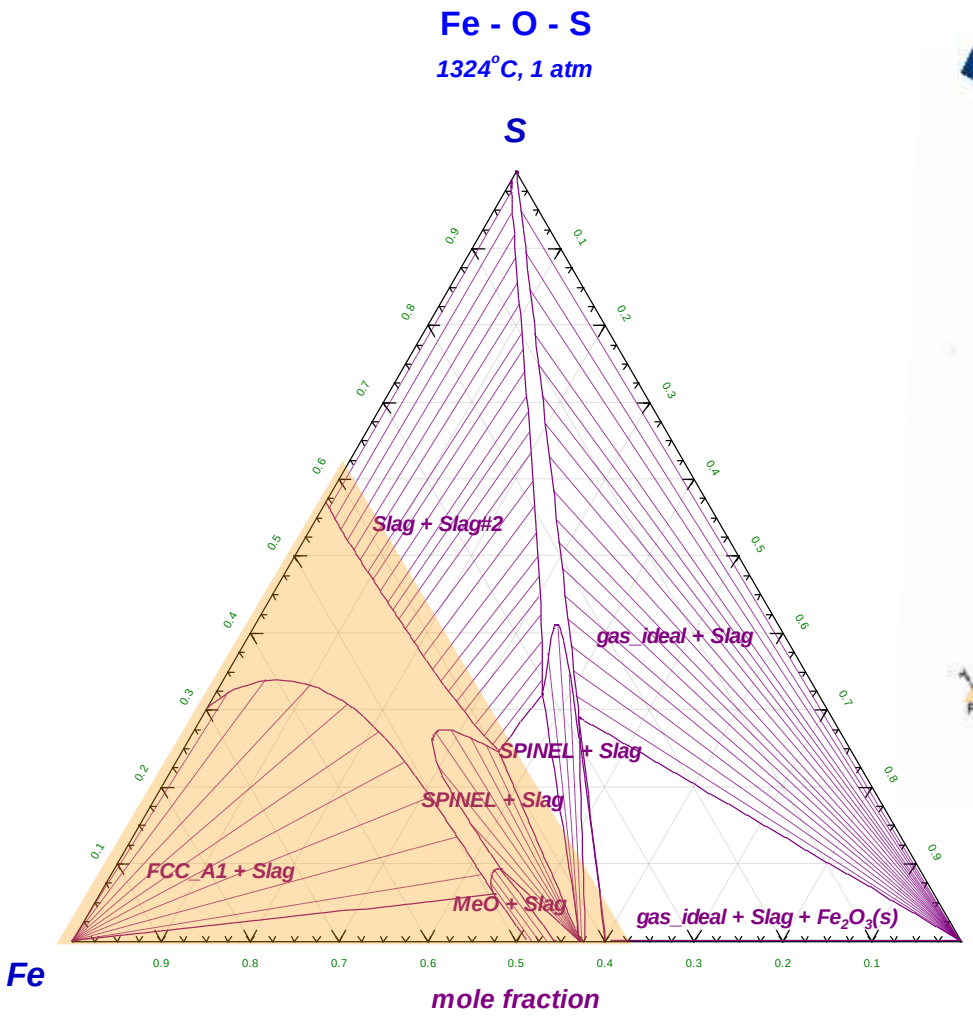
FeS-MgS phase diagram

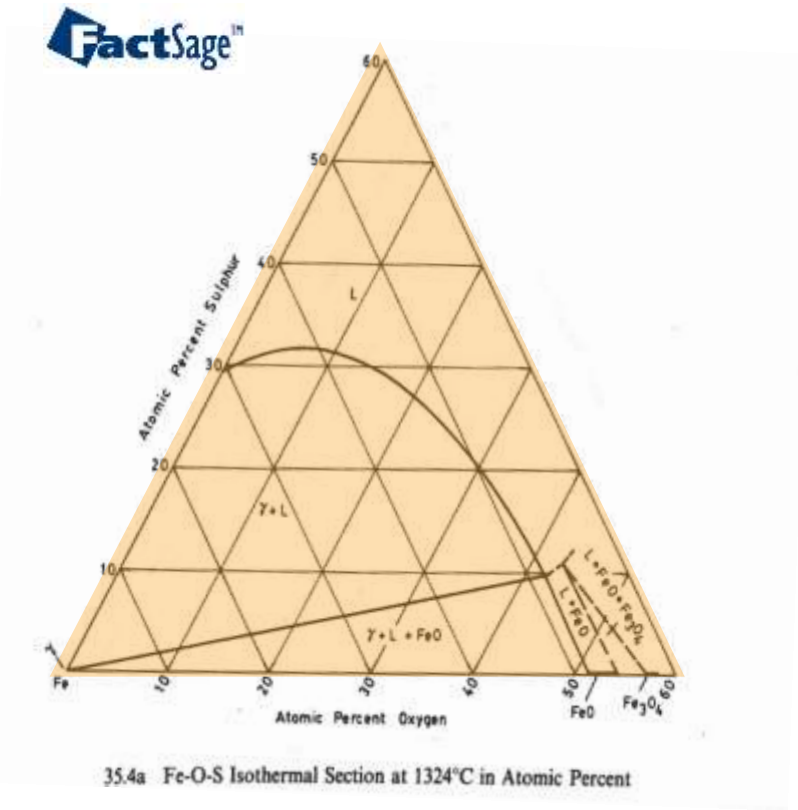




O. V. Andreev, A. V. Solov'eva, and T. M. Burkhanova, Zh. Neorg. Khim., 51 [11]
1938-1941 (2006); Russ. J. Inorg. Chem. (Engl. Transl.), 51 [11] 1826-1828 (2006).

Isothermal section in Fe-O-S at 1324ºC

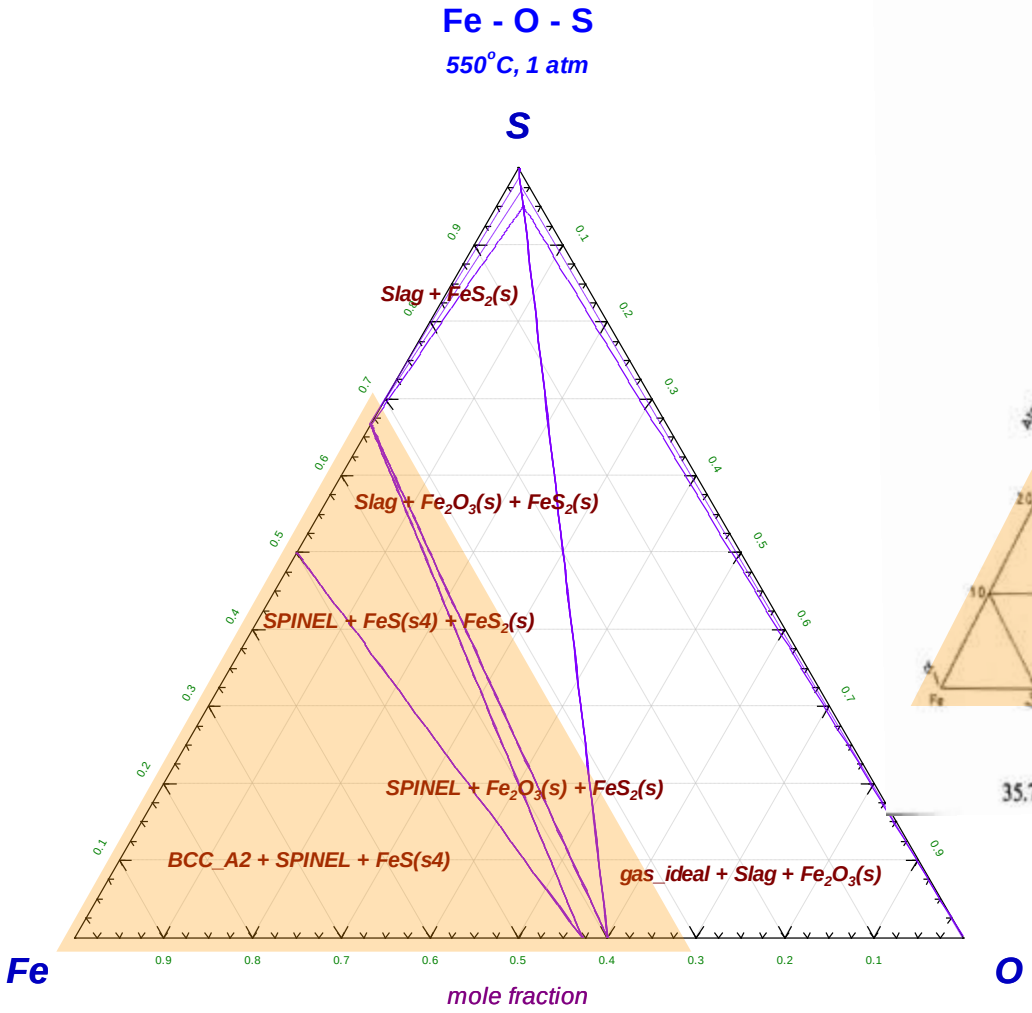


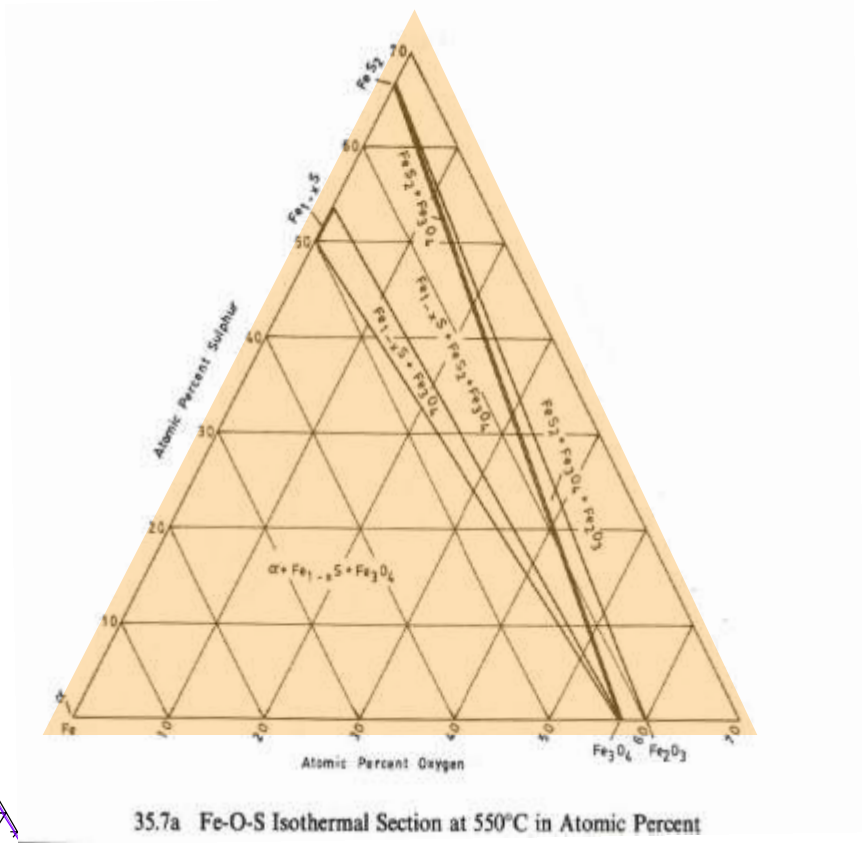


35.4a Fe-O-S Isothermal Section at 1324°C in Atomic Percent

V. Raghavan, Phase diagrams of Ternary Iron Alloys, Part 2, Ternary systems containing Iron and Sulphur, The Indian Institute of Metals, Calcutta,1988.

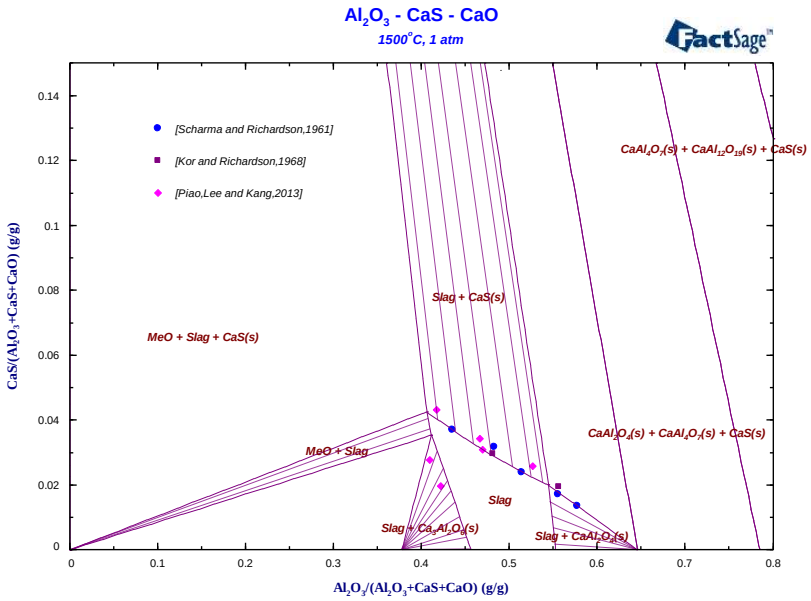
Isothermal section in Fe-O-S at 550ºC

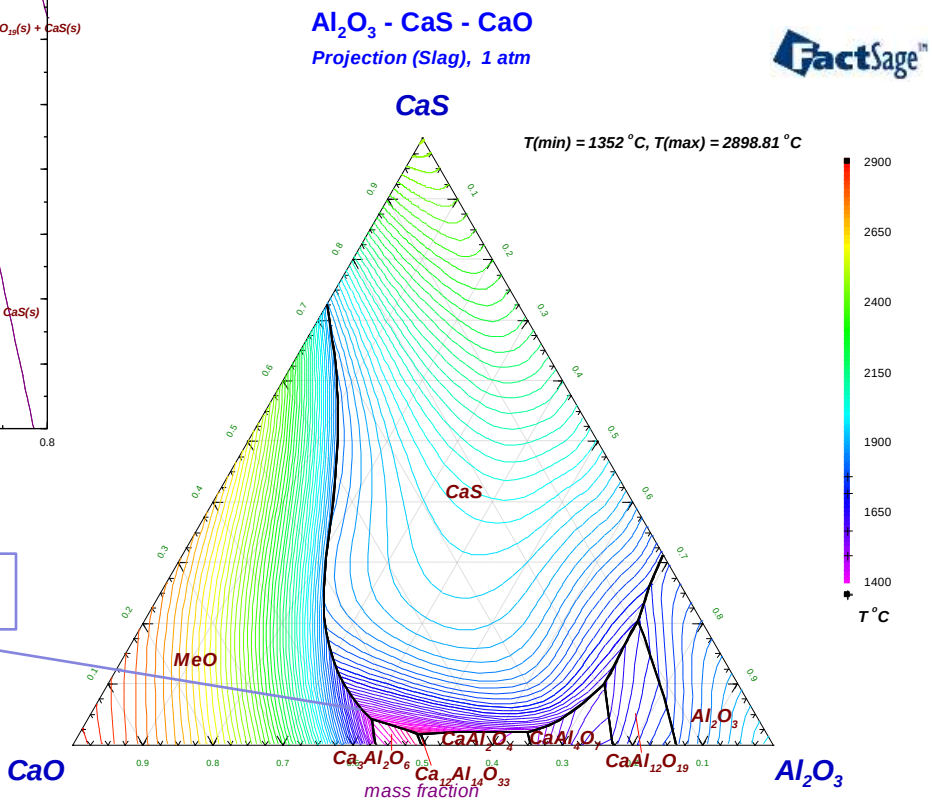




V. Raghavan, Phase diagrams of Ternary Iron Alloys, Part 2, Ternary systems containing Iron and Sulphur, The Indian Institute of Metals, Calcutta,1988.

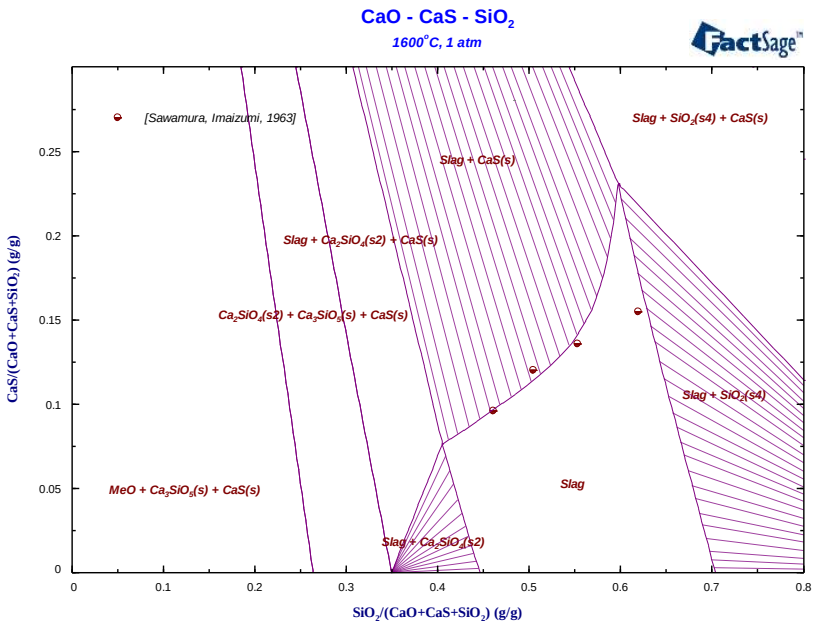
The Al_2O_3-CaO-CaS ternary system

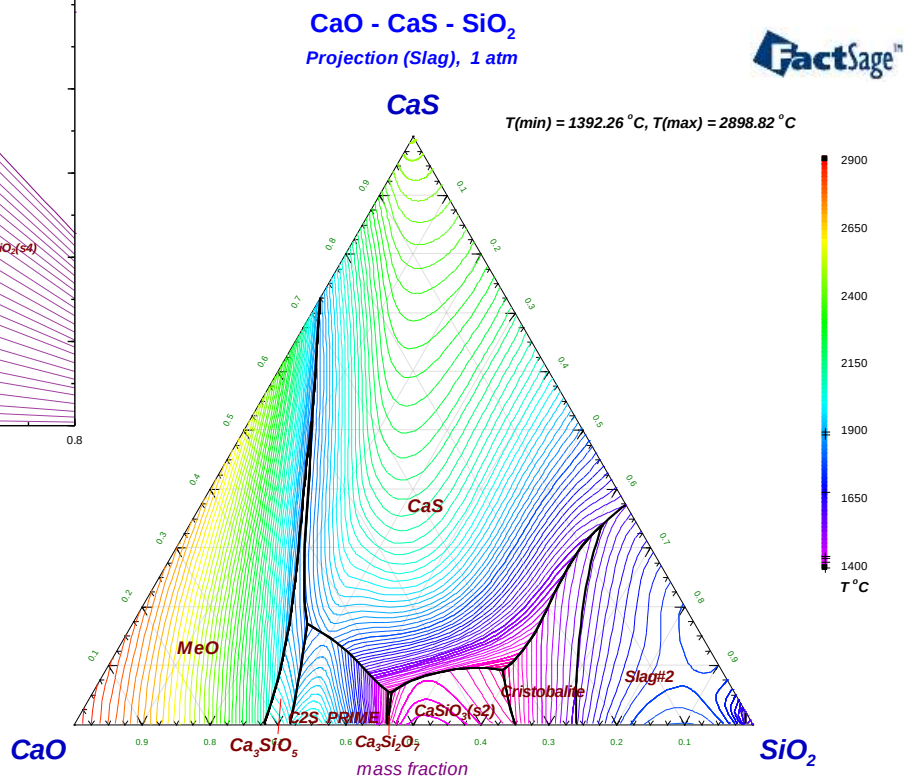




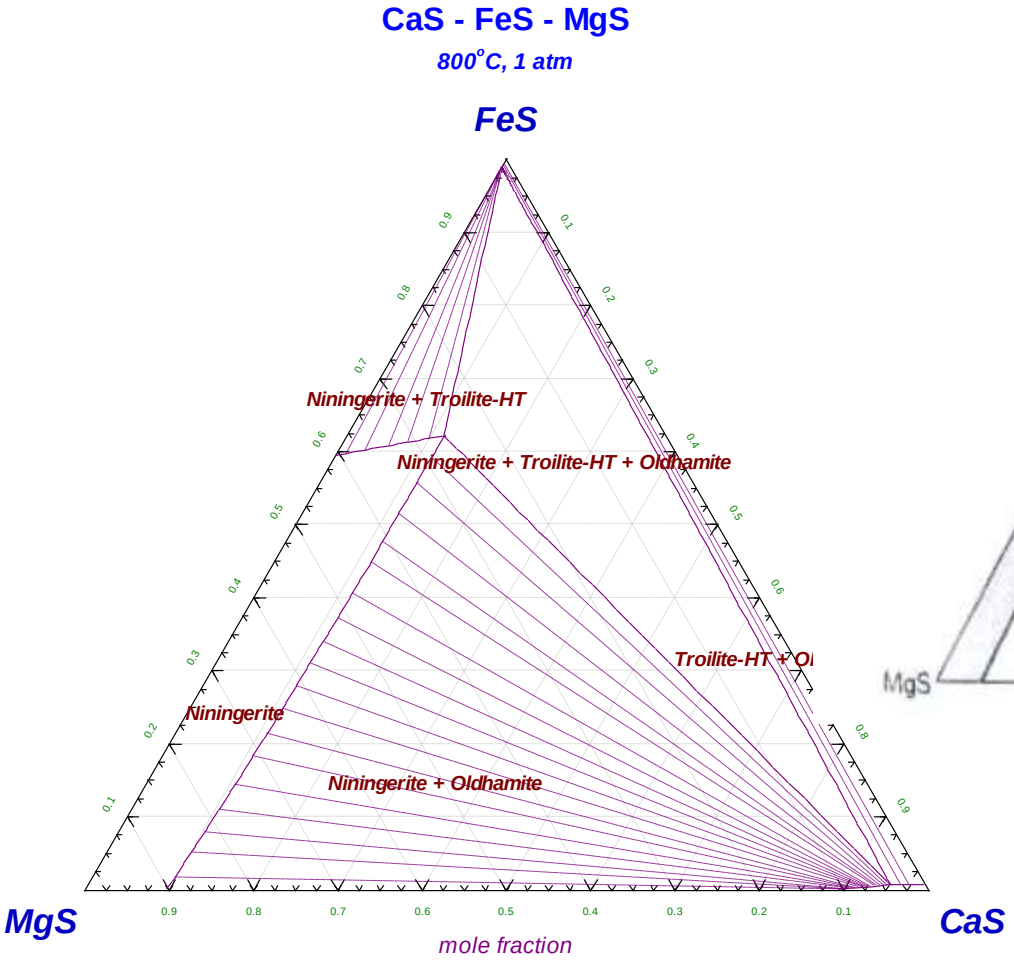
Calculated 1352 ° C
1350 ° C [Piao,2013]

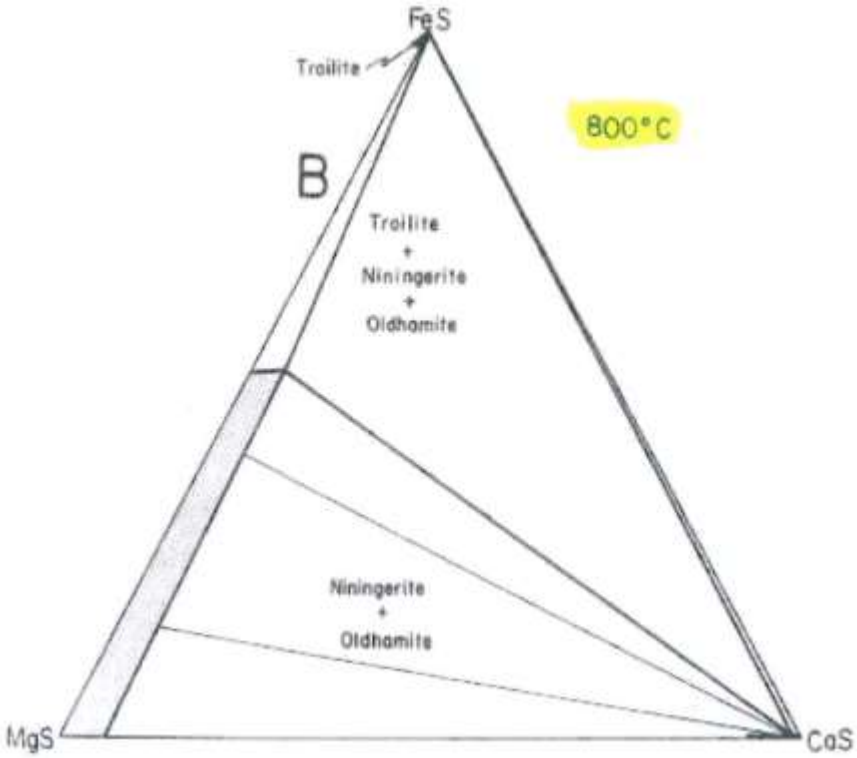
The CaO-CaS-SiO_2 ternary system





Isothermal section in CaS-FeS-MgS at 800ºC





B.J. Skinner, F.D. Luck, Amer. Mineral., Vol.56 (1971), pp. 1269-1296.

Addition of MnO_x (MnO + Mn, Mn_2O_3+O_2)

- The Mn-O binary system
- The Al_2O_3-MnO_x system
- The CaO-MnO_x system
- The CrO_x-MnO_x system
- The FeO_x-MnO_x system
- The MgO-MnO_x system
- The MnO_x-SiO_2 system

- The ternary CaO-FeO-MnO system
- The ternary CaO-MgO-MnO system
- The ternary MgO-MnO-SiO_2 system

Addition of MnO and Mn_2O_3

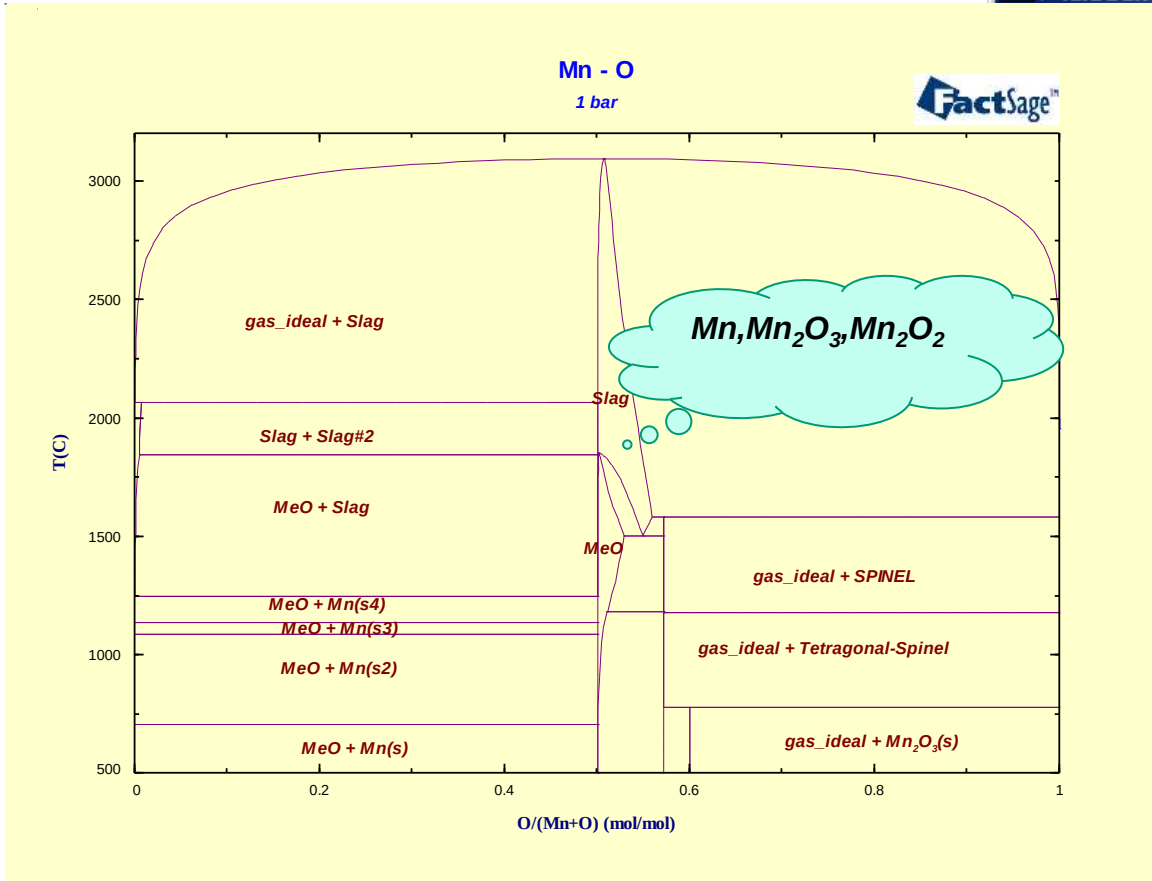
The associate species containing Mn were added in order to describe the liquid phase in the Al_2O_3-CaO-Cr_2O_3-FeO-Fe_2O_3-MgO-SiO_2 system containing MnO_x.

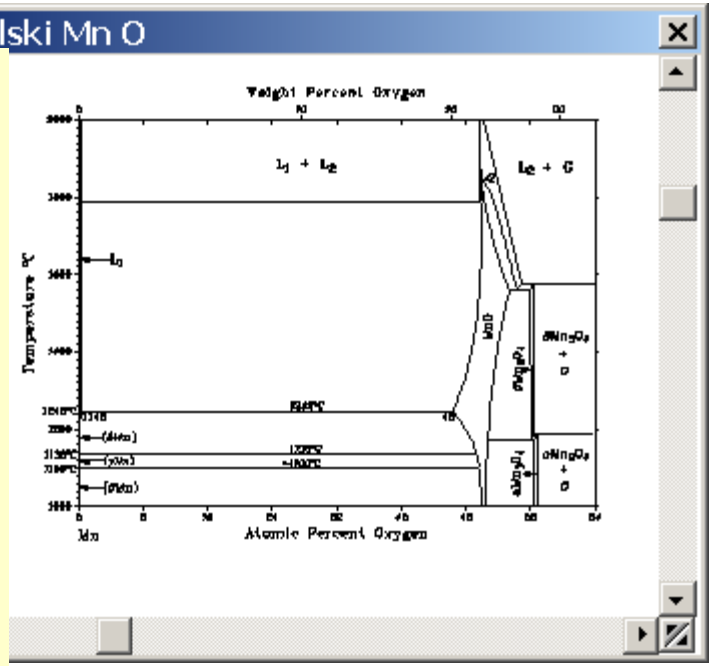
System	*Associate species*	*Description* MeO_x *: MnO (:MeO)*
Al_2O_3- MnO	Al_2MnO_4	1:1
Cr_2O_3 – MnO	Cr_2MnO_4	
Fe_2O_3 – MnO	Fe_2MnO_4	
MnO-SiO_2	$MnSiO_3$, Mn_2SiO_4 (like with Ca^{+2}, Fe^{+2} and Mg^{+2})	1:1 and 1:2
MgO-MnO-SiO_2	$MgMnSi_2O_6$	1:1:1

Modelling of Mn-containing phases

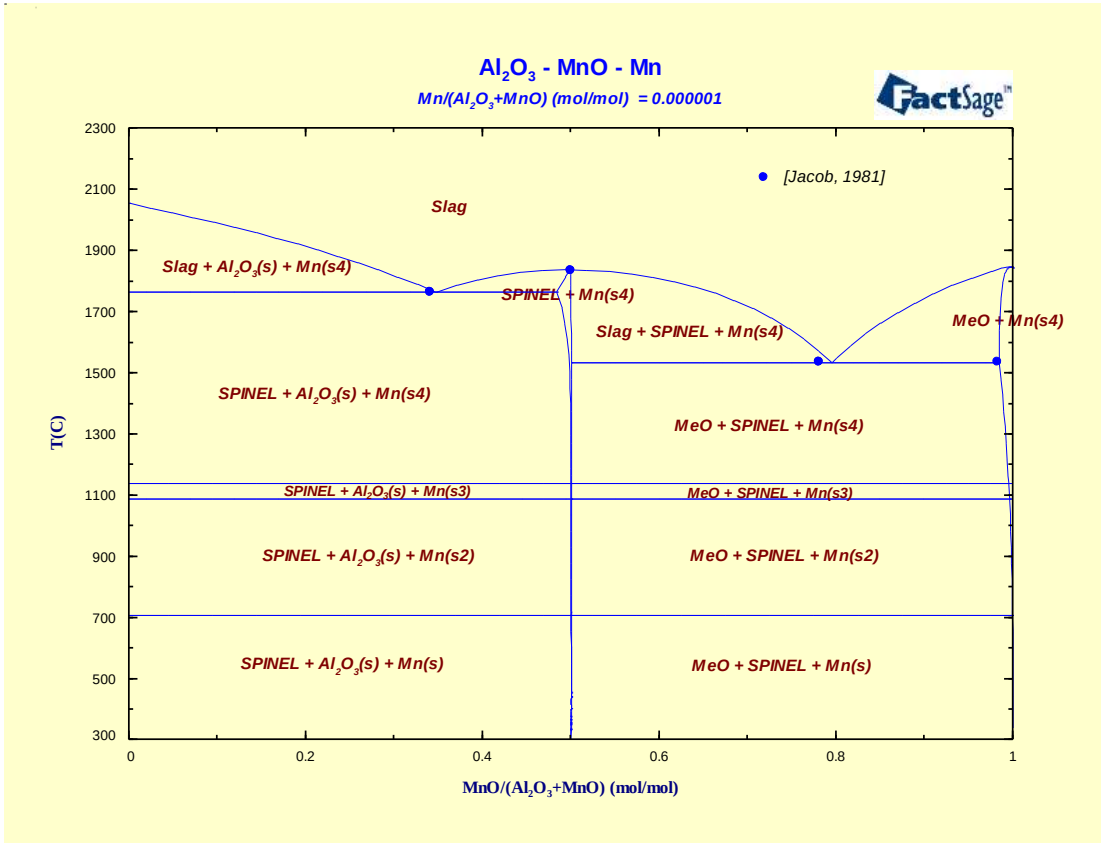
Phase	Description
MeO	$(Al^{+3},Ca^{+2},Cr^{+3},Mn^{+2},Mn^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Na^{+1},Va)(O^{-2})$
Cubic Spinel	$(Al^{+3},Cr^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2})(Al^{+3},Ca^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Mn^{+3},Mn^{+4},Va)2\ (Cr^{+2},Fe^{+2},Mg^{+2},Va)_2(O^{-2})_4$
Tetragonal Spinel	$(Cr^{+2},Cr^{+3},Mn^{+2},Mn^{+3})(Al^{+3},Cr^{+3},Fe^{+3},Mn^{+2},Mn^{+3},Va)_2(O^{-2})_4$
Corundum	$(Al^{+3},Cr^{+2},Cr^{+3},Fe^{+3},Mn^{+3})_2(Cr^{+3},Va)(O^{-2})_3$
Bixbyte	$(Cr^{+3},Fe^{+3},Mn^{+3})_2(O^{-2})_3$
Olivine	$(Ca^{+2},Fe^{+2},Mg^{+2},Mn^{+2})(Ca^{+2},Fe^{+2},Mg^{+2},Mn^{+2})(Si^{+4})(O^{-2})_4$
Rhodonite	$(Mg^{+2},Mn^{+2})(Si^{+4})(O^{-2})_3$
Protopyroxene	$(Ca^{+2},Mg^{+2},Mn^{+2})(Si^{+4})(O^{-2})_3$

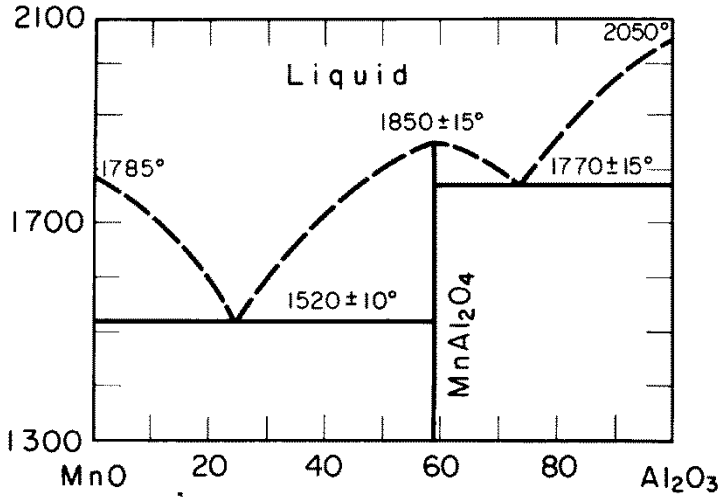
The binary Mn-O phase diagram



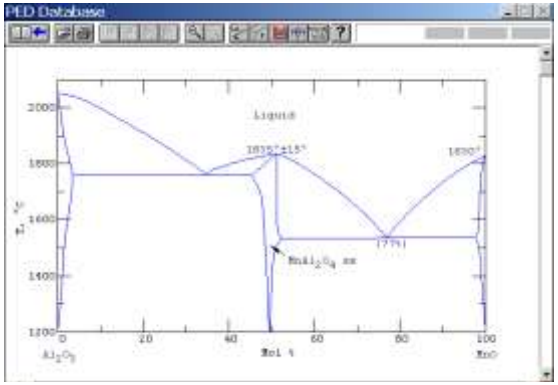


The Al_2O_3-MnO system in equilibrium with Mn





I.A. Novokhatskij, L.M. Lenev, A.A. Savinskaya, A.V. Gorokh, Zh. Neorg. Khim., 11 [2], (1966), pp. 427-428.



K.T. Jacob, Can. Metall. Q., 20 [1], (1981), pp. 89-92.

The CaO-MnO and MgO-MnO binary systems

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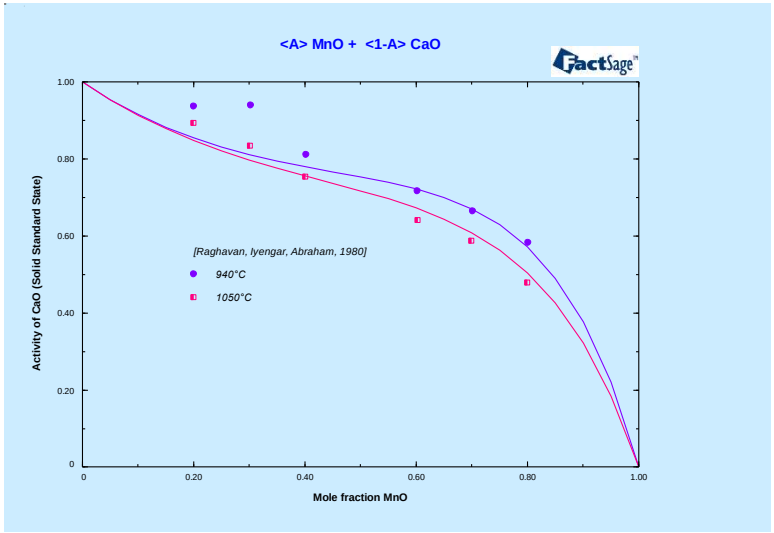
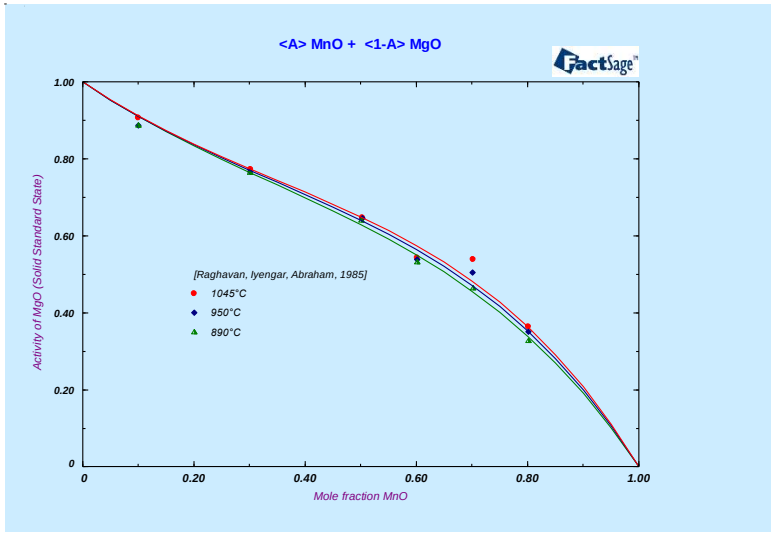
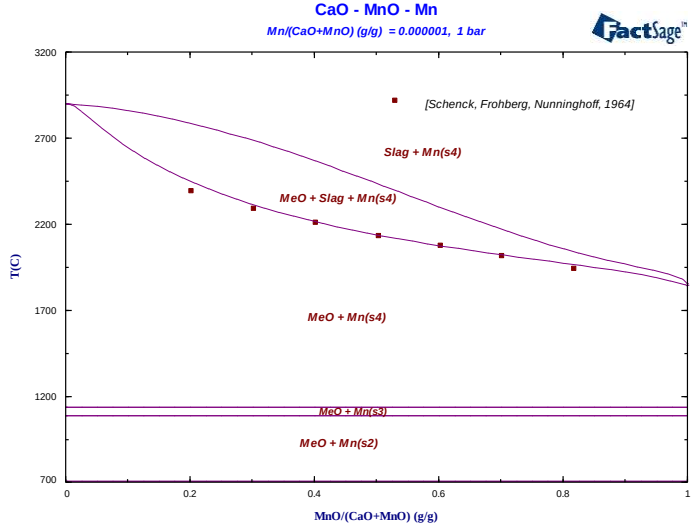
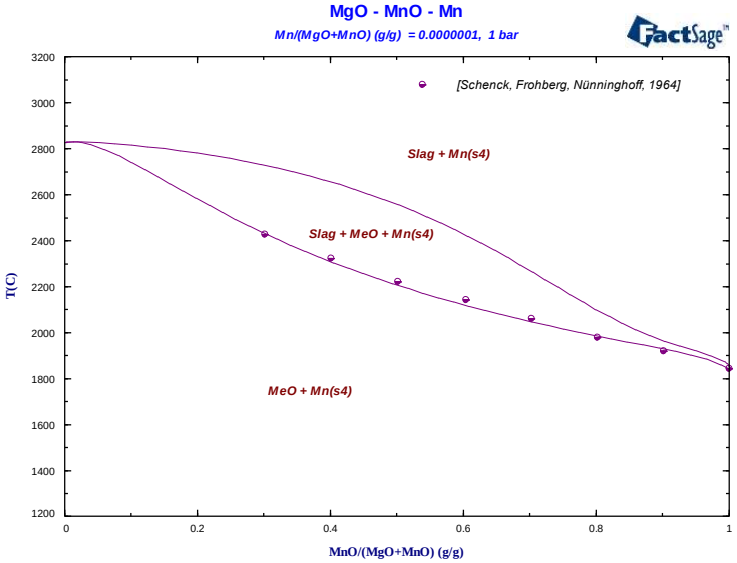
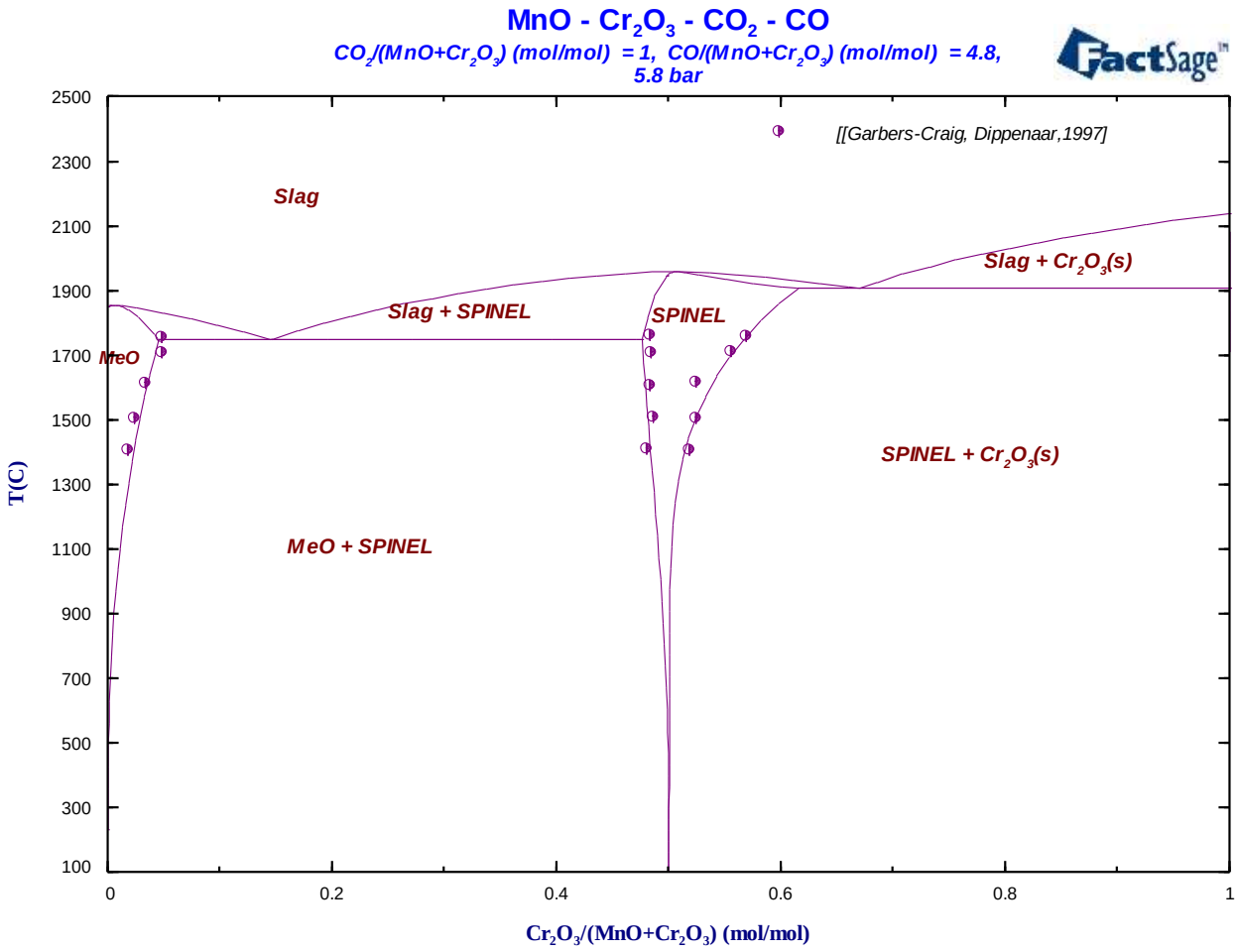




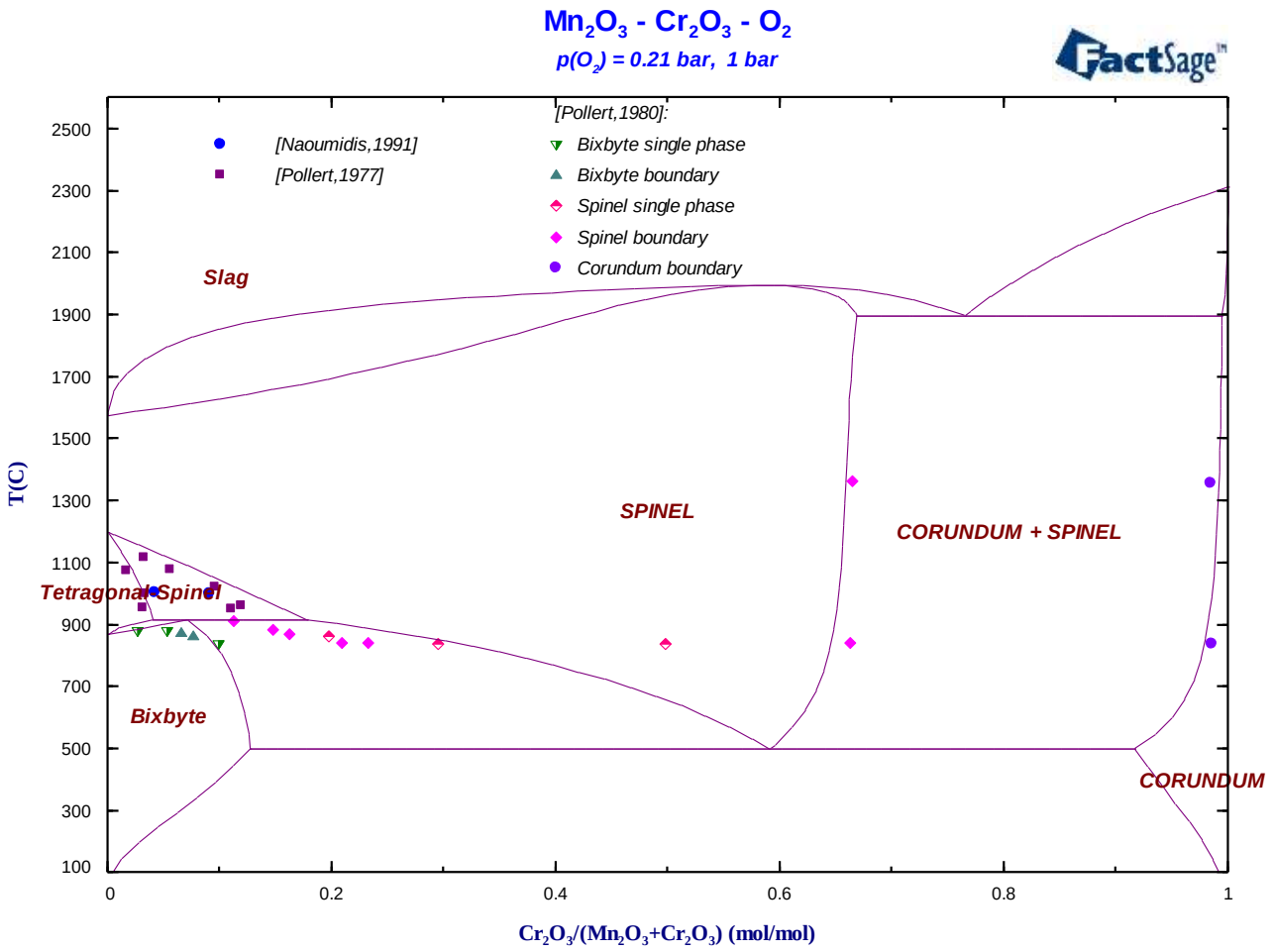




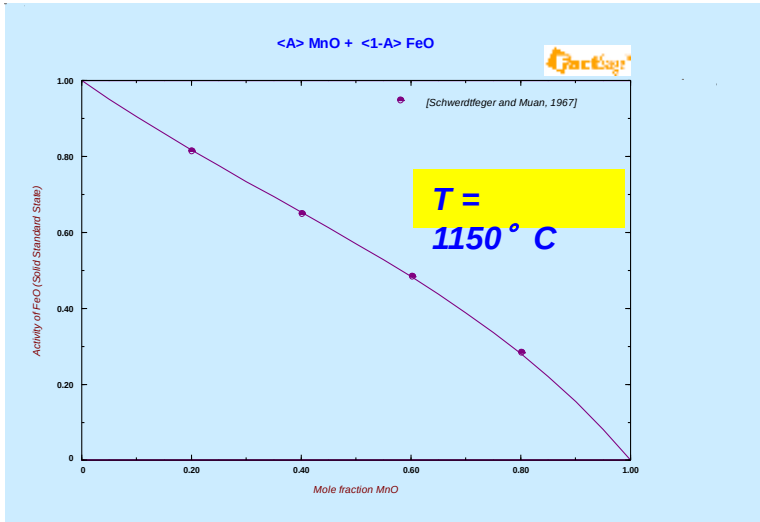
The Cr_2O_3-MnO system under CO/CO_2 = 4.8

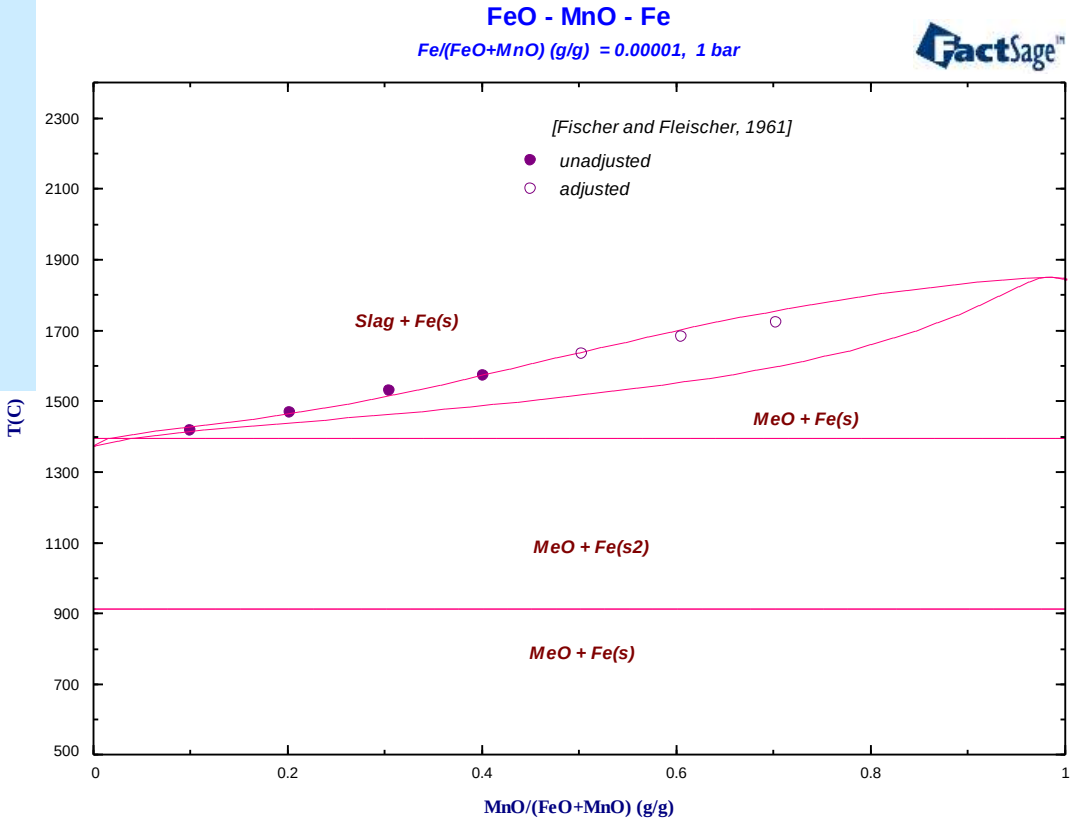


The Cr_2O_3-Mn_2O_3 system in air

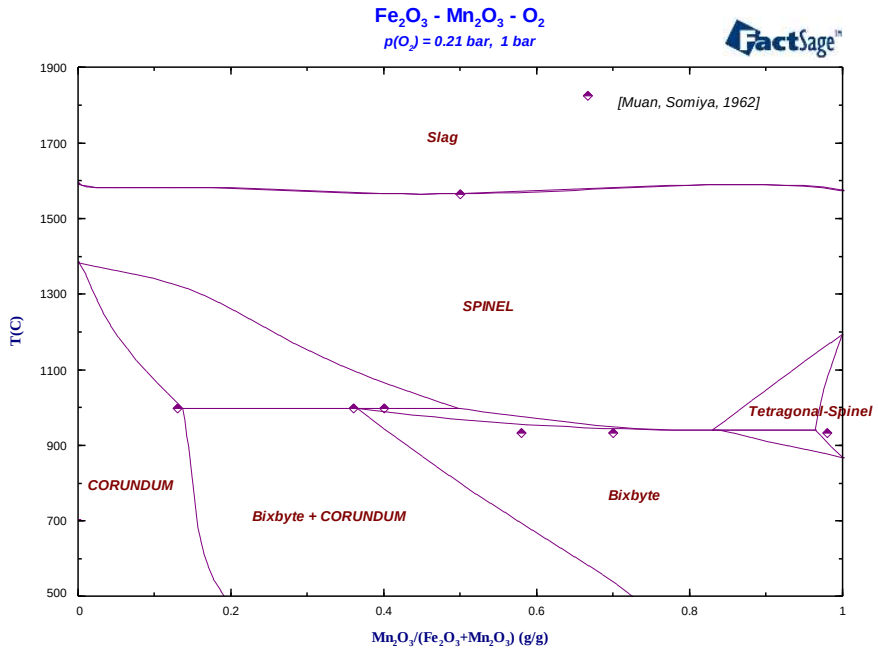


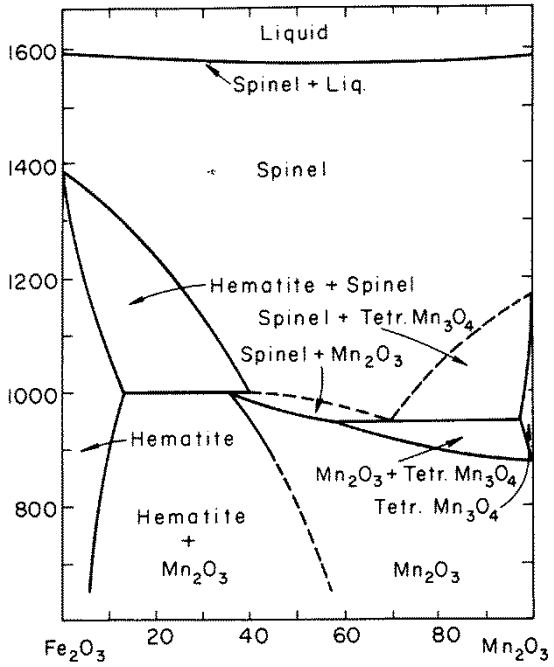
The FeO-MnO system in equilibrium with Fe





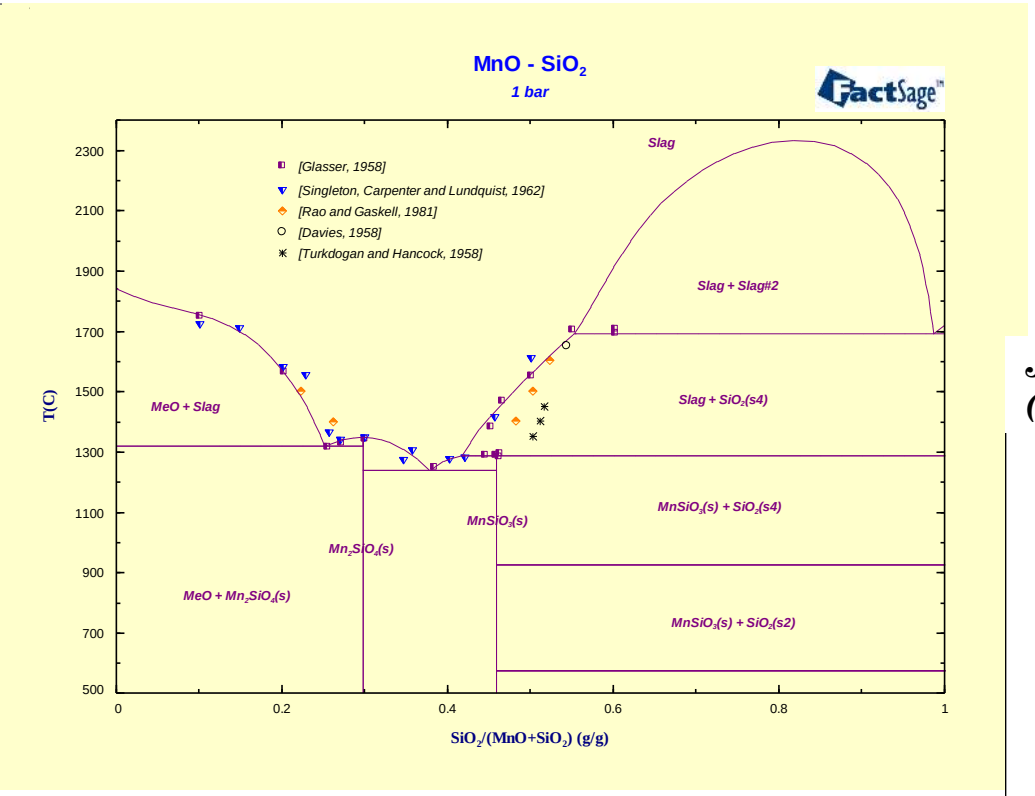
The Fe_2O_3-Mn_2O_3 system in air

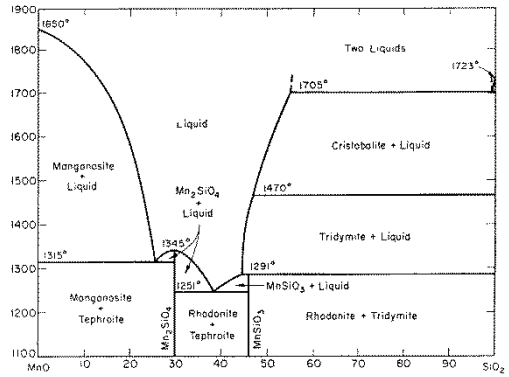




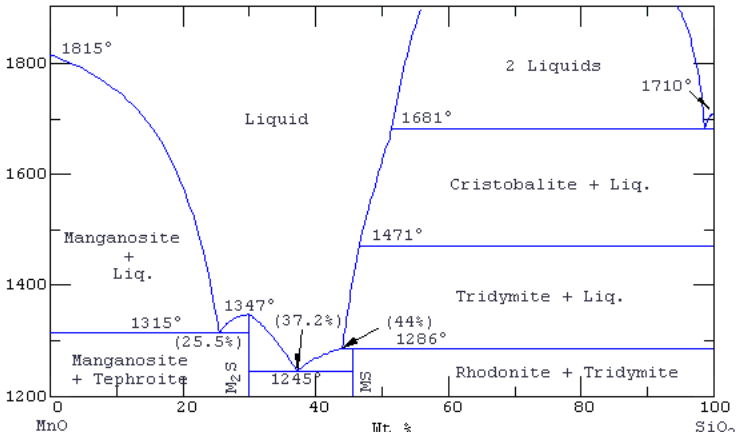
A. Muan, S. Somiya, Am. J. Sci., 260 [3], (1962), pp. 230-240.

The MnO-SiO_2 binary system



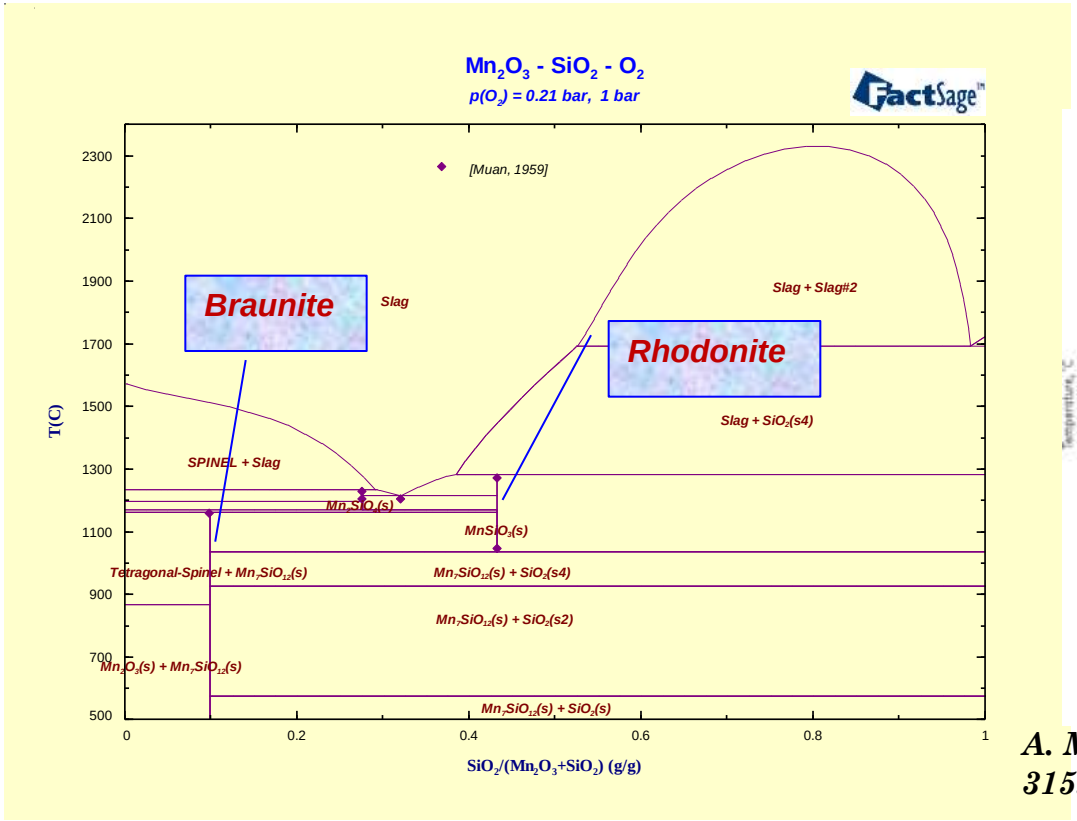


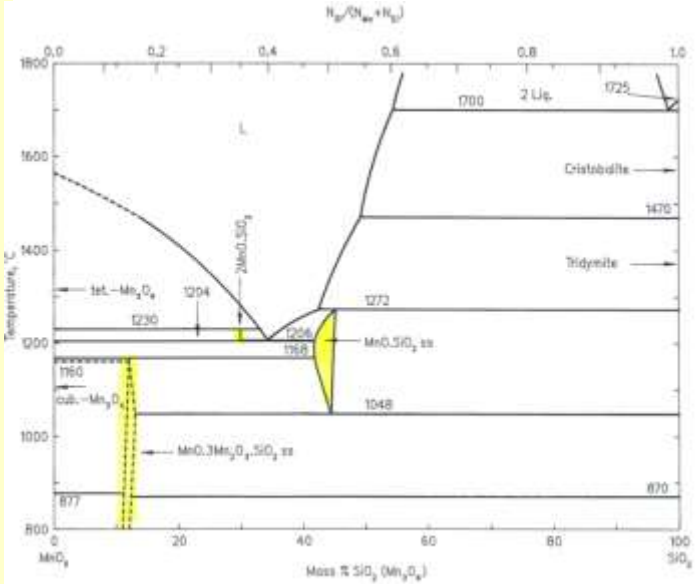
J. White, D.D. Howat, R. Hay, J.R. Tech. Coll. (Glasgow), 3, (1934), pp.231-240.



E.L. Singleton, L. Carpenetr, R.V. Lundquist, Rep. Invest.-U.S., Bur. Mines., No. 5938, (1962), pp. 1-31.

The Mn_2O_3-SiO_2 phase diagram in air



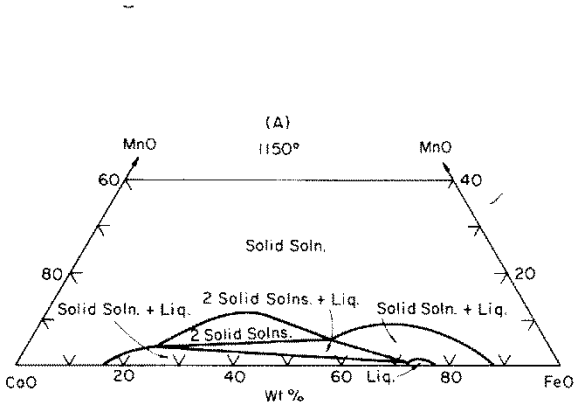


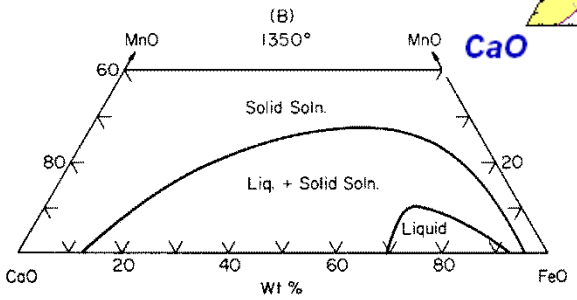
A. Muan, Am. J. Sci., 257 [4], (1959), pp. 297-315.

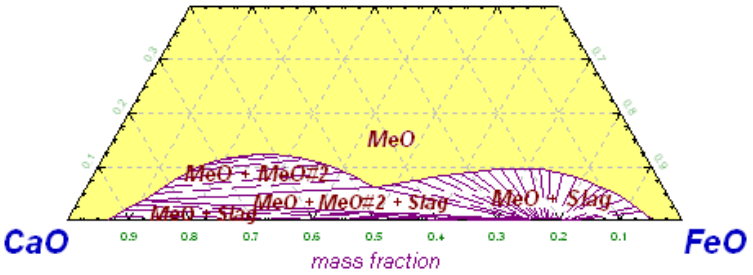
The heat capacities, H_f and S_f of Rhodonite *($MnSiO_3$)* and Braunite *(Mn_7SiO_{12})* were obtained by Robie, Huebner and Hemingway 1995.

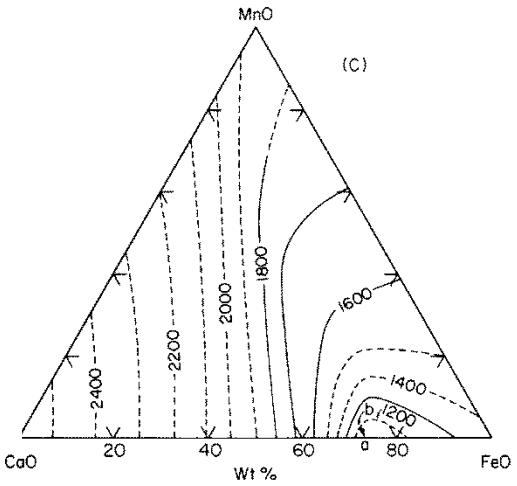
The CaO-FeO-MnO ternary system

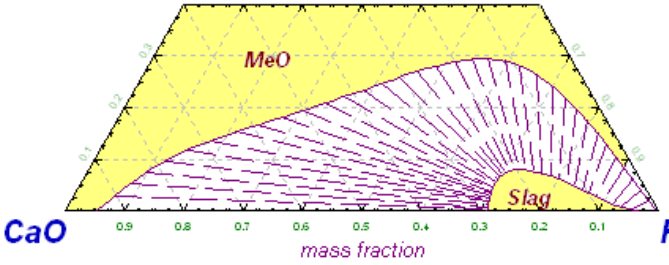
W.A. Fleischer, H.-J. Fischer, Arch. Eisenhüttenwes., 32 [5], (1961), pp. 305-313.

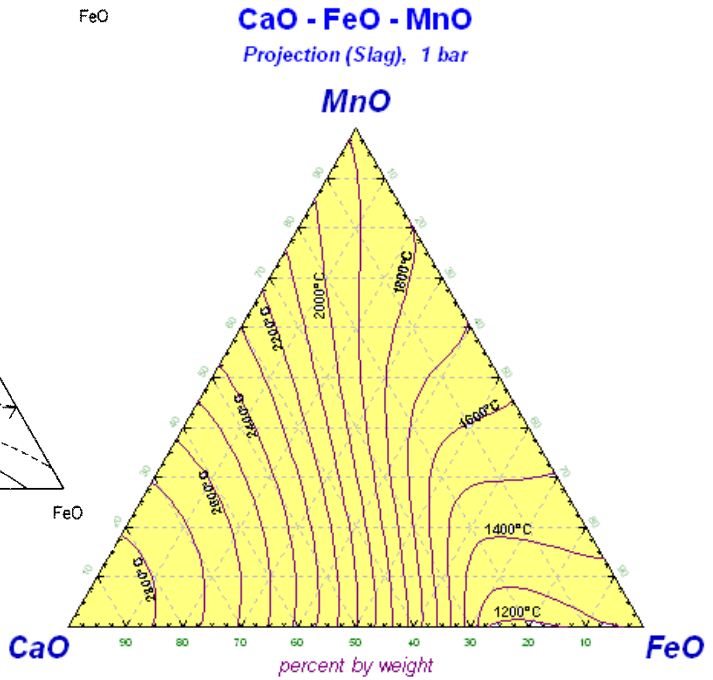




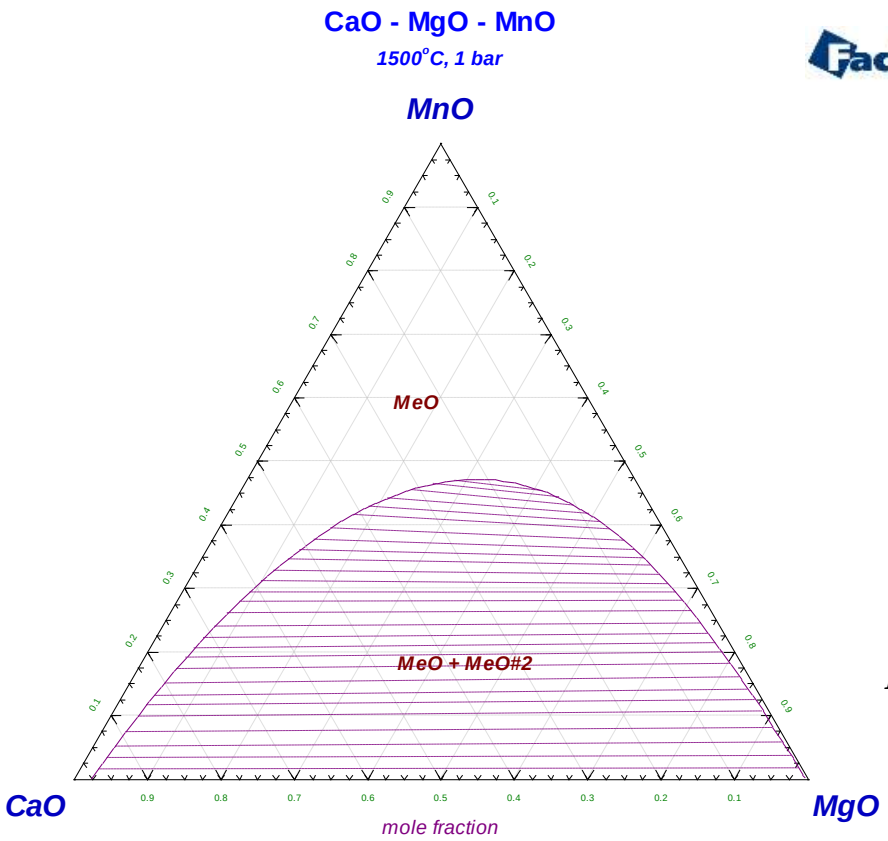




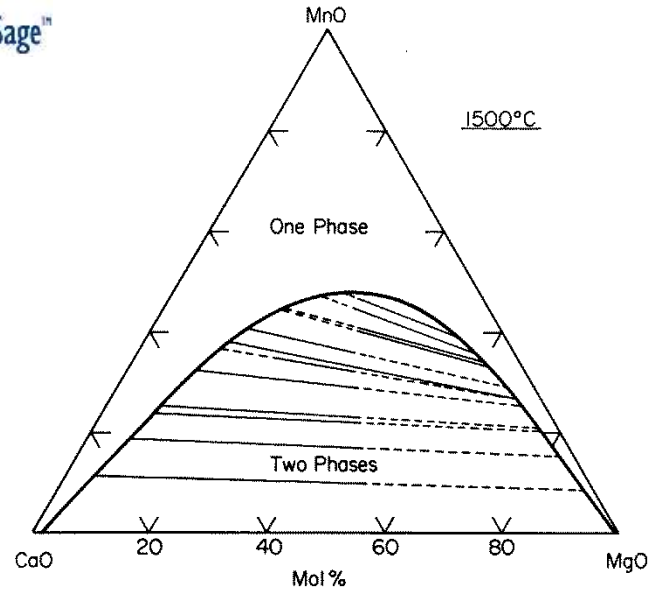




The CaO-MgO-MnO ternary system

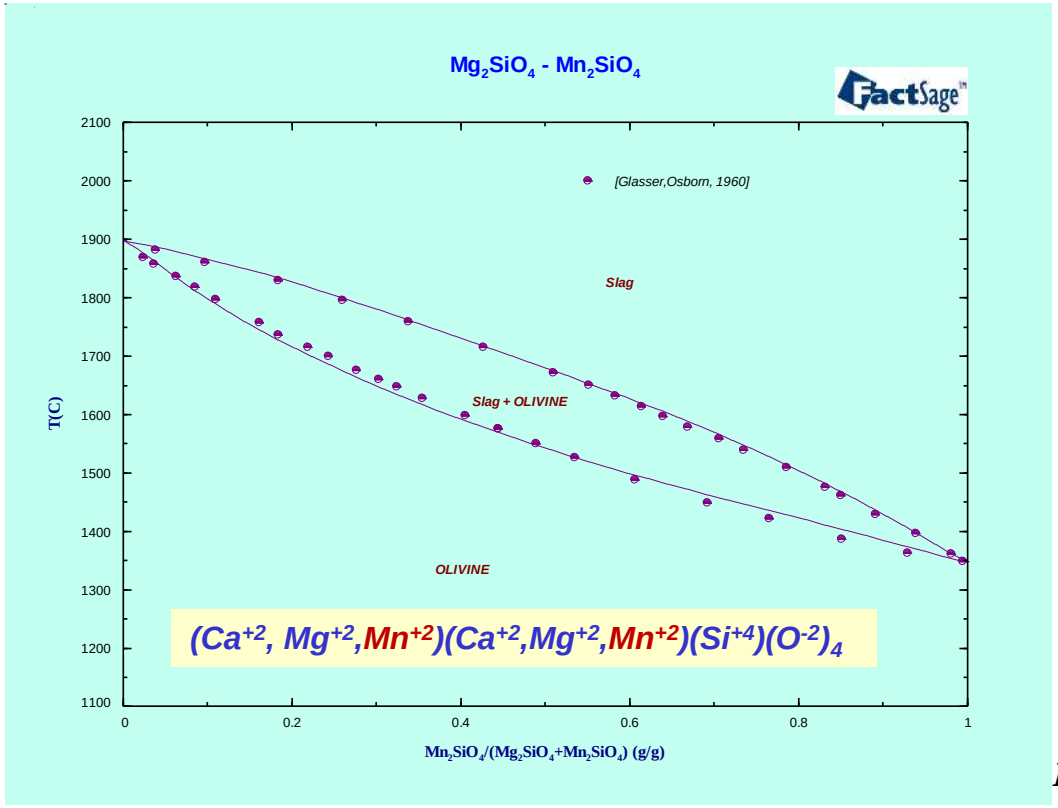


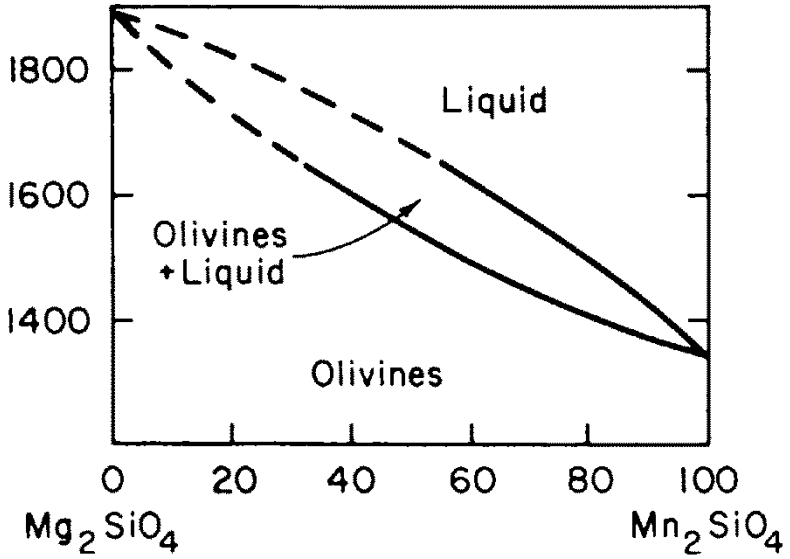
FactSage™



E. Woermann, A. Muan, Mat. Res. Bull. 5 [10], (1970), pp. 779-788.

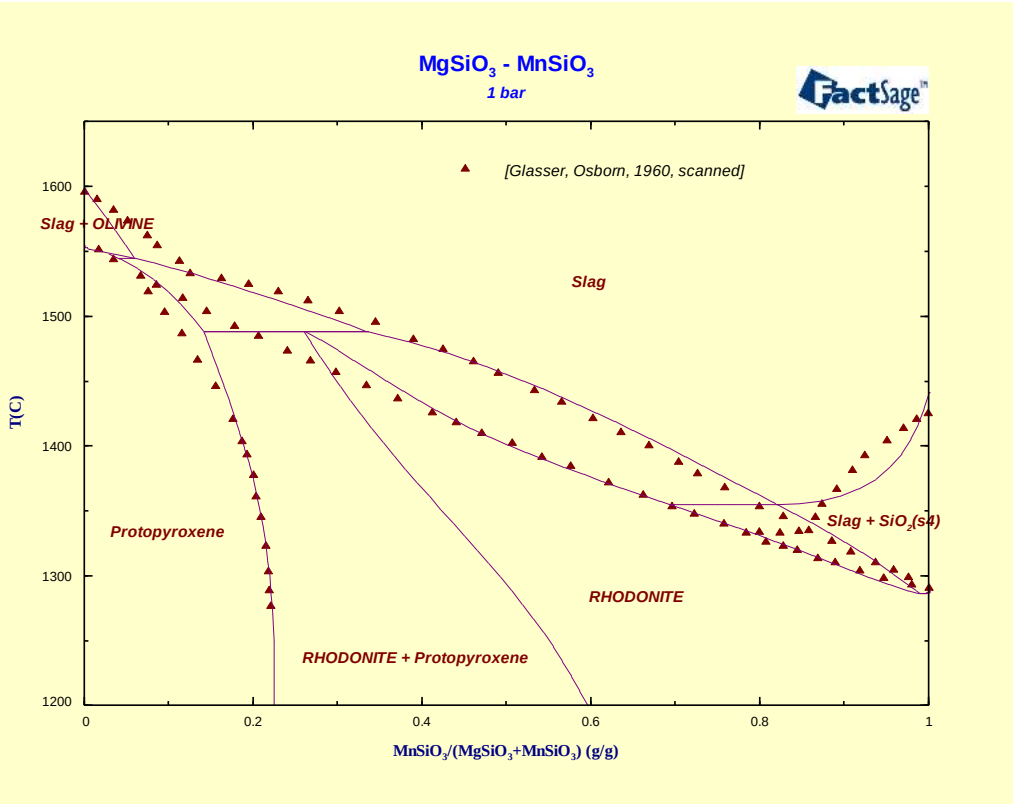
Isopletal orthosilicate section Mg_2SiO_4-Mn_2SiO_4

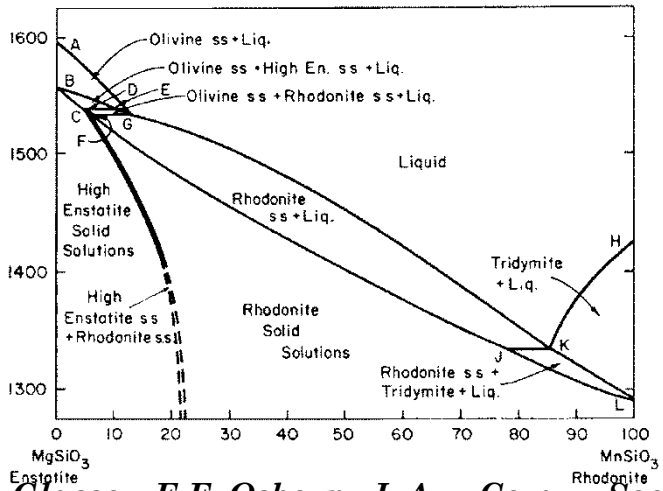




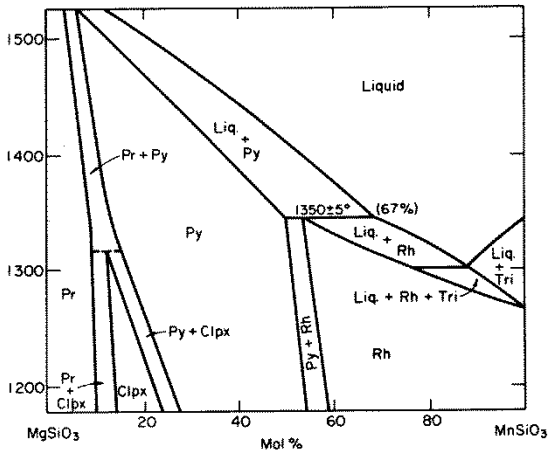
F.P. Glasser, E.F. Osborn, J. Am. Ceram. Soc., 43 [3], (1960), pp. 132-140.

Isopletal metasilicate section $MgSiO_3$-$MnSiO_3$



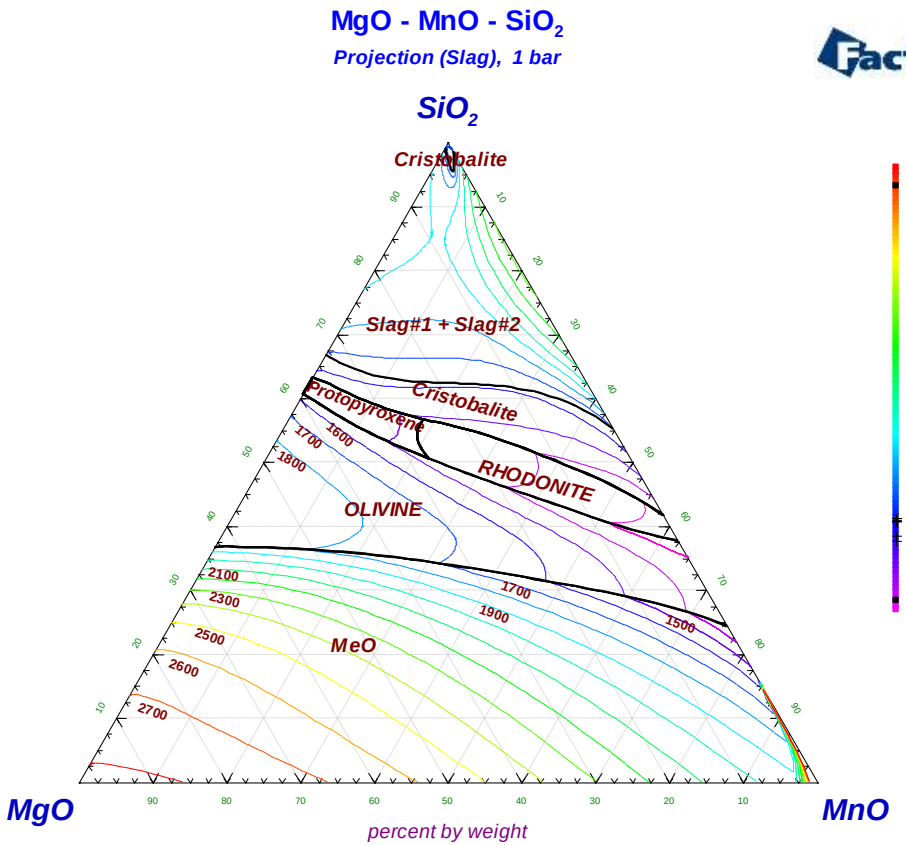


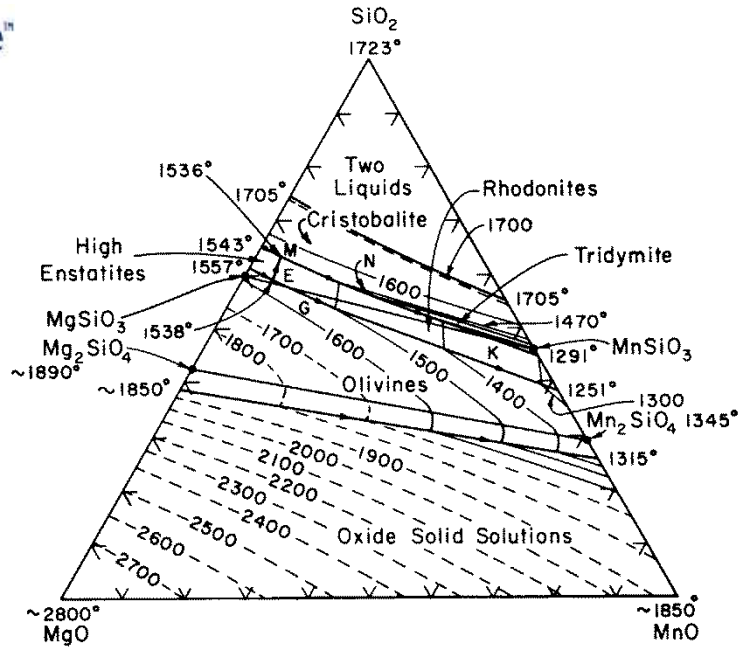
F.P. Glasser, E.F. Osborn, J. Am. Ceram. Soc., 43 [3], (1960), pp. 132-140.



J. Ito, Am. Mineral., 57 [5-6], (1972), pp.865-876.

Liquidus surface in MgO-MnO-SiO_2





F.P. Glasser, E.F. Osborn, J. Am. Ceram. Soc., 43 [3], (1960), pp. 132-140.

Conclusions

- The liquid phase in all subsystems was evaluated using associate species model,
- All systems were assessed using experimental phase diagram information.
- The 3 solid solution phases containing S (Oldhamite, Niningerite and Troilite-HT) were incorporated.
- MnO_x has so far been integrated into the reduced core system CaO-MgO-Al_2O_3-CrO_x-FeO-Fe_2O_3-SiO_2. All binary and 3 ternary systems were described.
- The stoichiometric phases $MnSiO_3$, Mn_2SiO_4 and Mn_7SiO_{12} were incorporated. The solubility ranges of 8 solid solution phases containing Mn (such as Cubic-Spinel, Tetragonal-Spinel, Bixbyte, Olivine, Rhodonite, Protopyroxene, Monoxide and Corundum) were described using the sublattice model.

Future developments

MeS-MeSO$_4$-MeO

Ternaries with ***MnO$_x$*** and Oxide Database

(Al$_2$O$_3$-CaO-CrO$_x$-FeO$_x$-K$_2$O-MgO-Na$_2$O-SiO$_2$)

Thanks for your attention !