Incorporation of MnO_x as well as Sulphides to the HotVeGas database

GTT-Technologies

GTT-Workshop, 2-4. Juli 2014, Herzogenrath

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Contents of presentation

- Introduction
- Addition of Sulphides
- Addition of MnO_x – new ternary systems
- Conclusions
- Future developments

HotVeGas Oxide Database

Workshop 2011
- Al_2O_3-CaO-CrO_x-FeO_x-MgO-SiO_2
- + K_2O + Na_2O

Workshop 2012
- + CaF_2
- + P_2O_5

Workhop 2013
- + binaries with MnO
- + CaS + FeS + MgS

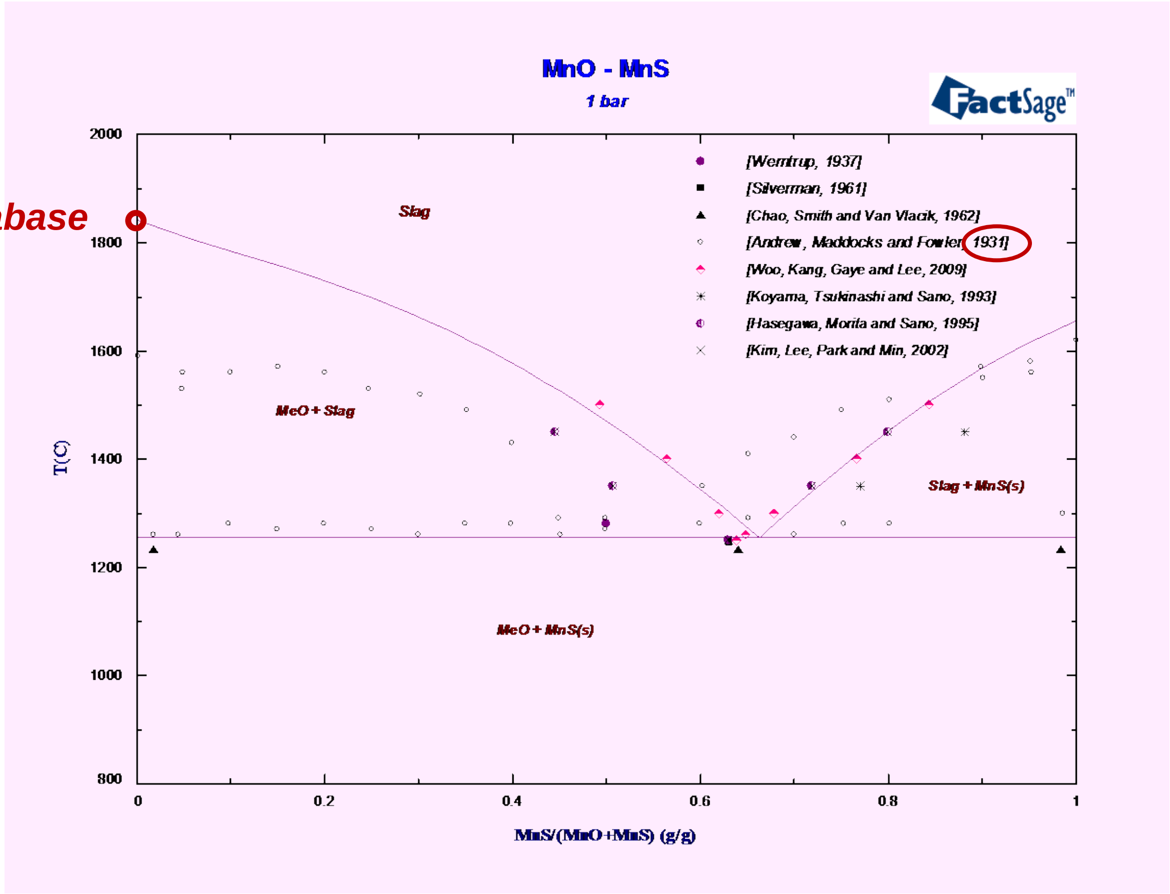
Workshop 2014
- + MnS
- + ternaries with MnO + Mn_2O_3

Addition of MnS

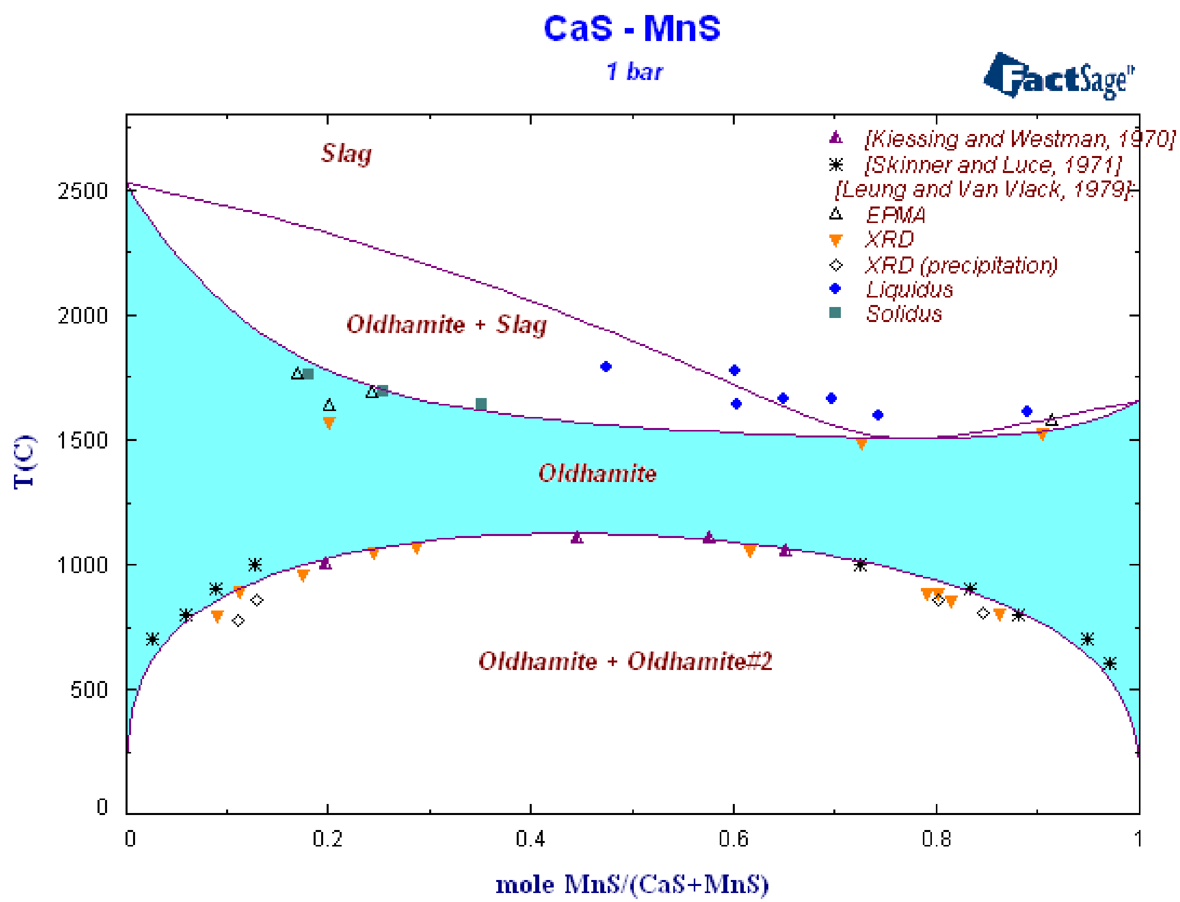
- Binary systems
  - The Mn-S and MnO-MnS phase diagrams
  - The CaS-MnS phase diagram
  - The FeS-MnS phase diagram
  - The proposed MgS-MnS and MnS-SiO_2 phase diagrams
  - The Al_2S_3-K_2S and K_2S-Na_2S phase diagrams
- Ternary systems
  - The ternary Al_2O_3 – MnO - MnS system
  - The ternary CaS – FeS - MnS system
  - The ternary CaS – MgS - MnS system
  - The ternary FeS – MgS - MnS system
  - The ternary MnO – MnS - SiO_2 system
- Quaternary system Al_2O_3 – MnO – MnS - SiO_2

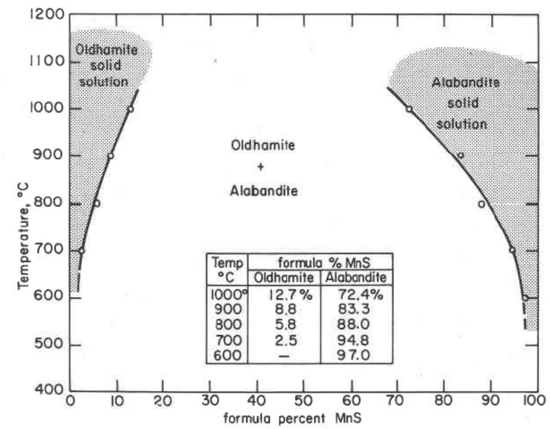
Mangan oxide - Mangan sulphide phase diagram

SGPS database



CaS-MnS phase diagram





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

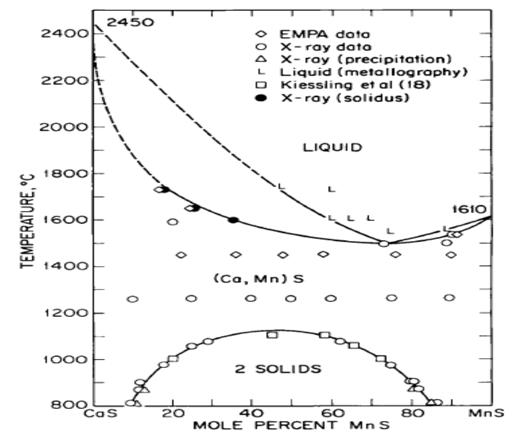
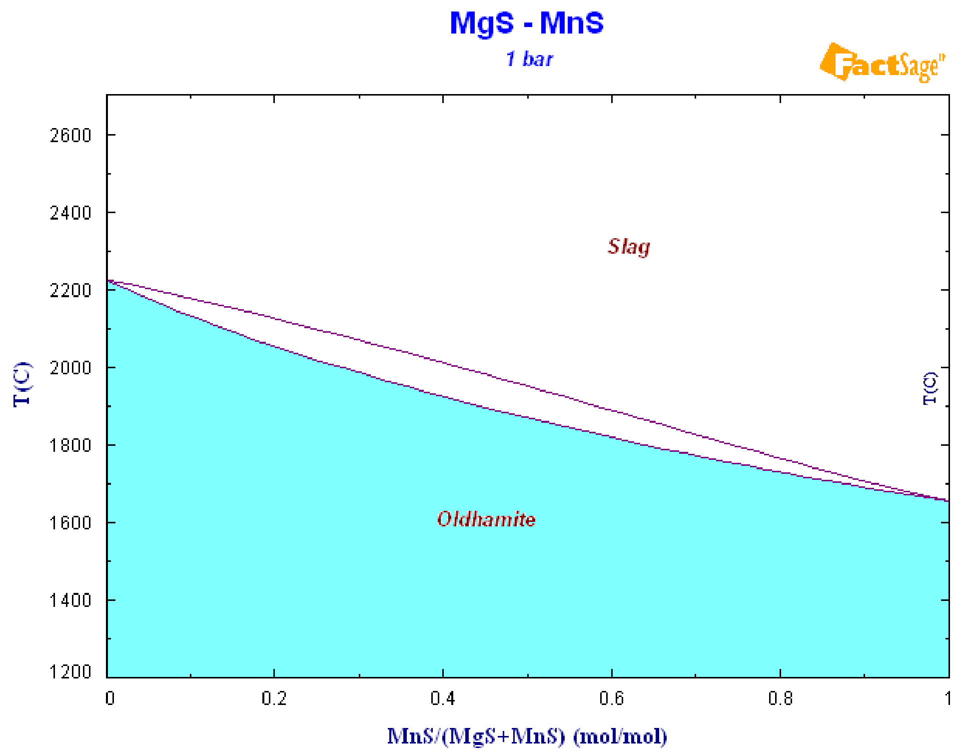
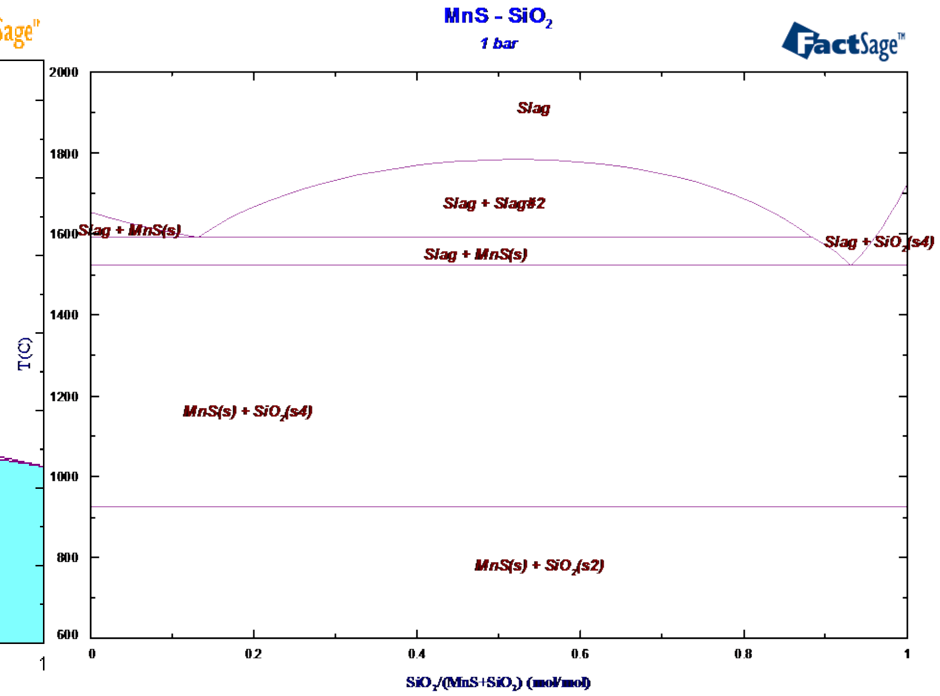


Fig. 1. The system CaS-MnS, drawn from results of this study, showing a miscibility gap and minimum melting point.

C.-H. Leung and L-H. van Vlack, J. Am. Ceram. Soc., 62 [11-12], (1979), pp.613-616.

Proposed MgS-MnS and $MnS-SiO_2$ phase diagrams





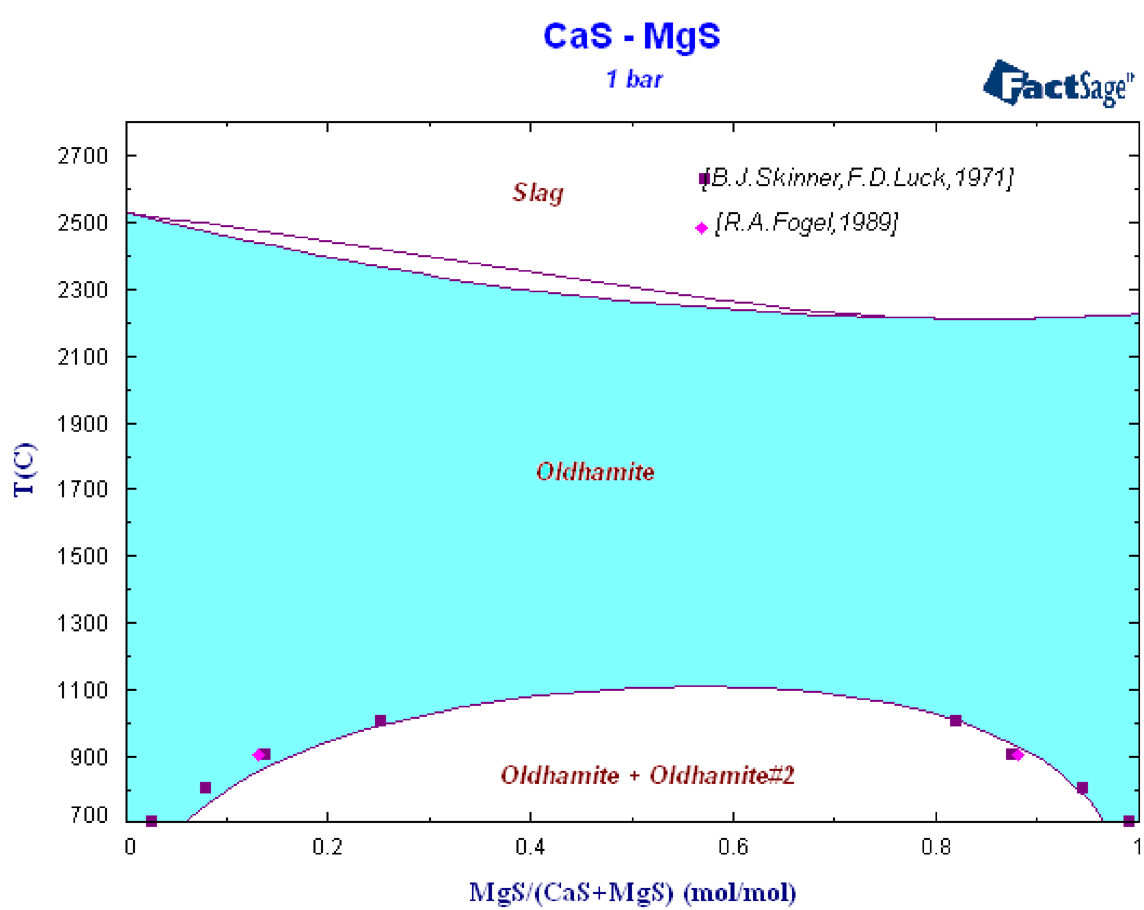
6) *MnS-MgS*

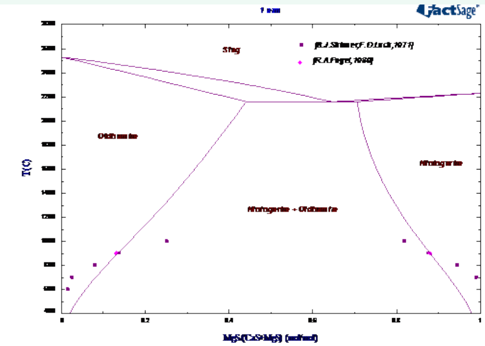
At all temperatures between 600°C and 1000°C, we found that MnS and MgS form a completely miscible solid solution.

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

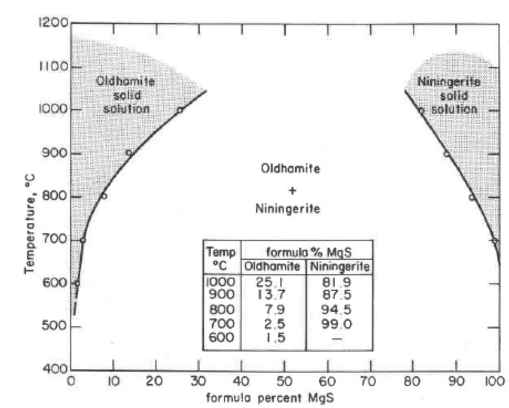
CaS-MgS phase diagram (revised)

CaS-MnS and **MgS-MnS** form completely miscible solid solution **Oldhamite**. **CaS-MgS** should have the same behaviour.



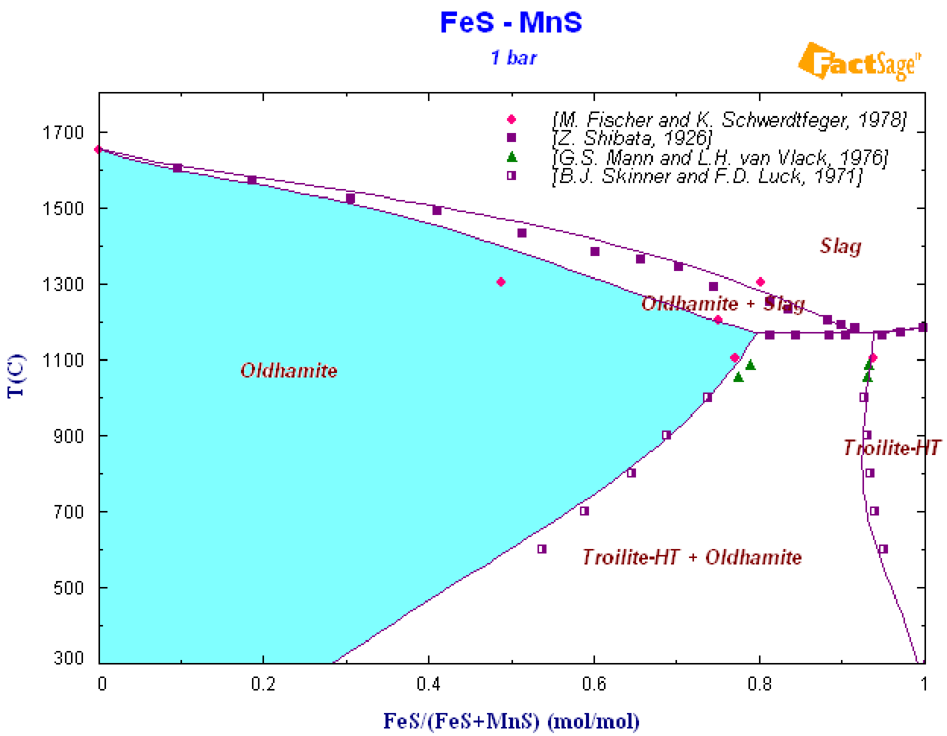


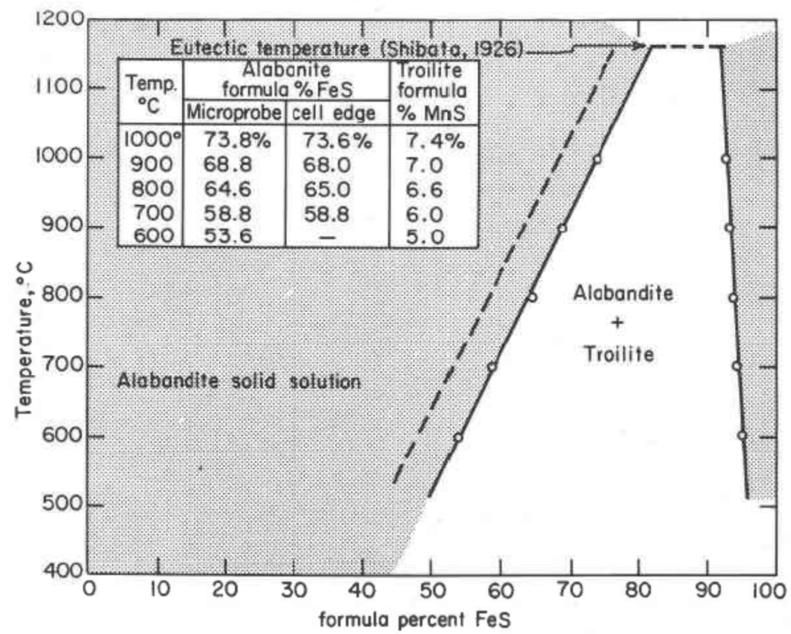
Previous calculation.



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

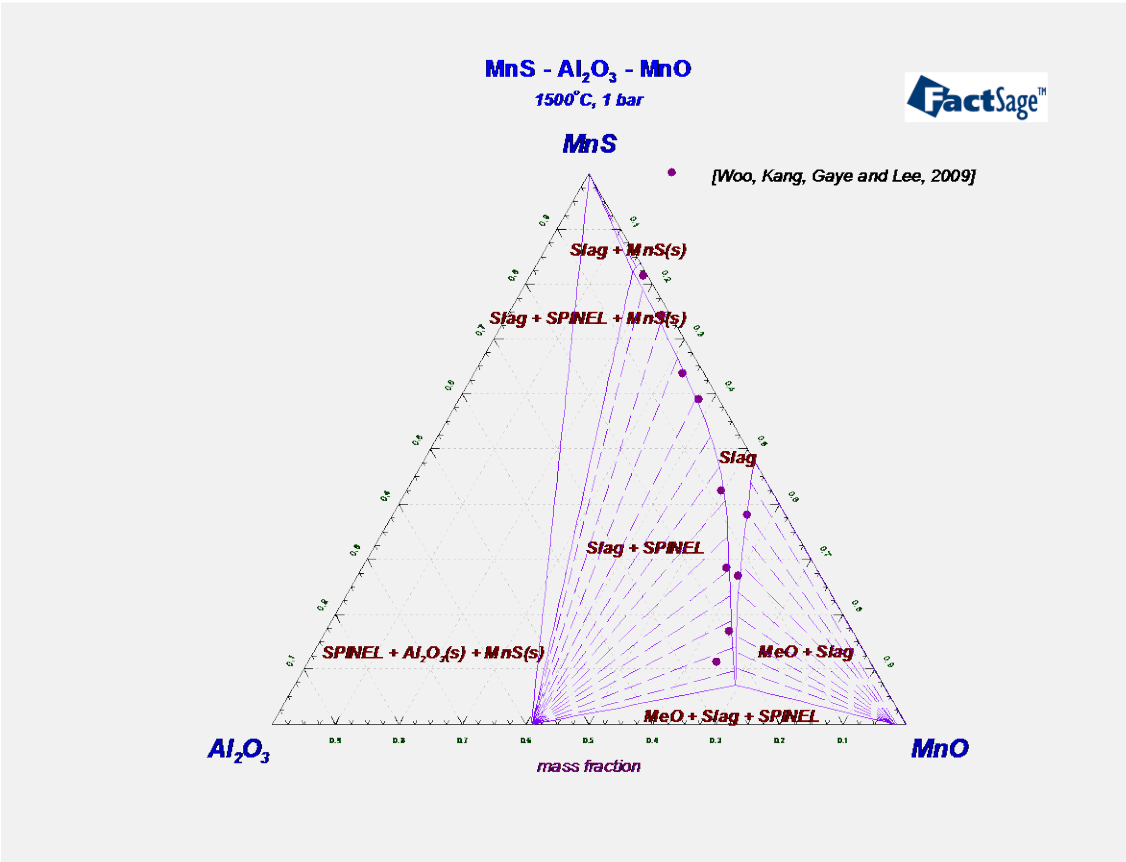
FeS-MnS phase diagram





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

The isothermal section at 1500° C in Al_2O_3-MnO-MnS



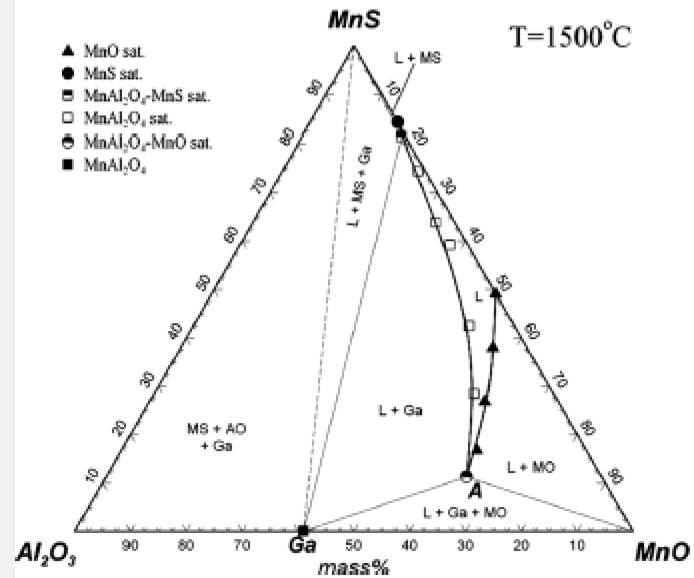
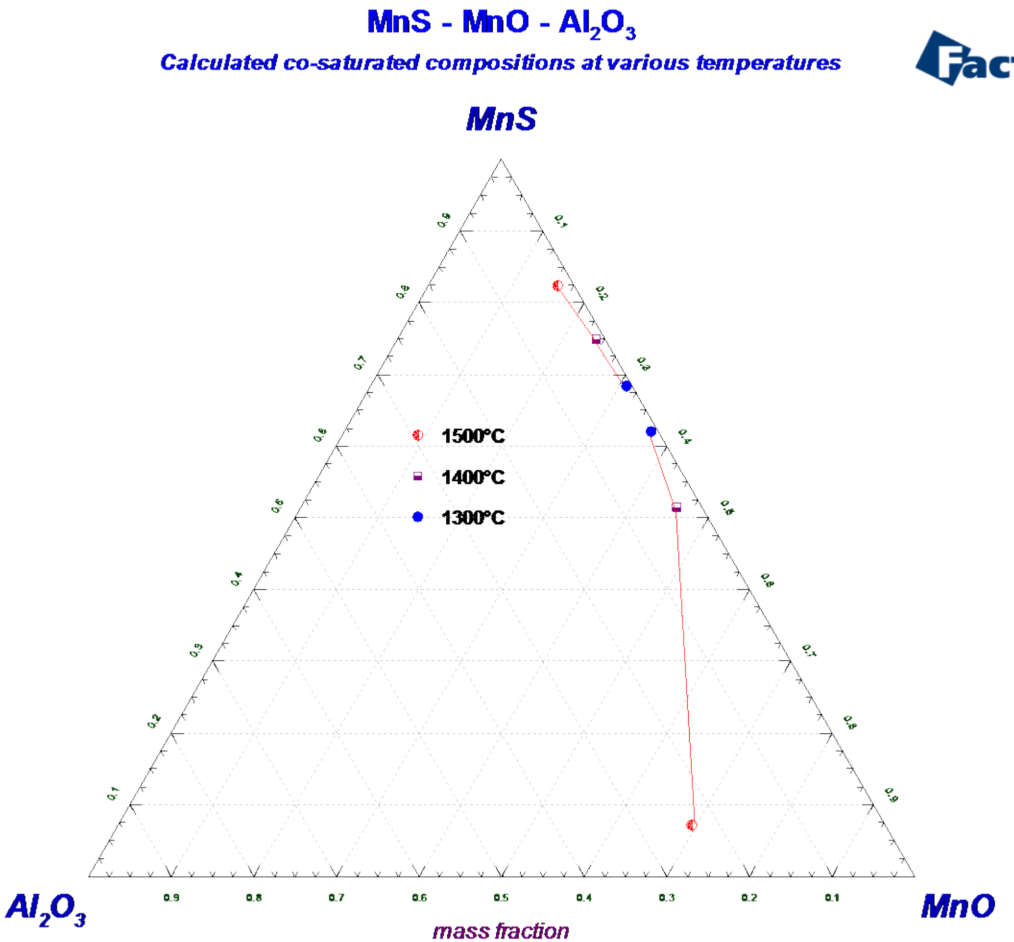


Fig. 9. Phase diagram of MnO–Al_2O_3–MnS system with experimentally determined phase equilibrium data in the present study. Legend: MS=MnS, MO=MnO, AO=Al_2O_3, Ga=$MnAl_2O_4$, L=Liquid.

D.-H. Woo, Y.-B. Kang, H. Gaye and H.-G. Lee, ISIJ Internat., Vol. 49 (2009), No. 10, pp. 1490-1497.

The Al_2O_3-MnO-MnS ternary system



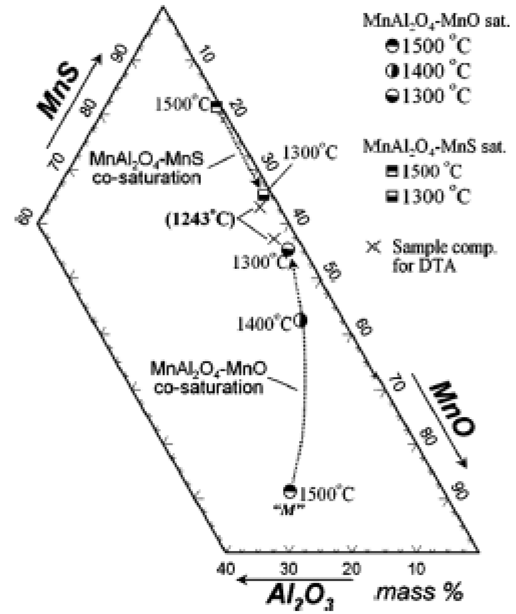


Fig. 10. Co-saturated compositions in the MnO–Al_2O_3–MnS system at various temperatures and sample compositions at which DTA analysis was performed.

D.-H. Woo, Y.-B. Kang, H. Gaye and H.-G. Lee, ISIJ Internat., Vol. 49 (2009), No. 10, pp. 1490-1497.

Isothermal sections in CaS-MgS-MnS

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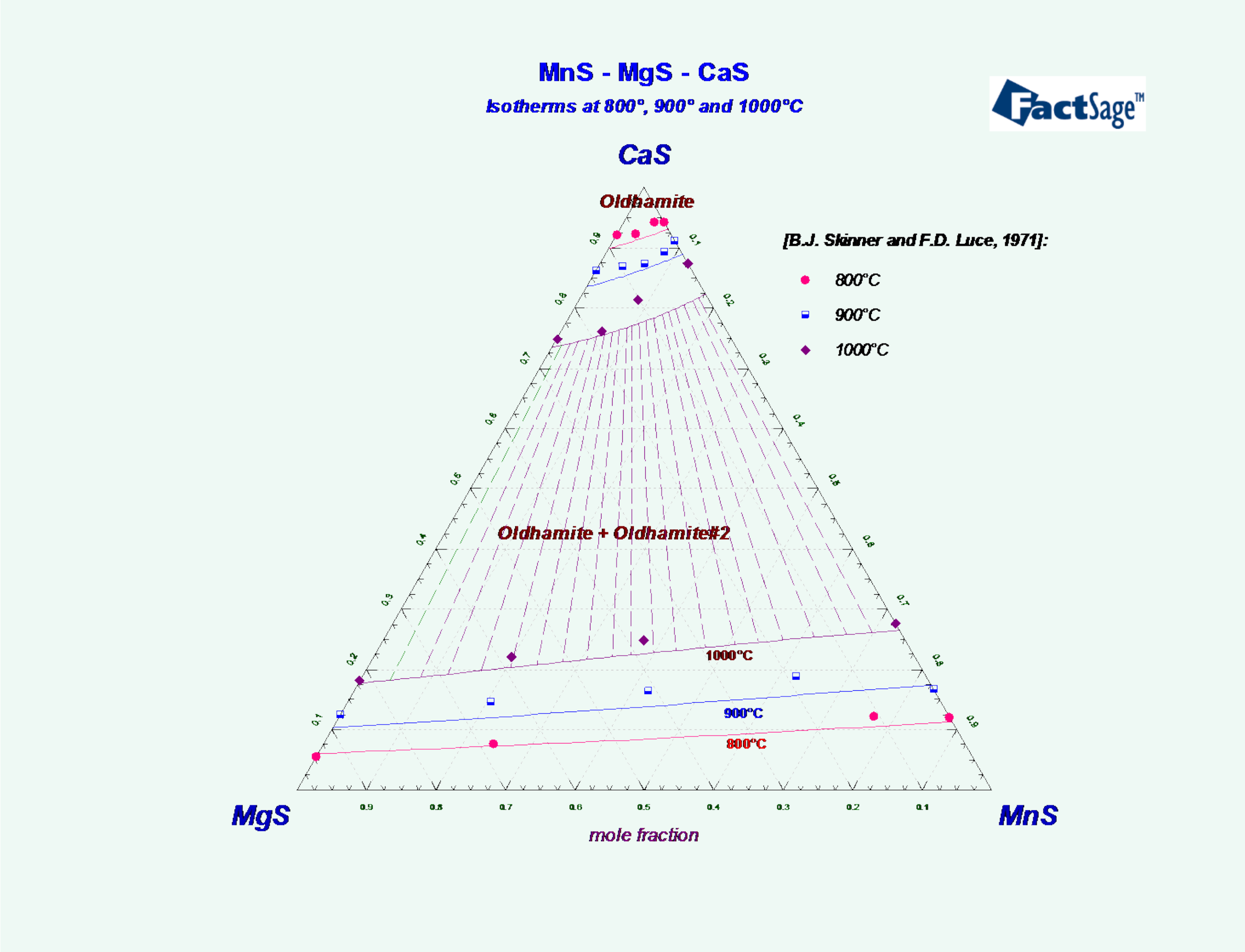
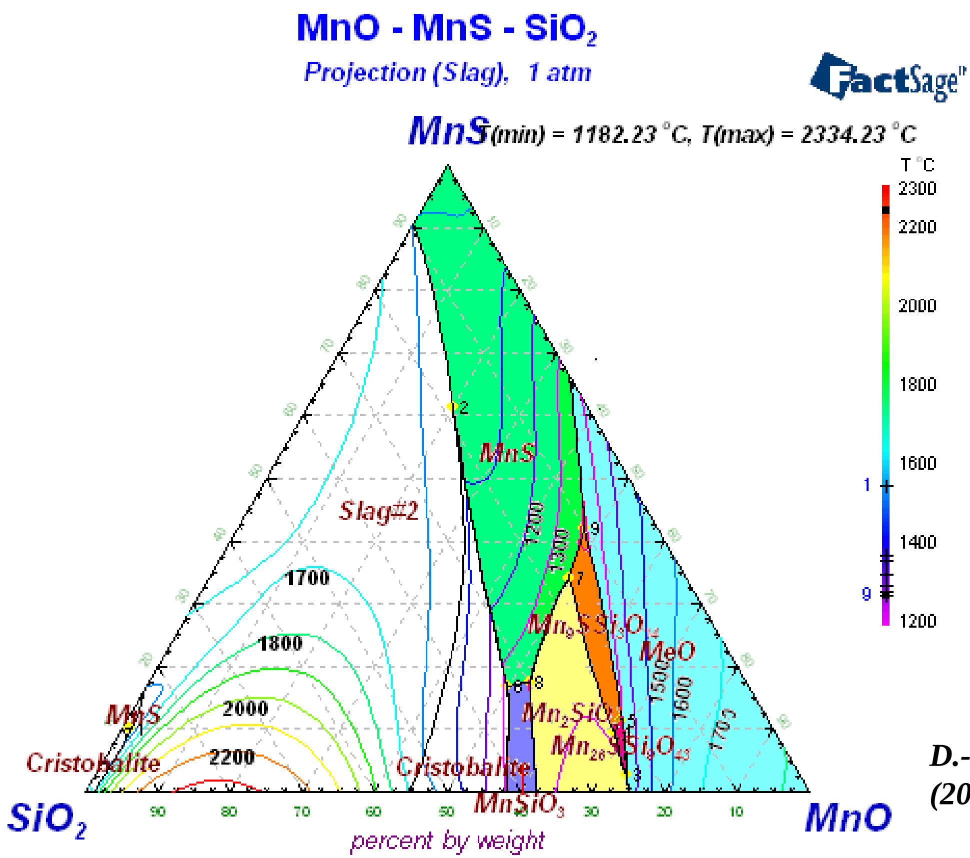
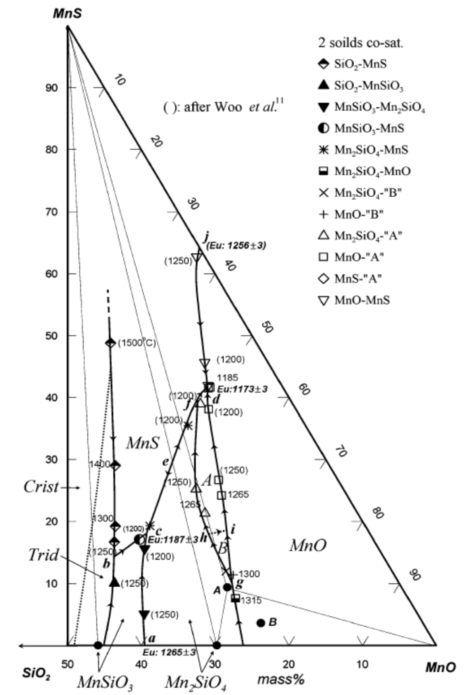


Liquidus surface in MnO-MnS-SiO_2

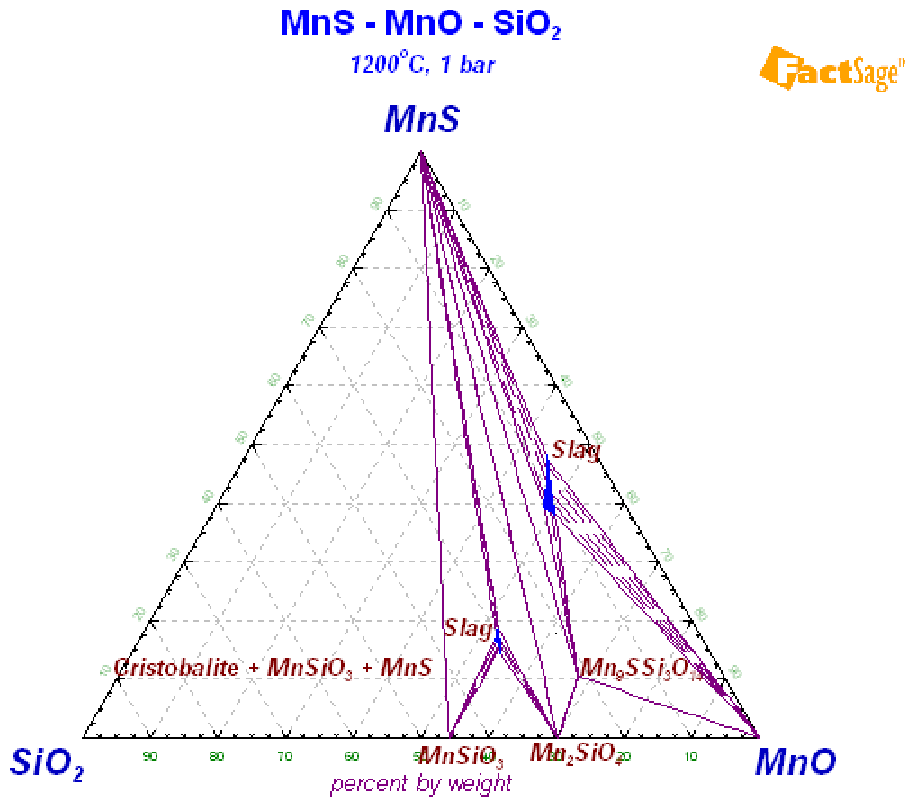


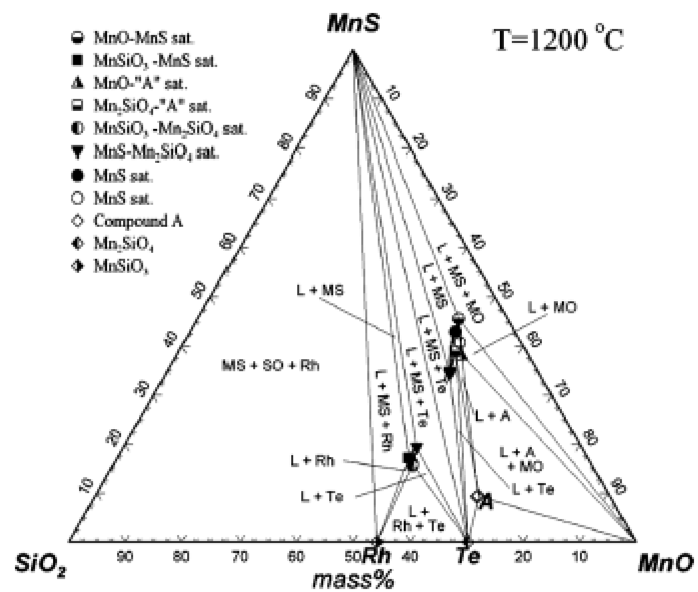


D.-H. Woo and H.-G. Lee, J. Am. Ceram. Soc., 93 [7], (2010), pp. 2008-2106.

8MnO·MnS·3SiO_2	*stoichiometric*	*modelled by GTT*
25MnO·MnS·9SiO_2	*stoichiometric*	*modelled by GTT*

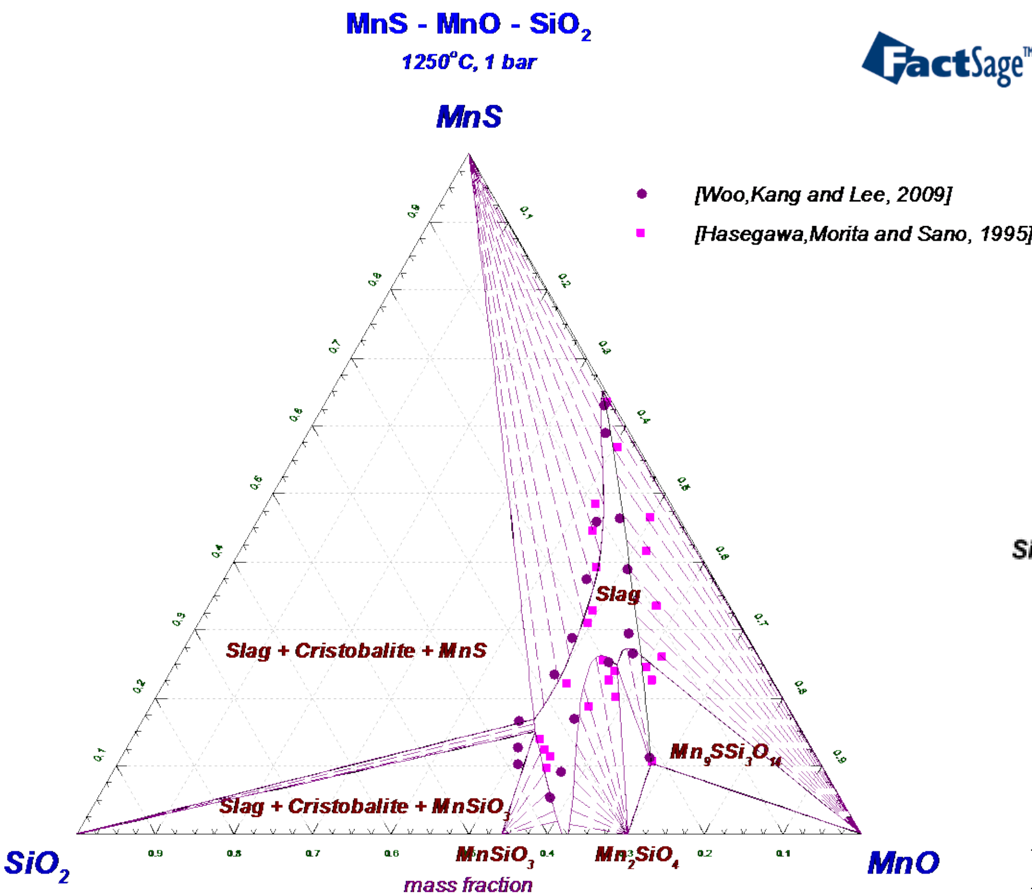
Isothermal section at 1200° C in MnO-MnS-SiO_2





D.-H. Woo, Y.-B. Kang, H.Gaye and H.-G. Lee, ISIJ Intern., 49 (2009), pp. 1490-1497.

Isothermal section at 1250°C in MnO-MnS-SiO_2



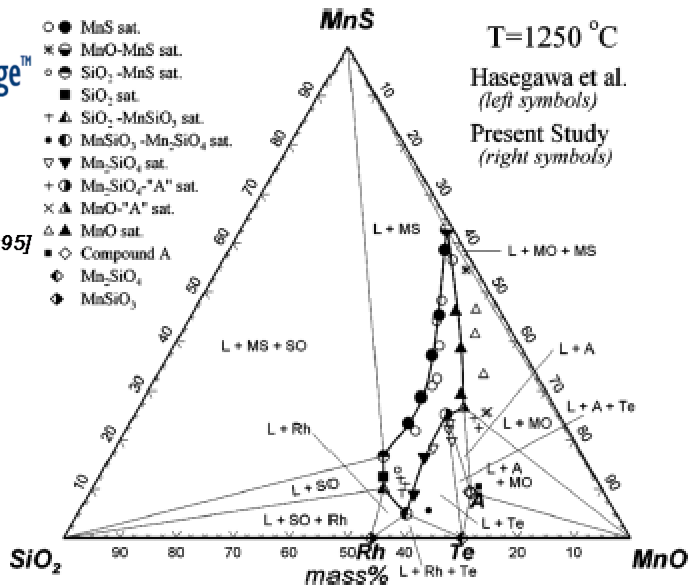
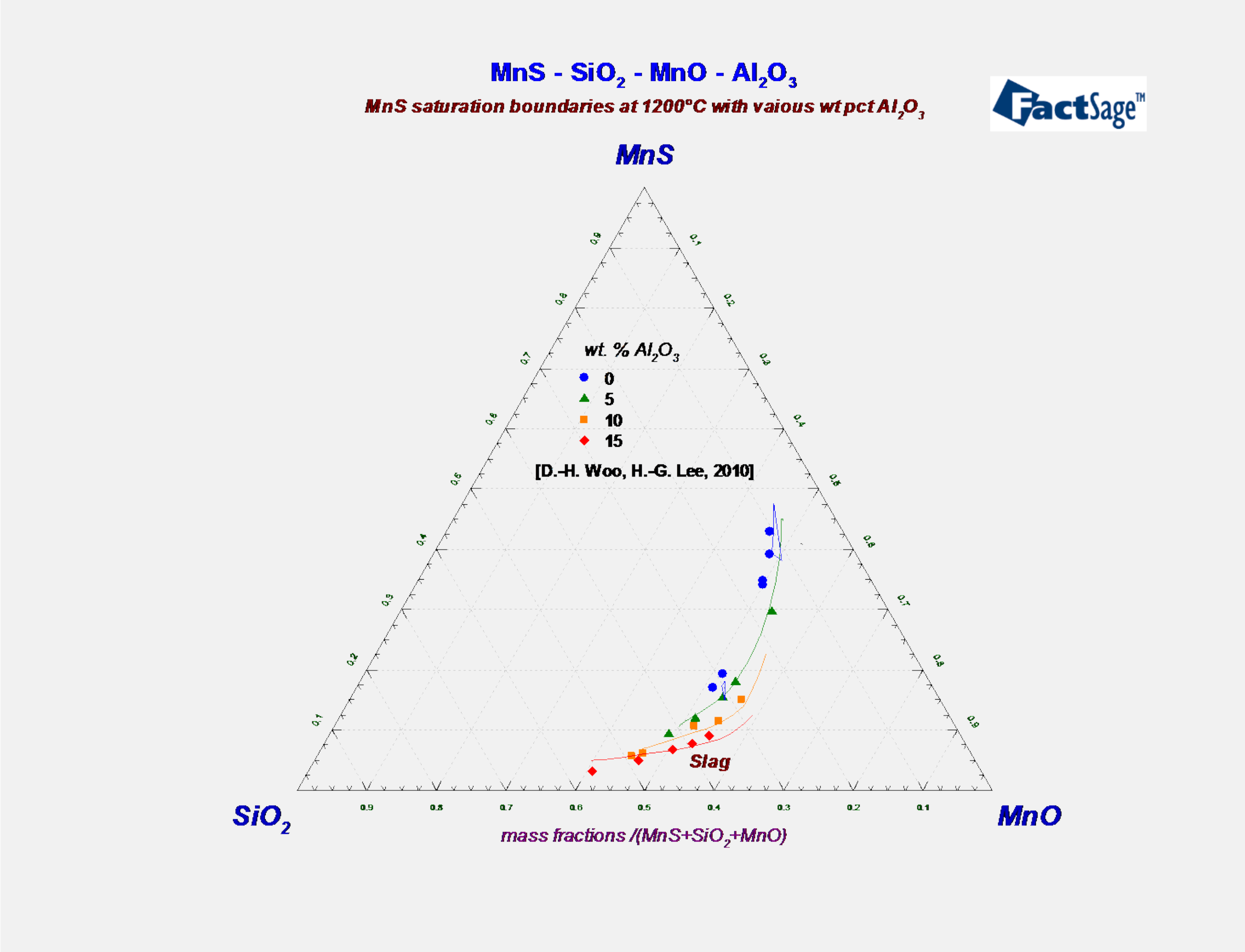


Fig. 12. Phase diagram of the MnO–SiO$_2$–MnS system with experimentally determined phase equilibrium data at 1 250°C. Composition of compound A was determined to be 67.0 mass% MnO, 23.6 mass% SiO$_2$ and 9.4 mass% MnS by EPMA analysis in the present study. Legend: MS=MnS, SO=SiO$_2$, MO=MnS, L=Liquid.

D.-H. Woo, Y.-B. Kang, H.Gaye and H.-G. Lee, ISIJ Intern., 49 (2009), pp. 1490-1497.

Quaternary Al_2O_3-MnO-MnS-SiO_2 at 1200° C



Ternary systems with the addition of MnO_x

- The ternary Al_2O_3-FeO_x-MnO_x system
- The ternary Al_2O_3-MnO-SiO_2 system
- The ternary CaO-MnO-SiO_2 system
- The ternary FeO-MnO-P_2O_5 system
- The ternary FeO_x-MnO_x-SiO_2 system

- The Iron-Cordierite phase in Al_2O_3-FeO-MgO-MnO-SiO_2

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	$(Mg^{+2},Mn^{+2},Ca^{+2},Fe^{+2})(Si^{+4})(O^{-2})_3$
Protopyroxene	$(Ca^{+2},Mg^{+2},Mn^{+2})(Si^{+4})(O^{-2})_3$
C2S-C3P	$(\underline{Ca^{2+}},Cr^{2+}, Mg^{2+},Mn^{+2})_3(\underline{Ca^{2+}},\underline{Va})_1(\underline{P^{5+}},\underline{Si^{4+}})_2 (O^{2-})_8$
C2S-Prime	$(\underline{Ca^{2+}},Mg^{2+},Fe^{2+},Mn^{+2})_3 (\underline{Ca^{2+}}, \underline{Va})_1(\underline{P^{5+}},\underline{Si^{4+}})_2(O^{2-})_8$
Cordierite	$(Al_2Si_5O_{18}{}^{10-})_1(Fe^{2+},Mg^{2+},Mn^{2+})_2(\underline{Al^{3+}},Mg^{2+})_1 (\underline{Al^{3+}},Si^{4+})_1$
Wollastonite	$(\underline{Ca^{2+}}, Fe^{2+}, Mg^{2+}, Mn^{2+})_1 (Si^{4+})_1 (O^{2-})_3$

The isothermal section at 800° C in Al_2O_3-MnO-SiO_2

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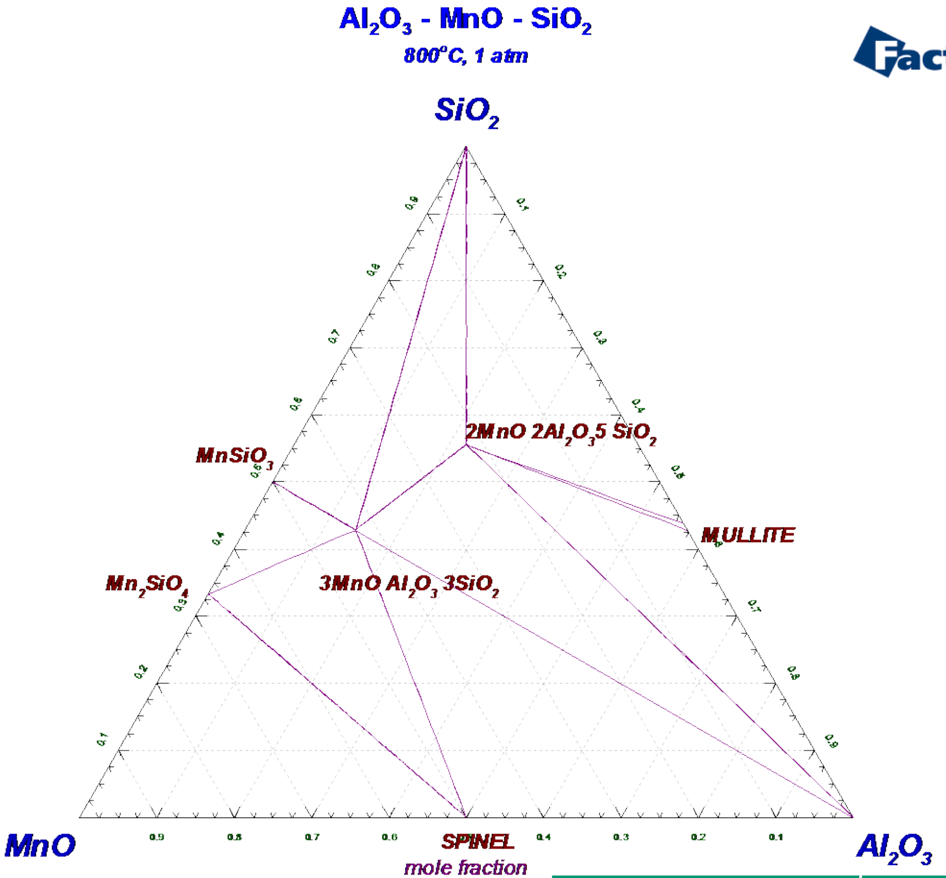
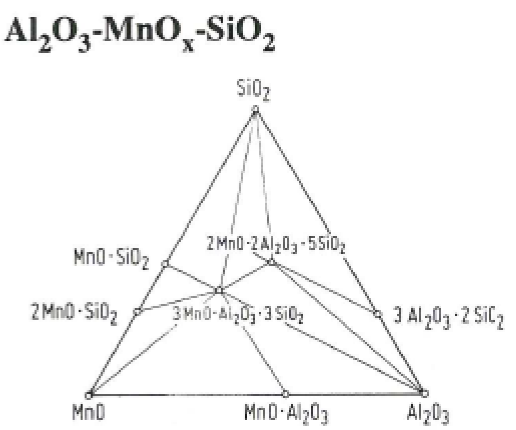
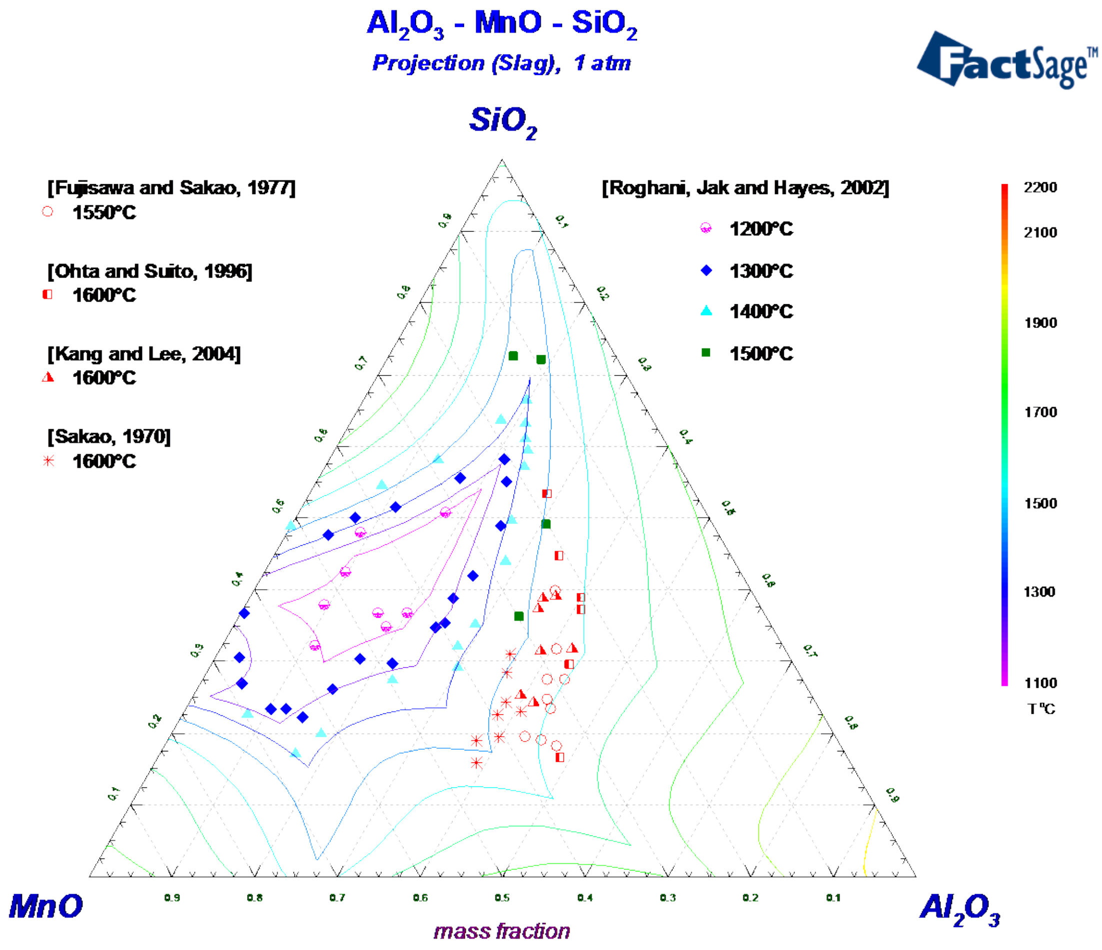




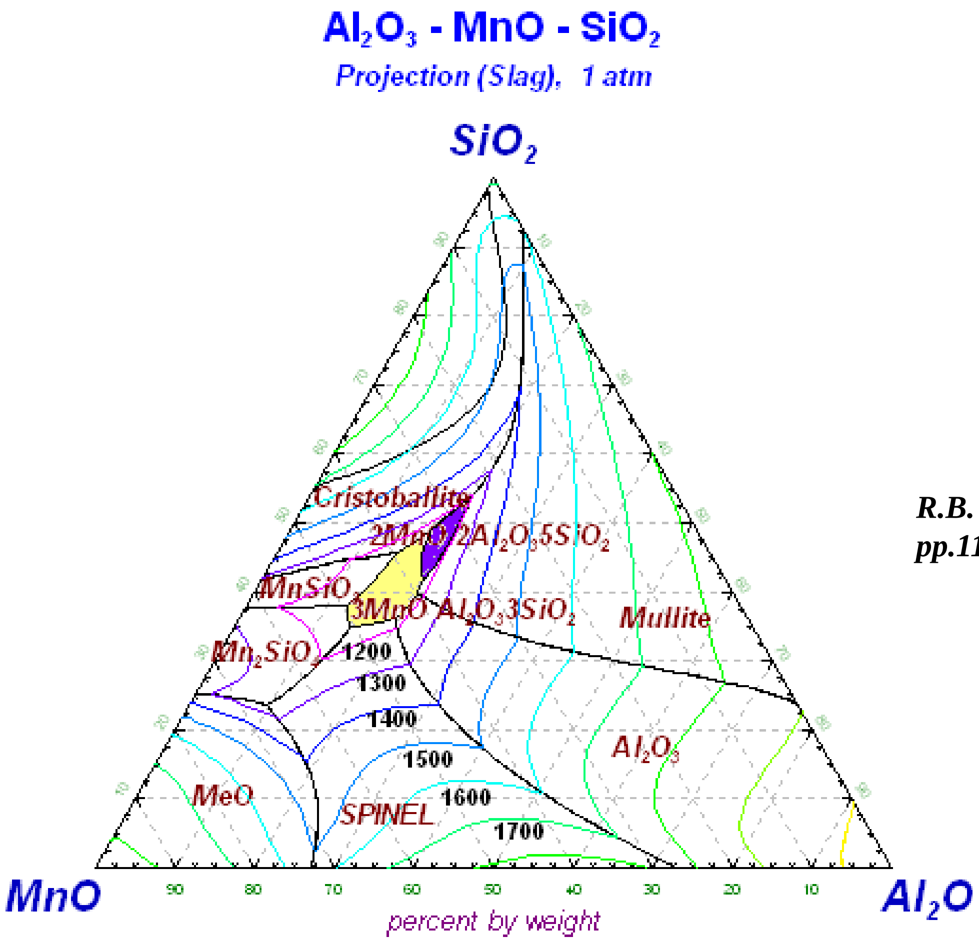
Slag Atlas, 2nd edition, Verlag Stahleisen GmbH,1995, p. 116.

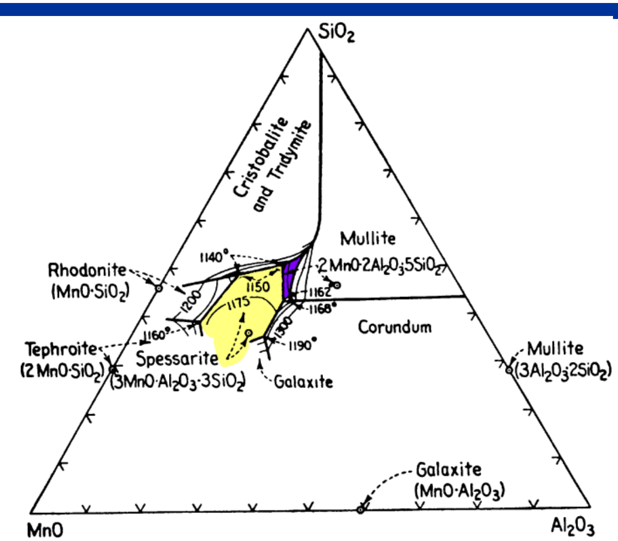
Phase	Description	Used data
Cubic spinel	$(Al^{+3},Mn^{+2})(Al^{+3},Mn^{+2},Mn^{+3},Mn^{+4})_2\ (O^{-2})_4$	GTT
Tetragonal spinel	$(Mn^{+2},Mn^{+3})(Al^{+3},Va,\ Mn^{+2},Mn^{+3})_2\ (O^{-2})_4$	GTT
$Al_4Mn_2Si_5O_{18}$	stoichiometric	FTOxide
$Al_2Mn_3Si_3O_{12}$	stoichiometric	FTOxide

The liquid lines in Al_2O_3-MnO-SiO_2

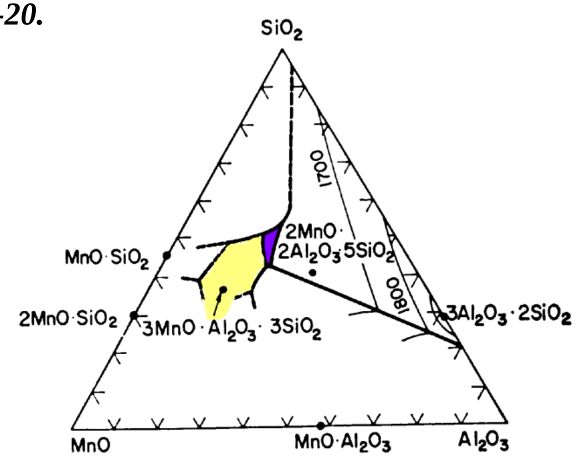


The liquidus surface in Al_2O_3-MnO-SiO_2



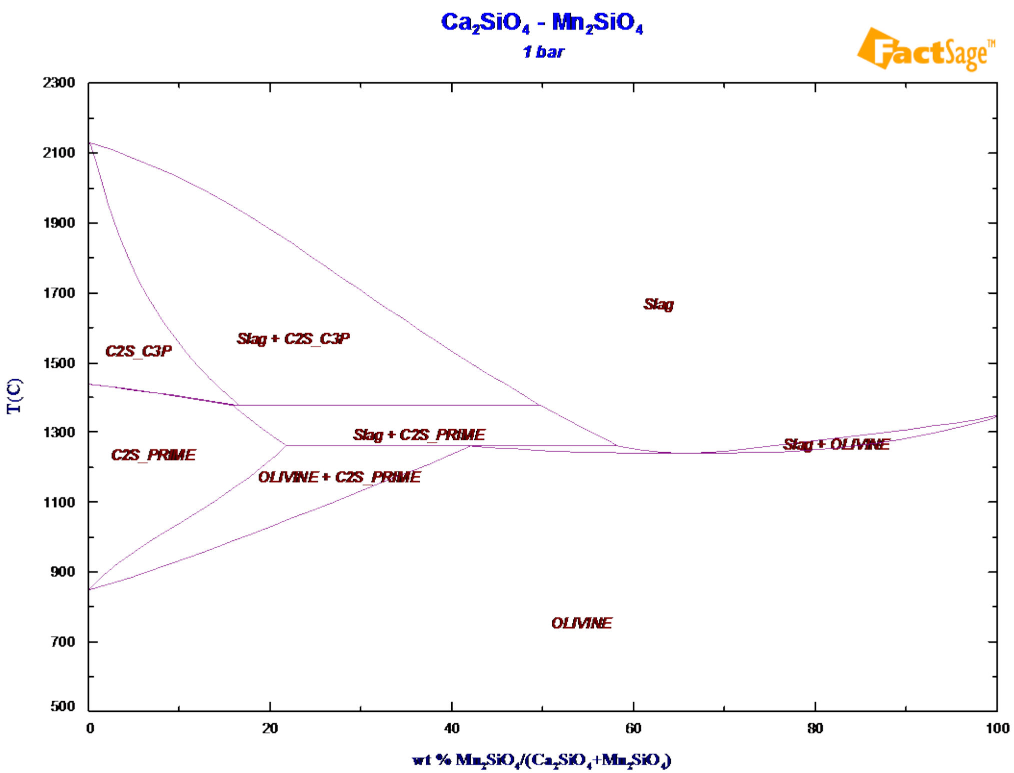


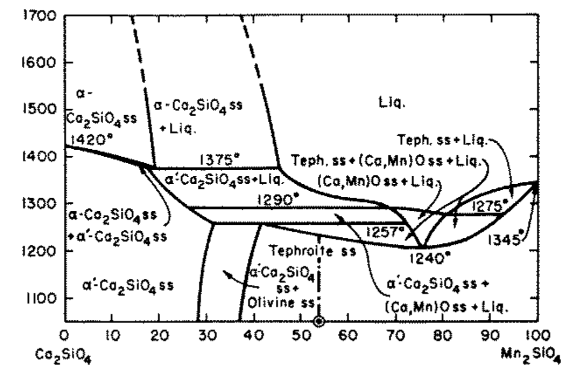
R.B. Snow, J. Amer. Ceram. Soc., 25 [1], (1943), pp.11-20.

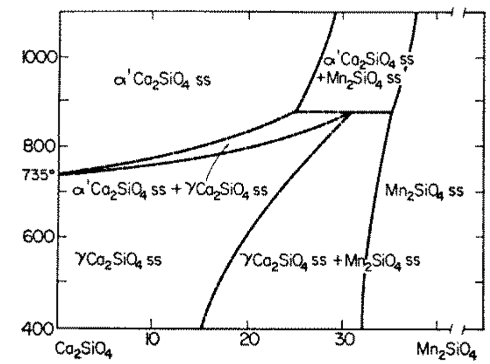


F.Y. Galakhov, Uch. Zap. Kazan. Gos. Univ., No.5, (1957), pp.525-531.

Orthosilicate section in $CaO\text{-}MnO\text{-}SiO_2$

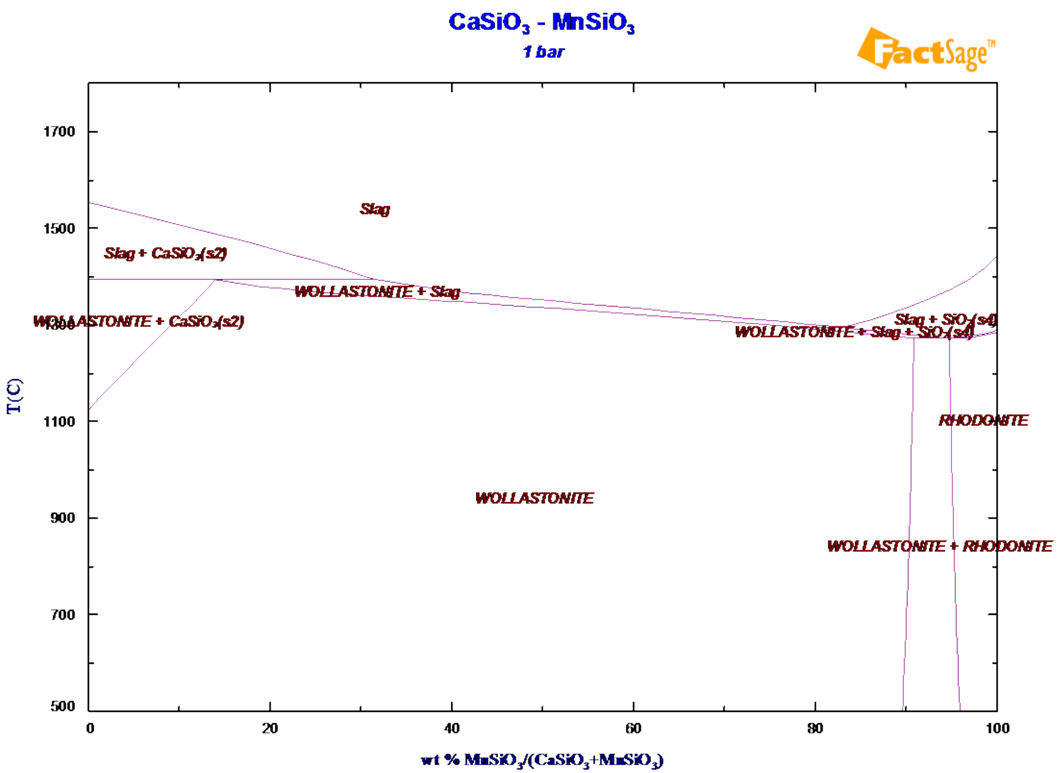






F.P. Glaser, Am. J. Sci., 259 [1], (1961), pp. 46-59.

Metasilicate section in $CaO\text{-}MnO\text{-}SiO_2$



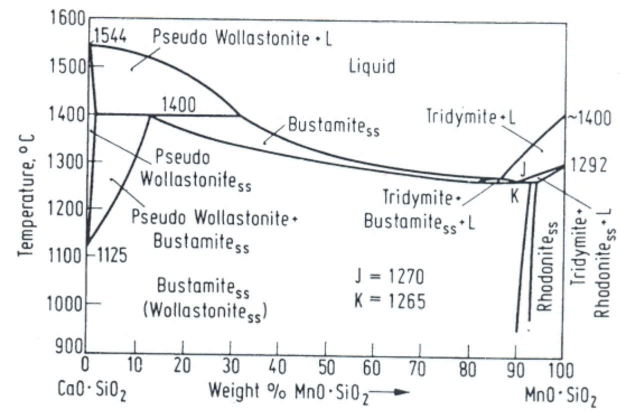
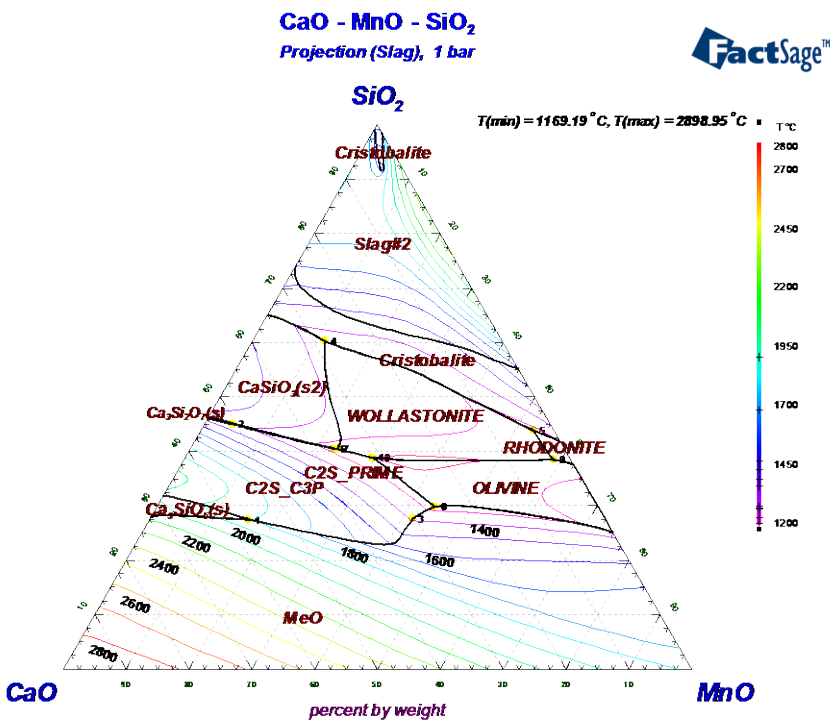
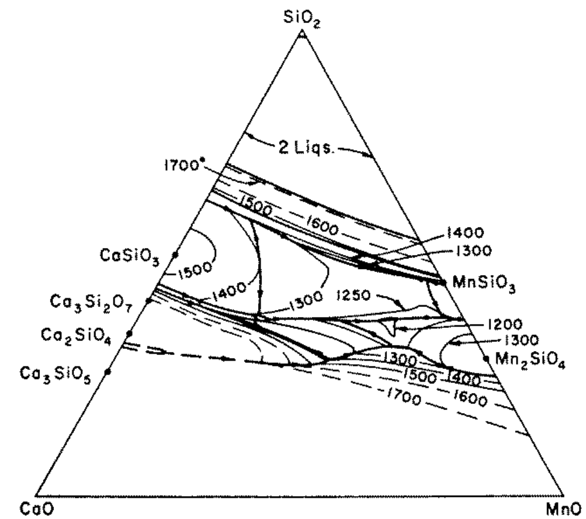


Fig. 3.257. Composition section $CaO{\cdot}SiO_2$-$MnO{\cdot}SiO_2$ after Glasser [1, 2]. Recently, a new ternary solution phase on the $CaO{\cdot}SiO_2$-$MnO{\cdot}SiO_2$ section was reported by Mikirticheva et al. [3].

F.P. Glaser, Am. J. Sci., 259 [1], (1961), pp. 46-59.

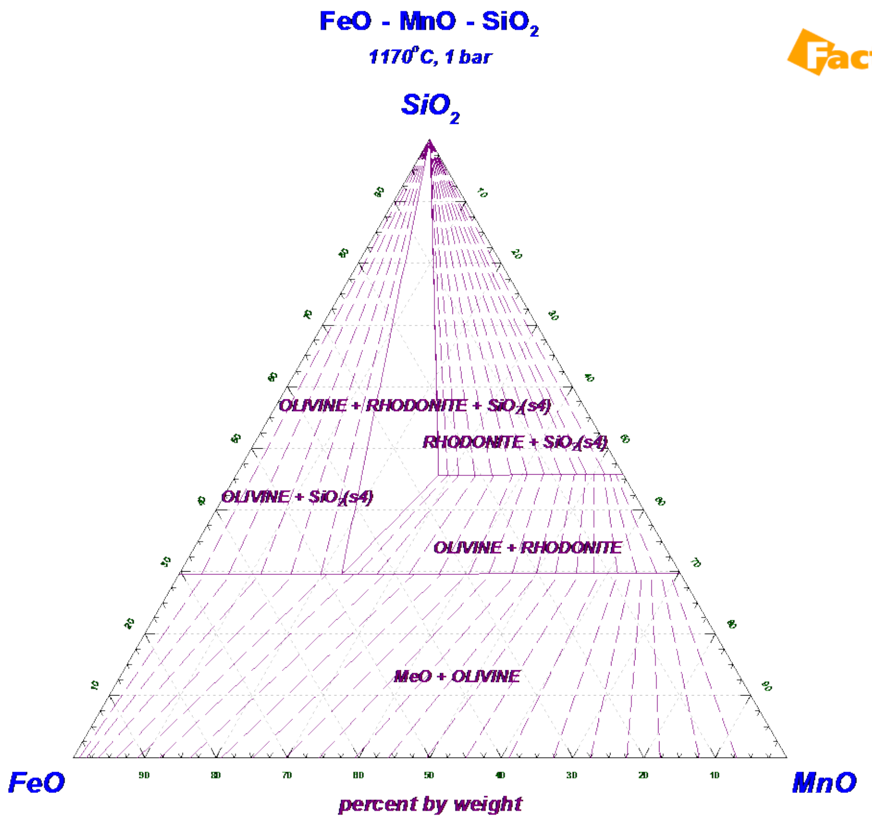
Liquidus surface in CaO-MnO-SiO_2

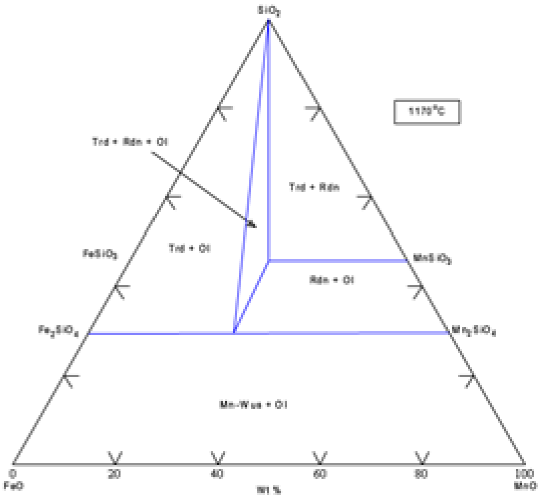




F.P. Glaser, Am. J. Sci., 259 [1], (1961), pp. 46-59.

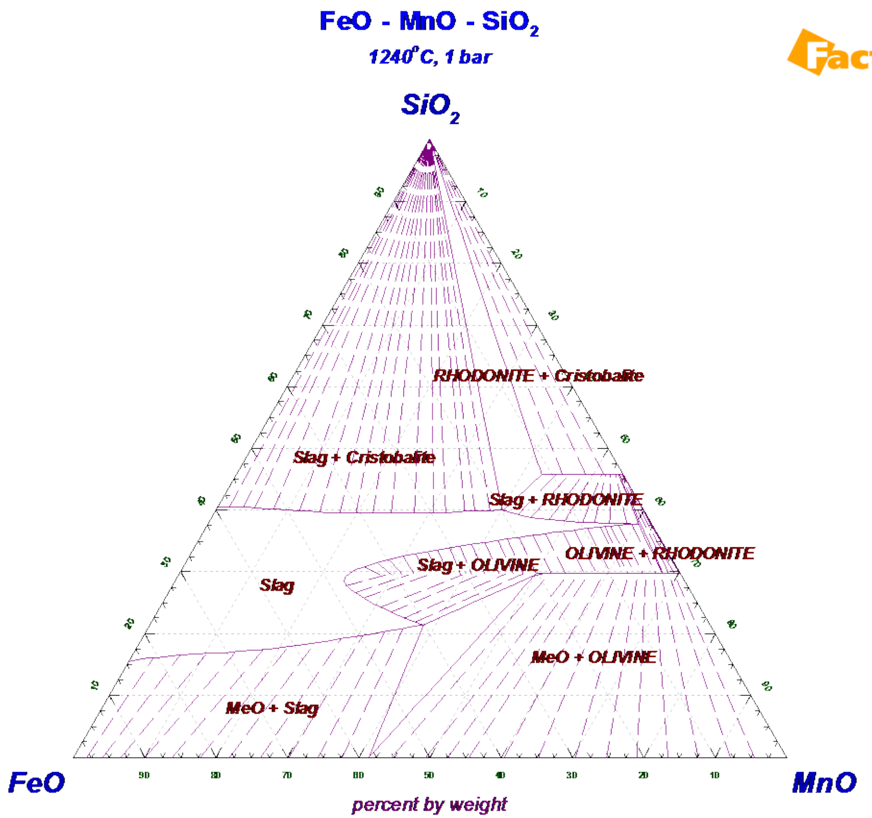
Isothermal section at 1170° C in FeO-MnO-SiO_2

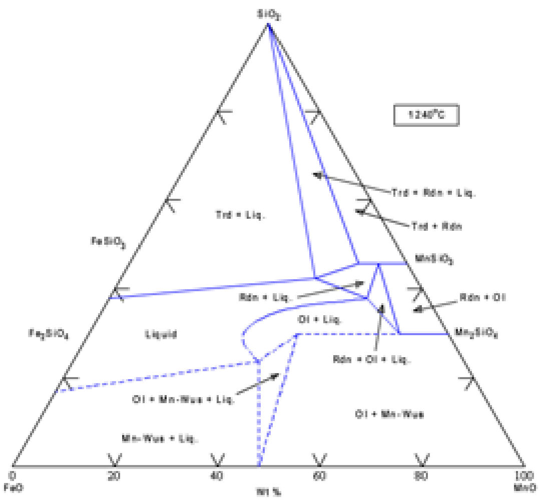




P. V. Riboud and A. Muan, Trans. Metall. Soc. AIME, 224 [1] 27-33 (1962).

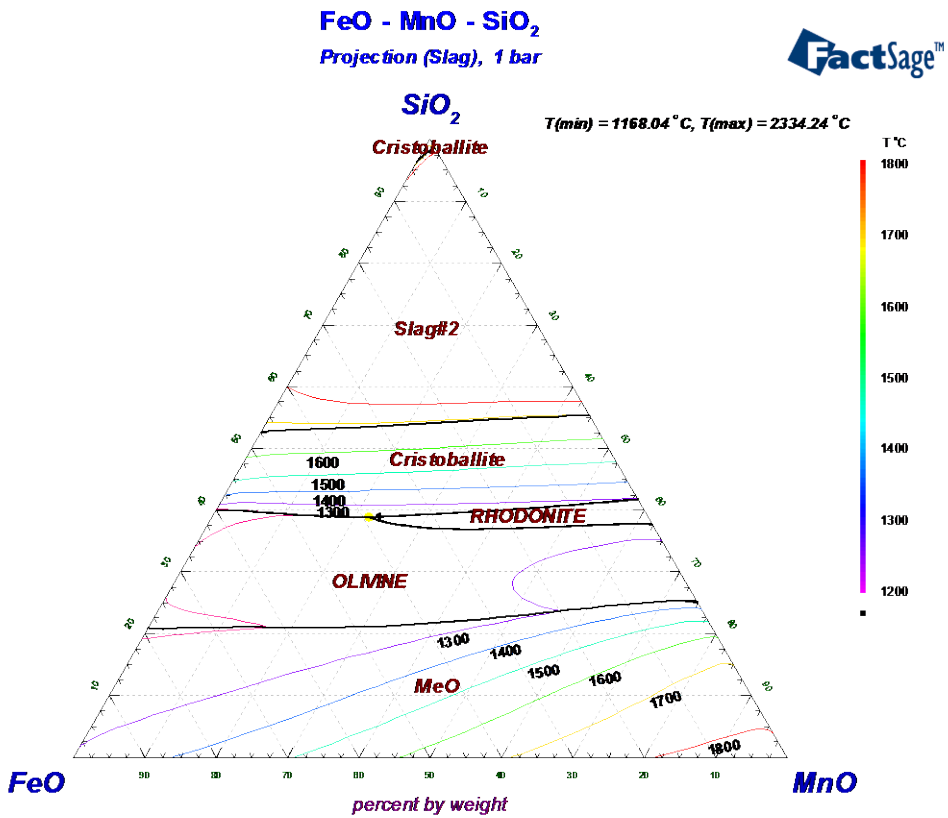
Isothermal section at 1240° C in FeO-MnO-SiO_2

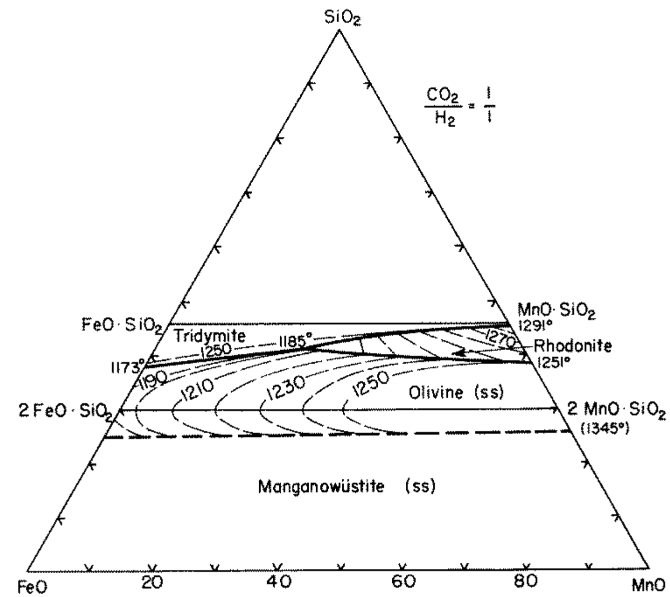




P. V. Riboud and A. Muan, Trans. Metall. Soc. AIME, 224 [1] 27-33 (1962).

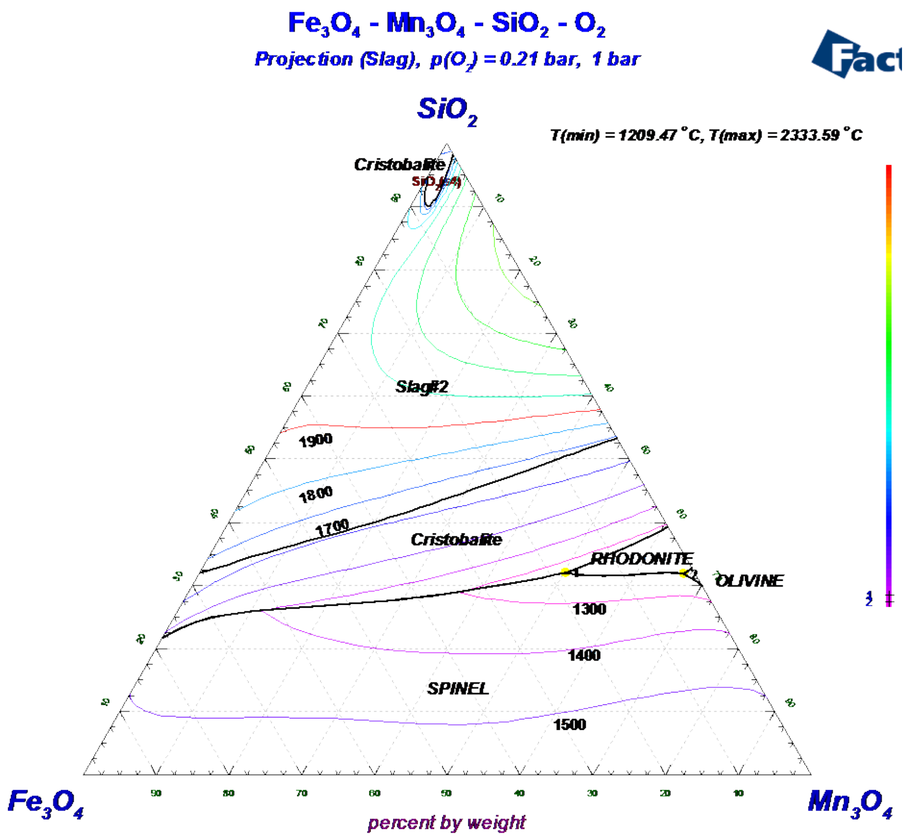
Liquidus surface in FeO-MnO-SiO$_2$

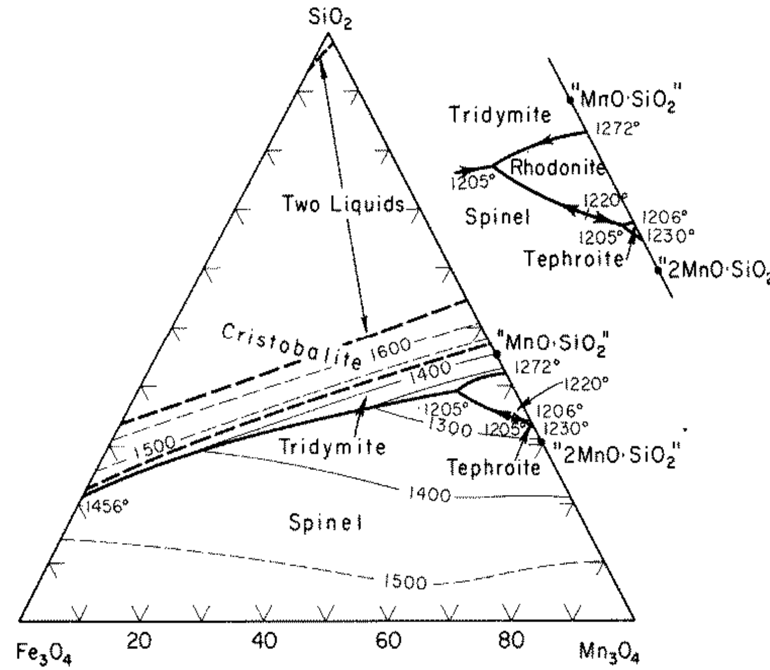




P. V. Riboud and A. Muan, Trans. Metall. Soc. AIME, 224 [1] 27-33 (1962).

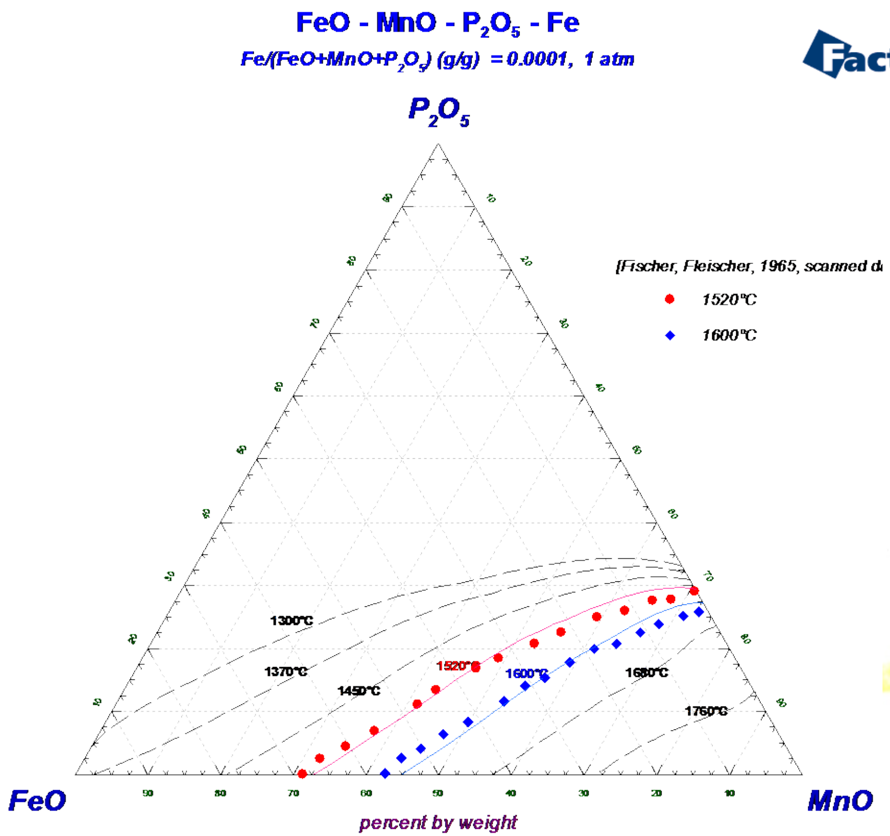
Liquidus surface in Fe_3O_4-Mn_3O_4-SiO_2 in air





A. Muan and S. Somiya, Am. Mineral., 46 [3-4] 364-378 (1961).

Part of liquidus surface in $FeO\text{-}MnO\text{-}P_2O_5$



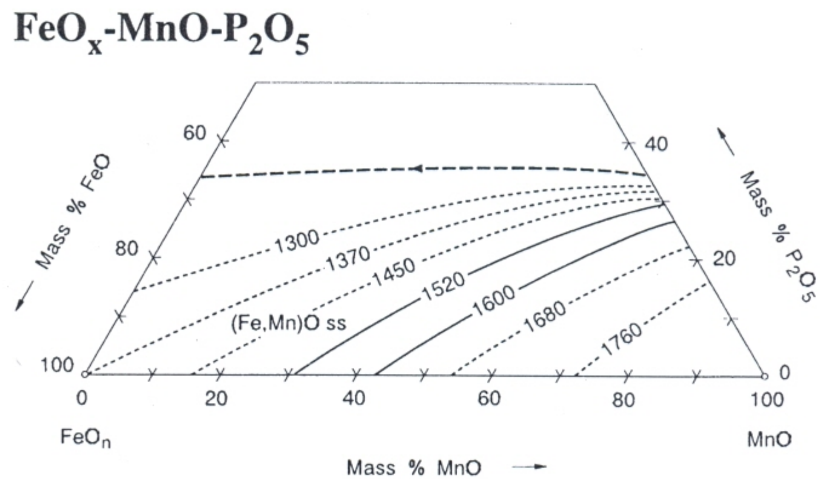


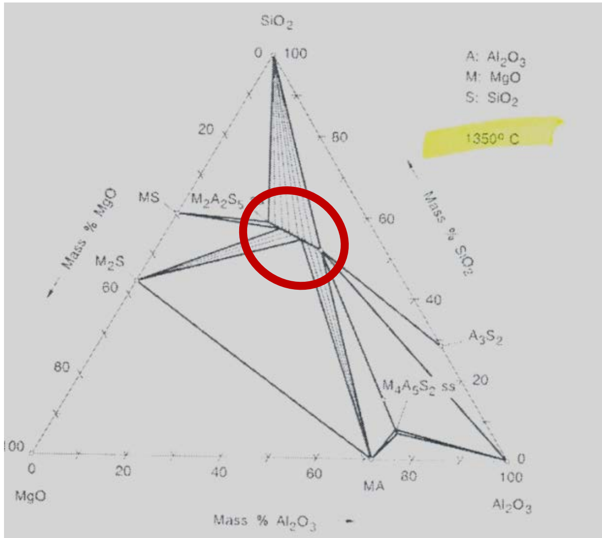
Fig. 3.285. The part of the liquidus surface in the system $FeO_n\text{-}MnO\text{-}P_2O_5$ in contact with metallic iron after Fischer, Fleischer [1].

References

[1] Fischer, W. A., H.-J. Fleischer: Arch. Eisenhüttenwes. 36 (1965) No. 11, p. 791/8

Cordierite in Al_2O_3-FeO-MgO-MnO-SiO_2

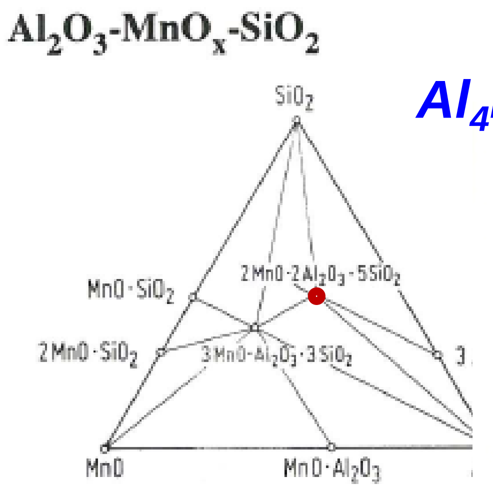
$Al_4Mg_2Si_5O_{18}$ (Cordierite)



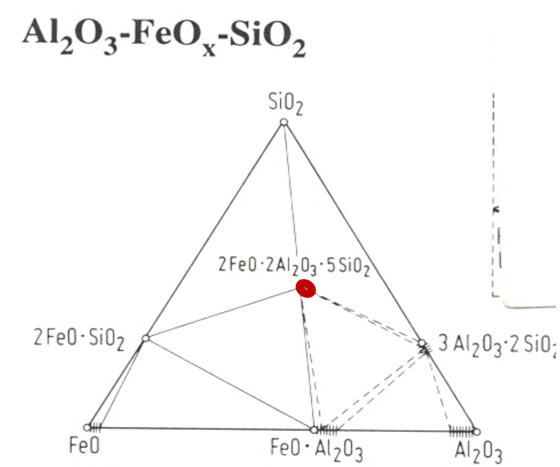
R.M. Smart, F.P. Glaser, Ceram. Int., 7 (1981), No.3,pp.90-97

Cordierite, which was discovered in 1813, is named after the French geologist Louis Cordier. The old name ***iolithe*** comes from the Greek words for violet and stone. Another old name is ***dichroite***, a Greek word meaning "two-colored rock“.

$Al_4Mn_2Si_5O_{18}$ (Mn-Cordierite)

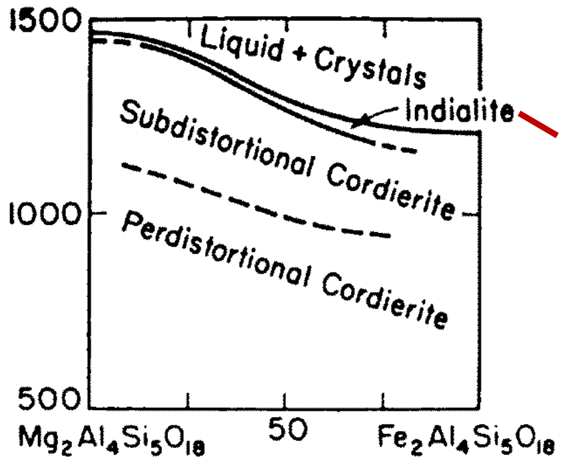


$Al_4Fe_2Si_5O_{18}$ (Iron-Cordierite)

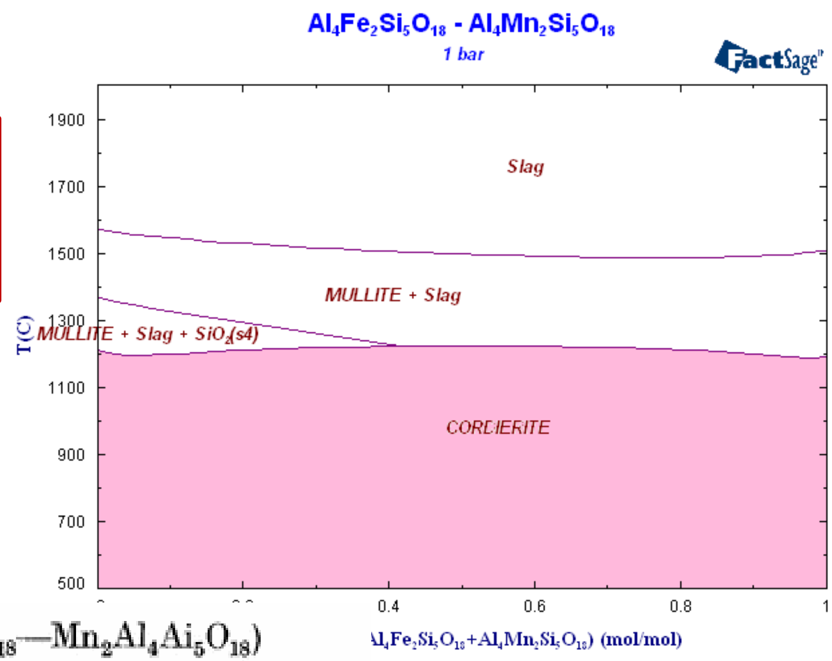


Slag Atlas, 2nd Ed., Verlag Stahl-Eisen, Düsseldorf, 1995.

Modelling of Cordierite in Al_2O_3-FeO-MgO-MnO-SiO_2



After the country of India, where this type of Cordierite is found.



A. Miyashimo, Am. J. Sci., 255 [1], (1957), pp.43-62.

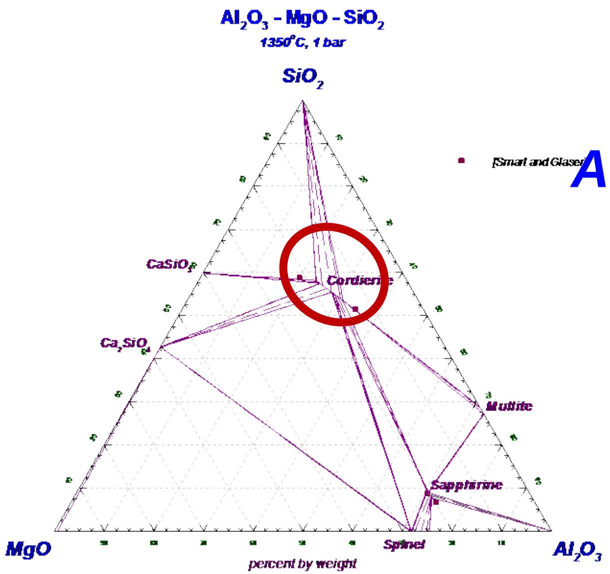
In the cordierite solid solution system ($Mg_2Al_4Si_5O_{18}$—$Fe_2Al_4Si_5O_{18}$—$Mn_2Al_4Ai_5O_{18}$) complete miscibility is obtained in laboratory experiments between the magnesium and iron end members and also between iron and manganese components (Eberhard, 1962). In nature, however, cordierite is usually enriched in magnesium

H.C. Dasgupta, F. Seifert and W. Schreyer, Contr. Mineral. And Petrol., 43, (1974), pp, 275-294.

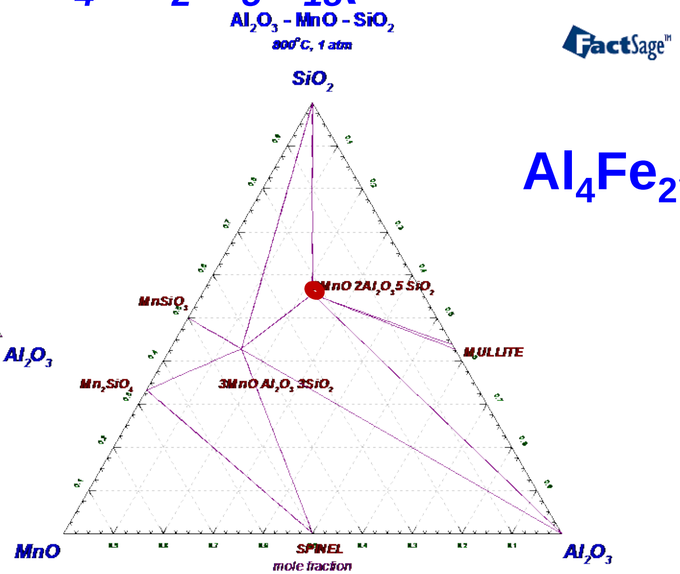
Cordierite : $(Al_2Si_5O_{18})^{6-}$ $(Fe^{2+}, Mg^{2+}, Mn^{2+})_2$$(\underline{Al}^{3+}, Mg^{2+})$$(\underline{Al}^{3+},Si^{4+})$

Cordierite in Al_2O_3-FeO-MgO-MnO-SiO_2

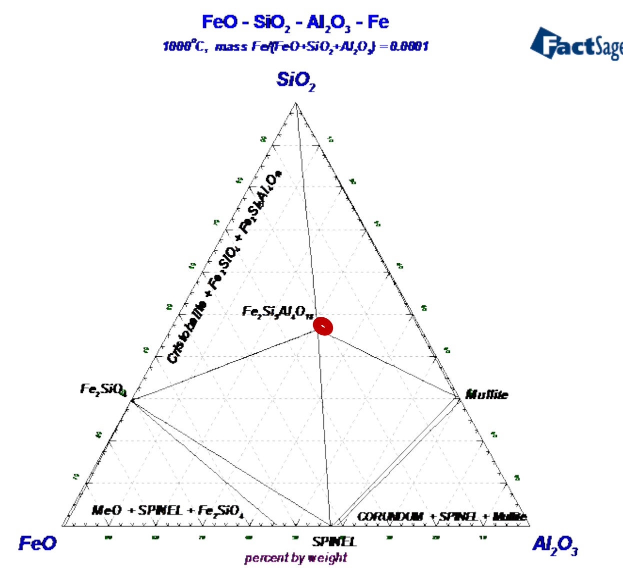
$Al_2Mg_2Si_5O_{18}$(<u>Al</u>,Mg)(<u>Al</u>,Si)



$Al_4Mn_2Si_5O_{18}$(Mn-Cordierite)



$Al_4Fe_2Si_5O_{18}$(Iron-Cordierite)



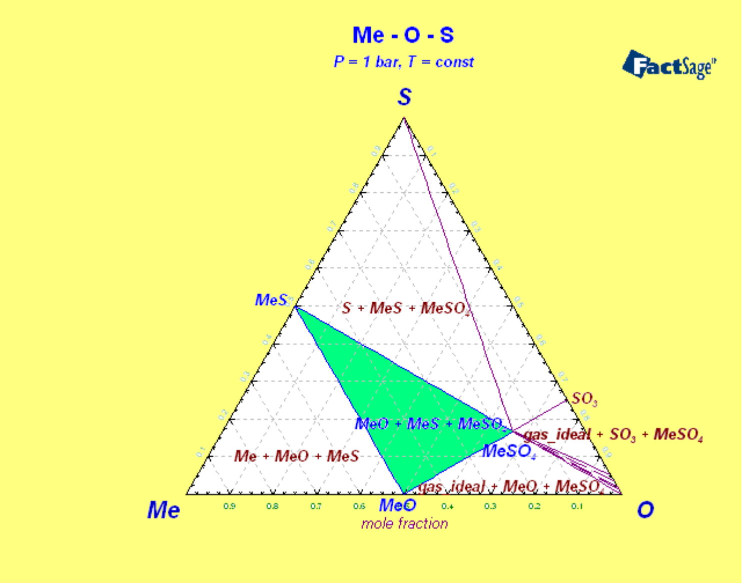
Conclusions

- The liquid phase in all subsystems was evaluated using associate species model,
- All systems were assessed using experimental phase diagram information.
- MnS has so far been integrated into the reduced core system CaS-FeS-MgS-MnO-Al_2O_3-SiO_2. All binaries, 5 ternary and 1 quaternary systems were described. The stoichiometric phases $8MnO \cdot MnS \cdot 3SiO_2$ and $25MnO \cdot MnS \cdot 9SiO_2$ were incorporated.
- The solubility ranges of 12 solid solution phases containing Mn were described using the sublattice model. 7 ternary systems were evaluated.

Future developments

Ternaries with $MeSO_4$ (using $MeO + SO_3 \rightarrow MeSO_4$)

- ***$MeS — MeSO_4(SO_3) — MeO$***
- ***$(Me1)SO_4—(Me2)SO_4 —(Me3)SO_4$***



Thanks for your attention !