Progress in data assessments for HotVegas project

GTT, 12th Annual Workshop, Herzogenrath, 16-18. Juni 2010

Klaus Hack, Tatjana Jantzen

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Introduction

The oxide system relevant to fuel ashes and slags which is suitable both for applications in the coal burning and in the gasification processes is treated.

Alkali and alkaline earth metal oxides as well as Al_2O_3 and SiO_2 form the material base:

→ Na_2O-K_2O-CaO-MgO-Al_2O_3-SiO_2

CaO-MgO-Al_2O_3-SiO_2 (GTT)

Na_2O-K_2O-Al_2O_3-SiO_2 (FZ Jülich)

Introduction

The associate species model was applied to the thermodynamic description of the liquid phase in the Al_2O_3-CaO-MgO-SiO_2 system.

System	Associate species
Al_2O_3-CaO	**Al_2CaO_4**
Al_2O_3-MgO	–
Al_2O_3-SiO_2	**$Al_6Si_2O_{13}$**
CaO-MgO	–
CaO-SiO_2	**$CaSiO_3$** **Ca_2SiO_4**
MgO-SiO_2	**$MgSiO_3$** **Mg_2SiO_4**
Al_2O_3-CaO-MgO	–
Al_2O_3-CaO-SiO_2	**$Al_4Ca_2Si_4O_{16}$**
Al_2O_3-MgO-SiO_2	**$Al_4Mg_2Si_5O_{18}$**
CaO-MgO-SiO_2	–

Behaviour of Spinel in Al_2O_3-CaO-MgO-SiO_2

E. F. Osborn, R.C. DeVries, K.H. Gee, H.M. Kraner, Trans. Am. Inst. MIn., Metall. Pet. Eng., 200, (1954), pp.33-45.

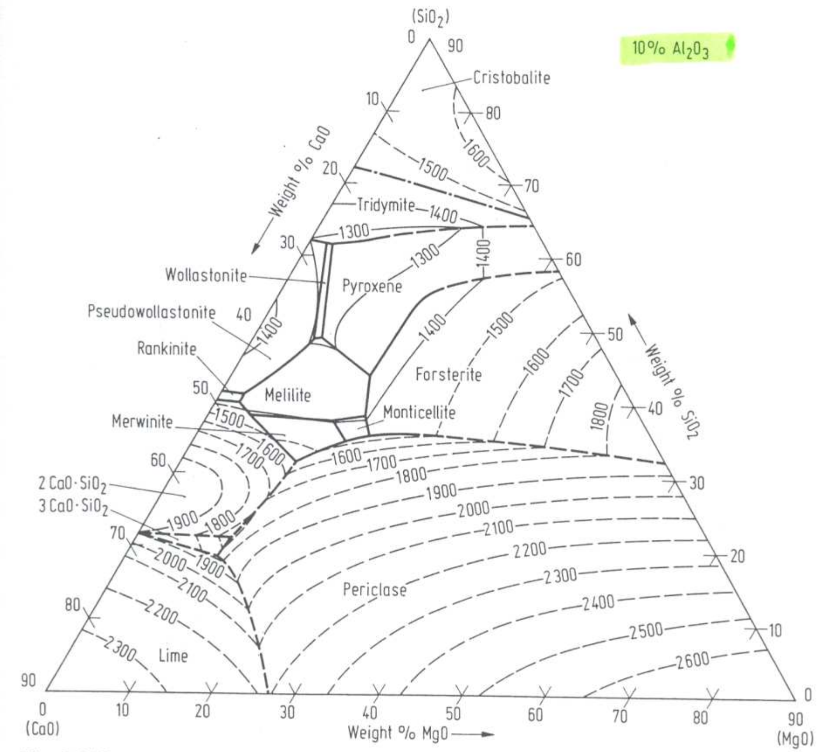
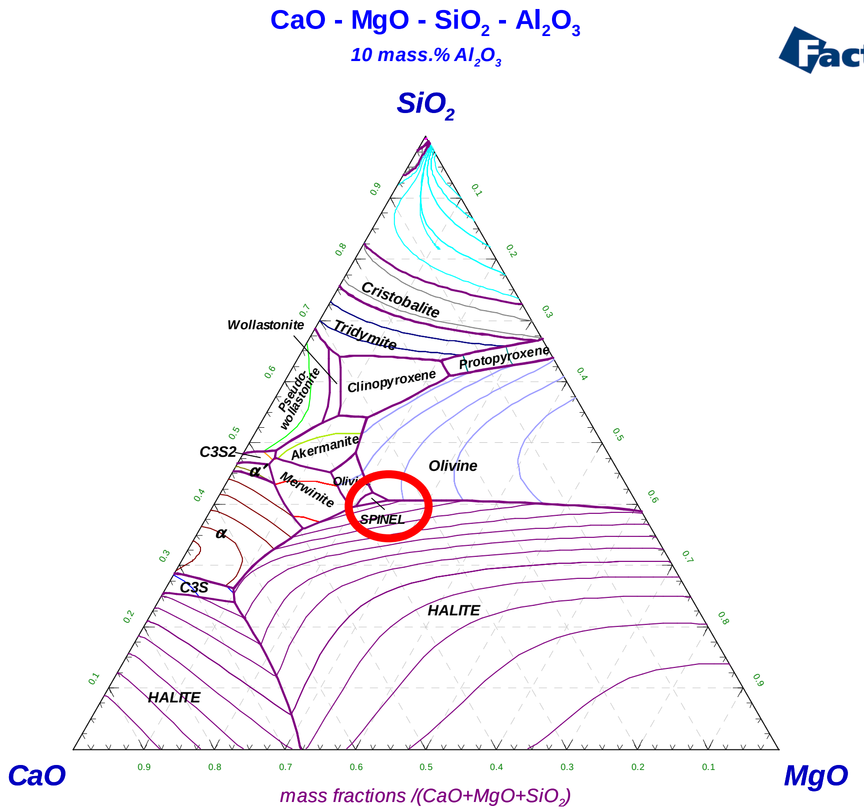
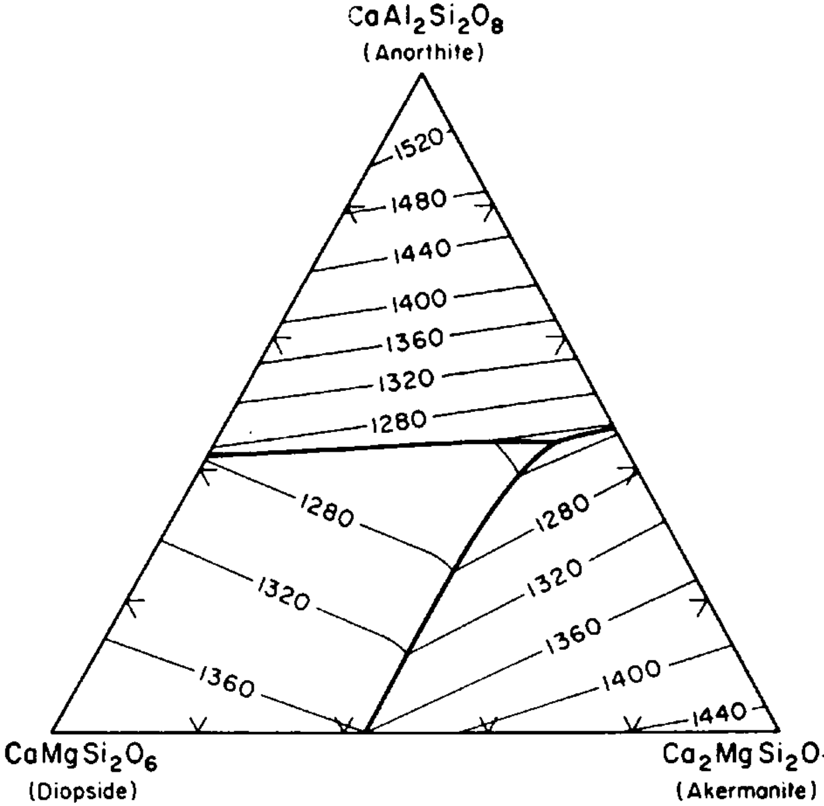


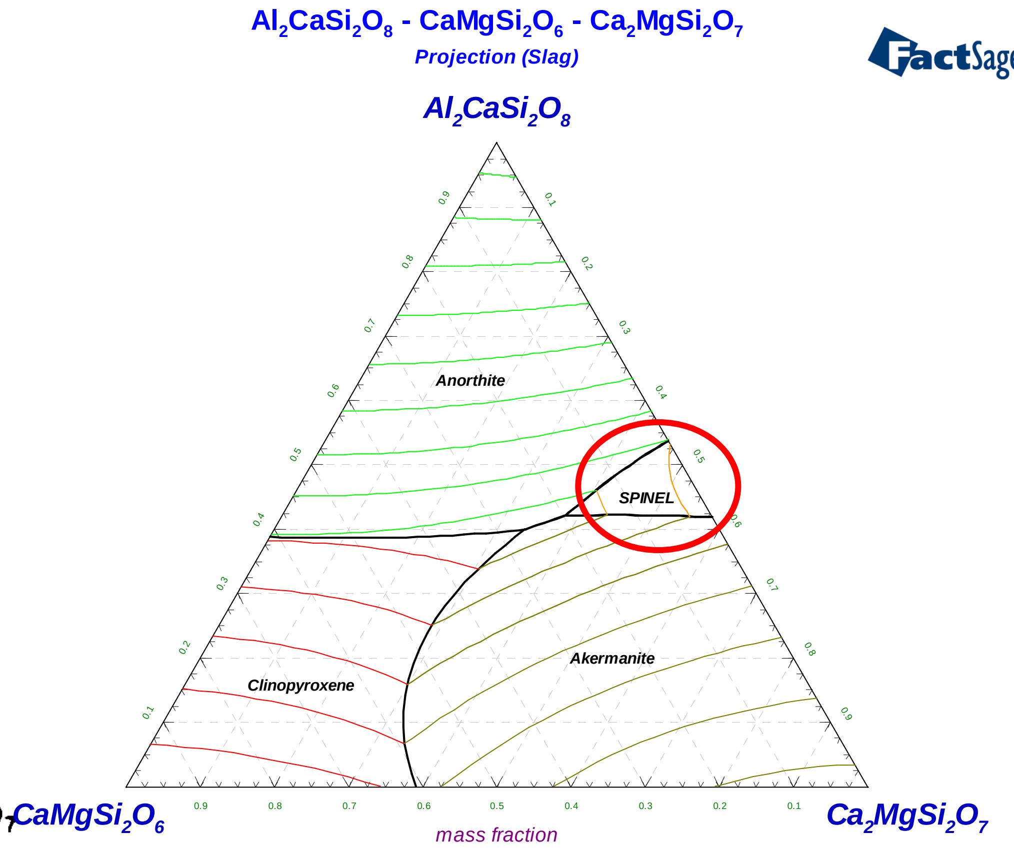
Fig. 3.318.



Behaviour of Spinel in Al_2O_3-CaO-MgO-SiO_2

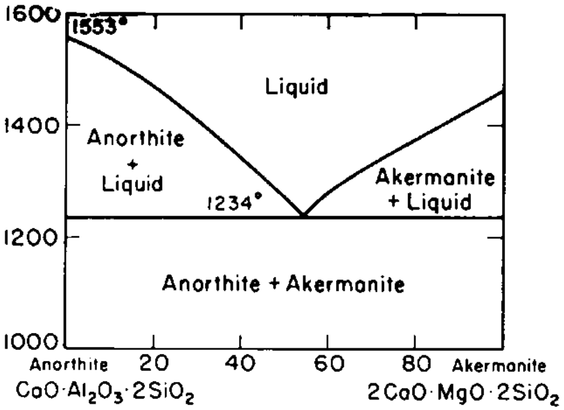
E.C. DeWys, W.R. Forster, Mineral. Mag., 31 [240], (1958), pp.736-743.



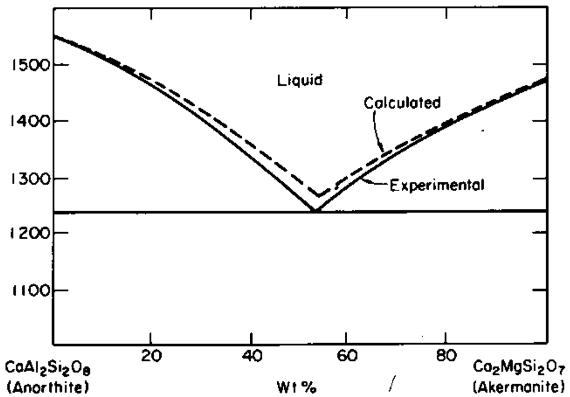


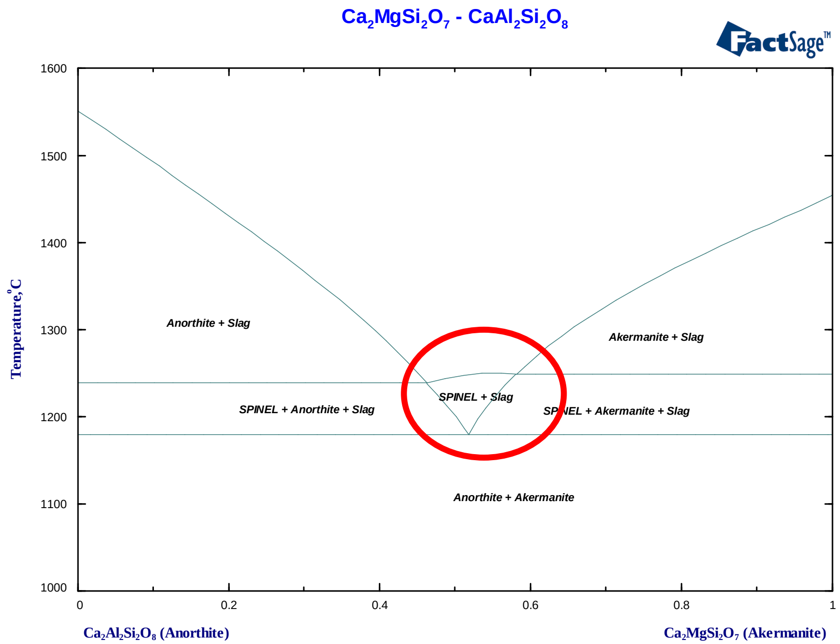
Behaviour of Spinel in Al_2O_3-CaO-MgO-SiO_2

E.C. DeWys, W.R. Foster, J. Am. Ceram. Soc., 39 [11], (1956), pp.372-376.



E.C. DeWys, W.R. Foster,, Mineral. Mag., 31 [240], (1958), pp.736-743.





Reassessment of Spinel in Al_2O_3-MgO

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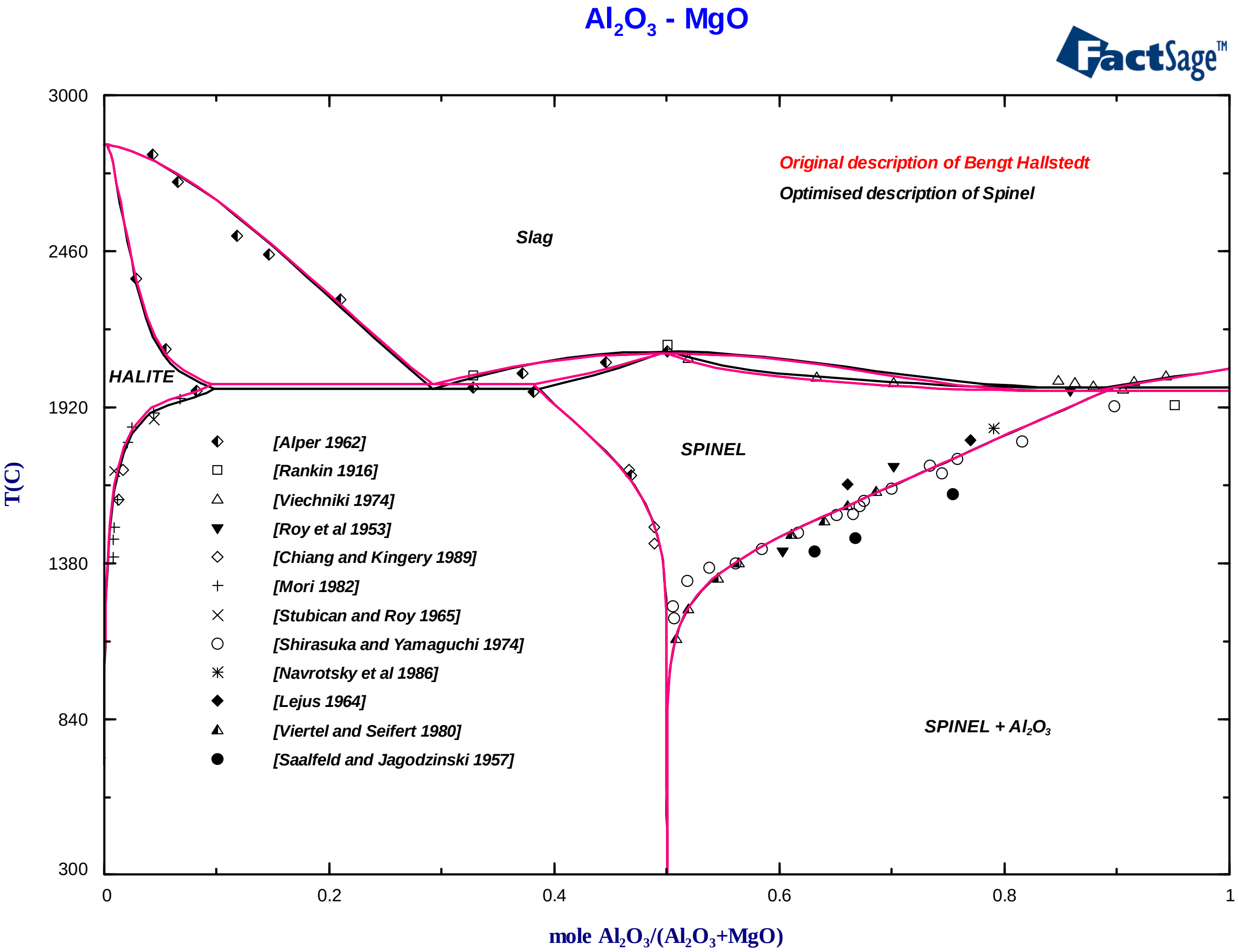
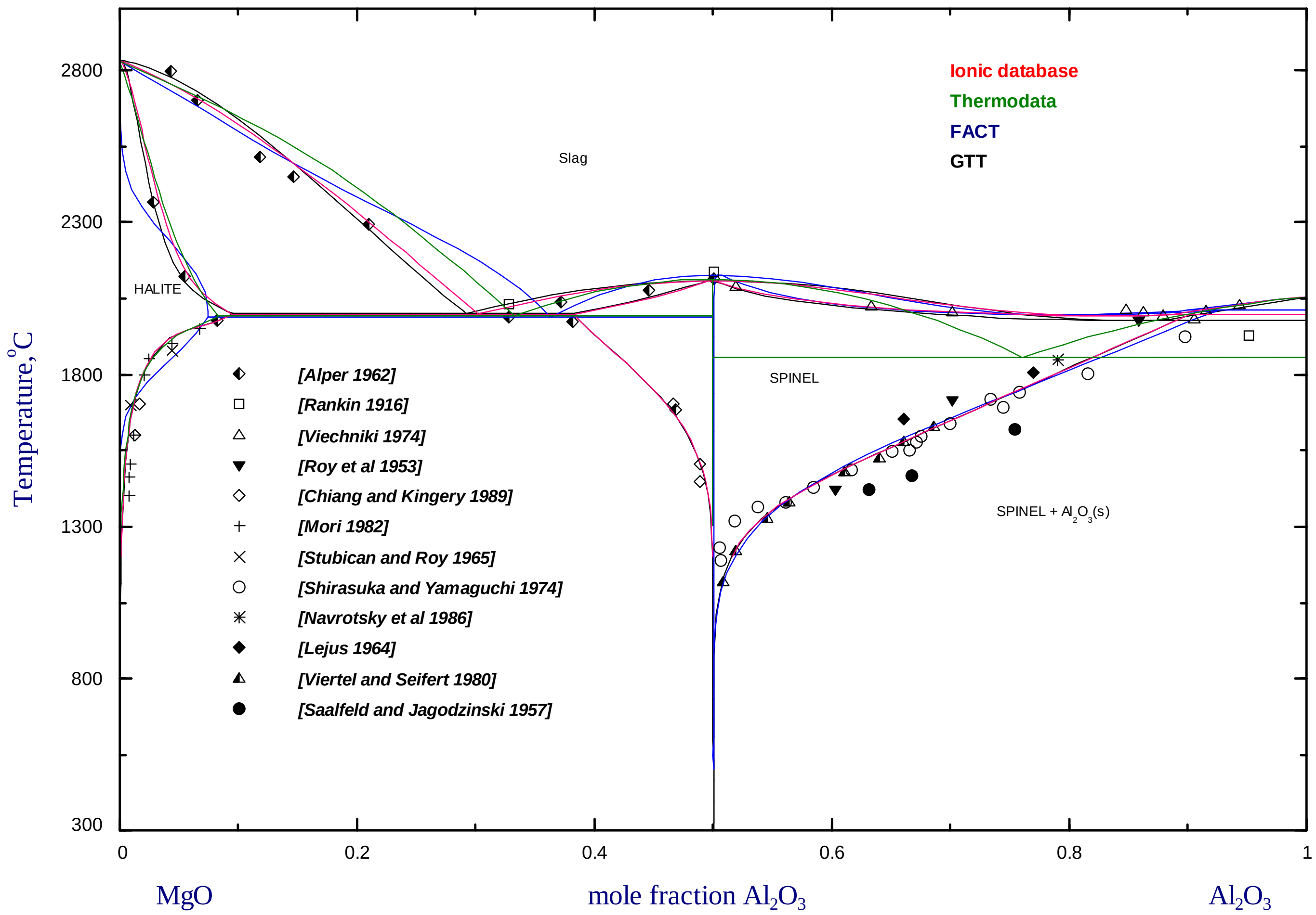


Comparison of databases

MgO - Al_2O_3



Isothermal sections in Al_2O_3-CaO-MgO

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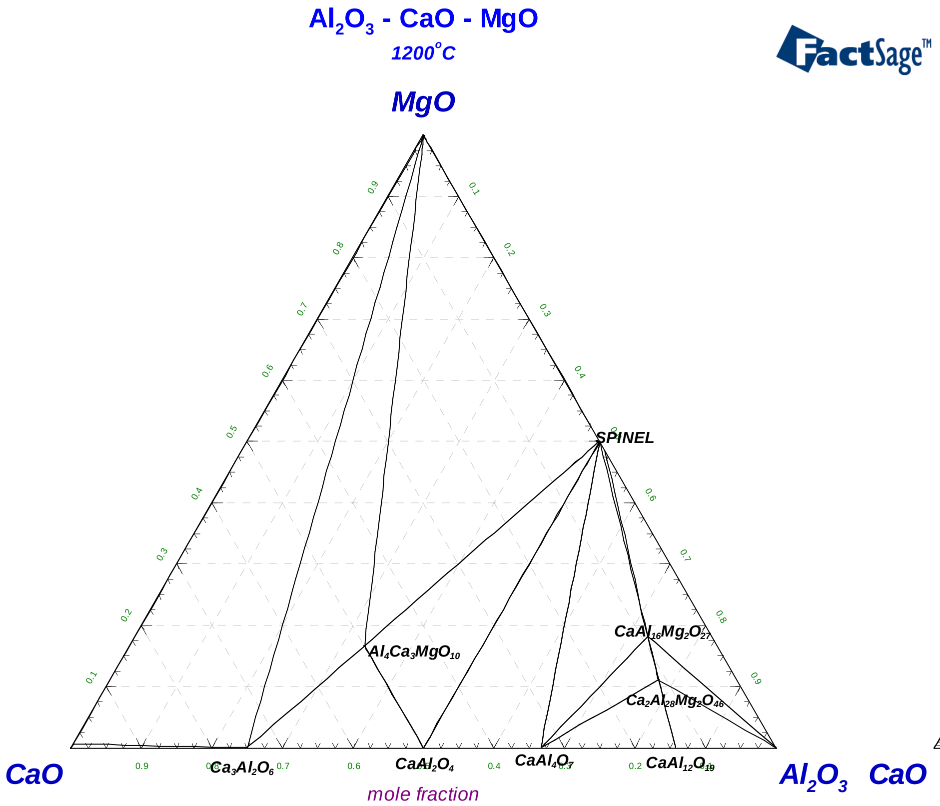
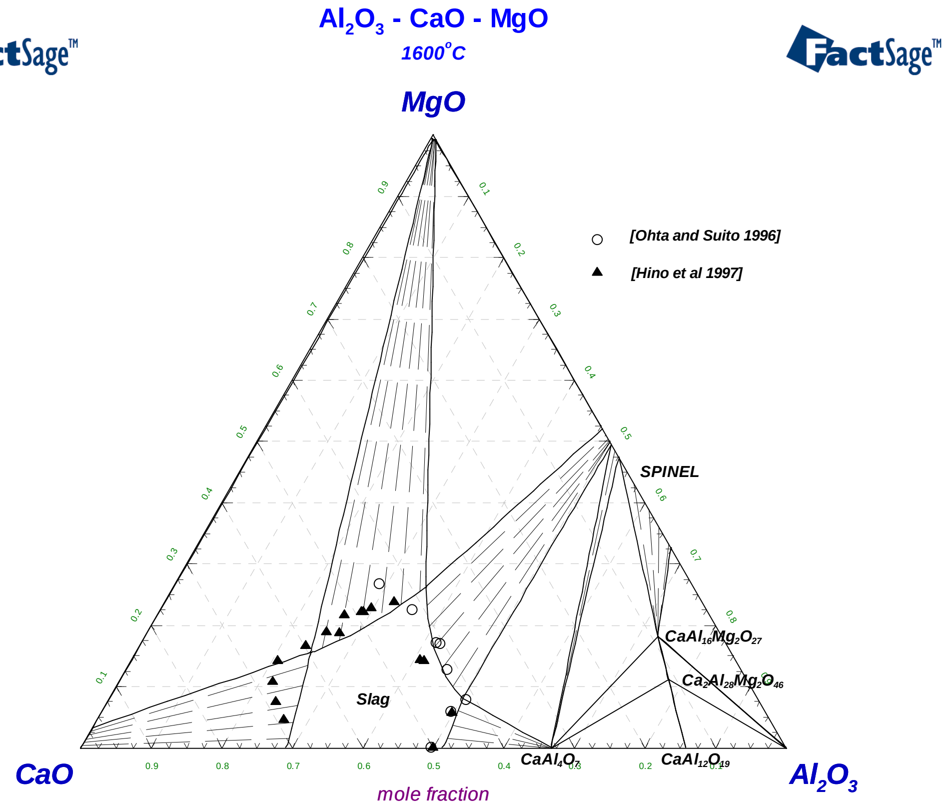
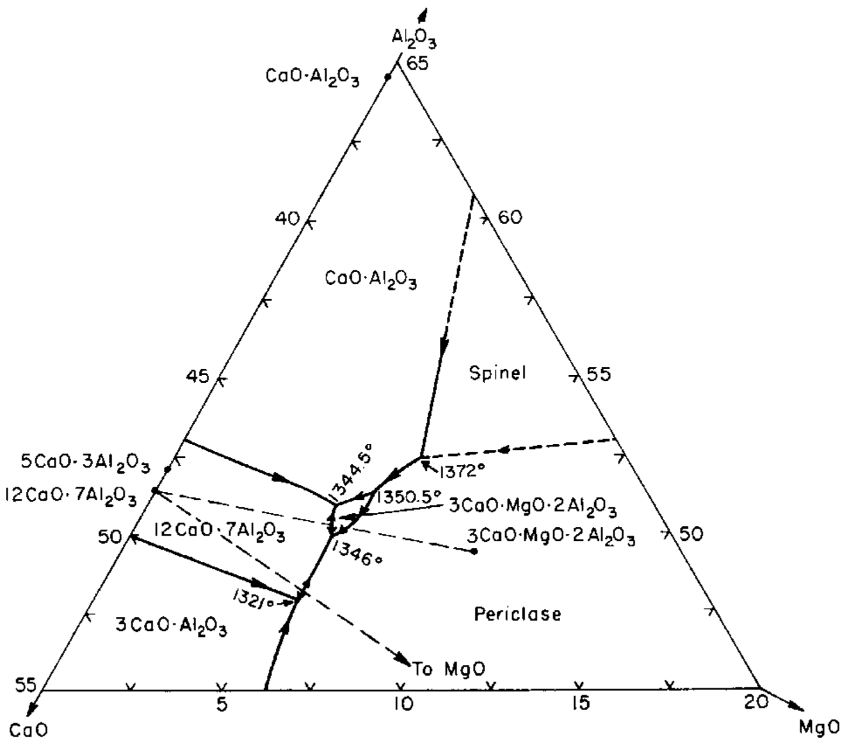
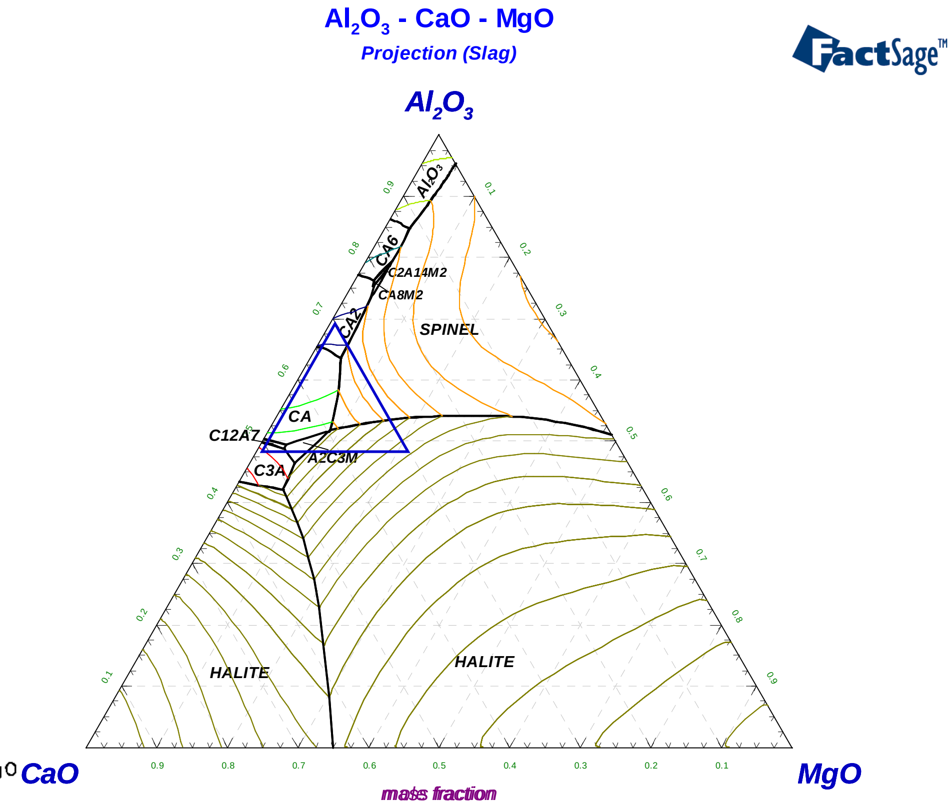




Liquidus surface in Al_2O_3-CaO-MgO

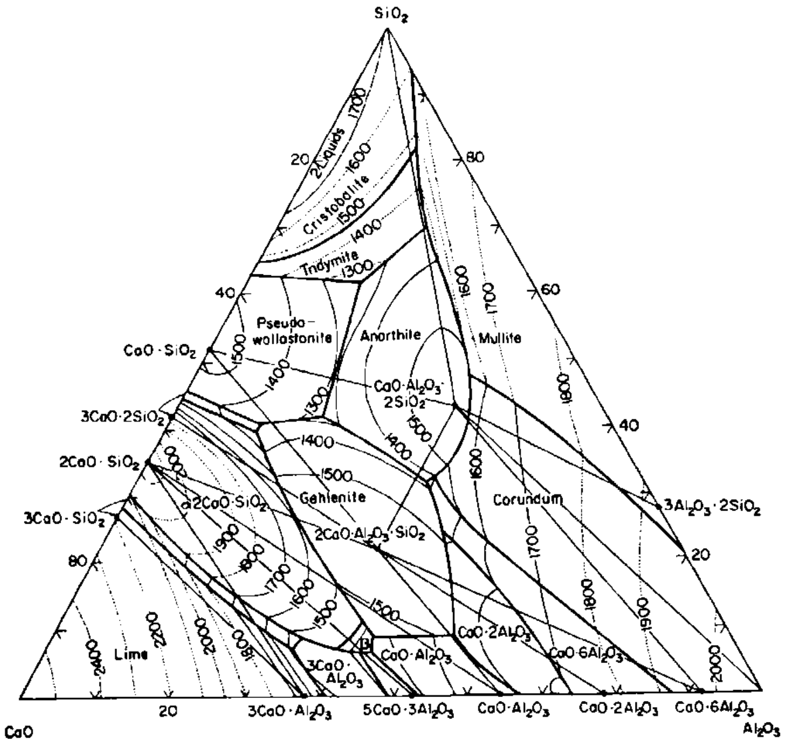
A.J. Majumdar, Trans.Br.Ceram.Soc., 63[7], (1964), pp. 347-364.

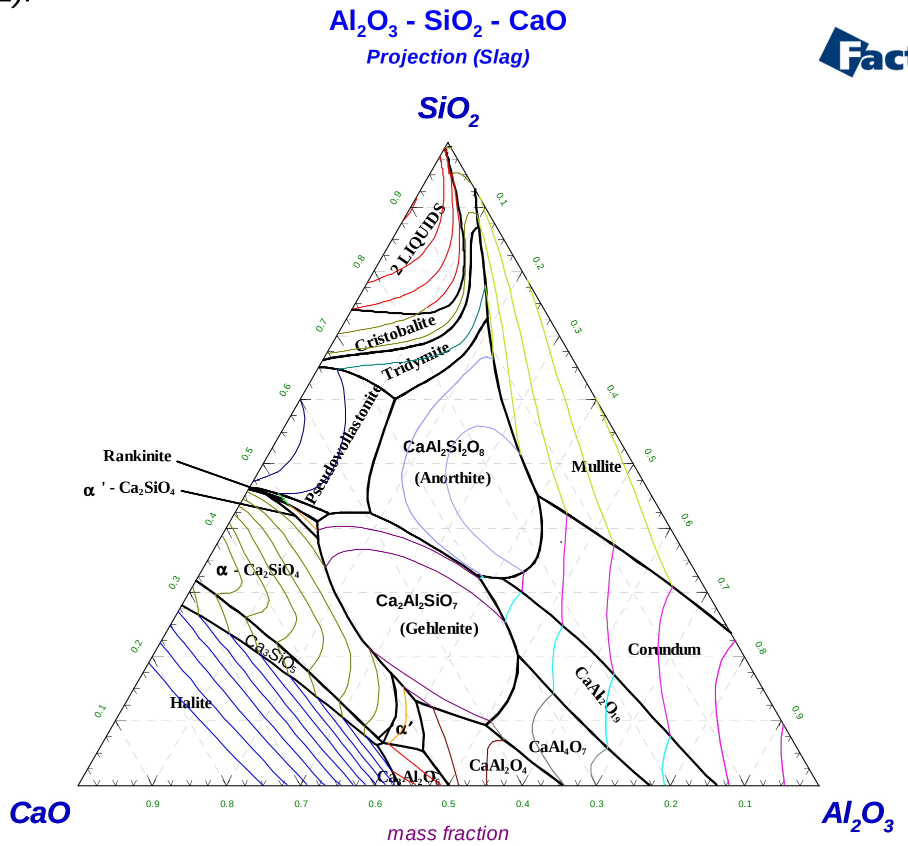




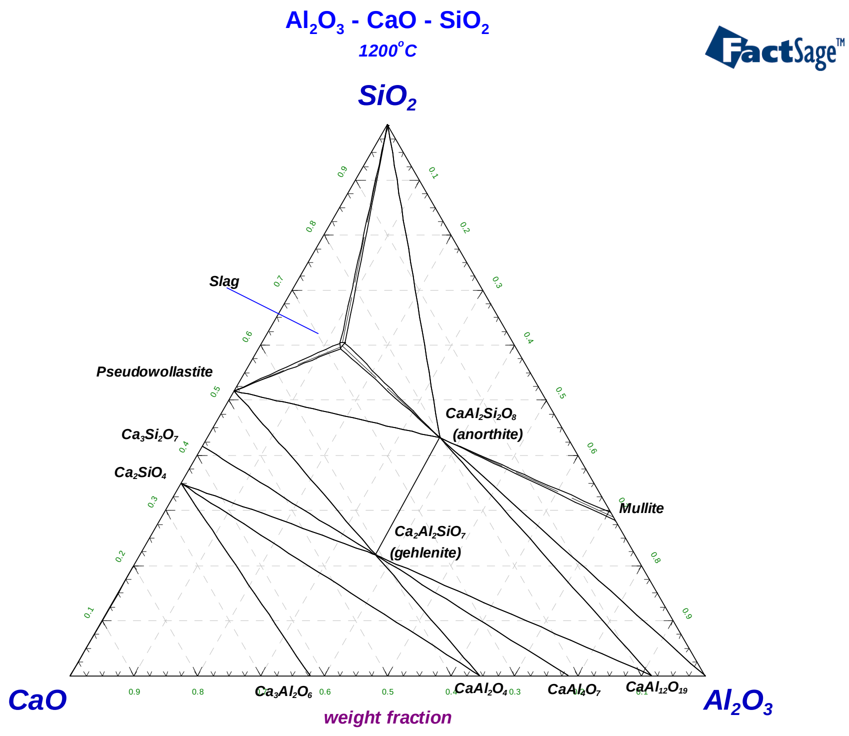
Liquidus surface in Al_2O_3-CaO-SiO_2

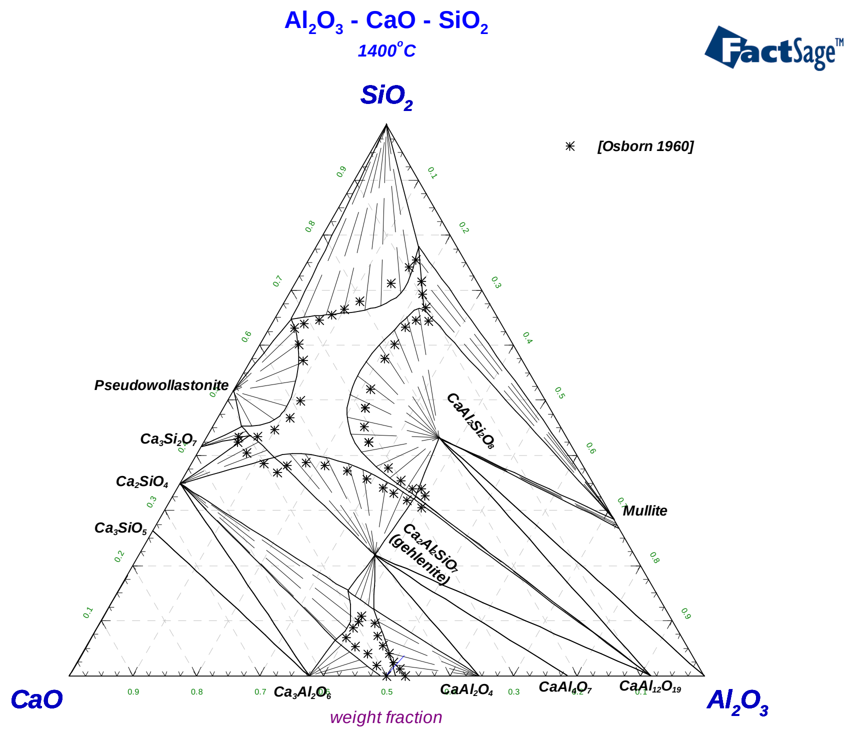
A.L. Gentile, W.R. Foster, private communication, (1961).





Isothermal sections in Al_2O_3-CaO-SiO_2





Isopleth section Anorthite - SiO_2

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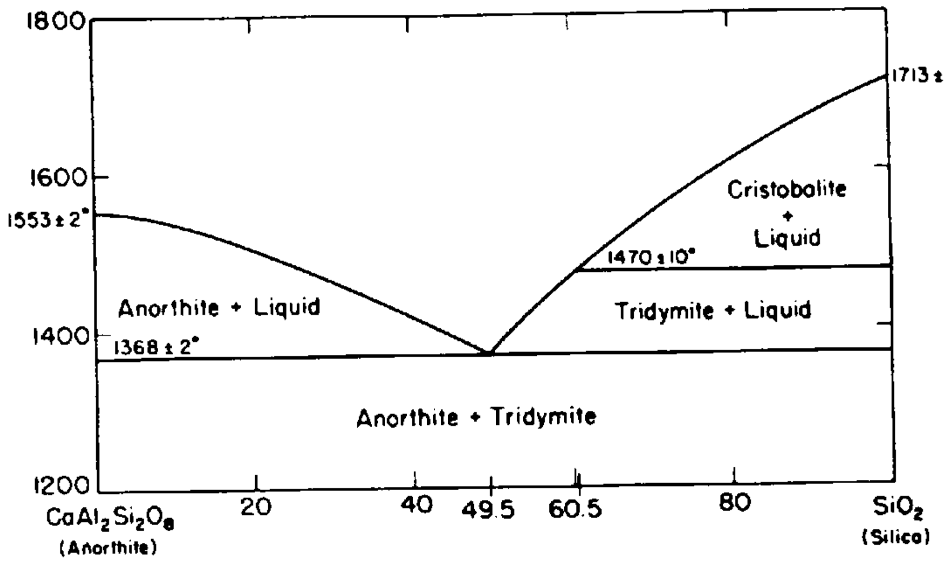
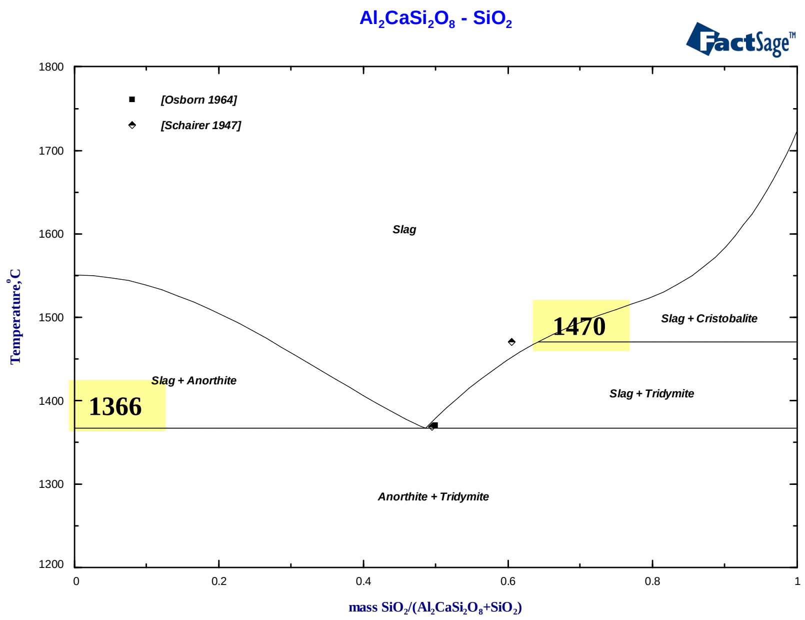
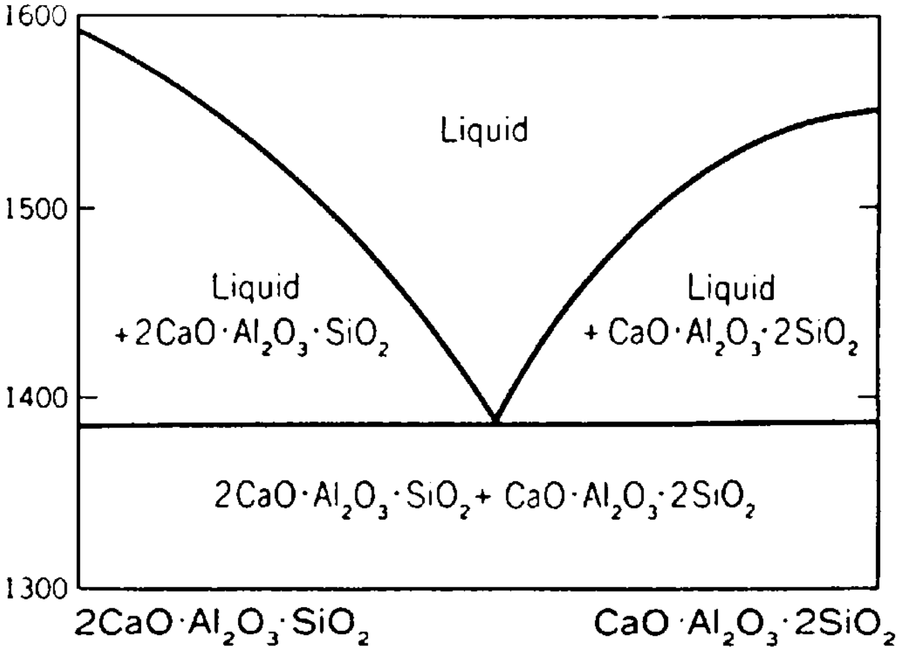
J.F. Schairer, N:l. Bowen, Bull.Comm.Geol.finl., 20 (1947), pp.67-87.

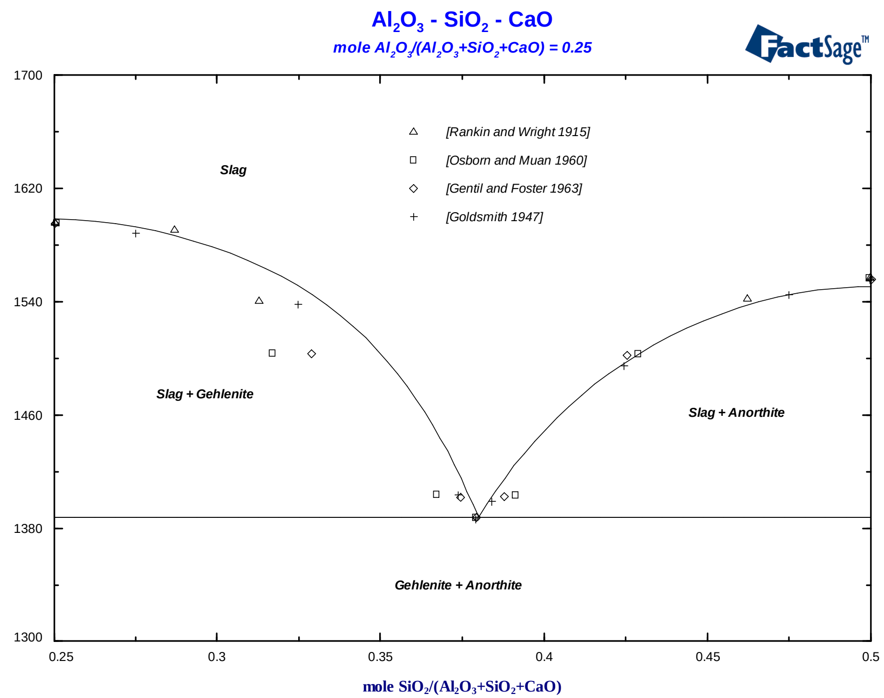




Isopleth section Anorthite - Gehlenite

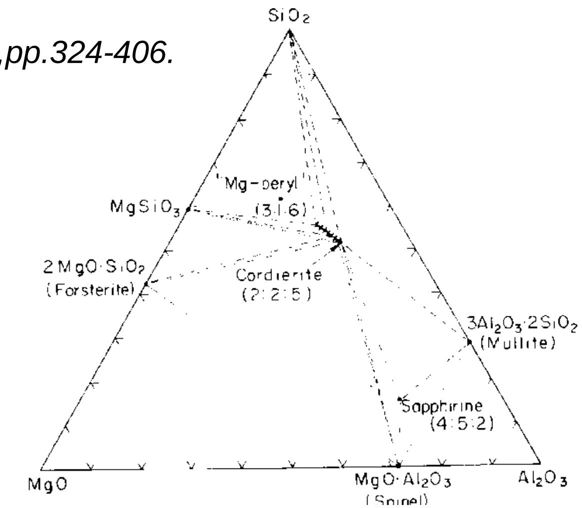
G.A. Rankin, F.E. Wright, Am.J.Sci., 189[39], (1915), pp.1-79.



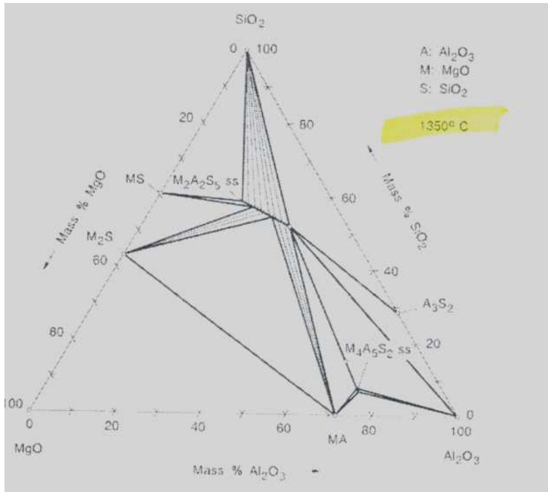


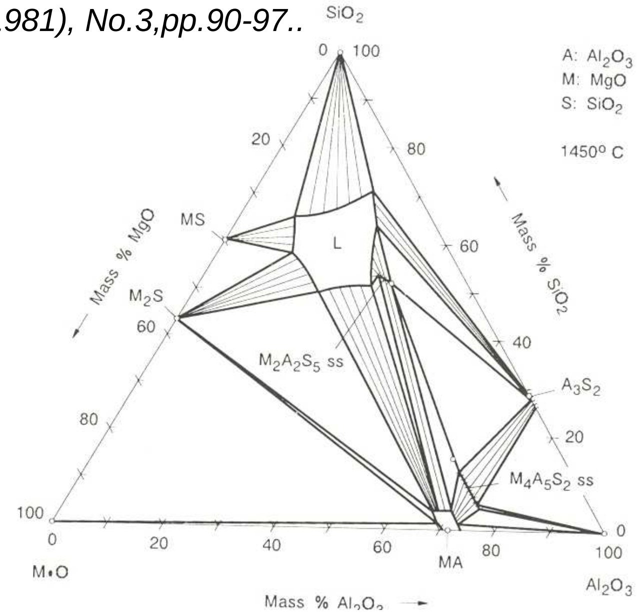
Modelling of Cordierite and Sapphirine in Al_2O_3-MgO-SiO_2 system : Motivation

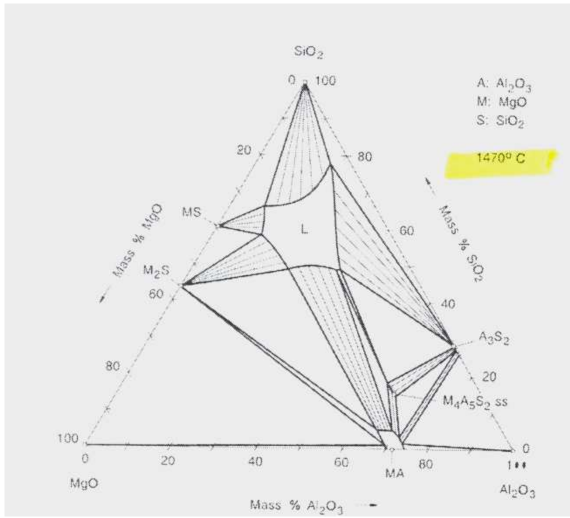
W.Schreyer, J.F. Schairer, J. Petrol., 2[3],(1961),pp.324-406.



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







Modelling of Cordierite and Sapphirine

$Al_4Mg_2Si_5O_{18}$

Cordierite : $(Al_2Mg_2Si_5O_{18})^{6-}$ $(\underline{Al}^{3+}, Mg^{2+})$ $(\underline{Al}^{3+}, Si^{4+})$

For the description of Cordierite and Sapphirine the reciprocal equation was applied:

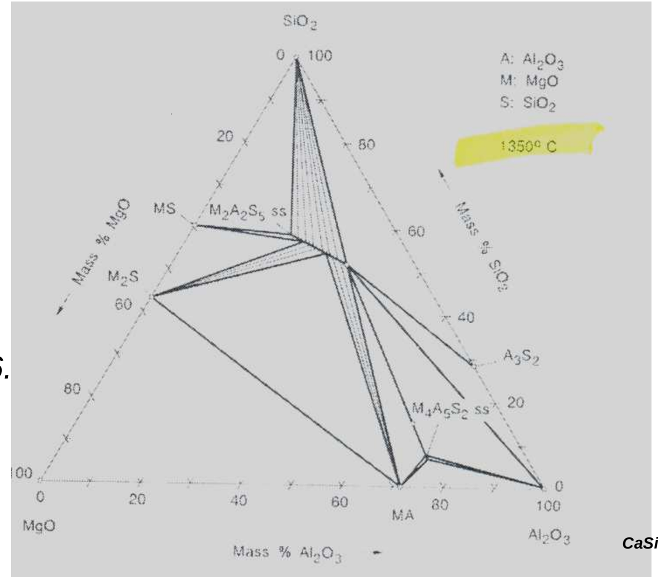
$$G(Al:Al) + G(Mg:Si) - G(Mg:Al) - G(Al:Si) = 0$$

$Al_{18}Mg_7Si_3O_{40}$

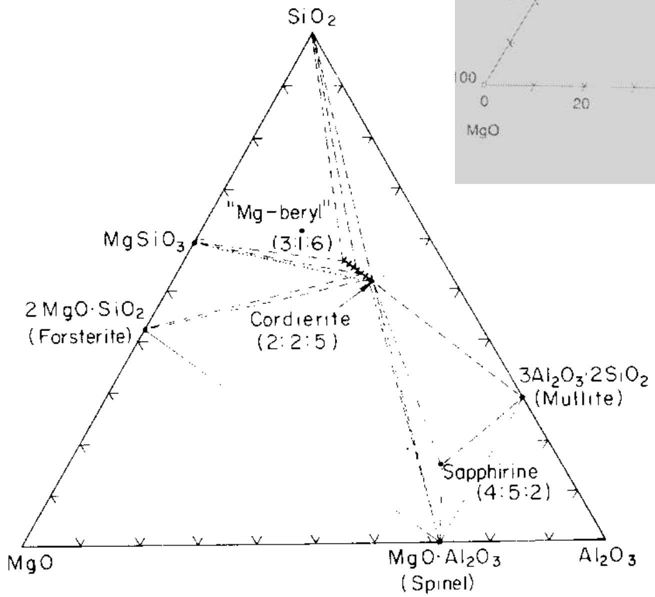
Sapphirine : $(Al_{36}Mg_{14}Si_3O_{80})^{12-}$ $(Al^{3+}, \underline{Si}^{4+})_3(Al^{3+}, \underline{Va})$

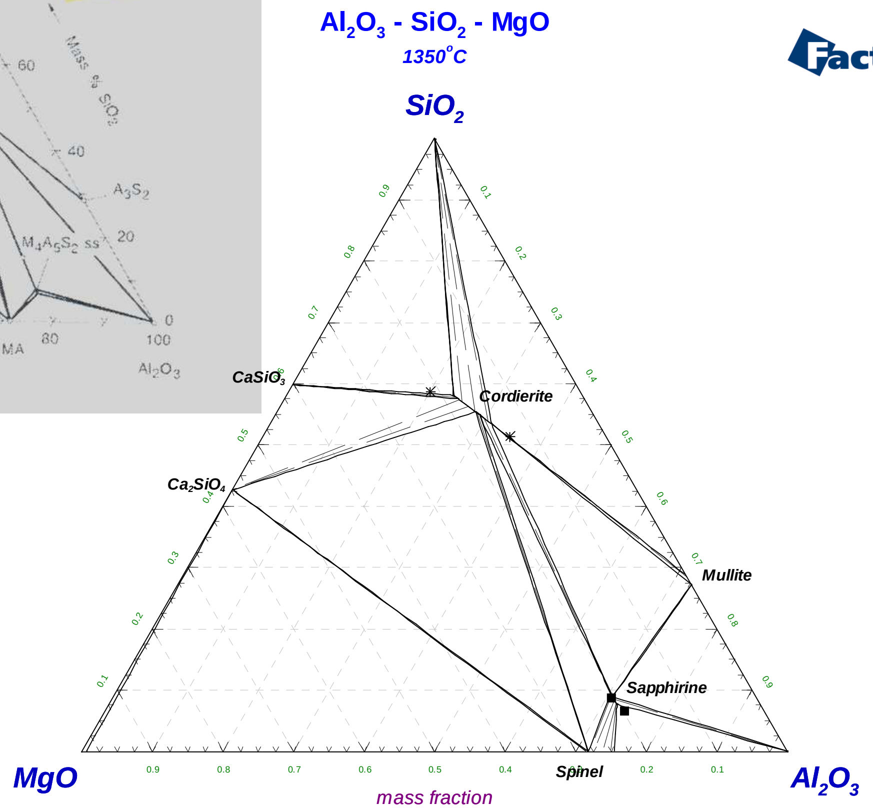
Isothermal section at 1350 °C

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



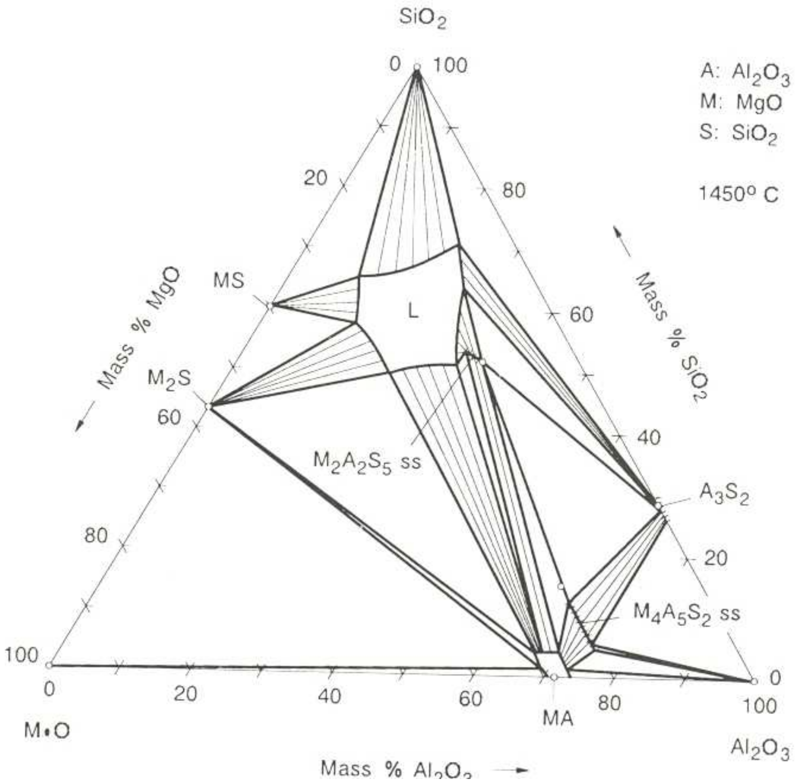
W.Schreyer, J.F. Schairer,
J. Petrol., 2[3],(1961),pp.324-406.

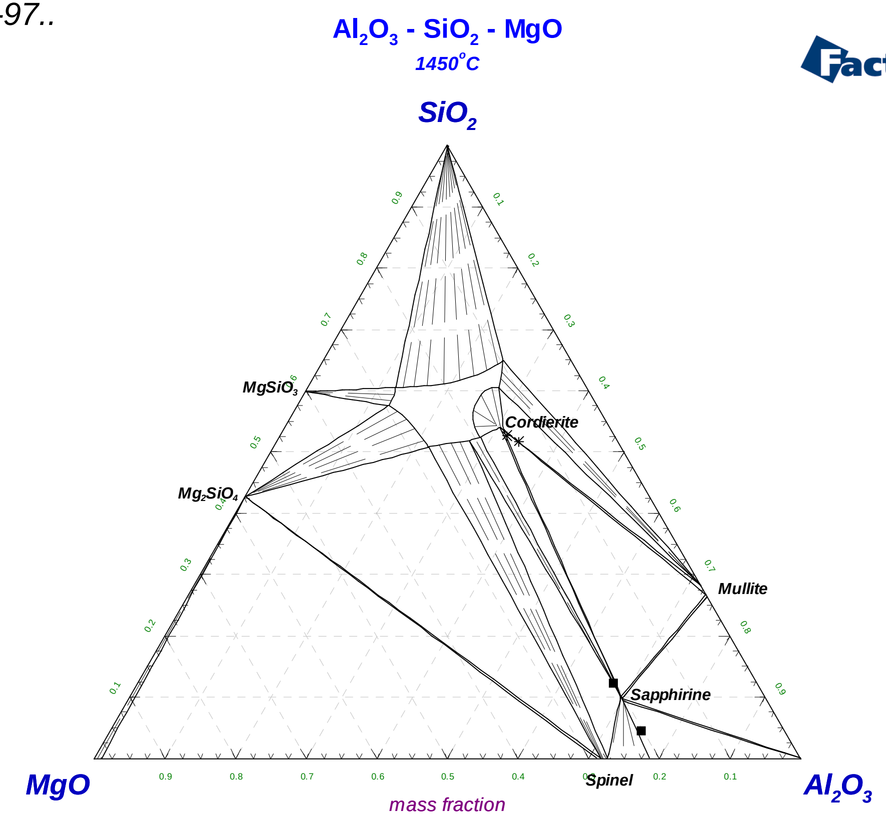




Isothermal section at 1450 ºC

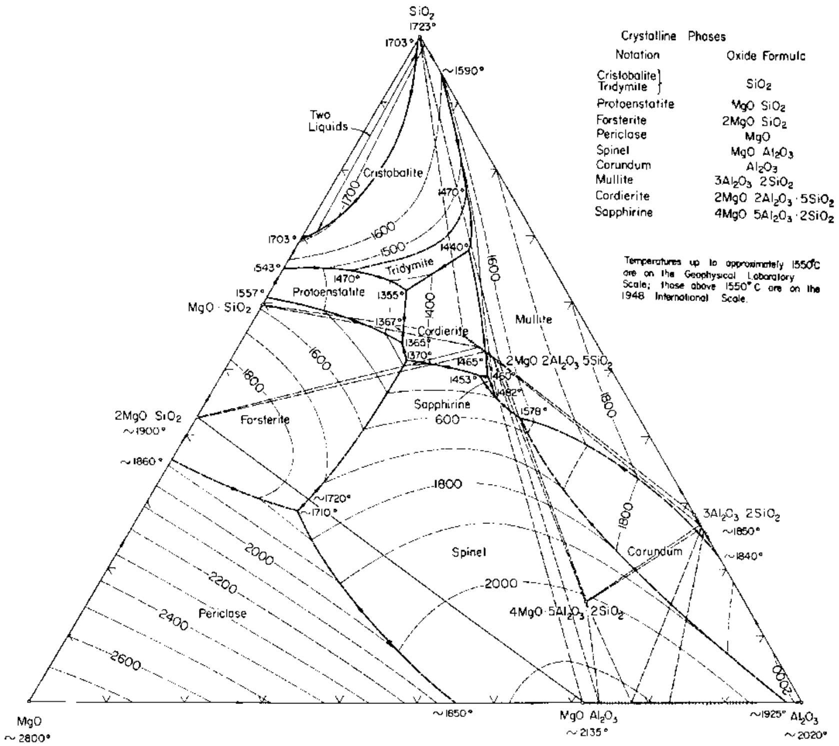
R.M.Smart, F.P. Glaser, Ceram. Int., 7 (1981), No.3,pp.90-97..

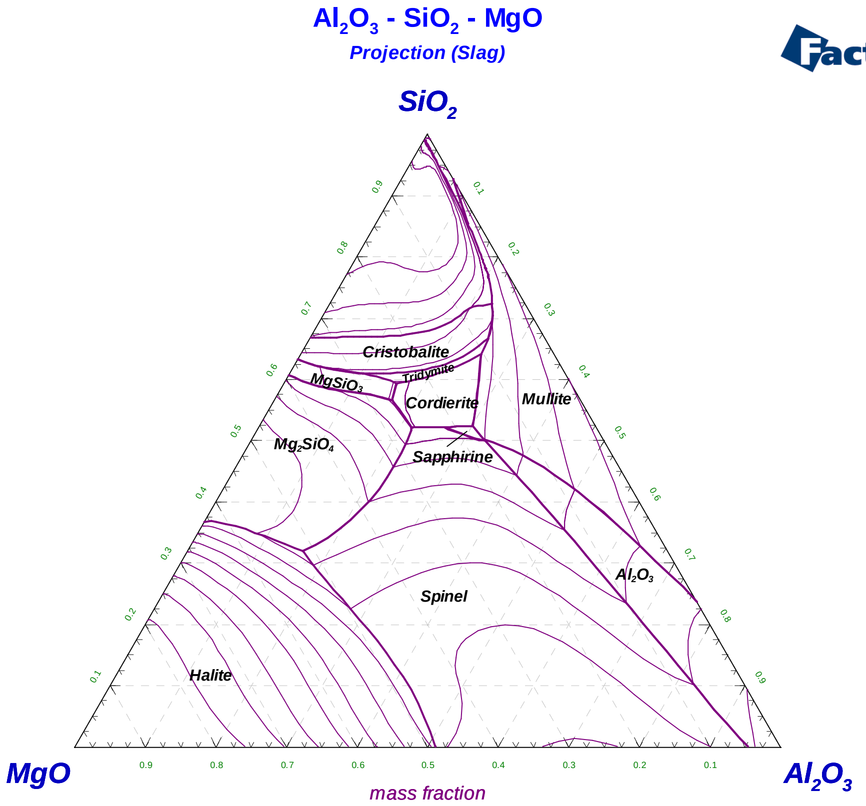




Liquidus surface in Al_2O_3-MgO-SiO_2

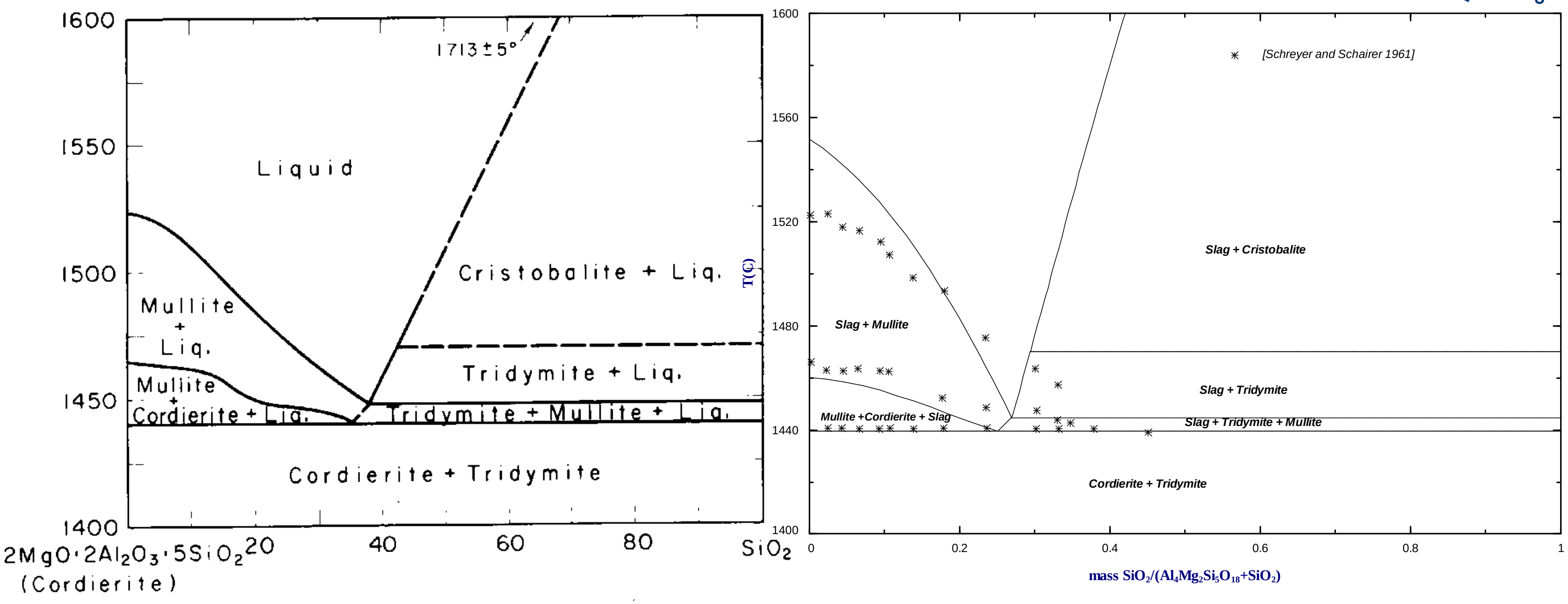
E.F. Osborn,A. Muan, private communication, (1960).





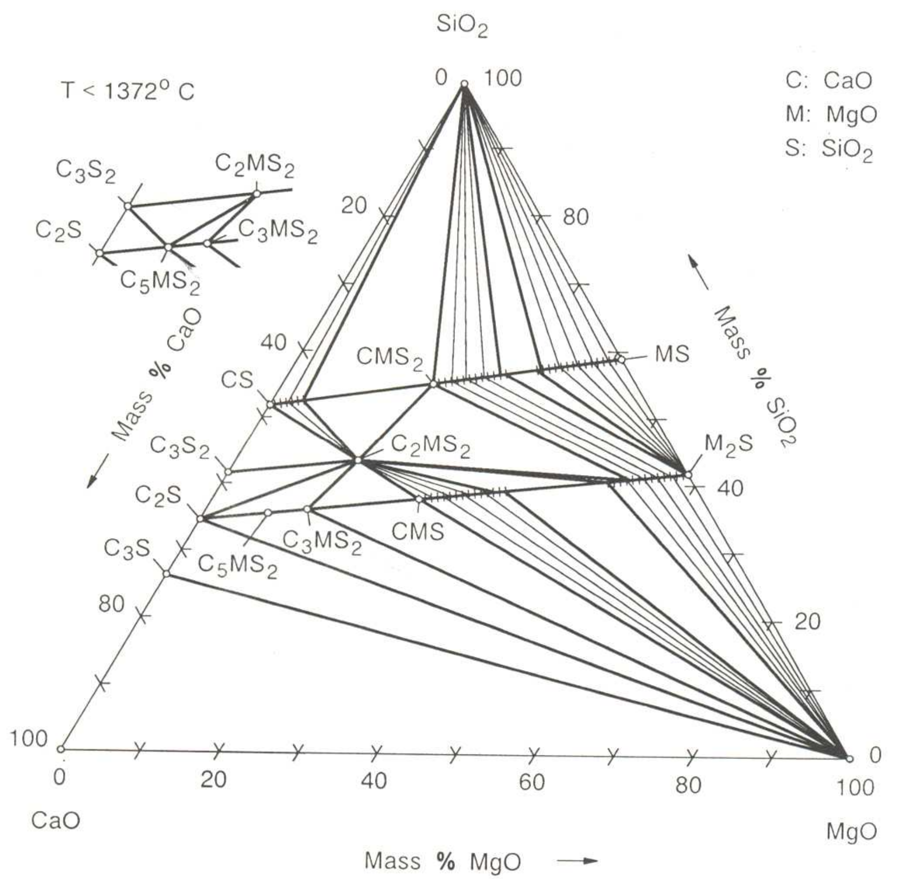
Isopleth section Cordierite - SiO_2

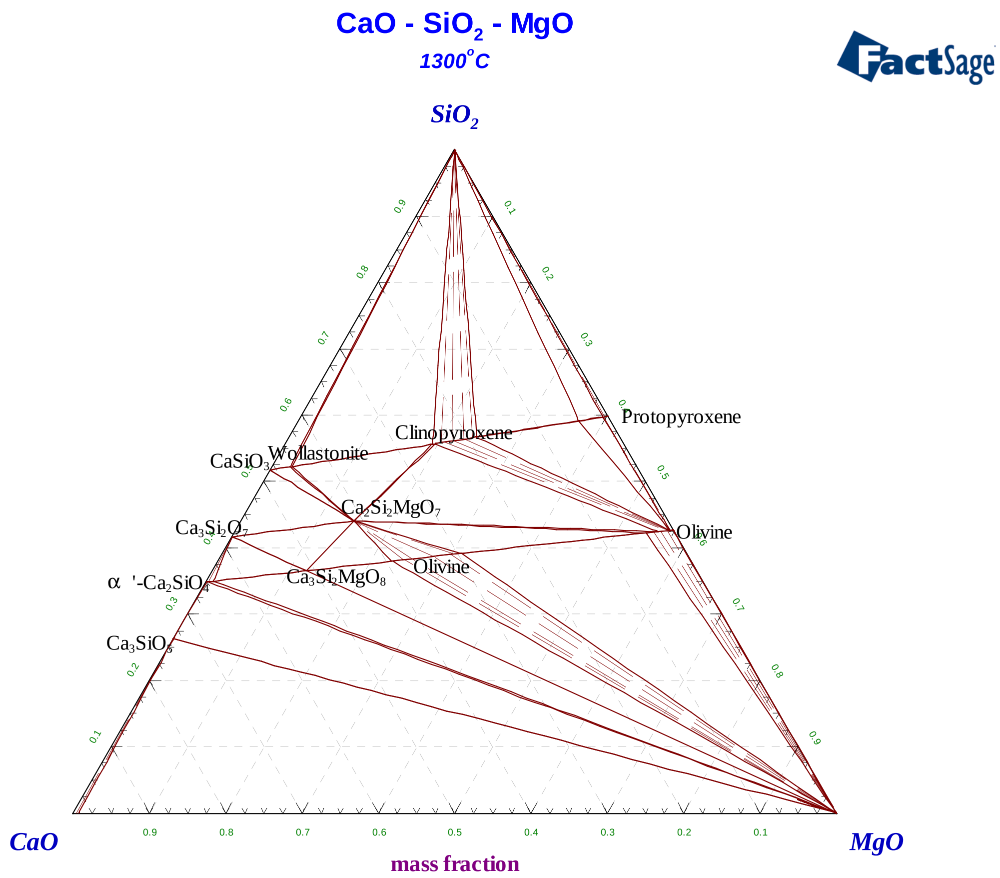
W.Schreyer, J.F. Schairer, J. Petrol., 2[3],(1961),pp.324-406.



Isothermal section at 1350°C

E.F. Osborn, A. Muan: Ceramic Foundation
1960, Publ. By Orton jr, Columbus/Ohio





Liquidus surface in CaO-MgO-SiO_2

E.F. Osborn, A. Muan: Ceramic Foundation
1960, Publ. By Orton jr, Columbus/Ohio

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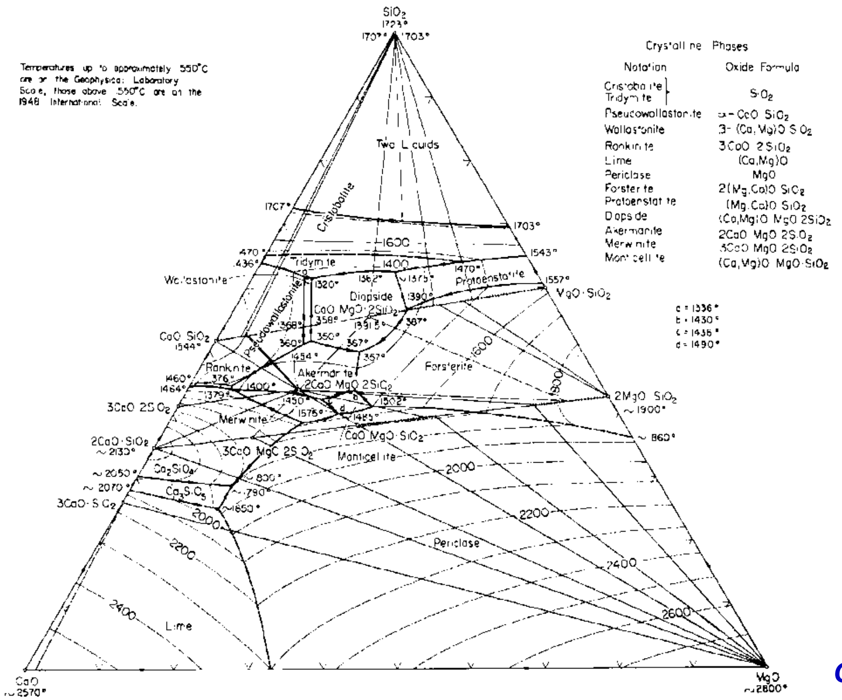
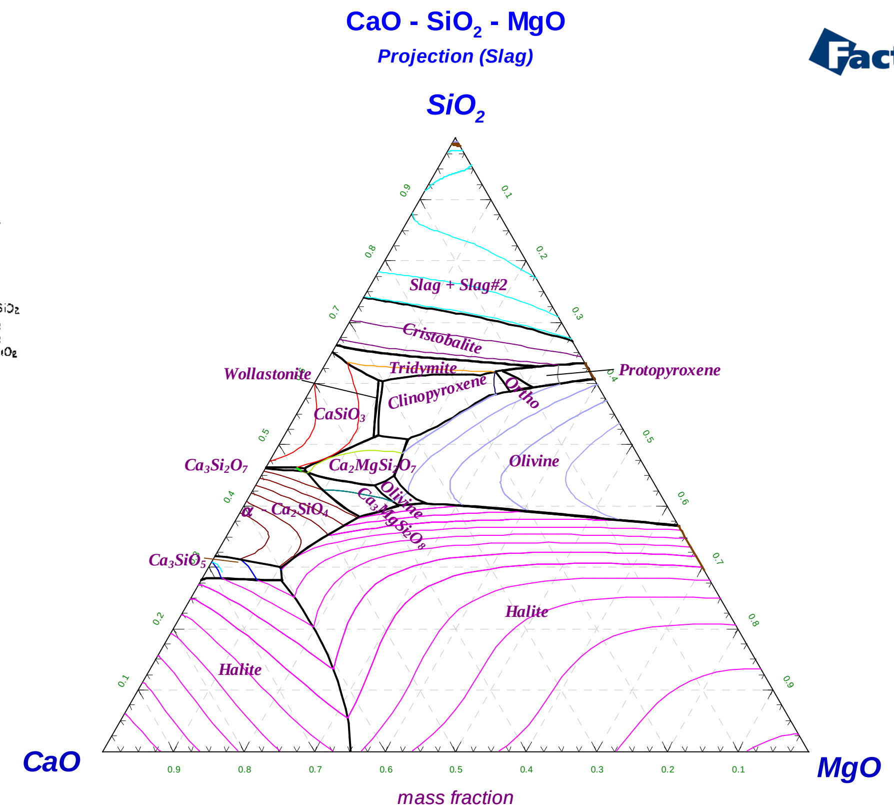
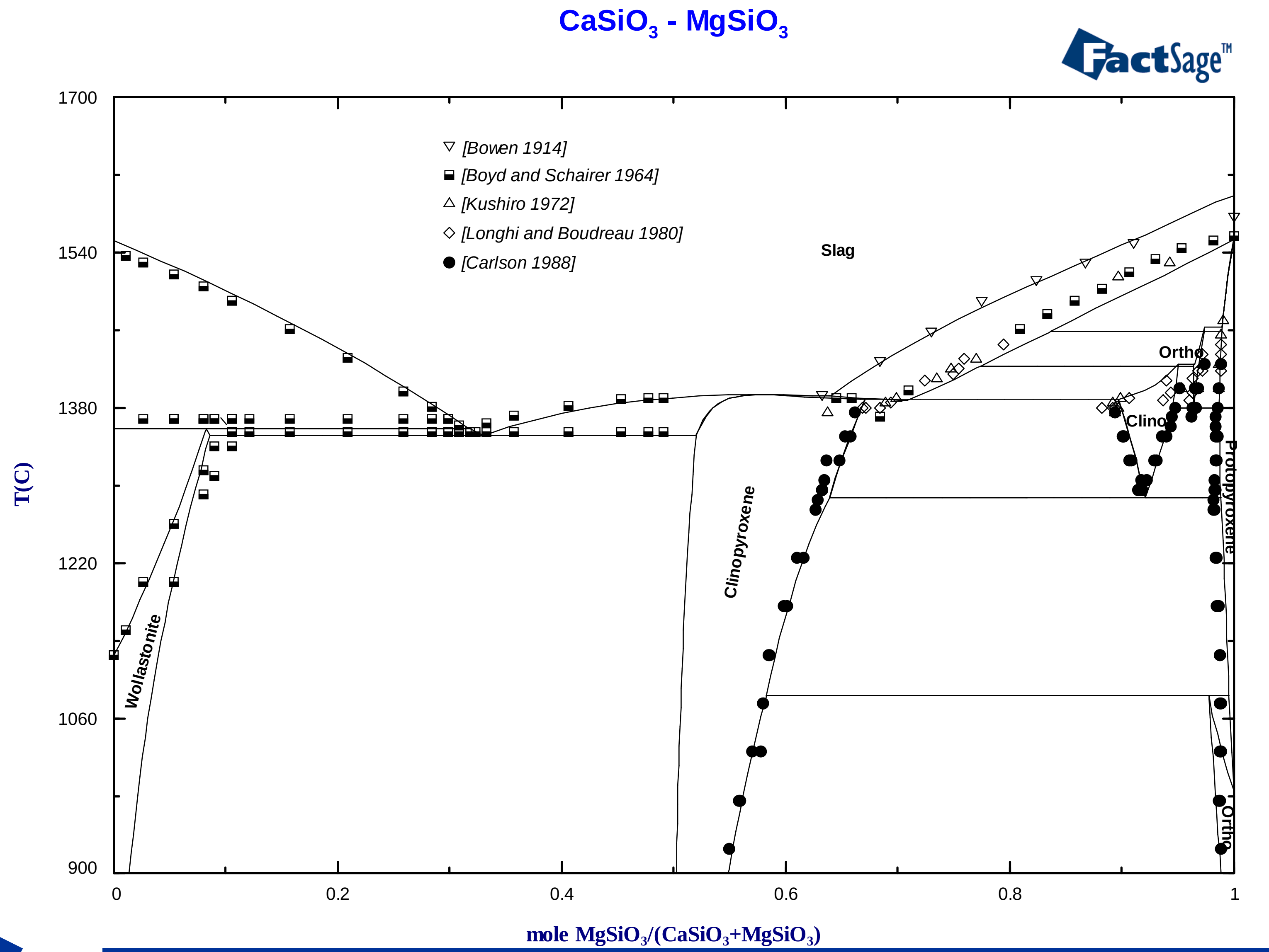
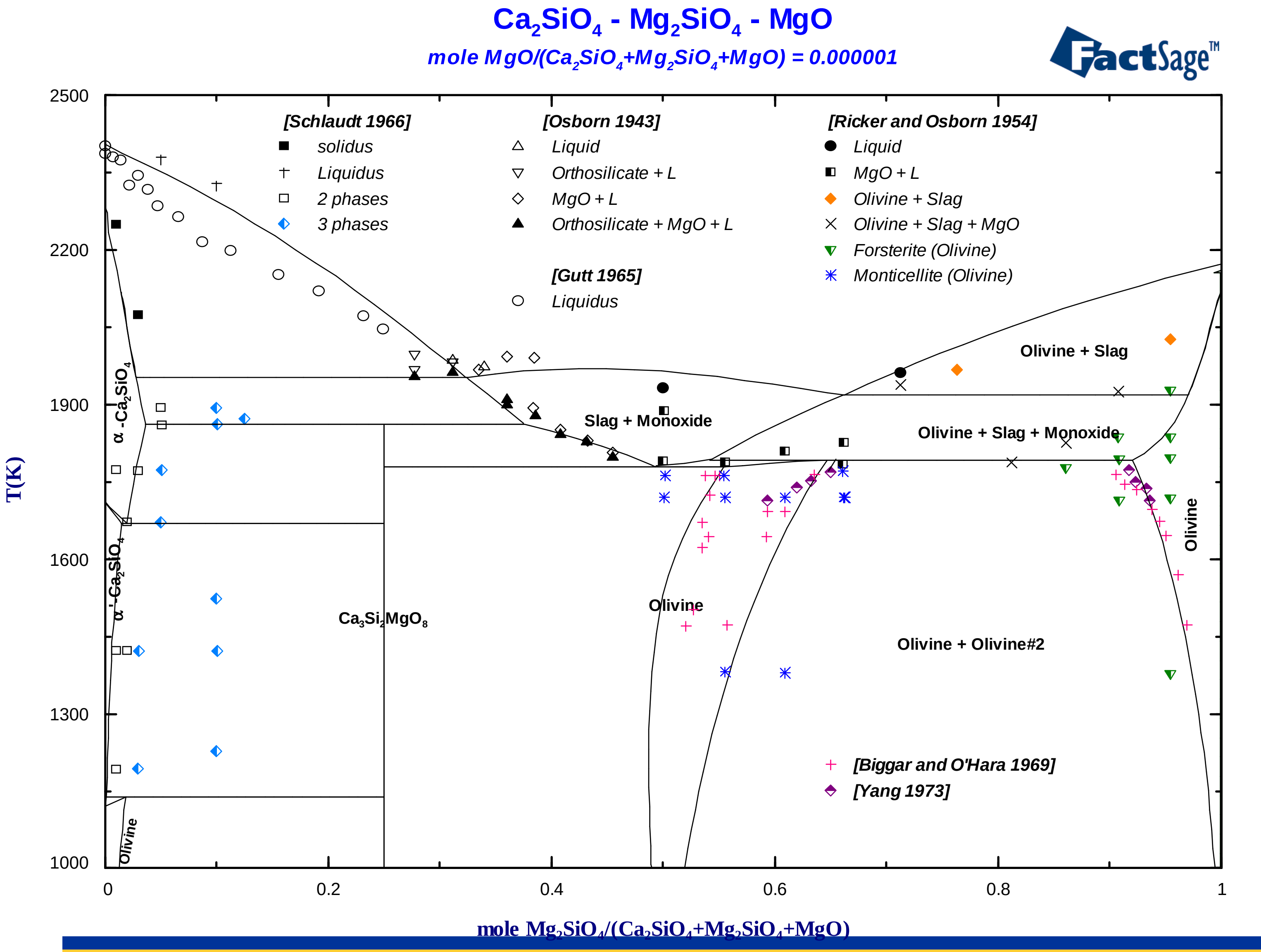




Metasilicate section $CaSiO_3$-$MgSiO_3$

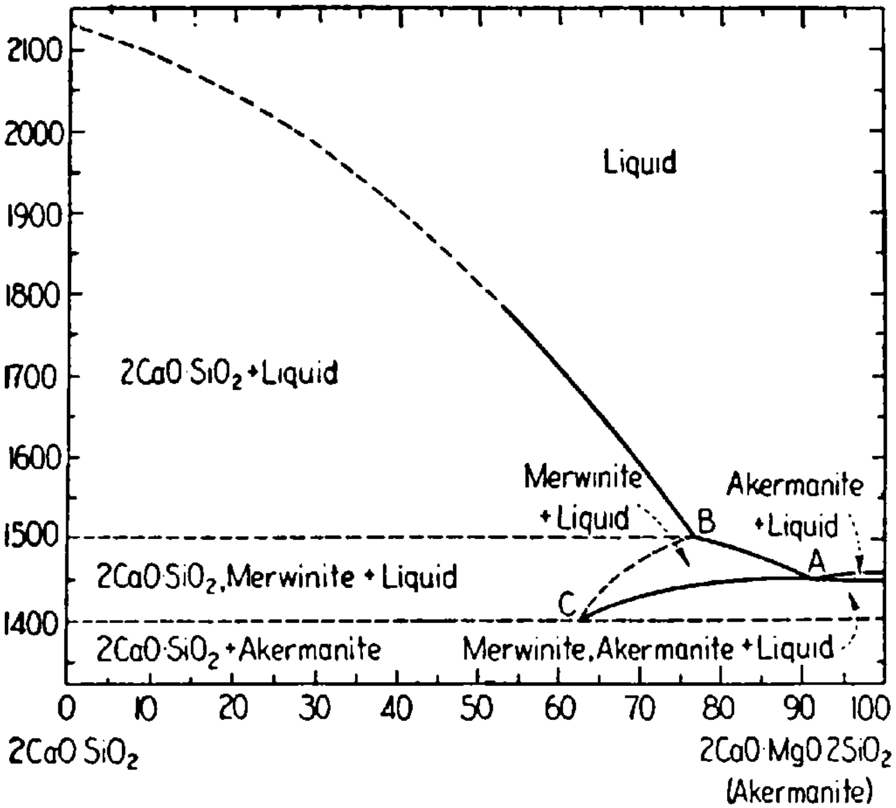


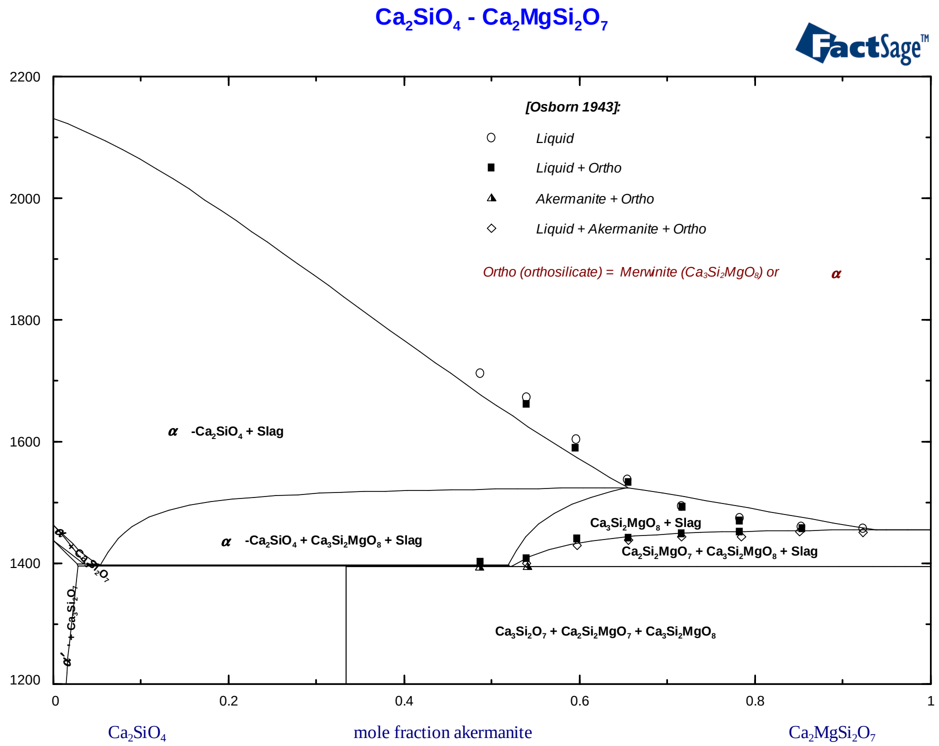
Orthosilicate section Ca_2SiO_4-Mg_2SiO_4



Isopleth section Ca_2SiO_4 - Åkermanite

E.F. Osborn, J. Am. Ceram. Soc.,26, (1943), pp.321-332.





Isopleth section $CaSiO_3$ - Åkermanite

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J.F. Schairer, N.L. Bowen, Am.J. Sci., 240[10], (1942), pp.725-742.

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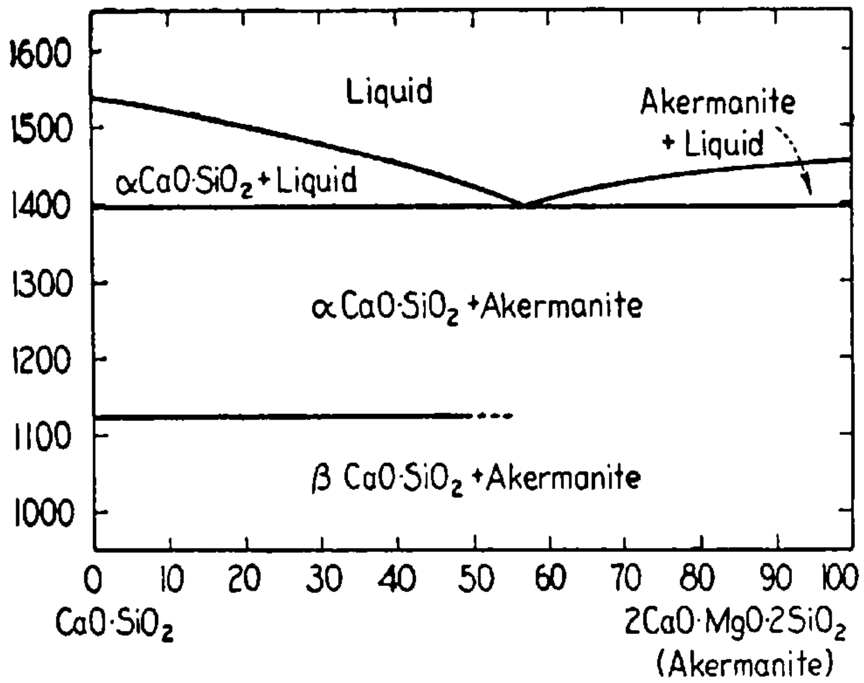
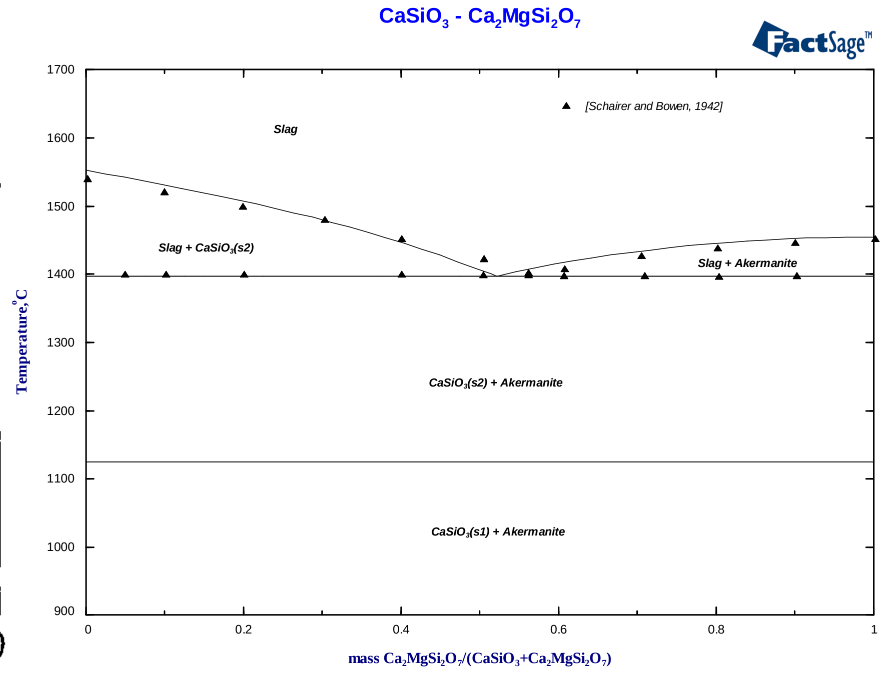




Quaternary system: Modelling of Melilite

Melilite refers to a mineral of the melilite group. Minerals of the group are solid solutions of several endmembers, the most important are **Gehlenite** and **Åkermanite**.
A generalised formula for common melilite is
(CaNa)2(AlMgFe2+)[(AlSi)SiO$_7$].

Discovered in 1793 near Rome,
it has a yellowish, greenish brown colour.

The name derives from the Greek words
meli (μέλι) ***"honey"*** and lithos (λίθους) ***"stone".***

Gehlenite and Åkermanite

Gehlenite, ($Ca_2Al[AlSiO_7]$), is a sorosilicate, Al-rich endmember of the melilite complete solid solution series with akermanite. It is named after Adolf Ferdinand Gehlen.

Å**kermanite** ($Ca_2Mg[Si_2O_7]$) is a melilite mineral of the sorosilicate group.
The mineral is named for Anders Richard Åkerman, a Swedish metallurgist.

Thermodynamic description of Melilite

Formula given in crystallographic atlas is
(CaNa)2(AlMgFe2+)[(AlSi)SiO$_7$].

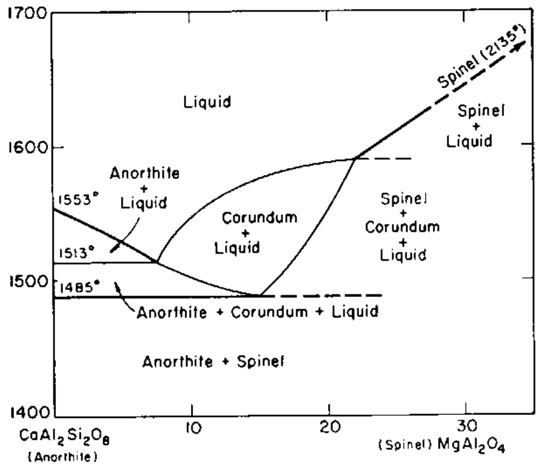
Thermodynamic description of melilite:
(Al^{3+},Mg^{2+})(Al^{3+},Si^{4+})($Ca_2SiO_7^{6-}$)

(Al^{3+})(Al^{3+})($Ca_2SiO_7^{6-}$) - Gehlenite

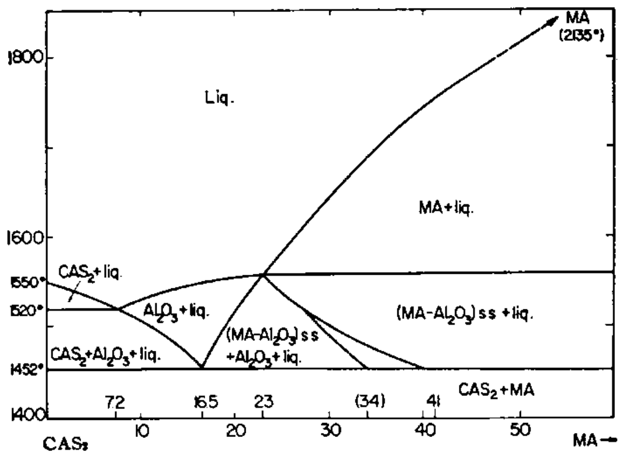
(Mg^{2+})(Si^{4+})($Ca_2SiO_7^{6-}$) - Å**kermanite**

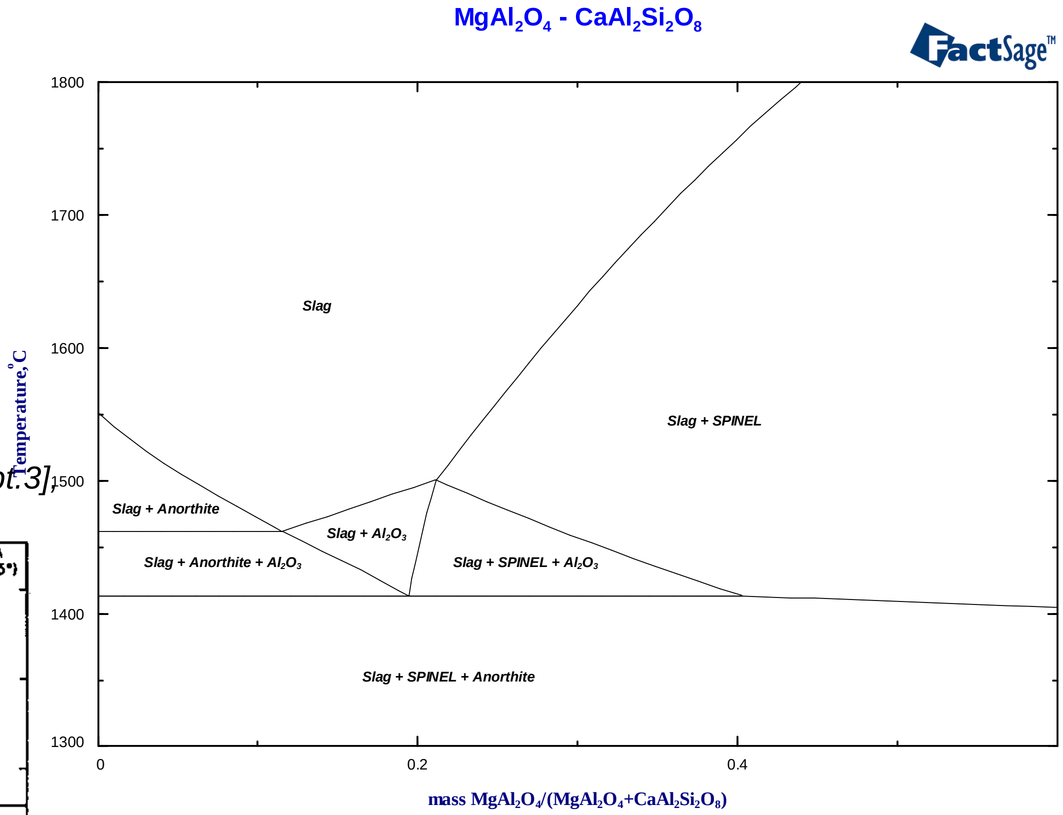
Quaternary system: Experiment and calculations

E.F. Osborn, R.C. DeVries, K.H. Gee, H.M. Kramer,
Trans. Am. Inst. MIn., Metall. Pet. Eng., 200 (1954), pp.33-45



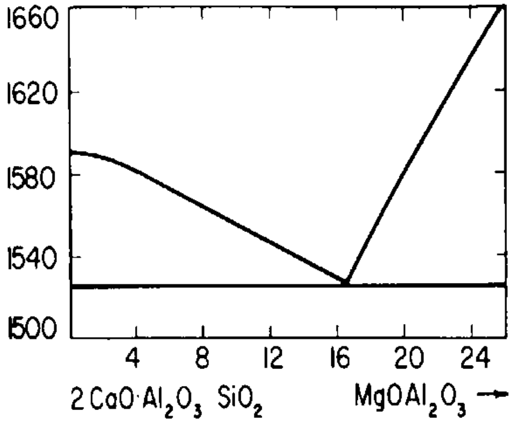
J.H. Welch, J. Iron Steel Inst., London, 183 [pt.3], (1956), pp.275-283.



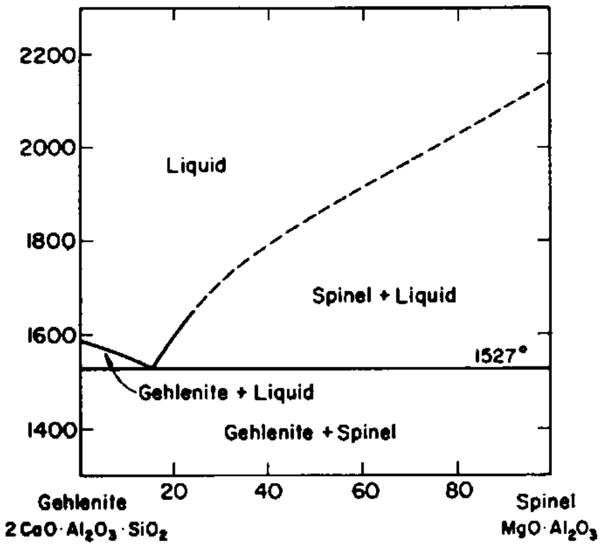


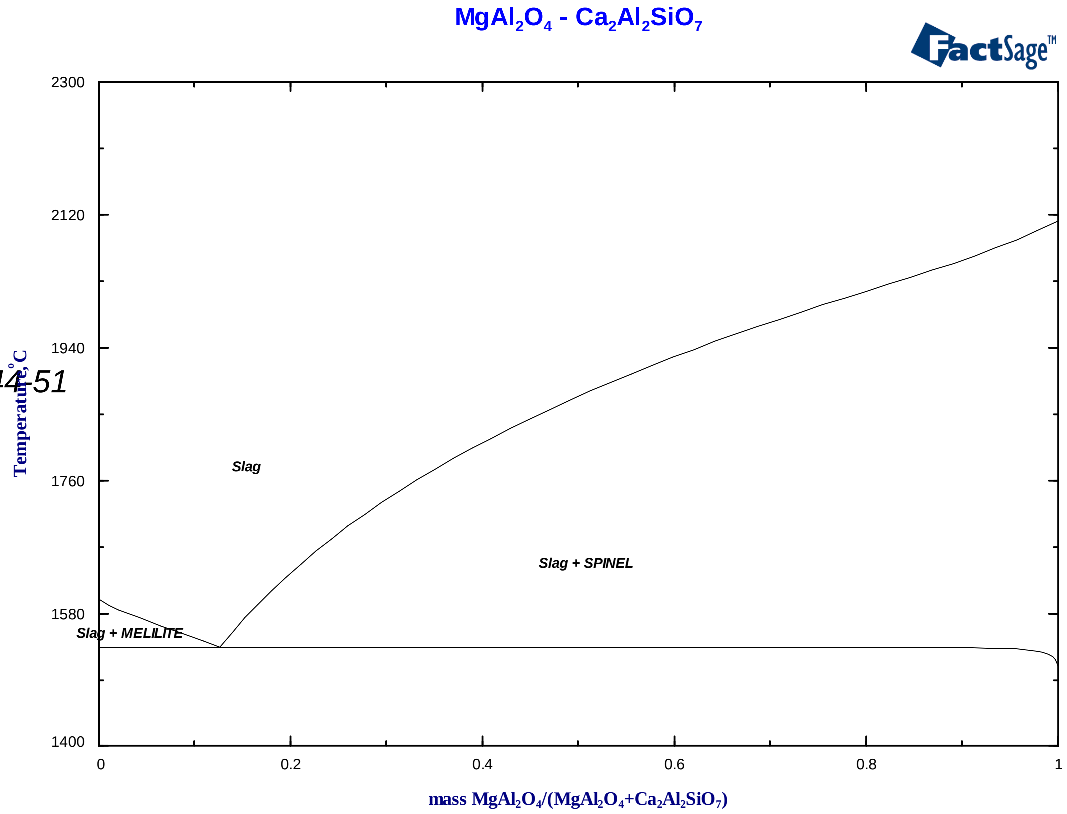
Quaternary system: Experiment and calculations

W.K. Gummer, J. Geol., 51 [8], (1943), pp.503-531.



A.T. Prince, J.Am.Ceram.Soc., 34[2], (1951), pp.44-51





Quaternary system: 10 mass.% Al_2O_3

E. F. Osborn, R.C. DeVries, K.H. Gee, H.M. Kraner, Trans. Am. Inst. MIn., Metall. Pet. Eng., 200, (1954), pp.33-45.

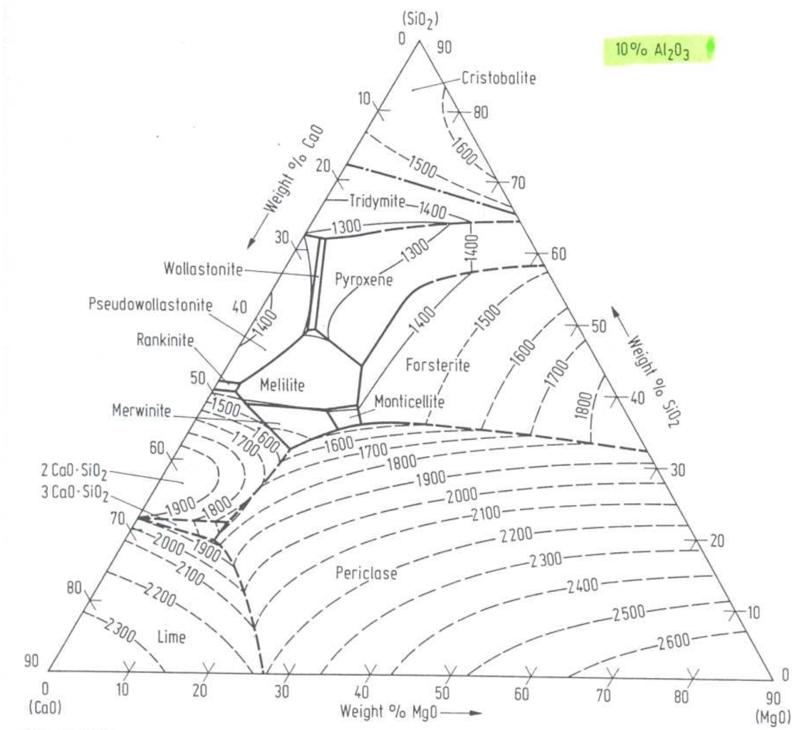
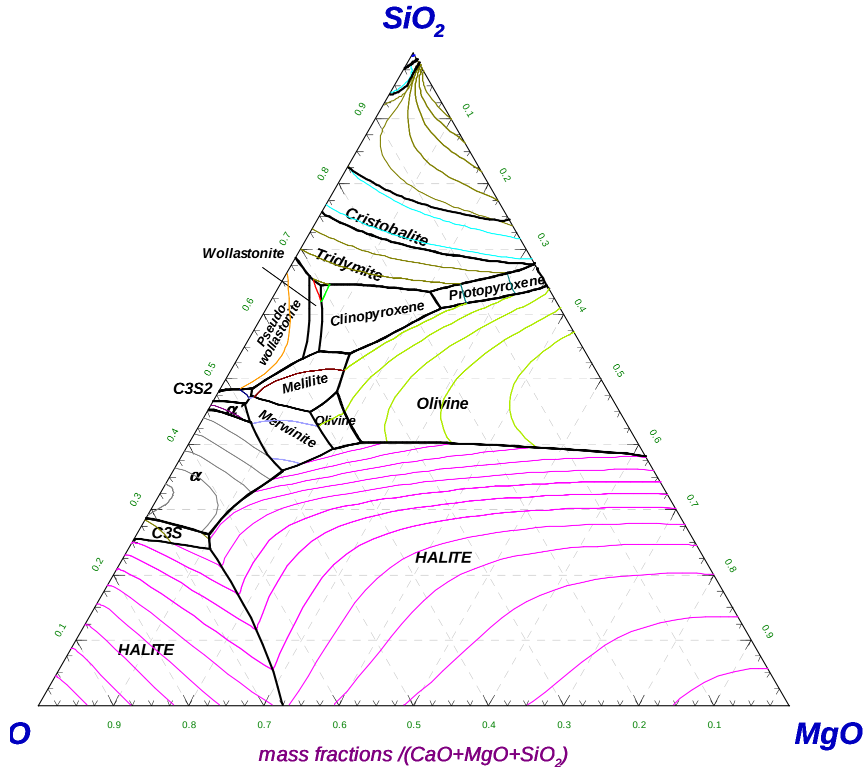


Fig. 3.318.



Spinel does not appear

Quaternary system: 15 mass.% Al_2O_3

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E. F. Osborn, R.C. DeVries, K.H. Gee, H.M. Kraner, Trans. Am. Inst. MIn., Metall. Pet. Eng., 200, (1954), pp.33-45.

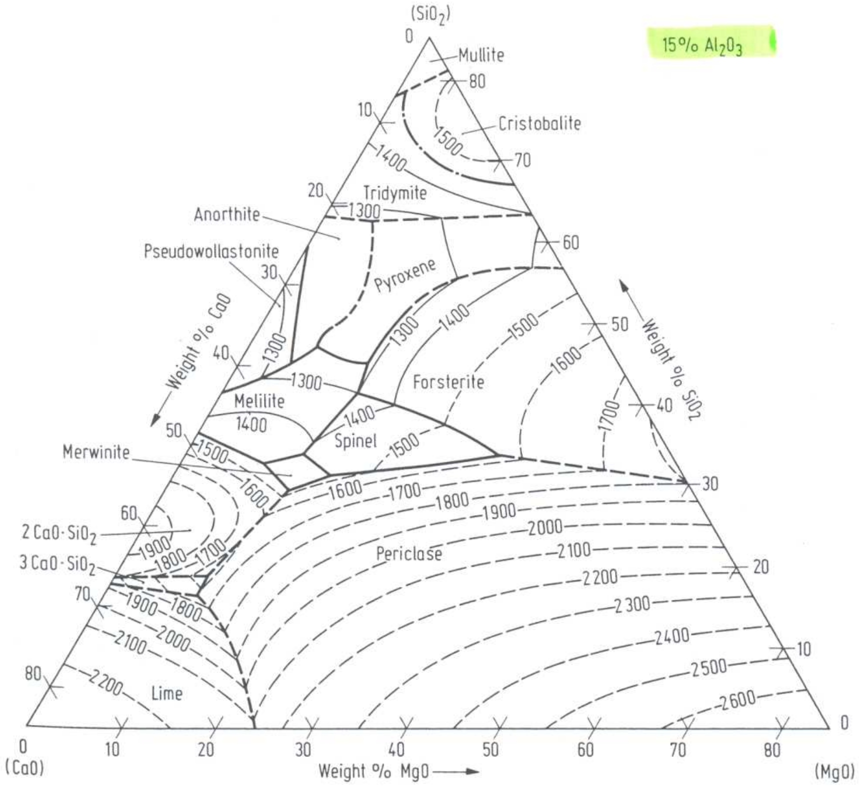
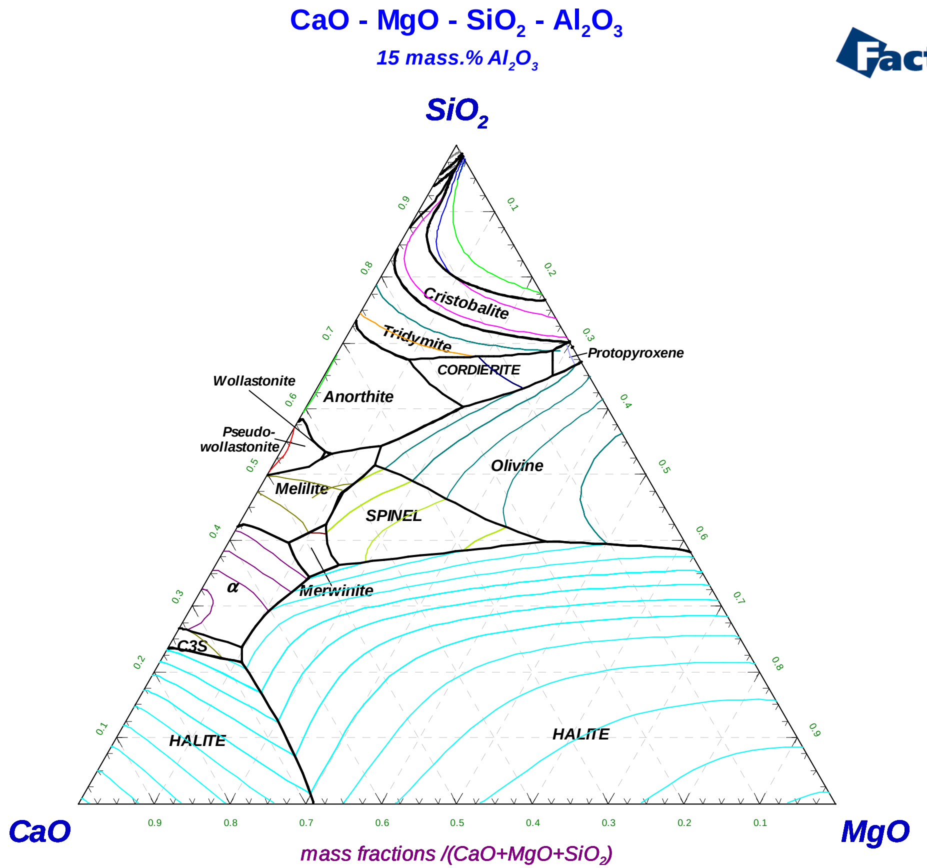


Fig. 3.319.



Quaternary system: 5 mass.% MgO

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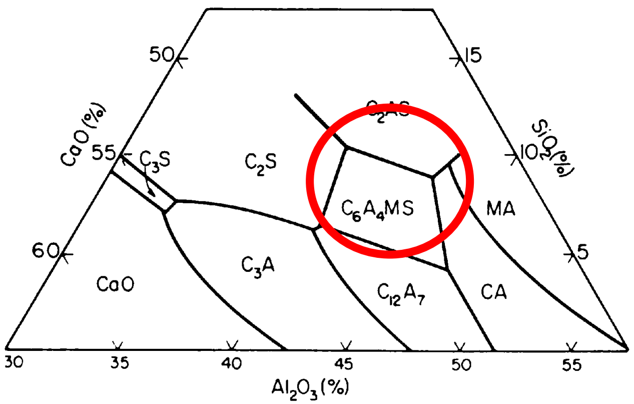
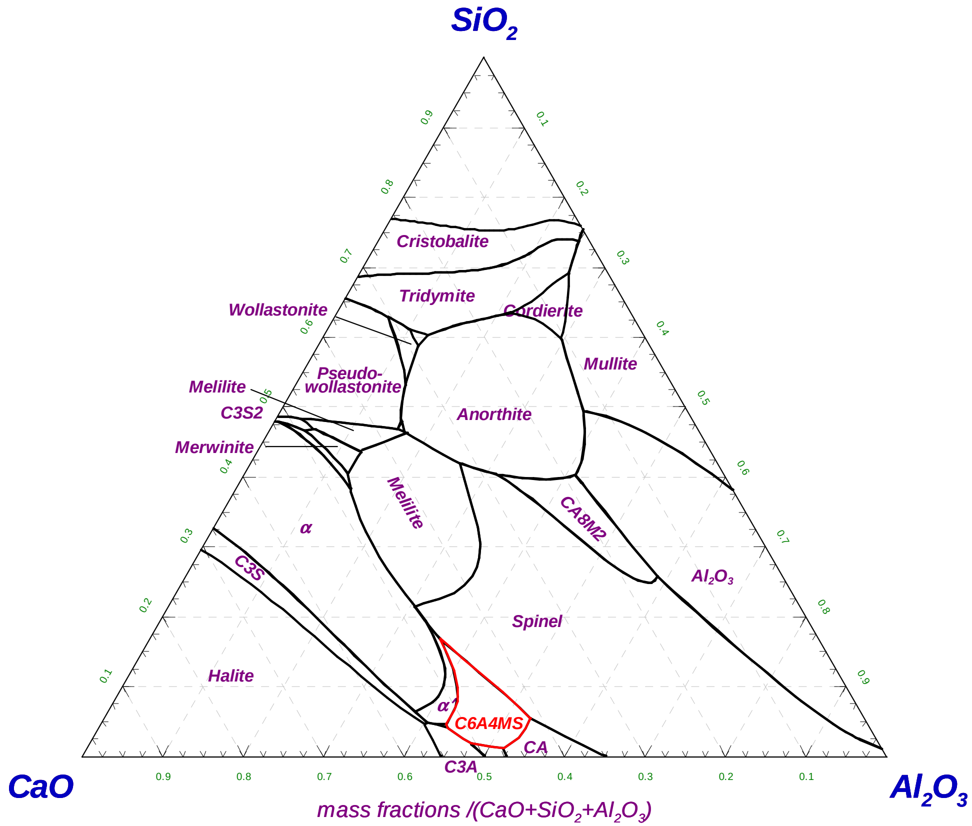
F.M. Lea, C.H. Desch, "The chemistry of cement and concrete", New York, (1956), pp.1-637.

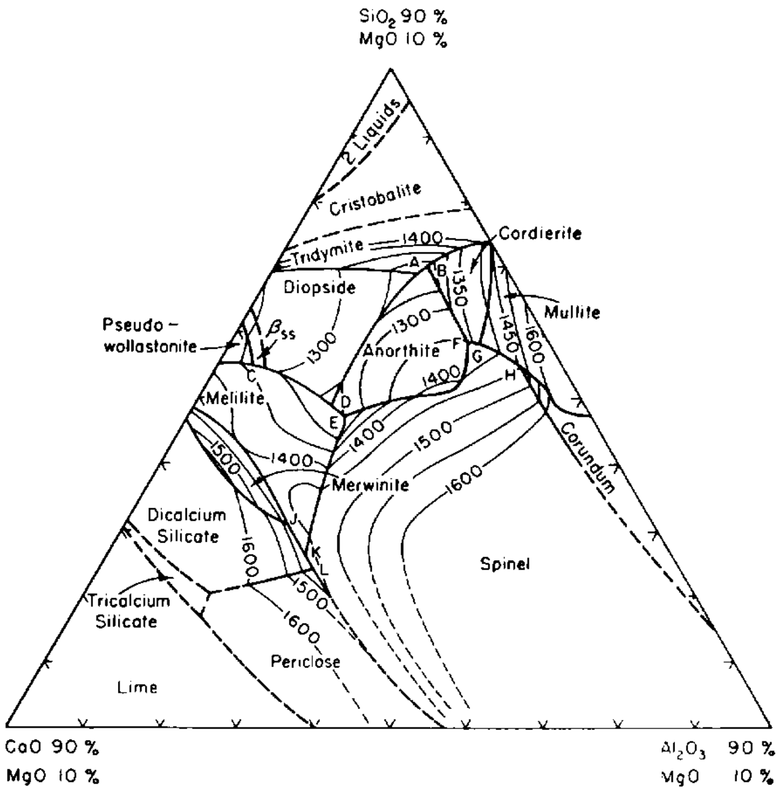


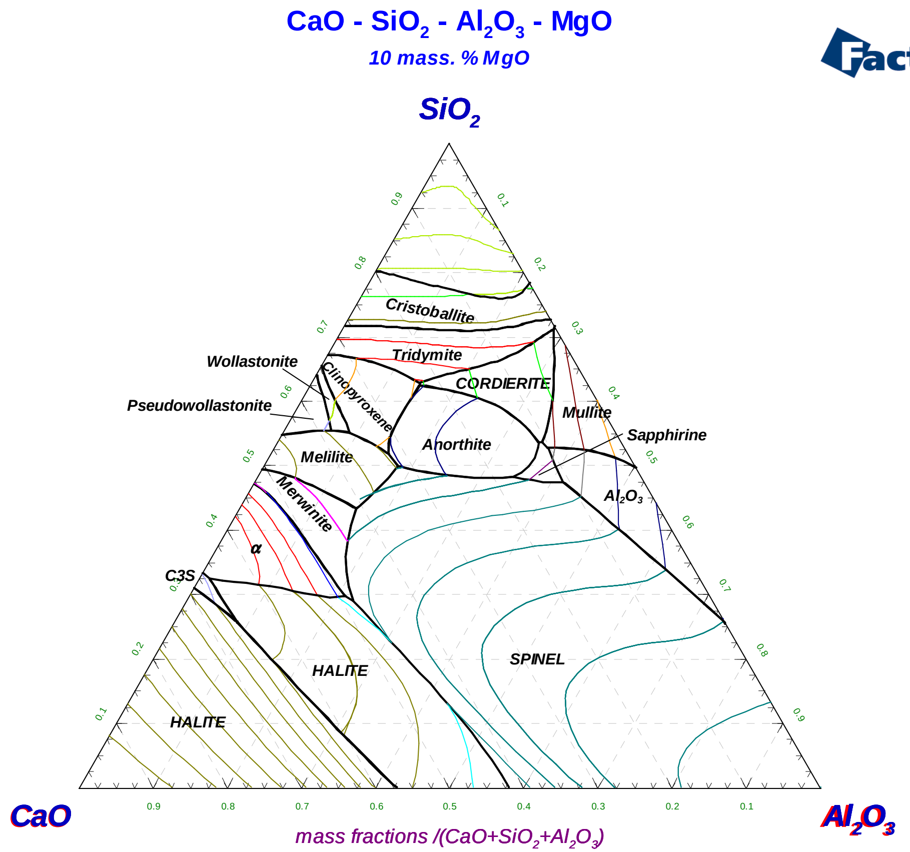
W.H. Gutt, A.D. Russell, J. Mater. Sci., 12 [9], (1977), pp.1869-1878.



Quaternary system: 10 mass.% MgO

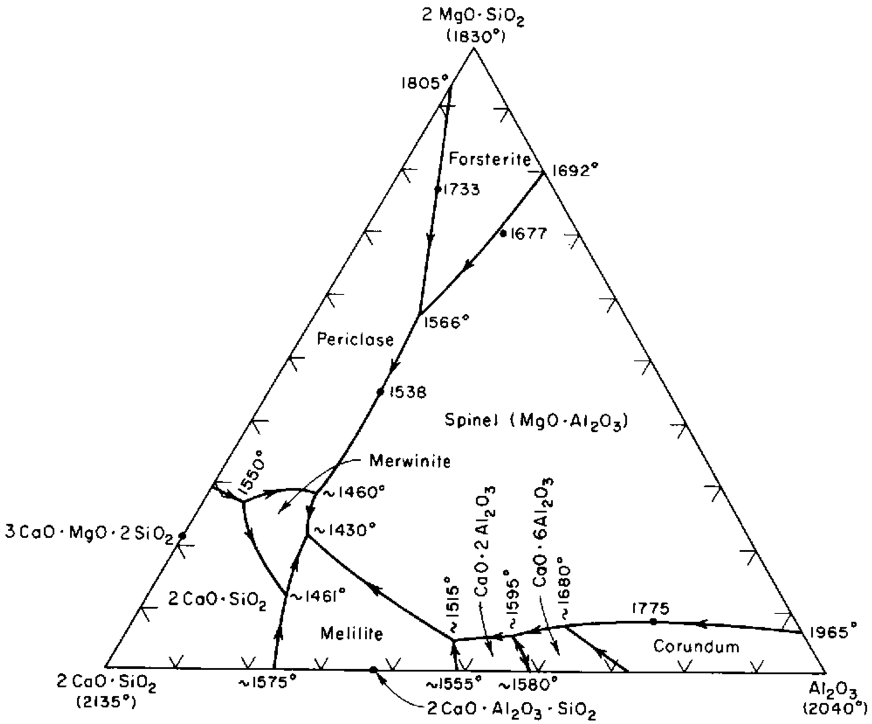
A.T. Prince, J. Am. Ceram. Soc., 37 [9], (1954), pp.402-408.

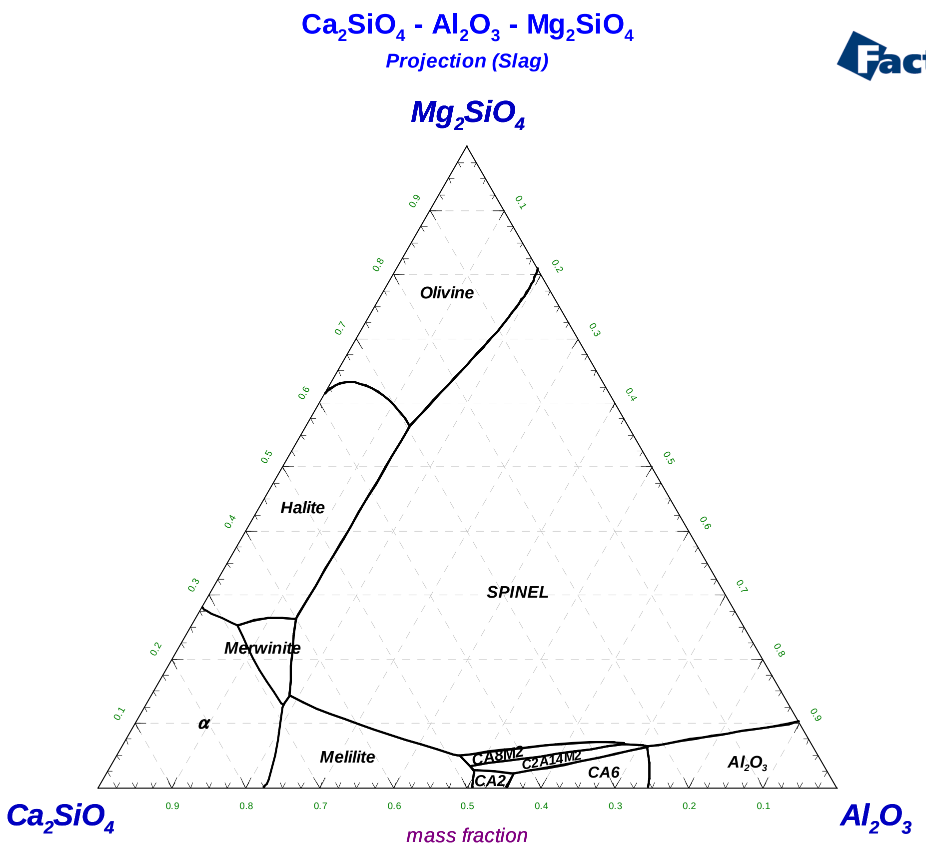




Quaternary system: Experiment and calculations

W. H. Gutt, J. Iron Steel Inst., London, 201 [Pt6], (1963), pp.532-536.

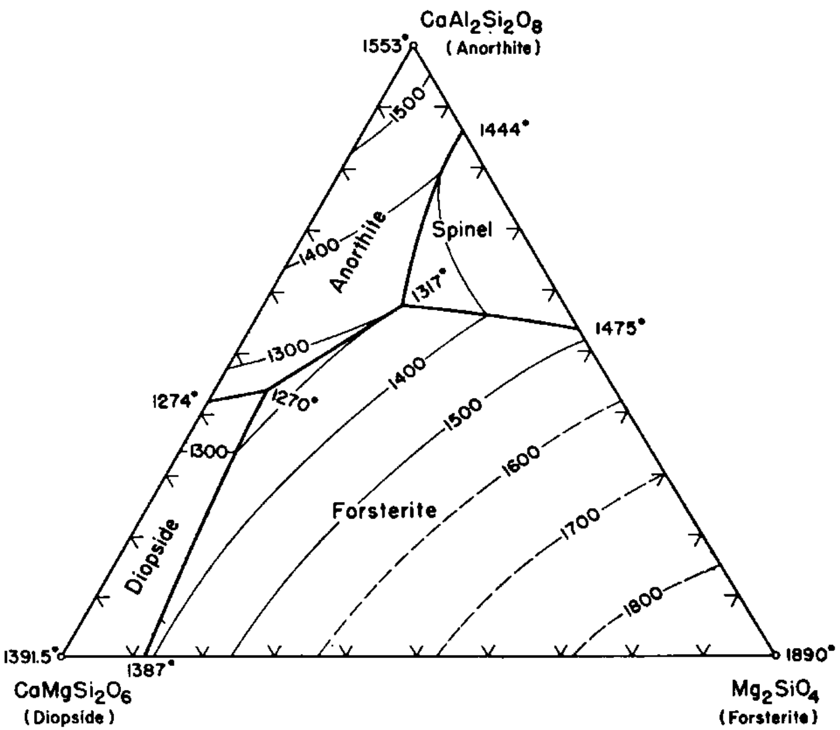


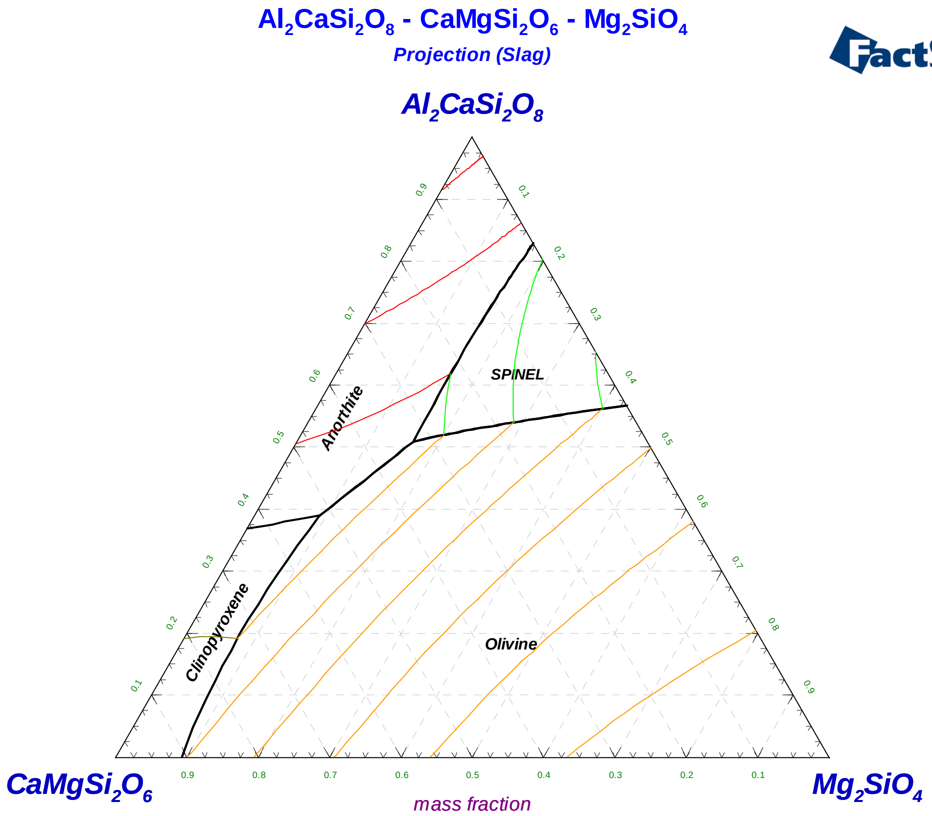


Quaternary system: Experiment and calculations

GTT-Technologies

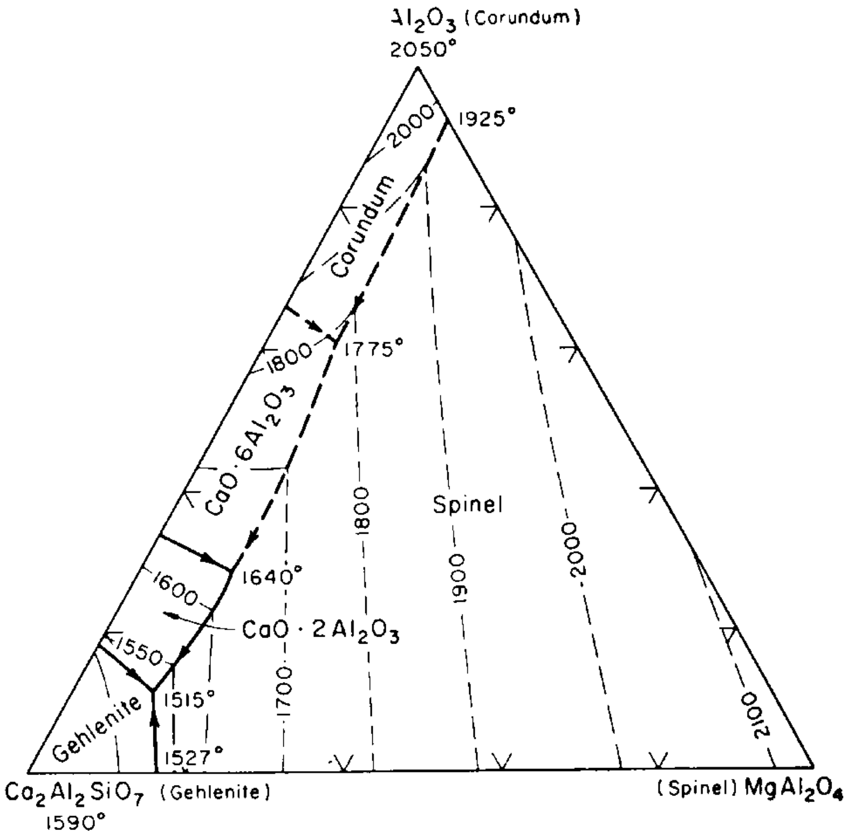
E.F. Osborn, D.B. Tait, Am. J. Sci., 250A [Bowen Vol.], (1952), pp. 413-433.

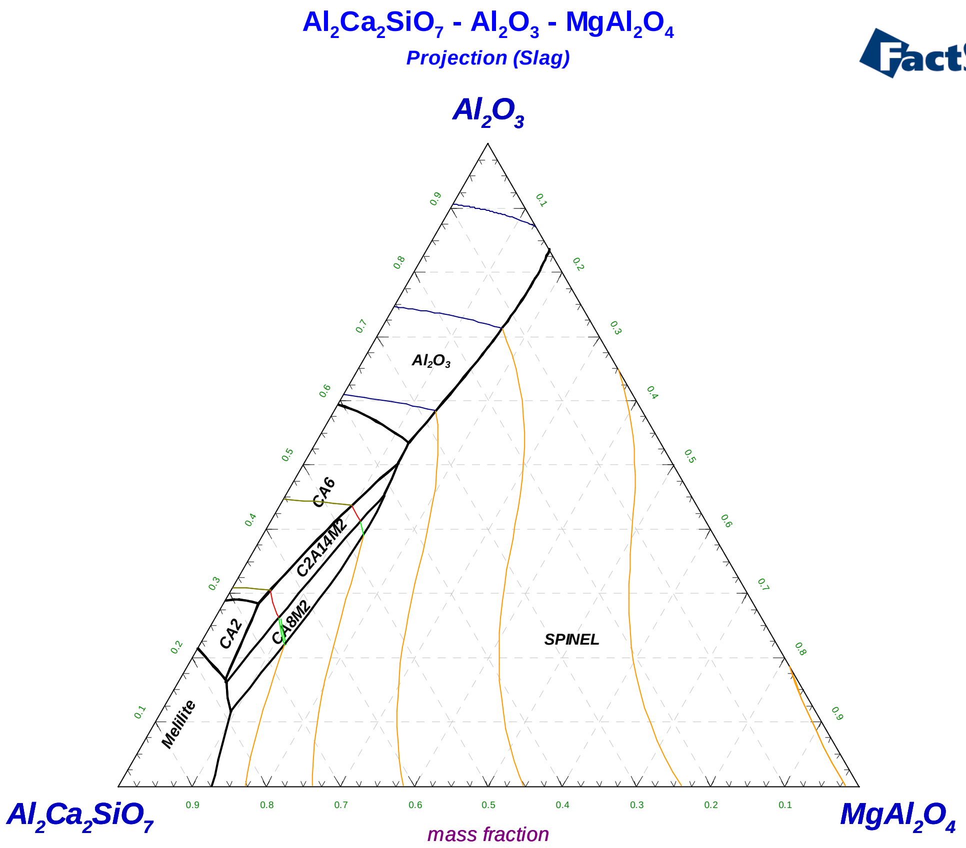




Quaternary system: Experiment and calculations

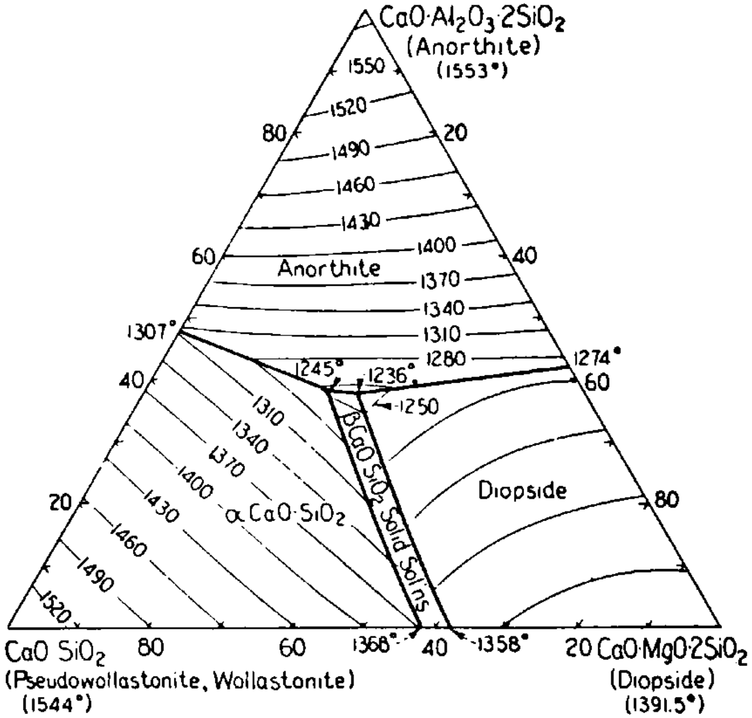
R.C. DeVries, E.F. Osborn, J. Ceram. Soc., 40[1], (1957), pp.6-15





Quaternary system: Experiment and calculations

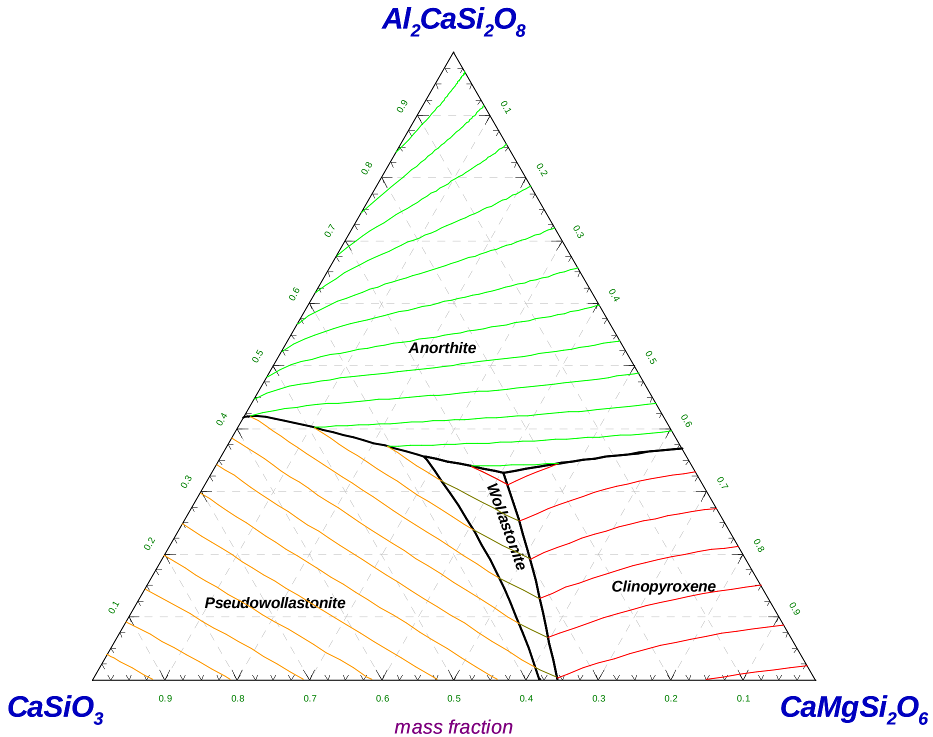
E.F. Osborn, Am. J. Sci., 240 [11], (1942), pp. 751-788.



$Al_2CaSi_2O_8$ - $CaMgSi_2O_6$ - $CaSiO_3$

Projection (Slag)

FactSage™



Conclusions

- All binary and ternary subsystems were evaluated using associate species model for the liquid phase.
- The binary Al_2O_3-MgO Spinel phase was re-optimised according to the available experimental data for the Al_2O_3-CaO-MgO-SiO_2 system.
- Cordierite $Al_4Mg_2Si_5O_{18}$ and Sapphirine $Al_{18}Mg_7Si_3O_{40}$ phases are described as solid solution phases because of experimentally determined wide solubility ranges.
- The quaternary Q-Phase $Al_8Ca_6MgSiO_{21}$ is involved.
- Melilite phase is present as quaternary solid solution phase with end members Åkermanite and Gehlenite.

Future developments

- Complete database for the Al_2O_3-CaO-K_2O-Na_2O-MgO-SiO_2 system combining the following databases:
  CaO-MgO-Al_2O_3-SiO_2 (GTT) and
  Na_2O-K_2O-Al_2O_3-SiO_2 (FZ Jülich)

- Expansion of the database by addition of such oxides as FeO and Fe_2O_3.

Thank you for your attention!