GTT Annual Users' Meeting 2016, June 29 - July 1

Database development for the HotVeGas project

Elena Yazhenskikh[1], Tatjana Jantzen[2], Klaus Hack[2], Michael Müller[1]

[1] Forschungszentrum Jülich, IEK-2 (Microstructure and properties of materials), Germany

[2] GTT-Technologies, Herzogenrath, Germany

Contents

HOTVEGAS

Motivation and aim of work

HOTVEGAS
Hochtemperaturvergasung und Gasreinigung

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GTT-TECHNOLOGIES

Aims:
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

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

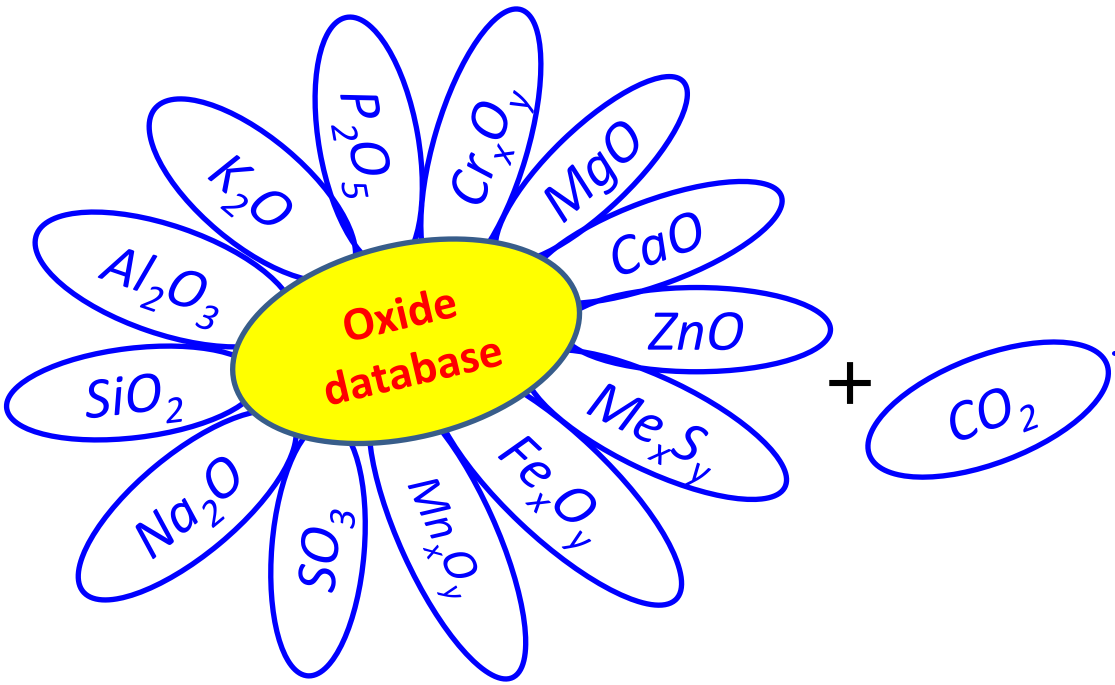
Contents	Slag atlas (11.0) Nov 2015
Binary systems	119
Ternary systems	98
Quaternaries	6
Slag components	149
Solid solution phases	85
Stoichiometric compounds	316

Including CO_2

Problem:

- Contradictory data on the mixtures silicate-carbonate-gas

After addition of the new associate species all systems (binary, ternary etc.) are assessed taking into account the available experimental information.



Oxide systems:
$(Me)_m(O)_n$-CO_2

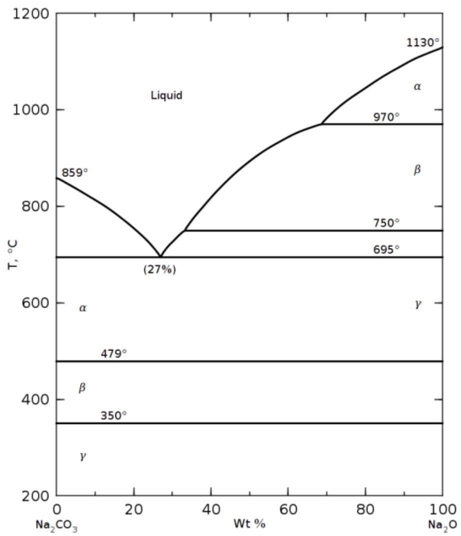
Carbonate systems:
$(Me1)_m(CO_3)_n$-$(Me2)_l(CO_3)_p$

Mixed systems:
e.g.$(Me1)_m(CO_3)_n$-$(Me2)_l(Si_xO_y)_p$

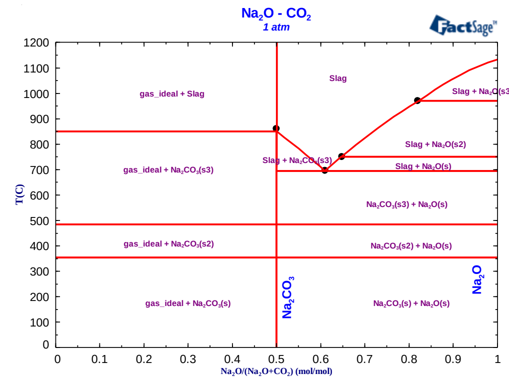
CO_2 is considered as oxide component in the database (similar to SiO_2, SO_3, etc.)

Oxide systems with CO_2

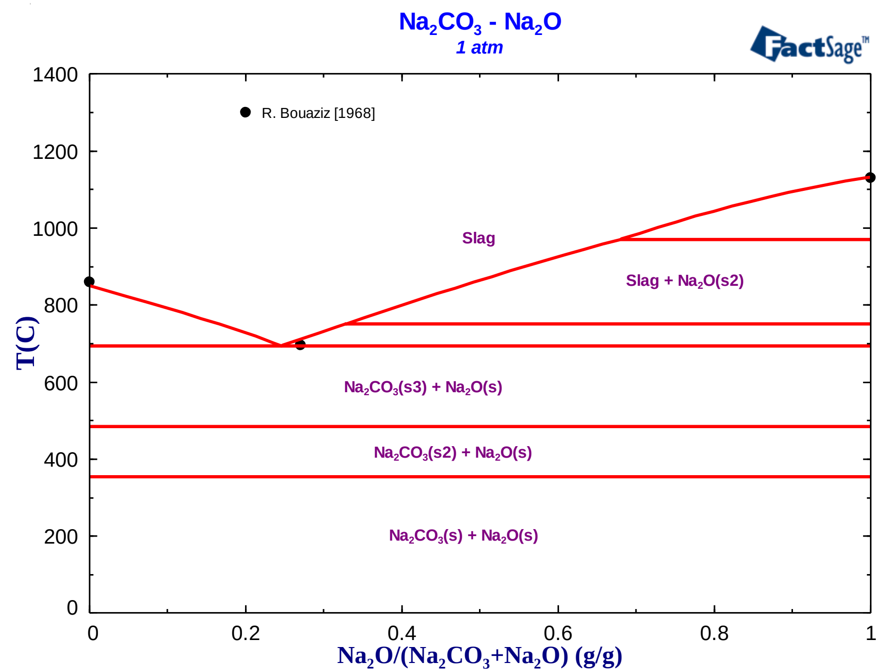
Binary system Na_2O-CO_2



R. Bouaziz and G. Papin, *C. R. Seances Acad. Sci., Ser. C*, **266** [21] 1530-1533 (1968).

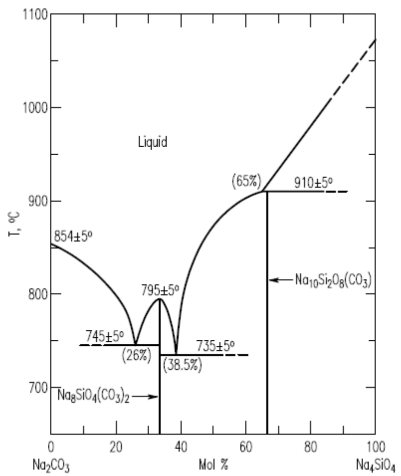


Preliminary calculation in the system Na_2O-CO_2



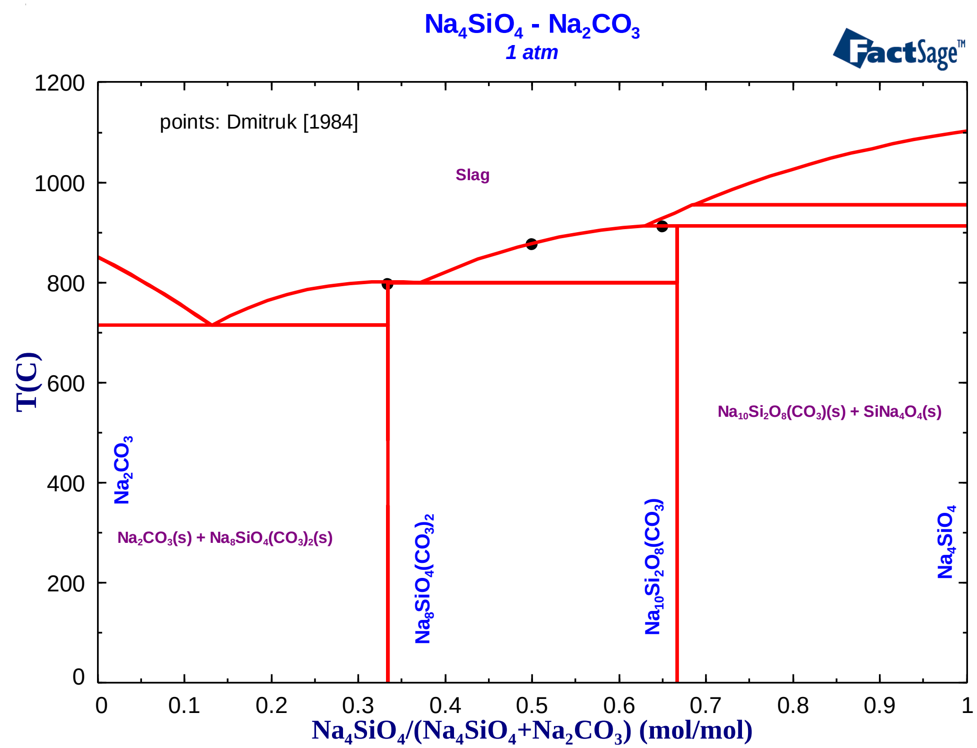
Slag: new species Na_2CO_3

Quasi-binary system Na_2CO_3-Na_4SiO_4



B. F. Dmitruk, 1984

Preliminary calculation of the system Na_4SiO_4-Na_2CO_3



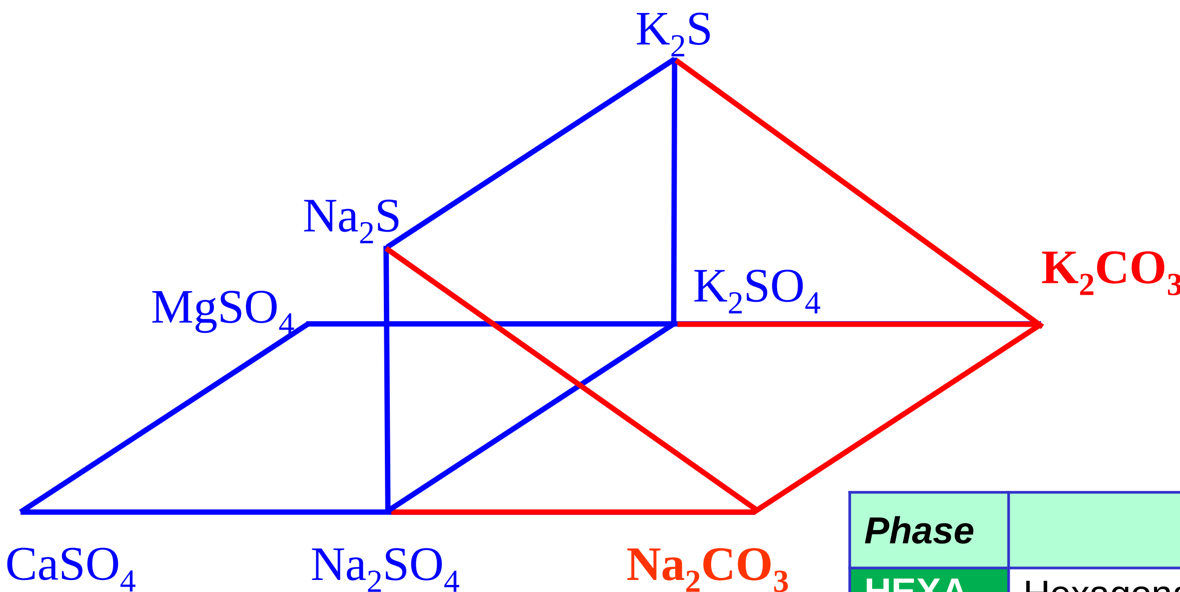
Slag: interaction parameter between Na_2CO_3 and Na_4SiO_4

New compounds:

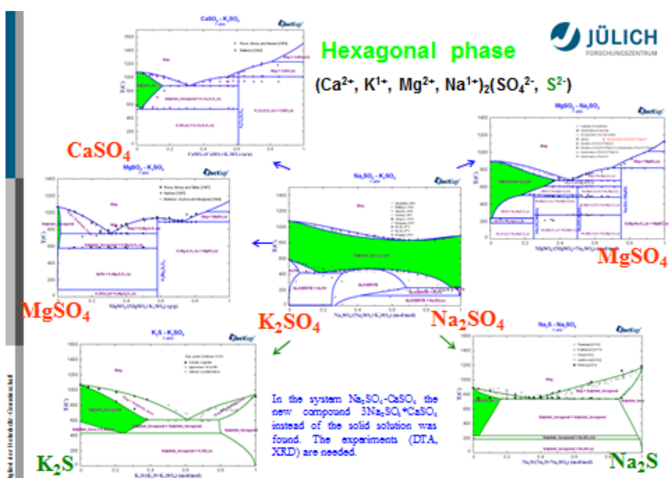
1:2 $Na_4SiO_4 * 2Na_2CO_3$

2:1 $2Na_4SiO_4 * Na_2CO_3$

Addition of alkali carbonates



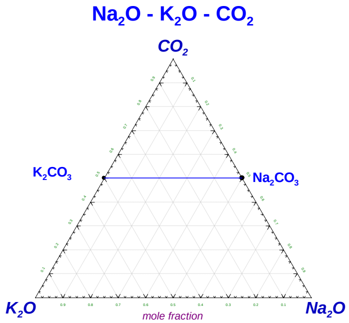
The species in the non-ideal associate solution containing CO_2 are added in order to describe the liquid phase. Solid solutions were considered using multi-sublattice model

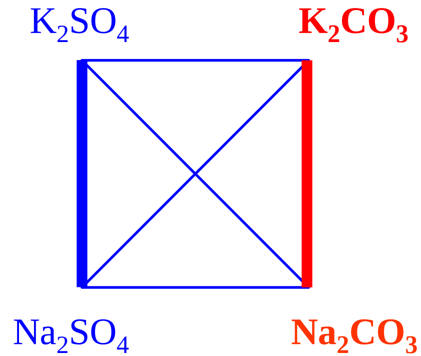


Phase	Description
HEXA	Hexagonal solution, HT: $(Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+})_2(SO_4^{2-}, S^{2-}, CO_3^{2-})$
HEX2	Intermediate, HT: $(K^{1+}, Na^{1+})_2(CO_3^{2-})_1$
MONO	Monoclinic, MT: $(K^{1+}, Na^{1+})_2(CO_3^{2-}, SO_4^{2-})_1$
MOLT	Monoclinic, based on Na_2CO_3_LT $(Na^{1+}, K^{1+})_2(CO_3^{2-})$
ALFA	Solution based on Na_2SO_4_MT and K_2SO_4_LT $(Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+})_2(SO_4^{2-}, S^{2-}, CO_3^{2-})$
HEXB	Sulphide hexagonal solution based on Alk_2S $(K^{1+}, Na^{1+})_2(S^{2-}, SO_4^{2-})$

Salt systems

System Na_2CO_3-K_2CO_3

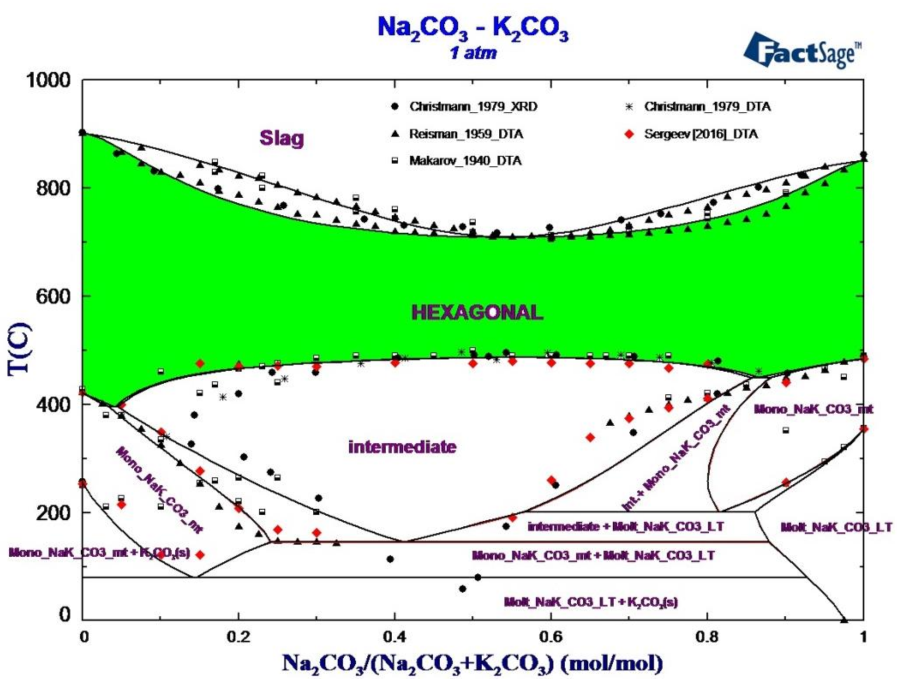


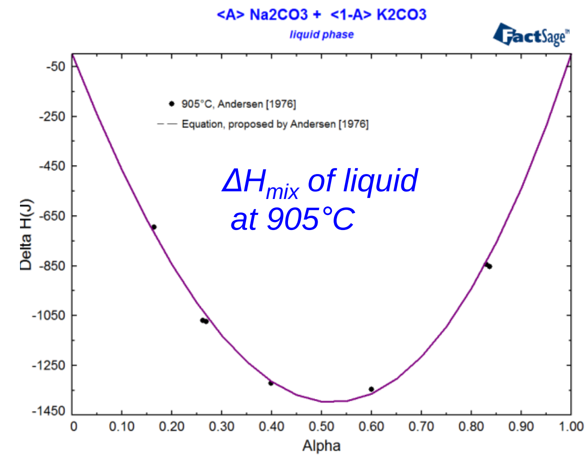


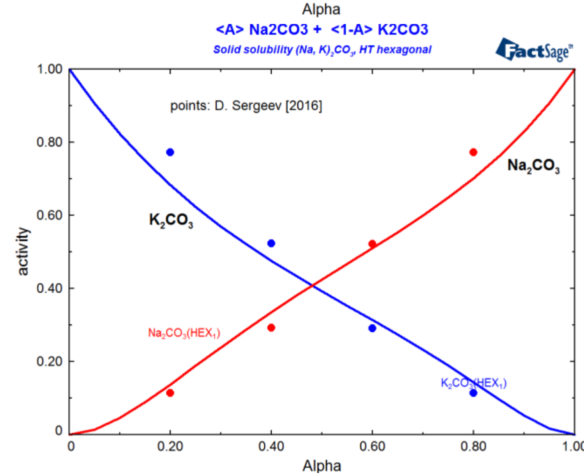
Slag: new species Na_2CO_3 and K_2CO_3

Hexagonal phase, HT

$(Ca^{2+}, \underline{K^{1+}}, Mg^{2+}, \underline{Na^{1+}}, Va)_2(\underline{SO_4}^{2-}, S^{2-}, \underline{CO_3}^{2-})$

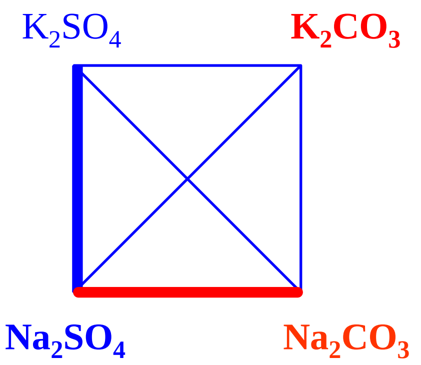


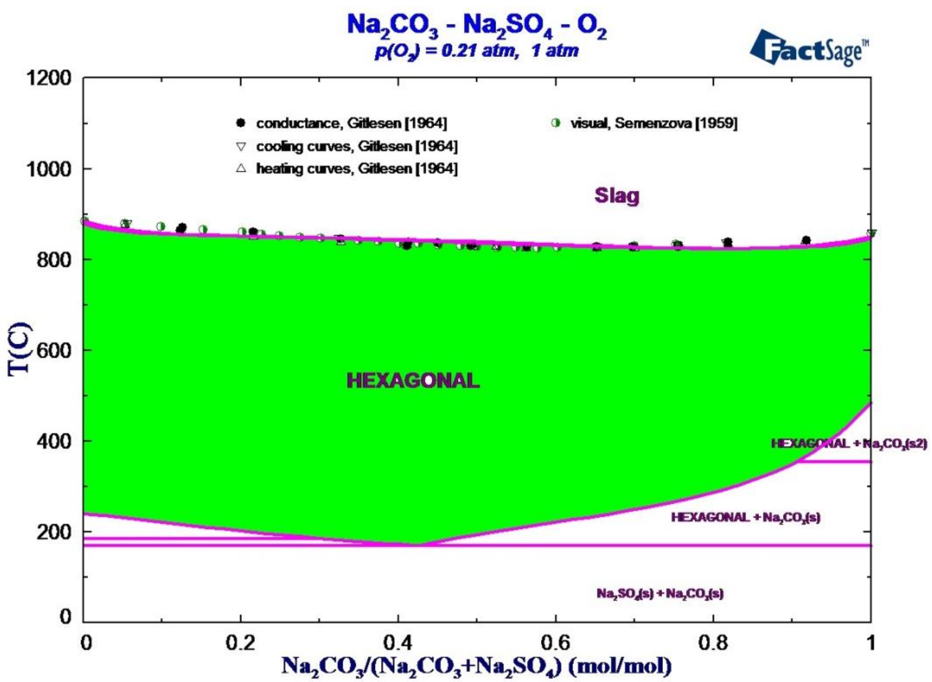


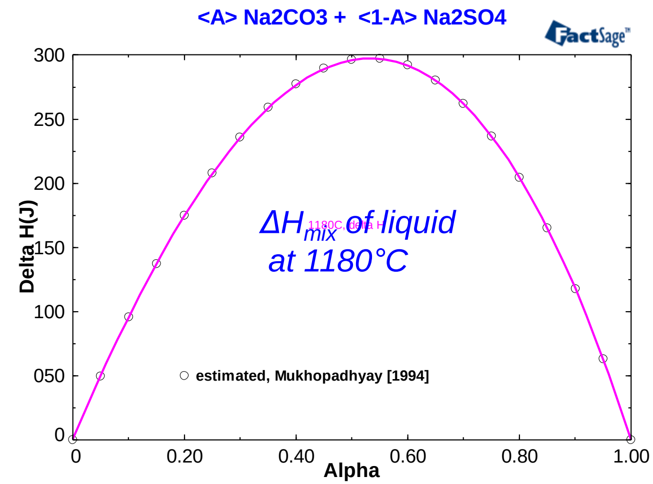


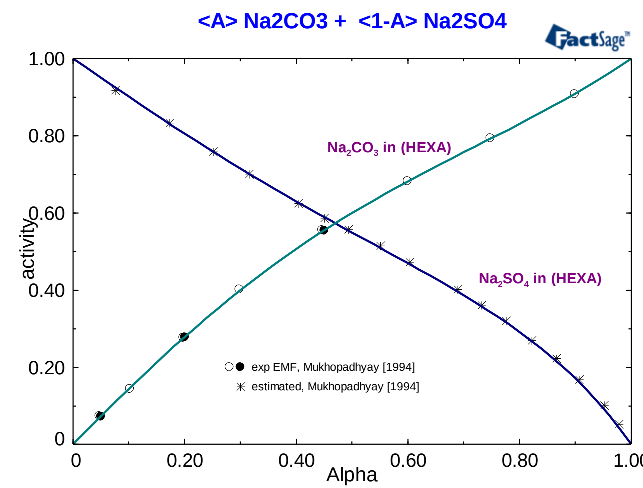
Activity in HEXA at 650°C

System Na_2CO_3-Na_2SO_4





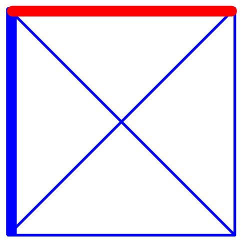




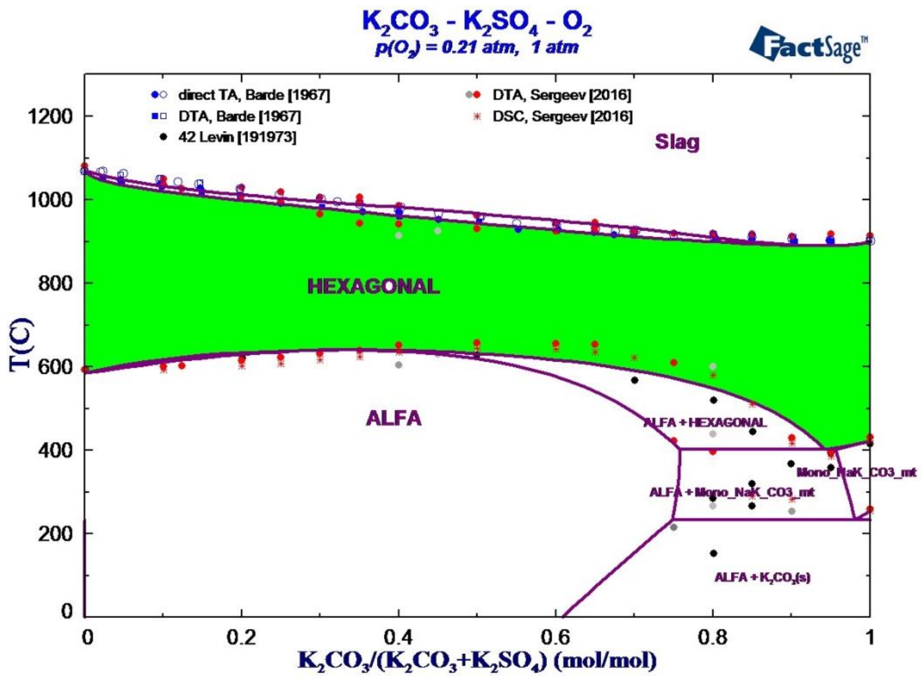
Activity in HEXA at 800°C

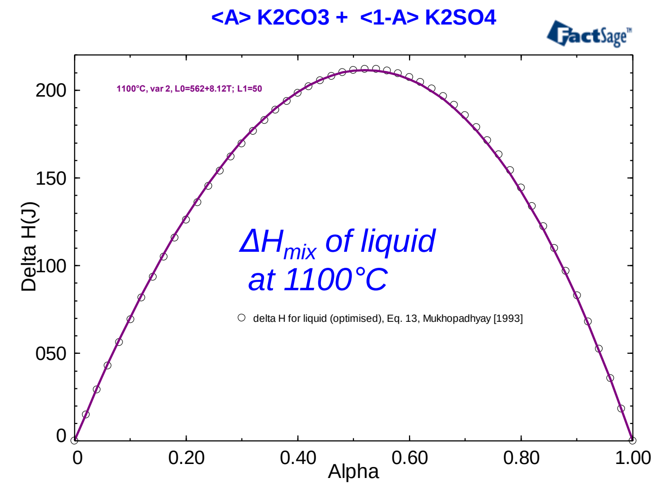
System K_2CO_3-K_2SO_4

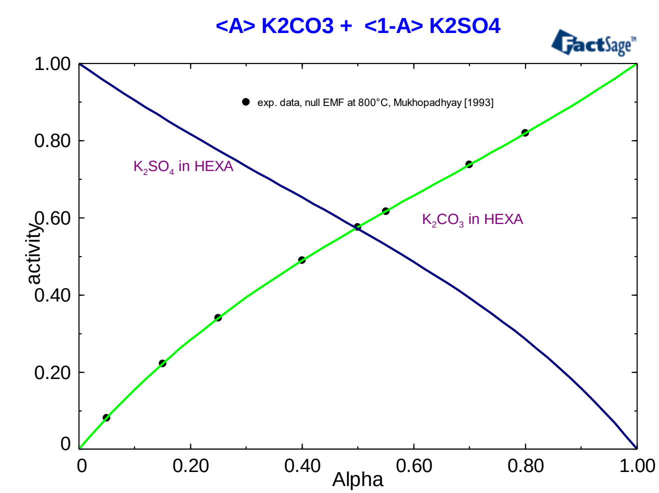
K_2SO_4 K_2CO_3



Na_2SO_4 Na_2CO_3

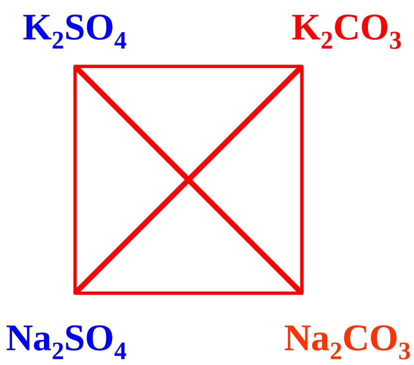


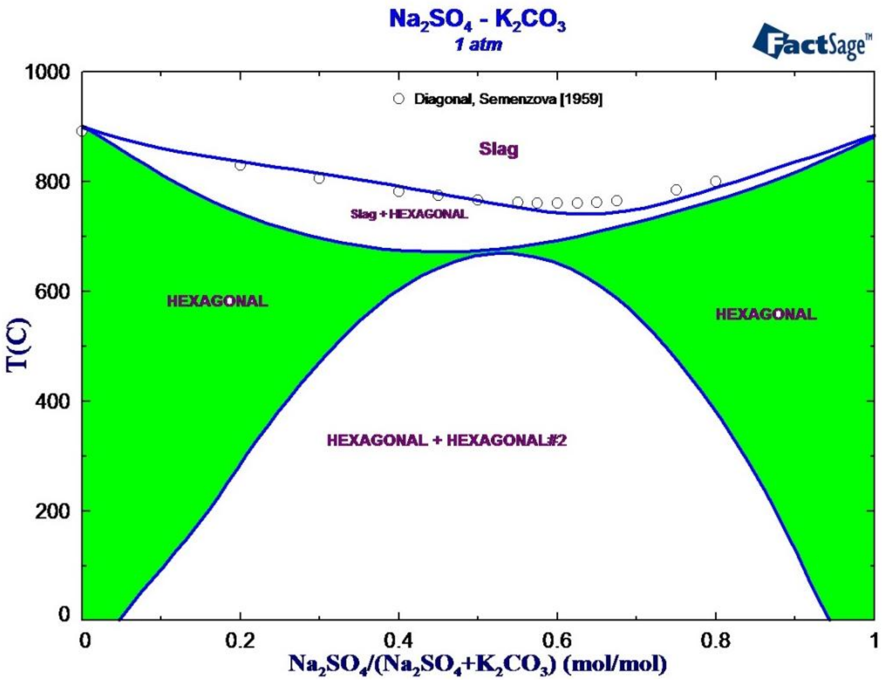


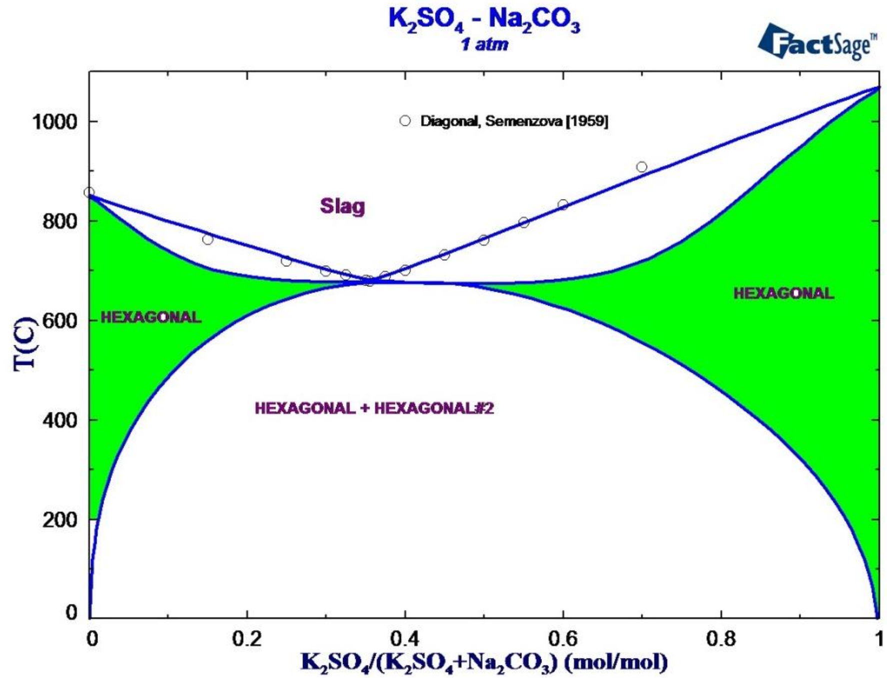


Activity in HEXA at 800°C

Diagonals in system Na^{1+}, K^{1+} ‖ CO_3^{2-}, SO_4^{2-}

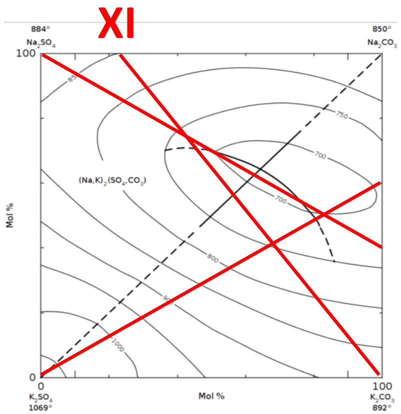




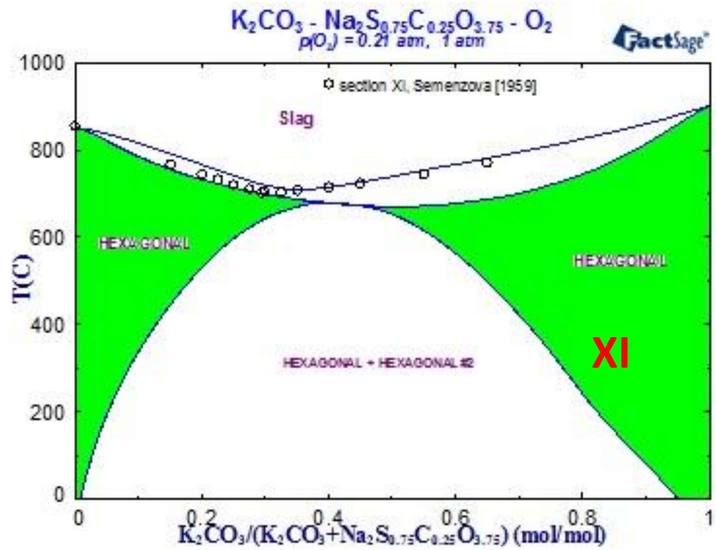


Calculations based on quasi-binary systems

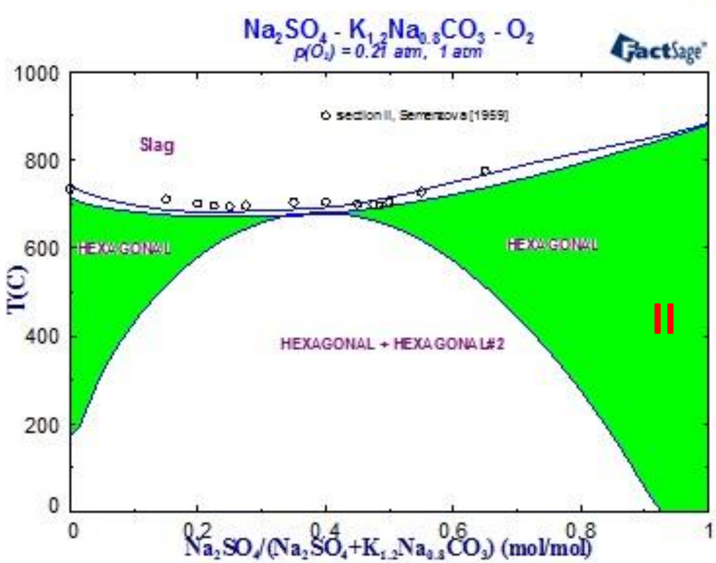
Sections in system Na^{1+}, $K^{1+} \| CO_3^{2-}$, SO_4^{2-}

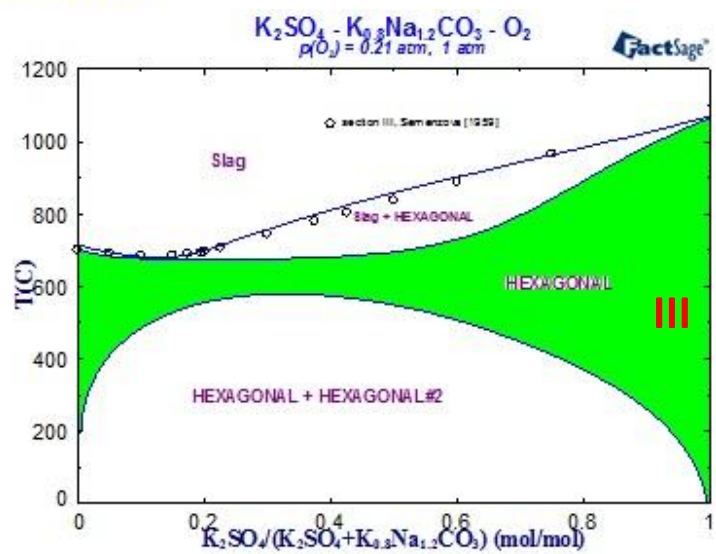


A.K. Semenzova, Zh. Neorg. Khim., ***4*** *[1] 144-147 (1959)*

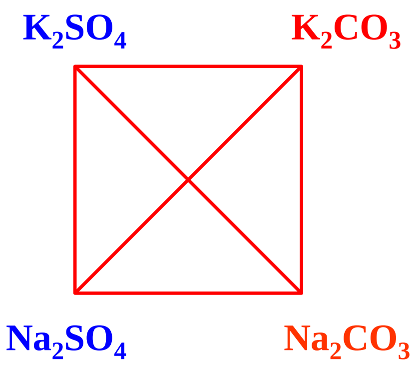


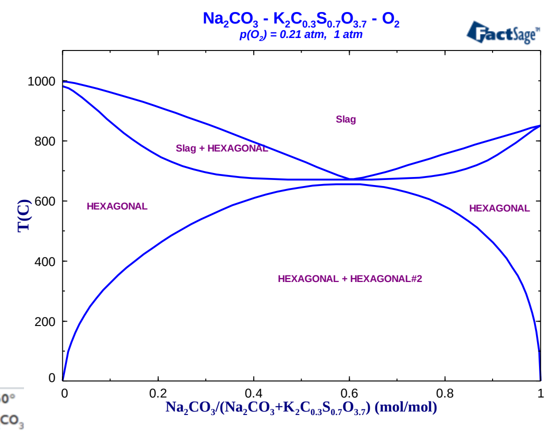
Calculations based on quasi-binary systems

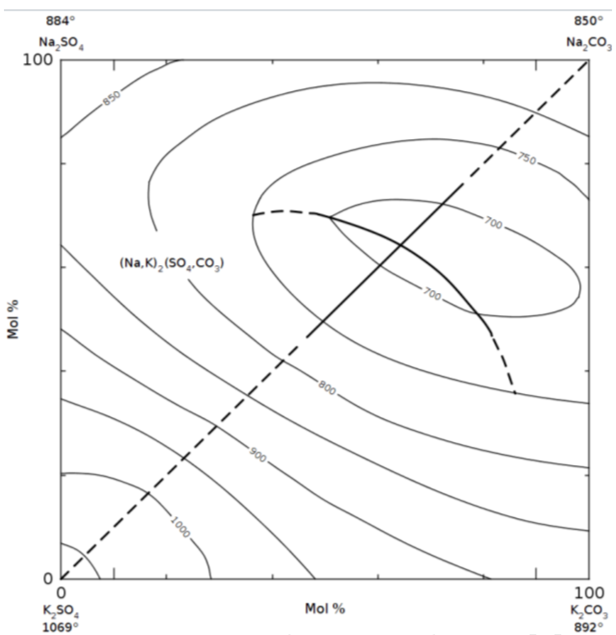




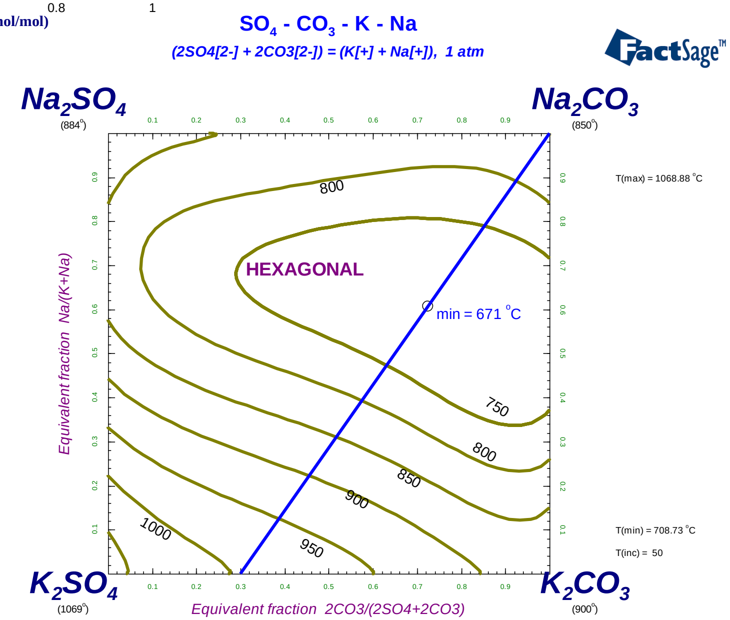
Reciprocal system Na^{1+}, K^{1+} ‖ CO_3^{2-}, SO_4^{2-}





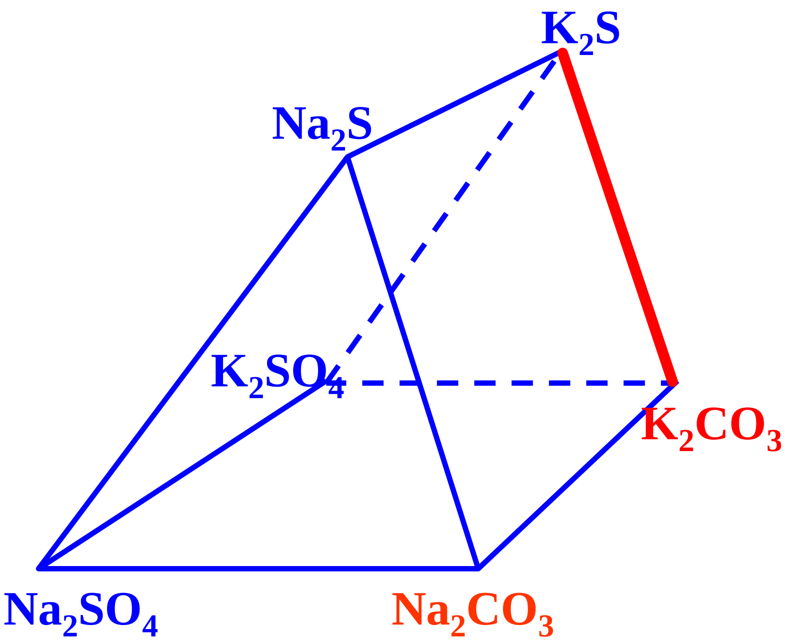


A.K. Semenzova, Zh. Neorg. Khim., **4** [1] 144-147 (1959)



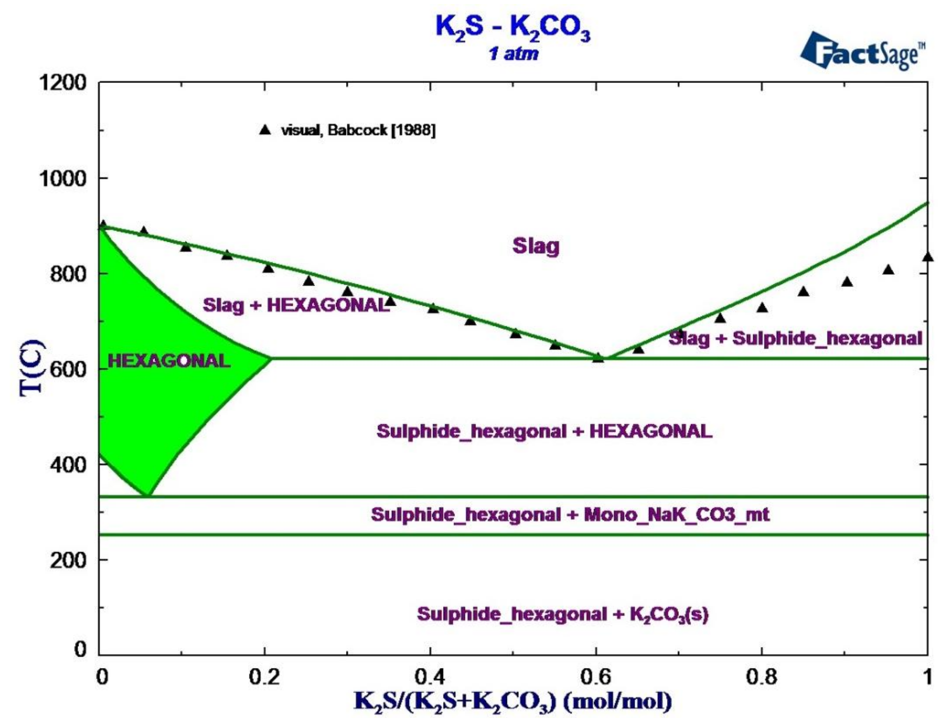
Salt systems

System Na^{1+}, K^{1+} ‖ CO_3^{2-}, SO_4^{2-}, S^{2-}



Hexagonal phase, HT

$(Ca^{2+}, \underline{K^{1+}}, Mg^{2+}, \underline{Na^{1+}}, Va)_2(SO_4^{2-}, S^{2-}, \underline{CO_3^{2-}})$



Mitglied der Helmholtz-Gemeinschaft

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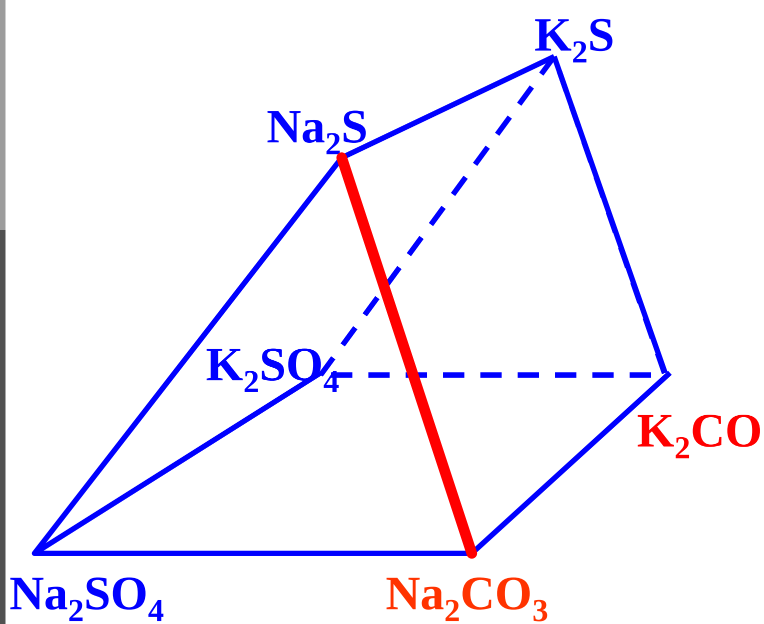
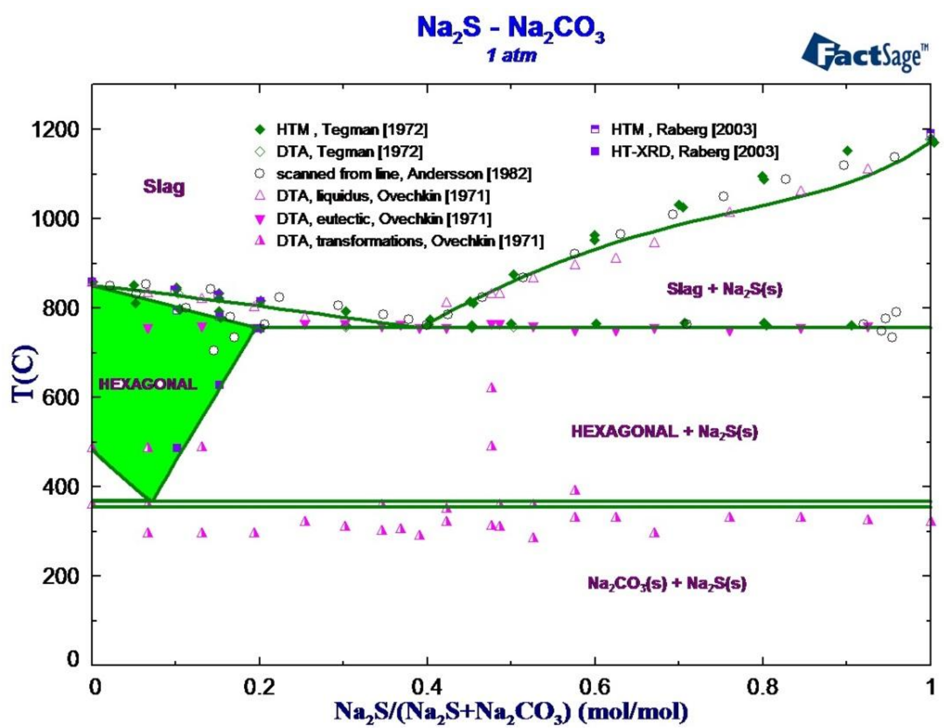
System Na^{1+}, K^{1+} ‖ CO_3^{2-}, SO_4^{2-}, S^{2-}



Hexagonal phase, HT

(Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+}, Va)$_2$(SO_4^{2-}, S^{2-}, CO_3^{2-})



Development of the sulphide database

binary systems

- S
- Cr-S
- Ca-S
- Mg-S
- Mn-S
- Fe-S

ternary systems

- Cr-Fe-S
- Mg-Mn-S
- Cr-Mn-S
- Fe-Mg-S
- Fe-Mn-S

quasi-ternary systems

- Me_1S-Me_2S-Me_3S

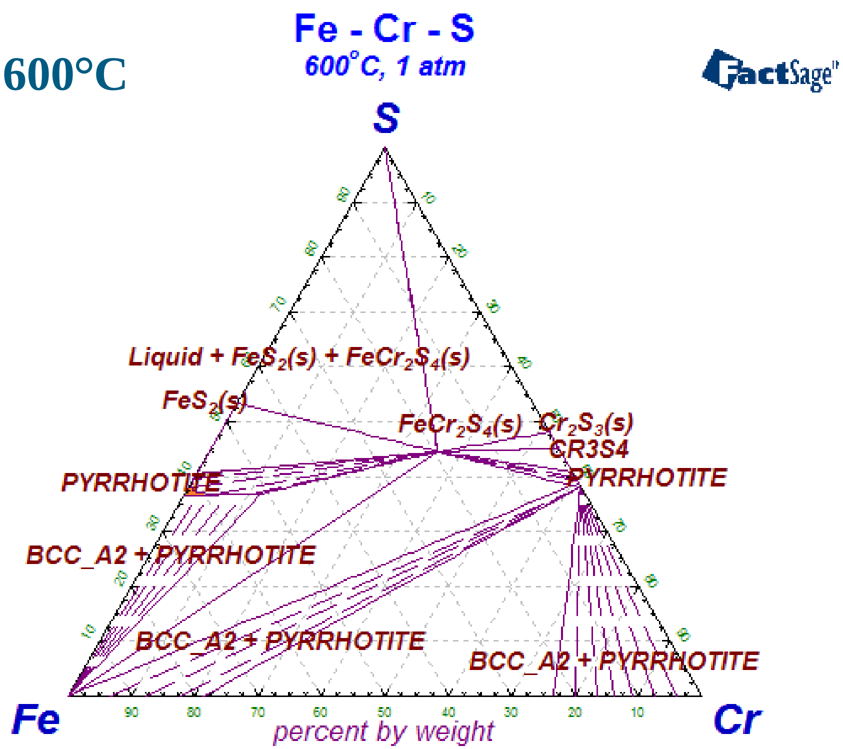
Phase	***Description***
Pyrrhotite	*(Cr, Fe, Mg, Mn, Va) S*
Oldhamite	*(Ca, Mg, Mn, Fe,Cr)(S)*
Thiospinel	*(Fe, Mn) $(Cr)_2(S)_4$*
Cr_3S_4	*(Fe, Cr, Mn) $(Cr)_2(S)_4$*

*T. Jantzen, K. Hack, E. Yazhenskikh, M. Müller, Evaluation of thermodynamic data and phase equilibria in the System Ca-Cr-Cu-Fe-Mg-Mn-S; Part I: Binary and quasi-binary subsystems; Calphad, in Press, Corrected Proof **(2016)***

Isothermal section in Cr-Fe-S

Properties	H_f, kJ/Mol	S_f, J/mol K	T_m, °C
Experimental	-457.31 [Kessler76] -566.8 [Petaev82] -488.4[Osadchij14]	207.1 [Petaev82] 187.53 [Osadchij14]	1440 [Indosova82] 1350 [ElGoresy]
Calculated	-570.279(FTMisc) -586.040[Waldner14] -542.835*	173.587(FTMisc) 198.082 [Waldner14] 167.883*	1440 (FTMisc) 1071 [Waldner14] 1437*

600°C



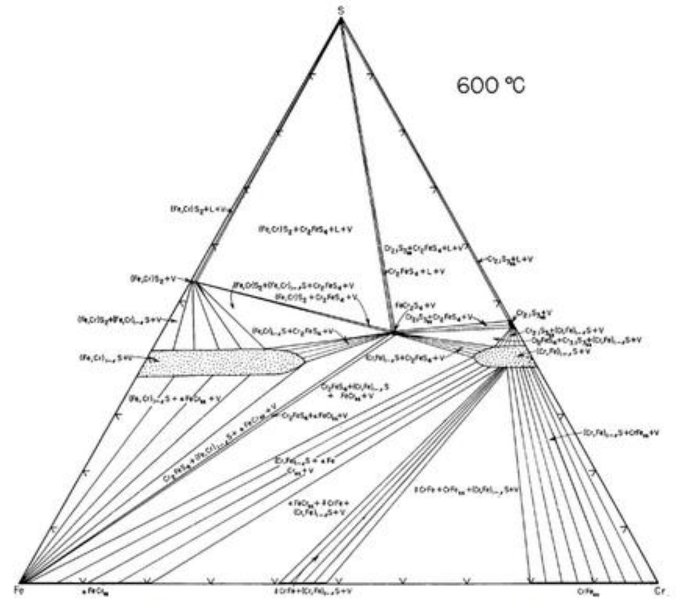


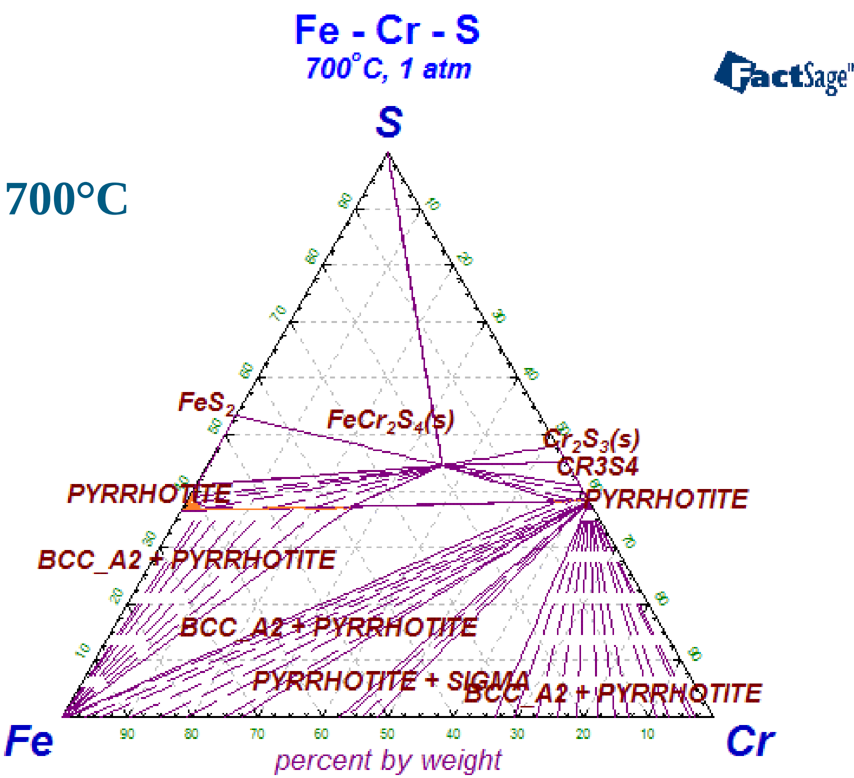
Fig. 7. Phase relations in the Cr-Fe-S system at 600°C. All assemblages are in equilibrium with vapor.

A. El Goresy, G. Kullerud: in Proc. Symp. Meteorite Res., P.M.D. Millman, ed., Reidel, Dordrecht, (1969), pp. 638-656.

Introduction $FeCr_2S_4$

Isothermal section in Cr-Fe-S

700°C



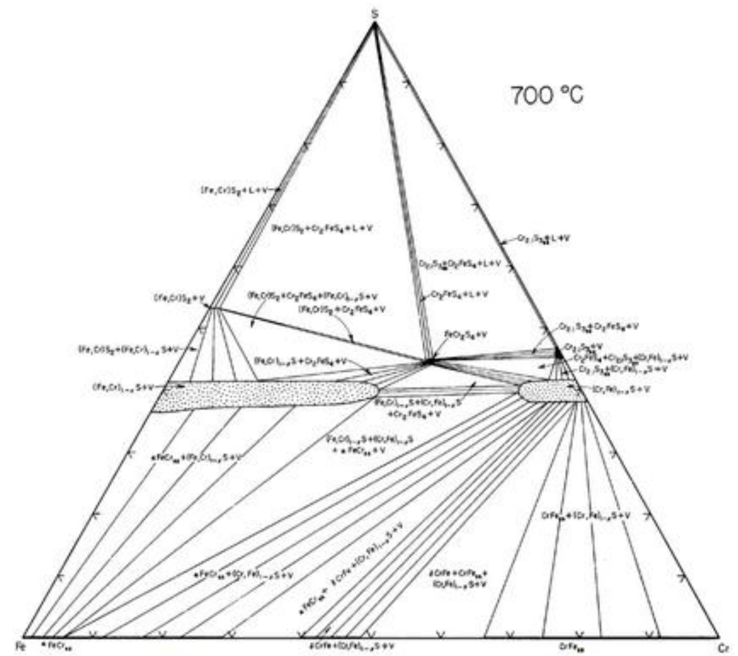
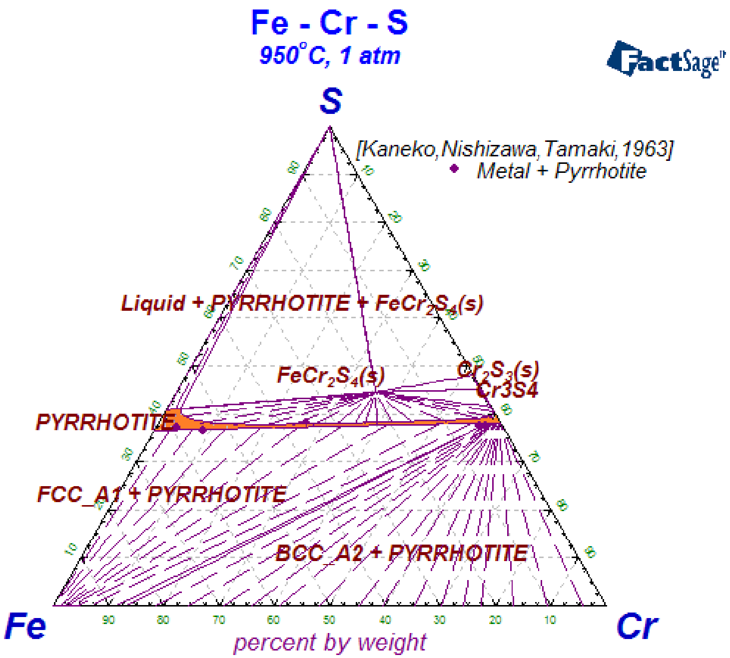


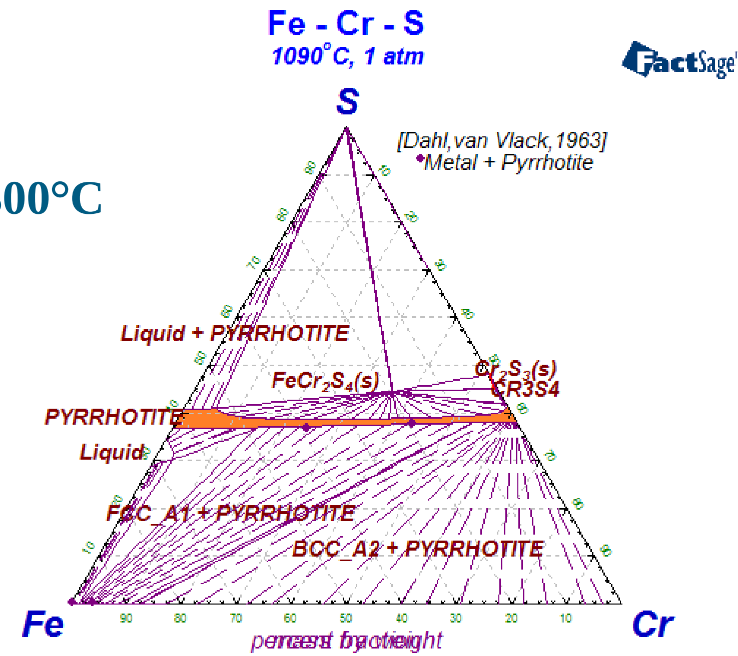
Fig. 6. Phase relations in the Cr-Fe-S system at 700°C. All assemblages are in equilibrium with vapor.

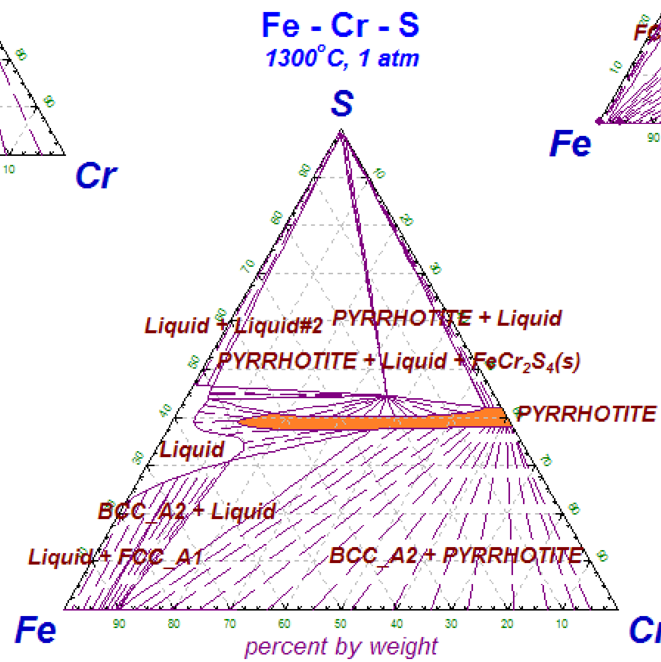
A. El Goresy, G. Kullerud: in Proc. Symp. Meteorite Res., P.M.D. Millman, ed., Reidel, Dordrecht, (1969), pp. 638-656.

Isothermal section in Cr-Fe-S

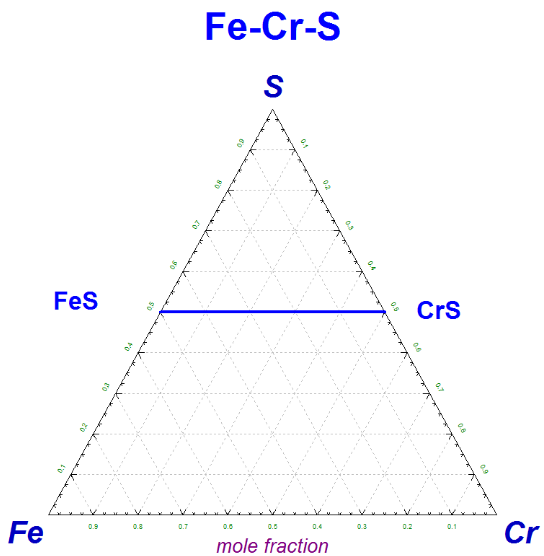


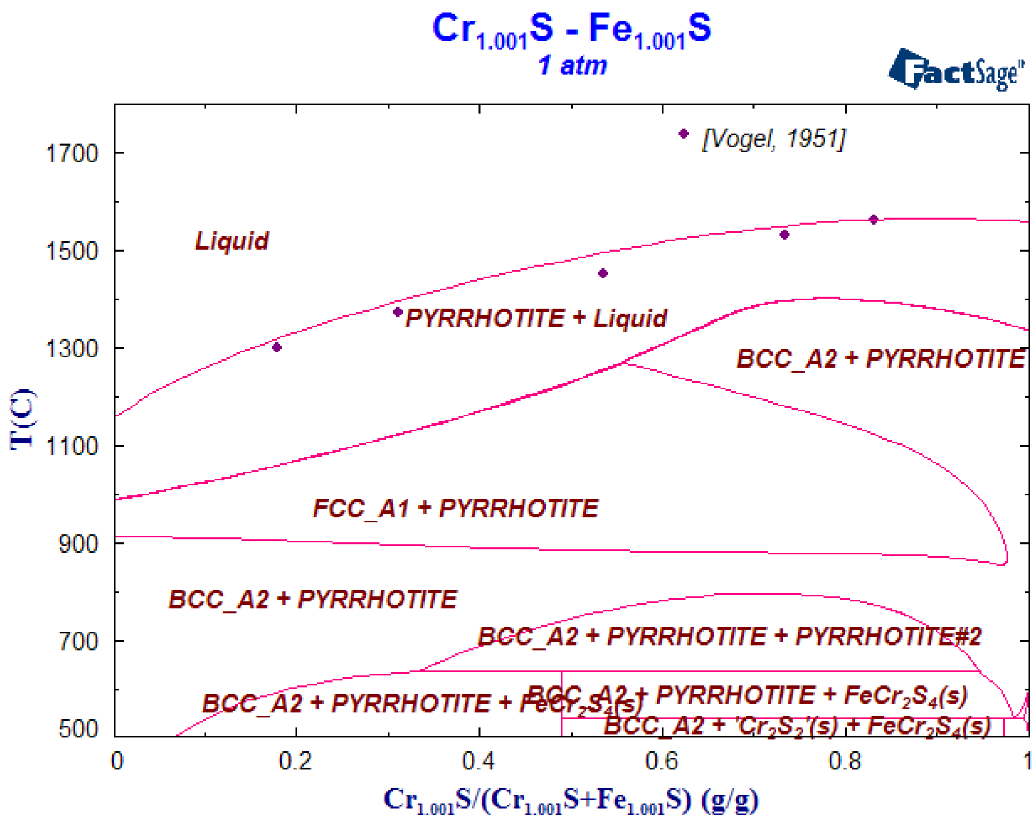
at 950, 1090, 1300°C





Isopleth section at ~50 mol % S in Cr-Fe-S





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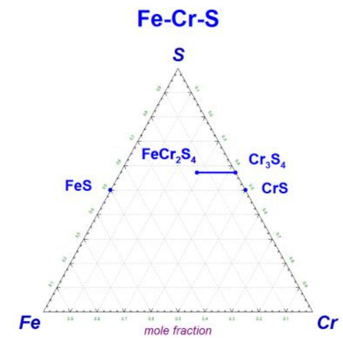
Solubility of Fe in Cr_3S_4



$(Cr^{+2}, Fe^{+2}, Mn^{+2})_1(Cr^{+3})_2(S^{-2})_4$

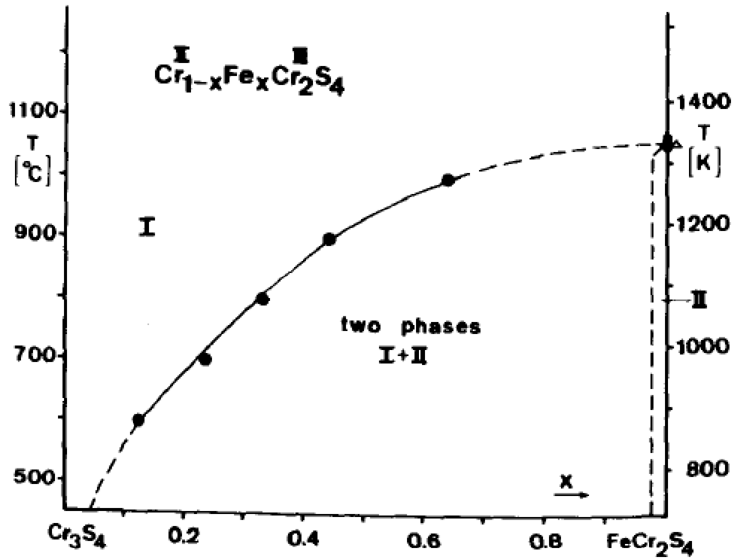
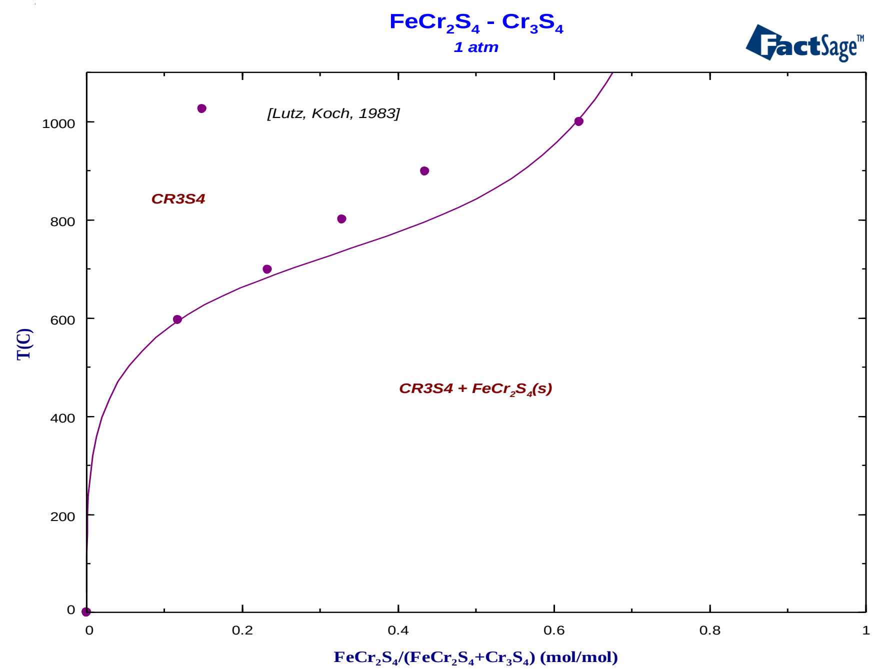


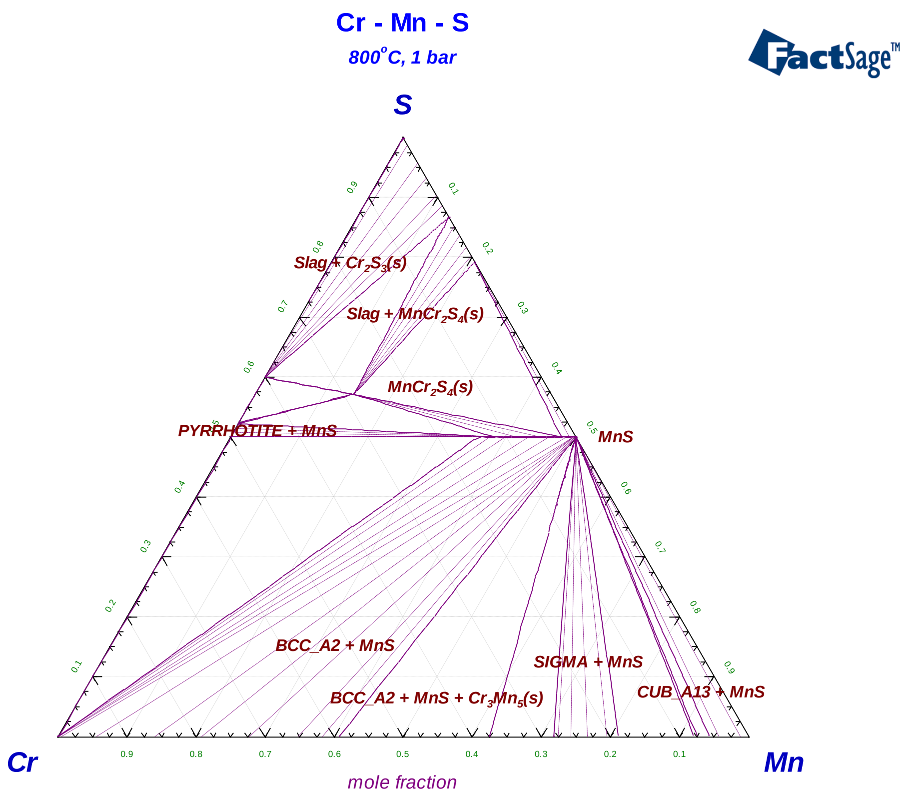
FIG. 2

Phase diagram of the system Cr_3S_4-$FeCr_2S_4$. Cr_3S_4 type I, spinel type, II, phase transition temperature given in ref. (1), ○, (4), □, and (5), △.



H.D. Lutz, U. Koch, H. Siwert, Mat. Res. Bull., 18 (1983), pp.1383-1389.

Isothermal section at 800°C in Cr-Mn-S



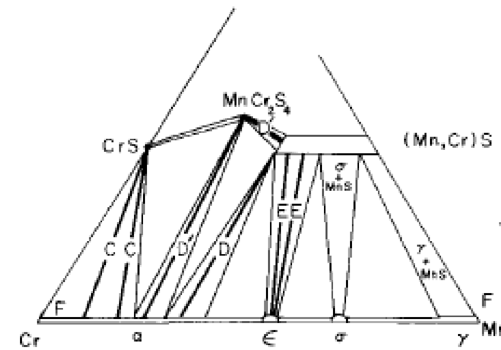
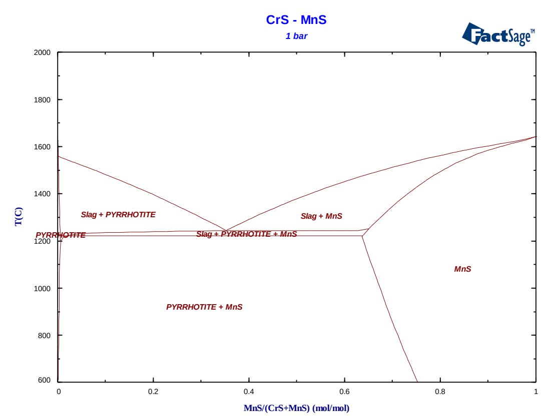
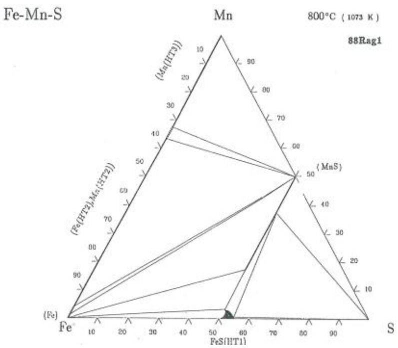


Fig. 8—Schematic representation of portion of Cr-Mn-S phase diagram at 800°C. Postulated tie lines for local equilibrium compositions of phases in contact during reaction are indicated, together with a continuity diagram. Dashed arrows show possible presence of $MnCr_2S_4$ in products.

Shatynski, S.R.; Hirth, J.P.; Rapp, R.A., Metall. Trans. A, 10A (5), 591-598 (1979) (16).

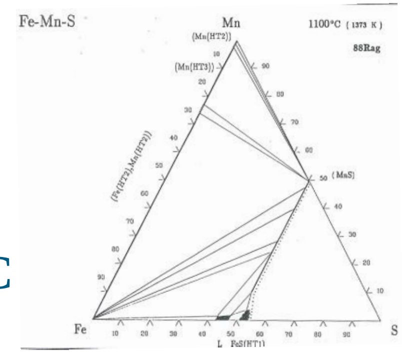


Isothermal section in Fe-Mn-S

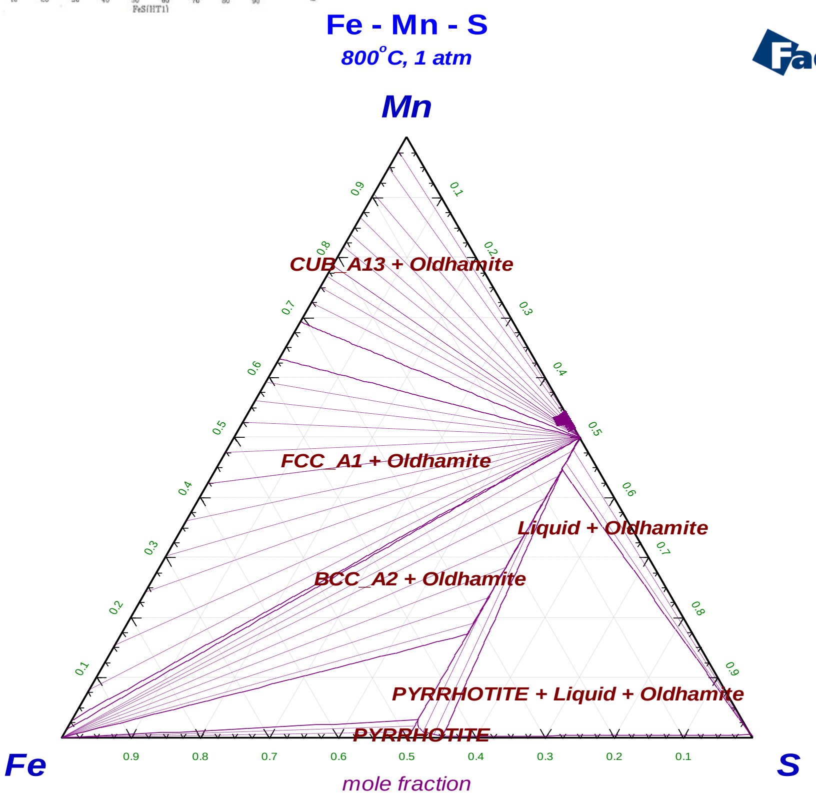


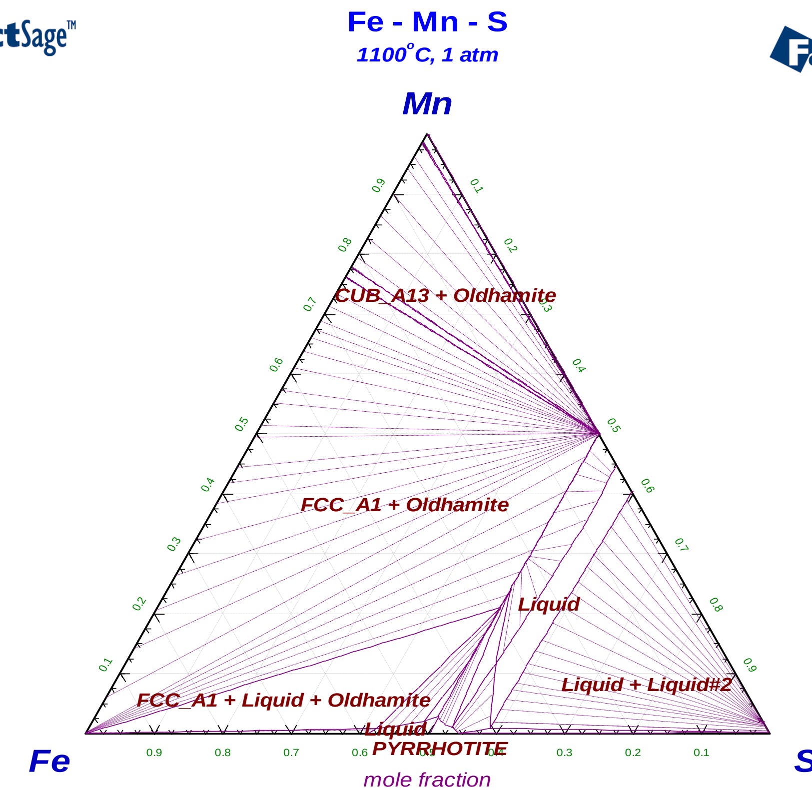
V. Raghavan, D.P. Antia, J. Alloy Phase Diagrams, India, 4[1], (1988), pp. 16-36.

at 800, 1100°C

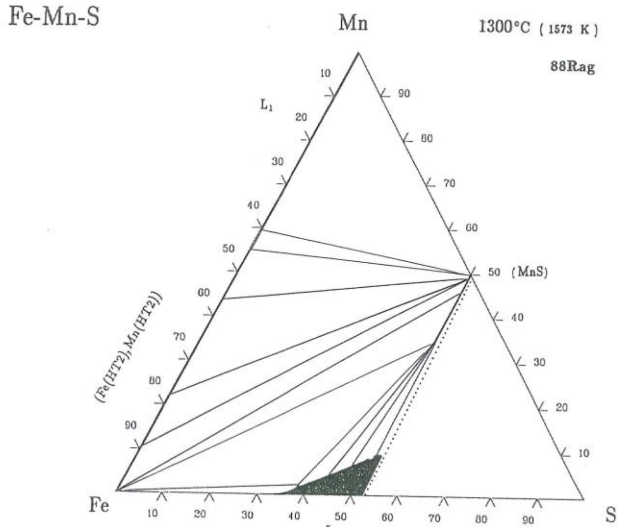


V. Raghavan, Phase Diagrams of Ternary Iron Alloys, The Indian Institute of Metals, Calcutta, India [2], (1988), pp. 154-173.



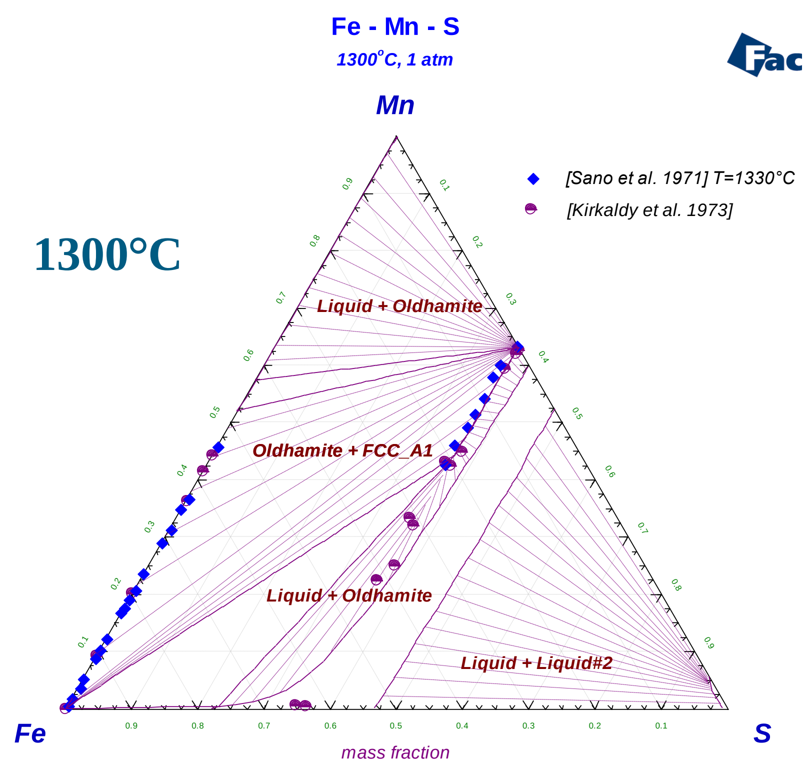


Isothermal section in Fe-Mn-S



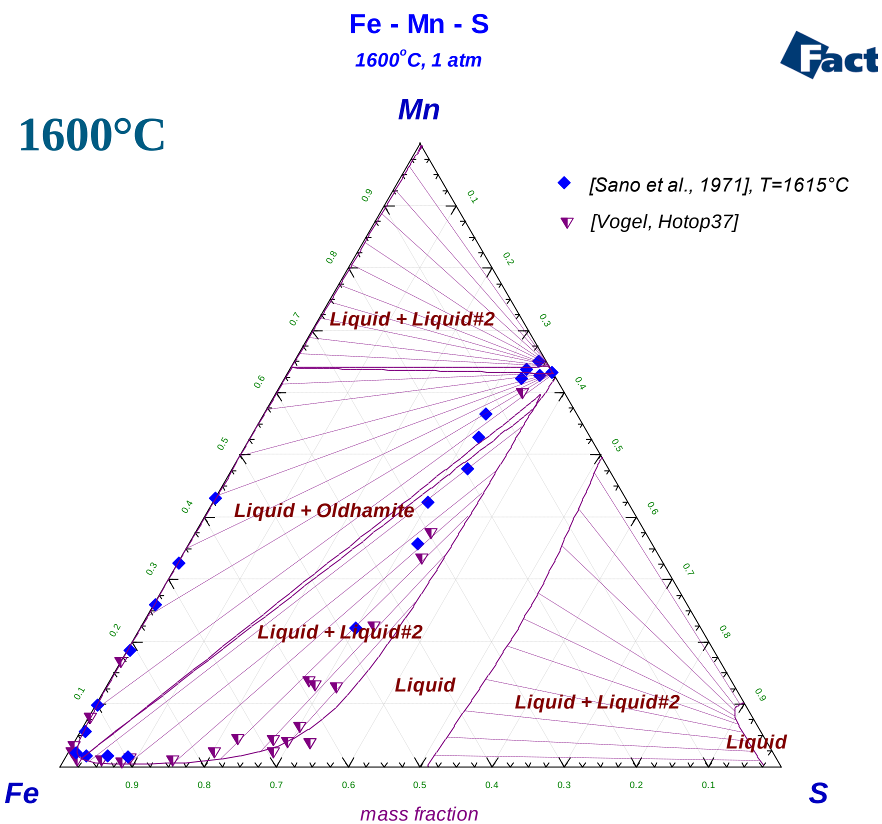
V. Raghavan, Phase Diagrams of Ternary Iron Alloys, The Indian Institute of Metals, Calcutta, India [2], (1988), pp. 154-173.

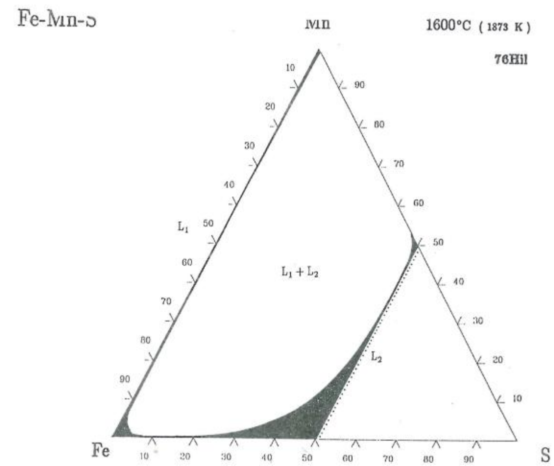
1300°C



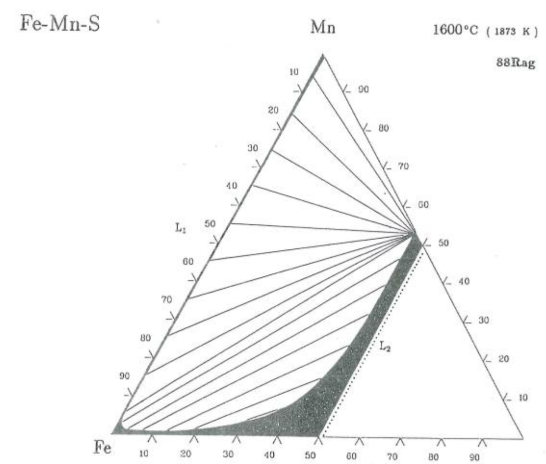
Isothermal section in Fe-Mn-S

1600°C



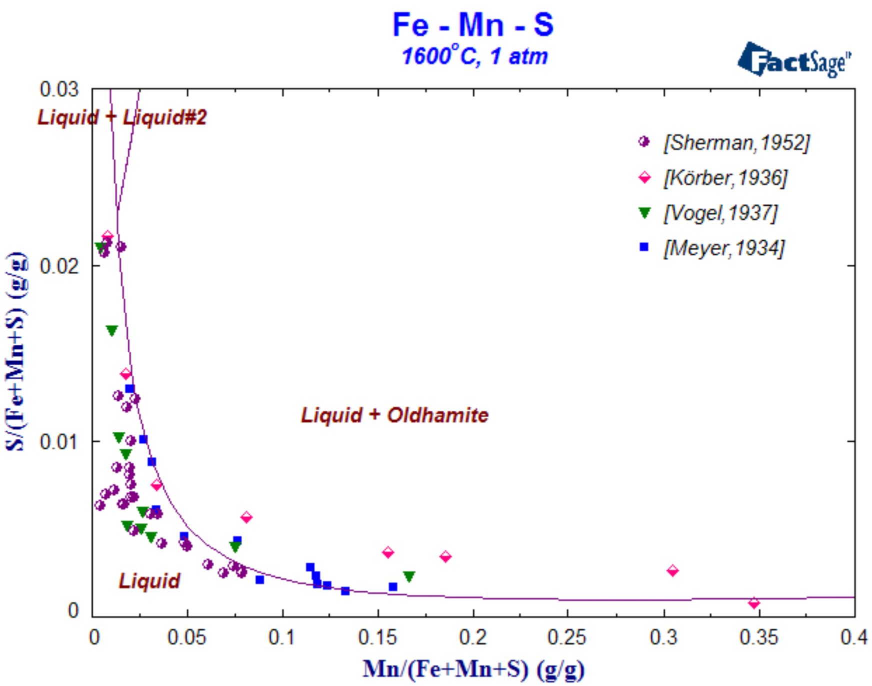


M. Hillert, L.-I. Staffansson, Metallurg. Transact., Section B: Process Metallurgy, 7B, (1976), pp. 203-211.



V. Raghavan, Phase Diagrams of Ternary Iron Alloys, The Indian Institute of Metals, Calcutta, India [2], (1988), pp. 154-173.

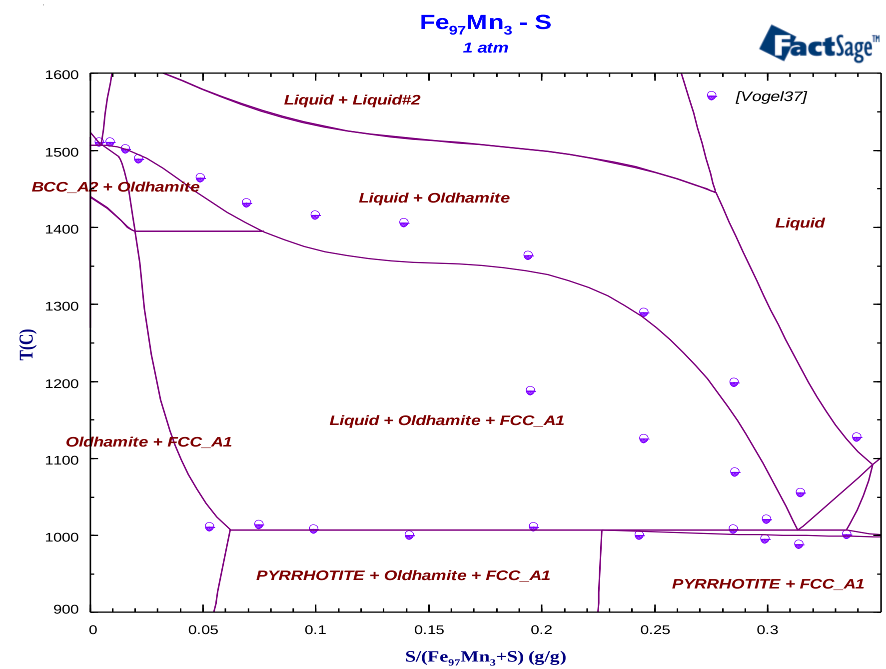
System Fe-Mn-S



1600°C

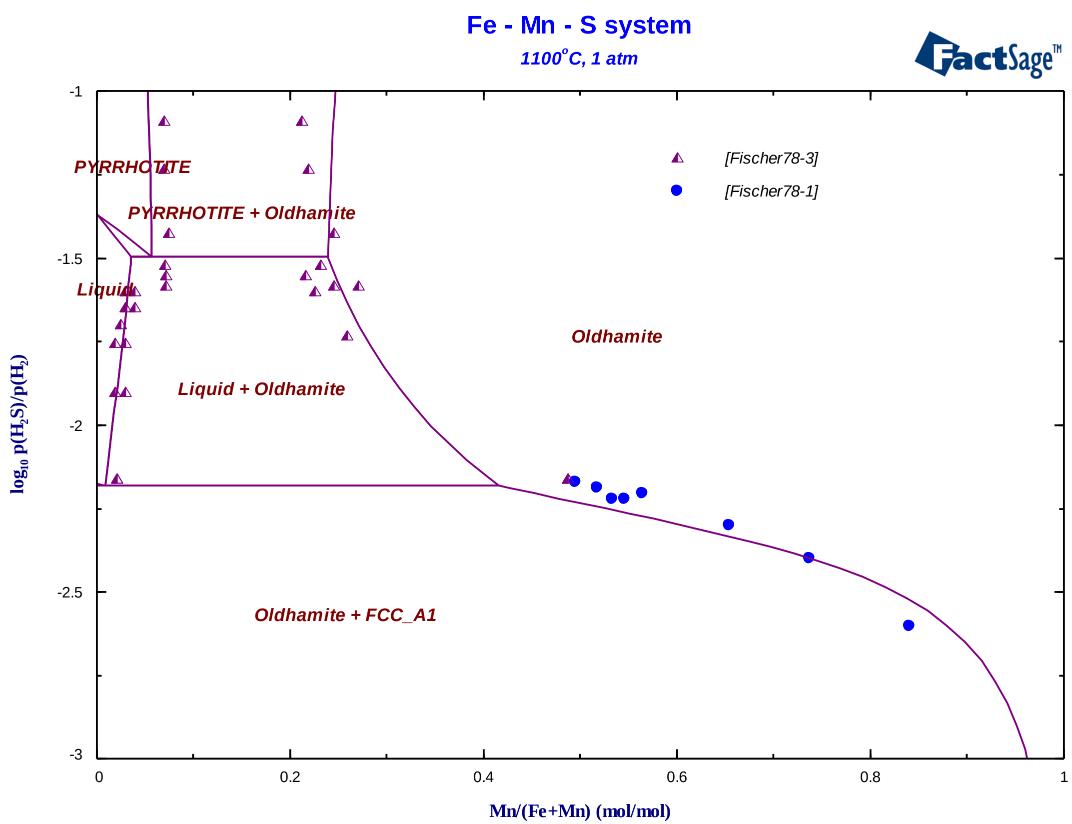
Solubility of Mn and S in Fe-rich liquid at 1600°C

Isopleth section Fe/Mn=97/3 in Fe-Mn-S



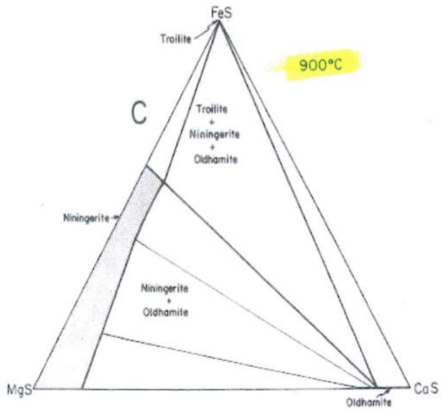
System Fe-Mn-S

1100°C

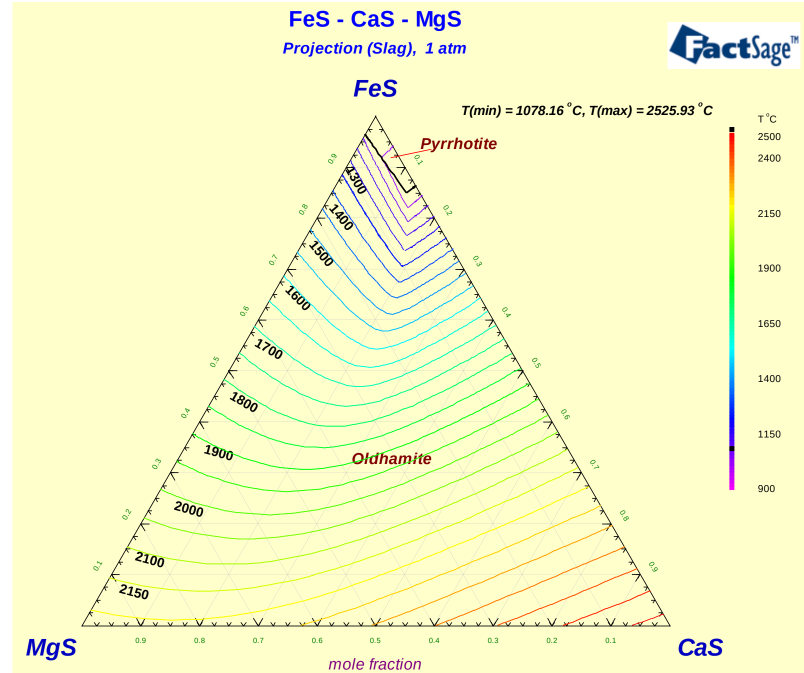


Relationship between S potential and Mn fraction

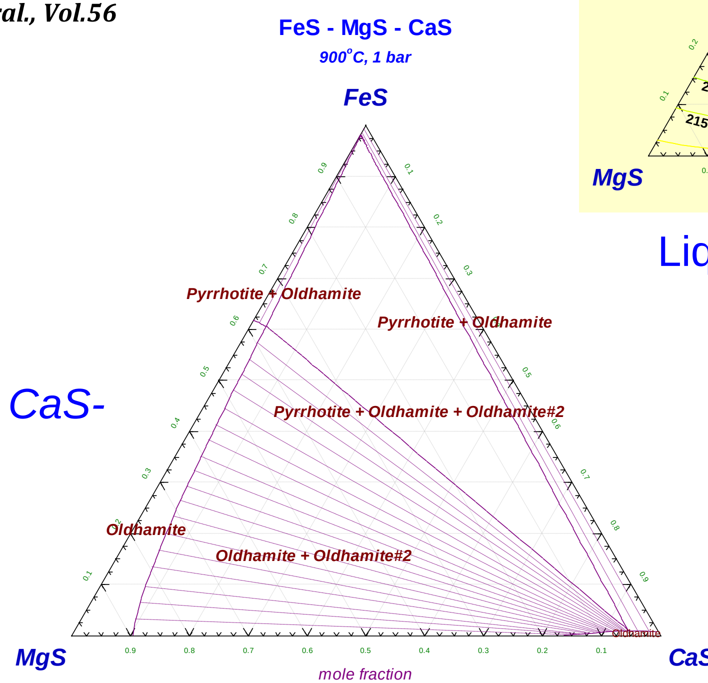
System CaS-FeS-MgS



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

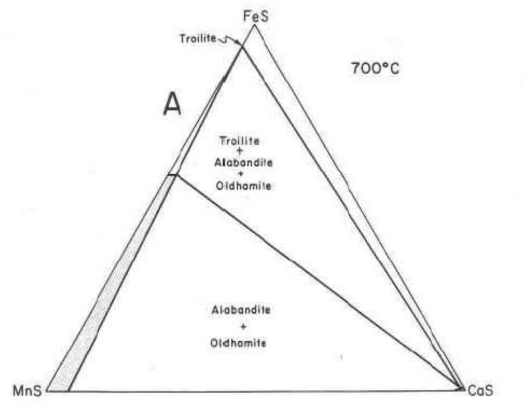


Liquidus surface in CaS-FeS-MgS



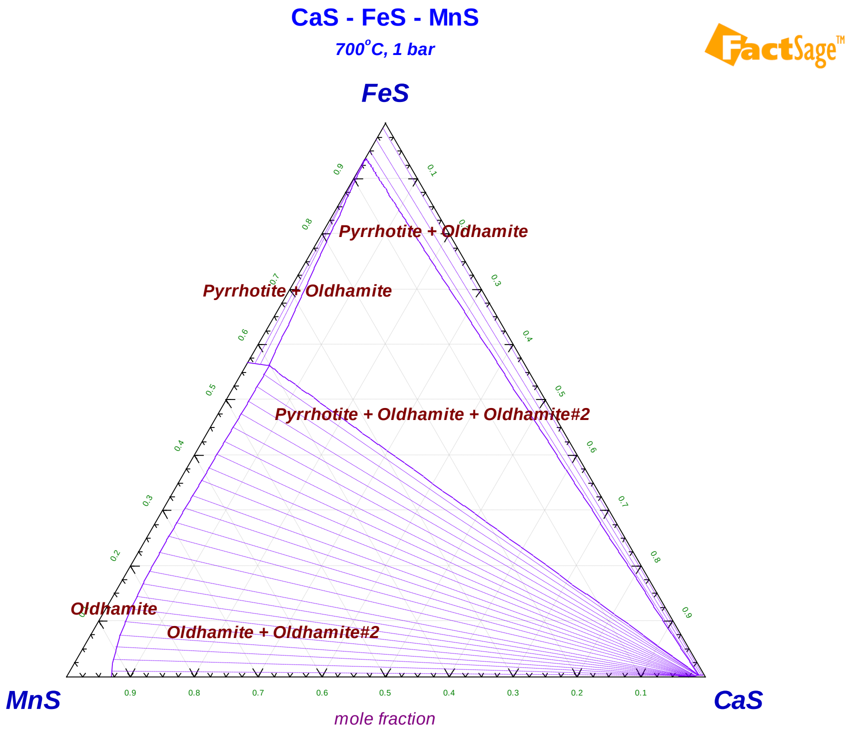
Isothermal section in CaS-FeS-MgS at 900^{o}C

System CaS-FeS-MnS



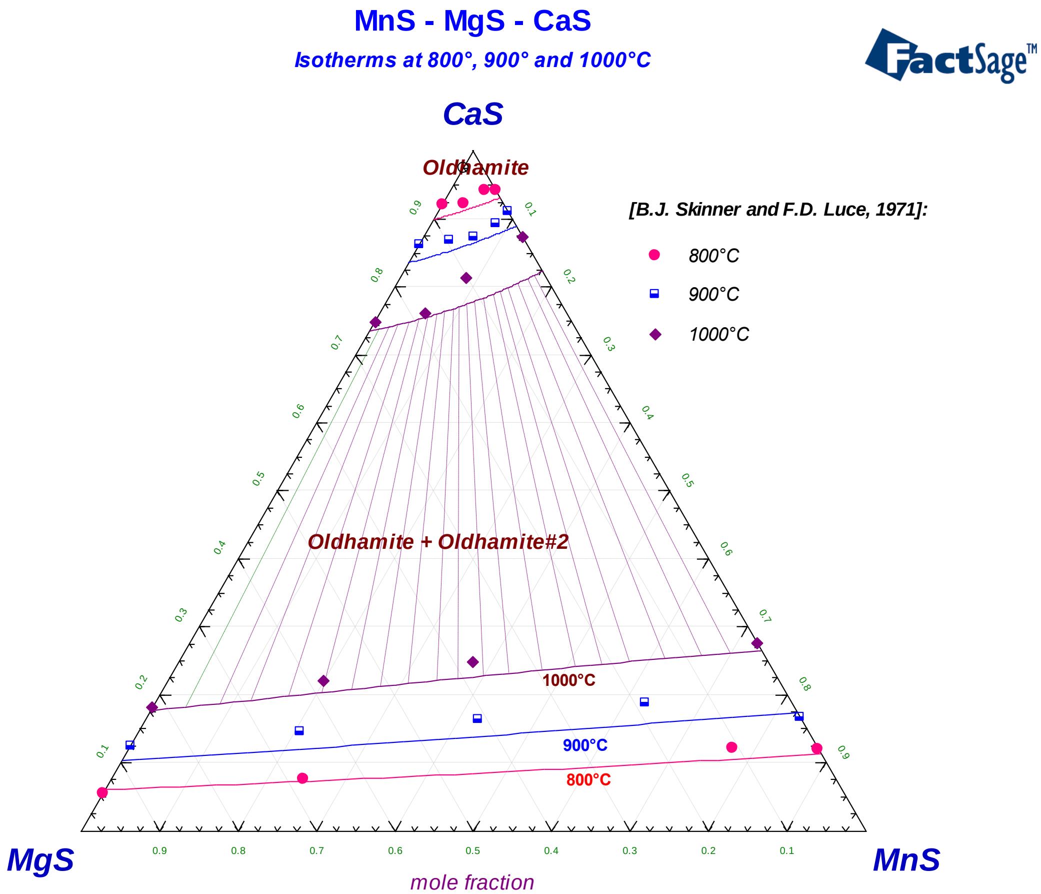
B.J. Skinner, F.D. Luck, Amer. Mineral., Vol.56 (1971), pp. 1269-1296.

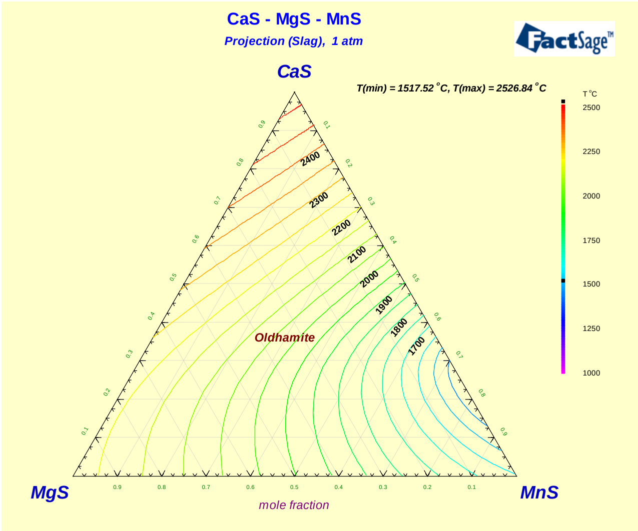
Isothermal section at 700°C in CaS-FeS-MnS



System CaS-MgS-MnS

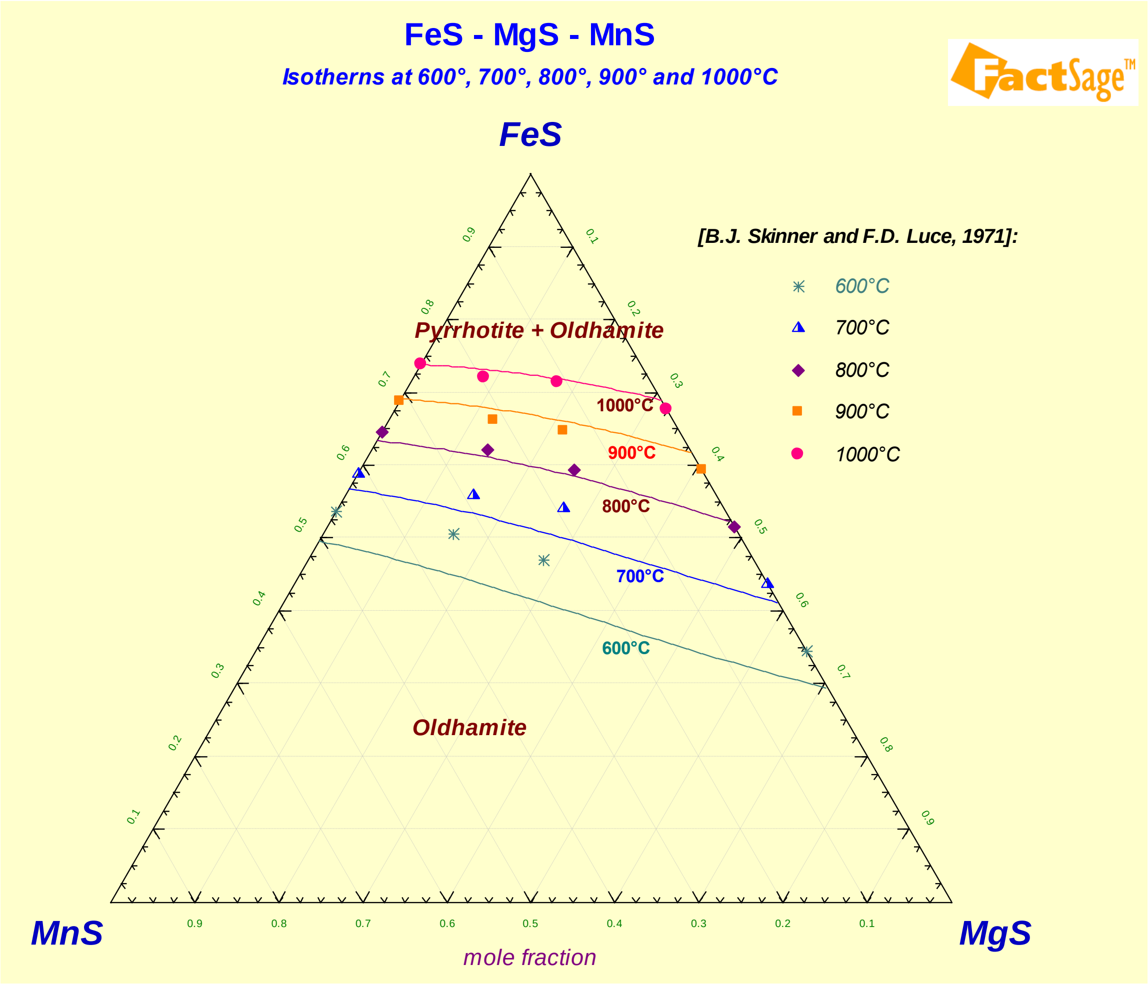
Isothermal sections in CaS-MgS-MnS





Liquidus surface in CaS-MgS-MnS (proposed)

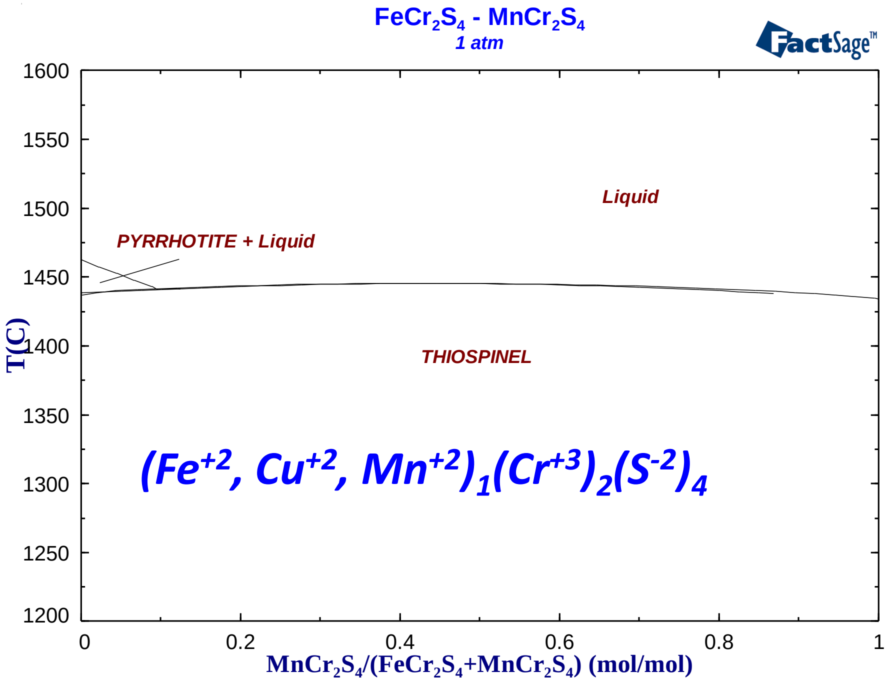
System FeS-MgS-MnS



Isothermal sections in FeS-MgS-MnS

Tiospinel in Cr-Fe-Mn-S

Sulfide	Name	Pearson Symbol	Space group	Tm, °C Exp.	Tm, °C Calc.
$FeCr_2S_4$	Daubreelite	cF56	Fd3m	1440 [Indosova82] 1350 [ElGoresy]	1437
$CuCr_2S_4$	Joegoldsteinite	cF56	Fm3m	1160 [94Sha]	1163
$MnCr_2S_4$	Cuprokalininite	cF56	Fm3m	-	1434



$(Fe^{+2}, Cu^{+2}, Mn^{+2})_1(Cr^{+3})_2(S^{-2})_4$

Sulfur spinels or thiospinels have a general formula AB_2S_4 where A is a divalent metal and B is a trivalent metal. Thiospinel in Sulfide database – solid solution phase with end-members $FeCr_2S_4$, $CuCr_2S_4$ and $MnCr_2S_4$

Conclusions

- ✓ Carbonate species have been included into the slag of the system Na_2O-K_2O-CO_2-S-SO_3. The liquid phase in all subsystems was evaluated using non-ideal associate species model (two cations per species).
- ✓ Alkali carbonates have been added to hexagonal phase with the corresponding parameters describing both solubilities in the cation and in the anion sublattices
- ✓ All systems were assessed using experimental phase diagram information.
- ✓ The mixed salt systems containing alkali carbonates, sulphides and sulphides have been calculated using the corresponding data
- ✓ The liquid phase in all subsystems Ca-Cr-Fe-Mn-Mg-S was evaluated using associate species model
- ✓ All systems (6 ternaries and 4 quasi-ternaries) were assessed using experimental phase diagram information and thermodynamic properties as far as available
- ✓ The solubility ranges of solid solution phases containing S (such as Pyrrhotite, Oldhamite, Thiospinel, Cr_3S_4) were described using the sublattice model

Outlook

- ✓ Thermodynamic assessment of further systems with CO_2
- ✓ Considering the mixed silicate-carbonate systems

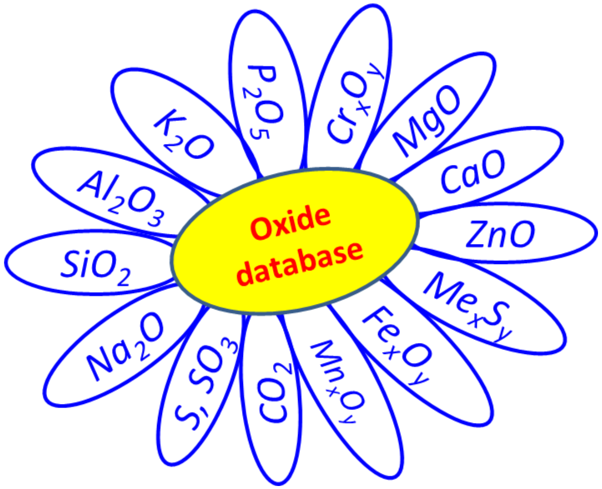
On behalf of all co-authors:

Thank you for your attention!

Vielen Dank für Ihre Aufmerksamkeit!

Благодарю за внимание!

HOTVEGAS



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