Sulfide Database: Evaluation of thermodynamic data and phase equlibria

GTT-Technologies, Herzogenrath

GTT-Workshop, 1-3. Juli 2015, Herzogenrath

K. Hack, T. Jantzen, E. Yazhenskikh, M. Müller

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- **Quasi-binary systems with Digenite**: Cu_2S-MgS and Cu_2S-MnS
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Sulphur in oxide glasses

Sulphur

Natural minerals may contain substantial quantities of sulphur.

Sulphur species are present in radioactive and toxic wastes.

Sulphide glasses can be used for high refractory index materials.

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

Introduction

The associate species containing S were added in order to describe the liquid phase containing metal sulphides.

System	Associate species
Ca-S	CaS
Cr– S	CrS
Cu-S	Cu_2S
Fe– S	FeS
Mg-S	MgS
Mn- S	MnS
Cu-Fe-S	$CuFeS_2/2$

Modelling of binary S-containing phases

System	Phase	Description	Source
Ca-S	Liquid	(Ca, CaS, S)	proposed by GTT
Cr-S	Liquid $Cr_{1.01}S$, Cr_3S_4 Cr_2S_3, Cr_5S_6,Cr_7S_8 Pyrrhotite	(Ca, CrS, S) stoichiometric stoichiometric (Va, Cr)S	modelled by GTT modelled by GTT modelled by GTT CrS(SGPS)
Cu-S	Liquid Cu_2S-I Cu_2S-II Digenite CuS	(Ca, Cu_2S, S) S (Va, Cu) S (Va, Cu) (S^{2-})(Va,Cu^{1+})(Va,Cu^{1+}) stoichiometric	modelled by GTT modelled by GTT modelled by GTT modelled by GTT SGPS
Fe-S	Liquid FeS (s1, s2) FeS_2 Pyrrhotite	(Fe, FeS, S) stoichiometric stoichiometric (Va, Fe)S	[Miettinen,Hallstedt98] < 50%S GTT > 50%S SGPS (H_f, C_p) SGPS [92Sun2]
Mg-S	Liquid	(Mg, MgS, S)	proposed by GTT
Mn-S	Liquid MnS, MnS_2	(Mn, MnS, S) stoichiometric	[Miettinen,Hallstedt98] < 50%S GTT > 50% S [Miettinen,Hallstedt98]

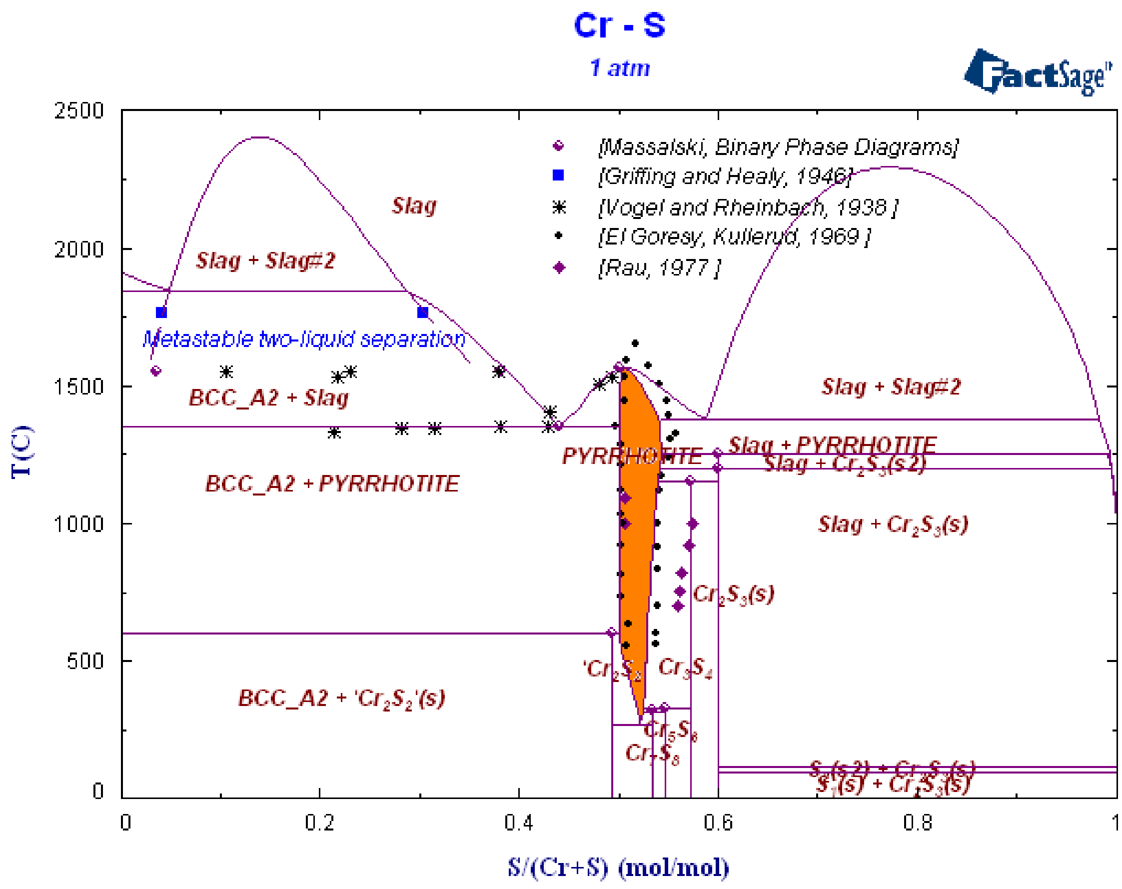
Modelling of ternary S-containing phases

System	Phase	Description	Used data
CaS - FeS	Oldhamite	(Ca, Fe)(S)	modelled by GTT
CaS - MgS	Oldhamite	(Ca, Mg)(S)	modelled by GTT
CaS - MnS	Oldhamite	(Ca, Mn)(S)	modelled by GTT
Cr-Fe-S	Cr_2FeS_4	stoichiometric	modelled by GTT
	Pyrrhotite	(Va, Cr, Fe)(S)	modelled by GTT
Cr-Mn-S	$MnCr_2S_4$	stoichiometric	modelled by GTT
	MnS	(Cr, Mn)S	modelled by GTT
Cu-Fe-S	Digenite	$(S^{2-})(Va,Cu^{1+})(Va,Cu^{1+},Fe^{2+})$	modelled by GTT
	Pyrrhotite	(Va, Fe, Cu)(S)	modelled by GTT
	$CuFeS_2$-HT	(Cu, Fe) FeS_2	modelled by GTT
	$CuFeS_2$ (s)	stoichiometric	SGPS
Cu_2S-MgS	Digenite	$(S^{2-})(Va,Cu^{1+})(Va,Cu^{1+},Mg^{2+})$	modelled by GTT
Cu_2S-MnS	Digenite	$(S^{2-})(Va,Cu^{1+})(Va,Cu^{1+},Mn^{2+})$	modelled by GTT
FeS-MgS	Pyrrhotite	(Va, Fe, Mg)(S)	modelled by GTT
	Oldhamite	(Fe, Mg)(S)	modelled by GTT
FeS-MnS	Oldhamite	(Fe, Mn)(S)	modelled by GTT
	Pyrrhotite	(Va, Fe, Mn)(S)	modelled by GTT

Modelling of S-containing phases

Phase	Description
Pyrrhotite	(<u>Cr,</u> <u>Fe</u>, Cu, Mg, Mn, Va) S
Cu_2S-I	(<u>Cu</u>, Va)$_2$ S
Cu_2S-II	(<u>Cu</u>,Va)$_2$ S
Digenite	(<u>Cu</u>$^{1+}$,Va) (<u>Cu</u>$^{1+}$,Fe^{2+},Mg^{2+},Mn^{2+}, Va) (S^{2-})
Oldhamite	(<u>Ca</u>, <u>Mg,</u> <u>Mn,</u> Fe)(S)
$CuFeS_2$-HT	(<u>Cu</u>, Fe) Fe(S)$_2$
MnS	(Cr, <u>Mn</u>) S

Binary Cr-S phase diagram



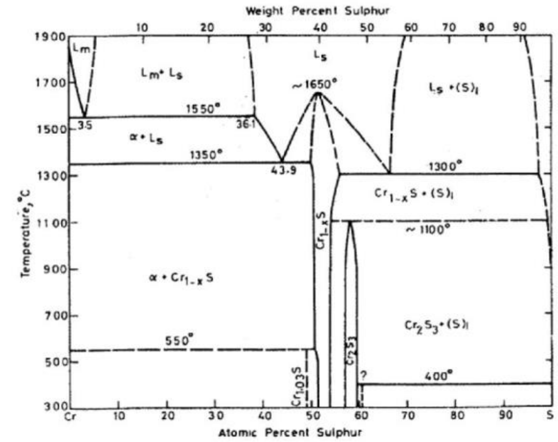
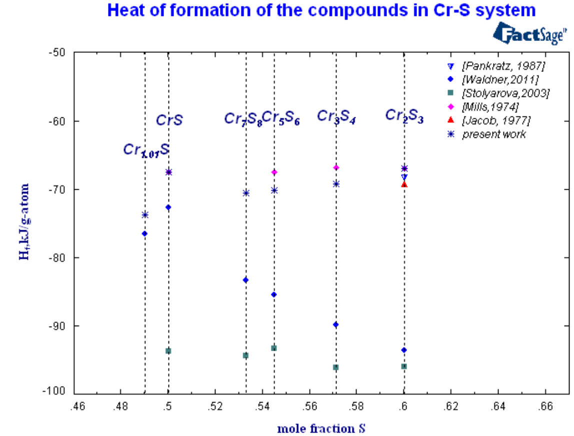
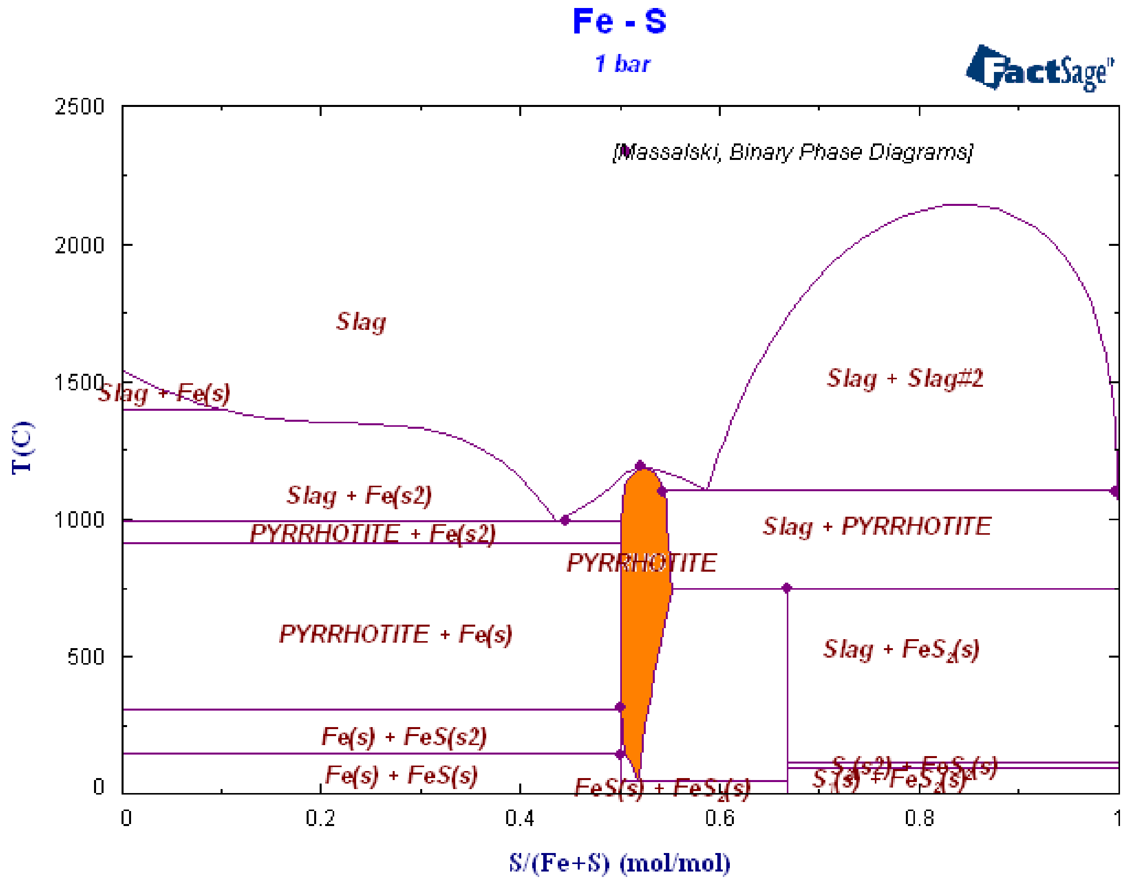


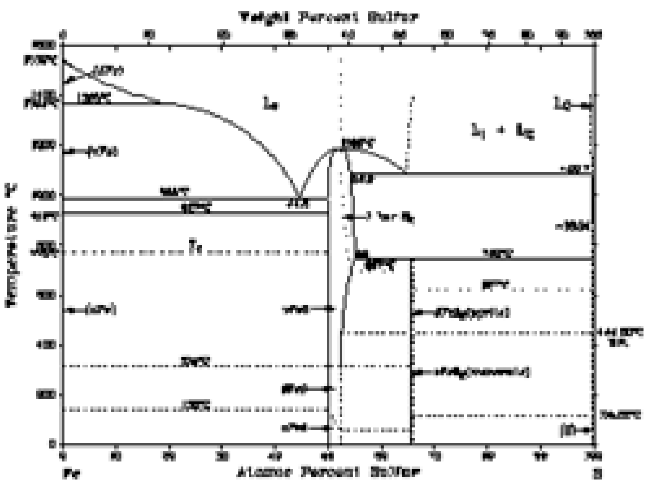
Fig 2.7 : Cr-S Phase Diagram (El Goresy and Kullerud,1969)

Heat of formation of the compounds in Cr-S system



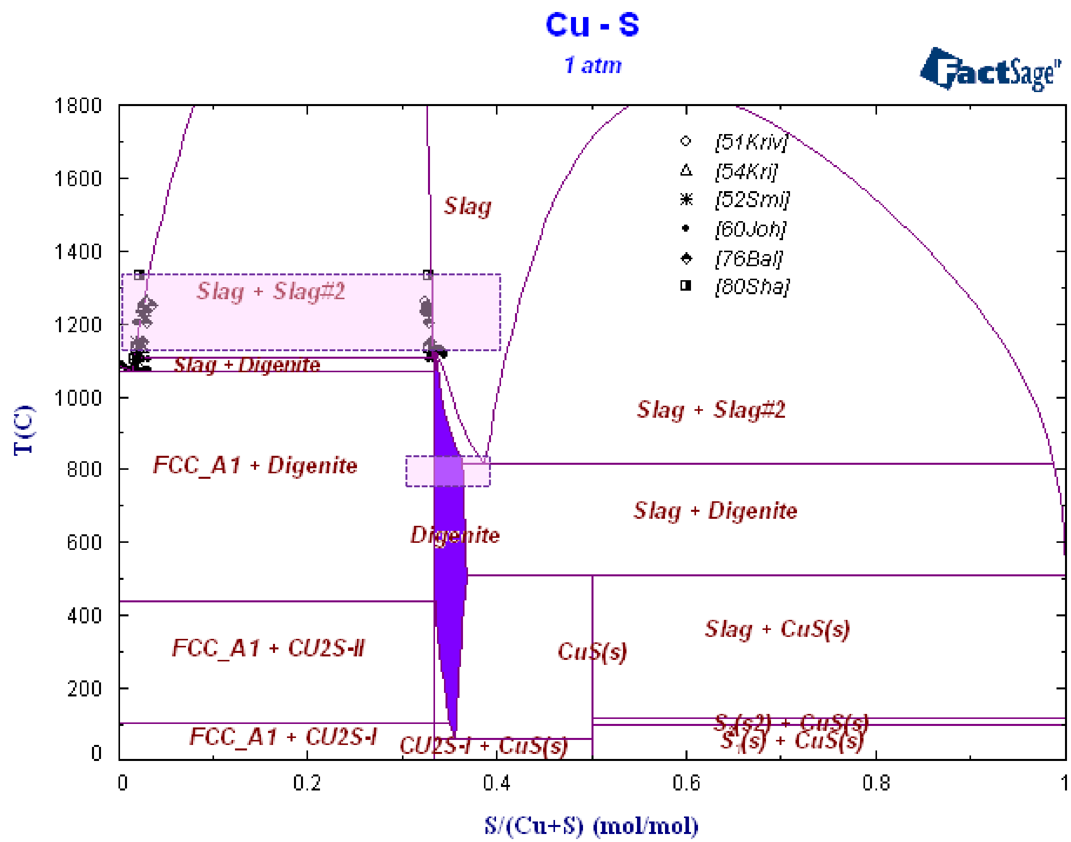
Binary Fe-S phase diagram

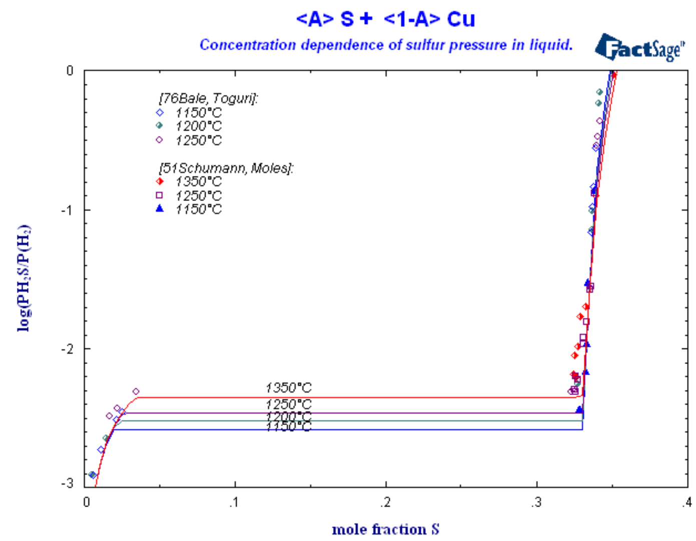


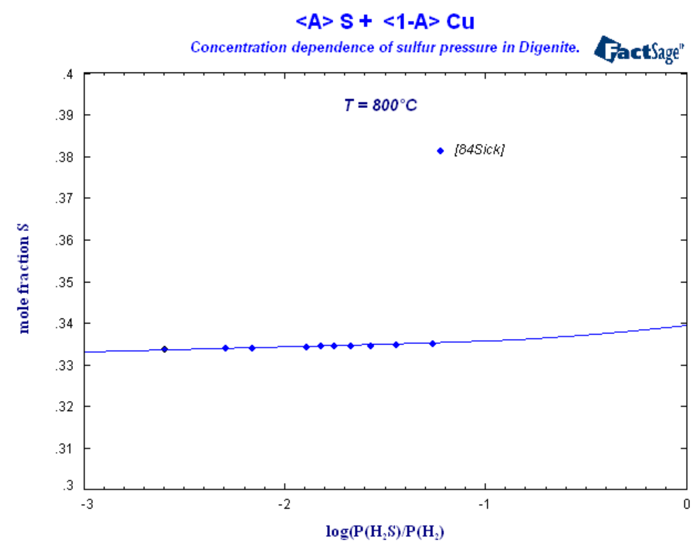


T.B. Massalski, Binary Alloy Phase Diagrams., ASM, 1990.

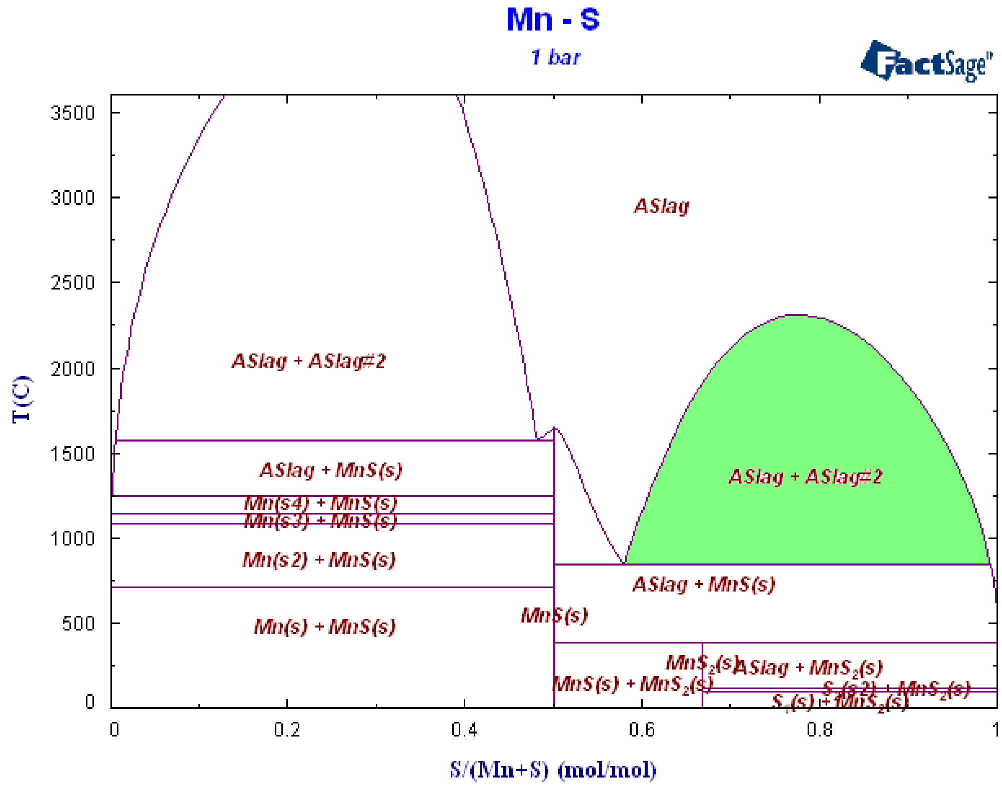
Binary Cu-S phase diagram

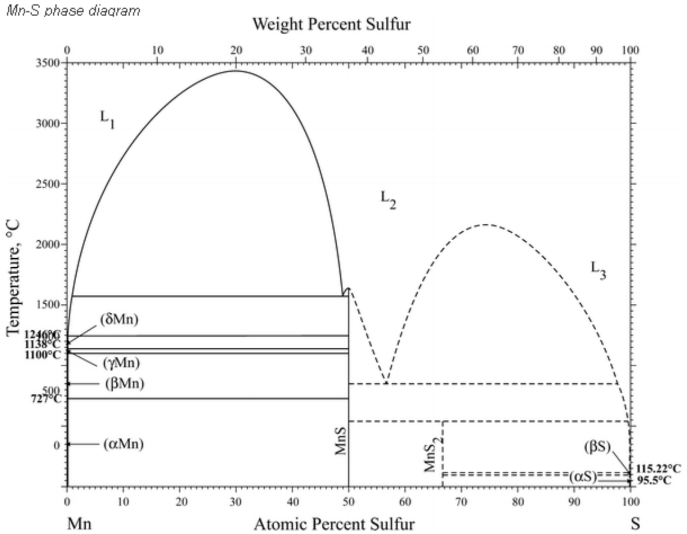






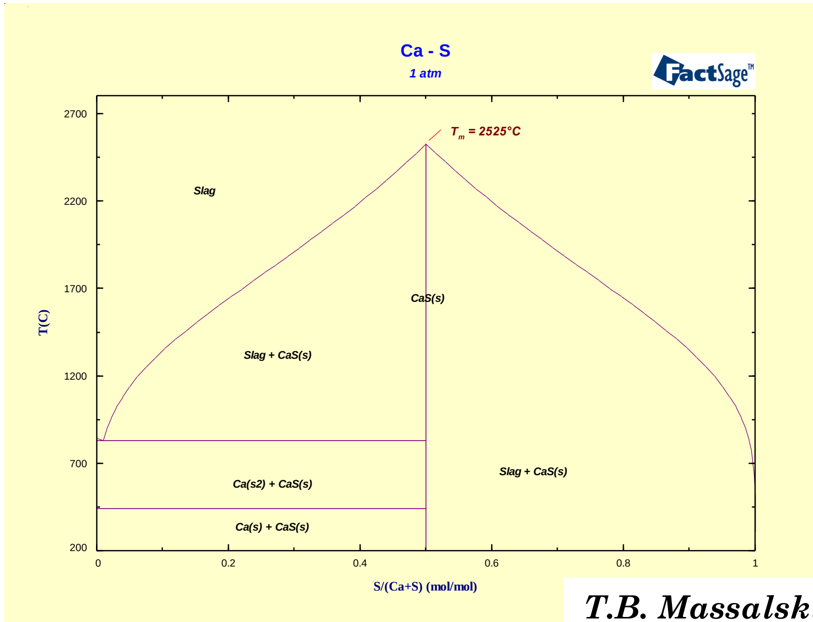
Binary Mn-S phase diagram

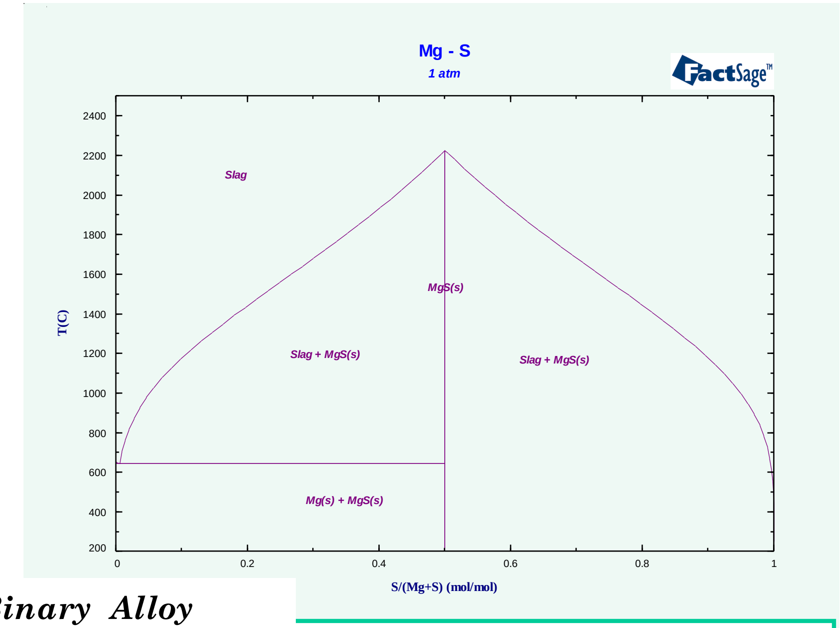




H. Okamoto, J. Phas. Equil. Diff., Vol. 32, 1 (2011), p.78.

Binary Ca-S and Mg-S phase diagrams





T.B. Massalski, Binary Alloy Phase Diagrams., ASM, 1990 .

Ca-S (Calcium-Sulfur)

Editor

No phase diagram is available for the Ca-S system. The crystal structure of CaS is the NaCl type [22Kus]. The melting point of CaS is 2525 °C [58Juz]. Polysulfides (*e.g.*, CaS_2, CaS_4, CaS_5, *etc.*, quoted in [86Vol] from literature of the early 19th century) could not be obtained thermally from elements [31Rob]. -H.O.

22Kus: H. Kuster, *Z. Phys.*, *23*, 257-262 (1922).
31Rob: P.L. Robinson and W.E. Scott, *J. Chem. Soc.*, *134*, 693-709 (1931).
58Juz: R. Juza and K. Bunzen, *Z. Phys. Chem. (Frankfurt)*, *17*, 82-99 (1958).
86Vol: A.E. Vol and I.K. Kagan, *Handbook of Binary Metallic Systems*, Vol. 4, N.V. Ageev, Ed., Amerind Publishing Co. Pvt. Ltd., New Delhi, 762-765 (1986).

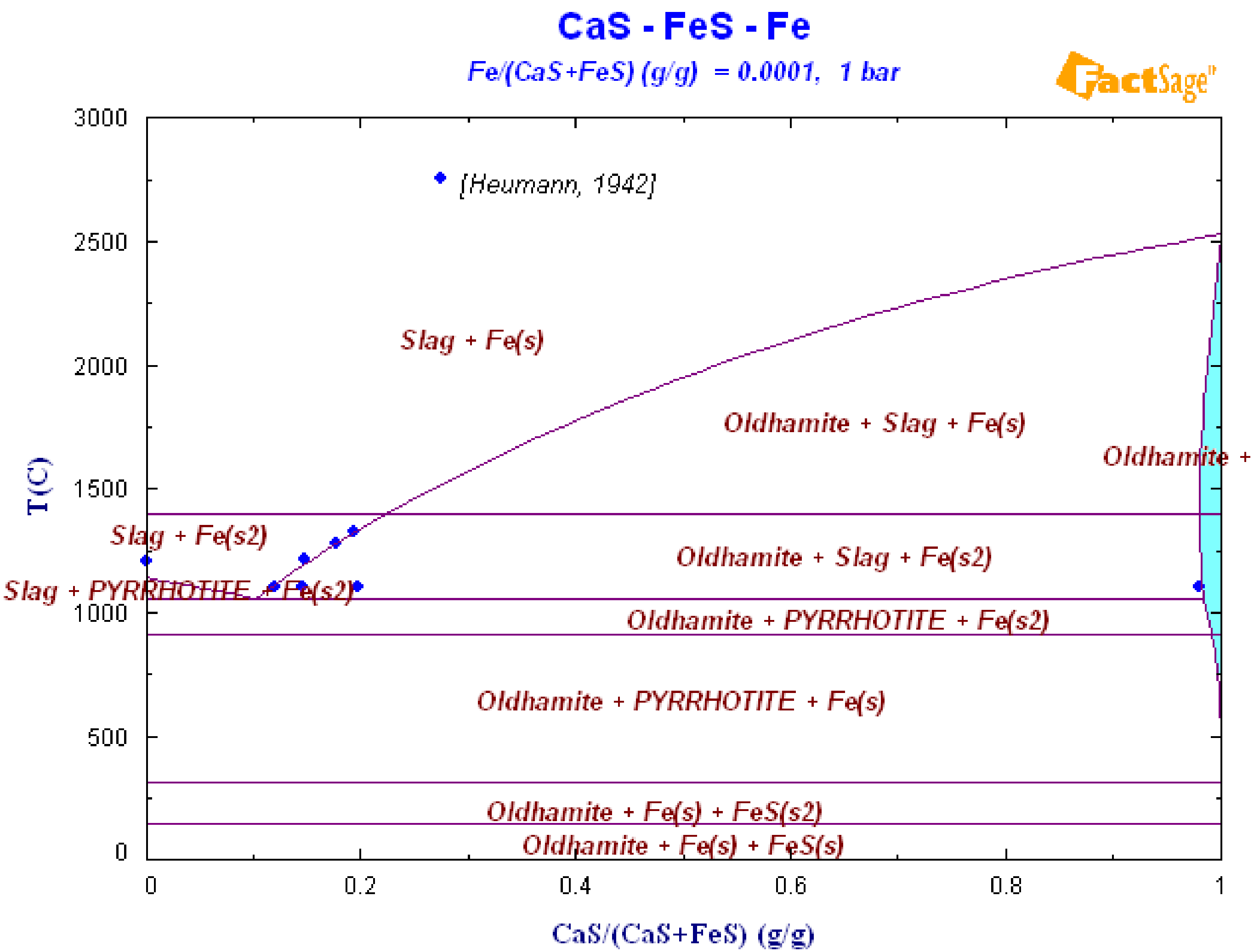
Mg-S (Magnesium-Sulfur)

A.A. Nayeb-Hashemi and J.B. Clark

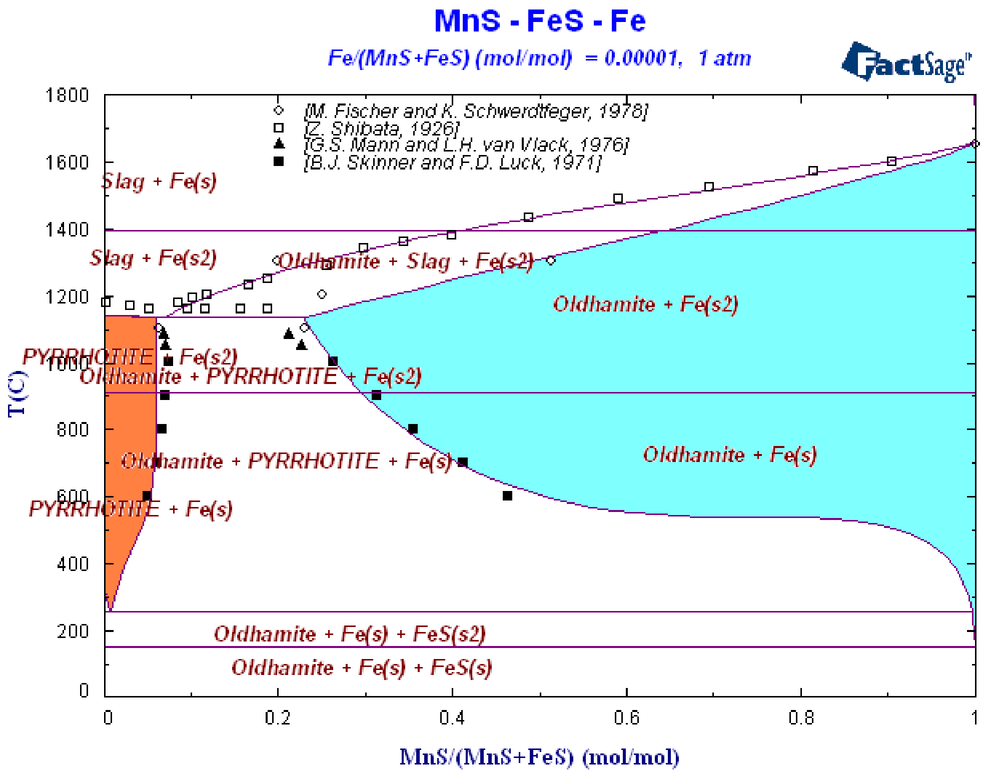
An assessed phase diagram for the Mg-S system has not been determined. The crystal structure of the only sulfide in this system, MgS, of the cubic, NaCl-type, was determined first by [23Hol]. [64Ber] also reported a hexagonal structure with lattice parameters *a* and *c* as 0.395 and 0.641 nm, respectively. The existence of magnesium sulfide with a hexagonal structure needs to be confirmed.

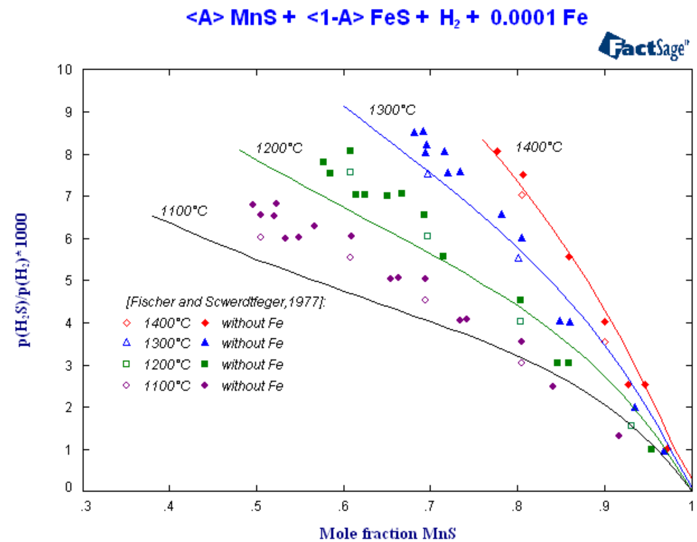
23Hol: S. Holgersson, *Z. Anorg. Chem.*, *126*, 179-182 (1923) in German.
27Bro: E. Broch, *Z. Phys. Chem.*, *127*, 446-454 (1927) in German.
27Hol: S. Holgersson, *Lunds Univ. Arsskr. 23*(9 and 17), (1927); quoted in [Hansen].
48Pri: W. Primak, H. Kaufmann, and R. Ward, *J. Am. Chem. Soc.*, *70*, 2043-2046 (1948).
56Gun: O.J. Guntert and A. Faessler, *Z. Kristallogr.*, *107*, 357-361 (1956) in German.
64Ber: G. Berthold, *Z. Phys.*, *181*, 333-343 (1964) in German.

CaS-FeS phase diagram

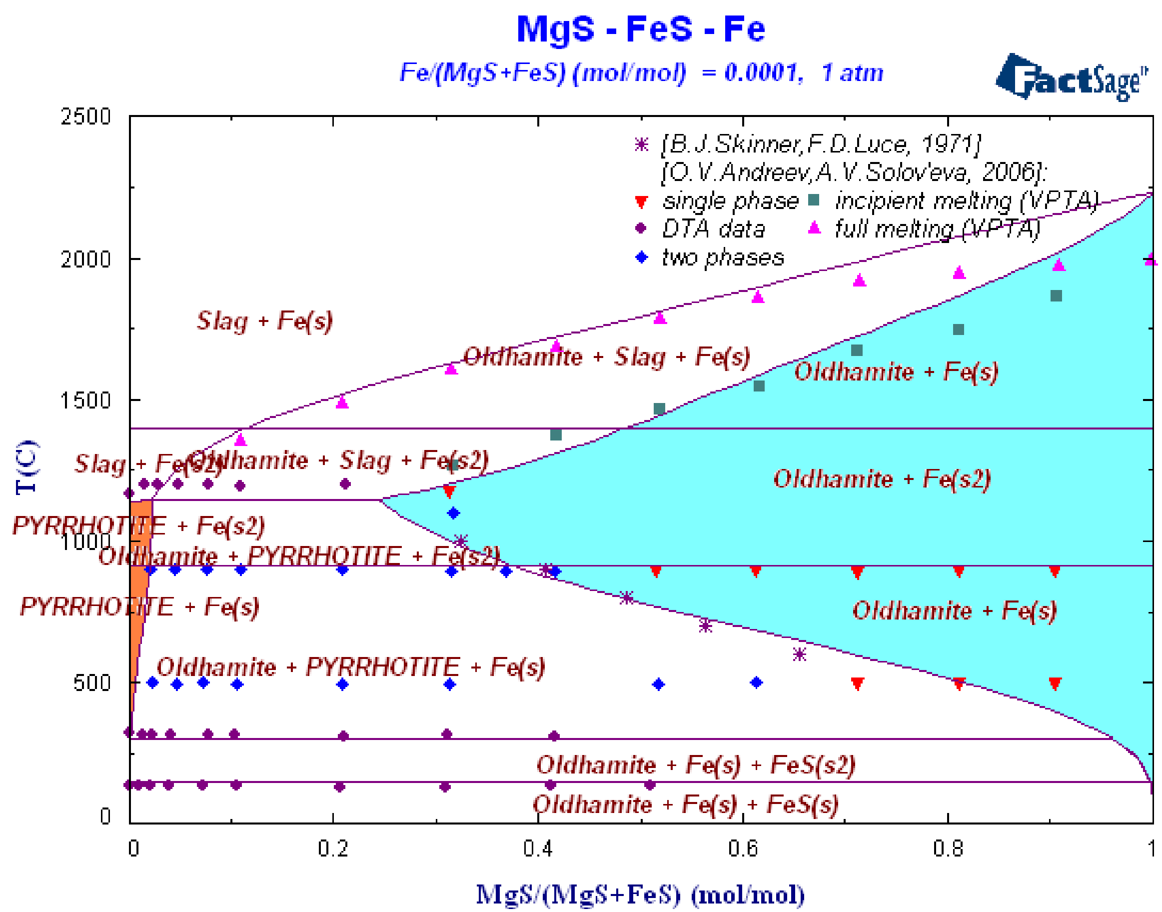


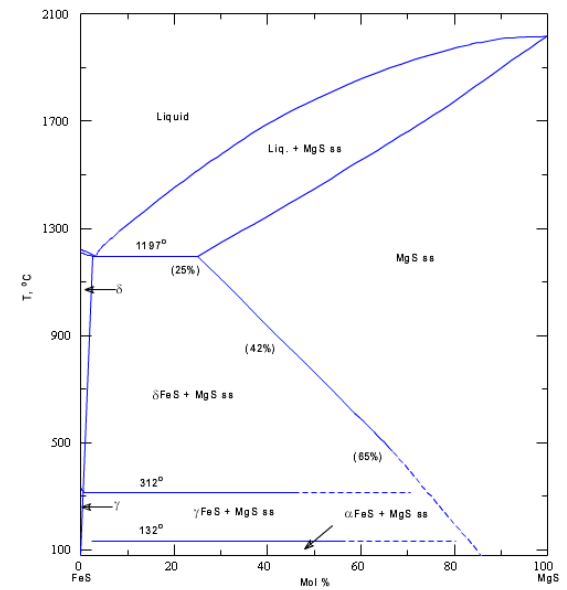
FeS-MnS phase diagram





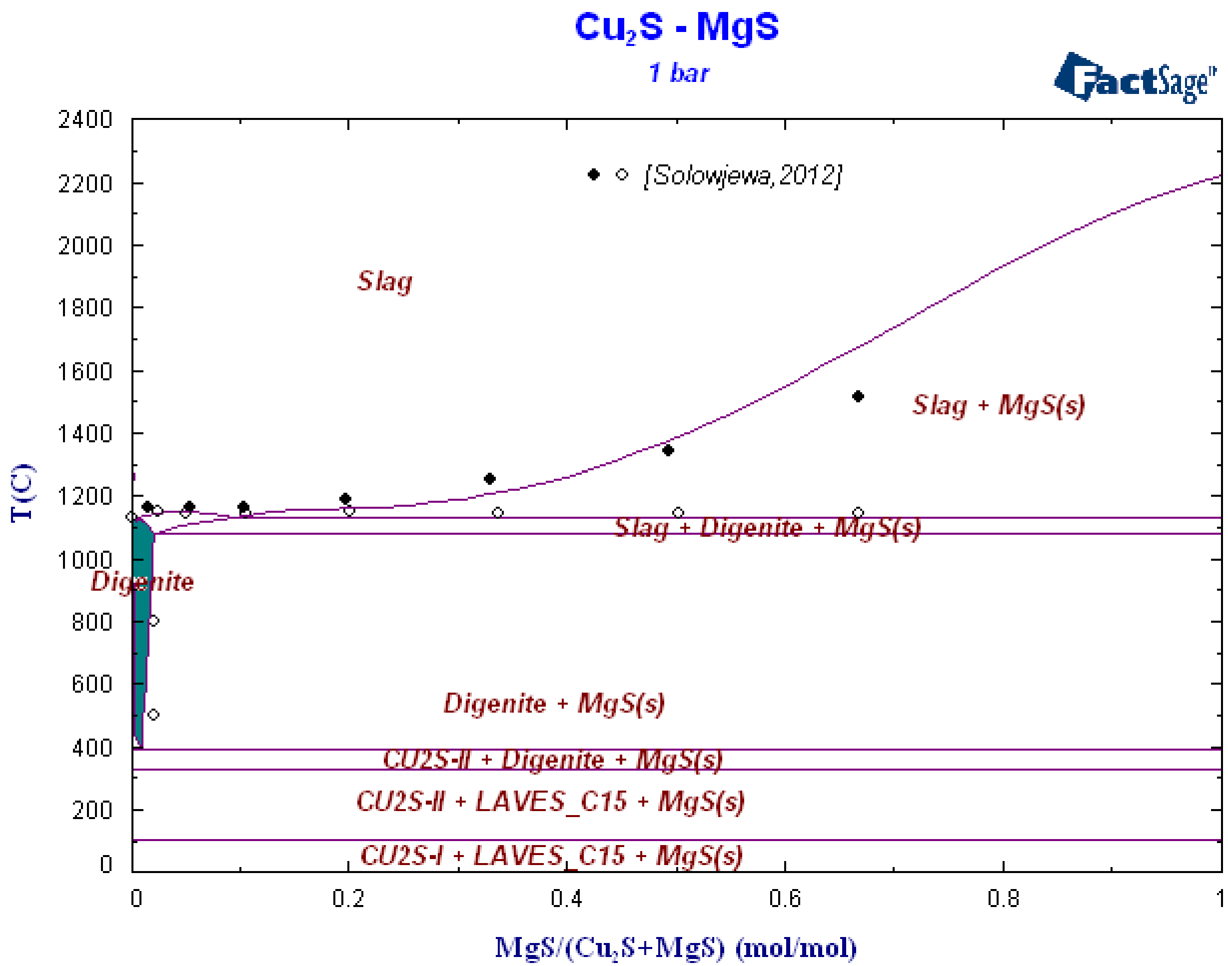
FeS-MgS phase diagram



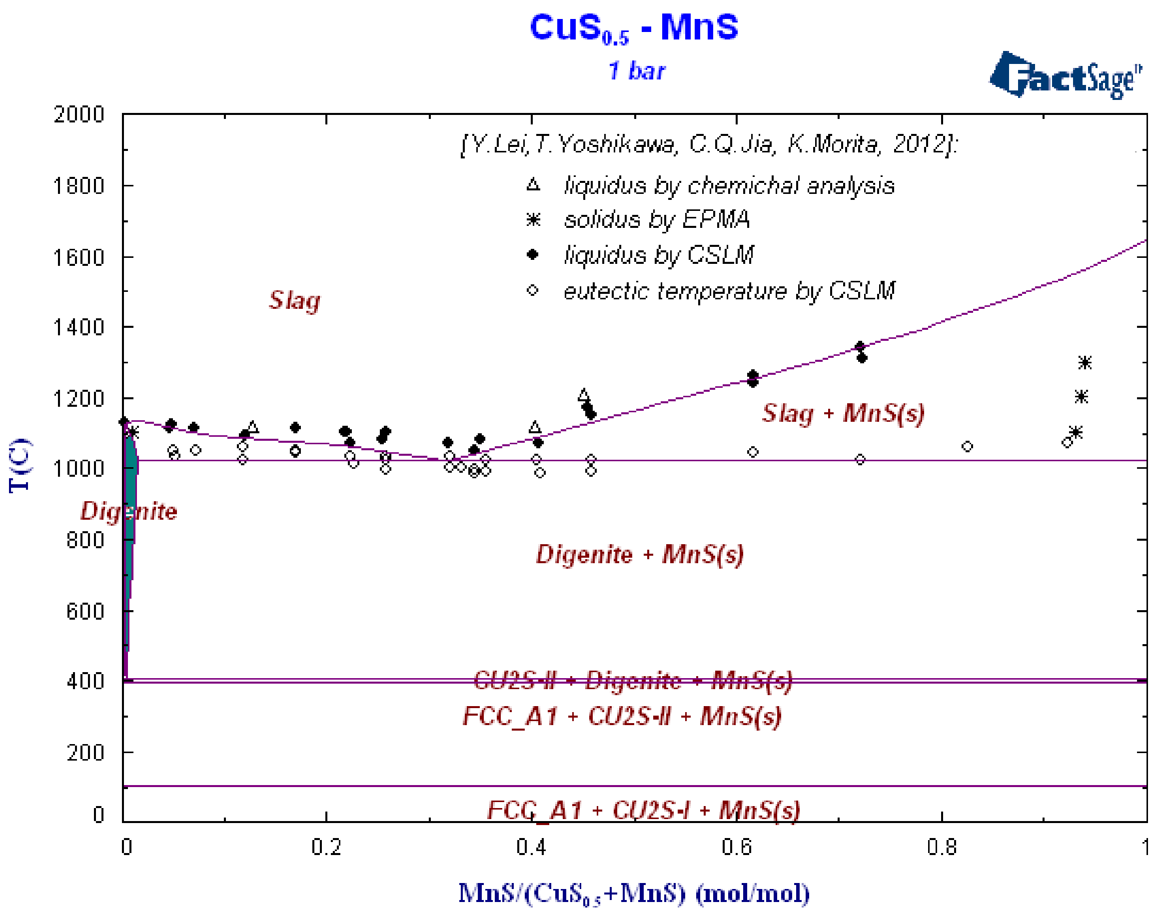


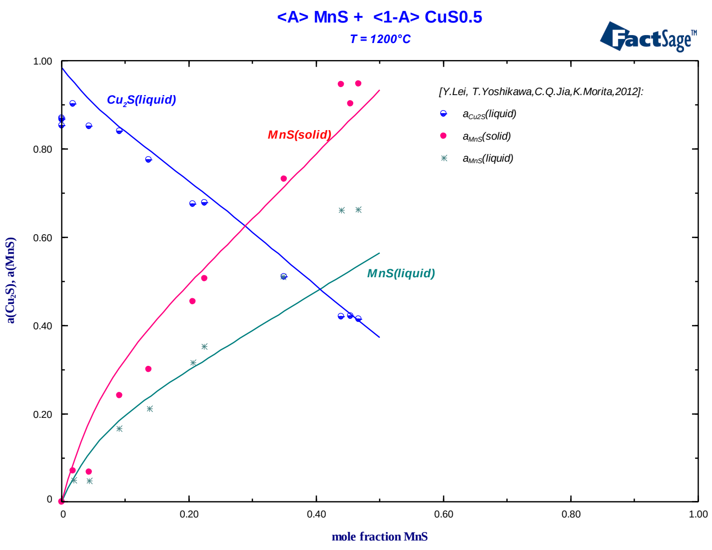
O. V. Andreev, A. V. Solov'eva, and T. M. Burkhanova, Zh. Neorg. Khim., 51 [11] 1938-1941 (2006); Russ. J. Inorg. Chem. (Engl. Transl.), 51 [11] 1826-1828 (2006).

Cu_2S-MgS phase diagram

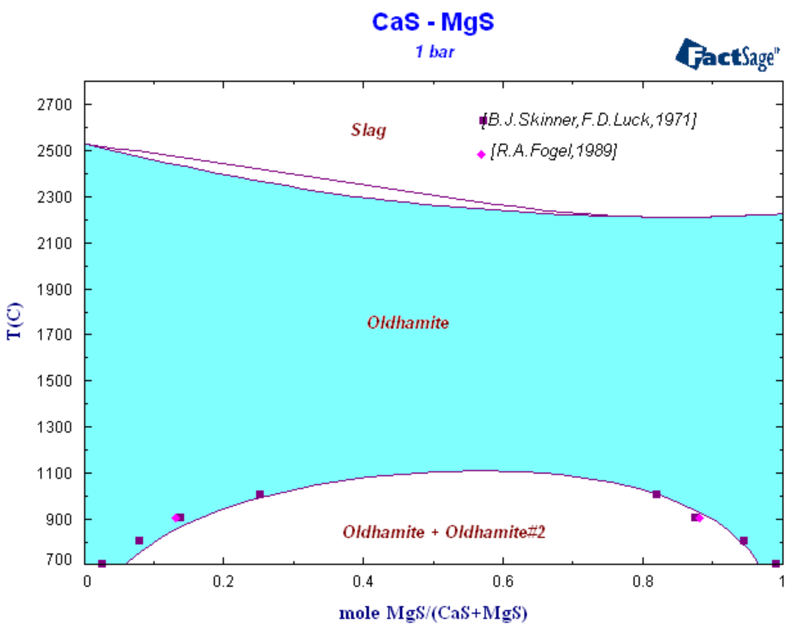


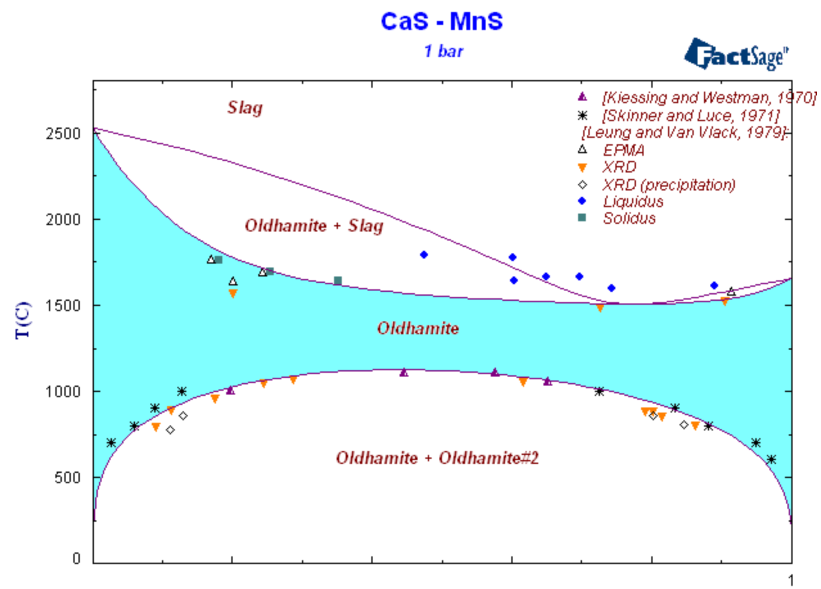
Cu_2S-MnS phase diagram





Quasi-binaries with Oldhamite





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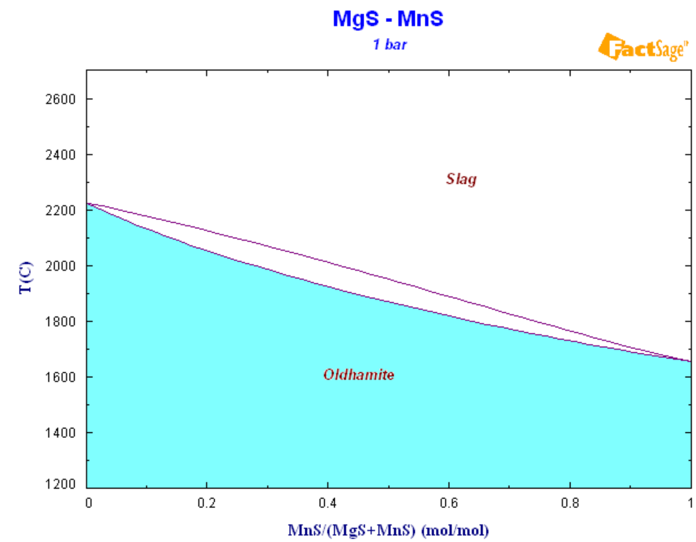

Sulfide	Pearson Symbol	Space group	Struktur-bericht	Prototype
CaS	cF8	$Fm\bar{3}m$	B1	NaCl
MgS	cF8	$Fm\bar{3}m$	B1	NaCl
MnS	cF8	$Fm\bar{3}m$	B1	NaCl

Isothermal sections at 700° C and 950° C in Cr-Fe-S

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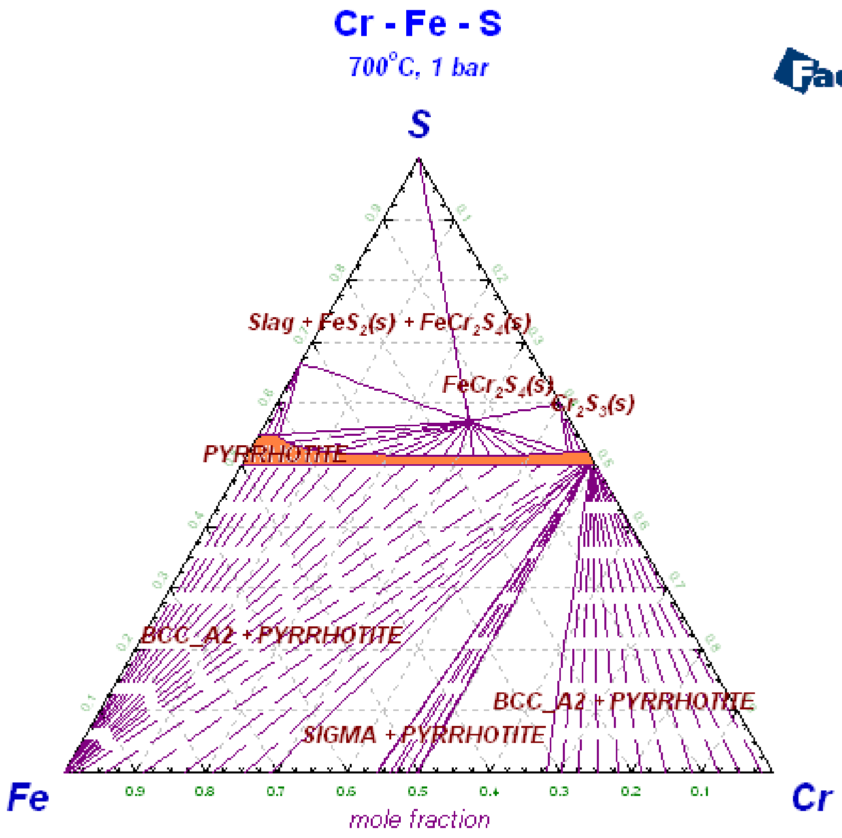

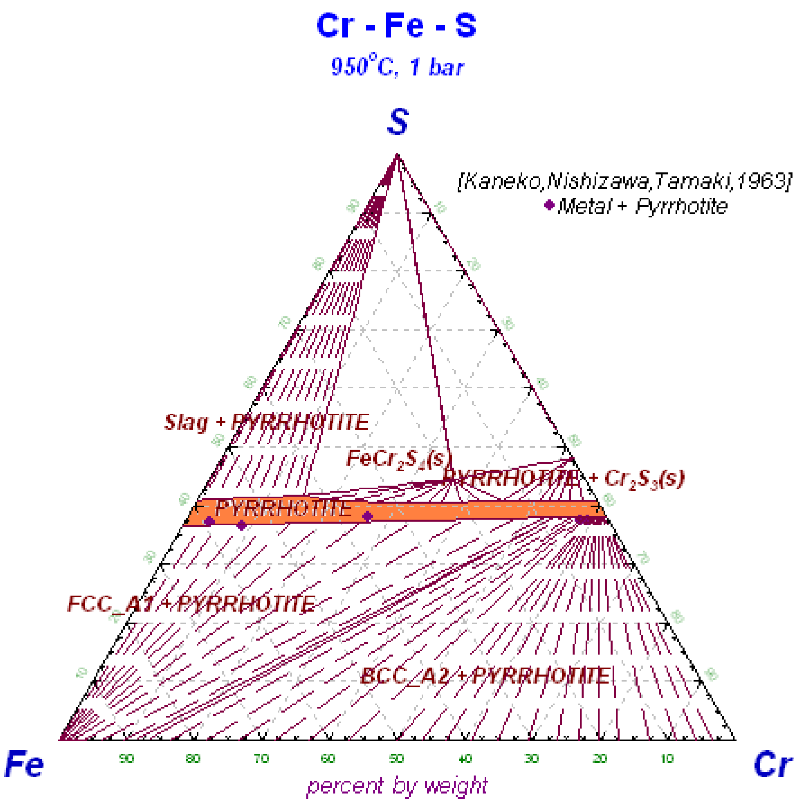

Isothermal sections at 1090° C and 1300° C in Cr-Fe-S

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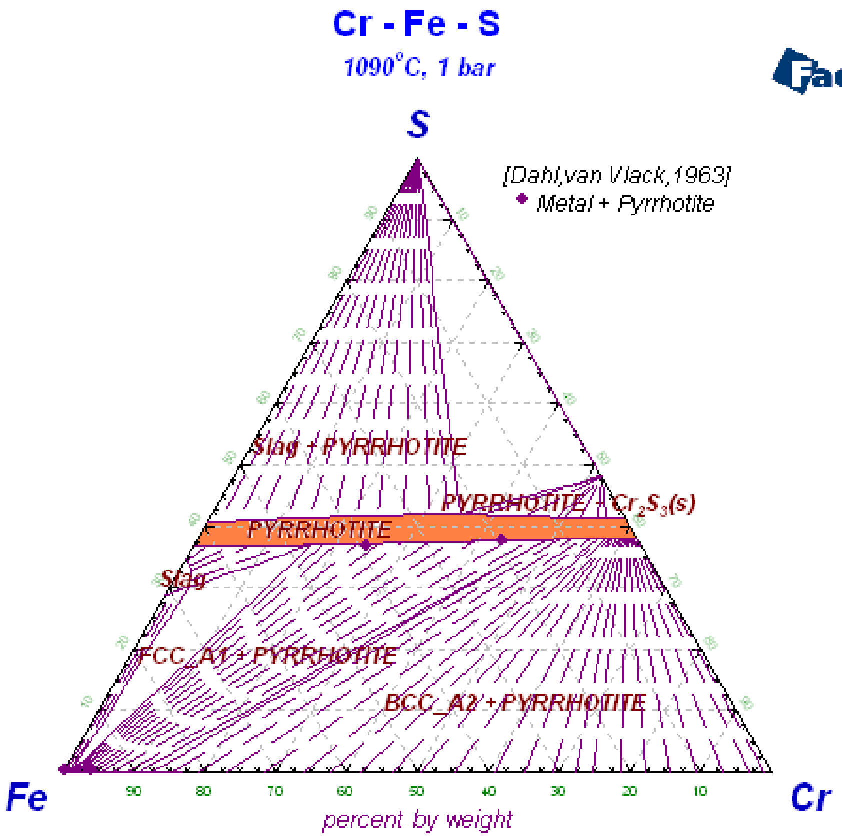
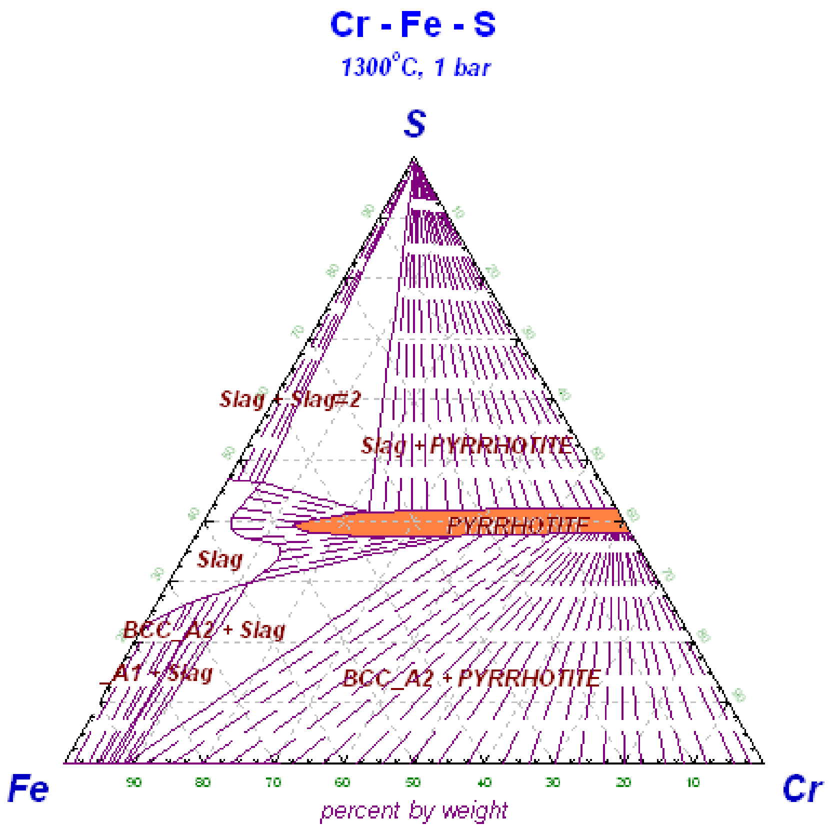
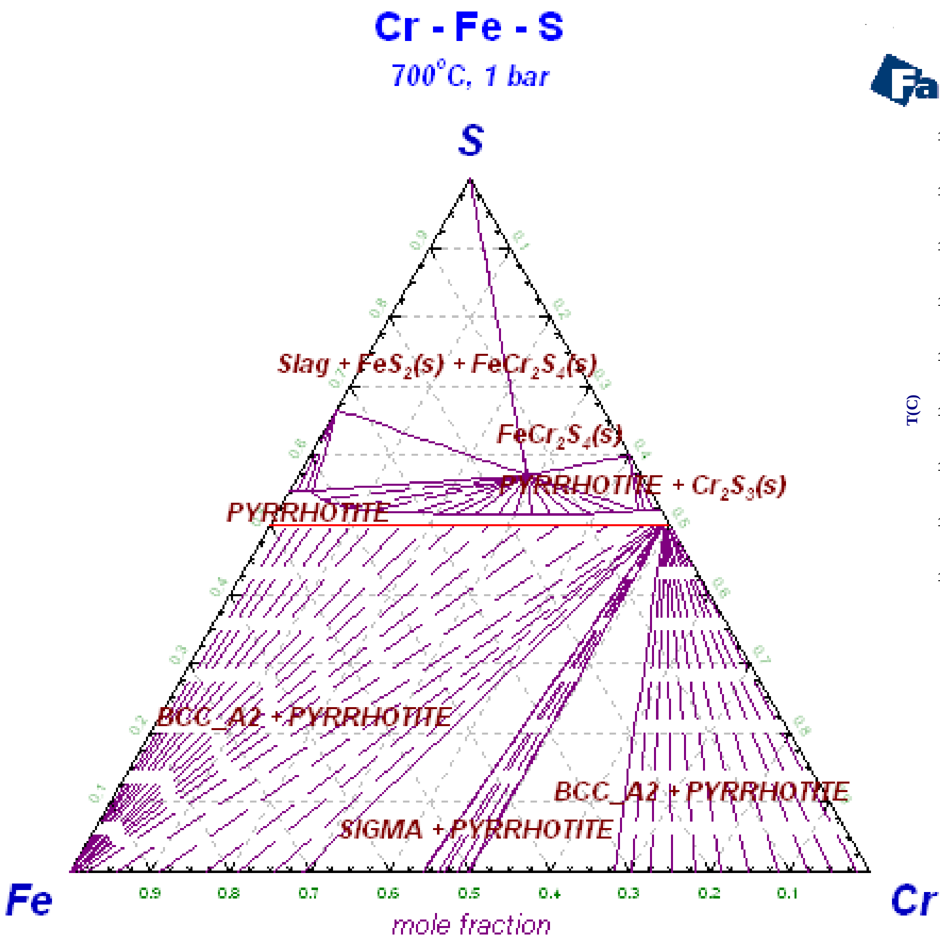
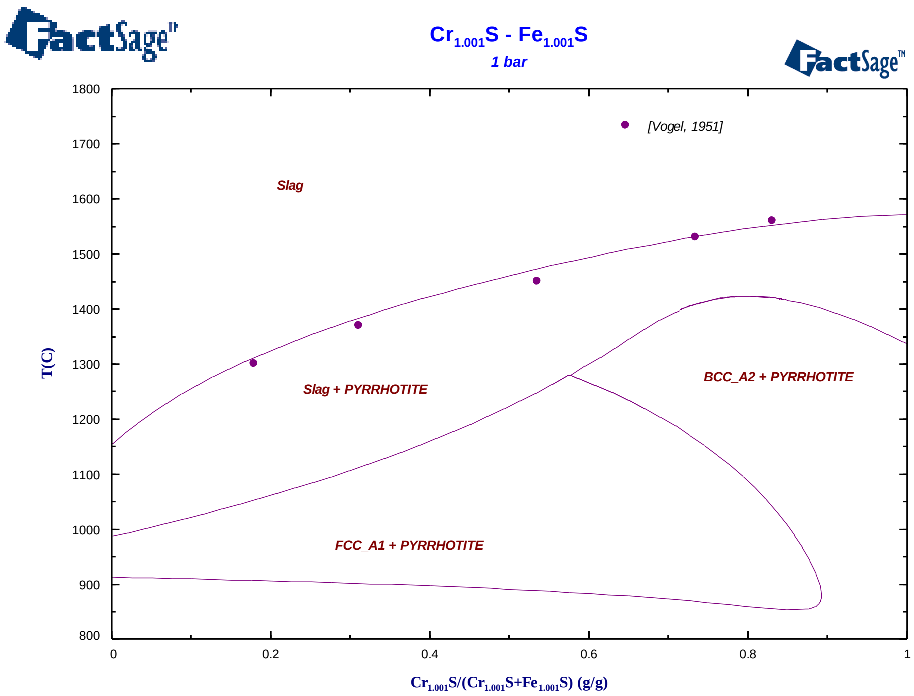




Isopleth section at ~50 mol % S in Cr-Fe-S





Isopleth section $FeCr_2S_4$-Cr_2S_3 in Cr-Fe-S

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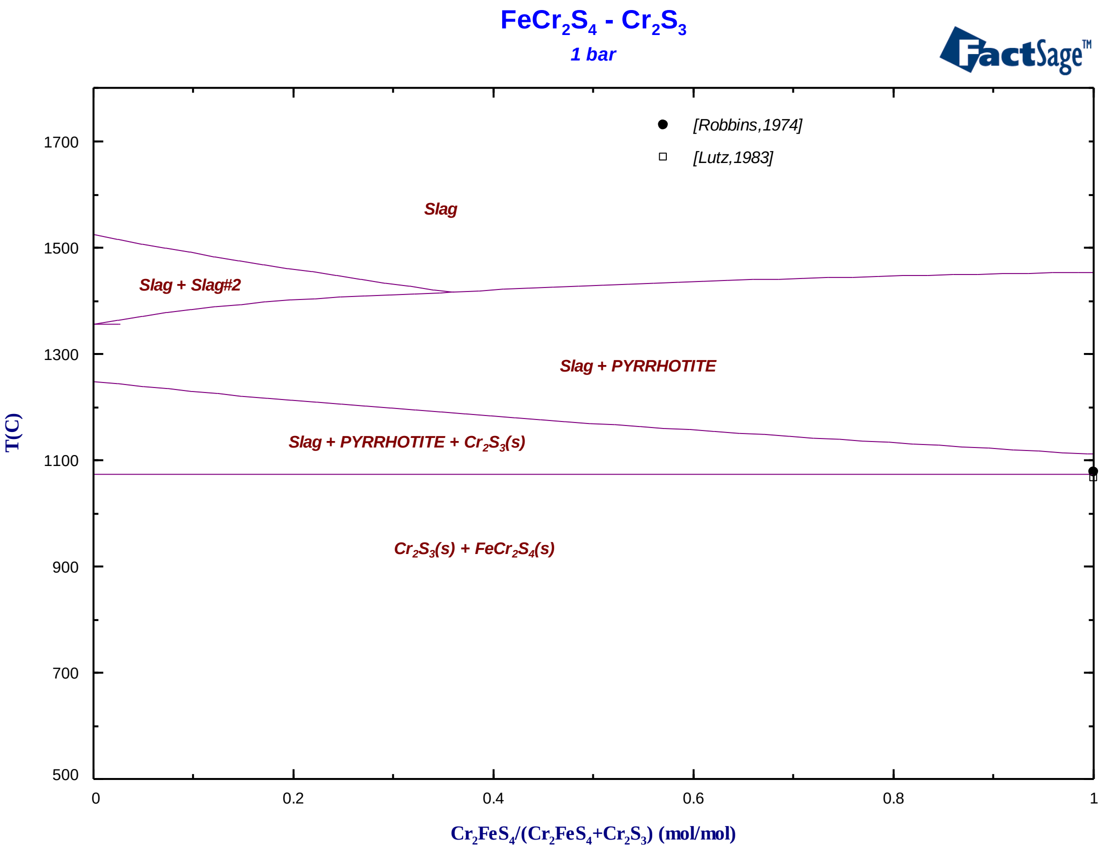
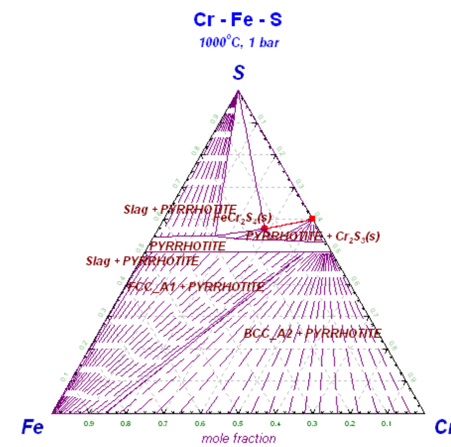
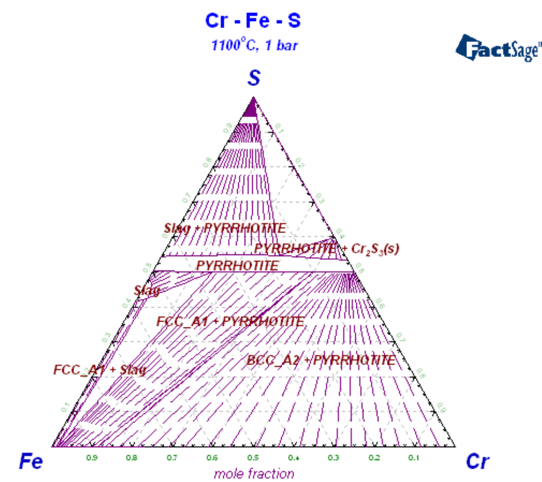
$FeCr_2S_4$ Daubreelite	H_f, kJ/Mol	S_f, J/mol K	T_m, ° C
Experimental	-457.31 [Kessler76] -566.8 [Petaev82]	207.1 [Petaev82]	1077 [Robbins74] 1067 [Lutz 83]
Calculated	-514.14	164.88	1073







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

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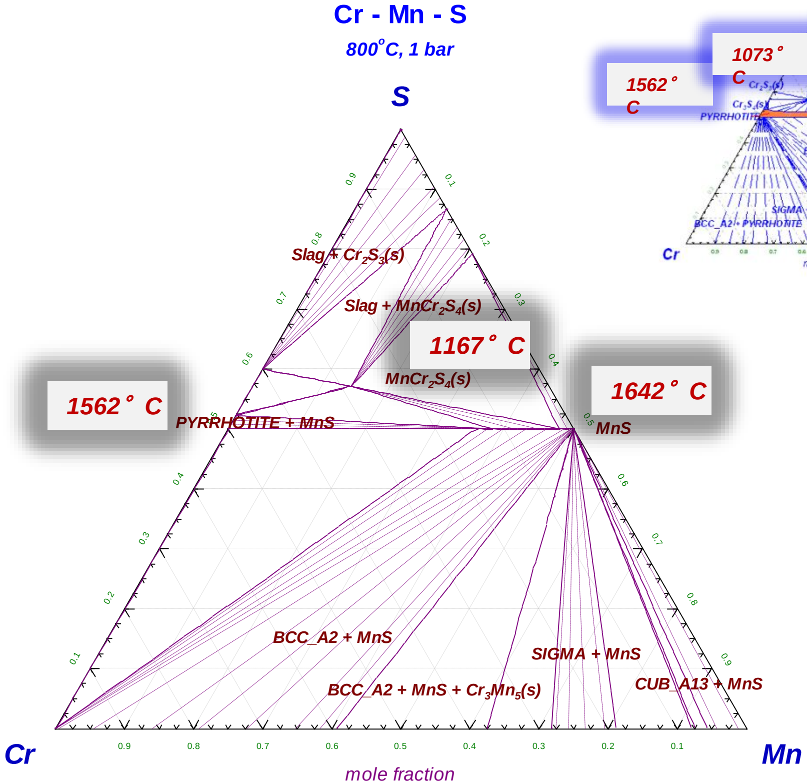
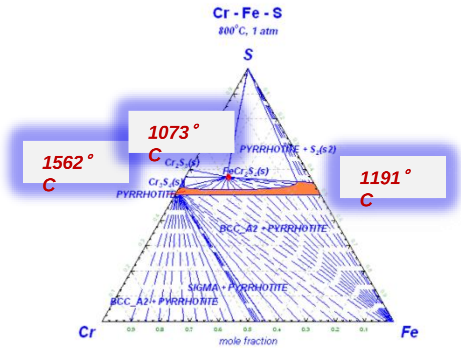




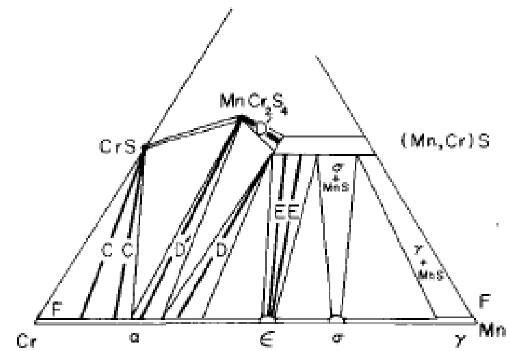
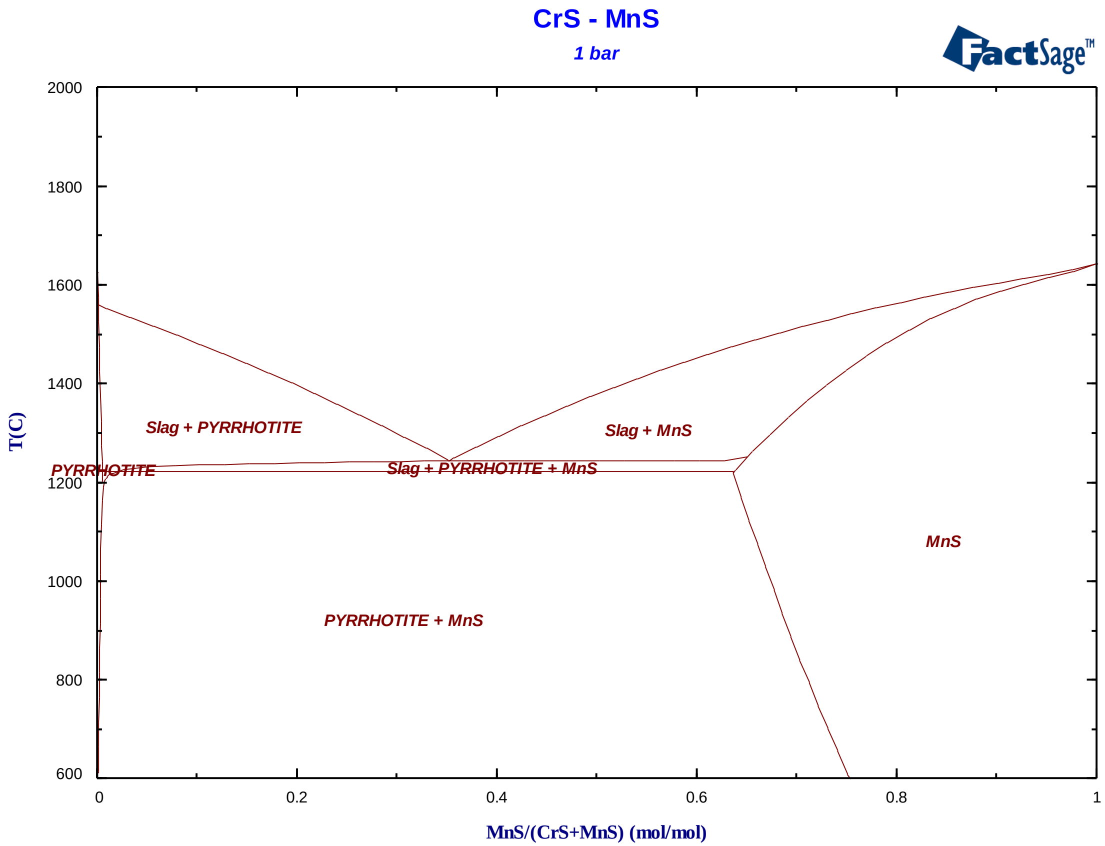


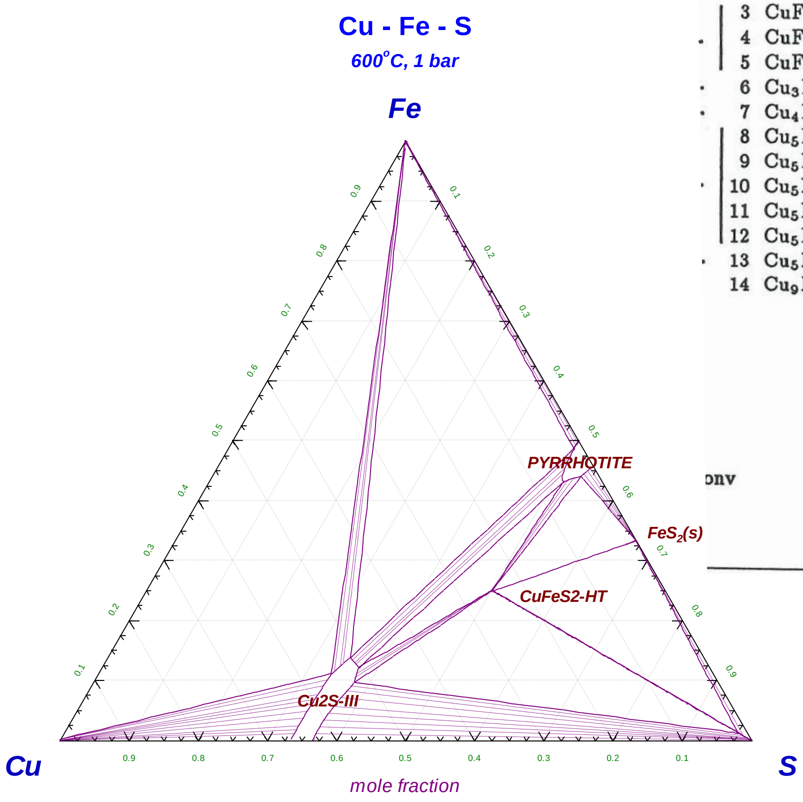
Fig. 8—Schematic representation of portion of Cr-Mn-S phase diagram at 800°C. Postulated tie lines for local equilibrium compositions of phases in contact during reaction are indicated, together with a continuity diagram. Dashed arrows show possible presence of $MnCr_2S_4$ in products.

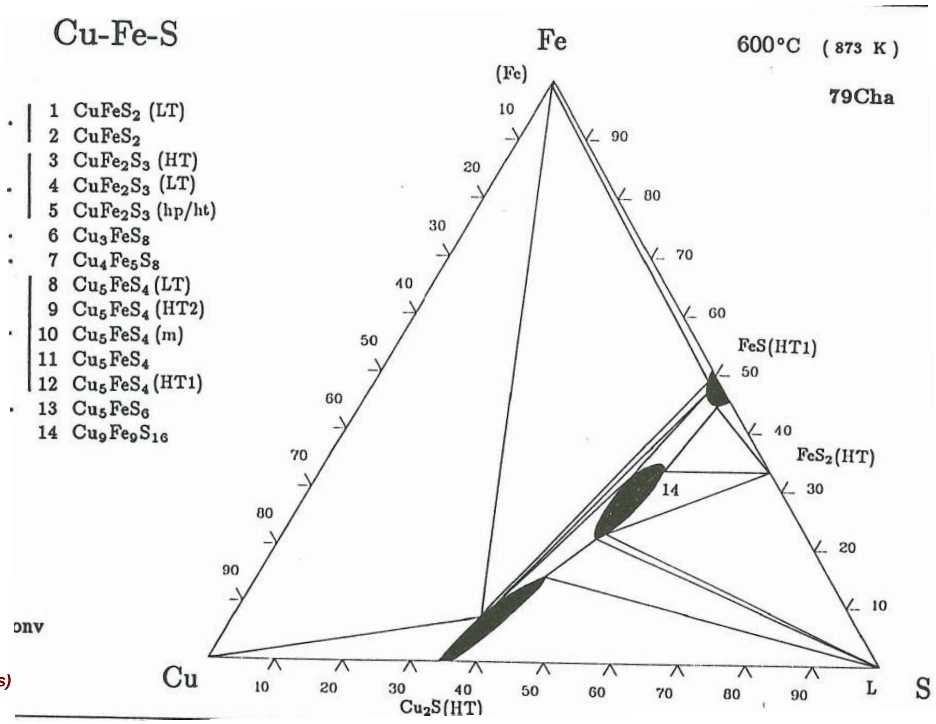
Shatynski, S.R.; Hirth, J.P.; Rapp, R.A., Metall. Trans. A, 10A (5), 591-598 (1979) (16).

Isopleth section CrS-MnS



Isothermal section at 600° C in Cu-Fe-S





Y.A. Chang, J.P. Neumann, U.V. Choudary, INCRA, Internat. Copper Research Assoc., Monograph VII, 1979, pp. 58-88.

Isothermal section at 800° C in Cu-Fe-S

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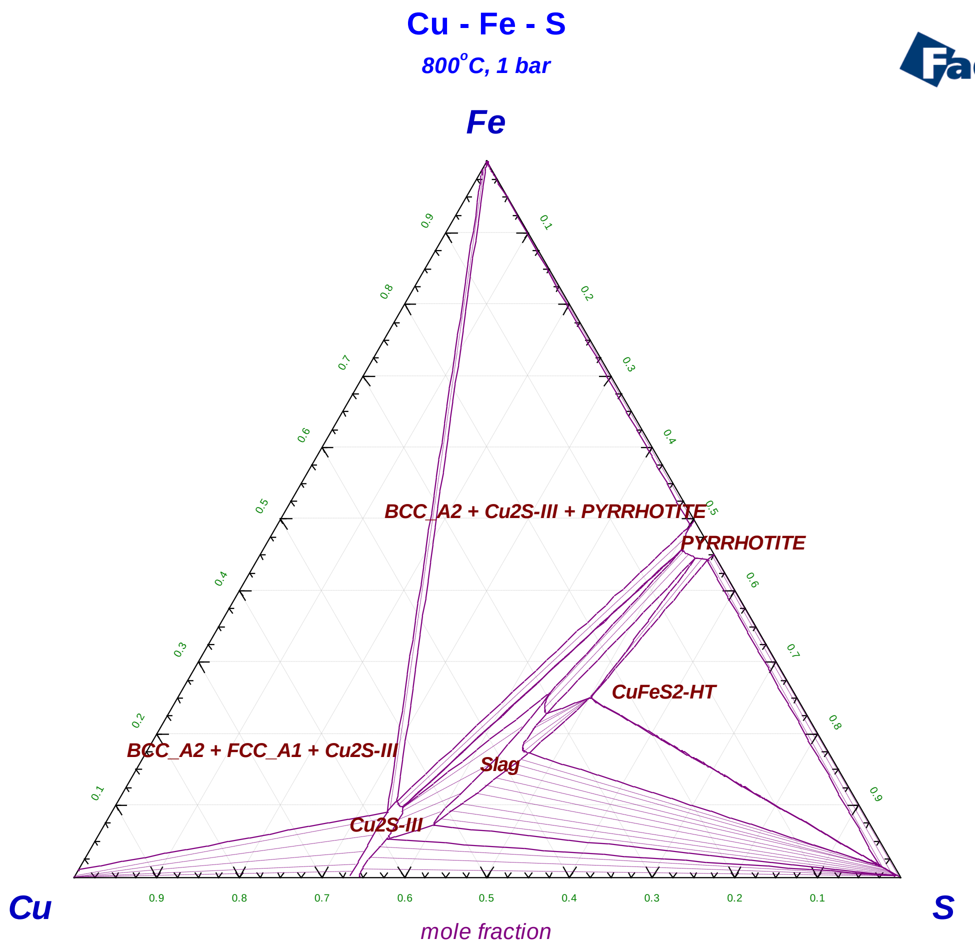
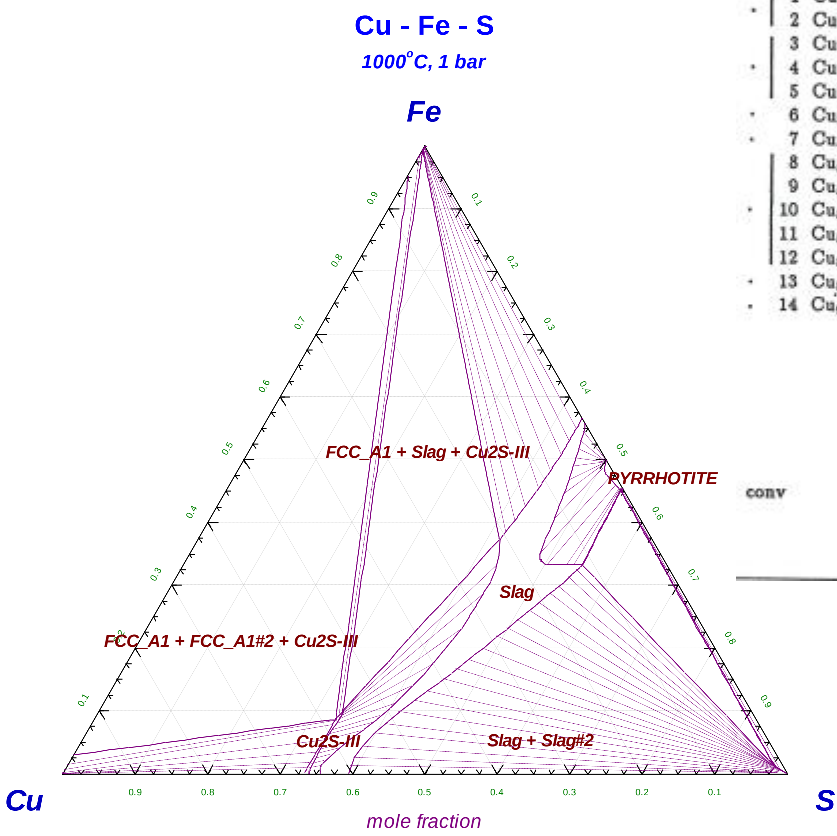
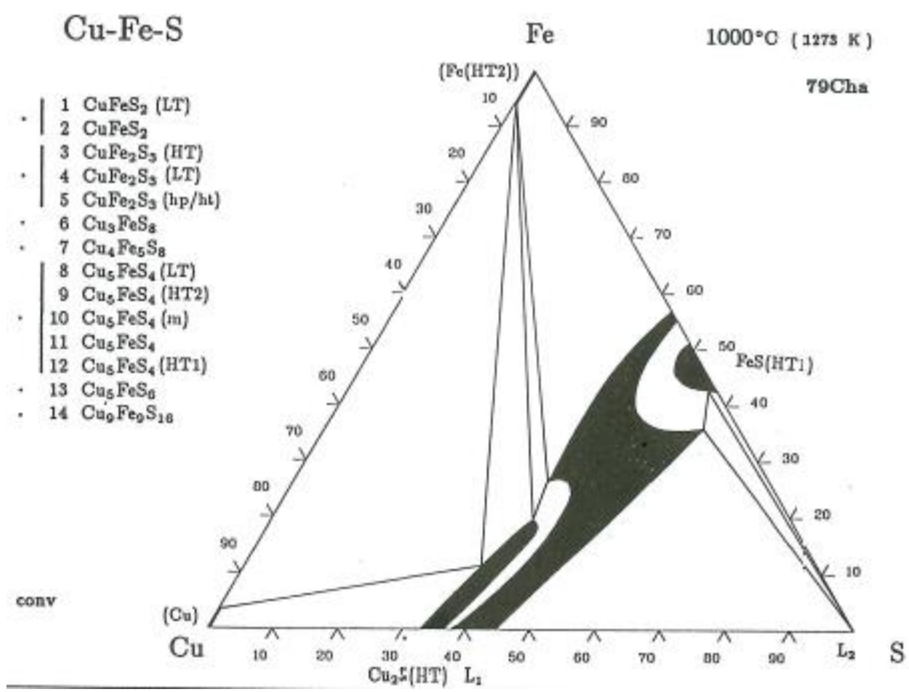


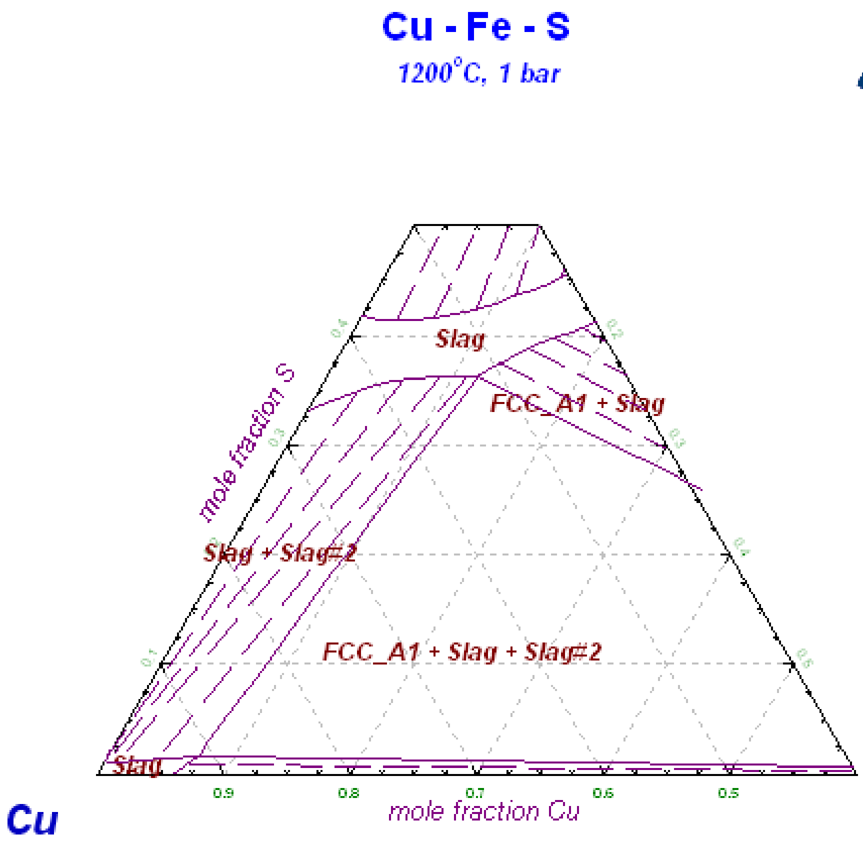
Isothermal section at 1000° C in Cu-Fe-S





Y.A. Chang, J.P. Neumann, U.V. Choudary, INCRA, Internat. Copper Research Assoc., Monograph VII, 1979, pp. 58-88.

Isothermal section at 1200° C in Cu-Fe-S



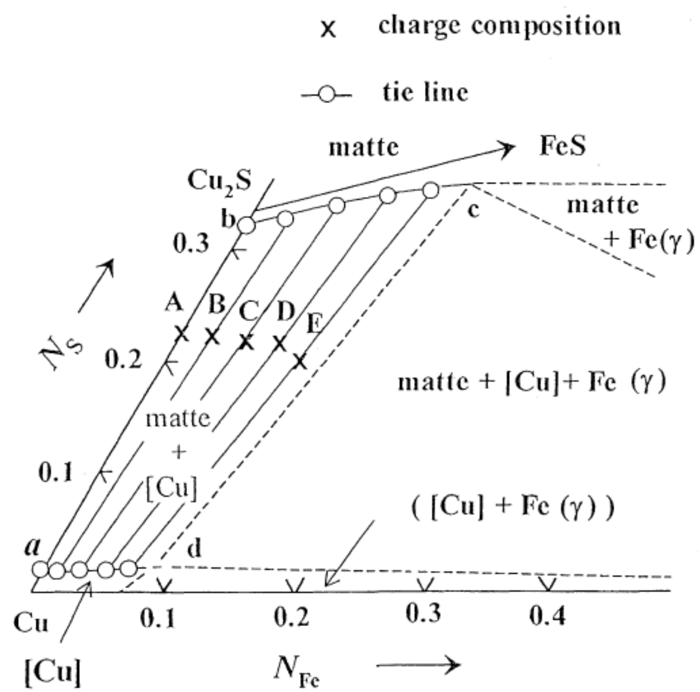


Fig. 1 A part of isothermal section in the Cu–Fe–S system at 1473 K.

D.G. Mendoza, M. Hino and K.Itagaki, Mater. Transact., Vol. 42, No. 11 [2001], pp.2427-2433.

Isopleth section $CuFeS_2$-$FeS_{1.08}$ in Cu-Fe-S

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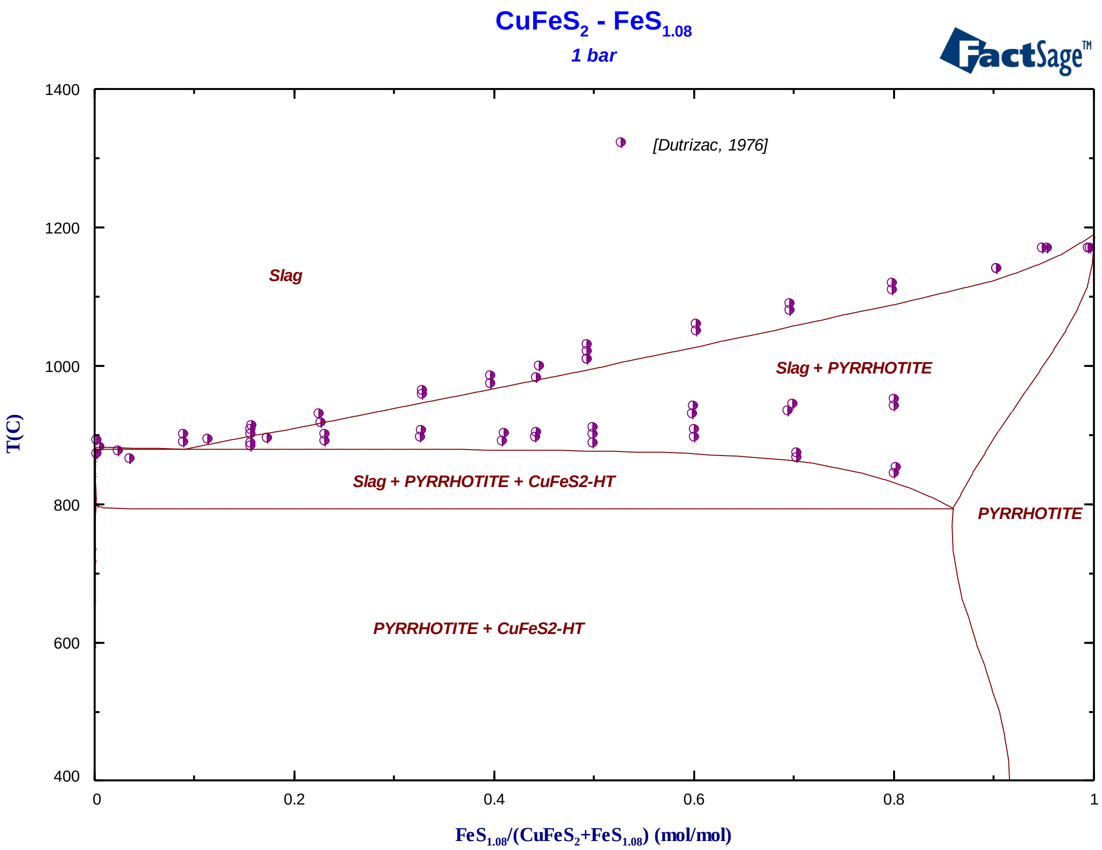

Conclusions

- The liquid phase in all subsystems was evaluated using associate species model,
- All systems were assessed using experimental phase diagram information and thermodynamic properties as far as available.
- The 8 solid solution phases and 19 stoichiometric phases containing S were incorporated.

Sailing close to the wind ...