DATABASE SELECTION FOR FERROUS APPLICATIONS

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FactSage databases for steelmaking applications

Brief History of Database Development
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In-Ho Jung and Marie-Aline Van Ende, “Computational Thermodynamic Calculations: FactSage from CALPHAD Thermodynamic Database to Virtual Process Simulation”, Metall. Mater. Trans. B, 2020, vol. 51, pp. 1851–1874. (Matall. Mater. Trans. 50th anniversary collection – invited paper)

I.-H. Jung, “Overview of the applications of thermodynamic databases to steelmaking processes”, Calphad, 2010, vol. 34, pp. 332-362.

Databases in FactSage

Brief History of FactSage Database Development

1976~2001: FACT → 2001~present: FactSage (a fusion of FACT + ChemSage)

< 1998 : FACT database (before 1998)

1999~2003 : FACT53 database

2000~2004 : FACT Consortium project (2000~2004): 16 companies
pyrometallurgy (ferrous, non-ferrous), hydrometallurgy-corrosion, glassmaking
- FACT53 database → FToxid, FTmisc, FThall, FTsalt, FThelg,..
- New alloy databases: FSstel, FSlite, FScopp, SGTE, ….

2004~2010 : Mini-consortiums
- Al consortium (Alcoa, Alcan, and Norsk-Hydro)
- Glass consortium (Corning, Schott, and Saint-Gobain)
- Light alloy (Al, Mg) consortium (Al consortium, GM, MagNET): FTlite

2009~present : Mini-consortiums
- Al consortium (3 companies), Glass consortium (3 companies)
- Steelmaking consortium: 11 companies → *Consortium database ('**CON3**')*

Databases in FactSage for Steelmaking Applications

FactPS (pure substances database): All gaseous species, stoichiometric solid and liquid species (organic, inorganic) → Similar to thermodynamic tables like JANAF, Barin-Kubaschewski. (When you need a "Gas" phase you always have to select this database).

FToxid: Frequently updated oxide database containing
- many solution phases (slag, spinel, monoxide, olivine, etc.)
- pure solid and liquid oxides, no gas phase

FTmisc: FeLq solution
- most reliable liquid steel database for steelmaking calculations (slags/refractories/gases/molten iron)

FSstel: solid and liquid steel phases (also includes a small number of gases, oxides, sulfides, nitrides, etc.)
- for steel solidification and alloy design.
- liquid steel: reasonable calculations for steelmaking applications

→ For steelmaking calculations:
priority: FToxid > FeLq > FactPS

(In the FactSage 6.4 and later versions, the best selections of compounds among multiple compound databases are provided automatically. But solutions must be selected carefully.)

FToxid database

The four character in red give the name of each solution phase

Main solution phases when T > 1550°C (steelmaking)

- **Slag (I option)**: CaO-MgO-Al_2O_3-SiO_2-FeO-Fe_2O_3-MnO-Mn_2O_3-Ti_2O_3-TiO_2…Na2O-K2O-Li2O-BaO-SrO-
  + Gas solubility such as S (SO_2), P, H (OH), N, C, F, …
  - All oxide components + sulfides: valid for liquid oxy-sulfide solution over a wide range
  - All oxide components + fluorides: mostly valid for (Ca,Al,Mg,Si,Na,K,Li//O,F): up to ~ 50% fluoride.

8.1 version: V oxide (V2+, 3+, 4+, 5+) in the CaO-MgO-Al2O3-SiO2-FeO-Fe2O3-Na2O slag for L_V calculation

- **Spinel (I option) (SPIN)**: (Mg,Fe,Mn,Co,Ni,Zn)(Al,Fe,Cr,Co,Mn,Va)$_2O_4$, extensive solid solution containing $MgAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$, $FeCr_2O_4$, Fe_3O_4, $FeAl_2O_4$, Cr_3O_4, $MnAl_2O_4$, $MnCr_2O_4$, $MnFe_2O_4$, etc.

- **a-, a'-Ca2SiO4 (aC2S, bC2S)**: Ca_2SiO_4 (C_2S)-rich solution with limited solubility of Mg_2SiO_4, Fe_2SiO_4, Mn_2SiO_4,etc.

- **Olivine (Oliv)**: Mg_2SiO_4, Fe_2SiO_4, etc. (Mg,Fe,Ca,Mn,Ni,Zn,Co,Cr,etc.)$_2SiO_4$, covering forsterite (Mg_2SiO_4), fayalite (Fe_2SiO_4), γ-Ca_2SiO_4, monticellite $CaMgSiO_4$, tephroite Mn_2SiO_4.

- **Corundum (CORU)**: (Al,Cr,Fe,Mn)$_2O_3$ solution, the solution of Al_2O_3, Cr_2O_3, Mn_2O_3 and Fe_2O_3. Solid miscibility gaps exist between the constituents.
- **Monoxide (halite) (MeO_)**: solution of CaO-MgO-FeO-MnO-NiO-Fe_2O_3-Al_2O_3-Cr_2O_3 etc. Major constituents: lime (CaO), periclase (MgO) and wustite (FeO).

FToxid database

- **Mn/Ti oxides**:
  i) ilmenite **(ILME):** ($FeTiO_3$(ilmenite)–Ti_2O_3–$MgTiO_3$–$MnTiO_3$ + Al_2O_3),
  ii) pseudo-brookite **(PSEU):** (Ti_3O_5–$FeTi_2O_5$-$MgTi_2O_5$–$MnTi_2O_5$),
  iii) Ti-spinel **(TiSp):** (Mg,Fe,Mn)[Mg,Fe,Mn,Ti,Al]$_2O_4$
  iv) Rutile (TiO_2):TiO_2 + Ti_2O_3-ZrO_2 solid solution

- **Mullite (Mull): non-stoichiometric** $Al_6Si_2O_{13}$ with possible solubility of B and Fe oxide.

- **Melilite** (Mel_): $Ca_2[Mg,Fe^{2+},Fe^{3+},Al](Fe^{3+},Al,Si)_2O_7$. Akermanite $Ca_2MgSi_2O_7$ and gehlenite $Ca_2Al_2SiO_7$ form the melilite solid solution stable below 1590 °C.

Main additional solution phases when T < 1550°C (solidification of slag):
(Including all above phases + additional phases below)

- **Wollastonite (Woll)**: (Ca,Mg,Mn)SiO_3, which is a $CaSiO_3$-rich phase stable below 1300 °C. Pseudo-wollastonite is stoichiometric $CaSiO_3$ stable below 1550 °C.
- **Pyroxene (pPyr, oPyr, cPyr)**: (Mg,Ca,Fe)[Mg,Fe]Si_2O_6, which is a $MgSiO_3$-rich phase stable below 1560 °C. Proto-, ortho-, low-clino-pyroxene exist. Clino-pyroxene is a $CaMg_2SiO_6$-rich phase, which is stable below 1390 °C.
- **Rhodonite (Rhod)**: (Mn,Ca)SiO_3, a $MnSiO_3$-rich solid stable below 1300 °C.

FToxid database

Main additional solution phases in the CaO-Al_2O_3-SiO_2-Fe_tO system at high PO_2 (air)

CAFS $Ca_2(Al,Fe)_8SiO_{16}$, **CAF6** $Ca(Al, Fe)_{12}O_{19}$, **CAF3** $Ca(Al,Fe)_6O_{10}$, **CAF2** $Ca(Al,Fe)_4O_7$
CAF1 $Ca(Al,Fe)_2O_4$, **C2AF** $Ca_2(Al,Fe)_2O_5$, **C3AF** $Ca_3(Al,Fe)_2O_6$

Main additional solution phases when T < 1550°C (mold flux, Na_2O-containing systems)

- **Nepheline (Neph)**: $NaAlSiO_4$ with excess SiO_2.
- **Carnegeite (Carn)**: $NaAlSiO_4$ with excess SiO_2.
- **NaAlO2 (NASl)**: low temperature - $NaAlO_2$ with excess $NaAlSiO_4$
- **NaAlO2 (NASh)**: high temperature - $NaAlO_2$ with excess $NaAlSiO_4$
- **Combeite (NCSO):** $Na_4CaSi_3O_9$ (bombeite) – $Na_2Ca_2Si_3O_9$ solid solution

- **Feldspar (Feld):** complete solution between Anorthite($CaAl_2Si_2O_8$)-Albite($NaAlSi_3O_8$)

- **NCA2**: $(Na_2,Ca)O{\cdot}Na_2O{\cdot}2Al_2O_3$ solid solution
- **C3A1**: $Ca_3Al_2O_6$ dissolving Na_2O, $(Ca,Na_2)1Ca_8Al_6O_{18}$ solution
- Many other Na, K, Li silicate solid solutions.

FTmisc (FeLq) and FSstel

FeLq

Liquid Fe containing Ag,Al,B,Ba,C,Ca,Ce,Co,Cr,Cu,H,Hf,La,Mg,Mn,Mo,N,Nb,Nd,Ni,O,P,Pb,Pd,S,Si, Sn,Ta,Th,Ti,U,V,W,Zr. This phase is better suited for calculations involving iron and steelmaking processes (optimized for iron-rich solutions only).

→ Based on the Unified Interaction Parameter Formalism (more advanced than classical Wagner Interaction Parameter Formalism) with associate model for deoxidation. Many interaction parameters between metallic elements are taken from JSPS (Japanese compilation)

→ Ca and Mg deoxidation were adjusted a bit (lower solubility limit of Ca and Mg) in FactSage 7.3.

FSstel database

- **FCC/BCC**: **Fe / Carbide / Nitride** are all treated as FCC phases
  - → Fe with N and C : use J option (possible 3-phase immiscibility) default option.
  - → Fe with N or C : use I option (possible 2-phase immiscibility).
  - → Also recommend to use I option for BCC phase. default option.

  See Fe-Ti-Nb-C-N example.

- **Liquid**: O, S, N, P are all described by MQM. Many binary and ternary liquid system are modeled by MQM.

- ***FCC ordered phase (FCC_L12), BCC ordered phase (BCC_B2)*** *slow down the calculations significantly. If not really interested in order/disorder transitions, do not select these phases.*

Carbon: when C content is lower than ~ 1%, Fe_3C (metastable) phase is normally formed instead of C (stable). So, in the selection of solid phases, “deselect” C solid.

Steelmaking Chemistry and Availability of Databases

The important chemical systems of non-metallic phases for steelmaking processes can be summarized as follows. All of these are modeled in the FactSage databases.

Database availability for general steelmaking processes:
Green: available in 7.0; Red: available 8.0; blue: available in 8.1

1) Molten slag for refining processes
a) CaO-FeO-Fe_2O_3-SiO_2-MgO-MnO-P_2O_5 system: BOF process
b) CaO-MgO-Al_2O_3-SiO_2-FeO-Fe_2O_3 system: ladle refining process
c) CaO-MgO-SiO_2-CaF_2 system: stainless steel refining
d) CaO-CrO-Cr_2O_3-MgO-SiO_2 system: AOD and VOD process for stainless steel
e) CaO-MgO-SiO_2-MnO-CrO-Cr_2O_3 system: high-Mn stainless steel
f) CaO-MgO-SiO_2-Al_2O_3-FeO-Fe_2O_3-V oxide system: V containing steel & Fe-V smelting process

2) Mold flux for casting processes
a) CaO-MgO-Al_2O_3-SiO_2-Na_2O-K_2O-Li_2O-F system: conventional process
b) BaO-SrO-CaO-MgO-Al_2O_3-SiO_2-Na_2O-B_2O_3 system: new candidate.

3) Non-metallic inclusions

a) CaO-Al_2O_3-MgO-CaS: conventional low carbon steels
b) MnO-SiO_2-Al_2O_3-CaO-MnS: wire steels and free cutting steels
c) MnO-SiO_2-Ti_2O_3-TiO_2-Al_2O_3: high strength steels
d) Al_2O_3-Ti_2O_3-TiO_2: interstitial-free (IF) steels
e) Ti-Nb-C-N: high-strength low-alloy (HSLA) steels containing Ti and Nb

4) Refractories

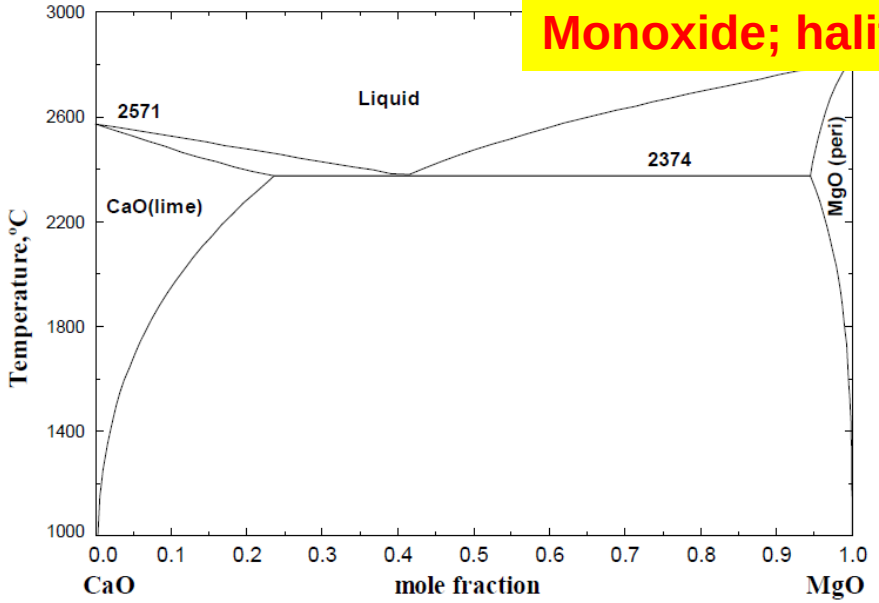
a) MgO-C: BOF and RH vessel refractories, ladle slag line
b) MgO-Al_2O_3: ladle castable
c) MgO-Cr_2O_3-FeO-Fe_2O_3-Al_2O_3: VOD and AOD refractories
d) Al_2O_3-ZrO_2-SiO_2-C: nozzle refractories and tundish plugs

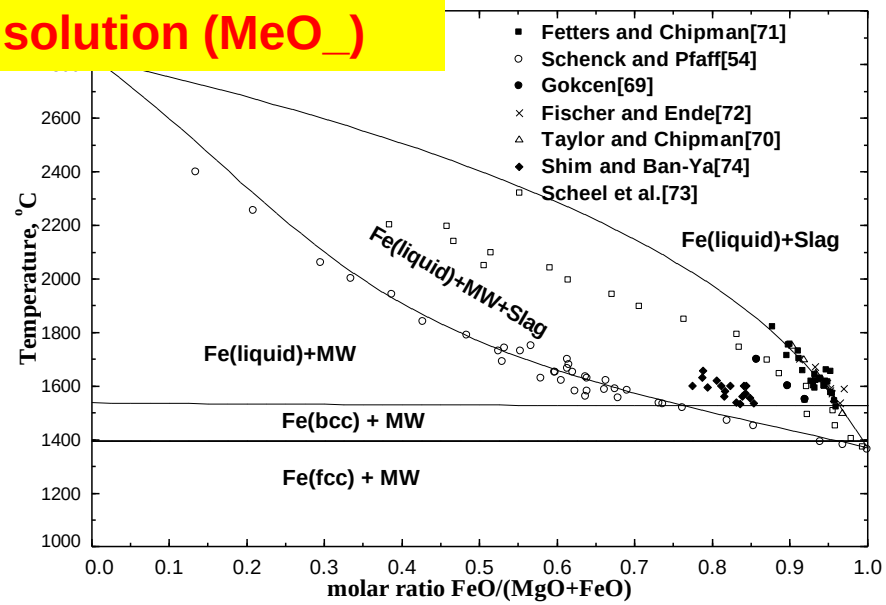
Most common phase diagrams for steelmaking applications

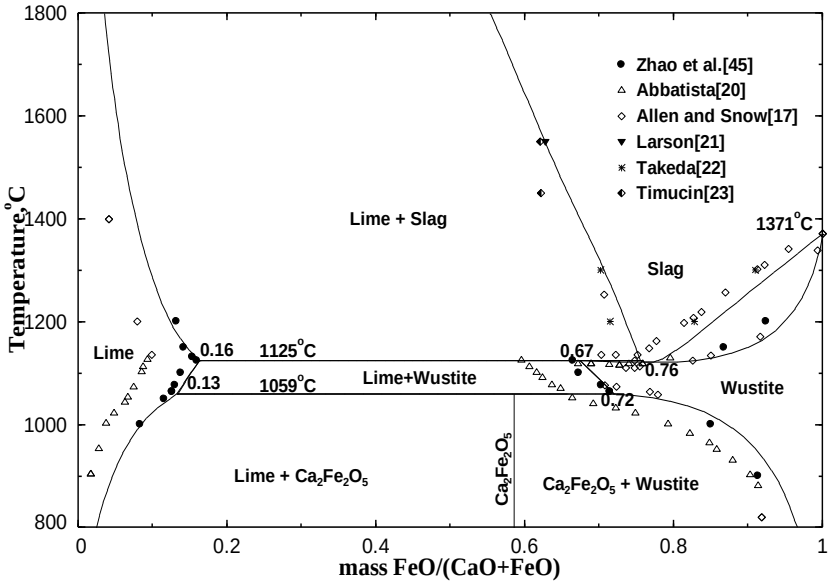
$CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3\text{-}FeO\text{-}Fe_2O_3\text{-}MnO$
$Na_2O\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2$
$MnO\text{-}Ti_2O_3\text{-}TiO_2$

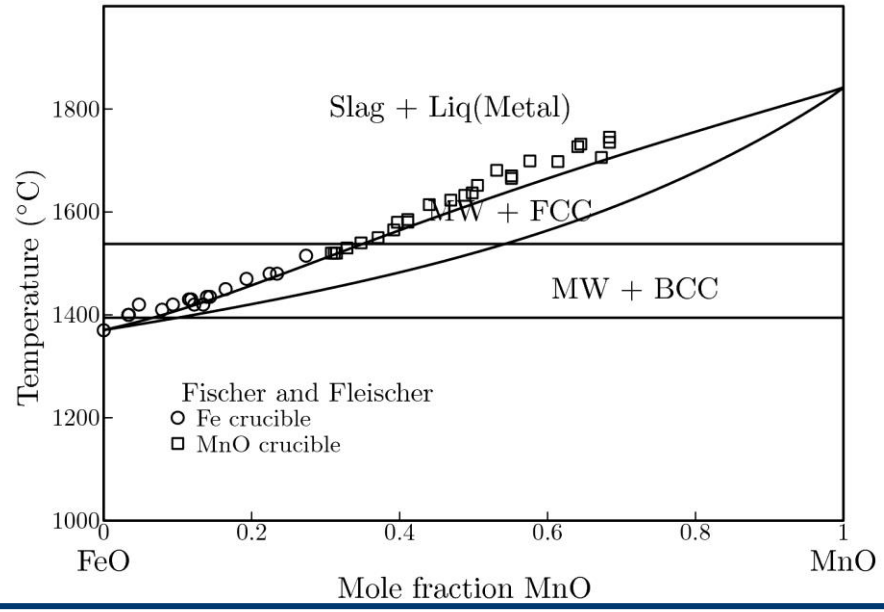
Important phases and phase diagrams

Monoxide; halite solution (MeO_)



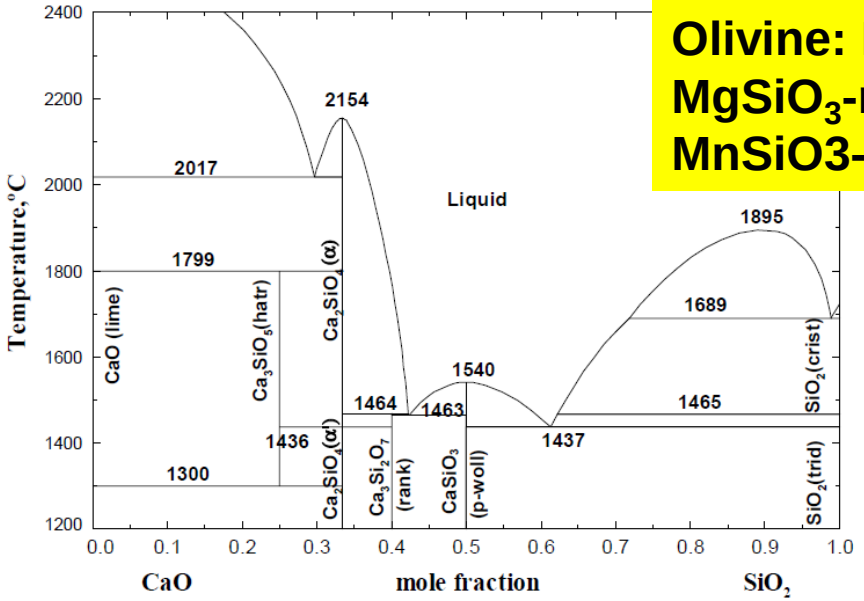


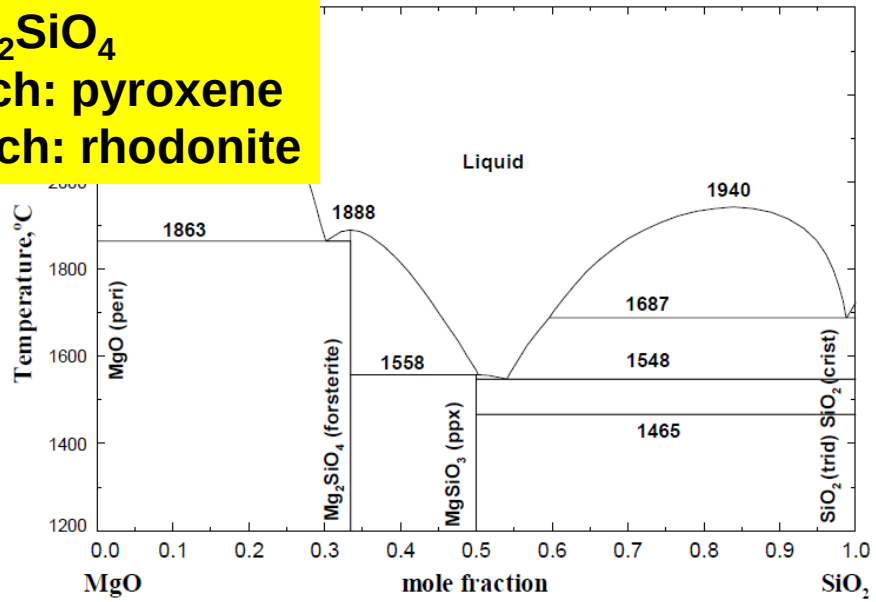


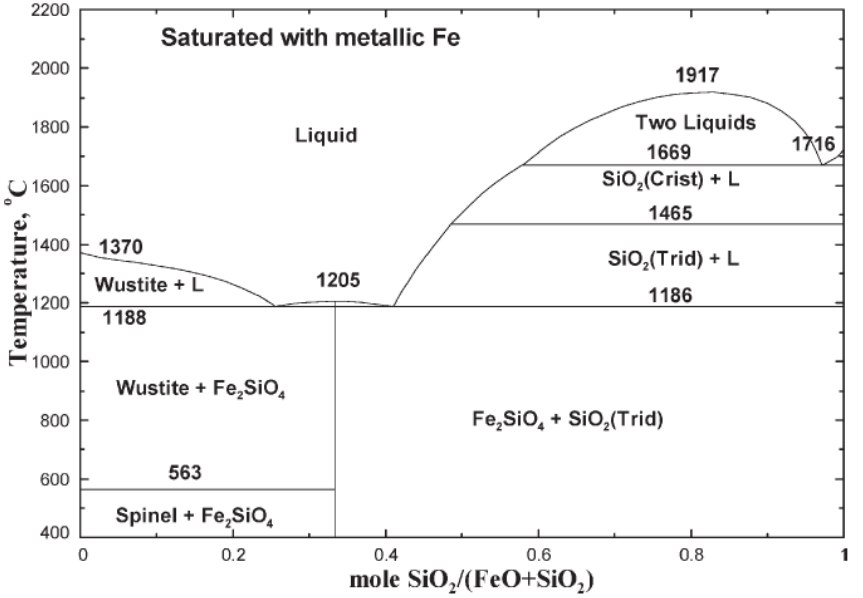


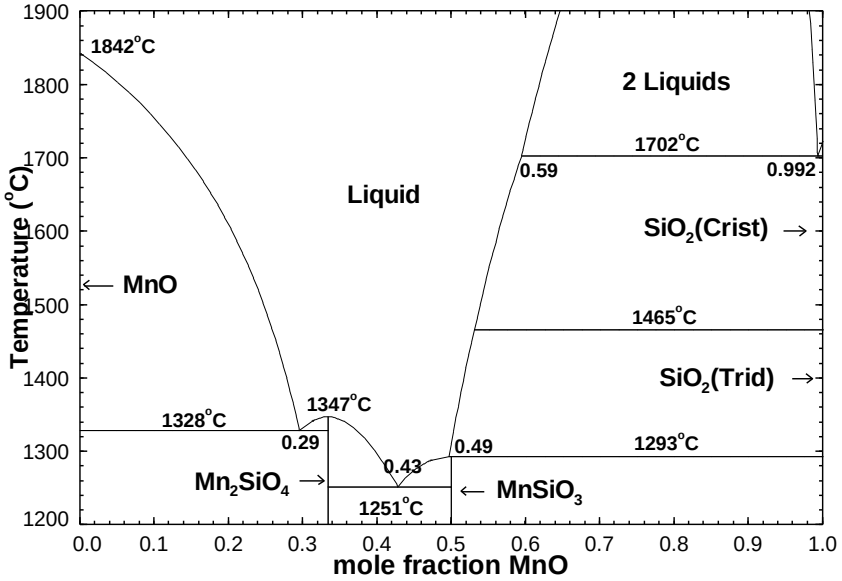
Important phases and phase diagrams

Olivine: M_2SiO_4
$MgSiO_3$-rich: pyroxene
MnSiO3-rich: rhodonite

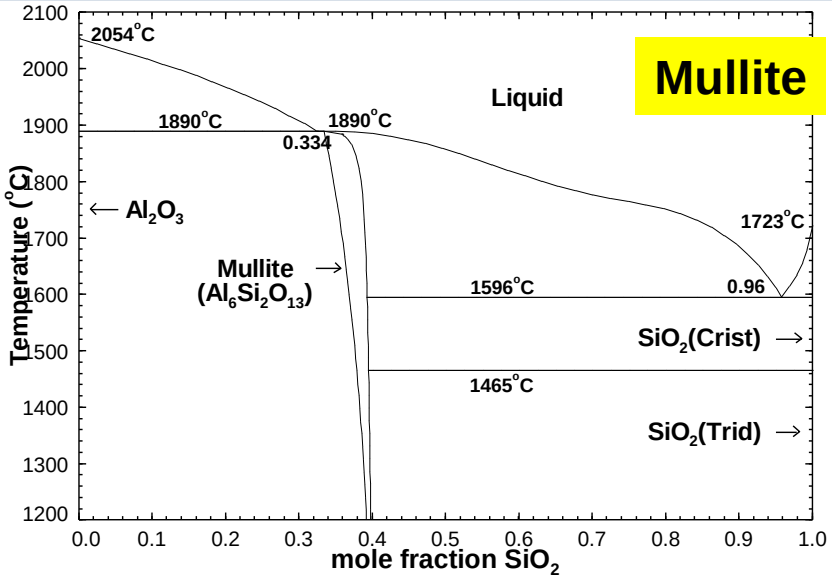


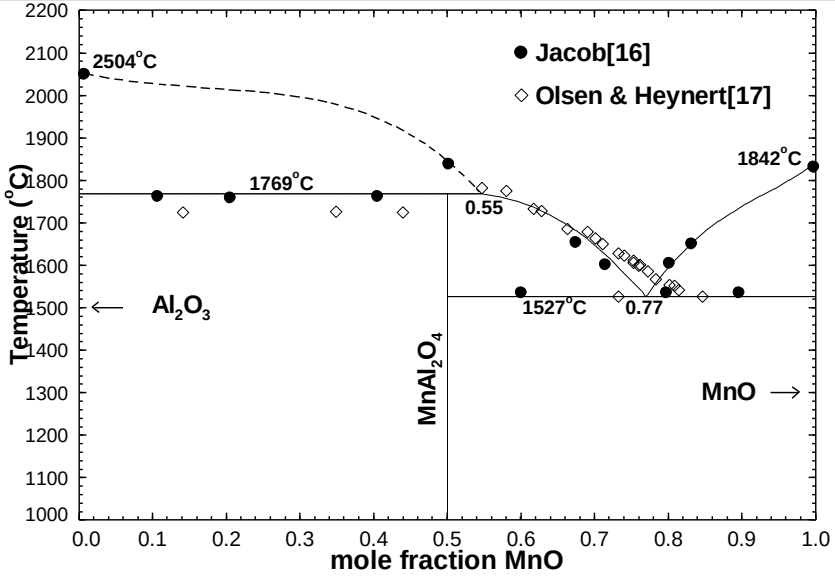




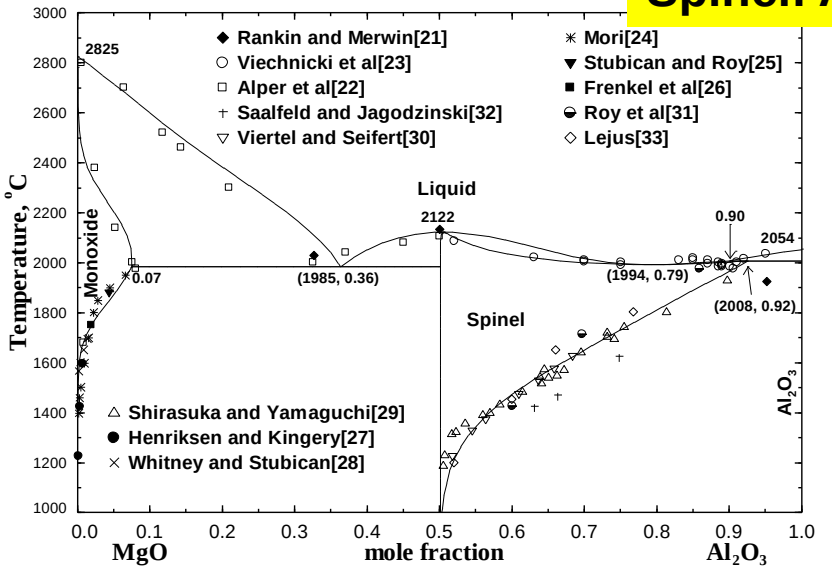


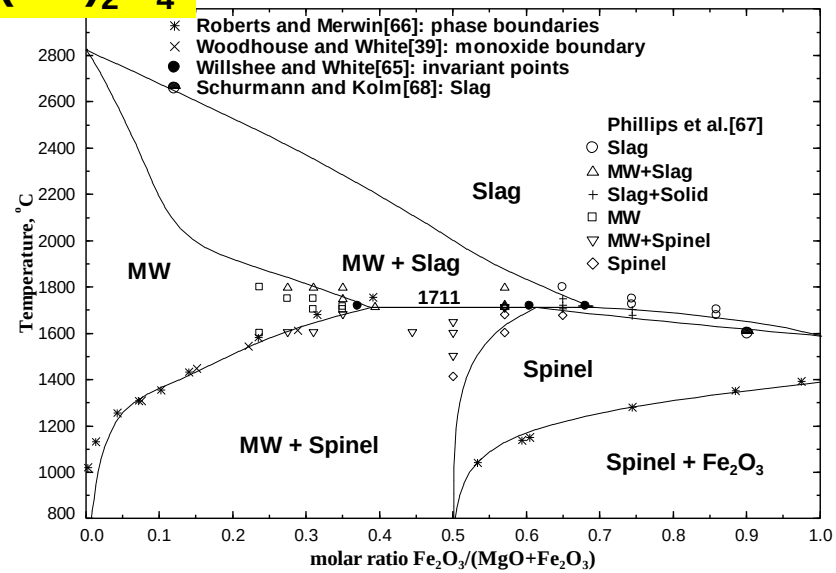
Important phases and phase diagrams





Spinel: $A^{2+}(B^{3+})_2O_4$





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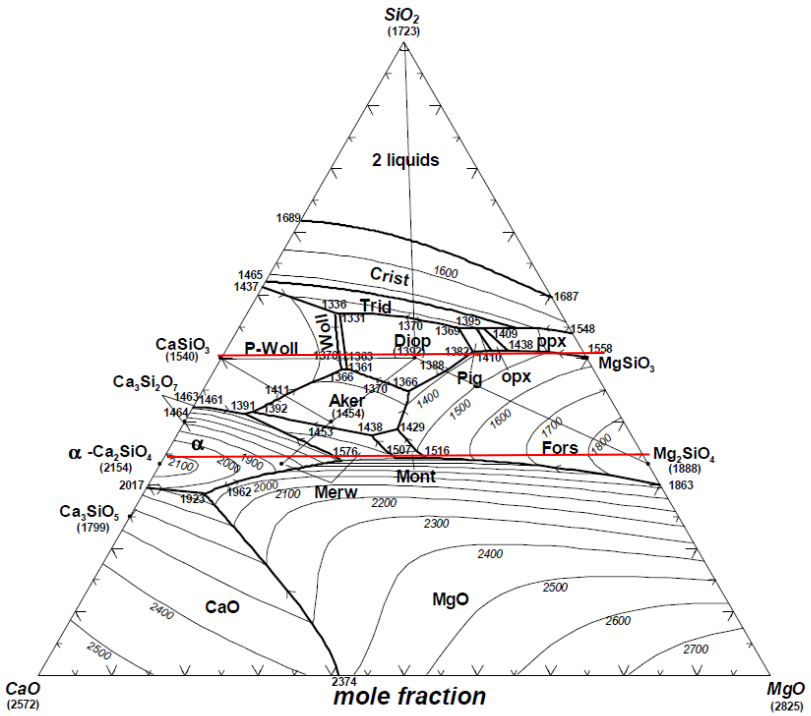

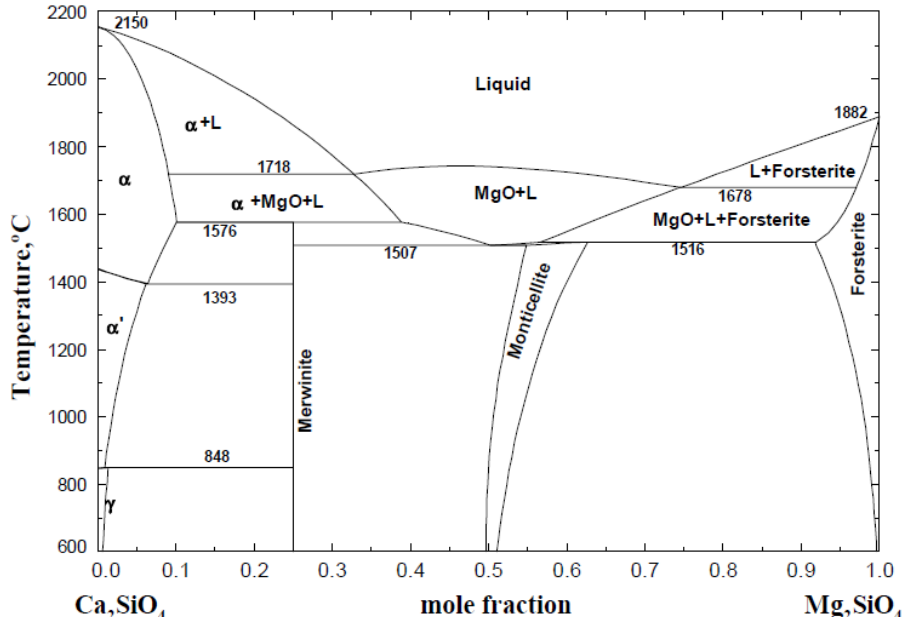

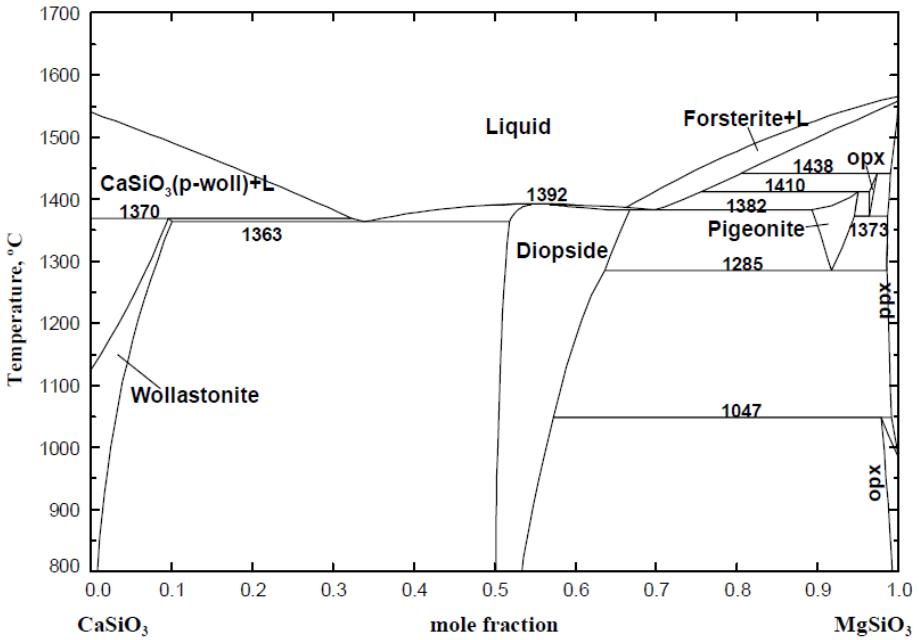

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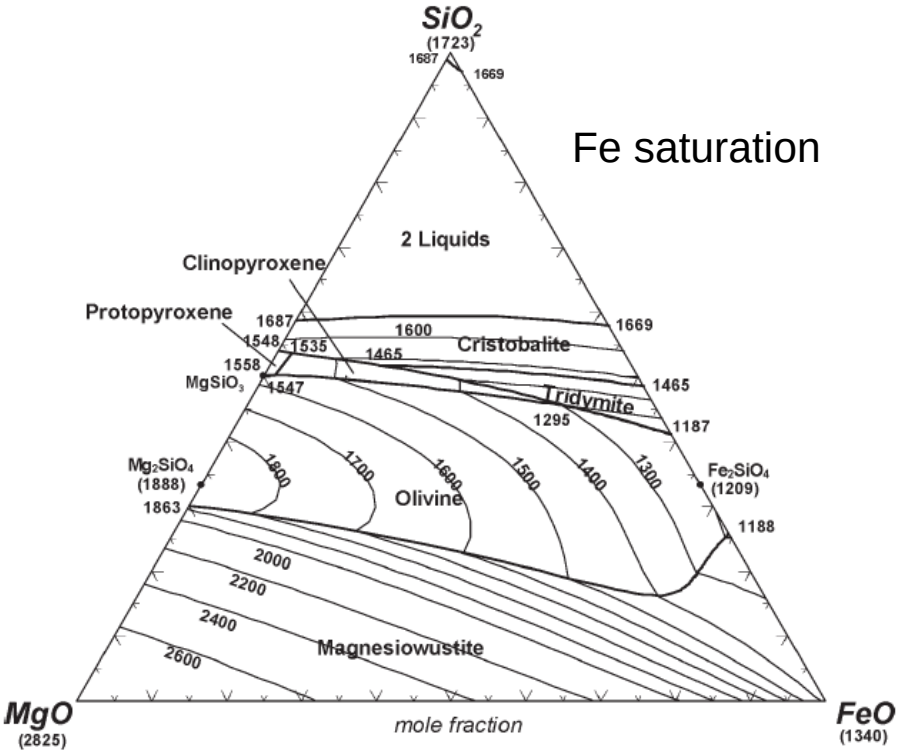
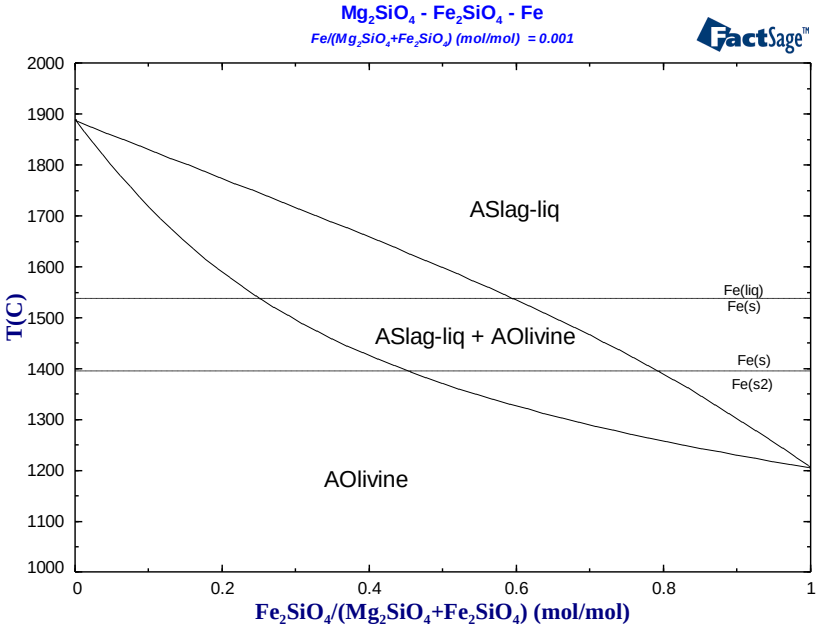
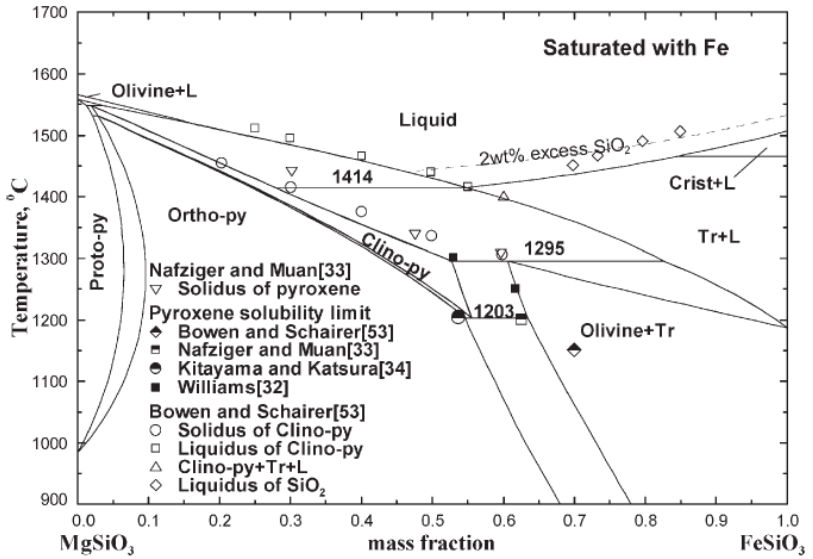


Fe saturation





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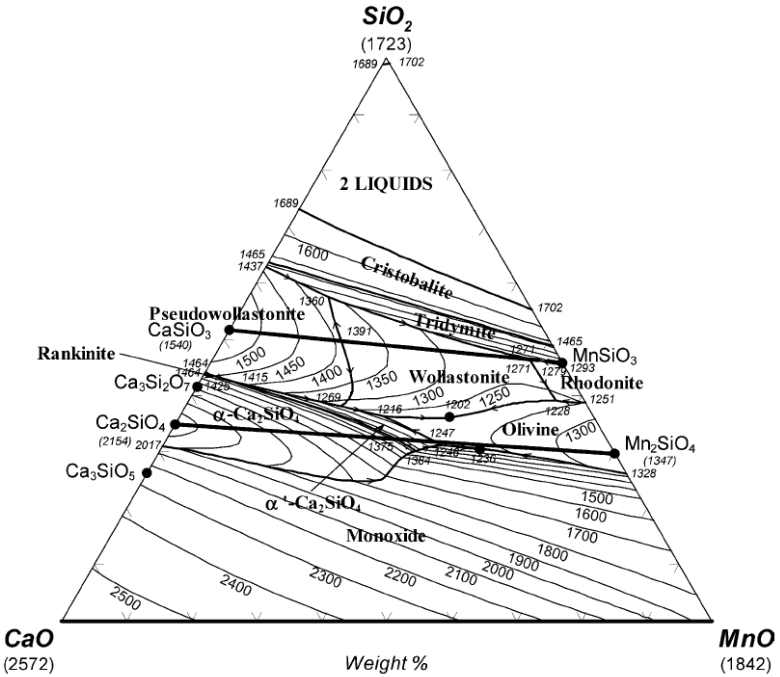

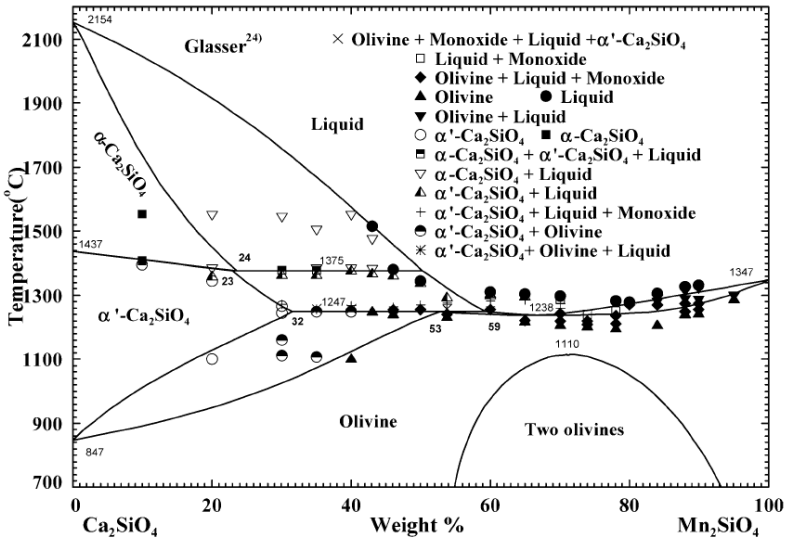

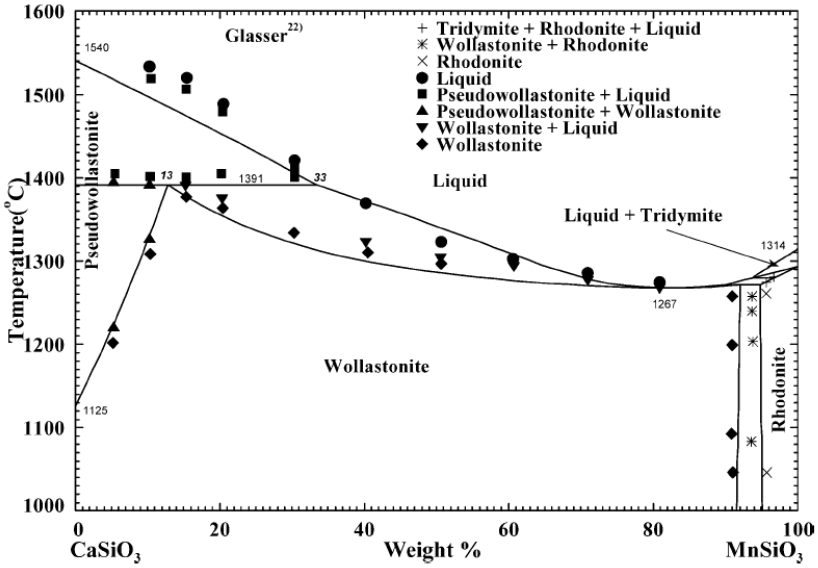

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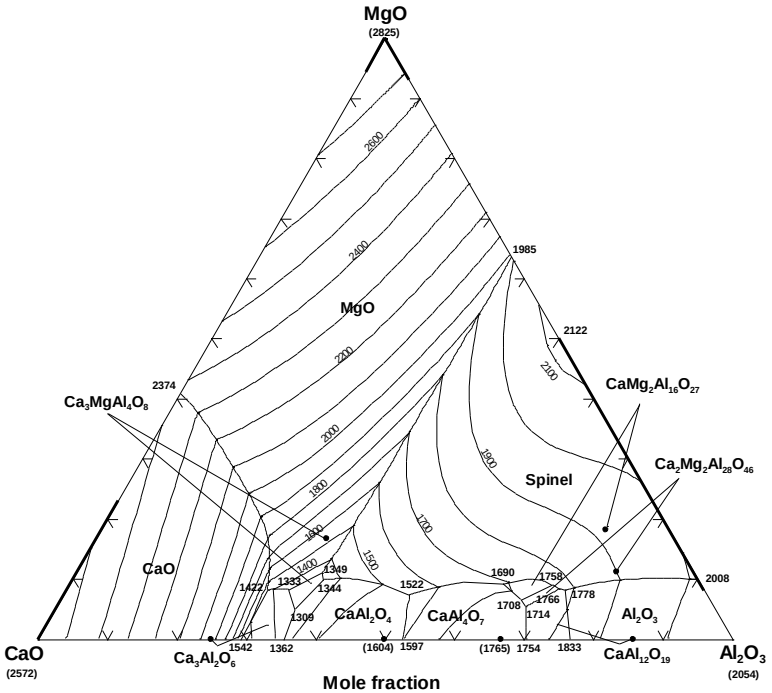

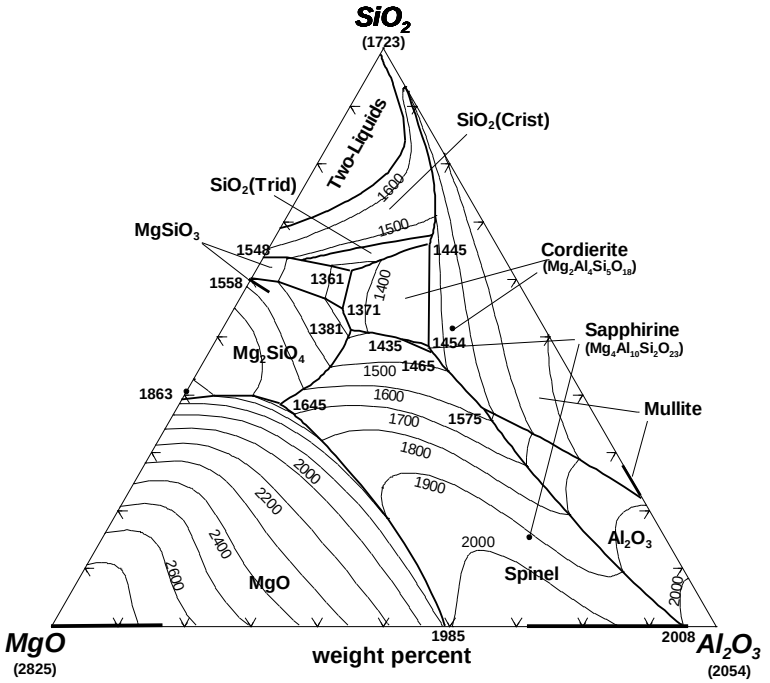

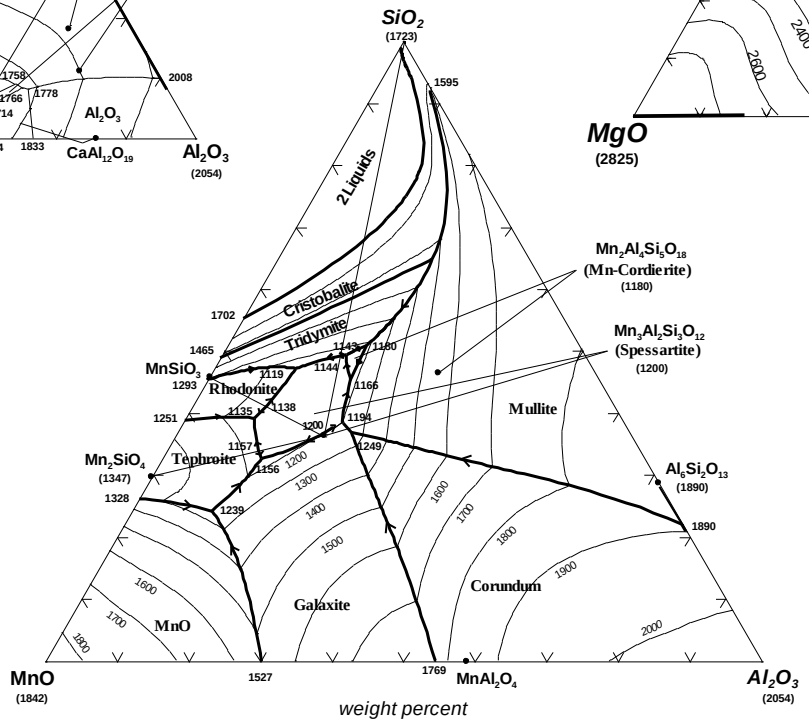

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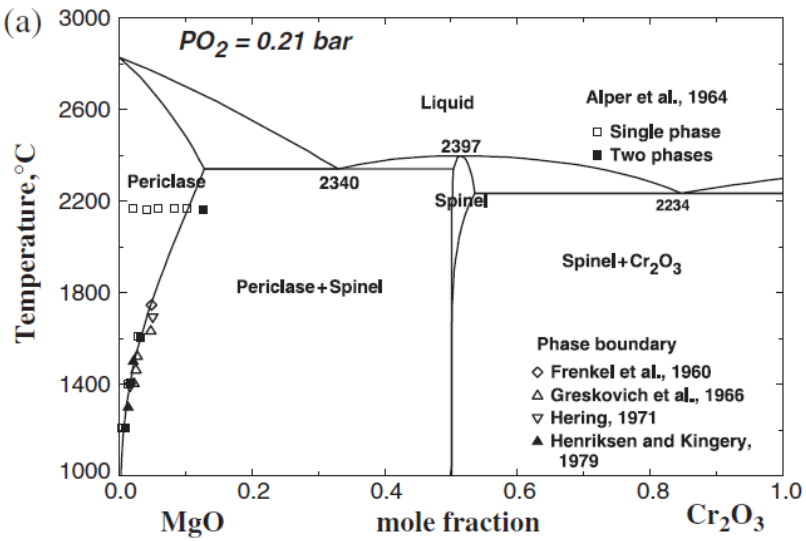
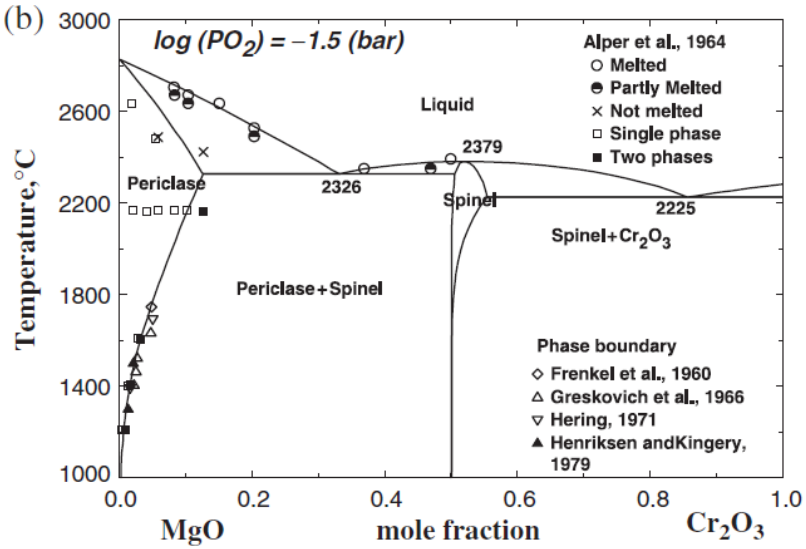
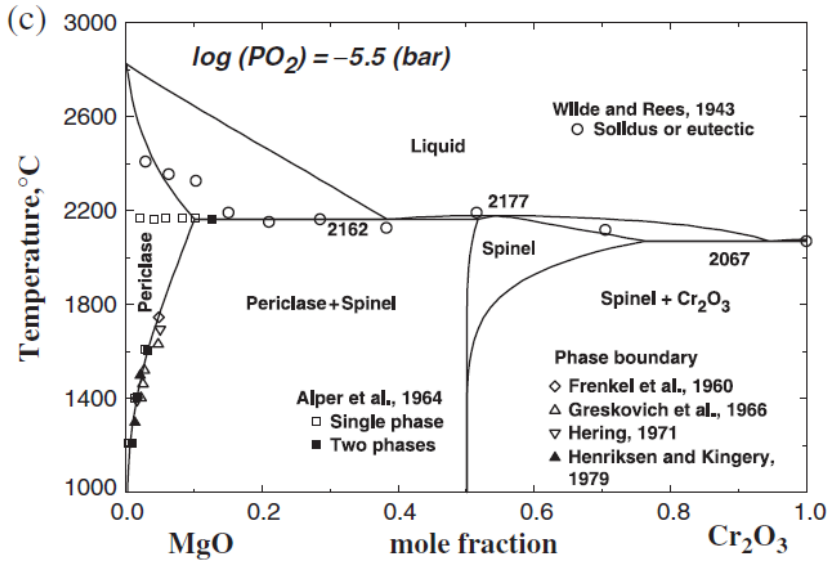
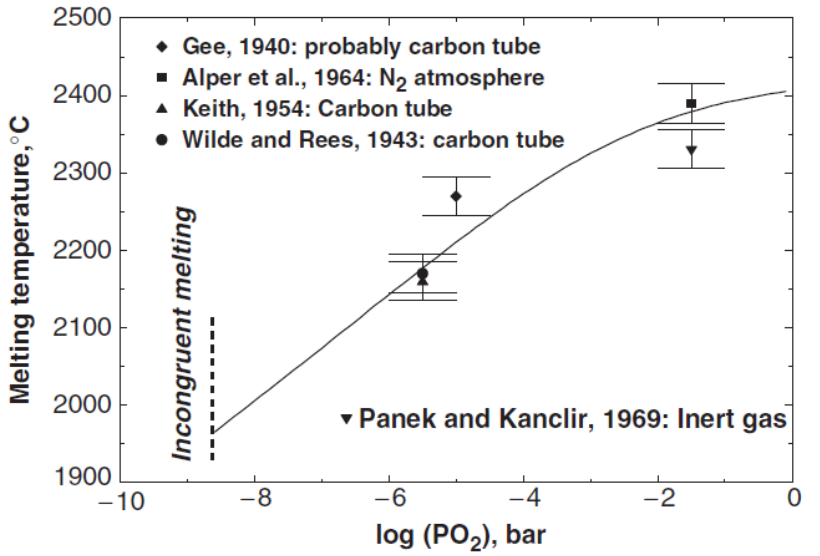
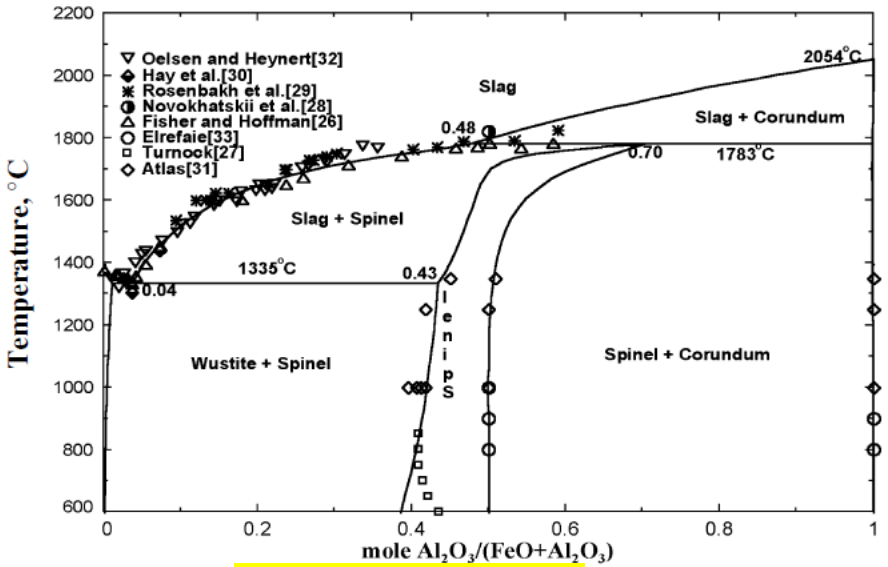




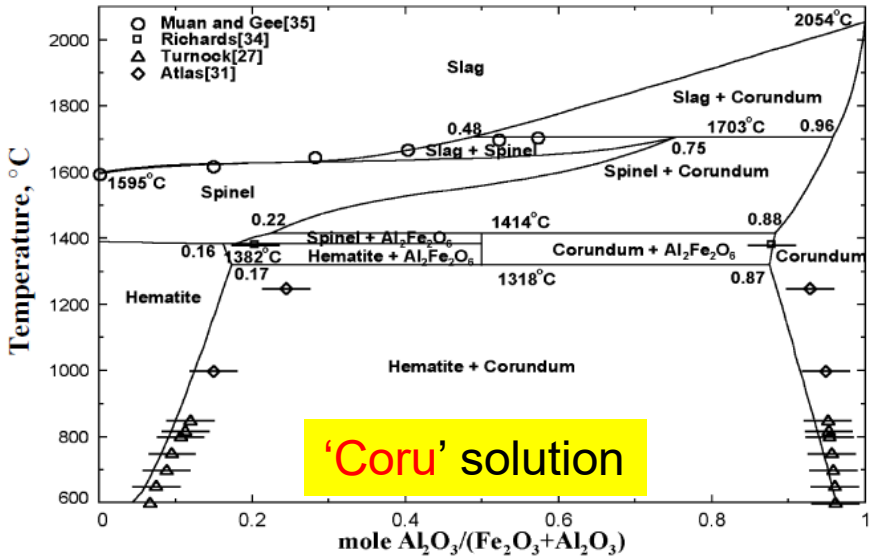




Important phases and phase diagrams

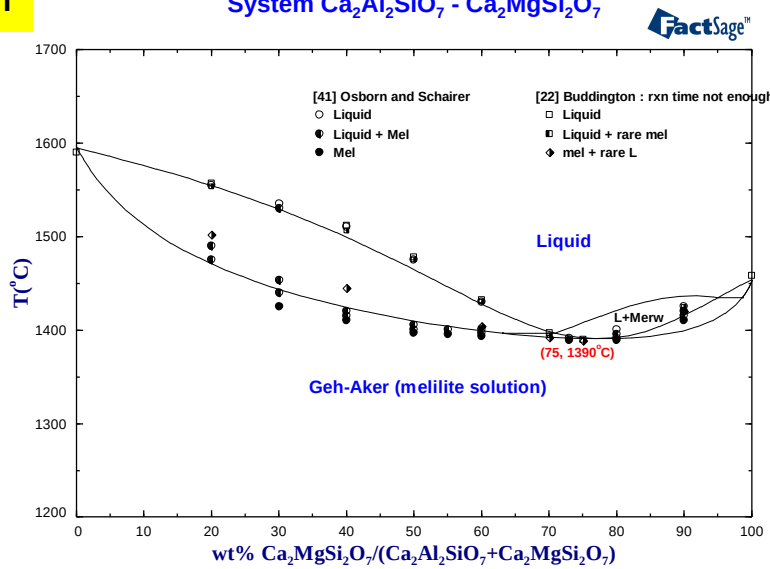


Spinel solution



'Coru' solution

System $Ca_2Al_2SiO_7$ - $Ca_2MgSi_2O_7$



Melilite solid solution

Important phases and phase diagrams

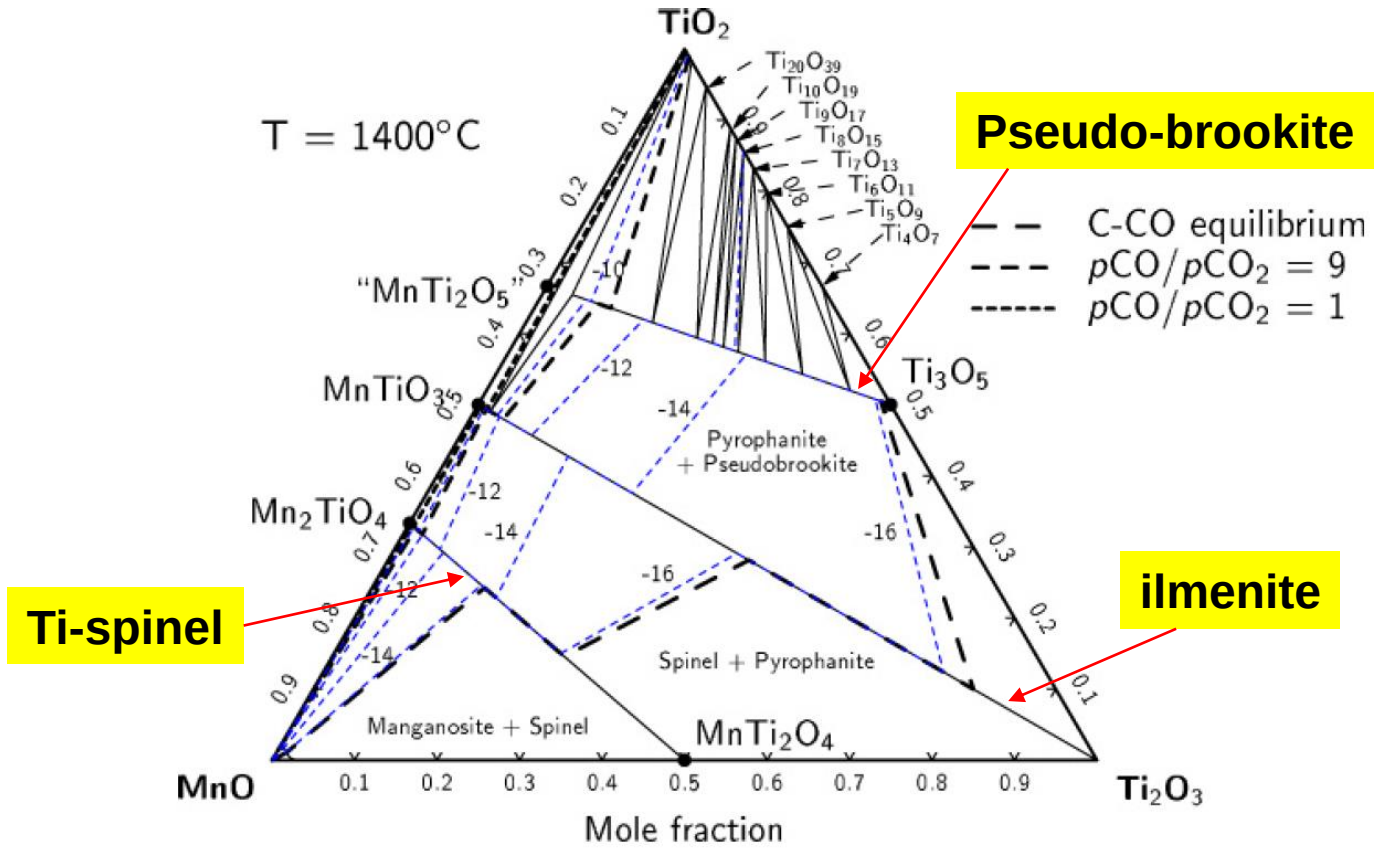


Fig. 5. Calculated isothermal section in the MnO–"TiO_2"–"Ti_2O_3" system at 1400 °C. Thin lines represent sections of phase equilibria under specified oxygen partial pressures (log pO_2 (bar)). Dashed lines denote sections of phase equilibria under $pCO/pCO_2 = 1$, 9 and C/CO equilibrium, respectively.

Important phases and phase diagrams

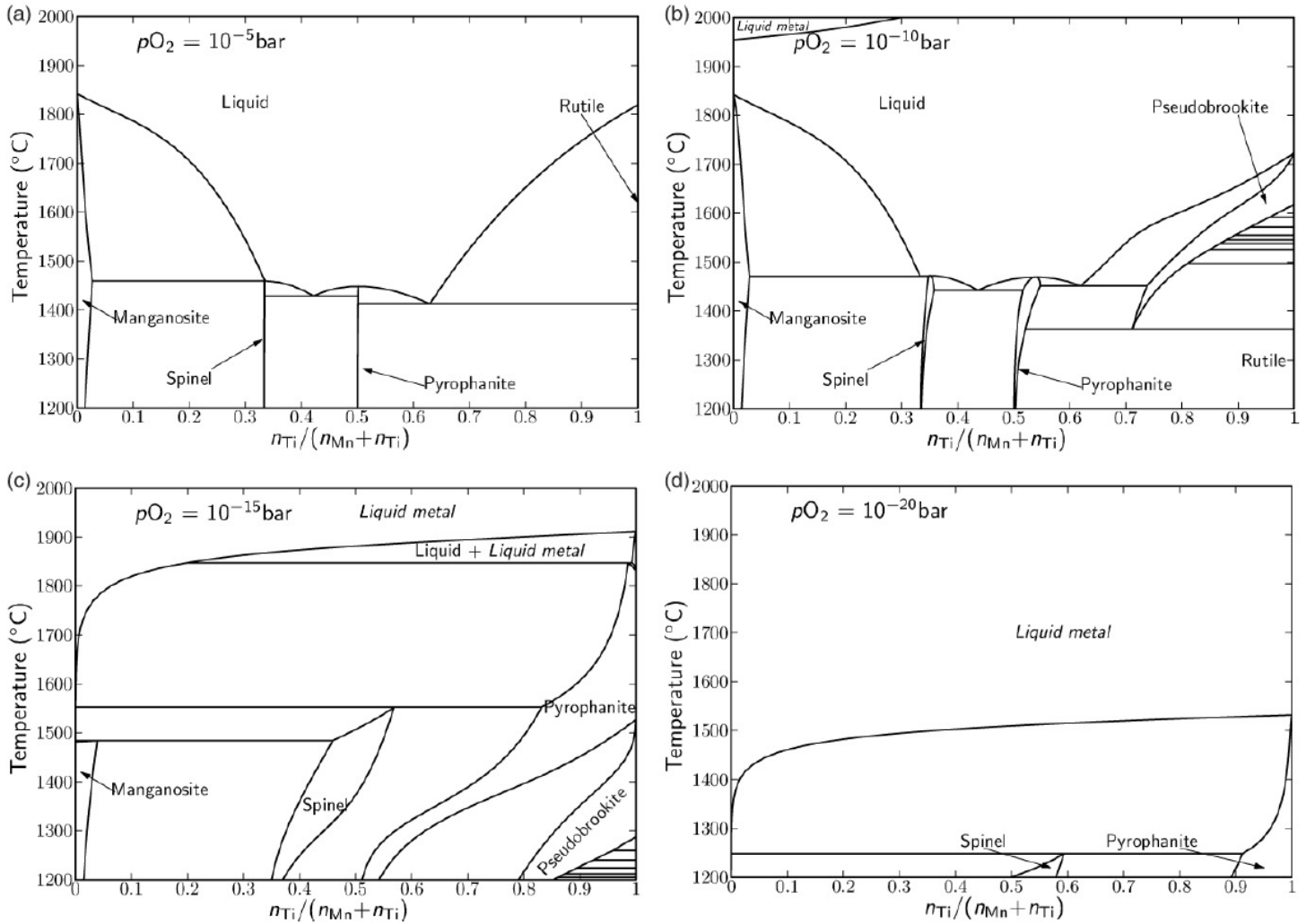
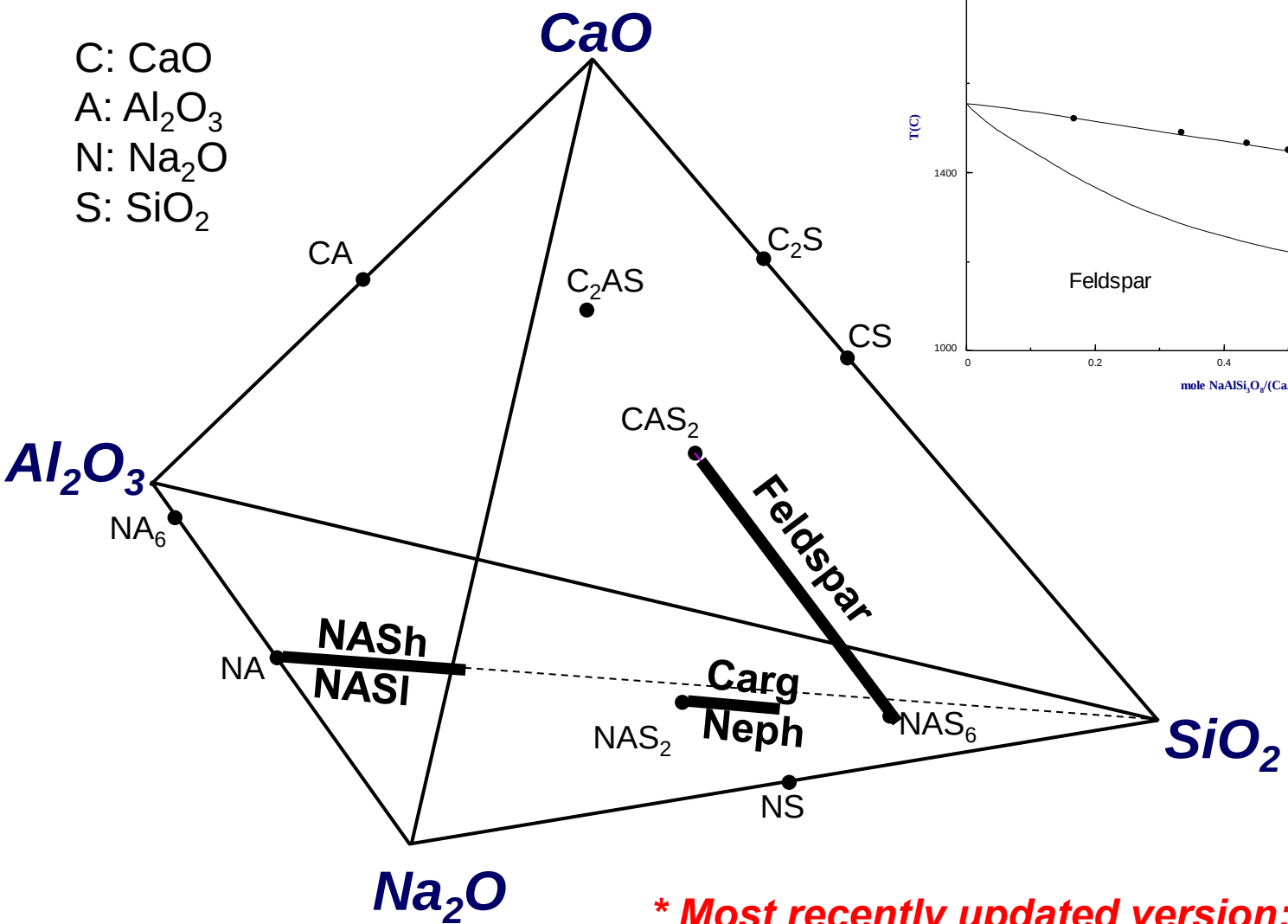
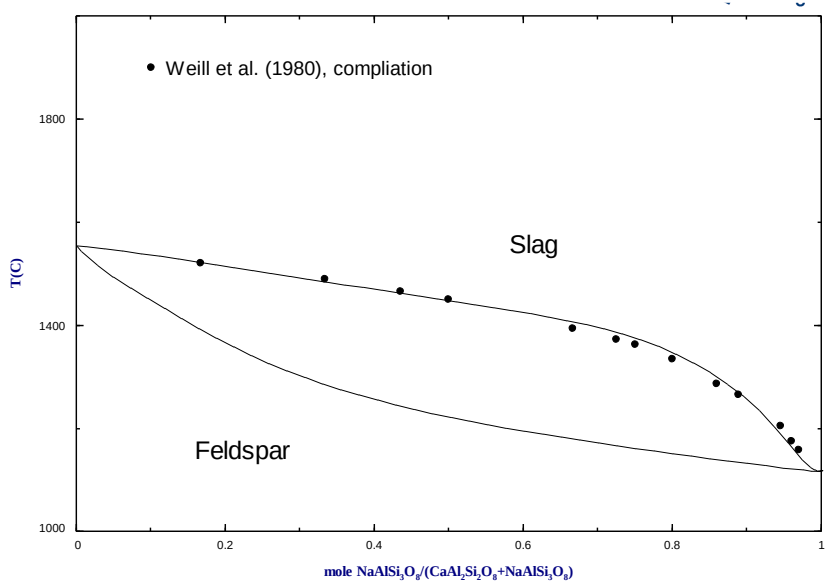


Fig. 7. Predicted phase diagrams of the Mn–Ti–O system under various oxygen partial pressures. (a) $pO_2 = 10^{-5}$ bar. (b) $pO_2 = 10^{-10}$ bar. (c) $pO_2 = 10^{-15}$ bar. (d) $pO_2 = 10^{-20}$ bar.

Na_2O-containing system: Na_2O-SiO_2-CaO-Al_2O_3

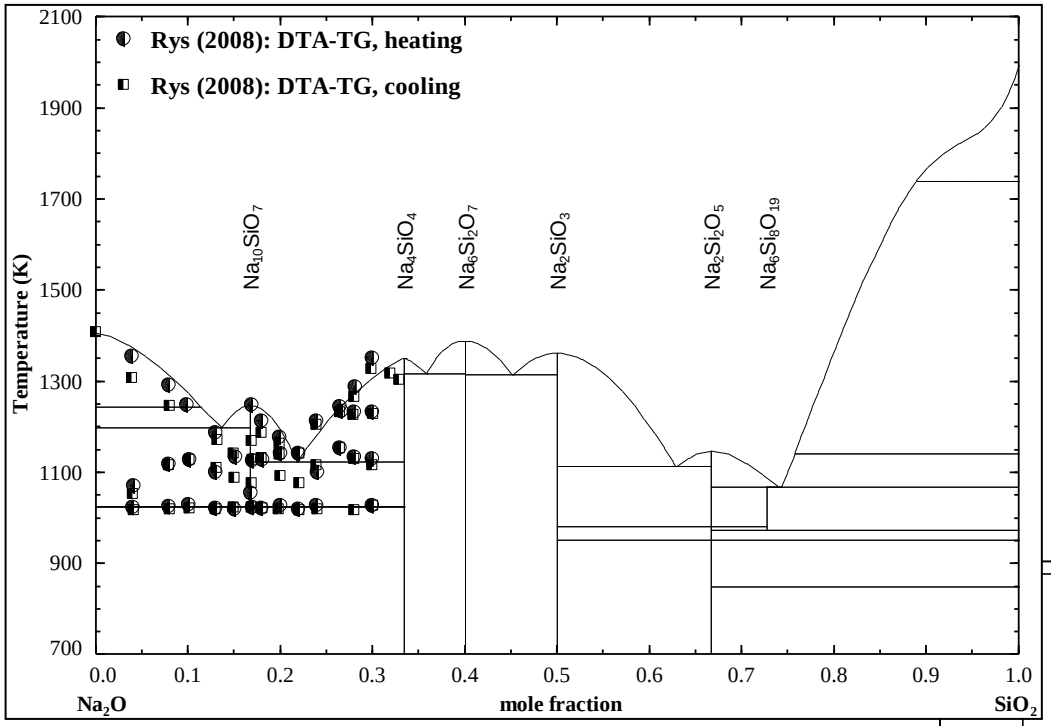
C: CaO
A: Al_2O_3
N: Na_2O
S: SiO_2

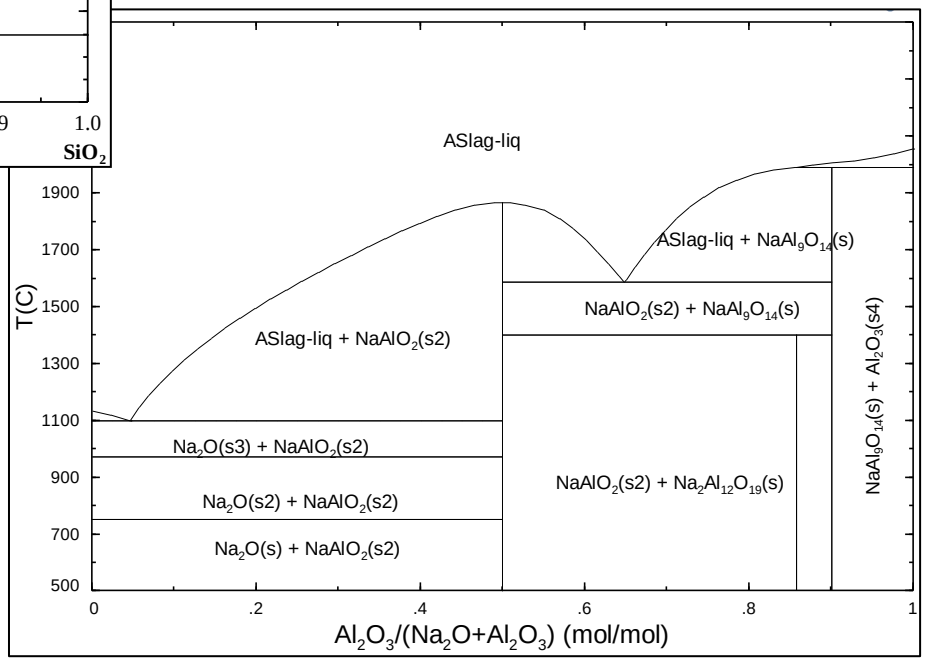




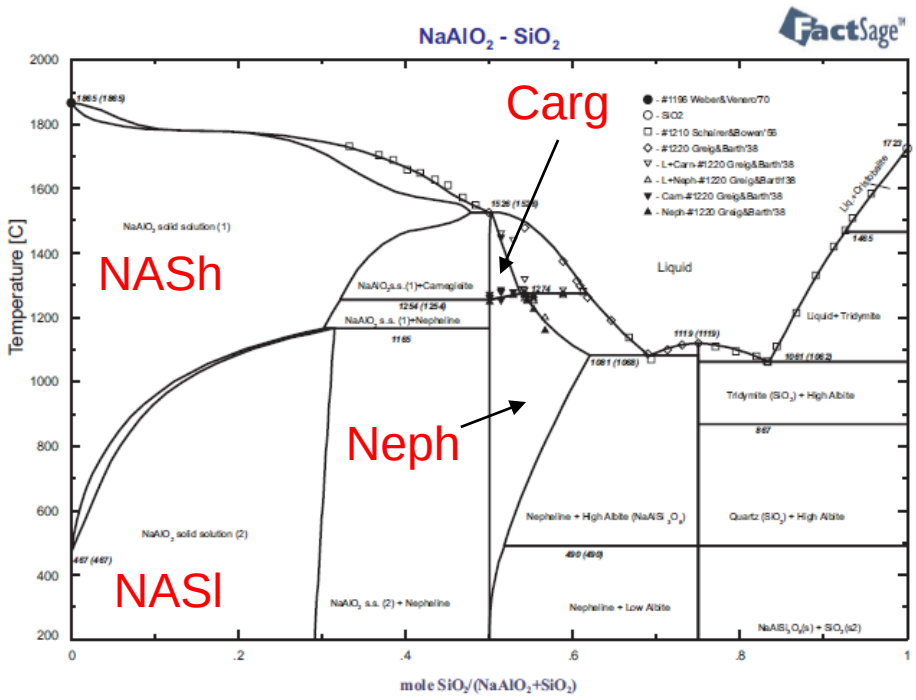
**** Most recently updated version: 'CON1' database***

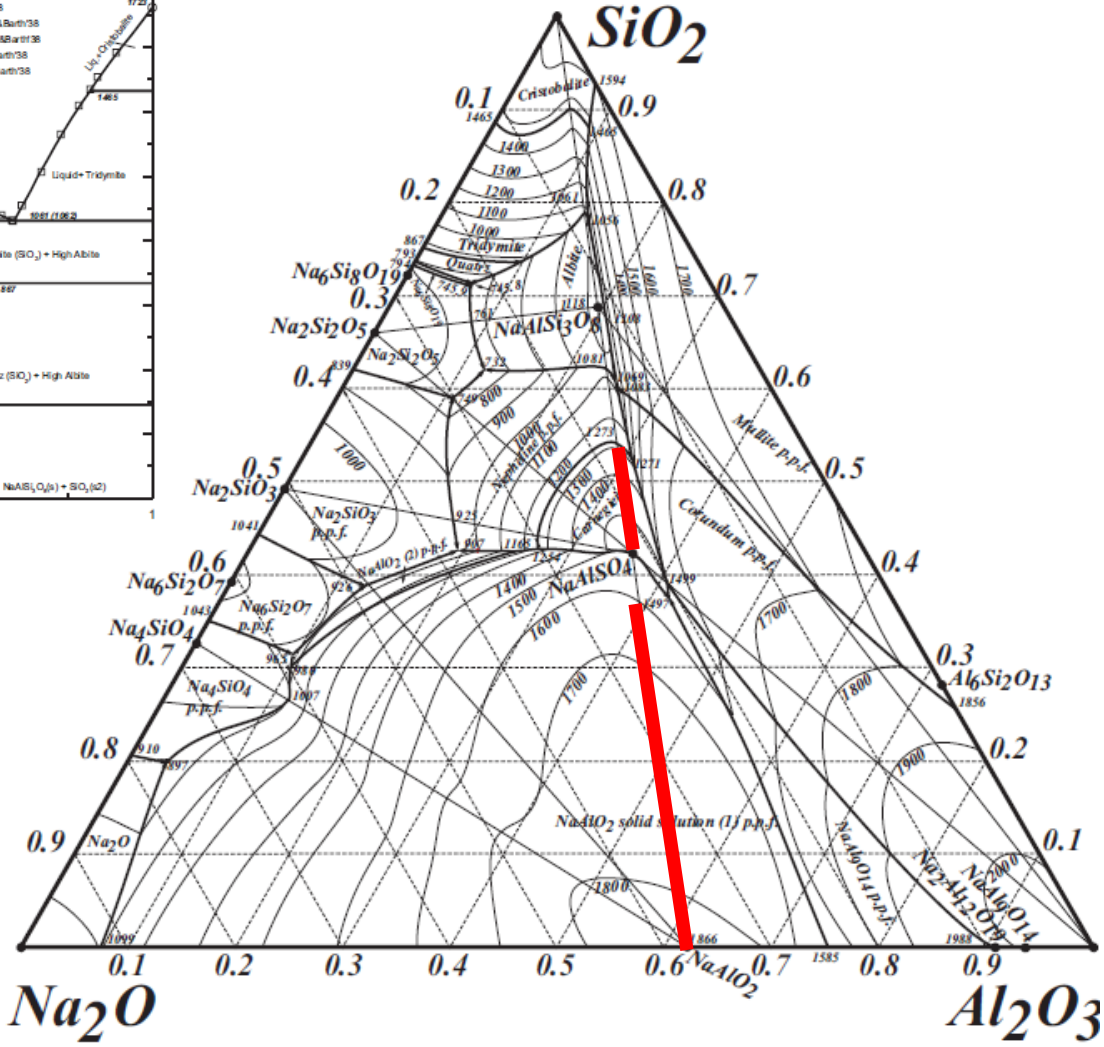
Important phases and phase diagrams: Na_2O-Al_2O_3-SiO_2 system





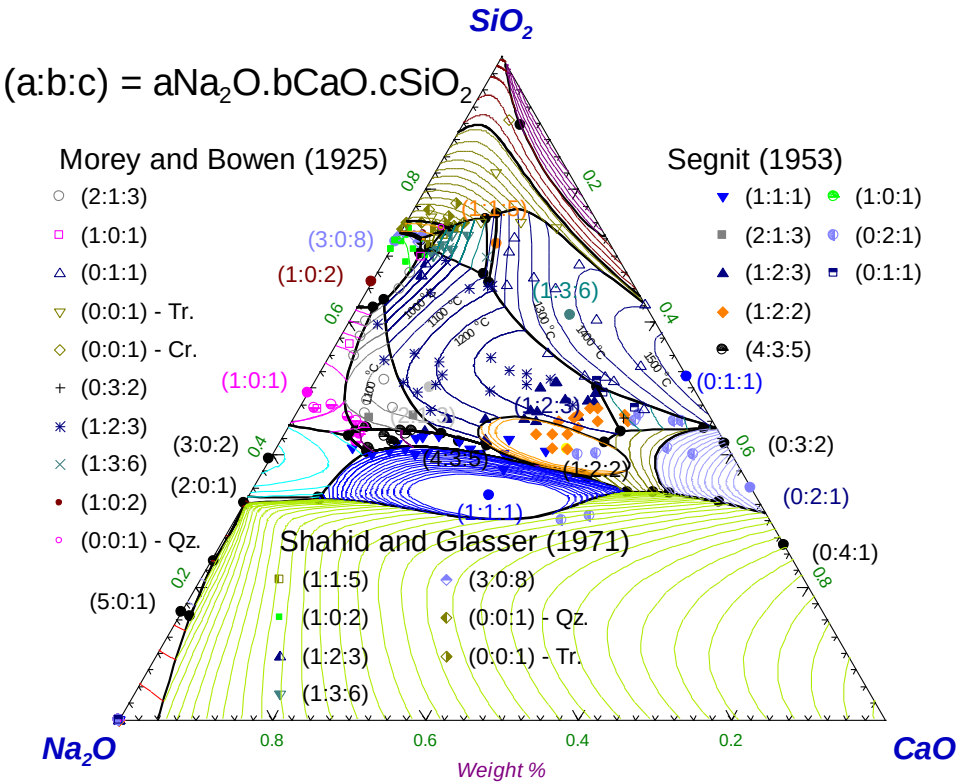
Important phases and phase diagrams: Na_2O-Al_2O_3-SiO_2 system

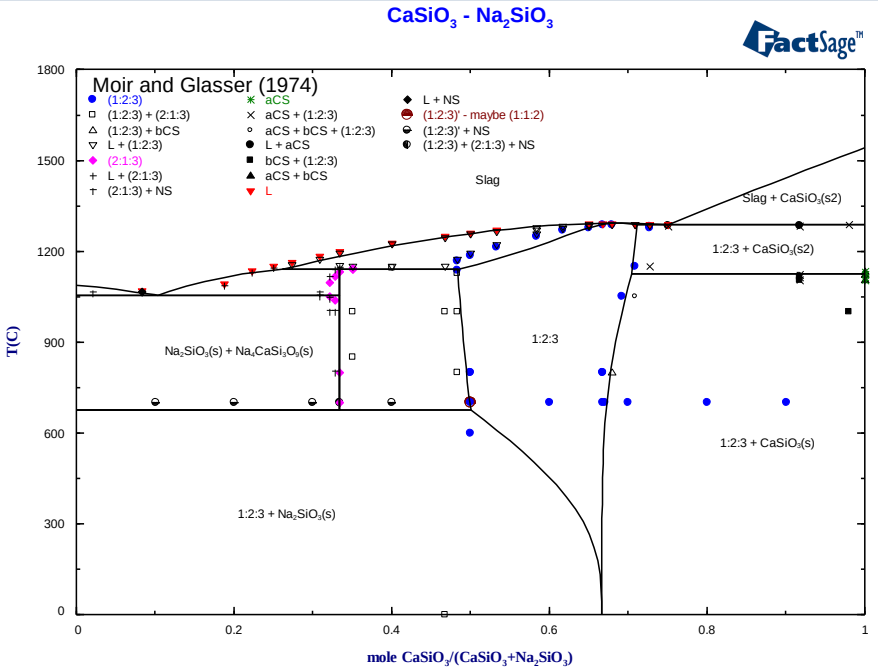


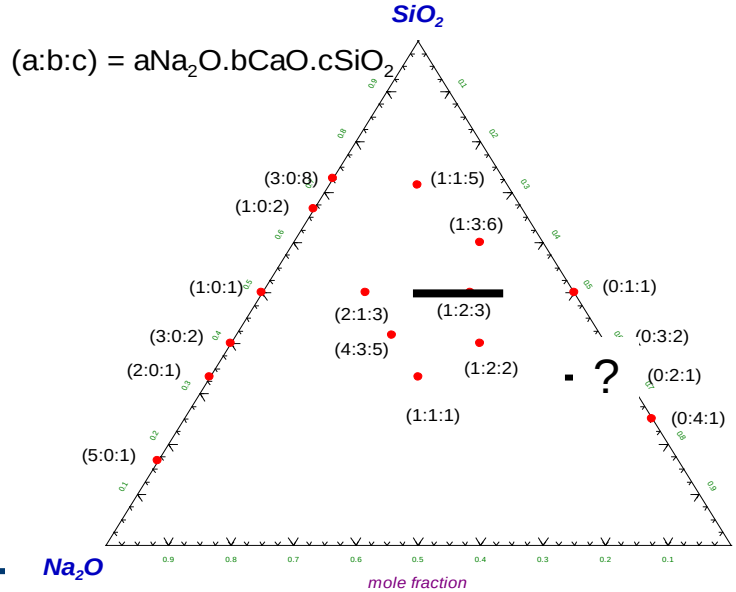


Important phases and phase diagrams: Na_2O-CaO-SiO_2 system

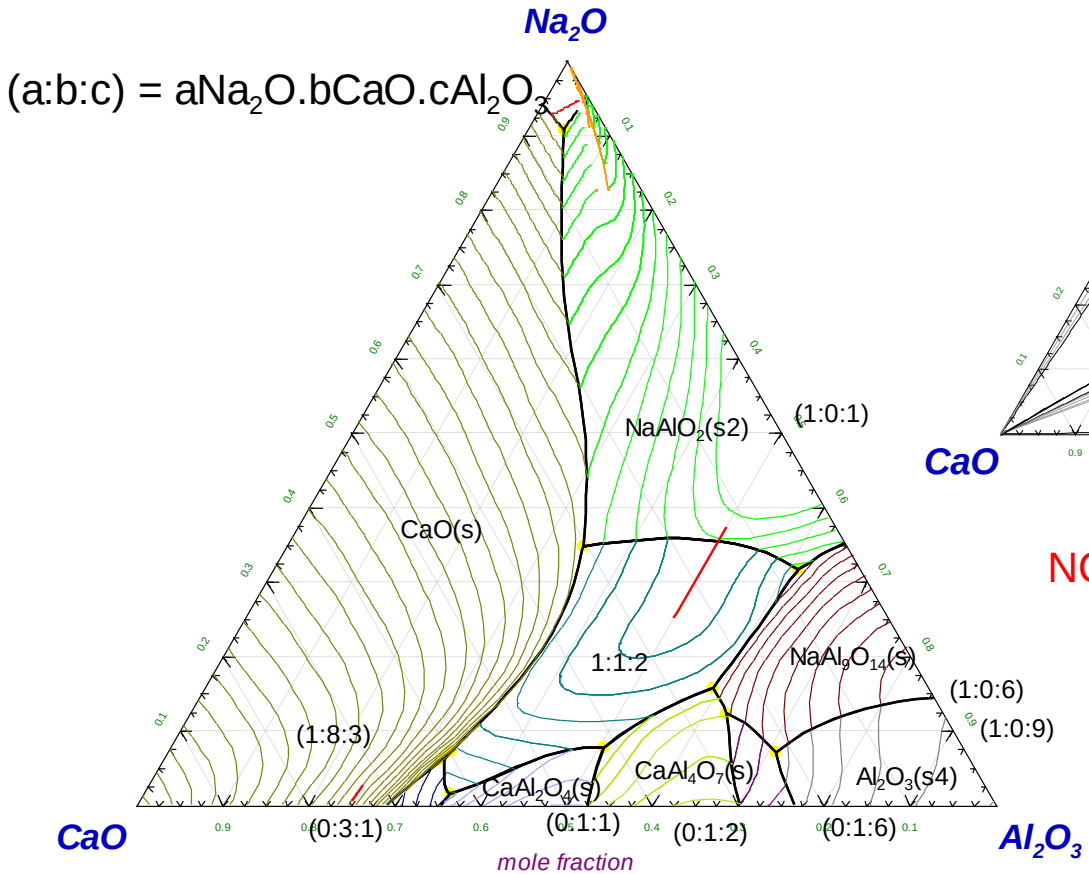
NCSO: 1:2:3 solid solution

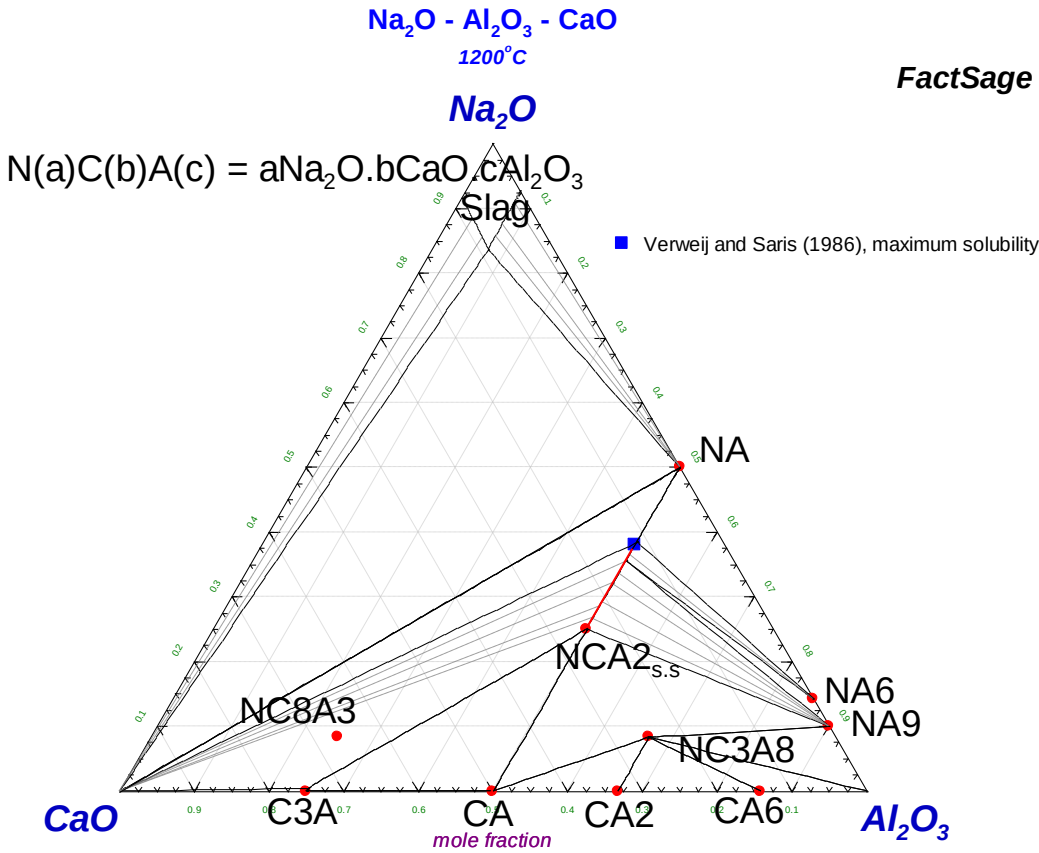






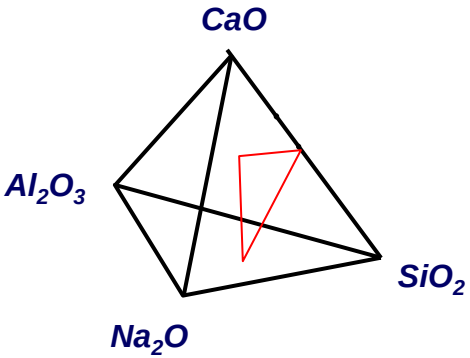
Important phases and phase diagrams: Na_2O-Al_2O_3-CaO system

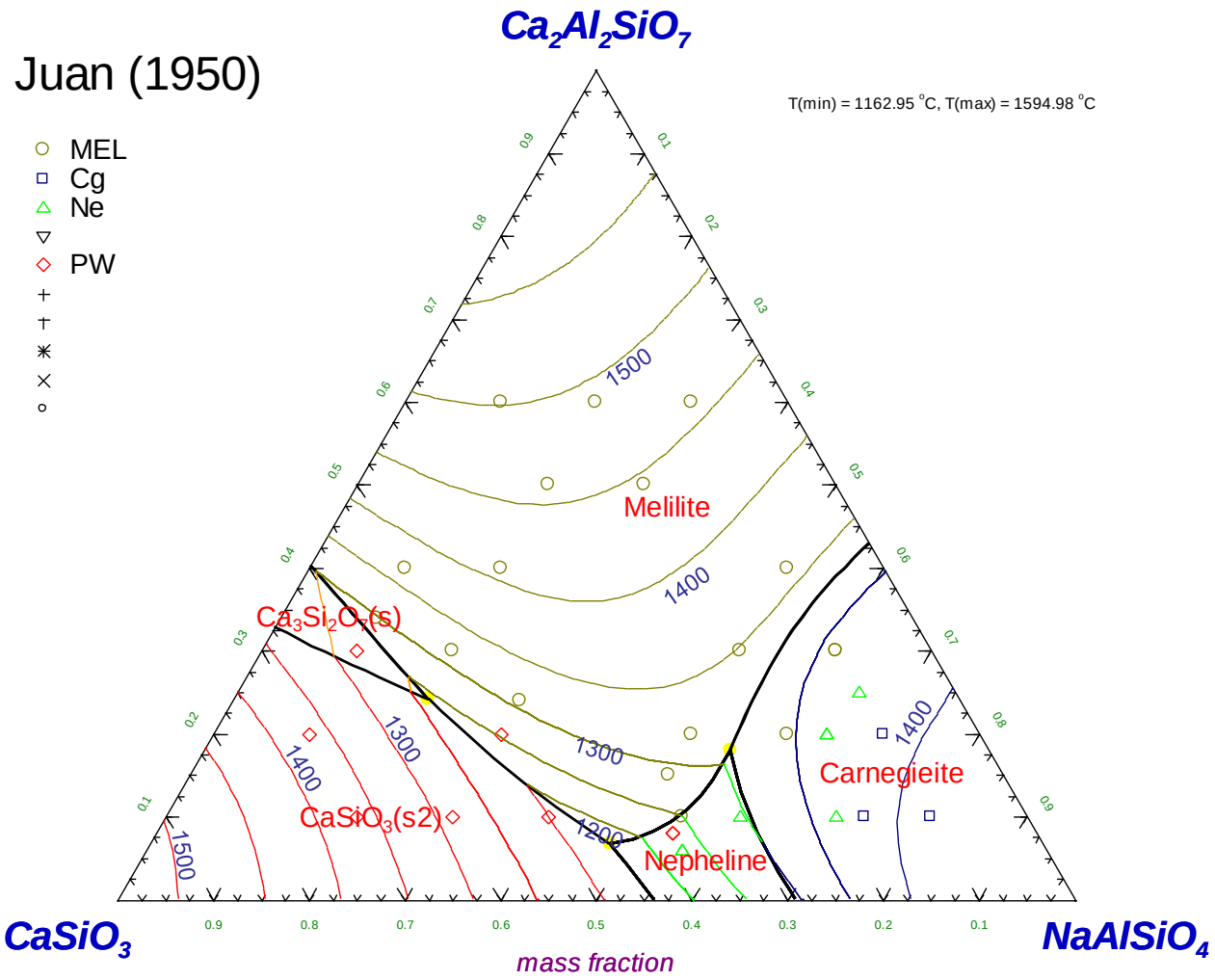




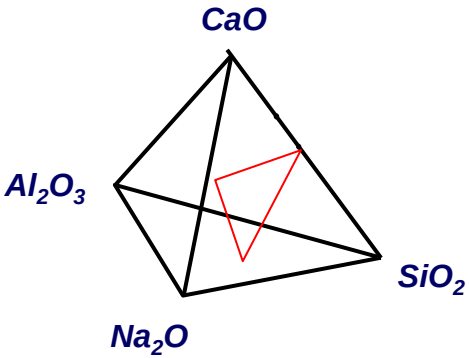
NCA2: $(Na_2,Ca)O \cdot Na_2O \cdot 2Al_2O_3$ solid solution

Important phases and phase diagrams: Na_2O-Al_2O_3-SiO_2-CaO system



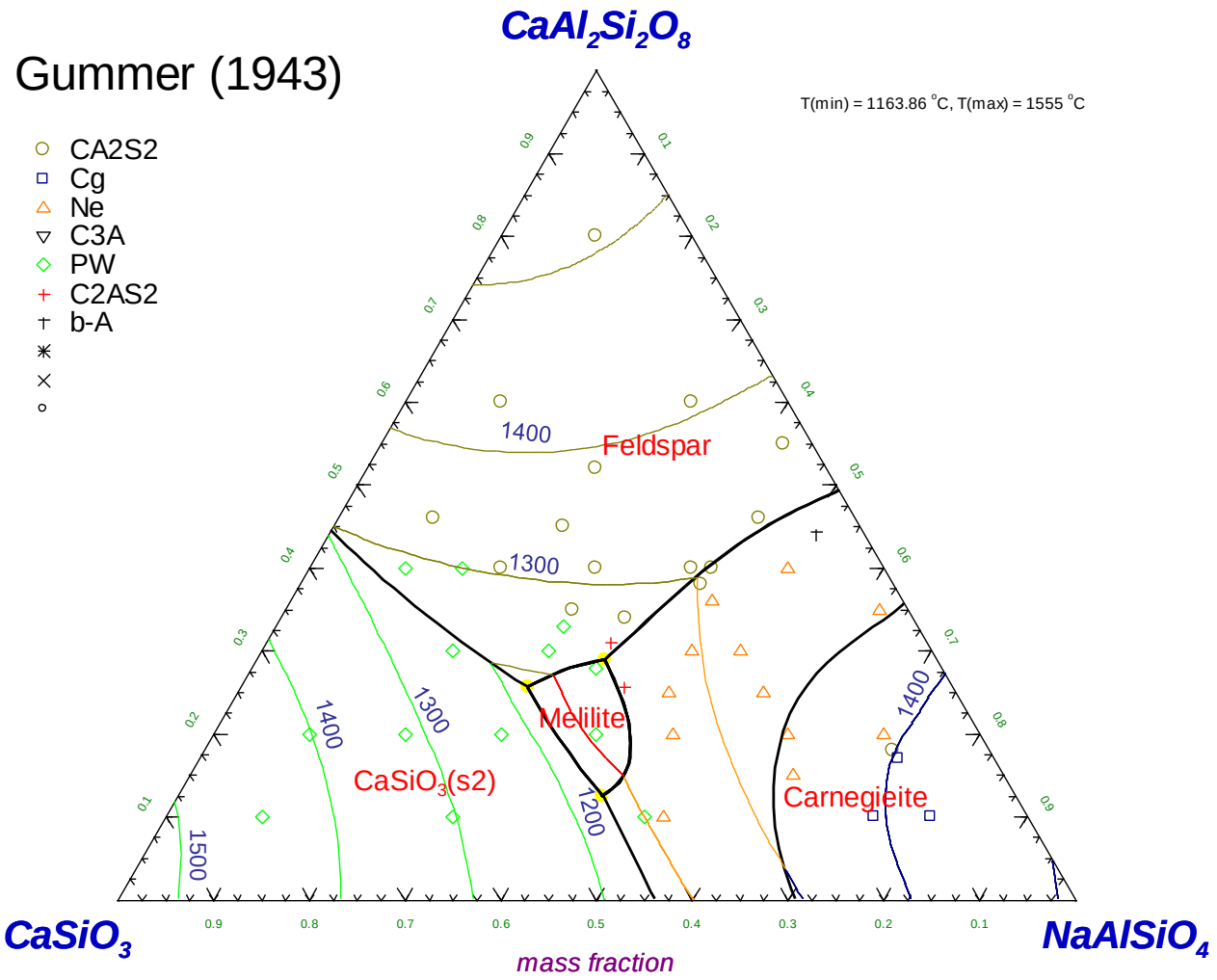


Important phases and phase diagrams: Na_2O-Al_2O_3-SiO_2-CaO system

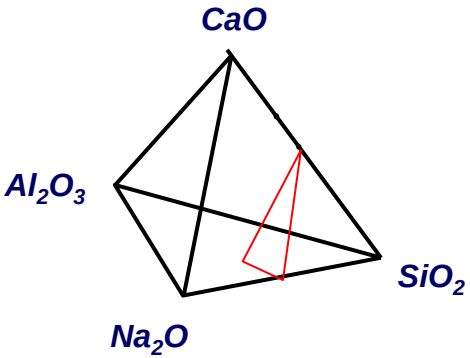


Gummer (1943)

- CA2S2
- Cg
- Ne
- C3A
- PW
- C2AS2
- b-A

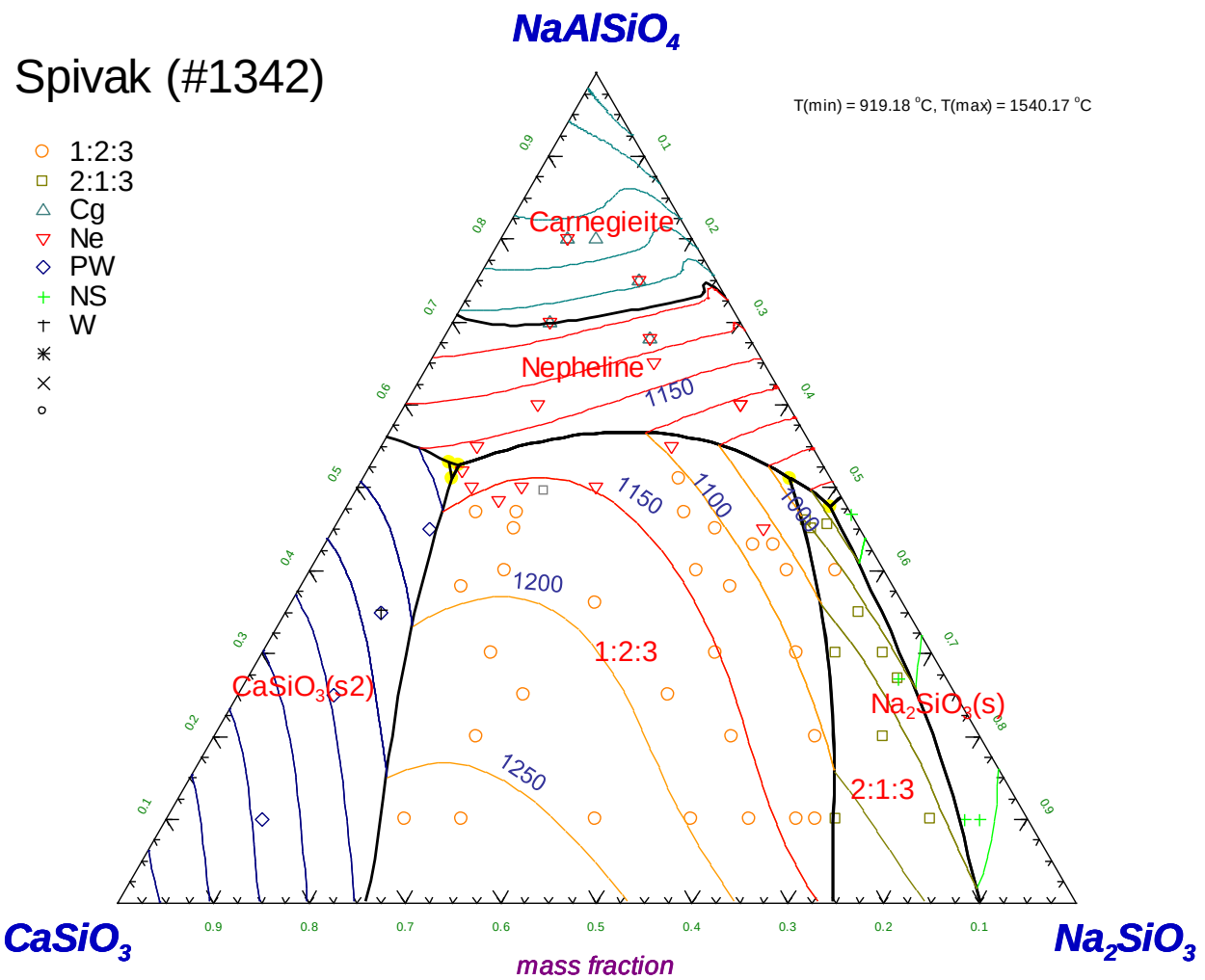


Important phases and phase diagrams: Na_2O-Al_2O_3-SiO_2-CaO system

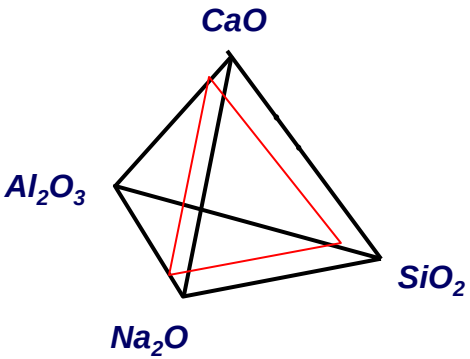


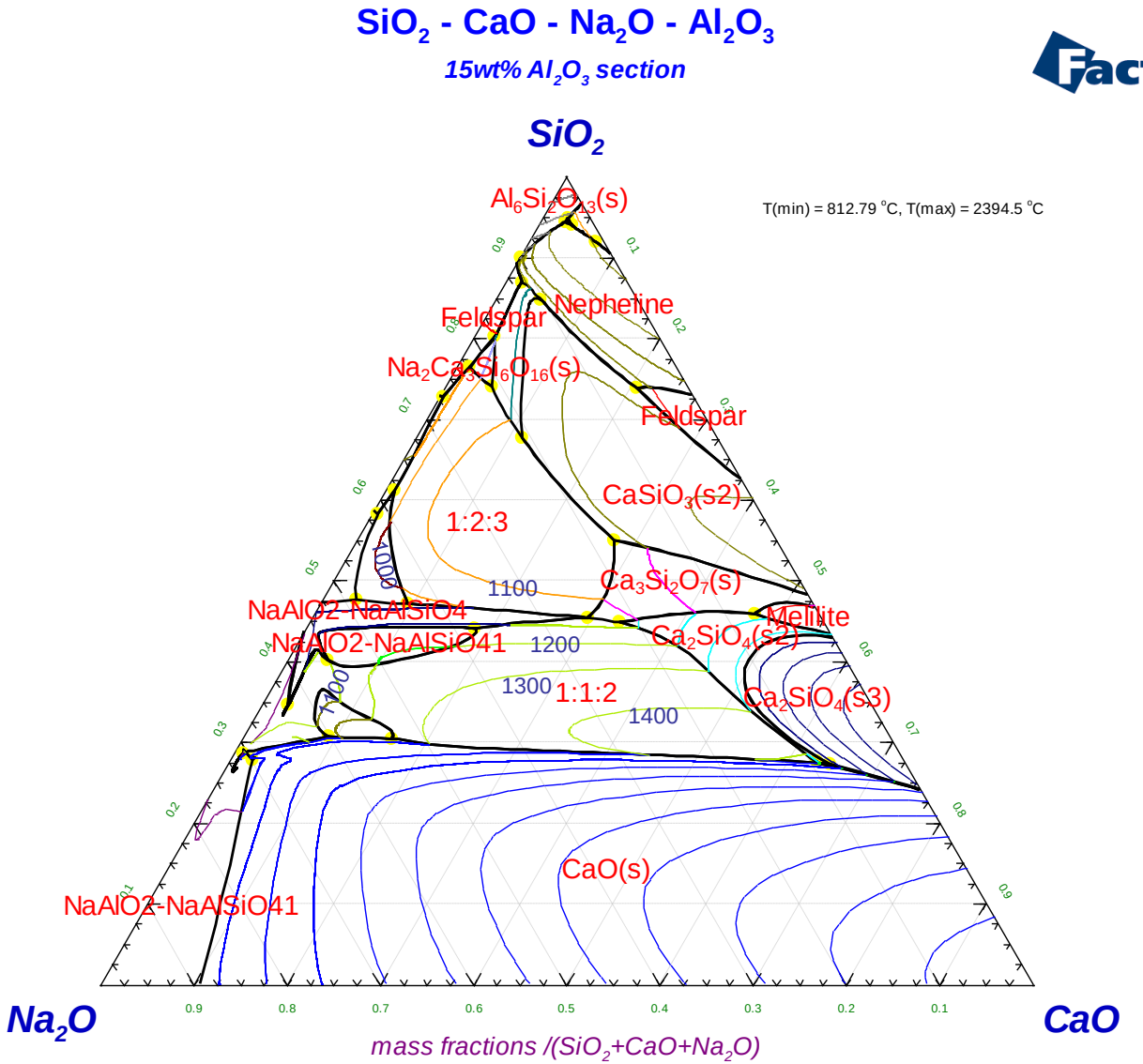
Spivak (#1342)

- 1:2:3
- 2:1:3
- Cg
- Ne
- PW
- NS
- W

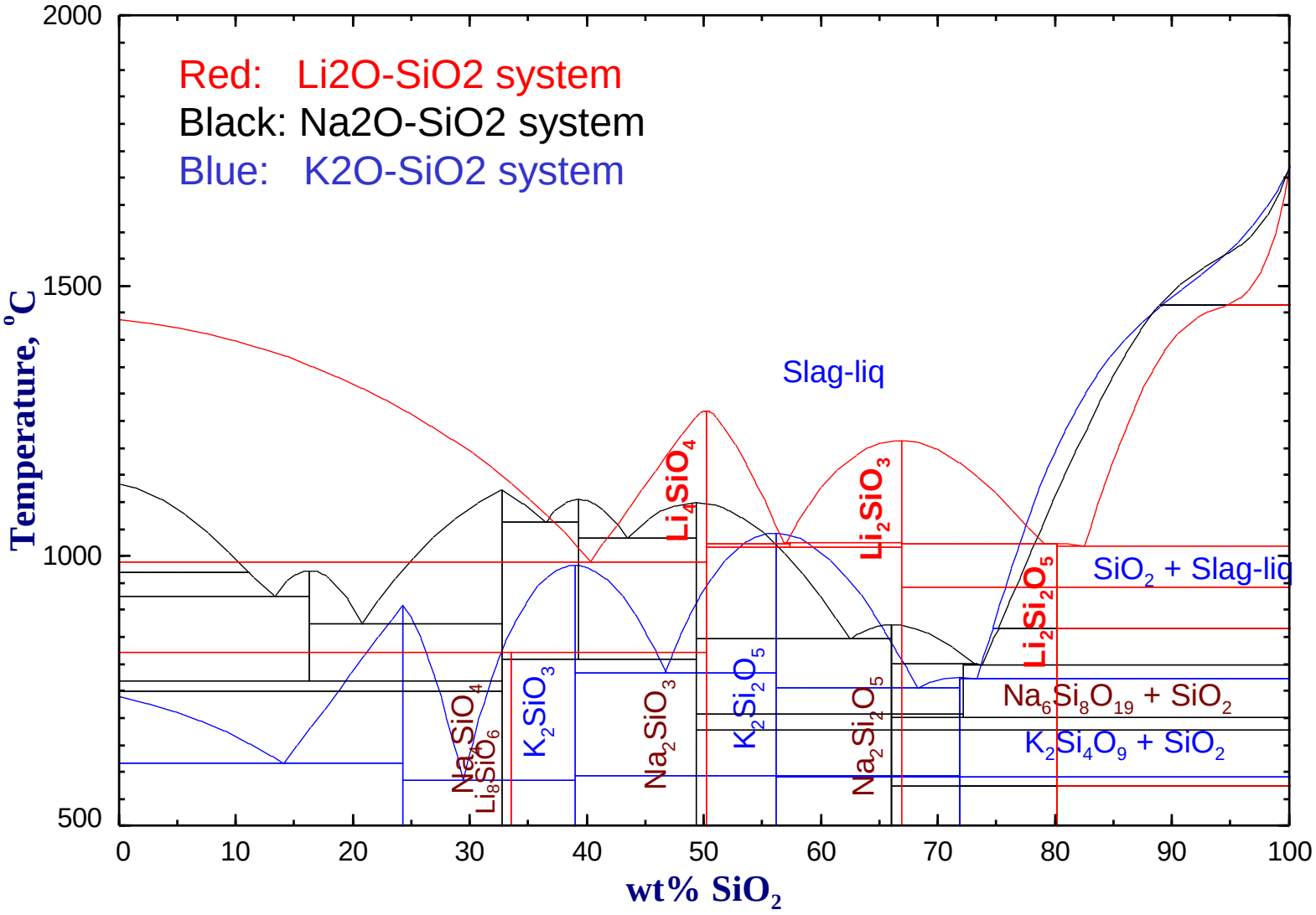


Important phases and phase diagrams: Na_2O-Al_2O_3-SiO_2-CaO system

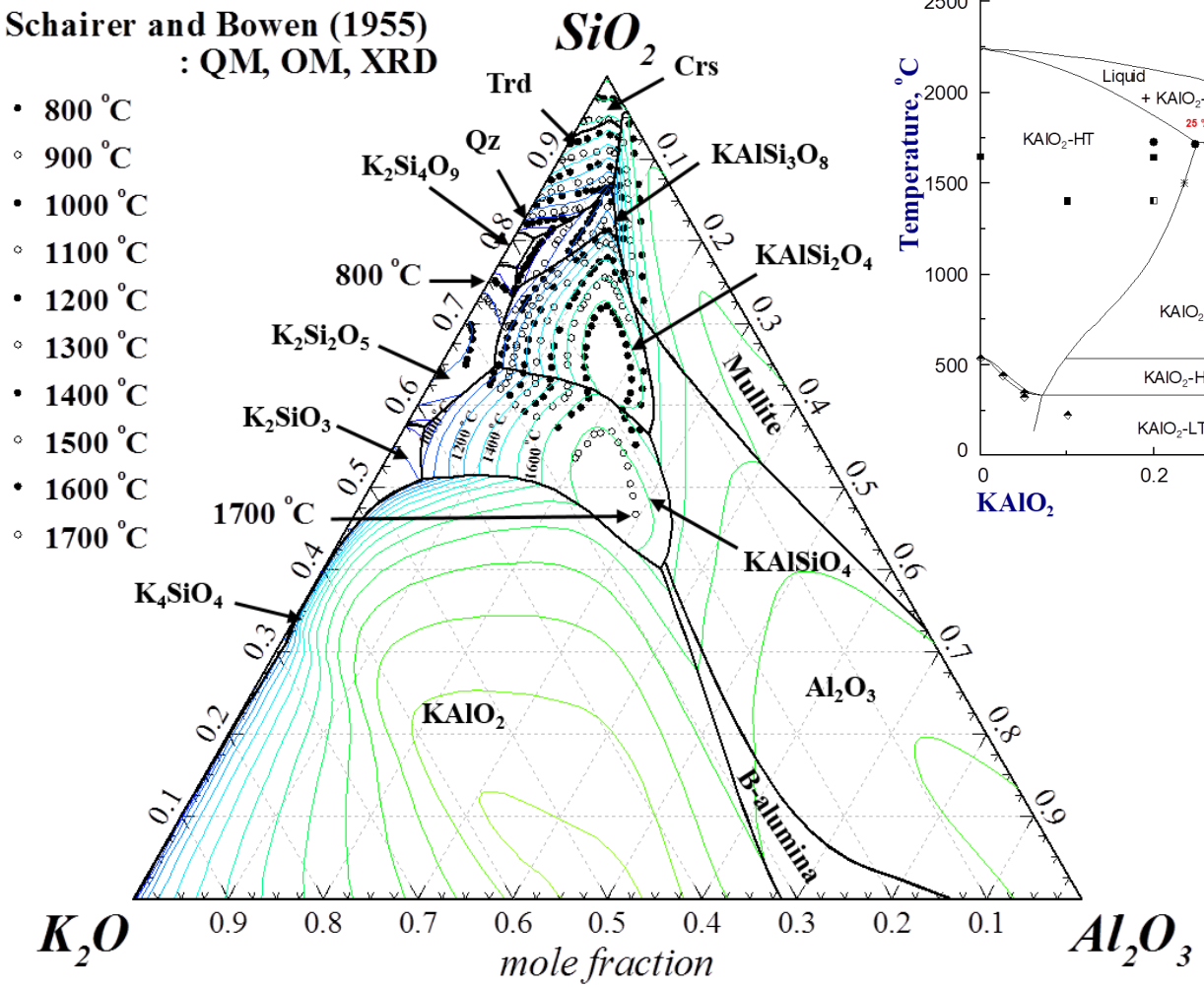


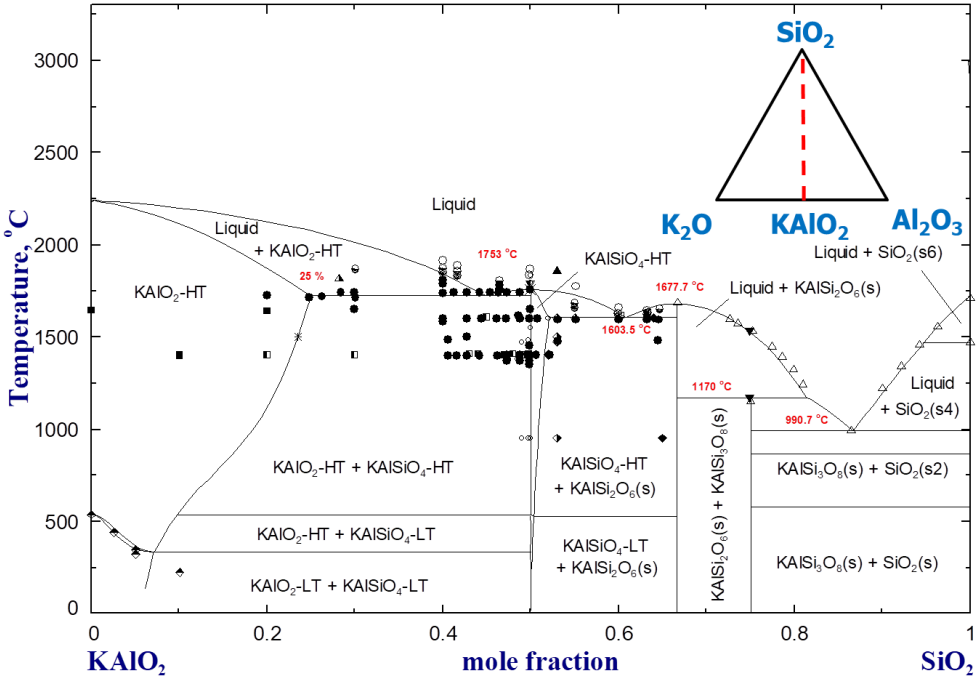


Important phases and phase diagrams: alkali-silicate system

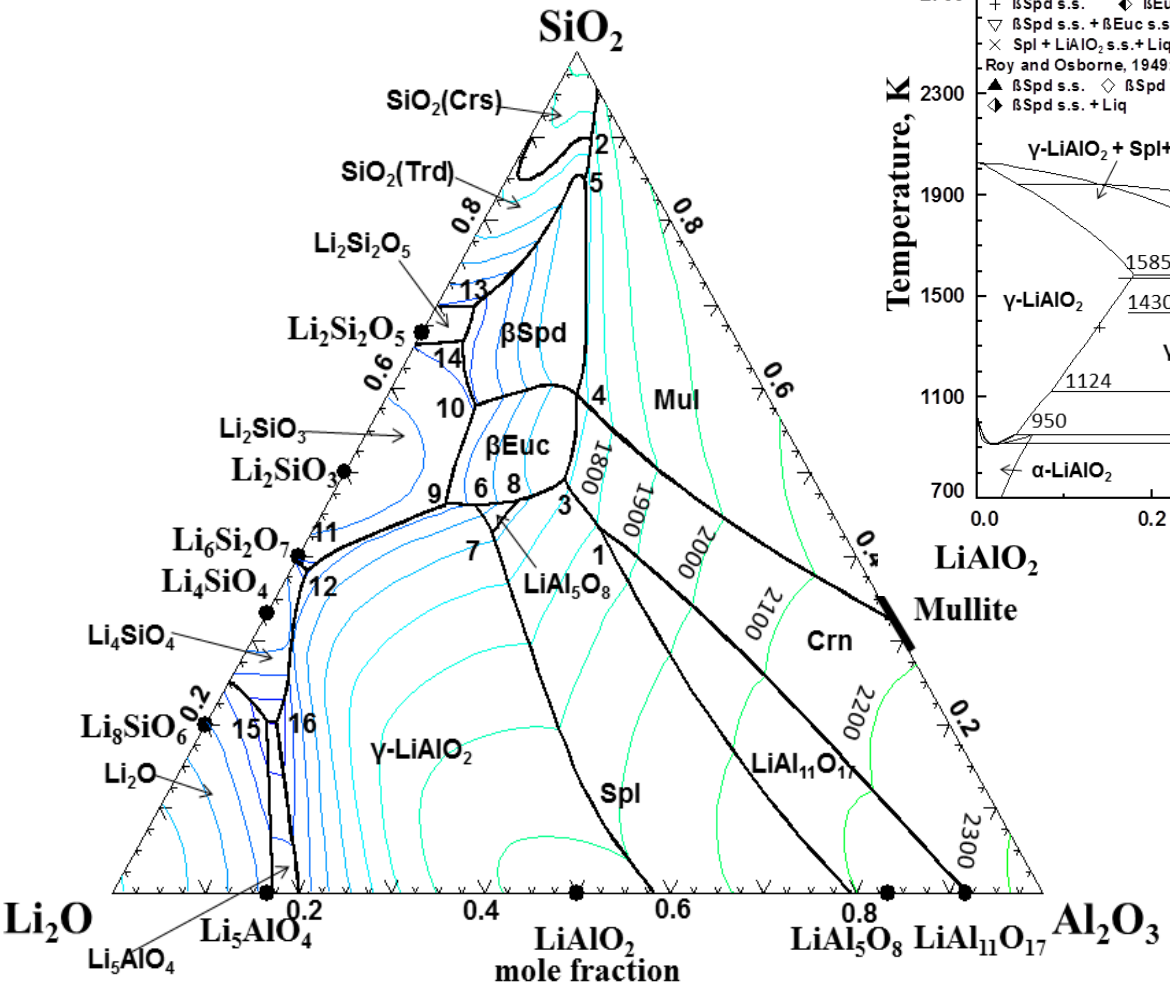


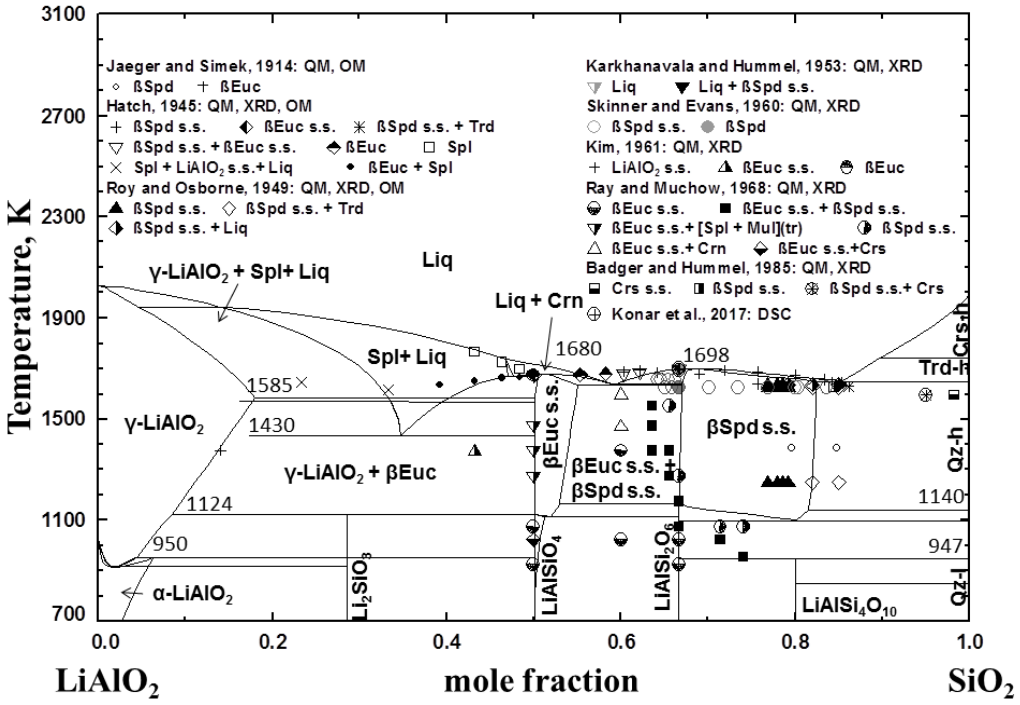
Important phases and phase diagrams: K_2O-Al_2O_3-SiO_2 system



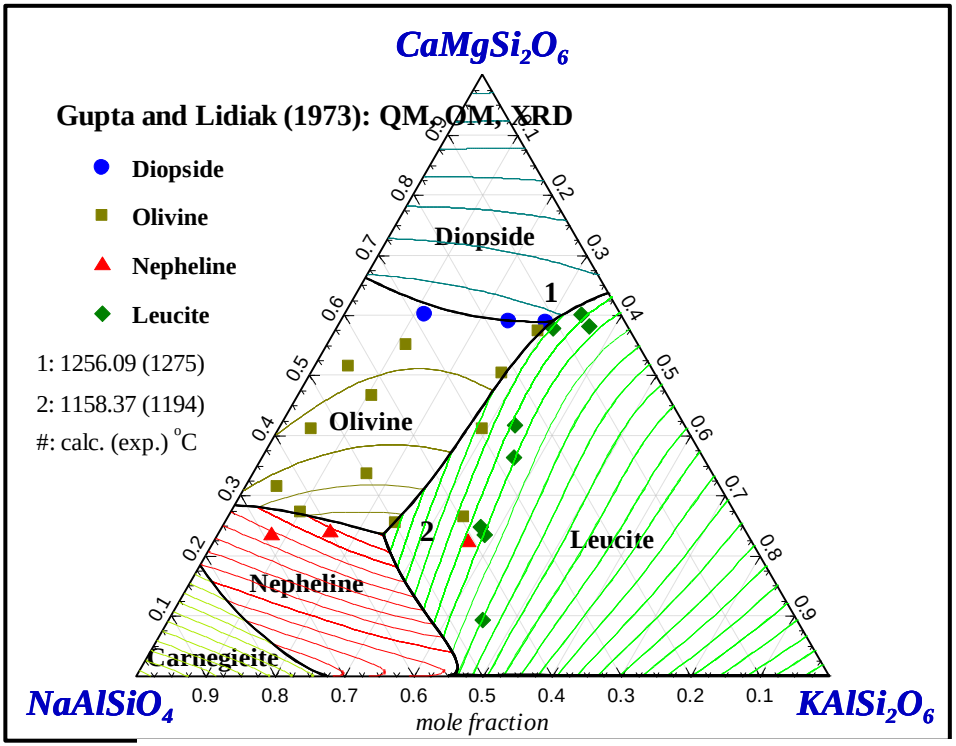


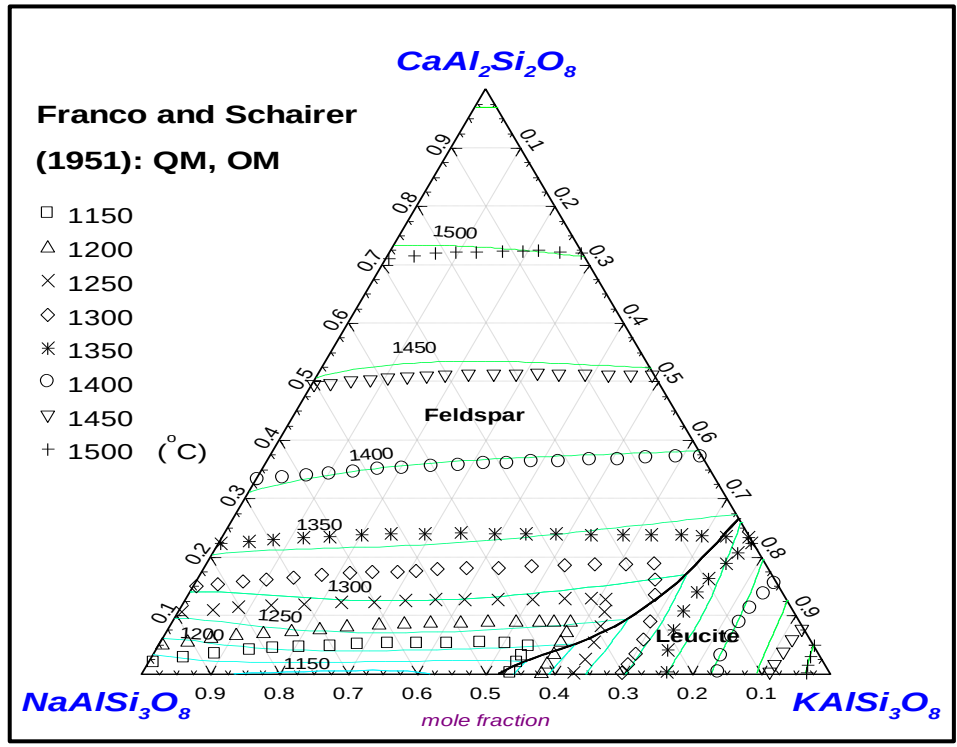
Important phases and phase diagrams: Li_2O-Al_2O_3-SiO_2 system

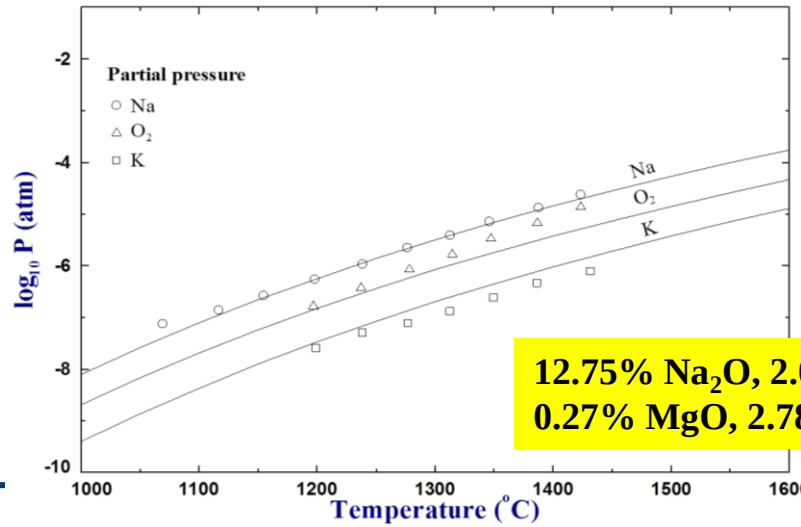




Important phases and phase diagrams: Na_2O-K_2O-Al_2O_3-SiO_2-CaO-MgO







12.75% Na_2O, 2.02% K_2O, 10.75% CaO, 0.27% MgO, 2.78% Al_2O_3, 71.39% SiO_2

Quasichemical Model for Short-Range Ordering

- **Used for the liquid oxide solution**

  SiO_2 – CaO – MgO – $AlO_{1.5}$ – FeO – $FeO_{1.5}$ – …

  - **Consider a random distribution of second-nearest-neighbor cation pairs.**
  - **Model parameters are the Gibbs energies of the pair-exchange reactions such as:**

  $[Ca\text{-}Ca]_{pair} + [Si\text{-}Si]_{pair} = 2\,[Ca\text{-}Si]_{pair}$ $\quad \Delta g_{CaSi} < 0$

  This is equivalent to $O^{2-} + O^o = 2O^-$

$$G = \left(n_{SiO_2} G^0_{SiO_2} + n_{CaO} G^0_{CaO} + \cdots\right) - T\,\Delta S^{config} + \sum_{n>m} n_{mn}\left(\Delta g_{mn}/2\right)$$

where : n_i, G_i^0 = number of moles and Gibbs energy of component i in solution

n_{mn} = number of moles of [m-n] pairs at equilibrium

ΔS^{config} = (Ising) entropy for random distribution of pairs = function of n_i and n_{mn}

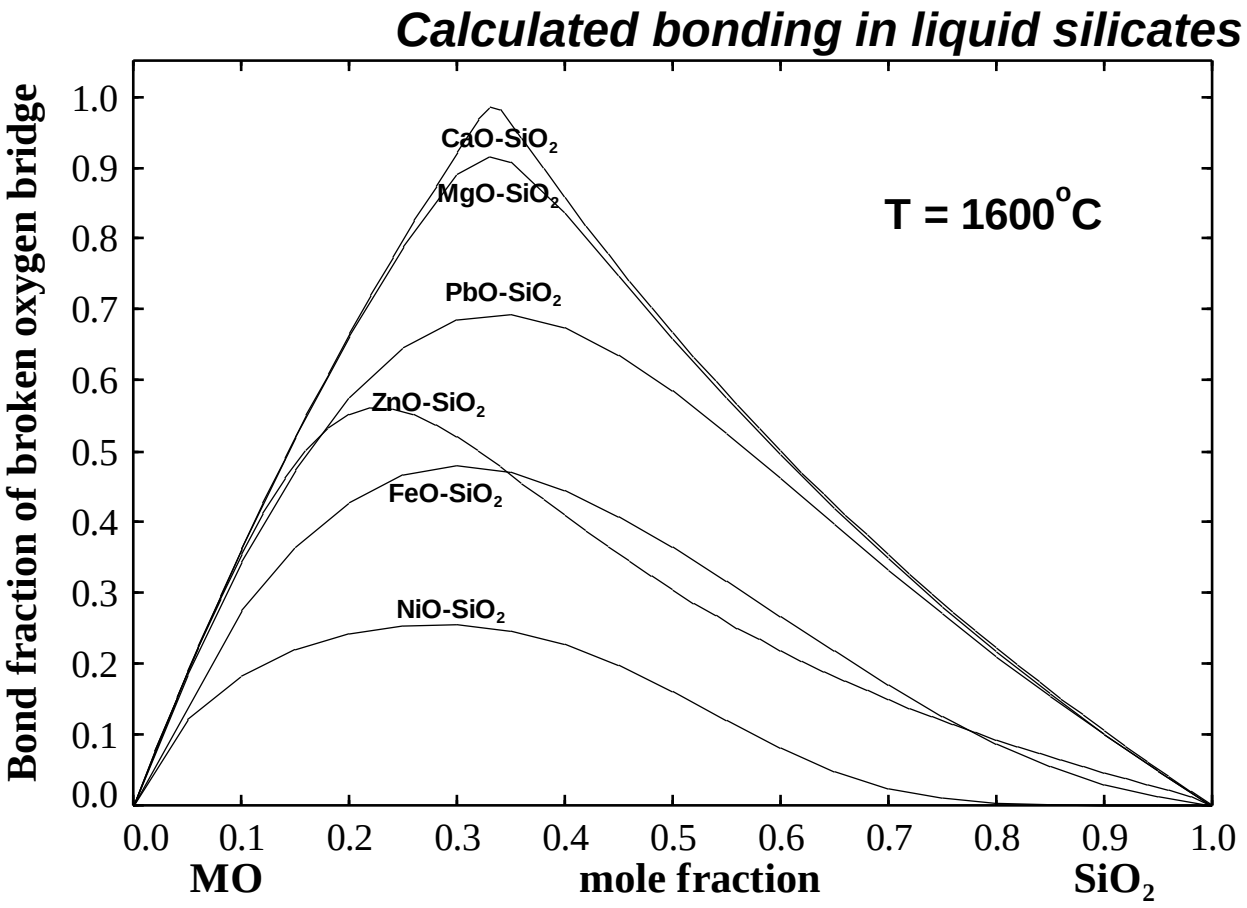
Δg_{mn} = binary model parameters (which may be functions of composition and T)

(The equilibrium values of n_{mn} are obtained by setting $\partial G/\partial n_{mn} = 0$ at constant n_i)

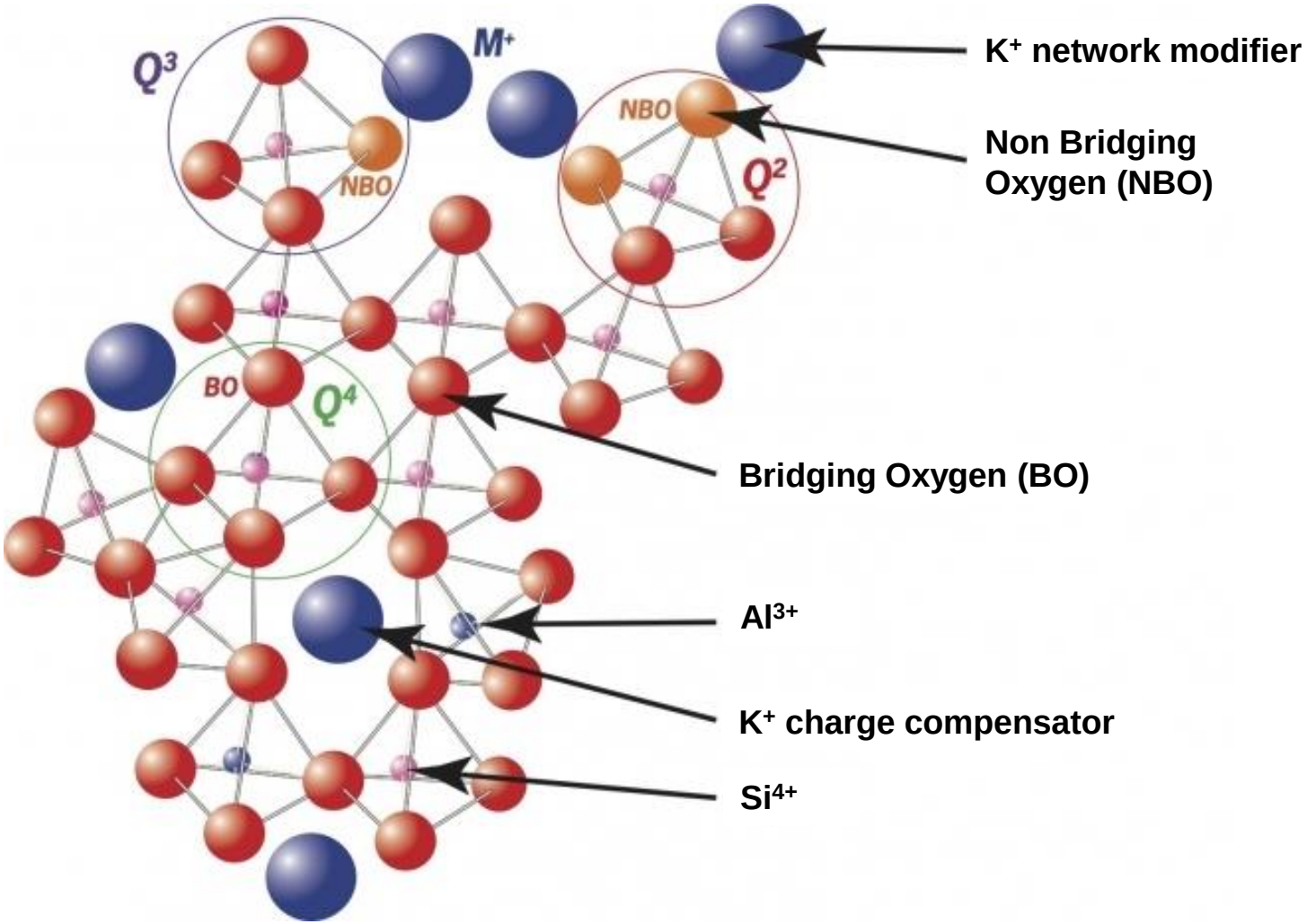
Silicate Slag: Network structure

-Consideration of Second Nearest Neighbor Short-Range-Ordering-

$$O^0 + O^{2-} = 2\ O^-$$

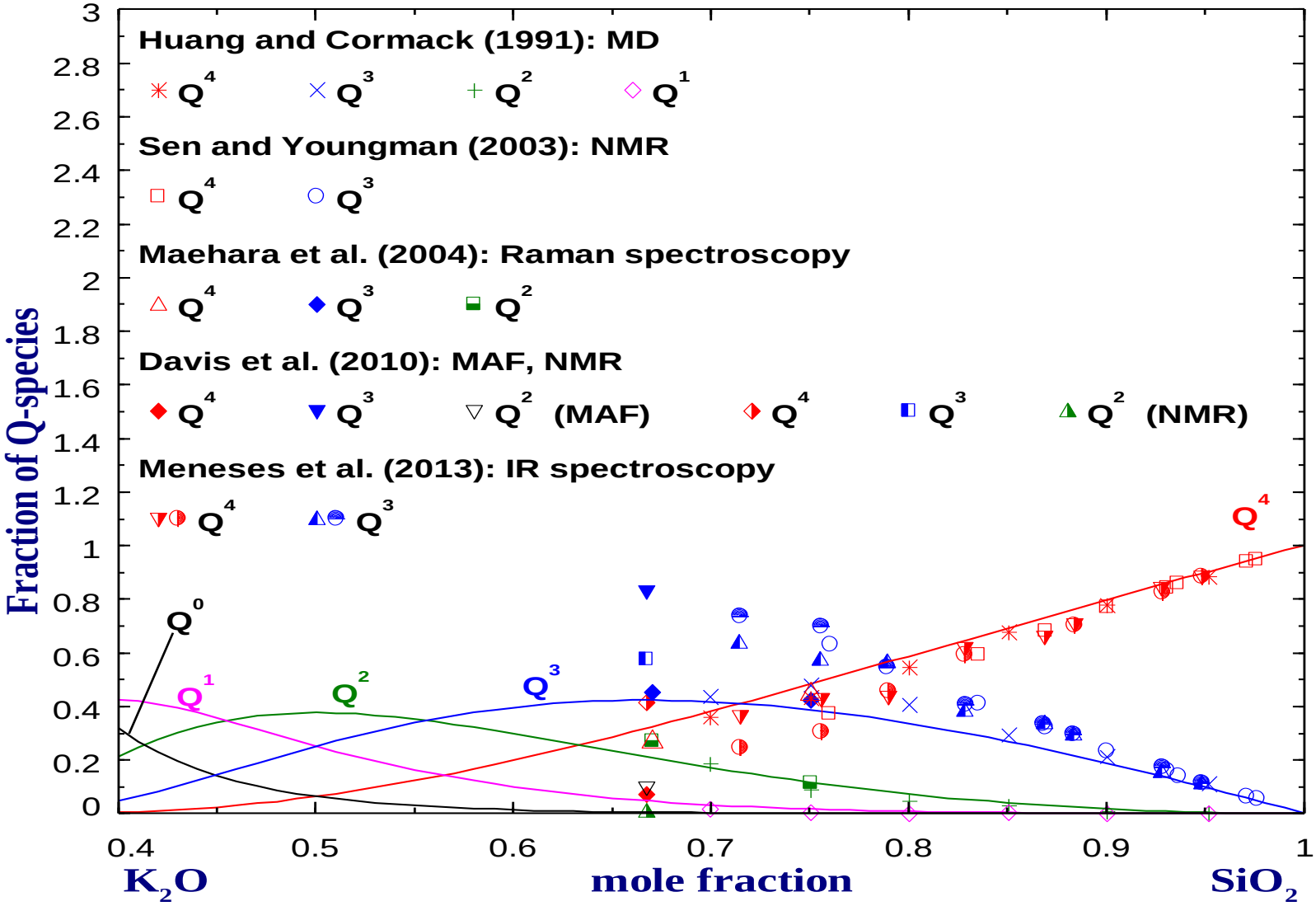


Q-species and charge compensation effect

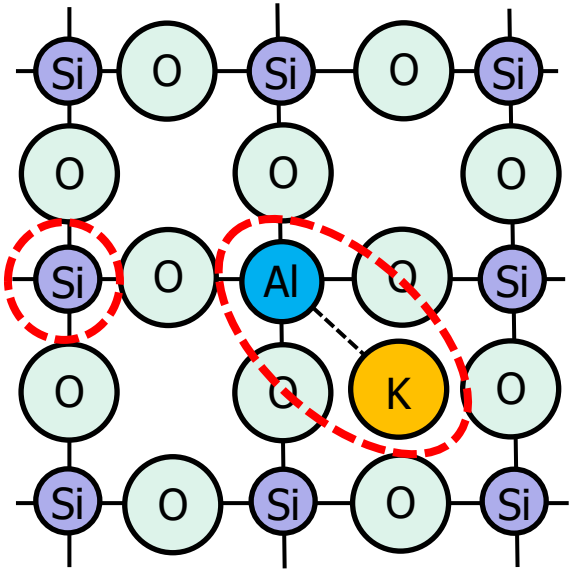


[Le CNRS Jan2014: http://www.insu.cnrs.fr/images/9757]

Calculated Q-species amount in K_2O-SiO_2 melt



The N_2O-SiO_2-Al_2O_3 system (N = Na, K, Li,…)



In the Model (MQM)

- Associate NAl^{4+} was introduced
- Replacement of Si^{4+} by Al^{3+} in quasi-lattice sites is assisted by N^{+}.

Closely reproduce the nature of the aluminosilicate melt

Charge compensation effect:

$Al^{3+} + N^{+} = NAl^{4+}$ replacing Si^{4+} in silicate melts

Application of Structural information from MQC model

Thermodynamic database(MQM)

Slag network structure

Good physical property model:
- **Model parameters for binary or ternary systems**
- **Accurate Prediction in higher order systems**

Physical properties
- **Viscosity**
- **Molar volume**
- **Electrical conductivity**

Others
- **Diffusivity**
- **Thermal conductivity**
- **…..**

Slag Viscosity: Structural Viscosity Model

Modified Quasichemical Model

→Bond fraction (Silicate network structure)

→Activation energy of bond breaking reaction: Binary parameters + Association energy for $M^{+}Al^{3+}$ replacing Si^{4+} in silicate network

→Prediction of multicomponent systems (oxide and oxy-fluoride)

→Heterogeneous (solid + liquid): Einstein-Rosco equation

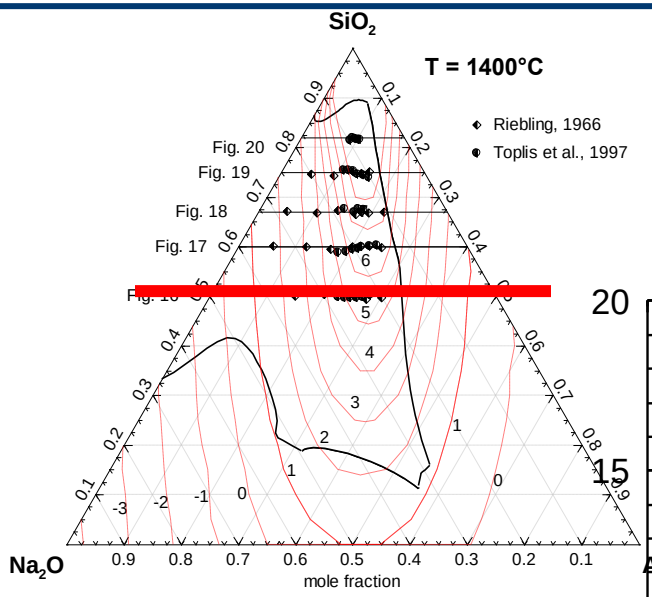
Database for molten slag

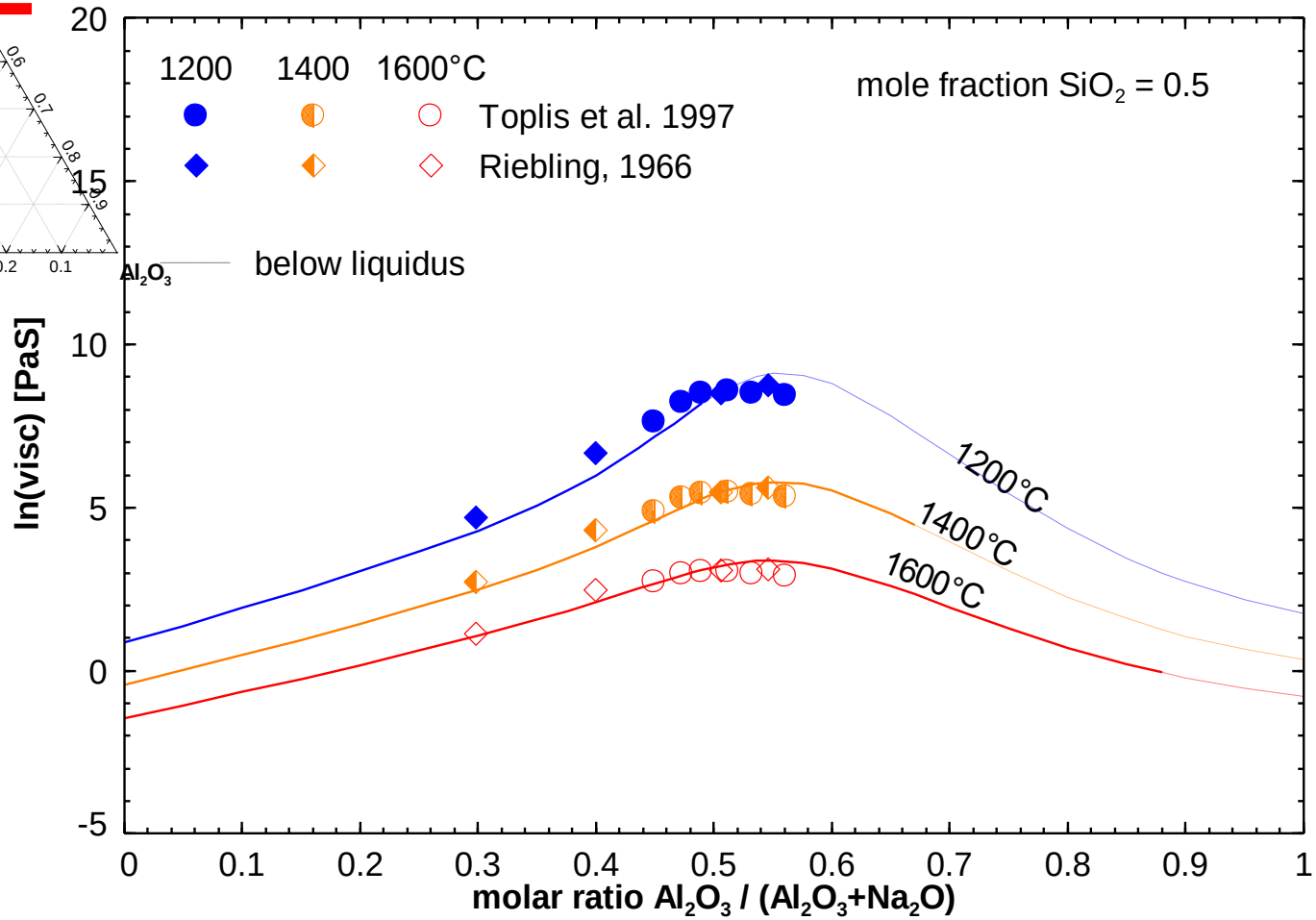
$CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3\text{-}FeO\text{-}Fe_2O_3\text{-}MnO\text{-}TiO\text{-}TiO_2\text{-}Na_2O\text{-}K_2O\text{-}Li_2O\text{-}B_2O_3\text{-}F$ (-PbO-NiO)

Database for glass (supercooled melt)

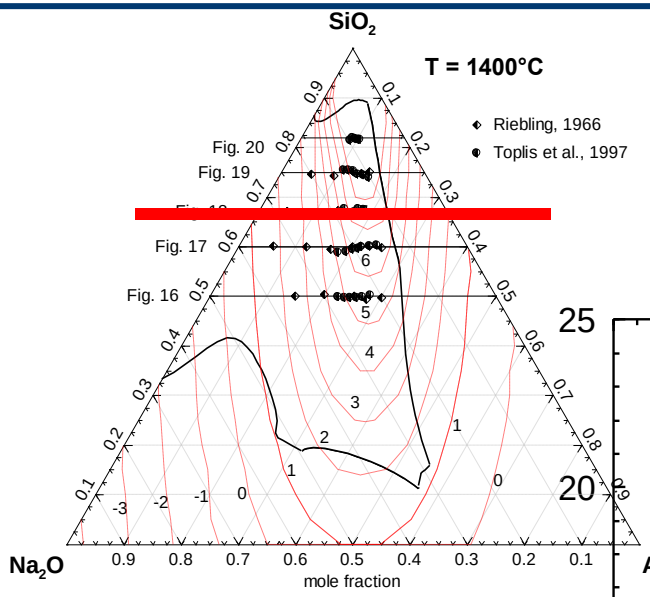
$CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3\text{-}Na_2O\text{-}K_2O\text{-}B_2O_3\text{-}PbO\text{-}\ldots$

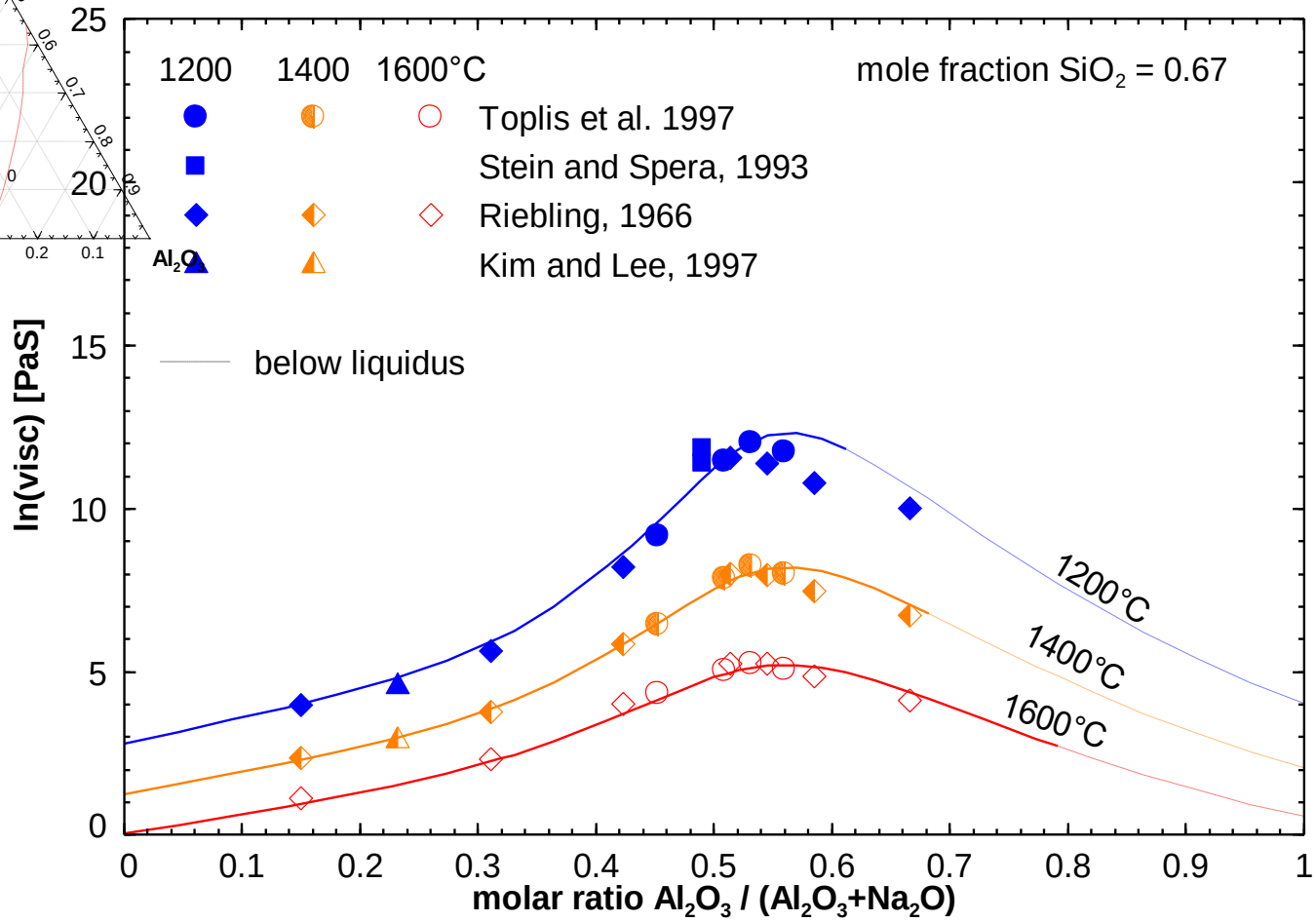
The Na_2O-Al_2O_3-SiO_2 system



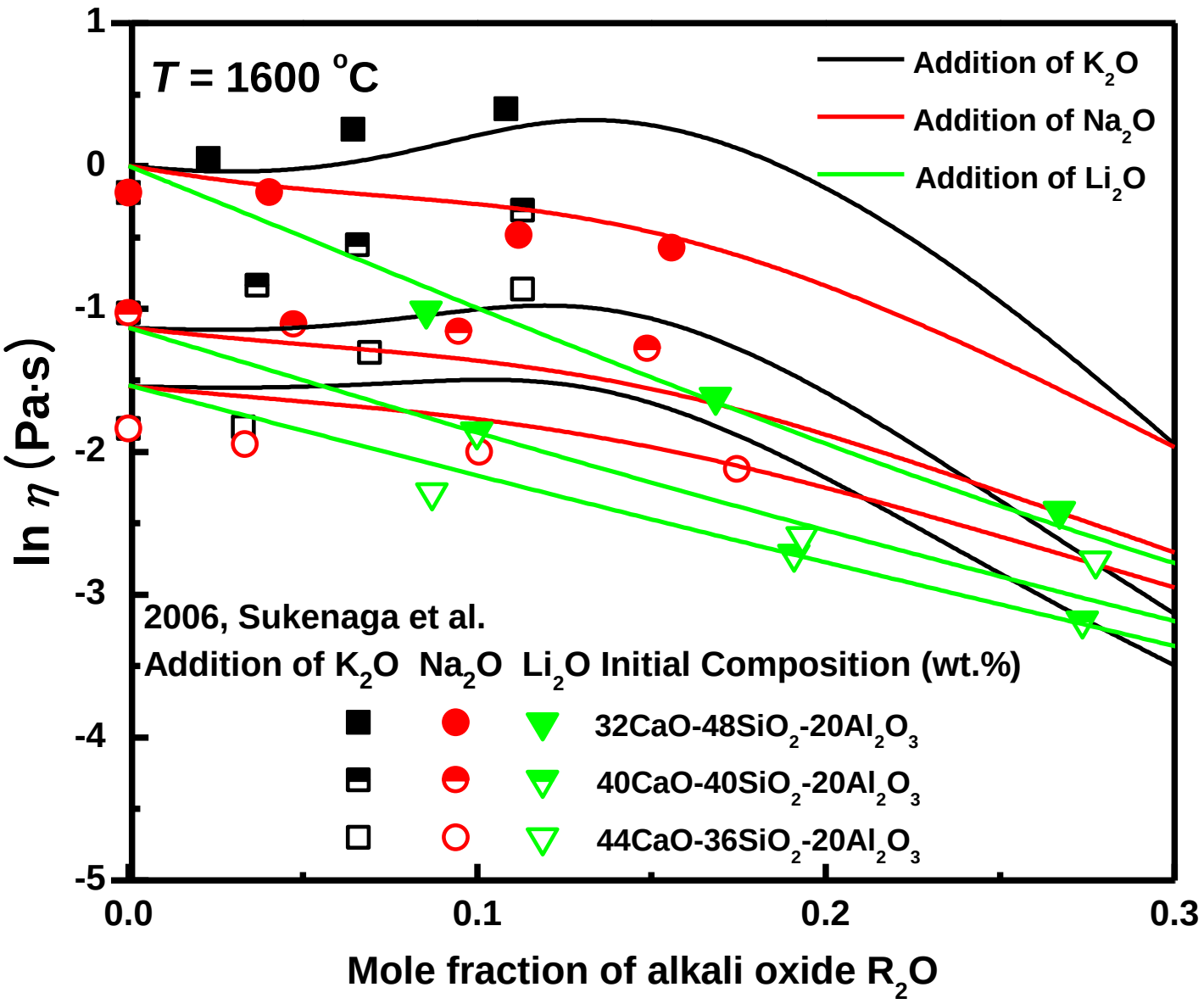


The Na_2O-Al_2O_3-SiO_2 system





Viscosity of $CaO-Al_2O_3-SiO_2-R_2O$ (R=K, Na, Li)



Viscosities of various systems