Structure and Thermodynamics of Liquid Oxides

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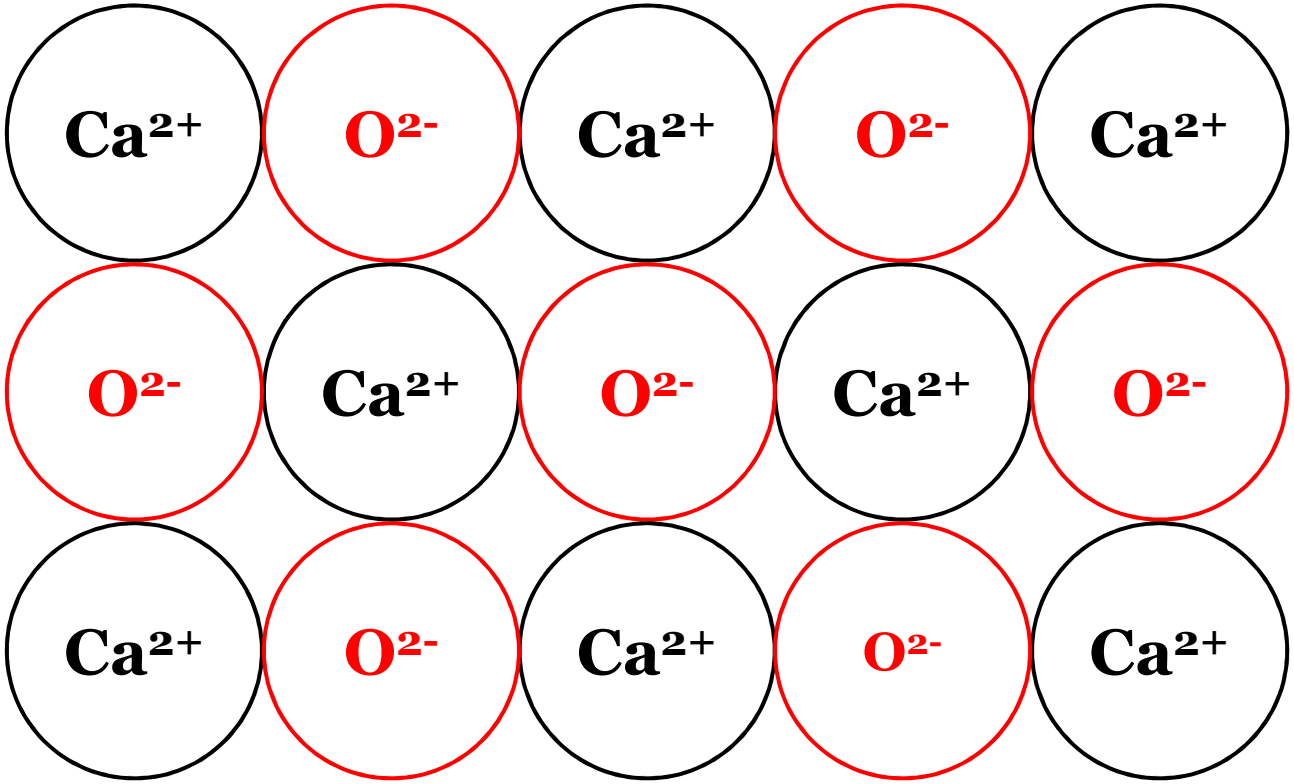
May 18, 2010

Ionic ("Basic") Oxides



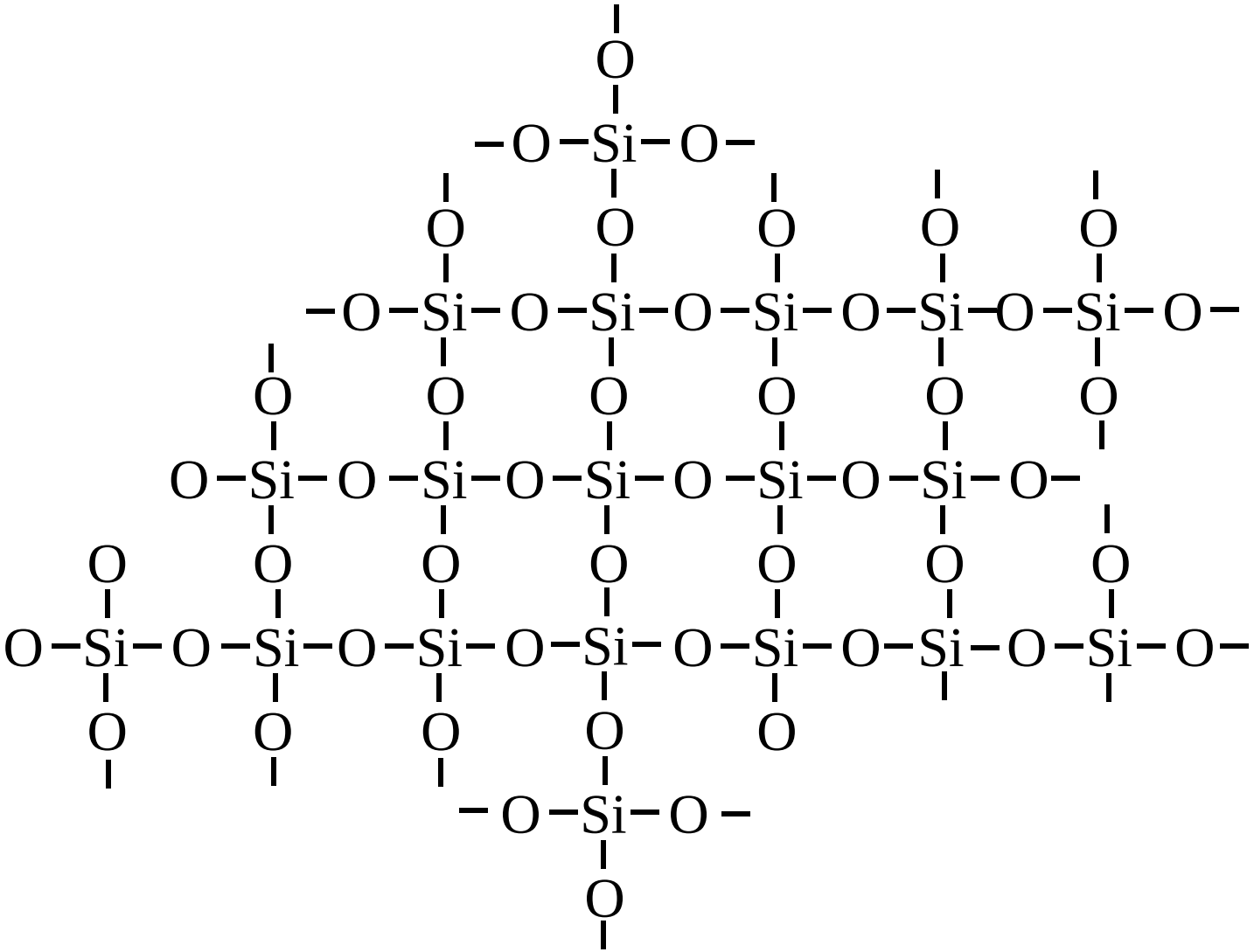
CaO, MgO, FeO, MnO, ...

Na_2O, K_2O, ...

Acidic Oxides (network formers)

- Tetrahedral:
  SiO_2, GeO_2
- Trigonal:
  B_2O_3
- Complex:
  P_2O_5

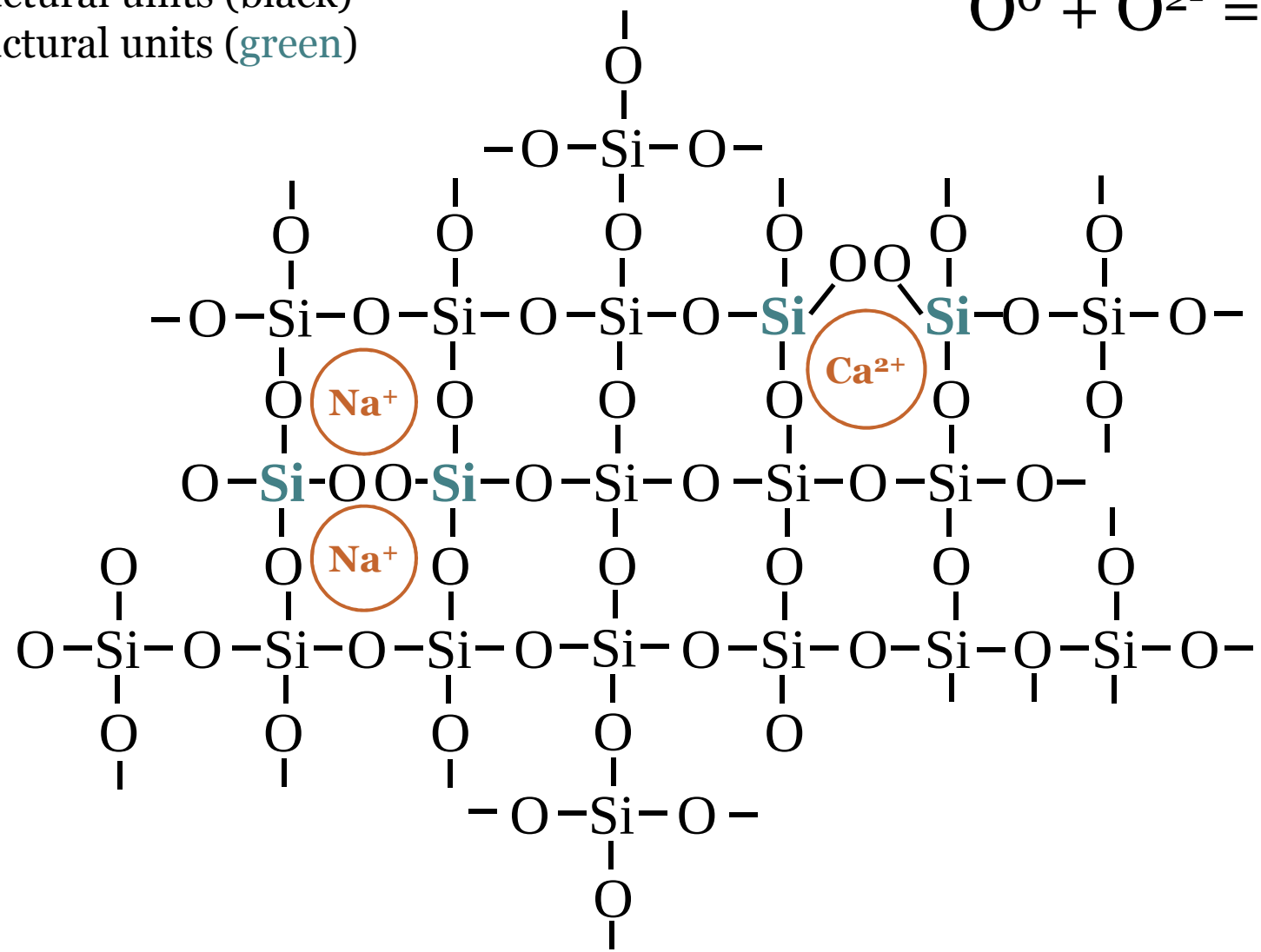
Structure of SiO_2



Network Modification by Basic Oxides

Q^4 structural units (black)
Q^3 structural units (green)

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



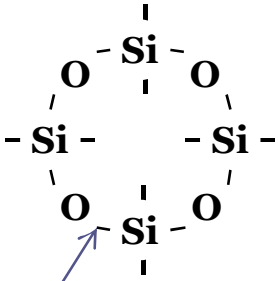
Structure of CaO-SiO_2 Liquid Solutions

Composition →

CaO — Ca_2SiO_4 — SiO_2

mainly
Ca^{2+}, O^{2-}, SiO_4^{4-}

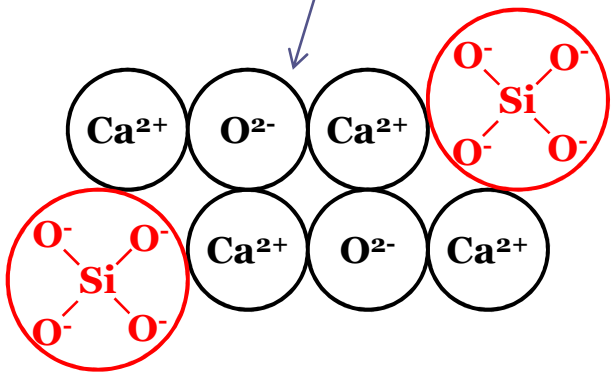
mainly
Ca^{2+},
SiO_4^{4-} (orthosilicate ions)

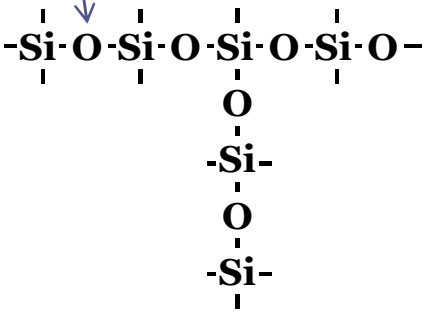


linear + branched
chain polymers

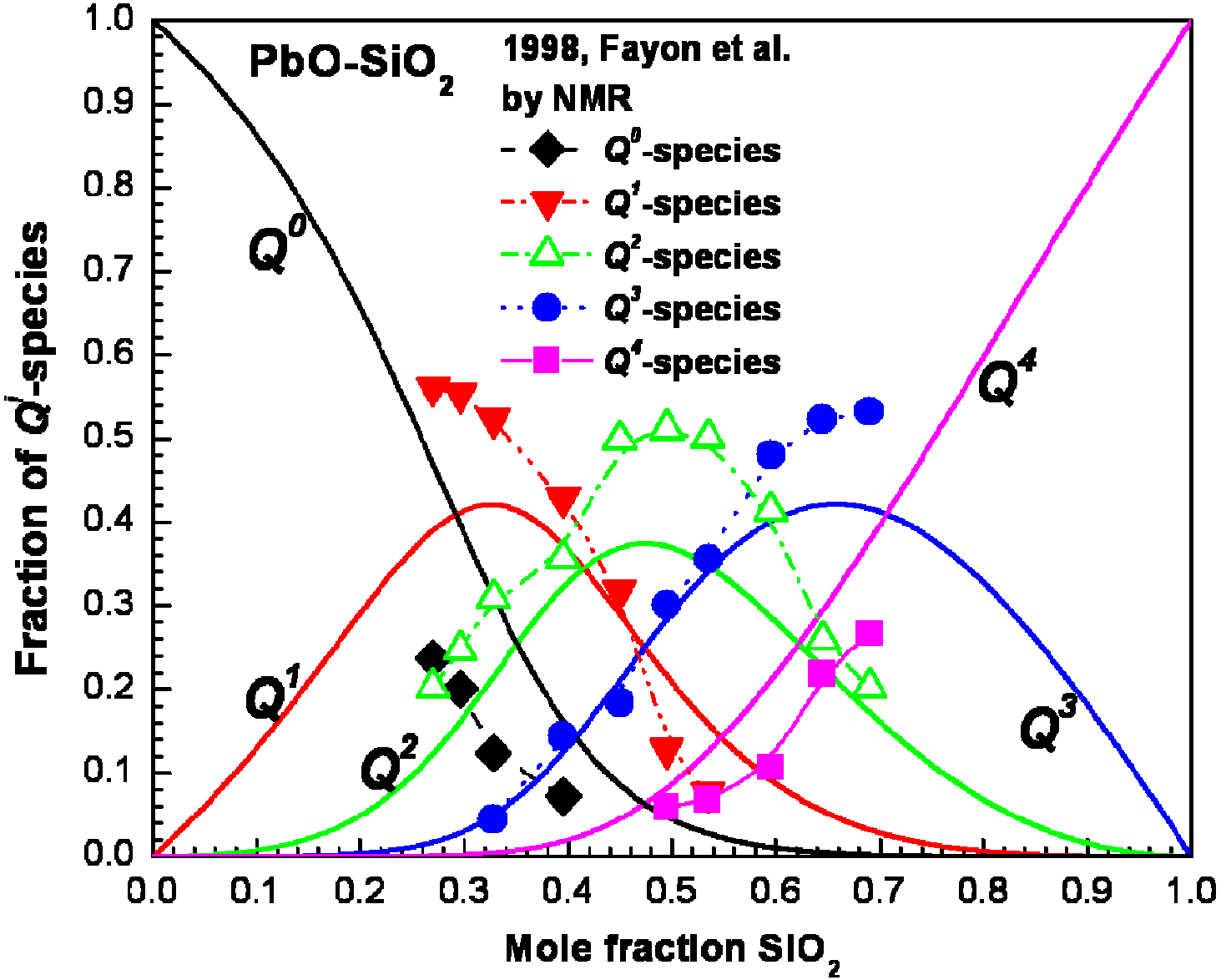
ring polymers

3-dimensional
network

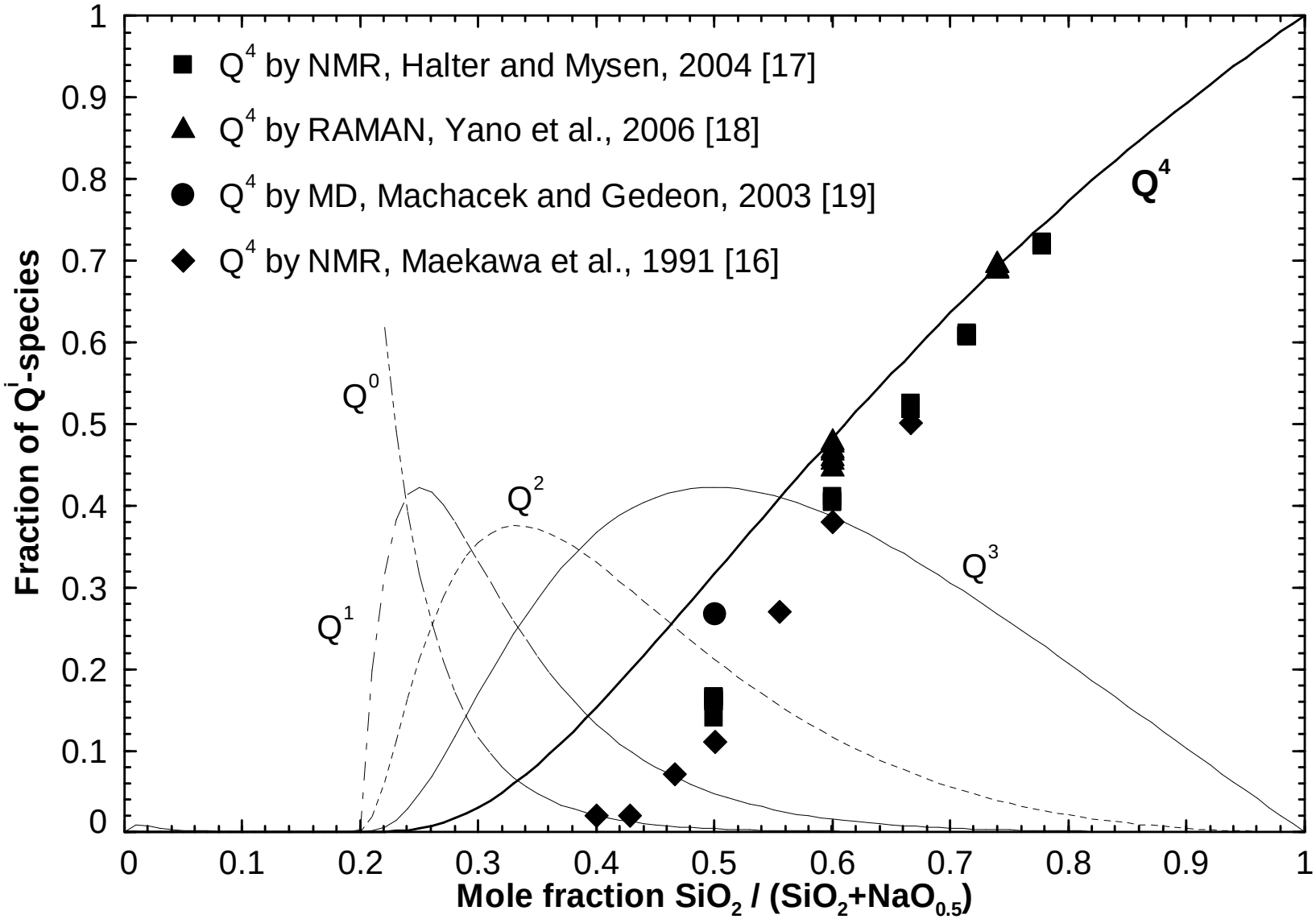




Fractions of Q Species as Measured by NMR



The System $NaO_{0.5}$-SiO_2
Measured Fractions of Q^4 Species



Thermodynamic Properties as Functions of Composition

$SiO_2 + 2MO = M_2SiO_4$ (M = Ca, Mg, Fe, Mn, ...)

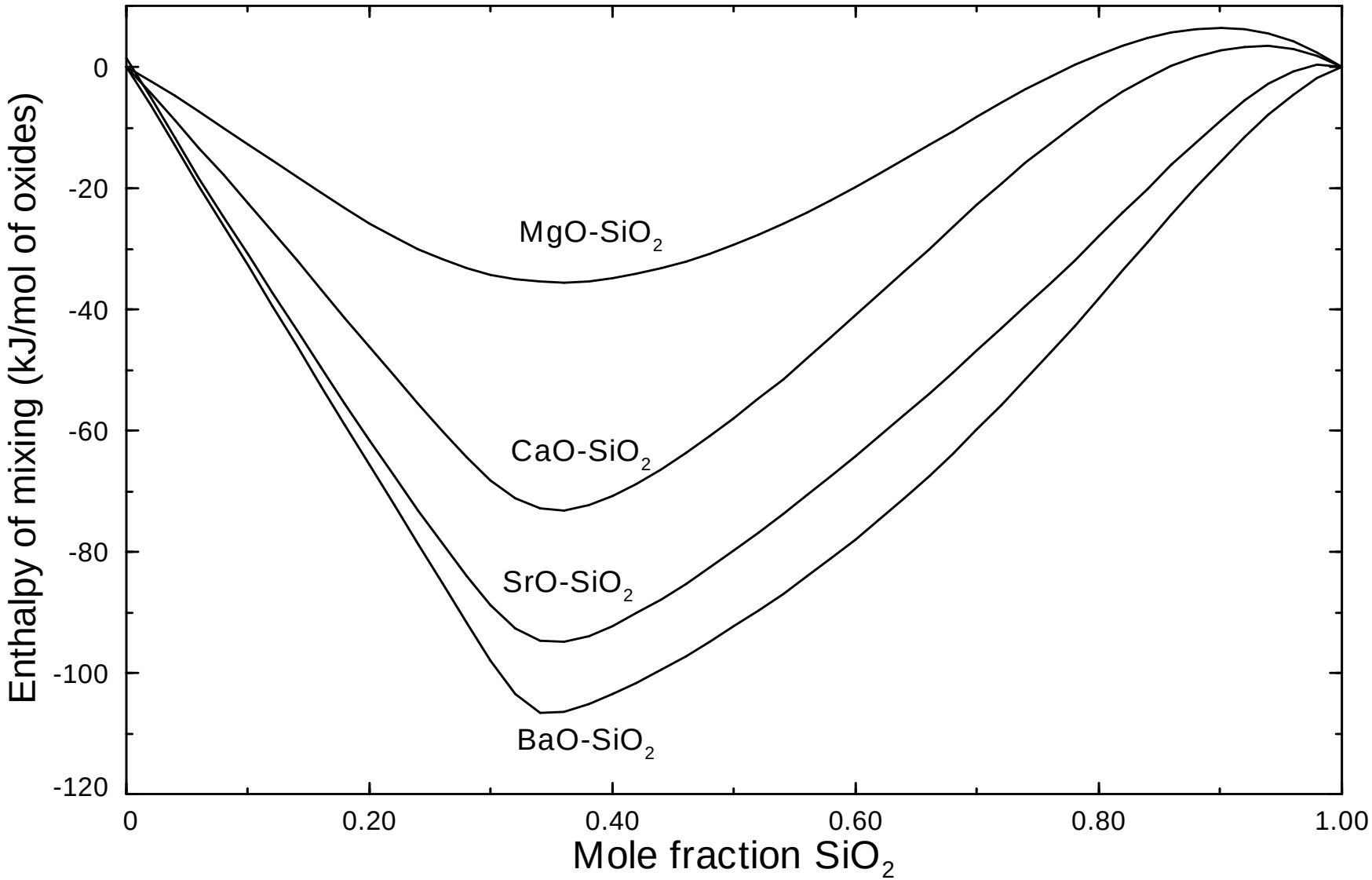
$SiO_2 + 2M_2O = M_4SiO_4$ (M = Li, Na, K, ...)

$Si - O - Si + O^{2-} = Si - O^- + {}^-O - Si$

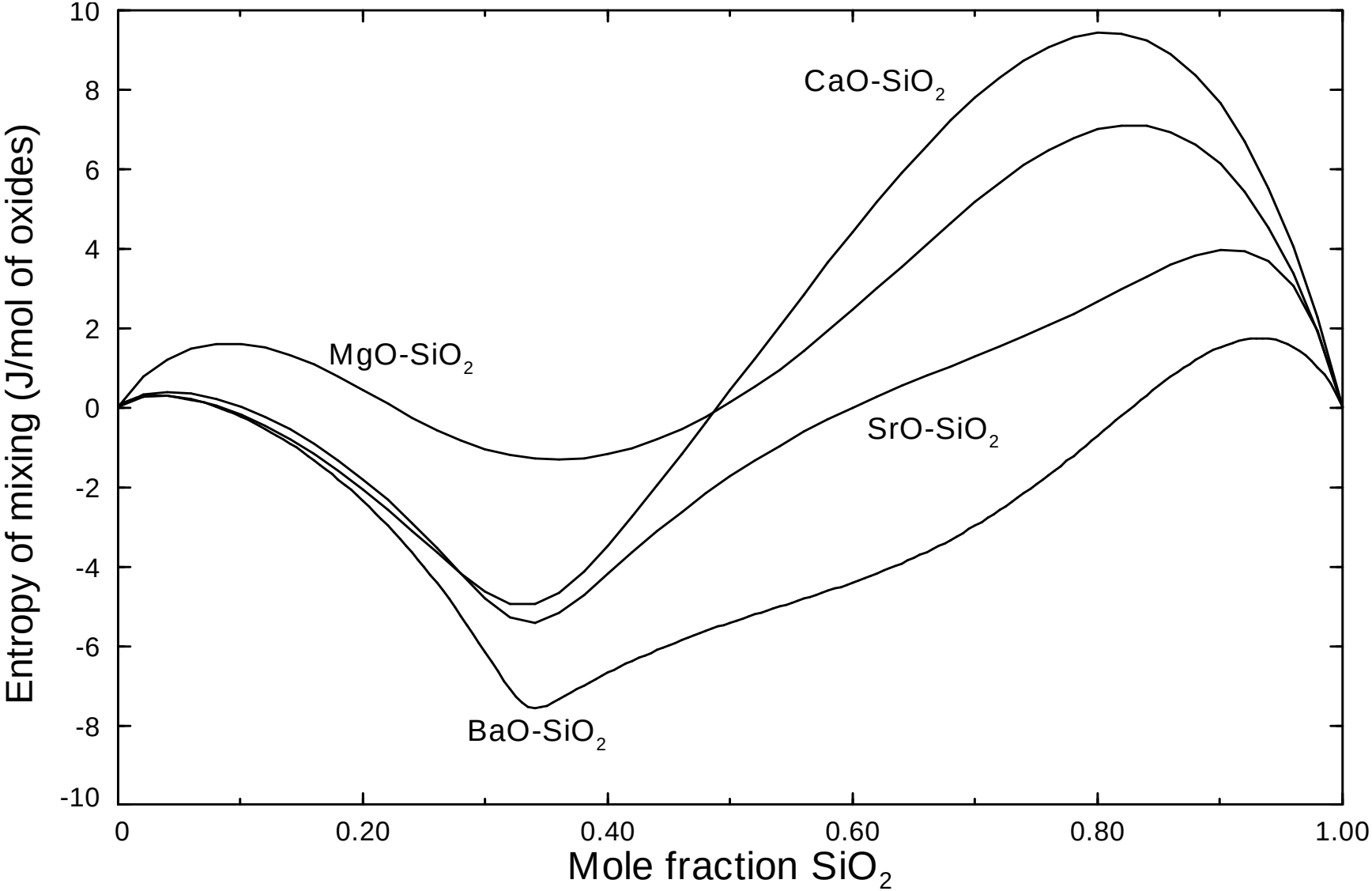
$O^0 + O^{2-} = 2O^-$

$\Delta H \ll 0$
$\Delta G \ll 0$

Enthalpy of Mixing in Liquid Alkaline-earth Silicates

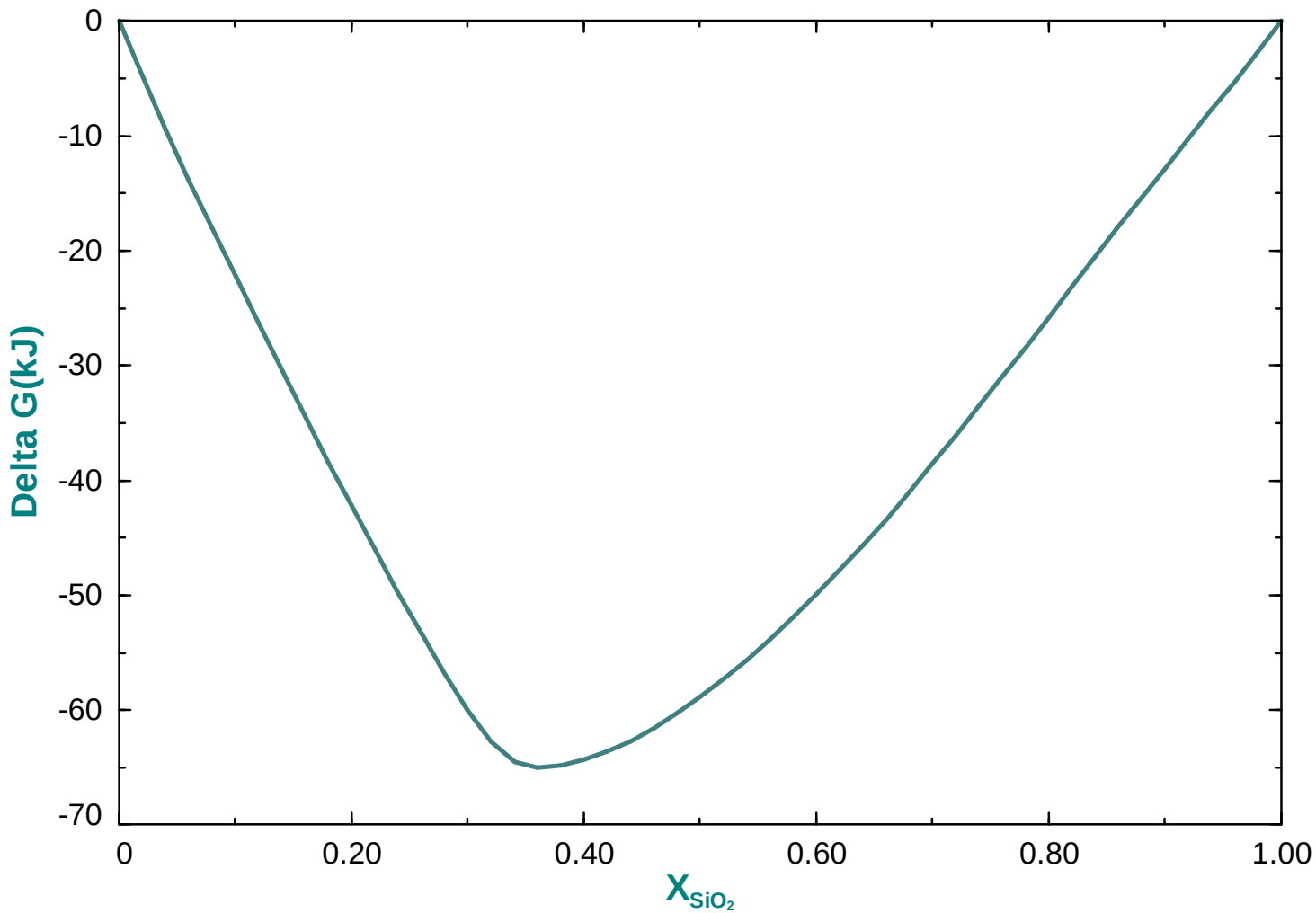


Entropy of Mixing in Liquid Alkaline-earth Silicates



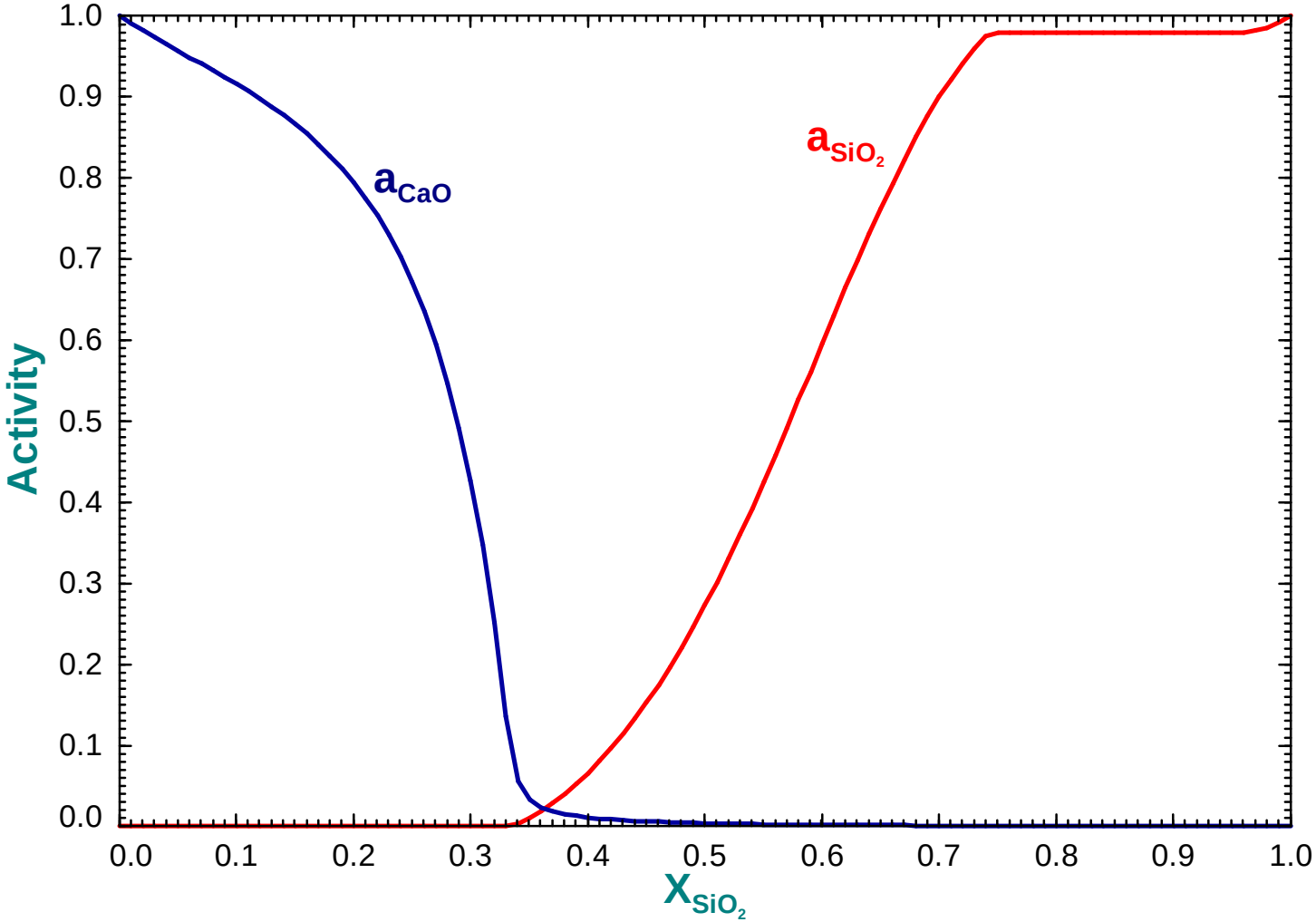
$CaO\text{-}SiO_2$ System:

ΔG vs X_{SiO_2} at 1750°C

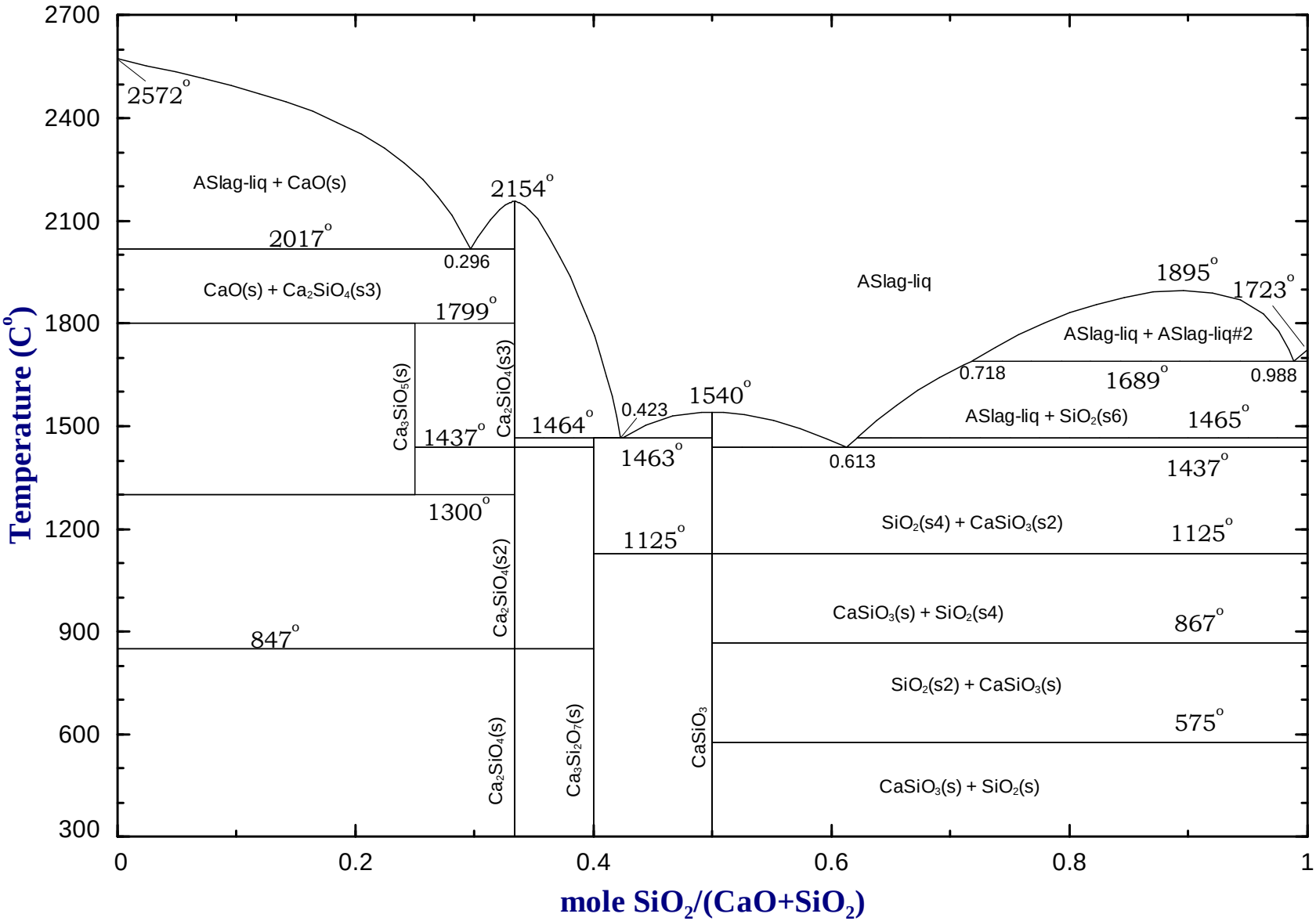


$CaO-SiO_2$ System:

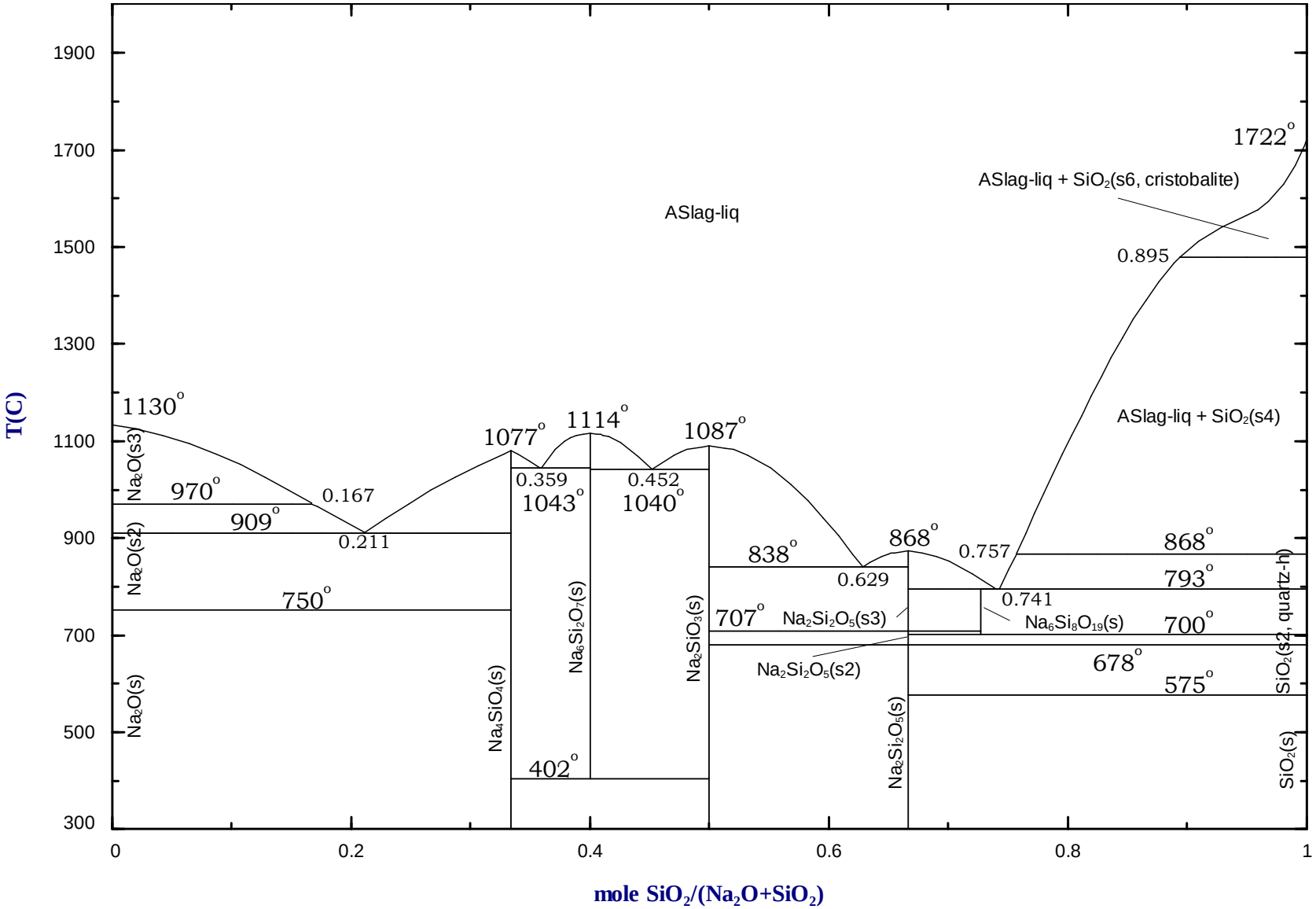
a_{SiO_2} and a_{CaO} vs X_{SiO_2} at 1750°C



CaO – SiO_2 Phase Diagram

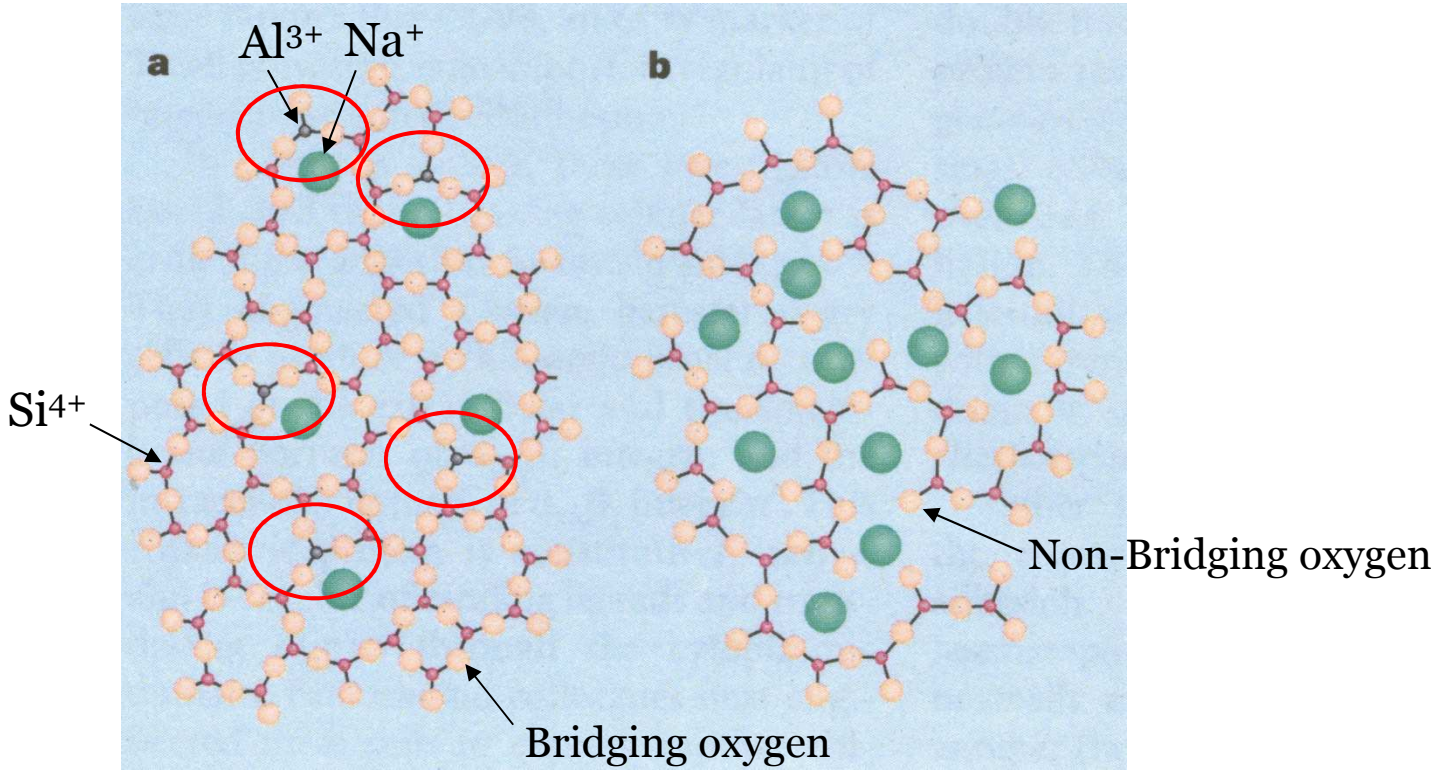


Na_2O – SiO_2 Phase Diagram



Systems with Al_2O_3 (amphoretic)

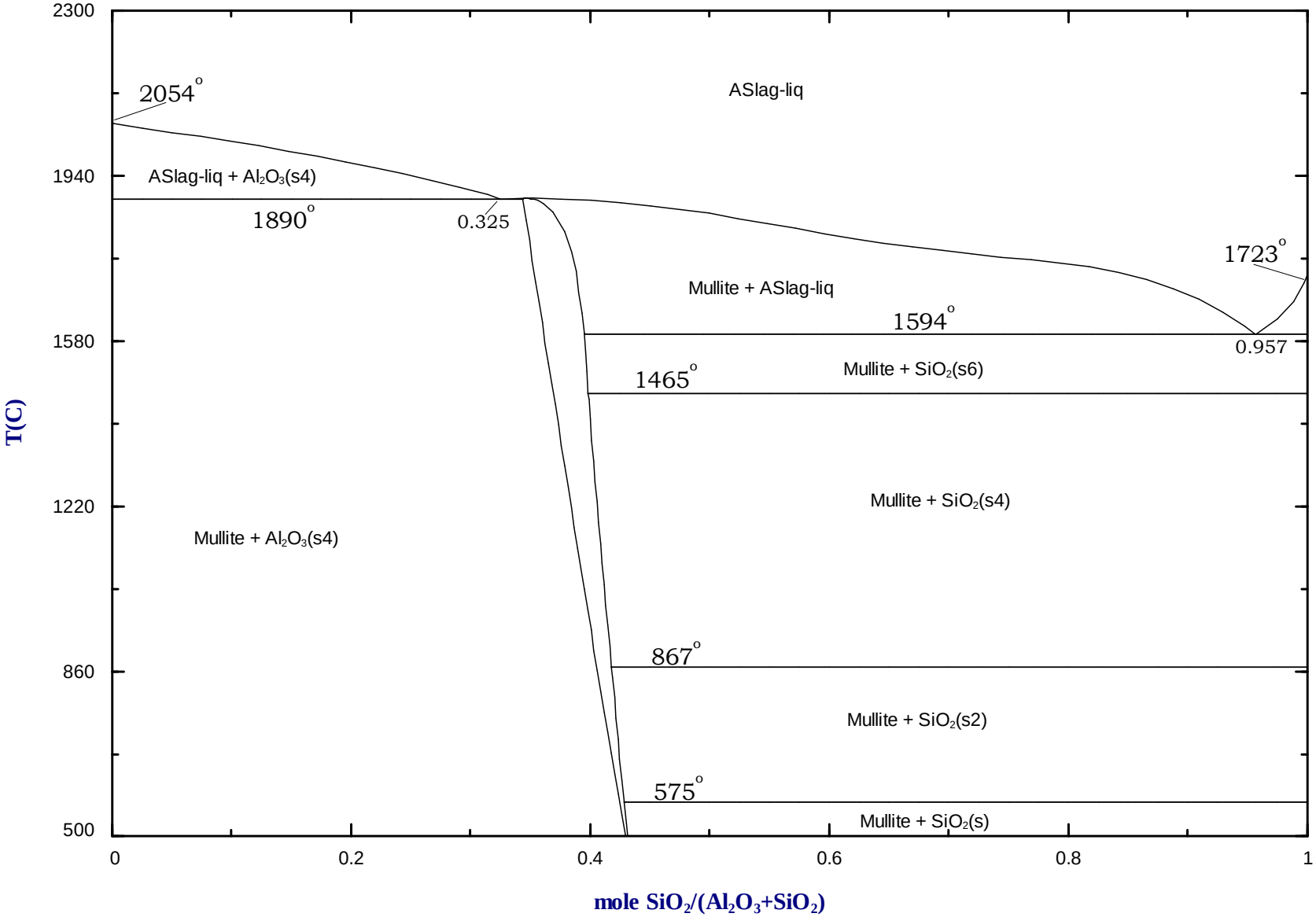
The Charge Compensation effect



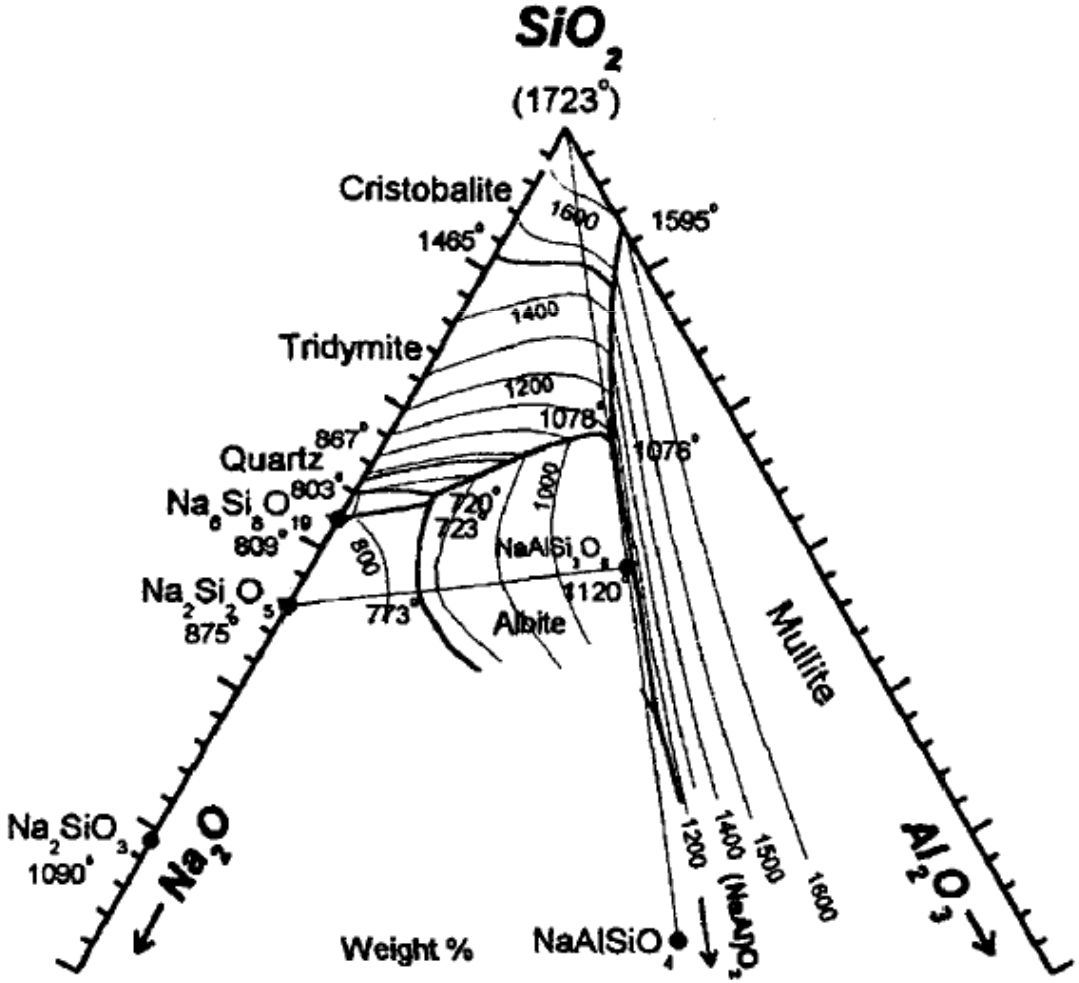
Al^{3+} can replace Si^{4+}
Na^{+} or K^{+} compensates the charge

2 Al^{3+} replace 2 Si^{4+}
Ca^{2+} or Mg^{2+} compensates the charge

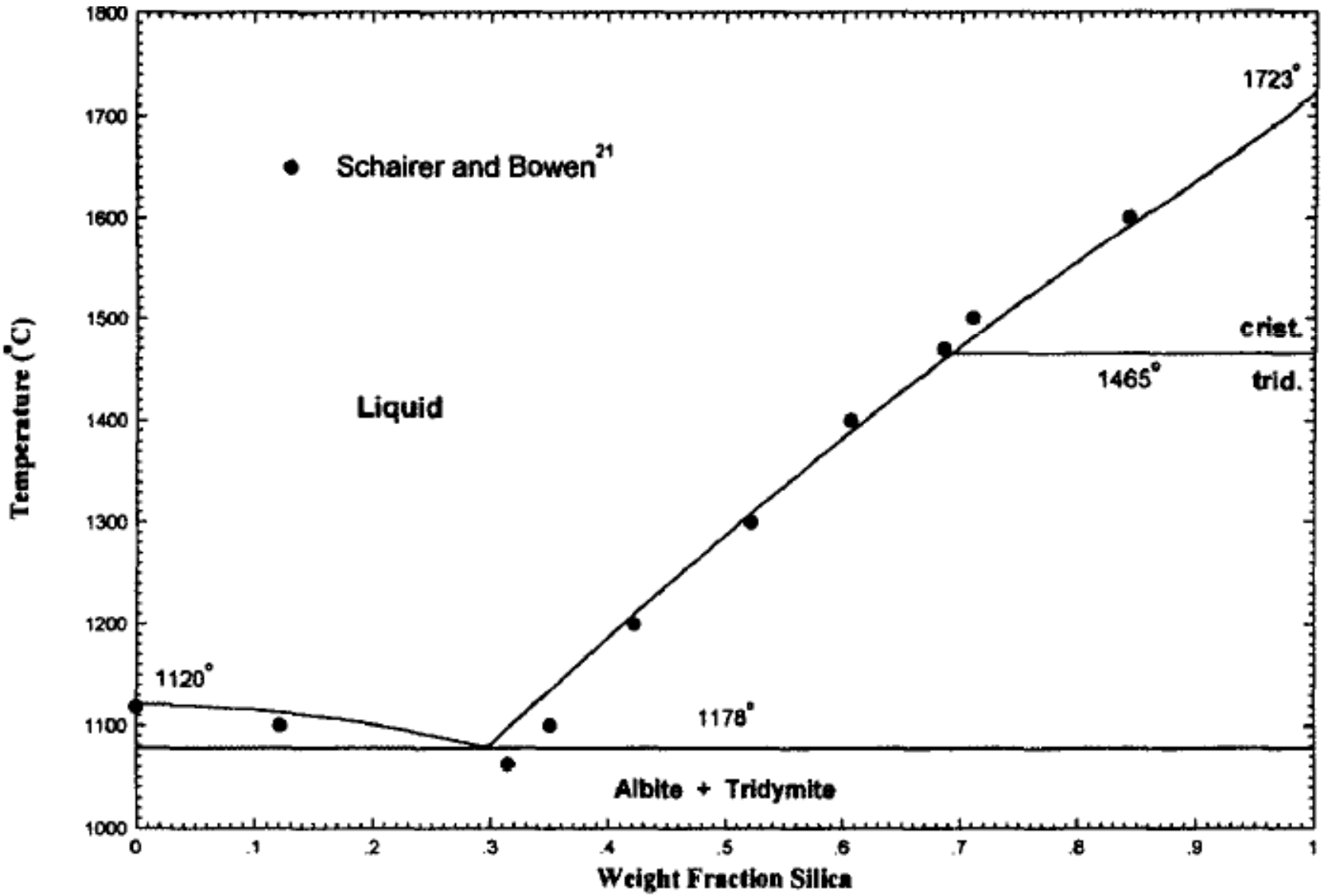
Al_2O_3 – SiO_2 Phase Diagram



Na_2O – SiO_2 - Al_2O_3 Phase Diagram (liquidus projection)



Albite($NaAlSi_3O_8$) – SiO_2



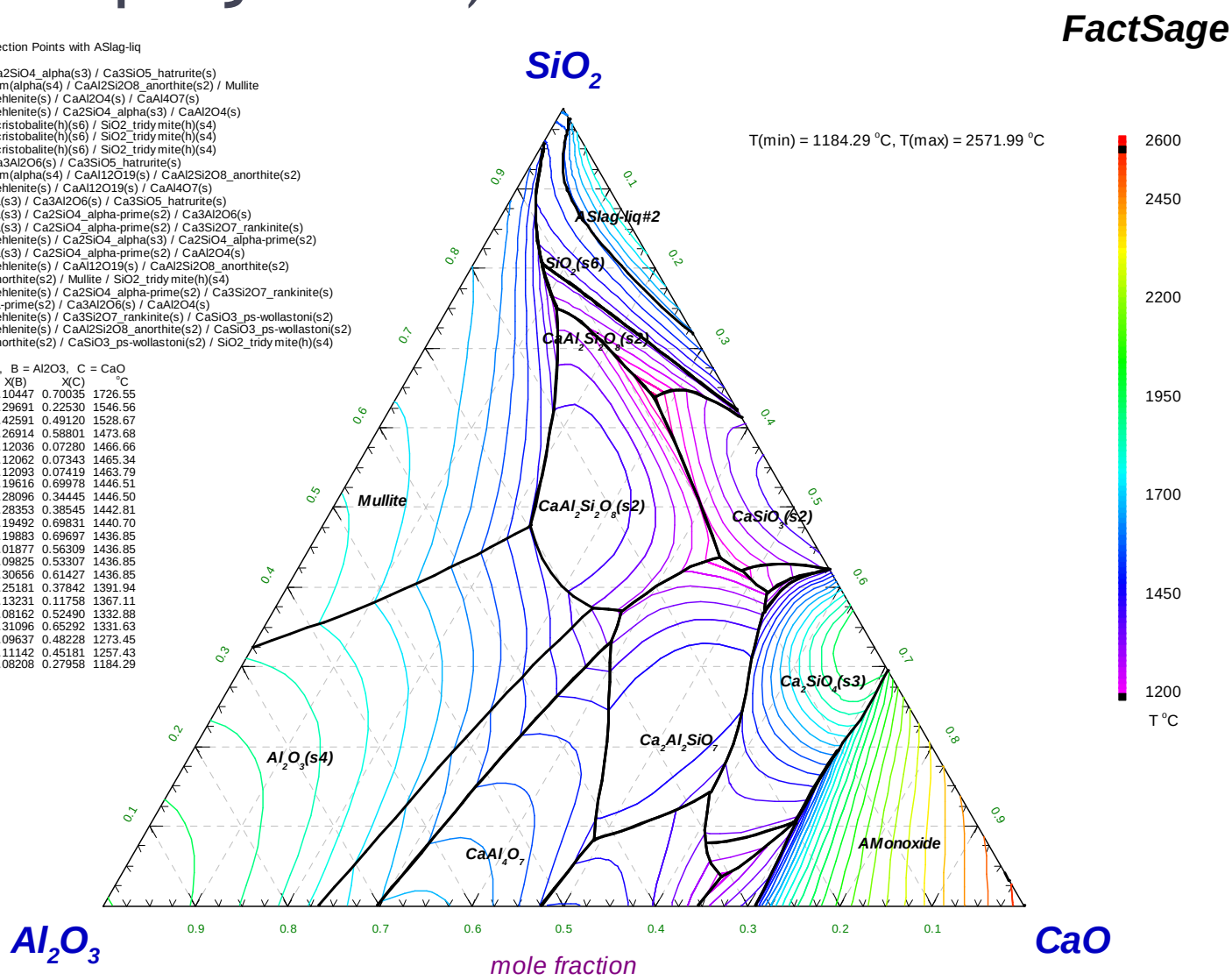
CaO – SiO_2 - Al_2O_3 Phase Diagram (liquidus projection)

Four-Phase Intersection Points with ASlag-liq

1: AMonoxide / Ca2SiO4_alpha(s3) / Ca3SiO5_hatrurite(s)
2: Al2O3_corundum(alpha(s4) / CaAl2Si2O8_anorthite(s2) / Mullite
3: Ca2Al2SiO7_gehlenite(s) / CaAl2O4(s) / CaAl4O7(s)
4: Ca2Al2SiO7_gehlenite(s) / Ca2SiO4_alpha(s3) / CaAl2O4(s)
5: Mullite / SiO2_cristobalite(h)(s6) / SiO2_tridymite(h)(s4)
6: Mullite / SiO2_cristobalite(h)(s6) / SiO2_tridymite(h)(s4)
7: Mullite / SiO2_cristobalite(h)(s6) / SiO2_tridymite(h)(s4)
8: AMonoxide / Ca3Al2O6(s) / Ca3SiO5_hatrurite(s)
9: Al2O3_corundum(alpha(s4) / CaAl12O19(s) / CaAl2Si2O8_anorthite(s2)
10: Ca2Al2SiO7_gehlenite(s) / CaAl12O19(s) / CaAl4O7(s)
11: Ca2SiO4_alpha(s3) / Ca3Al2O6(s) / Ca3SiO5_hatrurite(s)
12: Ca2SiO4_alpha(s3) / Ca2SiO4_alpha-prime(s2) / Ca3Al2O6(s)
13: Ca2SiO4_alpha(s3) / Ca2SiO4_alpha-prime(s2) / Ca3Si2O7_rankinite(s)
14: Ca2Al2SiO7_gehlenite(s) / Ca2SiO4_alpha(s3) / Ca2SiO4_alpha-prime(s2)
15: Ca2SiO4_alpha(s3) / Ca2SiO4_alpha-prime(s2) / CaAl2O4(s)
16: Ca2Al2SiO7_gehlenite(s) / CaAl12O19(s) / CaAl2Si2O8_anorthite(s2)
17: CaAl2Si2O8_anorthite(s2) / Mullite / SiO2_tridymite(h)(s4)
18: Ca2Al2SiO7_gehlenite(s) / Ca2SiO4_alpha-prime(s2) / Ca3Si2O7_rankinite(s)
19: Ca2SiO4_alpha-prime(s2) / Ca3Al2O6(s) / CaAl2O4(s)
20: Ca2Al2SiO7_gehlenite(s) / Ca3Si2O7_rankinite(s) / CaSiO3_ps-wollastoni(s2)
21: Ca2Al2SiO7_gehlenite(s) / CaAl2Si2O8_anorthite(s2) / CaSiO3_ps-wollastoni(s2)
22: CaAl2Si2O8_anorthite(s2) / CaSiO3_ps-wollastoni(s2) / SiO2_tridymite(h)(s4)

A = SiO2, B = Al2O3, C = CaO

	X(A)	X(B)	X(C)	°C
1:	0.19519	0.10447	0.70035	1726.55
2:	0.47779	0.29691	0.22530	1546.56
3:	0.08289	0.42591	0.49120	1528.67
4:	0.14285	0.26914	0.58801	1473.68
5:	0.80684	0.12036	0.07280	1466.66
6:	0.80594	0.12062	0.07343	1465.34
7:	0.80489	0.12093	0.07419	1463.79
8:	0.10406	0.19616	0.69978	1446.51
9:	0.37459	0.28096	0.34445	1446.50
10:	0.33102	0.28353	0.38545	1442.81
11:	0.10677	0.19492	0.69831	1440.70
12:	0.10420	0.19883	0.69697	1436.85
13:	0.41814	0.01877	0.56309	1436.85
14:	0.36868	0.09825	0.53307	1436.85
15:	0.07917	0.30656	0.61427	1436.85
16:	0.36977	0.25181	0.37842	1391.94
17:	0.75011	0.13231	0.11758	1367.11
18:	0.39348	0.08162	0.52490	1332.88
19:	0.03612	0.31096	0.65292	1331.63
20:	0.42135	0.09637	0.48228	1273.45
21:	0.43677	0.11142	0.45181	1257.43
22:	0.63835	0.08208	0.27958	1184.29



Species in Borate Melts

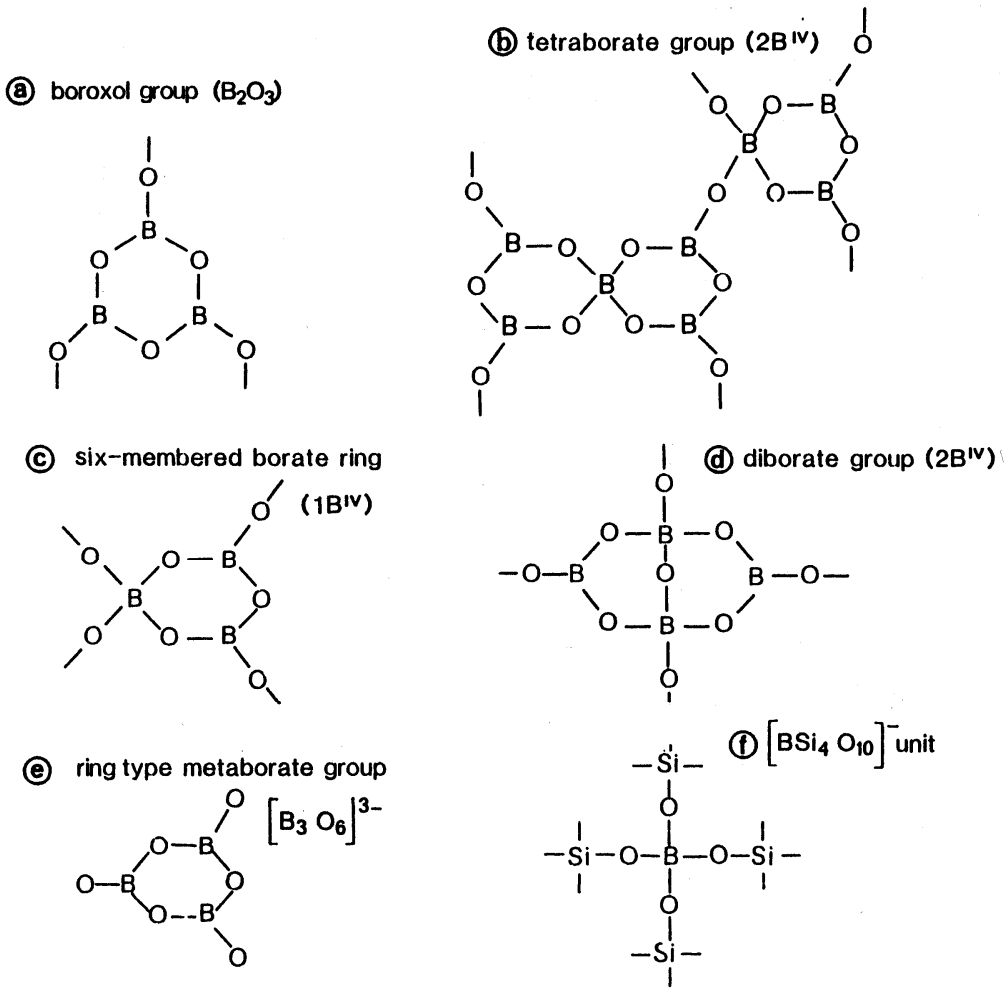
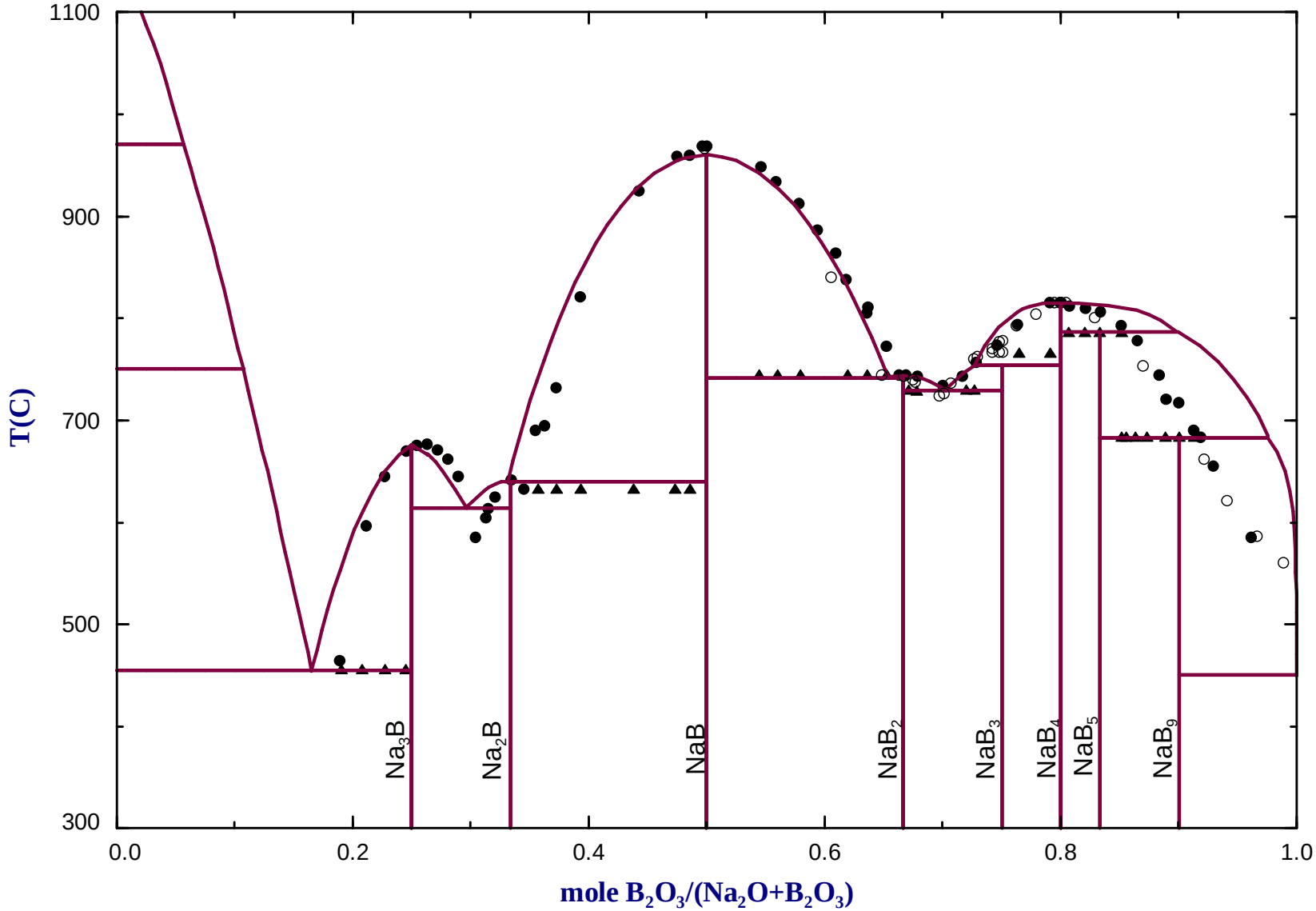


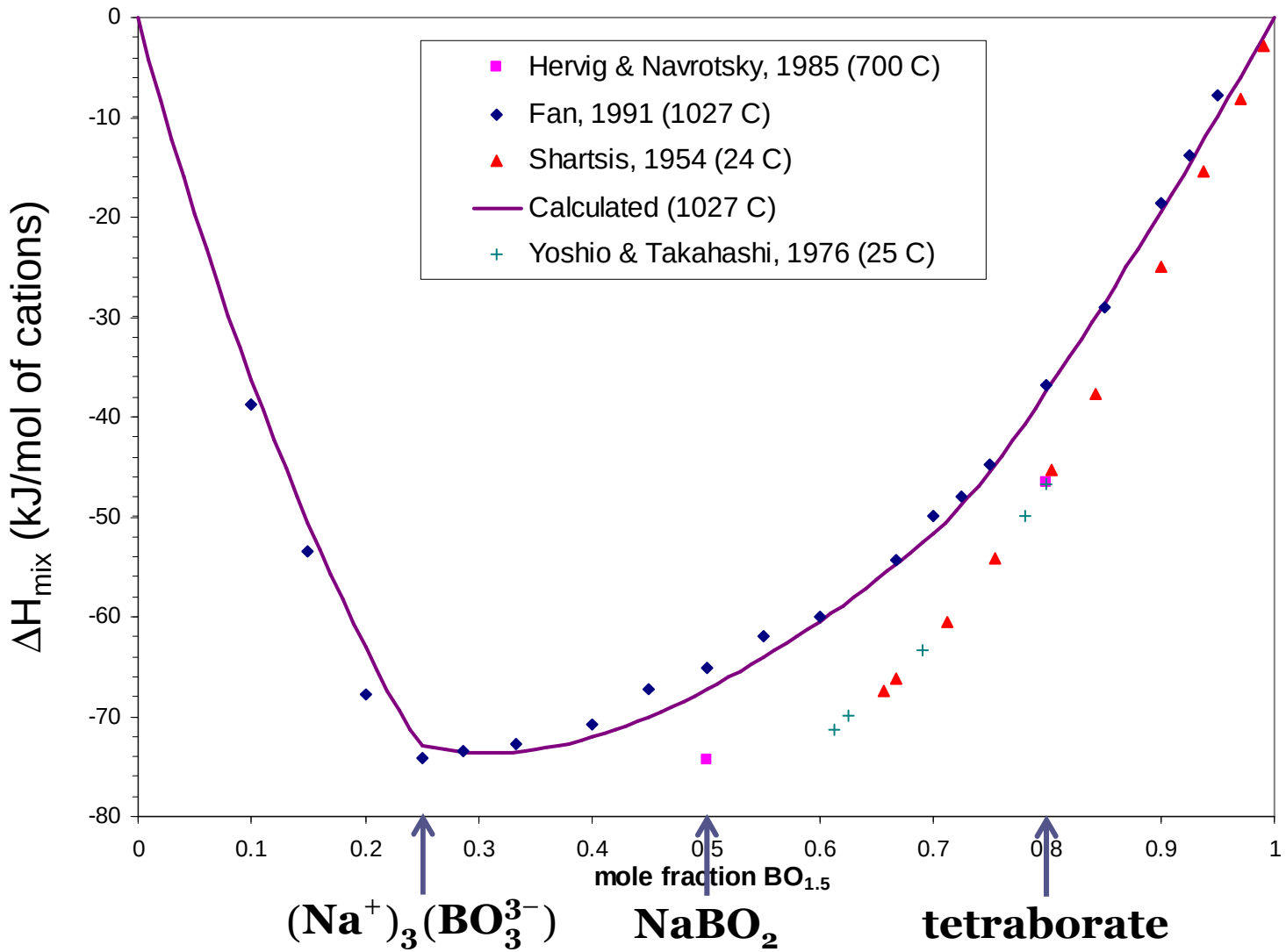
Figure 2. Species proposed by various authors for the structural role of boron in melts. (Used by permission of the editor of *Bulletin de Minéralogie*, from Pichavant, 1983a, Fig. 7, p. 208.)

Na_2O – B_2O_3 System:

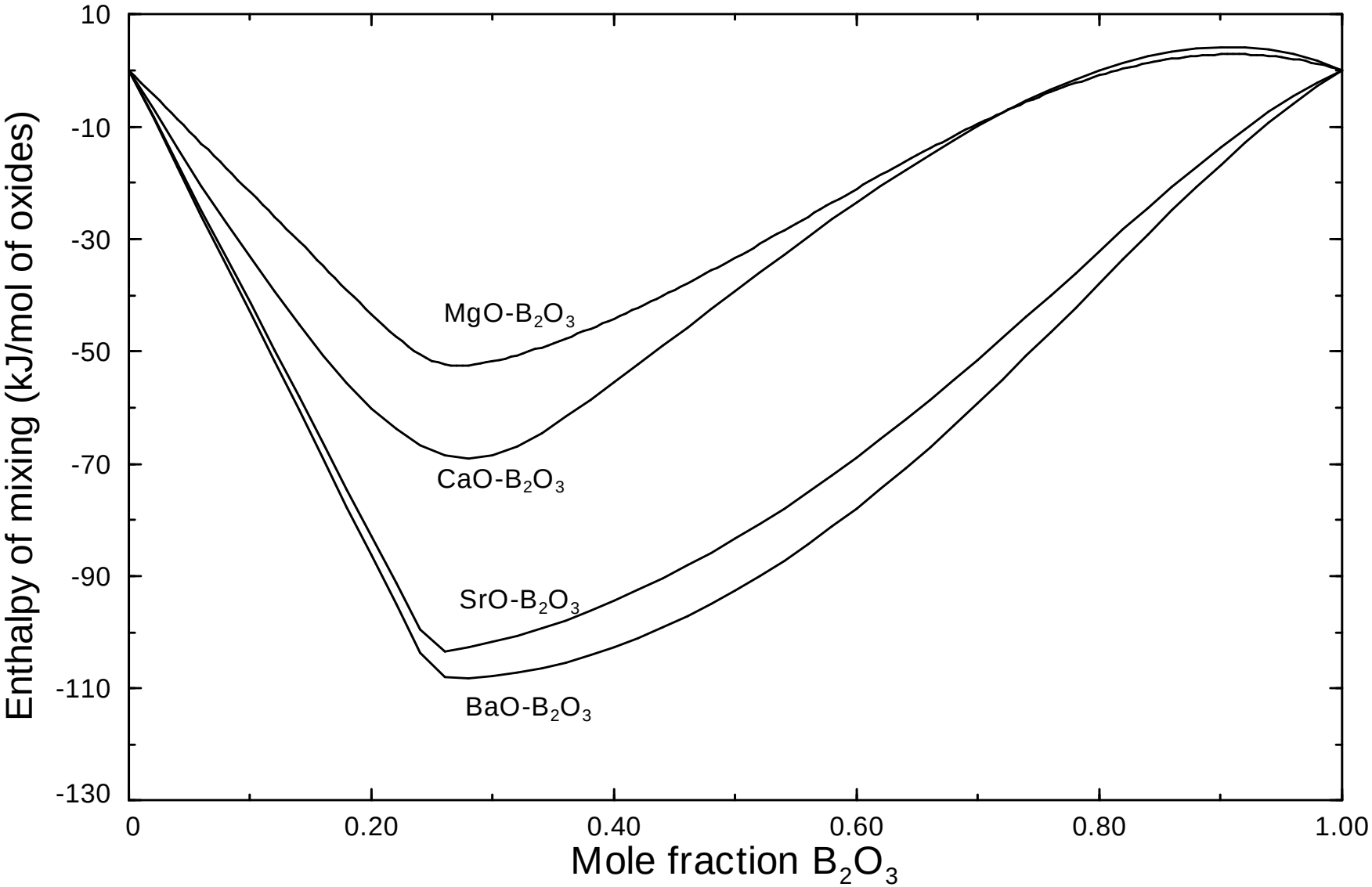
The Na_2O – B_2O_3 Phase Diagram



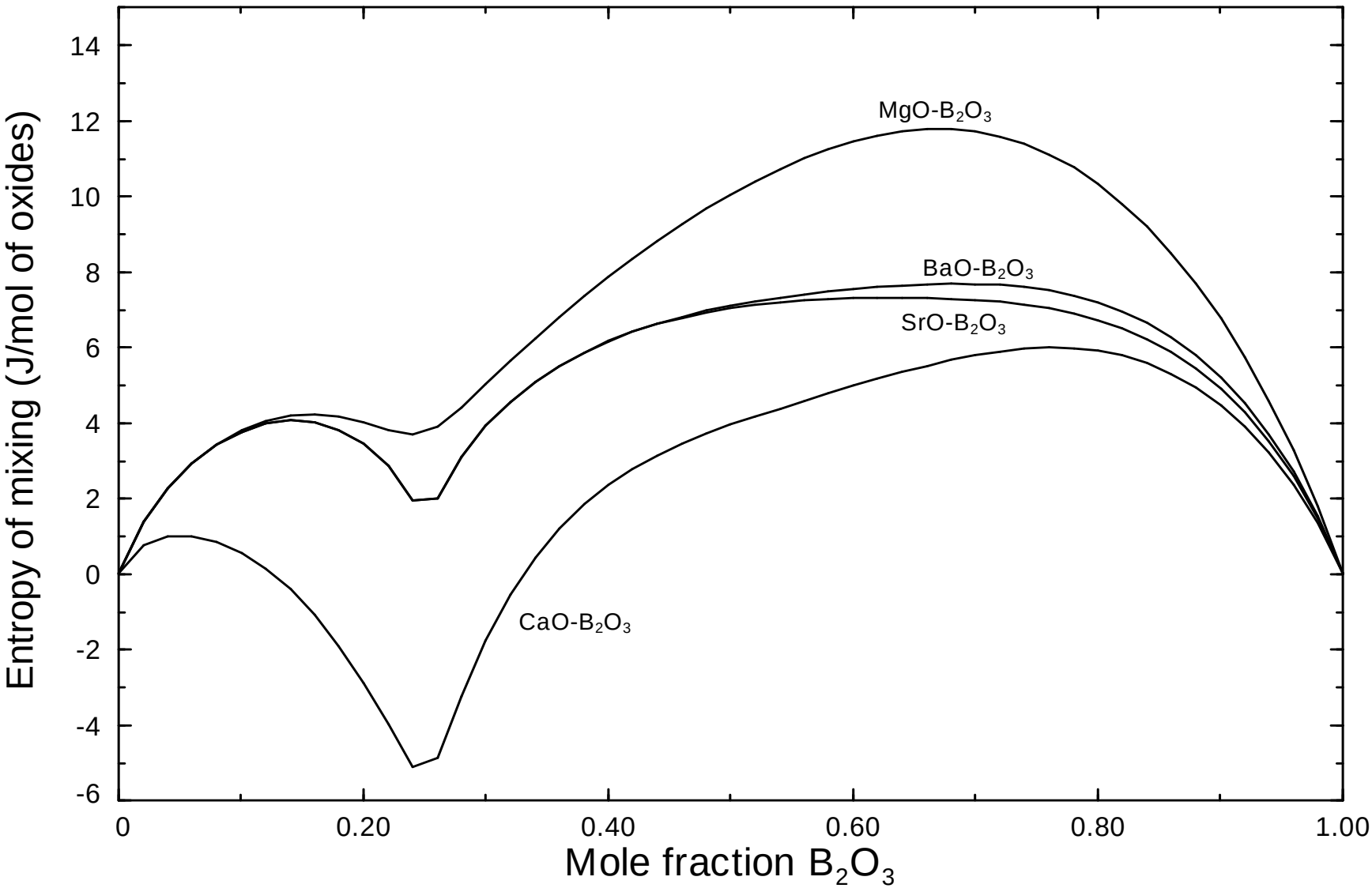
Na_2O – B_2O_3 System: Enthalpies of Mixing in the $Na_{0.5}O$ – $BO_{1.5}$ System



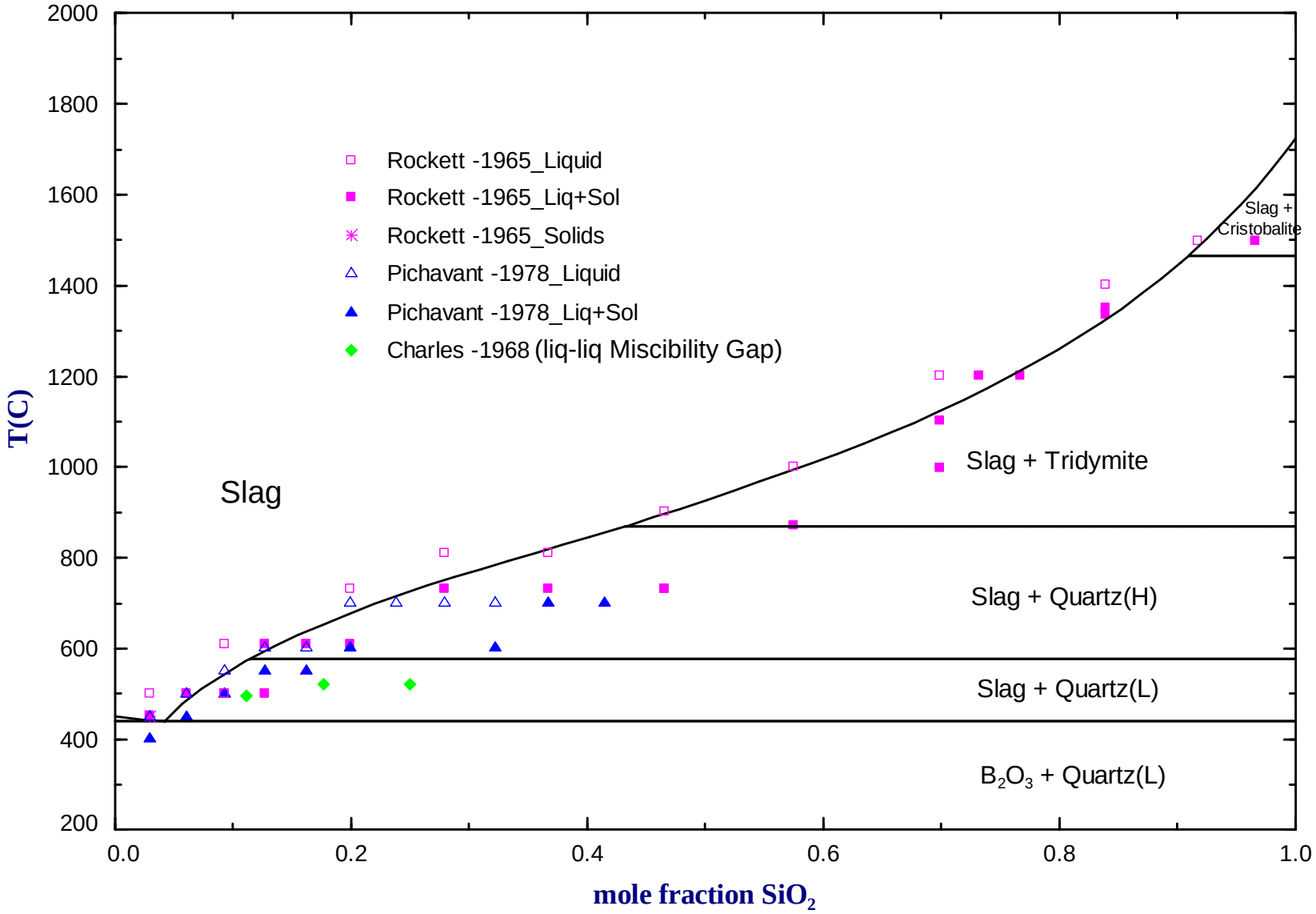
Enthalpy of Mixing in Liquid Alkaline-earth Borates



Entropy of Mixing in Liquid Alkaline-earth Borates

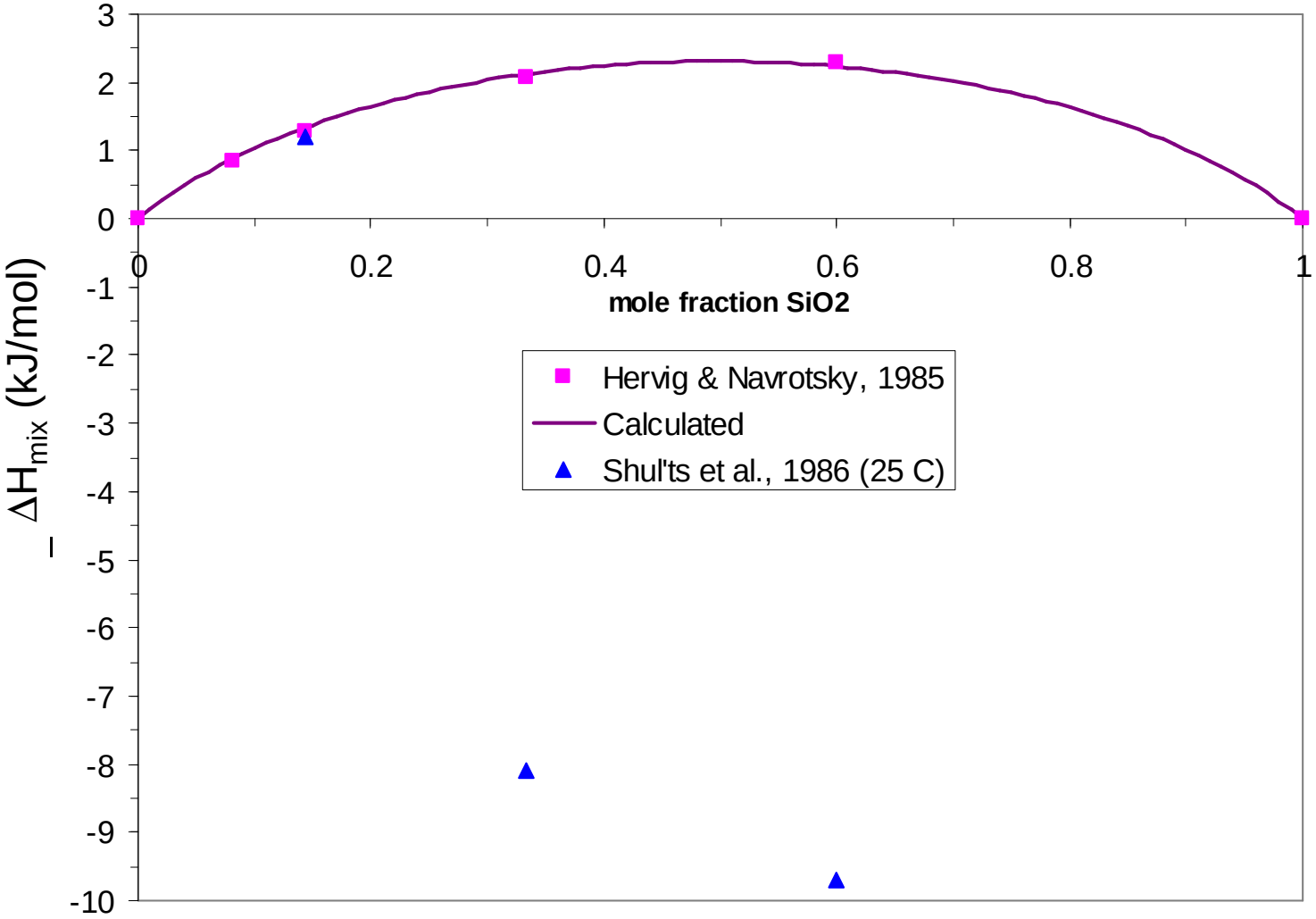


B_2O_3 -SiO_2 System: The $BO_{1.5}$ - SiO_2 Phase Diagram



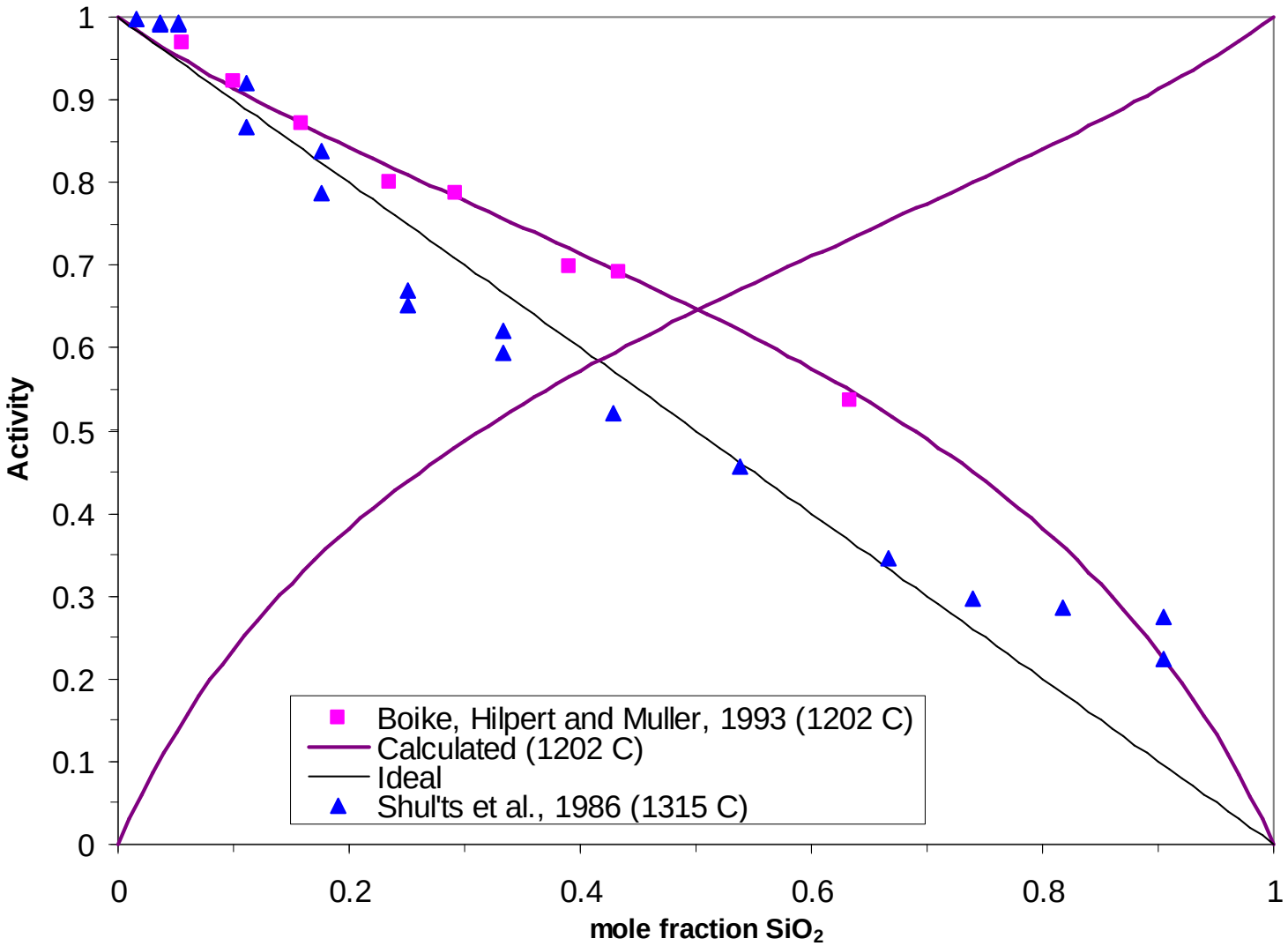
B_2O_3 –SiO_2 System:

Enthalpy of Mixing in the $BO_{1.5}$ – SiO_2 System at 700°C

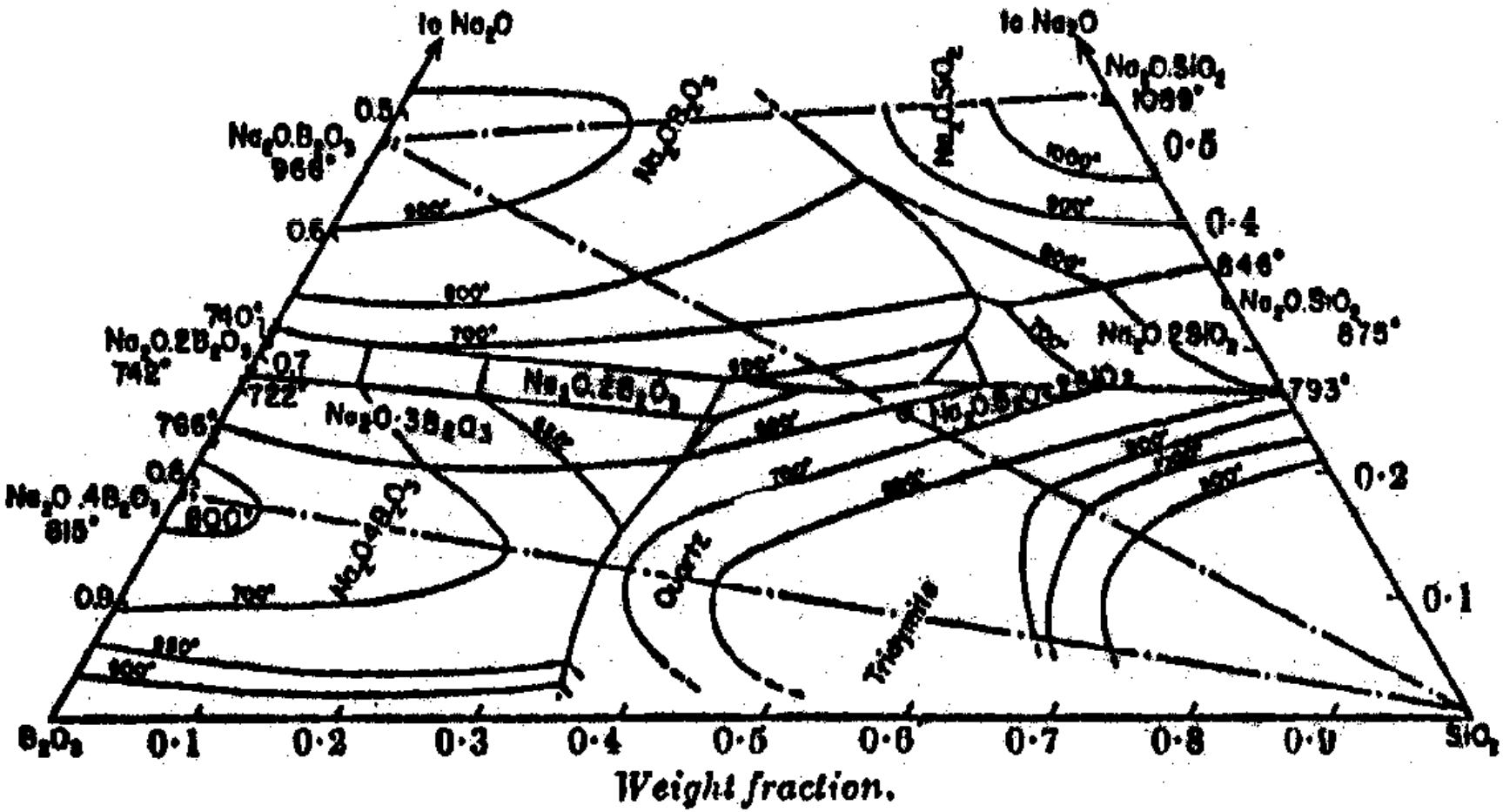


B_2O_3 -SiO_2 System:

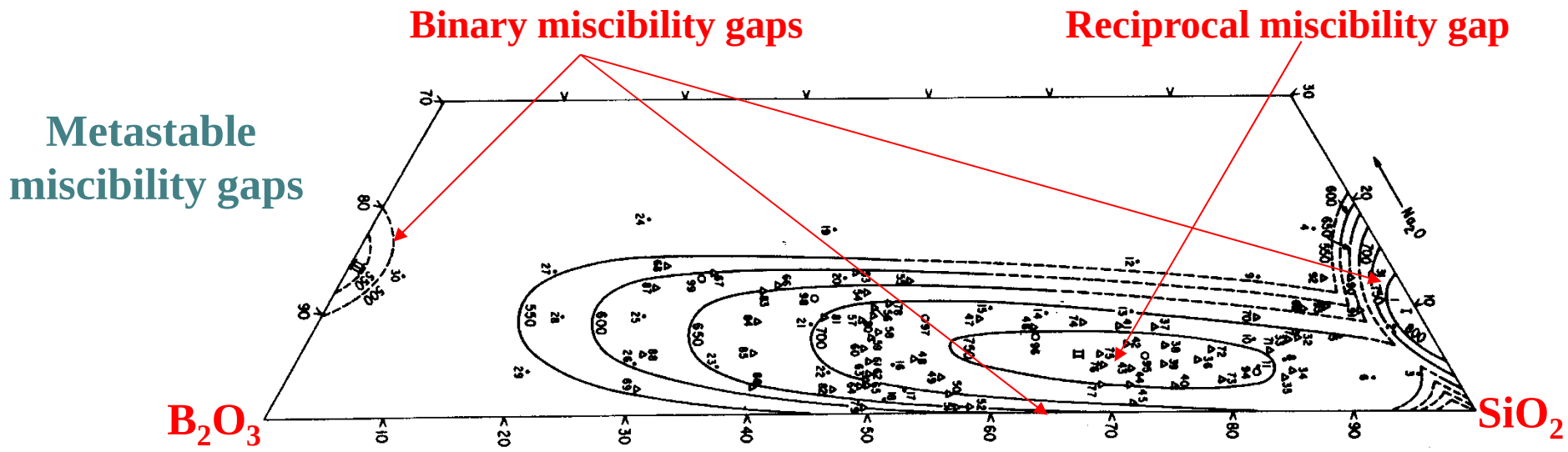
Activity of $BO_{1.5}$ in the $BO_{1.5}$ - SiO_2 Melts by Mass-spectroscopy



SiO_2-B_2O_3-Na_2O Liquidus Projection



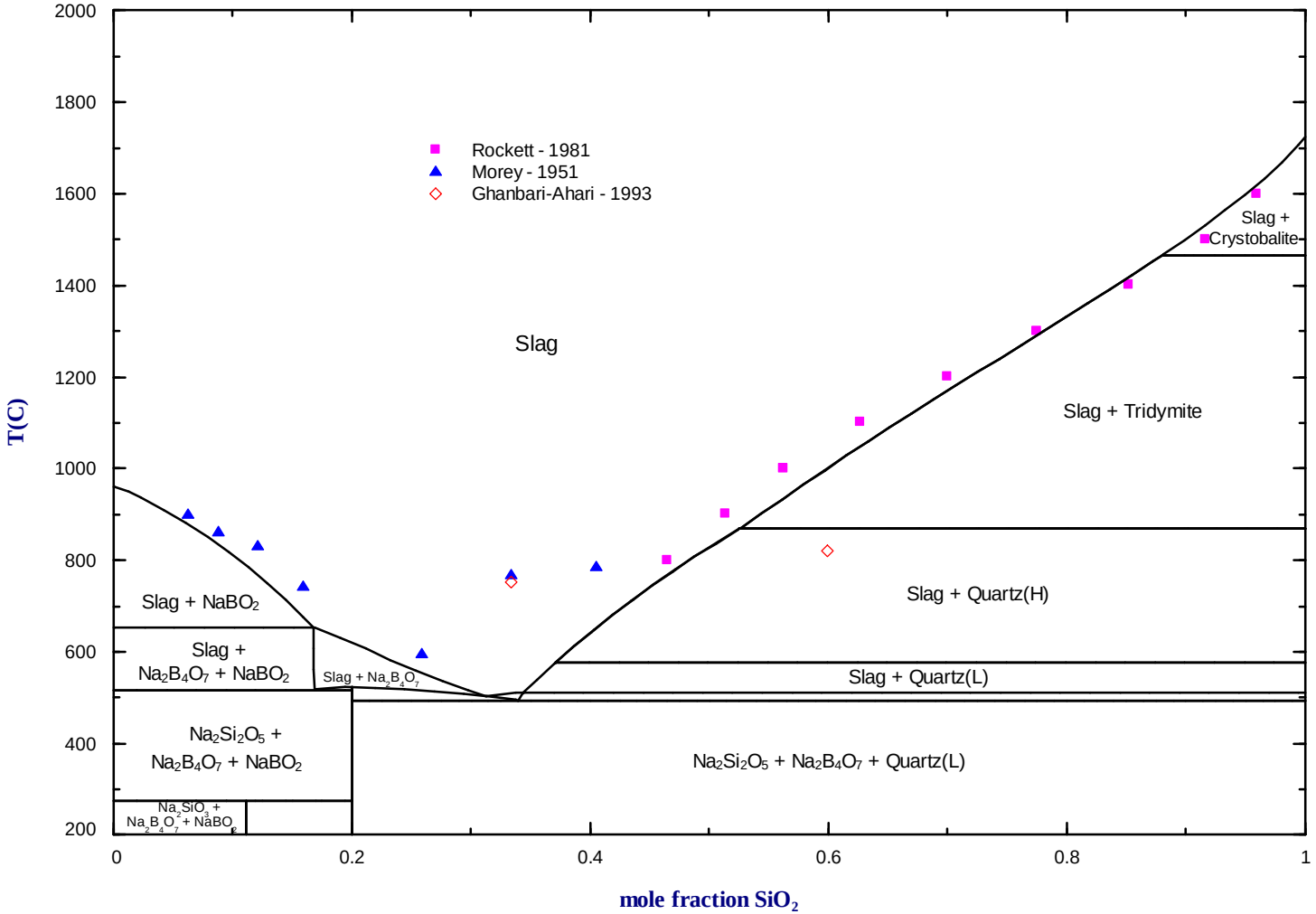
SiO_2-B_2O_3-Na_2O Subsolidus Miscibility Gap



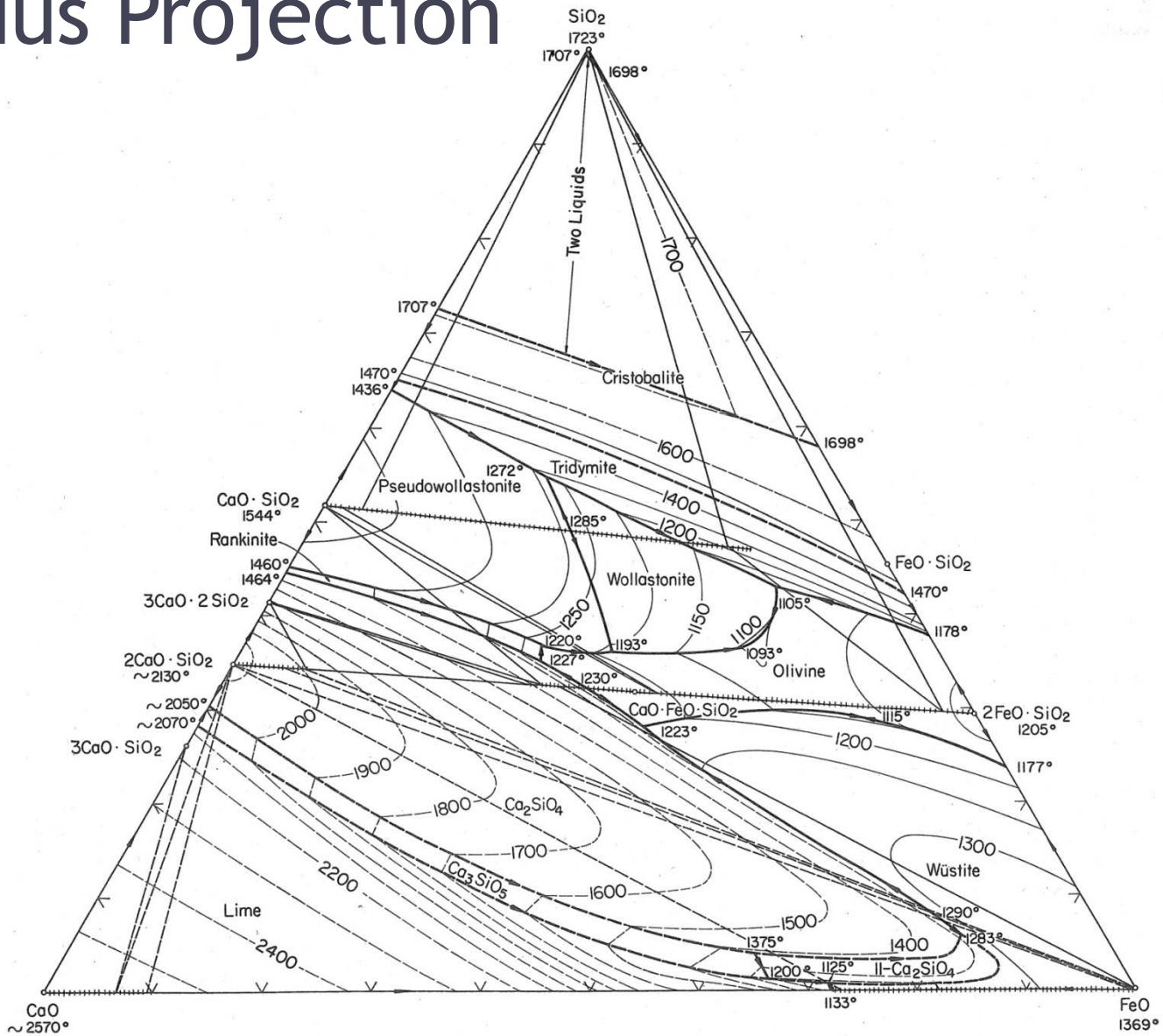
Na_2O-B_2O_3-SiO_2 System:

Liquidus along the $(NaBO_2)/2$-SiO_2 section

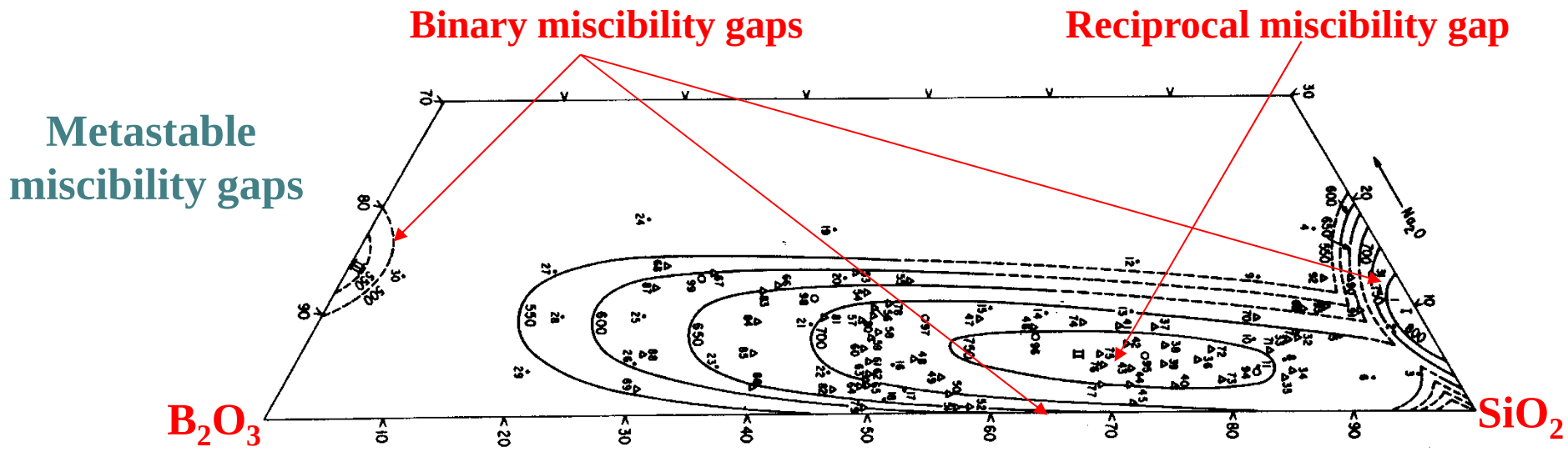
(close to an ideal liquid solution)



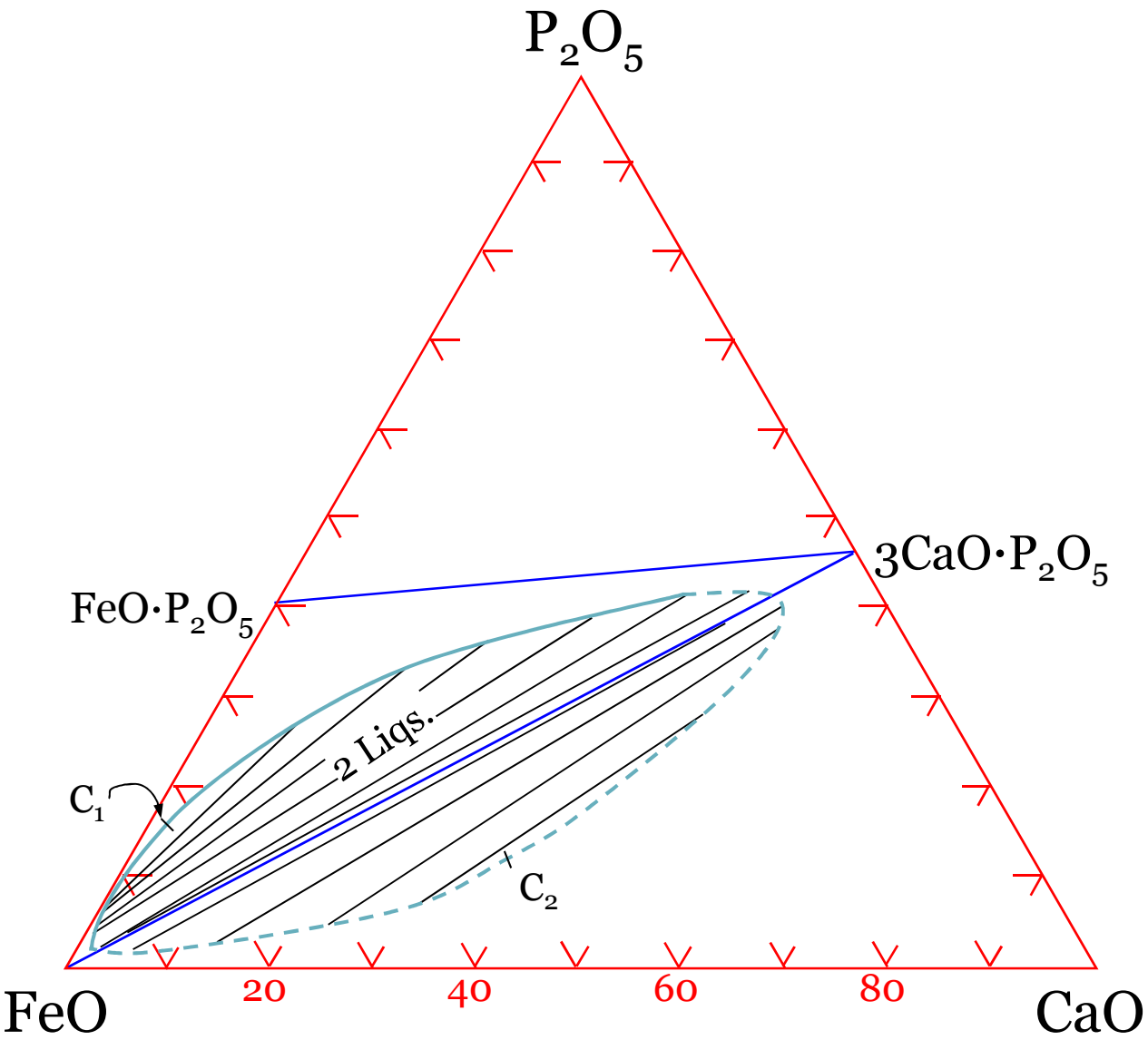
SiO_2-CaO-FeO Liquidus Projection



SiO_2-B_2O_3-Na_2O Subsolidus Miscibility Gap



$CaO-FeO-P_2O_5$ System



Thermodynamic Modeling of Solutions

The simplest example:

A "regular" solution in which the molecules of each component are randomly distributed on a quasilattice:

$$g(molar) = (x_1 g_1^0 + x_2 g_2^0 + x_3 g_3^0 + \ldots)$$
$$+ RT(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3)$$
$$+ \alpha_{12} x_1 x_2 + \alpha_{23} x_2 x_3 + \alpha_{31} x_3 x_1 + \ldots + \alpha_{123} x_1 x_2 x_3 + \ldots$$

where: x_i = *mole fraction of component i*

g°_i = *Gibbs function of pure component i*

α_{ij} = *empirical binary parameter of the model*

α_{123} = *empirical ternary parameter of the model*

α_{ij} represents the energy of forming *i-j* nearest neighbour bonds upon mixing.

α_{ij} may be expanded as an empirical power series:

$$\alpha_{ij} = \sum q_{ij}^{k} (x_i - x_j)^k$$

The empirical parameters q_{ij}^{k} are found by fitting experimental data.

- For molten oxides a more sophisticated model is required.
- We use the Modified Quasichemical Model (MQM).

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:

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

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

where : n_i, G^0_i = 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} = empirical binary model parameters
(which are functions of composition and temperature)
(The equilibrium values of n_{mn} are obtained by setting $\partial G/\partial n_{mn} = 0$ at constant n_i)
Binary model parameters are optimized by fitting experimental data.

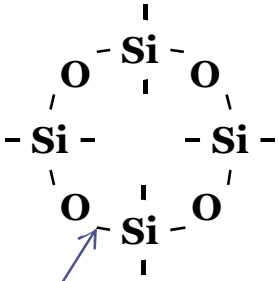
Structure of CaO-SiO_2 Liquid Solutions

Composition →

CaO — Ca_2SiO_4 — SiO_2

mainly
Ca^{2+}, O^{2-}, SiO_4^{4-}

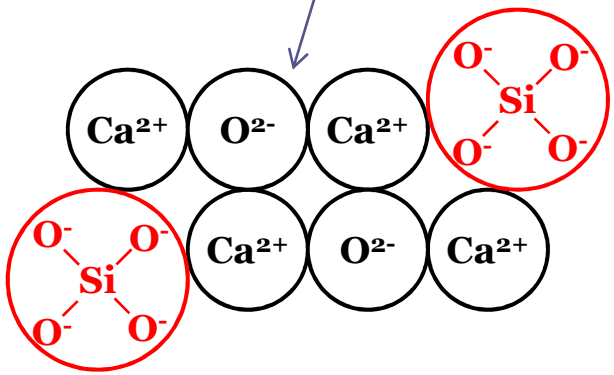
mainly
Ca^{2+},
SiO_4^{4-} (orthosilicate ions)

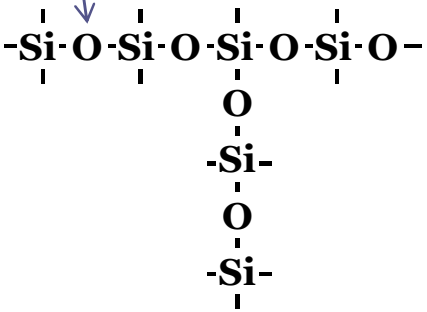


linear + branched
chain polymers

ring polymers

3-dimensional
network

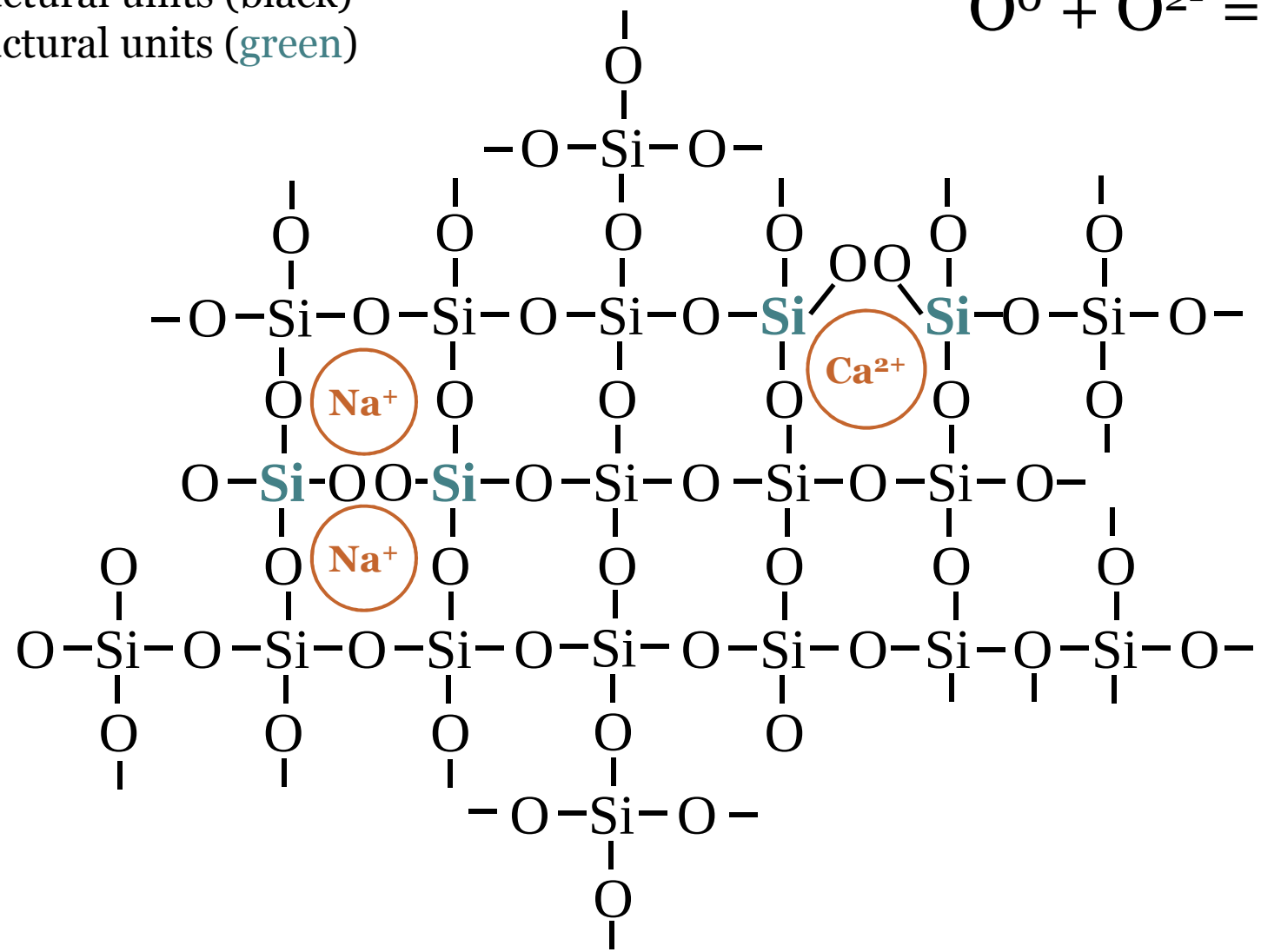




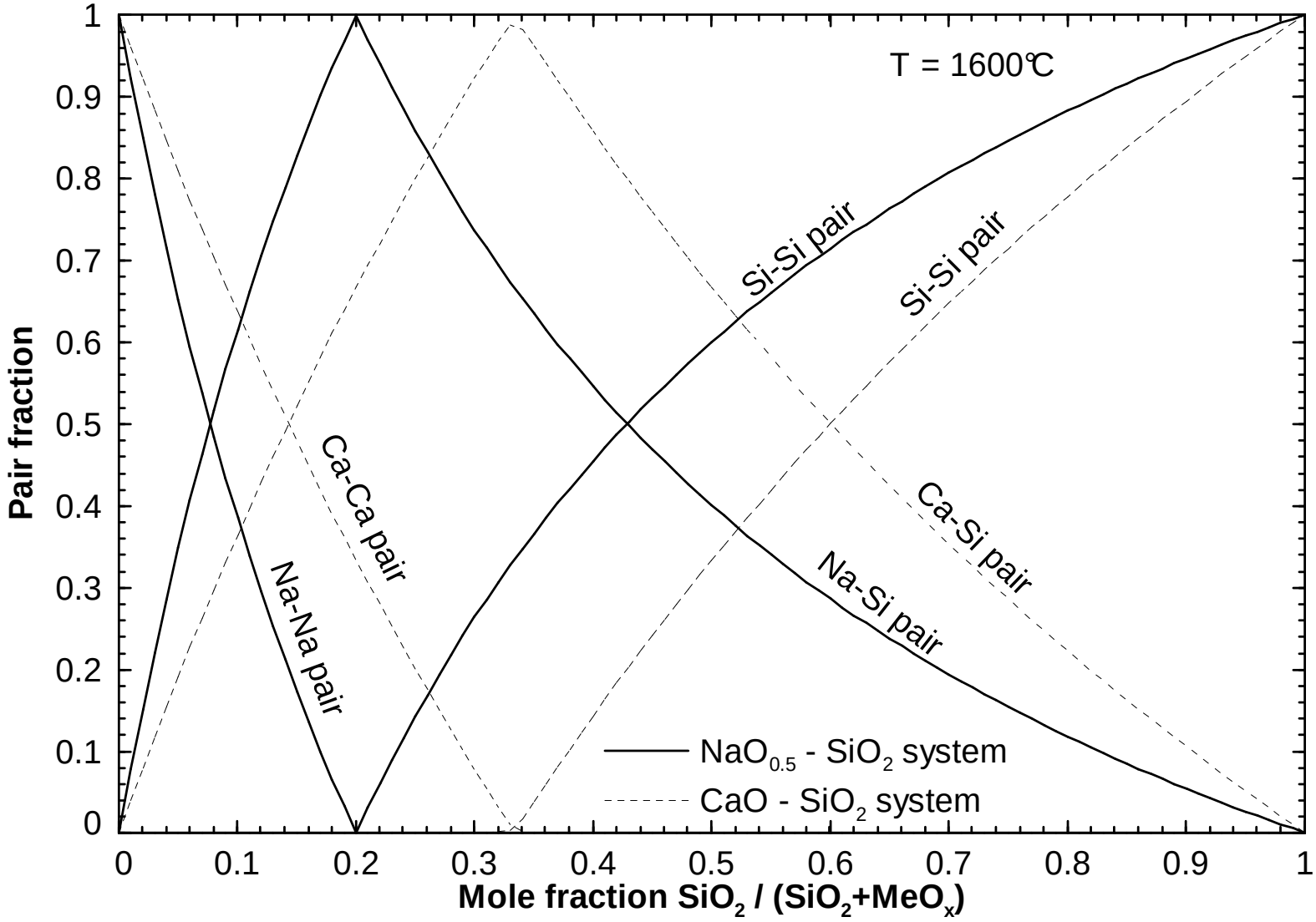
Network Modification by Basic Oxides

Q^4 structural units (black)
Q^3 structural units (green)

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



Pair Fractions in the Systems $CaO\text{-}SiO_2$ and $NaO_{0.5}\text{-}SiO_2$



Thermodynamic Database Development

Modeling and Phase Diagram Calculation in Oxide Systems

Several thermodynamic software/database packages with applications in materials science have been developed over the last 30 years.

- These packages all contain large **critically evaluated** databases for thousands of compounds and hundreds of solution phases, as well as user interfaces of varying degrees of user-friendliness.
  - **HSC Chemistry**
  - **MTS-NPL**
  - **Thermo-Calc**
  - **Thermodata**
  - **FactSage**

- **Thermochemical databases** contain parameters giving the **Gibbs energy**, **G**, of all compounds as functions of T (and P) and of all solutions as functions of T, (P) and composition. This is a complete description because all the other thermodynamic properties (H, C_p, μ, etc.) can be calculated by taking the appropriate derivatives of the G functions.
- **For a given set of constraints** (such as temperature, total pressure, total mass of each element) the ***software*** calculates the equilibrium conditions by **minimizing the total Gibbs energy** of the system. This is mathematically equivalent to solving all the equilibrium constant equations simultaneously.
- Data are automatically extracted as required from the databases.

How a thermodynamic database is developed by evaluation/optimisation

There are many kinds of chemical thermodynamic data for compounds and solutions:

- **Calorimetric data:**
  - **Heat capacity**
  - **Solution calorimetry**
  - **Enthalpy of mixing**
  - **…**
- **Vapour pressures**
- **Phase equilibria:**
  - **Solid/liquid/gas**
  - **Phase diagrams (T-P-Composition)**
- **Chemical potentials or activities**
  - **From electrochemical cells**
  - **From phase equilibria (vapour pressures, isopiestic, …)**
  - **…**
- **…(and so on)**

These diverse kinds of data are not independent of each other, but are related through the **GIBBS FUNCTIONS** of the phases.

For each phase (compound or solution):

G = G(T, P, Composition)

Then: $$H(\text{enthalpy or "heat"}) = \left[\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_{P,Composition}$$

$$C_p(\text{heat capacity}) = \left(\frac{dH}{dT}\right)_P$$

$$S(\text{entropy}) = -\left(\frac{\partial G}{\partial T}\right)_{P,composition}$$

$$\mu_i = \begin{matrix}(\text{chemical potential of} \\ \text{component } i \text{ of a solution})\end{matrix} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \quad (\text{where } n_i = \text{moles of } i)$$

When phases are in equilibrium:

$$\begin{aligned} \mu_i\,(\text{in phase } \alpha) &= \mu_i\,(\text{in phase } \beta) \text{ for all components } i \\ &= \mu_i\,(\text{in phase } \gamma) \\ &= \ldots \end{aligned}$$

…(and so on)

- Therefore, **in developing a database for a multicomponent chemical system, one assesses and evaluates** ALL **the data** SIMULTANEOUSLY **in order to obtain an optimal Gibbs function, G(T, P, Composition), for each phase.**
- The resultant database is then thermodynamically self-consistent.
- The optimized Gibbs functions are stored in the database (as sets of parameters).
  All thermodynamic properties and phase equilibria can then be calculated from these functions.

- **Step 1):** **Develop a mathematical model for each solution phase based upon the structure of the solution.**

  The simplest example:

  a "regular" solution in which the atoms or molecules of each component are randomly distributed.

$$G(molar) = \left(X_1 G_1^\circ + X_2 G_2^\circ + X_3 G_3^\circ + \cdots\right)$$
$$+RT\left(X_1 \ln X_1 + X_2 \ln X_2 + \cdots\right)$$
$$+\alpha_{12} X_1 X_2 + \alpha_{23} X_2 X_3 + \alpha_{31} X_3 X_1 + \cdots$$

Where: $X_i = mole\ fraction\ of\ component\ i$

$G_i^\circ = Gibbs\ function\ of\ pure\ component\ i$

$\alpha_{ij} = empirical\ parameters\ of\ the\ model$

- **Step 2):**

  Obtain the parameters of the models by simultaneous critical evaluation/optimization of all available data of all kinds (thermodynamic data, phase equilibria data, structural data) (generally for 2- and 3-component systems.)

- **Step 3):**

  Store parameters and use models to estimate properties of N-component phases using optimized 2- and 3-component parameters.

- **Step 4):**

  Calculate complex phase equilibria by minimization of the Gibbs energy of the total system.

  $G(\text{total system}) = n_\alpha G^\alpha + n_\beta G^\beta + n_\gamma G^\gamma + \ldots$

  Where: $n_\alpha, n_\beta, n_\gamma, \ldots$ = *numbers of moles of phases* $\alpha, \beta, \gamma, \ldots$ *at equilibrium*

  $G^\alpha, G^\beta, G^\gamma, \ldots$ = *molar Gibbs function of each phase*

The FACT OXIDE DATABASE

Components

- **Major:**
  - (completely evaluated and modeled at all compositions and temperatures)
    Al_2O_3 – CaO – FeO – Fe_2O_3 – MgO – SiO_2 –
- **Secondary:**
  - (extensively evaluated, particularly with the major components, and particularly over composition ranges of practical importance)
    B_2O_3 – CrO – Cr_2O_3 – MnO – Na_2O – NiO – PbO – Ti_2O_3 – TiO_2 – ZnO – ZrO_2 –
- **Minor:**
  - (evaluated for some combinations with other components)
    As_2O_3 – Cu_2O – K_2O – SnO

The FACT OXIDE DATABASE

Liquid Solution

- Modeled for all oxide components

Also: Non-oxide components (in dilute solution)

S, SO_4, PO_4, CO_3, H_2O, OH, F, Cl, Br, I

> 150 Solid Stoichiometric Compounds

The FACT Oxide Database

Major Oxide Solid Solutions

- **Spinel:** $(Al, Co^{2+}, Co^{3+}, Cr^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Mg, Ni^{2+}, Zn)$ $[Al, Co^{2+}, Co^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Mg, Ni^{2+}, Zn, \square]_2 O_4$
- **Pyroxenes:** $(Ca, Fe^{2+}, Mg)^{M2} (Fe^{2+}, Fe^{3+}, Mg, Al)^{M1} (Fe^{3+}, Al, Si)^{B} Si^{A} O_6$
- **Olivine:** $(Ca, Fe^{2+}, Mg, Mn, Ni, Co, Zn) [Ca, Fe^{2+}, Mg, Mn, Ni, Co, Zn] SiO_4$
- **Melilite:** $(Ca)_2 [Mg, Fe^{2+}, Fe^{3+}, Al, Zn] \{Fe^{3+}, Al, Si\}_2 O_7$
- **Monoxide:** $CaO - MgO - MnO - CoO - NiO - FeO$ $(+ Fe_2O_3 - Al_2O_3 - ZnO - Cr_2O_3)$
- **α-Ca2SiO4:** $\alpha\text{-}Ca_2SiO_4 (+ Fe_2SiO_4, Mg_2SiO_4, Mn_2SiO_4)$
- **α'-Ca2SiO4:** $\alpha'\text{-}Ca_2SiO_4 (+ Fe_2SiO_4, Mg_2SiO_4, Mn_2SiO_4, Pb_2SiO_4, Zn_2SiO_4)$
- **Wollastonite:** $CaSiO_3 (+ FeSiO_3, MgSiO_3, MnSiO_3)$
- **Corundum:** $Al_2O_3 - Cr_2O_3 - Fe_2O_3$
- **Ilmenite:** $(Fe^{2+}, Mg, Mn, Ti^{3+}) (Ti^{4+}, Ti^{3+})O_3$
- **Pseudobrookite:** $(Fe^{2+}, Mg, Mn, Ti^{3+}) (Ti^{4+}, Ti^{3+})_2 O_5$
- **26 other solid solutions**

Sublattice Model – Compound Energy Formalism

- **Used for solid solutions**
  - Example:

    Spinel Solution (A^{2+}, A^{3+}, B^{2+}, C^{3+}, ...)[A^{2+}, A^{3+}, B^{2+}, C^{3+}, ...]O_4

$$G = \sum_i \sum_j Y_i' Y_j'' G_{ij} - TS^{config} + G^E$$

$$where: Y_i', Y_j'' = site\ fractions\ on\ first\ and\ second\ sublattices$$

$$S^{config} = -R\left(\sum_i Y_i' \ln Y_i' + 2\sum_j Y_j'' \ln Y_j''\right) = configurational\ entropy$$

$$G^E = \sum_i \sum_j \sum_k Y_i' Y_j' Y_k'' L_{ij:k} + \sum_i \sum_j \sum_k Y_k' Y_i'' Y_j'' L_{k:ij}$$

(usually $G^E = 0$ or contains only a very few small parameters L_{ijk})

G_{ij} = "end-member Gibbs energies" (one for each ion pair)

The G_{ij} are the main parameters of the formalism.

(Sublattice Model – Compound Energy Formalism)

- End-member Gibbs energies G_{ij} are the **formalism parameters**.
- Some may be equal to Gibbs energies of real compounds,
- In other cases, certain linear combinations of the G_{ij} have physical significance, and these combinations are the **model parameters**.
  - Example:
    Fe_3O_4 spinel: $(Fe^{2+}, Fe^{3+})\,[Fe^{2+}, Fe^{3+}]_2O_4$
    - Four end-member Gibbs energies:

$$G_{Fe^{2+}Fe^{2+}}, G_{Fe^{2+}Fe^{3+}}, G_{Fe^{3+}Fe^{2+}}, G_{Fe^{3+}Fe^{3+}}$$

$$G_{Fe^{2+}Fe^{3+}} = \text{Gibbs energy of hypothetical normal } Fe_3O_4$$

$$I = G_{Fe^{3+}Fe^{3+}} + G_{Fe^{3+}Fe^{2+}} - 2G_{Fe^{2+}Fe^{3+}}$$

$$= \text{model parameter related to degree of inversion}$$

$$\Delta = G_{Fe^{2+}Fe^{2+}} + G_{Fe^{3+}Fe^{3+}} - G_{Fe^{3+}Fe^{2+}} - G_{Fe^{2+}Fe^{3+}}$$

$$= \text{model parameter related to reciprocal exchange of nearest-neighbor pairs}$$

$$\left(G_{Fe^{3+}Fe^{2+}} \text{ can be arbitrarily set equal to } G_{Fe^{2+}Fe^{3+}}\right)$$

Quasichemical Model for Short-Range Ordering

- **Used for the liquid 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:

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

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

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

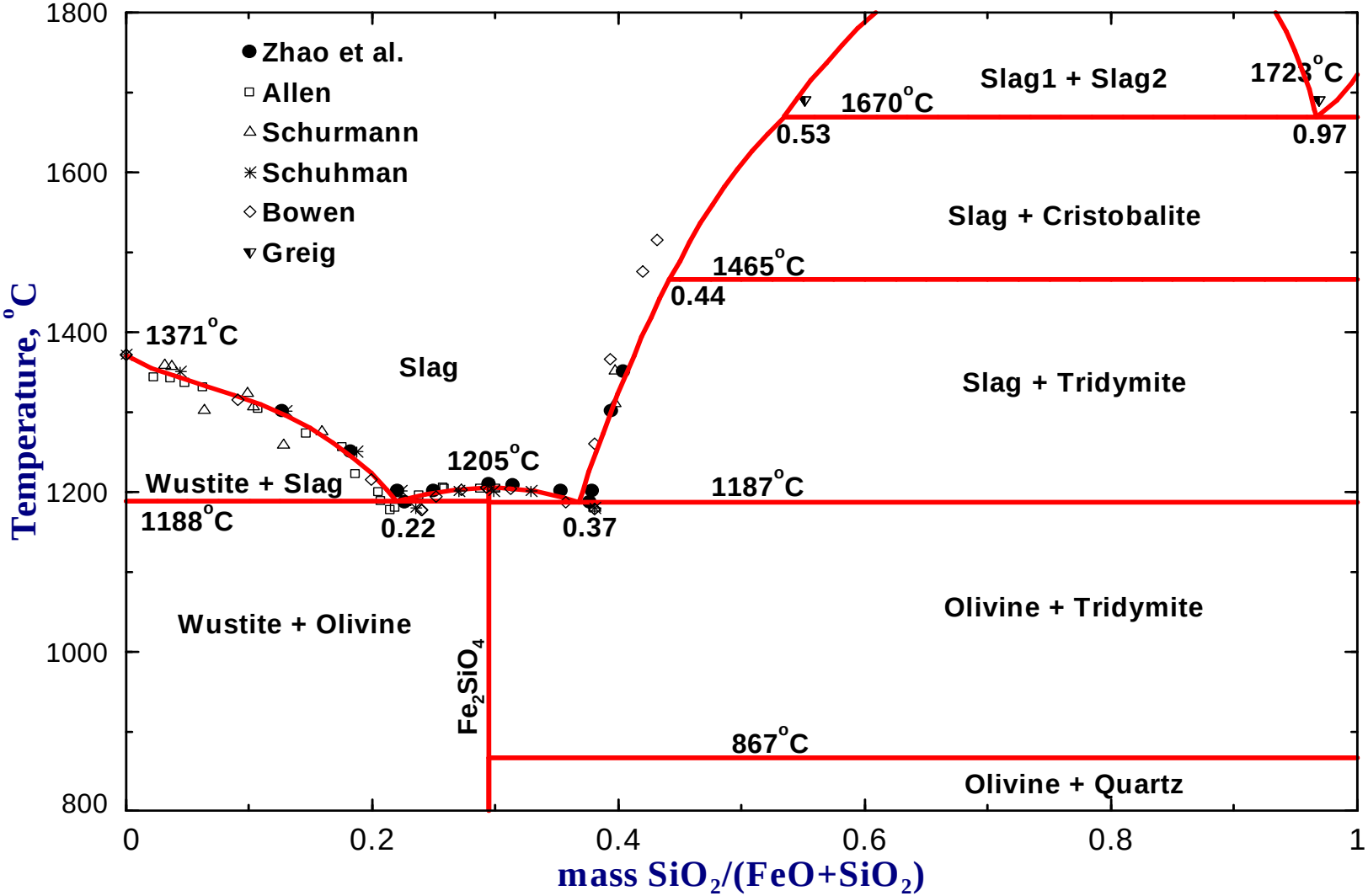
ΔS^{config} = (Ising) entropy for random distribution of pairs = function of n_i and n_{mn}

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

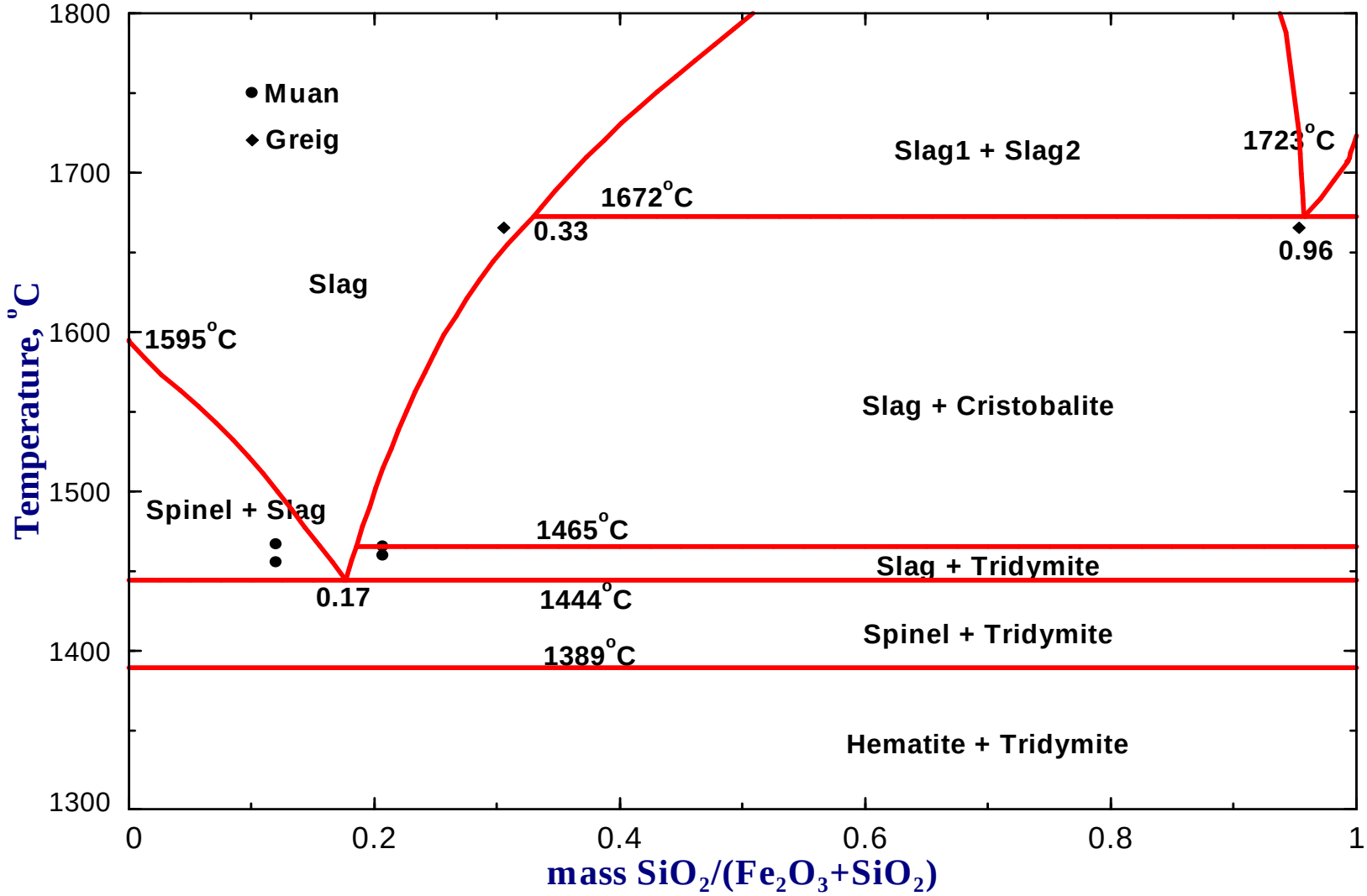
(The equilibrium values of n_{mn} are obtained by setting $\partial G/\partial n_{mn} = 0$ at constant n_i)

Some of the data critically evaluated and used in the modeling of the $SiO_2 – Al_2O_3 – CaO – FeO – Fe_2O_3$ system, and comparison with calculations from the resultant optimized database.

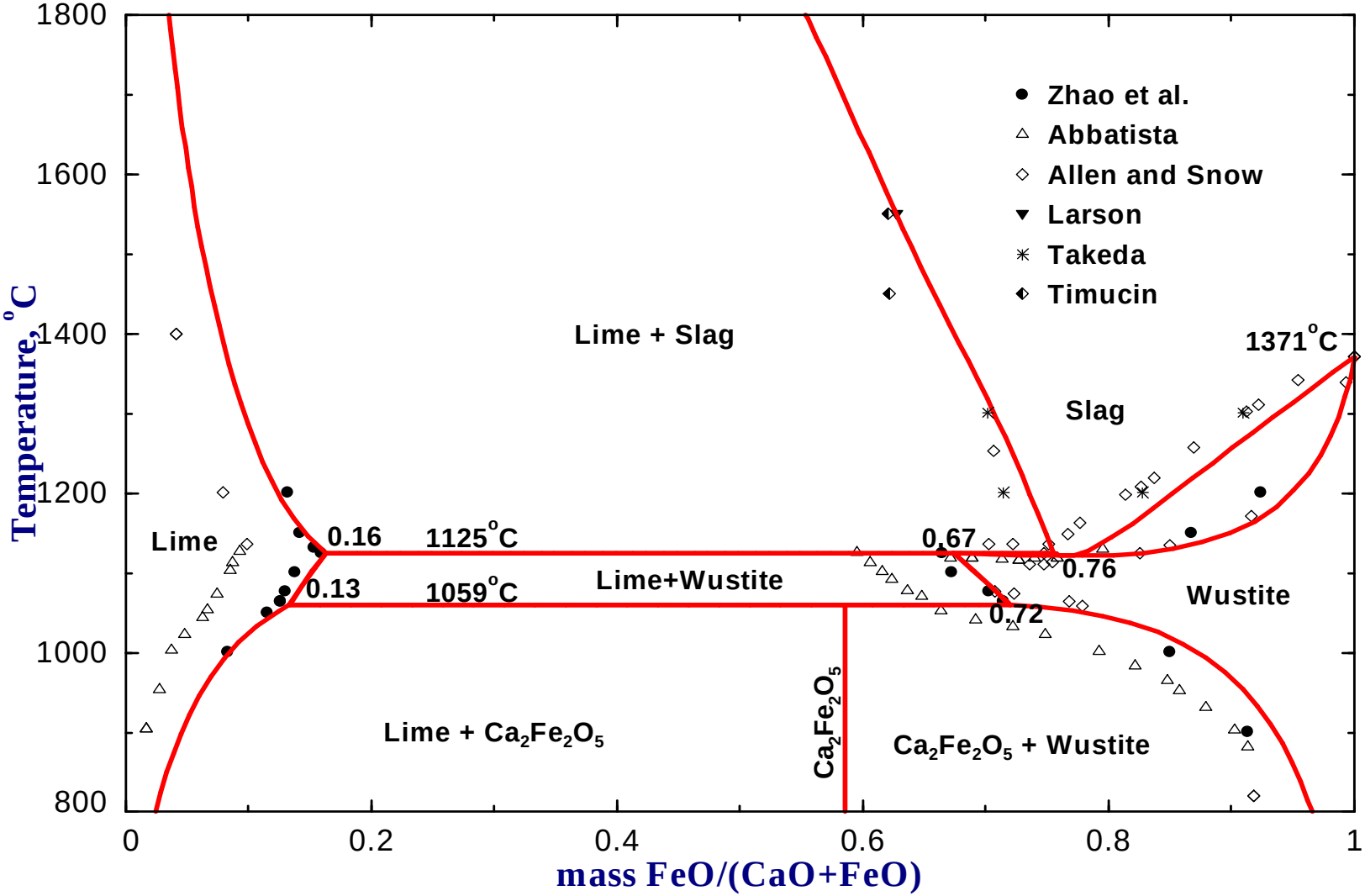
Calculated Fe-Si-O phase diagram in equilibrium with iron



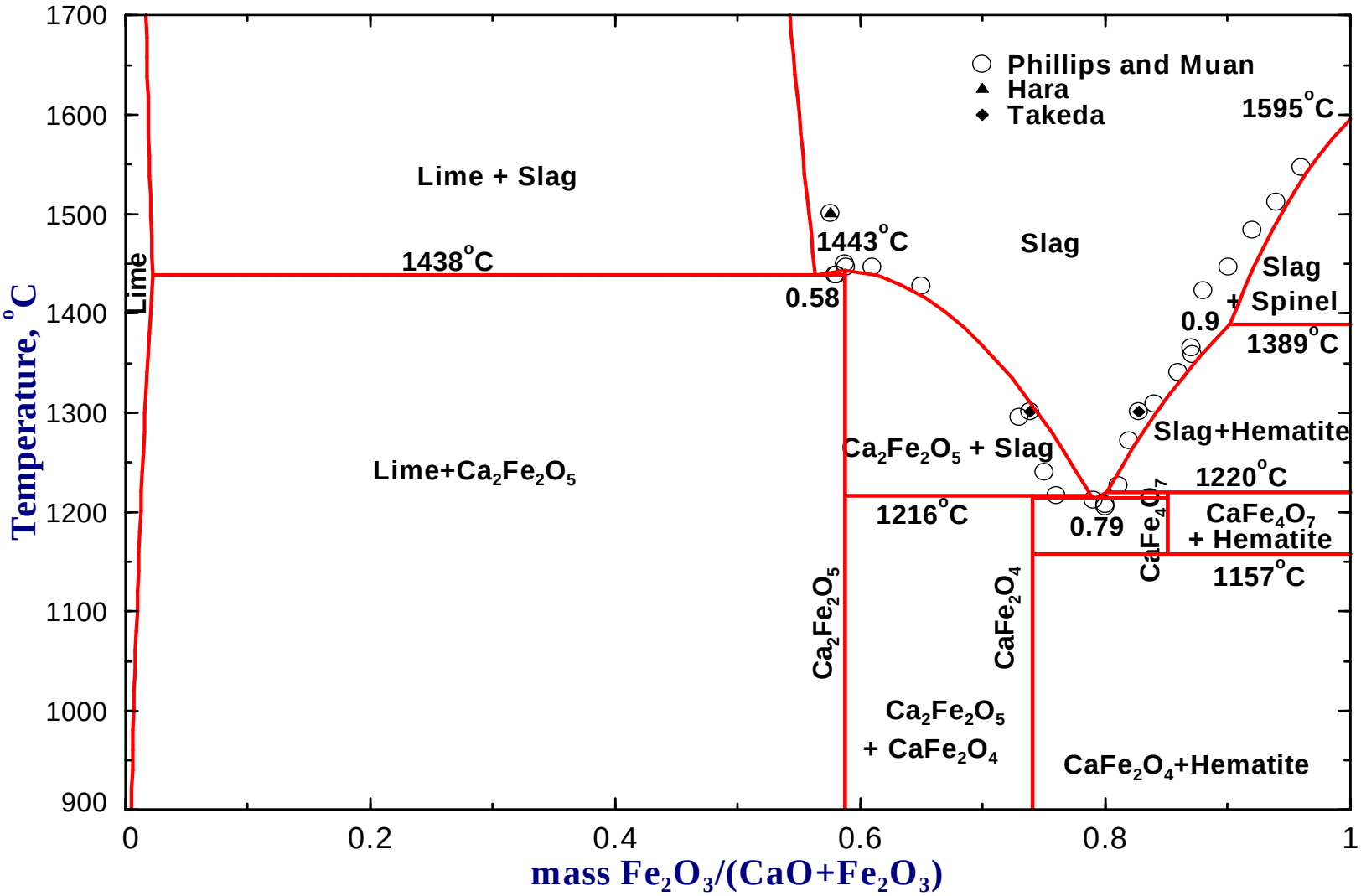
Calculated Fe-Si-O phase diagram in equilibrium with air



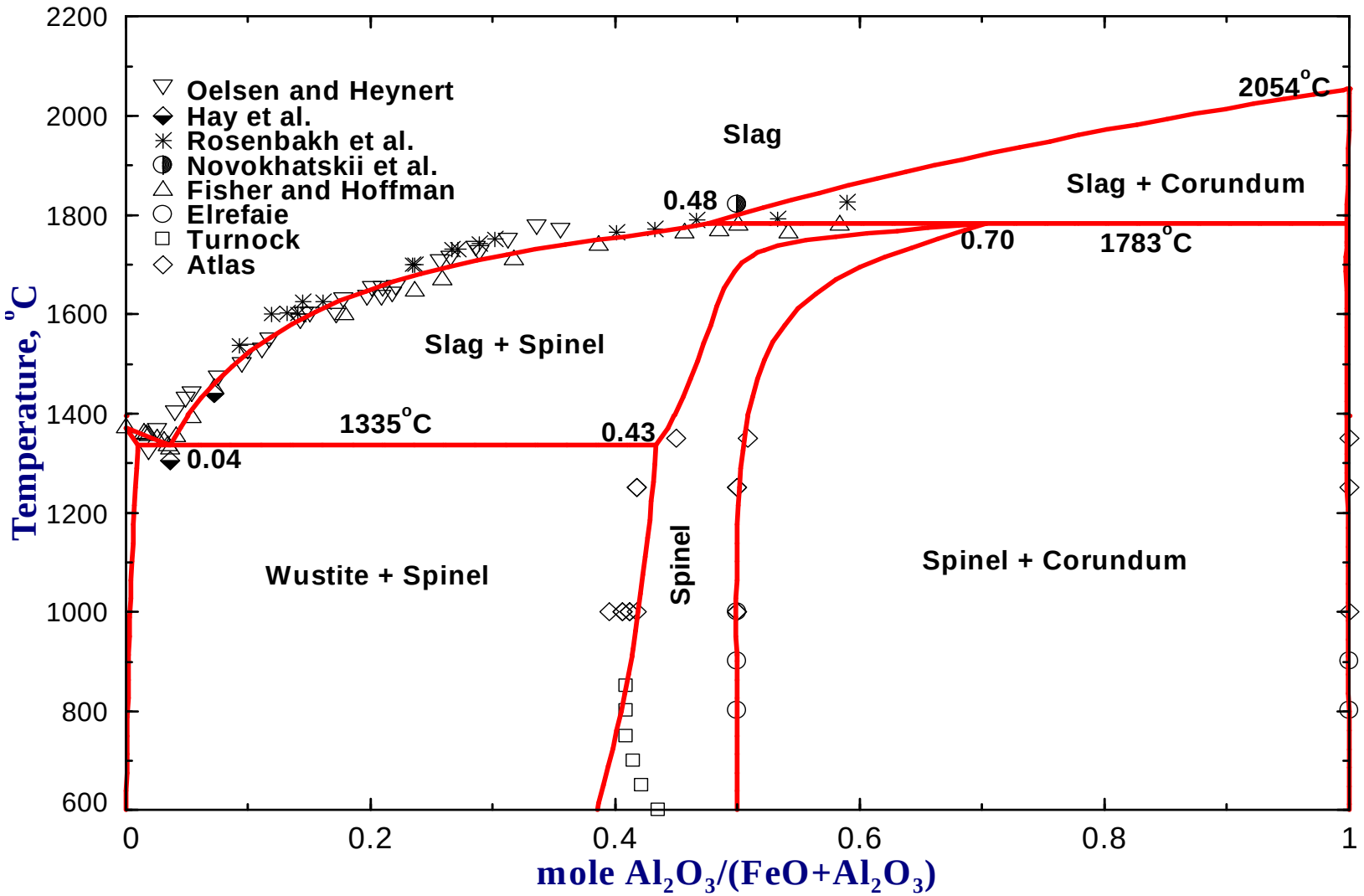
Calculated Ca-Fe-O phase diagram in equilibrium with iron



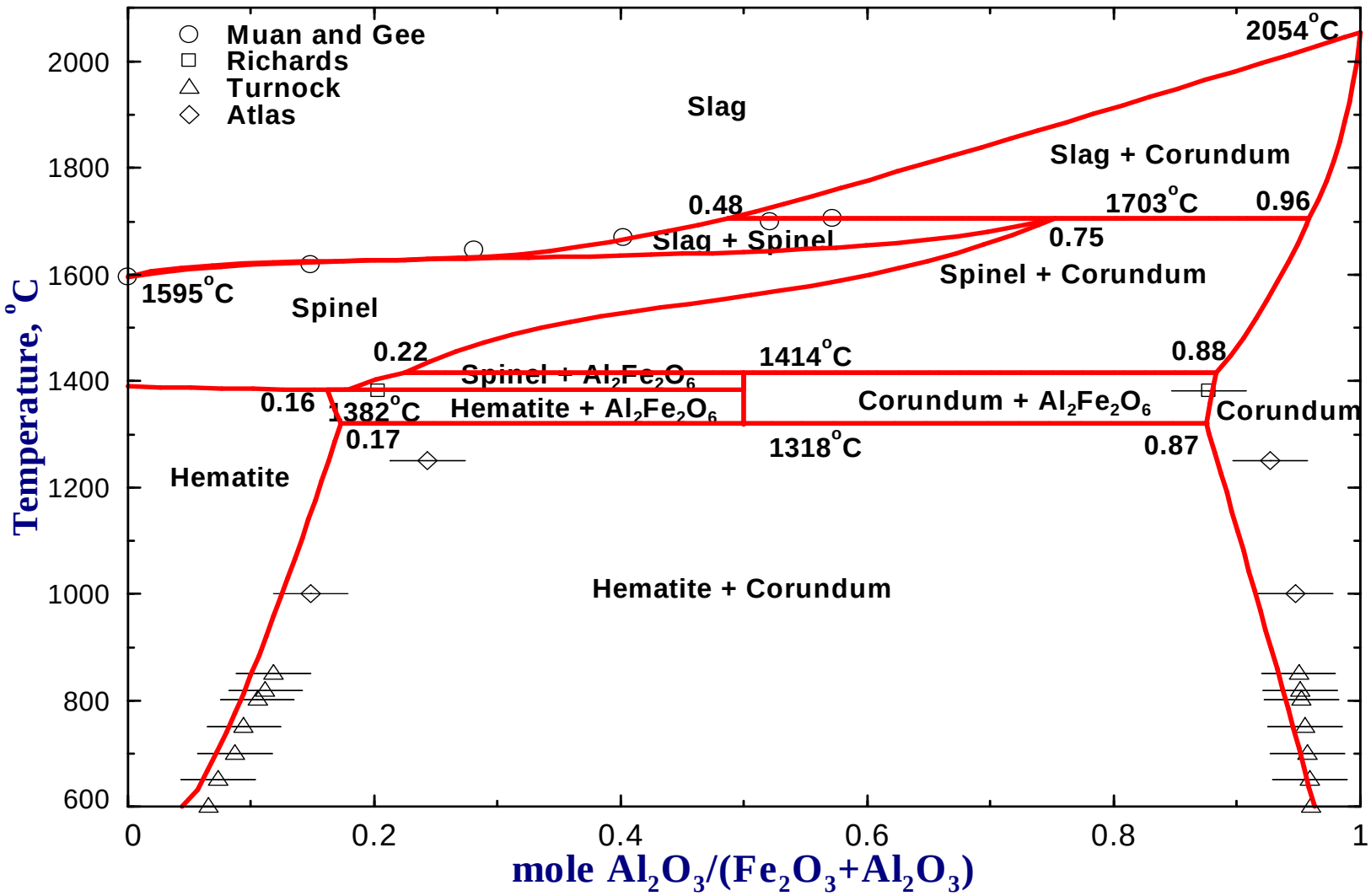
Calculated Ca-Fe-O phase diagram in equilibrium with air



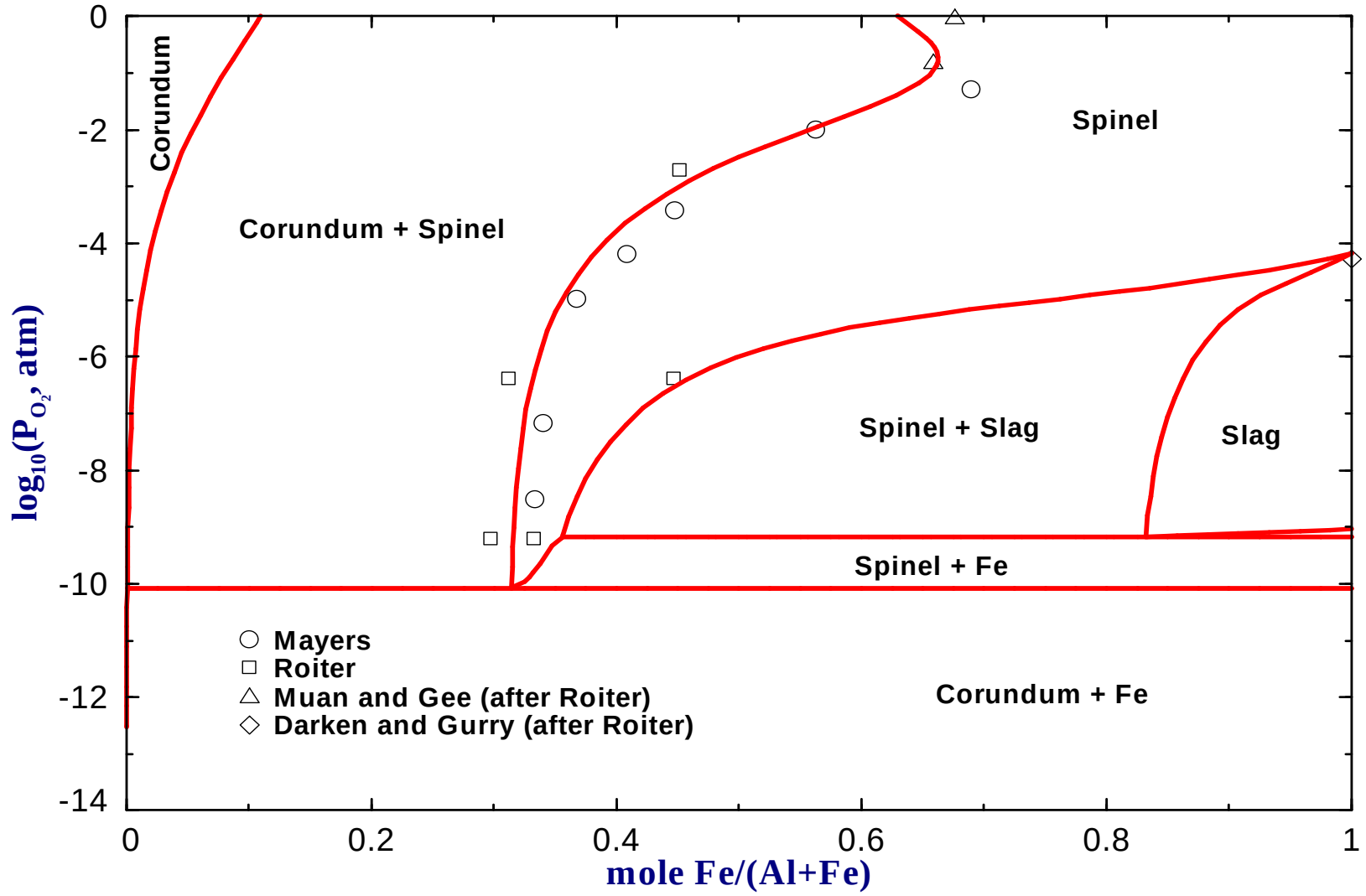
Calculated $FeO-Al_2O_3$ phase diagram in equilibrium with iron



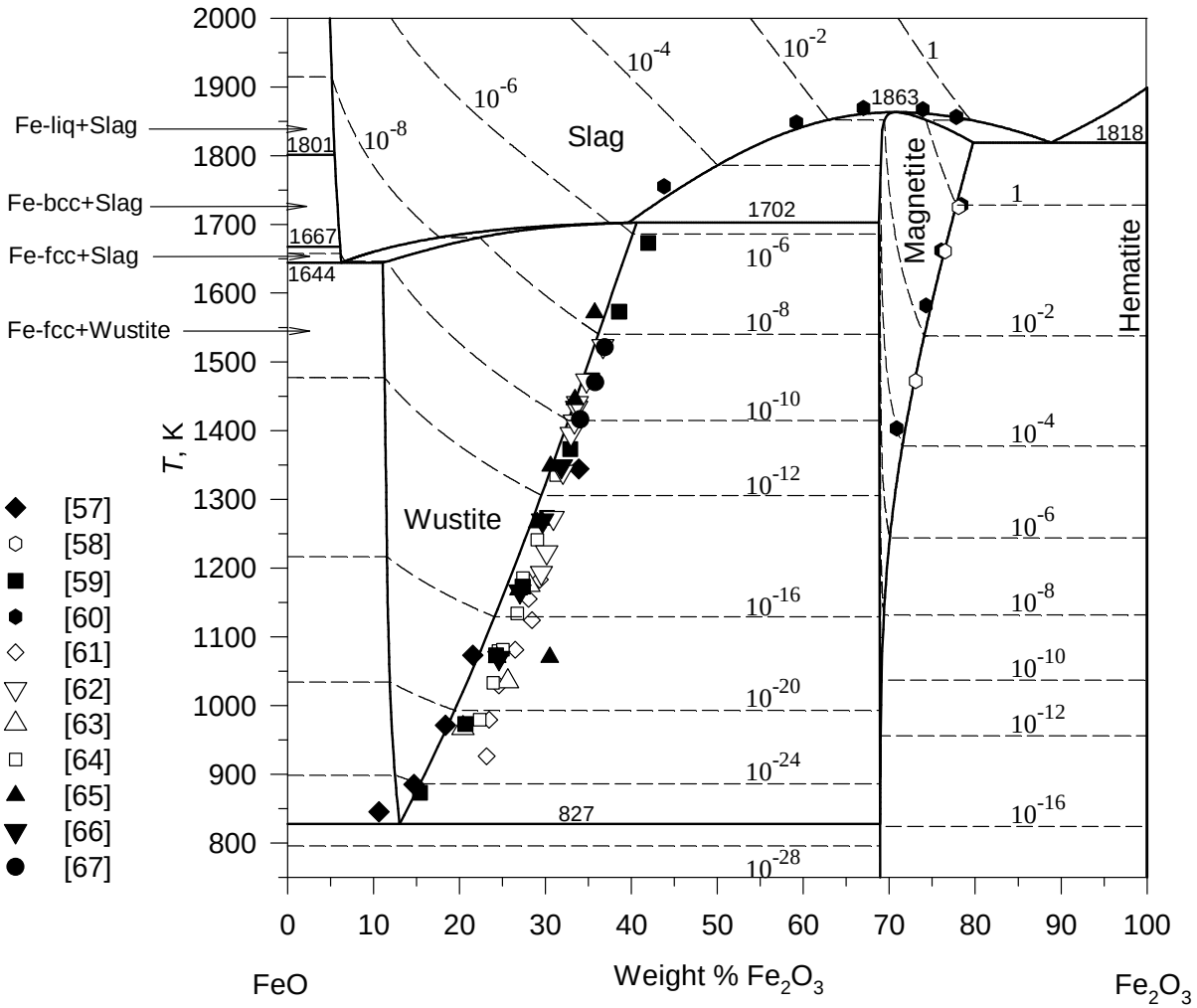
Calculated Al-Fe-O phase diagram in equilibrium with air



Calculated Al-Fe-O phase diagram at 1500°C

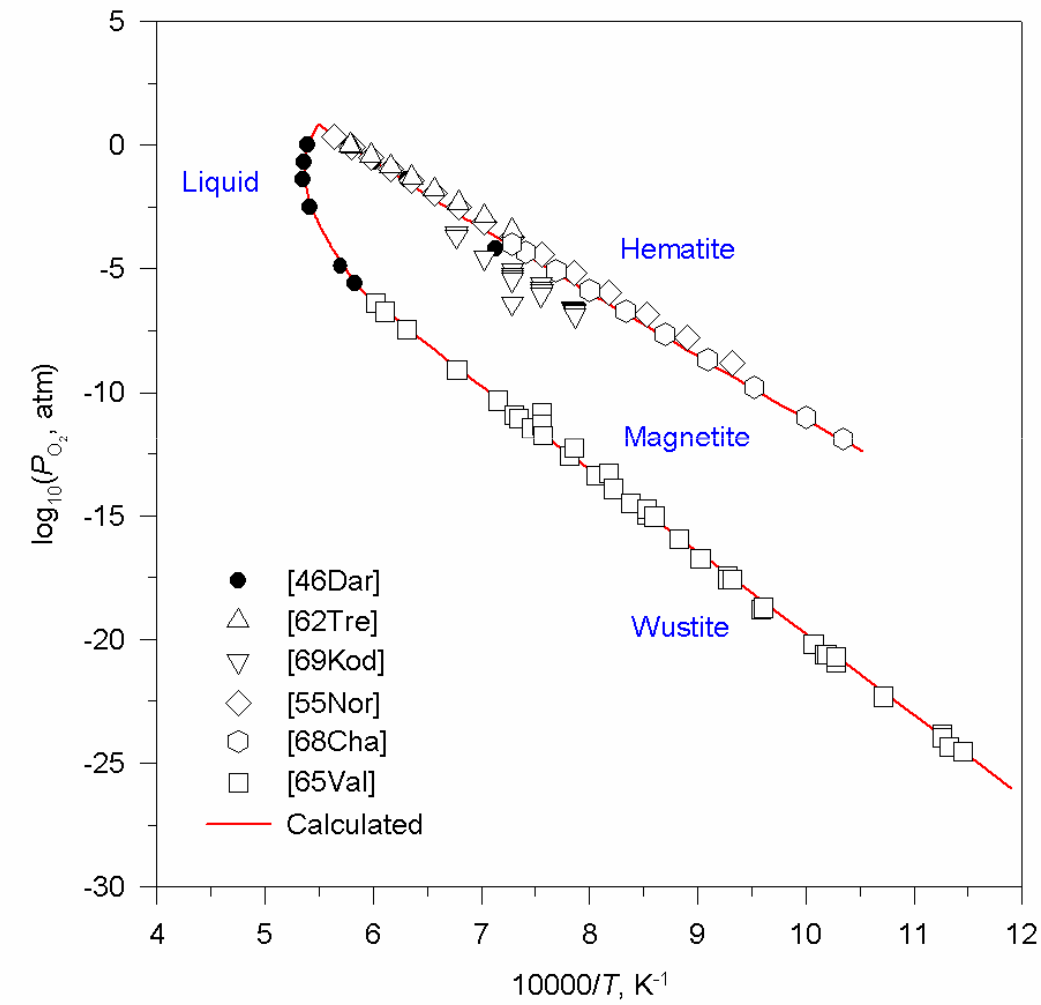


$FeO-Fe_2O_3$ phase diagram

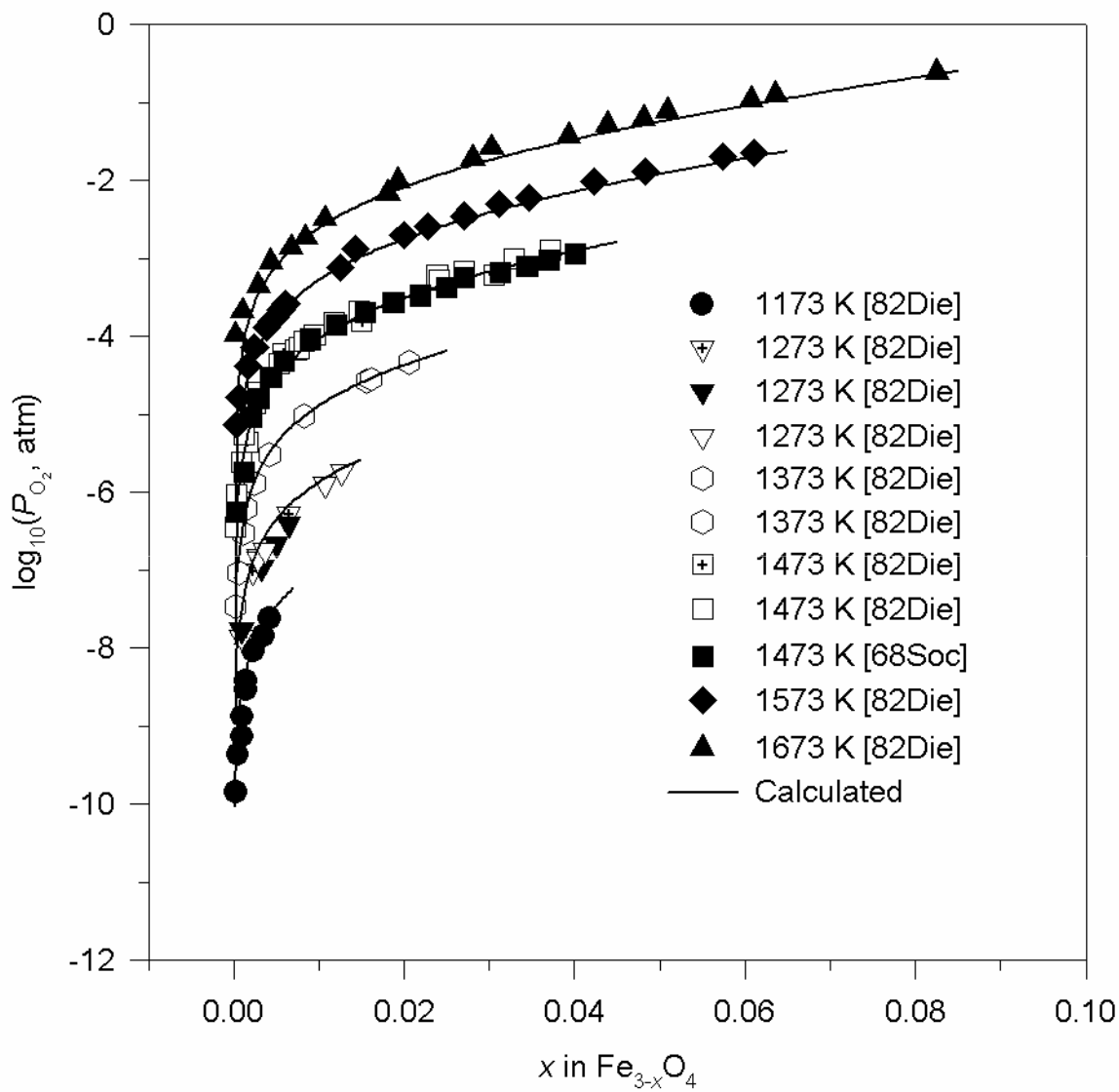


Selected experimental points and calculated lines and invariant temperatures. Dashed lines are calculated oxygen isobars (bar).

Fe-O System



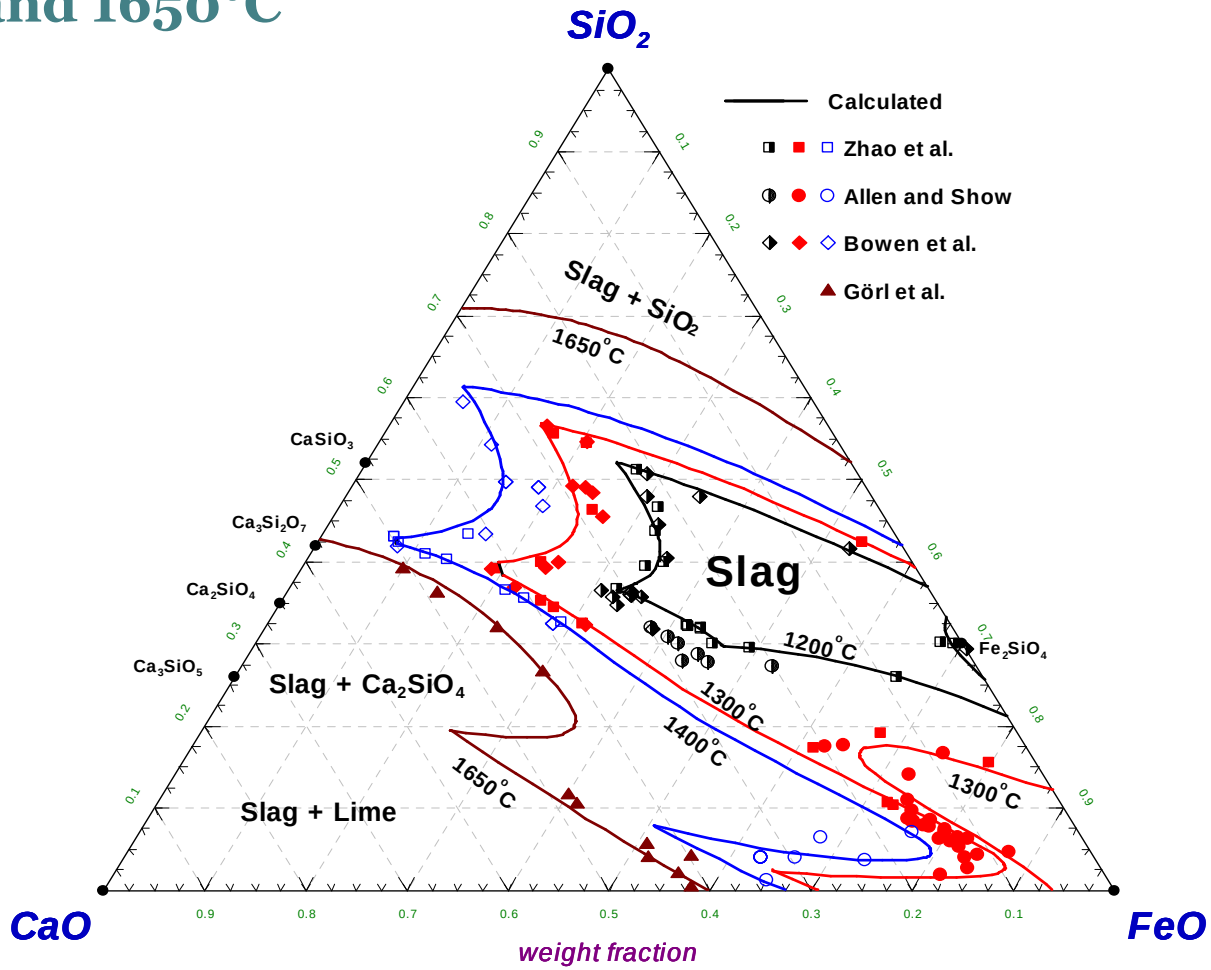
Oxygen partial pressure for two-phase equilibria with magnetite in the Fe-O system.



Experimental and calculated oxygen partial pressure over single-phase magnetite as a function of composition.

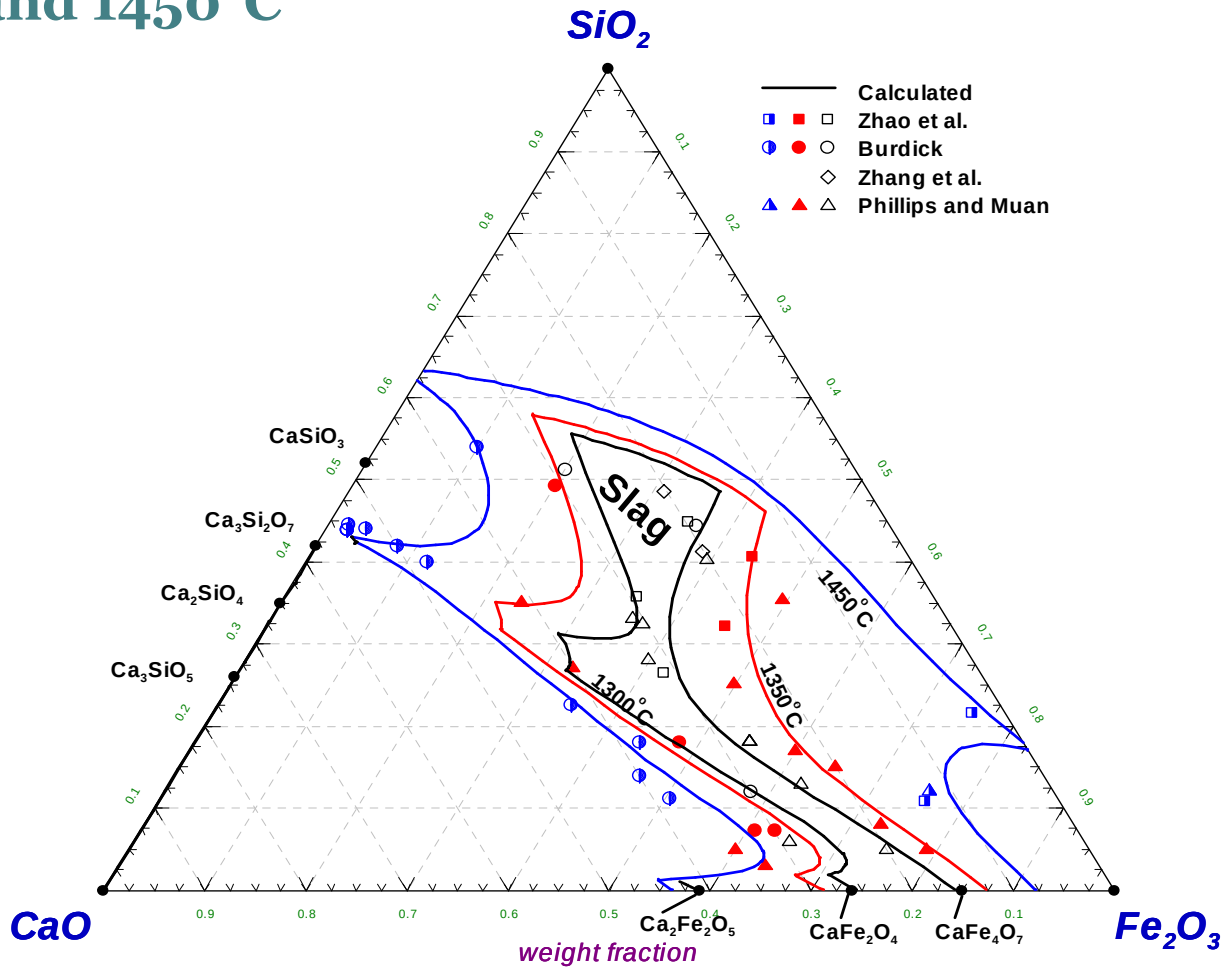
Liquidus of the Ca-Fe-Si-O system in equilibrium with iron

Temperatures between 1200°C and 1650°C



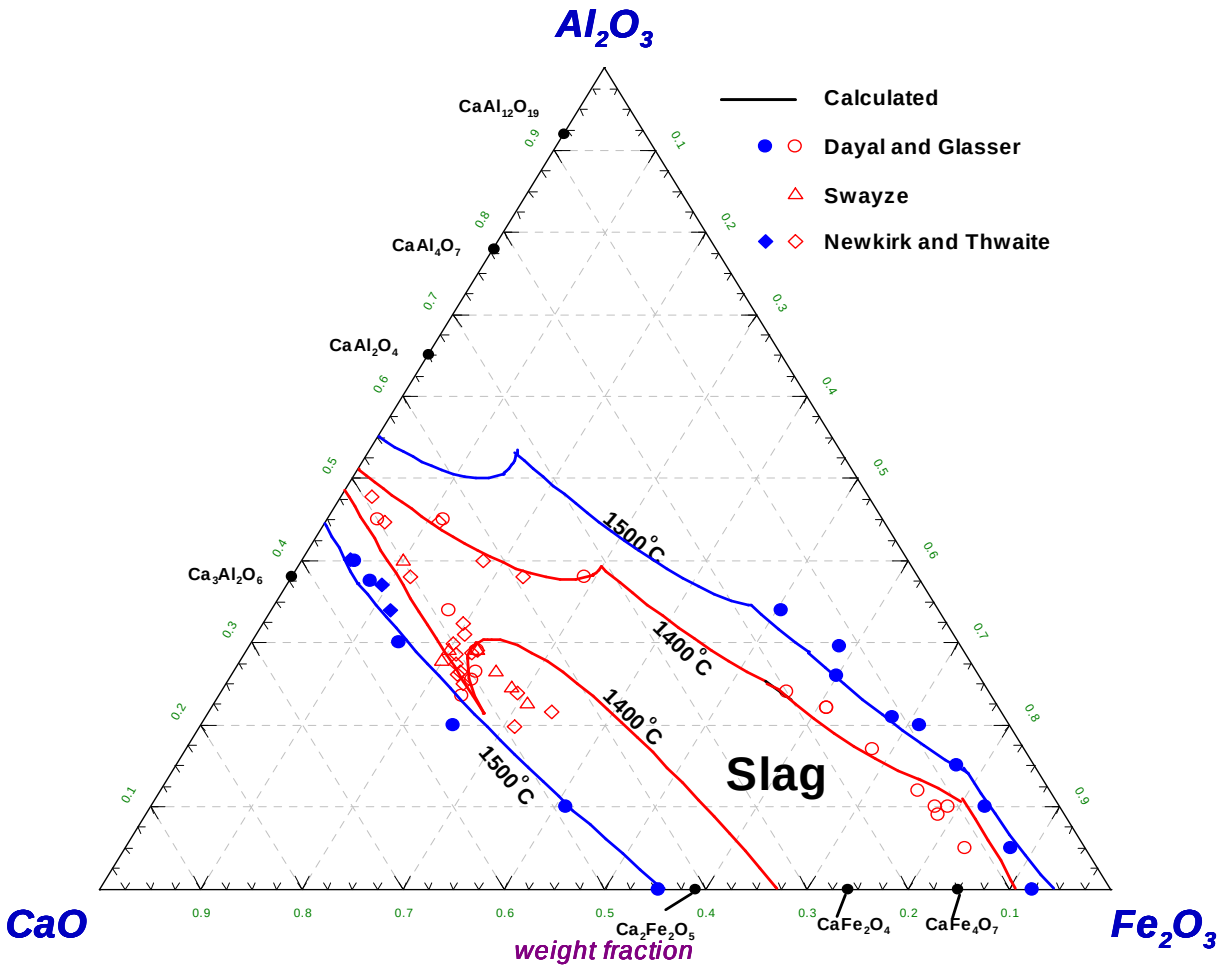
Liquidus of the Ca-Fe-Si-O system in equilibrium with air

Temperatures between 1300°C and 1450°C

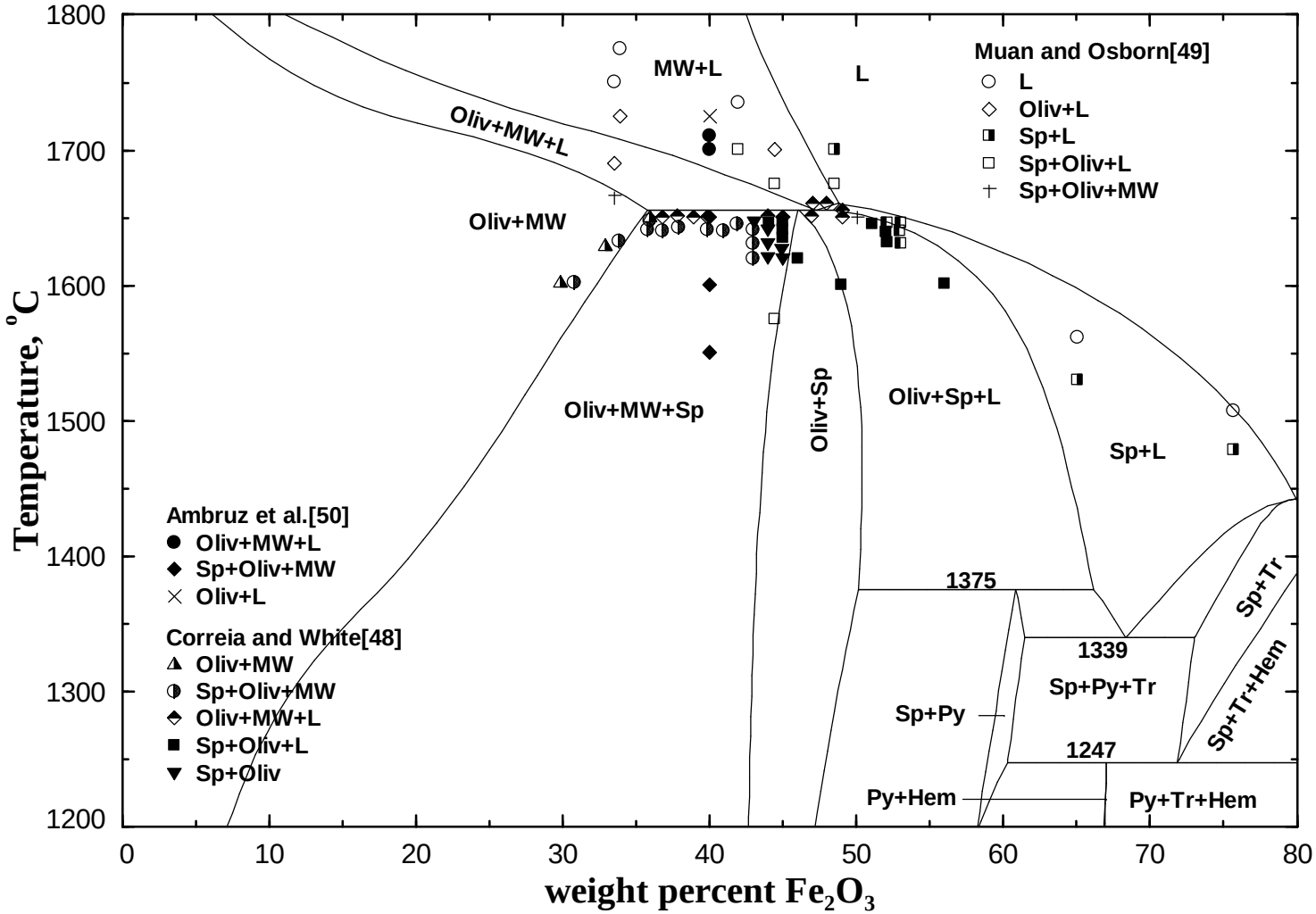


Liquidus of the Al-Ca-Fe-O system in equilibrium with air

At 1400°C and 1500°C



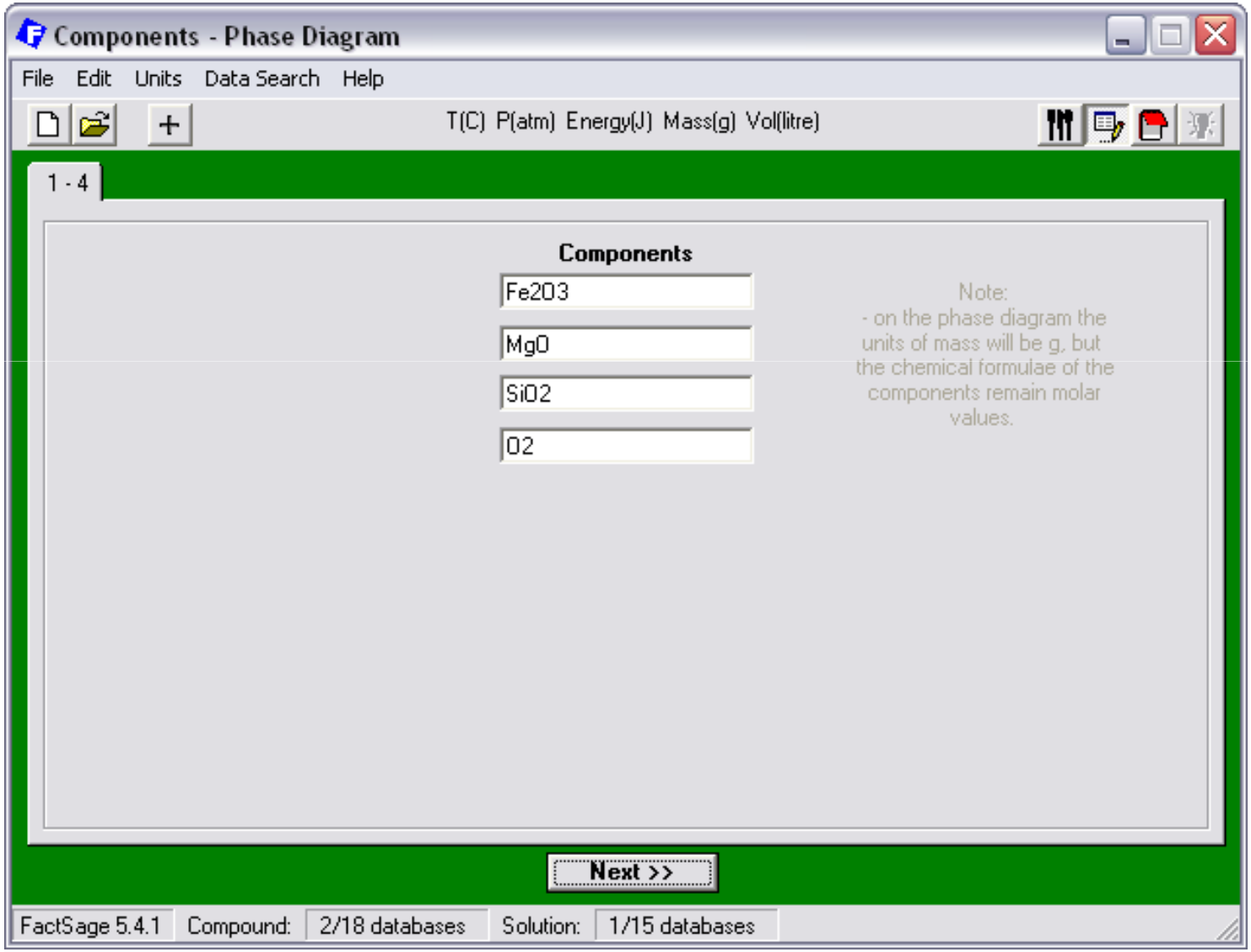
Calculating Multicomponent Phase Diagram Sections using the Oxide Database



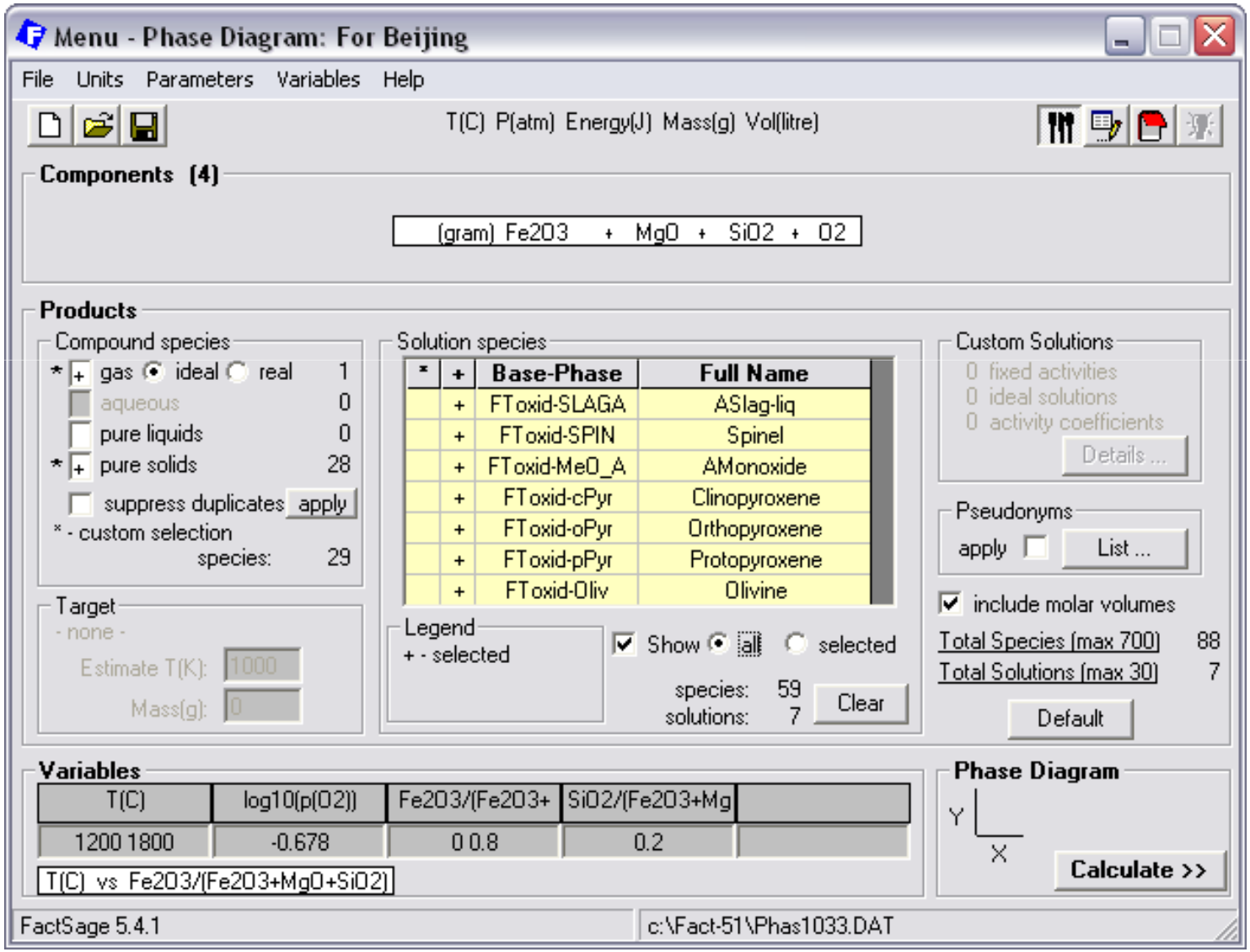
Calculated section of the Fe_2O_3-MgO-SiO_2-O_2 phase diagram in air at $SiO_2/(MgO+Fe_2O_3+SiO_2)$ = 20 weight %

- Inputs to the FactSage module required to generate the preceding diagram
- (data retrieved automatically from database)

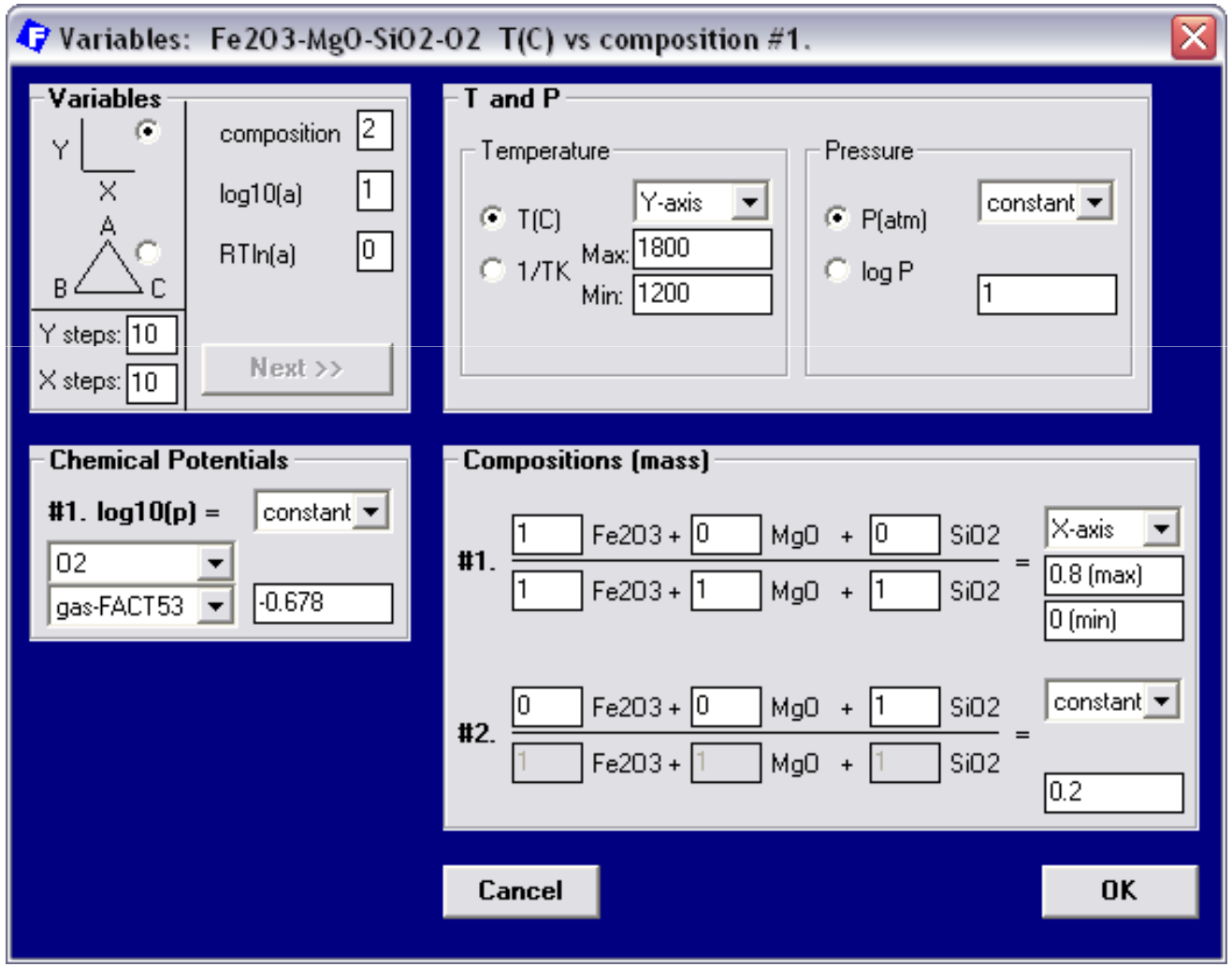
(1) Components



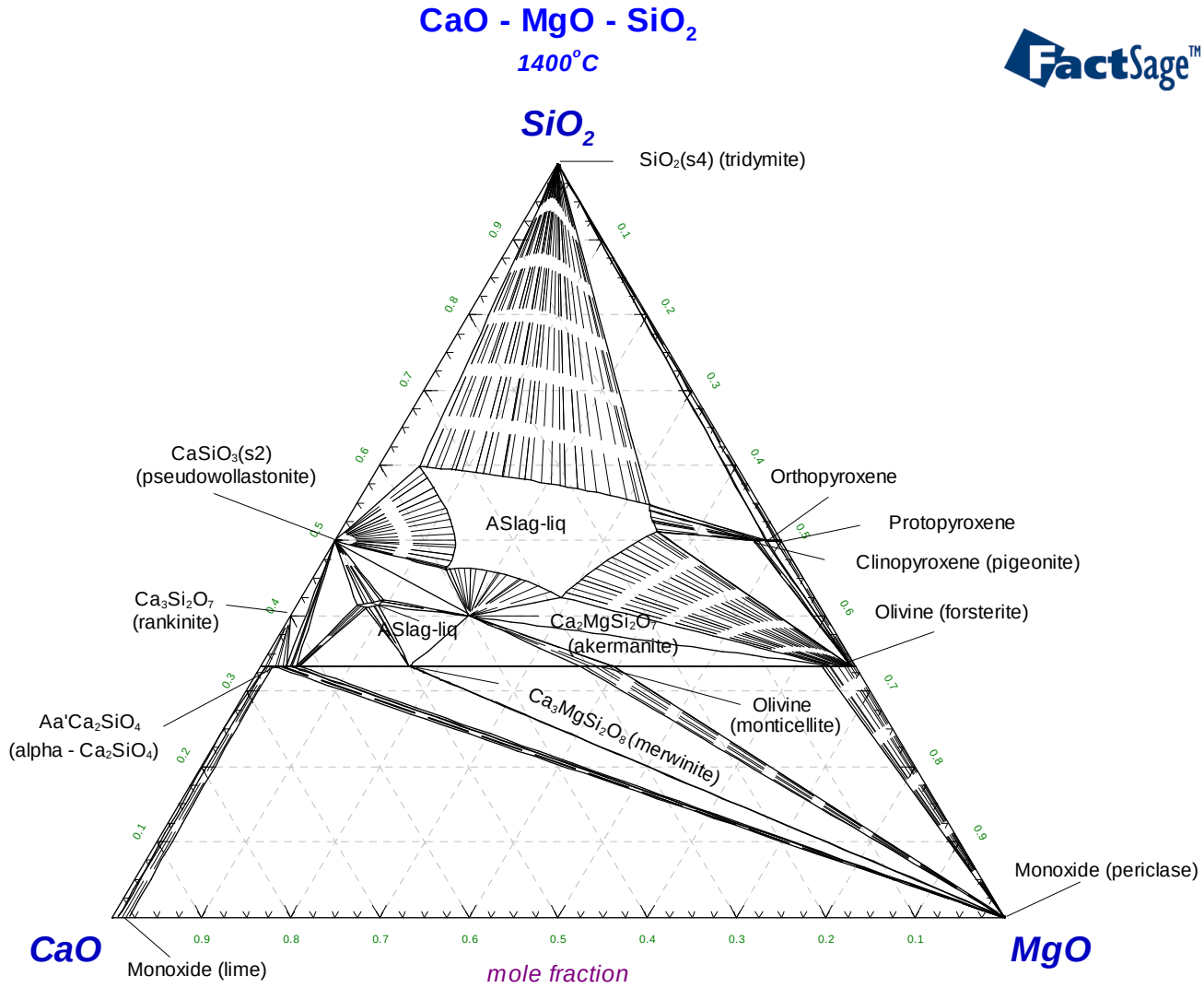
(2) Species Selection



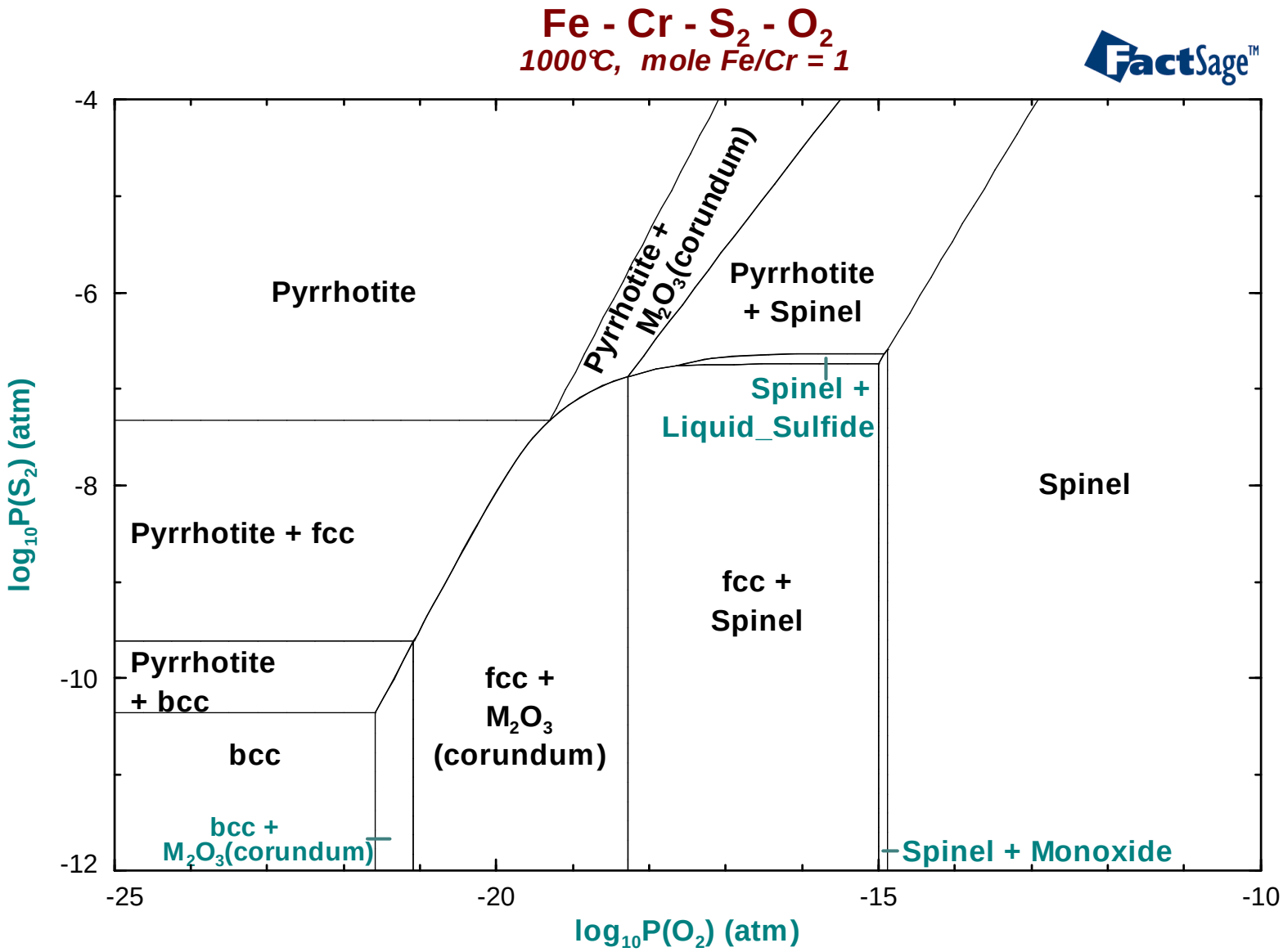
(3) Defining Variables



CaO – MgO – SiO_2 , 1400°C



Calculations using the Oxide Database in Conjunction with other Databases (such as Databases for Metallic Phases, Gases, Sulfides, etc.)


Fe - Cr - S2 - O2
1000℃, mole Fe/Cr = 1
FactSage™
Pyrrhotite
Pyrrhotite + M2O3(corundum)
Pyrrhotite + Spinel
Spinel + Liquid_Sulfide
Spinel
Pyrrhotite + fcc
fcc + Spinel
Pyrrhotite + bcc
fcc + M2O3 (corundum)
bcc
bcc + M2O3(corundum)
Spinel + Monoxide
log10P(S2) (atm)
log10P(O2) (atm)
-4
-6
-8
-10
-12
-25
-20
-15
-10

Equilibrium phase composition generated by placing cursor at the point $P(S_2) = 10^{-7}$, $P(O_2) = 10^{-15}$ in the preceding diagram and clicking

```
log10(p(S2)) (atm) = -7.00,  log10(p(O2)) (atm) = -15        1000.00 C
==================================================

0.00    mol    (0.99294E-07     S2
             +  0.33664E-07    SO2
             +  0.49582E-08    SO
             +     .
                   .
                   .
             +  0.10000E-14    O2
             +     .
                   .
                   .
              (1 atm, gas)


 +  0.32583  mol   Spinel
             Mole fraction of sublattice constituents in Spinel:
             Fe[2+]      0.87607     Stoichiometry = 1.0000
             Fe[3+]      0.12392
             Cr[3+]      0.30106E-05
             Cr[2+]      0.34690E-05
             ------------------------
             Fe[2+]      0.61961E-01  Stoichiometry = 2.0000
             Fe[3+]      0.17195
             Va[0]      0.19186E-08
             Cr[3+]      0.76609

 +  0.21232E-01 mol   (  0.94037            FeO
                      +  0.41724E-01     Fe2O3
                      +  0.17901E-01     Cr2O3
                      ( Monoxide)
```

Conclusions

- Thermodynamic databases have been developed which contain critically evaluated and modeled data for thousands of compounds and hundreds of multicomponent solutions.
- The evaluated data are generally reproduced by the models within the experimental error limits.
- The models permit extrapolation into regions of temperature and composition where data are unavailable.
- The databases are automatically accessed by user-friendly software that calculates complex multiphase equilibria in large multicomponent systems for a wide variety of input/output constraints.
- The databases contain parameters of models specifically developed for different types of solutions involving sublattices, ordering, etc.