# Thermochemical models of molten silicates and silicate vapor atmospheres on hot rocky exoplanets

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Outline

Thermochemical modeling of molten silicates

Thermodynamics of Solutions

Ideal Mixing of Complex Components Model

Some examples with the MAGMA code

Applications to hot rocky planets

# Thermochemical modeling of molten silicates

In general, activity $a_i$ and mole fraction $X_i$ are related via $a_i = \gamma_i X_i$

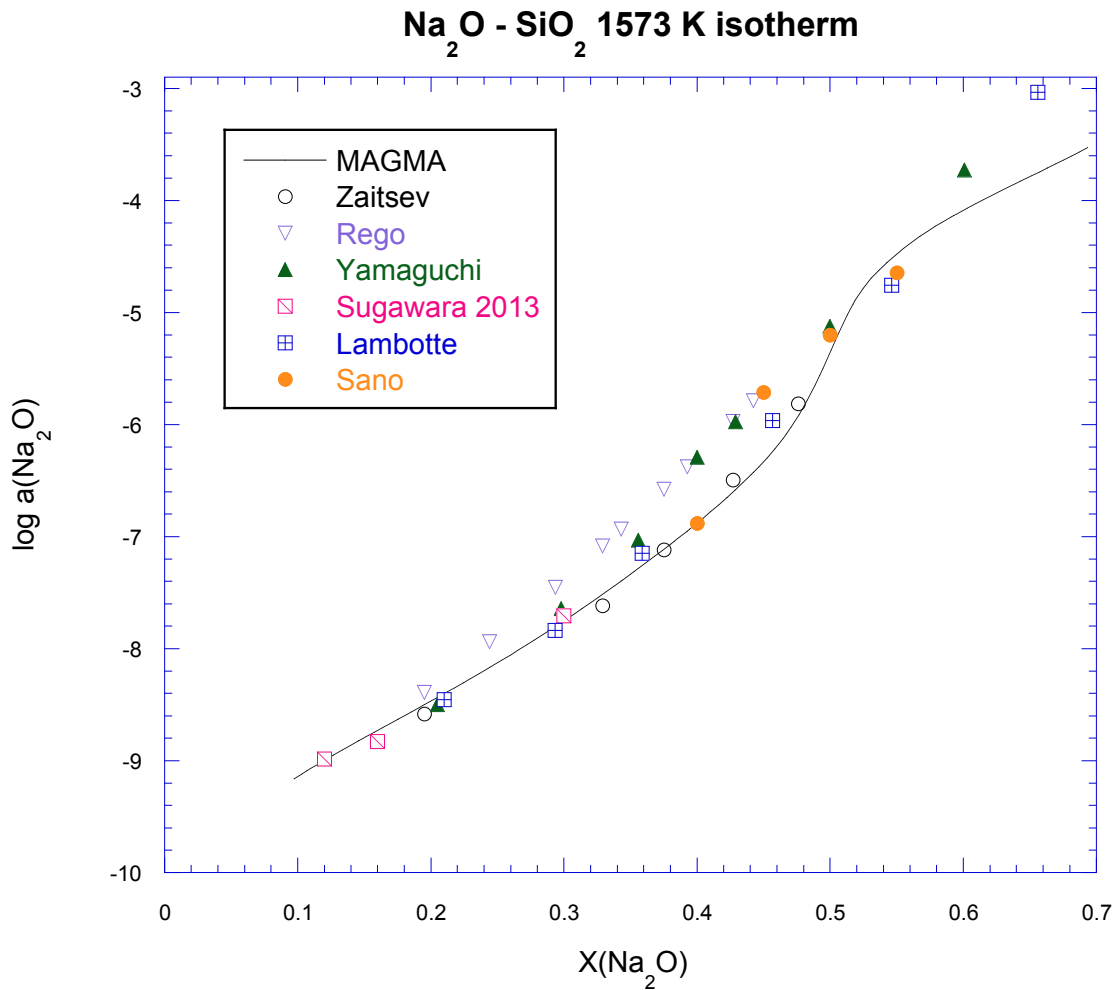with $\gamma_i = 1$ for ideal solutions and $\gamma_i \neq 1$ for non-ideal solutions

**Na$_2$O - SiO$_2$ 1573 K isotherm**



Figure shows activity << mole fraction for $Na_2O$

We want to compute a = f(T,P,X) for multicomponent silicate melts.

Then we can compute all other properties of the silicate melts.

Define some concepts and nomenclature for thermodynamics of

solutions before proceeding

# Thermodynamics of solutions

## Mole Fraction Notation

We express concentration as mole fraction $X_i$, e.g., for the $Na_2O$ – $SiO_2$ binary solution, the mole fraction of $Na_2O$ is

$$X_{Na_2O} = \frac{n_{Na_2O}}{n_{Na_2O} + n_{SiO_2}}$$

where n is the number of moles of $Na_2O$ or $SiO_2$, respectively.

The sum of mole fractions for a solution is unity. For example, considering molten soda-lime glass ($Na_2O$ – $CaO$ – $SiO_2$)

$$X_{Na_2O} + X_{CaO} + X_{SiO_2} = 1$$

Typical $Na_2O/SiO_2$ molar ratios in planetary materials:

| Object | $Na_2O/SiO_2$ molar ratio |
|---|---|
| Bulk silicate Moon | 0.0010 |
| Bulk silicate Earth | 0.0076 |
| Earth's crust | 0.052 |
| CI Chondrites (= solar ratio) | 0.029 |

The $SiO_2$-rich end of $Na_2O$ – $SiO_2$ melts is most relevant for us.

# Thermodynamics of solutions II.

## Gibbs Energy of Solution

Two or more components form solutions because it is energetically favorable to do so – the solution has a lower Gibbs energy G than the physical mixture of the two (or more) components.

$$\Delta G^M = G_{solution} - G_{mixture}$$

We call $\Delta G^M$ the Gibbs energy of mixing. For the $Na_2O - SiO_2$ binary,

$$\Delta G^M = n_{Na_2O}\left(\bar{G}_{Na_2O} - G^o_{m,Na_2O}\right) + n_{SiO_2}\left(\bar{G}_{SiO_2} - G^o_{m,SiO_2}\right)$$

$$\Delta G^M = n_{Na_2O}\left(RTlna_{Na_2O}\right) + n_{SiO_2}\left(RTlna_{SiO_2}\right)$$

The terms in the equations are the number of moles ($n_i$) of each component, the partial molal Gibbs energy of each component in the solution (e.g., $\bar{G}_{Na_2O}$), the molar Gibbs energy of each pure liquid oxide (e.g., $G^o_{m,Na_2O}$) at the same temperature, and the activity ($a_{Na_2O}$, $a_{SiO_2}$) of each component (see Solution Thermodynamics slide IV).

All the other thermodynamic properties of solutions can be derived by differentiation of $\Delta G^M$ the Gibbs energy of mixing using the fundamental equation dG = VdP – SdT and the Gibbs – Helmholtz equation G = H – TS.

## Thermodynamics of solutions III.

**Other Properties Derived From $\Delta G^M$**

For example, the entropy of mixing is given by the partial derivative at constant pressure (P) and composition (X)

$$\Delta S^M = -\left(\frac{\partial \Delta G^M}{\partial T}\right)_{P,X}$$

The volume of mixing is given by

$$\Delta V^M = \left(\frac{\partial \Delta G^M}{\partial P}\right)_{T,X}$$

The enthalpy (or heat) of mixing is given by

$$\Delta H^M = \left(\frac{\partial \Delta G^M/T}{\partial(1/T)}\right)_{P,X}$$

The constant pressure heat capacity $C_P$ $(\partial H/\partial T)$ of mixing is given by

$$\Delta C_P^M = -T\left(\frac{\partial^2 \Delta G^M}{\partial T^2}\right)_{P,X}$$

# Thermodynamics of solutions IV.

## Definition of Thermodynamic Activity

Thermodynamic activity (a) – henceforth activity – G.N. Lewis 1907

$$a = \frac{f}{f^*} \cong \frac{p}{p^*}$$

The activity of a material is approximately equal to the ratio of the

partial pressure (p) of the material at some P,T,X and the saturation

vapor pressure (p*) of the pure material at the same total pressure

(P) and temperature (T). The activity is exactly equal to the fugacity

ratio where f = $\Gamma$p with $\Gamma$=1 for ideal and $\Gamma \neq$ 1 for non-ideal gases. In

the absence of PVT data for many high temperature gases, we

assume $\Gamma$=1 for our discussion and define activity as

$$a = \frac{p}{p^*}$$

Example: At 1600 C (1873 K) the vapor pressure of pure liquid Fe is

0.0572 mm Hg and the Fe vapor pressure over molten Fe – Ni alloy

($Fe_{0.9}Ni_{0.10}$) is 0.05124 mm Hg. Calculate the activity of pure liquid Fe

and Fe in the molten alloy from these data.

$$a_{Fe(liq)} = \frac{0.0572}{0.0572} = 1 \text{ and } a_{Fe(alloy)} = \frac{0.05124}{0.0572} = 0.90$$
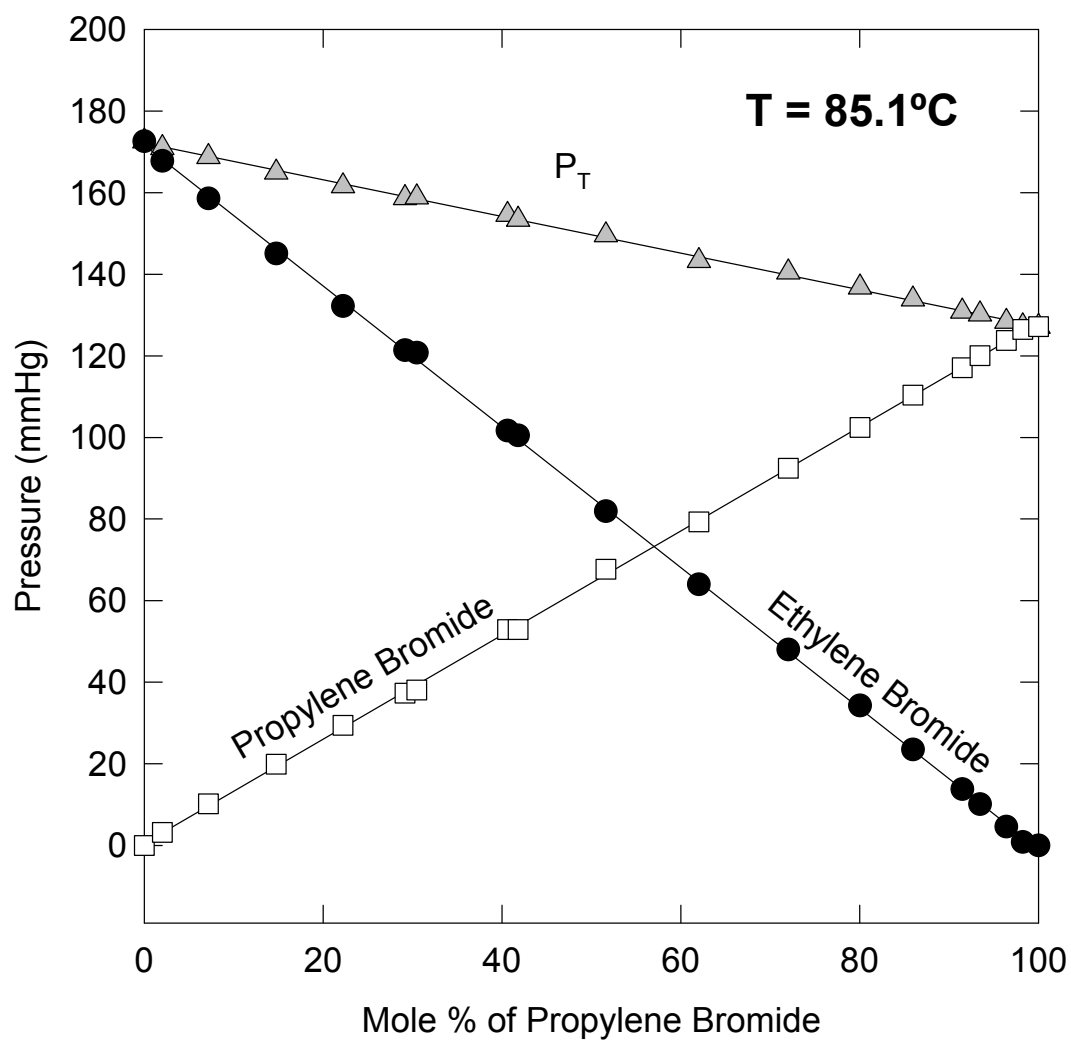
# Thermodynamics of solutions V.

**Ideal Solutions**

These follow Raoult's Law at all concentrations:

$$a_i = X_i = \frac{f_i}{f_i^o} \cong \frac{p_i}{p_i^o}$$

Ethylene and propylene bromide ($C_2H_4Br_2 - C_3H_6Br_2$) form an ideal solution ($p_i = X_i p_i^o$) giving a characteristic straight-line plot:

# Thermodynamics of solutions VI.

## Enthalpy of Mixing

Ideal solutions also are athermal

$$\Delta H^M = 0 = \left(\frac{\partial \Delta G^M/T}{\partial(1/T)}\right)_{P,X}$$

This is easy to understand if we use the definition of an ideal solution

and substitute into our expression for the Gibbs energy of mixing.

Any two components A and B in an ideal solution ($a_i = X_i$)

$$\Delta G^M = n_A(RT\ln a_A) + n_B(RT\ln a_B)$$

$$\Delta G^M = n_A(RT\ln X_A) + n_B(RT\ln X_B)$$

The ideal gas constant R, number of moles, and mole fractions are

constant, hence

$$\left(\frac{\partial \Delta G^M/T}{\partial(1/T)}\right)_{P,X} = \frac{\partial}{\partial(1/T)}R[n_A\ln X_A + n_B\ln X_B] = 0$$

Conversely non-ideal solutions have $\Delta H^M \neq 0$ because $\gamma_i \neq 1$

$$\left(\frac{\partial \Delta G^M/T}{\partial(1/T)}\right)_{P,X} = \frac{\partial}{\partial(1/T)}R[n_A\ln\gamma_A + n_B\ln\gamma_B] \neq 0$$

The next page shows $\Delta H^M$ for ideal and non-ideal solutions.

The large negative $\Delta H^M$ values for $Na_2O - SiO_2$ occur because
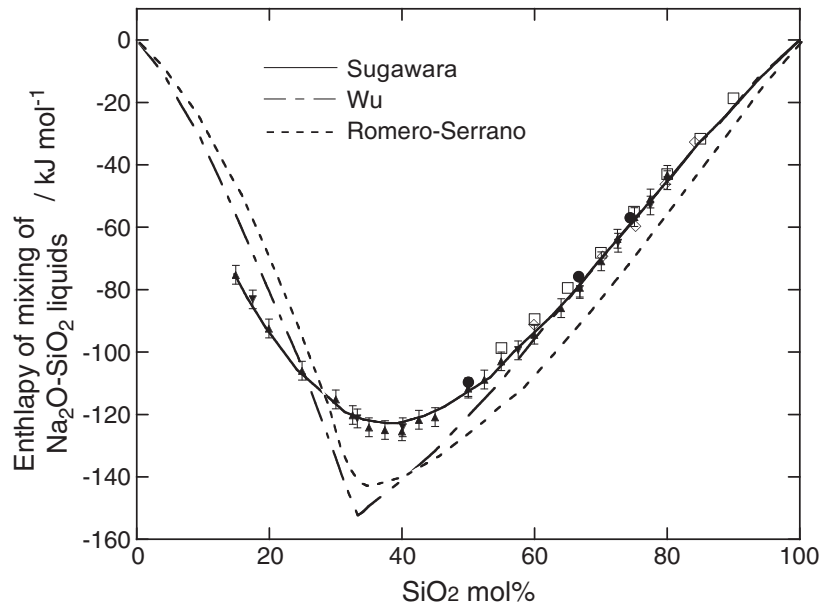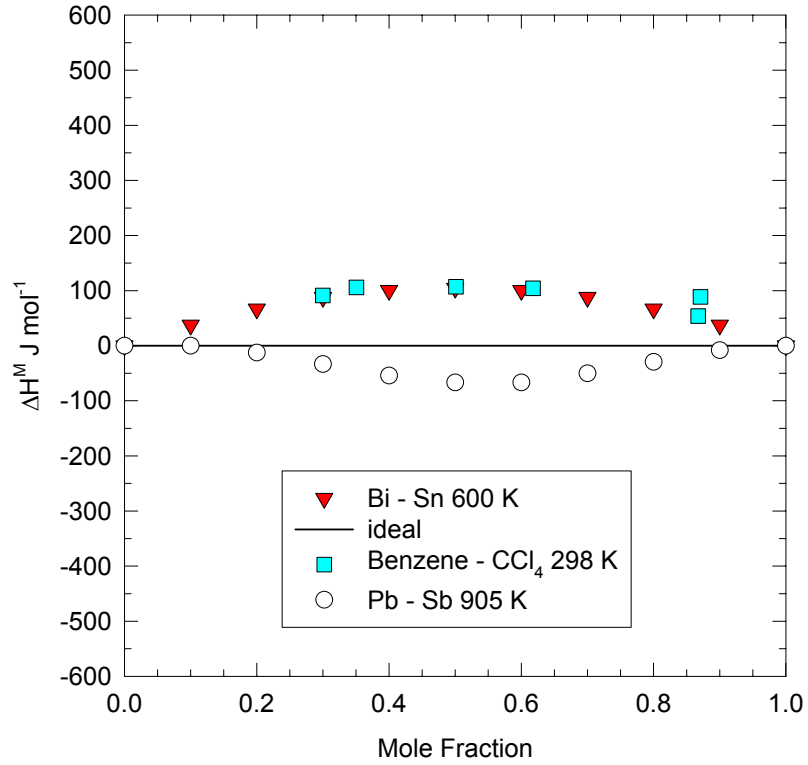
activity coefficients << 1 for $Na_2O$

**Fig. 2.** Enthalpy of mixing of $Na_2O$–$SiO_2$ liquids: ●, present study (DSC); ▲ (glass) and ▼ (gel), Fan [10] (Transpose-temperature drop calorimetry); □, Hovis et al. [35] (HF solution calorimetry); ◊, Rogez and Mathiue [51] (Lead borate solution calorimetry).

## Ideal Mixing of Complex Components (IMCC) Model

Developed by Hastie & colleagues at NIST(NBS) in 1980s

Very negative $\Delta H^M$ values (e.g., $Na_2O - SiO_2$) show $a_{oxide} \ll X_{oxide}$

The IMCC model computes

$$a_{oxide} = X^*_{oxide}$$

The $X^*_{oxide}$ is the mole fraction of unbound oxide in the melt

The activity coefficient is calculated from

$$\gamma_{oxide} = \frac{X^*}{X^T}$$

The $X^T$ is the total mole fraction of the oxide added to the melt.

Combination of these two equations is simply

$$a_{oxide} = \gamma_{oxide}X^T$$

The change from $X^T$ to $X^*_{oxide}$ is computed using chemical equilibria

between fictive components (aka pseudo-species) in the melt.

$K_2SiO_3$ (liq), $K_2Si_2O_5$ (liq), and $K_2Si_4O_9$ (liq) used for $K_2O - SiO_2$ melts
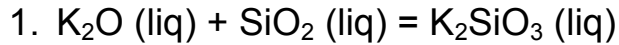

IMCC model – precursor of models by Allendorf, Spear & colleagues

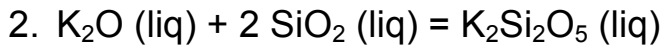Does not depend on actual (poorly known) speciation in the melts

Good agreement with experimental data (shown later)
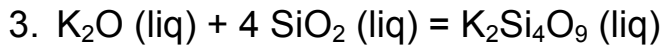
Can be modified for oxides with $\gamma_{oxide} > 1$

# MAGMA Code Example for $K_2O - SiO_2$ melts

1. $K_2O$ (liq) + $SiO_2$ (liq) = $K_2SiO_3$ (liq)

$$K_1 = \frac{a_{K_2SiO_3}}{a_{K_2O} a_{SiO_2}}$$

2. $K_2O$ (liq) + 2 $SiO_2$ (liq) = $K_2Si_2O_5$ (liq)

$$K_2 = \frac{a_{K_2Si_2O_5}}{a_{K_2O} a_{SiO_2}^2}$$
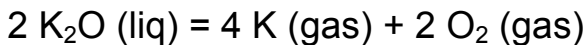
3. $K_2O$ (liq) + 4 $SiO_2$ (liq) = $K_2Si_4O_9$ (liq)

$$K_3 = \frac{a_{K_2Si_4O_9}}{a_{K_2O} a_{SiO_2}^4}$$

The equilibrium constants are calculated from literature data

The activity coefficient for $K_2O$ is given by

$$\gamma_{K_2O} = \frac{a_{K_2O}}{a_{K_2SiO_3} + a_{K_2Si_2O_5} + a_{K_2Si_4O_9}}$$

The activity of $K_2O$ calculated from the reactions above and from the

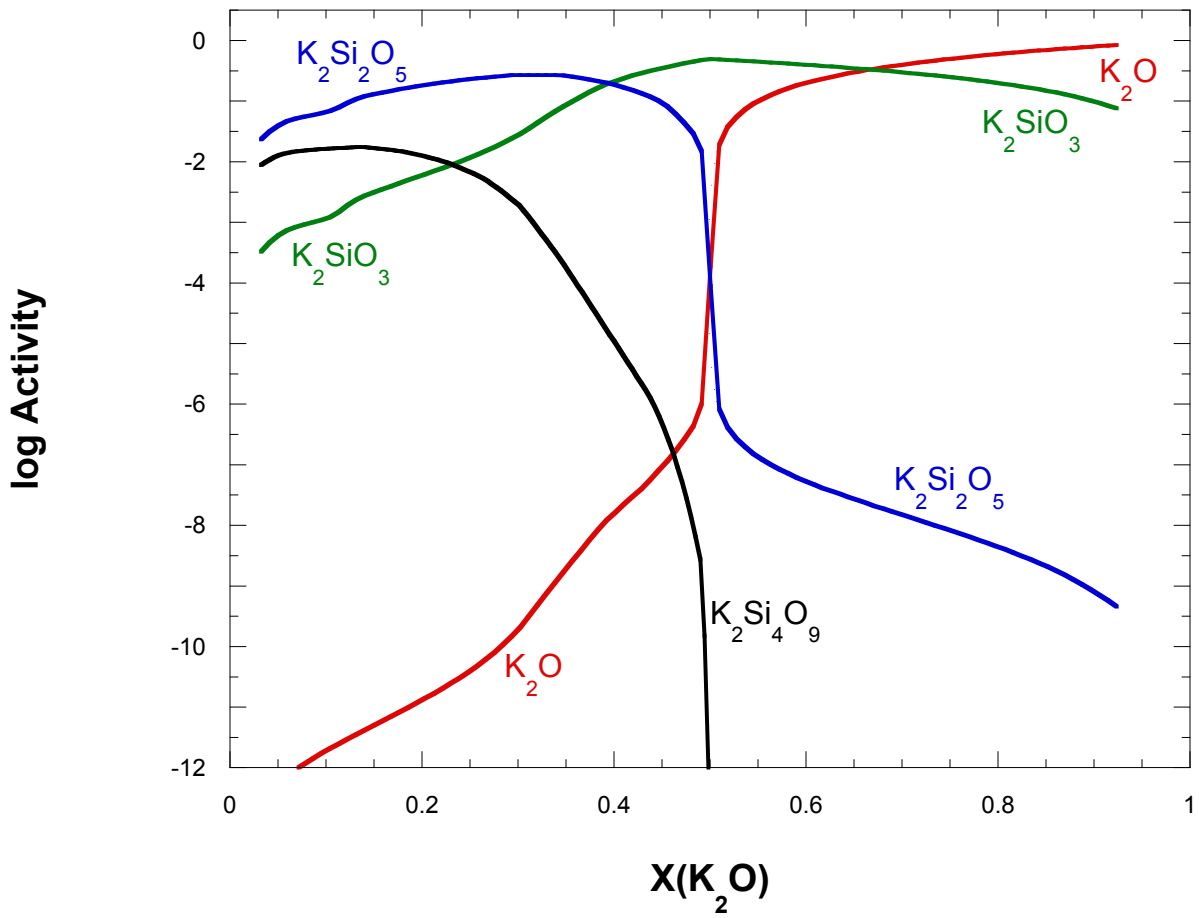vaporization reaction below must be equal.

2 $K_2O$ (liq) = 4 K (gas) + 2 $O_2$ (gas)

$$K_{vap} = \frac{P_K^4 P_{O_2}^2}{a_{K_2O}^2}$$

Gas phase equilibrium chemistry including thermal ionization, also

computed, e.g., K, $K_2$, $K^+$, $e^-$, KO, $K_2O$ for potassium

☞ See figure showing pseudo-species, 1500 K isotherm

$K_2O$ - $SiO_2$ pseudospecies 1500K

log Activity

$X(K_2O)$

$K_2Si_2O_5$

$K_2SiO_3$

$K_2O$

$K_2SiO_3$

$K_2Si_2O_5$

$K_2Si_4O_9$

$K_2O$

# MAGMA Code

Includes $SiO_2$, $MgO$, $FeO$, $CaO$, $Na_2O$, $K_2O$, $TiO_2$, and $Al_2O_3$

Most abundant oxides in silicates on Earth and other rocky planets

Consequence of two factors

– solar abundances of the elements

– geochemical affinity (atmophile, chalcophile, lithophile, siderophile)

Table 1
Species included in MAGMA code calculations

| Melt species | Vapor species |
|---|---|
| $SiO_2$, $MgO$, $FeO$, $CaO$, $Al_2O_3$, $TiO_2$, | $O$, $O_2$ |
| $Na_2O$, $K_2O$ | $Si$, $SiO$, $SiO_2$ |
| $MgSiO_3$, $Mg_2SiO_4$, $MgAl_2O_4$, $MgTiO_3$, $MgTi_2O_5$, | $Mg$, $MgO$ |
| $Mg_2TiO_4$, $Mg_2Al_4Si_5O_{18}$ | $Fe$, $FeO$ |
| $FeTiO_3$, $Fe_2SiO_4$, $FeAl_2O_4$ | $Ca$, $CaO$ |
| $CaAl_2O_4$, $CaAl_4O_7$, $Ca_{12}Al_{14}O_{33}$, $CaMgSi_2O_6$, | $Al$, $AlO$, $AlO_2$, |
| $Ca_2MgSi_2O_7$, $Ca_2Al_2SiO_7$, $CaAl_2Si_2O_8$, $CaTiO_3$, | $Al_2O$, $Al_2O_2$ |
| $Ca_2SiO_4$, $CaTiSiO_5$, $CaAl_{12}O_{19}$, $CaSiO_3$ | $Ti$, $TiO$, $TiO_2$ |
| $Al_6Si_2O_{13}$ | $Na$, $Na_2$, $NaO$, |
| $Na_2SiO_3$, $Na_2Si_2O_5$, $NaAlSiO_4$, $NaAlSi_3O_8$, | $Na_2O$, $Na^+$ |
| $NaAlO_2$, $Na_2TiO_3$, $NaAlSi_2O_6$ | $K$, $K_2$, $KO$, |
| $K_2SiO_3$, $K_2Si_2O_5$, $K_2Si_4O_9$, $KAlSiO_4$, | $K_2O$, $K^+$ |
| $KAlSi_3O_8$, $KAlO_2$, $KAlSi_2O_6$, $KCaAlSi_2O_7$ | $e^-$ |

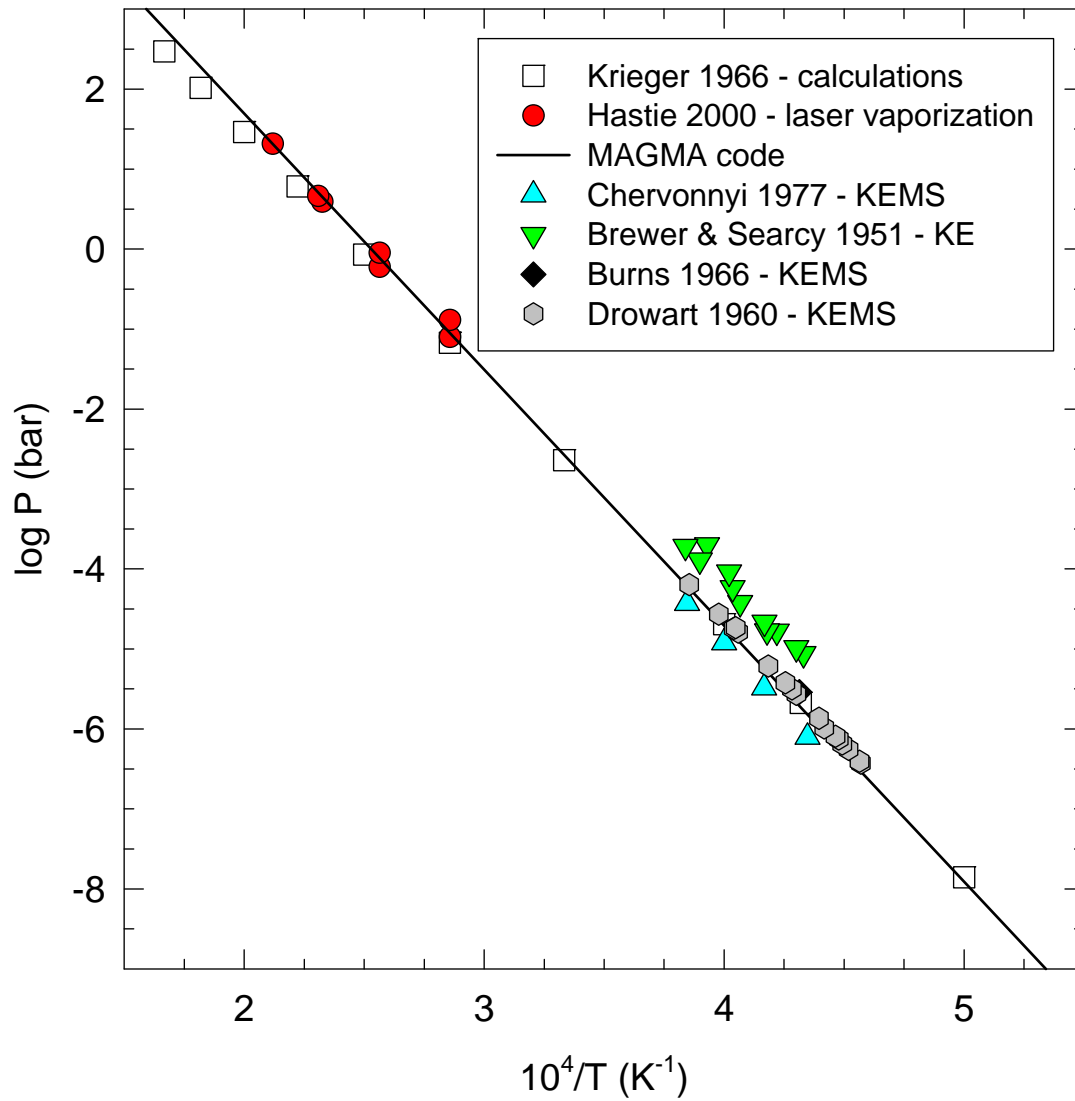Look at some examples of code calculations vs.

– experimental data

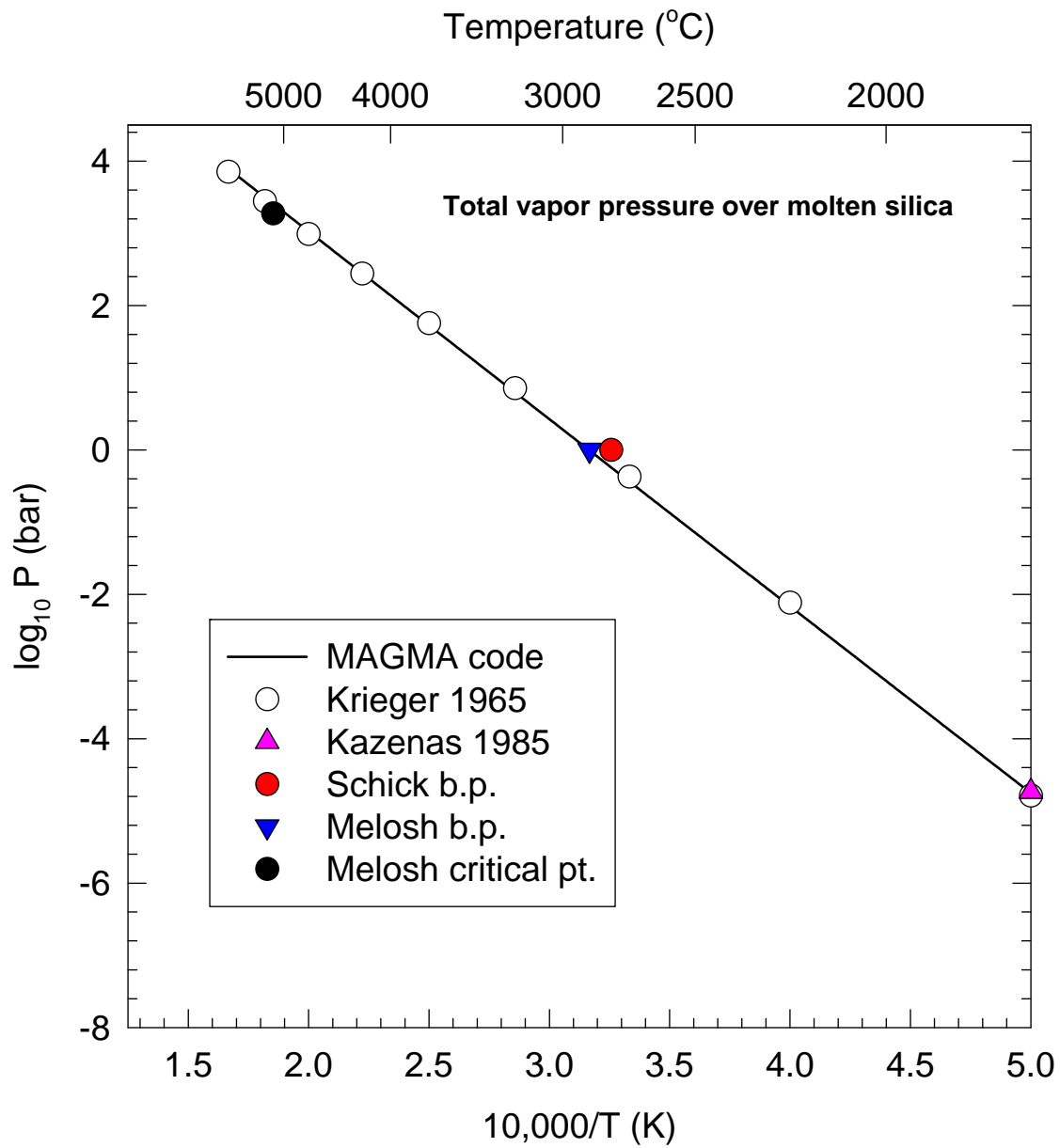– theoretical calculations by other groups

Vapor pressures of pure oxides

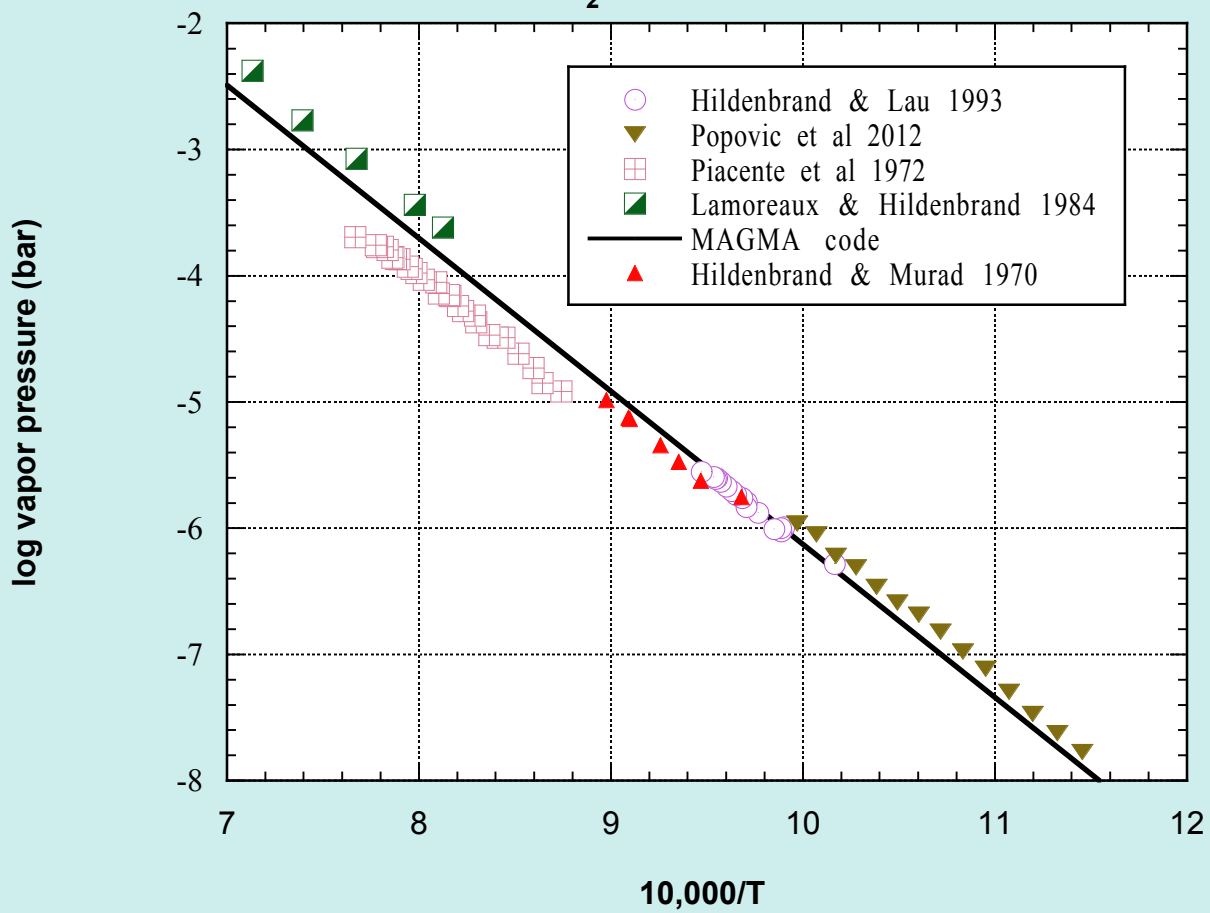$Na_2O$ – $SiO_2$ and $K_2O$ – $SiO_2$ binary systems

Multicomponent systems

**Alumina**
**Vapor Pressure**

Legend:
- □ Krieger 1966 - calculations
- ● Hastie 2000 - laser vaporization
- — MAGMA code
- ▲ Chervonnyi 1977 - KEMS
- ▼ Brewer & Searcy 1951 - KE
- ◆ Burns 1966 - KEMS
- ⬡ Drowart 1960 - KEMS

y-axis: log P (bar)

x-axis: $10^4/T$ $(K^{-1})$

$Al_2O_3PT.SPW$

Temperature ($^o$C)

**Total vapor pressure over molten silica**

- MAGMA code
- ○ Krieger 1965
- ▲ Kazenas 1985
- ● Schick b.p.
- ▼ Melosh b.p.
- ● Melosh critical pt.

$\log_{10}$ P (bar)

10,000/T (K)

SiO2vap.SPW

**Na$_2$O(s,liq) vapor P**

**Na₂Si₂O₅(liq) vapor P**
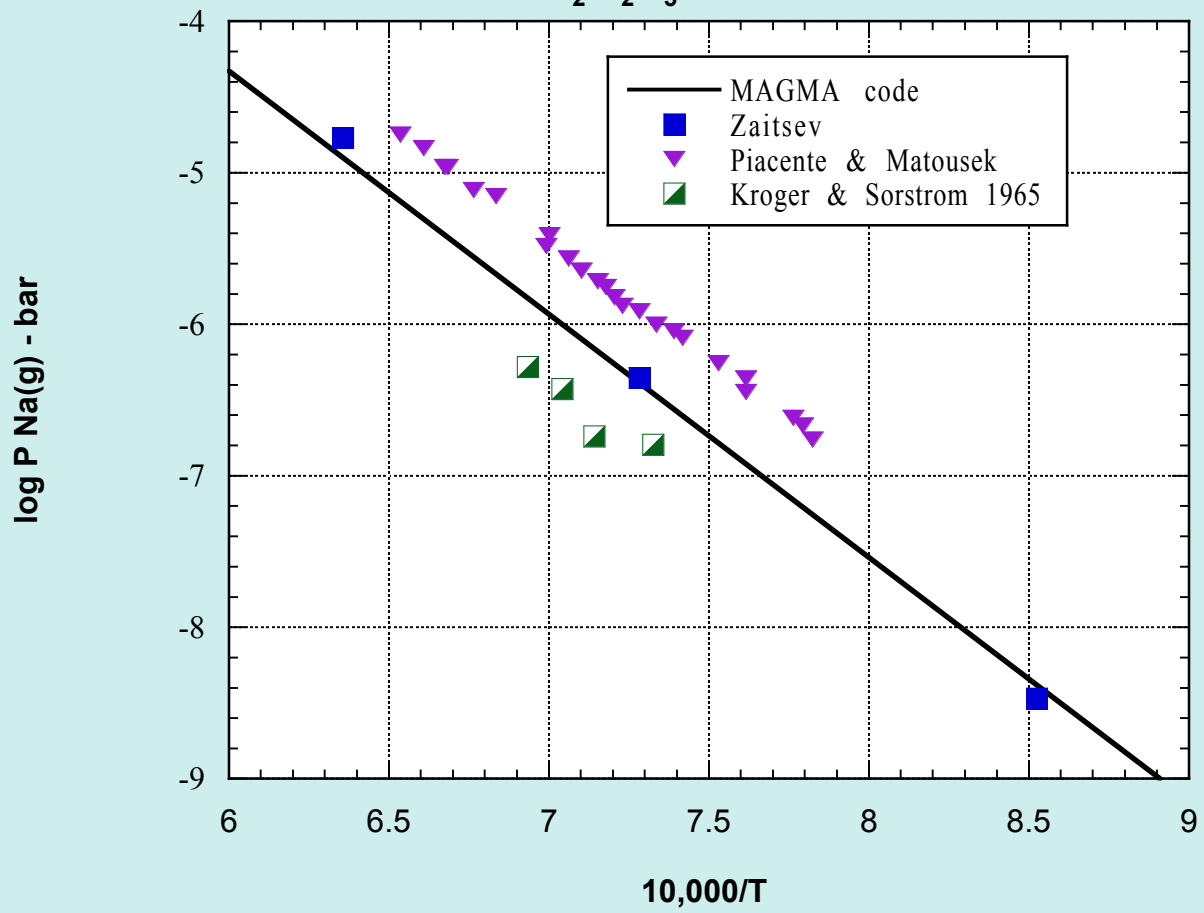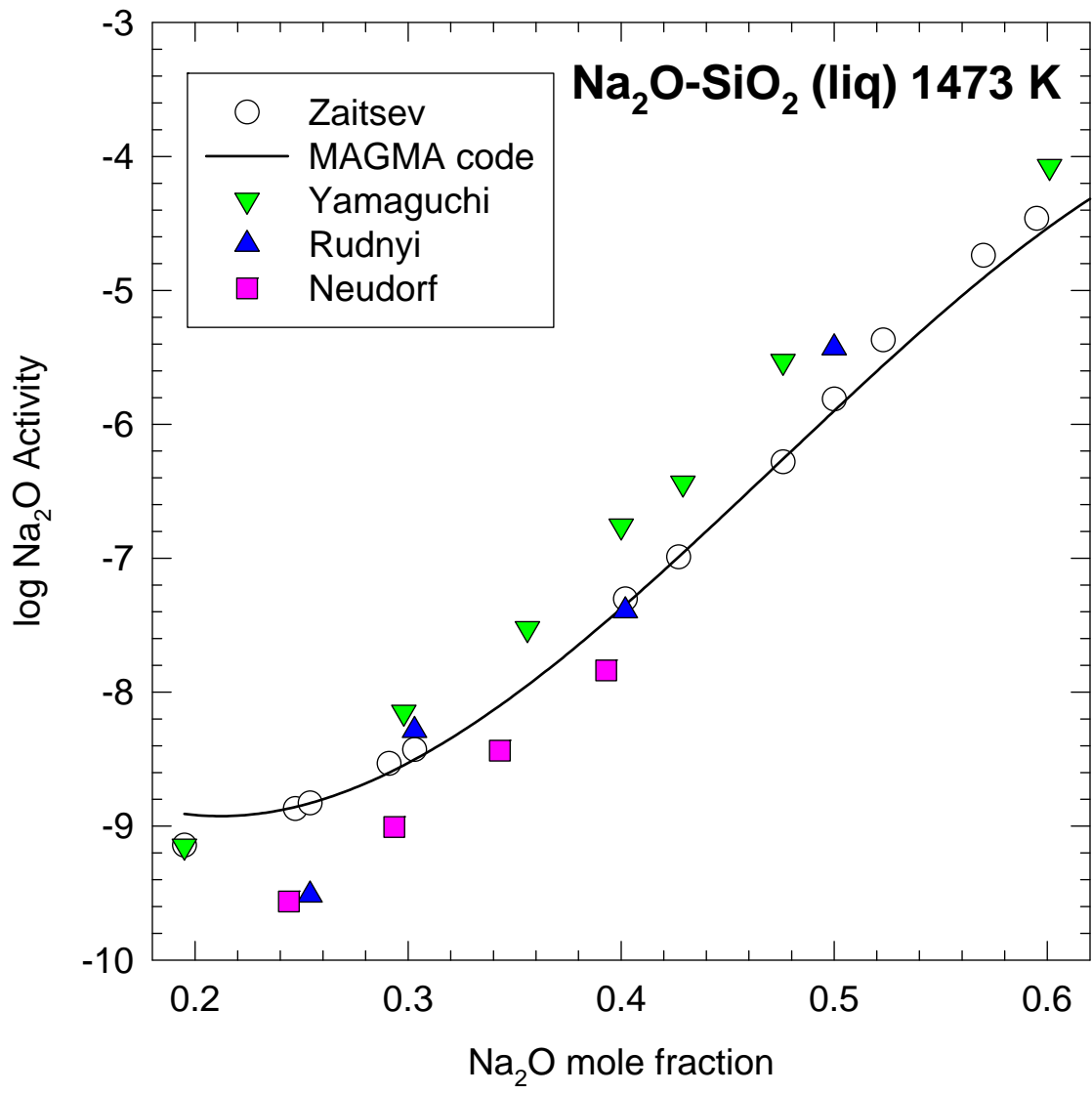
Na2OSiO2.SPW

Na$_2$O - SiO$_2$ 1573 K isotherm
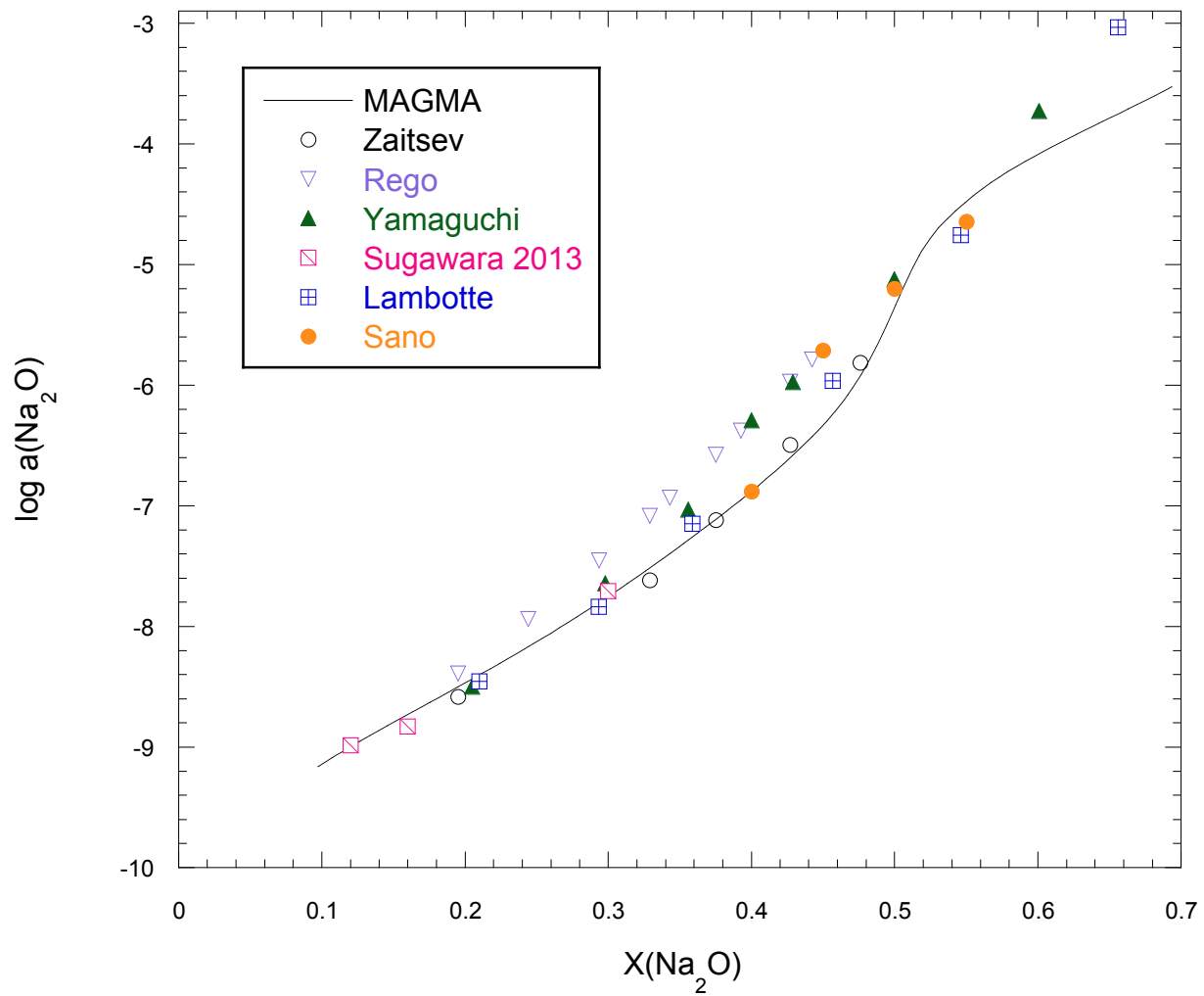
**K$_2$O-SiO$_2$ 1573K isotherm**
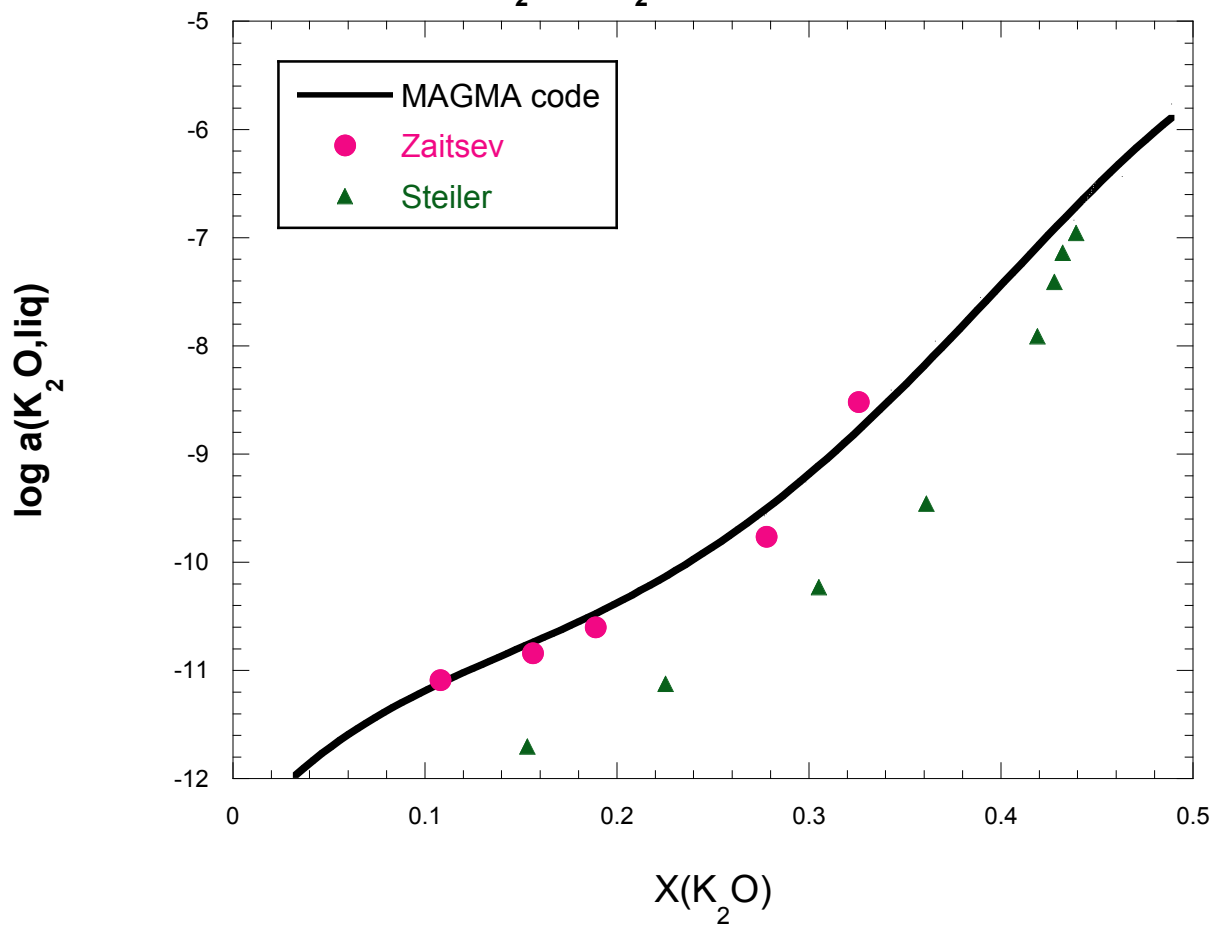
**Composition of saturated vapor
Bulk silicate Earth magma**
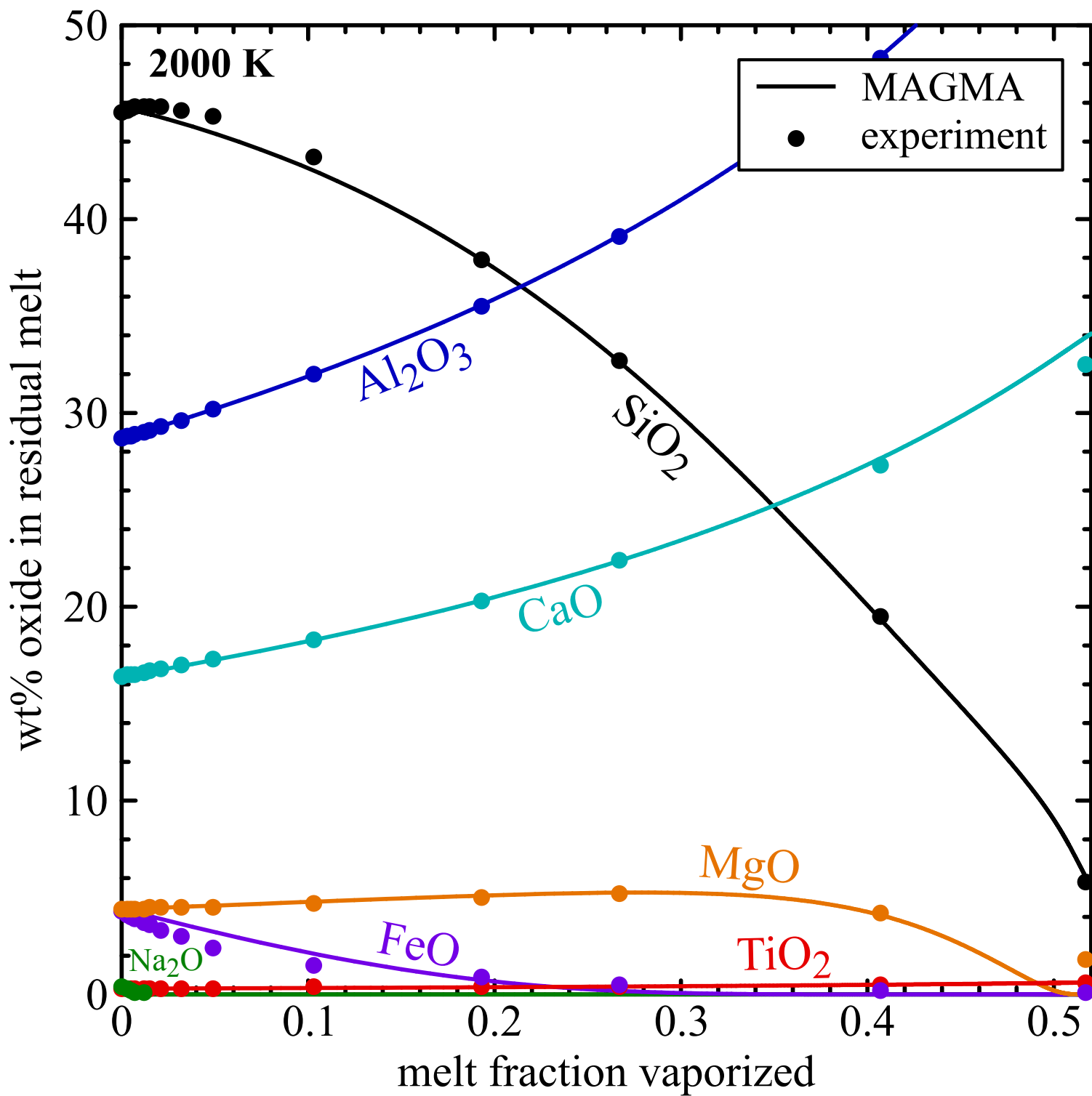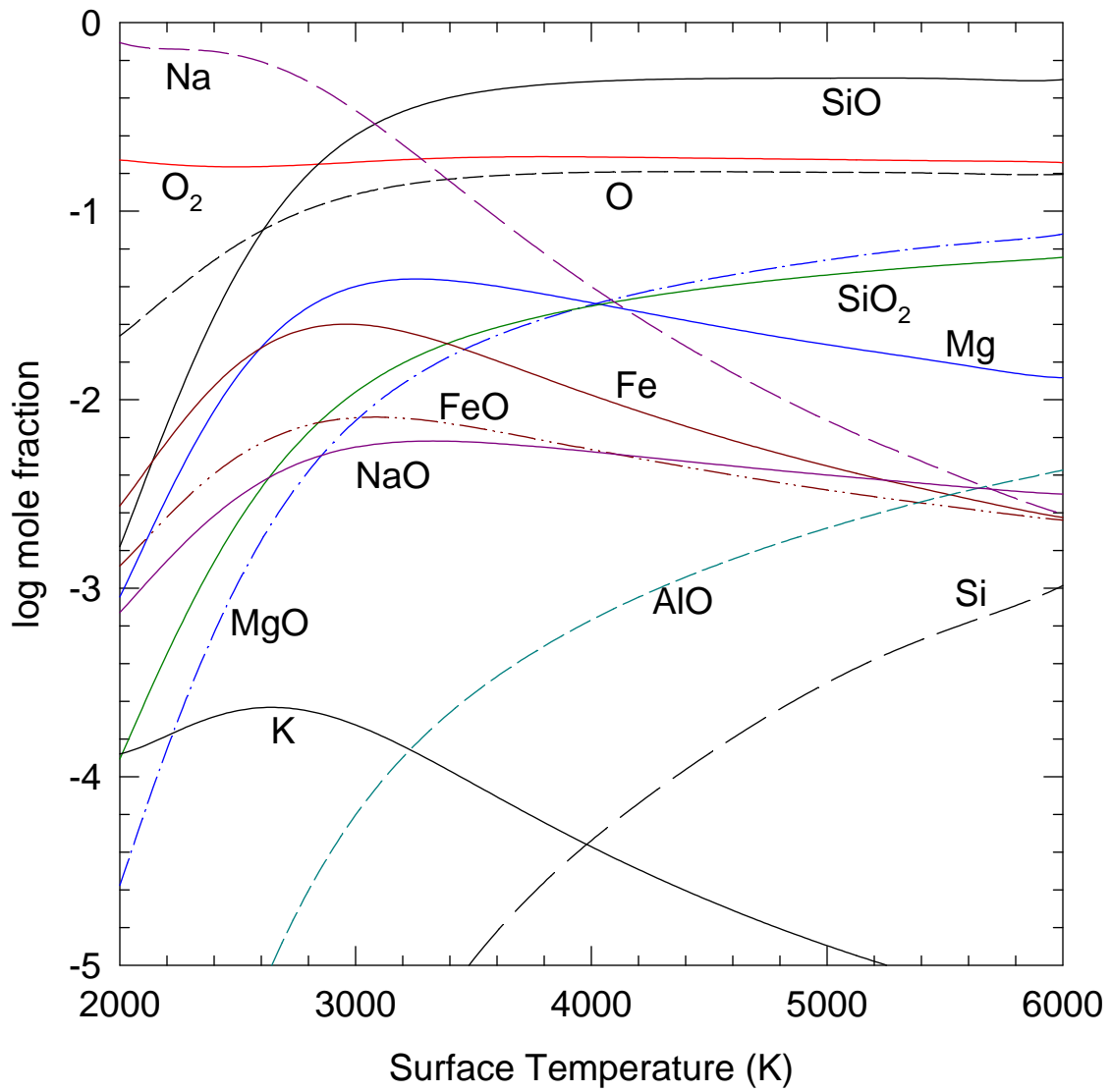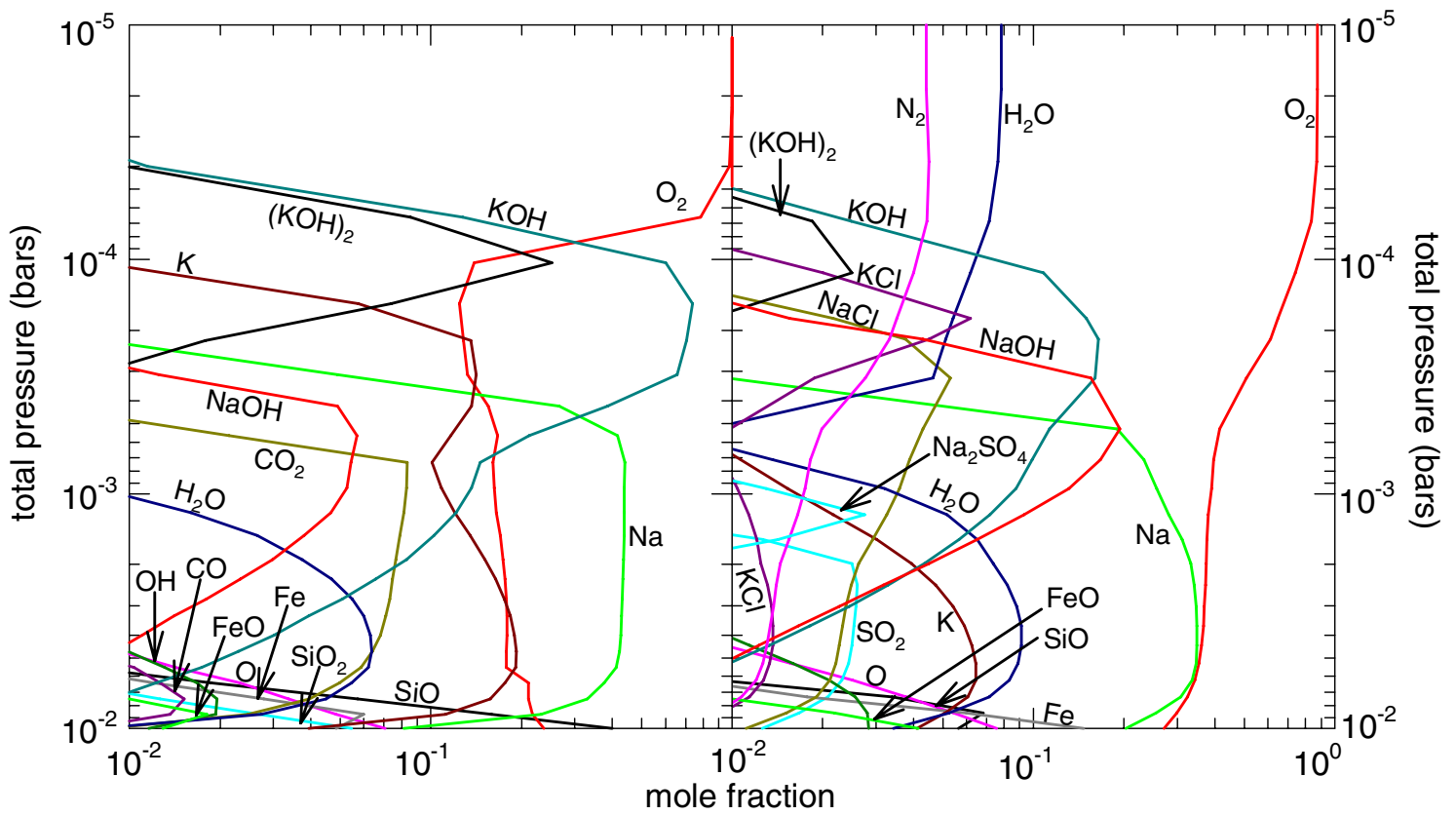
CoRoT-7b dry adiabatic P-T profiles
continental crust (left), BSE (right)
surface T 2500 K, surface P 0.01 bar

## Sodium oxide.

Sublimation and vaporization of $Na_2O$(s, liq) occur congruently and proceed mainly via the net reaction

$2Na_2O$ (s, liq) = $4Na$(g) + $O_2$ (g)
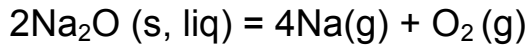
Only minor amounts of $NaO$, $Na_2O$, $Na_2O_2$, $NaO_2$ in the vapor.

The calculated vapor pressures from the MAGMA code for $Na_2O$(s) from 950 – 1405 K and for $Na_2O$ (liq) from 1405 – 2000 K are

$Na_2O$ (solid) 950 – 1405 K: $\log_{10}P$ (bar) = 5.995 – 12,124.1/T

$Na_2O$ (liquid) 1405 – 2200 K: $\log_{10}P$ (bar) = 5.091 – 10,854.4/T

These two equations give a triple point pressure of ~ 0.0023 bar and a one bar boiling point of 2132 K. At the boiling point the saturated vapor is ~ 78% $Na$(g), 19% $O_2$(g), 1.5% $NaO$(g), 1.0% $Na_2O$(g), and 0.5% all other gases ($O$, $O^+$, $Na^+$, $e^-$, $Na_2$).

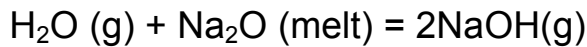## Water Vapor and Hydroxide Gases

In the absence of water the vaporization of alkali metals from silicate melts proceeds via net thermochemical reactions exemplified by

$$2Na_2O \text{ (melt)} = 4Na(g) + O_2(g)$$
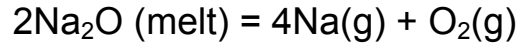
**Water**. Water vapor increases the amount of alkali metals in the gas phase over silicate melts via net thermochemical reactions such as

$$H_2O \text{ (g)} + Na_2O \text{ (melt)} = 2NaOH(g)$$

$$K_{OH} = \frac{P_{NaOH}^2}{P_{H_2O} a_{Na_2O}}$$

The ratio of the NaOH and Na gas pressures over a melt is

$$\frac{P_{NaOH}}{P_{Na}} = \left[ \frac{K_{OH} P_{H_2O}}{K_{vap} f_{O_2}^{-\frac{1}{2}}} \right]^{\frac{1}{2}} > 1$$

The NaOH/Na molar ratio is > 1 unless $P_{H_2O}$ is sufficiently small that

$$K_{vap} > K_{OH} P_{H_2O} f_{O_2}^{\frac{1}{2}}$$

Argent et al (1979) calculated Na gas speciation above a float glass melt (by moles: 12% $Na_2O$, 10% CaO, 6% MgO, 72% $SiO_2$) and found NaOH is the predominant Na gas at 1300 – 1800 K, in a gas containing (by volume) 0.5-4% $O_2$, 10-20% water vapor.

MAGMA code and hand calculations at 1600 K give

NaOH/Na molar ratio ~ 5.4

**Future plans**

1. Complete comparison of $K_2O - SiO_2$ binary with experimental data & other theoretical models

2. Include newer thermodynamic data for other key binaries

    a. $Na_2O - Al_2O_3$ and $K_2O - Al_2O_3$ binaries

    b. $CaO - Al_2O_3$ and $MgO - SiO_2$ binaries

    c. $MgO - SiO_2$ and $CaO - SiO_2$ binaries

3. Update $M_2O - SiO_2 - Al_2O_3$ ternary

4. Add S- and halogen-bearing gases into code

    ☛ Can be major species for alkalis – Schaefer et al (2012)

5. Add H-bearing gases into code – water, hydroxides, hydrides

    ☛ $1^{st}$ approximation – no water solubility in melts T > 2000 K

    ☛ No water solubility data in this T-range

Revisions motivated by newer thermodynamic data for liquid oxides and silicates and the need to compare different new datasets for the liquid oxides and silicates (e.g., geological vs. materials science)

**Some Suggestions for Experimental Studies**

Vaporization of peridotite rock – major constituent of Earth's mantle

(Using Earth as a starting point to study extrasolar rocky planets,

could also use the Moon, Mars, EPB or also study their analogs)

1. Chemistry & mineralogy of vaporization residue as a function of

    the fraction vaporized

2. Partial pressures of SiO, $O_2$, Na, K, Fe, Mg as f(T)

    a. Can compute activities of $SiO_2$, $Na_2O$, $K_2O$, "FeO", MgO

       in molten peridotite

    b. Determine vaporization coefficients for major gases

☞ gives observations to test and improve MAGMA code, also guides

future astronomical observations

Effect of water vapor on vaporization chemistry

1. Control $H_2O$ partial pressures during vaporization of peridotite

    and constrain the importance of hydroxides/oxyhydroxides for

    Na, K, Fe, Mg, Si gas chemistry

2. If #1 is not feasible, try olivine $Fo_{90}Fa_{10}$ (this is 90% $Mg_2SiO_4$

    Forsterite Fo – 10% $Fe_2SiO_4$ Fayalite, Fa) and study importance

    of $H_2O$ for Fe, Mg, Si gas chemistry

## References

This is an incomplete, but hopefully still useful, listing of references about vaporization and oxide activity measurements and MAGMA code applications.

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