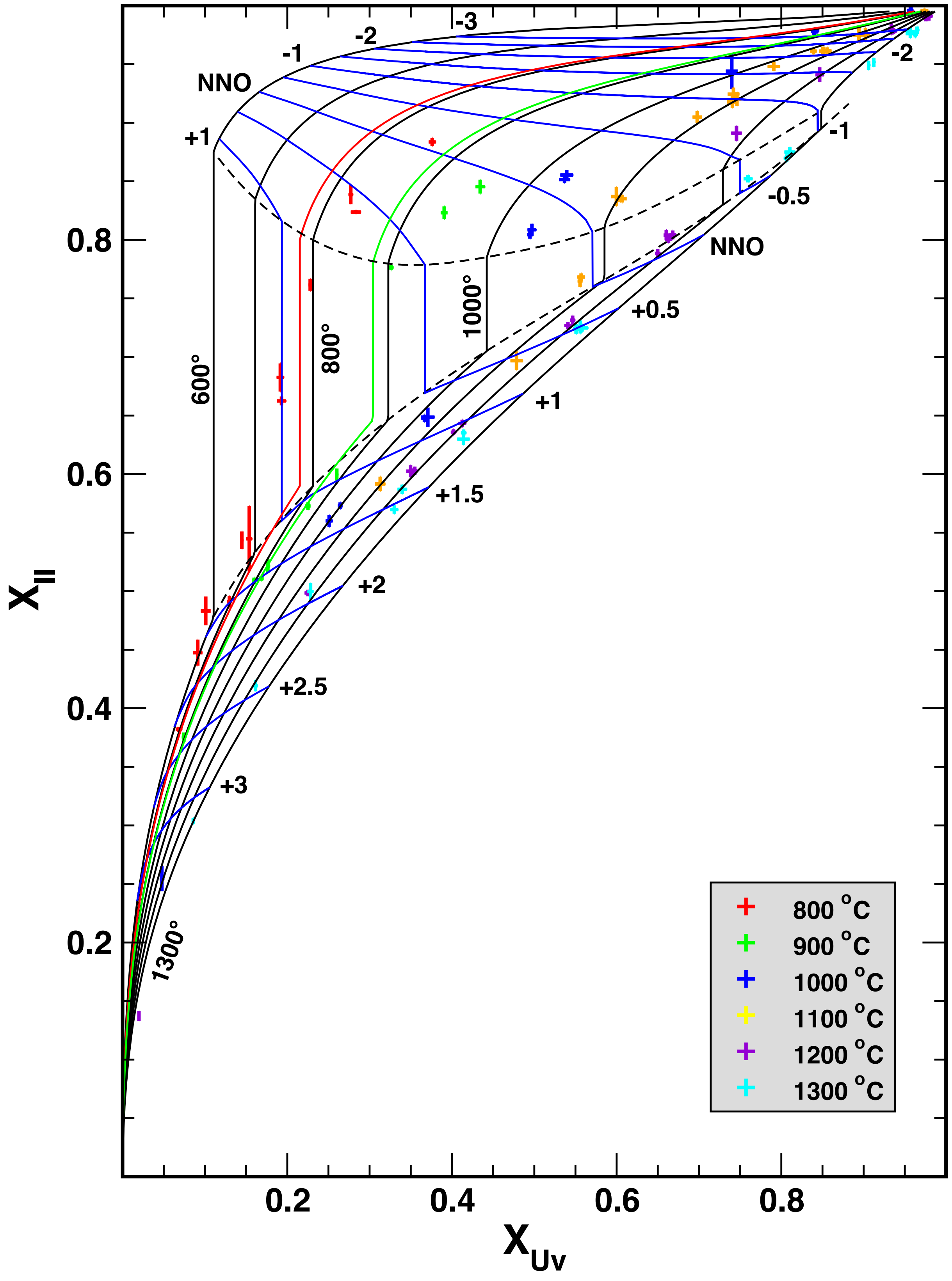
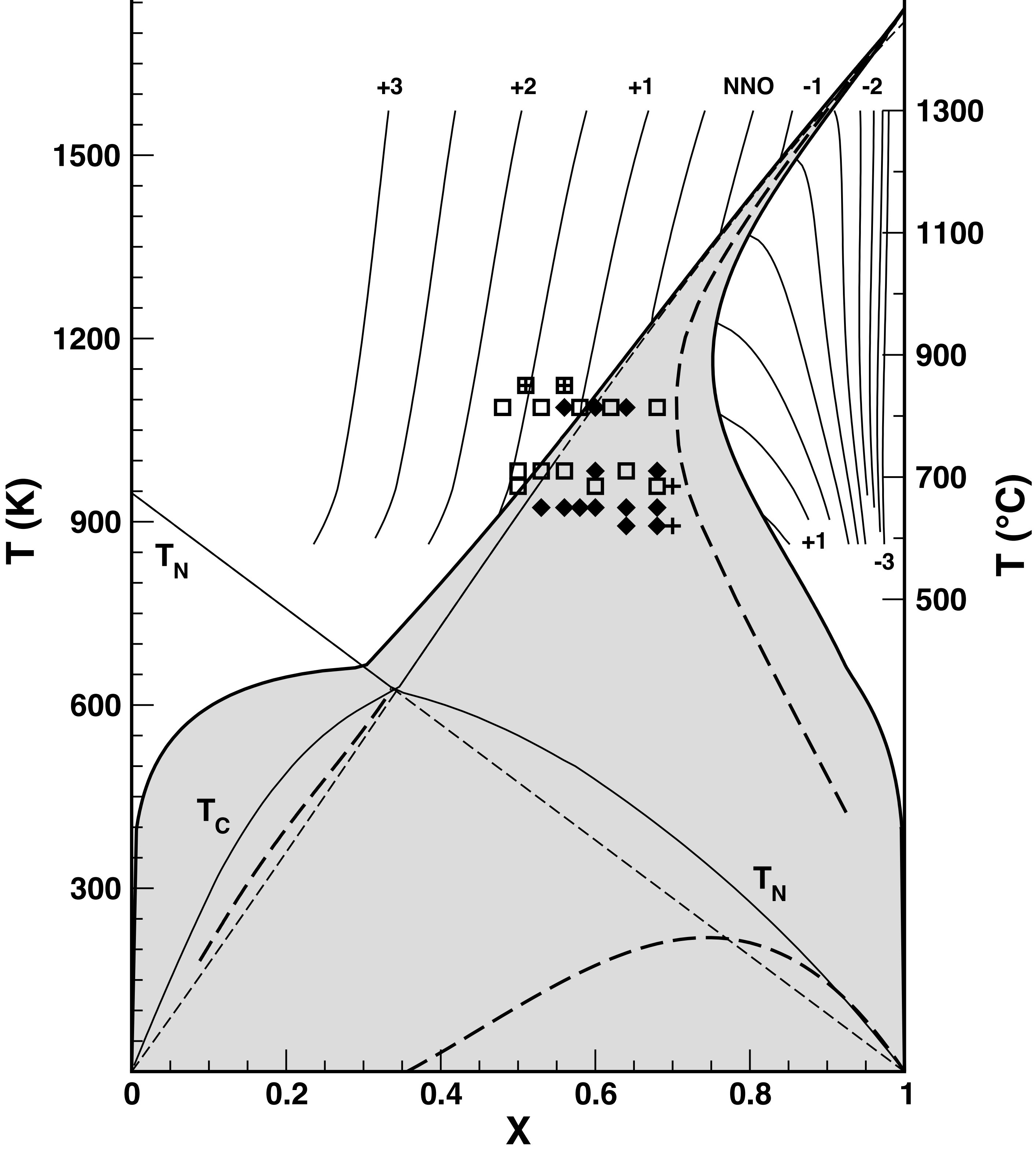
What are the critical aspects of calibration?

- **First and most important - Solid solution theory**
  - Why? Because there is more compositional variation in the solid solutions than in the magmas from which they form.
- **Second - Constraints on endmember properties**
  - Why? Because the “excess” solution properties and the “standard state” endmember properties are highly correlated, mostly due to common compositional restrictions on calibration data.
- **Third - Theory for the liquid state**
  - Why? Exact theory is not important because compositional spectrum of magmas being modeled is very limited. Exception: the effect of pressure.

Solid solution models



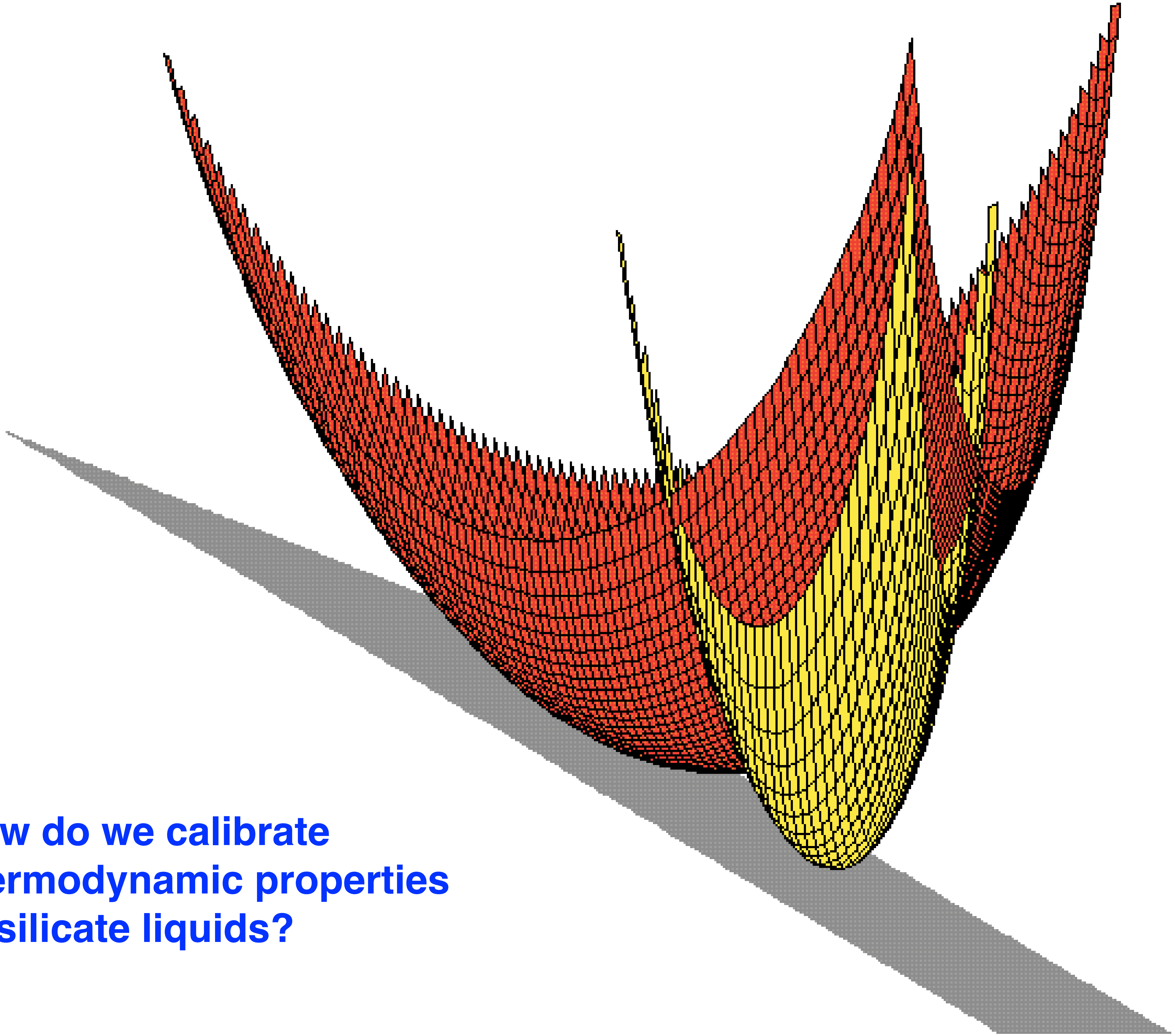


What are the critical aspects of calibration?

- **First and most important - Solid solution theory**
  - Why? Because there is more compositional variation in the solid solutions than in the magmas from which they form.
- **Second - Constraints on endmember properties**
  - Why? Because the “excess” solution properties and the “standard state” endmember properties are highly correlated, mostly due to common compositional restrictions on calibration data.
- **Third - Theory for the liquid state**
  - Why? Exact theory is not important because compositional spectrum of magmas being modeled is very limited. Exception: the effect of pressure.

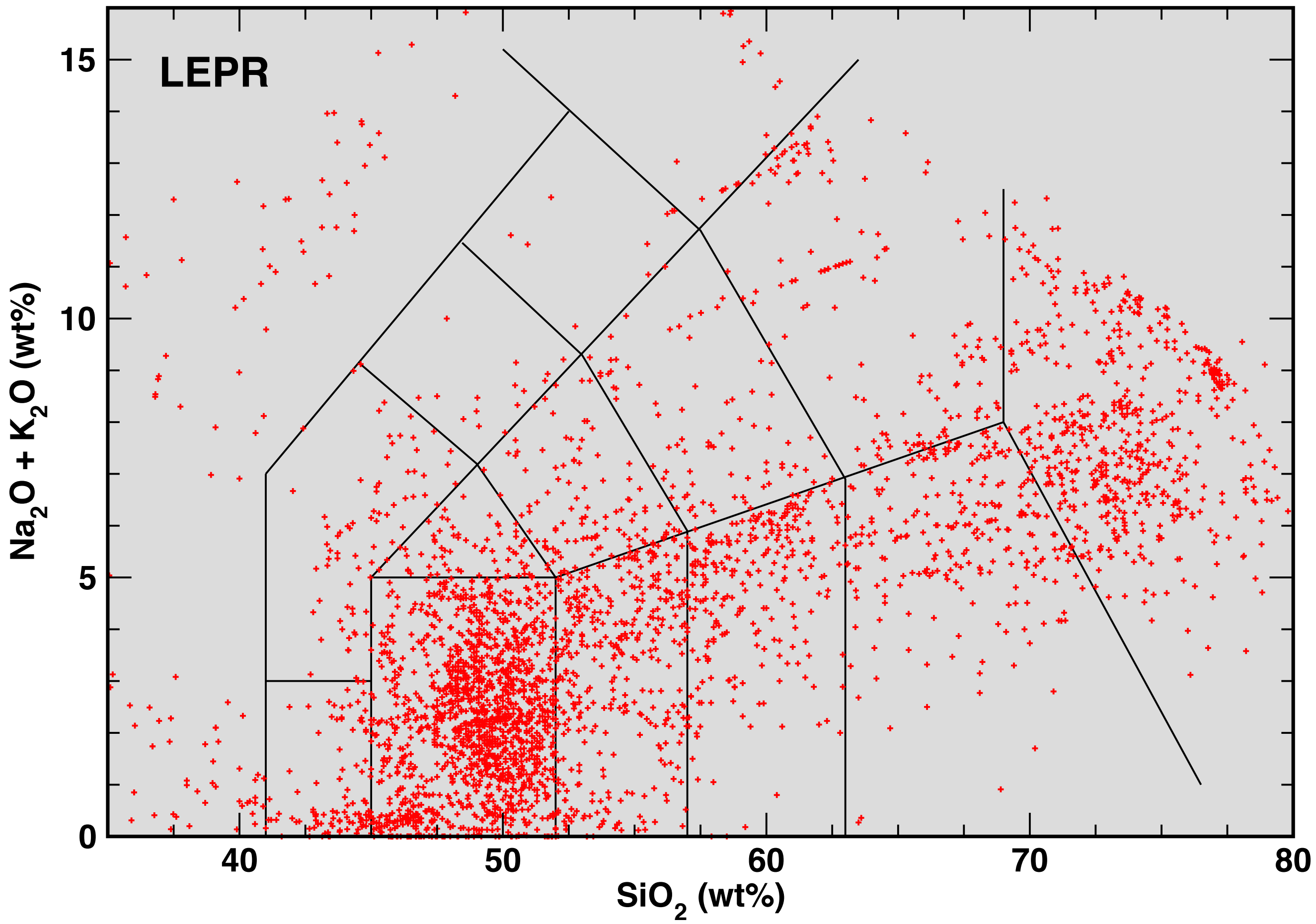
What are the critical aspects of calibration?

- **First and most important - Solid solution theory**
  - Why? Because there is more compositional variation in the solid solutions than in the magmas from which they form.
- **Second - Constraints on endmember properties**
  - Why? Because the “excess” solution properties and the “standard state” endmember properties are highly correlated, mostly due to common compositional restrictions on calibration data.
- **Third - Theory for the liquid state**
  - Why? Exact theory is not important because compositional spectrum of magmas being modeled is very limited. Exception: the effect of pressure.



How do we calibrate thermodynamic properties of silicate liquids?

Liquids

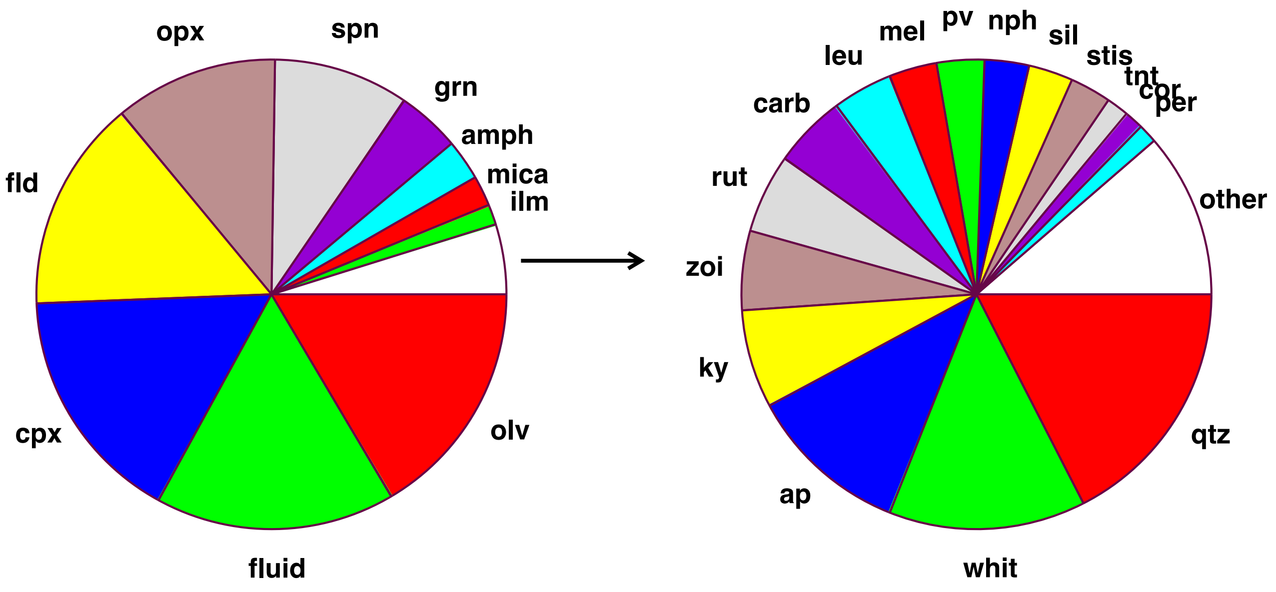


LEPR: Experimental database of solid-liquid phase equilibrium studies

Over 8,800 experiments that span the compositional spectrum of natural silicate liquids

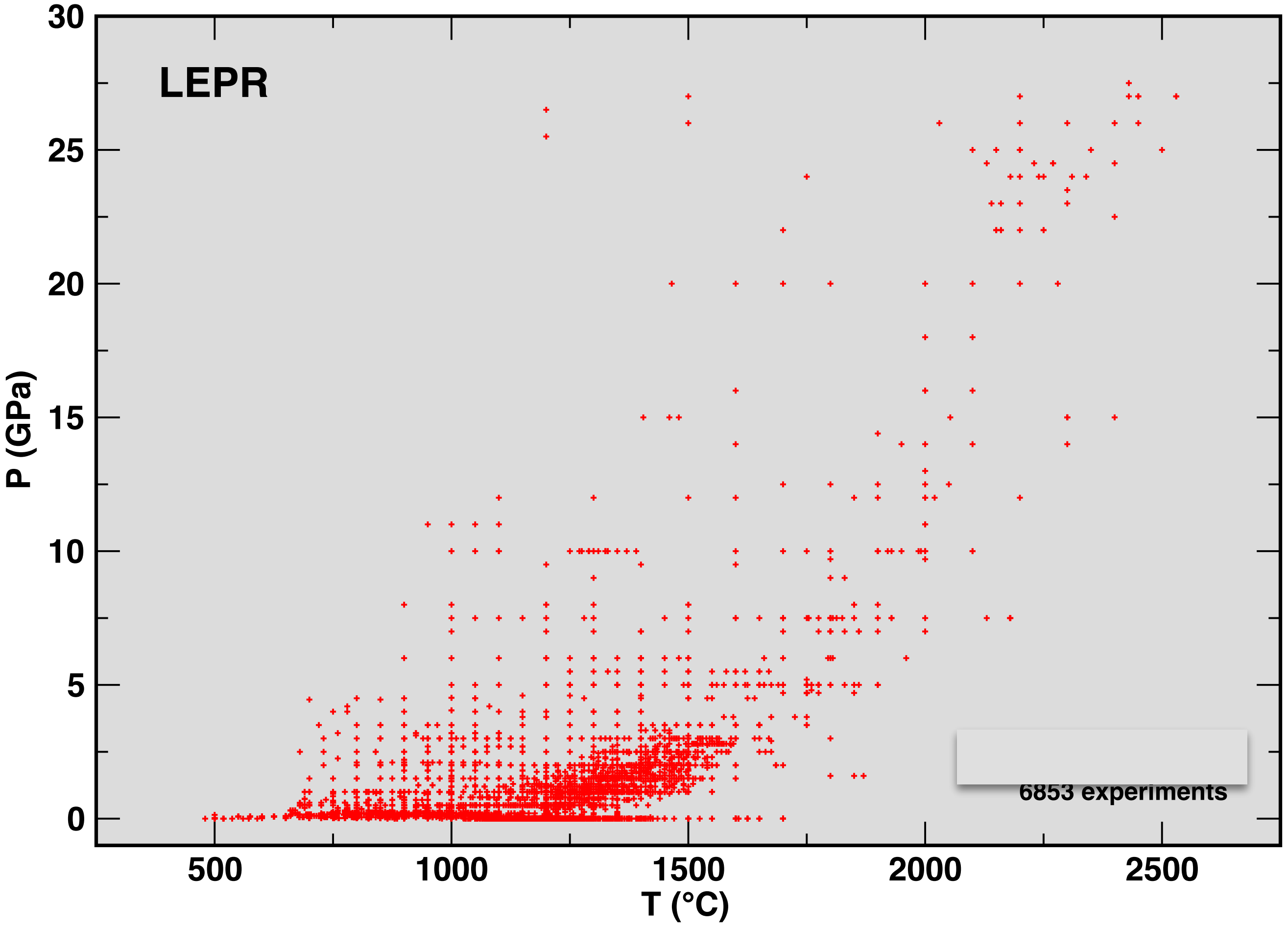
Available at http://lepr.ofm-research.org

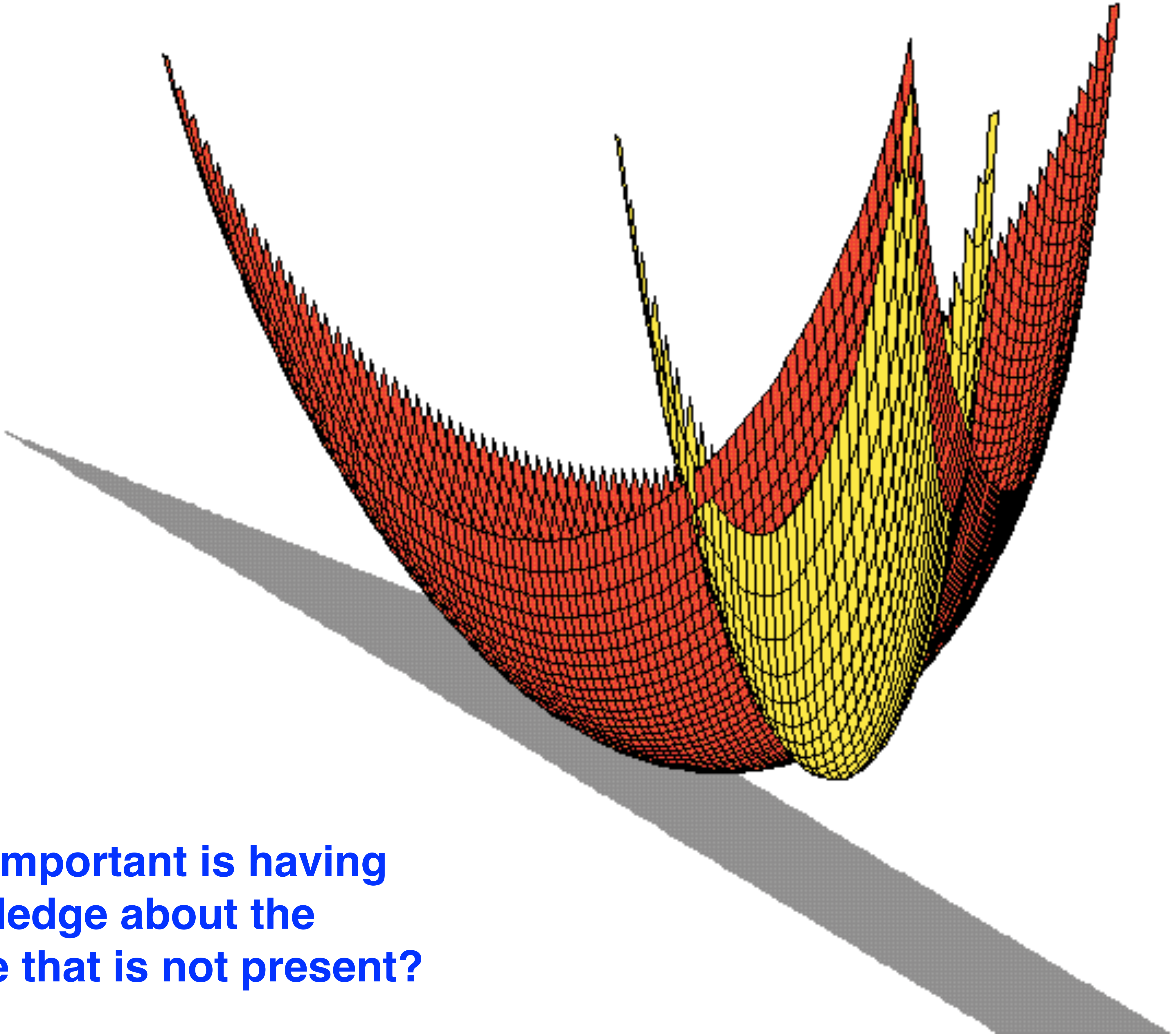
Solid phases



12,750

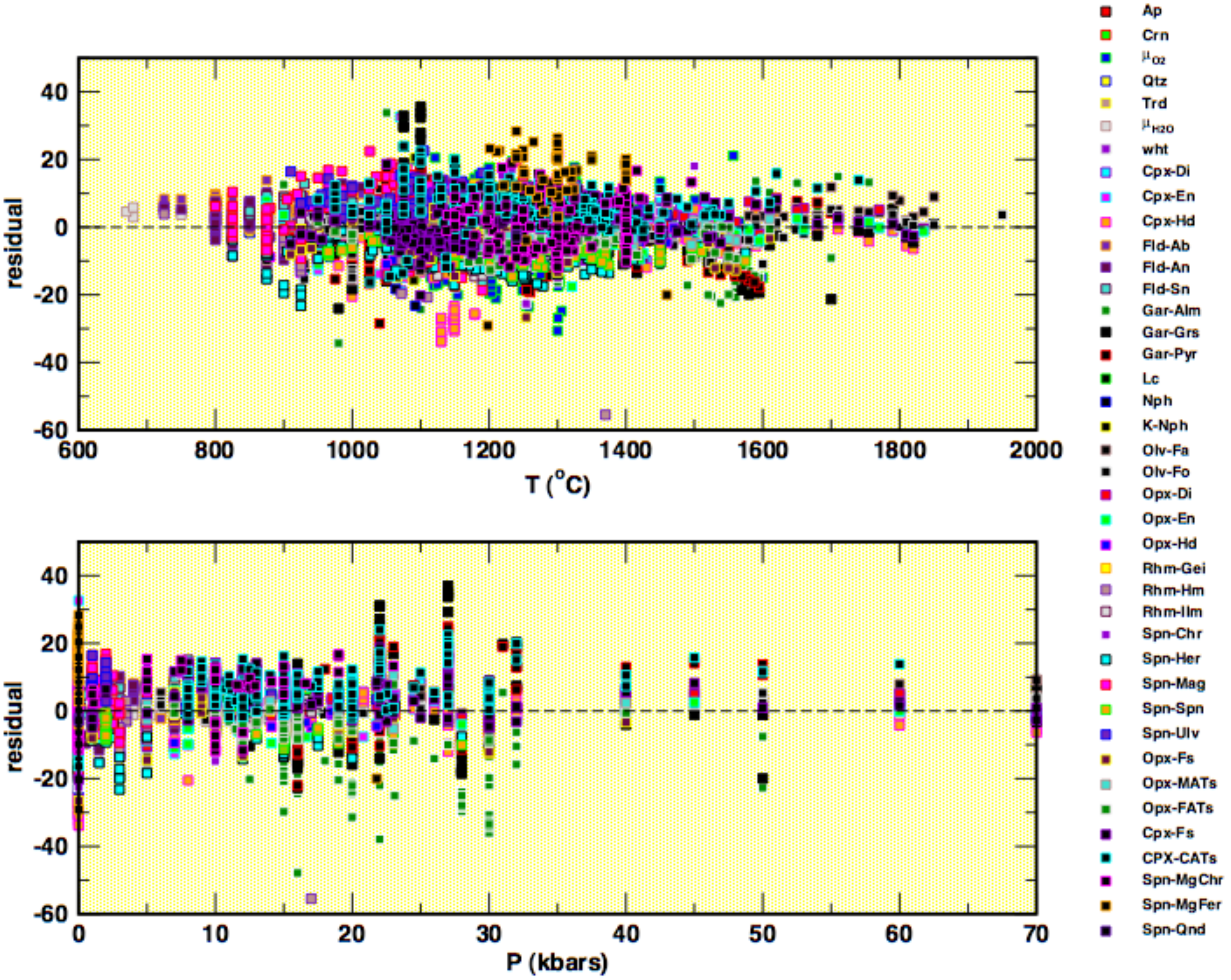
623



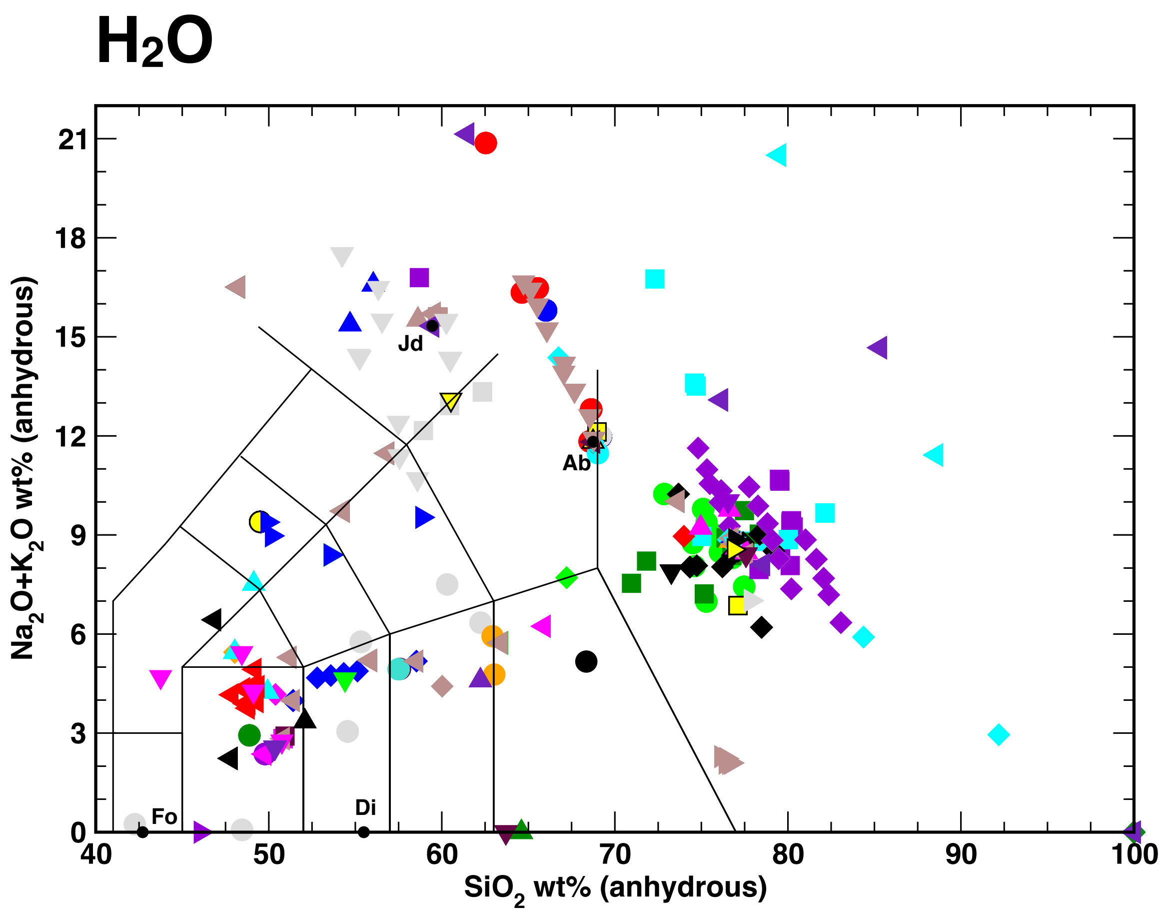


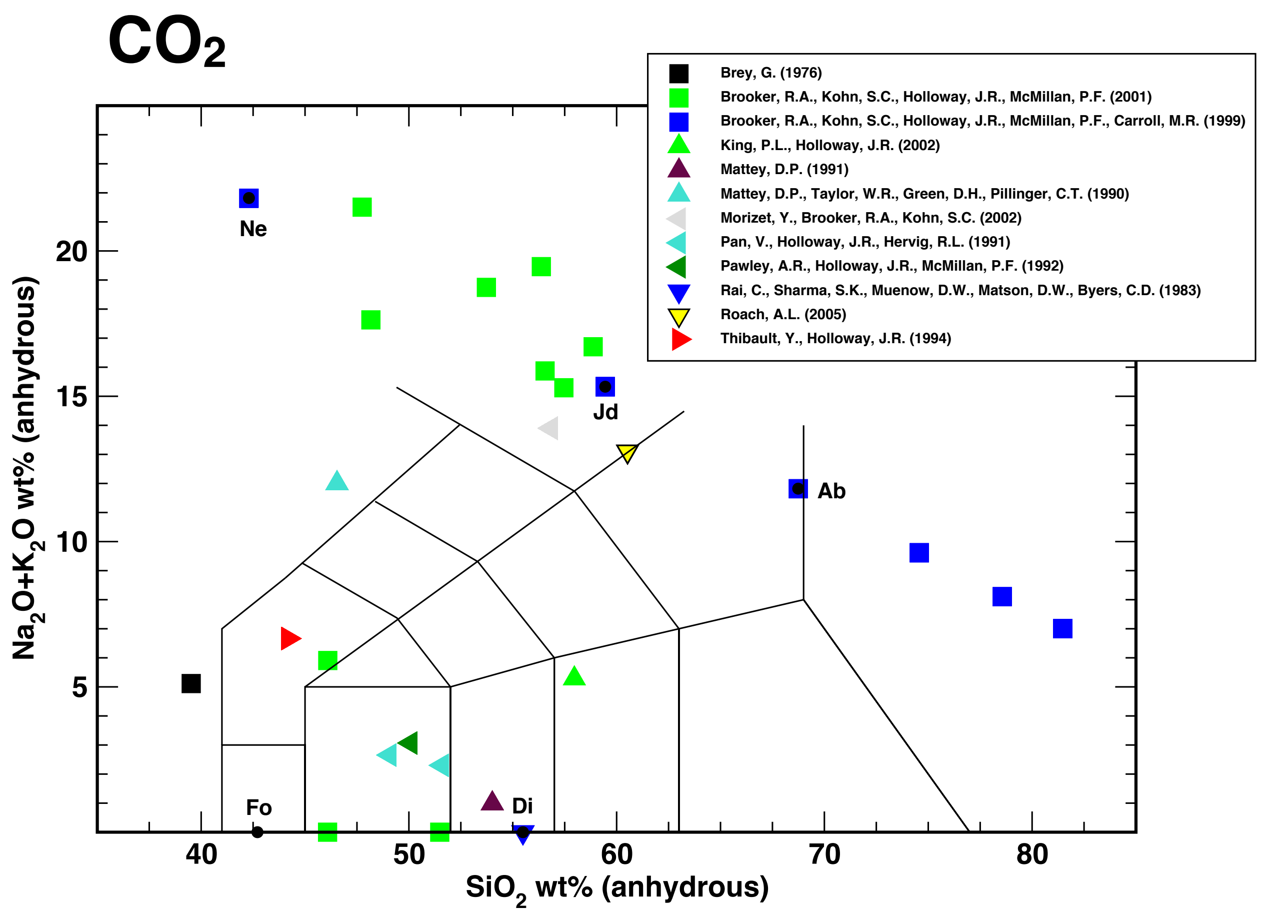
How important is having knowledge about the phase that is not present?

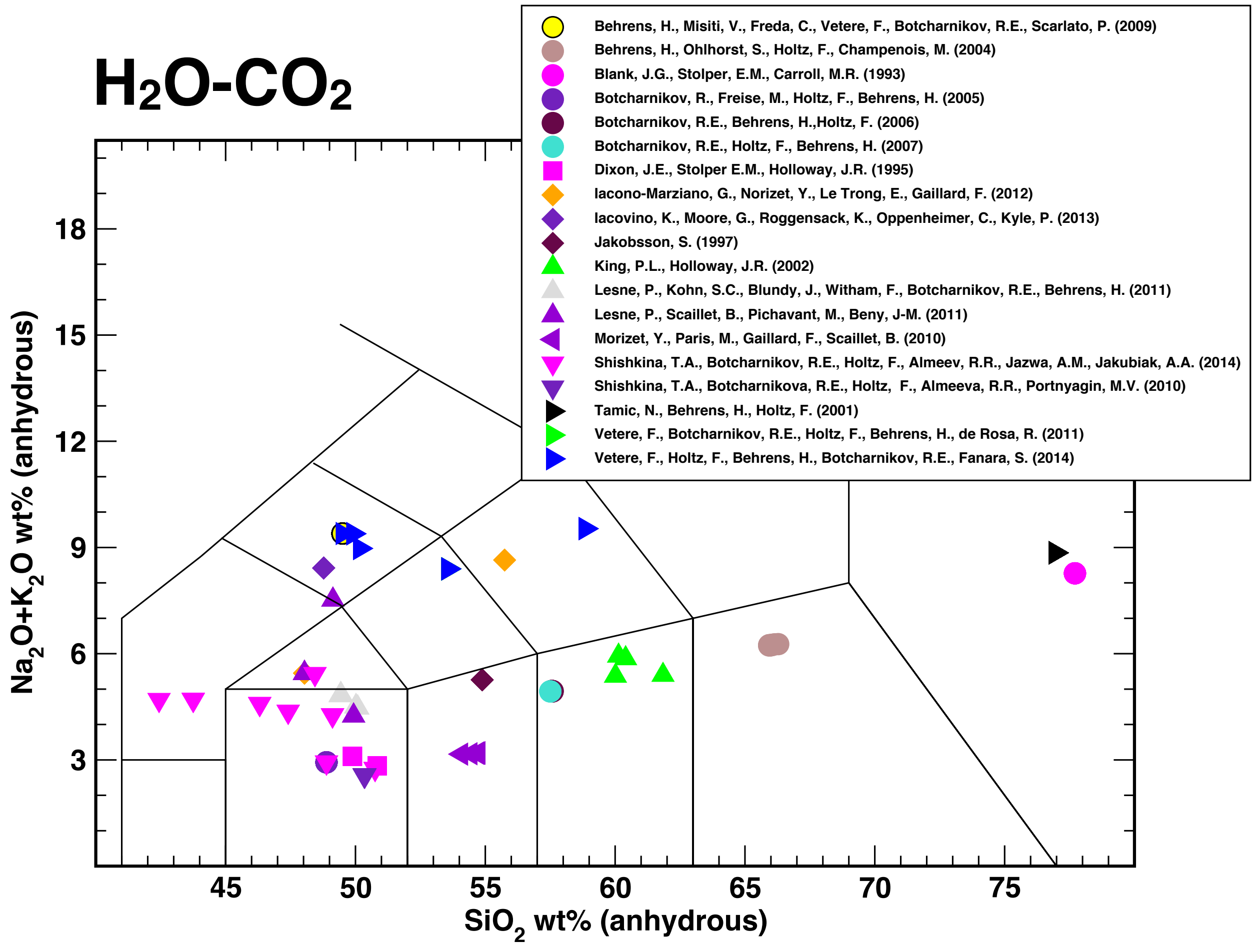
How do we obtain robust calibrations?



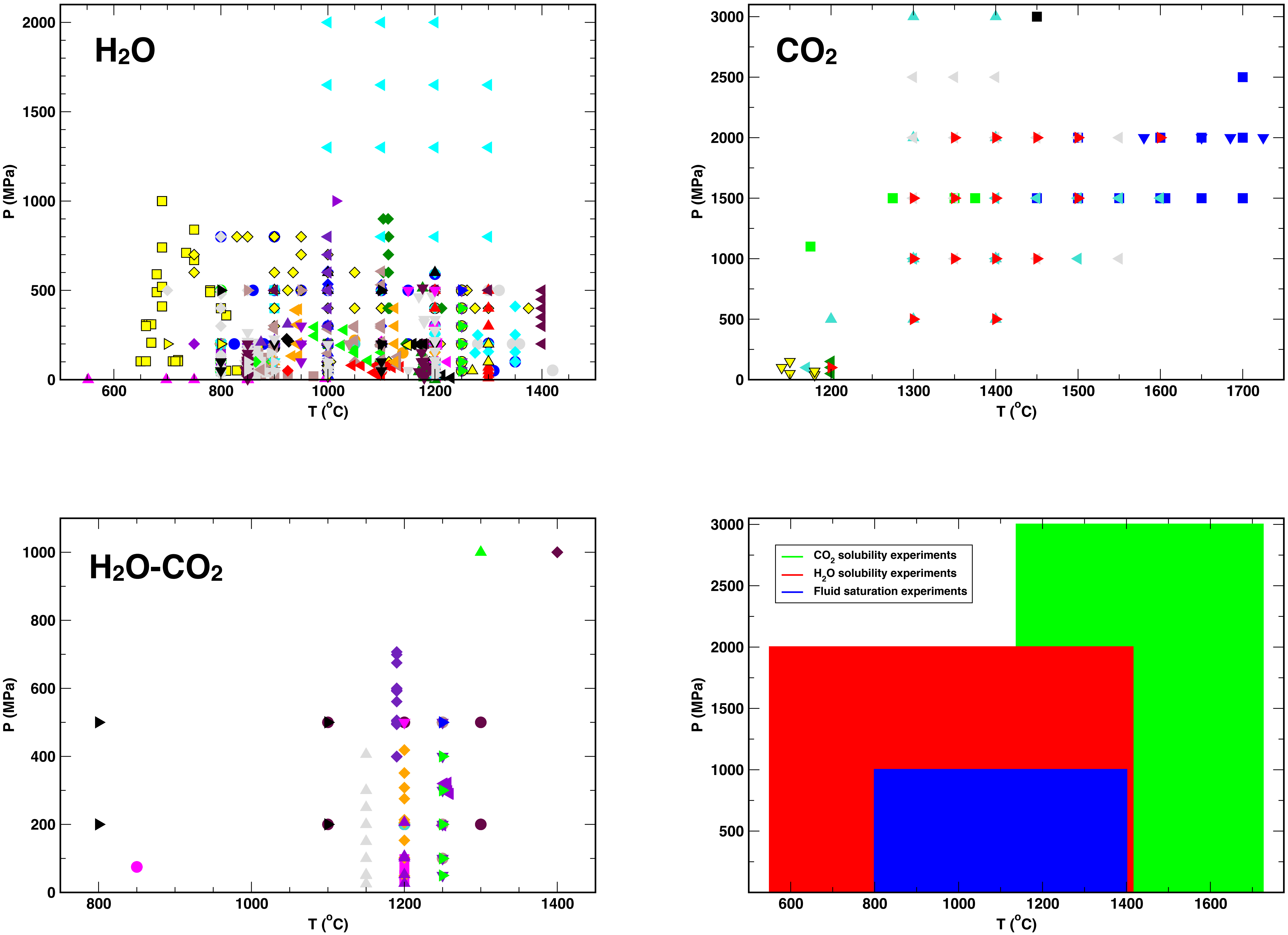
Model construction: Data







- Solubility of H_2O in silicate melts (on assumption of pure water fluid)
- Solubility of CO_2 in silicate melts
- Saturation conditions for mixed H_2O-CO_2 fluids


H₂O
P (MPa)
0
500
1000
1500
2000
T (°C)
600
800
1000
1200
1400
CO₂
P (MPa)
0
500
1000
1500
2000
2500
3000
T (°C)
1200
1300
1400
1500
1600
1700
H₂O-CO₂
P (MPa)
0
200
400
600
800
1000
T (°C)
800
1000
1200
1400
CO₂ solubility experiments
H₂O solubility experiments
Fluid saturation experiments
P (MPa)
500
1000
1500
2000
2500
3000
T (°C)
600
800
1000
1200
1400
1600

Thermodynamic model: melt phase

(regular associated solution, after MELTS)

Molar Gibbs free energy:

$$\bar{G} = \sum_{i=0}^{16} X_i \mu_i^o + RT \sum_{i=0}^{16} X_i \ln X_i + RT\left[X_{\mathrm{H_2O}} \ln X_{\mathrm{H_2O}} + \left(1 - X_{\mathrm{H_2O}}\right) \ln\left(1 - X_{\mathrm{H_2O}}\right) \right] + \frac{1}{2} \sum_{i=0}^{16} \sum_{j=0}^{16} W_{ij} X_i X_j$$

Condition of internal or homogeneous equilibrium:

$$0 = \mu_{\mathrm{SiO_2}}^o - \mu_{\mathrm{CaSiO_3}}^o - \mu_{\mathrm{CO_2}}^o + \mu_{\mathrm{CaCO_3}}^o + RT \ln \frac{X_{\mathrm{SiO_2}} X_{\mathrm{CaCO_3}}}{X_{\mathrm{CaSiO_3}} X_{\mathrm{CO_2}}} + \sum_{i=0}^{16} \left(W_{\mathrm{SiO_2},j} - W_{\mathrm{CaSiO_3},j} - W_{\mathrm{CO_2},j} + W_{\mathrm{CaCO_3},j} \right) X_i$$

Chemical potential of nonvolatile melt components and of CO_2:

$$\mu_{\mathrm{SiO_2}} = \mu_0 = \mu_{\mathrm{SiO_2}}^o + RT \ln X_{\mathrm{SiO_2}} + RT \ln\left(1 - X_{\mathrm{H_2O}}\right) + \sum_{i=0}^{16} W_{\mathrm{SiO_2},i} X_i - \frac{1}{2} \sum_{i=0}^{16} \sum_{j=0}^{16} W_{ij} X_i X_j$$

Chemical potential of H_2O:

$$\mu_{\mathrm{H_2O}} = \mu_{14} = \mu_{\mathrm{H_2O}}^o + RT \ln X_{\mathrm{H_2O}}^2 + \sum_{j=0}^{16} W_{\mathrm{H_2O},j} X_j - \frac{1}{2} \sum_{i=0}^{16} \sum_{j=0}^{16} W_{ij} X_i X_j$$

#	**Independent Component or Basis Species**
0	SiO_2
1	TiO_2
2	Al_2O_3
3	Fe_2O_3
4	Cr_2O_3
5	Fe_2SiO_4
6	$MnSi_{1/2}O_2$
7	Mg_2SiO_4
8	$NiSi_{1/2}O_2$
9	$CoSi_{1/2}O_2$
10	$CaSiO_3$
11	Na_2SiO_3
12	$KAlSiO_4$
13	$Ca_3(PO_4)_2$
14	H_2O
15	CO_2

Dependent Species

16	$CaCO_3$

Thermodynamic model: H_2O-CO_2 mixed fluid phase

(virial EOS of Duan and Zhang, 2006)

Chemical potential of CO_2:

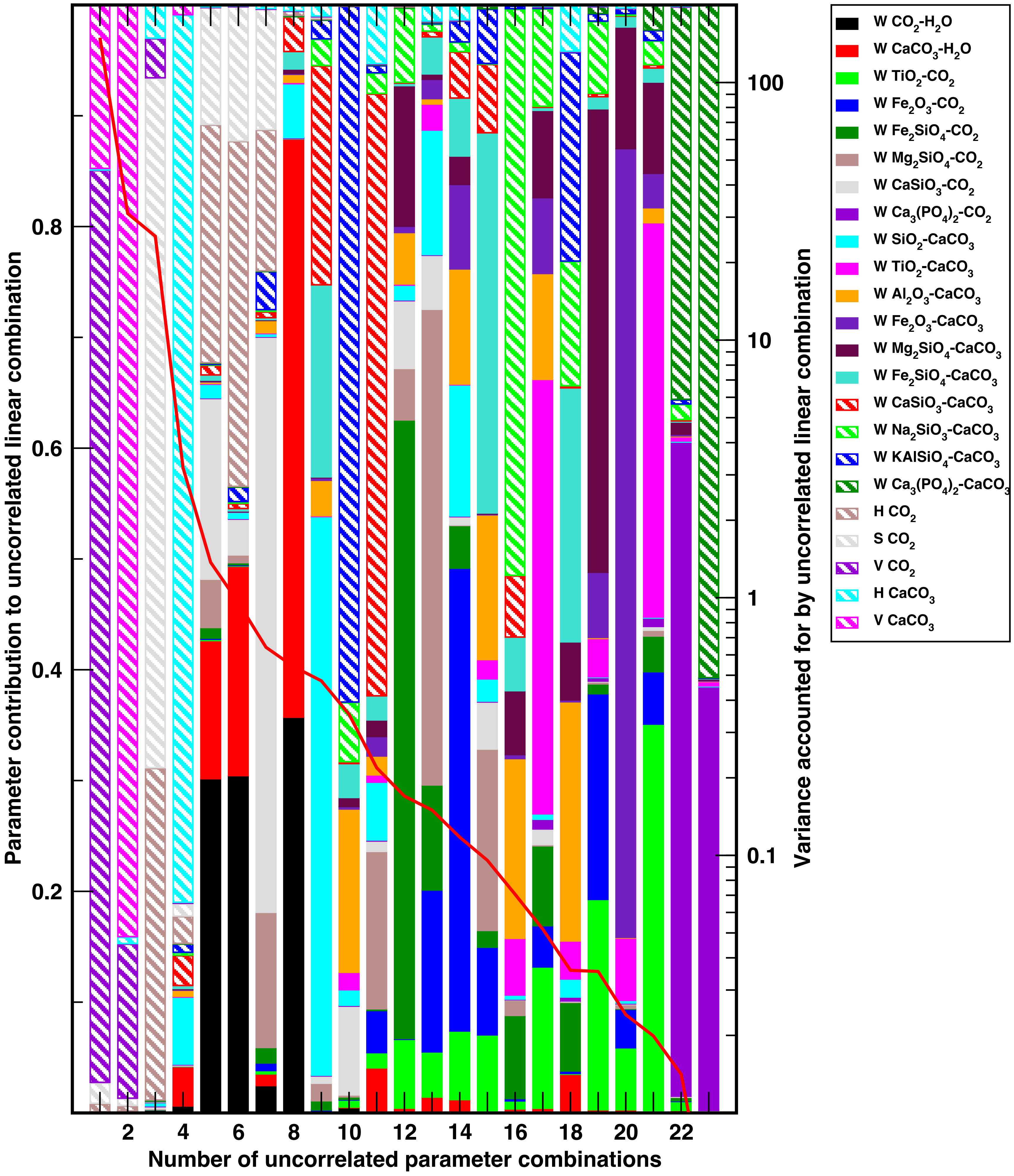
$$\mu_{\mathrm{SiO_2}} = \mu_0 = \mu^o_{\mathrm{CO_2}} + RT\ln X_{\mathrm{CO_2}} + RT\ln\left(1 - X_{\mathrm{H_2O}}\right) + \sum_{i=0}^{16} W_{\mathrm{CO_2},i} X_i - \frac{1}{2}\sum_{i=0}^{16}\sum_{j=0}^{16} W_{ij} X_i X_j$$

Chemical potential of H_2O:

$$\mu_{\mathrm{H_2O}} = \mu_{14} = \mu^o_{\mathrm{H_2O}} + RT\ln X^2_{\mathrm{H_2O}} + \sum_{j=0}^{16} W_{\mathrm{H_2O},j} X_j - \frac{1}{2}\sum_{i=0}^{16}\sum_{j=0}^{16} W_{ij} X_i X_j$$

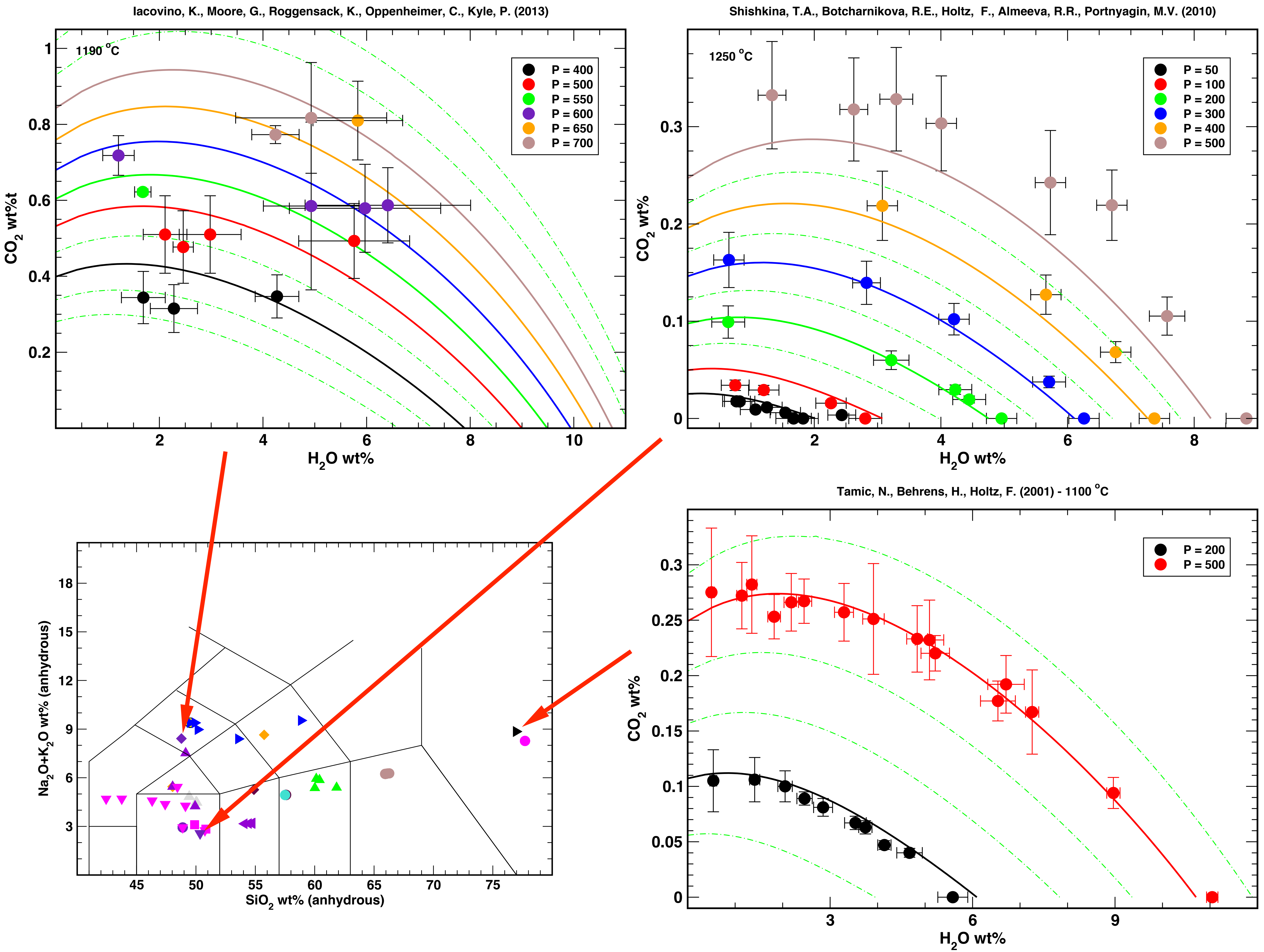
Condition of internal or homogeneous

$$0 = \mu^o_{\mathrm{SiO_2}} - \mu^o_{\mathrm{CaSiO_3}} - \mu^o_{\mathrm{CO_2}} + \mu^o_{\mathrm{CaCO_3}} + RT\ln\frac{X_{\mathrm{SiO_2}} X_{\mathrm{CaCO_3}}}{X_{\mathrm{CaSiO_3}} X_{\mathrm{CO_2}}} + \sum_{i=0}^{16}\left(W_{\mathrm{SiO_2},j} - W_{\mathrm{CaSiO_3},j} - W_{\mathrm{CO_2},j} + W_{\mathrm{CaCO_3},j}\right) X_i$$

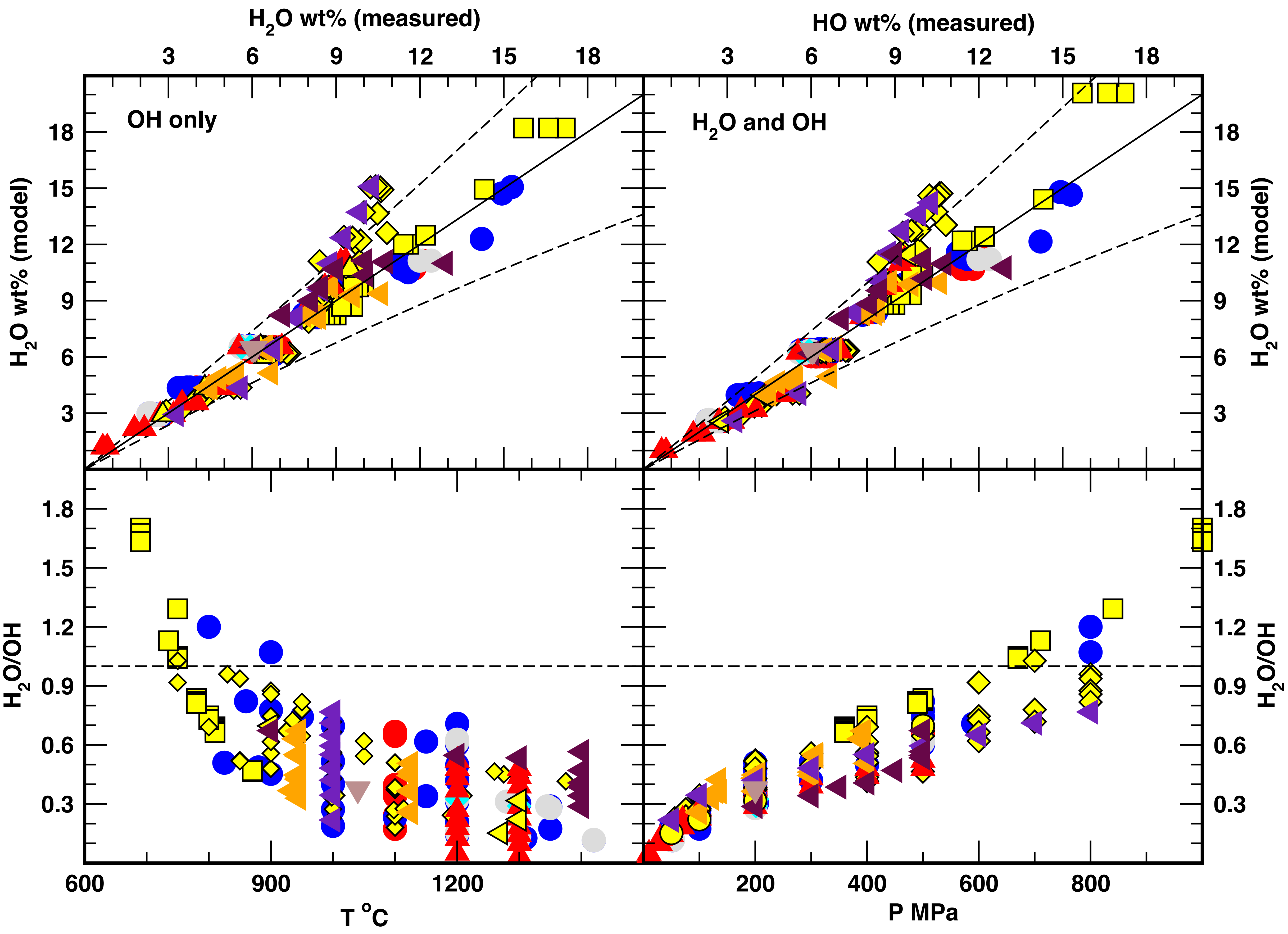


Fitting the model:

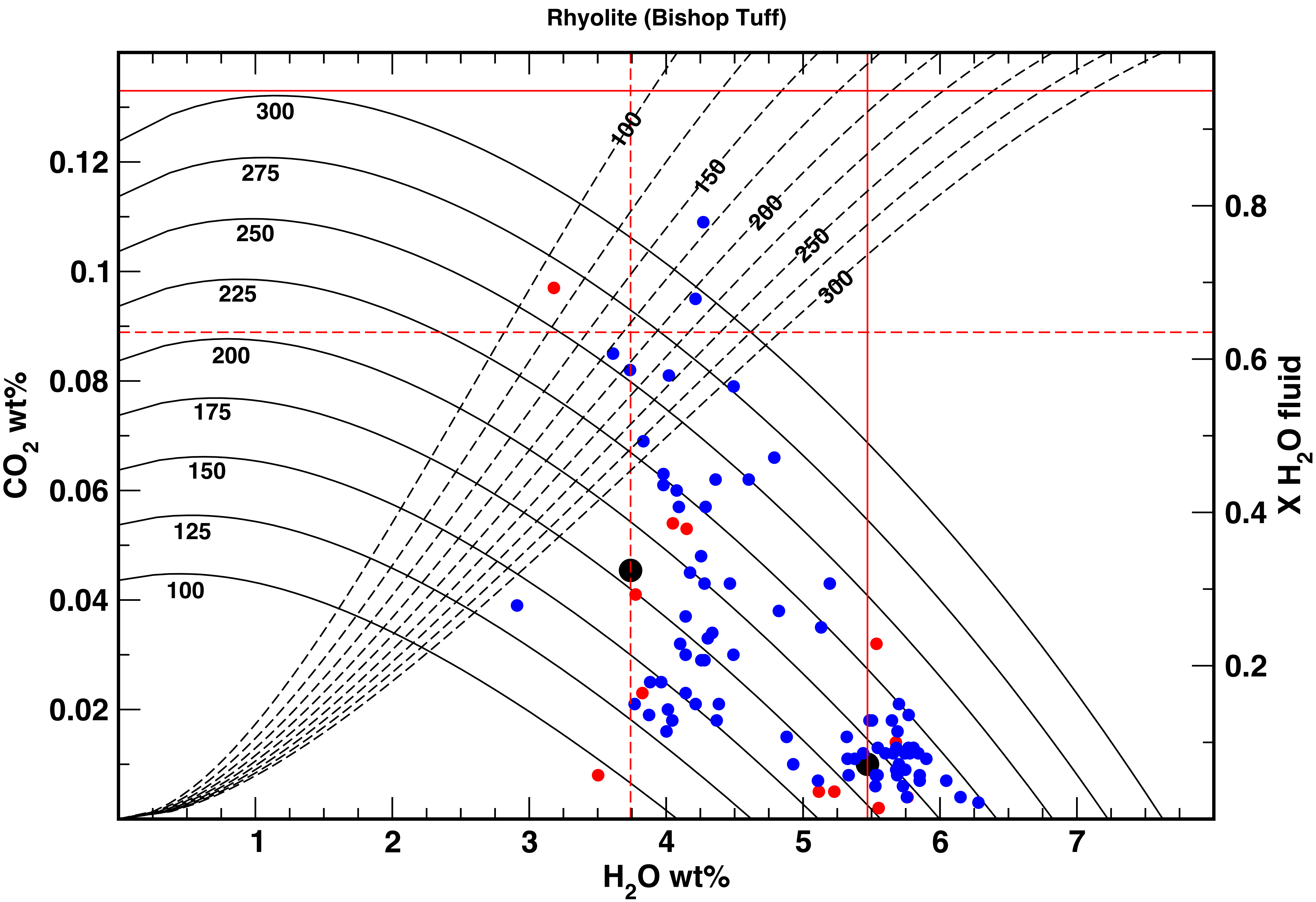
- Equate chemical potentials of the H_2O component in melt and fluid
- Optimize both standard state properties and interaction parameters for H_2O in the melt
- Equate chemical potentials of the CO_2 component in melt and fluid
- Optimize both standard state properties and interaction parameters for CO_2 in the melt. Because of the speciation, the optimization is non-linear.
- Singular Value analysis is used at each non-linear step to the residual minimum


Iacovino, K., Moore, G., Roggensack, K., Oppenheimer, C., Kyle, P. (2013)
1190 °C
P = 400
P = 500
P = 550
P = 600
P = 650
P = 700
CO2 wt%t
H2O wt%
Shishkina, T.A., Botcharnikova, R.E., Holtz, F., Almeeva, R.R., Portnyagin, M.V. (2010)
1250 °C
P = 50
P = 100
P = 200
P = 300
P = 400
P = 500
CO2 wt%
H2O wt%
Tamic, N., Behrens, H., Holtz, F. (2001) - 1100 °C
P = 200
P = 500
CO2 wt%
H2O wt%
Na2O+K2O wt% (anhydrous)
SiO2 wt% (anhydrous)

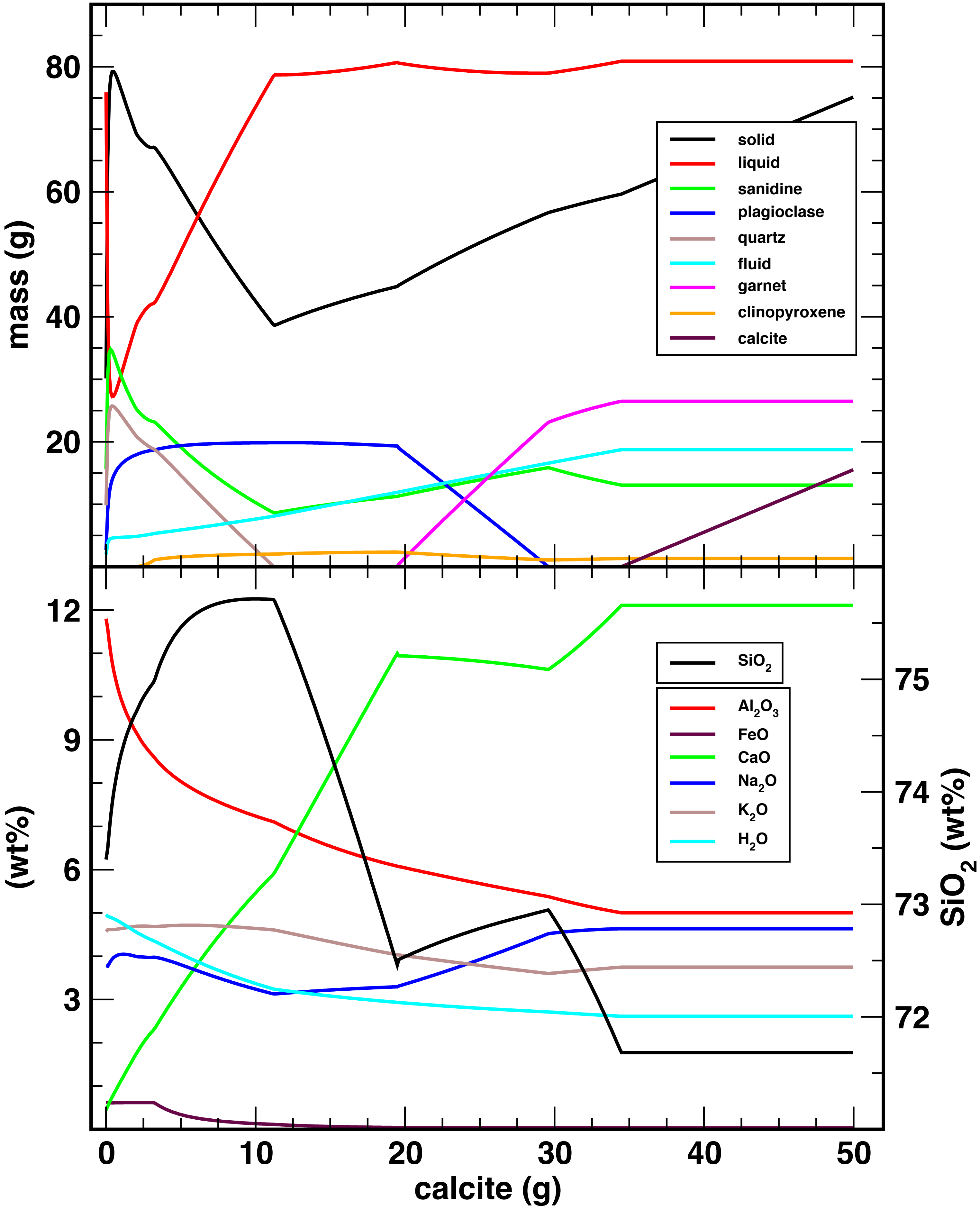
Model-Data recovery: the issue of speciation, case study $NaAlSi_3O_8$ (albite) liquid



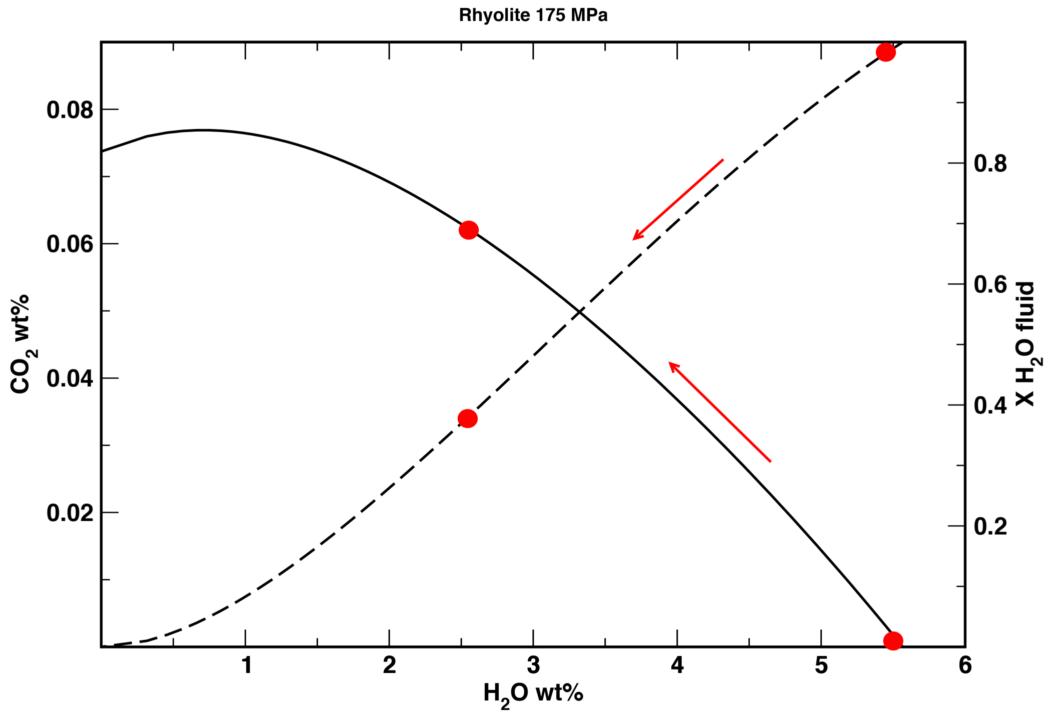
Application: melt inclusions in quartz phenocrysts in rhyolite magma

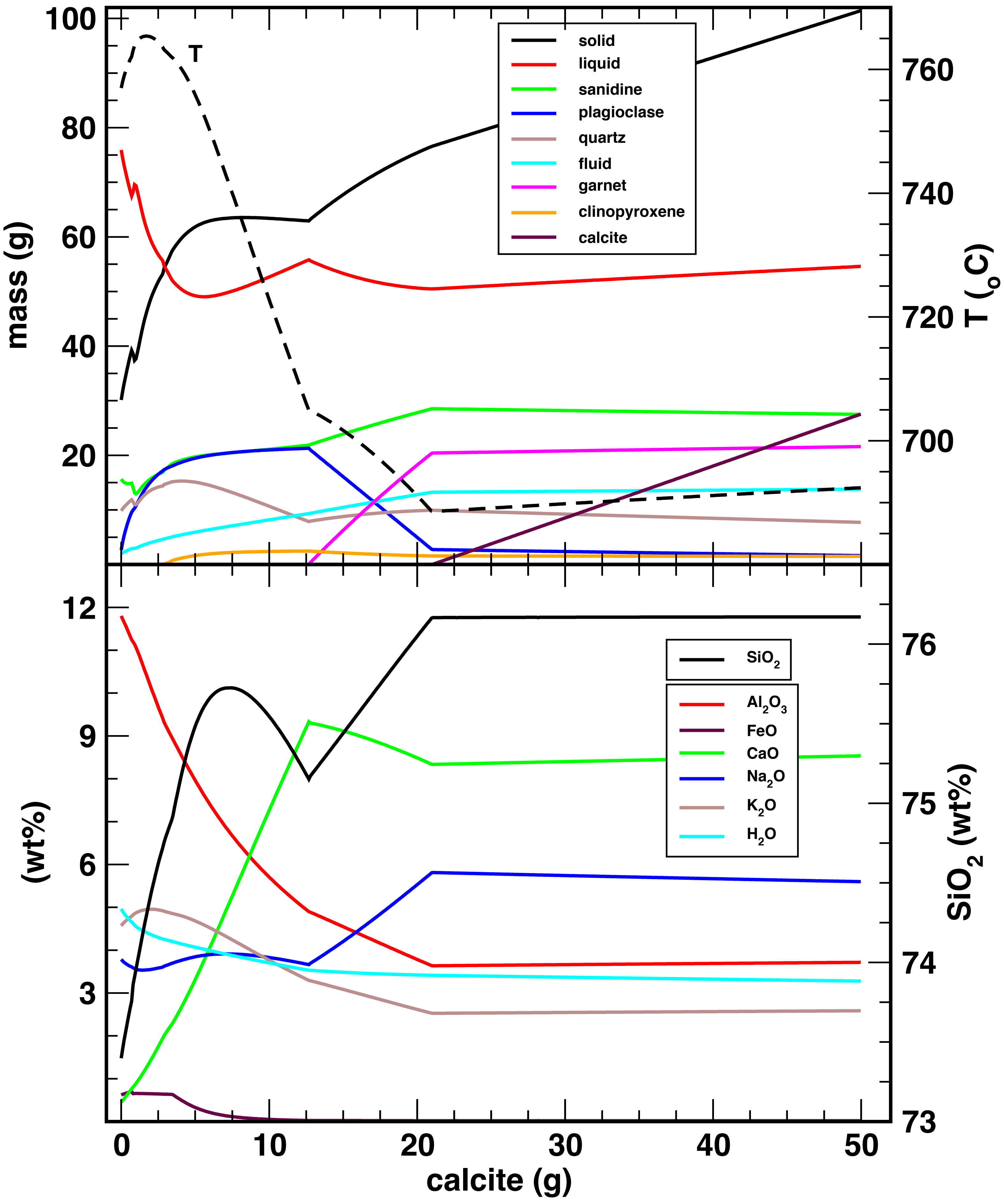


Assimilation of calcite into rhyolite magma



- Addition of calcite (CaCO3) initially induces crystallization, then remelting
- Plagioclase is stabilized at the expense of sanidine
- Addition lifts the system off of the quartz saturation surface, eventually stabilizing grossular garnet, ultimately saturating the magma with carbonate, while loosing plagioclase
- melt initially increases in SiO_2 concentration due to partitioning of H_2O to the fluid phase
- concentration of CaO in the melt rises, and SiO_2 diminishes, but not monotonically
- melt composition is ultimately “buffered” by the assemblage: fluid, sanidine, grossular, calcite, clinopyroxene





Assimilation of calcite into rhyolite magma, with isenthalpic (adiabatic) energy constraints; temperature is a dependent variable

- temperature initially rises, then falls ~4°C/g of assimilant until calcite reaches saturation
- ~ 20% less liquid at calcite saturation than in the isothermal case
- calcite saturates at lower extents of assimilation
- quartz is never lost from the assemblage
- plagioclase is never lost from the assemblage
- the SiO_2 content of the melt does not fall, as in the isothermal case
- as in the isothermal case, melt composition seizes to evolve once calcite appears as a product phase
- despite the lower temperatures, the abundance of dissolved volatile components in the melt is higher in the isenthalpic case because the coexisting fluid composition is not as CO_2-rich

Assimilation of calcite into rhyolite magma, with isochoric constraints; pressure is a dependent variable