# Why do we make thermodynamic models of magmatic phase relations?

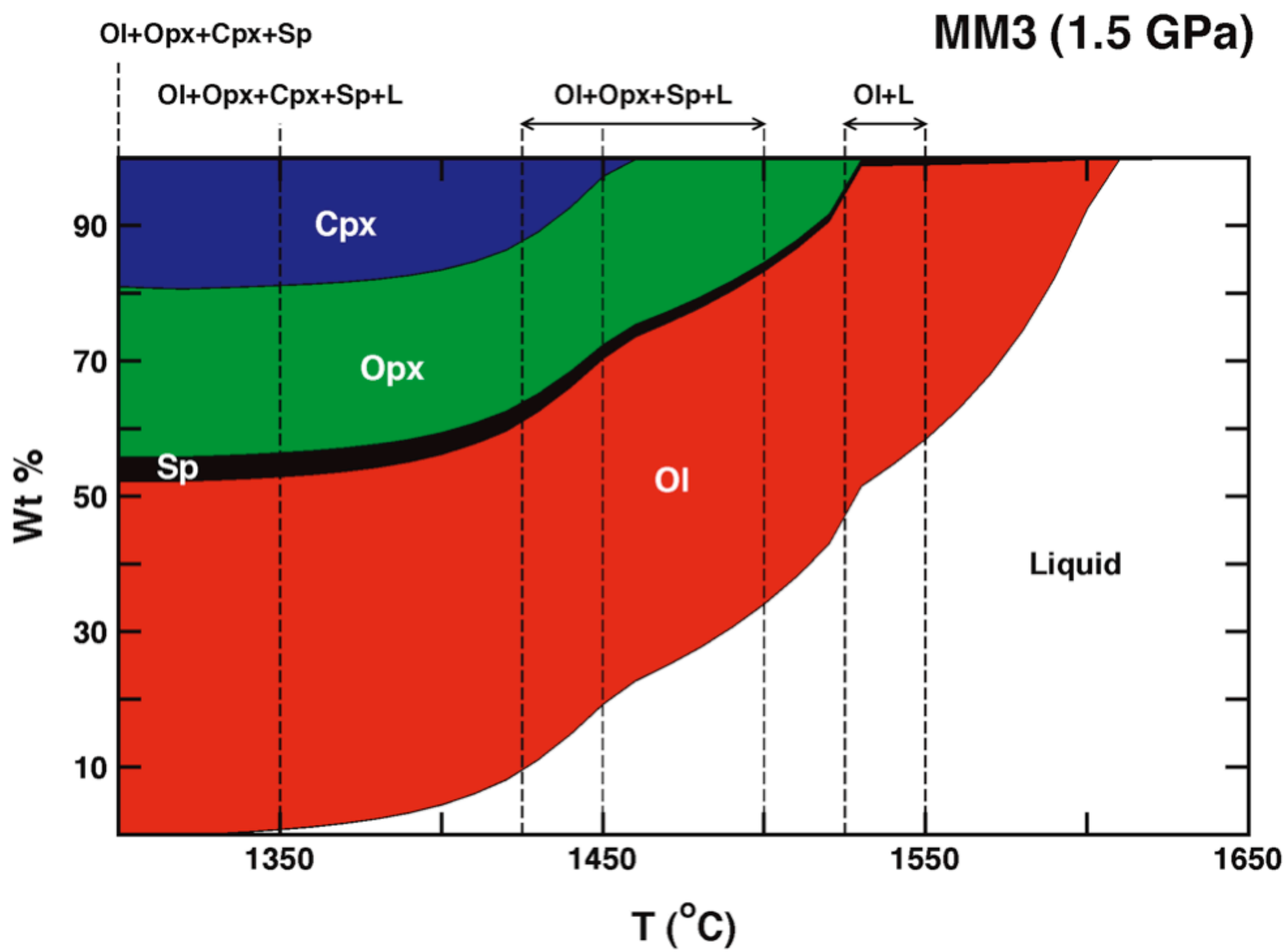
## Experiments are not always enough!

- **Reproduce or interpolate experiments**
  - In this context, models can be useful, but are often disappointing. The more multivariate a problem is, the more useful interpolation becomes. Models can be very useful in synthesizing multiple experimental sources.

- **To extrapolate experimental data**
  - The framework of thermodynamics is most useful in this case. Arbitrary functional forms with little theoretical basis may not extrapolate well in T, P and composition. Thermodynamical-based models of phase equilibria are always better extrapolators of experimental data.

# Example: melting of peridotite at shallow mantle pressures:

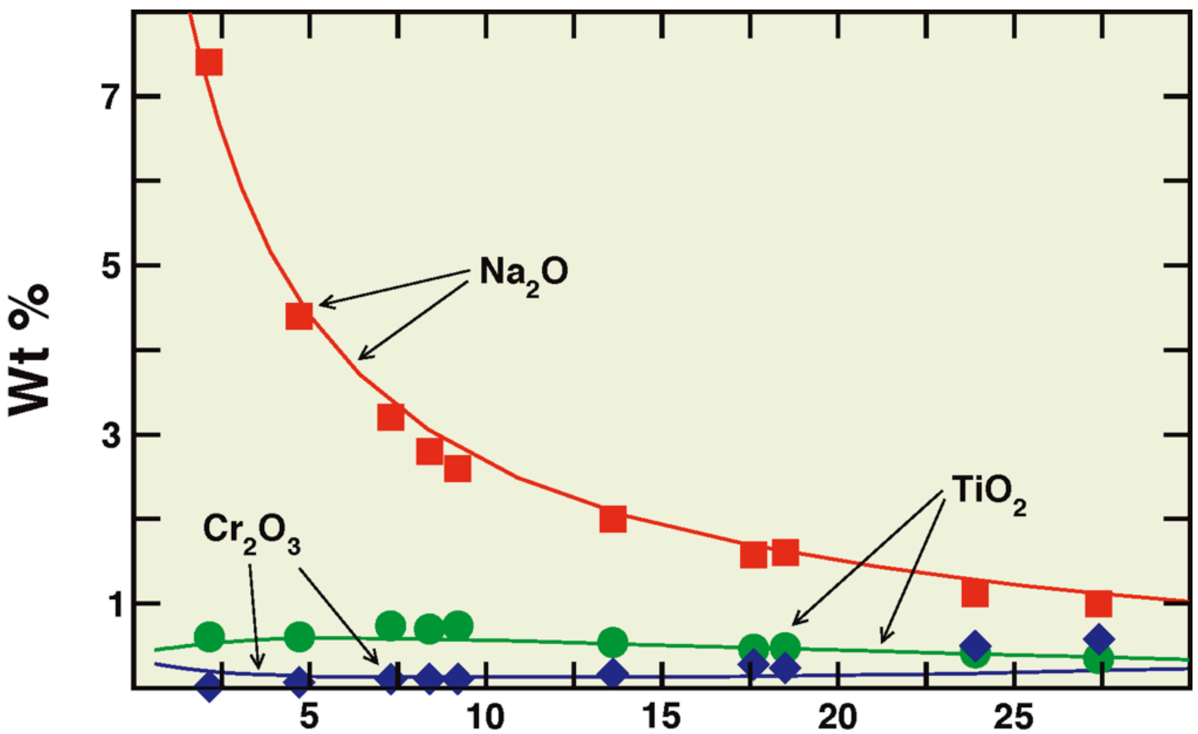
## Phase equilibria from 0-3 GPa

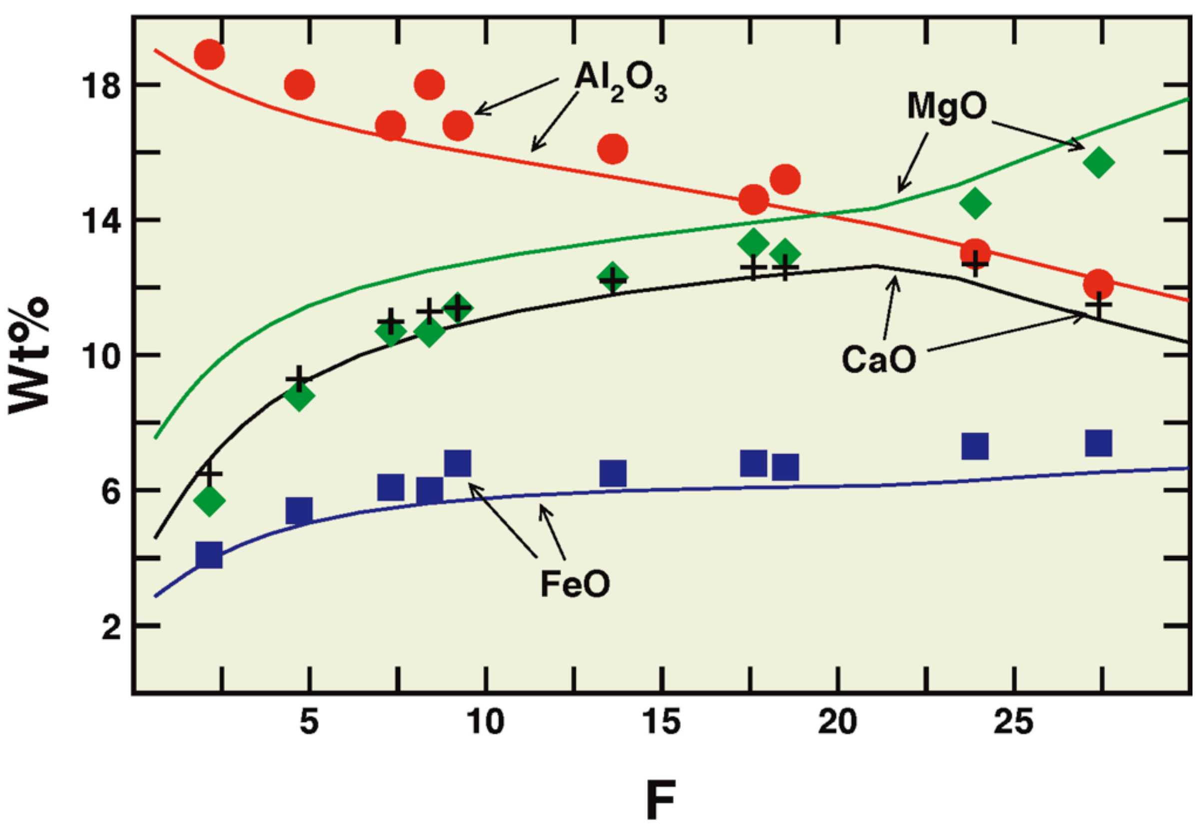



| | MM3 |
|---|---|
| $SiO_2$ | 45.47 |
| $TiO_2$ | 0.11 |
| $Al_2O_3$ | 4.00 |
| $Cr_2O_3$ | 0.68 |
| $FeO_T$ | 7.22 |
| MgO | 38.53 |
| CaO | 3.59 |
| $Na_2O$ | 0.31 |

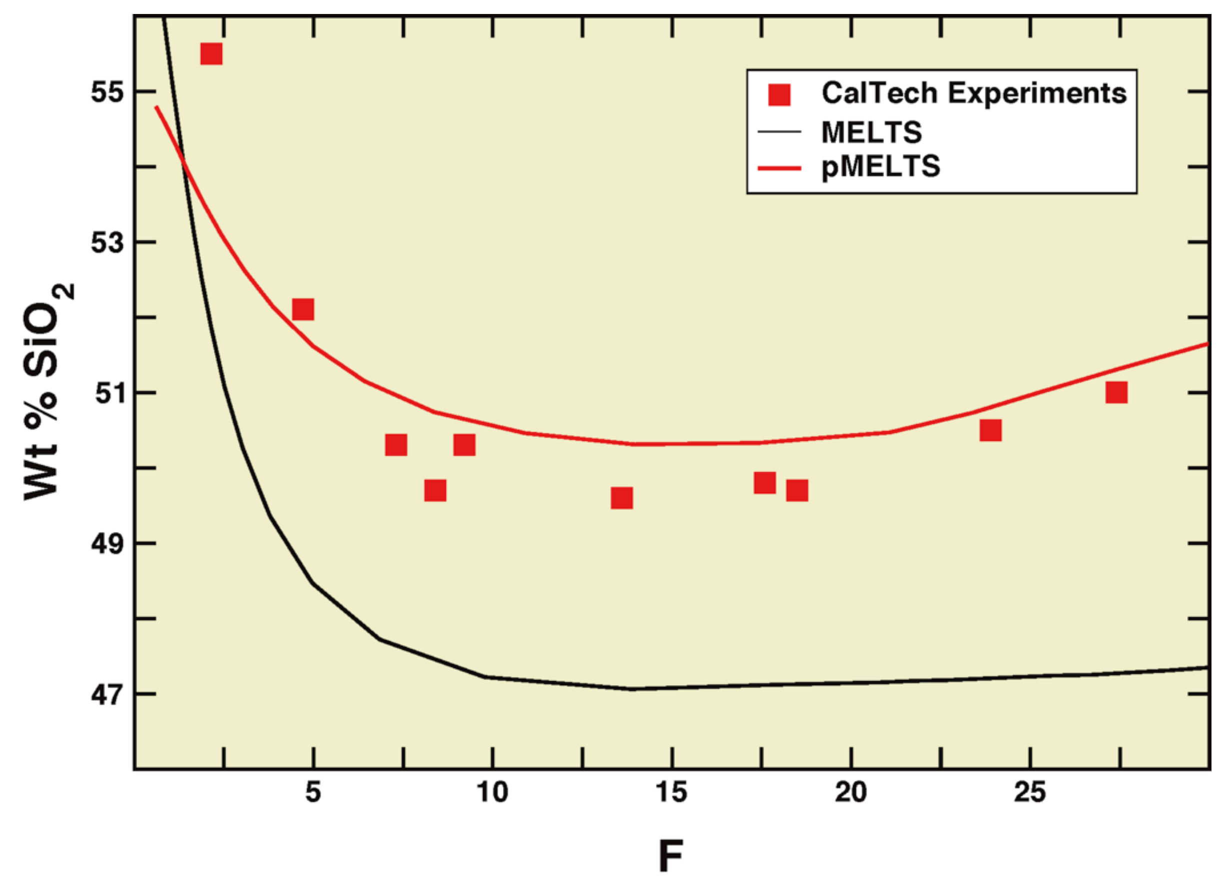
**Ol** Olivine
**Sp** Spinel
**Opx** Orthopyroxene
**Cpx** Clinopyroxene
**Plag** Plagioclase

# Phase equilibria from 0-3 GPa (con't)



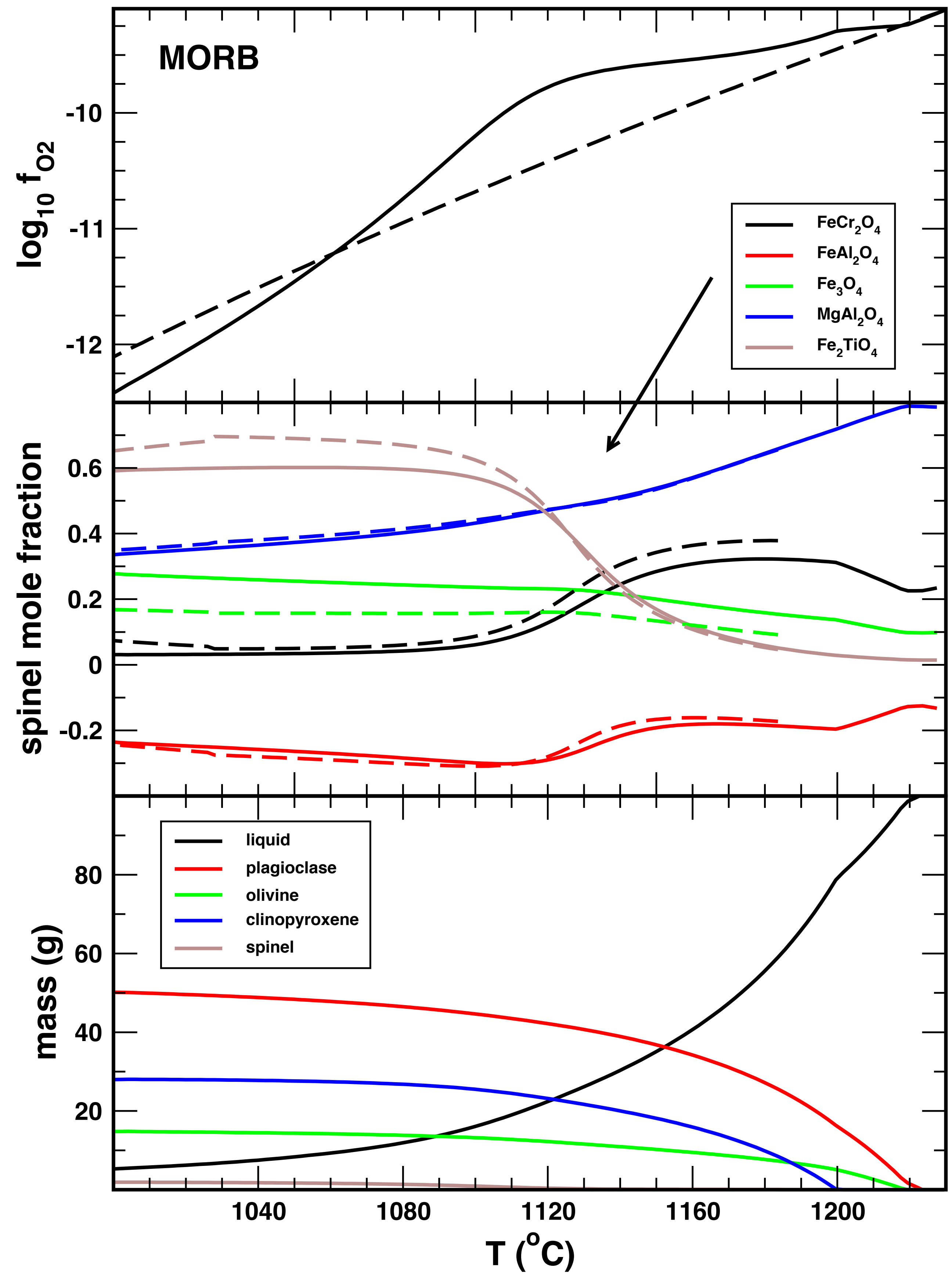




- Experimentally determined liquid compositions are indicated by symbols.
- Smooth curves are calculated using the pMELTS software package.

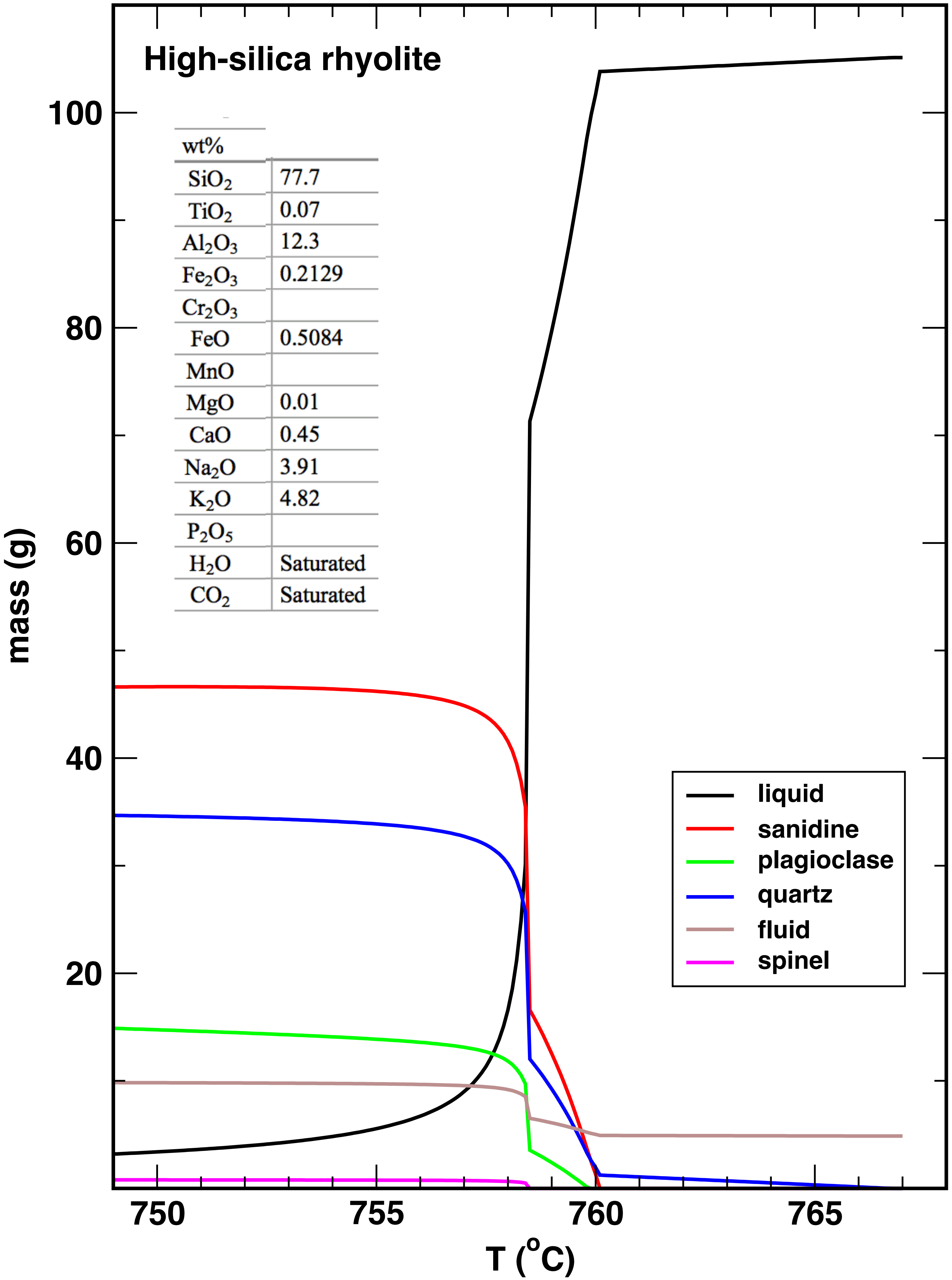


# Another example: crystallization of MORB composition liquid:

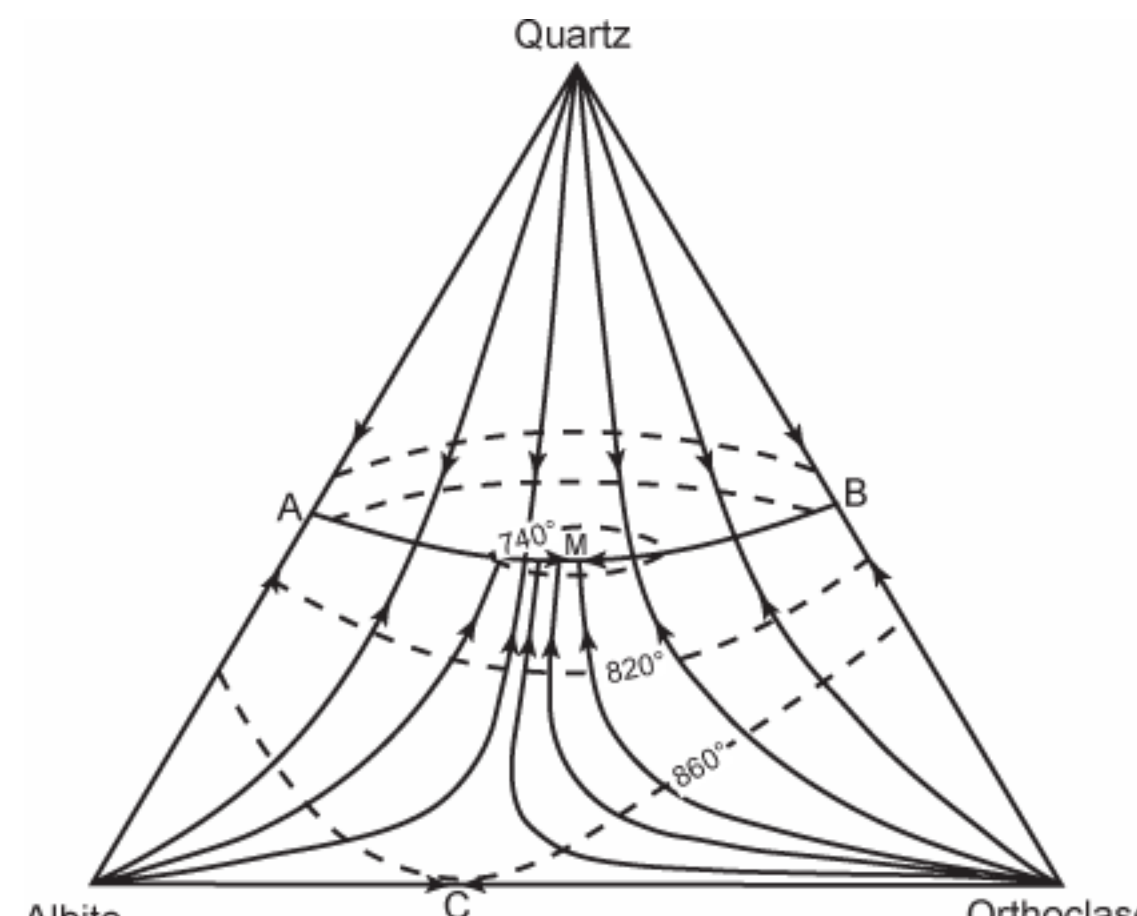
| wt% | MORB |
|---|---|
| $SiO_2$ | 48.68 |
| $TiO_2$ | 1.01 |
| $Al_2O_3$ | 17.64 |
| $Fe_2O_3$ | 0.89 |
| $Cr_2O_3$ | 0.0425 |
| FeO | 7.59 |
| MnO | |
| MgO | 9.1 |
| CaO | 12.45 |
| $Na_2O$ | 2.65 |
| $K_2O$ | 0.03 |
| $P_2O_5$ | 0.08 |
| $H_2O$ | 0.2 |
| $CO_2$ | |



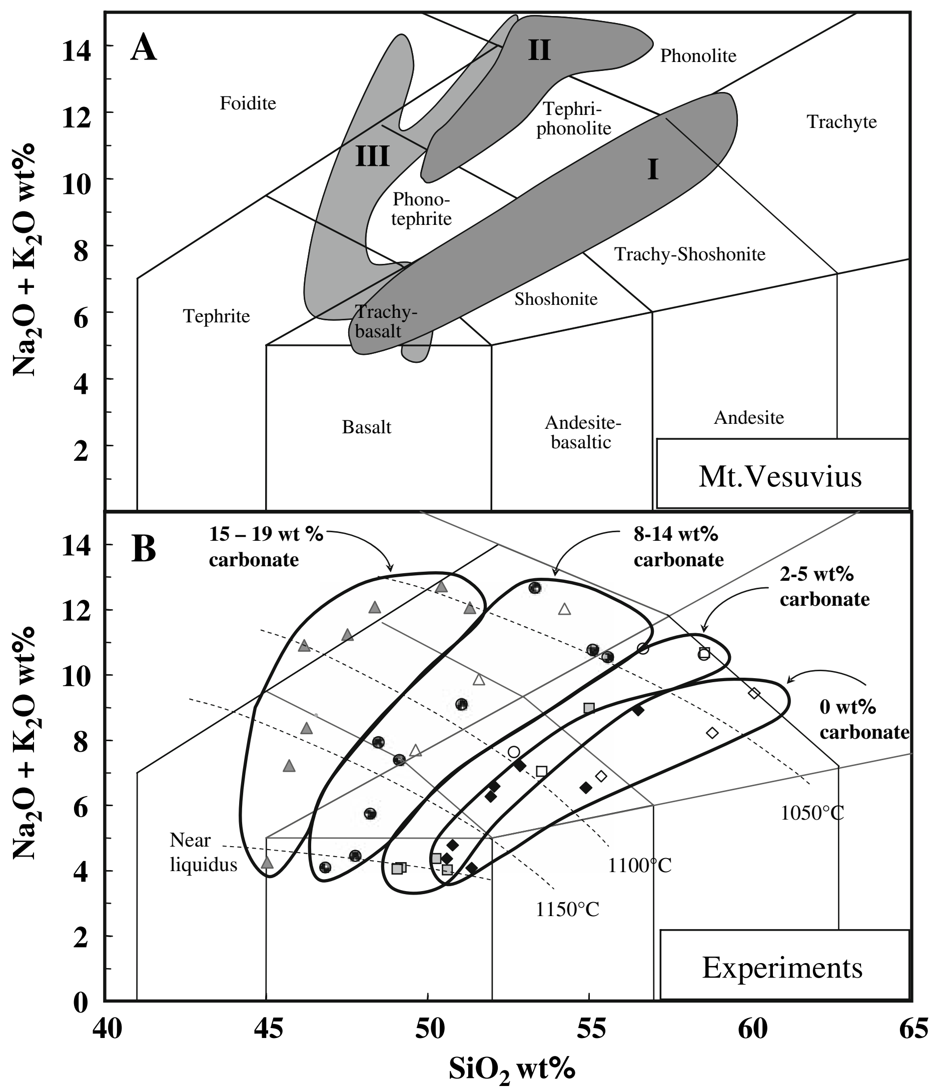
# Another example: rhyolite:



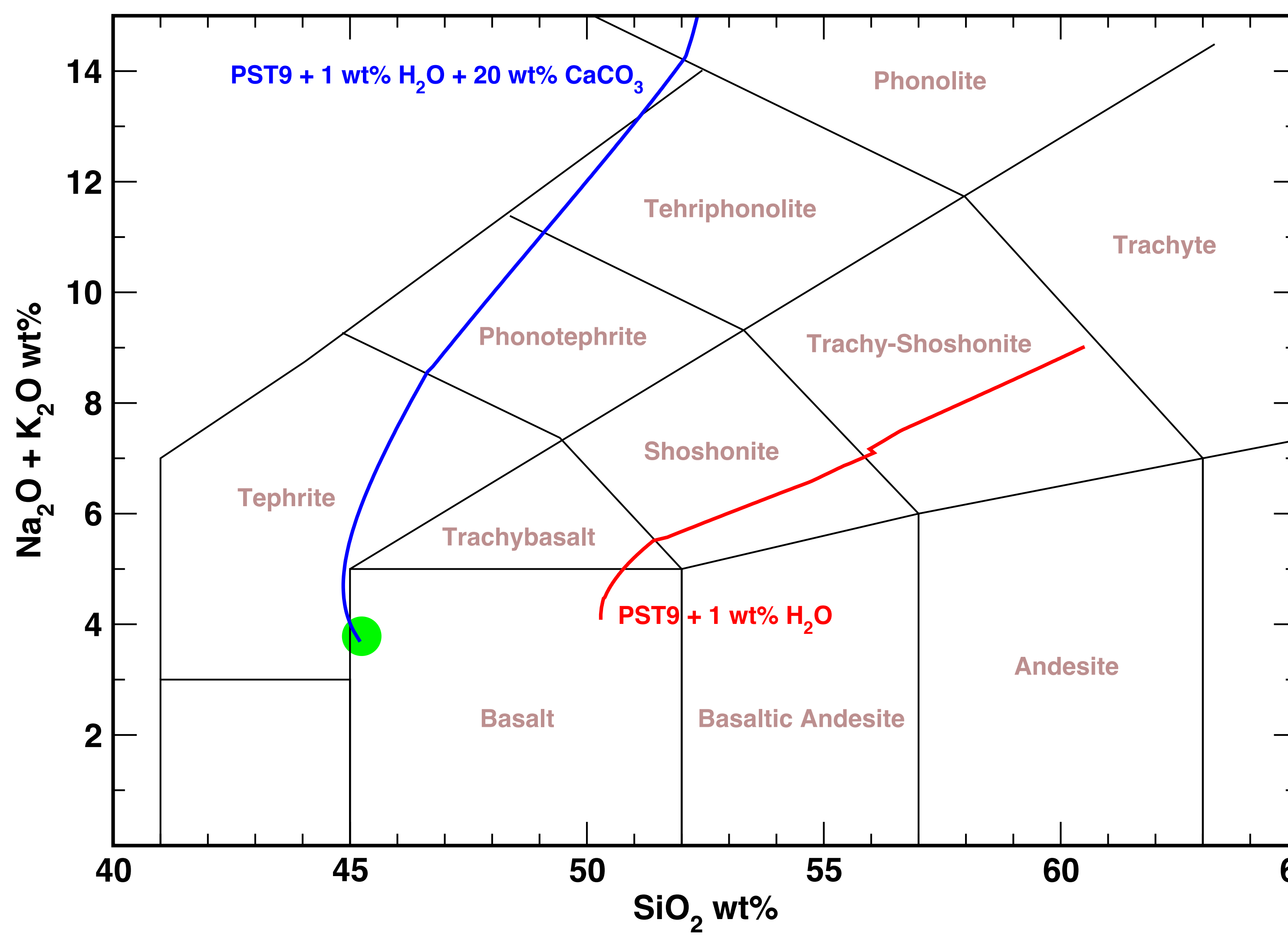

| wt% | |
|---|---|
| $SiO_2$ | 77.7 |
| $TiO_2$ | 0.07 |
| $Al_2O_3$ | 12.3 |
| $Fe_2O_3$ | 0.2129 |
| $Cr_2O_3$ | |
| FeO | 0.5084 |
| MnO | |
| MgO | 0.01 |
| CaO | 0.45 |
| $Na_2O$ | 3.91 |
| $K_2O$ | 4.82 |
| $P_2O_5$ | |
| $H_2O$ | Saturated |
| $CO_2$ | Saturated |



# Example: Daly hypothesis - Generation of tephrites and phonolites by assimilation of limestones into alkali basalts




after, Iacono-Marziano et al. (2008)

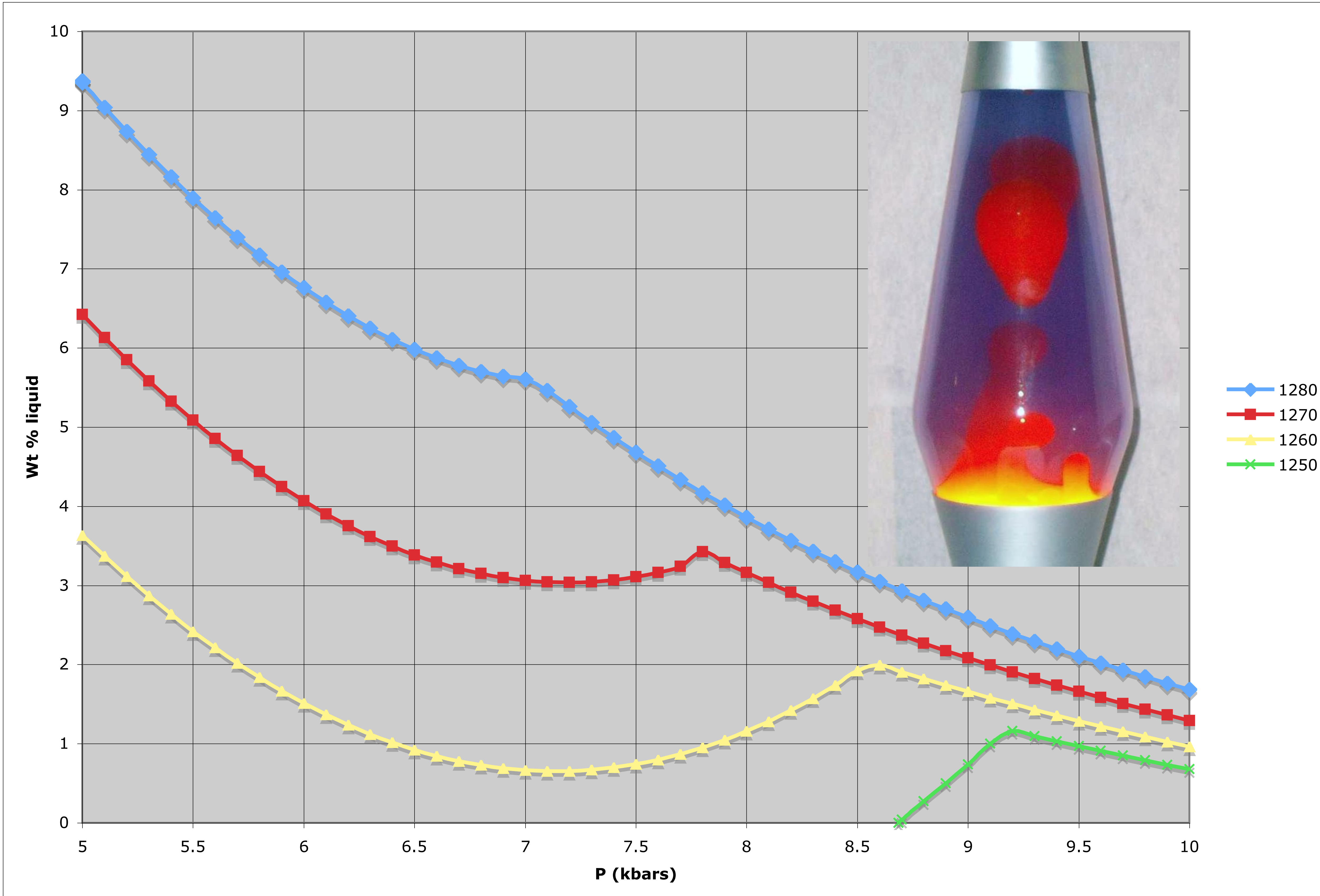



- (red curve) is PST-9 + 1 wt% H2O crystallization simulated using MELTS
- addition of 20 wt% CaCO3 to PST-9 + 1 wt% H2O generates the composition plotted as the green circle (compare to experiments)
- equilibrium crystallization of that carbonated composition generates the blue curve

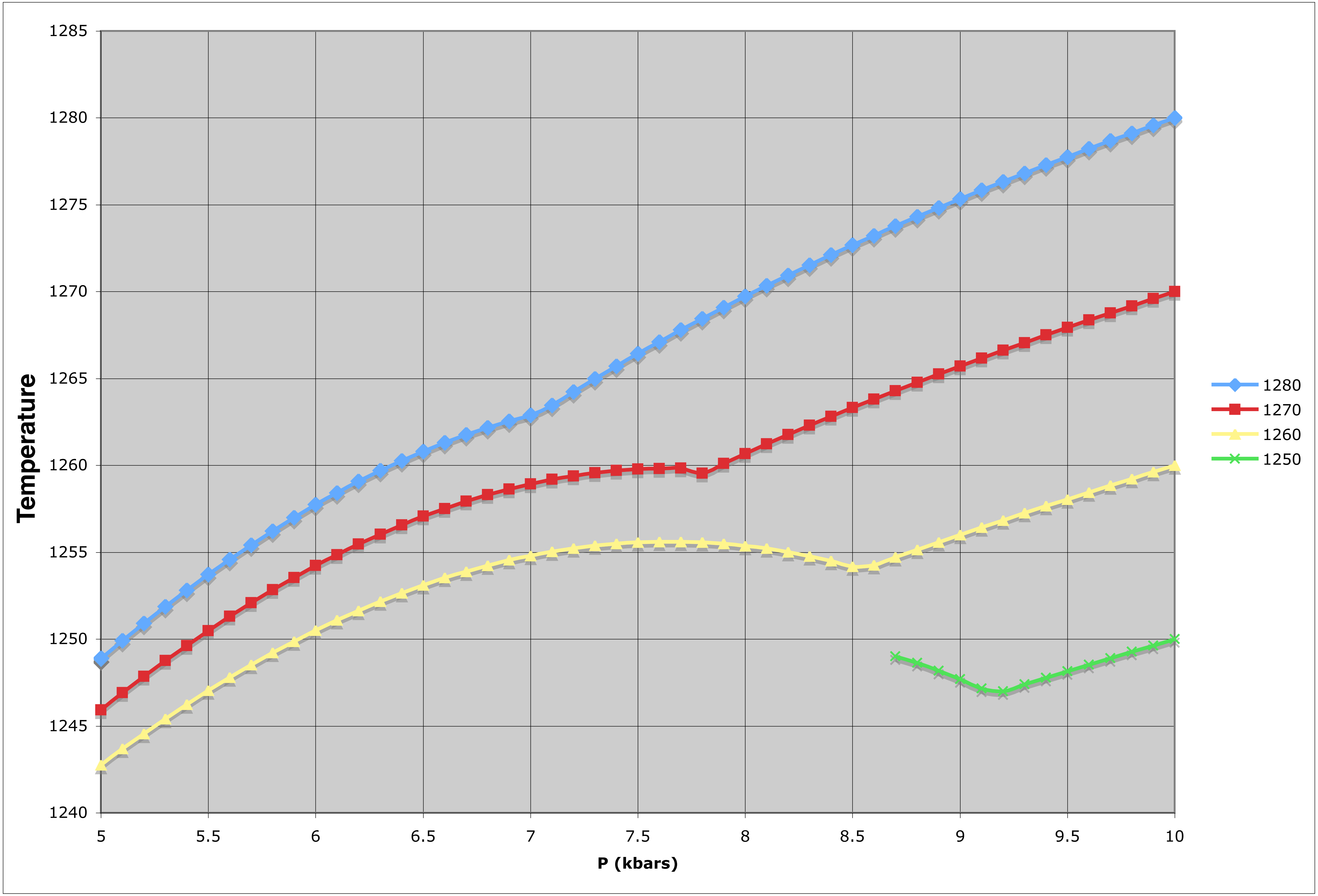
# But, what is the real advantage of thermodynamic models?

- **To investigate phenomena that are difficult or impossible to examine experimentally**
  - This is the key reason to develop a thermodynamic model. Examples:
    - We wish to model melting associated with adiabatic decompression, yet we cannot perform a sequence of melting experiments at fixed entropy content.
    - Experiments are done at fixed oxygen fugacity, but we are interested in evolution of the system at fixed oxygen content?
    - We wish to explore the consequences of crystallization under isochoric conditions, and it may not be possible to impose experimental constraints that mimic this condition.

# Example: Adiabatic melting (ΔQ = 0):



# … Adiabatic melting



**… Adiabatic melting**

$$\boxed{\begin{aligned} dS &\geq \frac{\cancel{d}q}{T} \\ dS &= \frac{dQ_{rev}}{T} \end{aligned}}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\left(\frac{\partial S}{\partial T}\right)_P \longrightarrow \frac{C_P}{T}$$

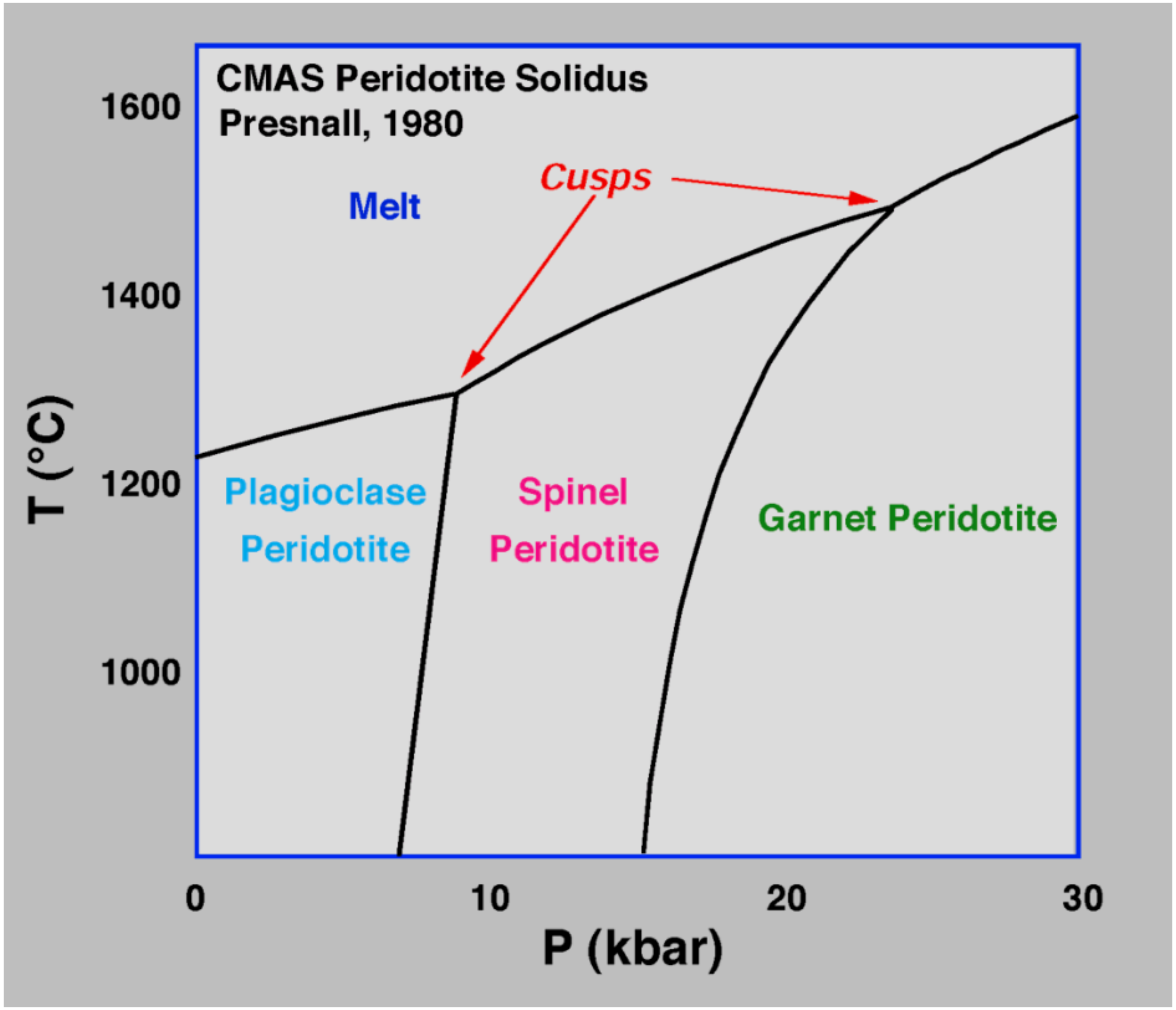
$$\left(\frac{\partial S}{\partial P}\right)_T \longrightarrow -\left(\frac{\partial V}{\partial T}\right)_P \longrightarrow V\alpha$$

$$\boxed{\begin{aligned} H &= E + PV \\ dH &= dE + PdV + VdP \\ &= dQ_{rev} - PdV + PdV + VdP \\ &= dQ_{rev} + VdP \end{aligned}}$$

$$0 = \frac{C_P}{T} dT - V\alpha dP$$

$$\boxed{\frac{dT}{dP}_{dQ=0} = \frac{V\alpha T}{C_P}}$$

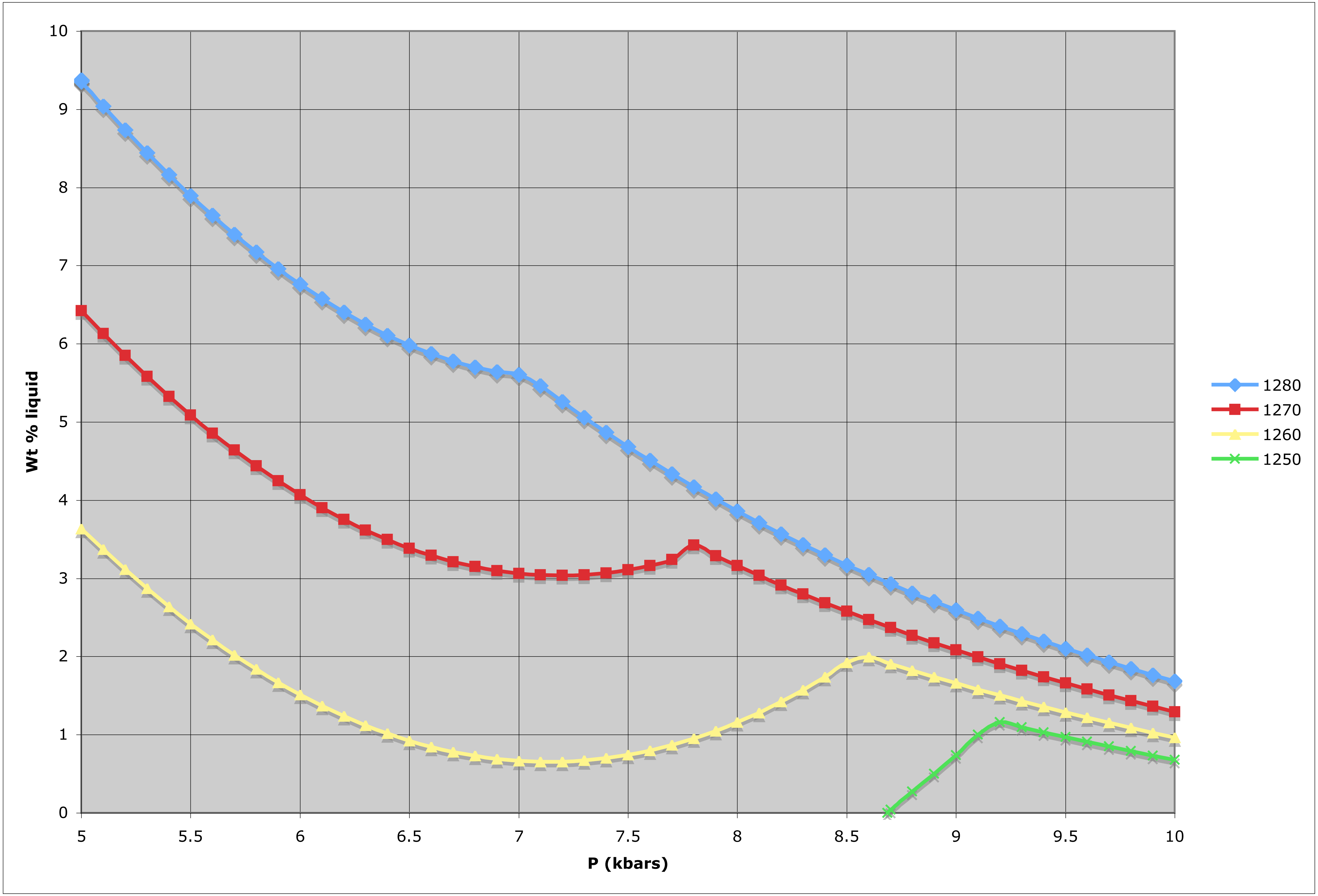
# … Adiabatic melting



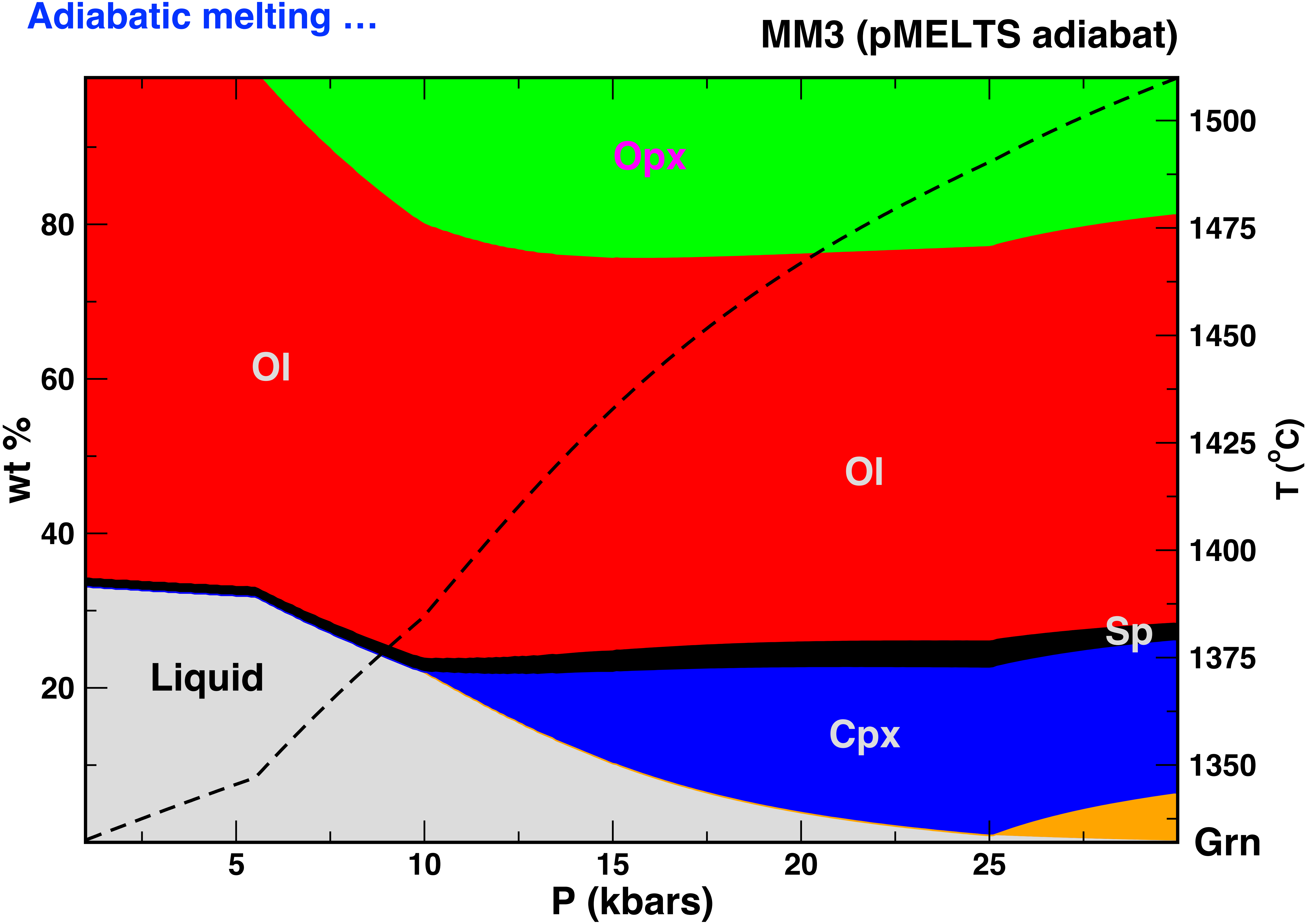

**Clapyron equation**

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S}$$

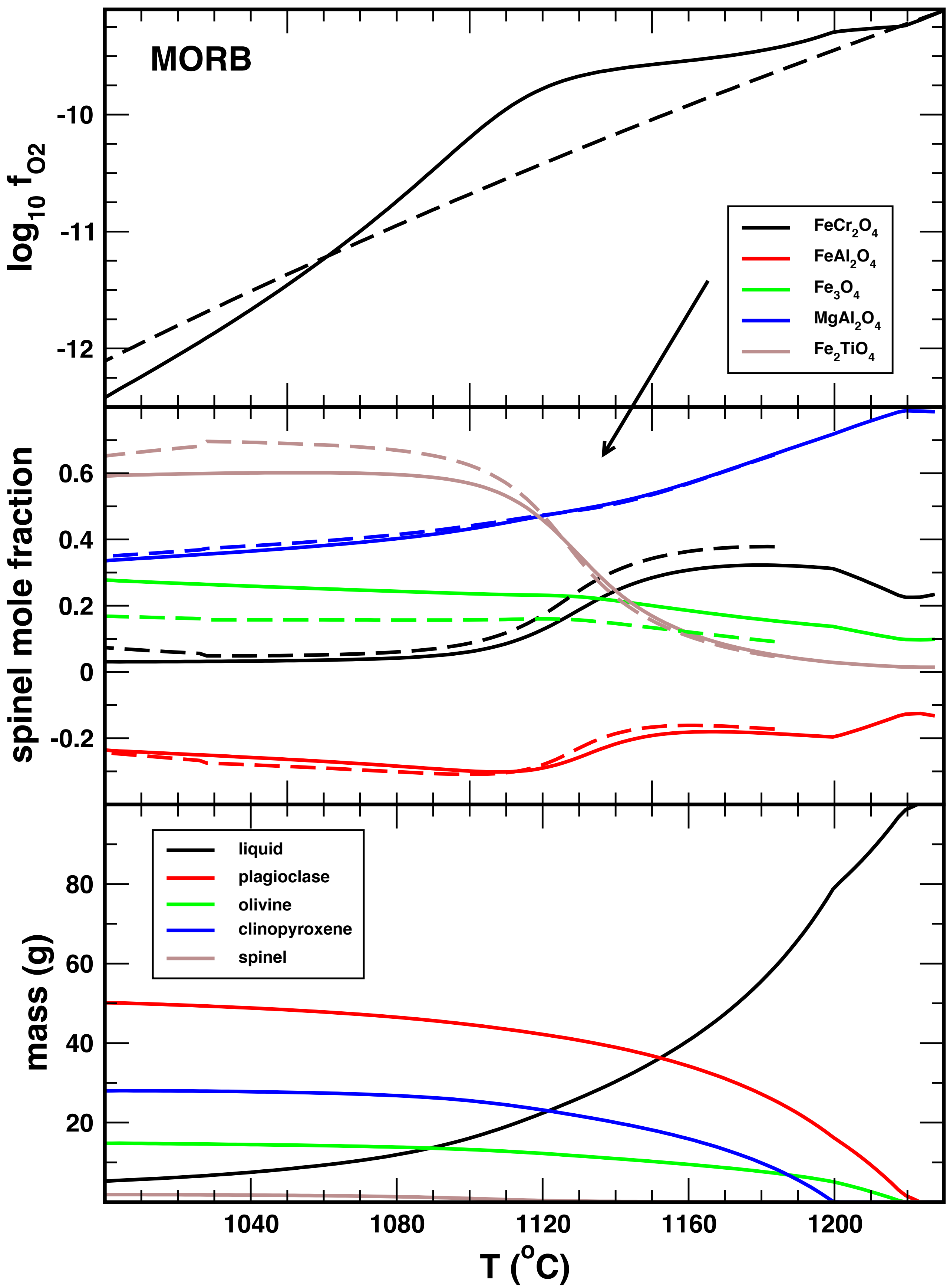
# Adiabatic melting …



Adiabatic melting …



# Example: Oxygen buffer: closed versus open system:

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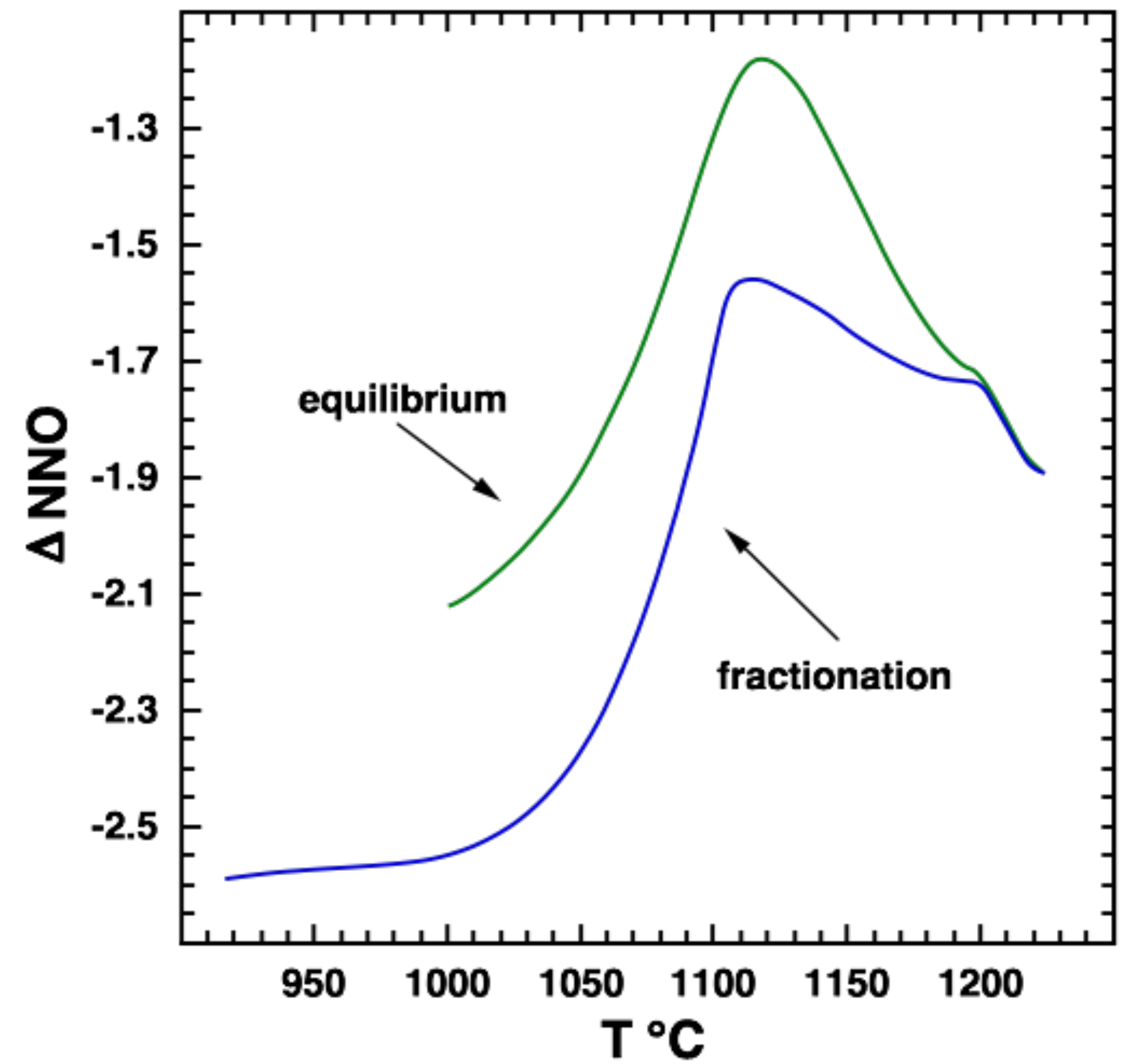
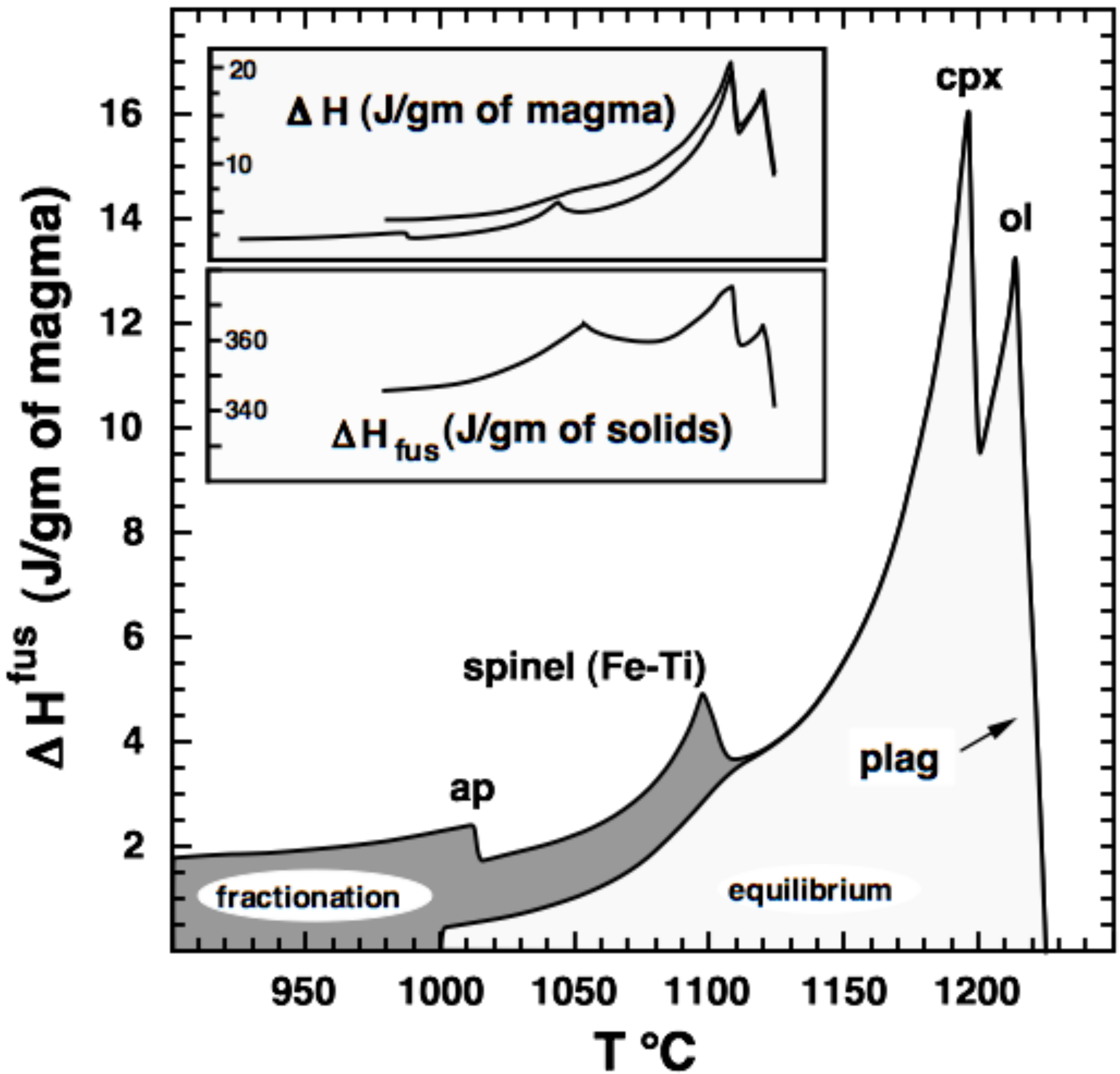
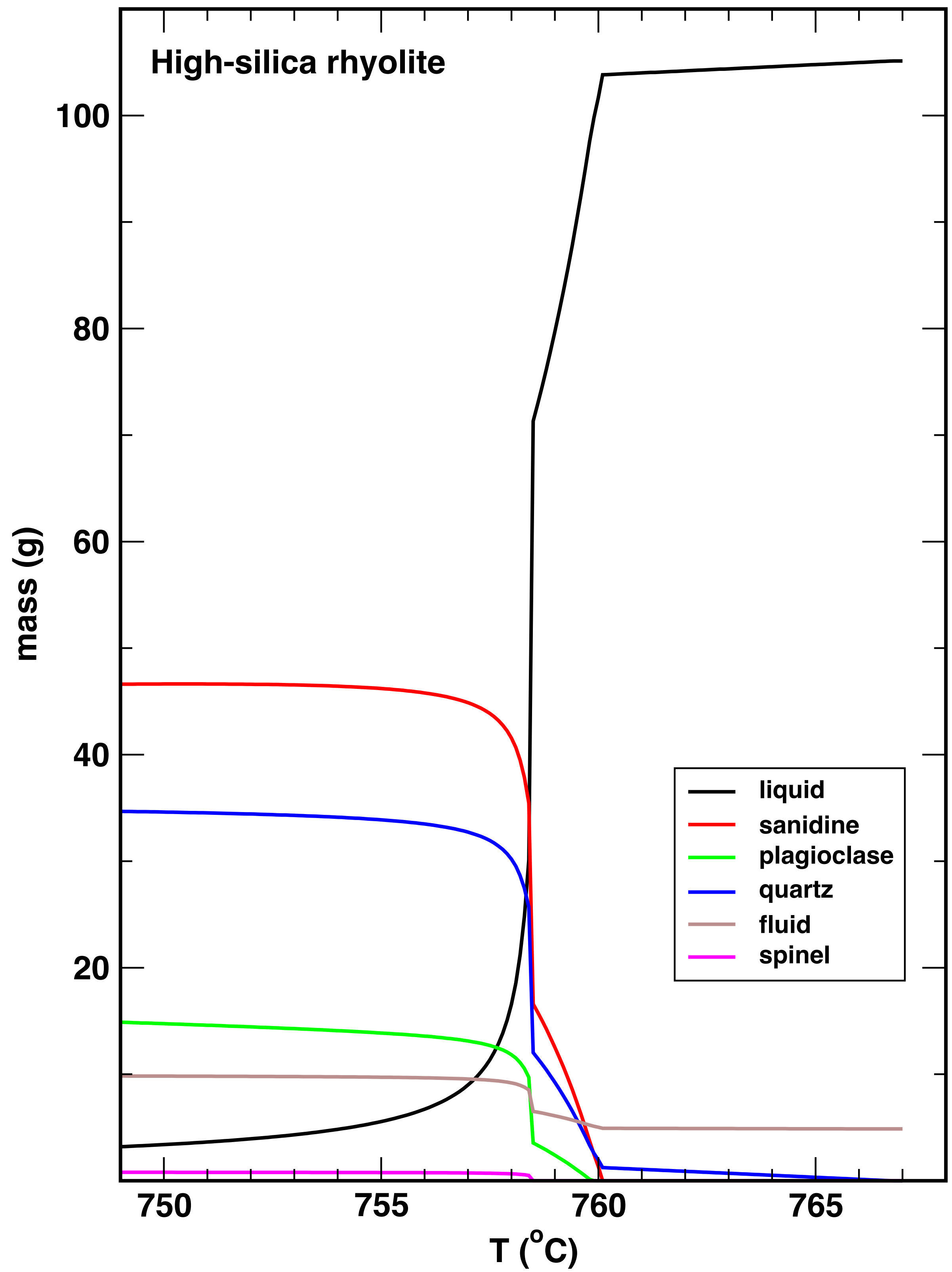
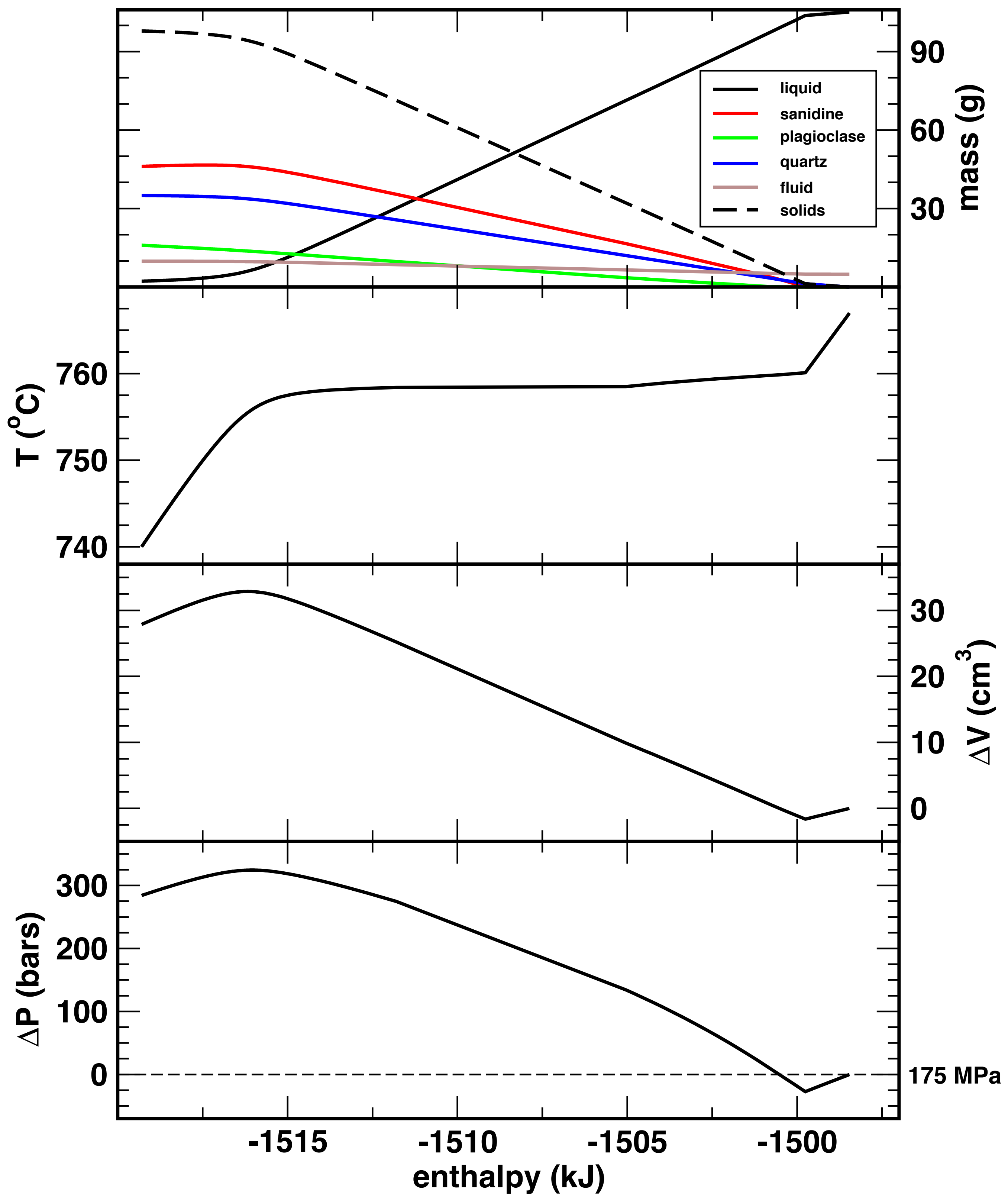


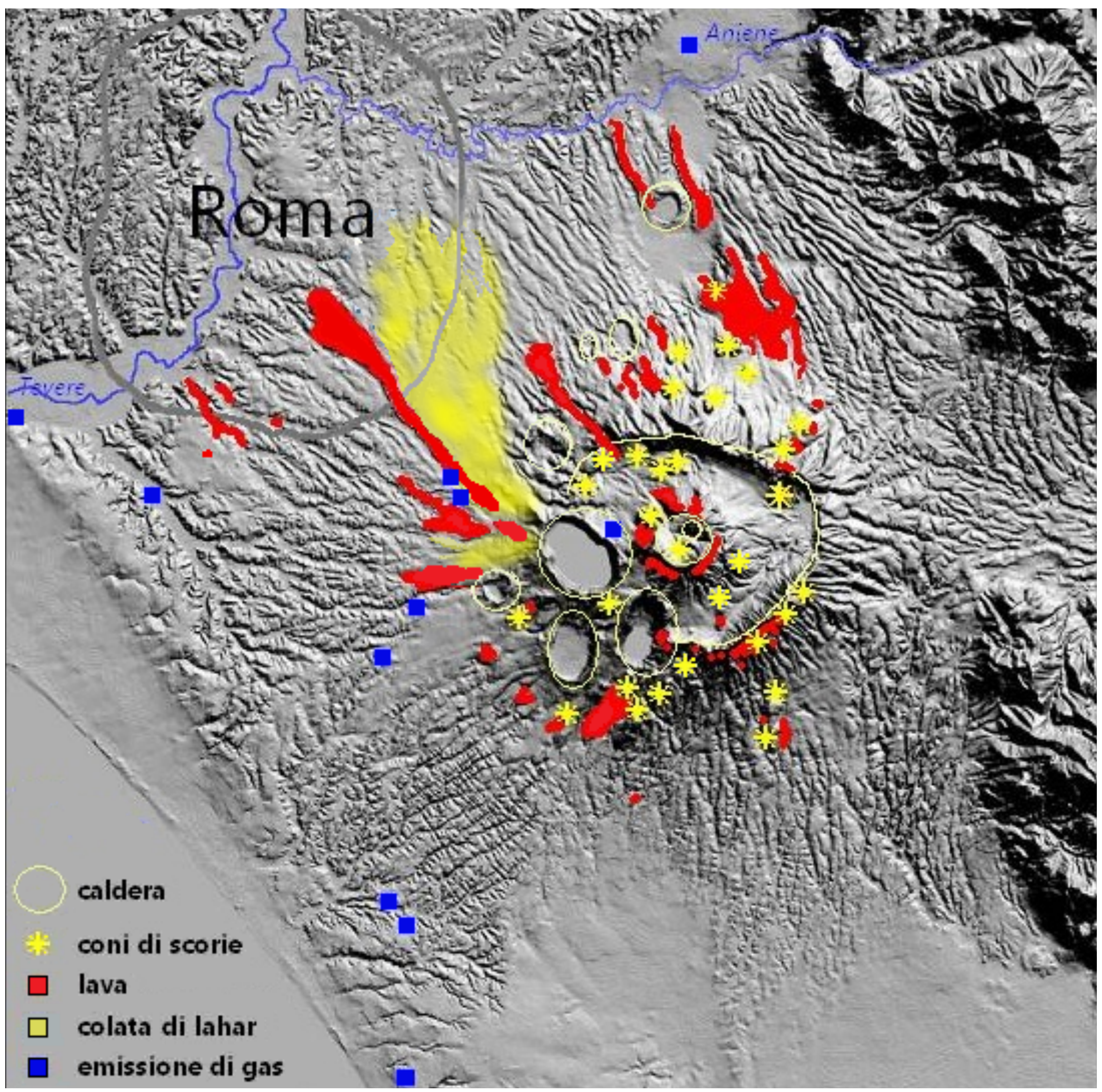
# Example: MORB crystallization: heat output:



# Example: High-silica rhyolite crystallization: heat output:



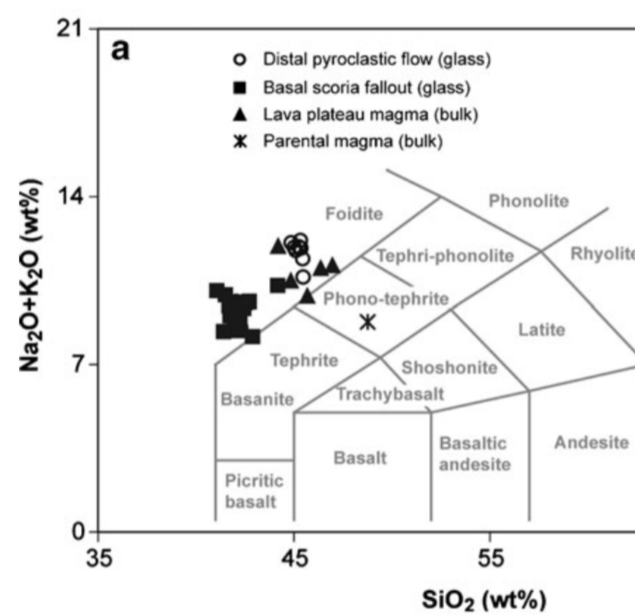



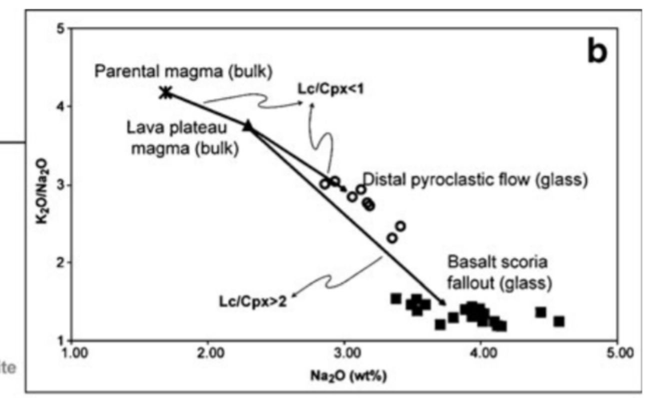



from: Daniele Bianchino, http://vulcanoalbano.altervista.org

# Colli Albani, Roman province

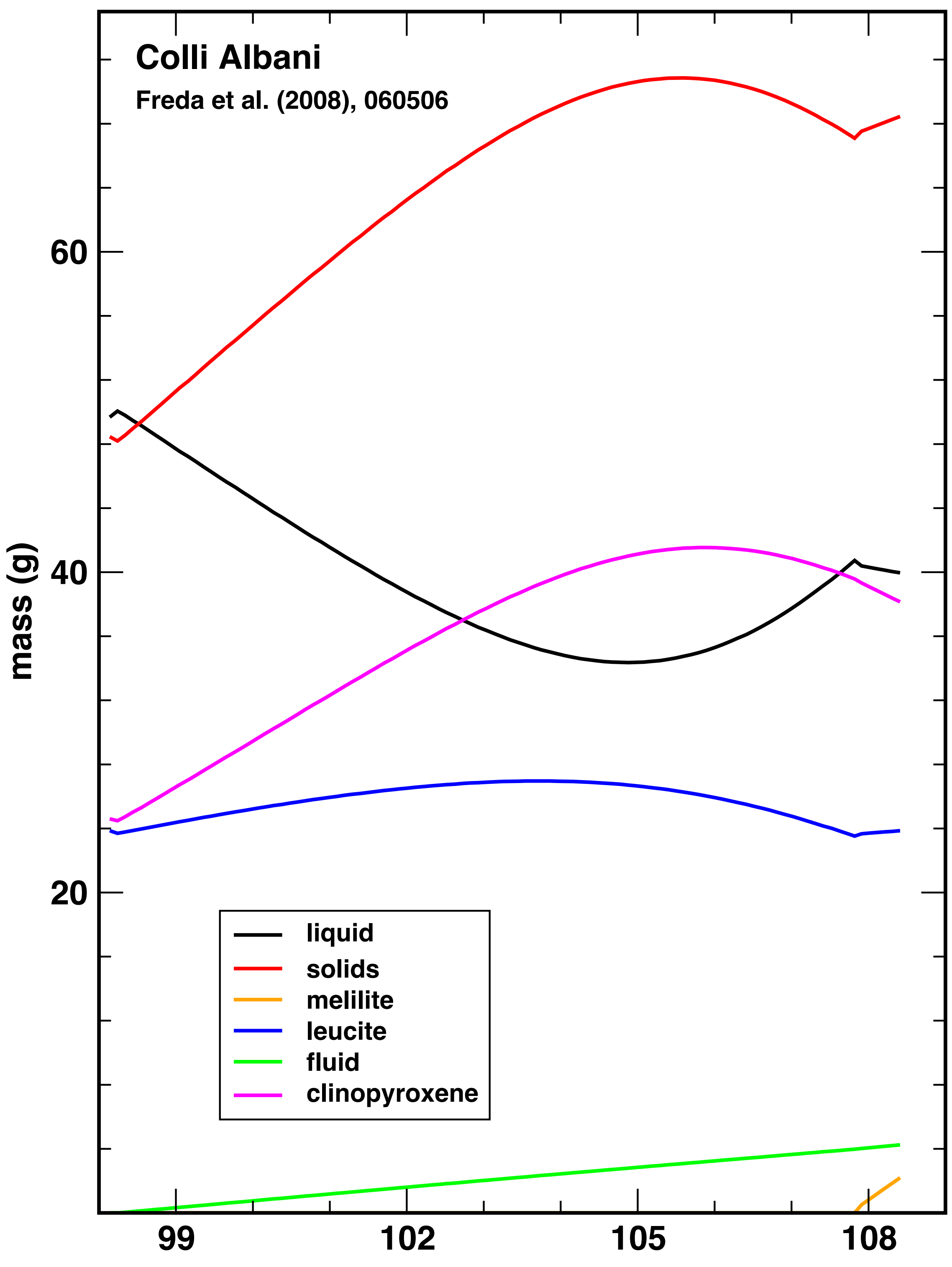
Composition from Freda et al. (2011, BV, 73:241-256)

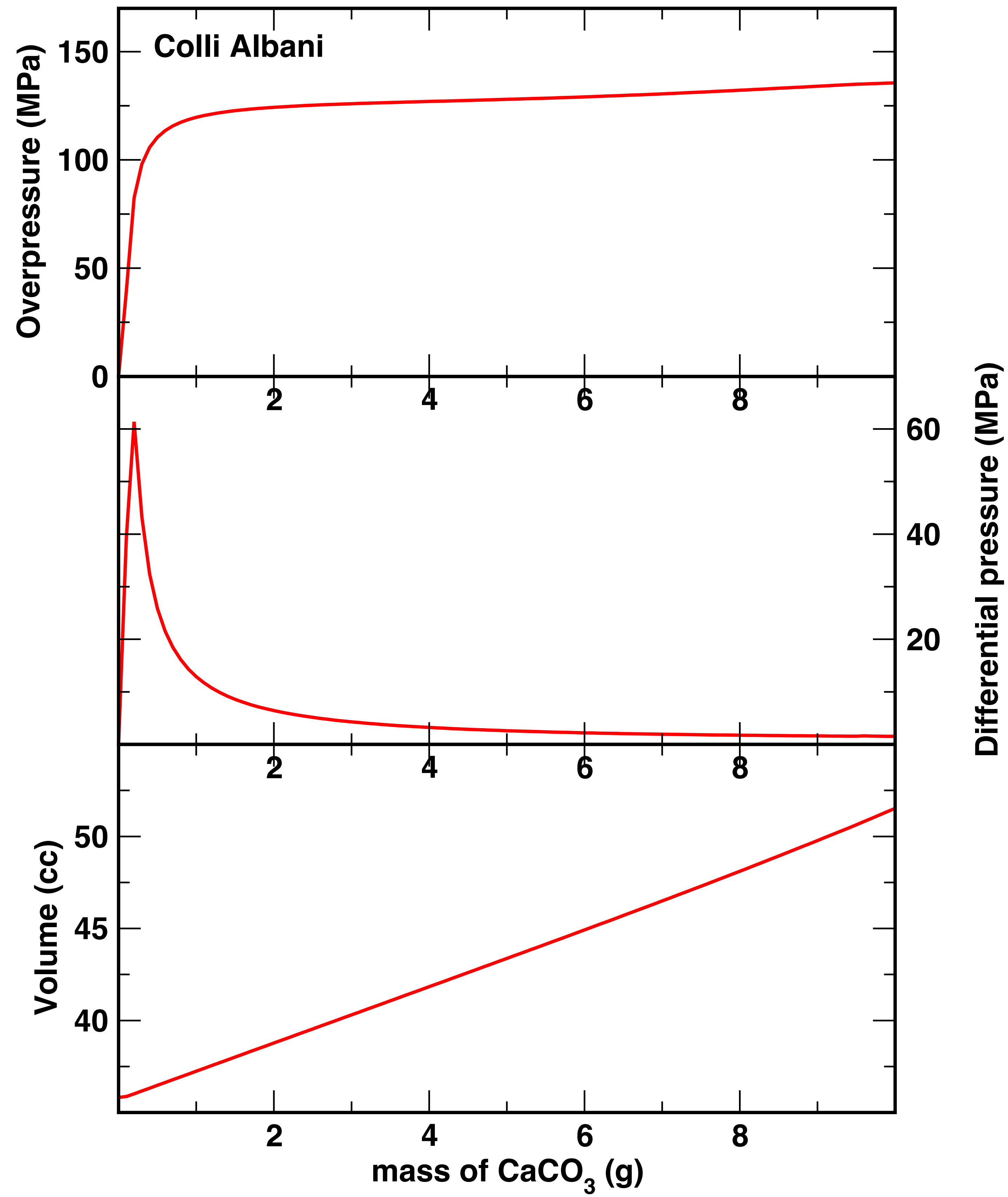


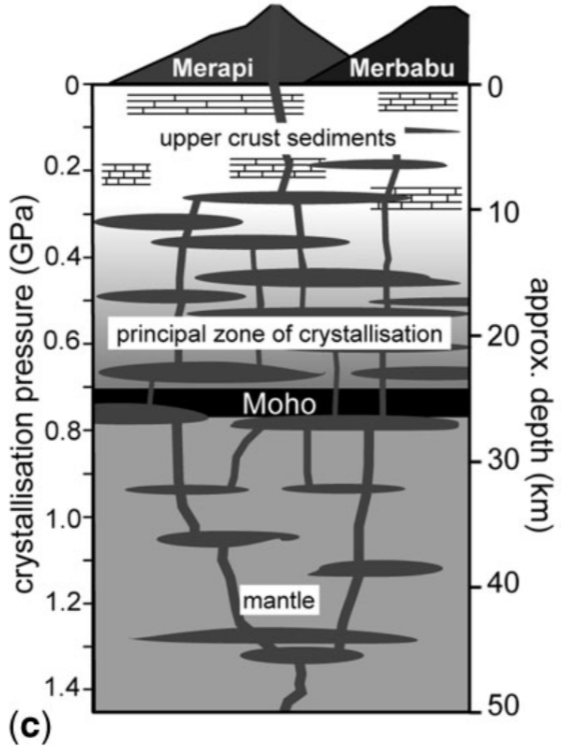

Geologic, petrographic and geochemical data with mass balance calculations, supported by experimental data for Colli Albani magma compositions, provide evidence for significant ingestion of carbonate wall rocks by the Pozzolane Rosse K-foiditic magma.

# Example: Colli Albani, calcite assimilation, 100 g initial magma, 1200 °C



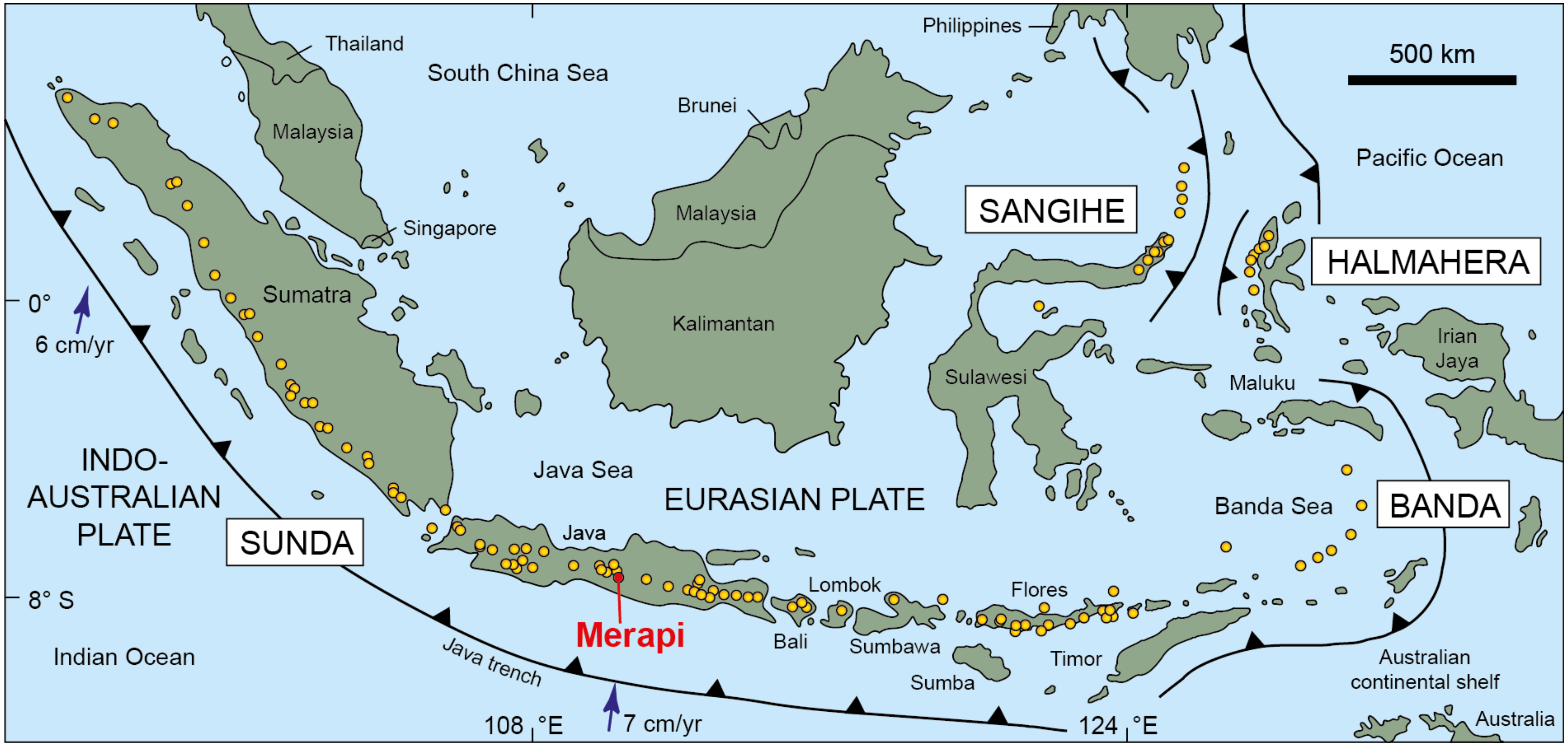



# Merapi, Indonesia




- **Parental magma: crystal-rich basaltic andesite, compared to the potassic-foidite from Alban Hills.**
- **Like Colli Albani, the explosivity of the eruptions of Merapi are fueled by assimilation of crustal carbonates**

**Composition for modeling is taken from Deegan et al. (2010, JP, 51:1027-1051)**



# Example: Merapi, Indonesia, calcite assimilation, 100 g initial magma, 1100 °C