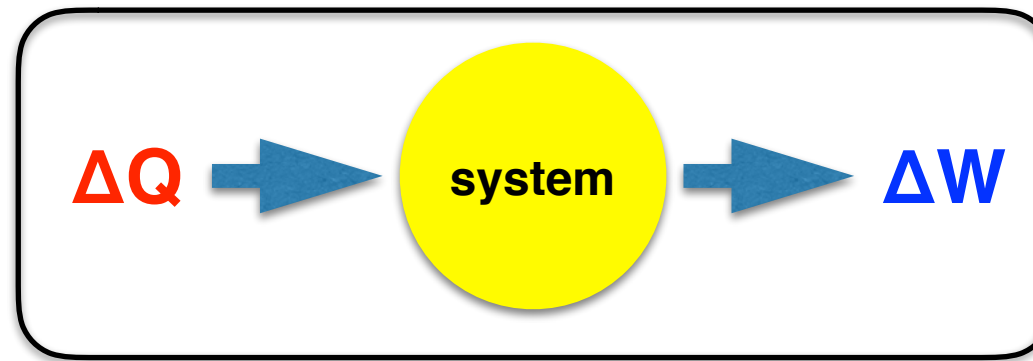


Thermodynamics



First law:

$$\Delta E = \Delta Q - \Delta W$$

Second law:

$$\Delta S \geq \Delta Q/T$$

$$\Delta S = \Delta Q_{\text{rev}}/T$$

Differential forms:

$$dE = dQ - dW$$

E, Internal Energy

ΔQ , heat transfer to the system

ΔW , work done by the system

T, absolute temperature

P, pressure

V, volume

S, entropy

\underline{A} , chemical affinity

ξ , reaction progress

$$\Delta Q = \Delta Q_{\text{rev}} + \Delta Q_{\text{irrev}}$$

de Donder

$$dQ = dQ_{\text{rev}} + dQ_{\text{irrev}}$$

$$dQ = dQ_{\text{rev}} - \underline{A}d\xi$$

$$dS = dQ_{\text{rev}}/T$$

$$dQ = TdS - \underline{A}d\xi$$

$$dW = PdV + \text{other work terms}$$

Combined first and second laws:

$$dE = TdS - PdV - \underline{A}d\xi$$

Legendre transforms:

Suppose $z = f(x, y)$, then

$$dz = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$

For convenience, we define two additional functions

$$M(x, y) = \left(\frac{\partial f}{\partial x} \right)_y \text{ and } N(x, y) = \left(\frac{\partial f}{\partial y} \right)_x,$$

so that dz may be written

$$dz = Mdx + Ndy. \quad (1)$$

Notice that the total derivative of the product, Mx , is given by the chain rule:

$$d(Mx) = Mdx + x dM. \quad (2)$$

If we subtract equation (2) from equation (1), we obtain:

$$dz - d(Mx) = Ndy - x dM \quad (3)$$

Since the operation of taking a derivative is distributive, equation (3) becomes:

$$d(z - Mx) = Ndy - x dM \quad (4)$$

This equation shows that $z - Mx$ is a function of the two variables, y and M . Adopting the definition

$$w = z - Mx = z - \left(\frac{\partial f}{\partial x} \right)_y x,$$

we say that w is a Legendre transform of z .

Legendre transform example:

As an example, take the expression for the internal energy resulting from the combined first and second laws of thermodynamics:

$$dE = TdS - PdV - \mathbf{A}d\xi, \quad (5)$$

which shows that $E = f(S, V, \xi)$

If we wish to construct a new state function with independent variables T , V and ξ , then we subtract

$$d(TS) = TdS + SdT$$

from equation (5) to obtain

$$d(E - TS) = -SdT - PdV - \mathbf{A}d\xi,$$

which provides the definition of a new thermodynamic potential called the Helmholtz free energy, $A = E - TS = f(T, V, \xi)$.

Thermodynamic potentials from Legendre transforms:

Closed system:

Gibbs free energy, G

minimization of $G(T, P, n_1 \dots n_c)$ yields V, S, H, A, E etc.

Enthalpy, $H = G + TS$

minimization of $H(S, P, n_1 \dots n_c)$ yields V, T, G, A, E etc.

Helmholtz free energy, $A = G - PV$

minimization of $A(T, V, n_1 \dots n_c)$ yields P, S, H, G, E etc.

Internal energy, $E = G - PV + TS$

minimization of $E(S, V, n_1 \dots n_c)$ yields P, T, H, A, G etc.

Open system:

Korzhinskii potential, $L = G - n_{O_2} \mu_{O_2}$

minimization of $L(T, P, \mu_{O_2}, n_1 \dots n_{c-1})$ yields $V, S, H, A, E, G,$ etc.

How do we do this minimization?

Where is the information about phases?

Answer:

**The minimization is done in the “integral” formulation
while the phase partitioning is derived from the
“differential” formulation**

The two formulations are equivalent!

Differential form:

$$dE = TdS - PdV - \underline{A}d\xi = \frac{\partial E}{\partial S}dS + \frac{\partial E}{\partial V}dV + \sum_i^c \frac{\partial E}{\partial n_i}dn_i$$

$$-\underline{A}d\xi = \sum_i^c \mu_i dn_i$$

$$dE = TdS - PdV + \sum_i^c \mu_i dn_i$$

$$dH = TdS + VdP + \sum_i^c \mu_i dn_i = \frac{\partial H}{\partial S}dS + \frac{\partial H}{\partial P}dP + \sum_i^c \frac{\partial H}{\partial n_i}dn_i$$

$$dA = -SdT - PdV + \sum_i^c \mu_i dn_i = \frac{\partial A}{\partial T}dT + \frac{\partial A}{\partial V}dV + \sum_i^c \frac{\partial A}{\partial n_i}dn_i$$

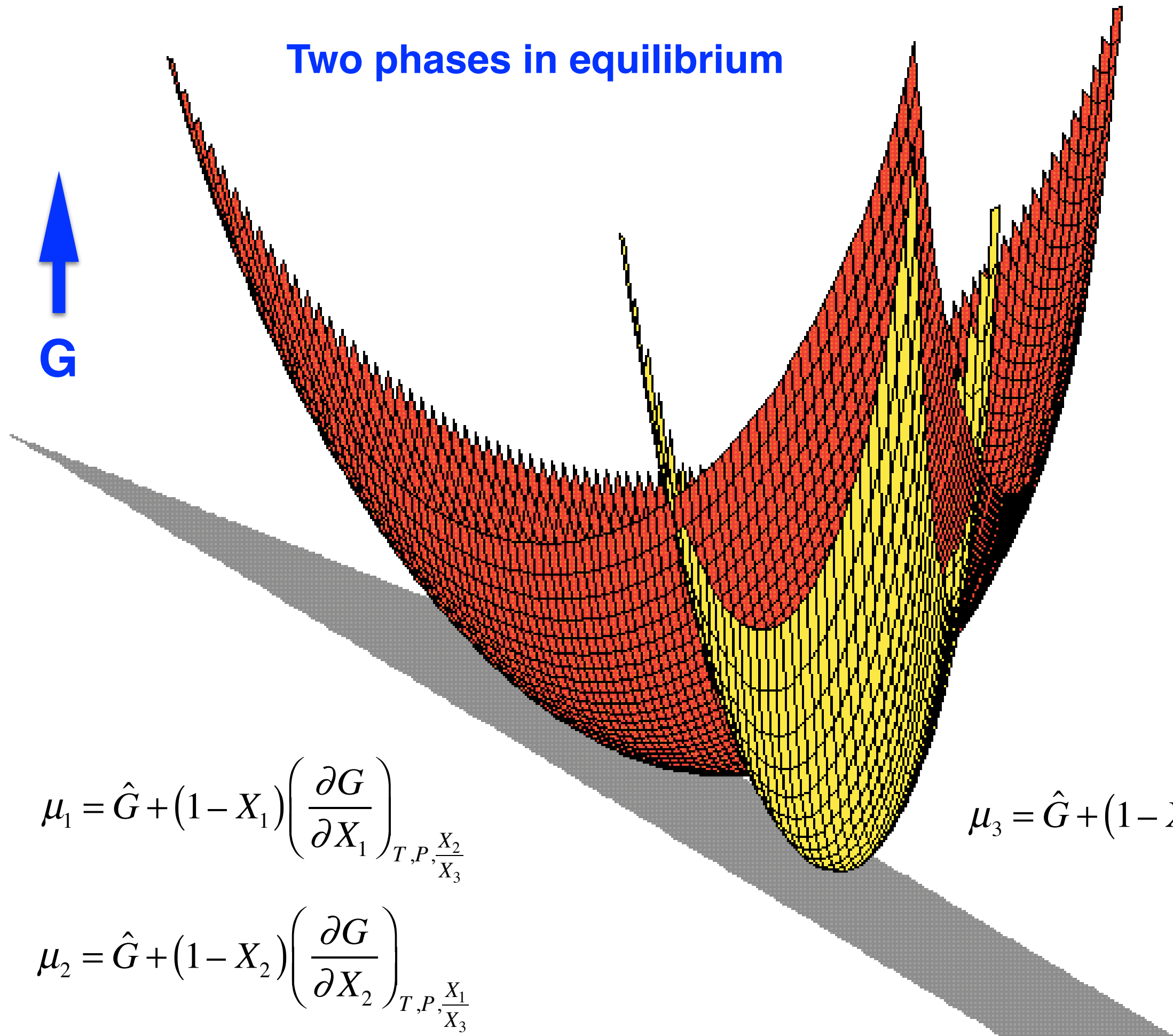
$$dG = -SdT + VdP + \sum_i^c \mu_i dn_i = \frac{\partial G}{\partial T}dT + \frac{\partial G}{\partial P}dP + \sum_i^c \frac{\partial G}{\partial n_i}dn_i$$

From the Gibbs free energy, by repeated Legendre transform, we obtain the Gibbs-Duhem equation:

$$0 = -SdT + VdP + \sum_i^c n_i d\mu_i$$

Two phases in equilibrium

↑
G



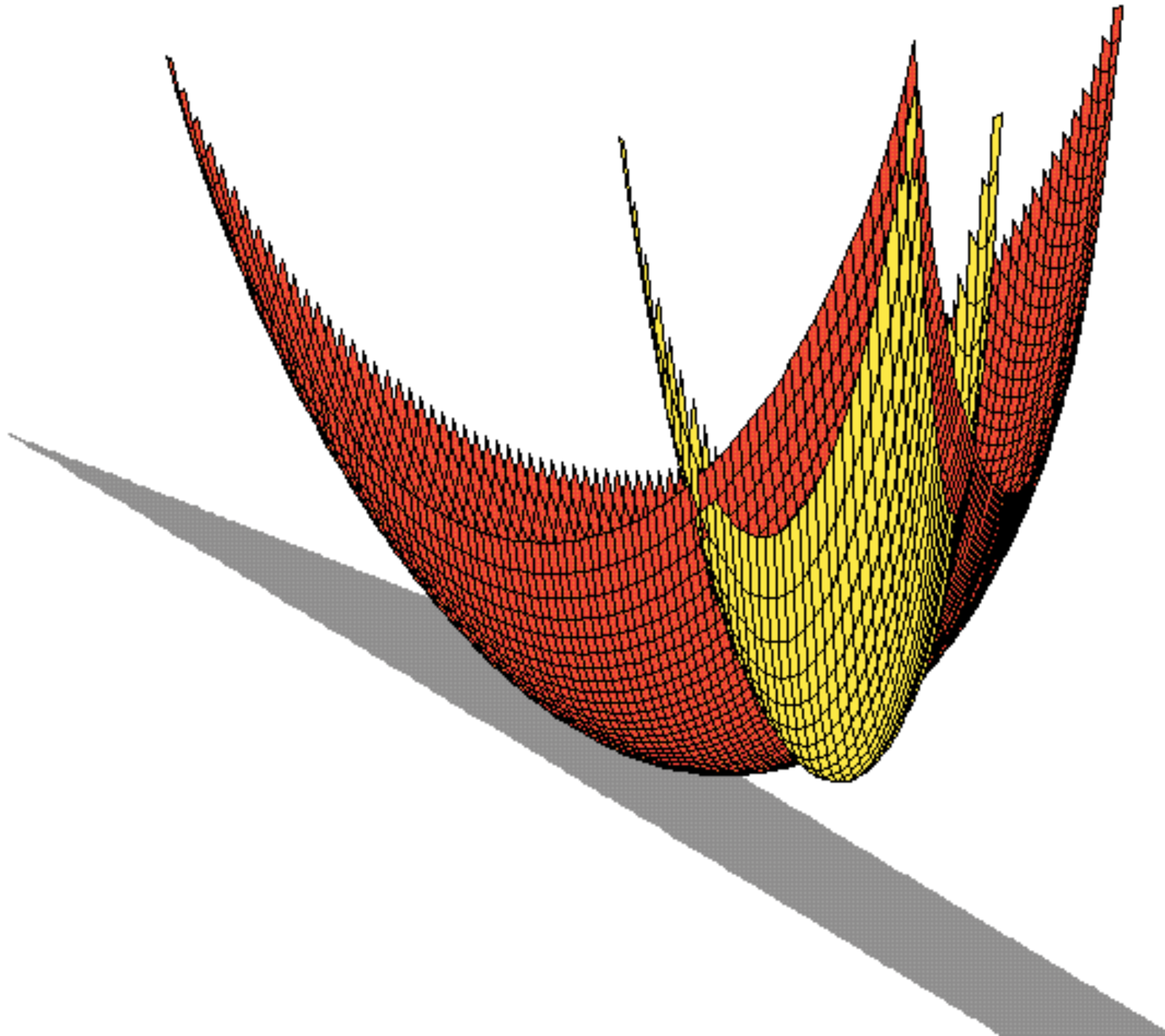
$$\mu_1 = \hat{G} + (1 - X_1) \left(\frac{\partial G}{\partial X_1} \right)_{T, P, \frac{X_2}{X_3}}$$

$$\mu_2 = \hat{G} + (1 - X_2) \left(\frac{\partial G}{\partial X_2} \right)_{T, P, \frac{X_1}{X_3}}$$

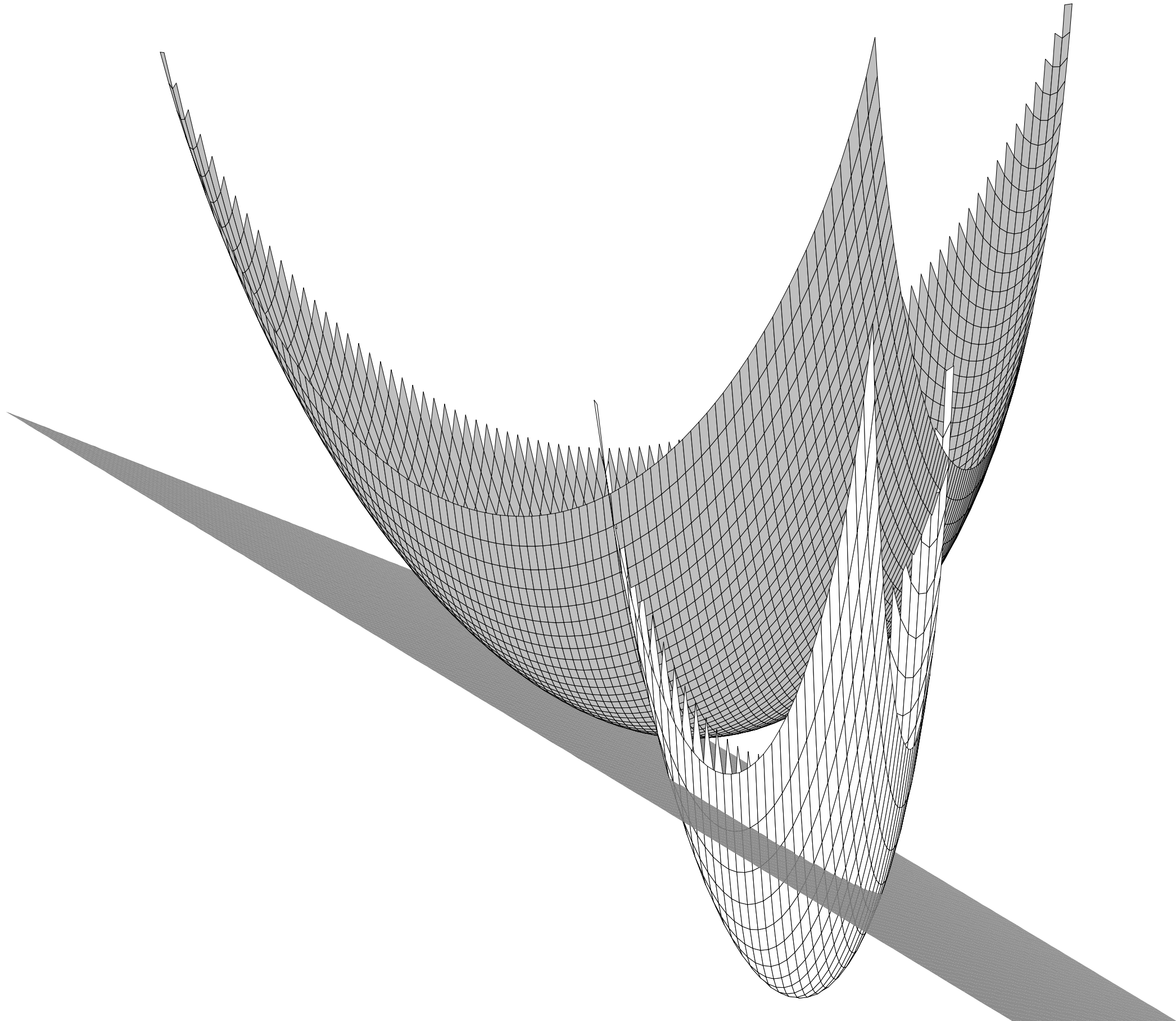
$$\mu_3 = \hat{G} + (1 - X_3) \left(\frac{\partial G}{\partial X_3} \right)_{T, P, \frac{X_1}{X_2}}$$

Two phases; one phase stable:

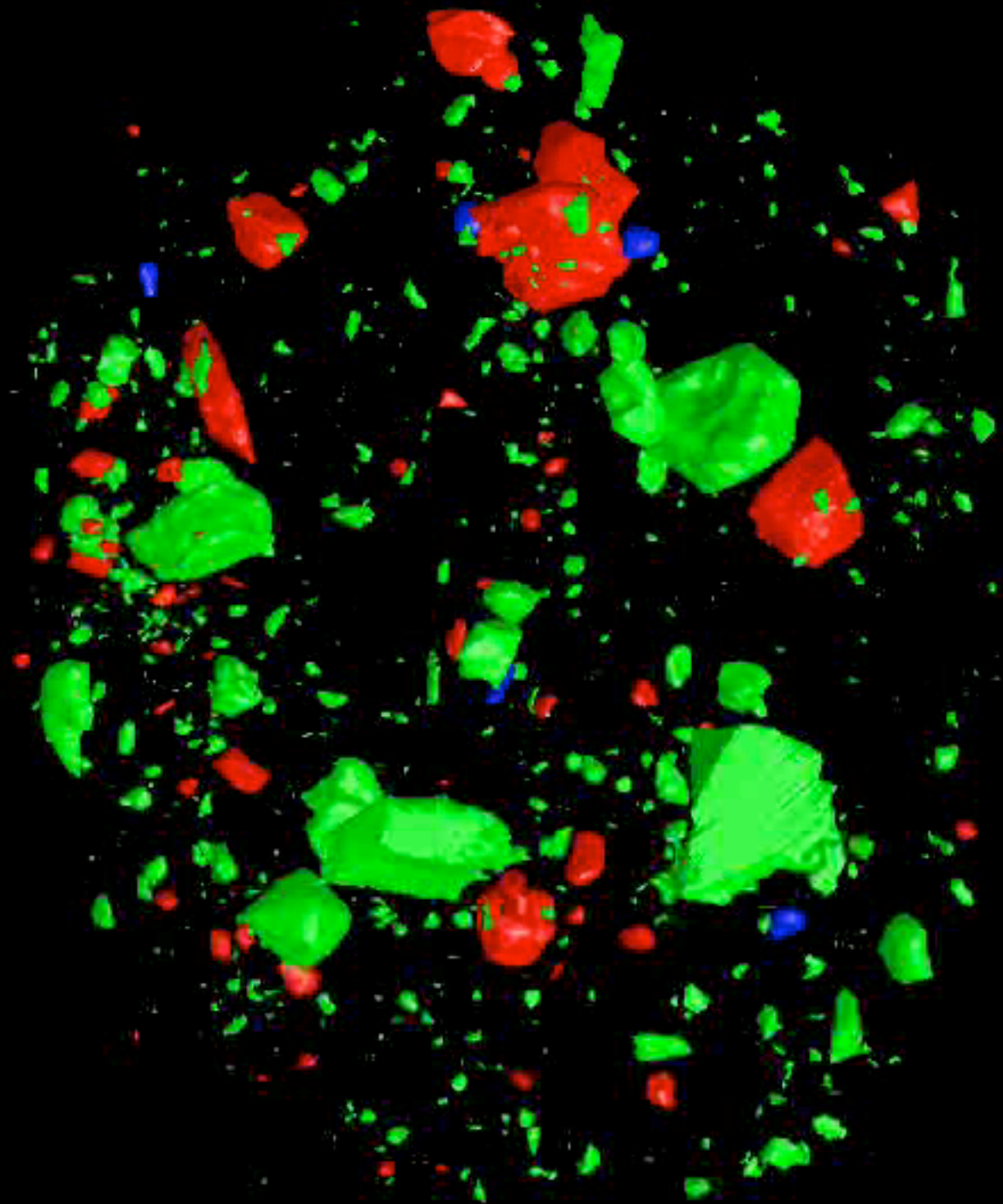
↑
G



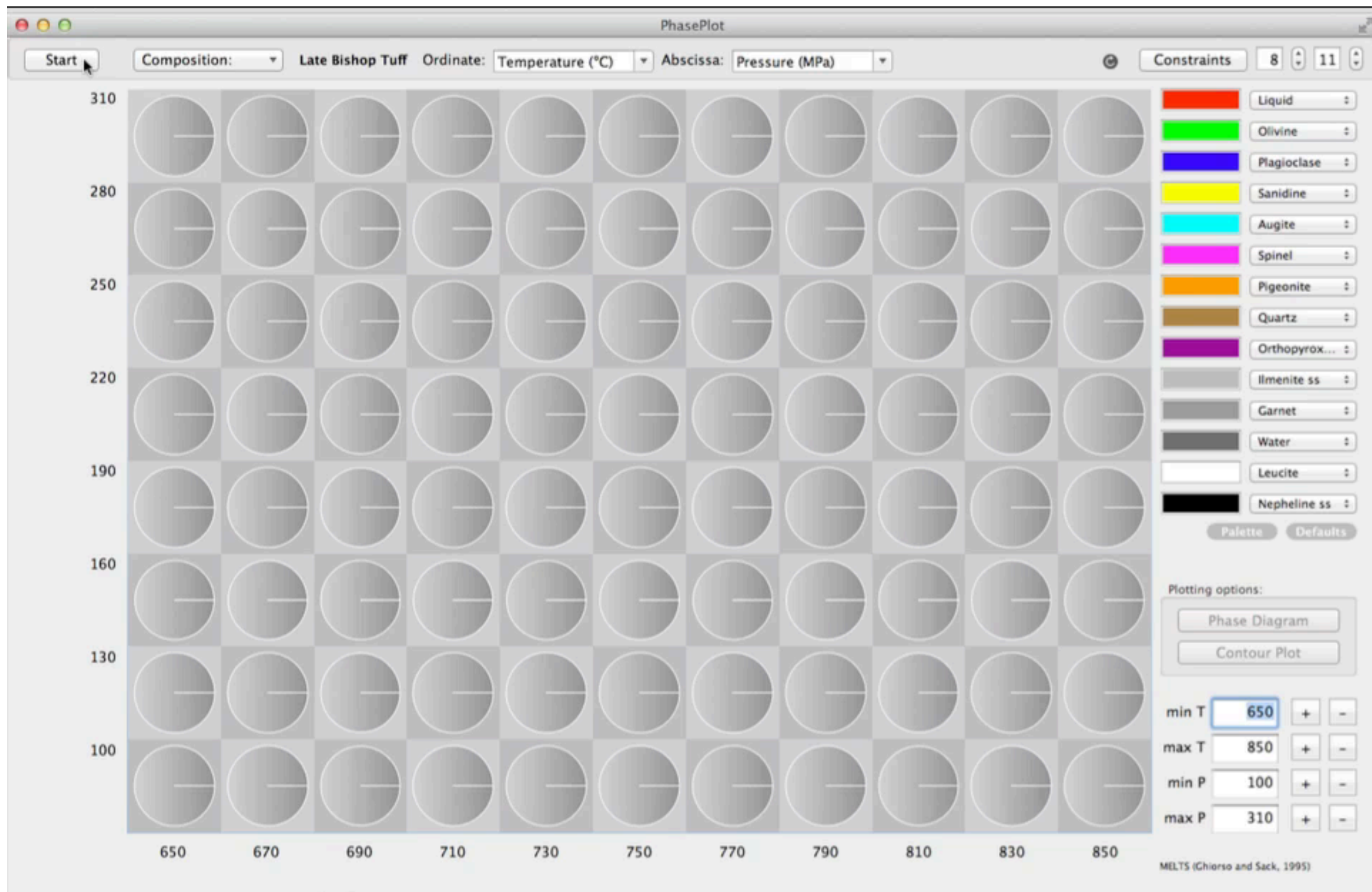
Two phases; disequilibrium:



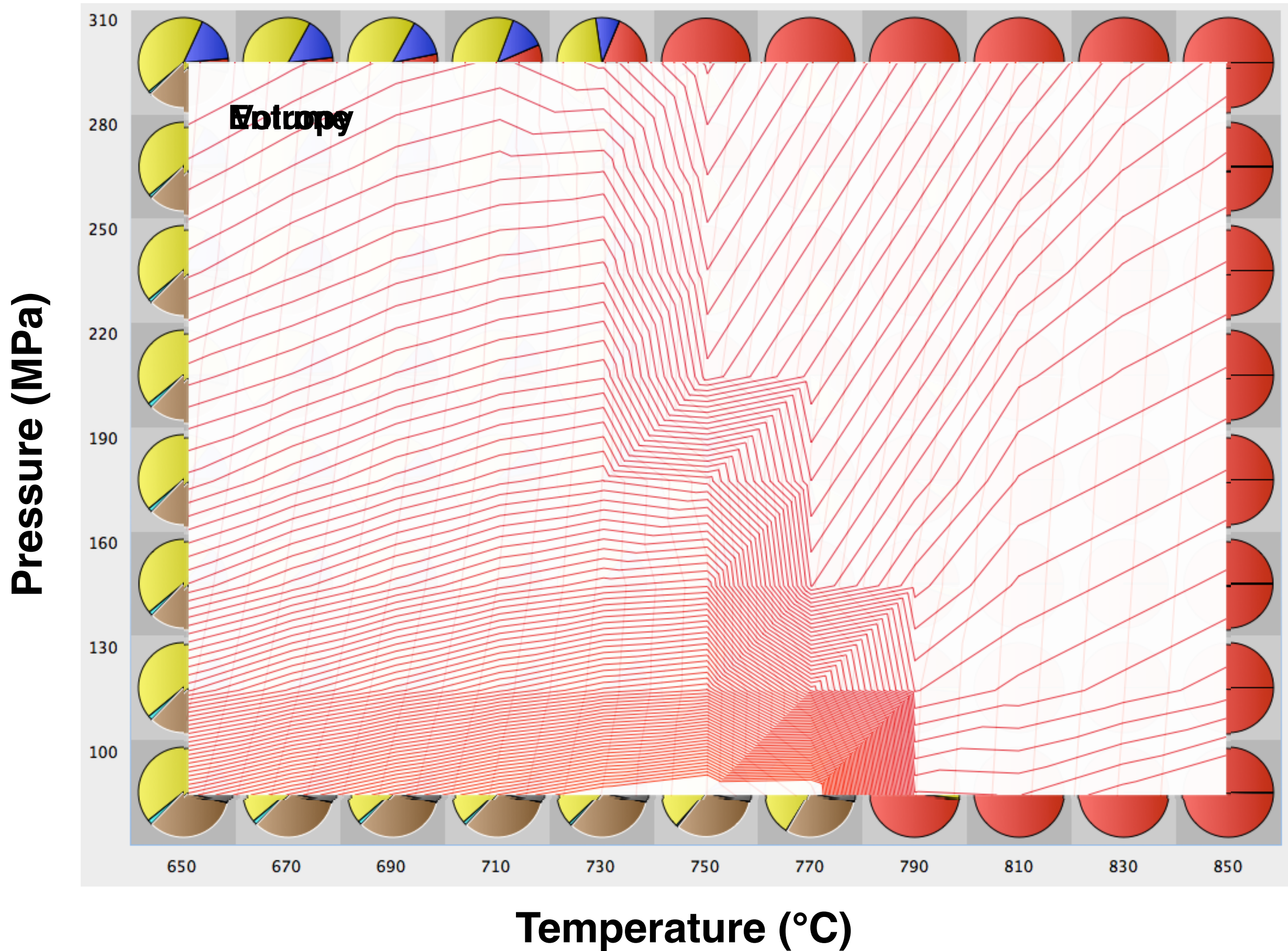
Examples: Results from the various thermodynamic potentials



High-silica rhyolite: Gibbs free energy

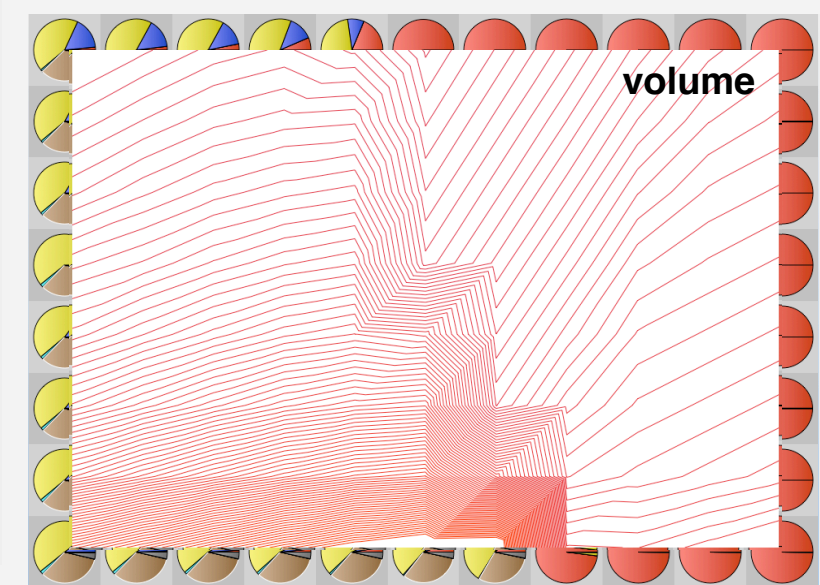
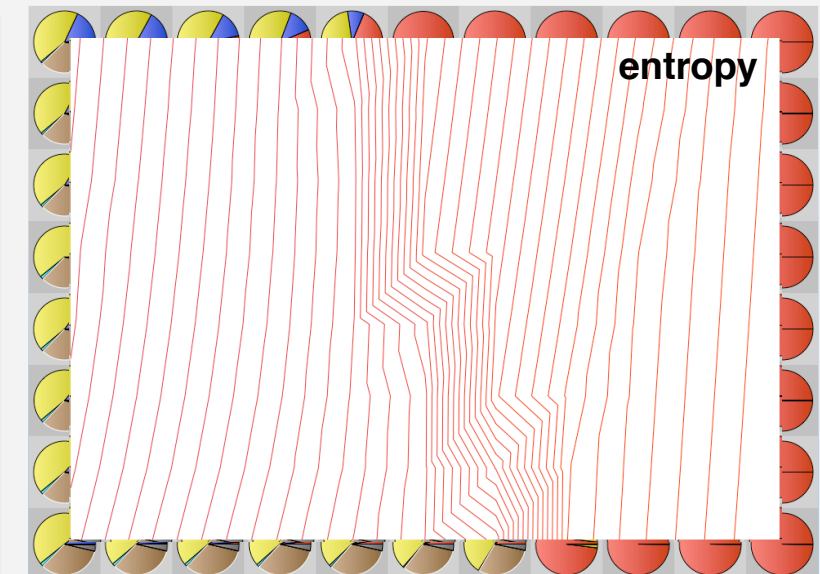
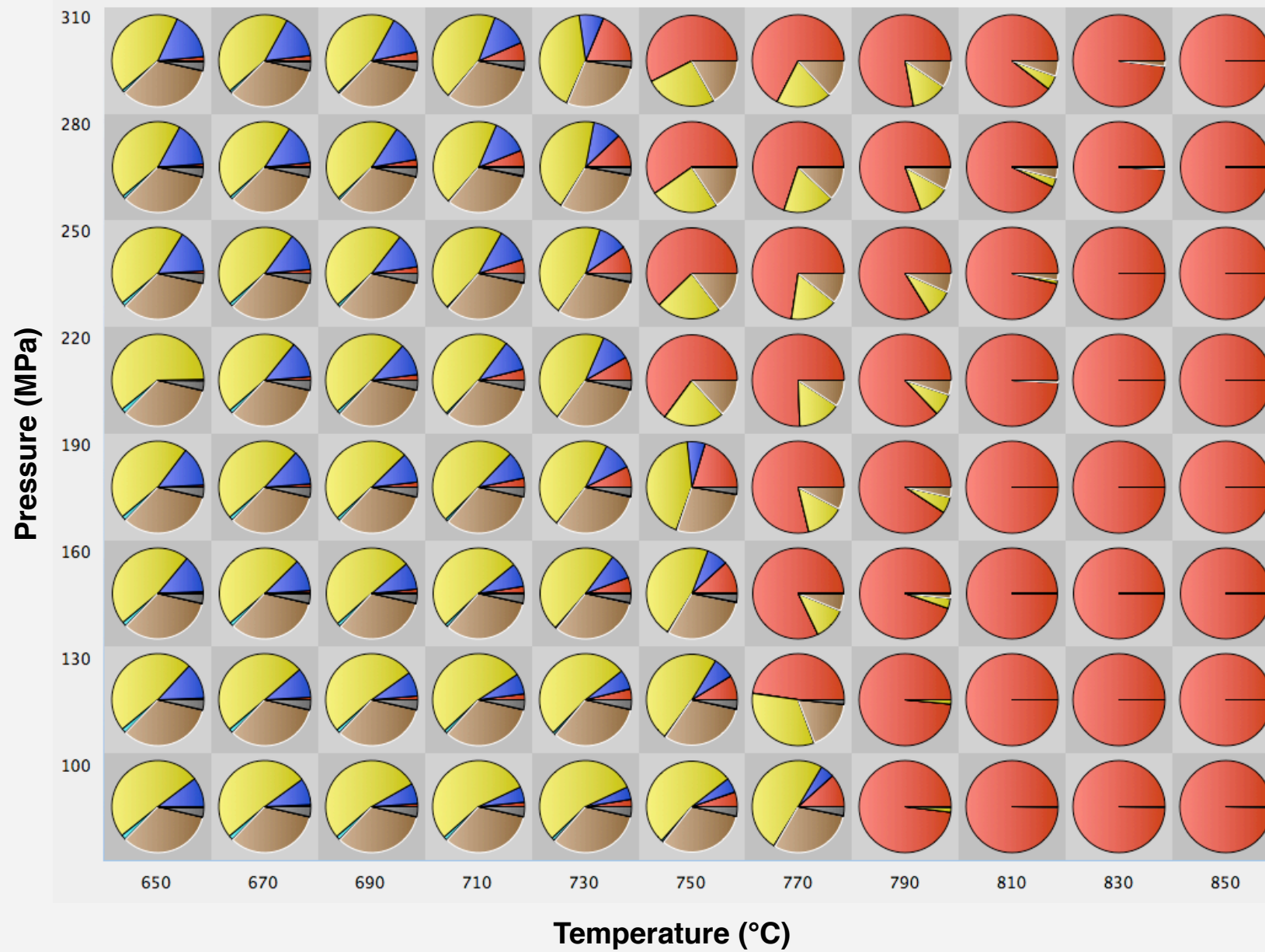


High-silica rhyolite: Gibbs free energy



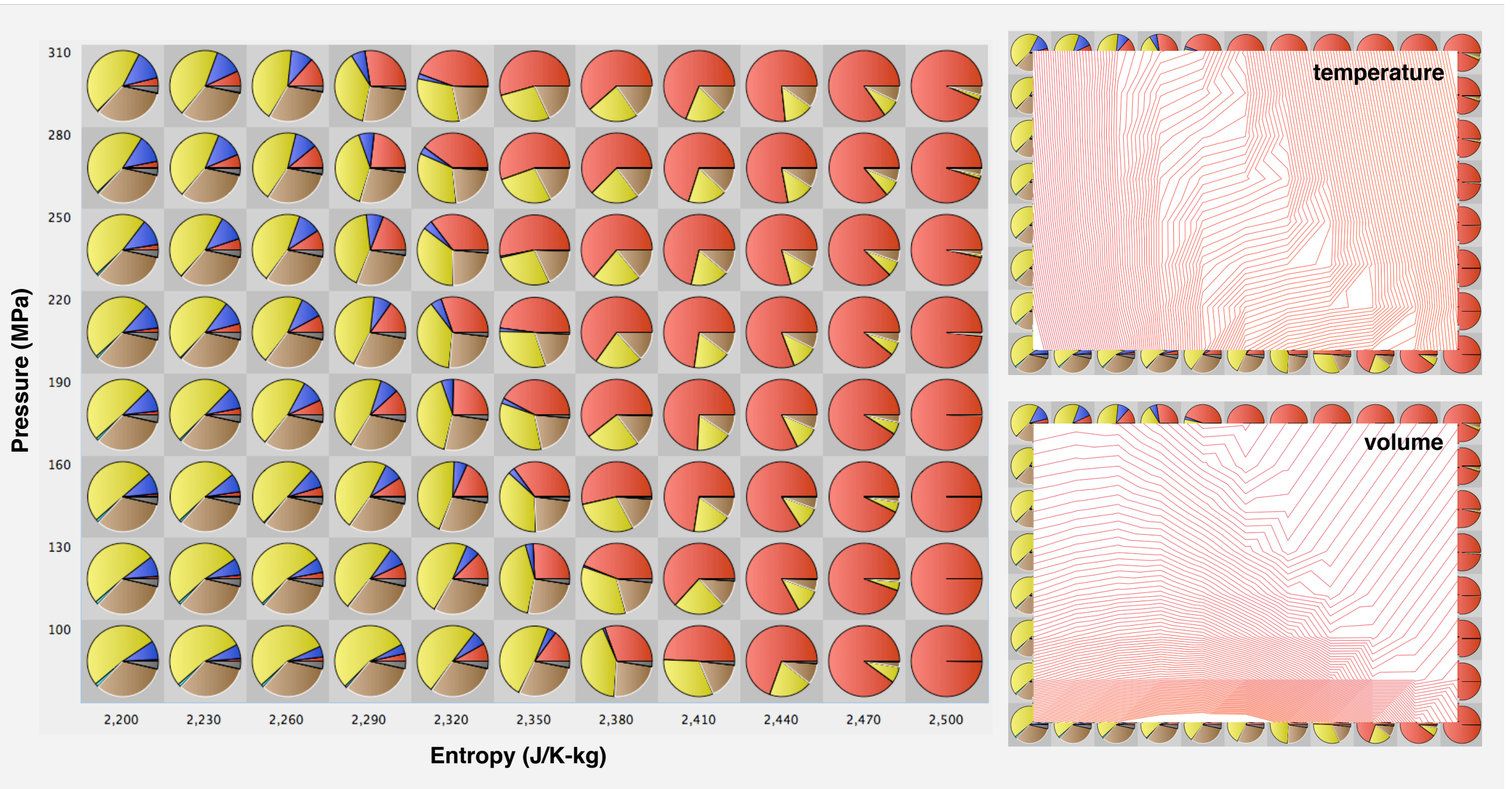
Gibbs free energy

minimization of $G(T, P)$ yields m, X, V , etc.



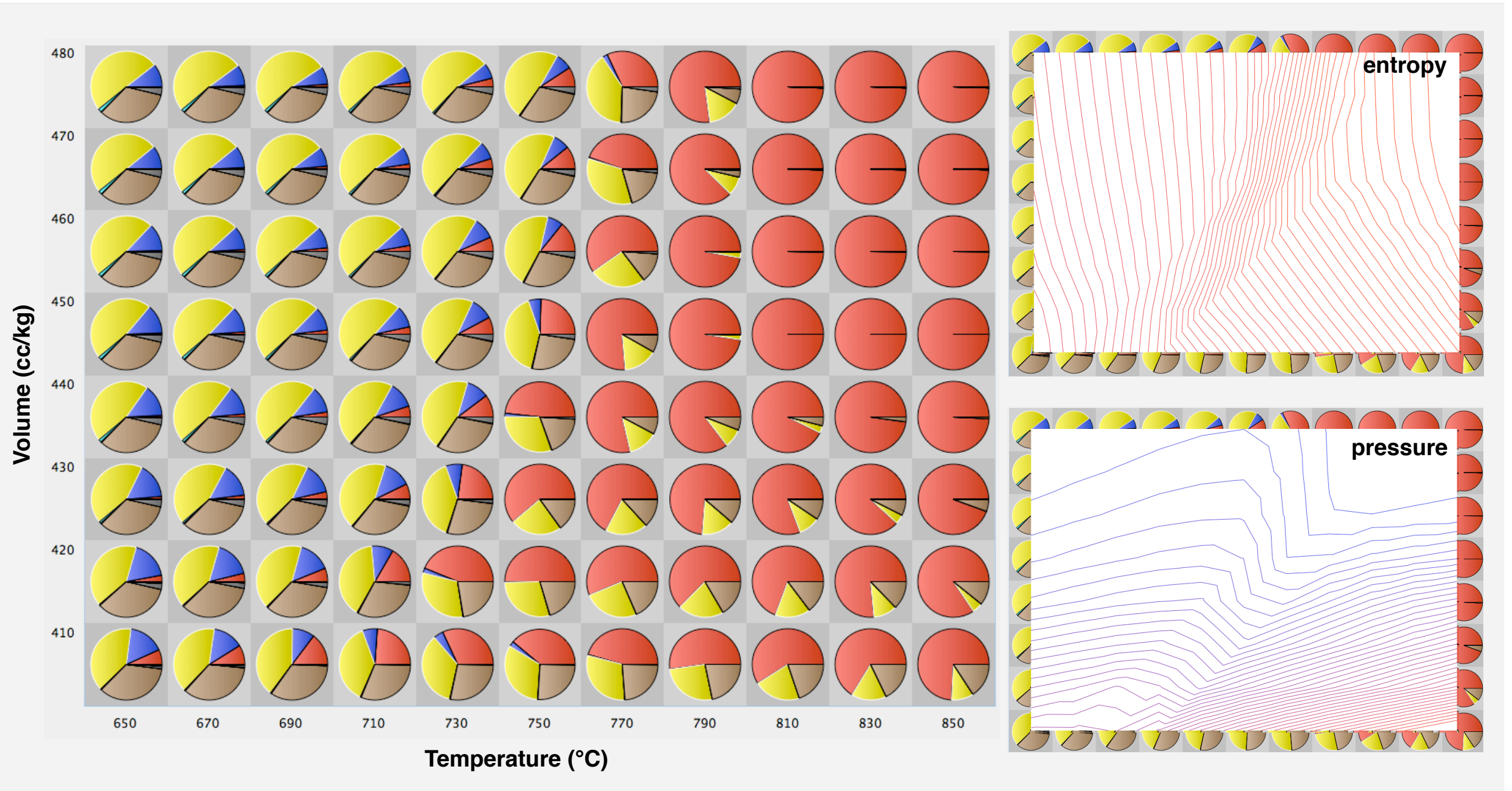
Enthalpy ($H = G - TS$)

minimization of $H(S, P)$ yields m, X, T , etc.



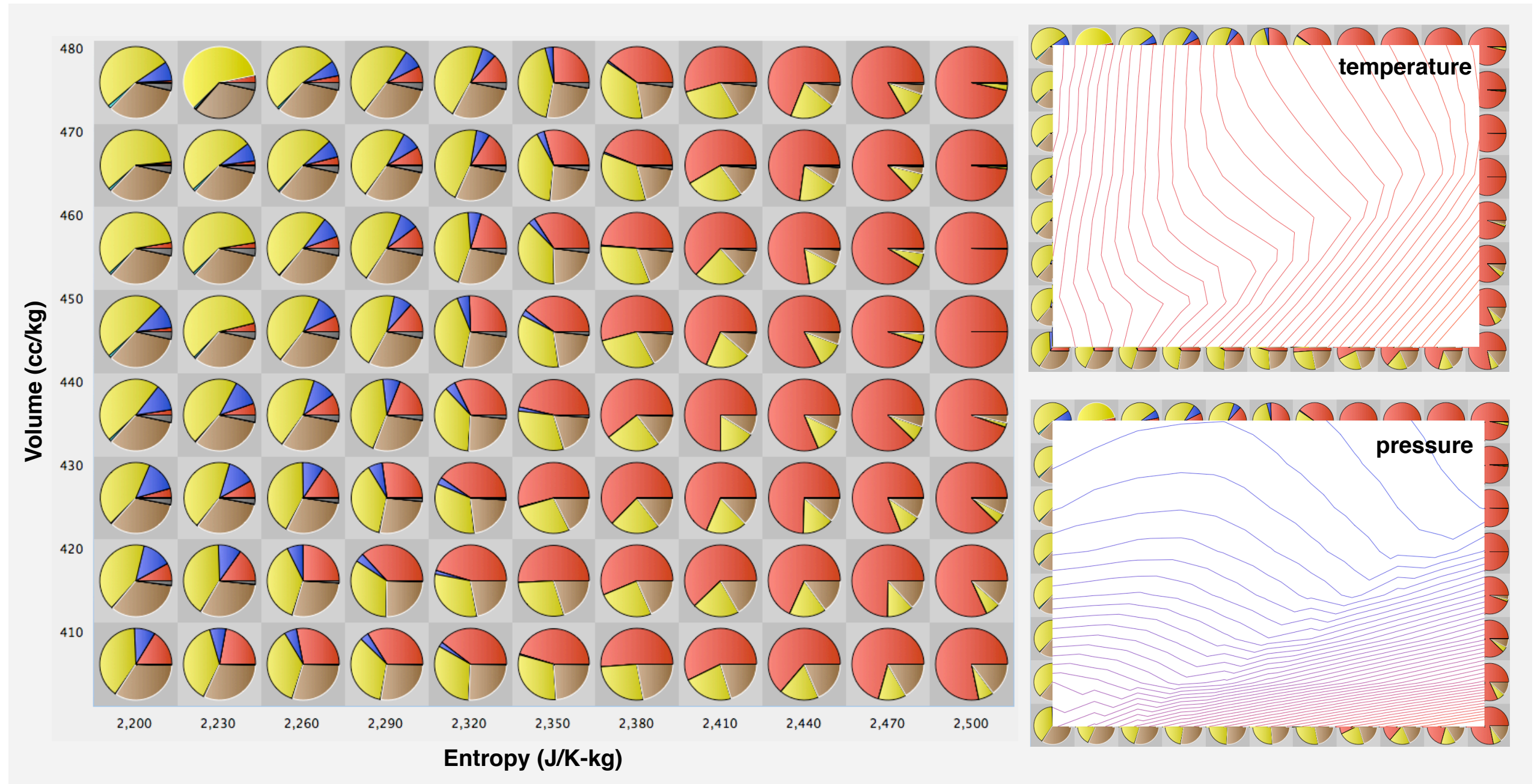
Helmholtz free energy ($A = G - PV$)

minimization of $A(T, V)$ yields m, X, P , etc.

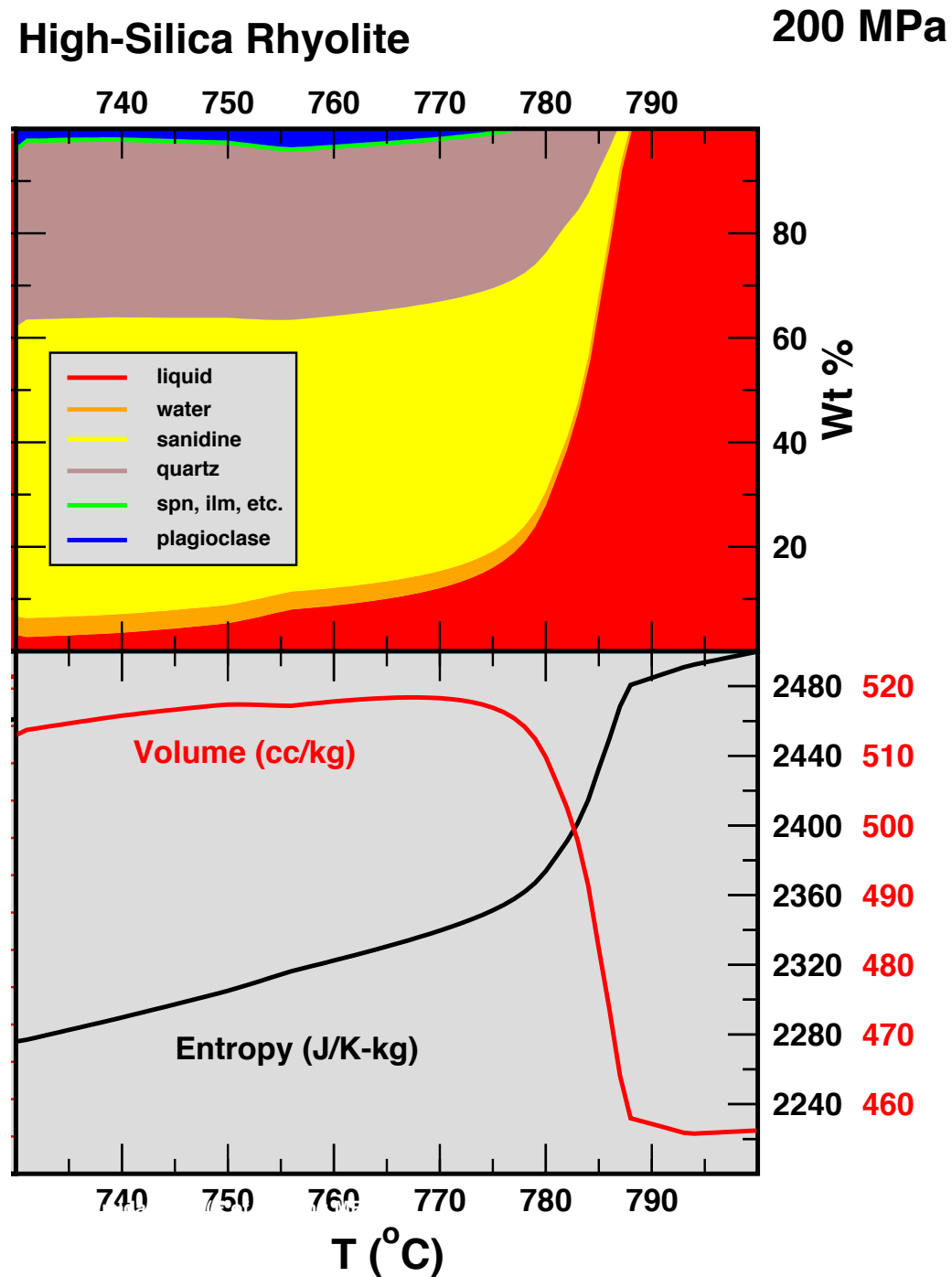


Internal energy ($E = G - PV + TS$)

minimization of $E(S, V)$ yields m, X, T, P , etc.

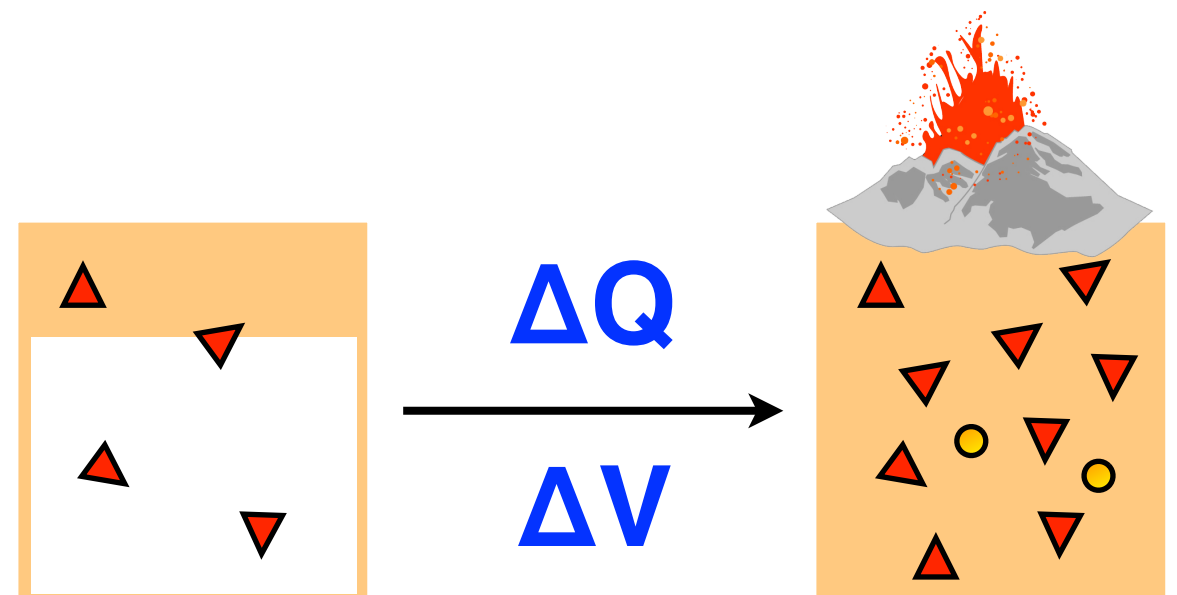
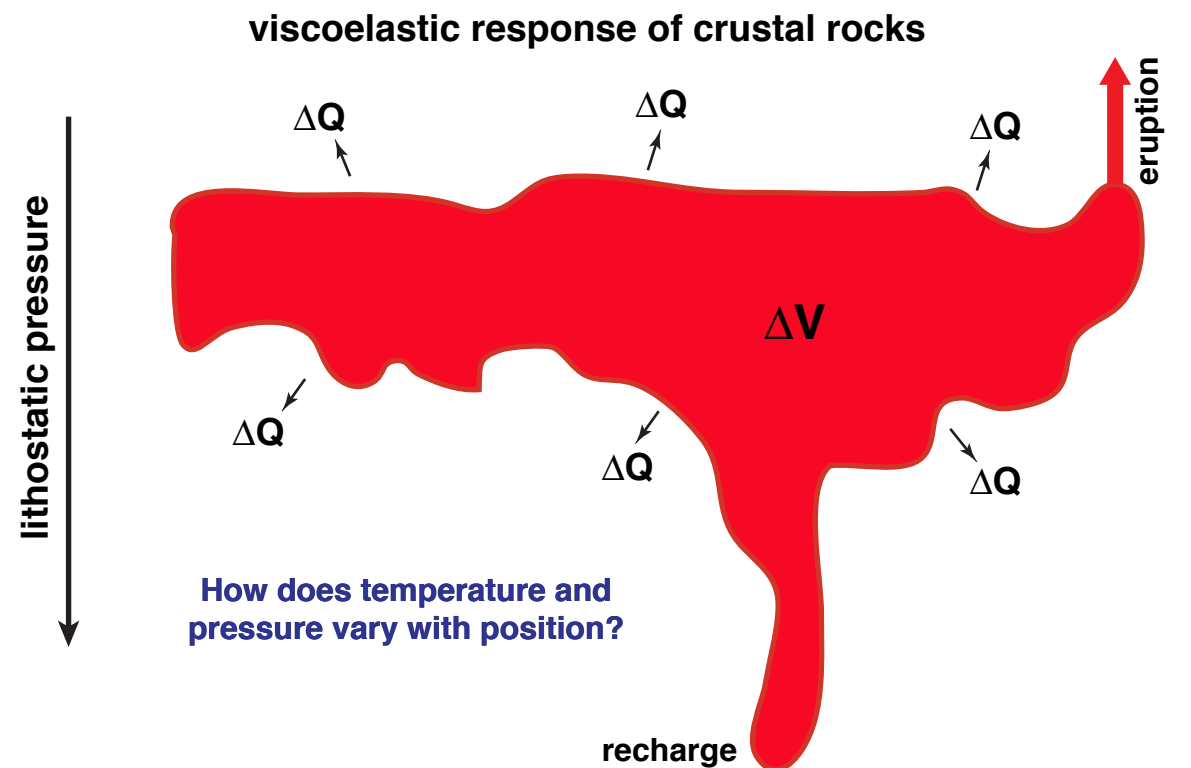


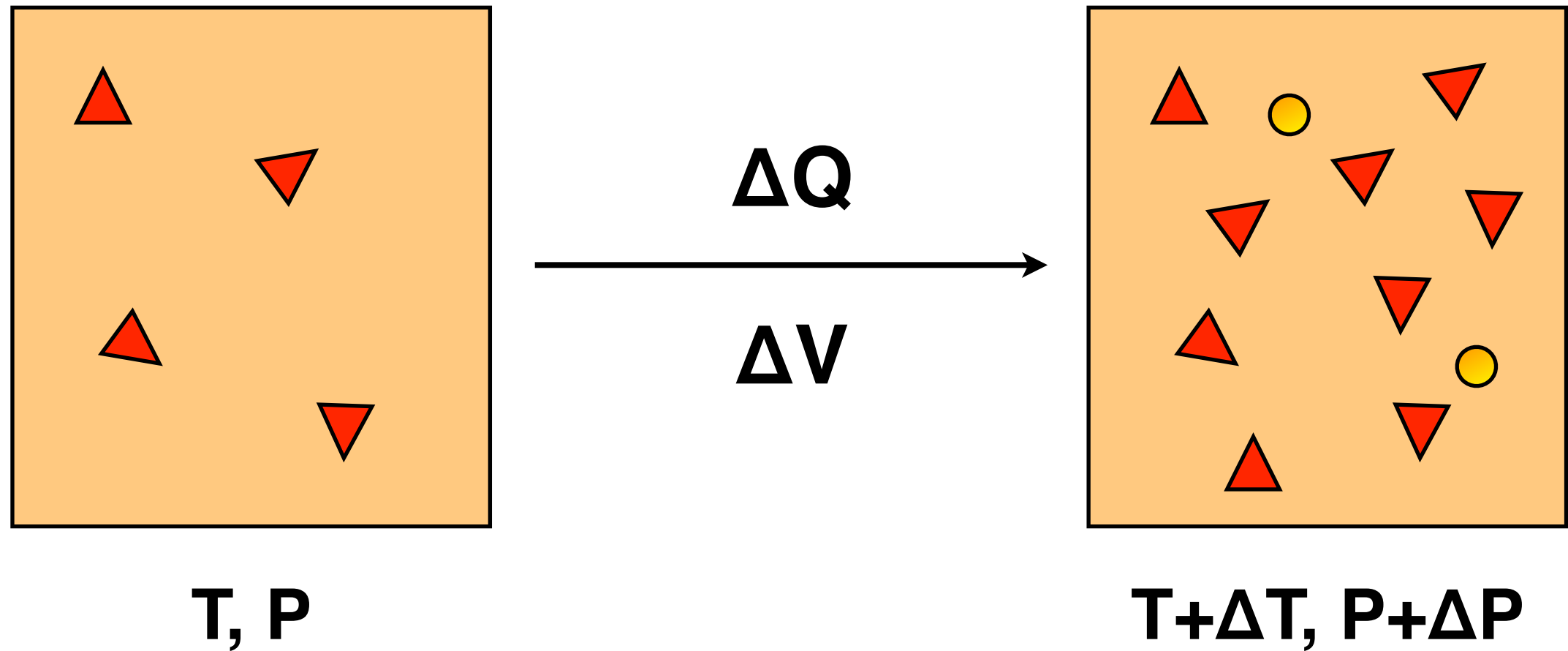
Helmholtz free energy minimization: modeling an eruption trigger



Because they are the natural variables for understanding the thermal and mechanical evolution of a magma body

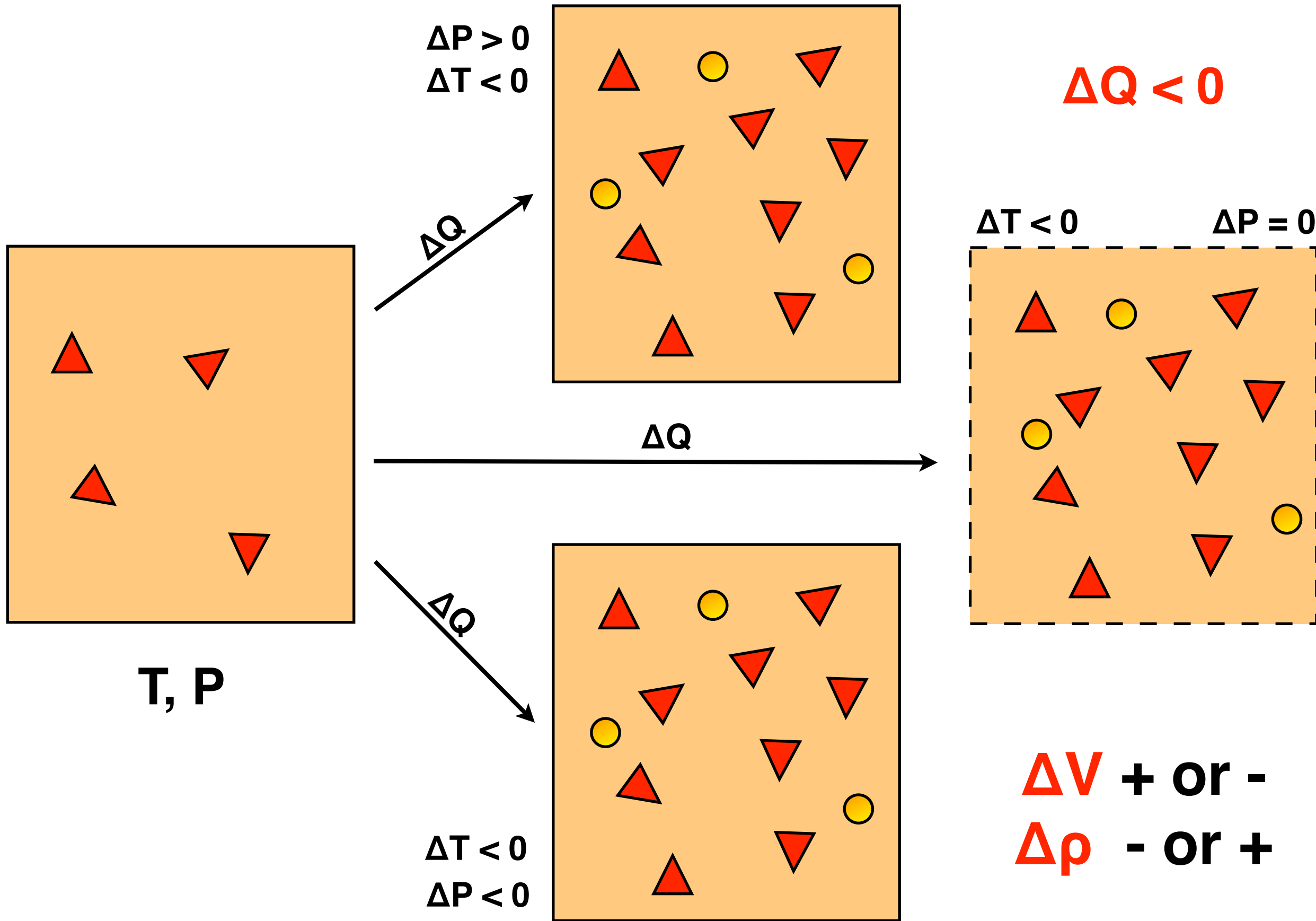
Why are entropy and volume important?



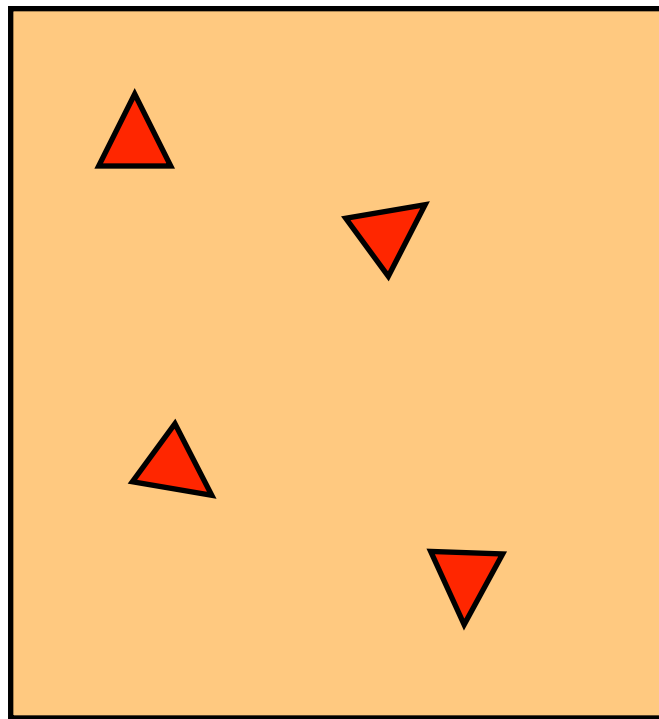


An eruption trigger must generate a large pressure differential between magma and country rock, so for evolving magmatic systems

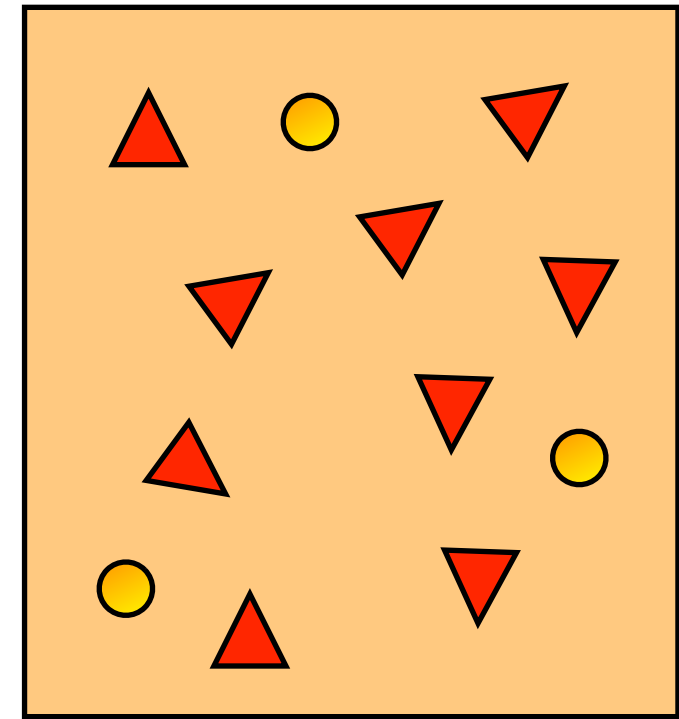
What is $\Delta T, \Delta P$?



Example: Assume that ΔV is zero:



T, P



T+ ΔT , P+ ΔP

$$\Delta P = \frac{(\text{mass crystallized}) \times (1/\rho_{\text{phase}} - 1/\rho_{\text{liquid}})}{\beta_{\text{system}}}$$

β = compressibility

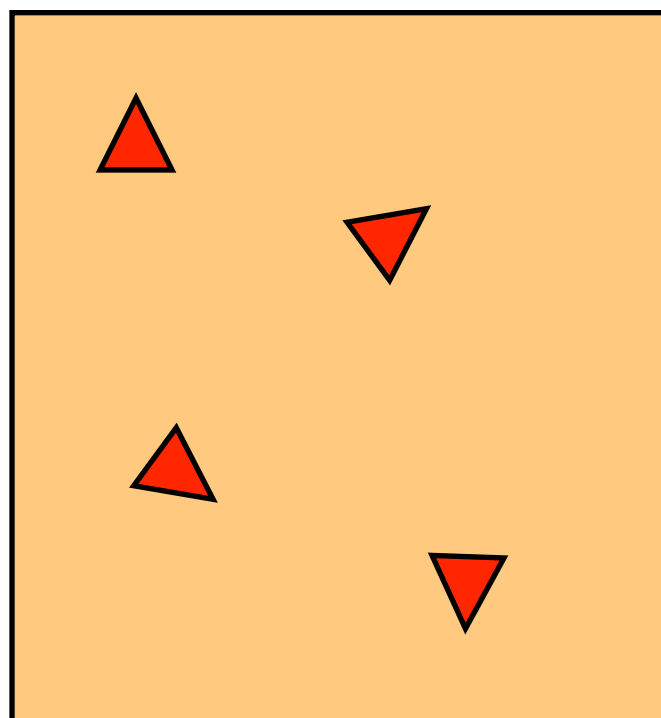
$\beta = 1/K$

K = bulk modulus

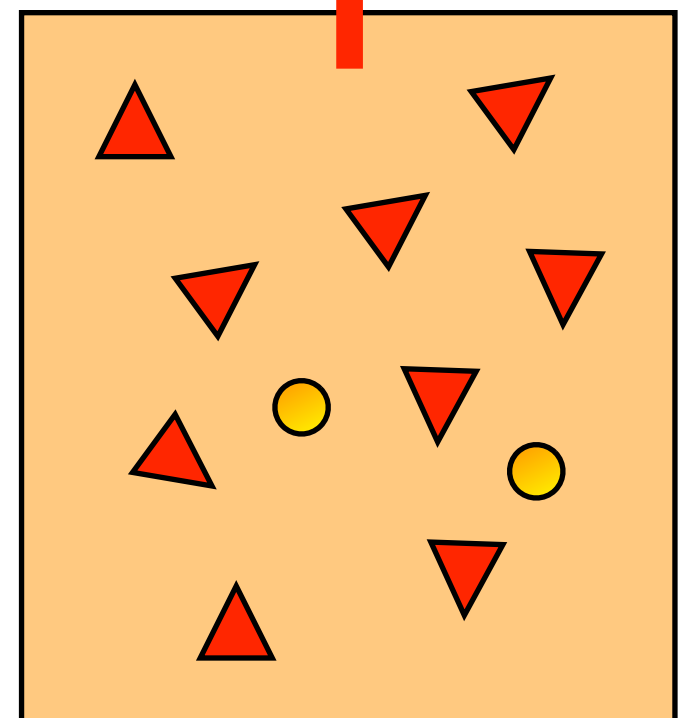
Is it possible to get ΔP large enough to over pressure the system, induce fracturing and thereby trigger an eruption?

Yes, if ...

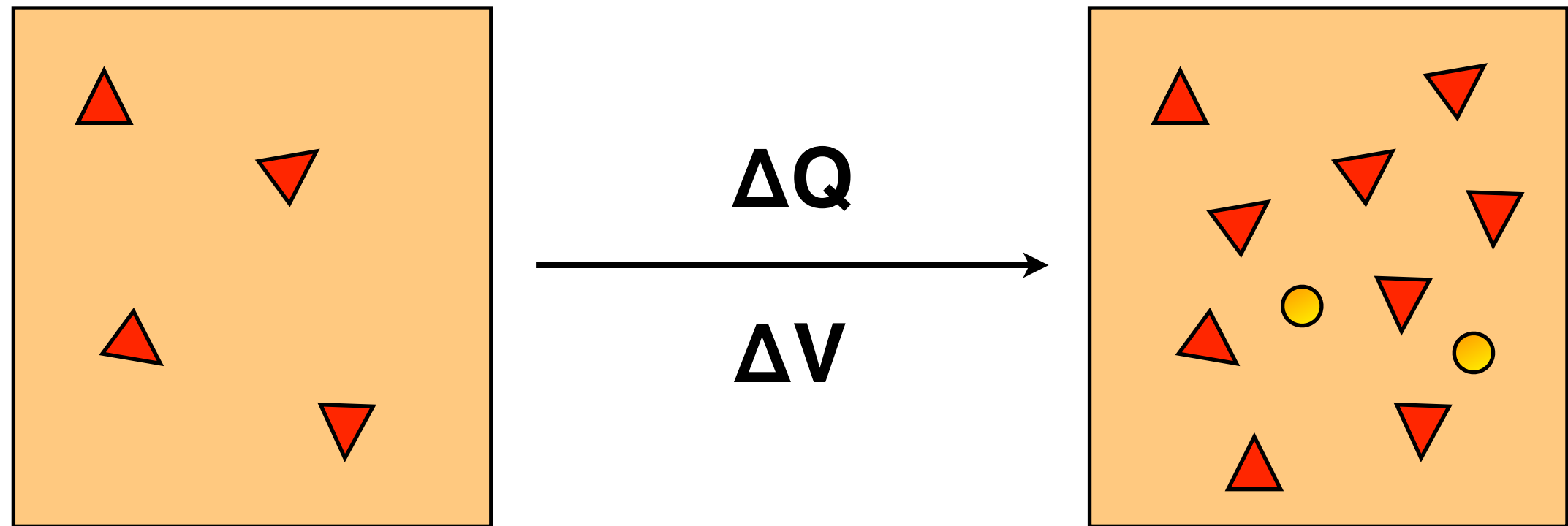
- mass crystallized is large
- $1/\rho_{\text{phase}} - 1/\rho_{\text{liquid}}$ is both large and positive, $\sim 3\%$
- β_{system} is very small, 10^{-4} bar^{-1} to 10^{-6} bar^{-1}
- $\Delta P \sim (\text{grams crystallized}) \times (0.01) / 10^{-6}$
- $\sim (\text{grams crystallized}) \times 10000 \text{ bars}$



ΔT



How do we obtain mass crystallized?



- What is the mass crystallized for a change in ΔQ and ΔV ?
- What are the compositions of those phases (i.e., phase density)?
- If the process is brought to chemical equilibrium, then what is the final temperature and pressure of the assemblage?

This process cannot be simulated experimentally

Experiments are conducted at fixed T and P

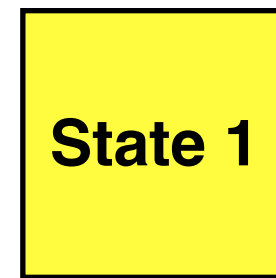
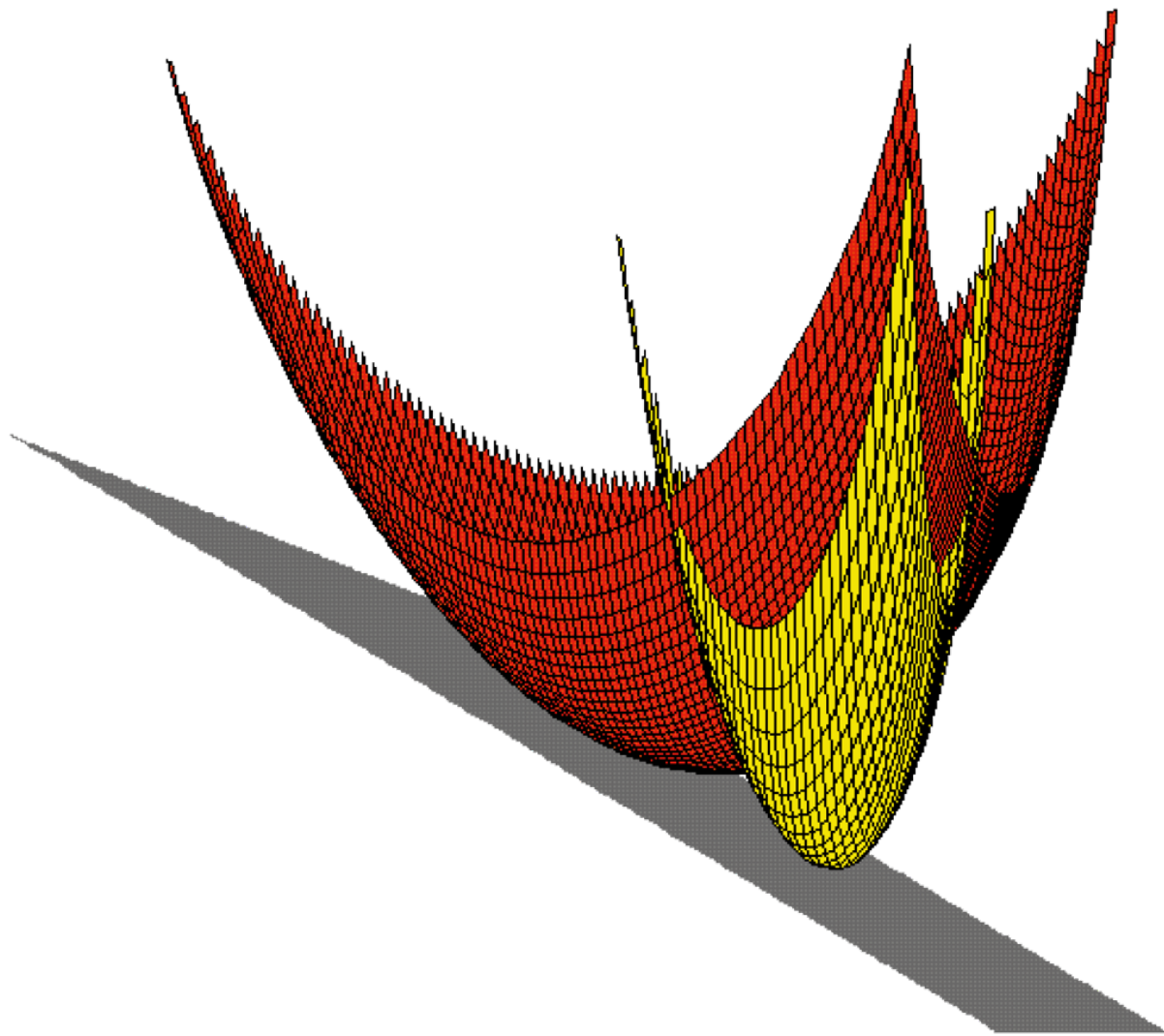
Thermodynamic calculations

Gibbs free energy

minimization of $G(T, P)$ yields $m, X, V, \text{etc.}$

Internal energy ($E = G - PV + TS$)

minimization of $E(S, V)$ yields m, X, T, P

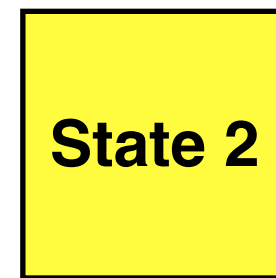


$$G(T_1, P_1)$$

$$E(S_1, V_1)$$

$$m_1, X_1, V_1, S_1$$

$$m_1, X_1, T_1, P_1$$

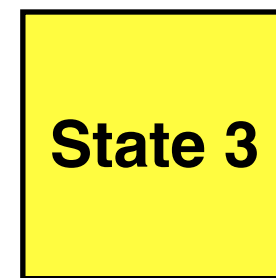


$$G(T_2, P_2)$$

$$E(S_2, V_2)$$

$$m_2, X_2, V_2, S_2$$

$$m_2, X_2, T_2, P_2$$



$$G(T_3, P_3)$$

$$E(S_3, V_3)$$

$$m_3, X_3, V_3, S_3$$

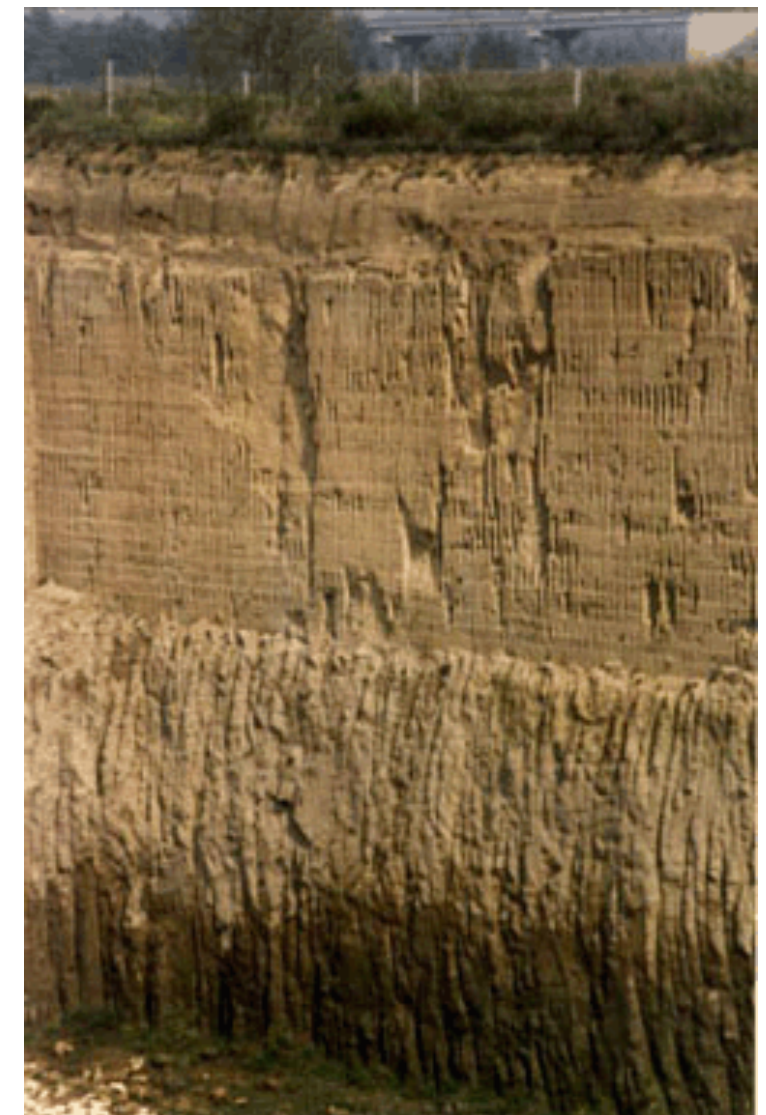
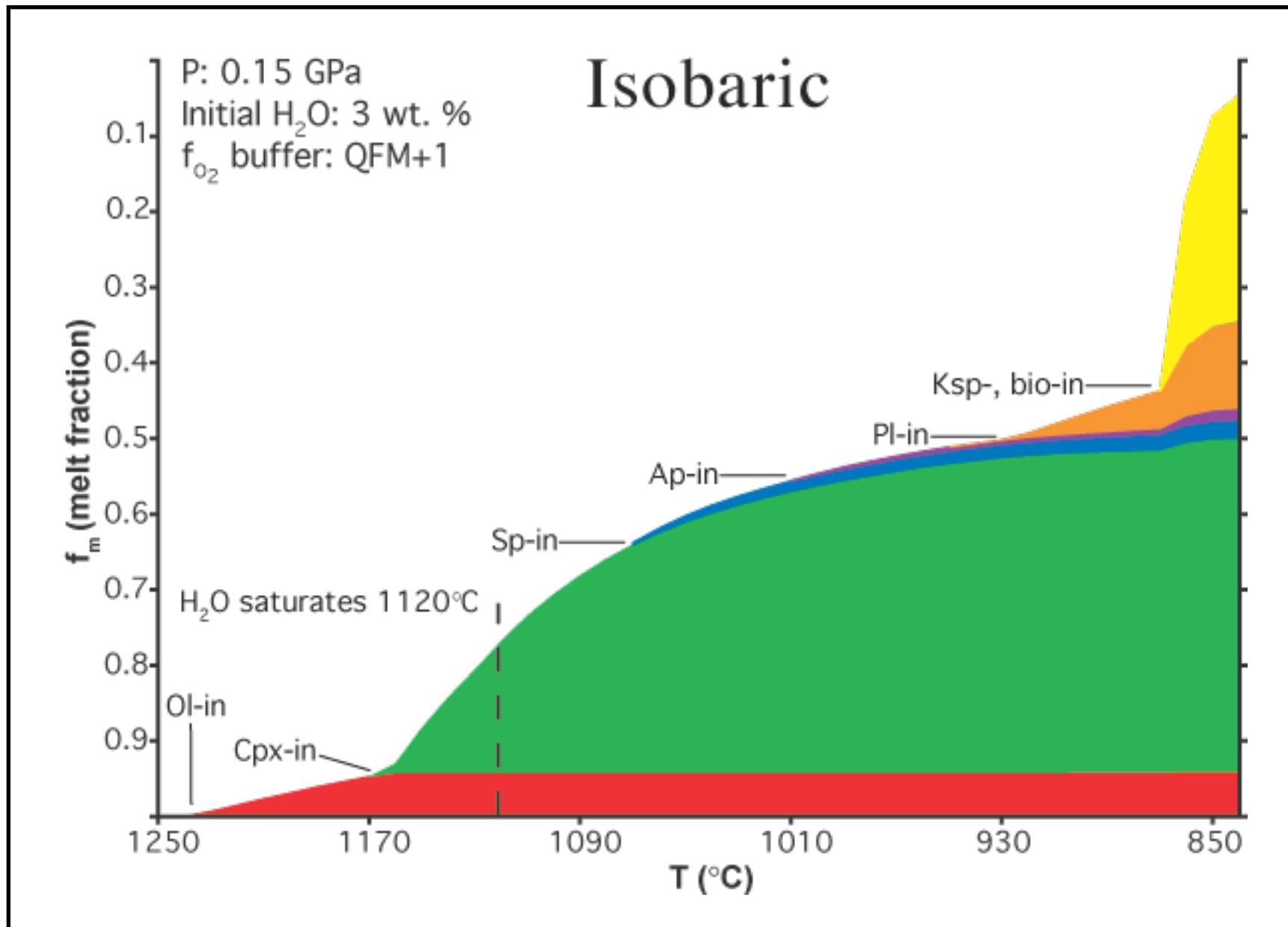
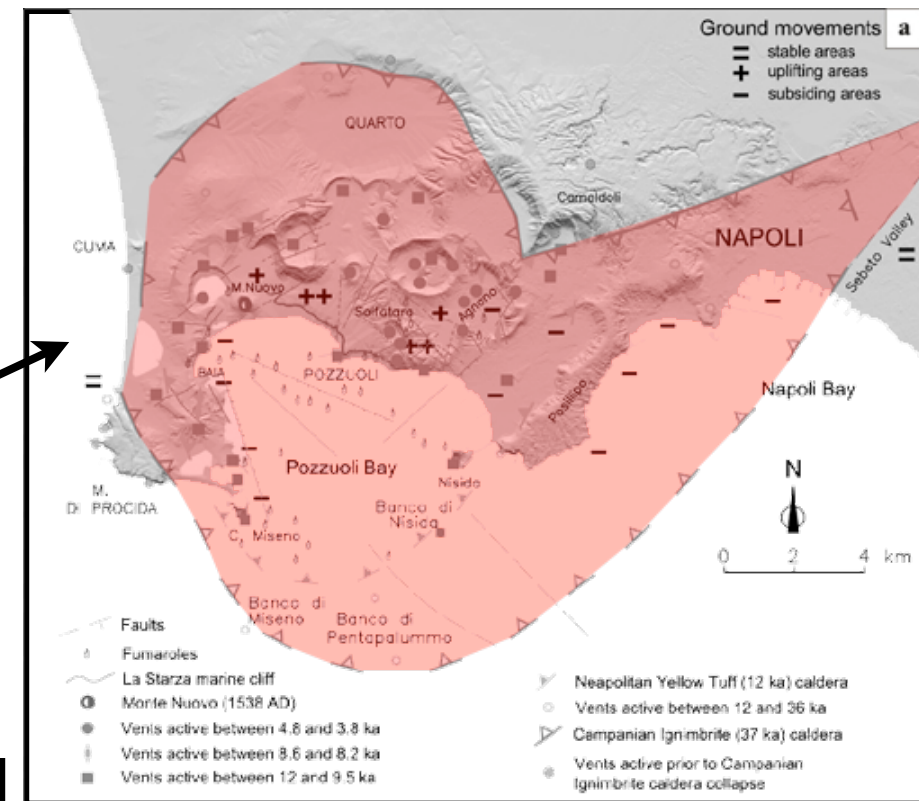
$$m_3, X_3, T_3, P_3$$

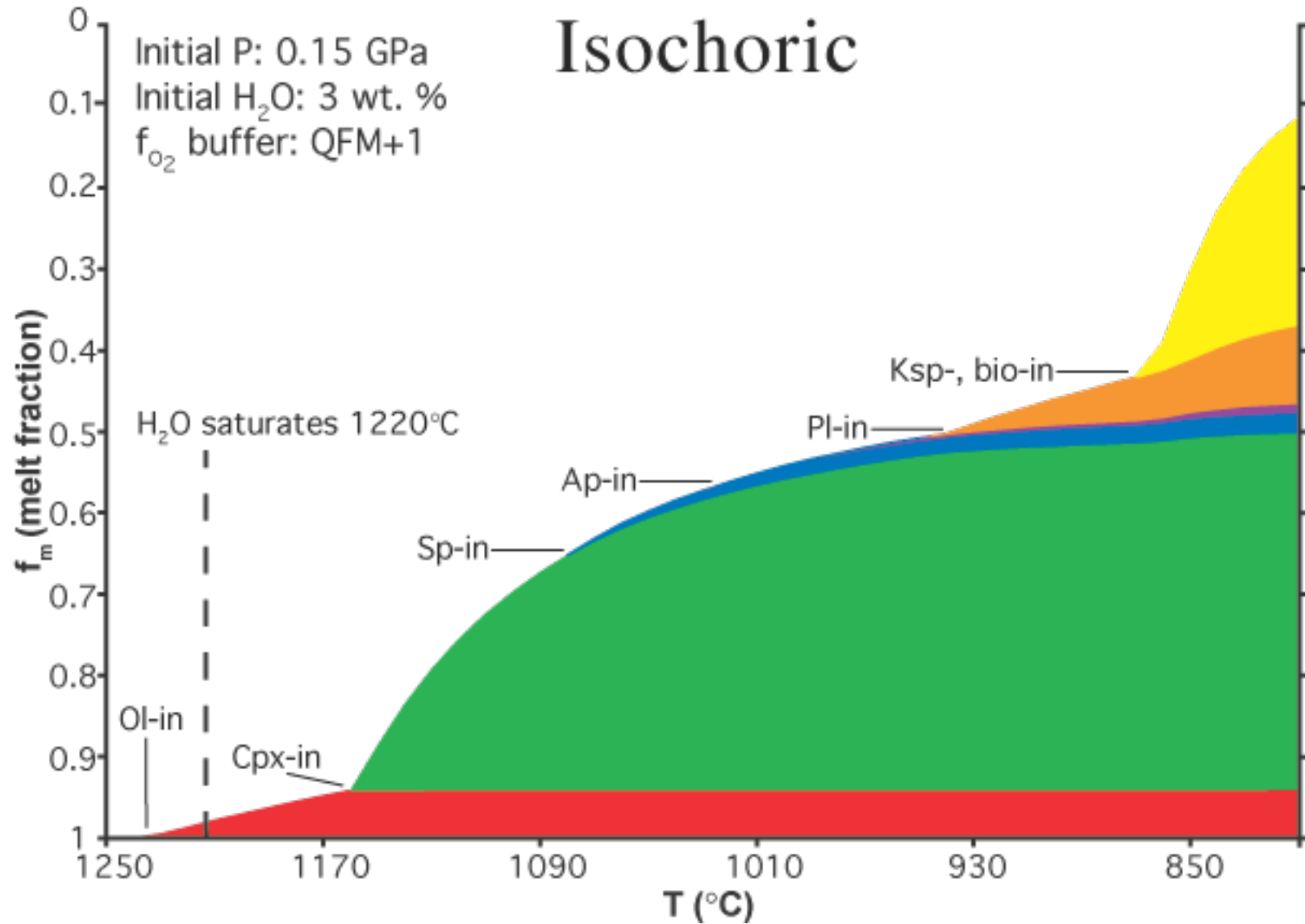
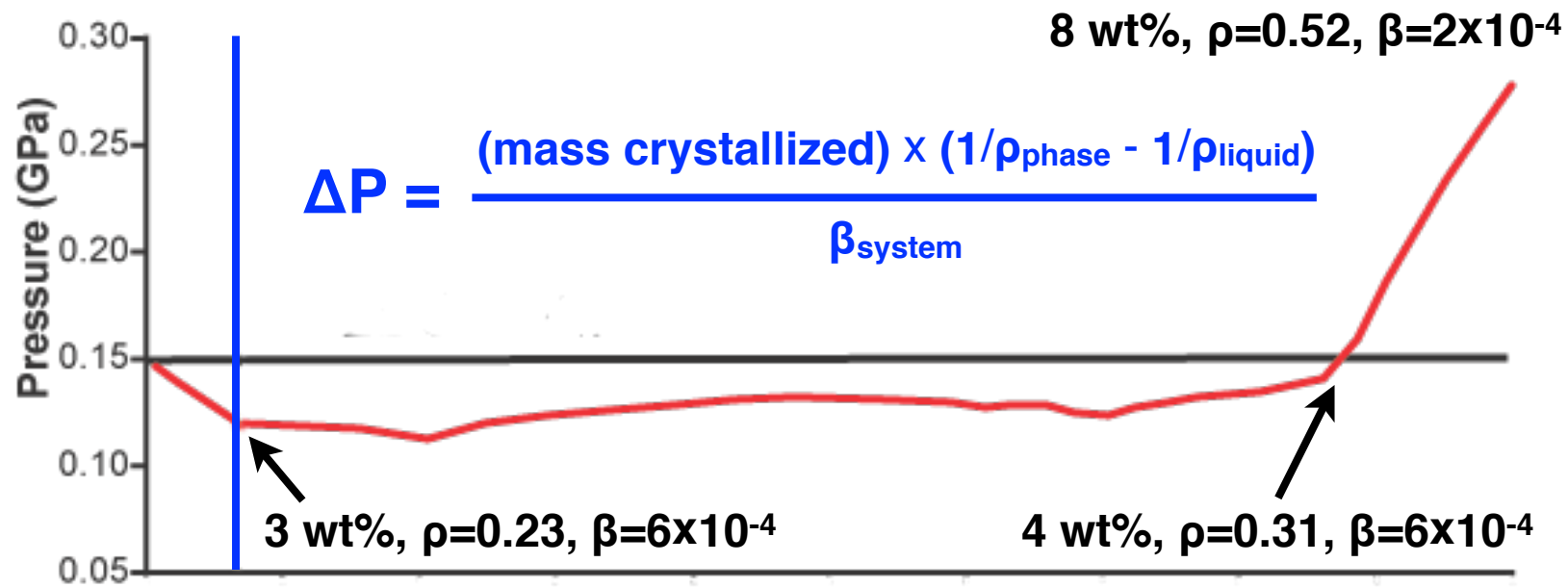
Campanian Ignimbrite

Fowler, Bohrson and Spera, 2007

Trachytic to phonolitic, ~39.3 ka, 200 km³

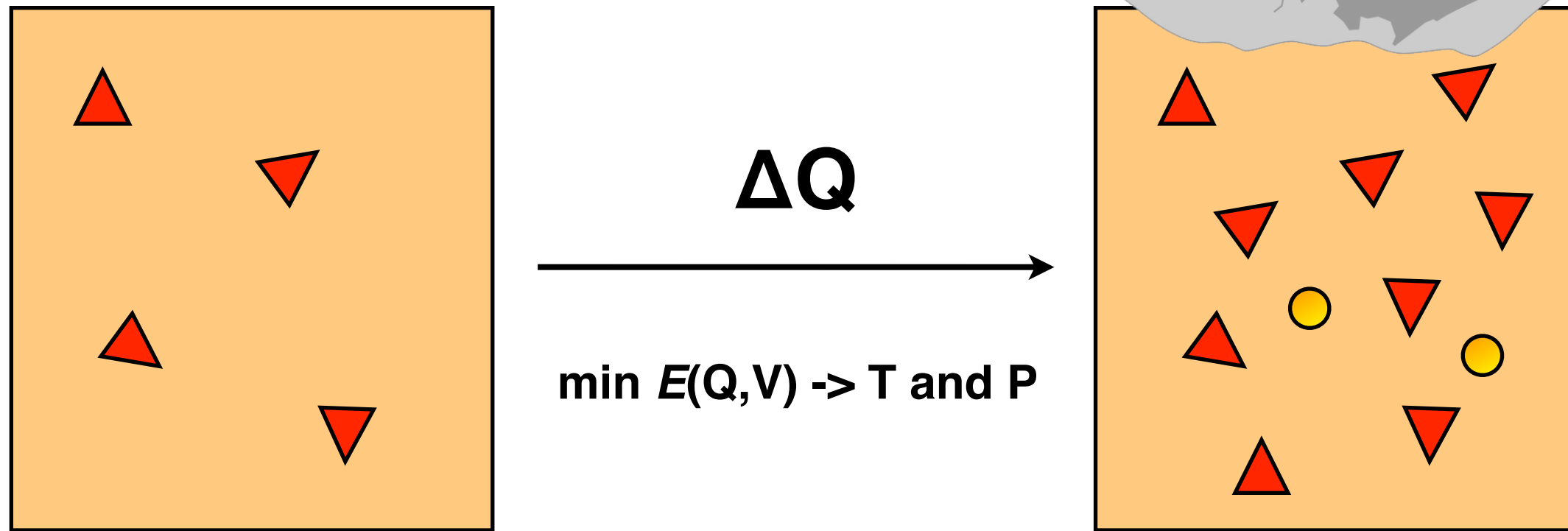
Campi Flegrei Volcanic Field, ~2000 km²





- Appearance of a vapor phase mitigates trend of decreasing P
- Why does pressure not increase rapidly when vapor is initially generated? (there are two reasons!)
- The trigger for the pressure increase is reaching the pseudo-invariant in the crystallization of the magma body.
- Increasing P increases the water content of magma and makes the vapor more dense.

A more realistic way to model this system ...?



- Yes, but it requires a fully coupled thermodynamic and dynamical model with no approximations regarding compressibility and uniformity of heat transfer
- Overpressure in the magma body now depends on the relative rates of crustal deformation and latent heat production

