Quantifying the influence of non-hydrostatic stress on polymorph equilibria

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1. Introduction

How does non-hydrostatic stress affect mineral equilibria?
- Debated topic since the work of Gibbs (1878) who developed the theory of equilibrium thermodynamics.
- Answering this question is critical for developing accurate thermodynamic models for highly stressed regions such as subduction zones and orogenic wedges.

Recently there have been three proposed ways for how stress influences mineral stability:

1. Mean stress
The mean stress, σ_m, or the average of the principal stresses, defines the thermodynamic pressure of the solid (Fig. 1a; Hobbs and Ord, 2016).

2. Normal stress
The stress normal to each interface, σ_n, defines the chemical potential on each interface. There is no single pressure value for the solid (Fig. 1b; Wheeler, 2014).

3. Hydrostatic stress
Stress has almost no effect on mineral stability, and constant pressure thermodynamics can be used (Fig. 1c; Powell et al., 2018).

Gibbs' (1878) non-hydrostatically stressed solid:

Solid in contact with fluids of different pressures (Fig. 2). Chemical potential at each solid interface is:

$$A_s + P_f V_s = \mu_s^f \quad (1)$$

Since A_s and V_s are constant for the solid and P_f differs between fluids, the chemical potential, μ, is different at each interface.
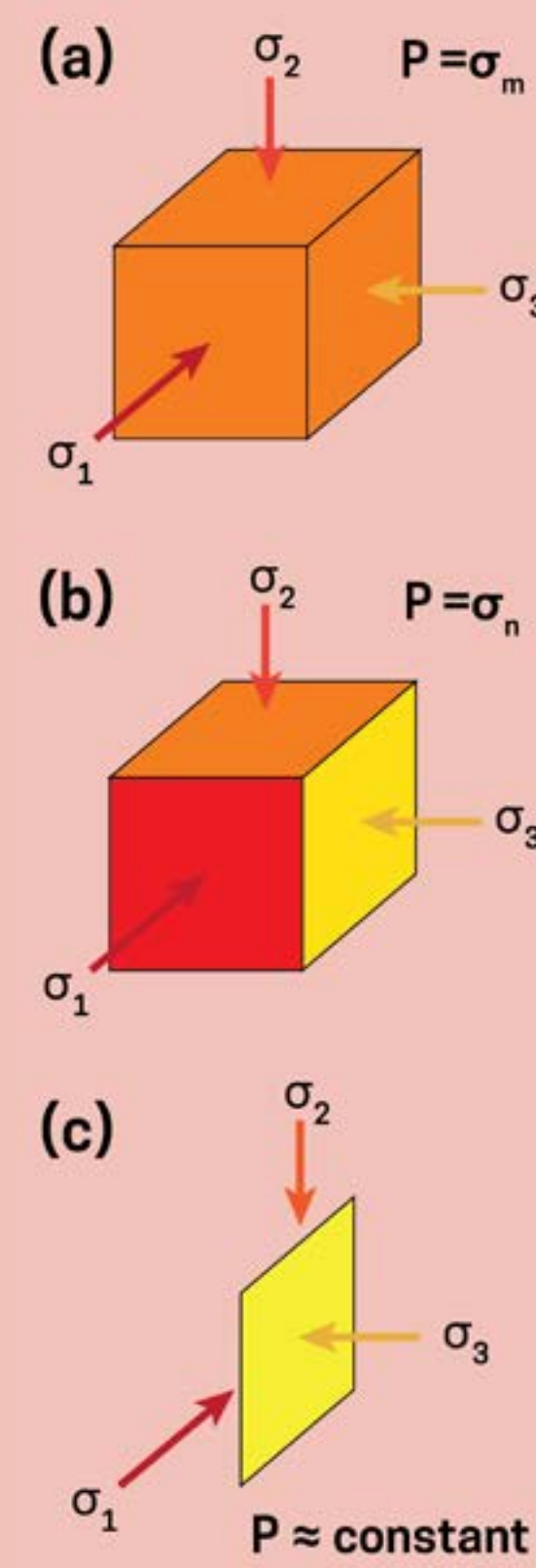
Conclusion: a mean stress approach is invalid (Fig. 1a).

Figure 1: Three approaches for how to treat mineral equilibria under non-hydrostatic stress. (a) Solid pressure is equal to the mean stress, σ_m. (b) The stress normal to each interface, σ_n, determines its stability. (c) Stress variation of σ_n and σ_n has little effect on interface stability and pressure is essentially constant.

Figure 2: Gibbs' (1878) thought experiment of a solid surrounded by fluids of different pressures. The chemical potential of the solid at each interface, μ, is determined by the fluid pressure, P_f.

2. Methods

Applying the work of Larché and Cahn (1985):
- Larché and Cahn's work follows and extends Gibbs' (1878) derivation to define chemical equilibrium for non-hydrostatically stressed, multi-component solids.
- Interface equilibrium between two non-hydrostatically stressed solids (from Larché and Cahn's equation 3.24):

$$A^\alpha - \sigma_n^\alpha V^\alpha = A^\beta - \sigma_n^\beta V^\beta \quad (2)$$

Equation (2) defines the condition for chemical equilibrium on a given interface between two single-component phases such as the polymorph pair calcite and aragonite (Fig. 3).

Numerically modeling polymorph interface stability:

Equation (2) can be solved as follows:
1. Helmholtz free energy at a given stress (A_σ):
$$A_\sigma = \Delta G_{f,T,P} - PV_{T,P} + \frac{1}{2}[\sigma_{ij}\varepsilon_{ij} - 3\sigma_P \varepsilon_P] \quad (3)$$
2. Volume at a given stress (V_σ):
$$V_\sigma = V_T(1 + \varepsilon_{ii}) \quad (4)$$
3. Normal stress (σ_n):
$$\sigma_n = \sigma_{ij} n_i n_j \quad (5)$$

Result: $A_\sigma^\alpha - \sigma_{ij}^\alpha n_i^\alpha n_j^\alpha V_T^\alpha(1 + \varepsilon_{ii}^\alpha) = A_\sigma^\beta - \sigma_{ij}^\beta n_i^\beta n_j^\beta V_T^\beta \left(1 + \varepsilon_{ii}^\beta\right)$ (6)

We numerically solve equation (6) for a range of stress tensors for different polymorph pairs to quantitatively demonstrate the influence of stress on interface stability.

Notes: the ij follow indicial notation and i follow summation convention. Compressive stresses are negative and strains, small. Phases are treated as isotropic which is valid to first order (Larché and Cahn, 1985). Additionally, in our discussion we do not consider more complex reaction phenomena such as those involving fluid films and interface-coupled dissolution-reprecipitation.

$\Delta G_{f,T,P}$ Gibbs free energy of formation at a reference pressure and temperature
P Pressure
$V_{T,P}$ Volume at reference pressure and temperature
σ_{ij} Cauchy stress tensor
ε_{ij} Small strain tensor
σ_P Hydrostatic pressure
ε_P Hydrostatic strain
V_T Volume at reference temperature and no pressure
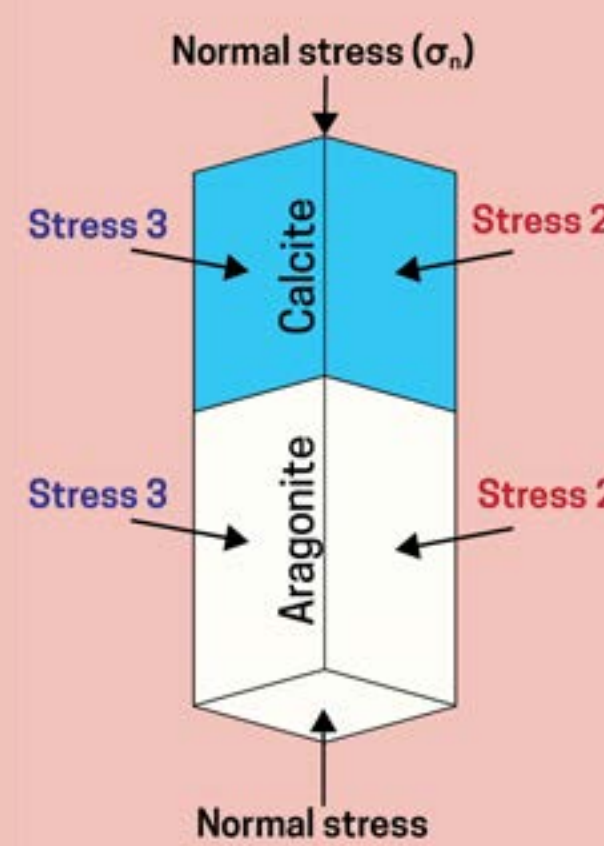n_i Interface normal vector

Figure 3: Applied stress orientations for interface equilibrium calculations. Two polymorphs (e.g., calcite and aragonite) are in contact at a given interface. The normal stress is normal to the interface while stresses 2 and 3 are parallel to the interface.

3. Results

Interface equilibrium diagrams (Fig. 4):
- Axes of diagrams in Figure 4 are the three principal stresses (Fig. 3)
- Contour surfaces represent the temperature of the interface necessary for chemical equilibrium at the given stress values (Fig. 4 top)
- CaCO$_3$ and C polymorph pairs (Figs. 4a-b) have isothermal surfaces with concave-down topologies while the SiO$_2$ polymorph pair has a saddle surface topology (Fig. 4c) because of the low poisson's ratio of quartz
- "X-Y" cross sections show the change in equilibrium temperature with changes in interface-parallel stresses (Stresses 2 and 3; Fig. 4 bottom)
- 0.1 GPa change in normal stress changes the equilibrium temperature by 20+ °C, consistent with Figure 1b (Fig. 4 top)
- 0.1 GPa change in interface-parallel stress changes the equilibrium temperature by less than a degree, consistent with Figure 1c (Fig. 4 bottom)

The approaches in both Figures 1b and 1c are correct, depending on the considered interface and stress variations
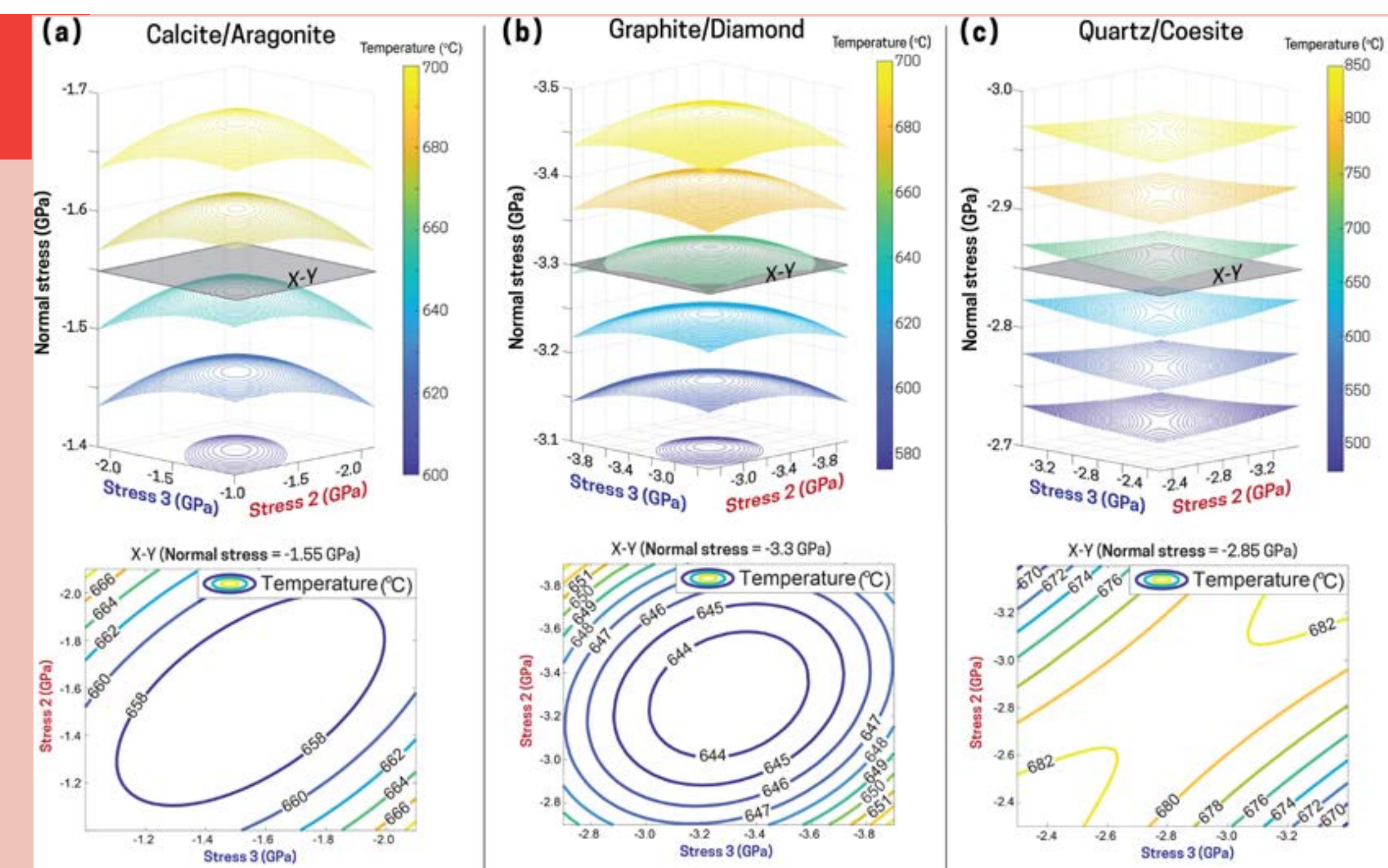

Figure 4: Interface equilibrium conditions for the polymorph pairs graphite/diamond (C), calcite/aragonite (CaCO3), and quartz/coesite (SiO2) using the setup in Figure 1. The top plots show equilibrium isothermal surfaces for the specified interface for a range of stress values. The isothermal surfaces show the possible stress values at which the given interface is at equilibrium for the given temperature. The bottom plots are cross sections at a fixed normal stress. The contours show the equilibrium temperature of the given interface at different values of stresses 2 and 3 (i.e., interface-parallel stresses). (a) Graphite and diamond (C). (b) Calcite and aragonite (CaCO3). (c) Quartz and coesite (SiO2).

4. Discussion

Normal stress determines interface stability to first order at a fixed temperature

Implications for solid-fluid reactions (Fig. 5a):
1. Pore fluids in rocks have a constant pressure
2. Fluids mediate chemical reactions
3. Equilibrium mineral assemblages will largely be controlled by the fluid pressure (Fig. 5a)

Implications for solid-solid reactions (Fig. 5b):
1. Direct solid-solid reactions will occur when a stress value crosses a reaction boundary (Fig. 6b)
2. Products will nucleate on interfaces normal to that stress value (Fig. 6c)
3. Minerals may grow parallel to the stress, depending on kinetics (Fig. 5b)

Figure 5: Controls on mineral equilibria for metamorphic systems with direct solid-fluid and solid-solid reactions. (a) In systems with interconnected pore fluids that mediate chemical reactions, the equilibrium mineral assemblages will be determined by the fluid pressure (P_f) which will be constant in each system. (b) In dry systems, the normal stress on each interface controls phase stability (Fig. 4). The maximum stress is in the aragonite stability field, and the minimum stress is in the calcite stability field. Large volume changes (ΔV) are associated with these polymorphic reactions.

Experimental evidence (Fig. 6):
- Quartz → coesite phase transformation under large non-hydrostatic stresses (Richter et al., 2016)
- Coesite forms when maximum stress exceeds the hydrostatic reaction boundary (Fig. 6b) even though mean stress remains below the reaction boundary (Fig. 6a)
- Coesite grains form normal to maximum stress and are subsequently rotated into the shear fabric (Fig. 6c) as indicated by the inset rose diagram

Interface-parallel stresses influence interface stability near reaction boundaries (Fig. 7)
- If a low-pressure polymorph is near a reaction boundary (Fig. 7a), interface-parallel stresses may be important
- For example, if interface-parallel stresses are decreased (Fig. 7b), the high-pressure polymorph will become more stable on an interface of constant normal stress (Fig. 7c)

Consequently, a stress decrease can make a high-pressure polymorph more stable compared to a low-pressure polymorph
- Opposite result of what is expected from a "mean stress" approach (Fig. 1a)

Implications for metamorphic systems:

1. Seismicity
- Polymorphic reactions normal to the maximum stress are a mechanism proposed for Mantle Transition Zone earthquakes (e.g., Green and Burnley, 1989)
- May operate in other direct polymorphic reactions

2. Seismic anisotropy
- Preferential nucleation of polymorphs relative to the principal stresses (Fig. 5b) may create crystallographic-preferred orientations in subducting marbles and quartzites

3. Reaction and growth kinetics
- Normal stress determines the thermodynamic driving force of a direct reaction
- The appropriate stress which generates the largest driving force should be used to model kinetics

4. Volume changes
- Large volume changes associated with polymorphic reactions (Fig. 5b) may cause deformation, uplift, and/or subsidence
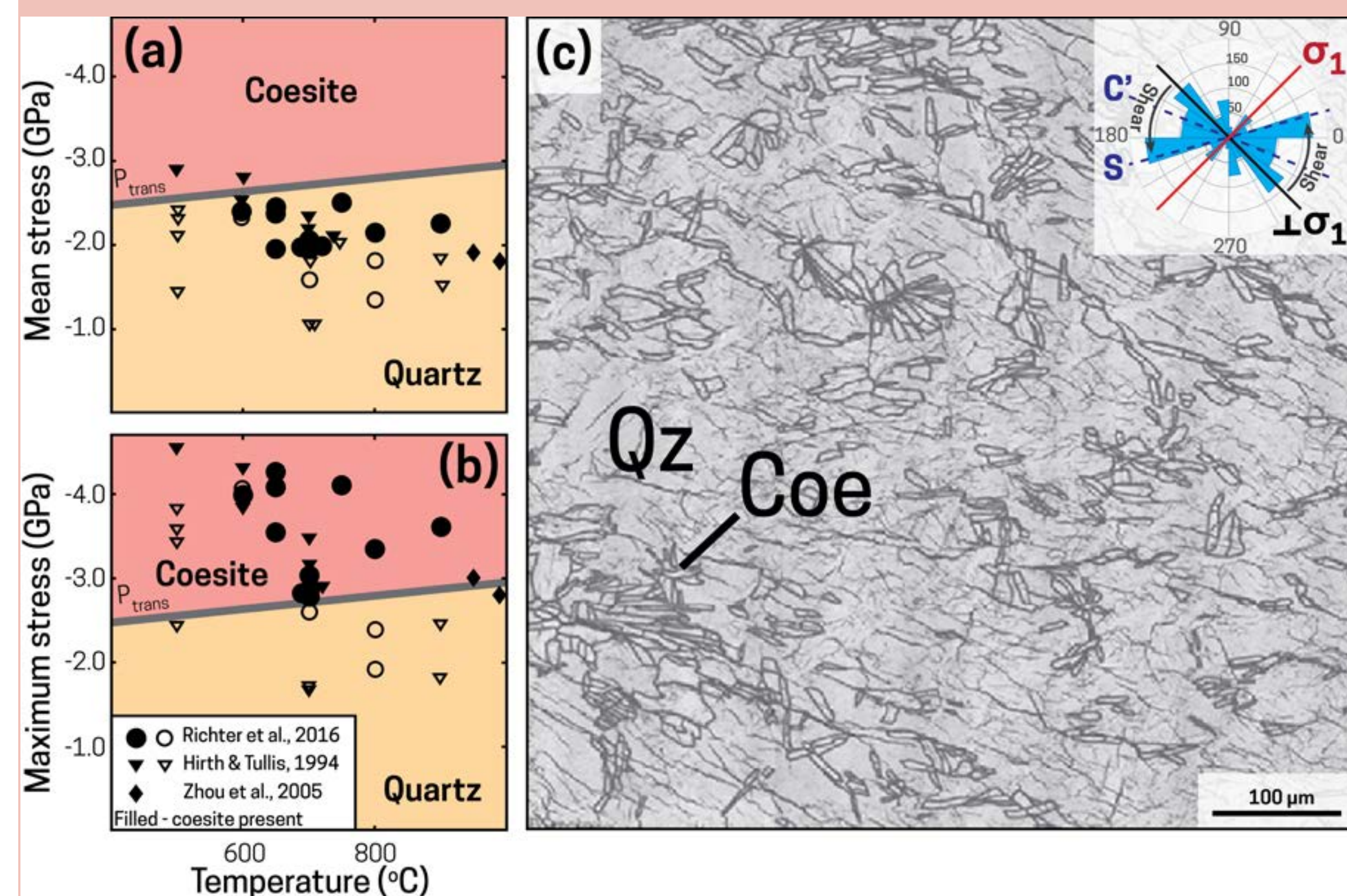

Figure 6: Quartz (Qz) uniaxial deformation experiments which formed coesite (Coe) using a modified Griggs apparatus. Figure modified after Richter et al. (2016). (a) The mean stress (($\sigma_1 + \sigma_2 + \sigma_3$)/3) plotted against the temperature for the given experiments where σ_1 is the maximum stress and σ_3 is the minimum stress (i.e., the confining pressure). The gray line (P_{trans}) denotes the pressure of the transition between quartz and coesite under hydrostatic stress conditions. The filled symbols are the experiments in which coesite formed. Many experiments which formed coesite have a mean stress below P_{trans}. (b) The maximum stress plotted against the temperature. The presence of coesite correlates strongly with maximum stress exceeding P_{trans}. (c) Scanning electron microscope image of coesite in deformed sample 435br after Richter et al., 2016. We created the inset rose diagram by measuring the angles of the long axes of the coesite grains. The resulting measurements indicate that the coesite grains nucleate on interfaces normal to the maximum stress ($\perp \sigma_1$) and are rotated by progressive shearing into the shear (C') and foliation (S) planes.

Figure 7: The effects of stress variation on polymorphs near reaction boundaries. (a) Calcite is hydrostatically stressed at calcite/aragonite equilibrium. The inset plot (top right) shows the qualitative isothermal surface for the calcite/aragonite equilibrium on the interface normal to the normal stress (σ_n; see Fig. 4). (b) Stresses 2 and 3 are decreased. The blue arrow in the inset plot shows the change in interface stability. (c) The interface normal to σ_n is now more stable as aragonite than calcite because the stress on the interface falls in the aragonite stability field (blue dot in the inset plot). Calcite remains stable on the interfaces normal to stresses 2 and 3. Thus, stress decrease can make a high-pressure polymorph more stable relative to a low-pressure polymorph.

5. Conclusions

1. Normal stress determines the stability of an interface to first order (Figs. 1b and 4)

2. Interface-parallel stresses have much smaller effects on interface stability (Figs. 1c and 4), however, they can still be important for phases near reaction boundaries (Fig. 7)

3. Mineral assemblages generated by reactions mediated by pore fluids of constant pressure will likely appear to be hydrostatic (Fig. 5a)

4. Direct solid-solid reactions under non-hydrostatic stress will:
   - Occur when stress crosses the reaction boundary (Figs. 5b and 6b)
   - Lead to nucleation of product phases on interfaces normal to that stress (Figs. 5b and 6c)
   - Lead to growth parallel to that stress, depending on kinetic factors

5. Polymorphic reactions under non-hydrostatic stress may generate seismicity, create seismic anisotropy, influence reaction kinetics, and cause deformation and subsidence/uplift
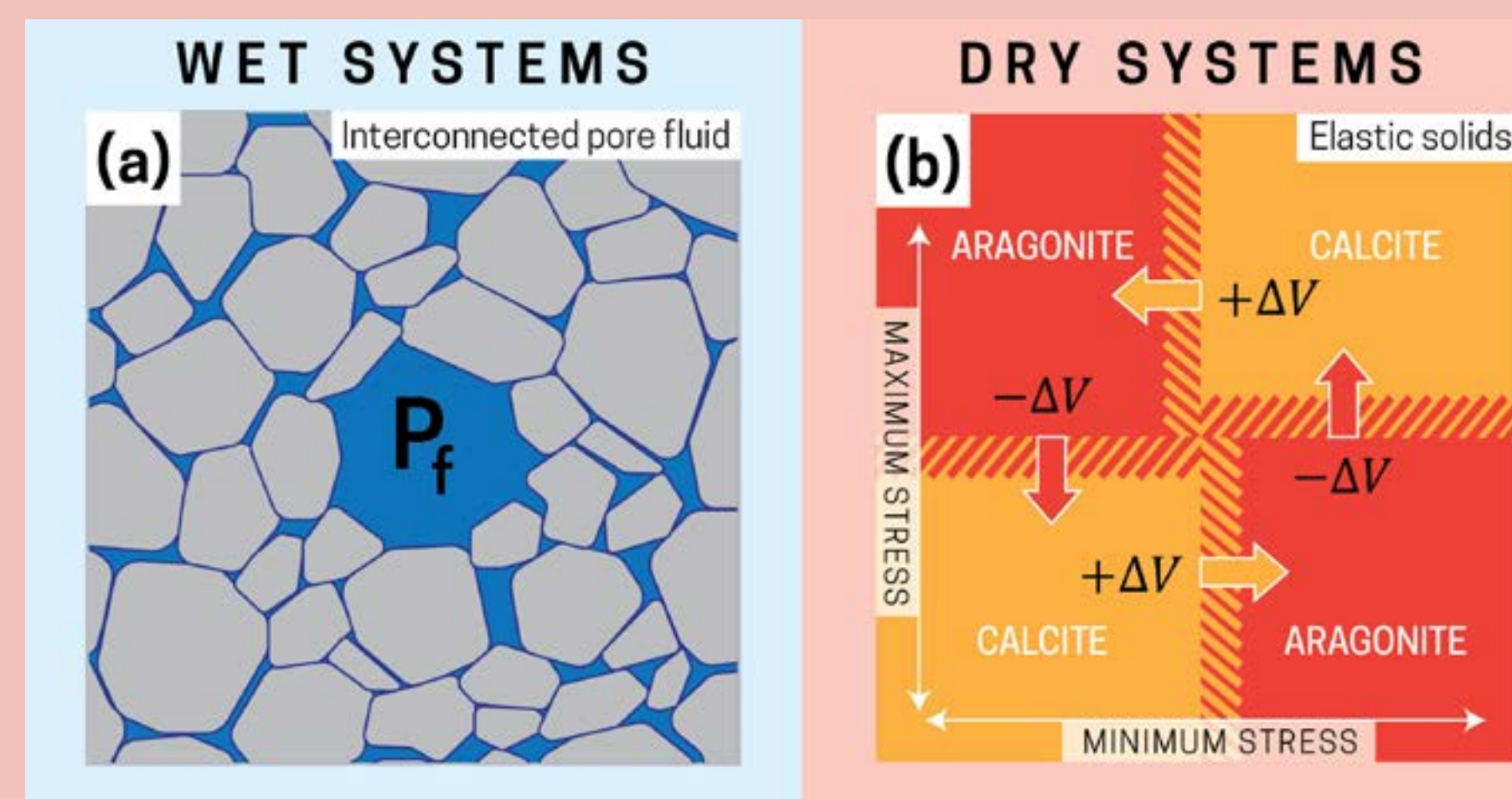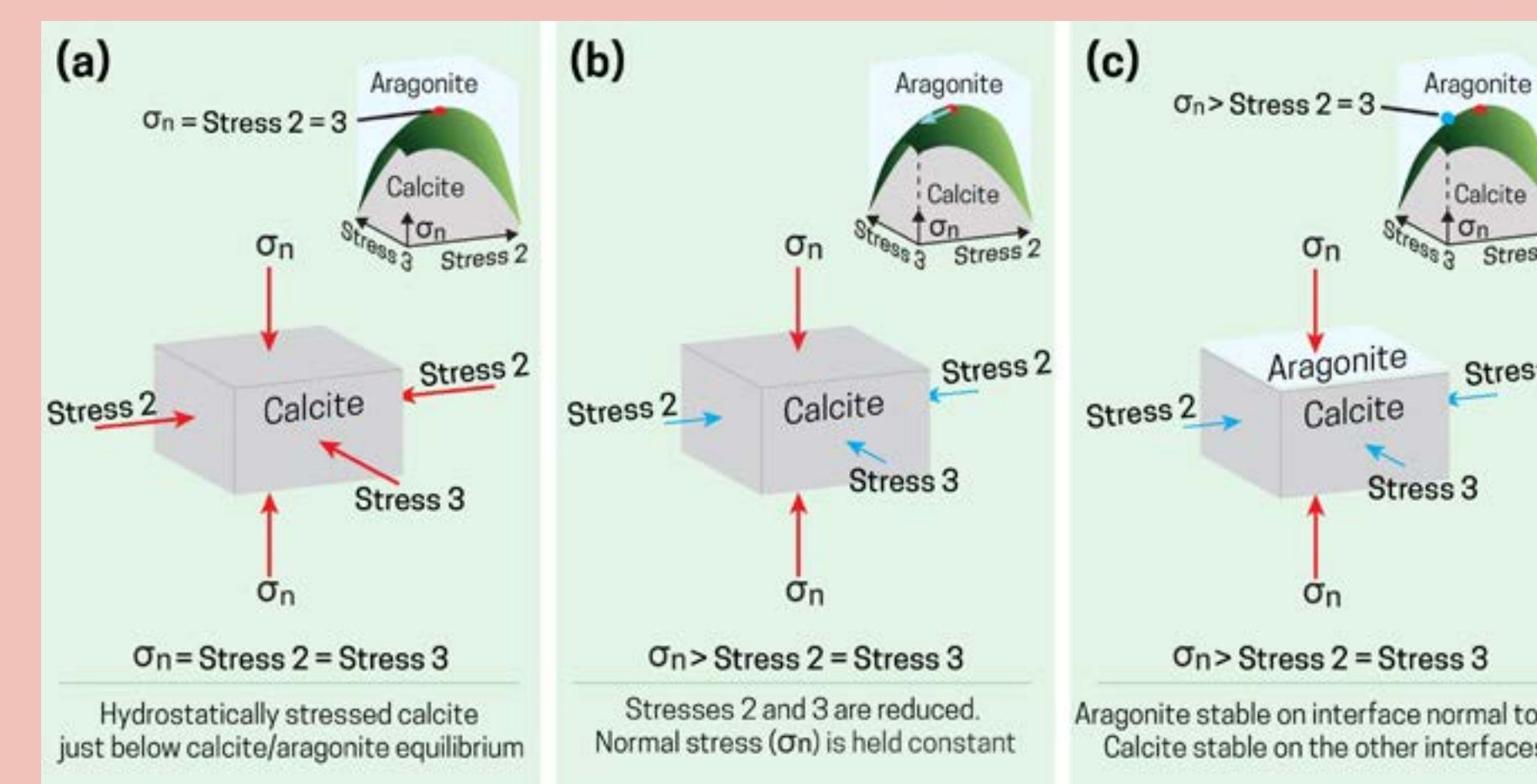
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