The effects of stress on reactions in the Earth: Sometimes rather mean, usually normal, always important

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Abstract
Stress affects chemical processes on all scales in the Earth but the magnitude of its effect is debated. Here, I give a new synthesis of the theory that describes the effects of stress on chemistry, elaborating upon work in Materials Science which is built from fundamental thermodynamic laws, and show its significance in Earth Science. There are separate but compatible relationships describing what happens (1) at interfaces and (2) within grains. (1) The main chemical effects of stress in the Earth are due to variations in normal stress along grain interfaces and between interfaces with different orientations. For reactions involving diffusion these variations give effects on mineral stability broadly equivalent to pressure changes of \(
\frac{\text{molar volume}}{\text{molar volume change during reaction}} \times \text{(stress variation)}
\)
. The volume ratio is generally large and so the effects of normal stress variations are always important since all stressed rocks have interfaces supporting different normal stresses. There is no global chemical equilibrium in a stressed system, so reaction kinetics contribute to ongoing evolution until stresses relax: this evolution can include deformation by diffusion creep and pressure solution, possibly with new mineral growth. These effects are relevant for predicting the conditions for reactions involving fluids, such as serpentinite formation and breakdown (relevant for the Earth’s volatile cycles) and for other reactions such as ringwoodite breakdown (relevant for understanding the 660 km mantle discontinuity). (2) Within stressed solid solution grains it is not possible to define chemical potentials of all chemical components since one has to be specified as “immobile.” The chemical potential of a “mobile” component such as an exchange vector can be defined. It depends on the “partial molar strain,” a second rank tensor defining the variation in unit cell geometry with composition. In cubic crystals the partial molar strain is isotropic and the chemical potential of a mobile component depends on mean stress. In other crystal systems the partial molar strain is anisotropic and the chemical potential depends on a “weighted” mean stress; orientation as well as magnitude of stress has an influence. I propose “chemical palaeopiezometry”—the possibility of measuring past stress levels via chemistry. Examples show that stress variations in hundreds of MPa to GPa are required to produce 2% variations in composition but high stresses and/or precise chemical analyses will allow this proposal to be tested. High stresses around inclusions and dislocations could be targeted. So, the weighted mean stress inside grains has an
1 | INTRODUCTION

It is undeniable that reactions in the Earth, with or without the involvement of fluids in pores, often occur under stress. I use the word reaction here in the broadest sense to include growth of new phases from old (either adjacent or separated), chemical change in existing phases and growth and dissolution of existing phases during diffusion creep and pressure solution. Stress in the Earth may be due to combinations of large-scale movements, distinct fluid pressures in pores or stresses induced by volume changes in reactions themselves. Since pressure (isostatic stress) is universally accepted to influence phase equilibria, from thermodynamic theory and direct observations, more general states of stress must also have effects on when and how new phases grow. This begs two questions: what is the mathematical framework in which to describe the thermodynamic effects of stress, and, using this, are those effects predicted to be important for representative differential stress levels in the Earth? If the effects are significant then they must be borne in mind when interpreting or predicting mineral assemblages in natural rocks, in applying the results of experiments, and in elucidating possible feedbacks between evolving stress and chemical reaction. These are not new questions, but have led to incompatible views from the 1960s through to today. My aims in this contribution are:

1. to summarize and elaborate upon the theory as established in Materials Science literature and put it in its Earth Science context;
2. to illustrate the qualitative and quantitative significance of the theory, and
3. to show how current debates can be illuminated by the theory.

In this contribution I show the relevance of works from outside Earth Science, which build on the fundamental tenets of thermodynamics. A knowledge of thermodynamics and of stress is necessary to understand the theory, and these topics are addressed in many texts. I first summarize some relevant quantities and relationships from hydrostatic thermodynamics (thermodynamics in systems under pressure but without differential stress). Any equation related to non-hydrostatic thermodynamics must reduce to a conventional hydrostatic equation when stress is isotropic. Next I summarize some relevant quantities and relationships for mechanical equilibrium, and then outline some controversies. Having provided this background, I show how a consistent theory for non-hydrostatic thermodynamics involves combinations of normal stress at interfaces and a weighted version of mean stress within grains to provide the quantitative basis for understanding reactions in stressed rocks. For simplicity this contribution is restricted to the description of small elastic strains which simplifies the mathematics (and is appropriate for many geological circumstances since minerals are not very compressible) and I address binary solid solutions with ideal mixing. For brevity I do not duplicate the derivations of the equilibrium conditions, since these are in the cited works; instead the focus is on the geological significance. As part of that aim some controversies will be addressed, and I finish by outlining some ways that these ideas can be further developed and applied.

1.1 | Hydrostatic thermodynamics

This is the conventional theory for the description of chemical equilibria in systems under simple pressure, where the force per unit area is the same in all directions. Table 1 summarizes relevant quantities and relationships, including some for exchange vectors (e.g. the exchange vector $\text{FeMg}_{-1}$ in orthopyroxene) because these are important for what follows. Defects play an important role in aspects of solid thermodynamics: in particular vacancies, which cannot be defined in a useful way in fluids, are important in crystals. They have zero chemical potential at crystalline surfaces but have a concentration in grain interiors given by Equation 10 (e.g. equation 3.64 of Balluffi, Allen, & Carter, 2005; section 2.2.1 of Poirier, 1985) because there is an energy penalty and an entropy benefit associated with their presence. In metals one can define an exchange vector such as $\text{MV}_{-1}$, and its associated chemical potential, an idea important in stressed systems. In partly ionic solids the behaviour of vacancies is more complicated (e.g. Kohlstedt, 2006) and is not discussed in detail in this contribution.

In what follows, the Helmholtz free energy $F$ plays an important role. For solids the dimensionless product $P k$ is usually small, so from Equation 8 it can be seen that $F$ is not sensitive to pressure—most of the pressure dependence of $G$ comes from the $P V$ term in Equation 2, not the $F$ term.
| Quantity or relationship | Symbol or equation | Source |
|--------------------------|-------------------|--------|
| Temperature              | T                 |        |
| Pressure                 | P                 |        |
| Entropy                  | S                 |        |
| Volume                   | V                 |        |
| Internal energy          | U                 |        |
| Moles of component $i$   | $N_i$             |        |
| Mole fraction of $i$     | $X_i$             |        |
| Coefficients defining a balanced reaction | $C_i$ where $\sum_i C_i(\text{species})_i = 0$ |        |
| Helmholtz free energy   | $F = U - TS$      | (1) NM3.64 |
| Gibbs free energy        | $G = F + PV$      | (2) NM3.70 |
| Compressibility (isothermal) | $k = \frac{1}{PV} \frac{\partial F}{\partial P} \bigg|_T = - \frac{1}{V} \frac{\partial V}{\partial P} \bigg|_T$ | (3) F9.73 |
| Value of property $Z$ at pressure $P$ $(T$ dependence is implicit) | $Z(P)$ | |
| Partial molar values of property $Z$ for component $i$ | $\check{Z}_i = \frac{\partial Z}{\partial N_i} \bigg|_{P,T,N_j}$ | (4) NM5.9 |
| Chemical potential of $i$ | $\mu_i = \check{G}_i = \frac{\partial G}{\partial N_i} \bigg|_{P,T} = \frac{\partial F}{\partial N_i} \bigg|_{V,T}$ | (5) NM5.13 |
| Partial molar volume of $i$ | $\check{V}_i = \frac{\partial \mu_i}{\partial P} \bigg|_T$ | (6) F9.77 |
| Partial molar quantity for pure $i$ end-member | $Z_i^0 = Z_i$ for brevity | |
| Pressure as a derivative | $P = \frac{\partial U}{\partial V} \bigg|_S = \frac{\partial F}{\partial V} \bigg|_T$ | (7) F9.9, 9.12 |
| $F$ for linear compressibility | $F = F(0) + \frac{1}{2} V\kappa P^2$ | (8) From Equation 3 |
| $\mu$ for single component | $\mu = \check{F} + P\check{V}$ | (9) |
| $\mu$ for ideal solution | $\mu_i = F_i + PV_i + RT \ln X_i$ | (10) NM5.39 |
| $\mu$ for exchange vector in ideal binary solution | $\mu_{1-0} = \mu_1 - \mu_0 = F_1 - F_0 + P(\check{V}_1 - \check{V}_0) + RT \ln \left( \frac{X}{1-X} \right)$ | (11) T7 and Equation 10 |

(Continues)
TABLE 1 (Continued)

| Quantity or relationship | Symbol or equation | Source |
|--------------------------|-------------------|--------|
| Affinity, for a reaction with products having \( C_i < 0 \) | \[ A = \sum_i C_i \mu_i(P) \] | (12) A18.57 |

\( G \) plays a central role in hydrostatic thermodynamics, taking the minimum possible value at equilibrium for fixed pressure and temperature. Except for affinity, Table 1 addresses equilibrium concepts. The kinetics of reaction can be considered in terms of the overall driving force or affinity, and various processes which operate, possibly involving local equilibria in a system with global or overall disequilibrium (Figure 1). This is relevant for this contribution because in stressed systems I argue that global chemical equilibrium cannot be attained, in which case the idea of local equilibrium is fundamental to describing them (Wheeler, 2014). That is true also for disequilibrium in systems under hydrostatic stress—they must be understood by quantifying each part of the overall reaction mechanism, for example, in Figure 1e the detachment of atoms from brucite, diffusion through the intervening phase and attachment to periclase.

1.2 | Stress

Table 2 shows some basic mechanical relationships and how some thermodynamic properties relate to stress. To illustrate some fundamental ideas, Figure 2 shows a calculated 2D example of grain scale stresses in a porous rock where the solid framework is carrying a load in addition to the fluid pressure \( P_f \) and the solid–solid boundaries are assigned a single value of normal stress \( P_s \). The differential stress (Figure 2a) and mean stress (Figure 2b) vary smoothly within grains in accord with \( \nabla \cdot \sigma = 0 \) (Irgens, 2008) but have discontinuities at boundaries (described by Equation 13). Stress trajectories are notional lines drawn parallel to principal stress directions, which assist in visualizing such stress states (Figure 2c). Gallagher, Friedman, Handin, and Sowers (1974) presented photoelastic pictures illustrating such heterogeneous states of stress.

Some works (e.g. equation 1 of Tajcmanova, Vrijmoed, & Moulas, 2015) use the word “pressure” for the mean stress in Equation 14. Thus, the word “pressure” may imply a state of isotropic stress in which case it must be uniform, or it may imply a general state of stress in which case the “pressure” is the mean stress and may vary from place to place as in Figure 2b. The precise meaning must be established from context, but use of the same word for two different things encourages the idea that mean stress can be substituted for pressure in various thermodynamic equations, an idea which is not necessarily true. The roles of normal stress (dependent on defining an interface) and mean stress in thermodynamics are a topic for debate but I emphasize now that their definitions are just that: definitions. They are not automatically imbued with any particular thermodynamic significance; any such significance needs to be demonstrated by building upon the fundamentals of thermodynamic theory.

1.2.1 | Stress at boundaries

Stresses at boundaries are important in non-hydrostatic thermodynamics, so require discussion here. Equation 13 allows for shear stress at boundaries but in rocks it is not clear what the magnitude of shear stress might be and under what conditions it may be significant. There is a scale issue here, for example, interfaces showing atomic steps (Pope & Chu, 1994; Risold, Trommsdorff, & Grobety, 2003) could appear to support mesoscale shear stress even if the local shear stresses are actually relaxed; undulating boundaries with locally relaxed shear stresses can be usefully modelled (Raj & Ashby, 1971). Indirect insight into shear stresses is given from diffusion creep experiments. Models for diffusion creep generally assume no shear stress at boundaries and successfully predict the cubic grain size dependence of viscosity (for Coble creep). Models with boundary stress give a different form for the grain size dependence (Wheeler, 2010), which has not been observed in experiments. As discussed below, Larché and Cahn (1985) deduce that on an incoherent interface there will be no shear stress at equilibrium.

There is much experimental evidence that in systems with fluids (e.g. water), these may be present as thin films along boundaries (Hickman & Evans, 1995; Israelachvili, 2011). When normal stress is greater than fluid pressure, narrow films persist even though a true fluid would be expelled before mechanical equilibrium is attained. Consequently, the grain boundary region is best considered as a stressed solid despite being (for example) rich in \( \text{H}_2\text{O} \) (Rutter, 1983). Israelachvili (1992) stated “Such molecularly thin films can behave more like a solid . . ., for example, being able to sustain a finite normal load . . .” implying that
mechanical equilibrium in such a region is as illustrated in Figure 2d (Wheeler, 1991). The normal stress is equal to that in the adjacent minerals. The transverse stress can be equal to the pore fluid pressure as implied in this simple sketch, which then ensures force balance.

Fluid films can exist even in single-component systems below their melting temperatures: “premelting.” For example, a liquid with properties akin to those of water can exist along ice boundaries below 0°C. Such films appear to have the same viscosity as water (Wettlaufer & Worster, 2006) and may flow as a result of freezing providing a sink (or melting providing a source) along boundaries. In multicomponent systems, it is not obvious how such inviscid films might be sustained in a stressed grain boundary and they are not discussed further.

The film illustrated in Figure 2d supports shear stress but not any shear stress parallel to the boundary. In general such solid-like films can support shear stress without sliding, for example, figure 36 of Israelachvili (1992), but above a certain value of shear stress, sliding begins. This generic model is based on experiments with numerous fluids; the data for shear stresses in aqueous films are limited and their behaviour complicated. Homola, Israelachvili, Gee, and McGuiggan (1989) showed that two undamaged mica surfaces separated by a thin (~0.5 nm) film of “environmental adsorbents” (essentially dry) moved at a shear stress of 25 MPa; if water was added this critical stress reduced to 10 MPa; with dissolved KCl this dropped further to <0.1 MPa for normal stresses >20 MPa. The shear velocities in these experiments were 0.2–2.0 μm/s or 6.3–63 m/year so that geologically enormous shear velocities are associated with modest shear stresses. As argued for dry grain boundaries, wet systems undergoing pressure solution show a flow law which is in accord with an assumption of zero shear stress along grain boundaries (Spiers et al., 1990). Tentatively, then, I assert that at “background” geological shear rates along aqueous boundary films, excluding fast events such as the passage of seismic waves, shear stresses parallel to the boundary are likely to be small—in the rest of this contribution it is assumed they are zero.

**1.2.2 | Stress and thermodynamic quantities**

Table 2 shows how some thermodynamic quantities depend on stress. Equation 17 maps to Equation 8 for a hydrostatic stress state, noting that \( k = s_{xxxyy} \) and as argued in Section 1.1, the dependence of \( F \) on stress is small because the compliances are small. The variation in \( F \) with stress is of the order (volume) \( \times \) (volumetric strain) \( \times \) (stress variation). So whatever detailed measure of stress is used in that phrase, the variation in \( F \) must be small in comparison to (volume) \( \times \) (stress variation), when elastic volumetric strains are small. For hydrostatic thermodynamics it implies, to reiterate, that for solids the \( PV \) term in \( G \) has the dominant influence on the value of \( G \). However, beyond this section, agreement is lacking in the development of non-hydrostatic
thermodynamics for Earth science, and different views must be outlined.

2 | INCOMPATIBLE VIEWS

There are several old and new debates, and examples of papers, which express one view without reference to other views. Disagreements are entangled, and I attempt to separate out some notable themes.

2.1 | Can $G$ and hence equilibrium be defined in a stressed system, or not?

Because $G$ plays a central role in hydrostatic thermodynamics some have attempted to generalize the mathematical description using $G$ to encompass stressed systems, so as to provide a general formulation of chemical equilibrium. For example, Macdonald (1957) proposed a generalized form for $G$ in which stress is coupled with elastic strain. He stated “The function $G$ … reduces to the familiar form of the Gibbs free energy for a hydrostatic pressure …” using a value for that pressure equal to mean stress. Similarly, Tajcmanova et al. (2015) proposed that, in stressed systems, mean stress be substituted for $P$ in the hydrostatic equation for $G$. They address the effects of stress variations solely through the effects of mean stress variations which, although they refer to them as “pressure” variations, relate to general states of stress.

In contrast, Kamb (1961) disagreed with Macdonald (1957) and asserted “it is not possible usefully to associate a chemical potential or Gibbs free energy with a non-hydrostatically stressed solid” and McLellan (1980), p. 193 said “… a complete generalization of this function $G$ [Gibbs free energy] cannot be achieved …” Larché and Cahn (1985) stated that in the context of formulating equilibrium conditions in stressed systems “It is dangerous to assert conditions for equilibrium under new restrictions (some type of free energy to be minimized or some potential to be constant) without a derivation that begins with the basic two laws” (those laws being that energy is conserved, and that entropy must increase or stay constant). The works defining $G$ referred to above must be assessed with the last statement in mind.

2.2 | Normal stress or mean stress?

The premise that local normal stress drives diffusion creep (Nabarro, 1948) and pressure solution (Rutter, 1983) leads to flow laws in satisfactory agreement with experiments in terms of stress and grain size dependence. Wheeler (2014) extended the theory which describes diffusion creep and pressure solution (both types of chemical mass transfer induced by differential stress) to include growth of new phases. That theory is based on the effects of normal stress (at various interfaces) on chemical potential, and addresses net transfer reactions which involve some long-range transport.

In an attempt to refute this, Fletcher (2015) provided a model system where overall reaction rate is controlled by mean stress, although his example is for a polymorphic reaction, thus involving only short-range transport across interfaces. Tajcmanova et al. (2015) applied the approach of Wheeler (2014) to a polymorphic reaction (quartz to...
coesite) and, similar to Fletcher (but with a different argument), decide that mean stress is what matters.

Hobbs and Ord (2016) also favour mean stress: “for an elastic solid at equilibrium the thermodynamic pressure is numerically equal to the mean stress and so the mean stress must be used in all considerations of the influence of thermodynamic pressure on thermodynamic equilibrium in stressed elastic solids” (p. 200). However, they also asserted (p. 193) “In some instances (Tajcmanova et al., 2014; Tajcmanova et al., 2015) it is claimed that the mean stress can be used in place of the total stress tensor. These kinds of arguments (in addition to being mechanically and mathematically unsound) can lead to very large errors in calculating the Clapeyron slopes for a mineral reaction . . .” So Hobbs and Ord disagreed with Wheeler; Tajcmanova et al. disagreed with Wheeler; but Hobbs and Ord also disagreed with Tajcmanova et al.

Root causes of controversy are not easy to disentangle.

2.3 Are the effects of stress on mineralogy and chemistry significant?

One should ask the pragmatic question: do the debates matter, if in any case the predictions are not quantitatively significant?

Wheeler (2014) argued that driving forces (affinities) in the order of (differential stress) × (molar volume) are predicted in stressed systems, and these are large in relation to the affinities in the order of (pressure) × (molar volume change during reaction) predicted in hydrostatic thermodynamics, and hence stress effects are important. In simple terms this is because V for a typical mineral is bigger than ΔV for a typical reaction. For example, a modest differential stress (e.g. 50 MPa) can have an effect on affinity equivalent to a pressure change in 500 MPa.

Connolly (2009) sought an equation of state for stressed solids. He considered the internal energy U for a particular

| Quantity or relationship | Symbol or equation | Source |
|--------------------------|-------------------|--------|
| Symmetric 2nd rank stress tensor (compression positive) | σ | |
| Principal stresses | σ1 > σ2 > σ3 | |
| Symmetric 2nd rank elastic strain tensor | E | |
| 4th rank compliance tensor (isothermal) | sI | |
| 4th rank compliance tensor (adiabatic) | sA | |
| Unit vector normal to an interface | n | |
| Force balance at interface between regions a and b | 0 = (σa − σb)n | (13) |
| Normal stress at interface | σn = n.(σn) | |
| Mean stress | σm = (σ1 + σ2 + σ3)/3 = tr σ/3 | (14) |
| Differential stress | σ1−σ3 | |
| Elasticity | | |
| Volume and stress | V(σ) = V(0)(1 + E^*) = V(0)(1 − s^*g_k_l_m_g_k_l) | (16) VJ3.36 |
| Helmholtz free energy and stress | F(σ) = F(0) + 1/2 V(0) s^*g_k_l_m_g_k_l | (17) VJ4.113 |
| Internal energy and stress | U(σ) = U(0) + 1/2 V(0) s^A_g_k_l_m_g_k_l | (18) W8.12 |
phase (his section 2.3) and showed that the effects of elastic strain on $U$ are small in relation to (pressure) $\times$ (volume) terms in thermodynamics—this is in accord with Section 1.2.2. Connolly concluded that mean stress can be substituted for pressure in the relevant equations, thus providing a recipe for deducing equilibrium in stressed systems, and implying that any additional stress effects are small. Tajcmanova et al. (2015) reiterated this view.

Hobbs and Ord (2016) had some different arguments. In the case of the thermodynamics of grain boundaries, and the analysis of pressure solution, they asserted that the effects of stress are smaller than those predicted by Wheeler (2014). Consider some solid–solid grain boundaries under normal stresses $\sigma_n$ with nearby pores which contain fluid at pressure $P_f$. Wheeler used equations based on $\sigma_n$ and then the driving force (affinity) for pressure solution depends on variations in $\sigma_n$. Hobbs and Ord used the mean stress inside the grain boundary film (p. 211) which in the (naïve) model of Figure 2d would equal $\frac{1}{3} (\sigma_n + 2P_f)$, rewritten using my convention that compressive stress is positive. The mean stress provides a smaller affinity related to normal stress variations from place to place, because it contains the factor 1/3. In another section a comparable point is made: they suggested (p. 228) that plausible stress states would perturb equilibria by an amount equivalent to a 20°C temperature change—not a major effect.

## 3 | LOCAL EQUILIBRIA IN STRESSED ROCKS

Having noted some disagreements, I now outline a view of non-hydrostatic thermodynamics based primarily on a paper which builds from first principles: Larché and Cahn (1985), abbreviated as LC. For brevity I do not give derivations; Table S1 tabulates where the key equations, with derivations, can be found in LC and other relevant works (McLellan, 1980; Paterson, 1973; Voorhees & Johnson, 2004) which although providing the same results present the derivations in quite different levels of detail. As well as notation differences, LC take tension as positive and define Helmholtz free energy per unit volume not per mole, so I have rewritten their equations in accord with Earth science convention. I omit discussion of surface and interface energy but their effects are usually comparatively small (Wheeler, 1991).

All of the equilibria discussed are local—they include interfaces with fluids and other solids, and grain interiors (Table 3; Figure 3). Sections 3.1–3.6 relate to the six numbered local equilibria.

### 3.1 | Solid adjacent to fluid

Consider a stressed solid, described for simplicity as being made from a single chemical component, adjacent to a fluid and in mechanical equilibrium (Figure 3a). The fluid cannot support shear stress and so one principal stress in the solid is perpendicular to the interface and has magnitude $\sigma_n$ which (from Equation 13) is equal to the fluid pressure $P_f$. The solid may support a tangential stress different to the normal stress. Then, there is a local description of chemical equilibrium at the interface given by

$$\mu = F + \sigma_n V = F + P_f V$$

This reduces to Equation 9 if stress is isotropic in the solid, as must be expected. Let us examine the effects of changing the tangential stress in the solid, while keeping the normal stress ($= \text{fluid pressure } P_f$) constant. The value of $V$ will change in accordance with Equation 16 and $F$ will change in accord with Equation 17; these variations are small as discussed above and so Equation 19 is approximately linear in $\sigma_n$. This is advantageous for modelling diffusion creep and pressure solution (Wheeler & Ford, 1989).
2007), which is discussed more later. Because the variations in V and \( F \) are small it can also be written:

\[
\mu = F^A + \sigma_n V^A = F^B + \sigma_n V^B
\]  

This means that we can use standard thermodynamic data to calculate chemical potentials at such interfaces. It does not mean that the Gibbs free energy is defined in this situation. It just means that the chemical potential can be conveniently approximated using a Gibbs free energy calculation. Equation 19 is most often referred to for explaining pressure solution: it does, but because pressure solution operates in part at stressed grain boundary films, rather than at surfaces in contact with fluid, discussion is postponed.

### 3.2 Single-component polymorphs at an incoherent interface

The key feature related to “incoherence” is that there are no shear stresses along the interface (LC equation 3.25). Figure 3b shows the idea, in general the lattices will not even be parallel or share any dimension. If the solids are called A and B, then LC equation 3.24 can be simplified, assuming a single chemical component, to

\[
\mu = F^A + \sigma_n V^A = F^B + \sigma_n V^B
\]  

The expression is exactly the same as Equation 19. Coherent interfaces are not discussed further here, however, see LC equation 3.27 and Robin (1974a).

If the two solids are in chemical disequilibrium, force balance (Equation 13) tells us that \( \sigma_n \) must be the same on both solids so the driving force for (affinity of) reaction is

\[
\mu^A - \mu^B = F^A - F^B + \sigma_n (V^A - V^B)
\]  

The normal stress is the main contribution to the affinity since, as argued previously, \( F \) is weakly dependent on stress.

### 3.3 Heterogeneously stressed solid solutions

In this section, I outline how equilibria within grains can be characterized; subsequent sections reconcile equilibria within grains with those at interfaces.

#### 3.3.1 Mobile and immobile components inside a grain

For a single-component stressed solid, if \( G \) can be defined (as some claim) then one would expect it to be numerically equal to chemical potential both inside and at the interfaces, so there should be a single value for chemical potential. However, Equation 19 implies that different values of chemical potential are found depending on interface orientation, even if stress is uniform. This is incompatible with the existence of a Gibbs free energy, in accord with the views of Kamb (1961) and McLellan (1980) as noted in Section 2.1.

However, there is a way forward to deal with multicomponent solids. The fundamental idea is an assertion that one “immobile” (sometimes called solid) chemical component forms a framework or network which cannot participate in chemical processes in the grain interior. Other “mobile” components (which may include vacancies) can diffuse and have thermodynamic properties defined under general states of stress. LC say “… we have defined a network solid as one in which there is an unambiguous method of locating the same place after diffusion, and where the thermodynamic properties are functions of the strain and local composition defined by this network,” referring to Larché and Cahn (1973). Also “There is thus not only no need to define a chemical potential of the solid [immobile] component, but it does not seem to be definable.”

The distinction between mobile and immobile components deserves illustration. \( H \) diffusing in Fe can be considered as a mobile component with Fe as the immobile framework (Li, Oriani, & Darken, 1966). Even in pure Fe, the presence of vacancies allows for a mobile component \( V_{Fe^{-1}} \) to be defined. Gradients in its chemical potential would then drive vacancy diffusion, relevant to, for example, diffusion creep. In minerals one can envisage in (for example) alkali feldspar an immobile aluminium silicate framework with mobile cations. The framework would be charged but to circumvent that it is possible to define the immobile component as NaAlSi\(_3\)O\(_8\) and the mobile component as an exchange vector KNa\(_{0.5}\) (Robin, 1974b, p. 65). In orthopyroxene, one could define immobile MgSiO\(_3\) and mobile FeMg\(_{1-x}\).

The mathematical formulation for the thermodynamics of the mobile components relies on defining a state of lattice strain using the immobile component. In hydrostatic thermodynamics we are familiar with the idea that partial molar volumes are important quantities. These define the extent to which, for example, substitutions in binary solutions alter the molar volume. If there are no non-linear mixing effects then

\[
\bar{V}_{1-o} = \frac{\partial V}{\partial X} = V_1 - V_0
\]  

and is independent of \( X \). Under stress, generalizations of the volume and partial molar volume become useful, taking into account the changes in all lattice parameters as a function of composition, not just the molar volume. The changes from a reference composition can be represented as a “compositional strain” (Voorhees & Johnson, 2004), induced only by...
substituting chemicals, not by stress. It is written as \( \mathbf{E}^c \) to distinguish it from \( \mathbf{E} \), the net strain that is induced by chemical and stress changes, and it depends on \( X \). A dimensionless tensor \( \mathbf{g} \) further characterizes the variation in lattice parameters with composition (LC equation 4.5)

\[
\frac{\partial E^c_{ab}}{\partial X} \, \sigma, T
\]

It has not been named in previous literature but its definition resembles that of a partial molar quantity very closely so I refer to it here as “partial molar strain.” As \( \mathbf{g} \) is a crystallographic property its symmetry is controlled by crystal symmetry, as is the case for other second rank tensor properties such as thermal conductivity (Nye, 1957). For example, it will be isotropic for cubic phases, have one unique value parallel to the symmetry axis for tetragonal, hexagonal and trigonal phases and will have three distinct values, but be aligned with crystal axes, for orthorhombic phases. If chemical variations have linear effects on lattice dimensions, and the changes are small (as assumed for simplicity in most of this contribution) then its trace is

\[
\text{tr } \mathbf{g} = \frac{V_1}{V_0} - 1
\]

and it is useful to define a normalized version of the tensor

\[
\tilde{\mathbf{g}} = \frac{\mathbf{g}}{\text{tr } \mathbf{g}}
\]

which always has unit trace and quantifies the difference in the way each lattice dimension depends on composition. Table 4 gives examples of partial molar strains in common solid solutions.

Consider orthopyroxene with end-member lattice parameters as in Table 4, in this orthorhombic case \( \mathbf{g} \) will be a diagonal tensor in the orthorhombic coordinate system. The component of \( \mathbf{g} \) parallel to \( b \) is about three times bigger than the other two. In other words enstatite does not dilate isotropically as Mg is replaced by Fe; it extends more parallel to the \( b \) axis. Consequently, \( \mathbf{g} \) is strongly anisotropic.

The chemical potentials of mobile components are defined using \( \mathbf{g} \). LC chose to define quantities called “diffusion potentials,” for example, \( M_{jk} \) which relate to two components (I

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**FIGURE 3** Subsystems with local equilibria a to f corresponding to 1 to 6, as in Table 3. All interfaces are incoherent. Red and blue dots represent end-members in solid solutions but can be taken as atoms or groups of atoms; blue is bigger and its end-member has a larger molar volume.
and $K$) but these are equivalent to the chemical potentials of exchange vectors, so LC equation 3.10 gives

$$M_{10} = \mu_{1-0} = \mu_1 - \mu_0$$  (26)

and I will rewrite using more familiar chemical potentials. LC derive a very general equation for the chemical potential so to simplify I assume that elastic coefficients are not themselves dependent on composition. I rewrite their (4.21) with the stress sign convention here (compression positive), for an ideal solution (so omitting activity coefficients), and using Helmholtz free energy (at zero pressure) rather than reference chemical potentials for end-members (see Wheeler, 1986 and Appendices S1 and S2 for a short derivation).

$$\mu_{1-0} = F_1 - F_0 + V_0 \eta_{a'b'} \sigma_{a'b'} + RT \ln \left( \frac{X}{1-X} \right)$$  (27)

The double dot product $\eta_{a'b'} \sigma_{a'b'}$ will be written in vector notation as $\eta : \sigma$. The difference in Helmholtz free energies is a constant under the assumptions made (Appendix S1). It is the middle term which shows the effect of stress. As a first example consider a cubic phase in which $\eta$ is isotropic and hence, noting that

$$\eta_{a'b'} \sigma_{a'b'} = (\text{tr}\eta) \sigma_m = \left( \frac{V_1}{V_0} - 1 \right) \sigma_m,$$

we obtain

$$\mu_{1-0} = F_1 - F_0 + \sigma_m (V_1 - V_0) + RT \ln \left( \frac{X}{1-X} \right)$$  (28)

This reads like Equation 11 except the mean stress is seen to take the numerical role of pressure and it reduces exactly to Equation 11 when stress is isotropic. Equation 28 seems to indicate that mean stress can be substituted for pressure but this is not the full story because it:

1. applies only for mechanically isotropic or cubic crystals;
2. applies only when the elastic coefficients are not themselves dependent on composition;
3. does not imply that a Gibbs free energy can be defined for the stressed crystal—only the chemical potential of the exchange vector can be defined in this binary solid solution example;
4. does not imply that mean stress can be used always instead of pressure since Equation 19, for example, shows normal stress plays the dominant role—they must somehow be reconciled.

Point 1 is illustrated by considering orthopyroxene. For this phase, using Table 4, the middle term in Equation 27 becomes (approximately)

$$V_0 \eta_{a'b'} \sigma_{a'b'} = (V_1 - V_0) (0.2 \sigma_{aa} + 0.6 \sigma_{bb} + 0.2 \sigma_{cc})$$  (29)

So the chemical potential is affected by a very weighted mean value of stress. The stress parallel to the $b$ axis has a relatively large effect, because the substitution of Fe for Mg has a relatively large effect on the $b$ axis length. Such “weighted” values of mean stress will prevail in minerals, which are mostly non-cubic. The assumption that mean stress in its strict definition has a general role is thus shown to be false. The dependence is on all three stresses and their orientation. Define weighted mean stress as

$$\sigma_m = \eta : \frac{\sigma}{\text{tr}\eta} = \tilde{\eta} : \sigma$$  (30)

which equals mean stress only if $\eta$ is isotropic, so Equation 27 becomes

| TABLE 4 | End-member volumes, unit cell parameters and “partial molar strains” for some representative solid solutions; for plagioclase see calculation in Appendix S3 |
| --- | --- | --- | --- |
| Unit cell volume (Å$^3$) | $a$ (Å) | $b$ (Å) | $c$ (Å) |
| Almandine | 1,531.2138 | 11.526 | 11.526 | 11.526 |
| Grossular | 1,664.4279 | 11.851 | 11.851 | 11.851 |
| $\eta$ | 0.0870 | 0.0282 | 0.0282 | 0.0282 |
| $\tilde{\eta}$ | 0.3333 | 0.3333 | 0.3333 |
| Enstatite | 832.1797 | 18.2280 | 8.8050 | 5.1850 |
| Ferrosilite | 875.6191 | 18.4180 | 9.0780 | 5.2370 |
| $\eta$ | 0.0522 | 0.0104 | 0.0310 | 0.0100 |
| $\tilde{\eta}$ | 0.2026 | 0.6025 | 0.1949 |
| Albite | 1,334.4000 | 8.1600 | 12.8700 | 14.2200 |
| Anorthite | 1,337.3000 | 8.1768 | 12.8768 | 14.1600 |
| $\eta$ | 0.0022 | 0.0206 | 0.0023 | 0.0161 |
| $\tilde{\eta}$ | 0.4482 | 1.0617 | 7.3865 |
| Eigenvectors (approx. Miller indices) | [10 -5 3] | [2 2 7] | [9 6 0] |
\[ \mu_{1-0} = F_1 - F_0 + \sigma_w(V_1 - V_0) + RT \ln \left( \frac{X}{1-X} \right) \]  
(31)

For orthopyroxene, then (approximately)

\[ \sigma_w = 0.2\sigma_{aa} + 0.6\sigma_{bb} + 0.2\sigma_{cc} \]  
(32)

Plagioclase provides a particularly informative illustration of the role of \( \eta \) (see Appendix S3 for calculations). The chemical potentials of albite and anorthite cannot be defined separately within a stressed crystal, but that of the exchange vector \( \text{CaAlNa}_{-1}\text{Si}_{-1} \) can be defined. As Table 4 shows, \( \bar{\eta} \) is very anisotropic with one eigenvalue \( >1 \) and two negative eigenvalues so we have, approximately,

\[ \sigma_w = 9.5\sigma_{pp} - 1\sigma_{qq} - 7.5\sigma_{rr} \]  
(33)

where the \( p, q \) and \( r \) directions are given by the eigenvectors of \( \eta \).

The significance of the behaviour of mobile components is now illustrated further using these minerals as examples. In each example I consider \( X \) varying from 0.10 to 0.12, a detectable variation, at 500°C. In terms of actual magnitude the effects of stress variations are likely to be small because of the small volume differences between end-members in the context of Equation 31—but the examples illustrate a basis for establishing whether that is always the case. There may be circumstances in which the effects are important and the chemistry then fingerprints stress levels.

3.3.2 | Heterogeneously stressed solid solution: garnet

Suppose we have a heterogeneously stressed solid solution crystal (Figure 3c). Within that crystal, ignoring its interfaces, we can define an equilibrium (only for the mobile component) by fixing the value of \( \mu_{1-0} \). Using Equation 31 the magnitudes of stress variation required to give significant chemical variations can be estimated. If the equilibrium values of \( X \) are given at points A and B then we obtain

\[ \sigma^A_w - \sigma^B_w = \frac{RT}{V_1 - V_0} \left( \ln \left( \frac{X^B_i}{1 - X^B_i} \right) - \ln \left( \frac{X^A_i}{1 - X^A_i} \right) \right) \]  
(34)

Take almandine–grossular with \( X_{\text{Ca}} \) varying from 0.10 to 0.12, then at 500°C we find that the variation in (in this case) \( \sigma_m \) required is 129 MPa, which if established (for the sake of illustration) by varying just one principal stress would require that value to vary by 386 MPa. There is an 8.7% volume difference between almandine and grossular (Table 4). If instead we consider almandine–pyrope, with \( X_{\text{Fe}} \) varying from 0.10 to 0.12 we find the variation in \( \sigma_m \) required is 682 MPa, because the volume difference in Equation 34 is much smaller. Very large stress heterogeneities are required to give significant variations in equilibrium composition.

3.4 | Solid solution grains of different orientation

3.4.1 | Orthopyroxene

Consider the geometry in Figure 3d in which the stress is the same in the two grains but \( \sigma_w \) is different because of the anisotropy of \( \bar{\eta} \). Suppose the \( a \) axis points out of the page while the \( a \) and \( b \) axes are rotated 90°, that Fe and Mg can exchange between the two crystals but nothing else can happen at the interface, and that \( \sigma_x = \sigma_z \) and the vertical stress \( \sigma_y = \sigma_x + Q \). We have

\[ \sigma^A_w = 0.2\sigma_x + 0.6\sigma_y + 0.2\sigma_z = \sigma_x + 0.6Q \]

and

\[ \sigma^B_w = 0.6\sigma_x + 0.2\sigma_y + 0.2\sigma_z = \sigma_x + 0.2Q \]

so

\[ \sigma^A_w - \sigma^B_w = 0.4Q \]

If we postulate a \( X_{\text{Ca}} \) as 0.1 in A and 0.12 in B we find the difference in \( \sigma_w \) required is 400 MPa (from Equation 34) so the required \( Q = 1 \) GPa, a very large differential stress. However, non-cubic solid solutions with much larger partial molar strains could potentially, using this idea, serve as chemical piezometers.

3.4.2 | Plagioclase

Applying Equation 34 to plagioclase, ignoring non-ideal mixing because just a rough estimate is required, we find that if \( X_{\text{An}} \) varies from 0.10 to 0.12 then a variation of 6 GPa in \( \sigma_w \) is needed; a number influenced by the small volume difference between the unit cells. It is difficult to believe such variations will exist. Using an (incorrect) calculation with mean stress, we would have to vary all stresses by 6 GPa or some by more than 6 GPa. Because of anisotropy, stress can then have an effect much larger than the incorrect calculations using mean stress would imply. For example, let us increase stress in all directions by 100 MPa, then \( \sigma_m \) and \( \sigma_w \) both increase by 100 MPa. The chemical potential of the exchange vector increases in accordance with Equation 31 because anorthite has a bigger molar volume (\( V_1 \)) than albite (\( V_0 \)). Instead let us impose a stress increase of 300 MPa in just one direction, given by the eigenvector associated with the maximum eigenvalue of \( \bar{\eta} \) (roughly [10, –5, 3]). This increases \( \sigma_m \) by 100 MPa (as stated earlier) but increases \( \sigma_w \) by 300 \times 9.45 = 2,840 MPa. In other words, because the \( a \) axis elongates considerably as anorthite substitutes for albite, the chemistry is particularly susceptible to stress changes in that direction. The effect is 28 times bigger than would be predicted by mean stress calculations. Stress increases in
other directions can, in contrast, decrease the chemical potential of the exchange vector. So, while it remains debatable whether such stress levels exist on the scale of mineral grains, a correct understanding of the partial molar strain and its anisotropy is essential to explore such possibilities.

### 3.5  Reconciliation of normal stress and weighted mean stress: solid solution next to fluid

Figure 3e illustrates the situation. Equation 19 showing dependence on normal stress appears to contradict Equation 28 showing dependence on weighted mean stress. They can be reconciled by noting that the chemical potential of the "immobile" component $K$ is not defined within the stressed solid, but it can be defined at an interface using those two equations together. So LC define an equilibrium of a solid solution with a fluid (their equation 3.15 rewritten)

$$\mu_K = F + \sigma_n V - \sum_{i\neq K} X_i \mu_{i-K}$$  \hspace{1cm} (35)

Note the similarity to Equation 19. At local equilibrium, $\mu_K$ as defined above at the interface is the same as equilibrium $\mu_K$ in the fluid, and each $\mu_{i-K}$ is the same in solid and fluid. In Appendix S4, discussing for simplicity an ideal binary solid solution, it is shown that

$$\mu_0 = F_0 + RT \ln(1 - X) + [V_0(1 - X) + V_1 X] \sigma_n + [V_0 - V_1] X \sigma_w = F_0 + RT \ln(1 - X) + V_0 \sigma_n + [V_0 - V_1] X (\sigma_w - \sigma_n)$$  \hspace{1cm} (36)

and

$$\mu_1 = F_1 + RT \ln X + [V_0(1 - X) + V_1 X] \sigma_n + [V_1 - V_0] \sigma_w = F_1 + RT \ln X + V_1 \sigma_n + [V_1 - V_0] X (\sigma_w - \sigma_n)$$  \hspace{1cm} (37)

The same expressions for $\mu_0$ and $\mu_1$ can be derived assuming either end-member 0 or end-member 1 is immobile. Thus, the arbitrary choice of which end-member is defined as immobile does not affect the mathematical outcome. In, for example, orthopyroxene, the key assumption used here for illustration is that the charged Si–O framework is immobile and Fe and Mg can move by exchange.

The second form of these equations allows us to see the effect of varying differential stress parallel to the interface while keeping $\sigma_n$ constant because $\sigma_w - \sigma_n$ depends on the differences between the tangential and normal stresses, together with $\tilde{n}$. If the two principal stresses parallel to the interface are $\sigma_1$ and $\sigma_2$ then

$$\sigma_w - \sigma_n = (\sigma_1 - \sigma_n) \tilde{n}_{11} + (\sigma_2 - \sigma_n) \tilde{n}_{22}$$

Inspecting Equation 36 shows that if $\sigma_w - \sigma_n$ is increased (more compressive stress parallel to interface) then if $V_0 - V_1 > 0$ the chemical potential of 0 is increased. In other words, if $\sigma_n$ is kept fixed, more compressive tangential stress increases the chemical potential of the less dense end-member. However, a large increase in $\sigma_w - \sigma_n$ is required to make the same change as a small increase in $\sigma_n$, because in the last term in Equation 36 we have $V_0 - V_1$ which is generally (as a survey of common solid solutions reveals) much smaller in magnitude than $V_0$ or $V_1$. Despite this the last term should not be omitted as a simplifying approximation because, for some local equilibria, further analysis highlights its importance. The next section gives an example.

### 3.6  Two different solid solutions

#### 3.6.1  Two different solid solution minerals

Figure 3f illustrates the situation. LC equation 3.23 defines the immobile component chemical potential at an interface and, when rewritten, is exactly the same as Equation 35. At equilibrium between two solid solutions, then, the chemical potential of any mobile component is the same in the two solids, and equilibrium for the immobile component (their equation 3.24 rewritten) means

$$\mu_K = F^K + \sigma_n V^K - \sum_{i\neq K} X_i^{A} \mu_{i-K}^{A} = F^K + \sigma_n V^K$$  \hspace{1cm} (38)

If we consider $A$ as a single chemical component then we have

$$\mu = F^K + \sigma_n V^K$$  \hspace{1cm} (39)

in this situation, and when adjacent to fluid (Equation 19), and when adjacent to an isochemical polymorph (Equation 21). It seems reasonable to claim, then, that this is the unambiguous definition of chemical potential of a stressed solid at any interface other than a coherent one. Equation 38 gives the relationship between the chemical potential of an immobile component at the interface between two different solid solutions, when that component is immobile in both.

LC do not actually discuss equilibria between solids with different immobile components, so I define here an extension to their theory. Suppose the immobile components are $K$ in A and $L$ in B, then at the interface

$$\mu_K = F^K + \sigma_n V^K - \sum_{i\neq K} X_i^{A} \mu_{i-K}^{A}$$  \hspace{1cm} (40)

and

$$\mu_L = F^L + \sigma_n V^L - \sum_{i\neq L} X_i^{B} \mu_{i-L}^{B}$$  \hspace{1cm} (41)

Suppose $K$ is mobile (as an exchange vector with $L$) in phase B, then at the interface there is buffering:

...
where the left hand side is defined at the interface and the right hand side within B.

As an example consider orthopyroxene, which can hold significant Al at low pressures via a Tschermak substitution, adjacent to garnet (which is assumed to be stoichiometric pyroxene), the reaction being

\[
\text{Mg}_2\text{Si}_2\text{O}_6 + \text{MgAl}_2\text{Si}_3\text{O}_8 = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}
\]

Let \( X \) be the mole fraction of ts, MgAl_2SiO_6. The orthopyroxene has two sites that can hold Mg but because Al substitutes for Mg only on the smaller M1 site, we have \( X_{\text{M1}} = X \) and \( X_{\text{M2}} = 1 - X \). So Wood and Banno (1973) Equation 7 shows \( a_{\text{ts}} = X \) and \( a_{\text{en}} = 1 - X \). Wood (1974) (Equation 3) defines the equilibrium using \( \Delta G \) at 1 bar. Using

\[
\Delta G(1\text{bar}, T) - (1\text{bar})\Delta V = \Delta F(1\text{bar}, T)
\]

this can be rewritten, for a fixed temperature and noting that \( \Delta F \) is not sensitive to pressure, as

\[
RT\ln(X(1 - X)) = \Delta F(1, T) + P\Delta V
\]  

(43)

where

\[ \Delta V = \bar{V}_p - \bar{V}_e - \bar{V}_t < 0, \]

so as \( P \) increases \( X \) decreases. This solid solution has a non-linear volume mixing effect so the partial molar volumes vary; for \( X = 0.05 \) we have \( \Delta V = -8.05 \times 10^{-6} \text{ m}^3/\text{mol} \) (Table 1 of Wood & Banno, 1973). In the non-hydrostatic analysis we must define the mobile component as the exchange vector tse, Al_2Mg_1Si_1 so

\[
2\text{Mg}_2\text{Si}_2\text{O}_6 + \text{Al}_2\text{Mg}_1\text{Si}_1 = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}
\]

and we require

\[
\mu_{\text{py}} - 2\mu_{\text{en}} = \mu_{\text{opx}}
\]  

(44)

At the interface we have, from Equation 28,

\[
\mu_{\text{opx}} = F_{\text{ts}} - F_{\text{en}} + \sigma_w(\bar{V}_{\text{ts}} - \bar{V}_{\text{en}}) + RT\ln\left(\frac{X}{1-X}\right)
\]  

(45)

The partial molar strain used here for calculating \( \sigma_w \) is for the Mg-ts substitution and is not the same as for Fe substitution, and the unit cell parameters are not a linear function of composition so the equations in Appendix S2 are used. For \( X = 0.05 \), \( \bar{\eta} = [0.25, 0.4, 0.35] \), using unit cell data from Arima and Onuma (1977). Assuming the same \( \partial V/\partial P \) for all phases, Equation 45 is rewritten using Equation 35 as

\[
F_{\text{py}} + V_{\text{py}}\sigma_n - 2(F_{\text{en}} + RT\ln(1 - X) + \bar{V}_{\text{en}}(1 - X) + \bar{V}_{\text{ts}}X\sigma_w) = F_{\text{ts}} - F_{\text{en}} + \sigma_w(\bar{V}_{\text{ts}} - \bar{V}_{\text{en}}) + RT\ln\left(\frac{X}{1-X}\right)
\]

(46)

Rearranging

\[
RT\ln(X(1 - X)) = F_{\text{py}} - F_{\text{en}} - F_{\text{ts}} + (V_{\text{py}} - 2(V_{\text{en}}(1 - X) + \bar{V}_{\text{ts}}X))\sigma_n - 2\bar{V}_{\text{en}}\sigma_w - \sigma_n(\bar{V}_{\text{ts}} - \bar{V}_{\text{en}}) = \Delta F + \Delta V\sigma_n + (1 - 2X)(\sigma_n - \sigma_w)(\bar{V}_{\text{ts}} - \bar{V}_{\text{en}})
\]  

(47)

For a hydrostatic situation \( \sigma_n = \sigma_w = P \) so Equation 47 reduces to Equation 43 but more generally we see the separate contributions of \( \sigma_n \) and \( \sigma_w \). For \( X = 0.05 \) we have \( \Delta V = -8.05 \times 10^{-6} \text{ m}^3/\text{mol} \) and \( \bar{V}_{\text{ts}} - \bar{V}_{\text{en}} = -3.9 \times 10^{-6} \text{ m}^3/\text{mol} \) which is comparable in magnitude. Changing composition from \( X = 0.05 \) to 0.07 could be caused by a reduction in hydrostatic pressure by 250 MPa at a nominal 500°C. It could also be caused by increasing \( \sigma_w \) by 577 MPa whilst keeping \( \sigma_n \) fixed, recalling that \( \bar{V}_{\text{ts}} - \bar{V}_{\text{en}} \) is negative (Figure 4). More Al rich solid solutions have chemistries more sensitive to differential stress.

**FIGURE 4** Tschermak substitution in orthopyroxene (right in each sketch) adjacent to garnet (left) showing the effects of normal stress and weighted mean stress. The smaller red “atoms” in orthopyroxene are a graphical representation of the Tschermak substitution with a visual reminder that this is associated with a volume decrease. (a) A situation in which stress parallel to the interface is low. (b) Increasing stress parallel to the interface increases the weighted mean stress and increases the Tschermak component in accord with Equation 47.
This means, although high stress levels are required (which may occur in particular situations discussed later), there is the potential here for the chemistry to record differential stress levels, and to define a palaeopiezometer based on chemistry.

### 3.6.2 Solid adjacent to grain boundary film

In Section 1.2 it was pointed out that grain boundaries may incorporate aqueous or other films and they should not be regarded as fluids but as stressed solids. If present these provide fast diffusion pathways (Rutter, 1976). So, to understand diffusion in grain boundaries we must somehow consider the diffusing chemicals as mobile components in a stressed solid. This begs a number of questions about the detailed structure of grain boundaries which are not easily answered. Can we model the region as crystalline and hence apply the above theory at all? What are the mobile and immobile components? What activity model should be used? However, simplified models for solutes in grain boundaries have been in use for some time and bypass all these problems. A key idea is that grain boundaries, since they have very small volume, are locally buffered by (i.e. are in local equilibrium with) the adjacent solids. If we consider a single-component solid for simplicity, Equation 39 then defines chemical potential for all interfaces except coherent ones and hence defines local chemical potential of the diffusing component in the grain boundary region.

Diffusion is linked to chemical potential gradient by an Onsager diffusion coefficient $L$ and a notional grain-boundary width $w$:

$$ C = -Lw\nabla \mu = -LVw\nabla \sigma_n \quad (48) $$

where $C$ is the diffusive flux in mol m$^{-1}$ s$^{-1}$ and the slight dependence of $F$ on stress is ignored. The mathematics is unchanged from treatments such as Rutter (1983) but the physical model behind it is clarified. That mathematical framework is sufficient to explain and quantify pressure solution and diffusion creep and leads to flow laws in accord with those deduced from experiments.

Boundary films show complicated properties: there are links between film thickness and normal stress (Israelachvili, 2011), and between surface and interface energies and film structure (Hickman & Evans, 1995); all relevant for $w$. Solutes have diffusion coefficients different to those in bulk fluid (Alcantar, Israelachvili, & Boles, 2003), relevant for $L$. Such properties have huge effects on the kinetics of diffusion through Equation 48 but not on the driving force. For example, Hickman and Evans (1995) discussed how high normal stress relates to thinner films (smaller $w$), and hence reduced diffusive fluxes (even if the diffusion coefficient is unaffected by stress). Nevertheless the driving force (their equation 4) is exactly in accord with Equation 39. In contrast, Kristiansen, Valtiner, Greene, Boles, and Israelachvili (2011) asserted that many mineral dissolution phenomena can be driven by electrochemical processes rather than a “pressure” (they mean normal stress)-driven process. However, Gratier, Dysthe, and Renard (2013) reinterpreted such work: “It is evident . . . that the electrochemical potential is extremely important in changing the dissolution rate of quartz . . .”, but the mathematical description “. . . shows that the strain rate is also proportional to a pressure–dependent factor, which is the thermodynamic driving force.” There is a very basic argument in favour of a single equation describing equilibrium chemical potential at the surface of a stressed solid. If the potential were different depending on the adjacent structure (free fluid, boundary film, solid . . .) then there would be permanent chemical potential differences in systems with free fluids and boundary films. Diffusion between films and free fluid would persist indefinitely—the implication of perpetual motion should engender caution (Sheldon, Wheeler, Worden, & Cheadle, 2004).

In the preceding sections I laid out an internally consistent theory for non-hydrostatic thermodynamics, derived by LC from first principles and addressing the six types of local equilibria shown in Figure 3. I now revisit the incompatible views described above.

### 4 HARMONIZATION OF INCOMPATIBLE VIEWS

I provide counter-arguments to those of Section 2 to illustrate how the theory I have outlined can be applied in a variety of situations.

#### 4.1 Can $G$ and hence equilibrium be defined in a stressed solid, or not?

$G$ cannot be defined in a stressed solid. Adding to the remarks of Kamb and LC, I consider diffusion creep and pressure solution. Unless one considers these processes as entirely divorced from the effects of stress and chemistry, they are relevant. They proceed, driven by stress, so long as differential stress persists. Consequently, perpetual disequilibrium characterizes stressed systems. The assertion by Tajcmanova et al. (2015) that Gibbs free energy can be used to define chemical equilibrium in stressed systems is not based on first principles, and does not provide any
opportunity to understand how pressure solution and reaction may occur together.

4.2 | Normal stress or mean stress?

We have a spectrum of quantitative links between stress and its thermodynamic effects.

1. Normal stress provides the most significant term in the expression for chemical potential at stressed interfaces, taking the solid chemistry as a single component. The same expression applies whether next to a fluid (Equation 19), a solid of identical composition (Equation 21) or a solid in which the mineral can dissolve.

2. For mobile components inside a stressed crystal, mean stress can be substituted for pressure in some thermodynamic equations (for mobile components) if the crystal is cubic (Equation 28).

3. A weighted mean stress can be substituted for pressure in some thermodynamic equations (for mobile components) for lower symmetry minerals (Equation 31). Mean stress is not a relevant quantity for quantifying the thermodynamics of such minerals. The phrase “rather mean” in the title of this contribution indicates that mean stress in its strict definition is only relevant for cubic minerals, and then only for their interiors not their interfaces.

4. For solid solution minerals, the chemical potentials of each component can be defined at interfaces and are functions of weighted mean stress and normal stress.

Fletcher (2015) analysed a model microstructure of two polymorphs arranged in a chessboard pattern to show that mean stress governs the evolution of the system. Implicit in this correct analysis is that there is disequilibrium, and reaction is ongoing. However, if one simply considers rectangular rather than square grains, we find instead of the mean stress that a weighted mean stress is what controls reaction (Wheeler, 2015a). This is loosely analogous to the discussion around Equation 27 (where an anisotropic lattice means that a weighted mean stress is involved) and Equation 28 (where an isotropic lattice means that a simple mean stress is involved). In the discussion of Fletcher’s idea, we see that an anisotropic microstructure means that a weighted mean stress is involved, and an isotropic microstructure means that a simple mean stress is involved.

Tajcmanova et al. (2015) applied the mathematics of Wheeler (2014) for a quartz — coesite transformation. For a differential stress of (in their example) 100 MPa they found deviations in the onset of reaction of ±1 GPa. Their mathematics is correct but their physical model, if made explicit (Figure 5), shows how the affinities they calculate are unlikely to be relevant. Wheeler (2014) did not discuss polymorphic transformations and his arguments are based on the requirement for long-range diffusive transport for reactions involving several phases. Figure 5 shows the transport pathways for forceful crystallization (path 1) and for incongruent pressure solution (path 2). But in this case, they are extremely unlikely to be relevant because the transformation can be accomplished simply by transport across, not along, grain boundaries (path 3).

In this case, Equation 22 tells us that the local $\sigma_n$ is the main stress-related factor controlling affinity. This is in accord with what Hirth and Tullis (1994) found in experiments where quartz transformed to coesite. But from the same experiments Tajcmanova et al. argued “The observation of coesite occurs under exactly the same maximum principal stress ($\sigma_1$) as predicted by hydrostatic thermodynamics (see experiments at 700°C) suggesting that in this case the effect of differential stress did not influence the location of the equilibrium.” There is a lack of logic in this sentence. Hydrostatic thermodynamics cannot by definition make any predictions about what may happen when there is differential stress. For that we need non-hydrostatic thermodynamics. What they are probably trying to say is this: the effect of $\sigma_1$ on coesite formation is numerically comparable to the effect of a hydrostatic pressure equal to $\sigma_1$. This fits with previous sections in this contribution: Equation 20 together with the approximation in Equation 23 suffice to explain this experiment.

Hobbs and Ord (2016) had “thermodynamic pressure” as key to their argument, which they claimed is equal to mean stress. The thermodynamic definition of pressure is $-\partial U/\partial V$ in hydrostatic thermodynamics (Equation 7) and their equation 2.4 (they quoted Callen p. 35). They rewrote

![FIGURE 5 Sketch showing the reaction pathways used in calculations by Tajcmanova et al. (2015). Black arrow tails show sites of dissolution, arrow bodies possible transport paths and arrow heads show sites of precipitation. 1 is akin to forceful crystallization and 2 to incongruent pressure solution. I suggest Path 3 is more plausible than either since no long-range transport of silica is involved.](image-url)
the energy $U$ (Equation 18) in two parts (p. 200, although in error they omitted the $1/2$)

$$U(\sigma) = U(0) - \frac{1}{2} V(0) \left( \tau_{\beta\beta} E'_{a\beta} + \sigma_\alpha E_{a\alpha} \right)$$  \hspace{1cm} (49)

The $E_{\alpha\beta}$ term is the fractional volume change and $E'$ is the deviatoric strain. They then asserted that $\partial U/\partial V$ is derived just from the second term and is equal to $-\sigma_{\alpha\alpha}$ citing Slattery and Lagoudas (2005), although that work does not in fact refer to mean stress. Moreover, since $\partial U/\partial V$ is a partial derivative, it needs to be clear what is being fixed as $V$ is varied because in general all six components of strain can vary. So far as I can tell, Hobbs and Ord are (implicitly) allowing only isotropic strain variations. For more general strain variations $\partial U/\partial V$ has a spectrum of values: from Equation 16 we have

$$dV = V(0)dE'_{a\alpha}$$  \hspace{1cm} (50)

and from Equation 18

$$dU = -V(0)\sigma_{\alpha\beta}dE'_{\beta\beta}$$  \hspace{1cm} (51)

Suppose we have a state of anisotropic stress. Let a particular volume change $dV$ be established by strain parallel to the $\sigma_3$ axis, so $V(0)dE'_{a3} = dV$ and the other strains are zero. Then these two equations show that $dU = -\sigma_{33}dV$. Now let the same volume change be enacted by strain parallel to $\sigma_1$ axis, then $dU = -\sigma_{11}dV$. It is obvious that $\partial U/\partial V$ can have different values depending on the different strains which can give rise to a particular volume change. It is incorrect of Hobbs and Ord to say it is equal to mean stress and in any case the usefulness of $\partial U/\partial V$ in non-hydrostatic thermodynamics has not been demonstrated from first principles.

### 4.3 Are the effects of stress on mineralogy and chemistry significant?

Connolly (2009) is correct that the effects of elastic strain on $U$ (or by analogy $F$) are small in relation to (pressure) $\times$ (volume) terms in thermodynamics. It is, however, a complete non-sequitur to assert then that mean stress can be substituted for pressure in the relevant equations adopted from hydrostatic thermodynamics. This is because he does not justify the nature or even existence of a $PV$-type term in non-hydrostatic thermodynamics. My discussion above shows that there is always some kind of “$\sigma_\alpha V$” term, a generalization of $PV$, in non-hydrostatic thermodynamics but that its nature depends on the type of local equilibrium being discussed. In both hydrostatic and non-hydrostatic thermodynamics we find

Chemical potential = (term related to Helmholtz free energy, rather insensitive to stress) + more significant (stress term) $\times$ (volume term)

The fact that the first term is insensitive to stress is of no value in justifying an incorrect form for the second term. It also should not be used to dismiss the general influence of stress on metamorphic evolution.

In an attempt to refute the arguments of Wheeler (2014), Hobbs and Ord (2016) focussed on the thermodynamic description of the grain boundary region. They asserted in their equation 3.25 that mean stress, which would equal $\frac{1}{3}(\sigma_n + 2P)$ in a (very simplified) model, will control the chemical potential of the adjacent solid. This term is smaller than $\sigma_n$ so they deduced the effect of stress is smaller than that predicted by Wheeler (2014) (0.4 of that value). However, I can find no justification in LC for the use of mean stress in their equation 3.25. As explained in Section 4.2, $-\partial U/\partial V$ does not have a unique value in a stressed system and it is arbitrary to assign it a value equal to mean stress.

The idea that mean stress will be the main influence on equilibrium has led to opposition to the claim that stress can have a large effect on metamorphic reaction. The discussion above shows that there is no equilibrium in stressed systems and that (weighted) mean stress often plays a secondary role in the chemical response to stress (e.g. Equation 34), although it is sometimes significant (e.g. Equation 47). The primary factor in the chemical response to stress in rocks is the normal stress across each interface, as shown by, for example, Equations 19, 21 and 36. To reiterate Wheeler (2014) briefly, the affinity $A$ of Equation 12 can be generalized to

$$A = \sum_i C_i \mu_i (\sigma_{nB})$$  \hspace{1cm} (52)

where $\sigma_{nB}$ indicates the normal stress at a particular interface $B$ which is buffering component $i$. Since there are many choices for interfaces for each component $i$, $A$ is multivalued. Taking end-members for simplicity, the $\mu_i$ are roughly linearly dependent on the $\sigma_n$ (Equation 20) so

$$A \cong A_0 + \sum_i C_i V_i / \sigma_{nB}$$  \hspace{1cm} (53)

In the hydrostatic situation all the normal stresses are equal to $P$ and this becomes

$$A \cong A_0 + P \Delta V$$  \hspace{1cm} (54)

In a stressed state in which some interfaces are under $\sigma_1$ (affecting chemical components denoted by $i$) and others under $\sigma_2$ (affecting chemical components denoted by $j$), so

$$A \cong A_0 + \sigma_1 \sum_i C_i V_i + \sigma_2 \sum_j C_j V_j.$$  \hspace{1cm} (55)

The volume terms here depend on which interfaces are chosen but the key point is that terms such as $\Sigma_i C_i V_i$ will
typically have a much bigger magnitude than $\Delta V$, hence varying a particular stress such as $\sigma_1$ will have a much bigger effect than varying the pressure $P$ in a hydrostatic situation. Consequently, I reassert that normal stress variations between different interfaces will have a major control on reaction affinities, as discussed in Section 2 above, and by Wheeler (2014).

I will now discuss the past success and the future potential of the theory outlined above for understanding chemical change in rocks.

## 5 | DISCUSSION

Figure 6a summarizes the local equilibria addressed in this contribution. Local equilibria give rise to local values for chemical potential which vary from place to place, giving a driving force for long-range transport, with examples of resulting reaction pathways in Figure 6b. This situation is just a generalization of the hydrostatic case illustrated in Figure 1c where we see two local equilibria (brucite against fluid, and fluid against periclase) and net disequilibrium with a transport pathway between the two minerals. Even locally there may be disequilibrium (as in Figure 1d, e) and it can be treated by quantifying each step in the reaction—for example, the overall reaction rate in Figure 1e is given by Lasaga (1986). In an analogous way, in experiments on olivine to spinel (Vaughan, Green, & Coe, 1984) there is obviously local disequilibrium (no diffusion required, but reaction is not instantaneous) and a reaction rate term can be defined based on Equation 22. In experiments on gypsum pressure solution, a rate term for precipitation can be defined (de Meer & Spiers, 1999) based on Equation 19.

Because there is no global equilibrium in stressed systems, there is a rich variety of possible behaviours depending on the relative rates of various processes. Even in hydrostatic systems we do not have a complete description of reaction kinetics. To generalize our understanding of kinetics to stressed systems will be an interesting challenge: in this contribution I have shown how to quantify the driving forces. My aim in this discussion is to stimulate new ways of interpreting mineralogical and chemical patterns in rocks where stress may have had an effect. Not all aspects of the theory have been tested by experiments, and even when they have, interpretations vary. Part of the problem is that—in my view—there is no equilibrium to be reached; all we will ever see in experiments is evolution, and any interpretation will be based on a picture involving processes as well as local equilibrium, with plenty of room for debate. Nevertheless, in the next section I note some possible tests as I consider the six local equilibria, and also highlight that atomistic models could play a role. I address the local equilibria in order, although the ones involving

![Figure 6](image-url)  
**Figure 6** Synthesis of how stress affects chemistry during metamorphism. In (a), six types of local equilibria are shown in accord with Table 3 and Figure 3. The solid arrows show local chemical exchange related to each local equilibrium. The open arrows indicate two $b$ axis orientations in orthopyroxene. In (b), long-range transport pathways are shown.
normal stress at interfaces are the most important. I then comment on the overall behaviour of stressed rocks.

5.1 | Particular equilibria

Local equilibrium (1), Equation 19, is not controversial and has been widely discussed. The approximation of Equation 20 is adequate if the phase is involved in some net reaction involving other minerals, for example, precipitation in a pore as part of pressure solution. However, for a simple situation of dissolution and precipitation, the small stress dependence of Helmholtz free energy can lead to instabilities and modifications of crystal surfaces as shown theoretically (Asaro & Tiller, 1972; Grinfeld, 1986) and in experiments (Misbah, Renard, Gratier, & Kassner, 2004).

Local equilibrium (2), Equation 22, is sufficient to explain polymorphic transformations under stress seen in experiments. As with other interface processes in hydrostatic thermodynamics, one can define a rate term based on departure from that equilibrium, of the form \( k(\mu^A - \mu^B) \) or a more complicated non-linear relationship. This is then dependent on normal stress. If a volume decrease occurs, then interfaces with the highest normal stress will have the highest reaction rates; on other interfaces reaction rates will be slower or even have the opposite sign. This scheme accounts for anisotropic growth in the olivine to spinel transformation of Mg$_2$GeO$_4$ (Vaughan et al., 1984). Their equation 2a, although derived in a very brief fashion, is the same as Equation 22. More recently, in experiments on coesite growth from quartz, Richter, Stunitz, and Heilbronner (2016) showed “In all cases, \( \sigma_1 \) triggered the quartz–to–coesite reaction as well as the reverse reaction, suggesting that \( \sigma_1 \) is the critical parameter for the quartz–to–coesite transformation.” For ice I to ice II, Kirby, Durham, and Stern (1991) said “The kinetic criterion for bulk transformation at a given T therefore depends on the maximum normal stress, \( \sigma_1 \), and the time under normal stress, for both hydrostatic and non-hydrostatic conditions.” These three experimental studies support the use of Equation 22. They do not provide the full story because the stress field will itself evolve in a non-uniform way as the product phase evolves (Moulas, Burg, & Podladchikov, 2014)—there will be feedback between reaction rate, morphological evolution and stress field. Consequently, the published experiments are not sufficient to engender agreement on the best mathematical description—at least models including stress field evolution as well as local equilibria are required. Further work is also required to clarify how it will help to explain other experimental results such as when reaction and diffusion creep occur together, for example, (Schubnel et al., 2013).

Local (grain scale) equilibrium (3), Equation 31, predicts that varying composition of solid solution minerals might relate to varying stress. The examples of Section 3.4 suggest that differential stresses of GPa are required before there is much chemical effect. However, there may be solid solutions in which \( \eta \) is significantly greater than in the minerals discussed there, and the effects of stress would accordingly be greater. In addition stresses of the order of GPa may form around inclusions, which are foci for stress if their elastic and thermal properties differ from those of the surrounding host mineral (Angel, Nimis, Mazzucchelli, Alvaro, & Nestola, 2015). There may be chemical patterns within the host grains that relate to such stress systems. Concentric zoning patterns on the scale of whole grains are likely to be in disequilibrium and related to growth, but non-concentric compositional patterns within individual grains could relate to stress. Variations might be subtle, and would link to stress only if they were “frozen in” before stress levels decreased. Around dislocations there are differential stresses in the order of (elastic modulus) \( \times (\)Burgers vector\()/(distance from dislocation)\). Even at a distance equivalent to 100 Burgers vectors, differential stresses of \( \sim 1 \) GPa are predicted and such stress fields give consequent chemical variations—the “Cottrell atmosphere” of impurities. Piazzolo et al. (2016) documented a possible geological occurrence. Mishin and Cahn (2016) showed how atomistic computer simulations of Al segregation on a dislocation in Ni are in agreement with LC theory and similar studies could be made of minerals. Local equilibrium (4) shows that under stress a correlation between crystal orientation and chemistry could be expected, again if mobile components equilibrated and were then frozen in: this is a testable idea. Plastic deformation and continuous chemical evolution as stress and temperature changed would of course complicate the signal. Nevertheless, there might be compositional variations in metamorphic rocks that have passed unnoticed or remain unexplained, but which could be used to deduce past stress levels—chemical palaeopiezometry.

Local equilibrium (5), of stressed solid solution with fluid, probably has comparable importance to local equilibrium (1).

5.2 | The general and most important aspects of how stress couples with chemistry

Local equilibrium (6), Equation 39, is general and the most important in this whole contribution. The arguments of Section 3.6 show that in essence Equation 39 is an unambiguous definition for chemical potential at any stressed interface (other than a coherent one which supports shear stress). In a strictly local way it can be used to define chemical palaeopiezometers such as in the garnet–orthopyroxene example, where garnet buffers the tschermak content of a stressed orthopyroxene. This is somewhat different to the previously mentioned chemical palaeopiezometers because it involves two different phases,
although it is founded on the same theory. More significantly, by defining stress-dependent chemical potentials Equation 39 also provides the basis for analysing long-range reaction pathways as well as local equilibria.

Some long-range reaction pathways are shown in Figure 6b. Some are drawn along interfaces as these are the main diffusive transport pathways at crustal conditions, although they could equally pass well through grain interiors when lattice diffusion prevails. What matters for the overall reaction affinity is the start and end positions, that is, which interfaces are involved with dissolution and precipitation.

Although not always stated and justified in quite the same way, Equation 39 has almost always been used to describe pressure solution and diffusion creep—to that extent, it is already tested. Variations in normal stress give rise to variations in chemical potential with lead to gradients and hence diffusion. For pressure solution (path (i)) Equation 39 gives the chemical potential directly in the grain boundary region, and can be used to derive the standard flow laws, which are in accord with experiments. If there is local disequilibrium in the grain boundary region, rate terms can be included for dissolution and/or precipitation, for example, de Meer and Spiers (1999). Nabarro Herring creep is accomplished by diffusion through the crystal lattice (path (i)), but in general this means the movement of vacancies. For simplicity consider a metal. The chemical potential of the exchange vector \( \text{MV}_{-1} \), is defined at an interface as equal to the chemical potential of the metal \( M \) at the interface using Equation 39, and in the stressed grain interior an expression similar to Equation 27 is used (see LC section 8.5.1 for details). For Coble creep, there has been no discussion at this level of detail and, as for pressure solution, there is ambiguity over the nature of the grain boundary region (which will be stressed). But, as for pressure solution, Equation 39 provides the standard description.

The behaviour of multiphase materials during diffusion creep is less well understood than that of single phase materials. Two phase experiments on harzburgite show lower strength than either mineral on its own, and development of crystallographic preferred orientation (Sundberg & Cooper, 2008). Extensive migration of olivine–orthopyroxene phase boundaries shows that this should be thought of not just as diffusion creep but as stress-induced reaction in which the two phases transform locally to one another. A quantitative explanation is relevant for large-scale problems such as characterizing the rheology of the lower mantle (two phases, probably deforming by diffusion creep). I assert that an appropriate theory, when established, will be based on Equation 39, because that links stress and chemistry. Further experiments analysing chemical evolution during the two-phase diffusion creep could provide tests, for example, the predictions in Wheeler (1987) about relative growth rates at particular interfaces. There is abundant evidence from rocks that pressure solution can be accompanied by other chemical processes (Wintsch & Yi, 2002), so I argue that the local chemical potentials used in conventional pressure solution theory (dissolution and precipitation of existing minerals) can also be used to quantify models for new mineral growth, as discussed in Wheeler (2014). Large-scale pathways (ii) and (iii) of Figure 6b, both of which enable the reaction sill\( ^{+}\text{opx} \rightarrow \text{grt} \) have different driving forces because the chemical potentials depend on which interface supplies the required chemical components. For example, path (ii) involves supply of orthopyroxene and sillimanite from an interface with high normal stress (high chemical potential) and growth of garnet at an interface with low normal stress (low chemical potential) so the overall affinity is large. In contrast path (ii), where reactants are supplied from a sillimanite–fluid interface at fluid pressure (which is low, so gives low chemical potential) an orthopyroxene interface at low normal stress (low chemical potential), and contribute to garnet growth at an interface with high normal stress (high chemical potential) has a smaller affinity. Which path will actually operate will depend on the detailed kinetics on each part of each path, for example, in Coble (path (i)) and Nabarro Herring creep (path (ii)) the affinity is the same but the paths are different because of the relative ease of diffusion along interfaces and through lattices.

The last paragraph is controversial so here is another way of looking at it. In Figure 6b paths were drawn without overlaps so that the processes represented could be discussed. Could the paths in fact overlap, combining transport related to reaction and diffusion creep? Of course. Will the diffusing chemicals “know” whether they are destined to contribute to growth of a new phase or an existing one? Of course not. They are just responding to local chemical potential gradients. I cannot conceive of a useful mathematical description in which there are two separate definitions of chemical potential at an interface, one dependent on normal stress to describe pressure solution and another separate definition for the same chemical at the same interface dependent on mean stress to describe reaction. In this contribution I have shown how there is a variety of expressions for chemical potential depending on combinations of normal and weighted mean stress but each expression relates to a distinct, although well-defined, local equilibrium. For each particular situation there is one value of chemical potential and for a quite general interface it is Equation 39.

5.3 | Future directions

There are clearly predictions here that could be tested in experiments and there is much mathematical development to be undertaken. I predict that Equation 39 will play a key role in understanding reactions where water is involved and is at
a different pressure to lithostatic—particularly likely during serpentinization near mid-ocean ridges because water must penetrate down into the mantle, and during serpentinite breakdown in subduction zones. In reactions which might not require diffusion, such as olivine → spinel in subduction zones, the effects of stress will be less prominent (Equation 22). However, since olivine is a solid solution its breakdown reaction may involve diffusion, and the upper to lower mantle transition definitely involves diffusion as ringwoodite breaks down to bridgmanite and ferropericlase. If stress influences these reactions it might provide new ways of explaining topography of the 410- and 660 km discontinuities, which is still debated (Schmerr & Garnero, 2007).

I have addressed the driving forces for change (departures from the conditions for local or larger scale equilibrium) but kinetics must be incorporated to produce a predictive and general model. I anticipate that such a model will include feedback between the driving forces for chemical change and the stress systems. This occurs in diffusion creep, where dissolution and precipitation feedback on stress systems so as to produce—in the simplest models—parabolic normal stress distributions along each interface. Feedback occurs even in the simplest kinetic models for metamorphism, for example, diffusion may control the rate of growth of a reaction rim, but as that rim widens the diffusive flux diminishes. Feedback between stress and reaction has large-scale significance. Nakajima et al. (2013) argued that the volume change related to eclogitization during subduction can be linked to earthquakes. They postulated that the eclogitized oceanic crust will, as a result of volume reduction, be in tension. While the volume reduction is undeniable, the way it is accommodated will ultimately depend on feedback between the eclogitization reactions and the stress system. Such predictions, and the interpretations of mineral assemblages and chemistry in stressed rocks, need to be underpinned by a coherent understanding of how stress links to reaction.

6 | SUMMARY

The effects of stress on chemistry are described via diverse but well-defined local equilibrium conditions. The weighted mean stress inside grains has an effect which is relatively minor although potentially valuable in explaining chemical variations. The normal stress at interfaces plays the main role in quantifying stress-related chemical processes and its effects are of significant magnitude.

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