

1 On equilibrium in non-hydrostatic metamorphic systems

2 R. Powell¹, K.A. Evans², E.C.R. Green³ & R.W. White^{4,5}

3 ¹School of Earth Sciences, University of Melbourne, Vic 3010, Australia

4 ²Dept Applied Geology, Curtin University, Bentley, WA 6845, Australia

5 ³Institute for Geochemistry and Petrology, ETH Zürich, Clausiusstrasse 25, CH 8092,
6 Zürich, Switzerland

7 ⁴Institute of Geoscience, University of Mainz, D-55099 Mainz, Germany

8 ⁵ now at School of Earth & Environmental Sciences, University of St Andrews, KY16 9AL,
9 Scotland, UK

10 Corresponding author: powell@unimelb.edu.au

11 **Short title:** Non-hydrostatic metamorphic systems

12 Abstract

13 Metamorphic geology has accumulated a huge body of observation on mineral
14 assemblages that reveal strong patterns in occurrence, summarised for example in the idea
15 of metamorphic facies. On the realisation that such patterns needed a simple explanation,
16 there has been considerable *a posteriori* success from adopting the idea that equilibrium
17 thermodynamics can be used on mineral assemblages to make sense of the patterns in
18 terms of, for example, the pressure and temperature of formation of mineral assemblages.
19 In doing so, a particularly simple implicit assumption is made, that mineral assemblages
20 operate essentially hydrostatically. Structural geologists have studied the same rocks for
21 different ends, but, remarkably, the phenomena they are interested in depend on
22 non-hydrostatic stress. We look at the effect of such behaviour on mineral equilibria. With
23 adoption of some plausible assumptions about how metamorphism in the crust works, the
24 consequence of minerals being non-hydrostatically stressed is commonly second order in
25 equilibrium calculations.

26 **KEYWORDS** elastic solids; equilibrium thermodynamics; lattice constraint;
27 non-hydrostatic stress

28 1 INTRODUCTION

29 In the study of crustal metamorphic rocks, the application of equilibrium thermodynamics
30 hinges on the interpretation of their petrographic features: the mineral assemblages,
31 mineral compositions and mineral textures. This interpretation relates to how the
32 petrographic features form, evolve and are preserved as a rock follows its
33 pressure–temperature path. Since the 1910s, with the classic work of Goldschmidt and
34 Eskola, the striking correspondence and correlation of mineral assemblage with rock-type
35 and orogenic “style” has been used to support the notion that the way to understand
36 metamorphic mineral assemblages is in terms of a preserved equilibrium (e.g. Thompson,
37 1955; Fyfe, Turner & Verhoogen, 1958). These observations and ideas form the basis of the
38 metamorphic facies concept (for a historical perspective, see Ch. 1 by F.J. Turner in Fyfe
39 *et al.*, 1958).

40 The “preserved equilibrium” view of metamorphic mineral assemblages has come to
41 form the *status quo* in metamorphic geology since that time, underpinning the use of
42 thermobarometry and phase diagrams to determine the “conditions of formation” of rocks
43 (the conditions from where the equilibrium was preserved, primarily the
44 pressure–temperature conditions). However, ideas do surface, or resurface, that challenge
45 the *status quo*. Such ideas include the effect of non-hydrostatic stress in minerals (e.g.
46 Wheeler, 2014). The importance of such ideas needs to be assessed and the order of
47 magnitude of their likely role evaluated.

48 As succinctly summarised in the very first section (1.1) of Balluffi, Allen and Carter
49 (2005), on the subject of kinetics and how equilibrium is achieved, most transport
50 phenomena occur more effectively the smaller the length-scale, so equilibrium is more likely
51 to apply on the small scale. Equilibrium at this small scale, if it applies, is called local
52 equilibrium. It was recognised as a guiding principle in material science in the 1940s (e.g.
53 Darken, 1942), and probably around that time by Korzhinskii in metamorphic geology, as
54 summarised in English in Korzhinskii (1959) calling it mosaic equilibrium (see also Fyfe *et al.*
55 *et al.*, 1958; Thompson, 1959). The idea of local equilibrium now suffuses all of metamorphic
56 geology, implicitly or explicitly, and underpins the “preserved equilibrium” view of
57 metamorphic mineral assemblages.

58 The primary justification of adopting a local equilibrium approach to metamorphism is
59 that it provides a simple explanation for the metamorphic patterns observed in
60 metamorphic belts. The main aim of this manuscript is to explore the incorporation of
61 non-hydrostatic thermodynamics into this local equilibrium approach.

62 2 OVERVIEW

63 A mineral or rock during orogeny can be considered to behave elasto-viscoplastically (see,
64 for example, de Souza Neto, Perić & Owen, 2008; Paterson, 2013), with deformation taking
65 place as a consequence of far-field stresses at the elevated temperatures involved. What is
66 observed in a metamorphic rock at the Earth's surface is a complex consequence of its
67 environment and its behaviour during its passage through an orogen. Elasto-viscoplastic
68 processes such as creep are responsible for the development of deformational
69 microstructure. With continuous overprinting, the observed microstructure is what
70 survives after elasto-viscoplastic processes have given way to elastic behaviour as
71 deformation ceases. In the domain of the structural geologist, microstructure can be
72 interpreted in terms of the processes likely to have operated (see for example Paterson,
73 2013, ch. 5–7). Paterson makes a primary distinction based on the scale of flow *sensu lato*
74 between processes on atomic, intragranular and granular scales (Paterson, 2013, p. 87).
75 Relevant examples relate to diffusion creep (e.g. Herring, 1950; Coble, 1963), the
76 development of preferred orientation of minerals (e.g. Kamb, 1969; Paterson, 1973),
77 pressure solution (e.g. Rutter & Elliot, 1976) and grain boundary sliding (e.g. Paterson,
78 2013, ch. 7). See also Hobbs & Ord (2015). Viscoplastic processes lead to deformation that
79 is permanent, i.e. it is dissipative (non-conservative), involving entropy production. It is
80 irreversible from a thermodynamic point of view and therefore not a valid subject for the
81 application of equilibrium thermodynamic calculations (e.g. Hobbs & Ord, 2016).

82 Dissipative processes are also involved in the chemical equilibration that accompanies
83 elasto-viscoplastic processes, for example the diffusion that flattens chemical potential
84 gradients, nucleation and growth of new minerals, and gain or loss of fluid. Such processes
85 may contribute to microstructure development, and feedbacks between chemical
86 equilibration and deformation are likely to occur at smaller scale with both involving
87 diffusion, e.g. diffusion creep (e.g. Mishin, Warren, Sekerka & Boettinger, 2013).

88 With the waning of orogeny, there is a transition from elasto-viscoplastic to elastic
89 behaviour in the minerals and rocks. Elastic behaviour is favoured over elasto-viscoplastic
90 behaviour at lower temperatures, and under fluid-absent conditions. The decrease of
91 far-field stresses when the nature and effect of the boundary conditions of the orogen
92 change, the lowering of temperature with exhumation, and the transition to fluid- or
93 melt-absent conditions, all combine to drive the transition from elasto-viscoplastic to
94 elastic behaviour. Although a non-hydrostatically-stressed elastic solid will tend to relax to
95 a hydrostatically-stressed state given enough time, this time may not be available in
96 relation to the orogenic timescales (e.g. Dabrowski, Powell & Podladchikov, 2015). In the

97 absence of relaxation, non-hydrostatically-stressed minerals may be in equilibrium, and
98 changes to their state can be treated as being thermodynamically reversible, as noted by,
99 for example, McLennan (1980), p106, and discussed by Reiner (1964) and Dealy (2010),
100 and is implicit in material science, for example Li, Oriani and Darken (1966) and
101 subsequent work. After mechanical dissipation has ceased and elastic behaviour
102 predominates, chemical equilibration may continue.

103 Thus, as a rock passes through an orogeny, it evolves via thermal, mechanical and
104 chemical dissipative processes. Considering a small volume of rock at a point in time, the
105 extant mineral assemblage will depend critically on the rates of the various dissipative
106 processes that contribute towards establishing equilibrium. A possibility is that
107 equilibrium can be established given the time available. If this is the case, and if the
108 mineral assemblage at this point in time could be observed, then equilibrium
109 thermodynamic methods as used in metamorphic petrology could be applied to it. Such
110 methods are applicable only to systems that are not behaving dissipatively, as emphasised
111 by Hobbs and Ord (2016).

112 The *status quo* view of metamorphism is that mineral assemblages evolve during
113 orogeny largely at chemical equilibrium on some length scale at least while there is fluid or
114 melt present. This view, an essentially macroscopic view of metamorphism, is commonly
115 implicit, but it underpins application of pseudosections and thermobarometry to mineral
116 assemblages in rocks. Classically, the view relates to what is described as progressive
117 metamorphism, involving essentially-continuous over-printing of mineral assemblages as
118 pressure and temperature change. In a stronger, local-equilibrium form, the over-printing
119 involves continuously-evolving equilibrium mineral assemblages. An argument for this view
120 of metamorphism is that mineral assemblages that appear to satisfy the textural and
121 mineral compositional criteria for equilibrium on some length-scale are preserved as records
122 of the metamorphic process. The majority of what is preserved in mineral assemblages
123 comes from relatively late in a rock's evolution, generally still at elevated temperature
124 judging by the nature of the mineral assemblages preserved (e.g. Guiraud, Powell & Rebay,
125 2001; White & Powell, 2002). How this preservation occurs—how and why mineral
126 assemblages stop evolving—is a key partly-unanswered question.

127 To understand the consequences of the idealised situation in which preserved mineral
128 assemblages were in local equilibrium, and in which the minerals were
129 non-hydrostatically-stressed at that time, the equilibrium thermodynamics of
130 non-hydrostatically-stressed elastic solids are considered in the next section. The aim is to
131 establish how important non-hydrostatic stress is for mineral equilibrium calculations.

132 Following the presentation of some illustrative calculations, the relevance of the results are
133 discussed briefly.

134 **3 THERMODYNAMICS OF EQUILIBRIUM**

135 In this section the equilibrium thermodynamics of elastic crystalline solids (i.e. minerals)
136 that may be hydrostatically or non-hydrostatically stressed is outlined. It is envisaged that
137 the system being considered has reached an equilibrium state, that is, no dissipative
138 processes are operating. The system is made up of grains of one or more solids, and may
139 also include fluid either continuously on grain boundaries, or isolated in pores, or both.
140 Fluid is also referred to as occurring as grains.

141 **3.1 Types of thermodynamic variable and equilibrium**

142 There is a distinction between types of thermodynamic variables (e.g. Münster, 1970,
143 §20–21; Callen, 1985, p35 *et seq.*). In a fluid the intensive variables, pressure, p ,
144 temperature, θ , and the chemical potentials, μ_ℓ , are scalars. Coexisting fluids at
145 equilibrium have the same values of the intensive variables (contact equilibrium of
146 Münster, 1970, p49). At equilibrium, there are no gradients in these intensive variables,
147 and there are no steps in the values of the intensive variables at grain boundaries. There is
148 a conjugate variable to each of these intensive variables, volume, V , to p , entropy, S , to θ ,
149 and number of moles of end-member ℓ , n_ℓ , to μ_ℓ . These extensive variables, while being
150 constant in each phase, are proportional to the amount of phase.

151 In a non-hydrostatically-stressed elastic solid, instead of mechanical equilibrium
152 involving the conjugate pair of scalars p and V , the thermodynamics is written in terms of
153 second-rank tensors for stress and strain (see the appropriate sections of a continuum
154 mechanics textbook, for example, Fung & Tong, 2001; Gurtin, Fried & Anand, 2010; Lai,
155 Rubin & Krempl, 2010; Malvern, 1969; Tadmor, Miller & Elliot, 2012, or Nye, 1985).
156 Minerals do not strain much elastically even with quite large stresses so it is reasonable to
157 use the small strain approximation in the thermodynamics in the way quantified by Gurtin
158 *et al.*, 2010, ch. 52, for example. In the case of small strain, the conjugate pair of variables
159 used are the Cauchy stress tensor, \mathbf{T} , and the infinitesimal strain tensor, \mathbf{E} (following the
160 notation of Gurtin *et al.*, 2010, with bold upright case used for second-rank tensors).
161 Whereas mechanical equilibrium in fluid involves constant p , the intensive variable, \mathbf{T} ,
162 need not be constant in an equilibrium (e.g. as illustrated in Llana-Fúnez, Wheeler &
163 Faulkner, 2012, fig. 1). Instead the criterion for mechanical equilibrium involves the

164 divergence of \mathbf{T} , with $\text{div } \mathbf{T} = 0$, in the absence of body forces, e.g. Gurtin *et al.*, 2010,
165 section 47.2. The probability of spatially heterogeneous stress-strain in an equilibrium
166 complicates the thermodynamics.

167 The mechanical equilibrium requirement across a grain boundary is a force balance. For
168 two fluids this is simply that their pressures, p , are the same. For a solid–fluid boundary,
169 force balance requires that the normal to the boundary must be a principal axis of the
170 stress tensor of the solid, with the magnitude of its principal stress being equal to p in the
171 fluid (e.g. Larché & Cahn, 1973; Sekerka & Cahn, 2004; Frolov & Mishin, 2010).
172 Solid–solid boundaries across which the lattices are discontinuous are classed as incoherent
173 (e.g. Malvern, 1969), whereas if the lattices of the two grains are continuous with one
174 another, the boundary is coherent. Grain boundaries intermediate between coherent and
175 incoherent are possible, as discussed by Larché and Cahn, 1978, p. 1586. If solid–solid
176 boundaries can slide (referred to as “greased”, Leo & Sekerka, 1989), then the normals to
177 the grain boundary must also be principal axes of the stress tensors in each solid at the
178 point of contact, and these principal stresses identical. If a boundary is deemed not to
179 slide, then the normals to the boundary do not have to correspond to principal axes of the
180 stress tensors in the solids. Constraints on the orientation of principal stresses in solids at
181 grain boundaries can be accommodated because stress can be heterogeneous in solids at
182 equilibrium. The physics becomes more complicated when grain boundaries are curved
183 (e.g. Leo & Sekerka, 1989; Cermelli & Gurtin, 1994). Planar incoherent greased grain
184 boundaries are assumed here for illustrative calculation purposes, as in Larché and Cahn,
185 (1973, 1985). Coherent grain boundaries and displacive reactions are not considered.

186 **3.2 Pressure, thermodynamic pressure, and mean stress**

187 In the previous section, pressure, p , has been used only for a fluid at equilibrium. It has a
188 rigorous definition for fluid that relates to the way internal energy changes with volume, as
189 expanded on below in the *Energies of an elastic solid* subsection. Because the word,
190 pressure, is used with a less restrictive meaning in the literature, p is referred to here as a
191 *thermodynamic pressure*, distinct from other usages of the term pressure. The
192 thermodynamic pressure is an intensive variable constant in an equilibrium. A feature of
193 the thermodynamics of solids that can be non-hydrostatically-stressed at equilibrium, is
194 that some of the scalar intensive variables involved are not defined everywhere, including
195 thermodynamic pressure (see later in this subsection), but where scalar intensive variables
196 are defined they are constant in an equilibrium. Solids that can be
197 non-hydrostatically-stressed at equilibrium are referred to simply as solids below.

198 In an equilibrium, separate grains of fluid are at the same thermodynamic pressure, p .
 199 However there is no equivalent scalar intensive variable to thermodynamic pressure within
 200 solids. Its role is taken by the stress tensor, \mathbf{T} . If, at a point within a solid, the coordinate
 201 axes are oriented parallel to the principal axes of \mathbf{T} , then the matrix of the stress tensor is
 202 diagonal and can be written

$$203 \quad \mathbf{T} = \begin{bmatrix} t_1 & 0 & 0 \\ 0 & t_2 & 0 \\ 0 & 0 & t_3 \end{bmatrix}$$

204 The *mean stress*, \bar{T} , is the average of the diagonal elements of the stress tensor, \mathbf{T} ,
 205 $\bar{T} = \frac{1}{3} \text{tr } \mathbf{T}$, where tr means trace. The mean stress is a third of the first principal invariant
 206 of the tensor, which means that it does not depend on the coordinates in which the matrix
 207 of the tensor is represented (e.g. Gurtin *et al.*, 2010, section 2.16). If the coordinates are
 208 organised as above, $\bar{T} = \frac{1}{3} (t_1 + t_2 + t_3)$. In the literature, negative of mean stress is called
 209 various sorts of pressure, or simply pressure, e.g. Connolly (2009), treating compression as
 210 negative.

211 In a solid grain in an equilibrium with fluid, in the limit of non-hydrostatic stress
 212 reducing to hydrostatic stress, with the difference between t_1 , t_2 and t_3 getting smaller and
 213 smaller, \bar{T} becomes equal to the pressure of the fluid, $-p$. The stress tensor in the
 214 hydrostatically-stressed solid can be written $\mathbf{T} = -p \mathbf{1}$, where $\mathbf{1}$ is the identity tensor, with
 215 ones on the diagonal. Alternatively it can be written as $t_i = -p$. The mean stress within a
 216 hydrostatically-stressed grain is uniform, equal to $-p$.

217 In contrast to p in a fluid, the mean stress, \bar{T} , in a solid is not a thermodynamic
 218 pressure, that is, it is not an intensive variable, constant in an equilibrium. Mean stress
 219 varies within a solid in an equilibrium if the solid is heterogeneously-stressed. There will be
 220 a step in the mean stress at grain boundaries in all but special cases. For example at the
 221 indicated point on the solid–fluid grain boundary in Figure 1, the mean stress in the solid,
 222 $\bar{T} = (t_1 + t_2 - p)/3$, can be larger or smaller than p in the fluid, depending on the magnitude
 223 of t_1 and t_2 . Here and below, t_3 is chosen to be the normal to the grain boundary.

224 Thermodynamic pressure is undefined within solid. A pressure in the solid at grain
 225 boundaries, meaning on the surface of the planar interface that is envisaged to represent a
 226 grain boundary, is $-t_3$ (Larché & Cahn, 1985, p336–337, corresponding to $-\omega$ in that
 227 reference). At solid–fluid boundaries this pressure is equal to p , the pressure in the fluid. It
 228 is different from the mean stress, the difference being $(t_1 + t_2 + 2p)/3$. At solid–solid grain
 229 boundaries the difference is $(t_1 - t_3)/3 + (t_2 - t_3)/3$ in each solid. In both cases the
 230 difference can vary along a grain boundary. Although mean stress is referred to routinely

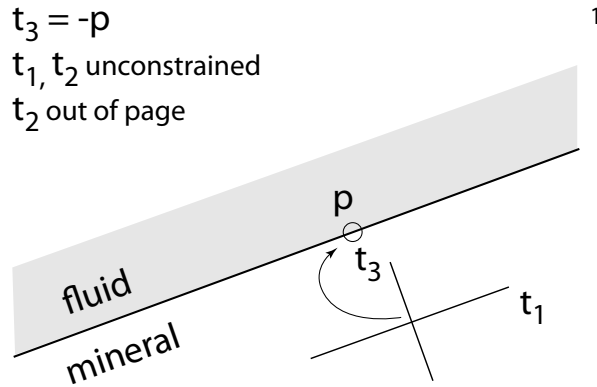


Figure 1: Summarising the stress relationships at a solid–fluid grain boundary, using the cross to represent the principal axes of the stress tensor at the indicated point on the boundary, the length of the lines representing the relative magnitude of the principal stresses. The principal stress t_3 , designated to be normal to the grain boundary, equals $-p$ along the boundary, but t_1 and t_2 may vary along the boundary.

231 as the pressure of a solid, the pressure that appears in the thermodynamics of grain
 232 boundaries (in the interface equilibrium relation, see below) is equal to $-t_3$.

233 As in Figure 1, each solid that abuts a fluid grain has a principal stress normal to the
 234 grain boundary equal to the negative of the pressure, $-p$, of the fluid grains as discussed
 235 above. As p is constant within an equilibrium, these normals have the same magnitude of
 236 stress. The non-hydrostatic stress in the solid at a point on a solid–fluid grain boundary
 237 can be referred to this p using

$$238 \quad q_1 = t_1 + p \quad \text{and} \quad q_2 = t_2 + p \quad (1)$$

239 (Sekerka & Cahn, 2004). In general q_1 and q_2 vary along solid–fluid grain boundaries, with
 240 the difference between the mean stress of the solid and the pressure of the fluid being
 241 $\frac{1}{3}(q_1 + q_2)$. If a solid abutting fluid is hydrostatically stressed, then $q_1 = q_2 = 0$ in the solid
 242 at the grain boundary. This q formalism is used below. Some aspects of thermodynamic
 243 pressure and mean stress are illustrated in Figure 2.

244 3.3 Small strain

245 Strain, for example in terms of change of size and shape of the unit cell in a crystalline
 246 solid, can be due to factors in addition to externally-applied stress. Such non-elastic strain
 247 is referred to as eigenstrain (Mura 1987, p. v), and can arise through for example
 248 temperature or composition change. For the small elastic strain in minerals it is reasonable
 249 to assume that minerals are linear elastic solids. In the absence of eigenstrain, stress and

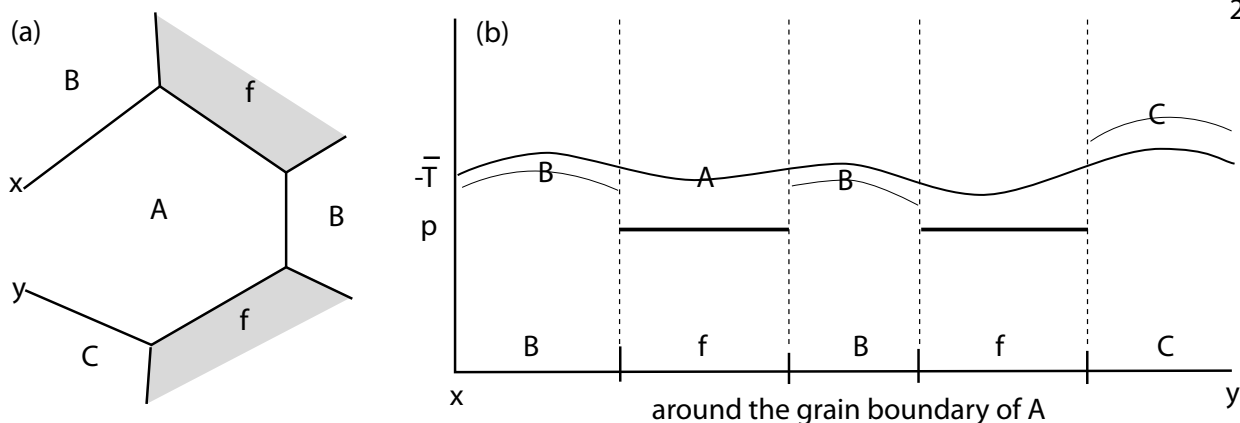


Figure 2: Schematic depiction of pressure–mean stress relations on grain boundaries involving heterogeneously non-hydrostatically-stressed solids, A, B, C, with fluid, f. (a) location of grain boundaries and fluid grains; (b) thermodynamic pressure (p) and variation of mean stress (as $-\bar{T}$) along the boundaries of A from x around to y. The horizontal thick lines show the fluid grains at a thermodynamic pressure, p . The mean stress around the perimeter of A is the continuous line. The thin line segments show the mean stress in the edge of the adjoining solid grains. The expression for the difference between the mean stress of the solid and the pressure of the fluid is given in the text. For example, at the fluid-A-C grain triple junction, the step of mean stress to p from A to fluid is $\frac{1}{3}(q_1^A + q_2^A)$ and from C to fluid is $\frac{1}{3}(q_1^C + q_2^C)$. The mean stress step between A and C at the fluid-A-C triple junction is just the difference between these two steps.

250 strain are related linearly by 4th order tensors, the compliance tensor, \mathbb{S} , and the stiffness
 251 tensor, \mathbb{C} , with the Voigt matrices of the tensors being the inverse of each another (e.g.
 252 Nye, 1985, p. 132). The relationships can be written

$$253 \quad \mathbf{T} = \mathbb{C}\mathbf{E} \quad \text{and} \quad \mathbf{E} = \mathbb{S}\mathbf{T} \quad (2)$$

254 The components of \mathbb{S} and \mathbb{C} depend on the crystal class of the mineral (e.g. Nye 1985, ch.
 255 8).

256 For the purpose of transparency of development and to see the order of magnitude of
 257 effects in illustrative calculations, it is assumed that the solids of interest are isotropic.
 258 This means that the number of adjustable parameters is minimised and the algebra is
 259 simple. For isotropic solids the principal axes of the strain tensor are coincident with those
 260 of the stress tensor, so if

$$261 \quad \mathbf{T} = \begin{bmatrix} t_1 & 0 & 0 \\ 0 & t_2 & 0 \\ 0 & 0 & t_3 \end{bmatrix} \quad \text{then} \quad \mathbf{E} = \begin{bmatrix} e_1 & 0 & 0 \\ 0 & e_2 & 0 \\ 0 & 0 & e_3 \end{bmatrix}$$

262 \mathbf{T} in terms of \mathbf{E} , and \mathbf{E} in terms of \mathbf{T} , using (2), with the bulk modulus, κ , and shear
 263 modulus, μ , are

$$264 \quad t_i = (\mathbf{CE})_i = \bar{\mathbf{E}}(3\kappa - 2\mu) + 2\mu e_i \quad \text{and} \quad e_i = (\mathbf{ST})_i = \bar{\mathbf{T}} \left(\frac{1}{3\kappa} - \frac{1}{2\mu} \right) + \frac{1}{2\mu} t_i \quad (3)$$

265 e.g. Gurtin *et al.* (2010), sect 52.5, with $\bar{\mathbf{E}} = \frac{1}{3} \text{tr } \mathbf{E}$. For hydrostatic stress, with
 266 $t_1 = t_2 = t_3$, strain is “spherical”, $e_i = \bar{\mathbf{T}}/(3\kappa)$, and $\text{tr } \mathbf{E} = \bar{\mathbf{T}}/\kappa$.

267 For an isotropic solid (and other solids whose crystallographic axes are orthogonal), and
 268 with the strain tensor aligned with the crystallographic axes, volume change as a function
 269 of strain is

$$270 \quad V - V_0 = V_0 ((1 + e_1)(1 + e_2)(1 + e_3) - 1) \approx V_0(e_1 + e_2 + e_3) = V_0 \text{tr } \mathbf{E} \quad (4)$$

271 with V_0 being the volume at zero strain, and at the temperature and composition of
 272 interest (so no eigenstrain is involved). The approximation in (4) results from ignoring
 273 terms higher than first order in e_k , as appropriate for small strain.

274 For an isotropic solid, referred to a fluid at fixed p at an interface, the volume of the
 275 solid is

$$276 \quad \frac{V}{V_0} = 1 + \text{tr } \mathbf{E} = 1 + \frac{1}{\kappa} \bar{\mathbf{T}} = 1 + \frac{1}{\kappa} \left(-p + \frac{q_1 + q_2}{3} \right) \quad (5)$$

277 An alternative derivation of the part of (5) that applies to a hydrostatically-stressed
 278 solid, i.e. with $q_1 = q_2 = 0$, starts with the equation of state for volume in terms of its
 279 temperature, θ , and pressure, p , at a reference state, $\{p_0, \theta_0\}$

$$280 \quad dV = V\alpha d\theta + \frac{V}{\kappa} dp$$

281 with α the thermal expansion, $1/V(\partial V/\partial\theta)_p$, and κ the bulk modulus as above, defined as
 282 $-V(\partial p/\partial V)_\theta$. The equation of state can be integrated to give V as a function of p and θ if
 283 κ and α are constants, and are large and small, respectively

$$284 \quad V \approx V_0 \left(1 + \alpha(\theta - \theta_0) - (p - p_0) \frac{1}{\kappa} \right) \quad (6)$$

285 with V_0 the volume at $\{p_0, \theta_0\}$, e.g., as in Holland and Powell (1990), p. 91. Commonly
 286 used are $p_0 = 0.001$ kbar and $\theta_0 = 298$ K, with a good approximation being $p_0 \approx 0$. Then
 287 the p term is seen to be the same as in (5), with $\bar{\mathbf{T}} = -p$, while the θ term is the thermal
 288 eigenstrain.

289 The simplest approximation for the compositional eigenstrain is that the volume of the
290 solid varies linearly with composition between the volumes of its end-members, implying
291 that there is no excess volume of mixing. The thermal and/or compositional eigenstrain
292 need only be considered if the effects of change of temperature and/or composition are
293 required.

294 **3.4 Lattice constraint**

295 For mineral equilibria calculations involving non-hydrostatically-stressed minerals, the
296 chemical potentials of the end-members of the minerals need to be formulated. The
297 chemical potentials are derived from an expression for internal energy appropriate for the
298 makeup and behaviour of the solid. The internal energy corresponding to the Gibbs energy
299 used for minerals in petrology, e.g. Powell, White, Green, Holland, and Diener (2014), has
300 a disadvantage in that it involves the implicit assumption that the solid is and remains
301 hydrostatically-stressed. Yet solids can be non-hydrostatically-stressed at equilibrium.
302 Even excluding processes involving nucleation such as recrystallisation, equilibration by
303 unrestricted diffusion in the lattice (as in diffusion creep) transforms a solid from being
304 non-hydrostatically stressed to hydrostatically stressed at equilibrium. For elastic solids to
305 hold non-hydrostatic stress at equilibrium, unrestricted diffusion in the lattice needs to be
306 prevented (e.g. Larché & Cahn, 1973, 1985; Cahn & Larché, 1983, Mullins & Sekerka,
307 1985). Larché and Cahn (1973) consider elastic solids to involve the conservation of lattice
308 points in a reference volume, referred to as the lattice (or network) constraint. Use of the
309 lattice constraint forces substitution of elements on sites in the lattice to be one-for-one: if
310 an element is taken out of a site, another element must be put into it. The lattice
311 constraint precludes unrestricted diffusion, allowing maintenance of non-hydrostatic stress
312 at equilibrium. The lattice constraint of Larché and Cahn (1973) is adopted here for
313 minerals. The lattice constraint is an example of what Gibbs (1906, p58) calls a passive
314 resistance, a feature of a material adopted to prevent a certain process or change.
315 Equilibrium is then subject to that resistance.

316 Adoption of the lattice constraint has a significant impact on the formulation of
317 equilibrium in elastic solids. With the lattice constraint, in a 1-site solid with atoms of
318 elements substituted on the site, like many alloys as considered by Larché and Cahn
319 (1973), the chemical potentials in the solid occur as μ of element *exchanges* on the site.
320 These μ are constant through an equilibrium. The μ of individual elements do not appear
321 in the thermodynamic description of the solid, only their differences. Extension to minerals
322 and end-members is made in the next paragraph. The μ in this work are mole-based: the

323 internal energy involved in Larché and Cahn (1973) is per volume, and the derivative of
324 this energy to give chemical potential is with respect to a molar density (moles per
325 volume). The μ are in kJ mole^{-1} .

326 The lattice constraint only applies in a solid, given that at grain boundaries, lattice
327 points can be created or lost, for example as a grain grows or is consumed. The distinction
328 between grains and grain boundaries is also fundamental to construction of the equilibrium
329 relations. At grain boundaries, with the lattice constraint not in effect there, the individual
330 μ are defined and are constant at equilibrium. These individual μ are consistent with the μ
331 of exchanges that are constant everywhere within the equilibrium. There is an additional
332 equilibrium relation—the interface equilibrium relation—that connects the
333 thermodynamics of solid with fluid, or solid with solid, across grain boundaries. The
334 interface equilibrium relation is outlined in detail below.

335 In a 1-site solid, such as an alloy, the chemical potentials are of exchanges of the
336 elements that substitute on the site. The minerals that make up rocks are multi-site, so
337 this needs to be taken into account in applying the lattice constraint to minerals. An
338 end-member of a mineral is a fixed chemical composition ‘formula unit’ that can be added
339 to or subtracted from the mineral without disrupting its stoichiometry and its
340 charge-balance. Generally this means that end-members have the stoichiometry of the
341 mineral. In a chosen chemical system, the compositional range of a mineral can be
342 completely described using an independent set of end-members in that system (e.g. Powell
343 *et al.*, 2014). For calculations, the system and the range of composition are constrained by
344 the availability of thermodynamic data for the end-members (e.g. Holland & Powell, 2011;
345 White, Powell, Holland, Johnson & Green, 2014).

346 The exchange of formula units of end-members in minerals is the lattice constraint
347 equivalent of exchanging elements on a site, as in Larché and Cahn (1973). End-members
348 can be chosen to represent such an exchange. Taking plagioclase as an example, for all
349 standard calculation purposes potassium-free plagioclase can be treated as a binary, in
350 terms of the additive end-members $\text{NaAlSi}_3\text{O}_8$ (albite, ab) and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite, an),
351 in $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$. Now, from a lattice constraint point of view, there is one
352 thermodynamically relevant end-member, the exchange end-member, $(\text{CaAl})_{-1}(\text{NaSi})$.
353 Internal equilibrium in a plagioclase grain is defined by constant $\mu_{(\text{CaAl})_{-1}(\text{NaSi})}$. The
354 chemical potentials of the additive end-members, $\mu_{\text{CaAl}_2\text{Si}_2\text{O}_8}$ and $\mu_{\text{NaAlSi}_3\text{O}_8}$, are not defined
355 in a plagioclase grain. However, at a grain boundary, both $\mu_{\text{CaAl}_2\text{Si}_2\text{O}_8}$ and $\mu_{\text{NaAlSi}_3\text{O}_8}$ are
356 defined, and are consistent with $\mu_{(\text{CaAl})_{-1}(\text{NaSi})} = \mu_{\text{NaAlSi}_3\text{O}_8} - \mu_{\text{CaAl}_2\text{Si}_2\text{O}_8}$ from the internal
357 equilibrium in the grain.

358 In a solid with n independent additive end-members, one of them, say ℓ , can be used as
 359 the common end-member in the exchanges. Then there is a set of independent $n - 1$
 360 exchange end-members, $\ell_{-1}k$. Internal equilibrium is defined by constant $\mu_{\ell_{-1}k}$. At a
 361 solid–fluid grain boundary, as well as $\mu_{\ell_{-1}k}$ being defined via the internal equilibrium, the
 362 interface equilibrium relation allows μ_{ℓ} to be determined, so that the chemical potentials of
 363 all of the additive end-members can be generated. Any end-member can be ℓ .

364 Now, a simpler notation is adopted for the end-member exchange variable, with $\ell_{-1}k$
 365 defined as $k\ell$, and $\mu_{\ell_{-1}k}$ defined as $\mu_{k\ell}$. So, for example, in plagioclase, $\mu_{(\text{CaAl})_{-1}(\text{NaSi})}$ is
 366 $\mu_{\text{ab an}}$, noting that the use of the plagioclase end-member name in the μ subscript means
 367 the *composition* of the formula unit with no implication of mineral structure. So $\mu_{\text{ab an}}^f$,
 368 with superscript f meaning fluid, means $\mu_{(\text{CaAl})_{-1}(\text{NaSi})}^f$. Also $\mu_{\text{ab an}} = \mu_{\text{pa ma}}$ by definition,
 369 given that both exchanges reduce to the same exchange, $(\text{CaAl})_{-1}(\text{NaSi})$, with pa =
 370 paragonite and ma = margarite.

371 3.5 Energies of an elastic solid

372 In this subsection, and the remainder of the section, a solid is assumed to be a linear
 373 hyperelastic elastic crystalline solid in which the lattice constraint applies, with the term
 374 hyperelastic defined below. Depending on context, this sort of material is referred to as
 375 “solid” or “elastic solid”.

376 In equilibrium thermodynamics, a fundamental equation relates the internal energy, U ,
 377 to a sufficient set of extensive variables. Whereas for a fluid, this fundamental equation
 378 involves only scalars (e.g. Alberty, 2001, eq. 1.1-2), for an elastic solid it does not, as
 379 discussed above. Instead, the fundamental equation involves the strain tensor, \mathbf{E} and the
 380 stress tensor, \mathbf{T} (Gurtin *et al.*, 2010, section 52.3), for small strain. For an arbitrary
 381 amount of homogeneously-stressed lattice-constraint solid, a sufficient set of extensive
 382 variables to consider the variation of the internal energy is entropy, S , strain, \mathbf{E} , and the
 383 number of moles of exchange end-members. V_0 is the volume of solid in the reference state:
 384 zero stress, at specified θ and composition. Then,

$$385 \quad dU = \left(\frac{\partial U}{\partial S} \right)_{\mathbf{E}, n_i} dS + \left(\frac{\partial U}{\partial \mathbf{E}} \right)_{S, n_i} : d\mathbf{E} + \sum_{k \neq \ell} \left(\frac{\partial U}{\partial n_{k\ell}} \right)_{\mathbf{E}, S, n_{i\ell} (i \neq k)} dn_{k\ell} \quad (7)$$

386 with $n_{k\ell}$ the number of moles of exchange end-member, k . The sum is over an independent
 387 set of exchanges. For a 1-end-member solid, there is no sum term as there are no
 388 exchanges. The colon symbol denotes the tensor inner product, with $\mathbf{A} : \mathbf{B} = \sum \sum A_{ij} B_{ij}$
 389 or in Einstein notation, $A_{ij} B_{ij}$. The variations in (7), like dS , relate strictly to quasi-static

390 processes, e.g. Callen (1985), Sect. 4.2. The derivatives in (7) can be identified with
 391 intensive variables, with the terms involving conjugate pairs of intensive and extensive
 392 variables, e.g. Callen (1985), Sect. 12-3, giving

$$393 \quad dU = \theta dS + V_0 \mathbf{T} : d\mathbf{E} + \sum_{k \neq \ell} \mu_{k\ell} dn_{k\ell} \quad (8)$$

394 in which the $\mu_{k\ell}$ are chemical potentials of exchange end-members, $k\ell$, involving
 395 end-member k substituting for end-member ℓ , as introduced in the *Lattice constraint*
 396 section above. Note that

$$397 \quad \mathbf{T} = \frac{1}{V_0} \left(\frac{\partial U}{\partial \mathbf{E}} \right)_{S, n_{k\ell}} \quad (9)$$

398 e.g. Gurtin *et al.* (2010), eq. 52.35. Relations such as (8,9) define hyperelasticity, the
 399 subset of elastic behaviours for which (8,9) are true (e.g. Gurtin *et al.*, 2010, p279).

400 In (8), $V_0 \mathbf{T} : d\mathbf{E}$ replaces $p dV$ in the expression for dU for a fluid, where the
 401 thermodynamic pressure in the fluid is defined by $p = -(\partial U / \partial V)_{S, n_i}$, (e.g. Callen, 1985,
 402 eq. 2.2). There is no equivalent derivation of a thermodynamic pressure within an elastic
 403 solid. Whereas $(\partial U / \partial V)_{S, \mathbf{E}_0, n_i}$, with the differentiation at constant deviatoric strain,
 404 $\mathbf{E}_0 = \mathbf{E} - \frac{1}{3} \text{tr} \mathbf{E}$, gives the mean stress (e.g. McLellan, 1980, eq. 8.3.2), this is not a
 405 thermodynamic pressure by the definition in the *Pressure* section above (c.f. Hobbs & Ord,
 406 2016, p. 200). Indeed, pressures with a range of different definitions can be generated,
 407 depending on what is held constant in $\partial U / \partial V$ instead of \mathbf{E}_0 . None of these are spatially
 408 constant within an equilibrium so none are thermodynamic pressures.

409 Legendre transforms allow energies to be generated that make the thermodynamics
 410 more easily used. The Legendre transform allows the variables in a conjugate pair in dU to
 411 be interchanged (Callen, 1985, p. 141 *et seq.*; Alberty, 2001). A Legendre transform of U
 412 with respect to θ , denoted \mathcal{L}_θ , gives a new energy, the Helmholtz energy, $F = \mathcal{L}_\theta U$ (e.g.
 413 McLellan, 1980, eq. 10.2.7)

$$414 \quad dF = -S d\theta + V_0 \mathbf{T} : d\mathbf{E} + \sum \mu_{k\ell} dn_{k\ell} \quad (10)$$

415 In a system at specified θ (rather than S), the Helmholtz energy (rather than U) is
 416 minimised at equilibrium. Gibbs energy is defined by a Legendre transform relating to the
 417 mechanical term in U . For a solid, Gibbs energy, $G = \mathcal{L}_{\mathbf{T}\theta} U$ (e.g. McLellan, 1980, eq.
 418 10.2.11), is

$$419 \quad dG = -S d\theta - V_0 \mathbf{E} : d\mathbf{T} + \sum \mu_{k\ell} dn_{k\ell} \quad (11)$$

420 A Maxwell relation generated from this equation is used below. For a fluid, G is defined as
 421 $\mathcal{L}_{p\theta}U$. However $\mathcal{L}_{p\theta}U$ cannot be used as a definition for G for an elastic solid because a
 422 thermodynamic pressure, p , is not defined in such solids.

423 The Gibbs-Duhem relation is an important relationship that indicates that at
 424 equilibrium the intensive variables cannot be varied independently. It arises from a
 425 complete Legendre transform of dU . For an homogeneously-stressed part within a solid the
 426 Gibbs-Duhem relation is

$$427 \quad 0 = -S d\theta - V_0 \mathbf{E} : d\mathbf{T} + \sum n_{k\ell} d\mu_{k\ell} \quad (12)$$

428 This also applies within a hydrostatically-stressed solid (Johnson & Schmalzried, 1992).
 429 Temperature, mean stress and the chemical potentials can be independently varied in a
 430 hydrostatically-stressed solid as \mathbf{T} is only partly characterised by $\bar{\mathbf{T}}$. This result is in
 431 contrast to fluids in which temperature, thermodynamic pressure and the chemical
 432 potentials cannot be varied independently.

433 **3.6 Chemical equilibrium involving an elastic solid**

434 The chemical potentials that are defined play a central role in characterising equilibrium
 435 because they are constant in an equilibrium. The relationships between chemical potential
 436 and mineral composition allow the compositions of minerals at equilibrium to be calculated.
 437 In a solid, chemical potentials of exchange end-members are defined and are constant.
 438 These can be used to look at the relationship between variations in stress and mineral
 439 composition. In a n -end-member solid there are $n - 1$ independent exchanges, and $n - 1$
 440 independent composition parameters. Different solid grains (i.e. different minerals) that
 441 are in equilibrium and involve the same exchanges will have the same μ of the exchanges.

442 In order to combine information from all of the end-members, not just exchange ones,
 443 the equilibrium in fluid and in solid–solid grain boundaries have to be determined. In these
 444 locations the chemical potentials of all the end-members are defined. The interface
 445 equilibrium relation—outlined later in this subsection—allows the extraction of the
 446 information on the chemical potentials of the individual additive end-members from the
 447 chemical potentials of the exchange end-members. Moreover it allows the chemical
 448 potential of the end-member in a 1-end-member solid, for example, SiO_2 in quartz, to be
 449 determined in fluid or at grain boundaries, reflecting the presence of, and equilibrium with,
 450 quartz, even though μ_{SiO_2} is not defined in quartz.

451 In a binary elastic solid, there is one chemical potential of an exchange end-member,

452 μ_{12} , in (11), with n_{12} the number of moles of the exchange end-member

$$453 \quad \mu_{12}(\mathbf{T}) = \left(\frac{\partial G}{\partial n_{12}} \right)_{\mathbf{T}, \theta} \quad (13)$$

454 written as $\mu_{12}(\mathbf{T})$ to indicate that this is a function of the state of stress, \mathbf{T} . To make
 455 calculations, it is advantageous to write $\mu_{12}(\mathbf{T})$ in terms of the properties of the
 456 hydrostatically-stressed additive end-members, 1 and 2, as might be gleaned from a
 457 thermodynamic dataset. The approach taken follows that of Larché and Cahn (1985), Sect.
 458 4.2, with equation numbers in square brackets here indicating the equations in that
 459 reference. A Maxwell relation, [4.13], derived from the differential form of G shown in
 460 equation (11), [4.12], with G called ϕ in Larché and Cahn (1985)

$$461 \quad V_{\ominus} \left(\frac{\partial \mathbf{E}}{\partial n_{12}} \right)_{\mathbf{T}, \theta} = - \left(\frac{\partial \mu_{12}(\mathbf{T})}{\partial \mathbf{T}} \right)_{\theta, n_{12}} \quad (14)$$

462 with V_{\ominus} being the volume in the \ominus reference state, see below. This equation says that the
 463 dependence of strain on composition is related to the dependence of chemical potential on
 464 stress. Integrating (14) from a reference state to the conditions of interest gives the
 465 corresponding strain as a function of composition. The most convenient reference state is
 466 the unstressed solid ($\mathbf{T} = \mathbf{0}$), at the temperature of interest, and for a reference
 467 composition, taken to be that of pure end-member 2. This reference state is denoted by the
 468 subscript, \ominus . The conventional reference state involving $\theta_0 = 298$ K is denoted by subscript
 469 0, with the transition between the two reference states, \ominus and 0, being via the thermal
 470 eigenstrain.

471 The strain, \mathbf{E} , can be decomposed into two parts (Larché & Cahn, 1973, p1056). The
 472 first is the compositional eigenstrain, $\mathbf{E}_{\mathbf{c}}$, associated with change of composition from that
 473 of V_{\ominus} to the composition of interest. The second part is the strain from the stress, $\mathbf{E} - \mathbf{E}_{\mathbf{c}}$.
 474 For linear elastic solids, $\mathbf{E} = \mathbf{E}_{\mathbf{c}} + \mathbb{S}\mathbf{T}$, [4.15].

475 Integrating the Maxwell relation, (14), from the unstressed state ($\mathbf{T} = \mathbf{0}$) to the state of
 476 stress of interest, \mathbf{T} , given strain as a function of composition, to give μ as a function of
 477 stress at the composition of interest is

$$478 \quad \int_{\mu_{12}|_0}^{\mu_{12}|\mathbf{T}} d\mu_{12}(\mathbf{T}) = -V_{\ominus} \int_{\mathbf{0}}^{\mathbf{T}} \left(\frac{\partial \mathbf{E}}{\partial n_{12}} \right) : d\mathbf{T}$$

479 the derivative being at constant θ . Substituting $\mathbf{E} = \mathbf{E}_{\mathbf{c}} + \mathbb{S}\mathbf{T}$, and integrating

$$480 \quad \mu_{12}(\mathbf{T}) - (\mu_{12})_{\ominus} = -V_{\ominus} \left(\frac{\partial \mathbf{E}_{\mathbf{c}}}{\partial n_{12}} \right) : \mathbf{T} - V_{\ominus} \frac{1}{2} \left(\frac{\partial \mathbb{S}}{\partial n_{12}} \right) \mathbf{T} : \mathbf{T} \quad (15)$$

481 in which $(\mu_{12})_{\ominus}$ is the chemical potential in the reference state. The derivative of \mathbb{S} is the
 482 4th rank tensor whose elements are the composition-dependence of the elements of \mathbb{S} . For
 483 an isotropic solid, the composition-dependence is of the bulk and shear moduli that make
 484 up \mathbb{S} .

485 For the illustrative calculations below, approximations can be made to simplify this
 486 equation, Appendix 1, (34). The aim is to be able to write chemical potentials of exchanges
 487 in non-hydrostatically-stressed solid in terms of properties of hydrostatically-stressed
 488 additive end-members. Then, for a standard state of the hydrostatically-stressed pure
 489 end-member at the temperature of interest and an arbitrary pressure, P , [4.23]

$$490 \quad \mu_{12}(\mathbf{T}) = G_1(P) - G_2(P) + R\theta \ln \frac{a_1}{a_2} - V_{12}(P + \bar{T}) \quad (16)$$

491 with $G_1(P)$ and $G_2(P)$ the Gibbs energies of end-members 1 and 2 at P and θ , a_1 and a_2
 492 the activities of 1 and 2, and V_{12} the difference between the volumes of 1 and 2, $V_1 - V_2$.
 493 This equation, (16), gives the chemical potential of the exchange end-member, 12, in the
 494 non-hydrostatically-stressed solid (as specified by \mathbf{T}) in terms of the properties of the
 495 end-members 1 and 2, in the G and V_{12} , and the composition of the solid in the ratio of the
 496 activities, a_1/a_2 . The pressure in (16) is chosen for the application of interest. At a
 497 solid–fluid grain boundary, P can be the pressure in the fluid, so $P = p$. For calculations
 498 within a solid, $P = -\bar{T}$ or $P = 0$ are obvious choices.

499 **3.7 Chemical equilibrium at grain boundaries**

500 At grain boundaries the lattice constraint is not active, and there the lattice can be created
 501 or consumed. So, along grain boundaries and within fluid the chemical potentials of the
 502 individual additive end-members are defined, and are constant at equilibrium (Larché &
 503 Cahn, 1973). An exchange μ in a grain boundary has the same constant value that it has
 504 in the solids and fluid at equilibrium, as illustrated in Figure 3. In this Figure, the
 505 end-member μ are arranged so that the differences between μ_{ab} and μ_{an} , and between μ_{pa}
 506 and μ_{ma} are the same, and the same as the exchange potential of $\mu_{(\text{CaAl})_{-1}(\text{NaSi})}$, which is
 507 the same as $\mu_{ab\ an}$ and $\mu_{pa\ ma}$.

508 Doing conventional calculations on a mineral assemblage involves (or can be reduced to)
 509 writing the chemical potentials of all of the end-members of the minerals and fluid in an
 510 equilibrium, or at least those end-members for which there are data in a thermodynamic
 511 dataset. If all phases are hydrostatically-stressed then the chemical potentials apply
 512 everywhere in the phases, while also applying at grain boundaries. However if any solids
 513 are non-hydrostatically-stressed, the chemical potentials of their additive end-members are

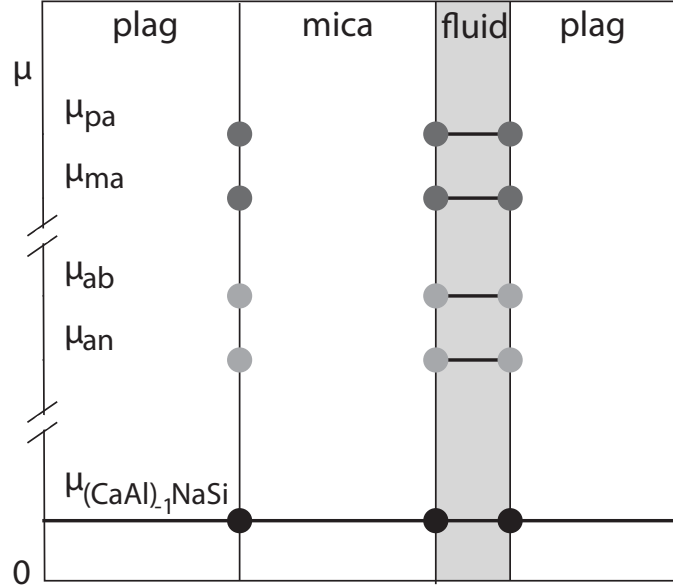


Figure 3: Chemical potential relationships in cross-section across several non-hydrostatically-stressed grains in an equilibrium, showing the constancy of the μ of exchange, $\mu_{(\text{CaAl})_{-1}(\text{NaSi})}$, with pa = paragonite, ma = margarite, an = anorthite and ab = albite. The μ of the additive end-members are only defined in the grain boundaries (dots) and in the fluid (solid line), whereas μ_{ex} is defined through all the minerals and fluid and is constant in the equilibrium.

514 only defined at grain boundaries or in the fluid. So, for example, the effect of having a
 515 non-hydrostatically-stressed grain of the 1-end-member solid, quartz, in a mineral
 516 assemblage is only seen in the grain boundaries or fluid, meaning that the presence of
 517 quartz allows a μ_{SiO_2} to be defined in the grain boundaries and in fluid, even though μ_{SiO_2}
 518 in the quartz grain is not defined. Considering plagioclase, at equilibrium $\mu_{(\text{CaAl})_{-1}(\text{NaSi})}$ is
 519 defined and constant everywhere, but $\mu_{\text{CaAl}_2\text{Si}_2\text{O}_8}$ and $\mu_{\text{NaAlSi}_3\text{O}_8}$ separately are only defined
 520 at grain boundaries (interfaces) or in fluid. It is the interface equilibrium relation that
 521 allows these separate μ to be calculated, stemming originally from Gibbs (1906), eq. 388.

522 The interface equilibrium relation for a binary elastic solid in equilibrium with a fluid is
 523 given by Larché and Cahn (1985), [3.14], incorporating [3.18]. Per mole

$$524 \quad F(\mathbf{T}) + pV(\mathbf{T}) - c\mu_1^f - (1-c)\mu_2^f = 0$$

525 with $F(\mathbf{T})$ and $V(\mathbf{T})$ being for the solid, p the pressure of the fluid at the interface, μ_1^f and
 526 μ_2^f the chemical potentials of 1 and 2 in the fluid, and c is the proportion of end-member 1
 527 in the solid. A more useful form of the interface equilibrium relation can be made using the
 528 fact that the chemical potential of exchange of 1 with 2 in the solid, $\mu_{12}^s(\mathbf{T})$, is equal to

529 $\mu_1^f - \mu_2^f$ in the fluid at the solid–fluid interface

$$530 \quad F(\mathbf{T}) + pV(\mathbf{T}) - c\mu_{12}^s(\mathbf{T}) = \mu_2^f \quad (17)$$

531 adding a superscript s to the μ for solid. Using the result for $F(\mathbf{T}) + pV(\mathbf{T})$ from Appendix
532 2, (41), and the result for $\mu_{12}(\mathbf{T})$ in (16), with $G(p)$ being at p and θ , (17) becomes

$$533 \quad \mu_2^f = c(G_1^s(p) + R\theta \ln a_1^s) + (1 - c)(G_2^s(p) + R\theta \ln a_2^s) + \\ 534 \quad \frac{V_0}{18\kappa}(q_1 + q_2)^2 + \frac{V_0}{6\mu}(q_1^2 - q_1q_2 + q_2^2) - \\ 535 \quad c(G_1^s(p) + R\theta \ln a_1^s - (G_2^s(p) + R\theta \ln a_2^s) - V_{12}(p + \bar{T})) \quad (18)$$

536 with V_0 the volume of the solid, unstressed at θ and at the composition of interest.

537 Simplifying (18), using $p + \bar{T} = \frac{1}{3}(q_1 + q_2)$

$$538 \quad \mu_2^f = G_2^s(p) + R\theta \ln a_2^s + \frac{1}{3}c(q_1 + q_2)V_{12} + \frac{V_0}{18\kappa}(q_1 + q_2)^2 + \frac{V_0}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \quad (19)$$

539 In combination with $\mu_{12}^f = \mu_{12}^s$ from (16), and μ_2^f from (19), the chemical potential of the
540 other end-member in the binary is

$$541 \quad \mu_1^f = G_1^s(p) + R\theta \ln a_1^s - \frac{1}{3}(1 - c)(q_1 + q_2)V_{12} + \frac{V_0}{18\kappa}(q_1 + q_2)^2 + \frac{V_0}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \quad (20)$$

542 Although only the chemical potential of the exchange is defined in the solid, the chemical
543 potentials of the two additive end-members are defined in the fluid by (19–20). The
544 chemical potentials are constant in the fluid and in grain boundaries at equilibrium.

545 For a 1-end-member solid involving end-member 1 the equivalent of (17) is

546 $F(\mathbf{T}) + pV(\mathbf{T}) = \mu_1^f$, which becomes, with the result from Appendix 2

$$547 \quad \mu_1^f = G_1^s(p) + \frac{V_0}{18\kappa}(q_1 + q_2)^2 + \frac{V_0}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \quad (21)$$

548 with V_0 the volume of end-member 1, unstressed at θ . Although the chemical potential of
549 the end-member is not defined in the solid, the chemical potential of the end-member is
550 defined in the fluid by (21). The chemical potential is constant in the fluid and in grain
551 boundaries at equilibrium.

552 The expressions, (19–21), apply at grain boundaries, so the chemical potentials are
553 written for the compositions of the solids there, as well as the stress relationships

554 represented by the terms in q_1 and q_2 . As q_1 and q_2 in a solid may vary along a grain
 555 boundary, constant μ_ℓ^f along the boundary means that q_1 and q_2 are constrained to covary.

556 The logic of (19–21) can be adapted to consider solid–solid grain boundaries (Larché &
 557 Cahn, 1985, sect. 3.5.2). Along solid–solid grain boundaries, the pressure to use in
 558 chemical potential expressions is the negative of the principal stress normal to the grain
 559 boundary, $-t_3$. So, for example, (21) becomes

$$560 \quad \mu_1^{gb} = G_1^s(-t_3) + \frac{V_0}{18\kappa}(q_1 + q_2)^2 + \frac{V_0}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \quad (22)$$

561 in which G_1^s is evaluated at θ and a pressure, $-t_3$, and the q definitions written as
 562 $q_1 = t_1 - t_3$ and $q_2 = t_2 - t_3$. This reduces to (1) for a solid–fluid grain boundary as then
 563 $p = -t_3$. As the pressure, $-t_3$, as well as q_1 and q_2 in each solid, may vary along a
 564 solid–solid grain boundary, constant μ_1^{gb} along the boundary means that these variables are
 565 constrained to covary in each solid. Equation 22, and the equivalent of (19–20), apply to
 566 solid–solid grain boundaries whether the equilibrium being considered is fluid-present or
 567 not.

568 Use of the interface equilibrium relation to determine the chemical potentials of all
 569 additive end-members in the solids, as reflected in fluid and in grain boundaries, depends
 570 on the disposition of grain boundaries in the context of the way stress varies in the solids in
 571 an equilibrium. This is in contrast to considering an equilibrium involving only
 572 hydrostatically-stressed phases. Then the disposition of grain boundaries is irrelevant (if
 573 the grain size is not very small and the boundaries are essentially planar), and the chemical
 574 potentials can be calculated without consideration of spatial information.

575 **4 ILLUSTRATIVE CALCULATIONS**

576 Simple forward calculations are shown here for equilibrium of elastic solids with and
 577 without fluid. In the calculations, minerals are treated as isotropic solids, allowing the
 578 effect of non-hydrostatic stress to be illustrated in a straightforward way. As outlined in
 579 Appendices 1 and 2, little is gained by using more complicated thermodynamic relations
 580 that include the effect of anisotropy.

581 First, calculations with *1-end-member solids* are considered, using kyanite + sillimanite
 582 with and without fluid as an example. If the minerals are hydrostatically stressed, then
 583 equilibrium coexistence occurs on a p – θ line. If temperature is fixed, then coexistence can
 584 only occur at one pressure. If one or both minerals are non-hydrostatically-stressed, the
 585 interface equilibrium relation gives the conditions of equilibrium coexistence which is a

586 pressure *range* at given θ .

587 Consider equilibrium coexistence of kyanite and sillimanite with fluid. At a kyanite-fluid
588 grain boundary at equilibrium using (21)

$$589 \quad \mu_{\text{Al}_2\text{SiO}_5}^f = G^{\text{ky}} + \left(\frac{V}{18\kappa}(q_1 + q_2)^2 + \frac{V}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \right)^{\text{ky}} \quad (23)$$

590 Similarly, at a sillimanite-fluid grain boundary

$$591 \quad \mu_{\text{Al}_2\text{SiO}_5}^f = G^{\text{sill}} + \left(\frac{V}{18\kappa}(q_1 + q_2)^2 + \frac{V}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \right)^{\text{sill}} \quad (24)$$

592 in which V is V_0 , the volume of the end-member at zero stress and the temperature of
593 interest. In an equilibrium involving kyanite + sillimanite + fluid, $\mu_{\text{Al}_2\text{SiO}_5}^f$ is constant, and
594 the fluid pressure is constant, p . Therefore (23) can be subtracted from (24), cancelling
595 $\mu_{\text{Al}_2\text{SiO}_5}^f$, giving

$$596 \quad 0 = G^{\text{sill}} - G^{\text{ky}} + \left(\frac{V}{18\kappa}(q_1 + q_2)^2 + \frac{V}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \right)^{\text{sill}} - \\ 597 \quad \left(\frac{V}{18\kappa}(q_1 + q_2)^2 + \frac{V}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \right)^{\text{ky}} \quad (25)$$

598 Linearising thermodynamic data for the kyanite = sillimanite reaction leads to,
599 $G^{\text{sill}} - G^{\text{ky}} \approx 6.876 - 0.011384\theta + 0.5445p$ kJ, at 7 kbar and 650°C (Holland & Powell,
600 2011, using the units, kJ, K and kbar adopted there). The kyanite + sillimanite
601 equilibrium coexistence surface involves p , θ , and four q values. The effect of some subsets
602 of these variables on the values of the other variables at equilibrium is now shown.

603 Envisage that equilibration occurs at 650°C, and that a non-hydrostatically-stressed
604 kyanite is coexisting with hydrostatically-stressed sillimanite, as might apply if the kyanite
605 is reacting to sillimanite as θ increases. With sillimanite hydrostatically stressed,
606 $q_1^{\text{sill}} = q_2^{\text{sill}} = 0$. Under these conditions the equilibrium relation is

$$607 \quad 0 = -3.631 + 0.5445p - \left(\frac{V}{18\kappa}(q_1 + q_2)^2 - \frac{V}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \right)^{\text{ky}} \quad (26)$$

608 in kJ, with p , q_1 and q_2 in kbar. To reiterate, the principal stresses of sillimanite and of
609 kyanite grains that are perpendicular to the solid-fluid grain boundaries, are equal in
610 magnitude, but opposite in sign, to p . As sillimanite in this example is taken to be
611 hydrostatically-stressed then sillimanite grains can be considered to have a pressure, p .
612 The state of non-hydrostatic stress in the kyanite grains at kyanite-fluid grain boundaries

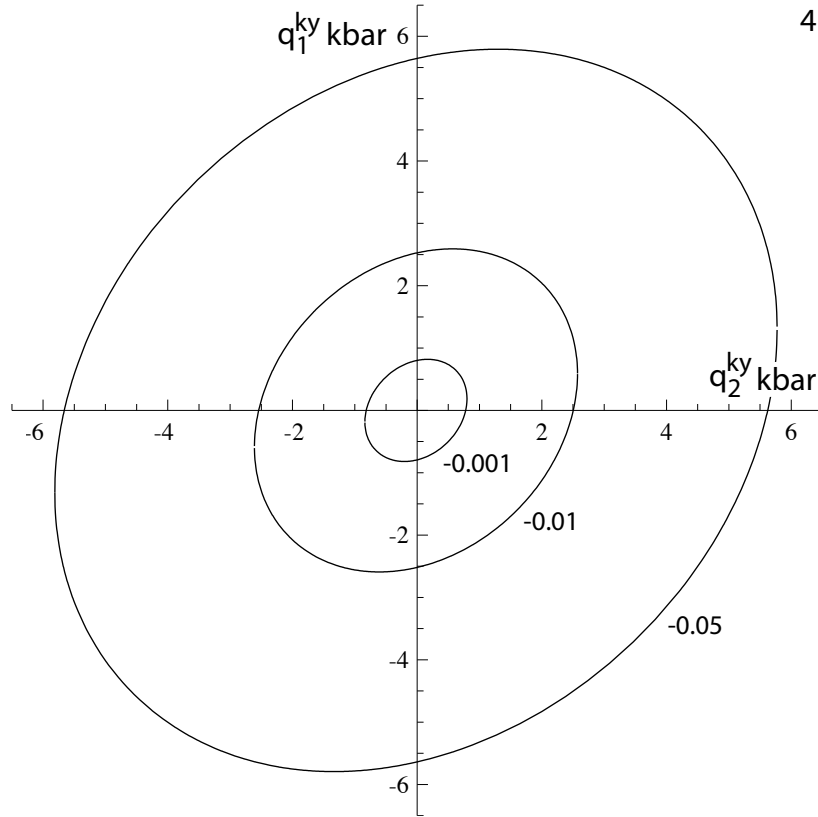


Figure 4: Kyanite-sillimanite surface of equilibrium coexistence, with fluid, in terms of q_1 and q_2 for kyanite, at 650°C . The ellipses are contours of p displacements from the ky=sill pressure at this temperature with both minerals hydrostatically stressed. Displacement of p , and q_1 and q_2 are in kbar. For sillimanite hydrostatically-stressed. For kyanite, $V/\kappa = 0.0028 \text{ kJ kbar}^{-2}$ and $V/\mu = 0.0042 \text{ kJ kbar}^{-2}$. The p displacements are very small compared to $2\sigma_p = 0.26 \text{ kbar}$ with dataset uncertainties, calculated for both minerals hydrostatically-stressed.

613 is represented by q_1^{ky} and q_2^{ky} , and generally will vary along those grain boundaries. This
 614 equation, (26), gives the conditions for equilibrium coexistence of kyanite + sillimanite,
 615 with fluid, in terms of p , q_1^{ky} and q_2^{ky} , as portrayed in Figure 4.

616 Considering relations at different grain boundaries in a kyanite + sillimanite + fluid
 617 system at equilibrium, a grain boundary between a non-hydrostatically-stressed grain of
 618 kyanite and fluid at equilibrium can be considered using (23). Linearising thermodynamic
 619 data for kyanite leads to, $G^{\text{ky}} \approx -2486.57 - 0.269125\theta + 4.4717p \text{ kJ}$, at 7 kbar and 650°C
 620 (Holland & Powell, 2011). With q_1 and q_2 in the range $\pm 5 \text{ kbar}$, the second two terms
 621 together in (23) are $< 0.03 \text{ kJ}$ and are always positive, using $V/\kappa = 0.0019 \text{ kJ kbar}^{-2}$ and
 622 $V/\mu = 0.0042 \text{ kJ kbar}^{-2}$ as in Figure 4. This is tiny compared with the pressure
 623 dependence of G^{ky} . Because the second two terms are always positive it means that a fluid
 624 in equilibrium with a non-hydrostatically-stressed kyanite is always supersaturated in

625 Al_2SiO_5 with respect to fluid in equilibrium with hydrostatically-stressed kyanite (a general
 626 result of Gibbs, 1906, p.197).

627 For the system with a specified fluid pressure, for example, with a pressure displacement
 628 of 0.01 kbar below the kyanite-sillimanite equilibrium with hydrostatically-stressed
 629 minerals, the covarying of q_1 and q_2 along kyanite-fluid grain boundaries is given by the
 630 0.01 ellipse in Figure 4. Given that hydrostatically-stressed sillimanite can also be
 631 considered to have a pressure, the same as the fluid pressure, the covarying of q_1 and q_2 at
 632 sillimanite-kyanite grain boundaries is given by the same ellipse. Along kyanite-kyanite
 633 grain boundaries, the pressure at the boundary, $-t_3$, can vary, as well as q_1 and q_2 in each
 634 of the adjacent grains at the grain boundary. From (23), the difference between the fluid
 635 pressure and the pressure at a kyanite-kyanite grain boundary is given by

$$636 \quad p + t_3 = \frac{0.005445 - \left(\frac{V}{18\kappa}(q_1 + q_2)^2 + \frac{V}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \right)^{\text{ky}}}{4.4717}$$

637 with 0.005445 kJ the $\mu_{\text{Al}_2\text{SiO}_5}^f$ difference corresponding to the displacement of the
 638 equilibrium by 0.01 kbar, and 4.4717 kJ/kbar the pressure dependence of G^{ky} . This
 639 pressure, $-t_3$, can be larger or smaller than the fluid pressure. With q_1 and q_2 in the range
 640 ± 5 kbar, $p + t_3$ is in the range -0.011 to 0.0012 kbar. This is a very small pressure range.

641 In this consideration of solid–solid grain boundaries in a fluid-present equilibrium, the
 642 pressure along the grain boundaries can be related to the fluid pressure, and is very similar
 643 to it. In the absence of fluid, the calculation can be recast to give the pressure at the grain
 644 boundaries directly. Again, the pressure range at the grain boundaries in an equilibrium is
 645 very small. The small pressure range in both these cases is due primarily to the pressure
 646 dependence of G being much larger than the contribution of the q terms.

647 If both sillimanite and kyanite are non-hydrostatically-stressed, and using the
 648 simplification for each mineral that $q_1 = q_2 = q$ to allow a two-dimensional representation,
 649 the surface of coexistence can be portrayed as in Figure 5. The calculations indicate again
 650 that kyanite + sillimanite coexistence can only occur over a very narrow pressure range at
 651 a fixed temperature, with the pressure range extending up and down pressure from the
 652 position of the kyanite = sillimanite univariant for both minerals hydrostatically-stressed,
 653 depending on whether the effect of the non-hydrostatic stress in kyanite dominates (up), or
 654 sillimanite (down).

655 A very small range of equilibrium coexistence of minerals involved in reactions that are
 656 univariant when the minerals are hydrostatically-stressed is a general result. The
 657 implication drawn is not dependent on the precise values of the moduli, κ and μ . For

658 example, halving the moduli, κ and μ do not invalidate the conclusion that the
659 contribution of the q terms to the thermodynamics is small. The lack of consistency of this
660 result with Wheeler (2014) is discussed in Appendix 3.

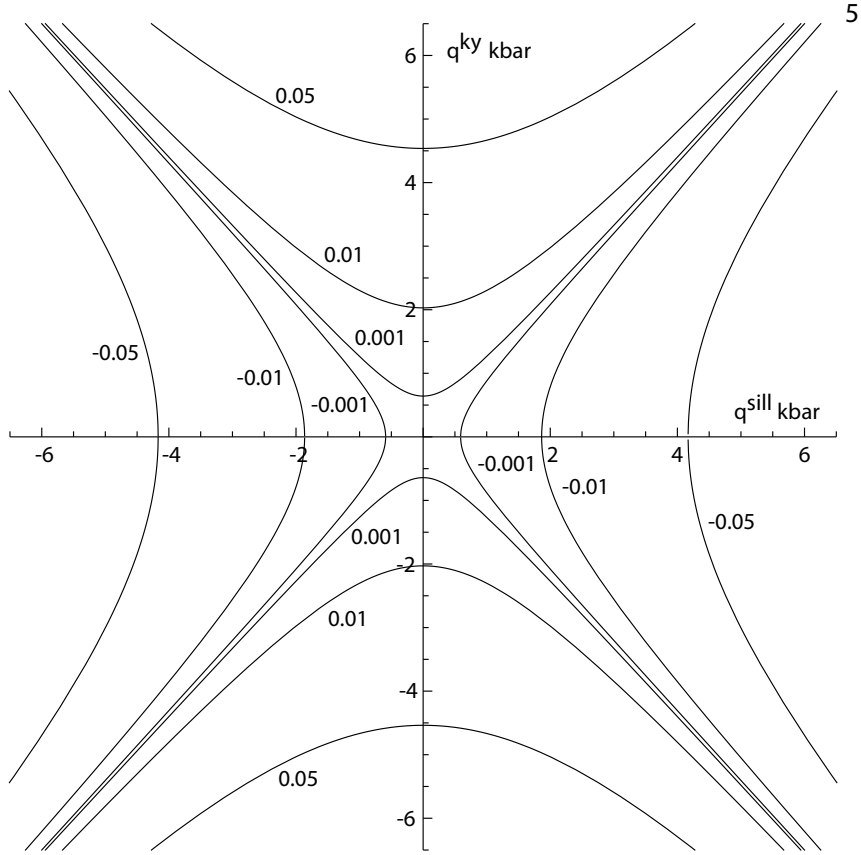


Figure 5: Kyanite-sillimanite surface of equilibrium coexistence, with fluid, at 650°C with both kyanite and sillimanite non-hydrostatically stressed, using (25) and simplifying with $q_1^{\text{ky}} = q_2^{\text{ky}} = q^{\text{ky}}$ and $q_1^{\text{sill}} = q_2^{\text{sill}} = q^{\text{sill}}$. The hyperbolae are for p displacements in kbar from the ky=sill pressure at this temperature if both minerals are hydrostatically stressed. For kyanite, $V/\kappa = 0.0019 \text{ kJ kbar}^{-2}$ and $V/\mu = 0.0042 \text{ kJ kbar}^{-2}$ and for sillimanite, $V/\kappa = 0.0030 \text{ kJ kbar}^{-2}$ and $V/\mu = 0.0054 \text{ kJ kbar}^{-2}$.

661 Next, calculations with *solid solutions* are considered. The example considered here is
662 that of the expected compositional heterogeneity in a mosaic of heterogeneously
663 non-hydrostatically stressed grains of a binary plagioclase in an equilibrium. At
664 equilibrium, $\mu_{(\text{CaAl})_{-1}(\text{NaSi})}$, i.e. $\mu_{\text{ab an}}$, defined by (16), is constant in each grain and
665 between grains, with each plagioclase grain having smoothly varying mean stress. The
666 occurrence of both mean stress and composition in the activity terms in (16), means that at
667 constant $\mu_{\text{ab an}}$ the grains must be compositionally-zoned. There will be composition steps
668 at grain boundaries corresponding to mean stress steps. Consider two points in grains

669 within the mosaic at equilibrium, A and B. The value of the exchange chemical potentials
 670 is the same everywhere, so

$$671 \quad \mu_{\text{ab an}}^{\text{A}} = \mu_{\text{ab an}}^{\text{B}} \quad (27)$$

672 where the superscripts A and B refer to the physical locations. For clarity, plagioclase is
 673 assumed to be an ideal solid solution, and x is substituted for a_{an} in (16) and $1 - x$ for a_{ab} .
 674 Simplifying, (27) becomes

$$675 \quad R\theta \ln \frac{1 - x^{\text{A}}}{x^{\text{A}}} - \bar{T}^{\text{A}} V_{\text{ab an}} = R\theta \ln \frac{1 - x^{\text{B}}}{x^{\text{B}}} - \bar{T}^{\text{B}} V_{\text{ab an}} \quad (28)$$

676 with $V_{\text{ab an}} = V_{\text{ab}} - V_{\text{an}}$.

677 In (28), if point A has a composition, x , at a mean stress, \bar{T} , and point B has the
 678 composition, $x + \Delta x$, at mean stress, $\bar{T} + \Delta \bar{T}$, then rearranging (28) gives

$$679 \quad \ln \frac{(1 - x)(x + \Delta x)}{x(1 - x - \Delta x)} = -\Delta \bar{T} \frac{V_{\text{ab an}}}{R\theta}$$

680 A series expansion of the left-hand side for Δx around zero gives

$$681 \quad \ln \frac{(1 - x)(x + \Delta x)}{x(1 - x - \Delta x)} \approx \frac{\Delta x}{x(1 - x)}$$

682 So, to a first approximation

$$683 \quad \Delta x = -x(1 - x) \frac{\Delta \bar{T} V_{\text{ab an}}}{R\theta} \quad (29)$$

684 with $V_{\text{ab an}} = 0.039 \text{ kJ kbar}^{-1}$ (at $\theta = 650^\circ\text{C}$ and 8 kbar), and with $x = 0.3$, $\theta = 650^\circ\text{C}$ and
 685 $\Delta \bar{T} = 3.3 \text{ kbar}$, $\Delta x \approx -0.0035$. Such a composition difference is similar to the random
 686 error associated with electron microprobe analysis of plagioclase composition. The
 687 difference between this result and that of Tajčmanová, Podladchikov, Powell, Moussas,
 688 Vrijmoed and Connolly (2014) is discussed in Appendix 4.

689 The plagioclase $V_{\text{ab an}}$ in (29) is relatively small, but such a V tends to be small for the
 690 majority of substitutions in minerals where there is significant substitution, so that large q
 691 tending to give rise to very small composition changes is a general result. Equation 29 is a
 692 general expression for the effect of variation in \bar{T} on an exchange equilibrium. The same
 693 logic as in (29) applies if there is more than one exchange operating in a mineral. If there
 694 are several minerals in the equilibrium with the same exchange, say $(\text{CaAl})_{-1}(\text{NaSi})$,
 695 Na_{-1}K , or Mg_{-1}Fe , then (29) applies in each of them. Given that the composition
 696 variation due to mean stress variation is so small, if minerals have obvious zoning then it is

697 unlikely to be because the minerals are non-hydrostatically stressed, unless the V term for
 698 the exchange is much larger than for plagioclase.

699 Continuing with this binary plagioclase example, consider now a plagioclase-fluid grain
 700 boundary. Application of the interface equilibrium relation, using (19, 20), and the
 701 assumption that plagioclase is an ideal solid solution, as above, gives

$$702 \quad \mu_{\text{an}}^f = G_{\text{an}}(p) + R\theta \ln(1 - x) + \frac{1}{3} x (q_1 + q_2) V_{\text{ab an}} +$$

$$703 \quad \frac{V_0}{18\kappa} (q_1 + q_2)^2 + \frac{V_0}{6\mu} (q_1^2 - q_1 q_2 + q_2^2) \quad (30)$$

$$704 \quad \mu_{\text{ab}}^f = G_{\text{ab}}(p) + R\theta \ln x - \frac{1}{3} (1 - x) (q_1 + q_2) V_{\text{ab an}} +$$

$$705 \quad \frac{V_0}{18\kappa} (q_1 + q_2)^2 + \frac{V_0}{6\mu} (q_1^2 - q_1 q_2 + q_2^2) \quad (31)$$

706 in which V_0 is the volume of plagioclase, unstressed, at the temperature and composition of
 707 interest. The μ^f values are the ones that would be used to calculate conditions of
 708 equilibrium with the end-members of other minerals coexisting with the plagioclase. The
 709 contribution to μ from non-hydrostatic stress, given by the last three terms in the
 710 equations, can be compared with the uncertainties on end-member chemical potentials
 711 given in thermodynamic data compilations. The uncertainties in G_{ab} and G_{an} are 3.36 and
 712 1.58 kJ, respectively, ($2\sigma_{\Delta_f H}$, Holland & Powell, 2011). Adding the latter three terms in
 713 the μ^f expressions, with $V = 10 \text{ kJ kbar}^{-1}$, $\kappa = 600 \text{ kbar}$, $\mu = 360 \text{ kbar}$, and q_1 and q_2 in
 714 the range $\pm 5 \text{ kbar}$, gives $< 0.35 \text{ kJ}$, small compared to the dataset uncertainties. The
 715 covarying relationship amongst x , q_1 and q_2 along plagioclase-fluid grain boundaries can be
 716 found from (29) and the mean stress definition. Specifying the fluid to be at $p = 8 \text{ kbar}$,
 717 and the plagioclase at a point on the grain boundary to have $x = 0.3$ and $q_1 = q_2 = -3$
 718 kbar (giving $\bar{T} = -10 \text{ kbar}$), then, by (29), $\Delta x = -0.0011 \bar{T}$. Then, from the mean stress
 719 definition, $q_2 = -q_1 + 3 \Delta \bar{T} - 6$. The logic for plagioclase-plagioclase grain boundaries
 720 follows the kyanite example above, with $-t_3$ being in a small range around p .

721 Can it be recognised if solid solutions were non-hydrostatically stressed at the time that
 722 textures and mineral compositions were preserved? The calculations above suggest that it
 723 might be difficult to do. Patterns of composition steps at grain boundaries might feasibly
 724 help, but, in a rock context, diffusive equilibration may change composition relations at
 725 grain boundaries after the assemblage as a whole has stopped evolving. The best
 726 opportunity might be provided by composition variation within grains of solid that involve

727 exchanges with the largest V_{ij} , which are likely to be ones involving more limited
728 substitutions. Calculations relating to such effects would need to involve a full exposition
729 of the thermodynamics, involving less simplified compliance tensors for minerals than those
730 used for illustrative purposes here, including p , θ and composition dependence of the
731 moduli involved.

732 An important difference in calculation methods between systems involving just
733 hydrostatically-stressed minerals, and systems involving non-hydrostatically-stressed
734 minerals, relates to the possibility of using straightforward energy minimisation techniques.
735 When all minerals are assumed to be hydrostatically stressed, Gibbs energy minimisation is
736 good for phase equilibrium calculations, as for example done by Perplex (Connolly 2009).
737 However, in non-hydrostatically stressed systems this is not an option. As shown by the
738 original energy minimisation in Larché and Cahn (1973), such a minimisation is non-trivial,
739 requiring the variational calculus. Given the heterogeneity of stress in general, there is no
740 direct way to calculate mineral proportions and compositions using energy minimisation.

741 The above illustrative calculations on non-hydrostatically-stressed minerals involve
742 forward calculations. In principle, inverse chemical potential-based calculation methods,
743 like average pressure (*avp*, Powell & Holland, 1994), can also be undertaken. Average
744 pressure can be calculated based on observed mineral compositions if the states of stress
745 are known in each mineral. Generally in rocks the states of stress are not known, and an
746 inverse method that specifically accounted for these would not be constrained. However,
747 chemical potentials, as in (30–31), and mineral composition, as in (29), are very insensitive
748 to the state of stress. Consequently, in applying inverse methods such as average pressure,
749 it is sufficient to assume that the minerals are hydrostatically-stressed.

750 Regardless of the actual or assumed state of stress in the minerals, the average pressure
751 will refer to the average of the pressure along the grain boundaries, and the fluid pressure if
752 the equilibrium is fluid-present. This is because it is the interface equilibrium relation for
753 the end-members in each mineral that specifies the chemical potentials at grain boundaries
754 (and in fluid if there is one). These are the chemical potentials used in the $\Delta\mu = 0$
755 relations that are then combined in an *avp* calculation. The mean stress in the minerals is
756 little reflected in the calculated average pressure.

757 The small difference between the thermodynamics of minerals in a
758 non-hydrostatically-stressed state and a corresponding hydrostatic state suggests that
759 various conventional thermodynamic calculations that assume hydrostatically-stressed
760 minerals will give useful results even if the minerals are non-hydrostatically-stressed. This
761 result provides an *a posteriori* justification for the adoption by Bruton and Helgeson (1983)

762 and Dahlen (1992) of their more restrictive approximation: making $F + pV$ in (17)
763 independent of stress, which, in terms of the formulation above means that V_0/κ and V_0/μ
764 are both taken to be zero, e.g. in (21).

765 **5 DISCUSSION and CONCLUSIONS**

766 As noted in the Introduction, the systematic nature of observations on metamorphic
767 mineral assemblages is consistent with a local equilibrium interpretation of what is seen.
768 The observations suggest *a priori* that non-hydrostatic stress in minerals does not have a
769 first order effect. The illustrative calculations using the thermodynamic development above
770 show that calculations that incorporate the equilibrium thermodynamics of
771 non-hydrostatically-stressed minerals give results that are little different from those
772 assuming hydrostatic stress. Making the usual assumption that, to first order, mineral
773 assemblages as preserved in rocks do represent equilibria on an appropriate length-scale,
774 the equilibrium methods developed above become directly applicable to rocks. Thus, the
775 presence of non-hydrostatically stressed minerals in rocks at the time that equilibrium is
776 preserved is unlikely to significantly affect the results of approaches commonly adopted in
777 mineral equilibria calculations, like thermobarometry, that involve the implicit assumption
778 that the minerals are hydrostatically stressed. The *a posteriori* success of such approaches,
779 along with their ability to account for the fundamental patterns of mineral assemblage
780 occurrence in orogens, is consistent with this. A view of metamorphism in which
781 non-hydrostatic effects dominate, as in Wheeler (2014), is inconsistent with both the
782 thermodynamic approach outlined here and the rock record itself.

783 Mineral assemblage evolution during progressive metamorphism, prior to mineral
784 assemblage preservation, accompanies elasto-viscoplastic processes accumulating permanent
785 deformation. The dissipative processes that need to take place to keep establishing an
786 approach to equilibrium appear to take place readily as pressure–temperature conditions
787 change. Such an approach to equilibrium is a necessary implication of many of the
788 observations on mineral assemblages that result from preservation. While dissipative
789 processes may leave no mark on the final preserved inferred-equilibrium mineral
790 assemblage, it may leave a record in features such as prograde-zoned porphyroblasts.

791 In general, overprinting equilibration is more complicated if the minerals are
792 non-hydrostatically stressed. At equilibrium, if all the minerals are hydrostatically stressed,
793 they are homogeneous and can be considered to have a pressure, the same in all of the
794 minerals, and equal to that in a fluid. As a consequence this pressure can be treated as a

795 boundary condition of the local equilibrium. This pressure might then be related to the
796 depth of metamorphism, or be understood in terms of larger scale tectonic processes. The
797 imposition of a pressure (and temperature) boundary condition is what allows Gibbs
798 energy minimisation to work for mineral equilibrium calculations. Boundary conditions for
799 elastic systems are, however, a more difficult problem, as discussed by, for example,
800 Truesdell and Noll (2004, p125 *et seq.*), and McLellan (1980, sections 19.3 and 22.4). In the
801 elastic case, the lack of homogeneity of stress-strain and the relevance of grain boundaries
802 means that the relation between boundary conditions and the behaviour of a local
803 equilibrium is indirect (e.g. Dahlen, 1992). In general, the connection can only be made via
804 the variational calculus (e.g. Larché & Cahn, 1973, 1978), and solution of the appropriate
805 partial differential equations. Detailed consideration of the processes involved in
806 equilibration itself is beyond our remit here.

807 The emphasis above is on equilibrium stated in terms of chemical potentials of the
808 end-members of minerals because that is the form that the variational calculus gives. The
809 approach of, for example, Powell and Holland (1994) and Powell, Holland and Worley
810 (1998), which is focussed on equilibrium in terms of the equilibrium relations, $\Delta\mu = 0$, for
811 balanced reactions between end-members, carries across to handling systems involving
812 non-hydrostatically stressed minerals, e.g. via (19).

813 There remain questions regarding *how* mineral assemblage development in progressive
814 metamorphism is curtailed and the resulting mineral assemblage preserved. The loss of
815 fluid around the start of cooling, Guiraud *et al.* (2001), or the loss of melt at higher
816 metamorphic grades, White and Powell (2002), is certainly significant. We speculate that
817 an additional effect comes from the evolution of elastic behaviour and chemical
818 equilibration during cooling, following elasto-viscoplastic behaviour giving way to elastic
819 behaviour.

820 ACKNOWLEDGEMENTS

821 RP acknowledges those several people who sent him Wheeler (2014) when it first came
822 online (knowing that he wouldn't have seen it otherwise). He thanks Lucie Tajčmanová for
823 her support in visiting ETH Zürich where, through conversations with Lucie and Yuri
824 Podladchikov, the original motivation for this work came. We thank Jamie Connolly and
825 Bruce Hobbs for discussions and the former for checking his elastic energy calculation in
826 Connolly (2009). We thank Bruce Hobbs (x2), John Wheeler, Ross Angel, Michel Guiraud
827 and three anonymous reviewers for their reviews of earlier versions of the paper. Editor,

828 Mike Brown, is thanked for his perseverance and patience.

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959 **APPENDIX 1: APPROXIMATION FOR CHEMICAL POTENTIALS OF**
 960 **EXCHANGE END-MEMBERS**

961 To use the general equation, (15), for calculations, approximations are needed. Following
 962 Larché and Cahn (1973), p1059, and Larché and Cahn (1985), p338, adopting isotropic
 963 constitutive relations, the eigenstrain is spherical. Then $V_{\ominus} \mathbf{E}_{\mathbf{c}}$ can be approximated for
 964 small eigenstrains (the first approximation in the next equation) by $(V - V_{\ominus})\mathbf{1}$, involving
 965 the volume, V , at θ in the unstressed state and at the composition of interest. At this
 966 point, $\partial\mathbb{S}/\partial n_{12} = 0$ is also assumed. Then

$$967 \quad \mu_{12}(\mathbf{T}) - (\mu_{12})_{\ominus} \approx -\frac{1}{3}(\mathbf{1} : \mathbf{T}) \left(\frac{\partial V}{\partial n_{12}} \right) \approx -\bar{T} (V_1 - V_2) \equiv -\bar{T} V_{12} \quad (32)$$

968 with V_{12} defined as the difference in the molar volumes of pure end-member 1 and 2,
 969 $V_1 - V_2$, at θ in the unstressed state, and in the absence of an excess volume of mixing (the
 970 second approximation). The assumptions leading to (32) result in the dependence of $\mu_{12}(\mathbf{T})$
 971 on \mathbf{T} reducing to a dependence on the first principal invariant of \mathbf{T} , i.e. the mean stress, \bar{T} .

972 Now to determine $(\mu_{12})_{\theta}$. Using a standard state of pure end-member at the θ of
 973 interest and an arbitrary pressure, P , denoted by superscript 0, and noting that the
 974 approximation $\partial\mathbb{S}/\partial n_{12} = 0$ means that the moduli in the compliance, \mathbb{S} , are composition
 975 independent, then, $(\mu_{12})_{\ominus}$ in (32) can be written

$$976 \quad (\mu_{12})_{\ominus} = \mu_1^0(0) - \mu_2^0(0) = \mu_1^0(P) - \mu_2^0(P) - P V_{12} \quad (33)$$

977 From (32,33), the chemical potential, $\mu_{12}(\mathbf{T})$, which is for the stressed state, can now be
 978 written in terms of the chemical potentials of the additive end-members, [4.23]

$$979 \quad \mu_{12}(\mathbf{T}) = \mu_1^0(P) - \mu_2^0(P) + R\theta \ln \frac{a_1}{a_2} - V_{12}(P + \bar{T}) \quad (34)$$

980 The various assumptions involved in this appendix can be relaxed at the cost of a much
 981 more complicated equation to replace (34). Generally, the added complexity involves only
 982 a minor modification of the effect of (34). However the assumption that the moduli are
 983 composition-independent is not a good approximation for some minerals, for example in
 984 plagioclase κ is strongly composition dependent (Brown, Angel & Ross, 2016). Treating
 985 plagioclase as isotropic, and with a composition dependent κ , $V_{\text{ab an}}$ in (29) is modified by a
 986 term $\frac{2\bar{T}}{\kappa^2} \frac{d\kappa}{dx}$. Even in this extreme case, this additional term is about half an order of
 987 magnitude less than $V_{\text{ab an}}$, so, while significant, it has no effect on the implications drawn
 988 from application of (29).

989 **APPENDIX 2: A USEFUL FORM FOR $F + pV$ IN THE INTERFACE**
 990 **EQUILIBRIUM RELATION**

991 The Helmholtz energy is required for the interface equilibrium relation. The derivation,
 992 which follows Larché and Cahn (1985) closely, needs to start with the Gibbs energy,
 993 because its differential has stress, not strain, as the natural variable. As a consequence,
 994 integration with respect to stress can be undertaken with the Gibbs energy but not the
 995 Helmholtz energy. The energies initially will be energy densities, with respect to a reference
 996 volume, V_0 (primed quantities in Larché & Cahn, 1985), with V_0 being the volume of the
 997 unstressed solid at the temperature and composition of interest. Lower case is used for
 998 such densities. The differential of the Gibbs energy density for a elastic solid, [4.12] (Larché
 999 & Cahn, 1985, with numbers in square brackets being their equations), from (11)

$$1000 \quad dg = -s d\theta - \mathbf{E} : d\mathbf{T} + \sum_{i \neq \ell}^n \mu_{i\ell} d\rho_i$$

1001 in which the ρ_i are number densities, with $n_i = V_0 \rho_i$. For a 1-end-member solid, the sum
 1002 disappears. This differential can be integrated from an arbitrary pressure P to \mathbf{T} (where P
 1003 will in due course be the pressure of a coexisting fluid p in the interface equilibrium
 1004 relation), [4.24]

$$1005 \quad g(\mathbf{T}) - g(P) = -\frac{1}{2} \mathbb{S} \mathbf{T} : \mathbf{T} + \frac{1}{2} (\mathbb{S} \mathbf{T} : \mathbf{T})|_{\mathbf{T}=-P\mathbf{1}} = -\frac{1}{2} \mathbb{S} \mathbf{T} : \mathbf{T} + \frac{1}{2} P^2 \mathbb{S} \mathbf{1} : \mathbf{1} \quad (35)$$

1006 with the energies indicated to be a function of stress (or pressure), and considering the
 1007 solid to be linear elastic, so $\mathbf{E} = \mathbb{S} \mathbf{T}$. Using the Legendre transform [4.11], $g = f - \mathbf{E} : \mathbf{T}$,
 1008 for $g(\mathbf{T})$ and also for $g(P)$ in (35) and rearranging gives, [4.25]

$$1009 \quad f(\mathbf{T}) = f(P) + \frac{1}{2} \mathbb{S} \mathbf{T} : \mathbf{T} - \frac{1}{2} P^2 \mathbb{S} \mathbf{1} : \mathbf{1} \quad (36)$$

1010 Given that, for a hydrostatically-stressed solid, [4.26]

$$1011 \quad f(P) = \frac{G(P)}{V_0} - P \frac{V|_{\mathbf{T}=-P\mathbf{1}}}{V_0} \quad (37)$$

1012 the Helmholtz energy density may be calculated from tabulated data of the molar Gibbs
 1013 energy as a function of P at specified θ and composition. This G relates to $\mathcal{L}_{p\theta}U$, whereas
 1014 (35) relates to $\mathcal{L}_{\mathbf{T}\theta}U$. Ultimately the $G(P)$ in (37) will be written as $\sum c_k \mu_k(p)$, in which
 1015 c_k is the proportion of end-member, k . In the case of a 1-end-member solid, $G(P)$ is just

1016 the Gibbs energy of the end-member. Now, given that the last term on the right-hand side
 1017 of (37) is $P(1 - P \mathbf{S} \mathbf{1} : \mathbf{1})$, then (36) becomes, [4.29]

$$1018 \quad f(\mathbf{T}) = \frac{G(P)}{V_0} + \frac{1}{2} \mathbf{S} \mathbf{T} : \mathbf{T} - P(1 - \frac{P}{2} \mathbf{S} \mathbf{1} : \mathbf{1}) \quad (38)$$

1019 In this equation, for an isotropic solid, [4.30], aligning the coordinates with the principal
 1020 axes of \mathbf{T} , and with $\{t_1, t_2, t_3\}$ along the diagonal of \mathbf{T}

$$1021 \quad \frac{1}{2} \mathbf{S} \mathbf{T} : \mathbf{T} = \frac{1}{18\kappa} (t_1 + t_2 + t_3)^2 + \frac{1}{6\mu} (t_1^2 + t_2^2 + t_3^2 - t_2 t_3 - t_1 t_2 - t_1 t_3)$$

1022 and

$$1023 \quad P(1 - \frac{P}{2} \mathbf{S} \mathbf{1} : \mathbf{1}) = P(1 - \frac{P}{2\kappa})$$

1024 assuming that κ and μ are constants.

1025 Now, the focus will shift to the Helmholtz energy of the solid at a solid–fluid grain
 1026 boundary as needed for the interface equilibrium condition. Then the principal stress
 1027 normal to the interface can be set to the pressure in the fluid, p . This principal stress is
 1028 chosen to be t_3 , so $p = -t_3$ (compression negative), without implication for the relative
 1029 magnitudes of t_1 , t_2 and t_3 . Now, P becomes the pressure in the fluid, $P = p$, and $\bar{\mathbf{T}}$ is
 1030 used for the mean stress in the solid at the interface. The development of Sekerka and
 1031 Cahn (2004) is brought in here, in parallel to that of Larché and Cahn (1985), with single
 1032 numbers in square brackets being Sekerka and Cahn (2004) equations. In the following
 1033 equations the only thing that relates to the fluid is its pressure, p . For an isotropic solid
 1034 (38) can now be written

$$1035 \quad f(\mathbf{T}) = \frac{G(p)}{V_0} + \frac{1}{2\kappa} (\bar{\mathbf{T}})^2 + \frac{1}{6\mu} (q_1^2 - q_1 q_2 + q_2^2) - p(1 - \frac{p}{2\kappa}) \quad (39)$$

1036 with $q_1 = t_1 - t_3$ and $q_2 = t_2 - t_3$, so that when the solid is hydrostatically stressed
 1037 $q_1 = q_2 = 0$.

1038 Now including the volume term needed in the interface equilibrium relation, forming
 1039 $f(\mathbf{T}) + p v(\mathbf{T})$, the additional term, $p v(\mathbf{T})$, is [35]

$$1040 \quad p v(\mathbf{T}) = p(1 + \mathbf{E} : \mathbf{1}) = p(1 + \mathbf{S} \mathbf{T} : \mathbf{1}) = p(1 + \frac{\bar{\mathbf{T}}}{\kappa}) \quad (40)$$

1041 Combining (39) and (40), and after some algebra, using $\bar{\mathbf{T}} = -p + \frac{1}{3}(q_1 + q_2)$

$$1042 \quad f(\mathbf{T}) + p v(\mathbf{T}) = \frac{G(p)}{V_0} + \frac{1}{18\kappa} (q_1 + q_2)^2 + \frac{1}{6\mu} (q_1^2 - q_1 q_2 + q_2^2)$$

1043 or in molar form

$$1044 \quad F(\mathbf{T}) + pV(\mathbf{T}) = G(p) + \frac{V_0}{18\kappa}(q_1 + q_2)^2 + \frac{V_0}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \quad (41)$$

1045 This equation is consistent with [6.4]. Also, as the two last terms are equal to zero for
1046 hydrostatically-stressed solids, with $q_1 = q_2 = 0$, then $F + pV = G$ as expected.

1047 Also from (39–41), the elastic energy density in the solid, $\frac{1}{2}\mathbb{S}\mathbf{T} : \mathbf{T}$, at a solid–fluid grain
1048 boundary with a fluid at p , can be written

$$1049 \quad \frac{p^2}{2\kappa} - \frac{p}{3\kappa}(q_1 + q_2) + \frac{1}{18\kappa}(q_1 + q_2)^2 + \frac{1}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \quad (42)$$

1050 which is quadratic in p , q_1 and q_2 . This reduces to $p^2/(2\kappa)$ when the solid is hydrostatically
1051 stressed. For kyanite at $p = 8$ kbar, with $\kappa = 1600$ kbar and $\mu = 1050$ kbar, and q_1 and q_2
1052 in the range ± 5 , the elastic energy density is < 0.032 kbar. Such energy densities are small,
1053 for example in the context of the dataset enthalpy uncertainty, $2\sigma_H/V_0 = 0.3$ kbar (see also
1054 Connolly, 2009). For anisotropic solids, the number of q terms in (41) and (42) depends on
1055 the crystal class. For example there are 9 independent moduli in the orthorhombic class, so
1056 9 terms in such equations, compared with the two, involving κ and μ , for isotropic solids.
1057 The q terms in (41) are always quadratic in q_1 and q_2 . The elastic energy density is always
1058 small for minerals regardless of crystal class.

1059 **Appendix 3: Discussion of Wheeler (2014)**

1060 Wheeler (2014) proposes that the effect of non-hydrostatic stress on mineral equilibria is
1061 much bigger than that suggested in the present work. The aim here is to show why the
1062 conclusions of the two studies are different.

1063 An example used by Wheeler is the breakdown of muscovite and quartz to K-feldspar,
1064 sillimanite and H₂O in the simple KASH system.



1066 Using (21) for each of the solids, *equilibrium* coexistence of mu + q + ksp + sill + H₂O at
1067 650°C, is given by

$$1068 \quad 0 = -6.50 + 1.92p + \sum r_\ell \left(\frac{V}{18\kappa}(q_1 + q_2)^2 + \frac{V}{6\mu}(q_1^2 - q_1q_2 + q_2^2) \right)^\ell \quad (43)$$

1069 in kJ, with the sum being over the non-hydrostatically-stressed solids involved, and r_i the
1070 reaction coefficients. The leading terms come from the thermodynamic data of Holland and

1071 Powell (2011), linearised at 650°C and 3.5 kbar, with a 2σ uncertainty on the constant
1072 term of 0.28 kJ, propagating to an uncertainty on pressure of the reaction at 650°C of 0.14
1073 kbar. As with ky+sill coexistence in the main text, there will be a very small range of p of
1074 coexistence of $\mu + q + \text{ksp} + \text{ky} + q + \text{H}_2\text{O}$ at specified θ , very close to the pressure
1075 for this KASH univariant at specified θ . For example, with quartz the only mineral
1076 non-hydrostatically-stressed in this equilibrium, and $q_1 = q_2 = 5$ kbar for the quartz, the
1077 last term is just -0.042 kJ, much smaller than the enthalpy uncertainty on the reaction.

1078 Wheeler (2014) is not concerned with equilibrium coexistence of the solids with fluid in
1079 reaction A, but rather with the temperature at which the $\mu + q$ breakdown reaction
1080 might occur, as shown in his fig. 2b. He is considering a system at a point in time in a
1081 dynamic dissipative process. He calculates a big range of temperature for the breakdown
1082 reaction by combining chemical potentials derived from spatially-separated minerals with
1083 different states of non-hydrostatic stress at solid–fluid grain boundaries. Wheeler uses an
1084 adaption of the interface equilibrium relation, $F + pV = \mu_1^f$, as used in deriving (17). He
1085 replaces p by the principal stress normal to the grain boundary of interest, $-t_3$ in the
1086 present work, giving $F - t_3V = \mu_1^f$, as implied by (22). This is legitimate given that the
1087 equality, $p = -t_3$, relates to mechanical equilibrium. But as a consequence his combination
1088 of the different chemical potentials relates to fluid on grain boundaries at *different* fluid
1089 pressures. Yet, as pointed out in the main body of the text, the fluid pressure is constant
1090 in an equilibrium. The argument may be extended to solid–solid grain boundaries, given
1091 that at equilibrium the pressure ($-t_3$) at such grain boundaries is close to the fluid
1092 pressure, as discussed in the main body of the text. Wheeler’s pressure differences are
1093 possible if the chemical potentials being combined do not all arise in the same equilibrium.
1094 The scenario considered by Wheeler should be envisaged as a set of spatially-separate
1095 smaller systems involving different equilibria, with chemical potential and pressure
1096 gradients between the systems. Such pressure and chemical potential gradients help to
1097 drive the dynamic dissipative process which will ultimately give rise to larger equilibrated
1098 systems by coalescence of the smaller systems. Only when this stage has been reached
1099 could Wheeler consider the equilibrium coexistence of the spatially-separated minerals
1100 participating in reaction A. If all the minerals occur together in equilibrium with the fluid
1101 on an appropriate length-scale, the fluid will have just one pressure, chemical potentials
1102 will be constant, and (43) will describe the equilibrium coexistence. Wheeler’s calculations
1103 attempt to reflect the details of what has been consumed and what has grown at particular
1104 grain boundaries at a point in time during the dynamic dissipative process. However, this
1105 is not directly relevant to the final mineral assemblage. In an equilibrium context,
1106 calculations with equations like (43) give a much more appropriate representation of

1107 equilibrium coexistence than Wheeler (2014) gives. His suggestion that there is a large
 1108 effect of non-hydrostatic stress on metamorphic mineral equilibria is erroneous.

1109 As an aside, it is unhelpful of Wheeler (2014) on his second page to repeat that a Gibbs
 1110 energy cannot be written for non-hydrostatically-stressed solids. As spelt out in the main
 1111 text in relation to (11), a Gibbs energy defined by $\mathcal{L}_{p\theta}U$ is not available in solid as there is
 1112 no thermodynamic pressure in solid. But a Gibbs energy can certainly be defined using
 1113 $G = \mathcal{L}_{T\theta}U$, (11). Nor is it correct to assert that a global equilibrium involving
 1114 non-hydrostatically-stressed solids and fluid is not attainable. The present work, and the
 1115 papers of Larché and Cahn (1973, 1978, 1985) on which much of the development is based,
 1116 show how such an equilibrium should be considered.

1117 **Appendix 4: Discussion of Tajčmanová *et al.* (2014)**

1118 In recent work, Tajčmanová *et al.* (2014) discuss compositional zoning in a monomineralic
 1119 plagioclase moat surrounding kyanite in high-grade felsic gneiss. The concentric zoning in
 1120 the plagioclase ranges from $x = 0.22$ at the outer edge of the moat to $x = 0.33$ at the inner
 1121 edge, with x the proportion of anorthite in the plagioclase, as in eq 28. Tajčmanová *et al.*
 1122 (2014) propose that the compositional zoning is due to the effect of a pressure gradient
 1123 across the moat, with chemical equilibrium attained so that chemical potential is constant
 1124 across the moat. Their approach is discussed here because it is inconsistent with the
 1125 thermodynamic formulation developed above, (28). Tajčmanová *et al.* (2014) introduce a
 1126 chemical potential expression to be considered constant in the proposed equilibrium

$$1127 \quad \frac{\mu_{ab}}{m_{ab}} - \frac{\mu_{an}}{m_{an}} \tag{44}$$

1128 with m_ℓ being the molecular mass of ℓ . They then use (44) to calculate the pressure
 1129 variation across the moat corresponding to the observed x relationships. The postulated
 1130 equilibrium relation in (44) can be rewritten as

$$1131 \quad \left(\frac{\mu_{ab}}{m_{ab}} - \frac{\mu_{an}}{m_{an}} \right)_A = \left(\frac{\mu_{ab}}{m_{ab}} - \frac{\mu_{an}}{m_{an}} \right)_B \tag{45}$$

1132 with A being in the inner edge of the moat and B in the outer edge. The development in
 1133 the present work generates (27), a superficially-similar equilibrium relation to (45), in
 1134 terms of the μ of an exchange, $\mu_{ab\ an}$, a consequence of the adoption of the lattice
 1135 constraint. The significant difference between (27) and (45) is the appearance of the
 1136 molecular masses in (45). Should the masses be there?

1137 Whereas mass-based chemical potentials, $\bar{\mu}_\ell = \mu_\ell/m_\ell$, are a notational convenience in
1138 writing energetics per unit mass, equilibrium relations are not generally in terms of
1139 mass-based chemical potentials. Gibbs, for example, uses mass-based chemical potentials
1140 but whenever equilibrium relations are derived, these $\bar{\mu}_\ell$ are multiplied by m_ℓ , giving μ_ℓ ,
1141 Gibbs (1906), e.g. the interface equilibrium relation, eq. 388.

1142 An equilibrium relation like (45) does arise if an external field that acts on mass, such
1143 as a gravitational field, is centred on the kyanite and imposes the pressure variation.
1144 External fields are characterised by a potential, ψ , a force per unit mass. Augmented
1145 chemical potentials, $\mu_i + m_i\psi$, are then constant in an equilibrium (Guggenheim, 1967, ch.
1146 9; Oppenheim & Kirkwood, 1961, ch. 15). For a binary plagioclase, separate augmented
1147 chemical potentials could then be written for albite and anorthite, involving ψ , each of
1148 which is constant across the moat. If the two augmented chemical potentials are
1149 subtracted, the result is (45). Although Tajčmanová *et al.* (2015), last paragraph of Sect.
1150 4.1, alludes to the plagioclase moat in terms of an external field, it is inconceivable that
1151 they derive (45) via augmented chemical potentials as there is no external field actually
1152 present.

1153 As there is no justification for involving molecular masses in (45), the use of (45) to
1154 predict compositional zoning is inappropriate. The observed compositional zoning is far
1155 too big to be accounted for by a mean stress gradient caused by variation in
1156 non-hydrostatic stress, as shown in the main text. Significant mineral compositional
1157 zonings like those around kyanite are most likely due to stranded μ gradients during
1158 mineral assemblage preservation, as argued, for example, by Štípská *et al.* (2010).