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The truth and beauty of chemical potentials

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Short title: Truth and beauty of chemical potentials

Abstract

This essay in honour of Mike Brown addresses aspects of chemical equilibrium and equilibration in rocks, with a focus on the role that chemical potentials play. Chemical equilibrium is achieved by diffusive flattening of chemical potential gradients. The idea of equilibration volume is developed, and the way equilibration volumes may evolve along a pressure-temperature path is discussed. The effect of the environment of an equilibration volume is key to understanding the evolution of the equilibration volume with changing conditions. The likely behaviour of equilibration volumes is used to suggest why preservation of equilibrium mineral assemblages and mineral compositions from metamorphism tends to occur. This line of logic then provides the conceptual support to conventional equilibrium thermodynamic approaches to studying rocks, using, for example, thermobarometry and pseudosections.

KEYWORDS chemical potential, elastic solids; equilibration volume, equilibrium thermodynamics

1 INTRODUCTION

This essay on chemical potentials is in honour of Mike Brown. Amongst other things, Mike has generated and maintained the 'space' within geology for the ongoing development of the metamorphic geology discipline, including via this Journal. The essay follows on from Powell, Guiraud & White (2005) "Truth and beauty in metamorphic mineral equilibria: conjugate variables and phase diagrams", in honour of D.M. Carmichael.

To interpret metamorphic rocks and understand metamorphic processes, a physicochemical framework is required in which to place observations on rocks. With such a framework, a view of how metamorphism occurs has been built up collectively in the metamorphic geology discipline. The view of metamorphism and metamorphic rocks adopted here, and explicitly or implicitly followed in most metamorphic papers, is outlined in detail in the Introduction and Overview sections in Powell, Evans, Green & White (2018). This paper is referred to as *nh18* below. Quoting from *nh18*: 'Since the 1910s, with the classic work of Goldschmidt and Eskola, the striking correspondence and correlation of mineral assemblage with rock-type and orogenic "style" has been used to support the notion that the way to understand metamorphic mineral assemblages is in terms of a preserved equilibrium (e.g. Thompson, 1955; Fyfe, Turner & Verhoogen, 1958)'. And 'The "preserved equilibrium" view of metamorphic mineral assemblages has come to form the *status quo* in metamorphic geology since that time...'. Integral to this paradigm of local equilibrium is that chemical potentials are constant over a length-scale mediated by diffusion. This paper will elaborate on the application of this view.

Every interpretation of mineral assemblage and mineral composition made under the thermodynamic equilibrium paradigm, including every thermodynamic calculation, makes implicit assumptions about the spatial variation of chemical potentials and the boundary conditions on the system considered. But because many of these assumptions are longstanding and little debated, the controls on chemical potential, and the features they impose on textures, are rarely discussed explicitly. This paper will elaborate on the implicit assumptions related to chemical potential and boundary conditions via a formal discussion of the central role of chemical potentials in equilibrium and equilibration in geological systems. Petrographic interpretations from the literature are reviewed in order to illustrate some common physical expressions of chemical potential behaviour.

What is chemical potential? For a system with multiple chemical components, the chemical potentials of these components describe the compositional dependence of the

relevant energy of the system. The energy then controls thermodynamic stability. A necessary condition for equilibrium is that the compositional dependence—the chemical potential—should be spatially constant. Consider temperature as an analogue for chemical potentials. In the same way that thermal equilibrium (constancy of temperature) is established by thermal equilibration involving the transfer of heat, chemical equilibrium is established by equilibration involving the transfer of matter (atoms and molecules), changing the proportions and compositions of the phases involved. As temperature is in relation to heat, so chemical potential is in relation to chemical composition. This essay begins with a formal discussion of the relationships between chemical potential, energy, and chemical composition.

2 EQUILIBRIUM and EQUILIBRATION

2.1 Equilibrium

Thermodynamic equilibrium is a concept that forms the cornerstone of quantitative metamorphic petrology. However, to gain insight into the thermodynamics of mineral assemblages, the physicochemical makeup of the materials involved must be simplified. Such models make the thermodynamics tractable. Results using the models then need to be assessed in the light of the differences between the predictions with the models and what is observed in real mineral assemblages. For example, an assumption that is used in the following is that grain boundaries are taken to be planar infinitely-thin interfaces between phases, that cannot hold shear-stress (they are "greased"), *nh18*, Sect. 3.1.

In metamorphic geology, in the greatest majority of calculations of mineral equilibria, mineral, melt and aqueous fluid phases have been treated thermodynamically as behaving in the same way mechanically, as though they are simple fluids, unable to hold shear stress. In this case the internal energy, U, of each phase is dependent on a minimal set of variables that are all scalars: entropy, S, volume, V, and composition, n_k, where n_k is the number of moles of end-member, k, e.g. Callen (1980) Sect. 1.10. The dependence of U on these variables can be formulated in terms of the intensive variables, temperature, θ, pressure, p, and the chemical potentials, μ_k, respectively, e.g. Callen (1980), Sect. 2.1; Alberty (2001), Sect. 1.1; and Appendix 1.1 below. The set of pairs of conjugate variables is $\{S, \theta\}$, $\{V, p\}$ and $\{n_k, \mu_k\}$ for this model of behaviour. This model permits the use of the Gibbs energy in calculations—it is the energy that is minimised at equilibrium at constant superimposed

pressure and temperature, e.g. Alberty (2001), Sect. 1.1; Appendix 1.1. This is then the basis of the familiar approach to rocks in which mineral equilibria are characterised by pressure and temperature and the compositions of the phases, with the compositions constant in the equilibrium.

In the model described above, solids at equilibrium are hydrostatically-stressed. However, it is relevant to consider the thermodynamics of solids that can be non-hydrostatically stressed at equilibrium, as undertaken in *nh18*. Any model of the solid that will allow this will need to involve a physicochemical constraint, a 'passive resistance' of Gibbs (1906), p58. The constraint adopted in *nh18* is the one developed by Larché and Cahn (1973) called the lattice (or network) constraint (*nh18*, Sect. 3.4). Applied to an elastic solid with a crystal lattice, the lattice constraint requires that atoms and vacancies can only move by interchanges. No new lattice sites are allowed to be created or lost within a grain of solid. In other words, there is a conservation of lattice sites within the solid. Such a solid is referred to as a *lattice-constraint* solid, in contrast to an *unconstrained* phase that is not constrained in this way and can only be hydrostatically-stressed at equilibrium. For a small-strain *lattice-constraint* solid, the set of pairs of conjugate variables are $\{S, \theta\}$, $\{V_0\mathbf{E}, \mathbf{T}\}$ and $\{n_{k\ell}, \mu_{k\ell}\}$, in which $\mathbf{E}$ is the infinitesimal strain tensor and V_0 is a reference volume, $\mathbf{T}$ is the Cauchy stress tensor, and $\mu_{k\ell}$ is the chemical potential of the exchange end-member involving the interchange of end-members k and ℓ (*nh18*, Sect. 3.1, 3.5; Appendix 1.1). In contrast to unconstrained solids, pressure and the chemical potentials of additive end-members do not appear in the expression for internal energy for lattice-constraint solids (*nh18*, p425). This and the consequences for equilibrium at grain boundaries are outlined in Appendix 1.3.

In an unconstrained phase with m independent end-members, there are m pairs in the minimal set, $\{n_k, \mu_k\}$. A lattice-constraint solid with m independent end-members can be represented by $m-1$ exchange end-members, and so involves $m-1$ pairs, $\{n_{k\ell}, \mu_{k\ell}\}$, with $k\ell$ in $n_{k\ell}$ and $\mu_{k\ell}$ having the meaning $k\ell_{-1}$. Adding a formula unit of an additive end-member to a grain increases the grain by the formula unit; adding a formula unit of an exchange end-member replaces one additive formula unit by another additive unit, leaving the number of formula units in the grain the same (*nh18*, Sect. 3.4).

The conventional definition of the chemical potential of any end-member, ℓ, used in metamorphic geology is

$$\mu_\ell = \left(\frac{\partial G}{\partial n_\ell}\right)_{p,T,n_{k\neq\ell}} .$$

This is for an unconstrained phase. In words, the chemical potential of an additive or exchange end-member is given by the rate of change of the Gibbs energy when the number of moles of the end-member is changed, while pressure, temperature and the number of moles of all other end-members is held constant. Outlined in Appendix 1.2–1.3 are other equivalent definitions for unconstrained phases and related definitions for lattice-constraint solids. A key result from Appendix 1.3 for a system involving unconstrained and lattice-constraint phases at equilibrium is that the chemical potentials of *all* end-members are defined on grain boundaries, and that these chemical potentials are all constant. For unconstrained phases—though not for lattice-constraint solids—the chemical potentials of all end-members are also defined throughout the interior of grains.

2.2 Equilibration

Features observed in rocks, such as zoned, oriented, and deformed grains, record processes that occurred during equilibration—thermal, mechanical, and chemical—as the rock adapted to changing pressures and temperatures by minimising its energy. Scalar intensive variables are constant in an equilibrium (Callen, 1985). Equilibration of scalar intensive variables involves flattening spatial gradients in those variables. A context for this is provided by classical irreversible thermodynamics (Appendix 1.5). The consequences of the flattening of gradients depend on the nature of the phases involved, and the relative rates of flattening.

In solids, thermal and mechanical equilibration are likely to occur faster on a given length-scale than chemical equilibration, e.g. Balluffi *at al.* (2005). For unconstrained solids, mechanical equilibrium is reached when hydrostatic pressure is attained. For lattice-constraint solids, the condition for mechanical equilibrium is that the divergence of the stress tensor is zero, which occurs when force-balance is attained for the system (*nh18*, Section 3.1). Owing to the relative rapidity of establishing thermal and mechanical equilibrium, in comparison to chemical equilibration, it is common to treat these processes as effectively instantaneous, and then consider chemical (i.e. diffusive) equilibration in solids in isolation, e.g. Larché & Cahn (1985), Sect. 7. Preservation of incomplete diffusive equilibration in rocks is considered below using this simplification.

3 APPLYING CHEMICAL POTENTIAL IDEAS TO ROCKS

The results of the development above are now incorporated into discussion of chemical potentials in the context of observations in thin section of metamorphic rocks.

3.1 Chemical potential landscapes

In a typical experiment on a reaction between minerals, the capsule contents are held at the experimental pressure and temperature. The starting materials are in general far from equilibrium, and equilibration occurs over the course of the experiment by evolution of the mineral assemblage. At any point in time as equilibration is underway, there is a spatial arrangement—"landscape"—of each chemical potential related to the distribution and compositions of the minerals in the experimental capsule. Each landscape flattens with time, via diffusive fluxes of the components from hills to valleys, changing the compositions and proportions of the minerals. If the experiment is continued long enough, with the pressure and temperature maintained, then equilibrium is reached when the chemical potentials flatten to become constant through the capsule. Once equilibrium is reached in the whole experimental capsule (assuming that the walls of the capsule are impermeable to all components), no further change will occur. Equilibrium thermodynamic modelling assumes that rocks have reached equilibrium in the same way that an experimental capsule does, when held at a constant pressure and temperature chosen for the experiment. But, during metamorphism, in contrast to the experimental case, rocks develop their mineral assemblages continuously with changing temperature and pressure, known as progressive metamorphism.

The continuously changing conditions involved in metamorphism complicate this experimental-capsule view of equilibrium. The idea of a chemical potential landscape is still useful, but such a landscape evolves with time, being dependent on temperature and pressure, even as diffusion acts to flatten relief. Moreover, unlike in an experimental capsule, there are no "walls" that constrain the part of a thin section that is being observed. The chemical potential landscapes go on, effectively, forever in space. Independent of these complexities, we can suppose *any* mineral growth or mineral composition change to be driven by the attempted flattening of chemical potential landscapes. As temperature and pressure change, the equilibrium mineral compositions change, and the discrepancy between actual and equilibrium mineral compositions induces

chemical potential gradients. The minerals change proportion and composition in response to these gradients in order to move towards the new equilibrium. If a new mineral nucleates, it grows if there are chemical potential gradients between it and the matrix that surrounds it that can be flattened by continued growth of the mineral.

To demonstrate that chemical equilibrium is broadly tracked by changing metamorphic conditions in the prograde history, at least on some length-scale, one need only invoke the very systematic metamorphic patterns that characterise orogenic belts, e.g. *nh18*, Sect 1 & 2. By extension, deformation that is concomitant with metamorphism must only affect or disrupt the chemical equilibration transiently. Deformation involves textural changes in rocks that are also, at least partially, continuously overprinted. Recrystallisation, for example as a consequence of deformation, can be thought of as an equilibration process, and is probably a key one at low metamorphic temperatures and in fluid-absent systems.

3.2 Equilibration Volume

What is the length-scale of local equilibration, or, conversely, the length-scale over which chemical potential landscapes in a rock will have significant relief? Answering this question is complicated because the scale depends on which component is being considered, which solids are involved, the grain-size of the solids and so on, even without accounting for the change of temperature and pressure. With respect to any given component, complications arise as a consequence of correlated effects amongst the components.

For each component, for example each oxide, the term *equilibration volume* (seen by geologists as an area around a point in the context of a thin section) relates to an interpreted length-scale for equilibrium. In practice, a single equilibration volume is commonly inferred in the form of a generalised length-scale for equilibrium for a specified set of components, rather than assessing the equilibration volume for each individual component. The size of the generalised equilibration volume is most constrained by the slower diffusers in the set. Of the major elements, alumina is commonly a candidate for slowest diffuser, with, consequently, the smallest individual equilibrium volume, e.g. Carmichael (1969), but silica is an alternative in quartz-absent rocks. The length-scale of equilibration of the slowest diffuser does not preclude equilibration of faster diffusing components on a much larger scale. Equilibration volumes, while being contiguous, may contain holes, to exclude minerals or parts of minerals not in the equilibrium. In the prograde, this would include, for example, the cores of zoned porphyroblasts (see next).

Grain-boundary diffusion is generally likely to be faster than intragranular diffusion, particularly in fluid-bearing systems. Therefore grain size is important in considering the rate of diffusive equilibration and size of the equilibration volume. During prograde evolution, if the matrix grain size is increasing as temperature increases, then equilibration along a pressure-temperature path tends to lead to unzoned minerals, with the exception of porphyroblasts. Growth zoning of porphyroblasts occurs when growth of the grain outstrips the ability of diffusive equilibration to equilibrate the interior of the porphyroblast with the matrix, while the porphyroblast margins remain in equilibrium with adjacent matrix. Porphyroblasts will grow if the equilibrium length-scale is short compared with the characteristic distance between neighbouring porphyroblasts. The rock will contain both porphyroblast-dominated and porphyroblast-free equilibration volumes, with distinct compositions, and a transitional zone between them, across which there were chemical potential gradients. Pseudosection calculations on mineral assemblage evolution might be done using the two compositions separately. In general pseudosection calculations are inappropriate for considering the transition zone, given that it is chemical potentials not composition that control the assemblage in the transition. If, instead of two pseudosections, a whole-rock bulk composition is used, the resulting pseudosection will typically predict porphyroblasts to be consumed by subsequent reaction during further heating, even though, in the rock, the porphyroblasts appear to remain in textural equilibrium with neighbouring phases.

During retrograde evolution in the absence of fluid infiltration, equilibration lengths decrease as temperature decreases, while grain-sizes are, at least initially, set by processes at peak metamorphic temperatures. Decreasing equilibration length-scale as a proportion of grain size means that maintenance of equilibrium is less likely. Attempted diffusive equilibration may then lead to arrested reaction textures, including coronas.

In general, evolution of mineral assemblages, from the perspective of equilibration volumes, can be thought of in terms of competing effects. On the one hand, larger equilibration volumes break down to smaller ones as a consequence of changing pressure and temperature, appearance of new minerals, and so on. On the other, smaller equilibration volumes coalesce by diffusive equilibration to make larger ones. During the prograde history, the effect of increasing temperature favours the latter, whereas during the retrograde history, the former is favoured, in the absence of fluid infiltration.

Equilibration volume is thus quintessentially a concept related to and defined by chemical potential, though chemical potential is barely mentioned in many petrological

studies which nonetheless use the equilibration volume idea. Explicit consideration of chemical potential landscapes and diffusive equilibration is a powerful approach in petrographic interpretation, especially in the case of textures representing incomplete flattening of chemical potential gradients (see section 3.4, Chemical Potentials and the Rock Record below). However, such principles cannot yet be used to *predict* most textural features. Constraining the myriad physicochemical parameters needed to make such predictions lies far beyond the current scope of the discipline.

3.3 Boundary Conditions

Boundary conditions constitute another formal aspect of thermodynamics that is rarely discussed explicitly in the metamorphic petrology literature. Yet the assumed boundary conditions have a profound effect on the predicted consequences of metamorphism for rocks.

To explore the influence of boundary conditions, the experimental capsule analogy is continued from above, with the contents of the capsule at equilibrium, and its walls closed to diffusion. If the temperature is changed, then the consequence of this change for the contents of the capsule depends on how the wall is controlled mechanically. On the one hand, the wall may be adjusted to control the pressure it imposes on the capsule contents. On the other, the wall may be fixed, so that the capsule contents may be physically constrained (boundary condition of *place*, Truesdell & Noll, 2004, p126). For a system composed of unconstrained phases, this is equivalent to a boundary condition of constant volume. The result of equilibration in the capsule will be different in these limiting cases. The way the wall is controlled is described in terms of *boundary conditions*, the boundary being the wall of the capsule.

The idea of boundary conditions can be carried across to equilibration volumes in a thin section. The "boundary" in the boundary conditions of an equilibration volume is necessarily imaginary. It can be thought of as enclosing as many grains or parts of grains as constitutes the equilibration volume. The evolution of an equilibration volume depends on the boundary conditions, as in the experimental capsule analogy above. The system within the "boundary" is assumed to be at equilibrium, as constrained by the boundary conditions.

In the limiting case of a fixed-pressure boundary condition, the pressure within unconstrained phases at equilibrium is the same as the fixed pressure at the boundary. In the alternative limiting case of the fixed-volume boundary condition, or the boundary

condition of place when lattice-constraint solids are involved, the pressure in unconstrained phases takes on a constant value within the boundary. This pressure is a function of the molar volumes of the phases, and their compressibilities. In these cases, grains of lattice-constraint solids may be non-hydrostatically stressed, having pressure relations at their grain margins with unconstrained phases as outlined in Appendix 1.3. Further consideration of mechanical boundary conditions is given in Truesdell & Noll (2004).

Equivalent limiting cases apply to the boundary conditions relating to chemical equilibrium. The chemical potential of a component may be imposed at the boundary, and takes this value everywhere within the boundary. This requires the composition within the boundary being able to change via diffusion through the boundary. Alternatively the composition within the boundary is held constant, and the chemical potential is a consequence of the changes of phase proportions and compositions that occur there as the system comes to equilibrium at the composition specified. The first case is that of external buffering, and the second that of internal buffering. In both cases, the chemical potential within the boundary is spatially invariant at equilibrium.

Practical situations are likely to be intermediate between the limiting cases for both the mechanical and chemical potential boundary conditions. Consider for example the case of external buffering, with the chemical potential of a component externally-superimposed on a boundary: if the "reservoir" that the chemical potential represents is finite, then the chemical potential superimposed is likely to change with time. Further, it is rare for all intensive variables to be externally buffered. More commonly, components that diffuse easily and that partition readily into fluids are likely to be externally buffered, whereas components that are slow to diffuse and disinclined to partition into fluids are likely to be internally buffered (Korzhinskii, 1959; Evans, Powell & Frost, 2013).

In the conventional view of prograde metamorphic mineral assemblages, implicit in almost all mineral equilibrium calculations, a constant pressure boundary condition is adopted. This, combined with the treatment of minerals as unconstrained solids, requires that pressure is constant throughout equilibration volumes. At constant pressure, the volume change of reaction is accommodated by the environment of the equilibration volume. This accommodation may be aided by fluid escape or ingress in fluid-bearing systems, or by concomitant deformation.

The constant-pressure boundary condition also warrants careful consideration when retrograde reactions are considered. Rocks that have progressively lost fluid during

prograde metamorphism become fluid-absent near their metamorphic peak, e.g. Guiraud, Powell & Rebay (2001); White & Powell (2002), where fluids may be aqueous, carbonic or silicate. Fluid addition is then needed for reversal of prograde reactions. In fluid-absent non-deforming systems, it is harder for mineral assemblages to change volume, as they need to do for reaction to occur. The limiting mechanical boundary-condition is then one of constant volume. Furthermore, fluid-absent rocks may involve significantly slower grain-boundary diffusion than rocks with fluid. Thus, growth of new minerals and diffusive equilibration between pre-existing minerals will tend to be inhibited. The latter will include an effect known as self-stress whereby diffusion causes non-hydrostatic stress in lattice-constraint solids (e.g. Larché & Cahn, 1985, Sect. 8.3). In the absence of fluid addition, the net effect is that, with decreasing temperature in the retrograde history, equilibration volumes become progressively smaller, with mineral assemblages becoming effectively "locked" to change. These effects contribute to preservation of high grade metamorphic assemblages at the Earth's surface (see below).

3.4 Chemical Potentials and the Rock Record

The previous sections outlined theoretical considerations related to chemical potentials, emphasizing that, within an equilibration volume, chemical potential landscapes are essentially flat—that is, chemical potentials are spatially constant. The primary record in rocks of the behaviour of chemical potentials is in the existence of recognisable equilibration volumes, via, for example, minerals having constant composition. There are, however, a number of metamorphic contexts in which *gradients* in chemical potential are preserved, having been locked into the rock before equilibration was complete. Indeed, preserved chemical potential gradients generate some of the most striking textures seen in thin section, such as coronas. They may also give valuable insight into equilibration processes that reach completion before the mineral assemblage and mineral compositions are preserved.

In the case of a preserved chemical potential gradient, the equilibration volume idea can be applied if, at each point in the preserved gradient, there is an (infinitely) thin equilibration volume, consistent with classical irreversible thermodynamics, e.g. Lebon *et al.* (2008), Ch. 2; Appendix 1.5. Moreover the chemical boundary condition of each such equilibration volume closely approaches the limiting case of external buffering, at least for faster diffusing components. Associated mineral assemblages can be predicted through

calculations predicated on thermodynamic equilibrium, mainly using calculated μ-μ diagrams as done in the cited papers summarised below.

This section describes some illustrative studies from the literature. Full details of the petrography, mineral chemistry and thermodynamic analysis of each example are given in the cited papers.

3.4.1 Chemical potential relationships during prograde metamorphism

During the prograde history of metamorphic rocks, diffusive equilibration is commonly effective at the thin-section length-scale, leaving scant trace of the chemical potential gradients that drove assemblage evolution. Nevertheless, evidence of equilibration and chemical potential gradients are sometimes preserved, as shown in the following examples.

The kyanite to sillimanite reaction on the prograde path in Barrovian metapelitic rocks is discussed in the seminal paper of Dugald Carmichael (Carmichael, 1969). The relationships are modelled in terms of calculated chemical potentials in White *et al.* (2008). Petrological observations suggest that kyanite does not break down directly to sillimanite under these conditions. In the published example, sillimanite has nucleated in biotite, rather than directly on kyanite, because the activation energy of nucleation is lower there. The presence of sillimanite sets up chemical potential gradients between parts of the rock that contain biotite+sillimanite and kyanite. From the calculations, difference in μ_{K_2O} between the parts of the rock is central, but gradients in all the chemical potentials are involved. The gradients cause the kyanite to be replaced by muscovite. If kyanite and sillimanite are still present in adjacent parts of the rock, then this most likely reflects preserved chemical potential gradients. If the kyanite is completely consumed by muscovite, the adjacent parts of the rock can form a single equilibration volume, with the chemical potential landscape flat.

An example of the influence of chemical potential gradients during prograde metamorphism is provided by White, Powell & Baldwin (2008), who consider the growth of a garnet porphyroblast. This is seen as a consequence of crossing a K_2O-FeO-MgO-Al_2O_3-SiO_2 (KFMASH) univariant reaction, with μ_{FeO} being typically lower at the porphyroblast than in the matrix, and μ_{MgO} being higher, driving diffusion of FeO to the growing porphyroblast and MgO away from it. These chemical potential differences are maintained, with continued garnet growth, until a reactant from the univariant reaction is lost. Then the chemical potential gradients may disappear and the

porphyroblast stops growing. Complications induced by metamorphism along a pressure-temperature path are discussed in White *et al.* (2008).

An example of preserved chemical potential gradient is recorded through a prograde partial melting reaction that took place in the aluminous metapelitic rocks at Round Hill, Broken Hill (Powell & Downes, 1990; White, Powell & Halpin, 2004). In the outcrop described, leucosome occurs only around sparsely-distributed garnets. In a KFMASH system view of the reaction, the textural development can be related to the passage of the rock through the divariant fields around the biotite + sillimanite = garnet + cordierite + melt univariant (with quartz and alkali feldspar in excess), and the crossing of the univariant itself. Chemical potential gradients set up by the garnet nucleation and growth caused melt to *form* around the garnet. Melt did not form away from the garnet and percolate to its observed position. At peak conditions, chemical potential gradients can be flattened once biotite, the main reactant in the melting reaction, is consumed.

3.4.2 Chemical potential gradients during retrograde metamorphism

In the retrograde history of metamorphic rocks, at conditions below 700° C, retrogression tends not to produce textures related to preservation of chemical potential gradients. Addition of fluid simply causes new lower temperature mineral assemblages at the conditions of the fluid ingress. At temperature above 700° C, diffusive re-equilibration is commonly incomplete and unrelated to fluid ingress or deformation, involving anhydrous minerals and undeformed textures. Corona textures are produced when the diffusion length-scale is shorter than the pre-existing grain size for at least some of the components. A classic example, involving reaction between sapphirine and quartz, is considered in White *et al.* (2008). Monomineralic layers of sillimanite and orthopyroxene grow between the sapphirine and quartz grains, representing preserved chemical potential gradients.

Kyanite in felsic granulite is commonly the focus of corona textures on cooling and/or decompression. The essential structure is a zoned plagioclase moat separating the kyanite from the matrix. Also symplectitic replacements of the kyanite by spinel+plagioclase and/or sapphirine+plagioclase are commonly involved. These are modelled in Štípská, Powell, White & Baldwin (2010) and in Baldwin, Powell, White, & Štípská, (2015). Unfortunately the elegant explanation of such textures in Tajčmanová, Podlatchikov, Powell, Moulas, & Vrijmoed (2014) founders on a units problem, as discussed in *nh18*, App. 4. Various other examples involving the development of retrograde textures are

considered in White & Powell (2011) and Doukkari, Diener, Ouzegane & Kienast (2018).

The behaviour of H_2O in migmatites at peak to retrograde conditions is considered in White & Powell (2010). In many migmatites the melt is physically separate from its solid residue host, as leucosomes. Chemical potential calculations show that as the melt in the leucosome/melt segregation starts to crystalise, μ_{H_2O} in the melt segregation becomes higher than that in the host. The chemical potential gradient in H_2O that this establishes causes diffusion of H_2O from the leucosome into the host on a decimetre scale, where biotite grows. Crystallisation of the melt leads to anhydrous quartzo-feldspathic leucosomes, containing for example unretrogressed garnet porphyroblasts. Melt loss from leucosomes can also result in anhydrous leucosomes and the absence of garnet retrogression (Powell & Downes, 1990; White *et al.*, 2004).

3.4.3 Chemical potential gradients across lithological boundaries

Reaction results if chemical potential gradients are set up across the boundary between adjoining rock types. Well-documented examples involve calc-silicate layers developed between marble and pelitic schist (e.g. Brady, 1977; Joesten, 1977). For effectively-infinite marble adjoining effectively-infinite pelitic schist, the width of the calc-silicate layers is constrained only by the duration of metamorphism, as the chemical potential gradients will never be flattened. However, if the marble layers are thin and the duration of metamorphism sufficiently long, chemical potential gradients may be fully flattened, with the marble completely transformed to calc-silicate.

A similar example was documented by Štípská, Powell, Racek & Lexa (2014). Here, chemical potentials from a felsic granulite/melt at 12 kbar and $> 900^\circ$ C were superimposed on an adjacent mafic granulite derived from an eclogite in a low-strain zone at peak metamorphic conditions. The mafic granulite contains eclogitic garnet in an orthopyroxene-diopsidic clinopyroxene-plagioclase-quartz matrix derived from original omphacite. The main components involved in the transformation of this mafic granulite were H_2O and K_2O, the oxides predicted to be the fastest diffusers, along with Na_2O. Acting on a metre scale, the chemical potentials locally transformed the mafic granulite to an intermediate composition, primarily through the growth of ternary feldspar, partly from plagioclase and partly interior to garnet. Little diffusion of Na_2O occurred as μ_{Na_2O} was similar in the felsic granulite and the mafic granulite. The transformation is inconsistent with the felsic melt infiltrating and reacting with the eclogite, because of decoupling of

K_2O (and H_2O) from other components would not occur in a simple mixture of felsic and mafic granulite. Intermediate-composition bands and bodies within related but high-strain felsic granulite may be due to such a transformation of eclogite by equilibration with the felsic granulite (Štípská *et al.*, 2014).

3.4.4 Chemical potential gradients in reworked assemblages

Two final examples occur in coarse-grained plutonic igneous rocks, primarily under the influence of fluid ingress. The first is a study of the serpentinisation reactions involved in the hydration of dunite, Evans *et al.* (2013). In that study, equilibrium volumes on the scale of mm-diameter protolith grains of olivine and orthopyroxene are recognised, with assemblages varying as a function of μ_{SiO_2}. These equilibrium volumes, or domains, are replaced by serpentine, brucite and magnetite, in the olivine domain, and by serpentine and talc in the orthopyroxene domain. The second example is provided by the textures involved in the transformation of coarse-grained plagioclase-orthopyroxene-clinopyroxene gabbro to garnet-omphacite eclogite across an apparent transformation front, Schorn & Diener (2017).

4 OUTSTANDING CONSIDERATIONS

One aspect of metamorphic mineral assemblage evolution that has received renewed attention recently is the idea of over-stepping of "reactions" (e.g. Spear & Pattison, 2017). In Spear & Pattison's terminology, a reaction is the appearance of a new mineral in an assemblage represented by an appearance-of-phase line in a pseudosection. Nucleation is kinetically controlled, so its consideration in terms of an equilibrium-thermodynamic energetic displacement as in Spear & Pattison, (2017) is not appropriate; it is implicit in the development of the conceptual model described above that local equilibrium on some length-scale is maintained while nucleation and growth of new minerals occurs, regardless of any over-stepping.

Over-stepping may occur, in some geological situations, with energetic consequences that are significant compared with the uncertainties involved in today's pseudosection modelling. However it is not clear currently how these energetic consequences could be estimated. Over-stepping as a consequence of homogeneous nucleation, for which good theoretical descriptions exist, is not applicable because heterogeneous nucleation is likely to

dominate over homogeneous nucleation on grain boundaries in metamorphic rocks, and there is little relevant theory regarding heterogeneous nucleation, Balluffi *et al.* (2005).

If over-stepping were common and significant, then its consequences would be different for different new minerals nucleating, and vary between rock compositions, mineral assemblage textures, etc. Thus, significant over-stepping would obscure or destroy the metamorphic patterns that are observed (e.g. *nh18*, Sect. 1). We conclude that over-stepping effects are unlikely to be commonly large in regional metamorphism.

The idea of the *preservation* of mineral assemblages and mineral compositions on cooling is so ubiquitous that the underlying implications are rarely considered. Yet it is unclear why preservation from metamorphism tends to correspond to local equilibrium, close to peak metamorphic conditions, and commonly on a many-grain scale, as opposed to the assemblage continuing to evolve far past peak conditions. If this preservation did not occur consistently, metamorphic patterns would be absent or obscured, and mineral equilibrium calculations would not give convincing results as commonly as they do. The intrinsic assumption, rarely articulated, is that equilibration occurs continuously along the prograde path but is then just switched off: a profound asymmetry of behaviour. A plausible explanation for the observed preservation is provided by the logic in the Boundary Conditions subsection, that a transition from a constant pressure boundary condition to a constant volume boundary condition for equilibration volumes occurs as mineral assemblages become fluid absent near the metamorphic peak, possibly also coinciding with the cessation of deformation. This is also consistent with reworking of such "locked" mineral assemblages on addition of fluid with renewed deformation. This causes reversion to constant pressure boundary conditions, dramatic increase in the size of equilibration volumes, and the appearance of new mineral assemblages that reflect local equilibrium.

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APPENDIX 1: Thermodynamic relations

Some key ideas from *nh18* needed in the text are summarised here, with some additional thermodynamics that are also needed in the text.

Appendix 1.1: Variable sets and energies

The fundamental relation used to express the internal energy, U, of a phase depends on how we have chosen to model the phase, each choice having its own minimal set of conjugate pairs of extensive and intensive variables. For the purpose of this discussion just two behaviours—unconstrained and lattice constraint—are of interest, but in other circumstances additional ones might be involved. In the unconstrained case, the minimal set involves pairs of scalars, $\{S, \theta\}$, $\{V, p\}$ and $\{n_k, \mu_k\}$, substantially simplifying the thermodynamic treatment. For a small-strain lattice constraint elastic solid, the minimal set involves $\{S, \theta\}$, $\{V_0\,\mathbf{E}, \mathbf{T}\}$ and $\{n_{k\ell}, \mu_{k\ell}\}$. The meaning of the symbols is given in the body of the text. For the meaning and behaviour of the tensors, $\mathbf{E}$ and $\mathbf{T}$, see *nh18*, Sect 3, or the references given there, e.g., Gurtin *et al.*, (2010). For finite strain the deformation gradient and the first Piola stress tensor can be used instead of $\mathbf{E}$ and $\mathbf{T}$ (e.g. Gurtin *et al.*, 2010, ch. 52). Those tensors reduce to $\mathbf{E}$ and $\mathbf{T}$ for small strain. The presence of tensors complicates the thermodynamic treatment. A scalar intensive variable is constant in an equilibrium, whereas a tensor intensive variable is not constant in an equilibrium. Instead the divergence of a tensor intensive variable is equal to zero everywhere within an equilibrium (in the absence of an external field that affects it).

The fundamental relation for an unconstrained phase, representing the dependence of U on the extensive variables in the minimal set, in a variation at equilibrium, is (e.g. Callen, 1960, eq. 2.2)

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{\ell} \left(\frac{\partial U}{\partial n_k}\right)_{V,S,n_{i(i\neq k)}} dn_k \tag{1}$$

The fundamental relation for a lattice-constraint solid is (e.g. *nh18*, eq. 7)

$$dU = \left(\frac{\partial U}{\partial S}\right)_{\mathbf{E},n_i} dS + \left(\frac{\partial U}{\partial \mathbf{E}}\right)_{S,n_i} : d\mathbf{E} + \sum_{k\neq\ell} \left(\frac{\partial U}{\partial n_{k\ell}}\right)_{\mathbf{E},S,n_{i\ell(i\neq k)}} dn_{k\ell} \tag{2}$$

Equation 2 is for a homogeneous part of the solid, allowing the strain to be represented by a simple $d\mathbf{E}$ term, given that strain can vary spatially within an equilibrium.

The derivatives in (1) and (2) can be identified with intensive variables, giving

$$dU = \theta\, dS - p\, dV + \sum \mu_k\, dn_k \tag{3}$$

and

$$dU = \theta\, dS + V_0\, \mathbf{T} : d\mathbf{E} + \sum_{k\neq\ell} \mu_{k\ell}\, dn_{k\ell} \tag{4}$$

respectively, with V_0 being a reference volume. The dependence of U on the extensive variables is given in terms of the intensive variables in the corresponding conjugate pair. The extensive variables can be thought of as natural variables.

The algebraic mechanism, the Legendre transform, allows the variables in a conjugate pair in dU to be exchanged thus changing the natural variable from the extensive to the intensive variable (Callen, 1985, p141 *et seq.*; Alberty, 2001). A Legendre transform of U with respect to θ—transforming the thermal term—denoted $\mathcal{L}_\theta$, gives a new energy, the Helmholtz energy, $F = \mathcal{L}_\theta U$, with θ now the natural variable, not S. The action of the transform on the right hand side of (3) is to replace the $\theta\, dS$ term by a $-S\, d\theta$ term, giving the Helmholtz energy expression for an unconstrained phase at equilibrium

$$dF = -S\, d\theta - p\, dV + \sum \mu_k\, dn_k \tag{5}$$

and for an homogeneous part of a lattice-constraint solid at equilibrium

$$dF = -S\, d\theta + V_0\, \mathbf{T} : d\mathbf{E} + \sum_{k\neq\ell} \mu_{k\ell}\, dn_{k\ell} \tag{6}$$

Transforming the thermal and mechanical terms in U gives the Gibbs energy. These transforms have a different effect for the two behaviours being considered because the mechanical contributions to U have a different form. The Gibbs energy for an unconstrained phase, $G = \mathcal{L}_{p\theta} U$, with p and θ now the natural variables, is

$$dG = -S\, d\theta + V\, dp + \sum \mu_k\, dn_k \tag{7}$$

For a lattice-constraint solid, $G = \mathcal{L}_{\mathbf{T}\theta} U$

$$dG = -S\, d\theta - V_0\, \mathbf{E} : d\mathbf{T} + \sum_{k\neq\ell} \mu_{k\ell}\, dn_{k\ell} \tag{8}$$

Given that Gibbs energy of a system is additive on its constituents, if all the phases in a system are unconstrained, the Gibbs energy of the system is minimised at equilibrium, as

the intensive variables are all scalar and are constant through the equilibrium. This then allows straightforward calculation of equilibrium in a system as in Connolly (2009). If any of the phases in the system are lattice-constraint solids, their stress tensors vary spatially in the equilibrium, so energies can no longer be minimised simply, requiring the variational calculus as in Larché & Cahn (1973), Sect. 3b.

Appendix 1.2: Chemical potential

Chemical potential is defined by for an unconstrained phase by

$$\mu_\ell = \left(\frac{\partial U}{\partial n_\ell}\right)_{S,V,n_{k\neq\ell}} = \left(\frac{\partial F}{\partial n_\ell}\right)_{\theta,V,n_{k\neq\ell}} = \left(\frac{\partial G}{\partial n_\ell}\right)_{\theta,p,n_{k\neq\ell}} \tag{9}$$

For a lattice-constraint solid the equivalent is

$$\mu_{k\ell} = \left(\frac{\partial U}{\partial n_{k\ell}}\right)_{\mathbf{E},S,n_{j\neq k,\ell}} = \left(\frac{\partial F}{\partial n_{k\ell}}\right)_{\mathbf{E},\theta,n_{j\neq k,\ell}} = \left(\frac{\partial G}{\partial n_{k\ell}}\right)_{\mathbf{T},\theta,n_{j\neq k,\ell}} \tag{10}$$

The equivalences arise because the Legendre transforms that convert U to F and G do not affect the chemical potential definition. In each case, the chemical potential relates to the the way the energy changes as a consequence of a change of the number of moles of the end-member, with the remaining natural variables in the energy held constant.

The chemical potential definitions in (9–10) involve the number of moles of the end-members in the phase, whereas conceptually it is useful to think in terms of the chemical potentials of components, e.g. oxides. The step from end-members to components can be illustrated with nominally 1-end-member phases as explored next using the Al-Si-O system. The key idea is that all phases are non-stoichiometric to some extent, as a consequence of defects, primarily vacancies. The following is most easily visualised for unconstrained phases but the conclusions are applicable more generally.

Chemical potentials are easier to visualise when composition is represented by mole fraction. For unconstrained phases, Gibbs energy can be used in energy-mole fraction diagrams, with pressure and temperature held constant. Then, on an molar Gibbs energy-mole fraction diagram, the chemical potentials of the end-members at the composition of a tangent to the curve for a phase are given by the values where the tangent intersects the compositions of the end-members, e.g. Powell (1978), Ch. 2, and as illustrated in Fig. 1. The G-x loops in Fig. 1 are qualitative, and exaggerated to illustrate that the phases are non-stoichiometric, with a range of composition across or near the

conventional composition for each phase. In fact, as a consequence, this conventional binary system, Al_2O_3-SiO_2 should be represented in a Al-Si-O ternary system as the phases will have a range of composition that may lie off the binary line across the ternary system. Kyanite, as a nominally 1-end-member Al_2SiO_5 phase, can be thought of as a model of the naturally-occurring mineral, kyanite.

Considering kyanite as presented in Fig. 1, if the nature and energetics of the defects in kyanite are known then the G-x loop can be generated. With the G-x loops, the μ_{SiO_2} of different assemblages as a function of the x of the system are indicated adjacent to the SiO_2-axis. For kyanite plus quartz or corundum, μ_{SiO_2} (and $\mu_{Al_2O_3}$) is fixed, whereas there is a range of μ_{SiO_2} (and $\mu_{Al_2O_3}$) for kyanite on its own, as its composition changes from coexistence with corundum to coexistence with quartz. It is important to realise that the values of μ_{SiO_2} and $\mu_{Al_2O_3}$ in kyanite are well established as a theoretical construct, even if with current knowledge they cannot be determined.

In Fig. 1 the range of composition of actual kyanite, or equivalently any nominally 1-end-member phase, is related to how strongly-curved the G-x loop is at its tip. The μ_{SiO_2} increases with SiO_2 in kyanite. In the conceptual limit the G-x loop can be reduced to a vertical line at the Al_2SiO_5 composition. Then the essential relationships remain, but without the relationship between μ and composition for the one-phase kyanite. The same applies to quartz and corundum if their G-x loops are reduced to vertical lines at SiO_2 and Al_2O_3 respectively. Thus, even for model 1-end-member phases, μ of components, in this case, oxides, are defined even if the phases are idealised.

In a binary system, if a phase involves an energetically-favourable, typically stoichiometric substitution, such as $FeMg_{-1}$, then the G-x loop is open and rounded, rather than strongly curved. This shape allows a wide range of possible compositions of the phase, depending on the G-x loops of possible coexisting minerals. In larger systems, the multi-dimensional G-x loops will be sharp in substitution directions that are energetically unfavourable, commonly non-stoichiometric, ones, but open and rounded in easy substitution directions. For example, consider plagioclase, conventionally idealised as binary anorthite-albite, $CaAl_2Si_2O_8$-$NaAlSi_3O_8$. In the system Na_2O-CaO-Al_2O_3-SiO_2, the plagioclase G-x loop will be rounded and open between the albite and anorthite compositions but sharp in other dimensions.

The main result of this Appendix section so far is that the chemical potentials of, say, oxides, are defined in all unconstrained phases. Given the convenience, and indeed

practical necessity, of considering model phases, for example Al_2SiO_5 for kyanite, or $CaAl_2Si_2O_8$-$NaAlSi_3O_8$ for plagioclase, it remains to be established how the statement of equilibrium in terms of constancy of the μ of, say, oxides, translates to equilibrium stated in terms of the μ of end-members of the phases in an equilibrium. With $\mu_{Al_2SiO_5}$ fixed by the presence of model kyanite in an equilibrium, then $\mu_{Al_2SiO_5} = \mu_{Al_2O_3} + \mu_{SiO_2}$, just from the geometry of the G-x diagram, Fig. 1, and the role of tangents to G-x loops. Then, given that $\mu_{Al_2O_3}$ and μ_{SiO_2} are constant in an equilibrium, so is $\mu_{Al_2SiO_5}$. If there are other phases in equilibrium with the kyanite, the end-members of each of these phases can be written in terms of a sum of μ of end-members, with multipliers from the number of oxides in the end-member formulae. The collected μ equivalences can be combined to make equilibrium relations just in terms of μ of the main end-members. A trivial example is coexisting kyanite, sillimanite and quartz giving one equilibrium relation, $\mu^{ky}_{Al_2SiO_5} = \mu^{sill}_{Al_2SiO_5}$. In this equilibrium, μ_{SiO_2} is specified by the presence of quartz, but $\mu_{Al_2O_3}$ is unspecified, although the fact that it is defined and constant in the equilibrium is used in generating the equilibrium relation. An alternative derivation of equilibrium relations is given in Appendix 1.4. THERMOCALC performs its calculations with an independent set of equilibrium relations between end-members of the phases in an equilibrium (Powell, Holland & Worley, 1998).

Appendix 1.3: Equilibrium within and between grains

Whereas the idea of pressure is firmly anchored in physics (as force acting perpendicularly on unit area), that does not mean that this quantity always plays a primary role in the thermodynamics of a phase. In *nh18*, the *thermodynamic* pressure is defined by

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,n_i} \tag{11}$$

This applies in an unconstrained phase, for which $\{V, p\}$ is a conjugate pair in the minimal set of variables, as defined in Appendix 1.1. In a lattice-constraint solid, $\{V, p\}$ does not appear in its minimal set, and the thermodynamic pressure is *not* defined. Depending on the orientation of the chosen plane in such a solid, the perpendicular force per unit area varies with the orientation and position of the plane. A scalar "pressure" that *can* be formed is the mean stress—the average of the principal stresses—which varies with position in a non-hydrostatically-stressed grain. However, this is not an intensive variable; it is not constant in an equilibrium as scalar intensive variables are (*nh18*, Sect. 3.2).

Chemical potential must also be considered differently in unconstrained and lattice-constraint phases. In unconstrained phases the chemical potentials of all end-members are defined and are constant in an equilibrium. Within lattice-constraint solids only the chemical potentials of exchange end-members are defined and constant in an equilibrium. The chemical potentials of additive end-members are not defined in a lattice-constraint solid.

For a lattice-constraint solid, the stricture of the lattice constraint does not apply on the grain boundary itself. Lattice points can be created or destroyed there, representing growth or dissolution of the grain. At grain boundaries, the chemical potentials of all end-members are defined, the connection to the chemical potentials of the exchange end-members in the solid being by the interface equilibrium, *nh18*, Sect. 3.7. The chemical potentials of all the end-members are constant in all grain boundaries and in all unconstrained phases in an equilibrium. The pressure used in the interface equilibrium is the negative of the principal stress normal to the grain boundary (for planar and greased boundaries), e.g. *nh18*, Eq. 22. This pressure varies in a grain boundary between lattice-constraint solids, but is constant and equal to the thermodynamic pressure with an unconstrained phase, at equilibrium. For chemical potentials to be constant in grain boundaries in an equilibrium, the range of pressures in the grain boundaries is constrained to be small, *nh18*, Sect. 3.7. The quantity "pressure" that is commonly understood to be reflected in an equilibrium mineral assemblage refers to this narrow range of pressures on grain boundaries, and not to some average of mean stress within the grains.

The creation or destruction of lattice points at a grain boundary is both the mechanism by which equilibrium stress relations are established at the grain boundaries of lattice-constraint solids, and that by which the chemical potentials of additive end-members reach constancy on grain boundaries at equilibrium (as above). Creation or destruction of lattice points within unconstrained phases is the mechanism by which the grains reach a state of constant pressure at equilibrium.

Appendix 1.4: Equilibrium relations

Equilibrium defined by energy minimisation leads to equilibrium relations in terms of chemical potentials corresponding to balanced chemical reactions between the end-members of phases. In systems containing lattice-constraint solids, minimising an energy is non-trivial, e.g. Larché & Cahn (1973), Sect. 3b. However in systems containing

only unconstrained phases at constant p and θ, the energy to minimise is the Gibbs energy, and the minimisation can be done in a straightforward way using Lagrangian multipliers, e.g. Smith & Missen (1982). This is a useful exercise as it shows that the chemical potentials of components are defined in such systems, and are constant at equilibrium.

The Gibbs energy in each phase is written in the usual way as a linear combination of the chemical potentials of end-members. Consider an equilibrium involving olivine (ol) and orthopyroxene (opx) in FeO–MgO– SiO_2. A model of the phases is chosen so that the end-members of olivine are Fe_2SiO_4 and Mg_2SiO_4 and of orthopyroxene are $Fe_2Si_2O_6$ and $Mg_2Si_2O_6$. The Fe-Mg order-disorder in olivine and opx is ignored for simplicity. The Gibbs energy in terms of the number of moles of the end-members in an arbitrary amount of system is

$$G = n^{\rm ol}_{\rm Fe_2SiO_4}\mu^{\rm ol}_{\rm Fe_2SiO_4} + n^{\rm ol}_{\rm Mg_2SiO_4}\mu^{\rm ol}_{\rm Mg_2SiO_4} + n^{\rm opx}_{\rm Fe_2Si_2O_6}\mu^{\rm opx}_{\rm Fe_2Si_2O_6} + n^{\rm opx}_{\rm Mg_2Si_2O_6}\mu^{\rm opx}_{\rm Mg_2Si_2O_6},$$

obtained from G being additive and also Euler's theorem, Callen (1980), Sect. 3.1. The composition of the system, in terms of the number of moles of the components (oxides), can be written in terms of the compositions of the end-members

$$\begin{aligned}
n_{\rm FeO} &= 2n^{\rm ol}_{\rm Fe_2SiO_4} + 2n^{\rm opx}_{\rm Fe_2Si_2O_6} \\
n_{\rm MgO} &= 2n^{\rm ol}_{\rm Mg_2SiO_4} + 2n^{\rm opx}_{\rm Mg_2Si_2O_6} \\
n_{\rm SiO_2} &= n^{\rm ol}_{\rm Fe_2SiO_4} + 2n^{\rm opx}_{\rm Fe_2Si_2O_6} + n^{\rm ol}_{\rm Mg_2SiO_4} + 2n^{\rm opx}_{\rm Mg_2Si_2O_6}
\end{aligned}$$

To minimise G at constant composition, the G is augmented with terms involving the Lagrange multipliers of the oxides, λ_i, and these composition identities

$$\begin{aligned}
G &+ \lambda_{\rm FeO}(n_{\rm FeO} - 2n^{\rm ol}_{\rm Fe_2SiO_4} - 2n^{\rm opx}_{\rm Fe_2Si_2O_6}) \\
&+ \lambda_{\rm MgO}(n_{\rm MgO} - 2n^{\rm ol}_{\rm Mg_2SiO_4} - 2n^{\rm opx}_{\rm Mg_2Si_2O_6}) \\
&+ \lambda_{\rm SiO_2}(n_{\rm SiO_2} - n^{\rm ol}_{\rm Fe_2SiO_4} - 2n^{\rm opx}_{\rm Fe_2Si_2O_6} - n^{\rm ol}_{\rm Mg_2SiO_4} - 2n^{\rm opx}_{\rm Mg_2Si_2O_6})
\end{aligned}$$

Minimising, by differentiating with respect to the number of moles of each end-member, and setting the results to zero, gives

$$\begin{aligned}
\mu^{\rm ol}_{\rm Fe_2SiO_4} &= 2\lambda_{\rm FeO} + \lambda_{\rm SiO_2} \\
\mu^{\rm ol}_{\rm Mg_2SiO_4} &= 2\lambda_{\rm MgO} + \lambda_{\rm SiO_2} \\
\mu^{\rm opx}_{\rm Fe_2Si_2O_6} &= 2\lambda_{\rm FeO} + 2\lambda_{\rm SiO_2} \\
\mu^{\rm opx}_{\rm Mg_2Si_2O_6} &= 2\lambda_{\rm MgO} + 2\lambda_{\rm SiO_2}
\end{aligned}$$

Eliminating the λ terms from these gives the expected exchange equilibrium relation in terms of the chemical potentials of the end-members of the phases

$$\mu^{\rm opx}_{\rm Fe_2Si_2O_6} + \mu^{\rm ol}_{\rm Mg_2SiO_4} = \mu^{\rm ol}_{\rm Fe_2SiO_4} + \mu^{\rm opx}_{\rm Mg_2Si_2O_6}$$

which corresponds to the balanced reaction between the end-members

$$\rm Fe_2Si_2O_6, opx + Mg_2SiO_4, ol = Fe_2SiO_4, ol + Mg_2Si_2O_6, opx$$

In this case there is just one equilibrium relation, but in general there are several, of number given by the nullspace of the composition matrix of the end-members in the equilibrium. Equilibrium relations are written generically as $\Delta\mu = 0$, with the Δ an operator such that $\Delta\mu \equiv \sum r_i\mu_i$, with r_i reaction coefficients.

A significant additional result of the derivations is that the Lagrangian multipliers can be identified with the chemical potentials of the components (in the above, oxides). It also implies that each is the same throughout the system at equilibrium, as this property is a key feature of Lagrangian multipliers in such a derivation (e.g. Larché & Cahn, 1973)

Appendix 1.5: Irreversible thermodynamics

The approach followed by, for example Powell *et al.* (2005) and White *et al.* (2008, 2011) follows that of Korzhinskii (1959) in taking it as self-evident that a local equilibrium approach, called mosaic equilibrium by Korzhinskii, can be followed. Thus, it is assumed that equilibrium ideas can be applied on some smaller scale, whereas disequilibrium occurs on some larger scale.

Classical irreversible thermodynamics provides an underpinning for the Korzhinskii approach, e.g. Kondepudi & Prigogine (1998), Part 4, and Lebon, Jou & Casas-Vázquez (2008), Ch. 2. Adopting the continuum physics view of considering a system in terms of particles or material points (e.g. Gurtin *et al.*, 2010, Sect. 5.1), in classical irreversible thermodynamics, the thermodynamics of each material point is considered precisely as it would be in equilibrium thermodynamics, that is, with the same minimal set of pairs of variables for the type of phase, and the same expression for the energies, e.g. (3–4). It is understood that the material points can interact with each other and therefore their properties and relative positions within the system may vary with time. With a dependence on boundary conditions, the behaviour of the system is predicated on the integral over space of the entropies of the material points, given the constraint of the

second law of thermodynamics that the overall entropy must increase (or not change). As formulated, the entropy constraint leads to equilibration processes that involve linear combinations of forces and fluxes, with rules that control how the fluxes may be coupled to forces. In the case of diffusive equilibration at thermal and mechanical equilibrium, the "forces" are the chemical potential gradients and the fluxes give rise to composition changes, with the fluxes coupled to all forces. The construction and use of μ-μ diagrams following the Korzhinski approach is consistent with classical irreversible thermodynamics.

Internal equilibria within phases correspond to reactions between end-members such as between species in a fluid, or for intracrystalline equilibria, e.g. $2\,Mg_{M1}Fe_{M2}Si_2O_6 = Mg_{M1}Mg_{M2}Si_2O_6 + Fe_{M1}Fe_{M2}Si_2O_6$ in orthopyroxene. These reactions can be written as $\Delta\mu = 0$ at equilibrium, as in Appendix 1.4. In classical irreversible thermodynamics, such internal equilibria, at thermal and mechanical equilibrium, can be written as $\Delta\mu = A$, where A is the affinity, e.g. Kondepudi & Prigogine (1998), p103 *et seq.*, following earlier work of de Donder. The magnitude of A represents the departure from equilibrium; on equilibration, $A = 0$. It is worthwhile noting that the word, affinity, is used in other ways in the metamorphic geology literature, all in the context of $\Delta\mu$ for reactions between end-members, but in ways that are inconsistent with the original meaning.

In the context of over-stepping of simple reactions, with just one reaction between end-members, introducing a phase not yet present in the assemblage, $\Delta\mu$ can be thought of as the integrated driving force for nucleation of the new phase (Hillert 2008, p142). $\Delta\mu$ then relates to the Gibbs energy difference between the metastable equilibrium, in which the new phase has not nucleated, and the stable one that includes the new phase. $\Delta\mu$ is not an affinity as defined by Kondepudi & Prigogine (1998). A finite value of $\Delta\mu$ does not indicate that the system is not in equilibrium, only that the equilibrium is a metastable one.

There is no length-scale involved in A: for A the $\Delta\mu$ considered is "at a point", spatially. If $\Delta\mu$ is used when there is a length-scale involved, when the phases are spatially separated, then it is critical to understand how the relevant μ vary with distance. If the phases are not in equilibrium with each other, chemical potential gradients will be present. The resulting $\Delta\mu$ is not an affinity, and, because of the μ gradients implied, is unlikely to be useful (c.f. Wheeler, 2014).

862 ## Figure Caption

Figure 1: Qualitative Gibbs energy–composition diagram for Al_2O_3-SiO_2 with exaggerated non-stoichiometric phases at fixed pressure and temperature.