

On equilibrium in non-hydrostatic metamorphic systems

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Abstract

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

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

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1 INTRODUCTION

In the study of crustal metamorphic rocks, the application of equilibrium thermodynamics hinges on the interpretation of their petrographic features: the mineral assemblages, mineral compositions and mineral textures. This interpretation relates to how the petrographic features form, evolve and are preserved as a rock follows its pressure–temperature path. 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). These observations and ideas form the basis of the metamorphic facies concept (for a historical perspective, see Ch. 1 by F.J. Turner in Fyfe *et al.*, 1958).

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

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

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

2 OVERVIEW

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

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

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

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

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

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

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

