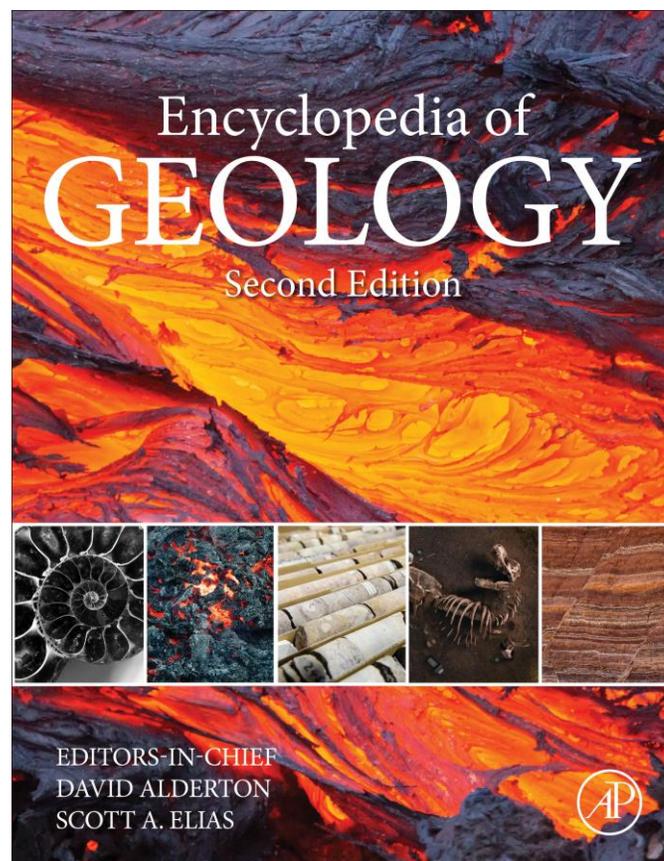


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## Composition Effects on Metamorphic Mineral Assemblages

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In most metamorphic rock types, a few (typically 3–6) mineral species make up 95–99% of a sample. Only a handful of meta-sedimentary types are mono-mineralic, such as (pure) marbles that may consist of only the mineral calcite, or pure quartzites that may contain only quartz. But the chemical composition of metamorphic rocks can be quite variable, and most of them do not correspond to the composition of a single mineral. So one may ask how many minerals and which mineral species make up such a rock. The concept of *metamorphic mineral assemblages* has been developed when these questions were addressed. It is a fundamental concept in petrology (the study of rocks). To grasp its significance properly, its historical roots and the evolution of thought are instructive.

### Conceptual Basis and Terminology

Early in the 20th century, contact metamorphic rocks in the Oslo area were systematically studied by Goldschmidt (1911). Where hot magmas (mostly syenites) had intruded a series of sedimentary rocks, particularly fine-grained metamorphic rocks (called hornfels) had developed. In these, Goldschmidt noted that minerals were systematically associated. Typically 3–4 specific minerals coexisted locally and some combinations never occurred in close spatial proximity. He found that the observed associations were determined by two factors: (1) the bulk chemical composition of the sedimentary precursor (shale, marl or limestone), and (2) the physical conditions of their metamorphic transformation, i.e. the temperature and pressure. Being aware of the work by Gibbs (1877) on chemical thermodynamics, Goldschmidt started to interpret mineral associations as products of chemical equilibration processes. He hypothesized that his rock samples were final products of an evolution in which some of the minerals originally present had reacted to form new mineral associations. He also realized that volatiles such as H<sub>2</sub>O or CO<sub>2</sub> had been participating in such transformation reactions and that fluid composition may delimit certain mineral associations (Goldschmidt, 1912).

#### An Important Aside

The term *mineral association*, as introduced by Goldschmidt, initially had a purely descriptive sense: Minerals systematically observed together, coexisting locally, often in grain contact. However, he then used the same term in an interpretive sense: Minerals considered to represent a state of local chemical equilibrium.

As interpretations should be distinguishable from observations, specific terms have come into use for the interpretive sense: either *mineral assemblage* or *paragenesis*. Current usage of these terms is not altogether consistent, but based on a survey among petrologists (May 2020), it is advocated to use either of these two terms when a local chemical interaction is implied. To avoid confusion, it is best to specify *equilibrium assemblage* (or *equilibrium paragenesis*) where appropriate; in other instances the term *disequilibrium assemblage* may even be appropriate. The term *mineral association* remains purely descriptive, denoting spatial proximity of different mineral species but not implying that the minerals involved had chemically interacted, thus reducing disequilibria or eventually reaching chemical equilibrium.

This terminological principle has made progress in the literature since the 1960s, but it has not been strictly followed. In the present text, to clarify the connotation, the term (metamorphic) *mineral assemblage* is consistently used wherever locally coexisting minerals are interpreted to have chemically interacted; the term *equilibrium assemblage* is used when a (hypothetical) state of chemical equilibrium is implied.

Goldschmidt realized, upon careful examination of thin sections in a petrographic microscope, that the mineral assemblages satisfy the *Phase Rule*, as postulated by Gibbs (1877) for systems at chemical equilibrium:

$$P + F = C + 2$$

$P$  denotes the number of phases, so the mineral species (and possibly a fluid phase) in the rock sample;  $C$  is the number of chemical components, such as oxides: CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, etc. in the sample domain examined, and  $F$  denotes the degrees of freedom, which includes the physical variables, essentially temperature and pressure. Goldschmidt regarded these two variables as fixed at the scale of

a rock sample, and he thus formulated the *Mineralogical Phase Rule*: The number of minerals in an equilibrium assemblage cannot exceed the number of components.

In summary, Goldschmidt's study (1911, his PhD thesis) viewed metamorphic rocks as composed of mineral assemblages, so he found the conditions of chemical equilibrium satisfied. As he identified 18 different assemblages in the hornfels samples studied, his case study offered a first clue of how composition (specifically: the local bulk composition) controls metamorphic mineral assemblages. An elegant way to visualize this insight was devised by Eskola (1920), who—working with Goldschmidt—used chemographic methods, such as the ACF diagram (Fig. 1).

Minerals and assemblages in a four-component composition space are depicted in Fig. 1, showing a projection from quartz ( $\text{SiO}_2$ ) onto the triangle ACF (A:  $\text{Al}_2\text{O}_3$ , C:  $\text{CaO}$ , F:  $\text{FeO} + \text{MgO}$ ; molar units). Stars indicate three hypothetical rock compositions (R1, R2, R3) discussed in the text, colored fields identify the respective mineral assemblages.

All of the mineral assemblages Goldschmidt observed in his samples included quartz; the proportions of the other three oxide components determine which other phases (minerals) make up the local assemblage (at fixed physical conditions). In Fig. 1 these mineral assemblages correspond either to a tie-line indicating

3 phases: andalusite + cordierite (+ quartz)

or diopside + grossular (+ quartz)

etc.

or to a triangle within ACF

4 phases: grossular + wollastonite + diopside (+ quartz)

etc.

Suppose that the compositions of two rocks are represented by R1 and R2 in Fig. 1, the stable mineral assemblages are immediately evident; the (molar) proportion of the minerals in each assemblage may be read off as well (except for quartz):

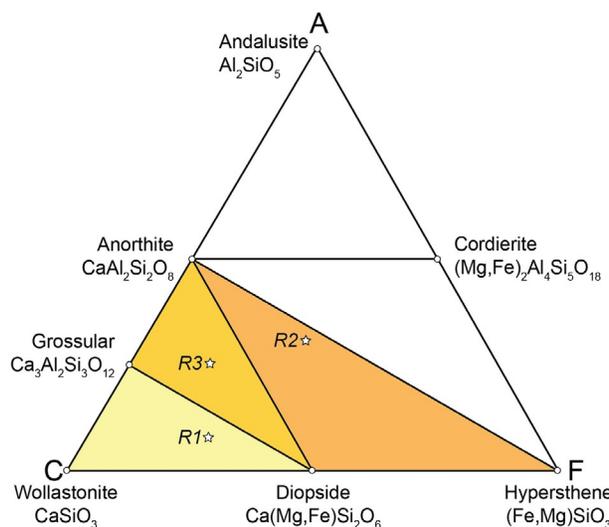
R1: 20% grossular, 30% wollastonite, 50% diopside

R2: 60% anorthite, 10% diopside, 30% hypersthene.

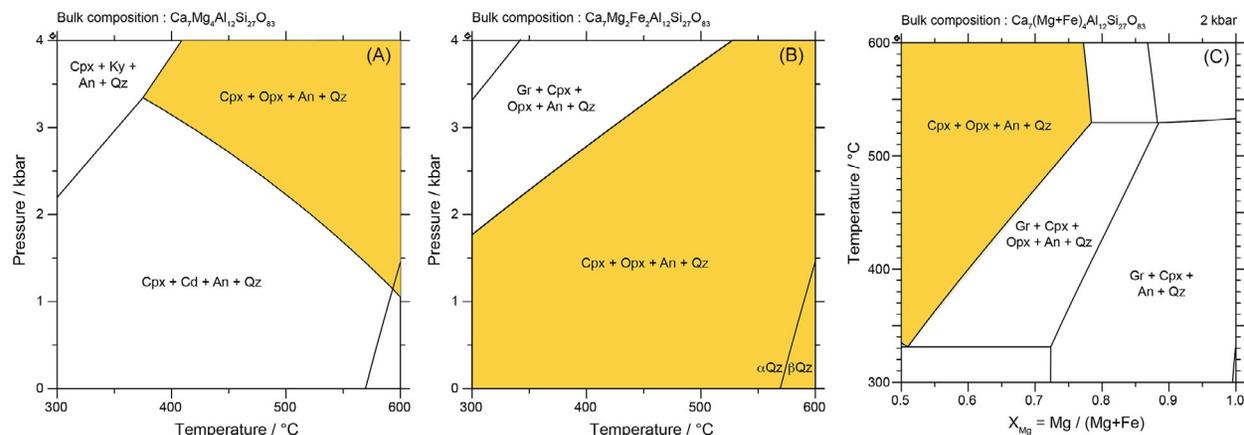
Some information is lost whenever a chemographic diagram involves projection. As the ACF-diagram requires a projection from  $\text{SiO}_2$ , the amount of quartz cannot be inferred from Fig. 1, i.e. the position of the star does not change whether R1 contains a lot of quartz or hardly any. Note that each mineral assemblage is fully characterized by the phases present, but it says nothing about their proportions.

Fig. 2 shows a model example to document how calculated stability limits of a specific mineral assemblage depend on bulk composition. Depicted is a simple model based on one calc-silicate assemblage observed by Goldschmidt (1911); the minerals in his hornfels samples could not yet be analyzed. In Fig. 2, only the effect of Mg-Fe substitution is explored; the diagrams show this assemblage to be stable over a large range of P-T conditions, and the stability limits clearly depend on composition.

Subsequent investigations have found that equilibrium was not universally achieved or preserved in metamorphic rocks. In fact, metamorphic samples found on the Earth's surface must have ceased to equilibrate at some point, else mineral assemblages (formed at high temperature and pressure) would hardly ever be preserved. Despite these reservations, the concept of mineral assemblages remains fundamental in several respects. It helps us understand how the minerals present reflect the bulk chemical



**Fig. 1** ACF-diagram. Minerals and assemblages in a 4-component composition space, shown in a projection from quartz ( $\text{SiO}_2$ ) onto the triangle ACF (A:  $\text{Al}_2\text{O}_3$ , C:  $\text{CaO}$ , F:  $\text{FeO} + \text{MgO}$ ; molar units). Stars indicate three hypothetical rock compositions (R1, R2, R3) discussed in the text, colored fields identify the respective mineral assemblages.



**Fig. 2** Assemblage diagrams. Calculated phase relations depicting the conditions where a specific mineral assemblage is predicted to be stable, depending on the bulk composition used in the model. Orange fields mark the same calc-silicate assemblage (R3 in Fig. 1): hypersthene (Opx) + diopside (Cpx) + anorthite (An) + quartz (Qz). White fields correspond to different assemblages, some of them including garnet (Gr). P-T fields are for the pure Mg-system in (A) and for a composition with Mg/Fe = 0.5 in (B). Thermal stability limits of assemblages are shown in (C) as a function of the mole fraction  $X_{Mg} = Mg / (Mg + Fe)$  at 2 kbar pressure. Diagrams were calculated using THERIAK/DOMINO (de Capitani and Petrakakis, 2010) and the internally consistent thermodynamic database updated from Berman (1988); <https://titan.minpet.unibas.ch/minpet/theriak/prog190309/>.

composition of a rock, and vice versa. Assemblages reflect fundamental relations between mineral stability and the physical conditions a rock encountered at some point in time.

### From the Static Equilibrium Concept to Metamorphic Evolution

Rock metamorphism is primarily induced by large-scale tectonic changes, processes that occur over very long time intervals, commonly  $10^5$  to  $>10^6$  years. The physical conditions (pressure and temperature) to which rocks are exposed will change in the course of time, and metamorphic processes occur in response. At the scale of an individual rock sample, chemical reactions and local physical processes include:

- the partial or complete replacement of minerals by new ones.
- loss of volatiles generated when hydrous minerals, carbonates etc. break down.
- recrystallization of minerals, often leading to textural coarsening.
- stress-induced deformation, including pressure-induced compaction.

As rocks are potentially reactive chemical systems, they may adapt to continually changing conditions. Thus, an initial set of minerals may undergo a sequence of chemical reactions during a protracted metamorphic evolution. These reactions may be entirely solid-state or they may, at certain stages, involve a fluid, i.e. a volatile solution phase made up of various components. Mobile components may be exported to neighboring rock volumes (or imported from them), in which case the system must be considered open. In any case, chemical transport will occur (by diffusion) within the system. Large-scale deformation may, either episodically or continually, induce small-scale textural changes.

Any metamorphic sample should thus be viewed as the end product of a long and perhaps complex evolution. Indeed, when studied in detail, most metamorphic rocks preserve not a single (equilibrium?) state, but at least some evidence of successive metamorphic changes. Careful documentation commonly reveals a mosaic of multiple (equilibrium?) states. During metamorphism, pressure ( $P$ ) and temperature ( $T$ ) vary over time ( $t$ ). To characterize a metamorphic evolution, the term used is *PTt-path* (or *PTDt-path*, if discrete stages of deformation ( $D$ ) are identified as well).

Of course, such ambitions go far beyond what Goldschmidt and Eskola had imagined. However, the early realization that metamorphic processes in rocks tend to reduce disequilibrium (i.e. the Gibbs Free Energy) remains a solid working hypothesis, even if thermodynamic equilibrium has not been fully attained or is not fully preserved. A wide spectrum of methods has been developed to recognize and quantify successive stages of metamorphic evolution, as outlined below. However far these theoretical and technical advances have come from Goldschmidt's original concept of one fossil equilibrium state, his idea of mineral assemblages still is at the core of most approaches now used. These provide detailed insight on how chemical composition affects mineral assemblages and how these, in turn, reflect physical conditions. The power to unravel metamorphic rocks as greatly expanded by a wealth of conceptual, analytical, and theoretical tools, as eloquently summarized by Spear et al. (2016).

Compelling clues to metamorphic evolution are often discernable from textures and compositional zoning in minerals. Systematic petrographic microscopy in thin sections remains an essential tool to determine the evolutionary sequence among minerals and recognize potential local assemblages. In addition, detailed chemical analyses of mineral composition, both for major

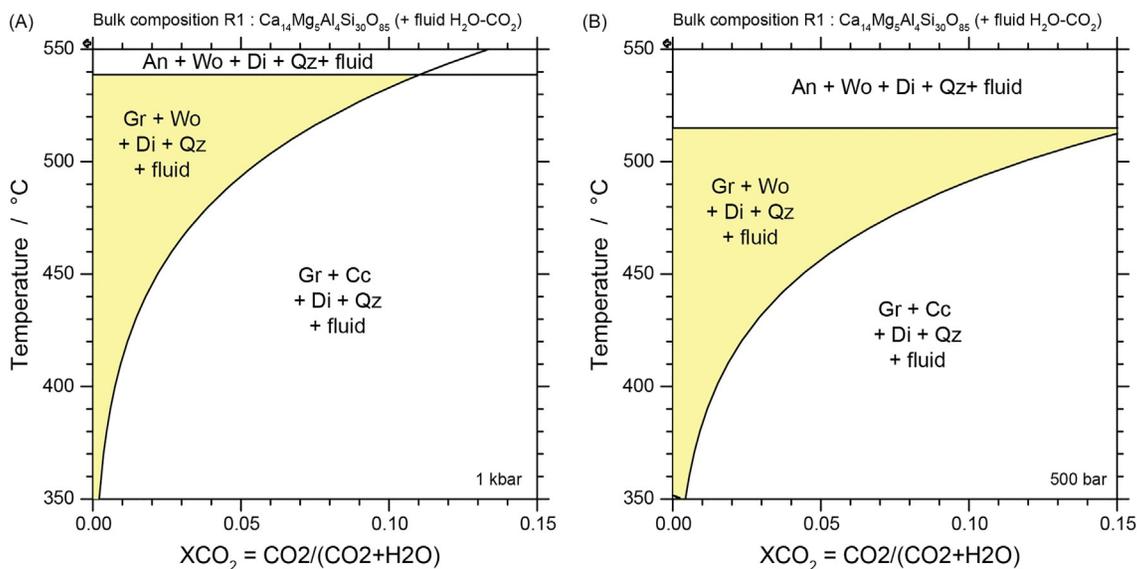
elements and trace elements, are indispensable. Such data form the basis for *thermobarometry*, i.e. methods that quantify the *P-T* conditions for a certain stage of the metamorphic evolution (e.g., Plunder et al., 2012). In addition, isotopic microanalysis may allow the age of such stages to be determined, hence to define parts of a *PTt*-path (e.g., Engi et al., 2017; Yakymchuk et al., 2017) and to extract rates of metamorphic processes. Studies indicate that the duration of individual stages of metamorphism may be much shorter than previously thought.

### Effects of Fluids on Metamorphic Mineral Assemblages

By definition, metamorphic rocks form essentially by solid-state processes that transform some *protoliths*, i.e. precursor rocks. Metamorphism may involve a fluid phase, commonly hydrous in composition. At the high-temperature end of metamorphic conditions, partial melting processes do occur, and the transition from metamorphism to magmatism is continuous. In the present article, melts (of silicate, carbonate or sulfide composition) are not discussed, and the term *fluid* refers to a volatile phase (of relatively low density), such as is commonly involved in metamorphic processes.

The presence (or absence) and composition of such a fluid phase during metamorphic processes has significant effects on the formation, evolution, and preservation of mineral assemblages. Two influences dominate: (1) during the prograde *PT*-path of a metamorphic evolution, as temperature is increasing, a series of breakdown reactions is usually induced wherever the protoliths contain hydrate or carbonate minerals. Where and when fluid is liberated, reaction kinetics are favorable, and equilibrium assemblages readily form, often by devolatilization reactions. By contrast, where fluid is scarce, in initially dry protoliths, equilibrium may not be attained as reaction kinetics are less favorable. For example, in coarse-grained magmatic protoliths metastable mineral relics may survive metamorphism up to fairly high temperature, except where external fluid can access due to localized deformation (e.g., Jamveit et al., 2019). (2) Another effect of fluids on the evolution of metamorphic assemblages is due to the chemical composition of fluids. Whereas locally generated fluid will be in equilibrium with the local mineral assemblage, this is rarely the case if fluid enters from a different source rock. Chemical fluid-rock interaction may thus affect the local assemblage. In fluid-dominated (open) systems, characteristic metasomatic series will develop (Putnis and Austrheim, 2010; Bach et al., 2013), which are characterized by high-variance mineral assemblages (e.g. mono- or bi-mineralic zones).

Fig. 3 explores the effect of fluid composition on stability relations, this time for the assemblage grossular + wollastonite + diopside (R1 in Fig. 1). It is evident that this assemblage is severely limited by the  $\text{CO}_2$ -content of the fluid. The fluid composition typically is buffered by the mineral assemblage (Greenwood, 1975) in closed systems, such as the calc-silicate hornfelses studied by Goldschmidt (1911). However, the limits shown in Fig. 3 are equally pertinent in open systems, i.e. with reactive fluid transfer through a body of rock.



**Fig. 3** Assemblage diagrams (with  $\text{CO}_2$ - $\text{H}_2\text{O}$  fluid). Calculated phase relations depicting the conditions where mineral assemblage R1 (see Fig. 1) is predicted to be stable, depending on the composition of a  $\text{CO}_2$ - $\text{H}_2\text{O}$  fluid. Yellow fields mark the same calcsilicate assemblage: grossular (Gr) + wollastonite (Wo) + diopside (Cpx) + quartz (Qz) + fluid. White fields correspond to assemblages in which either Gr is missing or Wo is replaced by calcite (Cc). Calculations as in Fig. 2.  $\text{CO}_2$  and  $\text{H}_2\text{O}$  denote moles of the respective species. Note the pressure difference.

## The Chemical Composition of Minerals During a Metamorphic Evolution

Minerals are characterized by a well-defined crystal structure, but the composition of most minerals is not fixed. In fact, most rock-forming minerals are *solid solutions*: The same mineral species may, within certain limits, vary in composition. For example, most of the minerals shown in Fig. 1 are in fact solid solutions: The composition of hypersthene is shown as  $(\text{Mg,Fe})\text{SiO}_3$ , indicating that it may vary from  $\text{MgSiO}_3$  to  $\text{FeSiO}_3$ , and similarly for cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ – $\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ). If compositions outside the four-component system depicted in Fig. 1 are also considered, then anorthite is but one endmember of the mineral plagioclase, a solid solution that can vary in composition from  $\text{CaAl}_2\text{Si}_2\text{O}_8$  to  $\text{NaAlSi}_3\text{O}_8$ . Similarly, grossular is but one endmember of garnet, a particularly important solid solution  $(\text{Ca,Fe}^{2+},\text{Mg,Mn})_3(\text{Al,Fe}^{3+})_2\text{Si}_3\text{O}_{12}$  present in many metamorphic rocks. In general, the thermodynamic stability of any mineral is strongly dependent on its composition. Excellent means are available to examine such effects; most widely used are various diagrams that portray the chemical stability of assemblages and the reactions among them. Such diagrams are calculated using databases containing thermodynamic models of rock-forming minerals and fluids. They are widely used to interpret data from well characterized metamorphic rocks, to substantiate reaction sequences inferred from the mineral textures and compositions preserved in a rock sample, or to quantify the conditions of equilibration (e.g. thermobarometry, fluid composition, redox conditions).

Two caveats are in store: (1) All of the relations shown in Figs. 2 and 3 hinge on the assumption of (local) chemical equilibrium, so they display the conditions under which equilibrium assemblages can form. Whether this is realistic for a given set of samples, needs to be tested, as emphasized earlier. (2) Though the use of such diagrams is well established, it should be kept in mind that thermodynamic models are continually evolving—usually improving—but they do have limitations and uncertainties. Predicted phase relations are not Truth, just models to be applied with scrutiny.

Since local phase relations in rocks may or may not correspond to preserved states of chemical equilibrium, testing the assumption of equilibrium is essential. The tools available are continually evolving, but they rest on just a few basic principles.

## Criteria and Tests of Equilibrium

Three main types of criteria and various methods are used to examine whether, how, and when a metamorphic rock sample, during its evolution, may have attained (or closely approached) one or more states of equilibrium:

Textural criteria

Compositional Criteria (chemical and/or isotopic)

Modeling criteria

These are commonly used in combination, and the same criteria are useful also to understand the specific factors that may have limited equilibration or essentially terminated metamorphic transformations at some stage of the evolution. This is most likely the case on the retrograde path, after metamorphism reached its thermal peak, but it may also be relevant on the prograde path, especially in fluid-starved rocks, at low temperatures, and in the evolution from coarse-grained protoliths. In metamorphic rocks it is usually possible to identify not just a single state, but a series of stages of the evolution. Where several such stages can be discerned, the first task is to document the minerals that formed or were coexisting at each stage (Lanari and Engi, 2017). Secondly, one can aim to estimate at what physical conditions this happened, and thirdly one may try to date one or more stages. Each of these steps is—yet again—based on the concept of mineral assemblages.

### Textural Criteria

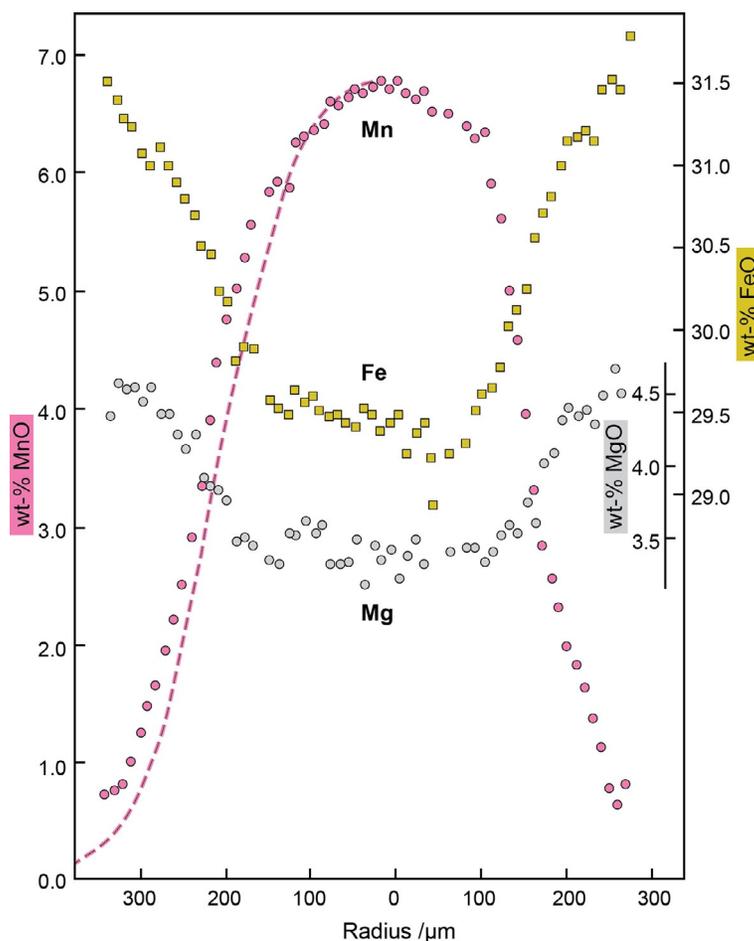
Metamorphic recrystallization often leads to an increase in grain size, and grain boundaries tend to become more regular. Fully equilibrated textures, such as mosaic fabrics with planar grain boundaries or equant grains are, however, not commonly found. But mutual grain boundaries among minerals hold important clues and require careful examination (Vernon, 1977). Regular, clean grain boundaries devoid of embayments or fine-grained alteration, may indicate local equilibrium. But many metamorphic textures include complexities such as corroded mineral relics or inclusions of one type of mineral in another. Elaborate criteria are used to understand such relations, especially in deformed rocks (Vernon, 1978), where microstructural characteristics (shape-preferred orientation, pressure shadows, etc.) can be used to relate local mineral assemblages or mineral compositions to tectonic processes (Airaghi et al., 2017). In many metamorphic belts, especially those associated with orogeny, rocks show evidence of several deformation stages. These may be analyzed using mostly geometric (micro-textural) criteria. However, such rocks typically indicate a sequence of metamorphic stages as well, and these may be related to different orogenic cycles. To understand or quantify complexities as are commonly preserved in poly-metamorphic rocks, micro-chemical analyses are indispensable.

### Compositional Criteria

A proper characterization of mineral assemblages hinges upon micro-chemical data from EPMA (electron probe microanalysis), perhaps augmented by LA-ICP-MS data for trace elements and in situ isotopic analysis. As polymineralic rocks are chemically

heterogeneous—neighboring grains usually differ in composition—and many protoliths comprise domains of very unequal composition, chemical exchange among phases is a pre-requisite to equilibration. The spatial and temporal scale of such exchange will delimit the size of potential equilibrium domains. At single grain scale, chemical heterogeneity or zoning is commonly evident because most rock-forming minerals are solid solutions. It may seem unlikely that principles of equilibrium thermodynamics could be a fruitful hypothesis in such situations, but over half a century of research shows otherwise. Much effort has gone into recognizing sequences of assemblages in *local (spatial) domains* and for several (*temporal) stages*, by applying careful chemical (and in some cases isotopic) analyses.

Chemical (or isotopic) inhomogeneity within a mineral grain is incompatible with the notion of complete equilibration, except where unmixing may be the cause (such phase separation can occur in strongly non-ideal solid solutions, e.g. alkali feldspar or Fe-Ti oxides). But in many—indeed most—other minerals chemical or isotopic zoning patterns are often observable. Such patterns may differ greatly in geometry, and deciphering these internal textures has turned out to be critical to understanding where chemical interaction took place and may have led to *local* equilibration. Zoning patterns often are fairly regular, more or less centrosymmetric, and such radial patterns may result from near-equilibrium growth processes. For instance, Hollister (1966) documented symmetric Mn-Fe-Mg zoning profiles in garnet (Fig. 4) and found that these are well described by Rayleigh fractionation of manganese during prograde growth of minerals. Sequestration of certain elements (those with high partition coefficients) into a growing crystal, such as garnet, leads to the steady depletion of these in the matrix. Microchemical zoning profiles such as observed by Hollister indicate that the matrix acted as a (more or less homogeneous) reservoir, from which a sequence of peripheral zones kept overgrowing a nucleus under local near-equilibrium conditions. Zoned porphyroblasts thus are able to preserve successive metamorphic stages and may reflect the physical conditions prevailing at the time of growth. If chemical zoning is regular and concentric as in Fig. 6A, one may assume that near-equilibrium conditions were probably maintained at the periphery of growing phases during their growth. But zoning in porphyroblasts often is neither concentric nor simple. Complications may be due to processes following the initial growth of the mineral and may indicate complexities (fluid influx, local deformation, etc.). Other



**Fig. 4** Growth zoning. Chemical zoning of Fe, Mn, and Mg in garnet porphyroblast. Concentrations (as oxide weight-%) from electron microprobe analysis; data and the Rayleigh fractionation model from Hollister (1966) indicate that during growth manganese was “distilled” from a matrix reservoir, which became correspondingly depleted. Rims were sequentially added to the porphyroblast, thus preventing substantial interaction of the core and the matrix. The grain did not homogenize, retaining its record of growth conditions.

complications may arise due to exchange and/or net-transfer reactions (Kohn and Spear, 2000) on the retrograde P-T path. For instance, composite garnet grains reported from various orogenic belts, show one or more Mn-rich internal rims deposited on inner garnet with irregular surfaces indicating corrosion (partial dissolution) followed by renewed garnet growth (Kouketsu et al., 2014; SY1460 in Laurent et al., 2018). Garnet is often viewed as a faithful “blackbox” of the P-T evolution, although as temperature increases, so does diffusion length, and partial homogenization may alter any chemical zoning present (e.g., Caddick et al., 2010). In high-grade metamorphic rocks potential memory loss must be considered, especially if the data are to be used for thermobarometry (Berman, 1991; Powell and Holland, 2008, 2010). For example, one may evaluate the shape of zoning profiles for elements with very unequal diffusivity (e.g. divalent and trivalent cations), to examine which of them have been seriously affected by diffusion.

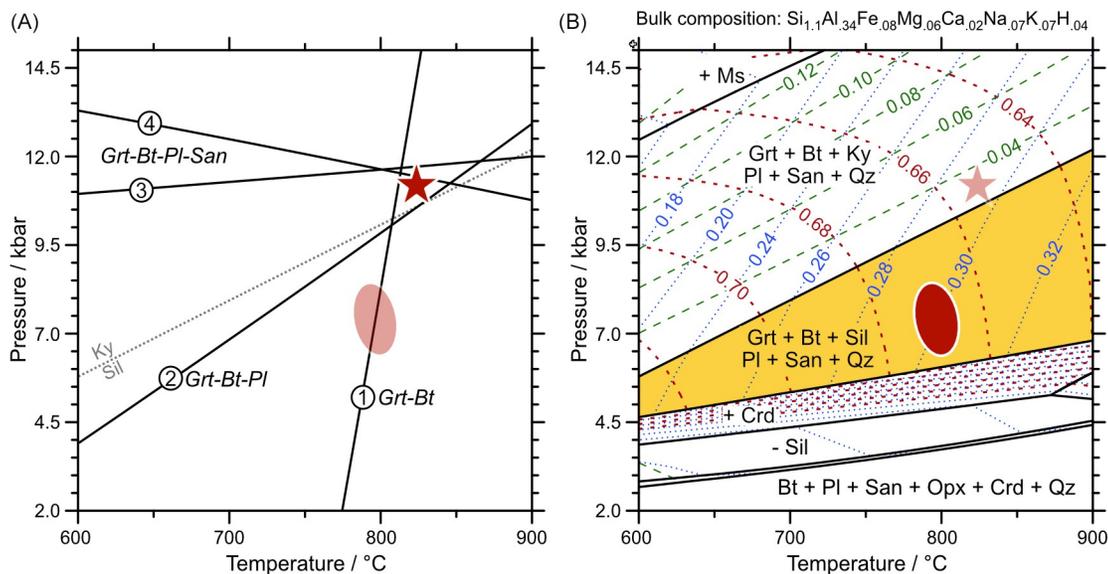
Where individual mineral grains show significant compositional heterogeneity and zoning appears to be irregular, metamorphic transformations either have never reached near-equilibrium conditions or, if a local assemblage did form, it was subsequently disturbed. Depending on the scale of the inhomogeneity and the complexity of mineral intergrowths, textural criteria alone may be insufficient to distinguish between these two possibilities. In these (common) cases, additional leverage from quantitative modeling has proven most valuable.

### Modeling criteria

Thermodynamic data (including solution models) are now available for most rock-forming minerals and relevant fluids. Over time, the scope of such databases keeps improving, as does a variety of flexible software packages making use of them (e.g., Berman, 1988; Connolly, 1990, 2009; de Capitani and Brown, 1987; de Capitani and Petrakakis, 2010; Holland and Powell, 1988, 1998, 2011; Lanari and Duisterhoeft, 2018; Spear et al., 2017) to predict stable phase assemblages in increasingly realistic model systems.

Basically two types of models are used:

- (1) Thermobarometry based on a set of computed phase equilibria chosen so as to match the identity and composition of minerals that coexist in a sample, ideally in direct grain-contact. *P-T* conditions are inferred by assuming that a combination of these equilibria were simultaneously satisfied, hence the approach is termed *multi-equilibrium* method. The dispersion of the *P-T* intersections (Fig. 5A) serves as a test of this assumption, but with no assurance that the phases represent a stable assemblage at these conditions.
- (2) Forward models of equilibrium phase relations calculated for a specified chemical composition, and in an appropriate *P-T* range (or any other physical parameter set chosen). To define a suitable bulk composition, chemical analyses are needed, either of the bulk sample or of the observed association of minerals and their modal abundances; moreover, the chemical component



**Fig. 5** Thermobarometry: forward versus inverse modeling. (A) Multi-equilibrium method (Berman, 1991; Berman, 2007) applied to the assemblage Grt-Bt-Pl-San-Qz-H<sub>2</sub>O. A selection of four equilibria is shown in the figure: (1) Alm + Phl = Prp + Ann; (2) 3 Alm + 3 Eas + 2 Grs + 6 Qz = 2 Prp + 6 An + 3 Ann; (3) 2 San + Grs + 2 Alm + 2 H<sub>2</sub>O = 2 Ann + 3 An + 3 Qz; (4) Grs + 2 San + 2 Prp + 2 H<sub>2</sub>O = 3 Qz + An + Phl. The red star represents the interpreted P-T conditions for this assemblage in the kyanite stability field. The gray dashed line shows the Ky-Sil reaction. Phases: Bt: biotite, Grt: garnet, Pl: plagioclase, Qz: quartz, Sil: sillimanite; endmember components: Alm: almandine, An: anorthite, Ann: annite, Eas: eastonite, Grs: grossular, Phl: phlogopite, Prp: pyrope, San: sanidine. (B) Constant-composition phase diagram (aka “pseudo-section”) calculated using a bulk rock composition of the same metapelite (TG8C-03) and the thermodynamic data in JUN92.bs (<https://titan.minpet.unibas.ch/minpet/theriak/prog190309/>) with addition of an extended biotite model taken from BED92.v1 (Duisterhoeft, 2017). Garnet isopleths are shown by dashed lines for three endmembers (red: almandine, blue: pyrope, green: grossular). The red ellipse marks the intersection of isopleths, interpreted to reflect *P-T* conditions for the assemblage Grt-Bt-Sil-Qz.

space is usually simplified to account for (limitations of) the thermodynamic models available. The computed phase relations and calculated stability limits are then compared against those observed in the sample(s). Such equilibrium diagrams allow interpretations formulated from well characterized samples to be tested, but initial models often show discrepancies between observed and predicted phase relations that reflect an inadequate bulk composition in the models. Some adjustment or iterative correction is often necessary, until the appropriate bulk composition is found (Lanari and Engi, 2017). Provided the observed (local) assemblage does have a stability field, one can then attempt to quantify metamorphic conditions more precisely. The method most commonly used is based on the intersection of equilibrium isopleths (Evans, 2004).

In most cases, thermobarometric results based on the two methods should yield comparable results. However, in the *multi-equilibrium* approach the  $P$ - $T$  dependence of the equilibria utilized is not always consistently formulated (e.g., explicit formulations from experimental studies are used), while forward modeling is (or should be) based on a set of consistent thermodynamic data. If compositional effects on assemblages are handled differently, this may produce a systematic discrepancy in the  $P$ - $T$  results obtained.

Even where an internally consistent database is used for modeling, the results may be sensitive to which equilibria are considered for thermobarometry. Fig. 5 shows an example of multiply overprinted metapelites from the Higher Himalayan Crystalline Sequence exposed in Sikkim, India. Metamorphic conditions for one sample (TG8C-03) from Rubatto et al. (2013) were investigated by Lanari and Duesterhoeft (2018). This sample exhibits a mineral association made of garnet, biotite, sillimanite, quartz, plagioclase, K-feldspar and ilmenite. Two methods are used to test if these minerals may represent an equilibrium assemblage and, if so, at what  $P$ - $T$  conditions (Fig. 5A and B). In the sample chosen, plagioclase and K-feldspar were interpreted by Lanari and Duesterhoeft (2018) to have formed during prograde metamorphism in the kyanite stability field, whereas garnet and biotite have partially re-equilibrated during decompression when sillimanite became stable. The same mineral compositions were used in (A) and (B), yet the two approaches reflect different  $P$ - $T$  conditions because (A) does not consider the observed aluminosilicate polymorph (sillimanite), while (B) does and relies on the composition of garnet.

### Final Account: Equilibrium?

Where a forward model, despite appropriate refinements of the bulk composition, indicates no stability field for an observed mineral association in an isochemical phase diagram, the discrepancy may indicate inadequacies in the thermodynamic data or models used. Alternatively, it may indicate disequilibrium, and kinetic considerations are required to explore its scale and extent.

While it is certainly possible to find evidence for disequilibrium, it is sobering but essential to emphasize that even judicious application of all the methods outlined above cannot conclusively prove that equilibrium was attained at any stage of a metamorphic evolution of a sample. But absence of evidence (for disequilibrium) is not evidence of the absence, thus the notion of equilibrium remains a hypothesis. It is important to explore the consequences and then consider possible extensions of the model.

Depending on the complexity of the  $P$ - $T$ - $D$  history of samples, the methods outlined above may or may not allow a series of metamorphic stages to be identified on the basis of local mineral assemblages. The ultimate aim often is to relate these to tectonics or models of crustal evolution. In tectonically complex situations, such as prevail in subduction systems or orogens, local assemblages pose particular challenges. Deformation and episodic fluid flux may occur jointly, and localized metamorphic processes may be initiated, possibly at relatively short time scales. Mineral inclusions or relics from certain stages of such evolutions are commonly preserved, and these may provide evidence for at least some of the growth stages of a zoned host mineral, notably in porphyroblasts of robust minerals, such as garnet. To relate any such relics to a host composition and to identify potential inclusion assemblages, the use of compositional maps—rather than just spots along profiles—has proven invaluable. These are derived from X-ray maps obtained by electron microprobe or analytical SEM (Lanari and Duesterhoeft, 2018).

When used in conjunction with the criteria outlined above, compositional maps may first be of use to recognize local phase relations and textures, i.e. to determine at what spatial scale these may (or may not) represent local equilibrium assemblages. Maps showing the spatial distribution of the minerals, combined with suitable maps of their compositions, are easily compared with isochemical phase diagrams (calculated for the relevant  $P$ - $T$  space) to infer to what extent the notion of local equilibrium is tenable or to recognize a frozen-in reaction.

Typical cases involve porphyroblasts hosting inclusions of relic phases that have been screened from further reaction by the armor provided by a robust host. However, complete assemblages are rarely preserved—often only one or two phases survive—and thus the leverage provided by isochemical diagrams is all the more important: the sparse relics available can be compared with phase compositions of complete assemblages. A tricky part of this approach is to define the *reactive bulk composition* for the model, i.e. to delimit domains in which chemical interaction among minerals could have led to the development of equilibrium assemblages (Lanari and Engi, 2017). Since maps support the simultaneous consideration of chemical and textural criteria (in 2D), such as grain orientation, mutual inclusion relationships, modal abundance distribution, etc., it is sometimes possible to identify several generations of assemblages and use these to quantify some stages of the evolution (by thermobarometry).

It should be emphasized that the mere identification of mineral inclusions (e.g. by micro-Raman analysis) in a host phase may aid in deciphering earlier metamorphic stages, provided the assemblage in which the inclusions formed is properly understood. For instance, it may be critical to be sure which  $\text{Al}_2\text{SiO}_5$ -polymorph or Fe-Ti oxide is preserved within specific garnet growth zones. However, a single phase is far less precise as a witness than an (even partly preserved) assemblage. The challenge may be to know

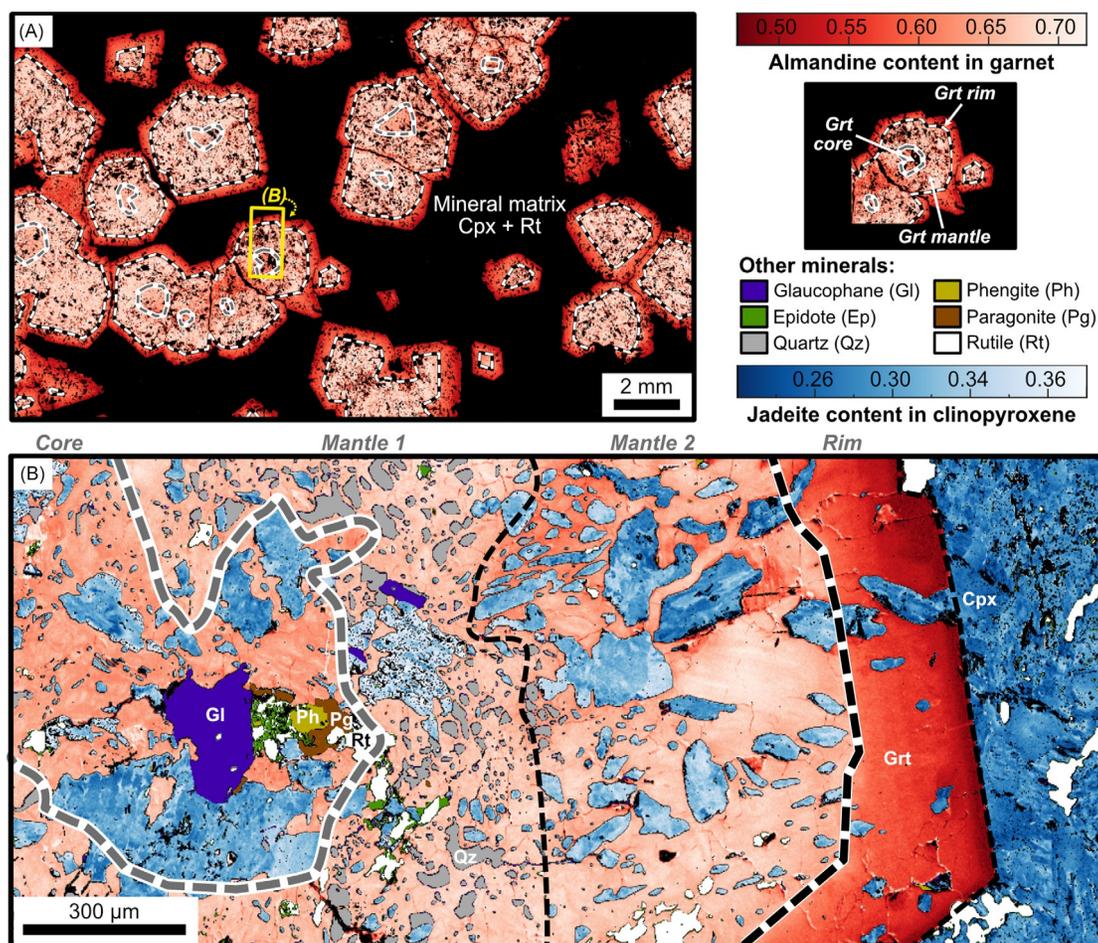
what composition is adequate to model the evolution of a small domain or an accessory phase that may contain large proportions of trace elements.

Cases where such efforts have proven successful include the following: (i) Prograde assemblages identified in high-grade samples, (ii) partly preserved high-temperature or high-pressure stages that remain in strongly retrogressed samples, (iii) significant relics of an earlier orogeny found in polymetamorphic samples.

### Pushing the Concept of Equilibrium Mineral Assemblages to its Kinetic Limits

The concept of equilibrium mineral assemblages has proven to be a useful model, but like all models, it has limitations. One such limitation derives from nucleation barriers. Certain typical textures indicate that deviations from thermodynamic equilibrium may commonly occur during the evolution of metamorphic rocks, but these deviations may not show up as obvious chemical disequilibria in samples studied.

Such limitations become most apparent where textures are not easily interpretable, for instance where some mineral species are very sparse or of much larger grain size than others. Consider the case of poikiloblastic garnet, i.e. the fairly common type of porphyroblast with many inclusions. This may (or may not) represent a partially preserved prograde assemblage. To test if it does, compositional maps of a sample domain are powerful since the chemical compositions of each locally preserved mineral can be compared to one or more complete model assemblages. In the specific case shown in Fig. 6, the map shows a domain in a



**Fig. 6** Mineral inclusions as relics of equilibrium assemblages. (A) Garnet porphyroblast shows approximately concentric chemical zones (in Fe-Mg-Ca, here the Fe-endmember almandine is shown in red); the Na-content of clinopyroxene (cpx) is shown in hues of blue. (B) Four garnet zones (core, mantle1, mantle2 and rim) contain a sequence of partly corroded relics. Loury et al. (2018) recognized these as partially preserved assemblages by comparing relics and their compositions to an isochemical phase diagram: Cpx-Gl-Ph-Pg-Rt-Qtz in the garnet core constitutes a (fully hydrated) low-temperature eclogite assemblage; subsequent overgrowth of garnet rims lead to the sequential loss of the following phases: Pa (missing) in mantle1, Pg + Ph in mantle2, Pg + Ph + Gl in rim. Some Gl and cpx grain boundaries preserve growth features, and cpx compositions suggest a systematic evolution from one Grt zone to the next. Dashes indicate approximate zone boundaries. Modified from Fig. 9b in Lanari P and Duesterhoeft E (2018) Modeling metamorphic rocks using equilibrium thermodynamics and internally consistent databases: Past achievements, problems and perspectives. *Journal of Petrology*, 60: 19–56 and Loury C, Rolland Y, Guillot S, Mikolaichuk AV, Lanari P, Bruguier O and Bosch D (2015) Crustal-scale structure of south Tien Shan: Implications for subduction polarity and Cenozoic reactivation. In: Brunet MF, McCann T and Sobel ER (eds.) *Geological Evolution of Central Asian Basins and the Western Tien Shan Range*. London: Geological Society. cpx: sodic clinopyroxene, Gl: glaucophane, Grt: garnet, Pg: paragonite, Ph: phengite, Qz: quartz, Rt: rutile.

hydrous low-temperature eclogite sample from the South Tien Shan Range (Kyrgyzstan) documented by Loury et al. (2015). At first sight, the geometrically and chemically complex inclusions in the zoned porphyroblast are hardly suggestive of equilibrium states in the relic assemblage. Simple, clean grain boundaries are missing, mineral relics show corroded surfaces, and irregular chemical zones add confusion. Yet, upon close inspection, some regularity is discernable, and systematic comparison with calculated phase diagrams may indicate which previous stage(s) the inclusions may be representing. In Fig. 6B, clinopyroxene shows variable compositions, though these appear linked to the (evolving) composition of garnet, so may just reflect very local growth conditions. The choice of an appropriate bulk composition for modeling the evolution of relic assemblages during growth of a (zoned) porphyroblast is a non-trivial exercise: It is necessary to consider the sequestration of nutrients for growing one phase from the matrix while replenishing the reservoir by partial resorption of the previously formed phases. Specific models that take account of these combined effects have been developed and applied for garnet (Lanari et al., 2014).

Despite the success of refined thermodynamic equilibrium methods, the need to develop approaches that consider kinetics remains. The need is well established, even for high temperature metamorphism, and especially in dry protoliths (e.g., Austrheim, 1987, 1990). Kinetic limitations to the continued equilibration of rocks, even on their prograde P-T path, include nucleation barriers and growth-limitations due to slow chemical transport. Considering these limitations is particularly relevant when porphyroblasts are analyzed, since large grains usually imply rapid growth, which may result from reaction overstepping.

Models of garnet growing after significant overstepping indicate that zoning patterns may rarely be distinguishable from zoning produced by continuous garnet grown under near-equilibrium conditions (Spear et al., 2017). If so, it is unrealistic to infer the amount of actual overstepping from zoning profiles. However, it can be assessed by methods that do not depend on chemical equilibrium, such as inclusion thermobarometry (Kohn, 2014). In the case of garnet porphyroblasts, the amount of overstepping has been found substantial in some studies (Spear et al., 2014), on the order of several kbar in pressure or tens of degrees in temperature.

The consequences are not yet fully understood. Certainly the reaction mechanisms in the evolution of metamorphic textures need further study, and the delayed appearance of certain critical minerals in prograde reaction sequences requires consideration.

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