The metamorphosis of metamorphic petrology

Frank S. Spear

*Department of Earth and Environmental Sciences, JRSC 1W19, Rensselaer Polytechnic Institute,
110 8th Street, Troy, New York 12180-3590, USA*

David R.M. Pattison

Department of Geoscience, University of Calgary, 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada

John T. Cheney

Department of Geology, Amherst College, Amherst, Massachusetts 01002, USA

ABSTRACT

The past half-century has seen an explosion in the breadth and depth of studies of metamorphic terranes and of the processes that shaped them. These developments have come from a number of different disciplines and have culminated in an unprecedented understanding of the phase equilibria of natural systems, the mechanisms and rates of metamorphic processes, the relationship between lithospheric tectonics and metamorphism, and the evolution of Earth's crust and lithospheric mantle. Experimental petrologists have experienced a golden age of systematic investigations of metamorphic mineral stabilities and reactions. This work has provided the basis for the quantification of the pressure-temperature *(P-T)* conditions associated with various metamorphic facies and eventually led to the development of internally consistent databases of thermodynamic data on nearly all important crustal minerals. In parallel, the development of the thermodynamic theory of multicomponent, multiphase complex systems underpinned development of the major methods of quantitative phase equilibrium analysis and *P-T* estimation used today: geothermobarometry, petrogenetic grids, and, most recently, isochemical phase diagrams.

New analytical capabilities, in particular, the development of the electron microprobe, played an enabling role by providing the means of analyzing small volumes of materials in different textural settings in intact rock samples. It is now understood that most (if not all) metamorphic minerals are chemically zoned, and that this zoning contains a record of sometimes complex metamorphic histories involving more than one period of metamorphism. The combination of careful field studies, detailed petrographic analysis, application of diverse methods of chemical analysis, and phase equilibrium modeling has resulted in at least a first-order understanding of the metamorphic evolution of nearly every metamorphic belt on the planet. Additionally, the behavior of fluids in the crust, although still not fully understood, has been examined experimentally, petrographically, chemically, isotopically, and via geodynamic modeling, leading to recognition of the central role fluids play in metamorphic processes.

The plate-tectonic revolution placed metamorphic facies types into a dynamic new context—one in which the peak metamorphic conditions were seen as the interplay of thermal perturbations due to tectonic and magmatic processes, thermal relaxation via conduction, and exhumation rates. The discovery of coesite and diamond from demonstrably supracrustal rocks revealed an extent of recycling between Earth's surface and the mantle that was previously unimagined. Numerous ultrahigh-pressure and ultrahigh-temperature terranes have now been recognized, forcing a reconsideration of the diversity and vigor of lithospheric processes that permit the formation and exhumation of rocks showing such extreme metamorphic conditions.

Revolutions in the field of geochronology have had a fundamental impact on metamorphic studies in that it is now possible to obtain ages from different parts of age-zoned minerals, thereby permitting absolute time scales to be constructed for the rates of metamorphic recrystallization and their tectonic driving forces. Application of diffusion and kinetic theory is providing additional insights into the time scales of metamorphic recrystallization, which are emerging to be shorter than previously suspected.

Many unanswered questions remain. As thermodynamic and kinetic theory evolves and new analytical methods emerge, augmenting the fundamental contributions of fieldwork and petrography, metamorphic petrology will continue to provide unique and irreplaceable insights into Earth processes and evolution.

INTRODUCTION AND HISTORICAL PERSPECTIVE

Fifty years ago (ca. 1965—about the time Spear began to be interested in geology as a career), the fundamental goals of metamorphic petrology were not particularly different from what is practiced today. At the forefront of the science, there was the enquiry into what metamorphic rocks could tell us about how the crust has evolved. However, the revolutions that have occurred throughout the geosciences in terms of global tectonics, new instrumentation, application of fundamental theoretical developments, and blending of once highly specialized and diverse subdisciplines have resulted in transformations in the field that have led to broad new understanding of the evolution of metamorphic terranes. Practitioners from 50 years ago would undoubtedly recognize the core of the science but would equally be amazed at the range of available tools and the degree of insight into metamorphic parageneses.

Reading over F.J. Turner and J. Verhoogen's *Igneous and Metamorphic Petrology* (2nd ed.; 1960), it is impressive to appreciate the depth of understanding of the scope, and the important issues, of metamorphic petrology. While it is true that this era of metamorphic studies was focused on classification of rocks into various categories and especially on differentiating the metamorphic facies, the principal factors affecting metamorphism such as pressure (P, depth), temperature (T), fluid pressure, surface tension, and strain were all recognized as significant. It was understood and appreciated that the metamorphic facies concept implied a close approach to equilibrium by rocks at their peak temperatures and that these relationships could be described, explained, and predicted by chemical thermodynamics. J.B. Thompson Jr. (1955) had laid out the thermodynamic

basis for the mineral facies concept in 1955. The importance of kinetics in governing whether a new mineral assemblage would nucleate and grow was acknowledged. Also appreciated was the relative rapidity of kinetic processes during prograde metamorphism and the relative sluggishness during retrograde metamorphism, presumably owing to the availability of copious quantities of H_2O released during heating and the absence of fluids during cooling.

What was missing, however, was the array of tools—analytical, theoretical, and conceptual—required to move the field to the next stages of truly quantitative material science. Electron microprobes were just becoming available to the community. Mass spectrometry was in its infancy, and it would be a number of decades before geochronology could be directed at metamorphic processes. Understanding of relatively simple thermodynamics and phase equilibria was universal, but the extension to multicomponent, multiphase systems had not been developed. Computers capable of performing the sorts of calculations that would be needed were just being conceived, and the crust of Earth, even during orogenesis, was considered a relatively static environment as the first compelling evidence for plate tectonics had yet to be unveiled.

Minerals in *P-T-X* (Composition) Space—The Impact of Experimental Studies on Metamorphic Petrology

Historical Setting

In the early 1960s, experimental petrology was blossoming into a major force in the geosciences. Tuttle and Bowen (1958) had just published their seminal study on the origin of granites, resolving the controversy surrounding the magmatic origin of

The metamorphosis of metamorphic petrology

granites, and Yoder and Tilley (1962) had published their treatise on the origin of basalt magmas, just in time for the discovery of seafloor spreading and a renewed interest in ocean floor volcanism. Experimental studies were being conducted on common metamorphic phases such as micas, pyroxenes, amphiboles, Fe-Ti oxides, staurolite, chloritoid, garnet, and cordierite, so that the broad ranges of metamorphic *P-T* conditions could finally be quantified.

Al$_2$SiO$_5$ System

One of the most important sets of phase boundaries in metamorphic petrology involves the Al$_2$SiO$_5$ polymorphs andalusite, sillimanite, and kyanite. The invariant point involving all three— the Al$_2$SiO$_5$ triple point—is fortuitously located in a part of *P-T* space commonly attained in crustal metamorphism. The simple presence of one or more of the polymorphs therefore provides first-order constraints on *P-T* conditions.

The qualitative *P-T* relationships amongst the polymorphs were established early on and were based on field relationships (e.g., andalusite being common in low-pressure contact aureoles, and sillimanite becoming dominant at higher metamorphic tem-

perature in the same aureoles) and volume measurements (e.g., kyanite, with the smallest molar volume, being stable at higher pressure). Based on such relationships, Miyashiro (1949) was the first to propose the shape of an inverted "Y" for the Al$_2$SiO$_5$ phase diagram. From the late 1950s through the early 1970s, several experimental studies on the Al$_2$SiO$_5$ triple point were conducted (e.g., Clark et al., 1957; Clark, 1961; Newton, 1966a, 1966b; Richardson et al., 1969; Holdaway, 1971), and continued through the 1990s (e.g., Bohlen et al., 1991; Kerrick, 1990; Holdaway and Mukhopadhyay, 1993). Estimates of the Al$_2$SiO$_5$ triple point ranged widely, with most falling in the range 500–620 °C, 3.8–5.5 kbar (Fig. 1). Discrepancies among these estimates were not unexpected, because of the small free energy difference between andalusite and sillimanite, and it led to assessment of the relatively subtle influences of factors such as order-disorder, grain size, and minor elements on the phase boundary (e.g., Salje, 1986; Kerrick, 1990; Hemingway et al., 1991).

Largely due to the quality of the experiments and the detailed explanation of the methods, the triple point of Holdaway (1971) was adopted by most metamorphic petrologists for over 20 years. However, inconsistencies remained between the
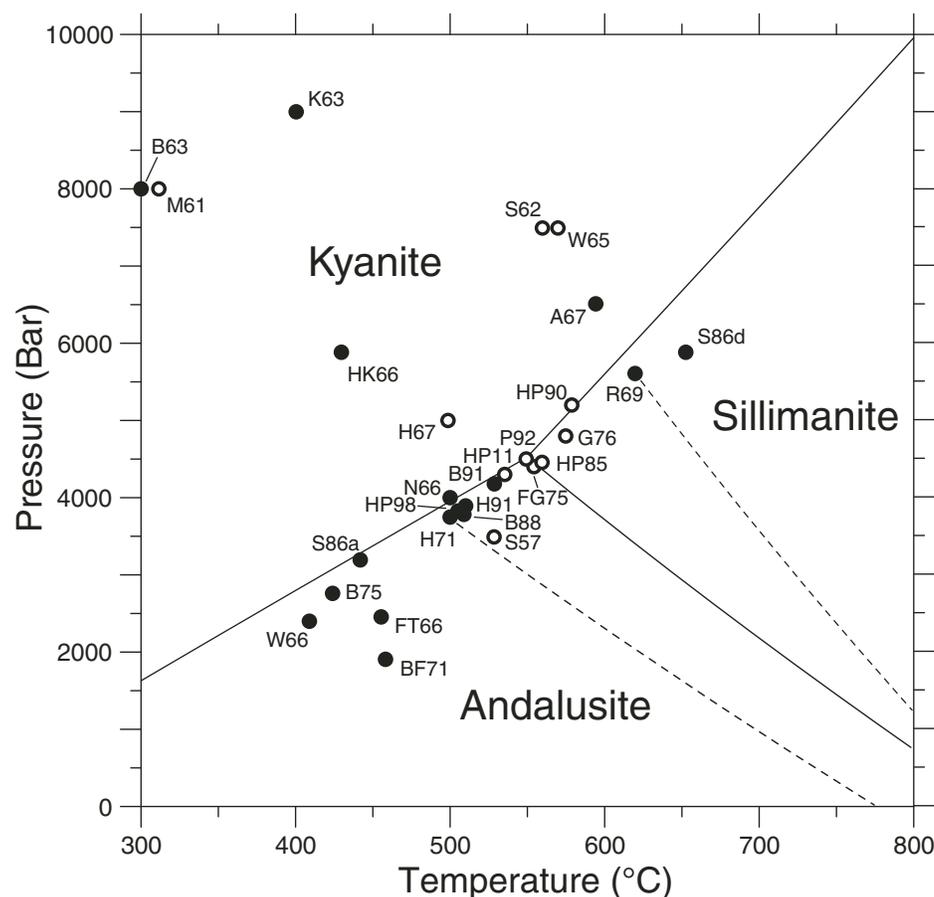

Figure 1. Estimated positions of the Al$_2$SiO$_5$ triple point. Filled circles—estimates from experiments augmented with thermochemical constraints. Open circles—estimates from combined field, phase equilibria, experimental, and thermochemical constraints. Solid lines—triple point and two-phase boundaries from the study of Pattison (1992). Dashed lines—position of the andalusite-sillimanite boundary from the two most widely cited experimental determinations, those of Richardson et al. (1969) and Holdaway (1971). Abbreviations: A67 (Althaus, 1967); B63 (Bell, 1963); B75 (Bowman, 1975); B88 (Berman, 1988); B91 (Bohlen et al., 1991); BF71 (Brown and Fyfe, 1971); FG75 (Froese and Gasparrini, 1975); FT66 (Fyfe and Turner, 1966); G76 (Greenwood, 1976); H67 (Hietanen, 1967); H71 (Holdaway, 1971); H91 (Hemingway et al., 1991); HK66 (Holm and Kleppa, 1966); HP85 (Holland and Powell, 1985); HP90 (Holland and Powell, 1990); HP98 (Holland and Powell, 1998); HP11 (Holland and Powell, 2011); K63 (Khitarov et al., 1963); M61 (Miyashiro, 1961); N66 (Newton, 1966a); P92 (Pattison, 1992); R69 (Richardson et al., 1969); S86a (Salje, 1986; his curve "a" for coarse sillimanite); S86d (Salje, 1986; his curve "d" for fibrolitic sillimanite); S57 (Schuiling, 1957); S62 (Schuiling, 1962); W66 (Weill, 1966); W65 (Winkler, 1965).

Holdaway (1971) triple point location and certain observations of natural parageneses. One notable inconsistency is the occurrence of andalusite-bearing granites (Clarke et al., 1976, 2005), which is prohibited based on the location of the andalusite-sillimanite boundary in Holdaway's experiments. Pattison (1992) reviewed the experimental and natural data that constrain the triple point and concluded that it must lie at conditions close to 550 °C, 4.5 kbar. Although this might not seem very different from Holdaway's values of 501 °C, 3.76 kbar, it makes a significant difference to estimated depths of emplacement of intrusions that develop andalusite-bearing sequences in their contact aureoles, as well as to regional andalusite-sillimanite–type sequences. The increased stability field for andalusite appears more consistent with other calculated and observed metamorphic parageneses and is generally accepted today.

Other Experimental Studies

The 1960s through 1980s were the golden age of experimental petrology. In the 1960s and 1970s, pioneering studies using natural minerals provided some of the first constraints on the *P-T* ranges of common mineral assemblages of metamorphic rocks (e.g., Hirschberg and Winkler, 1968; Hoschek, 1969). Later, greater emphasis was placed on experiments using synthetic minerals of restricted composition that better allowed extraction of thermodynamic data. Many studies were conducted in a wide range of chemical systems (see summaries and references in Holland and Powell, 1985, 1990, 1998, 2011; Berman, 1988). Experimental techniques were explored and refined, with the gold standard of experimental reliability being the reversed experiment using crystalline starting materials (e.g., Newton, 1966a). Earlier experimental studies crystallized minerals or groups of minerals from glass starting materials, but these experiments were susceptible to kinetic artifacts because glass is very unstable relative to crystallized solid phases. Reversals, by contrast, involved putting the crystalline products and reactants

of a reaction together into an experimental capsule, and bracketing the equilibrium by noting the *P-T* conditions under which the reactants grew at the expense of the products, and vice versa (e.g., Koziol and Newton, 1988).

At the same time, experiments were being conducted on element fractionation between solid solution phases, such as Fe-Mg fractionation among minerals like garnet, biotite, and cordierite (see discussion on geothermobarometry later herein). A different concept of reversibility evolved for such experiments that was also based on the principle of bracketing, but it involved bracketing of composition rather than *P-T* conditions (e.g., Ferry and Spear, 1978; Fig. 2). The approach involved pairs of experiments conducted at the same *P-T* conditions, in which mineral compositions on either side of the estimated equilibrium compositions were inserted in each experiment. The expectation was that the newly formed mineral compositions from each experiment would migrate toward the intermediate, possibly equilibrium, composition from opposite compositional directions. Even if a gap remained, the experiments in theory provided brackets. In practice, bracketing depends on an equilibration mechanism by solid diffusion, an unlikely situation in fluid-fluxed experiments such as these. If equilibration is by solution-precipitation (in which the out-of-equilibrium inserted minerals dissolve into, and the newly formed mineral compositions precipitate from, an intergranular medium), the sense of compositional bracketing is lost (Pattison, 1994). Nevertheless, many successful calibrations were based on such experiments because they generally returned consistent results.

f$_{O_2}$-T *Equilibria*

It was well understood that elements with variable valence states over typical crustal conditions would display different geochemical behavior. Eugster (1959), in his groundbreaking paper "Reduction and oxidation in metamorphism," outlined the fundamental principles of redox equilibria as they pertained to
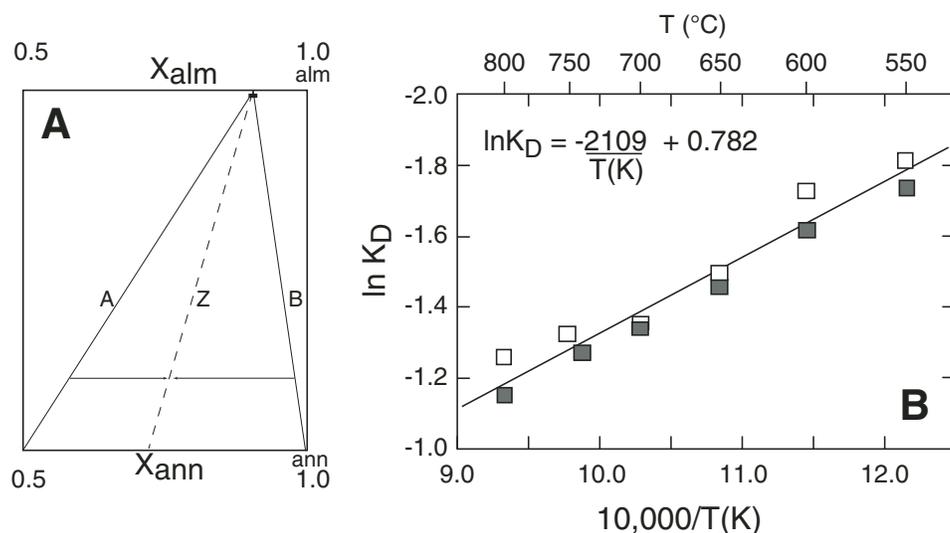

Figure 2. (A) Design of experiments for Fe-Mg exchange reaction (from Ferry and Spear, 1978, their figure 2). Biotite of different composition was equilibrated with garnet of the same composition (tie lines A and B). The approach to equilibrium was established by both experiments converging to a similar biotite composition (tie line Z). (B) ln *K* vs. 1/*T* plot for garnet-biotite partitioning experiments (Ferry and Spear, 1978, their figure 3). alm—almandine; ann—annite.

metamorphic assemblages, which spawned decades of research into the relationship between oxygen fugacity (f_{O_2}) and observed mineral assemblage.

Of these elements, Fe is clearly the most dominant in typical metamorphic rocks, and it was paramount in experimental studies involving Fe-bearing minerals that the f_{O_2} of the experiment be controlled. The most common approach was to use what was known as a solid oxygen fugacity buffer (Eugster, 1957), such as quartz-fayalite-magnetite, which controlled the f_{O_2} via the equilibrium $3Fe_2SiO_4 + O_2 = 3SiO_2 + 2Fe_3O_4$. This buffer assemblage was isolated in the outer part of a two-capsule assembly, and equilibrium with H_2O ($H_2 + O_2 = H_2O$) resulted in control of hydrogen fugacity (f_{H_2}) in this outer capsule. This hydrogen equilibrated with the inner capsule by diffusion through the permeable capsule wall (e.g., Ag, Pt, or Ag-Pd), and equilibrium with H_2O in the inner capsule in turn buffered f_{O_2}.

Figure 3 shows the f_{O_2}-T diagram displaying the stability of the Fe-biotite annite (Eugster and Wones, 1962) from a series of such experiments. The fact that the upper f_{O_2} stability of annite crosses the solid oxygen fugacity buffers indicates that considerable ferric iron can be incorporated into annite, especially at low temperatures.
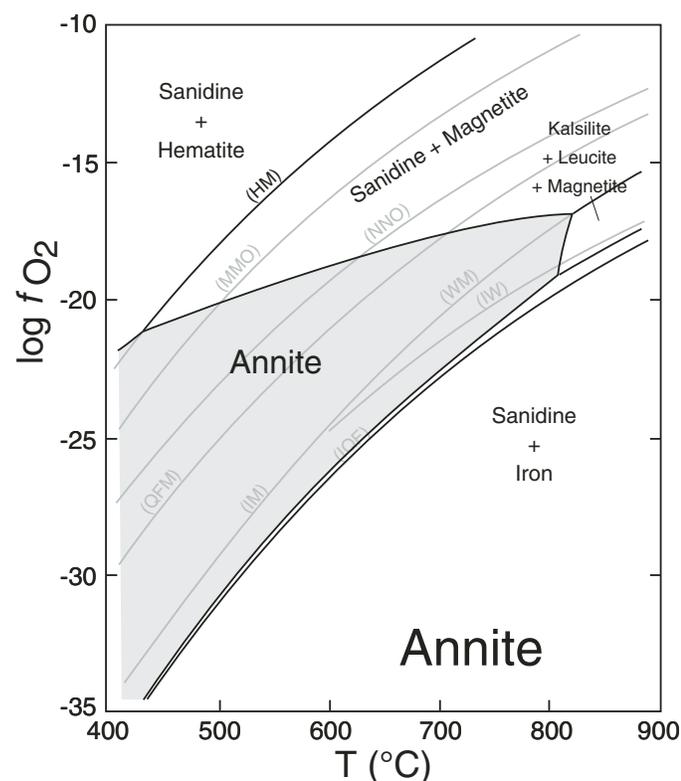

Figure 3. f_{O_2}-T diagram showing the stability of the Fe-biotite annite ($KFe_3AlSi_3O_{10}[OH]_2$), after Eugster and Wones (1962). HM—hematite-magnetite; MMO—manganese-manganese oxide; NNO—nickel-nickel oxide; QFM—quartz-fayalite-magnetite; WM—wüstite-magnetite; IM—iron-magnetite; IW—iron-wüstite buffer; IQF—iron-quartz-fayalite.

The f_{O_2} in the inner capsules of these experimental studies was controlled externally, and it is not surprising that considerable discussion ensued in the petrologic literature about the external control of f_{O_2} on observed mineral assemblages. However, it was soon recognized that the quantities of oxygen under discussion were miniscule (e.g., pO_2 [partial pressure of oxygen] values ranging from 10^{-15} to 10^{-30} bars) and that typical metamorphic mineral assemblages themselves possessed considerable redox buffering capacity due to elements of difference valence, especially Fe. Consequently, it was appreciated that most variations in f_{O_2} among nearby mineral assemblages were inherited from the original sedimentary precursor (e.g., Rumble, 1978). Nevertheless, control of f_{O_2} is a necessary consideration in any experimental study on variable redox systems, and evaluation of the redox state of any assemblage is critical to correctly assess the conditions of its formation. Unfortunately, even today, metamorphic studies are hampered by the difficulty in measuring the relative amounts of oxidized and reduced species of an element—most notably the Fe^{2+}/Fe^{3+} in typical metamorphic minerals—because they cannot be distinguished on the electron microprobe.

Geothermometry and Geobarometry

A parallel development in the analysis of metamorphic mineral assemblages and the *P-T* conditions under which they formed arose from theoretical considerations and the observation in field studies that element fractionations between solid solution phases varied systematically across a range of metamorphic grade (e.g., Ramberg, 1952; Kretz, 1959). Examples included Fe-Mg fractionation among minerals like garnet, biotite, and cordierite, or Ca-Mg partitioning between calcite and dolomite. These trends, if quantified, offered the potential to estimate metamorphic temperature simply from measuring elemental concentrations in the coexisting minerals of interest. The calibration of temperature-sensitive element fractionations between minerals, and its application to metamorphic rocks, became a major focus of metamorphic petrology in the 1970s and 1980s, giving rise to the subdiscipline of geothermometry (Essene, 1982, 1989). Pressure-sensitive element fractionations, involving elements that affect the molar volume of minerals such as Ca in garnet and plagioclase and Al in micas and amphiboles, were also recognized from field studies (Kretz, 1959). Experimental and natural investigation of these trends (e.g., Ghent, 1976; Newton, 1983) gave rise to the complementary subdiscipline of geobarometry. The combined approach—geothermobarometry—became the dominant means of estimating the peak conditions of metamorphic rocks for ~20 years, to some degree supplanting evaluation of *P-T* conditions via mineral assemblages and petrogenetic grids.

Calibration of many individual pressure- or temperature-sensitive equilibria, and different calibrations of the same equilibria (e.g., garnet-biotite), resulted in a mushrooming of geothermobarometric methods that could be applied to individual samples (Essene, 1982, 1989). Judging the precision, accuracy, and, quite commonly, the inconsistencies between *P-T* results arising from several methods applied to the same rock became

a major problem. A major conceptual advance was the recognition that with internally consistent thermodynamic databases and attendant activity-composition (*a-X*) relations, *P-T* estimates could be made using all possible equilibria that could be written between minerals in a rock (e.g., Berman, 1991), rather than selective (and subjective) choice of individually calibrated equilibria, which in some cases were inconsistent with each other. Disadvantages were (1) that the more mineral end members that were considered, the greater was the scatter of results (e.g., Fig. 4), giving rise to the problem, "which of the many equilibria are the most reliable?"; and (2) that many of the individual equilibria were linearly dependent on each other, meaning they provided no more information than a much smaller subset of linearly independent equilibria. In addition, errors were strongly correlated among many of the equilibria. These problems were solved with a statistical best-fit analysis using least squares involving either the equilibria themselves (Powell and Holland, 1994), or the constituent mineral end members (Gordon, 1992) and their associated uncertainties. The result, for a given sample, was a single multi-equilibrium or multispecies *P-T* estimate with an associated uncertainty ellipse of specified confidence (e.g.,

Fig. 4), the robustness of which could be investigated using various sensitivity techniques.

In theory, geothermobarometry obviated the need to consider the rest of the phase equilibria of the rock. One of the authors of this chapter remembers an animated conversation with a prominent petrologist/geochemist in 1986 in which this individual insisted that there was no longer any need to be concerned with mineral assemblages, phase equilibria, and the like because *P* and *T* could be obtained directly by geothermobarometry. An undesirable outcome was the proliferation of papers providing elemental ratios of certain phases but otherwise incomplete documentation of mineral assemblages, textures, and full mineral compositions.

Three major considerations called into question the view of geothermobarometry as the panacea to *P-T* estimation of metamorphic rocks: (1) the context-free, "black box" aspect of geothermobarometry, with no explicit checks on the reasonableness of the result; (2) the typically large uncertainties (>±50 °C, >1 kbar) associated with the *P-T* estimates, sometimes resulting in no improvement on what could be inferred from simple phase diagram analysis; and (3) the question as to whether all relevant elements in the phases being measured equilibrated at a single *P-T* condition (usually inferred to be peak temperature conditions), and even if they did, whether they were preserved from peak conditions. The latter problem is particularly a concern for high-grade metamorphic rocks because of the likelihood of down-temperature diffusive reequilibration as the rocks cool from peak conditions, and it was termed in this context as the "granulite uncertainty principle" by Frost and Chako (1989). Despite these caveats, traditional and multi-equilibrium, multispecies geothermobarometry is sometimes the only means by which to estimate *P-T* conditions of some metamorphic rocks, especially those in which the mineral assemblage does not change very much over significant tracts of *P-T* space.

Calibration of the temperature dependence of the fractionation of stable isotopes between minerals resulted in the development of numerous isotopic geothermometers that are potentially applicable to a wide range of metamorphic rocks (see reviews in O'Neil, 1986; Valley, 1986; Chacko et al., 2001). The most common mineral thermometers involve isotopes of oxygen and carbon. As is the case with traditional multi-equilibrium geothermobarometry, black-box application of isotopic geothermometry is ill advised. Nevertheless, with judicious choice of thermometers and targeted sampling methods, good results can be obtained. These techniques have been of particular importance in temperature estimation of igneous and high-grade metamorphic rocks (e.g., Farquhar et al., 1993; Valley, 2001) and in samples for which reaction histories are well understood (Kohn and Valley, 1998).

New research activity in the field of geothermometry continues today with major emphasis on the distribution of trace elements in major and accessory phases as thermometers. Examples include the solubility of Y in garnet (Pyle and Spear, 2000; Pyle et al., 2001), the solubility of Y in monazite (e.g., Gratz and Heinrich,
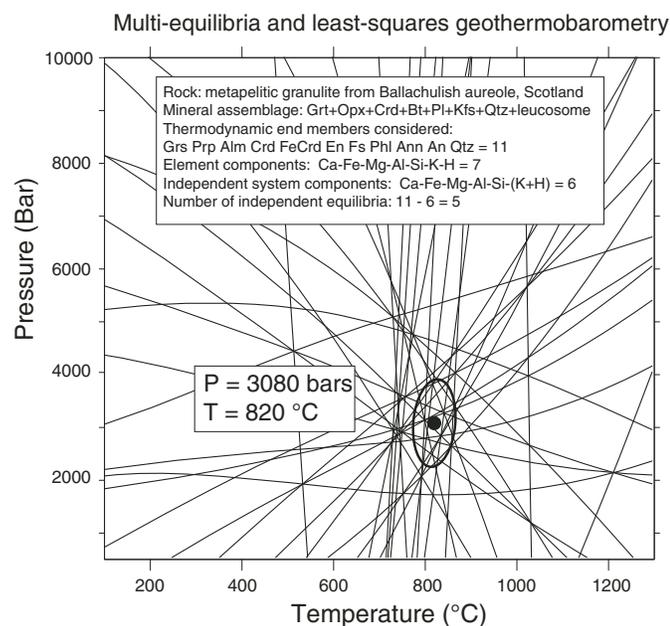

Figure 4. Comparison of pressure-temperature (*P-T*) estimates for a single rock using multi-equilibria thermobarometry (TWQ; Berman, 1991, lines) and the least-squares, individual-species approach of Gordon (1992) that incorporates uncertainties on the thermodynamic data (ellipses). The latter is similar in approach to the AvePT approach of Powell and Holland (1994, e.g., their figure 4), which involves least-squares optimization of equilibria rather than individual species. The error ellipse is the 68.3% confidence region assuming a 1 kJ estimate for the 1σ errors on the molar free energy of the individual thermodynamic end members (species). The rock is a metapelitic granulite from the Ballachulish aureole, Scotland (Pattison and Harte, 1988). The thermodynamic end members are those of the TWQ1.02 database (Berman, 1991). Abbreviations after Kretz (1983).

1997; Heinrich et al., 1997; Andrehs and Heinrich, 1998), Ti in quartz (Wark and Watson, 2006; Thomas et al., 2010), Zr in rutile (Zack, et al., 2004; Watson et al., 2006), and Ti in zircon (Watson et al., 2006). Trace-element thermometers have the advantage of chemical simplicity and, as opposed to exchange thermometers, only require the analysis of a single phase. However, the analysis of trace-element concentrations requires sophisticated analytical equipment and procedures, and it is often difficult to accurately assess the activity of the trace element in the rock during recrystallization (e.g., Ti activity in the absence of rutile). A further concern is whether these trace elements, some of which are tetrahedrally coordinated, equilibrate between modally minor minerals in natural rocks and, if they do, whether this equilibration is continuous or is restricted to discrete intervals of marked recrystallization. Nevertheless, these new thermometers have the potential to open new avenues of research.

Development of Activity Models for Metamorphic Phases

Experimentally derived thermodynamic data on end members and calibration of thermobarometers were only two parts of the necessary development for the quantitative calculation of metamorphic phase equilibria. An essential subset of this endeavor was the determination of a-X relations for minerals for which compositions in natural rocks differed from those used in experiments (for example, natural Ca-Fe^{2+}-Mg-Mn-Al-Fe^{3+} garnet vs. Fe-end-member almandine used in many experiments). Various a-X formalisms were devised to take account of the energetic effects of mixing of different components in phases showing solid solution. Although variations in assumed activity models for typical phases might only result in variations of a few kilojoules, these variations can exert as great or greater control on metamorphic phase equilibria calculations as the end-member thermodynamic data. Models for complex solid solutions (and melts) paralleled the development of thermodynamic theory and are still under development.

Determining a-X relations for a given phase is an inexact exercise (Powell and Holland, 1993). It involves first separating the energetic effects of mixing into ideal (configurational) and nonideal (excess or interaction) energy terms, which in turn represents a nonunique exercise based on inferences about crystallographically controlled element partitioning, volume behavior in solid solutions, and coupling behavior. In considering the configurational entropy contribution, it had long been recognized that the simple relationship equating activity to mole fraction (the classical "ideal solution" model) needed to be modified for ionic solutions in which the multiplicity of the crystallographic site in the mineral formula was other than one. Considerations of the entropy of mixing of ionic species led to the familiar expressions for ideal ionic solutions where the activity is proportional to the mole fraction of the ionic species raised to the power of the site multiplicity (e.g., Kerrick and Darken, 1975). It was also recognized that many ionic substitutions required more than one substituting species to maintain charge balance, as, for example, in the plagioclase feldspars. The simplest approach was to assume

absolute coupling of the two species, in which case one could be ignored. However, this model might result in violations of the Al-avoidance principle, so further refinements were in order (e.g., Kerrick and Darken, 1975). Furthermore, many phases of petrologic interest exhibited solution behavior on more than one crystallographic site, resulting in end-member phase components that were not all linearly independent. A classic example is the calcic pyroxene components enstatite-ferrosilite-diopside-hedenbergite. Because thermodynamics dictate that the choice of components is arbitrary, then accounting must be done for the inevitable fact that the end-member free energies in these types of solutions are not all coplanar. This led to the development of the reciprocal solution model as discussed by Wood and Nicholls (1978). An alternative approach to modeling multisite crystals is the so-called distribution of species approach (e.g., Engi, 1983). Although distribution of species models are de rigueur in aqueous systems, they have not been developed for many crystalline solutions. Still another approach to modeling multisite solid solutions, and particularly solutions that display intrasite ordering, was developed by Powell and Holland (1993; see also Holland and Powell, 1996a, 1996b)—the so-called symmetric formalism—in which a macroscopic regular solution model among the chemical and ordered end members is employed to accommodate the ordering and the non-coplanarity of the end members.

It was also recognized that many petrologically important phases exhibit nonideal behavior, as, for example, in the alkali feldspars or white micas. The theory of nonideal solution models for solids had been developed in the chemical literature, and the first application to systems of petrologic interest was by J.B. Thompson (1967), in which the basis for the regular solution model (the so-called Margules formulation) was laid out. Initial applications were to the alkali feldspars (Thompson and Waldbaum, 1969b; Waldbaum and Thompson, 1969), the halite-sylvite system (Thompson and Waldbaum, 1969a), and the muscovite-paragonite system (Eugster et al., 1972; Chatterjee and Froese, 1975; Chatterjee and Flux, 1986). Excess energy terms have now been estimated for nearly all common metamorphic crystalline solutions.

The final step is finding sufficiently constrained mineral compositions at known P-T conditions to allow the mixing parameters of the chosen model to be fitted. In the early days of thermodynamic databases, typically involving minerals in simpler chemical systems than at present, the key components of a-X models for important, relatively simple, phases like garnet were determined experimentally (e.g., Koziol and Newton, 1989; Koziol, 1990). However, the impossibility of investigating experimentally all possible compositional variations in phases of petrological interest, especially complex phases like amphiboles and sheet silicates, has meant that increasingly a-X relations are based on mineral compositions in natural rocks (e.g., Diener et al., 2007). The obvious danger in this approach is that assumptions need to be made concerning, first, the degree of equilibration amongst the phases in the natural rocks and, second, the reliability of the putative P-T conditions at which equilibration

occurred. These considerations extend to thermodynamic properties of mineral end members that are derived from natural minerals using assumed *a-X* relations. An important consequence is that the end-member data themselves are then tied to the *a-X* models employed in their derivation, which can lead to problems of inconsistency if other *a-X* models are employed. Yet, there seems to be no alternative if thermodynamic descriptions of phases in increasingly complex chemical systems are desired.

Metamorphism also often involves a fluid phase, and thermodynamic models and calibration of *a-X* relations for metamorphic fluids required considerable development. Tabulations of fugacities were published for pure H_2O in the 1960s (e.g., Anderson, 1967; Burnham et al., 1969), for CO_2 in 1975 (Shmulovich and Shmonov, 1975), and for H_2O-CO_2 mixtures in 1980 (Walther and Helgeson, 1980). The first successful equation of state (EOS) for the full range of common supercritical fluids was the modified Redlich-Kwong equation adapted by Holloway (1977). The *a-X* relations for mixed fluids, including common H_2O-CO_2 mixtures, were determined by Kerrick and Jacobs (1981).

Significant advances are continuing to this day in measuring the solubilities of various species in aqueous solutions at elevated temperatures and pressures (e.g., Manning, 1994; Manning and Aranovich, 2014; Newton and Manning, 2000; Schmulovich et al., 2001, 2006; Walther and Helgeson, 1977). Recent highlights include development of models for aqueous and carbonic fluids at mantle conditions (e.g., Manning et al., 2013; Manning, 2013; Sverjensky et al., 2014a) and models for CO_2 cycling between crustal and mantle reservoirs (e.g., Sverjensky et al., 2014b; Facq et al., 2014; Ague and Nicolescu, 2014; Manning, 2014). In addition, significant insights into the geochemical and physical properties of fluids in the crust are areas of ongoing research (discussed in the following).

Evolution of Internally Consistent Thermodynamic Data Sets

Concomitant with the rise in experimental studies was the analysis of the experimental results using chemical thermodynamics (see next section). The formalism of equilibrium thermodynamics allowed extrapolation of experimental results beyond the conditions under which they were conducted, especially to lower temperatures more characteristic of crustal metamorphism, where experimental run times become prohibitively long. In addition, it was quickly appreciated that, with enough experimental studies involving common minerals, augmented with calorimetric and volume determinations (e.g., Robie and Waldbaum, 1968; Robie et al., 1978), thermodynamic parameters for individual minerals rather than just reactions could be calculated (e.g., Helgeson et al., 1978). In theory, the position of reactions unexplored experimentally could then be calculated.

Some of these early data compilations resulted in incongruities in slope or position between calculated reactions that, for example, violated topological constraints such as Schreinemakers' rule. The final step in this evolution was the derivation of internally consistent databases, in which thermodynamic data were derived simultaneously from all experimental, calorimetric, volume, and other data (Powell, 1978; Berman, 1988; Holland and Powell, 1985, 1990, 1998, 2011). The development of internally consistent thermodynamic databases involving most of the significant phases and chemical components of natural metamorphic rocks represents one of the major advances in metamorphic petrology of the past 50 years.

One unintended and unfortunate result of the rise of comprehensive internally consistent databases has been the relative demise of experimental phase equilibrium studies pertaining to crustal metamorphism since about the early 1990s. Existing thermodynamic data and *a-X* relationships can in theory predict the position of most mineral assemblages and mineral reactions of interest, so that the incentive to engage in painstaking and time-consuming experimental studies has been reduced. However, it seems likely that as the limits of reprocessing the same experimental data are reached, combined with the difficult-to-quantify uncertainties associated with end members or *a-X* properties derived from natural assemblages, targeted experimental phase equilibrium studies will be needed to resolve incongruities between prediction and observation.

DEVELOPMENT OF THERMODYNAMIC THEORY AND APPLICATIONS

By the early 1960s, it had become well established that metamorphic rocks broadly adhered to the tenets of equilibrium thermodynamics. Following the pioneering work of Goldschmidt, several decades of discussion and debate eventually led to the seminal contribution of J.B. Thompson, "The thermodynamic basis for the mineral facies concept" (Thompson, 1955), which elegantly laid out the rigorous basis for evaluation of the thermodynamic relations that govern the natural occurrences of metamorphic rocks. Coupled with Thompson's equally impactful contribution on the graphical analysis of pelitic schists (Thompson, 1957), the stage was set for major steps forward in the quantitative analysis of metamorphic phase equilibria.

However, it was not entirely straightforward how to proceed. Although the theory of chemical thermodynamics as applied to complex multicomponent systems was well known, especially with respect to single-phase equilibria significant for the development of rocket propulsion systems (e.g., for a review, see van Zeggeren and Storey, 1970), how to apply these concepts to heterogeneous systems of complex silicate minerals was not immediately grasped by the petrologic community. Calculations involving individual reactions among phases of fixed composition were relatively straightforward, and Goldschmidt (1912) had laid out the fundamentals for the reaction calcite + quartz = wollastonite + CO_2 more than 60 years earlier. However, metamorphic rocks involved solid solution phases with considerable crystal chemical complexity as well as fluids (e.g., H_2O-CO_2 mixtures) at supercritical conditions. Several lines of development were required before application of chemical thermodynamics to natural systems would become fully quantitative.

Development of the Theory of Heterogeneous Equilibria

Whereas it was clear from the time of Goldschmidt's pioneering contributions how to formulate individual heterogeneous reaction among phases of fixed composition, it was uncertain how to formulate the equilibrium relations for an entire metamorphic assemblage with numerous solid solution phases. Gibbs (1928) had already formulated the completely general conditions of equilibrium for heterogeneous multicomponent systems (see following). He went on to derive the phase rule as an afterthought. However, early applications focused upon the special case, commonly taught in chemistry courses focused upon equilibrium in unary systems containing solid, liquid, and/or gas phases, and this presentation persists in several modern geochemistry and petrology texts in which the equilibrium condition:

$$\mu_i^a = \mu_i^b = \mu_i^g, \tag{1}$$

is incorrectly presented as a general result. However, it was unclear how to properly formulate these equilibrium relations when the components of different phases were not similar.

Much of the development of understanding of the proper application of the principles of Gibbs to metamorphic equilibria came from the teachings of J.B. Thompson during the 1960s and 1970s. Indeed, many preeminent petrologists can boast of having taken "JBT's course" in metamorphic phase equilibria at Harvard University. One of the fundamental tenets of this course was the conveyance of the Gibbs derivation and the understanding that for every stoichiometric equation among the components of the phases, there is an analogous equation among the chemical potentials of those components. There are a minimum number of such equations (equal to the difference between the components of the system and the components of the phases or $C_i - Cj$ in the notation of Thompson). This statement includes the special case of $\mu_i^a = \mu_i^b = \mu_i^g$ corresponding to stoichiometric equations such as $(Ab)^{plag} = (Ab)^{ksp}$. The detailed history of these developments is difficult to chronicle but was beautifully summarized in the *Reviews in Mineralogy* volume and short course "Characterization of Metamorphism through Mineral Equilibria (Ferry, 1982). In the first chapter, J.B. Thompson (1982) laid out the fundamentals of the algebraic formulation of composition space (see also, Greenwood, 1975b; Spear et al., 1982a), reiterated the distinction between components of phases and components of systems (Thompson, 1967), introduced the concepts of additive and exchange components to the petrologic community, described the matrix manipulations used to transform composition space, and emphasized the need to use independently variable phase components in the formulation of heterogeneous phase equilibria. The short course presentation by Thompson, however, contained an additional gem that was apparently developed subsequent to the manuscript version. In his lecture, Thompson described to the audience how the system of linearly independent governing equilibria could be derived from what is known as a Gauss-Jordan reduction of the system of equations that describe all of the independently variable phase components in terms of the system components—what are known as the null-space reactions. In addition, the rank of the system of equations conveniently provided the number of linearly independent system components needed to describe the variability of the phases. Prior to this, the systems of equations had been derived by inspection (e.g., Rumble, 1973, 1976; Spear et al., 1982b). Thompson provided the formal means by which to derive these expressions for any equilibrium assemblage and thus opened the door to computer applications. In hindsight, of course, this was not an entirely new development (e.g., van Zeggeren and Storey, 1970), but its introduction to the metamorphic community was new and profound.

With these tools, computer applications could be generalized and extended to all metamorphic systems. For example, Spear and Selverstone (1983) developed a method, which later became known as the Gibbs method, to back out the changes in P and T that would give rise to a measured garnet zoning profile. This initial approach applied the method of differential thermodynamics, which only required entropy, volume, and activity models for the phases of interest, because enthalpies were insufficiently well known for most metamorphic phases. As internally consistent databases became available (see discussion in previous section), these applications were extended to directly calculate the equilibrium phase assemblages at any conditions desired by the user. This same approach is widely used today in the programs THERMOCALC (Powell et al., 1998), TWEEQU (Berman and Brown, 1992), and Gibbs (Spear and Menard, 1989). The integrated methods of analytical petrology and thermodynamics were summarized by Spear in his 1993 textbook (Spear, 1993).

Phase Equilibria and the Petrogenetic Grid

Bowen's (1940) concept of the petrogenetic grid—a series of univariant reactions dividing *P-T* space into domains within which certain mineral assemblages were stable—advanced considerably in the 1970s through 1990s. Of particular note is the work of Trommsdorff and Evans (1972, 1974), which led to a petrogenetic grid for the $CaO\text{-}MgO\text{-}SiO_2\text{-}H_2O\text{-}CO_2$ system that links serpentinites and marbles (Trommsdorff and Connolly, 1990). The most important rock type for which petrogenetic grids were calculated was metapelite, because of the several readily identifiable index minerals. The most common chemical system for metapelites, accounting for 95% or more of their composition, is the KFMASH system (K-Fe-Mg-Al-Si-H, with enough O to provide electroneutrality, commonly written as $K_2O\text{-}FeO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$). Equilibria in this system have been described as the "backbone" of any metapelitic phase diagram (Thompson, 1957; Spear and Cheney, 1989; Powell and Holland, 1990). KFMASH only involves six chemical components, three of which (H-Si-K) can be assumed to be in excess in rocks with quartz (Si) and muscovite or K-feldspar (K) and that, during reaction, liberate H in the form of hydrous fluid or silicate melt. Even so, metapelites vary widely in the proportion of the remaining three components, Al, Fe, and Mg.

Spear et al.

Several grids for pelitic schists were proposed based on experimental determinations of key reactions and from observations of natural assemblages (e.g., Guidotti, 1970, 1974; Guidotti et al., 1975) and their field distributions (e.g., Albee, 1965b, 1968, 1972; Bickle and Archibald, 1984; Brown, 1975; Carmichael, 1978; Harte and Hudson, 1979; Hess, 1969; Holdaway and Lee, 1977; Kepezhinskas and Khlestov, 1977; Koons and Thompson, 1985; Labotka, 1981; Pattison and Harte, 1985; Percival et al., 1982; Spear and Franz, 1986; Thompson, 1976; Thompson and Thompson, 1976) and employing the geometric constraints of Schreinemakers (e.g., Zen, 1966). The earliest of these is the schematic grid of Albee (1965b) shown in Figure 5A. Although constraints on the grid based on experiments were few, Albee (1965b) identified some of the key petrogenetic indicator reactions such as the reactions bounding staurolite stability in the KFASH system, the stability of cordierite in the KMASH system, and the important KFMASH reactions garnet + chlorite + muscovite = staurolite + biotite + H_2O and staurolite + chlorite + muscovite = Al_2SiO_5 + biotite + H_2O. These reactions appear on all subsequent grids, as does the invariant point Al_2SiO_5 + chloritoid + staurolite + garnet (+ quartz + muscovite + H_2O). The Harte and Hudson (1979) grid (Fig. 5B) incorporated these reactions and invariant point and added additional detail to the grid based on additional experimental studies and observations from the Barrovian and Buchan terranes of Scotland. Their placement of the KFASH invariant point cited earlier at 18 kbar, 580 °C is quite respectably close to the preferred conditions of ~14 kbar, 600 °C (Fig. 5C). Although the low-pressure part of the Harte and Hudson (1979) grid has been modified based on detailed studies of the parageneses around contact aureoles (e.g., Pattison and Tracy, 1991; Pattison and Vogl, 2005), the parageneses predicted in the medium-pressure part of their grid remain largely unchanged.

Problems included the limited number of experimentally determined reactions compared to the wide range of observed mineral assemblages, and gauging the reliability and internal consistency of the experimentally determined reactions. The advent of comprehensive thermodynamic databases in the 1980s dramatically changed the situation, allowing the calculation of petrogenetic grids that were internally consistent (e.g., Spear and Cheney, 1989; Powell and Holland, 1990) and that allowed calculation of reactions relevant to rocks that had not been
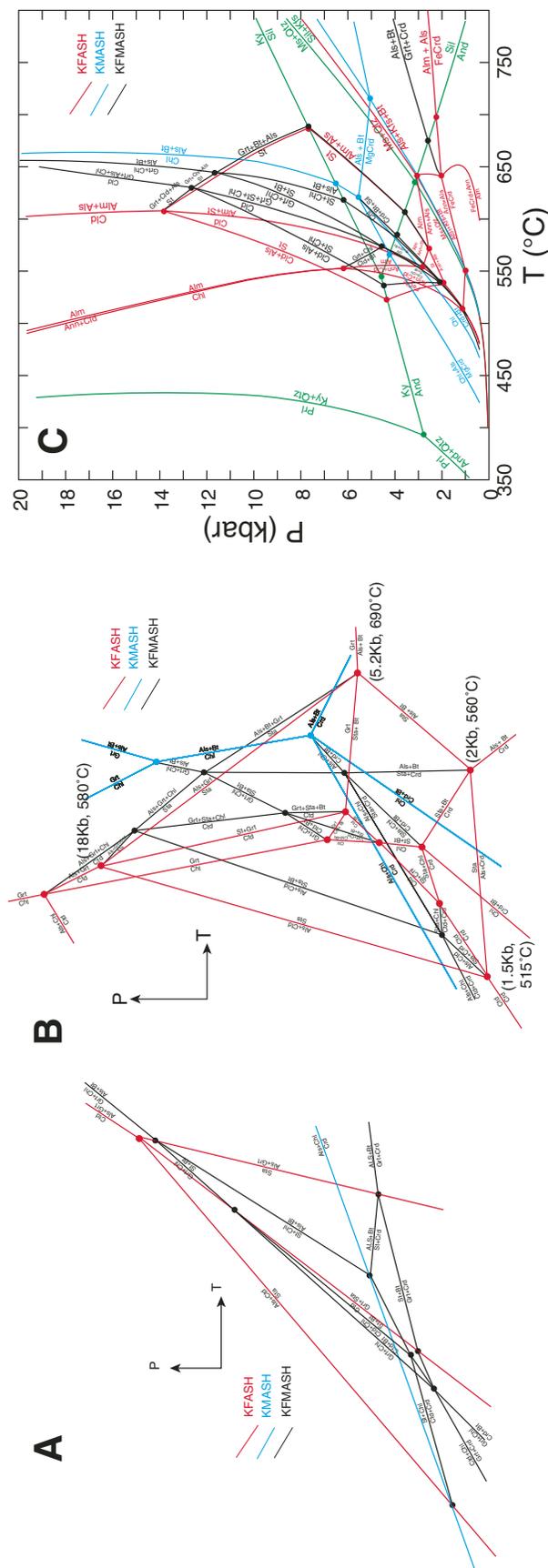

Figure 5. Development of petrogenetic grids for metapelites. (A) The first published grid for pelites (Albee, 1965b). (B) The first semiquantitative grid (Harte and Hudson, 1979). (C) Recent grid constructed from the internally consistent data set of Berman (1988) as modified by Pattison et al. (2002) and Spear and Pyle (2010). The grids of Albee (1965a) and Harte and Hudson (1979) have been redrafted and color-coded to make comparison with the modern grid simpler. Green lines—ASH reactions, red lines—KFASH reactions, blue lines—KMASH reactions, and black lines—KFMASH reactions. Abbreviations are: A = Al_2O_3, S = SiO_2, H = H_2O, K = K_2O, F = FeO, M = MgO. Mineral abbreviations after Kretz (1983).

determined experimentally. For example, the grid in Figure 5C was calculated based on the data set of Berman (1988), but a similar grid is predicted by the thermodynamic data sets of Holland and Powell (1985, 1990, 1998; Powell and Holland, 1990). Nevertheless, modifications to improve the grid, especially at low pressure, are ongoing.

Because a petrogenetic grid is a projection onto the *P-T* plane of all stable (i.e., minimum free energy) equilibria in the chemical system of interest, the resultant petrogenetic grid for KFMASH is a complex web of lines that can be difficult to interpret. Many of the univariant reactions are not "seen" (meaning, do not lie within the composition space) of a given rock, and reactions that are divariant or of higher variance (continuous reactions) that may have occurred in the rock are not directly visible on the grid. For this reason, interpretation of rocks using the petrogenetic grid commonly requires the complementary use of chemographic diagrams such as the AFM diagram (Thompson, 1957; Spear and Cheney, 1989). A second problem is that, as each additional component, such as Mn, is added to the chemical system to make it a better model of natural rock compositions, the number of reactions increases nonlinearly, such that the resultant petrogenetic grid can become quite complex. The same problem arises even in KFMASH if quartz-absent mineral assemblages as well as quartz-bearing mineral assemblages are portrayed on the same diagram.

Isochemical Phase Diagrams

The problems of extending phase diagrams to more complex and realistic chemical systems, and of providing mineral assemblage constraints to complement *P-T* estimates from geothermobarometry, led to another major advance, namely, the addition of mass balance constraints to thermodynamic constraints in the calculation of phase diagrams. The mathematical formulation of

phase equilibria involving a linearly independent set of equilibrium relations plus mass balance equations leads to a system of equations with a variance of only two—known as Duhem's theorem (e.g., Prigogine and Defay, 1954). Mass balance constraints permitted the additional calculation of mineral amounts in the assemblage (e.g., Brown and Skinner, 1974; Spear, 1988) and the calculation of modal abundance diagrams and forward modeling of metamorphic paragenesis. Early applications of these systems were limited to evaluating whether, for example, garnet might grow or be consumed along a specific *P-T* path (e.g., Spear et al., 1990).

Extension to entire *P-T* diagrams was pioneered by R. Powell and coworkers (Powell et al., 1998), although the original conception of such diagrams dates back to Hensen (1971). The result was a new type of phase diagram specific to the bulk composition of interest, or to a restricted range of bulk compositions, that portrayed only those mineral assemblages, reactions, and mineral compositions that are "seen" by that bulk composition or bulk compositions. The term introduced by Powell for these diagrams—"pseudosection"—has theoretical justification but may engender confusion in other science disciplines; here we will simply refer to them as isochemical phase diagrams. An example is shown in Figure 6. Lines represent the loci of *P-T* points where the assemblage changes either by continuous or discontinuous reaction. Rigorously, they are lines where the modal abundance of a phase goes to zero. Regions surrounded by lines are where a particular phase or assemblage of phases is stable (e.g., Fig. 6B) and can be contoured for mineral abundance (modes) and composition, as shown for garnet in Figure 6C. These diagrams show mineral assemblages as a function of controlling parameters, but the reactions responsible for changes in these assemblages are, in many cases, not obvious.

Two main approaches have been adopted to calculate phase diagrams from internally consistent thermodynamic databases.
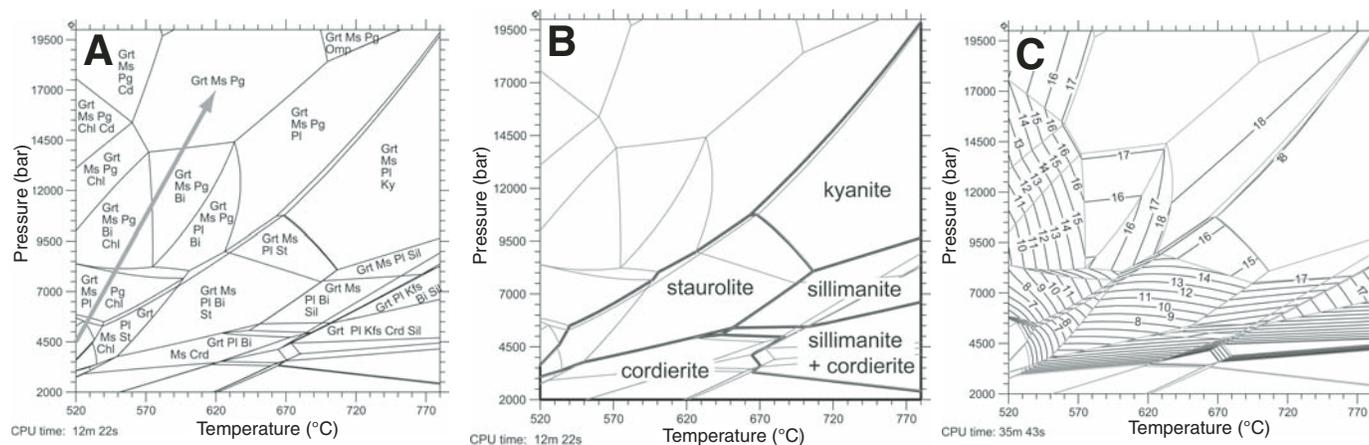

Figure 6. Examples of isochemical phase diagrams for a metapelite in the KFMASH system from de Capitani and Petrakakis (2010). (A) Pressure-temperature (*P-T*) diagram showing distribution of mineral assemblages. All assemblages contain quartz and H_2O. (B) *P-T* diagram showing stabilities of specific phases based on A. (C) *P-T* contoured for the volume % (mode) of garnet. CPU—central processing unit. Mineral abbreviations after Kretz (1983). Used with permission.

The earliest of these involves solving the system of equilibrium and mass balance equations in the assemblage of interest and building up the isochemical phase diagram using Schreinemakers' analysis (e.g., THERMOCALC—Powell et al., 1998). The second method incorporates free energy minimization to determine the most stable mineral assemblage at a specified *P* and *T* (e.g., THERIAK/DOMINO—de Capitani and Brown, 1987; de Capitani and Petrakakis, 2010; PERPLEX—Connolly and Petrini, 2002; Connolly, 2009). Phase boundaries over a range of *P-T* conditions are determined by interpolating between the stable mineral assemblages. These latter methods are generally highly automated.

Isochemical phase diagrams have revolutionized the analysis of metamorphic rocks because, in theory at least, they provide constraints on mineral assemblage stability as well as the compositions of the minerals in the rock of interest. In addition, the automated phase diagram calculators (e.g., THERIAK/ DOMINO and PERPLEX) allow almost limitless petrologic experimentation. Phase diagrams can be calculated rapidly for a given bulk composition and chemical system, and then recalculated for slightly varying compositions, in simpler or more complex chemical systems, using different *a-X* models, and so on. They also allow calculation of a wide range of physical rock parameters of interest to geophysicists such as density and bulk modulus (e.g., Connolly, 2009).

The relative ease of calculating phase diagrams introduces a nagging concern, namely, whether our ability to calculate these diagrams has outstripped our critical assessment of their predictions. A dynamic tension has emerged, that continues to the present, when incongruities between predicted phase equilibria and natural constraints present themselves: Does the problem lie with the thermodynamic data (including the *a-X* models)? Does it lie with modeling a complex natural rock with a too-simple chemical system (the implication being that the energetic effects of elements not considered in the model system in fact have a significant influence on the stability or composition of the minerals in question)? Has there been an error in the interpretation of the natural rocks, such as misidentification of minerals or mineral compositions considered to be in equilibrium? Have kinetic factors impeded the attainment of equilibrium? These questions will continue to lie at the heart of future phase equilibrium analysis of metamorphic rocks.

Interplay of Equilibrium and Kinetics

Whereas the above topics focus on phase equilibria, an area of recently increasing interest is the interplay between equilibrium and kinetics in controlling the mineral assemblages and textures of metamorphic rocks. To some degree, phase equilibrium studies of metamorphic rocks and kinetic studies of metamorphic recrystallization have evolved separately. Those concerned with *P-T* estimation based on mineral assemblages and compositions have relied on the idea that rocks evolve along *P-T* paths never far from local equilibrium, with the metamorphic facies princi-

ple being the underpinning rationale for this approach. The tremendous advances in metamorphic phase equilibrium analysis, described earlier herein, are predicated on this assumption.

In parallel, great strides were being made in understanding the rates and mechanisms of rock recrystallization and their controlling kinetic factors: nucleation, dissolution, growth, intracrystalline diffusion, intergranular transport, metasomatism, and fluid presence or absence (e.g., Brady, 1975, 1977; Frantz and Mao, 1979; Lasaga, 1979, 1981, 1983, 1986; Lasaga and Kirkpatrick, 1981; Lasaga et al., 1977; Walther and Wood, 1984; Ridley and Thompson, 1986; Rubie and Thompson, 1985; Chakraborty and Ganguly, 1992; Rubie, 1998; Carlson, 1989). Dugald Carmichael published a remarkably insightful paper in 1969, based entirely on petrographic analysis, showing how metasomatic cation-exchange reactions proceeding in different microscopic domains of a single thin section added up to give the overall balanced chemical reaction implied by the mineral assemblage (Carmichael, 1969). This insight changed the way metamorphic reaction progress was conceived, and it led to impressive developments in quantifying texture development in metamorphic rocks undergoing nucleation, growth, and consumption of porphyroblasts (e.g., Yardley, 1977b; Foster, 1999). A noteworthy Mineralogical Society meeting in 1985 on kinetics and metamorphic processes led to the publication of an influential volume of *Mineralogical Magazine* (1986; volume 50; e.g., Lasaga, 1986)) that triggered much subsequent research in this field.

To many petrologists working under the assumption that rocks are never far from local equilibrium, these kinetic studies, although of fundamental interest in understanding metamorphic rock evolution, did not significantly affect their goals of using mineral assemblages and mineral compositions to understand the *P-T* or pressure-temperature-time (*P-T-t*) evolution of metamorphic rocks. This view has recently been changing. A dramatic petrological example of the need to consider kinetic controls on metamorphic mineral assemblage development was published by Austrheim (1987), in which large tracts of granulite on the island of Holsnoy, Norway, were demonstrated to be metastable with respect to eclogite, with the latter developing at the expense of the granulite only where fluid influx catalyzed the otherwise kinetically impeded transformation reaction. For the granulites on Holsnoy, the metamorphic facies principle failed in that the stable mineral assemblage was not developed in the rocks. Whereas kinetic impediments to reaction are widely acknowledged in retrograde metamorphism, there is increasing evidence that they need to be considered in prograde metamorphism as well. Any reaction needs to be overstepped to some degree to build up sufficient energy (reaction affinity) to overcome the kinetic impediments to reaction, and the rate at which this energy builds up varies widely from reaction to reaction (Pattison et al., 2011), something that is not apparent on an equilibrium phase diagram. Waters and Lovegrove (2002) provided the first convincing petrological demonstration of the importance of this phenomenon in prograde metamorphism in their study of the Bushveld aureole, in which they inferred that stable, low-entropy,

chloritoid-consuming reactions were overstepped by 80–90 °C before being overtaken, in terms of reaction affinity and reaction progress, by high-entropy, metastable chlorite-consuming reactions. Other examples, over a range of scales, have demonstrated that ignoring kinetic factors in rock recrystallization may lead to petrologically significant misinterpretation (Carlson et al., 2015, and references therein).

In parallel, increasingly sophisticated studies focusing on the size and distribution of porphyroblasts, accompanied by numerical models that simulate these textures, have produced quantitative estimates of the departure from equilibrium required to account for these textures (e.g., Cashman and Ferry, 1988; Carlson, 1989; Kelly et al., 2013). Predictions from these models are of a magnitude (up to several tens of degrees) that petrologists can no longer ignore. Thus, we foresee a period of dynamic research in the next decade concerned with the interplay between equilibrium and kinetics in metamorphism. Of the latter, the contribution and importance of rock deformation must be added, such as suggested by Bell and Hayward (1991).

FROM ELECTRON GUNS TO LASERS— THE IMPACT OF ANALYTICAL CAPABILITIES ON METAMORPHIC PETROLOGY

Electron Microprobe

Traditional methods of chemical analysis involved first separating mineral phases by disaggregation, magnetics, heavy liquids, and handpicking. This was a tedious process and virtually impossible to get perfect: There were almost always bits of other materials in the mineral separate. In addition, it was clear even in the 1960s that many metamorphic minerals were compositionally zoned. While presenting an analytical challenge, chemical zoning in metamorphic minerals is a key to unlocking the history of the crust. What was needed was an instrument for chemical analysis of small volumes of minerals.

Raymond Castaing is credited with building the first modern electron microprobe (1948–1951), which consisted of an electron beam focused on a small region of a sample to produce X-rays, a crystal spectrometer (originally a quartz crystal) to discriminate X-rays by wavelength through Bragg diffraction, and an X-ray counter. The first commercial microprobe was produced by Cameca in 1958, and numerous varieties were produced by other manufacturers in ensuing years, although only two companies produce microprobes today (Cameca and JEOL).

Electron probe microanalysis was applied to metamorphic petrology in the 1960s and is still the mainstay of chemical microanalysis. The early microprobes were finicky, and an operator had to be on good terms with the probe gremlins to have any hope of getting good analyses. The instruments were unstable, and the beam current would drift notoriously. Early instruments had only 1–3 spectrometers, so a 10 element analysis would take numerous days to collect the required suite of data. The optics were poor, and finding one's way around a sample was a significant challenge. Online data reduction was far in the future, and counts on standards and unknowns had to be processed by hand with the assistance of large mainframe computers (and punch cards) to perform the data corrections for fluorescence and adsorption. We harbor many fond (and not so fond) memories of all-night sessions on the electron microprobe to collect precious data in support of a thesis project. At the electron microprobe laboratory at the University of California–Los Angeles (UCLA), where the first author was a graduate student in the early 1970s, the standard operating protocol was to collect data on a typewriter: standard-unknown-standard for three elements at a pass (which was a large step forward from writing down counts from the nixie tubes). After three such sessions to collect data for nine elements (Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe), the values for standards and unknowns were averaged, and $I_{unknown}/I_{standard}$ intensity ratios were computed. These were then typed onto punch cards, and the pile was assembled with the Bence-Albee data reduction program and carried to the UCLA mainframe (with a then state-of-the-art 360 kilobytes of memory), where the cards were handed to an operator and, with luck, the results might be available the next day. More commonly, one had made a mistake, requiring the offending card to be fixed and resubmitted. It is small wonder that relatively few chemical analyses of minerals were published during this early era, and it provides an added perspective of appreciation to pioneering works of Hollister (1966) and Atherton and Edmunds (1966), which reported the first electron probe study of garnet zoning.

It is interesting to note that the chemical data on garnet, chloritoid, chlorite, biotite, and muscovite for the very first published AFM diagram (Albee, 1965a) were obtained on mineral separates using X-ray fluorescence, not an electron microprobe. It is small wonder that Albee at Caltech was instrumental in developing the most sophisticated electron probe laboratory in the country and, along with A.E. Bence, developing the data reduction scheme used for oxides for the next 20 years (Bence and Albee, 1968).

The microprobe quickly replaced other methods for determination of mineral chemistry and became a mainstay of field-based, observation-rooted, and mineralogically focused petrologic studies (Evans and Guidotti, 1966; Guidotti, 1970, 1974; Cheney and Guidotti, 1979; Thompson et al., 1977a, 1977b).

Modern electron microprobes operate with the same principles as the early instruments, but they are far more stable, due to better electronics, and computer automation permits unattended data collection and real-time data reduction. Analyses can be examined for quality as soon as the analysis is completed, and research directions can be adjusted continuously as results are obtained.

One of the major developments in the use of the electron microprobe that has greatly enhanced the field is the ability to collect composition maps of metamorphic mineral assemblages. X-ray maps had been possible by beam scanning since the early days, but limitations to the Bragg focusing geometry of the crystal spectrometers limited their usefulness. It was the development of the high-precision, computer-controlled *x-y-z* stage that
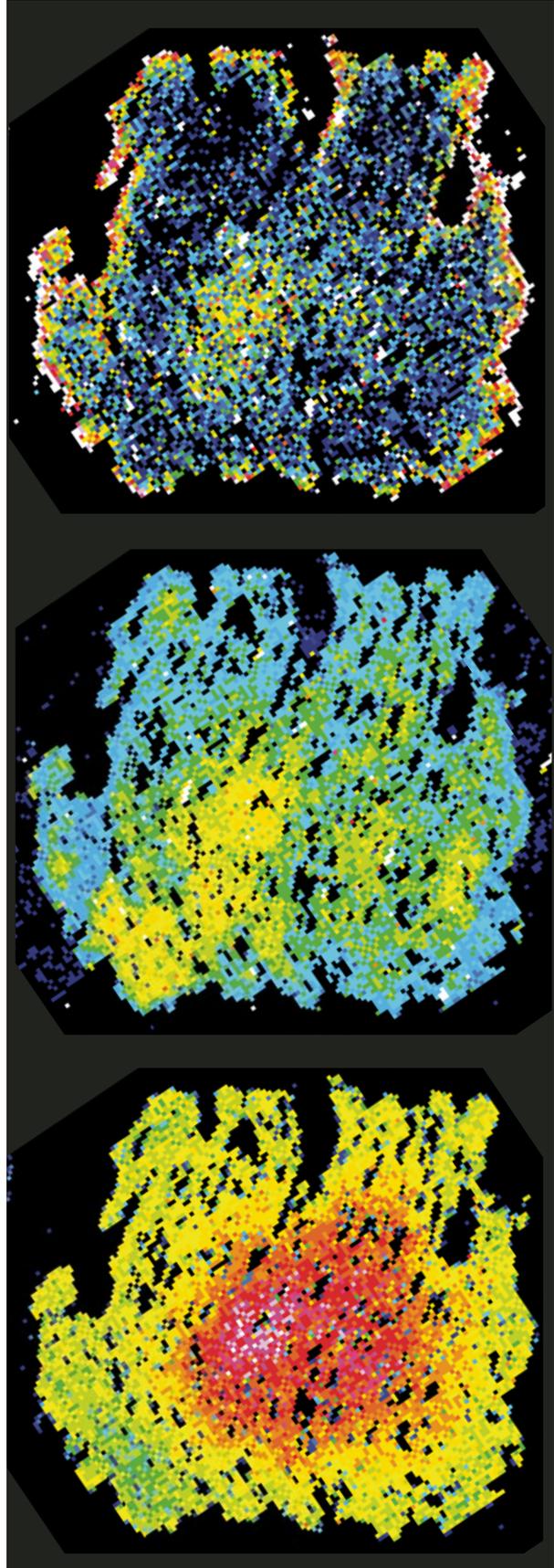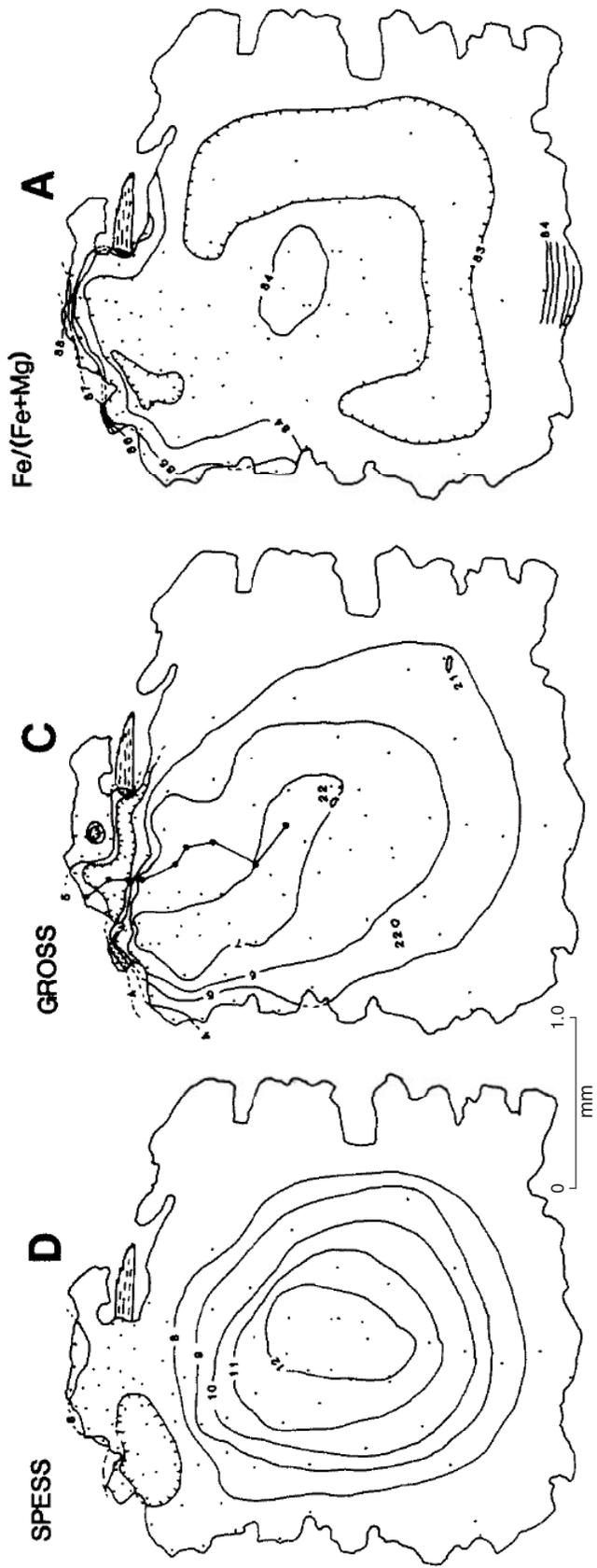
Figure 7. Top row: Sketch of a garnet crystal from a pelitic schist contoured for composition using spot analyses, from Spear and Rumble (1986). Bottom row: X-ray maps of the same garnet.

The metamorphosis of metamorphic petrology

permitted large-area composition maps to become routine. Early microprobe automation systems (e.g., Tracor Northern ca. 1985) provided software to generate X-ray maps using their energy dispersive spectroscopy (EDS) detector, and one of the authors (Spear) wrote a program using Tracor Northern's language "Flextran" to collect wavelength dispersive spectroscopy (WDS) X-ray maps using the JEOL 733 at Rensselaer. The program performed well but slowly, although maps could be collected unattended and thus run overnight (this may seem like a quaint development from today's perspective).

The first X-ray maps published by the authors were, of course, of garnet (Fig. 7). To put into perspective the improvement in characterization of the chemical zoning of garnet that X-ray mapping provided, compare the images in Figure 7. Figure 7A (reproduced from Spear and Rumble, 1986) was created by contouring ~100 spot analyses on a photomosaic of a garnet from a staurolite-kyanite schist from Vermont. In contrast, Figure 7B is an X-ray map of the same garnet collected with a pixel size of around 20 μm/pixel and a total of ~10,000 pixels to describe the garnet zoning. The hand-contoured diagram took days to complete, whereas the X-ray maps were collected in a few hours with little user effort, and they show subtle, fine-scale variations in zoning that are invisible on the hand-contoured maps.

Images that depict the compositional variation in phases such as garnet are aesthetically pleasing, but far more importantly, they are critical to the interpretation of chemical zoning. Hollister (1966) made the insightful interpretation of the "bell-shaped" Mn zoning in garnet from the Kwoiek, British Columbia, Canada, region as arising from Rayleigh fractionation during garnet growth (Fig. 8). Hollister's original contribution can be credited with introducing to the metamorphic community the notion that part of a rock's history could be gleaned from examination of the chemical zoning in garnet, and by extension, other minerals. Tracy et al. (1976) extended the interpretation of garnet zoning to a sequence of rocks from central Massachusetts. Samples from the staurolite-kyanite zone (Fig. 9A) displayed concentric zoning with Mn depletions similar to that reported by Hollister (1966) and were interpreted as representative of growth zoning. Samples from higher-grade rocks displayed two types of zoning. Concentric zoning of resorbed garnet with Mn increasing toward the rim (Fig. 9B) was interpreted as resulting from diffusion driven by retrograde net transfer reactions (ReNTR in the terminology of Kohn and Spear, 2000). Zoning of only Fe and Mg adjacent to biotite (Fig. 9C) was interpreted as resulting from diffusion in response to Fe-Mg retrograde exchange (ReER in the terminology of Kohn and Spear, 2000; see also Yardley, 1977a). These pioneering studies used spot analyses to characterize garnet zoning. In Hollister's study, ~50 analyses were collected along a line traverse, and in Tracy et al.'s study, on the order of 100 spot analyses were made to generate hand-drawn contour maps. Clearly, X-ray mapping provides a faster, cheaper, and easier method for characterizing chemical zoning in phases, which is critical to petrologic interpretations.

An example from high-grade rocks from the Valhalla Complex, British Columbia, Canada (Fig. 10), displays garnet zoning very similar to that described by Tracy et al. as resulting from diffusion driven by back reaction and resorption of garnet with a crystallizing melt (Spear and Parrish, 1996). The X-ray map also reveals a wide variation in the Fe/Mg of biotite. It had often been assumed that one obtains an accurate estimate of the peak temperature in high-grade rocks, i.e., those in which prograde garnet growth zoning has been homogenized due to internal diffusion, by coupling the composition of the garnet core (which was assumed not to have been affected by retrograde diffusion) with the composition of the matrix biotite. However, retrograde net transfer reactions significantly modified the composition of the matrix biotite to the extent that this approach yielded unreasonable temperatures over 1000 °C (Spear and Parrish, 1996). An accurate assessment of the peak temperature (~820 °C) using garnet-biotite thermometry could only be made by finding either a sample that did not undergo retrograde reaction, or by seeking a biotite composition that was isolated from this reaction (e.g., encased in plagioclase or quartz). Without the compositional distributions observed in the X-ray maps, these types of interpretations would be extremely difficult to make.

Other developments in computer automation, imaging capabilities, and spectrometer design have steadily improved electron microprobes. Imaging using backscattered electrons, which produce an image based on the average atomic number of a material,
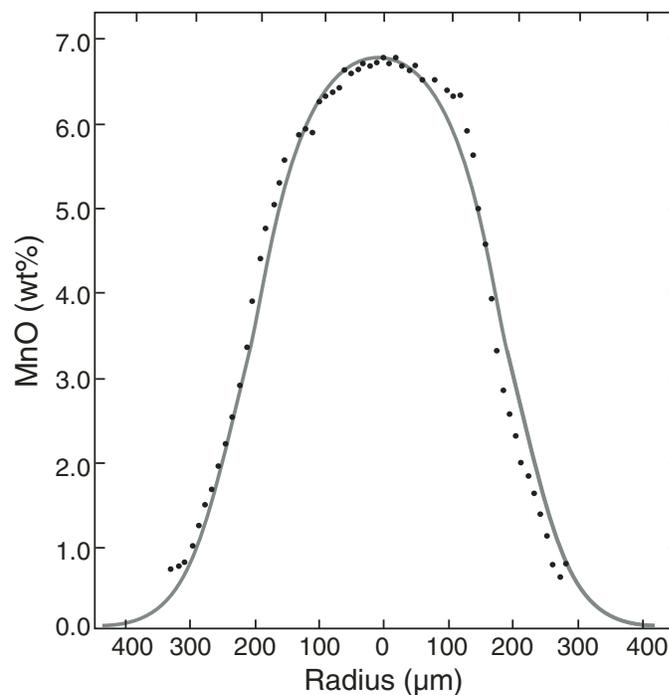

Figure 8. Plot of weight percent MnO vs. radius for a garnet from the Kwoiek area, British Columbia. Dots show measured MnO values, and curve shows the calculated profile assuming the simple Rayleigh fractionation model. Modified after Hollister (1966).

Xalm x 100   Xprp x 100

A

80
82
84 86

11

11

7
8
9 10
10

0 mm 1

4
3 2
1

8
6
4
2

Xgrs x 100   Xsps x 100

Xalmandine x 100   Xpyrope x 100   Xspessartine x 100

B

73

73
74 73
77 76 75

18
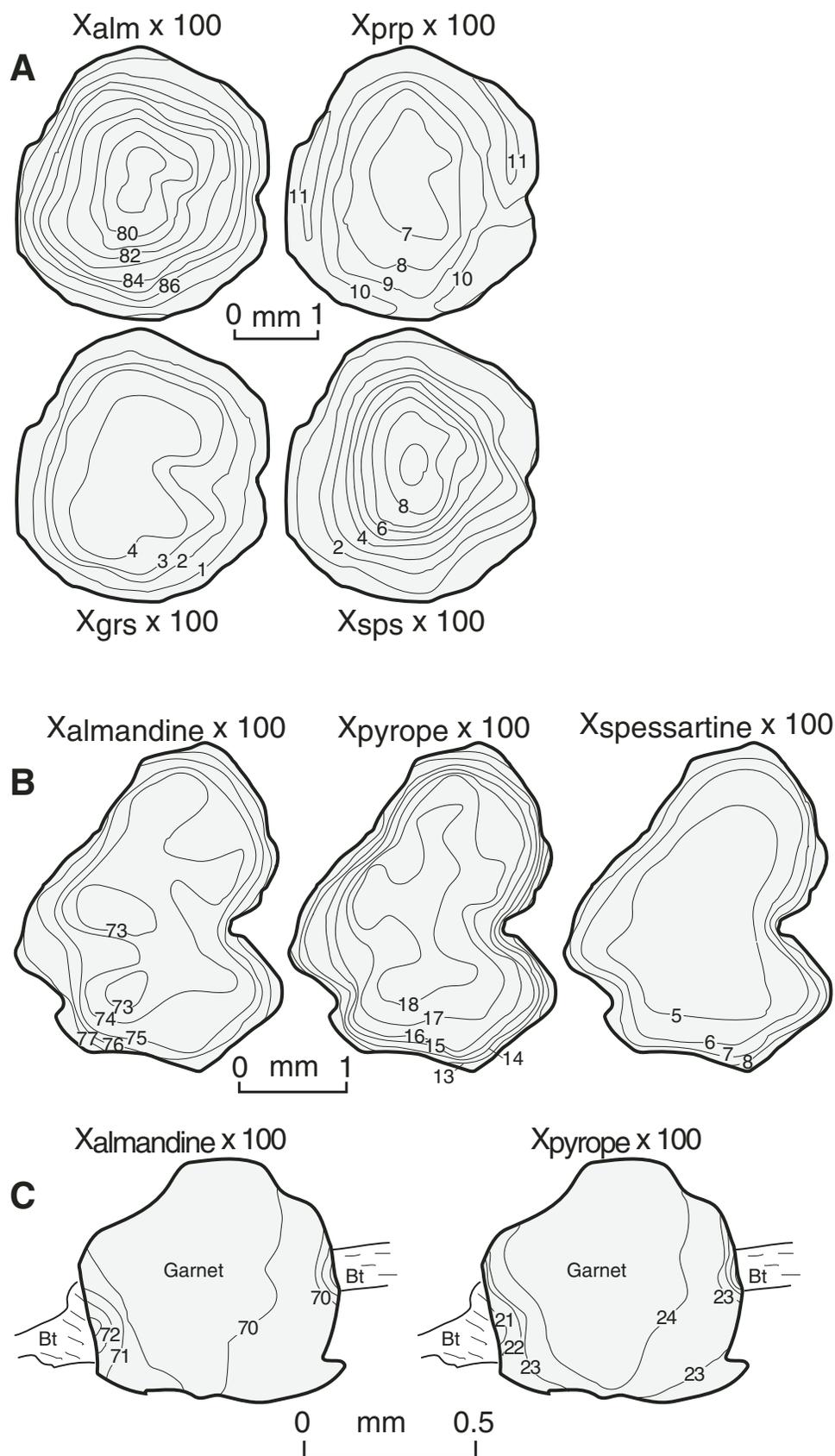17
16 15
13 14

5

6
7 8

0 mm 1

Figure 9. (A) Contours of chemical zoning in a garnet from the staurolite-kyanite zone of central Massachusetts, United States (sample 908 from Tracy et al., 1976). This type of zoning is interpreted as growth zoning. (B) Contours of chemical zoning in garnet from the sillimanite + muscovite + K-feldspar zone in central Massachusetts, United States (sample 933B from Tracy et al., 1976). This type of zoning is interpreted as diffusion zoning in response to net transfer and exchange reactions. (C) Contours showing chemical zoning in a garnet from the garnet + cordierite zone in central Massachusetts, United States (sample FW 407 from Tracy et al., 1976). This is interpreted as diffusion zoning in response to only Fe-Mg exchange reaction between garnet and biotite (Bt).

Xalmandine x 100   Xpyrope x 100

C

Garnet Bt

70

Bt 72
71

70

Garnet Bt

21
22
23

24

23

23 23

0 mm 0.5
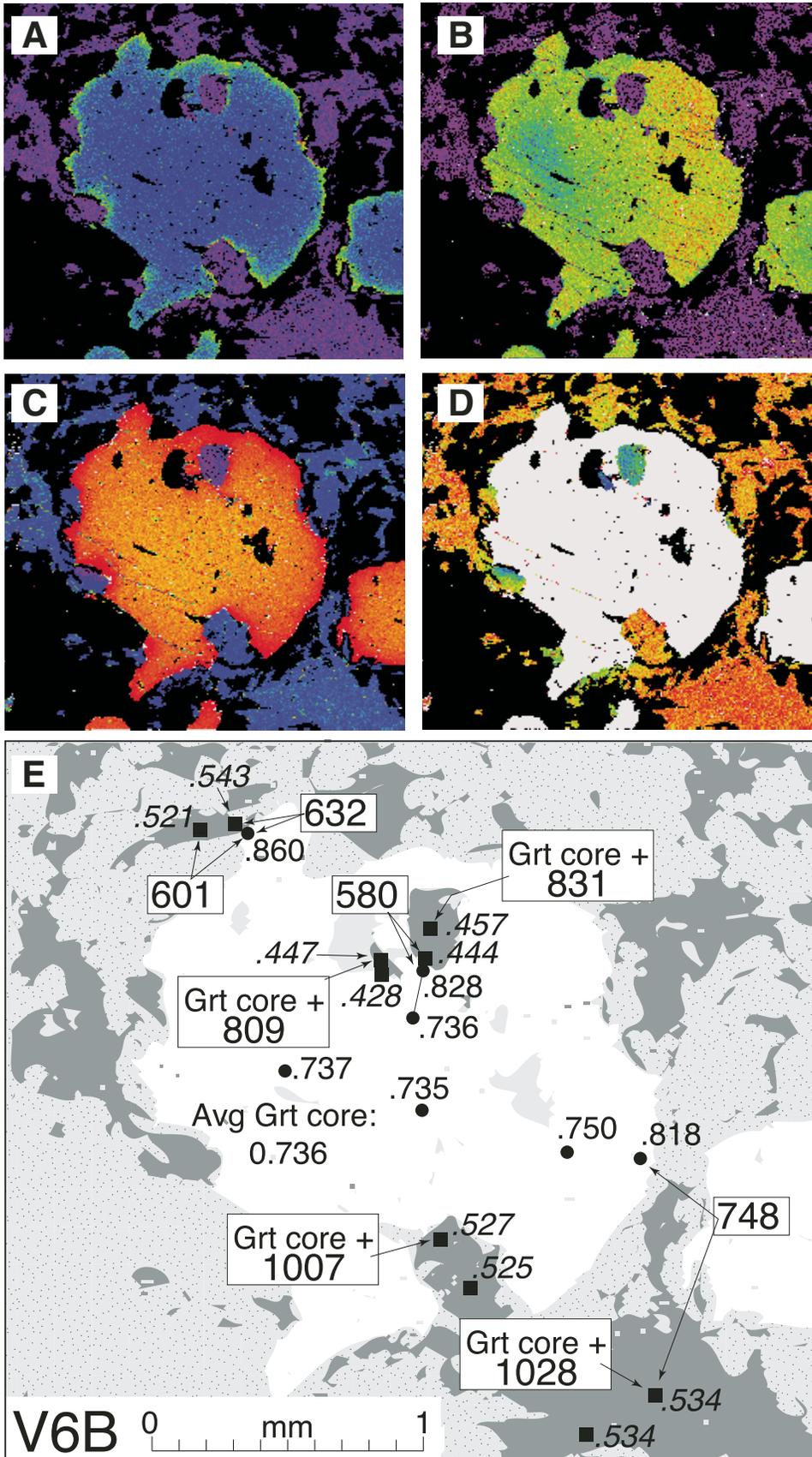
The metamorphosis of metamorphic petrology

Figure 10. X-ray maps of (A) Mn; (B) Ca; (C) Fe/(Fe + Mg) enhanced to show garnet (Grt) zoning; (D) Fe/(Fe + Mg) enhanced to show biotite compositional variation. (E) Sketch of garnet showing Fe/(Fe + Mg) of biotite (black squares) and temperatures obtained from garnet-biotite thermometry using various combinations of biotite and garnet compositions. Sample V6B is from the Valhalla complex, British Columbia (after Spear and Parrish, 1996; Spear, 2004).

are routine, sometimes to the elimination of an optical microscope except for the purpose of focusing. Cathodoluminescence imaging provides formerly invisible maps of trace-element distributions in zircon, feldspar, and quartz. New electron source filaments such as the LaB_6 gun provide a much brighter electron source with a smaller spot size, especially at high currents, providing a greater signal for analysis of minor and trace elements. New spectrometers with either extra large crystals (e.g., the Cameca Ultrachron) or modified Rowland circle geometries (e.g., the JEOL h-spectrometer) have improved detectability limits to under 10 ppm for some trace elements. New algorithms for fitting backgrounds have improved analysis of complex rare earth element (REE) phosphates such as monazite (e.g., Williams et al., 1999, 2006) and furthered development of chemical dating of monazite (e.g., Montel et al., 1996; Suzuki and Adachi, 1991; Williams et al., 1999). The incorporation of a field emission gun (FEG) as an electron source holds the promise of even finer spatial resolution, thus permitting the analysis of smaller phases and thin films.

It is difficult to predict future developments in electron microprobe analysis. The technique is quite mature. Many recent improvements have been made because of improvements in computer automation, and these have also reached a level of maturity. Most future developments in this method are anticipated to be incremental rather than revolutionary, but the impact of the electron microprobe on the field of metamorphic petrology has been nothing less than profound.

Other Analytical Advances

As noted already, chemical analyses of metamorphic minerals to be used in thermodynamic analysis are of limited value unless they come from parts of the mineral in which the texture and compositional zoning are known. The secondary ion mass spectrometer (SIMS) and laser-ablation–inductively coupled plasma–mass spectrometer (LA-ICP-MS) both fit this requirement and are additionally well suited for both trace-element and isotopic studies and are having major impacts in the realm of petrochronology (see following section).

Several other novel analytical techniques have advanced the understanding of metamorphic recrystallization. The development of high-resolution computed X-ray tomography, the same technology used in brain scanners, has revolutionized our ability to make three-dimensional, nondestructive images of the size and distribution of porphyroblasts and other heterogeneities in rocks, and to analyze them quantitatively (Carlson and Denison, 1992). Electron backscatter diffraction has permitted examination of differences in crystallographic orientation of minerals, with implications for growth and deformation mechanisms (e.g., Prior et al., 1999). This technique extends to different zones of individual crystals such as garnet, allowing inferences to be made concerning their nucleation and growth history and, in some cases, the interaction of mineral growth with deformation (e.g., Robyr et al., 2009). Raman spectroscopy, another rela-

tively new technique, has been applied to metamorphic rocks in an increasing number of ways: to measure valence differences in polyvalent elements like iron; to examine the sites in minerals at which individual ions reside; and to identify microscopic inclusions in garnet, zircon, and other phases. One especially noteworthy application of Raman spectroscopy has been the development of the graphite thermometer (Beyssac et al., 2002), based on changes in the degree of crystallinity of graphitic carbon as temperature increases, a technique that is of particular use for estimating temperature in low-grade rocks and those containing no distinctive mineral assemblages. Raman spectroscopy is also being used to determine the conditions of entrapment of an inclusion mineral in a host phase (e.g., quartz inclusions in garnet), a method that should enjoy considerable application in thermobarometry (e.g., Kohn, 2014).

FLUIDS IN THE CRUST

It was well understood that metamorphism involved the devolatilization of the crust as evidenced by water-rich muds being transformed into relatively dry schists and gneisses. However, the details of the ways in which fluids and rocks interacted in the crust were, and still are, very much in debate. J.B. Thompson Jr., in his landmark 1957 paper on the graphical analysis of pelitic schists, pointed out that the phase relations of many (most?) pelitic schists could be represented graphically by a projection through the component H_2O. The implication of this observation was that the chemical potential of H_2O (or "relative humidity" as Thompson referred to it) was constant among assemblages over a restricted outcrop area. The constancy of μ_{H_2O} led many petrologists to assume that its value must be externally controlled by some unseen, but omnipresent reservoir, although Thompson never implied this in his paper. Views about the external control of μ_{H_2O} were reinforced by another major contribution by D.S. Korzhinskii (1959) in which he described the efficacy of "perfectly mobile components" in determining what mineral assemblages would be stable. These views, prevalent during the 1960s, spawned considerable research into the mobility of elements, especially volatile ones, in the crust, and the reader is referred to Thompson (1970) and Rumble (1982) for reviews of the debate at that time. A.B. Thompson (1983) challenged the view of ubiquity of free fluid in metamorphosing rocks by suggesting that a free fluid phase may only have saturated grain boundaries during periods of significant dehydration reaction, punctuating much longer periods of absence of a free fluid.

Investigations of the behavior of fluids in the crust focused on a number of major approaches. The first of these approaches was to evaluate the consistency of the hypothesis of externally controlled μ_{H_2O} through graphical and analytical analysis of the phase equilibria of natural assemblages. Albee (1965a) published the first AFM diagram using natural assemblages from Lincoln Mountain, Vermont (Fig. 11A). The regular array of mineral assemblages on the AFM diagram was interpreted as being consistent with equilibrium among phases in each

assemblage and with external control of μ_{H_2O}. Rumble (1974), in a theoretical tour de force, developed an algebraic method (which later came to be known as the Gibbs method) in which differences in the chemical potential of volatile components could be quantified based on variations in mineral chemistry. His landmark study of quartzites from Black Mountain, New Hampshire (Rumble, 1978; Fig. 11B) documented gradients in the chemical potentials of H_2O and O_2 among different silicate-oxide assemblages and verified that, rather than external control of these components, their values were most likely buffered by the solid mineral assemblages.

The concept of buffering was certainly not new in physical chemistry, although in application to geologic systems, the term "buffering" was typically used to describe "fixing" a chemical potential. Buffering in the acid-base sense is more of a retardation of the effects of adding an external agent. A similar conceptual framework emerged from these studies of fluid-rock interactions. An early application of the concept by Guidotti (1974) explained the occurrence of an ostensibly univariant assemblage across a mappable zone in the Rangeley Lakes area of NW Maine. A fluid might infiltrate a rock, and, if that fluid is out of equilibrium with the rock, reactions will proceed. The extent to which the rock is altered by this infiltration depends on the amount of material infiltrated and the buffer capacity of the rock. The theoretical basis for application of this concept to metamorphic mineral assemblages was eloquently formalized by H.J. Greenwood (1975a), in which he presented arguments that mineral assemblages are

more likely to buffer pore-fluid composition than the converse, and he presented equations to quantify the buffer capacity of a specific assemblage. J.M. Ferry, in a series of landmark papers (Ferry, 1980, 1983, 1986, 1987, 1988, 1991; Baumgartner and Ferry, 1991), developed this methodology and pioneered its application to natural assemblages. Based on observed modal variations in typical calc-pelites, Ferry was able to calculate the amount of fluid, and hence the fluid flux, required to drive mixed-volatile reactions. Calculated fluid fluxes were locally unexpectedly large, with some estimates in the range of 10^3 mol fluid cm^{-2}. Assuming around 20 cm^3/mole for H_2O, this figure equates to 5×10^4 cm^3 of fluid having passed through every square centimeter of rock in order to drive the reactions as observed. This appears to be a very large quantity and clearly carries major implications for fluid transport in the crust, perhaps especially the degree to which fluid may be channeled (Walther and Orville, 1982; Walther 1990; Yardley and Valley, 1997; Manning, 2004; Yardley, 2009; Yardley and Bodnar, 2014).

The physics of fluid flow through metamorphic rocks has also been a subject of considerable research over the past several decades. The fact that sediments lost volatiles during metamorphism was unequivocal. However, the mechanism(s) by which this happened was (were) not known. Studies by Etheridge and coworkers (e.g., Etheridge et al., 1983, 1984) set out to document high fluid pressures during "typical" metamorphic devolatilization, with implications for significant fluid transport by advection. During the same period, studies of contrasting wetting
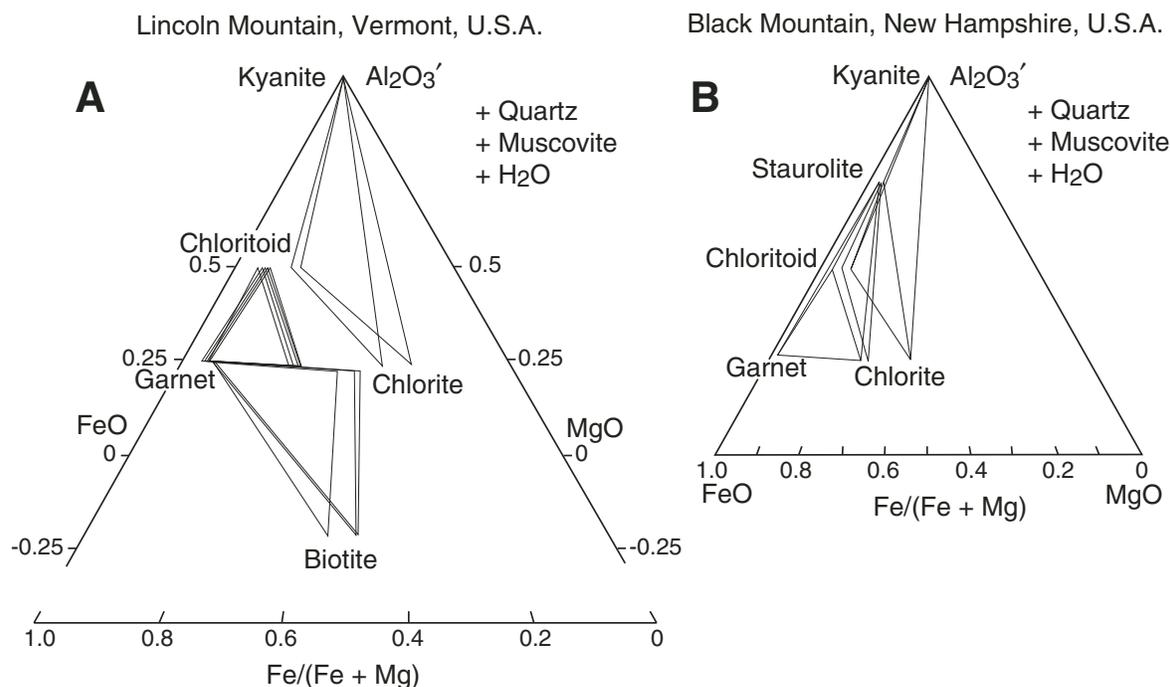

Figure 11. (A) AFM diagram (Thompson projection) of pelitic assemblages from Lincoln Mountain, Vermont, consistent with external control of μ_{H_2O}, after Albee (1965a). (B) AFM diagram of pelitic assemblages from Black Mountain, New Hampshire, consistent with internal buffering of μ_{H_2O}, after Rumble (1978).

characteristics of H_2O and CO_2 fluids (e.g., Watson and Brenan, 1987; Holness and Graham, 1991) provided experimental constraints on the types of permeability to be expected in the crust and helped pave the way for sophisticated transport modeling of fluid-rock interactions (e.g., Baumgartner and Ferry, 1991; Balashov and Yardley, 1998).

Another approach involved application of stable isotope analyses (primarily oxygen and carbon) to determine the degree to which stable isotope compositions varied across an outcrop. Again, Rumble (1978) pioneered this work in application to "typical" metamorphic rocks by demonstrating that quartz from different beds on Black Mountain differed in $\delta^{18}O$ by as much as 2.5‰, consistent with the absence of a pervasive, externally derived fluid that flowed across layers and homogenized isotopic compositions. These types of isotopic studies do not, however, preclude extensive channeled or layer-parallel fluid flow (e.g., Kohn and Valley, 1998). Since then, the application of stable isotopes has mushroomed and revolutionized our understanding of fluid-rock interaction and fluid flow in metamorphic terrains (see review volumes of Valley et al., 1986; Valley and Cole, 2001; Valley, 2003).

Studies of fluid inclusions provided direct observation and measurement of fluid composition and density, which provided new insights into the relationships between metamorphism and fluid evolution. For example, J. Touret (1971) was the first to recognize a transition from dominantly H_2O-rich fluid inclusions to dominantly CO_2-rich fluid inclusions across the amphibolite-to-granulite facies transition, thus fueling the debate as to the causes of granulite-facies and ultrahigh-temperature metamorphism (see following). L.S. Hollister and coworkers demonstrated numerous applications of fluid inclusion research to the metamorphic community (e.g., Hollister, 1981; Hollister and Crawford, 1981; Hollister and Burruss, 1976). Research on fluid inclusions is still very much going on today, with applications as diverse as hydrothermal ore deposition and paleoclimate studies.

METAMORPHISM AND CRUSTAL EVOLUTION

As discussed in the introduction, the study of metamorphic rocks is the study of the evolution of the crystalline crust on which humans live. The past 50 years have resulted in tremendous progress in our understanding of the evolution of this crust, in large part thanks to the many local and regional studies of metamorphic rocks and the processes responsible for their formation. Along with the insights into the petrogenesis of specific terranes, some broad areas of new understanding have emerged. This section will attempt to summarize some of these new insights.

Contact Metamorphism

Contact aureoles around igneous intrusions, although spatially limited and reflective of local rather than regional processes, have nevertheless been of great importance to the development of concepts and techniques of metamorphic petrology

both before and since 1960. Aureoles represent relatively simple metamorphic settings in which the direction of increasing grade is clear and the metamorphic cycle of heating and cooling takes place more rapidly than in regional terrains, leading to sensibly isobaric metamorphic field gradients. In some aureoles, decussate textures imply recrystallization in the absence of significant deviatoric stress. These have made contact aureoles ideal natural laboratories in which to investigate a range of petrologic questions, occupying an intermediate position between laboratory experiments and more complicated regional metamorphic terrains. An indication of the range of investigations that have exploited these attributes is the *Contact Metamorphism* volume edited by D.M. Kerrick (Kerrick, 1991).

Variations in the prograde sequence of mineral assemblages in aureoles as a function of pressure were used to systematize low-pressure metapelitic (Pattison and Tracy, 1991) and serpentinite (Trommsdorff and Evans, 1972) phase equilibria for which there were few or contradictory constraints. They were used to demonstrate internal versus external fluid buffering in metacarbonates, with broader implications for crustal fluid flow (Rice, 1977a, 1977b; Ferry, 1991); to demonstrate differences between water-consuming melting versus dehydration melting (Pattison and Harte, 1988); to better understand the petrogenesis of accessory minerals used for geochronology (Ferry, 1996, 2000); to constrain homogeneous and heterogeneous reaction kinetics (Joesten, 1991; Kerrick et al., 1991; Waters and Lovegrove, 2002); and many other applications. Beyond these petrologic applications, aureoles around intrusions have been of regional tectonic importance because their mineral assemblages allow relatively precise estimates of the depth of emplacement. When this information is combined with the age of the intrusion, they have provided depth-time "pins" for the evolution of the crust during orogenesis (e.g., Archibald et al., 1983).

Interplay between Recrystallization and Deformation

It was long recognized that metamorphic recrystallization and rock deformation occurred in intimate association in regionally metamorphosed belts, as revealed by porphyroblastic schists and gneisses in which porphyroblasts sometimes overprinted (postdated) the dominant foliation in the rock, and in other cases were wrapped by the external fabric (implying that the porphyroblasts had developed prior to matrix flattening). In the 1970s and 1980s especially, there was a flourishing of increasingly sophisticated analysis of microstructures, involving comparison of microscopic textures preserved within porphyroblasts and those present in the surrounding matrix (Vernon, 1978, 1989). These investigations led to the discernment of complex histories involving sometimes several episodes of mineral growth and deformation, termed by Cees Passchier as "microtectonics." This became the title of his classic 2005 text on the subject (Passchier and Trouw, 2005). An important subsequent step was to link the microstructures with macroscopic deformation features visible in outcrops, and mappable regionally. This information contributed

significantly to unraveling the interplay between deformation and heat flow, represented by metamorphic recrystallization, in orogenic belts.

In the 1980s, a vigorous debate evolved concerning the interpretation of porphyroblast microstructures and what they implied about strain relationships between porphyroblasts and matrix. Spiral-shaped inclusion trails in porphyroblasts such as garnets were long interpreted as indicating rotation of the porphyroblasts as they grew within a matrix undergoing shear strain (Rosenfeld, 1970). This interpretation was questioned by Tim Bell (Bell, 1985; Bell and Johnson, 1989), leading to over two decades of debate in the literature that is still ongoing (e.g., Bell et al., 1992; Passchier et al., 1992; Johnson, 1993, 1999, 2009; Bell and Bruce, 2007; Fay et al., 2008, 2009; Sanislav, 2009).

Migmatites, Granulites, and Melt Generation

There have been major advances in our understanding of the role of partial melting in crustal evolution. In the early 1960s, it was generally believed that the formation of migmatites involved injection of granitic material from nearby plutons with associated metasomatic introduction of K, Na, and Si (e.g., Turner and Verhoogen, 1960). Today, processes involved in the formation of migmatites have become accepted as a fundamental part of the metamorphic continuum, integral to both the drying out and stabilization of cratonic cores, and to the generation and segregation of felsic magmas (Brown, 1994; Sawyer et al., 2011). In fact, characterizing partial melting has become as much an area of metamorphic research as of igneous research, with the focus on the actual reactions and segregation mechanisms involved in the generation and ascent of magma.

Whereas much of the volatile content of sediments is lost during diagenesis and progressive metamorphism in the subsolidus *P-T* region, the final dehydration episode experienced by many rocks occurs during partial melting. Early studies of partial melting focused on the role of H_2O activity in generating crustal melting, which is not surprising inasmuch as experimental studies were often conducted under vapor-saturated conditions (e.g., Thompson and Algor, 1977; Thompson and Tracy, 1979). The role of dehydration melting of common hydrous silicates such as muscovite and biotite was beginning to be appreciated in the 1980s following important experimental works by Huang and Wyllie (1975), Vielzeuf and Holloway (1988), and Beard and Lofgren (1991), among others, and theoretical analysis by A.B. Thompson (1982) and Powell (1983) (see discussions in Spear et al., 1999). It became apparent from these studies that fluids produced by dehydration melting reactions dissolved completely into the melt that was produced and were then either released back into the rock as the melt crystallized, driving retrograde reactions, or removed from the source region by extraction of the melt.

Partial melting, especially dehydration melting, is now recognized as the governing process in the simultaneous formation of upper-amphibolite- and granulite-facies rocks, representing the relatively anhydrous residue of the melting process, and gra-

nitic melt, the latter of which escapes the source region. The generation of a viscous melt phase within high-grade rocks at mid- to lower-crustal depths creates significant changes to their rheology, in particular melt weakening, leading to the possibility of ductile flow (Arzi, 1978; Rosenberg and Handy, 2005). Ductile flow of partially molten mid- to lower-crustal rocks has potentially major geodynamic consequences (Brown, 2001; Jamieson et al., 2002), such as the hypothesized model of "channel flow" beneath the Himalayas (e.g., Beaumont et al., 2001; Jamieson et al., 2004).

Migmatites represent the frozen record of the complex interplay among melt generation, melt segregation, rock deformation, and melt extraction. They display a range of distinctive structures and textures that differ from subsolidus metamorphic rocks. Mehnert's (1968) classic account of migmatites remained the authoritative text until about the 1990s, when new observational, analytical, experimental, and conceptual advances led to a deeper understanding of the processes involved (e.g., Waters, 1988; Brown, 1994; Brown et al., 1995a, 1995b). To catalogue these new observations, an entire atlas of migmatitic structures and textures in the context of partial melting was published by E.W. Sawyer (Sawyer, 2008). In addition to macroscopic features indicative of anatexis, subtle yet distinctive microscopic features indicative of anatexis were increasingly recognized (e.g., Vernon and Collins, 1988; Sawyer, 1999, 2001), even in mafic granulites that formed deep (>10 kbar) in the lower crust (Hartel and Pattison, 1996). Complementary to these textural studies was the recognition of inclusions of trapped melt (now glass) in certain minerals in migmatites, especially garnet, providing direct evidence of the melt phase that was generated during partial melting (Cesare et al., 2009).

Although partial melting is considered to be the dominant process involved in the formation of granulite-facies rocks, the 1980s witnessed a vigorous debate over the relative roles of partial melting, and infiltration of carbonic fluids, in their formation. Both processes could produce the characteristic low-a_{H_2O} conditions implied by phase equilibria. The carbonic-infiltration process (e.g., Newton, 1985) was inspired by the spectacular, dark-colored, diffuse, deformation-controlled channels, veins, and patches of orthopyroxene-bearing rock ("charnockite") that variably overprinted migmatitic gray gneisses in quarries in southern India and Sri Lanka in the regional amphibolite-granulite transition zone (e.g., Janardhan et al., 1982). Fluid infiltration was unmistakable in these localities, but the larger question was whether this process could reasonably be extended to the formation of regional-scale tracts of granulite-facies rocks, implying massive fluid infiltration of portions of the lower crust. Although this latter view has not gained broad acceptance, and the debate has subsided, the presence and role of low-a_{H_2O} fluids in the lower crust continue to be researched (e.g., Newton and Manning, 2010).

Metamorphism and Plate Tectonics: Subduction Tectonics

During the early 1960s, the prevailing interpretation of the tectonic significance of metamorphic rocks was that the

distribution of mineral assemblages or metamorphic facies observed on the ground represented the crustal geotherm at the time of metamorphism. In the case of contact aureoles, this was a reasonable assumption because the spatial relationship between the metamorphosed aureole and the plutonic heat source was clear, and the time scale of heating and cooling was short compared to regional processes. Nevertheless, a similar relationship was also assumed for regionally metamorphosed (e.g., Barrovian) rocks. Indeed, in the first edition of his classic textbook *Metamorphic Petrology* (Turner, 1968, p. 41), F.J. Turner stated, "…it is usually possible to recognize in a regular zonal progression the 'frozen in' expression of a single gradient." These ideas had evolved by the second edition (Turner, 1981, p. 46), where he stated, "The zonal sequence of mineral assemblages in rocks of the same general composition, in fact, constitutes a record of some particular temperature-pressure gradient." Turner continued to emphasize that it is a fallacy to view "…the metamorphic gradient as a fossil depth-controlled geothermal gradient" principally because the instantaneous gradient in the crust is not likely to be homogeneous across an orogenic belt, and the geothermal gradient is most certainly variable depending on the tectonic environment. Similar ideas were implicit in Miyashiro's "metamorphic facies series" concept or "baric types" (Miyashiro, 1961, 1973; see also Carmichael, 1978). Whereas it was recognized that different tectonic environments would result in different facies series or field gradients, the fundamental realization that tectonic processes (e.g., folding and thrusting) might perturb the geothermal gradient in highly complex ways does not seem to have been recognized.

The discovery of symmetric magnetic anomalies on the seafloor (Vine and Matthews, 1963) that led to the acceptance of seafloor spreading and the emergence of plate-tectonic theory revealed the lithosphere to be considerably more mobile than previously believed. In particular, the recognition that collisional plate boundaries resulted in subduction and recycling of the lithosphere into the mantle prompted geophysicists to examine the thermal consequences of this process. The first published thermal structure of subducting plates (Minear and Toksoz, 1970) revealed that even at the modest plate-tectonic velocity of 1 cm/yr (10 km/m.y.), the subducting slab would carry down cool material, resulting in a downward bowing of the isotherms in subduction zones (Fig. 12). It was generally believed that blueschist-facies assemblages recorded conditions of relatively low temperature and high pressure (e.g., Miyashiro, 1961; Ernst, 1963; Ernst and Seki, 1967), and these pioneering thermal models of subduction regimes provided quantitative models for ways in which such *P-T* conditions could be realized on Earth, leading to a wealth of new studies that correlated the distribution of blueschists to ancient subduction zones. The first of these was published by W.G. Ernst (1970), in which he associated the thermal structure of a typical subduction zone with metamorphism of the Franciscan blueschist belt. A series of papers describing the apparent *P-T* histories of other blueschist terranes soon followed (e.g., Ernst, 1971a, 1971b, 1972, 1973a, 1973b). These relations were beautifully summarized by Ernst (1976b) in a diagram in which the metamorphic facies are superimposed upon the thermal structure of a convergent margin (Fig. 13). It was also recognized that the distribution of metamorphic facies in a terrane (e.g., zeolite facies to blueschist facies to eclogite facies) could be used to infer the polarity of an ancient subduction zone (Ernst, 1971b) because the dip of a subduction zone should be in the direction of increasing metamorphic grade. This observation led to mapping of the distribution of ancient subduction zones through time (Ernst, 1972).
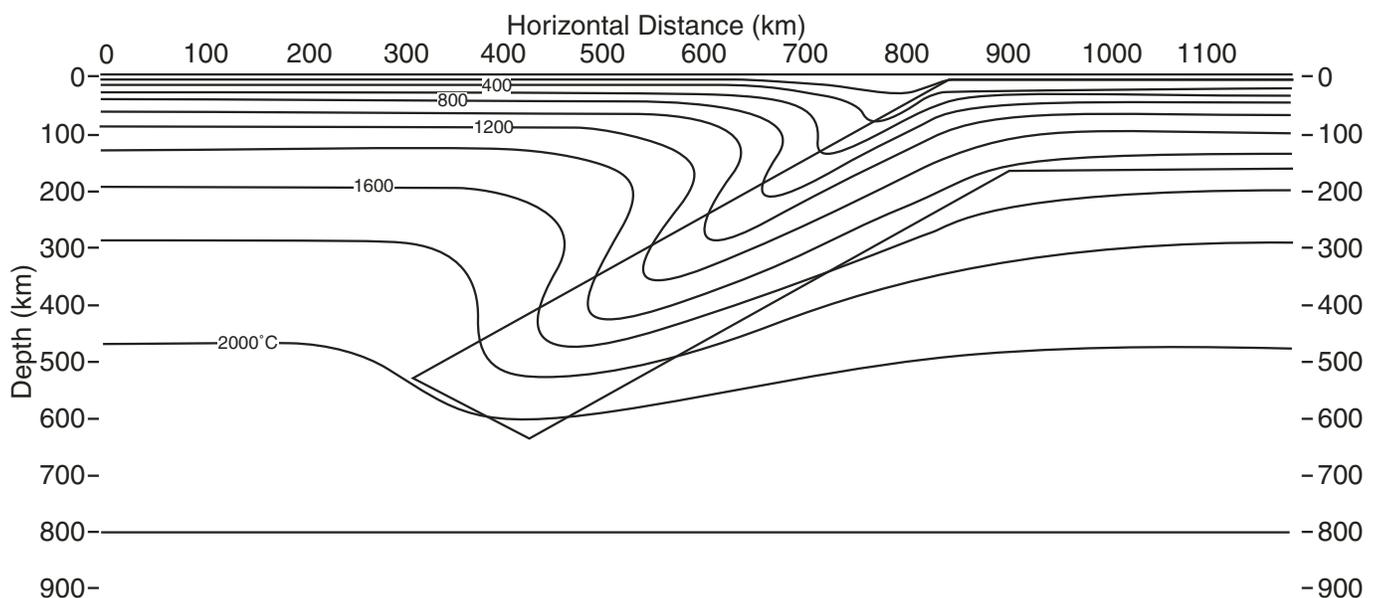

Figure 12. Thermal structure of a subducting slab (1 cm/yr, conductive heat transfer only), adapted from Minear and Toksoz (1970). Used with permission.

The metamorphosis of metamorphic petrology

The theory of plate tectonics also provided an explanation for Miyashiro's (1961) observation of paired metamorphic belts in which low-*T*, high-*P* metamorphic rocks were often juxtaposed against high-*T*, low-*P* metamorphic terranes. Blueschist-facies (low-*T*, high-*P*) metamorphism was now known to be characteristic of subduction complexes, whereas the nearby high-*T*, low-*P* metamorphism could be related to the associated island arc. Mike Brown, in a series of papers in the late 2000s (Brown, 2006, 2007, 2008, 2010), argued that these distinctive features could be used to assess the timing of onset of plate tectonics in Earth history. In his analysis, the earliest occurrence of dual thermal environments suggestive of subduction was in the Neoarchean.

Although subduction and consequent down-bowing of isotherms provided the mechanism for generation of low-*T*, high-*P* blueschist-facies metamorphism, it was recognized at an early stage that rocks that are subducted must eventually be returned to the surface if they are to be examined by the petrologist. Nevertheless, a detailed understanding of the mechanisms for exhumation of deeply subducted rocks is still very much debated. Mechanisms such as rise due to buoyancy forces (England and Holland, 1979), underplating of an accretionary wedge and exhumation against a buttress (Platt, 1987), accretionary wedge corner flow (Cloos, 1982, 1985; Shreve and Cloos, 1987), and lithosphere slab breakoff (Davies and von Blanckenburg, 1995;
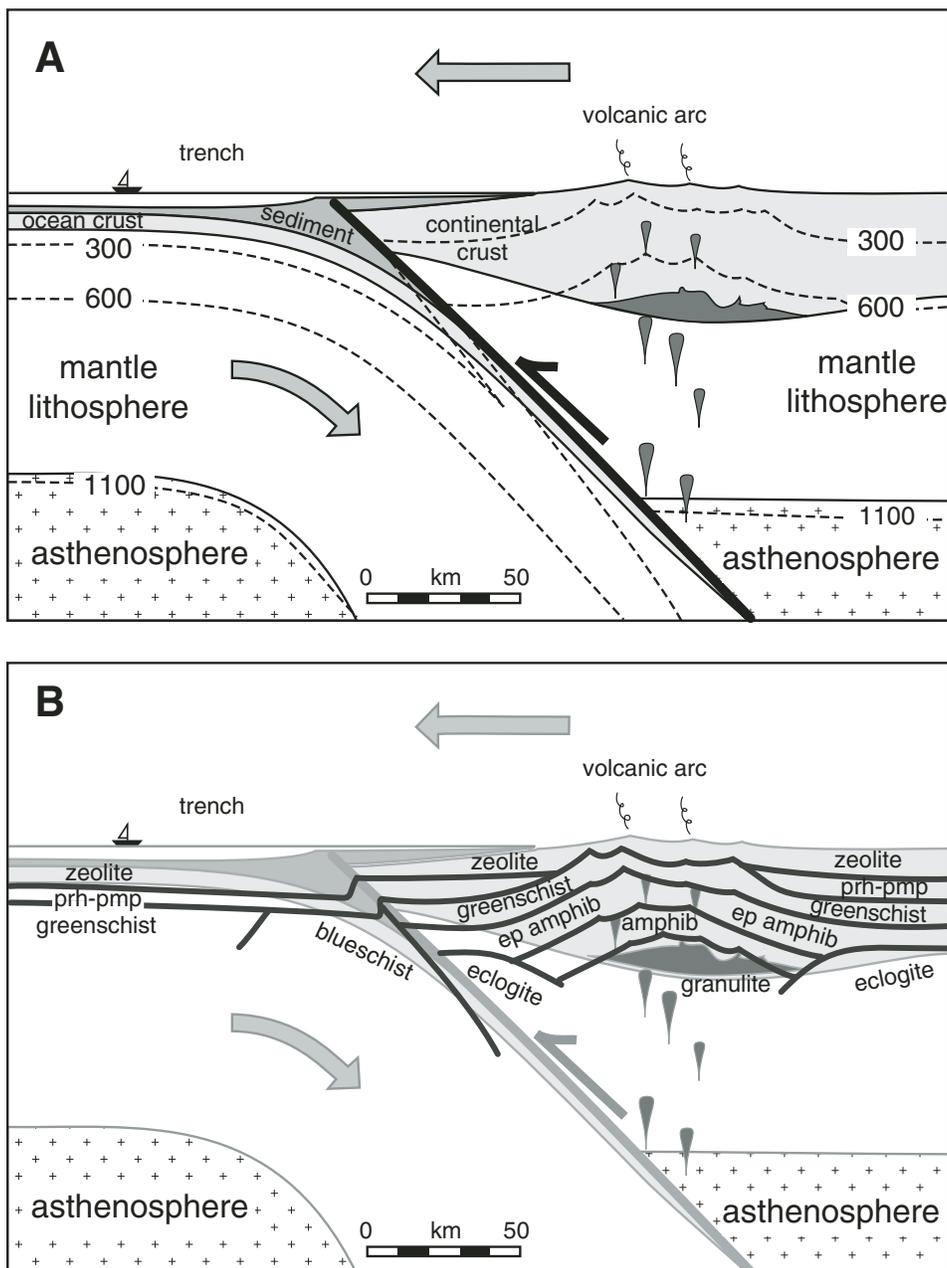

Figure 13. Schematic cross section of an ocean-island arc collision zone. (A) Isotherms are bowed downward in the subduction zone because cool oceanic lithosphere is being subducted. Isotherms in the arc are bowed upward because of the advection of heat by rising magmas. (B) The distribution of metamorphic facies in the subduction zone and island arc. High pressure-temperature (*P-T*) facies series are encountered in the subduction zone, and low *P-T* facies series are encountered in the arc. Figure is after Ernst (1976b). Abbreviations: prh—prehnite; pmp—pumpellyite; ep—epidote; amphib—amphibole.

Hacker et al., 2013) have all been proposed, and it may be that different mechanisms operate in different collisional settings. An approach to deciphering the tectonics underlying the burial and exhumation of subduction complexes has been to infer the detailed *P-T* trajectory followed by the rocks based on the observed sequence of mineral parageneses in both the prograde and retrograde assemblages. The first such *P-T* trajectory was published by Ernst (1973b) for blueschist-facies rocks from the Alps. The *P-T* trajectories for a number of ancient subduction complexes were compiled by Ernst (1988) and divided into two broad types: Franciscan type and Alpine type (Fig. 14). With Franciscan-type trajectories, the rocks follow a *P-T* path during exhumation that closely follows the burial path. In Alpine-type trajectories, the rocks follow an exhumation path that is nearly isothermal or involves significant heating and is typified by significant greenschist- or amphibolite-facies overprinting.
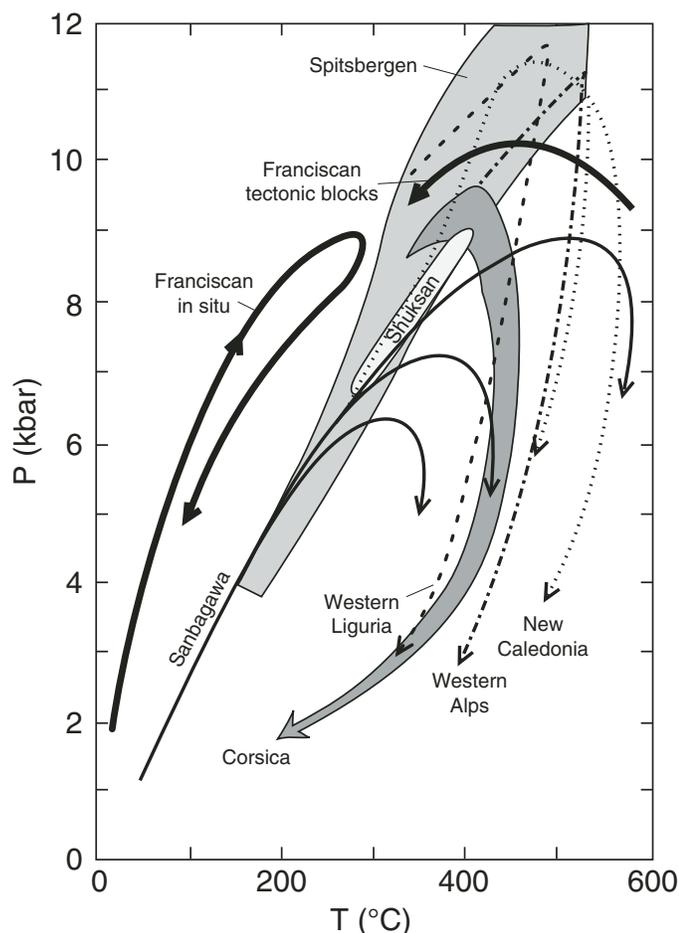

Figure 14. Pressure-temperature (*P-T*) diagram showing *P-T* paths from subduction complexes. Western Alps–type *P-T* paths are characterized by a period of nearly isothermal decompression following the peak pressure, whereas Franciscan-type *P-T* paths are characterized by a retrograde path that is very nearly the same as the prograde path. Figure is after Ernst (1988).

A key constraint in distinguishing these two exhumation paths is the presence or absence of aragonite in the assemblage. Aragonite is the stable $CaCO_3$ polymorph under blueschist-facies conditions, and a kinetic study by Carlson and Rosenfeld (1981) documented that crossing back into the calcite field at greenschist-facies conditions would result in aragonite readily converting back to calcite. Thus, the presence of aragonite required crossing this boundary at temperatures below 200 °C, i.e., a *P-T* trajectory similar to the burial path. Franciscan blueschists contain aragonite, whereas Alpine-type blueschists contain only calcite.

Metamorphism and Plate Tectonics: Continental Orogenesis

Although the relationship between subduction and low-*T*, high-*P* metamorphism was well established by the early 1970s, similar appreciation of the thermal evolution of continental orogenesis was slower to emerge. The first quantitative assessment of the thermal implications of overthrusting during collisional orogeny was published by Oxburgh and Turcotte in 1974 (Oxburgh and Turcotte, 1974). This milestone contribution laid out the fundamental relationships that govern heat flow in a one-dimensional (1-D) crustal section following instantaneous overthrusting, but it was little appreciated by most metamorphic petrologists. Six years later, Phil England, a graduate student of Ron Oxburgh's, published, along with Steve Richardson, "The influence of erosion upon the mineral facies of rocks from different metamorphic environments" (England and Richardson, 1977), in which they outlined the *P-T* path a rock would traverse following instantaneous thrusting (the Oxburgh and Turcotte initial condition) and subsequent erosion to eventual exposure at Earth's surface (Fig. 15). They described how the evolution of geotherms following thrusting coupled with erosion would result in a *P-T* path that was clockwise in shape and argued that the peak metamorphic assemblage would most likely be that representative of maximum entropy—typically coincident with the condition of maximum temperature or maximum dehydration. Rocks initially at different crustal depths would experience similarly shaped *P-T* paths but acquire peak metamorphic conditions at different *P-T* conditions and at different times.

This remarkable insight led to a true paradigm shift in the understanding of metamorphism and metamorphic rocks. No longer was the metamorphic field gradient representative of specific geothermal gradients, either steady state or transient. Rather, the metamorphic field gradient was envisioned to be a complex array of maximum *T* points that arose from continuously evolving geotherms and erosional exhumation following tectonic perturbations. These ideas were further developed and expanded upon in a classic pair of papers by Phil England and Alan Thompson (England and Thompson, 1984; Thompson and England, 1984). In addition, Brady (1988) showed that, contrary to intuition, the role of fluid flow in the thermal evolution of metamorphic terranes is negligible.

The Oxburgh and Turcotte (1974) and England and Richardson (1977) thermal models were 1-D and consequently were limited in how accurately they could be used to model natural metamorphic terranes, because there was no way that rocks undergoing metamorphism in a 1-D model could all be exposed at the surface at the same time. At the very least, the 1-D models would need to be tilted to provide for the observed exposures of metamorphic field gradients.

One consequence of modeling orogenesis in 1-D with a single crustal-scale thrust was the necessity to invoke time scales ranging over tens of millions of years to achieve the peak *P-T*

conditions that were observed in nature (see Fig. 15). Geochronology had not advanced to the point where fine-scaled metamorphic chronologies could be established, yet the exposure of relatively young metamorphic belts in relatively recent mountain belts such as the Alps and Himalaya was evidence that the time scales implied by the 1-D thermal models were unrealistically long. Recent evidence for much shorter time scales of regional metamorphism, including in the classic Barrovian type area itself, has accumulated through thermochronological studies involving several different isotopic systems (e.g., Viete et al., 2013), and from dating of cores and rims of garnet porphyroblasts (e.g.,
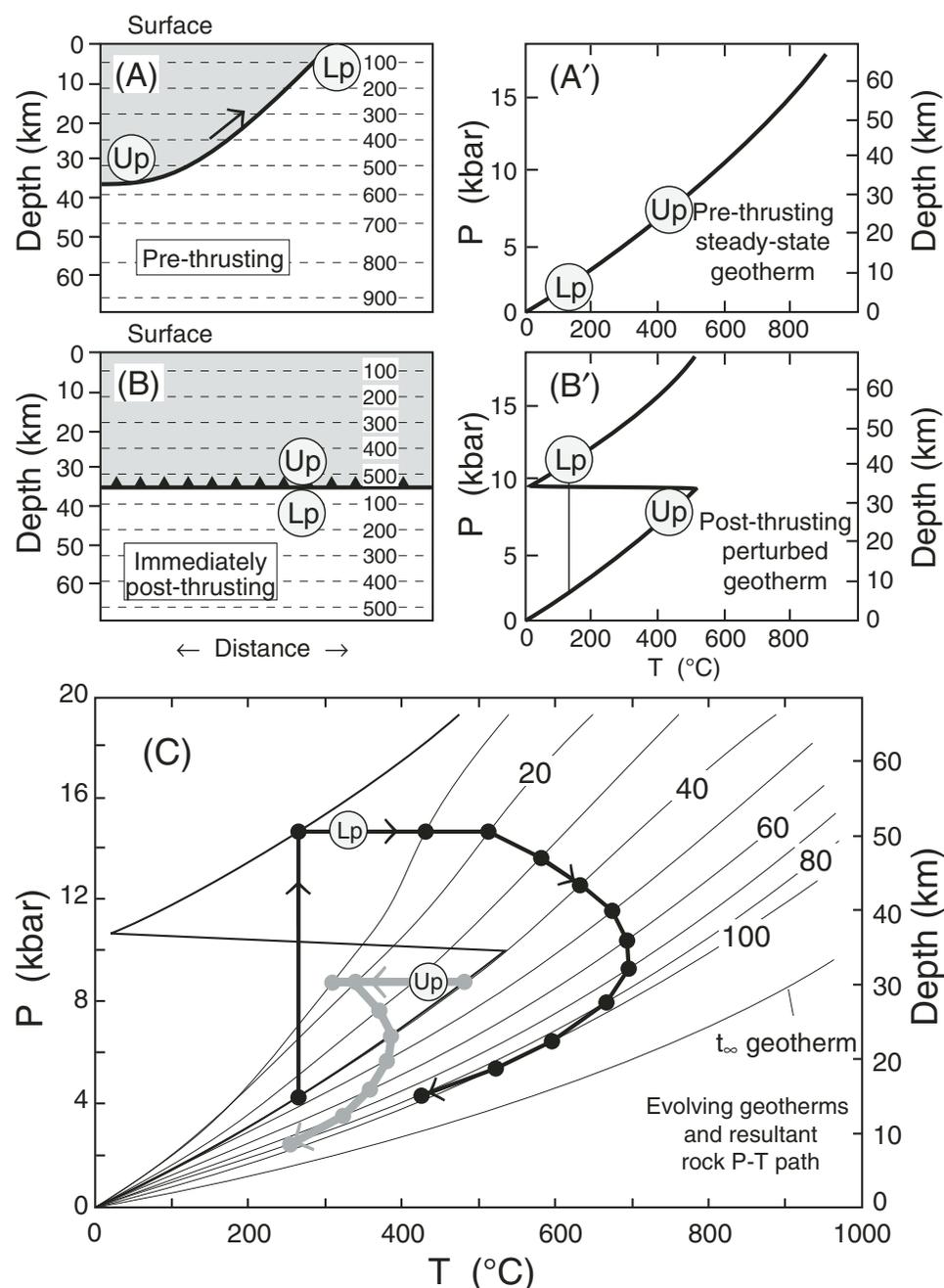

Figure 15. Illustration of the overthrust model. (A and A′) Prethrusting. Cross section (left) shows isotherms and position of future thrust. Pressure-temperature (*P-T*) diagram (right) shows initial, prethrusting geotherm. (B and B′) Immediately post-thrusting. Cross section (left) shows position of thrust and repetition of isotherms. *P-T* diagram (right) shows "sawtooth" geotherm characteristic of instantaneous overthrusting. (C) *P-T* diagram showing the evolution of geotherms with time and the *P-T* paths followed by lower-plate (LP) and upper-plate (UP) rocks. Time lag between thrusting and onset of erosion = 20 Ma. Uplift rate = 0.35 mm yr^{-1}, k = 2.25 W m^{-1} K^{-1}, $Q*$ = 30 mW m^{-2}, A = 2.0 μW m^{-3}; t_∞ is the hypothetical steady-state geotherm after infinite time for a doubly thick crust; this geotherm is never attained because uplift and erosion act to thin the crust. Figure is based on England and Richardson (1977) and England and Thompson (1984), modeled using program THICKEN by S. Peacock (in Spear et al., 1991).

Baxter et al., 2002). These authors attributed the rapidity of the regional metamorphic event to the involvement of magmas within a regime characterized by crustal thickening.

Nevertheless, these models changed the thinking of much of the metamorphic petrology community because it was recognized that *P-T* paths could contain much valuable information about the tectonic burial and exhumation history of a metamorphic belt. Over the next 30 years, a considerable amount of research effort was (and still is) expended toward establishing not only the peak *P-T* conditions experienced by a metamorphic rock, but also the *P-T* path the rock traveled in its journey through a collisional orogenic event (e.g., Spear and Peacock, 1989; Brown, 1993).

Two dominant themes emerged from these studies. Rocks that exhibited Barrovian-type metamorphism (i.e., kyanite to sillimanite parageneses) were inferred to have followed predominantly clockwise *P-T* paths, similar to the predictions of the 1-D thermal models of England and Richardson (1977). A second general class of *P-T* paths for regional metamorphism was observed to be predominantly counterclockwise, in which early high-*T*, low-*P* metamorphism was followed by loading and eventual exhumation (e.g., andalusite-sillimanite parageneses). In these terranes, it was apparent that the low-*P* metamorphism was associated with high heat flow into the terranes, as might be caused by the influx of magmas or hot fluids, by crustal thinning, or by high radioactive heat production. In fact, some terranes such as the Acadian metamorphic belt of New England, exhibit both clockwise and counterclockwise *P-T* paths in relatively close juxtaposition (Fig. 16).
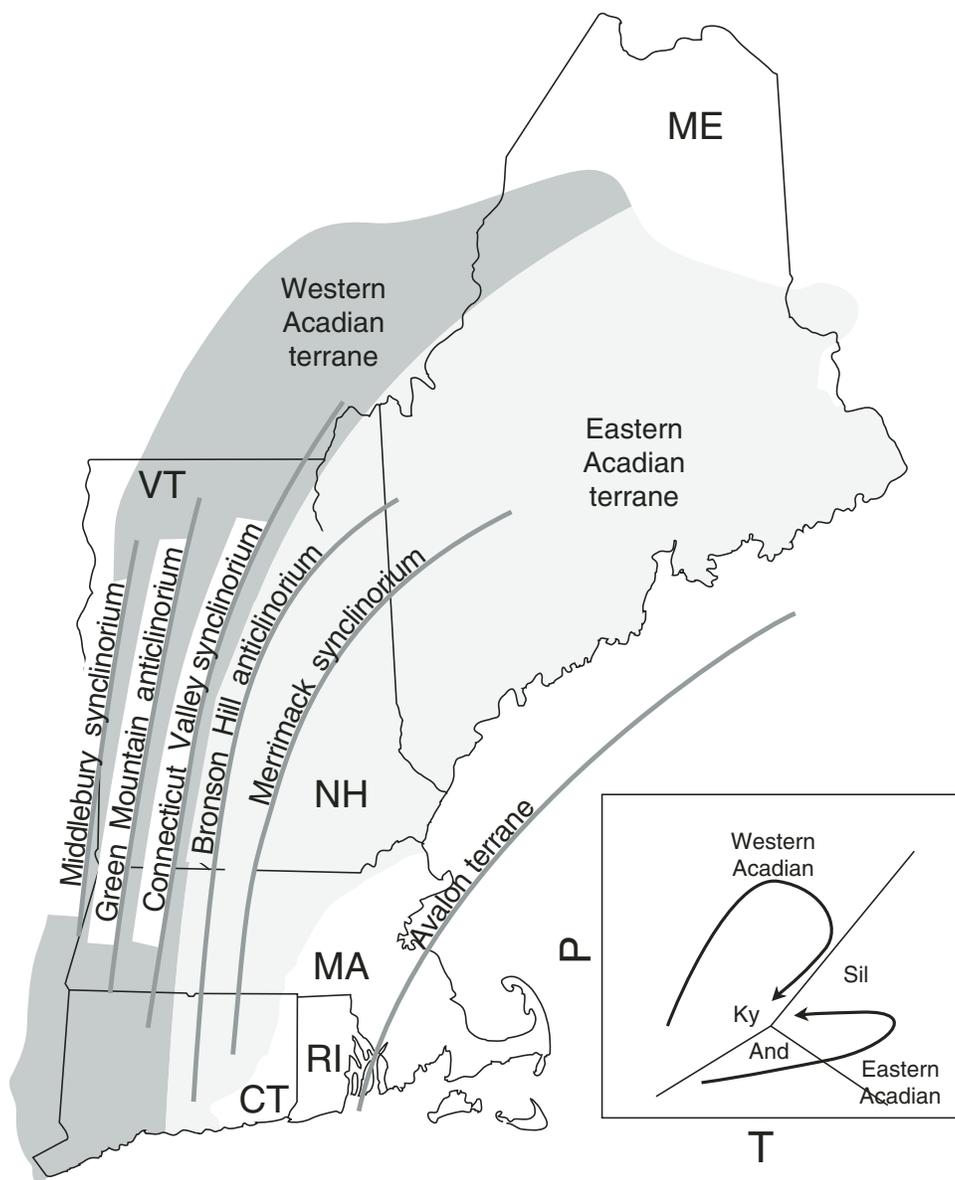

Figure 16. Map of New England, United States, showing the distribution of the major tectonic elements. Abbreviations for states are CT—Connecticut, MA—Massachusetts, RI—Rhode Island, NH—New Hampshire, ME—Maine, VT—Vermont. Inset shows schematic pressure-temperature (*P-T*) paths for the western Acadian terrane (Connecticut Valley synclinorium), which are clockwise, and the eastern Acadian terrane (Merrimack synclinorium), which are counterclockwise. Ky—kyanite; And—andalusite; Sil—sillimanite. Figure is from Spear (1993).

Debate on the significance of clockwise versus counterclockwise *P-T* paths was not restricted to studies of midcrustal conditions. It was recognized during the 1980s that granulite-facies terranes around the globe might have experienced either clockwise or counterclockwise paths, as was elegantly summarized by Bohlen (1987) and Harley (1989). Prograde *P-T* paths in granulites are difficult to constrain because most prograde features are eradicated at the peak metamorphic conditions. As reviewed by Harley (1989), granulite-facies rocks have experienced two broad types of retrograde paths: either isothermal decompression (ITD) or isobaric cooling (IBC). Both of these types of paths were predicted in the seminal paper by England and Richardson (1977), in which crustal thickening by magma injection into the upper crust was presumed to be the major cause of subsequent isobaric cooling. It was subsequently realized that extension of "normal" crust could also result in an elevated geotherm, which could give rise to an overall counterclockwise *P-T* path.

Discovery of Coesite, Diamond, and Ultrahigh-Pressure (UHP) Metamorphism

One of the most profound discoveries of metamorphic petrology during the past 50 years was the discovery in metamorphic rocks of the first coesite in the Alps (Chopin, 1984) and the Norwegian Caledonides (Smith, 1984), and then even more spectacularly, diamond in northern Kazakhstan (Sobolev and Shatsky,

1990) and Dabie Shan, China (Okay, 1993). Previously, these minerals were believed to occur only in mantle xenoliths and meteorite impact craters. Their presence in supracrustal rocks, most commonly as small inclusions within garnet, led to the startling realization that surficial rocks could be subducted to depths of 120 km or more and then returned to the surface. This led to a renewed appreciation of the vigor of plate-tectonic recycling.

Described as UHP metamorphism, there are now known to be more than 20 UHP (coesite-bearing) terranes on the planet (Fig. 17; for reviews of global UHP terranes, see Liou et al., 2004; Chopin, 2003; Carswell and Compagnoni, 2003; Rumble et al., 2003; Gilotti, 2013). Most UHP terranes appear to be associated with continent-continent collisions that have occurred since the beginning of the Paleozoic. Vertical exhumation rates of UHP terranes have been documented at up to several centimeters per year; if exhumation occurs up along a subduction suture that dips 20°, then exhumation velocity along the suture must be around three times faster—very fast indeed!

Ultrahigh-Temperature (UHT) Metamorphism

UHT metamorphism is a term coined by Simon Harley (1998) to describe regional metamorphism at temperatures in excess of 900 °C. Unlike the unexpected discoveries of coesite and diamond in metamorphic rocks, UHT metamorphic rocks had been known and studied extensively for some time (e.g., Ellis et al., 1980; Harley, 1985, 1989), but estimating the peak
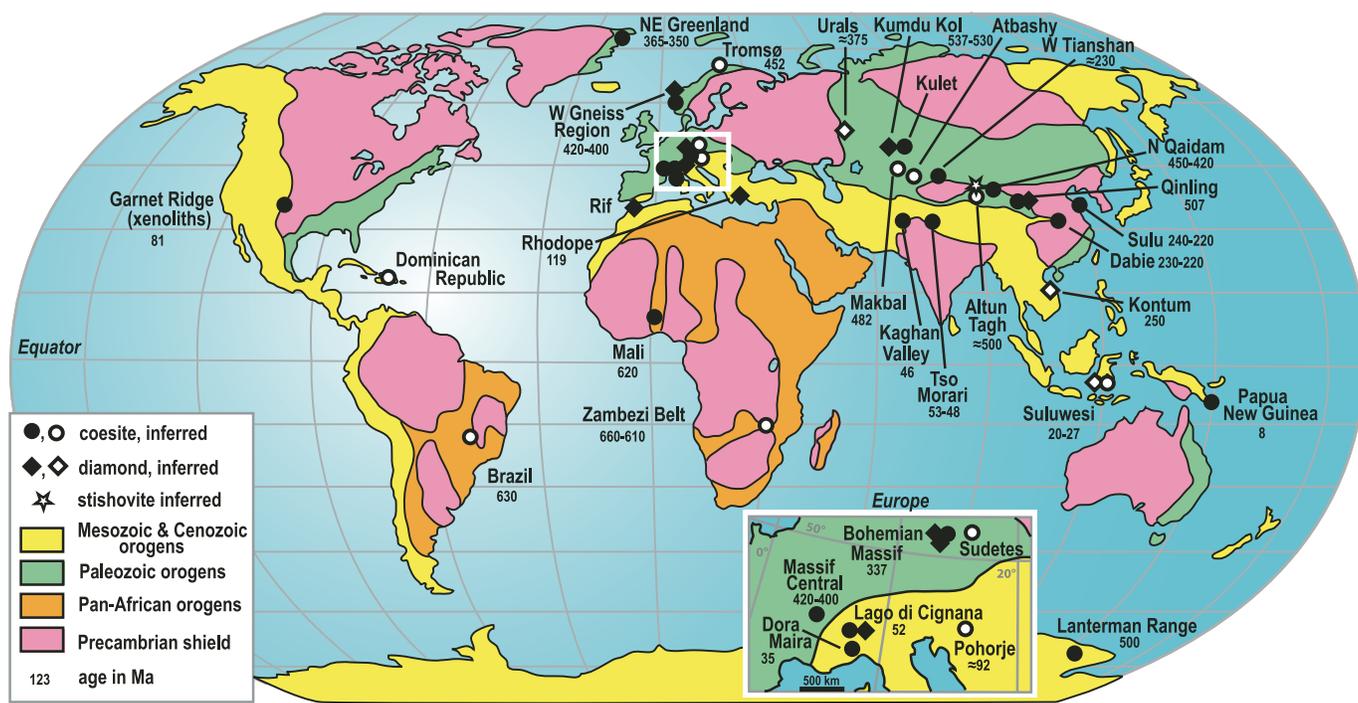

Figure 17. World map showing distribution of known ultrahigh-pressure (UHP) terranes. Numbers are ages of metamorphism in Ma. Figure is from Gilotti (2013); used with permission.

P-T conditions of granulites was problematic because of the evidence for resetting of cation-exchange geothermometers on cooling from peak conditions (e.g., Pattison and Begin, 1994). Controversies abounded for decades as to the accurate record of peak metamorphic temperatures experienced by granulite-facies rocks (e.g., Harley, 1989; Frost and Chako, 1989; Spear and Florence, 1992; Fitzsimons and Harley, 1994; Pattison et al., 2003). It was not until important new experimental data were obtained on diagnostic UHT minerals and mineral associations, such as sapphirine, osumilite, and orthopyroxene + sillimanite, and the generation of internally consistent thermodynamic data sets extracted from these experiments, that the true *P-T* conditions of these extreme metamorphic conditions could be accurately calculated (e.g., Kelsey et al., 2003, 2004, 2005).

Much research continues today on the distribution and evolutionary history of UHT rocks (for reviews, see Harley, 2008; Kelsey, 2008; Kelsey and Hand, 2015). To date, there are 58 UHT terranes recognized globally (Fig. 18). Although the *P-T* conditions of many of these terranes are now well established, there remains uncertainty as to the longevity of UHT metamorphism, with estimates based on a variety of geochronometers ranging from less than 10 to more than 100 m.y. The largest controversies center on the thermal-tectonic causes of UHT metamorphism. Normal crustal geotherms perturbed by tectonic thickening are incapable of producing the required *P-T* conditions except under exceptional scenarios (Harley, 1989), so additional heat sources such as magmatic underplating, asthenospheric upwelling, or increased radioactive heat generation have been suggested as necessary conditions. Most recently, Brown (2014) has linked the findings from UHT terranes to Precambrian lithosphere evolution.

Metamorphism and Ore Deposits

In a more applied field, study of the influence of metamorphic processes on the genesis and modification of ore deposits, and on strategies for ore exploration, has increased markedly in the past 50 years (e.g., Spry et al., 2000). It has long been recognized that rocks spatially associated with hydrothermal ore deposits (e.g., porphyries, seafloor exhalative deposits) are of an unusual composition due to the metasomatic effects of the passage of large volumes of fluids through the host rocks. When metamorphosed, these produce distinctive and unusual metamorphic mineral assemblages that can then be used as indicators, or "vectors," to mineralization (Bonnet and Corriveau, 2007). The classic example is the development of rocks containing anomalous occurrences or abundances of cordierite, Fe/Mg-amphibole, and other Fe-Mg-Al minerals (e.g., "dalmatianite"), indicative of alkali-depleted metasomatic rocks that formed in the feeder zones to volcanic exhalative deposits prior to metamorphism (e.g., Franklin, 1984). A side benefit, from a metamorphic/tectonic perspective, is that these unusual bulk compositions sometimes result in mineral associations that preserve a more sensitive record of the *P-T* conditions and *P-T* evolution of the region

in which they are found than the more abundant "ordinary" metavolcanic and metasedimentary host rocks (e.g., Diener et al., 2008).

There has been increasing recognition of the role of metamorphic processes in the formation of orogenic gold deposits. These are a major type of gold deposit found in deformed and metamorphosed rocks of accretionary and collisional orogens, of which Precambrian greenstone-hosted gold deposits are perhaps the best known (Tomkins, 2013). A series of papers (Powell et al., 1991; Phillips, 1993; Phillips and Powell, 2010) showed that the compositions of fluids generated in metamorphosed volcanic and sedimentary rocks at the greenschist-to-amphibolite facies transition closely match those of the fluids associated with these deposits. The gold and related metals are interpreted to have been leached from the host rocks and transported to the sites of deposition at shallower levels by the metamorphic fluids. Tomkins (2010) extended this idea by incorporating the role of pyrite as a metamorphic reactant mineral, the breakdown of which during metamorphism yields high-S fluids ideally suited to carry gold.

A novel application of metamorphic petrology to ore geology was the recognition of metamorphic sulfide melting (Frost et al., 2002; Tomkins et al., 2007). Prior to these studies, ore remobilization was understood in terms of two processes: hydrothermal remobilization and deformation-induced, solid-state remobilization. These studies showed that the low melting temperature of certain sulfide and especially sulfosalt mineral assemblages permitted them to melt and migrate under metamorphic conditions as low as the greenschist facies (sulfide migmatites). Recognition of this process explained a number of perplexing ore deposits hosted in high-grade metamorphic rocks containing internally segregated accumulations of gold and associated sulfosalt minerals characteristic of low-temperature epithermal deposits (e.g., Hemlo, Ontario; Tomkins et al., 2004).

PETROCHRONOLOGY—PUTTING THE "*t*" IN *P-T-t* PATHS

The term "petrochronology" refers to establishing the relative and absolute time frames for metamorphic processes—that is, quantifying the small "*t*" in *P-T-t* paths. As mass spectrometry and geochronology have developed over the past 50 years, the ability to assess geologic time has become increasingly accurate. As a consequence, the general duration of metamorphic "events" is becoming quite well known. In addition, it has become increasingly apparent that a precise constraint on the time scales of various metamorphic processes—that is, the rates of these processes—could provide significant insights into the tectonic processes that drive crustal evolution.

There are two broad ways to consider the implementation of the discipline of petrochronology: either from inferences gleaned from plate tectonics and thermal modeling, or from direct or indirect determination of the absolute or relative ages of points along a *P-T* path or the duration of segments of the *P-T* path.
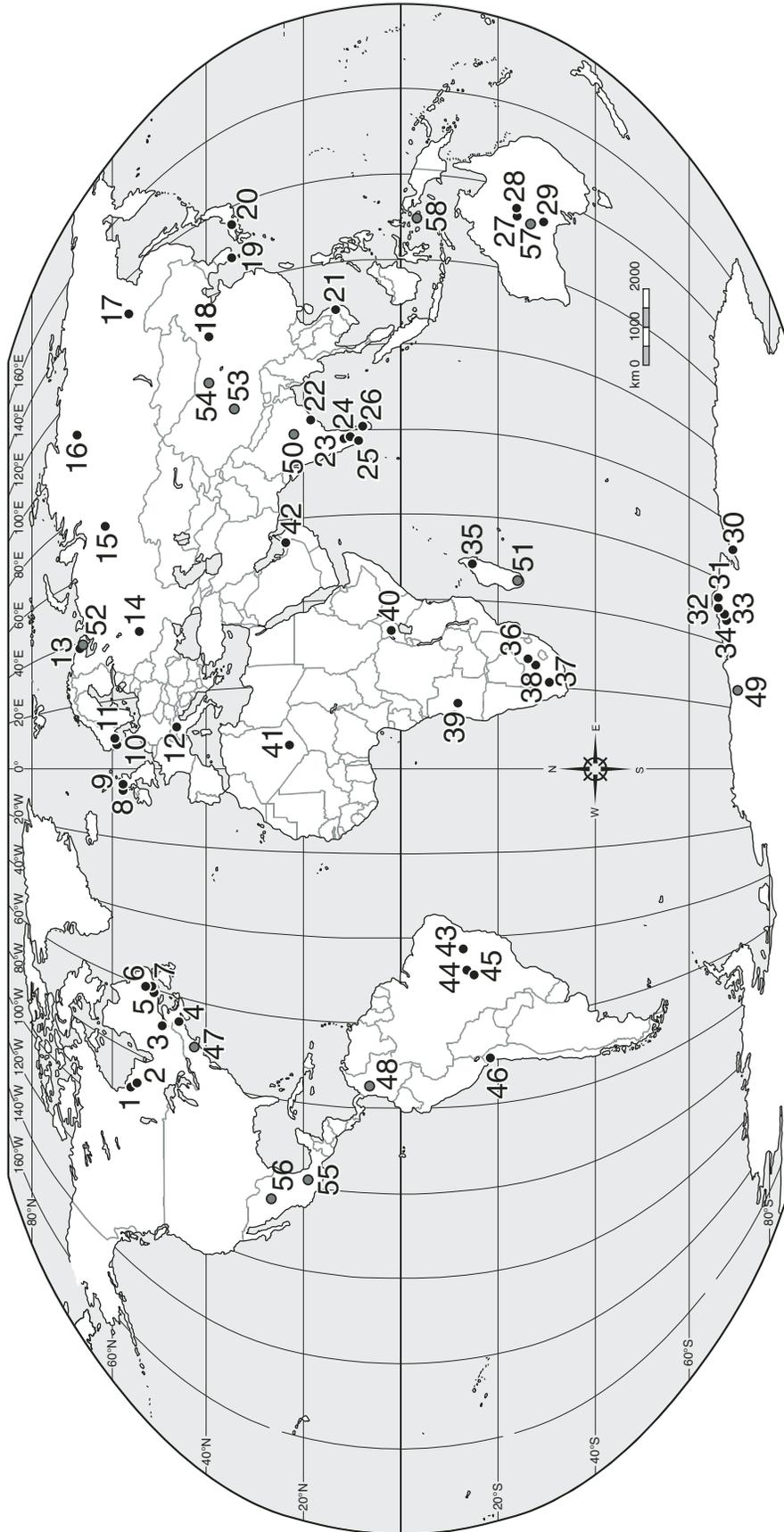
Figure 18. World map of exposed ultrahigh-temperature metamorphic rocks (including xenoliths in some cases). See Kelsey and Hand (2015) for key numbers and discussion. Figure is from Kelsey and Hand (2015); used with permission.

Insights from Plate-Tectonic and Thermal Modeling

Plate-tectonic rates have been established for the last 200 m.y. based on magnetic anomalies on the seafloor and provide a first-order constraint on the rates of metamorphic processes that are driven by plate tectonics (e.g., subduction and continental collisions). Maximum plate convergent rates are on the order of 10 cm/yr, and it is reasonable to suppose that this represents an upper bound on the rates of orogenic tectonic processes.

Thermal models have been employed for decades to help understand the thermal evolution of metamorphic rocks. Modeling of thermal aureoles around dikes and plutons is quite mature (e.g., Harrison and Clarke, 1979), and the general time scales of contact metamorphism are quite well constrained by application of these models (e.g., Harrison and Clarke, 1979; Furlong et al., 1991; McFarlane et al., 2003). Considerable research into the hydrothermal circulation and consequent mass transfer around plutons is still in progress.

Thermal modeling of subduction processes date from the early days of plate-tectonic theory and is still very much ongoing (e.g., Minear and Toksoz, 1970; Peacock, 1991, 2003). All of the early models and most current ones involve steady-state subduction and are not focused directly on constraining the duration of metamorphic crystallization and exhumation. Nevertheless, they provide a time frame within which to evaluate rates of metamorphic processes.

Thermal modeling of continental orogenesis dates from the pioneering works of Oxburgh and Turcotte (1974) and England and Richardson (1977) (see earlier discussion). In these early studies, it was assumed that instantaneous continental overthrusting involved the entire crust, so time scales for the thermal perturbation caused by this overthrusting to decay was on the order of tens of millions of years (i.e., $t = h^2/\kappa = [35{,}000 \text{ m}]^2/10^{-6} \text{ m}^2 \text{ s}^{-1} = 39$ Ma). Although rarely stated explicitly, this time frame was tacitly accepted by the metamorphic community as reflecting the time scale for regional metamorphism. As noted already, direct dating of regional metamorphic terrains increasingly suggests that this model time frame is longer than observed.

Direct Measurement and Process Modeling— Geochronologic Methods

Assessment of the validity of the above models can only be made through direct observation, analysis, and modeling of the rocks themselves. Direct determination of the *T-t* histories of metamorphic rocks can be divided into two broad classes of endeavor—direct measurement of the radiometric age of a metamorphic mineral (e.g., geochronology), and inference of the rate of a metamorphic process by analysis of a kinetic property of the system (e.g., diffusion).

Early geochronologic studies of metamorphic minerals often involved the K-Ar system, which later evolved into Ar-Ar geochronology (for an excellent introduction and review, see

McDougall and Harrison, 1988). As early as the mid-1960s, it was recognized by Stan Hart (Hart, 1964) that proximity to a later intrusion would cause a metamorphic mineral such as hornblende, biotite, muscovite, or K-feldspar to lose the radiogenic daughter product (Ar), and thus exhibit an age much younger than the formation age (Fig. 19). The cause was interpreted to be the thermal diffusion effects caused by the nearby pluton, and the concept of "closure temperature" of a mineral was born. This concept was subsequently formalized by Dodson (1974, 1986) and is still the backbone of interpretation of geochronologic results from minerals that have undergone a complex thermal history. Mineral closure ages reflect the time at which a mineral passed through its closure temperature, and for the most part, these ages have been used to infer cooling histories of metamorphic terranes.

A complementary approach is the analysis of fission-track ages from minerals (especially apatite, titanite, zircon) in metamorphic and igneous rocks. Fission tracks caused by radioactive decay anneal with time and, because the process is diffusive and thus thermally activated, also express closure temperatures.

Inasmuch as the common K-bearing phases (amphibole, biotite, muscovite, and K-feldspar) have closure temperatures ranging from over 500 °C to below 200 °C, and fission-track closure temperatures for titanite, zircon, and apatite range from a few hundred to below 100 °C, these combined studies have been able to reveal rather detailed *T-t* histories for the late stages of exhumation of metamorphic terranes.

Dating the prograde metamorphic path has proven to be somewhat more difficult. There are a number of accessory minerals that have closure temperatures above the maximum temperature experienced by many metamorphic rocks (e.g., zircon,
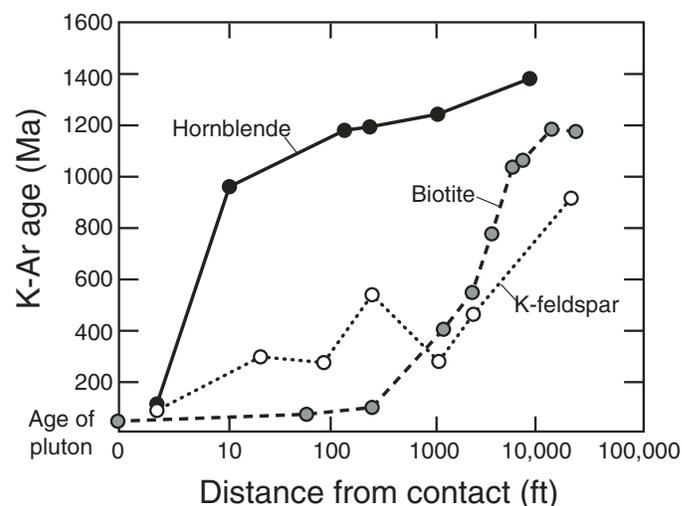

Figure 19. Plot of measured K-Ar ages of hornblende, biotite, and K-feldspar as a function of distance from the contact of a young (55 Ma) pluton. The fact that the ages get older with distance from the pluton is interpreted to signify that the minerals have lost radiogenic daughter product (^{40}Ar) as a consequence of heating by the pluton. Figure is after Hart (1964).

monazite, baddeleyite, titanite, rutile, and garnet), and it was initially hoped that ages on these minerals would provide a precise time scale for metamorphic processes (e.g., Parrish, 1990; Heaman and Parrish, 1991). Two issues confounded this approach, however. First, it became clear that accessory phases such as zircon and monazite can be age-zoned, so ages on bulk separates represent a weighted average of the different ages. Second, it was not clear on what part of the metamorphic *P-T* path a particular accessory mineral formed, and thus what the age represented.

A major step forward in the field of petrochronology came as the ability to obtain ages on small analytical volumes in a texture-sensitive context emerged. This capability developed in part as a result of new instrumentation such as SIMS and LA-ICP-MS, which can today provide isotopic analysis on spots as small as 10 μm (e.g., Compston et al., 1984; Harrison et al., 1995; Cheney et al., 2004). Nearly simultaneously, there came the recognition that reasonably precise monazite ages could be obtained via the chemical dating method using the electron microprobe (e.g., Suzuki and Adachi, 1991; Montel et al., 1996). These developments were critical because it had been recognized that accessory minerals useful for geochronology—zircon and monazite in particular—often contain evidence for multiple growth stages. An age on an entire grain separate would necessarily then be a mixture of the ages of these different growth events. The new work flow for petrochronology of accessory minerals involved first imaging a suite of grains by an appropriate imaging technique (typically cathodoluminescence [CL] for zircon and X-ray mapping of Y and Th for monazite) and then attempting to obtain ages for discrete textural or chemical regions using the appropriate beam technique. For example, Figure 20 shows Y maps of monazite grains from migmatites of west-central New Hampshire. Four generations of monazite growth are indicated, each having been produced by a different reaction during the metamorphic evolution (Pyle and Spear, 2003; Pyle et al., 2005).

Developments in instrumentation, analytical methods, and petrologic interpretation are all very much on the forefront of petrochronology investigations today.

Different isotopic systems have been applied to other metamorphic minerals. One of the earliest studies to attempt to directly determine the age of garnet crystallization as well as rate of garnet growth was by Christensen et al. (1989) using the Rb/Sr system. Whereas the analytical protocols of the day provided sufficient precision to determine the age of the garnet studied to a few million years, it was also necessary to make assumptions about the isotopic evolution of the matrix, which was much more difficult to constrain for the Rb/Sr system. In contrast, the Sm/Nd system is not as susceptible to changes in the isotopic composition of the matrix because most of the Sm resides in the garnet. The first Sm/Nd ages of garnet from metamorphic rocks (Vance and O'Nions, 1990, 1992; Vance and Holland, 1993 demonstrated that this approach held great promise. E. Baxter and coworkers (e.g., Pollington and Baxter, 2010, 2011) have improved the analytical precision to better than 1% and developed a microsampling technique that allows distinct growth zones in a garnet to be dated. Coupled with an estimated *P-T* path for the same garnet, this method potentially yields a complete *P-T-t* history for that portion over which garnet grew. The Lu/Hf system has also been used to date garnets, with the resulting age being heavily weighted toward the garnet core as it fractionates most of the rock's Lu budget.

The analytical methods discussed here all hold great promise for dating specific metamorphic phases and thus providing absolute and relative time scales for metamorphic processes. However, they all require that an accurate pressure and temperature be known for the growth of the phase being dated. This is not too difficult in the case of garnet, as this phase is incorporated in much of metamorphic geothermobarometry (see earlier discussion). However, much less is understood about the
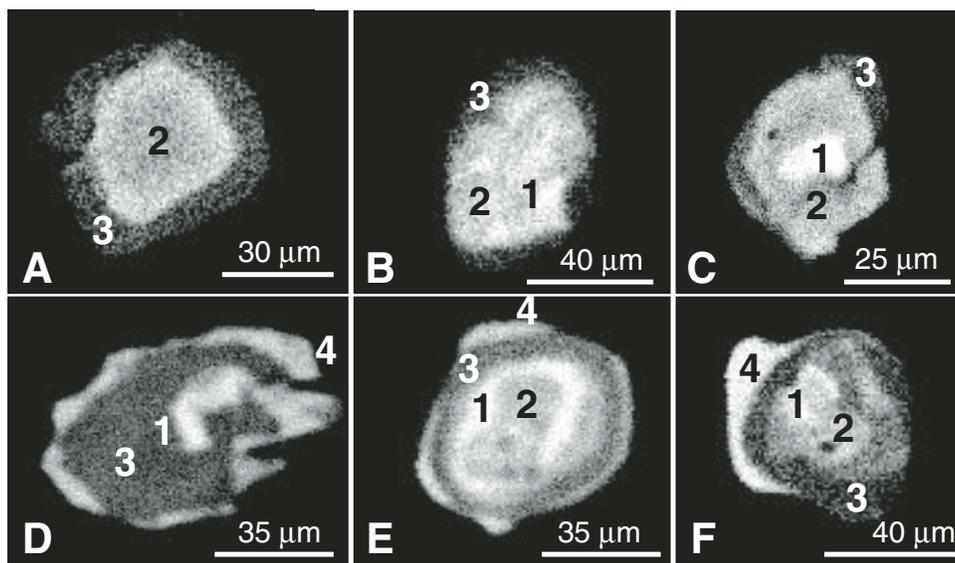

Figure 20. X-ray maps of Y distribution in monazite grains from migmatites in west-central New Hampshire reveal four generations of monazite growth (1–4), from Pyle and Spear (2003).

paragenesis of accessory minerals in metamorphic rocks. For example, monazite is known to grow at conditions around the staurolite isograd in rocks that previously contained allanite (e.g., Smith and Barreiro, 1990; Spear and Pyle, 2002; Wing et al., 2003; Janots et al., 2008), but it can also grow at very low grades in pelites low in Ca that do not produce allanite (e.g., Kingsbury et al., 1993). Monazite can also grow during crystallization of migmatite leucosomes (e.g., Pyle and Spear, 2003). However, beyond these broad generalizations, it is difficult to more precisely constrain the temperature and pressure of monazite growth. In a related vein, considerable progress is being made relating monazite growth to deformation events (e.g., Williams et al., 2007).

Zircon petrogenesis in metamorphic rocks is even more problematic. A notable exception is the study of Fraser et al. (1997), in which the growth of zircon was directly related to the replacement of garnet by cordierite during a high-temperature decompression reaction, with the garnet being the source of the zirconium for the zircon. Williams (2001) and Rubatto et al. (2001) studied the behavior of monazite and zircon in prograde metamorphic sequences in Australia. Attempts to incorporate accessory phases into thermodynamic modeling of metamorphic phase equilibria represent a promising new development (Kelsey et al., 2008; Spear and Pyle, 2010; Spear, 2010; Kelsey and Powell, 2011).

In addition, although analytical precision and accuracy are continually improving, there is a limit to the ability of geochronology to directly discriminate ages for any particular system. Even with an accuracy of 1%, a monazite dated at 500 Ma will carry an age uncertainty of ±5 Ma, and this uncertainty may, in fact, span the entire metamorphic episode.

Direct Measurement and Process Modeling—Kinetic Methods

An alternative approach utilizes the fact that kinetic processes, and diffusion in particular, are thermally activated (see discussion of kinetics earlier herein). Therefore, any process that is kinetically activated will occur most rapidly at the highest temperature.

Diffusion modeling of metamorphic systems has undergone tremendous development over the past 50 years. Diffusion is the underlying processes in the quantification of closure temperature (e.g., Dodson, 1974, 1986). Diffusion modeling of zoned minerals such as garnet has also been used successfully to infer cooling rates of metamorphic terranes (e.g., Lasaga et al., 1977; Lasaga, 1983; for an excellent review, see Chakraborty, 2008). The initial conditions in such studies are typically assumed to be that of a homogeneous garnet at the metamorphic peak. The boundary condition is then modeled as an exchange or net transfer reaction, and the diffusion profile is matched to a cooling rate (e.g., Spear, 2004). Studies such as these provide constraints on the cooling rate at temperatures above the closure temperatures for Ar/Ar or fission tracks, thus enabling a more complete *T-t* history to be determined for the exhumation path.

This approach has been extended in recent years to situations where the initial conditions are established before the metamorphic peak. Examples include metamorphic overgrowths on detrital minerals (e.g., apatite and garnet), an initial chemical zoning profile in a mineral such as garnet that can be predicted from phase equilibria calculations, or an interpretation of the compositional consequences of a prograde metamorphic reaction (i.e., one that results in a dramatic compositional change that is then modified by diffusion). These studies constrain the *T-t* history of a part of the *P-T* path near the metamorphic peak, including a part of the prograde path. It is interesting that several of these fairly recent studies have concluded that the metamorphic "episode" (i.e., near-peak conditions) happened over time scales shorter than 1 m.y.—quite a contrast to the previously assumed time scales of several tens of millions of years.

TOWARD THE FUTURE—MAJOR QUESTIONS IN METAMORPHIC PETROLOGY

It would be impossible to conclude such a retrospective without speculating on future directions for the field, although we certainly do not claim any access to a crystal ball. Advances in the past 50 years have been driven by many factors—the discovery of plate tectonics, developments of new analytical equipment, developments in thermodynamics and kinetics, new mineralogical discoveries, and many superb field-based studies—and it must be assumed that future developments will arise from similar quarters. Nevertheless, there are major thematic questions about metamorphic processes and the constraints they provide for our understanding of Earth evolution that will undoubtedly occupy future researchers. Next, we attempt to outline some of these questions.

Metamorphism and Earthquakes

Several researchers have recognized that metamorphic dehydration reactions associated with subduction of oceanic lithosphere could be the cause of transitory fluid pulses capable of triggering intermediate-depth seismic events (e.g., Hacker et al., 2003). John and Schenk (2006) and John et al. (2009) examined thermal and mechanical feedbacks involved in pseudotachylyte development in eclogitized rocks, in which the pseudotachylyte was interpreted as the petrological manifestation of seismic events. The efficacy of these mechanisms for earthquake generation is still an active area of study.

Metamorphism and Climate Change

Metamorphic processes have been identified as both a potential cause, and potential means of mitigation, of climate change, albeit on different time scales. Carbon dioxide released from metamorphosed carbonate and calc-silicate sequences by magmatic and tectonic processes have been identified as a possible contributing factor to long-term secular variations in climate

through Earth history (e.g., Selverstone and Gutzler, 1993; Kerrick and Caldeira, 1999; Kerrick, 2001). Skelton (2011) and Evans (2011) examined rates of fluid production during regional metamorphism and concluded that orogenically triggered fluxes may exceed background levels of silicate weathering, with the resultant potential to perturb CO_2 levels in the exosphere. On the more human time scale of anthropogenically caused climate change, several studies have highlighted the potential of industrial-scale simulation of metamorphic carbonation reactions in ultramafic rocks as a means to capture and store CO_2 produced from power plants that burn fossil fuels (e.g., Lackner et al., 1995; Metz et al., 2005; Hansen et al., 2005; Kelemen and Matter, 2008; Wilson et al., 2009; Zevenhoven et al., 2011; Power et al., 2013). One of the beauties of this development is the way in which it evolved from a somewhat esoteric subdiscipline of metamorphic petrology.

What Is the Driving Force for Metamorphism?

It is well established that P and T change during the evolution of a metamorphic rock, but is this the only driving force? Is fluid escape and infiltration a significant mechanism on a regional scale? Significant volumes of fluid are driven off by prograde metamorphic reactions: What are the fate and transport path of this fluid? What role does strain play? Do rocks only recrystallize under strain? It appears that strain enhances recrystallization, but what is the mechanism by which this happens and to what extent is it significant?

How Much Overstepping Occurs During Metamorphism?

Overstepping is necessary to nucleate new phases and to drive reactions, but what is the degree of overstepping, and how common is it? Is prograde metamorphism characterized by a continuous series of near-equilibrium steps, or is it more episodic, characterized by a few major recrystallization intervals separated by periods of nonreaction in which the energy of reaction is not sufficient to overcome kinetic barriers to progress? How can one tell from the texture or chemistry of minerals? Is overstepping more common in contact versus regional metamorphism because of faster heating rates, or is a more fundamental difference whether the rocks are being subjected to strain as they are recrystallizing? How rapid is metamorphic recrystallization?

What Are the Mechanisms by Which Metamorphic Rocks Recrystallize?

Minerals break down, and new ones grow, and chemical potential gradients are the general mechanism by which material moves around and gets reassembled, but how does this work on a nanoscale? What does a grain boundary look like? What is the composition of a grain boundary, and how does it vary with grain boundary structure and the identities of the host phases? How does the composition of material in a grain boundary change as external conditions (P and T) change? How rapidly do the compositions of grain boundaries equilibrate as conditions change? Is there anything that resembles a bulk fluid present in a metamorphic rock? Does it exist only in pockets or along grain boundaries? Are grain boundaries wet (have a bulk fluid along them), or are they characterized by the dispersion of OH groups?

How Does a Texture Form?

Textures form because minerals recrystallize in strain fields, but how does this happen on an atomistic scale? Can we develop quantitative models of texture formation that will provide a means to interpret deformation structures?

Tectonic Processes

What is the level of resolution of the time scales and rates of tectonic processes that metamorphic rocks can reveal? Are metamorphic rocks sufficiently homogenized that information at this resolution is lost? What are the limits on the time scales that can be resolved using either geochronology or kinetic theory?

What Does the Crust Undergoing Metamorphism Today Look Like?

Where are domains of Buchan and Barrovian metamorphism forming today? Can we image parts of the lower crust where partial melting may be affecting rheology and tectonic rates? Why is the lower crust conductive? Are fluids present in the lower crust?

How Do Fluids Escape?

Metamorphism involves the drying out of the crust. How does this happen? A back-of-the-envelope calculation indicates that massive amounts of fluid must exit from a crust undergoing metamorphism. Is this exfiltration pervasive or channeled? Do fluids exiting from one rock influence the metamorphism of another? If fluids are channeled, where do they end up? Do these fluids affect any major geochemical cycles?

Fluid Escape in Subduction Zones

What phases are responsible for fluid expulsion in subduction zones? Under what conditions does fluid release occur (near equilibrium, or only after considerable overstepping)? How do fluids flux into the mantle, and do they promote melting and generation of andesite volcanics? Does fluid release trigger deep earthquakes?

Metamorphism in Early Earth

Were there metamorphic rocks in the Hadean Eon? What did they look like, and what do they tell us about early Earth? Do they require a cycle of sedimentation (and presumably running water)? What do the oldest metamorphic rocks tell us about early

Earth and the advent of plate tectonics? How have metamorphic rocks evolved through time?

ACKNOWLEDGMENTS

REFERENCES CITED

Ague, J.J., and Nicolescu, S., 2014, Carbon dioxide released from subduction zones by fluid-mediated reactions: Nature Geoscience, v. 7, p. 355–360, doi:10.1038/ngeo2143.

Albee, A.L., 1965a, Phase equilibria in three assemblages of kyanite-zone pelitic schists, Lincoln Mtn. quadrangle, central Vermont: Journal of Petrology, v. 6, p. 246–301, doi:10.1093/petrology/6.2.246.

Albee, A.L., 1965b, A petrogenetic grid for the Fe-Mg silicates of pelitic schists: American Journal of Science, v. 263, p. 512–536, doi:10.2475/ajs.263.6.512.

Albee, A.L., 1968, Metamorphic zones in northern Vermont, *in* Zen, E.-a., White, W.S., Hadley, J.B., and Thompson, J.B., Jr., eds., Studies of Appalachian Geology, Northern and Maritime: New York, John Wiley, p. 329–341.

Albee, A.L., 1972, Metamorphism of pelitic schists: Reaction relations of chloritoid and staurolite: Geological Society of America Bulletin, v. 83, p. 3249–3268, doi:10.1130/0016-7606(1972)83[3249:MOPSRR]2.0.CO;2.

Althaus, E., 1967, The triple point andalusite-sillimanite-kyanite; an experimental and petrologic study: Contributions to Mineralogy and Petrology, v. 16, no. 1, p. 29–44, doi:10.1007/BF00371606.

Anderson, G.M., 1967, Specific volumes and fugacities of water, App. 1, *in* Barnes, H.L., ed., Geochemistry of Hydrothermal Ore Deposits: New York, Holt, Rinehart and Winston, p. 632–635.

Andrehs, G., and Heinrich, W., 1998, Experimental determination of REE distributions between monazite and xenotime: Potential for temperature-calibrated geochronology: Chemical Geology, v. 149, p. 83–96, doi:10.1016/S0009-2541(98)00039-4.

Archibald, D.A., Glover, J.K., Price, R.A., Farrar, E., and Carmichael, D.M., 1983, Geochronology and tectonic implications of magmatism and metamorphism, southern Kootenay Arc and neighbouring regions, southeastern British Columbia: Part I. Jurassic to mid-Cretaceous: Canadian Journal of Earth Sciences, v. 20, p. 1891–1913, doi:10.1139/e83-178.

Arzi, A.A., 1978, Critical phenomena in the rheology of partially melted rocks: Tectonophysics, v. 44, p. 173–184, doi:10.1016/0040-1951(78)90069-0.

Atherton, M.P., and Edmunds, W.M., 1966, An electron microprobe study of some zoned garnets from metamorphic rocks: Earth and Planetary Science Letters, v. 1, p. 185–193, doi:10.1016/0012-821X(66)90066-5.

Austrheim, H., 1987, Eclogitization of lower crustal granulites by fluid migration through shear zones: Earth and Planetary Science Letters, v. 81, p. 221–232, doi:10.1016/0012-821X(87)90158-0.

Balashov, V.N., and Yardley, B.W.D., 1998, Modeling metamorphic fluid flow with reaction-compaction permeability feedbacks: American Journal of Science, v. 298, p. 441–470, doi:10.2475/ajs.298.6.441.

Baumgartner, L.P., and Ferry, J.M., 1991, A model for coupled fluid-flow and mixed-volatile mineral reactions with applications to regional metamorphism: Contributions to Mineralogy and Petrology, v. 106, p. 273–285, doi:10.1007/BF00324557.

Baxter, E.F., Ague, J.J., and DePaolo, D.J., 2002, Prograde temperature-time evolution in the Barrovian type-locality constrained by Sm/Nd garnet ages from Glen Clova, Scotland: Journal of the Geological Society, London, v. 159, p. 71–82, doi:10.1144/0016-76901013.

Beard, J.S., and Lofgren, G.E., 1991, Dehydration melting and water-saturated melting of basaltic and andesitic greenstones and amphibolites at 1, 3, and 6.9 kbar: Journal of Petrology, v. 32, p. 365–401, doi:10.1093/petrology/32.2.365.

Beaumont, C., Jamieson, R.A., Nguyen, M.H., and Lee, B., 2001, Himalayan tectonics explained by extrusion of low viscosity crustal channel coupled to focused surface denudation: Nature, v. 414, p. 738–742, doi:10.1038/414738a.

Bell, P.M., 1963, Aluminum silicate system: Experimental determination of the triple point: Science, v. 139, p. 1055–1056.

Bell, T.H., 1985, Deformation partitioning and porphyroblast rotation in metamorphic rocks: A radical reinterpretation: Journal of Metamorphic Geology, v. 3, p. 109–118, doi:10.1111/j.1525-1314.1985.tb00309.x.

Bell, T.H., and Bruce, M.D., 2007, Progressive deformation partitioning and deformation history: Evidence from millipede structures: Journal of Structural Geology, v. 29, p. 18–35, doi:10.1016/j.jsg.2006.08.005.

Bell, T.H., and Hayward, N., 1991, Episodic metamorphic reactions during orogenesis—The control of deformation partitioning on reaction sites and reaction duration: Journal of Metamorphic Geology, v. 9, p. 619–640, doi:10.1111/j.1525-1314.1991.tb00552.x.

Bell, T.H., and Johnson, S.E., 1989, Porphyroblast inclusion trails: The key to orogenesis: Journal of Metamorphic Geology, v. 7, p. 279–310, doi:10.1111/j.1525-1314.1989.tb00598.x.

Bell, T.H., Johnson, S.E., Davis, B., Forde, A., Hayward, N., and Wilkins, C., 1992, Porphyroblast inclusion-trail orientation data: *eppure-non-son-girate*!: Journal of Metamorphic Geology, v. 10, no. 3, p. 295–307, doi:10.1111/j.1525-1314.1992.tb00084.x.

Bence, A.E., and Albee, A.L., 1968, Empirical correction factors for the electron microanalysis of silicates and oxides: The Journal of Geology, v. 76, p. 382–403, doi:10.1086/627339.

Berman, R.G., 1988, Internally-consistent thermodynamic data for minerals in the system $Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2$: Journal of Petrology, v. 29, p. 445–522, doi:10.1093/petrology/29.2.445.

Berman, R.G., 1991, Thermobarometry using multi-equilibrium calculations; a new technique, with petrological applications: Canadian Mineralogist, v. 29, p. 833–855.

Berman, R.G., and Brown, T.H., 1992, Thermobarometry with estimation of equilibration state [TWEEQU]; a software package for IBM or compatible personal computers: Calgary, Alberta, Geological Survey of Canada Open File Report 2534.

Beyssac, O., Goffe, B., Chopin, C., and Rouzaud, J.N., 2002, Raman spectra of carbonaceous material in metasediments: A new geothermometer: Journal of Metamorphic Geology, v. 20, p. 859–871, doi:10.1046/j.1525-1314.2002.00408.x.

Bickle, M.J., and Archibald, N.J., 1984, Chloritoid and staurolite stability: Implications for metamorphism in the Archean Yilgarn block, western Australia: Journal of Metamorphic Geology, v. 2, p. 179–203, doi:10.1111/j.1525-1314.1984.tb00295.x.

Bohlen, S.R., 1987, Pressure-temperature-time paths and a tectonic model for the evolution of granulites: The Journal of Geology, v. 95, p. 617–632, doi:10.1086/629159.

Bohlen, S.R., Montana, A.L., and Kerrick, D.M., 1991, Precise determinations of the equilibria kyanite = sillimanite and kyanite = andalusite and a revised triple point for Al_2SiO_5 polymorphs: American Journal of Science, v. 76, p. 677–680.

Bonnet, A.-L., and Corriveau, L., 2007, Alteration vectors to metamorphosed hydrothermal systems in gneissic terranes, *in* Goodfellow, W.D., ed., Mineral Deposits of Canada—A Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods: Geological Association of Canada, Mineral Deposits Division, Special Publication 5, p. 1035–1049.

The metamorphosis of metamorphic petrology

Bowen, N.L., 1940, Progressive metamorphism of siliceous limestone and dolomite: The Journal of Geology, v. 48, no. 3, p. 225–274, doi:10.1086/624885.

Bowman, A.F., 1975, An Investigation of Al_2SiO_5 Phase Equilibrium Utilizing the Scanning Electron Microscope [Ph.D. thesis]: Eugene, University of Oregon, 80 p.

Brady, J.B., 1975, Reference frames and diffusion coefficients: American Journal of Science, v. 275, no. 8, p. 954–983, doi:10.2475/ajs.275.8.954.

Brady, J.B., 1977, Metasomatic zones in metamorphic rocks: Geochimica et Cosmochimica Acta, v. 41, p. 113–125, doi:10.1016/0016-7037(77)90191-0.

Brady, J.B., 1988, The role of volatiles in the thermal history of metamorphic terranes: Journal of Petrology, v. 29, p. 1187–1213, doi:10.1093/petrology/29.6.1187.

Brown, E.H., 1975, A petrogenetic grid for reactions producing biotite and other Al-Fe-Mg silicates in the greenschist facies: Journal of Petrology, v. 16, p. 258–271.

Brown, G.C., and Fyfe, W.S., 1971, Kyanite-andalusite equilibrium: Contributions to Mineralogy and Petrology, v. 33, no. 3, p. 227–231, doi:10.1007/BF00374065.

Brown, M., 1993, *P-T-t* evolution of orogenic belts and the causes of regional metamorphism: Journal of the Geological Society, London, v. 150, no. 2, p. 227–241, doi:10.1144/gsjgs.150.2.0227.

Brown, M., 1994, The generation, segregation, ascent and emplacement of granite magma—The migmatite-to-crustally-derived-granite connection in thickened orogens: Earth-Science Reviews, v. 36, p. 83–130, doi:10.1016/0012-8252(94)90009-4.

Brown, M., 2001, Orogeny, migmatites and leucogranites: A review: Journal of Earth System Science, v. 110, p. 313–336.

Brown, M., 2006, Duality of thermal regimes is the distinctive characteristic of plate tectonics since the Neoarchean: Geology, v. 34, p. 961–964, doi:10.1130/G22853A.1.

Brown, M., 2007, Metamorphic conditions in orogenic belts: A record of secular change: International Geology Review, v. 49, p. 193–234, doi:10.2747/0020-6814.49.3.193.

Brown, M., 2008, Characteristic thermal regimes of plate tectonics and their metamorphic imprint throughout Earth history, *in* Condie, K., and Pease, V., eds., When Did Plate Tectonics Begin on Planet Earth?: Geological Society of America Special Paper 440, p. 97–128, doi:10.1130/2008.2440(05).

Brown, M., 2010, Paired metamorphic belts revisited: Gondwana Research, v. 18, p. 46–59, doi:10.1016/j.gr.2009.11.004.

Brown, M., 2014, The contribution of metamorphic petrology to understanding lithosphere evolution and geodynamics: Geoscience Frontiers, v. 5, p. 553–569, doi:10.1016/j.gsf.2014.02.005.

Brown, M., Rushmer, T., and Sawyer, E.W., 1995a, Introduction to special section: Mechanisms and consequences of melt segregation from crustal protoliths: Journal of Geophysical Research, v. 100, p. 15,551–15,563, doi:10.1029/95JB01253.

Brown, M., Averkin, Y.A., McLellan, E.L., and Sawyer, E.W., 1995b, Melt segregation in migmatites: Journal of Geophysical Research, v. 100, no. B8, p. 15,655–15,679, doi:10.1029/95JB00517.

Brown, T.H., and Skinner, B.J., 1974, Theoretical prediction of equilibrium phase assemblages in multicomponent systems: American Journal of Science, v. 274, p. 961–986, doi:10.2475/ajs.274.9.961.

Burnham, C.W., Holloway, J.R., and Davis, N.F., 1969, Thermodynamic Properties of Water to 1000 C and 10,000 Bars: Geological Society of America Special Paper 132, 96 p.

Carlson, W.D., 1989, The significance of intergranular diffusion to the mechanisms and kinetics of porphyroblast crystallization: Contributions to Mineralogy and Petrology, v. 103, p. 1–24, doi:10.1007/BF00371361.

Carlson, W.D., and Denison, C., 1992, Mechanisms of porphyroblast crystallization: Results from high-resolution computed X-ray tomography: Science, v. 257, p. 1236–1239, doi:10.1126/science.257.5074.1236.

Carlson, W.D., and Rosenfeld, J.L., 1981, Optical determination of topotactic aragonite-calcite growth kinetics: Metamorphic implications: The Journal of Geology, v. 89, p. 615–638, doi:10.1086/628626.

Carlson, W.D., Pattison, D.R.M., and Caddick, M.J., 2015, Beyond the equilibrium paradigm: How consideration of kinetics enhances metamorphic interpretation: The American Mineralogist, v. 100, doi:10.2138/am-2015-5097.

Carmichael, D.M., 1969, On the mechanism of prograde metamorphic reactions in quartz-bearing pelitic rocks: Contributions to Mineralogy and Petrology, v. 20, p. 244–267, doi:10.1007/BF00377479.

Carmichael, D.M., 1978, Metamorphic bathozones and bathograds: A measure of the depth of post-metamorphic uplift and erosion on the regional scale: American Journal of Science, v. 278, p. 769–797, doi:10.2475/ajs.278.6.769.

Carswell, D.A., and Compagnoni, R., eds., 2003, Ultrahigh Pressure Metamorphism: Chantilly, Virginia, Mineralogical Society of America, European Mineralogical Union Notes 5, 508 p.

Cashman, K.V., and Ferry, J.M., 1988, Crystal size distribution (CDS) in rocks and the kinetics and dynamics of crystallization: III. Metamorphic crystallization: Contributions to Mineralogy and Petrology, v. 99, p. 401–415, doi:10.1007/BF00371933.

Cesare, B., Ferrero, S., Salviolo-Mariani, E., Pedron, D., and Cavallo, A., 2009, "Nanogranite" and glassy inclusions: The anatectic melt in migmatites and granulites: Geology, v. 37, p. 627–630, doi:10.1130/G25759A.1.

Chacko, T., Cole, D.R., and Horita, J., 2001, Equilibrium oxygen, hydrogen and carbon isotope fractionation factors applicable to geologic systems, *in* Valley, J.W., and Cole, D.R., eds., Stable Isotope Geochemistry: Reviews in Mineralogy Volume 43: Washington, D.C., Mineralogical Society of America, p. 1–81, doi:10.2138/gsrmg.43.1.1.

Chakraborty, S., 2008, Diffusion in solid silicates: A tool to track timescales of processes comes of age: Annual Review of Earth and Planetary Sciences, v. 36, p. 153–190, doi:10.1146/annurev.earth.36.031207.124125.

Chakraborty, S., and Ganguly, J., 1992, Cation diffusion in aluminosilicate garnets—Experimental determination in spessartine-almandine diffusion couples, evaluation of effective binary diffusion coefficients, and applications: Contributions to Mineralogy and Petrology, v. 111, p. 74–86, doi:10.1007/BF00296579.

Chatterjee, N.D., and Flux, S., 1986, Thermodynamic mixing properties of muscovite-paragonite crystalline solutions at high temperatures and pressures, and their geological applications: Journal of Petrology, v. 27, p. 677–693, doi:10.1093/petrology/27.3.677.

Chatterjee, N.D., and Froese, E., 1975, A thermodynamic study of the pseudo-binary join muscovite-paragonite in the system $KAlSi_3O_8$-$NaAlSi_3O_8$-Al_2O_3-SiO_2-H_2O: The American Mineralogist, v. 60, p. 985–993.

Cheney, J.T., and Guidotti, C.V., 1979, Muscovite + plagioclase equilibria in sillimanite + quartz bearing metapelites, Puzzle Mountain area, northwest Maine: American Journal of Science, v. 279, p. 411–434, doi:10.2475/ajs.279.4.411.

Cheney, J.T., Webb, A.A.G., Coath, C.D., and McKeegan, K.D., 2004, In situ ion microprobe [207]Pb/[206]Pb dating of monazite from Precambrian metamorphic suites, Tobacco Root Mountains, Montana, *in* Brady, J.B., Burger, H.R., Cheney, J.T., and Harms, T.A., eds., Precambrian Geology of the Tobacco Root Mountains, Montana: Geological Society of America Special Paper 377, p. 151–179.

Chopin, C., 1984, Coesite and pure pyrope in high-grade blueschists of the western Alps; a first record and some consequences: Contributions to Mineralogy and Petrology, v. 86, p. 107–118, doi:10.1007/BF00381838.

Chopin, C., 2003, Ultrahigh-pressure metamorphism: Tracing continental crust into the mantle: Earth and Planetary Science Letters, v. 212, p. 1–14, doi:10.1016/S0012-821X(03)00261-9.

Christensen, J.N., Rosenfeld, J.L., and De Paolo, D.J., 1989, Rates of tectonometamorphic processes from rubidium and strontium isotopes in garnet: Science, v. 244, p. 1465–1469, doi:10.1126/science.244.4911.1465.

Clark, S.P., 1961, A redetermination of equilibrium relations between kyanite and sillimanite: American Journal of Science, v. 259, p. 641–650, doi:10.2475/ajs.259.9.641.

Clark, S.P., Robertson, E.C., and Birch, A.F., 1957, Experimental determination of kyanite-sillimanite equilibrium relations at high temperatures and pressures: American Journal of Science, v. 255, p. 628–640, doi:10.2475/ajs.255.9.628.

Clarke, D.B., McKenzie, C.B., and Muecke, G.K., 1976, Magmatic andalusite from the South Mountain Batholith, Nova Scotia: Contributions to Mineralogy and Petrology, v. 56, p. 279–287, doi:10.1007/BF00466826.

Clarke, D.B., Dorais, M., and 34 others, 2005, Occurrence and origin of andalusite in peraluminous felsic igneous rocks: Journal of Petrology, v. 46, p. 441–472, doi:10.1093/petrology/egh083.

Cloos, M., 1982, Flow mélanges: Numerical modeling and geologic constraints on their origin in the Franciscan subduction complex, California: Geological Society of America Bulletin, v. 93, p. 330–345, doi:10.1130/0016-7606(1982)93<330:FMNMAG>2.0.CO;2.

Cloos, M., 1985, Thermal evolution of convergent plate margins: Thermal modeling and reevaluation of isotopic Ar-ages for blueschists in the Franciscan

complex, California: Tectonics, v. 4, no. 5, p. 421–433, doi:10.1029/TC004i005p00421.

Compston, W., Williams, I.S., and Meyer, C., 1984, U-Pb geochronology of zircons from Lunar Breccia 73217 using a sensitive, high mass resolution ion microprobe: Proceedings of the 14th Lunar and Planetary Science Conference, Part 2: Journal of Geophysical Research, v. 89, p. B525–B534, doi:10.1029/JB089iS02p0B525.

Connolly, J.A.D., 2009, The geodynamic equation of state: What and how: Geochemistry Geophysics Geosystems, v. 10, no. 10, doi:10.1029/2009GC002540.

Connolly, J.A.D., and Petrini, K., 2002, An automated strategy for calculation of phase diagram sections and retrieval of rock properties as a function of physical conditions: Journal of Metamorphic Geology, v. 20, p. 697–708, doi:10.1046/j.1525-1314.2002.00398.x.

Davies, J.H., and von Blanckenburg, F., 1995, Slab breakoff: A model of lithosphere detachment and its test in the magmatism and deformation of collisional orogens: Earth and Planetary Science Letters, v. 129, p. 85–102, doi:10.1016/0012-821X(94)00237-S.

de Capitani, C., and Brown, T.H., 1987, The computation of chemical equilibrium in complex systems containing non-ideal solutions: Geochimica et Cosmochimica Acta, v. 51, p. 2639–2652, doi:10.1016/0016-7037(87)90145-1.

de Capitani, C., and Petrakakis, K., 2010, The computation of equilibrium assemblage diagrams with Theriak/Domino software: The American Mineralogist, v. 95, p. 1006–1016, doi:10.2138/am.2010.3354.

Diener, J.F.A., Powell, R., White, R.W., and Holland, T.J.B., 2007, A new thermodynamic model for clino- and orthoamphiboles in the system Na_2O-CaO-FeO-MgO-Al_2O_3-SiO_2-H_2O-O: Journal of Metamorphic Geology, v. 25, no. 6, p. 631–656, doi:10.1111/j.1525-1314.2007.00720.x.

Diener, J.F.A., Powell, R., and White, R.W., 2008, Quantitative phase petrology of cordierite-anthophyllite gneisses and related rocks: Journal of Metamorphic Geology, v. 26, p. 795–814, doi:10.1111/j.1525-1314.2008.00791.x.

Dodson, M.H., 1974, Kinetic processes and thermal history of rocks: Carnegie Institution of Washington Yearbook, v. 74, p. 210–217.

Dodson, M.H., 1986, Closure profiles in cooling systems, *in* Freer, R., and Dennis, P.F., eds., Materials Science Forum, Volume 7: Aedermannsdorf, Switzerland, Trans Tech Publications, p. 145–153.

Ellis, D.J., Sheraton, J.W., England, R.N., and Dallwitz, W.B., 1980, Osumilite-sapphirine-quartz granulites from Enderby Land, Antarctica—Mineral assemblages and reactions: Contributions to Mineralogy and Petrology, v. 72, p. 123–143, doi:10.1007/BF00399473.

Engi, M., 1983, Equilibria involving Al-Cr spinel: Mg-Fe exchange with olivine; experiments, thermodynamic analysis and consequences for geothermometry: American Journal of Science, v. 284, p. 29–71.

England, P.C., and Holland, T.J.B., 1979, Archimedes and the Tauern eclogites: The role of buoyancy in the preservation of exotic eclogite blocks: Earth and Planetary Science Letters, v. 44, p. 287–294, doi:10.1016/0012-821X(79)90177-8.

England, P.C., and Richardson, S.W., 1977, The influence of erosion upon the mineral facies of rocks from different metamorphic environments: Journal of the Geological Society, London, v. 134, p. 201–213, doi:10.1144/gsjgs.134.2.0201.

England, P.C., and Thompson, A.B., 1984, Pressure-temperature-time paths of regional metamorphism: Part I. Heat transfer during the evolution of regions of thickened continental crust: Journal of Petrology, v. 25, p. 894–928, doi:10.1093/petrology/25.4.894.

Ernst, W.G., 1963, Petrogenesis of glaucophane schists: Journal of Petrology, v. 4, no. 1, p. 1–30, doi:10.1093/petrology/4.1.1.

Ernst, W.G., 1970, Tectonic contact between the Franciscan mélange and the Great Valley sequence—Crustal expression of a late Mesozoic Benioff zone: Journal of Geophysical Research, v. 75, no. 5, p. 886–901, doi:10.1029/JB075i005p00886.

Ernst, W.G., 1971a, Do mineral parageneses reflect unusually high-pressure conditions of Franciscan metamorphism?: American Journal of Science, v. 270, p. 81–108, doi:10.2475/ajs.270.2.81.

Ernst, W.G., 1971b, Metamorphic zonations on presumably subducted lithospheric plates from Japan, California and the Alps: Contributions to Mineralogy and Petrology, v. 34, p. 43–59, doi:10.1007/BF00376030.

Ernst, W.G., 1972, Occurrence and mineralogic evolution of blueschist belts with time: American Journal of Science, v. 272, p. 657–668, doi:10.2475/ajs.272.7.657.

Ernst, W.G., 1973a, Blueschist metamorphism and *P-T* regimes in active subduction zones: Tectonophysics, v. 17, p. 255–272, doi:10.1016/0040-1951(73)90006-1.

Ernst, W.G., 1973b, Interpretive synthesis of metamorphism in the Alps: Geological Society of America Bulletin, v. 84, p. 2053–2078, doi:10.1130/0016-7606(1973)84<2053:ISOMIT>2.0.CO;2.

Ernst, W.G., 1976a, Mineral chemistry of eclogites and related rocks from the Voltri Group, western Liguria, Italy: Schweizerische Mineralogische und Petrographische Mitteilungen, v. 56, p. 293–343.

Ernst, W.G., 1976b, Petrologic Phase Equilibria: San Francisco, California, W.H. Freeman and Company, 333 p.

Ernst, W.G., 1988, Tectonic history of subduction zones inferred from retrograde blueschist *P-T* paths: Geology, v. 16, p. 1081–1084, doi:10.1130/0091-7613(1988)016<1081:THOSZI>2.3.CO;2.

Ernst, W.G., and Seki, Y., 1967, Petrologic comparison of the Franciscan and Sanbagawa metamorphic terranes: Tectonophysics, v. 4, no. 4–6, p. 463–478, doi:10.1016/0040-1951(67)90011-X.

Essene, E.J., 1982, Geologic thermometry and barometry, *in* Ferry, J.M., ed., Characterization of Metamorphism through Mineral Equilibria, Volume 10: Washington, D.C., Mineralogical Society of America, p. 153–206.

Essene, E.J., 1989, The current status of thermobarometry in metamorphic rocks, *in* Daly, J.S., Cliff, R.A., and Yardley, B.W.D., eds., Evolution of Metamorphic Belts: Oxford, Blackwell Scientific Publications, p. 1–44, doi:10.1144/GSL.SP.1989.043.01.02.

Etheridge, M.A., Wall, V.J., and Vernon, R.H., 1983, The role of the fluid phase during regional metamorphism and deformation: Journal of Metamorphic Geology, v. 1, p. 205–226, doi:10.1111/j.1525-1314.1983.tb00272.x.

Etheridge, M.A., Wall, V.J., Cox, S.F., and Vernon, R.H., 1984, High fluid pressures during regional metamorphism and deformation: Implications for mass transport and deformation mechanisms: Journal of Geophysical Research, v. 89, no. B6, p. 4344–4358, doi:10.1029/JB089iB06p04344.

Eugster, H.P., 1957, Heterogeneous reactions involving oxidation and reduction at high pressures and temperatures: The Journal of Chemical Physics, v. 26, p. 1760–1761, doi:10.1063/1.1743626.

Eugster, H.P., 1959, Reduction and oxidation in metamorphism, *in* Ableson, P.H., ed., Researches in Geochemistry: New York, Wiley, p. 397–426.

Eugster, H.P., and Wones, D.R., 1962, Stability relations of the ferruginous biotite, annite: Journal of Petrology, v. 3, p. 82–125, doi:10.1093/petrology/3.1.82.

Eugster, H.P., Albee, A.L., Bence, A.E., Thompson, J.B., Jr., and Waldbaum, D.R., 1972, The two-phase region and excess mixing properties of paragonite-muscovite crystalline solutions: Journal of Petrology, v. 13, p. 147–179, doi:10.1093/petrology/13.1.147.

Evans, B.W., and Guidotti, C.V., 1966, The sillimanite-potash feldspar isograd in western Maine, U.S.A.: Contributions to Mineralogy and Petrology, v. 12, p. 25–62, doi:10.1007/BF02651127.

Evans, K.A., 2011, Metamorphic carbon fluxes: How much and how fast?: Geology, v. 39, p. 95–96, doi:10.1130/focus012011.1.

Facq, S., Daniel, I., and Sverjensky, D.A., 2014, Aqueous carbonate speciation in equilibrium with aragonite under subduction zone conditions: Geochimica et Cosmochimica Acta, v. 132, p. 375–390, doi:10.1016/j.gca.2014.01.030.

Farquhar, J., Chacko, T., and Frost, B.R., 1993, Strategies for high-temperature oxygen isotope thermometry: A worked example from the Laramie anorthosite complex, Wyoming, USA: Earth and Planetary Science Letters, v. 117, p. 407–422, doi:10.1016/0012-821X(93)90093-O.

Fay, C., Bell, T.H., and Hobbs, B.E., 2008, Porphyroblast rotation versus nonrotation: Conflict resolution!: Geology, v. 36, p. 307–310, doi:10.1130/G24499A.1.

Fay, C., Bell, T.H., and Hobbs, B.E., 2009, Porphyroblast rotation versus nonrotation: Conflict resolution! [Reply]: Geology, v. 37, no. 2, doi:10.1130/G25630Y.1.

Ferry, J.M., 1980, A case study of the amount and distribution of heat and fluid during metamorphism: Contributions to Mineralogy and Petrology, v. 71, p. 373–385, doi:10.1007/BF00374708.

Ferry, J.M., ed., 1982, Characterization of Metamorphism through Mineral Equilibria: Reviews in Mineralogy Volume 10 (Ribbe, P.H., series ed.): Washington, D.C., Mineralogical Society of America, 397 p.

Ferry, J.M., 1983, On the control of temperature, fluid composition, and reaction progress during metamorphism: American Journal of Science, v. 283-A, p. 201–232.

Ferry, J.M., 1986, Reaction progress: A monitor of fluid-rock interaction during metamorphic and hydrothermal events, *in* Walther, J.V., and Wood, B.J.,

The metamorphosis of metamorphic petrology

eds., Fluid-Rock Interactions during Metamorphism: New York, Springer Verlag, p. 60–88, doi:10.1007/978-1-4612-4896-5_3.

Ferry, J.M., 1987, Metamorphic hydrology at 13-km depth and 400–550°C: The American Mineralogist, v. 72, p. 39–58.

Ferry, J.M., 1988, Infiltration-driven metamorphism in northern New England, USA: Journal of Petrology, v. 29, p. 1121–1159, doi:10.1093/petrology/29.6.1121.

Ferry, J.M., 1991, Dehydration and decarbonation reactions as a record of fluid infiltration, *in* Kerrick, D.M., ed., Contact Metamorphism: Reviews in Mineralogy Volume 26: Washington, D.C., Mineralogical Society of America, p. 351–394.

Ferry, J.M., 1996, Three novel isograds in metamorphosed siliceous dolomites from the Ballachulish aureole, Scotland: The American Mineralogist, v. 81, p. 485–494, doi:10.2138/am-1996-3-422.

Ferry, J.M., 2000, Patterns of mineral occurrence in metamorphic rocks: The American Mineralogist, v. 85, p. 1573–1588, doi:10.2138/am-2000-11-1201.

Ferry, J.M., and Spear, F.S., 1978, Experimental calibration of the partitioning of Fe and Mg between biotite and garnet: Contributions to Mineralogy and Petrology, v. 66, p. 113–117, doi:10.1007/BF00372150.

Fitzsimons, I.C.W., and Harley, S.L., 1994, The influence of retrograde cation exchange on granulite *P-T* estimates and a convergence technique for the recovery of peak metamorphic conditions: Journal of Petrology, v. 35, p. 543–576, doi:10.1093/petrology/35.2.543.

Foster, C.T., 1999, Forward modeling of metamorphic textures: Canadian Mineralogist, v. 37, p. 415–429.

Franklin, J.M., 1984, Characteristics of alteration associated with Precambrian massive sulfide deposits, *in* Morton, R.L., and Groves, D.A., eds., Volcanic Rocks, Hydrothermal Alteration and Associated Massive Sulfide and Gold Deposits: Duluth, University of Minnesota–Duluth, Short Course Notes, p. 92–105.

Frantz, J.D., and Mao, H.K., 1979, Bimetasomatism resulting from intergranular diffusion: II. Prediction of multimineralic zone sequences: American Journal of Science, v. 279, p. 312–323, doi:10.2475/ajs.279.3.302.

Fraser, G., Ellis, D., and Eggins, S., 1997, Zirconium abundance in granulite-facies minerals, with implications for zircon geochronology in high-grade rocks: Geology, v. 25, p. 607–610, doi:10.1130/0091-7613(1997)025<0607:ZAIGFM>2.3.CO;2.

Froese, E., and Gasparrini, E., 1975, Metamorphic zones in the Snow Lake area, Manitoba: Canadian Mineralogist, v. 13, Part 2, p. 162–167.

Frost, B.R., and Chako, T., 1989, The granulite uncertainty principle: Limitations on thermobarometry in granulites: The Journal of Geology, v. 97, p. 435–450, doi:10.1086/629321.

Frost, B.R., Mavrogenes, J.A., and Tomkins, A.G., 2002, Partial melting of sulfide ore deposits during medium- and high-grade metamorphism: Canadian Mineralogist, v. 40, p. 1–18, doi:10.2113/gscanmin.40.1.1.

Furlong, K.P., Hanson, R.B., and Bowers, J.R., 1991, Modeling thermal regimes, *in* Kerrick, D.M., ed., Contact Metamorphism: Reviews in Mineralogy Volume 26: Washington, D.C., Mineralogical Society of America, p. 437–506.

Fyfe, W.S., and Turner, F.J., 1966, Reappraisal of the metamorphic facies concept: Contributions to Mineralogy and Petrology, v. 12, p. 354–364, doi:10.1007/BF00616820.

Ghent, E.D., 1976, Plagioclase-garnet-Al$_2$SiO$_5$ quartz: A potential geobarometer-geothermometer: The American Mineralogist, v. 61, p. 710–714.

Gibbs, J.W., 1928, The Scientific Papers of J. Willard Gibbs. Volume 1. Thermodynamics: New Haven, Connecticut, Yale University Press, 434 p.

Gilotti, J.A., 2013, The realm of ultrahigh-pressure metamorphism: Elements, v. 9, p. 255–260.

Goldschmidt, V.M., 1912, Die Gesetze der Gesteinsmetamorphose: Norsk Videnskapsselskaps Skrifter I. Matematisk-Naturvidenskapelig Klasse, v. 22, 16 p.

Gordon, T.M., 1992, Generalized thermobarometry: Solution of the inverse chemical equilibrium problem using data for individual species: Geochimica et Cosmochimica Acta, v. 56, p. 1793–1800, doi:10.1016/0016-7037(92)90310-F.

Gratz, R., and Heinrich, W., 1997, Monazite-xenotime thermobarometry: Experimental calibration of the miscibility gap in the system CePO$_4$-YPO$_4$: The American Mineralogist, v. 82, p. 772–780, doi:10.2138/am-1997-7-816.

Greenwood, H.J., 1975a, Buffering of pore fluids by metamorphic reactions: American Journal of Science, v. 275, p. 573–593, doi:10.2475/ajs.275.5.573.

Greenwood, H.J., 1975b, Thermodynamically valid projections of extensive phase relationships: The American Mineralogist, v. 60, p. 1–8.

Greenwood, H.J., 1976, Metamorphism at moderate temperatures and pressures, *in* Bailey, D.K., and Macdonald, R., eds., The Evolution of the Crystalline Rocks: New York, Academic Press, p. 187–259.

Guidotti, C.V., 1970, The mineralogy and petrology of the transition from lower to upper sillimanite zone in the Oquossoc area, Maine: Journal of Petrology, v. 11, p. 277–336, doi:10.1093/petrology/11.2.277.

Guidotti, C.V., 1974, Transition from staurolite to sillimanite zone, Rangely quadrangle, Maine: Geological Society of America Bulletin, v. 85, p. 475–490, doi:10.1130/0016-7606(1974)85<475:TFSTSZ>2.0.CO;2.

Guidotti, C.V., Cheney, J.T., and Conatore, P.D., 1975, Coexisting cordierite + biotite + chlorite from the Rumford quadrangle, Maine: Geology, v. 3, p. 147–148, doi:10.1130/0091-7613(1975)3<147:CCBCFT>2.0.CO;2.

Hacker, B.R., Peacock, S.M., Abers, G.A., and Holloway, S.D., 2003, Subduction factory 2. Are intermediate-depth earthquakes in subducting slabs linked to metamorphic dehydration reactions?: Journal of Geophysical Research, v. 108, no. B1, 2030, doi:10.1029/2001JB001129.

Hacker, B.R., Gerva, T.V., and Gilotti, J.A., 2013, Formation and exhumation of ultrahigh-pressure terranes: Elements (Quebec), v. 9, p. 289–293, doi:10.2113/gselements.9.4.289.

Hansen, L.D., Dipple, G.M., Gordon, T.M., and Kellett, D.A., 2005, Carbonated serpentinite (listwanite) at Atlin, British Columbia: A geological analogue to carbon dioxide sequestration: Canadian Mineralogist, v. 43, p. 225–239, doi:10.2113/gscanmin.43.1.225.

Harley, S.L., 1985, Garnet-orthopyroxene bearing granulites from Enderby Land, Antarctica: Metamorphic pressure-temperature-time evolution of the Archaean Napier complex: Journal of Petrology, v. 26, p. 819–856, doi:10.1093/petrology/26.4.819.

Harley, S.L., 1989, The origins of granulites: A metamorphic perspective: Geological Magazine, v. 126, p. 215–247, doi:10.1017/S0016756800022330.

Harley, S.L., 1998, On the occurrence and characterization of ultrahigh-temperature crustal metamorphism, *in* Treloar, P.J., and O'Brien, P., eds., What Drives Metamorphism and Metamorphic Reactions?: Geological Society, London, Special Publication 138, p. 81–107, doi:10.1144/GSL.SP.1996.138.01.06.

Harley, S.L., 2008, Refining the *P-T* records of UHT crustal metamorphism: Journal of Metamorphic Geology, v. 26, p. 125–154, doi:10.1111/j.1525-1314.2008.00765.x.

Harrison, T.M., and Clarke, G.K.C., 1979, A model of the thermal effects of igneous intrusion and uplift as applied to Quottoon pluton, British Columbia: Canadian Journal of Earth Sciences, v. 16, no. 3, Part 1, p. 411–420.

Harrison, T.M., McKeegan, K.D., and Le Fort, P., 1995, Detection of inherited monazite in the Manaslu leucogranite by [208]Pb/[232]Th ion microprobe dating: Crystallization age and tectonic implications: Earth and Planetary Science Letters, v. 133, p. 271–282, doi:10.1016/0012-821X(95)00091-P.

Hart, S.R., 1964, The petrology and isotopic-mineral age relations of a contact zone in the Front Range, Colorado: The Journal of Geology, v. 72, p. 493–525, doi:10.1086/627011.

Harte, B., and Hudson, N.F.C., 1979, Pelite facies series and the temperatures and pressures of Dalradian metamorphism in E. Scotland, The Caledonides of the British Isles, *in* Harris A.L., Holland, C.H., and Leake, B.E., eds., The Caledonides of the British Isles—Reviewed: Geological Society, London, Special Publication 8, p. 323–337.

Hartel, T.H.D., and Pattison, D.R.M., 1996, Genesis of the Kapuskasing (Ontario) migmatitic mafic granulites by dehydration melting of amphibolite: The importance of quartz to reaction progress: Journal of Metamorphic Geology, v. 14, p. 591–611, doi:10.1046/j.1525-1314.1996.00404.x.

Heaman, L., and Parrish, R., 1991, U-Pb geochronology of accessory minerals, *in* Heaman, L., and Ludden, J.N., eds., Applications of Radiogenic Isotope Systems to Problems in Geology: Mineralogical Association of Canada Short Course Handbook 19, p. 59–102.

Heinrich, W., Andrehs, G., and Franz, G., 1997, Monazite-xenotime miscibility gap thermometry: I. An empirical calibration: Journal of Metamorphic Geology, v. 15, p. 3–16, doi:10.1111/j.1525-1314.1997.t01-1-00052.x.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K., 1978, Summary and critique of the thermodynamic properties of rock-forming minerals: American Journal of Science, v. 278A, p. 299.

Hemingway, B.S., Robie, R.A., Evans, H.T.J., and Kerrick, D.M., 1991, Heat capacities and entropies of sillimanite, fibrolite, andalusite, kyanite, and quartz and the Al$_2$SiO$_5$ phase diagram: The American Mineralogist, v. 76, p. 1597–1613.

Hensen, B.J., 1971, Theoretical phase relations involving cordierite and garnet in the system MgO-FeO-Al_2O_3-SiO_2: Contributions to Mineralogy and Petrology, v. 33, p. 191–214, doi:10.1007/BF00374063.

Hess, P.C., 1969, The metamorphic paragenesis of cordierite in pelitic rocks: Contributions to Mineralogy and Petrology, v. 24, p. 191–207, doi:10.1007/BF00376047.

Hietanen, A., 1967, On the facies series in various types of metamorphism: The Journal of Geology, v. 75, no. 2, p. 187–214, doi:10.1086/627246.

Hirschberg, A., and Winkler, H.G.F., 1968, Stabilitatsbeziehungen zwischen chlorit, cordierit und almandin bei der metamorphose: Contributions to Mineralogy and Petrology, v. 18, p. 17–42, doi:10.1007/BF00371984.

Holdaway, M.J., 1971, Stability of andalusite and the aluminum silicate phase diagram: American Journal of Science, v. 271, p. 97–131, doi:10.2475/ajs.271.2.97.

Holdaway, M.J., and Lee, S.M., 1977, Fe-Mg cordierite stability in high-grade pelitic rocks based on experimental, theoretical and natural observations: Contributions to Mineralogy and Petrology, v. 63, p. 175–198, doi:10.1007/BF00398778.

Holdaway, M.J., and Mukhopadhyay, B., 1993, A reevaluation of the stability relations of andalusite; thermochemical data and phase diagram for the aluminum silicates: The American Mineralogist, v. 78, p. 298–315.

Holloway, J.R., 1977, Fugacity and Activity of Molecular Species in Super Critical Fluids, *in* Frazer, D.G., ed., Thermodynamics in Geology: Dordrecht, Netherlands, D. Reidel Co., p. 161–181.

Holland, T.J.B., and Powell, R., 1985, An internally consistent thermodynamic dataset with uncertainties and correlations: 2. Data and results: Journal of Metamorphic Geology, v. 3, p. 343–370, doi:10.1111/j.1525-1314.1985.tb00325.x.

Holland, T.J.B., and Powell, R., 1990, An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: The system K_2O-Na_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O_2: Journal of Metamorphic Geology, v. 8, p. 89–124, doi:10.1111/j.1525-1314.1990.tb00458.x.

Holland, T.J.B., and Powell, R., 1996a, Thermodynamics of order-disorder in minerals: I. Symmetric formalism applied to minerals of fixed composition: The American Mineralogist, v. 81, p. 1413–1424, doi:10.2138/am-1996-11-1214.

Holland, T.J.B., and Powell, R., 1996b, Thermodynamics of order-disorder in minerals: II. Symmetric formalism applied to solid solutions: The American Mineralogist, v. 81, p. 1425–1437, doi:10.2138/am-1996-11-1215.

Holland, T.J.B., and Powell, R., 1998, An internally-consistent thermodynamic dataset for phases of petrological interest: Journal of Metamorphic Geology, v. 16, p. 309–343, doi:10.1111/j.1525-1314.1998.00140.x.

Holland, T.J.B., and Powell, R., 2011, An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids: Journal of Metamorphic Geology, v. 29, p. 333–383, doi:10.1111/j.1525-1314.2010.00923.x.

Hollister, L.S., 1966, Garnet zoning: An interpretation based on the Rayleigh fractionation model: Science, v. 154, p. 1647–1651, doi:10.1126/science.154.3757.1647.

Hollister, L.S., 1981, Information intrinsically available from fluid inclusions, *in* Hollister, L.S., and Crawford, M.L., eds., Fluid Inclusions: Applications to Petrology: Mineralogical Association of Canada Short Course Handbook 6, p. 1–12.

Hollister, L.S., and Burruss, R.C., 1976, Phase equilibria of fluid inclusions from the Khtada Lake metamorphic complex: Geochimica et Cosmochimica Acta, v. 40, p. 163–175, doi:10.1016/0016-7037(76)90174-5.

Hollister, L.S., and Crawford, M.L., eds., 1981, Fluid Inclusions: Applications to Petrology, Volume 6: Mineralogical Association of Canada Short Course Handbook 6, 304 p.

Holm, J.L., and Kleppa, O.J., 1966, The thermodynamic properties of the aluminum silicates: The American Mineralogist, v. 51, p. 1608–1622.

Holness, M.B., and Graham, C.M., 1991, Equilibrium dihedral angles in the system H_2O-CO_2-$NaCl$-calcite, and implications for fluid flow during metamorphism: Contributions to Mineralogy and Petrology, v. 108, p. 368–383, doi:10.1007/BF00285944.

Hoschek, G., 1969, The stability of staurolite and chloritoid and their significance in metamorphism of pelitic rocks: Contributions to Mineralogy and Petrology, v. 22, p. 208–232, doi:10.1007/BF00387954.

Huang, W.L., and Wyllie, P.J., 1975, Melting reactions in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2 to 35 kbar, dry and with excess water: The Journal of Geology, v. 83, p. 737–748, doi:10.1086/628165.

Jamieson, R.A., Beaumont, C., Nguyen, M.H., and Lee, B., 2002, Interaction of metamorphism, deformation and exhumation in large convergent orogens: Journal of Metamorphic Geology, v. 20, p. 9–24, doi:10.1046/j.0263-4929.2001.00357.x.

Jamieson, R.A., Beaumont, C., Medvedev, S., and Nguyen, M.H., 2004, Crustal channel flows: 2. Numerical models with implications for metamorphism in the Himalayan-Tibetan orogen: Journal of Geophysical Research, v. 109, B06407, doi:10.1029/2003JB002811.

Janardhan, A.S., Newton, R.C., and Hansen, E.C., 1982, The transformation of amphibolite facies gneiss to charnockite in southern Karnataka and northern Tamil Nadu, India: Contributions to Mineralogy and Petrology, v. 79, p. 130–149, doi:10.1007/BF01132883.

Janots, E., Engi, M., Berger, J., Allaz, J., Schwarz, O., and Spandler, C., 2008, Prograde metamorphic sequence of REE minerals in pelitic rocks of the central Alps: Implications for allanite-monazite-xenotime phase relations from 250 to 610 °C: Journal of Metamorphic Geology, v. 26, p. 509–526, doi:10.1111/j.1525-1314.2008.00774.x.

Joesten, R.L., 1991, Kinetics of coarsening and diffusion-controlled mineral growth, *in* Kerrick, D.M., ed., Contact Metamorphism: Reviews in Mineralogy Volume 26: Washington, D.C., Mineralogical Society of America, p. 507–582.

John, T., and Schenk, V., 2006, Interrelations between intermediate-depth earthquakes and fluid flow within subducting oceanic plates: Constraints from eclogite-facies pseudotachylytes: Geology, v. 34, p. 557–560, doi:10.1130/G22411.1.

John, T., Medvedev, S., Rüpke, L.H., Podladchikov, Y., Andersen, T.B., and Austrheim, H., 2009, Generation of intermediate-depth earthquakes by self-localizing thermal runaway: Nature Geoscience, v. 2, p. 137–140, doi:10.1038/ngeo419.

Johnson, S.E., 1993, Testing models for the development of spiral-shaped inclusion trails in garnet porphyroblasts—To rotate or not to rotate, that is the question: Journal of Metamorphic Geology, v. 11, no. 5, p. 635–659, doi:10.1111/j.1525-1314.1993.tb00178.x.

Johnson, S.E., 1999, Porphyroblast microstructures: A review of current and future trends: The American Mineralogist, v. 84, p. 1711–1726, doi:10.2138/am-1999-11-1202.

Johnson, S.E., 2009, Porphyroblast rotation and strain localization: Debate settled! [Reply]: Geology, v. 37, p. 663–666, doi:10.1130/G25729A.1.

Kelemen, P.B., and Matter, J., 2008, In situ carbonation of peridotite for CO_2 storage: Proceedings of the National Academy of Sciences of the United States of America, v. 105, p. 17,295–17,300, doi:10.1073/pnas.0805794105.

Kelly, E.D., Carlson, W.D., and Ketcham, R.A., 2013, Magnitudes of departures from equilibrium during regional metamorphism of porphyroblastic rocks: Journal of Metamorphic Geology, v. 31, p. 981–1002, doi:10.1111/jmg.12053.

Kelsey, D.E., 2008, On ultrahigh-temperature crustal metamorphism: Gondwana Research, v. 13, p. 1–29, doi:10.1016/j.gr.2007.06.001.

Kelsey, D.E., and Hand, M., 2015, On ultrahigh temperature crustal metamorphism: Phase equilibria, trace element thermometry, bulk composition, heat sources, timescales and tectonic settings: Geoscience Frontiers, v. 6, p. 311–356, doi:10.1016/j.gsf.2014.09.006.

Kelsey, D.E., and Powell, R., 2011, Progress in linking accessory mineral growth and breakdown to major mineral evolution in metamorphic rocks: A thermodynamic approach in the Na_2O-CaO-K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O-TiO_2-ZrO_2 system: Journal of Metamorphic Geology, v. 29, p. 151–166, doi:10.1111/j.1525-1314.2010.00910.x.

Kelsey, D.E., White, R.W., and Powell, R., 2003, Orthopyroxene-sillimanite-quartz assemblages; distribution, petrology, quantitative *P-T-X* constraints and *P-T* paths: Journal of Metamorphic Geology, v. 21, p. 439–453, doi:10.1046/j.1525-1314.2003.00456.x.

Kelsey, D.E., White, R.W., Holland, T.J.B., and Powell, R., 2004, Calculated phase equilibria in K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O for sapphirine-quartz-bearing mineral assemblages: Journal of Metamorphic Geology, v. 22, p. 559–578, doi:10.1111/j.1525-1314.2004.00533.x.

Kelsey, D.E., White, R.W., and Powell, R., 2005, Calculated phase equilibria in K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O for silica-undersaturated sapphire-bearing mineral assemblages: Journal of Metamorphic Geology, v. 23, p. 217–239, doi:10.1111/j.1525-1314.2005.00573.x.

Kelsey, D.E., Clark, C., and Hand, M., 2008, Thermobarometric modeling of zircon and monazite growth in melt-bearing systems: Examples using model metapelitic and metapsammitic granulites: Journal of Metamorphic Geology, v. 26, p. 199–212, doi:10.1111/j.1525-1314.2007.00757.x.

The metamorphosis of metamorphic petrology

Kepezhinskas, K.B., and Khlestov, V.V., 1977, The petrogenetic grid and sub-facies for middle-temperature metapelites: Journal of Petrology, v. 18, p. 114–143, doi:10.1093/petrology/18.1.114.

Kerrick, D.M., 1990, The Al_2SiO_5 polymorphs, *in* Ribbe, P.H., ed., The Al_2SiO_5 Polymorphs: Reviews in Mineralogy Volume 22: Washington, D.C., Mineralogical Society of America, p. 406.

Kerrick, D.M., ed., 1991, Contact Metamorphism: Reviews in Mineralogy Volume 26: Washington, D.C., Mineralogical Society of America.

Kerrick, D.M., 2001, Present and past nonanthropogenic CO_2 degassing from the solid Earth: Reviews of Geophysics, v. 39, p. 565–585, doi:10.1029/2001RG000105.

Kerrick, D.M., and Caldeira, K., 1999, Was the Himalayan orogen a climatically significant coupled source and sink for atmospheric CO_2 during the Cenozoic?: Earth and Planetary Science Letters, v. 173, p. 195–203, doi:10.1016/S0012-821X(99)00229-0.

Kerrick, D.M., and Darken, L.S., 1975, Statistical thermodynamic models for ideal oxide and silicate solid solutions, with application to plagioclase: Geochimica et Cosmochimica Acta, v. 39, p. 1431–1442, doi:10.1016/0016-7037(75)90122-2.

Kerrick, D.M., and Jacobs, G.K., 1981, A modified Redlich-Kwong equation for H_2O, CO_2, and H_2O-CO_2 mixtures at elevated pressures and temperatures: American Journal of Science, v. 281, p. 735–767, doi:10.2475/ajs.281.6.735.

Kerrick, D.M., Lasaga, A.C., and Raeburn, S.P., 1991, Kinetics of heterogeneous reactions, *in* Kerrick, D.M., ed., Contact Metamorphism: Reviews in Mineralogy Volume 26: Washington, D.C., Mineralogical Society of America, p. 583–672.

Khitarov, N.I., Pugin, V.A., and Slutsky, A.B., 1963, Sootnosheniya mezhdu andaluzitom, kianitom i sillimanitom v usloviyakh umerennykh temperatur i davlenii: Геохимия (Geokhimiya), v. 3, p. 219–228.

Kingsbury, J.A., Miller, C.F., Wooden, J.L., and Harrison, T.M., 1993, Monazite paragenesis and U-Pb systematics in rocks of the eastern Mojave Desert, California, U.S.A.: Implications for thermochronometry: Chemical Geology, v. 110, p. 147–167, doi:10.1016/0009-2541(93)90251-D.

Kohn, M.J., 2014, "Thermoba-Raman-try": Calibration of spectroscopic barometers and thermometers for mineral inclusions: Earth and Planetary Science Letters, v. 388, p. 187–196, doi:10.1016/j.epsl.2013.11.054.

Kohn, M.J., and Spear, F.S., 2000, Retrograde net transfer reaction insurance for *P-T* estimates: Geology, v. 28, p. 1127–1130, doi:10.1130/0091-7613(2000)28<1127:RNTRIF>2.0.CO;2.

Kohn, M.J., and Valley, J.W., 1998, Obtaining equilibrium oxygen isotope fractionations from rocks: Theory and examples: Contributions to Mineralogy and Petrology, v. 132, p. 209–224, doi:10.1007/s004100050418.

Koons, P.O., and Thompson, A.B., 1985, Non-mafic rocks in the greenschist, blueschist and eclogite facies: Chemical Geology, v. 50, p. 3–30, doi:10.1016/0009-2541(85)90109-3.

Korzhinskii, D.S., 1959, Physiochemical Basis of Analysis of the Paragenesis of Minerals: New York, Consultants Bureau, Inc., 142 p.

Koziol, A.M., 1990, Activity-composition relationships of binary Ca-Fe and Ca-Mn garnets determined by reversed, displaced equilibrium experiments: The American Mineralogist, v. 75, p. 319–327.

Koziol, A.M., and Newton, R.C., 1988, Redetermination of the anorthite breakdown reaction and improvement of the plagioclase-garnet-Al_2SiO_5-quartz geobarometer: The American Mineralogist, v. 73, p. 216–223.

Koziol, A.M., and Newton, R.C., 1989, Grossular activity-composition relationships in ternary garnets determined by reversed displaced-equilibrium experiments: Contributions to Mineralogy and Petrology, v. 103, p. 423–433, doi:10.1007/BF01041750.

Kretz, R., 1959, Chemical study of garnet, biotite and hornblende from gneisses of S.W. Quebec, with emphases on distribution of elements in coexisting minerals: The Journal of Geology, v. 67, p. 371–402, doi:10.1086/626594.

Kretz, R., 1983, Symbols for rock-forming minerals: American Mineralogist, v. 68, p. 277–279.

Labotka, T.C., 1981, Petrology of an andalusite-type regional metamorphic terrane, Panamint Mountains, California: Journal of Petrology, v. 22, p. 261–296, doi:10.1093/petrology/22.2.261.

Lackner, K.S., Wendt, C.H., Butt, D.P., Joyce, E.L., and Sharp, D.H., 1995, Carbon dioxide disposal in carbonate minerals: Energy, v. 20, p. 1153–1170, doi:10.1016/0360-5442(95)00071-N.

Lasaga, A.C., 1979, Multicomponent exchange and diffusion in silicates: Geochimica et Cosmochimica Acta, v. 43, p. 455–469, doi:10.1016/0016-7037(79)90158-3.

Lasaga, A.C., 1981, Rate laws of chemical reactions: Reviews in Mineralogy, v. 8, p. 1–66.

Lasaga, A.C., 1983, Geospeedometry: An extension of geothermometry, *in* Saxena, S.K., ed., Kinetics and Equilibrium in Mineral Reactions: New York, Springer-Verlag, p. 81–114, doi:10.1007/978-1-4612-5587-1_3.

Lasaga, A.C., 1986, Metamorphic reaction-rate laws and development of isograds: Mineralogical Magazine, v. 50, no. 357, p. 359–373, doi:10.1180/minmag.1986.050.357.02.

Lasaga, A.C., and Kirkpatrick, R.J., 1981, Kinetics of Geochemical Processes: Reviews in Mineralogy Volume 8: Washington, D.C., Mineralogical Society of America, 398 p.

Lasaga, A.C., Richardson, S.M., and Holland, H.D., 1977, The mathematics of cation diffusion and exchange between silicate minerals during retrograde metamorphism, *in* Saxena, S.K., and Bhattacharji, S., eds., Energetics of Geological Processes: New York, Springer-Verlag, p. 353–388, doi:10.1007/978-3-642-86574-9_15.

Liou, J.G., Tsujimori, T., Zhang, R.Y., Katayama, I., and Maruyama, S., 2004, Global UHP metamorphism and continental subduction/collision: The Himalayan model: International Geology Review, v. 46, p. 1–27, doi:10.2747/0020-6814.46.1.1.

Manning, C.E., 1994, The solubility of quartz in H_2O in the lower crust and upper-mantle: Geochimica et Cosmochimica Acta, v. 58, no. 22, p. 4831–4839, doi:10.1016/0016-7037(94)90214-3.

Manning, C.E., 2004, The chemistry of subduction-zone fluids: Earth and Planetary Science Letters, v. 223, no. 1–2, p. 1–16, doi:10.1016/j.epsl.2004.04.030.

Manning, C.E., 2013, Thermodynamic modeling of fluid-rock interaction at mid-crustal to upper-mantle conditions: Reviews in Mineralogy and Geochemistry, v. 76, p. 135–164, doi:10.2138/rmg.2013.76.5.

Manning, C.E., 2014, A piece of the deep carbon puzzle: Nature Geoscience, v. 7, p. 333–334, doi:10.1038/ngeo2152.

Manning, C.E., and Aranovich, L.Y., 2014, Brines at high pressure and temperature: Thermodynamic, petrologic and geochemical effects: Precambrian Research, v. 253, p. 6–16, doi:10.1016/j.precamres.2014.06.025.

Manning, C.E., Shock, E.L., and Sverjensky, D.A., 2013, The chemistry of carbon in aqueous fluids at crustal and upper-mantle conditions: Experimental and theoretical constraints: Reviews in Mineralogy and Geochemistry, v. 75, p. 109–148, doi:10.2138/rmg.2013.75.5.

McDougall, I., and Harrison, T.M., 1988, Geochronology and Thermochronology by the $^{40}Ar/^{39}Ar$ Method: New York, Oxford, 212 p.

McFarlane, C.R.M., Carlson, W.D., and Connelly, J.N., 2003, Prograde, peak, and retrograde *P-T* paths from aluminum in orthopyroxene: High-temperature contact metamorphism in the aureole of the Makhavinekh Lake Pluton, Nain Plutonic Suite, Labrador: Journal of Metamorphic Geology, v. 21, p. 405–423, doi:10.1046/j.1525-1314.2003.00446.x.

Mehnert, K.R., 1968, Migmatites and the Origin of Granitic Rocks: New York, Elsevier, 394 p.

Metz, B., Davidson, O., de Coninck, H.C., Loos, M., and Meyer, L.A., 2005, IPCC Special Report on Carbon Dioxide Capture and Storage: Cambridge, UK, Cambridge University Press, 422 p.

Minear, J.W., and Toksoz, M.N., 1970, Thermal regime of a downgoing slab and new global tectonics: Journal of Geophysical Research, v. 75, p. 1397–1419, doi:10.1029/JB075i008p01397.

Miyashiro, A., 1949, The stability relation of kyanite, sillimanite, and andalusite, and the physical conditions of the metamorphic processes: Journal of the Geological Society of Japan, v. 55, p. 218–223, doi:10.5575/geosoc.55.218.

Miyashiro, A., 1961, Evolution of metamorphic belts: Journal of Petrology, v. 2, p. 277–311, doi:10.1093/petrology/2.3.277.

Miyashiro, A., 1973, Metamorphism and Metamorphic Belts: London, George Allen & Unwin Ltd., 492 p.

Montel, J.-M., Foret, S., Veschambre, M., Nicollet, C., and Provost, A., 1996, Electron microprobe dating of monazite: Chemical Geology, v. 131, p. 37–53.

Newton, R.C., 1966a, Kyanite-andalusite equilibrium from 700° to 800°C: Science, v. 153, p. 170–172, doi:10.1126/science.153.3732.170.

Newton, R.C., 1966b, Kyanite-sillimanite equilibrium at 750°C: Science, v. 151, p. 1222–1225, doi:10.1126/science.151.3715.1222.

Newton, R.C., 1983, Geobarometry of high-grade metamorphic rocks: American Journal of Science, v. 283-A, p. 1–28.

Newton, R.C., 1985, Temperature, pressure and metamorphic fluid regimes in the amphibolite facies to granulite facies transition zones, *in* Tobi, A.C., and Touret, J.L.R., eds., The Deep Proterozoic Crust in the North

Atlantic Provinces: Dordrecht, Netherlands, Reidel Publishing Company, p. 75–104, doi:10.1007/978-94-009-5450-2_6.

Newton, R.C., and Manning, C.E., 2000, Quartz solubility in the H_2O-NaCl and H_2O-CO_2 solutions at deep crust–upper mantle pressures and temperatures: 2–15 kbar and 500–900°C: Geochimica et Cosmochimica Acta, v. 64, p. 2993–3005, doi:10.1016/S0016-7037(00)00402-6.

Newton, R.C., and Manning, C.E., 2010, Role of saline fluids in deep-crustal and upper-mantle metasomatism: Insights from experimental studies: Geofluids, v. 10, p. 58–72, doi:10.1111/j.1468-8123.2009.00275.x.

Okay, A.I., 1993, Petrology of a diamond and coesite-bearing metamorphic terrain, Dabie Shan, China: European Journal of Mineralogy, v. 5, no. Jul.–Aug., p. 659–675.

O'Neil, J.R., 1986, Theoretical and experimental aspects of isotopic fractionation, *in* Valley, J.W., Taylor, J.P., and O'Neil, J.R., eds., Stable Isotopes in High Temperature Geological Processes: Reviews in Mineralogy Volume 16: Washington, D.C., Mineralogical Society of America, p. 1–40.

Oxburgh, E.R., and Turcotte, D.L., 1974, Thermal gradients and regional metamorphism in overthrust terrains with special reference to the eastern Alps: Schweizerische Mineralogische und Petrographische Mitteilungen, v. 54, p. 641–662.

Parrish, R., 1990, U-Pb dating of monazite and its application to geological problems: Canadian Journal of Earth Sciences, v. 27, p. 1431–1450, doi:10.1139/e90-152.

Passchier, C., and Trouw, R.A.J., 2005, Microtectonics (2nd ed.): New York, Springer Verlag, 366 p.

Passchier, C.W., Trouw, R.A.J., Zwart, H.J., and Vissers, R.L.M., 1992, Porphyroblast rotation—Eppur si muove?: Journal of Metamorphic Geology, v. 10, no. 5, p. 283–294.

Pattison, D.R.M., 1992, Stability of andalusite and sillimanite and the Al_2SiO_5 triple point: Constraints from the Ballachulish aureole, Scotland: The Journal of Geology, v. 100, p. 423–446, doi:10.1086/629596.

Pattison, D.R.M., 1994, Are reversed Fe-Mg exchange and solid solution experiments really reversed?: The American Mineralogist, v. 79, p. 938–950.

Pattison, D.R.M., and Begin, N.J., 1994, Zoning patterns in orthopyroxene and garnet in granulites: Implications for geothermometry: Journal of Metamorphic Geology, v. 12, p. 387–410, doi:10.1111/j.1525-1314.1994.tb00031.x.

Pattison, D.R.M., and Harte, B., 1985, A petrogenetic grid for pelites in the Ballachulish and other Scottish thermal aureoles: Journal of the Geological Society, London, v. 142, p. 7–28, doi:10.1144/gsjgs.142.1.0007.

Pattison, D.R.M., and Harte, B., 1988, Evolution of structurally contrasting anatectic migmatites in the 3-kbar Ballachulish aureole, Scotland: Journal of Metamorphic Geology, v. 6, p. 475–494, doi:10.1111/j.1525-1314.1988.tb00435.x.

Pattison, D.R.M., and Tracy, R.J., 1991, Phase equilibria and thermobarometry of metapelites, *in* Kerrick, D.M., ed., Contact Metamorphism: Reviews in Mineralogy Volume 26: Washington, D.C., Mineralogical Society of America, p. 105–206.

Pattison, D.R.M., and Vogl, J.J., 2005, Contrasting sequences of metapelitic mineral-assemblages in the aureole of the tilted Nelson Batholith, British Columbia: Implications for phase equilibria and pressure determination in andalusite-sillimanite type settings: Canadian Mineralogist, v. 43, p. 51–88, doi:10.2113/gscanmin.43.1.51.

Pattison, D.R.M., Spear, F.S., DeBuhr, C.L., Cheney, J.T., and Guidotti, C.V., 2002, Thermodynamic modelling of the reaction muscovite + cordierite = Al_2SiO_5 + biotite + quartz + H_2O: Constraints from natural assemblages and implications for the metapelitic petrogenetic grid: Journal of Metamorphic Geology, v. 20, p. 99–118, doi:10.1046/j.0263-4929.2001.356.356.x.

Pattison, D.R.M., Chacko, T., Farquhar, J., and McFarlane, C.R.M., 2003, Temperatures of granulite-facies metamorphism: Constraints from experimental phase equilibria and thermobarometry corrected for retrograde exchange: Journal of Petrology, v. 44, p. 867–900, doi:10.1093/petrology/44.5.867.

Pattison, D.R.M., de Capitani, C., and Gaidies, F., 2011, Petrological consequences of variations in metamorphic reaction affinity: Journal of Metamorphic Geology, v. 29, no. 9, p. 953–977, doi:10.1111/j.1525-1314.2011.00950.x.

Peacock, S.M., 1991, Numerical simulation of subduction zone pressure-temperature-time paths: Constraints on fluid production and arc magmatism: Philosophical Transactions of the Royal Society of London, ser. A, Mathematical and Physical Sciences, v. 335, p. 341–353, doi:10.1098/rsta.1991.0050.

Peacock, S.M., 2003, Thermal structure and metamorphic evolution of subducting slabs, *in* Eiler, J., ed., Inside the Subduction Factory: American Geophysical Union Geophysical Monograph 138, p. 7–22.

Percival, J.A., Carmichael, D.M., and Helmstaedt, H., 1982, A petrogenetic grid for calcium and alkali-deficient bulk compositions: Geological Survey of Canada Current Research A, v. 82-1A, p. 169–173.

Phillips, G.N., 1993, Metamorphic fluids and gold: Mineralogical Magazine, v. 57, p. 365–374, doi:10.1180/minmag.1993.057.388.02.

Phillips, G.N., and Powell, R., 2010, Formation of gold deposits: A metamorphic devolatilization model: Journal of Metamorphic Geology, v. 28, p. 689–718, doi:10.1111/j.1525-1314.2010.00887.x.

Platt, J.P., 1987, The uplift of high-pressure–low-temperature metamorphic rocks: Philosophical Transactions of the Royal Society of London, ser. A, v. 321, p. 87–103, doi:10.1098/rsta.1987.0006.

Prior, D.J., Boyle, A.P., Brenker, F., Cheadle, M.C., Day, A., Lopez, G., Peruzzo, L., Potts, G.J., Reddy, S., Spiess, R., Timms, N.E., Trimby, P., Wheeler, J., and Zetterström, L., 1999, The application of electron backscatter diffraction and orientation contrast imaging in the SEM to textural problems in rocks: American Mineralogist, v. 84, p. 1741–1759, doi:10.2138/am-1999-11-1204.

Pollington, A.D., and Baxter, E.F., 2010, High resolution Sm-Nd garnet geochronology reveals the uneven pace of tectonometamorphic processes: Earth and Planetary Science Letters, v. 293, p. 63–71, doi:10.1016/j.epsl.2010.02.019.

Pollington, A.D., and Baxter, E.F., 2011, High precision microsampling and preparation of zoned garnet porphyroblasts for Sm-Nd geochronology: Chemical Geology, v. 281, p. 270–282, doi:10.1016/j.chemgeo.2010.12.014.

Powell, R., 1978, Equilibrium Thermodynamics in Petrology: London, Harper & Row, 284 p.

Powell, R., 1983, Fluids and melting under upper amphibolite facies conditions: Journal of the Geological Society, London, v. 140, p. 629–633, doi:10.1144/gsjgs.140.4.0629.

Powell, R., and Holland, T., 1990, Calculated mineral equilibria in the pelite system, KFMASH (K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O): The American Mineralogist, v. 75, p. 367–380.

Powell, R., and Holland, T., 1993, On the formulation of simple mixing models for complex phases: The American Mineralogist, v. 78, p. 1174–1180.

Powell, R., and Holland, T., 1994, Optimal geothermometry and geobarometry: The American Mineralogist, v. 79, p. 120–133.

Powell, R., Will, T.M., and Phillips, G.N., 1991, Metamorphism in Archaean greenstone belts: Calculated fluid compositions and implications for gold mineralisation: Journal of Metamorphic Geology, v. 9, p. 141–150, doi:10.1111/j.1525-1314.1991.tb00510.x.

Powell, R., Holland, T., and Worley, B., 1998, Calculating phase diagrams involving solid solutions via non-linear equations, with examples using THERMOCALC: Journal of Metamorphic Geology, v. 16, p. 577–588, doi:10.1111/j.1525-1314.1998.00157.x.

Power, I.E., Wilson, S.A., and Dipple, G.M., 2013, Serpentinite carbonation for CO_2 sequestration: Elements (Quebec), v. 9, p. 115–121, doi:10.2113/gselements.9.2.115.

Prigogine, I., and Defay, R., 1954, Chemical Thermodynamics: London, Longmans, Green and Co., 543 p.

Prior, D.J., Boyle, A.P., Brenker, F., Cheadle, M.C., Day, A., Lopez, G., Peruzzo, L., Potts, G.J., Reddy, S., Spiess, R., Timms, N.E., Trimby, P., Wheeler, J., and Zetterström, L., 1999, The application of electron backscatter diffraction and orientation contrast imaging in the SEM to textural problems in rocks: The American Mineralogist, v. 84, p. 1741–1759.

Pyle, J.M., and Spear, F.S., 2000, An empirical garnet (YAG)-xenotime thermometer: Contributions to Mineralogy and Petrology, v. 138, p. 51–58, doi:10.1007/PL00007662.

Pyle, J.M., and Spear, F.S., 2003, Four generations of accessory phase growth in low-pressure migmatites from SW New Hampshire: The American Mineralogist, v. 88, p. 338–351, doi:10.2138/am-2003-2-311.

Pyle, J.M., Spear, F.S., Rudnick, R.L., and McDonough, W.F., 2001, Monazite-xenotime-garnet equilibrium in metapelites and a new monazite-garnet thermometer: Journal of Petrology, v. 42, p. 2083–2107, doi:10.1093/petrology/42.11.2083.

Pyle, J.M., Spear, F.S., Cheney, J.T., and Layne, G., 2005, Monazite ages in the Chesham Pond nappe, SW New Hampshire, USA: Implications for assembly of central New England thrust sheets: The American Mineralogist, v. 90, p. 592–606, doi:10.2138/am.2005.1341.

Ramberg, H., 1952, Chemical bonds and distribution of cations in silicates: The Journal of Geology, v. 60, p. 331–355, doi:10.1086/625982.

Rice, J.M., 1977a, Contact metamorphism of impure dolomitic limestone in the Boulder aureole, Montana: Contributions to Mineralogy and Petrology, v. 59, p. 237–259, doi:10.1007/BF00374555.

Rice, J.M., 1977b, Progressive metamorphism of impure dolomitic limestone in the Marysville aureole, Montana: American Journal of Science, v. 277, p. 1–24, doi:10.2475/ajs.277.1.1.

Richardson, S.W., Gilbert, M.C., and Bell, P.M., 1969, Experimental determination of kyanite-andalusite and andalusite-sillimanite equilibria: The aluminum silicate triple point: American Journal of Science, v. 267, p. 259–272, doi:10.2475/ajs.267.3.259.

Ridley, J., and Thompson, A.B., 1986, The role of mineral kinetics in the development of metamorphic microtextures, *in* Walther, J.V., and Wood, B.J., eds., Fluid-Rock Interactions during Metamorphism: New York, Springer Verlag, p. 80–97.

Robie, R.A., and Waldbaum, D.R., 1968, Thermodynamic Properties of Minerals and Related Substances at 298.15 K (25.0°C) and One Atmosphere (1.013 Bars) Pressure and at Higher Temperatures: U.S. Geological Survey Bulletin 1259, 256 p.

Robie, R.A., Hemingway, B.S., and Fisher, J.R., 1978, Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures: U.S. Geological Survey Bulletin 1452, 456 p.

Robyr, M., Carlson, W.D., Passchier, C., and Vonlanthen, P., 2009, Microstructural, chemical and textural records during growth of snowball garnet: Journal of Metamorphic Geology, v. 27, p. 423–437, doi:10.1111/j.1525 -1314.2009.00824.x.

Rosenberg, C.L., and Handy, M.R., 2005, Experimental deformation of partially melted granite revisited; implications for the continental crust: Journal of Metamorphic Geology, v. 23, p. 19–28, doi:10.1111/j.1525-1314.2005.00555.x.

Rosenfeld, J.L., 1970, The geometrical arrangement of material included in garnets, *in* Rosenfeld, J.L., ed., Rotated Garnets in Metamorphic Rocks: Geological Society of America Special Paper 129, p. 25–50.

Rubatto, D., Williams, I.S., and Buick, I.S., 2001, Zircon and monazite response to prograde metamorphism in the Reynolds Range, central Australia: Contributions to Mineralogy and Petrology, v. 140, p. 458–468, doi:10.1007/PL00007673.

Rubie, D.C., 1998, Disequilibrium during metamorphism: The role of nucleation kinetics, *in* Treloar, P.J., and O'Brien, P.J., eds., What Drives Metamorphism and Metamorphic Reactions: Geological Society, London, Special Publication 138, p. 199–214.

Rubie, D.C., and Thompson, A.B., 1985, Kinetics of metamorphic reactions at elevated temperatures and pressures: An appraisal of available experimental data, *in* Thompson, A.B., and Rubie, D.C., eds., Metamorphic Reactions: Kinetics, Textures and Deformation: New York, Springer-Verlag, p. 27–79, doi:10.1007/978-1-4612-5066-1_2.

Rumble, D., III, 1973, Fe-Ti oxide minerals from regionally metamorphosed quartzites of eastern New Hampshire: Contributions to Mineralogy and Petrology, v. 42, p. 181–195, doi:10.1007/BF00371584.

Rumble, D., III, 1974, The Gibbs phase rule and its application in geochemistry: Journal of the Washington Academy of Sciences, v. 64, p. 199–208.

Rumble, D., III, 1976, The use of mineral solid solutions to measure chemical potential gradients in rocks: The American Mineralogist, v. 61, p. 1167–1174.

Rumble, D., III, 1978, Mineralogy, petrology and oxygen isotope geochemistry of the Clough Formation, Black Mountain, western New Hampshire, U.S.A.: Journal of Petrology, v. 19, p. 317–340, doi:10.1093/petrology/19.2.317.

Rumble, D., III, 1982, The role of perfectly mobile components in metamorphism: Annual Review of Earth and Planetary Sciences, v. 10, p. 221–233, doi:10.1146/annurev.ea.10.050182.001253.

Rumble, D., Liou, J.G., and Jahn, B.M., 2003, Continental crust subduction and UHP metamorphism, *in* Rudnick, R.L., ed., The Crust, Volume 3: Oxford, UK, Elsevier, p. 293–319.

Salje, E., 1986, Heat capacities and entropies of andalusite and sillimanite: The influence of fibrolitization on the phase diagram of the Al_2SiO_5 polymorphs: The American Mineralogist, v. 71, p. 1366–1371.

Sanislav, I.V., 2009, Porphyroblast rotation and strain localization: Debate settled!: Comment: Geology, v. 37, p. e204.

Sawyer, E.W., 1999, Criteria for the recognition of partial melting: Physics and Chemistry of the Earth, v. 24, p. 269–279, doi:10.1016/S1464 -1895(99)00029-0.

Sawyer, E.W., 2001, Melt segregation in the continental crust: Distribution and movement of melt in anatectic rocks: Journal of Metamorphic Geology, v. 19, p. 291–309, doi:10.1046/j.0263-4929.2000.00312.x.

Sawyer, E.W., 2008, Atlas of Migmatites: Canadian Mineralogist Special Paper 9, 371 p.

Sawyer, E.W., Cesare, B., and Brown, M., 2011, When the continental crust melts: Elements (Quebec), v. 7, p. 229–234, doi:10.2113/ gselements.7.4.229.

Schuiling, R.D., 1957, A geo-experimental phase-diagram of Al_2SiO_5 (sillimanite, kyanite, andalusite): Proceedings of the Koninklijke Nederlandse Academie van Wetenschappen. Series B: Physical Sciences, v. 60, no. 3, p. 220–226.

Schuiling, R.D., 1962, Die petrogenetische Bedeutung dur drei Modifikationen von Al_2SiO_5: Neues Jahrbuch für Mineralogie, Monatch, p. 200–214.

Selverstone, J., and Gutzler, D.S., 1993, Post–125 Ma carbon storage associated with continent-continent collision: Geology, v. 21, p. 885–888, doi:10.1130/0091-7613(1993)021<0885:PMCSAW>2.3.CO;2.

Shmulovich, K.I., and Shmonov, V.M., 1975, Fugacity coefficients for CO_2 from 1.0132 to 10,000 bar and 450–1300 K: Geochemistry International, v. 12, p. 202–205.

Shmulovich, K.I., Graham, C.M., and Yardley, B.W.D., 2001, Quartz, albite and diopside solubilities in H_2O-NaCl and H_2O-CO_2 fluids at 0.5–0.9 GPa: Contributions to Mineralogy and Petrology, v. 141, p. 95–108, doi:10.1007/s004100000224.

Shmulovich, K.I., Yardley, B.W.D., and Graham, C.M., 2006, Solubility of quartz in crustal fluids: Experiments and general equations for salt solutions and H_2O-CO_2 mixtures at 400–800 degrees C and 0.1–0.9 GPa: Geofluids, v. 6, no. 2, p. 154–167, doi:10.1111/j.1468 -8123.2006.00140.x.

Shreve, R.L., and Cloos, M., 1987, Dynamics of sediment subduction, mélange formation, and prism accretion: Journal of Geophysical Research, v. B91, p. 10,229–10,245.

Skelton, A., 2011, Flux rates for water and carbon during greenschist facies metamorphism: Geology, v. 39, p. 43–46, doi:10.1130/G31328.1.

Smith, D.C., 1984, Coesite in clinopyroxene in the Caledonides and its implications for geodynamics: Nature, v. 310, p. 641–644, doi:10.1038/310641a0.

Smith, H.A., and Barreiro, B., 1990, Monazite U-Pb dating of staurolite grade metamorphism in pelitic schists: Contributions to Mineralogy and Petrology, v. 105, p. 602–615, doi:10.1007/BF00302498.

Sobolev, N.V., and Shatsky, V.S., 1990, Diamond inclusions in garnets from metamorphic rocks: A new environment for diamond formation: Nature, v. 343, p. 742–746, doi:10.1038/343742a0.

Spear, F.S., 1988, The Gibbs method and Duhem's theorem: The quantitative relationships among *P*, *T*, chemical potential, phase composition and reaction progress in igneous and metamorphic systems: Contributions to Mineralogy and Petrology, v. 99, p. 249–256, doi:10.1007/BF00371465.

Spear, F.S., 1993, Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths: Washington, D.C., Mineralogical Society of America, 799 p.

Spear, F.S., 2004, Fast cooling and exhumation of the Valhalla metamorphic core complex: International Geology Review, v. 46, p. 193–209, doi:10.2747/0020-6814.46.3.193.

Spear, F.S., 2010, Monazite-allanite phase relations in metapelites: Chemical Geology, v. 279, p. 55–62, doi:10.1016/j.chemgeo.2010.10.004.

Spear, F.S., and Cheney, J.T., 1989, A petrogenetic grid for pelitic schists in the system SiO_2-Al_2O_3-FeO-MgO-K_2O-H_2O: Contributions to Mineralogy and Petrology, v. 101, p. 149–164, doi:10.1007/BF00375302.

Spear, F.S., and Florence, F.P., 1992, Thermobarometry in granulites: Pitfalls and new approaches: Journal of Precambrian Research, v. 55, p. 209–241.

Spear, F.S., and Franz, G., 1986, *P-T* evolution of metasediments from the eclogite zone, south-central Tauern Window, Austria: Lithos, v. 19, p. 219–234, doi:10.1016/0024-4937(86)90024-1.

Spear, F.S., and Menard, T., 1989, Program GIBBS: A generalized Gibbs method algorithm: The American Mineralogist, v. 74, p. 942–943.

Spear, F.S., and Parrish, R., 1996, Petrology and petrologic cooling rates of the Valhalla complex, British Columbia, Canada: Journal of Petrology, v. 37, p. 733–765, doi:10.1093/petrology/37.4.733.

Spear, F.S., and Peacock, S.M., 1989, Metamorphic Pressure-Temperature-Time Paths: Washington, D.C., American Geophysical Union, Short Course in Geology, 102 p.

Spear, F.S., and Pyle, J.M., 2002, Apatite, monazite, and xenotime in metamorphic rocks, *in* Kohn, M.J., Rakovan, J., and Hughes, J.M., eds., Phosphates: Geochemical, Geobiological, and Materials Importance: Reviews in Mineralogy and Geochemistry Volume 48: Washington, D.C., Mineralogical Society of America, p. 293–335.

Spear, F.S., and Pyle, J.M., 2010, Theoretical modeling of monazite growth in a low-Ca metapelite: Chemical Geology, v. 273, no. 1–2, p. 111–119, doi:10.1016/j.chemgeo.2010.02.016.

Spear, F.S., and Rumble, D., III, 1986, Pressure, temperature and structural evolution of the Orfordville Belt, west-central New Hampshire: Journal of Petrology, v. 27, p. 1071–1093, doi:10.1093/petrology/27.5.1071.

Spear, F.S., and Selverstone, J., 1983, Quantitative *P-T* paths from zoned minerals: Theory and tectonic applications: Contributions to Mineralogy and Petrology, v. 83, p. 348–357, doi:10.1007/BF00371203.

Spear, F.S., Ferry, J.M., and Rumble, D., 1982a, Algebraic formulation of phase equilibria: The Gibbs method, *in* Ferry, J.M., ed., Characterization of Metamorphism through Mineral Equilibria: Reviews in Mineralogy Volume 10: Washington, D.C., Mineralogical Society of America, p. 105–152.

Spear, F.S., Rumble, D., III, and Ferry, J.M., 1982b, Linear algebraic manipulation of *n*-dimensional composition space, *in* Ferry, J.M., ed., Characterization of Metamorphism through Mineral Equilibria: Reviews in Mineralogy Volume 10: Washington, D.C., Mineralogical Society of America, p. 53–104.

Spear, F.S., Kohn, M.J., Florence, F., and Menard, T., 1990, A model for garnet and plagioclase growth in pelitic schists: Implications for thermobarometry and *P-T* path determinations: Journal of Metamorphic Geology, v. 8, p. 683–696, doi:10.1111/j.1525-1314.1990.tb00495.x.

Spear, F.S., Peacock, S.M., Kohn, M.J., Florence, F.P., and Menard, T., 1991, Computer programs for petrologic *P-T-t* path calculations: The American Mineralogist, v. 76, p. 2009–2012.

Spear, F.S., Kohn, M.J., and Cheney, J.T., 1999, *P-T* paths from anatectic pelites: Contributions to Mineralogy and Petrology, v. 134, p. 17–32, doi:10.1007/s004100050466.

Spry, P.G., Marshall, B., and Vokes, F.M., 2000, Metamorphic and metamorphogenic ore deposits: Reviews in Economic Geology, v. 11, p. 163–201.

Suzuki, K., and Adachi, M., 1991, Precambrian provenance and Silurian metamorphism of the Tsubonosawa paragneiss in the South Kitakami terrane, northeast Japan, revealed by the chemical Th-U-total Pb isochron ages of monazite, zircon and xenotime: Geochemical Journal, v. 25, p. 357–376, doi:10.2343/geochemj.25.357.

Sverjensky, D.A., Harrison, B., and Azzolini, D., 2014a, Water in the deep Earth: The dielectric constant and the solubilities of quartz and corundum to 60 kb and 1,200°C: Geochimica et Cosmochimica Acta, v. 129, p. 125–145, doi:10.1016/j.gca.2013.12.019.

Sverjensky, D.A., Stagno, V., and Huang, F., 2014b, Important role for organic carbon in subduction zone fluids in the deep carbon cycle: Nature Geoscience, v. 7, p. 909–913, doi:10.1038/ngeo2291.

Thomas, J.B., Watson, E.B., Spear, F.S., Shemella, P.T., Nayak, S.K., and Lanzirotti, A., 2010, TitaniQ under pressure: The effect of pressure and temperature on Ti-in-quartz solubility: Contributions to Mineralogy and Petrology, v. 160, p. 743–759, doi:10.1007/s00410-010-0505-3.

Thompson, A.B., 1976, Mineral reactions in pelitic rocks: II. Calculation of some *P-T-X*(Fe-Mg) phase relations: American Journal of Science, v. 276, p. 425–454, doi:10.2475/ajs.276.4.425.

Thompson, A.B., 1982, Dehydration melting of pelitic rocks and the generation of H_2O-undersaturated granitic liquids: American Journal of Science, v. 282, p. 1567–1595, doi:10.2475/ajs.282.10.1567.

Thompson, A.B., 1983, Fluid-absent metamorphism: Journal of the Geological Society, London, v. 140, p. 533–547, doi:10.1144/gsjgs.140.4.0533.

Thompson, A.B., and Algor, J.R., 1977, Model systems for anatexis of pelitic rocks: I. Theory of melting reactions in the system $KAlO_2$-$NaAlO_2$-Al_2O_3-SiO_2-H_2O: Contributions to Mineralogy and Petrology, v. 63, p. 247–269, doi:10.1007/BF00375575.

Thompson, A.B., and England, P.C., 1984, Pressure-temperature-time paths of regional metamorphism: II. Their influence and interpretation using mineral assemblages in metamorphic rocks: Journal of Petrology, v. 25, p. 929–955, doi:10.1093/petrology/25.4.929.

Thompson, A.B., and Tracy, R.J., 1979, Model systems for anatexis of pelitic rocks: II. Facies series melting and reactions in the system CaO-$KAlO_2$-$NaAlO_2$-Al_2O_3-SiO_2-H_2O: Contributions to Mineralogy and Petrology, v. 70, p. 429–438, doi:10.1007/BF00371049.

Thompson, A.B., Lyttle, P.T., and Thompson, J.B., Jr., 1977a, Mineral reactions and A-Na-K and A-F-M facies types in the Gassetts Schist, Vermont: American Journal of Science, v. 277, p. 1124–1151, doi:10.2475/ajs.277.9.1124.

Thompson, A.B., Tracy, R.J., Lyttle, P., and Thompson, J.B., Jr., 1977b, Prograde reaction histories deduced from compositional zonation and min-

eral inclusions in garnet from the Gassetts Schist, Vermont: American Journal of Science, v. 277, p. 1152–1167, doi:10.2475/ajs.277.9.1152.

Thompson, J.B., Jr., 1955, The thermodynamic basis for the mineral facies concept: American Journal of Science, v. 253, p. 65–103, doi:10.2475/ajs.253.2.65.

Thompson, J.B., Jr., 1957, The graphical analysis of mineral assemblages in pelitic schists: The American Mineralogist, v. 42, p. 842–858.

Thompson, J.B., Jr., 1967, Thermodynamic properties of simple solutions, *in* Abelson, P.H., ed., Researches in Geochemistry, Volume 2: New York, Wiley, p. 340–361.

Thompson, J.B., Jr., 1970, Geochemical reaction and open systems: Geochimica et Cosmochimica Acta, v. 34, p. 529–551, doi:10.1016/0016-7037(70)90015-3.

Thompson, J.B., Jr., 1982, Composition space: An algebraic and geometric approach, *in* Ferry, J.M., ed., Characterization of Metamorphism through Mineral Equilibria: Reviews in Mineralogy Volume 10: Washington, D.C., Mineralogical Society of America, p. 1–31.

Thompson, J.B., Jr., and Thompson, A.B., 1976, A model system for mineral facies in pelitic schists: Contributions to Mineralogy and Petrology, v. 58, p. 243–277, doi:10.1007/BF00402355.

Thompson, J.B., Jr., and Waldbaum, D.R., 1969a, Analysis of the two-phase region halite-sylvite in the system NaCl-KCl: Geochimica et Cosmochimica Acta, v. 33, p. 671–690, doi:10.1016/0016-7037(69)90114-8.

Thompson, J.B., Jr., and Waldbaum, D.R., 1969b, Mixing properties of sanidine crystalline solutions: III. Calculations based on two-phase data: The American Mineralogist, v. 54, p. 811–838.

Tomkins, A.G., 2010, Windows of metamorphic sulfur liberation in the crust: Implications for gold deposit genesis: Geochimica et Cosmochimica Acta, v. 74, p. 3246–3259, doi:10.1016/j.gca.2010.03.003.

Tomkins, A.G., 2013, On the source of orogenic gold: Geology, v. 41, p. 1255–1256, doi:10.1130/focus122013.1.

Tomkins, A.G., Pattison, D.R.M., and Zaleski, E., 2004, The Hemlo gold deposit, Ontario: An example of melting and mobilization of a precious metal-sulfosalt assemblage during amphibolite facies metamorphism and deformation: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 99, p. 1063–1084, doi:10.2113/gsecongeo.99.6.1063.

Tomkins, A.G., Pattison, D.R.M., and Frost, B.R., 2007, On the initiation of metamorphic sulfide anatexis: Journal of Petrology, v. 48, p. 511–535, doi:10.1093/petrology/egl070.

Touret, J., 1971, Le facies granulite en Norvège Méridionale: II. Les inclusions fluides: Lithos, v. 4, p. 423–436, doi:10.1016/0024-4937(71)90125-3.

Tracy, R.J., Robinson, P., and Thompson, A.B., 1976, Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts: The American Mineralogist, v. 61, p. 762–775.

Trommsdorff, V., and Connolly, J.A.D., 1990, Constraints on phase diagram topology for the system: CaO-MgO-SiO_2-H_2O-CO_2: Contributions to Mineralogy and Petrology, v. 104, p. 1–7, doi:10.1007/BF00310641.

Trommsdorff, V., and Evans, B.W., 1972, Progressive metamorphism of antigorite schist in the Bergell tonalite aureole (Italy): American Journal of Science, v. 272, p. 423–437, doi:10.2475/ajs.272.5.423.

Trommsdorff, V., and Evans, B.W., 1974, Alpine metamorphism of peridotitic rocks: Schweizerische Mineralogische und Petrographische Mitteilungen, v. 54, p. 333–352.

Turner, F.J., 1968, Metamorphic Petrology (1st ed.): New York, McGraw-Hill, 524 p.

Turner, F.J., 1981, Metamorphic Petrology (2nd ed.): New York, McGraw-Hill, 524 p.

Turner, F.J., and Verhoogen, J., 1960, Igneous and Metamorphic Petrology (2nd ed.): New York, McGraw-Hill, 694 p.

Tuttle, O.F., and Bowen, N.L., 1958, Origin of Granite in Light of Experimental Studies in the System $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O: Geological Society of America Memoir 74, 153 p.

Valley, J.W., 1986, Stable isotope geochemistry of metamorphic rocks, *in* Valley, J.W., Taylor, J.P., and O'Neil, J.R., eds., Stable Isotopes in High Temperature Geological Processes: Reviews in Mineralogy Volume 16: Washington, D.C., Mineralogical Society of America, p. 445–490.

Valley, J.W., 2001, Stable isotope thermometry at high temperatures, *in* Valley, J.W., and Cole, D.R., eds., Stable Isotope Geochemistry: Reviews in Mineralogy and Geochemistry Volume 43: Washington, D.C., Mineralogical Society of America, p. 365–414.

The metamorphosis of metamorphic petrology

Valley, J.W., 2003, Oxygen isotopes in zircon, *in* Hanchar, J.M., and Hoskin, P.W.O., eds., Zircon: Reviews in Mineralogy Volume 53: Washington, D.C., Mineralogical Society of America, p. 343–385.

Valley, J.W., and Cole, D.R., eds., 2001, Stable Isotope Geochemistry: Reviews in Mineralogy Geochemistry Volume 43: Washington, D.C., Mineralogical Society of America, 662 p.

Valley, J.W., Taylor, J.P., and O'Neil, J.R., eds., 1986, Stable Isotopes in High Temperature Geological Processes: Reviews in Mineralogy Volume 16: Washington, D.C., Mineralogical Society of America, 570 p.

Vance, D., and Holland, T., 1993, A detailed isotopic and petrological study of a single garnet from the Gassetts schist, Vermont: Contributions to Mineralogy and Petrology, v. 114, p. 101–118, doi:10.1007/BF00307868.

Vance, D., and O'Nions, R.K., 1990, Isotopic chronometry of zoned garnets: Growth kinetics and metamorphic histories: Earth and Planetary Science Letters, v. 97, p. 227–240, doi:10.1016/0012-821X(90)90044-X.

Vance, D., and O'Nions, R.K., 1992, Prograde and retrograde thermal histories from the central Swiss Alps: Earth and Planetary Science Letters, v. 114, p. 113–129, doi:10.1016/0012-821X(92)90155-O.

van Zeggeren, F., and Storey, S.H., 1970, The Computation of Chemical Equilibrium: London, Cambridge University Press, 176 p.

Vernon, R.H., 1978, Porphyroblast-matrix microstructural relationships in deformed metamorphic rocks: Geologische Rundschau, v. 67, no. 1, p. 288–305, doi:10.1007/BF01803268.

Vernon, R.H., 1989, Porphyroblast-matrix microstructural relationships: Recent approaches and problems, *in* Daly, J.S., Cliff, R.A., and Yardley, B.W.D., eds., Evolution of Metamorphic Belts: Geological Society, London, Special Publication 43, p. 83–102, doi:10.1144/GSL.SP.1989.043.01.05.

Vernon, R.H., and Collins, W.J., 1988, Igneous microstructures in migmatites: Geology, v. 16, p. 1126–1129, doi:10.1130/0091-7613(1988)016<1126:IMIM>2.3.CO;2.

Vielzeuf, D., and Holloway, J.R., 1988, Experimental determination of the fluid-absent melting relations in the pelitic system: Consequences for crustal differentiation: Contributions to Mineralogy and Petrology, v. 98, p. 257–276, doi:10.1007/BF00375178.

Viete, D.R., Oliver, J.H., Fraser, G.L., Forster, M.A., and Lister, G.S., 2013, Timing and heat sources for the Barrovian metamorphism, Scotland: Lithos, v. 177, p. 148–163, doi:10.1016/j.lithos.2013.06.009.

Vine, F.J., and Matthews, D.H., 1963, Magnetic anomalies over oceanic ridges: Nature, v. 199, p. 947–949, doi:10.1038/199947a0.

Waldbaum, D.R., and Thompson, J.B., Jr., 1969, Mixing properties of sanidine crystalline solutions: IV. Phase diagrams from equations of state: The American Mineralogist, v. 54, p. 1274–1297.

Walther, J.V., 1990, Fluid dynamics during progressive regional metamorphism, *in* Bredehoft, J.D., and Norton, D.L., eds., The Role of Fluids in Crustal Processes: Washington, D.C., National Academy of Sciences, p. 64–71.

Walther, J.V., and Helgeson, H.C., 1977, Calculation of the thermodynamic properties of aqueous silica and solubility of quartz and its polymorphs at high pressures and temperatures: American Journal of Science, v. 277, p. 1315–1351, doi:10.2475/ajs.277.10.1315.

Walther, J.V., and Helgeson, H.C., 1980, Description and interpretation of metasomatic phase relations at high pressures and temperatures: 1. Equilibrium activities of ionic species in nonideal mixtures of CO_2 and H_2O: American Journal of Science, v. 280, p. 575–606, doi:10.2475/ajs.280.7.575.

Walther, J.V., and Orville, P.M., 1982, Volatile production and transport in regional metamorphism: Contributions to Mineralogy and Petrology, v. 79, p. 252–257, doi:10.1007/BF00371516.

Walther, J.V., and Wood, B.J., 1984, Rate and mechanism in prograde metamorphism: Contributions to Mineralogy and Petrology, v. 88, p. 246–259, doi:10.1007/BF00380169.

Wark, D.A., and Watson, E.B., 2006, TitaniQ: A titanium-in-quartz geothermometer: Contributions to Mineralogy and Petrology, v. 152, p. 743–754, doi:10.1007/s00410-006-0132-1.

Waters, D.J., 1988, Partial melting and the formation of granite facies assemblages in Namaqualand, South Africa: Journal of Metamorphic Geology, v. 6, p. 387–404, doi:10.1111/j.1525-1314.1988.tb00430.x.

Waters, D.J., and Lovegrove, D.P., 2002, Assessing the extent of disequilibrium and overstepping of prograde metamorphic reactions in metapelites from the Bushveld complex aureole, South Africa: Journal of Metamorphic Geology, v. 20, no. 1, p. 135–149, doi:10.1046/j.0263-4929.2001.00350.x.

Watson, E.B., and Brenan, J.M., 1987, Fluids in the lithosphere: 1. Experimentally-determined wetting characteristics of CO_2-H_2O fluids and their implications for fluid transport, host-rock physical properties, and fluid inclusion formation: Earth and Planetary Science Letters, v. 85, p. 496–515.

Watson, E.B., Wark, D.A., and Thomas, J.B., 2006, Crystallization thermometers for zircon and rutile: Contributions to Mineralogy and Petrology, v. 151, no. 4, p. 413–433, doi:10.1007/s00410-006-0068-5.

Weill, D.F., 1966, Stability relations in the Al_2O_3-SiO_2 system calculated from solubilities in the Al_2O_3-SiO_2-Na_3AlF_6: Geochimica et Cosmochimica Acta, v. 30, p. 223–237, doi:10.1016/0016-7037(66)90109-8.

Williams, I.S., 2001, Response of detrital zircon and monazite, and their U-Pb isotopic systems, to regional metamorphism and host-rock partial melting, Cooma complex, southeastern Australia: Australian Journal of Earth Sciences, v. 48, p. 557–580, doi:10.1046/j.1440-0952.2001.00883.x.

Williams, M.L., Jercinovic, M.J., and Terry, M.P., 1999, Age mapping and dating of monazite on the electron microprobe: Deconvoluting multistage tectonic histories: Geology, v. 27, p. 1023–1026, doi:10.1130/0091-7613(1999)027<1023:AMADOM>2.3.CO;2.

Williams, M.L., Jercinovic, M.J., Goncalves, P., and Mahan, K., 2006, Format and philosophy for collecting, compiling, and reporting microprobe monazite ages: Chemical Geology, v. 225, p. 1–15, doi:10.1016/j.chemgeo.2005.07.024.

Williams, M.L., Jercinovic, M.J., and Hetherington, C.J., 2007, Microprobe monazite geochronology: Understanding geologic processes by integrating composition and chronology: Annual Review of Earth and Planetary Sciences, v. 35, p. 137–175, doi:10.1146/annurev.earth.35.031306.140228.

Wilson, S.A., Dipple, G.M., Power, I.M., Thom, J.M., Anderson, R.G., Raudsepp, M., Gabites, J.E., and Southam, G., 2009, Carbon dioxide fixation within mine wastes of ultramafic-hosted ore deposits: Examples from the Clinton Creek and Cassiar chrysotile deposits, Canada: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 104, p. 95–112, doi:10.2113/gsecongeo.104.1.95.

Wing, B.A., Ferry, J.M., and Harrison, M., 2003, Prograde destruction and formation of monazite and allanite during contact and regional metamorphism of pelites: Petrology and geochronology: Contributions to Mineralogy and Petrology, v. 145, p. 228–250, doi:10.1007/s00410-003-0446-1.

Winkler, H.G.F., 1965, Petrogenesis of Metamorphic Rocks (translated from German): Berlin, Springer-Verlag, 220 p.

Wood, B.J., and Nicholls, J., 1978, The thermodynamic properties of reciprocal solid solutions: Contributions to Mineralogy and Petrology, v. 66, p. 389–400, doi:10.1007/BF00403424.

Yardley, B.W.D., 1977a, An empirical study of diffusion in garnet: The American Mineralogist, v. 62, p. 793–800.

Yardley, B.W.D., 1977b, The nature and significance of the mechanism of sillimanite growth in the Connemara schists, Ireland: Contributions to Mineralogy and Petrology, v. 65, p. 53–58, doi:10.1007/BF00373570.

Yardley, B.W.D., 2009, The role of water in the evolution of the continental crust: Journal of the Geological Society, London, v. 166, p. 585–600, doi:10.1144/0016-76492008-101.

Yardley, B.W.D., and Bodnar, R.J., 2014, Fluids in the continental crust: Geochemical Perspectives, v. 3, no. 1, p. 1–127, doi:10.7185/geochempersp.3.1.

Yardley, B.W.D., and Valley, J.W., 1997, The petrologic case for a dry lower crust: Journal of Geophysical Research–Solid Earth, v. 102, no. B6, p. 12,173–12,185, doi:10.1029/97JB00508.

Yoder, H.S., Jr., and Tilley, C.E., 1962, Origin of basalt magmas: An experimental study of natural and synthetic rock systems: Journal of Petrology, v. 3, p. 342–532, doi:10.1093/petrology/3.3.342.

Zack, T., Moraes, R., and Kronz, A., 2004, Temperature dependence of Zr in rutile: Empirical calibration of a rutile thermometer: Contributions to Mineralogy and Petrology, v. 148, p. 471–488, doi:10.1007/s00410-004-0617-8.

Zen, E.-a., 1966, Construction of Pressure-Temperature Diagrams for Multicomponent Systems After the Method of Schreinemakers: A Geometric Approach: U.S. Geological Survey Bulletin 1225, 56 p.

Zevenhoven, R., Fagerlund, J., and Songok, J.K., 2011, CO_2 mineral sequestration: Developments toward large-scale application: Greenhouse Gases: Science and Technology, v. 1, p. 48–57.

Geological Society of America Special Papers Online First

The metamorphosis of metamorphic petrology

Frank S. Spear, David R.M. Pattison and John T. Cheney

E-mail alerting services	click www.gsapubs.org/cgi/alerts to receive free e-mail alerts when new articles cite this article
Subscribe	click www.gsapubs.org/subscriptions to subscribe to Geological Society of America Special Papers
Permission request	click www.geosociety.org/pubs/copyrt.htm#gsa to contact GSA.

Notes

THE GEOLOGICAL SOCIETY OF AMERICA