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.
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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.

$Al_2SiO_5$ System

One of the most important sets of phase boundaries in metamorphic petrology involves the $Al_2SiO_5$ polymorphs andalusite, sillimanite, and kyanite. The invariant point involving all three—the $Al_2SiO_5$ 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 temperature 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 $Al_2SiO_5$ phase diagram. From the late 1950s through the early 1970s, several experimental studies on the $Al_2SiO_5$ 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 $Al_2SiO_5$ 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 $Al_2SiO_5$ 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 (Schulinding, 1957); S62 (Schulinding, 1962); W66 (Weill, 1966); W65 (Winkler, 1965).
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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.

\[ \text{ln} K_D = -2109 + 0.782 \frac{T(K)}{10,000} \]

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) In 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 $3\text{Fe}_2\text{SiO}_4 + \text{O}_2 = 3\text{SiO}_2 + 2\text{Fe}_3\text{O}_4$. This buffer assemblage was isolated in the outer part of a two-capsule assembly, and equilibrium with $\text{H}_2\text{O}$ ($\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}$) resulted in control of hydrogen fugacity ($f_{H_2O}$) 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 $\text{H}_2\text{O}$ 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.

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., $p\text{O}_2$ [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 $\text{Fe}^{2+}/\text{Fe}^{3+}$ 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

![Figure 3. $f_{O_2}$-$T$ diagram showing the stability of the Fe-biotite annite (KFe$_3$AlSi$_3$O$_{10}$[OH]$_2$), after Eugster and Wones (1962). HM—hematite-magnetite; MMO—manganese-manganese oxide; NNO—nickel-nickel oxide; QFM—quartz-fayalite-magnetite; WM—wustite-magnetite; IM—iron-magnetite; IW—iron-wüstite buffer; IQF—iron-quartz-fayalite.](image-url)
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-diffusion isotopic 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., Graetz and Heinrich, 1991), and...
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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-diopsid-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 H2O in the 1960s (e.g., Anderson, 1967; Burnham et al., 1969), for CO2 in 1975 (Shmulovich and Shmonov, 1975), and for H2O-CO2 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 H2O-CO2 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; Shmulovich 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 CO2 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 Waldbaan, 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 + CO2 more than 60 years earlier. However, metamorphic rocks involved solid solution phases with considerable crystal chemical complexity as well as fluids (e.g., H2O-CO2 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:

$$\mu_i^e = \mu_i^l = \mu_i^g,$$  (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 \( C_i - C_j \) in the notation of Thompson). This statement includes the special case of \( \mu_i^e = \mu_i^l = \mu_i^g \) 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 \( P\text{-}T \) 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-MgO-SiO₂-H₂O-CO₂ system that links serpentinites and marbles (Trommsdorff and Connolly, 1990). The most important rock type for which petrologic 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 K₂O·FeO·MgO·Al₂O₃·SiO₂·H₂O). 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.
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 + H2O and staurolite + chlorite + muscovite = Al2SiO5 + biotite + H2O. These reactions appear on all subsequent grids, as does the invariant point Al2SiO5 + chloritoid + staurolite + garnet (+ quartz + muscovite + H2O). 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 = Al2O3, S = SiO2, H = H2O, K = K2O, F = FeO, M = MgO. Mineral abbreviations after Kretz (1983).
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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 Hol-
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 inter-
pret. 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 vis-
ible 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 sys-
tem 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 assem-
blage constraints to complement P-T estimates from geothermo-
barometry, 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 equilib-
rium relations plus mass balance equations leads to a system of
equations with a variance of only two—known as Duhem’s theo-
rem (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. Pow-
ell 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 com-
position 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 dia-
agrams—“pseudosection”—has theoretical justification but may
ingender 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 com-
position, 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 H2O. (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
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 Petrakis, 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 heart of future phase equilibrium analysis of metamorphic rocks under-going 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 granite on the island of Holsnøy, Norway, were demonstrated to be metastable with respect to eclogite, with the latter developing at the expense of the granite only where fluid influx catalyzed the otherwise kinetically impeded transformation reaction. For the granulites on Holsnøy, 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,
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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).

Electrode 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 Iunknown/Ifstandard 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 Atherstone 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.
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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, 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).](image-url)
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).
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 LaB₆ 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 there 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 relatively 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 H₂O. The implication of this observation was that the chemical potential of H₂O (or “relative humidity” as Thompson referred to it) was constant among assemblages over a restricted outcrop area. The constancy of μH₂O 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 μH₂O were reinforced by another major contribution by D.S. Korzhinski (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 μH₂O 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 $\mu_{H_2O}$. 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 $5 \times 10^4$ 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
characteristics of $\text{H}_2\text{O}$ and $\text{CO}_2$ 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 $\delta^{18}\text{O}$ 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 $\text{H}_2\text{O}$-rich fluid inclusions to dominantly $\text{CO}_2$-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
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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 H2O 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 granitic 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-aH2O 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-aH2O 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).
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.](image-url)
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.

A key constraint in distinguishing these two exhumation paths is the presence or absence of aragonite in the assemblage. Aragonite is the stable CaCO3 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.

![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).](https://example.com/figure14.png)
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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$^{-3}$; $t_\infty$ 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).]
Spear 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
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 sapphire, osmutilite, 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 “q” 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.
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., $t = h^2/k = [35,000 \text{ m}]^2/10^{-6} \text{ m}^2 \text{ s}^{-1} = 39 \text{ Ma}$). 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,
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 pseudotachylite development in eclogitized rocks, in which the pseudotachylite 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
The metamorphism of metamorphic petrology

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?

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