3.07 Geochemical Zoning in Metamorphic Minerals

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3.07.1 INTRODUCTION

Rock’s encode the sum of Earth processes that affected them during their “lifetimes,” and the purpose of most geological studies is to invert that information to refine our understanding of those processes. A metamorphic rock records not just a peak $P–T$ condition, a single cooling rate, or a simple texture, but rather has undergone an evolving history of changes in $P$ and $T$, mineral abundances, rim compositions, and textures, acting over its metamorphic lifespan, in response to heat flow, stress and strain, and inter- and intragranular movement of material. The greatest advances in understanding metamorphic rocks have been achieved through a recognition that
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3.07.2 MAJOR ELEMENTS

3.07.2.1 Rayleigh Distillation

Rayleigh distillation describes the partitioning of a chemical species (element, molecular species, isotope, etc.) between two reservoirs during a distillation process, i.e., the preferential transfer of material from one reservoir to another (Rayleigh, 1896). If a geochemical species is especially compatible within a mineral, then as the mineral grows, the concentration of that species in the matrix and toward the rim of the mineral will decrease during metamorphism. The rock matrix and the growing crystals are the reservoirs from which and into which the species is being transferred. The rock matrix is compositionally homogeneous and if the mineral undergoes perfect fractional crystallization, so that it preserves a perfect compositional record of its growth, its compositions will conform to Equation (1) (Hoefs, 1997):

\[ C_i^M = \alpha_i C_i^R f^{\alpha_i - 1} \]  

where \( C_i^M \) is the concentration of the species \( i \) in the mineral, \( \alpha_i \) is the fractionation factor (partition coefficient) for species \( i \) in the mineral relative to the rock, \( C_i^R \) is the initial concentration in the rock matrix, and \( f \) is the fraction of the species \( i \) remaining in the rock. For \( \alpha_i > 1 \) (i.e., the species partitions into the mineral), the instantaneous concentration of the species in the mineral will exponentially decrease, asymptotically approaching 0. A linear traverse across such a grain should be characteristicly “bell shaped.” For \( \alpha_i < 1 \) (i.e., the species partitions into the matrix), the instantaneous concentration will increase, because mineral growth depletes the matrix in other components, increasing the concentration of the less-preferred species.

Hollister (1966, 1969) first proposed that manganese zoning in garnets could be understood in terms of Rayleigh distillation. He recast Equation (1) in terms of weight percent MnO in the garnet (\( C_{Mn}^{Grt} \)) and in the manganese-bearing minerals of the rock (\( C_{Mn}^{R} \)), and the weight fraction of garnet (\( W_{Grt} \)) relative to the other manganese-bearing minerals in the rock (\( W_o \)):

\[ C_{Mn}^{Grt} = \alpha_{Mn} C_{Mn,0}^{R} \left(1 - \frac{W_{Grt}}{W_o}\right)^{\alpha_{Mn} - 1} \]  

He then showed that the manganese zoning profiles in garnets from Kwiolek, British Columbia could be fit with Rayleigh distillation models for \( \alpha_{Mn} \) values in the range 15–40 (Figure 1). Although manganese in garnet is the type example of Rayleigh distillation during metamorphism, other minerals that strongly partition an element can also show qualitatively similar chemical depletions from cores to rims (Figure 2).
Hollister’s work was critical to later interpretations, because Rayleigh distillation implies perfect preservation of compositions, i.e., that compositions were not modified during or after mineral growth by processes such as diffusion, dissolution–reprecipitation, and recrystallization. Ever since Hollister’s classic paper, “bell-shaped” Mn-profiles in garnets have been cited as prima facie evidence for the preservation of growth zonation. Although bell-shaped profiles are expected for Rayleigh distillation, they are not proof positive that a mineral has faithfully retained its original composition, because compositions may change during or after growth, and still exhibit a general trend of decreasing manganese from core to rim. Furthermore, in Rayleigh distillation sensu stricto the value of $\alpha$ is constant. Partitioning of elements depends on temperature ($T$), and because changes in $T$ will drive mineral growth, $T$ and $\alpha$ are likely to change as the mineral grows. In fact, the best fit to the Kwoiek profiles has a continuously decreasing value of $\alpha_{\text{Mn}}$ from core to rim, which Hollister (1969) ascribed to an increase in $T$ as the garnets grew. Compositional patterns in minerals (e.g., Figures 1 and 2) are usually the sum of several contributing processes; their formation is therefore better termed “fractional crystallization” than “Rayleigh distillation.”

### 3.07.2.2 Equilibrium Partitioning and Growth Zoning Models

The matrix of a metamorphic rock is not well stirred and homogeneous. It is better described as an assembly of chemically distinct minerals that simultaneously change mode and composition during metamorphism. Furthermore, if growth is driven by a change in pressure ($P$) or $T$, element partitioning changes as the mineral grows. Modeling these effects requires assessing the changes in abundance and composition of each mineral in a rock, as well as any $P$ or $T$ changes attending mineral growth. This was first accomplished in a fully quantitative fashion by Spear (1988), using a differential thermodynamic technique that he dubbed the Gibbs’ method (Spear et al., 1982). In this approach, changes in mineral composition and mode are determined from a starting set of compositions, modes, and $P$–$T$ conditions, as a function of the thermodynamic properties of the minerals (entropy, volume, and mixing parameters), compositions, and changes in $P$ and $T$. Numerous publications have refined these models for interpreting geochemical zoning patterns (e.g., Spear and Selverstone, 1983; Spear, 1988; Spear et al., 1990a, b, 1995, 1999; Wang and Spear, 1991; Spear and Florence, 1992; Kohn, 1993a; Young, 1993; Menard and Spear, 1996; Kohn et al., 1997; Spear and Markussen, 1997; Pyle and Spear, 2003). An “integrated” form of this approach is also possible (Spear, 1993) and was implemented by Powell et al. (1998) as an extension of their work on internally consistent compositions.

In thermodynamically based models, it is critical to account for the $P$- and $T$-dependence of the partitioning of elements among minerals, as well as the mass balance of reactions among minerals. A set of equations corresponds to each of these requirements. The principles have been detailed elsewhere (Spear, 1993), and so the equations are simply presented here.

The equations that describe element partitioning are the differentials of the thermodynamic expression of equilibrium for each independent reaction:

$$dG = 0 = \left(R \ln K_{eq} - \Delta S + RT \frac{\partial \ln K_{eq}}{\partial T}\right) dT$$

$$+ \left(\Delta V + RT \frac{\partial \ln K_{eq}}{\partial P}\right) dP$$

$$+ RT \sum_j \frac{\partial \ln K_{eq}}{\partial X_j} dX_j$$

(3)

where $\Delta S$ and $\Delta V$ are the changes in molar entropy and volume for each reaction, $R$ is the gas constant, $dT$, $dP$, and $dX_j$ are the changes in temperature, pressure, and mole fraction of the phase component $j$, and $K_{eq}$ is the equilibrium constant:

$$K_{eq} = \prod_j (a_j)^{n_j}$$

(4)

where $a_j$ and $n_j$ are the activity and the stoichiometric coefficient of the phase component $j$ involved in the reaction. Each mineral is also subject to a stoichiometric constraint, because the sum of mole fractions must equal 1, which in differential form is

$$\sum_j dX_j = 0$$

(5)

The variance of the combined set of equations of the types shown in Equations (3) and (5) is equivalent to the thermodynamic degrees of freedom ("the number of chemical components") plus 2 (for $P$ and $T$) minus "the number of minerals"). This set of equations involves only intensive variables, and is important for inferring $P$–$T$ paths from chemical zoning.

It is often convenient to assume a closed chemical system, which imposes one mass balance constraint for each chemical component. In differential form, each equation is

$$dm_i = 0$$

$$= \sum_k M_k \sum_j n_{i,j} dX_{j,k} + \sum_k \left(\sum_j n_{i,j} X_{j,k}\right) dM_k$$

(6)

where $m_i$ and $n_{i,j}$ are the number of moles of each chemical component $i$ (e.g., SiO$_2$, Al$_2$O$_3$, etc.) in the rock and in each phase component (j) of each mineral (k), respectively, $M_k$ is the number of moles of the mineral $k$ in the rock (i.e., proportional to its mode), $X_{j,k}$ is the mole fraction of the phase component $j$ in the mineral $k$, and the summation is over all minerals in the rock. This equation simply reflects the transfer of material as accomplished via changes to mineral compositions (first summation in $dX_{j,k}$) and modes (second summation in $dM_k$). Combining equations of the type shown in Equation (6) with the equilibrium and stoichiometric constraints yields a set of equations with a linear algebraic and thermodynamic variance of only 2, a result known as Duhem’s theorem (Spear, 1988). Duhem’s theorem implies that, after specifying starting conditions ($P$, $T$, $X$, and $M$), one can, for example, specify a $\Delta P$ and $\Delta T$ and predict changes in mineral composition and mode with thermodynamic and mass balance rigor. This permits contouring of $P$–$T$ space with mineral compositions and modes, to see graphically how compositions and abundances change with changing $P$–$T$ conditions (Figure 3; e.g., Spear et al., 1982, 1990b; Spear and Silverstone, 1983; Kohn, 1993a; Spear, 1993; Spear and Markussen, 1997; Pyle and Spear, 2003).

Strictly speaking, a zoning profile that is developed during growth depends on the $P$–$T$ path of the rock because fractional crystallization is path dependent. Therefore, contour diagrams are completely accurate only for equilibrium crystallization models, in which minerals are compositionally homogeneous. Although such diagrams may not predict chemical zoning precisely, nonetheless they reveal compositional and modal trends that help interpret metamorphic mineral growth and composition change. To a first order, Rayleigh distillation would appear to be a dominant process controlling $X_{\text{SpS}}$ and $X_{\text{Prp}}$ (where SpS and Prp represent spessartine (Mn$_3$Al$_2$Si$_3$O$_4$) and pyrope (Mg$_3$Al$_2$Si$_3$O$_12$), respectively), because neither show maxima or minima over the contoured region (Figure 3). However, $X_{\text{Alm}}$ (Alm = almandine (Fe$_3$Al$_2$Si$_3$O$_12$)) shows obvious non-Rayleigh behavior, even though iron is strongly preferred by garnet. In fact, the trends in $X_{\text{Alm}}$, $X_{\text{SpS}}$, and $X_{\text{Prp}}$ are described quite well in terms of iron, magnesium, and manganese phase equilibria. The end-member reactions that form garnet from chlorite + quartz occur at low, intermediate, and high temperatures for the magnesium-, iron-, and magnesium endmembers, respectively (Wang and Spear, 1991). Thus, with increasing $T$, phase equilibria demand that manganese continually decreases, magnesium continually increases, and iron shows a maximum in the vicinity of the iron-endmember reaction.
These diagrams illustrate that Rayleigh distillation is not particularly useful for explaining Fe–Mg–Mn systematics, even though there are major differences in the partitioning of these elements between garnet and the matrix minerals. Instead, reaction locations in the Fe–Mg–Mn garnet system better explain the overall trends. More realistic models of intracrystalline zoning combine thermodynamic equilibrium and mass balance with fractional crystallization (Spear, 1988, 1993). An example involving an isobaric temperature increase (Figure 4) illustrates how fractional crystallization profiles deviate from equilibrium models. Most importantly, manganese decreases faster than predicted by equilibrium models, causing iron and magnesium to increase faster. The actual zoning patterns reflect both phase equilibria and chemical kinetics.

Although no theoretical model can capture the idiosyncracies of every rock, there are now hundreds of examples of garnets whose chemical zonation follows the basic patterns depicted in Figure 4 of decreasing manganese, increasing magnesium, and decreasing Fe/(Fe + Mg) from core to rim. This implies that thermodynamic equilibrium and fractional crystallization are plausible drivers of chemical zonation, and that both thermodynamics and mass balance must be accounted for to explain compositional zonation patterns quantitatively. The occurrence of profiles that have a Rayleigh-like appearance in one or more elements (Figure 1) is evidence that
fractional crystallization has occurred, but not that compositions are perfectly preserved, or that simple Rayleigh distillation models are accurate.

3.07.2.2.1 P–T paths

The retrieval of metamorphic P–T paths is a major application of quantitative modeling of chemical zonation in metamorphic garnets. If the chemical zonation encoded in a garnet is a reflection of the changes in P and/or T that drove garnet growth, then in principle one can invert the zonation profile to infer those P and T changes. That is, if \( \Delta P \) and \( \Delta T \) cause \( \Delta X_{jk} \), one should be able to use the \( \Delta X_{jk} \) that are preserved as chemical zoning to infer the original \( \Delta P \) and \( \Delta T \). This approach is computationally simple if mass balance constraints are imposed. Duhem’s theorem requires a variance of only 2, so zonation in only two components of the garnet (two \( \Delta X_{jk} \)) are necessary to retrieve \( \Delta T \) and \( \Delta P \). However, it is difficult to verify that the mass of a chemical component has remained constant. For example, the whole-rock Na\(_2\)O and CaO contents depend on bulk plagioclase content and composition. If plagioclase cores are nonreactive, the effective bulk composition that the garnet “sees” as it grows may be substantially depleted in Na\(_2\)O and/or CaO compared to the whole rock. Plagioclase nonreactivity affects calcium mass balance, which influences \( X_{Grs} \) trends in garnet (Spear et al., 1990b). This problem may be evident in plagioclase compositional zoning, but difficult to model quantitatively. Consequently, most workers use only the equations that involve intensive variables (\( dP \), \(dT \), and \( dX_{jk} \)). The linear algebraic variance of the set of equations is then equivalent to the thermodynamic variance, which ordinarily means that changes in several mole fractions must be measured to resolve \( dP \) and \( dT \). In the case of typical garnet-grade metapelites, the thermodynamic variance is 4, so four independent \( dXs \) must be measured. Only three of the major mole fractions in garnet are independent, so changes in the mole fraction of another mineral component would need to be measured to model a P–T path. The calculated path can be very sensitive to the choice of the fourth \( dX \) (Kohn, 1993b). For example, \( dX_{Ann} \) (\( Ann = \) annite (KFe\(_3\)AlSi\(_3\)O\(_{10}(OH)_2) \)) and \( dX_{Phl} \) (\( Phl = \) phlogopite (KMg\(_3\)AlSi\(_3\)O\(_{10}(OH)_2) \)) in biotite are poor choices numerically because they do not resolve changes in pressure, whereas \( dX_{An} \) (\( An = \) anorthite (CaAl\(_2\)Si\(_2\)O\(_8) \)) in plagioclase is numerically preferable.

The first detailed P–T path determined by inversion of a zoning profile was from the Tauern Window, Austria (Figure 5; Selverstone et al., 1984). The rock has an unusual, low-variance assemblage, so in fact only two independent \( dX_{jk} \) were needed to retrieve a path. Two logical pairings are \( X_{Alm} – X_{Grs} \) and \( X_{Sps} – X_{Grs} \), because \( X_{Sps} \) and \( X_{Alm} \) are both sensitive to temperature (e.g., Figure 3), whereas \( X_{Grs} \) is moderately sensitive to pressure. The different path calculations show very similar P–T evolution—exhumation by \(-3 \) kbar with heating of \(-20 \) °C (Figure 5(b); open symbols)—suggesting that the model assumptions are valid, i.e., that chemical equilibrium was attained among minerals, and

![Figure 5](image-url)
garnet faithfully retained a record of changing composition. Subsequent updates to mixing models and thermodynamic data (Berman, 1988; Holland and Powell, 1998; Pattison et al., 2002), especially for water, suggest that the change in $\Delta T$ was $\sim 75$ °C, although differences between calculations using the thermodynamic databases and models are now imperceptible. Most importantly, none of these modifications affect the original conclusion of Selverstone et al. that the garnet grew during exhumation with heating (Figure 5(b)).

The recovery of the Tauern Window $P$–$T$ path (Selverstone et al., 1984) was revolutionary because the geodynamics community had predicted that exhumation with heating would be the result of overthickening, relaxation of isotherms, and exhumation in collisional orogens (England and Richardson, 1977). England and Thompson (1984) published a now-classic thermal modeling study the same year as Selverstone et al. (1984), in which they investigated numerically the $P$–$T$ implications of overthickening during orogenesis. The convergent series of publications in petrology and geodynamics (Spear and Selverstone, 1983; Spear et al., 1984; Selverstone et al., 1984; England and Thompson, 1984; Thompson and England, 1984) have linked these two fields inseparably, so that today most metamorphic petrologists justify $P$–$T$ path research on the basis of its ability to inform geodynamic and tectonic processes.

### 3.07.2.3 Diffusion

Diffusion is a thermally activated process, whereby a chemical or isotopic species moves down a chemical potential gradient (usually from high to low concentration), at a rate dependent on the diffusion coefficient, $D$. This applies to the progressive decrease of growth zoning in a mineral as a rock heats, and to diffusive fluxes into or out of the surface of a mineral as processes in the matrix alter the rim composition relative to the mineral interior. The diffusion coefficient is formally defined as the proportionality constant between flux rate ($J$) and concentration gradient ($\nabla C$):

$$J = -D\nabla C$$  \hspace{1cm} (7)

and is an exponential function of temperature:

$$D = D_o e^{-E_a/kT}$$  \hspace{1cm} (8)

where $D_o$ is a pre-exponential constant, $E$ is the activation energy, $R$ is the gas constant, and $T$ is absolute temperature. For cations, $E$ generally depends weakly on pressure and $f_{O_2}$ (for minerals that contain iron and other redox sensitive elements). Commonly, the $P$-dependence is expressed as an activation volume contribution to $E$, and results are adjusted to a particular $f_{O_2}$ buffer, for example, the graphite–$O_2$ buffer (Loomis, 1978a,b; Loomis et al., 1985; Chakraborty and Ganguly, 1991, 1992; Chakraborty and Rubie, 1996; Ganguly et al., 1998a). These corrections are especially important for reconciling experimental data that are collected at different $P$ and $f_{O_2}$.

The diffusion coefficient can also depend on composition, and this gives rise to three different types of diffusion coefficients (e.g., see Chakraborty and Ganguly (1991)):

(i) tracer diffusion describes movement of an element at infinite dilution (e.g., iron in “pure” forsterite);

(ii) self-diffusion describes movement of an element in the absence of a chemical potential gradient (e.g., iron in pure fayalite), as determined via measurement of isotope diffusion rates; and

(iii) interdiffusion describes movement of one element in exchange for another (e.g., Fe–Mg interdiffusion in a forsterite–fayalite solid solution).

Tracer and self-diffusion do not cause appreciable chemical compositional changes. Consequently, geologic applications to major and minor element zoning ubiquitously involve interdiffusion. However, there is generally not a single interdiffusion coefficient in a multicomponent mineral. Rather, for an $n$-component mineral, the concentration gradient ($\nabla C$) and chemical flux rate ($J$) are $(n-1)$ vectors related via an $(n-1) \times (n-1)$ diffusion coefficient matrix (Lasaga, 1979). Each term in $\nabla C$ and $J$ refers to a chemically independent component, and the dimensionality is reduced because the flux rate of one component can be expressed in terms of rates of the other $(n-1)$ components. Lasaga (1979) described how to derive the diffusion coefficient matrix from self-diffusion coefficients, if the thermodynamic mixing properties of the different components are known. Assuming ideal solid solutions, each component in the matrix ($D_{ij}$) is

$$D_{ij} = D_i^\ast \delta_{ij} - \left[ \frac{D_i^\ast C_i z_i z_j}{\sum_k D_{kj}^\ast C_k z_k^2} \right] \left[ D_j^\ast - D_p^\ast \right]$$  \hspace{1cm} (9)

where $z_i$ is the charge on the cation $i$, $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$, and $D^\ast$ is the self-diffusion coefficient. More complex equations apply for nonideal solid solutions. Some geologic problems can be reduced essentially to binary exchange, for example, for Fe–Mg interdiffusion in silicates. For a binary nonideal solution, the expression for the interdiffusion coefficient is

$$D_{ij} = \left[ \frac{D_i^\ast D_j^\ast \left[ 1 + \left( \frac{\partial \ln \gamma_i}{\partial \ln X_i} \right)_{P,T} \right]}{X_i D_i^\ast + X_j D_j^\ast} \right]$$  \hspace{1cm} (10)

where $i$ and $j$ are the interdiffusing species, $X_i$ and $X_j$ are the mole fractions of components $i$ and $j$, respectively, and $\gamma_i$ is the activity coefficient of
Thus, most generally, cation diffusion calculations must account for the $T$, $P$, $f_{O_2}$, and $X$-dependence of the diffusion coefficient, including the mixing properties of the mineral. Few, if any, applications actually account explicitly for all these effects; instead, simplifications are made, for example, assuming that solutions are ideal, that $f_{O_2}$ is buffered, and/or that $D_i^f$ and $D_j^f$ are approximately equal (which eliminates cross-terms in Equation (9)). Chakraborty and Ganguly (1991, 1992) suggested using an effective binary diffusion coefficient with a single $D_0$ and $E$ that describes interdiffusion of two species over the composition range in the sample studied. In part, these simplifications are useful because even the best diffusion experiments, when extrapolated to metamorphic conditions, yield uncertainties in $D$ of $\pm 1–2$ orders of magnitude. Errors arising from other assumptions are relatively small. Furthermore, many diffusion calculations are limited not by model simplifications, but by uncertainties in the assignment of initial concentrations or changes in rim compositions.

### 3.07.2.3.1 Diffusional flattening of manganese growth profiles in garnet

If an increase in temperature drives garnet growth, fractional crystallization implies that the garnet will develop a core–rim manganese decrease. However, increasing temperature also increases the diffusion rates, and this affects the overall manganese pattern and composition of the rim region. There is competition between fractional crystallization and the core–rim diffusive flux to decrease and increase manganese at the rim. At a sufficiently high temperature, garnet compositions are homogenized. The degree of homogenization can be plotted geographically and, in principle, related to the temperature–time history. Several studies have documented progressively flatter manganese profiles in garnets at progressively higher metamorphic grades (e.g., Anderson and Olimpio, 1977; Woodsworth, 1977; Yardley, 1977; Dempster, 1985; Carlson and Schwarze, 1997).

Investigation of polymetamorphic rocks of the Llano Uplift (Carlson and Schwarze, 1997; Carlson, 2002) illustrates both diffusional flattening of high-manganese cores and near-rim diffusion profiles imposed via thermal overprinting and mineral resorption. For garnet crystals with radii of $\sim 0.5–1$ mm, the degree of manganese flattening depends on peak metamorphic temperatures and grain size (Figure 6). Samples that were collected directly adjacent to plutons have completely flattened core profiles, and the smaller garnets in a single rock exhibit flatter manganese profiles than the larger garnets (Figure 6). Both results are consistent with growth of garnets with manganese-enriched cores that were subsequently flattened as temperature increased, either during the first metamorphic event for samples far from plutons, or during a contact metamorphic overprint for samples at pluton margins. The increase in manganese at the rims of the garnets is the result of postpeak metamorphic garnet resorption, and the repartitioning of manganese among matrix minerals and the garnet rim. Rim zoning impacts many applications, including “geospeedometry” (the use of diffusion changes to track time).

**Figure 6** (a) Plots of garnet MnO content (wt.%) versus distance across central sections of crystals from different localities in the Llano Uplift polymetamorphic block, Texas. Garnets show increased core–rim flattening with increasing temperature (either peak conditions for prograde event or proximity to plutons during static overprinting event). (b) Garnet MnO content versus distance across central sections of crystals of different sizes from a single locality. Garnets show increased core–rim flattening with decreasing grain size. All data are consistent with diffusive modification of earlier-formed growth profiles (sources Carlson and Schwarze, 1997; Carlson, 2002).
of diffusion profiles for estimating cooling rates, and thermobarometry (the determination of metamorphic \( P-T \) conditions).

3.07.2.3.2 Geospeedometry

Lasaga (1983) outlined a technique that he dubbed “geospeedometry” for inverting chemical diffusion profiles at the rims of minerals to infer cooling rates. The basic diffusion equation is

\[
\frac{\partial c}{\partial t} = D(t) \frac{\partial^2 c}{\partial x^2} \quad (11)
\]

where \( c \) is the concentration of the species of interest (e.g., magnesium in garnet), \( D \) is the diffusion coefficient, \( t \) is time, and \( x \) is distance. The difficulty in solving this equation is that \( D \) is a function of \( T \) (Equation (8)), which changes with time. However, Equation (11) can be made analytically tractable through a series of transformations, if linear cooling is assumed \((\text{Lasaga, 1983; Lindström et al., 1991})\). First, Lasaga (1983) introduced a compressed time variable \((t')\):

\[
t' = \frac{1}{\gamma} (1 - e^{-\gamma t}) \quad (12)
\]

where \( t \) is time, and \( \gamma \) is given by

\[
\gamma = \frac{E_s}{RT_{\text{init}}} \quad (13)
\]

\( E \) is the activation energy, \( s \) is the cooling rate (“speed” of cooling), \( R \) is the gas constant, and \( T_{\text{init}} \) is the initial temperature. He then nondimensionalized time \((t')\) and distance \((x')\) as

\[
t'_r = \frac{D_{\text{init}}}{a^2} t' \quad (14)
\]

\[
x'_r = \frac{x}{a} \quad (15)
\]

where \( a \) is the characteristic distance of the diffusing grain (e.g., the grain radius). These substitutions transform Equation (11) to

\[
\frac{\partial c}{\partial t'} = \frac{\partial^2 c}{\partial x'^2} \quad (16)
\]

In principle, one must solve Equation (16) for all minerals in the rock that are diffusively limited from equilibrating. However, many applications involve Fe–Mg exchange between garnet and biotite, and because biotite is almost always homogeneous with respect to Fe/Mg, one need only solve for the diffusion profile in the garnet.

Equation (16) can be solved for \( \gamma \) and hence \( s \) subject to the constraint of equilibrium partitioning on the rim of the garnet due to exchange with another mineral:

\[
K_D(t) = K_{D,\text{init}} \exp \left( -\frac{\Delta H_s}{RT_{\text{init}}^2} t \right) \quad (17)
\]

where \( K_D \) is the distribution coefficient for the exchange (e.g., for Fe/Mg between garnet and biotite), and \( \Delta H \) is the enthalpy of reaction. Lasaga’s original approach has been improved both theoretically and computationally \((\text{Lindström et al., 1991; Lasaga and Jiang, 1995; Ganguly and Tirone, 1999; Jaoul and Sautter, 1999; Ganguly et al., 2000})\).

Two fundamental cautions are, however, warranted. First, the diffusion profile really results from an integrated diffusional history (e.g., \( \text{Ganguly et al., 2000})\):

\[
\gamma = \frac{D(T_{\text{init}})}{\int_0^t D(\tau) d\tau} \quad (18)
\]

which corresponds to an infinite number of cooling paths. Linear cooling (i.e., Equation (13)) is only one solution of Equation (18). Thus, one must interpret the results within the context of the most likely thermal history, for example, linear cooling versus steadily increasing or decreasing rates. Second, Lasaga’s transformation of variables essentially converts the problem into a description of the position-dependent closure temperature \([T_s(x)])\). If the matrix remains compositionally homogeneous (e.g., very small and very large amounts of garnet and biotite, respectively), then a general analytical solution exists \((\text{Dodson, 1986; McDougall and Harrison, 1988})\):

\[
T_s(x) = \frac{E/R}{\ln[eRT_s^2D_s^2/a^2/E_s] + 4S_2(x)} \quad (19)
\]

where \( e \) is the exponential of Euler’s constant, \( 4S_2(x) \) is a position-dependent term, \( x \) is the fractional distance from the mineral center, and the other terms are as described above. The position-dependent temperatures (and hence compositions) recorded along the zoning profile depend on the logarithm of cooling rate. The insensitivity of the composition profile to \( s \) leads to large uncertainties in retrieved \( s \). This problem is further compounded by the large uncertainties in \( D \) because of the large extrapolation of experimental data to metamorphic conditions. For many problems, the uncertainty in the calculated cooling rate may amount to several orders of magnitude \((\text{Lindström et al., 1991})\). Ganguly et al. (2000) have provided an example of geospeedometric calculations for the rocks of the Sikkim Himalaya (NE India). They emphasized that composition profiles should be measured perpendicular to the grain edge, whereas edges may “dip” with respect to the plane of the section, thus requiring correction of
The diffusion profile for the crystal boundary orientation (Figure 7). However, for correctly oriented grains it is relatively straightforward to solve for $g^2_2$: $1 < 10^{14}$. One could then use Equation (13) to infer $s^2_2$, but a uniform cooling rate may not be applicable over the entire temperature range during which Fe–Mg exchange is evident. Instead, Ganguly et al. (2000) used the product $a^2_2 \cdot g^2_2 = D(T_o)$ as a constraint in a one-dimensional thermal model linking cooling with exhumation. From this, they inferred accelerated cooling from an initial rate of $15^\circ C$ Myr$^{-1}$ at $800^\circ C$, to $100^\circ C$ Myr$^{-1}$ by $450^\circ C$. The retrieved cooling rate depends directly on the diffusion coefficient, and because experimental uncertainties in $D$ for divalent cations in garnet are well over an order of magnitude at $T \approx 800^\circ C$, this directly translates into an error in the retrieved cooling rate. That is, if $D$ is not known to better than a factor of 10, neither is $s$ (Lindström et al., 1991).

### 3.07.2.4 Combination of Retrograde Diffusional Exchange and Reaction

Interpretation of near-rim composition profiles depends critically on the nature of retrograde reactions (Robinson, 1991; Spear and Florence, 1992; Figure 8). These belong to two classes. First, exchange reactions (ERs) involve the exchange of two elements between two minerals, for example, Fe–Mg exchange between garnet and biotite (almandine + phlogopite = annite + pyrope). Retrograde exchange reactions do not significantly change mineral modes, and cause divergence of mineral compositions. Second, net-transfer reactions (NTRs) involve production and consumption of minerals, i.e., a net transfer of material among mineral reservoirs. Unlike ERs, NTRs cause mineral compositions to shift in the same direction. Thus, a decrease in magnesium and increase in iron towards the rim of a garnet (e.g., Figure 7) could result from retrograde Fe–Mg exchange between garnet and biotite (an ReER), or retrograde reaction between several minerals, such that they all shift towards iron-richer compositions (an ReNTR; Figure 8). The physical difference between them is that an ReER does not change the position of mineral rims perceptibly, whereas an ReNTR causes mineral resorption or growth. Therefore, it is critical in any geospeedometry study either to verify petrologically that ReNTRs have not occurred, or to characterize the amount by which the boundaries of minerals have moved.

One way of identifying ReNTRs in garnets is to examine their manganese profiles. Because garnet partitions manganese so strongly, growth of garnet causes manganese to decrease towards the rim, whereas resorption will cause it to increase (Figure 8). Therefore, higher manganese at rims is prima facie evidence for the dissolution of garnet via ReNTRs, whereas a flat or decreasing manganese profile at the rim indicates only ReERs. This is evident in diffusion profiles in garnet around biotite inclusions, where iron and magnesium are zoned, but manganese is not (e.g., Spear and Parrish, 1996). Carlson (2002) ascribed composition profiles in garnet rims from the Llano Uplift, Texas, to both ReERs and ReNTRs. These rocks are unusual, because spectacular retrograde coronas permit identification of the original rim locations (Figure 9). Composition profiles show increases in iron and decreases in magnesium towards garnet rims, as expected for diffusional re-equilibration of the garnet rim during cooling (Figure 10).
However, the coronal textures and the increase in manganese towards the garnet rims (Figure 10) both unequivocally indicate operation of one or more garnet-consuming ReNTRs, so that the rim of the garnet has not remained stationary. If this fact was not recognized, application of geospeedometry to the Fe–Mg profiles would yield an apparent cooling rate that is too fast. An estimate of the amount of garnet resorption from the size of the coronas permits a rigorous accounting of mass fluxes (particularly manganese), and fitting of the composition profiles. By accounting quantitatively for both ReERs and ReNTRs, Carlson (2002) refined the relative diffusion rates for calcium, iron, magnesium, and manganese, which in turn permitted reconciliation of the observed

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**Figure 8** Diagrams illustrating the change in Fe/(Fe + Mg) for garnet and biotite during retrograde reactions (Spear, 1993; Kohn and Spear, 2000). (a, b) High-grade, diffusionally homogenized garnets. G1 and B1 are peak compositions; G2 and B2 are retrograde compositions. (a) Effects of retrograde exchange reactions (ReERs). On an Al2O3–FeO–MgO diagram, garnet and biotite compositions diverge with decreasing temperature. The compositions corresponding most closely to peak conditions are the garnet with highest Mg/Fe and biotite with highest Fe/Mg. Because of slow $D_{Fe-Mg}$ in garnet, but fast $D_{Fe-Mg}$ in biotite, biotite remains homogeneous while a diffusion profile is established at the garnet rim. Pairing of garnet core (G1) with matrix biotite (B2) yields a temperature below the peak. (b) Effects of retrograde net transfer reactions (ReNTRs). On an Al2O3–FeO–MgO diagram, garnet rim and biotite compositions move towards higher Fe/(Fe + Mg) during retrograde garnet dissolution. The compositions corresponding most closely to peak conditions are the garnet with highest Mg/Fe and biotite with lowest Fe/Mg. However, the original biotite may not be present, and pairing of matrix biotite (B3) with garnet core (G1) yields too high a temperature. (c) Diagrams for lower-grade conditions illustrating the change to Fe/(Fe + Mg) and Mn in garnet, and Fe/(Fe + Mg) in biotite during retrograde reactions. Dashed line shows original profile at peak conditions. General decrease in $X_{Sp}$ towards rim is result of prograde growth. ReERs (right side) cause an increase in garnet Fe/(Fe + Mg) at rim, which forms a compositional trough near the grain edge (right side). No change in Mn occurs. Pairing of garnet trough composition with matrix biotite yields a temperature below the peak because garnet and biotite have shifted to higher and lower Fe/(Fe + Mg), respectively. ReNTRs (left side) cause an increase in both Fe/(Fe + Mg) and Mn in garnet, which forms compositional troughs near the grain edge in both profiles (left side). Pairing of garnet trough composition with matrix biotite may yield a temperature that is too high because both garnet and biotite shift to higher Fe/(Fe + Mg) (Kohn and Spear, 2000) (reproduced by permission of GSA from Geology, 2000, 28, 1127–1130).
profiles with the independently constrained cooling rate.

Most garnets lack coronas, and resorption may only be evident either texturally from embayed margins or geochemically from near-rim manganese increases. Without direct markers of original rim locations, the extent of reaction is difficult to characterize quantitatively. Therefore, Carlson’s work cautions against application of geospeedometry except in special cases where the garnet rim has not moved, or the amount of garnet resorption is independently determinable. In the case of the garnets from Sikkim analyzed by Ganguly et al. (2000), the small increases in manganese towards garnet rims (Figure 7(b)) imply that garnet has dissolved somewhere in the rock (albeit not necessarily at those particular rims). If dissolution has shortened the near-rim profiles, then calculated cooling rates assuming no resorption will be too fast.

### 3.07.2.5 Thermobarometric Implications

Thermobarometry, or the calculation of $P–T$ conditions from mineral compositions, is not based on mineral zoning, nor does it directly inform processes that cause geochemical zoning. Nonetheless, $P–T$ calculations in metamorphic rocks usually require selecting compositions from minerals that are compositionally heterogeneous. How one selects compositions from a zoned mineral can strongly influence retrieved $P$ and $T$, and that issue is worth discussion.

$P–T$ conditions are ordinarily calculated based on the $T$-dependence of a cation partitioning equilibrium (e.g., Fe–Mg exchange between garnet and biotite), and the $P$-dependence of a net-transfer equilibrium (e.g., anorthite = grossular + aluminosilicate + quartz). Most barometers have moderate slopes, so the calculated $P$ depends moderately on $T$. The basic problem

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**Figure 9** Photomicrograph of spectacularly well-developed corona around relict garnet from Llano Uplift, Texas. The coronas permit identification of the original rim position of the garnet (assuming isovolumetric replacement), which in turn allows quantification of the amount of garnet that was resorbed during cooling (source Carlson and Schwarze, 1997).

**Figure 10** Zoning profiles collected at the outer edges of garnets from rocks with much less pronounced coronas show diffusional patterns over the outer $\sim$50 µm. However, the coronal texture and increase in Mn towards rim unequivocally indicate operation of an ReNTR, which must have consumed part of the diffusion profile as it was growing. Thus, the apparent extent of diffusion is much lower than if the rim had been static. These profiles can be fitted to infer relative rates of cation diffusion (source Carlson, 2002).
lies in choosing the best compositions from which one calculates $T$ (Robinson, 1991; Spear, 1991, 1993, chapter 17; Spear and Florence, 1992; Kohn and Spear, 2000, figure 8). A higher $\text{Mg}/\text{Fe}$ ratio in garnet or $\text{Fe}/\text{Mg}$ ratio in biotite will result in a higher computed $T$. If only ReERs have occurred, then compositions have diverged and all calculated temperatures will be below the peak. Therefore, the highest $T$ will be the best estimate of peak conditions, and, of all compositions expressed in a rock, will correspond to the highest $\text{Mg}/\text{Fe}$ in garnet and highest $\text{Fe}/\text{Mg}$ in biotite. In contrast, if ReNTRs have occurred, then compositions have shifted simultaneously. Consumption of (iron-rich) garnet causes biotite and the garnet rim to shift to more iron-rich compositions. If the iron-enriched matrix biotite is then paired with relict, magnesium-rich garnet, temperatures exceeding peak conditions can be calculated (Spear, 1991; Spear and Parrish, 1996; Kohn and Spear, 2000). Commonly, matrix biotite is rather homogeneous compositionally, so the main difficulties are selecting garnet compositions and assessing how much biotite compositions could have changed. In high-grade garnets, the highest $\text{Mg}/\text{Fe}$ (lowest $\text{Fe}/(\text{Fe} + \text{Mg})$) ordinarily occurs in the core (Figures 7 and 8). In lower-grade garnets, the lowest $\text{Fe}/(\text{Fe} + \text{Mg})$ occurs in an $\text{Fe}/(\text{Fe} + \text{Mg})$ trough, whose location results from competition between prograde growth of garnet, which causes $\text{Fe}/(\text{Fe} + \text{Mg})$ to decrease, and ReERs or ReNTRs, which commonly cause $\text{Fe}/(\text{Fe} + \text{Mg})$ to increase (Figure 8(c)). Similar troughs are observed in manganese for the same reasons (Figure 8(e)).

Within this context, Kohn and Spear (2000) developed a semiquantitative “ReNTR insurance policy.” Because the increases in manganese towards garnet rims predominantly result from garnet resorption, the excess manganese in the rim region relative to the lowest manganese reflects the amount of garnet that was resorbed. The manganese-based estimate of this resorbed volume permits resurrection of the original composition of the matrix biotite prior to the ReNTR. This revised biotite composition can then be paired with the highest $\text{Mg}/\text{Fe}$ composition garnet to better estimate peak $P$–$T$ conditions prior to garnet resorption. This approach is analogous to Carlson’s inference of material fluxes and resulting ReNTR correction of mineral compositions (Carlson, 2002), except that his calculations were texturally based, whereas Kohn and Spear’s were based on X-ray maps of manganese distributions. Application of ReNTR insurance to most rocks in the author’s research collection indicates relatively small corrections: 10–20 °C compared to uncorrected compositions. However, in some cases corrections can be as large as 200 °C (Kohn and Spear, 2000). Virtually all garnets exhibit retrograde manganese increases towards their rims, so ReNTR insurance should be adopted for most rocks, as it permits identification and remedial petrologic action, if necessary. Although both Carlson (2002) and Kohn and Spear (2000) developed their approaches for amphibolite-facies ReNTRs, the implications can be generalized to all metamorphic facies in which diffusion-facies ReNTRs can affect mineral compositions during cooling (Spear and Florence, 1992).

### 3.07.2.6 Kinetically Limited Transport within the Rock Matrix

Compositional zoning in a mineral depends on rates of crystal growth, “nutrient” supply, and “waste” removal. In the previous discussions, it was implicitly assumed that matrix compositions are homogeneous and that equilibrium among grain edges occurs on scales that are large compared to individual crystals. Although this may be true, limited transport of some elements through the matrix can profoundly impact chemical zoning. If diffusion of nutrients limits the rate of crystal growth (diffusion control), then there should be a simple relationship for the spacing between compositional contours ($C$) versus radius ($R$), as normalized to the largest grain in the rock (Kretz, 1974). A different rate-limiting mechanism, such as adsorption and addition of chemical species to the growing crystal surface (interface control), yields a different normalized radius-rate ($C^*$ versus $R^*$) relationship. This concept has been developed extensively by Carlson and co-workers (Carlson, 1989, 1991; Carlson et al., 1995; Denison and Carlson, 1997; Denison et al., 1997; Chernoff and Carlson, 1997, 1999), who have shown that $C$ versus $C^*$ diagrams commonly conform to diffusion control. It is important to recognize that a $C$ versus $C^*$ plot assumes different diffusivities for different elements (Figure 11). Specificially some element must be homogeneous over the sampled region of the rock, and so can be used to monitor the growth rate of different crystals as a function of crystal size, i.e., serve as a geochemical proxy for time (Kretz, 1974; Carlson, 1989), whereas transport of another element diffusionally limits growth (Carlson et al., 1995). For example, slow aluminum diffusion could cause diffusion limited growth, whereas the fast diffusion of manganese provides a time marker. The success of diffusion control in explaining many radius-rate data apparently supports this paradigm.

Other zoning studies further suggest radically different intergranular diffusivities for different elements, and a strong dependence of the
behavior of particular elements on temperature. For example, X-ray maps collected by Yang and Rivers (2001) show that some elements in garnet behave systematically, for example, manganese, whereas others have patterns that mimic the original texture of the rock, for example, chromium. If intergranular diffusion of manganese is fast, then the rim of growing garnets always has the same manganese content, and grains are zoned systematically. But if intergranular diffusion of chromium is extremely slow, then local mineralogical differences in chromium content due to textural variability in mica and/or oxide abundance directly control the local supply of chromium to different edges of growing garnets, and grains become zoned heterogeneously. At low grade, even manganese zoning can be quite heterogeneous (Daniel and Spear, 1998; Spear and Daniel, 1998, 2001). This presumably reflects extremely slow intergranular rates of diffusion, which causes locally heterogeneous supply of manganese.

Rates of intergranular chemical transport are extremely important because they govern the length scales over which equilibrium occurs. For example, the generally systematic behavior of manganese zoning in most garnets (albeit not garnet cores studied by Daniel and Spear (1998)) implies that equilibrium can be assumed over several grain diameters, and that equilibrium thermodynamics can be applied to the rock as a whole. However, the heterogeneous zonation of chromium implies that its distribution is dominated by local effects, and hence is much less easily modeled. These differences in element mobility become increasingly important for many trace elements which are believed to have transport behavior more like chromium and less like manganese, and for accessory minerals, whose occurrence is controlled by the distribution of trace elements.

3.07.2.7 Dissolution–Reprecipitation

Theoretical models suggest that some minerals are driven thermodynamically to change composition, yet are prevented from re-equilibrating via diffusion by extremely slow cation diffusivities. One common example is plagioclase. Anorthite and albite end-members are linked via a coupled substitution (CaIVAlNa\textsubscript{2}Si\textsubscript{2}), and so diffusive re-equilibration of X\textsubscript{An} requires exchange of tetrahedral aluminum and silicon, a process which is extremely slow (Grove et al., 1984). Therefore, the ubiquitous zonation in X\textsubscript{An} must be caused by a mechanism other than diffusion. The texture of many plagioclase grains suggests that they change composition via dissolution of old grains and reprecipitation of new grains or as overgrowths (Figures 12 and 13).

Plagioclase compositional change is intimately tied to garnet growth and consumption as required by calcium mass balance in the rock (Figure 14). Garnet and plagioclase are commonly the only calcium-bearing silicates in a rock. Growth or consumption of calcium-bearing garnet, therefore, consumes or produces the anorthite component of plagioclase. Plagioclase cannot adjust composition diffusionaly, so thermodynamics drives grain dissolution and reprecipitation. Such direct modal and compositional links among minerals must be accounted for when interpreting chemical zoning patterns. Even if the overall mode and composition of reactive plagioclase changes systematically, local dissolution or precipitation can happen continuously or sporadically, leading to different textures in different grains (Figures 12 and 13). Compositional zoning in a single grain can be perplexing or even misleading unless X-ray maps or backscattered electron images of many grains are collected and the overall sense of zoning compared with theoretical expectations. If a mineral contains an essential constituent that is shared by other minerals in the rock,
and if that constituent has an extremely slow intracrystalline diffusivity, then chemical or modal changes in the other minerals will drive dissolution–reprecipitation reactions.

3.07.3 STABLE ISOTOPES

There are relatively few studies of stable isotope zoning in metamorphic minerals, because the required measurements are more difficult than for major elements. This section will focus on
oxygen, because there are more studies of oxygen isotope zoning, and because oxygen transport is more readily modeled. Growth zoning, diffusion zoning, and dissolution–reprecipitation are best documented for this element.

Isotopic compositions are usually expressed in per mil notation, relative to a standard, such as Standard Mean Ocean Water (SMOW):

$$\delta^{18}O(i) = \left( \frac{R_i - R_{SMOW}}{R_{SMOW}} \right) \times 1,000$$ (20)

where \( R_i \) and \( R_{SMOW} \) are the ratios of \(^{18}\text{O} \) to \(^{16}\text{O} \) in the material \( i \) and SMOW, respectively. Partitioning between two materials, \( i \) and \( j \), is usually expressed in terms of a fractionation factor, \( \alpha_{i-j} \), where

$$1,000 \ln \alpha_{i-j} \sim \delta^{18}O(i) - \delta^{18}O(j) = \Delta_{ij}$$ (21)

Partitioning is almost solely dependent on absolute temperature:

$$\Delta_{ij} = \frac{A_{ij}}{T} + \frac{B_{ij}}{T^2} + C_{ij}$$ (22)

where \( A, B, \) and \( C \) are constants. For the partitioning of oxygen among many silicates and oxides, \( B \) and \( C \) are nearly zero and can be ignored, but for fluids all terms must be used (e.g., see summary by Chacko et al. (2001)). Pressure dependence is strongly subsidiary to the effect of temperature, and is similar in most minerals (Polyakov and Kharlashina, 1994), so that mineral–mineral \( \Delta s \) are nearly \( P \)-independent. Equation (22) indicates that the isotopic compositions of minerals tend to converge with increasing temperature.

### 3.07.3.1 Growth Zoning

Many orthosilicates have slow oxygen diffusion rates and can readily develop growth zoning, whereas many sheet and tectosilicates have fast diffusion rates and control the oxygen isotope mass balance of a rock. A rigorous theoretical approach for predicting changes in the isotopic composition of minerals was derived independently (Kohn, 1993a; Young, 1993), by incorporating a set of oxygen isotope partitioning equilibria and mass balance equations into the differential thermodynamics method. These equations maintain partitioning equilibrium:

$$d\Delta_{ij} = \left( \frac{-2A_{ij}}{T^3} + \frac{-B_{ij}}{T^2} \right) dT$$ (23)

(ignoring pressure dependence) and oxygen isotope mass balance:

$$d\delta^{18}O_{sys}N_{sys} = \sum_{k=1}^{n} M_k N_k d\delta^{18}O_k + \sum_{k=1}^{n} N_k \delta^{18}O_k dM_k = 0$$ (24)

where \( \delta^{18}O_{sys} \) is the whole-rock oxygen isotopic composition, \( N_{sys} \) is the total number of moles of oxygen in the system, \( M_k \) and \( N_k \) are the number of moles and the number of moles of oxygen in the \( k \)th mineral, and \( \delta^{18}O_k \) is the \( \delta^{18}O \) of the \( k \)th mineral. For a rock with \( n \) minerals, there are \( n \) new variables (\( \delta^{18}O_k \)), and \( n \) new equations—\((n-1)\) in the form of Equation (23), and one in the form of Equation (24). Thus, the total linear algebraic variance of the combined system of thermodynamic mass balance and isotope partitioning equations remains 2, and changes in only two variables (e.g., \( dP \) and \( dT \)) need to be specified to model changes in \( \delta^{18}O_k \).

When mineral modes change slowly due to continuous reaction over a large temperature range, the temperature dependence of isotopic partitioning controls compositions (Figure 15). For example, garnet in a model metapelite that contains biotite and chlorite simply increases in \( \delta^{18}O \) with increasing temperature because it has a lower \( \delta^{18}O \) value than the whole rock, and mineral compositions converge with increasing temperature. However, at nearly discontinuous reactions, such as

$$\text{garnet} + \text{chlorite} + \text{muscovite} = \text{biotite} + \text{staurolite} + \text{quartz} + \text{H}_2\text{O}$$ (25)

mineral modes change so rapidly that isotopic mass balance (Equation (24)) controls compositions, as indicated by the coincidence of compositional and modal slopes for the staurolite-in reaction. However, such reactions also rapidly exhaust a reactant, so their isotopic influence is ordinarily rather small. Models of growth zoning can be constructed by incorporating fractional crystallization. Generally, in a closed system, the strongest prograde isotope zoning will result from continuous reactions that occur over a large temperature range. Even so, predicted growth zoning is subdued, and resolution of the small changes in isotopic composition indicated by the models requires an analytically and spatially precise technique. Such profiles could not be routinely measured until the advent of miniaturized laser fluorination systems (Sharp, 1990, 1992).

Oxygen isotope zoning in garnet was documented by the early 1990s (Chamberlain and Conrad, 1991, 1993; Young and Rumble, 1993; Jamtveit and Hervig, 1994), but Kohn et al. (1993) described the first isotopic zoning profiles that clearly conformed with independent predictions of growth models. The observed monotonic \( \sim 0.5\%e \) increase
in $\delta^{18}O$ from core to rim (Figure 16) is consistent with prograde growth over the 75 °C temperature interval that had been inferred from major element zoning. Staurolite from the same sample had no resolvable zoning in its interior, which again was consistent with closed-system models. The internal consistency between the theoretical models and observed zonation in this study implies that isotopic partitioning was maintained during prograde metamorphism, and that the rock was closed to infiltration by an isotopically disequilibrium fluid. Conversely, one of the main objectives of measuring oxygen isotope zoning profiles is to identify open system processes by seeking out core–rim isotopic trends that cannot be explained by closed-system models (Chamberlain and Conrad, 1991, 1993; Young and Rumble, 1993; Jamtveit and Hervig, 1994; Kohn and Valley, 1994; Van Haren et al., 1996; Crowe et al., 2001; Skelton et al., 2002).

### 3.07.3.2 Diffusion

Different minerals have radically different oxygen diffusivities (see review by Cole and Chakraborty (2001)), so there is potentially a wealth of petrologic information encoded in the stable isotopic products of diffusion. The effects of diffusive exchange on bulk mineral compositions are widely studied. This is, in large part, an outgrowth of the seminal work of Giletti (1986). Giletti (1986) used the closure temperature concept of Dodson (1973) together with the temperature dependence of isotope partitioning and oxygen isotope mass balance to describe the changes to bulk mineral composition that occur in a rock during cooling. To a first order, his model is accurate for slowly cooled rocks. However, the analytical expression of Dodson (1973) requires a uniform matrix reservoir, whereas the matrix...
adjusts its partitioning character as minerals successively close to isotope exchange. Therefore, Eiler et al. (1992, 1993) modified Giletti’s model to account for modes, grain sizes, and diffusive profiles. The Eiler et al. models are more rigorous, explain more observations, especially from mineralogically uncommon rocks, and predict isotopic zoning profiles in each mineral. Jenkin et al. (1994) independently modeled and explored mode and grain size effects using a similar approach.

An important feature of oxygen diffusion rates is their very strong dependence on water fugacity, $f_{H_2O}$ (for a detailed discussion, see Cole and Chakraborty (2001, pp. 126–155)), although there are several alternative explanations for this behavior (e.g., Elphick and Graham, 1988; Zhang et al., 1991; Graham and Elphick, 1990; McCallum 1995; Doremus, 1998, 1999). Regardless, the $f_{H_2O}$ history strongly influences diffusion rates and isotopic compositions, and should be taken into account explicitly in diffusion models (Kohn, 1999). Conversely, if grain size, grain geometry, and cooling rate are independently determined, differences in isotopic composition or zoning patterns can potentially reveal variations in $f_{H_2O}$ that are difficult to ascertain from mineralogy alone (e.g., Edwards and Valley, 1995).

There are few published oxygen isotope diffusion profiles in natural samples, mainly due to analytical difficulties. The length scale of a natural diffusion profile is commonly of the order of several μm to ~100 μm, and the magnitude of the isotopic change is small (<1‰) except in the outer few microns. Thus, excellent spatial and/or analytical precision is required to demonstrate that an isotopic profile exists, let alone that it is the product of diffusion. Ion microprobe analysis has excellent spatial resolution (ca. 10 μm), but is relatively imprecise analytically (±1‰), whereas microsampling in combination with laser fluorination is analytically precise (±0.1‰), but has much poorer spatial resolution (~250 μm). Both techniques underwent rapid analytical improvements at the end of the twentieth century (e.g., Young et al., 1998a,b; Valley et al., 1998) and may soon permit relatively routine measurement of natural diffusion profiles. Oxygen zoning trends reported due to diffusional exchange have been measured in calcite (Wada, 1988; Arita and Wada, 1990; Graham et al., 1998; Wada et al., 1998), magnetite (Valley and Graham, 1991; Eiler et al., 1995), and garnet (Burton et al., 1995).

Granulite facies calcite from the Hida metamorphic belt, Japan, exhibits one of the best-documented isotope profiles that is at least in part due to diffusional exchange (Wada, 1988; Arita and Wada, 1990; Graham et al., 1998). The marbles are modally dominated by extremely coarse-grained calcite. Graphite is the only other mineral present. No oxygen diffusion profile is to be expected, because there is no other mineral with which the marble could exchange. The discovery of near-rim $\delta^{18}O$ decreases (Wada, 1988), therefore, implies that the rock was infiltrated by an isotopically distinct fluid. Profiles for un-recrystallized calcite margins are well matched by error-function curves (Figure 17), as expected for diffusion-controlled isotopic equilibration (Graham et al., 1998).

### 3.07.3.3 Dissolution–Reprecipitation

Hot fluids readily dissolve and transport material, both in hydrothermal systems (see Chapter 3.15) and in deeper metamorphic environments (see Chapter 3.06). If such fluids are isotopically distinct, then stable isotopes can help define fluid–rock reactions. Isotopic processes at deeper levels are likely to be rather subtle, because temperatures are high, timescales are long, and different oxygen reservoirs may not be very distinct isotopically. Therefore, isotopic studies of contact metamorphism provide some of the best examples of the mechanisms by which fluids and rocks interact and exchange oxygen.

The Tertiary Skye igneous complex has been well studied isotopically. It contains multiple, shallow-level intrusions, which established successive hydrothermal systems involving low $\delta^{18}O$ meteoric water (Forester and Taylor, 1977; Elsenheimer and Valley, 1993; Valley and Graham, 1996). Ion microprobe analyses of quartz from an older, highly altered pluton (Valley and Graham, 1996) elucidate exchange mechanisms (Figure 18). Cathodoluminescience images reveal healed microcracks, and the lowest $\delta^{18}O$ values are either in or adjacent to these healed cracks,
indicating that igneous quartz grains were fractured and infiltrated by a fluid with very low $\delta^{18}O$ value. Quartz adjacent to these fractures probably exchanged oxygen diffusively. The fractures were then sealed with very low $\delta^{18}O$ quartz precipitated from the fluid. These data imply that in metamorphic settings with high strain rates and low temperatures, dissolution–reprecipitation is a likely mechanism for producing isotopic heterogeneities.

3.07.4 TRACE ELEMENTS

Trace element zoning is probably ubiquitous in metamorphic minerals. Pioneering analysis by Hickmott and co-workers established trace element zoning as a sensitive monitor of $P$–$T$ histories (Hickmott et al., 1987; Hickmott and Spear, 1992), changes in major mineral assemblages (Hickmott and Spear, 1992), abrupt breakdown of trace element-rich minerals (Hickmott and Shimizu, 1990), and infiltration of fluids (Hickmott et al., 1992; Hervig and Peacock, 1989). However, the need for an ion microprobe probably deterred most petrologists from making such measurements. Renewed interest has been spurred by the recognition that some trace elements can be investigated with the electron microprobe (Spear and Kohn, 1996) or LA–ICPMS (e.g., Bea et al., 1996), and by an increased petrologic and geochronologic focus on accessory minerals whose stability depends on the availability of trace elements.

Unlike major elements, which can homogenize at high $T$ via simple interdiffusion and exchange with matrix minerals, trace elements often have different charges than the major elements for which they substitute. These differences are expected to impede diffusion. For example, to maintain charge balance, the $^{IV}P$–$^{IV}Si$, $^{VII}Na$–$^{VII}Mg$, $^{VIII}Y$–$^{VIII}Mg$, and $^{VI}Ti$–$^{VI}Al$ exchanges all require coupled substitution of other cations on other sites, such as $^{IV}Al$–$^{IV}Si$. This may permit the preservation of trace element zonation in minerals that lack obvious major element zonation.

3.07.4.1 Growth Zoning

Pyle and Spear (2003) have presented the only thermodynamically based petrogenetic models for the distribution of trace elements, specifically for yttrium in garnet coexisting with monazite, xenotime, apatite, and the typical silicates of a calcium-poor metapelite. Their differential thermodynamic models expand the theoretical treatment described above for major elements, to include yttrium and phosphates. Of particular interest is the zonation of yttrium predicted in garnet in a prograde metamorphic sequence, and the demise of xenotime as an accessory mineral. Garnet is a common target of yttrium zoning studies because it readily accommodates yttrium as “YAG” (Y$_3$Al$_5$O$_{12}$), where substitution of $\text{Y}^{3+}$ for divalent cations in the cubic site is charge balanced by substitution of $\text{Al}^{3+}$ for $\text{Si}^{4+}$ in the tetrahedral site. Dramatic yttrium zoning in one garnet (Figure 19) is correlated with the rim-ward disappearance of xenotime inclusions, and could be modeled in reference to changing accessory mineral abundances (Pyle and Spear, 1999, 2003). Xenotime buffers yttrium in garnet, but garnet growth also consumes xenotime. If the mode of xenotime is sufficiently low, it will eventually disappear, and further growth of garnet then rapidly depletes the remaining matrix minerals in yttrium. These effects yield high yttrium in garnet cores, while xenotime is present, and a sharp dropoff in yttrium as matrix xenotime disappears.

A full theoretical prediction for a specific bulk composition (Figure 20; Pyle and Spear, 2003) has intriguing implications for the control exerted by major minerals on accessory mineral stability (e.g., Ferry, 2000), and for the repartitioning of trace elements among major and accessory minerals at different $P$ and $T$. For example, the increase in monazite abundance at the expense of apatite with decreasing $P$ accords with

Figure 18 Digitized cathodoluminescence image of Skye quartz grain analyzed for $\delta^{18}O$ via ion microprobe. Dots are analytical spots; numbers are $\delta^{18}O$ in per mil (V-SMOW). Analytical error is approximately ±1‰. Backscattered electron images and oxygen X-ray maps show that the cracks are now completely healed, and so the cathodoluminescence contrast reflects different generations of quartz. Isotopic compositions are extremely low in the region dominated by healed microfractures, indicating the importance of newly precipitated quartz, possibly coupled with diffusive exchange of surrounding quartz with low $\delta^{18}O$ contact metamorphic fluids (source Valley and Graham, 1996).
observations in ultra-high pressure metamorphic (UHP) terranes that monazite exsolves from apatite during exhumation (Liou et al., 1998). However, other studies suggest that trace element zoning in many garnets is strongly affected by other processes, and that equilibrium models, while useful as a benchmark, may not be as widely applicable for trace elements as for major elements or stable isotopes.

3.07.4.2 Diffusion

No clear examples of diffusion profiles in garnet have been identified. This could reflect either extremely slow diffusivities (e.g., Cherniak, 1998), or simply a lack of natural samples amenable to investigation combined with difficulty of measuring trace element profiles compared to those of major elements. However, Hervig and Peacock (1989) presented an excellent case for lithium diffusion in porphyroclastic quartz from a mylonite (Figure 21). Ion microprobe analysis reveals a “bell-shaped” distribution, with relatively high concentrations in the center and near-zero concentrations on the rim. This profile probably reflects the initial growth of lithium-enriched quartz, followed by diffusive loss of the lithium to an infiltrating, lithium-poor fluid during deformation. Preservation of the profile is surprising because...
experimentally determined lithium diffusivities in quartz are extremely fast (Verhoogen, 1952; White, 1970). Either laboratory determinations of lithium diffusivities are nearly 10 orders of magnitude too fast, because of a different diffusion mechanism, or fluid is required to enhance diffusion, and was present only intermittently during mylonitization. If lithium diffusion rates were better known, the duration of fluid infiltration during mylonitization could potentially be recovered.

3.07.4.3 Dissolution–Reprecipitation

Trace elements can provide a sensitive monitor of dissolution and reprecipitation or regrowth. As summarized by Yang and Rivers (2002; Figure 22), if an element is compatible in a mineral, then resorption will increase the concentration of the element at the rim. Subsequent regrowth will cause a depletion, leading to an annulus in that element (see also Hickmott et al. (1987), Spear et al. (1990a), Kohn et al. (1997), and Pyle and Spear (1999)). If instead an element is incompatible, resorption will cause its decrease at the mineral rim. Subsequent regrowth will produce an increase, leading to a moat. The development and preservation of an annulus or moat depends on the partition coefficient (the degree of compatibility), the amount of material dissolved and then regrown, and trace element diffusivities. Of particular interest is that if diffusivities are extremely slow, the step on the inner side of the annuli and moats should be extremely sharp, whereas if diffusion is non-negligible, back-diffusion towards the mineral core will round the profile.

A staurolite-grade garnet from New Hampshire exhibits a yttrium annulus in garnet (Pyle and Spear, 1999; Figure 23). Most garnets in staurolite-bearing rocks are predicted to have originally grown in an assemblage containing garnet + chlorite + biotite (Spear et al., 1990b). At the staurolite-in isograd, garnet and chlorite are consumed via the staurolite-in reaction (Equation (25)). After chlorite is completely consumed, garnet can regrow, via continuous staurolite and biotite breakdown. This provides a thermodynamic driving force to produce the observed yttrium annulus. Interestingly, the annulus is not completely sharp at the inner boundary, but is rounded on a scale of 10 μm to ~100 μm. This likely implies that yttrium diffusivity cannot be several orders of magnitude slower than that of divalent cations, and that REE diffusion rates determined in natural-composition garnets (Coghlan, 1990; Ganguly et al., 1998b; Van Orman et al., 2002) are more likely to be applicable to rocks than the rates determined in Y₃Al₅O₁₂ by Cherniak (1998).

3.07.4.4 Kinetically Limited Transport within the Rock Matrix

Trace element annuli and spikes in garnets have been found over a range of metamorphic grades (Lanzirotti, 1995; Spear and Kohn, 1996; Pyle and Spear, 1999; Chernoff and Carlson, 1999; Pyle et al., 2001; Yang and Rivers, 2002). In some
instances they are ascribed to transport limitations. For example, garnets from Picuris quartzites have ytterbium, yttrium, phosphorous, titanium, and scandium annuli or moats that are spatially coincident with calcium spikes (Chernoff and Carlson, 1999; Figure 24). Kinetically limited intergranular transport of these elements is expected to produce chemically and mineralogically distinct zones concentric about each growing porphyroblast (Chernoff and Carlson, 1997, 1999). As the zones grow outward through time, they begin to impinge on each other, possibly causing abrupt changes in local mineralogy. If a trace phosphate or other mineral within one of these zones suddenly reacts out, the local concentration of many elements—including phosphorous, calcium, and REEs—can change suddenly. Petrologic interpretations may be further refined by using the shape of the profiles (Figure 22), which elements are enriched, and whether element enrichments versus depletions are systematic with respect to garnet compatibility (Yang and Rivers, 2002). For example, a sudden enrichment in LREEs could reflect the breakdown of apatite, allanite, or monazite, enrichment in MREEs could reflect breakdown of epidote, and enrichment in HREEs could reflect the breakdown of xenotime or zircon (Yang and Rivers, 2002). Identification of the reactions which occurred in a particular rock requires careful characterization of textures, zoning patterns, and mineral inclusion suites.

3.07.5 RADIOGENIC ISOTOPES
(AGE VARIABILITY)

Radiogenic isotopes are, of course, commonly measured in metamorphic minerals to obtain mineral isochron ages (see Chapter 3.08). However, sample size requirements restrict most isotopic measurements to bulk mineral separates; core versus rim isotopic variability is rarely investigated. Nonetheless, some inferences regarding isotopic trends are obtainable for measured concentration variations in parent isotopes, or from direct measurements of two or more isotopic compositions from large crystals that exhibit systematic zoning of other elements.

3.07.5.1 Growth Zoning

Because most radiogenic isotopes and their parent isotopes are trace elements and/or have large ionic radii, charge balance and/or physical arguments imply that they should have slow diffusivities. Some of the most extensively studied systems include Rb–Sr, Sm–Nd, U–Pb, and Lu–Hf in garnet, and U–Th–Pb in monazite, and experimental studies indeed indicate slow diffusion rates, and hence a high potential to retain original growth compositions (Coghlan, 1990; Smith and Giletti, 1997; Ganguly et al., 1998b; Cherniak et al., 2000; Van Orman et al., 2002). Although growth zoning of parent isotopes is sometimes obvious and easily resolvable (e.g., thorium in monazite; Figure 2), direct measurements of growth profiles in daughter isotopes have not been made with even remotely similar spatial resolution.

Strontium isotopes in garnet provide an interesting means of investigating the timescale over which a mineral grows. Garnet contains very little rubidium, and strontium diffusion rates are extremely slow (Coghlan, 1990; Burton et al., 1995). If isotopic partitioning takes place at equilibrium, garnet will record the matrix $^{87}\text{Sr}/^{86}\text{Sr}$ during
growth. A high $^{87}\text{Rb}/^{86}\text{Sr}$ ratio in the matrix assures that its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increases with time. Progressive growth of a garnet should, therefore, record a progressively higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio towards the rim. The magnitude of the $^{87}\text{Sr}/^{86}\text{Sr}$ change reflects the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of the matrix, and the duration of garnet growth ($\Delta t$). Even if garnet contains a small amount of rubidium, or contains small inclusions of rubidium-bearing minerals, its isotopic composition will change slowly, and the intersection of the garnet and matrix growth curves will define the time of garnet growth. Christensen et al. (1989, 1994) were able to exploit $^{87}\text{Sr}/^{86}\text{Sr}$ differences among different segments of individual garnet grains to determine the $\Delta t$ for crystal growth (Figure 25). Their results demonstrate that regional metamorphic garnets grow over a period of 5–30 Myr, in accordance with thermal model predictions for the timescale of temperature increases of $\sim 50 \, ^{\circ}\text{C}$ in overthrust terranes (e.g., England and Thompson, 1984).

3.07.5.2 Diffusion

The principles of diffusional zoning in radiogenic isotopes follow many of those for major elements and stable isotopes. Just as for stable isotopes, measurement of diffusion profiles in radiogenic isotopes is much more difficult than growth zoning, and instead bulk analysis of different coexisting minerals has been used to assess the magnitude of diffusional re-equilibration (Giletti and Casserly, 1994; Jenkin et al., 1995, 2001; Jenkin, 1997). Similarly, core versus rim isotopic compositions of garnet coronas adjacent to orthopyroxene and plagioclase have been used
to infer closure temperatures for the Sm–Nd and Rb–Sr systems relative to U–Pb (Burton et al., 1995).

In contrast to these relatively crude studies, Grove and Harrison (1999) showed that diffusional zoning of $^{208}\text{Pb}$ in monazite could be measured with high spatial and analytical resolution via ion microprobe. Because monazite has such a high concentration of thorium, sufficient $^{208}\text{Pb}$ is produced to permit relatively straightforward measurements (Harrison et al., 1995). Grove and Harrison (1999) analyzed the cores of crystals using sectioned, polished grains, and the outer few microns of other crystals, using depth profiling. In depth profiling, grains with good crystal faces are pressed into a soft mounting medium. The primary ion beam is used to sputter a crater into the face of a crystal, and isotopic compositions are collected continuously. These compositions are periodically averaged, and since the sputter rate is known (from the depth of the crater and total sputter time), the depth corresponding to each of these compositions can be determined. Depth profiling into the faces of crystals from a rock from the Greater Himalayan Sequence, Nepal, yields a monotonically increasing apparent age (Figure 26(a)), which can be inverted to obtain a temperature–time history (Figure 26(b)). The retrieved cooling path is generally compatible with other chronologic data, and reveals details of the cooling history that are otherwise difficult to resolve.

In principle, diffusion zoning profiles for radiogenic isotopes are inherently much better than major element profiles at resolving cooling histories. Each point on a composition profile fundamentally reflects temperature for major elements via cation exchange thermometry with matrix minerals versus time for radiogenic elements (specifically $T_c(x)$; Equation (19)). Retrieval of $t$ from zoning profiles depends

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**Figure 25** (a) Sr isotope composition of segments from a large garnet and its rock matrix, illustrating very slow change in isotopic composition of garnet relative to matrix. Intersection of garnet and matrix Sr-evolution curves yields ages. (b) Apparent age versus distance from core for same garnet, showing a $\sim 20$ Myr time difference. This implies a $\sim 0.23$ mm Myr$^{-1}$ radial growth rate, and nucleation and rim ages of $\sim 62$ Ma and $\sim 30$ Ma, respectively. Rectangles reflect measurement errors (source Christensen et al., 1994).

**Figure 26** (a) Age variation versus depth for ion microprobe depth profiles collected from the faces of Himalayan monazite grains, showing apparent diffusive loss of $^{208}\text{Pb}$ towards rim, and consequent age increase towards core. Solid curve is best fit to the data. Dashed lines show implied compositional trends for bounds on cooling history. Vertical bars are analytical errors. (b) Inferred temperature–time history, based on composition profile in (a). Solid line is best fit to data, dashed lines are bounds. White boxes are temperature–time points based on peak metamorphic conditions, and $^{40}\text{Ar}/^{39}\text{Ar}$ cooling age from biotite. Size of boxes reflects age and temperature uncertainties (Grove and Harrison, 1999) (reproduced by permission of GSA from Geology, 1999, 27, 487–490).
directly on temperature, cooling rate, and diffusion parameters, so has large uncertainty. $T_c(x)$ depends on their logarithm, so has much smaller uncertainty. Thus, cooling rates inferred from major elements are much more uncertain than those inferred from radiogenic isotopes.

### 3.07.5.3 Dissolution–Reprecipitation

Accessory minerals commonly contain high concentrations of radioactive elements, and are a common target of radiogenic isotope measurements. Specific elements include uranium (zircon, apatite, titanite, monazite, xenotime, allanite) and thorium (monazite and allanite). Each accessory mineral is stabilized in a rock via a single element or suite of related elements, specifically phosphorous (apatite), REE (allanite, monazite, xenotime), zirconium (zircon), and titanium (titanite). Trace elements also occur in the major minerals (particularly phosphorous, zirconium, and titanium), so accessory minerals participate directly in major mineral reactions (Pyle and Spear, 1999, 2000, 2003; Ferry, 2000; Pyle et al., 2001; Spear and Pyle, 2002; Wing et al., 2003; Kohn and Malloy, in press). However, the slow diffusion of many elements in accessory minerals as verified experimentally (e.g., Cherniak, 1995, 2000; Cherniak et al., 1997) implies that dissolution–reprecipitation must be a common mechanism for changing compositions, and that different zones within single grains should have different elemental and isotopic compositions.

Monazite ubiquitously exhibits this type of behavior. Backscattered electron images and yttrium, thorium, and uranium X-ray maps nearly always reveal complex zonation (e.g., Parrish, 1990; DeWolf et al., 1993; Zhu et al., 1997; Zhu and O’Nions, 1999; Williams et al., 1999; Pyle et al., 2001; Townsend et al., 2001; Williams and Jercinovic, 2002; see Figures 27 and 28), and several studies have demonstrated significant age differences between these chemically distinct domains (e.g., DeWolf et al., 1993; Zhu et al., 1997; Zhu and O’Nions, 1999; Williams et al., 1999; Townsend et al., 2001; Figures 27 and 28). Extreme compositional and age heterogeneity implies that the analysis of a bulk mineral separate or even of a single grain is not very useful.

![Figure 27](a, b) Th and U X-ray maps; (c) age map; and (d) age histogram for monazite grain from the western gneiss region, Norway, as measured via the electron microprobe, showing correlation of ages (and implied isotopic composition) with some chemically delineated zones within grains (Williams et al., 1999) (reproduced by permission of GSA from Geology, 1999, 27, 1023–1026).
geochronologically, because data from zones of different origin and age are then averaged. By analogy, geochronologists have long since recognized the domainal behavior of zircon and its ages, and we cannot now imagine analyzing bulk zircon separates, or even single whole grains without first characterizing their internal chemistry via backscattered electron imaging or cathodoluminescence. Conversely, because there is a direct link between major mineral reactions and accessory mineral abundance and chemistry (Pyle and Spear, 1999, 2000, 2003; Ferry, 2000; Wing and Ferry, in press; Kohn and Malloy, in press), different zones within an accessory mineral grain can potentially be linked to different reactions. The most fruitful research will be to link chemical zones in accessory minerals with metamorphic reactions, determine ages for those zones, and deduce the timing of mineral reactions and hence the overall mineralogical evolution of metamorphic rocks (Spear and Pyle, 2002; Harrison et al., 2002).

3.07.6 CASE STUDY: FALL MOUNTAIN, NEW HAMPSHIRE

Garnets in rocks from the Fall Mountain nappe, southwestern New Hampshire, have been analyzed for intracrystalline zoning in major elements, trace elements, and stable isotopes (Spear et al., 1990a; Spear and Kohn, 1996; Kohn et al., 1997; Pyle and Spear, 1999, 2000). Each type of zoning reveals important details about thermal evolution, tectonism (loading), and mineral reactions. Major and trace elements show evidence for at least four and possibly five generations of garnet growth, whereas oxygen isotope profiles monitor fluid infiltration and/or open system behavior (Figures 29–31). All generations of garnets, the important reactions that produce or consume garnet, and oxygen isotope trends are summarized in Figure 32.

Garnet cores (Grt1 + Grt2) are believed to have grown at low pressure (andalusite field), but flat profiles in manganese, iron, and magnesium (although not calcium; Figures 29 and 30) indicate that these rocks reached a sufficiently high temperature to homogenize manganese, iron, and magnesium by diffusion (Spear et al., 1990a, 1995). The existence of Grt1 is suggested by patchy zoning in calcium in garnet cores (Figure 29), by phase equilibrium arguments (Spear et al., 1995), and by trace-element compositions in some relict cores (Pyle and Spear, 1999). Grt3 grew during partial melting, which is indicated both macroscopically in migmatitic textures, and by the occurrence of trace element discontinuities towards the rims of some garnets (Figure 29). Most importantly, the abrupt increase in chromium (Figure 29) is diagnostic of a mica-breakdown reaction, specifically the muscovite + plagioclase + quartz dehydration-melting reaction. Although this reaction does not produce or consume garnet, it increases the chromium content of the matrix.

Figure 28 Backscattered electron image and age measurements for complexly zoned monazite crystals from contact metamorphosed Ireteba granite, Nevada. Crystallization age of the pluton is ~65 Ma. Subsequent infiltration of fluids perhaps as young as ~16 Ma apparently dissolved and reprecipitated new monazite in an extremely complex fashion. Ages determined via ion microprobe, and have typical uncertainties of a few percent (source Townsend et al., 2001).
phases, and further heating produces garnet with increasing chromium contents (Figure 29) via continuous biotite dehydration–melting (Spear and Kohn, 1996; Kohn et al., 1997; Spear et al., 1999). The occurrence of these melting reactions after earlier, low-P metamorphism, rather than dehydration reactions that produce K-feldspar, implies an increase in pressure. Because garnet cores are unzoned in $\delta^{18}$O (Figure 31), this loading and garnet core growth apparently occurred nearly isothermally.

On the retrograde path, cooling and melt crystallization produced biotite at the expense of garnet. This ReNTR consumed most Grt3, causing an increase in manganese concentration at the rims of garnets, which diffused back towards garnet cores. At the muscovite dehydration–melting reaction, muscovite reformed (the melt fully crystallized), and in the resulting solid-state assemblage garnet started to grow again with

Figure 29 X-ray maps of Mn, Ca, Fe/(Fe + Mg) (“FM”), Cr, and Sc in garnets from Fall Mountain, New Hampshire. White box indicates area of major element maps. Different generations of growth can be linked to prograde reaction history, to better understand mineralogical changes attending metamorphism and anatexis, and overall $P–T$ evolution. Black line shows location of composition traverse plotted in Figure 30 (source Kohn et al., 1997).

Figure 30 Electron microprobe compositional traverse across garnet in Figure 29, showing relatively flat core, pronounced Mn “humps,” and high-Ca rims. Vertical lines separate different garnet generations, as inferred compositionally. Third-generation garnet is not present, but is evident from Cr-zoning in other garnets (Figure 29) (source Kohn et al., 1997).
cooling, to produce Grt$_4$. Garnet growth was accompanied by a decrease in manganese content towards the rim, and differential thermodynamic modeling of this zonation indicates isobaric cooling (Spear et al., 1990a). The combination of Grt$_3$ consumption followed by Grt$_4$ growth resulted in the pronounced manganese “hump” (Spear et al., 1990a; Kohn et al., 1997), just as annuli in trace elements can result from dissolution followed by regrowth (Figure 22). The decrease in $\delta^{18}$O towards garnet rims is simply the result of garnet growth during cooling (Figure 31). High-calcium garnet overgrowths (Grt$_5$) are believed to reflect late-stage fluid infiltration, as emplacement of the nappe caused dewatering of structurally lower metapelites. The $\delta^{18}$O composition of quartz, muscovite, and biotite in different rocks provides additional evidence for low-$T$ infiltration.

What is interesting about this work is that no one zoning study could possibly have resolved all the details of the mineralogical and $P$–$T$ evolution. Specifically, (a) major elements indicated general $P$–$T$ conditions, high temperatures (compositional homogenization), retrograde resorption followed by growth during isobaric cooling, and late-stage overgrowths; (b) trace elements indicated the importance of dehydration–melting reactions; and (c) stable isotopes indicated an isothermal pressure increase, cooling during Grt$_4$ growth, and a general absence of open system behavior throughout most of the rocks’ history. Clearly, a combination of zoning studies provides a much better picture of the $P$–$T$, mineralogical, and tectonic evolution than any one zoning study. Two particularly interesting results of this work are given as follows.

**Figure 31** Oxygen isotope profile across garnet porphyroblasts, showing homogeneous core, and pronounced decrease in $\delta^{18}$O towards rims. The homogeneous core implies growth at relatively constant temperature, whereas the decreasing $\delta^{18}$O is interpreted to result from growth during cooling. Solid boxes show individual measurements. Dashed line is theoretical prediction assuming an absence of infiltration by an isotopically distinct fluid. Inset shows sketch of garnets analyzed. Horizontal lines are saw cuts used to subsample garnets. Short vertical lines show size of each subsample (source Kohn et al., 1997).

**Figure 32** $P$–$T$ diagram showing important reactions, isopleths of oxygen isotope compositions (thin vertical lines), and inferred $P$–$T$ path, as deduced from the major element, trace element, and oxygen isotope zoning in garnet porphyroblasts. The parallelogram at the end of the $P$–$T$ path is the thermobarometrically derived estimate of final $P$–$T$ conditions (source Kohn et al., 1997).
(i) Fluids were “recycled” during high-grade metamorphism from hydrous minerals to dispersed melt pockets during heating, and then back to hydrous minerals during cooling (Kohn et al., 1997).

(ii) Accessory mineral abundance and the trace element compositions of major silicates are very strongly influenced by melting reactions. This is perhaps not surprising given the high phosphorus solubility in most felsic melts.

3.07.7 DISCUSSION AND CONCLUSIONS

It is perhaps self-evident from this review that the most powerful application of geochemical zoning involves combining theoretical models (both forward and inverse) with detailed geochemical measurements. Theory readily accommodates only end-member processes, however, and recent research has confirmed that minerals do not exhibit end-member equilibrium or disequilibrium behavior with respect to element partitioning and geochemical zoning. It has long been recognized that minerals do not grow without overstepping a reaction (e.g., Lasaga, 1986, 1989). The degree to which a reaction is overstepped and compositions are equilibrated within a rock volume clearly depends on many variables, and reaction overstepping can be quite small for some elements in regional metamorphic rocks, or quite profound, especially in contact metamorphic rocks (Lasaga, 1986, 1989). Thus, some elements may equilibrate on the scale of a thin section (e.g., iron, magnesium, manganese in high-grade rocks), whereas others may not (e.g., REEs). Deciphering these effects from the geochemical record first requires understanding the basic phase equilibria of a rock, and how elements partition and repartition in an equilibrium sense as mineral abundances and species change. Equilibrium processes do explain some chemical behavior quite well, and inversion of composition profiles can yield information on \( P-T \) evolution, cooling rates, etc. Conversely, trace elements show local concentration heterogeneities, indicating poor equilibration, at least over length scales of millimeters. In isotope studies, equilibrium partitioning is difficult to verify, and is commonly simply assumed. Any behavior outside equilibrium models is then assigned to open system effects.

The fastest growing areas, in the early 2000s, are studies of geochemical zoning that deal with trace and radiogenic elements. Interest in this field is driven in part by a propensity of minerals to retain growth zoning in trace elements, but also because of geochronologic interests. One highlight of this work is the realization that all minerals, not just accessories, control trace element behavior. Accessory mineral compositions (and therefore preserved ages) are undoubtedly, yet complexly, related to major mineral reactions. The advent of geochronologic microanalysis of inclusions and zones in grains has inspired a new generation (at least) of petrologic research. However, assigning chronologic significance to an accessory mineral grain or even a single zone within it requires identifying the mineral reaction(s) responsible for its growth. In metamorphic rocks whose petrologic and reaction histories are unknown, geochronologic interpretation is perilous or, in some cases, pointless.

Several areas deserve additional study, especially in kinetics and in the phase equilibria of accessory minerals. Some minerals and elements probably equilibrate rapidly because of fast inter- and intragranular diffusion rates (e.g., oxygen). For other elements (e.g., strontium, neodymium, etc.) there is, in the early 2000s, very little information available. If different elements do not equilibrate on the scale of a thin section, then different regions on this scale could have different isotopic compositions. There are as yet no systematic data for the effects of water fugacity on cation diffusion rates. There could be major differences between diffusive behavior during heating when water is being liberated and \( f_{H_2O} \) is high, and during cooling, when water is being consumed and \( f_{H_2O} \) rapidly decreases. The links among major and trace mineral reactions, modal abundances, and compositions are also paramount for understanding metamorphic geochemistry. There are several examples of chemical zoning, such as annuli, that are extremely common in trace elements, but rare in major elements. Some annuli can be explained by equilibrium and mass balance processes, and some cannot. A significant effort is required to explore the systematics of accessory mineral chemistry and its relation to major mineral reactions and abundances.

New technologies always yield new insights. The increasing availability of laser ablation ICPMS and ion microprobes, and more general application of electron microprobes for mapping and analyzing minor and trace elements, implies that petrologists have a substantially larger suite of elements and isotopes at their disposal than ever before. Zoning patterns in trace elements and isotopes will undoubtedly reveal insights into growth processes, diffusion, and kinetics. Nonetheless, interpretation of the new data will require a full understanding of the many processes, equilibrium or otherwise, that lead to geochemical zoning in metamorphic minerals.

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