

PRESSURE-TEMPERATURE-TIME PATHS

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INTRODUCTION

The past decade has been a time of unprecedented improvement in our ability to reconstruct the thermal evolution of orogenic belts. Like many instances of rapid advancement in science, this achievement can be traced to the convergence of disparate research directions. The new field of thermochronology (the study of the time-temperature evolution of rocks) derived from the realization by geochronologists that many mineral-isotopic systems could be used to determine the time of cooling of a terrain through a series of predictable temperatures (e.g. Armstrong 1966, Wagner et al 1977, Harrison & McDougall 1980, Berger & York 1981). Petrologists have made great progress in their ability to discern the pressure-temperature history of metamorphic rocks through the improvement of conventional thermobarometric techniques [see Bohlen & Lindsley (1987) and Essene (1989) for reviews] and the development of important new approaches to relating changes in mineral chemistry to changes in environmental parameters (Spear & Selverstone 1983, St-Onge 1987). From a theoretical standpoint, several geophysical papers in the mid- to late-1970s and early 1980s explored heat transfer processes in orogenic belts and the role of these in the development and preservation of metamorphic mineral assemblages (Oxburgh & England 1974, Bickle et al 1975, Bird et al 1975, England & Richardson 1977, Toksoz & Bird 1977, England & Thompson 1984, among others).

The integration of geochronologic and petrologic techniques allows us

to recover the pressure-temperature-time (PTt) paths of metamorphic terrains, and numerical experiments on heat transfer permit us to use PTt paths to constrain the thermal evolution of an orogenic belt. Clearly, there is an intimate relationship between the thermal and tectonic processes operating during orogenesis. Thus, if we can reconstruct the thermal history of a mountain belt, then it should be possible to constrain better the tectonic evolution of the orogen. This paper reviews the current state of our capability to recover PTt paths and identifies fertile ground for future research in this field.

TIME-TEMPERATURE PATHS

One of the most fundamental assumptions inherent in the use of an isotopic chronometer to determine the crystallization age of a rock is that the system must close with respect to gain or loss of both parent and daughter isotopes at the time of crystallization. Although this premise may be reasonable for quickly cooled volcanic rocks, it has been shown empirically that more slowly cooled systems, such as metamorphic minerals, commonly lose some fraction of the radiogenic daughter product until they cool below a critical temperature range (Tilton et al 1958, Armstrong 1966, Harper 1967). Early laboratory and field studies of this phenomenon demonstrated that isotopic open-system behavior in minerals can be successfully modeled as a volume diffusion process (Evernden et al 1960, Hart 1964, Hanson & Gast 1967, Turner 1968, Giletti 1974a).

Closure Temperature Theory

Dodson (1973) established a mathematical formalism to describe the transition from open- to closed-system behavior for geochronologic systems. His definition of the closure temperature for such systems is illustrated in Figure 1*a,b*. Suppose that a mineral (m_1) initially containing a radioactive parent isotope and no radiogenic daughter crystallizes at a temperature so high that the radiogenic daughter produced by parent decay can diffuse out of the mineral as fast as it is produced. Under such conditions of purely open-system behavior, the daughter/parent ratio in the mineral remains effectively zero. After it cools sufficiently, the mineral will exhibit purely closed-system behavior: All daughter produced through parent decay will be retained in the system and the daughter/parent ratio will be a roughly linear function of time. Recognizing that the transition from an open to a closed system is a continuous process, we can predict the form of the (daughter/parent) vs time curve for the mineral-isotopic system (the heavy curve labeled " m_1 " in Figure 1*a*).

If we were to measure the daughter/parent ratio in m_1 today and calculate

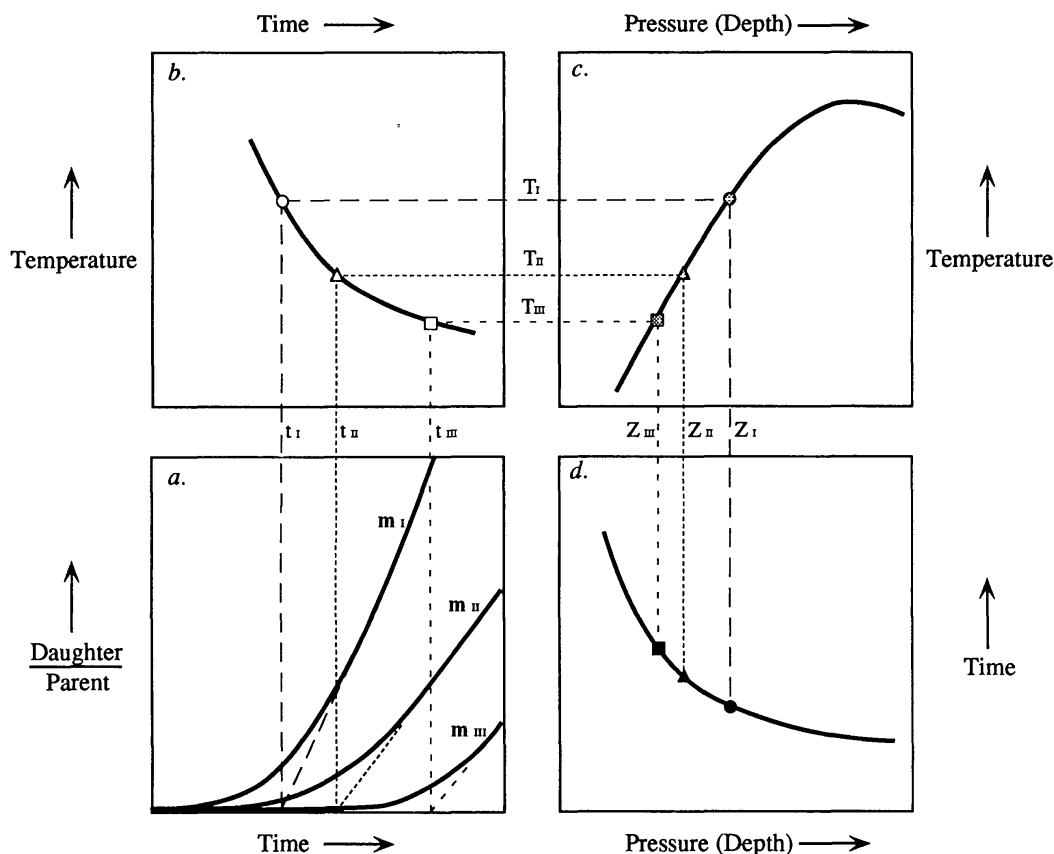


Figure 1 Procedure for recovering depth-time (Zt) paths from petrologic and geochronologic data. For three mineral-isotopic systems (I, II, and III) in a metamorphic sample, frame *a* shows the accumulation of radiogenic daughter isotopes at the expense of radioactive parent isotopes; the methodology for extracting closure temperatures for the three systems (T_I , T_{II} , and T_{III}) is explained in the text. Frame *b* illustrates construction of a temperature-time (Tt) curve for the sample using the apparent ages (t_I , t_{II} , and t_{III}) of the systems at T_I , T_{II} , and T_{III} . The system closure temperatures are transferred in frame *c* to a pressure-temperature (PT) curve derived from petrologic data; their positions may be used to find depths at the time of system closure (Z_I , Z_{II} , and Z_{III}) using an appropriate lithostatic pressure gradient. Finally, these depths are plotted in frame *d* against t_I , t_{II} , and t_{III} in order to constrain a portion of the Zt path of the sample.

its isotopic age, we would, in effect, be extrapolating the quasi-linear portion of the (daughter/parent) vs time curve back to its time intercept (t_I on Figure 1*a*). This time has no special kinetic significance; it does not correspond to the crystallization age of m_I , the time at which fully open-system behavior ceased, or the time at which fully closed-system behavior began. It may be thought of simply as the “apparent” age of the mineral. The temperature of the mineral at the recorded age (T_I in Figure 1*b*) is defined as the closure temperature for the system. Dodson (1973) showed that if volume diffusion was the primary mechanism of daughter loss, then the closure temperature can be expressed by the formula

$$T_1 = \frac{\frac{E_1}{R} + 2T_1}{\ln \left[\frac{\left(\frac{A_1 R T_1^2 D_{ol}}{a_1^2} \right)}{\left(\frac{E_1 dT}{dt} \right)} \right]}, \quad (1)$$

where R is the gas constant, D_{ol} and E_1 are, respectively, the preexponential constant and activation energy describing diffusivity of the daughter isotope in the system, A_1 is a constant describing diffusion geometry in the system, a_1 is the characteristic dimension over which diffusion occurs, and dT/dt is the cooling rate of the system. This equation must be solved iteratively because T_1 appears on both sides, but any reasonable initial guess for T_1 results in convergence after a few iterations. Although Equation (1) was derived assuming that $1/T$ increases linearly with time over the cooling interval in question, Lovera et al (1989) demonstrated that this assumption is not critical to the applicability of the equation to natural samples.

Given experimental data pertaining to diffusion of a radiogenic isotope in a mineral, Equation (1) permits calculation of the closure temperature for the mineral-isotopic system if we assume a cooling rate. Figure 2 illustrates the functional relationship between closure temperature and cooling rate for Ar diffusion in hornblende, biotite, and muscovite. Closure temperature is not strongly dependent on cooling rate for rates in excess of about 10 K m.y.^{-1} ; thus, closure temperature can be thought of as being essentially constant in tectonic settings characterized by rapid cooling (e.g. the contact zones of syntectonic plutons). In environments such as collisional belts being unroofed by erosion, where cooling rates can be substantially less than 10 K m.y.^{-1} , relatively minor errors in the assumed cooling rate can cause significant errors in calculated closure temperature. For example, the difference in closure temperatures for Ar diffusion in hornblende at 90 and 100 K m.y.^{-1} is about 2 K , but the difference between 0.1 and 10 K m.y.^{-1} closure temperatures is over 75 K (Figure 2).

Thermochronologic information can also be obtained using the fission track method of dating (Fleischer et al 1975), which is based on the observation that the density of tracks of crystallographic damage produced by ^{238}U fission in a mineral is proportional to U concentration and age. It has been shown through many laboratory experiments that fission tracks can be made to shorten or disappear by heating (e.g. Wagner 1968, Naeser & Faul 1969), implying that fission tracks in minerals that crystallized at

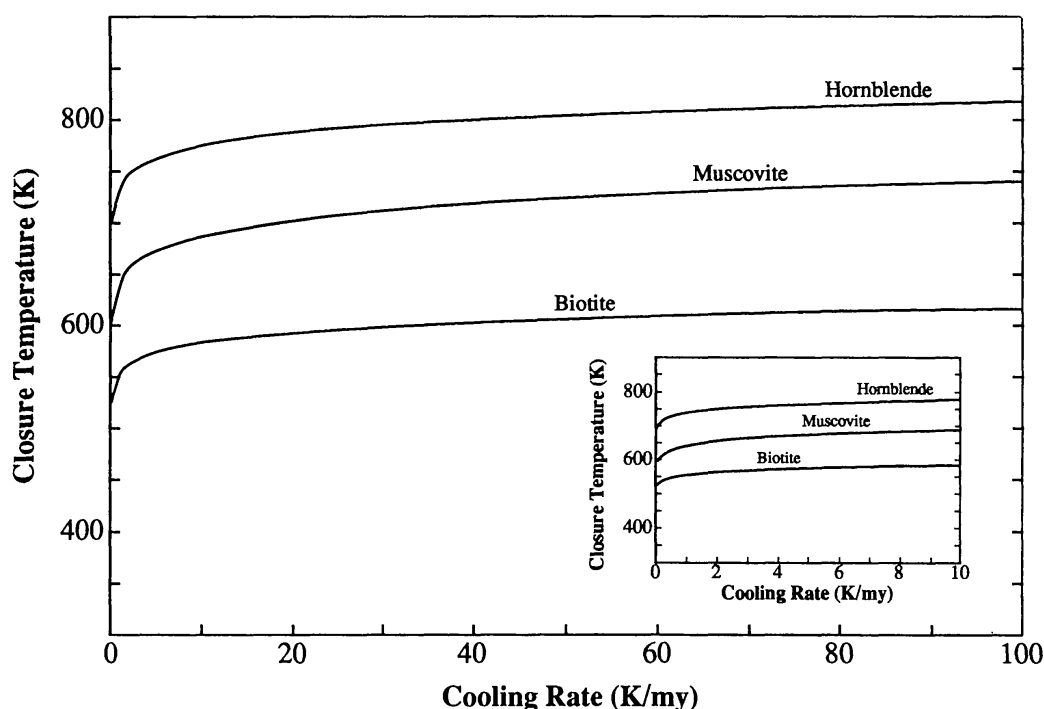


Figure 2 Closure temperature of the K-Ar system as a function of cooling rate for hornblende, muscovite, and biotite. The curves were obtained from Equation (1) using experimental diffusion data from Harrison (1981), Robbins (1972), and Harrison et al (1985). The inset is an enlargement of the larger diagram at slow cooling rates ($< 10 \text{ K m.y.}^{-1}$).

high temperature will anneal by diffusion of ions displaced by uranium fission back into the zone of damage until the sample cools below some critical temperature range (Naeser 1979). The closure temperature of fission track annealing in a mineral can be calculated using numerical methods (Haack 1977, Dodson 1979) or can be estimated from empirical studies of apparent fission track age gradients in deep boreholes (e.g. Naeser & Forbes 1976).

Applications

Table 1 lists estimated closure temperatures at a nominal cooling rate of 10 K m.y.^{-1} for a number of useful mineral-isotopic systems. The uncertainties in these values are not easily constrained. Rigorous propagation of errors in experimentally derived diffusion or annealing data through Equation (1) suggests closure temperature errors of a few tens of kelvins. However, diffusion data are available for only a limited range of mineral compositions, and some studies have documented a clear dependence of diffusion rate (and therefore closure temperature) on major element composition. For example, note in Table 1 that the estimated

Table 1 Approximate closure temperatures for mineral-isotopic systems

Decay scheme	Mineral	Closure T (K)	Method ^a	Reference
U-Pb	Zircon	> 1025	M	Ghent et al 1988
U-Pb	Monazite	980	M	Parrish 1988
U-Pb	Allanite	975–925	M	Parrish 1990
Sm-Nd	Grossularite	950 ^b	X	Harrison & Wood 1980
U-Pb	Sphene	875	M	Ghent et al 1988
Sm-Nd	Almandine-rich garnet	> 800	M	Vance & O’Nions 1990
U-Pb	Almandine-rich garnet	≥ 800	M	Mezger et al 1989
K-Ar	Hornblende	780	X	Harrison 1981
Rb-Sr	Muscovite	780	M	Wagner et al 1977
Sm-Nd	Pyrope	720 ^b	X	Harrison & Wood 1980
K-Ar	Muscovite	690	X	Robbins 1972
U-Pb	Rutile	680	M	Mezger 1989
K-Ar	Phlogopite	680	X	Giletti 1974b
K-Ar	K-feldspar	640–440 ^c	X	Lovera et al 1989
U-Pb	Apatite	625	M	Ghent et al 1988
Rb-Sr	Biotite	600	M	Wagner et al 1977
K-Ar	Biotite	580	X	Harrison et al 1985
Rb-Sr	Orthoclase	580–470 ^d	X	Misra & Venkatasubramanian 1977
Fission track	Garnet	580	X	Haack 1977
Fission track	Sphene	570	M	Harrison & McDougall 1980
Rb-Sr	Microcline	550–440 ^d	X	Misra & Venkatasubramanian 1977
Fission track	Epidote	540	X	Haack 1977
Fission track	Zircon	450	M	Harrison & McDougall 1980
Fission track	Apatite	380	X, M	Parrish 1983

^a The letters “X” and “M” refer to “experimental” and “empirical,” respectively. “Experimental” denotes that the closure temperature was estimated from Equation (1) using experimentally obtained cation diffusion or fission track annealing data, reasonable estimates of effective diffusion dimension and diffusion geometry for the system in question, and a nominal cooling rate of 10 K m.y.^{−1}. “Empirical” means that the closure temperature estimate was derived from field studies in which independent thermobarometric and/or thermochronologic data constrain the approximate temperature of the mineral-isotopic system at the time of closure.

^b These estimates were made using the experimental data of Harrison & Wood (1980) for Sm diffusion in garnet and therefore implicitly assume that the diffusion behavior of Nd in garnet is essentially the same as that of Sm. See Humphries & Cliff (1981) for a similar argument.

^c A wide range of closure temperatures has been estimated for K-feldspars, and recent studies have shown that individual feldspar samples may contain multiple diffusion domains of different sizes having different closure temperatures. The 640–440 K range referred to here was derived by Lovera et al (1989) for the Chain of Ponds pluton in northwestern Maine, USA.

^d Rb-Sr closure temperatures for orthoclase and microcline were calculated assuming the range of effective Ar diffusion dimensions estimated by Lovera et al (1989).

closure temperature for phlogopite [$\text{Mg}/(\text{Mg} + \text{Fe}) = 0.96$] is nearly 100 K higher than that for biotite [$\text{Mg}/(\text{Mg} + \text{Fe}) = 0.44$] based on the experimental work of Giletti (1974b) and Harrison et al (1985), respectively. The effective diffusion dimensions of natural phases can vary because of deformational history, structural state, exsolution, or fine-scale inter-

growths (e.g. Foland 1974, Zeitler & Fitz Gerald 1986, Onstott & Peacock 1987, Baldwin et al 1990); this variability in turn has a major effect on actual closure temperatures. Despite these difficulties, numerous field applications suggest that the closure temperatures listed in Table 1 are acceptable estimates to within 50–75 K.

If geochronologic data can be obtained for several systems with different closure temperatures from a single structural level within an orogen (e.g. systems I, II, and III in Figure 1), then it should be possible to reconstruct a portion of the temperature-time (Tt) path for that level (Figure 1*b*). For example, high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ data for hornblende, muscovite, and biotite from an outcrop of pelitic schist intruded by a metamorphosed mafic sill could permit recovery of the Tt path for the outcrop over a 200-K temperature interval (Figure 2).

The principal limitation in deriving Tt histories stems from a lack of high-quality diffusion data for many systems. Some of the empirically estimated closure temperatures in Table 1 are little more than educated guesses based on few data. Unfortunately, good laboratory diffusion experiments are difficult and time consuming; see Giletti (1974a) or McDougall & Harrison (1988) for a discussion of the many potential pitfalls. A singular exception to the overall depressing state of our knowledge of diffusion rates for geochronologically interesting species is the case of Ar diffusion in feldspar. Because feldspar is anhydrous, the incremental vacuum heating experiment inherent to $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology is also a diffusion experiment when a feldspar sample is being analyzed. Berger & York (1981) demonstrated that the fraction of Ar released during each temperature step of the experiment could be used to define the quantity D_1/a_1^2 , where D_1 is the diffusion coefficient for Ar at the appropriate temperature. Theoretically, plots of D_1/a_1^2 against reciprocal temperature for a variety of steps should yield linear arrays representative of the Arrhenius relationship,

$$\frac{D_1}{a_1^2} = \left(\frac{D_{01}}{a_1^2} \right) \exp(-E_1/RT), \quad (2)$$

such that D_{01}/a_1^2 and E_1 derived through regression analysis can be used with Equation (1) to estimate closure temperature for each dated feldspar sample.

One of the most exciting developments in recent years in thermochronologic research has been the recognition that Ar in many feldspars is trapped in multiple diffusion domains of differing dimensions (Zeitler 1987, Heizler & Harrison 1988). A number of researchers using the approach described in the previous paragraph noted that Ar fractions

from the low-temperature steps of feldspar experiments defined linear arrays on plots of D_1/a_1^2 against $1/T$, but that high-temperature fractions deviated from the trend. Commonly, such behavior was attributed to structural breakdown of the feldspar at high temperatures during the experiment, and thus only the low-temperature steps were used to extract a closure temperature (e.g. Harrison et al 1986, Heizler et al 1988). Zeitler (1987) demonstrated that high-temperature deviations from the linear array were more likely a consequence of the release of additional Ar components held in energetically different diffusion domains, and Lovera et al (1989) developed the mathematical formalism for extracting the age and diffusion characteristics (and thus closure temperature) of each domain. Through judicious choice of the heating schedule for a feldspar experiment, it is possible to extract multiple temperature-time points on the cooling curve of the sample. The potential power of this approach was demonstrated convincingly by Lovera et al (1989), who showed that feldspars from the Chain of Ponds pluton in northwestern Maine recorded the cooling history of the intrusive body over the 640–440 K temperature range.

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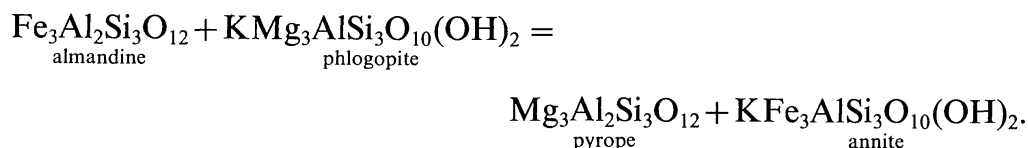
The most fundamental axiom of metamorphic petrology is that the laws of equilibrium thermodynamics provide a useful context for study of the crystallization of minerals in a metamorphic sample (Goldschmidt 1911, Eskola 1920). If these laws are applicable to a metamorphic assemblage, then they permit the estimation of environmental parameters, such as pressure and temperature, at the time of equilibration (Bowen 1940, Thompson 1955). The common occurrence of compositionally zoned minerals suggests that whole-sample equilibrium is rarely attained during metamorphism, and any thermodynamic treatment of metamorphic samples must include a presumption about the scale of equilibrium. The common assumption, supported by the internal consistency of results in numerous field studies, is that the compositions of the outermost rims of porphyroblasts reflect the pressure-temperature (*PT*) conditions at the time of last equilibration of a metamorphic sample. Recovering the *PT* history of a sample during metamorphism thus involves at least two procedures: determining the conditions of final equilibration of porphyroblasts in the sample using mineral rim thermobarometry, and estimating the *PT* trajectory of the sample prior to final equilibration from the chemistry of zoned porphyroblasts and their inclusions. In some samples, the existence of fluid inclusions permits recovery of a portion of the *PT* path followed by a sample after final mineral rim equilibration.

Mineral Rim Thermobarometry

Consider an amphibolite facies pelitic schist sample containing the assemblage garnet-biotite-muscovite-plagioclase-kyanite-quartz. It is possible to write a variety of stoichiometric relationships between mineral components in this sample; two of particular interest are



and



These reactions will be referred to, respectively, as GASP (*G*arnet-*A*luminum silicate-*S*ilica-*P*lagioclase) and GARB (*G*ARNET-*B*iotite) for simplicity. For any balanced chemical equation involving mineral components, the condition of heterogeneous equilibrium mandates that the difference in Gibbs free energy (ΔG) between the left-hand and right-hand sides of the equation is zero. When some or all of the mineral components are part of solid solutions, this requirement leads to the following relationship:

$$\Delta G = 0 = \Delta H - T\Delta S + (P - 0.1)\Delta V + RT \ln K, \quad (3)$$

where ΔH , ΔS , and ΔV are reaction enthalpy, entropy, and volume changes, respectively, and all variables have SI dimensions (temperature and pressure are in kelvins and megapascals, respectively). The equilibrium constant (K) is a function of the compositions of the minerals involved in the equilibrium and their solution properties. If (a) the enthalpy, entropy, and volume change of a reaction are known independently, (b) mineral compositions are measured using the electron microprobe, and (c) appropriate solution models are assumed, then Equation (3) may be used to define a unique curve in P vs T space. Some equilibria have unusually small dP/dT slopes, and their relative insensitivity to temperature makes them useful as geologic barometers; others have unusually large dP/dT slopes and are thus useful thermometers. By simultaneously solving equations like (3) with significantly different dP/dT slopes, one can obtain a robust estimate of the equilibration temperature and pressure of a sample. The end-member reactions GASP and GARB, with nominal slopes of 2.2 and 7.1 MPa K⁻¹, are excellent candidates for such an exercise (Ghent 1976, Ferry & Spear 1978, Hodges & McKenna 1987, McKenna & Hodges 1988). Space does not permit a comprehensive tabulation of the many

equilibria that have proven useful as thermobarometers for natural assemblages, but excellent reviews of these equilibria and discussions of the perils and pleasures of thermobarometry may be found in Powell (1985), Essene (1989), and Spear & Peacock (1989).

Several methods may be used to “calibrate” (or determine ΔH , ΔS , and ΔV for) a thermobarometric reaction. These include the *experimental* approach, where the position of the reaction is determined through a series of experiments at elevated T and P [see Chapter 2 of Ernst (1976) for a review of common experimental techniques]; the *thermodynamic* approach, where tabulated data for the molar volume and enthalpy and entropy of formation of the components of interest (Robie et al 1978, Helgeson et al 1978, Berman 1988, Holland & Powell 1990) are used to estimate ΔH , ΔS , and ΔV of the reaction; and the *empirical* approach, where equilibrium constants are calculated from compositional data for a number of natural samples, equilibrium T and P for the samples are estimated using other well-calibrated thermobarometers, and finally thermodynamic constants are extracted from statistical analysis of the data set (e.g. Hodges & Crowley 1985). Each method has its strengths and weaknesses. Experimental calibrations are generally the most reliable, although some systems are difficult to work with experimentally. Moreover, application of the results to chemically complex natural systems can be difficult. Empirical calibrations are less troublesome in this regard, but they are inherently less precise because of their dependency on thermobarometric data derived from other equilibria. Theoretically, the thermodynamic approach should be the most powerful; it should be possible to establish uniquely the equilibration pressure and temperature of a sample by simultaneously solving all possible equilibria inherent to the system using any one of the available internally consistent thermodynamic data bases to calibrate each equilibrium (Berman & Brown 1988, Powell & Holland 1988). In my opinion, this technique has largely not realized its potential because of the difficulties involved in critically evaluating the calorimetric and phase equilibrium data used to derive thermodynamic data bases. Despite the precautions taken by careful workers such as Berman (1988) and Holland & Powell (1990) to incorporate uncertainties in input parameters into their compilations, the fact remains that internal consistency is not necessarily the same as accuracy.

Table 2 illustrates this point by comparing pressures calculated using alternative thermodynamic and experimental calibrations of GASP at a temperature of 775 K assuming that all phases are pure. Although there is substantial variation in the results obtained using different thermodynamic data sets, the three most recent compilations (Halbach & Chatterjee 1984, Berman 1988, Holland & Powell 1990) yield quite similar pressures at

Table 2 Comparison of GASP calibrations at 775 K^a

Calibration	Method ^b	ΔH (J mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)	ΔV ($\times 10^{-5}$ m ³)	P (MPa)
Helgeson et al 1978	C-C, PE	-48,221	-153	-6.62	1062
Robie et al 1978	C-C	-21,740	-133	-6.62	1234
Halbach & Chatterjee 1984	LP	-37,173	-129	-6.63	952
Berman 1988	MP	-45,809	-139	-6.59	940
Holland & Powell 1990	LS	-41,540	-136	-6.61	964
Koziol & Newton 1988	EX1	-48,500	-151	-6.62	1035
McKenna & Hodges 1988	EX2	-41,000	-146	-6.62	1090
				Average	1040
				SD	103

^a Thermodynamic constants for all calibrations except Koziol & Newton (1988) and McKenna & Hodges (1988) correspond to tabulated values at 298.15 K and 0.1 MPa. Correction for deviation from the standard state using appropriate heat capacity, expansivity, and compressibility values would lower the pressure estimates in the last column by less than 50 MPa (cf Essene 1989).

^b Abbreviations—C-C: compilation weighted toward calorimetric data; C-C, PE: compilation based on both calorimetric and phase equilibrium data; LP: derived from experimental data through linear programming (cf Gordon 1973); MP: derived from experimental data through mathematical programming (Berman et al 1986); LS: derived from experimental data through least-squares regression (cf Holland & Powell 1990); EX1: based on the GASP experiments of Koziol & Newton (1988); EX2: derived through regression analysis of five compatible experimental studies of the GASP, including that of Koziol & Newton (1988).

775 K, averaging 950 MPa. The GASP equilibrium is one of the best-characterized metamorphic reactions, having been the subject of at least six experimental studies. Calibrations derived from the most recent (Koziol & Newton 1988) and statistical analysis of the five best experimental data sets (McKenna & Hodges 1988) yield pressures at 775 K of 1035 and 1090 MPa, respectively. Although a difference of roughly 100–150 MPa between the thermodynamic and experimental calibrations may not seem large in light of the uncertainties in rim thermobarometry discussed below, it is barely within the precision limits of either the Koziol & Newton (1988) or the McKenna & Hodges (1988) calibrations, and it is well outside the uncertainty calculated by propagating the correlated errors estimated by Holland & Powell (1990) for their data base.

Rim Thermobarometry of Variably Retrograded Samples

It is relatively common to find petrographic evidence in high-grade samples of retrograde re-equilibration of mineral rims during cooling from the metamorphic peak. In many cases, the degree of retrogression varies from sample to sample at a single structural horizon. Provided that the samples reequilibrated at different times during cooling, rim thermobarometry can define a portion of the retrograde *PT* path of the horizon. Examples of this

phenomenon in the northern Scandinavian Caledonides were described by Hodges & Royden (1984), Crowley & Spear (1987), and Steltenpohl & Bartley (1987).

One of the greatest dangers in using this method to recover PT paths is the possibility that not all thermobarometric reactions are equally susceptible to retrograde operation (Ghent et al 1988, Frost & Chacko 1989). Consider three variably retrograded pelitic samples (A, B, and C) from a single structural horizon (Figure 3). If all three contain the model assemblage discussed in the previous section, then it should be possible to calculate the final equilibration PT of each by simultaneously solving GARB and GASP. GARB is an *exchange* reaction that simply describes Fe and Mg partitioning between garnet and biotite; operation in either a prograde or a retrograde sense produces changes in Fe/Mg in both phases

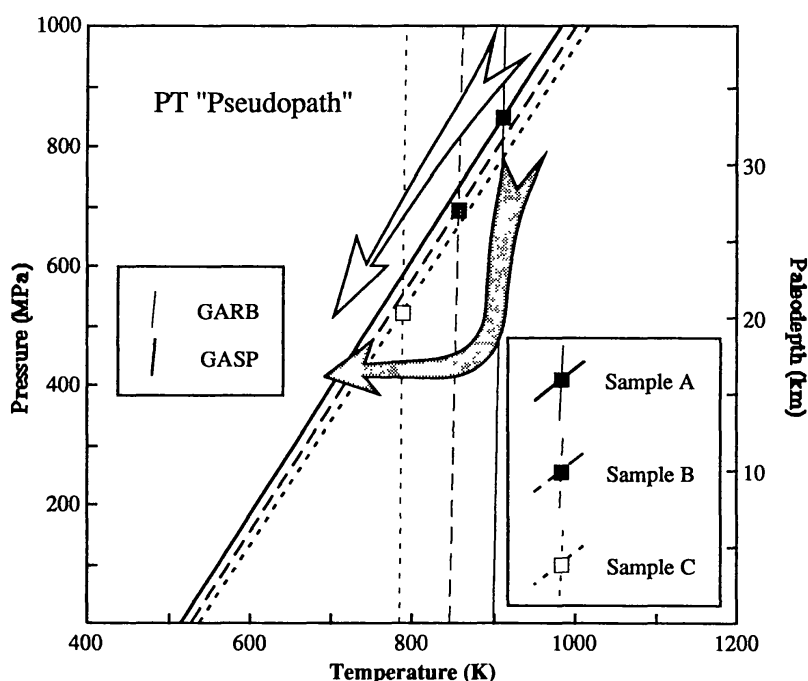


Figure 3 Illustration of how a meaningless PT array (a PT "pseudopath") can arise as a result of the distinctive kinetic behavior of different thermobarometers. GARB and GASP equilibrium curves (*thin* and *thick lines*, respectively) are derived from mineral rim compositions in slowly cooled samples A, B, and C. *Square symbols* (black for sample A, shaded for sample B, and white for sample C) illustrate the apparent equilibrium PT for each sample. Similarities between the GASP curves for these samples, as compared with the major differences between GARB curves, reflect the fact that GARB has operated in a retrograde sense in some samples during cooling whereas GASP has not. The pseudopath (indicated by the *unpatterned arrow*), subparallel to the GASP curve, is entirely an artifact of the differential closure of the two thermobarometers and has no relationship to the true PT path of the sample (*shaded arrow*).

but does not require recrystallization and does not induce changes in the modal proportions of minerals. GASP, on the other hand, is a *net-transfer* reaction; its operation requires the dissolution, nucleation, and growth of various phases. Generally speaking, net-transfer reactions are more sluggish than their exchange counterparts. Suppose that GARB operated in a retrograde fashion in our three samples but GASP did not for kinetic reasons. Positions of the GASP equilibrium for each sample, derived from Equation (3), are similar, but the GARB curves have been shifted commensurate with the amount of retrogression in each sample. Simultaneous solution of GARB and GASP for these samples yields an array of *PT* points in Figure 3 that is roughly parallel to the GASP equilibrium curve. Unfortunately, the “pseudopath” defined by these points has no relation to the *PT* trajectory actually pursued by the structural horizon during retrogression.

The most effective defense against pseudopaths is careful petrography and comparison of the results of retrograde rim thermobarometry with those derived from other techniques of *PT* path reconstruction (Selverstone & Chamberlain 1990). Even though the *PT* path obtained by rim thermobarometry by Hodges & Royden (1984) was broadly similar in slope to the GASP equilibrium, samples lying at lower temperatures on the trend showed petrographic evidence of the GASP reaction operating in a retrograde fashion, precluding the scenario illustrated in Figure 3. Moreover, Gibbs method analysis (see below) of garnet zoning in samples from this region has yielded *PT* trajectories that are consistent with the paths defined by rim thermobarometric studies (Hubbard & Hodges 1984, Crowley & Spear 1987).

Path Estimation from Zoned Porphyroblasts

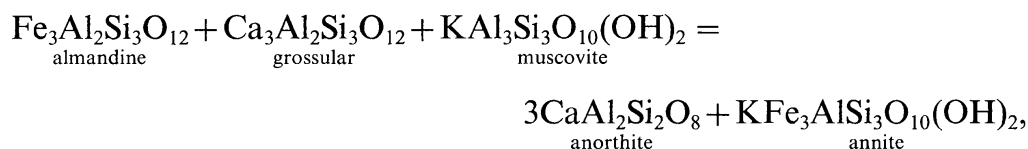
Metamorphic petrologists traditionally have used the reaction textures that are commonly preserved in metamorphic rocks to infer *PT* paths. Petrographic evidence of changes in the stable mineral assemblage with time can be mapped into *PT* space using petrogenetic grids. Tracy et al (1976) and Thompson et al (1977) demonstrated that compositionally zoned minerals and their inclusions can be important indicators of changes in *PT* during metamorphism. Recently, two new techniques—solid inclusion thermobarometry and thermodynamic modeling of porphyroblast zoning—have greatly improved our ability to quantify *PT* paths.

SOLID INCLUSION THERMOBAROMETRY Some large porphyroblasts in metamorphic rocks contain inclusions of other minerals. If equilibria involving components of these phases and their host have been calibrated as thermobarometers, then it is theoretically possible to calculate the *PT* conditions

of entrapment. By way of example, suppose that a garnet porphyroblast in the hypothetical pelitic schist sample introduced above contains a composite inclusion of biotite + plagioclase + kyanite + quartz. By measuring compositions at the interfaces of the biotite, the plagioclase, and the garnet that surrounds them, the *PT* conditions of entrapment can be calculated through simultaneous solution of GARB and GASP. This information, along with the conditions of final rim equilibration deduced through rim thermobarometry, constrain two points along the *PT* trajectory of the sample.

One of the earliest (and still one of the most impressive) applications of solid inclusion thermobarometry was that of St-Onge (1987). Poikiloblastic garnets in six pelitic schist samples (garnet + biotite + plagioclase + muscovite + quartz + sillimanite \pm kyanite) from the Wopmay orogen of Canada contained abundant composite inclusions of biotite + plagioclase + quartz, and garnets in one sample also contained kyanite and sillimanite inclusions. Arguing that all samples were saturated with Al_2SiO_5 throughout the period of garnet growth, St-Onge used GARB and GASP to obtain between 6 and 17 estimates of *PT* during garnet growth for each sample. Evidence that the basic methodology was sound came from the broad consistency between the resulting *PT* paths and both local geologic constraints and the theoretical morphology of *PT* trajectories resulting from crustal thickening (England & Richardson 1977).

Unfortunately, inclusion suites containing all of the necessary phases for thermobarometry are relatively uncommon. It is often necessary to assume that phases not observed as inclusions were nonetheless part of the equilibrium assemblage and were either pure or had minor compositional variability that was inconsequential to the thermobarometric calculations. An example of this approach may be found in the study by Hodges & Silverberg (1988) of pelitic samples from the Garhwal region of the Indian Himalaya. One sample, characterized by the subassemblage garnet + biotite + plagioclase + muscovite + quartz, contained garnets with composite biotite + plagioclase + quartz inclusions. The absence of aluminum silicate precluded use of GASP for either rim or inclusion thermobarometry, but the presence of muscovite permitted the alternative use of the GMPB (Garnet-Muscovite-Plagioclase-Biotite) barometer:



which was calibrated empirically by Ghent & Stout (1981) and Hodges & Crowley (1985). The position of the GMPB equilibrium in *PT* space is a

very weak function of muscovite composition; large variations in the latter produce changes of only a few tens of megapascals in GMPB pressures calculated at constant temperature. Making the assumption that muscovite was stable at the time of equilibration of the inclusion suite with its garnet host, Hodges & Silverberg (1988) estimated PT conditions at that time by applying GARB and GMPB using the composition of *matrix* muscovite. Although invalid in a strict thermodynamic sense, the results of this exercise were corroborated independently by thermodynamic modeling using the Gibbs method.

THERMODYNAMIC MODELING OF PORPHYROBLAST ZONING Traditionally, metamorphic petrologists have used the integrated forms of thermodynamic equations such as (3) to determine the values of intensive variables like P and T . It is equally possible to employ the differential forms of these equations in order to establish *changes* in intensive variables during metamorphism. This approach has tremendous potential in the study of zoned porphyroblasts; if we can establish the conditions of final rim equilibration for a sample through traditional thermobarometry, then it should be possible to use changes in porphyroblast chemistry and the composition of solid inclusions to monitor changes in P and T during garnet growth. Two variants of this technique have evolved over the past few years: Gibbs method modeling (Spear & Selverstone 1983) and differential thermobarometry (Spear 1989).

The Gibbs method refers to a general thermodynamic formalism for relating intensive variables in a system at equilibrium through a set of linear differential equations (Spear et al 1982). This set includes three types of thermodynamic functions describing the conditions of heterogeneous and homogeneous equilibrium.

The first type of equation stems from the observation of Gibbs (1875) that any stoichiometric relationship between phase components in a system implies the same relationship between the derivatives of their chemical potentials (μ). For the GASP equilibrium, this equation would be

$$0 = d\mu_{\text{grs}} + 2d\mu_{\text{ky}} + d\mu_{\text{qtz}} - 3d\mu_{\text{an}}.$$

Although it is possible to write as many differential equations of this form as there are possible reactions among phase components, only a linearly independent subset of these is used for Gibbs method analysis.

The second class of equations describes the conditions of homogeneous equilibrium for each phase in the system. In the case of $(\text{Fe,Mg,Ca,Mn})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnet:

$$0 = S^{\text{garnet}} dT - V^{\text{garnet}} dP + X_{\text{alm}} d\mu_{\text{alm}} + X_{\text{prp}} d\mu_{\text{prp}} + X_{\text{grs}} d\mu_{\text{grs}} + X_{\text{sps}} d\mu_{\text{sps}},$$

where S^{garnet} and V^{garnet} are the molar entropy and volume of the garnet solid solution, and the quantities designated by X are mole fractions of almandine (alm), pyrope (prp), grossular (grs), and spessartine (sps) in the solution.

The final group of equations introduces differential compositional variables. For plagioclase that is a solid solution of albite and anorthite, we have

$$0 = -(\mathrm{d}\mu_{\text{an}} - \mathrm{d}\mu_{\text{ab}}) - (S_{\text{an}} - S_{\text{ab}}) \mathrm{d}T + (V_{\text{an}} - V_{\text{ab}}) \mathrm{d}P + \left(\frac{\partial^2 G^{\text{plagioclase}}}{\partial X_{\text{an}}^2} \right)_{PT} \mathrm{d}X_{\text{an}},$$

where $G^{\text{plagioclase}}$ is the molar Gibbs free energy of the plagioclase solution, S_{an} and S_{ab} refer to the partial molar entropies of the anorthite and albite components, and V_{an} and V_{ab} correspond to their partial molar volumes.

The three classes of equations can be combined into a linear system with a mathematical variance equivalent to the thermodynamic variance of the petrologic system under investigation. Consider our model pelitic schist once again. This sample can be reasonably described by the system $\text{K}_2\text{O}-\text{CaO}-\text{Na}_2\text{O}-\text{FeO}-\text{MnO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Assuming reasonable compositional variations in the equilibrium assemblage garnet + biotite + muscovite + plagioclase + kyanite + quartz + water, the phase rule (Gibbs 1906) tells us that this sample has a thermodynamic variance of four. Using the Gibbs method, we can write a system of thermodynamic equations with the same variance; by specifying the values of four independent unknowns in the system, we can calculate values for the remaining variables. Suppose that a zoned garnet in the sample contains an inclusion of plagioclase. If we presume that all of the phases in the matrix assemblage maintained equilibrium throughout the period of garnet growth, then we can use the change in X_{an} between the rim of matrix plagioclase and the plagioclase inclusion, along with rim to core changes in three independent garnet mole fractions (e.g. X_{alm} , X_{prp} , and X_{grs}), to solve for changes in P and T (ΔPT) during garnet growth.

The differential thermobarometry technique also involves deriving a system of thermodynamic equations with a variance equal to the phase rule variance of the sample, but the equations are of two different classes. The first derives from the simple observation that the mole fractions of all components in a phase must sum to one; thus, $\sum \mathrm{d}X_i = 0$ for all components i in a phase. The second class includes the differentiated equivalents of Equation (3) for reactions between phase components. A linearly independent subset of these equations and one equation of the first class for each phase in the sample combine to form the necessary system of

equations. Differential thermobarometry and the Gibbs method yield exactly the same information about ΔPT , but differential thermobarometry is computationally simpler.

A NOTE OF CAUTION Inclusion thermobarometry, the Gibbs method, and differential thermobarometry all share one characteristic: the axiomatic belief that porphyroblast zoning accurately records changes in mineral compositions as a sample passes through successive equilibrium states during its PT evolution. The unfortunate fact is that classical equilibrium thermodynamics is independent of kinetic constraints and a real rock is not. If the porphyroblasts that we examine in metamorphic rocks had truly maintained equilibrium with their surroundings under changing PT conditions, then they would not be zoned. The fact that they commonly are implies that there is a hidden assumption associated with using them to reconstruct PT paths: As new material is added to a porphyroblast during growth, the older part of the crystal and any inclusions therein are chemically insulated from the rest of the system. Although this hypothesis may be correct for greenschist or amphibolite facies samples, it may be inappropriate for higher grade samples. At sufficiently high temperatures, intragranular volume diffusion will work to eliminate compositional gradients in zoned minerals. For garnet, the mineral most commonly used for PT path determination, empirical studies have indicated that growth zoning can be completely eliminated in samples heated above roughly 900 K (Tracy et al 1976, Anderson & Olympio 1977, Woodsworth 1977, Yardley 1977), making it impossible to reconstruct the early PT history of the sample using the techniques discussed above. In many cases, however, retrograde rims form on high-temperature garnets during cooling from maximum temperatures (Tracy 1982), and inclusion thermobarometry, Gibbs method analysis, and differential thermobarometry can be used to recover a portion of the retrograde PT path for such samples (Crowley & Spear 1987, Hodges & Silverberg 1988, Spear 1989).

If a pelitic sample experiences maximum temperatures of 800–925 K for sufficiently long periods during metamorphism, the diffusion rate of cations in garnet is such that inclusions trapped during growth can partially or completely reequilibrate with their host (Hodges & Spear 1981, Thompson & England 1984, Spear & Peacock 1989). Any attempt to model the PT path of such a sample using inclusion data will yield meaningless information. Fortunately, we can evaluate the possibility of reequilibration through a net-transfer mechanism with petrographic examination. Testing for reequilibration through an exchange reaction requires careful microprobe traverses across host-inclusion interfaces.

Before leaving the subject of zoned porphyroblasts, we should consider

ways in which they have been used to infer PT paths when appropriate inclusions are absent. Although these approaches are more universally applicable than those described above, the potential for error in their use is quite high. There is a great temptation to use zoning in different minerals as compositional monitors. For example, suppose that our model pelitic schist contains inclusion-free garnets but we find that the matrix plagioclase is zoned. We might consider using core to rim compositional changes in both phases for either Gibbs method or differential thermobarometric analysis. The problem with this approach is that it requires the assumption that the cores of the two phases were once in equilibrium. There is no way to critically evaluate this hypothesis, and it seems quite likely that the garnet and plagioclase did not nucleate at the same time or grow at the same rate.

Another dangerous technique involves the use of core compositions in zoned porphyroblasts with rim composition of matrix phases for thermobarometry. This method is frequently applied to upper amphibolite and granulite facies pelitic samples that contain abundant biotite and garnets with homogeneous cores and narrow retrograde rims. Biotites in such samples are commonly unzoned, and their composition is often used with the core garnet composition to estimate one GARB temperature and with the rim garnet composition to estimate another. The resulting temperatures are interpreted as indicating the amount of cooling that occurred between garnet homogenization and final rim equilibration. The implicit assumption here is that the biotite effectively acted as an infinite reservoir for Fe-Mg exchange during retrogression because the volume of garnet participating in the reaction was small (Tracy et al 1976). It should be possible to test this hypothesis for a particular sample using extensions of the Gibbs method that include mass balance constraints (Spear 1988, Spear & Florence 1990). Unless such tests are made, PT path interpretations made using this technique should be viewed with skepticism.

In the final analysis, all of the techniques used to extract PT path data from zoned porphyroblasts require substantially more assumptions than does rim thermobarometry. Whether or not these assumptions are philosophically palatable is a subject for debate (e.g. Frost 1988). In my opinion, the two most useful tests of these assumptions for a particular application are internal consistency and geologic feasibility. Whenever possible, different techniques of path reconstruction should be used for the same samples and the results should be compared (e.g. Hodges & Silverberg 1988, Selverstone & Chamberlain 1990). If a number of samples from a single structural level in an orogenic belt yield similar PT trajectories, then it is hard to imagine that the paths are artifacts of sample-specific problems with the assumptions involved. If a path implies a tectonic scenario that

is consistent with fundamental structural constraints, then it should be tentatively accepted as an additional constraint; if it is not consistent, then the burden of proof associated with path reconstruction becomes unbearable.

Fluid Inclusion Thermobarometry

A fluid phase is an essential part of most metamorphic assemblages. Some of this fluid may be trapped in metamorphic minerals during their growth (as primary inclusions) or during the healing of later fractures (as secondary inclusions). Various laboratory techniques may be used to establish the composition, density, and homogenization temperature of an inclusion at atmospheric pressure (Roedder 1984). From experimental phases equilibrium data for the pertinent system, it is possible to establish the density-specific curve (isochore) in PT space that must pass through the conditions at which the inclusion was trapped. If either the temperature or pressure of entrapment can be constrained independently (e.g. through rim thermobarometry), then the isochore may be used as either a barometer or a thermometer. In rare cases, coeval inclusions of different compositions can yield estimates of both P and T of entrapment (Roedder & Bodnar 1980).

Because secondary fluid inclusions are commonly trapped at temperatures and pressures well below those recorded by rim thermobarometers, they can place important constraints on the late-stage PT evolution of metamorphic terrains (Hollister 1979). In some cases, multiple generations of fluid inclusions in a sample define distinct isochores. By knowing the sequence of entrapment, it is possible to reconstruct the general PT trajectory of the sample as it crossed the isochores (Hollister et al 1979). Excellent examples of the use of fluid inclusions in unroofing studies may be found in Hollister (1982), Selverstone et al (1984), Selverstone & Spear (1985), Hames et al (1989), and Sisson et al (1989).

PT Path Error Estimation

Many PT paths determined using the techniques described above have been published in the literature, but few authors attempt a realistic assessment of the uncertainties involved. This is less a matter of negligence than an admission that many of the associated uncertainties cannot be quantified given present knowledge.

UNCERTAINTIES IN RIM THERMOBAROMETRY Beyond the question of whether or not mineral rim compositions measured in a particular sample represent equilibrium, there are three sources of uncertainty in con-

ventional thermobarometry: analytical errors, errors in solution modeling, and calibration errors.

Hodges & McKenna (1987) and Steltenpohl & Bartley (1987) have described how Monte Carlo techniques may be used to propagate analytical uncertainties (including counting statistics as well as compositional variabilities in natural samples) through thermobarometric calculations into uncertainty ellipses in PT space. Although the magnitudes of the resulting PT uncertainties obviously vary depending on data quality and the relative dP/dT slopes of the thermobarometers used, most careful studies result in 2-SD errors on the order of 20–50 K and 100–150 MPa.

Any application of Equation (3) requires an assumption about the thermodynamic behavior of mineral solutions for calculating activities. Although many experimental and empirical studies have been aimed at understanding the solution properties of common rock-forming minerals, a lack of consensus remains. Garnet solution modeling, an integral part of most thermobarometric studies, is especially plagued in this regard: Over the past ten years, different models have been proposed for quaternary garnet solutions by Newton & Haselton (1981), Hodges & Spear (1982), Ganguly & Saxena (1984), and Berman (1990), and there have been numerous other papers published on solution properties of binary and ternary subsystems in garnet. Unfortunately, the variations in their results cannot be transformed into a numerical estimate of the error involved in garnet solution modeling because different workers often used different, mutually exclusive assumptions about solution behavior.

Different methods of calibration lead to different magnitudes of error in the thermodynamic constants appearing in Equation (3). The uncertainties in experimental calibrations have been analyzed by Demarest & Haselton (1981), Hodges & McKenna (1987), and McKenna & Hodges (1988). Propagation of these through thermobarometric equations leads to 2-SD errors of well over 100 K and 200 MPa in the best of circumstances, although thermobarometric studies of metamorphic terrains where PT can be estimated independently from phase equilibrium considerations (e.g. Hodges & Spear 1982) suggest that most thermobarometers are more reliable than rigorous propagation of experimental uncertainties would suggest. The errors associated with empirical calibrations have been reviewed by Hodges & Crowley (1985). In general, these are substantially larger than errors in experimental calibrations because the former are derived in part from application of the latter to natural samples. As alluded to previously, uncertainties in thermodynamic calibrations are difficult to establish because most thermodynamic data sets are not accompanied by error estimates, and it is likely that the uncertainties that have been estimated (e.g. Holland & Powell 1990) are minimal because appropriately

large errors were not assumed for the experiments from which the data base was derived.

The above uncertainties relate to both the precision and the accuracy of rim thermobarometry, and it is important to appreciate fully the distinction between the two. The *precision* of a *PT* estimate refers to errors obtained by propagating analytical uncertainties alone. The *accuracy* refers to propagation of these errors as well as uncertainties in solution models and calibration methods. The precision of rim thermobarometry is generally quite good, but the accuracy must be substantially poorer. For most studies, adequate answers to important tectonic questions depend more on differences in *PT* between samples than on absolute pressures and temperatures. If the same equilibria and the same solution models are used for all samples, then only precision limits need to be considered. In such cases, it is possible to establish relative depths of equilibration to within a few kilometers and relative temperatures to within a few tens of degrees.

UNCERTAINTIES IN *PT* PATHS OBTAINED FROM ZONED PORPHYROBLASTS The uncertainties of individual *PT* estimates derived from solid inclusion thermobarometry are similar to those that characterize rim thermobarometry. The field of uncertainty associated with changes in *PT* conditions from the time of inclusion equilibration to the time of rim equilibration may be obtained simply by using Monte Carlo techniques. Potential errors in both the Gibbs method and differential thermobarometry include those derived from analytical methods and the choice of thermodynamic constants and solution models. Empirically, uncertainties in solution models have little effect on *PT* path calculations (Spear 1989). Because uncertainties in thermodynamic constants are not well known, there have been no attempts to propagate such uncertainties through Gibbs method or differential thermobarometric calculations. As pointed out by Spear (1989), such uncertainties would be irrelevant to comparative studies of *PT* paths from mineralogically similar samples from different structural levels in an orogen. Spear & Rumble (1986) have illustrated the effect of propagating analytical uncertainties through Gibbs method calculations. They found that the basic geometric features of paths are preserved despite substantial scatter.

UNCERTAINTIES IN FLUID INCLUSION STUDIES Roedder (1984) presents a detailed overview of the sources of uncertainty in fluid inclusion thermometry and barometry. Some of the most important are (a) an imperfect knowledge of the density and composition of a fluid at the time of its entrapment; (b) the potential for postentrapment changes in density or composition (e.g. by decrepitation or diffusion); (c) various experimental problems with laboratory analysis; and (d) uncertainties in the phase

equilibria of fluid systems. Some laboratory methods are available for making accurate measurements of fluid inclusion composition, but most of these are not widely available. The possibility of decrepitation, though especially important in regional metamorphic terrains, is hard to evaluate for most samples. Analytical difficulties can be minimized with proper refinement of techniques, and errors in establishing homogenization temperatures for inclusions at atmospheric pressure are on the order of a few tens of degrees at most (Roedder 1984). To my knowledge, there has been no rigorous analysis of the uncertainties associated with extrapolating experimentally derived P - T -composition relationships to derive isochores from laboratory analysis of high-temperature fluid inclusions. Most papers presenting fluid inclusion data contain no attempt to evaluate uncertainties.

DEPTH-TIME PATHS

Pressures obtained through thermobarometric techniques can be converted to equilibration depths (Z) by assuming a nominal lithostatic load with a density of 2750 kg m^{-3} : $Z(\text{km}) = 0.037P(\text{MPa})$. Thus, a PT path effectively defines a depth-temperature (ZT) path (Figure 1c). If such a path and a Tt trajectory (Figure 1b) can be reconstructed for a particular structural horizon, then it should be possible to “map” the times at which the horizon passed through specific depths (Figure 1d). The resulting depth-time (Zt) curve is the ultimate goal of PTt path analysis. The slope of this curve defines the rate of approach of the horizon to the surface of the Earth. This is often incorrectly referred to as the uplift rate for the horizon. “Uplift” properly pertains to changes in the elevation of something relative to a surface with fixed coordinates; for example, we speak of the “uplift of a marine terrace relative to sea level.” Changes in depth inferred from a Zt curve are essentially changes in the amount of lithostatic load and should be referred to as “denudation” or “unroofing.”

Many attempts have been made to extract denudation rates directly from Tt data without integrating PT data (e.g. Clark & Jäger 1969, Wagner et al 1977, Parrish 1983, Copeland et al 1987). The most common approach involves the assumption of a specific, stable geothermal gradient during unroofing, such that a cooling rate defined for a sample by Tt data may be divided by the geothermal gradient to obtain an unroofing rate. A second approach requires the collection of thermochronologic data from a variety of elevations in an area of high relief. Given different apparent ages obtained for a particular mineral-isotopic system at different elevations, an unroofing rate is calculated by dividing the age difference by the elevation change. Both of these methods can be dangerous because they

require the assumption of a uniform geothermal gradient that is stable throughout the unroofing interval being analyzed. One of the most profound results of numerical experiments on the thermal structure of metamorphic terrains is that geothermal gradients during orogenesis are complex in both two and three dimensions. The time scale of tectonically induced thermal perturbations is on the order of many tens to hundreds of millions of years (England & Thompson 1984). This is essentially the same as the time scale of orogenesis itself; thus, it seems very unlikely that anything remotely resembling an equilibrium thermal gradient persists for any appreciable length of time in an evolving orogen.

The integration of PT and Tt data provides a much more robust estimate of unroofing rates because it is independent of any assumptions about the thermal structure of the lithosphere. Unfortunately, the appropriate data for this exercise are seldom available because most Tt and PT studies focus on different temperature ranges. The most reliable thermobarometers involve phases that are stable under amphibolite to granulite facies conditions. The kinetics of thermobarometric reactions is such that most reactions are incapable of recording retrograde PT path information at temperatures below about 775 K (Hodges & Spear 1981, Thompson & England 1984, Spear & Peacock 1989). Table 1 shows that the vast majority of mineral-isotopic systems have closure temperatures approximately equal to or lower than 775 K. As a consequence, most Tt paths published in the literature correspond to the 775–380 K interval, while most published PT paths correspond to exclusively higher temperatures.

One solution to this unfortunate situation is to simply extrapolate at constant slope either the Tt curve to higher temperatures or the PT curve to lower temperatures. This approach also implies an extremely simplistic view of the thermal evolution of orogenic belts, and it must be used with extreme caution (if at all). An alternative solution has been suggested by Royden & Hodges (1984). They showed that it is possible to reconstruct mathematically the lower temperature portions of the thermal history of a metamorphic terrain from higher temperature PT data given an arbitrary initial thermal structure. Their mathematical formalism was derived assuming a constant unroofing rate over the temperature interval of interest, but a predictable change in the unroofing rate with time could also be incorporated into the equations. If Tt data are available for a specific structural horizon, then this technique may be used to extract the approximate PT path for the appropriate temperature interval and thus solve for the unroofing rate. Linear programming analysis of the Royden & Hodges (1984) approach indicates that the results obtained from it are relatively insensitive to reasonable errors in input parameters 20 m.y. after the initial thermal perturbation (McNutt & Royden 1987); for shorter time scales,

very precise thermobarometric data are required from more than one structural level for robust estimates of the low-temperature PT path.

PLACING PTt PATHS IN THEIR STRUCTURAL CONTEXT

Regionally metamorphosed samples characteristically contain one or more deformational fabrics. For many years it has been common practice among metamorphic petrographers to use textural criteria to establish the relative timing of porphyroblast growth and fabric development (Zwart 1962, Spry 1969). Unfortunately, it is not always easy to relate observed textures to the timing of final chemical equilibration or to open- vs closed-system behavior for geochronometers. For example, textural evidence may show that garnet and biotite in a sillimanite-grade sample grew synkinematically with respect to an early schistosity, but the GARB temperature calculated for the sample could correspond to conditions during retrograde reequilibration at garnet grade. Similarly, the $^{40}\text{Ar}/^{39}\text{Ar}$ age of the biotite would reflect passage of the sample through the closure temperature for the mineral-isotopic system substantially after schistosity development. These difficulties aside, petrographic observations can provide important corroboration of PT trajectories obtained through rim thermobarometry of retrograded samples, inclusion thermobarometry, or thermodynamic modeling. For many retrograde paths, it may be possible to relate late-metamorphic deformational fabrics to the thermal events responsible for retrograde reequilibration.

THE FUTURE

Despite recent advances in PTt path reconstruction, developments in our methodology have greatly outpaced improvements in our knowledge of the necessary input parameters. Our greatest ignorance continues to lie in the field of geochemical kinetics. Kinetic experiments are tedious, but they are absolutely essential if we wish to better define the closure temperatures of thermochronologic systems or to establish a rigorous understanding of the limitations of our techniques for PT path reconstruction.

Even with our presently limited appreciation of kinetic constraints, we can use PTt paths to place important constraints on tectonic processes. Recent examples of the power of combining the techniques described in this paper may be found in Hollister (1979), Spear et al (1984), Selverstone (1985), Spear & Rumble (1986), Hodges et al (1988), Chamberlain et al (1989), Hames et al (1989), Hubbard (1989), and Hubbard & Harrison (1989). The future challenge is to improve our record of integrating these

techniques. We must focus on better definition of the high-temperature portions of Tt curves (using systems like U-Pb monazite, U-Pb allanite, and Sm-Nd garnet) and the low-temperature portions of PT curves (using fluid inclusions more aggressively). We must also increase the use of inverse methods to extract unroofing rates from PTt data. Finally, we must remember that any PTt study is virtually useless without an adequate appreciation of the tectonic setting of a suite of samples. The techniques described in this review may have their roots in classical geochemistry, but their application lies squarely in the domain of continental tectonics. Future improvements in our understanding of the evolution of metamorphic terrains will depend on conscientious efforts to integrate petrologic and geochronologic studies with the traditional mainstay of continental tectonics—field structural geology.

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236 HODGES

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