

THERMOBAROMETRY USING MULTI-EQUILIBRIUM CALCULATIONS: A NEW TECHNIQUE, WITH PETROLOGICAL APPLICATIONS*

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ABSTRACT

An "internally consistent method" (Powell 1985) for performing thermobarometric calculations is described in which all possible equilibria implied by a given mineral assemblage are computed using an internally consistent set of thermodynamic data for end members and mixing properties. Results are presented graphically and as best estimates determined by weighted averaging of the graphical results. Several examples illustrate that convergence of all equilibria in a single P-T region correlates well with textural and chemical indications of equilibrium, suggesting that this technique makes it possible to reasonably assess the state of equilibration of samples for systems in which the thermodynamic properties appear to be well described. One implication is that portions of P-T paths may be reconstructed from rocks that display disequilibrium textures but that pass this test for local equilibrium. The general applicability of this technique is presently limited by the accuracy of thermodynamic data, particularly for solid solutions, but should expand as these properties are refined in the future. This method facilitates the refinement process by (1) highlighting which minerals are most incompatible in each calculation and thus may be in need of refinement, (2) illustrating the sensitivity of results to different solution-models and offering the chance to correlate these differences with petrographic observations, and (3) providing a means to select "well-equilibrated" samples that can be used to refine thermodynamic properties in the absence of appropriate experimental data.

Keywords: thermobarometry, metamorphic, pressure, temperature, P-T paths, thermodynamic properties, software.

SOMMAIRE

Ce travail porte sur une méthode à compatibilité interne (Powell 1985) d'effectuer des calculs thermobarométriques; tous les équilibres possibles impliqués par un assemblage de minéraux sont calculés au moyen d'une banque de données thermodynamiques à compatibilité interne pour les pôles et les propriétés de mélange

impliquant ces pôles. Les résultats sont présentés graphiquement et interprétés comme étant les meilleurs estimés, tels que déterminés par une moyenne pondérée des résultats graphiques. Plusieurs exemples montrent que la convergence de tous les équilibres dans un secteur unique de P et T concorde bien avec les indicateurs texturaux et chimiques de l'équilibre. La technique facilite donc l'évaluation de l'état d'équilibre pour un échantillon dans un système où les propriétés thermodynamiques sont bien décrites. Des segments de tracés d'évolution en termes de P et T peuvent ainsi être reconstruits pour des échantillons qui manifestent des textures de déséquilibre mais qui réussissent quand même ce test de l'existence d'un équilibre local. L'exactitude des données thermodynamiques, particulièrement pour les solutions solides, limite présentement l'applicabilité générale de cette technique; son applicabilité ira en s'améliorant à mesure que ces propriétés deviennent mieux connues. Cette approche facilite le processus de l'affinement de données: 1) elle indique quelles des phases minérales sont le plus incompatibles dans chaque cas calculé, et ainsi en mesure d'être affinées; 2) elle illustre la sensibilité des résultats au choix des différents modèles de solution et offre ainsi la chance d'établir une corrélation de ces différences avec les observations pétrographiques, et 3) elle permet la sélection d'échantillons "bien équilibrés" qui peuvent à leur tour servir dans un affinement des propriétés thermodynamiques en l'absence de données expérimentales.

(Traduit par la Rédaction)

Mots-clés: thermobarométrie, métamorphique, pression, température, évolution P-T, données thermodynamiques, logiciel.

INTRODUCTION

One of the primary goals of petrology is to quantify accurately petrogenetic conditions and relate them to geological processes. For metamorphic petrologists, a great deal of attention has been focused on determination of peak conditions of metamorphism, and much experimental and theoretical work has been expended on the important task of calibration of equilibria that can be used for the purpose of thermobarometry. Spear

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(1989) provided a recent comprehensive review. Most recently, petrologists have been increasingly adopting a more dynamic perspective, in which the focus is on the changing P-T conditions that a rock experienced over time, as it is this information that is important in formulating models of crustal evolution linking metamorphism and plutonism to tectonic processes (England & Richardson 1977, England & Thompson 1984). Significant advances have been made recently in relating compositional zonation in minerals to pressure (P) - temperature (T) changes (Selverstone & Spear 1985, Spear 1989); these calculations rely on traditional thermobarometric techniques (described below) to provide the absolute P-T conditions. For high-grade rocks that do not preserve compositional zonation, other methods of determining P-T paths are required.

As one consequence of the recognition that rocks may trap some record of their path of changing P-T conditions, petrologists must apply the most stringent tests of equilibrium in order to obtain reliable thermobarometric data. Most commonly, petrographic observations, data on chemical partitioning, and intra- and intersample consistency are used to argue for the attainment of equilibrium (e.g., Zen 1963, Vernon 1976, 1977, Spear 1989). This paper presents a new technique for performing thermobarometric calculations in which the equilibration state of a sample may be assessed by comparison of the positions of all equilibria implied by a given assemblage. Although limitations are imposed by the dependency of results on the quality of thermodynamic data input, examples presented below suggest that these data are of sufficient quality in some mineral systems to allow this test to be applied usefully; some implications for determining portions of P-T paths are explored. For other systems, involving minerals with less well-defined thermodynamic properties at present, this technique can assist in refining these properties by (a) providing a method to select "well-equilibrated" samples that can be used to place constraints on thermodynamic properties that are poorly constrained by experiment, (b) highlighting those mineral components that are most incompatible in each set of calculations and whose thermodynamic properties may be in need of refinement, and (c) helping to evaluate solution models of minerals through comparisons of results obtained with alternative models.

THERMODYNAMIC RELATIONS

For a system at chemical equilibrium, the chemical potentials of all system components (e.g., i) are equal in all phases (A, B, C):

$$\mu_i^A = \mu_i^B = \mu_i^C = \dots \quad (1)$$

For a balanced chemical reaction among n end members of each phase (i.e., phase components) (ϕ_i), given by:

$$\sum_i^n \nu_i \phi_i \quad (2)$$

where ν_i is the stoichiometric reaction coefficient, the thermodynamic relation that must be satisfied for chemical equilibrium is:

$$\Delta_r G^* = -RT \ln K \quad (3)$$

$\Delta_r G^*$ is the standard state Gibbs free energy of reaction at P and T, R is the gas constant, and K is the equilibrium constant, given by:

$$K = \prod_i^n a_i^{\nu_i} \quad (4)$$

with a_i equal to the activity of phase component i. The Gibbs free energy of reaction is computed from:

$$\Delta_r G^* = \sum_i^n \nu_i \Delta_f G_i^* \quad (5)$$

where $\Delta_f G^*$, the Gibbs free energy of formation of any phase component at P and T, is given by:

$$\Delta_f G^* = \Delta_f H^0 + \int_{298}^T C_p dT - T[S^0 + \int_{298}^T (C_p/T) dT] + \int_1^P V dP \quad (6)$$

$\Delta_f H^0$ and S^0 are the standard state enthalpy of formation and entropy at 1 bar and 298 K, C_p is the heat capacity, and V the volume.

Substitution of eqns (5) and (6) into (3), omitting C_p and volume-derivative terms, yields the standard form for a geothermometer or geobarometer (Δ_r refers to a reaction property):

$$T = \frac{(\Delta_r H^0 + \Delta_r V^0(P-1))}{(\Delta_r S^0 - R \ln K)} \quad (7a)$$

$$P = \frac{(-RT \ln K - \Delta_r H^0 + T \Delta_r S^0)}{\Delta_r V^0} \quad (7b)$$

In a system with c system components and n end members of the phases, the maximum number of

possible reactions that can be used as thermobarometers is given by:

$$n! / [(c+1)!(n-(c+1))!] \quad (8)$$

Owing to compositional degeneracies, the actual number of unique reactions may be some number less. Of these, there are only $n - c$ independent reactions. Any of the other possible reactions can be generated from linear combinations of the independent reactions, although the set of independent reactions is not unique.

REVIEW OF THE THERMOBAROMETRY PROBLEM

The most common method of thermobarometric analysis [see Spear (1989) for a review] is through application of a minimum of two independently calibrated equations (7), whether they are calibrated directly using experimental results or indirectly from empirical observations of $\ln K$ variations in natural assemblages. Ideally, these equilibria have slopes that are independent of pressure (geothermometer) and temperature (geobarometer), so that uncertainties in determination of either P or T are not translated into uncertainties in the other variable. This technique introduces three main problems:

1. *Internal consistency*: A major problem with the classical technique is the lack of internal consistency in the calculations. As one reflection of this problem, three separately calibrated equilibria, only two of which are independent, will in general not intersect at the invariant point required by thermodynamic consistency. An important consequence of this inconsistency is that effects of disequilibrium may not be recognized from the thermobarometric results, as discussed below. In addition, inspection of equation (7) indicates that two independently calibrated thermobarometers will in general imply something different about the thermodynamic properties (both standard state and solution) of any phases or phase components that participate in both equilibria. Since both sets of properties for a given phase cannot be correct, the P and T defined through intersection of both equilibria also cannot be correct in detail.

2. *Verification*: The most severe problem is that thermobarometry based on the intersection of two equilibria offers no way to check the validity of the results, in particular the validity of the critical assumption that all minerals that comprise thermobarometers equilibrated at the same pressure and temperature (here referred to as the "equilibrium assumption"). Without a quantitative way

to assess this assumption, support for thermobarometric results must come from intra- and intersample consistency and independent geological evidence.

3. *Ambiguity*: A final problem is that of deciding which formulation of each particular thermobarometer one will use. The garnet - biotite equilibrium, for example, has at least seven different calibrations (Spear 1989, p. 13), among which it is difficult for the lay-petrologist and the expert to decide objectively. This situation has led many geologists to use several, many, or all different formulations, and rely on other geological evidence, intersample consistency, or simply geological intuition (!) to select preferred results. In many cases, the process of having to select among the various calibrations defeats the original goal of obtaining a quantitative or independent P-T estimate.

Powell (1985) referred to the traditional thermobarometric approach as the "directly calibrated method", and introduced an improved "internally consistent method" that has been further developed by Powell & Holland (1988). With this method, the consistency problem is avoided by computing an average pressure for a given sample from an independent set of equilibria, all of which are computed using one set of thermodynamic data. A discussion of the technique of derivation of the data is beyond the scope of this paper (see, for example, Berman *et al.* 1986, Holland & Powell 1990), but the calibration of thermodynamic data will, in the ideal case, account for each of the different sets of experiments and constraints imposed by natural assemblages used in the different calibrations of each thermobarometer. An additional advantage of the "internally consistent method" is that new experimental data for thermobarometer A, for example, have the potential of improving thermobarometric results using other equilibria if the experiments are used to revise the thermodynamic data-base. An ambiguity problem similar to that described above will arise, however, when alternative sets of standard state or solution data are available. In this case, the comparisons can help to elucidate the effects of different data-sets or models, thus leading to the continuous improvement of these data and the thermobarometric applications utilizing them.

PROPOSED METHOD FOR THERMOBAROMETRY

General description

In order to address the problems described above, this paper presents an alternative "internally

consistent" thermobarometric technique to that described by Powell (1985) and Powell & Holland (1988). With the present method, referred to as TWEEQU (Thermobarometry With Estimation of EQUilibration state), the positions of all possible equilibria implied by a given mineral assemblage are computed in $P - T - X(\text{CO}_2)$ - activity space by the TWQ program, plotted for visual inspection and interpretation, and utilized to compute an average pressure and temperature (or other intensive variable) simultaneously from all intersections (INTERSX program). The TWEEQU calculations, described in more detail in Appendix I, are performed utilizing a set of internally consistent thermodynamic data for end members and solution properties so that thermobarometric consistency is guaranteed. If three conditions are met: (1) thermodynamic data are perfect, (2) compositional data are perfect, and (3) all minerals last equilibrated at the same pressure and temperature, all equilibria will intersect at a single P-T point (Fig. 1), or, stated another way, a single P and T satisfies eqn. 3 for all equilibria. This is one consequence of the usual definition of equilibrium in terms of the equivalence of chemical potentials of all system components (eqn. 1). Significant deviations from this ideal case lead one to question the validity of the results and analyze the geological (and possibly thermodynamic) input data with the aim of discovering which of these three assumptions is in error. There is unfortunately much room for

circular reasoning, it being impossible to conclude in any one calculation whether, for example, inaccurate thermodynamic data, compositional data, or disequilibrium may have caused discrepant results. Some of the examples discussed in the next section, however, illustrate that, when results for several or many rocks are compared to each other and to petrographic observations, these three sources of potential error can commonly be discriminated with some degree of confidence. Even where the source of error cannot be pinpointed, it is important to recognize that one or more of the basic assumptions have been compromised, and weight the thermobarometric results accordingly. As further experimental work and analysis of data on natural assemblages lead to improved thermodynamic data in the future, one can expect to be able to resolve the source of discrepant thermobarometric results with greater confidence. It should also be noted that, because of its dependence on thermodynamic data, this technique must to some extent continue to rely on, and indeed can be complemented by, individually calibrated thermobarometers that may involve minerals or account for data not incorporated in the thermodynamic calibrations.

A major difference between the technique described here and that of Powell & Holland (1988) is that the latter calculates average pressures based on an independent set of equilibria, rather than pressures and temperatures from all equilibria. As different results are produced with each different independent set that forms the basis of the calculations, the choice of independent set affects the final numerical result. The equilibria that are best suited to form the independent set are those with the smallest uncertainties and which are least sensitive to errors in input data (those with the largest $\Delta_r S$, $\Delta_r V$, and smallest $\ln K$). Because uncertainties in activities comprise the largest source of error (Powell & Holland 1988, Holland & Powell 1990, Kohn & Spear 1991) and because these errors are magnified to different extents in each equilibrium by virtue of the different reaction-coefficients (eqn. 4), it is difficult to derive a general strategy for selection of the optimal set of independent equilibria. Moreover, once consideration is given to errors caused by geological processes that may have operated to perturb the equilibrium composition of any phase (e.g., re-equilibration during cooling, interaction with fluids), an optimal set becomes impossible to predict *a priori*. This can be illustrated by considering a hypothetical ideal case in which all equilibria intersect at a single point, $P_{\text{true}} - T_{\text{true}}$ (Fig. 1). In this example construed with the equilibria listed in Table 1, there are three independent

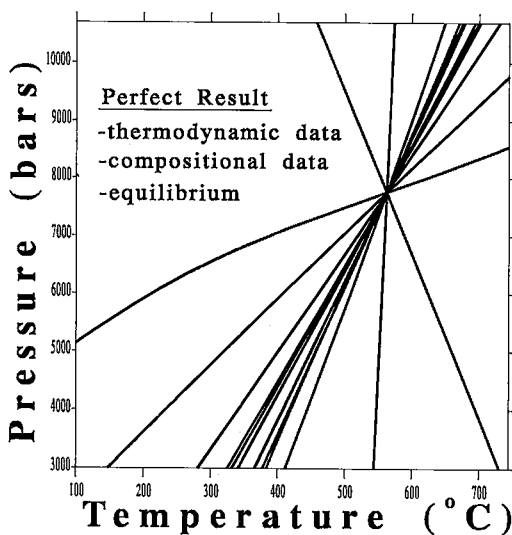


FIG. 1. P-T diagram showing ideal thermobarometric results in a case where the thermodynamic data and compositional data are perfect, and all minerals equilibrated at the same P-T conditions.

TABLE 1. TWEEQU RESULTS FOR CALC-SILICATE RPI3 (HOLLAND & POWELL 1990)

Mineralogy: Chl-Bt-Ms-Grt-Pl-Ep-Cc-Qtz

Assemblage used in TWEEQU calculations: Chl-Bt-Ms-Grt-Pl-Ep-Qtz

Previous P-T results: P=7.5 ± 0.5 kbar @ assumed 520 °C (Powell & Holland (1988)

P=7.2 ± 0.3 kbar @ assumed 530 °C (Holland & Powell (1990)

Averaged TWEEQU results[§]: P=7.2 ± 0.3 kbar / T=533 ± 15 °C (3 independent reactions)

Outliers: Equilibria 1, 9, 10 (end-members in common: annite, almandine)

Equilibrium 6 controls P-T determination (excluding annite)

Averaged TWEEQU results[#]: P= 6.8 ± 0.6 kbar / T=467 ± 32 °C (3 independent reactions)

Outliers: Equilibrium 9 (contains reliability level 3 end-members: annite, clinozoisite)

Equilibria plotted in Figure 3	Δ_p S	Δ_r V
1: Alm + Phl = Prp + Ann	-13.7	-0.31
2: 5 Prp + 24 Czo + 3 Qtz = 33 An + 3 Cln + 5 Grs	-842.7	-67.23
3: Prp + Ms + Grs = 3 An + Phl	-119.2	-7.26
4: 3 Qtz + 5 Alm + 24 Czo + 5 Phl = 5 Grs + 3 Cln + 33 An + 5 Ann	-911.1	-68.77
5: Ms + Grs + Alm = Ann + 3 An	-132.9	-7.57
6: 6 Prp + 11 Ms + 16 Grs + 3 Cln = 3 Qtz + 24 Czo + 11 Phl	-469.0	-12.68
7: 5 Phl + 24 Czo + 3 Qtz = 18 An + 3 Cln + 10 Grs + 5 Ms	-246.5	-30.91
8: 3 Qtz + 24 Czo + 5 Ms + 10 Prp = 5 Phl + 3 Cln + 48 An	-1438.9	-103.55
9: 11 Ms + 16 Grs + 3 Cln + 11 Alm = 3 Qtz + 11 Ann + 24 Czo + 5 Prp	-619.6	-16.08
10: 11 Ms + 16 Grs + 3 Cln + 6 Alm = 3 Qtz + 6 Ann + 24 Czo + 5 Phl	-551.1	-14.53
11: 3 Qtz + 5 Alm + 24 Czo + 5 Ms + 5 Prp = 3 Cln + 48 An + 5 Ann	-1507.3	-105.09
12: 3 Qtz + 10 Alm + 24 Czo + 5 Ms + 5 Phl = 3 Cln + 48 An + 10 Ann	-1575.8	-106.64

[§] Results using Holland & Powell (1990) thermodynamic data and activities; [#] Results using thermodynamic data of Berman (1988; 1990) with ideal mixing in biotite; ± for TWEEQU results is 1σ imprecision; Δ_p S in J·K⁻¹; Δ_r V in J·bar⁻¹; abbreviations from Kretz (1983); Cln = Clinocllore

reactions among ten phase components. Uncertainties in activities, whether due to analytical errors or retrograded mineral compositions, have been simulated using random perturbations between 0 and ±2% in the mole fractions of cations that contribute to the activities of each solid-solution component. For each of 500 sets of perturbed compositions, all equilibria were computed and then processed with the INTERSX program to determine average pressures as well as the difference (Δ_p) between P_{true} and the position of each equilibrium at T_{true} . Inspection of equation (7b) indicates that pressures should vary least from P_{true} for those equilibria that have the smallest changes in lnK and the largest changes in Δ_r V. Accordingly, average pressures were computed for each sample using a weighting factor, W, for each equilibrium given by

$$W = \frac{\Delta_r V}{\ln K'} \quad (9)$$

where K' differs from the equilibrium constant in that the activities of equation 4 are raised to the absolute values of the reaction coefficients. This term has the effect of giving the most weight to those equilibria that have the smallest reaction-coefficients and site multiplicities and that involve minerals closest to end-member compositions.

The results of a Monte Carlo analysis of this system (Fig. 2) show that there is an imprecise

correlation between W and the equilibria that most frequently comprise one of the three closest to P_{true} . Thus, although there is no one set of three equilibria that is best suited to retrieval of the true P-T in all cases, the good correlation of decreasing difference in pressure averaged for all 500 perturbed samples ($\Delta_{p,av}$) with increasing W means that the $\Delta_{p,av}$ are roughly equal for independent sets formed from any of the seven equilibria (Fig. 2) that are least sensitive to compositional perturbations.

The simulation results indicate that $\Delta_{p,av}$ computed from the weighted average of all equilibria (0.05 kbar) is about half the magnitude of $\Delta_{p,av}$ based on an unweighted average of all equilibria, (0.12 kbar), but is equal to $\Delta_{p,av}$ based on the average of the set of independent equilibria (#3, 5, 8 of Table 1) with the smallest $\Delta_{p,av}$. For nonoptimum independent sets formed from the seven equilibria least sensitive to input errors (Fig. 2), $\Delta_{p,av}$ is not significantly worse (0.07 versus 0.05 kbar), but the Δ_p calculated for each of the 500 perturbed samples is higher than Δ_p calculated from the weighted average of all equilibria for about 70% of the samples. The weighted average based on all equilibria, therefore, appears to provide the most stable solution unless the optimum set of independent equilibria can be chosen unambiguously. For this reason, the technique proposed here is to compute the average P-T using *all* possible

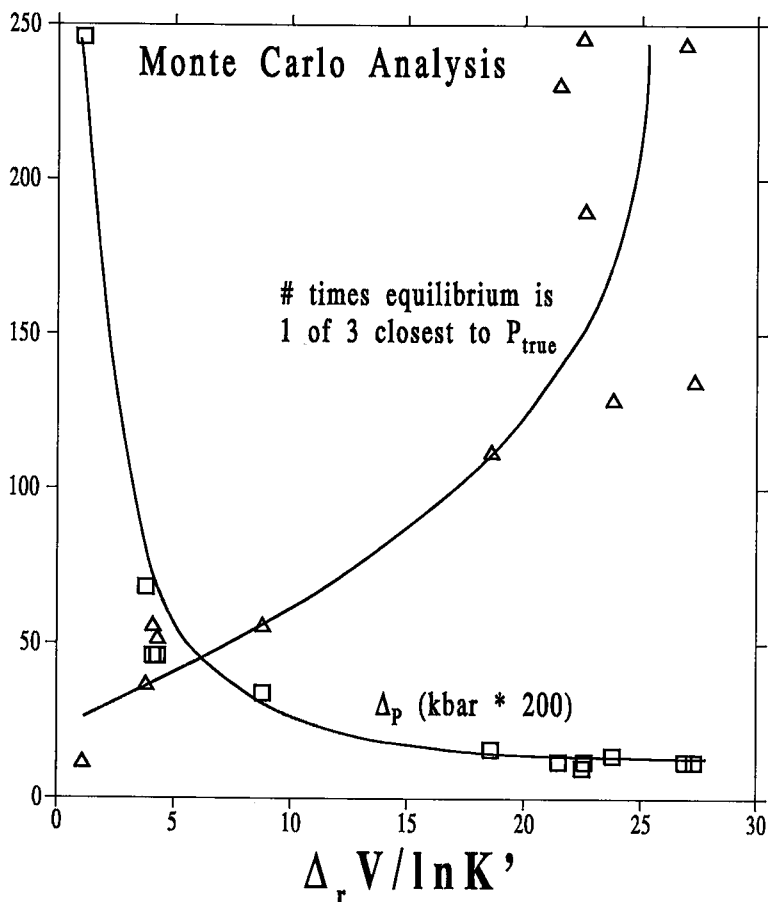


FIG. 2. Results of a Monte Carlo simulation of calculations of average pressure using mineral compositions perturbed from perfect case (Fig. 1). Average deviation in pressure (Δp_{av} ; squares) is well correlated with weighting factor (eqn. 9) for each equilibrium. A less precise correlation is observed with the number of times a given reaction is one of the three closest to the "true" pressure (triangles; see text).

equilibria implied by a given mineral assemblage. The INTERSX program computes averages and the amount of scatter (expressed as a standard deviation) of the diagram variables from all intersections (including indifferent ones) among all equilibria, both stable and metastable. The averages are weighted toward the best-constrained intersections by using a weighting factor, $|\beta \cdot W_i \cdot W_j|$, with

$$W_i = \frac{\Delta_r S_k \cdot \Delta_r V_k}{\ln K'_k} \quad (10)$$

where β is the acute angle of intersection between equilibria i and j , and K' is defined above.

It is important to appreciate that equilibria that occur furthest from the true P-T of equilibration

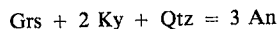
contain phase components for which one of the three basic assumptions have been most compromised. Indeed, one of the main reasons for computing all equilibria, as opposed to an independent set, is to determine if any of the phase components used in a particular calculation are significantly at odds with these three assumptions and to omit them from further calculations, unless reassessment of all input data is permissive of other combinations of "equilibrium" compositions of minerals. There are several ways the TWEEQU analysis fulfills this task. The first is by visual inspection of graphical thermobarometric results, which is the easiest way of recognizing outlying equilibria. A second way is with the INTERSX program, which repeats the averaging calculations

excluding one phase component and then one phase at a time. Powell & Holland (1988) also used this technique to filter the results of their averaging calculations. INTERSX results are highlighted when the scatter in the results decreases significantly (less than one-third) or when the average is more than 2σ outside of the average, considering all equilibria. Another effective method performed by the INTERSX program is finding those phase components in common to any outlying equilibria, operationally defined as those equilibria that differ from the average P-T by more than 1.5σ . A warning is given when the excluded phase component or phase components common to the outlying equilibria have less reliable thermodynamic data, which alerts the user to the possibility that the aberrant results were produced for this reason. Thermodynamic data have been assigned three levels of reliability, similar to those proposed by Holland & Powell (1990): (1) data that are well constrained and consistent with a large body of experimental data, and are expected to change little in the future, (2) data that are constrained by few experiments, among which some contradictions may exist, or for which some estimated thermodynamic parameters are more uncertain, and (3) data that are considered preliminary because of large inconsistencies among experimental studies or because their retrieval involved major assumptions about mixing properties.

Uncertainties

Although standard deviations computed by the INTERSX program give a measure of imprecision that allows an assessment of the overall consistency of the results in terms of the three critical assumptions to thermobarometry, it is important to note that these standard deviations do not represent statistically valid uncertainties. Overall uncertainties are exceedingly difficult to assess quantitatively because errors in standard state and solution data are systematic, depending on which model and data set is adopted, and cannot be accommodated by standard statistical techniques. Additional problems are encountered in the definition of uncertainties in thermodynamic data retrieved from phase-equilibrium data (see discussion of Berman *et al.* 1986), which are characterized by non-Gaussian probability distributions (Demarest & Haselton 1981, Kolassa 1990). The "overall" uncertainties calculated by Powell & Holland (1988) by propagation of systematic errors in thermodynamic data and random errors due to analytical uncertainties (Powell & Holland 1988, p. 177) appear to lead to overly pessimistic estimates

of uncertainty in comparison to estimates based on the compatibility of different geobarometers. For example, Powell & Holland (1988) computed overall uncertainties (2σ) of about 3 kbar for the GASP equilibrium:



yet calculations of GASP pressures repeatedly produce results that place rocks with one aluminosilicate polymorph in its appropriate field of stability and rocks with two aluminosilicates thought to be at equilibrium within about 0.5 kbar of the appropriate phase-boundary (e.g., Fig. 13 of Berman 1990). Such comparisons suggest that a more reasonable estimate of overall uncertainty is generally around 1 kbar (2σ), except for assemblages with Ab-rich plagioclase, for which activity coefficients are poorly known. The uncertainties calculated by Hodges & McKenna (1987) and McKenna & Hodges (1988) also appear overly pessimistic, at least in part because they consider only the uncertainties associated with the phase-equilibrium data they used to determine the position of the GASP equilibrium. These uncertainties are reduced substantially through consideration of other phase-equilibrium and calorimetric data that constrain the thermodynamic properties of the phases in this equilibrium. The above estimates of uncertainty based on barometer compatibility are supported by the recent analysis of Kohn & Spear (1991), which suggests overall errors of 1.6–2.4 kbar for the GASP equilibrium, with about 1 kbar stemming from the uncertainty in estimated temperature.

The method favored here focusses on what is the largest source of systematic error for most equilibria, that stemming from uncertainties in solution models (Holland & Powell 1988, Holland & Powell 1990, Kohn & Spear 1991). As this type of error produces systematic differences in results, their effects are best discovered and explored by performing different sets of calculations with alternative proposed solution-models that are compatible with standard state thermodynamic properties. Through comparison of these different sets of calculations, it should be possible to gain important insights that will eventually help to refine and improve the solution models. This process will be further aided by the selection of "well-equilibrated" samples using the TWEEQU approach. Within each set of calculations using different solution-models, the random errors related to analytical data are best quantified using Monte Carlo techniques, described by Lieberman & Petrakakis (1991). A similar technique can be applied to derive overall thermobarometric uncer-

tainties when uncertainties in standard state and solution properties are better defined (Engi *et al.* 1990).

Assessment of equilibrium

Poorly defined uncertainties in thermodynamic data, particularly solution properties, seriously compromise the ability to quantitatively assess the state of equilibration of samples on an individual basis. In addition, because each equilibrium has different uncertainties, and different reaction-properties that translate into different sensitivities to errors in input data, a single limit on pressure and temperature for the amount of intersection scatter cannot be established as the criterion to assess equilibration state. Ideally, equilibration state should be determined by comparison of calculated scatter in the intersection with that stemming solely from calibration and analytical uncertainties. Until the calibration uncertainties are better defined, the strategy recommended here is that confidence can be gained using the TWEEQU technique when the thermodynamic data pass the first-order test of producing results for specific systems and phase components with (a) little scatter when classic "equilibrium" textures (*e.g.*, Vernon 1976, 1977, Spear 1989) are observed, and (b) good consistency among different domains of single samples and among samples thought to have the same metamorphic and deformational history. Calculations for a set of samples should define the criteria used to define the "equilibrium" case, and TWEEQU results for samples of similar bulk-composition with ambiguous textures can be taken with some degree of confidence. Examples discussed below indicate that reasonable criteria for satisfaction of the equilibrium assumption correspond to INTERSX 1σ standard deviations of $\pm 0-40^\circ\text{C}$ and 0.2-0.5 kbar.

It should be noted that the expectation that all equilibria intersect at a single pressure and temperature (Fig. 1) is unjustified in view of the different closure-temperature (T_C) and resistance to retrogression of each equilibrium (Lasaga 1983, Ghent *et al.* 1988). For example, equilibria that depend on the Al content of orthopyroxene may record higher pressures and temperatures than equilibria that involve only the Fe and Mg end members (*e.g.*, Aranovich & Podlesskii 1989) because of the larger kinetic barriers to re-equilibration of Al distribution. Nevertheless, there are three reasons why the kind of equilibrium test described above should be reasonable. First, closure temperatures depend on grain size and cooling rate, and thus may be operationally quite similar for many samples at common geological rates of cooling.

Second, uncertainties in thermodynamic data, particularly activity - composition relationships, are larger than many expected differences in T_C , precluding the general interpretation at the present time of thermobarometric differences in terms of T_C differences. As these uncertainties are reduced, this type of interpretation may prove feasible and may allow geological rates of cooling to be determined from detailed study of thermobarometric differences. Third, and perhaps most convincing, is the empirical observation that thermobarometric results suggesting attainment of equilibrium are well correlated in a variety of mineral systems with textural and chemical criteria for equilibrium. A number of these results are discussed in detail below.

APPLICATIONS

Thermobarometric results for RP13, a calc-silicate rock considered by Holland & Powell (1990) to be "remarkably well equilibrated", offer a good opportunity to illustrate the TWEEQU technique. This software facilitates calculations using different thermodynamic data-bases; Table 1 and Figure 3 show TWEEQU results for this rock using thermodynamic data and activities of phase components from Holland & Powell (1990). The calculations are based on non-fluid-phase components that are also given in the TWEEQU data-base. Immediately obvious from the inconsistency in the position of invariant point A with the other equilibria shown in Figure 3 is that one of the three basic thermobarometric assumptions has been violated. The same conclusion is reflected in the large 1σ scatter (1.5 kbar, 65°C) calculated with the INTERSX program when all equilibria are included. This program proceeds to calculate that three equilibria (#1, 9, 10 of Table 1) are more than 1.5σ outside of the average P-T, and that these three equilibria have almandine and annite in common. The position of invariant point A is controlled by the garnet - biotite Fe-Mg exchange equilibrium, which gives temperatures much lower than that (520°C) preferred by Powell & Holland (1988) on the basis of calcite - dolomite thermometry. The INTERSX program focusses attention on annite, because it has a reliability level of three, suggesting that the problems may be related to this phase component. Calculations repeated without this phase component give the P-T of invariant point B, but the program warns that an independent P or T estimate is advised since there is no means of checking this P-T determined from the intersection of only two independent equilibria. An important difference with the THERMOCALC procedures (Powell & Holland 1988) is that the

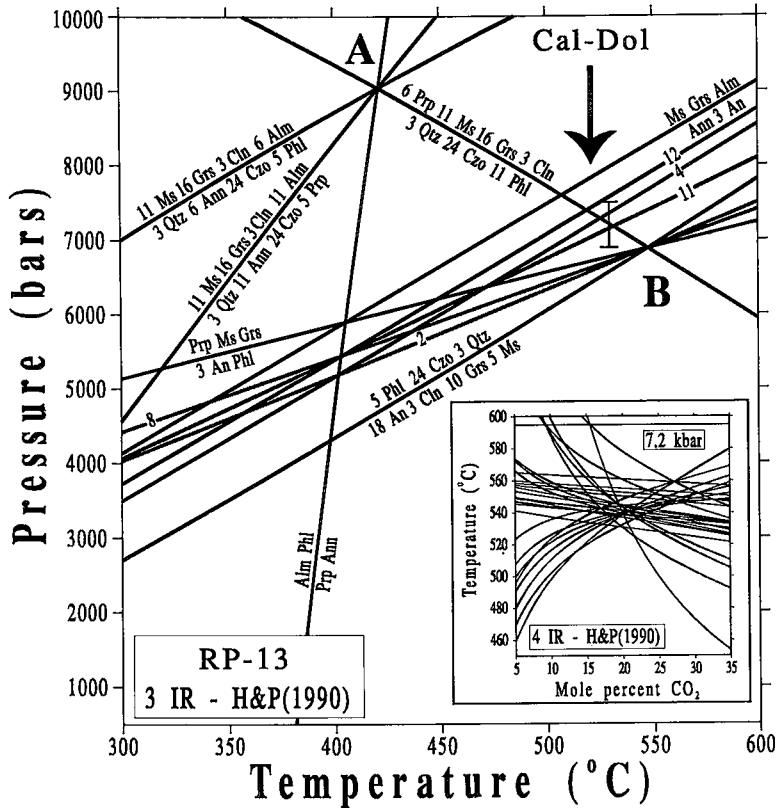


FIG. 3. TWEEQU results for calc-silicate RP-13 (Holland & Powell 1990). Box in lower left corner indicates there are three independent equilibria (3 IR), and that calculations were made using the thermodynamic data of Holland & Powell (1990). Arrow shows the preferred temperature of Powell & Holland (1988) (520°C) based on calcite-dolomite thermometry. I bar shows the 2σ average bracket associated with pressure (Holland & Powell 1990). Numbered curves refer to equilibria identified in Table 1. See text for discussion of invariant points A and B. Inset shows TWEEQU results in T- $X(\text{CO}_2)$ section at 7.2 kbar, omitting annite from the calculations.

TWEEQU results suggest that annite is a probable bad actor in RP13, and should not be included for the most accurate thermobarometric calculations. The TWEEQU calculations alone do not make it clear, however, whether it is a bad actor because of compositional data or thermodynamic data. Calculations using the TWEEQU thermodynamic data (Berman 1988, 1990, McMullin *et al.* 1991) and the same activities as given by Holland & Powell (1990) yield low garnet - biotite temperatures as well (about 430°C at 7 kbar), which suggests that the problem lies with the activity of annite. Holland & Powell (1990) calculated the activity of annite taking account of a wet-chemical analysis giving Fe^{3+} . If all Fe is calculated as Fe^{2+} , the activity of annite is raised, and a garnet - biotite temperature between 480 and 510°C is produced

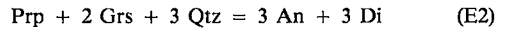
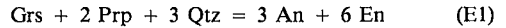
with the TWEEQU thermodynamic data, depending on whether nonideal (McMullin *et al.* 1991) or ideal mixing is assumed for biotite. This suggests that much of the problem illustrated in Figure 3 is likely a calibration problem based on different states of oxidation in retrieved thermodynamic data for annite and in these thermobarometric applications. In the examples that follow, all Fe is treated as Fe^{2+} because thermodynamic data were retrieved with this same assumption (Berman 1988, Berman 1990, McMullin *et al.* 1991). When annite is excluded from the analysis of RP13, TWEEQU calculations in a T- $X(\text{CO}_2)$ section at 7.2 kbar yield a very precise estimate of $X(\text{CO}_2)$ of 0.18 ± 0.03 (Fig. 3, inset).

It is interesting to note that results using the TWEEQU thermodynamic data produce a similar

discrepancy between the positions of invariant points A and B, but with invariant point A at lower pressure than invariant point B. This difference, highlighted by the TWEEQU technique (Table 1), is a direct consequence of the different properties for clinozoisite in the two data-bases. Holland & Powell (1990) recommended that clinozoisite is 4 kJmol^{-1} more stable than indicated by the experimental results of Jenkins *et al.* (1983), a change that would improve the overall consistency of the TWEEQU calculation for RP13. As suggested by Holland & Powell (1990), feedback from other thermobarometric applications is needed to further evaluate this change. In the meantime, this example serves as an important reminder that thermobarometric calculations with alternative internally consistent data-bases offer one of the best methods to discover systematic errors in calibration. This step is particularly important for verification of the state of equilibration of samples used for the purpose of refining any thermodynamic properties.

Geothermobarometry

Much attention has been focussed recently on the calibration of geobarometers that are compatible with one another. In granulites, for example, Newton & Perkins (1982) presented calibrations for the equilibria:



and recommended a +2 kbar correction be applied to the Cpx-bearing equilibrium in order to obtain similar pressures with the Opx-bearing equilibrium. Powell & Holland (1988) showed that their calibration of thermodynamic data for these minerals leads to quite reasonable agreement of these two barometers in applications to granulites from southern India (Harris *et al.* 1982), assumed to have equilibrated at 750°C. Equilibria E1 and

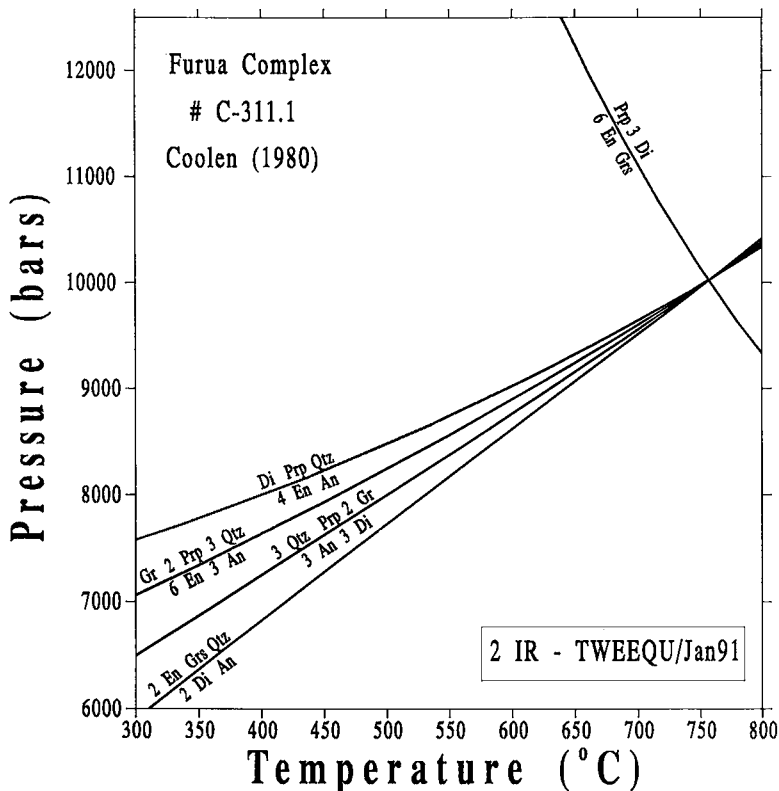
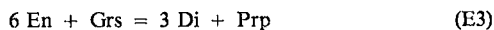


FIG. 4. TWEEQU results in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS) for first-generation phases in granulite C-311.1 from the Furua Complex, computed with the January, 1991 TWEEQU thermodynamic data. Two of five equilibria shown are independent (2 IR).

E2 are two of five equilibria that intersect in an invariant point (Fig. 4), the temperature of which is defined largely by the position of the equilibrium



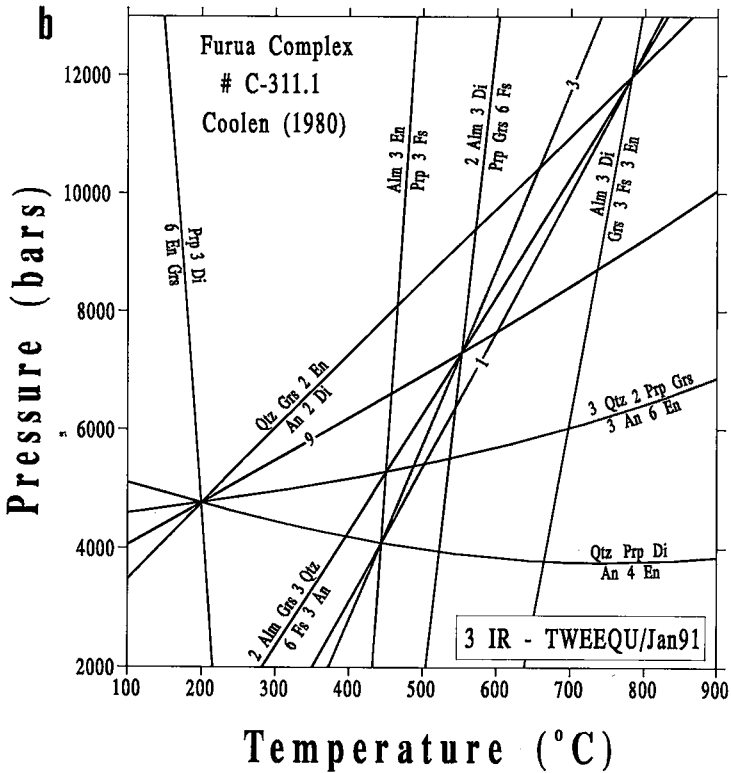
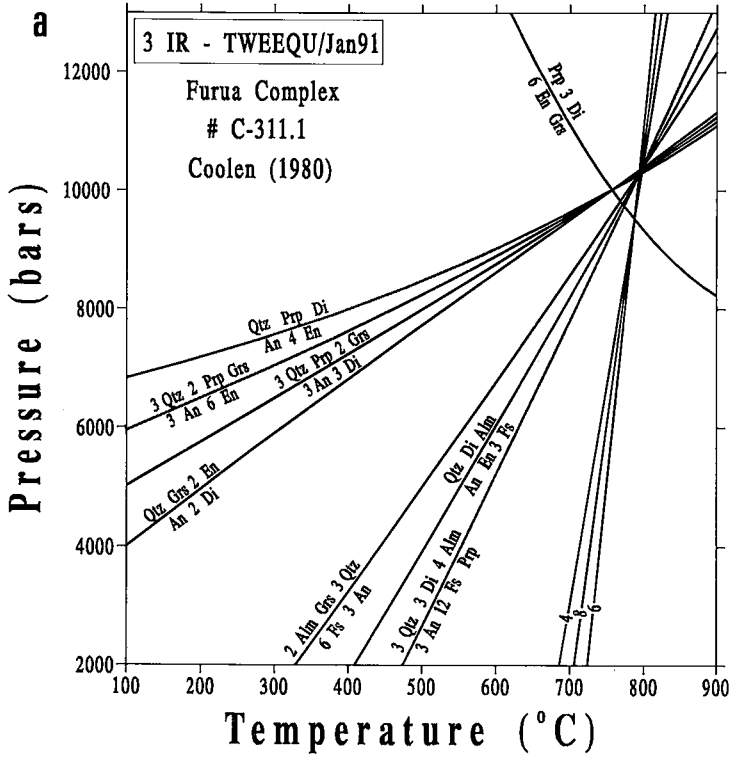
Owing to the very small $\Delta_r V$ of reaction (0.16 Jbar⁻¹), the position of this equilibrium is highly uncertain [2σ between 40 and 50 kbar based on calculations of Powell & Holland (1988, their Table 6)]. Nevertheless, Figure 4 serves to illustrate that the problem of achieving compatibility of barometers is in fact a problem of being able to retrieve an accurate estimate of the temperature of equilibration, the temperature at which the barometers intersect. For some mineral systems, like that illustrated in Figure 4, which involve extremely small $\Delta_r V$ or $\Delta_r S$ equilibria, the stringency of this test of thermodynamic data is too demanding to be of practical value. However, many other systems, in which the most temperature-dependent equilibria are not as sensitive to errors in input data (larger values of $\Delta_r V$ or $\Delta_r S$), do afford a reasonable opportunity to determine pressure and temperature simultaneously. Efforts to assure the compatibility of barometers defined for Fe and Mg end members (*e.g.*, Moecher *et al.* 1988) will always fail at some level until they test the ability of thermodynamic data to retrieve an accurate temperature, as well as a pressure, of equilibration.

The main application of the TWEEQU software lies in performing general thermobarometric calculations in which temperature as well as pressure are determined simultaneously wherever possible. The necessary criteria are that at least two of the equilibria implied by a given mineral assemblage intersect at a reasonably high angle (optimally 90°C), and are not overly sensitive to errors in input data. It is not necessary to have two equilibria with the ideal P- and T-independent slopes. One of the largest classes of equilibria that are useful for temperature estimation are those that involve Fe-Mg exchange, many of which have been calibrated independently as geothermometers. Because the $\Delta_r V$ of these equilibria is generally much smaller than that of other equilibria, calculation of these geothermometers is an extremely sensitive test of the quality of the thermodynamic data, although a test not independent of input mineral compositions and the assumption of equilibrium among these minerals. Because of this sensitivity, the greatest confidence in results is obtained when there are two or more independent equilibria that both yield a consistent temperature. Equilibria involving fluid species have not been used to estimate P-T conditions in the examples discussed below because

such calculations depend on the generally unknown activities of the fluid species.

Coolen (1980) reported chemical data for two-pyroxene granulites of the Furua Complex, Tanzania that contain two texturally distinct parageneses, distinguished by first- (M1) and second-generation (M2) garnet and pyroxene. For first-generation phases, all equilibria involving the assemblage Cpx-Opx-Grt-Pl-Qtz except E3, the equilibrium with the smallest $\Delta_r V$ of the 11 equilibria (3 independent), intersect in a very tight cluster not only defining pressure and temperature simultaneously, but also adding a degree of confidence to the result (Fig. 5a, Table 2). This confidence is what is lacking from traditional thermobarometric methods because of the common use of only two equilibria. On the other hand, the clustering of intersections shown in Figure 5a allows one to conclude that the three basic thermobarometric assumptions appear to be satisfied in this case. This conclusion is further supported by the similar, but less perfect, results produced for different samples from the Furua Complex, which show scatter up to $\pm 40^\circ\text{C}$ and 1 kbar in the positions of these intersections, except those with equilibrium E3. That such results are obtained from samples of the Furua Complex and from other granulite terranes with a range in bulk composition ($0.49 < X_{\text{Alm}} < 0.65$) suggests that the thermodynamic data are not seriously in error for these phase components in this compositional range and that the consistency in the positions of all equilibria results from the attainment of chemical equilibrium among these phases. Results including biotite produce a large amount of scatter, most likely attributed to retrogression of the biotite, modally the least abundant phase.

Although chemical equilibrium is impossible to prove, a number of tests must be met to be consistent with it. One important test is the counterexample that phases in apparent textural disequilibrium display results with substantial scatter. Figure 5b shows results for the same sample as Figure 5a, but for the case where "second-generation" (Coolen 1980) garnet and orthopyroxene are included in the calculation together with "first-generation" clinopyroxene. Assuming little error in compositional or thermodynamic data, the scatter in results of $\pm 150^\circ\text{C}$ and 4 kbar illustrates the effects of chemical disequilibrium that are implied by Coolen's (1980) textural observations. The ability of the TWEEQU technique to produce the range in results shown in Figures 5a and 5b is a necessary criterion to allow one to discriminate between equilibrium and disequilibrium. Although trivial in this case because of their obvious petrographic differences (Coolen



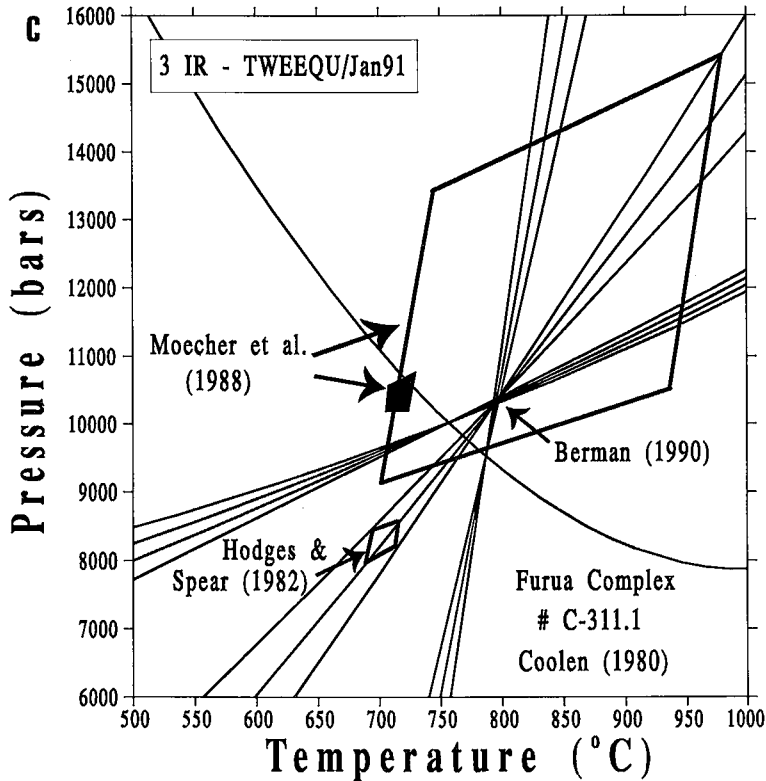


FIG. 5. a. TWEEQU results in the CMFAS system (F: FeO) for first-generation phases in granulite C-311.1 from the Furua Complex, computed with the January, 1991 TWEEQU thermodynamic data. Numbered equilibria (3 independent) are listed in Table 2. b. TWEEQU results in the CMFAS system for first-generation clinopyroxene and second-generation garnet and orthopyroxene in granulite C-311.1 from the Furua Complex, computed with the January, 1991 TWEEQU thermodynamic data. Numbered equilibria (3 independent) are listed in Table 2. Note the wide scatter in the positions of all equilibria, indicative of the disequilibrium assemblage. c. TWEEQU results in the CMFAS system for first-generation phases in granulite C-311.1 from the Furua Complex. Curves were computed with the January, 1991 TWEEQU thermodynamic data (including garnet model of Berman 1990). Open polygons show the range of intersections for the same equilibria using the garnet calibrations of Hodges & Spear (1982) and Moecher *et al.* (1988). Small filled polygon shows range of intersections for mixed first- and second-generation phases computed with the garnet calibration of Moecher *et al.* (compare with Fig. 5b).

1980), the importance of this ability becomes paramount in the most common situation petrologists are faced with, that of ambiguous petrographic textures. Particularly critical is the ability to test which mineral compositions might be in equilibrium where zoned minerals are present.

A major problem in interpreting results like those shown in Figures 5a and 5b is the sensitivity of results to thermodynamic data, particularly alternative solution-models. This sensitivity is

difficult to analyze rigorously because of the systematic differences among the data with which they are calibrated. The TWEEQU method has been set up to facilitate comparisons of the effect of different solution models on all equilibria. Figure 5c compares results for first-generation phases in the same Furua Complex rock, using the garnet mixing properties of Moecher *et al.* (1988), Hodges & Spear (1982), and Berman (1990, Fig. 5a). Results with the first two calibrations are

TABLE 2. TWEEQU RESULTS FOR MAFIC GRANULITE C-311.1 (COOLEN 1980)

Mineralogy: Opx-Cpx-Grt-Pl-Qtz-Mc-Scp-Hbl-Bt-Asp-Mag-Ilm
 Assemblage used in TWEEQU calculations: Opx-Cpx-Grt-Pl-Qtz
 Original P-T estimate: P=7.8 kbar / T=773-836 °C (Coolen 1980)
 Average TWEEQU results: P=10.2 kbar \pm .05 / T=795 \pm 3 °C (3 independent reactions)
 Outliers: Equilibrium 10

Equilibria plotted in Figures 4-5	Δ_S	Δ_V
1: Qtz + Di + Alm = An + En + 3 Fs	-28.0	-2.59
2: 3 Qtz + Grs + 2 Alm = 3 An + 6 Fs	-109.0	-7.32
3: 3 Qtz + 3 Di + 4 Alm = 3 An + 12 Fs + Prp	-100.5	-8.07
4: Alm + 3 Di = Grs + 3 Fs + 3 En	25.0	-0.45
5: Qtz + Grs + 2 En = An + 2 Di	-53.0	-2.14
6: Alm + 3 En = Prp + 3 Fs	-16.5	-0.29
7: Qtz + Prp + Di = An + 4 En	-11.5	-2.30
8: 2 Alm + 3 Di = Prp + Grs + 6 Fs	8.5	-0.74
9: 3 Qtz + Prp + 2 Grs = 3 An + 3 Di	-117.5	-6.58
10: Prp + 3 Di = 6 En + Grs	41.5	-0.16
11: 3 Qtz + 2 Prp + Grs = 3 An + 6 En	-76.0	-6.74

\pm for TWEEQU results is 1 σ imprecision; Δ_S in J-K⁻¹; Δ_V in J-bar⁻¹; abbreviations from Kretz (1983)

summarized by showing the boxes that enclose the range of all intersections, excluding equilibrium E3. Not only is a different average P-T produced with each different calibration, but the conclusion of equilibrium would not be supported by the calculations utilizing the Moecher *et al.* (1988) calibration. This calibration incorporates the main features of those of Ganguly & Saxena (1984) and Anovitz & Essene (1987). As discussed in detail by Berman (1990) and Berman & Koziol (1991), these calibrations are incompatible with recent reversed phase-equilibrium data in the Prp-Alm, Grs-Alm, and Grs-Prp-Alm systems (Koziol & Bohlen 1990, Lee & Ganguly 1988, Koziol 1990, Koziol & Newton 1989). Similarly, the calibration of Hodges & Spear (1982) is inconsistent with experimental data on the Grs-Alm join (Koziol 1990). It is instructive to note that TWEEQU results using the Moecher *et al.* (1988) calibration give a very tight cluster of intersections when the same combination of first- and second-generation phases is used (black box in Fig. 5c) as in the calculations shown in Figure 5b. Clearly, one needs to establish confidence in thermodynamic data before conclusions regarding the state of equilibration of a sample can be regarded with anything but skepticism.

Ferry (1980) has described chlorite- to sillimanite-zone pelites of the Waterville Formation that have undergone one metamorphic event postdating most of the deformation. The sub-assemblage Ms-Bt-Grt-Pl-And/Sil-Qtz was assumed by Ferry (1980) to be in equilibrium when petrographically observed within a 2.5 cm diameter area without evidence of textural disequilibrium, such as inclusions of one mineral in another or mantling relationships (Ferry 1976). Results using the January, 1991 TWEEQU thermodynamic data (Berman 1988, Berman 1990, McMullin *et al.* 1991) show excellent intrasample consistency between the six possible equilibria (three independent), with

most samples showing scatter in intersections of less than $\pm 15^\circ\text{C}$ and 0.30 kbar (Fig. 6, Table 3). Intersample consistency also suggests that equilibrium was maintained in these samples. The overall accuracy of the thermobarometric results is supported by the general agreement between the calculated andalusite - sillimanite boundary (Berman 1988) and the distribution of the andalusite-zone (light triangles) and sillimanite-zone (bold triangles) samples (Fig. 6).

Two samples display less precise results (20-40°C and 0.44-0.76 kbar scatter). The results for sillimanite-bearing sample #1104-1 fall largely in the stability field of kyanite. This sample has the most sodic plagioclase (An_{9,3}), strongly suggesting that activity coefficients given by the Fuhrman & Lindsley (1988) calibration are too low for Ab-rich plagioclase. In contrast, plagioclase-independent pressures for this same sample based on equilibrium 5 of Table 3 (Qtz-Grt-Aluminosilicate-Ms-Bt, *i.e.*, SGAM: McMullin *et al.* 1991) fall in the sillimanite field. The same explanation cannot apply to sample 674-A, which contains a plagioclase of composition An₄₂. Although slightly more magnesian (within $X_{\text{Fe}} = 0.03$), the overall similarity of its mineral chemistry to that of the other samples suggests that calibration errors should not be significantly different for this sample and that the discrepant results are likely due to disequilibrium.

Pelitic rocks from the Monashee Mountains, British Columbia, studied in detail by Journeay (1986), have assemblages characteristic of the St-Sil zones of the Barrovian facies series. Ms-Bt-Grt-Pl-Ky-Qtz assemblages occur stratigraphically about 1 km below the Monashee Décollement, a major crustal scale shear-zone. Deformation continued after the growth of kyanite and garnet porphyroblasts, but petrographic observations concerning the state of equilibration are ambiguous. Figure 7 summarizes TWEEQU results using unpublished analytical data for some of these samples and the same equilibria shown in Figure 6 and Table 3. Although all samples were collected within a 1-km area, they record temperatures from 650 to 950°C. The fact that the bulk composition of these rocks is very similar to those used to calibrate thermodynamic data for biotite (McMullin *et al.* 1991) and to the Waterville Formation pelites with plagioclase greater than An₁₅ suggests that the problem is not one related to calibration of thermodynamic data. To the contrary, disequilibrium is suggested by the wide discrepancy (4-10 kbar) in the positions of the two main barometers, equilibria 1 (GASP = Grt-Ky-Qtz-Pl) and 5 (SGAM) of Table 3. The position of the GASP equilibrium, generally close to the kyanite - sillimanite boundary (Fig. 7), is broadly consistent

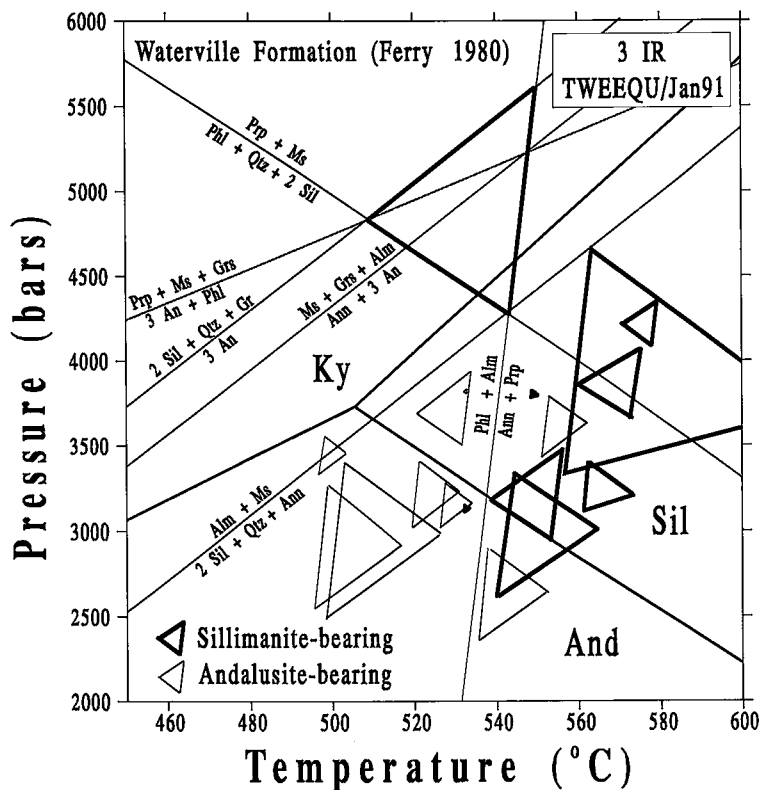


FIG. 6. Summary of TWEEQU results in the KCMFASH system (K: K_2O , H: H_2O) for 18 samples of Waterville Formation pelite, computed with the January, 1991 TWEEQU thermodynamic data. Light and dark triangles, defined by the intersections of equilibria 1–3 of Table 3, show the range of intersections among all six equilibria (3 independent) for andalusite- and sillimanite-zone samples, respectively.

TABLE 3. TWEEQU RESULTS FOR WATERVILLE FORMATION PELITES (FERRY 1980)

Equilibria plotted in Figures 6, 7, 10	Δ_S	Δ_V
1: 2 Sil + Qtz + Grs = 3 An	-111.1	-5.45
2: Prp + Ms = Phl + Qtz + 2 Sil	-8.2	-1.81
3: Phl + Alm = Ann + Prp	-13.7	-0.31
4: Ms + Grs + Alm = Ann + 3 An	-132.9	-7.57
5: Alm + Ms = 2 Sil + Qtz + Ann	-21.8	-2.12
6: Prp + Ms + Grs = 3 An + Phl	-119.2	-7.26

Δ_S in J-K⁻¹; Δ_V in J-bar⁻¹; abbreviations from Kretz (1983)

with the occurrence of these kyanite-bearing samples just downgrade of the sillimanite zone. The likely explanation for the discrepant SGAM pressures and the extreme spread in Grt–Bt temperatures is that biotite is out of equilibrium

with the other mineral phases in these rocks. This may be the result of retrogression of biotite caused by interaction with late fluids introduced through access along the Monashee Décollement. Alternatively, the disequilibrium assemblage may have been produced by mechanical repositioning during post-metamorphic shearing.

Pigage (1976) gave detailed compositional data for St–Sil zone pelites of the Settler Schist, British Columbia, that contain the assemblage Grt–Ms–Bt–Pl–Qtz–Rt–Ilm ± St ± Ky/Sil. Pigage (1976) reported that syn- to post-tectonic metamorphic recrystallization produced sharp crystal margins with little alteration, but that “textural evidence for equilibrium is inconclusive”. Chemical homogeneity on a thin-section scale and uniform distribution-coefficients between samples are suggestive, however, of attainment of equilibrium. TWEEQU calculations based on 21 equilibria (4 independent) support this conclusion (Fig. 8, Table 4). For each

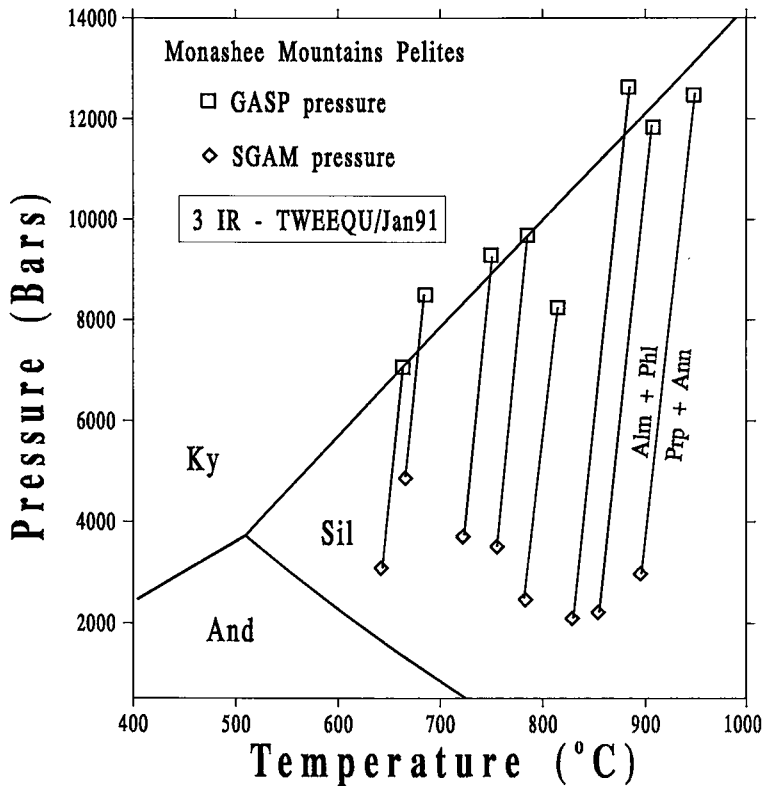


FIG. 7. Summary of TWEEQU results in the KCMFASH system for Monashee Mountain pelites, computed with the January, 1991 TWEEQU thermodynamic data. The wide range in Grt-Bt temperatures and extreme discrepancy between pressures computed with the GASP (squares) and SGAM (triangles) equilibria suggest disequilibrium. Note the difference of scale with Figure 6.

of six samples that contain Ky or Sil, the computed scatter is less than $\pm 25^\circ\text{C}$ and 0.45 kbar. Average values of P-T display excellent intersample agreement (inset in Fig. 8), and indicate an inverted metamorphic gradient, with a temperature increase, and pressure decrease from south to north paralleling the distribution of metamorphic isograds. Support for the overall accuracy comes from the fact that TWEEQU results all plot narrowly in the kyanite field, in agreement with the occurrence of kyanite in all samples except #7, which contains sillimanite.

Tracy (1978) studied migmatitic pelites within the Bronson Hill anticlinorium in west-central Massachusetts, four of which contain the same subassemblage, Grt-Ms-Bt-Pl-Qtz-Rt-Ilm-Sil, as the Settler schist, in addition to pyrrhotite and graphite \pm chalcopyrite. Equilibrium is suggested by the mutual contact of all minerals within a small

area and by uniform chemical partitioning among phases (Tracy 1978). Zoned garnet, modally less than 1%, is the only mineral that shows significant inhomogeneity on a thin-section scale. TWEEQU results based on 21 equilibria (Fig. 9, thin-ruled polygons) using rim compositions of the garnet show a similar degree of scatter as the Settler schist samples (Fig. 8) for only one sample (#595C). The much larger scatter for the other rocks is reflected in the position of the GRAIL (Grt-Rt-Sil-Ilm-Qtz) equilibrium 2-4 kbar higher in pressure than GASP or SGAM. Use of core compositions of the garnet produces a somewhat larger scatter at higher P-T conditions. The INTERSX program finds that six equilibria (#6, 7, 8, 13, 15, 18 of Table 4) are significant outliers. That all six involve rutile and ilmenite suggests that one or both of these minerals in low modal abundance is out of equilibrium with the other minerals. Eliminating these minerals from

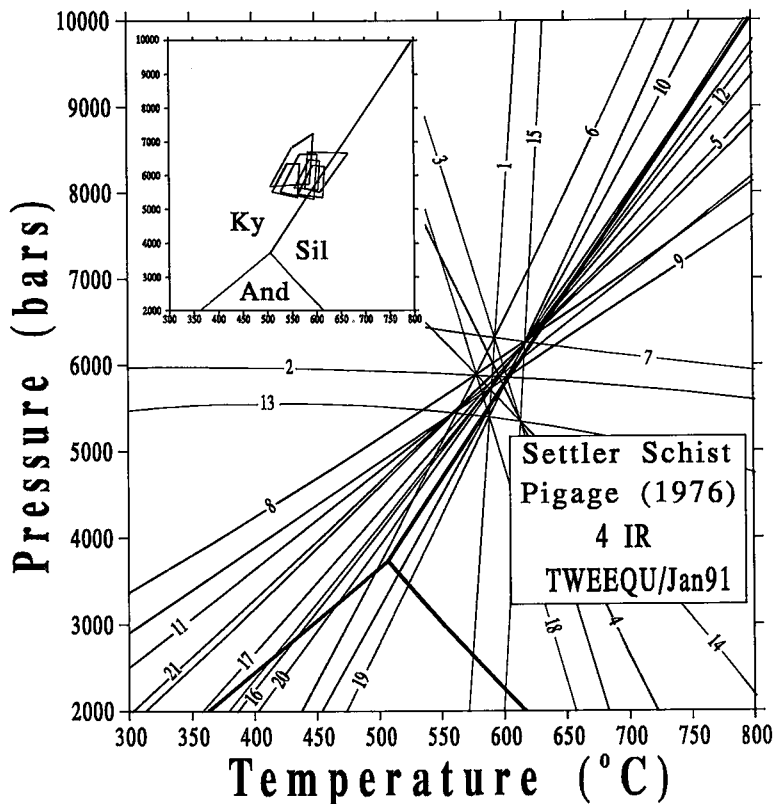


FIG. 8. TWEEQU results in the KCMFASTH system (T: TiO₂) for sample 5 of the Settler Schist, computed with the January, 1991 TWEEQU thermodynamic data. All equilibria (4 independent) are listed in Table 3. Inset shows the range of intersections for all six samples that contain Ky-Sil.

TABLE 4. TWEEQU RESULTS FOR SETTLER SCHIST PELITES (PIGAGE 1976)

Mineralogy: Ms-Bt-Grt-Pl-Qtz-Rt-Ilm (± Ky, Sil, St, Chl)
 Assemblage used in TWEEQU calculations: Ms-Bt-Grt-Pl-Ky/Sil-Qtz-Rt-Ilm
 Previous P-T estimate: P = 6-8 kbar / T = 550-700 °C (Pigage, 1976)
 Average TWEEQU results (6 samples): P = 5.7-7.1 kbar / T = 554-618 °C
 (4 independent reactions)

Equilibria plotted in Figure 8	$\Delta_r S$	$\Delta_r V$
1: Alm + Phl = Prp + Ann	-13.7	-0.31
2: 6 Rt + 2 Prp + Grs + 2 Ann = 3 An + 6 Ilm + 2 Phl + 3 Qtz	-119.4	-8.89
3: 6 Rt + Prp + 2 Ann = 6 Ilm + Ms + Phl + 3 Qtz	0.1	-1.62
4: 3 Rt + Prp + Ann = 3 Ilm + Phl + 2 Qtz + Sil	5.5	-1.77
5: 6 Rt + Grs + 2 Alm = 3 An + 6 Ilm + 3 Qtz	146.7	-9.51
6: 2 Alm + Phl + 6 Rt = 3 Qtz + Prp + Ms + 6 Ilm	-27.5	-2.24
7: Alm + Ann + 6 Rt = 3 Qtz + Ms + 6 Ilm	-13.8	-1.93
8: Alm + 3 Rt = Si + 2 Qtz + 3 Ilm	-19.2	-2.08
9: Prp + Ms + Grs = 3 An + Phl	-119.2	-7.26
10: Grs + 6 Ilm + 2 Ms + 3 Qtz = 6 Rt + 3 An + 2 Ann	-119.1	-5.64
11: 3 Sil + 3 Rt + Prp + 2 Grs + Ann = 6 An + 3 Ilm + Phl	-222.2	-12.47
12: 2 Sil + Qtz + Grs = 3 An	-108.3	-5.35
13: Prp + 2 Ms + 3 Ilm = Ann + Phl + 3 Rt + 3 Sil	-16.3	-2.06
14: Prp + Ms = Phl + Qtz + 2 Sil	-10.9	-1.91
15: 3 Ilm + Ms + Qtz = Sil + 3 Rt + Ann	-5.4	-0.14
16: Ms + Grs + Alm = Ann + 3 An	-132.9	-7.57
17: 3 Sil + 3 Rt + 2 Grs + Alm = 6 An + 3 Ilm	-235.9	-12.78
18: 3 Ilm + 2 Ms + 2 Prp = 3 Sil + 3 Rt + 2 Phl + Alm	-2.6	-1.75
19: 2 Ms + 3 Ilm + Alm = 2 Ann + 3 Rt + 3 Sil	-30.0	-2.37
20: Ms + Alm = Ann + Qtz + 2 Sil	-24.6	-2.22
21: 3 Sil + 3 Rt + Grs + Ann = 3 An + 3 Ilm + Ms	-102.9	-5.21

$\Delta_r S$ in J-K⁻¹; $\Delta_r V$ in J-bar⁻¹; abbreviations from Kretz (1983)

the calculations leads to much less scatter in the results based on three independent equilibria (Table 3) for each sample (Fig. 9, bold triangles). Much improved consistency among all equilibria is obtained with a reduced activity of rutile (inset in Fig. 9), which might be attributed to dilution by a small amount of nonstoichiometric components (no analytical data are given for rutile by Tracy 1978). Similar improvement is obtained with increased activity of ilmenite, possibly reflecting continued retrograde exchange of ilmenite with sulfide minerals.

Calculation of P-T paths

Because of their tectonic significance (England & Richardson 1977, England & Thompson 1984), a great deal of effort has been focussed on determining P-T paths from zoned minerals (Spear

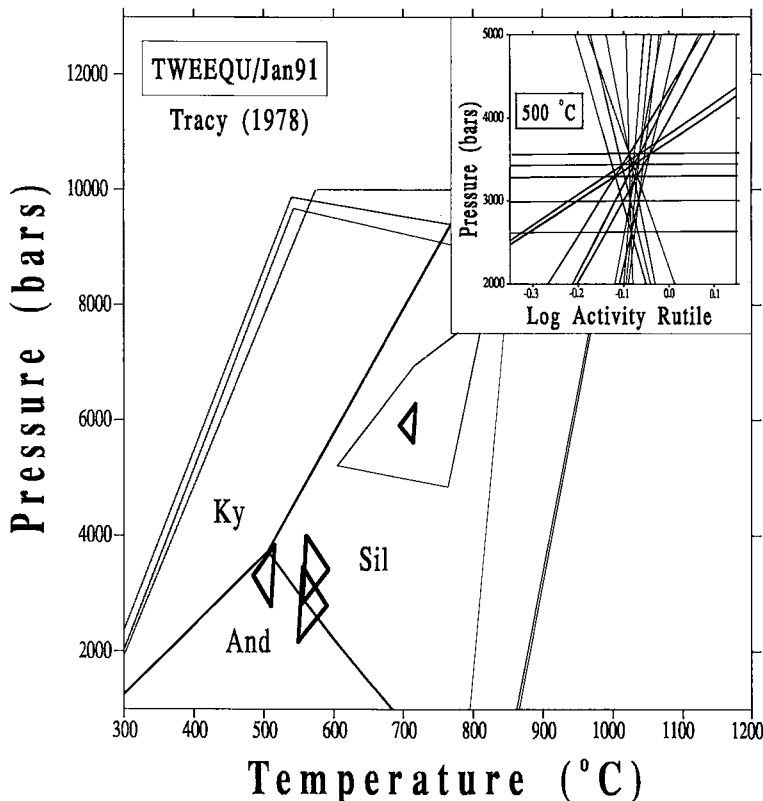


FIG. 9. Summary of TWEEQU results in the KCMFASTH system for four pelitic samples with the assemblage Grt–Ms–Bt–Pl–Qtz–Rt–Ilm–Sil (Tracy 1978), computed with the January, 1991 TWEEQU thermodynamic data. Thin-ruled polygons show the range of intersections among 21 equilibria (4 independent) listed in Table 4. Bold triangles show the range of intersections among six equilibria (3 independent) listed in Table 3 that do not involve ilmenite and rutile. Inset shows P–Activity(rutile) diagram computed at 500°C for sample 534r (see text for discussion).

& Selverstone 1983, Thompson & England 1984, Selverstone & Spear 1985, St. Onge 1987, Spear 1989). In high-grade rocks, however, prograde compositional zonation has been erased by diffusional equilibration. This has led some investigators (*e.g.*, Bohlen 1987, Anovitz & Essene 1990, Indares & Martignole 1990) to infer the retrograde portion of P–T paths from thermobarometry applied to garnet cores and thin rims that show retrograde compositional zonation. A major problem with this type of analysis is the reliance on the assumption that all minerals involved in the thermobarometric equilibria maintained equilibrium through the retrograde event. This assumption is in fact unlikely, given the very different kinetic mechanisms and hence lower expected closure temperatures for Fe–Mg exchange geother-

mometers than net-transfer barometric reactions (*e.g.*, Ghent *et al.* 1988, Frost & Chacko 1989). Frost & Chacko (1989) showed, for example, that re-equilibration of only the Fe–Mg exchange equilibria produces apparent near-isobaric cooling paths even if the P-sensitive equilibria undergo no re-equilibration.

Given the expectation that some temperature- and pressure-sensitive equilibria may close at different temperatures, it becomes necessary for petrologists to decipher P–T paths from the study of inclusions that may remain (*e.g.*, Selverstone & Chamberlain 1990) or to establish that both sets of equilibria reached equilibrium at the same pressure and temperature in order for the results to be trusted (no matter how reasonable the calculated retrograde paths appear). The technique described

in this paper lends itself to this problem because it offers a general way to test this assumption of equilibrium. In addition, given confidence in the thermodynamic data used, one can look for textural signs of disequilibrium to try to reconstruct P-T paths from samples or portions of samples that have locally re-equilibrated at different times along a prograde or retrograde path.

St-Onge (1987) derived a P-T path from analysis of mineral inclusions in a zoned garnet, but the full advantage of the TWEEQU technique cannot be gained in this example because only two independent equilibria can be written for the Grt-Bt-Ky-Pl-Qtz assemblage present in these rocks. Hodges & Royden (1984) have calculated a P-T path for a portion of the northern Scandinavian Caledonides from pelitic samples that apparently underwent different histories of retrogression. Although the scatter for three rocks using the

equilibria listed in Table 3 is significantly greater than obtained for other "well-equilibrated" suites of samples (e.g., Figs. 6 and 8), TWEEQU results (Fig. 10) appear to indicate that many of their samples did re-equilibrate fully at temperatures between 475 and 600°C. Although it may be tempting to conclude that the distribution of samples parallel to the slope of the GASP equilibrium is an artifact of Fe-Mg exchange to lower temperature without GASP re-equilibration, consideration of the effects of Fe-Mg exchange on the SGAM equilibrium in the manner described by Frost & Chacko (1989) shows that this conclusion is unjustified. The extent of Fe-Mg exchange necessary to reduce the temperature of the 725°C sample of Hodges & Royden (1984) by the observed 250°C (increasing X_{Fe} in Grt or decreasing X_{Fe} in Bt by about 0.14) produces a shift in the SGAM barometer between 4 and 8 kbar. The magnitude

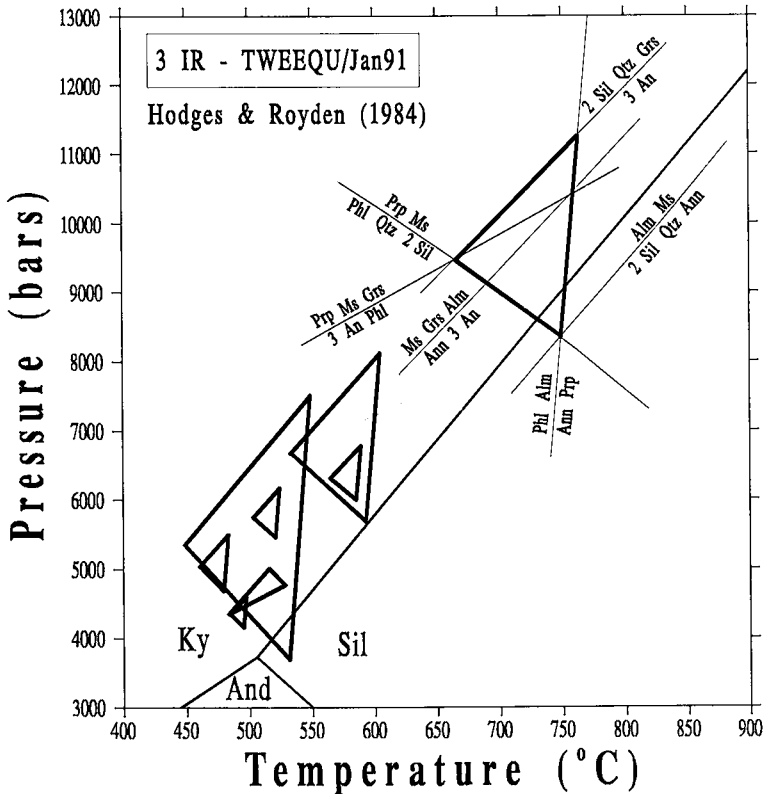


FIG. 10. TWEEQU results in the KCMFASH system for pelites from the northern Scandinavian Caledonides, computed with the January, 1991 TWEEQU thermodynamic data. Triangles, defined by the intersections of equilibria 1-3 of Table 3, show the range of intersections of all equilibria (3 independent). See text for discussion.

of this effect should clearly be discernible within reasonable expectations of uncertainties in calibration. The TWEEQU results, therefore, support the notion that these samples have frozen in a record of a portion of the retrograde P-T path, although the exact P-T trajectory derived here is somewhat less steep than that derived by Hodges & Royden (1984).

CONCLUSIONS

The thermobarometric technique proposed in this paper offers a test of the critical assumption that all minerals used in a calculation last equilibrated at the same pressure and temperature. The correlation of convergent TWEEQU results with independent indications of equilibrium in some of the examples discussed above suggests that this technique makes it possible to reasonably assess the state of equilibration of samples for systems in which the thermodynamic properties appear to be well described. The number of situations in which independent evidence for equilibrium is ambiguous underscores the importance of being able to apply this thermobarometric test in a general way. In addition, the technique offers the means to reconstruct portions of P-T paths from appropriate samples.

Although this analysis is hindered by poorly described uncertainties in thermodynamic data, as these uncertainties become better known, they can be incorporated into the analysis in the same way as Lieberman & Petrakakis (1991) describe for compositional errors. At present, this technique will prove most useful in systems that involve minerals with the smallest uncertainties in calibration, but its general applicability should expand as thermodynamic properties continue to be refined in the future. This method facilitates the refinement process by (1) highlighting which minerals are most incompatible in each calculation and may be in need of refinement, (2) illustrating the sensitivity of results to different solution-models and offering the chance to correlate these differences with petrographic observations, and (3) providing a means to select "well-equilibrated" samples that can be used to refine thermodynamic properties in the absence of appropriate experimental data. It is hoped that feedback from users of this software will increase the pace of improvements in the thermodynamic data, which in turn will provide an increasing ability to gain insights into petrological problems and to reconstruct geological histories.

The TWEEQU software may be obtained from the author by sending a self-addressed envelope, 5-1/4" or 3-1/2" floppy disc, and \$20 Canadian in

cheque form, payable to "Receiver General of Canada", in order to cover handling costs.

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APPENDIX:
DESCRIPTION OF THE TWEEQU SOFTWARE

The general expression for equilibrium (3) is a nonlinear equation in P and T that defines a locus of points in P-T space that must be solved by iterative techniques. The thermobarometric method advocated here presents all solutions, both graphically, in the form of P-T- $X(\text{CO}_2)$ -activity diagrams, and analytically, based on the graphical results. All calculations are performed by a computer program (TWQ) modified as described below from the GEØ-CALC software package for computation of phase diagrams (Berman *et al.* 1987, Brown *et al.* 1988). Details of the various algorithms used by this software can be found elsewhere (Brown *et al.* 1988), and only a brief summary is given here.

Operation of this software is facilitated by an extremely user-friendly interface. The only information required of the user is the choice of type of diagram (any combination of P, T, $X(\text{CO}_2)$, activity), the desired range of these variables in the diagram, the chemical system and phase components to include in the calculations. For most applications, all components of phases thought to have equilibrated at the same P and T are selected. The TWQ program generates all possible reaction-stoichiometries using linear algebraic methods, and, after reading an accompanying file containing all thermodynamic data and mineral compositions, follows standard root-finding procedures within the selected P-T space to locate points on each equilibrium curve in turn. Results are written to an ASCII file that is read by separate programs that allow the graphical results to be viewed on a video monitor or hard-copy device (dot matrix or laser printer), or to be analyzed by the INTERSX program.

Whereas the GEØ-CALC software implements a strategy for calculating metastability and removing metastable equilibria and extensions, the present method is simplified by not having to test for stability since every equilibrium curve is equally valid for thermobarometric purposes regardless of its stability level. The main modification of the GEØ-CALC software, however,

involves the incorporation of generalized Margules-type solution equations (Berman & Brown 1984) to describe activity coefficients of multisite minerals. Their incorporation allows accurate displacement of all equilibria using P-T-dependent models that describe the nonideal mixing along with mineral compositions read from a user-specified file. These mixing models are defined in an external file that can be modified to add other solid-solution phases or alternative mixing models for a given solution phase. At run time, the educated user can usefully select between alternative solution-models in order to explore the ramifications on the thermobarometric results. Details of these procedures are given in a documentation file that accompanies this software.

The January, 1991 TWEEQU data-base includes standard state thermodynamic properties of Berman (1988) with modifications and additions of Berman (1990), Mäder & Berman (1991), and McMullin *et al.* (1991). Nonideal mixing is accounted for using the calibrations of Berman (1990) for garnet, McMullin *et al.* (1991) for biotite, Furrman & Lindsley (1988) for plagioclase, and Chatterjee & Froese (1975) for muscovite. Ideal two-site mixing is assumed for ortho- and clinopyroxene (Newton 1983). In order to facilitate comparisons with alternative data-bases, the program can accommodate other data-bases with a variety of equations of state (*e.g.*, Holland & Powell 1990). This feature is particularly useful to explore the sensitivity of thermobarometric results to uncertainties in standard state thermodynamic data. One caveat, however, is that some standard state and mixing properties are tied together from their method of calibration, and this internal consistency must be preserved. For example, Berman (1990) derived annite properties from the garnet - biotite exchange data of Ferry & Spear (1978), assuming a newly derived set of garnet mixing parameters and ideal Fe-Mg mixing in biotite. Use of a different set of mixing properties for garnet requires use of different properties for annite in order to maintain consistency with the experimental data.