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Error propagation for barometers: 2. Application to rocks

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ABSTRACT

A new evaluation is made of the uncertainty in pressure when a barometer is applied to an assemblage in a rock. Sources of error considered include: accuracy of the experimentally located, barometric end-member reaction, volume measurement errors, analytical imprecision, uncertainty of electron microprobe standard compositions and α-factors, thermometer calibration errors, variation in garnet and plagioclase activity models, and compositional heterogeneity of natural minerals. Whereas calibration and analytical errors can be treated statistically, variability in activity models and natural compositional heterogeneity probably cannot be.

Our estimates (1σ or quarterwidth) of the propagated uncertainties in pressure corresponding to these sources of error based on analysis of five barometers are barometer calibration uncertainties of ±300 to ±400 bars, volume measurement errors of ±2.5 to ±10 bars, analytical imprecision of ±55 to ±185 bars, thermometer calibration inaccuracy of ±250 to ±1000 bars, variability in activity models of ±60 to ±1500 bars, and natural compositional heterogeneity (sample dependent, but reportedly) of ±150 to ±500 bars. Assuming 1% uncertainties in analytical standard compositions and α-factors results in propagated errors of ±40 bars and ±150 bars (1σ) for the GASP barometer when the same standards and when different standards are used respectively for analyzing unknown phases. The accuracy of a barometer as applied to rocks may typically range from ±600 to ±3250 bars (1σ or quarterwidth), with the most significant sources of error being uncertainty in thermometer calibration and poorly constrained activity models. Continued experimental and empirical work aimed at minimizing thermometer uncertainties and better constraining activity-composition relations should substantially reduce the propagated uncertainty.

INTRODUCTION

As more geologists become interested in studying tectonic processes using petrologic methods, the evaluation of the uncertainties of pressure and temperature estimates of rocks becomes increasingly important. These uncertainties stem from two basic sources: calibration and application. While calibration errors for barometers have been addressed (Hodges and McKenna, 1987; McKenna and Hodges, 1988; Kohn and Spear, 1991), a comprehensive analysis of application errors has not yet been made.

The purpose of this paper is to discuss and propagate errors that arise when a barometer is applied to rocks. This study is a companion to the work of Kohn and Spear (1991), which describes the precision and accuracy of experimentally located end-member reactions. Sources of error considered in detail in this paper include measurement of compositions, natural compositional heterogeneity, estimation of temperature, and poorly constrained activity models. In this paper, the term "precision" will be used to describe reproducibility or randomly distributed errors, as contrasted with "systematic uncertainties"; the term "accuracy" will be used to describe the combination of precision and systematic uncertainties.

METHOD

The method employed in the analysis presented below involves application of the error propagation expression:

$$\sigma_P^2 = \sum_i \sum_j \left(\frac{\partial P}{\partial X_i}\right)\left(\frac{\partial P}{\partial X_j}\right)\sigma_i\sigma_j\rho_{ij} \quad \text{(+ higher order terms)} \tag{1}$$

where P is pressure, the X_i and X_j are the independent variables of which pressure is a function, σ_i and σ_j are the standard deviations of the independent variables, and ρ_{ij} is the correlation coefficient between the ith and jth variables. For barometers, the equation that describes the relationship among P, T, and composition may be written as

$$P = b + mT - \mathrm{R}T \ln K_{\mathrm{eq}}/\Delta V \tag{2}$$

where T and R are temperature and the gas constant, m, b, and ΔV are the slope, intercept, and change of volume of the end-member barometric reaction, and K_{eq} is the product of the activities of the mineral phase components involved in the equilibrium, raised to their respective stoichiometric coefficients. For convenience, we have ig-

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nored changes of heat capacities, compressibilities, and thermal expansivities for the reaction.

Application of Equation 1 to Equation 2 results in the expression:

$$\sigma_P^2 = \sigma_b^2 + T^2\sigma_m^2 + 2\rho_{mb}T\sigma_m\sigma_b + \left(\frac{\sigma_{\Delta V}\mathrm{R}T\ln K_{\mathrm{eq}}}{(\Delta V)^2}\right)^2 + \left(m - \frac{\mathrm{R}\ln K_{\mathrm{eq}}}{\Delta V^2}\right)^2(\sigma_{T,\,\mathrm{Calib}}^2 + \sigma_{T,\,\mathrm{Compo}}^2) + \left(\frac{\mathrm{R}T}{\Delta V}\right)^2 \sum_i \sum_j \alpha_i\alpha_j\nu_i\nu_j\left(\frac{\sigma_{x_i}}{x_i}\right)\left(\frac{\sigma_{x_j}}{x_j}\right)\rho_{x_i x_j} \quad (3)$$

where α_i, ν_i, x_i, and σ_{x_i} are the site multiplicity, stoichiometric coefficient, mole fraction, and uncertainty in the mole fraction of the ith phase component in the reaction of interest. It should be noted that we have ignored any correlation arising from compositional dependence between T and K_{eq} associated with their dependence on composition for reasons that are described below. The first three terms on the right hand side of Equation 3 all reflect uncertainties in barometer calibration and may be grouped into a single term $[(\sigma_{P,\mathrm{Calib}})^2]$. The fourth term is the error introduced because of uncertainties in volume. The fifth term on the right side of Equation 3 represents the contribution of the uncertainty in a temperature that has been estimated using geothermometry; this term consists of two parts that correspond to the effects on the overall error in temperature arising from uncertainties in the measurement of composition (i.e., $\sigma_{T,\mathrm{Compo}}$ resulting from σ_{x_i}), and simple thermometer calibration errors ($\sigma_{T,\mathrm{Calib}}$). The sixth term represents the propagation of uncertainties in composition, and each σ_{x_i} represents a combination of analytical imprecisions and systematic analytical errors. The purpose of the following sections is to describe the propagation of the errors in Equation 3 in the order: (1) barometer calibration errors ($\sigma_{P,\mathrm{Calib}}$), (2) volume uncertainties ($\sigma_{\Delta V}$), (3) analytical imprecisions (σ_{x_i} and hence $\sigma_{T,\mathrm{Compo}}$), (4) systematic analytical errors (σ_{x_i} and $\sigma_{T,\mathrm{Compo}}$), and (5) thermometer calibration errors ($\sigma_{T,\mathrm{Calib}}$). Additional considerations are made for activity coefficient variability and compositional inhomogeneities of minerals in rocks.

Barometer calibration accuracy

Kohn and Spear (1991) have described a method whereby the uncertainty in the pressure of experimentally determined, barometric end-member reactions ($\sigma_{P,\mathrm{Calib}}$) can be calculated, and the interested reader is referred to that paper for a more complete discussion. Their results suggest that the accuracy of end-member reaction positions for tightly reversed experimental data has a magnitude of about ±300 to ±400 bars (1σ). It should be noted that this value is much smaller than that estimated by Hodges and McKenna (1987), which we believe to be the result of differences in dealing with systematic experimental uncertainties (see also McKenna and Hodges, 1988).

Volume uncertainties

Because volumes may be measured extremely precisely (0.05–0.1%), their uncertainties do not significantly affect σ_P. For example, for typical values of $\mathrm{R}T\ln K_{\mathrm{eq}}/\Delta V$ ranging from 5000 to 10000 bars, the contribution of $\sigma_{\Delta V}$ to σ_P is only ±2.5 to ±10 bars.

Analytical precisions

Determination of the contribution of the σ_{x_i} to σ_P requires a detailed knowledge of the σ_{x_i} and ρ_{ij}. While errors on elemental abundances are obtainable from electron microprobe counting statistics, these errors will generally not represent the uncertainty in mineral components (i.e., σ_{x_i}) because of (1) normalization of measured wt% oxides to a particular mineral oxide formula, and (2) normalization to mole fractions. As described in Appendix 1, the effect of different operators using the microprobe on different days with different operating procedures and standards will also increase the uncertainty in mole fractions. Similarly, although the measured wt% oxides are largely uncorrelated, normalization can introduce substantial correlation among the mineral components (i.e., $\rho_{ij} \neq 0$).

We have estimated uncertainties in mineral components (σ_{x_i}) and correlation coefficients (ρ_{ij}) both empirically and by using a Monte Carlo procedure. Our empirical estimates for one composition were derived by analyzing a single spot on a garnet 100 times in succession for the elements Si, Al, Mg, Fe, Mn, and Ca. No systematic change in the concentration of each element during the course of the analyses was detected. Table 1 presents the average composition of the garnet (column 1), the measured standard deviations of the mole fractions (column 2), and the counting statistics errors for the weight percents MgO, FeO, MnO, and CaO (column 4). Each counting statistics error depends on the counting time, beam current, and spectrometer on which the counts were collected. Counting time and flag current were 40 s and 15 nA, respectively, for each analysis, and the spectrometers are tabulated with their respective elements.

Also shown in Table 1 is the measured correlation coefficient matrix for the 100 analyses. The correlation coefficient between two quantities X and Y may be estimated from the relationship (Draper and Smith, 1981, p. 44):

$$\rho_{ij} = \frac{\sum(X_i - \mu_X)(Y_i - \mu_Y)}{\left[\sum(X_i - \mu_X)^2\right]^{1/2}\left[\sum(Y_i - \mu_Y)^2\right]^{1/2}}$$

where X_i and Y_i represent measured values, and μ_X and μ_Y are the averages of the n measurements of X and Y.

A Monte Carlo technique was also used to derive a theoretical estimate of the standard deviations in mole fractions and correlation coefficients between mole fractions by using a procedure analogous to that of Steltenpohl and Bartley (1987). The mean garnet composition

TABLE 1. Average composition and statistics of single spot on garnet

	Average composition (mole fraction) (1)	Measured standard deviation (mole fraction) (2)	Monte Carlo standard deviation (mole fraction) (3)	Counting statistics errors (wt%) (4)
Pyrope (TAP)	0.0670	7.91×10^{-4} (1.18%)	8.11×10^{-4} (1.21%)	(1.31%) (MgO)
Almandine (LIF)	0.4904	2.35×10^{-3} (0.48%)	2.45×10^{-3} (0.50%)	(0.69%) (FeO)
Spessartine (LIF)	0.2284	2.08×10^{-3} (0.91%)	2.15×10^{-3} (0.94%)	(1.10%) (MnO)
Grossular (PET)	0.2142	1.74×10^{-3} (0.81%)	1.71×10^{-3} (0.80%)	(1.14%) (CaO)

Correlation matrices (ρ)

	(Measured)				(Monte Carlo)			
	Prp	Alm	Sps	Grs	Prp	Alm	Sps	Grs
Pyrope	1.000	−0.221	−0.157	0.020	1.000	−0.238	−0.109	−0.002
Almandine	−0.221	1.000	−0.624	−0.514	−0.238	1.000	−0.670	−0.480
Spessartine	−0.157	−0.624	1.000	−0.265	−0.109	−0.670	1.000	−0.244
Grossular	0.020	−0.514	−0.265	1.000	−0.002	−0.480	−0.244	1.000

Note: Number of analyses used for average composition and measured standard deviation and correlation matrix = 100. Number of iterations used for Monte Carlo estimates = 2000. Prp = pyrope, Alm = almandine, Sps = spessartine, Grs = grossular.

in wt% oxides was first calculated. This analysis was randomly perturbed within the limits of errors allowed by the counting statistics for each element, the new analysis was converted to cations, and mole fractions of pyrope, almandine, spessartine, and grossular were calculated. The perturbations were repeated 2000 times using a random number generator with normal distribution, and four single column arrays of 2000 randomly perturbed mole fractions of garnet were created. Correlation coefficients and standard deviations for garnet mole fractions were calculated as above and the results are in Table 1.

Three aspects should be noted concerning the data in Table 1. First, the relative errors resulting from counting statistics for the elements MgO, FeO, MnO, and CaO (column 4) always exceed the measured relative errors in the corresponding garnet mole fractions (column 2). This is simply a result of the normalization employed when determining garnet mole fractions, and it should be noted that this observation does not necessarily apply for all minerals, particularly those in which a single element may be distributed over several sites (e.g., Giaramita and Day, 1990).

Second, the mole fraction of any single garnet component is moderately negatively correlated to the other garnet components. The only exception is the empirical correlation coefficient between grossular and pyrope, which is not significantly different from 0. The negative correlation among mole fractions is expected, because the sum of the mole fractions was normalized to 1. It is also not surprising that the components associated with those elements in greatest concentration (almandine and spessartine) are the most strongly correlated.

Finally, the excellent correspondence between theoretical Monte Carlo and empirical values for the standard deviations and correlation coefficients suggests that the theoretical technique is a valid method of calculating analytical precisions and correlations for mineral components. Accordingly, we have used the Monte Carlo method for calculating analytical precisions and correlation coefficients in the remainder of this paper.

The negative correlation between components of the same mineral has interesting implications for error propagation of barometers and thermometers. Barometers commonly have components of the same mineral on the same side of the equilibrium; for example, in the reaction annite + 3 anorthite = muscovite + almandine + 2 grossular, the two garnet components are both products. Therefore, the stoichiometric coefficients (ν's) of components in the same mineral will usually have the same sign, and cross correlation between those components will tend to decrease the propagated error in pressure relative to the first two terms in Equation 3, as noted by Hodges and McKenna (1987). Although not described explicitly in this paper, exchange thermometers have components of the same mineral on opposite sides of the equilibrium (for example, almandine + phlogopite = pyrope + annite). In this case, both ρ_{ij} and either ν_i or ν_j will be negative, tending to increase propagated errors, in contrast to the discussion of Hodges and McKenna (1987).

An example. For estimating the contribution of analytical precision to uncertainties in pressure estimates, we selected four different barometers, representing a range of equilibria that have been applied to natural rocks. The barometers chosen were: garnet-rutile-sillimanite-ilmenite-quartz (GRAIL; Bohlen et al., 1983), garnet-plagioclase-clinopyroxene-quartz (GPCQ: Mg end-member; Powell and Holland, 1988), garnet-kyanite-quartz-plagioclase (GASP; Koziol and Newton, 1988), and garnet-biotite-muscovite-quartz-sillimanite (GBMQS: Fe end-member; Hodges and Crowley, 1985; Holdaway et al., 1988). For this exercise, the garnet composition was chosen to be $Prp_{15}Alm_{60}Sps_{05}Grs_{20}$, reflecting a typical garnet composition in metabasites. Plagioclase was assumed to be $An_{35}Ab_{65}$, biotite 40% annite and 60% phlogopite, clinopyroxene 65% diopside and 35% hedenbergite, and ilmenite pure. Volumes were taken from end-member measurements at standard temperature and pressure. Standard deviations and correlation coefficients for mineral mole fractions were calculated with the Monte Carlo technique by assuming that errors attributable to count-

Table 2. Predicted standard deviation and correlation of mineral mole fractions for compositions used in an example of error propagation

Component	Seed analysis (mole fraction)	Standard deviation (mole fraction)	Garnet correlation matrix			
			Prp	Alm	Sps	Grs
Pyrope	0.15	0.0012(0.82%)	1.000	−0.504	−0.055	−0.050
Almandine	0.60	0.0022(0.36%)	−0.504	1.000	−0.400	−0.674
Spessartine	0.05	0.0011(2.2%)	−0.055	−0.400	1.000	−0.104
Grossular	0.20	0.0017(0.85%)	−0.050	−0.674	−0.104	1.000
Anorthite	0.35	0.0028(0.80%)				
Annite	0.40	0.0022(0.55%)				
Diopside	0.65	0.0027(0.42%)				

ing statistics were consistent with the composition of the phase and operating conditions of 15 kV and 15 nA (Table 2). Garnet and plagioclase activities were modeled using the expressions of Hodges and Spear (1982) and Newton et al. (1980) respectively.

The propagated errors in pressure using these assumptions at a temperature of 900 K are presented in Table 3 for the different barometers. Each imprecision is broken down into the uncertainties arising from the dependence of σ_P on σ_{x_i} as they in turn affect ln K_{eq} and T in Equation 2. The 1σ precision in temperature for most thermometers ($\sigma_{T,\mathrm{Compo}}$) is approximately ±4 to ±6 °C (Kohn and Spear, unpublished data), and virtually independent of pressure. Because we did not wish to choose a particular geothermometer for calculating temperatures, we have simply multiplied the slope of the barometer by this uncertainty in temperature to estimate the importance of thermometer imprecision resulting from analytical errors. However, it should be noted that depending on which thermometer and barometer are being used, minor cross correlation may occur as a result of the composition dependence of both T and ln K_{eq}.

As can be seen in Table 3, the total effect of analytical imprecision on σ_P ranges from about ±55 to ±185 bars, of which ±10 to ±170 bars is associated with imprecise temperatures, while ±40 to ±70 bars is caused by the explicit dependence of pressure on the barometric equilibrium constant. Physically, the total propagated imprecision corresponds to the uncertainty in pressure for a sample with either compositionally homogeneous minerals or single mineral analyses, using one barometer and one thermometer. The GBMQS barometer has a large range in the pressure uncertainty associated with $\sigma_{T,\mathrm{Compo}}$ because the two empirical calibrations of it (Hodges and Crowley, 1985; Holdaway et al., 1988) indicate rather different slopes for the reaction.

Table 3. Propagated errors in calculated P at 900 K for four barometers assuming the analytical precision in Table 2

Barometer:	ΔV (J/bar)	Contribution from $\sigma_{T,\mathrm{Compo}}$ in Eq. 3 (bars)	Contribution from σ_{x_i} in Eq. 3 (bars)	Total precision (bars)
GRAIL	1.86	30–40	45	55–60
GPCQ	6.87	10–20	65	65–70
GASP	6.62	80–120	40	90–125
GBMQS	2.08	80–170	70	105–185

The above discussion emphasizes that, for many barometers, the analytical uncertainty in pressure is strongly influenced by the precision to which temperature can be determined (see also Hodges and McKenna, 1987). In particular, ignoring correlation coefficients among mole fractions can potentially lead to an underestimate of the temperature uncertainty by a factor of $(2)^{1/2}$ (from Eq. 1), and as is evident from Table 3, this can lead to a significant underestimation of the uncertainty in pressure.

Accuracy of analytical standards

There are generally two different philosophies of how electron microprobes should be standardized: (1) many different standards should be used, similar to the minerals being analyzed, so that uncertainties of extrapolation to unknown composition are minimized, and (2) few standards should be used, so that the potential compositional inaccuracy resulting from using many standards is minimized. Essentially, the concerns of error propagation are whether the α-factors for matrix effects or the true compositions of the standards are better known, and how such uncertainties propagate into errors in pressure.

If many different standards are used, then their compositional uncertainties may be easily propagated using a Monte Carlo technique as was done for counting statistics precision above. For example, assuming (1) a garnet standard for garnet, a plagioclase standard for plagioclase, and a biotite standard for biotite, (2) a 1% uncertainty in the element standards for each, (3) no correlation between uncertainties in weight percents, and (4) the compositions in Table 2, an uncertainty of ±155 bars (1σ) is derived for the GASP reaction at 900 K. An error of ±45 bars is associated with uncertainty of grossular and anorthite components and ±150 bars results from $\sigma_{T,\mathrm{Compo}}$ for the garnet-biotite thermometer. These calculations assume that compositional extrapolation from the standards is so small that it does not contribute to the propagated uncertainty.

The effects of using a single standard for each element in all minerals requires assessing the propagation of both the uncertainty in the composition of the standards and the uncertainty in the α-factors. Such calculations depend on what standards are being used, and we have simply assumed similar oxide and silicate standards as are used at Rensselaer Polytechnic Institute. Using the compositions in Table 2 and assuming 1% uncertainties in the standard compositions and the α-factors, we estimate the propagated uncertainty in pressure to be approximately ±40 bars for the GASP reaction at 900 K. The uncertainties in X_{Grs} and X_{An} contribute ±35 bars of uncertainty, while the uncertainty in temperature introduces ±25 bars. Alternatively, the propagated uncertainty can be broken into the contributions of the compositional uncertainty of the standards (±30 bars) and the assumed 1% uncertainty in α-factors (±30 bars).

Comparing the values calculated for the two philosophies, we find that the uncertainty in the ratio $X_{\mathrm{Grs}}/X_{\mathrm{Am}}$ is insensitive to the standardization technique. However, $\sigma_{T,\mathrm{Compo}}$ is much smaller when the same standards are used, and consequently, the uncertainty in pressure is decreased. It should be noted that any uncertainty in standard compositions or α-factors will not be observed in data collected at a single facility with the same standardization, but may become important when comparing data collected at different analytical facilities.

Thermometer calibration accuracy

Kohn and Spear (unpublished data) have found that propagating calibration uncertainties and variability in solution models for three exchange thermometers involving garnet and other minerals results in calibration accuracies ($\sigma_{T,\mathrm{Calib}}$) of about ±50 °C. If it is assumed that this uncertainty is typical, then the contribution of thermometer calibration errors to the error in pressure may be ±250 to ±1000 bars. This calculation assumes that barometers have slopes ranging from about 5 to 20 bars/°C, and the actual value for a specific barometer will depend on its slope at the P-T condition of interest.

Activity models

Errors in activity coefficients cannot be evaluated statistically in the general absence of direct comprehensive experimental data. However, one empirical approach is to examine the effect of several of the activity models used commonly for the determination of pressures. Specifically, we investigated some of the models that have been proposed for the anorthite component in plagioclase, and for the grossular, pyrope, and almandine components in garnet. These components were chosen because they are very commonly used in barometry.

To examine the variability of activity coefficients for garnet, the models of Perkins (1979), Hodges and Spear (1982), Ganguly and Saxena (1984), Anovitz and Essene (1987, their model 1), and Berman (1990) were applied to the compositions $\mathrm{Prp}_{15}\mathrm{Alm}_{65}\mathrm{Sps}_{05}\mathrm{Grs}_{15}$ (garnet G1) and $\mathrm{Prp}_{05}\mathrm{Alm}_{80}\mathrm{Sps}_{10}\mathrm{Grs}_{05}$ (garnet G2) (Table 4). To test the variability of activity coefficients for anorthite, the models of Orville (1972), Saxena and Ribbe (1972; data from Orville, 1972), Newton et al. (1980), and Hodges and Royden (1984) were applied to the compositions An_{30} and An_{50} (Table 4). The models and compositions were chosen as representative of the ranges described in the literature. The midpoint and quarterwidth of the range of activity coefficients at 900 K for each mineral component considered are also presented in Table 4.

It should be understood that the midpoint of the range of activity coefficients is not any more correct than that estimated using any one activity model. Therefore, the different activity models cannot be assumed to represent any statistical measure of the variability of an activity coefficient. For this reason, we have chosen to ignore the possibility of correlation among activity coefficients resulting from their compositional dependence.

The almandine activity coefficient is by far the most agreed upon value among those considered, and exhibits a range quarterwidth of not more than 2%. This good agreement among different models is in part due to consideration of only almandine-rich garnet compositions. Anorthite activity coefficients are also fairly well agreed upon and do not exceed a range quarterwidth of 10% about the midpoint. The relative uncertainty in the pyrope activity coefficient (up to 30% quarterwidth) is considerably larger than that of any other mineral component considered, but grossular activity coefficients are in dispute for grossular-poor garnet compositions (with a range quarterwidth of about 15%).

For a given activity model, it is possible to calculate a pressure correction for the barometric equilibrium according to the equation

$$\Delta P = \sum \alpha_i \nu_i RT \ln \gamma_i / \Delta V. \tag{5}$$

As can be seen in Table 4, the uncertainty in pressure introduced by the variability in activity models can be substantial, and for the models, compositions, and barometers considered, the quarterwidths range from ±60 bars for the GRAIL barometer to ±1475 bars for the GPCQ barometer (garnet and plagioclase variability combined). In the GPCQ and GASP reactions, the largest potential error in pressure is dominated by the uncertainties in grossular and pyrope activity coefficients, and the minimum and maximum errors correspond to the grossular-pyrope–rich (G1) and grossular-pyrope–poor (G2) compositions respectively. This problem with the GPCQ reaction was also noted by Powell and Holland (1988). Poor agreement on the proper value for pyrope activity causes 60% of the extremely large error for the GPCQ reaction, and if both grossular and pyrope activity coefficients were in as little dispute as the activity coefficient of anorthite in An_{50} plagioclase, the total potential error arising from activity coefficients for the GPCQ reaction would be reduced by a factor of 2–3. However, for barometers that involve more of the pyrope component (e.g., the Mg–end-member garnet-plagioclase-orthopyroxene-quartz barometer), propagated uncertainties may be even larger.

Grossular activity models have a small effect on the uncertainty of the GASP reaction for grossular-rich compositions (G1), but have a strong influence at grossular-poor compositions (G2). Therefore, this barometer is potentially very inaccurate at low P, high T conditions, where the mole fraction of grossular in garnet is less than 5%.

TABLE 4. Ranges of activity coefficients of garnet and plagioclase components

	Garnet						
	Perkins (1979)	Hodge and Spear (1982)	Ganguly and Saxena (1984)	Anovitz and Essene (1987)	Berman (1990)	Range midpoint	Range quarterwidth
G1:$Prp_{15}Alm_{65}Sps_{05}Grs_{15}$							
Pyrope	3.110	1.149	2.691	2.501	1.295	2.130	0.491(23%)
Almandine	1.034	0.976	0.951	0.988	0.970	0.993	0.021(2%)
Spessartine	1.034	0.976	1.150	1.106	0.961	1.063	0.044(4%)
Grossular	1.201	1.149	1.095	1.311	1.292	1.203	0.054(4%)
ΔP GASP (bars)	+620	+470	+310	+920	+870	+620	150
ΔP GRAIL (bars)	+400	−290	−610	−150	−370	−100	260
ΔP GPCQ (bars)	+4900	+1360	+3830	+4770	+2520	+3130	885
G2:$Prp_{05}Alm_{80}Sps_{10}Grs_{05}$							
Pyrope	4.006	1.053	3.694	3.559	1.208	2.530	0.739(30%)
Almandine	1.004	0.997	0.984	0.992	0.996	0.994	0.005(1%)
Spessartine	1.004	0.997	1.055	1.034	0.999	1.026	0.015(1%)
Grossular	1.179	1.053	0.602	0.872	1.109	0.891	0.144(16%)
ΔP GASP (bars)	+560	+180	−1720	−460	+350	−580	570
ΔP GRAIL (bars)	+50	−40	−190	−100	−50	−70	60
ΔP GPCQ (bars)	+5610	+510	+950	+3250	+1290	+3060	1275

	Plagioclase					
	Orville (1972)	Saxena and Ribbe (1972)	Newton et al. (1980)	Hodges and Royden (1984)	Range midpoint	Range quarter width
An_{30}						
Anorthite	1.276	1.355	1.603	1.342	1.440	0.082(6%)
ΔP GASP (bars)	−830	−1030	−1600	−1000	−1240	205
ΔP GRAIL (bars)	—	—	—	—	—	—
ΔP GPCQ (bars)	−800	−990	−1540	−960	−1190	200
An_{50}						
Anorthite	1.276	1.265	1.444	1.342	1.355	0.045(3%)
ΔP GASP (bars)	−830	−800	−1250	−1000	−1030	110
ΔP GRAIL (bars)	—	—	—	—	—	—
ΔP GPCQ (bars)	−800	−770	−1200	−960	−990	105

Uncertainty in *P* from activity models (bars)	
GASP	260–775
GRAIL	60–260
GPCQ	990–1475

Note: ΔP's are all relative to an ideal solution model.

This situation could be greatly improved by better constraints on grossular activities for very dilute solutions.

The GRAIL reaction is rather insensitive to almandine activity models because (1) less extrapolation from the pure almandine end-member was required for the compositions used above, and (2) almandine activities for Fe-rich garnet compositions are more generally agreed upon. However, any error in the almandine activity coefficient at almandine-poor compositions is magnified by the relatively small ΔV of reaction, which is three to four times smaller than the ΔV of reactions for equilibria involving grossular and anorthite.

Natural compositional inhomogeneities and geologic precision

Few, if any, natural samples contain compositionally homogeneous minerals, and specific mineral compositions will be a complex function of the geologic history that the rock has undergone. For example, compositions will depend to varying degrees on the *P-T,* strain, and the history of fluid infiltration in the rock. Yet another source of uncertainty faced by the petrologist is the choice of which compositions to use for thermobarometry. As compositional heterogeneity is specific to a given rock and its geologic evolution, we prefer to describe the resulting contribution to the uncertainty in thermobarometric estimates as the "geologic precision" (see also McIntyre et al., 1966; Brooks et al., 1972; Spear and Rumble, 1986).

Although statistical approaches have been advocated in the past to describe the geologic precision (e.g., Steltenpohl and Bartley, 1987; Hodges and McKenna, 1987), there are four reasons why we believe a statistical treatment should be avoided. First, the selection of the data that will be used for thermobarometry is dependent on the interpretation developed by the petrologist in studying the rock and consequently will depend on his or her possibly arbitrary criteria by which those analyses are chosen. For example, one petrologist might collect garnet analyses as close to the rim as possible, reasoning that this physical position is most likely to have been in equilibrium with the matrix phases. Another might choose to use those analyses that correspond to a minimum in the Fe/(Fe + Mg) ratio or spessartine content near the rim, thinking that such compositions best represent the rim composition of the garnet at the peak of metamorphism. Such differences in petrologic models are not typically conducive to statistical treatments.

Second, even if criteria are chosen that are agreeable to every petrologist for a single rock, the true compositional

TABLE 5. Summary of error sources and their propagated effects (bars)

Error source	Range of propagated error	GASP	GRAIL	GPCQ	GBMQS
Analytical (total, 1σ)	55–185	90–125	55–60	65–70	105–185
Barometer K_{eq} (1σ)	40–70	40	45	65	70
Temperature imprecision (1σ)	10–170	80–120	30–40	10–20	80–170
Thermometer Calibration (1σ)	250–1000	1000	350	250	
Barometer Calibration (1σ)	300–750*	350–380	350		
Total statistically treatable errors (1σ)	400–1260	1050–1080	500		
Activity models (quarterwidth)	50–1500	260–775	60–260	990–1475	
Compositional heterogeneity (quarterwidth)	150–500	250–500	150–200	150–200	
Total uncertainty	600–3250	1560–2350	710–960		

* The upper value for this range is not bounded, and ±750 bars is simply an estimate based on the internal consistency of thermodynamic data bases for barometric reactions involving grossular and anorthite.

distribution corresponding to those criteria may not follow a mathematical form that is treatable statistically from the finite number of data collected. For example, the actual composition of a garnet rim region may vary complexly as a result of the proximity of matrix ferromagnesian phases, localized retrograde garnet growth or consumption, fluid availability to facilitate reactions, etc. The relatively small number of analyses that a petrologist is likely to collect on any given sample may not adequately define the true mathematical form of compositional variation consistent with a single criterion. A statistical treatment of the compositions will then be mathematically erroneous.

Third, there is no reason why the number and distribution of analyses corresponding to a particular model in any way represents the likelihood of equilibrium. Even if a statistically meaningful number of analyses are collected that are consistent with a single petrologic model, there is still the critical assumption that this distribution has some physical significance regarding the best composition for thermobarometry. Ascribing such physical meaning to the measured distribution seems to us unwise.

Finally, in many cases, a statistical approach will actually be contradictory with petrologic models, which tend to weight more heavily those compositions at the extremes of measured distributions. For example, the garnet or plagioclase exhibiting the minimum in spessartine or anorthite content may be deemed the most likely to have been in equilibrium with the other phases based on a petrologic model. Because virtually every statistical treatment of the data will tend to center weight the analyses and the thermobarometric combination of analyses, the petrologic importance of the extreme compositions will be devalued.

As a final note in this discussion, if a single petrologic criterion is used in selecting analyses, if one believes that some mathematical form of the compositional variation is derivable from the analyses collected, and if one is willing to ascribe some petrologic meaning to the compositional distribution, then the influence of the correlation between mineral components must be considered before statistics can be applied. This aspect was deliberately ignored by Hodges and McKenna (1987), and consequently their technique can over- or underestimate the corresponding geologic precision, depending on which thermometers and barometers are being used. Furthermore, if standard errors derived from multiple analyses are reported for mineral compositions, then correlation coefficient matrices for each mineral should also be presented.

One useful method of calculating geologic precisions is simply to solve the thermobarometric equilibria using the measured compositions to produce a P-T parallelogram, whose bounds represent the maximum and minimum limits consistent with the small set of compositional data chosen as potentially representing equilibrium. The philosophical implication of the parallelogram is that no one analysis or combination of analyses is a statistically better measure of equilibrium conditions than another, so that the extremes of the parallelogram have no more or less validity than any other position within the parallelogram, at least within the limits of the data chosen as being consistent with the petrologic model. Although we recognize that there will always be some arbitrariness to the values that may be calculated, examples of this technique are abundant in the literature, and the quarter widths of the pressure uncertainties are often on the order of ±150 to ±500 bars for well-characterized samples.

These typical geological precisions reported for rocks only consider natural inhomogeneity and do not take into account any systematic errors in the thermometer calibrations or any analytical errors. The fact that this range is about twice the analytical precision of pressure estimates indicates that at present our ability to measure mineral compositions is much better than our ability to understand mineral zoning in natural rocks and to correlate compositions. Future plots of thermobarometric

TABLE 6. Compositions of minerals from a natural sample

	Garnet	Biotite	Plagioclase
Si	2.981	2.516	2.739
Al	2.016	1.758	1.247
Ti	—	0.152	—
Mg	0.369	1.148	—
Fe	2.201	1.353	0.012
Mn	0.287	0.006	—
Ca	0.155	0.000	0.258
Na	—	0.063	0.759
K	—	0.973	0.006

Note: Sample location is latitude 54°45′19″ S, longitude 69°36′20″ W.

results might display both the *P-T* parallelogram resulting from the geologic precision and the error ellipse corresponding to the propagated electron microprobe errors; this would allow a direct comparison of sample heterogeneity (parallelogram) and analytical precision (ellipse).

DISCUSSION

Accuracy of pressure estimates

Each source of uncertainty and the range of its propagated effect on pressures is listed in Table 5. Five columns are presented corresponding to a possible typical range of uncertainties in pressure and to the individual GASP, GRAIL, GPCQ, and GBMQS barometers.

Combining these uncertainties into an estimate of the accuracy of a pressure estimate depends on the assumed distributional behavior of each source of error. The analytical precision and calibration errors probably have nearly Gaussian distributions, and so their combined effects may be taken as the square root of the sums of the squares of their individual propagated uncertainties; the range of this value is tabulated as a subtotal in Table 5. For reasons described above, we believe that neither compositional heterogeneity nor variability in activity models are statistical measures, and so believe it is appropriate simply to add the propagated quarterwidths derived from variability in activity models and from compositional heterogeneity to the total 1σ uncertainty derived from the statistical error sources. This combination results in accuracies of ±600 to ±3260 bars, which corresponds to an uncertainty in crustal depth of ±2.1 to ±11.4 km. Other assumptions about the distribution of the geologic imprecision and variability in activity models decrease this uncertainty somewhat; an assumed square wave distribution results in paleodepth uncertainties of ±1.6 to ±6.8 km (1σ), while an assumed Gaussian distribution produces uncertainties of ±1.5 to ±6.6 km (1σ). Thus overburden uncertainties estimated solely from rigorous propagation of thermobarometric errors may range from about ±1.5 to +11.4 km, or 5–30% of the thickness of normal continental crust.

Example

As a depiction of some of the uncertainties described above, we present an example from an upper amphibolite grade pelitic schist with the assemblage garnet + sillimanite + muscovite + biotite + plagioclase + quartz. Relevant data are presented in Table 6, and some of the measures of uncertainty are plotted in Figure 1. As can be seen, the mean *P-T* estimate using GASP barometry and garnet-biotite thermometry is about 6.4 kbar and 620 °C.

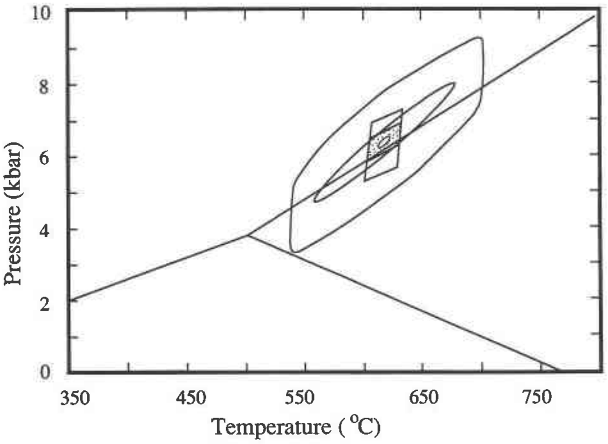

Fig. 1. Measures of thermobarometric uncertainty (1σ or quarterwidth) for a natural sample using GASP barometry and garnet-biotite thermometry. The small ellipse, small stippled parallelogram, and large parallelogram represent propagated uncertainties resulting from analytical imprecision, natural compositional heterogeneity, and different activity models, respectively. The long thin ellipse is the propagated calibration errors for barometric and thermometric end-member reactions. Largest bounded region is combination of all uncertainties.

The analytical precision of the pressure estimate (small ellipse in Fig. 1) is about ±150 bars (1σ). This value exceeds those calculated for the analytical precision for the GASP barometer above because the very low grossular and anorthite contents of the garnet and plagioclase increase the analytical uncertainty. Of additional interest in Figure 1 are the long, thin ellipse that represents the combined calibration uncertainties of the GASP barometer and garnet-biotite thermometer (±1700 bars; 1σ), the small shaded parallelogram that represents the compositional heterogeneity of the analyses chosen for thermobarometry (±500 bars; quarterwidth), and the large parallelogram that indicates the effects of variable activity models (±900 bars; quarterwidth). As can be seen, activity models and uncertainties in thermometer calibration dominate the estimated total uncertainty in the thermobarometrically derived pressure for this sample, which is about ±3100 bars (1σ or quarterwidth).

We emphasize that the uncertainties described in this paper are only for pressures determined from thermobarometers, and that the error field defined for a thermobarometer may violate other constraints derived from phase equilibria or physical necessity. Of course, for this sample, an additional important constraint on the pressure of equilibration is the presence of sillimanite as the aluminosilicate in this rock; the kyanite to sillimanite transition is accurately located in *P-T* space (e.g., Holdaway, 1971), and limits the pressure to approximately 3.75 kbar at 500 °C and 10 kbar at 800 °C. This single phase equilibrium constraint implies that the maximum *P-T* range for the equilibration of the sample falls within the lower part of the field of uncertainty. That is, phase equilibria limit the magnitude of the pressure uncertainty for this sample.

The general consistency of a thermobarometric calibration with phase equilibria or physical constraints can be used to estimate better its uncertainty. For example, the fact that the Ferry and Spear (1978) calibration of the garnet-biotite thermometer indicates temperatures that are in general accord with phase equilibrium (e.g., Hodges and Spear, 1982) suggests that the calibration is better than rigorous propagation of its calibration errors (i.e., the errors reported by Ferry and Spear, 1978, may be overestimated). As is obvious from Figure 1 and from the discussion above, inaccuracies in thermometer calibration can be a substantial source of uncertainties in pressure; if the Ferry and Spear (1978) calibration is perfectly accurate, then the pressure uncertainty derived from thermobarometry and phase equilibrium constraints for the rock considered would be reduced to ±1000 bars (1σ or quarterwidth), even considering the effect of activity model variability.

Uncertainty in pressure differences

In spite of the substantial absolute error of barometers, many metamorphic processes are best identified from differences in pressures and temperatures, and changes in pressure and temperature may be much better characterized. If a single barometer is used to calculate a difference in pressure, then any experimental uncertainties cancel out, and differences in pressure of equilibration may be calculated by considering only the effects of the geologic precision, analytical errors, and activity coefficients (see Hodges and McKenna, 1987; Powell and Holland, 1988).

In order to calculate the effect of activity coefficients, the variability in changes of pressure corresponding to the different activity models must be assessed. For the garnet compositions and activity models considered in Tables 2 and 4, the uncertainty (quarterwidth) in the estimated changes in pressure (ΔP's) at a constant temperature and activity of anorthite is approximately ±5% to ±10% of the total change in pressure. For example, suppose it is desired to know the difference in pressure recorded by garnet compositions G1 and G2 (Table 4). Using the GPCQ reaction, the mean change in pressure at constant plagioclase composition is 11900 bars, and the difference between the maximum and minimum pressure changes is about 3500 bars; that is, the quarterwidth of the calculated pressure differences (875 bars) is roughly 7% of the total. Similar values are obtained from more realistic, natural compositions from zoned garnets (Kohn and Spear, unpublished data; see also Powell and Holland, 1988).

Therefore, the minimum difference in pressure that could be resolvable may be taken as the sum of the geologic precision (±150 to ±500 bars) and the analytical uncertainty (±70 to ±305 bars) augmented by 5–10% for activity model variability, or ±230 to ±890 bars (1σ or quarterwidth). This corresponds to a difference or change in crustal depth based solely on thermobarometry of approximately ±0.8 to ±3.1 km.

If different barometers are used to calculate differences in pressure, then any uncertainties in the calibrations uncertainties must be considered, as well as the differences among activity models. Obviously, it will be advantageous to apply calibrations that employ the same activity models, to use the same thermometer calibration, and to consider assemblages with similar bulk compositions, in which case, measurable differences in pressure (1σ or quarterwidth) may be as small as ±230 bars.

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APPENDIX 1. NOTE ON TRUE ANALYTICAL IMPRECISIONS

Although errors calculated from the counting statistics of data obtained using an electron microprobe could be interpreted to represent the precision of a chemical analysis, it is likely that analyses collected by different operators on different machines with different standards will be more variable than the statistics of a single analysis would imply. In an effort to quantify partially some of these effects, we have examined analyses of Kakanui hornblende that were collected immediately after initial standardization over a period of two years on the JEOL 733 electron microprobe at Rensselaer Polytechnic Institute. The average of our measured compositions is presented in Appendix Table 1 (column 1), with the typical counting statistics error in each oxide component (column 2), and the standard deviation of each wt% oxide about the mean analysis (column 3). As can be seen, each element has a measured uncertainty that exceeds the counting statistics error by a factor ranging from 1.5 (Ti) to 5.3 (Mg).

Three aspects should be understood about these analyses. (1) While the first approximately 50 analyses of Kakanui hornblende were collected with some variability in standards, the remaining analyses were collected using similar standards. (2) Operating conditions were virtually identical for over 95% of the analyses. (3) Because the purpose of analyzing the hornblende was to check the standardization, the uncertainties reported in column 3 are certainly maxima. If an oxide wt% was significantly different from its expected value, then we assume that the operator restandardized for that element after the analysis.

Part of the increased error is undoubtedly due to natural compositional inhomogeneity; this possibility was evaluated by D. Wark (personal communication, 1988), who collected 43 consecutive analyses across a single grain of the standard. The measured variability in each element represents the combined effects of counting statistics and compositional heterogeneity and is also presented in Appendix Table 1 (column 4); however, as can be seen, these uncertainties fail to account for the bulk of the observed deviation of the last two years' analyses. Therefore, we believe the increase in compositional uncertainty over the counting statistics error and natural inhomogeneity mostly represents the effects of different operators (e.g., focusing differences), the quality of the initial standardization, and random machine errors over the two year period, but some of the uncertainty no doubt reflects the standards used. We have additionally conducted two other (unpublished) studies on garnet standards with similar results.

It is interesting that the mean composition measured (column 1) differs from the wet chemical analysis supplied by the Smithsonian Institution (column 5), especially regarding Al content (see also the results and discussion of Rucklidge et al., 1971 and Reed and Ware, 1975, as well as the mean analysis presented by Giaramita and Day, 1990). This difference indicates that compositional uncertainties are even larger when different analytical techniques are compared.

These data imply that the total analytical imprecision of a barometer should be increased over the propagated errors from counting statistics by a factor of approximately 2–3 if one wishes to include the possibility of the collection of data by different operators or on different days. Of course, the increased uncertainty will not be observed if data are collected by the same operator on a single day and will be minimized for large data sets if the same operator collects the data using the same standardization over a limited time period. However, error beyond uncertainties ascribed to counting statistics must be considered when comparing data collected at two different microprobe facilities, for example when performing regression diagnostics on combined data sets.

APPENDIX TABLE 1. Average composition and statistics of Kakanui Hornblende standard

	Average composition (wt%) (1)	Counting statistics errors (2)	Measured errors (3)	Variability of consecutive analyses* (4)	Wet chemical analysis (5)
SiO_2 (TAP)	40.24	0.121(0.30%)	0.398(0.99%)	0.18(0.44%)	40.37
Al_2O_3 (TAP)	14.26	0.051(0.36%)	0.227(1.6%)	0.09(0.60%)	14.90
TiO_2 (LIF)	4.76	0.137(2.9%)	0.199(4.2%)	0.14(2.9%)	4.72
MgO (TAP)	12.64	0.054(0.43%)	0.291(2.3%)	0.14(1.1%)	12.80
FeO (LIF)	10.61	0.115(1.1%)	0.219(2.1%)	0.16(1.5%)	10.92
MnO (LIF)	0.09	0.011(11.9%)	0.029(31.2%)	0.02(16.2%)	0.09
CaO (PET)	10.08	0.073(0.72%)	0.256(2.5%)	0.11(1.1%)	10.30
Na_2O (TAP)	2.70	0.039(1.4%)	0.097(3.6%)	0.08(2.8%)	2.60
K_2O (PET)	2.07	0.037(1.8%)	0.070(3.4%)	0.05(2.4%)	2.05

Note: Number of analyses used for average composition and measured errors = 325. Number of analyses used for natural inhomogeneity = 43. Wet chemical analysis supplied by Smithsonian Institution.

* Includes both counting statistics errors and natural compositional heterogeneity.