APPENDIX 1

PRECISION OF THE PROPOSED BAROMETER

The generalized equation for estimating error (1σ) in pressure for a barometric equation of the type

$$P = \left(\Delta H - T\Delta S + RT \ln K_{eq}\right)/(-\Delta V)$$

or, $P = b + mT - RT \ln K_{eq} / \Delta V$, (A1)

where $b = -(\Delta H / \Delta V)$ and $m = (\Delta S / \Delta V)$ are the intercept and slope of the barometer respectively can be expressed as (Kohn and Spear 1991b)

$$\sigma_P^2 = \left[\sigma_b^2 + T^2\sigma_m^2 + 2\rho_{mb}T\sigma_m\sigma_b\right] + \left[\left(\frac{\sigma_{\Delta V}RT\ln K_{eq}}{(\Delta V)^2}\right)^2\right] + \left[\left(m - \frac{R\ln K_{eq}}{\Delta V^2}\right)^2 \left(\sigma_{T,Calib}^2 + \sigma_{T,Compo}^2\right)\right]$$

$$+ \left[\left(\frac{RT}{\Delta V}\right)^2 \sum_{i=1}^{i=n}\sum_{\substack{j=1 \\ j\neq i}}^{j=n} \alpha_i\alpha_j\vartheta_i\vartheta_j\left(\frac{\sigma_{x_i}}{X_i}\right)\left(\frac{\sigma_{x_j}}{X_j}\right)\rho_{X_iX_j}\right]$$ (A2)

In Equation (A2), X_i is the mole fraction. σ_{X_i} is the error (standard deviation) in the X_i^{th} variable and $\rho_{X_iX_j}$ is the correlation coefficient between i^{th} and j^{th} variables. α_i and ϑ_i are site-multiplicity and stoichiometric coefficients. All parameters in Equation (A2) were derived based on the methodology given in Kohn and Spear (1991b). The four terms within parentheses in Equation (A2) reflect uncertainties in barometer calibration (σ_P^{baro}), uncertainty in ΔV ($\sigma_P^{\Delta V}$), uncertainty in input temperature obtained from thermometers (σ_P^{thermo}), and uncertainty in composition (σ_P^{Comp}) respectively (Kohn and Spear 1991b).

In the expression of σ_P^{baro}, σ_b^2, and σ_m^2 are estimated by dividing the errors in $\Delta \hat{H}$ and ΔS (column 2 of Table 7), by ΔV, which was calculated using Equation (xiv) at specific

experimental *P-T* condition, i.e. $\sigma_b^2 = \left(\dfrac{\sigma_{\Delta\hat{H}}}{\Delta V_{P_{exp},T_{exp}}}\right)^2$ and $\sigma_m^2 = \left(\dfrac{\sigma_{\Delta S}}{\Delta V_{P_{exp},T_{exp}}}\right)^2$. For $\sigma_P^{\Delta V}$ (2nd term,

Eq. A2), $\sigma_{\Delta V}$ is formulated by finding out the derivatives of $V_{P,T}$ (Eq. xiv) with respect to P

and T using the simple error propagation equation $\sigma_Y = \sqrt{\left(\dfrac{\partial Y}{\partial U}\right)^2 \cdot \sigma_U^2 + \left(\dfrac{\partial Y}{\partial V}\right)^2 \cdot \sigma_V^2}$ where

$Y = f(U,V)$.

Hence $\sigma_{\Delta V} = \sqrt{\left(\dfrac{\partial V_{P,T}}{\partial T}\right)_P^2 \cdot \sigma_T^2 + \left(\dfrac{\partial V_{P,T}}{\partial P}\right)_T^2 \cdot \sigma_P^2}$.

For the barometric reaction, $Tr + Ts + 2Ab = 2Prg + 8\ Qtz$, K_{eq} for Equation (xv) is

expressed as

$$2RT \ln\left[\frac{16 X_{Na}^A X_{Al}^{T1}}{X_V^A X_{Si}^{T1} X_{Ab}}\right] - 98.698 X_{Na}^A - 33.213 X_K^A - 20.338 X_{Na}^{M4} - 39.101 X_{Fe2+}^{M13} + 100.392 X_{Al}^{M2}$$

$$+ 131.03 X_{Fe2+}^{M2} + 82.479 X_{Fe3+}^{M2} - 118.653 X_{Al}^{T1} - 2RT \ln \gamma_{Ab}$$

The third term (σ_P^{thermo}) in Equation (A2) includes the terms $\sigma_{T,Calib}$ (calibration uncertainty of

simple thermometer, assumed to be ±50 ºC) and $\sigma_{T,Compo}$ (uncertainty in measurement of

composition), cf. Kohn and Spear (1991b). $\sigma_{T,Compo}$ is calculated by multiplying the slope

($m = (\Delta S / \Delta V)$) of the reaction by the precision of temperature (assumed to be ± 5 ºC) for

most barometer (Kohn and Spear 1991b).

To ascertain the effect compositional uncertainty (σ_P^{Comp}), the oxides wt% of amphibole

in the chosen experimental runs (PB9 and S5, Table 5) were randomly perturbed (random

numbers showing normal distribution) within the given standard errors of the analytical data

(2 mol%) using the Monte-Carlo technique (Anderson 1976). Fifty iterations (cf. Anderson

1976) were performed. These fifty randomly generated amphiboles were then recast using the formulation of Leake et al. (1997). For each, the cation site fractions were obtained from the scheme given in Table 3. Equation (iv) was then applied for the determination of mole fraction (X_{Tr}, X_{Ts}, X_{Prg},) of the amphibole end-members. Similar approach was adopted for the determination of mole fraction of albite (X_{Ab}). Average mole fraction and uncertainty (standard deviation) in mole fraction ($\sigma_{X_{Tr}}$, $\sigma_{X_{TS}}$, $\sigma_{X_{Prg}}$, $\sigma_{X_{Ab}}$) is presented in Appendix Table 1a; the correlation matrix for the fifty randomly generated compositional data is shown in Appendix Table 1b. Because, the amphibole end-members on either side of the barometer reaction and plagioclase end-members (Ab-An) are related by $Na_1Al_1V_{-1}Si_{-1}$ and $Na_1Si_1Ca_{-1}Al_{-1}$ exchange vectors, respectively, the site-multiplicities (α_i) of X_{Tr}, X_{Ts}, X_{Prg}, and X_{Ab} in the fourth term of Equation (A2) are taken to be 1 (cf. Todd 1998). For the phases involved in the present formulation the 4th term can be expressed as $\left(\dfrac{RT}{\Delta V}\right)^2 \cdot X_{Comp}$, where X_{Comp} can be expanded as

$$
\left[\alpha_{Tr}\alpha_{Ts}\vartheta_{Tr}\vartheta_{Ts}\left(\frac{\sigma_{x_{Tr}}}{X_{Tr}}\right)\left(\frac{\sigma_{x_{Ts}}}{X_{Ts}}\right)\rho_{X_{Tr}X_{Ts}}\right] + \left[\alpha_{Tr}\alpha_{Prg}\vartheta_{Tr}\vartheta_{Prg}\left(\frac{\sigma_{x_{Tr}}}{X_{Tr}}\right)\left(\frac{\sigma_{x_{Prg}}}{X_{Prg}}\right)\rho_{X_{Tr}X_{Prg}}\right] +
$$

$$
\left[\alpha_{Tr}\alpha_{Ab}\vartheta_{Tr}\vartheta_{Ab}\left(\frac{\sigma_{x_{Tr}}}{X_{Tr}}\right)\left(\frac{\sigma_{x_{Ab}}}{X_{Ab}}\right)\rho_{X_{Tr}X_{Ab}}\right] + \left[\alpha_{Ts}\alpha_{Prg}\vartheta_{Ts}\vartheta_{Prg}\left(\frac{\sigma_{x_{Ts}}}{X_{Ts}}\right)\left(\frac{\sigma_{x_{Prg}}}{X_{Prg}}\right)\rho_{X_{Ts}X_{Prg}}\right] +
$$

$$
\left[\alpha_{Ts}\alpha_{Ab}\vartheta_{Ts}\vartheta_{Ab}\left(\frac{\sigma_{x_{Ts}}}{X_{Ts}}\right)\left(\frac{\sigma_{x_{Ab}}}{X_{Ab}}\right)\rho_{X_{Ts}X_{Ab}}\right] + \left[\alpha_{Prg}\alpha_{Ab}\vartheta_{Prg}\vartheta_{Ab}\left(\frac{\sigma_{x_{Prg}}}{X_{Prg}}\right)\left(\frac{\sigma_{x_{Ab}}}{X_{Ab}}\right)\rho_{X_{Prg}X_{Ab}}\right]
$$

The 1σ errors in σ_P^{baro}, $\sigma_P^{\Delta V}$ σ_P^{thermo}, and σ_P^{comp} and the cumulative uncertainty for the two chosen experimental runs are listed in Appendix Table 1c.

Further, an attempt was made to estimate the error arising from uncertainty in Fe^{3+} in amphiboles calculated using the average ferric estimation scheme of Leake et al. (1997). An uncertainty of 10% in $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio was assumed for hornblende (cf. Kohn and Spear 1991b). The Fe^{3+} and Fe^{2+} values were recalculated at 10% uncertainty on both the higher and the lower side of the mean value. Using the two limiting values, cations were re-allocated to the respective sites using the scheme of Leake et al. (1997). For the two compositions, the pressures were re-estimated from the barometric Equation (xv) at the experimental T. The pressures corresponding to the extreme compositions were computed to be 1.5 kbar and 2.8 kbar for the experimental run S5 (for which P_{com} = 2.1 kbar, assuming no error in the $Fe^{3+}/Fe^{3+}+Fe^{2+}$ ratio). The respective values for the experimental run PB9 (P_{com} = 9.4 kbar) were 9.0 kbar and 9.8 kbar. Therefore, the deviation from the P_{com} value was 700 bar (S5) and 400 bar (PB9) for 10% uncertainty in $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio.

APPENDIX TABLE 1

Results of Monte-Carlo simulation (50 iterations) of compositional parameters in the two chosen experimental runs (S5 and PB9, Table 5). (a) Mole fractions and standard errors, (b) correlation matrix of amphibole end-members (*Tr*, *Ts*, and *Prg*), and albite in plagioclase feldspar, and (c) 1σ error in σ_P^{baro}, $\sigma_P^{\Delta V}$ σ_P^{thermo}, σ_P^{comp}, and the cumulative uncertainty for the barometric Equation (xv).

Appendix Table 1a

	S5		PB9	
	X_i	σ_X	X_i	σ_X
	Mean	StDev	Mean	StDev
X_{Tr}	0.0424	0.0065	0.0011	0.0003
X_{Ts}	0.0028	0.0019	0.0039	0.0014
X_{Prg}	0.0098	0.0033	0.0169	0.0037
X_{Ab}	0.5000	0.0000	0.4982	0.0300

Appendix Table 1b

S5	X_{Tr}	X_{Ts}	X_{Prg}	X_{Ab}
X_{Tr}	1.0000			
X_{Ts}	0.0953	1.0000		
X_{Prg}	-0.0020	-0.1736	1.0000	
X_{Ab}	-0.6245	0.4246	0.3654	1.0000

PB9	X_{Tr}	X_{Ts}	X_{Prg}	X_{Ab}
X_{Tr}	1.0000			
X_{Ts}	0.2176	1.0000		
X_{Prg}	-0.2689	0.2227	1.0000	
X_{Ab}	-0.0122	-0.0301	-0.2473	1.0000

Appendix Table 1c

	S5	PB9
P, T	1 kbar, 701 ^{0}C	10 kbar, 925 ^{0}C
σ_P^{baro} (bars)	18	17
$\sigma_P^{\Delta V}$ (bars)	8	17
σ_P^{thermo} (bars)	6	23
σ_P^{comp} (bars)	1882	730
$\sum 1\sigma$ (bars)	1914	787

APPENDIX 2

SCHEME FOR CALCULATING PRESSURE USING COEXISTING HORNBLENDE AND PLAGIOCLASE IN SAMPLE 73-20C OF SPEAR (1982)

P	5.5 kbar	Cation proportion calculated	
T	535 °C	after Leake et al. (1997)	
	Amphibole		
SiO_2	42.23	Si	6.16
TiO_2	0.38	Ti	0.04
Al_2O_3	16.61	Al	2.86
Cr_2O_3	0.00	Cr	0.00
Fe_2O_3	0.00	Fe3+	0.51
FeO	18.79	Fe2+	1.78
MnO	0.11	Mn	0.01
MgO	8.32	Mg	1.81
CaO	10.18	Ca	1.59
Na_2O	2.01	Na	0.57
K_2O	0.25	K	0.05
X_{Ab}	0.70		

Calculated site fractions using the scheme in Table 3

X_{Na}^A	X_K^A	X_{Na}^{M4}	X_{Fe2+}^{M13}	X_{Al}^{M2}	X_{Fe2+}^{M2}	X_{Fe3+}^{M2}	X_{Si}^{T1}	X_{Al}^{T1}	X_V^A
0.361	0.047	0.104	0.496	0.517	0.102	0.257	0.543	0.457	0.593

Choice of ΔV for the barometers

For the natural assemblage 73-20C (Spear, 1982), the P-T values recommended are 5.5 kbar, 535ºC. The ΔV of the barometer reaction (A) at this P-T condition obtained using Equation (xiv) is -1.64949 KJ kbar^{-1}. However, for the natural assemblages P and T conditions are not precisely known. In such a case, ΔV of the reaction (A) can be computed at 8 kbar, 800ºC, which are mean values for the range of experimental P-T conditions. The linearised ΔV value ($\Delta V_{8\ kbar,\ 800\ ºC}$) is -1.72433 KJ kbar^{-1}. In the following section, a test will be made for the chosen natural assemblage to check the compatibility in the pressure values retrieved from the

proposed barometers (P_1 and P_2) for ΔV calculated at author's recommended *P-T*, and at linearised *P-T* condition.

<div align="center">Pressure computed at 575 °C, 5.5 kbar from Equation (xv)</div>

$$P_1 \text{ (kbar)} = [-9.326 + 0.01462T(\text{K}) + RT \ln K_{\text{ideal}} - 98.698X_{Na}^{A} - 33.213X_{K}^{A} - 20.338X_{Na}^{M4}$$
$$-39.101X_{Fe}^{M13} + 100.392X_{Al}^{M2} + 131.03X_{Fe}^{M2} + 82.479X_{Fe3+}^{M2} - 118.653X_{Al}^{T1}$$
$$-2RT \ln \gamma_{Ab}]/(1.64949)$$

P_1 (at 535 °C) = 5.4 kbar, $\Delta P = P_{\text{computed}} - P_{\text{author}} = $ - 0.1 kbar

<div align="center">Pressure computed at 575 °C, 5.5 kbar from Equation (xvi)</div>

$$P_2 \text{ (kbar)} = [-1.869 + 0.0076T(\text{K}) + RT \ln K_{\text{ideal}} - 102.692X_{Na}^{A} - 35.251X_{K}^{A} - 15.969X_{Na}^{M4}$$
$$-40.499X_{Fe}^{M13} + 93.069X_{Al}^{M2} + 130.750X_{Fe}^{M2} + 74.226X_{Fe3+}^{M2} - 104.402X_{Al}^{T1}$$
$$-2RT \ln \gamma_{Ab}]/(1.64949)$$

P_2 (at 535 °C) = 5.7 kbar, $\Delta P = P_{\text{computed}} - P_{\text{author}} = 0.2$ kbar

<div align="center">Pressure computed at mean *P - T* value, 800 °C, 8 kbar from Equation (xv)</div>

$$P_1 \text{ (kbar)} = [-9.326 + 0.01462T(\text{K}) + RT \ln K_{\text{ideal}} - 98.698X_{Na}^{A} - 33.213X_{K}^{A} - 20.338X_{Na}^{M4}$$
$$-39.101X_{Fe}^{M13} + 100.392X_{Al}^{M2} + 131.03X_{Fe}^{M2} + 82.479X_{Fe3+}^{M2} - 118.653X_{Al}^{T1}$$
$$-2RT \ln \gamma_{Ab}]/(1.72433)$$

P_1 (at 800 °C) = 5.2 kbar, $\Delta P = P_{\text{computed}} - P_{\text{author}} = $ - 0.3 kbar

<div align="center">Pressure computed at mean *P - T* value, 800 °C, 8 kbar for barometer Equation (xvi)</div>

$$P_2 \text{ (kbar)} = [-1.869 + 0.0076T(\text{K}) + RT \ln K_{\text{ideal}} - 102.692X_{Na}^{A} - 35.251X_{K}^{A} - 15.969X_{Na}^{M4}$$
$$-40.499X_{Fe}^{M13} + 93.069X_{Al}^{M2} + 130.750X_{Fe}^{M2} + 74.226X_{Fe3+}^{M2} - 104.402X_{Al}^{T1}$$
$$-2RT \ln \gamma_{Ab}]/(1.72433)$$

P_2 (at 800 °C) = 5.5 kbar, $\Delta P = P_{\text{computed}} - P_{\text{author}} = 0.0$ kbar