

# APPENDIX 1

## PRECISION OF THE PROPOSED BAROMETER

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

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

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

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)

$$\begin{aligned} \sigma_p^2 = & \left[ \sigma_b^2 + T^2 \sigma_m^2 + 2\rho_{mb} T \sigma_m \sigma_b \right] + \left[ \left( \frac{\sigma_{\Delta V} RT \ln K_{eq}}{(\Delta V)^2} \right)^2 \right] + \left[ \left( m - \frac{R \ln K_{eq}}{\Delta V^2} \right)^2 (\sigma_{T, \text{Calib}}^2 + \sigma_{T, \text{Compo}}^2) \right] \\ & + \left[ \left( \frac{RT}{\Delta V} \right)^2 \sum_{i=1}^{i=n} \sum_{\substack{j=1 \\ j \neq i}}^{j=n} \alpha_i \alpha_j \vartheta_i \vartheta_j \left( \frac{\sigma_{x_i}}{X_i} \right) \left( \frac{\sigma_{x_j}}{X_j} \right) \rho_{x_i x_j} \right] \end{aligned} \quad (\text{A2})$$

In Equation (A2),  $X_i$  is the mole fraction.  $\sigma_{X_i}$  is the error (standard deviation) in the  $X_i^{\text{th}}$  variable and  $\rho_{X_i X_j}$  is the correlation coefficient between  $i^{\text{th}}$  and  $j^{\text{th}}$  variables.  $\alpha_i$  and  $\vartheta_i$  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 ( $\sigma_p^{\text{baro}}$ ), uncertainty in  $\Delta V$  ( $\sigma_p^{\Delta V}$ ), uncertainty in input temperature obtained from thermometers ( $\sigma_p^{\text{thermo}}$ ), and uncertainty in composition ( $\sigma_p^{\text{Comp}}$ ) respectively (Kohn and Spear 1991b).

In the expression of  $\sigma_p^{\text{baro}}$ ,  $\sigma_b^2$ , and  $\sigma_m^2$  are estimated by dividing the errors in  $\Delta \hat{H}$  and  $\Delta S$  (column 2 of Table 7), by  $\Delta V$ , which was calculated using Equation (xiv) at specific

experimental  $P$ - $T$  condition, i.e.  $\sigma_b^2 = \left( \frac{\sigma_{\Delta \hat{H}}}{\Delta V_{P_{\text{exp}}, T_{\text{exp}}}} \right)^2$  and  $\sigma_m^2 = \left( \frac{\sigma_{\Delta S}}{\Delta V_{P_{\text{exp}}, T_{\text{exp}}}} \right)^2$ . For  $\sigma_p^{\Delta V}$  (2<sup>nd</sup> 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  $\sigma_Y = \sqrt{\left( \frac{\partial Y}{\partial U} \right)^2 \cdot \sigma_U^2 + \left( \frac{\partial Y}{\partial V} \right)^2 \cdot \sigma_V^2}$  where

$$Y = f(U, V).$$

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

For the barometric reaction,  $Tr + Ts + 2Ab = 2Pr_g + 8 Qtz$ ,  $K_{eq}$  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 ( $\sigma_p^{thermo}$ ) in Equation (A2) includes the terms  $\sigma_{T, \text{Calib}}$  (calibration uncertainty of simple thermometer, assumed to be  $\pm 50$  °C) and  $\sigma_{T, \text{Compo}}$  (uncertainty in measurement of composition), cf. Kohn and Spear (1991b).  $\sigma_{T, \text{Compo}}$  is calculated by multiplying the slope ( $m = (\Delta S / \Delta V)$ ) of the reaction by the precision of temperature (assumed to be  $\pm 5$  °C) for most barometer (Kohn and Spear 1991b).

To ascertain the effect compositional uncertainty ( $\sigma_p^{Comp}$ ), 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 ( $\alpha_i$ ) 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 4<sup>th</sup> term can be expressed as  $\left(\frac{RT}{\Delta V}\right)^2 \cdot X_{Comp}$ , where

$X_{Comp}$  can be expanded as

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

The  $1\sigma$  errors in  $\sigma_P^{baro}$ ,  $\sigma_P^{\Delta V}$ ,  $\sigma_P^{thermo}$ , and  $\sigma_P^{comp}$  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  $\text{Fe}^{3+}$  in amphiboles calculated using the average ferric estimation scheme of Leake et al. (1997). An uncertainty of 10% in  $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$  ratio was assumed for hornblende (cf. Kohn and Spear 1991b). The  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  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  $P_{\text{com}} = 2.1$  kbar, assuming no error in the  $\text{Fe}^{3+}/\text{Fe}^{3+}+\text{Fe}^{2+}$  ratio). The respective values for the experimental run PB9 ( $P_{\text{com}} = 9.4$  kbar) were 9.0 kbar and 9.8 kbar. Therefore, the deviation from the  $P_{\text{com}}$  value was 700 bar (S5) and 400 bar (PB9) for 10% uncertainty in  $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$  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)  $1\sigma$  error in  $\sigma_P^{baro}$ ,  $\sigma_P^{\Delta V}$ ,  $\sigma_P^{thermo}$ ,  $\sigma_P^{comp}$ , and the cumulative uncertainty for the barometric Equation (xv).

**Appendix Table 1a**

	<b>S5</b>		<b>PB9</b>	
	$X_i$	$\sigma_x$	$X_i$	$\sigma_x$
	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**

<b>S5</b>	$X_{Tr}$	$X_{Ts}$	$X_{Prg}$	$X_{Ab}$
$X_{Tr}$	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

  

<b>PB9</b>	$X_{Tr}$	$X_{Ts}$	$X_{Prg}$	$X_{Ab}$
$X_{Tr}$	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 $^{\circ}$ C	10 kbar, 925 $^{\circ}$ C
$\sigma_P^{baro}$ (bars)	18	17
$\sigma_P^{\Delta V}$ (bars)	8	17
$\sigma_P^{thermo}$ (bars)	6	23
$\sigma_P^{comp}$ (bars)	1882	730
$\Sigma 1\sigma$ (bars)	1914	787

## APPENDIX 2

### SCHEME FOR CALCULATING PRESSURE USING COEXISTING HORNBLLENDE 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 <sub>2</sub>	42.23	Si	6.16
TiO <sub>2</sub>	0.38	Ti	0.04
Al <sub>2</sub> O <sub>3</sub>	16.61	Al	2.86
Cr <sub>2</sub> O <sub>3</sub>	0.00	Cr	0.00
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	2.01	Na	0.57
K <sub>2</sub> O	0.25	K	0.05
X <sub>Ab</sub>	0.70		

#### Calculated site fractions using the scheme in Table 3

X <sub>Na</sub> <sup>A</sup>	X <sub>K</sub> <sup>A</sup>	X <sub>Na</sub> <sup>M4</sup>	X <sub>Fe2+</sub> <sup>M13</sup>	X <sub>Al</sub> <sup>M2</sup>	X <sub>Fe2+</sub> <sup>M2</sup>	X <sub>Fe3+</sub> <sup>M2</sup>	X <sub>Si</sub> <sup>T1</sup>	X <sub>Al</sub> <sup>T1</sup>	X <sub>V</sub> <sup>A</sup>
0.361	0.047	0.104	0.496	0.517	0.102	0.257	0.543	0.457	0.593

#### Choice of $\Delta V$ for the barometers

For the natural assemblage 73-20C (Spear, 1982), the  $P$ - $T$  values recommended are 5.5 kbar, 535°C. The  $\Delta V$  of the barometer reaction (A) at this  $P$ - $T$  condition obtained using Equation (xiv) is -1.64949 KJ kbar<sup>-1</sup>. However, for the natural assemblages  $P$  and  $T$  conditions are not precisely known. In such a case,  $\Delta V$  of the reaction (A) can be computed at 8 kbar, 800°C, which are mean values for the range of experimental  $P$ - $T$  conditions. The linearised  $\Delta V$  value ( $\Delta V_{8 \text{ kbar}, 800 \text{ °C}}$ ) is -1.72433 KJ kbar<sup>-1</sup>. 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  $\Delta V$  calculated at author's recommended  $P$ - $T$ , and at linearised  $P$ - $T$  condition.

Pressure computed at 575 °C, 5.5 kbar from Equation (xv)

$$P_1 \text{ (kbar)} = [-9.326 + 0.01462T(\text{K}) + RT \ln K_{\text{ideal}} - 98.698X_{\text{Na}}^A - 33.213X_K^A - 20.338X_{\text{Na}}^{M4} \\ - 39.101X_{\text{Fe}}^{M13} + 100.392X_{\text{Al}}^{M2} + 131.03X_{\text{Fe}}^{M2} + 82.479X_{\text{Fe}^{3+}}^{M2} - 118.653X_{\text{Al}}^{T1} \\ - 2RT \ln \gamma_{\text{Ab}}]/(1.64949)$$

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

Pressure computed at 575 °C, 5.5 kbar from Equation (xvi)

$$P_2 \text{ (kbar)} = [-1.869 + 0.0076T(\text{K}) + RT \ln K_{\text{ideal}} - 102.692X_{\text{Na}}^A - 35.251X_K^A - 15.969X_{\text{Na}}^{M4} \\ - 40.499X_{\text{Fe}}^{M13} + 93.069X_{\text{Al}}^{M2} + 130.750X_{\text{Fe}}^{M2} + 74.226X_{\text{Fe}^{3+}}^{M2} - 104.402X_{\text{Al}}^{T1} \\ - 2RT \ln \gamma_{\text{Ab}}]/(1.64949)$$

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

Pressure computed at mean  $P$  -  $T$  value, 800 °C, 8 kbar from Equation (xv)

$$P_1 \text{ (kbar)} = [-9.326 + 0.01462T(\text{K}) + RT \ln K_{\text{ideal}} - 98.698X_{\text{Na}}^A - 33.213X_K^A - 20.338X_{\text{Na}}^{M4} \\ - 39.101X_{\text{Fe}}^{M13} + 100.392X_{\text{Al}}^{M2} + 131.03X_{\text{Fe}}^{M2} + 82.479X_{\text{Fe}^{3+}}^{M2} - 118.653X_{\text{Al}}^{T1} \\ - 2RT \ln \gamma_{\text{Ab}}]/(1.72433)$$

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

Pressure computed at mean  $P$  -  $T$  value, 800 °C, 8 kbar for barometer Equation (xvi)

$$P_2 \text{ (kbar)} = [-1.869 + 0.0076T(\text{K}) + RT \ln K_{\text{ideal}} - 102.692X_{\text{Na}}^A - 35.251X_K^A - 15.969X_{\text{Na}}^{M4} \\ - 40.499X_{\text{Fe}}^{M13} + 93.069X_{\text{Al}}^{M2} + 130.750X_{\text{Fe}}^{M2} + 74.226X_{\text{Fe}^{3+}}^{M2} - 104.402X_{\text{Al}}^{T1} \\ - 2RT \ln \gamma_{\text{Ab}}]/(1.72433)$$

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