

**Full Length Research Paper**

## A Computer Programme for Estimation of Pressure Conditions in Metamorphic Rocks: Thermodynamic Basis and Uncertainties

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### ABSTRACT

Metamorphic processes tend to increase the degree of in homogeneity of preexisting natural system. Application of revised and recent thermodynamic parameters under equilibrium state help in determining precise thermobarometric estimates. In the present paper we have discussed thermodynamic modeling and uncertainties associated with it along with error propagation techniques. A new computer programme involving Garnet- Biotite-Plagioclase-Quartz equilibria. For a meaningful interpretation of P-T estimates, the uncertainties attached to these geological thermobarometry require further treatment by basic error propagation equation or involving Monte-Carlo error propagation routines.

### INTRODUCTION AND APPROACH

The process of change brought about in the rocks in respect of temperature, pressure and the activity of the fluids is termed as metamorphism and stated as Mohan et.al (1993):

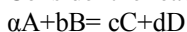
$$M = f(P, T, X_i), \quad i = 1 \text{ to } n_l$$

Under the fluid-absent state, the value of P, T in 2-D space can be uniquely defined through the equation of a straight line  $y = mx + c$ .

$$x = c_1 - c_2 / m_1 - m_2 \text{ and } y = m_2 c_1 - m_1 c_2 / m_2 - m_1.$$

This would form a basis for thermodynamic modeling of reaction equilibria.

Consider the reaction,



Under the condition of chemical equilibrium,

$$G^{P,T} = G^\circ + nRT \ln a$$

Where,

$G^\circ$  is standard molar Gibbs energy at 1 bar and specified temperature.

$n$  is the number of moles.

$R$  is Universal gas constant (1.987 cal  $k^{-1}$ ).

$a$  is activity of a phase component in that phase.

$G_A, G_B, G_C, G_D$ , for the above reaction are

$$G_A = G_A^\circ + \alpha RT \ln a_A$$

$$G_B = G_B^\circ + bRT \ln a_B$$

Thus

$$G_A + G_B = G_A^\circ + G_B^\circ + RT (\ln a_A^\alpha \cdot a_B^b), \text{ and}$$

$$G_C + G_D = G_C^\circ + G_D^\circ + RT (\ln a_C^c \cdot a_D^d).$$

Under equilibrium state

$$G_A^\circ + G_B^\circ + RT (\ln a_A^\alpha \cdot a_B^b) = G_C^\circ + G_D^\circ + RT (\ln a_C^c \cdot a_D^d).$$

Rearranging we have

$$(G_C^\circ + G_D^\circ) - (G_A^\circ + G_B^\circ) = -RT (\ln a_C^c \cdot a_D^d / a_A^\alpha \cdot a_B^b), \text{ which gives}$$

$$\Delta G_R^\circ = -RT \ln K$$

Where  $\Delta G_R^\circ$  is the molar Gibbs energy change of the reaction and  $K$  is equilibrium constant.  $\Delta G^\circ$  is approximately linear in temperature and pressure and may be replaced by

$A + BT + CP$ , Thus:

$$0 = A + BT + CP + RT \ln K$$

or,

$$\Delta G_{p, T=0} = \Delta H_{1, T} - T \Delta S_{1, T} + \Delta V (P-1) + RT \ln K$$

This is a simplified equation of standard state for a mineral equilibrium, where  $\Delta H, \Delta S, \Delta V$  denote changes in enthalpy, entropy and volume respectively. However, each of these terms need to be expanded to obtain a complete expression. To begin with, when a substance is heated at constant pressure, its enthalpy increases in

approximate proportion to its increase in temperature and is expressed by a characteristic constant of proportionality, the heat capacity (Cp).so long the trend in the increment is linear, the following approximation holds good  

$$(\delta H / \delta T)P = Cp$$

But when the entire range, is considered then we get

$$\int_{298}^T dH = \int_{298}^T (a+bT+cT^{-2}+dT^{-0.5}+eT^2)dT$$

(where a, b, c, d, e are experimentally determined constants for the phase of interest and T is the absolute temperature).

$$H^T = H^{298} + \int_{298}^T (a+bT+cT^{-2}+dT^{-0.5}+eT^2)dT$$

Similarly,

$$S^T = S^{298} + \int_{298}^T (aT^{-1}+b+cT^{-3}+dT^{-1.5}+eT) dT$$

(since d H=T d S)

Likewise simplification of the volume term is valid so long we assume that for geological calculations the volume of solids are independent of P-T. Also, because for solid–solid reactions, thermal expansion and compressibility tend to offset each other. Otherwise a rigorous execution requires it as function of P-T with the help of coefficient of isobaric thermal expansion ( $\alpha$ ) and isothermal compressibility ( $\beta$ ). The complex expression for volume term may be written as follows:

$$\int_1^P V_T(P)dT = v_{298}^0 [1 + \alpha_0(T-298) + \alpha_1/2(T^2-298^2) - \{ \beta_0/2 + \beta_1/6(P+2) \} (P-1)] (P-1)$$

The last factor, RT ln K is a combination of following;

$$RT \ln K = RT \ln (K_D \gamma)$$

Where  $K_D$  is distribution coefficient and  $\gamma$  is activity coefficient. If we assume ideal mixing, then,  $\gamma=1$ , but the complex nature of many solid solutions found in minerals demand for non ideal mixing.

The total molar Gibbs energy ( $G_T$ ) given by

$$G_T = G_{ID} + G_{EX}$$

Ideal excess

Mixing gibbs energy

Where  $G_{EX} = X_1X_2(W_{G1}X_2 + W_{G2}X_1)$

This is called a sub regular approximation where W is the Fit Parameter or Margules Parameter that helps in dealing with systems in which the phase separation occurs. They can be expanded to two-parameter margules model for a binary solution or regular ternary solution model.

Finally, to obtain the thermometric and barometric expression, we need to rearrange the simplified thermodynamic equation of standard state under equilibrium.

Thus,

$$(P-1)V/RT + \ln K_D = -\Delta H/RT + \Delta S/R$$

A graphical plot of  $\{ (P-1) \Delta V/RT + \ln K_D \}$

Verses  $1/T$  ( $^{\circ}K$ ) yields slope ( $-\Delta H/R$ ) and an intercept at  $0^{\circ} K (+\Delta S/R)$ , analogous to the equation of straight line discussed earlier. The expression for T ( $^{\circ}K$ ) and involve large V, P (bars) are stated below;

$$T (^{\circ}K) = -\Delta H - (P-1) \Delta V/R \ln K_D - \Delta S$$

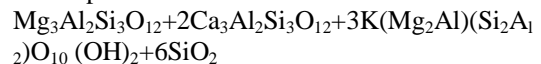
And

$$P (\text{bars}) = 1 + T (\Delta S - R \ln K_D) - \Delta H/\Delta V$$

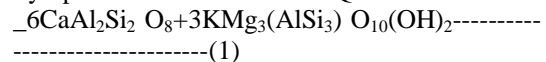
For a good thermometer, the exchange reaction should have small  $\Delta V$  and steep slope in P-T diagram. Likewise, for a good barometer, the net-transfer reaction should involve large  $\Delta V$ ,  $\Delta H$  and gentle slope in P-T diagram.

Garnet- Biotite-Plagioclase-Quartz equilibria provide a good geobarometric expression for pressure estimates in pelitic schists. In the present paper we develop a new computer programme for the above equilibria using the model of Wu et al. 2004. The GBPQ barometry is based on the following Mg and Fe-model equilibria (Höisch, 1990, 1991).

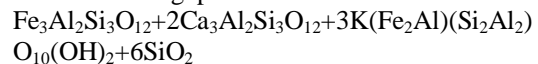
The expression for P1 and P2



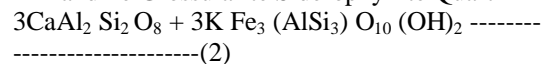
Pyrope Grossularite Enstatite Quartz



Anorthite Phlogopite and



Almandine Grossularite Siderophyllite Quartz



Anorthite Phlogopite

## COMPUTER PROGRAMMES

PROGRAM NAME: GBPQ.EXE

begin: CLS

BEEP

INPUT "Enter fe,mg,mn and ca of garnet", fegrt,  
mggrt, mngrt, cagrt

INPUT "Enter fe, mg,ti,AlVI of biotite", febt,  
mgbt, tib, albt

INPUT "Enter Ca,Na and K of plagioclase",  
caplag, naplag, kplag

i = fegrt + mngrt + mggrt + cagrt

fegrt = fegrt / i

mggrt = mggrt / i

cagrt = cagrt / i

almgrt = (fegrt ^ 3)

pygrt = (mggrt ^ 3)

grgt = (cagrt ^ 3)

spsgrt = (mngrt ^ 3)

i = febt + mgbt + tib + albt

febt = febt / i

mgbt = mgbt / i

tib = tib / i

albt = albt / i

annbt = (febt ^ 3)

phlbt = (mgbt ^ 3)

easbt = (27 / 4) \* ((mgbt ^ 2) \* albt)

sidrbt = (27 / 4) \* ((febt ^ 2) \* albt)

i = caplag + naplag + kplag

caplag = caplag / i

naplag = naplag / i

kplag = kplag / i

anplag = ((.25 \* caplag) \* (1 + caplag) ^ 2)

abplag = naplag

orplag = kplag

k1 = ((caplag ^ 6) \* (1 + caplag) ^ 12) \* (mgbt ^ 3)

k1 = k1 / (1259712# \* (mggrt ^ 3) \* (cagrt ^ 6) \* (albt ^ 3))

k2 = ((caplag ^ 6) \* (1 + caplag) ^ 12) \* (febt ^ 3)

k2 = k2 / (1259712# \* (fegrt ^ 3) \* (cagrt ^ 6) \* (albt ^ 3))

caa = ((.337 \* fegrt ^ 2) - (18.983 \* mggrt ^ 2) - (9.5725 \* fegrt \* mggrt) - (19.34 \* fegrt \* cagrt))

caa = caa - (4.665 \* fegrt \* mngrt) - (25.746 \* mggrt \* cagrt) - (38.938 \* mggrt \* mngrt) + (11.006 \* fegrt ^ 2 \* mggrt)

caa = caa - (.674 \* fegrt ^ 2 \* cagrt) - (11.986 \* mggrt ^ 2 \* fegrt) + (37.966 \* mggrt ^ 2 \* cagrt)

caa = caa + (46.02 \* mggrt ^ 2 \* mngrt) + (19.34 \* cagrt ^ 2 \* fegrt) + (25.746 \* cagrt ^ 2 \* mggrt)

caa = caa + (46.02 \* mngrt ^ 2 \* mggrt) + (19.145 \* fegrt \* mggrt \* cagrt) + (45.53 \* fegrt \* mggrt \* mngrt)

caa = caa + (9.333 \* fegrt \* cagrt \* mngrt) + (77.876 \* mggrt \* cagrt \* mngrt)

cab = ((.04 \* fegrt ^ 2) + (.068 \* mggrt ^ 2) + (.065 \* mngrt ^ 2) - (.0515 \* fegrt \* mggrt) + (.27 \* fegrt \* cagrt))

cab = cab + (.1765 \* fegrt \* mngrt) + (.28 \* mggrt \* cagrt) + (.207 \* mggrt \* mngrt) + (.13 \* cagrt \* mngrt) - (.1 \* fegrt ^ 2 \* mggrt)

cab = cab - (.08 \* fegrt ^ 2 \* cagrt) - (.048 \* fegrt ^ 2 \* mngrt) + (.068 \* mggrt ^ 2 \* fegrt) - (.136 \* mggrt ^ 2 \* cagrt)

cab = cab - (.076 \* mggrt ^ 2 \* mngrt) - (.27 \* cagrt ^ 2 \* fegrt) - (.28 \* cagrt ^ 2 \* mggrt) - (.13 \* cagrt ^ 2 \* mngrt)

cab = cab - (.048 \* mngrt ^ 2 \* fegrt) - (.076 \* mngrt ^ 2 \* mggrt) - (.13 \* mngrt ^ 2 \* cagrt)

cab = cab + (.103 \* fegrt \* cagrt \* mggrt) - (.14 \* fegrt \* mggrt \* mngrt)

cab = cab - (.353 \* fegrt \* cagrt \* mngrt) - (.414 \* mggrt \* cagrt \* mngrt)

cac = ((-1304! \* fegrt ^ 2) + (66114! \* mggrt ^ 2) + (1425! \* mngrt ^ 2) + (31326.5 \* fegrt \* mggrt) + (39864! \* fegrt \* cagrt))

cac = cac + (12356! \* fegrt \* mngrt) + (51518 \* mggrt \* cagrt) + (88610.5 \* mggrt \* mngrt) + (2850! \* cagrt \* mngrt) - (23244 \* fegrt ^ 2 \* mggrt)

cac = cac + (2608! \* fegrt ^ 2 \* cagrt) - (3234! \* fegrt ^ 2 \* mngrt) + (11344! \* mggrt ^ 2 \* fegrt) - (132228! \* mggrt ^ 2 \* cagrt)

cac = cac - (82498! \* mggrt ^ 2 \* mngrt) - (39864! \* cagrt ^ 2 \* fegrt) - (51518! \* cagrt ^ 2 \* mggrt) - (2850! \* cagrt ^ 2 \* mngrt)

cac = cac - (3234! \* mngrt ^ 2 \* fegrt) - (82498! \* mngrt ^ 2 \* mggrt) - (2850! \* mngrt ^ 2 \* cagrt)

cac = cac - (62653! \* fegrt \* cagrt \* mggrt) - (91682! \* fegrt \* mggrt \* mngrt)

cac = cac - (24712! \* fegrt \* cagrt \* mngrt) - (177221! \* mggrt \* cagrt \* mngrt)

fca = ((5.993 \* mggrt ^ 2) - (9.67 \* cagrt ^ 2) - (11.006 \* fegrt \* mggrt) + (.674 \* fegrt \* cagrt))

fca = fca - (9.5725 \* mggrt \* cagrt) - (22.765 \* mggrt \* mngrt) - (4.6665 \* mggrt \* mngrt)

$$\begin{aligned}
 & \text{cagrt} * \text{mngrt}) + (11.006 * \text{fegrt}^2 * \text{mggrt}) \\
 \text{fca} &= \text{fca} - (.674 * \text{fegrt}^2 * \text{cagrt}) - (11.986 * \\
 & \text{mggrt}^2 * \text{fegrt}) + (37.966 \\
 & * \text{mggrt}^2 * \text{cagrt}) \\
 \text{fca} &= \text{fca} + (46.02 * \text{mggrt}^2 * \text{mngrt}) + (19.34 \\
 & * \text{cagrt}^2 * \text{fegrt}) + \\
 & (25.746 * \text{cagrt}^2 * \text{mggrt}) \\
 \text{fca} &= \text{fca} + (46.02 * \text{mngrt}^2 * \text{mggrt}) + \\
 & (19.145 * \text{fegrt} * \text{mggrt} * \text{cagrt}) + \\
 & (45.53 * \text{fegrt} * \text{mggrt} * \text{mngrt}) \\
 \text{fca} &= \text{fca} + (9.333 * \text{fegrt} * \text{cagrt} * \text{mngrt}) + \\
 & (77.876 * \text{mggrt} * \text{cagrt} * \\
 & \text{mngrt}) \\
 \text{fcb} &= ((-.034 * \text{mggrt}^2) + (.135 * \text{cagrt}^2) + \\
 & (.024 * \text{mngrt}^2) + (.1 * \\
 & \text{fegrt} * \text{mggrt}) + (.08 * \text{fegrt} * \text{cagrt})) \\
 \text{fcb} &= \text{fcb} + (.048 * \text{fegrt} * \text{mngrt}) - (.0515 * \\
 & \text{mggrt} * \text{cagrt}) + (.07 * \text{mggrt} * \\
 & \text{mngrt}) + (.1765 * \text{cagrt} * \text{mngrt}) \\
 \text{fcb} &= \text{fcb} - (.1 * \text{fegrt}^2 * \text{mggrt}) - (.08 * \text{fegrt}^2 \\
 & * \text{cagrt}) - (.048 * \text{fegrt}^2 \\
 & * \text{mngrt}) \\
 \text{fcb} &= \text{fcb} + (.068 * \text{mggrt}^2 * \text{fegrt}) - (.136 * \\
 & \text{mggrt}^2 * \text{cagrt}) - (.076 * \\
 & \text{mggrt}^2 * \text{mngrt}) \\
 \text{fcb} &= \text{fcb} - (.27 * \text{cagrt}^2 * \text{fegrt}) - (.28 * \text{cagrt}^2 \\
 & * \text{mggrt}) - (.13 * \text{cagrt}^2 \\
 & * \text{mngrt}) \\
 \text{fcb} &= \text{fcb} - (.048 * \text{mngrt}^2 * \text{fegrt}) - (.076 * \\
 & \text{mngrt}^2 * \text{mggrt}) - (.13 * \\
 & \text{mngrt}^2 * \text{cagrt}) \\
 \text{fcb} &= \text{fcb} + (.103 * \text{fegrt} * \text{mggrt} * \text{cagrt}) - (.14 * \\
 & \text{fegrt} * \text{mggrt} * \text{mngrt}) - \\
 & (.353 * \text{fegrt} * \text{cagrt} * \text{mngrt}) - (.414 * \text{mggrt} * \\
 & \text{cagrt} * \text{mngrt}) \\
 \text{fcc} &= ((-5672! * \text{mggrt}^2) + (19932! * \text{cagrt}^2) \\
 & + (1617 * \text{mngrt}^2) + \\
 & (23244! * \text{fegrt} * \text{mggrt}) - (2608 * \text{fegrt} * \text{cagrt})) \\
 \text{fcc} &= \text{fcc} + (3234! * \text{fegrt} * \text{mngrt}) + (31326.5 * \\
 & \text{mggrt} * \text{cagrt}) + (45841! * \\
 & \text{mggrt} * \text{mngrt}) + (12356 * \text{cagrt} * \text{mngrt}) \\
 \text{fcc} &= \text{fcc} - (23244 * \text{fegrt}^2 * \text{mggrt}) + (2608 * \\
 & \text{fegrt}^2 * \text{cagrt}) - (3234 * \\
 & \text{fegrt}^2 * \text{mngrt}) \\
 \text{fcc} &= \text{fcc} + (11344! * \text{mggrt}^2 * \text{fegrt}) - \\
 & (1332228# * \text{mggrt}^2 * \text{cagrt}) - \\
 & (82498! * \text{mggrt}^2 * \text{mngrt}) \\
 \text{fcc} &= \text{fcc} - (39864! * \text{cagrt}^2 * \text{fegrt}) - (51518 * \\
 & \text{cagrt}^2 * \text{mggrt}) - (2850 \\
 & * \text{cagrt}^2 * \text{mngrt}) \\
 \text{fcc} &= \text{fcc} - (3234 * \text{mngrt}^2 * \text{fegrt}) - (82498 * \\
 & \text{mngrt}^2 * \text{mggrt}) - (2850 \\
 & * \text{mngrt}^2 * \text{cagrt}) \\
 \text{fcc} &= \text{fcc} - (62653! * \text{fegrt} * \text{mggrt} * \text{cagrt}) - \\
 & (91682 * \text{fegrt} * \text{mggrt} *
 \end{aligned}$$

$$\begin{aligned}
 & \text{mngrt}) - (24712 * \text{fegrt} * \text{cagrt} * \text{mngrt}) - \\
 & (177221 * \text{mggrt} * \text{cagrt} * \text{mngrt}) \\
 \text{mga} &= ((-5.503 * \text{fegrt}^2) - (12.873 * \text{cagrt}^2) \\
 & - (23.01 * \text{mngrt}^2) + \\
 & (11.986 * \text{fegrt} * \text{mggrt}) - (9.5725 * \text{fegrt} * \\
 & \text{cagrt})) \\
 \text{mga} &= \text{mga} - (22.765 * \text{fegrt} * \text{mngrt}) - (37.966 * \\
 & \text{mggrt} * \text{cagrt}) - (46.02 * \\
 & \text{mggrt} * \text{mngrt}) - (38.938 * \text{cagrt} * \text{mngrt}) \\
 \text{mga} &= \text{mga} + (11.006 * \text{fegrt}^2 * \text{mggrt}) - (.674 \\
 & * \text{fegrt}^2 * \text{cagrt}) - \\
 & (11.986 * \text{mggrt}^2 * \text{fegrt}) \\
 \text{mga} &= \text{mga} + (37.066 * \text{mggrt}^2 * \text{cagrt}) + \\
 & (46.02 * \text{mggrt}^2 * \text{mngrt}) + \\
 & (19.34 * \text{cagrt}^2 * \text{fegrt}) \\
 \text{mga} &= \text{mga} + (25.746 * \text{cagrt}^2 * \text{mggrt}) + \\
 & (46.02 * \text{mngrt}^2 * \text{mggrt}) + \\
 & (19.145 * \text{cagrt} * \text{mggrt} * \text{fegrt}) \\
 \text{mga} &= \text{mga} + (45.53 * \text{fegrt} * \text{mggrt} * \text{mngrt}) + \\
 & (9.333 * \text{fegrt} * \text{cagrt} * \\
 & \text{mngrt}) + (77.876 * \text{mggrt} * \text{cagrt} * \text{mngrt}) \\
 \text{mgb} &= ((.05 * \text{fegrt}^2) + (.14 * \text{cagrt}^2) + \\
 & (.038 * \text{mngrt}^2) - (.068 * \\
 & \text{fegrt} * \text{mggrt}) - (.0515 * \text{fegrt} * \text{cagrt})) \\
 \text{mgb} &= \text{mgb} + (.07 * \text{fegrt} * \text{mngrt}) + (.136 * \\
 & \text{mggrt} * \text{cagrt}) + (.076 * \text{mggrt} \\
 & * \text{mngrt}) + (.207 * \text{cagrt} * \text{mngrt}) \\
 \text{mgb} &= \text{mgb} - (.048 * \text{fegrt}^2 * \text{mngrt}) + (.068 * \\
 & \text{mggrt}^2 * \text{fegrt}) - (.136 * \\
 & \text{mggrt}^2 * \text{cagrt}) \\
 \text{mgb} &= \text{mgb} - (.28 * \text{cagrt}^2 * \text{mggrt}) - (.13 * \\
 & \text{cagrt}^2 * \text{mngrt}) - (.048 * \\
 & \text{mngrt}^2 * \text{fegrt}) \\
 \text{mgb} &= \text{mgb} - (.076 * \text{mngrt}^2 * \text{mggrt}) - (.132 * \\
 & \text{mngrt}^2 * \text{cagrt}) + (.103 \\
 & * \text{cagrt} * \text{mggrt} * \text{fegrt}) \\
 \text{mgb} &= \text{mgb} - (.14 * \text{fegrt} * \text{mggrt} * \text{mngrt}) - \\
 & (.353 * \text{fegrt} * \text{cagrt} * \text{mngrt}) - \\
 & (.414 * \text{mggrt} * \text{cagrt} * \text{mngrt}) \\
 \text{mgc} &= ((11622! * \text{fegrt}^2) + (25759! * \text{cagrt}^2) \\
 & + (41249! * \text{mngrt}^2) - \\
 & (11344! * \text{fegrt} * \text{mggrt}) + (31326.5 * \text{fegrt} * \\
 & \text{cagrt})) \\
 \text{mgc} &= \text{mgc} + (45841! * \text{fegrt} * \text{mngrt}) + \\
 & (132228! * \text{mggrt} * \text{cagrt}) + \\
 & (82498! * \text{mggrt} * \text{mngrt}) + (8610.5 * \text{cagrt} * \\
 & \text{mngrt}) \\
 \text{mgc} &= \text{mgc} - (23244 * \text{fegrt}^2 * \text{mggrt}) + (2608 \\
 & * \text{fegrt}^2 * \text{cagrt}) - \\
 & (3234! * \text{fegrt}^2 * \text{mngrt}) \\
 \text{mgc} &= \text{mgc} + (11344! * \text{mggrt}^2 * \text{fegrt}) - \\
 & (132228! * \text{mggrt}^2 * \text{cagrt}) - \\
 & (82498! * \text{mggrt}^2 * \text{mngrt}) \\
 \text{mgc} &= \text{mgc} + (39864! * \text{cagrt}^2 * \text{fegrt}) - \\
 & (51518! * \text{cagrt}^2 * \text{mggrt}) - \\
 & (2850! * \text{cagrt}^2 * \text{mngrt})
 \end{aligned}$$

```

mgc = mgc - (3234! * mngrt ^ 2 * fegrt) -
(82498! * mngrt ^ 2 * mggrt) -
(2850! * mmgrt ^ 2 * cagrt)
mgc = mgc - (62653! * fegrt * mggrt * cagrt) -
(91682! * fegrt * mggrt *
mngrt) - (24712! * fegrt * cagrt * mngrt)
mgc = mgc - (177221! * mggrt * cagrt * mngrt)
fa = ((20.6 * abplag ^ 2 * orplag) + (20.6 *
orplag ^ 2 * abplag ^ 2) - (10.3 *
abplag * orplag) + (20.6 * abplag * anplag *
orplag))
orplag ^ 2 * anplag) - (.12 * orplag ^ 2) - (.76 *
abplag * orplag))
fb = fb + (1.52 * abplag * anplag * orplag)
fc = ((-16942 * abplag ^ 2 * anplag) - (54640 *
abplag ^ 2 * orplag) -
(56452! * anplag ^ 2 * abplag) - (94792 * anplag
^ 2 * orplag))
fc = fc - (37620 * orplag ^ 2 * abplag) - (104936
* orplag ^ 2 * anplag) +
(8471 * abplag ^ 2) + (52468 * orplag ^ 2)
fc = fc + (56452 * abplag * anplag) + (100045.5
* abplag * orplag) +
(94792 * anplag * orplag) - (200091! * abplag *
orplag * anplag)
PRINT "xfe,xmg,xca and Xmn of grt", fegrt;
mggrt; cagrt; mngrt
PRINT "xfe,xmg,xtiand xalVi biotite", febt;
mgbt; tib; albt
PRINT "Xca,Xna and Xk", caplag; naplag, kplag
PRINT
"Caa,Cab,Cac,Fca,Fcb,Fcc,Mga,Mgb,Mgc,Fa,Fb
& Fc", caa; cab;
cac; fca; fcb; fcc; mga; mgb; mgc; fa; fb; fc
p: INPUT " temperature deg.c", t
t = t + 273
r = 8.314
CLS
FOR choice% = 1 TO 2
SELECT CASE choice%
CASE 1
PRINT "GBPQP1 Wu et.al(2004) ";
k1 = LOG(k1)
p1 = ((-24450.7) + (40.238 * t) + (59256.2 *
febt) + (5173.9 * (mgbt - albt))
+ (6393.4 * tib))
p1 = p1 + (.081 * (t * ((-r * k1) - (6 * fa) + mga
+ (2 * caa) - (788.7 * febt))
- ((6 * fc) + mgc + (2 * cac))))
p1 = p1 / 1 - (.081 * (-6 * fb + mgb + 2 * cab))
CASE 2
PRINT "GBPQP1 Wu et.al(2004) ";
k2 = LOG(k2)
p1 = ((-19871!) + (30.75 * t) + (66622.5 * (febt -
albt)) + (1363.1 * mgbt) -
(74704.2 * tib))

```

```

p1 = p1 + (.081 * (t * ((-r * k2) - (6 * fa) + fca +
(2 * caa) - (840.9 * febt) +
(52.2 * mgbt) + (840.9 * albt) + (111.2 * tib)) -
((6 * fc) + fcc + (2 * cac))))
p1 = p1 / 1 - (.081 * ((-6 * fb) + fcb + (2 * cab)))
END SELECT
PRINT p1; "bars "; p1 / 1000; "kbar"
NEXT choice%
END

```

However these geobarometric calibrations require reliable thermodynamic data set which should be internally consistence. An agreement between the experimentally determined reversal brackets and the calorimetric data within a range of plus or minus two standard deviations of the mean, provides an internally consistent data set. For this purpose, linear programming is employed that solves for n variables  $P_1, P_2, \dots, P_n$ , such that the linear objective function,

$$F_1 = q_1P_1 + q_2P_2 \dots + q_n P_n$$

assume a minimum value subject to two types of constraints.

$l_i < P_i < u_i$ , with  $i= 1$  to  $n$ .

$l_i$  and  $u_i$  denote the lower and upper bounds for the variable  $P_i$  and  $m$  general constraints of the form

$$\begin{aligned}
 I_1 &\leq a_{11}P_1 + \dots + a_{1n} P_n \leq u_1 \\
 I_2 &\leq a_{21}P_1 + \dots + a_{2n} P_n \leq u_2 \\
 I_m &\leq a_{m1}P_1 + \dots + a_{mn} P_n \leq u_m
 \end{aligned}$$

$q_i$  and  $a_{ij}$  are constant. It is important that  $l_i$  must be less than or equal to  $u_i$ ; when the two bound become identical, we have an equality. Moreover, the upper and the lower bound of the constraints are such that either can be  $\pm\infty$ . In many cases we need to optimize a non-linear (e.g. quadratic) objective function to a set of linear constraints using the following algorithm of the general form,

$$F_n = \sum_i \sum_j r_{ij} P_i P_j + \sum_i q_i P_i$$

It goes without saying that different sources of errors attached to thermo barometry either due to calibration or analytical technique, deserve a careful consideration for a meaningful discussion (Spear and Peacock, 1989; Spear and Florence, 1992). Error propagation formula is useful in such cases, which, for a function  $F$  of the variables gives  $Z_1, Z_2, Z_3$  etc., gives,

$$\sigma F^2 = (\delta F/\delta Z_1) \sigma Z_1^2 + (\delta F/\delta Z_2) Z_2^2 + 2 \sum_i \sum_j \rho Z_i Z_j (\delta F/\delta Z_i) (\delta F/\delta Z_j) \sigma Z_i^{0.5} \sigma Z_j^{0.5}$$

If we consider a sample of n values  $X_1, X_2, \dots, X_n$  drawn at random from normally distributed population, the sample mean is defined as (cf Johar and Srivastava 2006):

$$\bar{X} = X_1 + X_2 + \dots + X_n/n.$$

The standard deviation is defined as

$$S = \sqrt{\sum_{i=1}^n (X_i - \bar{X})^2 / (n-1)}$$

Where as sample variance  $S^2$  is given by

$$S^2 = \sum_{i=1}^n (X_i - \bar{X})^2 / (n-1)$$

If the secondary variable Y is a function of  $X_1, X_2, \dots, X_p$  which can be written as

$$Y = f(X_1, X_2, \dots, X_p)$$

Then the variance of Y can be estimated using the approximation (Bevington and Robinson 1992):

$$\sigma^2 Y = \text{Var } Y = \sum (\sigma Y / \delta X_i)^2 \text{Var } X_i + 2 \sum_{i=1}^p \sum_{j=1}^{i-1} (\delta Y / \delta X_i) (\delta Y / \delta X_j) \text{Cov } X_i X_j \dots (3)$$

where Var  $X_i$  is the variance of the invariable and Cov  $X_i X_j$  is the covariance between the  $i^{\text{th}}$  and  $j^{\text{th}}$  variable.

Equation (1) can be written in simplified form (if it is assume that covariance is zero)

$$\text{Var } Y = \sigma^2 Y = \sum_{i=1}^p (\delta Y / \delta X_i)^2 \text{Var } X_i \dots (4)$$

The above equation (4) is commonly used for calculating the variance of a function.

A further generalized matrix form of equation (3) is (Powell, 1985; Albarede, 1995):

$$V(Y) = J V(x) J^T$$

where J is Jacobian or matrix of first partial derivative of the y (P or T function),

V(y) is the variance-covariance matrix of the output elements,

V(x) is variance-covariance matrix of data vector x, and T denotes transpose.

Roddick (1987) emphasized that inspite of deriving the complete set of partial derivatives, the above could be easily achieved by numerical partial differentiation.

A computationally simpler approach involves Monte-Carlo propagation of compositional uncertainties (Anderson, 1976, Hodges and Crowley 1985) which is based on repeated calculation of a result, each time having input data changed by a random selection from its

error probability distribution. This method is valid only when the variables subject to uncertainty are independent.

Worley and Powell (2000) developed a method known as  $\Delta$ PT approach for the rigorous propagation of uncertainties. Further this method is independent of thermobarometric techniques and a-x models. This method has been applied to most recently used THERMOCALC (Holland and Powell 1998) thermo barometry.

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