Geothermobarometer based on coexisting garnet-orthopyroxene-plagioclase-quartz equilibria

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ABSTRACT

The garnet-orthopyroxene-plagolcase-quartz pairs are commonly found in the assemblages of basic granulites/charnockite and hence are suitable for estimating equilibrium temperature and pressure of most metamorphic rocks. The temperature based on garnet-orthopyroxene Fe-Mg exchange reaction and pressure based on net transfer reaction of garnet-orthopyroxene-plagioclase-quartz equilibria, mainly based on reactions, using the equation given by different workers.

i. 1/2 Ferrosilite + 1/3 Pyrope = 1/2 Enstatite + 1/3 Almandine.

ii. Ferrosilite + Anorthite = 2/3 Almandine + 1/3 Grossularite + Quartz

iii. Enstatite + Anorthite = 2/3 Pyrope + 1/3 Grossularite + Quartz.

The author developed software in visual basic with the executable code MPET3.EXE

Keywords: Exchange reaction, Net transfer reaction, Geothermobarometer, Granulite

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INTRODUCTION

One of the main goal of metamorphic petrology is to determine the pressure-temperature evolution of rocks in metamorphic terrains. Within this frame work, application of "geothermobarometry" in estimating the temperature and pressure conditions at which metamorphic rocks were once equilibrated has gained remarkable recognition in recent years. Impressive thermodynamic data sets and constantly improving activity models of minerals have substantially contributed to the success of rapidly evolving network (Knowledge) of (on) geothermobarometry. These P-T sensors have thus opened new vista for metamorphic petrology and eventually led to a much better understanding of metamorphic conditions prevailing in an area. Several geothermobarometers have been formulated during the last 35 years for garnet-orthopyroxene-plagioclasequartz assemblage (Thomas, H., 1995, 2003, 2005, 2006 and 2008). In order to make the calculation faster, the authors have developed a program, "MPET3" for pressure-temperature calculations, using the various formulations given by different workers.

The Fe-Mg exchange reaction between garnet (Gt) and orthopyroxene (Opx) (GOtherm) using equations given by Dhal (1980); Raith et al. (1983); Harley (1984); Sen and Bhattacharya (1984); Lee and Ganguly (1984); Perchuk et al. (1985); Lee and Ganguly (1988); Anovich and Podlesskii (1989); Perchuk and Lavrente'va (1990); Bhattacharya et al. (1991); and Lal (1993). The Fe-Mg exchange reaction of

garnet-orthopyroxene is as follows:

(i)
$$1/2 \text{ Fe}_2 \text{Si}_2 \text{O}_6 + 1/3 \text{ Mg}_3 \text{Al}_2 \text{Si}_3 \text{O}_{12} = 1/2 \text{ Mg}_2 \text{Si}_2 \text{O}_6 + 1/3 \text{ Fe}_3 \text{Al}_2 \text{Si}_3 \text{O}_{12}$$

1/2 Ferrosilite + 1/3 Pyrope = 1/2 Enstatite + 1/3 Almandine

To explain geobarometry properly, the authors have considered the net transfer reaction of garnet-orthopyroxene-plagioclase-quartz (GOPQ) equilibria. These mineral pairs are commonly found in the assemblages of basic granulites/ charnockite and hence are suitable for estimating equilibrium pressure of most metamorphic rocks. For this the authors have considered the equations of Newton (1978); Wells (1979); Newton and Perkins III (1982); Raith et al. (1983); Bohlen et al. (1983); Perkins and Chipera (1985); Moecher et al. 1988); Eckert et al. (1991); Bhattacharya et al. (1991); Holland and Powell (1985); calculated by Eckert et al. (1993); Berman (1988) calculated by Eckert et al. (1993); Berman (1990); calculated by Eckert et al. (1993) and Lal (1993). The equations of equilibrium are given below:

(ii)
$$Fe_2Si_2O_6 + CaAl_2Si_2O_8 = 2/3 Fe_3Al_2Si_3O_{12} + 1/3 Ca_3Al_2Si_3O_{12} + SiO_2$$

Ferrosilite + Anorthite = 2/3 Almandine+1/3 Grossularite + Quartz

(iii)
$$Mg_2Si_2O_6 + CaAl_2Si_2O_8 = 2/3Mg_3Al_2Si_3O_{12} + 1/3$$

 $Ca_3Al_2Si_3O_{12} + SiO_2$

Enstatite + Anorthite = 2/3 Pyrope + 1/3 Grossularite + Quartz

The program is written in Visual Basic and the executable code of the computer program is MPET3.EXE.

GARNET-ORTHOPYROXENE EXCHANGE THERMOMETERS

Exchange thermometers mainly imply the exchange of Fe and Mg between coexisting silicates. Exchange thermometers are characterized by small ΔV compared to large ΔH so that equilibrium constant isopleths have rather steep slope. A ratio of exchange cation in one phase divided by the same ratio in the second phase is generally taken as equilibrium constant for exchange-reactions. As an example Fe-Mg exchange between garnet and orthopyroxene is defined as K=(Fe/Mg)Gt/(Fe/Mg)Opx. This expression of partitioning of a pair of elements between two minerals is commonly referred to as distribution coefficient (KD).

This Fe-Mg exchange equilibrium has been formulated by a number of workers by obtaining standard state thermodynamic data either by empirical method or by experiments involving the crystalline solutions (garnet and orthopyroxene) between the two cations Fe and Mg. A brief description of various models is summarized as follows:

Dhal (1980)

Dhal (1980) proposed an empirical calibration for the garnetpyroxene geothermometer. The expression for geothermometer is as follows:

$$T(K) = [(1391 + 1509(X_{Fe} - X_{Mg})^{Gt} + 2810(X_{Ca}^{Gt}) + 2855(X_{Mn}^{Gt})/RlnK_{D}]$$

Where .

$$\begin{split} &K_{_{D}} = (X_{_{Fe}}/X_{_{Mg}})^{Gt} * (X_{_{Mg}}/X_{_{Fe}})^{Opx} = (Fe/Mg)^{Gt} * (Mg/Fe)^{Opx} \\ &i = (Ca + Mg + Fe + Mn)^{Gt}; \ X_{_{Mg}}^{\quad Gt} = (Mg/i)^{Gt}; \ X_{_{Ca}}^{\quad Gt} = (Ca/i)^{Gt}; \\ &X_{_{Mn}}^{\quad Gt} = (Mn/i)^{Gt} \ and \ X_{_{Fe}}^{\quad Gt} = (Fe/i)^{Gt} \\ &X_{_{Mg}}^{\quad Opx} = Mg/Mg + Fe); \ X_{_{Fe}}^{\quad Opx} = Fe/(Fe + Mg) \end{split}$$

Raith et al. (1993)

Raith et al. (1983) proposed an empirical calibration for granulites facies rocks. The expression for geothermometer is as follows:

$$T(K) = [1684/(InK_D + 0.334)]$$

Where, KD is same as defined by [4] Dahl (1980) for this as well as the subsequently discussed geothermometer.

Harley (1984)

Harley (1984) experimentally investigated the partitioning of Fe and Mg between garnet and orthopyroxene and aluminous pyroxene in the P-T range of 5-30 Kb and 800-1200 °C in the FeO-MgO-Al₂O₃-SiO₂ (FMAS) and CaO-FeO-MgO-Al₂O₃-SiO₂ system. Within error of the experimental data, orthopyroxene can be regarded as microscopically ideal. The effect of calcium on the Fe-Mg partitioning between garnet and orthopyroxene can be attributed to non-ideal Ca-Mg interaction in the garnet described by interactions terms:

 $W_{\text{Ca-Mg}}^{~~Gt}$ - $W_{\text{Ca-Fe}}^{~~Gt}$ = 1400 \pm 500 Cal/mol per site. The expression for geothermometer is as follows:

$$T(K) = [(3740 + 1400(X_{Ca}^{Gt}) + 22.86 P (Kb))/(RlnK_D + 1.96)]$$

Sen and Bhattacharya (1984)

They formulated the orthopyroxene-garnet geothermometer for which the values of ΔH° , ΔS° and ΔV° are:

 $\Delta H1000K = -2.713K$ Cal/mole; $\Delta S1000K = -0.787$ Cal/K mole and $\Delta V0298K = -0.221$ Cal/bar.

The expression of geothermometer is as follows:

$$\begin{split} T(K) &= [(2713 + 3300(X_{Ca}^{~Gt}) + 195(X_{Fe} - X_{Mg})^{Gt} + 0.022(P-1))/\\ &(1.9872 * InK_{D} + 0.787 + 1.5(~X_{Ca}^{~Gt}))] \end{split}$$

Their expression for geothermometer includes interaction parameters (W) for Ca as well as Fe-Mg mixing in garnet.

Lee and Ganguly (1984)

Lee and Ganguly (1984) experimentally determined the Fe-Mg exchange for garnet-orthopyroxene pairs. Empirical adjustment form natural data in terms of Ca and Mn lead to the following expression.

$$T(K) = [(2187+1510(X_{Ca}-X_{Mn})^{Gt}+8.6*P(Kb))/(InK_{D}+1.071)]$$

Perchuk et al. (1995)

The calibrated value for Fe-Mg exchange reaction given by [15] Perchuk et al. (1981) is as follows:

$$\Delta H^o_{970}$$
 K = - 4766 Cal.; ΔS^o_{970} K = -2.654 Cal/K and ΔV_{298} K = - 0.0234 Cal/bar

Besides the non-ideal mixing of Ca in garnet, they also considered the interaction parameters of alumina and Fe⁺²- Mg mixing in orthopyroxene in their equation for geothermometer.

$$\begin{split} T(K) &= [(4766 + 2533*(X_{Fs} - X_{En})^{Opx} - 5214*X_{Al}^{Opx} + 5704*\\ X_{Ca}^{Gt} + 0.023*P(bar))/(RlnK_D + 2.65 + 1.86*(X_{Fs} - X_{En})^{Opx} + \\ 1.242*X_{Ca}^{Gt}] \\ Where & i = (Fe + Mg + Al/2)\\ X_{Fe}^{Opx} &= Fe/i \; ; \; X_{Mg}^{Opx} = Mg/i \; and \; X_{Al}^{Opx} = Al/2 \; / \; i \end{split}$$

Lee and Ganguly (1988)

They refined their earlier equation proposed in 1984, through their experimental data Fe-Mg exchange reaction between garnet and orthopyroxene.

$$T(K) = [(1981 + 1509.66*(X_{Ca}-X_{Mn})^{Gt} + 11.91*P(Kb))/(InK_{D} + 0.97)]$$

Aranovich and Podlesskii (1989)

They proposed an empirical calibration for garnet orthopyroxene assemblage:

$$\begin{split} T(K) &= [((P\text{-}1)*0.02342 + 4766 - A + (X_{Fe}\text{-}X_{Mg})^{Opx}*2372 - 5204*X_{Al}^{Opx})/(RInK_D + 2.654 + B + 1.69*(X^{Fe}\text{-}X^{Mg})^{Opx})] \end{split}$$
 where

$$A = \begin{bmatrix} -626*X2_{Ca} - 6642*X_{Fe}*X_{Ca} - 8100*X_{Mg}*X_{Ca} + X_{Ca}*(X_{Mg} - X_{Fe})*1051.5 \end{bmatrix}$$

$$B = \begin{bmatrix} 1.266*X^{2}_{Ca} + 2.836*X_{Fe}*X_{Ca} + 3.0*X_{Mg}*X_{Ca} + X_{Ca}*(X_{Mg} - X_{Fe})*(-0.908) \end{bmatrix}$$

Perchuk and Lavrente'va (1990)

They proposed the following expression for garnet orthopyroxene geothermometer based on experimental data and thermodynamics.

$$\begin{split} T(K) &= [(4066 - 347*(X_{Mg} - X_{Fe})^{OPX} - 17484*X_{Al}^{OPX} \\ &+ 5769X_{Ca}^{Gt} + 23.42*P(Kb))/(1.987*InK_{D} + 2.143 + \\ &0.0929*(X_{Mg} - X_{Fe})^{OPX} - 12.8994*X_{Al}^{OPX} + 3.846*X_{Ca}^{Gt})] \\ Where &i = (Fe + Mg + Al/2) \\ X_{Fe}^{Opx} &= Fe/i; X_{Mo}^{Opx} = Mg/i \ and \ X_{Al}^{Opx} = (Al/2)/i \end{split}$$

Bhattacharya et al. (1991)

The expression for Gt-Opx geothermometer proposed by them is as follows:

$$T(K) = [(1611 + 0.012(P-1) + 906X_{Ca}^{Gt} + A + 477(2*X_{Mg}-1)) + (1000 + 0.796)]$$

$$(InK_D + 0.796)]$$

The above expression can be used to estimate temperature from orthopyroxene-garnet pairs subject to the following conditions: I. Grossularite contents in garnet should be < 30 mol %, II. Spessartine content should be low ($X_{Mn} < 0.05$) such as Mg/Mg <3, III. Pressure should be less then 15Kb. At higher pressure the excess volume of mixing in Ca-Fe and Ca-Mg binaries in garnet could markedly affect the In KD-T relations:

Lal (1993)

Lal (1993) proposed the empirical calibration for garnet orthopyroxene thermo-meter. His equation is applicable for crustal rocks containing garnet with low Mn content (<5 mol %) as well as mantle derived rocks ($Cr_2O_2 < 5$ wt%).

$$\begin{split} T(K) &= \left[(3367 + (P\text{-}1)*0.024 - A - 948*(X_{Fe}\text{-}X_{Mg})^{Opx} - 1950 \right. \\ &X_{Al}^{Opx)} / (1.987*InK_D + 1.634 + B - 0.34*(X_{Fe}\text{-}X_{Mg})^{Opx)} \right] \\ Where, \end{split}$$

$$A = [-1256*X_{Mg}^{2} - 2880*X_{Fe}^{2} + 8272*(X_{Mg}^{4}X_{Ca})^{Gt} + 812*X_{Ca}^{Gt*}(X_{Mg}^{4} - X_{Fe}^{2})^{Gt} + 90X_{Ca}^{2} - 2340*X_{Ca}^{Gt*}(X_{Fe}^{4} + X_{Mg}^{4}) - 3047*X_{Mg}^{4}X_{Ca}^{2} - 1813*X_{Fe}^{4}X_{Ca}^{4} + X_{Ca}^{2}*(X_{Fe}^{4} - X_{Mg}^{4})^{4}(-4498)].$$

$$\begin{split} B = & [1.0*X_{Mg}^2 + 1.7*X_{Fe}^2 - 5.4*X_{Fe}*X_{Mg} - 0.35*X_{Ca}*(X_{Mg} - X_{Fe}) + 1.5*X_{Ca}^2 + 1.666*X_{Ca}*(X_{Fe} + X_{Mg}) + 0.332*X_{Fe}*X_{Ca} + X_{Ca}*(X_{Fe} - X_{Mg})*1.516] \end{split}$$

GARNET-ORTHOPYROXENE-PLAGIOCLASE-QUARTZ EQUILIBRIA

Vapour-absent, solid-solid, net transfer equilibria serve as potential geobarometer as they involve substantial volume change and have small positive slope in P-T space. The assemblage garnet-orthopyroxene-plagioclase-quartz in basic granulites represents a potential geobarometer. The four-phase assemblage is represented by the reaction (Thomas 1995, 2003, 2005, 2006 and 2008; Joshi et al. 1993):

$$P_{Mg}$$
 Reaction: $CaAl_2Si_2O_8 + Mg_2Si_2O_6 = 2/3 Mg_3Al_2Si_3O_{12} + 1/3 Ca_3Al_2Si_3O_{12} + SiO_2$
Anorthite + Enstatite = 2/3 Pyrope + 1/3 Grossularite +

Quartz

$$K_{1} = \mathbf{a}_{Ca}^{Gt*} (\mathbf{a}_{Mg}^{Gt})^{2} / \mathbf{a}_{An}^{plag*} \mathbf{a}_{Mg}^{Opx}; K_{B1} = \mathbf{a}_{Ca}^{Gt*} (\mathbf{a}_{Mg}^{Gt})^{2} / \mathbf{a}_{An}^{plag*} (\mathbf{a}_{Mg}^{Opx})^{2}$$

 P_{Fe} Reaction: $CaAl_2Si_2O_8 + Fe_2Si_2O_6 = 2/3 Fe_3Al_2Si_3O_{12} + 1/3 Ca_3Al_2Si_3O_{12} + SiO_2$

Anothite + Ferrosilite = 2/3 Almandine + 1/3 Grossularite + Ouartz

$$K_2 = {m a}_{Ca}^{Gt*} ({m a}_{Fe}^{Gt})^2 / ({m a}_{An}^{plag*} {m a}_{Fe}^{Opx}); \ K_{2B} = {m a}_{Ca}^{Gt*} ({m a}_{Fe}^{Gt})^2 / ({m a}_{An}^{plag*} ({m a}_{Fe}^{Opx})^2)$$

To desired barometry properly the author separated the equations given by different workers on the basis of garnet (Thomas 2006) and orthopyroxene activities:

(i) Regular Solution model for activities of garnet

$$\begin{aligned} & \mathbf{a}_{\text{Ca}}^{\text{Gt}} = X_{\text{Ca}}^{*} \exp \left[\{ W_{\text{CaFe}}^{*} (X_{\text{Fe}}^{2})^{\text{Gt}} + W_{\text{CaMg}}^{*} (X_{\text{Mg}}^{2})^{\text{Gt}} + (W_{\text{CaFe}}^{} + W_{\text{CaMg}}^{} - W_{\text{FeMg}}^{})^{*} X_{\text{Fe}}^{\text{Gt}} * X_{\text{Mg}}^{}^{\text{Gt}} \} / \text{RT} \right] \end{aligned}$$

$$\begin{aligned} & \boldsymbol{a}_{Mg}^{~~Gt} = \boldsymbol{X}_{Mg} * exp \left[\{ \boldsymbol{W}_{CaMg} * (\boldsymbol{X}_{Ca}^{~2})^{Gt} + \boldsymbol{W}_{FeMg} * (\boldsymbol{X}_{Fe}^{~2})^{Gt} + (\boldsymbol{W}_{CaMg} \\ & + \boldsymbol{W}_{FeMg} - \boldsymbol{W}_{CaFe}) * \boldsymbol{X}_{Ca}^{~Gt} * \boldsymbol{X}_{Fe}^{~Gt} \} / RT \right] \end{aligned}$$

$$\begin{array}{l} {{\bm{a}_{{{\text{Fe}}}}}^{\text{Gt}}} = {X_{{{\text{Fe}}}}}* \exp \left[{\{{{W_{{\text{CaFe}}}}^*}\left({{X_{{\text{Ca}}}}} \right)^{\text{Gt}} + {W_{{{\text{FeMg}}}}}*\left({{X_{{{\text{Mg}}}}}^2} \right)^{\text{Gt}} + \left({{W_{{\text{CaFe}}}}} + {W_{{{\text{FeMg}}}}} \right)^{\text{Gt}}} \right] \\ {W_{{{\text{FeMg}}}}} - {W_{{{\text{CaMg}}}}})* \; {X_{{{\text{Ca}}}}}^{\text{Gt}} * X_{{{\text{Mg}}}}^{\text{Gt}}} / RT \\ \end{array}$$

(ii) Regular Solution model for activities of orthopyroxene:

$$\begin{array}{l} {{\bm{a}_{{\rm{Mg}}}}^{{\rm{Opx}}}} = {\rm{ }}{{\rm{ }}{{\rm{ }}{{\rm{ }}{\rm{ }}{\rm{$$

$$\begin{aligned} & \mathbf{a}_{\text{Fe}}^{\text{Opx}} = X_{\text{Fe}}^{*} \exp \left[\{ W_{\text{MgFe}}^{*} (X_{\text{Mg}}^{\text{Opx}})^{2} + W_{\text{FeAl}}^{*} (X_{\text{Al}}^{\text{Opx}})^{2} + (W_{\text{MgFe}}^{*} + W_{\text{FeAl}}^{*} - W_{\text{MgAl}}^{\text{Opx}} X_{\text{Mg}}^{\text{Opx}} X_{\text{Al}}^{\text{Opx}} \} / RT \right] \end{aligned}$$

$$X_{Mg}^{\ Opx}=Mg/i;\ X_{Fe}^{\ Gt}=Fe/i\ ;\ X_{Al}^{\ Opx}=(Al/2)/i\ and\ i=(Mg+Fe+Al/2)$$

(iii) Sub-regular solution model of garnet mixing by Ganguly and Saxena (1984) and Thomas (2006):

$$\begin{aligned} & \mathbf{a}_{\text{Mg}}^{\text{Gt}} = \mathbf{X}_{\text{Mg}} * \exp * \left\{ \left[\mathbf{X}_{\text{Fe}}^{2} \left[\mathbf{W}_{\text{MgFe}} + 2 * \mathbf{X}_{\text{Mg}} * \left(\mathbf{W}_{\text{FeMg}} - \mathbf{W}_{\text{MgFe}} \right) \right] + \right. \\ & \left. \mathbf{X}_{\text{Ca}}^{2} * \left[\mathbf{W}_{\text{MgCa}} + 2 * \mathbf{X}_{\text{Mg}} * \left(\mathbf{W}_{\text{CaMg}} - \mathbf{W}_{\text{MgCa}} \right) \right] + \mathbf{X}_{\text{Fe}} * \mathbf{X}_{\text{Ca}} * \left[1/2 * \left(\mathbf{W}_{\text{FeMg}} + \mathbf{W}_{\text{MgFe}} + \mathbf{W}_{\text{CaMg}} + \mathbf{W}_{\text{MgCa}} - \mathbf{W}_{\text{FeCa}} - \mathbf{W}_{\text{CaFe}} \right) + \mathbf{X}_{\text{Mg}} * \left(\mathbf{W}_{\text{FeMg}} - \mathbf{W}_{\text{MgFe}} + \mathbf{W}_{\text{CaMg}} - \mathbf{W}_{\text{MgCa}} \right) + \left(\mathbf{X}_{\text{Fe}} - \mathbf{X}_{\text{Ca}} \right) * \left(\mathbf{W}_{\text{FeCa}} - \mathbf{W}_{\text{CaFe}} \right) - \left(1 - 2 * \mathbf{X}_{\text{Mg}} \right) * \mathbf{C}_{123} \right] \right] / R * T \end{aligned}$$

$$\begin{aligned} & \mathbf{a}_{\text{Ca}}^{\text{Gt}} = X_{\text{Ca}}^{*} \exp^{*} \left\{ \left[X_{\text{Mg}}^{2} * \left[W_{\text{CaMg}} + 2^{*} X_{\text{Ca}}^{*} \left(W_{\text{MgCa}}^{} - W_{\text{CaMg}}^{} \right) \right] \right. \\ & + X_{\text{Fe}}^{2} * \left[W_{\text{CaFe}}^{} + 2^{*} X_{\text{Ca}}^{*} \left(W_{\text{FeCa}}^{} - W_{\text{CaFe}}^{} \right) \right] + X_{\text{Mg}}^{*} X_{\text{Fe}}^{*} * \left[1/2 * \left(W_{\text{MgCa}}^{} + W_{\text{CaMg}}^{} + W_{\text{FeCa}}^{} + W_{\text{CaFe}}^{} - W_{\text{MgFe}}^{} - W_{\text{FeMg}}^{} \right) + X_{\text{Ca}}^{*} \left(W_{\text{MgCa}}^{} + W_{\text{CaMg}}^{} + W_{\text{FeCa}}^{} - W_{\text{CaFe}}^{} \right) + \left(X_{\text{Mg}}^{} - X_{\text{Fe}}^{} \right) * \left(W_{\text{MgFe}}^{} - W_{\text{FeMg}}^{} \right) - \left(1-2 \left(X_{\text{Ca}}^{} \right) * C_{123}^{} \right) \right] / R^{*}T \end{aligned}$$

$$\begin{aligned} & \mathbf{a}_{\text{Fe}}^{\text{ Gt}} = \ X_{\text{Fe}} * \exp * \{ [X_{\text{Mg}}^{2} \ [W_{\text{FeMg}} + 2 * X_{\text{Fe}} * (W_{\text{MgFe}} - W_{\text{FeMg}})] \\ & + X_{\text{Ca}}^{2} * [W_{\text{FeCa}} + 2 * X_{\text{Fe}} * (W_{\text{CaFe}} - W_{\text{FeCa}})] + X_{\text{Mg}} * X_{\text{Ca}} * [1/2 * (W_{\text{MgFe}} + W_{\text{FeMg}} + W_{\text{CaFe}} + W_{\text{FeCa}} - W_{\text{MgCa}} - W_{\text{CaMg}}) + X_{\text{Fe}} * (W_{\text{MgFe}} - W_{\text{FeMg}} + W_{\text{CaFe}} - W_{\text{FeCa}}) + (X_{\text{Mg}} - X_{\text{Ca}}) * (W_{\text{MgCa}} - W_{\text{CaMg}}) - (1-2 * X_{\text{Fe}}) * C_{123}]] / R*T \} \end{aligned}$$

Where,

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$$X_{Mg}^{~~Gt}=Mg/i;~X_{Fe}^{~~Gt}=Fe/i~;~X_{Ca}^{~~Gt}=Ca/i~and~i=(Mg+Mn+Fe+Ca)^{Gt}$$

Equations based on regular solution models Newton (1978)

Newton (1978) presented a barometer on the basis of experimental and thermodynamic studies and his formulation is as follows:

$$\begin{aligned} & P_{_{Mg}} = 1 + \left[1370 + T*(7.03 + RInK_{_{1}})\right] / 0.538 \\ & Where, \ K_{_{1}} = \boldsymbol{a}_{_{Ca}}^{^{Gt}}*(\boldsymbol{a}_{_{Mg}}^{^{Gt}})^{2} / \boldsymbol{a}_{_{An}}^{^{Plag}}*\boldsymbol{a}_{_{Mg}}^{^{Opx}} \end{aligned}$$

Newton used in his equation the activity of garnet based on regular solution mode.

 $\begin{array}{l} \mbox{Where $W_{\mbox{\tiny CaMg}} = 3200$ Cal; $W_{\mbox{\tiny CaFe}} = 0$; $W_{\mbox{\tiny MgFe}} = 2500$ Cal and ${\bf a}_{\mbox{\tiny An}}^{\mbox{\tiny Opx}} = X_{\mbox{\tiny An}}^{\mbox{\tiny An}} * 1.28$; ${\bf a}_{\mbox{\tiny Mg}}^{\mbox{\tiny Opx}} = X_{\mbox{\tiny Mg}}^{\mbox{\tiny M_1}} * X_{\mbox{\tiny Mg}}^{\mbox{\tiny M_2}} \mbox{\tiny (Formula based on 6 oxygen basis) and $X_{\mbox{\tiny Mg}} = Mg/(Mg + Fe)$} \\ X_{\mbox{\tiny Mg}}^{\mbox{\tiny MI}} = [1 - (Al^{\mbox{\tiny Vi}} + Fe^{+3} + Ti + Cr)] * X_{\mbox{\tiny Mg}}; $X_{\mbox{\tiny Mg}}^{\mbox{\tiny M2}} = [1 - (Mn + Ca + Na + K)] * X_{\mbox{\tiny Mg}}; $R = 1.987$ cal/mol. \\ \end{array}$

Wells (1979)

Wells (1979) has given an equation for barometer based on empirical studies, his equation is as follows:

$$P_{Mg} = 1 + [3300 + T * (6.26 + RlnK_1)] / 0.56771$$

Where K_1 , \mathbf{a}_{An}^{plag} and \mathbf{a}_{Mg}^{Opx} same as given in Newton (1978) and $W_{CaMg} = 3820$ Cal; WCaFe = 1000 Cal and $W_{MgFe} = 0$ for activities of garnet.

Revision by Raith et al. (1983)

Raith et al. (1983) revised the equation given by Wells (1979), they revised on the basis of activities. They used the garnet activity same as in Newton and Perkins (1982) and aMgOpx same as in Newton (1978) and activity of anorthite in plagioclase is given below:

$$\mathbf{a}_{An}^{plag} = X_{An} * (1 - X_{An}/4) * exp [(1 - X_{An})2 (2050 + 9392 * X_{An}) / RT]$$

Newton and Perkins III (1982)

Newton and Perkins III (1982) gave thermodynamic calibration of geobarometer based on the assemblage's garnet-plagioclase-orthopyroxene-quartz. The equation proposed by them is given below:

$$P_{Mg} = 1 + [2237 + T * (7.417 + RlnK_1)] / 0.567$$

Where K_1 is same as Newton (1978), \mathbf{a}_{Mg}^{Opx} same as in Newton (1978) model \mathbf{a}_{An}^{Plag} same as in Wells (1979) model and activity of garnet calculated through regular solution model. They used the margulus.

$$W_{_{CaMg}} = 3300$$
 - 1.5 * T(K) Cal; $W_{_{CaFe}} = 0$ Cal and $W_{_{MgFe}} = 0$

Eckert et al. (1991)

Eckert et al. (1991) investigated the ΔH of reaction and recalibrated the garnet-pyroxene-plagioclase-quartz geobarometer in the CMAS systems by solution calorimetry.

The equation proposed by them is given below: $P_{M\sigma} = 1 + [1958 + T* (7.4092 + RlnK_1)] / 0.5399$

Where K_1 , a_{Mg}^{Opx} and aAnplag same as Newton and Perkins III (1982).

Bohlen et al. (1983)

Bohlen et al. (1983) proposed the equation based on thermodynamics and phase equilibria. The equation proposed by them is as follows:

$$P_{E_p} = 1 + [T * (9.1255 + RlnK_2) - 3705] / 0.6115$$

Where $K_2 = a_{Ca}^{Gt} * (\boldsymbol{a}_{Fe}^{Gt})^2 / (\boldsymbol{a}_{An}^{Plag} * \boldsymbol{a}_{Fe}^{Opx})$ and activity of garnet calculated through regular solution model:

$$\begin{split} W_{_{CaMg}} &= 4507.6 - 1.2 * T(K) \; Cal; \; W_{_{CaFe}} = 1377.6 - 1.2 * T(K) \\ Cal \; and \; W_{_{MgFe}} &= 3807.6 - 1.2 * T(K); \; \boldsymbol{a}_{_{An}}^{^{plag}} = X_{_{An}} * 1.28 \; and \\ X_{_{An}} &= Ca/(Ca + Na + K)^{Plag} \end{split}$$

$$\mathbf{a}_{Fe}^{Opx} = X_{Fe}M_1 * X_{Fe}M_2, X_{Fe}M_1 = [1 - (Al^{vi} + Fe + 3 + Ti + Cr] * X_{Fe}];$$

$$X_{Fe}^{\ M2}$$
 = [1- (Mn + Ca + Na + K) * X_{Fe}]* X_{Fe} and $X_{Fe}^{\ }$ = Fe/(Mg + Fe)^{Opx}

Perkins and Chipera (1985)

Perkins and Chipera (1985) gave an empirical calibration for garnet-orthopyroxene -plagioclase-quartz barometry. They calculated the activity of garnet through sub-regular mixing in garnet at 750°C using equation given by Ganguly and Saxena, (1984). They solution used the following margulus parameters for activity:

$$W_{FeMg} = 200 \text{ Cal}; W_{MgFe} = 2500; W_{CaMg} = 2515.5; W_{MgCa} = -534.5; W_{CaFe} = -2164.5; W_{FeCa} = 3085.5 \text{ and } C123 = 0, \, \boldsymbol{a}_{Mg}^{Opx}$$
 as in Newton (1978) and $\boldsymbol{a}_{Fe}^{Opx}$ as in Bohlen et al. (1983).

The proposed equation is as follows:

$$\begin{split} &P_{\text{Mg}} = 1 + [\text{T*} (7.335 + \text{RlnK}_{1}) + 1310] / 0.5408 \\ &\text{Where } K_{1} = \mathbf{a}_{\text{Ca}}^{\text{Gt}} * (\mathbf{a}_{\text{Mg}}^{\text{Gt}})^{2} / \mathbf{a}_{\text{An}}^{\text{Plag}} * \mathbf{a}_{\text{Mg}}^{\text{Opx}} \\ &P_{\text{Fe}} = 1 + [\text{T*} (8.364 + \text{RlnK2}) - 2247] / 0.5849 \\ &\text{Where } K2 = \mathbf{a}_{\text{Ca}}^{\text{Gt}} * (\mathbf{a}_{\text{Fe}}^{\text{Gt}})^{2} / (\mathbf{a}_{\text{An}}^{\text{Plag}} * \mathbf{a}_{\text{Fe}}^{\text{Opx}}) \\ &\text{and } \mathbf{a}_{\text{An}}^{\text{plag}} = X_{\text{An}} (1 - X_{\text{An}})^{2} / 4 * \exp[(1 - X_{\text{An}})^{2} * (2050 + 9392 * X_{\text{An}}) / (1.987 * 1023)] \end{split}$$

Moecher et al. (1988)

Moecher et al. (1988) proposed the empirical calibration for pyroxene-garnet-plagioclase-quartz geobarometer. They calculated the activity of garnet through subregular solution mixing in garnet using equation of Ganguly and Saxena (1984). $\mathbf{a}_{\mathrm{Mg}}^{\mathrm{Opx}}$ as in Newton (1978), $\mathbf{a}_{\mathrm{Fe}}^{\mathrm{Opx}}$ as in Bohlen et al. (1983) and $\mathbf{a}_{\mathrm{An}}^{\mathrm{Plag}}$ same as in wells (1979). They used the margulus parameters for garnet activity which is as follows:

$$\begin{aligned} &W_{\text{FeMg}} = 200 \text{ Cal; } W_{\text{MgFe}} = 2500; W_{\text{CaMg}} = 4047\text{-}1.5\text{*T; } W_{\text{MgCa}} = \\ &1000\text{-}1.5\text{*T; } W_{\text{CaFe}} = 150\text{-}1.5\text{*T; } W_{\text{FeCa}} = 4038\text{-}1.5\text{*T and } C_{123} \\ &= \text{-}\ 4640 \end{aligned}$$

The equation given by them is as follows:

$$\begin{split} &P_{_{Fe}} = 1 + \left[T * (9.353 + RlnK_{_{2}}) - 3244\right] / 0.61233 \\ &Where \; K_{_{2}} = \boldsymbol{a}_{_{Ca}}^{^{Gt}} * (\boldsymbol{a}_{_{Fe}}^{^{Gt}})^{2} / \, \boldsymbol{a}_{_{An}}^{^{Plag}} * \, \boldsymbol{a}_{_{Fe}}^{^{Opx}} \end{split}$$

Aranovich and Podlesskii (1989)

Aranovich and Podlesskii (1989) gave the equation for simultaneously operating reactions. They calculated the activity of garnet through sub-regular solution of mixing in garnet using equation of Ganguly and Saxena (1989). They used the margulus parameter for activity of garnet as follows:

$$W_{_{FeMg}} = 0$$
 Cal; $W_{_{MgFe}} = 0$; $W_{_{CaMg}} = 4050$ - 1.5*T; $W_{_{MgCa}} = 1000$ - 1.5*T;

 $W_{CaFe} = -3321 + 1.481*$ T; $W_{FeCa} = 374 - 0.234*$ T and $C_{123} = 0$ and calculated the activity of Mg in Opx (\mathbf{a}_{Mg}^{Opx}), through regular solution model of orthopyroxene mixing model.

Where
$$W_{MgFe} = -2372 + 1.69*T$$
; $W_{FeAl} = -6441$ and $W_{MgAl} = -1237$.

The proposed equation is given below:

$$\begin{split} &P_{_{Mg}} = 1 + [522 + T* (8.794 + RlnK1B) / (0.56156 + \\ &0.285* (X_{_{Al}}{^{Opx}})^2 - 1/3* \left[(0.075 - 4.566* (0.2 - X_{_{Ca}}{^{Gt}})^2) \right]) \end{split}$$

Where

where ,
$$\begin{split} &X_{Al}^{Opx} = (Al/2) \, / \, [(Al/2) + Mg + Fe^2]; \\ &\mathbf{a}_{An}^{~~plag} = X_{An}^{~~*} \exp \{ (1 - X_{Ca})^2 * [W_{CaNa}^{~} + 2 * X_{Ca}^{~*} * (W_{NaCa}^{~} - W_{CaNa}^{~})] \} / \, (R * T) \\ &W_{CaFe}^{~} = 3321 + 1481 * T; \, W_{FeCa}^{~} = 374 - 0.234 * T \, \text{and} \, \, C_{123}^{~} = 0; \\ &W_{CaNa}^{~} = 1980 - 1.526 * \, T \, Cal; \\ &W_{NaCa}^{~} = 6860 - 3.784 * T \, Cal \end{split}$$

Bhattacharya et al. (1991)

Bhattacharya et al. (1991) gave an improved set of a-X parameters for Fe-Mg-Ca garnets and refinements of the orthopyroxene-garnet-plagioclase-quartz barometer. They calculated the activity of garnet through sub-regular solution mixing in garnet at 1000 K using equation of Ganguly and Saxena (1984) and aAnPlag at 750°C as given in Perkins and Chipera (1985). They used the margulus values for garnet activity as follows:

$$\begin{split} &W_{\text{FeMg}} = 270 \text{ Cal; } W_{\text{MgFe}} = 1482; W_{\text{CaMg}} = 1800; W_{\text{MgCa}} = 1800; \\ &W_{\text{CaFe}} = 0; W_{\text{FeCa}} = 0 \text{ and } C_{123} = 0 \\ &P_{\text{Mg}} = 1 + \left[T^* \left(7.417 + \text{Rln} K_{1B} \right) + 2237 \right] / 0.567 \\ &Where \ K_{1B} = \mathbf{a_{\text{Ca}}}^{\text{Gt}} * \left(\mathbf{a_{\text{Mg}}}^{\text{Gt}} \right)^2 / \left(\mathbf{a_{\text{An}}}^{\text{Plag}} * \left(\mathbf{a_{\text{Mg}}}^{\text{Opx}} \right)^2 \right) \\ &P_{\text{Fe}} = 1 + \left[T^* \left(8.153 + \text{Rln} K_{2B} \right) - 2153 \right] / 0.5928 \\ &Where \ K_{2B} = \mathbf{a_{\text{Ca}}}^{\text{Gt}} * \left(\mathbf{a_{\text{Fe}}}^{\text{Gt}} \right)^2 / \left(\mathbf{a_{\text{An}}}^{\text{Plag}} * \left(\mathbf{a_{\text{Fe}}}^{\text{Opx}} \right)^2 \right) \\ &\mathbf{a_{\text{Mg}}}^{\text{Opx}} = X_{\text{Mg}} * \exp \left[984 * \left(X_{\text{Mg}}^{\text{Opx}} \right)^2 / \left(1.987 * 1000 \right) \right] \text{ and } \\ &\mathbf{a_{\text{Fe}}}^{\text{Opx}} = X_{\text{Fe}} * \exp \left[984 * \left(X_{\text{Mg}}^{\text{Opx}} \right)^2 / \left(1.987 * 1000 \right) \right] \end{split}$$

Lal (1993)

Lal (1993) gave an internally consistent recalibrations of mineral equilibria for geothermobarometry involving garnetorthopyroxene-plagioclase-quartz assemblages. He calculated the activity of garnet through sub-regular solution mixing in garnet using equation of Ganguly and Saxena (1984), where he used the margulus values as follows:

$$\begin{split} W_{\text{FeMg}} &= -1256 + 1.0 * \text{T; W}_{\text{MgFe}} = 2880 - 1.7 * \text{T; W}_{\text{CaMg}} = 4047 \\ &- 1.5 * \text{T; W}_{\text{MgCa}} = 1000 - 1.5 * \text{T; W}_{\text{CaFe}} = -723 + 0.332 * \text{T; W}_{\text{FeCa}} \\ &= 1090 \text{ and C}_{123} = -4498 + 1.516 * \text{T,} \end{split}$$

Activity of Mg and Fe in Opx ($\mathbf{a}_{\text{Mg}}^{\text{Opx}}$ and $\mathbf{a}_{\text{Fe}}^{\text{Opx}}$) calculated through regular solution model of orthopyroxene mixing model,

Where; $W_{MgFe} = 948 - 0.34 * T$; $W_{FeAl} = -1950$ and $W_{MgAl} = 0$ and activity of anorthite in plagioclase (\mathbf{a}_{An}^{plag}) same as in Wells (1979) see model 2b. The equation proposed by him is given below:

$$\begin{split} &P_{_{Mg}} = 1 + \left[T * (5.376 + RlnK_{_{2}}) + 3985\right] / 0.5614 \\ &P_{_{Fe}} = 1 + \left[T * (8.644 + RlnK_{_{2B}}) + 2749\right] / 0.60946 \end{split}$$

Holland and Powell (1985) calculated by Eckert et al. (1993)

Holland and Powell (1985) gave an internally consistent thermodynamic data set with uncertainties and correlations and Eckert et al. (1993) recalibrated based on thermo-chemically.

$$P_{Mg} = 1 + [T * (6.525 + RlnK_1) + 2632] / 0.5399$$

Where \mathbf{a}_{Ca}^{Gt} , \mathbf{a}_{Mg}^{Gt} , \mathbf{a}_{An}^{Plag} and \mathbf{a}_{Mg}^{Opx} same as in Newton and Perkins (1982).

Holland and Powell (1990) calculated by Eckert et al. (1993)

Holland and Powell (1990) gave an enlarged and updated internally consistent thermodynamic data set with uncertainties and correlations: the system K₂O-Na₂O-CaO-MgO-MnO-FeO-Fe₂O₃-Al₂O₃-TiO₂-SiO₂-C-H₂-O₂ and Eckert et al. (1993) recalibrated thermochemically.

$$P_{Mg} = 1 + [T * (6.931 + RlnK1) + 2513] / 0.5478$$

Where \mathbf{a}_{Ca}^{Gt} ; \mathbf{a}_{Mg}^{Gt} ; \mathbf{a}_{An}^{plag} and \mathbf{a}_{Mg}^{Opx} same as in Newton and Perkins (1982).

Berman (1988) calculated by Eckert et al. (1993)

Berman (1988) gave an internally-consistent thermodynamic data for minerals in the system NaO₂-K₂O-CaO-MgO-FeO -Fe₂O₃-Al₂O₃-SiO₂-H₂O-CO₂ and also calculated the activity of garnet using Ca-Fe-Mg ternary sub-regular solution of mixing in garnet (Berman 1990) calculated at constant pressure of 7Kbar equation is given below, and Eckert et al. (1993) recalibrated the Berman equation thermochemically.

$$PMg = 1 + [T * (7.459 + RlnK_1) + 1269] / 0.54995$$

Where a_{An}^{Plag} , a_{Mg}^{Opx} same as in Newton and Perkins (1982) and

$$\begin{aligned} & \mathbf{a}_{\mathrm{Mg}}^{\mathrm{Gt}} = X_{\mathrm{Mg}} * \exp * \{ [W_{112}(X_{\mathrm{Ca}}^{2} - 2 * X_{\mathrm{Ca}}^{2} * X_{\mathrm{Mg}}) + W_{112} * (2 * X_{\mathrm{Ca}}^{*} * X_{\mathrm{Mg}}^{} - 2 * X_{\mathrm{Ca}}^{} * X_{\mathrm{Mg}}^{}) + W_{113} * (-2 * X_{\mathrm{Ca}}^{2} * X_{\mathrm{Fe}}^{}) + W_{133} * (-2 * X_{\mathrm{Ca}}^{} * X_{\mathrm{Fe}}^{}) + W_{233} * (2 * X_{\mathrm{Mg}}^{} * X_{\mathrm{Fe}}^{} - 2 * X_{\mathrm{Mg}}^{} * X_{\mathrm{Fe}}^{}) + W_{233} * (X_{\mathrm{Fe}}^{2} - 2 * X_{\mathrm{Mg}}^{} * X_{\mathrm{Fe}}^{}) + W_{123} * (X_{\mathrm{Ca}}^{} * X_{\mathrm{Fe}}^{} - 2 * X_{\mathrm{Ca}}^{} X_{\mathrm{Mg}}^{} * X_{\mathrm{Mg}}^{} * X_{\mathrm{Fe}}^{}) / (R^{*}T) \} \end{aligned}$$

$$\begin{aligned} & \boldsymbol{a}_{\text{Ca}}^{\text{Gt}} = X_{\text{Ca}} * exp * \{ [W_{112}(2*X_{\text{Ca}} * X_{\text{Mg}} - 2*X_{\text{Ca}} ^2 * X_{\text{Mg}}) + W_{122} \\ & * (X_{\text{Mg}}^{2} - 2*X_{\text{Ca}} * X_{\text{Ca}} * X_{\text{Mg}}^{2}) + W_{113} * (2*X_{\text{Ca}} * X_{\text{Fe}} - 2*X_{\text{Fe}} * X_{\text{Fe}} * X_{\text{Fe$$

Table 1: Electron micro probe analyses (Wt%) and structural formula of garnet and orthopyroxene in basic granulite from Thana, District Bhilwara, Rajasthan. (Source: Thomas 1995).

Oxides	Garnet Sample No H90/2, Point 10	Orthopyroxene Sample No H90/2, Point 08	Plagioclase Sample No. H90/2 Point	
SiO ₂	37.926	51.408	56.539	
TiO ₂	0.003	0.254	0.000	
Al ₂ O ₃	21.208	1.116	27.461	
Cr ₂ O ₃	0.016	0.063	0.000	
Fe ₂ O ₃	0.678	0.418	0.000	
FeO	26.927	28.285	0.081	
MnO	1.344	0.499	0.000	
MgO	4.319	17.499	0.000	
CaO	7.970	1.161	10.165	
Na ₂ O	0.000	0.051	5.826	
K ₂ O	0.000	0.000	0.135	
TOTAL	100.389	100.754	100.207	
Cation	Cation	Cation	Cation	
Si	5.9583	1.9625	2.5365	
Ti	0.0003	0.0073	0.0000	
Al	3.9269	0.0502	1.4520	
Cr	0.0020	0.0019	0.0000	
Fe ⁺³	0.0801	0.0120	0.0000	
Mg	1.0113	0.9957	0.0000	
Ca	1.3415	0.0475	0.4886	
Mn	0.1788	0.0162	0.0000	
Fe	3.5378	0.9030	0.0031	
Na	0.0000	0.0037	0.5068	
K	0.0000	0.0000	0.0077	

Table 2: Temperature (in °C) calculated at 7000 bars from garnet-orthopyroxene thermometer for the assemblages of basic granulites (H90/2) from Shivpura area, District Bhilwara, Rajasthan.

S. No.	Authors		KD	InK _D	Temperature °C			
	1/2 Ferrosilite + 1/3 Pyrope = 1/2 Enstatite + 1/3 Almandine							
1.	DAHL (1980)		3.8574	1.3500	742			
2.	RAITH et al. (1983)		3.8574	1.3500	705			
3.	HARLEY (1984)		3.8574	1.3500	634			
4.	SEN and BHATTACHAR	YA (1984)	3.8574	1.3500	694			
5.	LEE and GANGULY (198	4)	3.8574	1.3500	811			
6.	PERCHUK et al. (1985)		3.8574	1.3500	814			
7.	LEE and GANGULY (1988)		3.8574	1.3500	780			
8.	ARANOVICH and PODLESSKII (1989)		3.8574	1.3500	753			
9.	PERCHUK and LAVRENTE'VA (1990)		3.8574	1.3500	681			
10.	BHATTACHARYA et al. (1991)		3.8574	1.3500	698			
11.	LAL (1993)		3.8574	1.3500	728			
	XFe (OPX)	XMg (OPX)	XAl (OPX)					
	0.469384	0.517569	0.013047					
	XFe (Gt)	XMg (Gt)	XCa (Gt)	XMn (Gt)				
	0.582891	0.166623	0.221027	0.029459				

Table 3: Pressure in (Kb) calculated at 1023 K from garnet-orthopyroxene-plagioclase-quartz barometer for the assemblages of granulites (H90/2) from Shivpura area, District Bhilwara, Rajasthan (Thomas 2005).

Author	lnK _D	Pressure (Kb) Calculated for P _{Mg} Reaction				
Anorthite + Enstatite = 1/3 Grossularite + 2/3 Pyrope + Quartz						
Newton (1978)	-1.436597	10.49				
Wells (1979)	-2.23514	9.9				
Raith et al. (1983)	-2.826595	6.97				
Newton and Perkins III (1982)	-2.826595	7.19				
Eckert et al. (1991)	-2.826595	7.02				
Perkins and Chipera (1985)	-2.102059	8.36				
Holland and Powell, (1985) calculated by Eckert et al. (1993)	-2.826595	6.6				
Holland and Powell, (1990) calculated by Eckert et al. (1993)	-2.826595	7.64				
Berman (1988) calculated by Eckert et al. (1993)	-2.511311	6.9				
Aranovich and Podlesskii (1989)	3.061691	4.3				
Bhattacharya et al. (1991)	2.740128	7.5				
Lal (1993)	2.58783	7.53				
Author	lnK _D	Pressure (Kb) Calculated for P _{Fe} Reaction				
Anorthite + Ferrosilite = 1/3 Grossularite + 2/3 Almandine + Quartz						
Bohlen et al. (1983)	-0.357622	8.02				
Perkins and Cipera (1985)	-0.613129	8.66				
Moecher et al. (1988)	-0.412138	8.96				
Bhattacharya et al. (1991)	-0.825801	7.64				
Lal (1993)	-0.387665	8.71				

$$\begin{split} &X_{\text{Ca}}^{\,2}) + W_{_{133}} * (X_{\text{Fe}}^{\,2} - 2 * X_{_{\text{Ca}}} * X_{\text{Fe}}^{\,2}) + W_{_{223}} * (-2 * X_{_{\text{Mg}}}^{\,2} * X_{_{\text{Fe}}} \\) + W_{_{223}} * (-2 * X_{_{\text{Fe}}}^{\,2} * X_{_{\text{Mg}}}) + W_{_{123}} * (X_{_{\text{Mg}}} X_{_{\text{Fe}}} - 2 * X_{_{\text{Ca}}} * X_{_{\text{Mg}}} X_{_{\text{Fe}}})] \\ / R * T \} \\ &Where, \quad W_{_{112}} = 1774 - 1.5 * T; \, W_{_{122}} = 5569 - 1.5 * T; \, W_{_{113}} \\ = 1714 - 0.405 * T; \, W_{_{133}} = 259 - 0.405 * T; \, W_{_{223}} = 24; \, W_{_{233}} = 329; \, W_{_{123}} = 4834 - 1.9017 * T. \end{split}$$

PROGRAM DESCRIPTION

The software consists of three programs as it is clear from; it prompts the user for the choice of:

- 1. Gt-Opx exchange reaction (GOTherm)
- 2. Gt-Opx-Plag-Qz equilibria (GOPQ)
- 3. Exit

If the temperature calculation is intended through (GOTherm) garnet-orthopyroxene exchange reaction enter the option No. 1. It automatically proceeds into the program (GOtherm) for calculation. Besides this, GOTherm also consists of three subprograms. On running, it prompts the user three choices, viz., ENTER DATA; CALCULATE and DISPLAY RESULTS and EXIT from GOtherm.

The first choice is ENTER DATA when opted asks for file name. The file selected is opened and displayed on the screen. If the file asked for does not exist then a file by the asked name is automatically created. The program then asks for data. The data requirement is in the form of structural formula units or atomic formula units (a.f.u.) of Fe, Mn, Mg, Ca for garnet and Fe, Mg, Mn, Ca, Al and Na for orthopyroxene. Pressure (in bars) at which the temperature is to be calculated is also required. The data entry operation can be terminated by entering 0 (zero) at the S. No. prompt.

The second choice, CALCULATED AND DISPLAY RESULTS however requires the data file name. The program first displays the data file contents and then proceeds for calculation of temperature through different models. This program may be looked upon as an operational block, which performs the specific operations on the data to give output in a fixed format (Table 2).

The third option is for termination of the program and return to the main program. In a similar way, if the user wishes to calculate pressure through garnet orthopyroxene -plagioclase-quartz equilibria (GOPQ), option no.2 is too entered. The program automatically enters into the subprogram (GOPQ) for pressure calculation. It also works like GOTherm. The data requirement in this program is also in the form structural formula units or atomic formula unit (a.f.u.) of Fe, Mn, Mg, Ca for garnet, Ca,Na, K for plagioclase and Fe, Mg, Mn, Ca, Aliv,

Alvi, Fe3, Cr, Ti, K and Na for orthopyroxene.

Temperature (in K) at which the pressure is to be calculated is also required. The data ENTRY operation can be terminated by entering 0 (zero) at the S. No. prompts. Rest other options work like GOTherm subprogram.

PROGRAM VALIDATION

To validate the program, several data had been manually calculated (Thomas 1995, 2005; Joshi et. al. 1993, Thomas 2006 and 2008) and reprocessed. It was observed that all the results are same as manually calculated. For example, one set of data is given in (Table 1) and the results obtained are shown in (Table 2 and 3). Through there is some variation among the results obtained from individual models. This discrepancy might be due to that fact that some of the models are based on empirical studies, some on thermodynamically and experimental work. Obviously, the experimentally calibrated models should be the preferred geothermobarometers. But according to author's observation garnet -orthopyroxene Fe-Mg exchange thermometer and garnet -orthopyroxene -plagioclase -quartz barometer of Bhattacharya et al. (1991) and Lal (1993) yield temperature and pressure estimates which agree with independent petrologic temperature constraints. These models take into accounts non-ideal Fe-Mg mixing in orthopyroxene and should be preferred over the other models, since it shows very little compositional dependence.

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