<u>CHAPTER – 7</u>

PART A- GEOTHERMOMETRY AND GEOBAROMETRY

7.A.1 Introduction

Application of the models of geothermometry and geobarometry is very useful in metamorphic petrology in estimating P–Tconditions. An estimate of the P–Tcondition is a challenging exercise for the rocks because they underwent different metamorphism episodes. The mineral compositions are not free from re-equilibration during cooling, which affects the peak composition by cation exchanges. It is established that the mineral compositions in natural rocks are difficult to interpret and expected to get the 'preserve equilibrium distributions' of all elements of concern from peak conditions. This 'difficult-to-quantify' compositional variability affects the precision and accuracy of thermobarometry approaches more seriously than the mineral assemblage approach.

The minerals and textural development of each rock occur along a pressuretemperature-time path during metamorphism. The thermal peak conditions of metamorphism on the path are an evident pressure-temperature point of interest. Because the kinetics of the reaction is most likely temperature sensitive, the maximum temperature point is chosen. Using geothermometry and geobarometry models to pinpoint this spot would be ideal. However, this very much depends on the interpretation of how the observed textural relations in minerals are developed.

7.A.2 Thermodynamic Basis

The theoretical basis of 'geothermobarometry' is straightforward. The term "geothermobarometry" refers to the use of the pressure and temperature dependence of the equilibrium constant as the basic standard to infer metamorphic temperatures and pressures of equilibration. A fundamental thermodynamic expression is written as:

 $\Delta G(P,T,X) = 0 = \Delta H(298,1) + \int_{298}^{T} \Delta C_p \, dT + \int_{1}^{P} \Delta V dP - T[\Delta S(298,1) + \int_{298}^{T} (\Delta C_p \, /T) dT] +$

RTlnK.....(1)

Where,

 Δ H: change in enthalpy

 ΔS : change in entropy

 ΔV : change in volume

dP: change in pressure

C_P: heat capacity

T: absolute temperature in K

P: pressure in bars

R: gas constant=1.987 cal

The equilibrium constant for a sample is calculated by characterizing the compositions of coexisting minerals in microprobes. Detailed treatment of thermodynamicparameters of the standard state equation (1) and their inter-relationship is given excellent coverage in the fundamental books on thermodynamics.

7.A.3 Presumption

The fact that the mineral phases are in equilibrium is a basic assumption for geothermobarometry. The concept of an equilibrium state in a metamorphic rock assumes that a heterogeneous system is in equilibrium. While it is possible to demonstrate that an assemblage is not in equilibrium, proving that phases in a rock developed in equilibrium is more complicated. All thermodynamic relationships and derivation presuppose the concept of equilibrium, thermodynamics does not provide criteria of equilibrium, and it describes features of equilibrium. In order to apply thermodynamics, this concept must be allowed.

7.A.4 Geothermobarometers

The estimation of pressure and temperature conditions at which rock is formed is represented as geobarometry and geothermometry and jointly termed geothermobarometry. The fundamental premise of Geothermobarometers is related to the mineral assemblage of rocks and reactions that show considerable temperature sensitivity (large ΔS , ΔH) and small pressure sensitivity (large ΔV), and geobarometers are reactions that show significant pressure sensitivity (large ΔV) and small temperature sensitivity (small ΔS and ΔH). Whichever thermodynamic equation that has large ΔS and small ΔV can be used as a geothermobarometer, while thermodynamic expression having high ΔV and low ΔS can be used as a geobarometer. Hence geothermometer is always more or less parallel to P-axis and an ideal geobarometer is parallel to T-axis in the *P*–*T* diavariant field. Ideally, vapour-absent, solid-solid reactions are best accorded as geobarometers.

Geothermobarometers are mainly based on two types of calibrations. Empirical calibrations rely on measurements of the equilibrium constant obtained from natural data. Experimental calibrations rely on measurements of the equilibrium constant as a function of pressure and temperature in experiments conducted under controlled laboratory conditions. Because the change of the equilibrium constant with T and P is usually better limited in them, carefully reversed experimental calibrations are undoubtedly more accurate. These experiments are generally conducted under ideal conditions, and the activity composition relationships are unwell defined. This is a disadvantage to experimental calibration. Though empirical calibrations include non-ideality of the solid solution phases, they are not as superior compared to experimental calibration. The simple reason is that empirical calibration.

7.A.5 Reaction Terminology

Geothermobarometers are based on specific metamorphic reactions. Different types of chemical reactions relevant to thermobarometry are discussed in thissection.

7.A.5.1 Exchange Reactions

Several geothermometers use exchange reactions as their basis. A heterogeneous reaction involving only exchange components between two minerals is known as an exchange reaction. Consider the following reaction that describes the exchange of Fe and Mg.

 $Fe_{3}Al_{2}Si_{3}O_{12} + KMg_{3}AlSi_{3}O_{10}(OH)_{2} \rightleftharpoons Mg_{3}Al_{2}Si_{3}O_{12} + KFe_{3}AlSi_{3}O_{10}(OH)_{2}....(2)$

Almandine Phlogopite Pyrope Annite This reaction is reduced to only FeMg-1 exchange components by substracting like components.

Fe $Mg_{(-1)}$ garnet = Fe $Mg_{(-1)}$ biotite

The interchanging of two similar atoms occurs in exchange equilibria. Hence, it is called an exchange reaction.

7.A.5.2 Net Transfer Reactions

Several geothermometers are based on net transfer reactions. Net-transfer reactions are the transfer of one or more components from one phase to another, resulting in the consumption of old phases or the production of new ones, or reactions that cause the production and consumption of phases by transferring components from reactant phases to product assemblage phases. The ΔV reaction is substantial, and the equilibrium constant is pressure sensitive because these reactions produce massive volume changes. Solid-solid net transfer reactions are hence ideal geobarometers. Consider the following reaction that describes anorthite's upper pressure stability:

 $3CaAl_2Si_2O_8 \rightleftharpoons Ca_3Al_2Si_3O_{12} + 2Al_2SiO_5 + SiO_2....(2)$

Anorthite Grossular Kyanite Quartz

7.A.6 Geothermometry

There are two types of thermometers in general: (i) exchange geothermometers and (ii) solvus thermometers.

Ion exchange (Fe-Mg; Fe-Ti) between coexisting silicates is the main focus of exchange geothermometers. Because exchange reactions have a small ΔV reaction compared to a large ΔS reaction, equilibrium constant isopleths exhibit a steep slope. The distribution coefficient is a term used to describe partitioning a pair of elements between two minerals (K_D). The K_D for the FeMg-1 exchange reaction between garnet and biotite is defined as $K_D=[Fe/Mg]_{Grt}$./[Mg/Fe]_{Bt}.

Solvus thermometers are based on the compositional variability of two coexisting, structurally linked phases that are tied to the T-X space's miscibility gap (solvus). Because miscibility gaps are temperature dependent, they are often used as thermometers. Solvus thermometry is frequently applied to mineral pairings such as orthopyroxene-clinopyroxene and plagioclase-alkali feldspar.

7.A.7 Geobarometry

Because they involve significant volume changes and have a slight positive slope in P-T space, vapour-absent, solid-solid, net transfer equilibria serve as potential geobarometers. The computed pressure from such equilibria uses temperatures obtained from the exchange or other thermometers. In a synopsis of the geobarometers, most of them involving garnet tend to maintain the thermobarometric information because of their strong refractory nature. The application of these barometers calls for well-defined thermodynamic models of activity-composition relationship. The conflict on using different activity models for common anhydrous phases such as garnet, plagioclase, orthopyroxene etc., accounts for the extend in the calculated P-T conditions. Essene (1989) and Spear (1989) provide an excellent comprehensive synthesis of them.

7.A.8 Problem/ Errors in Geothermobarometry

Any quantitative science, including geothermobarometry, requires careful examination of the propagation of errors. Thermobarometry, however, is not without its pitfalls and calculations without some estimate of uncertainty are meaningless. That is why, the results of geothermobarometry have been only partially satisfying the petrologists. For estimating the metamorphic conditions based on very precise data, new calibrations are being worked out by petrologists to get ideal models of geothermobarometry. Important factors that contribute as sources of errors in thermobarometry have been studied by Hodges and McKenna (1987); Spear (1989); Kohn and Spear (1991). There are several sources of errors/ pitfalls in thermobarometry, which are summarized below:

7.A.8.1 Evaluation of Chemical Equilibrium

A crucial requirement for thermobarometry is the assumption of chemical equilibrium between the phases. For this reason, it is desirable to look for sub-assemblages in different domains of the same rock that show local equilibrium or mosaic equilibrium. As a result, equilibrium can be proven or denied. As a result, failure of the following tests, which are aimed to prove disequilibrium in a rock, provides an indirect check on equilibration conditions. One easy way is to cross the tie-lines for selected assemblages' topological projections. It is consistent with equilibrium when tie-lines do not intersect. Another test is the partitioning of elements in a pair of coexisting minerals. Whether the distribution coefficient pattern is systematic or random, equilibrium or disequilibrium is indicated.

Mineral zoning patterns (composition profiles) serve as a test case for determining which component of the zoned mineral is in equilibrium with the matrix phase of the rock.

7.A.8.2 Re-equilibration during Retrogression

We only get peak metamorphic conditions from thermobarometric calculations in a few circumstances. They usually record lower temperatures as a result of re-equilibration

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during retrogression. The rim compositions of garnet touching biotite exhibit indications of severe Fe-Mg resetting and so fail to record peak temperatures, according to studies on cationic exchange equilibria. Even Fe-Mg exchange thermometry on most refractory phases, such as the core composition of garnet and orthopyroxene grain in contact, may not record peak conditions due to resetting, according to Pattison and Begin (1994a, b). Due to the exsolution property, two-feldspar thermometers frequently give low temperatures. To reach geologically appropriate temperatures, Bohlen and Essene (1977) employed the reintegration of exsolved lamellae method.

7.A.8.3 Quality of Thermobarometric Formulations

There are two sorts of calculations: experimental and thermodynamic. Although our knowledge of mineral thermodynamics and calorimetric data has greatly improved, it is far from complete. Volume corrections for solid-solid equilibria are often overlooked. Poor mixing models, substantial thermodynamic variations between the natural and its poor analogue or synthetic phase, and experimental data without tight bracketed reversed results can all degrade calibration quality.

7.A.8.4 Extrapolations

At extremely high P-T settings, the number of reaction equilibria has been investigated experimentally. To apply these equilibria at much lower P-T conditions, an extended projection reaction slope in an area outside the critical limits is required, which is a risky inference. Calculations of propagating uncertainty are unexpectedly (very) large in such instances.

7.A.8.5 Restraints and Sensitivity of thermobarometers

The P-T span of many thermobarometric formulations is restricted. As a geothermometer, the commonly occurring garnet-biotite exchange equilibria have nearly 18 different calibrations. Some clearly state that these thermometers only apply over a specific

compositional range. Ferry and Spear (1978) restricted their ideal mixing model to rocks with low Ca and Mn garnets. Corrections for the Grossular component in garnet, known to mix nonideally with pyrope, are included in the calibrations of Hodges and Spear (1982) and Perchuk and Lavrent'eva (1983). As a result, they produce higher temperatures than Ferry and Spear (1978).

7.A.8.6 Analytical errors in Microprobe data

The microprobe technique has the significant drawback of only determining total iron. The contents of Fe^{2+} and Fe^{3+} are determined using ideal structural formulas and various recasting procedures. Unfortunately, such stoichiometry-based recalculation procedures are sensitive to even modest analytical mistakes in SiO₂ and Al₂O₃ estimations, mainly when Fe^{3+} content is low. Based on total iron, model temperatures are frequently computed using Fe-Mg distribution equilibria. When only considering Fe^{2+} , these estimates can differ by up to 100°C.

7.A.8.7 Effect of other components in solid solutions

Generally, thermobarometers are simple mineral chemistry-based, but mostnatural minerals show a prominent departure toward complex solid solutions. Theideal end-member in the complex solid solution may be calculated from thestructural formulae in the different and arbitrary ways of recasting procedures. Therecasting procedure strongly depends on the quality of analyses and requires knowledge of Fe^{2+} and Fe^{3+} contents.

7.A.8.8 Effect of cation order/disorder

Cation disorder has a significant impact on thermobarometry. The experimental data on sapphirine stability shows the metastable disordered phase, whereas this phase is orderly in gradually cooled natural samples. Before sapphirine reactions should be exploited for quantitative thermobarometry, more crystal chemistry work on the material is required.

7.A.8.9 Error Analyses

It combines the precision and accuracy of P-T readings and necessitates a thorough study before establishing a meaningful thermobarometric interpretation. For example, for most geobarometers, the total uncertainty in pressure is represented by a series of independent errorsources.

 σ P-total = σ P-statistical + σ P activity models + σ P sample heterogeneity

Many researchers have detailed estimates on thermobarometry propagating uncertainty (Hodges and McKenna, 1987; Kohn and Spear, 1991). Precision refers to reproducibility or errors that are randomly distributed. It relates to analytical uncertainty during microprobe analyses. The accuracy of the P-T estimate is a measure of how closely the estimate matches the actual P-T conditions. However, estimating the accuracy of the P-T estimate is problematic since the error sources that contribute to it are not well constrained.

7.A.8.10 Blocking effect

Continual reactions can reset thermobarometers during post-peak metamorphic conditions as the rocks cool. When the temperature drops low enough, the reactions eventually shut down. Blocking (closing) temperature is the temperature recorded by a thermometer that has been reset during cooling. When using thermometry on high-grade rocks, keep in mind that most cation exchange thermometers have closure temperatures lower than the granulite facies; therefore, they are prone to reset upon cooling.

7.A.9 Concluding Remarks

From the above discussion, it is clear that the application of geothermobarometry requires prior knowledge of phase equilibria, reaction texture history and chemical evolution of the rock for a successful interpretation. The abilities of petrologists are reflected in choosing the appropriate thermobarometers and in selecting mineral points for arriving at the best P-T results. Only very rigorous and careful work and a bit of fortune enable us to address thermobarometry satisfactorily. The following pages give details of various relevant

geothermobarometric expressions applicable to metamorphic rocks. For most thermobarometers, computation of P and T are in bars and Kelvin, respectively, unless otherwise specified.

PART B- GEOTHERMOBAROMETRY

This section details different geothermobarometers used to estimate the temperaturepressure conditions of metamorphism in the study area. Thermodynamic expressions and equations are discussed earlier in this chapter's first part. The different geothermometers and geobarometers are:

7.B.1 Geothermometers

7.B.1.1 Garnet-biotite geothermometry

The following equation gives the Fe-Mg partitioning between garnet and biotite on an 11 oxygen basis.:

repetition.

$$K_D = (Fe/Mg)^{Grt}$$
 . $(Mg/Fe)^{Bt}$ Or $(X_{Fe}/X_{Mg})^{Grt}$. $(X_{Mg}/X_{Fe})^{Bt}$

$$X_{Fe}^{Grt} = \frac{Fe}{i}, X_{Mg}^{Grt} = \frac{Mg}{i}, X_{Ca}^{Grt} = \frac{Ca}{i}, X_{Fe}^{Grt} = \frac{M}{i}$$

Where $i = (Fe + Mg + Mn + Ca)^{Grt}$

$$X_{Fe}^{Bt} = \frac{Fe}{Fe + Mg}, X_{Mg}^{Bt} = \frac{Mg}{Fe + Mg}, X_{Al}^{Bt} = \frac{Al}{Al + Fe + Mg + Mn + Ti + Cr}, X_{Ti}^{Bt} = \frac{Ti}{Al + Fe + Mg + Mn + Ti + Cr}$$

Thompson (1976) and Perchuck et al., (1985) calibrated the equation on an empirical basis, whereas Holdaway and Lee (1977) proposed a calibration based on experimental work of pure Fe end-member exchange reaction along with thermochemical data and K_D obtained from the natural rocks. Goldman and Albee (1977) used stable oxygen-isotope temperature to derive the equation in their calibration. The reliable geothermometer proposed by Ferry and

Spear (1978) is based on the numerical analysis of experimental data of rocks containing garnet biotite assemblages. Based on the experimental data, several refined models have been established by various workers to determine the temperature of Fe-Mg exchange relation between the coexisting garnet and biotite. The models are as follows:

Models

Thompson (1976)

The Fe-Mg exchange reaction between garnet and biotite was fitted by least square to linear expression; Y = a + b/t.

Here, **a** gives the intercept $(+\Delta S/R)$ and **b** is the slope $(-\Delta H/R)$ of the reaction.

For the exchange reaction,

$$Y = n/nK_D + (P-1)\Delta V/RT$$
 or $(\Delta S/R) - \Delta H/RT = n/nK_D + (P-1)\Delta V/RT$

After rearranging the equation:

$$T = \frac{\left[-\frac{\Delta H}{R} - \frac{(P-1)\Delta V}{R}\right]}{\left(\frac{n}{nK_D}\right) - \frac{\Delta S}{R}}$$

Thompson (1976) found the following thermochemical parameters for the Fe-Mg exchange equilibria:

 $\Delta S/R = -1.560 \text{ cal/K}, \Delta H/R = -2739.646 \text{ cal}, \Delta V/R = -0.0234 \text{ cal/bar}$

Using these thermochemical data for the exchange reaction, the thermometric expression is given as:

$$T = \frac{[2739.646 + 0.0234 (P - 1)]}{[lnK_{D} + 1.560]}$$

As this model is based on empirical Fe-Mg distribution coefficient, it is particularly sensitive to non-ideality among these phases. It was observed that the values ln K_D (Fe-Mg) determined for garnet-biotite pairs from high-grade metamorphic rocks show a systematic displacement with increasing Ti in biotite.

Holdaway and Lee (1977)

They expressed the equation after putting the value of ΔH , ΔS and ΔV in the following equation:

$$\Delta H - T\Delta S + (P-1)\Delta V = -RT lnK_D$$

They formulated the geothermobarometer by substituting;

 $\Delta H = -6150$ cal,

 $\Delta S = -3.93$ cal/deg,

 $\Delta V = -0.0246$ cal/bar

$$T = \frac{[3095 + 0.0124 (P - 1)]}{(\ln K_{\rm D} + 1.98)}$$

Where P is in bars and K_D is the same as given in Thompson (1976).

Ferry and Spear (1978)

Ferry and Spear (1978) were the first to calibrate a geothermometer based onexperimental data and plotted their results in ln K_D vs l/T plot. Combining thepreferred values for $\Delta S = -1.554$ Cal/K, $\Delta H = -4151$ Cal, and $\Delta V = 0.019$ cal/bar in the equation (B), a polybaric and polythermal expression for Fe-Mg partitioning between biotite and garnet can be obtained.

$$T = \frac{[4151 + 0.019 (P - 1)]}{(\ln K_{D} + 1.554)]}$$

Perchuk et al., (1985)

The earlier model of Perchuk et al. (1981) did not consider the effect of Ca and Mn components in garnet. During a later refinement in 1985, they considered $W_{Fe-Mg} = 0$ and $W_{Ca-Mg}-W_{Ca-Fe} = 5704$ - 1.242 + T°K. Since the Fe-Mn and Fe-Mg solid solutions are close to ideal, they assumed that Ca-Mg-Mn solutions are also ideal. Thus after considering all these values, they have redefined this geothermometer as given below:

$$T = \frac{[3720 + 2871 X_{Ca}^{Gt} + 0.038]}{[\ln K_{\rm D} + 0.625 X_{Ca}^{Gt} + 2.868]}$$

Bhattacharya et al., 1992

Bhattacharya used the parameters of Ganguly and Saxena (1984); for the pyropealmandine asymmetric regular solutions as inputs in the non-ideal phlogopite-annite binary system in the temperature range 550°C-950°C. This geothermometer was an improved thermometer based on the updated activity-composition relationship in Fe-Mg-Ca garnet solid solutions. The resulting equations are:

T(HW) =

$$\frac{\left[20286+0.0193P-\left\{2080(X_{Mg}^{Gt})^{2}-6350(X_{Fe}^{Gt})^{2}-13807\left(X_{Ca}^{Gt}\right)\left(1-X_{Mn}^{Gt}\right)+8540\left(X_{Fe}^{Gt}\right)\left(X_{Mg}^{Gt}\right)\left(1-X_{Mn}^{Gt}\right)+4215(X_{Ca}^{Gt}\right)\left(X_{Mg}^{Gt}-X_{Fe}^{Gt}\right)+4441\left(2X_{Mg}^{Bt}-1\right)\right]}{\left[13.138+8.3143lnK_{D}+6.276\left(X_{Ca}^{Gt}\right)\left(1-X_{Mn}^{Gt}\right)\right]}$$

T(GS) =

$$\frac{\left[13538+0.0193P-\left\{136(X_{Mg}^{Gt})^{2}-10460(X_{Fe}^{Gt})^{2}-13807\left(X_{Ca}^{Gt}\right)\left(1-X_{Mn}^{Gt}\right)+19246\left(X_{Fe}^{Gt}\right)\left(X_{Mg}^{Gt}\right)\left(1-X_{Mn}^{Gt}\right)+5649(X_{Ca}^{Gt})\left(X_{Mg}^{Gt}-X_{Fe}^{Gt}\right)+7972\left(2X_{Mg}^{Bt}-1\right)\right]}{\left[6.778+8.3143lnK_{D}+6.276\left(X_{Ca}^{Gt}\right)\left(1-X_{Mn}^{Gt}\right)\right]}$$

Gessman et al., 1997

For the Fe-Mg exchange between garnet and biotite in the temperature range 600– 800°C at 0.2 GPa, Gessman employed new experimental data. He analyzed the Fe-Mg-Al mixing characteristics of biotite and recalibrated the garnet-biotite geothermometer. The expression used as a geothermometer is:

$$T = [-57594 + 0.236(P - 1) + (230 + 0.01P) \times (X_{Mg}^{2Ct} - 2X_{Mg}^{2Ct}X_{Fe}^{2Gt}) \times (3720 + 0.06P) \\ \times (2X_{Mg}^{2Ct}X_{Fe}^{2Gt} - X_{Fe}^{2Gt}) - 7548(X_{Mg}^{Bt} - X_{Mg}^{Bt}) - 56572X_{Al}^{Bt}]/[-24.44 - 3RlnK_{D}] - 273.15$$

Where,

$$K_D = \left(\frac{X_{Fe}}{X_{Fe}}\right)^{Gt} / \left(\frac{X_{Fe}}{X_{Fe}}\right)^{Bt}$$

K_D is the distribution coefficient.

Holdaway et al., 1997

The garnet-biotite geothermometer was re-calibrated utilizing Margules parameters for iron-magnesium-calcium garnet, Mn interactions in garnet, and Al interactions in biotite, as well as the Fe oxidation state of both minerals. The equation for the geothermometer is:

$$T = \frac{[41952 + 0.311P + G + B]}{10.35 - 3RlnK_D}$$

Where R=8.31441 and P is in the bar, and G and B, evaluated in terms of Margules parameters, are given by

$$G = 3RTln\left(\frac{\gamma_{Mg}^{Gt}}{\gamma_{Fe}^{Gt}}\right), B = 3RTln\left(\frac{\gamma_{Fe}^{Bt}}{\gamma_{Mg}^{Bt}}\right)$$

Where G and B are Margules parameters for garnet and biotite respectively.

Kaneko and Miyano (2004)

Kaneko and Miyano made several assumptions for calibrating garnet-biotite thermometers. Fe^{3+} is present in the octahedral sites of garnet and biotite and is assumed to be 3% of the total Fe (Fe^T) in the case of garnets. Two cases were considered. The first case, where Fe^{3+} in biotite is present. The second case where Fe^{3+} is absent in biotite, i.e. all Fe cations are present as ferrous Fe. The resulting equations for the garnet-biotite thermometers for the two cases are as follows:

(a) Case A; assuming the presence of Fe^{3+} in biotite

$$T = \frac{\left[-37612.9 + (-0.295 + W_V^{Gt})(P - 1) + W_H^{Gt} - 16234.6(X_{Mg}^{Bt} - X_{Fe}^{Bt}) - 262165.9X_{Al}^{Bt} - 310990X_{Ti}^{Bt}\right]}{-5.160 - 3RlnK_D^{(1)} + W_S^{Gt} - 12.066(X_{Mg}^{Bt} - X_{Fe}^{Bt}) - 300.664X_{Al}^{Bt} - 370.39X_{Ti}^{Bt}}$$

(b) Case B; assuming the absence of Fe^{3+} in biotite

$$T = \frac{\left[-3889.9 + (-0.295 + W_V^{Gt})(P - 1) + W_H^{Gt} - 15667.5(X_{Mg}^{Bt} - X_{Fe}^{Bt}) - 256595.2X_{Al}^{Bt} - 310990X_{Ti}^{Bt}\right]}{-7.880 - 3RlnK_D^{(1)} + W_S^{Gt} - 12.238(X_{Mg}^{Bt} - X_{Fe}^{Bt}) - 309.871X_{Al}^{Bt} - 370.39X_{Ti}^{Bt}}$$

7.B.1.2 Garnet-orthopyroxene geothermometry

Garnet-orthopyroxene Fe-Mg exchange reaction is also extensively used for the calibration of geothermometers of the granulite facies rocks. The Mg-Feexchange equilibrium was firstly calibrated empirically by Dahl (1980). The exchange reaction used in the calibrations is as follows:

$$Mg_{3}Al_{2}Si_{3}O_{12} + 3FeSiO_{3} \rightleftharpoons Fe_{3}Al_{2}Si_{3}O_{12} + 3MgSiO_{3}....(2)$$

Pyrope Ferrosilite Almandine Enstatite

Sen and Bhattacharya (1984) proposed their expression for the reaction on the basis of thermochemical data. The preferred geothermometric models used for the calculation of the temperature of metamorphism in the study area are those calibrated by Sen and Bhattacharya (1984), Harley (1984), Lee and Ganguly (1988) and Bhattacharya et al. (1991).

Models

Lee and Ganguly (1988)

Lee and Ganguly calibrated the geothermometers on the experimental dataobtained from the experiment in the (FMASH) system. They carried out experiments at 20-25 kbar pressure and 975-1400°C temperature. They used Caand Mn corrections in garnet given by Ganguly and Saxena (1984). This modeling variably gives high-temperature estimates. The expression for the thermometer is:

$$T = \frac{[1981 + 0.0119(P - 1) + 1510(X_{Ca} + X_{Mn})^{Gt}]}{[lnK_D + 0.97]}$$

Bhattacharya et al. (1991)

Based on phase equilibrium and calorimetric experiments, Bhattacharya et al. (1991) have developed the Fe-Mg exchange garnet-orthopyroxene thermometer. Their thermometric equation for Fe-Mg partitioning between garnet and orthopyroxene for reaction (2) with interaction parameters (Δ W'S), calculated at 1000 K, is as under:

$$T = \frac{1611 + 0.021P + 906X_{Ca}^{Gt} + [A] + 477(2X_{Mg}^{Opx} - 1)}{RlnK_{D} + 0.796}$$

Where K_D is the same as given in Harley (1984) and

 $[A] = -1220(X_{Ca}^{Gt}) \cdot (X_{Ca}^{Gt}) \cdot 441X_{Ca}^{Gt}(X_{Ma}^{Gt} - X_{Fe}^{Grt}) - 136(X_{Mg}^{Grt})^2 + 746(X_{Fa}^{Grt})^2$

Perchuk et al. (1985)

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

$$\Delta H_{970}^0 K = -4766 \ Cal.; \ \Delta S_{970}^0 K = -2.654 \ \frac{Cal}{K} \ and \ \Delta V_{298} K = -0.0234 \ Cal/bar$$

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

$$T(K) = [(4766 + 2533 \times (X_{Fs} - X_{En})^{opx} - 5214 \times X_{Al}^{opx} + 5704 \times X_{Ca}^{Gt} + 0.023 \times P(bar))/(RlnK_D + 2.65 + 1.86 \times (X_{Fs} - X_{En})^{opx} + 1.242 \times X_{Ca}^{Gt}]$$

Where i = (Fe + Mg + Al/2)

$$X_{Fe}^{Opx} = \frac{Fe}{i}$$
; $X_{Mg}^{Opx} = \frac{Mg}{i}$; and $X_{Al}^{Opx} = \frac{Al}{2}/i$

Aranovich and Berman (1997)

To define the solubility of Al_2O_3 in ferrosilite in equilibrium with almandine garnet, Aranovich and Berman (1997) used reversed-phase equilibrium data gathered over the *P*–*T* range of 12–20 kbar at 850–1100°C.

$$T = \frac{\left[-\Delta H_a^0 - 3H_{Fs}^x - H_{0k}^x + H_{Alm}^x - P(\Delta V_a^0 - 3V_{Fs}^x - 3V_{0k}^x + V_{Alm}^x)\right]}{RlnK_a - \Delta S_a^0 - 3S_{Fs}^x - 3S_{0k}^x + S_{Alm}^x}$$

Carson and Powell (1997)

Carson and Powell (1997) presented a geothermometer based on the Fe–Mg exchange between coexisting garnet and orthopyroxene expressed as pressure as follows:

$$P = 1/22.86\left[\frac{RT\ln(1 - X_{Mg}^{Gt} - X_{Ca}^{Gt})(X_{Mg}^{Opx})}{(X_{Mg}^{Gt})(1 - X_{Mg}^{Opx})}\right] + 1.96T - 3740 - 1400X_{Ca}^{Gt}$$

Where P is pressure in kilobar, and T is the temperature in kelvin.

Nimis and Grütter (2010)

Using mineral compositions of the best equilibrated natural ultramafic rocks in combination with P and T values calculated using the two-pyroxene thermometer and Al in Opx thermometer, Nimis and Grütter (2010) suggested the following formula.

$$T = \frac{\{1215 + 17.4P + 1495(X_{Ca}^{Gt} + X_{Mn}^{Gt})\}}{(lnK_D + 0.732)}$$

7.B.1.3 Garnet-cordierite geothermometry

Several efforts have been made to calibrate Fe-Mg partitioning between garnet and cordierite as thermometer and barometer. Unfortunately, the existing models ofCurrie (1971, 1974), Hensen and Green (1971, 1972, 1973), Hutcheon et al. (1974), Thompson (1976), Perchuk (1977), Holdaway and Lee (1977), Wells (1979), Wells and Richardson (1979), Perchuk and Lavrent'va (1981), Perchuk et al. (1981), Bhattacharya et al. (1988), Aranovich and Podlesskii (1989) and Nichols et al. (1992) show significant inconsistencies. Newton and Wood (1979) illustrated the effect of the hydration state of cordierite on its stability. The model of Martignole and Sisi (1981) also considers the water content of cordierite.

According to Ellis (1980), the present geothermometers imply equilibration at the temperature of 500°–600°C for the granulites from Enderby land, Antarctica, although the width of the two-phase field separating the three-phase fields is reasonably small. This, combined with a few more discrepancies, suggests thatthe evaluation or numerous conflicting theories for garnet-cordierite equilibria stillrequires unambiguous and accurate data.

The exchange reaction:

 $1/3Mg_3Al_2Si_3O_{12} + 1/2Fe_2Al_4Si_5O_{18} = 1/3Fe_3Al_2Si_3O_{12} + 1/3 Mg_2Al_4Si_5O_{18}....(3)$ Mg-Garnet Fe-Cordierite Fe-Garnet Mg-Cordierite The distribution coefficient (K_D) is given by the expression:

$$K_{D} = (X_{Fe}/X_{Mg})^{Grt} \cdot (X_{Mg}/X_{Fe})^{Crd}$$
$$X_{Mg}^{Grt} = \frac{Mg}{i}, X_{Ca}^{Grt} = \frac{Ca}{i}, X_{Fe}^{Grt} = \frac{M}{i}$$

Where i = (Fe + Mg + Mn + Ca)

$$X_{Fe}^{Crd} = \frac{Fe}{Fe + Mg}, X_{Mg}^{Crd} = \frac{Mg}{Fe + Mg}$$

Several models have been introduced by several workers.

Models

Thompson (1976)

A plot of the ln K_D^{Fe-Mg} vs 1/T (K) using the core compositions of coexisting garnetcordierite pairs from natural samples and obtained linear relation for equation (3) after least square analysis.

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

and he obtained the following thermodynamic data:

$$\Delta V/R = -0.0155$$
 cal/bar

 $\Delta S/R$ = -0.896 cal/K/mole

$$\Delta H/R = 2725$$
 cal/mole

Using these data, he formulated the following equation for geothermometry:

$$T = \frac{[2725 + 0.0155(P - 1)]}{lnK_D + 0.896}$$

Holdaway and Lee (1977)

Using the following thermodynamic parameters, Holdaway and Lee (1977) proposed a geothermometer based on experimental and natural data of coexisting garnet-cordierite phases.

 Δ H=-6150 Cal

 ΔS =-2.69 Cal/deg

 ΔV =-0.0303 Cal/bar

$$T = \frac{[3095 + 0.0152(P - 1)]}{lnK_{D} + 1.354}$$

Perchuk et al. (1981)

Perchuk and co-workers have refined their geothermometer based on the experimental work of Aranovich and Podlesskii (1981).

$$T = \frac{[2729]}{lnK_D + 0.802}$$

Perchuk et al. (1985)

Perchuk et al., (1985) formulated an equation for calculation of temperature of metamorphism for Aldan granulites as:

$$T = \frac{[3087 + 0.018(P - 1)]}{lnK_D + 1.342}$$

Bhattacharya et al. (1988)

Bhattacharya et al. (1988) used naturally occurring garnet and cordierite to derive an equation for thermometer using the interchange energy of Fe-Mg mixing in cordierite and the free energy change of the exchange equilibrium:

$$T = \frac{\left[1814 + 0.0152(P-1) + 1122(X_{Mg} - X_{Fe})Crd + 1258(X_{Fe} - X_{Mg})Gt + 1510(X_{Ca} - X_{Mn})Gt\right]}{1.354 + lnK_D}$$

Aranovich and Podlesskii (1989)

The proposed geothermometer based on experimental data in the CFMAS system is given below:

$$T = \frac{[3087 + 0.0178(P - 1) - A]}{lnK_D + 1.343 + B}$$

Where,

$$A = -315(X_{Ca}^{Grt})^2 - 3343(X_{Fe}^{Grt}, X_{Ca}^{Grt}) - 4076(X_{Mg}^{Grt}, X_{Ca}^{Grt}) + X_{Ca}^{Grt}(X_{Mg}^{Grt} - X_{Fe}^{Grt}).529$$

$$B = +0.637(X_{Ca}^{Grt})^2 + 1.427(X_{Fe}^{Grt}, X_{Ca}^{Grt}) + 1.510(X_{Mg}^{Grt}, X_{Ca}^{Grt}) + X_{Ca}^{Grt}(X_{Mg}^{Grt} - X_{Fe}^{Grt}).0.457$$

Perchuk (1991)

Perchuk (1991) has attempted to construct an internally consistent thermometer adopting nearly ideal solid solution models for garnet-cordierite pairs as:

$$T = \frac{[3020 + 0.0176(P - 1) + 1074 \times X_{Ca}^{Gt}]}{lnK_{D} + 1.287}$$

Nichols et al. (1992)

Nichols et al. (1992) used experimentaldata based on non-ideal mixing on internally consistent gahnite-spinel-cordierite-garnetequilibria in FMASHZ system to formulate an the equation for the garnet-cordierite pair.

$$T = \frac{[2268 + 0.012632(P - 1) - C - A]}{lnK_{D} + 0..62889 + b}$$

Dwivedi et al. (1998)

Dwivedi et al. (1988) used a multiple linear regression method to develop a garnetcordierite thermometer that estimated Fe-Mg non-ideality in cordierite. Their calibration was based on the ternary margules parameters of Holdaway et al. (1997) and the quaternary parameters of Berman (1990) for garnets.

$$T1 = \frac{\left[27018 + 0.13(P - 1) - 2024(X_{Fe} - X_{Mg}) - Crd - A\right]}{\left[RlnK_D + 12.8 + B\right]}$$
$$T2 = \frac{\left[26932 + 0.13(P - 1) - 887(X_{Fe} - X_{Mg}) - Crd - c\right]}{\left[RlnK_D + 12.36 + D\right]}$$

Kaneko and Miyano (2004)

Kaneko and Miyano (2004) calibrated a garnet-cordierite thermometer utilizing Fe²⁺-Mg cation exchange data. They recently assessed non-ideal mixing features of garnet in terms of iterative multiple least square regressions of the experimental results.

$$T(K) = \frac{\left[-26144 + (-0.122 + W_V^{Gt}) \times (P - 1) + W_H^{Gt} - 80.449 \times (X_{Fe} - X_{Mg})Crd\right]}{\left[-12.7094 - RlnK_D + W_S^{Gt} + 1.642(X_{Fe} - X_{Mg})Crd\right]}$$

7.B.1.4 Garnet-clinopyroxene geothermometry

Garnet-Clinopyroxene thermometry developed by Ellis and Green (1979) is based on the experimental Fe-Mg exchange equilibria studies. Thermometric model for the Fe-Mg exchange reaction:

$$1/3 Mg_3 Al_2 Si_3 O_{12} + Ca Fe Si_2 O_6 = 1/3 Fe_3 Al_2 Si_3 O_{12} + Ca Mg Si_2 O_6....(4)$$

Pyrope Headenbergite Almandine Diopside

The distribution coefficient function of temperature, pressure and X_{Ca} of garnet is given by K_D , obtained from the mineral compositions. In the present calculation, the mole fraction of Fe²⁺ in the three equivalent divalent sites of garnet structure and mole fraction of Fe in cpx is considered, assuming the minerals are ideal (after Ellis and Green, 1979).

Models

Ellis and Green (1979)

The distribution coefficient (K_D) is a function of pressure, temperatureand X_{Ca} of garnet, which can be obtained from the mineral compositions. Experimentally, Ellis and Green (1979) developed garnet-clinopyroxene thermometry for the Fe-Mg exchange reaction (4). Their thermometric model for Fe-Mg exchange reaction:

$$T = [3104X_{Ca}^{Gt} + 3030 + 10.86 \text{ P}]/([lnK_D + 1.9034])$$

Where, $K_D = (X_{Fe}/X_{Mg})^{Grt}$. $(X_{Mg}/X_{Fe})^{Cpx}$

Ravana (2000)

They incorporated the effect of X_{Mn}^{Grt} using data from natural Mn-rich garnet– clinopyroxene pairs. Their thermometric model for Fe-Mg exchange reaction:

 $T = \frac{\left[\left(1939.9+3270X_{Ca}^{Grt}-1396(X_{Ca}^{Grt})^{2}+3319X_{Mn}^{73Grt}-3535(X_{Mn}^{Grt})^{2}+1105X_{Mg\#}^{Grt}-3561(X_{Mg\#}^{Grt})^{2}\right)-2324(X_{Mg\#}^{Grt})^{3}+169.4P\right)\right]}{\ln K_{D}+1.223} - 273$

Where, $K_D = (Fe^{2+}/Mg)^{Gt}/(Fe^{2+}/Mg)^{Cpx}$,

 $X_{Ca}^{Gt} = Ca/(Ca+Mn+Fe^{2+}+Mg)$ in garnet, $X_{Mn}^{Gt} = Mn/(Ca+Mn+Fe^{2+}+Mg)$ in garnet, and $X_{Mn\#}^{Gt} = Mg/(Mg+Fe^{2+})$ in garnet.

Ganguly (1979)

Ganguly (1979) examined the effects of Mn in addition to other variables, Fe/Mg, Ca and pressure. This formulation is based on experimental and thermochemical data. This formulation is:

$$T = \frac{1586X_{Ca}^{Gt} + 1308X_{Mn}^{Gt} + 4801 + 11.07 \text{ P}}{([\ln K_{D} + 1.9034])}$$

Dahl (1980)

This thermometer has been empirically derived from a granulite terrane in southwest Montana. The formulation is:

$$T = \left[2482 + 1509 \left(X_{Fe}^{Gt} - X_{Mg}^{Gt}\right) + 2810 X_{Ca}^{Gt} + 2855 X_{Mn}^{Gt}\right] / [\text{RlnK}_{\text{D}}]$$

7.B.1.5 Amphibole-plagioclase geothermometry:

Blundy and Holland (1990) developed an amphibole-plagioclase thermometer based on the reaction:

$$NaCa_2Mg_5Si_4(AlSi_3)O_{22}(OH)_2 + 4SiO_2 = Ca_2Mg_5Si_8O_{22}(OH)_2 + NaAlSi_3O_8$$

Edenite Quartz Tremolite Albite

Holland and Blundy (1994)

Holland and Blundy (1994) developed thermometers for application to coexisting amphibole and plagioclase. The thermometer takes into account non-ideal mixing in both amphibole and plagioclase and is calibrated against an extensive data set of natural and synthetic amphiboles. The thermometric equation is:

$$T = \frac{\left[-76.95 + 0.79P + Y_{ab} + 39.4X_{Na}^{A} + 22.4X_{K}^{A} + (41.5 - 2.89P).X_{Al}^{M2}\right]}{-0.0650 - R.\frac{\ln\left(27.X^{A}.X_{Sl}^{Ti}.X_{Ab}^{Plg}\right)}{256.X_{Na}^{A}.X_{Il}^{Ti}}}$$

Where the Y_{ab} term is given by: $X_{ab} > 0.5$ then $Y_{ab} = 0$

Otherwise $Y_{ab} = 12.0(1-X_{ab})^2 - 3.0 \text{ kJ}$

R = 0.0083144 kJ/K/mol $\Delta H = -76.95 \pm 1.8 \text{kJ}$ $\Delta S = -0.065 \pm 0.002 \text{ kJ/K}$ $\Delta V = 0.79 \text{ kJ/kbar}$

7.B.2 Geobarometers

7.B.2.1 Garnet-biotite -plagioclase-quartz geobarometers

The GBPQ barometry is based on the following Mg- and Fe-model equilibria: $Mg_3Al_2Si_3O_{12}+2Ca_3Al_2Si_3O_{12}+3K(Mg_2Al)(Si_2Al_2)O10(OH)_2+6SiO_2=6CaAl_2Si_2O_8+3KMg_3(AlSi_3)O10(OH)_2$ pyrope grossular eastonite quartz anorthite Phlogopite.....(5) And $Fe_3Al_2Si_3O_{12} + 2Ca_3Al_2Si_3O_{12} + 3K(Fe_2Al)(Si_2A_{12})O_{10}(OH)_2 + 6SiO_2 = 6CaAl_2Si_2O_8 + 3KFe_3(AlSi_3)O_{10}(OH)_2$

 $almandine \quad grossular \quad siderophyllite \quad quartz \quad anorthite \quad annite...(6)$

Wu et al. (2006)

Inserting activity models of garnet, biotite and plagioclase into equation 5 and 6, Wu et al., described two pressure dependent models of GBPQ barometry:

$$\begin{split} & P(1)(\text{bars}) = 1 - \frac{\Delta_1 H^0}{\Delta_1 V^0} + T(K) \left(\frac{\Delta_1 S^0}{\Delta_1 V^0}\right) + 3 \left(X_{Fe}^{Bt} + X_{Mg}^{Bt} - X_{Al}^{Bt}\right) \left(\frac{W_{MgAl}^{Bt}}{\Delta_1 V^0}\right) + \\ & 3X_{Ti}^{Bt} \left[\frac{W_{AlTi}^{Bt} - W_{MgTi}^{Bt}}{\Delta_1 V^0}\right] + \left(\frac{1}{\Delta_1 V^0}\right) \left[T(K)(-RlnK_1^{ideal} - 6Fa + Mga + 2Caa - 788.73X_{Fe}^{Bt} + P(-6Fb + Mgb + 2Cab) - 6Fc + Mgc + 2Cac + 667683.0X_{Fe}^{Bt}] \end{split}$$

And

$$\begin{split} & P(2)(\text{bars}) = 1 - \frac{\Delta_2 H^0}{\Delta_2 V^0} + T(K) \left(\frac{\Delta_2 S^0}{\Delta_2 V^0}\right) + 3 \left(X_{Fe}^{Bt} + X_{Mg}^{Bt} - X_{Al}^{Bt}\right) \left(\frac{W_{MgAl}^{Bt}}{\Delta_2 V^0}\right) + \\ & 3X_{Ti}^{Bt} \left[\frac{W_{AlTi}^{Bt} - W_{MgTi}^{Bt}}{\Delta_2 V^0}\right] + \left(\frac{1}{\Delta_2 V^0}\right) \left[T(K) \left(-Rln K_2^{ideal} - 6Fa + Fea + 2Caa - 840.918 X_{Fe}^{Bt} + 52.188 X_{Mg}^{Bt} + 840.918 X_{Al}^{Bt} + 1111.17 X_{Ti}^{Bt}\right) + P(-6Fb + Feb + 2Cab) - 6Fc + Fec + \\ & 2Cac + 736677.0 X_{Fe}^{Bt} - 68994.0 X_{Mg}^{Bt} - 736677.0 X_{Al}^{Bt} - 93297.0 X_{Ti}^{Bt}\right] \quad \text{Where,} \end{split}$$

$$K_{1}^{ideal} = \left[(X_{An}^{Plg})^{6} (X_{Phl}^{Bt})^{3} \right] / \left[(X_{Py}^{Grt}) (X_{Grs}^{Grt}) (X_{En}^{Bt})^{3} (X_{Qz}^{Qz})^{6} \right]$$

$$K_{2}^{ideal} = \left[(X_{An}^{Plg})^{6} (X_{ann}^{Bt})^{3} \right] / \left[(X_{alm}^{Grt}) (X_{Grs}^{Grt}) (X_{Sid}^{Bt})^{3} (X_{Qz}^{Qz})^{6} \right]$$

$$X_{Fe}^{Bt} = Fe^{2+} / (Fe^{2+} + Mg + Al^{VI} + Ti), X_{Mg}^{Bt} = Mg / (Fe^{2+} + Mg + Al^{VI} + Ti)$$

$$X_{Al}^{Bt} = Al^{VI} / (Fe + Mg + Al^{VI} + Ti), X_{Ti}^{Bt} = Ti / (Fe + Mg + Al^{VI} + Ti)$$

$$X_{Fe}^{Grt} = Fe^{2+} / (Fe^{2+} + Mg + Ca + Mn), X_{Mg}^{Grt} = Mg / (Fe^{2+} + Mg + Ca + Mn)$$

$$X_{Ca}^{Grt} = Ca / (Fe^{2+} + Mg + Ca + Mn), X_{Mn}^{Grt} = Mn / (Fe^{2+} + Mg + Ca + Mn),$$

$$X_{An}^{Plg} = 0.25X_{Ca}^{Plg} (1 + X_{Ca})^{2},$$

$$W^{Plg} \qquad Ca \qquad W^{Plg} \qquad K$$

$$X_{Ca}^{Plg} = \frac{Ca}{Ca + Na + K} \qquad X_{K}^{Plg} = \frac{K}{Ca + Na + K}$$

7.B.2.2 Garnet-orthopyroxene-plagioclase-quartz geobarometers

The garnet-orthopyroxene-plagioclase-quartz equilibrium is a goodgeobarometer due to large volume exchange (ΔV). The Mg-end member reactioninvolved in the equilibrium is: P_{Mg}

 $3Mg_{2}SiO_{3} + 3CaAl_{2}Si_{2}O_{8} = Ca_{3}Al_{2}Si_{3}O_{12} + 2Mg_{3}Al_{2}Si_{3}O_{12} + 3SiO_{2}.....(7)$ Enstatite Anorthite Grossular Pyrope Quartz

Newton (1978), Perkins III and Newton (1985) and Newton and Perkins III (1982) calibrated the reaction (7) using the thermodynamic data available at thattime.

Similarly, for the CaO-FeO-Al₂O₃-SiO₂ (CFAS) system Bohlen et al. (1983a) experimentally calibrated two reactions (a & b) and combined them to derive the thermodynamic expression for the geobarometry of almandine-ferrosilite-plagioclase-quartz (Fe-end member) equilibrium (4).

 $Fe_2SiO_4 + SiO_2 = Fe_2Si_2O_6$ (a)

Fayalite Quartz Ferrosilite

 $CaFe_2Al_2Si_3O_{12}=Fe_2SiO_4+CaAl_2Si_2O_8$ (b)

Garnet Fayalite Anorthite

Considering the non-ideal mixing of Ca-Fe in garnet, they calibrated the end member reaction (8).

Ca₃Al₂Si₃O₁₂ + 2Fe₃Al₂Si₃O₁₂=3Fe₂SiO₄ + 3CaAl₂SiO₈.....(8) Grossular Almandine Fayalite Anorthite After adding the reactions (a) and (4) results in the following reaction **P**_{Fe}

$$3FeSiO_3 + 3CaAl_2Si_2O_8 = Ca_3Al_2Si_3O_{12} + 3Fe_3Al_2Si_3O_{12} + 3SiO_2 \quad \dots \dots \dots (9)$$

Ferrosilite Anorthite Grossular Almandine Quartz

These vapour-absent, solid-solid net-transfer equilibria involve large volumechanges and, therefore it makes brilliant geobarometers.

Several workers have presented various calibrations of P_{Mg} and P_{Fe} reactions.Perkins III and Chipera (1985) and Moecher et al. (1988) calibrated new geobarometers for the reactions (7) and (5) based on the different models of non-ideal mixing in garnet derived from the thermodynamic and experimental data. Recently Bhattacharya et al. (1991) calibrated the two geobarometry for above end-member reactions using the thermochemical data for the reaction (7) and adding the experimental data of Bohlen et al. (1983a) of the reactions (a) and (8) for the reaction (9). They assumed the ideal mixing of Ca and Fe in Garnet. The distribution coefficient for P_{Mg} and P_{Fe} reactions are denoted by K₁ and K₂, respectively.

$$K_{1} = (a_{Ca}^{Grt}) \cdot (a_{Mg}^{Grt})^{2} / (a_{An}^{Pl}) \cdot (a_{Mg}^{Opx})$$
$$K_{2} = (a_{Ca}^{Grt}) \cdot (a_{Fe}^{Grt})^{2} / (a_{An}^{Pl}) \cdot (a_{Fe}^{Opx})$$

Regular solution in Garnet

$$a_{Ca}^{Grt} = X_{Ca}^{Grt} \cdot \exp\{\left[W_{CaFe}(X_{Fe}^{2})^{Grt} + W_{CaMg}(X_{Mg}^{2})^{Grt} + \left(W_{CaFe} + W_{CaMg} - W_{MgFe}\right)X_{Fe}^{Grt} \cdot X_{Mg}^{Grt}\right)\right]/RT\}$$

$$a_{Mg}^{Grt} = X_{Mg}^{Grt} \cdot \exp\{\left[W_{CaMg}(X_{Ca}^{2})^{Grt} + W_{MgFe}(X_{Fe}^{2})^{Grt} + \left(W_{CaMg} + W_{MgFe} - W_{CaFe}\right)X_{Ca}^{Grt} \cdot X_{Fe}^{Grt}\right)\right]/RT\}$$

$$a_{Fe}^{Grt} = X_{Fe}^{Grt} \cdot \exp\{\left[W_{CaFe}(X_{Ca}^{2})^{Grt} + W_{MgFe}(X_{Mg}^{2})^{Grt} + \left(W_{CaFe} + W_{MgFe} - W_{CaMg}\right)X_{Ca}^{Grt} \cdot X_{Mg}^{Grt}\right)\right]/RT\}$$

Regular solution in orthopyroxene

$$a_{Mg}^{opx} = X_{Mg} \cdot \exp\{\left[W_{MgFe}(X_{Fe2+}^{opx})^2 + W_{MgAl}(X_{Al}^{opx})^2 + (W_{MgFe} + W_{MgAl} - W_{FeAl})\}X_{Fe2+}^{opx} \cdot X_{Al}^{opx})\right]/RTa_{Fe}^{opx}$$

$$= X_{Fe} \cdot \exp\{\left[W_{MgFe}(X_{Mg}^{opx})^2 + W_{FeAl}(X_{Al}^{opx})^2 + (W_{MgFe} + W_{FeAl} - W_{MgAl})\}X_{Mg}^{opx} \cdot X_{Fe2+}^{opx})\right]/RT$$

$$/RT$$

Where, $X_{Mg}^{Opx} = \frac{Mg}{i}$, $X_{Fe2+}^{Opx} = \frac{Fe2+}{i}$, $X_{Al}^{Opx} = [\frac{\Sigma_{2}^{Al}}{i}]$, $i = (Mg + Fe^{2+} + Al/2)$

Models

Perkins III and Chipera (1985)

Perkins III and Chipera (1985) have calibrated two internally consistent geobarometers for Mg - and Fe end-member reactions (7) and (9).

The derived thermodynamic parameters for

Mg-reaction:

$$\Delta H = 1310 \text{ cal}, \Delta S = -7.355 \text{ cal K-1}, \Delta V = -0.5408 \text{ cal bar-1}$$

Fe-reaction:

 $\Delta H = -2247$ cal, $\Delta S = -8.364$ cal K-1, $\Delta V = -0.5849$ cal bar-1

are substituted in the equation of the standard state to obtain the barometric expression.

$$P_{Mg} = 1 + \frac{[T(7.355 + RlnK_1) + 1310]}{0.5408}$$
$$P_{Fe} = 1 + \frac{[T(8.364 + RlnK_2) - 2247]}{0.549}$$

The expression for geobarometry given in above equations havebeen derived from the graphic plot and equations given by Perkins III and Newton (1981).

Perchuk and Lavrente'va (1990)

They proposed the following expression for garnetorthopyroxene geothermometer based on experimental dataand thermodynamics.

$$T = \frac{\left[4066 - 347 \times \left(X_{Mg} - X_{Fe}\right)^{Opx} - 17484X_{Al}^{Opx} + 5769X_{Ca}^{Gt} + 23.42 \times P\right]}{1.987 lnK_{D} + 2.143 + 0.0929 \left(X_{Mg} - X_{Fe}\right)^{Opx} - 12.8994X_{Al}^{Opx} + 3.846X_{Ca}^{Gt}}$$

Where i=(Fe+Mg+Al/2)

$$X_{Fe}^{Opx} = Fe/i;$$

 $X_{Mg}^{Opx} = Mg/i$
 $X_{Al}^{Opx} = Al/2/i$

Bhattacharya et al. (1991)

Bhattacharya and co-workers calibrated geobarometric models for garnetorthopyroxene- plagioclase-quartz. In their calibration, they derived new interaction parameters for garnet and orthopyroxene and substituted these values in the geobarometric equation of Newton and Perkins III (1982) and Perkins III and Chipera (1985). Their geobarometric expressions for Mg and Fe end member reactions are as follows:

$$P_{Mg} = 1 + \frac{[T(7.417 + RlnK_1') + 2237]}{0.567}$$
(13)
$$P_{Fe} = 1 + \frac{[T(8.153 + RlnK_2') + 2135]}{0.5928}$$
(14)

The equilibrium constant K'_1 and K'_2 are exposed as $(a_{Sio2}^{Qtz} = 1.0 \text{ for quartz})$ $K'_1 = a_{Ca}^{Grt} \cdot (a_{Mg}^{Grt})^2 / a_{An}^{Pl} \cdot (a_{Mg}^{Opx})^2;$ $K'_2 = a_{Ca}^{Grt} \cdot (a_{Fe}^{Grt})^2 / a_{An}^{Pl} \cdot (a_{Fe}^{Opx})^2$

The activity of anorthite at 750 °C is taken from Perkins III and Chipera (1985).

$$a_{Mg}^{opx} = X_{Mg}^{opx} \cdot \exp[948(X_{Fe}^{opx})^2/1.987.1000]$$

$$a_{Fe}^{opx} = X_{Fe}^{opx} \cdot \exp[948(X_{Mg}^{opx})^2/1.987.1000]$$

$$X_{Mg} = Mg/ (Mg + Fe^{2+}), X_{Fe2+} = Fe^{2+}/ (Mg + Fe^{2+})$$

Lal (1993)

Lal (1993) have been calibrated both Fe- and Mg end-member reactions basedon combining large published experimental data sets (FMAS, n = 104 and CFMAS, n = 78) applicable over a wide P-T range. The internally consistent calibrations by Lal

(1993) produce congruent results for P_{Fe} and P_{Mg} end-members.

$$P_{Mg} = 1 + \frac{[T(5.376 + RlnK_1) + 3985]}{0.5614}$$
$$P_{Fe} = 1 + \frac{[T(8.644 + RlnK_2) - 2249]}{0.60946}$$

Garnet activity has been calculated using the sub-regular solution mixing modelby Ganguly

and Saxena (1984).

where,

 $W_{\text{FeMg}} = -1256 + 1.0T, W_{\text{MgFe}} = 2880 - 1.7T,$

 $W_{MgCa} = 1000 - 1.5 \text{ T}, W_{CaMg} = 4047 - 1.5 \text{ T}, W_{CaFe} = -723 + 0.332 \text{ T},$

 $W_{FeCa} = 1090, C_{123} = -4498 + 1.516T$

For the orthopyroxene activity calculations, a regular solution model is used.

where,

 $W_{MgFe} = 948 - 0.34T, W_{FeAl} = -1950, W_{MgAl} = 0$

The activity of anorthite is taken from Newton and Perkins III (1982).

7.B.2.3 Garnet-clinopyroxene-plagioclase-quartz geobarometers

The garnet-plagioclase-clinopyroxene-quartz assemblage represents a potential geobarometer. Thermodynamic calibrations for these assemblages have been formulated by Newton and Perkins (1982), giving consistent results for the samples containing both pyroxenes. For the continuous reaction:

From the activity relations given by Newton and Perkins (1982): activities of garnet components, plagioclase activities, and diopside (cpx) activities are determined. The ideal two-site model, which gives good results in many applications, is used here for the pyroxene components, for which the cation site assignments for clinopyroxene followed here are: Ca, Na, Mn and Fe²⁺ in M2 site and Al^{vi}, Ti, Fe³⁺, Mg and the remaining Fe²⁺ in the M1 site.

Models

Newton and Perkins (1982)

Perkins and Newton (1981) and Newton and Perkins (1982) calibrated this geothermometer in the CaO-Al₂O₃-MgO-SiO₂ system. Their geobarometric expression for the reaction (10) is:

$$P(\pm 1500 \text{kbar}) = 675 + 17.929 \text{ T (K)} + 3.5962 \text{ T (K)} \ln \text{K} (\pm 1.90 \text{kbar})$$
Where, $K = (a_{Ca}^{Grt})^2 .(a_{Mg}^{Grt})/(a_{An}^{Plg})^2 .(a_{CaMg}^{Cpx})$

$$a_{Mg}^{Grt} = X_{Mg}^{Grt} . \exp [(3300 - 1.5 \text{T})(X_{Ca}^{Grt})^2 + X_{Ca}^{Grt} . X_{Fe}^{Grt}]/\text{Rt}$$

$$a_{Ca}^{Grt} = X_{Ca}^{Grt} . \exp [(3300 - 1.5 \text{T})(X_{Mg}^{Grt})^2 + X_{Mg}^{Grt} . X_{Fe}^{Grt}]/\text{Rt}$$

$$a_{Ca}^{Plg} = [\frac{X_{Ca}(1 + X_{Ca})^2}{4} .\exp [\frac{(1 - X_{Ca})^2}{RT}(2050 + 9393X_{Ca})]$$

Eckert et al. (1991)

They used the equations of the Newtons and Perkins III (1982) and developed new calibration for clinopyroxene-garnet-plagioclase-quartz geobarometer in thesystem CaO-Al₂O₃-FeO-MgO-SiO₂ based on thermodynamic data set. Their geobarometric expression for the reaction (1) is:

 $P(kbar) = 2.60 + 0.01718 T (K) + 0.003596 T (K) lnK (\pm 1.90kbar)$

where,

 $K = (a_{Ca} \ . \ a_{Mg})^{Grt} / (a_{Ca})^{Plg} \ . \ (a_{CaMg})^{Cpx}$

7.B.2.4 Amphibole-plagioclase-quartz geobarometers

Bhadra and Bhattacharya (2007)

A new garnet-free, hornblende-plagioclase barometer has been formulated by Bhadra and Bhattacharya (2007) based on the reaction:

Tremolite + tschermakite + 2albite = 2 pargasite + 8 quartz.....(11)

A linear least-square fit to the coexisting hornblende and plagioclase composition in the experiments yields the following barometric expressions:

$$\begin{split} P_1(kbar) &= \left[-9.326 + 0.01462T(K) + RTlnK_{ideal} - 98.698X_{Na}^A - 33.213X_K^A \right. \\ &- 20.338X_{Na}^{M4} - 39.101X_{Fe2+}^{M13} + 100.392X_{Al}^{M2} + 131.03X_{Fe2+}^{M2} \right. \\ &+ 82.479X_{Fe3+}^{M2} - 118.653X_{Al}^{Ti} - 2RTln\gamma Ab \right] / (-\Delta V) \end{split}$$

And

$$\begin{split} P_2(kbar) &= \left[-1.869 + 0.00762T(K) + RTlnK_{ideal} - 102.692X_{Na}^A - 35.251X_K^A \right. \\ &- 15.969X_{Na}^{M4} - 40.499X_{Fe2+}^{M13} + 93.069X_{Al}^{M2} + 130.750X_{Fe3+}^{M2} \right. \\ &+ 74.226X_{Fe3+}^{M2} - 104.402X_{Al}^{Ti} - 2RTln\gamma Ab \left] / (-\Delta V) \end{split}$$

Where,

$$K_{ideal} = [\frac{[16(X_{Na}^{A}).(X_{Al}^{Ti})]}{(X_{Na}^{A})(X_{Si}^{Ti})(X_{Ab})}]^{2}$$

 X_{Ab} and γ_{Ab} are the mole fraction and activity coefficient of albite in plagioclase, respectively, and ΔV is the volume change for the reaction.

7.B.2.5 Garnet-cordierite-sillimanite-quartz geobarometers

Garnet and cordierite are known to coexist only over a relatively narrow pressurerange; as a result, many workers have attempted to calibrate Fe/Mg partitioning between garnet and cordierite as geothermometers i.e. Currie (1971), Hensen and Green (1973), Thompson (1976), Tracy et al (1976), Hensen (1977), Holdaway and Lee (1977), Newton and Wood (1979), Martignole and Sisi (1981), Lonker (1981), Aranovich and Podlesskii (1989). Both Fe and Mg end-members have been used for calibration. One of the major problems in these equilibria is the presence of water in the structural channels of cordierite. Hence the geobarometers have been calibrated bysome at $XH_2O = 1.0$ and by a few others at $XH_2O = 0.0$. Few workers have calibrated two different models for $XH_2O = 1.0$ and $XH_2O = 0.0$. There are two end-member reactions, i.e. Mg and Fe. The Mg-end-member reaction is:

 $3Mg_2Al_4Si_5O_{18}=2Mg_3Al_2Si_3O_{12}+4Al_2SiO_5+5SiO_2$ (PMg).....(12)

Mg-Cordierite Pyrope Sillimanite Quartz

The Fe end-member reaction is:

 $3Fe_2Al_4Si_5O_{18} = 2Fe_3Al_2Si_3O_{12} + 4Al_2SiO_5 + 5SiO_2(\mathbf{P}_{Fe})$ (13)

Fe-Cordierite Almandine Sillimanite Quartz

The distribution coefficient for P_{Mg} and P_{Fe} reactions are given by K_{D1} and K_{D2} respectively.

 $K_{D1} = X_{Ma}^{Crd} / X_{Ma}^{Grt}; K_{D2} = X_{Fe}^{Crd} / X_{Fe}^{Grt}$

Models

Wells (1979)

He calibrated geobarometers for both Fe and Mg end-members on the basis of the experimental works of Currie (1971) and Weisbrod (1973) under the conditions $P_{H2O} =$ Ptotal. Wells (1979) did not use any solution model for garnet mixing. The formulation for Mg end-member at $X_{H2O} = 1$ is:

$$P_{Mg} = 1 + \frac{[T(23.67 + 6RlnK_{D1}) + 16773]}{3.6481}$$

The formulation for Fe end-member at $X_{H2O} = 1$ is:

$$P_{\text{Fe}} = 1 + \frac{[T(-9.44 + 6RlnK_{D2}) + 21801]}{3.8256}$$

Aranovich and Podlesskii (1983, 1989)

They calibrated the geobarometer for the Mg end-member equilibrium for barometry based on experimental data in CMAS system. They also considered the effect of fluid contents (X_{H2O} and X_{CO2}) along the structural channels of cordierite and used the sub-regular solution model for the calculation of activity of Mg in garnet, taking W_{FeMg} and W_{MgFe} to be zero.

$$P_{Fe} = 1 + \frac{[T(27.588 - 6RlnK_1) - 36 + 3(2414 - 1.9552T)X_{H20} + 3(17.883 - 0.828679T)X_{CO2}]}{2.7128}$$

where,
$$K_1 = X_{Mg}^{Crd} / a_{Mg}^{Grt}$$

 $X_{H2O} = (H_2O/H_2O+CO_2)$ mole
 $X_{CO2} = (1-X_{H2O})$
 $a_{Mg}^{Grt} = X_{Mg}$. exp {[$(1 - 2X_{Mg})X_{Ca}^2 W_{MgCa} + 2X_{Mg}X_{Ca}(1 - X_{Mg})W_{CaMg} - 2X_{Ca}.X_{Fe}(X_{Ca}W_{FeCa} + X_{Fe}W_{CaFe}) + (1 - 2X_{Mg})X_{Ca}X_{Fe}. C]/Rt$ }
 $W_{CaMg} = 4050 - 1.5T$, $W_{MgCa} = 1000 - 1.5T$, $W_{CaFe} = -3321 + 1.418T$,
 $W_{FeCa} = 374 - 0.234T$, C = 1051.5 -0.908T

Perchuk et al. (1985)

He formulated two geobarometers for Mg end-member reaction, one assuming water activity to be 0.0 ($P_{H2O} = 0$) and the other 1.0 ($P_{H2O} = 1$). They used garnet mixing using the regular solution model. The expression for calculation of geobarometric formulation for P_{Mg} at $P_{H2O} = 0$:

$$P_{Mg} = 1 + \frac{[T(27.72 + 6RlnK_1) - 306]}{3.82962}$$

The expression for calculation of geobarometric formulation for P_{Mg} at $P_{H2O} = 1$:

$$P_{Mg} = 1 + \frac{[T(27.72 + 6RlnK_1) - 306 + (2504 - 2T)]}{2.74443}$$

They also used the following method of calculating the activity of Mg in garnet:

$$a_{Mg}^{Grt} = X_{Mg}^{Grt}$$
. exp [(3300–1.5T)(X_{Ca}^{Grt})² +(5704–1.242T) X_{Ca}^{Grt} . X_{Fe}^{Grt}]/Rt
Where K₁= $X_{Mg}^{Crd}/X_{Mg}^{Grt}$

Lal (1991)

Lal (1991) calibrated the following equation for the assemblage garnet-cordierite sillimanite- quartz for the Mg end-member reaction (12) at ($X_{H2O} = 0$).

$$P_{\text{Fe}} = 1 + \frac{[T(20.22 - 6RlnK_{D1}) + 8230]}{3.6262}$$

Where $K_{D1} = X_{Mg}^{Crd} / X_{Mg}^{Grt}$

PART C- APPLICATION OF GEOTHERMOBAROMETERS AND AVERAGE P-T

Understanding the thermal state of the lithospheric mantle in the past or present requires accurate estimation of the P-T conditions. Naturally, precise and exact thermometers and barometers are necessary to get dependable P-T calculations (Tam et al. 2012). The estimated pressure and temperature conditions obtained from the different existing models of geothermobarometry are represented in diagrams and described as follows and illustrated in Figures 7.1-7.10:

7.C.1 Pelitic granulite

The various conventional geothermobarometry pairs such as garnet–orthopyroxene and garnet–biotite geothermometers and garnet–orthopyroxene–plagioclase-quartz and garnet-biotite-plagioclase-quartz geobarometers have been used for evaluating the temperature and pressure conditions for pelitic granulites (Grt-Opx-Bt-Sil). Table 7.1 represents the temperature and pressure estimates of pelitic granulites with various proposed models. For the pelitic granulite, the estimated temperature by Grt-Bt thermometry provides prograde temperatures of 639°C–697°C for garnet core and biotite included in garnet and 615°C–661°C for garnet and matrix biotite, whereas pressure of 5.8 kbar at 700°C using the garnet-biotite-plagioclase-quartz geobarometer (GBPQ). Similarly, Grt-Opx thermometry provides peak temperatures of 760°C–841°C for core values and 713°C–829°C for rim values of garnet and orthopyroxene and peak pressure has been observed as 6.43–7.42 kbar at 800°C using the garnet–orthopyroxene–plagioclase-quartz (GOPQ) barometer.

For Grt-Opx-Crd-Bt-Sil pelitic granulites, we have used conventional geothermobarometry pairs such as, garnet-biotite, garnet-orthopyroxene and garnetcordierite geothermometers garnet-biotite-plagioclase-quartz, as well as garnetorthopyroxene-plagioclase-quartz and garnet-cordierite-sillimanite-quartz geobarometers for evaluating the temperature and pressure conditions. Table 7.2 represents the temperature and pressure estimates of pelitic granulites with various proposed models. For the pelitic granulite, the estimated temperature by Grt-Bt thermometry provides prograde temperatures of 640°C–692°C for garnet core and biotite included in garnet and 605°C–660°C for garnet and matrix biotite, whereas pressure of 5.79 kbar at 650°C using the garnet-biotite-plagioclase-quartz geobarometer (GBPQ). Similarly, Grt-Opx thermometry provides peak temperatures of 762°C–845°C for core values and 712°C–825°C for rim values of garnet and orthopyroxene and peak pressure has been observed as 6.49–7.49 kbar at 800°C using the garnet-cordierite geothermometer provides the retrograde temperature of 508°C–604°C for garnet core and cordierite included in garnet and 489°C–588°C for garnet and matrix cordierite, whereas garnet-cordierite-sillimanite-quartz geobarometer was used to estimate the pressure and it ranges from 4.24 to 4.89 kbar.

7.C.2 Garnet-biotite gneisses

P-T conditions are essential to understanding the metamorphic evolution under which a rock was formed. We have tried to obtain the pressure and temperature conditions through which these granulites create the most suitable minerals to achieve meaningful metamorphic *P-T* conditions. The various conventional geothermobarometry pairs such as, garnet–biotite geothermometers and garnet-biotite-plagioclase-quartz geobarometers have been used for evaluating the temperature and pressure conditions for Grt-Bt gneiss rocks. Table 7.3 represents the temperature and pressure estimates of Grt-Bt gneisses with various proposed models. For the Grt-Bt gneiss, the garnet–biotite exchange geothermometer was applied to inclusion and matrix biotite. It provides 595°C–656°C from biotite present as inclusion in garnet and 578°C–618°C from matrix biotite and pressure of 5.0 kbar at 600°C using the garnet-biotite-plagioclase-quartz geobarometer (GBPQ).



1000 Temperature°C 800 600 T1 (Perchuk et al., 1985) T2 (Aranovich and Berman, 1997) T3 (Nimis and Grutter, 2010) 400 T4 (Carson and Powell, 1997) Temperature (mean±error) Pelitic granulites (M-9, PM-2) Core=814±16°C 200 Rim=769±22°C 0 PM-2 PM-2 M-9 M-9 Sample No. (R) (R) (C) (C)

Figure 7.1 Coexisting Garnet-biotite pairs and derivative temperatures for different rocks.

Figure 7.2 Coexisting Garnet-orthopyroxene pairs and derivative temperatures for different rocks.

7.C.3 Amphibolites

We attempted to constrain the *P*–*T* conditions of various metamorphic stages for garnet-bearing and garnet-absent amphibolites, which is critical for understanding the metamorphic evolution of any rock type. The various geothermobarometry proposed models are used to estimate the pressure and temperature of amphibolites and are listed in Table 7.4. In the garnet-bearing amphibolites, the garnet-biotite pair was used to define a temperature of the pre-peak stage from garnet and biotite rim compositions, where biotite exists as inclusion within the garnet; it shows 539 to 597°C at 5.5 kbar. Ferry & Spear (1978) show a relatively

low temperature (539°C), while Thompson (1976) shows a high temperature (597°C). However, the pressure of metamorphism, according to the garnet-biotite-plagioclase-quartz geobarometer, is 5.32 kbar at 600°C (Wu et al. 2004). The Grt-Cpx geothermometer can measure the temperature of the peak metamorphic stage; Ellis & Green (1979) found 834°C, and Ravna (2000) found 760°C at 7.0 kbar pressure. At this stage, we have taken probe data from the garnet core portion as well as clinopyroxene to achieve the peak P-T conditions. Simultaneously, GCPQ (Grt-Cpx-Pl-Qz) geobarometry calculated 7.42 and 6.46 kbar pressures at a constant temperature of 800°C using Newton & Perkins (1982) and Eckert et al. (1991) models, respectively. Afterwards, garnet and clinopyroxene are unstable during postpeak metamorphism, which can be caused by retrograde metamorphism. We used the Holland & Blundv (1994) model to constrain the temperature condition as 556°C at 4.5 kbar pressure, as measured by an Amp-Pl geobarometer, during the post-peak metamorphism. However, the pressure condition for post-peak metamorphism is estimated to be 5.04 kbar at 550°C by Bhadra & Bhattacharya (2007) using an Amp-Pl-Qz geobarometer model. Using a few selected models, we estimated P-T conditions in garnet-absent amphibolites. The amphibole-plagioclase geothermometer provides two distinct temperature and pressure conditions based on the chemical compositions of the rim and core portions. The Holland & Blundy (1994) model predicts 517°C and 685°C from the rim and core compositions, respectively, whereas the Bhadra & Bhattacharya (2007) model of the Amp-Pl-Qz geobarometer predicts 5.21 and 6.78 kbar pressure from the rim and core portions.



Figure 7.3 Coexisting Garnet-cordierite pairs and derivative temperatures for different rocks.



Figure 7.4 Coexisting Garnet-clinopyroxene pairs and derivative temperatures for different rocks.



Figure 7.5 Coexisting Amphibole-plagioclase pairs and derivative temperatures for different rocks.











Figure 7.8 Coexisting Garnet-clinopyroxene-plagioclase-quartz pairs and derivative pressure for different rocks.



Figure 7.9 Coexisting Amphibole-plagioclase-quartz pairs and derivative pressure for different rocks.



Figure 7.10 Coexisting Garnet-orthopyroxene-plagioclase-quartz pairs and derivative pressure for different

rocks.

Sample	Thermometers		T(°C)	Models	Barometer	P/kbar	Models
PM2	Grt-Bt (5.5	Grt-	697	Kaneko and Miyano (2004)	Grt-Bt-Pl-	5.82	Wu et al. (2004)
	kbar)	Bt(In)	670	Bhattacharya et al. (1992)	Qz		
			639	Gessman et al. (1997)	(700°C)		
			668	Holdaway et al. (1997)			
		Grt-	661	Kaneko and Miyano (2004)			
		Bt(M)	633	Bhattacharya et al. (1992)			
			615	Gessman et al. (1997)			
			640	Holdaway et al. (1997)			
PM2	Grt-Opx (6.5	Grt-	834	Perchuk et al. (1995)	Grt-Opx-	7.42	Perchuk and Lavrente'va
	kbar)	Opx(C)			Pl-Qz		(1990)
			760	Aranovich and Berman	(800°C)	6.46	Bhattacharya et al. (1991)
				(1997)	4		
			818	Nimis and Gutter (2010)	-	6.43	Lal (1993)
			841	Carson and Powell (1997)			
		Grt-Opx	765	Perchuk et al. (1985)			
		(R)	713	Aranovich and Berman			
				(1997)			
			778	Nimis and Gutter (2010)			
			829	Carson and Powell (1997)			
K-2	Grt-Bt (6.0	Grt-	600	Kaneko and Miyano (2004)	Grt-Bt-Pl-	5.95	Wu et al. (2004)
	kbar)	Bt(In)	596	Bhattacharya et al. (1992)	Qz		
			642	Gessman et al. (1997)	(700°C)		
			620	Holdaway et al. (1997)			
		Grt-	563	Kaneko and Miyano (2004)			
		Bt(M)	544	Bhattacharya et al. (1992)			
			588	Gessman et al. (1997)			
			589	Holdaway et al. (1997)			

Table 7.1 Pressure and temperature estimates of the Grt-Opx pelitic garnulites (PM2) and Grt-Bt-Sill (K-2) through conventional geothermobarometers.

Sample	Thermometers		T(°C)	Models	Barometer	P/kbar	Models
M-9	Grt-Bt (5.5 kbar)	Grt-	692	Kaneko and Miyano (2004)	Grt-Bt-Pl-	5.79	Wu et al. (2004)
		Bt(In)	669	Bhattacharya et al. (1992)	Qz (650°C)		
			640	Gessman et al. (1997)			
			666	Holdaway et al. (1997)			
		Grt-	660	Kaneko and Miyano (2004)			
		Bt(M)	623	Bhattacharya et al. (1992)			
			605	Gessman et al. (1997)			
			630	Holdaway et al. (1997)			
M-9	Grt-Opx (6.5	Grt-	835	Perchuk et al. (1985)	Grt-Opx-Pl-	7.49	Perchuk and Lavrente'va (1990)
	kbar)	Opx(C)	762	Aranovich and Berman (1997)	Qz (800°C)		
			820	Nimis and Gutter (2010)		6.54	Bhattacharya et al. (1991)
			845	Carson and Powell (1997)			
		Grt-	761	Perchuk et al. (1995)		6.49	Lal (1993)
		Opx (R)	712	Aranovich and Berman (1997)			
			775	Nimis and Gutter (2010)			
			825	Carson and Powell (1997)			
M-9	Grt-Crd (5 kbar)	Grt-Crd	556	Kaneko and Miyano (2004)	Grt-Crd-Sil-	4.74	Dwivedi et al. (1997)
		(In)	526	Nichols et al. (1992)	Qz (600°C)	4.89	Aranovich and Podlesskii (1989)
			604	Dwivedi et al. 1998		4.35	Nichols et al. (1992)
			508	Perchuk (1991)		4.24	Wells (1979)
		Grt-Crd	518	Kaneko and Miyano (2004)			
		(M)	494	Nichols et al. (1992)]		
			489	Dwivedi et al. 1998	1		
			588	Perchuk (1991)			

 Table 7.2 The conventional geothermobarometry estimates of Grt-Opx-Crd pelitic granulites (M-9) from the Mauranipur region.

Sample	Thermometers		T(°C)	Models	Barometer	P/kbar	Models
M-1A	Grt-Bt (5	Grt-	656	Thompson (1976)	Grt-Bt-Pl-	5.00	Wu et al. (2004)
	kbar)	Bt(In)	626	Holdaway and Lee (1977)	Qz		
			595	Ferry and Spear (1978)	(600°C)		
			608	Perchuk et al. (1985)			
		Grt-	618	Thompson (1976)			
		Bt(M)	594	Holdaway and Lee (1977)			
			578	Ferry and Spear (1978)			
			589	Perchuk et al. (1985)			

Table 7.3 The conventional geothermobarometry estimates of Grt-Bt gneisses (M-1A) from the Mauranipur region.

Table 7.4 The conventional geothermobarometry estimates of Garnet-bearing amphibolites (B-6) and Garnet-absent amphibolites (K-1) from the Babina and Mauranipur regions.

Garnet-bearing amphibolites (B-6)									
Thermometers	T(°C) Models		Barometers	P(kbar)	Models				
Grt–Bt (5.5 kbar)	597	Thompson (1976)	Grt-Bt-Pl-Qz (600°C)	5.32	Wu et al. (2004)				
570		Holdaway and Lee (1977)							
	539	Ferry and Spear (1978)							
	568	Perchuk et al. (1985)							
Grt–Cpx (7.0 kbar)	834	Ellis and Green (1979)	Grt-Cpx-Pl-Qz (800°C)	7.42	Newton and Perkins (1982)				
	760	Ravna (2000)		6.46	Eckert et al. (1991)				
Amp –Pl (4.5 kbar)	556	Holland and Blundy (1994)	Amp-Pl-Qz (550°C)	5.04	Bhadra and Bhattacharya (2007)				
Garnet-absent amphibolites (K-1)									
Amp(R) - Pl(R) (5.0	517	Holland and Blundy (1994)	Amp-Pl-Qz (600°C)	5.21	Bhadra and Bhattacharya (2007)				
kbar)									
Amp(C) - Pl(C) (6.0)	685	Holland and Blundy (1994)	Amp-Pl-Qz (700°C)	6.78	Bhadra and Bhattacharya (2007)				
kbar)									