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MPET4: a computer program for coexisting garnet-clinopyroxene-plagioclase-quartz geothermobarometry

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ABSTRACT

The paper deals with the computer program to calculate temperature (in °C) and pressure (in kbar) based on assemblages garnet-clinopyroxene-plagioclase-quartz, and following reactions:

(a) 1/3 Pyrope + Hedenbergite = 1/3 Almandine + Diopside,
(b) Anorthite + Diopside = 2/3 Grossularite + 1/3 Pyrope + Quartz,
(c) Anorthite + Hedenbergite = 2/3 Grossularite + 1/3 Almandine + Quartz.

The program is written in Microsoft Quick Basic for IBM XT/AT compatible machines running MS-DOS Version 3.0 or higher. The user can acquire a copy of program by sending the author a 3.5"/5.25" DD/HD floppy diskette. The executable code of the computer program is MPET4.EXE.

INTRODUCTION

Several geothermometers and geobarometers have been formulated during the last 20 years for garnet-clinopyroxene-plagioclase-quartz assemblage. With the improvement of geothermobarometers, the activity composition relations poses a problem of formulation because of non-ideality for most of the minerals and garnet in particular. In order to make the calculations faster, the author has developed a program, "MPET4", for pressure-temperature calculations, using different formulations given by different workers.

The Fe-Mg exchange reactions between garnet (Gt) and clinopyroxene (Cpx) given by Mysen and Heier (1972), Raheim and Green (1974), Ellis and Green (1979), Ganguly (1979), Wells (1979), Dahl (1980), Ganguly and Saxena (1987) and Yang (1994) are used for geothermometric calculations. The Fe-Mg exchange reaction of garnet-clinopyroxene is as follows:

$$1/3Mg_3Al_2Si_3O_{12}+CaFeSi_2O_6 = 1/3\ Fe_3Al_2Si_3O_{12}+CaMgSi_2O_6 \quad \text{..... (a)}$$
Pyrope + Hedenbergite = Almandine + Diopside

To explain geobarometry properly, the author had considered the net transfer reaction of garnet-clinopyroxene-plagioclase-quartz (GCPQ) equilibria. These mineral pairs are commonly found in the assemblages of metabasic and hence are suitable for estimating equilibrium pressure of most metamorphic rocks.

For this, the author has considered the Newton and Perkins (1982), Eckert et al. (1991), Holland and Powell (1985) calculated by Eckert et al. (1993), Holland and Powell (1990) calculated by Eckert et al. (1993), Berman (1988) calculated by Eckert et al. (1993) and Berman (1988) using Ca-Mg-Fe subregular solution of mixing in garnet of Berman (1990) calculated by Eckert et al. (1993) and Moecher et al. (1988). The equation of equilibrium is as follows:

Anorthite + Diopside = 2/3 Grossularite + 1/3 Pyrite + Quartz ..... (b)
Anorthite+Hedenbergite=2/3 Grossularite+1/3 Almandine+Quartz ... (c)

BACKGROUND OF GARNET-CLINOPYROXENE GEOTHERMOMETERS

Distribution of ferrous iron and magnesium between coexisting silicate minerals is the basis of important geothermometers for metamorphic rocks of wide interest. The exchange reaction is:

$$1/3\ Mg_3Al_2Si_3O1_2+CaFeSi_2O_6 = 1/3\ Fe_3Al_2Si_3O_{12}+CaMgSi_2O_6 \quad \text{.....(a)}$$
Pyrope + Hedenbergite = Almandine + Diopside

The partition coefficient, $K_D = (Fe/Mg)^{Gt} / (Fe/Mg)^{cpx}$, has been shown in both natural and synthetic assemblages to be large and strongly temperature dependent. Two general experimental calibrations of the exchange thermometer have been carried out in mafic systems (Raheim and Green, 1974; Ellis and Green, 1979). In addition, several semi-empirical and theoretical studies by Mysen and Heier (1972), Ganguly (1979), Wells (1979), Dahl (1980), Ganguly and Saxena (1987) and Yang (1994) have been based on a selective input of experimental data and attempted reproduction of expected temperatures of natural parageneses.

Raheim and Green (1974) presented a geothermometer, on the basis of experimental studies and natural observations. Their formulation is:

$$T(K) = \frac{(3686 + 28.35*P)}{(\ln K_D + 2.33)}$$

Mysen and Heier (1972) proposed an empirical calibration for the garnet-clinopyroxene thermometer:

$$T(K) = \frac{2475}{(\ln K_D + 0.781)}$$

where K_D is same as defined by Raheim and Green (1974) for this as well as the subsequently discussed thermometer.

Ellis and Green (1979) presented a geothermometer on the basis of experimental studies. They considered the effect of Ca upon garnet-clinopyroxene. Their formulation is as follows:

$$T(K) = \frac{(3104*X_{Ca}^{gt} + 3030 + 0.01086*(P-1))}{(\ln K_D + 1.9034)}$$

Ganguly (1979) has examined the effects of Mn, Ca and P and gave the following formulation, based on integrated thermochemical and experimental data:

$$T(K) = \frac{(4801 + 11.07*P(kb) + 1586*X_{Ca}^{gt} + 1308*X_{Mn}^{gt})}{(\ln K_D + 2.93)}$$

Wells (1979) has also presented a geothermometer for calculation of equilibrium temperature of the granulite facies assemblages from the composition of coexisting garnet and clinopyroxene. Assuming that the departures from ideal mixing in the pyroxene and garnet phases are mutually cancelled out, Wells gave the following equation:

$$T(K) = \frac{(24440 + 0.06524*(P-1))}{(13.41 - 3*R\ln K_D)}$$

Dahl (1980) presented a geothermometer on the basis of empirical studies and his formulation is as follows:

$$T(K) = \frac{(1170+0.01107x(P-1)+ 759.44x(X_{Fe}-X_{Mg})+1414xX_{Ca}^{gt}+1437xX_{Mn}^{gt})}{\ln K_D}$$

Ganguly and Saxena (1987) modified the equation given by Ganguly, 1979 on the basis of empirical studies and the modified equation is given below:

$$T(K) = \frac{(4100 + 0.01107*(P-1) + 1510*(X_{Ca}+X_{Mn})^{gt})}{(\ln K_D + 2.40)}$$

Yang (1994) presented a geothermometer on the basis of empirical studies and his formulation is as follows:

$$T(K) = \frac{[1987.98 + (0.01766*P) - (1629*X_{Ca}*X_{Ca}) + (3648.55*X_{Ca}) - (6.59*MgNo)]}{(\ln K_D + 1.076)}$$

where, MgNo = (100 x MGGT) / (MGGT + FEGT)

BACKGROUND OF GARNET-CLINOPYROXENE-PLAGIOCLASE-QUARTZ GEOBAROMETERS

The assemblage garnet-clinopyroxene-plagioclase-quartz in basic granulites represent a potential geobarometer. The four-phase assemblage is represented by the reactions:

$$CaAl_2Si_2O_8 + CaMgSi_2O_6 = 2/3\,Ca_3AlSi_3O_{12} + 1/3\,Mg_3Al_2Si_3O_{12} + SiO_2$$

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

$$K1 = \frac{(a_{Ca}^{gt})^2 * a_{Mg}^{gt}}{(a_{An}^{Plag} * a_{Diop}^{Cpx})}$$

$$CaAl_2Si_2O_8 + CaFeSi_2O_6 = 2/3\,Ca_3AlSi_3O_{12} + 1/3\,Mg_3Al_2Si_3O_{12} + SiO_2$$

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

$$K1 = \frac{(a_{Ca}^{gt})^2 * a_{Fe}^{gt}}{(a_{An}^{Plag} * a_{Hed}^{Cpx})}$$

These reactions have large volume changes and hence are highly suitable for geobarometry. Newton and perkins (1982) have also calibrated reaction as:

$$P_{Mg} = 1 + \frac{(T*(9.493 + RlnK1) + 373)}{0.55258}$$

According to Newton and Perkins (1982), the combined uncertainties in the thermochemically measured standard Gibbs energies lead to uncertainty of 1700 bars for this barometer at a given temperature.

Moecher et al. (1988) presented a geobarometer on the basis of thermodynamic studies and their formulation are as follows:

$$P_{Mg} = 1 + \frac{[T*(*11.314 + RlnK1) - 1103]}{0.5411} \text{ and}$$

$$P_{Fe} = 1 + \frac{[T*(12.773 + RlnK2) - 4924]}{0.5588}$$

Eckert et al. (1991) gave the pH of reaction and recalibrated the garnet-pyroxene-plagioclase-quartz geobarometers in the CMAS systems by solution calorimetry.

$$P_{Mg} = 1 + \frac{[T*(9.4885 + RlnK1) + 1491]}{0.53200}$$

Holland and Powell (1985) gave the geobarometer based on an internally consistent themodynamic dataset, which Eckert et al. (1993) calibrated thermochemically.

$$P_{Mg} = 1 + \frac{[T*(8.891 + RlnK1) + 1224]}{0.53203}$$

Holland and Powell (1990) gave the geobarometer based on an internally consistent the thermodynamic dataset with uncertainties and correlations: In K_2O-NaO-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O_2 system, which Eckert et al., 1993, recalibrated thermochemically and gave the equation given below:

$$P_{Mg} = 1 + \frac{[T*(10.2055 + RlnK1) + 733]}{054254}$$

Berman (1988) presented the internally-consistent thermodynamic data for stoichiometric minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-SiO_2-TiO_2-H_2O-CO_2, which Eckert et al. (1993) recalculated thermochemically and gave the equation:

$$P_{Mg} = 1 + \frac{[T*(10.1577 + RlnK1) + 315]}{0.54135}$$

PROGRAM DESCRIPTION

The software consists of three programs as it is clear from the program flowchart (Fig. 1). Being an interactive package, it prompts the user for a choice of:

(1) Gt-Cpx exchange reaction (GCtherm)
(2) Gt-Cpx-Plag-Qz equilibria (GCPQ)
(3) Exit.

If the temperature calculation is intended through garnet-clinopyroxene exchange reaction, enter the Option No. 1. It automatically proceeds into the subprogram <<GCtherm>> for calculation.

Beside this, GCtherm also consists of three subprograms as shown on the flowchart (Fig. 1). On running, it prompts the user three choices, viz., "ENTER DATA", "CALCULATE AND DISPLAY RESULTS" and "EXIT" from GCtherm. The first choice is "ENTER DATA", when opted asks for a file name. The selected file 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, Mg, Ca, Mn for garnet and Fe and Mg, for clinopyroxene. 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 (CALCULATE AND DISPLAY RESULTS), however requires the data file name. The program first displays the data file contents 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 provide the output in a fixed format.

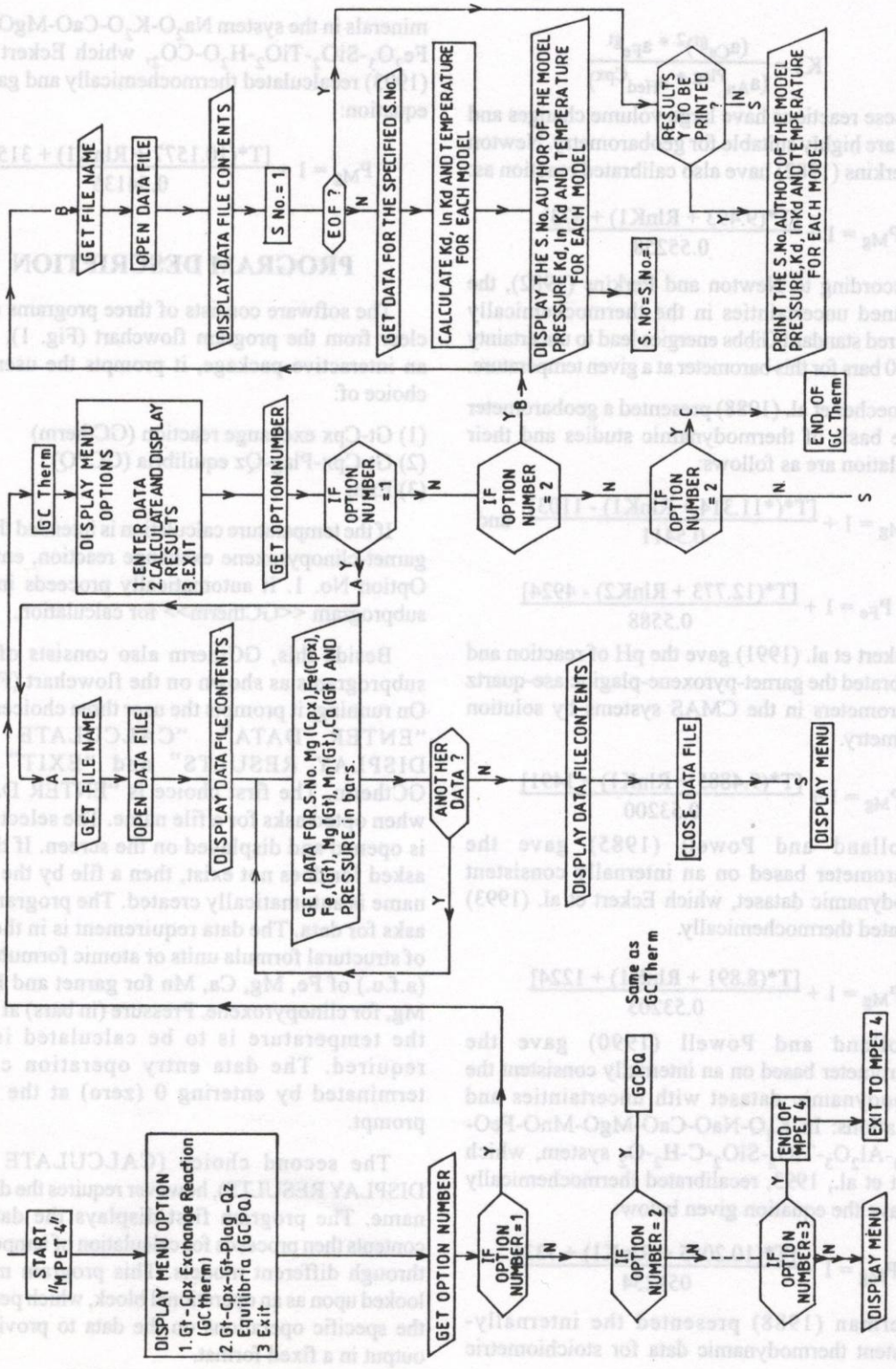

Fig. 1: Program Flowchart.

The third option terminates the program and return to the main menu.

In a similar way, if the user wishes to calculate pressure through garnet-clinopyroxene-plagioclase-quartz equilibria (GCPQ), option No. 2 is to be entered. The program automatically enters into the subprogram (GCPQ) for pressure calculation. It also works like GCtherm subprogram. The data requirement in this program is also in the form of structural formula units or atomic formula units (a.f.u.) of Fe, Mg, Ca, Mn for garnet, Ca, Na, K for plagioclase and Fe, Mg, Ca, Al^6, Fe^3, Cr and Ti for clinopyroxene. 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. prompt. Rest of the options are also work like Gotherm subprogram. Copy of the computer program "MPET4" (Executable code; MPET4.EXE) can be acquired from the author by sending a unformatted 3.5"/5.25" disk.

PROGRAM VALIDATION

Validation of the computer program (MPET4), several data had been manually calculated (Thomas, 1991) and reprocessed through this computer program. 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. Although there is some variation among the results obtained from individual formulation. This discrepancy might be due to the fact that some of the formulations are based on the empirical studies, some on experimental works. Comparison of different calibrations require more enhaustive discussion, therefore, the author feels that experimentally calibrated formulations should be the preferred geothermobarometer.

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Table 1: Electron micro-probe analyses (Wt%) and structural formulae (24 Oxygen basis) of garnet, (6 Oxygen basis) of clinopyroxene and (8 Oxygen basis) of plagioclase in basic granulite from Thana, District Bhilwara, Rajasthan.

Oxides	H90/9 Clinopyroxene point 44	H90/9 Garnet point 46	H90/9 Plagioclase point 47
SiO_2	50.707	37.536	56.334
TiO_2	0.801	0.000	0.000
Al_2O_3	1.977	21.483	27.280
FeO	11.355	28.001	0.151
MnO	0.136	0.908	0.000
MgO	12.559	6.037	0.000
CaO	20.526	6.898	9.979
K_2O	0.008	0.000	0.092
Na_2O	0.916	0.000	5.995
Total	98.986	100.863	99.649
Si	1.9227	5.8563	2.5404
Ti	0.0228	0.0000	0.0000
Al	0.0884	3.9501	1.4499
Fe^3	0.0882	0.0818	0.0000
Mg	0.7098	1.4038	0.0000
Ca	0.8339	1.1531	0.4734
Mn	0.0044	0.1200	0.0000
Fe	0.2620	3.5626	0.0057
Na	0.0674	0.0000	0.5242
K	0.0004	0.0000	0.0053

Table 2: Temperature (in °C) calculated by GCtherm subprogram.

Pressure (bars) 7000	K_D	$\ln K_D$	Temperature (°C)
1/3 Pyrope + Hedenbergite == 1/3 Almandine + Diopside			
Mysen and Heier (1972)	6.8754	1.9279	640
Raheim and Green (1974)	6.8754	1.9279	639
Ellis and Green (1979)	6.8754	1.9279	687
Ganguly (1979)	6.8754	1.9279	797
Wells (1979)	6.8754	1.9279	727
Dahl (1980)	6.8754	1.9279	660
Ganguly and Saxena (1987)	6.8754	1.9279	763
Yang (1994)	6.8754	1.9279	574

$X_{Fe(Gt)}$	$X_{Mg(Gt)}$	$X_{Ca(Gt)}$	$X_{Mg(Gt)}$	$X_{Fe(Cpx)}$	$X_{Mg(Cps)}$
0.570975	0.224986	0.184806	0.019232	0.269703	0.730397

Table 3: Pressure (in kbar) calculated by GCPQ subprogram.

Temperature (K) 923	$1nK_D$	Pressure (Kbar)
Anorthite+Diopside = 2/3 Grossularite + 1/3 Pyrope + Quartz		
Newton and Perkins (1982)	-3.3443	5.43
Moecher et al. (1988)	-2.6835	8.17
Eckert et al. (1991)	-3.3443	7.74
Holland and Powell (1985) calculated by Eckert et al. (1993)	-3.3443	6.20
Holland and Powell (1990) calculated by Eckert et al. (1993)	-3.3443	7.41
Berman (1988) calculated by Eckert et al. (1993)	-3.3443	6.57
Berman (1988) calculated by Eckert et al. (1993) using Ca-Fe-Mg subregular solution of mixing in garnet. Berman (1990)	-2.9841	7.79
Anorthite + Hedenbergite = 2/3 Grossularite + 1/3 Almandine+Quartz		
Moecher et al. (1988)	-1.4480	7.53

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