

Garnet-biotite pair: a suitable geothermometer

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ABSTRACT

The garnet-biotite pairs are commonly found in the pelitic assemblage right from upper green schist to granulites facies and hence are suitable for estimating equilibrium temperature for most metamorphic rocks. Several geothermometer has been proposed since long based on garnet - biotite Fe-Mg exchange reaction '1/3 Almandine + 1/3 Phlogopite = 1/3 Annite + 1/3 Pyrope'. The authors has developed a software in visual basic to calculate the temperature based on this pair using the formulation given by different works.

Keywords: Exchange reaction, Geothermometer, Garnet-Biotite.

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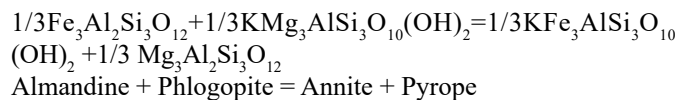
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INTRODUCTION

Geologists have for a long time attempted to estimate the temperature of formation of igneous and metamorphic rocks or estimating quantitatively the metamorphic condition at which the observed minerals assemblage attained equilibrium. The composition of equilibrium temperature of an assemblage in a rock is referred to as geothermometer. Traditionally geothermometry involves calculation of distribution coefficient (K_D) from mineral compositions and these K_{DS} are used alternately in one or more calibrations which have been proposed thermodynamically for the equilibrium assemblages. Thermometric models are based on the thermodynamic dataset (ΔH° , ΔS° , ΔV° , ΔG°) for the end-member reactions. These data have been obtained empirically, calorimetrically and by reaction reversals. A thermodynamic data set, compatible with both calorimetry and reaction reversals is called an internally consistent dataset. This internally consistent thermodynamic dataset, are the base for P-T calculations. Several geothermometer have been formulated during the last 45 years. In order to make the calculations faster the authors have developed Software "Gt-Bio.EXE", for temperature calculation, using different published geothermometer formulations given by different workers for garnet-biotite geothermometer. The Software is developed in visual basic and setup file is Gt-bio.Exe.

GARNET-BIOTITE EXCHANGE THERMOMETRY

If the system is closed, the partitioning of Fe and Mg between garnet and biotite can be given by the following exchange reaction:



For this the equilibrium constant, K_D , T at some P and T is given by:

$$K_D, T = (a_{\text{Pyr}}^{\text{Gt}})^{1/3} * (a_{\text{Ann}}^{\text{Bio}})^{1/3} / (a_{\text{Alm}}^{\text{Gt}})^{1/3} * (a_{\text{Phlo}}^{\text{Bio}})^{1/3}$$

Where 'a' refers to the activity of component and the superscripts refer respectively to garnet and biotite phases. If both garnet and biotite behave as ideal 3 site solid solutions then, taking standard states to be the pure phases at the P and T of interest, the $K_{(P, T)}$ corresponds to the empirical distribution coefficient,

$$K_D = (X_{\text{Mg}}^{\text{Gt}} * X_{\text{Fe}}^{\text{Bio}}) / (X_{\text{Fe}}^{\text{Gt}} * X_{\text{Mg}}^{\text{Bio}})$$

Where,

$$X_{\text{Fe}}^{\text{GT}} = \text{Fe} / (\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca})$$

$$X_{\text{Mg}}^{\text{GT}} = \text{Mg} / (\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca})$$

$$X_{\text{Mn}}^{\text{GT}} = \text{Mn} / (\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca})$$

$$X_{\text{Ca}}^{\text{GT}} = \text{Ca} / (\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca})$$

$$X_{\text{Al}}^{\text{Bio}} = \text{Al} / (\text{Al}^{\text{vi}} + \text{Fe} + \text{Mg} + \text{Mn} + \text{Ti} + \text{Cr}),$$

$$N_{\text{Al}} = (\text{Al}-1)/2 \text{ based on 11 oxygen, P in bars and } T^\circ\text{C} = T(\text{K}) - 273.15$$

The different models which were used for this software are summarized in Table 1:

PROGRAM DESCRIPTION

This software consists of two programs as it is clear from the software window. It is an interactive package. On running, it prompts the user for choice of:

- Gt-Bio Ex. Rec.
- Exit

Table 1: Name of scientists, ΔH , ΔS , and ΔV of the different models of garnet-biotite exchange reaction.

S. No.	Name of Scientist	ΔH	ΔS	ΔV
1.	Thompson (1976)	2740	1.156	0.0234
2.	Holdaway and Lee (1977)	3095	1.978	0.0124
3.	Ferry and Spear (1978)	2089	0.782	0.0096
4.	Perchuk (1977, 1981)	3416.4	2.30128	
5.	Pigage and Greenwood (1982)	2089	0.782	0.00956
6.	Hodges and Spear (1982)	2089	0.782	0.00956
7.	Perchuk and Lavrenteva (1983)	3875	2.868	0.0124
8.	Perchuk et al. (1985)	3720	2.868	0.0191
9.	Indares and Martignole (1985) (a) Newton and Haselton (1981) Garnet Mixing (b) Ganguly and Saxena (1984) Garnet mixing	2089 2089	0.782 0.782	0.00956 0.00956
10.	Hoinkes (1986)	2089	0.782	0.00956
11.	Aranovich et al. (1988)	3873	2.609	0.0124
12.	Dasgupta et al. (1991)	2156	0.93105	0.01238
13.	Bhattacharya et al. (1992) (a) Ganguly and Saxena (1984) Garnet mixing (b) Hackler and Wood (1989) Garnet mixing	1628 1628	0.81522 0.81522	0.00232 0.00232

If the user wants to calculate temperature through garnet-biotite reaction, select the Option of Garnet-Biotite Exchange Reaction. It will show the proceed into the program Gt-Bio Ex. Rec. for Add record, Edit record, Delete record and Display result. For detail operation of software please see the program window given below:

Starting screen

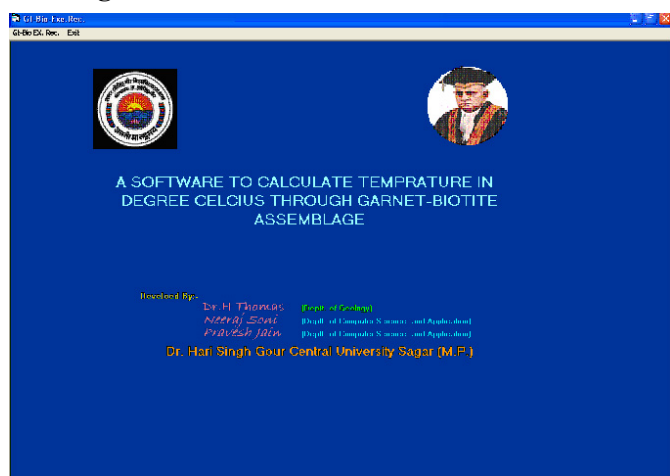


Fig. 1: Starting screen of software.

Software Window

This is the main window of the software. It has following two menu/subprogram i.e.

- Gt-Bio Ex. Rec.
- Exit

1. Garnet biotite exchange reaction: This menu contains four sub-menu, (Fig. 2) these are:

1. Add record

2. Edit record
3. Delete record
4. Display result

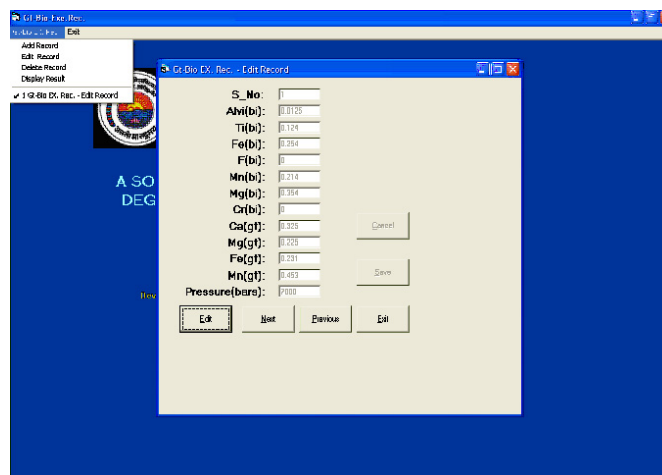


Fig. 2: From (Add record) menu one can add the data/record

To add the data, click on the Gt-Bio Ex. Rec. menu and choose Add Record from the given submenu. The window will appear to add the data; the following steps have to follow:

1. To add the new data click on the add button
2. Fill all the values in the correct format

The first choice is “Add record”. In this choice the data requirement is in the form of structural formula units or atomic formula units (a.f.u.) Fe, Mg, Mn, Ca for garnet (Gt); Al^{vi}, Ti, Fe⁺³, Fe⁺², Mg, Mn, Cr and F for biotite (Bio) and pressure in bars at which the temperature is to be calculated (Fig. 3 and Fig. 4).

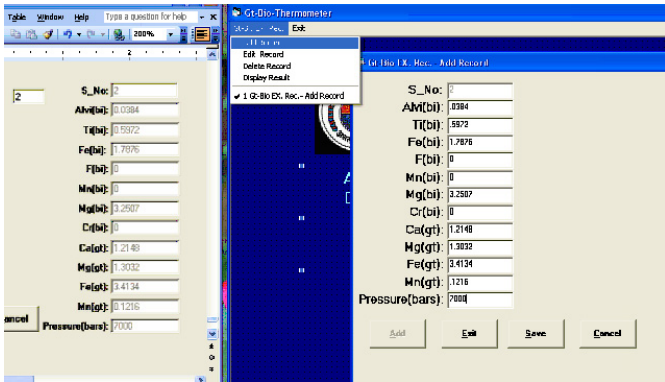


Fig. 3: Add or edit the data.

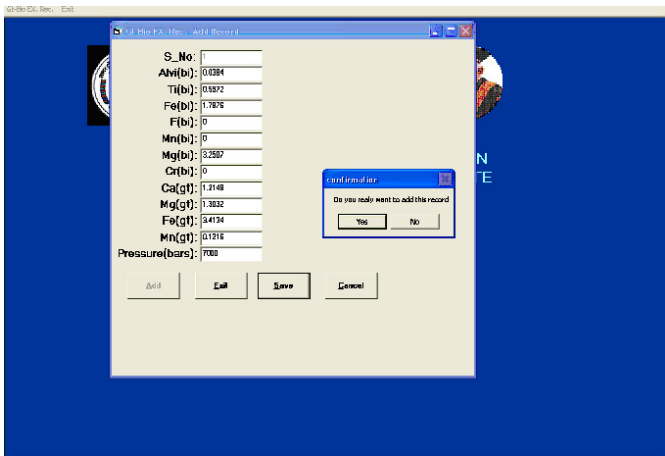


Fig. 4: Add and save the data.

3. To save the record click in the Save Button.
4. To avoid the addition, click on the Cancel Button.
5. To exit from the window click on the Exit Button.

Edit the record

To edit the record select the Gt-Bio Ex. Rec. menu or simply the options list are appears select the Edit Record (Fig. 4 and Fig. 5) options from the given submenu. The window will appear to add the record, these following steps

1. Click on the edit button
2. Edit the record
3. Click on the save button, if you do not want to change the record click on the cancel or exit button.

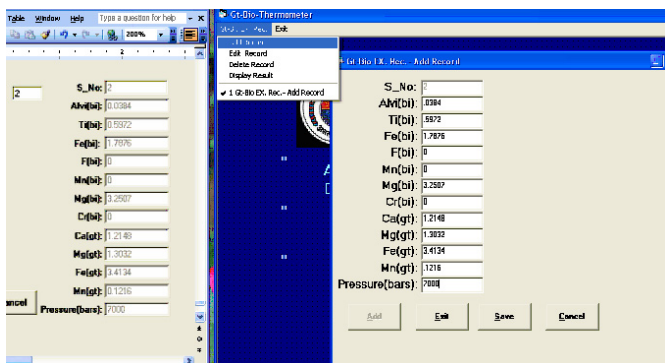


Fig. 5: Menu for edit record.

Delete the record

To delete the record select the Gt-Bio Ex Rec. menu the options list are appears select the Delete Record (Fig.6) options from the given submenu. The window will appear to add the record, these following steps

1. Move the record by click on the next and previous button to select the record to be deleted.
2. Click on the delete button the dialog box will appear Click on yes if you want to delete the record otherwise on No
3. Click on exit button.

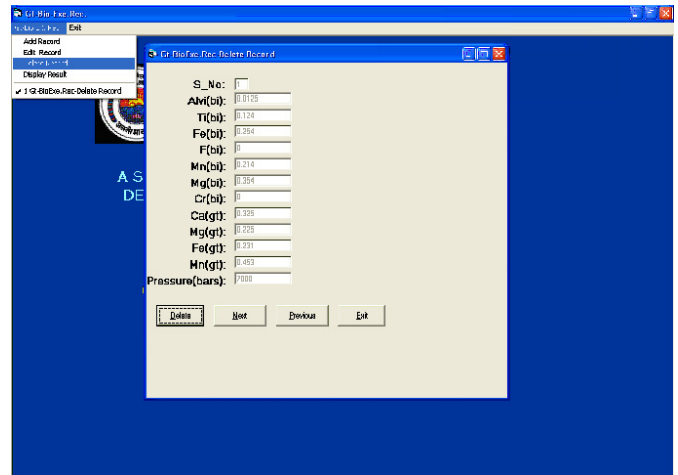


Fig. 6: Menu for the delete the record.

View the result

To view the Result selects the Gt-Bio Ex Rec. menu and select the Display Result options (Fig.7 and 8) from the given submenu. The window will appear to Search the record, these following steps:

1. Enter the serial no. of the record of which result you want view.
2. Click on the OK button.

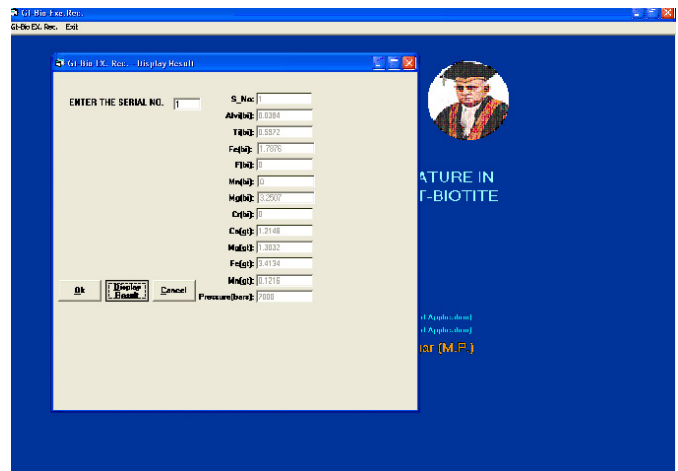
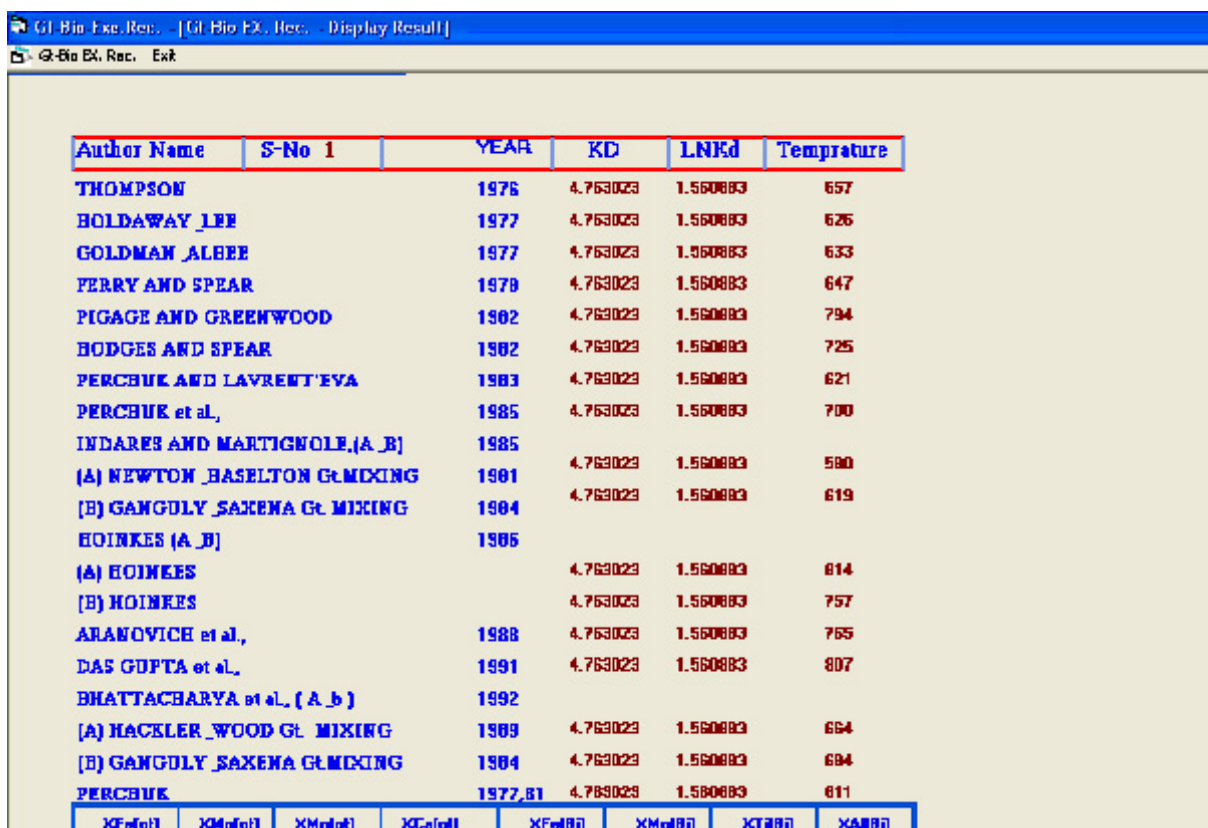


Fig. 7: Menu to view the selects Result.

The choice “display result” however, requires the data file name and provide the result in fixed format.



Author Name	S-No 1	YEAR	KD	LNkd	Temperature
THOMPSON		1976	4.763023	1.560883	657
HOLDAWAY_LEE		1977	4.763023	1.560883	626
GOLDMAN_ALBEE		1977	4.763023	1.560883	633
FERRY AND SPEAR		1979	4.763023	1.560883	647
PIGAGE AND GREENWOOD		1982	4.763023	1.560883	794
HODGES AND SPEAR		1982	4.763023	1.560883	725
PERCHUK AND LAVRENT'YVA		1983	4.763023	1.560883	621
PERCHUK et al.		1985	4.763023	1.560883	700
INDARES AND MARTIGNOLE,(A_B]		1985			
(A) NEWTON_BASELTON G.MIXING		1981	4.763023	1.560883	590
(B) GANGULY_SAXENA G. MIXING		1984	4.763023	1.560883	619
HOINKES (A_B]		1986			
(A) HOINKES			4.763023	1.560883	814
(B) HOINKES			4.763023	1.560883	757
ARANOVICH et al.		1988	4.763023	1.560883	765
DAS GUPTA et al.		1991	4.763023	1.560883	807
BHATTACHARYA et al. (A_b]		1992			
(A) HACKLER_WOOD G. MIXING		1989	4.763023	1.560883	664
(B) GANGULY_SAXENA G.MIXING		1984	4.763023	1.560883	684
PERCHUK		1977,81	4.763023	1.560883	611

Fig. 8: Menu display result in fixed format.

SOFTWARE VALIDATION

For the validation of the “Software,” several data have been manually processes (Thomas 1994, 1995, 1995, 2005 and 2008; Joshi et al. 1993) and also reprocessed through this Software and found the identical result. One set of data is given in Table 2 and results are shown in Table 3 in a fixed format with temperature based on different workers along with K_D , $\ln K_D$, X_{Fe} , X_{Mg} , X_{Mn} , and X_{Ca} for garnet and X_{Fe} , X_{Mg} , X_{Ti} and X_{Al} for biotite. Some variation is noticed in the results obtained from different calibrations. This discrepancy might be due to the fact that some of the formulations are based on the empirical studies and some on experimental work. Comparison of different calibration requires more exhaustive discussion, therefore, the authors feels that experimentally calibrated models should be the preferred geothermometer.

Table 2: Electron probe analyses (Wt %) and structural formulae (24 oxygen basis) of garnet and (22 oxygen basis) of biotite in pelitic granulite from Shivpura, District Bhilwara, Rajasthan; Thomas 2005)

Oxide	Garnet	Biotite
SiO ₂	37.158	37.569
TiO ₂	0.039	3.523
Al ₂ O ₃	21.056	17.147
Cr ₂ O ₃	0.037	0.052
Fe ₂ O ₃	0.240	0.00

Table 2 (contd.):

Oxide	Garnet	Biotite
FeO	33.778	12.766
MgO	5.278	14.744
MnO	0.508	0.00
CaO	1.365	0.00
K ₂ O	0.0	9.815
Na ₂ O	0.0	0.156
Total	99.459	99.587
	Cations 24 (O)	Cations 22 (O)
Si	5.9484	5.5147
Ti	0.0047	0.3889
Al ^{iv}	2.0514	2.4853
Al ^{vi}	1.9212	0.4811
Cr	0.0047	0.0060
Fe ⁺³	0.0289	0.00
Fe ⁺²	4.5220	1.5671
Mg	1.2595	3.2259
Mn	0.0689	0.00
Ca	0.2341	0.00
K	0.00	1.8377
Na	0.00	0.0445

Table 3: Temperature in (°C) calculated at 7000 bars by Gt-Bio.EXE.

S. No.	Authors	K_p	$\ln K_p$	Temperature (°C)			
1.	Thompson (1976)	4.763023	1.560883	657			
2.	Holdaway and Lee (1977)	4.763023	1.560883	626			
3.	Goldman and Albee (1977)	4.763023	1.560883	633			
4.	Ferry and Spear (1978)	4.763023	1.560883	647			
5.	Pigage and Greenwood (1982)	4.763023	1.560883	794			
6.	Hodges and Spear (1982)	4.763023	1.560883	725			
7.	Perchuk and Lavernteva (1983)	4.763023	1.560883	621			
8.	Perchuk (1985)	4.763023	1.560883	700			
9.	Indares and Martignole (A and B) (1985) A. Newton and Haselton 1981 Garnet mixing B. Ganguly and Saxena 1984 Garnet mixing	4.763023 4.763023	1.560883 1.560883	580 619			
10.	Hoinkes (A and B) (1986) A. Hoinkes B. Hoinkes	4.763023 4.763023	1.560883 1.560883	814 757			
11.	Aranovich et al. (1988)	4.763023	1.560883	765			
12.	Das Gupta et al. (1991)	4.763023	1.560883	807			
13.	Bhattacharya et al. (A and B) (1992) A. Hackler and Wood 1989 Garnet mixing B. Ganguly and Saxena 1984 Garnet mixing	4.763023 4.763023	1.560883 1.560883	664 684			
14.	Perchuk (1977, 1981)	4.763023	1.560883	611			
$X_{Fe(gt)}$	$X_{Mg(gt)}$	$X_{Mn(gt)}$	$X_{Ca(gt)}$	$X_{Fe(bio)}$	$X_{Mg(bio)}$	$X_{Ti(bio)}$	$X_{Al(bio)}$
0.56391	0.215298	0.020089	0.200694	0.354802	0.645198	0.105254	0.006768

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