Journal of Nepal Geological Society, 2019, vol. 58 (Sp. Issue), pp. 61–68
DOI: https://doi.org/10.3126/jngs.v58i0.24574

Valid garnet-biotite thermometer: A comparative study

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ABSTRACT

The abundance of garnet-biotite pair in a wide range of rocks mainly from upper green schist to granulite facies has made it one of the most widely used pairs for estimation of temperature at which once rocks equilibrated. In last four decades, more than 20 thermometer models of garnet-biotite pair have been proposed. To find the suitability of models, twenty-one thermometers formulated by a number of scholars since 1976 is considered. 27 sample data of granulites from the global literature were collected and processed through the "Gt-Bio.EXE" software. We conclude that four models are the most valid and reliable of these kinds of thermometers: Perchuk and Lavrente'va (1983); Thompson (1976); Ferry and Spear (1978) and Holdaway and Lee (1977).

Keywords: Geothermometer, Exchange reactions, Fe-Mg partitioning, Granulite, Comparative study

Paper Received: 7 Jan 2019 **Paper Accepted:** 20 Mar 2019

INTRODUCTION

Distribution of ferrous iron and magnesium between coexisting silicate minerals is the basis of important geothermometers for metamorphic rocks. Of wide interest is the distribution between garnet and biotite as the thermometer ranging for a wide range of rocks from greenschist to granulites. In last four decades, more than twenty thermometers have been proposed for garnet-biotite pair including both empirical and experimental calibrations. Several thermobarometric studies have been undertaken in the past few years, which led to the development of a range of thermometers such as garnet-biotite thermometer (Wu and Cheng, 2006); garnet-clinopyroxene thermometer (Jahnson et al., 1983; Fu et al., 1998); garnet - orthopyroxene thermometer (Thomas et al., 2018).

For last four decades, several experiments led to the development of GB thermometry. (Frost, 1962) had used the Fe-Mg distribution between garnet and biotite to qualitatively determine the grade of metamorphic rocks. (Kretz, 1964) stated that the Fe-Mg distribution between garnet and biotite may be a function of pressure and temperature without stating any formulation.

However, the calibrations are diverse and may be confusing to petrologists in choosing a suitable version. With the development of geothermometric studies, it appears necessary to undertake a review of this thermometer every decade or so. In order to recommend the best calibration for geologists, the authors have compared twenty one garnet - biotite thermometer models proposed since 1976 applicable on granulites facies of rocks. The partitioning of the Fe^{+2} and Mg, expressed by the distribution coefficient between coexisting garnet and biotite, has clearly shown that this distribution is a function of both physical conditions as well as compositional variations of the phases involved (Thompson, 1976; Holdaway and Lee, 1977; Goldman and Albee, 1977; Ferry and Spear, 1978; Pigage and Greenwood, 1982; Hodges and Spear, 1982; Perchuk and Lavrente'va, 1983; Perchuk et al., 1985; Indares and Martignole a and b, 1985; Hoinkes, a and b, 1986; Aranovich et al., 1988; Dasgupta et al., 1991; Bhattacharya et al., a and b, 1992; Perchuk, 1977, 1981; Holdaway et al., 1997; Gessman et al., 1997 and Kaneko and Miyano, a and b, 2004):

$$\begin{array}{l} 1/3\ Fe_3Al_2Si_3O_{12} + 1/3\ KMg_3AlSi_3O10(OH)_2 \\ (1/3\ \text{Almandine}) + (1/3\ \text{Phologopite}) \\ \rightleftharpoons 1/3\ Mg_3Al_2Si_3O_{12} + 1/3\ KFe_3AlSi_3O_{10}(OH)_2 \\ (1/3\ \text{Pyrope}) + (1/3\ \text{Annite}) \end{array}$$

The distribution of Fe and Mg between the phase's garnet and biotite is a function of pressure and temperature. As a general rule, the partitioning of elements between phases decreases as temperature increases: that is, K_D approaches 1 and lnK_D approaches 0.

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

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

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,

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

Where,

X_{Fe}^{GT} = Fe/(Fe+Mg+Mn+Ca); X_{Mg}^{GT} = Mg/(Fe+Mg+Mn+Ca) ; X_{Fe}^{BT} = Fe/(Fe+Mg) ; X_{Mg}^{BT} = Mg/(Fe+Mg)

Several models of geothermometer have been formulated for garnet-biotite pair by a number of workers since 1976 to till dates which are summaried below:

Thompson (1976) attempted to calculate isobaric Fe-Mg section from available experimental and thermo-chemical data in the KFMASH system, calculated at PH_2O = 5 kb for reactions involving garnet - biotite - staurolite - chlorite - cordierite - quartz - muscovite assemblages. Holdaway and Lee (1977) have given an empirical calibration of the garnet-biotite geothermometer applicable to high grade metamorphism of pelitic rocks. Ferry and Spear (1978) carried out experimental calibration with garnet-biotite ratio as 49/1 and ΔH = 12,454 cal; ΔS = 4.662 Cal/K mole to gave a polythermal polybaric equation. Perchuk (1977, 1981) calibrated an equation using distribution coefficient as a factor without using pressure effect in the equation. Goldman and Albee (1977) used the isotopic and chemical data for thirteen metamorphic rocks containing garnet and biotite to investigate the dependence of the Mg-Fe partition upon temperature to give an emperical calibration. Hodges and Spear (1982) incorporated (Ferry and Spear, 1978) data set in their calibrations along with alternative calibration using a consistent set of solution models to formulate an equation. Pigage and Greenwood (1982) gave an empirical equation for coexisting garnet - biotite with sillimanite plus kyanite using XCaGT and XMnGT as variables in the equation. Perchuk and Lavrente'va (1983) undertook an experimental calibration using natural minerals and biotite with a high Al content. Their equation avoids the problem of non-ideality by working directly with the natural minerals. Perchuk et al. (1985) formulated an equation for calculation of temperature of metamorphism for Aldan granulites using X_{Ca}^{Gt} as variable in the equation. Indares and Martignole (1985) proposed two new calibration of (Newton and Haselton, 1981) and (Ganguly and Saxena, 1984) based upon the correction for Al and Ti and the interaction of Ca in Fe - Mg garnets. Hoinkes (1986) gave two equations evaluating the Ca content in the metapelites of staurolite in zone, supporting non-ideal mixing of the grossular with almandine - pyrope solid solution. Aranovich et al. (1988) reformulated the equation using the experimental data set of Perchuk and Lavrente'va (1983). Dasgupta et al. (1991) gave a new formulation developed through statistical regression of the reversed experimental data of Ferry and Spear (1978) using available thermo-chemical data for quaternary Fe-Mg-Ca-Mn garnet solid solution and for the excess free energy terms, associated with the mixing of Al and Ti, in octahedral sites in biotite solid solution. Bhattacharya et al. (1992) gave two new formulations using (Ganguly and Saxena, 1984) and (Hackler and Wood, 1989) of garnet - biotite thermometer using the non-ideal mixing in the phlogopite-annite binary system. Gessman et al. (1997) used new experimental data for the Fe-Mg exchange between garnet and biotite using the Fe-Mg-Al mixing properties of biotite to give new calibration. Holdaway et al. (1997) recalibrated the equation using recently obtained Margules parameters for ternary Fe-Mg-Ca garnet, Mn interactions in garnet, Al interactions in biotite as well as the Fe oxidation state of both minerals. Kaneko and Miyano (2004) derived two equations, one as the presence of ferric Fe in biotite in relation to the coexisting Fe-oxide phases and second assuming the absence of ferric Fe in biotite, both evaluated in terms of iterative multiple least-square regressions of the experimental results.

RESULTS AND DISCUSSION

For the validation of the software (Thomas, 1995; Thomas and Paudel, 2017) and comparative study of different models, 27 sample data of granulites (Table 1: Bohlen and Essene, 1980; Harris et al.,1982; Hodge and Spear, 1982; Keinast and Ouzegane, 1987; Perchuk, 1989; Sharma et al, 1989; Riciputi et al., 1990; Barth and May, 1992; Sen and Bhattacharya, 1992; Buchernurminen and Ohta, 1993; Liangzhao and Shiqin, 1993; Dasgupta et al., 1994; Fareduddin et al., 1994; Kumar and Chacko, 1994; Thomas,1995; Knudsen, 1996; Muhongo and Tuisku, 1996; Shaw and Arima, 1996; Bindu,1997; Ellis and Hiroi, 1997; Raith et al., 1997; Bose et al., 2001; Pattison et al., 2003; Sommer et al., 2008; Tadokaro et al., 2008; Gross et al., 2009; Yang et al., 2015) have been processed through "Gt-Bio.EXE" software. A comparison of the calculated lnK_D and 1/T for different geothermometric models has been done. The K_D, lnK_D, X_{Fe} Gt, X_{Mg} Gt, X_{Ca} Gt, X_{Mn} Gt, X_{Mg} Bt, X_{Fe} Bt, X_{Al} Bt and, X_{Ti} Bt of different rocks samples by different authors are shown in Table 1 and the plots of lnK_D vs 1/T plot are shown in Figs. (1a-u) along with temperature distribution of specific models are shown in Table 2.

The data selected in this way was used to check the temperature dependence of the distribution coefficient.

Perchuk and Lavarente'va, 1983 (Fig. 1a) graph of lnK_D vs 1/T has been plotted as lnK_D = 1875/ T (°C) – 1.470 with R^2 = 0.997;

Thompson, 1976 (Fig. 1b) as lnK_D = 1567/ T (°C) – 0.425 with R^2 = 0.996;

Ferry and Spear, 1978 (Fig. 1c) as lnK_D = 1020/ T (°C) – 0.040 with R^2 = 0.992;

Holdaway and Lee, 1977 (Fig. 1d) as lnK_D = 1402/ T (°C) – 0.723 with R^2 = 0.963;

Hoinkes, 1986(b) (Fig. 1e) as lnK_D = 1032/ T (°C) – 0.003 with R^2 = 0.951;

Perchuk, 1977; 1981 (Fig. 1f) as lnK_D = 1271/ T (°C) – 0.591 with R^2 = 0.926;

Hoinkes, 1986 A, (Fig. 1g) as lnK_D = 1038/ T (°C) + 0.063with R^2 = 0.921;

Kaneko and Miyano, 2004(b) (Fig. 1h) as lnK_D = 1570/ T (°C) –1.07 with R^2 = 0.909;

Indares and Martingole, (a. Newton and Haselton, 1981), 1985 (Fig. 1i) as lnK_D = 882.6/ T (°C) -0.070 with R^2 = 0.903;

Perchuk et al., 1985 (Fig. 1j) as lnK_D = 1740/ T (°C) – 1.234 with R^2 = 0.871;

Hodges and Spear, 1982 (Fig. 1k) as lnK_D = 1044/ T (°C) – 0.048 with R^2 = 0.870;

Holdaway et al., 1997 (Fig. 1l) as lnK_D = –759.1/ T (°C) + 2.607 with R^2 = 0.855;

Pigage and Greenwood, 1982 (Fig. 1m) as lnK_D = 1210/ T (°C) – 0.158 with R^2 = 0.851; Aranovich et al., 1988 (Fig. 1n) as lnKD = 1264/ T (°C) – 0.332 with R^2 = 0.780;

Bhattacharya et al., 1992 (a) (Fig. 1o) as lnK_D = 985/ T (°C) – 0.089 with R^2 = .767;

Indares and Martingole, (b. Ganguly and Saxena, 1984), 1985 (Fig. 1p) as lnK_D = 837.3/ T (°C) + 0.028 with R^2 = 0.674;

Dasgupta et al., 1991 (Fig. 1q) as lnK_D = 523.8/ T (°C) + 0.729 with R^2 = 0.659;

Kaneko and Miyano, 2004 (a) (Fig. 1r) as lnK_D = 1364/ T (°C) -0.655 with R^2 = 0.652; Goldman and Albee, 1977 (Fig. 1s) as lnKD = 747.5/ T (°C) + 0.240 with R^2 = 0.647;

Gessman et al., 1997 (Fig. 1t) as lnK_D = 844.9/ T (°C) + 0.236 with R^2 = 0.599; and Bhattacharya et al., 1992 (b) (Fig. 1u) as lnK_D = 402.3/ T (°C) + 0.819 with R^2 = 0.526.

On the basis of different plots, it is observed that Perchuk and Lavrente'va (1983); Thompson (1976); Ferry and Spear (1978) and Holdaway and Lee (1977) are showing very good relation between lnKD vs 1/T and maximum points are coming in best fit lines and has high regression values.

CONCLUSION

Among the twenty-one geothermometer models of garnet-biotite equilibrium considered for this comparative study, Perchuk and Lavrente'va (1983); Thompson (1976); Ferry and Spear (1978) and Holdaway and Lee (1977) are showing the highest regression values and maximum points (values of temperature) are coming in best fit lines (Figs. 1a-d). So, these models can be considered empirically as the most appropriate ones to be used for the calculation of temperature.

Table 1: Data of K_D, lnK_D, X_{Fe} Gt, X_{Mg} Gt, X_{Ca} Gt, X_{Mn} Gt, X_{Mg} Bt, X_{Fe} Bt, X_{Al} Bt and, X_{Ti} Bt of different rocks samples by different authors

Data of different authors	KD	LNKD	X_{Fe}(GT)	X_{Mg}(GT)	X_{Mn}(GT)	X_{Ca}(GT)	X_{Fe}(BT)	X_{Mg}(BT)	X_{Ti}(BT)	X_{Al}(BT)
1. Fareduddin et al., 1994	6.5854	1.8849	0.683162	0.151777	0.021754	0.143308	0.405997	0.594003	0.085745	0.029296
2. Sharma et al., 1989	4.4993	1.5039	0.581613	0.193871	0.012581	0.211935	0.400040	0.599960	0.100088	0.020720
3. Sen and Bhattacharya, 1992	4.0973	1.4103	0.613666	0.350065	0.010687	0.025583	0.299643	0.700357	0.056345	0.070562
4. Perchuk,1989	6.2770	1.8369	0.760623	0.18748	0.023678	0.028219	0.392593	0.607407	0.017389	0.371606
5. Bose et al., 2001	11.4956	2.442	0.566195	0.014509	0.349655	0.069641	0.772458	0.227542	0.063475	0.123322
6. Harris et al., 1982	3.9128	1.3642	0.585634	0.325906	0.058863	0.029598	0.314717	0.682830	0.107725	0.023033
7. Muhongo and Tuisku, 1996	3.6956	1.3071	0.517309	0.295791	0.018040	0.168861	0.321225	0.678775	0.089482	0.022152
8. Barth and May, 1992	3.3232	1.2009	0.575908	0.214851	0.028713	0.180528	0.446472	0.553528	0.125373	0.006848
9. Riciputi et al.,1990	2.7304	1.0045	0.570910	0.364404	0.031746	0.032759	0.364666	0.635334	0.056667	0.149000
10. Liangzhao and Shiqin,1993	3.2373	1.1747	0.601329	0.335548	0.006645	0.056478	0.356322	0.643678	0.073333	0.056667
11. Kumar and Chacko,1994	3.0268	1.1075	0.717260	0.240430	0.023842	0.018469	0.496975	0.503625	0.100652	0.049602
12. Keinast and Ouzegane,1987	4.1082	1.413	0.542448	0.444255	0.007842	0.005455	0.229120	0.770880	0.103177	0.013924
13. Dasgupta et al., 1994	4.9774	1.6049	0.535802	0.371289	0.018163	0.074747	0.224763	0.775237	0.070607	0.011233
14.Tadokaro et al., 2008	4.9868	1.6068	0.636270	0.335276	0.005828	0.022626	0.275654	0.724346	0.087427	0.058166
15. Buchernurminen and Ohta, 1993	4.9351	1.5964	0.795918	0.159864	0.017007	0.027211	0.502203	0.497797	0.086806	0.012500
16. Gross et al., 2009	3.3293	1.2028	0.700997	0.255814	0.132890	0.029900	0.451477	0.548523	0.100000	0.535710
17. Shaw and Arima, 1996	6.9161	1.9339	0.681116	0.184140	0.026882	0.107863	0.348459	0.654541	0.069143	0.021051
18. Yang et al., 2015	6.8372	1.9224	0.653333	0.286667	0.033330	0.026667	0.250000	0.750000	0.043860	0.114035
19. Raith et al., 1997	3.7479	1.3212	0.520392	0.420881	0.016313	0.042414	0.248062	0.751938	0.072414	0.037931
20. Knudsen, 1996	4.5030	1.5047	0.676768	0.292929	0.010101	0.020202	0.339093	0.660907	0.098039	0.076649
21. Ellis and Hiroi, 1997	2.7227	1.0016	0.668901	0.253016	0.043566	0.034517	0.492641	0.507359	0.105982	0.022476
22. Bindu, 1997	3.9599	1.3762	0.708169	0.264493	0.010211	0.017128	0.403394	0.596606	0.123702	0.035890
23. Bohlen and Essene, 1980	3.6507	1.2949	0.698552	0.132705	0.109801	0.058942	0.590480	0.409520	0.061833	0.152667
24. Thomas, 1995	6.9285	1.9356	0.726952	0.233728	0.013454	0.025867	0.309824	0.690176	0.080045	0.065651
25. Sommer et al., 2008	4.2565	1.4485	0.622074	0.274247	0.030100	0.073579	0.347640	0.652360	0.038732	0.137324
26. Pattison et al., 2003	3.1028	1.1323	0.516667	0.380000	0.066670	0.036667	0.304688	0.695313	0.083624	0.020906
27. Hodge and Spear, 1982	7.4259	2.0050	0.730000	0.100000	0.140000	0.030000	0.495726	0.504273	0.025729	0.168096

Table 2: Data of the Calculated Temperature (ºC) of different rocks samples by different authors

Data of different authors	Thompson (1976)	Holdway and Lee (1977)	Goldman and Albee (1977)	Ferry and Spear (1978)	Pigage and Greenwood (1982)	Hodges and Spear (1982)	Perchuk and Laverante'va (1983)	Perchuk et al. (1985)	Indares and Martingole (1985a)	Indares and Martingole (1985b)	Hoinkes (1986a)
1. Fareduddin et al., 1994	682	551	497	535	631	590	560	608	482	499	640
2. Sharma et al., 1989	819	641	647	670	824	752	633	717	611	647	850
3. Sen and Bhattacharya, 1992	858	666	629	710	735	721	653	641	627	613	744
4. Perchuk,1989	697	561	622	550	579	561	569	560	507	442	576
5. Bose et al., 2001	534	447	379	396	572	420	473	484	346	488	435
6. Harris et al., 1982	879	679	618	732	789	744	663	653	572	597	772
7. Muhongo and Tuisku, 1996	906	695	756	759	898	826	676	740	686	725	956
8. Barth and May, 1992	959	728	710	814	977	886	701	772	683	734	1043
9. Riciputi et al.,1990	1071	794	888	934	986	947	750	741	822	803	999
10. Liangzhao and Shiqin,1993	973	736	704	829	879	852	707	712	721	714	920
11. Kumar and Chacko,1994	1010	758	612	868	900	876	723	707	690	681	901
12. Keinast and Ouzegane,1987	857	665	599	709	718	711	652	630	550	537	716
13. Dasgupta et al., 1994	779	615	600	630	690	660	613	627	561	574	708
14. Tadokaro et al., 2008	778	614	556	629	648	639	612	600	509	491	654
15. Buchernurminen and Ohta, 1993	782	617	469	633	661	644	614	604	509	482	664
16. Gross et al., 2009	958	727	1384	813	925	826	700	690	650	635	861
17. Shaw and Arima, 1996	667	540	489	521	597	562	552	582	476	494	602
18. Yang et al., 2015	670	543	526	524	556	534	554	544	470	463	547
19. Raith et al., 1997	899	691	685	752	794	770	673	670	650	651	812
20. Knudsen, 1996	818	640	565	670	689	678	633	619	525	502	694
21. Ellis and Hiroi, 1997	1073	795	658	936	998	730	751	743	748	769	1004
22. Bindu, 1997	874	675	549	726	745	733	660	644	535	517	749
23. Bohlen and Essene, 1980	912	699	639	765	879	789	679	685	674	717	849
24. Thomas, 1995	666	540	472	520	542	530	552	542	425	412	542
25. Sommer et al., 2008	842	655	688	694	763	723	645	659	652	649	782
26. Pattison et al., 2003	996	750	744	853	929	868	717	711	719	762	916
27. Hodge and Spear, 1982	645	526	482	501	583	512	540	532	467	510	524

Table 2: Continued.

Data of different authors	Hoinkes (1986b)	Aranovich et al. (1988)	Dasgupta et al. (1991)	Bhattacharya et al. (1992a)	Bhattacharya et al. (1992b)	Perchuk, (1977, 1981)	Holdaway et al. (1997)	Gessman et al. 1997	Kaneko and Miyano (2004a)	Kaneko and Miyano (2004b)
1. Fareduddin et al., 1994	597	659	635	588	603	537	1006	532	563	547
2. Sharma et al., 1989	788	770	812	679	697	620	715	636	655	637
3. Sen and Bhattacharya, 1992	718	712	815	642	638	643	684	683	670	641
4. Perchuk,1989	550	496	437	575	591	546	978	820	583	548
5. Bose et al., 2001	414	465	274	343	217	384	1153	530	452	438
6. Harris et al., 1982	743	753	813	656	661	635	659	661	674	653
7. Muhongo and Tuisku, 1996	865	815	937	713	736	665	642	685	716	693
8. Barth and May, 1992	929	840	909	741	759	690	534	759	722	704
9. Riciputi et al.,1990	952	816	937	749	753	744	472	985	744	706
10. Liangzhao and Shiqin,1993	860	805	920	711	713	707	545	790	732	702
11. Kumar and Chacko,1994	865	795	828	726	728	720	468	874	721	697
12. Keinast and Ouzegane,1987	710	747	841	623	610	643	713	601	663	643
13. Dasgupta et al., 1994	669	728	818	610	615	594	851	537	639	618
14. Tadokaro et al., 2008	634	675	721	601	598	599	818	596	616	595
15. Buchernurminen and Ohta, 1993	631	651	571	620	632	599	741	637	604	589
16. Gross et al., 2009	819	777	808	704	706	697	525	1313	641	605
17. Shaw and Arima, 1996	564	646	645	573	591	526	1090	497	553	537
18. Yang et al., 2015	529	580	616	548	555	526	1110	544	564	538
19. Raith et al., 1997	777	780	907	660	661	662	665	666	703	676
20. Knudsen, 1996	671	680	706	628	628	621	728	669	630	607
21. Ellis and Hiroi, 1997	947	834	919	757	761	743	426	897	768	744
22. Bindu, 1997	723	727	735	659	661	653	630	702	652	633
23. Bohlen and Essene, 1980	786	666	651	669	658	644	515	915	667	637
24. Thomas, 1995	521	598	590	555	569	531	1107	522	551	532
25. Sommer et al., 2008	729	716	760	654	663	630	697	749	658	626
26. Pattison et al., 2003	875	830	976	714	728	691	557	751	760	733
27. Hodge and Spear, 1982	500	514	463	518	513	491	1068	630	542	516

However, Perchuk and Lavrente'va (1983) is the best among them as the regression correlation coefficient value; R^2 is close to 1 which indicates that the maximum points are coming in best fit line. Therefore, the temperature value obtained by the Perchuk and Lavrente'va (1983) model is more accurate as compared to others.

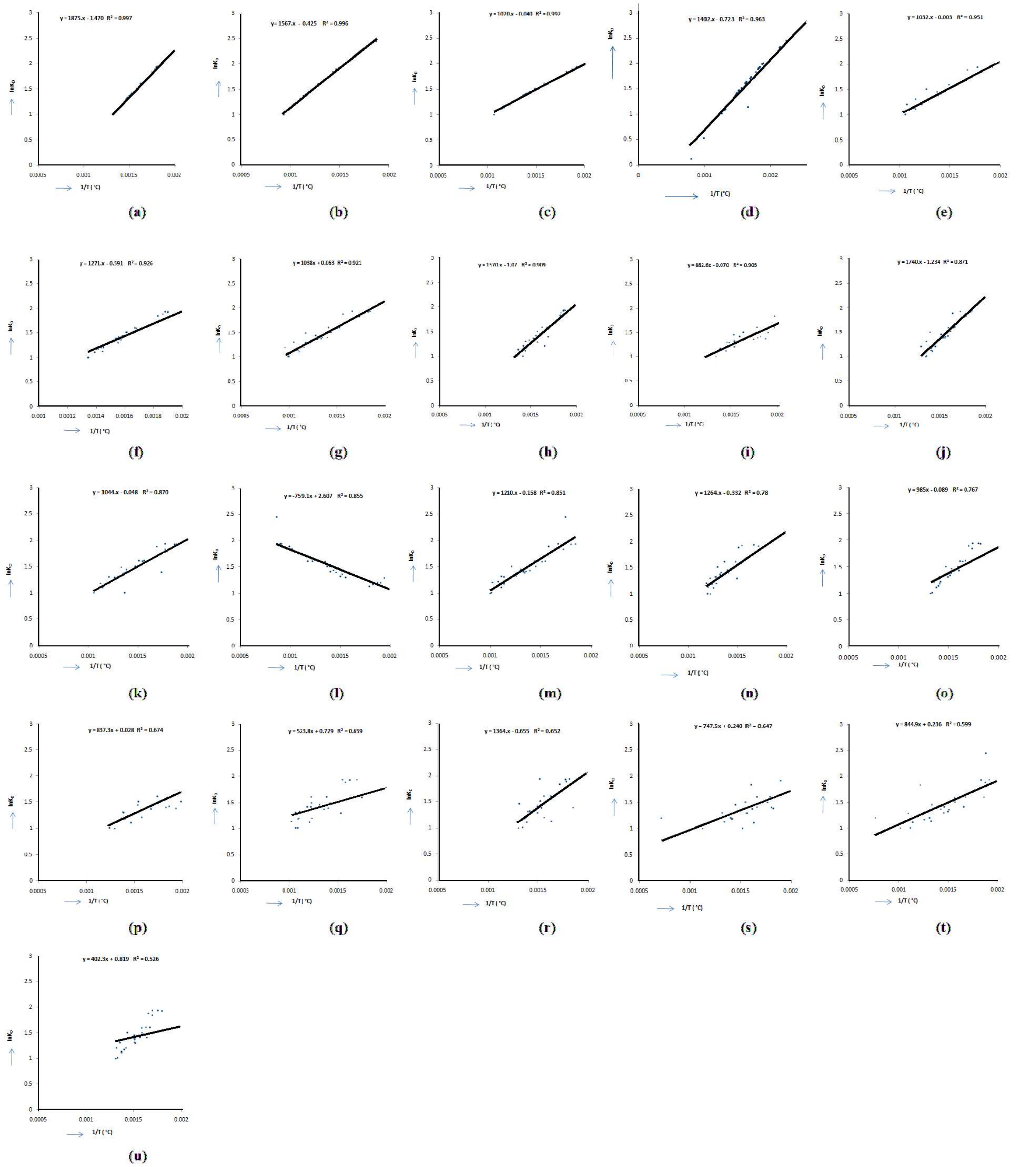

Fig. 1: (a) Perchuk and Lavarente'va, 1983, (b) Thompson, 1976, (c) Ferry and Spear, 1978, (d) Holdaway and Lee, 1977, (e) Hoinkes, 1986(b), (f) Perchuk, 1977; 1981, (g) Hoinkes, 1986 a, (h) Kaneko and Miyano, 2004(b), (i) Indares and Martingole, (a. Newton and Haselton, 1981), 1985, (j) Perchuk et al., 1985, (k) Hodges and Spear, 1982, (l) Holdaway et al., 1997, (m) Pigage and Greenwood, 1982, (n) Aranovich et al., 1988, (o) Bhattacharya et al., 1992, (p) Indares and Martingole, (b. Ganguly and Saxena, 1984), 1985, (q) Dasgupta et al., 1991, (r) Kaneko and Miyano, 2004 (a), (s) Goldman and Albee, 1977, (t) Gessman et al., 1997, and (u) Bhattacharya et al., 1992 (b)

ACKNOWLEDGEMENT

The authors thank the Head, Department of Applied Geology, Doctor Harisingh Gour Vishwavidyalaya, Sagar (M.P.) and the Department of Science and Technology, New Delhi, India for providing facilities as including PURSE- Phase -II for conducting present research work. The authors express sincere thanks to the reviewer, Prof., University of Torino, Italy, for his critical and constructive reviews which significantly improved the focus and clarity of the manuscript.

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