Pressure - temperature conditions of a garnet-biotite gneiss, Minnesota River Valley

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Introduction

This study applies chemical analyses of homogeneous grains to geothermobarometric models in order to determine the pressure and temperature conditions under which a garnet-biotite gneiss from western Minnesota, was metamorphosed. Resultant temperature and pressure conditions can then extrapolated into hypotheses of the tectonic environment in which the rocks were metamorphosed. Previous geothermobarometry on these rocks by Moecher and Medaris (1986) indicates temperature and pressure ranges of 650-700° C and 4.5-7.5 kbar.

Distribution of Mg and Fe between the garnet and biotite phases is largely a function of temperature and pressure, as the partitioning of elements decreases with increasing temperature. Zoning, differences in concentration of elements such as Mg and Fe from core to rim of a particular grain, often occurs in non-equilibrium mineral assemblages. At higher temperatures, the energetic distinction between elements decreases and crystals show less of a preference for one element over another. In this way, mineral grains become relatively homogeneous with respect to Fe and Mg (Spear, 1995). Zoned garnets often show higher concentrations of Fe near the rim and Mg in the core, indicating diffusion of Mg into the biotite at lower temperatures (Woodsworth, 1977).

Chemical analyses of minerals in a garnet-biotite gneiss from Granite Falls, in the Minnesota River Valley (MRV), were obtained with a scanning electron microprobe. Geothermometry was then conducted on molar oxide percentages of garnet, biotite,

plagioclase, and orthopyroxene, using garnet-biotite and garnet-orthopyroxene exchange reactions and garnet-plagioclase-orthopyroxene-quartz and garnet-plagioclase-biotitequartz net transfer equilibria reactions. Geothermobarometric models generated in this study largely agree with the results of Moecher and Medaris (1986).

Geologic Setting

The Precambrian garnet-biotite gneiss is located in the Minnesota River Valley and outcrops just south of Granite Falls, along State Highway 67 (Fig. 1). As part of the North American Craton at the southern edge of the Canadian Shield, it is among the oldest rocks in the United States at approximately 3.6 Ga (Grant, 1972). The garnetbiotite gneiss formed at the same time as the granitic Morton gneiss and a nearby hornblende-pyroxene gneiss (Southwick, 2002).

The MRV garnet-biotite gneiss is a dark, medium-grained, roughly equigranular, well-foliated gneiss that contains light-gray, coarser-grained, granular compositional banding, and is characterized by abundant pink to red garnet. Planar minerals within the rock, such as biotite, have a preferred orientation, and lineations apparent on foliation surfaces consist of parallel minerals and axes of small folds. The gneiss has been assigned to granulite facies metamorphism by previous researchers (Grant, 1972) on the basis of its rock chemistry.

The structure within the Granite Falls outcrop is relatively uniform, with foliations striking several degrees north of east and dipping ~40 degrees south. The northern contact between these rocks and the hornblende-pyroxene gneiss is well exposed and is

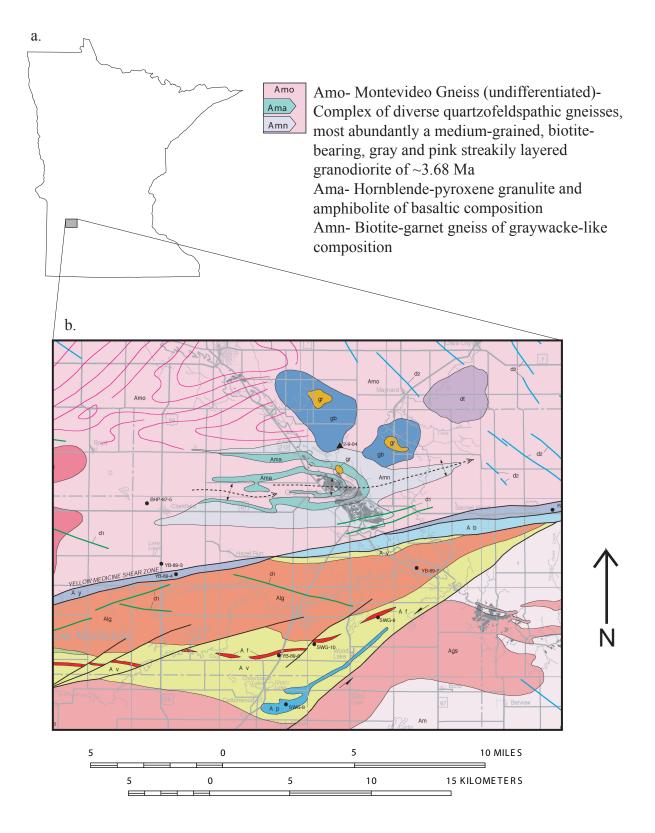


Fig. 1- a. Map of Minnesota, showing area of location map. b. Geologic map of Granite Falls area and sampling site of garnet-biotite gneiss (Southwick 2002).

basically marked by the appearance of garnet. The southern contact is deduced to be a fault (Goldich et al., 1961).

The garnet-biotite, hornblende-pyroxene, and granitic Morton gneiss units share a similar history. All were formed in close proximity about 3.6 Ga (Grant 1972). The garnet-biotite protolith may have formed from sediments derived from volcanic activity related to the emplacement of the hornblende-pyroxene and granitic gneiss protoliths. The rocks traveled across a Precambrian ocean and were accreted to the southern margin of the proto-North American Craton approximately 2.7 Ga (Southwick 1996). At the time, these rocks lay under the mountain belt that was forming at the southern edge of the continent. Almost a billion years later (~2.7 Ga) volcanic activity related to the Penokean orogeny caused intrusion of local stratigraphy; however the garnet-biotite gneiss was not disturbed by this event (Grant 1972).

Methods

Oriented samples of the garnet-biotite gneiss were taken from an outcrop in the Minnesota River Valley, just south of Granite Falls on State Highway 67. An oriented thin section of Sample 6 was analyzed by a JEOL 8900 Electron Probe Microanalyzer with an accelerating voltage of 15 kV and a beam diameter of 5 microns at the sample surface. To ensure that data reflected equilibrium conditions of all minerals, intergrown euhedral grains with sharp contacts were chosen from probe analysis whenever possible (Himmelberg and Phinney, 1967) (Fig. 2).

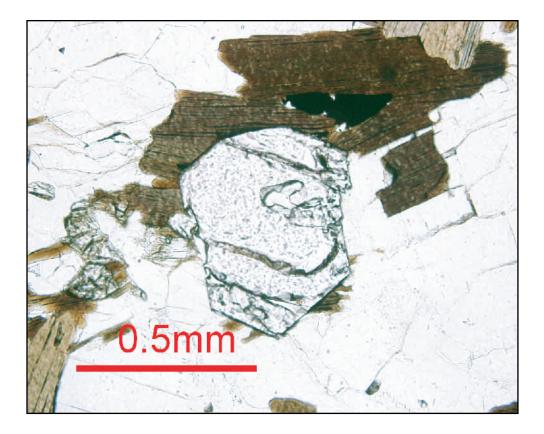


Figure 2- Garnet surrounded by biotite and plagioclase. Garnet faces are relatively sharp, indcating that the two adjacent minerals probably formed in equilibrium.

A series of points were analyzed across garnet-biotite and garnet-plagioclase boundaries, as well as core-rim lines within individual garnets and orthopyroxene grains. A total of 37 points within individual garnets were taken, along with 10 points across 2 garnetbiotite boundaries, 15 points across 3 garnet-plagioclase boundaries, and 9 points within 2 orthopyroxene grains. X-ray maps of a euhedral garnet, along with biotite and plagioclase grains were taken for Al, Fe, Ca, Mg, and Mn to determine if the garnets were zoned relative to those elements.

Representative chemical analyses of each mineral were chosen from raw SEM data, and weight percent oxides were converted to molar percentages (Table 1). These representative mineral compositions were then used in two computer modeling programs, GTB (Spear, 1996) and TWQ (Berman and Brown), to estimate pressure and temperature conditions under which the garnet-biotite gneiss formed.

Initially in GTB, all possible calibrations were used (Bohlen, 1983; Douce, 1993; Eckert et al., 1991; Ferry and Spear, 1978; Ferry et al., 1990; Ganguly and Saxena, 1984; Gessman, 1997; Harley, 1984; Hodges and Spear, 1982; Hoisch, 1990; Holdaway, 1997; Indares and Martignole, 1985; Kleeman and Reihnardt, 1994; Lee and Ganguly, 1988; Moecher, 1988; Newton and Perkins, 1982; Perchuk and Lavrent'eva, 1984; Perkins and Chipera, 1985; Powell and Holland, 1987; Sen and Bhattacharya, 1984; Wood, 1975). FeO₂O₃ content in the garnet-biotite gneiss is minimal (Himmelberg and Phinney, 1967; Moecher et al., 1986), so all chemically analyzed iron was assumed to be FeO. The primary reactions used for temperature analysis, the garnet-biotite exchange reaction, is as follows: almandine (Fe₃Al₂Si₃O₁₂) + phlogopite (KMg₃AlSi₃O₁₀(OH)₂) = pyrope (Mg₃Al₂Si₃O₁₂) + annite (KFe₃AlSi₃O₁₀(OH)₂). The primary barometer, garnet-

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Wei	ght percen	t Oxides	Gar	net/Biotit	e Gneiss							
	1											
	Transect	SiO ₂	Al_2O_3	TiO ₂	FeO	MgO	MnO	CaO	K2O	Na ₂ O	Cr ₂ O ₃	Total
Garnet 1	Rim 1	38.39	22.31	0.00	33.21	5.79	1.02	1.89	0.03	0.04	0.05	102.72
	2	38.45	22.21	0.01	33.37	5.88	1.03	1.94	0.01	0.00	0.09	102.98
	Core 3	38.46	22.32	0.04	33.61	5.82	1.09	1.89	0.03	0.00	0.06	103.30
	4	38.10	22.12	0.00	33.68	5.60	1.03	1.85	0.02	0.00	0.02	102.41
	Rim 5	34.97	19.41	0.00	31.88	5.40	0.92	2.03	0.07	0.03	0.06	94.77
Garnet 2	Rim 1	38.40	22.28	0.00	32.62	5.78	1.06	2.41	0.02	0.02	0.06	102.64
	2	38.29	22.28	0.00	32.54	5.99	1.10	2.19	0.03	0.00	0.02	102.43
	Core 3	27.64	15.59	0.00	28.32	4.45	0.92	1.71	0.06	0.10	0.04	78.81
	4	38.31	22.67	0.02	33.49	5.84	1.01	1.72	0.02	0.04	0.05	103.16
	Rim 5	38.76	22.39	0.00	34.05	5.23	1.13	2.01	0.04	0.02	0.06	103.68
Garnet 3	Rim 1	38.18	22.48	0.02	33.97	5.33	1.26	1.72	0.00	0.05	0.08	103.09
	2	38.50	22.47	0.00	33.75		1.22	1.67	0.01	0.06	0.08	103.32
	Core 3	34.72	19.35	0.02	32.04		1.02	1.55	0.04	0.08	0.03	94.69
	4	38.43	22.48	0.00	33.45		1.10	1.74	0.03	0.06	0.05	102.95
	Rim 5	38.17	22.43	0.00	32.72	5.80	1.14	1.89	0.04	0.03	0.00	102.23
Garnet 4	Rim 1	38.30	22.08	0.00	33.74	5.30	1.22	1.68	0.04	0.03	0.00	102.39
	2	38.03	22.34	0.01	34.20	4.95	1.20	1.85	0.03	0.01	0.02	102.66
	Core 3	38.07	22.28	0.00	34.24	4.89	1.31	1.77	0.01	0.00	0.07	102.62
	4	37.82	22.19	0.00	33.92	4.73	1.31	1.90	0.03	0.00	0.09	101.99
	Rim 5	38.13	21.98	0.01	33.00	4.93	1.28	2.31	0.06	0.03	0.09	101.82
Garnet 5	Rim 1	38.31	22.16	0.00	33.44	6.02	1.06	1.74	0.03	0.02	0.08	102.85
	2	38.05	22.38	0.00	33.38	6.01	1.15	1.69	0.02	0.00	0.03	102.70
	Core 3	38.11	22.35	0.00	32.63	6.19	1.15	1.67	0.01	0.04	0.06	102.19
	4	38.64	22.41	0.03	32.78	6.04	1.06	1.77	0.05	0.00	0.01	102.79
	Rim 5	37.77	22.28	0.00	31.77	5.79	1.01	2.18	0.00	0.04	0.02	100.85
Garnet 6	Rim 1	37.92	22.09	0.05	34.47	4.83	1.14	1.70	0.02	0.05	0.10	102.37
	2	38.08	22.33	0.00	34.30	4.78	1.19	1.71	0.01	0.05	0.13	102.55
	Core 3	43.54	20.81	0.04	26.41	3.44	0.84	1.39	3.16	0.54	0.05	100.22
	4	38.40	22.22	0.05	34.41	4.88	1.24	1.94	0.01	0.00	0.12	103.28
	Rim 5	38.72	22.25	0.02	33.38	4.88	1.20	2.21	0.06	0.00	0.08	102.80
Garnet 7	Rim 1	38.37	22.35	0.00	32.83	5.64	1.18	1.67	0.02	0.00	0.04	102.10
	2	38.28	22.32	0.00	32.87	5.73	1.01	1.81	0.01	0.05	0.05	102.12
	Core 3	37.75	21.87	0.00	31.71	5.58	1.10	1.75	0.05	0.11	0.05	99.97
	4	38.27	22.46	0.00	32.54	5.89	1.16	1.78	0.03	0.00	0.00	102.12
	Rim 5	38.30	22.53	0.00	32.44	5.85	1.09	1.99	0.03	0.07	0.00	102.30
Gt/Opx	1	34.32	16.94	0.00	29.57	5.48	0.89	1.58	0.04	0.13	0.01	88.95
	2	73.70	1.13	0.04	4.41	1.50	0.09	0.25	0.19	0.03	0.00	81.34
				c				c				-
	Minimum	27.64	1.13	0.00	4.41	1.50	0.09	0.25	0.00	0.00	0.00	78.81
	Maximum	73.70	22.67	0.05	34.47		1.31	2.41	3.16	0.54	0.13	103.68
	Average	38.77	21.20	0.01	32.03		1.08	1.80	0.12	0.05	0.05	100.44
	Sigma	6.30	3.72	0.02	4.95	0.86	0.20	0.34	0.52	0.09	0.03	5.72

Table 1: Weight percent oxides of transects across garnet.

plagioclase-orthopyroxene-quartz is: $3\text{FeSiO}_3 + 3\text{CaAl}_2\text{Si}_2\text{O}_8 = 2\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 3\text{SiO}_2$ (Moecher, 1988; Newton and Perkins, 1982; Perkins and Chipera, 1985; Powell and Holland, 1987) or: $3\text{MgSiO}_3 + 3\text{CaAl}_2\text{Si}_2\text{O}8 = 2\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 3\text{SiO}_2$ (Perkins and Chipera, 1985; Powell and Holland, 1987; Wood, 1975).

After examination of initial results, unreasonably low temperature estimates were eliminated from GTB analysis. Additionally, all but those barometers with the flattest slopes were eliminated, as steeply-sloping barometers are highly dependent on temperature and therefore are not as reliable for pressure determination. The Clapeyron equation $(dP/dT = \Delta S/\Delta V)$ demonstrates how the ideal geothermometer has a low entropy and high volume in order to result in a steeply sloping or near vertical reaction line, whereas the ideal geobarometer has high entropy and low volume and a nearly flat reaction line (Winter, 2001).

With TWQ, a program that calculates pressure-temperature conditions through theoretical Gibbs free energy properties, graphs were plotted for the garnet-biotite gneiss based on molar percentages of magnesium, aluminum, silicon, hydrogen, calcium, potassium, iron, and oxygen. Thirteen trials were run with exclusion of various minerals and different calibrations (H and P, 1990; Haar, 1984; K and J, 1981). Minerals that remained constant throughout the analysis were almandine, anorthite, grossular, pyrope, phlogopite, annite, and quartz. Minerals that were experimented with in various combinations were aluminum-orthopyroxene, ferrosilite, potassium feldspar, and orthoenstatite. These trials were run with and without water as a variable, under both metastable and stable conditions.

Results

Hand samples of the garnet-biotite gneiss exhibit pronounced foliation and subtle lineations on foliation surfaces. The outcrop off Highway 67 near Granite Falls showed signs of having undergone obvious plastic and brittle deformation; certain zones were highly folded and faulted. Petrographic analysis of the oriented thin section revealed the following bulk rock chemistry: Plag – 55%, Biotite – 15%, Garnet – 8%, Orthopyroxene – 10%, Quartz – 10%, Iron sulfides – 2%. Stoichiometry of representative mineral analyses from the SEM is as follows: garnet: 102.89%, biotite: 96.29%, orthopyroxene: 100.60%, plag: 99.59%. SEM transect points across garnet, biotite, plagioclase, and orthopyroxene (Fig. 3) as well as x-ray maps (Fig. 4), indicate that individual mineral grains are homogeneous with respect to Fe/Fe+Mg.

GTB results for garnet-biotite and garnet-orthopyroxene thermometers and garnetplagioclase-orthopyroxene-quartz and garnet-plagioclase-biotite-quartz barometers using all possible calibrations was widespread, ranging from 530-800° C and .8 to 9.3 kbars (Fig. 5). As the probable minimum temperature needed for the garnets in these rocks to equilibrate is 700° (Winter, 2001; Woodsworth, 1977), those calibrations that resulted in temperatures under 650° C were eliminated, leaving five garnet-biotite calibrations (Ferry and Spear, 1978; Ferry et al., 1990; Gessman, 1997; Hodges and Spear, 1982; Holdaway, 1997; Winter, 2001; Woodsworth, 1977) over 700° C. Three garnet–plagioclase– orthopyroxene-quartz barometers (Eckert et al., 1991; Newton and Perkins, 1982; Powell

Percent Molar Fe/(Fe+Mg) in Garnet

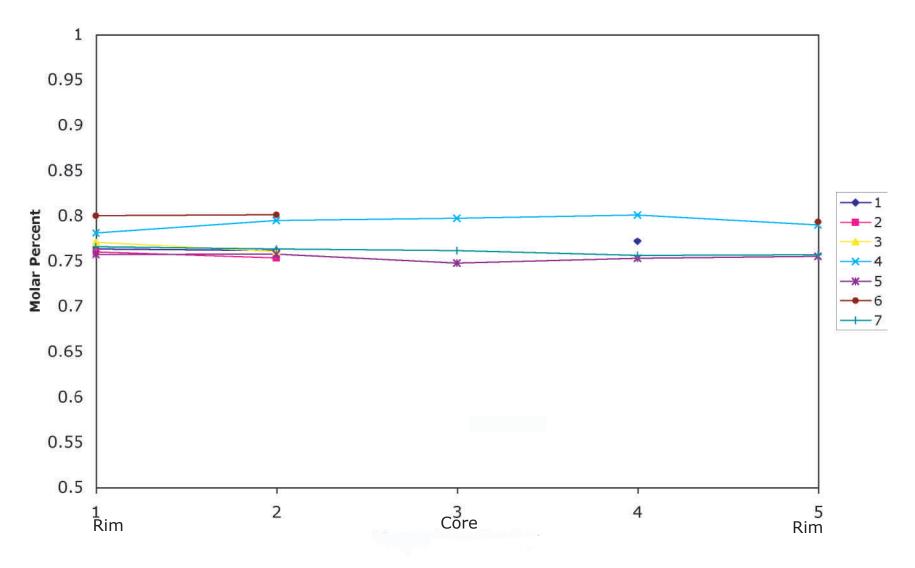
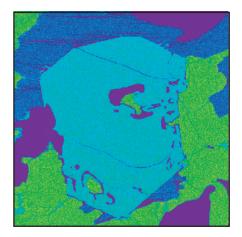
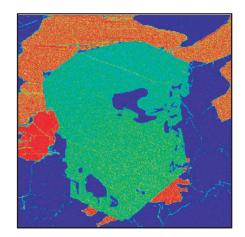


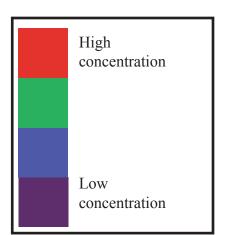
Figure 3 - Molar Percent Fe/(Fe + Mg) for garnet in MRV garnet-biotite gneiss. Transects across garnets reveal lack of zoning.

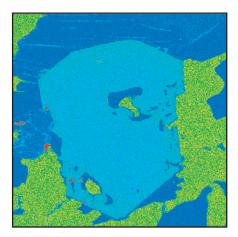


Aluminum

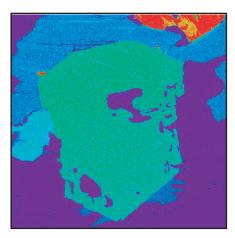


Magnesium





Calcium



Iron



Manganese

Figure 4 – X-ray map of mineral grains from Figure 2, garnet with biotite above and plagioclase below. Lack of zoning in garnets is displayed by nearly complete homogenization of various elements throughout the grain.

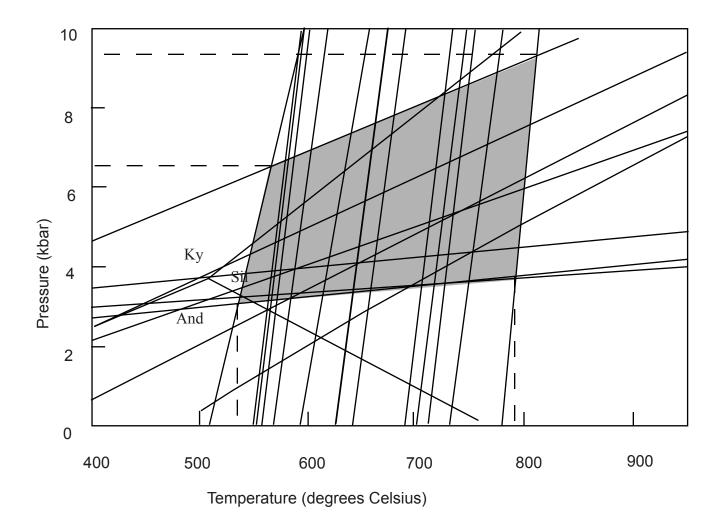


Fig. 5- Plot of geothermometry of MRV garnet-biotite gneiss with respect to Al2SiO5 triple junction based on representative mineral analyses using experimental data from all possible garnet-biotite and garnet-opx thermometers, and garnet-plag-opx-quartz and garnet-plag-biotite-quartz barometers in Frank Spear's GTB program.

and Holland, 1987) with markedly flatter slopes than the others were considered the most reliable, and were chosen to be used for further analysis. The newly narrowed GTB calibrations indicated temperatures of ~700-800° C and ~3.5-4.5 kbars pressure (Fig. 6).

TWQ analysis provided similar results to GTB. Using analyses from reactions driven by almandine, grossular, and pyrope garnet, al-orthopyroxene, annite, phlogopite, anorthite, orthoenstatite, and quartz, an equilibrium pressure of 4.2 kbars and temperature of 725° C was obtained (Fig. 7). Analyses that included reactions with the mineral ferrosilite gave results that offered a much wider range in equilibrium temperature and pressure ($600^\circ - 900^\circ$ C, and 4.0 - 7.0 kbars).

Discussion

The mineral assemblage (garnet, biotite, quartz, orthopyroxene, and plagioclase), when viewed in conjunction with the GTB diagrams, show that the garnet-biotite gneiss underwent metamorphism of granulite facies conditions. This is consistent with previous work in the area for these rocks (Bauer, 1980).

Due to the high grade metamorphism that the Precambrian Minnesota River Valley rocks experienced, their origins can only be construed from their bulk compositions. The high Al-content in the mineral assemblage indicates that the garnet-biotite gneiss is probably derived from a sedimentary protolith (Goldich et al., 1961; Grant, 1972). However, the nearby hornblende-pyroxene gneiss most likely came from some sort of mafic plutonic protolith. The same is true for the granitic gneiss, although the protolith would have had to have been a felsic pluton (Grant, 1972).

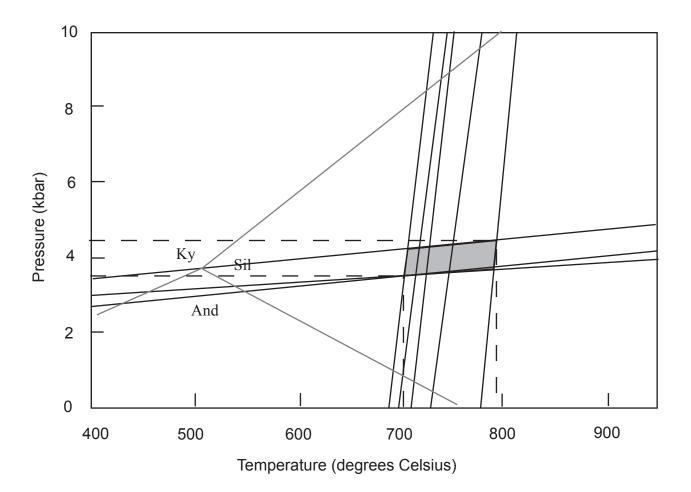


Fig. 6- Plot of geothermometry of MRV garnet-biotite gneiss with respect to Al2SiO5 triple boundary based on representative mineral analyses using experimental data from selected garnet biotite thermometers (Ferry and Spear 1978, Hodge and Spear 1982, Ferry and Spear with Berman 1990, Holdaway et al. 1997, and Gessman et al. 1997) and garnet-plag-opx-quartz barometer (Newton and Perkings 1982, Powell and Holland 1987, and Eckert, Newton and Kleppa 1991) in Frank Spear's GTB program.

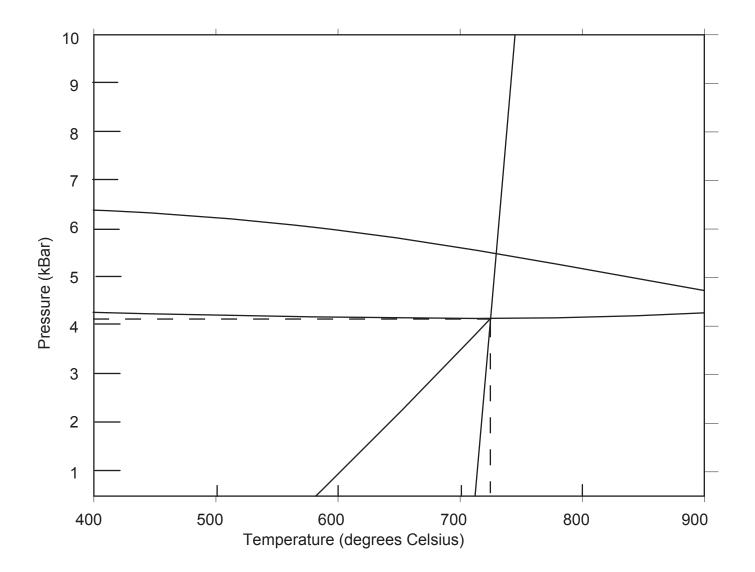


Fig. 7- Plot of theoretical geothermometry of MRV garnet-biotite gneiss using representative mineral analyses based on reactions of almandine, Al-opx, annite, anorthite, grossular garnet, orthoenstatite, phlogopite, pyrope, and quartz, following Haar et al. 1984.

Previous work in the area has shown that there is a small amount of zoning in the garnets, most likely due to retrograde metamorphism (Moecher et al., 1986). However, in this study, homogeneity of mineral grains from core to rim and between garnet and biotite grains indicates a lack of zoning and that these rocks formed in equilibrium (Fig. 3, Fig. 4). According to Woodsworth (1977) these rocks probably had to reach temperatures of at least 650 or 700° Celsius in order for garnet and orthopyroxene to achieve equilibrium. Lack of zoning indicates that retrograde metamorphism probably did not occur in these rocks (Himmelberg and Phinney, 1967; Moecher et al., 1986; Woodsworth, 1977) except locally, perhaps as a result of the 1.8 bya tectonism (Himmelberg and Phinney, 1967).

When the data were plotted on TWQ diagrams, pressure-temperature estimates for this assemblage were 4.2 kBar at 725°C. Ferrosilite was determined unnecessary for this analysis due to the small amount that was present in the sample and the large fluctuations that it caused in the analysis. Omitting ferrosilite resulted in a much more straightforward pressure vs. temperature figure that produced one set of equilibrium conditions instead of many. Wide distribution of reactions using ferrosillite indicates that its properties may be poorly constrained, and is therefore unreliable. Only two reactions were plotted by TWQ, which is less than ideal, but as the junction of equilibrium conditions falls within the range of pressures and temperatures generated by GTB, the two analyses taken together lend credibility to the resultant P-T conditions.

Assuming a pressure gradient of.27 kbar/km, the GTB result of 4 kbar indicates a depth of ~16-17 km. If a constant metamorphic gradient is assumed, the slope would be steeper than for most granulite facies rocks (Moecher et al., 1986), with a gradient of

~50°C/km. Alternatively, a rising pluton may have locally raised the geothermal gradient in order to accommodate calculated GTB and TWQ temperatures (Winter, 2001) (Fig. 8). The active tectonism occurring in the region at the time lends plausibility to the pluton hypothesis. The Sacred Heart granite, dated at ~2.7 billion years (Grant, 1972) and located close to the garnet-biotite gneiss, may have been the pluton in question.

The results of project could have been adversely affected by several factors. In the initial data analysis no SEM calibration was available for garnet, and therefore a calibration for ilmenite was used in its place. This could have been the reason the values reported for the stoichiometry of garnet were slightly off (2.98 SiO₂ instead of 3.0 SiO₂, and 2.02 Al₂O₃ instead of 2 Al₂O3). The molar weight of garnet (102.89%) was also slightly higher than the ideal value of 100%. However, the pressure-temperature calculations we generated with this data match previous studies in this area, so the difference in the calibration doesn't seem to have negatively affected the results. The calculations for plagioclase, orthopyroxene, and biotite were calibrated correctly and stoichiometry fell within the expected margin of error.

Results could also have been affected by errors inherent in the GTB calibrations. Granulite facies barometers and thermometers tend to have large uncertainties due to the large solid solution pressure/temperature ranges they encompass (Spear, 1995). Additionally, GTB compensates for unexpected compositional variations in the minerals and interactions of the barometers and thermometers to some degree as the barometers depend on the thermometers to calculate the pressure, and vice versa (Spear, 1995). All

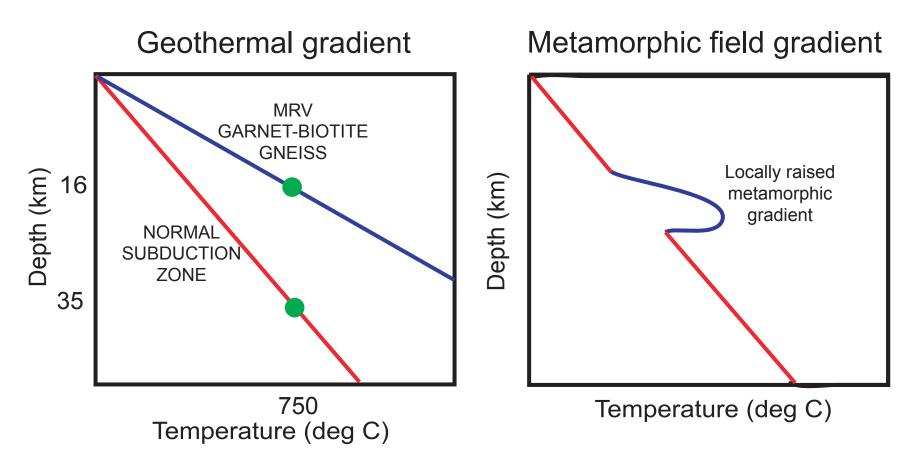


Fig. 8- a) Schematic plot of apparent geothermal gradient seen in garnet-biotite gneiss vs. the expected geothermal gradient for a subduction zone. b) An alternative hypothesis explains the discrepancy with a normal geothermal gradient raised locally by a pluton.

iron in the minerals was assumed to be ferric, due to the variability of the ferrous iron calculations, in accordance with Moecher (1986). Since the level of ferrous iron is so low in the MRV garnet-biotite gneiss (Moecher et al., 1986), the exclusion of ferrous iron should only have had only a negligible effect on the results.

The orthopyroxene-garnet thermometers used in GTB plotted much lower than expected, around 500°C. There are several possibilities that could explain this discrepancy. The first, that the MRV garnet data collected from the SEM could have been inaccurate, doesn't seem likely, given the accuracy of the biotite-garnet thermometer. A second possibility is that the orthopyroxene values reported by the SEM and used in the calculations were not accurate. This is a stronger possibility, since relatively few orthopyroxene SEM points were taken. It is possible that the compositional differences of orthopyroxene could have been normalized if more transect points had been taken. A third possibility is simply that properties of the garnetorthopyroxene reaction have not been thoroughly researched and calibrated for granulite facies rocks.

Conclusions

The garnet-biotite gneiss in the Minnesota River Valley most likely formed at a depth of 16 - 17 km, under pressures of 4.5 kbar, and at temperatures ranging from 700 – 800° C. The high temperatures found in a relatively shallow area of the crust can likely be explained by a local rising pluton. Due to the lack of zoning, this particular area probably did not undergo retrograde metamorphism during a later event.

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