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## Comparison of garnet-biotite, calcite-graphite, and calcite-dolomite thermometry in the Grenville Orogen; Ontario, Canada

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**Abstract** The Elzevir Terrane of the Grenville Orogen in southern Ontario contains metapelites and abundant graphitic marbles that were regionally metamorphosed from the upper greenschist to upper amphibolite facies. Comparative thermometry was undertaken with widely used calibrations for the systems garnet-biotite, calcite-dolomite, and calcite-graphite. Temperatures that are obtained from matrix biotites paired with prograde garnet near-rim analyses are usually consistent with those determined using calcite-graphite thermometry. However, calcite-graphite thermometry occasionally yields low temperatures due to lack of equilibration of anomalously light graphite. Application of calcite-graphite and garnet-biotite systems may yield temperatures up to 70 °C higher than calcite-dolomite in amphibolite facies rocks. Calcite-dolomite temperatures most closely approach those from calcite-graphite and garnet-biotite when the samples contain a single generation of dolomite and calcite grains contain no visible dolomite exsolution lamellae. However, some of these samples yield temperatures considerably lower than temperatures calculated from calcite-graphite and garnet-biotite thermometry, indicating that the calcite-dolomite thermometer may have been partially reset during retrogression. Estimated peak metamorphic temperatures of regional metamorphism between Madoc (upper greenschist facies) and Bancroft (upper amphibolite facies) range from 500 to 650 °C. These results place the chlorite-staurolite isograd at 540 °C, the kyanite-sillimanite isograd at 590 °C, and the sillimanite-K-feldspar isograd at 650 °C. Although each thermometer may

have an absolute uncertainty of as much as  $\pm 50$  °C, the 50 to 60 °C temperature differences between the isograds are probably accurate to 10 to 20 °C. An incomplete picture of the thermal gradients can result from the application of only one thermometer in a given area. Simultaneous application of several systems allows one to recognize and overcome the inherent limitations of each thermometer.

### Introduction

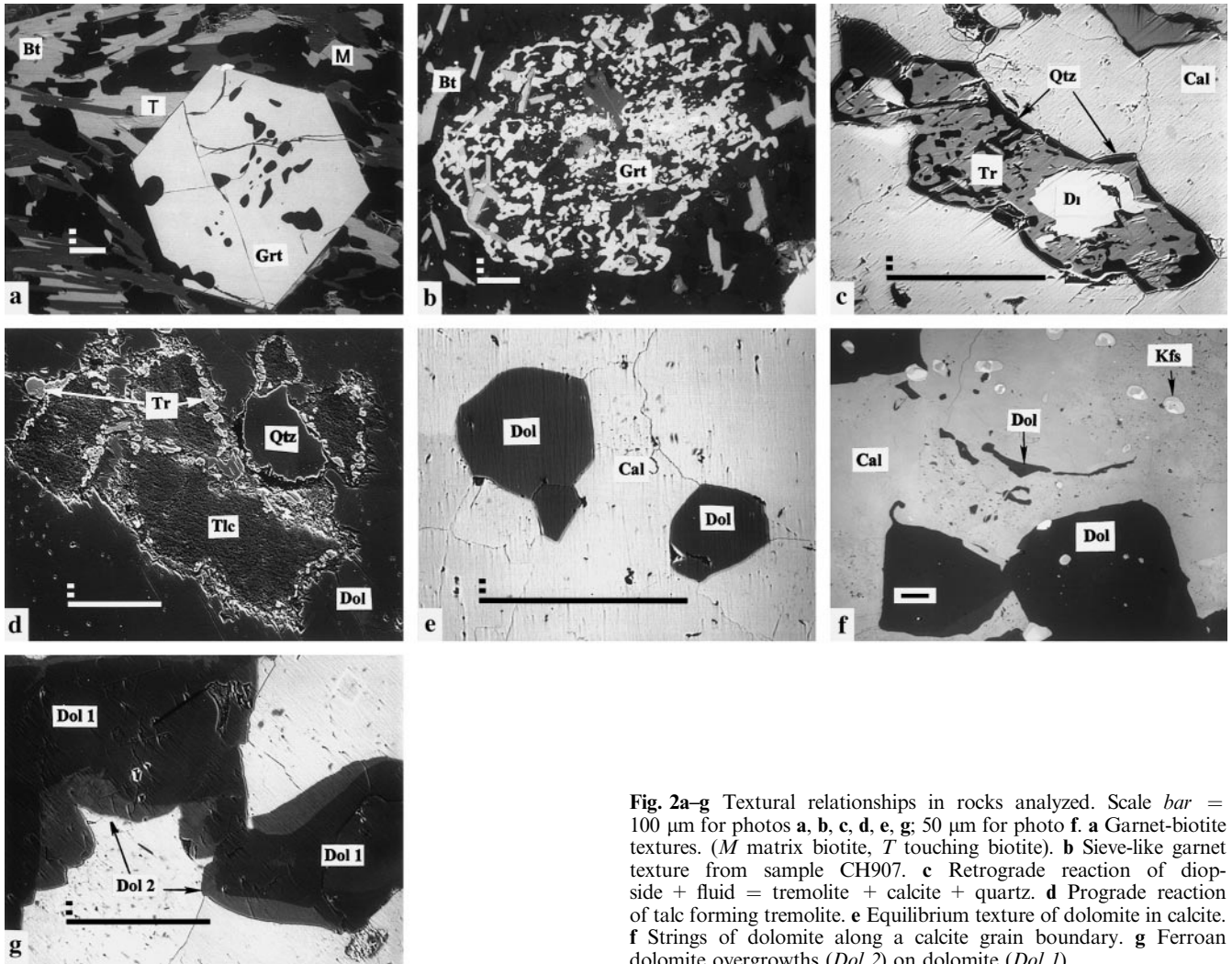
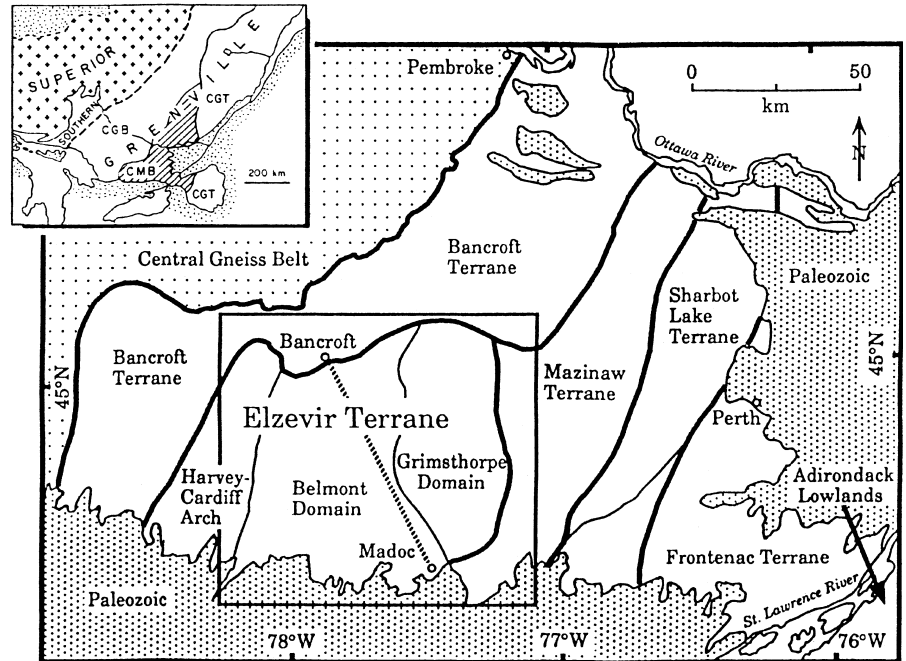
The Grenville Orogen in southern Ontario is subdivided into two distinct lithotectonic packages, the Gneiss Belt and the Metasedimentary Belt (MB). The area of focus for this study is located in the Elzevir Terrane of the MB. It comprises the Belmont Domain, Grimsthorpe Domain, eastern Harvey-Cardiff Arch, and southwestern Mazinaw Domain of Easton (1992) (Fig. 1). Portions of the MB have been mapped by the Ontario Geological Survey (1991 and references therein). Common rock types include metapelites, graphitic marbles, metavolcanic rocks and metamorphosed felsic and mafic intrusive rocks. Peak metamorphic conditions ranged from the upper greenschist to the upper amphibolite facies (Wynne-Edwards 1972; Carmichael et al. 1978) in the Elzevir Terrane and were reached at ca. 1040 Ma (Mezger et al. 1993). Slow time-averaged cooling rates of 1 to 4 °C/million years have been estimated from chronological studies (Cosca et al. 1991; Mezger et al. 1993).

Geothermometers are widely used to make quantitative estimates of peak metamorphic temperatures. In a given area the application of geothermometry is limited by bulk compositional constraints, and commonly only one or two thermometers are available in a given field area. It is therefore important to test the reliability of individual thermometers, which can be evaluated by a comparison of several thermometers. In this study we compare widely accepted calibrations of three thermometers, garnet-biotite, calcite-graphite, and calcite-dolomite to determine how well they correlate in a

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**Fig. 1** Tectonic map of south-eastern Ontario, Canada. [*GB* Gneiss Belt, *MB* Metasedimentary Belt (*white*)]. Paleozoic cover is shown in *gray*. The *box* outlines the area of study shown in Figs. 5–8, and the *dashed line* indicates the traverse for Fig. 6. After Easton (1992)



**Fig. 2a–g** Textural relationships in rocks analyzed. Scale bar = 100  $\mu\text{m}$  for photos a, b, c, d, e, g; 50  $\mu\text{m}$  for photo f. a Garnet-biotite textures. (*M* matrix biotite, *T* touching biotite). b Sieve-like garnet texture from sample CH907. c Retrograde reaction of diopside + fluid = tremolite + calcite + quartz. d Prograde reaction of talc forming tremolite. e Equilibrium texture of dolomite in calcite. f Strings of dolomite along a calcite grain boundary. g Ferroan dolomite overgrowths (*Dol 2*) on dolomite (*Dol 1*)

regionally metamorphosed area. Each thermometer uses a distinctly different mechanism to record temperatures: garnet-biotite is related to the partitioning of Mg and Fe between garnet and biotite, calcite-graphite is dependent on the fractionation of  $^{13}\text{C}$  versus  $^{12}\text{C}$  between calcite and graphite, and calcite-dolomite is controlled by the Mg content in calcite equilibrated with dolomite. Previous thermometric data have been obtained using calcite-dolomite (Sobol 1973; Allen 1976; Dunn 1989), calcite-graphite (van der Pluijm and Carlson 1989; van der Pluijm 1991; Dunn and Valley 1992), and garnet-biotite (LeClair 1982).

## Petrography

Polished thin sections were examined under a standard petrographic microscope to determine their suitability for thermobarometric analyses. Texturally, most garnets are subhedral to euhedral with the notable exception of sample CH907. In this sample the garnets have a poikiloblastic texture comprised of 20–50  $\mu\text{m}$  blebs that are separated by quartz, plagioclase, and biotite. Collectively the blebs have the shape of a 300–500  $\mu\text{m}$  subhedral to euhedral garnet (Fig. 2a and b). Biotite grains free of chlorite or muscovite interlayers were chosen for analysis.

Marbles in the study area show complex textural relationships. Silicates commonly show textural evidence of retrogression, especially in the higher grade areas. For example, diopside is reacting to form tremolite-quartz-calcite in a sample 10 km southwest of Bancroft (Fig. 2c). Textures suggestive of prograde reactions are much less common than retrograde textures; an example is shown in Fig. 2d where tremolite forms a rim around talc. Three types of dolomite were observed: equilibrium textures where the dolomite and calcite grain boundaries intersect at approximately  $120^\circ$  (Fig. 2e), irregularly shaped dolomites occurring either as long sinuous shapes or small blebs along calcite grain boundaries (Fig. 2f), or an early generation of dolomite with an overgrowth of ferroan dolomite (Fig. 2g).

## Analytical techniques

### Garnet-biotite

Compositions of coexisting garnet and biotite were determined with wavelength dispersive spectrometry (WDS) using a Cameca MBX electron microprobe and a selection of natural and synthetic mineral standards. Garnets were analyzed at a 15 kV accelerating voltage and a 10 nA current with the beam in point mode. Biotites were analyzed at 12 kV and 10 nA with the beam rastered over a 3  $\mu\text{m}$  wide square. No significant volatilization or migration of K was noted in biotites after 400 seconds of analysis. Back-scattered electron (BSE) microphotographs were taken to insure that biotite analyses would be free of chlorite and muscovite lamellae and to avoid pitted surfaces. Garnet profiles were obtained by stepping across the grains with approximately 100  $\mu\text{m}$  between analyses, with the rims being more densely sampled within 200  $\mu\text{m}$  of the grain edges (Fig. 3). Selected analyses of garnet are provided in Table 1 and biotite in Table 2; complete listings are in Appendix B of Rathmell (1993).

Two populations of biotites, those in the matrix and those in contact with garnets, may yield different garnet-biotite temperatures (Indares and Martignole 1985; Edwards and Essene 1988). In many MB metapelitic garnets, Mn has a classical bell shaped profile, and the Mg# [Mg/(Mg + Fe)] profile is a mirror image of the Mn profile. This is interpreted as prograde growth zonation with a retrogressive rim (Tracy 1982). Garnet zoning profiles were

obtained for most samples; a representative profile is shown in Fig. 3. The highest metamorphic temperatures are obtained by coupling analyses of matrix biotites to garnet analyses with the greatest Mg#, which are usually found ca. 100  $\mu\text{m}$  from the garnet edge.

### Calcite-graphite

For each sample approximately 100 cc of 2 mm sized crushed marble was dissolved in 38% HCl. Floating graphite was collected from the surface of the acid and large flakes were recovered from the residue if present. The graphite was combusted in the presence of CuO at 850  $^\circ\text{C}$  for 3 hours to form  $\text{CO}_2$  (Coplen et al. 1983), which was then purified and analyzed on a Delta-S mass spectrometer. Carbon standards NBS 21 (spectrographic graphite) and NBS 22 (hydrocarbon oil) were also processed with each batch of samples. The average  $\delta^{13}\text{C}$  of NBS 21 was  $-27.72$  which is within 0.07 per mil of the accepted value of  $-27.79$  per mil and NBS 22 was  $-29.56$  which is within 0.18 per mil of the accepted value of  $-29.74$  per mil. Replicate  $\delta^{13}\text{C}$  values for duplicate splits of Grenville graphites averaged within 0.14 per mil of each other. Thin section chips were stained with an Alizarin red/HCl solution to identify calcite grains suitable for analysis. The stain was removed by polishing prior to drilling the calcite with a 0.5 mm dental burr. These powdered carbonate samples were analyzed for carbon and oxygen isotopes on a Finnigan-Mat 251 mass spectrometer with an automated Kiel Carbonate Device. The carbonate standard NBS 19 was analyzed repeatedly with the unknowns; its  $\delta^{13}\text{C}$  was within  $0.05 \pm 0.03$  and its  $\delta^{18}\text{O}$  within  $0.06 \pm 0.05$  per mil of accepted values (Coplen et al. 1983). Replicate values for ten duplicate splits of Grenville calcites averaged within 0.04 per mil for  $\delta^{13}\text{C}$  and 0.10 per mil for  $\delta^{18}\text{O}$ . Combining the variations in the  $\delta^{13}\text{C}$  of coexisting calcite and graphite yields a 10  $^\circ\text{C}$  change ( $2\sigma$ ) in calculated temperatures. See Appendix A in Rathmell (1993) for a detailed discussion of the procedures used for analysis of calcite and graphite.

Most marble samples have very low concentrations of graphite (less than 1–2%). No attempt was made to measure graphite modes because of their fine grain size in most samples. Graphite was not detectable in many of the lower grade marbles with the microprobe. However, when the floating residue was treated with HCl and HF acids and then analyzed by powder X-ray diffraction (XRD), the low grade samples produced a sharp peak at 3.36  $\text{\AA}$ , i.e., well-ordered graphite. High magnification scanning electron microscope (SEM) photographs of purified graphite residues from the lowest grade samples reveal graphite flakes ranging in diameter from 0.5 to 5  $\mu\text{m}$ . A medium grade marble commonly contains graphite flakes that are 10–20  $\mu\text{m}$  in diameter, and a high grade marble has 50–100  $\mu\text{m}$  graphite flakes. The grain size of graphite appears to increase with increasing grade, but a detailed analysis has not been undertaken. Most of the graphite grains are too small to investigate isotopic zoning (Wada 1988; Kitchen and Valley 1995).

### Calcite-dolomite

Calcite and dolomite grains were analyzed on the Cameca microprobe using WDS at 15 kV and 7 nA. The beam was rastered over a 15  $\mu\text{m}$  square to minimize beam damage and reintegrate small dolomite lamellae. Analyzed elements included Ca, Mg, Mn, Fe, and Sr, with oxygen and carbon calculated assuming stoichiometric values (Essene 1983). The temperature for each sample was calculated by taking an average of the highest Mg# analyses of several different grains. Dolomite lamellae are occasionally too large to reintegrate with a 15  $\mu\text{m}$  rastered beam. In these samples quantitative energy dispersive spectrometry (EDS) was used with a 60  $\mu\text{m}$  square or larger raster to reintegrate the exsolution. Calcite and dolomite analyses are given in Table 5, and marble assemblages and a summary of calcite-dolomite temperatures are included in Table 6.

**Table 1** Garnet analyses

	CH 4c-o 11	CH907 4	KA9116 11	CH91117 14	KA91121 4	CH91133 15	KA91142 9	BB91155 20,57 $\mu$	BB91159 6	GH9201 8	BA9202 19	CH9203 36
Wt% Oxide												
SiO <sub>2</sub>	37.13	37.40	37.60	38.08	37.81	37.77	37.34	37.54	37.75	38.61	37.59	37.93
TiO <sub>2</sub>	0.02	0.02	0.03	0.06	0.10	0.10	0.00	0.18	0.00	0.01	0.01	0.00
Al <sub>2</sub> O <sub>3</sub>	21.14	21.00	20.78	21.05	21.05	21.48	20.94	20.83	20.92	21.43	20.80	21.42
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.11	0.02	0.01	0.02	0.02	0.00	0.01	0.00	0.00
FeO	38.46	21.30	35.17	26.65	35.22	27.30	33.88	24.82	37.86	31.38	27.29	33.87
MnO	0.67	15.23	1.63	4.27	1.82	1.16	1.45	5.39	0.46	1.53	8.28	0.46
MgO	2.08	0.50	1.58	2.45	3.15	2.88	3.18	0.98	2.32	4.99	2.95	3.51
CaO	0.60	4.26	3.46	7.48	1.10	8.62	1.93	9.57	0.40	3.22	2.23	3.15
Total	100.10	99.70	100.25	100.15	100.27	99.31	98.73	99.33	99.72	101.18	99.14	100.34
# of Ions												
Si	3.008	3.033	3.031	3.004	3.027	3.001	3.026	3.018	3.052	3.017	3.036	3.013
Al	2.018	2.007	1.974	1.981	1.986	2.011	2.000	1.974	1.994	1.974	1.979	2.006
Ti	0.001	0.001	0.002	0.003	0.006	0.006	0.000	0.011	0.000	0.000	0.001	0.000
Cr	0.000	0.000	0.000	0.010	0.001	0.000	0.001	0.002	0.000	0.001	0.000	0.000
Mg	0.251	0.060	0.189	0.270	0.376	0.341	0.384	0.118	0.280	0.581	0.355	0.416
Fe	2.606	1.444	2.372	1.812	2.359	1.814	2.296	1.669	2.560	2.051	1.843	2.250
Mn	0.046	1.046	0.111	0.271	0.124	0.078	0.100	0.367	0.031	0.101	0.566	0.031
Ca	0.052	0.370	0.299	0.646	0.094	0.734	0.167	0.825	0.035	0.270	0.193	0.268
Mol %												
Almandine	88.2	49.5	79.8	59.3	79.9	61.1	77.9	56.0	88.1	68.3	62.3	75.9
Grossular	1.8	12.7	10.1	21.0	3.1	24.7	5.6	27.6	1.2	9.0	6.5	9.0
Pyrope	8.5	2.1	6.4	9.7	12.7	11.5	13.0	4.0	9.6	19.3	12.0	14.0
Spessartine	1.6	35.8	3.7	9.6	4.2	2.6	3.4	12.3	1.1	3.4	19.2	1.0
Uvarovite	0.0	0.0	0.0	0.4	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.0
Mg#	0.088	0.040	0.074	0.141	0.138	0.158	0.143	0.066	0.099	0.221	0.161	0.156

Normalized to 12 oxygen atoms per formula unit bi = garnet analysis is adjacent to a biotite grain: Mg# = Mg/(Mg + Fe)

For sample BB91155, the number of microns to the edge of the garnet is given for analyses that correspond to the right hand rim of Figure 2

## Evaluation of available thermometers

### Garnet-biotite

Selected garnet and biotite analyses are presented in Tables 1 and 2 respectively; complete listings are in Rathmell (1993). Various calibrations of the garnet-biotite thermometer were tested, including Ferry and Spear (1978), Hodges and Spear (1982), Perchuk and Lavrent'eva (1983), Perchuk and Aranovich (1984), Indares and Martignole (1985), Hoinkes (1986), Williams and Grambling (1990), Dasgupta et al. (1991), Bhattacharya and Raith (1987), Bhattacharya et al. (1992), and Patiño-Douce et al. (1993) (Table 2). The garnet-biotite thermometer of Patiño-Douce et al. (1993), which also takes into account the effects of mixing of Mg, Fe<sup>2+</sup>, Al and Ti in the octahedral layer of biotite and their exchange with garnet, was used to calculate garnet-biotite temperatures throughout the study area. A program (Thermobarometry version 2.0 by M.J. Kohn and F.S. Spear, provided by F.S. Spear) was used to calculate temperatures of garnet-biotite pairs from their chemical analyses. Analyses of biotite from the electron microprobe do not take into account the possibility of a ferric iron component. Therefore the garnet-biotite data were reprocessed assuming 8% of the iron as ferric iron, following Guidotti and Dyar (1991). The resultant garnet-biotite temperatures decreased, on the average, by

about 30 °C. We have accepted the 8% Fe<sup>3+</sup> value as more likely correct for the purposes of garnet-biotite thermometry, rather than assuming all iron as ferrous, for the reasons given by Guidotti and Dyar (1991) and report the corrected analyses in Table 2.

### Calcite-graphite

Since graphite is a refractory phase with a high melting point it is very difficult to conduct meaningful isotopic exchange experiments which involve graphite. Even natural assemblages may fail to attain equilibrium partitioning, especially at low temperatures or brief durations of diffusion (Valley and O'Neil 1981). Several versions of the temperature dependence of <sup>13</sup>C/<sup>12</sup>C partitioning between calcite and graphite have been proposed, including those that were empirically derived in comparison with other geothermometers (Valley and O'Neil 1981; Wada and Suzuki 1983; Morikiyo 1984; Dunn and Valley 1992; Kitchen and Valley 1995) and those that were obtained from experimental measurements and/or theoretical considerations (Chacko et al. 1991; Scheele and Hoefs 1992; Polyakov and Khavlashina 1995). Experiments, even those conducted at high temperatures, have incomplete equilibration combined with small fractionations and are difficult to interpret in terms of equilibrium partitioning. Systematic comparisons of the various calcite-graphite calibrations were

CH9204 46	KA9206 25	BB9207 8	BA9211 7	BA9212 11	CH9214 5	GH9215C 8	BF9216 44	CH9217 9	WF9219 21	BB9223A 25
38.14	37.13	37.32	37.53	38.16	37.32	38.14	38.61	38.18	37.23	37.25
0.03	0.05	0.05	0.00	0.03	0.05	0.00	0.03	0.00	0.00	0.01
21.10	21.11	20.87	20.98	21.10	20.90	20.86	21.44	20.91	20.97	20.81
0.06	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
31.18	37.06	26.10	33.66	24.84	29.48	28.81	28.36	27.42	37.19	37.11
2.77	1.68	11.37	4.09	9.05	5.52	3.32	0.74	8.48	0.45	0.57
3.78	1.53	1.09	2.08	4.36	1.22	1.26	4.87	2.57	3.63	2.61
2.90	2.03	4.35	2.47	2.56	5.58	9.20	6.84	2.17	0.53	0.71
99.97	100.59	101.14	100.81	100.12	100.07	101.58	100.89	99.73	99.99	99.08
3.033	3.000	3.000	3.012	3.025	3.010	3.015	3.007	3.062	2.999	3.031
1.978	2.010	1.980	1.985	1.971	1.987	1.944	1.968	1.977	1.991	1.996
0.002	0.000	0.000	0.000	0.002	0.003	0.000	0.002	0.000	0.000	0.001
0.004	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
0.449	0.180	0.130	0.248	0.515	0.146	0.148	0.565	0.307	0.436	0.317
2.074	2.500	1.750	2.259	1.647	1.989	1.905	1.847	1.839	2.505	2.525
0.187	0.110	0.770	0.278	0.608	0.377	0.222	0.049	0.576	0.031	0.040
0.247	0.180	0.370	0.213	0.217	0.482	0.779	0.570	0.187	0.045	0.062
70.2	84.1	57.8	75.4	55.1	66.4	62.4	60.9	63.2	83.0	85.8
8.2	5.9	12.3	7.1	7.2	16.1	25.5	18.8	6.4	1.5	2.1
15.2	6.2	4.3	8.3	17.3	4.9	4.9	18.7	10.6	14.5	10.8
6.3	3.9	25.5	9.3	20.4	12.6	7.3	1.6	19.8	1.0	1.3
0.2	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
0.178	0.068	0.069	0.099	0.238	0.069	0.072	0.234	0.143	0.148	0.112

reported by Morrison and Barth (1993) and Kitchen and Valley (1995). They concluded that the empirical calibration of Dunn and Valley (1992) is in best agreement with other metamorphic geothermometers, and therefore only the latter calibration is employed here.

#### Calcite-dolomite

The calcite-dolomite solvus was evaluated by Anovitz and Essene (1987) using available experimental reversals. They also provided an updated correction for the effect of Fe on calcite-dolomite thermometry. All calcite-dolomite temperatures have been corrected for Fe using Anovitz and Essene (1987), even though the corrections are small (< 10 °C) in the temperature range considered in this study.

## Discussion

#### Garnet-biotite

Garnet-bearing assemblages and a summary of garnet-biotite temperatures are given in Table 3. A location map for all samples analyzed in this study is shown in Fig. 4. Temperature data using the calibration of Patiño-Douce et al. (1993) are shown on a regional map in Fig. 5a. Temperatures range from approximately 500 °C near Madoc to over 650 °C just south of Bancroft and along

the western margin just east of Apsley. Retrograde temperatures for the same samples from touching garnet-biotite pairs were, on average, about 100 °C lower than peak temperatures. Garnet-aluminosilicate-silica-plagioclase (GASP) barometry for samples KA91142 and CH4c-o yields a pressure of 550 MPa, and BA9223A gives 500 MPa (Kozioł and Newton 1988; Essene 1989). Based mainly on occurrences of Al<sub>2</sub>SiO<sub>5</sub> polymorphs, Anovitz and Essene (1990) concluded that pressures in the area vary from 400 to 600 MPa. A variation of 100 MPa produces a change of only 10 °C in the calculated garnet-biotite temperatures. An average pressure estimate of 500 MPa was used in the calculations.

Garnet-biotite isotherms display a bend in the western part of the area that forms a salient pointing to the east (Fig. 5a). The shape of the garnet-biotite salient is mimicked by the muscovite-quartz/sillimanite-K-feldspar isograd (Fig. 5d) (Carmichael et al. 1978). Sample CH907, located 10 km east of Coe Hill, yields a garnet-biotite temperature of 400 °C whereas another sample, CH9204, less than 3 km away from CH907 yields a garnet-biotite temperature of 620 °C (Fig. 5a). The sieve-like texture of the garnets in sample CH907 may be responsible for the low garnet-biotite temperatures (Fig. 2b). The individual garnet blebs are less than 50 µm in diameter, so the entire garnet has probably been retrogressed, resulting in the low temperature estimate. In other samples, garnet rim profiles show that the outer 50–200 µm of the garnet may be affected by retrogression (Fig. 3).

**Table 2** Biotite analyses

	CH 4c-o 10, m	CH907 1, m	KA9116 3, m	CH91117 2, m	KA91121 1, m	CH91133 6, m	KA91142 3, m	BB91155 7, m	BB91159 1, m	KA91163 5, m	GH9201 1, m	BA9202 8, m
<i>Wt% oxide</i>												
SiO <sub>2</sub>	33.58	34.84	34.37	35.55	35.42	37.10	35.98	34.42	33.88	36.35	37.32	35.22
TiO <sub>2</sub>	2.25	1.84	1.59	2.22	1.56	2.37	1.57	2.86	2.54	1.82	1.84	1.99
Al <sub>2</sub> O <sub>3</sub>	18.48	17.42	18.44	15.84	18.24	15.16	19.03	14.19	19.26	18.37	17.14	18.53
Cr <sub>2</sub> O <sub>3</sub>	0.05	0.01	0.00	0.13	0.08	0.04	0.00	0.00	0.05	0.01	0.17	0.00
Fe <sub>2</sub> O <sub>3</sub>	1.93	1.98	1.97	1.67	1.56	1.62	1.62	2.29	1.84	1.31	1.32	1.61
FeO	22.23	22.75	22.68	19.25	17.98	18.69	18.62	26.38	21.12	15.06	15.22	18.54
MnO	0.02	0.50	0.00	0.07	0.04	0.09	0.02	0.17	0.06	0.36	0.00	0.17
MgO	6.69	6.30	7.24	10.79	10.05	11.59	9.55	5.91	7.31	11.08	14.12	9.32
BaO	0.15	0.06	0.12	0.00	0.11	0.52	0.00	0.09	0.07	0.27	0.30	0.19
CaO	0.02	0.00	0.05	0.20	0.00	0.00	0.00	0.12	0.03	0.03	0.00	0.00
Na <sub>2</sub> O	0.23	0.05	0.13	0.19	0.33	0.25	0.15	0.06	0.17	0.16	0.15	0.14
K <sub>2</sub> O	9.64	9.78	9.28	8.18	9.61	9.04	9.67	9.48	9.13	9.76	9.02	9.62
F	0.37	0.57	0.61	0.38	0.32	1.58	0.61	0.20	0.38	0.37	0.28	0.40
Cl	0.04	0.03	0.07	0.07	0.00	0.03	0.00	0.79	0.01	0.06	0.00	0.27
O = F	-0.16	-0.24	-0.26	-0.16	-0.14	-0.66	-0.26	-0.08	-0.16	-0.15	-0.12	-0.17
O = Cl	-0.01	-0.01	-0.02	-0.02	0.00	-0.01	0.00	-0.18	0.00	-0.01	0.00	-0.06
Total	95.51	95.88	96.27	94.36	95.16	97.41	96.56	96.70	95.69	94.85	96.76	95.77
<i># of ions</i>												
Si	2.63	2.73	2.67	2.75	2.71	2.80	2.71	2.74	2.62	2.75	2.75	2.69
Al (iv)	1.37	1.27	1.33	1.25	1.29	1.20	1.29	1.26	1.38	1.25	1.25	1.31
Al (vi)	0.33	0.33	0.35	0.19	0.35	0.15	0.40	0.07	0.37	0.39	0.24	0.36
Ti	0.13	0.11	0.09	0.13	0.09	0.13	0.09	0.17	0.15	0.10	0.10	0.11
Cr	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Fe <sup>3+</sup>	0.11	0.12	0.12	0.10	0.09	0.09	0.09	0.14	0.11	0.07	0.07	0.09
Fe <sup>2+</sup>	1.46	1.49	1.47	1.24	1.15	1.18	1.17	1.76	1.36	0.95	0.94	1.18
Mn	0.00	0.03	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.02	0.00	0.01
Mg	0.78	0.73	0.84	1.24	1.15	1.31	1.07	0.70	0.84	1.25	1.55	1.06
Ba	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.01	0.01	0.01
Ca	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Na	0.03	0.01	0.02	0.03	0.05	0.04	0.02	0.01	0.03	0.02	0.02	0.02
K	0.96	0.98	0.92	0.81	0.94	0.87	0.93	0.96	0.90	0.94	0.85	0.94
A site	1.02	1.01	0.95	0.84	1.01	0.92	0.97	0.99	0.95	0.99	0.88	0.98
F	0.09	0.14	0.15	0.09	0.08	0.38	0.15	0.05	0.09	0.09	0.07	0.10
Cl	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.11	0.00	0.01	0.00	0.04
OH	1.46	1.38	1.54	1.74	1.49	1.31	1.42	1.53	1.51	1.33	1.75	1.42
Garnet for T	gt # 11	up gt # 4	CR gt 11	LC gt # 14	LL gt # 4	ML gt # 15	LL gt # 9	9LR gt # 20	UL gt # 6	sm rt gt # 23	gt 8	up rt gt 19
P (kb)	5	5	5	5	5	5	5	5	5	5	5	5
T °C PD et al.	560	400	540	580	540	630	600	630	550	560	580	640
T °C FS	610	400	530	580	570	590	620	610	610	500	590	680
T °C HS	620	450	570	670	580	710	640	730	610	590	630	710
T °C PA	610	490	580	590	590	650	630	600	610	550	600	650
T °C PA Mn	610	420	570	570	580	640	620	570	610	480	590	600
T °C IM	470	520	480	640	480	630	530	710	520	630	550	690
T °C H	630	470	610	720	600	750	680	760	620	620	680	760
T °C BR	640	360	600	850	750	930	800	560	670	850	880	840
T °C DSGF	490	400	480	660	510	680	550	660	480	570	630	630
T °C BMSR	600	260	540	590	590	640	620	500	610	490	620	590
Mg # of bi	0.330	0.312	0.344	0.479	0.478	0.504	0.457	0.269	0.362	0.547	0.603	0.452

Number of ions on the basis of 220 equivalents, hydroxyl site occupancy = 4: Mg# = Mg/(Mg + Fe): gt = touching garnet, m = matrix

PD = Patino-Douce et al. (1993), FS = Ferry and Spear (1978), HS = Hodges and Spear (1982), IM = Indares and Martignole (1985), H = Hoinkes (1986), BR = Bhattacharya and Riath (1987), DSGF = Dasgupta et al. (1991), BMSR = Bhattacharya et al. (1992)

PA = Perchuk and Aranovich (1984), PA Mn = Perchuk and Aranovich (1984) with Mg# = Mg/(Mg + Fe + Mn) (see text for discussion)

\*H<sub>2</sub>O has been calculated but is not shown in the table

## Calcite-graphite

Isotopic data for calcite and graphite and the corresponding temperatures are shown in Table 4. These data and calcite-graphite temperatures from Dunn and Valley

(1992) are shown on a regional map in Fig. 5b. A temperature minimum of < 450 °C is located to the west of Madoc and the temperatures increase radially away from it. As with the garnet-biotite data, the 650 °C isotherm cuts just south of Bancroft and turns to a N-S orienta-

CH9203 5, m	CH9204 5, m	KA9206 10, m	BB9207 1, m	BA9211 6, m	BA9212 5, m	CH9214 5, m	GH9215C 8, m	BF9216 8, m	CH9217 7, m	WF9219 9, m	BB9223A 6, m
36.11	36.36	34.84	34.82	34.90	36.84	34.59	34.51	36.32	34.75	34.93	35.19
1.71	1.44	1.55	1.59	4.59	0.20	2.20	2.26	2.39	3.22	3.98	1.58
18.95	16.98	18.42	17.77	18.35	18.09	17.21	16.31	16.51	17.94	17.05	19.02
0.07	0.00	0.00	0.00	0.05	0.00	0.02	0.00	0.05	0.04	0.11	0.08
1.51	1.40	1.97	1.73	1.71	1.28	2.11	2.30	1.34	1.71	1.80	1.78
17.34	16.12	22.62	19.84	19.64	14.71	24.26	26.41	15.42	19.71	20.64	20.46
0.00	0.03	0.00	0.22	0.10	0.25	0.15	0.11	0.00	0.23	0.00	0.00
10.31	13.72	6.99	9.13	6.41	12.66	5.90	5.32	13.45	8.67	7.22	8.36
0.27	0.11	0.10	0.07	0.13	0.23	0.08	0.09	0.13	0.01	0.14	0.21
0.00	0.19	0.01	0.02	0.02	0.01	0.00	0.03	0.00	0.00	0.00	0.00
0.17	0.57	0.24	0.19	0.08	0.14	0.08	0.04	0.50	0.06	0.07	0.32
9.17	8.29	9.03	9.70	9.70	9.45	9.60	9.51	8.82	9.96	9.92	9.07
0.49	0.13	0.54	0.83	0.53	0.74	0.42	0.79	0.00	0.20	0.77	0.54
0.02	0.02	0.05	0.03	0.05	0.04	0.87	0.06	0.01	0.00	0.65	0.13
-0.21	-0.05	-0.23	-0.35	-0.22	-0.31	-0.18	-0.33	0.00	-0.08	-0.32	-0.23
0.00	0.00	-0.01	-0.01	-0.01	-0.01	-0.20	-0.01	0.00	0.00	-0.15	-0.03
95.91	95.31	96.12	95.58	96.03	96.14	97.11	97.40	94.94	96.42	96.81	96.48
2.72	2.73	2.70	2.69	2.67	2.74	2.70	2.71	2.73	2.65	2.69	2.68
1.28	1.27	1.30	1.31	1.33	1.26	1.30	1.29	1.27	1.35	1.31	1.32
0.40	0.23	0.38	0.31	0.33	0.33	0.29	0.22	0.20	0.27	0.24	0.39
0.10	0.08	0.09	0.09	0.26	0.11	0.13	0.13	0.14	0.18	0.23	0.09
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
0.09	0.08	0.11	0.10	0.10	0.07	0.12	0.14	0.08	0.10	0.10	0.10
1.09	1.01	1.46	1.28	1.26	0.92	1.59	1.73	0.97	1.26	1.33	1.30
0.00	0.00	0.00	0.01	0.01	0.02	0.01	0.01	0.00	0.01	0.00	0.00
1.16	1.54	0.81	1.05	0.73	1.40	0.69	0.62	1.51	0.99	0.83	0.95
0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.02	0.08	0.04	0.03	0.01	0.02	0.01	0.01	0.07	0.01	0.01	0.05
0.88	0.79	0.89	0.96	0.95	0.90	0.96	0.95	0.85	0.97	0.98	0.88
0.93	0.88	0.95	1.01	1.00	0.94	0.99	0.98	0.93	1.01	1.02	0.95
0.12	0.03	0.14	0.21	0.14	0.18	0.11	0.20	0.00	0.05	0.19	0.13
0.00	0.00	0.01	0.00	0.01	0.01	0.12	0.01	0.00	0.00	0.09	0.02
1.45	1.87	1.51	1.45	0.98	1.42	1.36	1.47	1.75	1.46	1.02	1.47
gt 36	gt 46	gt 25	big gt 8	gt 7	gt 11	gt 5	gt 8	gt 44	gt 9	up gt 21	gt 25
5	5	5	5	5	5	5	5	5	5	5	5
590	620	500	490	650	620	600	720	660	620	700	560
600	530	510	420	630	660	590	650	650	680	810	600
640	570	540	460	660	690	660	770	730	710	820	610
610	560	560	510	630	650	600	650	620	640	730	610
610	540	560	460	610	590	570	620	610	590	730	610
520	520	450	500	490	690	620	720	630	660	580	480
690	600	560	480	710	740	720	820	810	760	830	620
840	830	570	550	730	940	590	620	1010	790	820	710
550	580	440	450	490	670	560	650	720	620	620	500
630	580	520	380	570	620	500	550	680	580	720	610
0.494	0.583	0.336	0.430	0.348	0.585	0.285	0.248	0.589	0.419	0.365	0.401

tion along the western margin of the area. A bend in the isotherms similar to that in the garnet-biotite data may also be inferred based on the sparse calcite-graphite data in the area. Powder XRD data show that even graphite from very low grade samples is fully crystallized and well ordered, suggesting that organic material has been transformed to graphite. As the lowest grade samples contain fully crystallized graphite, it was assumed that most of the graphites from higher grade rocks were also fully ordered. The samples chosen for isotopic analysis do not have mylonitic textures, so resetting during late crystallization (van der Pluijm and Carlson 1989; van der

Pluijm 1991) was probably minor, although resetting during early retrogression with subsequent grain boundary recovery cannot be ruled out. Exchange of calcite with late fluids without reequilibration of the graphite could also occur, but cathodoluminescent observations of thin sections do not reveal any evidence for access of late fluids. The refractory nature of graphite also suggests that it may equilibrate during prograde metamorphism that is accompanied by strong deformation at temperatures somewhat below the thermal maximum; however, such graphite will not subsequently reequilibrate at peak temperatures. Careful separation and analysis of graph-

Table 3 Pelite Assemblages

Sample #	Gt	Bi	Qz	Plag	Ksp	Amph	St	Mu	Chl	Ru	Ilim	Py	Zc	Ap	Mon	Xn	Other	T (°C) PD et al.	UTM
CH 4c-o	x	x	x	x	-	-	x	x	-	-	-	-	-	-	-	-	Sil, Tour	590	745715
CH907	x	x	x	x	-	-	-	r	-	x	x	x	x	x	-	-	Cc, Sph	410	878710
BB913C	-	x	x	x	x	-	-	-	-	x	x	-	-	x	x	-	Cc, Sph, Tour	-	992305
KA9116	x	x	x	-	-	-	x	x	r	-	x	-	x	-	-	-	All, Ctd, Dol, Mt	560	082385
KA9122	-	x	x	x	-	-	-	-	-	-	-	-	-	-	-	-	Cc, Tour	-	066328
KA9129	-	-	x	-	-	-	x	x	x	x	x	-	x	x	x	-	Ctd, Mt	-	024330
BB9131	-	x	x	x	-	-	-	x	-	-	-	-	-	-	-	-	Cc	-	959499
BB9146	-	x	x	x	-	-	-	-	-	-	-	-	-	-	-	-	-	-	817395
CH9160	-	x	x	x	x	-	-	x	-	-	-	-	-	-	-	-	-	-	850786
CH9162	-	x	x	x	-	x	-	-	-	-	-	-	-	-	-	-	-	-	859746
CH9163	-	x	x	-	-	x	-	-	-	-	-	-	-	-	-	-	Cc	-	859746
CH9168	-	x	-	-	x	-	-	-	-	-	-	-	-	-	-	-	EP	-	898684
CH9172	-	x	x	-	-	-	-	x	-	-	-	-	-	x	-	-	-	-	011800
GH9177	-	-	x	x	x	x	-	-	-	-	-	-	-	-	-	-	-	-	288813
GH9180	-	-	-	x	-	x	-	-	-	-	-	-	-	-	-	-	-	-	345803
WF9182	-	x	x	x	-	x	-	-	-	-	-	-	-	-	-	-	-	-	338876
BA9192	-	x	x	x	-	-	-	-	-	-	x	-	-	-	-	-	Px	-	815915
BA9196	-	x	x	x	x	-	-	-	-	-	-	-	-	-	-	-	-	-	938988
CH9105	-	x	x	x	-	-	-	x	-	-	-	-	-	-	-	-	-	-	747719
CH9109	-	x	x	x	-	-	-	x	-	-	-	-	-	-	-	-	-	-	761646
CH9117	x	x	x	x	-	x	-	-	-	x	x	-	-	x	-	-	Mt	600	632746
KA91121	x	x	x	-	-	-	x	x	r	-	x	x	x	x	x	-	Cpy, Mt	560	294412
KA91122	-	x	x	-	-	x	-	-	-	-	-	x	-	x	-	-	Tour	-	270521
CH91129	-	x	x	x	-	x	-	x	r	-	-	x	-	x	-	-	Sil	-	745715
CH91133	x	x	-	x	-	x	-	-	r	x	x	x	-	x	-	-	Cc	680	641673
KA91139	x	x	x	x	x	-	-	x	r	-	-	x	-	x	x	x	Cc, Tour	-	315394
KA91140	x	x	x	x	x	-	-	x	r	-	-	x	-	x	-	-	Cc	-	315394
KA91142	x	x	x	x	x	-	-	x	r	-	-	-	x	x	x	x	Bar, Ser, Sil	640	315394
BB91144	-	-	x	-	-	-	-	-	x	-	-	-	-	-	-	-	Cc	-	759349
BB91145B	-	-	x	-	-	-	-	-	x	-	-	-	-	-	-	-	Cc	-	732316
BB91150	-	-	-	x	x	x	-	-	-	-	-	-	-	-	-	-	Cc	-	701421
BB91151	-	x	-	x	-	x	-	-	-	-	-	-	-	-	-	-	Cc	-	747541
BB91155	x	x	-	x	-	x	-	-	-	-	x	x	x	x	-	-	Sph	670	669528
BB91159	x	x	x	-	-	-	x	r	r	x	x	-	x	x	x	x	Tour	590	702421
BB91160	-	-	x	-	-	-	-	x	x	-	x	-	-	-	-	-	Mt	-	762323
BB91162	-	x	x	x	-	-	-	x	-	x	-	x	-	x	-	-	Cc, Ep	-	817396
KA91163	x	x	x	x	x	-	-	r	r	-	-	x	x	x	-	-	All, Cc, Mt, Tour	560	163361
BB91164	-	x	x	x	-	-	-	r	r	-	-	-	-	-	-	-	Tour	-	992305
BA91165	-	x	-	x	-	-	-	-	-	x	-	-	-	-	-	-	Cc, PX	-	725916
GH9201	x	x	x	x	-	x	-	r	r	-	x	x	-	x	-	-	Cpy, Mt, Ser, ZnS	600	345805
BA9202	x	x	x	x	-	-	-	r	-	x	x	x	x	x	x	x	Tour	680	918971
CH9203	x	x	x	x	-	x	x	-	r	-	x	x	-	-	-	-	Cc	620	025802
CH9204	x	x	-	x	-	x	-	-	r	-	x	x	x	-	-	-	Cpy	620	860735





**Table 5** Carbonate Analyses

	BA904A cc 3	BA904A dol 1	CH908A cc 3	KI909 cc 2	BF917 cc 7	BF917 dol 1	KA9121 cc 9	KA9121 dol 1	CF9134 cc 5	CF9134 dol 1	CH9166 cc 1
Wt% Oxide											
FeO	0.14	0.85	0.14	0.78	0.04	0.09	0.01	0.05	0.04	0.08	0.05
MnO	0.06	0.06	0.00	0.04	1.05	4.49	0.67	4.04	0.95	5.94	1.09
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.76	21.01	0.99	1.44	1.78	18.16	1.33	19.02	1.10	17.49	2.04
CaO	55.41	31.25	55.64	53.71	52.16	30.56	52.78	30.31	53.41	30.46	51.54
CO <sub>2</sub>	44.44	48.02	44.83	44.22	43.54	46.60	43.29	47.04	43.73	46.68	43.37
Total	100.82	101.20	101.59	100.18	98.56	99.90	98.09	100.46	99.24	100.65	98.09
# of Ions											
Mg	0.037	0.955	0.048	0.071	0.089	0.851	0.067	0.883	0.055	0.818	0.103
Fe	0.004	0.022	0.004	0.022	0.029	0.118	0.019	0.105	0.027	0.155	0.031
Mn	0.002	0.002	0.000	0.001	0.001	0.002	0.000	0.001	0.001	0.002	0.001
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	1.957	1.021	1.948	1.906	1.880	1.029	1.913	1.011	1.917	1.024	1.865
Mol%											
CaCO <sub>3</sub>	97.9	51.1	97.4	95.3	94.0	51.5	95.7	50.6	95.9	51.2	93.3
MgCO <sub>3</sub>	1.9	47.8	2.4	3.6	4.5	42.5	3.4	44.1	2.8	40.9	5.1
FeCO <sub>3</sub>	0.2	1.1	0.2	1.1	1.5	5.9	1.0	5.2	1.3	7.8	1.5
MnCO <sub>3</sub>	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1
T °C	340	–	400	480	515	–	465	–	440	–	540

Normalized to two +2 cations per formula unit: cc = calcite, dol = dolomite  
 Temperatures calculated using Anovitz and Essene (1987)

ite flakes grown in different orientations in deformed marbles could be used to test this hypothesis.

Anomalously high calcite-graphite temperatures may be due to the presence of a cryptic contact aureole, i.e., an aureole caused by an intrusion that is not exposed. Dunn and Valley (1992) found that high calcite-graphite temperatures are preserved in contact aureoles even when overprinted by subsequent regional metamorphism in the range of 500–550 °C. Samples for calcite-graphite thermometry were collected at least two kilometers away from any mapped intrusive bodies to avoid contact aureole effects, although igneous bodies not exposed at the surface may have perturbed some samples.

Four marble samples show anomalously low carbon ( $\delta^{13}\text{C}$  of –23 to –25 per mil), suggesting that they failed to equilibrate with matrix calcite (Table 4). These samples yield apparent temperatures of only 180–230 °C even though they were collected in areas that are above the sillimanite isograd. They clearly failed to attain equilibrium partitioning of carbon isotopes and were ignored in the contouring of isotherms.

#### Calcite-dolomite

The calcite-dolomite thermometer is prone to resetting during deformation and retrogression (Essene 1983). Textures observed with BSE reveal retrogression of magnesian calcite forming ferroan dolomite overgrowths and exsolution of dolomite (Figs. 2f–g). Irregularly shaped dolomites that form along calcite grain boundaries probably represent dolomite that exsolved within the calcite and then migrated out of the host grain (Fig. 2f). Calcite-dolomite temperatures from the center

of exsolved grains were compared to those from grains with little or no exsolution. Analyses from points 1, 6, and 7 in an unexsolved grain (Fig. 2g) yield temperatures of 530, 540, and 540 °C respectively, while analyses from points 8 and 9 with abundant exsolution give 510 and 450 °C, respectively. This indicates that some Mg was lost from the cores of calcites during the process of exsolution. Therefore, calcite grains were selected for thermometry that showed little or no dolomite exsolution. Calcite-dolomite temperature data from Sobol (1973), Allen (1976), Dunn and Valley (1992), and this study are shown on a map along with interpreted isotherms (Fig. 5c). Temperatures are lowest near Madoc (<450 °C), and increase toward Bancroft. The 600 °C isotherm for calcite-dolomite runs through Bancroft and then trends NE–SW through the western part of the study area.

#### Comparative thermometry

Garnet-biotite and calcite-graphite thermometry yield very similar contour maps for the study area. Both indicate a low temperature core centered to the west of Madoc with temperature increasing to the north, northwest, and northeast. It is interpreted that both have a bend in the northwest that closely approximates the sillimanite + K-feldspar isograd of Carmichael et al. (1978) (Fig. 5d). The apparent isotherms for calcite-dolomite thermometry trend NE–SW and have a distinctly different shape from garnet-biotite and calcite-graphite contours. The location of the thermal minimum near Madoc for calcite-dolomite is the same as the other thermometers, but the 600 °C and 650 °C isotherms are

CH9166 dol 1	CH9171 cc 4	BA9183 cc 3	BA9189 cc 14	BA9197 cc 8	CH91107 cc 7	KA91118 cc 7	KA91118 dol 3	KA91138 cc 4	KA91138 eds cc 1	KA91118 wds cc 1
0.07	0.15	0.16	0.07	0.12	0.04	0.08	0.06	0.02	0.00	0.03
5.15	1.72	0.04	0.07	0.25	0.68	0.06	0.22	0.00	0.00	0.02
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18.29	2.09	2.54	2.57	2.92	2.30	2.80	21.54	2.13	2.26	2.26
30.25	51.04	52.93	51.86	51.64	52.41	52.87	30.85	52.67	53.53	52.79
46.89	43.48	44.44	43.58	43.94	44.08	44.63	47.90	43.67	44.48	43.92
100.65	98.48	100.12	98.15	98.87	99.51	100.43	100.57	98.49	100.27	99.01
0.852	0.105	0.125	0.129	0.145	0.114	0.137	0.982	0.107	0.111	0.112
0.134	0.048	0.001	0.002	0.007	0.019	0.002	0.005	0.000	0.000	0.000
0.002	0.004	0.005	0.000	0.003	0.001	0.002	0.002	0.002	0.001	0.001
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.012	1.842	1.869	1.867	1.845	1.866	1.859	1.011	1.893	1.889	1.887
50.6	92.1	93.5	93.4	92.2	93.3	93.0	50.5	94.7	94.5	94.3
42.6	5.3	6.3	6.4	7.3	5.7	6.8	49.1	5.3	5.6	5.6
6.7	2.4	0.1	0.1	0.3	0.9	0.1	0.3	0.0	0.0	0.0
0.1	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.0	0.0	0.0
–	550	580	575	> 600	560	600	–	540	550	550

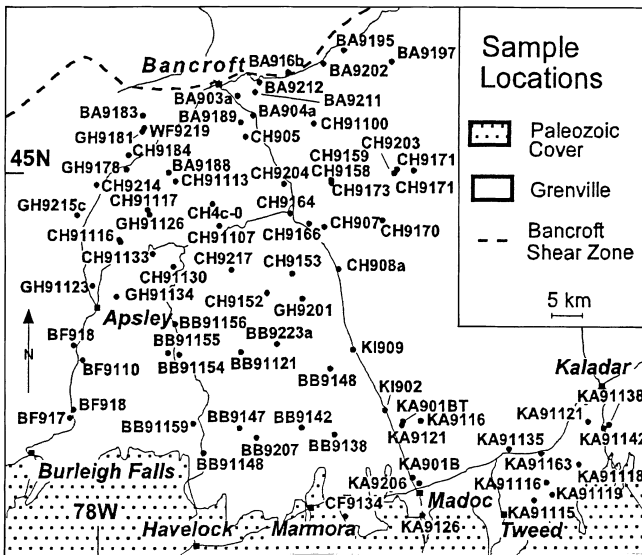


Fig. 4 Location map of all samples analyzed for thermometry

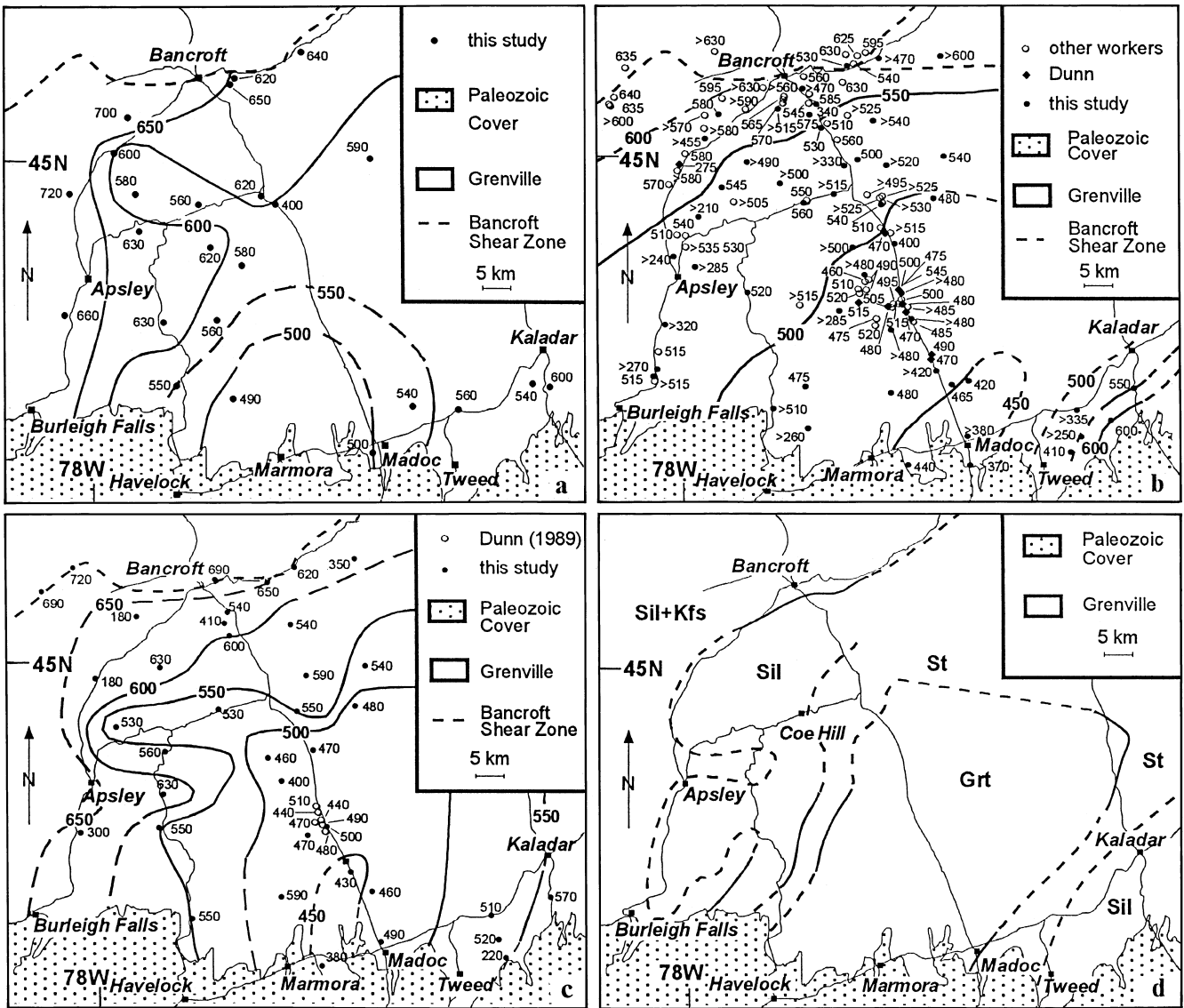
shifted north toward Bancroft and have a NE–SW orientation instead of a N–S orientation.

Temperatures for all three thermometers within 5 km of either side of a transect from Madoc to Bancroft are plotted in Fig. 6. Although some of the low values are from samples where calcite and dolomite appear to be in textural equilibrium (Fig. 2h), many of the low temperature results for calcite-dolomite are from dolomite-absent samples and therefore only represent minimum temperatures. Dunn and Valley (1992) found a high temperature spike in the calcite-graphite data in the contact aureole of the Tudor gabbro that is not shown in the figure. They found that calcite-graphite thermometry

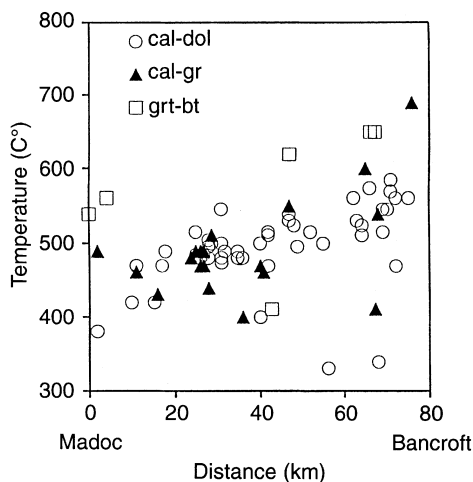
preserves a record of the approximately 1250 Ma intrusion through the Grenville overprint, while calcite-dolomite systematics were completely reset during subsequent regional metamorphism. All three thermometers are generally in agreement at the low temperature end of the profile, but the calcite-graphite and garnet-biotite data indicate higher temperatures than the calcite-dolomite trend in the high temperature region.

The positions of the pelitic isograds (Fig. 5d) and the garnet-biotite isotherms (Fig. 5a) are consistent with each other. The staurolite isograd occurs at 540 °C, the sillimanite isograd 590 °C, and the sillimanite + K-feldspar isograd at 650 °C. A  $590 \pm 30$  °C temperature for the kyanite–sillimanite transition indicates a pressure of  $600 \pm 80$  MPa (Bohlen et al. 1991). At 650 °C and 600 MPa the sillimanite + K-feldspar isograd is located at an  $X_{H_2O}$  of approximately 0.7 (Kerrick 1972). The apparently reduced activity of  $H_2O$  at this isograd may be related to systematically low estimates of temperature, or to dilutional effects of additional components in the fluid (Edwards and Essene 1988).

Garnet-biotite and calcite-graphite thermometry yield results that are consistent with each other and with the pelitic isograds. Therefore, they appear to be reliable indicators of peak metamorphic conditions. Based on the garnet-biotite and calcite-graphite thermometry, calcite-dolomite thermometry has been reset by approximately 50 to 100 °C in the higher grade parts of the field area. Consequently, calcite-dolomite thermometry by itself is not sufficient accurately to constrain metamorphic field gradients in middle to upper amphibolite facies rocks. Different calibrations of garnet-biotite thermometers may yield variable results that are related to the neglect of  $Fe^{3+}$  in biotite both in the calibration and in the natural samples, dissimilar treatment of im-



**Fig. 5a-d** Maps of isotherms for each thermometer with major roads shown for reference. Isotherms are *dashed* where inferred. **a** Map of garnet-biotite temperatures from this study; **b** map of calcite-graphite thermometry based on data from Dunn (1989) and this study; **c** calcite-dolomite thermometry based on data from Dunn and Valley (1992) and this study; **d** map of pelitic isograds [*Grt* garnet, *St* staurolite, *Sil* sillimanite, *Kfs* K-feldspar (Carmichael et al. 1978)]



**Fig. 6** Garnet-biotite, calcite-graphite, and calcite-dolomite temperatures plotted along a traverse from Madoc to Bancroft. Data points used were within 5 km on either side of a traverse from Madoc to Bancroft

portant additional components (Ca, Mn in garnet; F, Al, Cl, Ti, Mn in biotite), or different calibrations of  $K_D$  versus  $T$  for  $Mg/Fe^{2+}$ . Most calcite-graphite temperatures seem to be representative of peak metamorphic conditions, but considering the remaining uncertainties in various calibrations of calcite-graphite thermometry, simultaneous application of another thermometer is desirable when possible. Each thermometer applied in this study has drawbacks that limit its usefulness to determine peak metamorphic temperatures when used alone. However in combination they produce a reliable picture of the thermal conditions that existed at the peak of regional metamorphism.

**Table 6** Marble Assemblages

Sample	Cc	Dol	Qz	Tc	Tr	Phl	Di	Ru	Sph	Mu	Plag	Ksp	Py	Gr	Ap	Other	Ce-Dol T(°C)*	UTM
KI902B	x	-	x	-	-	x	-	x	x	x	x	x	x	-	x	Bi,Chl, Mon,Zc	>410	983444
BA903A	x	-	x	-	x	r	x	-	x	-	-	x	x	x	x	-	>420	767915
BA904A	x	2	x	-	r	-	x	x	x	-	x	x	x	x	x	Hyal,Thor	340	795887
CH908A	x	x	x	-	-	x	-	x	-	-	-	x	x	x	x	-	390	916657
KA914C	x	-	x	-	-	-	-	-	-	x	x	x	x	-	x	-	>380	025324
BA916B	x	x	-	-	x	x	-	-	-	-	-	-	x	-	-	Chi,Oliv, Serp	530	849939
BF917	x	x	x	-	-	x	-	x	x	-	x	-	x	-	x	Chl,Zc	515	278422
BF918	x	-	-	-	2	x	-	-	x	-	x	x	x	-	x	Zc	>270	274441
BF9110	x	-	x	-	-	x	x	-	x	-	x	x	x	x	-	All	>320	282525
KA9113	x	x	-	-	-	-	-	x	-	x	x	x	x	-	-	-	420	044419
KA9121	x	x	x	-	-	x	-	x	-	-	x	-	x	-	-	Chl,Cpy	465	019415
KA9126	x	-	x	-	-	-	-	-	-	x	x	-	x	-	x	-	>370	038275
CF9134	x	x	x	x	x	x	-	-	x	-	x	x	x	-	x	All,Chl	440	915285
BB9138	x	x	x	-	-	-	-	x	-	x	x	x	x	-	x	Chl	480	921384
BB9147	x	2	x	-	-	-	-	x	-	-	x	-	-	-	x	Fl,Mt	475	767422
BB9148	x	-	x	-	-	-	-	-	x	-	x	-	-	-	x	Chl	>480	918512
CH9153	x	-	x	-	-	x	-	x	-	x	x	-	-	-	-	Chl, Cpy, Zc	>500	850651
CH9158	x	2	x	-	-	x	-	x	-	x	x	-	x	-	x	-	500	871794
CH9159	x	2	x	-	-	x	-	x	-	x	x	-	x	-	x	Tour, Zc	510	916784
CH9164	x	-	x	-	-	x	-	-	x	-	x	-	-	-	-	All, Chl, Ep	>515	826733
CH9166	x	x	x	-	-	x	-	-	-	x	x	-	-	-	-	All, Chl, Zc	540	900717
CH9170	x	x	x	-	-	-	-	-	-	x	x	-	x	-	x	-	480	989726
CH9171	x	x	x	-	-	x	-	x	-	x	x	-	x	-	x	All, Cpy, Zc	540	012795
CH9173	x	-	x	-	-	x	-	x	-	x	x	-	x	-	x	Chl, Ilm	>495	981775
GH9181	x	-	x	-	x	x	-	x	x	-	x	-	x	-	-	Scp	>455	339830
BA9183	x	x	-	r	x	-	x	-	-	-	-	-	-	-	-	Bar, Dan, Gl, Moly	570	360874
BA9188	x	x	x	-	r	r	Fe	-	x	x	x	-	x	-	x	Zc	>515	734874
BA9189	x	x	x	r	r	r	x	-	-	x	x	-	x	-	x	-	575	786870
BA9195	x	2	-	-	r	r	x	-	-	-	x	-	x	-	x	Cpy	>470	908963
BA9197	x	-	x	-	r	-	x	-	-	-	-	x	x	-	-	Cpy	>600	004964
BA9198	x	x	x	-	-	x	-	x	-	-	-	x	x	-	x	Chl, Zc	<250	977896
CH91107	x	x	x	-	r	x	x	-	-	x	x	x	x	-	x	Zc	560	773718
CH91113	x	-	x	-	x	x	-	-	x	-	x	-	x	-	x	Zc	>500	737769
KA91115	x	2	-	x	x	x	-	x	-	-	-	-	-	-	Cl	410	201298	
CH91116	x	2	x	-	x	x	-	x	x	-	x	-	x	-	x	Mt	545	634748
KA91116	x	-	x	-	-	-	-	x	x	x	x	-	x	-	x	Chl	>250	233324
KA91118	x	x	x	x	x	x	-	-	-	-	-	-	-	-	-	-	600	278344
BB91121	x	-	x	-	-	-	-	x	-	x	x	x	-	-	x	Zc	>285	826542
GH91123	x	-	x	-	-	-	x	-	x	-	x	x	x	-	x	Cpy, Zc	>240	289637
GH91134	x	-	x	-	x	x	-	-	x	-	x	x	x	-	x	-	>285	332662
KA91135	x	-	-	-	x	x	-	-	x	-	-	-	x	-	x	-	>335	212362
KA91138	x	x	-	-	x	-	-	-	-	-	-	-	x	-	-	Fl, Mt	550	315395
BB91148	x	-	x	-	-	-	-	-	-	x	-	x	x	-	x	-	>510	709384
BB91156	x	2	x	x	-	x	-	-	-	x	x	-	x	-	x	Chl	520	671582

See Table 3 for abbreviations

In addition, Cele = celestite, Cls = celsian, Dan = danburite, Di = Diopside, Fl = fluorite, Gl = galena, Gr = graphite, Hb = hornblende, Hyal = hyalophane, Moly = molybdenite, Oliv = olivine, Phl = phlogopite, Serp = serpentinite, Tc = talc, Thor = thortite, Tr = tremolite, 2 = two generations of phase present, Fe = iron rich form of phase present, Cl = chlorine rich form of phase present

\* = Calibration from Anovitz and Essence (1987)

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