

Garnet-biotite-cordierite thermometry and barometry in the Cashel thermal aureole, Connemara, Ireland

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ABSTRACT. A number of geothermometers and geobarometers involving coexisting garnet, biotite, and cordierite have been used to calculate the pressures and temperatures of metamorphism of the Cashel thermal aureole in Connemara. Temperatures from the garnet-biotite thermometer show a wide variation between calibrations, and are markedly different from those obtained from the garnet-cordierite thermometer. These variations, together with the possibility of extensive re-equilibration between garnet and cordierite rims and biotite, indicate that the use of exchange reaction thermometry, for these rocks at least, may be invalid. The various calibrations of the garnet-cordierite-sillimanite-quartz geobarometer give reasonably consistent pressure estimates which, after allowance for partial pressures of water, indicate pressures of metamorphism of about 5 ± 1 kb.

In the pelitic hornfelses that surround the Cashel-Lough Wheelaun ultrabasic intrusion of Central Connemara (Leake and Skirrow, 1960; Leake, 1969) cordierite and garnet frequently occur together, often in equilibrium with biotite or sillimanite or both. The pressure dependence of garnet and cordierite compositions in the assemblage garnet-cordierite-sillimanite-quartz, and the temperature dependence of Fe-Mg partitioning between garnet, biotite, and cordierite enable these rocks to be used to calculate the pressure-temperature conditions of the thermal event. The intrusion of the ultrabasic magma was synchronous with the D2 stage of the regional deformation (Leake, 1969), and consequently pressures derived from the Cashel aureole rocks are relevant to studies of the regional metamorphism which has been overprinted by the thermal effects of the intrusion.

Four rocks, 1502, 1502A, 1698, and 1698A, collected by B. E. Leake, have been used in the present study. Their locations are listed in Leake and Skirrow (1960). Samples 1502 and 1502A are from an enclave of metasedimentary rocks within the ultrabasic intrusion, while samples 1698 and

1698A come from within 10 m of the contact. In all four samples, cordierite, garnet, biotite, and sillimanite coexist with magnetite together with varying amounts of quartz and plagioclase feldspar. Most samples contain between 20 and 30% quartz and feldspar. Cordierite is by far the dominant ferromagnesian phase, constituting in all cases over 50% of the rock and up to 70% of the total ferromagnesian phase content. Apart from sample 1698, in which biotite forms 25% of the total ferromagnesian content, the rocks generally contain little more biotite than 5 to 10% of the total ferromagnesian content. In all samples cordierite is generally between 1 and 2 mm in diameter, though individual grains may reach 4 or 5 mm diameter. Garnet normally occurs as isolated grains often 4 mm and rarely up to 8 mm in diameter. The cordierites in sample 1698A have been extensively altered and pinitized. Microprobe analyses of the coexisting phases have been carried out on the energy-dispersive microprobe designed and housed in the Department of Earth Sciences, University of Cambridge, using an 80 sec. counting time, accelerating voltage of 20 kV, specimen current of 50 nA and take-off angle of 40 deg. All phases are homogeneous although within a few microns of the rim X_{Mg}^{garn} decreases sharply while X_{Mg}^{cord} shows a significant increase. Mineral analyses are listed in Tables I-III, and compositions plotted on an AFM diagram in fig. 1.

Partitioning of Fe and Mg between the phases garnet, biotite, and cordierite is temperature dependent and has been calibrated to produce three two-phase exchange reaction thermometers with low ΔV_r , high ΔS_r , and a steep (sub-vertical) slope in P - T space. Thompson (1976) and Holdaway and Lee (1977) have both produced empirical calibrations of the garnet-biotite and garnet-cordierite thermometers, while Ferry and Spear (1978) have published an experimentally determined calibration of the former thermometer.

TABLE I. Representative garnet analyses

	1502	1503	1502	1502	1502	1502B	1502B	1502B
SiO ₂	38.44	38.13	37.69	38.70	38.48	39.21	39.08	39.26
Al ₂ O ₃	22.10	22.16	21.77	21.98	22.33	21.67	22.11	21.97
FeO	33.84	33.07	32.12	32.22	32.24	32.75	32.99	32.82
MgO	4.72	4.73	5.76	55.53	5.27	4.97	4.65	5.23
MnO	1.04	1.06	0.88	1.00	0.92	1.01	1.03	1.06
CaO	1.06	1.31	1.40	1.55	1.53	1.40	1.38	1.45
Total	101.20	100.46	99.62	101.04	100.42	100.94	100.93	101.75
Si	3.00	2.99	3.02	3.01	3.01	3.00	3.06	3.01
Al	2.03	2.05	1.89	2.02	2.03	2.05	1.99	2.01
Fe	2.21	2.17	2.19	2.10	2.11	2.13	2.15	2.12
Mg	0.55	0.55	0.56	0.64	0.62	0.58	0.54	0.60
Mn	0.07	0.07	0.06	0.07	0.06	0.07	0.07	0.07
Ca	0.09	0.11	0.12	0.13	0.13	0.12	0.12	0.12
Mg/(Mg+Fe)	0.20	0.20	0.24	0.23	0.23	0.21	0.20	0.22

	1698A	1698A	1698A	1698	1698	1698	1698	1698
SiO ₂	38.03	37.49	37.49	37.78	37.88	37.86	37.86	37.63
Al ₂ O ₃	22.50	22.62	22.68	22.10	21.71	21.85	22.04	21.68
FeO	34.23	32.54	33.96	33.82	33.53	34.17	32.84	32.99
MgO	4.19	4.39	4.61	4.53	4.29	4.34	4.98	5.00
MnO	1.94	1.98	2.03	1.71	1.81	1.86	1.80	1.76
CaO	1.19	1.11	1.16	1.14	1.14	1.03	1.12	1.34
Total	100.89	102.03	101.93	101.08	100.26	101.11	100.64	100.58
Si	2.97	2.94	2.94	2.98	3.01	2.99	2.98	2.98
Al	2.07	2.09	2.09	2.05	2.03	2.03	2.05	2.03
Fe	2.23	2.26	2.22	2.23	2.23	2.26	2.16	2.20
Mg	0.49	0.51	0.54	0.53	0.50	0.51	0.59	0.56
Mn	0.13	0.13	0.14	0.11	0.12	0.13	0.12	0.12
Ca	0.10	0.09	0.10	0.10	0.10	0.09	0.10	0.10
Mg/(Mg+Fe)	0.18	0.19	0.20	0.19	0.18	0.18	0.21	0.20

Analyses are calculated to 12 oxygen atoms.

TABLE II. Representative cordierite analyses

	1502	1502	1502	1502	1502	1502B	1502B	1502B
SiO ₂	48.88	49.17	49.27	48.97	49.27	48.86	48.56	49.20
Al ₂ O ₃	33.03	33.04	33.55	33.03	33.19	33.33	33.64	33.04
FeO	7.89	8.23	8.53	8.24	8.35	8.08	8.27	8.45
MgO	8.30	8.94	8.26	8.11	8.10	8.37	8.52	8.35
Total	98.10	99.38	99.61	98.35	98.91	98.64	98.99	99.04
Si	5.02	5.00	5.00	5.03	5.03	5.00	4.96	5.02
Al	4.00	3.96	4.02	3.99	4.00	4.00	4.05	3.98
Fe	0.68	0.70	0.72	0.71	0.71	0.69	0.71	0.72
Mg	1.27	1.36	1.25	1.24	1.23	1.28	1.30	1.27
Mg/(Mg+Fe)	0.65	0.66	0.63	0.64	0.63	0.65	0.65	0.64

	1698A	1698A	1698A	1698	1698	1698	1698	1698
SiO ₂	49.77	46.13	48.13	48.41	48.04	47.77	48.66	47.43
Al ₂ O ₃	34.11	32.59	33.23	33.47	33.29	33.89	33.42	32.98
FeO	9.55	11.45	8.26	8.17	8.66	8.52	8.68	8.70
MgO	6.66	6.74	7.80	7.86	7.95	7.76	7.56	7.58
MnO	0.00	0.00	0.14	0.17	0.10	0.13	0.14	0.14
Total	100.09	96.91	97.66	98.08	98.04	98.07	98.46	96.83
Si	5.04	4.89	4.98	4.99	4.97	4.93	5.00	4.97
Al	4.07	4.08	4.06	4.07	4.06	4.13	4.05	4.07
Fe	0.81	1.02	0.72	0.70	0.75	0.74	0.75	0.76
Mg	1.00	1.07	1.22	1.21	1.22	1.19	1.16	1.18
Mn	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Mg/(Mg+Fe)	0.55	0.51	0.63	0.63	0.62	0.62	0.61	0.61

Analyses are calculated to 18 oxygen atoms.

TABLE III. Representative biotite analyses

	1502	1502	1502B	1502B	1502B	1502B	1698A	1698	1698	1698
SiO ₂	36.03	36.68	35.51	35.12	34.93	33.44	35.18	34.37	34.47	
Al ₂ O ₃	17.70	18.63	18.39	18.00	18.70	20.62	18.75	17.92	18.31	
FeO	1.58	3.03	3.49	3.65	3.38	2.27	4.35	4.52	4.53	
MgO	20.40	20.11	21.25	21.59	21.86	22.64	20.26	21.05	20.72	
MnO	10.69	8.62	6.05	8.01	8.10	8.18	8.31	8.45	7.87	
K ₂ O	8.78	8.59	8.61	8.61	7.98	6.68	9.15	9.02	9.11	
Total	95.13	95.86	95.30	95.18	94.95	95.83	96.60	95.33	95.03	
Si	2.75	2.76	2.71	2.70	2.68	2.56	2.66	2.64	2.65	
Al	1.59	1.65	1.66	1.63	1.69	1.87	1.68	1.62	1.66	
Ti	0.09	0.17	0.20	0.21	0.20	0.13	0.25	0.26	0.26	
Fe	1.30	1.27	1.36	1.38	1.40	1.45	1.28	1.35	1.33	
Mg	1.21	0.99	0.92	0.92	0.93	0.94	0.94	0.97	0.90	
X	0.85	0.82	0.84	0.87	0.78	0.85	0.88	0.89	0.90	
Mg/(Mg+Fe)	0.48	0.44	0.40	0.40	0.40	0.39	0.42	0.42	0.40	

Analyses are calculated to 11 oxygen atoms

not been calculated for 1698A from the cordierite-garnet thermometer due to the altered nature of the cordierite in that sample. Temperatures obtained from calibration 1c, which is the only experimental calibration among the five, are higher than those obtained from the other calibrations. This calibration (Ferry and Spear 1978) has a markedly different slope ($\ln K$ v. T) from the other calibrations of the biotite-garnet thermometer. At low values of $\ln K$, corresponding to high values of T , the defined value of T changes increasingly rapidly and the accurate definition of the slope becomes increasingly more important. Thompson's calibration (1976) of this thermometer is heavily weighted at the low-temperature end and extrapolated by best fit techniques to higher temperature regions where any errors at the low-temperature end will become grossly magnified. This is even more likely to happen with his calibration of the garnet-cordierite thermometer (1976, p. 249) where the broad scatter on the calibration diagram probably invalidates his best-fit line. Realistic errors on Thompson's calibrations of both thermometers must be in the region of $\pm 50^\circ$ at 500°C increasing

to $\pm 100^\circ$ at 1000°C . Indeed Bohlen and Essene (1980) commented that cation-exchange thermometers are too inconsistent, imprecise, and inaccurate to be used for quantitative thermometry. Bearing in mind the probable large errors at higher temperatures on Thompson's (1976) and Holdaway and Lee's (1977) empirical calibrations and that Ferry and Spear's (1978) calibration is the only experimentally determined one, it may be intimated that realistic temperatures derived for the present rocks will be in the region of $850^\circ \pm 100^\circ\text{C}$.

A further complication to direct thermometry is raised by the possibility of continued re-equilibration during cooling either by continued exchange reaction or by diffusion. The sharp increase in $X_{\text{Fe}}^{\text{Gar}}$ adjacent to the rim indicates that some such readjustment may well have occurred. In view of the large size of the garnet and cordierite grains it is likely that any such re-equilibration will have been limited to the near-rim areas with the interior of the grains remaining constant and unaffected by diffusion. The re-equilibration of garnet and cordierite rims should have had a very marked effect on the composition of the smaller

TABLE IV. *Calculated pressures and temperatures*

Calibration		Sample			
		1502	1502B	1698A	1698
(a)	1a	724-882	850-908	814-871	766-879
	1b	688-819	793-840	763-710	723-816
	1c	750-988	938-1028	882-971	810-982
	2a	679-813	693-751		679-778
	2b	659-770	671-720		659-742
(b)	700°C				
	3a	5322-5782	5473-5645		5243-5517
	3b	5886-6529	6098-6339		5776-6160
	3c	5664-6111	5812-5979		5588-5854
(c)	1000°C				
	3a	4756-5358	5954-5180		4653-5012
	3b	5348-6190	5626-5941		5204-5706
	3c	5298-5882	5490-5709		5198-5545
(d)	3d	5336-5929	5532-5753		5235-5588
	K_1	3.69-2.49	2.67-2.36	2.91-2.55	3.29-2.51
	K_2	7.76-5.39	7.43-6.30		7.76-5.88
	K_3	2.24-1.92	2.14-2.02		2.05-1.87

(a) Temperature ranges for each rock from the garnet-biotite (1a-1c) and garnet-cordierite (2a-2b) thermometers ($^\circ\text{C}$).

(b) Pressure ranges calculated for each rock from the four calibrations (3a to 3d) of the garnet-cordierite-sillimanite-quartz barometer with T at 700°C (bars).

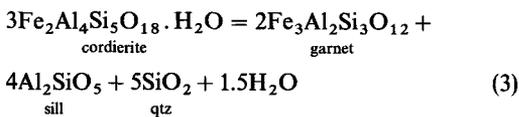
(c) As (b) but with T set to 1000°C (bars).

(d) Range of values of K_1 , K_2 , and K_3 used in the calculations.

biotite crystals especially in those rocks which contain very little biotite. The similarity, though, of K_1 and K_2 (Table IV, (d)) between those rocks with high (25%) and low (5%) biotite contents may be considered to be remarkable and could indicate that biotite was not affected by re-equilibration. However, continuing down temperature reaction between garnet and biotite should result in an increase in X_{Mg}^{bite} while similar continuing reaction between biotite and cordierite should have the opposite effect and it is possible that if the latter were continued after the former ceased the result would be fortuitous values of K_1 which would indicate apparently sensible temperatures of reaction. As such it appears that temperatures from the garnet-biotite thermometer in this instance could be somewhat misleading.

In the likely event that the interiors of the garnet and cordierite crystals remained constant during cooling the calibrations of the garnet-cordierite thermometers, if reliable, should provide sensible temperatures. The indicated range of $660-810^\circ \pm 75^\circ C$ is not, however, very useful. From considerations of the regional metamorphism the lower values which come from calibration 2b appear to be excessively low, while the upper values from calibration 2a have already been questioned on account of the scatter on Thompson's (1976) calibration diagram. It would appear that thermometry in the present rocks may not be very revealing, and that the results should be treated with a great deal of circumspection.

The homogeneous cores of the garnet and cordierite crystals are likely to lend themselves to a sensible attempt at barometry. Pressures may be derived from the calibration of the reaction:



$$P = \frac{27808 - (15.103 - 6R \ln K_3)T}{3.886} \pm 500 \text{ bars} \quad (3a)$$

(Thompson, 1976)

$$P = 7631 + (4.2877 \ln K_3 - 4.59)T \pm 500 \text{ bars} \quad (3b)$$

(Holdaway and Lee, 1977)

$$P = \frac{1 + 13818 - (6.38 - 6 \ln K_3)T}{2.01609} \pm 400 \text{ bars} \quad (3c)$$

(Wells and Richardson, 1980)

$$\text{where } K_3 = \frac{X_{Fe}^{Gar}}{X_{Fe}^{Cord}}$$

3a is an empirical calibration, 3b is experimentally calibrated, and 3c was derived from a consideration of the experimental data of Richardson (1968), Weisbrod (1973), and Holdaway and Lee (1977).

Pressures have been calculated for three rocks from all calibrations using the maximum range of K_3 at temperatures of 700° and $1000^\circ C$. These temperatures were chosen as they should span the probable range of interest. In view of the low levels of Mn and Ca in the garnet, ideal mixing between Fe and Mg has been assumed for this phase as well as for cordierite. Rock 1698A has been ignored due to the extensive alteration of the cordierite. Pressures calculated at $1000^\circ C$ are about 300 to 500 bars lower than those calculated at $700^\circ C$, the total range of pressures being about 5.5 ± 1 kb. This error bar should account for errors in both calibration and probe analyses, the latter being more than accounted for by the range of K_3 used. It is noticeable that the lowest pressures derived are from calibration 3a, the only empirical calibration of the three used. Pressures are listed in Table IV and the range plotted on a bar diagram in figs. 2b and 2c.

These pressure calibrations all assume the presence of H_2O within the cordierite lattice. The effect of varying amounts of water within the cordierite lattice has been examined by Newton and Wood (1979) who showed that decreasing water content will result in a lower equilibrium pressure at a specific temperature for a set value of K_3 . Newton and Wood derived an equation to account for the effect of water content on the calculated equilibrium pressure. On the theoretical basis they outlined an equation which has been derived to calculate equilibrium pressures:

$$P = 5933 + (3.018 \ln K_3 - 3.415 - 0.604 \ln(1 - X)^3)T \quad (3d)$$

The term $5933 + (3.018 \ln K_3 - 3.415)T$ is the calculated position of the anhydrous analogue of reaction 3 and is consistent with both the experimental data of Holdaway and Lee (1977) and Richardson (1968) and the hydration theory of Newton and Wood (1979). The correction term $(-0.604 \ln(1 - X)^3)T$ accounts for the hydration state of cordierite, where X is defined by Newton and Wood (1979) as a function of the water content of cordierite. In this instance the water content of cordierite has been taken to be 1.8% or equivalent to $\frac{1}{2}$ mol H_2O in the formula unit. This value is consistent with the graphical plot of the P - T dependence of water in cordierite (Newton and Wood, 1979) as well as with the microprobe analyses. It is slightly higher than the water content of an Fe-rich cordierite analysed from similar rocks by Evans and Leake (1970). In direct contrast to those derived from the other barometric calibrations the resultant pressures are not temperature dependent and fall within the 5.5 ± 1 kb bracket established earlier (Table IV, Fig. 2).

All these pressure estimates have assumed $P_{\text{tot}} = P_{\text{H}_2\text{O}}$. In the present rocks which from the degree of desilication, fall well within the field of partial melting, it is likely that $P_{\text{H}_2\text{O}}$ is considerably less than P_{tot} . In the absence of another hydrous reaction which may be used in conjunction with reaction 3 to generate an intersection point in $P_{\text{H}_2\text{O}}-T$ space, more oblique methods must be used to approximate P_{tot} for the state $P_{\text{H}_2\text{O}} < P_{\text{tot}}$. An equation modified from Holdaway and Lee (1977) may be derived relating $X_{\text{H}_2\text{O}}$ to P_{tot} such that:

$$2.7805P_i = (4.0061 - 1.2256X_{\text{H}_2\text{O}})P_f \quad (4)$$

where P_i is the pressure already calculated and P_f is a corrected pressure for a condition where $X_{\text{H}_2\text{O}} \leq 1$. Table V has been constructed from equation 4. Setting $X_{\text{H}_2\text{O}} = 0$ gives the minimum anhydrous pressure (P_f) that may be related to the initial calculated hydrous pressure (P_i).

TABLE V. Values of P_f for net values of P_i and $X_{\text{H}_2\text{O}}$.

$X_{\text{H}_2\text{O}}$	P_i				
	6500	6000	5500	5000	4500
0.9	6226	5747	5268	4789	4310
0.7	5741	5299	4857	4416	3974
0.5	5326	4916	4506	4097	3687
0	4511	4164	3817	3470	3123

Calculated from equation 4 derived from Holdaway and Lee (1977).

A similar type of correction may be derived from the theory of Newton and Wood (1979):

$$P_i = P_f + \frac{1.2RT}{\Delta V_r} \ln \frac{(1 - X_f)^3}{(1 - X_i)^3} \quad (5)$$

where X_i and X_f are values of X , the water content of cordierite as defined by Newton and Wood (1979), at pressures P_i and P_f respectively. For the values of K_3 measured here the minimum value of P_f assuming fully anhydrous cordierite is about 1 kb less than P_i . This correction is considerably less than that derived from equation 4 for $X_{\text{H}_2\text{O}} = 0$. For a more realistic condition of $P_{\text{H}_2\text{O}} = 0.5 P_{\text{tot}}$ the value of P_f derived from equation 5 at values at T between 700 and 1000 °C will be no more than 300 to 500 bars less than P_i , which correction again is considerably less than that which would be indicated by application of equation 4.

We may conclude from this that after applying a realistic, though by necessity approximate, correction for the partial pressure of water in equilibrium with the hornfels, a realistic equilibrium pressure for the thermal event in the Cashel aureole is in the region of 5 ± 1 kb.

Discussion

In the vicinity of the Cashel ultrabasic bodies the thermal effects of the intrusions completely overprint the regional metamorphism, with the early stages of which the intrusions are concurrent. The resulting set of mineral assemblages are unique in the area. Large homogeneous crystals of garnet and cordierite have grown, in association with biotite and sillimanite, in rocks which have undergone considerable desilication. There can be little doubt that these assemblages are representative of conditions very near to the thermal maximum. Northwards as the effects of the thermal overprint decrease the cordierite disappears and the garnet becomes increasingly smaller and more typical of the common Connemara garnets which are richer in Mn (Yardley *et al.*, 1980). Two miles to the north of the intrusions the regional metamorphic rocks contain garnets richer in Mn and much metasedimentary migmatite derived by partial melting. Temperatures in this area must be fairly close to 700 °C (Treloar, in prep.). Those near to the intrusion must be appreciably higher than this and the Temperatures derived from the two-phase exchange reaction thermometers used above must be viewed in this context. The empirical calibrations of the cordierite-garnet thermometer appear increasingly dubious in this respect, not only on the grounds of the calibration scatter but also of relative magnitude. The application of the garnet-biotite thermometer is also fraught with hazards not only in the variation exhibited between the empirically and experimentally derived calibrations, but also in the possible degree of biotite re-equilibration.

The associated effects of varying partial pressures of water and water content of cordierite tend to compromise pressures derived from the garnet-cordierite-sillimanite-quartz barometer. For the Cashel rocks the (unlikely) assumption of $P_{\text{H}_2\text{O}} = P_{\text{tot}}$ gives a calculated pressure in the range of 5.5 ± 1 kb. In the conditions more likely to have obtained in the aureole rocks ($P_{\text{H}_2\text{O}} \approx 0.5 P_{\text{tot}}$) calculated pressures will be in the region of 5 ± 1 kb. In the likely event that the interiors of the large garnet and cordierite grains were not seriously affected by diffusion during cooling (i.e. the grains grew as large homogeneous crystals and retained their compositions) values of $\ln K_3$ are likely to be representative of the thermal maximum with the

result that the derived pressures may be treated with a fair degree of confidence.

This pressure still raises a problem concerning the presence of andalusite. Evans and Leake (1970) described this phase on textural criteria as being associated with the thermal maxima. It is possible, however, that in fact the andalusite is considerably later than this and is associated with growth at lower pressures and temperatures during post-D3 uplift.

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