RELATIONSHIP BETWEEN ROCK TYPE, METAMORPHIC GRADE, AND FLUID-PHASE COMPOSITION IN THE GRENVILLE SUPERGROUP, LIMERICK TOWNSHIP, ONTARIO

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ABSTRACT

The study area in Limerick Township in the southern Grenville Province consists of a sequence of late Proterozoic metabasalts, noncalcareous and calcareous quartzofeldspathic granofels, and marbles intruded by two gabbro complexes. During the Grenville Orogeny, metamorphism of marble produced assemblages that are below the titanite, actinolite – calcite, and hornblende – K-feldspar isograds, but above the hornblende – K-feldspar isograd in the quartzofeldspathic units and amphibolites. Calcite–dolomite and two-feldspar geothermometry, and calculation of the displacement of intersecting equilibria due to solid-solution, bracket equilibrium temperatures between 535 and 550°C in the marbles and between 402 and 543°C or higher in rocks with low carbonate contents. $X(CO_2)$ is estimated between 0.45 and 0.55 in the marbles and less than 0.10 in the carbonate-poor units. The relationship between metamorphic grade and rock type is due to a decrease in $X(CO_2)$ from the marble to the less calcareous units. This relationship may be due to: 1) internal buffering of the fluid by the isogradic reactions to high $X(CO_2)$ values in the marbles and low $X(CO_2)$ values in the carbonate-poor units, or 2) buffering of the fluids at low $X(CO_2)$ by the isogradic reactions during infiltration of H_2O-rich fluids through the carbonate-deficient and carbonate-absent rocks.

Keywords: isograds, marble, granofels, intersecting equilibria, metamorphic grade, pore-fluid composition, Grenville, Limerick Township, Ontario.

SOMMAIRE

Dans le canton de Limerick (Ontario), dans la partie sud de la province du Grenville, une séquence d'âge Protérozoïque tardif de métabasaltes, granofels quartzofeldspathiques avec calcaires ou non, et marbres est recoupée par deux complexes gabbroïques. Pendant l'orogenèse grenvillienne, le métamorphisme des marbres a donné des assemblages qui se trouvent au dessous des isogrades titanite, actinote – calcite, et hornblende – feldspath potassique, mais au dessus de ce dernier isograde dans les unités quartzofeldspathiques et les amphibolites. La géothermométrie, utilisant les équilibres impliquant calcite et dolomite et les deux feldspaths, ainsi que le calcul des déplacements des intersections des réactions dus aux solutions solides présentes, indiquent des températures d'équilibre entre 535 et 550°C dans les marbres et 402 et 543°C ou plus dans les lithologies pauvres en carbonate. La valeur de $X(CO_2)$ serait entre 0.45 et 0.55 dans les marbres et moins de 0.10 dans les milieux pauvres en calcaire. La relation entre degré de métamorphisme et lithologie reflète la diminution du $X(CO_2)$ du marbre vers les unités moins riches en calcaire. Cette relation pourrait être attribuée 1) à un tamponnage interne de la phase fluide par les réactions isogradiques à des valeurs élevées de $X(CO_2)$ dans les marbres et des valeurs inférieures dans les unités pauvres en carbonate, ou 2) à un tamponnage des fluides à des valeurs faibles de $X(CO_2)$ par les réactions isogradiques suite à l'infiltration de fluides aqueux au travers des unités pauvres ou sans carbonate.

Mots-clés: isogrades, marbre, granofels, intersection d'équilibres, degré de métamorphisme, composition de la phase aqueuse interstitielle, Grenville, canton de Limerick, Ontario.

INTRODUCTION

Experimental investigations (*e.g.,* Skippen 1971, 1974, Slaughter *et al.* 1975) and theoretical studies (*e.g.,* Greenwood 1962, 1967, 1975) of mixed-volatile equilibria have made possible the interpretation of metamorphosed, interlayered calcareous, pelitic and quartzofeldspathic sedimentary rocks. The temperature of mixed-volatile equilibria is dependent not only on pressure but on fluid composition, especially the ratio of H_2O to CO_2, or $X(CO_2)$. "High-grade" areas defined by mixed-volatile isograds, therefore, do not necessarily indicate regions of high temperature, unlike dehydration reactions in nongraphitic pelitic rocks. Mixed-volatile isograds may, and often do, reflect variations in $X(CO_2)$.

Carmichael (1970) found that isograds based on mixed-volatile reactions intersect one another in Lake Township in the southern Grenville Province, Ontario. This was interpreted to be the result of migration of H_2O from the Whetstone granite into the wallrocks. Moore & Kerrick (1976) described a similar situation in the Alta aureole in Utah.

Locally, in southeastern Maine, interbedded pelites, micaceous quartzites and calcareous rocks strike parallel to the direction of the thermal gra-
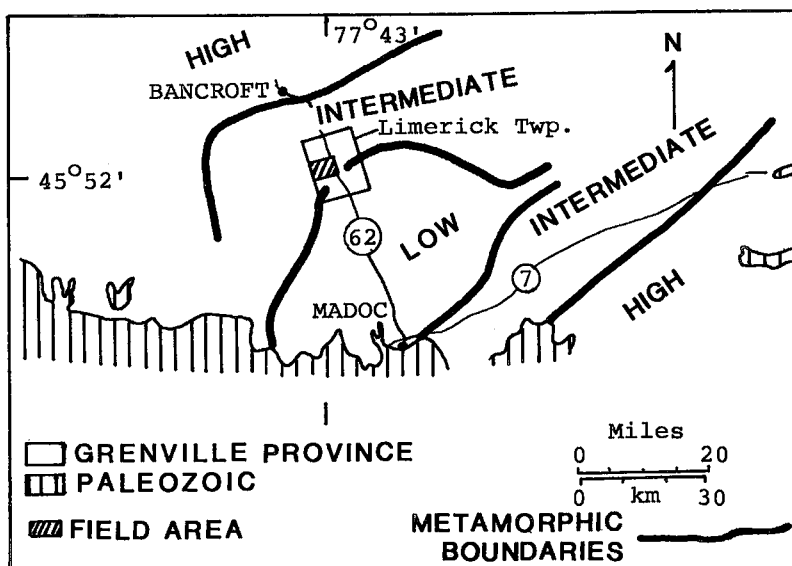
FIG. 1. The field area is located in Limerick Township, southern Ontario, 100 km northeast of Toronto (after Lumbers 1964). The field area of Allen (1976) is located in Tudor Township, immediately south of Limerick Township, and that of Carmichael (1970) in Lake Township, immediately southwest of Limerick Township.

dient. Calc-silicate isograds are extremely irregular and form local, high-grade areas related to centres of intrusion, and exhibit local cross-cutting relationships. Ferry (1976, 1980) interpreted these patterns as the result of a high flux of heat related to the plutons, introduction of H_2O from the intrusive bodies, dehydration of the pelitic rocks, and internal control of the fugacities of H_2O and CO_2 by the mineral assemblages.

In Grenville marble and calcareous metasedimentary rocks in Tudor Township, southern Ontario (Fig. 1), Allen (1976) observed an increase in metamorphic grade toward a series of metamorphosed tonalite, trondhjemite, granodiorite, and gabbro intrusive bodies. This was attributed to a decrease in $X(CO_2)$ of the intergranular gas-phase toward the igneous contact, *i.e.*, the relic of a pre-Grenville, contact-metamorphic aureole.

GENERAL GEOLOGY

A sequence of Grenville amphibolites and quartzofeldspathic and calcareous rocks surrounds the Thanet and Jocko Lake gabbro complexes (Lumbers 1967, 1969, LeAnderson 1978a, b) approximately 22 km south of Bancroft, Ontario, in Limerick Township (Figs. 1, 2). The areas studied by Carmichael (1970) and Allen (1976) lie to the southwest and south, respectively (Fig. 1).

The most commonly observed sequence of rock units is amphibolite, rusty (sulfidic) quartzofeldspathic schist, quartzofeldspathic granofels, calcar-

eous quartzofeldspathic granofels, and marble (Fig. 2). The Brinklow Lake and Ormsby Junction amphibolite belts consist predominantly of massive amphibolites of assumed volcanic origin. Volumetrically minor, calcareous, locally schistose amphibolite may have formed through the reworking of volcanic rocks and introduction of clastic material. The calcareous horizons are in greatest abundance in the Ormsby Junction amphibolite belt. An age of 1310 Ma was obtained by Silver & Lumbers (1966) on zircon from the mafic Tudor metavolcanic rocks south of the study area. The similarity of the Tudor volcanic rocks and associated rock units to those in Limerick Township gives an approximate age of the rocks in the study area.

Rusty schists surround the amphibolite belts and occur as discontinuous lenses in them and in the other units. Small, exhalative massive-sulfide deposits containing pyrite, pyrrhotite, sphalerite and chalcopyrite occur in the rusty schists adjacent to the amphibolites. Their composition, clastic host-rocks, and association with mafic volcanic rocks suggest that they are Besshi-type deposits (Franklin *et al.* 1981). Furthermore, it is likely that the volcanic rocks were the heat source for the deposits. This indicates that the amphibolites are the oldest unit in the field area.

The quartzofeldspathic granofels is generally arkosic in composition and is assumed to represent clastic sediments. Calcereous quartzofeldspathic granofels contains similar assemblages in addition to up to 10% calcite and dolomite. Lenses and layers of each rock type are found in the others.
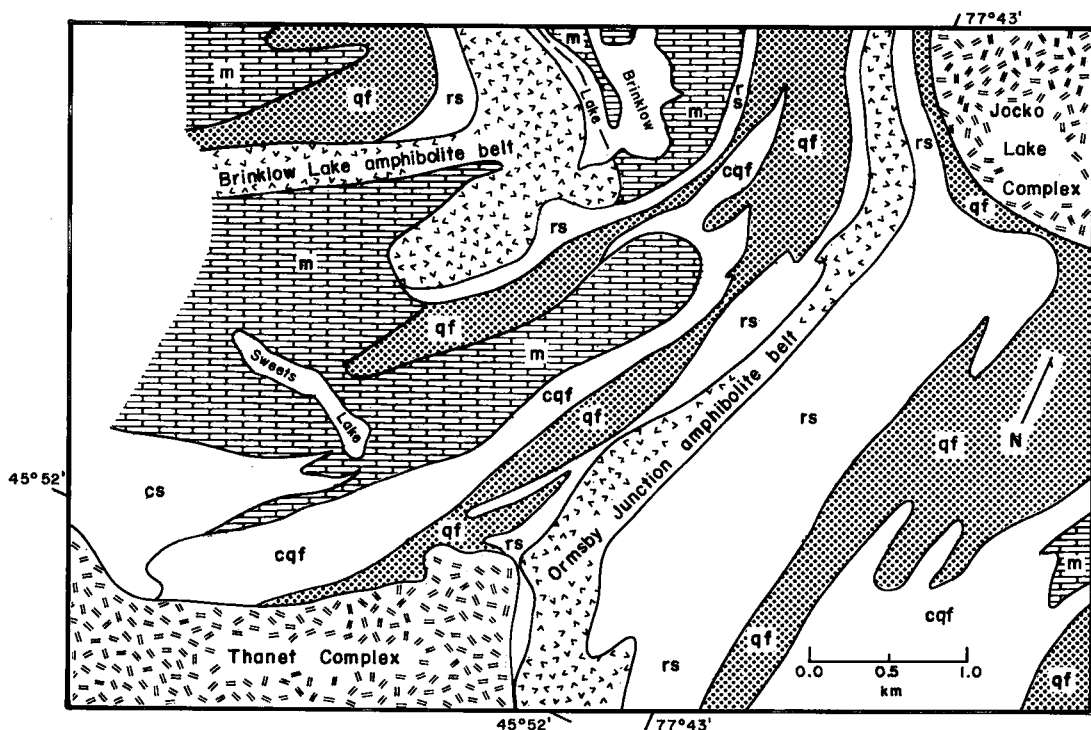
FIG. 2. Generalized geological map of the study area (after LeAnderson 1978a). Symbols: rs rusty schists, qf quartzofeldspathic granofels, cqf calcareous quartzofeldspathic granofels, m marble, cs calcsilicate.

Marble makes up the youngest of the sedimentary units and is present in four areas (Fig. 2). The mineralogy, color and texture are a function of metamorphic grade. Below the actinolite–calcite isograd the marble is grey and commonly contains chlorite, biotite, calcite, dolomite, quartz, plagioclase, titanite, pyrrhotite, sphalerite, rutile, graphite and, locally, epidote, ilmenite and pyrite. Calcic amphibole, ranging from colorless tremolite to dark green actinolite, appears at the actinolite–calcite isograd. Above this isograd the marbles are mostly very fine grained and grey-green. Hornblende, epidote, microcline and diopside appear with increasing grade at the expense of chlorite, dolomite and biotite (mineral compositions are given in LeAnderson 1978a). Layers and lenses of sulfidic schist, quartzofeldspathic and calcareous quartzofeldspathic granofels are ubiquitous. A calc-silicate horizon, intermediate in composition between the calcareous quartzofeldspathic granofels and marble, is located in the southwestern part of the area (Fig. 2).

The northeastern corner of the 1200 Ma (Berger & York 1981) Thanet gabbro complex is exposed in the map area (Fig. 2). Based on gradational internal contacts and intrusions of hybrid magma, Lumbers (1967) suggested that the majority of the intrusive units were emplaced over a short period of time. The Jocko Lake complex (Fig. 2) consists of metapyrox-

enite and hornblende metagabbro (Lumbers 1967); its age is unknown but assumed to be approximately that of the Thanet complex. A premetamorphic date for the Thanet complex (Berger & York 1981) and metamorphic textures in both indicate that the complexes were emplaced prior to the Grenville metamorphic event.

Numerous granitic pegmatites occur in the Ormsby Junction Amphibolite Belt immediately northeast of Highway 62. No other intrusions occurred.

During the Grenville orogeny, the Grenville Supergroup was buried, deformed, and metamorphosed. The metamorphic grade is in the upper greenschist facies near Madoc (Fig. 1) and increases to upper amphibolite facies to the west, north and east. Paleozoic rocks are exposed to the south. Temperatures calculated using the calcite–dolomite geothermometer for rocks in Tudor Township, south of the study area, range from 400 to 550°C (Allen 1976), and from 475 to 630°C to the north, in the Bancroft area (Sobol & Essene 1973).

An estimation of load pressure at the time of metamorphism is made from the distribution of the aluminum silicate minerals and the Al_2SiO_5 phase diagram of Holdaway (1971). Aluminum silicate minerals were not observed in the study area, but andalusite is found approximately 10 km to the north-northeast (Lumbers 1967). Andalusite is also

found 16 km to the southwest in central Lake Township, 8 km east of the kyanite–sillimanite isograd (D.M. Carmichael, pers. comm., 1973). Pressure in central Lake Township was probably close to that of the aluminum silicate triple point. In the absence of more definitive data, it is assumed that the pressure of the study area was less than, but perhaps close to, that defined by the triple point.

The pressure of the triple point determined by Holdaway (1971) is 3.76 ± 0.3 kbar at a temperature of 501 ± 20°C. Calorimetric work (Anderson *et al.* 1977) and a thermodynamic analysis of the aluminum silicate system (Day & Kumin 1980) support Holdaway's data, as does the assemblage epidote–sillimanite found in the Reading Prong, N.Y., area by Murray (1976). The pressure in the map area, therefore, is assumed not to have exceeded 4 kbar, the figure used in the calculations.

ANALYTICAL TECHNIQUES

Mineral analyses were obtained at Queen's University using an ARL–EMX electron microprobe equipped with an energy-dispersion system and a PDP-11 computer. The system was operated at an accelerating voltage of 15 kV and an emission current of 100 μA. Raw data were reduced using the Multiple Least Squares computer program (written by Northern Scientific for the PDP-11 computer) with the methods and constants of Bence & Albee (1968).

Oxide totals of 98–102% were considered acceptable for analyses of anhydrous minerals. Acceptable totals for the hydrous minerals were determined by subtracting the average water content using data listed by Deer *et al.* (1962a, b, 1963). The reproducibilities of the mole fractions of Al, Mg, Ca, Na and K in their respective sites are less than or equal to 0.01 for the minerals studied, except for Ca in epidote ($X^p_{Ca} = \pm 0.02$; LeAnderson 1978a). The results of the chemical analyses, activity models, and calculated activities are given in LeAnderson (1978a, 1981).

ISOGRADS

Five isograds were mapped in the calcareous rocks based on model reactions ("isoreactiongrads" of Winkler 1974). In order of increasing grade, they are:
(1) rutile + calcite + quartz = titanite + CO_2
(2) 5 dolomite + 8 quartz + H_2O =
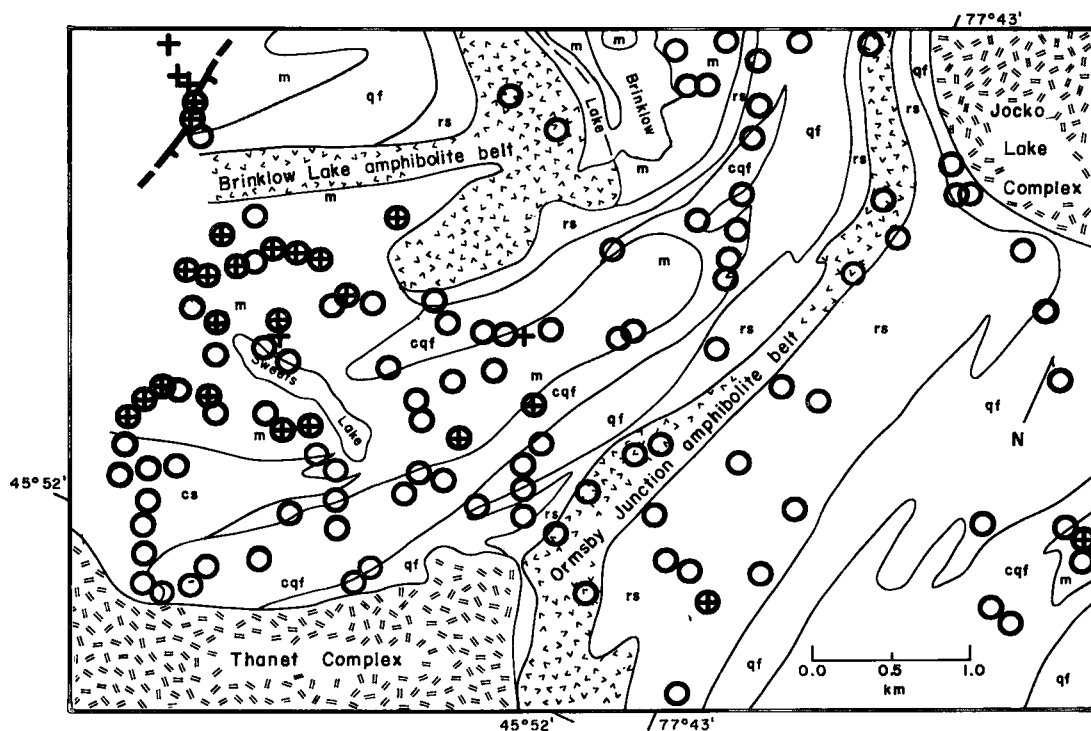$$\text{tremolite} + 3 \text{ calcite} + 7 \text{ } CO_2$$

FIG. 3. The titanite isograd, based on the model titanite-producing reaction (1) (see text). A plus indicates the reactant assemblage, a circle, the product assemblage, and a plus and circle, samples with both the reactant and product assemblages. Hachures are drawn on the high-grade side of the isograd. For clarity, isograds are not drawn around the two occurrences of the reactant assemblage in the marble.

(3) 5 phlogopite + 6 calcite + 24 quartz =
      3 tremolite + 5 K-feldspar + 6 CO_2 + 2 H_2O.
(4) tremolite + 3 calcite + 2 quartz =
      5 diopside + 3 CO_2 + H_2O.
(5) 3 tremolite + 6 calcite + K-feldspar =
      12 diopside + phlogopite + 6 CO_2 + 2 H_2O.

Although most of the minerals are members of solid-solution series, the model reactions may be used as a basis for the isograds provided that the phases in the model reactions are members of the same solid-solution series. The model reactions are labeled according to the product phases, and the isograds by the product minerals.

An assemblage is used as a constraint on an isograd only if the minerals involved in the model reaction were in equilibrium during metamorphism. The assumption of equilibrium applies equally to calculations that use chemical compositions of coexisting minerals. The range of composition for each mineral analyzed in single samples in this study is generally greater than the reproducibility of the analyses. This suggests that adjacent grains of the same mineral, e.g., hornblende–hornblende, did not equilibrate with one another. Nevertheless, plots of analytical means of coexisting minerals, e.g., diopside–hornblende, on mole fraction versus mole fraction and mole fraction versus distribution-coefficient diagrams, suggest that at least on the scale of a thin section, equilibrium between minerals was closely approached (LeAnderson 1978a). Thus we assume that these assemblages represent mosaic equilibrium (Osberg 1971); this hypothesis is supported by the presence of mosaic textures (LeAnderson 1978a).

The titanite isograd marks the appearance of titanite in rutile-bearing, siliceous, calcareous rocks. The isograd occurs in the northwest corner of the map area and around two samples in the west-central part of the area (Fig. 3). There are only five occurrences of the assemblage rutile – calcite – quartz, but numerous occurrences of the four-phase assemblage. This may reflect buffering of the gas phase, participation of plagioclase in the reaction (the titanite contains between 1.7 and 4.2% Al_2O_3; LeAnderson 1978a), or both.

The actinolite – calcite isograd, based on the model tremolite – calcite reaction (2), defines four low-grade areas in the northwestern and southeastern corners, and the central and west-central parts of the map area (Fig. 4). It coincides with the titanite isograd at several localities. Calcite inclusions in actinolite at this grade provide supporting evidence that actinolite was produced by this reaction or one similar to
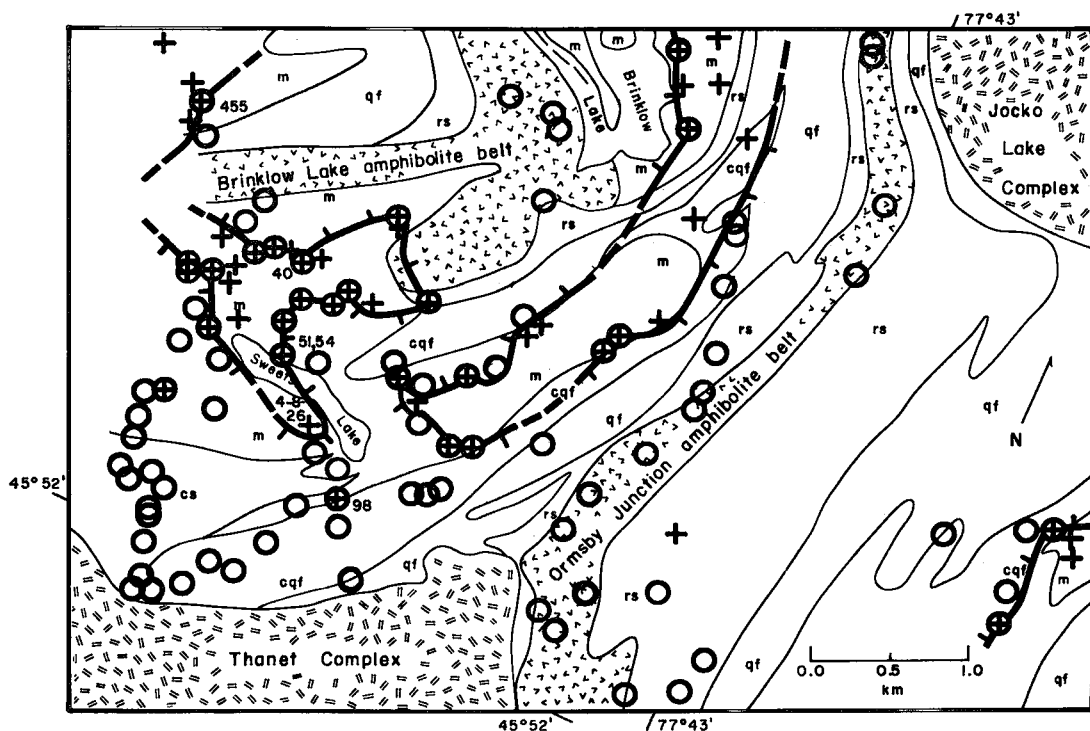

FIG. 4. The actinolite–calcite isograd, based on the model tremolite- and calcite-producing reaction (2). See Figure 3 for explanation. The numbers refer to samples for which temperatures were calculated using the calcite – dolomite geothermometer (see Table 4).

it. The numerous occurrences of the assemblage quartz – dolomite – actinolite – calcite may be the result of buffering of the gas phase by the reaction, the presence of Fe and Al in actinolite, or both. The Fe and Al may have been contributed by dolomite, plagioclase, or chlorite (LeAnderson 1978a).

An isograd based on the model reaction 2 zoisite + CO_2 = calcite + 3 anorthite + H_2O could not be mapped. It is represented in the field by the assemblage epidote – plagioclase – calcite. Below the actinolite – calcite isograd, however, the high-grade [high temperature and high $X(CO_2)$] assemblage plagioclase – calcite is very common, whereas above this isograd, epidote – calcite predominates.

The hornblende – K-feldspar isograd is based on the model tremolite – K-feldspar reaction (3). The isograd lies between the actinolite – calcite and diopside isograds and defines high-grade areas in the Brinklow Lake amphibolite belt and around the Thanet complex (Fig. 5). It does not occur around the Ormsby Junction Amphibolite Belt or the Jocko Lake complex because of the absence of rocks of appropriate bulk-composition. Numerous occurrences of the assemblage biotite – calcite – quartz – hornblende – K-feldspar near the Thanet complex may indicate local compositional control or buffering of the $X(CO_2)$ of the fluid phase.

The temperature of isogradic reactions depends in part on mineral composition. The effect of mineral composition on the temperature of the hornblende – K-feldspar and diopside reactions was determined by calculation of the displacement of the corresponding ph–cc–qtz–tr–kf and tr–cc–qtz–di equilibria (mineral-phase abbreviations are given in Table 1) at an $X(CO_2)$ of 0.10 and a pressure of 4 kbar using the activity models listed in Table 1. The temperature displacement of the equilibria is correlated with the magnesium content of hornblende ($X_{Mg}^{Ca-amph}$; Table 2) because: hornblende exhibits the greatest variation in composition of the minerals in the diopside reaction (isograd); the magnesium concentration has the greatest effect on $a_{tr}^{Ca-amph}$; and the magnesium content is related to the color of the mineral, a feature readily observable in hand specimen and thin section.

The displacement of the ph–cc–qtz–tr–kf equilibrium was calculated using the experimentally determined equilibrium-constant of Hoschek (1973) (see LeAnderson 1978a). The hornblende – K-feldspar isograd does not appear to be very sensitive to mineral composition; a change of about 0.20 in $X_{Mg}^{Ca-amph}$ is necessary to displace the equilibrium by 40°C. Furthermore, for hornblende containing Na, Al and Fe, such as the hornblende in this study
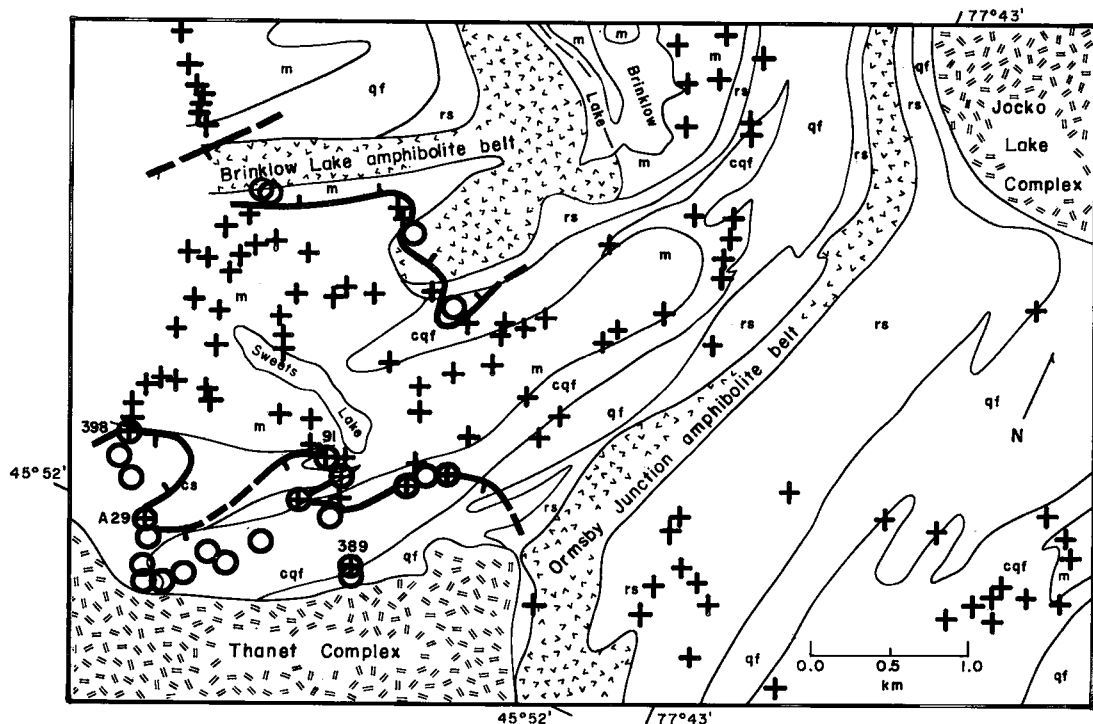

FIG. 5. The hornblende – K-feldspar isograd, based on the model tremolite- and K-feldspar-producing reaction (3). See Figure 3 for explanation. The numbers refer to samples used in the calculation of the displacement of the ph–cc–qtz–tr–kf equilibrium and intersection of the ph–cc–qtz–tr–kf, tr–cc–qtz–di and cc–an–zo equilibria (Tables 2, 5).

(LeAnderson 1978a, 1981), there is little or no displacement at an $X_{Mg}^{Ca-amph}$ of 0.50, but the curve is displaced to lower temperatures at $X_{Mg}^{Ca-amph}$ less than 0.50, and to higher temperatures at $X_{Mg}^{Ca-amph}$ higher than 0.50. Differences in $X_{Mg}^{Ca-amph}$ of about 0.10 or less in an area with even a shallow thermal gradient would have little effect on the isograd pattern. Nevertheless, a series of hornblende – K-feldspar isograds based on specific compositions of hornblende would reduce the effects of composition on the isograd patterns and assist in interpretation of spatial variations in temperature and fluid composition.

Using samples coincident with the mapped position of the hornblende – K-feldspar isograd, Carmichael (1970) calculated the following reaction:

biotite + calcite + quartz + epidote + plagioclase = hornblende + K-feldspar + titanite + magnetite (or hematite).

Because constant pressure is assumed, an isograd based on this reaction is sensitive only to variations in temperature and $X(CO_2)$.

Unfortunately, neither magnetite nor hematite is present in samples related to this isograd. Nevertheless, an isograd based on the silicate minerals in the reaction is still less sensitive to variables other than temperature and $X(CO_2)$ than the hornblende – K-feldspar isograd in Figure 5 because more minerals and, therefore, fewer degrees of freedom are involved. Although based on fewer samples, the hornblende – K-feldspar – titanite isograd (Fig. 6) has the same general pattern as the hornblende – K-feldspar isograd.

The diopside isograd based on reaction (4) lies between the hornblende – K-feldspar and diopside – phlogopite isograds around the two gabbro com-

TABLE 2. CALCULATED DISPLACEMENT OF PH-CC-QTZ-TR-KF AND TR-CC-QTZ-DI EQUILIBRIA DUE TO SOLID SOLUTION

ph-cc-qtz-tr-kf equilibrium

Sample Number	$X_{Mg}^{Ca-amph.}$	Displacement at $X(CO_2)$ = 0.1
389	0.30	-40°C
91	0.51	0°C
A 29	0.58	$+10^{\circ}$C

tr-cc-qtz-di equilibrium

Sample Number	$X_{Mg}^{Ca-amph.}$	Displacement at $X(CO_2)$ = 0.1
A 29	0.58	$+10^{\circ}$C
A 28	0.58	$+20^{\circ}$C
398	0.52	$+30^{\circ}$C
121	0.49	$+40^{\circ}$C
139	0.48	$+40^{\circ}$C
A 34	0.45	$+40^{\circ}$C

Sample locations and rock types are given in Figures 5 and 7. See text for explanation and Table 1 for the activity models and mineral abbreviations.

plexes (Figs. 7, 10). The isograd coincides with the hornblende – K-feldspar and diopside – phlogopite isograds at several localities (Fig. 10).

Common occurrences of the assemblage hornblende – calcite – quartz – diopside are probably the result of Na, K, Al and Ti substitutions in hornblende and, to a lesser extent, in diopside (LeAnderson 1978a). The sensitivity of the diopside isograd to mineral composition is displayed as a function of $X_{Mg}^{Ca-amph}$ (Table 2) at an $X(CO_2)$ of 0.10 using the

TABLE 1. ACTIVITY MODELS OF END-MEMBER COMPONENTS IN MINERALS

$$a_{KMg_3AlSi_3O_{10}(OH)_2}^{bi} = (K)(Mg/3)^3(OH/2)^2$$

$$a_{Ca_2Mg_5Si_8O_{22}(OH)_2}^{Ca-amph} = (1/X_{Na+K}^A)(Ca/2)^2(Mg/5)^5(OH/2)^2$$

$$a_{CaCO_3}^{cc} = (X_{Ca}) = Ca/(Ca + Mn + Fe + Mg)$$

$$a_{KAlSi_3O_8}^{kf} = (X_K) = K/(K + Na + Ca + Mn + Mg)$$

$$a_{CaAl_2Si_2O_8}^{pl} = X_{An}^{pl}\gamma \text{ where An } = (Ca + Mn + Mg)/(Ca + Mn + Mg + Na + K)$$
$$\text{and } \gamma = 1.276, \text{ Orville (1972)}$$

$$a_{Ca_2AlAl_2Si_3O_{12}(OH)}^{ep} = (Ca/2)^2(1-Fe^{3+} + Mn)(Si/3)^3$$

$$a_{CaMgSi_2O_6}^{di} = (Ca)(Mg)(Si/2)^2$$

See LeAnderson (1978a) for derivation of activity models. The mineral phase abbreviations used here, in the text, and remaining Tables and Figures are an = anorthite, bi = biotite, Ca-amph = calcium amphibole, cc = calcite, di = diopside, dol = dolomite, ep = epidote, kf = potassium feldspar, ph = phlogopite, pl = plagioclase, qtz = quartz, rut = rutile, ttn = titanite, tr = tremolite and zo = zoisite.
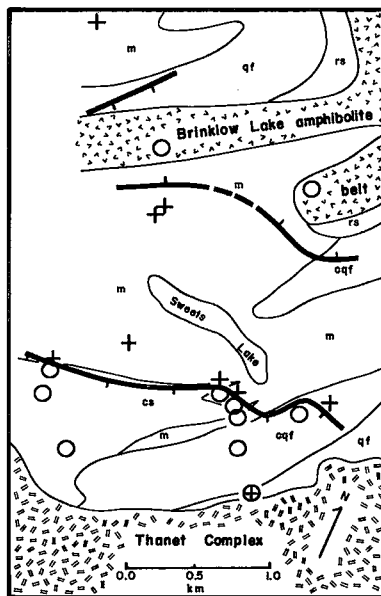

FIG. 6. The hornblende – K-feldspar – titanite isograd. See Figure 3 for explanation and the text for derivation of the isogradic reaction.
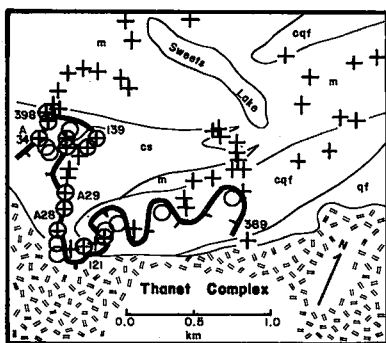
FIG. 7. The diopside isograd, based on the model diopside-producing reaction (4). See Figure 3 for explanation. The diopside isograd is also present around the Jocko Lake complex based on one occurrence of diopside near the contact with the complex. The position of this isograd is shown in Figure 10. The numbers refer to samples used in the calculation of the displacement of tr-cc-qtz-di equilibrium and intersection of the ph-cc-qtz-tr-kf, tr-cc-qtz-di, and cc-an-zo equilibria (Tables 2, 5).
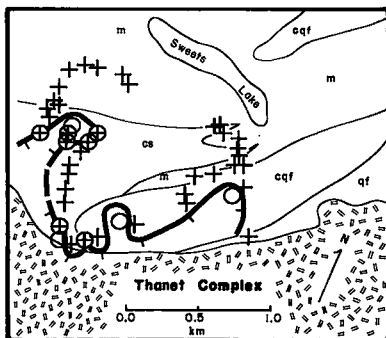

FIG. 8. The diopside – microcline – plagioclase – epidote – titanite isograd. See Figure 3 for explanation and the text for derivation of the isogradic reaction.
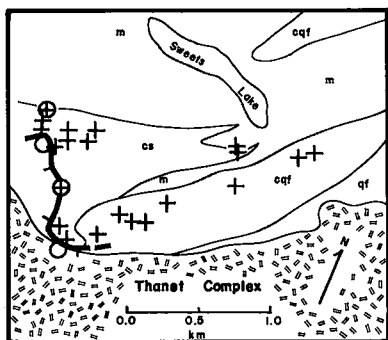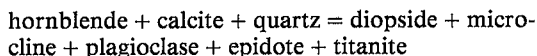

FIG. 9. The diopside – biotite isograd, based on the model diopside- and phlogopite-producing reaction (5). See Figure 3 for explanation.

experimentally determined equilibrium-constant of Skippen (1974) (see LeAnderson 1978a, 1981). As expected, even small differences in $X_{Mg}^{Ca\text{-}amph}$ result in large shifts in the position of the equilibrium curves. Such shifts profoundly affect the position of the isograd even if there are relatively steep thermal gradients.

An isograd based on the following reaction:

hornblende + calcite + quartz = diopside + microcline + plagioclase + epidote + titanite

was mapped (Fig. 8) because it is a closer approximation to the naturally occurring reaction. It defines the same high- and low-grade areas as the diopside isograd.

The diopside – biotite isograd, based on the model diopside – phlogopite reaction (5), is the highest-grade isograd and lies near, and locally coincides with, the diopside and hornblende – K-feldspar isograds near the Thanet complex (Figs. 9, 10).

In summary, the isograds define low-grade areas below the titanite, actinolite – calcite, and hornblende – K-feldspar isograds (Figs. 3, 4, 5, 10) in the marble, and an increase in grade toward and into the quartzofeldspathic units and the two amphibolite belts, and toward the gabbro complexes (Fig. 10). The general range of metamorphic grade for each rock type is as follows: 1) marble: generally from below the titanite isograd to below the hornblende – K-feldspar isograd; 2) quartzofeldspathic units and amphibolite belts: generally above the actinolite – calcite isograd; 3) calc-silicate units: generally from above the actinolite – calcite or hornblende – K-feldspar isograd to above the diopside – phlogopite isograd. The grade around the gabbro complexes, where isograds could be mapped, ranges from above the hornblende – K-feldspar isograd to above the diopside – biotite isograd.

CALCULATION OF UNIVARIANT EQUILIBRIA IN ISOBARIC T–X(CO₂) SPACE FOR THE MODEL SYSTEM

Equilibrium constants for the model isogradic reactions and related equilibria in the system K_2O–Al_2O_3–CaO–MgO–SiO_2–H_2O–CO_2 were calculated using the standard enthalpies, entropies, volumes, and heat capacities listed in the internally consistent data-set of Helgeson et al. (1978). The derived constants listed in Table 3 result from combining standard thermodynamic relations with the Maier–Kelley form of the heat-capacity equation (Helgeson et al. 1978). Isobaric T–$X(CO_2)$ univariant curves and their associated invariant points (Fig. 11) were generated at a total pressure of 4 kbar using a BASIC program that solves the equation:
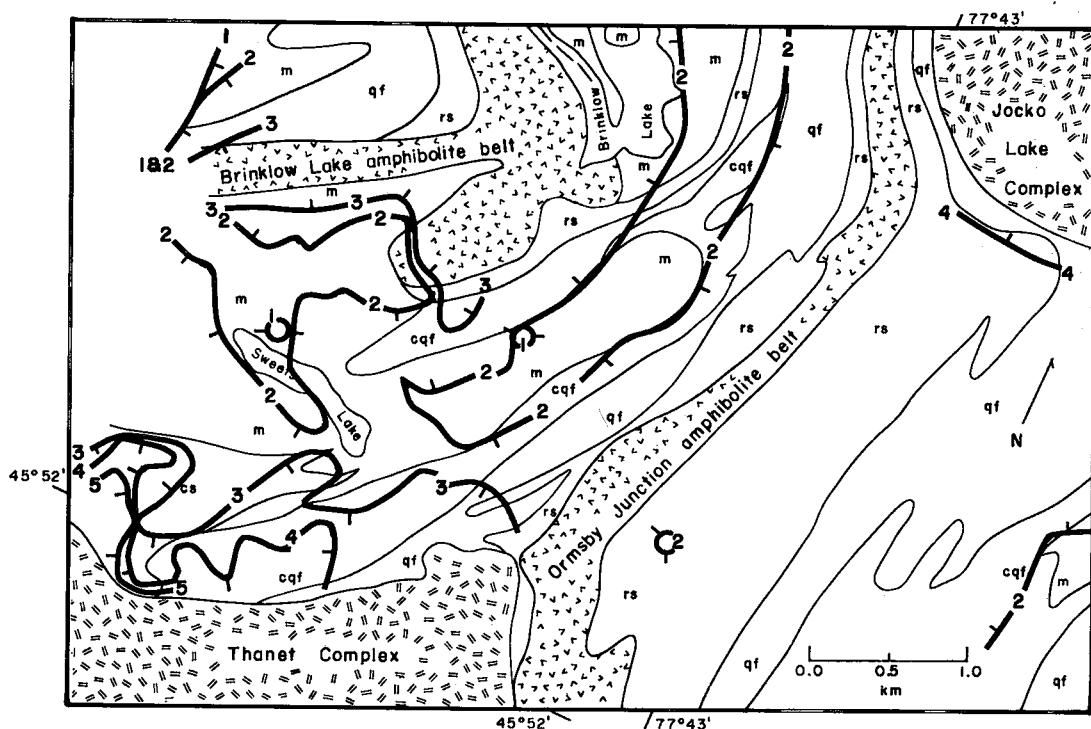
Fig. 10. Composite isograd map. The isograds are numbered the same as the corresponding reactions given in the text and Figures 3, 4, 5, 7, 9. The hornblende – K-feldspar – titanite and diopside – microcline – plagioclase – epidote – titanite isograds are not plotted. Hachures are on the high-grade side of the isograds.

$$\ln K_{P,T} = 0 = \ln K_{1,T} - \frac{(P-1)\Delta V_s}{RT} +$$

$$\nu_{CO_2} \ln(P\Gamma^{mix}_{CO_2} X_{CO_2}) + \nu_{H_2O} \ln[P\Gamma^{mix}_{H_2O}(1-X_{CO_2})] \quad (1)$$

where $K_{P,T}$ and $K_{1,T}$ are the equilibrium constants for the reaction at P and T and at 1 bar and T, respectively; ΔV_s is the volume change for the pure mineral phases in the reaction as written; ν_{CO_2} and ν_{H_2O} are the stoichiometric coefficients for CO_2 and H_2O, respectively; $\Gamma^{mix}_{CO_2}$ and $\Gamma^{mix}_{H_2O}$ are the fugacity coefficients for CO_2 and H_2O in the nonideal CO_2–H_2O fluid, calculated according to a hard-sphere modified Redlich–Kwong equation of state (Kerrick & Jacobs 1981, Jacobs & Kerrick 1981a). The program uses an iterative method to solve for the equilibrium $X(CO_2)$ at fixed P and T.

Equilibrium (1) does not appear in Table 3 because data for rutile and titanite are not included in the compilation of Helgeson *et al.* (1978). The approximate position of the titanite equilibrium at 4 kbar is shown as a dashed line in Figure 11 based on the position of the titanite isograd. The position of the equilibrium in Figure 11 is in good agreement with the position determined experimentally by Jacobs & Kerrick (1981b).

The model equilibria can be used to estimate both temperatures and fluid compositions provided that

the equilibrium constants are modified to account for the activities of the standard-state components in the mineral phases. This may be done by solving the equation:

$$\ln K_{P,T} - \ln(\Pi_{i=1,j}a_i^{\nu_i}) = 0 \quad (2)$$

where $K_{P,T}$ refers to pure phases (equation 1); j represents the total number of phases with variable activities in the reactions; a_i is the activity of the ith standard-state component in the ith phase, and ν_i is the stoichiometric coefficient of the ith phase.

We have neglected CH_4 as a possible fluid-phase component although, under some conditions, CH_4 can be a major constituent in the system C–O–H–S (Ohmoto & Kerrick 1977). CH_4 concentrations are highest in graphite-bearing rocks at low $X(CO_2)$. Where present in significant amounts, CH_4 can lower the temperature of invariant points by tens of degrees. The invariant point corresponding to the assemblage grossular – zoisite – calcite – anorthite – quartz (not present in Fig. 11) is lowered by 40°C at 2 kbar (Ohmoto & Kerrick 1977). The assumption that $P_{total} = P(H_2O) + P(CO_2)$ is reasonable for the calculations in this study because the high-grade rocks, which were characterized by low $X(CO_2)$ values, do not contain graphite.

TABLE 3. COEFFICIENTS FOR EQUILIBRIA PLOTTED IN FIGURE 11

$$\log K_{p_s,T} = a(\log T - 0.4343) - bT + c/2T^2 - d/T + e + hP$$

Reaction Number	constants					
	a	$b \times 10^3$	$c \times 10^{-5}$	$d \times 10^{-4}$	e	h
2	16.257	10.939	-1.491	2.3299	19.1224	0.6248
3	52.111	17.613	-19.025	1.8438	-64.5981	0.7903
4	8.937	4.530	-3.509	1.5147	11.8141	0.5153
5	11.027	7.349	-4.618	3.2665	41.2736	1.0786
6	-0.298	0.049	0.837	0.3041	6.0467	-0.3526
7	9.237	7.641	0.405	5.0909	77.5539	-1.0370
8	8.042	4.676	-0.998	2.4269	29.9541	-0.5425
9	50.321	17.905	-14.002	3.6683	-28.3178	-1.3253
10	17.152	10.793	-4.002	1.4176	0.9823	1.6826
11	-0.668	3.041	2.910	1.0292	24.3930	0.2168
12	0.227	2.895	0.399	0.1169	6.2530	1.2745

The standard state for all equilibrium constants is 1 bar and T for fluid ($H_2O + CO_2$) and P and T for pure mineral phases. Thermodynamic data and mineral stoichiometry are taken from Helgeson et al. (1978). P is in kilobars and T is in kelvins.

The topology of the isobaric $T-X(CO_2)$ grid presented in this paper differs from that calculated by LeAnderson (1978a, 1981). The earlier version used mostly experimental data, and did not incorporate either heat-capacity equations or models to reflect a nonideal fluid. For example, in Figure 11, reactions (3) and (4) do not intersect. However, if the data of Skippen (1974) are used for the diopside equilibrium and those of Hoschek (1973) for the tremolite – K-feldspar equilibrium, an intersection is obtained (LeAnderson 1978a, 1981).

Using the data of Helgeson et al. (1978), the cc–an–zo equilibrium (reaction 6) plots at a higher $X(CO_2)$ than when the experimental data of Johannes & Orville (1972) are used; it plots close to the position of the equilibrium determined experimentally by Allen & Fawcett (1982). In the model system, the cc–an–zo equilibrium intersects the phl–cc–qtz–tr–kf, tr–cc–qtz–di, and tr–cc–kf–di–ph equilibria, which generates cc-absent equilibria at each intersection (Fig. 11). Similarly, cc-absent equilibria are generated by the intersection of the cc–an–zo equilibrium with the dol–kf–ph–cc and dol–qtz–tr–cc equilibria (Fig. 11).

CONDITIONS OF METAMORPHISM

The isograds record an increase in grade from the marble into the quartzofeldspathic units and the two amphibolite belts, as well as toward the two gabbro complexes. Prehnite is not present in the study area. This absence, and the presence of coexisting amphibole – epidote – diopside – zoisite – quartz, indicate a lower-temperature limit during metamorphism of approximately 350°C. These phases are related by the reaction prehnite + tremolite = diopside + zoisite + quartz + H_2O, which was calculated at 2 and 5 kbar by Rice (1983) using the data of Helgeson et al. (1978). The absence of grossular and presence of coexisting epidote, plagioclase and quartz suggest a maximum temperature in the upper

500°C range based on the reaction clinozoisite + quartz = grossular + anorthite + H_2O (Boettcher 1970, Bird & Helgeson 1981).

The temperature of metamorphism for the marble is calculated using the $MgCO_3$ content for coexisting calcite and dolomite. The $MgCO_3$ content of calcite in equilibrium with dolomite is strongly dependent on temperature and is not significantly affected by pressure in the range 1–10,000 bars (Goldsmith & Newton 1969). The effects of $FeCO_3$ and $MnCO_3$ on the solvus are not known, but are not considered significant for mole fractions less than 1%, the content of $FeCO_3$ and $MnCO_3$ in the calcite in this study (LeAnderson 1978a).

The rim of calcite grains in six samples of low-grade marble (Fig. 4) was analyzed. Grains with sutured margins or included dolomite blebs, or grains that are in contact with elongate dolomite grains that may represent exsolved dolomite, were not analyzed. Temperatures calculated using the relationship:

$$T°C = (\log MgCO_3 + 0.223)10^3/1.727$$

(Sheppard & Schwarcz 1970) range from 535 to 595°C (Table 4). A range between 5 and 170°C for individual samples may indicate re-equilibration of calcite during retrograde metamorphism (Hutcheon & Moore 1973). However, the highest temperatures calculated are for samples with the greatest range in temperatures, which suggests that Mg-rich domains were inadvertently analyzed in some grains. If so, the temperature of metamorphism of the marbles was probably between approximately 535 and 550°C.

Temperatures are calculated for five samples of high-grade calc-silicate and calcareous quartzofeldspathic granofels near the Thanet complex (Table 5, Figs. 5, 7) using the two-feldspar geothermometer of Whitney & Stormer (1977) and by calculation of the displacement of intersecting equilibria (LeAnderson 1978a, b, 1981). The activity models are given
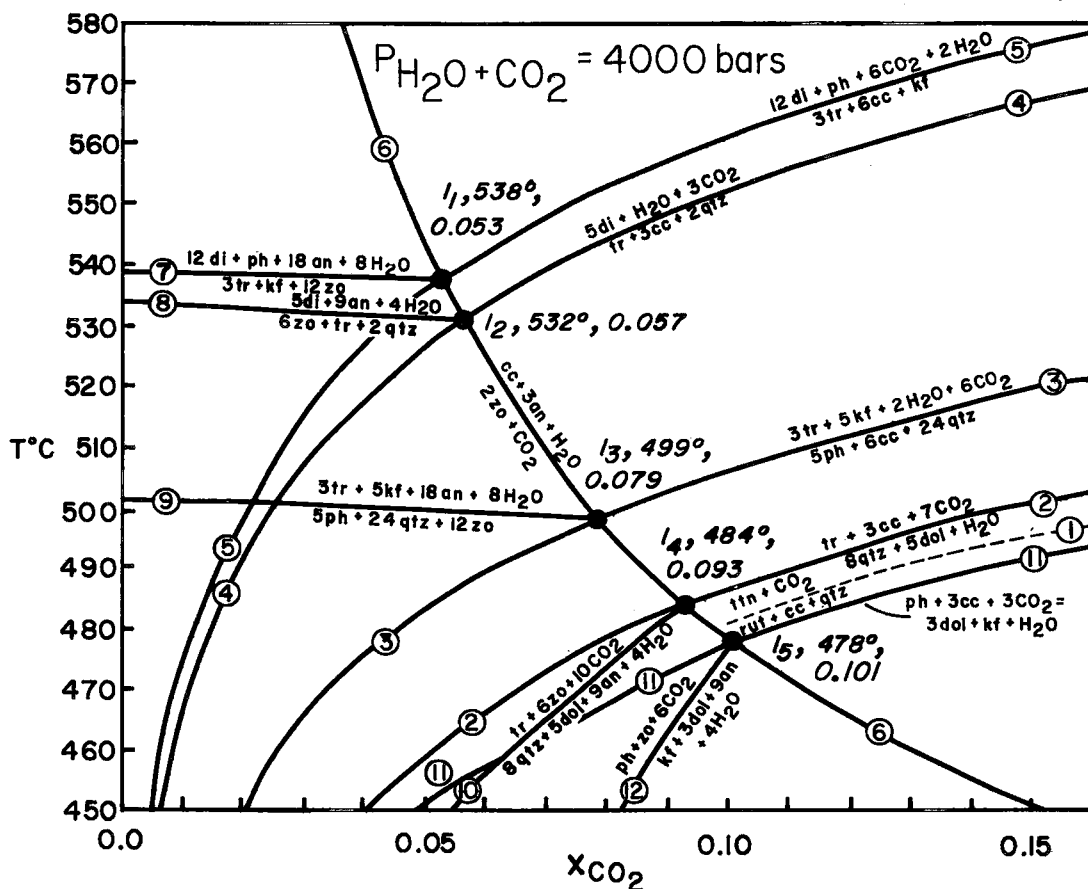
FIG. 11. The T–$X(CO_2)$ grid at 4 kbar. Equilibrium constants are from Helgeson *et al.* (1978) (Table 3). Equilibria 1–5 are used as model reactions for the isograds (Figs. 3–10). The abbreviations for the mineral phases are listed in Table 1.

in Table 1. The equilibria involved are cc–an–zo and ph–cc–qtz–tr–kf (sample 389), cc–an–zo and tr–cc–qtz–di (A28 and A34), and tr–cc–qtz–di and ph–cc–qtz–tr–kf (A29 and 398). The temperatures calculated using the experimentally determined equilibrium-constants of Skippen (1974) (tr–cc–qtz–di), Hoschek (1973) (ph–cc–qtz–tr–kf) and Johannes & Orville (1972) (cc–an–zo) and the two-feldspar geothermometer of Whitney & Stormer (1977) (LeAnderson 1978a, 1981) are given in Table 5, together with the temperatures calculated using the data of Helgeson *et al.* (1978) (Table 3).

Temperatures calculated for samples A28 and 389, using the experimental data of Johannes & Orville (1972), are unrealistically low (LeAnderson 1978a, 1981) and are not considered further. However, temperatures calculated for these same samples using the two-feldspar geothermometer and the data of Helgeson *et al.* (1978) at 4 kbar are reasonable and in agreement for each sample, although the temperatures calculated for A28 are higher than for 389.

TABLE 4.   TEMPERATURES CALCULATED FOR THE LOW-GRADE MARBLE USING CALCITE-DOLOMITE GEOTHERMOMETRY

Sample Number	Number of Analyses	$X^{cc}_{MgCO_3}$	Calculated Range (°C)	Temperature Maximum (°C)
98	3	0.0408–0.0505	50	535
4-8-26	3	0.0505–0.0510	5	540
455	3	0.0404–0.0532	70	550
40	4	0.0404–0.0619	110	590
51	8	0.0323–0.0638	170	595
54	1	0.0638	---	595

$X^{cc}_{MgCO_3}$ = Mg/(Mg + Ca + Fe + Mn).

$T°C$ = (log $MgCO_3$ + 0.223)/0.001727 (Sheppard & Schwarcz 1970).

Sample locations are given in Figure 4.

Temperatures for A29 and 398 could not be obtained using the data of Helgeson *et al.* (1978) because the tr–cc–qtz–di and ph–cc–qtz–tr–kf equilibria do not intersect. Intersection can be obtained, however, with a slight increase in the

TABLE 5.   CALCULATED TEMPERATURE (°C) AND X(CO₂) VALUES FOR FIVE HIGH-GRADE SAMPLES

Sample Number	Feldspar Geother- mometer	Intersecting equilibria at 4 kbar (LeAnderson 1978a, 1978b, 1981)	Intersecting equilibria at 4 kbar (this study)	Intersecting equilibria at 3 kbar (this study)
A28	500-543	355-405	487-517	447-492
	--- ---	0.007-0.02	0.001-0.02	0.001-0.02
389	412-457	340-400	402-432	365-400
	--- ---	0.007-0.02	0.015-0.04	0.01-0.02
A34	462-498	440-505	537-607	497-557
	--- ---	0.02-0.09	0.035-0.10	0.02-0.07
A29	494-535	440-450	--- ---	--- ---
	--- ---	0.03-0.04		
398	443-484	430-450	--- ---	--- ---
	--- ---	0.02-0.03		

The first row for each sample number gives the calculated temperature range in °C. The second row for each sample number gives the calculated range in X(CO₂) (intersecting equilibria only). Intersecting equilibria are cc-an-zo and tr-cc-qtz-di (A28 and A34); cc-an-qtz and ph-cc-qtz-tr-kf (389); ph-cc-qtz-tr-kf and tr-cc-qtz-di (A29 and 398). No meaningful intersections were obtained for samples A29 and 398 at either 3 or 4 kbar using the data in Helgeson et al. (1978), owing to the nearly parallel relation of the curves in T-X(CO₂) space. Samples A29, 398, A28 and A34 are calcsilicates and sample 389 a calcareous quartzofeldspathic granofels. The sample locations are given on Figures 5 and 7 and mineral abbreviations in Figure 1.

entropy of reaction within the experimental constraints for either equilibria or, possibly, by using different activity-models. In view of the steep slope of both reactions, there is no good justification for making such arbitrary changes, because the resulting uncertainty in the temperature of intersection is very great. However, the temperatures calculated for A29 and 398 using both the two-feldspar geothermometer and the experimentally determined equilibrium-constants cited above are within the range calculated for samples A28 and 389, although the temperature calculated for A29 using the two-feldspar geothermometer is higher than that calculated at 4 kbar using the experimentally determined equilibrium-constants. The temperatures calculated for A34 using the two-feldspar geothermometer and the experimentally determined equilibrium-constants are in agreement, but the temperature obtained for this sample using the data of Helgeson et al. (1978) is the highest of all the temperatures calculated.

In summary, it appears that the temperature near the Thanet complex ranged from approximately 402 (389) to 543°C (A28) and possibly higher (up to 607°C; A34). Thus, the temperature range was greater, and the average lower, than for the marble, which reveals a range of 535 to 550°C.

The $X(CO_2)$ values for the five samples near the Thanet complex ranged from less than 0.01 to approximately 0.10. The $X(CO_2)$ for the marble was approximately 0.45 to 0.55 based on the temperature range of 535 to 550°C and the calculated position of the model qtz–dol–tr–cc equilibrium using the data of Helgeson et al. (1978). The presence

of calcite and plagioclase in the marble, and of calcite and epidote in rocks with low amounts of carbonate, related through the cc–an–zo equilibrium (6) (Fig. 11), is in agreement with this.

The spatial relationship between the isograds and rock type indicates a genetic relationship. Furthermore, a decrease in $X(CO_2)$ of approximately 0.3 to 0.5 is responsible for the increase in metamorphic grade from the marble toward the carbonate-deficient rocks near the Thanet complex, even though the temperature decreased several tens of degrees. Based on these relationships, we infer that the increase in grade toward the Jocko Lake complex and amphibolite belts is also due to a decrease in $X(CO_2)$. The inverse relationship between grade and carbonate content may be due to: 1) internal buffering of the $X(CO_2)$ of the fluid by the isogradic reactions. All five reactions produce CO_2 or produce more CO_2 than H_2O. Owing to the positive slope of the isogradic reactions in isobaric $X(CO_2)$ space at low values of $X(CO_2)$ (Fig. 11), rocks with a high carbonate content, for example marble, would likely produce greater amounts of CO_2 than the carbonate-poor rocks. This would explain the high $X(CO_2)$ and low grade in the marble, and low $X(CO_2)$ and high grade in the carbonate-poor rocks; or 2) buffering during the influx of external H_2O-rich fluids. The quartzofeldspathic rocks and amphibolite belts may have been more permeable than the marble, which would have allowed for extensive infiltration of H_2O-rich fluids in the carbonate-poor rocks and maintenance of low $X(CO_2)$ values, a situation documented elsewhere

by Ferry (1980, 1983). Influx of heat accompanying the influx of fluid would also explain the wider range of temperature in the calc-silicates and calcareous quartzofeldspathic granofels than in the marble.

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