Comparative geothermometry based on major-element and oxygen isotope distributions in Precambrian metamorphic rocks from southwestern Montana

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Abstract

Mineral assemblages in the Kelly and Carter Creek areas of the Ruby Range, southwestern Montana, indicate orthopyroxene-zone and sillimanite-K feldspar-zone metamorphism, respectively. Because the two areas are small and contain diverse lithologies, they are ideal for a comparative study of mineral-pair geothermometers and grade indicators. For the Kelly area, various major-element methods (clinopyroxene-orthopyroxene, garnet-orthopyroxene, garnet-hornblende, garnet-biotite, and K feldspar-plagioclase) yield a consensus peak temperature estimate of 745±50°C. For the Carter Creek area, garnet-clinopyroxene, garnet-hornblende, garnet-biotite, and K feldspar-plagioclase methods plus assemblage data yield 675±45°C.

Coexisting quartz and magnetite in metamorphic iron-formations from the two areas yield anomalously low temperature estimates of 530±15°C and 475±25°C, respectively, based on oxygen isotopic fractionations of 8.41±0.30 per mil and 9.92±0.20 per mil. Similarly, Mg distributions between calcite and dolomite in metadolomites from the Kelly area yield estimates of ca. 545°C. These lower temperatures are probably the result of (1) solid-state diffusion of chemical species between minerals or (2) recrystallization of quartz, magnetite, and carbonates (i.e., the non-refractory minerals) during retrograde or subsequent low-grade metamorphism. Another low estimate (545°C) is obtained from rim compositions of coexisting garnet and cordierite in one magnesian meta-pelite sample from the Kelly area. This estimate is consistent with the observation of cordierite coronas on garnet, a texture that suggests retrograde origin for the cordierite.

These data show it cannot be assumed a priori that a given geothermometer will record peak metamorphic temperature. Instead, the bimodal discordance of estimates presented here reflects the varied response of different mineral pairs to a given metamorphic and tectonic history.

Introduction

Many published geothermometers are based upon the temperature-dependence of major-element or isotope distributions between coexisting minerals. An inherent danger confronting the petrologist who uses such methods is the tendency to regard calculated temperatures as estimates of peak thermal conditions in an area, without due consideration for possible alternatives. The primary purpose of this communication, therefore, is to evaluate the precision, accuracy, sensitivity, petrologic significance, and limitations of selected mineral-pair geothermometers.

Geologic setting

The Ruby Range is a northeast-southwest-trending block whose highly deformed and metamorphosed Precambrian (Pre-Beltian) core was exposed by Laramide uplift and subsequent erosion. Sillimanite-K feldspar-zone metamorphism prevailed.
Botholiths and Tertiary intrusives in Madison County, Montana (after Cordua, 1973). The Kelly and Carter Creek areas of the Ruby Range are the primary sample sites for this study. These areas are named for Precambrian metamorphic iron-formations contained therein. One sample (sample RMS-22) is from the Stone Creek area, located approximately half-way between the two main areas.

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throughout most of the range, including the Carter Creek area (ca. 9 km² in area), as evidenced by mineral assemblages in pelitic rocks. However, in the northeast part of the area, which includes the Kelly iron deposit (ca. 1 km² in area), assemblages in mafic gneisses and iron-formations indicate that the orthopyroxene isograd was reached. Mineral assemblages in the two areas are summarized in Table 1.

Both areas are situated within a thick sequence of metamorphosed dolomites, mafic gneisses, iron-formations, pelitic and semi-pelitic rocks, and quartzites. These rocks, collectively termed "Cherry Creek" rocks by Heinrich (1960), are thought to have attained their high-grade metamorphic character approximately 2700 m.y. ago, during the Beartooth orogeny (H. L. James, personal communication). The "Cherry Creek" rocks are conformably underlain by the Dillon pelitic gneiss unit, which in turn is underlain by a sequence of "pre-Cherry Creek" schists and gneisses. The regional foliation of the Pre-Beltian units parallels bedding, striking northeast–southwest.

Table 1. Summary of mineral assemblages in the Kelly and Carter Creek areas of the Ruby Range

<table>
<thead>
<tr>
<th>Mafic gneisses: Kelly assemblages = la-lc; Carter Cr. assemblages = ld-lh.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a) and (or lab) + sal + hbl + CaMg alm + qtz + ilm + (apa, mag, zirc) * Sample RMK-13,-17,-26,-271,-272, and -77.</td>
</tr>
<tr>
<td>1b) and + CaMg alm + qtz + hyp + hbl + bio + (sal) + (mag, ilm, zirc). Sample RMK-273 and -51.</td>
</tr>
<tr>
<td>1c) lab + hbl + sal + hyp. Sample RMK-122.</td>
</tr>
<tr>
<td>1d) mic + scap + hbl + sal + CaMg alm + sp + cal + (graph, qtz, zirc). Samples RMK-11 and -12.</td>
</tr>
<tr>
<td>1e) sal + FeMn gross + and + cal + sp + (apa). Sample RMK-71.</td>
</tr>
<tr>
<td>1f) hbl + and + cum + CaMg alm + qtz + ilm + (apa). Samples RMK-77,-97, and -123.</td>
</tr>
<tr>
<td>1g) hbl + qtz + (or) + MgCa (or CaMg) alm + cum + ilm. Samples RMK-15D and -103A.</td>
</tr>
<tr>
<td>1h) gedr + Mg alm + qtz + and + bio. Samples RMK-19E1 and -19E2.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Iron-formations: Kelly assemblages = 2a-2b; Carter Cr. assemblages = 2c-2d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a) qtz + mag + eul + (FeCa spess). Sample RMK-48.</td>
</tr>
<tr>
<td>2b) qtz + mag + Fe-aug (or aug) + Fe-hyp (or eul) + CaMn (or MnCa) alm + (Mn-ilm, cal). Samples RMK-371,-372, -46,-60,-76, and -80.</td>
</tr>
<tr>
<td>2c) qtz + mag + hem + Fe-hyp + cum + hbl (or act) + (mic, cal, apa). Sample RMK-44.</td>
</tr>
<tr>
<td>2d) qtz + mag + hem + diop (or hyp) + ab + Na trem + rieb + (mic, cal, apa). Samples RMK-37 and -135.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Meta-pelites: Kelly and Carter Cr. assemblage.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a) qtz + mic perth + olig + MgMn (or Mg) alm + bio + cord + sill + (ilm, rut, mag, zirc, apa, cal, mu (relict), and/or ky (relict)). Samples RMK-66,-98, and -127; RMC-30,-84,-93,-112, and -151.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Meta-dolomites: Kelly assemblage.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a) cal + dol + fo + sal + phl. Sample RMK-136.</td>
</tr>
</tbody>
</table>

**Brackets [ ] indicate accessory phases. Abbreviations: ab = albite; alm = almandine; and = andesine; andr = andradite; apa = apatite; aug = augite; biot = biotite; cal = calcite; cord = cordierite; cum = cummingtonite; diop = diopside; dol = dolomite; eul = eulite; fo = forsterite; gedr = gedrite; graf = graphite; gross = grossularite; grun = grunerite; hem = hematite; hbl = hornblende; hyp = hypersthene; ilm = ilmenite; ky = kyansite; lab = labradorite; mag = magnetite; mic = microcline; mu = muscovite; olig = oligoclase; perth = perthite; phl = phlogopite; qtz = quartz; rieb = riebeckite; rut = rutile; sal = salite; scap = scapolite; serp = serpentine; sill = sillimanite; sph = sphene; trem = tremolite; zirc = zircon.**
Table 2. Metamorphic temperature estimates for the Kelly and Carter Creek areas of the Ruby Range

<table>
<thead>
<tr>
<th>Mineral-pair</th>
<th>Temperature estimates (°C) (Kelly area)</th>
<th>Temperature estimates (°C) (Carter Creek area)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak</td>
<td>Retrograde</td>
<td>Peak</td>
</tr>
<tr>
<td>Cpx-opx</td>
<td>770±30 (9)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cpx-opx</td>
<td>700±30 (9)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Gar-cpx</td>
<td>760±40 (3)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Gar-cpx</td>
<td>74±50 (5)</td>
<td>690±35 (5)</td>
<td>665±60 (3)</td>
</tr>
<tr>
<td>Gar-hb</td>
<td>74±50 (4)</td>
<td>&lt;740±50 (4)</td>
<td>645±70 (6)</td>
</tr>
<tr>
<td>Gar-bi</td>
<td>760±50 (1)</td>
<td>635±50 (3)</td>
<td>665±50 (3)</td>
</tr>
<tr>
<td>Ksp-plag**</td>
<td>735±70 (1)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Sili-ksp</td>
<td>630±40 (4)</td>
<td>---</td>
<td>630±40 (9)</td>
</tr>
<tr>
<td>Gar-cpx</td>
<td>665±50 (1)</td>
<td>545±50 (1)</td>
<td>---</td>
</tr>
<tr>
<td>Cal-dol</td>
<td>545±50 (1)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Qtz-mag</td>
<td>540±15 (3)</td>
<td>---</td>
<td>490±20 (3)</td>
</tr>
<tr>
<td>Qtz-mag</td>
<td>530±15 (3)</td>
<td>---</td>
<td>475±25 (3)</td>
</tr>
<tr>
<td>Consensus peak temp.</td>
<td>74±50°C</td>
<td>675±45°C</td>
<td>---</td>
</tr>
</tbody>
</table>

The value reported for each geothermometer represents either the temperature range indicated by the various samples analyzed, or the published uncertainty of the method (if known) applied to the average temperature obtained by that method. Number of samples analyzed is given in parentheses next to each temperature estimate. Abbreviations: cpx = clinopyroxene, opx = orthopyroxene, gar = garnet, hb = hawthorne, bi = biotite, ksp = Kfeldspar, plag = plagioclase, cd = cordierite, dol = dolomite, qtz = quartz, mag = magnetite, and sill = sillimanite.

**It cannot be stated with certainty that these estimates reflect peak conditions (see text for explanation); consequently, these estimates are not figured into the consensus peak temperature for the Kelly area. Gar-cpx estimates assume P= 6 kbar (Kelly) and 6.0-6.7 kbar (Carter Creek).

and dipping to the northwest. Widespread alteration of prograde assemblages indicates that Precambrian greenschist- to lower amphibolite-facies metamorphism occurred in the Ruby Range. Whether this metamorphism occurred during the waning stages of the 2700 m.y. event or represents a separate event cannot be discerned from field or petrographic evidence. However, Gillis (1966) has reported a number of 1600 m.y. mineral dates for the area. Also, Reid and Greenwood (1968) have documented a 670 m.y. event in Idaho, which may have affected basement rocks in Montana as well. These dates indicate a polymetamorphic history for the area.

The “Cherry Creek” rocks of the Kelly and Carter Creek areas were mapped in detail by James et al. (1969) and James and Wier (1972a, b). Additional details on the stratigraphy, structure, and petrology of these rocks are given in Heinrich (1960), Dahl (1977), and Garihan (1979).

Analytical procedures

Electron microprobe procedures

Chemical analyses for nine oxide components were performed on coexisting minerals in some thirty polished thin sections using the 3-spectrometer ETEC Autoprobe at Indiana University; operating conditions and analytical procedures were identical to those described in Klein (1974). Representative analyses of minerals—too numerous to list here—are catalogued in Dahl (1977). Averaged (mean) microprobe analyses (uncorrected for generally small amounts of Fe**) were used in the calculation of distribution coefficients which, in turn, were referred to the published mineral-pair geothermometers and grade indicators itemized in Table 2 and Figure 2.

Oxygen isotopic procedures

Quantitative oxygen extraction of quartz and magnetite from iron-formation was performed by the BrF₃ method described by Clayton and Mayeda (1963). Liberated oxygen was then passed over a heated graphite disc for quantitative conversion to CO₂. Isotopic composition of the CO₂ was determined with a 15-cm, 60°-sector mass spectrometer equipped with a double inlet and a double collector similar to that described by McKinney et al. (1950). Oxygen yields of 100±3 percent were obtained for all quartz runs and most of the magnetite runs. Some yields for magnetite runs were as low as 85 percent,
but no detectable error was introduced in measured isotope ratios, as determined by comparison with replicate runs that gave 100 percent yields. Most runs were performed in replicate, and a 95 percent confidence limit of ±0.12 per mil was recorded for δ18O in most samples.

Geothermometric results and discussion

**Introduction**

Metamorphic temperature estimates based upon nine different mineral pairs are presented in Table 2 and Figure 2. These estimates are discussed individually in the following sections.

**Clinopyroxene-orthopyroxene**

Rim compositions of coexisting pyroxenes in mafic granulite gneisses and iron-formations from the Kelly area were referred to two widely-used pyroxene geothermometers. The first of these methods—that of Wood and Banno (1973)—uses an equation based on Davis and Boyd’s (1966) experimental determination of the diopside–enstatite solvus. Their equation contains an empirical correction for the FeO content of orthopyroxene and assumes ideal mixing of the MgSiO3 component in diopside coexisting with orthopyroxene. The Wood–Banno method yields a mean temperature estimate of 770±70°C for the Kelly area, based on nine pyroxene-bearing samples. The ±70°C uncertainty reflects the range of individual estimates; a ±60°C uncertainty is placed on the method by Wood and Banno. The more Mg-rich pyroxene pairs from the mafic granulite gneiss assemblages consistently give the higher temperatures in the above range, whereas pyroxenes from the iron-formations yield the lower temperatures. A similar trend was observed and explained by Wells (1977). Hewins (1975) concluded that the Wood–Banno geothermometer may read too high by as much as 50°C for granulite-facies assemblages. Indeed, the temperature range calculated by this method is higher than that predicted by any other method (see Table 2 and Fig. 2).

Ross and Huebner (1975) performed heating experiments on natural, exsolved pyroxenes at various temperatures under controlled oxygen fugacity (iron–wustite buffer) at 1 atm. Electron microprobe analyses of these exsolved pyroxenes permitted them to contour the pyroxene solvus for temperature on a Wo–En–Fs diagram. Dahl (in preparation) showed that pyroxene pairs from the Kelly area plot along the 700°C isotherm defined by Ross and Huebner [as do pyroxene pairs from the nearby Tobacco Root Mountains (Imme and Klein, 1976)]. Mori and Green (1976) suggest that the diopside–enstatite solvus is insensitive to variations in load pressure (Pv) below 900°C. If this relationship extends also to pyroxenes containing Fe, it follows that the 700°C estimate need not be corrected for pressure. Ross and Huebner place a ±100°C uncertainty on estimates obtained by their method.

**Garnet-orthopyroxene**

The sub-assemblage garnet–orthopyroxene is common in the mafic granulite gneisses and iron-formations of the Kelly area, and neither mineral exhibits chemical zonation. Although a geothermometer based on this mineral pair has never been calibrated, Dahl (in preparation) found that the value of Kp(Fe/Mg; gar–opx) is dependent on temperature and on the Mn content in garnet (MnGar). By plotting data
from various world-wide localities on a graph of $K_0$ vs. $Mn^{ost}$, it was possible to infer relative metamorphic temperatures among these areas from the relative positions of their respective isotherms. Because the isotherm for the Kelly area merged with an isotherm defined by garnet-orthopyroxene-bearing gneisses from the Venezuelan Guyana shield (Doughan, 1974), it was concluded that these two areas experienced similar peak metamorphic temperatures. Thus, Doughan’s estimate of 760±40°C, which was partly based on garnet-cordierite geothermometry, is tentatively applied here as an indirect estimate for the Kelly area. This estimate agrees well with the consensus peak estimate of 745±50°C for the Kelly area given in Table 2, although it must be stated that the effects of load pressure on isotherms in $K_0$-$Mn^{ost}$ space are not known. These effects are assumed to be small.

Garnet-clinopyroxene

This mineral pair, like garnet-orthopyroxene, is common in the mafic granulite gneisses and iron-formations of the Kelly area. It is found also in several calcite-bearing samples of mafic gneiss from the Carter Creek area.

Räheim and Green (1974) experimentally calibrated the distribution coefficient $K_0(Fe/Mg; gar-cpx)$ as a geothermometer for eclogites, using mineral mixes and artificial tholeiitic glasses as starting materials. Their piston-cylinder experiments yielded the temperature-dependence of $K_0$ from 600°C to 1400°C at 30 kbar, and the pressure-dependence of $K_0$ from 20 to 40 kbar at 1100°C. Based on straight-line trends at these conditions, they extrapolated their results to other pressures and temperatures in the eclogite field and, tentatively, to conditions within the garnet granulite field. One difficulty involved in applying this geothermometer to garnet-clinopyroxene-bearing rocks of the Ruby Range is that these rocks formed at load pressures well below the 20-40 kbar range studied by Räheim and Green, as evidenced by the abundance of sillimanite (and not kyanite) in associated meta-pelites. A second difficulty is that a marked dependence of $K_0$ on $Mn^{ost}$ exists among the low-Mn mafic granulite gneisses and the relatively high-Mn iron-formations of the Kelly area (Dahl, in preparation). Thus, to obtain a temperature estimate for the Kelly area, it is necessary to choose only $K_0$ values that correspond to the range of Mn contained in Räheim and Green’s experimentally-derived garnets. Accordingly, $K_0$ values of 5.5 (core) and 6.6 (rim) were chosen; they yield respective temperature estimates of 700°C and 660°C (assuming $P_L = 8$ kbar) for the Kelly area.

A second garnet-clinopyroxene geothermometer was calibrated empirically by Mysen and Heier (1972), using published analyses of low-Mn garnet-clinopyroxene pairs together with the published equilibration temperature for each assemblage. As noted by Räheim and Green, this approach depends on the validity of the $P_L$-$T$ estimates for the different metamorphic terrains, and most of these estimates carry large uncertainties. Secondly, the range of pressure estimates (6 to 36 kbar) is so large that, even if the pressure effect on $K_0$ is small, data over so large a pressure range probably cause some of the broad scatter observed in Mysen and Heier’s calibration. Thirdly, their calibration is based on chemical analyses of separated minerals, and the possibility of chemical zoning in these minerals adds uncertainty to estimated $K_0$ values. To allow for these three sources of error, Mysen and Heier place a ±60°C uncertainty on temperature estimates obtained by their method. The Mn-normalized core and rim $K_0$ values from the Kelly area, when referred to Mysen and Heier’s geothermometer, yield respective estimates of 790±60°C and 725±60°C. These estimates are significantly higher than those obtained by Räheim and Green’s method, which may in part reflect the high-pressure (mean ≈20 kbar) assemblages used in Mysen and Heier’s calibration. Indeed, Räheim and Green’s calibration of $K_0$ as a function of $P_L$ and $T$ shows that, for load pressures of 21 and 8 kbar, a $K_0$ value of 6.6 yields respective temperatures of 745°C and 655°C. This means that for the Kelly area ($P_L = 8$ kbar), temperatures estimated by the Mysen and Heier geothermometer are probably somewhat high.

The petrologic significance of core and rim temperature estimates remains to be resolved. Clinopyroxene (salite) and almandine in the mafic granulite gneisses of the Kelly area generally appear to be in textural equilibrium, but coronas of garnet-quartz symplectic in clinopyroxene grains in contact with plagioclase are not uncommon, as shown in Figure 3. This texture, along with zoning profiles in andesine, suggests that the overall garnet-forming reaction:

\[
\text{CaMg almandine} + \text{quartz} + \text{andesine(II)} \rightarrow \text{salite} + \text{andesine(I)}
\]

was in progress. Manna and Sen (1974) studied similar coronal garnets in granulite gneisses from Saltora, India, and concluded that the garnets formed from clinopyroxene during isobaric cooling of gabbroic
magma at great depth. Thus, the 660°C and 725°C estimates, which are based upon rim $K_0$ values, may represent the temperature of last equilibration between garnet and its parent clinopyroxene during isobaric cooling. A mean temperature of 690±35°C is reported in Table 2.

The petrologic significance of core compositions is ambiguous, because clinopyroxenes in the mafic granulite gneisses exhibit bell-shaped zoning profiles for the elements Na, Al, Fe, and Mg, whereas the garnets mantling these pyroxenes (see Fig. 3) are typically unzoned. The rims of these pyroxenes are depleted in Na, Al, and Fe and enriched in Mg relative to the cores (Dahl, 1977; Fig. 13). These profiles are consistent with the textural evidence that almandine in mafic gneisses formed at the expense of clinopyroxene. Prior to garnet growth, however, it is likely that the clinopyroxene was chemically homogeneous (as are pyroxenes in the iron-formations) and had a composition similar to the present core composition. It follows from the pyroxene zoning profiles described above that the first garnet grains to form would have equilibrated with clinopyroxenes whose rims were less depleted in Fe and less enriched in Mg than the present rims (i.e., the Fe/Mg ratio at the rims was once higher than that observed today). If this were the case at the time of first garnet growth, then the value of the rim $K_0$ (Fe/Mg; gar–cpx) must have been lower than it is now, indicating a temperature higher than that of final equilibration. Thus, the garnet–clinopyroxene core and rim “temperatures” may give a qualitative indication as to the direction of temperature change during garnet growth from clinopyroxene, but it cannot be stated that the core “temperature” represents peak metamorphic conditions. The uncertainty concerning this estimate is noted in Table 2 and Figure 2.

It should be possible to derive a metamorphic temperature estimate for the Carter Creek area, based on local occurrences of coexisting garnet and clinopyroxene. Garnet–clinopyroxene pairs in mafic gneisses from the Carter Creek area differ, however, from their Kelly area counterparts in that (1) both minerals are chemically unzoned (except in sample RMC-71, in which a prograde zoning profile is preserved in the garnet), (2) they are never found in a coronal relationship, (3) both are much more calcic, and (4) they exhibit significantly higher $K_0$ values (ca. 11.5; Dahl, in preparation). Dahl concluded that the higher $K_0$ values for the Carter Creek samples resulted from a combination of lower metamorphic temperature and the much higher calcium content of the garnets ($Ca^{10}$). Thus, comparison of Kelly and Carter Creek garnet–clinopyroxene pairs of approximately equal Mn content, combined with knowledge of the effect of $Ca^{10}$ on $K_0$ for amphibolite-facies rocks (Banno, 1970), permits a tentative peak temperature estimate of 665°C for the Carter Creek area. This estimate is concordant with other estimates of peak temperature for the area, as shown in Table 2 and Figure 2.

In summary, the temperature estimates obtained from garnet–clinopyroxene pairs are consistent with the other estimates given in Table 2 and shown in Figure 2. However, rigorous application of the available gar–cpx geothermometers is difficult for the reasons outlined above.

Garnet–hornblende

Coexisting garnet and hornblende are common in mafic gneisses from both the Kelly and Carter Creek areas. Saxena (1968) showed that $K_0$(Fe) for this mineral pair is a function of metamorphic grade. According to his empirical calibration, based upon published compositional data, garnet–hornblende pairs
in epidote-amphibolite-facies rocks have $K_D$ values of about 9.0, whereas in granulite-facies rocks, $K_D$ values of approximately 4.7 are typical. These calibration curves are shown in Figure 4, along with garnet-hornblende data from the Ruby Range. Three data points representing granulite-facies assemblages of the Kelly area plot directly on Saxena's curve for granulites. On the other hand, six data points representing the upper-amphibolite-facies assemblages of the Carter Creek area define a band that plots at somewhat lower grade than the granulite trend. Using $P_T$ boundaries assigned by Turner (1968, p. 366) for the various metamorphic facies, the granulite-facies trend defined in Figure 4 for the Kelly area is assigned a broad peak temperature range of $740 \pm 80^\circ C$. Similarly, the upper-amphibolite-facies trend of the Carter Creek samples corresponds to a peak temperature range of $645 \pm 70^\circ C$. These temperature ranges are concordant with other estimates given in Table 2 and Figure 2.

The trends in Figure 4 are based on core $K_D$ values. Rim compositions of both garnet and hornblende are slightly different from core compositions, and probably indicate incipient mass transfer of Fe and Mg between the two minerals, in response to declining temperatures of metamorphism. This conclusion is supported by antithetic compositional profiles in the two minerals and by the fact that rim $K_D$ values (not shown in Fig. 4) are invariably a little higher than the corresponding core values. Apparent retrograde (rim) temperatures are reported in Table 2.

**Garnet–biotite**

Coexisting garnet and biotite are common in pelitic rocks of the Kelly and Carter Creek areas. Values of $K_D(\text{Fe/Mg; gar–bi})$ for these rocks, and corresponding temperature estimates obtained from the theoretical geothermometer of Thompson (1976), are presented in Table 3 for both core and rim compositions. In most samples, temperatures based on core $K_D$ values are higher than those based on rim values, and mass transfer of Fe and Mg at garnet–biotite contacts is inferred on the basis of antithetic compositional profiles determined by the electron microprobe. Thus, core compositions probably reflect peak temperatures, and rim compositions reflect temperatures that were set during retrograde cooling. This
Table 3. Metamorphic temperature estimates based on core and rim values of $K_D(\text{Fe}/\text{Mg}; \text{gar-bi})$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rim</th>
<th>Core</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_D$</td>
<td>$T(\degree C)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kelly</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMK-511</td>
<td>4.53</td>
<td>620</td>
</tr>
<tr>
<td>RMK-512</td>
<td>4.31</td>
<td>640</td>
</tr>
<tr>
<td>RMK-66</td>
<td>4.26</td>
<td>640</td>
</tr>
<tr>
<td>RMK-127</td>
<td>5.96</td>
<td>543**</td>
</tr>
<tr>
<td>Carter</td>
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<td>RMC-30</td>
<td>5.46</td>
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<td>585</td>
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<tr>
<td>RMC-93</td>
<td>4.75</td>
<td>605</td>
</tr>
<tr>
<td>RMC-84</td>
<td>5.72</td>
<td>560</td>
</tr>
</tbody>
</table>

Temperatures are calculated from Thompson’s (1976) calibration. Approximate uncertainties are ±50\degree C.

* Prograde vs. retrograde zoning in garnet is figured from the criteria of Sturt (1962) -- n.a. = not analysed.

** Data from these samples are not figured into the average temperature estimates, as explained in the text.

Conclusion is supported by the criteria of Sturt (1962) for garnet zoning, namely, that garnets which contain more Ce+Mn and less Fe+Mg in their rims than in their cores exhibit retrograde zoning. The nature of garnet zoning in each sample is included in Table 3.

Thompson’s geothermometer yields mean peak estimates of 760±50\degree and 665±50\degree C for the Kelly and Carter Creek areas, respectively (±50\degree C is the uncertainty quoted by Thompson for the method). These estimates are concordant with peak estimates obtained by other methods, as indicated in Table 2. Samples RMK-127 and RMC-84 are not included in the averages because, in these samples, high $Mn^{\text{Gaz}}$ values appear to have contributed to high values of $K_D$, resulting in artificially low temperature estimates. The core $K_D$ of sample RMC-93 is also ignored, because garnet in this sample exhibits a prograde zoning profile, making it impossible for the core $K_D$ to represent peak metamorphic conditions.

K feldspar–plagioclase

Stormer (1975) calculated the $P-T$ dependence of albite distribution between coexisting alkali feldspar and plagioclase, using published Margules parameters for alkali feldspar (sanidine) and assuming ideal mixing in plagioclase. Strictly speaking, this geothermometer is applicable only to sanidine–plagioclase pairs, because it has been shown experimentally (Müller, 1971) that the albite content of alkali feldspar coexisting with plagioclase is highly dependent on its structural state. Alkali feldspar in meta-pelites from the Ruby Range occurs primarily as microcline, and application of Stormer’s geothermometer to microcline–plagioclase pairs in the Kelly and Carter Creek areas yields respective estimates of 675\degree (assuming $P_t=8$ kbar) and 620\degree C (assuming $P_t=6$ kbar). These temperatures, which are somewhat low compared to the consensus peak estimates given in Table 2 for the two areas, indicate that Stormer’s sanidine–plagioclase geothermometer should not be applied to microcline–plagioclase pairs.

Whitney and Stormer (1977) recalibrated the two-feldspar geothermometer using Margules parameters for microcline (instead of for sanidine). This new method yields much higher estimates of 790\degree and 700\degree C for the Kelly and Carter Creek areas, respectively. According to Whitney and Stormer, however, microcline is not stable at temperatures much in excess of 500\degree C, and where it is found in high-grade metamorphic rocks, it probably transformed from feldspar that originally crystallized as orthoclase. Furthermore, they state that temperature values for feldspars crystallizing as orthoclase would probably lie between those defined for sanidine and microcline. Therefore, I suggest that alkali feldspars in meta-pelites of the Ruby Range originally crystallized in the range 675–790\degree (i.e., 735 ± 60\degree C) and 620–700\degree C (i.e., 660 ± 40\degree C), respectively. These results are consistent with the consensus estimates reported in Table 2 and Figure 2.

Application of two-feldspar thermometry requires not only an accounting of feldspar structural state, but also consideration of an analytical difficulty, namely, chemical inhomogeneity of feldspars. Plagioclase in the Ruby Range meta-pelites usually exhibits weak normal zoning, and the coexisting K feldspar is commonly perthitic, with some parts of
the grains slightly more perthitic than others. It is not clear, therefore, which feldspar compositions were in equilibrium at peak metamorphic conditions. The temperatures reported above were calculated on the basis of bulk K feldspar compositions (determined by the mean of repeated cross-sectional analyses of perthitic grains) and plagioclase core compositions. Such a procedure yields maximum estimates of temperature.

**Garnet–cordierite**

Four garnet–cordierite pairs in one Mg-rich metapelite (sample RMK-98) from the Kelly area yield rim $K_p$ (Fe/Mg; gar–cd) values of 11.6. This $K_p$, when applied to the theoretical garnet–cordierite geothermometer of Thompson (1976), results in a final equilibrium temperature of $545 \pm 50^\circ C$ (uncertainty quoted by Thompson), which is significantly lower than the consensus peak estimate of $745 \pm 50^\circ C$. In thin section, undeformed cordierite grains containing sillimanite and kyanite fragments are found as coronas on moderately-fractured, Mg-rich almandine porphyroblasts. This texture suggests that cordierite formed in the continuous reaction:

$$\text{almandine} + \text{sillimanite (and kyanite)} + \text{quartz} \rightleftharpoons \text{cordierite} \quad (2)$$

Rims of almandine grains in sample RMK-98 are markedly depleted in Mg and enriched in Fe relative to the cores. This zoning is probably the result of chemical potential gradients induced by the crystallization of coronal cordierite.

According to the experimental work of Hensen and Green (1973), the above reaction is highly sensitive to changes in load pressure, with decreasing load pressure favoring the growth of cordierite. Furthermore, Hollister (1977) suggested that almandine–coronal cordierite textures may signify uplift events. For the Ruby Range, therefore, it is tentatively concluded that coronal cordierite formed from almandine in response to a decrease in load pressure, which occurred during Precambrian uplift and erosion following the high-grade metamorphism. The $545^\circ C$ garnet–cordierite temperature, then, must reflect thermal conditions at some time during the uplift event. The exact timing of this event is not clear; it could have occurred during the waning stages of the 2700 m.y. metamorphism, or during the subsequent greenschist–lower amphibolite-facies metamorphism ($1600 \text{ m.y.}, 670 \text{ m.y.}$).

Because reaction 2 has proceeded to the extent that only small fragments of almandine remain, it is not likely that the interiors reflect the composition of almandine at peak metamorphic conditions. Therefore, temperature estimates based on these compositions are of doubtful significance and are not figured into the consensus peak estimate for the Kelly area.

**Calcite–dolomite**

Sheppard and Schwarcz (1970) used the experimental carbonate solvus data of Goldsmith and Heard (1961) and Goldsmith and Newton (1969) to derive a least-squares expression for the temperature-dependence of Mg distribution between coexisting calcite and dolomite at $400^\circ C < T < 1075^\circ C$ and $P_L < 2 \text{ kbar}$. For $P_L = 10 \text{ kbar}$, the calculated solvus temperature is too high by about $25^\circ C$ (Goldsmith and Newton, 1969). Variable amounts of Fe$^{2+}$, Mn$^{2+}$, and Sr$^{2+}$ in calcites affect temperature estimates, but not at concentrations less than 1–2 mole percent (Sheppard and Schwarcz, 1970). For chemically unzoned, low Fe–Mn–Sr calcite–dolomite pairs in metadolomite sample RMK-136 (Kelly area), six pair analyses yield temperatures in the range $545 \pm 45^\circ C$. This estimate is far below the consensus peak estimate of $745 \pm 50^\circ C$, but is concordant with the garnet–cordierite temperature obtained from sample RMK-98. Carbonates are highly susceptible to recrystallization. Thus, it is possible that calcite and dolomite in sample RMK-136 underwent recrystallization (perhaps in response to a deformational pulse) during retrograde or subsequent low-grade metamorphism. Similar reasoning may explain a low calcite–dolomite temperature of $590^\circ C$ reported by Sheppard and Schwarcz for a granulite-facies metadolomite from the Grenville Province. However, these low temperature estimates may reflect inaccuracy in the original calibration as applied to high-grade rocks.

**Quartz–magnetite**

Oxygen isotopic compositions ($\delta^{18}O$) and calculated fractionations ($\Delta_{O-M}$) for coexisting quartz and magnetite are presented in Table 4 for six iron-formation samples from the Ruby Range. The calculated values of $\Delta_{O-M}$ for the Kelly samples are significantly less than those for the Carter Creek samples. The temperature-dependence of $\Delta_{O-M}$ was calibrated by Becker and Clayton (1976), using a combination of calculation and experimental mineral–water equilibrium data. Isotopic temperatures based upon their calibration fall in the ranges $530 \pm 15^\circ C$ (Kelly) and $475 \pm 25^\circ C$ (Carter Creek). These estimates are in good agreement with those calculated by the method of Bottinga and Javoy (1973) (see Table 2 and Fig.
Table 4. Oxygen isotopic compositions, fractionations, and temperatures for coexisting quartz and magnetite in iron-formations from the Ruby Range

<table>
<thead>
<tr>
<th>Locality</th>
<th>Sample</th>
<th>( \delta^{18}O_{\text{qtz}} ) (oo)</th>
<th>( \delta^{18}O_{\text{mag}} ) (oo)</th>
<th>( \lambda_{\text{Q-M}} )</th>
<th>Isotopic temp. (°C)</th>
<th>Isotopic temp. range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kelly</td>
<td>RMK-46</td>
<td>12.85 ± 0.12 (2)</td>
<td>4.35 ± 0.12 (2)</td>
<td>8.43 ± 0.17</td>
<td>528 ± 10</td>
<td>530 ± 15</td>
</tr>
<tr>
<td></td>
<td>RMX-60</td>
<td>11.05 ± 0.12 (2)</td>
<td>2.77 ± 0.12 (2)</td>
<td>8.23 ± 0.17</td>
<td>537 ± 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RMK-76</td>
<td>11.50 ± 0.12 (2)</td>
<td>2.84 ± 0.12 (2)</td>
<td>8.60 ± 0.17</td>
<td>520 ± 10</td>
<td></td>
</tr>
<tr>
<td>Carter Creek</td>
<td>RMC-37</td>
<td>17.74 ± 0.12 (2)</td>
<td>7.77 ± 0.12 (2)</td>
<td>9.85 ± 0.17</td>
<td>460 ± 10</td>
<td>475 ± 25</td>
</tr>
<tr>
<td></td>
<td>RMC-44</td>
<td>18.24 ± 0.12 (2)</td>
<td>8.94 ± 0.12 (2)</td>
<td>9.18 ± 0.17</td>
<td>495 ± 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RMC-135</td>
<td>18.99 ± 0.17 (1)</td>
<td>8.86 ± 0.12 (2)</td>
<td>9.99 ± 0.21</td>
<td>455 ± 10</td>
<td></td>
</tr>
</tbody>
</table>

Temperatures obtained from the calibration of Becker and Clayton (1976). Uncertainties listed reflect only those inherent in the corresponding fractionations (\( \lambda_{\text{Q-M}} \)). 95% confidence limits and number of runs (in parentheses) are indicated for each \( \delta^{18}O \) value. Low temperatures for samples RMC-37 and -135 may be due in part to fine magnetite grain sizes (mean 0.1 mm), compared to 0.6 mm for the other four samples.

2). Clearly, however, these temperatures must be regarded as poor indicators of peak metamorphic conditions, since they fall some 200°C below all other independent estimates. Mineralogical evidence is consistent with this conclusion. Specifically, meta-pegmites associated with the iron-formations indicate that \( P_{L-T} \) conditions of at least sillimanite–K feldspar–zone metamorphism were attained throughout the Ruby Range. The minimum thermal stability of sillimanite + K feldspar at \( P_L = 6 \) kbar is roughly 700–715°C at \( a_{H_{2}O} = 1 \) (Chatterjee and Johannes, 1974; Kerrick, 1972) and 630°C at \( a_{H_{2}O} = 0.25 \) (Wintsch, 1975). Thus, even if \( a_{H_{2}O} \) were as low as 0.25, the minimum peak temperature in the Ruby Range was approximately 630°C—far above the isotopic temperature. Furthermore, the common occurrences of the sub-assemblage garnet±clino.pyroxene±ortho.pyroxene in iron-formations and mafic gneisses of the Kelly area are clear indicators of granulite-facies metamorphism.

The low isotopic temperatures are probably the result of (1) solid-state diffusion of oxygen isotopes between quartz and magnetite during retrograde metamorphism, or (2) recrystallization of quartz and magnetite during retrograde or subsequent low-grade metamorphism. Alternatively, the low estimates point to errors at the high-temperature ends of published quartz–magnetite calibration curves. In the following discussion, however, it is assumed that these calibration curves are accurate and applicable to the Ruby Range iron-formations.

Let us first consider model (1), illustrated in Figure 5 for the Kelly area. During the sedimentary and diagenetic stages, equilibrium between quartz and magnetite was presumably maintained through mineral–water isotopic exchange with a common pore fluid. Continuous mineral–water isotopic re-equilibration, favored by fine quartz–magnetite grain sizes, probably took place in response to gradually increasing metamorphic temperatures. By the peak of metamorphism (745 ± 50°C in the Kelly area), quartz and magnetite were recrystallized into coarser grains (mean diameter 0.6 mm), and water was effectively removed by (1) the completion of dehydration reactions and (2) the diminution of pore space brought on by compaction and deformation. Temperatures were now probably high enough, however, for quartz–magnetite equilibrium to be maintained directly by solid-state diffusion of isotopes. This process probably maintained the equilibrium even as temperatures began to decline, at first keeping up with the change in temperature. But as temperatures decreased further, the kinetics of solid-state diffusion must have become increasingly less favorable, such that diffusion of isotopes slowed and eventually ceased, “freezing in” an apparent isotopic “temperature” of 530 ± 15°C in the Kelly area. Actual temperature continued to decline as the metamorphic event drew to a close.

Evidence in support of model (1) is provided by experimental diffusion data. Choudhury et al. (1965) studied the diffusion of oxygen in quartz at 667°C and determined diffusion coefficients (\( D \)) of \( 10^{-15} \) cm²/sec (perpendicular to the c axis) and
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If, as suggested by Clayton et al. (1968), quartz is among the most resistant of all minerals to isotopic exchange, then it follows that diffusion of oxygen in quartz is the rate-limiting factor in isotopic exchange with a coexisting mineral, such as magnetite. Thus, we can estimate the minimum exchange rate (i.e., the maximum transfer time) of oxygen between coexisting quartz and magnetite in terms of quartz diffusion data alone. If quartz and magnetite grains (0.6 mm mean diameter) were in isotopic equilibrium at 667°C, and temperature were then to drop 10°C very slowly, the maximum time required to effect isotopic re-equilibration would be roughly equal to the time required for oxygen to diffuse from the core of a quartz grain to the rim of an adjacent magnetite grain. This time, calculated from known grain sizes and the larger $D$ value given above, is approximately 1400 years.

Thus, if the retrograde cooling rate were no greater than 1°C per 140 years over the assumed 10°C interval, isotopic re-equilibration could keep pace with the temperature decrease. However, steadily decreasing diffusion rates over a larger temperature span would cause the diffusion to lag behind the temperature decrease and eventually cease entirely, as shown schematically in Figure 5. In the absence of diffusion data for quartz at temperatures other than 667°C, a more quantitative diffusion model cannot be presented. However, the above calculations indicate that in a regionally-metamorphosed terrain, retrograde cooling over hundreds of thousands of years could result in significant oxygen isotopic re-equilibration between quartz and magnetite.

In terms of model (1), the significantly higher temperatures preserved by ferromagnesian silicate pairs (Fig. 2) indicate that, during retrograde cooling, solid-state diffusion of Fe and Mg between these silicates was much more sluggish than oxygen diffusion between quartz and magnetite. This relationship is shown in Figure 5 by the dashed lines labelled “GAR-CPX-OPX” and “QTZ-MAG.” If the model is correct, then it follows that $D$ values for Fe and Mg in garnet, pyroxene, hornblende, and biotite at a given temperature are much lower than those for oxygen in quartz and magnetite. The test for this prediction awaits the experimental determination of Fe–Mg diffusion coefficients for the ferromagnesian silicates at various temperatures.

An alternative model to explain the low oxygen isotopic temperatures is illustrated in Figure 5 [model (2)]. According to this model, isotopic temperatures in the two areas may have been set originally near the peak of the high-grade metamorphic event (M1), but were subsequently reset by recrystallization of quartz and magnetite under retrograde conditions. Recrystallization may have occurred in response to a deformational pulse in the waning stages of the high-grade event, resulting in a higher retrograde temperature for the Kelly area than for the Carter Creek area. Alternatively, recrystallization in the two areas occurred during a subsequent low-grade event (M2), as discussed in earlier sections. Garnet, pyroxene, and other refractory silicates in the Kelly assemblages were perhaps more resistant to recrystallization than quartz and magnetite, and for this reason, they persisted as metastable relics that record the 745 ± 50°C peak temperature of the high-grade event. This selective recrystallization model is shown schematically in Figure 5 by the diverging
dashed lines labelled “GAR–CPX–OPX” and “QTZ–MAG.”

Support for model (2) comes from Wilson et al. (1970), who estimated peak metamorphic temperatures of 780°C for pyroxene granulites from the Musgrave Ranges, Central Australia. Post-metamorphic intrusion of the Ernabella Adamellite caused recrystallization of plagioclase, quartz, and magnetite in these granulites, resulting in quartz–magnetite and plagioclase–magnetite isotopic “temperatures” of around 550°C. Preservation of pyroxene at this temperature, however, suggests that this mineral did not recrystallize; dissolution of pyroxene at 550°C would most likely have culminated in amphibole crystallization.

Regardless of which of the two models in Figure 5 is applicable, it is noteworthy that re-equilibration of oxygen isotopes in the anhydrous Kelly iron-formation assemblages occurred despite the apparent lack of a fluid phase during retrograde metamorphism. Higher $P_{H_2O}$ in the Carter Creek iron-formation (evidenced by a much higher modal amphibole/pyroxene ratio) may have facilitated oxygen isotopic exchange down to lower retrograde temperatures than in the Kelly iron-formation. In addition, the lower temperatures may be due in part to finer magnetite grain sizes. In samples RMC-37 and RMC-135, the mean magnetite grain size is 0.1 mm, compared to 0.6 mm in sample RMC-44 and in the three Kelly samples. Retrograde effects in very fine-grained magnetites were also reported by Shieh and Taylor (1969). Quartz grain sizes in the six samples studied are relatively uniform, ranging from 0.5 to 1.0 mm.

Conclusions

Mineral-pair geothermometry (based on six different pairs) and the coexistence of sillimanite and K feldspar in meta-pelites indicate peak metamorphic temperatures of 745 ± 50°C and 675 ± 45°C for the Kelly and Carter Creek areas, respectively. These temperatures are consistent with the observed occurrences of orthopyroxene-zone and sillimanite–K feldspar-zone assemblages in the two areas. Furthermore, each mineral pair common to the two areas appears sensitive to the small metamorphic temperature difference inferred from mineral assemblages. The ±45–50°C uncertainty in temperature is determined from Figure 2 by defining the widest temperature range consistent with all the individual ranges shown for a given area. This uncertainty may help to define the limits of precision attainable for geothermometry in other high-grade terrains.

Concordant estimates of peak temperature are expected within a small area if (1) all geothermometers are accurately calibrated and applicable to the rocks in question, (2) all methods do in fact record peak conditions, (3) compositional and pressure effects on major-element and isotope distributions are negligible (or, if not, are taken into account), and (4) chemical equilibrium was approached during the exchange of species between coexisting minerals. The discordant estimates reported in Table 1 and Figure 2 indicate violation of one or more of these conditions. Orderly isotope distributions between quartz and magnetite (Table 4) suggest a close approach to chemical equilibrium [condition (4)]. Similarly, orderly element distributions between the rims of coexisting garnets and cordierites (in sample RMK-98) and between calcites and dolomites (in sample RMK-136) suggest attainment of equilibrium on a very local scale. Condition (3) is approximately satisfied, judging from the known chemistries of the mineral pairs and the known pressure effects on fractionation factors (Clayton et al., 1979) and distribution coefficients. With regard to condition (1), there is no guarantee that the geothermometers giving discordant results in Figure 2 are accurately calibrated for high-temperature applications. If the published calibrations are accepted at face value, however, then the bimodal discordance shown in Figure 2 must indicate that different geothermometers record different “temperatures” [i.e., condition (2) is violated].

Indeed, the interpretation of oxygen isotopic “temperatures,” for example, has long been a controversial subject. Some investigators (e.g., Taylor and Epstein, 1962, 1963; Taylor et al., 1963) have maintained that these temperatures represent nearly peak thermal conditions. Other workers (e.g., James and Clayton, 1962; Perry and Bonnichsen, 1966; Anderson et al., 1971; Swulius, 1976) have concluded that minerals re-equilibrate by exchange of oxygen isotopes during retrograde cooling, thereby “freezing in” temperatures that may be significantly lower than peak temperatures. Deines (1975) has stated that the thermal significance of oxygen isotopic temperatures remains to be resolved.

Isotopic data from the Ruby Range iron-formations support the re-equilibration hypotheses. Specifically, it is thought that resetting of quartz–magnetite temperatures occurred in response to (1) solid-state diffusion of oxygen between quartz and magnetite during retrograde metamorphism or (2) recrystallization of the two minerals during retrograde or subsequent low-grade metamorphism. Garnet, py-
roxene, hornblende, biotite, and feldspars were perhaps more resistant to diffusion of chemical species and/or to recrystallization, and therefore retained compositions indicative of near-peak thermal conditions. Recrystallization at low temperature may also explain the low calcite-dolomite temperature reported for the Kelly area.

The temperature of final equilibration recorded for garnet–cordierite pairs (545 ± 50°C) is some 200° lower than the consensus peak estimate for the Kelly area. Because Thompson’s (1976) geothermometer has been successfully applied in numerous high-grade terrains, however, the low estimate for the Kelly area is not thought to reflect major inaccuracies in his calibration. Instead, textural and chemical evidence suggests that cordierite in the Kelly area meta-pelites formed during retrograde metamorphism. The continuous reaction by which cordierite in the meta-pelites formed from garnet [reaction (2)] is favored by a decrease in load pressure, and could indicate a Precambrian uplift event post-dating the high-grade metamorphism. The concordant temperatures obtained from calcite-dolomite, quartz-magnetite, and garnet–cordierite pairs (ca. 545 ± 50°C) may represent thermal conditions at some time during this event.

The results reported in this paper may help to resolve the petrologic significance of geothermometric data for other high-grade terrains. However, generalities regarding the exchange of chemical species during metamorphic events may not be entirely valid, inasmuch as different fluid partial pressures, different cooling rates, and different superimpositions of thermal and deformational maxima combine to make each metamorphic terrain unique.

Acknowledgments

This work is part of a doctoral dissertation presented to Indiana University. I am most grateful to Professor C. Klein, Jr. for his critical reviews of earlier versions of the manuscript and for his help in interpretation of the results. Drs. H. L. James, D. G. Towell, D. B. Wenner, and R. P. Wintsch read an earlier version of the manuscript and made many helpful suggestions. Special thanks are due to Professor E. C. Perry, Jr. of Northern Illinois University for the use of his oxygen isotope laboratory. I thank Messrs. R. L. Purcell, J. Tolen, G. R. Ringer, H. N. Geizer, and W. B. Barber for drafting and photography, and Lynn V. Dahl and Susan McCauslin for typing of the manuscript.

Field and laboratory support for this study were provided by NSF grants DES-72-01665 and EAR 76-11740 to Professor Klein. The electron microprobe was obtained on NSF grant GA-37109 to Professor Klein, with joint funds from the Indiana University Foundation.

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Manuscript received, October 2, 1978; accepted for publication, June 26, 1979.