[AMERICAN JOURNAL OF SCIENCE, VOL. 282, JUNE, 1982, P. 886-919]

FLUID FLOW DURING METAMORPHISM AT THE BEAVER BROOK FOSSIL LOCALITY, NEW HAMPSHIRE

D. RUMBLE, III,* J.M. FERRY,**
T. C. HOERING,* and A. J. BOUCOT***

ABSTRACT. *Rocks at the Beaver Brook fossil locality were regionally metamorphosed at 3.5 kb and 600°C. Metamorphic fluids were water rich, $X_{H_2O} > 0.80$ (mole fraction), and contained variable amounts of CO_2 and CH_4 as controlled by the buffer capacity of different mineral assemblages in individual sedimentary beds. The minimum amount of fluid that flowed through the beds during metamorphism has been estimated using mineralogic and oxygen isotopic evidence. The mineralogic evidence is the extent to which decarbonation reactions have gone to completion as measured by petrographic modal analysis. The isotopic evidence is the inferred metamorphic change in the oxygen isotopic composition of fossil brachiopods. Fluid-rock ratios of 1.5 to 4.0 (minimum estimate, by volume) are obtained from the mineralogic evidence, and ratios of 4.0 to 6.0 from the isotopic evidence. The large amounts of fluid flow observed at Beaver Brook are believed to be a consequence of metamorphic decarbonation reactions. These reactions, not in themselves capable of producing the computed amounts of fluid, nevertheless, are responsible for enhancing permeability sufficiently so that fluid flow could occur.*

INTRODUCTION

An important chemical effect of metamorphism on a rock is to change its content of the volatile components H_2O and CO_2. Such changes require fluid flow between adjacent rocks and, ultimately, fluid flow from the deeply buried zone of active metamorphism to the Earth's surface. Evidence from rocks of fluid flow during metamorphism has not been commonly recognized. One possible explanation for this oversight is the concentration of petrologists on mineral reactions that buffer the composition of fluids within rocks during metamorphism. Such studies, however, are an essential groundwork for investigating fluid flow during metamorphism, because the extent to which buffer reactions have gone to completion records the volume of fluid that has flowed through rocks during a metamorphic event.

This report examines a number of lines of evidence for fluid flow during metamorphism through rocks exposed in the cascades of Beaver Brook on the slopes of Mount Moosilauke, N. H. The most important evidence is (1) the extent to which decarbonation reactions have gone to completion, as measured by petrographic modal analysis and (2) the inferred metamorphic change in ^{18}O content of fossil brachiopods. From each of the lines of evidence, it is possible to estimate the minimum, time-integrated flux of fluid through the rocks during the metamorphic

* Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C., 20008
** Department of Geology, Arizona State University, Tempe, Arizona, 85281
*** Department of Geology, Oregon State University, Corvallis, Oregon, 97331

episode. Results agree within an order of magnitude and indicate volumetric fluid-rock ratios of 1.5 to 6.0 during metamorphism. The results of this study agree with other recent investigations that show appreciable volumes of fluid involved in metamorphism (Ferry, 1980a; Bowman, Essene, and O'Neill, 1980).

The report begins with a description of the geology, petrography, geothermometry, and geobarometry of the Beaver Brook locality in order that the reader may evaluate the evidences for fluid flow in relation to the metamorphic history of the area. The presence of metamorphosed fossils in rocks of the locality is emphasized, because their occurrence constrains the rocks' isotopic composition prior to metamorphism, and the rocks' pre-metamorphism isotopic composition is a key element in documenting fluid flow through the rocks. The report next summarizes evidence for fluid flow through the rocks during metamorphism and presents estimates of the amounts of fluid involved. Finally the significance of the evidence is discussed in terms of a model of metamorphism that relates devolatization reactions, rock porosity, and rock permeability.

METHODS OF STUDY

Samples were collected using an ATLAS COPCO portable jack hammer equipped with a rock drilling bit and quarryman's tools (wedges and feathers). The sample traverses listed in table 1 and located on figure 2 were cut from single blocks of rock. Sample traverse AA consists of 5 2.5-cm diam polished thin sections distributed evenly along a 14 cm long line oriented perpendicular to sedimentary bedding. Thin section domains AA-4-1 and AA-4-2 are 2 to 3 mm in diam and are from two different rock layers in the same thin section. Sample traverse R is made up of 3 polished thin sections located along a line that is 8 cm long and is perpendicular to bedding. Thin section domains R-1-1-1 and R-1-1-2 are from the same thin section in which two different rock layers occur. Similarly, the pairs of domains (R-1-2-1 and R-1-2-2) and (R-1-3-2 and R-1-3-1) are from different rock layers in two thin sections. Sample traverse DD consists of 3 partly overlapping thin sections distributed along a 6.5 cm line oriented perpendicular to bedding. Sample domains DD-1-1, DD-1-2, and DD-1-3 are from different rock layers in the same thin section. Domain DD-1-2 is located along the contact between diopside-bearing calc-silicate and amphibolite. Domains DD-3-1 and DD-3-2 are from the same thin section. Sample traverse EE is made up of 3 thin sections along a 8 cm line oriented perpendicular to the contact between dike and wall rock. Domains EE-2-2 and EE-2-1 are from the same thin section and are located on opposite sides of the contact between anorthosite and diopsidic calc-silicate. The samples of each traverse are listed in table 1 in the order in which they occur along the line of traverse.

Chemical analyses of minerals were made with the automated MAC electron microprobe analyzer at the Geophysical Laboratory (Finger and Hadidiacos, 1972). Natural and synthetic carbonate and silicate minerals were used as analytical standards. The Bence-Albee correction scheme was used to calculate chemical compositions from X-ray intensity data

TABLE 1
Mineral assemblages, chemical and isotopic data

Traverse:	AA						R						DD					
Sample no.:	1	2	3	4-1	4-2	5	1-1-1	1-1-2	1-2-1	1-2-2	1-3-2	1-3-1	1-1	1-2	1-3	2	3-1	3-2
Rock type:	gcs(f)	gcs(f)	gcs	gcs	dcs	am	gcs(f)	dcs	dcs	gcs	dcs	am	dcs	dcs/am	am	dcs	am	dcs
Q*	14.3(1)	+	+	+	+	14.3(1)	14.9(2)	+	+	+	14.3(1)	+	+	+	+	+	+	+
Cc	+	+	+	+			+			+								
Wo							+											
Gt†	80(1)	80(2)	+	77(1)		44(1)	88(5)			86(1)								
Czo‡	66(2)	55(6)	+	64(2)	55(4)	56(4)		64(1)	60(4)	69(1)	58(2)		58(1)	60(3)	55(6)	56(3)		63(5)
Cpx§	76(4)	51(3)	+	50(1)	95(20)		86(1)	80(1)	80(5)	67(11)	122(16)		78(2)	116(5)		103(9)		90(4)
Amp§					49(3)	49(1)					75(3)	77(3)		58(4)	68(8)	59(3)	63(11)	49(1)
Pl‖					94(1)	94(1)		95(1)	94(1)		93(1)	94(1)	97(1)	93(1)	93(1)	94(2)	95(2)	94(1)
G		+	+	+	+	+		+	+	+	+	+	+	+	+	+	+	+
Sp	+	+	+	+	+	+		+	+	+	+	+	+	+	+	+	+	+
Po	+	+	+	+	+	+					+	+						
Mu**																		
Bi§																		
Kspt†																		
Il						+												
Rut																		
St																		
Si																		
WR††	11.8(1)					12.9(1)	12.0(2)				12.5(3)							

* Numerical entry is $\delta^{18}O_{SMOW}$; number in parentheses is 1 *esd* of least unit cited; "+" signifies mineral is present; blank means mineral is absent.

† Numerical entry is mol % grossular.

‡ Numerical entry is mol % $Ca_2Al_3Si_3O_{12}(OH) = (Al - 2)/(Fe + (Al - 2))$, in $Ca_2Al_3Si_3O_{12}(OH)$–$Ca_2FeAl_2Si_3O_{12}(OH)$ solid solution.

§ Numerical entry is Mg/Fe (atomic) × 100.

‖ Numerical entry is mol % $CaAl_2Si_2O_8$.

** Numerical entry is K/(K + Na) (atomic) × 100.

†† Numerical entry is mol % $KAlSi_3O_8$.

‡‡ Numerical entry is $\delta^{18}O_{SMOW}$ of whole rock.

Note: abbreviations given at bottom of table continuation.

Traverse:	EE				CG	M	N	QV	184	184A
Sample no.:	1	2-2	2-1	3						
Rock type:	an	an	dcs	dcs	Kqm	ms	ms	qv	ms	ms
Q*	14.2(1)	14.2(1)	+	14.4(1)	14.3(1)	14.6(1)	14.6(1)	13.8(2)	+	+
Cc										
Wo										
Gt†									+	
Czo‡	67(5)	53(9)	58(2)	57(4)						
Cpx§			91(1)	84(3)						
Amp§	16l(8)		68(10)	72(12)						
Pl‖	98(1)	93(4)	92(1)	96(1)	19(1)	+	83/67			
G	+	+	+	+	+					
Sp	+	+	+	+			+			
Po	+	+	+	+		+	+			
Mu**					95(1)				+	+
Bi§					47(1)	+	66(1)		+	+
Ksp††					87(1)					
Il						+	+		+	+
Rut									+	
St									+	+
Si										+
WR‡‡					13.0(1)	12.2(1)	12.8(1)		12.7(2)	13.2(1)

Rock type abbreviations: gcs, grossular calc-silicate; (f), fossil bearing; dcs, diopside calc-silicate; am, amphibolite; an, anorthosite; Kqm, Kinsman quartz monzonite; ms, mica schist; qv, quartz vein.

Mineral abbreviations: Q, quartz; Cc, calcite; Wo, wollastonite; Gt, garnet; Czo, clinozoisite; Cpx, clinopyroxene; Amp, amphibolite; Pl, plagioclase; G, graphite; Sp, sphene; Po, pyrrhotite; Mu, muscovite; Bi, biotite; Ksp, potash feldspar; Il, ilmenite; Rut, rutile; St, staurolite; Si, sillimanite.

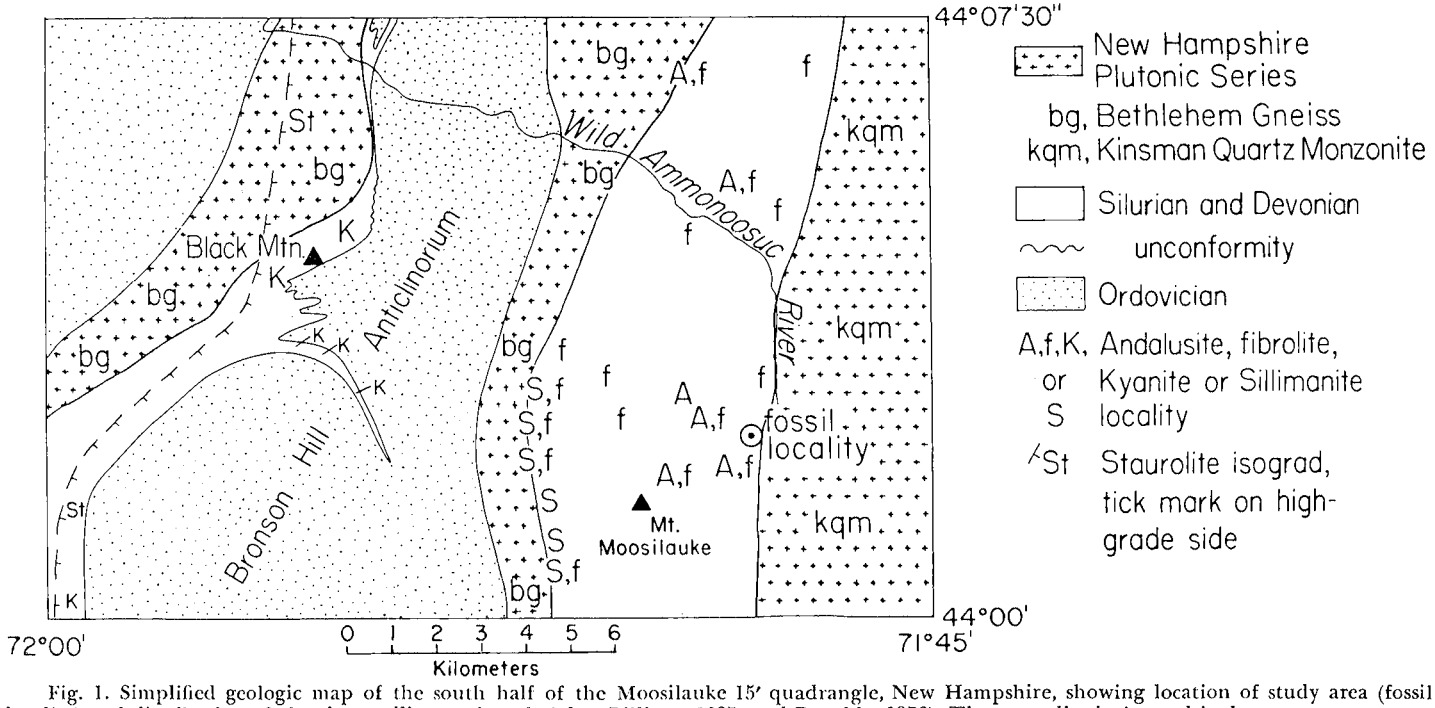

Fig. 1. Simplified geologic map of the south half of the Moosilauke 15′ quadrangle, New Hampshire, showing location of study area (fossil locality) and distribution of aluminum silicate minerals (after Billings, 1937; and Rumble, 1973). The staurolite-in isograd is shown.

(Bence and Albee, 1968; Albee and Ray, 1970). Analytical conditions were 15 Kv and 20 na sample current on benitoite. The size of domains in thin section chosen for analysis was 2 to 3 mm in diam, just large enough to include all the minerals of a given assemblage. The chemical analyses reported in table 1 are averages of 3 to 4 spot analyses of each mineral in each sample domain.

Thermodynamic calculations of P, T, and fluid phase composition were made according to the methods described by Ferry (1976). The thermodynamic modeling of mineral solid solutions and the thermodynamic data used in calculations are discussed in appendices 1 and 2. Methods of calculating oxygen isotope metasomatism are described in appendix 3.

Oxygen isotope analyses were made on minerals and whole rock powders from rock chips 4 to 8 cm^3 in volume. The location of samples for isotopic analysis corresponds closely to the location of samples prepared for microprobe analysis. The size of samples processed for isotopic analysis was kept as small as possible, so that the scale of isotopic measurements would be commensurate with the 2.5 cm diam, round polished thin sections used for microprobe analysis. Whole rock and mineral separates were analyzed using the BrF_5 technique of Clayton and Mayeda (1963). The $\delta^{18}O_{smow}$ value of National Bureau of Standards isotope reference material no. 28 equals 10.0 per mil according to the calibration adopted in this study (Friedman and Gleason, 1973).

Volumetric proportions of minerals in mineral assemblages were measured by counting 1000 points on a rectangular grid in thin section. Molar proportions of minerals were calculated from modal analyses and molar volume data (Robie, Bethke, and Beardsley, 1967) assuming linear volume-composition relations for solid solutions.

GEOLOGY AND PETROLOGY

The rocks of Beaver Brook were correlated by Billings (1937) with the Early Devonian Littleton Formation. Recent paleontologic assessment of fossils found at the locality (Boucot and Rumble, 1980) confirms the stratigraphic assignment. The contact between the Littleton Formation and the main pluton of the Kinsman Quartz Monzonite lies 200 m east of the fossil locality (fig. 1). The quartz monzonite has no contact aureole nor does it have a chill zone against its country rocks; moreover, the gneissic layering of the border of the pluton is parallel to schistosity in the country rock (Billings, 1937). Thus, the pluton was intruded either prior to or during regional metamorphism. A whole rock Rb-Sr isochron for the Kinsman yields an age of 411 ± 19 m.y. (Lyons and Livingston, 1977). Regional metamorphism of the area occurred during the interval 410 to 380 m.y. (Naylor, 1971). The radiometric ages support the geologic evidence that intrusion of the quartz monzonite took place before or during regional metamorphism.

The presence of primary muscovite and quartz in the main pluton of the quartz monzonite (as well as in the dike exposed at Beaver Brook, see fig. 2) suggests that the Kinsman was intruded and crystallized at a pres-

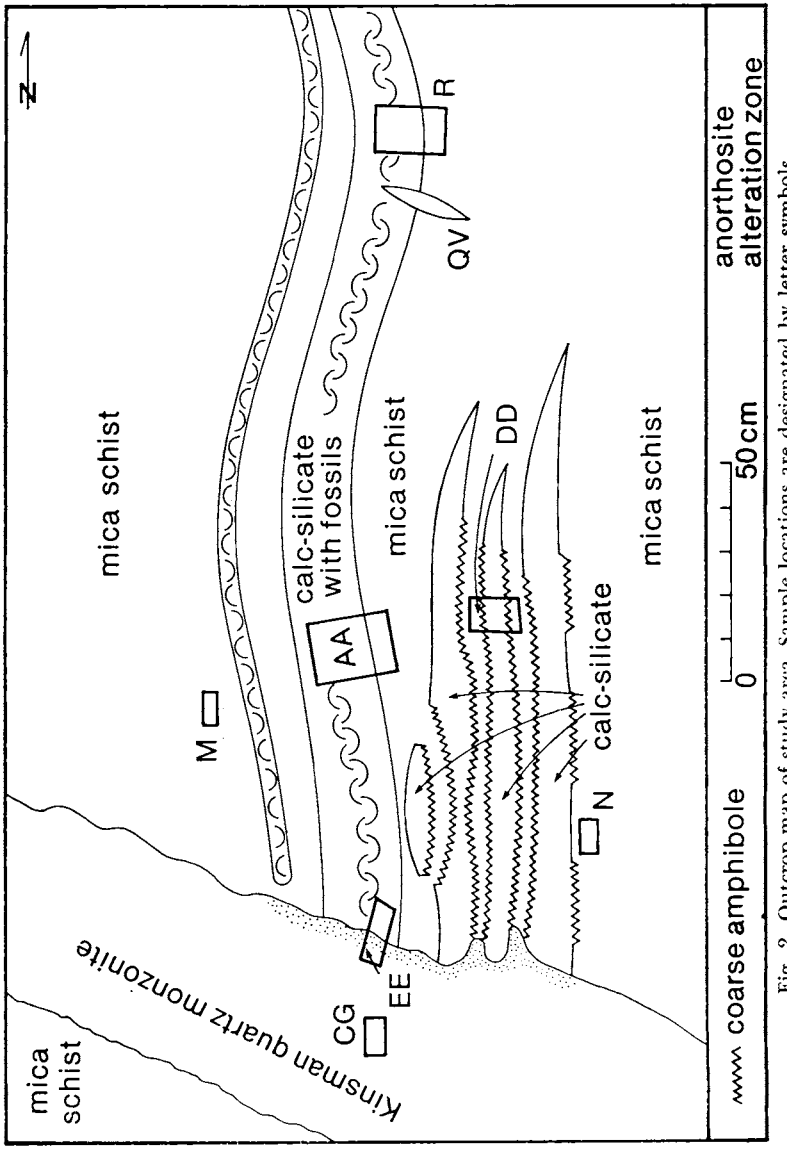

Fig. 2. Outcrop map of study area. Sample locations are designated by letter symbols.

sure greater than that of the intersection of the breakdown curve of muscovite + quartz and the minimum melting curve of granite. For $X_{H_2O} = 1.0$ the intersection is at 3.8 kb and 650°C, for $X_{H_2O} = 0.8$ the intersection is at 5 kb and 660°C (Kerrick, 1972, p. 954, fig. 5). Thus, it is likely that the Kinsman was intruded under P-T conditions not very different from those inferred for regional metamorphism. If this is true and if intrusion occurred during regional metamorphism, then it should not be surprising that no evidence of thermal effects of the intrusion on its wall rocks or of the wall rocks on the intrusion has been found. An hypothesis for the origin of the Kinsman Quartz Monzonite by Thompson and others (1968, p. 208) states that the pluton was derived from ignimbrites that were originally interstratified with Littleton sediments but were mobilized by partial fusion during regional metamorphism. Their hypothesis is consistent with evidence that suggests the Kinsman was emplaced during regional metamorphism. Accordingly, we assume that the Beaver Brook mineral assemblages and their oxygen isotopic composition reflect the influence of regional metamorphism, alone.

There is no evidence of repeated events of deformation and metamorphism such as refolded folds or secondary cleavage in the Beaver Brook rocks. It is necessary to consider the possibility of polyphase deformation and metamorphism, nevertheless, because it is known to have occurred in nearby areas (Rumble and Oertel, 1978; Thompson and others, 1968). In western New Hampshire, rocks of Early Devonian age were deformed and metamorphosed during the period 410 to 380 m.y. (Naylor, 1971). The events of polyphase metamorphism and deformation that did occur are all related in the sense that they are successive stages of a single orogenic episode including subsidence, sedimentation, metamorphism, and deformation — the Acadian orogeny. The methods we have used to measure fluid flow give the amounts of fluid integrated over the whole duration of Acadian regional metamorphism.

Four genera of Early Devonian brachiopods have been identified, including *Acrospirifer, Leptocoelia, Atrypa,* and either *Leptostrophia* or *Protoleptostrophia* (Boucot and Rumble, 1980). A high-spired gastropod of unidentifiable genus, similar to *Loxonema,* has also been found. The bed containing the fossils is 5 to 10 cm thick and is the innermost layer within a banded, tan or pink, calc-silicate unit (20 to 30 cm thick) which is interbedded with gray mica schist (fig. 2). Shells are aligned parallel to bedding, are disarticulated but unbroken and little sheared. The shells of the organisms are now composed of either quartz and calcite or wollastonite, calcite, and quartz; their impressions are made of grossular, diopside, clinozoisite, and sphene (table 1). Partial silicification of the shells probably took place during diagenesis, judged by the fact that silicified brachiopods are common in unmetamorphosed carbonate rocks (Moore, Lalicker, and Fischer, 1952, p. 5). Another possibility, that silica was deposited in the shells by aqueous solutions during metamorphism, cannot be proven or disproven. If it were possible to prove that silica was brought into the shells during metamorphism then synmetamorphic sil-

icification would be still another line of evidence for the flow of fluid during metamorphism. We have chosen the more "conservative" alternative and assumed that silicification occurred before metamorphism.

The center of the dike that truncates the fossil bed contains quartz, plagioclase (An_{19}), muscovite, biotite, potash feldspar, and graphite; thus, it is similar to the Kinsman Quartz Monzonite (fig. 2 and table 1). The margin of the dike has been altered to anorthosite containing plagioclase, An_{95}, everywhere it is in contact with calc-silicate. There is no alteration of the dike where it cross-cuts mica schist (fig. 2 and table 1). The grains of anorthite in the anorthosite zone are pseudomorphs of quartz plus An_{95} after primary microcline and oligoclase (An_{19}). The composition of the anorthite in the anorthosite zone is the same as that in calc-silicate rocks in contact with the anorthosite. It is concluded that the dike rock was intruded prior to metamorphism and that the anorthosite zone formed during metamorphism.

ATTAINMENT OF CHEMICAL AND ISOTOPIC EQUILIBRIUM

Calculations of the intensive parameters of metamorphism such as P, T, and fluid composition assume that observed mineral assemblages were in chemical equilibrium at a given time under conditions of deep burial. Evidence discussed in this section shows that mineral assemblages tended toward attainment of chemical and oxygen isotopic equilibrium during metamorphism.

Textures of the metasedimentary rocks show evidence of the attainment of equilibrium in a single episode of deformation and recrystallization. There are no reaction selvages at the points of contact between adjacent grains of different minerals; there are no minerals that rim or appear to replace other minerals; and there is no secondary cleavage. Grains of a given mineral are of uniform size. Grain boundaries are smooth, and where the boundaries of three grains of the same mineral intersect their angles of intersection are approx 120°. Textures of the metamorphosed quartz monzonite stand in contrast to those of the metasedimentary rocks. Grains of the same mineral in the dike are unequal in grain size. Furthermore, there are myrmeketic intergrowths of anorthite and quartz in the anorthosite that are pseudomorphs after oligoclase and microcline.

Chemical evidence suggests that there was a tendency for minerals to achieve homogeneous and heterogeneous equilibrium on a scale of 2 to 3 mm. Inspection of table 1 shows that most minerals in each thin section domain are homogeneous, judged by the criteria that the estimated standard deviations (esd) of inhomogeneous minerals are greater than 5 percent of the average values of chemical parameters reported in the table. Plagioclase, muscovite, biotite, and potash feldspar in all samples are homogeneous. Of 6 analyzed garnets, only 1 is inhomogeneous; of 15 clinopyroxenes, 5 are inhomogeneous; of 12 amphiboles, 6 are inhomogeneous; and of 18 clinozoisites, 9 are inhomogeneous. Even the most inhomogeneous minerals are not strongly so. Garnet R-1-1-1, for example,

shows the following chemical variation: total Fe as FeO 2 to 5 wt percent, Al_2O_3 20 to 22 wt percent, and CaO 35 to 37 wt percent. In clinozoisite AA-2, total Fe as FeO varies 6.2 to 7.7 wt percent and Al_2O_3 28.5 to 26.8 wt percent. Similarly, the major elements of clinopyroxene AA-4-2 and amphibole EE-3 vary 3 to 5 wt percent. The effects of the numerical uncertainty in mineral composition caused by inhomogeneity have been evaluated by propagating the uncertainties through the calculations of metamorphic temperature. An uncertainty of ± 30°C in metamorphic T is due to inhomogeneity, as shown by the maximum length of error bars in figure 5.

Evidence of the attainment of heterogeneous cation exchange equilibrium is given in figure 3. It may be seen that there is a tendency toward a uniform value for K_D for average compositions of mineral pairs. Additional confirmation of the hypothesis of chemical equilibrium comes from the recognition that there are neither reaction relationships nor crossing tie-lines between mineral assemblages at Beaver Brook (compare Greenwood, 1967a). For example, the plagioclase and amphibole-bearing assemblages cannot be made isochemically from the calc-silicate assemblages (table 1).

The uniformity of oxygen isotopic analyses of quartz separated from rock types cropping out at the fossil locality suggests that oxygen isotopic equilibrium was attained between different rock types and over distances of several meters (table 1 and fig. 4). The mean value of quartz from Beaver Brook is $\delta^{18}O_{smow} = +14.4 \pm 0.2$ per mil. Such a high degree of

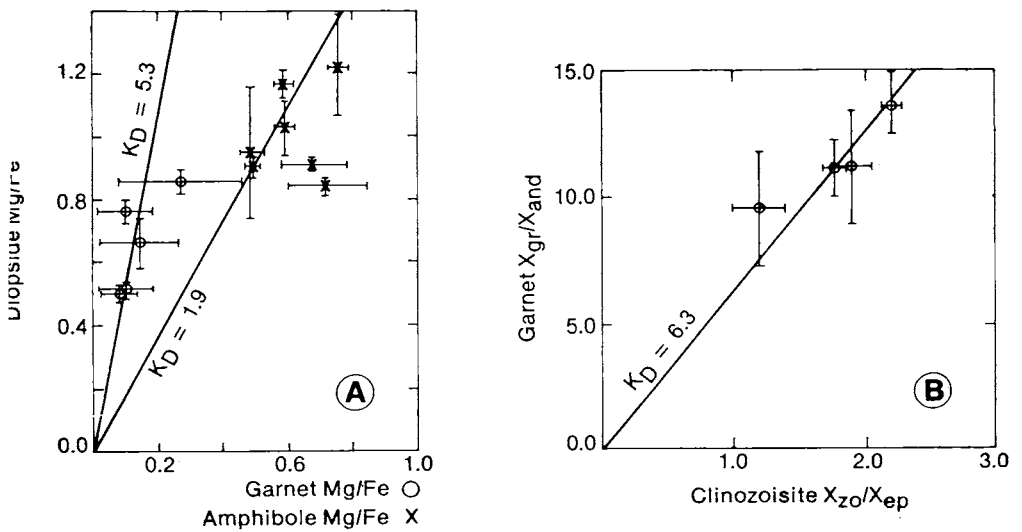

Fig. 3. Exchange equilibrium diagrams. (A) shows Fe/Mg partitioning between diopside, garnet, and amphibole. (B) shows partitioning of Fe^{3+} and Al between clinozoisite and garnet. X_{gr} is the gram formula weight (gfw) fraction of $Ca_3Al_2Si_3O_{12}$ in garnet. X_{and} is the gfw fraction of $Ca_3Fe^{3+}Si_3O_{12}$ in garnet. X_{zo} is the gfw fraction of $Ca_2Al_3Si_3O_{12}(OH)$ in clinozoisite. X_{ep} is the gfw fraction of $Ca_2Fe^{3+}Al_2Si_3O_{12}(OH)$ in clinozoisite. Horizontal and vertical lines through data points have lengths equal to 2 times estimated standard deviation.

homogeneity is all the more remarkable, when it is considered that quartz from the dike and quartz from the fossil shells may have differed by as much as 12.0 per mil prior to metamorphism. Muscovite-bearing granitic rocks, such as the dike rock, typically have whole rock values of +10 to 14 per mil with quartz 1 to 2 per mil higher than whole rock values (Taylor, 1977). Quartz from unmetamorphosed, silicified Devonian brachiopods similar to those at Beaver Brook gives a value of 24.0 ± 2.8 per mil (Savin and Epstein, 1970). The hypothesis that oxygen isotopic equilibrium was attained between minerals during metamorphism at Beaver Brook can be tested by comparing the computed versus measured $\delta^{18}O$ whole rock values listed in table 2. Whole rock values were computed assuming isotopic equilibrium was achieved at 600°C and using the measured $\delta^{18}O$ of quartz, the measured modal abundances of minerals, the ^{18}O fractionation curves of Friedman and O'Neill (1977) and the equation

$$\delta^{18}O_{(\text{whole rock})} = \sum_i X_i \delta^{18}O_i$$

(Craig, 1953, p. 87). In the equation, X_i is the atomic fraction of oxygen

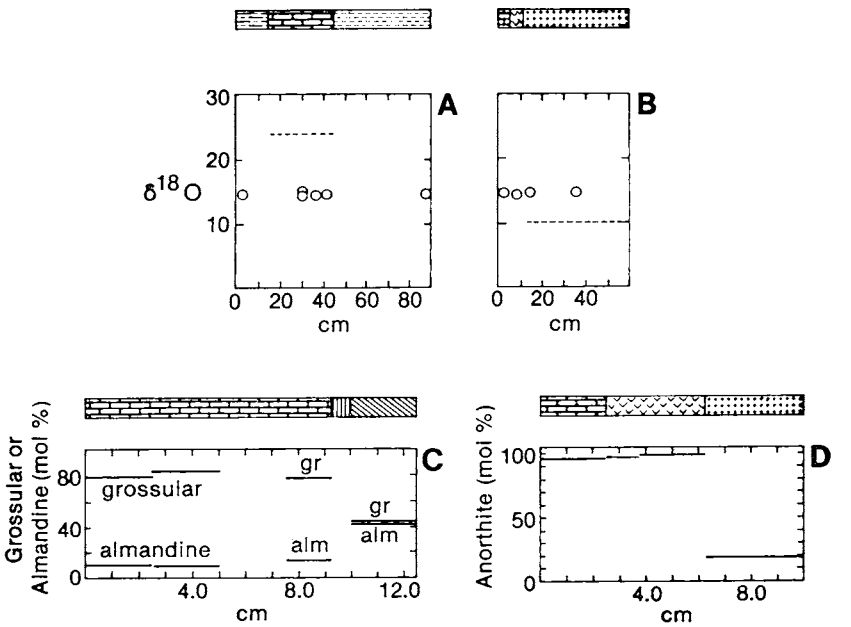

Fig. 4. (A) shows $\delta^{18}O$ values versus distance perpendicular to bedding for traverses AA and R, combined, and samples M and N. Circles show measured data points. Dashed lines give inferred pre-metamorphic isotopic composition. The dashed pattern denotes mica schist, the brick work calc-silicate. (B) is a plot of $\delta^{18}O$ values versus distance perpendicular to the dike/country rock contact for traverse EE and sample CG. The "V" pattern is anorthosite; the "+" pattern is Kinsman quartz monzonite. (C) is a plot of garnet composition versus distance perpendicular to bedding for traverse AA. The vertical ruled pattern is non-garnetiferous calc-silicate, the diagonal ruled pattern is amphibolite. (D) is a plot of plagioclase composition versus distance perpendicular to the dike/country rock contact for traverse EE and sample CG.

TABLE 2
Estimated temperature, fluid composition, and fluid/rock

Traverse:	AA					R			DD			EE		CG
Sample no.:	1	2	4-1	4-2	5	1-1-1	1-2-2	1-3-2	1-2	2	3-2	2-1	3	
Rock type:	gcs(f)	gcs(f)	gcs	dcs	am	gcs(f)	gcs	dcs	dcs/am	dcs	dcs	dcs	dcs	Kqm
Temperature, °C	≤590	≤610	≤590	625-612	617-610		≤585	590-575	604-592	607-595	604-593	568-555	582-562	509-529
Fluid composition (at 600°C)														
X_{H_2O} (mol %)	81	82	80	85-81	85-81	91-84	82	85-81	85-81	85-81	85-81	85-81	85-81	57-85
X_{CO_2} (mol %)	16	14	17	7-16	7-16	9	14	7-16	7-16	7-16	7-16	7-16	7-16	
X_{CH_4} (mol %)	3	4	3	8-3	8-3	0-7	4	8-3	8-3	8-3	8-3	8-3	8-3	
Fluid/rock in atoms of O {in cm^3}														
$\delta^{18}O$: infiltration*	4{6}	4{6}				3{5}								2-3 {3-5}
Modal analysis†	0.7{1.5}	1{2}				2{4}								
Fluid mixing‡														2{3}
Calculated [vs. measured]														
$\delta^{18}O_{quartz}$ (‰)	14.5[14.3]	14.5				14.9[14.9]								14.1 [14.3]
$\delta^{18}O_{whole\ rock}$ (‰)	12.6[11.8]	12.6				12.4[12.0]								13.3 [13.0]

* Calculated according to method of app. 3.
† Calculated according to method of J. M. Ferry (1980b).
‡ See text.

in mineral "i" relative to the total number of oxygen atoms in the whole rock, and $\delta^{18}O_i$ is the oxygen isotopic composition of mineral "i." Calculated values of $\delta^{18}O$ (whole rock) at 600°C agree, within 0.3 to 0.6 per mil, with measured whole rock values (table 2). Computations at other temperatures give poorer agreement. For a constant $\delta^{18}O$ value of quartz (the measured value) calculated whole rock values decrease 0.5 to 1.0 per mil for a decrease in T of 100°C. The agreement between calculated and measured $\delta^{18}O$ whole rock values at 600°C and their poorer agreement at other temperatures supports the hypothesis that oxygen isotopic equilibrium between minerals was attained during metamorphism at Beaver Brook.

Chemical equilibrium and oxygen isotopic equilibrium were achieved on markedly different scales during metamorphism at Beaver Brook. The distance over which equilibrium between chemical components of minerals occurred was limited to a few millimeters. Plots of mineral composition versus distance for two traverses (fig. 4, C and D) show that substantial differences in mineral composition between different rock types persist across distances of a few millimeters. In contrast, $\delta^{18}O$ values of quartz are uniform over distances of several meters (fig. 4, A and B).

GEOBAROMETRY/GEOTHERMOMETRY

The pressure from which the Beaver Brook rocks were quenched is estimated to have been 3.5 ± 0.3 kb. Inspection of figure 1 shows that the fossil occurrence is located in the andalusite + fibrolite zone, 8 km east of the nearest kyanite outcrops and 3 km east of the outcrop trace of the isobar of the Al_2SiO_5 invariant point (Thompson and Norton, 1968; Rumble, 1973). Pressure could not have been much less than that of the invariant point during metamorphism because the fossil locality is close to the outcrop trace of the invariant point isobar. Experimentally determined coordinates of the invariant point are 5.5 kb at 622°C (Richardson, Gilbert, and Bell, 1969) and 3.8 kb at 500°C (Holdaway, 1971). We chose to assume a P during metamorphism of 3.5 kb, consistent with the experimental determination of Holdaway (1971). A choice of higher P, consistent with the measurements of Richardson, Gilbert, and Bell (1969) does not materially affect our conclusions. Increasing P from 3.5 to 4.5 kb results in an increase of estimated metamorphic T from 600° to 635°C; estimated fluid compositions are changed by 1 to 2 mol percent.

The temperature at which the Beaver Brook rocks were quenched is calculated to have been 600° ± 40°C. The mineral assemblages used to calculate T are quartz–clinozoisite–plagioclase–grossular (sample AA-5) and quartz–clinozoisite–amphibole–diopside–plagioclase (sample AA-4, DD-1, DD-2, DD-3, EE-2, EE-3, R-1-3). Conditions of $P_{CO_2} + P_{H_2O} = P =$ 3500 bars were assumed. Addition of 10 mol percent CH_4 to fluid lowers estimated temperature by 8°C, an amount taken into account in the stated uncertainty of the T estimate. Thermochemical data and equations used were those compiled by Ferry (1976). A discussion of alternative thermochemical data bases is presented in appendix 2. Mineral equilibria were corrected for solid solution effects as outlined in appendix 1.

The ubiquity of clinozoisite indicates that metamorphic fluids were H_2O-rich at 3.5 kb in the T range of 500° to 675°C (Kerrick and Ghent, 1979). Dehydration equilibria, such as those represented by the two assemblages listed above, are useful geothermometers because the temperature of equilibrium at 3.5 kb changes very little as a function of fluid composition at high X_{H_2O} (compare fig. 5). Specifically, the maximum temperature limit of the assemblage quartz–clinozoisite–amphibole–diopside–plagioclase, corrected for solid solution effects (app. 1), is 605° ± 25°C, the temperature at which these minerals are in equilibrium with pure H_2O (fig. 5A). The minimum temperature limit of the assemblage is 595° ± 25°C, the temperature at which clinozoisite in the assemblage would react with CO_2 in fluid to form anorthite + calcite + H_2O (fig. 5A). The maximum and minimum T limits of the assemblage quartz–clinozoisite–plagioclase–grossular, using similar reasoning and correcting for non-ideality in garnet solid solution (see app. 1), are 620°C and 610° (fig. 5B). Although it is not a useful geothermometer in H_2O-rich fluids, the assemblage quartz–calcite–clinozoisite–grossular does require a maximum temperature limit of 595°C during metamorphism at the sample locality (fig. 5C).

The compositions of coexisting microcline and plagioclase in the quartz monzonite give temperatures of 529°C at 3.5 kb according to the microcline-low albite geothermometer of Whitney and Stormer (1977, p. 688) and Ferry (1978, p. 1047) and 509°C according to the sanidine-plagioclase geothermometer (Stormer, 1975) as modified by S. W. Lonker (ms) using the thermodynamic data of Thompson and Hovis (1979). It has

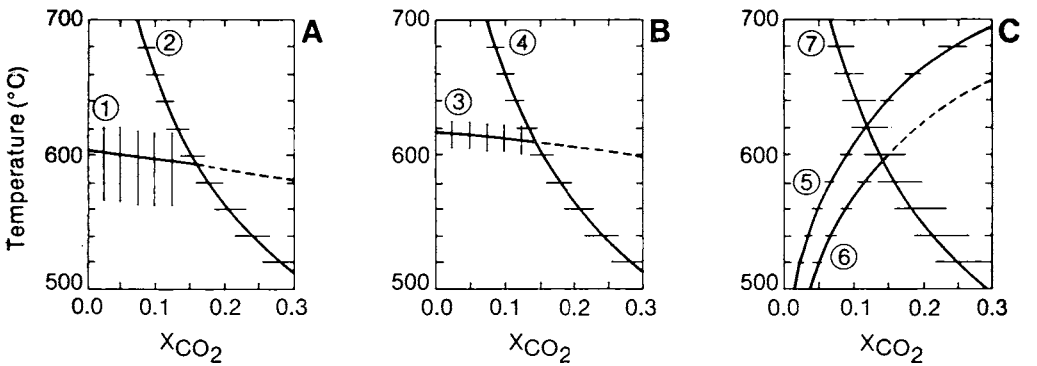

Fig. 5. T-X_{CO_2} diagrams at 3.5 kb. The positions of equilibrium curves (heavy lines) were computed from average values of the equilibrium constants for solid reactants and products (K_s) of the assemblages listed below. Corrections for solid solution effects are explained in app. 1. The short horizontal and vertical lines show the uncertainty in location of the equilibrium curves for a range of 2σ about the average value of K_s. In (A), equilibrium 1 is Amp + 6Czo + 2Q = 5Cpx + 9Pl + $4H_2O$, and equilibrium 2 is 2Czo + CO_2 = 3Pl + Cc + H_2O (samples AA-4-2, R-1-3-2, DD-1-2, DD-2, DD-3-2, EE-2-1, and EE-3). (B) shows equilibrium 3, 4Czo + Q = 5Pl + Gt + $2H_2O$ and equilibrium 4, 2Czo + CO_2 = 3Pl + Cc + H_2O (sample AA-5). In (C), equilibrium 5 is Cc + Q = Wo + CO_2 (sample R-1-1-1). Equilibrium 6 is 2Czo + 5Cc + 3Q = 3Gt + $5CO_2$ + H_2O, and equilibrium 7 is 2Czo + CO_2 = 3Pl + Cc + H_2O (samples AA-1, AA-2, AA-4-1, and R-1-2-2). Mineral abbreviations given in table 1. Dashed lines are metastable extensions.

been noted in other studies of amphibolite facies metamorphic rocks that the two-feldspar geothermometer yields lower T estimates than other geothermometers (compare Thompson, 1975; Thompson, Lyttle, and Thompson, 1977; Ferry, 1980b). Possible causes for the discrepancy are discussed by Ferry (1980b).

FLUID COMPOSITIONS

Compositions of fluids in equilibrium with mineral assemblages present during metamorphism in Beaver Brook rocks were calculated from expressions of Ohmoto and Kerrick (1977) and Ferry (1976) and with the assumption of ideal mixing of components in the fluids. Calculations were performed for conditions of P = 3.5 kb and T = 600°C; mineral equilibria were corrected for solid solution effects as outlined in app. 1. Uncertainties in P-T estimates lead to small uncertainties in calculated fluid compositions. Recalculation of fluid compositions at 4.5 kb and 635°C results in changes of 1 to 2 mol percent in the content of H_2O, CO_2, and CH_4.

The elemental and species compositions of fluids recorded by various assemblages at Beaver Brook differ by small but measurable amounts. As noted above, the ubiquity of clinozoisite requires metamorphic fluids to have been H_2O-rich. Decarbonation equilibria are useful monitors of fluid compositions for H_2O-rich fluids, because temperature has a small effect on equilibrium fluid compositions at high X_{H_2O} (fig. 5C). The assemblage quartz–calcite–grossular–clinozoisite–graphite (samples AA-1, AA-2, AA-4-1, R-1-2-2) was in equilibrium with a fluid of composition $X_{H_2O} = 0.81$, $X_{CO_2} = 0.15$, and $X_{CH_4} = 0.04$ (figs. 5C, 6). Calculations on which figure 6 is based show that other C-H-O fluid species occurred in negligible concentrations ($X_i < 0.01$). The assemblage quartz–calcite–wollastonite (R-1-1-1) records equilibrium with a fluid of $X_{CO_2} = 0.09$ (fig. 5C). Although there is no graphite in R-1-1-1 to uniquely define X_{H_2O} and X_{CH_4}, these fluid constituents must have been in the range $X_{H_2O} = 0.84$-0.91 and $X_{CH_4} = 0.0$-0.07 (figs. 5C and 6).

Dehydration equilibria are poor monitors of fluid composition in H_2O-rich fluids, because temperature and solid solution effects have a large effect on calculated equilibrium fluid compositions at X_{H_2O}. Despite the difficulty of directly obtaining reliable estimates of fluid composition from dehydration reactions, it is nevertheless possible to establish narrow limits on fluid compositions from related equilibria. All samples of the assemblage quartz–clinozoisite–diopside–amphibole–plagioclase contain graphite (AA-4, DD-1, DD-2, DD-3, EE-2, EE-3, R-1-3-2). Fluids in equilibrium with this assemblage lie on the graphite saturation surface of figure 6 and are characterized by $X_{H_2O} < 0.84$. The lower limit of X_{H_2O} for this assemblage is 0.81, the fluid composition at which clinozoisite reacts with C-O-H fluids in equilibrium with graphite to form anorthite + calcite (fig. 6).

The composition of fluid in equilibrium with the quartz monzonite dike is constrained by:

1. the presence of graphite in the dike;
2. the occurrence of muscovite + quartz instead of sillimanite + K-feldspar.

These constraints require that the fluid had a composition in the range $0.84 > X_{H_2O} > 0.57$.

Measurable differences in fluid composition persisted during metamorphism at the Beaver Brook locality over distances of a centimeter (table 2). Along sample traverse R, for example, the assemblage quartz–calcite–wollastonite records $X_{CO_2} = 0.09$ (R-1-1-1), whereas the assemblage quartz–calcite–clinozoisite–grossular records $X_{CO_2} = 0.14$ (R-1-2-2) (figs. 5C and 6). Fluid compositions estimated from dehydration equilibria in the rocks in contact with the bed of fossils have X_{H_2O} in the range 0.81 to 0.84, but the exact composition of fluid in equilibrium with individual samples cannot be calculated precisely. Equilibration between chemical

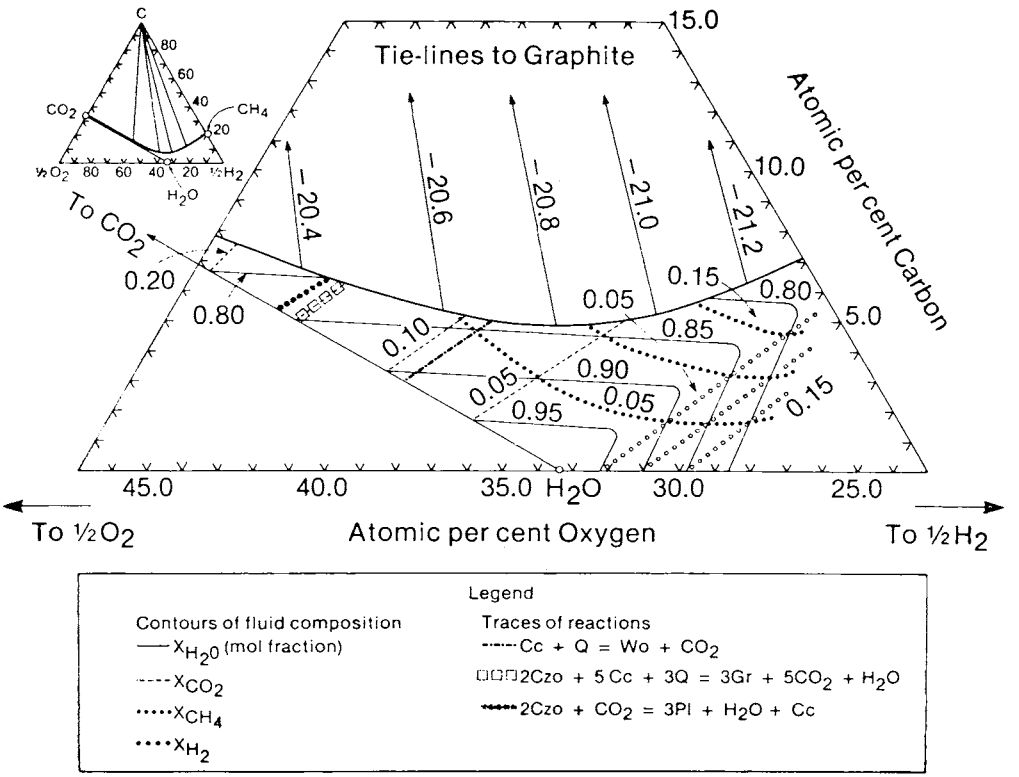

Fig. 6. Phase diagram of the system C–O–H at 3.5 kb, 600°C. The small triangle shows the entire C–O–H diagram. The heavy line is the graphite saturation curve, and the straight lines from it to the graphite corner are two phase tie-lines. The large trapezoidal diagram is an enlargement of the H_2O-rich region. Contours of fluid composition are drawn in the one-phase fluid field. Tie-lines labeled with log f_{O_2} are shown in the two-phase, graphite-fluid region. The traces of three decarbonation or combined decarbonation/dehydration reactions are given. Dehydration reactions lie parallel to contours of X_{H_2O}. Average compositions of mineral solid solutions were used to plot the positions of metamorphic reactions.

components of minerals was limited to distances of a few millimeters (see above). The equilibration of chemical species in fluid, likewise, was limited to distances of a few centimeters, as controlled by the buffer capacity of different mineral assemblages. In a later section of this paper, the measured extent of reaction progress of buffer reactions is used to estimate the amount of fluid that flowed through buffer assemblages.

Calculations of fluid compositions rest on two separate sets of data: (1) chemical analyses of minerals and (2) thermodynamic data for end-member components and solid solution models of the minerals. Each of these data sets has its own characteristic uncertainties that affect numerical results in different ways (app. 2). It is desirable to test the validity of calculations of fluid composition by using a method of data analysis that is independent of thermodynamic data and independent of P-T estimates. The method of Korzhinskii (1959) has been used to construct a μH_2O versus μCO_2 diagram from average measured mineral compositions in different assemblages. Although nine phases in the 9 component system SiO_2-Al_2O_3-Fe_2O_3-FeO-MgO-CaO-Na_2O-CO_2-H_2O are represented, only 4 different curves emanate from the invariant point because of the compositionally degenerate reaction quartz + calcite = wollastonite + CO_2. The diagram is intended to show graphically how 3 of the most common mineral assemblages at Beaver Brook are related to each other by additions or subtractions of H_2O and CO_2. The algebraic analysis of mineral composition space upon which figure 7 is based was carried out with the FORTRAN program REACTION (Finger and Burt, 1972). It may be seen that the results of thermodynamic calculations of fluid composition are consistent with figure 7; the assemblage quartz–calcite–clinozoisite–grossular–diopside–graphite plots at higher μCO_2 than does quartz–calcite–wollastonite. The assemblage quartz–clinozoisite–amphibole–diopside–plagioclase–graphite overlaps the stability fields of both calc-silicate assemblages.

EVIDENCE FOR FLUID FLOW DURING METAMORPHISM

There are mineralogic and oxygen isotopic data that are evidence for fluid flow during metamorphism of the Beaver Brook rocks. The mineralogic data include quenched decarbonation reactions in calc-silicate rocks, the presence of graphite in the quartz monzonite, and the development of an anorthosite zone in the dike at its contact with calc-silicate rock. The isotopic data are both the low $\delta^{18}O$ values of the fossiliferous beds and the high $\delta^{18}O$ values of the quartz monzonite dike. It should be kept in mind that the methods used to measure the time-integrated volume of fluid flow are only sensitive to those fluids that interact chemically or isotopically with rock. The calculated values of fluid-rock ratio, therefore, are minimum estimates. The computed values of fluid-rock ratio discussed below are 1 to 3 orders of magnitude greater than the measured porosity of metamorphic rocks. Norton and Knapp's (1977) data suggest porosity is 5 percent or less. For this reason, the large amounts of fluid calculated to have interacted with Beaver Brook rocks must have flowed through them.

Decarbonation reactions.—In order to utilize quenched decarbonation reactions as evidence of fluid flow during metamorphism, two possible models of fluid behavior during metamorphism are first identified and discussed. One model of fluid behavior considers that small volumes of rock (for example, 100 cm^3) equilibrate *only* with fluid generated by devolatization reactions within the sample. A second model considers that small volumes of rock equilibrate with a fluid, part of which is derived internally from devolatization reactions and part of which is from sources external to the small rock volume. The first model will be called the "distillation model," and the second model the "infiltration model." These names were chosen in order to emphasize that the models used to investigate fluid flow petrographically are the same as the models used to compute oxygen isotope metasomatism (see app. 3).

The distillation model can be rejected for metamorphism at Beaver Brook because of the discrepancy between compositions of fluid generated within samples and the composition of fluid with which mineral equilibria indicate the specimens were in equilibrium. For example, domain

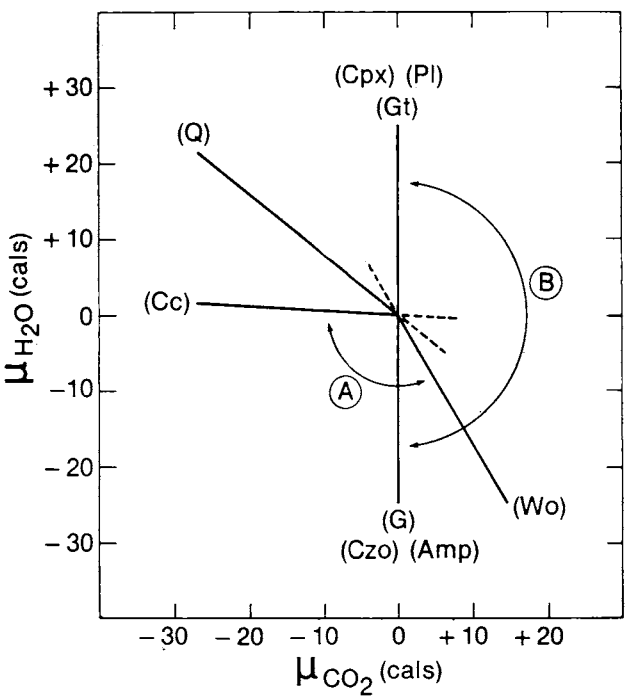

Fig. 7. $\mu H_2O - \mu CO_2$ diagram for 9 phases in the system SiO_2-Al_2O_3-Fe_2O_3-FeO-MgO-CaO-CO_2-H_2O-Na_2O at constant P, T. Univariant curves are labeled with abbreviation (table 1) of missing phases. Vertical curve labeled (Cpx), (Gt), (Pl), above, and (G), (Czo), (Amp), below, is the degenerate equilibrium Cc + Q = Wo + CO_2. Circular arrow labeled "B" shows sector over which the assemblage Q-Cc-Czo-Gt-Di-G is stable. Arrow "A" shows sector over which the assemblage Q-Czo-Di-Amp-Pl-G is stable. Average compositions of mineral solid solutions were used to construct the diagram.

R-1-1-1 contains the assemblage calcite–quartz–wollastonite which is evidence that the reaction

$$\text{calcite} + \text{quartz} = \text{wollastonite} + CO_2 \qquad \text{(R5)}$$

proceeded in the rock during metamorphism. There is evidence for no other mineral reactions. The fluid in equilibrium with the assemblage in R-1-1-1 is characterized by $X_{CO_2} = 0.09$ (figs. 5C and 6). Clearly this sample equilibrated not just with fluid produced internally (whose composition would be $X_{CO_2} = 1$) but with a mixture of internally-produced fluid components (CO_2) and fluid components derived from external sources ($H_2O + CH_4$). Similar discrepancies between compositions of fluid generated by reactions in rocks and the compositions of fluid with which minerals were in equilibrium are also noted for samples containing the assemblage quartz–calcite–grossular–clinozoisite–graphite (AA-1, AA-2, AA-4-1, R-1-2-2). The distillation model is inconsistent with the progress of decarbonation reactions observed petrographically. In rocks such as those of this study whose total porosity is less than 5 percent (Norton and Knapp, 1977, fig. 6, p. 923), reaction R5 in a system closed to externally derived H_2O would scarcely have produced a detectable amount of wollastonite before grain boundaries would have become saturated with CO_2; reactants would then have been stabilized with respect to products, and reaction would have stopped. Finally, the distillation model cannot account for the change in oxygen isotope composition of the fossils that is inferred to have occurred during metamorphism (see below; fig. 8; app. 3).

The foregoing discussion is not only evidence against the distillation model but also is strong evidence *for* the infiltration model of fluid behavior. Additional evidence for the infiltration model is the observation that carbonate-bearing calc-silicate rocks constitute less than 1 percent of the Littleton Formation. The bulk of the Littleton Formation is mica schist and micaceous quartzite. Thus the volume of H_2O released by dehydration of rocks in the immediate vicinity of the fossil locality would be enormous relative to the volume of the calc-silicate rocks. It seems implausible that 20 to 30 cm thick beds of calc-silicate could remain isolated, for the duration of the metamorphic event, from the copious amount of H_2O driven off from surrounding schists and quartzites.

The above mineralogical, chemical, and geological arguments favor an infiltration system model in which the calc-silicate rocks at Beaver Brook equilibrated with a fluid, part of which was generated by mineral reactions within the rock and part of which was derived from sources external to the calc-silicates. Further, the arguments favor that the externally-derived components were largely H_2O. If the externally-derived fluid, as a simplification, is considered to be *pure* H_2O, then the amount and volume of externally-derived fluid that interacted with the calc-silicate rocks can be estimated with knowledge of the mineral reac-

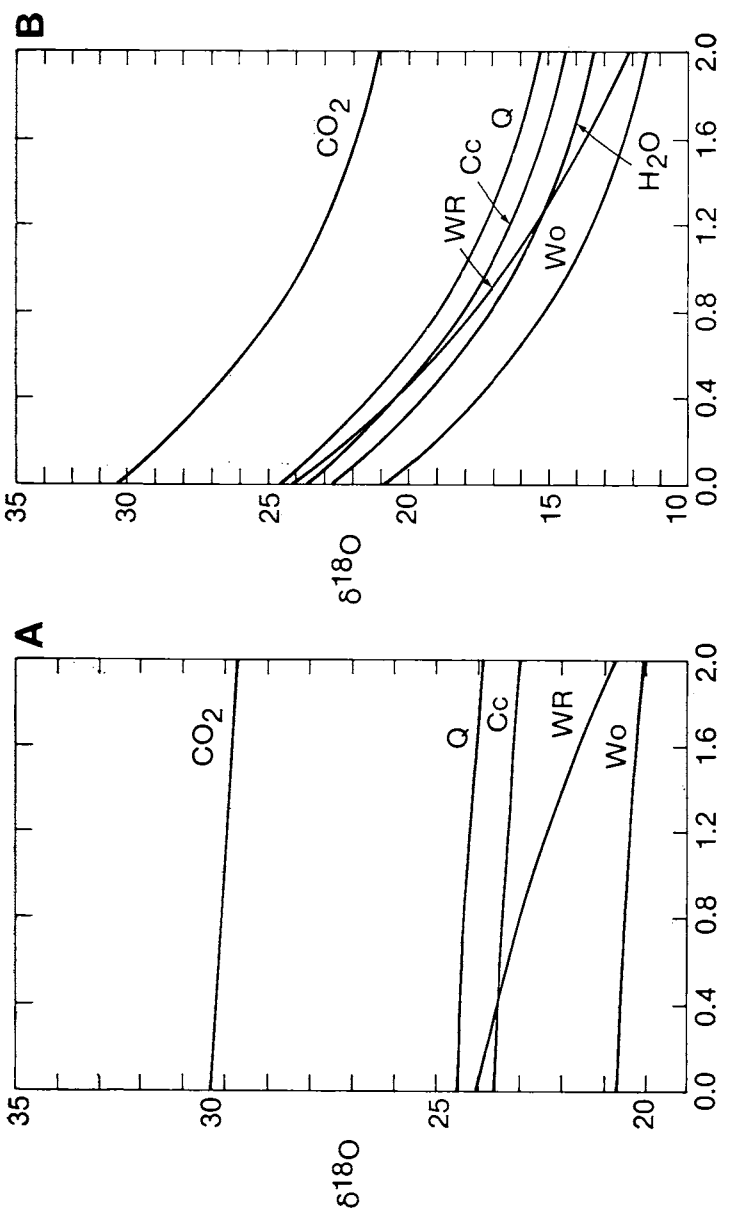

Fig. 8. Plots of $\delta^{18}O$ versus number of gram formula weight (gfw) units of wollastonite formed in the reaction Cc + Q = Wo + CO_2. (A) shows expected changes in $\delta^{18}O$ as a function of reaction progress in the case where Rayleigh distillation is operative. Fluid is pure CO_2, corresponding to model (1) described in text. (B) gives expected changes in $\delta^{18}O$ in a rock infiltrated by H_2O with a $\delta^{18}O$ value of 12.5 per mil corresponding to model (2) described in text. Amount of infiltrating H_2O is related to amount of wollastonite formed because fluid composition is constrained to maintain an equilibrium value of X_{CO_2} for the reaction Cc + Q = Wo + CO_2. Initial amounts of Cc and Q are 2.11 and 2.49 gfw units, respectively, as would be found in 100 cm^3 of sample R-1-1-1. Initial whole rock $\delta^{18}O$ = 24.0 per mil.

tions that proceeded in the rocks during metamorphism. The equation used in the calculation is (Ferry, 1980a)

$$V_{H_2O}^{ext} = V_{H_2O}\left[\frac{n_{CO_2}^{rxn} - X_{CO_2}^{eq}\,(n_{CO_2}^{rxn} + n_{H_2O}^{rxn})}{X_{CO_2}^{eq}}\right] \qquad (1)$$

where $V_{H_2O}^{ext}$ is the volume of externally derived H_2O, V_{H_2O} is the molar volume of H_2O under metamorphic P-T conditions, n_i^{rxn} is the number of moles of fluid component "i" produced by mineral reaction in a reference volume of rock, and $X_{CO_2}^{eq}$ is the equilibrium value of X_{CO_2} for the mineral reaction. The n_i^{rxn} are computed from reaction stoichiometry and the extent of reaction progress measured by petrographic modal analysis of reactant and product minerals. Specifying the externally-derived fluid as *pure* H_2O is a conservative action, because calculated amounts of fluid are then *minimum* estimates. The results of such calculations for the Beaver Brook rocks are presented in table 2, expressed as amounts of fluid per reference amount of rock (fluid-rock ratios). Fluid-rock ratios of 2.27 (oxygen atom basis) or 4.4 (volume basis using the molar volume of H_2O at 600°C; 3.5 kb) are obtained for one sample containing the quartz–calcite–wollastonite assemblage (R-1-1-1). Calculations assumed that reaction (R5) (now quenched in the rock) was the sole reaction that the rock experienced during metamorphism and that the reaction occurred at T = 600°C; P = 3.5 kb. Assuming progressive decarbonation over a temperature interval culminating at 600°C requires even larger fluid-rock ratios. An uncertainty of ± 2 mol percent in the value of $X_{CO_2}^{eq}$ leads to an uncertainty in volumetric fluid rock ratio of ± 1.2.

Two sets of fluid-rock ratios have been calculated using eq (1) for samples containing the assemblage quartz–calcite–clinozoisite–grossular–diopside–graphite (AA-1, AA-2, AA-4, R-1-2-2). One set assumes that the reaction:

$$2\ \text{clinozoisite} + 5\ \text{calcite} + 3\ \text{quartz} = 3\ \text{grossular} + 5\ CO_2 + H_2O \qquad (R6)$$

(now quenched in the rock) was the sole reaction that the rock experienced and that it occurred at 600°C; 3.5 kb. This first set of fluid-rock ratios averages 0.16 (oxygen basis) or 0.26 (volume basis). The assumptions involved in calculation of the first set of fluid-rock ratios are not plausible. Certainly other reactions besides (R6) occurred that formed the clinozoisite and diopside in the samples. There remains, however, no record of what these reactions were. A second set of fluid rock ratios was calculated by assuming that all Fe, Ca, and Mg now in calc-silicate minerals was originally contained in carbonates prior to metamorphism, and that for every mole of Ca, Fe, and Mg now in calc-silicate minerals, one mole of CO_2 was produced by decarbonation during metamorphism. The composition of fluid in equilibrium with the rocks during decarbonation was assumed to be that of fluid in equilibrium with the assemblage quartz–clinozoisite–calcite–grossular–graphite. Without having to specify exactly

what reactions were involved, fluid-rock ratios for samples AA-1 and AA-2 could then be calculated at conditions of P = 3.5 kb; T = 600°C: 0.7 to 1.0 (oxygen basis) or 1.5 to 2.0 (volume basis) (table 2). The second set of calculated fluid-rock ratios agrees within a factor of approx two with fluid-rock ratios estimated from the calcite–quartz–wollastonite rock (R-1-1-1).

Graphite in the quartz monzonite dike.—Because carbon or carbon-bearing species have low solubility in granitic magmas at pressures near 3500 bars (Mysen, 1977), the presence of graphite in the quartz monzonite may be evidence for contamination of the dike rock with some carbon-bearing material. The main pluton of the Kinsman quartz monzonite contains three types of graphite (Rumble, unpub.): (1) spherulitic aggregates, 5 μm in diameter, of very small graphite grains sparsely distributed in the center of silicate mineral grains (compare Ramdohr, 1969, figs. 324 and 325, p. 391); (2) micaceous flakes of graphite, 150 μm long, located along grain boundaries of silicate minerals; and (3) irregular aggregates of graphite grains of variable size (but no larger than 50 μm in diameter) that occur along the grain boundaries of and within silicate mineral grains. The first type of occurrence may well represent primary magmatic graphite. The third type of occurrence appears to be related to secondary hydration of the quartz monzonite, because graphite of this type tends to occur within or adjacent to retrograded minerals and such graphite is more abundant in retrograded rocks. In none of the samples studied has any evidence been seen of oxidation or reduction of biotite or ilmenite, the chief iron-bearing minerals of the quartz monzonite. Graphite found in the Beaver Brook dike rock corresponds to types (2) and (3), however, retrograde metamorphism is not manifest. The petrographic evidence is believed to be consistent with the hypothesis that graphite is present in the dike rock, because the quartz monzonite was contaminated by carbon-bearing material. Three possible mechanisms of contamination are envisioned. First, contamination could have occurred by stoping and magmatic assimilation of graphitic country rock (metasediment). This mechanism is rejected, because no partially consumed blocks of metasediment have been found in the dike itself and such blocks are rare in the main Kinsman Quartz Monzonite pluton. A second possible mechanism of contamination is the reduction of CO_2-bearing fluids by minerals in the dike rock. This second mechanism is rejected, because there is no textural or mineralogic evidence for oxidation/reduction reactions in the dike rocks. A third possible mechanism of contamination involves the precipitation of graphite caused by the mixing within the dike of two or more C-H-O fluids, in equilibrium with graphite but with different CO_2/CH_4 ratios. The strong curvature of the graphite-saturation boundary at H_2O-rich fluid compositions in figure 6 demonstrates the feasibility of this third mechanism. Further, a simple calculation demonstrates that graphite can be precipitated by mixing two different fluids that are likely to have existed at the Beaver Brook locality during metamorphism. If 150 cm^3 of fluid in equilibrium with minerals and graphite in domain

R-1-1-1 ($X_{HO_2} = 0.84$, $X_{CO_2} = 0.09$, $X_{CH_4} = 0.07$) are mixed with 150 cm³ of fluid in equilibrium with minerals in AA-1, AA-2, AA-4, and R-1-2-2 ($X_{H_2O} = 0.82$, $X_{CO_2} = 0.15$, $X_{CH_4} = 0.04$) at 600°C, 3.5 kb, and log f_{O_2} = −20.5 to −20.6, 0.5 cm³ of graphite precipitates, an amount comparable to that observed in 100 cm³ of quartz monzonite. For these reasons, the origin of graphite in the dike rock is attributed to the mechanism involving mixing of two or more fluids of different compositions. The above calculation implies a fluid-rock ratio of approx 3 (volume basis) in order to form amounts of graphite similar to those actually found in the quartz monzonite dike (table 2).

The anorthosite zone.—The presence of a reaction zone of anorthosite at the margin of the quartz monzonite dike where it is in contact with calc-silicate rock is evidence for the infiltration of Ca-bearing aqueous solutions from the calc-silicate wall rock into the dike during metamorphism. Myrmeketic anorthite pseudomorphs after alkali feldspar in the anorthosite suggest that the anorthosite zone formed by the reaction

$$2\,(Na,K)AlSi_3O_8 + CaCl_2 = CaAl_2Si_2O_8 + 4\,SiO_2 + 2\,(Na,K)Cl$$

The development of the anorthosite zone from unaltered quartz monzonite is evidence for fluid flow during metamorphism, because the geometry, mineralogy, and chemistry of the zone indicates that it formed by infiltration metasomatism.

Hofmann (1972, p. 82) lists two criteria that characterize infiltration as opposed to diffusion metasomatism. First, infiltration metasomatism involves one-way mass transfer, whereas diffusion involves two-way mass transfer. At Beaver Brook the metasomatic effects are observed only in the dike rock; there is no metasomatic alteration of the calc-silicate wall rock. Such evidence of one-way mass transfer favors infiltration metasomatism at the Beaver Brook locality. Second, infiltration metasomatism produces sharp replacement fronts in mineral solid solutions and between separate adjacent mineral assemblages not in equilibrium with each other. A sharp replacement front exists in plagioclase at the contact between anorthosite and quartz monzonite. Plagioclase changes in composition from An_{95} to An_{19} within a distance of 1 to 2 mm across the contact (fig. 4). Experimental investigation shows that the isotherm for Na-Ca exchange between aqueous chloride solutions and plagioclase has the correct curvature at 3.5 kb and 600°C (Orville, 1972; personal commun., 1980) appropriate to the development of sharp replacement fronts during infiltration metasomatism. The limited mutual solubility of potash feldspar and calcic plagioclase "automatically" gives rise to a sharp replacement front during infiltration (Hofmann, 1972). The anorthosite zone, therefore, is a third line of evidence for fluid flow during metamorphism at the Beaver Brook locality. The anorthosite zone is important evidence, because it not only documents the existence of fluid flow but also the direction of flow: calcic aqueous solutions flowed from calc-silicate wall rocks into the quartz monzonite dike.

Oxygen isotopic composition of fossiliferous rocks.—The low $\delta^{18}O$ values of the fossiliferous beds relative to unmetamorphosed equivalents are evidence for interaction of the fossiliferous rocks with large volumes of O-bearing fluid during metamorphism. In order to calculate the volume of fluid involved, it is necessary first to know the pre-metamorphic $\delta^{18}O$ values of the rocks. It is also necessary to specify a mechanism of fluid-rock interaction that best accounts for measured isotopic compositions.

The pre-metamorphic isotopic composition of the fossil bed can be estimated rather accurately. The average $\delta^{18}O$ value of quartz from silicified Devonian brachiopods is + 24.0 ± 2.8 per mil (Savin and Epstein, 1970); the average $\delta^{18}O$ value of unsilicified Devonian marine limestones is + 23 ± 1.5 per mil (Keith and Weber, 1964). Evidently, diagenetic silicification does not alter greatly the oxygen isotopic composition of fossil brachiopods. For purposes of the calculations, an initial value of + 24 per mil has been chosen for the pre-metamorphic oxygen isotope composition of the fossiliferous bed at Beaver Brook. The post-metamorphic, measured value of the fossil bed is + 12.0 per mil (table 1). In the calculations of infiltration isotope exchange given below, the oxygen isotopic composition of infiltrating H_2O is + 12.5 per mil. The value of $\delta^{18}O$ for H_2O was chosen, because it is the composition of H_2O in oxygen isotope equilibrium at 600°C with the mica schists enclosing the fossiliferous rocks. Choosing a lower value for $\delta^{18}O_{H_2O}$, such as + 11.9 per mil in equilibrium at 600°C with the cross-cutting quartz vein, sample QV, results in fluid-rock ratios 14 percent lower than those reported in table 2. Choosing a lower value for the pre-metamorphic oxygen isotope composition of the fossils, such as 21 per mil, lowers calculated fluid-rock ratios by 10 percent.

Three mechanisms of fluid-rock interaction have been investigated using numerical methods (see app. 3): (1) Rayleigh distillation with fluid as pure CO_2 produced solely by decarbonation reactions within the fossil bed; (2) combined Rayleigh distillation and infiltration of sufficient H_2O into the fossil bed so that the H_2O/CO_2 of fluid produced by mixtures of externally-derived H_2O and internally-derived CO_2 equals the equilibrium value of the ongoing reaction; (3) infiltration of H_2O-CO_2 fluid (with equilibrium H_2O/CO_2) into the fossil bed with no decarbonation reactions within the bed. Results of model calculations indicate that the present-day oxygen isotope composition of the fossil bed could have been achieved only by the infiltration of large quantities of fluid either accompanied or unaccompanied by decarbonation reactions (models 2 and 3 above) (fig. 8). Calculations using either model (2) or model (3) give similar fluid-rock ratios.

Fluid-rock ratios required to explain measured isotopic composition of the fossil bed have been calculated assuming model (2) at 600°C and 3.5 kb: fluid/rock = 3 to 4 (oxygen atom basis) or 5 to 6 (volume basis) (fig. 8; table 2). Repeating the model calculations at temperatures lower than 600°C results in poor agreement between calculated final whole rock

and measured whole rock compositions and between calculated quartz compositions and measured quartz compositions.

Oxygen isotopic composition of the quartz monzonite dike.—The high $\delta^{18}O$ values of the quartz monzonite dike rock relative to "fresh" equivalents are evidence for interaction of the quartz monzonite with large volumes of O-bearing fluid during metamorphism. The pre-metamorphic oxygen isotopic composition of the quartz monzonite cannot be estimated very accurately. Most unaltered plutonic granitic rocks are known to have a range of $\delta^{18}O$ whole rock values of + 7.0 to + 10.0 per mil, but muscovite-bearing granitic rocks usually have values > + 10.0 per mil (Taylor, 1977). The range of uncertainty in estimating the pre-metamorphic isotopic composition of the quartz monzonite overlaps with its measured composition. In the following calculations of fluid-rock ratios, it is assumed that the oxygen isotope composition of the dike was altered by infiltration, without the formation of new minerals. There is no petrographic evidence of reaction between minerals of the dike except in the anorthosite zone. There is evidence, however, that quartz and feldspar have recrystallized, because they no longer have an igneous-like texture. The oxygen isotopic composition of infiltrating H_2O is assumed to be + 12.5 per mil, a value in equilibrium at 600°C with the dike's country rocks. Fluid-rock ratios required to explain measured isotopic composition of the quartz monzonite have been calculated at 600°C and 3.5 kb (app. 3); because of uncertainty in the dike's pre-metamorphic isotopic composition, results must be regarded with some skepticism. If the whole rock isotopic composition of the dike before metamorphism was + 10.0 per mil or + 12.0 per mil, calculated fluid-rock ratios of 3.0 or 2.0 (oxygen atom basis), respectively, are required to match measured isotopic composition of quartz in the dike rocks (table 2).

EVALUATION OF DIFFERENT EVIDENCES OF FLUID FLOW

The most definitive evidences of fluid flow through the Beaver Brook rocks during metamorphism are the quenched decarbonation reactions, the anorthosite zone, and the ^{18}O depletion of the fossil bed. Evidence contained in the dike rock is less certain because the contamination of the dike rock with graphite and its enrichment in ^{18}O could have happened prior to intrusion and crystallization. There is agreement within a factor of 1.4 between the estimate of minimum fluid-rock ratio for domain R-1-1-1, quartz–calcite–wollastonite, calculated from reaction progress, 2.3 (oxygen atom basis), and that calculated from ^{18}O depletion, 3.3 (oxygen atom basis). There is worse agreement between the results for the decarbonation reaction in the assemblage quartz–calcite–clinozoisite–grossular–diopside–graphite (samples AA-1 and AA-2). The estimate of fluid-rock ratio based on reaction progress is 0.7 to 1.0 (oxygen atom basis). Oxygen isotope depletion, however, implies a fluid-rock ratio of 4.0 (oxygen atom basis). The discrepancy arises because the isotope data are a measure of the integrated fluid-rock ratio throughout the entire history of the rock. The reaction progress estimate is an "order-of-magnitude"

approximation, because the history of decarbonation is not known well enough to make a more accurate calculation.

The results of our study demonstrate that substantial amounts of fluid flowed through a 20 to 30 cm thick bed of calc-silicate during metamorphism at a depth of 13 km. Definitive evidence on the direction of fluid flow is lacking. The distribution of the anorthosite in the dike suggests that a component of fluid flow was parallel to bedding. The uniform oxygen isotope composition of quartz from the calc-silicate and quartz from the mica schist implies that there may have been some flow across bedding. The specific pathways along which fluid flowed cannot be identified unequivocally. There are no ramifying networks of quartz veins or mineralized fractures visible in outcrop. Examination of a 10 × 15 cm polished slab cut perpendicular to bedding shows a few healed fractures 2 to 3 cm long, but these do not extend across the entire thickness of a single sedimentary bed, and they are not interconnected. It is probable, therefore, that much of the fluid flow occurred through relatively unbroken rock, along grain boundaries.

ROCK PERMEABILITY DURING METAMORPHISM

It has been shown that the calc-silicate and dike rocks at Beaver Brook experienced substantial amounts of fluid flow during metamorphism at a depth of 13 km. The absence of ramifying networks of quartz veins or healed fractures in the outcrop suggests that much of the flow took place along mineral grain boundaries through relatively unbroken rock. These results raise the problem of how to account for the permeability that made it possible for flow to occur. Evidence of a specific mechanism for enhancing permeability — devolatization reactions (Fyfe, Price, and Thompson, 1978, p. 309) — may be best brought out by comparing the Beaver Brook rocks to rocks through which little fluid flow occurred during metamorphism.

Quartzites and quartz-mica schists exposed at Black Mountain (northwest quarter of fig. 1) stand in contrast to the Beaver Brook rocks with regard to fluid-rock interaction during metamorphism. Quartz and magnetite within single sedimentary beds were in localized oxygen isotope exchange equilibrium during metamorphism but these minerals were not in equilibrium from one bed to the next (Rumble, 1978, p. 329). The fractionation of ^{18}O between quartz and magnetite from different beds is constant ($1000 \ln \alpha = 9.5 \pm 0.3$), but $\delta^{18}O$ values of quartz and magnetite vary over a range of 2.5 per mil. The calculated value of fluid-rock ratio required to bring the quartz from the different beds to a uniform $\delta^{18}O$ is 0.7 (atomic oxygen basis). This value was obtained by using Taylor's single-pass model (1977, p. 524; compare app. 3) and assuming that the Black Mountain quartz richest in ^{18}O ($\delta^{18}O = 13.8$ per mil) was changed to the mean value of all quartz samples (12.6 per mil) by infiltration with H_2O ($\delta^{18}O = 8.0$ per mil) in oxygen isotope equilibrium with the quartz poorest in ^{18}O. Larger values of fluid-rock ratio can be obtained by choosing the $\delta^{18}O$ of infiltrating H_2O to be more nearly in equilibrium with

the rock being infiltrated; smaller values are realized when infiltrating H_2O is farther out of equilibrium. The important point to be made is that using fluids known to have been present at Black Mountain during metamorphism, pervasive oxygen isotope equilibrium could have been achieved by fluid-rock ratios one-fifth to one-tenth of those observed at Beaver Brook. Yet, such flow did not take place. Why did fluid flow occur at Beaver Brook and not at Black Mountain during metamorphism?

The rocks at Beaver Brook and Black Mountain are similar in many respects: they are both of Siluro-Devonian stratigraphic age and experienced regional metamorphism of equal duration. Rocks from the two localities were metamorphosed under P conditions that differed by no more than 1 kb and T that differed by no more than 100°C. What is different about the two localities is that at Beaver Brook the quantity of volatile components released by mineral reactions during metamorphism far exceeded that released at Black Mountain. At Beaver Brook, sample domain R-1-1-1 released 21 percent, by weight, CO_2; dehydration of Black Mountain rocks could have produced no more than 1 percent, by weight, of H_2O. These observations suggest that the magnitude of fluid flow and the intensity of devolatization reactions are positively correlated during metamorphism. It is to be emphasized that the correlation is not merely 1:1, because the amount of fluid that flowed through the rocks is far greater than that released by devolatization reactions. Such a correlation between evidence for fluid flow and intensity of metamorphic devolatization reactions has been reported by Rye and others (1976) who found ^{18}O depletion of marbles to be most extreme in beds where decarbonation reactions produced calc-silicate minerals.

The observed correlation between the occurrence of large fluid flow during metamorphism and the intensity of devolatization reactions can be explained by considering the likely effects of such reactions on rock permeability. Experiments have shown that permeability depends strongly on pore pressure and rock porosity (Brace, 1972). Metamorphic devolatization reactions would enhance permeability in two ways: first, such reactions would maintain or increase fluid pressure to values equal to lithostatic pressure; and second, metamorphic reactions would tend to increase porosity because the volume occupied by solid mineral products is usually less than that of reactants. The following reaction mechanism is envisaged. Consider the fossil shells at an early stage of metamorphism below the T at which wollastonite forms. The fossils consist of quartz and calcite whose grain boundaries are wetted, probably, by H_2O. As temperature increases toward its metamorphic maximum, small amounts of wollastonite will form. Reaction will cease, however, as soon as the amount of CO_2 released by decarbonation has diluted grain boundary H_2O to a value of X_{CO_2} equal to the equilibrium one. In order for an additional increment of reaction to occur without exceeding the maximum T of metamorphism, the reaction product CO_2 saturating grain boundaries must be flushed out. Product CO_2 would be flushed out by a

new aliquot of more or less pure H_2O derived from a source external to the reaction site. The H_2O is believed to flow through the rocks in response to either small, local P gradients or buoyancy forces. The key step in the process is the momentary enhancement of permeability caused by decarbonation that makes it possible for H_2O to remove CO_2.

It is concluded that the substantial differences in fluid flow between the Black Mountain and Beaver Brook rocks were caused by differences in rock permeability during metamorphism. These differences in rock permeability, in turn, were caused by variations in the intensity of metamorphic devolatization reactions as controlled by rock bulk composition, pressure, and temperature.

ACKNOWLEDGMENTS

We thank J. D. Frantz, B. R. Frost, A. Hofmann, and H. S. Yoder, Jr., who contributed to this study through discussion and criticism. The support of National Science Foundation grants EAR-7919769 (Rumble and Hoering) and EAR-7722771 (Ferry), and of a Cottrell Grant from the Research Corporation (Ferry), is gratefully acknowledged. J. M. Stonehouse, G. Carlson, and F. S. Spear helped collect samples. C. V. Guidotti discovered the fossils. F. L. Steele, of the Society for the Protection of New Hampshire Forests, gave permission to collect specimens.

APPENDIX 1

Mineral solid solutions

Clinozoisite is a binary solution of the components $Ca_2Al_2AlSi_3O_{12}(OH)$-$Ca_2Al_2Fe^{3+}Si_3O_{12}(OH)$. All Fe determined by microprobe analysis was assumed to be Fe^{3+}. The activity of $Ca_2Al_2AlSi_3O_{12}(OH)$ was calculated as

$$a_{czo} = (\text{Al-2})/(\text{Fe} + (\text{Al-2}))$$

where Fe and Al stand for the total number of Fe and Al atoms in the mineral formula normalized to 12.5 anhydrous oxygen atoms. In this solution model it is assumed that there is an ordered distribution of Fe into one site whose multiplicity is unity. Our model for a_{czo} is equivalent to that of Bird and Helgeson (1980, p. 916, eq 22), who showed that it adequately represents experimental and thermochemical data on the clinozoisite component in epidote solid solutions over the T range 25° to 600°C and for the composition range of Beaver Brook clinozoisites (Bird and Helgeson, 1980, p. 929, fig. 12). If a disordered distribution of Fe is assumed over 3 sites (Ferry, 1976, p. 141), the temperatures of the equilibrium curves used for geothermometry decrease by 10°C.

Garnet is a 5-fold solution of the components $Ca_3Al_2Si_3O_{12}$-$Ca_3Fe_2^{3+}Si_3O_{12}$-$Fe_3^{2+}Al_2Si_3O_{12}$-$Mn_3Al_2Si_3O_{12}$-Mg-$Al_2Si_3O_{12}$, with the last two components present in amounts less than 3 mol percent. Ferric iron was estimated by recasting microprobe analyses in terms of 8 cations, assigning sufficient Fe^{2+} to the divalent site to make a total of 3 cations, and assigning the remaining Fe as Fe^{3+} to the trivalent site. For grossular-rich garnets (AA-1, 2, 4-1; R-1-1-1, 1-2-2) the following ideal activity model was assumed

$$a_{gr} = (X_{Ca})^3 (X_{Al})^2$$

where X_{Ca} is the atomic fraction of Ca in the divalent site, and X_{Al} is the atomic fraction of Al in the trivalent site. Intermediate grossular-almandine garnets (AA-5) were assumed to mix as a regular symmetric solution. A correction for non-ideal mixing was made using the data of Cressey, Schmid, and Wood (1978) to obtain values of a_{gr} for the composition of garnet AA-5 at temperatures of 900°, 1000°, and 1100°C. Values of a_{gr} appropriate to the temperature range 570° to 640°C were obtained by linear least squares extrapolation of the high-temperature data. Corrections for garnet solid solution effects have a big effect on the calculated temperature of the reaction

clinozoisite + quartz = plagioclase + garnet + H_2O: assuming ideal mixing of garnet, the calculated curve for AA-5 is 15°C lower than the pure endmember equilibrium curve; assuming the non-ideal corrections described above, the curve for AA-5 is 42°C higher than the pure endmember curve.

Diopside is a binary $CaMgSi_2O_6$–$CaFeSi_2O_6$ solution that is assumed to mix ideally: $a_{di} = X_{Ca,M2}\, X_{Mg,M1}$, where $X_{Ca,M2}$ is the atomic fraction of Ca in M2 and $X_{Mg,M1}$ is the atomic fraction of Mg in M1.

Amphibole is a calcic multi-component solution that is assumed to mix ideally: site populations of cations were calculated according to Robinson and others (1973). Activity of the tremolite component is given by

$$a_{tr} = X_{\square}\, X^2_{Ca,M4}\, X^3_{Mg,\,M1+M3}\, X^2_{Mg,M2}$$

where $X_{\square}$ = atomic fraction of vacancy in A site, $X_{Ca,M4}$ = atomic fraction Ca in M4, $X_{Mg,M1+M3}$ = atomic fraction Mg in M1+M3 sites, and $X_{Mg,M2}$ = atomic fraction Mg in M2.

Plagioclase is a binary solution of $CaAl_2Si_2O_8$–$NaAlSi_3O_8$ with possible solvus gap in the range An_{83}–An_{97}. Plagioclase was assumed to mix ideally in the range An_{90}–An_{100} (Orville, 1972).

APPENDIX 2

Thermodynamic data

The thermodynamic data of Ferry (1976, app. 2, p. 135) were used to calculate equilibrium curves. The equilibrium constants quoted by Ohmoto and Kerrick (1977) were used to compute gas phase equilibria. Gas species were assumed to mix ideally. The fugacity coefficients of Burnham, Holloway, and Davis (1969) were used for H_2O, of Burnham and Wall (personal commun) for CO_2, and of Ryzhenko and Volkov (1971) for CO, H_2, and CH_4. A critical comparison of these with other data sets is given below.

Gas phase equilibria.—At 600°C and 3.5 kb, there is no noticeable difference between the graphite saturation surface computed from the K_D expressions of Ohmoto and Kerrick (1977) and that from the expressions of Deines and others (1974) when plotted on a 10 cm isothermal, isobaric C–O–H equilateral triangle. The use of the γ_{CO_2} values of Shmulovich and Shmonov (1975) instead of those of Burnham and Wall (personal commun.) does not change the shape or position of the graphite saturation surface on an isothermal, isobaric, C–O–H triangle but does shift f_{O_2} contours slightly toward more CO_2-rich compositions. The position of the calcite + quartz = wollastonite + CO_2 equilibrium curve at 3.5 kb and 600°C shifts by 1.0 mol percent toward more CO_2-rich compositions on a T-X_{CO_2} diagram if the γ_{CO_2} values of Shmulovich and Shmonov (1975) are used instead of those of Burnham and Wall (personal commun.). The effects of non-ideal corrections on the computed C–O–H phase diagram (fig. 6) at 3.5 kb and 600°C are not very great where the fluid phase is dominantly H_2O + CO_2; non-ideal effects become more important with increasing CH_4 content. A comparison of the graphite saturation surface as computed with the ideal mixing model and as computed by Frost (1979, p. 1039, fig. 2; p. 1041, fig. 3) with the Redlich-Kwong mixing model (Holloway, 1977) gives the following results: At 2 kb and 600°C the ideal and non-ideal models agree within 2 mol percent X_{CO_2} for $X_{CH_4} < 10$ mol percent; at 5 kb and 600°C the models agree within 5 mol percent X_{CO_2} for $X_{CH_4} < 10$ mol percent. Disagreement between the two models for both pressures is greater for $X_{CH_4} >$ 10 mol percent but that is of no concern to this study because fluids at Beaver Brook contain < 10 mol percent CH_4. The model of ideal mixing of H_2O and CO_2 in fluid was tested by predicting the T-X_{CO_2} coordinates of the equilibrium quartz–wollastonite–calcite measured by Jacobs and Kerrick (1979) at 6 kb. The predicted coordinates agree within 10°C with the experimental determination.

Calcite + quartz = wollastonite + CO_2.—The computed curves of Ferry at 1 and 2 kb agree ± 10°C with the experimental brackets of Greenwood (1967b) and at 6 kb with the bracket of Kerrick and Jacobs (1978). Curves computed with the data of Helgeson and others (1978) are in agreement with Ferry (1976) at 1 kb, are 10°C higher than Ferry's at 2 kb, and 40°C higher at 6 kb. The data of Robie, Hemingway, and Fisher (1978) produce curves that are 50°C below the brackets of Greenwood (1967b) at 1 and 2 kb. The revised data of Haas, Robinson, and Hemingway (1979) for wollastonite together with the data of Robie, Hemingway, and Fisher (1978) give curves that are within 10°C of Kerrick and Jacobs (1978) bracket but 40° to 50°C too low at 1 and

2 kb. At 600°C and 3.5 kb, the T-X_{CO_2} equilibrium curve computed from Helgeson and others (1978) is 1.0 mol percent more H_2O-rich than Ferry's (1976) curve.

Clinozoisite + quartz = plagioclase + garnet + H_2O and tremolite + clinozoisite + quartz = diopside + plagioclase + H_2O.—Curves computed for the pure end member reactions from Helgeson and others (1978) data are 10°C lower than Ferry's curves at 3.5 kb. The data of Robie, Hemingway, and Fisher (1978), as revised by Haas, Robinson, and Hemingway (1979), give equilibrium temperatures that are 100° to 150°C lower than those of Helgeson and Ferry. The anorthite values of Charlu, Newton, and Kleppa (1978) together with Helgeson's data also produce curves that are much too low.

Clinozoisite + quartz = plagioclase + garnet + H_2O.—Calculated curves of Ferry (1976) and Helgeson and others (1978) for pure endmembers agree within ± 10°C for the brackets of Newton (1966) at 2 kb and Boettcher (1970) at 4 and 5.3 kb and within ± 200 bars with Newton's (1966) bracket at 650°C. Substituting the anorthite values of Charlu, Newton, and Kleppa (1978) in Helgeson's data gives temperatures 100° to 150°C too low, as do the data of Robie, Hemingway, and Fisher (1978) and Haas, Robinson, and Hemingway (1979).

Clinozoisite + CO_2 = plagioclase + calcite + H_2O.—Curves of T-X_{CO_2} for pure endmembers computed from Helgeson and others (1978) are 1.5 mol percent more H_2O rich at 600°C and 3.5 kb than Ferry's (1976) curves.

APPENDIX 3

Isotope fractionation during dehydration and decarbonation

Oxygen isotope fractionation during metamorphism was computed for different models of fluid/rock interaction considering the following factors: (1) temperature, (2) proportions of H_2O and CO_2 in metamorphic fluids (compare Ohmoto, 1972), (3) changing amounts of reactant and product minerals, and (4) rock porosity. Isotopic fractionation factors were taken from the compilation of Friedman and O'Neill (1977). Mole fractions of H_2O and CO_2 in metamorphic fluids were estimated from phase equilibria (see text) and used to calculate the isotopic fractionation between bulk fluid and whole rock. The effect of changing amounts of reactant and product minerals on bulk fluid versus whole rock fractionation was computed from reaction stoichiometry and reaction progress. Rock porosity was considered by insuring that at each increment of reaction an amount of fluid no greater than 1 percent by volume was added to or subtracted from the reacting minerals.

Rayleigh distillation is a process in which the products of a reaction are isolated from reactants immediately after formation. Such a process is likely to occur during metamorphism, because the volatile products of metamorphic reactions are driven away from the reaction site by small, local pressure gradients or buoyancy. Therefore, products H_2O and CO_2 do not remain in isotopic equilibrium with the rock from which they were released. Rayleigh distillation for isotopic fractionation in a two-phase system is described by the following equation (Broecker and Oversby, 1971, p. 166):

$$\delta_{initial} - \delta_{final} = 1000(F^{\alpha-1} - 1) \qquad \text{(A1)}$$

where $\delta_{initial} - \delta_{final}$ gives the change in reactant composition, F is the fraction of uncoverted reactant, and α ($\cong \delta_{whole\ rock} - \delta_{fluid}$) is the partitioning of isotopes between product and reactant. Eq (A1) is inadequate to deal with devolatization reactions, however, because it is valid only for constant α. The value of α changes continuously throughout the course of an isothermal, multi-phase, multi-component devolatization reaction in response to changing proportions of minerals as may be seen in the following equation:

$$\Delta_{WR-FL} = \sum_{i} X_i \Delta_{i-Q} - \sum_{f} X_f \Delta_{f-Q} \qquad \text{(A2)}$$

where $\Delta_{WR-FL} = \delta^{18}O$ (whole rock) $- \delta^{18}O$ (bulk fluid) and is approximately equal to α; X_f is the atomic fraction of oxygen in fluid species "f" relative to the total number of oxygen atoms in fluid; X_i is the atomic fraction of oxygen in mineral "i" relative to the total number of oxygen atoms in the minerals; and Δ_{i-Q} or $\Delta_{f-Q} = \delta^{18}O$ (mineral or fluid species) $- \delta^{18}O$ (quartz) and is a function of temperature. Accordingly, a numerical scheme was devised to calculate the effects of Rayleigh distillation taking into account all the factors influencing α.

The computer model of this work uses the principle of conservation of mass to compute the isotopic effects of isothermal devolatization reactions for very small increments of reaction progress. The calculations are reiterated with continually updated values so that what is finally obtained is the approximation of smooth curves by short, straight line segments. The convergence of the computation scheme was checked by using smaller and smaller increments of reaction progress. The isothermal model of Rayleigh distillation is as follows: computation begins with a rock of given $\delta^{18}O$ (whole rock) and given temperature. Let a small, specified increment of devolatization take place at chemical and isotopic equilibrium. The rock now consists of product and reactant minerals together with a small amount of fluid phase with which it is in equilibrium. The value of $\delta^{18}O$ (quartz) is calculated with the equation

$$\delta^{18}O_Q = \delta^{18}O_{WR} - \sum_i \Delta_{i-Q} X_i - \sum_f \Delta_{f-Q} X_f \qquad \text{(A3)}$$

where the subscripts Q and WR refer to quartz and whole rock, respectively, X_i is the atomic fraction of oxygen in mineral "i" relative to the total oxygen in minerals *plus* fluid, X_f is the atomic fraction of oxygen in fluid species "f" relative to the total oxygen in fluid *plus* minerals, and Δ_{i-Q} and Δ_{f-Q} are defined as in eq (A2). The next step is to remove the fluid products of reaction and compute a new value of $\delta^{18}O_{WR}$ with the equation

$$\delta^{18}O_{WR} = \sum_i X_i \delta^{18}O_i \qquad \text{(A4)}$$

where X_i is the atomic fraction of oxygen in mineral "i" relative to the total oxygen in minerals *alone* and $\delta^{18}O_i = \Delta_{i-Q} + \delta^{18}O_Q$. At this point, another increment of devolatization takes place, and computation returns to eq (A3). Reiteration continues until the desired extent of reaction progress is reached. Test calculations of isothermal Rayleigh distillation in a two-phase system in which α is constant show agreement of $\pm$ 0.1 per mil for up to 70 percent completed reaction and $\pm$ 0.5 per mil for 90 percent completed reaction between a simplified version of the computer program of this study and the analytic form of Rayleigh's equation with constant α (see eq A1).

Isotopic infiltration is a process whereby the minerals in rock exchange isotopes with fluid flowing through the rock. By this means a rock may come to be in isotopic equilibrium with an external reservoir. Such a process is likely to occur during metamorphism, because the volatile species released by metamorphic reactions must pass through other rocks in order to reach the Earth's surface. The numerical procedure described above was modified to compute the effects of infiltration either alone or combined with Rayleigh distillation. The isothermal infiltration of isotopes without devolatization reactions is computed as follows: consider a rock at given T with a given $\delta^{18}O$ (whole rock) and empty pores. To these pores add a small, specified amount of H_2O and CO_2 with specified $\delta^{18}O$ not in equilibrium initially with the rock. The fluid is allowed to come to isotopic equilibrium with the minerals of the rock. In this case, in which infiltration occurs without devolatization reactions, the H_2O and CO_2 are added in the correct ratio to be in equilibrium with the mineral assemblage in the rock. Now compute the mean isotopic composition of the system consisting of whole rock plus fluid using the equation

$$\delta^{18}O_{(system)} = \sum_f X_f \delta^{18}O_f + X_{WR}\delta^{18}O_{WR} \qquad \text{(A5)}$$

where the X_f's are defined as in eq (A3) and X_{WR} is the atomic fraction of oxygen in all the minerals in the rock relative to total oxygen in rock *plus* fluid. Then, $\delta^{18}O_Q$ is calculated with the equation

$$\delta^{18}O_Q = \delta^{18}O_{(system)} - \sum_f \Delta_{f-Q} X_f - \sum_i \Delta_{i-Q} X_i$$

where X_i and X_f are defined in eq (A3) and Δ_{f-Q} and Δ_{i-Q} are as in eq (A2). At this point, the previously infiltrated, small increment of fluid is removed from the rock. A new value of $\delta^{18}O_{WR}$ is computed from the equation

$$\delta^{18}O_{WR} = \sum_i X_i \delta^{18}O_i$$

where X_i and $\delta^{18}O_i$ are defined as in eq (A4). A new increment of fluid is added to the rock, computation returns to eq (A5), and reiteration continues until the desired

degree of infiltration alteration of $\delta^{18}O_{WR}$ has been achieved. Test calculations of infiltration into a rock *not* undergoing devolatization using the computer model of this study give results in agreement with fluid-rock ratios computed using Taylor's (1977, p. 524) "open system" or "single-pass" model.

References

Albee, A. L., and Ray, L., 1970, Correction factors for electron probe micro-analysis of silicates, oxides, carbonates, phosphates, and sulfates: Anal. Chemistry, v. 42, p. 1408-1414.

Bence, A. E., and Albee, A. L., 1968, Empirical correction factors for the electron microanalysis of silicates and oxides: Jour. Geology, v. 76, p. 382-403.

Billings, M. P., 1937, Regional metamorphism of the Littleton-Moosilauke area, New Hampshire: Geol. Soc. America Bull.: v. 48, p. 463-566.

Bird, D. K., and Helgeson, H. C., 1980, Chemical interaction of aqueous solutions with epidote-feldspar mineral assemblages in geologic systems. I. Thermodynamic analysis of phase relations in the system CaO-FeO-Fe_2O_3-Al_2O_3-SiO_2-H_2O-CO_2: Am. Jour. Sci., v. 280, p. 907-941.

Boettcher, A. L., 1970, The system CaO-Al_2O_3-SiO_2-H_2O at high pressures and temperatures: Jour. Petrology, v. 11, p. 337-379.

Boettcher, A. L., and Wyllie, P. J., 1968, Melting of granite with excess water to 30 kb pressure: Jour. Geology, v. 76, p. 235-254.

Boucot, A. J., and Rumble, D., 1980; Regionally metamorphosed (high sillimanite zone, granulite facies) Early Devonian brachiopods from the Littleton Formation of New Hampshire: Jour. Paleontology, v. 54, p. 188-195.

Bowman, J. R., Essene, E. J., and O'Neill, J. R., 1980, Origins and evolution of metamorphic fluids in dolomitic marbles, Elkhorn, Montana [abs.]: EOS, v. 61, p. 391.

Brace, W. F., 1972, Pore pressure in geophysics, *in* Heard, H. C., Borg, I. Y., Carter, N. L., and Raleigh, C. B., Flow and Fracture in Rocks: Am. Geophys. Union Geophys. Mon., v. 16, p. 265-273.

Broecker, W. S., and Oversby, V. M., 1971, Chemical Equilibria in the Earth: New York, McGraw-Hill, 318 p.

Burnham, C. W., Holloway, J. R., and Davis, N. F., 1969, Thermodynamic properties of water to 1000°C and 10,000 bars: Geol. Soc. America Spec. Paper 132, 96 p.

Charlu, T. V., Newton, R. C., and Kleppa, O. J., 1978, Enthalpy of formation of some lime silicates by high-temperature solution calorimetry, with discussion of high pressure phase equilibria: Geochim. et Cosmochim. Acta, v. 42, p. 367-375.

Clayton, R. N., and Mayeda, T. K., 1963, The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis: Geochem. et Cosmochim. Acta, v. 27, p. 43-52.

Craig, H., 1953, The geochemistry of the stable carbon isotopes: Geochim. et Cosmochim. Acta, v. 3, p. 53-92.

Cressey, G., Schmid, R., and Wood, B. J., 1978, Thermodynamic properties of almandine-grossular garnet solid solutions: Contr. Mineralogy Petrology, v. 67, p. 397-404.

Deines, P., Nafziger, R. H., Ulmer, G. C., and Woermann, E., 1974, Temperature-oxygen fugacity tables for selected gas mixtures in the system C–H–O at one atmosphere total pressure: Pennsylvania State Univ. Exp. Sta. Bull. 88, 129 p.

Ferry, J. M., 1976, P, T, f_{CO_2}, and f_{H_2O} during metamorphism of calcareous sediments in the Waterville-Vassalboro area, south-central Maine: Contr. Mineralogy Petrology, v. 57, p. 119-143.

———— 1978, Fluid interaction between granite and sediment during metamorphism, south-central Maine: Am. Jour. Sci., v. 278, p. 1025-1056.

———— 1980a, A case study of the amount and distribution of heat and fluid during metamorphism: Contr. Mineralogy Petrology, v. 71, p. 373-385.

———— 1980b, A comparative study of geothermometers and geobarometers from pelitic schists in south-central Maine: Am. Mineralogist, v. 65, p. 720-732.

Finger, L. W., and Burt, D. M., 1972, REACTION, a Fortran IV computer program to balance chemical reactions: Carnegie Inst. Washington Year Book 71, p. 616-620.

Finger, L. W., and Hadidiacos, C. G., 1972, Electron microprobe automation: Carnegie Inst. Washington Year Book 71, p. 598-600.

Friedman, I., and Gleason, J. D., 1973, A new silicate intercomparison standard for ^{18}O analysis: Earth Planetary Sci. Letters, v. 18, p. 124.

Friedman, I., and O'Neill, J. R., 1977, Compilation of stable isotope fractionation factors of geochemical interest: U. S. Geol. Survey Prof. Paper 440-KK, 9 p.

Frost, B. R., 1979, Mineral equilibria involving mixed volatiles in a C–O–H fluid phase: the stabilities of graphite and siderite: Am. Jour. Sci., v. 279, p. 1033-1059.

Fyfe, W. S., Price, N. J., and Thompson, A. B., 1978, Fluids in the Earth's Crust: Amsterdam, Elsevier, 383 p.

Greenwood, H. J., 1967a, The N-dimensional tie-line problem: Geochim. et Cosmochim. Acta, v. 31, p. 465-490.

———— 1967b, Wollastonite: stability in H_2O-CO_2 mixtures and occurrence in a contact metamorphic aureole near Salmo, British Columbia: Am. Mineralogist, v. 52, p. 1669-1680.

Haas, J. L., Robinson, G. R., Jr., and Hemingway, B. S., 1979, Thermodynamic data for CaO-Al_2O_3-SiO_2-H_2O system [abs.]: EOS, v. 60, p. 968.

Helgeson, H. C., Delany, J. M., Nesbitt, H. W., and Bird, D. K., 1978, Summary and critique of the thermodynamic properties of rock-forming minerals: Am. Jour. Sci., v. 278-A, 229 p.

Hofmann, A., 1972, Chromatographic theory of infiltration metasomatism and its application to feldspars: Am. Jour. Sci., v. 272, p. 69-90.

Holdaway, M. J., 1971, Stability of andalusite and sillimanite and the aluminum silicate phase diagram: Am. Jour. Sci., v. 271, p. 97-131.

Holloway, J. R., 1977, Fugacity and activity of molecular species in super-critical fluids, *in* Fraser, D. G., ed., Thermodynamics in Geology: Boston, D. Reidel, p. 161-181.

Jacobs, G. K., and Kerrick, D. M., 1979, Experimental study of decarbonation equilibria in H_2O-CO_2 mixtures: an evaluation of the mixing properties of H_2O-CO_2 fluids [abs.]: Geol. Soc. America Abs. with Programs, v. 11, p. 450.

Keith, M. L., and Weber, J. N., 1964, Carbon and oxygen isotopic composition of selected limestones and fossils: Geochim. et Cosmochim. Acta, v. 28, p. 1787-1816.

Kerrick, D. M., 1972, Experimental determination of muscovite + quartz stability with $P_{H_2O} < P_{total}$: Am. Jour. Sci., v. 272, p. 946-958.

Kerrick, D. M., and Ghent, E. D., 1979, P-T-X_{CO_2} relations of equilibria in the system CaO-Al_2O_3-SiO_2-CO_2-H_2O, *in* Zharikov, V. A. and others, eds., Problems of physicochemical petrology: Moscow, Acad. Sci., p. 32-52.

Kerrick, D. M., and Jacobs, G. K., 1978, Experimental and thermodynamic analysis of decarbonation equilibria in P-T-X_{CO_2} space [abs]: EOS, v. 59, p. 402.

Korzhinskii, D. S., 1959, Physicochemical Basis of the Analysis of the Paragenesis of Minerals: New York, Consultants Bur., 142 p.

Lonker, S. W., ms, 1979, Conditions of metamorphism in high grade pelites from the Frontenac axis, Ontario, Canada: Ph.D. thesis, Harvard Univ., Cambridge, Mass.

Lyons, J. B., and Livingston, D. E., 1977, Rb-Sr age of the New Hampshire Plutonic Series: Geol. Soc. America Bull., v. 88, p. 1808-1812.

Moore, R. C., Lalicker, C. G., and Fischer, A. G., 1952, Invertebrate Fossils: New York, McGraw-Hill, 766 p.

Mysen, B. O., 1977, The solubility of H_2O and CO_2 under predicted magma genesis conditions and some petrological and geophysical implications: Revues Geophysics Space Physics, v. 15, p. 351-361.

Naylor, R. S., 1971, Acadian orogeny: an abrupt and brief event: Science, v. 172, p. 558-560.

Newton, R. C., 1966, Some calc-silicate equilibrium relations: Am. Jour. Sci., v. 264, p. 204-222.

Norton, D., and Knapp, R., 1977, Transport phenomena in hydrothermal systems: the nature of porosity: Am. Jour. Sci., v. 277, p. 913-936.

Ohmoto, H., 1972, Systematics of sulfur and carbon isotopes in hydrothermal ore deposits: Econ. Geology, v. 67, p. 551-578.

Ohmoto, H., and Kerrick, D., 1977, Devolatization equilibria in graphitic systems: Am. Jour. Sci., v. 277, p. 1013-1044.

Orville, P. M., 1972, Plagioclase cation exchange equilibria with aqueous chloride solutions: results at 700°C and 2000 bars in the presence of quartz: Am. Jour. Sci., v. 272, p. 234-272.

Ramdohr, P., 1969, The ore minerals and their intergrowths: Oxford, Pergamon, 1174 p.

Richardson, S. W., Gilbert, M. C., and Bell, P. M., 1969, Experimental determination of kyanite-andalusite and andalusite-sillimanite equilibria; the aluminum silicate triple point: Am. Jour. Sci., v. 267, p. 259-272.

Robie, R. A., Bethke, P. M., and Beardlsey, K. M., 1967, Selected x-ray crystallographic data, molar volumes, and densities of minerals and related substances: U. S. Geol. Survey Bull. 1248.

Robie, R. A., Hemingway, B. S., and Fisher, J. R., 1978, Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar pressure and at higher temperatures: U. S. Geol. Survey Bull. 1452, 456 p.

Robinson, K., Gibbs, G. V., Ribbe, P. H., and Hall, M. R., 1973, Cation distribution in three hornblendes: Am. Jour. Sci., v. 273-A, p. 522-535.

Rumble, D., 1973, Andalusite, kyanite, and sillimanite from the Mt. Moosilauke region, New Hampshire: Geol. Soc. America Bull., v. 84, p. 2423-2430.

———— 1978, Mineralogy, petrology, and oxygen isotopic geochemistry of the Clough Formation, Black Mountain, Western New Hampshire, U.S.A.: Jour. Petrology, v. 19, p. 317-340.

Rumble, D., and Oertel, G., 1978, Strain and metamorphism: metaclastic rocks from New Hampshire: Jour. Geology, v. 87, p. 69-86.

Rye, R. O., Schuiling, R. D., Rye, D. M., and Jansen, J. B. H., 1976, Carbon, hydrogen, and oxygen isotope studies of the regional metamorphic complex at Naxos, Greece: Geochim. et Cosmochim. Acta, v. 40, p. 1031-1049.

Ryzhenko, B. N., and Volkov, V. P., 1971, Fugacity coefficients of some gases in a broad range of temperatures and pressures: Geochim. Internat., v. 8, p. 468-481.

Savin, S. M., and Epstein, S., 1970, The oxygen isotopic composition of coarse-grained sedimentary rocks and minerals: Geochim. et Cosmochim. Acta, v. 34, p. 323-329.

Shmulovich, K. I., and Shmonov, V. M., 1975, Fugacity coefficients for CO_2 from 1.0132 to 10,000 bars and 450°-1300°K: Geochim. Internat., v. 12, p. 202-206.

Stormer, J. C., Jr., 1975, A practical two-feldspar geothermometer: Am. Mineralogist, v. 60, p. 667-674.

Taylor, H. P., 1977, Water/rock interactions and the origin of H_2O in granitic batholiths: Geol. Soc. Jour., v. 133, p. 509-558.

Thompson, A. B., 1975, Mineral reactions in a calc-mica schist from Gassetts, Vermont, USA: Contr. Mineralogy Petrology, v. 53, p. 105-127.

Thompson, A. B., Lyttle, P. T., and Thompson, J. B., Jr., 1977, Mineral reactions and A-Na-K and A-F-M facies types in the Gassetts Schist, Vermont: Am. Jour. Sci., v. 277, p. 1124-1151.

Thompson, J. B., Jr., and Hovis, G. L., 1979, Entropy of mixing in sanidine: Am. Mineralogist, v. 64, p. 57-65.

Thompson, J. B., Jr., and Norton, S. A., 1968, Paleozoic regional metamorphism in New England and adjacent areas, *in* Zen, E-An, and others, eds., Studies of Appalachian Geology, Northern and Maritime: New York, Intersci., p. 319-327.

Thompson, J. B., Jr., Robinson, P., Clifford, T. N., and Trask, N. J., Jr., 1968, Nappes and gneiss domes in west-central New England, *in* Zen, E-An, and others, eds., Studies of Appalachian Geology, Northern and Maritime: New York, Intersci., p. 203-218.

Whitney, J. A., and Stormer, J. C., Jr., 1977, The distribution of $NaAlSi_3O_8$ between coexisting microcline and plagioclase and its effect on geothermometric calculations: Am. Mineralogist, v. 62, p. 687-691.

Zen, E-An, 1963, Components, phases, and criteria of chemical equilibrium in rocks: Am. Jour. Sci., v. 261, p. 929-942.