American Mineralogist, Volume 68, pages 334–354, 1983

Mineral reactions and element migration during metamorphism of calcareous sediments from the Vassalboro Formation, south-central Maine

JOHN M. FERRY

Department of Geology
Arizona State University
Tempe, Arizona 85287

Abstract

Whole-rock chemical data for a suite of metamorphosed carbonate rocks from a single stratigraphic unit indicate that K, Na, and CO_2 were progressively lost from the rocks during the metamorphic event. Average rocks collected at the highest grades contain only 18% as much K and only 31% as much Na as do average rocks collected at the lowest grades. Extraction of Na and K occurred over a wide range of metamorphic grades, but extraction of Na began at lower grade conditions than did extraction of K. The chemical data and petrological arguments are consistent with no mass transfer of Fe, Mg, Ti, Si, or Ca relative to a constant aluminum reference frame. Consideration of the compositions and proportions of minerals in the metamorphic rocks, and of whole-rock chemistry leads to the inferred mechanisms by which K and Na were lost. Sodium was probably lost through a mineral–fluid hydrolysis reaction that destroyed the albite component of plagioclase and produced quartz, anorthite, and a soluble Na-bearing fluid species. Potassium was probably lost independently through a mineral–fluid hydrolysis reaction that destroyed biotite and formed calcic amphibole, sphene, anorthite, and a soluble K-bearing fluid species. The reactions indicate that H_2O was progressively lost during metamorphism, as well as K, Na, and CO_2. The observed amount of mass transport of K and Na requires that 1–10 rock volumes of fluid interacted with the carbonate rocks during metamorphism. The large fluid volumes and the observed hydrolysis reactions lead to a model that considers regional metamorphism in the area as possible large-scale acid metasomatism.

Introduction

The possibility of mass transfer during metamorphism has been the basis for lively debate among petrologists for decades. Metamorphic petrologists commonly view metamorphism as an isochemical process, *i.e.*, a process which occurs at constant composition with the exception of the loss of certain volatile compounds (principally H_2O and CO_2). The modern concept of isochemical metamorphism is largely based on Shaw's (1955) pioneering study of the metamorphosed Littleton Formation in New Hampshire. He found (with the exception of H_2O) no statistically significant difference between concentrations of major elements in a group of low-grade metamorphic rocks and concentrations in a group of high-grade rocks from that formation. Isochemical metamorphism has been confirmed in a number of more recent studies (*e.g.*, Yardley, 1977; Stanton and Williams, 1978). The concept of isochemical metamorphism is the foundation of many practices among metamorphic petrologists. For example, the concept leads to the modeling of prograde mineral reactions as simple mass-balance relations among mineral formulas ($\pm CO_2$ $\pm H_2O$), and it is the basis for considering the mineralogical evolution of a metamorphic rock as the trajectory of a single fixed bulk composition through a petrogenetic grid.

There are, however, numerous studies which have documented transport of at least some elements (besides, of course, CO_2 and H_2O) related to a metamorphic event (*e.g.*, Misch, 1949; Senior and Leake, 1978; Tanner and Miller, 1980; Velde and Brusewitz, 1982). Unfortunately these studies do not address certain important aspects of allochemical (=non-isochemical) metamorphism such as (1) the mineral–fluid reactions by which transported elements are released and/or fixed, (2) the scale over which element migration occurs. This report begins with documentation of a case for allochemical metamorphism developed from whole-rock chemical analyses, mineral composition data, and modes for a suite of metamorphosed impure carbonate rocks from south-central Maine. Metamorphic processes almost quantitatively extracted the alkalis, K and Na, from medium- and high-grade rocks. Whole-rock chemical patterns are similar to those in a recent study of progressively metamorphosed impure carbonate rocks from Scotland (Tanner and Miller, 1980) and suggest that allochemical metamor-

0003–004X/83/0304–0334$02.00

phism may be quite common for certain rock types in certain metamorphic environments. The report next utilizes mineral composition data and modes to determine those mineral–fluid reactions which released the alkalis from the carbonate-bearing rocks during the metamorphic event. Finally this report and a companion paper (Ferry, 1982) consider the scale and mechanism by which migration of K and Na occurred during metamorphism. Based, in part, on earlier studies which document interaction of the calc-silicate rocks in Maine with large volumes of aqueous metamorphic fluid (Ferry, 1980a), I conclude that the principal transport process was infiltration. Thus metamorphism of the carbonate-bearing rocks is considered to be an example of large-scale infiltration metasomatism.

Geological setting

Analyzed samples were all collected from the Silurian Vassalboro Formation in south-central Maine (Fig. 1). The Vassalboro Formation is composed of interbedded argillaceous sandstone, argillaceous carbonate rock, and minor shale and their metamorphic equivalents. Compositional layering is on a scale of 2–15 cm. The metasediments are folded into tight isoclinally refolded recumbent folds (Osberg, 1979). Axes of the isoclinal folds trend NE–SW, and almost everywhere in outcrop lithologic layering is near vertical with a NE–SW strike. Porphyroblasts cross-cut schistosity associated with the isoclinal folds and indicate that metamorphism followed almost all deformation. The metasediments are intruded by synme-

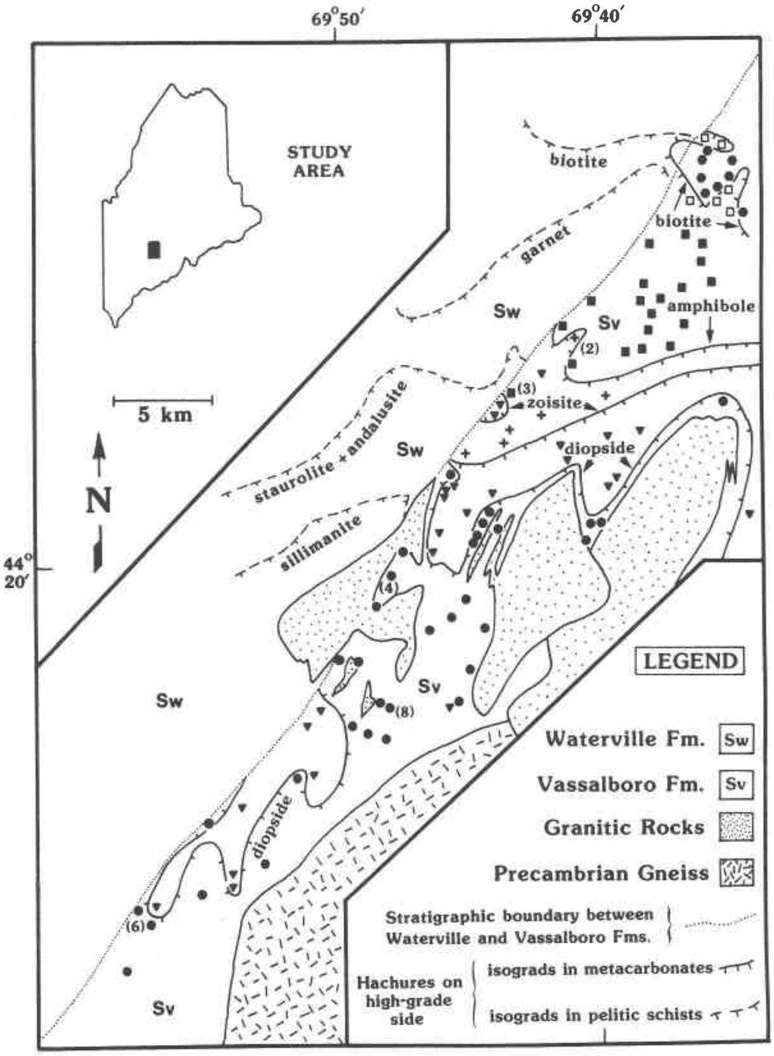

Fig. 1. Geologic sketch map of area studied. Symbols are locations of outcrops sampled. Hexagons: ankerite zone; squares: biotite zone; crosses: amphibole zone; triangles: zoisite zone; circles: diopside zone. Numbers in parentheses indicate number of samples collected at an outcrop, if more than one. The amphibole zone contains two anomalous outcrops: one contains rocks with the mineralogy of biotite zone samples; the other contains rocks with the mineralogy of zoisite zone samples. Data from Osberg (1968, 1979, pers. comm.); Ferry (1980a).

tamorphic quartz monzonite and granodiorite stocks. The grade of metamorphism, with reference to pelitic schists, varies from chlorite-zone conditions in the northernmost portion of Figure 1 to sillimanite-zone conditions in the south. Geochronologic work on both the granitic and metamorphic rocks indicates that the metamorphism and emplacement of the granites occurred during the Devonian Acadian Orogeny (Dallmeyer, 1979; Dallmeyer and VanBreeman, 1981). Evidence for three Acadian metamorphic episodes (one well to the west of the present area) has been reported for rocks of the western part of the Augusta Quadrangle by Novak and Holdaway (1981). They suggest that low-variance assemblages and limited textural evidence of disequilibrium imply the presence of two metamorphic episodes (possibly M_2 and M_3 of Guidotti, 1970) in an area 10–30 km west of the exposure of the Vassalboro Formation in Figure 1. If there were two metamorphic events in the present area, they were closely spaced in time and *P–T* conditions and the rocks in question appear to have entirely equilibrated to the last and most pervasive event (M_3, Holdaway *et al*, 1982). The stratigraphy, structural geology, and metamorphism of the Vassalboro Formation have been discussed in more detail by Osberg (1968), as well as in references cited previously.

Metamorphism of impure carbonate rocks in the Vassalboro Formation has been described by Ferry (1976a,b, 1978, 1980a). The Vassalboro Formation in Figure 1 is divided into five metamorphic zones based on the mineralogy of the metacarbonate rocks. Boundaries of the zones are isograds based on the first appearance of biotite, calcic amphibole, zoisite, and diopside in the rocks (Ferry, 1976a). Zones are named according to the name of the isograd that bounds the lower-grade side of the zone. The northernmost zone will be referred to as the ankerite zone. Ferry (1976a) mapped a microcline–amphibole isograd between the zoisite and diopside isograds and a scapolite isograd at grades higher than the diopside isograd in a portion of Figure 1. Both isograds are omitted from this report because in the larger area of Figure 1 there are too few microcline-bearing and scapolite-bearing rocks to accurately locate the isograds. In earlier reports (Ferry, 1976a,b) I presented reactions to account for the prograde mineral changes that were based on an assumption of isochemical metamorphism. Later work has now proven that metamorphism was not isochemical. While the reactions proposed earlier are still believed to have occurred, they constitute an incomplete description of mineral reactions which occurred during the metamorphic event. Specifically, additional reactions are required to account for the allochemical nature of the metamorphism. Consequently, results presented here supersede earlier ones. Because isograds were given names based on the inferred isochemical reactions that they represent, it seems appropriate at this time to also revise the nomenclature of the isograds. The isograds along which biotite and calcic amphibole first appear in the metacarbonates will simply be referred to as the biotite and amphibole isograds, respectively. Isograds based on the first appearance of zoisite and diopside will retain their original names. Revised nomenclature in no way changes the position of the isograds or mineral assemblages previously reported in each zone.

Because of the relationship between the strike of lithologic layering and the isograds of the Vassalboro Formation, the area in Figure 1 is an ideal location to investigate what chemical changes occur during metamorphism. While individual beds cannot be traced over the entire range of metamorphic grades, similar lithologies from the same stratigraphic unit can be followed from ankerite- through diopside-zone conditions. Such an arrangement between structure and metamorphic gradient minimizes variations in original sedimentary rock composition with changes in grade, thereby maximizing the opportunity of detecting any whole-rock chemical changes associated with the metamorphism.

Pressure, temperature, and fluid composition

Estimates of pressure and temperature attained during metamorphism in the study area are summarized by Ferry (1976b, 1980b). Pressure was 3500±200 bars in the diopside zone, based on four different geobarometers in rocks from the adjacent Waterville Formation. Temperatures ranged from ~375°C at the biotite isograd to 520–575°C in the diopside zone.

The composition of CO_2–H_2O fluids in equilibrium with metacarbonate rocks from the zoisite and diopside zones has been previously reported (Ferry, 1976b; 1978; 1980a). The ubiquitous presence of zoisite in rocks from the zoisite and diopside zones requires H_2O-rich equilibrium fluids ($X_{CO_2} = 0.04–0.3$). The occurrence of sphene, as opposed to rutite + calcite + quartz, in metacarbonate rocks from the biotite and amphibole zones indicates that equilibrium metamorphic fluids were H_2O-rich in the low-grade portion of the terrain, as well (Jacobs and Kerrick, 1981). At inferred temperature conditions of 400–440°C in the biotite zone, the occurrence of sphene restricts metamorphic fluid compositions to $X_{CO_2} \leq 0.10$; at inferred conditions of 440–500°C in the amphibole zone the composition of CO_2–H_2O fluid in equilibrium with sphene-bearing rocks was $X_{CO_2} \leq 0.30$. The compositions of metamorphic fluids in equilibrium with rocks in the ankerite zone could not be characterized.

Methods of investigation

Approximately 200 samples of metacarbonate rock were collected from all five zones of the Vassalboro Formation. Only those samples containing a carbonate mineral are considered in this study. Of the ~200 samples, 115 of the freshest with calcite and/or ankerite were chosen for further chemical and petrographic study. Locations of the 115 samples are shown in Figure 1.

Thin sections were prepared from rock specimens that correspond in outcrop to individual layers of carbonate rock. At some outcrops more than one layer was sampled. Most samples appear homogeneous in hand specimen. Mineral assemblages were identified from petrographic observation of the thin sections. Compositions of minerals were obtained by electron microprobe analysis either at Harvard University (methods described by Ferry, 1976a) or at the Geophysical Laboratory (methods described by Ferry, 1980a). The same natural and synthetic minerals were used as standards for all analyses.

Modal amounts of minerals in most specimens were determined by counting 500–1000 points in thin section. Modes for muscovite, ankerite, calcite, biotite, plagioclase, amphibole, zoisite, and diopside were later determined in selected samples by counting 1000 points. Volume amounts of minerals were converted to molar amounts (per reference volume of rock) using molar volume data (Robie *et al.*, 1967; Hewitt and Wones, 1975; McOnie *et al.*, 1975).

Chemical analyses of rock samples for major-element metal oxides were performed using inductively coupled argon–plasma methods by Technical Service Laboratories (TSL), Mississauga, Ontario (A. Debnam and W. Grondin, analysts). The application of this technique to the chemical analysis of rocks has been recently described by Church (1981). Samples for chemical analysis, approximately 5 cm^3 in volume, were cut from hand specimens as close as possible to where chips were removed to prepare thin sections. Table 1 lists analyses of a Mount Hood andesite which is used as a secondary standard in the XRF laboratory in the Department of Chemistry at Arizona State University (ASU). Table 1 consists of the average of two analyses of the andesite performed by TSL and an average of three analyses of the same material performed at ASU by X-ray fluorescence methods (A. Yates, analyst). Agreement between the two averages is good for all oxides except SiO_2, and is a measure of the reliability of the analyses of the carbonate rocks. Analyses for SiO_2 by TSL appear to be too low by approximately 1.25 weight percent. Consequently 1.25% SiO_2 was added to all analyses made by TSL of metacarbonate rock. The addition of 1.25% SiO_2 raised the sum of oxide percents from an average of slightly less than 99% to an average very near 100%. Whole-rock samples were also analyzed by TSL for total carbonate carbon. Samples were fused at over 1800°C in a LECO combustion furnace. The total amount of carbon was then measured in the effluent gases using a LECO 4000A carbon analyzer. Samples were next leached in acid to remove the carbonate carbon and a second measurement was made of total carbon in the acid-leached residue. Total carbonate carbon is reported as the difference between the two measurements of total carbon.

Table 1. Composition (weight percent) of a Mount Hood andesite. TSL refers to the average of two analyses by Technical Service Laboratories. ASU refers to the average of three analyses performed at Arizona State University.

	TSL	ASU
SiO_2	58.83	60.07
Al_2O_3	17.55	17.89
Fe_2O_3	6.73	6.59
CaO	6.09	6.08
MgO	2.81	2.91
Na_2O	4.34	4.07
K_2O	0.99	1.14
TiO_2	1.06	0.93
MnO	0.11	0.12
P_2O_5	0.24	0.20
LOI	0.35	0.03
Total	99.10	100.03

Mineralogy and mineral chemistry

Average modes of metacarbonates in each of the five zones from the Vassalboro Formation are presented in Table 2 and Figure 2. Table 3 lists the composition of minerals in the carbonate-bearing rocks averaged over those samples from one or several of the zones. Because the mineralogy of these rocks has been described previously (Ferry, 1976a) only a brief summary follows here.

Ankerite zone

Metamorphosed carbonate rocks in the ankerite zone contain the assemblage ankerite + quartz + albite + muscovite±calcite±chlorite. Accessory minerals include various combinations of pyrite, pyrrhotite, apatite, tourmaline, ilmenite, and graphitic material. All plagioclase is albite with an average of one mole percent anorthite component.

Biotite zone

Metamorphosed carbonate rocks in the biotite zone contain the assemblage biotite + quartz + plagioclase + calcite + chlorite±muscovite±ankerite. Accessory minerals include combinations of pyrite, pyrrhotite, apatite, tourmaline, ilmenite, sphene, and graphitic material. Samples from the biotite zone may be readily divided into two groups. One group, located close to the biotite isograd (open squares, Fig. 1), contains abundant ankerite, little biotite (<2.7 modal percent), and albite (An_0–An_3). Ankerite-bearing samples are referred to as rocks from the lower biotite zone in Table 2 and elsewhere. The second group of rocks (filled squares, Fig. 1) contains no ankerite, abundant biotite (5.7–29.6 modal percent), and significantly more calcic plagioclase (An_{10}–An_{62}). The second group occupies the higher-grade portion of the biotite zone and rocks in it are referred to as from the upper biotite zone in Table 2 and elsewhere.

Amphibole zone

Metamorphosed carbonate rocks in the amphibole zone contain the assemblage calcic amphibole + quartz + plagioclase + calcite + biotite±chlorite. Accessory minerals include combinations of pyrrhotite, apatite, tourma-

Table 2. Average modes of metamorphosed carbonate rocks in each metamorphic zone. Numbers in volume percent.

	Ankerite Zone		Lower Biotite Zone		Upper Biotite Zone		Amphibole Zone		Zoisite Zone		Diopside Zone	
Mineral	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.
Carbonate	27.1	20.4	21.3	8.7	12.7	13.5	6.1	3.8	10.6	12.4	11.2	10.0
Quartz	30.8	3.1	30.7	5.9	35.1	7.6	37.2	12.5	38.6	7.6	38.4	7.9
Plagioclase	25.1	11.1	27.7	5.7	27.6	5.9	32.4	5.6	15.8	10.4	18.4	8.4
Muscovite	14.5	6.2	15.8	2.0	3.4	4.3	0.0	0.0	0.1	0.2	0.0	0.0
Chlorite	1.2	2.4	2.1	2.6	1.9	2.2	1.1	1.2	0.0	0.0	0.0	0.0
Biotite	0.0	0.0	1.0	0.9	17.7	5.5	14.8	6.6	3.1	5.5	0.3	1.1
Amphibole	0.0	0.0	0.0	0.0	0.0	0.0	5.9	1.9	15.2	4.7	11.9	5.6
Zoisite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	12.1	9.8	11.6	8.4
Diopside	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.1	4.9
Microcline	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8	3.7	0.8	2.4
Scapolite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.3	tr	0.3
Sphene	0.0	0.0	tr	0.0	0.6	0.5	1.9	1.1	2.0	1.0	2.0	0.9
Tourmaline	tr	0.0	0.1	0.1	0.1	0.1	tr	0.1	0.1	0.1	0.1	0.1
Apatite	tr	0.0	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.2
Opaques	1.4	0.6	1.4	0.3	1.0	1.1	0.7	0.5	0.2	0.3	0.1	0.2
Garnet	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	tr	0.1	tr	0.2

line, ilmenite, sphene, and graphitic material. The formulas for all calcic amphiboles in Table 3 have been slightly simplified by omitting approximately 0.1 K atom. Plagioclase varies in composition from An_{33} to An_{95} with an average of A_{70} for all feldspars analyzed from the amphibole zone.

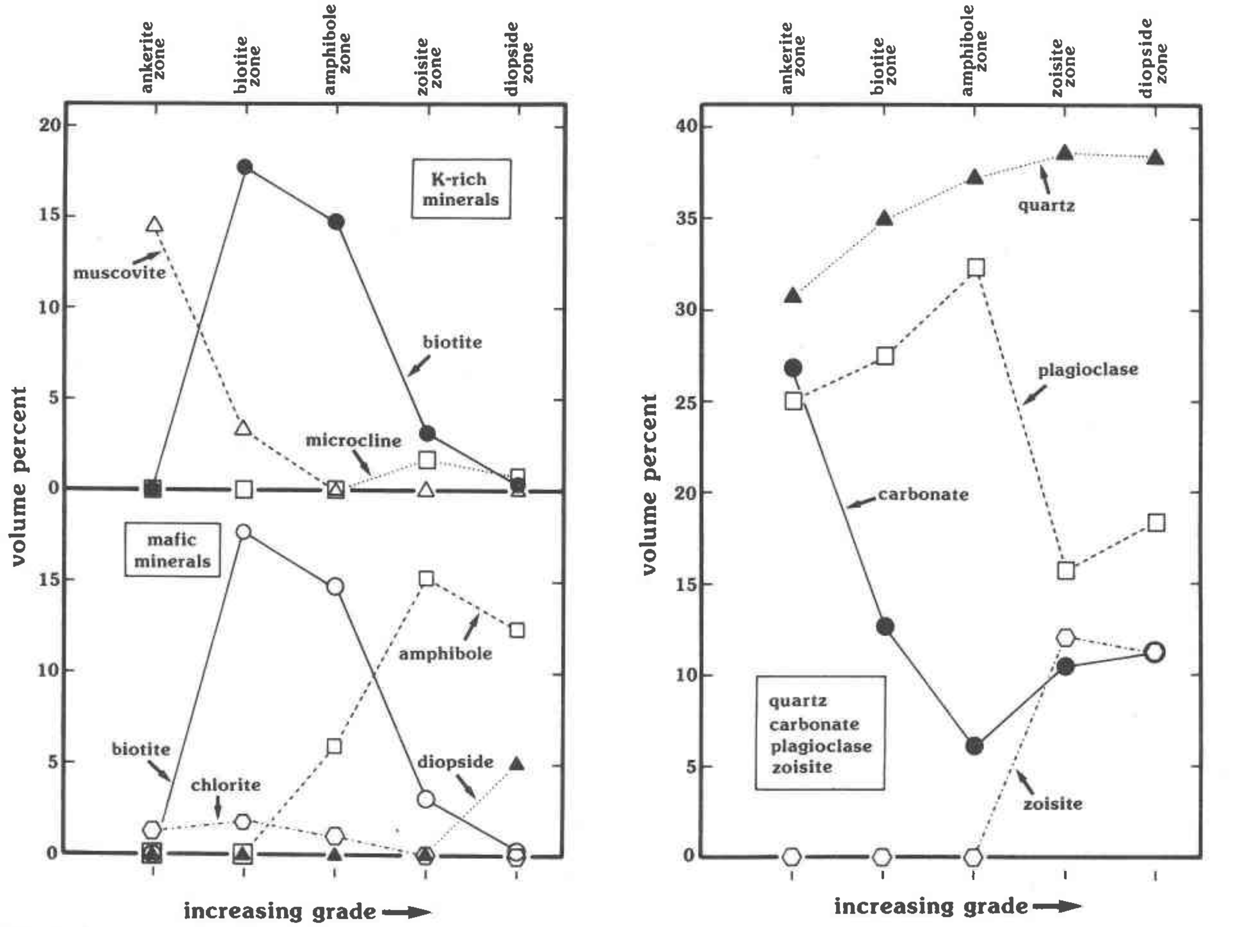

Fig. 2. Average modes of metacarbonate rocks in each metamorphic zone. Data for the biotite zone refers to upper biotite zone.

Table 3. Average composition of minerals in metamorphosed carbonate rocks.

Mineral	Zone	Composition
Ankerite	Average: Ankerite and Biotite Zones	$Ca(Fe,Mg,Mn)(CO_3)_2$
Calcite	1. Average: Ankerite and Biotite Zones	$Ca_{0.93}(Fe,Mg,Mn)_{0.07}CO_3$
	2. Average: Biotite and Amphibole Zones	$Ca_{0.96}(Fe,Mg,Mn)_{0.04}CO_3$
	3. Average: Amphibole, Zoisite, and Diopside Zones	$Ca_{0.97}(Fe,Mg,Mn)_{0.03}CO_3$
Biotite	1. Average: Biotite Zone	$(K_{0.88}Na_{0.02})\{(Fe,Mg,Mn)_{2.33}Ti_{0.12}Al_{0.40}\}(Al_{1.22}Si_{2.78})O_{10}(OH)_2$
	2. Average: Biotite, Amphibole, and Zoisite Zones	$(K_{0.89}Na_{0.02})\{(Fe,Mg,Mn)_{2.36}Ti_{0.10}Al_{0.38}\}(Al_{1.22}Si_{2.78})O_{10}(OH)_2$
Amphibole	1. Average: Amphibole and Zoisite Zones	$Na_{0.19}Ca_{1.93}(Fe,Mg,Mn)_{4.60}Ti_{0.05}Al^{VI}_{0.43}Al^{IV}_{0.82}Si_{7.18}O_{22}(OH)_2$
	2. Average: Zoisite Zone	$Na_{0.15}Ca_{1.93}(Fe,Mg,Mn)_{4.67}Ti_{0.03}Al^{VI}_{0.38}Al^{IV}_{0.68}Si_{7.32}O_{22}(OH)_2$
	3. Average: Zoisite and Diopside Zones	$Na_{0.16}Ca_{1.94}(Fe,Mg,Mn)_{4.58}Ti_{0.03}Al^{VI}_{0.44}Al^{IV}_{0.75}Si_{7.25}O_{22}(OH)_2$
Diopside	Average: Diopside Zone	$Ca_{0.97}Na_{0.01}(Fe,Mg,Mn)_{1.01}Al^{VI}_{0.01}Al^{IV}_{0.01}Si_{1.99}O_6$
Chlorite	Average: Ankerite, Biotite, and Amphibole Zones	$(Fe,Mg,Mn)_{4.50}Al_{2.70}Si_{2.71}O_{10}(OH)_8$
Muscovite	Average: Ankerite and Biotite Zones	$(K_{0.90}Na_{0.05})\{(Fe,Mg,Mn)_{0.23}Ti_{0.03}Al_{1.78}\}(Al_{0.85}Si_{3.15})O_{10}(OH)_2$
Microcline	Average: Zoisite and Diopside Zones	$Or_{0.94}Ab_{0.06}$
Plagioclase	Average: Ankerite Zone	An_{01}
	Average: Biotite Zone	An_{29}
	Average: Amphibole Zone	An_{70}
	Average: Zoisite Zone	An_{74}
	Average: Diopside Zone	An_{79}
Zoisite	Average: Zoisite and Diopside Zones	$Ca_{2.00}(Al_{2.68}Fe_{0.32})Si_{3.00}O_{12}(OH)$
Scapolite	Average: Zoisite and Diopside Zones	$Ca_{3.01}Na_{0.96}K_{0.03}Al_{5.01}Si_{6.99}O_{24}CO_3$
Sphene	Biotite, Amphibole, Zoisite, and Diopside Zones	$CaTiSiO_5$
Ilmenite	All Zones	$(Fe,Mg,Mn)TiO_3$
Quartz	All Zones	SiO_2

Zoisite zone

Metamorphosed carbonate rocks in the zoisite zone contain the assemblage zoisite + calcic amphibole + quartz + plagioclase + calcite±biotite±K–feldspar. Accessory minerals include combinations of muscovite, scapolite, garnet, pyrrhotite, apatite, tourmaline, sphene, and graphitic material. The formula for zoisite in Table 3 has been slightly simplified by omitting 0.01 Mg and 0.01 Mn atoms. Microcline occurs in 22% of the samples studied from the zoisite zone. Plagioclase varies in composition from An_7 to An_{97} with an average of An_{74} for all feldspars analyzed in the zoisite zone. Zoisite has a composition usually associated with monoclinic crystals (clinozoisite); zoisite, however, has the optical properties of orthorhombic crystals in thin section.

Diopside zone

Metamorphosed carbonate rocks in the diopside zone contain the assemblage diopside + zoisite + calcite + quartz + plagioclase + calcic amphibole±biotite±K–feldspar. Accessory minerals include combinations of scapolite, garnet, pyrrhotite, apatite, tourmaline, sphene, and graphite. Microcline and scapolite occur in only a small percentage of rocks studied from the diopside zone (17% and 4%, respectively). Plagioclase varies in composition from An_{27} to An_{98} with an average of An_{79} for all feldspars analyzed in the diopside zone.

Whole-rock chemistry

Average chemical compositions of metamorphosed carbonate rock from each of the five zones are listed in

Table 4. During analysis of the whole-rock samples, iron is oxidized to Fe_2O_3; consequently total iron is reported as Fe_2O_3. CO_2 was not determined for all samples. Data for CO_2, therefore, are reported separately because the average CO_2 content of samples analyzed for CO_2 is different from the average CO_2 content of samples analyzed for metallic oxides. The compositions of only eight samples from the ankerite zone were determined. In order to evaluate chemical changes that are induced by metamorphism, however, it is desirable to have data on as large a population of unmetamorphosed or weakly-metamorphosed rocks as possible. To augment the population of weakly-metamorphosed rocks, analyses of six rocks from the lower biotite zone were included with those of the ankerite zone. The six samples from the lower biotite zone are only incipiently metamorphosed. They contain exactly the same mineral assemblages as do rocks from the ankerite zone with the exception of 0.1–2.7 modal percent biotite (Table 2). Compositions of minerals in the six rocks are indistinguishable from mineral compositions observed in rocks of the ankerite zone. The larger population that includes both rocks from the ankerite zone and those six from the lower biotite zone more reliably characterizes the chemistry of the Vassalboro Formation prior to the greenschist–amphibolite facies metamorphic event.

In order to compare the composition of metamorphic rocks from different zones, some basis for comparison must be established. Previous studies (Carmichael, 1969; Thompson, 1975) have used a constant aluminum reference frame. This reference frame is sensible because the small solubility of Al in aqueous fluids (Frantz *et al.*, 1981) implies relatively little mass transport of the element during metamorphic and hydrothermal events. An aluminum-based reference frame was therefore adopted in this study. The ratios of the atomic concentrations of major elements to that of aluminum were calculated for each analyzed sample, and these ratios were averaged for all samples from each zone. Results are plotted in Figure 3. Figure 3 reveals that there is no detectable change in

Table 4. Average whole-rock chemical composition (weight percent) of metamorphosed carbonate rocks in each metamorphic zone.

	Ankerite Zone		Biotite Zone		Amphibole Zone		Zoisite Zone		Diopside Zone	
	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
SiO_2	62.64	44.55-72.80	65.51	50.94-74.89	64.37	46.62 75.92	64.72	45.93-76.33	65.28	52.87-74.15
Al_2O_3	9.85	7.84-13.21	10.67	6.97 14.18	10.74	9.36 11.88	10.06	7.25 12.53	10.03	7.96 14.08
Fe_2O_3*	3.72	2.07 5.43	3.90	2.43-6.03	4.06	3.24 4.70	3.66	2.75-4.95	3.74	2.79-4.52
CaO	8.27	1.01 19.82	7.46	1.56-20.44	10.52	4.96-23.06	12.45	4.75-24.96	13.05	4.95 21.08
MgO	1.99	1.33-3.21	2.27	1.31-3.89	2.41	1.98-2.68	2.27	1.54-3.49	2.21	1.53-2.85
Na_2O	2.27	1.62-3.24	2.03	1.04-3.52	1.04	0.55-2.04	0.99	0.30-2.01	0.74	0.32-2.03
K_2O	1.64	0.74-2.70	1.82	0.87-3.82	0.97	0.22-1.63	0.56	0.11-2.01	0.29	0.12-2.28
TiO_2	0.64	0.45-0.84	0.70	0.49-1.03	0.68	0.61-0.83	0.66	0.48-1.04	0.67	0.49-1.02
MnO	0.32	0.06-1.41	0.13	0.04-0.35	0.19	0.07-0.47	0.18	0.07 0.45	0.19	0.06-0.42
P_2O_5	0.10	0.01-0.17	0.16	0.10-0.33	0.16	0.10-0.19	0.14	0.07-0.25	0.15	0.06-0.25
LOI†	8.47	2.46 16.76	5.14	0.95-13.52	4.61	0.83-12.15	4.24	0.34-13.49	3.47	0.34-10.92
Total	99.91		99.79		99.75		99.93		99.82	
n§	14		21		7		25		48	
CO_2	9.84	3.55-18.40	5.00	0.92-14.90	7.04	1.68-14.10	6.13	0.40-15.30	3.97	0.81-11.30
n§	12		20		5		17		43	

* all Fe as Fe_2O_3; † loss on ignition; § number of samples analyzed.

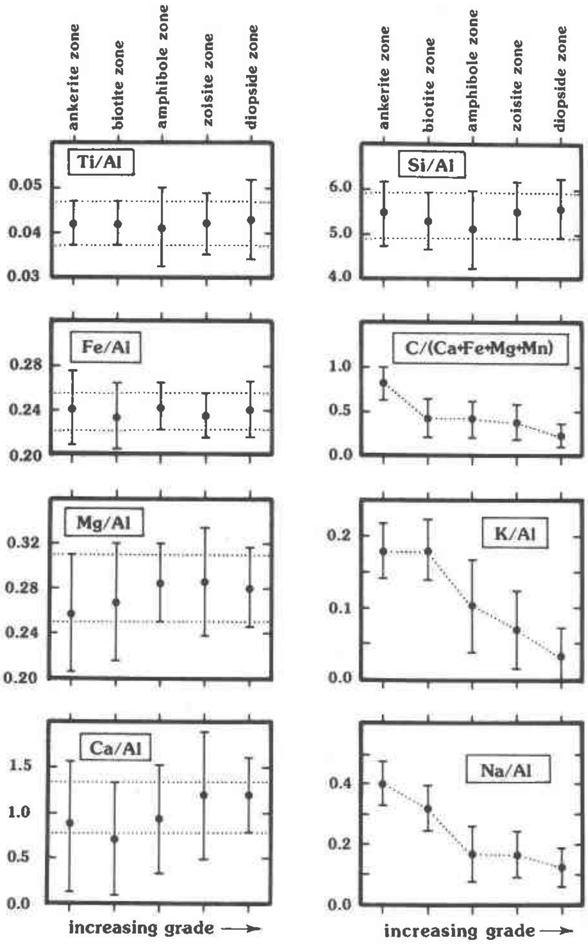

Fig. 3. Average atomic ratio of i/Al and of C/(Ca+Mg+Fe+Mn) for metacarbonate rocks in each metamorphic zone, where i = K, Na, Si, Ca, Fe, Mg, Ti. Data for the ankerite zone includes samples from the lower biotite zone; data for the biotite zone refers to samples from the upper biotite zone (see text). Length of error bar represents two standard deviations.

whole-rock Fe/Al, Mg/Al, Ti/Al, or Si/Al with increasing grade of metamorphism. Because Mg/Al and Fe/Al show no changes, whole-rock Fe/(Fe+Mg) also shows no change. Results in Figure 3, however, indicate that K/Al and Na/Al decrease dramatically with increasing metamorphic grade. Relative to aluminum, diopside zone metacarbonates contain, on the average, only 31% as much Na and only 18% as much K as do rocks from the ankerite zone. Some rocks in the diopside zone are highly depleted in alkalis; the most Na-depleted rock contains 14% as much Na as the average rock in the ankerite zone; the most K-depleted rock contains only 7% as much K as the average rock in the ankerite zone. Relative to aluminum, the calcium content of the metacarbonate rocks is quite variable (unlike the other ratios, the standard deviations of average Ca/Al are nearly as large as the average values themselves). Average Ca/Al of rocks in the zoisite and diopside zones is slightly larger than average Ca/Al in the other three zones.

As would be expected from decarbonation reactions, there is a decrease in whole-rock carbon content with increasing grade of metamorphism. Because all carbonate carbon originally was in the rock as Ca–Fe–Mg–Mn carbonates (ankerite±calcite), the carbon contents of rocks are compared in Figure 3 using the variable C/(Ca+Mg+Fe+Mn) rather than the variable C/Al. The average value of C/(Ca+Mg+Fe+Mn) is less than one in the ankerite zone because in these rocks some Fe, Mg, and Mn is contained in muscovite and chlorite as well as in carbonate. Metacarbonate rocks in the diopside zone contain, on the average, 30% as much carbonate carbon as do rocks in the ankerite zone (relative to Ca+Mg+Fe+Mn).

The statistical significance of differences in average i/Al between the metamorphic zones was assessed using Student's t test (Leabo, 1972). Differences were taken as significant if they occurred at a >98% confidence level. Average Na/Al and K/Al are significantly less in the amphibole, zoisite, and diopside zones than in the ankerite zone. Average K/Al and Na/Al in the zoisite and diopside zones are less than K/Al and Na/Al in the ankerite zone at a >99.9% confidence level. Average C/(Ca+Mg+Fe+Mn) is significantly less in all other zones than C/(Ca+Mg+Fe+Mn) in the ankerite zone. In contrast, Ti/Al, Fe/Al, Mg/Al, and Si/Al in the biotite, amphibole, zoisite, and diopside zones are not different from corresponding values in the ankerite zone at more than a 95% confidence level. In the diopside zone Ca/Al is different from that in the ankerite zone at a 95–98% confidence level. This difference is believed to be due to a sample bias made during sample collection. Only carbonate-bearing rocks were collected. Carbonate-bearing rocks in the diopside zone, on the average, initially contained more carbonate and higher Ca/Al than carbonate-free rocks in the diopside zone because prograde metamorphic reactions produced calc-silicate minerals at the expense of carbonate. By similar logic, carbonate-bearing rocks in the diopside zone, on the average, should have higher Ca/Al than rocks with carbonate at lower grades which have experienced less mineral reaction. This sample bias is believed to be the cause of the somewhat greater average values of whole-rock Ca/Al in the diopside and zoisite zones than average Ca/Al in the ankerite, biotite, and amphibole zones.

The sample bias responsible for higher average Ca/Al of samples collected in the zoisite and diopside zones is important because it potentially could be an explanation for the decrease in average whole-rock Na/Al and K/Al with increasing grade. It could be argued, for example, that the chemical trends in Figure 3 are a result of preferentially collecting Na-poor, K-poor, Ca-rich lithologies at high grades and of collecting a mixture of lithologies with variable Na-, K-, and Ca-contents at low grades. Figure 4 illustrates why sample bias during collec-

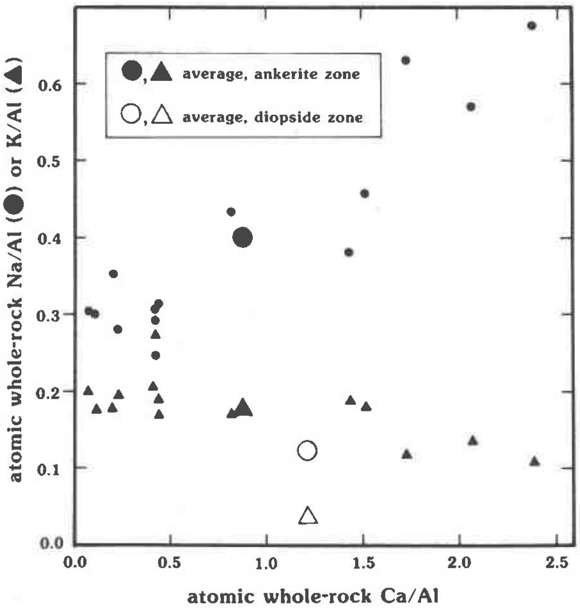

Fig. 4. Plot of Na/Al (small circles) and K/Al (small triangles) *vs.* Ca/Al for metacarbonate rocks from the ankerite and lower biotite zones of Fig. 1. Large symbols are average values for the ankerite and diopside zones.

tion of the rocks could not explain the difference in Na/Al and K/Al between the low-grade and high-grade metacarbonate rocks. For rocks in the ankerite and lower biotite zone, there is no change in K/Al with Ca/Al up to a value of Ca/Al ~ 1.6 (which is greater than the average Ca/Al of rocks in the diopside and zoisite zones). The variable Na/Al actually *increases* with increasing Ca/Al in the low-grade rocks. Even though selective sampling of Ca-rich metacarbonates at high grades can explain the slightly higher average values of Ca/Al in the diopside and zoisite zones, such a bias could not explain the large depletion in whole-rock Na/Al and K/Al of high-grade samples relative to those collected at low grades.

In principle, then the dramatic changes in Na/Al, K/Al, and C/(Ca+Mg+Fe+Mn) with increasing metamorphic grade could be due either to sedimentary or metamorphic processes. Three arguments are presented in favor of metamorphic processes. First, changes in K/Al and Na/Al occur over distances of ~10 km along strike of beds. Within each zone samples were collected along similar distances across strike and much less variation in K/Al, Na/Al, and C/(Ca+Mg+Fe+Mn) was observed. It would be an unusual set of sedimentary processes that produce greater variations in rock composition along strike of beds than across beds. Second, the chemical compositions of rocks in the ankerite zone are very similar to those of calcareous graywackes (Pettijohn, 1975) which the ankerite-zone rocks resemble texturally and mineralogically as well. In contrast, K/Al and Na/Al of rocks from the amphibole, zoisite, and diopside zones are unlike those for *any* common sedimentary rock (*cf.* analyses in Pettijohn, 1975). The chemistry of rocks in the three zones, therefore, does not appear to be a result of common sedimentary processes. Third, there is a close correlation between the Na/Al and K/Al of carbonate-bearing rocks and metamorphic grade in the area. For example, rocks with low K/Al (<0.10) and low Na/Al (<0.20) are never found in the ankerite zone but only in the amphibole, zoisite, and diopside zones. Conversely, rocks with high K/Al (>0.10) or high Na/Al (>0.30) constitute only 8% of the samples found in the diopside zone but are ubiquitous in the ankerite and lower biotite zones. This close relationship between rock chemistry and metamorphic grade suggests that the relationship developed during metamorphism rather than during sedimentation and diagenesis. In light of these three arguments, it seems more reasonable to attribute observed differences in K/Al and Na/Al of rocks from different zones to metamorphic processes.

If little or no mass transport of aluminum occurs during metamorphism, then changes in K/Al and Na/Al as a function of metamorphic grade may be interpreted as mass transport of Na and K during the metamorphic event. Evidently metamorphic processes leached alkalis from the rocks. There is no positive evidence that Mg, Fe, Ti, or Si were transported during regional metamorphism because no significant changes in Mg/Al, Fe/Al, Ti/Al, and Si/Al were observed as a function of increasing grade. Changes in Ca/Al are interpreted in terms of sample bias during collection of the metacarbonate rocks rather than in terms of mass transport of Ca during metamorphism. Because it is believed that there is no positive evidence for mass transfer of Ca, Fe, and Mg, the decrease in average C/(Ca+Mg+Fe+Mn) may be interpreted as progressive loss of CO_2 from the rocks during metamorphism (Mn-content of rocks is small, usually <0.5 weight percent). The observed decrease in the carbonate carbon content of the rocks is a natural consequence of decarbonation reactions that proceeded in the rocks during the metamorphic event.

Although there is no evidence for mass transport of Ti, Fe, Mg, and Si, it cannot necessarily be inferred from the data that Ti, Fe, Mg, and Si were absolutely immobile during metamorphism. Generally the standard deviations of the four ratios, Ti/Al, Fe/Al, Mg/Al and Si/Al, are approximately 10% of the value of the mean in each zone. Consequently there *could* have been mass transport of Ti, Fe, Mg, or Si relative to Al, if such mass transport were limited to less than ~10% of the amount of the element initially present in the carbonate-bearing rocks. The data of this study probably could not detect such a small change in major element whole-rock chemistry. Generally the standard deviation of Ca/Al is approximately equal to the mean Ca/Al in each zone. Consequently quite substantial transport of Ca relative to Al *could* have occurred during metamorphism. Because of the high "noise level" of measured Ca/Al in each zone (*i.e.*, large standard deviations), mass transfer of Ca simply would not be detectable.

The change in whole-rock chemistry described here is very similar to the results of a study of regionally metamorphosed carbonate rocks from Scotland (Tanner and Miller, 1980). They studied carbonate rocks metamorphosed over a range of conditions which appear to correspond to those between the biotite and diopside zones in Figure 1. The similarity between rocks from the area in Figure 1 and those from Scotland is not exact, however, because the rocks from Scotland contain zoisite at all grades studied. Tanner and Miller found that low-grade biotite-bearing rocks were characterized by Na/Al = 0.13–0.58 (average: ~0.21) and K/Al = 0.02–0.14 (average: ~0.06). High-grade diopside- and hornblende-bearing calc-silicate rocks were characterized by Na/Al = 0.03–0.30 (average: ~0.08) and K/Al = 0–0.05 (average: ~0.03). In carbonate-bearing rocks from the Vassalboro Formation average Na/Al changes from ~0.32 in the biotite zone to ~0.12 in the diopside zone while average K/Al changes from ~0.18 to ~0.03 in the same interval. In both studies the absolute values of Na/Al and K/Al are similar and the magnitude of the changes are similar: over a comparable range of metamorphic conditions Na/Al decreases by approximately 60–70% and K/Al decreases by approximately 50–80%. The two studies suggest that loss of Na and K during progressive regional metamorphism of impure carbonate rocks may be quite a common phenomenon.

Mineral reactions

Because minerals in a rock are a reflection of the rock's chemical composition, changes in rock chemistry must be accompanied by changes in the rock's mineralogy. In this section the prograde mineral reactions that occurred during metamorphism are derived from whole-rock chemical, mineral chemical, and modal data. The reactions identify the mechanisms by which Na, K, and CO_2 were lost from the carbonate rocks during the metamorphic event.

General considerations

Speciation of the metamorphic fluid. Before the prograde mineral reactions are discussed, the identity of the principal Na- and K-bearing species in the metamorphic fluid must be determined. Those reactions which liberate K and/or Na will have different forms depending on the chemical species which accommodate the released K and Na. Four possibilities are envisioned. First, K and Na could have existed in the fluid as oxides, K_2O and Na_2O. The oxides, however, would be very reactive with aqueous fluids and are unlikely to have existed in other than trace concentrations. Second, K and Na could have existed as various hydrated or carbonated species (*e.g.*, KOH, NaOH, $KHCO_3$, $NaHCO_3$, K_2CO_3, *etc.*). Studies of fluid inclusions from regionally metamorphosed calc-silicate rocks (Crawford *et al.*, 1979; Sisson *et al.*, 1982), however, do not report significant concentrations of these species in the trapped fluids. They report that trapped metamorphic fluids are aqueous brines with dissolved alkalis present as chlorides. Third, K and Na could exist as charged species in the fluid, $K+$ and $Na+$. Ions, however, are almost completely associated in aqueous fluids at the *P–T* conditions of metamorphism (Helgeson, 1969; Helgeson *et al.*, 1981; Frantz *et al.*, 1981). The fourth and most likely possibilility is that K and Na principally occurred as associated chloride complexes (KCl and NaCl) in the metamorphic fluid. Although the conclusion is based on inference rather than direct observation, it is consistent with the following information: (a) fluids in equilibrium with the carbonate-bearing rocks of the Vassalboro Formation were H_2O-rich, (b) aqueous fluids in fluid inclusions from calc-silicate rocks contain substantial dissolved chlorine, which is the principal anion and (c) aqueous chloride solutions coexisting with metamorphic minerals are largely composed of associated chloride complexes at the elevated pressures and temperatures of metamorphism.

Based on these considerations, the K- and Na-bearing fluid species which appear in the mineral reactions that follow are tentatively chosen as KCl and NaCl. Future studies may reveal that other species may have been a better choice. Because KCl and NaCl participate in the mineral reactions, some other chloride species must appear on the opposite side of the mineral reaction. NaCl and KCl are not balanced in the reactions by $MgCl_2$, $FeCl_2$, $SiCl_4$, or $TiCl_4$ because the decrease in (Na+K)/Al would then require an increase of Mg/Al, Fe/Al, Si/Al, or Ti/Al which is not observed in the whole–rock chemical data (Fig. 3). KCl and NaCl might be balanced by $CaCl_2$: a decrease in (K+Na)/Al by 0.42 would require an increase of Ca/Al by 0.21 which is consistent with the increase in average whole-rock Ca/Al between the ankerite and diopside zones. In detail, however, decreases in average (Na+K)/Al are poorly correlated with increases in Ca/Al. Average (Na+K)/Al and Ca/Al, for example, *both* decrease between the ankerite and biotite zones (Fig. 3). Between the ankerite and amphibole zones average (Na+K)/Al decreases by 0.30 while average Ca/Al increases by only 0.03. The increase in average Ca/Al of 0.28 between the amphibole and zoisite zones is accompanied by a decrease in average (Na+K)/Al of only 0.04. It seems unlikely therefore that loss of NaCl and KCl was coupled to gains in $CaCl_2$ during metamorphism. Metallic chloride complexes other than $FeCl_2$, $MgCl_2$, $TiCl_4$, $CaCl_2$, and $SiCl_4$ were not chosen to balance NaCl and KCl because their participation in mineral reactions would have required addition of these metallic elements to the rock in quantities far greater than their observed concentration in the metacarbonate rocks. Chlorine in all of the mineral reactions has therefore been balanced with HCl, as is commonly done in studies of mineral–fluid reactions (*e.g.*, Helgeson, 1967). The simplest model reactions, consistent with available data, are ones involving KCl and NaCl balanced by HCl.

Conservation of elements in mineral phases. Arguments, based on data in Figure 3, have been made earlier that metamorphism occurred at constant whole-rock content of Al, Fe, Mg, Si, and Ti and with loss of K, Na, and C. Data in Figure 3 show an increase in average whole-rock Ca/Al with increasing grade of metamorphism. The increase in Ca/Al was intrepreted not in terms of addition of Ca to high-grade metacarbonate rocks but in terms of a sample bias resulting from collection in the field of only carbonate-bearing specimens. Consequently in all mineral reactions which follow, the elements Al, Fe, Mg, Si, Ti, and Ca will be conserved in the mineral phases. Amounts of Na, K, and C not required to form product minerals in the reactions are used to form the volatile species NaCl, KCl, and CO_2.

Mineral formulas in the mineral reactions. The average mineral compositions in Table 3 are used in the mineral reactions which follow. Average compositions obscure small, real differences in mineral composition between different samples from the same metamorphic zone and between samples in different zones. These compositional differences are controlled by cation–exchange equilibria. The main goal of the study was to characterize the net-transfer reactions that created and destroyed minerals during prograde metamorphism. Cation–exchange reactions only change the composition of minerals; they in no way affect the *number of moles* of minerals present. Consequently exchange reactions were ignored in writing the reactions that describe creation or destruction of minerals in the carbonate-bearing rocks (with the exception of the cation–exchange reaction which controls plagioclase composition). This same concept has been elegantly championed elsewhere (Thompson, 1981; Thompson *et al.*, 1982), although I hasten to point out that Thompson's treatment of mineral reactions substantially differs in detail from the one adopted in this study. The composition of plagioclase changes greatly during progressive metamorphism of the carbonate-bearing rocks. In addition, there are systematic changes in plagioclase composition with progress of the prograde mineral reactions. For this reason, Reactions (1)–(11), which follow, utilize the plagioclase components, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$, rather than average plagioclase composition. Use of the components, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$, then rationalizes the change in plagioclase composition during metamorphism in terms of the mineral reactions which occurred.

Distribution of the prograde mineral reactions. The distribution of prograde mineral Reactions (1)–(11) within the metamorphic zones of the Vassalboro Formation is illustrated in Figure 5.

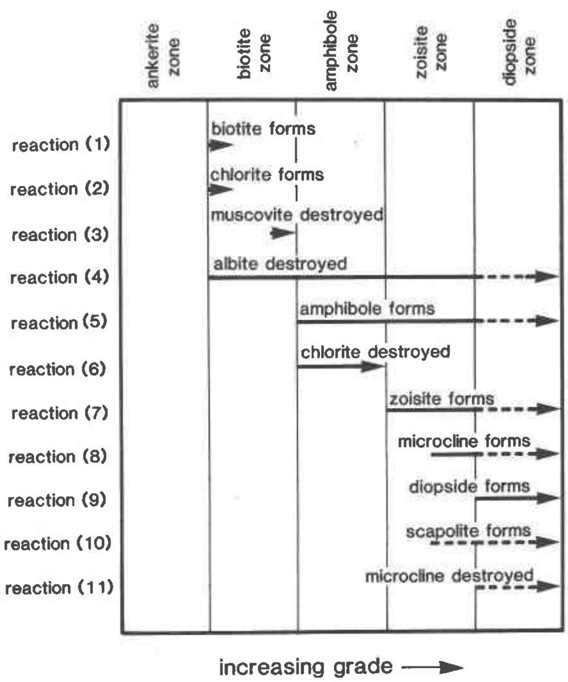

Fig. 5. Distribution of mineral reactions in metamorphosed carbonate rocks within the various metamorphic zones. Dashed line indicates the reaction occurred in some but not all samples.

Mineral reactions in the biotite zone

Mineral reactions in the biotite zone account for the difference between the mineralogy of carbonate-bearing rocks in the ankerite and biotite zones. The principal change is the appearance of biotite and a significant increase in the $CaAl_2Si_2O_8$-content of plagioclase. Chlorite probably was produced in the biotite zone for two reasons: (a) the average chlorite content of rocks in the biotite zone is greater than the average chlorite content of rocks from the ankerite zone, and (b) not all rocks from the ankerite zone contain chlorite while every metacarbonate rock from the biotite zone does. No carbonate-bearing rock from the amphibole zone contains ankerite or muscovite. Mineral reactions in the biotite zone must therefore have consumed all ankerite and muscovite in the metacarbonate rocks. Finally, mineral reactions in the biotite zone must account for the difference in average whole-rock Na/Al between rocks in the biotite and ankerite zones.

Formation of biotite. Modal data in Figure 2 and Table 2 indicate that increases in modal biotite content are accompanied by decreases in modal muscovite and carbonate content. Chlorite is not abundant in most rocks in either the biotite or ankerite zones. Muscovite and carbonate, but not chlorite, are therefore important participants in the reaction. Average plagioclase composition in rocks of the upper biotite zone is An_{29} while average plagioclase in the ankerite zone is An_1. Formation of biotite evidently was accompanied by production of $CaAl_2Si_2O_8$. Data in Figure 3 indicate that the formation of biotite occurred at constant whole-rock K (relative to Al). A reaction that produces biotite and $CaAl_2Si_2O_8$ at the expense of muscovite and ankerite at constant Al, K, Fe, Mg, Ti, Ca, and Si and loss of Na and CO_2 is:

$$\begin{aligned}&0.98 \text{ muscovite} + 2.23 \text{ ankerite} + 0.65 \text{ quartz}\\ &\quad + 0.09 \text{ ilmenite} + 0.03\ HCl + 0.01\ H_2O\\ &= 1.00 \text{ biotite (1)} + 1.89 \text{ calcite (1)} + 0.48\ CaAl_2Si_2O_8\\ &\quad + 0.03\ NaCl + 2.57\ CO_2 \qquad (1)\end{aligned}$$

Reaction (1), and all others which follow, utilizes averages of actual compositions of minerals in the rocks (Table 3); numbers in parentheses refer to a particular formula when more than one for that mineral is presented in Table 3. The reaction (and all others in the report) are slightly imbalanced for some elements because reaction coefficients are rounded to the nearest 0.01.

Reaction (1) is similar to a reacation proposed by Hewitt (1973) to model the formation of biotite in metamorphosed carbonate rocks from Connecticut.

Formation of chlorite. The formation of chlorite in the biotite zone has been modeled by a reaction which consumes muscovite and ankerite, produces biotite, and conserves K, Fe, Mg, Ti, Ca, and Si (Fig. 3, Table 2):

$$\begin{aligned}&2.77 \text{ muscovite} + 11.04 \text{ ankerite} + 0.26 \text{ ilmenite}\\ &\quad + 1.86 \text{ quartz} + 0.08\ HCl + 4.02\ H_2O\\ &\quad = 1.00 \text{ chlorite} + 2.83 \text{ biotite (1)} + 11.87 \text{ calcite (1)}\\ &\quad + 0.08\ NaCl + 10.21\ CO_2 \qquad (2)\end{aligned}$$

Reaction (2) is similar to the model reaction used by Ferry (1976a) as a basis for mapping the biotite isograd in Figure 1. The principal difference is that Reaction (2) takes into account the actual compositions of minerals in the rocks (Table 3). The small amount of chlorite in metacarbonate rocks from the upper biotite zone (Table 2) indicates that Reaction (2), however, is inadequate to account for the observed amount of biotite in these same rocks. Most biotite in the carbonate-bearing rocks was produced by Reaction (1).

Destruction of muscovite. Most rocks in the biotite zone contain muscovite but the mineral is entirely absent in rocks from the amphibole and diopside zones and occurs in trace amounts in only three rocks from the zoisite zone. Reactions (1) and (2) are important mechanisms by which muscovite was consumed during metamorphism. All rocks in the upper biotite zone lack ankerite and most contain muscovite. A mineral reaction therefore must have consumed muscovite in ankerite-free rocks from the upper biotite zone. Ankerite-free rocks in the upper biotite zone contain, as principal minerals, plagioclase + calcite + quartz + biotite. Destruction of muscovite must have involved some combination of these minerals. The reaction could not have converted muscovite to biotite at constant K because biotite is the only K-rich mineral other than muscovite and because biotite is the only abundant mafic mineral (there is no mineral in sufficient abundance for the required Fe + Mg + Mn in biotite). A possible reaction that consumes muscovite, involves plagioclase + calcite + quartz, and conserves Fe, Mg, Ti, Ca, Si, and Al is:

$$\begin{aligned}&1.00 \text{ muscovite} + 1.28 \text{ calcite (2)} + 0.84\ HCl\\ &\quad = 0.12 \text{ biotite (1)} + 0.02 \text{ sphene} + 0.36 \text{ quartz}\\ &\quad + 1.22\ CaAl_2Si_2O_8 + 0.79\ KCl + 0.05\ NaCl\\ &\quad + 1.30\ H_2O + 1.28\ CO_2. \qquad (3)\end{aligned}$$

The reaction, which occurred in the transition from conditions of the upper biotite zone to those at higher grades, is consistent with the observed decrease in Na/Al and K/Al in that interval (Fig. 3).

Destruction of $NaAlSi_3O_8$. Reactions (1)–(3) release a soluble Na species (NaCl) but the amount of NaCl released by the reactions is far too little to account for the decrease in Na/Al with the change in grade of metamorphism between the ankerite and upper biotite zones (Fig. 3). Some other reaction must have been involved. The principal repository of Na in rocks of the ankerite zone is albite. Biotite, chlorite, calcite, sphene, and $CaAl_2Si_2O_8$ (the crystalline products of Reactions 1–3) contain little or no Na. The decrease in whole-rock Na/Al with increasing grade must therefore be related to the destruction of $NaAlSi_3O_8$ without concomitant formation of new, prograde, Na-rich minerals.

Modal data for rocks in the ankerite and upper biotite zone reveal that the reaction which consumed $NaAlSi_3O_8$ also produced $CaAl_2Si_2O_8$. Reaction (3) occurred in the transition between the upper biotite and amphibole zones. In the transition between the ankerite and upper biotite zones Reactions (1) and (2) occurred, but only Reaction (1) produced $CaAl_2Si_2O_8$. On the average rocks from the upper biotite zone contain 17.7 and 27.6 modal percent biotite and plagioclase An_{29}, respectively. On the average 1000 cm^3 carbonate-bearing rock from the upper biotite zone thus contains 1.18 moles biotite and 0.80 moles $CaAl_2Si_2O_8$. Even if all 1.18 moles biotite were produced by Reaction (1), no more than $1.18 \times 0.48 = 0.57$ moles $CaAl_2Si_2O_8$ in the average rock from the upper biotite zone can be accounted for by Reactions (1) and (2). The "excess" $0.80–0.57 = 0.23$ moles $CaAl_2Si_2O_8$ is inferred to be related to the reaction which consumed $NaAlSi_3O_8$ during metamorphism. Similar agruments, which consider the calcite content of rocks from the ankerite and upper biotite zones, suggest that the destruction of $NaAlSi_3O_8$ was also associated with destruction of calcite.

A mineral reaction that destroys albite and calcite and forms $CaAl_2Si_2O_8$ at constant Al and Si is

$$\begin{aligned}&2\ NaAlSi_3O_8 + CaCO_3 + 2\ HCl = CaAl_2Si_2O_8\\ &\qquad + 4 \text{ quartz} + 2\ NaCl + CO_2 + H_2O \qquad (4)\end{aligned}$$

Reaction (4) is the principal mechanism by which Na was lost from the carbonate rocks during metamorphism. Although Reaction (4) was deduced from data for rocks in the ankerite and biotite zones, it proceeded under conditions of the amphibole, zoisite, and diopside zones, as well. Tanner and Miller (1980) also identified the prograde conversion of albite to anorthite component of plagioclase as the mechanism by which Na was lost from Moinian calc-silicate pods in Scotland.

Reaction (4) explains two peculiarities of the modal and mineral composition data. First the reaction explains why rocks in the upper biotite zone contain more $CaAl_2Si_2O_8$ than would be expected from the action of Reactions (1) and (2) alone. Second, Reaction (4), along with Reaction (1), explains how plagioclase composition can change during metamorphism from An_1 in the ankerite zone to an average of An_{29} in the upper biotite zone without a substantial increase in the modal plagioclase content of rocks. The net production of plagioclase by Reaction (1) was simply offset by a net consumption of plagioclase by Reaction (4).

Transition from the ankerite zone to upper biotite zone: average overall reaction. In the transition from conditions of the ankerite zone to conditions of the upper biotite zone rocks underwent varying degrees of Reactions (1), (2), and (4). There was no detectable change in the K-content of carbonate rocks in this interval; Reaction (3) therefore proceeded very little, if at all. The wide range in modes of rocks from the upper biotite zone (see standard deviations, Table 2) indicates that Reactions (1), (2), and (4) were uncoupled and progressed to different degrees in different rock samples collected in the biotite zone. The different degrees of reaction progress are consonant with the high variance of assemblages participating in each reaction. Modal data for rocks in Table 2, however, can be used to formulate the average overall reaction which occurred during the transition from the ankerite zone to the upper biotite zone (see Brimhall, 1979 for further discussion). The overall reaction is simply some appropriate combination of Reactions (1), (2), and (4). First, progress variables ξ_1 and ξ_2, are defined for Reactions (1) and (2) respectively.

$$\xi_2 \equiv \text{(moles chlorite in upper biotite zone–moles chlorite in ankerite zone)/1000 cm}^3\text{ metamorphosed rock} \quad \text{(a)}$$

$$\xi_1 \equiv [\text{(moles biotite in upper biotite zone)/1000 cm}^3\text{ metamorphosed rock}] - 2.83\xi_2 \quad \text{(b)}$$

Values of ξ_1 and ξ_2 may be calculated for an average rock in the upper biotite zone from data in Table 2: $\xi_2 = 0.033$; $\xi_1 = 1.08$ (moles/1000 cm^3 rock). The average overall mineral reaction is $\Sigma_i[\Sigma_j \nu_j(j)]\xi_i = 0$, where ν_j is the stoichiometric coefficient of species (j) in Reactions (1), (2), and (4) (positive for products; negative for reactants) and the ξ_i are defined as above. The sum is taken over all (j) species which participate in each of the i Reactions, (1), (2), and (4). The progress of Reaction (4), ξ_4, was calculated so that (a) the average overall reaction was balanced with a reactant plagioclase of composition An_1 and with a product plagioclase of composition An_{29} (Table 3) and (b) after reaction the resulting rock contained the amount of $CaAl_2Si_2O_8$ required by average modal and mineral composition data for plagioclase in rocks from the upper biotite zone. Accordingly, 1000 cm^3 of average carbonate-bearing rock in the upper biotite zone was produced from the average carbonate-bearing rock in the ankerite zone by the following overall reaction:

$$1.15 \text{ muscovite} + 2.78 \text{ ankerite} + 0.11 \text{ ilmenite} + 2.49 \text{ plagioclase } (An_1) + 0.54\ HCl = 1.18 \text{ biotite} + 0.03 \text{ chlorite} + 2.18 \text{ calcite} + 0.25 \text{ quartz} + 2.75 \text{ plagioclase } (An_{29}) + 0.54\ NaCl + 0.11\ H_2O + 3.37\ CO_2. \quad \text{(A)}$$

Reaction (A) ignores the small composition difference between calcite in Reactions (1), (2), and (4). Individual metacarbonates in the biotite zone experienced different relative degrees of progress of Reactions (1), (2), and (4) and hence overall reactions different than (A). Reaction (A), however, gives a generalized account of the mineralogical and chemical changes which occurred as carbonate-bearing rocks were progressively metamorphosed in the transition between conditions of the ankerite and upper biotite zones. Reaction (A) is consistent with the observed avearage modal and chemical changes which occurred in this interval (Table 2; Figs. 2, 3). In particular Reaction (A) rationalizes the decreases in Na/Al and C/(Ca+Fe+Mg+Mn) which occurred in rocks between the ankerite and upper biotite zones.

Mineral reactions in the amphibole zone

Mineral reactions in the amphibole zone account for the difference between the mineralogy of carbonate-bearing rocks in the biotite and amphibole zones. The principal change is the appearance of calcic amphibole and a significant increase in the $CaAl_2Si_2O_8$-content of plagioclase. Chlorite was probably consumed in the amphibole zone because, on the average, rocks from the amphibole zone contain less modal chlorite than those of the upper biotite zone. No carbonate-bearing rocks in the amphibole zone contain muscovite. Muscovite, observed in rocks from the upper biotite zone, must therefore have been consumed in the transition from metamorphic conditions of the biotite zone to those of the amphibole zone. Mineral reactions must also account for the decrease in average whole-rock Na/Al and K/Al between rocks in the upper biotite and amphibole zones.

Formation of calcic amphibole. Modal data in Table 2 for the upper biotite, amphibole, and zoisite zones, indicate that increases in modal amphibole are accompanied by decreases in modal biotite. Chlorite is not abundant in most rocks in either the biotite or amphibole zones. Ankerite is absent in rocks of the upper biotite zone. Calcic amphibole therefore principally formed at the expense of biotite rather than chlorite or ankerite. No K-rich mineral, however, appears in rocks from the amphibole zone as biotite disappears. Average plagioclase composition in rocks of the amphibole zone is An_{70} while average plagioclase in the upper biotite zone is An_{29}. Formation of calcic amphibole evidently was accompanied by production of $CaAl_2Si_2O_8$. A reaction that produced amphibole and $CaAl_2Si_2O_8$ at the expense of biotite at constant Fe, Mg, Ti, Ca, Si, and Al and loss of K and CO_2 is

$$1.90 \text{ biotite } (2) + 3.16 \text{ calcite } (2) + 3.53 \text{ quartz} + 0.15\ NaAlSi_3O_8 + 1.69\ HCl = 1.00 \text{ amphibole } (1) + 0.14 \text{ sphene} + 0.97\ CaAl_2Si_2O_8 + 1.69\ KCl + 3.16\ CO_2 + 1.74\ H_2O \quad (5)$$

Reaction (5) is different from the mineral reaction previously proposed to account for the formation of amphibole in the metacarbonate rocks (Ferry, 1976a). The earlier reaction produced amphibole and $CaAl_2Si_2O_8$ at the expense of chlorite, calcite, and quartz. Rocks in the biotite zone contain far too little chlorite to account for the amount of amphibole observed in rocks from the amphibole and zoisite zones (Table 2).

In the amphibole zone no new K-rich minerals formed along with amphibole. Figure 2 indicates that the conversion of biotite to amphibole principally occurred in the amphibole and zoisite zones. These zones represent the metamorphic conditions at which most of the K was lost from the metacarbonates (Fig. 3). The correlation between decreasing whole-rock K/Al and progress of Reaction (5) leads to the conclusion that reaction (5) is the principal mechanism by which K was liberated from the carbonate-bearing rocks during metamorphism. Tanner and Miller (1980) also identified the prograde conversion of biotite to calcic amphibole as the mechanism by which K was lost from Moinian calc-silicate pods in Scotland.

Destruction of chlorite. All rocks from the biotite zone contain chlorite, yet it is absent from all samples in the zoisite and diopside zones. Modal data in Figure 3 indicate that chlorite disappears in metacarbonate rocks in the amphibole zone. Rocks in the amphibole zone contain, as principal minerals, plagioclase + calcite + quartz + amphibole±biotite. Destruction of chlorite, therefore, must have involved some combination of these minerals. The reaction that consumed chlorite must have produced amphibole because biotite is consumed in the amphibole zone (Reaction 5) and because calcic amphibole is the only other mafic mineral in the rocks. A possible reaction that satisfies these constraints and conserves Fe, Mg, Al, Si, Ti, and Ca in minerals is:

$$1.00 \text{ chlorite} + 2.94 \text{ calcite } (2) + 5.73 \text{ quartz} + 0.05 \text{ ilmenite} + 0.19\ NaAlSi_3O_8 = 1.02 \text{ amphibole } (1) + 0.86\ CaAl_2Si_2O_8 + 2.94\ CO_2 + 2.98\ H_2O \quad (6)$$

Reaction (6) is very similar to the model reaction used by Ferry (1976a) as a basis for mapping the amphibole isograd in Figure 1. The principal difference is that Reaction (6) takes into account the actual compositions of minerals in the rocks. The small amount of chlorite in metacarbonate rocks from the upper biotite zone (Table 2) indicates that Reaction (6), however, is inadequate to account for the observed amount of amphibole in rocks from the amphibole zone and from higher grades. Most amphibole in the carbonate-bearing rocks was produced by Reaction (5). Reaction (6) did occur; it was simply a quantitatively less significant contribution to the amphibole content of rocks.

Destruction of muscovite and $NaAlSi_3O_8$. Carbonate-bearing rocks from the amphibole zone contain no muscovite. Muscovite disappeared from the metacarbonates in the transition from the upper biotite zone to the amphibole zone by Reaction (3). Consideration of the amount and composition of plagioclase in rocks from the amphibole zone leads to the conclusion that $NaAlSi_3O_8$ was consumed and $CaAl_2Si_2O_8$ produced by Reaction (4) in the amphibole zone (as well as in the biotite zone). The argument for progress of Reaction (4) in the amphibole zone is similar to that made for Reaction (4) in the biotite zone and is not repeated.

Transition from the upper biotite zone to amphibole zone: average overall reaction. In the transition from conditions of the upper biotite zone to conditions of the amphibole zone rocks underwent varying degrees of Reactions (3)–(6). Modal data for rocks in Table 2, however, can be used to formulate the average overall reaction which occurred during the transition. The overall reaction is an appropriate combination of reactions (3)–(6). Progress variables, ξ_3, ξ_5, and ξ_6 were definded for reactions (3), (5), and (6) respectively;

$$\xi_3 \equiv -(\text{moles muscovite in amphibole zone–moles muscovite in upper biotite zone})/1000\ \text{cm}^3 \text{ metamorphosed rock} \quad (c)$$

$$\xi_6 \equiv -(\text{moles chlorite in amphibole zone–moles chlorite in upper biotite zone})/1000\ \text{cm}^3 \text{ metamorphosed rock} \quad (d)$$

$$\xi_5 \equiv [(\text{moles amphibole in an amphibole zone})/1000\ \text{cm}^3 \text{ metamorphosed rock}] - 1.02\xi_6 \quad (e)$$

Values of ξ_3, ξ_5, ξ_6 were calculated for an average rock in the amphibole zone from data in Table 2: $\xi_3 = 0.24$; $\xi_5 = 0.17$; $\xi_6 = 0.04$ (moles/1000 cm^3 rock). The average overall reaction is $\Sigma_i[\Sigma_j \nu_j(j)]\xi_i = 0$ summed over Reactions (3)–(6). The value for ξ_4 was calculated, similarly as was done for reaction (A), so that the average overall reaction was balanced with a reactant plagioclase of composition An_{29} and with a product plagioclase of composition An_{70} (Table 3). Accordingly, 1000 cm^3 of average carbonate-bearing rock in the amphibole zone was produced from the average rock in the upper biotite zone by the following overall reaction:

$$0.30 \text{ biotite} + 0.04 \text{ chlorite} + 0.24 \text{ muscovite} + 3.50 \text{ plagioclase } (An_{29}) + 1.71 \text{ calcite} + 1.98\ HCl = 0.21 \text{ amphibole} + 0.03 \text{ sphene} + 2.23 \text{ quartz} + 3.22 \text{ plagioclase } (An_{70}) + 0.49\ KCl + 1.50\ NaCl + 1.71\ CO_2 + 1.47\ H_2O \quad (B)$$

Reaction (B) ignores the small composition difference between calcite in Reactions (3)–(6). Reaction (B) gives a generalized account of the mineralogical and chemical changes which occurred as carbonate-bearing rocks were progressively metamorphosed in the transition from conditions of the upper biotite zone to those of the amphibole zone. In particular, Reaction (B) rationalizes the substantial decrease in both K/Al and Na/Al which occurred in rocks metamorphosed through this transition (Fig. 3).

Mineral reactions in the zoisite zone

Mineral reactions in the zoisite zone account for the difference between the mineralogy of carbonate-bearing rocks in the amphibole and zoisite zones. The principal change is the appearance of zoisite in all rocks and of microcline in 22% of the samples studied. A slight increase in the $CaAl_2Si_2O_8$-content of plagioclase occurs. Amphibole was produced because the amphibole-content of rocks in the zoisite zone is greater than the amphibole-content of rocks from the amphibole zone. Because no rocks from the zoisite zone contain chlorite, chlorite must have been consumed in the transition from metamorphic conditions of the amphibole zone to those of the zoisite zone. Mineral reactions must also account for the decrease in average whole-rock K/Al between rocks in the amphibole and zoisite zones.

Formation of zoisite. Data indicate that increases in modal zoisite are accompanied by decreases in modal plagioclase (Fig. 2, Table 2). When zoisite appears in the metacarbonate rocks, no other new mineral accompanies it. A reaction that produces zoisite at the expense of plagioclase at constant Fe, Mg, Ti, Ca, Si, and Al is:

$$\begin{aligned}&0.07\ \text{Fe–component of amphibole} + 0.59\ \text{Fe–component of calcite} + 1.31\ CaAl_2Si_2O_8 + 0.01\ HCl + 0.59\ H_2O \\ &= 1.00\ \text{zoisite} + 0.002\ \text{sphene} + 0.10\ \text{quartz} + 0.01\ NaCl + 0.59\ CO_2 + 0.16\ H_2 \qquad (7)\end{aligned}$$

Because zoisite contains some iron, a source for that iron must appear in the reaction that forms zoisite. The only mineral that contains substantial iron and that occurs in all zoisite-bearing rocks is calcic amphibole. The iron component of calcite probably contributed a small amount of iron to zoisite as well. Reaction (7) is a redox reaction because iron in zoisite is ferric while amphibole formulas have been recalculated assuming all iron is ferrous. If amphiboles in the carbonate-bearing rocks contain small amounts of ferric iron and if this ferric iron was the source of iron in zoisite, then the real zoisite-forming reaction may be a simple hydration-decarbonation reaction. Reaction (7) produces a small amount of sphene and an Na-bearing species because the natural calcic amphiboles contain Ti and Na. NaCl was chosen as the Na-bearing species because of the general trend of Na-loss during progressive metamorphism illustrated in Figure 3.

Reaction (7) is very similar to a model reaction used by Ferry (1976a) as a basis for mapping the zoisite isograd in Figure 1. The principal difference is that Reaction (7) accounts for the iron content of natural zoisite and therefore involves other minerals besides plagioclase, calcite, and zoisite.

Formation of microcline. Some rocks in the zoisite and diopside zones contain microcline. The appearance of microcline in the metacarbonate rocks was the basis of a microcline-amphibole isograd in an earlier study (Ferry, 1976a). Study of the Vassalboro Formation over a larger area, however, has revealed that microcline is uncommon in rocks from the zoisite and diopside zone. Reaction (5) explains why this is so: because of Reaction (5) most high-grade metacarbonate rocks are too depleted in K to develop *any* K-rich mineral.

Although microcline is absent or not abundant in most rocks, some assessment may be made of the inferred mineral reaction that produced it. Microcline appears in the zoisite zone where rocks contain, as principal minerals, zoisite + plagioclase + quartz + calcite + amphibole ± biotite. Microcline must have developed, therefore, from some combination of these minerals as participants in the reaction. Biotite is the only possible source of K; if biotite were consumed at constant Fe + Mg + Mn, amphibole must have been produced. A reaction that produces microcline and amphibole at the expense of biotite at constant Fe, Mg, Mn, Ca. Al, Ti, and Si is:

$$\begin{aligned}&1.06\ \text{biotite (2)} + 1.28\ \text{calcite(3)} + 3.94\ \text{quartz} + 0.13\ NaAlSi_3O_8 = 1.00\ \text{microcline} + 0.55\ \text{amphibole(3)} + 0.09 \\ &\text{sphene} + 0.08\ CaAl_2Si_2O_8 + 0.50\ H_2O + 1.28\ CO_2. \qquad (8)\end{aligned}$$

Reaction (8) is very similar to a model reaction proposed earlier (Ferry 1976a) to account for the formation of microcline in the carbonate rocks during metamorphism. The principal difference is that Reaction (8) considers the actual composition of minerals in the rocks. Calcic amphibole was produced from biotite in the carbonate rocks by two independent Reactions (5) and (8). One conserves K while the other does not. Rocks that were closed to K-transport produced amphibole principally by Reaction (8). Rocks from which all or almost all K was extracted under amphibole- and zoisite-zone conditions produced amphibole principally by Reaction (5). Rocks in which some but not all K was extracted produced amphibole by a combination of the two reactions.

Formation of amphibole. Carbonate-bearing rocks in the zoisite zone on the average have greater amphibole contents and smaller biotite contents than metacarbonate rocks in the amphibole zone. The difference implies continued formation of calcic amphibole in microcline-free rocks in the zoisite zone by Reaction (5).

Destruction of chlorite and $NaAlSi_3O_8$. The absence of chlorite in rocks from the zoisite zone suggests complete consumption of chlorite by Reaction (6) during the transition from metamorphic conditions of the amphibole zone to those of the zoisite zone. Consideration of the amount and composition of plagioclase in the zoisite zone indicates that a very small amount of $NaAlSi_3O_8$ was consumed and $CaAl_2Si_2O_8$ produced by Reaction (4) in the zoisite zone. The evidence for progress of Reaction (4) is similar to that for progress of Reaction (4) in the biotite zone.

Transition from the amphibole zone to the zoisite zone: average overall reaction. In the transition from conditions of the amphibole zone to conditions of the zoisite zone rocks underwent varying degrees of Reactions (4)–(8). Modal data for rocks in Table 2 can be used to formulate the average overall reaction which occurred during the transition. The overall reaction is an appropriate combination of Reactions (4)–(8). Progress variables ξ_5, ξ_6, ξ_7, and ξ_8 were defined for Reactions (5)–(8):

$$\xi_8 \equiv \text{(moles microcline in zoisite zone)/1000 cm}^3\text{ metamorphosed rock} \qquad \text{(f)}$$

$$\xi_7 \equiv \text{(moles zoisite in zoisite zone)/1000 cm}^3\text{ metamorphosed rock} \qquad \text{(g)}$$

$$\xi_6 \equiv -\text{(moles chlorite in amphibole zone)/1000 cm}^3\text{ metamorphosed rock} \qquad \text{(h)}$$

$$\xi_5 \equiv [\text{(moles amphibole in zoisite zone–moles amphibole in amphibole zone)/1000 cm}^3\text{ metamorphosed rock}] - 1.02\xi_6 + 0.07\xi_7 - 0.55\xi_8 \qquad \text{(i)}$$

Values of ξ_5, ξ_6, ξ_7, ξ_8 were calculated for an average rock in the zoisite zone from data in Table 2: $\xi_8 = 0.17$; $\xi_7 = 0.89$; $\xi_6 = 0.05$; $\xi_5 = 0.25$ (moles/1000 cm^3 rock). The average overall reaction is $\Sigma_i[\Sigma_j \nu_j(j)]\xi_i = 0$ summed for Reactions (4)–(8). The value of ξ_4 was calculated, similarily as for Reaction (A), so that the average overall reaction was balanced with a reactant plagioclase of composition An_{70} and with a product plagioclase of composition An_{74} (Table 3). Accordingly, 1000 cm^3 of average carbonate-bearing rock in the zoisite zone was produced from the average rock in the amphibole zone by the following overall reaction:

0.66 biotite + 0.05 chlorite + 1.85 calcite + 1.12 quartz + 2.66 plagioclase (An_{70}) + 0.76 HCl = 0.34 amphibole + 0.89 zoisite + 0.17 microcline + 0.05 sphene + 1.57 plagioclase (An_{74}) + 0.43 KCl + 0.33 NaCl + 1.85 CO_2 + 0.32 H_2O + 0.14 H_2. (C)

Reaction (C) ignores the compositional differences in calcite and amphibole between Reactions (4)–(8). It gives a generalized account of the mineralogical and chemical changes which occurred as carbonate-bearing rocks were progressively metamorphosed in the transition between conditions of the amphibole zone and the zoisite zone.

Reaction (C) predicts a decrease in the calcite content of metacarbonate rocks between the amphibole and zoisite zones. Figure 2, however, indicates an average *increase* in the calcite content of the metacarbonates over this interval. The data in Figure 2 are not taken as an indication that Reaction (C) is incorrect. Rather, the apparent increase in average calcite content of rocks between the amphibole and zoisite zones is interpreted in terms of the large range in the calcite contents of rocks collected within any particular zone. Table 2 shows that the standard deviation of the carbonate contents of rocks from each zone is approximately of the same magnitude as the value of the average carbonate content itself. Consequently, differences in the average carbonate content of rocks between the different zones is not significant statistically. The low calcite content of rocks from the amphibole zone is believed to simply be the result of a statistically insignificant chance sampling of a group of rocks which contained, on the average, a small amount of calcite. The increase in average calcite content of rocks between the amphibole and zoisite zones, however, may also be related to the sample bias, discussed earlier, introduced by the collection of only carbonate-bearing specimens in the field.

Reaction (C) rationalizes the decrease in whole-rock K/Al between the amphibole and zoisite zone observed in Figure 3. The reaction, however, also predicts a small decrease in average Na/Al which is not observed in the whole-rock chemical data (Fig. 3). Reaction (C) does correctly predict, though, that changes in Na/Al between the amphibole and zoisite zones should be much less than changes between the ankerite and upper biotite zones (Reaction A) or between the upper biotite and amphibole zones (Reaction B). The slight inconsonance between Reaction (C) and whole-rock chemical data for Na/Al is probably due either to small errors in the chemical analyses, errors in the modal data (upon which reaction C is based) or both.

Mineral reactions in the diopside zone

Mineral reactions in the diopside zone account for the difference between the mineralogy of carbonate-bearing rocks in the zoisite and diopside zones. The principal change is the appearance of diopside. Scapolite appears in 4% of the rocks collected in the diopside zone. A slight increase in the average anorthite content of plagioclase occurs. Comparison of the average modal mineralogy of rocks in the diopside and zoisite zones (Table 2) suggests that small amounts of biotite, zoisite, and microcline were consumed. Mineral reactions in the diopside zone must also account for the difference in average whole-rock K/Al between rocks in the zoisite and diopside zone.

Formation of diopside. Data show that increases in modal diopside are accompanied by decreases in modal amphibole (Fig. 2, Table 2). Biotite and microcline are not present in all diopside-bearing rocks, but amphibole is. Diopside, therefore, principally formed at the expense of amphibole rather than biotite or microcline. A reaction that produces diopside at the expense of calcic amphibole at constant Ca, Fe, Mg, Ti, Si, and Al and with loss of Na and CO_2 is:

0.22 amphibole (3) + 0.70 calcite (3) + 0.67 quartz + 0.03 HCl = 1.00 diopside + 0.01 sphene + 0.12 $CaAl_2Si_2O_8$ + 0.03 NaCl + 0.23 H_2O + 0.70 CO_2 (9)

Reaction (9) is very similar to a model reaction used by Ferry (1976a) as a basis for mapping the diopside isograd in Figure 1. The principal difference is that reaction (9) considers actual rather than idealized mineral compositions.

Formation of scapolite. One rock in the zoisite zone and 3 rocks in the diopside zone contain scapolite. The appearance of scapolite in the metacarbonate rocks was the basis of a scapolite isograd in an earlier study (Ferry, 1976a). Study of the Vassalboro Formation over a larger area, however, has revealed that scapolite is very uncommon in the diopside and zoisite zones. Scapolite must have formed at the expense of plagioclase because of scapolite's composition (Table 3). Plagioclase, coexisting with scapolite, is always more sodic than An_{67}. It is difficult to establish even the reaction mechanism by which scapolite formed because scapolite is uncommon and occurs in small amounts. Two quite different mechanisms are possible. The first and simplest involves destruction of plagioclase by a mechanism which continuously changes plagioclase composition with progress of the reaction:

$$0.99\ NaAlSi_3O_8 + 2.01\ CaAl_2Si_2O_8 + CaCO_3 + 0.03\ KCl = 1.00\ \text{scapolite} + 0.03\ NaCl \quad (10a)$$

Reaction (10a) consumes KCl because most scapolite-bearing rocks contain no mineral source for K (*i.e.*, biotite or microcline).

The second mechanism involves destruction of plagioclase (with X mole fraction anorthite component, $X < 0.67$) at constant composition to form scapolite and a soluble Na-bearing species:

$$\left(\frac{5.01}{1+X}\right)\text{plagioclase} + \left(\frac{3.01-2X}{1+X}\right)CaCO_3 + 0.03\ KCl + \left(\frac{4.02-6X}{1+X}\right)HCl = 1.00\ \text{scapolite} + \left(\frac{8.04-12X}{1+X}\right)\text{quartz} + \left(\frac{4.05-5.97X}{1+X}\right)NaCl + \left(\frac{2.01-3X}{1+X}\right)CO_2 + \left(\frac{2.01-3X}{1+X}\right)H_2O. \quad (10b)$$

The two reaction mechanisms remain only a speculation. Without a collection of scapolite-rich metacarbonate rocks, the validity of reactions (10a) and (10b) cannot be confirmed.

Destruction of biotite, zoisite, and microcline. The decrease in the average modal abundance of biotite, zoisite and microcline between the zoisite and diopside zones (Table 2) suggests consumption of the three minerals in the diopside zone during metamorphism. Biotite was probably consumed by Reaction (5) as at lower grades. Zoisite was probably consumed by Reaction (7)—the reverse of the process by which zoisite was produced in the zoisite zone. Microcline was probably consumed by a reaction analogous to Reaction (4):

$$2\ \text{microcline} + CaCO_3 + 2\ HCl = CaAl_2Si_2O_8 + 4\ \text{quartz} + 0.12\ NaCl + 1.88\ KCl + CO_2 + H_2O \quad (11)$$

Reaction (11) utilizes the composition of microcline in Table 3. It conserves Ca, Al, and Si but not Na, K, or CO_2 in consonance with whole-rock chemical data in Figure 3.

Transition from the zoisite zone to the diopside zone: average overall reaction. In the transition from conditions of the zoisite zone to conditions of the diopside zone, rocks underwent varying degrees progress of Reactions (4), (5), (7), (9), and (11). Modal data for rocks in Table 2, however, can be used to formulate the average overall reaction which occurred during the transition (an appropriate combination of Reactions (4), (5), (7), (9), and (11)). Progress variables, ξ_5, ξ_7, ξ_9, and ξ_{11} were defined for Reactions (5), (7), (9), and (11), respectively:

$\xi_{11} \equiv -0.5$ (moles microcline in diopside zone–moles microcline in zoisite zone)/1000 cm^3 metamorphosed rock (j)

$\xi_9 \equiv$ (moles diopside in diopside zone)/1000 cm^3 metamorphosed rock (k)

$\xi_7 \equiv$ (moles zoisite in diopside zone–moles zoisite in zoisite zone)/1000 cm^3 metamorphosed rock (l)

$\xi_5 \equiv$ [(moles amphibole in diopside zone–moles amphibole in zoisite zone)/1000 cm^3 metamorphosed rock] + $0.22\xi_9 + 0.07\xi_7$ (m)

Values of ξ_5, ξ_7, ξ_9, and ξ_{11} were calculated for an average carbonate-bearing rock in the diopside zone from data in Table 2: $\xi_{11} = 0.09$, $\xi_9 = 0.76$, $\xi_7 = -0.04$; $\xi_5 = 0.05$ (moles/1000 cm^3 rock). The average overall reaction is $\Sigma_i[\Sigma_j \nu_j(j)]\xi_i = 0$ summed for Reactions (4), (5), (7), (9), and (11). The value for ξ_4 was calculated similarly as was done for Reaction (A) so that the average overall reaction was balanced with a reactant plagioclase of composition An_{74} and with a product plagioclase of composition An_{79} (Table 3). Accordingly, 1000 cm^3 of average carbonate-bearing rock in the diopside zone was produced from the average rock in the zoisite zone by the following overall reaction:

0.12 amphibole + 0.09 biotite + 0.04 zoisite + 0.09 microcline + 0.67 calcite + 0.61 quartz + 1.68 plagioclase (An_{74}) + 0.13 HCl + 0.03 NaCl + 0.01H_2 = 0.76 diopside + 0.01 sphene + 1.83 plagioclase (An_{79}) + 0.16 KCl + 0.67 CO_2 + 0.29 H_2O (D)

Reaction (D) rationalizes the decrease in average whole-rock K/Al between the zoisite and diopside zones. The reaction, however, also predicts essentially no change in whole-rock Na/Al and a decrease in the calcite content of carbonate-bearing rocks in the same interval. Metacarbonates in the diopside zone on the average contain more calcite and have lower whole-rock Na/Al than do rocks in the zoisite zone (Fig. 3, Table 2). The slight discrepancy between Reaction (D), whole-rock data for Na/Al, and modal data for calcite are believed to be due simply to either small errors in the chemical analyses, small errors in the modal data or both. The small increase in average calcite content of rocks between the zoisite and diopside zones may also be related to the sample bias introduced by the collection of only carbonate-bearing specimens in the field.

Discussion

Mass transfer during metamorphism

Mass transport of CO_2 and H_2O, released from rocks during metamorphism by decarbonation and dehydration reactions, is a well-established phenomenon. An important contribution of this report is documentation that mass transport of other elements (K and Na) must occur as well, at least in some circumstances of regional metamorphism. Carbonate rocks in the ankerite zone contain, on the average, approximately 2.5 moles albite and 1 mole muscovite/1000 cm^3 rock. During the course of metamorphism, an average of 69% of the Na initially in the albite and 82% of the K initially in muscovite is extracted from the rocks. One liter of average metacarbonate rock in the diopside zone therefore lost approximately 1.7 moles Na and 0.8 moles K during its metamorphic evolution. The mechanisms by which K and Na were extracted have been identified. Sodium was lost principally through the destruction of albite according to Reaction (4). The reaction occurred over metamorphic conditions ranging from those of the biotite to those of the diopside zone. Sodium therefore was depleted continuously at grades higher than the biotite isograd. Figure 3 and Reactions (A)–(D), however, indicate that Na loss was more severe in the biotite and amphibole zones than in the zoisite and diopside zones. Potassium was lost principally through the destruction of biotite according to Reaction (5). The reaction occurred over metamorphic conditions ranging from those of the amphibole zone through those of the diopside zone. Potassium therefore was depleted continuously at grades higher than the amphibole isograd.

Loss of K and loss of Na from the metacarbonate rocks were not coupled. K-loss and Na-loss were controlled by different mechanisms (reactions), and they were initiated at different metamorphic conditions. Depletion of Na in metacarbonate rocks began under biotite-zone conditions while there is no evidence for significant depletion of K until amphibole-zone metamorphic conditions were attained. Furthermore, in the diopside zone, some rocks have very low Na/Al but have near normal K/Al (*i.e.*, like average K/Al in the ankerite zone). Other samples in the diopside zone have near normal Na/Al but very low K/Al. Whatever ultimately controlled the extraction of alkalis from the carbonate rocks was able, during the same episode of metamorphism, to preferentially remove K from some rocks and Na from others. Most rocks at high grades, however, are substantially depleted in both K and Na.

Mechanisms of mass transport and fluid-rock ratios during metamorphism

The rocks which are interbedded with the calc-silicates of the Vassalboro Formation are mica schists and micaceous sandstones. A very similar sequence of interbedded calc-silicate rocks and mica schists crops out in the adjacent Waterville Formation (Fig. 1). In a companion study (Ferry, 1982) the mechanism by which K and Na were transported out of the carbonate-bearing rocks was investigated. Two possible mechanisms were identified: (a) transport of K and Na from metacarbonate rock into adjacent mica schist by diffusion down chemical potential gradients and (b) transport of K and Na from metacarbonate rock by a through-flowing metamorphic fluid (infiltration). The possibility for mass transport by diffusion was evaluated by quantitatively determining the difference in μ_{K_2O}, μ_{Na_2O}, $\mu_{Al_2O_3}$, μ_{FeO}, μ_{MgO}, μ_{MnO}, μ_{SiO_2}, μ_{H_2O} and μ_{CO_2} between interbedded schist and calc-silicate rock in the same outcrop. Chemical potential differences were calculated from mineral equilibria involving garnet, quartz, plagioclase, and biotite in the contrasting lithologic types. Results indicate that over the range of metamorphic conditions at which mass transfer of K and Na occurred, chemical potential differences were of the wrong algebraic sign to account for the mass transport by diffusion down chemical potential gradients. If any transport of K and Na occurred by diffusion down chemical potential gradients, the gradients would have driven K and Na from schist into calc-silicate rock. The calc-silicate rocks would have become *enriched* in Na and K, not depleted in the two elements.

The apparent inability of diffusion, to account for transport of K and Na out the carbonate-bearing rocks is the principal argument for mass transfer by infiltration. There is additional, indirect evidence that infiltration was the mechanism for K and Na transfer. Studies of the petrology of metamorphosed impure carbonate rocks both from the Vassalboro Formation (Ferry, 1980a) and elsewhere (Rumble *et al.*, 1982; Rice and Ferry, 1982) indicate that impure carbonate rocks are commonly infiltrated by large volumes of H_2O-rich fluid during metamorphism. The source(s) of the fluid, however, is unknown. Rumble *et al.* (1982), for example, demonstrated that regionally metamorphosed calc-silicate rocks from western New Hampshire were infiltrated by 4–6 rock volumes H_2O fluid. Carbonate-bearing rocks from the Vassalboro Formation were infiltrated by up to 3–4 rock volumes H_2O fluid during the metamorphic event (Ferry, in preparation; these values are based on methods described by Ferry, 1980a). Apparently metamorphism of impure carbonate-bearing rocks (and those from the Vassalboro Formation, in particular) may be accompanied by infiltration involving large volumes of aqueous fluids. It does not therefore seem unreasonable to relate to this infiltration the loss of K and Na from calc-silicate rocks of the Vassalboro Formation. The infiltrating fluid was probably the transport mechanism which removed K and Na from the carbonate-bearing rocks during metamorphism.

Quantitative estimates of the volume of fluid which infiltrated the metacarbonate rocks of the Vassalboro Formation may also be made from chemical and mineralogical data in Figure 3 and Table 2. Average metamorphic conditions were P = 3500 bars and $T \sim 500°C$ when infiltration occurred. Figure 6 illustrates the volume of H_2O fluid at 3500 bars, 500°C necessary to transport 0.5–1.0 moles K as a function of the mole fraction of K in that fluid. For reference, the composition of brines from the Salton Sea geothermal field are identified (Helgeson, 1968). For these rather concentrated brines, 1–3 rock volumes of fluid are required. Regardless then of the speciation of natural metamorphic fluids, it appears that at least one rock volume of fluid was required to achieve the observed levels of depletion in K by infiltration. The diagram furthermore refers to a perfectly efficient extraction process. For example, 2.2 rock volumes brine with $X_K = 0.01$ can transport 1 mole K at 500°C, 3500 bars. The brine can *extract* 1 mole of K from a rock, however, only if the fluid contains *no* K before it interacts with the rocks and 0.01 X_K after fluid-rock interaction. It is unlikely that natural extraction processes are so efficient. Fluid-rock ratios in Figure 6 therefore are minimum estimates; the figure indicates that the metacarbonate rocks interacted with *at least* one and perhaps 10 or more rock volumes aqueous fluid during the metamorphic event. Treated in the same manner as K in Figure 6, data on the loss of Na from the carbonate-bearing rocks requires infiltration of at least 0.5–1.0 rock volumes of fluid to account for the inferred loss of ~1–2 moles Na/1000 cm^3 from the metacarbonates during metamorphism.

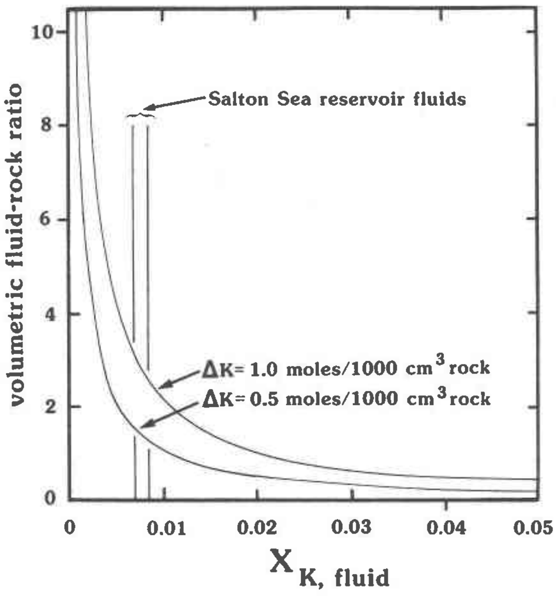

Fig. 6. Volume of fluid (per reference rock volume) required to transport 0.5–1.0 moles K as a function of potassium concentration in the fluid. Vertical lines refer to compositions of fluids from the Salton Sea geothermal system.

If infiltration is the mechanism by which K and Na were extracted from the metacarbonate rocks of the Vassalboro formation, it is appropriate to wonder if the infiltration affected other rock types in the area as well. This subject is taken up in detail elsewhere (Ferry, 1982). Although the carbonate rocks show substantial depletion in K and Na with increasing grade of metamorphism, the schists with which they are interbedded do not. The reason for this disparity in chemical behavior is believed to be related to the flow pattern of metamorphic fluid. The carbonate-bearing layers are thought to have behaved as metamorphic aquifers. Fluid flow (and consequent chemical changes) was much greater in the carbonate units than in the adjacent, less permeable schists. Rumble *et al.* (1982) present a model of reaction-enhanced permeability to account for the greater permeability of metacarbonate rocks compared to pelitic schists.

Hydrolysis vs. dehydration reactions

It has long been known that the high temperature stability limit of hydrous minerals is lower for decomposition by hydrolysis reactions than for isochemical decomposition by dehydration. This led Eugster (1970) to propose that petrologists should see hydrous alkali-rich minerals such as muscovite breakdown in metamorphic rocks first by hydrolysis and then, at higher grades, by isochemical dehydration.

Eugster's prediction may be confirmed in a remarkable fashion by the behavior of biotite in the metacarbonate rocks from the Vassalboro Formation. If the principal K-bearing fluid species is KCl and *if* KCl is balanced in the prograde mineral-fluid reactions by HCl, then biotite began to decompose in the amphibole zone by hydrolysis Reaction (5). Only at higher grades and at higher temperatures in the zoisite zone did biotite decompose isochemically by dehydration Reaction (8). A remarkable aspect of metamorphism of the Vassalboro Formation is the important role that hydrolysis reactions played in the mineralogical evolution of the rocks. If the assumptions upon which Reactions (4) and (5) are based are correct, most of the amphibole and much of the $CaAl_2Si_2O_8$ in the calc-silicate rocks were produced by hydrolysis Reactions (4) and (5).

Regional metamorphism as large scale acid metasomatism

Pressure and temperature are conventionally considered the principal *external* variables that, along with bulk rock composition, control which minerals develop in a rock during metamorphism. This study demonstrates that additional controls are the composition and amount of externally-derived fluid that interacts with rock during the metamorphic event. In particular, the carbonate rocks of the Vassalboro Formation developed their particular set of minerals not only because a certain set of *P–T* conditions were attained during metamorphism but also because the rocks were infiltrated by large volumes of aqueous fluid that was low in its K and Na content. If reactions (4) and (5) are correct, the infiltrating fluids were acid as well as H_2O-rich and low in K and Na. It was probably the interaction of the rocks with the acid fluid that drove reactions such as (4) and (5) during the metamorphic event. In this regard regional metamorphism of the Vassalboro Formation might be regarded as an example of large-scale acid metasomatism.

Additional studies should determine whether acid metasomatism is a general metamorphic process or not. In addition, further research would evaluate to what degree the development of minerals during metamorphism is controlled by the interplay of hydrolysis *vs.* dehydration-decarbonation.

Acknowledgments

Research was supported by a Cottrell Grant from Research Corporation and NSF grants EAR 77-22771 and 80-20567 (Earth Sciences Section). Electron microprobe analyses were obtained at the Geophysical Laboratory with the kind permission of H. S. Yoder, Jr., Director. An earlier version of the paper was substantially improved by reviews from D. M. Carmichael and R. C. Newton.

References

Brimhall, G. H., Jr. (1979) Lithologic determination of mass transfer mechanisms of multiple-stage porphyry copper mineralization at Butte, Montana: Vein formation by hypogene leaching and enrichment of potassium-silicate protore. Economic Geology, 74, 556–589.

Carmichael, D. M. (1969) On the mechanism of prograde metamorphic reactions in quartz-bearing pelitic rocks. Contributions to Mineralogy and Petrology, 20, 244–267.

Church, S. E. (1981) Multi-element analysis of fifty-four geochemical reference samples using inductively coupled plasma-atomic emission spectrometry. Geostandards Newsletter, 5, 133–160.

Crawford, M. L., Kraus, D. W., and Hollister, L. S. (1979) Petrologic and fluid inclusion study of calc-silicate rocks, Prince Rupert, British Columbia. American Journal of Science, 279, 1135–1159.

Dallmeyer, R. D. (1979) Chronology of igneous and metamorphic activity in south-central Maine. In Osberg, P. H. and Skehan, J. W., Editors, The Caledonides in the U.S.A., p. 63–72. Weston Observatory of Boston College, Weston, Massachusetts.

Dallmeyer, R. D. and VanBreeman, O. (1981) Rb–Sr whole-rock and $^{40}K/^{39}Ar$ mineral ages of the Togus and Hallowell quartz monzonite and Three Mile Pond grandodiorite plutons, south-central Maine: Their bearing on post-Acadian cooling history. Contributions to Mineralogy and Petrology, 78, 61–73.

Eugster, H. P. (1970) Thermal and ionic equilibria among muscovite, K-feldspar, and aluminosilicate. Fortschritte der Mineralogie, 47, 106–123.

Ferry, J. M. (1976a) Metamorphism of calcareous sediments in the Waterville-Vassalboro area, south-central Maine: Mineral reactions and graphical analysis. American Journal of Science, 276, 841–882.

Ferry, J. M. (1976b) P, T, f_{CO_2}, and f_{H_2O} during metamorphism of calcareous sediments in the Waterville-Vassalboro area, south-central Maine. Contributions to Mineralogy and Petrology, 57, 119–143.

Ferry, J. M. (1978) Fluid interaction between granite and sediment during metamorphism, south-central Maine. American Journal of Science, 278, 1025–1056.

Ferry, J. M. (1979) A map of chemical potential differences within an outcrop. American Mineralogist, 64, 966–985.

Ferry, J. M. (1980a) A case study of the amount and distribution of heat and fluid during metamorphism. Contributions to Mineralogy and Petrology, 71, 373–385.

Ferry, J. M. (1980b) A comparative study of geothermometers and geobarometers in pelitic schists from south-central Maine. American Mineralogist, 65, 720–732.

Ferry, J. M. (1982) A comparative geochemical study of pelitic schists and metamorphosed carbonate rocks from south-central Maine, U.S.A. Contributions to Mineralogy and Petrology, 80, 59–72.

Frantz, J. D., Popp, R. K., and Boctor, N. Z. (1981) Mineral-solution equilibria—V. Solubilities of rock-forming minerals in supercritical fluids. Geochimica et Cosmochimica Acta, 45, 69–77.

Guidotti, C. V. (1970) Metamorphic petrology, mineralogy, and polymetamorphism in a portion of N. W. Maine. In Boone, G. M., Editor, 1970 New England Intercollegiate Geological Conference, 62nd Annual Meeting, Fieldtrip B-1, 1–29.

Helgeson, H. C. (1967) Solution chemistry and metamorphism. In P. H. Abelson, Editor, Researches in Geochemistry, Vol. 2, p. 362–404. John Wiley, New York.

Helgeson, H. C. (1968) Geologic and thermodynamic characteristics of the Salton Sea geothermal system. American Journal of Science, 266, 129–166.

Helgeson, H. C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American Journal of Science, 266, 729–804.

Helgeson, H. C., Kirkham, D. H., and Flowers, G. C. (1981) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb. American Journal of Science, 281, 1249–1516.

Hewitt, D. A. (1973) The metamorphism of micaceous limestones from south-central Connecticut. American Journal of Science, 273-A, 444–467.

Hewitt, D. A. and Wones, D. R. (1975) Physical properties of some synthetic Fe–Mg–Al trioctahedral biotites. American Mineralogist, 60, 854–862.

Holdaway, M. J. and Guidotti, C. V. (1981) Polymetamorphism in medium- to high-grade pelitic metamorphic rocks, west-central Maine. Geological Society of America Bulletin, 93, 572–584.

Jacobs, G. K. and Kerrick, D. M. (1981) Devolitilization equilibria in $H_2O–CO_2$ and $H_2O–CO_2–NaCl$ fluids: An experimental and thermodynamic evaluation at elevated pressures and temperatures. American Mineralogist, 66, 1135–1153.

Leabo, D. A. (1972) Basic Statistics. Richard D. Irwin, Inc., Homewood, Illinois.

McOnie, A. W., Fawcett, J. J., and James, R. S. (1975) The stability of intermediate chlorites of the clinochlore-daphnite series at 2 kbar P_{H_2O}. American Mineralogist, 60, 1047–1062.

Misch, P. (1949) Metasomatic granitization of batholithic dimensions. American Journal of Science, 247, 209–245.

Novak, J. M. and Holdaway, M. J. (1981) Metamorphic petrology, mineral equilibria, and polymetamorphism in the Augusta Quadrangle, south-central Maine. American Mineralogist, 66, 51–69.

Osberg, P. H. (1968) Stratigraphy, structural geology, and metamorphism of the Waterville-Vassalboro area, Maine. Maine Geological Survey Bulletin, 20.

Osberg, P. H. (1979) Geologic relationships in south-central Maine. In P. H. Osberg and J. W. Skehan, Eds., The Caledonides in the U.S.A., p. 37–62. Weston Observatory of Boston College, Weston, Massachusetts.

Pettijohn, F. J. (1975) Sedimentary Rocks. Harper and Row, New York.

Rice, J. M. and Ferry, J. M. (1982) Buffering, infiltration, and the control of intensive variables during metamorphism. In J. M. Ferry, Ed., Characterization of Metamorphism through Mineral Equilibria. Reviews in Mineralogy, Volume 10, Mineralogical Society of America, Washington, D. C.

Robie, R. A., Bethke, P. M., and Beardsley, K. M. (1967) Selected X-ray crystallographic data, molar volumes, and densities of minerals and related substances. U.S. Geological Survey Bulletin 1248.

Rumble, D., Ferry, J. M., Hoering, T. C., and Boucot, A. J. (1982) Fluid flow during metamorphism at the Beaver Brook fossil locality, New Hampshire. American Journal of Science, 282, 886–919.

Senior, A. and Leake, B. E. (1978) Regional metasomatism and the geochemistry of the Dalradian metasediments of Connemara, Western Ireland. Journal of Petrology, 19, 585–625.

Shaw, D. M. (1956) Geochemistry of pelitic rocks. Part III. Major elements and general geochemistry. Bulletin of the Geological Society of America, 67, 919–934.

Sisson, V. B., Crawford, M. L., and Thompson, P. H. (1981) CO_2-brine immiscibility at high temperatures, evidence from calcareous metasedimentary rocks. Contributions to Mineralogy and Petrology, 78, 371–378.

Stanton, R. L. and Williams, K. L. (1978) Garnet compositions at Broken Hill, New South Wales, as indicators of metamorphic processes. Journal of Petrology, 19, 514–529.

Tanner, P. W. G. and Miller, R. G. (1980) Geochemical evidence for loss of Na and K from Moinian calc-silicate pods during prograde metamorphism. Geological Magazine, 117, 267–275.

Thompson, A. B. (1975) Calc-silicate diffusion zones between marble and pelitic schists. Journal of Petrology, 16, 314–346.

Thompson, J. B., Jr. (1981) An introduction to the mineralogy and petrology of the biopyriboles. In D. R. Veblen, Ed., Amphiboles and other Hydrous Pyriboles—Mineralogy, p. 141–188. Reviews in Mineralogy, Volume 9A, Mineralogical Society of America, Washington, D. C.

Thompson, J. B., Jr., Laird, J., and Thompson, A. B. (1982) Reactions in amphibolite, greenschist, and blueschist. Journal of Petrology, 23, 1–27.

Velde, B. and Brusewitz, A. M. (1982) Metasomatic and nonmetasomatic low grade metamorphism of Ordovician metabentonites in Sweden. Geochimica et Cosmochimica Acta, 46, 447–452.

Yardley, B. W. D. (1977) Relationship between the chemical and modal compositions of metapelites from Connemara, Ireland. Lithos, 10, 235–242.

Manuscript received, December 9, 1981;
accepted for publication, November 5, 1982.