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MINERAL REACTIONS AT BOUNDARIES BETWEEN AMPHIBOLITE AND MARBLE IN THE SOUTHERN GRENVILLE PROVINCE, QUEBEC, CANADA

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Abstract

In a high-grade metamorphic terrane north of Ottawa, in the southern Grenville Province of Quebec, numerous reaction-zones from 4 to 20 mm wide have formed at boundaries between amphibolite and marble. Rock compositions are used to identify elements that were added to or removed from two of these zones, and electron-microprobe data on minerals are used to construct reaction equations, which provide additional information on gains and losses. Near the village of Otter Lake, a K-feldspar-bearing amphibolite, composed of aluminous calcic amphibole [$Mg/(Mg + Fe^{2+}) = 0.66$] and K-feldspar [$Na/(Na + K) = 0.07$] with minor titanite, reacted with calcite–quartz marble to produce a 6-mm zone of calcic pyroxene [$Mg/(Mg + Fe^{2+}) = 0.68$] and scapolite [$Ca/(Ca + Na + K) = 0.71$; $Cl:S:CO_2 = 0.1:0.1:0.8$]. Sodium, Cl, and S were introduced, and Fe, K, Rb, Ba, F, H_2O and CO_2 were removed. Near Gracefield, amphibolite composed of pargasitic amphibole [$Mg/(Mg + Fe^{2+}) = 0.50$], plagioclase [$Ca/(Na + Ca) = 0.20$] and minor ilmenite reacted with calcite–dolomite marble to produce a 10-mm subzone of mainly amphibole [$Mg/(Mg + Fe) = 0.83$, increasing toward marble to 0.87] and scapolite [$Ca/(Na + Ca) = 0.37$], with minor plagioclase [$Ca/(Na + Ca) = 0.27$] and calcite, and a 7-mm subzone (adjacent to marble) composed almost entirely of biotite [$Mg/(Mg + Fe) = 0.87$, increasing toward marble, to 0.92]. Here, K, P, Zn, Rb, Ba, Cl, and H_2O were introduced, and Na, Sr, and CO_2 were removed. Estimates of gains and losses per cm^3 of reaction zone (both occurrences) fall in the range of 9000 to 2000 μmol for H_2O and CO_2, 2000 to 600 μmol for Na, K, and Fe, and <200 μmol for trace elements. In the Otter Lake occurrence, approximately 3 μmol of each of Si, Al, Fe, and Mg passed through the reaction zone from amphibolite to marble, relative to 12 μmol of pyroxene produced, whereas 5 μmol of Ca moved in the opposite direction. In reactions of the kind here described, the rate of migration of atoms that were added to the reaction sites, and the rate of migration of atoms through the reaction zones, have possibly both determined the overall rate of crystallization.

Keywords: amphibolite, marble, reaction zone, calcic amphibole, calcic pyroxene, scapolite, biotite, Grenville Province, Quebec.

Sommaire

Dans un socle affecté par une recristallisation métamorphique de forte intensité au nord d'Ottawa, dans le secteur sud de la Province du Grenville du Québec, plusieurs zones de réaction allant de 4 à 20 mm de large ont été formées à l'interface entre amphibolite et marbre. La composition des roches sert à identifier quels éléments ont été ajoutés ou soustraits de deux de ces zones, et les données obtenues sur les minéraux avec la microsonde électronique servent à construire les équations pour représenter les réactions, ce qui permet d'évaluer davantage les ajouts et les pertes. Près du village de Otter Lake, une amphibolite à feldspath potassique, faite d'amphibole calcique alumineuse [$Mg/(Mg + Fe^{2+}) = 0.66$] et de feldspath potassique [$Na/(Na + K) = 0.07$], avec titanite accessoire, a réagi avec le marbre à calcite–quartz pour produire une zone de 6 mm de pyroxène calcique [$Mg/(Mg + Fe^{2+}) = 0.68$] et de scapolite [$Ca/(Ca + Na + K) = 0.71$; $Cl:S:CO_2 = 0.1:0.1:0.8$]. Le Na, Cl et S ont été introduits, et le Fe, K, Rb, Ba, F, H_2O et CO_2 ont été perdus. Près de Gracefield, une amphibolite contenant une amphibole pargasitique [$Mg/(Mg + Fe^{2+}) = 0.50$], plagioclase [$Ca/(Na + Ca) = 0.20$] et ilménite accessoire a réagi avec un marbre à calcite–dolomite pour produire un premier liseré de 10 mm d'un assemblage surtout composé d'amphibole [$Mg/(Mg + Fe) = 0.83$, augmentant vers le marbre jusqu'à 0.87] et scapolite [$Ca/(Na + Ca) = 0.37$], avec plagioclase [$Ca/(Na + Ca) = 0.27$] et calcite accessoires, et un autre de 7 mm adjacent au marbre composed presqu'entièrement de biotite [$Mg/(Mg + Fe) = 0.87$, augmentant vers le marbre, jusqu'à 0.92]. Dans ce cas, le K, P, Zn, Rb, Ba, Cl et H_2O ont été introduits, et le Na, Sr et CO_2 ont été perdus. Les bilans de gains et de pertes par cm^3 dans les deux zones de réaction étudiées indiquent une mobilisation de 9000 à 2000 μmol de H_2O et CO_2, de 2000 à 600 μmol de Na, K et Fe, and <200 μmol des éléments traces. A Otter Lake, environ 3 μmol de Si, Al, Fe, et Mg ont traversé la zone de réaction de l'amphibolite au marble, par rapport à 12 μmol de pyroxène produit, tandis que 5 μmol de Ca ont migré dans la direction opposée. Dans de telles réactions, le taux de migration des atomes ajoutés aux sites de réaction, ainsi que des atomes traversant ces zones de réaction, auraient ensemble déterminé le taux global de cristallisation.

(Traduit par la Rédaction)

Mots-clés: amphibolite, marbre, zone de réaction, amphibole calcique, pyroxène calcique, scapolite, biotite, Province du Grenville, Québec.

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INTRODUCTION

Mineral zones a few mm to several cm wide, separating marble from schist or gneiss, are commonly observed in metamorphic terranes, and have been described by Eskola (1922), Thompson (1975), Glassley (1983), Todd & Evans (1993), López Sánchez-Vizcaíno & Soto (2002), among others. Reaction zones at boundaries between marble and amphibolite are less common; one occurrence in California was described by Kerrick (1977), who found three subzones, with different combinations of calcic pyroxene, calcic amphibole, garnet, and epidote. In general, reaction zones have attracted much attention because reactant and product minerals are available for study, and because the zones provide information on the displacement of atoms under metamorphic conditions. Theoretical aspects have been dealt with by Thompson (1959), Brady (1977), Frantz & Mao (1979) and Joesten & Fisher (1988).

While carrying out field studies in southwestern Quebec, the writer recognized two kinds of zones between marble and amphibolite, one with calcic pyroxene (hereafter referred to as pyroxene), and one with biotite, locally accompanied by calcic amphibole (hereafter referred to as amphibole), and one zone of each kind is described in this report. The aim is to identify the elements that were added to or removed from the reaction zones, based on rock compositions in terms of major and eight trace elements, as established by X-ray-fluorescence analysis, and to construct reaction equations based on electron-microprobe data on the minerals. The reaction equations should provide additional information on gains and losses, especially for C, H, F, and Cl. Growth of the reaction zones, and the displacement of major and trace elements during reaction-zone crystallization, will also be considered.

GEOLOGICAL SETTING

The regions about the town of Gracefield, 70 km north of Ottawa, and about the village of Otter Lake, 70 km northwest of Ottawa, and the intervening terrane, lie within the southern Grenville Province of the Canadian Precambrian Shield. This part of the province is characterized by the presence of highly deformed marble, garnet biotite sillimanite gneiss, quartzite, amphibolite, and a variety of other units, including metagabbro, granite, and syenite (Aubert de la Rüe 1956, Baker 1977, Kretz 1977). The metamorphic grade is upper amphibolite to locally lower granulite facies (7 kbar, 700°C), and reaction zones described below presumably formed near the peak of metamorphism. The principal tectonic-metamorphic events that affected this terrane occurred between approximately 1220 and 920 Ma (Rivers 1997).

METHODS

Mineral proportions were determined by point-count analysis of thin sections and stained slabs. Following Chayes (1956), 0.95 confidence limits to these estimates, as listed in the relevant tables, are approximately 10 ± 3 and 50 ± 5 volume percent. The density of rock fragments, also listed in the tables, was measured by the standard method of weighing the fragments in water and in air; the uncertainty is ± 0.02 g/cm^3.

Rock samples were analyzed using fused discs and a Philips PW 2400 X-ray-fluorescence spectrometer at the University of Ottawa. The precision s (0.95 confidence limits) of the results can be expressed by use of the equation $\pm 1.96\ s = \pm\ \mathrm{k}c^{2/3}$ (Kretz & Hartree 1998), where c is concentration (weight % oxide in the case of a major element, or ppm in the case of a trace element), and k is equal to 0.002 (Mn), 0.0046 (Si, Ti, Al, Fe, Mg, Ca, K), 0.010 (Na), 0.029 (Sr), 0.071 (V, Zn, Y, Zr), and 0.15 (P, Rb); Ba was not evaluated. For example, 0.95 confidence limits to some of the constituents that were determined in amphibolite (see below) are: 50.2 ± 0.2% SiO_2, 18.7 ± 0.1% Al_2O_3, 8.21 ± 0.04% CaO, 0.34 ± 0.01% K_2O wt%, and 1160 ± 10 ppm Sr and 36 ± 2 ppm Y. The proportion of FeO was determined by titration (Wilson method), with an uncertainty of approximately ±0.10 wt%.

Electron-microprobe analyses of minerals were made at Carleton University (Sample 1) and at McGill University (Sample 2), by use of standard procedures. Most of the results presented below are mean concentrations of two spot analyses (x_1, x_2), one on each of two closely spaced crystals. Between-spot differences for a given element can be described by use of standard deviation (s), calculated as $s^2 = \Sigma\ (x_1 - x_2)^2\ /\ 2N$, where N is the number of pairs of compositions (all at approximately the same level of concentration) converted to percent relative standard deviation. These numbers were found to range from 1% (at 50 wt% SiO_2), to 2% (at 20 wt% Al_2O_3 and CaO), to 3% (at 1 wt% Na_2O and K_2O). They are approximately twice as large as those resulting from analytical precision (Potts *et al.* 1983), and hence the variation is very small. Only locally was within-crystal variation detected, *e.g.*, slight normal zoning in plagioclase crystals in amphibolite in Sample 2.

THE CONSERVATION PROBLEM

While examining a reaction zone (B in Fig. 1) that has crystallized at the boundary of two bodies of rock (A and C), it is of interest to identify those elements that remained within the confines of the zone, and those that were either added to or removed from the zone. This can be done only if the location of the original A–C interface (β in Fig. 1) is known.

In a previous study (Kretz 2000), an equation was derived to assist in locating the interface, provided rock compositions are available for major and several trace elements, and this derivation is here quickly reproduced.

Consider a prismatic volume of rock measuring 1 cm × 1 cm in cross-section, extending from amphibolite (A), through a reaction zone (B), and into marble (C), as in Figure 1. Line β marks the position of the original interface, and distances *a* and *c* are normalized to make $a' + c' = 1.0$. The density of A, B, and C is denoted d^A, d^B, and d^C g/cm^3, and for each chemical element, concentration (expressed as weight percent, weight fraction, or ppm) in A, B, and C is denoted w^A, w^B, and w^C. The change in volume during the transformation, $A' + C' \rightarrow B$ (Fig. 1) is described by use of a factor *f* (*e.g.*, $f = 1.0$ where there is no change in volume, and $f = 0.90$ when there is a 10% decrease in volume). Now for each element (*e.g.*, Na) that is locally conserved, the number of grams of Na in volume A' + the number of grams of Na in volume C' are equal to the number of grams of Na in volume B, *i.e.*,

$$d^A w^A a' + d^C w^C c' = f\,[d^B w^B (a' + c')], \qquad (1)$$

assuming that the concentration of the element (Na) in volume A' was the same as presently found in volume A, adjoining the reaction zone (Fig. 1), and similarly for C' and C. Recalling that $a' + c' = 1.0$, and rearranging terms, one obtains

$$a' = \frac{f d^B w^B - d^C w^C}{d^A w^A - d^C w^C} \qquad (2)$$

and

$$w^B = \frac{d^A w^A a' - d^C w^C \left(1 - a'\right)}{f d^B} \qquad (3).$$

Various arguments, to be described below, can be advanced to arrive at an estimate of *f*, for example the volume change (ΔV) for the reaction equation, calculated from molar volume data.

Now applying equation (2), if several elements, including trace elements, all yield nearly the same values of *a'*, one can suppose that *a'* is located, and all of these elements remained within the boundaries of the reaction zone. The remaining elements, with different *a'* values, are then inferred to have been added to or removed from the reaction zone, especially so if the *a'* values are less than zero or larger than 1.0.

A simple reaction is now examined, to bring into focus some of the questions that arise in the study of reaction zones, and to demonstrate that under exceptional conditions, equation (2) cannot be used for major elements. Consider a zone of spinel that has crystallized at the boundary separating periclase and corundum. Thus, in Figure 1, A is MgO, B is $\mathrm{MgAl_2O_4}$, and C is $\mathrm{Al_2O_3}$, and the reaction equation is:

$$\begin{array}{llll} 0.10\,\mathrm{MgO} + & 0.10\,\mathrm{Al_2O_3} \Rightarrow & 0.10\,\mathrm{MgAl_2O_4} & \qquad (4) \\ 1.125\ \mathrm{cm^3} & 2.558\ \mathrm{cm^3} & 3.977\ \mathrm{cm^3} & \end{array}$$

for which the volume change (ΔV) at 298 K, 1 bar is +0.294 cm^3 ($f = 1.08$). The Gibbs energy change (ΔG) for this reaction at 25°C to 730°C (1 bar) is large (approximately –2.4 kJ; data from Robie *et al.* 1979), and, indeed, the widespread occurrence of spinel confirms that if reaction (4) occurs at all, it must be displaced to the right.

Applying equation (2) to this example, using as concentration terms the weight fractions of Mg, Al, O, or MgO, $\mathrm{Al_2O_3}$, all yield *a'* values of 0.305. The calculated value of *a'* (0.305) would locate the original MgO–$\mathrm{Al_2O_3}$ interface accurately, had growth of the reaction zone occurred by the transfer of small, 1 μmol volumes of MgO from α to γ, as an equal number of small, 1 μmol volumes of $\mathrm{Al_2O_3}$ was transferred from γ to α (Fig. 1). This, however, is not a realistic mechanism of reaction. Indeed, Carter (1961) has demonstrated experimentally that the reaction proceeds instead by the transfer of Mg and Al atoms as follows,

$$\begin{array}{lcccl} & | & \Leftarrow 2\mathrm{Al} & | & \\ \mathrm{MgO} & | & & | & \mathrm{Al_2O_3}, \\ & | & 3\ \mathrm{Mg} \Rightarrow & | & \end{array}$$

which is referred to as the Wagner mechanism. The transfer occurs by diffusion down small concentration-gradients in the spinel structure, with vacancies playing an important role. Thus the half reactions are:

at α,

$$\begin{array}{ll} 0.10\,\mathrm{MgO} + 0.05\,\mathrm{Al} \Rightarrow & \\ 1.125\ \mathrm{cm^3} & \\ 0.025\,\mathrm{MgAl_2O_4} + 0.075\,\mathrm{Mg}, & \qquad (5) \\ \quad 0.994\ \mathrm{cm^3} & \end{array}$$

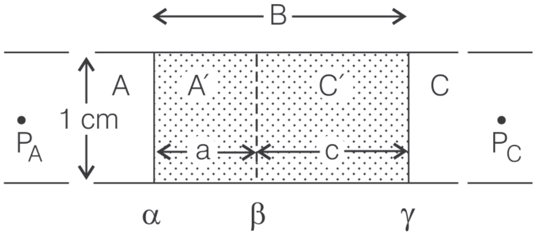

FIG. 1. Model reaction zone (B) at boundary between amphibolite (A) and marble (C); β marks the location of the original A–C contact plane; P_A and P_C are reference points.

and at γ,

$$\begin{array}{ll} 0.10\ Al_2O_3 + 0.075\ Mg \Rightarrow & \\ \quad 2.558\ cm^3 & \\ 0.075\ MgAl_2O_4 + 0.05\ Al & (6). \\ \quad 2.983\ cm^3 & \end{array}$$

Now the volume of spinel produced at γ exceeds that produced at α by a factor of 3.0 (*i.e.*, a' is 0.25 rather than 0.30), and γ advances to the right three times as fast as α advances to the left (Fig. 1). From data in equations (5) and (6), the volume change at α is -0.131 cm^3 per 0.10 mol of spinel, and at γ, $+0.425$ cm^3 per 0.10 mol of spinel produced, and β is therefore displaced to the left. There is an additional (indeterminate) displacement resulting from the overall increase in volume [$+0.294$ cm^3 per 0.10 mol of spinel (eq. 4), *i.e.*, $f = 1.08$], which results from the separation of reference points P_A and P_C (Fig. 1).

When dealing with the more complex reactions that occurred at boundaries between bodies of rock, it is less likely that stoichiometric restrictions of the kind described above played a major role in determining the rate of advance of α relative to γ. In what follows, equation (2) will be applied with caution to major elements, and without reservation to trace elements.

While scanning a table of data for A, B and C, the concentration of an element in the reaction zone (B) might be found to be very much larger than, or smaller than, that in A and C. It is then obvious that this element was not conserved. A calculation of a' (eq. 2) for this element would give meaningless results, but equation (3) would remain useful to obtain an estimate of the amount of the element that was added to or removed from the reaction zone.

TABLE 1. PROPORTION, WIDTH, AND DENSITY OF MINERALS, SAMPLE 1 (OL 593)

	Amphibolite A	Reaction zone B	Marble C
Calcic pyroxene	-	58	13
Calcic amphibole	65	< 1	-
Biotite	< 1	-	-
Epidote	4	< 1	1
Titanite	5	7	1
K-feldspar	23	-	1
Scapolite	-	34	10
Quartz	2	-	10
Calcite	-	-	64
Apatite	< 1	< 1	-
Pyrite	< 1	< 1	< 1
Width, mm	12	6	15
Density, g cm^{-3}	3.09	3.13	2.84
Points counted	600	295	600

Modal proportions expressed in vol.%.

RESULTS

Sample 1 (*Otter Lake*)

Sample 1 is from a small west-facing cliff, 3 km southeast of the village of Otter Lake, near and to the north of Route 303, at 45°50.4'N, 76°23.5'W. The outcropping consists mainly of marble (calcite, pyroxene, scapolite) with fragments and layers (some folded and disjointed) of amphibolite and granulite (pyroxene, hornblende, feldspar, scapolite, titanite, garnet) as well as isoclinally folded quartz–feldspar layers. Also present are bodies of skarn (pyroxene, scapolite, titanite, allanite, apatite) cut by pink calcite veins. This association of rocks, some of which have obviously been affected by metasomatism, lies within the Otter Complex (Kretz 1994), which consists mainly of veined gneiss of granitic composition.

In the study sample (Fig. 2), a reaction rim of pyroxene, scapolite, and titanite 6 mm wide occurs at the

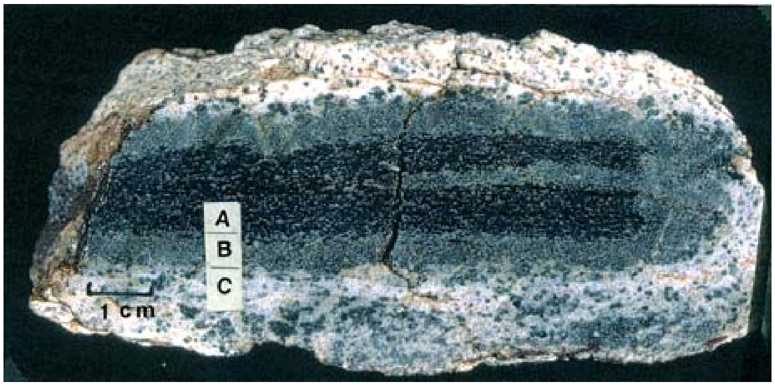

FIG. 2. Sample 1, showing amphibolite (A), reaction zone (B) and marble (C).

boundary of amphibolite and marble. Unlike most bodies of amphibolite in the Otter Lake area, this one contains K-feldspar in place of plagioclase, and it too appears to have been affected by a metasomatic event, which is assumed to have occurred prior to formation of the reaction rim. Note that the rim must have formed after the amphibolite layer became disjointed.

All minerals present in amphibolite (A), reaction zone (B) and marble (C) are listed in Table 1, and microstructures are illustrated in Figure 3. Epidote, as elsewhere in the field area, is viewed as a retrograde mineral that appeared after the rim had crystallized. Another sample from the same outcropping was examined microscopically and was found to be very similar to Sample 1.

The chemical composition of A, B, and C in Sample 1 is indicated in Table 2. Notice that several elements show a step-wise increase or decrease from A to C, which is viewed as evidence that both amphibolite and marble contributed to the crystallization of the reaction zone. Thus the zone was evidently produced by reaction of amphibole, K-feldspar, and calcite to yield pyroxene and scapolite.

Application of equation (2) with *f* initially taken as 1.0 produces *a*' values for all of Si, Al, P, V, Zn, and Y in range of 0.91 to 0.98, placing β (Fig. 1) near the boundary with marble (Table 3). A second solution is obtained by allowing *f* to decrease by increments until *a*' for Si (0.94) and *a*' for Ca (0.54) converge, which they do at $f = 0.86$, $a' = 0.66$. This value of *f* (0.86) agrees with that calculated from the reaction equation (below) and is now adopted. A similar solution is obtained ($f = 0.83$, $a' = 0.69$) by convergence of Al and Ca.

Note that with *f* taken at 0.86 (Table 3), *a*' values for several elements lie not far from 0.66 (range 0.58 to 0.85). The conclusion to be drawn regarding the remaining elements is that Fe, K, Rb, and Ba were removed from the reaction zone as Na was added, by amounts that can be calculated (Table 3) by use of equation (3).

Compositions of minerals in Sample 1 are reported in Table 4. The ratio $Fe^{3+} / (Fe^{2+} + Fe^{3+})$ in amphibolite (Table 2) is 0.36, from which it is possible to estimate this ratio in the contained amphibole. Then the ratio $Mg / (Mg + Fe^{2+})$ in this mineral is 0.66, and with 6.5 Si atoms in the formula, the composition falls at the bound-

TABLE 2. CHEMICAL COMPOSITION OF SAMPLE 1

	A Amphibolite	B Reaction zone	C Marble
SiO_2 wt%	47.6	45.7	27.2
TiO_2	1.91	1.92	0.27
Al_2O_3	12.4	11.5	4.17
Fe_2O_3	4.6	2.2	1.1
FeO	7.4	5.1	1.0
MnO	0.109	0.062	0.042
MgO	8.17	6.26	1.88
CaO	9.87	20.5	36.6
Na_2O	0.83	1.36	0.30
K_2O	4.52	0.45	0.51
P ppm	1140	1040	179
V	218	200	30
Zn	132	129	67
Rb	100	< 10	15
Sr	574	646	784
Y	27	26	10
Zr	120	139	96
Ba	400	42	106

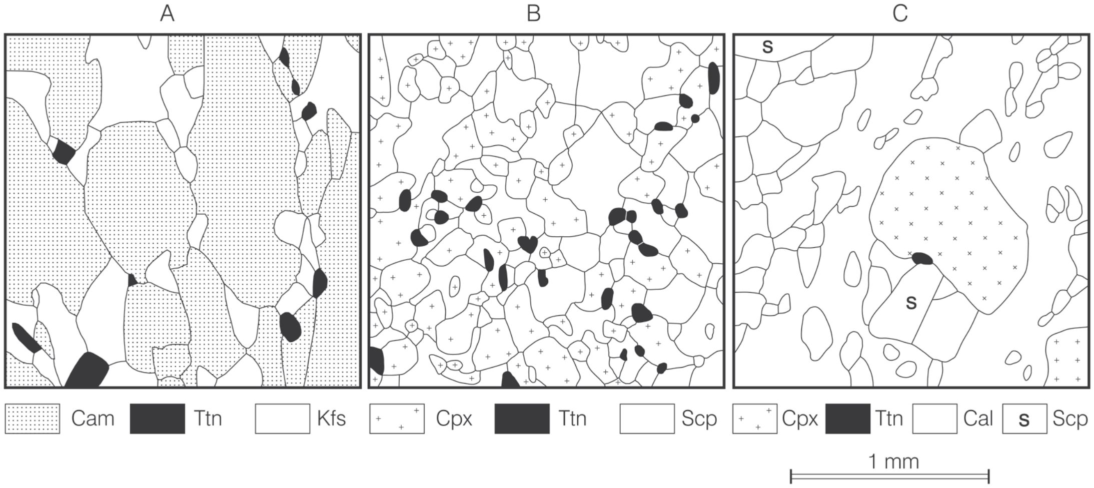

FIG. 3. Microstructure of amphibolite (A), reaction zone (B) and marble (C) in Sample 1; in frame C, calcite is mainly very fine-grained.

ary of edenite and magnesiohastingsite. In pyroxene, if one assumes that little or no Fe^{3+} is present, Mg / (Mg + Fe^{2+}) is 0.68, and applying the 50% rule, this is diopside. The composition of this mineral in marble is similar to that in the reaction zone, but is more variable. The stoichiometry of scapolite agrees well with that determined by Evans *et al.* (1969), and with a ratio Ca / (Ca + Na + K) = 0.71, this is meionite. Both Cl and S are present (Table 4), whereas F could not be detected.

The mineral formulas are now used to construct the following proposal for the chemical reaction that produced the reaction zone in Sample 1.

$$\begin{aligned}
&\text{amphibole + K-feldspar + calcite}\\
&+ \text{quartz} + (\text{Na, Cl, S})\\
&\longrightarrow \text{pyroxene + scapolite} + (\text{K, Fe, Ti, F, H, C})\\[1ex]
&3\ Ca_{1.97}\ Na_{0.34}\ K_{0.34}\ (Mg_{2.47}\ Fe_{2.03}\ Mn_{0.02}\ Ti_{0.07}\\
&Al_{0.52})\ Al_{1.50}\ Si_{6.50}\ O_{22}\ (F_{0.20}\ Cl_{0.032}\ OH_{1.77})\\
&+ 1\ K_{1.80}\ Na_{0.14}\ Al_{2.06}\ Si_{5.95}\ O_{16}\\
&+ 10\ Ca_{0.99}\ Mg_{0.01}\ Fe_{0.004}\ Mn_{0.01}\ CO_3\\
&+ 9\ Si\ O_2\\
&+ (0.80\ Na + 0.05\ Cl + 0.15\ S)\\
&\longrightarrow 12\ (Ca_{0.98}\ Na_{0.03}\ Mg_{0.63}\ Fe_{0.30}\ Mn_{0.003}\ Ti_{0.003}\\
&Al_{0.053})\ Al_{0.04}\ Si_{1.96}\ O_6\\
&+ 1.5\ (Na_{1.07}\ K_{0.05}\ Ca_{2.77})\ Al_{4.95}\ Si_{7.05}\ O_{24}\ Cl_{0.10}\\
&F_{0.00}\ (SO_4)_{0.10}\ (CO_3)_{0.8}\\
&+ (2.7\ K + 2.5\ Fe + 0.2\ Ti\\
&+ 0.6\ F + 2.7\ H_2O + 8.8\ CO_2) \qquad (7)
\end{aligned}$$

This equation is nearly balanced for Si, Al, Ca, and Mg. It requires the addition of Na and removal of K and Fe, in agreement with expectations based on the bulk composition (Table 3). Some of the Cl that entered scapolite was derived from amphibole, the remainder and all of the S were introduced. The minor excess Ti possibly contributed to the formation of additional titanite. All F that was present in amphibole evidently escaped, as did H and C, presumably as H_2O and CO_2.

TABLE 3. APPLICATION OF THE CONSERVATION EQUATION TO SAMPLE 1

	a'		w^B (f = 0.86; a' = 0.66)			
	f = 1.0	f = 0.86	calculated	found	change	
Si	0.94	0.66				
Ti	1.0	0.85				
Al	0.91	0.72				
Fe	0.54	0.44	7.37	5.43	- 1.9	wt%
Mn	0.34	0.21				
Mg	0.72	0.58				
Ca	0.54	0.66				
Na	2.0	1.66	0.55	1.01	+ 0.46	
K	- 0.003	- 0.02	3.00	0.37	- 2.63	
P	0.91	0.76				
V	0.92	0.77				
Zn	0.98	0.72				
Rb	- 0.07	- 0.08	81	< 10	- 80	ppm
Sr	0.45	1.08				
Y	0.96	0.76				
Zr	1.6	1.0				
Ba	- 0.81	- 0.2	342	42	- 300	

By use of molar volume data for minerals (at 298 K, 1 bar) of simplified composition, as compiled by Berman (1988), the volume change for reaction equation (7) is f = 0.81, *i.e.*, a 19% decrease, in good agreement with the above estimate of 0.86 (Table 3). The equation produces a pyroxene : scapolite volume ratio of 1.6, the same as that found (Table 1), and an amphibole : K-feldspar volume ratio of 3.8, compared with 2.8, as found. The volume ratio quartz : calcite in the equation (0.56) is larger than that measured in the marble (0.19).

The reaction zone is Sample 1 is nearly uniform with regard to mineral proportions and microstructure, and contacts with amphibolite and marble are moderately sharp. Given that the original amphibolite–marble contact was at *a'* approximately equal to 0.66, as calculated above, then one can imagine growth of the reaction zone

TABLE 4. COMPOSITION OF MINERALS, SAMPLE 1

	Amphibolite (A)		Reaction zone (B)		Marble (C)	
	Cam	Kfs	Cpx	Scp	Cpx	Cal
SiO_2 wt%	43.3	65.8	52.1	47.2	52.1	
Al_2O_3	11.4	19.3	2.07	28.1	1.29	
TiO_2	0.6		0.13		0.05	
FeO_T	16.1*	0.14	9.61	0.03	10.7	0.30
MnO	0.16		0.11	0.01	0.15	0.06
MgO	11.1		11.2	0.00	11.4	0.33
CaO	12.2	0.02	24.3	17.3	23.3	56.0
Na_2O	1.15	0.80	0.40	3.68	0.31	
K_2O	1.75	15.6		0.27		
BaO		0.15				
Cl	0.13			0.39		
F	0.41			0.00		
SO_3				0.91		
Si *apfu*	6.50	5.95	1.96	7.05	1.98	
^{IV}Al	1.50	2.06	0.04	4.95	0.02	
Σ	8.0	8.0	2.0	12.0	2.0	
^{VI}Al	0.52		0.053		0.037	
Ti	0.07		0.003		0.001	
Fe	2.03	0.01	0.30	0.004	0.34	0.004
Mn	0.02		0.003	0.002	0.005	0.001
Mg	2.47		0.63	0.00	0.64	0.008
Σ	5.1					
Ca	1.97	0.002	0.98	2.77	0.95	0.987
Na	0.34	0.14	0.03	1.07	0.023	
K	0.34	1.8		0.05		
Ba		0.005				
Σ	2.64	10.0	2.0	3.9	2.0	1.0
Cl	0.032			0.10		
F	0.20			0.00		
OH**	1.77					
S				0.10		
C**				0.8		
Σ	2.0			1.0		

* $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ = 0.36 (see text); ** by difference.

(*i.e.*, an increase in width) occurring by advance of α into amphibolite and of γ into marble, with the rate of advance of α exceeding that of γ by a factor of 2.

Sample 2 (*Gracefield*)

Sample 2 is from a folded layer of amphibolite, 17 cm wide, in marble (Fig. 4). The amphibolite and marble are exposed in a north-facing road-cut, 8 km northeast of Gracefield, and ~100 m east of a bridge across the Gatineau River, *i.e.*, at 46° 07.0'N, 75° 54.7'W. The site lies within a 15-minute quadrangle mapped by Aubert de la Rüe (1956), and within a smaller area that for many years was studied by undergraduate students from the University of Ottawa. More recent mapping was done by Langlais (1994).

Biotite is conspicuously present at the margin of the exposed layer of amphibolite (Fig. 4), but the amount varies, and locally it is absent. Sample 2 is a rock fragment that includes the entire width of the amphibolite layer and extends 7 cm into the adjoining marble. In this sample, there is a subzone (B1) with abundant amphibole, 10.1 mm wide, adjacent to amphibolite, and another (B2) with abundant biotite, 6.6 mm wide, adjacent to marble, for a total width of 16.7 mm. From mineral assemblages and proportions, as listed in Table 5, a complex change evidently occurred at the amphibolite–marble boundary, in which K was introduced, plagioclase was consumed, and amphibole, scapolite and biotite were produced. The abundant Mg present in biotite was presumably obtained from dolomite, which is not present in the study sample, but occurs two decimeters from the reaction zone, in calcite – dolomite – olivine – spinel marble and pure dolomite marble.

Variation in microstructure along a traverse beginning in amphibolite, passing through the reaction zone, and extending into marble, is illustrated in Figure 5, where five frames labeled a, c, e, f, g are located along the abscissa in Figure 6. The first frame (a) shows the typical mosaic microstructure of amphibolite, frames c and e lie within the amphibole-rich subzone (B1), f is in the biotite-rich subzone (B2), and g is on the boundary between B2 and marble.

The chemical composition of amphibolite (A), marble (C), and the entire reaction zone (B) in sample 2 is indicated in Table 6. Notice that as in Sample 1, a step-wise increase or decrease is observed for many elements, from A to C, which is again viewed as evidence that portions of both A and C contributed to the crystallization of B.

Application of the conservation equation (2), with f = 1.0, produces the results in Table 7. All of Si, Ti, Al, Fe, V, and Zr yield a' values in the range 0.38 to 0.72, with a mean of 0.58. This mean defines almost exactly the boundary between subzones B1 and B2, which is measured at 0.60. It seems unlikely, therefore (given that a' is a function of f) that an appreciable change in volume has occurred. Values of a' for most remaining elements fall outside of the range 0.1 to 1.0, and of these, K, P, Zn, Rb, and Ba were evidently introduced, whereas Sr, and possibly Na (a' = 0.38) were removed; results for Mn are inconclusive.

Although dolomite is not present in the 2-cm-wide zone of marble that was analyzed, this mineral almost certainly participated in formation of the reaction zone, and the result for Mg in Table 7 (a' = –10.3) is therefore viewed as being erroneous. A substitution of the 92 volume % of calcite in marble (Table 5) by the same volume of dolomite, yields a'(Mg) = 0.4 and a'(Ca) = 0.7, and brings these two elements into the group (above) that yields a realistic a' value of 0.58 (mean).

Data on mineral composition in Sample 2 are listed in Tables 8 and 9. The atom fraction Fe^{3+} / (Fe^{2+} + Fe^{3+}) in amphibolite (rock) is 0.14 (Table 6), which, upon subtraction of Fe^{2+} residing in ilmenite (taken as $Fe^{2+}TiO_3$), increases to 0.19. This value provides an estimate for the Fe^{3+} content of the contained amphibole. The ratio Mg / (Mg + Fe^{2+}) in amphibole of subzone A1 (Table 8) is therefore 0.50. Crystals that are located along a line that extends into the reaction zone contain progressively more Mg and Si, and less ^{IV}Al, Fe, and Ti (Table 8, Fig. 6); these compositions fall in the field of pargasite. Biotite (phlogopite) varies sympathetically (Table 8, Fig. 6).

Within amphibolite and subzone B1, the Ca/(Na + Ca) value of plagioclase is 0.20 (Table 9), increasing to 0.27 (oligoclase), whereas this ratio in scapolite is near 0.37. In marble, near the reaction zone, scapolite occurs as a rim about crystals of biotite (Fig. 5, frame g), and farther from the reaction zone, similar rims consist of plagioclase, both with relatively high Na (Table 9).

Mineral compositions (Tables 8, 9) are now used to construct an equation for the reaction in Sample 2. In this equation, amphibole and biotite formulas (a, b, c,

TABLE 5. PROPORTION, WIDTH, AND DENSITY OF MINERALS, SAMPLE 2 (FC 14-8)

	Amphibolite	Reaction zone			Marble
	A	B1*	B2*	B	C
Calcic pyroxene	-	-	-	-	4
Calcic amphibole	31	53	-	32	4
Biotite	-	15	89	45	< 1
Plagioclase	63	4	-	2	< 1
Scapolite	1	12	< 1	7	-
Calcite	2	13	11	12	92
Ilmenite	2	-	-	-	-
Apatite	2	2	< 1	1	-
Width, mm	10	10.1	6.6	16.7	20
Density, g cm^{-3}	2.91			3.00	2.77
Points counted	632	317	353		683

* subzones. Modal proportions expressed in vol.%.

etc.) are from Table 8; formulas for other minerals were calculated from the data of Table 9. The equation is,

plagioclase a + amphibole a + ilmenite
+ dolomite + (K, Cl, H)
→ scapolite c + amphibole d + biotite f
+ calcite c + (Na, C),

$$
\begin{aligned}
&1.0\ Na_{2.33}\ K_{0.021}\ Ca_{0.62}\ Al_{3.62}\ Si_{8.39}\ O_{24}\\
&+ 0.5\ Ca_{1.65}\ Na_{1.11}\ K_{0.16}\ Mg_{1.85}\ Fe_{2.29}\ Ti_{0.31}\ Al_{0.49}\\
&Al_{2.03}\ Si_{5.97}\ O_{22}\ (OH)_2\\
&+ 0.1\ FeTiO_3\\
&+ 7.6\ Ca\ Mg\ (CO_3)_2\\
&+ (1.7\ K + 0.02\ Cl + 2.5\ H_2O)\\
&\rightarrow 0.2\ Na_{2.37}\ K_{0.01}\ Ca_{1.59}\ Al_{4.16}\ Si_{7.84}\ O_{24}\ Cl_{0.1}\\
&(CO_3)_{0.9}\\
&+ 1.0\ Ca_{1.66}\ Na_{1.10}\ K_{0.13}\ Mg_{3.42}\ Fe_{0.65}\ Ti_{0.16}\ Al_{0.77}\\
&Al_{1.85}\ Si_{6.15}\ O_{22}\ (OH)_2\\
&+ 1.0\ K_{1.62}\ Na_{0.41}\ Mg_{5.06}\ Fe_{0.45}\ Ti_{0.15}\ Al_{0.32}\ Al_{2.20}\\
&Si_{5.80}\ O_{20}\ (OH)_4\\
&+ 7.4\ Ca_{0.95}\ Mg_{0.04}\ Fe_{0.01}\ CO_3\\
&+ (0.91\ Na + 7.6\ CO_2). \qquad (8)
\end{aligned}
$$

Note the following points:

1. Given that the original amphibolite–marble boundary coincided approximately with the present B1–

FIG. 4. Folded layer of amphibolite in marble; Sample 2 is from the left contact of the left limb, at pencil, which is 13 cm long; the reaction zone here is 1.7 cm wide and is visible below the pencil point; a wider and more complex zone is present at the "upper" contacts of both limbs.

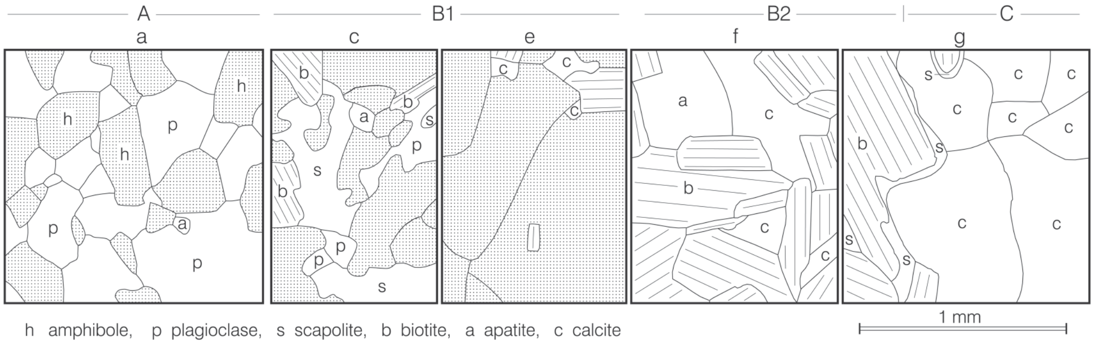

FIG. 5. Microstructure of Sample 2; frames a, c, e, f, g, are located in Figure 6 on the abscissa. The first frame (a) is in amphibolite (A), c and e are in reaction subzone B1, f is in subzone B2, and g is on the boundary of B2 and marble (C).

B2 boundary, then the abundant amphibole in subzone B1 (Table 5) means that some amphibole was produced. This mineral therefore appears in equation (8) as both a reactant, and (in larger amount and with a different composition) as a product.

2. As noted above, dolomite almost certainly provided most of the Mg now present in biotite and newly crystallized amphibole, and it is therefore brought into the equation.

3. Ilmenite, which is present in amphibolite but not in subzone B1, was evidently consumed.

4. Chlorine in the scapolite formula is taken to be the same as in Sample 1. In equation (8), Cl is introduced, and the CO_3 for scapolite is locally derived.

Equation (8), as written, is balanced approximately for Si, Al, Fe (total, with ferrous > ferric), Ti, and O, with the ratio of the number of atoms on the left to the number of atoms on the right falling between 0.94 and 1.2. This ratio for the remaining elements can, of course, be made equal to 1.0. The addition of K and removal of Na are in agreement with above conclusions, based on rock composition (Table 7).

By use of molar volume data (as for equation 7), the volume change for equation (8) is found to be very small ($f = 0.98$), in agreement with $f = 1.0$, deduced above. The volume ratio plagioclase a : amphibole a in the equation is 2.2, compared with 2.0 observed (Table 5), and for amphibole e : scapolite c, it is 4.0, compared with 4.4, observed. The equation produces much more calcite than is present in the reaction zone; most of this excess calcite presumably crystallized in adjoining marble, to replace the dolomite that was brought into the equation.

Equation (8) provides an explanation for the larger Mg/Fe of amphibole within the reaction zone relative to that in the amphibolite (amphibole d and e, Table 8), but it does not explain the composition gradients in amphibole and biotite within the reaction zone, as plotted in Figure 6. A more complex equation would be needed to do so. One may note, however, that although crystals of amphibole at c and at e (separated by 4 mm) differ in composition and are obviously not at equilibrium with each other, an approach to Fe–Mg *exchange* equilibrium (amphibole–biotite) evidently occurred at sites c and e, and also at site d. Thus, assuming that the

TABLE 6. CHEMICAL COMPOSITION OF SAMPLE 2

	A Amphibolite	B Reaction zone	C Marble
SiO_2 wt%	50.2	34.4	6.04
TiO_2	1.4	0.99	0.061
Al_2O_3	18.7	12.9	0.69
Fe_2O_3	1.06	1.17	0.07
FeO	6.04	2.65	0.84
MnO	0.065	0.030	0.047
MgO	3.20	15.55	4.55
CaO	8.21	13.9	47.5
Na_2O	6.38	2.42	0.15
K_2O	0.34	3.52	0.060
P ppm	3800	5310	35
V	91	59	14
Zn	90	102	31
Rb	< 10	61	< 10
Sr	1160	132	343
Y	36	11	<10
Zr	192	106	23
Nb	18	12	<10
Ba	605	840	40

TABLE 7. APPLICATION OF THE CONSERVATION EQUATION TO SAMPLE 2

	a'	$w^B(f = 1.0; a' = 0.60)$			
	$f = 1.0$	calculated	found	change	
Si	0.67				
Ti	0.72				
Al	0.70				
Fe	0.48				
Mn	- 0.70				
Mg	- 10.3 (0.4)*				
Ca	0.83 (0.7)*				
Na	0.38	2.79	1.8	- 1.0	wt%
K	+ 12.8	0.18	2.92	+ 2.74	
P	+ 1.5	3330	5310	+ 1980	ppm
V	0.61				
Zn	+ 1.25	64	102	+ 38	
Rb	> 170	~ 4	61	+ 57	
Sr	- 0.23	800	130	- 670	
Y	~ 0.20				
Zr	0.51				
Ba	1.5	370	840	+ 470	

* Dolomite in place of calcite.

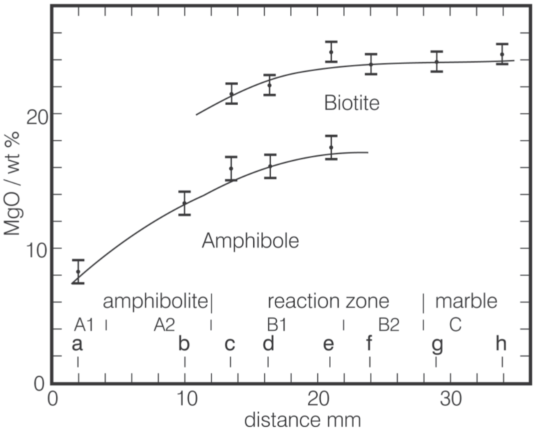

FIG. 6. Variation in Mg content of amphibole and biotite along a traverse through the reaction zone in Sample 2; letters a to h locate microstructures (Fig. 5) and sites of electron-microprobe analyses (Tables 8, 9).

value $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ is 0.81 for both minerals, the distribution coefficient, K_D (Fe^{2+}/Mg; biotite/amphibole) at sites c, d, and e (Fig. 6) is 1.3, 1.3, and 1.0. The expected value (Kretz 1978) is 1.0. Some changes in the composition of crystals could have occurred after reaction (8) came to a close.

Although boundaries of the reaction zone in Sample 2 can be located accurately, on the basis of the minerals present, it is apparent from the above data and interpretations that certain changes evidently occurred for some distance beyond the reaction zone, into the amphibolite on one side and into the marble on the other. Thus the composition of amphibole in amphibolite changed within a few mm of the reaction zone, and in marble, crystals of dolomite for distances of 10 to 20 cm evidently became involved in the reaction.

TABLE 8. COMPOSITION OF AMPHIBOLE AND BIOTITE IN SAMPLE 2

	Amphibolite		Reaction zone				Marble	
	A1	A2	B1			B2	C	
Site (Fig. 6):	a	b	c	d	e	f	g	h
Ca amphibole								
SiO_2 wt%	40.0	40.9	42.9	43.5	44.9			
Al_2O_3	14.7	15.5	15.4	15.7	14.2			
TiO_2	2.70	2.62	1.17	1.55	1.04			
FeO_T	18.3	9.49	5.80	5.52	4.72			
MgO	8.32	13.4	15.9	16.2	17.6			
CaO	10.3	10.7	10.6	11.0	11.6			
Na_2O	3.84	4.07	4.35	4.04	3.80			
K_2O	0.84	0.76	0.63	0.69	0.77			
Si *apfu*	5.97	5.97	6.16	6.15	6.30			
^{IV}Al	2.03	2.03	1.84	1.85	1.70			
^{VI}Al	0.49	0.64	0.77	0.77	0.65			
Ti	0.31	0.29	0.13	0.16	0.11			
Fe	2.29	1.16	0.70	0.65	0.56			
Mg	1.85	2.91	3.40	3.42	3.69			
Ca	1.65	1.68	1.63	1.66	1.75			
Na	1.11	1.15	1.21	1.10	1.04			
K	0.16	0.14	0.12	0.13	0.14			
Biotite								
SiO_2 wt%			38.1	39.4	41.6	40.6	41.1	40.8
Al_2O_3			18.2	16.2	13.9	15.0	14.2	13.3
TiO_2			1.80	2.19	1.31	1.47	1.84	1.95
FeO_T			5.93	5.51	3.65	3.83	3.94	4.03
MgO			21.5	22.2	24.7	23.8	23.9	24.5
CaO			0.01	0.08	0.02	0.02	0.00	0.00
Na_2O			1.77	1.23	1.49	1.48	1.44	1.45
K_2O			8.41	9.17	8.79	8.91	9.14	9.03
Si *apfu*			5.45	5.44	5.89	5.80	5.86	5.84
^{IV}Al			2.55	2.54	2.11	2.20	2.14	2.16
^{VI}Al			0.52	0.19	0.21	0.32	0.25	0.08
Ti			0.20	0.23	0.14	0.15	0.20	0.21
Fe			0.71	0.63	0.43	0.45	0.47	0.48
Mg			4.58	4.74	5.22	5.06	5.08	5.23
Ca			0.00	0.01	0.00	0.00	-	-
Na			0.49	0.34	0.41	0.41	0.39	0.40
K			1.54	1.68	1.59	1.62	1.66	1.65

Formulae based on Σ(Si, Al, Ti, Fe, Mg) = 13 *apfu* (amphibole), 14 *apfu* (biotite).

Growth of the reaction zone in Sample 2 can now be visualized as beginning at the amphibolite–marble contact, in response to an influx of K, H, and Cl. Crystals of the product minerals nucleated at the interface, and growth occurred of amphibole and scapolite crystals 'into' amphibolite, and of most of the biotite crystals 'into' marble, to give rise to subzones B1 and B2; some calcite crystallized in subzone B1 (Table 5). With continued reaction , the width of subzone B1 increased more rapidly than that of B2 by a factor of 1.5.

DISPLACEMENTS OF ATOMS

Reaction equation (7) for Sample 1, combined with estimates of the location of the original amphibolite–marble boundary ($a' = 0.66$) can be used to construct half-reactions, analogous to (5) and (6) above, that occurred at the outer margins (α, γ) of the reaction zone. These half-reactions identify those elements that migrated through the zone, from α to γ and from γ to α, as reaction was in progress, and they also provide estimates of the numbers of atoms that were displaced. The results of this calculation appear in Figure 7, where displacements are in units of μmol of element per 12 μmol of pyroxene produced (equation 7). Atoms of oxygen and other elements not indicated in Figure 7 also were displaced. A similar but more complex displacement of atoms must have occurred within the reaction zone of Sample 2.

TABLE 9. COMPOSITION OF PLAGIOCLASE, SCAPOLITE AND CALCITE IN SAMPLE 2

	Amphibolite		Reaction zone				Marble	
	A1	A2	B1			B2	C	
Site (Fig. 6):	a	b	c	d	e	f	g	h
Plagioclase								
SiO_2 wt%	62.6	62.5		61.0				65.2 *
Al_2O_3	22.9	22.7		23.9				20.9
CaO	4.29	4.15		5.57				1.95
Na_2O	8.99	9.24		8.52				10.35
K_2O	0.12	0.05		0.02				0.00
Ca/(Na + Ca)	0.21	0.20		0.27				0.094
Scapolite								
SiO_2 wt%		53.9	53.3	55.5			58.5 *	
Al_2O_3		23.4	24.0	23.6			22.0	
CaO		9.40	10.1	8.40			5.42	
Na_2O		8.70	8.29	9.44			11.1	
K_2O		0.14	0.06	0.13			0.15	
Ca/(Na + Ca)		0.37	0.40	0.33			0.21	
Calcite								
CaO wt%				52.3	53.5	52.6		52.3
MgO				2.8	1.8	2.4	3.0	2.2
FeO_T				0.70	0.56	0.58	0.73	0.63
Mg/(Ca + Mg)				0.069	0.045	0.060		0.055

* rim about biotite crystal.

TABLE 10. GAINS (+) AND LOSSES (−) IN SAMPLES 1 AND 2, CALCULATED FROM ROCK COMPOSITION (I) AND MINERAL COMPOSITION (II), IN UNITS OF μmol / cm^3 OF REACTION ZONE

	Sample 1		Sample 2	
	I	II	I	II
Fe	− 1060	− 1930		
Na	+ 630	+ 620	− 1300	− 1000
K	− 2100	− 2080	+ 2100	+ 1860
P			+ 190	
Zn			+ 2	
Rb	− 3		+ 2	
Sr			− 23	
Ba	− 7		+ 10	
F		− 460		
Cl		+ 39		+ 22
S		+ 116		
H_2O		− 2080		+ 2740
CO_2		− 6780		− 8320

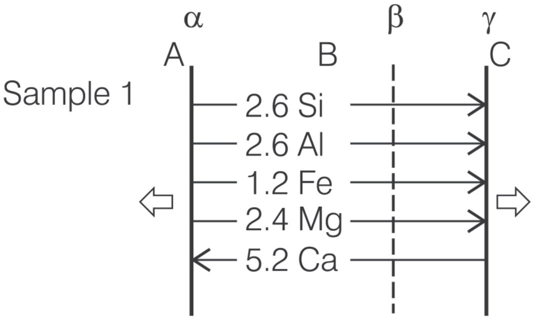

FIG. 7. Calculated displacement of atoms in Sample 1; numbers are μmol of element relative to 12 μmol of pyroxene produced (eq. 7).

The various gains and losses that were calculated above, from rock and mineral compositions, are summarized in Table 10, where numbers are in units of μmol of element per 1 cm^3 of reaction zone. In general, elements that could be calculated by *both* methods agree fairly well. Thus rock and mineral compositions support and supplement each other.

Note (Table 10) that Rb and Ba "followed" K from the reaction zone in Sample 1 and into the reaction zone in Sample 2. That Rb and Ba are geochemically similar to K is well known and is illustrated, for example, in the following distribution formulas, obtained from gneiss and amphibolite of the Otter Lake area:

Rb: Bt 2.3 Kfs 23 Pl 1.0 Hbl,

Ba: Kfs 4.0 Bt 12 Pl 1.0 Hbl,

where the numbers are distribution ratios, for example ppm Rb in Kfs / ppm Rb in Pl = 23 (Kretz *et al.* 1999).

Those elements that apparently remained within the confines of the reaction zones in both samples are Si, Ti, Al, V, Y and Zr. That all have a valence of 3 or 4 rather than 1 or 2 might be relevant to the ease of displacement of these atoms.

DISCUSSION

It is instructive to define two groups of reaction zones, based on whether or not a significant gain or loss occurred during crystallization. A model for Group I (*no* gain or loss of metals) is the system

A	B	C
periclase	spinel	corundum

described above. A possible model for Group II (conspicuous gain or loss) is the equilibrium

$$1.5\ KAlSi_3O_8 + H = 0.5\ KAl_3Si_3O_{10}(OH)_2 + 3\ SiO_2 + K,$$

which was studied experimentally by Hemley & Jones (1964), with phases arranged as follows:

A	B	C	gain K
muscovite	K-feldspar	quartz	loss H.

In this hypothetical system (an aqueous phase need not be present), growth of the reaction zone (K-feldspar) at the boundary of muscovite and quartz occurs as atoms of K are introduced, and atoms of H are removed, along unspecified paths.

The following two reaction zones form examples of Group I; evidently a loss occurred, but only of CO_2.

Joesten (1974):

A	B	C	
quartz	wollastonite	calcite	loss CO_2

Kerrick (1977):

A	B1	B2	B3	C	
hornblende	tremolite	diopside	diopside	calcite	loss CO_2
plagioclase	epidote	epidote	garnet	quartz	
	plagioclase				

Additional examples are provided by Thompson (1975), Sack (1982) and Owen (1993).

In many studies, the problem of gains and losses is not examined in detail, but a loss of potassium from the following three reaction-zones can be deduced, and they form examples of Group II.

Schrijver (1973):

A	B	C	
orthopyroxene	orthopyroxene	plagioclase	loss (K, H_2O)
Ca pyroxene	Ca pyroxene	K-feldspar	
Ca amphibole	Ca amphibole	quartz	
biotite	plagioclase		
plagioclase			

Auwera (1993):

A	B1	B2	C	
orthopyroxene	orthopyroxene	Ca pyroxene	orthopyroxene	loss (K, Rb)
Ca pyroxene	plagioclase	plagioclase	Ca pyroxene	
hornblende			plagioclase	
biotite			K-feldspar	
plagioclase				

Abart *et al*. (2001):

A	B1	B2	B3	C	
Ca pyroxene	Ca pyroxene	Ca pyroxene	Ca pyroxene	calcite	gain Cl
hornblende		garnet	scapolite	Ca pyroxene	loss K
garnet					

Additional examples are provided by Glassley (1983), Tuisku (1992), and Kretz (2000).

The two samples from the present study fall in Group II, and compared to other reaction zones, they form examples of extreme gains and losses.

Sample 1:

A	B	C	
amphibole	pyroxene	calcite	gain (Na Cl S)
K-feldspar	scapolite	quartz	loss (Fe K Rb F
titanite	titanite	pyroxene	H_2O CO_2)
scapolite			

Sample 2:

A	B1	B2	C	
amphibole	amphibole	biotite	calcite	gain (K Rb Cl H_2O)
plagioclase	biotite	calcite	(dolomite)	loss (Na CO_2)
ilmenite	scapolite		pyroxene	
	calcite		amphibole	

These extremes could be attributed to the very long time that the study terrane resided at high temperatures, providing favorable conditions for transport of atoms over large distances. The source of the atoms that were introduced to Samples 1 and 2 is not known, but numerous examples of large bodies of scapolite-bearing skarn and other kinds of rock that were apparently affected by metasomatism are present in the Otter Lake area (Kretz 1977, 2004) and elsewhere in the southern Grenville Province.

For reaction zones of Group I, phase-equilibrium considerations can be applied to explain the formation and sequence of subzones (Thompson 1959). For example, the sequence, B1 to B3 in the sample described by Kerrick (1977) shown above is one of decreasing Ca/(Al + Mg + Fe). This aspect has been dealt with in detail (assuming the presence of a fluid phase) by Frantz & Mao (1979). The crystallization of Group II reaction zones requires certain threshold values for the "availability" of the added atoms, and the "ease of escape" of the removed atoms. Also, the paths of approach of the added atoms could determine the spatial distribution of product crystals. For example, in Sample 2, the presence of biotite adjacent to marble was possibly controlled by the arrival of K atoms from the direction of marble, but the ease of transport of major metals within the reaction zone must also have played a role.

The terms "availability" and "ease of escape" were used in the above paragraph. If the nature of each transported species was known (simple ions, complex ions, or molecules) and the nature of the phase in which these species resided (fluid, vapor, or solid crystal-boundary phase), one could use "chemical potential" or "activity" in place of these terms. But the information is not available. This argument applies equally well to the metals that were transported through the reaction zones of the present study (Fig. 7) during crystallization. Here, although displacement of the atoms almost certainly occurred by diffusion, and although diffusion always occurs down gradients in chemical potential, the nature of the diffusing particles and the nature of the paths are not known. Information of this kind can only be obtained through careful experimental work such as that carried out by Carter (1961), referred to above. Hence the procedure of assigning values to chemical potential, to chemical potential gradients, and to relative diffusion or Onsager coefficients for various "components" (*e.g.*, Sack 1982, Joesten & Fisher 1988, Abart *et al.* 2001) was not attempted in the present study.

CONCLUDING REMARKS

Centimeter-scale mineral zones at boundaries between bodies of metamorphic rock of contrasting chemical composition provide a unique opportunity to study solid-to-solid mineral-producing transformations. It is possible, within a single thin section, to obtain compositions of all reactant and product minerals, and the formulas can then be used to construct a reaction equation.

It is important to try to locate the original boundary between the two bodies of rock, because if located correctly, rock compositions can be used to identify those elements that were added to the reaction zone, those that were removed, and those that remained within the confines of the reaction zone. Location of the boundary is facilitated by use of a conservation equation (eq. 2), which requires that at least some of several elements that are determined were neither lost nor gained, a condition that was evidently satisfied in the two samples here described. Information on gains and losses is absolutely essential to a complete picture of the nature of the mineral reactions.

Thus, in Sample 1, Na was added and K was removed, and other elements, including trace elements, were added or removed. Reaction equations provide additional information regarding gains and losses, especially for F, Cl, H, and C. Compared with reaction zones elsewhere, those described here are extreme in the gains and losses that occurred.

As reaction progressed, and the reaction zones increased in width, atoms of some elements must have migrated through the reaction zones, from amphibolite to marble and from marble to amphibolite. Reaction equations can identify these elements, which in Sample 1 are Si, Al, Fe, Mg toward marble, and Ca toward amphibolite. These displacements, which presumably occurred by diffusion, possibly operated in concert with the availability of introduced atoms, to determine the time when reaction was initiated, the reaction rate, and the time of termination.

The particles that moved to, from, and within the reaction zones were possibly simple or complex ions, rather than units such as MgO and Al_2O_3. To minimize conjecture, the various elements that were dealt with in the present study were, for the most part, treated as atoms.

It is well known that during regional metamorphism, reactant crystals do not need to be in contact to react with each other; an example is the reaction of olivine with plagioclase to produce coronas of orthopyroxene, hornblende, and spinel. But it is nevertheless remarkable that in reaction zones between bodies of rock, reactant crystals continue to react with each other even where separated by 1 cm or more. In Sample 2, it was necessary to conclude that crystals in amphibolite, in the presence of introduced K, reacted with crystals of dolomite in marble, at a distance of several cm. This finding can be viewed in relation to the inherent random movement of all atoms and the availability of very long periods of time, but certainly, it is not yet fully understood.

Information is now available on reaction zones in several metamorphic terranes, especially on the chemical composition of the minerals that are present, and the rearrangement of elements within the zones. Detailed studies are now needed on the microstructure of these zones (*i.e.*, crystal shape, size, orientation, and distribution), which could provide valuable information on reaction mechanisms.

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