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METASOMATISM IN A CHEMICAL GRADIENT AND THE FORMATION OF CALC-SILICATE BANDS*

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ABSTRACT. Mineral assemblages with different bulk chemical compositions in the system K_2O–CaO–MgO–Al_2O_3–SiO_2–H_2O–KCl–($\pm CO_2$) were juxtaposed in experimental capsules and held at 600°C and 2000 bars for 14 to 28 days in the presence of salt solutions. Two initial geometries were used: a single contact between calcite and a synthetic pelite consisting of muscovite, phlogopite, and quartz, and a sequence of the assemblages, wollastonite–diopside–anorthite–sanidine–quartz, diopside–tremolite–anorthite–sanidine–quartz, tremolite–phlogopite–anorthite–sanidine–quartz, and phlogopite–muscovite–anorthite–sanidine–quartz, which are the stable five-mineral-phase assemblages spanning the composition range between wollastonite and the synthetic pelite in the CO_2-free system at 600°C and 2000 bars. Samples with both initial geometries tended to form similar new zonations consisting of sequences of mostly three- and four-mineral-phase assemblages discontinuously crossing part or all of the composition range between calcite or wollastonite and the synthetic pelite.

Formation of the new zonations required differential movement of K, Ca, Mg, and probably Al during the runs. The rate of their formation was increased greatly by higher temperature, increased pore fluid, and higher salt concentration in the pore fluid. Metasomatic transport apparently proceeded almost entirely through the pore fluid.

The compositions of 2N chloride solutions in equilibrium with the stable five-mineral-phase assemblages in the composition range between wollastonite and the synthetic pelite were determined. Approximate equilibrium constants calculated from these data were used to calculate the approximate local buffering effect on the solution phase of each mineral assemblage zone in the experimental samples.

A model is proposed in which aqueous species diffuse through pore fluids down activity gradients controlled by local equilibration between fluid and solid phases. As the process continues, more rapidly moving components shift until their chemical potentials are buffered outside some of the mineral assemblage zones, and the number of phases within those zones decreases.

Two zoned calc-silicate bands from kyanite grade rocks of western Connecticut show compositional variations that strongly suggest differential movement similar to that observed in the experimental study occurred during metamorphism. Calc-silicate band samples from sillimanite grade rocks of southeastern Maine contain sequences of simple mineral assemblages very closely resembling those produced in the experimental runs. Primary fluid inclusions in the metamorphic minerals give evidence of the presence of a fluid phase during metamorphism. It is concluded that a metasomatic process analagous to that observed in the experimental study played a significant part in the formation of the zoned calc-silicate bands.

INTRODUCTION

Metasomatism has been defined by Thompson (1959) as, ". . . any process involving a change in the bulk chemical composition of the mineral assemblage". Chemical species may move differentially in a system by flow mechanisms or by diffusion down their own chemical

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* Part of a dissertation submitted to the faculty of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Geology (Vidale, 1968).

potential gradients. The chemical potential gradients may be established by gradients in temperature, total pressure, various partial pressures, chemical composition, gravitational potential, and possibly other gradients as well. This study deals only with diffusion driven by a gradient in chemical composition.

Thompson (1959) noted that marble-schist contacts commonly contain sequences of simple mineral assemblages, and that the chemical compositions of the assemblage zones make a depositional origin unlikely while the simplicity of their mineral assemblages suggests that some components of the system may have been "mobile" (Korzhinsky, 1936). The principal object of this study was to observe what happened in experimental samples containing a contact between calcite and a synthetic pelite. The starting configuration and composition were known, displacement of chemical elements was observed, and variables that affected metasomatic transport were changed one at a time.

EXPERIMENTAL DATA

The experimental work was carried out in the system K_2O–CaO–MgO–Al_2O_3–SiO_2–H_2O–$KCl(\pm CO_2)$, which includes the major elements found in Shaw's typical pelite (Shaw, 1956) and those in limestone except for Fe and Na. Fe was omitted to avoid problems of oxidation state. Na was omitted to simplify the system; it would normally be present in the plagioclase. It is believed the conclusions drawn from this study are valid despite the simplified composition used.

The pressure chosen was 2000 bars. The temperature chosen was 600°C, which is just below that for the breakdown of muscovite in the presence of quartz at 2000 bars P_{H_2O} (Evans, 1965). Excess quartz was present in all runs.

Starting materials and apparatus.—Quartz, muscovite, phlogopite, calcite, wollastonite, tremolite, diopside, grossular, anorthite, and sanidine were synthetic minerals prepared hydrothermally from gels, quartz and tremolite were natural minerals, and calcite was a standard chemical reagent. The salt solutions used were prepared from chemical reagents and deionized water. The mineral mix used to represent a simplified pelite consisted of 1:1:1: by weight synthetic muscovite, synthetic phlogopite, and quartz.

The experimental runs were made in twelve-inch "cold-seal" bombs (Tuttle, 1949) heated externally by horizontal resistance furnaces. Temperature was controlled to within ±5°C, and pressure to within ±5 percent. The temperature gradient in the bombs over the 20 mm length of the experimental capsules was less than 1°C. The fact that the final zonation of the samples was the same whichever end faced the front end of the bomb was considered evidence that the temperature gradient did not significantly affect the zonation.

Determination of stable mineral assemblages.— At 600°C and 2000 bars, calcite reacts with quartz to form wollastonite ($CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$) until the CO_2/H_2O ratio in the fluid phase is 1:3 (Greenwood, 1967). The assemblage, quartz, calcite, and wollastonite will then act as a buffer, maintaining the CO_2/H_20 ratio at 1:3 during a run if the above reaction is reversible. It was considered reversible in this study because, at a contact between calcite and "pelite", a layer of wollastonite formed in the edge of the calcite zone in the early stages of the runs, and in later stages, when excess CO_2 had been produced by other mineral reactions, the edge of the wollastonite layer next to the "pelite" zone reverted to calcite.

The composition tetrahedron of figure 1 shows the stable mineral assemblages in the composition range between wollastonite (or calcite and wollastonite) and the "pelite" at 600°C and 2000 bars in the presence of excess quartz. These assemblages tended to form from any combination of the minerals of figure 1 whose bulk chemical composition fell within the appropriate range. (The only sluggish reactions in the presence of 0.4N chloride solution were those forming tremolite.) Each five-mineral assemblage was held at 600°C and 2000 bars in the presence of 2N chloride solution for 28 days, the length of the longest experimental runs. No changes in mineralogy could be detected by X-ray or optical examination. It was concluded that these were equilibrium assemblages.

No salts were present as solid phases in the experimental samples; the salt solutions used were always less than half saturated under the experimental conditions.

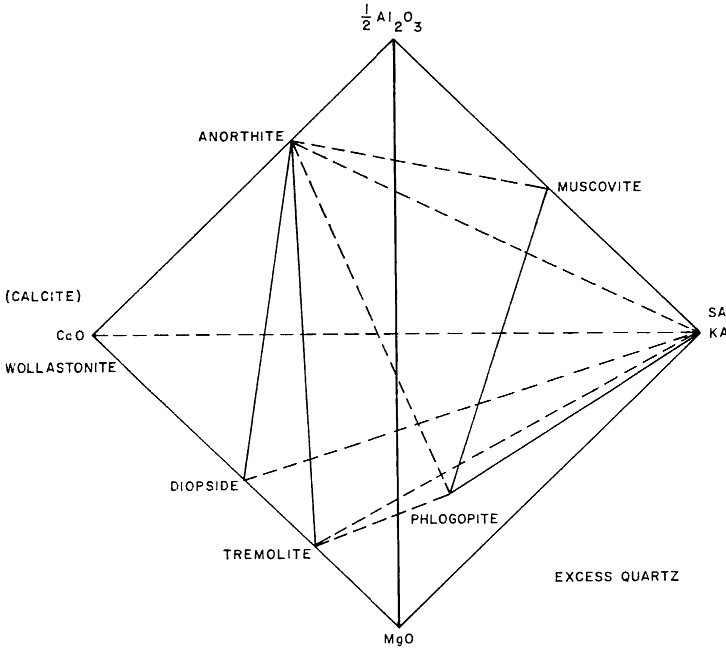

Fig. 1. Equilibrium assemblages at 6000° and 2000 bars, $P_{fluid} = P_{total}$.

Experimental procedure for the zoned samples.—A 20 mm length of platinum or gold tubing (3 mm od, 0.125 mm wall thickness) was boiled 5 minutes in Fisher RBS 25 cleaning solution and 5 minutes in 3N HCl, rinsed, dried, and welded shut at one end. Solution, usually 10 μl, was added by hypodermic syringe before any solids were added.

Initial geometries with a contact between calcite and "pelite" were prepared as follows: approximately 50 mg of $CaCO_3$ were added to the capsule and tamped down as tightly as possible, 20.0 mg of "pelite" (1:1:1 by weight muscovite, phlogopite, and quartz) were added and tamped down, and approximately 100 mg of quartz were added and tamped down. Both the $CaCO_3$ and the mica mix had been ground for 1 hour under acetone in an automatic mortar so that different starting mixes would be as similar in grain size as possible. The quartz powder had been ground briefly in a hand mortar and served both to insure an excess of quartz in the runs and to facilitate the grinding of thin sections to the proper thickness.

Initial geometries consisting of a sequence of stable assemblages of decreasing Ca content were prepared by adding and tamping down approximately 100 mg of quartz, 10 mg of wollastonite–diopside–anorthite–sanidine–quartz mix, 10 mg of diopside–tremolite–anorthite–sanidine–quartz mix, 10 mg of tremolite–phlogopite–anorthite–sanidine–quartz mix, 10 mg of phlogopite–muscovite–anorthite–sanidine–quartz mix, and approximately 25 mg of quartz. The quartz powder had been ground briefly as above, and the mixes had been ground 1 hour under acetone in an automatic mortar.

The final addition of quartz filled the capsule to within 5 mm of the top. The capsule was then wrapped in wet tissue to prevent loss of volatiles, and the top was welded shut.

After a run, the capsule was gently clipped open at both ends, dried at 110°C, and impregnated under vacuum with epoxy resin. When the resin had hardened, the block was cut with a 0.010 inch jeweler's saw mounted in a milling machine so that the capsule was halved lengthwise. One half was remounted in epoxy face down, ground, and prepared as a thin section. The second half was reserved for X-ray samples or for preparation of a second thin section.

The minerals were usually identified optically in thin section. Grains of calcite, wollastonite, and phlogopite were large enough to identify easily. Diopside was usually fine-grained but could be located by its high index of refraction and strong birefringence. Tremolite formed needles with a 20° maximum extinction angle. Careful sodium cobaltinitrate staining for K made the fine-grained potassium feldspar clearly visible. Muscovite occurred in fine-grained aggregates with a distinctive "watery" appearance. Anorthite was extremely fine-grained and difficult to identify. Its presence was confirmed in a few cases by drilling the zone out of the second half of the capsule with a dentist's drill and analyzing by powder X-ray diffraction. Modal analyses were never feasible in these experimental samples because of the small grain size.

TABLE 1

Experimental zonation at a single contact

Starting configuration: Assemblage	Thickness, mm
calcite (50 mg)	
1:1:1 muscovite–phlogopite–quartz (20 mg)	3.0
quartz (excess)	
Zonation sequence A: 10 μl, 0.4N KCl, 600°C, 2000 bars, 14 days	
calcite	
calcite–wollastonite	0.1
calcite–wollastonite–diopside	0.1
diopside–tremolite–quartz–(anorthite)*	0.1
tremolite–quartz–(anorthite)	0.2
tremolite–phlogopite–quartz–(anorthite)	0.4
phlogopite–quartz–(anorthite)	0.9
phlogopite–quartz–sanidine–(anorthite)	0.4
muscovite–phlogopite–quartz–sanidine–(anorthite)	1.1
quartz	
Zonation sequence B: 10 μl, 0.4N KCl, 600°C, 2000 bars, 28 days	
calcite	
calcite–wollastonite	0.2
calcite–wollastonite–diopside	0.1
diopside–tremolite–quartz–(anorthite)	0.1
tremolite–quartz–(anorthite)	0.4
tremolite–phlogopite–quartz–(anorthite)	0.3
phlogopite–quartz–(anorthite)	0.3
phlogopite–quartz–sanidine–(anorthite)	1.9
quartz	
Zonation sequence C: 5 μl, 0.4N KCl, 600°C, 2000 bars, 14 days	
calcite	
calcite–wollastonite	0.1
calcite–wollastonite–diopside	0.1
diopside–tremolite–quartz–(anorthite)	0.1
tremolite–phlogopite–quartz–(anorthite)	0.1
phlogopite–quartz–(anorthite)	0.2
phlogopite–quartz–sanidine–(anorthite)	1.0
muscovite–phlogopite–quartz–sanidine–(anorthite)	1.6
quartz	
Zonation sequence D: 1 μl, 0.4N KCl, 600°C, 2000 bars, 14 days	
calcite	
calcite–wollastonite	0.1
phlogopite–quartz–(anorthite)	0.4
muscovite–phlogopite–quartz–sanidine–(anorthite)	2.6
Zonation sequence E: 10 μl, 0.4N KCl, 550°C, 2000 bars, 28 days	
calcite	
calcite–wollastonite	0.2
diopside–tremolite–quartz–sanidine–(anorthite)	0.1
tremolite–phlogopite–quartz–sanidine–(anorthite)	0.2
phlogopite–quartz–sanidine–(anorthite)	0.2
muscovite–phlogopite–quartz–sanidine–(anorthite)	2.5
quartz	
Zonation sequence F: 10 μl, 0.4N KCl, 650°C, 2000 bars, 14 days	
calcite	
calcite–wollastonite–grossular	0.5
diopside	0.5
anorthite	1.1
sanidine–quartz	1.4
quartz	

TABLE 1 (continued)

Assemblage	Thickness, mm
Zonation sequence G: 10 μl, H_2O, 600°C, 2000 bars, 14 days	
calcite	
calcite–wollastonite	0.1
muscovite–phlogopite–quartz	3.1
quartz	
Zonation sequence H: 10 μl, 2N KCl, 600°C, 2000 bars, 14 days**	
calcite	
calcite–wollastonite	0.1
diopside–tremolite–quartz–(anorthite)	0.1
tremolite–quartz–(anorthite)	0.3
tremolite–phlogopite–quartz–sanidine–(anorthite)	0.3
phlogopite–quartz–sanidine–(anorthite)	0.4
muscovite–phlogopite–quartz–sanidine–(anorthite)	1.5
quartz	

* (Anorthite) indicates that a very fine-grained groundmass is present that does not stain for potassium. It is assumed to be anorthite.

** There has been a significant increase in total sanidine in these assemblages from reaction between the solid phases and the initial 2N KCl solution.

Six-tenths weight percent graphite powder was frequently included in the "pelite" layer or in alternate mineral assemblage layers as a marker. A large number of duplicate runs were made with and without graphite and in platinum and in gold capsules to determine if there were any catalytic or other effect of the graphite or metals on the mineral reactions. None could be observed. There was no noticeable change in the abundance or the distribution of the graphite, and it appears to have functioned as a truly inert marker.

Experimental zonation.—Table 1 gives the starting configuration for capsules containing a contact between calcite and "pelite" and describes the final zonation sequences observed as the experimental conditions were varied. Many duplicate runs were made: the final configurations proved closely reproducible.

Zonation sequence A formed when capsules prepared with 10 μl 0.4N KCl were held at 600°C and 2000 bars for 14 days. These conditions were considered "standard", and the following zonation sequences were produced as the "standard" conditions were varied one at a time.

Zonation sequence B was observed after 28 days and showed both greater overall reaction and a spreading of the three-phase zone, tremolite–quartz–anorthite, relative to the other zones.

Zonation sequences C and D showed the effect of decreasing the amount of pore solution to 5 μl and 1 μl. Less extensive reaction was observed with 5 μl, and almost no reaction with 1 μl. When more than 10 μl of solution were added, massive mineral grains appeared next to the capsule wall, and cavities bordered by large grains appeared within the mineral matrix, suggesting that pore space volume had been exceeded. If 10 μl of solution measured at 25°C and 1 bar filled the pore space at 600°C and 2000 bars, the calculated ratio of pore volume to solid volume in the experimental capsule is 35/65. Thirty five percent pore space is consistent with the amount of impregnating epoxy resin observed.

TABLE 2

Growth of new zones from a starting sequence of assemblages

Assemblage	Thickness, mm
Initial zonation sequence: (position of initial contacts shown by graphite marker placed in alternate layers)	
quartz	
wollastonite–diopside–anorthite–sanidine–quartz	1.0
diopside–tremolite–anorthite–sanidine–quartz	1.1
tremolite–phlogopite–anorthite–sanidine–quartz	1.1
phlogopite–muscovite–anorthite–sanidine–quartz	1.2
quartz	
Final zonation sequence A: 10 μl, 0.4N KCl, 595°C, 2000 bars, 17 days	
quartz	
diopside–sanidine–quartz–(anorthite)*	2.0
diopside–tremolite–sanidine–quartz–(anorthite)	0.2
tremolite–sanidine–quartz–(anorthite)	1.0
tremolite–phlogopite–sanidine–quartz–(anorthite)	0.3
phlogopite–sanidine–quartz–(anorthite)	0.3
phlogopite–muscovite–sanidine–quartz–(anorthite)**	0.7
quartz	
Final zonation sequence B: 10 μl, 0.4N KCl, 595°C, 2000 bars, 30 days	
quartz	
diopside–sanidine–quartz–(anorthite)	2.2
tremolite–sanidine–quartz–(anorthite)	1.2
tremolite–phlogopite–sanidine–quartz–(anorthite)***	1.4
quartz	

* (Anorthite) indicates that a very fine-grained groundmass is present that does not stain for potassium. It is assumed to be anorthite.

** The proportion of sanidine increases toward this end.

*** The proportion of sanidine increases greatly toward this end.

Zonation sequences E and F showed the effects of lower and higher temperatures. Twenty eight-day runs were made at 550°C, and 14-day runs at 650°C. Little reaction occurred at 550°C, even in 28 days. At 650°C there was total reaction in 14 days and almost complete segregation into monomineralic zones including a miniature "anorthosite".

Zonation sequences G and H showed the effect of changing the concentration of salt in the pore solution. A narrow band of wollastonite and nothing else formed in the runs using pure water, whereas in the runs using 0.4N chloride solution (zonation sequence A) a sequence of mineral assemblage zones formed at the contact. The runs using 2N chloride solution showed zones of width similar to those formed using 0.4N solution, but the much greater abundance and size of tremolite grains suggested significantly more transport and reaction.

Table 2 gives the final zonation sequences observed when the starting geometry consisted of a sequence of mineral assemblages of decreasing Ca content, approximating a gradational contact in which the stable mineral assemblages had formed locally.[1] Four-mineral-phase zones developed between the five-mineral phase zones and spread with time, while the proportion of sanidine grains to others progressively decreased in the Ca-rich end of the capsule and increased in the Ca-poor end.

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[1] Starting with a gradational contact was not successful because the mixed unstable assemblages reacted very rapidly under the experimental conditions, forming metastable diopside as well as tremolite wherever tremolite was a stable phase.

TABLE 3

Differential movement in the zoned capsules

A. Single initial contact with 10 μl, 0.4N KCl run at 600°C, 2000 bars for 28 days
Initial configuration:

calcite	muscovite phlogopite quartz	quartz

Final Configuration:

———————— calcite
— calcite–wollastonite
— calcite–wollastonite–diopside
— diopside–tremolite–quartz–(anorthite)[1]
— tremolite–quartz–(anorthite)
— tremolite–phlogopite–quartz–(anorthite)
— phlogopite–quartz–(anorthite)
————— phlogopite–quartz–sanidine–(anorthite)

Displacement:

K	→	No K-bearing minerals remain in the left half of the former "pelite" zone and a high concentration of sanidine appears in the right end.
Ca	→	Ca-bearing minerals appear throughout the former "pelite" zone.
Mg	←	Diopside appears in the former calcite zone and a high concentration of diopside and tremolite in the left end of the former "pelite" zone.
Si	←	Diopside and wollastonite appear in the former calcite zone.
Al	←	Anorthite may be present in the former calcite zone (see text).
H	←	H may have moved to balance the large shift of K and Ca (see text).

B. Initial assemblage sequence with 10 μl, 0.4N KCl run at 595°C, 2000 bars for 30 days
Initial configuration:

quartz	woll diop an san qtz	diop trem an san qtz	trem phlog an san qtz	phlog musc an san qtz	quartz

Final Configuration:

——————— diopside–quartz–sanidine–(anorthite)[1]
————— tremolite–quartz–sanidine–(anorthite)
——————— tremolite–phlogopite–quartz–sanidine–(anorthite)
——————————→ proportion of sanidine to other minerals increasing greatly

Displacement:

K	——	The proportion of sanidine to other minerals has decreased on the left and increased on the right.
Ca	→	&/or Mg ← The new assemblages on the left contain a higher proportion of Mg and the new assemblages on the right a higher proportion of Ca than the initial assemblages did.

[1] (Anorthite) indicates that a very fine-grained groundmass is present that does not stain for potassium. It is assumed to be anorthite.

Differential movement of chemical constituents.—The samples prepared with a single contact between calcite and "pelite" always showed net displacement of K, Ca, Mg, and Si after the runs (table 3A). The final configuration required a shift of K in the original "pelite" zone away from the calcite-"pelite" contact since no K-bearing minerals remained in the end by the calcite and a large quantity of sanidine appeared in the end away from the calcite.[2] Ca moved in the same direction to form Ca-bearing minerals. Si moved from the "pelite" zone into the calcite zone where no Si had been present initially to form wollastonite and diopside. Mg moved into the calcite zone to form diopside, and it probably moved within the "pelite" zone to form the somewhat dense accumulation of diopside and tremolite observed near the initial contact.

Displacement of Al from the "pelite" zone into the calcite zone was always observed in the higher temperature runs and may have occurred in all runs. A zone containing garnet formed in the edge of the initial calcite zone at 650°C (table 5), at 700°C, and at 600°C in one preliminary run. Grossular proved metastable under the conditions of these experiments, reacting with quartz to form wollastonite and anorthite (Vidale, 1968). Anorthite may have been present in this zone in all runs but could not be identified optically because of small grain size and small quantity, or by X-ray because of the problem of sampling a narrow zone adjacent to a zone very rich in anorthite.

The samples prepared with a sequence of assemblages showed similar displacements of K, Ca, and Mg after the runs (table 3B). The proportion of sanidine to the other mineral phases was progressively decreased in the Ca-rich end and increased in the Ca-poor end during the runs (table 2), indicating a shift of K toward the Ca-poor end. The final mineral assemblages required a decrease of Ca/Mg ratio in the Ca-rich end and an increase in the Ca-poor end, indicating movement of Ca toward the Ca-poor end, movement of Mg away from it, or both.

The composition of the fluid phase in the CO_2-free system.—Cation concentrations were determined for 2N chloride solutions coexisting at 600°C and 2000 bars with the assemblages: wollastonite–diopside–anorthite–sanidine–quartz, diopside–tremolite–anorthite–sanidine–quartz, tremolite–phlogopite–anorthite–sanidine–quartz, and phlogopite–muscovite–anorthite–sanidine–quartz. Similar determinations for 0.4N chloride solutions were attempted, but the analytical error proved too great in the case of the more dilute solutions.

Thirty mg of 2N chloride solution were allowed to react with 100 mg of mineral mix for times ranging from 14 to 28 days. Both the starting mix and the final solid phases were always checked optically and by X-ray diffraction pattern. Varying the length of the runs had no effect on the final fluid composition. Five different 2N starting solutions were used: HCl, KCl, $CaCl_2$, $MgCl_2$, and $AlCl_3$. All gave the same final fluid composition for the same mineral assemblage. Equilibrium is assumed to have been achieved during these runs.

The concentrations of K, Ca, and Mg in the solutions were determined by atomic absorption spectrometry. The Al concentration was shown to be less than 0.04 by the same method. $SiCl_4$ in the solution was assumed negligible, and H (as HCl) was determined by difference

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[2] The concentration and volume of KCl solution added initially to both types of capsules was chosen low enough that there would not be significant formation of new mineral phases when the solution phase equilibrated with the solids.

when the sum of the other chloride concentrations showed good precision in a series of runs.

TABLE 4

Solution compositions at 600°C, 2000 bars, and 2 normal chloride concentration

A.

Assemblage:	Wollastonite–diopside–anorthite–sanidine–quartz	Diopside–tremolite–anorthite–sanidine–quartz	Tremolite–phlogopite–anorthite–sanidine–quartz	Phlogopite–muscovite–anorthite–sanidine–quartz
$K/(K+Ca+Mg)$*	0.692 ± 0.006**	0.709 ± 0.009	0.715 ± 0.007	0.701 ± 0.005
$Ca/(K+Ca+Mg)$	0.304 ± 0.006	0.282 ± 0.011	0.257 ± 0.004	0.233 ± 0.001
$Mg/(K+Ca+Mg)$	0.003 ± 0.002	0.012 ± 0.015	0.028 ± 0.005	0.070 ± 0.009
K	1.44	1.41	1.37	1.28
Ca	0.55	0.53	0.49	0.43
Mg	0.01	0.03	0.05	0.13
H (in HCl)	0.00	0.03	0.09	0.16
Al	<0.04	<0.04	<0.04	<0.04

* K, Ca, and Mg represent concentrations of the respective cations in equivalents per 1000 g of H_2O. The diluted solutions were analyzed by atomic absorption. Analyst: Rosemary Vidale.

** Standard deviation

Table 4 gives the values of $K/(K+Ca+Mg)$, $Ca/(K+Ca+Mg)$, and $Mg/(K+Ca+Mg)$ and the concentrations of KCl, $CaCl_2$, $MgCl_2$, and HCl present in 2N chloride solutions in equilibrium with the mineral assemblages at 600°C and 2000 bars. The concentration data for the two Ca-poor assemblages is significantly better than that for the other two (Vidale, 1968).

CONCLUSIONS FROM THE EXPERIMENTAL DATA

Formation of zones in the experimental capsules was greatly accelerated by increased pore fluid, suggesting that diffusion of reacting species through the fluid phase was the rate-limiting step in the process. Since local reactions were much more rapid than diffusion, local equilibrium could be approached between pore fluid and solid in each zone. Concentration gradients in the pore fluid were thus controlled by a sequence of local equilibria. Species diffused down the activity gradients, and minerals formed or broke down as the migrating species were taken out of or put into the fluid by the buffering local assemblages. A similar mechanism was proposed by Orville (1962) for metasomatism in quartz-feldspar systems.

A model for describing the experimental metasomatism.—A useful model for describing the experimentally produced metasomatism in a chemical gradient is illustrated by figure 2. This model represents a detailed analysis of a specific case of the general model proposed by Thompson (1959).

Figure 2A shows one possible course of evolution of zonation sequence in the CO_2-free system. Figure 2B gives the approximate activities

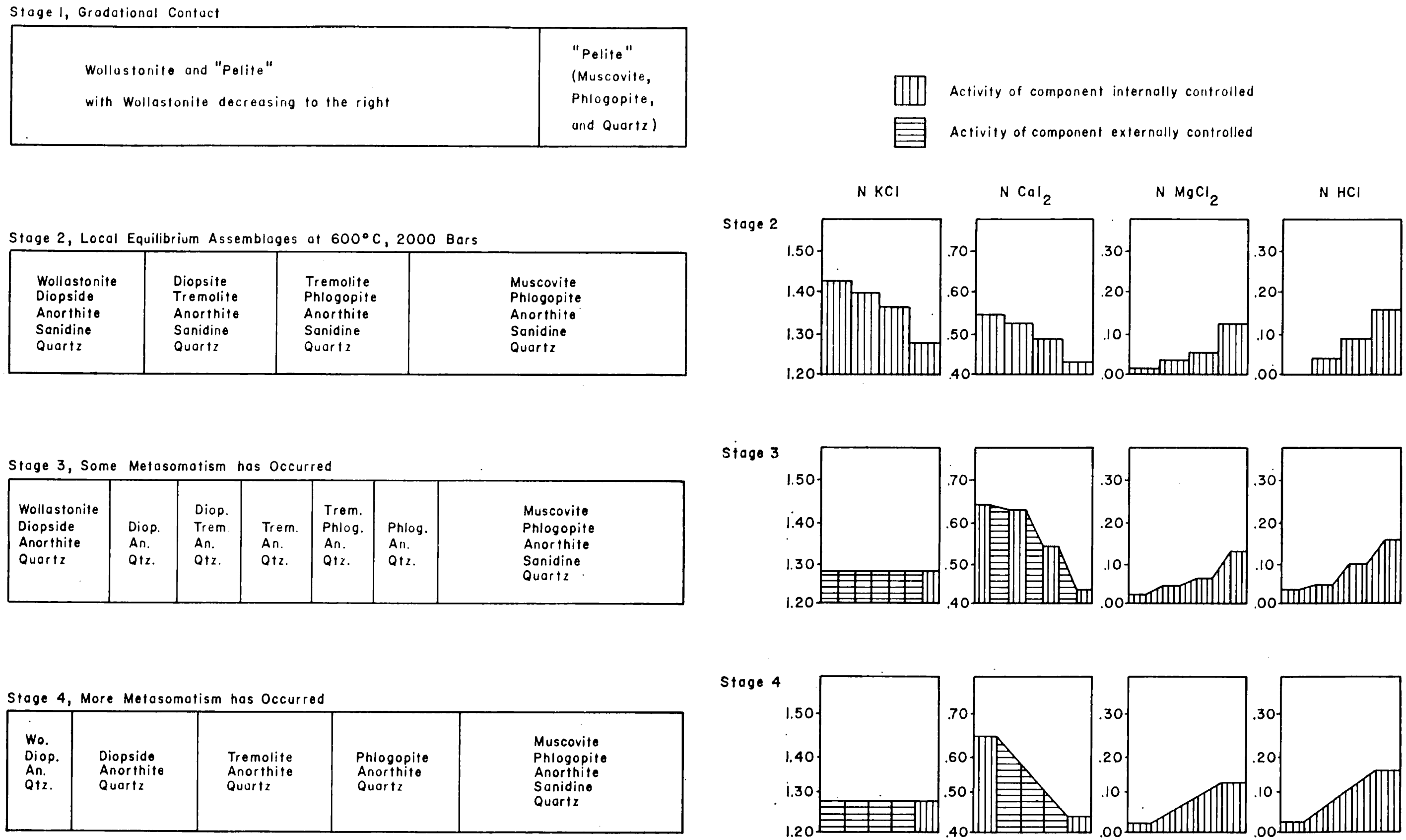

Fig. 2. Model for the evolution of a zonation sequence. A, solid phase assemblage; B, corresponding fluid phase composition at 600°C, $P_{fluid} = P_{total} = 2000$ bars for 2 normal chloride solution.

of KCl, $CaCl_2$, $MgCl_2$, and HCl in each assemblage zone shown in 2A. The activities for the five–mineral–phase assemblages are taken from the experimentally determined solution compositions, and the activities for the other assemblages were determined from equilibrium constant expressions calculated from the experimental data.[3]

In figure 2A, a gradational contact between wollastonite and "pelite" (stage 1) first equilibrates locally to a sequence of five–mineral–phase assemblages (stage 2) which correspond to the five-phase assemblages spanning the composition range between wollastonite and the muscovite-phlogopite join in figure 1. Activities of KCl, $CaCl_2$, $MgCl_2$, and HCl tend to be buffered to the values indicated in figure 3B for each of the four assemblages.

KCl, $CaCl_2$, $MgCl_2$, and HCl diffuse through the pore fluid, first across the assemblage contacts where their activity drops most sharply and ultimately into the assemblage regions where the activities are buffered to the lowest values.[4] As the diffusing species move out of or into mineral assemblage zones, cations are added to or subtracted from the pore fluid by the assemblages as they tend to restore the equilibrium activities (or, in other words, as they buffer the solution activities). Some minerals are used up in the process and others form, and a net transport of cations is achieved.

In stage 3, K has shifted until all sanidine is gone from the first three zones, and the KCl activity for the whole sequence is buffered by the five-phase assemblage, phlogopite–muscovite–anorthite–sanidine–quartz. Ca has moved significantly near the stage 2 assemblage contacts, and three-phase assemblages now appear where the $CaCl_2$ activity gradient is externally determined by the bounding four-phase assemblages.

K is now a "mobile" component (Korzhinsky, 1936) of the three- and four-phase zones where its activity is externally controlled, but it is an "inert" component (Korzhinsky, 1936) of the five-phase zone where its activity is internally controlled. Ca is a "mobile" component of the three-phase zones where its activity is completely determined by boundary conditions, but it is an "inert" component of all the other zones.

Stage 4 shows the effect of further transport of Ca. The three-phase zones have broadened and met, as a continuous $CaCl_2$ activity gradient has been established between the wollastonite–diopside–anorthite–quartz buffering assemblage and the phlogopite–muscovite–anorthite–sanidine–quartz buffering assemblage.

A gradient in HCl activity persists although HCl or H^+ might be expected to move most easily because of small size or because of effective transport by a mechanism of coupling and uncoupling of H^+ in water

[3] Conductivity studies on inorganic salts show solution species at 600°C and 2000 bars to be predominantly molecular rather than ionic (Franck, 1956a, 1956b, 1961; Quist, Frank, and Jolley, 1963; Quist and Marshall, 1966; Quist, Marshall, and Jolley, 1965). In this study, activities were assumed approximately equal to concentrations because of the molecular nature of species and because of the lack of activity coefficient data in this high temperature range.

[4] Diffusion in the pore fluid may be described by Fick's 1st Law which states that the flux of any species is equal to its diffusion coefficient times its activity gradient.

molecules. Each "mobile" component, however, may be an exchange reaction such that electrical neutrality is maintained where ions are diffusing or total chloride concentration remains uniform where chloride molecules are diffusing. For example, the movement that balances that of KCl may be predominantly a shift of HCl, the KCl diffusion being the slow step in the process.

Stages 3 and 4 are similar to the sequences observed after the experimental runs. Further metasomatism in the model could follow a number of paths depending on what other components move and would end when the whole system is in equilibrium, with only a layer of phlogopite–anorthite–quartz next to the muscovite–phlogopite–anorthite–sanidine–quartz "country rock". On the other hand, metasomatic transport of this type may be effectively quenched at an intermediate stage by a drop in temperature, a decrease in pore space, or dilution of the salt in the pore fluid by H_2O (or CO_2)[5] released from solid phase reactions.

PETROGRAPHIC DATA

Rock samples were collected at contacts between Ca-rich layers and pelitic schist or micaceous gneiss in a number of areas in New England and New York. Where possible, samples consisting of single calcareous layers bounded on both sides by schist or gneiss were taken. Over 50 different contacts were examined in thin section. The purpose of this part of the study was to record the metamorphic grade of the samples and to describe their geometry, mineralogy, and, in two cases, their chemical composition.

Geometry and mineralogy of typical calc-silicate bands.—A sequence of distinct zones was found in all samples from kyanite and sillimanite grade rocks. Tables 5 and 6 list two kyanite grade bands and two sillimanite grade bands and give the thickness of the zones and their mineralogy.

Samples #RMV-7-65 and #RMV-9-65 are typical of the kyanite grade calc-silicate bands examined. A symmetric sequence of zones commences with the central calcite-bearing zone and is followed by an epidote-rich zone or zones, an amphibole-rich zone, a biotite schist, and a two-mica schist.

Samples #RMV-50-65 and #RMV-31-65 are typical of the sillimanite grade calc-silicate bands examined. Epidote is absent, and the assemblages, diopside–plagioclase–quartz, amphibole–plagioclase–quartz, and biotite–plagioclase–quartz, are common.

Additional data on samples RMV-765 and RMV-9-65.—Samples #RMV-7-65 and #RMV-9-65 (both of kyanite grade) were chosen for more detailed analysis because they were the least altered broad calc-silicate bands among the samples examined. Unfortunately, no unaltered sillimanite grade bands of sufficient width for meaningful sampling of zones were collected despite considerable effort to find such bands.

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[5] The principal effect of adding CO_2, which is non-polar, to this system at 600°C would probably be to decrease the fugacity of water.

TABLE 5

Zonation of two kyanite grade calc-silicate bands

Sample #RMV-7-65, a kyanite grade calc-silicate band from the Hartland Formation, Thomaston Quadrangle, Conn., collected from the north side of Conn. Route 109, 2.6 miles west of the junction between 109 and U.S. Routes 6 and 202.

Zone	Mineral Assemblage*	Thickness, cm
1	qtz–plag(An16-21)**–biot–musc–kspar	
2	qtz–plag(An21-26)–biot	4.3
3	qtz–plag(altered)–ep–amph–sph	3.1
4	qtz–plag(An28-33)–ep–amph–sph–gar	1.2
5 (center)	qtz–ep–amph–gar–diop–cal	1.3
4′	qtz–plag(An30-35)–ep–amph–sph–gar	0.5
3′	qtz–plag(An23-28)–ep–amph–sph	2.5
2′	qtz–plag(An21-26)–biot	5.5
1′	qtz–plag(An18-20)–biot–musc–kspar	

Sample #RMV-9-65, a kyanite grade calc-silicate band from a schist layer in the amphibolite unit between the Stratis Schist and the Monroe Gneiss, Naugatuck Quadrangle, Conn., collected from the east side of Conn. Route 8, 0.6 mile north of the Seymour access road. A diamond drill core and a hand sample were taken about 10 feet apart. The schist was badly weathered on one side of the band.

Zone	Mineral Assemblage*	Thickness, cm	
		Core	Hand Sample
1	qtz–plag(An25)***–biot–musc–gar–po		
2	qtz–plag(An25-45)–biot–gar	5	
3	qtz–plag(altered)–gar–amph–ep–kspar–sph	1	2
4	qtz–gar–amph–ep–sph–diop	3	1.5
5	qtz–gar–amph–ep–diop	2	2
6 (center)	qtz–plag(An88)–amph–ep–diop–sph–cal	10	7
5′	qtz–gar–amph–ep–diop	2	2
4′	qtz–gar–amph–ep–sph–diop	1	2
3′	qtz–plag(altered)–gar–amph–ep–kspar–sph		1.5

* The following abbreviations have been used:

amph	amphibole	ep	epidote + zoisite	plag	plagioclase
biot	biotite	gar	garnet	po	pyrrhotite
cal	calcite	kspar	potassium feldspar	qtz	quartz
diop	diopside	musc	muscovite	sph	sphene

** An-content of plagioclase was determined by refractive index of mineral separate.

*** An-content of plagioclase was determined by method of Michel-Levy.

Table 7 gives modes and chemical analyses of the zones in #RMV-7-65, and table 8 gives modes and chemical analyses for #RMV-9-65. The modes are only approximate since the zones are not homogeneous on the scale of one or two thin sections. Representative samples for the chemical analyses of the zones were obtained by taking cuts from ground 50-g slabs from each zone. All slabs in each sequence came from a single hand specimen except for zone I of #RMV-9-65; it was sampled several feet along strike from the rest in order to obtain an unweathered 50-g slab.

TABLE 6

Zonation of two sillimanite grade calc-sillicate bands

Sample #RMV-50-65, a sillimanite grade calc-silicate band from Portland East Quadrangle, Maine, collected from the Riprap quarry on the west side of U.S. Route 1 in the town of Falmouth about 1.5 miles north of Maine Turnpike Interchange 9.

Zone	Mineral Assemblage*	Thickness, cm
1	qtz–plag(An38)**–biot–musc–kspar	
2	qtz–plag(An47)–biot	1.4
3	qtz–plag–biot–kspar	0.2
4	qtz–plag(An56)–amph	0.7
5 (center)	qtz–plag(An65)–amph–diop	2.0
4′	qtz–plag(An55)–amph	0.6
3′	qtz–plag–biot–kspar	0.2

Sample #RMV-31-65, a sillimanite grade calc-silicate band from Orrs Island Quadrangle, Maine, collected from a calc-silicate granulite in the Sebascodegan Formation on the east side of Long Point, Sebascodegan Island.

Zone	Mineral Assemblage*	Thickness, cm
1	qtz–plag–biot	
2	qtz–plag–amph	0.5
3	qtz–plag–diop	0.8
4 (center)	qtz–plag–diop–gar–cal	1.0
3′	qtz–plag–diop	0.7
2′	qtz–plag–amph	

* The following abbreviations have been used:

amph	amphibole	diop	diopside	musc	muscovite
biot	biotite	gar	garnet	plag	plagioclase
cal	calcite	kspar	potassium feldspar	qtz	quartz

** The An-content of plagioclase was determined by refractive index of mineral separate.

Plagioclase compositions were traced across the biotite schist zone and 25 mm into the two-mica schist zone of both samples. The plagioclase of #RMV-7-65 was analyzed by electron probe and changed from An$_{30\pm4}$ to An$_{18\pm2}$ across the biotite zone, then remained at An$_{16\pm2}$ for the first 25 mm of the two-mica zone. The maximum zoning within plagioclase grains corresponded to the spread in composition among grains at a given location. Within grains, An-content increased outward but not very symmetrically. Maximum An-content of the plagioclase in #RMV-9-65 was determined by the method of Michel-Levy and decreased from An$_{45}$ to An$_{25}$ across the biotite zone and remained at An$_{25}$ in the two-mica zone (core section). The spread in composition at a given location in the sample could not be determined.

Fluid inclusions.—Inclusions in the metamorphic minerals, consisting of liquid and a gas bubble, are evidence that fluid was present in the rock during metamorphism. These were observed in nearly all the samples examined. Their size and random occurrence suggest primary inclusion, recording the presence of a fluid at the time of growth. There are also numerous small and clearly secondary fluid inclusions that are concentrated along planes crossing grains.

TABLE 7

Modes and chemical analyses of the zones in sample #RMV-7-65

A. Modes (based on 1600 points counts each)

	Schist	(1)	(2)	(3)	(4)	(5)
Quartz	59.4	52.1	45.5	66.8	65.4	64.4
Plagioclase	15.2	29.9	36.7	15.3	9.2	trace
Muscovite	15.7	2.1	1.0			
Biotite	9.4	13.9	16.1			
Pyrrhotite	0.2	0.1	0.4			
Apatite	0.2	0.3	0.4			
Potassium feldspar		1.9				
Zoisite + clinozoisite				8.7	16.2	14.4
Amphibole				7.0	5.3	2.3
Sphene				1.2	1.1	
Garnet				0.4	1.4	2.9
Calcite					0.8	14.5
Diopside						1.0

B. Chemical Analyses*

Zone	SiO_2	Al_2O_3	Fe_2O_3**	CaO	K_2O	TiO_2	MnO	MgO	Na_2O	Total
(1)	79.0	10.5	2.6	1.40	1.53	0.48	0.06	1.40	2.70	99.0
(2)	83.3	8.8	1.8	1.70	0.80	0.19	0.06	1.05	2.16	99.9
(3)	90.0	5.2	0.6	3.25	0.28	0.0	0.06	0.80	0.42	100.6
(4)	84.2	5.9	1.2	5.64	0.16	0.0	0.14	0.85	0.38	98.4
(5)	75.5	7.0	1.5	10.9	0.0	0.07	0.23	0.90	0.10	96.2

* SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O, TiO_2, and MnO were determined by X-ray fluorescence using a fusion-heavy absorber method. U.S. Geol. Survey Rept. #66-WF-30. Analysts: Rosemary Vidale and James Lindsay. MgO and Na_2O were determined by atomic absorption. Analyst: Rosemary Vidale.

** Total Fe

Primary fluid inclusions usually contain specks of solids too small to resolve clearly optically, and it is probable, but not proved, that they are soluble salts present in the fluid during metamorphism and precipitated during cooling when their solubility was exceeded.

EVIDENCE FOR METASOMATISM IN THE NATURAL ROCK SAMPLES

Petrographic evidence for metasomatism.—Several features of the calc-silicate bands examined in this study are considered evidence for metasomatic transport. The first is the symmetry of the mineral assemblage zones in many of the bands. The width of the zones as well as their mineralogy tends to be symmetric about the center. Gradational depositional contacts could produce duplicate mineral assemblages on the two sides, but it is quite unlikely that the zone widths would be similar.

A second feature is the fact that many of the zones contain relatively few mineral phases. For these zones, some of the components may have been "mobile", with their chemical potentials externally controlled (Korzhinsky, 1936; Thompson, 1959).

A third feature is the fact that the chemical compositions of the analyzed zones (tables 7 and 8) do not show continuous variation between the composition of the center of the bands and that of the surrounding rock as would be expected in a simple gradational contact. Each chemical element seems to vary independently of the others as if differential movement had occurred after deposition.

TABLE 8

Modes and chemical analyses of the zones in sample #RMV-9-65

A. Modes (based on 1600 point counts each)

	(1)	(2)	(3)	(4)	(5)	(6)
Quartz	33.5	20.0	34.2	27.1	7.3	5.7
Plagioclase	12.3	47.4	10.0			16.8
Muscovite	24.4	0.4				
Biotite	22.0	23.7	0.7			
Pyrrhotite	2.2	0.1				
Apatite	0.2	0.2				
Potassium feldspar	trace	trace	1.8			
Zoisite + clinozoisite		0.2	1.2	11.4	65.6	23.3
Amphibole			29.1	7.2	6.2	29.4
Sphene			3.4	2.5	0.5	1.2
Garnet	5.4	8.2	19.6	42.6	8.2	
Diopside				9.2	12.2	11.1
Calcite						12.6

B. Chemical Analyses* (given as wt percent of the oxides)

Zone	SiO_2	Al_2O_3	Fe_2O_3**	CaO	K_2O	TiO_2	MnO	MgO	Na_2O	Total
(1)***	63.4	16.2	8.0	1.24	4.52	0.74	0.69	2.05	0.78	97.6
(2)	64.1	15.8	7.0	3.81	1.98	0.86	0.51	2.10	2.22	98.4
(3)	61.2	16.2	6.9	8.06	0.75	0.80	0.73	2.00	0.80	97.5
(4)	55.5	18.6	7.1	13.0	0.30	0.63	1.02	1.65	0.68	98.4
(5)	52.2	20.5	4.1	17.5	0.25	0.19	0.16	2.10	0.58	97.6
(6)	48.8	17.9	6.5	19.1	0.20	0.24	0.22	3.95	0.62	97.5

* SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O TiO_2, and MnO were determined by X-ray fluorescence using a fusion-heavy absorber method. U.S.G.S. Report #66--WF-30. Analysts: Rosemary Vidale and James Lindsay. MgO and Na_2O were determined by atomic absorption. Analyst: Rosemary Vidale.

** Total Fe

*** The sample for zone (1) was collected several feet away from the samples for the other zones.

Similarities between natural and experimental samples.—The zonation observed in typical sillimanite grade calc-sillimanite bands (table 1) is very similar to that produced in the experimental runs (tables 4 and 5). Simple phase assemblages commonly observed in rock and experimental samples are diopside–plagioclase–quartz, amphibole–plagioclase–quartz, and biotite (or phlogopite)–plagioclase–quartz. The fact that these are known to form metasomatically in the experimental samples is considered further evidence that they also formed by a metasomatic process in the rocks.

The presence of primary fluid inclusions in metamorphic minerals of the rock samples gives evidence that pore fluid was present during metamorphism. While the rocks no doubt contained far less fluid than the 35 percent in the experimental samples, the very strong dependence of experimental metasomatism on pore fluid content suggests that any fluid present during metamorphism would have been the principal diffusion medium. It is believed, therefore, that the model used to describe the experimental metasomatism may prove useful for natural metasomatism as well.

CONCLUSIONS

Zonation closely resembling that in calc-silicate bands was produced experimentally by a metasomatic process. Differential movement of chemical elements in the experiments was increased by increased temperature, increased proportion of pore fluid to solid, and increased concentration of salt in the pore fluid.

A model has been suggested in which an initial chemical composition gradient becomes a sequence of metamorphic mineral assemblages, each of which locally buffers the pore fluid composition. Chemical species diffuse through the pore fluid down their own activity gradients. The chemical composition of the zones changes, and, as the chemical potentials of diffusing species become externally controlled, the number of mineral phases decreases.

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