

ALKALI METASOMATISM AND FELDSPARS

By

PHILIP M. ORVILLE

Cornell University, Ithaca, New York [1]

Introduction

For the purpose of this paper we shall define a metasomatic process as any process that results in a change in the bulk chemical composition of a mineral assemblage (rock) below the zone of weathering and sedimentation. Metasomatism can then be regarded as a matter of scale; that is, how much rock we include within the system we are considering. Metasomatism on the scale of a single thin section will not necessarily be metasomatism on the scale of a hand specimen and metasomatism of any rock unit will no longer be metasomatism when a sufficiently large volume of the earth is included in the system.

Some amount of transport of material is involved in all recrystallization phenomena and, independent of the scale, we can consider recrystallization to involve dissolution or replacement of material at a source where the chemical potentials for certain substances are high, transportation of these substances along potential gradients within the rock, and fixation at a sink where their chemical potentials are low. We call it metasomatism where source and sink are far apart and metamorphic recrystallization or metamorphic differentiation where close together.

The reactions by which mineral phases grow, disappear or change in composition in a rock must involve the crystalline phases and chemical species (ions, atoms, molecules, complexes etc.) dispersed in some medium (vapor phase, intergranular film, or the crystal lattice itself). It is generally accepted that metamorphic recrystallization takes place primarily through the intermediary of a volatile-rich intergranular fluid that may be present as a phase when $P_{\text{volatiles}} \geq P_{\text{con-}}$

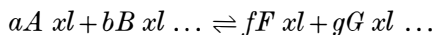
[1] Present address: Yale University, New Haven, Conn.

fining or as a volatile-rich film adsorbed on crystal surfaces when $P_{\text{volatiles}} < P_{\text{confining}}$. Some diffusion of material must take place directly through crystal lattice in order to form, for example, plagioclase exsolution lamellae within perthite. The scale of the perthite texture, however, suggests that the limit of effective transport of Na ions by this mechanism is no more than a few millimeters. Diffusion of material through either a volatile-rich phase or volatile-rich surface film (referred to together as "intergranular fluid" in this paper) will take place along gradients in activities (and in general, in concentrations) of the diffusing substances. It is entirely possible that a major part of the material present in crystalline phases in most regionally metamorphosed rocks has passed through a state of solution in a volatile-rich intergranular fluid. Only a very small weight proportion of the nonvolatile constituents will ever be in solution at one time, but the cumulative transfer of material from smaller grain to larger grain, from less stable to more stable phases, and from more stressed grain to less stressed grain will produce, in the end, a major reworking of the original rock constituents. Throughout this process reactions involving crystal phases and a volatile-rich fluid will have prevailed. It is not an overstatement to say that the equilibria for these reactions are as fundamental to our understanding of metamorphic rocks and processes as equilibria between silicate melt and crystal phases are to our knowledge of igneous rocks and processes.

Metamorphic recrystallization reactions

Equilibrium reactions that involve a crystalline phase or phases and a single fluid phase can be divided into four types depending on the way crystalline substances and substances in solution in the fluid phase enter into the reactions. Specified in the most general way they are:

- 1) *solubility-precipitation reactions*
 $aAx + bB \text{ xl} \dots \rightleftharpoons lL \text{ sol} + mM \text{ sol} \dots$
- 2) *exchange reactions*
 $aA \text{ xl} + bB \text{ xl} \dots + lL \text{ sol} + mM \text{ sol} \dots \rightleftharpoons fF \text{ xl} + gG \text{ xl} \dots$
 $+ vV \text{ sol} + wW \text{ sol} \dots$
- 3) *decomposition-addition reactions*
 $aA \text{ xl} + bB \text{ xl} \dots \rightleftharpoons fF \text{ xl} + gG \text{ xl} \dots + lL \text{ sol} + mM \text{ sol} \dots$

4) *reconstitution reactions*

where $aA \text{ xl}$, $bB \text{ xl}$, ... represent a , b , ... moles, respectively, of substances A , B , ..., each in a specific crystalline phase of specified composition, and $lL \text{ sol}$, $mM \text{ sol}$, ... represent l , m , ... moles, respectively, of substances L , M , ... in solution in the fluid phase. At constant temperature, T , constant pressure, P , and constant compositions of the crystalline phases, $X \text{ xl}$, equilibrium expressions for the reactions are:

- 1) $K_{T,P,X \text{ xl}} = a_L^l \cdot a_M^m \dots$
- 2) $K_{T,P,X \text{ xl}} = (a_V^v \cdot a_W^w \dots) / (a_L^l \cdot a_M^m \dots)$
- 3) $K_{T,P,X \text{ xl}} = a_L^l \cdot a_M^m \dots$
- 4) $K_{T,P,X \text{ xl}} = 1$

where a is the activity of the substance in the fluid. All equilibria above are functions of pressure, temperature and compositions of crystalline phases and all but reconstitution reactions are functions of the activities of substances in solution in the fluid phase. If all crystalline phases involved in a reaction are pure substances (phases that cannot vary in composition) then activities of the crystalline substances are all equal to unity and the equilibrium will depend only on temperature, pressure and (again excepting reconstitution reactions) activities of substances in solution.

Solubility-precipitation reactions must be important during metamorphic recrystallization in which porphyroblastic growth leads to a general coarsening of texture with only local transport of material. Transport of large quantities of material over long distances is hampered by the low solubility of the rock forming minerals (excepting only the evaporite minerals) in an H_2O -rich fluid phase, even at high temperature and pressure. This severely limits the concentration gradients that can be established to permit diffusion of substances through a static fluid medium and requires very large volumes of fluid to transport a significant amount of material in a flowing medium. Even so, the abundance of quartz veins in metamorphic terranes and observations in the laboratory that demonstrate extreme mobility of SiO_2 under hydrothermal conditions (Bowen and Tuttle (1949)) suggest that considerable amounts of silica may be moved in solution during metamorphism.

Exchange reactions may be particularly important in metasomatism since they commonly involve substances having high solubilities (salts and acids of Cl^- , SO_4^{2-} , HCO_3^- etc.) in a volatile-rich phase. The higher solubilities of these substances relative to the bulk solubilities of silicates permit proportionally larger concentration gradients to be established in the solution. This gives a greater capacity per unit time for transfer of material by diffusion in a static fluid medium and a greater capacity per unit volume for transfer of material by a flowing fluid medium. Many reactions that involve only exchange of cations between crystal and fluid phases will proceed at approximately constant volume of crystalline phases in accordance with Lindgren's "law of constancy of volume" (Lindgren (1918)) because the number of oxygen atoms in crystalline products and reactants remains constant. Standard cell calculations (Barth (1948)) for *any* pair of rocks can be incorporated into a cation exchange reaction in which one rock composition is changed to another rock composition by addition and subtraction of the appropriate cations. The mere fact that it is possible to write such a reaction proves nothing about the origin of either rock, however.

Most decomposition-addition reactions of geological interest involve H_2O or CO_2 as the soluble material that is lost or added to the crystal phases. Exceptions include the formation of sodalite group minerals by addition of NaCl , Na_2SO_4 , CaSO_4 or Na_2S to material of nepheline composition and the formation of scapolite by addition of NaCl and CaCO_3 to material of plagioclase composition. Aside from the direct metasomatism resulting from loss or addition of H_2O and CO_2 to a rock, decomposition-addition reactions feed the intergranular fluid with volatiles during progressive metamorphism, thereby providing a medium within which other soluble materials may be transported by diffusion or flow. A decomposition-addition reaction is not the only way in which H_2O can be lost or added (as determined by a chemical analysis) to a mineral assemblage. A cation exchange reaction in which H^+ ions are exchanged for metal cations will achieve the same result.

The first three types of reactions are metasomatic on at least the smallest scale because the bulk compositions of crystalline phases on the two sides of the equation are not equal. The reconstitution type of reaction represents isochemical recrystallization but it does not

necessarily represent the actual chemical reactions that have taken place. The net result of any given reconstitution reaction can be achieved by some combination of reactions of the first three types in which soluble substances appearing as reactants in certain reactions are exactly balanced by the same substances as products in other reactions. Any set of reactions taking place within a chemically closed system in which the fluid phase is a trivial fraction of the mass must approximate a reconstitution reaction.

Source and composition of intergranular fluid

Possible sources of the volatile and soluble materials present in rocks during metamorphism include:

- 1) connate water
- 2) evaporite salts within a sedimentary sequence
- 3) volatiles released by decomposition reactions during progressive metamorphism
- 4) volatiles released from crystallizing magma
- 5) volatiles passing through crust as a result of degassing of the mantle.

Connate water

The connate waters of marine sediments can be expected to be saline but not necessarily identical in composition with normal sea water. The results of Goldberg and Arrhenius (1958) suggest that significant chemical interaction between clastic particles of pelagic sediments and sea water has taken place, producing quite different ratios and total concentration of elements dissolved in the pore water compared to normal sea water. Maxwell ((1960) p. 111) gives analyses of connate waters from wells at depths of 5000 to 9000 feet on the Texas Gulf Coast that show total soluble salt contents of 6 to 13 weight per cent (normal sea water approximately 3 weight per cent). Other analyses, for example those quoted by Chilingar (1958), for Russian oil field waters, show little if any increase in total salt concentration compared to normal sea water.

Evaporite salts

Sedimentary rocks that contain an appreciable fraction of evaporite minerals are widespread areally and chronologically in the geologic

record. Winkler and von Platen (1958) have shown that reaction takes place readily between halite and kaolinite rich clay to give plagioclase and HCl vapor at a temperature of about 390 °C at 2000 bars pressure, and experiments of Hemley, Meyer and Richter (1961) show that clay minerals can be converted to albite at temperatures as low as 200–300 °C in the presence of solutions having a high ${}^m\text{NaCl}/{}^m\text{HCl}$ ratio.

Red bed sequences that consist predominantly of shale and arkose commonly contain interbedded evaporites and disseminated evaporite minerals. Moderate metamorphism, either contact or regional, of such a sequence of rocks would undoubtedly produce reaction between evaporite and silicate minerals, either directly or through the intermediary of a saturated hydrous solution.

Thick, halite-rich evaporite sequences buried at considerable depth commonly escape upward as diapiric domes by virtue of their buoyancy and plasticity within the sedimentary crust. It is clear, therefore, that some evaporites are lost from the metamorphic cycle but it is hardly possible that all are lost in this way, particularly where evaporites and shales or sandstones are thinly interbedded.

Engel and Engel ((1953) p. 1033) report small amounts of halite and anhydrite in drill cores from a marble sequence in the Balmat area, northwest Adirondacks, in the Grenville metamorphic province. Evidence of present existence of evaporite minerals in other moderate to high grade metamorphic terraines is lacking, but so, for the most part, are diamond drill cores taken from below the zone of action of meteoric water. Evidence of the former presence of evaporite minerals in a metamorphic terraine founders on a lack of criteris. Shaw ((1960) p. 282), however, concludes, on the basis of his exhaustive geochemical study of natural scapolites, "It is evident that the principal requirement for scapolite to form is a diminution of $P_{\text{H}_2\text{O}}$ and concomitant increase in one or all of P_{CO_2} , P_{Cl_2} , P_{SO_3} ," and he suggests (Shaw (1960) p. 284) as one possibility, that regional scapolitization has taken place only where the original sedimentary sequence contained significant amounts of evaporite minerals.

Decomposition reactions

H_2O and CO_2 are produced in substantial amounts by decomposition reactions during regional metamorphism and must therefore make

up a major, probably predominant, fraction of the intergranular fluid during the period when these volatiles are being actively evolved.

Magmatic water

Rubey ((1951) p. 1136), has presented a summary of analyses of gases obtained from volcanoes, rocks heated at high temperature in the laboratory, and fumaroles. These analyses show H_2O to be by far the dominant volatile with CO_2 next in importance, followed by variable amounts of CO , H_2 , N_2 , Ar , SO_2 , S_2 (or H_2S), Cl_2 (or HCl), and F_2 (or HF). Equilibria prevailing between the volatile components will be quite different at high pressure within the earth's crust. Krauskopf (1959) has calculated the equilibrium proportions of volatiles in a "magmatic gas" at $600^\circ C$ with P_{H_2O} equal to 1000 atmospheres, the gas having approximately the average composition of the analyses presented by Rubey. Gases with partial pressures greater than 1 atmosphere (in addition to H_2O) were found to include CO_2 (50 atm.), HCl (10 atm.), N_2 (10 atm.), H_2S and SO_2 (total 30 atm. with H_2S dominant in reducing environment, and SO_2 dominant in oxidizing environment), and H_2 (up to 40 atm. in reducing environment but negligible in oxidizing environment). It is important to note that these calculations do not take into account any interaction between crystal phases and volatiles. Cation exchange reactions between HCl and alkalis in silicate phases will produce significant amounts of KCl and $NaCl$ in solution in the fluid phase and greatly reduce the amount of HCl present.

Degassing of mantle

If the mantle of the earth has degassed at a uniform rate during geologic time, the composition of "excess" volatiles in the outer shells of the earth should give us an estimate of the average composition of all volatiles that have passed through the crust from below. By "excess" volatiles we mean those volatile materials now at or near the surface of the earth which are present in amounts greater than could have been supplied by weathering of crystalline rocks. The most recent estimate of this "excess" is that of Rubey ((1951) p. 116), which shows that for every 1000 parts by weight of H_2O there are 55 parts

CO₂, 18 parts Cl, 2.5 parts N, 1.3 parts S, and 0.8 parts of all other volatiles (H, B, Br, Ar, F). Note the general similarity of the "excess" volatiles to the "magmatic gas" above and the occurrence of Cl (or HCl) as an important constituent.

Fluid inclusions

Nearly all minerals from every rock type except unaltered lavas contain some fluid-filled inclusions. Smith (1953) gives a bibliography of the extensive literature dealing with fluid inclusions as applied to geothermometry and Roedder (1958) summarizes the results of more recent investigations directed toward determination of their chemical compositions. All studies of fluid inclusions in minerals of metamorphic rocks, hydrothermal veins and pegmatites are in essential agreement that they consist of a concentrated (commonly 2-5 molar) hydrous solution of various salts, commonly with some CO₂ present as gas. Principal cations in solution are Na⁺, K⁺, Ca⁺⁺, and Li⁺, and principal anions are Cl⁻, SO₄⁼, and CO₃⁼. In some instances the solutions are saturated and crystals of alkali chloride are present as well.

Roedder (1958) analyzed the soluble salts extracted from fluid

Table 1. Summary of Partial Analyses of Ions in Fluid-filled Inclusions in Quartz from Metamorphic and Hydrothermal Environments (from Roedder (1958) Tables 2 and 3).

Eleven samples were analyzed by Roedder but one sample, chert nodules in late Paleozoic limestone, was not used in computing values given in this table.

Ion analyses given in mg/per kg of original quartz sample. Ratios of ions are molar ratios.

	Minimum	Maximum	Average
Na ⁺ mg./kg.	32	125	96
K ⁺ mg./kg.	30	155	101
Li ⁺ mg./kg.	0.1	1.2	.93
Cl ⁻ mg./kg.	27	151	96
SO ₄ ⁼ mg./kg.	6	140	36
.....			
<i>m</i> Na/ <i>m</i> K	1.38	2.40	1.64
<i>m</i> Cl/ <i>m</i> SO ₄	1.9	33	12

inclusions in quartz representing a variety of metamorphic environments. His results, summarized in Table (1), show Na^+ , K^+ , Cl^- and SO_4^{2-} to be the dominant ions in solution with the molar proportion of Na^+ generally greater than K^+ , and Cl^- greater than SO_4^{2-} . Total soluble salts extracted from each quartz sample were 300–400 mg/kg. of starting material. This is equivalent to about 0.2 weight per cent of 4–5 molar alkali chloride solution in the original sample.

Some fluid inclusions are definitely secondary and apparently mark the paths of partially or wholly healed fracture planes through the mineral grain. Others appear to be primary and probably represent the best means we have at present of sampling the “intergranular fluid” present during metamorphic recrystallization.

Applicability of equilibrium data to metasomatic reactions

Complete internal equilibrium in a thermodynamic system requires that all intensive variables (pressure, temperature and chemical potential of each component in the system) must be uniform throughout the system. This requires, in addition to constant pressure and temperature, that any phase that can vary in composition have the same composition throughout the system and that all phases are compatible with one another. Thompson ((1959) p. 430) has pointed out, following the line of reasoning of Korzhinskij (1959), that although a large volume of rock will commonly contain mutually incompatible phases and therefore cannot have been in complete internal equilibrium, any small part of the larger thermodynamic system can generally be considered to be substantially in internal equilibrium providing that the incompatible phases are nowhere in actual contact. The same assumption of local equilibrium can be made for a rock mass that contains gradients in temperature, pressure and composition of a particular phase if variation is continuous from point to point and no actual discontinuities in temperature, pressure or composition exist.

The success of the phase rule approach in treating metamorphic mineral assemblages is consistent with, although it does not prove, the assumption of local internal equilibrium in most metamorphic rocks.

A total metasomatic process cannot be regarded as an equilibrium process because it will, in general, involve a larger volume of rock than that for which complete internal equilibrium can be assumed. If local equilibrium prevails, however, the specific chemical reactions taking place between crystal phases and the H₂O-rich intergranular fluid *will* closely approach equilibrium. In this event, the intergranular fluid within a particular small volume of rock will be compatible with the presence and with the particular compositions of mineral phases within that volume. Changes in pressure, temperature, or composition of any phase (including the intergranular fluid) will result in reaction between fluid and mineral phases to return the system to equilibrium under the changed conditions. The equilibria determined between a water-rich fluid phase containing salt in solution and crystalline phases under different pressures, temperatures, and chemical conditions can be used to predict the chemical reactions that will occur if the physical or chemical environment is changed in a particular way.

Experimental investigations of alkali exchange reactions

In view of the high alkali salt concentration found in fluid inclusions and in many connate waters it seems reasonable to expect that exchange reactions between alkali ions in hydrous solution and alkali-silicate phases might be important in nature. A number of investigators (Gruner (1944); O'Neil (1948); Eskola, Vuoristo and Rankama (1937); Wyart and Sabatier (1956); Winkler and von Platen (1958, 1962)) have shown in the laboratory that reaction takes place readily between hydrous solutions of sodium, potassium and calcium salts and feldspar, mica and clay phases at low to moderate temperatures and pressures and they have discussed the significance of these reactions in such processes as alkali metasomatism, hydrothermal alteration, spilitization and metamorphic recrystallization.

Mica-feldspar systems

The experiments of Hemley (1959) are the first in which the equilibria were determined unambiguously under controlled physical

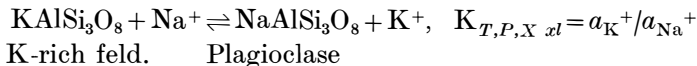
The very strong temperature dependence of these reactions is significant in any discussion of alkali metasomatism within a thermal gradient and this will be returned to later in this paper.

At low temperature, spontaneous hydrolysis reaction will take place between pure water and K-feldspar. This consists of a cation exchange reaction in which H ions are exchanged for K ions of the feldspar. A mica or clay mineral, together with excess silica will be formed and the solution becomes depleted in H⁺ ions and enriched in K⁺.

Hemley, Meyer and Richter (1961) have recently published equilibrium curves for coexistence of albite and paragonite, and paragonite and pyrophyllite as functions of temperature and $^m\text{NaCl}/^m\text{HCl}$.

Alkali feldspars

Experimental investigation of cation exchange equilibria in the feldspars has been reported briefly (Orville (1959, 1960)) and will be presented in detail in a forthcoming publication (Orville, in press). The reaction of most interest to our discussion here is,



in which a K-rich feldspar is in equilibrium with a plagioclase feldspar of specified anorthite-content at a specified temperature and pressure. Equilibrium between two pure alkali feldspars is a special case of this reaction in which the anorthite-content of the plagioclase phase is zero. The features of this work that are most significant in the context of this paper are:

- 1) the readiness with which reaction proceeds at moderate temperature
- 2) the effect of temperature on the vapor-two feldspar equilibrium
- 3) the effect of Ca-content of the plagioclase phase on the vapor-two feldspar equilibrium.

The experiments were carried out in sealed platinum tubes using standard hydrothermal techniques. Starting materials for most runs consisted of synthetic alkali feldspar, crystallized hydrothermally from glass of appropriate composition, and solution 2 molar in total

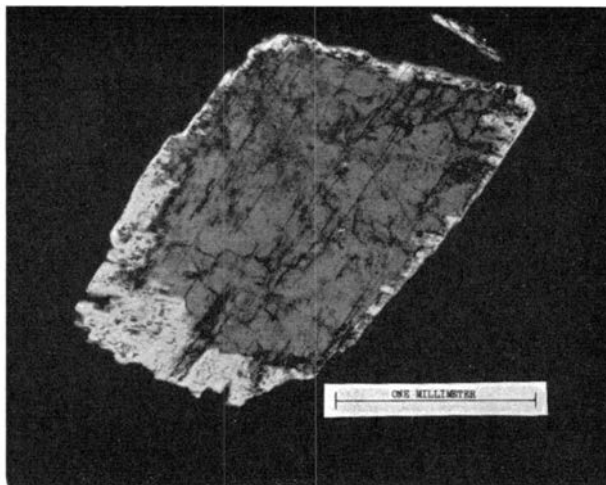


Figure 2. Thinsection photomicrograph of microcline (dark) rimmed by crystallographically continuous Na-rich feldspar (light). Crossed polarizers. Replacement rim produced by reaction with 2 molar NaCl solution at 600 °C, 2000 bars total pressure.

alkali chlorides. The compositions and amounts of the starting materials are known and the compositions of the fluid and crystalline end products are determined by flame photometer and the $\bar{2}01$ X-ray powder technique, respectively (Bowen and Tuttle (1950); Orville (1958)).

The manner in which one feldspar is replaced by another can be seen in Figure (2). The grain shown is a cleavage fragment of microcline approximately 2 mm. in maximum dimension which has reacted with 2 molar NaCl solution and has been partly replaced by Na-feldspar in crystallographic continuity with the original feldspar. This reaction took place at 600 °C and 2000 bars total pressure in 12 hours. In experiments with very fine-grained synthetic feldspar starting material, significant replacement of one feldspar by another in the presence of 2 molar alkali chloride solution takes place at 300 to 400 °C and 2000 bars total pressure in several days. In experiments at 600–670 °C and 2000 bars total pressure, the vapor phase that coexists with two alkali feldspar phases attains an essentially constant alkali ratio after only a few hours.

Figure (3) shows the compositions of coexisting synthetic alkali feldspars and vapor phase at 600 ° and 700 °C at 2000 bars total pres-

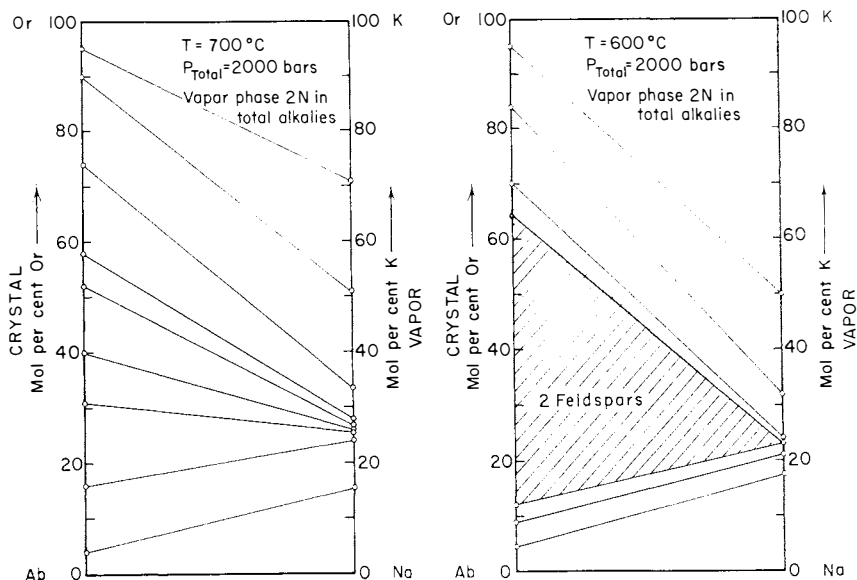


Figure 3. Vapor-crystal tielines for final assemblages at 700° and 600 °C at 2000 bars total pressure. Vapor phase 2 molar in total alkali chlorides. Compositions of phases shown by circles.

sure. At 700 °C there is a continuous series of alkali feldspars, each member of the series in equilibrium with a different composition of vapor phase. At 600 °C the feldspar series is broken by a wide immiscibility gap from $Or_{11}Ab_{89}$ to $Or_{64}Ab_{36}$ and feldspars of these compositions coexist with a vapor phase of the composition $K_{23}Na_{77}$ over a wide range of bulk compositions in the system. All equilibrium assemblages that contain feldspar whose bulk composition falls within the immiscibility gap at a particular temperature constitute an invariant assemblage in which two alkali feldspars of fixed composition coexist with a vapor phase of fixed composition.

Figure (4) shows that the composition of the vapor phase coexisting with two alkali feldspars is strongly temperature dependent. Solutions 0.2 molar in total alkali chloride gave the same result within experimental error as 2 molar solutions, therefore the ratio ${}^mKCl/{}^mNaCl$ for the fluid of the invariant assemblage is nearly independent of total concentration and can be considered an equilibrium constant at fixed pressure and temperature.

Laboratory data are lacking for equilibria at temperatures below 400 °C but the compositions of water reported by White (1955) for samples obtained at depth in hot spring systems show extreme potassium depletion relative to sodium. Thermal waters in the Upper Basin, Yellowstone Park, sampled by Fenner (1936) at a depth of 400 feet at 180 °C have a $mK/m(K+Na)$ ratio of only .03 yet this same water is actively replacing sodic oligoclase in the dacite country rock by K-rich feldspar. Therefore the solution that would coexist in equilibrium with two feldspars must be even poorer in potassium than that which is present.

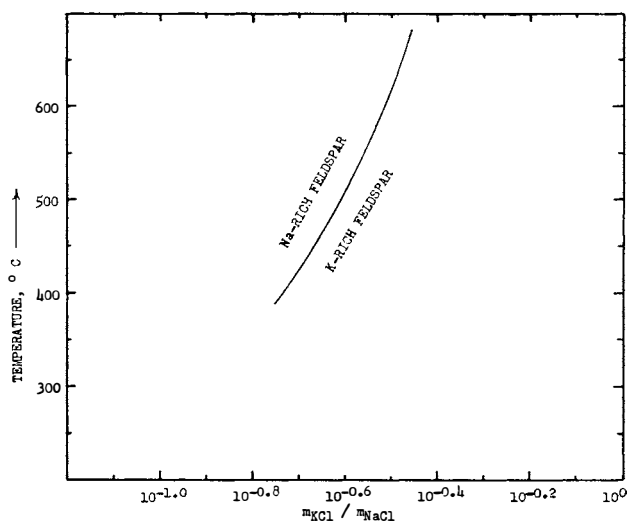
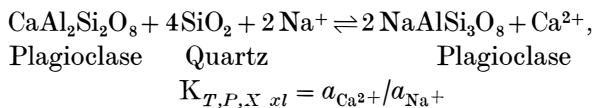


Figure 4. Plot of the experimental equilibrium quotient versus temperature for the two alkali feldspar exchange reaction at 2000 bars total pressure.

Plagioclase and ternary feldspars

It has been shown experimentally (Eskola, Vuoristo and Rankama (1937)) that anorthite reacts readily with sodium carbonate solution and silica to give albite and calcite at about 300 °C and 220 bars. I have carried out experiments at the Geophysical Laboratory and currently at Cornell University to determine equilibria for the reaction,



This reaction is considerably less rapid at any given temperature than the alkali feldspar cation exchange reaction, probably because complete reorganization of the feldspar structure is required due to the radically different Al/Si ratios on the two sides of the equation. Pure albite is in equilibrium with pure NaCl solution, pure anorthite plus quartz with pure CaCl₂ solution, and intermediate plagioclases with solutions having intermediate ${}^m\text{Ca}/{}^m\text{Na}$ ratios. In order for the reaction to go from left to right, excess SiO₂ must be present in the system. In the absence of excess SiO₂, pure anorthite or any intermediate plagioclase can coexist with 2 molar alkali chloride solution (no CaCl₂ present) at 700 °C and 2000 bars total pressure for an indefinite period with no apparent exchange reaction taking place between anorthite in the crystal and NaCl and KCl in the fluid phase. This is also consistent with observations of Wyart and Sabatier (1958).

Only a few preliminary cation exchange experiments have been carried out in the ternary feldspar system. These experiments show, however, that the ${}^m\text{K}/{}^m\text{Na}$ ratio in the vapor coexisting with two feldspars increases as the anorthite-content of the plagioclase phase increases. This is shown in a schematic way in Figure (5) in which lines

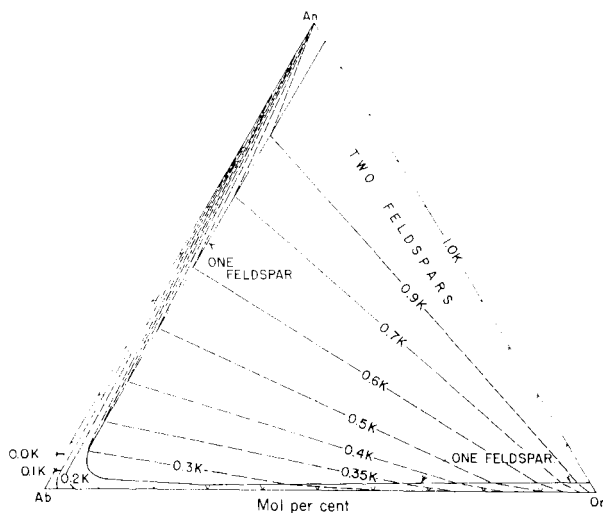


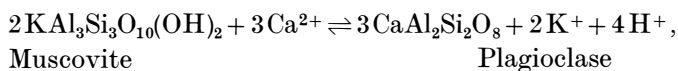
Figure 5. Hypothetical isothermal, isobaric section of the ternary feldspar system. Alkali ratio, K , ($K = {}^m\text{KCl}/({}^m\text{KCl} + {}^m\text{NaCl})$) of vapor phase coexisting with one or two feldspar phases shown by dashed contour lines.

of constant ${}^m\text{K}/{}^m(\text{Na} + \text{K})$ in the vapor phase are superimposed on the ternary feldspar phase diagram at some specified temperature and pressure. Vapor compositions along the Ab-Or sideline are based on experimental data at 700 °C and 2000 bars but the extent of the two feldspar field, the positions of feldspar tielines, and the compositions of vapor in equilibrium with two feldspars within the ternary diagram, although reasonable, are entirely conjectural. All that Figure (5) really tells us about the ternary feldspar system is that, for any pair of vapor-two feldspar assemblages at a given temperature and pressure the vapor in equilibrium with the feldspar pair having the less anorthite-rich plagioclase phase will have the lower ${}^m\text{K}/{}^m(\text{K} + \text{Na})$ ratio.

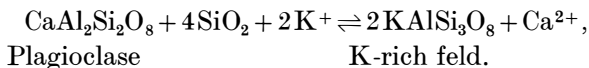
Other cation exchange reactions

There are a number of cation exchange reactions involving alkali silicates that may be important in nature for which no data at all are presently available.

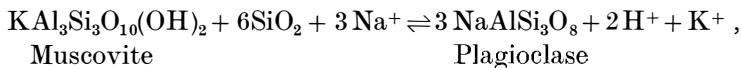
These include:



$$K_{T,P,X} = a_{\text{K}^+}^2 \cdot a_{\text{H}^+}^4 / a_{\text{Ca}^{2+}}^3 ;$$



$$K_{T,P,X} = a_{\text{Ca}^{2+}} / a_{\text{K}^+}^2 ;$$



$$K_{T,P,X} = a_{\text{Na}^+}^3 / a_{\text{H}^+}^2 \cdot a_{\text{K}^+}$$

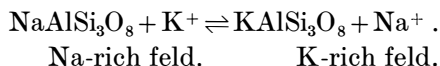
The first of these reactions may be responsible for the very common concentration of sericite alteration in the more anorthite-rich cores and zones of zoned plagioclase crystals. The second reaction (from right to left) was suggested by Becke (1908) as the reaction responsible for myrmekite. His observations that myrmekite intergrowths of quartz and plagioclase replace K-feldspar and that the proportion of quartz intergrown with plagioclase increases with the anorthite-content of the invading plagioclase are consistent with this reaction.

Alkali metasomatism

If the cation exchange equilibria described in the previous section are effective in nature, then the simple coexistence of muscovite, K-feldspar, plagioclase (of specified anorthite-content) and quartz at a specified temperature and pressure will determine the mutual activity ratios of K^+ , Na^+ , H^+ and Ca^{2+} ions in the intergranular fluid. The relatively high rate at which equilibrium is approached in the laboratory suggests that the assumption of local equilibrium in nature is justified for a wide range of geologic environments.

Transport by flowing fluid

Figure (4) shows that the vapor phase in equilibrium with two alkali feldspars becomes progressively poorer in potassium as the temperature is lowered. This temperature dependence provides a potential for alkali metasomatism in the presence of a thermal gradient. Alkali-bearing fluid in equilibrium with two alkali feldspars at high temperature will, upon cooling, be capable of replacing a certain amount of Na-rich feldspar by K-rich feldspar by the reaction,



This is in accord with observations at the Upper Basin in Yellowstone (discussed previously) and other hot spring areas (White (1955)) that Na-rich feldspar is commonly replaced by K-rich feldspar in rocks undergoing hydrothermal alteration near the surface of the earth.

At the Upper Basin the thermal spring water is approximately .03 molar in total alkali chloride. If this water was originally in equilibrium at depth with two alkali feldspar phases at 600 °C, 640 kg of fluid would be capable of replacing 1 kg of Na-rich feldspar by K-rich feldspar by the time its temperature had fallen to 180 °C [1]. Since

[1] Assuming that the data given in Figure (4) for cation exchange equilibria in the alkali feldspar system are applicable, ${}^mK/{}^mNa$ at 600 °C will be 0.30 and ${}^mK/(Na + K) = 0.23$. At 180 °C the water has ${}^mK/(Na + K) = {}^mK/{}^mNa = 0.03$. Therefore $(0.23 - 0.03) \times 0.03 = 0.006$ moles of potassium will have been lost from each kg of solution between 600° and 180 °C. If all this change in potassium-content has been due to replacement of Na-rich feldspar by K-rich feldspar, then $0.006 \times 262 = 1.57$ g. of Na-rich feldspar will have been replaced by each kg. of solution, since one mole of potassium will replace one mole (262 g.) of albite by the reaction $NaAlSi_3O_8 + K^+ \rightleftharpoons KAlSi_3O_8 + Na^+$. Replacement of one kg of Na-rich feldspar will require $1000/1.57 = 640$ kg of solution.

only a small proportion of the H_2O discharged at Upper Basin and other thermal springs is of igneous origin, the greater part consisting of meteoric water (White (1957)), the original concentration of alkali salts will have been higher than 0.03 molar. If the solutions given off at depth approximated the material of fluid inclusions in salt concentration (about 3 molar) only 6.4 kg of the original igneous fluid would be needed to accomplish the replacement of 1 kg of Na-rich feldspar.

The porphyroblastic growth of K-feldspar in country rock adjacent to a granite intrusion and in the outer portions of the intrusion itself can be accounted for in the same way. Volatiles that escape from a hot two-feldspar granite into cooler rock cannot reach equilibrium with both Na-rich feldspar and K-rich feldspar until the K/Na ratio in the fluid phase is lowered. This can be accomplished by replacement (not necessarily pseudomorphously) of Na-rich feldspar by K-rich feldspar and also by sericitization of plagioclase.

The effect of anorthite-content of the plagioclase phase on the two-feldspar alkali exchange equilibrium was ignored in the discussion above, the assumption being made that either anorthite was absent or that anorthite content of plagioclase was the same in all the rocks discussed. Increasing anorthite-content of the plagioclase phase corresponds to increasing K/Na ratio in the vapor phase (Figure 5) and is therefore parallel to the effect of increasing temperature. In an isothermal system in which local equilibrium prevails, alkali-bearing solutions passing from a more calcic plagioclase two feldspar assemblage will be capable of replacing plagioclase in the less calcic plagioclase assemblage by K-feldspar. Solutions moving from the less calcic to the more calcic plagioclase assemblage will be capable of replacing K-feldspar in the more calcic plagioclase assemblage by plagioclase.

Transport by diffusion in static fluid

If it is assumed that local equilibrium is maintained between crystal phases and alkali-bearing fluid within a two feldspar rock mass subjected to a thermal gradient and that the anorthite-content of the plagioclase phase is either zero or uniform, the K/Na ratio in the fluid phase must increase with increasing temperature. If substances dissolved within the intergranular fluid are free to diffuse throughout the volume of rock, it is clear that potassium will migrate toward the cooler portion

of the rock mass and sodium toward the hotter portions. This migration of alkalis will disturb the local equilibria established between crystal and fluid phases and cation exchange reaction between feldspar phases and alkalis in solution will take place throughout the rock mass. Na-rich feldspar will be replaced by K-rich feldspar in the cooler portion and K-rich feldspar replaced by Na-rich feldspar in the hotter portion. If anorthite is assumed to be entirely absent from the feldspar phases, reciprocal movement of sodium and potassium through the fluid phase along the thermal gradient will take place until the two alkali feldspar-fluid assemblage is restricted to a single isotherm. This isotherm will separate the higher temperature Na-rich feldspar rock from the lower temperature K-rich feldspar rock. The initial and final states of this rock are shown diagrammatically in Figure (6).

Figures (6) through (12) represent the initial and final states of rocks in which alkali metasomatism has been assumed to take place by the combined effects of cation exchange reactions and diffusion of substance along concentration gradients in a static intergranular fluid. The bottom section of each diagram should be regarded as a cross section through a volume of rock that is a chemically closed but thermally open system. Thermal gradients, where assumed to be present, are from side to side with the highest temperature on the right side of the diagram. The modal composition of each rock is shown diagram-

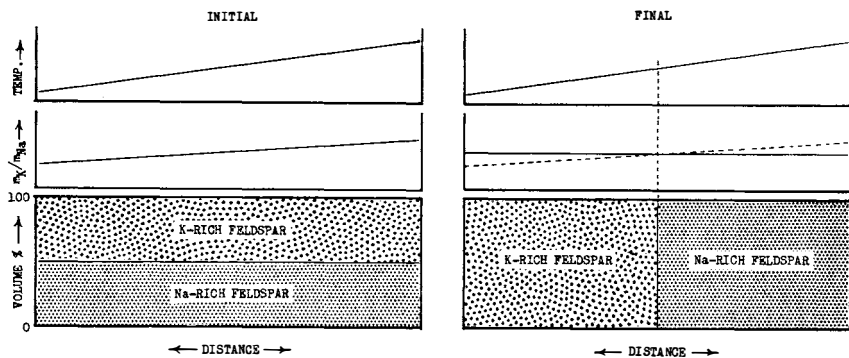
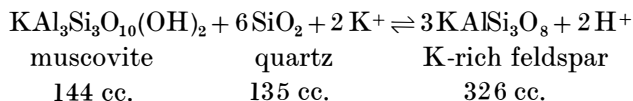


Figure 6. Initial and final states of a rock mass consisting of equal volumes of Na-rich and K-rich alkali feldspars (no anorthite present). Pressure constant, temperature increasing to right. Exchange reaction between the two alkali feldspars is presumed to take place. Isotherm at which K-rich and Na-rich feldspars coexist in final state is indicated by a vertical dashed line.

matically from one side of the rock volume to the other. It has been assumed that local equilibrium prevails between the intergranular fluid and crystalline phases, and that diffusion through the intergranular fluid will eventually allow all concentrations (actually, potentials) of substances in solution to be equalized throughout the volume. Variation, if any, in temperature, cation ratios in the intergranular fluid, and anorthite-content of the plagioclase phase from one side of the rock to the other is shown in the upper part of each diagram.

Figure (6) represents a rock mass consisting of equal volumes of K-rich and Ab-rich alkali feldspars (no anorthite present) in the presence of a thermal gradient. In the initial state the K/Na ratio in the intergranular fluid is variable and the modal composition is constant from side to side. In the final state the K/Na ratio in the fluid is constant but K-rich feldspar is segregated in the low temperature portion and Na-rich feldspar is segregated in the high temperature portion of the volume. The plot of K/Na ratio in the initial diagram can be read as a K/Na versus temperature stability diagram for the alkali feldspars, with K-rich feldspar stable above the curve, Na-rich feldspar stable below, and the curve itself representing the stable coexistence of both phases. The diagram that represents the final state in this system shows that the line representing a uniform K/Na ratio in the fluid lies in the K-rich feldspar field on the low temperature side, lies in the Na-rich feldspar field on the high temperature side, and intersects the two feldspar stability curve at the isotherm along which the two feldspars coexist.

Figure (7) is constructed on the same assumptions as Figure (6) and shows initial and final states for a rock consisting of equal volumes of muscovite, K-rich feldspar and quartz. The data of Hemley (Figure 1) show that the K/H ratio in the vapor phase increases with increasing temperature. Volume relations in the reaction,



are such that a unit volume of muscovite reacts with 0.95 volumes of quartz to give K-rich feldspar. If less than this amount of quartz is present, the reaction will stop unless SiO₂, as well as potassium, is introduced from outside. In the specific case diagrammed in Figure (7)

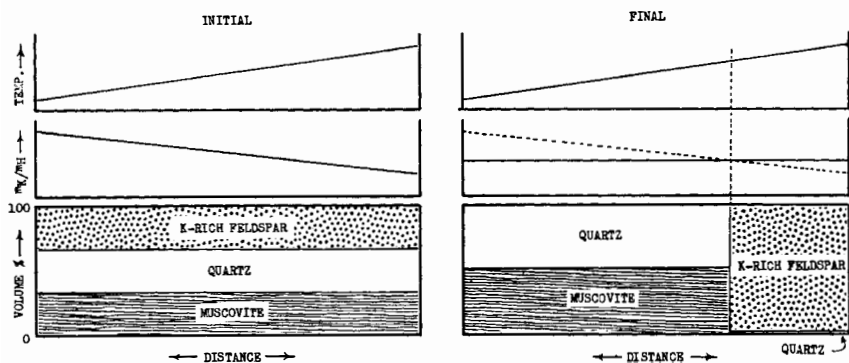


Figure 7. Initial and final states of a rock mass consisting of equal volumes of muscovite, quartz and K-feldspar (no albite or anorthite present). Pressure constant, temperature increasing to right. Exchange reaction between muscovite and K-feldspar is presumed to take place. Isotherm at which K-feldspar and muscovite coexist in final state is indicated by a vertical dashed line.

there is a slight excess of quartz over that required for the reaction and the final K-feldspar rich rock at the hotter end of the system will still contain a small amount of quartz.

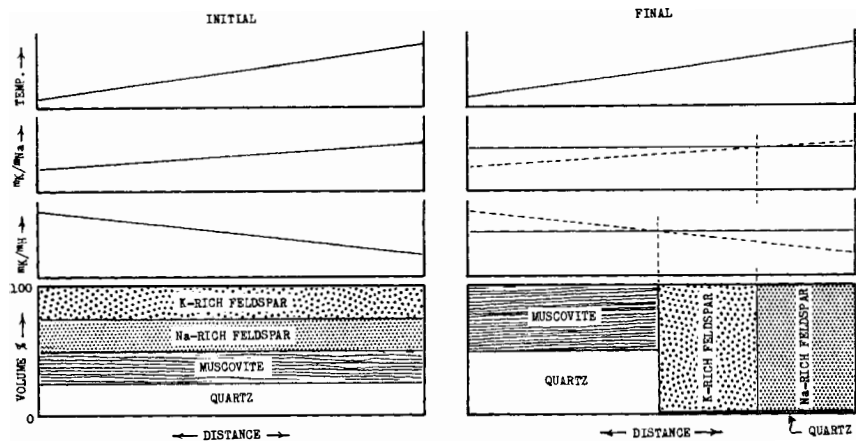


Figure 8. Initial and final states of a rock mass consisting of equal volumes of muscovite, quartz, K-rich feldspar and Na-rich feldspar (no anorthite present). Pressure constant, temperature increasing to right. Sodium-potassium exchange reaction between the two alkali feldspars and potassium-hydrogen exchange reaction between muscovite and K-rich feldspar are presumed to take place. Isotherms at which K-rich and Na-rich feldspars, and K-rich feldspar and muscovite coexist are indicated by vertical dashed lines.

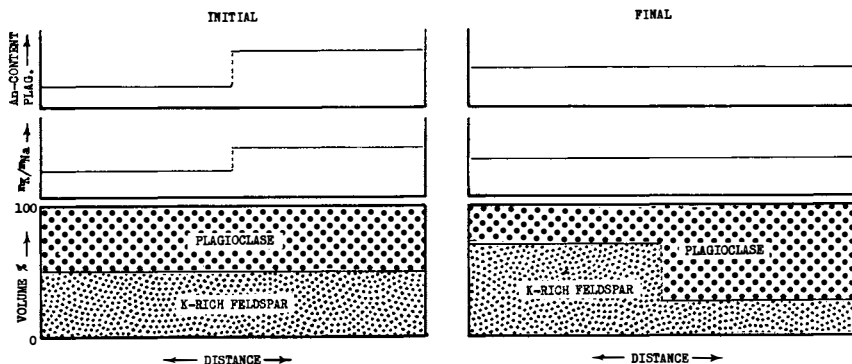
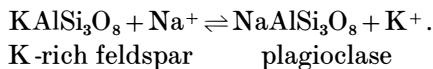


Figure 9. Initial and final states of a rock mass consisting of equal volumes of K-rich feldspar and plagioclase, the plagioclase having a discontinuous change in anorthite-content. Pressure and temperature constant. Sodium-potassium exchange reaction between the alkali feldspar components in K-rich feldspar and plagioclase is presumed to take place.

In Figure (8) both reactions treated in previous diagrams are assumed to take place within a single rock volume that consists of equal volumes of muscovite, quartz, K-rich feldspar and Na-rich feldspar. The configuration of phase assemblages shown in the final stage is the only one consistent with uniform concentrations of K^+ , Na^+ and H^+ in the intergranular fluid.

Figures (9) and (10) show initial isothermal rock volumes consisting of equal volumes of plagioclase with variable anorthite-content and K-rich feldspar. In Figure (9) the change in anorthite-content is discontinuous, in Figure (10) it is continuous. The laboratory data indicate that in the absence of free SiO_2 , only sodium and potassium will be able to exchange between crystal and fluid phases by the reaction,



Replacement of K-rich feldspar by Na-rich feldspar in the originally anorthite-rich plagioclase rock and replacement of plagioclase by K-rich feldspar in the originally anorthite-poor plagioclase rock will eventually equalize the anorthite-contents of the plagioclase phase throughout the rock volume. Phase homogeneity will have been achieved at the expense of modal homogeneity.

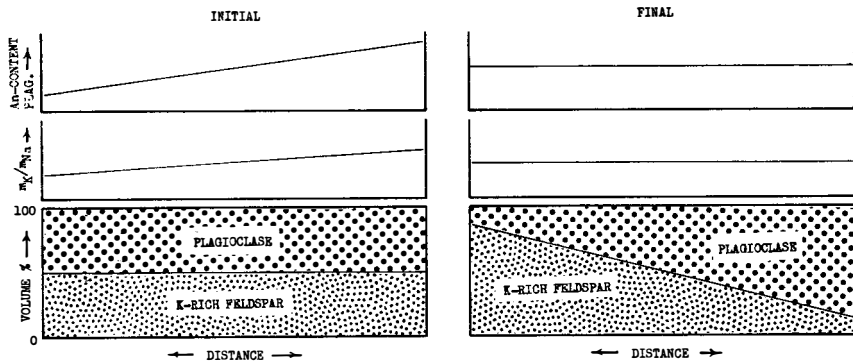


Figure 10. Initial and final states of a rock mass consisting of equal volumes of K-rich feldspar and plagioclase, the plagioclase increasing in anorthite-content to the right. Pressure and temperature constant. Sodium-potassium exchange reaction between the alkali feldspar components in K-rich feldspar and plagioclase is presumed to take place.

Figure (11) shows an isothermal rock volume that consists of equal volumes of quartz and plagioclase, the anorthite-content of the plagioclase being discontinuously variable. In the presence of free quartz, homogenization of the plagioclase phase can take place by the reaction,

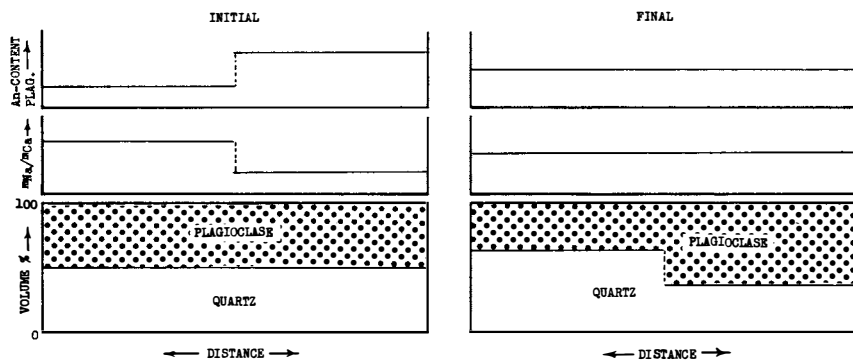
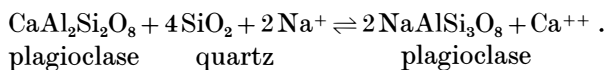


Figure 11. Initial and final states of a rock mass consisting of equal volumes of quartz and plagioclase, the plagioclase having a discontinuous change in anorthite-content. Pressure and temperature constant. Sodium-calcium exchange reaction between the two compositions of plagioclase phase is presumed to take place.

The initial discontinuity on both the anorthite-content of plagioclase and the $^{m}\text{Ca}/^{m}\text{Na}$ ratio should be quickly eliminated because at that point the concentration gradients for both sodium and calcium will be infinitely large. Sodium and calcium concentrations can be uniform throughout the rock body only when the anorthite-content of the plagioclase phase is uniform throughout.

Figure (12) represents an isothermal rock mass consisting of equal volumes of quartz, K-rich feldspar and a plagioclase phase that is discontinuously variable in anorthite-content. Plagioclase homogeneity could be achieved by either or both of the reactions assumed to take place in Figures (10) and (11) above. Both reactions will result in an increased proportion of plagioclase phase in the originally anorthite-rich plagioclase volume, but one reaction achieves this at the expense of K-rich feldspar, the other at the expense of quartz. There is no way at present to predict the relative efficiency of these reactions, therefore the final quartz and K-rich feldspar modal proportions across the rock volume cannot be specified.

There is no point in proceeding further with diagrams of this type. We cannot begin to treat metasomatism systematically in a rock

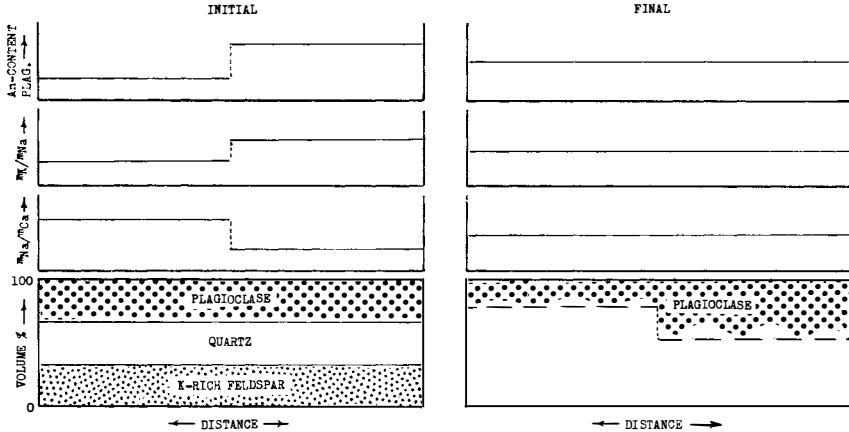


Figure 12. Initial and final states of a rock mass consisting of equal volumes of quartz, K-rich feldspar and plagioclase, the plagioclase having a discontinuous change in anorthite-content. Pressure and temperature constant. Sodium-calcium exchange reaction between the two compositions of plagioclase, and sodium-potassium exchange reaction between the alkali feldspar components in K-rich feldspar and plagioclase are presumed to take place.

consisting of quartz, K-rich feldspar, muscovite and plagioclase of variable anorthite-content. We have some important clues from equilibrium studies in the simpler systems but there are great gaps in our knowledge.

No attempt will be made to discuss the systems diagrammed in Figures (6) through (12) on the basis of the Phase Rule or the thermodynamics of systems which contain mobile components. Thompson (1959, p. 434), on the basis of a graphical treatment of metasomatism somewhat similar to that presented here, concluded, "First, that a diffusional process can actually produce discontinuities in bulk composition where none existed before; second, that there appears to be a tendency for metasomatic reactions to reduce the number of phases in an assemblage." This statement is equally true of the metasomatic systems considered here.

Rate of transport in metasomatism

The experimental data show clearly that a potential is developed for alkali transfer within a thermal gradient in a rock that contains an alkali-bearing intergranular fluid and two alkali feldspars or muscovite, quartz and K-rich feldspar. It can also be demonstrated that a potential exists for transfer of Na, K and Ca in an isothermal system if plagioclase of varying anorthite-content coexists with quartz, K-rich feldspar and a salt-bearing intergranular fluid. Many other exchange reactions doubtless take place during metamorphism. In general, we can predict that each of these various equilibria will vary with temperature, pressure and composition of the crystalline phases involved in the reaction and that a potential for metasomatism will exist if any of these parameters vary from point to point in a rock mass. Whether significant amounts of a particular substance will be transferred within and between rock masses in response to these potentials will depend upon:

- 1) The extent to which the equilibria in which the soluble substance is involved are changed by the temperature, pressure or composition differences that exist in the rock.
- 2) The rate at which exchange reactions take place between the substance in solution and the crystalline phases.

3) The absolute concentration of the substance in the intergranular fluid.

4) The rate at which the substance will diffuse through the intergranular fluid for a given concentration gradient (the diffusivity).

Diffusion rates

There are almost no experimental data on diffusion rates of substances in H₂O-rich fluid under geologically interesting conditions and the theoretical treatment of the problem has been little more than guesswork (see Walton (1960) for a summary of the problem). We are primarily interested in the relative diffusion rates of different substances in the same fluid medium and we can do little more than make the assumption that the diffusion rates (diffusivity) of all substances in the intergranular fluid will be of about the same order of magnitude. There is some basis for this assumption since the radii of molecules and hydrated ions that are likely to be present in the intergranular fluid are similar (in the range of 1 to 3 or 4 Å). Complex interactions among species of particles and between particles and the medium are likely to take place and their effects cannot be predicted. This may not be too serious a limitation on our treatment of metasomatism in the light of Walton's conclusion (Walton (1960) p. 395) that, "the basic diffusion rates are so rapid that the real rate controls in the geologic realm are likely to be factors that limit effective activity gradients.... Complex coupled reactions may be involved which control the relationship of the rate at which the diffusing particle enters the vapor phase to the rate at which it is removed elsewhere in the system. The reaction at either interface may produce a product layer and diffusivity in the product layer will influence the rate of further reactions."

Experimental metasomatism

It is not likely that any of the four factors listed above will prevent alkali metasomatism from taking place in the appropriate geological environments, because it has been possible to induce significant reciprocal alkali transfer in the laboratory (Orville, in press) in a matter of days over a distance of several centimeters with a 30 °C temperature differential.

Sealed platinum tubes 4 cm. long that contained a mixture of

Na-rich and K-rich feldspars and a 2 molar alkali chloride solution were held at 2000 bars total pressure with a temperature of 630 °C at one end and 600 °C at the other end of the tube. This experiment is shown schematically in Figure (13). After 6 days the low temperature end of the tube had become significantly enriched in K-feldspar and the 630° end in Na-feldspar. In a typical experiment, the original bulk feldspar composition at both ends of the tube was $Or_{45}Ab_{55}$; after 6 days the 600° feldspar mixture had a bulk composition of $Or_{48}Ab_{52}$ and the 630° mixture, $Or_{42}Ab_{58}$. Shorter runs showed less difference in composition between the two ends and longer runs showed more (although the rate of change decreases with time). Experiments in which pure H_2O was used instead of 2 molar alkali chloride solution showed no difference in composition between the two ends of the tube after 6 days. The presence of alkali salts in the fluid phase appears to be a necessary condition for significant transfer of alkalis under the condition of these experiments, and, very likely, in nature as well.

Concentration gradients

Fick's equation for mass transport along a concentration gradient in a fluid is,

$$n_M = -D_M A \frac{(\Delta m_M)t}{l},$$

where n is the number of moles of a substance, M , diffused through a cross-section area, A , in time, t , D_M is the diffusivity of the substance in the fluid, and Δm_M is the change in molal concentration of M over a distance l . If we make the assumption that differences in diffusivity of the various substances in the intergranular fluid are slight, the amount of M transferred through a given cross section area in a given time will depend directly on the concentration gradient, $\Delta m_M/l$.

If substances L and M are involved in an exchange reaction of the two alkali feldspar or muscovite-K-feldspar type,

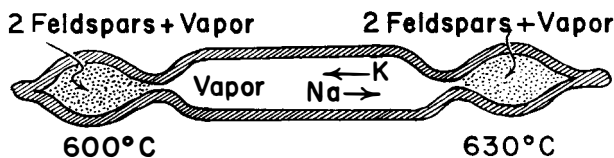


Figure 13. Cross-section of charge in alkali transfer experiment.

$aA_{xl} + bB_{xl} \dots + L \rightleftharpoons gG_{xl} + hH_{xl} \dots + M$, then $K_{T,P,X_{xl}} = a_M/a_L$,

and if at constant pressure and composition of the crystal phases,

$K_T = m_M/m_L$ and $m_M + m_L = c$, where c is a constant, then,

$$K_T = m_M/(c - m_M)$$

and, solving for m_M ,

$$m_M = c K_T/(1 + K_T).$$

In the presence of a temperature difference, $\Delta T = (T_2 - T_1)$, over a distance l , $\Delta m_M = c[K_{T_2}/(1 + K_{T_2}) - K_{T_1}/(1 + K_{T_1})]$. If we arbitrarily pick ΔT and an average temperature, T_{average} , such that K_{T_1}/K_{T_2} is equal to 0.9 and 0.975 corresponding to $\Delta T \simeq 25^\circ$ and 8° , respectively at about 500°C for the alkali feldspar equilibrium plotted in Figure (4) or $\Delta T \simeq 8^\circ$ and 2°C respectively at about 500°C for the muscovite-K-feldspar equilibrium plotted in Figure (1), then the function,

$$\frac{\Delta m_M}{c} = \varrho = [K_{T_2}/(1 + K_{T_2}) - K_{T_1}/(1 + K_{T_1})],$$

can be evaluated for a range of values of $K_{T_{\text{average}}}$. The results are plotted in Figure (14).

Since $\Delta m_M = c\varrho$, the diffusion gradient will be at a maximum for

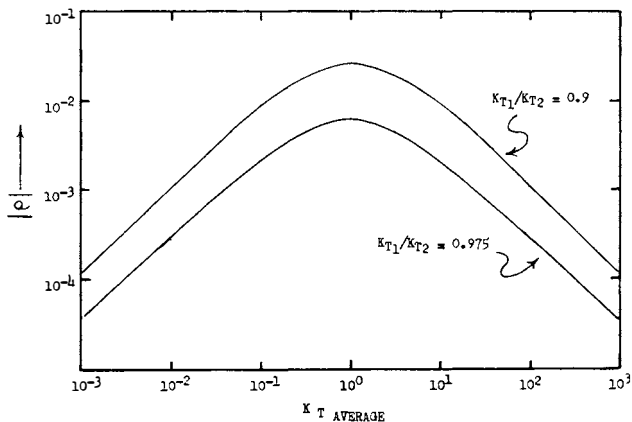


Figure 14. The absolute value of the function

$$\varrho, (\varrho = K_{T_2}/(1 + K_{T_2}) - (K_{T_1}/(1 + K_{T_1}))) \text{ for } K_{T_1}/K_{T_2} = 0.9 \text{ and } 0.975,$$

plotted against $K_{T_{\text{average}}}$.

a given value of c when $K_{T_{\text{average}}} = \text{unity}$, or, in other words, when both soluble substances involved in the reaction are present in about equal amounts.

Substances that are present in high concentration and that are involved in cation exchange reactions having reaction constants not too far from unity will clearly be at an advantage in achieving significant concentration gradients in the intergranular fluid during metamorphism. Insofar as metasomatism takes place by diffusion through a static intergranular fluid, these substances will be the most likely to move in significant quantities, and the reactions which use these substances will be most important in metasomatism.

If we accept the premise that fluid inclusions represent a "quenched" equilibrium state of the intergranular fluid present during metamorphism, then the elements found within them in high concentrations should be of more than passing interest to us. We know that H_2O and CO_2 enter and leave rocks during metamorphism and it shouldn't surprise us that they make up the volatile fraction of fluid inclusions. The only cations commonly present in fluid inclusions in metamorphic minerals in significant concentration are sodium, potassium and calcium. These three may be present in subequal amounts or, more commonly, Ca may be nearly absent. Sodium is almost invariably present in higher molar concentration than potassium and this is consistent with experimentally determined equilibria in the feldspar systems.

Field studies confirm that feldspars are of great importance in metasomatism and, in view of the abundance of feldspars in almost all types of rock, it is reasonable to assume that the feldspar phases exert a dominating influence on the composition of the intergranular fluid. The feldspar phases will therefore be directly affected by changes in composition of the intergranular fluid as a result of diffusion of material from portions of the rock where somewhat different conditions of equilibrium prevail.

Intergranular fluid in metasomatism

The intergranular fluid contains salts of strong acids in solution. On the assumption that local equilibrium is achieved between the intergranular fluid and crystal phases, the composition of the intergranular fluid will be determined by the mineral assemblage at a

particular point in the rock mass. The cations which predominate in the intergranular fluid will be those that participate in cation exchange with abundant mineral phases that have reaction constants, $K_{T,P,X}$, not too far from unity. A great deal more experimental data for exchange reactions involving mineral phases is needed but it seems reasonable to assume that the predominance of sodium, potassium and, to a lesser extent, calcium, in fluid inclusions is a reflection of the importance of exchange equilibria involving feldspar, and perhaps mica, phases.

The intergranular fluid makes up a trivial fraction of the mass of metamorphic rocks and its function in metasomatism is not as a reservoir of metasomatising materials, but as a channel through which some substances move freely and other materials only slightly or not at all. The rocks themselves must provide the reservoir for materials transferred in large amounts during metasomatism.

We can broadly distinguish the following roles of the intergranular fluid during metasomatism:

1. *Solvent medium for minerals.*

Solution-precipitation reactions produce very small concentration gradients so only local diffusion is possible through a static fluid medium. Large amounts of material can be moved only if a large volume of flowing fluid is available.

2. *Catalytic transfer of cations.*

Cation exchange reactions between substances normally present in high concentration in the intergranular fluid, principally chlorides, sulfates and carbonates of sodium, potassium and calcium, can produce large concentration gradients and substantial amounts of these cations can diffuse through a static fluid medium. Hydrolysis exchange reaction between water and silicate phases will be important for low temperature and dilute solutions.

3. *Constituent of minerals.*

Decomposition-addition reactions result in H_2O and CO_2 "metasomatism" during regional metamorphism and may also be responsible for scapolitization by addition of $NaCl$ or $CaCO_3$ to material of plagi-

class composition. At low temperatures and in dilute salt solutions H_2O provides a source of H^+ ions by hydrolysis exchange reactions with silicate phases.

4. *Flowing medium.*

Provides rapid transport of material in solution in one direction only. Transfer of material from rock to fluid and back to rock may take place from dilute solutions by solution-precipitation reactions or from more concentrated salt solutions by exchange reactions.

Acknowledgements

Research upon which this discussion is based was supported, in part, by the National Science Foundation (Grant # NSF G-14303). I greatly appreciate the many helpful suggestions offered by Dr. Daniel Barker (presently at Yale University) at various stages in the preparation of the manuscript.

Discussion

Olav H. J. Christie (Oslo)

It seems as if fundamentally different processes may lead to very similar results. Dr. Orville has shown us that an albite mantled K-feldspar may be produced by action of a NaCl solution upon K-feldspar. Mantled feldspars may possibly also be formed in a way similar to that found by Sahama for nepheline-kalsilite mixed crystals (see page 168). The consolidation of the individual perthite lamellae and their migration towards the surface seems to be less pronounced for feldspars than for the nephelines. Nevertheless it should be borne in mind that albite mantled K-feldspars may form by this mechanism, and therefore would seem to correspond to the lowest energy state within a limited low temperature range.

15th August, 1962.

Discussion

Schuling (Utrecht)

I should like to make a qualifying comment on your statement that plagioclase-feldspars tend to become of similar composition in a

metamorphic complex. When studying banded amphibolites of Rognstrand, Southern Norway, we found that, whereas the normal composition of the plagioclase was An_{40} , there was one narrow band, $\frac{1}{2}$ –1 cm. across, containing pure albite. In a massive of augen gneisses in Southern France (Dome de l'Agout) with oligoclase small metasedimentary intercalations occurring as bands as thin as 5 cm., which we called "cipolins résiduels" contained a plagioclase of up to 96% anorthite. Clearly, in both cases, no homogenization of the plagioclase across the banding had taken place; these examples only demonstrate the extreme difference in transport of material across and along the banding.

REFERENCES

- ALTHAUS, E., and WINKLER, HELMUT G. F. (1962): Experimentelle gesteinsmetamorphose—VI. *Geochim. Cosmochim. Acta*, vol. 26 (1962) pp. 145.
- BARTH, T. F. W. (1948): Oxygen in rocks: a basis for petrographic calculations. *Jour. Geol.*, vol. 56 (1948) pp. 50.
- BECKE, F. (1908): Über Myrmekit. *Mineral. Petr. Mitt.*, vol. 27 (1908) pp. 377.
- BOWEN, N. L. and TUTTLE, O. F. (1949): The system $M_2O-SiO_2-H_2O$. *Geol. Soc. Amer. Bull.*, vol. 60 (1949) pp. 439.
- and TUTTLE, O. F. (1950): The system $NaAlSi_3O_8-KAlSi_3O_8-H_2O$. *Jour. Geology*, vol. 58 (1950) pp. 489.
- CHILINGAR, G. V. (1958): Chemical composition of oil-field waters from Apsheron Peninsula, Azerbaidzhan S S R: A summary. *Geochim. Cosmochim. Acta*, vol. 14 (1958) pp. 168.
- ENGEL, A. E. J. and ENGEL, CELESTE G. (1953): Grenville Series in the northwest Adirondack Mountains, New York, Part I. *Geol. Soc. Amer. Bull.*, vol. 64 (1953) pp. 1013.
- ESKOLA, P., VUORISTO, U. and RANKAMA, K. (1937): An experimental illustration of the spilite reaction. *Comm. géol. Finlande Bull.* 119 (1937) pp. 61.
- FENNER, C. N. (1936): Bore-hole investigations in the Yellowstone Park. *Jour. Geology*, vol. 44 (1936) pp. 225.
- GOLDBERG, E. D. and ARRHENIUS, G. O. S. (1958): Chemistry of Pacific Pelagic Sediments. *Geochim. Cosmochim. Acta.*, vol. 13 (1958) pp. 153.
- GRUNER, J. W., (1944): Hydrothermal alteration of feldspar in acid solution between 300° and 400° C. *Econ. Geology*, vol. 39 (1944) pp. 578.
- HEMLEY, JULIAN J. (1959): Some mineralogical equilibria in the system $K_2O-Al_2O_3-SiO_2-H_2O$. *Amer. Jour. Sci.*, vol. 257 (1959) pp. 241.
- HEMLEY, JULIAN J., MEYER, CHARLES, and RICHTER, D. H. (1961): Some alteration reactions in the system $Na_2O-Al_2O_3-SiO_2-H_2O$. *United States Geol. Survey Prof. Paper* 424-D, pp. 338.
- KORZHINSKIJ, D. S. (1959): The Physicochemical Basis of the Analysis of the Paragenesis of Minerals. Consultants Bureau, Inc. (1959) 142 p.

- KRAUSKOPF, KONRAD B. (1959): The use of equilibrium calculations in finding the composition of a magmatic gas phase. *in* *Researches in Geochemistry*, P. H. Abelson, editor. John Wiley & Sons, pp. 260.
- LINDGREN, W. (1918): Volume changes during metamorphism. *Jour. Geology*, vol. 26 (1918) pp. 542.
- MAXWELL, J. C. (1960): Experiments on compaction and cementation of sand: *in* *Rock deformation*, David Griggs and John Handin, Editors, *Geol. Soc. Amer. Memoir* 79, pp. 105.
- O'NEIL, T. F., (1948): The hydrothermal alteration of feldspar at 250–400° C. *Econ. Geology*, vol. 43 (1948) pp. 167.
- ORVILLE, P. M. (1958): Feldspar investigations. Annual Report, Director Carnegie Inst. Wash., pp. 206.
- (1959): Feldspars. Annual Report, Director Carnegie Inst. Wash., pp. 118.
- (1960): Alkali feldspar-alkali chloride hydrothermal ion exchange. Annual Report, Director Carnegie Inst. Wash., pp. 104.
- (in press): Alkali ion exchange between vapor and feldspar phases. *Amer. Jour. Sci.*
- ROEDDER, EDWIN (1958): Technique for the extraction and partial chemical analysis of fluid filled inclusions from minerals. *Econ. Geology*, vol. 53 (1958) pp. 235.
- RUBEY, W. W. (1951): Geologic history of sea water. *Geol. Soc. Amer. Bull.*, vol. 62 (1951) pp. 1111.
- SHAW, DENIS M. (1960): The geochemistry of scapolite, Part II. *Jour. Petrology*, vol. 1 (1960) pp. 261.
- SMITH, F. G. (1953): Historical development of inclusion thermometry. University of Toronto Press, 149 p.
- THOMPSON, JAMES B., JR. (1959): Local equilibrium in metasomatic processes. *in* *Researches in Geochemistry*, P. H. Abelson, editor. John Wiley & Sons, pp. 427.
- WALTON, M. S., (1960): Molecular diffusion rates in supercritical water vapor estimated from viscosity data. *Amer. Jour. Sci.*, vol. 258 (1960) pp. 385.
- WHITE, DONALD E. (1955): Thermal springs and epithermal ore deposits. *Econ. Geology*, 50th Anniversary Volume (1955) pp. 99.
- WHITE, D. E. (1957): Thermal waters of volcanic origin. *Geol. Soc. Amer. Bull.*, vol. 68 (1957) pp. 1637.
- WINKLER, HELMUT G. F. and VON PLATEN, HILMAR (1958): Experimentelle gesteinsmetamorphose—II: *Geochim. Cosmochim. Acta*, vol. 15 (1958) pp. 91.
- WYART, J. and SABATIER, G. (1956): Transformations mutuelles des feldspaths alcalins. *Bull. Soc. franç. Minéral. et Crist.*, v. 79 (1956) pp. 574.
- WAYART, J. and SABATIER, G. (1958): Mobilité des ions silicium et aluminium dans les cristaux de feldspath: *Bull. Soc. franç. Minéral. et Crist.*, v. 81 (1958) pp. 223.