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SYNTECTONIC OXIDATION

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ABSTRACT. A reduction in grain size caused by deformation increases surface area and allows spontaneous surface exchange reactions which adsorb $H^+(aq)$ to take place. This increase in pH can be the driving force for oxidation reactions under certain geologic conditions. Conditions favorable to the process are low porosity, low permeability, low water/rock ratio, waning but high grade metamorphic conditions, and moderate strain rates.

Several lines of evidence lend support to the proposal. Tectonic and petrographic evidence and mass balance calculations suggest that oxidation reactions in blastomylonites in eastern Connecticut have been driven by this process. The positive correlation of an increase in Fe_2O_3/FeO ratio and other metasomatic changes with a decrease in grain size in a mylonite gneiss from Willimantic, Conn., the occurrence of increased Mg/Fe ratio of silicates, and aeromagnetic anomalies in shear zones are all in agreement with this hypothesis.

INTRODUCTION

The composition of the diagenetic or metamorphic fluid is frequently buffered (Fisher, 1970; Kerrick, 1974; Merino, 1975) by the host mineral assemblage. In particular the fugacity of O_2 appears to be buffered by solid reactions such as

$$2\ Fe_3O_4 + \tfrac{1}{2}\ O_2 = 3\ Fe_2O_3$$

in all cases where the situation can be assessed (Zen, 1963; Floran and Papike, 1978). However, it is also possible that in small scale shear zones for short periods of time (relative to chemical equilibration time) surface exchange reactions may dominate the composition of the fluid. In these situations the altered fluid composition can influence the solid assemblage, and the mineral assemblage may be permanently modified.

Mechanism.—One of the primary features of ductile shear zones is a reduction of grain size and therefore an increase in the surface area. This allows surface exchange reactions of the form:

$$K(surface) + H^+(aq) = H(surface) + K^+(aq) \qquad (1)$$

to take place, where $\log K = \log (a_{H(surface)}\ a_{K^+(aq)}) - \log (a_{K(surface)}\ a_{H^+(aq)})$. Such reactions decrease the a_{H^+} in the aqueous solutions adjacent to these newly exposed surfaces. This phenomenon is called abrasion pH by Stevens and Carron (1948). They show that crushing a variety of minerals under distilled water for a fixed period of time causes the pH to change from 7 to the extreme values of 1 to 12. However, no common silicate produces abrasion pH values smaller than 6, and most produce alkaline solutions. Among the common rock forming minerals quartz has the lowest abrasion pH (6-7). Phyllosilicates have values ranging from 7 to 8 (muscovite) to 10 to 11 (phlogopite), feldspars average 8.5, amphiboles and pyroxenes 9.5, olivine, 10 to 11, and carbonates 8.5.

These abrasion pH values vary as the exchange constants analogous to reaction 1 vary. Few exchange constants are known with accuracy, but those for muscovite and sanidine at 25°C and 1 bar are $10^{7.4}$ and

$10^{9.5}$ respectively (Garrels and Howard, 1959), indicating that the surface exchange of H^+ for K^+ is essentially complete. Low temperature experiments with silica gel (Dugger and others, 1964) and silicate glass (Eisenman, 1962) show that these surfaces prefer H^+ to a large variety of other cations. Existing thermodynamic and higher temperature experimental data suggest that silicate surfaces continue to be highly H^+ selective at high P–T conditions (Wintsch, Merino, and Blakely, 1980). Thus if deformation causes a reduction in grain size, either by dynamic recrystallization or by brittle fracturing (White, 1976), these newly exposed mineral surfaces will adsorb H^+ and increase the pH of the adjacent fluids, even at high grade metamorphic conditions.

The significance of abrasion pH in shear zones is that an aqueous fluid initially in equilibrium with its host mineral assemblage will be forced out of equilibrium by cation exchange on the newly exposed surfaces. This exchange decreases the a_{H^+} and increases the activities of the alkalis and alkaline earths. These effects combine to increase the a_{K^+}/a_{H^+}, $a_{Ca^{++}}/a^2_{H^+}$ et cetera from values initially buffered by the mineral assemblage to higher values and produce relatively alkaline solutions.

Under normal prograde metamorphic conditions, the metamorphic fluid is probably not forced far from equilibrium compositions. In this case the fluids will react with the assemblage causing the growth of larger grains at the expense of smaller grains. This will cause an ultimate *increase* in the grain size and will release adsorbed H^+ from the surfaces, remove cations from the aqueous fluid, and return the system to equilibrium. The likely effect of the initial grain size reduction and concomitant surface exchange would be to hasten the overall coarsening process.

If, on the other hand, the reduction in grain size causes an increase in pH at a faster rate than coarsening processes can decrease it, then values of the variables a_{K^+}/a_{H^+} et cetera in the fluid may be raised, possibly into the stability field or a new mineral. If this occurs, then the original assemblage will dissolve into these alkaline solutions. This dissolution releases the adsorbed H^+ and increases its aqueous activity, and the new mineral will precipitate from these fluids, causing a reduction in the activity of the cations. These effects combine to decrease the cation/H^+ activity ratio, until equilibrium among minerals and fluid is again established. In this case, however, a new mineral is added to the assemblage, and its growth is not dependent on changes in temperature or pressure but on pH increases caused by grain size reduction.

Surface exchange reactions can dominate the composition of the fluid most efficiently when the porosity of the rock is low. A given area of surface exchange will adsorb a given number of moles of H^+ ions, and so the smaller the volume of fluid, the larger the relative effect on pH. Similarly. if the permeability is low, the alkaline solutions produced by surface exchange will not be free to migrate and mix with fluids of buffered compositions. These two conditions are best met in high grade metamorphism. During prograde metamorphism many reactions release

H_2O which would add to the volume of available fluid and reduce the relative importance of surface exchange. Thus waning metamorphic conditions in which H_2O is fixed by retrograde reactions would increase the potential effect of surface exchange on fluid composition.

The ultimate mineral assemblage produced by increases in pH will be determined by the relative rate of pH increase. This rate is, in turn, dependent on the rate of grain size reduction. A new mineral will crystallize in a deforming assemblage only if the rate of decrease in grain size by deformational processes exceeds the rate of increase in grain size by coarsening processes. Coarsening is faster at higher temperatures, so grain size reduction must be relatively faster in high grade rocks to allow surface exchange to dominate the fluid composition and cause new minerals to crystallize. The moles of new mineral formed are directly proportional to the moles of H^+ exchanged; the exact relationship will depend on the specific reaction taking place. Wintsch (1975) has proposed that increases in pH may be responsible for the growth of alkali and plagioclase feldspar porphyroblasts in blastomylonites. I propose here that this process may also be responsible for the oxidation of biotite.

PHASE EQUILIBRIA

In order to assess the effect of pH changes on mineral asemblages, appropriate activity diagrams showing either a_{H^+} or a_{cation}/a_{H^+} ratio as intensive variables must be obtained. Supercritical pE-pH diagrams showing the stability of biotite solid solutions in equilibrium with sanidine, muscovite, and Al_2SiO_5 have been constructed by Wintsch (1980) and are shown here as figures 1 and 2. The diagrams are constructed for 500°C, 2kb, $a_{K^+} = 10^{-2}$, and quartz saturation, but the topological relations will hold at any P and T within the muscovite stability field. On these diagrams, lines of -1 slope constitute isopleths of constant f_{H_2}, f_{H_2O}, and f_{O_2}. Large fugacities of O_2 occur in the upper right corner, and large H_2 and small O_2 and H_2O fugacities are present in the lower left corner of figures 1 and 2. Following the suggestion of Carmichael (1969) all reactions in figures 1 and 2 are balanced conserving aluminum.

The relative stability realtions of muscovite, sanidine, and andalusite can be shown by reactions:

$$\underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + 6SiO_2 + 2K^+ = 3\,\underset{\text{sanidine}}{KAlSi_3O_8} + 2H^+ \qquad (1)$$
$$\text{quartz}$$

and

$$3\,\underset{\text{andalusite}}{Al_2SiO_5} + 3\,SiO_2 + 3\,H_2O + 2K^+ = \underset{\text{muscovite}}{2KAl_3Si_3O_{10}(OH)_2} + 2H^+ \qquad (2)$$
$$\text{quartz}$$

These reactions are identified by the circled numbers on figures 1 and 2. Reaction 1 does not involve electrons and is vertical. Reaction 2 is sensitive to the f_{H_2O} and is displaced to higher pH values in the fluid of reduced f_{H_2O} in the lower left side of figures 1 and 2. The equilibrium

constants for these reactions are calculated using the computer program SUPCRT described by Helgeson and others (1978, p. 202).

The stability of annite–phlogopite solid solutions in magnetite + sanidine bearing assemblages is limited by the reaction

$$\underset{\text{annite component}}{0.5\ K_2Fe_6Al_2Si_6O_{20}(OH)_4} = \underset{\text{sanidine}}{KAlSi_3O_8} + \underset{\text{magnetite}}{Fe_3O_4} + 2H^+ + 2e^- \quad (3)$$

and is known from the experimental work of Wones and Eugster (1965). Reaction 3 may be combined with reactions 1 and 2 to allow the calculation of the stability of these solid solutions in the muscovite and Al_2SiO_5 stability fields respectively by the reactions:

$$\underset{\text{annite component}}{1.5\ K_2Fe_6Al_2Si_6O_{20}(OH)_4} = \underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + \underset{\text{magneite}}{3Fe_3O_4} \quad (4)$$

$$+ \underset{\text{quartz}}{6SiO_2} + 2K^+ + 4H^+ + 6e^-$$

$$\underset{\text{annite component}}{K_2Fe_6Al_2Si_6O_{20}(OH)_4} = \underset{\text{andalusite}}{Al_2SiO_5} + \underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{quartz}}{5SiO_2} + H_2O \quad (5)$$

$$+ 2K^+ + 2H^+ 4e^-$$

Figure 2 is analogous to figure 1, except that it shows the stability of aluminous biotites taken from the experimental work of Rutherford (ms and personal commun.). The composition contours of biotite solid solution refer to the mole percent of annite in the biotite solid solution. Biot 1.00, 0.92, 0.83, and 0.75 have 2, 3, 4, and 5 aluminum atoms/formula unit of biotite respectively as written in reactions 3, 4, and 5 and appropriately less but equal amounts of Fe and Si.

DISCUSSION

The thesis of this paper is that within the geological constraints outlined above, the pH of the metamorphic fluid may be raised by surface exchange reactions. The effect of pH increases on several biotite bearing assemblages is shown by the arrows in figures 1 and 2. These arrows are independent of pE, because the activity of the electron is not affected by surface exchange. Thus at constant or nearly constant pE any increase in pH will lead to an increase in f_{O_2} and to the oxidation of iron. Increases in pH can be caused by grain size reduction. Thus the oxidation of iron can be a syntectonic process. Several lines of evidence supporting the syntectonic oxidation of iron are present in the blastomylonite–gneisses of eastern Connecticut.

Reaction textures.—Many textural relationships suggesting incomplete replacement reactions are present in the blastomylonitic Tatnic Hill Formation in the Norwich-Putnam and Willimantic areas of eastern Connecticut. Alkali and plagioclase feldspar porphyroblasts commonly surround large muscovite flakes with highly irregular, serrated edges and contain small islets of muscovite in optical continuity

with the larger grains. This texture, combined with the local absence of quartz, suggests the partial replacement of muscovite + quartz by reaction 1. This reaction could have been brought about by an increase in pH in an original muscovite-bearing, sanidine-free assemblage. This would move the fluid composition in the direction of arrow A of figures 1 and 2 (Wintsch, 1975) and drive reaction 1 to the right. The replacement of Al_2SiO_5 by muscovite occurs to a lesser extent in these blastomylonites than the above reaction and has been identified by Eugster (1970) and Kwak (1971) among others in many terrains. Theoretically, this reaction could also be driven by pH increases (arrow B, fig. 1).

Analogous textural relationships exist with biotite. Biotite commonly occurs as inclusions in microcline and plagioclase and in many samples has the same highly irregular grain boundaries that inclusions of muscovite have in the previous example. Plate 1-A shows an example of a biotite inclusion in a microcline porphyroblast, with a thin layer of

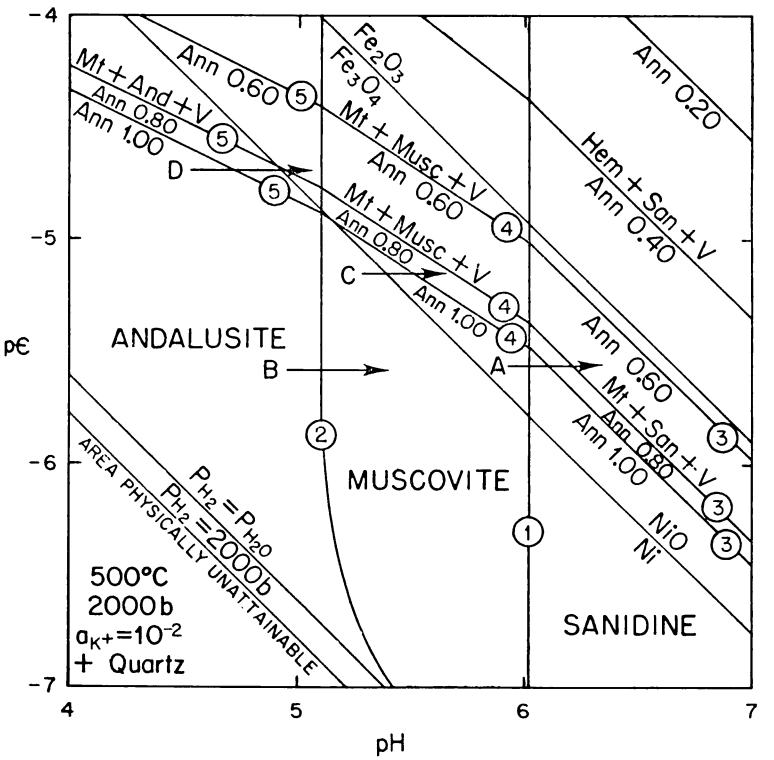


Fig. 1. A pE–pH diagram showing the stabilities of andalusite, muscovite, sanidine, magnetite, hematite, and biotite solid solutions, constructed from the data of Wones and Eugster (1965) after Wintsch (1980). Contours of biotite–phlogopite solid solution are given in terms of Fe/Fe+Mg. At constant pE grain size reduction of mineral assemblages A, B, C, and D will cause the pH to rise in the direction of the arrows. This will cause muscovite to replace Al_2SiO_5, sanidine to replace muscovite, and also bring about the oxidation of the iron in biotite (see text). Circled numbers refer to reactions in text.

muscovite and several grains of magnetite lining the edges of the biotite crystal and also partially surrounded by microcline. Plate 1-B shows a biotite crystal partially included in a plagioclase porphyroblast. Muscovite and magnetite define the border between the two. Hematite occurs as blades parallel to the (001) direction of the larger muscovite crystal at its boundary with the host biotite crystal. These textural relations suggest the partial replacement of biotite by these feldspars with the growth of magnetite and muscovite as by-products of the replacement.

Microprobe analyses show that the aluminum content of biotite is close to three atoms per formula unit (see reactions 3-5), equivalent to an annite content of 0.93 to 0.90 mole percent. Plagioclase is An_{23-27}, and microcline contains Ab_{5-10}. These analyses have been averaged and

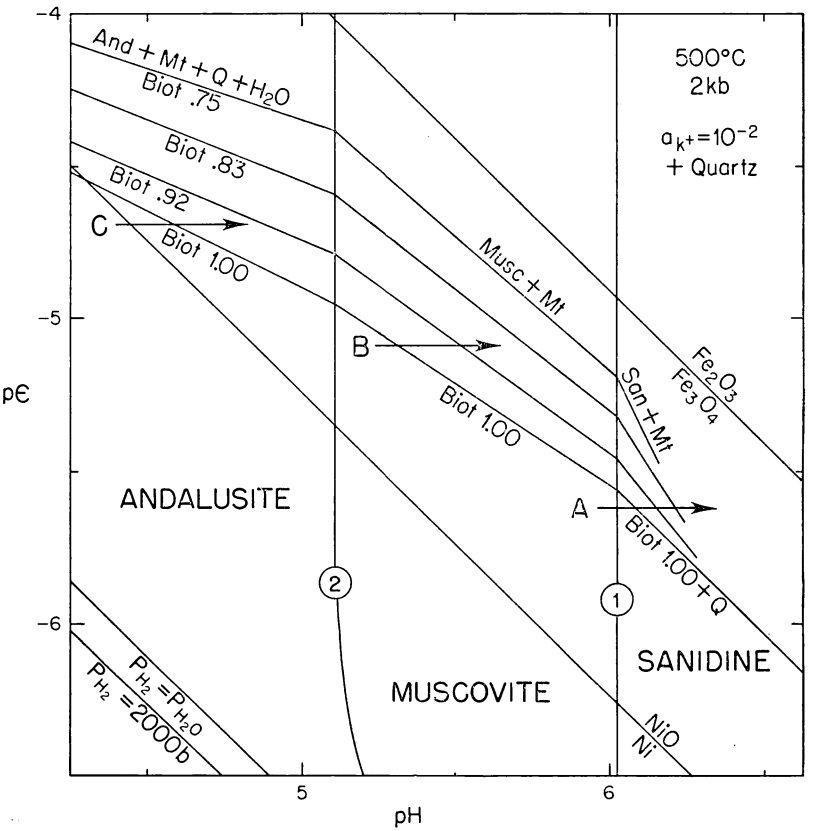


Fig. 2. A pE–pH diagram similar to figure 1 except showing the stability of aluminous biotite contoured in terms of $Fe^{VI}/Fe^{VI} + Al^{VI}$, constructed from the data of Rutherford (ms) after Wintsch (1980). Surface exchange following grain size reduction of biotite bearing assemblages containing muscovite or andalusite will increase the pH, as indicated by the arrows. This, in turn, will reduce the amount of iron and increase octahedral aluminum in biotite and in the sanidine field will first increase and then decrease the aluminum content.

simplified to allow the replacement reactions inferred from plate 1 to be written:

$$6\ K_2Fe_{5.5}Al_3Si_{5.5}O_{20}(OH)_4 + 23\ SiO_2 + 2\ H_2O + 6\ K^+ = \quad (6)$$
$$18\ KAlSi_3O_8 + 11\ Fe_3O_4 + 28\ H^+ + 22\ e^-$$

and

$$5\ K_2\ Fe_{5.5}Al_3Si_{5.5}O_{20}(OH)_4 + 5.5\ SiO_2 + 9\ Na^+ + 3\ Ca^{++} + 1\ 2/3\ H_2O$$
$$= 12\ Na_{0.75}Ca_{0.25}Al_{1.25}Si_{2.75}O_8 + 9\ 1/6\ Fe_3O_4 + 10\ K^+ + 23\ 1/3\ H^+ +$$
$$18\ 1/3\ e^- \quad (7)$$

Again following Carmichael (1969) the reactions are balanced on aluminum. Of immediate significance is the appearance of H^+ as a reaction product; reduction in the a_{H^+} at constant temperature and pressure will clearly drive these reactions to the right and bring about the replacement of biotite and oxidation of ferrous iron.

The replacement of biotite via reaction 6 (arrow heads of A, figs. 1 and 2) consumes SiO_2, H_2O, and K^+, as well as biotite, and would be limited by the activities of these components. The ΔV of reaction 6 is + 5 percent (ignoring the volume of ions), and thus a local pressure increase on the growing microcline + magnetite assemblage is also potentially limiting. A local pressure gradient has the added effect of contributing to a chemical potential gradient of the aqueous species away from the replacement site, which would point toward K^+, the ion with the largest partial molal volume (Helgeson and Kirkham, 1976) as the limiting variable. Quartz is present in the asemblage of plate 1-A, and thus the activity of SiO_2 was buffered here, and there is no evidence for a gradient in the a_{H_2O}. The a_{K^+} would, however, be locally reduced as reaction 6 proceeds. If this were the case, then the muscovite–K-feldspar boundary of figures 1 and 2 (reaction 1) would be shifted to the higher pH values of the arrowheads of A and would eventually lead to the local stabilization of muscovite as is present in plate 1-A. Although an increase in the volume of the product assemblage and an increase in the a_{e^-} remain potential limiting variables, a low a_{K^+} appears to explain the texture of plate 1-A adequately.

The replacement of biotite by plagioclase via reaction 7 (see pl. 1-B) is limited by low activities of SiO_2, Na^+, Ca^{++}, and H_2O and by high activities of K^+, H^+, and e^-. In this case the plagioclase bearing assemblage is 1 percent by volume smaller than the biotite bearing assemblage, and thus volume would not be a limiting factor. However, this negative volume of reaction would contribute to chemical potential gradients of the aqueous species *toward* the growing plagioclase porphyroblast. By analogy with reaction 6, the activities of Na^+ and Ca^{++} are potentially limiting variables. Unlike reaction 6, however, K^+ is a reaction product, and the a_{K^+} and particularly the ratio of activities of $K^+/Na^+ + Ca^{++}$ would have risen in the texture of plate 1-B with reaction progress. Apparently the local a_{K^+}/a_{H^+} ratio in the vicinity of plate 1-B was in the muscovite stability field, because muscovite and not

K-feldspar is present in the assemblage. The potassium bearing part of the overall reaction is represented by arrows C (fig. 1) and B (fig. 2).

Intergrowths of biotite with muscovite and magnetite are also very common in these rocks, but reaction relationships are usually not easily identified. Muscovite flakes occassionally cut biotite, but the reverse is never true, suggesting that muscovite replaces biotite. A possible reaction is:

$$6\ K_2Fe_{5.5}Al_3Si_{5.5}O_{20}\ (OH)_4 + 2\ H_2O$$
$$= 6\ KAl_3Si_3O_{10}\ (OH)_2 + 11\ Fe_3O_4 + 15\ SiO_2 + 6\ K^+ + 16\ H^+ + 22\ e^- \quad (8)$$

A reduction in the a_{H^+} would drive this reaction to the right, as is shown by arrow C (fig. 1) and arrow B (fig. 2). The product assemblage is 7 percent by volume smaller than the reactant assemblage (neglecting volumes of ions) indicating that an increase in pressure would also drive reaction 8 to the right.

Replacement textures involving biotite, sillimanite, and magnetite are abundant in portions of the Tatnic Hill Formation. In this assemblage biotite occurs as inclusions in magnetite, and larger flakes are cut by both magnetite and sillimanite. These features suggest the replacement reaction:

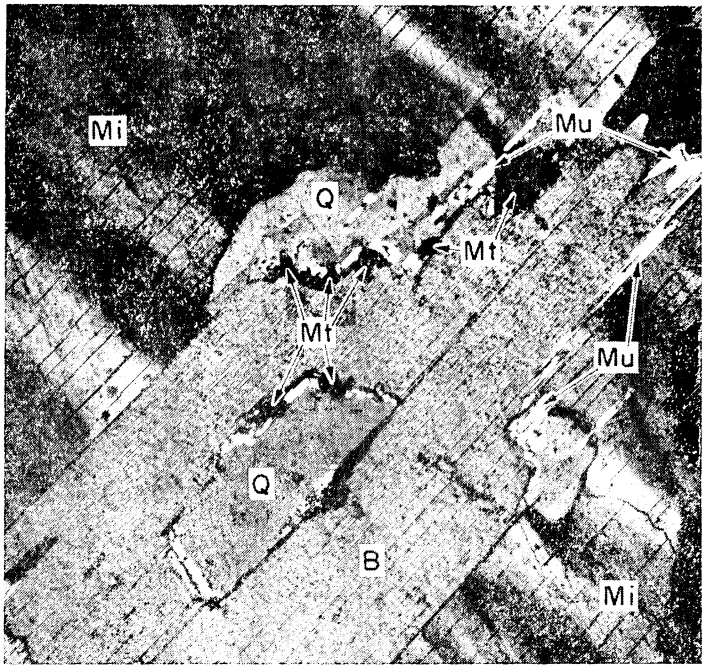
$$6\ K_2Fe_{5.5}Al_3Si_{5.5}O_{20}\ (OH)_4$$
$$= 9\ Al_2SiO_5 + 11\ Fe_3O_4 + 24\ SiO_2 + 7\ H_2O + 2K^+ + 10H^+ + 22\ e^- \quad (9)$$

The reaction will be driven to the right by a decrease in the activities of any of the fluid components, and because the product assemblage (neglecting fluid components) is 18 percent smaller than the replaced biotite, also by an increase in pressure. The effect of a decrease in the a_{H^+} on the assemblage is shown in arrow D (fig. 1) and arrow C (fig. 2.)

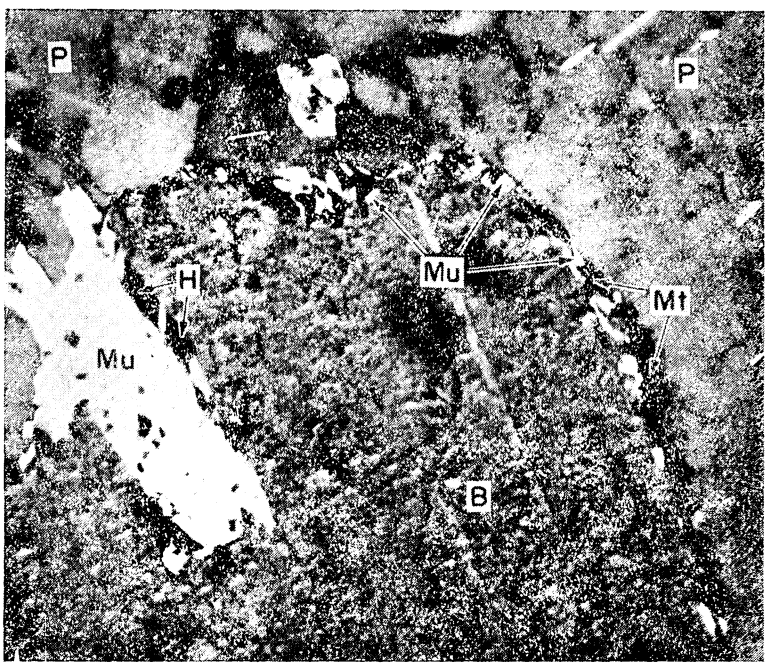
On theoretical grounds it is clear that all four of the above biotite replacement reactions could have been driven to the right by an increase in pH, but the question remains as to whether surface exchange could have been responsible for the pH increases. To answer this question a mass balance calculation has been performed.

Quantitative mass balance cannot be calculated for any of these reactions, because equilibrium constants for these reactions are not known. Order of magnitude calculations are possible given the following conditions. For every atom of iron oxidized, 1 electron is released to the aqueous fluid. The proportion of hydrogen ions necessary to counter the increase in a_{e^-} is multiplied by a factor of 10 raised to the ratio of reaction coefficients of e^-/H^+ in each reaction; the activity of the other aqueous species is ignored. In most cases this underestimates the decrease in a_{H^+} needed to drive these reactions and to a first approximation may be adequate. A starting rock is assumed to have an average grain size of 1 mm^3 and contain 20 volume percent each of feldspar and biotite, whose surfaces are H^+ selective. In some cases this underestimates the

PLATE 1



A. Microstructural relationships among biotite (B), muscovite (Mu), microcline (Mi), magnetite (Mt), and quartz (Q) from the blastomylonitic Yantic member of the Tatnic Hill Formation, Yantic, Conn. The replacement of biotite by microcline + magnetite ± muscovite is suggested by this intergrowth. Long dimension of plate is 1.17 mm.



B. Microstructural relationships among biotite (B), plagioclase (P), muscovite (Mu), magnetite (Mt), and hematite (H), from the blastomylonitic lower member of the Tatnic Hill Formation, Norwichtown, Conn. Note the armoring of the biotite by a trail of magnetite + hematite. Albite twinning is present in the upper left corner of the photomicrograph. Long dimension of plate is 1.25 mm.

number of potential H^+ exchange sites. A grain size reduction from 1 mm^3 to 0.1 mm^3 exposes 2×10^{14} surface sites and adsorbs the same number of H^+ ions per cubic mm. In cases of more intense grain size reduction, this also underestimates the number of H^+ ions adsorbed. Given these conditions, the volume of rock necessary to produce 1 mm^3 of magnetite (3×10^{19} ferrous atoms oxidized) is calculated; no ferric iron is allowed in the original rock. This volume of magnetite overestimates the amount of magnetite observed by a factor of 2 to 5. It is assumed that the magnetite crystal forms in the center of this volume, and that increases in pH anywhere within the volume drive the reaction at the center. The radii of spheres of rock necessary to adsorb the hydrogen ion so calculated for reactions 3 to 9 are shown in table 1. In view of the overall calculation, these radii probably represent maximum volumes of rock necessary to drive the reactions by surface exchange.

Table 1 shows that H^+ ion adsorption on silicate surfaces in a sphere of rock as small as 1.2 cm radius may drive the replacement of 1.9 mm^3 of Ann 0.92 by feldspar (reactions 6 and 7). Substantially larger volumes of rock are necessary to provide sufficient exchange sites for the replacement of Ann 0.92 by sillimanite (reaction 9). This larger radius of 17.4 cm reduces to 12.8, if it is allowed that 20 volume percent of the rock is biotite, and that biotite grain size is reduced from $1 \times 1 \times 1$ mm to $0.1 \times 0.1 \times 0.01$ mm. However, even the liberal estimates of volumes required from table 1 are compatible with observations of the Tatnic Hill Formation. Never does more than one major cluster of magnetite crystals occur in one thin section, and in outcrop clots of magnetite are frequently separated by tens of centimeters. Thus surface exchange reactions *are* capable of driving these reactions.

One last consideration in the development of these textures is the problem of time. The exchange reactions that occur on newly exposed surfaces are instantaneous reactions, which destroy mineral-fluid equilibria immediately. The dissolution and precipitation of minerals in this fluid is a relatively slow process, and the net reactions (1-9) are ionic and probably diffusion controlled, also a slow process. A sudden rapid decrease in grain size would meet the restrictions of the above calculations but would shift the solution compositions far from equilibrium with the solids. This situation is not likely to produce the textures

TABLE 1
Calculated radii of spheres (cm)*

Reactant	Product			
	Sanidine	Plagioclase	Muscovite	Sillimanite
Ann 1.00	(3)** 3.21	3.21	(4) 10.2	(5) 14.9
Ann 0.92	(6) 1.21	(7) 1.21	(8) 9.24	(9) 17.4

* Calculated radius of spherical rock volume necessary to produce 1 mm^3 of magnetite by surface exchange (see text).

** (#) Refers to reaction number in text.

observed because dissolution and precipitation (nucleation) would occur at many sites in these calculated volumes and not lead to the growth of porphyroblasts at the centers of these spheres. A slow, steady state creep better explains observations, because grain size reduction and therefore pH increase would then be a slow, continuous process. In this case the rate of pH increase destroying equilibrium is closer to the rate of diffusion and crystal growth reestablishing equilibrium. Upon nucleation, the magnetite-bearing assemblages would establish local chemical potential gradients which would drive the diffusion of reactant cations toward the growing assemblage and allow the growth of relatively large, isolated porphyroblasts at the centers of the larger volumes of rock (table 1). A steady supply of these cations as well as a sink for H^+ would be assured by surface exchange accompanying the slow, continuous grain size reduction.

Petrographic evidence for the syntectonic growth of these assemblages comes from rotated porphyroblasts of plagioclase (Wintsch, 1975) and magnetite with inclusions of muscovite and biotite variably rotated out of the orientation of the foliation. This implies that displacement parallel to the foliation and a grainsize reduction by a factor of 0.5 to 0.2 took place simaltaneously with crystal growth. The actual amount of time involved in the production of these blastomylonites is unknown. However, metamorphic and structural arguments of Wintsch (1979) suggest at least several and perhaps many million years were involved in the development of these blastomylonites — a time clearly sufficient to accommodate the "slow" growth of these porphyroblasts. Thus petrographic, tectonic, and mass balance considerations support the syntectonic oxidation of the biotite in the blastomylonites of the Tatnic Hill Formation.

TABLE 2

Chemical analyses (wt %) of mylonitic gneisses, Willimantic fault zone, Hosmer Mountain, Willimantic, Conn.

	W12A-1	W12A-2	W12A-3	W12A-4	W12A-5
SiO_2	68.2	63.8	45.4	62.5	46.9
Al_2O_3	13.7	15.7	29.2	18.2	19.3
Fe_2O_3	0.41	0.05	3.58	0.12	0.51
FeO	3.48	6.48	7.94	4.38	10.90
TiO_2	0.91	0.97	1.49	0.75	2.84
CaO	3.97	3.70	1.02	5.03	5.36
MgO	2.77	3.40	4.03	2.34	6.33
Na_2O	2.68	1.87	0.59	2.93	0.84
K_2O	1.80	2.55	3.05	2.05	4.20
MnO	0.07	0.21	0.24	0.11	0.11
CO_2	0.05	0.04	0.04	0.10	0.05
S	0.068	0.029	0.430	0.009	N.D.
$H_2O(-)$	0.11	0.14	0.52	0.10	0.15
$H_2O(+)$	0.73	1.12	2.44	0.93	2.04
Total	98.84	99.92	99.45	99.54	99.38

Analyst: M. E. Coller

Willimantic fault.—Another line of evidence compatible with the syntectonic oxidation hypothesis comes from the mylonite–gneiss at Hosmer Mtn., Willimantic, which forms the base of the Willimantic fault zone (Wintsch, 1979, p. 379). Major oxides of five samples across this shear zone are given in table 2. Sample W12A-3 has the highest Fe_2O_3/FeO ratio and contains hematite as well as magnetite. These oxides are selectively located along the boundaries of and in the cleavages of relatively large biotite crystals. This location is compatible with a high pH of the fluid in the vicinity of the biotite surface. The variation of grain size across this shear zone is compared to the Fe_2O_3/FeO ratio in figure 3. The reciprocal correlation between grain size and ferric iron content is consistent with the oxidation of the iron by surface adsorption of H^+.

Surface exchange on micas and feldspars decreases the a_{H^+} but also increases the activities of Ca^{++}, Na^+, and K^+. SiO_2 is more soluble in the high pH solutions produced (Anderson and Burnham, 1967), and its concentration will also increase. The increase in the activities of these species in a deforming rock will establish a locally high chemical potential of these components and cause the diffusion of these species away from the shear zone. These elements will thus be lost from the shear zone unless they are precipitated from solution by reactions such as 6 or 7.

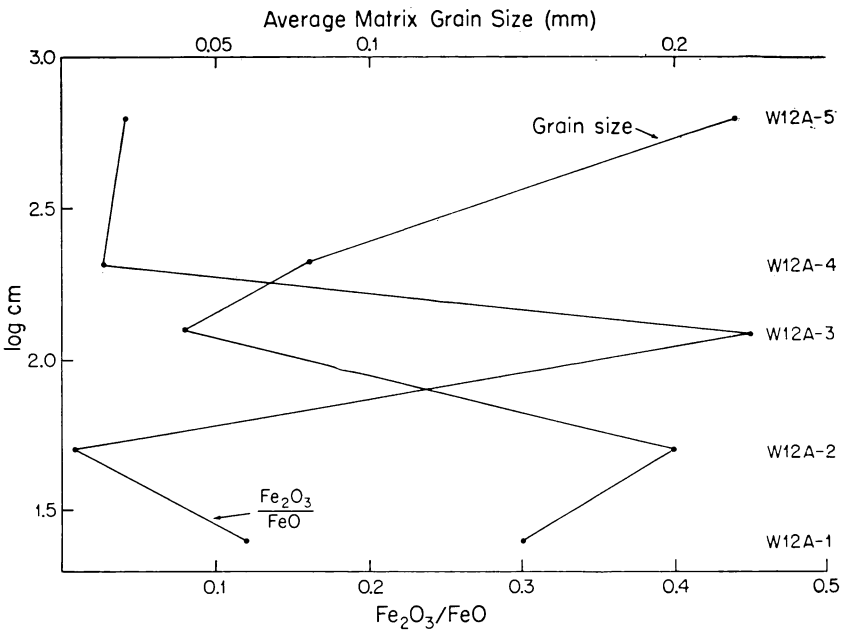


Fig. 3. The relationships among average matrix grain size, Fe_2O_3/FeO wt ratio and position across a mylonite gneiss from Hosmer Mtn., Willimantic, Conn. Sample numbers refer to analyses of table 2. The positive correlation between small grain size and large Fe_2O_3/FeO ratio is compatible with the hypothesis that surface exchange is responsible for a high pH and for the oxidation of iron.

Figure 4 shows the abundance of several major oxides relative to Al_2O_3 from the Hosmer Mtn. shear zone. SiO_2, Na_2O, CaO, and possibly MgO are less abundant in the finer grained sample W12A-3, while K_2O, FeO, TiO_2, MnO, and H_2O show no appreciable change across the shear zone. This follows the trend predicted by surface exchange except for K_2O. However, biotite surrounds and embays porphyroclasts of garnet in W12A-3, suggesting the replacement of garnet by biotite. Using microprobe analyses and balancing on Al_2O_3, the following metastomatic reaction may be constructed:

$$\begin{aligned} &3.53\ Fe_{2.19}Mg_{0.39}Mn_{0.20}Ca_{0.22}Al_{2.00}Si_{3.00}O_{12} \\ &+ 2.84\ K^+ + 3.96\ Mg^{++} + 0.39\ Ti^{+4} + 9.54\ H_2O \\ &= 2\ K_{1.42}\ (Fe_{2.665}Mg_{2.669}Mn_{0.02}Ti_{0.198}Al_{0.65})\ Al_{2.88}Si_{5.12}O_{20}\ (OH)_4 \qquad (10) \\ &+ 0.35\ SiO_2 + 0.80\ Fe_3O_4 + 0.70\ Mn^{++} + 0.78\ Ca^{++} + 11.08\ H^+ + 1.60\ e^- \end{aligned}$$

The reaction shows that K^+, Mg^{++}, and Ti^{+4} are consumed by the growth of biotite, which may help explain the retention of these elements in the shear zone. The foliation adjacent to these garnet prophyroclasts is distorted and sometimes rotated around the garnet, suggesting that the garnet acted as a local stress riser. In this regard, the product assemblage (neglecting ions) is 13 percent smaller than the garnet, and thus local high stress as well as reduction of a_{H^+} by surface exchange may have contributed to driving reaction 10 to the right. Reactions fixing Na^+ and Ca^{++} (for example 6,7) are not observed in this shear zone, which is compatible with their removal from it.

The possibility exists that the metasomatism in this shear zone may have been caused by the introduction of oxidizing fluids with low initial concentrations of alkalis and alkaline earths, as inferred by Beach (1976) for shear zones in Scotland. This interpretation does not seem likely for the shear zone at Hosmer Mtn., however, because it is part of a low angle ductile fault zone (Wintsch, 1979), and high angle brittle faults which might provide avenues for these fluids have not been identified. Moreover, magnetite, hematite, graphite, and pyrrhotite are all present in the shear zone and suggest a highly variable fluid composition on the scale of cm. This is not compatible with the massive intrusion of oxidizing fluids in an open system. It is also possible that these blastomylonites may have been oxidized by meteoric waters under near surface conditions. Although many outcrops of these blastomylonites are rusty-weathering, this is due to the oxidation of pyrrhotite. Surface weathering could not account for the syntectonic amphibolite facies assemblages that contain magnetite and hematite.

A more detailed analysis of the data in table 2 is not warranted, because it is likely that the undeformed precursors of these rocks had different compositions. Thus a detailed mass balance among the samples, as presented by Kerrich and others (1977) is not justified. However, the geochemical trends observed across the shear zone are too large to be

accounted for by primary sedimentary differences and in fact are in qualitative agreement with those predicted by surface exchange.

Aeromagnetic anomalies.—This model of syntectonic oxidation in high grade rocks predicts that the modal abundances of ferric iron bearing phases will increase with grain size reduction. If the major iron oxide produced is magnetite, then aeromagnetic anomalies should be associated with shear zones. In the high grade shear zones of central Massachusetts (Alvord and others, 1976) the positions of aeromagnetic highs do coincide with shear zones, and anomaly profiles have been used to infer the dips (Castle and others, 1976). These latter authors note that the anomalies stem chiefly from differences in the magnetite content of the individual rock masses. They believe that sharply truncated magnetic lineaments provide compelling evidence of faulting, and that there is a 'lesser likelihood that relatively long and linear magnetic boundaries may also coincide with faults" (Castle and others, 1976, p. 6). These studies were conducted in rocks on strike with and correlated with the Tatnic Hill Formation in the Norwich-Putnam area. In this regard the data in the preceding sections tend to support these geophysical interpretations.

Mg/Fe ratio.—The oxidation of the iron-bearing component of biotite by the reactions discussed above is a continuous reaction that reduces the Fe/Mg ratio in the remaining biotite. An example of this

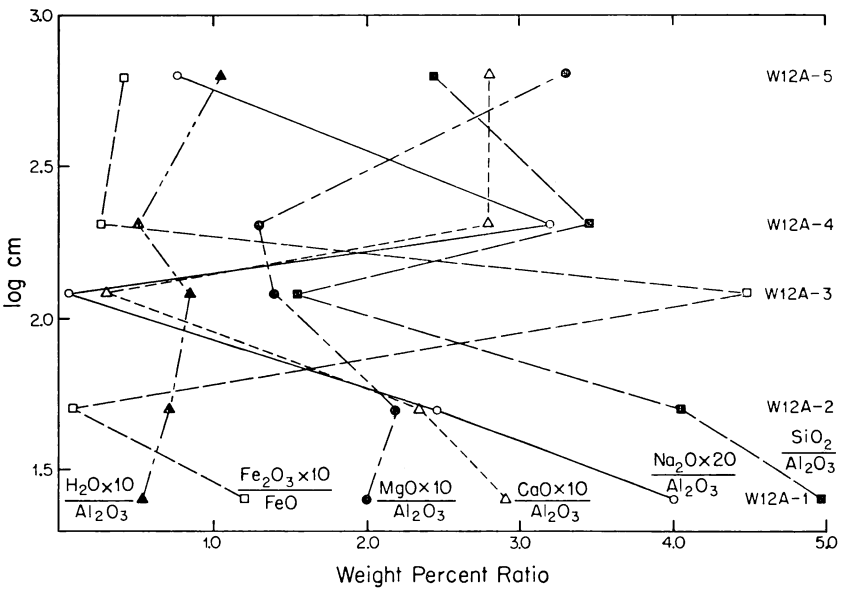


Fig. 4. The relationship between several wt percent ratios and position across a mylonite–gneiss from Hosmer Mtn., Willimantic, Conn. The decrease in amounts of SiO_2, Na_2O, and CaO relative to Al_2O_3 are compatible with the hypothesis that surface exchange releases alkalies and alkaline earths to the fluid, which increases their local concentration. This, in turn, causes the migration of these elements out of the shear zone (see text).

effect is present in the Pennsylvanian age biotite zone metasediments of the Narragansett basin, Rhode Island. The composition of biotites from the Providence area from Wiechmann (ms) is shown in figure 5. None of the biotite contains more than 0.40 mole percent MgO except those from a shear zone (fig. 5). These biotites also contain less aluminum than the others (Ann 0.91 versus ~ Ann 0.86). All samples except the shear zone sample contain disseminated carbonaceous material and ilmenite, suggesting a relatively low f_{O_2}. The shear zone sample, on the other hand, contains magnetite, epidote, ilmenite, and no disseminated carbon, suggesting a higher f_{O_2} was present during the crystallization of this assemblage. The anomalously high magnesium content of the biotite in the shear zone may be attributed to the syntectonic oxidation of the ferrous iron in the biotite to form magnetite and epidote. There is some evidence that the lower aluminum content of the biotite may also be compatible with oxidation in relatively alkaline environments (Wintsch, 1980), but more work on aluminous biotite is necessary to document this.

Other shear zones.—A variety of shear zones have been studied by Beach (1973, 1976), Beach and Fyfe (1972), Beach and Tarney (1978), Bryant (1966, 1967), and Kerrich and others (1977). Strong geochemical trends do not emerge from these studies, but in general K_2O, TiO_2, H_2O, and usually ferric and total iron increase, SiO_2, CaO, and Na_2O usually decrease, and MgO is variable (all relative to Al_2O_3) in shear zones relative to the undeformed rock. The net gain or loss of any element will be dependent on mineral reactions taking place, which may be complex (Beach, 1973), but which are not usually assessed. Without data on the mechanical behavior of these shear zones and without the above petrologic information, detailed comparison is not meaningful. It is nevertheless interesting to view these studies in the light of the model proposed here. Only some of the mineral reactions proposed

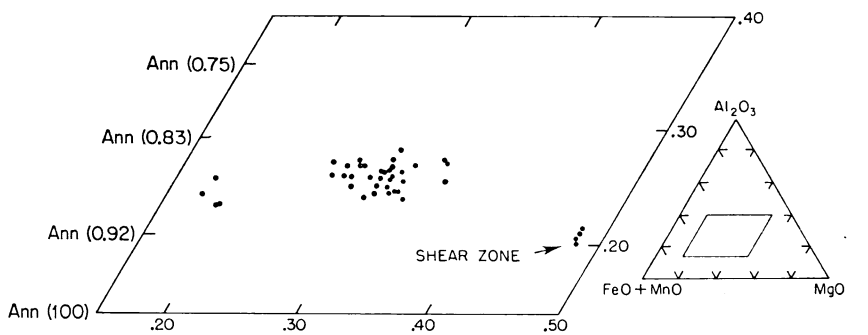


Fig. 5. The distribution of biotite compositions from the biotite zone, Providence area, R. I. from Wiechmann (ms). All samples contain disseminated carbon and ilmenite except those from the shear zone, which contain magnetite and epidote and are carbon free. This assemblage as well as the high magnesium and possibly the low aluminum content of the biotite from the shear zone are compatible with oxidation of the biotite-bearing assemblage by surface exchange following grain size reduction.

(Bryant, 1966; Beach, 1973; Gresens, 1974) are driven by a decrease in a_{H^+}; many are driven by an increase in a_{H^+}. Most authors of these studies attribute the metasomatism in these shear zones to the introduction of oxidizing fluids. However, the evidence for this is not compelling, and at least the participation of surface exchange in the metasomatism of these shear zones cannot at this point be ruled out.

CONCLUSIONS

The significance of the syntectonic oxidation model is the proposal of grain size as a petrologic variable. Through its effect on surface exchange, deformation may ultimately be responsible for not only the mode but also the composition of minerals, the mineral assemblages, and even the bulk composition. Theoretically pH increases should occur in all shear zones, but other processes such as introduction of fluids in open systems and coarsening by annealing may dwarf the effect of surface exchange on fluid composition. However, syntectonic oxidation by surface exchange apparently has occurred in southern New England and may have participated in the geochemical evolution of other shear zones as well.

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