

SUMMARY AND CONCLUSIONS

The results of this theoretical analysis indicate that direct gibbsite formation probably occurs under conditions of high soil permeability and good soil drainage. Also gibbsite formation probably does not occur where the soil pH is less than about 4.3 or where the initial concentration of dissolved silica exceeds $10^{-4.6}$ moles/liter. The analysis further indicates that alteration of K-feldspar to K-mica probably does not occur without antecedant production of kaolinite. In general, the analysis demonstrates that the formation of clay minerals in the zone of weathering involves the complex interplay of parent material, pH, rates of soil drainage, kinetics of dissolution of primary silicates and precipitation of clays, initial composition of the soil solution, and biologic factors. There is probably no simple universal sequence of alteration products in the zone of weathering, the exact sequence of formation and relative proportions of clays in a particular situation being determined by the above factors.

REFERENCES

- GARDNER, L. R. (1970) A chemical model for the origin of gibbsite from kaolinite. *Amer. Mineral.* 55, 1380-1389.
- HELGESON, H. C., R. M. GARRELS, AND F. T. MACKENZIE (1969) Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions—II. Applications. *Geochim. Cosmochim. Acta* 33, 455-481.
- LODDING, W. (1961) Gibbsite vermiforms in the Pensauken Formation of New Jersey. *Amer. Mineral.* 46, 394-401.
- ROBIE, R. A., AND D. R. WALDBAUM (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U. S. Geol. Surv. Bull.* 1259.

American Mineralogist
Vol. 57, pp. 300-316 (1972)

STABILITY OF BIOTITE: A DISCUSSION

ROBERT F. MUELLER, *National Aeronautics and Space Administration, Goddard Space Flight Center, Greenbelt, Maryland 20771*

ABSTRACT

Distribution data for magnesium and iron from a variety of ferro-magnesium silicates and coexisting biotites indicate that the mixing properties of these constituents in biotite and the other silicates do not deviate greatly from the ideal solution (activity coefficients within a factor or two of unity). This result is in conflict with some inferences which have been drawn from experimental data on the phlogopite-annite system. Examination of these experimental data

and the models used to interpret them lead to the conclusion that the assignment of a large negative deviation from ideality is unwarranted. However, the distribution of Mg^{2+} and Fe^{2+} is greatly perturbed by variations in the abundances of extraneous ions such as Al^{3+} and Si^{4+} . These characteristics of the biotite solid solutions have important implications in the interpretation of igneous and metamorphic rocks.

INTRODUCTION

The question of the thermodynamic stability relations of the biotite group of minerals is of great interest to petrologists because these minerals are important components of a variety of igneous and metamorphic rocks.

The data bearing on this question consist of compositional relations among natural biotites and coexisting minerals as well as direct experimental data and the data on thermodynamic properties obtained from thermochemistry. Although the data from natural assemblages have been widely used in the interpretation of rocks and in the construction of solution models, they have been largely ignored in the interpretation of the results of laboratory experiments.

Experimental data on biotite are still largely confined to the phlogopite-annite series, which is understandable since the stability relations are highly dependent on the compositional variations of such ions as Al^{3+} , Fe^{3+} , Si^{4+} , etc. Some variations involving Mg^{2+} and Fe^{2+} versus Fe^{3+} occur even within the restricted compositional field of the phlogopite-annite series and these have been discussed in the important studies of Eugster and Wones (1962) and of Wones and Eugster (1965). Among the results of these works is the broad delineation of the stability field of the phlogopite-annite series with respect to temperature, oxygen fugacity and certain ranges of fluid pressure. These authors also attempted to draw certain inferences from these variables, the compositional parameter $Fe/(Fe + Mg)$ and the nature of the biotite solid solution. They concluded through the application of solution theory to their activity measurements that the phlogopite-annite series, regarded as a pseudobinary solution, is highly non-ideal with activity coefficients as small as 10^{-3} . It is clear that such a wide deviation from the ideal solution should have profound effects not only on the distribution of elements among coexisting minerals but also on the stability relations with respect to temperature, oxygen fugacity, and fluid pressure. Wones and Eugster (1965) in fact attempted to show the effect of this non-ideal behavior on element distributions of certain natural assemblages. However, their illustrations were of a qualitative nature and were drawn from only a small and select part of the existing literature.

Although some of Wones and Eugster's inferred large deviations from ideality are attributable to their choice of the "molecular" component involving Fe_3 and Mg_3 , large deviations still remain even when their data are normalized to Fe^{2+} and Mg^{2+} ions. It is therefore essential that their assumptions be reexamined and that their results be compared in some detail with the independent data from biotites which coexist with other ferromagnesian silicates in natural assemblages which closely approached equilibrium during crystallization.

DISTRIBUTION OF IRON AND MAGNESIUM AMONG BIOTITES AND OTHER MINERALS

The distribution data for biotites may be divided into those for igneous rocks and those for metamorphic rocks. Because of the mechanism of crystallization of igneous minerals from melts and the many possibilities of mechanical separation and interruption of crystallization of the minerals, their use in distribution studies is usually more limited than minerals of metamorphic rocks. Many independent studies—to be referred to later—now have shown that metamorphic minerals generally exhibit a high degree of equilibrium with respect to element distributions.

Some confusion arises in evaluating and comparing distribution data which may on one hand distinguish between ferrous and ferric iron and on the other hand fail to make this distinction. The distinction between the two oxidation states of iron is an important one if determination of the oxidation state itself is involved or if $\text{Fe}^{3+}/\text{Fe}^{2+}$ is high. If however, only distribution equilibrium is being considered, and if the ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ is sufficiently low, considerations of the ratio may not be necessary. For example, if both minerals of a coexisting pair contain similar and low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios, the difference between the distribution curves obtained by considering and ignoring this ratio will not be great since the two sets of distribution points will be separated by only a small translation subparallel to the curve.

The first precise and detailed study of the distribution of magnesium and iron between biotite and coexisting ferromagnesian silicates was made by Kretz (1959) who found that on a total iron basis these elements were almost equally distributed between biotite and hornblende but that iron was concentrated relative to magnesium in the coexisting garnet. Within the range of uncertainty the data for coexisting biotites and hornblendes may be approximated by the relation

$$D^{\text{bi}-\text{hb}} = \frac{X_{\text{Fe}}^{\text{hb}} X_{\text{Mg}}^{\text{bi}}}{\Delta_{\text{Mg}}^{\text{hb}} X_{\text{Fe}}^{\text{bi}}} \simeq 1 \quad (1)$$

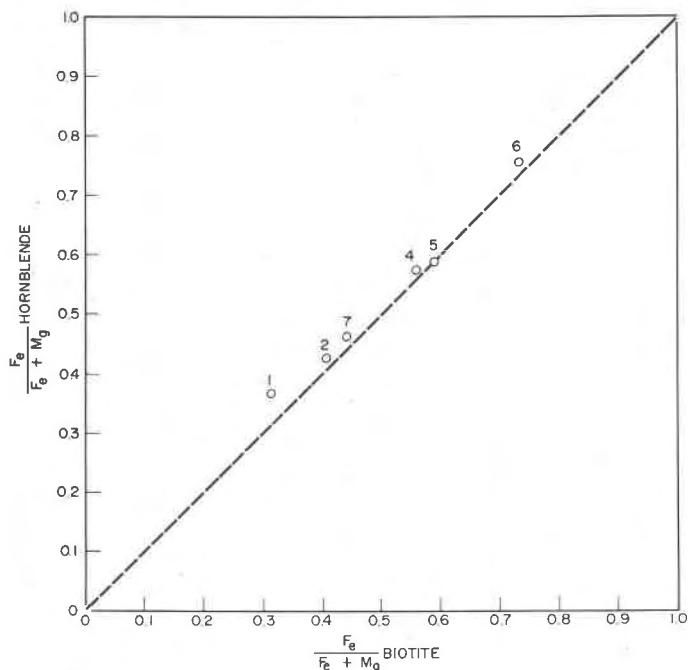


FIG. 1. Distribution of magnesium and total iron between coexisting biotites and hornblendes from charnockites of Varberg, Sweden (after Saxena, 1968b).

in which D^{bi-hb} is the distribution coefficient and the x 's are the atomic fractions in hornblende (hb) and in biotite (bi) as indicated by the superscripts. On the other hand, the distribution of Mg and Fe between biotite and garnet was found to be highly dependent on the concentration of other constituents such as manganese in the garnet.

Later studies of Kretz (1960), Albee *et al.* (1965), Hounslow and Moore (1967), Annersten (1968), Saxena (1968a, b) and Sen and Chakraborty (1968) generally confirm and extend the relations found by Kretz. In particular, the extensive data and compilations of Sen and Chakraborty (1968) and of Saxena (1968a, b) confirm the strong dependence of the distribution of Mg and Fe between garnet and the other ferromagnesian minerals on the compositional variation of such elements as Mn, Ca, Al, and Si. Saxena (1968b) has shown (Figs. 1 to 4) that the distributions between biotite and other ferromagnesian silicates are very orderly and correspond rather closely to the distribution curve represented by the ideal solution. As was shown also by Saxena (1968a), if a single facies is considered and there are no perturbation effects coexisting garnets and biotites approximate the relation

$$D^{ga-bi} = \frac{X_{Fe}^{ga} X_{Mg}^{bi}}{X_{Mg}^{ga} X_{Fe}^{bi}} \quad (2)$$

in which D^{ga-bi} is a constant.

In the case of the epidote amphibolite facies D^{ga-bi} is approximately 9.0 while for the granulite facies it is about 5.6. The specimens of Figures 1-4 from the Charnockites represent a highly homogeneous set of samples so that thermal and other perturbations are minimal. In them even the small amount of scatter and deviation from the ideal distribution curves may be accounted for by systematic variations in Al^{IV} and Al^{VI} , which as we shall see, perturb the Mg-Fe distributions. For example, the biotites represented by points 4 and 5 contain much more Al^{IV} than do the others.

The near ideal character of the biotite solid solution of the Mg and Fe components is also indicated by the data of Hounslow and Moore (1967). Among their examples the data for coexisting biotite and staurolite in particular are highly uniform and indicate only a very slight deviation from a model which ascribes ideality to both solid solutions. Similarly in the case of the data of Albee *et al.* (1965) consistency with this model is shown.

In summary it might be said that when perturbations due to elements other than Mg and Fe are small, the distribution curves for biotites coexisting with other silicates indicate a very close approach to the ideal solution for this mineral as well as the coexisting ferromagnesian silicates. We show later that this characteristic results from the intrinsic mixing properties of Fe^{2+} and Mg^{2+} irrespective of the perturbations by other constituents. This picture is consistent with an early interpretation of the mixing properties of these ions in pyroxenes and cummingtonites (Mueller, 1961). This general picture of near ideal mixing of the Mg^{2+} and Fe^{2+} components of the whole crystal has also been substantiated by the recent work of Saxena and Ghose (1971) on orthopyroxene. In the latter case the deviation from ideality is associated at least in part with the strong tendency for ordering of Mg^{2+} and Fe^{2+} into two nonequivalent lattice sites, Mg^{2+} being concentrated in the $M(1)$ site, whereas Fe^{2+} is concentrated in the $M(2)$ site. Deviation from ideality in orthopyroxene is most marked in the low temperature experimental range ($\sim 500^\circ C$) and almost vanishes as T approaches $1000^\circ C$. However, even at $500^\circ C$ the activity coefficients of $MgSiO_3$ and $FeSiO_3$ do not exceed 2 over more than 80 percent of the compositional range and for most of the range they are less than 1.3. It is important to note that in the minerals which enter into Figures 1 to 4 the degree of structural non-equivalence of the lattice sites of

Mg^{2+} and Fe^{2+} is less marked than in the case of orthopyroxene (Steinfink, 1962; Ghose, personal communication). In the case of hornblende, the only mineral with a high degree of nonequivalence, the most distorted site $M(4)$ is almost filled with calcium. Thus the mineral pairs represented present a good test for the ideality of biotite.

VARIATION OF ALUMINUM CONTENT WITH RESPECT
TO THE ASSEMBLAGE

It has been known for some time that biotite exhibits considerable variation in aluminum content and that this characteristic is related to the mineral assemblage in which it occurs. Since the aluminum content affects the distributions, as shown by the work of Saxena (1968b) and others, it is clear that it has an important effect on stability relations. Because of the still very limited experimental data it is difficult to assess the alumina content of biotites in terms of pressures and temperatures of crystallization; however at least the qualitative relations of aluminum content to bulk compositional variations can in many cases be deduced.

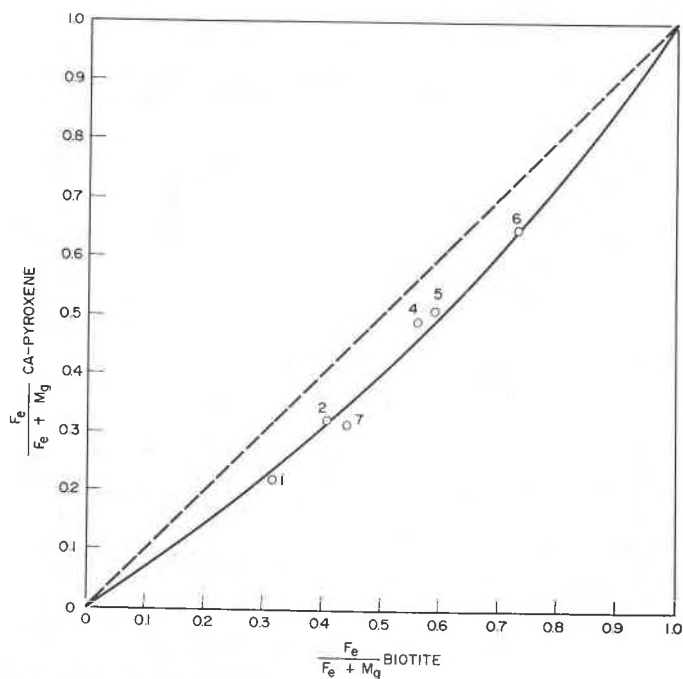


FIG. 2. Distribution of magnesium and total iron between coexisting biotites and ca-pyroxenes from charnockites of Varberg, Sweden (after Saxena, 1968b).

The relatively simple compositional characteristics of the phlogopite-annite series are most closely approached in biotites of skarns and other rocks with no excess alumina or Al_2SiO_5 . Generally also the rocks of the calc-alkali igneous series are characterized by biotites which do not differ greatly from phlogopite-annite, since such rocks are seldom peraluminous. Typical examples of the latter type of biotites from the southern California and Sierra Nevada batholiths were presented by Larsen and Draisin (1948) and by Dodge, Smith, and Mays (1969) respectively.

The peraluminous biotites, especially those termed "eastonites" are characteristic of aluminum-rich schists and gneisses and are frequently in association with polymorphs of Al_2SiO_5 or corundum. Such biotites frequently contain in excess of 20 weight percent Al_2O_3 . Examples may be found in the works of Chinner (1960), Hounslow and Moore (1967), and Sen and Chakraborty (1968). Generally in suites of rocks which exhibit a variability of Al_2O_3 content and which contain both alumi-

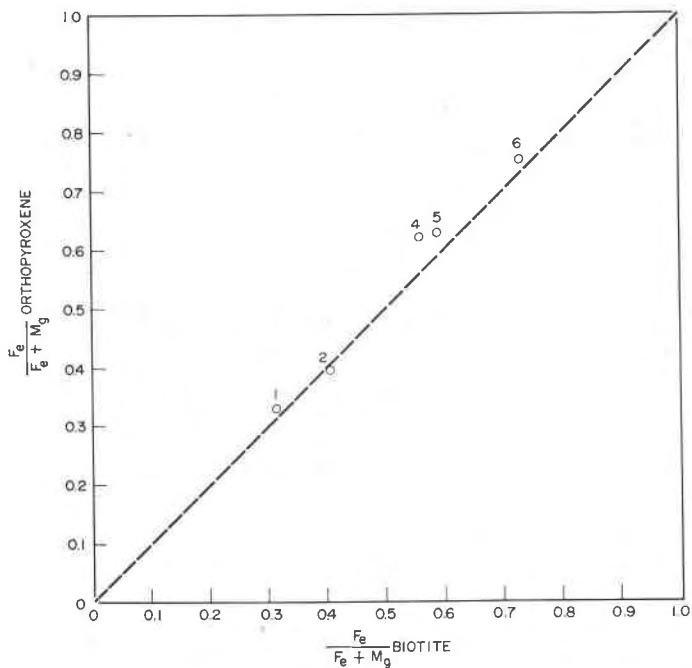


FIG. 3. Distribution of magnesium and total iron between coexisting biotites and orthopyroxenes from charnockites of Varberg, Sweden (after Saxena, 1968b).

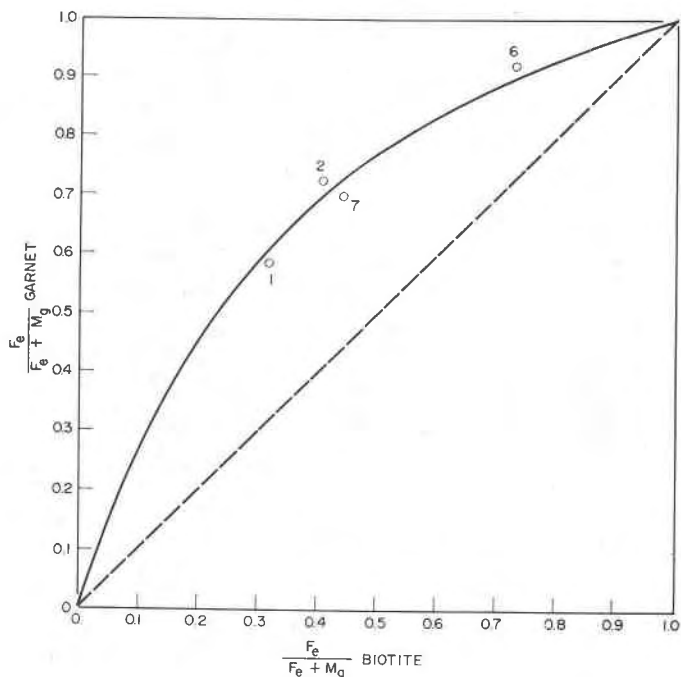


FIG. 4. Distribution of magnesium and total iron between coexisting biotites and garnets from charnockites of Varberg, Sweden (after Saxena, 1968b).

num-poor and aluminum-rich assemblages the biotites which coexist with Al_2SiO_5 polymorphs show distinctly higher Al_2O_3 contents. This is illustrated by the suite of upper amphibolite facies gneisses studied by Kretz (1959) as shown in Table 1. That the composition of biotites in such rocks is not simply related to the bulk Al_2O_3 content is however indicated by the observations of Chinner (1960). It is clear from his observations and from theoretical considerations that the composition of biotite reflects the oxygen and water fugacities as well. Chinner in fact established that the Mg and Mn contents of biotites (and other silicates as well) increase relative to Fe^{2+} as the degree of oxidation of a rock is increased, since Fe^{2+} is then oxidized to form higher oxides. It may be shown that analogous reactions also govern the Al_2O_3 content of biotite. As an example we may consider the reaction

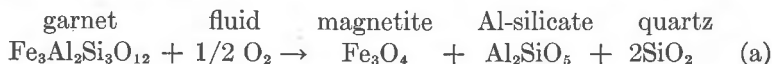
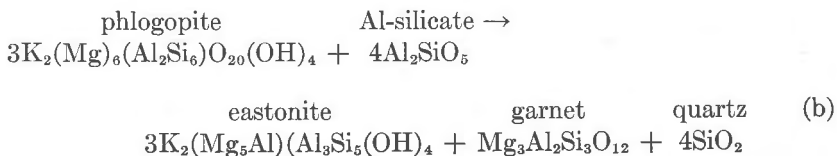


Table 1
 Aluminum-Content of Biotites in Rocks With and Without
 Sillimanite (Kretz, 1959)

Specimen Ref. Number	Al ₂ O ₃ in Biotite	Specimen Ref. Number	Al ₂ O ₃ in Biotite
1	12.7	13	—
2	14.5	14	15.2
3	13.3	15	17.6
4	13.5	16	17.4
5	14.2	17	14.2
6	15.5	18	16.0
7	14.6	19	14.2
8	13.4	20	16.2
9	16.3	21	17.0 (Sil)
10	17.0	22	18.3 (Sil)
11	17.0 (Sil)	23	17.0 (Sil)
12	—	24	17.2 (Sil)
		25	19.5 (Sil)

(Sil) indicates sillimanite is present.

In this reaction Al₂SiO₅ is regarded not necessarily as precipitated sillimanite, kyanite or andalusite but as a component available for other reactions. Thus the Al₂SiO₅ produced by the oxidation of ferrous aluminum silicate—in this case garnet, can react with the phlogopite or annite components of biotite to produce a biotite more enriched in alumina:



The Al_2SiO_5 will appear as an Al_2SiO_5 polymorph only when its chemical potential exceeds the value necessary for precipitation. At values less than this it dissolves in biotite and enriches this mineral in Al_2O_3 . Consequently for each P - T condition the ratio eastonite/(phlogopite + annite) may be continuously increased as the fugacity of oxygen is increased. In the field of stability of muscovite increased precipitation of this mineral will be an accompanying effect as was noted by Chinner (1960).

EVALUATION OF EXPERIMENTAL DATA

Wones and Eugster (1965) arrived at several conclusions about the character of the phlogopite-annite solution which bear in an important way on the stability relations and compositional behavior of biotites in general. Their conclusions are:

1. That the series is really quasi-ternary and consists of phlogopite, annite, and "oxybiotite" ($\text{KFe}_3^{3+}\text{AlSi}_3\text{O}_{12}(\text{H}_{-1})$) components.

2. That the quasi-ternary system may be approximated by a quasi-binary system in which the phlogopite and oxybiotite components are considered as a single component.

3. That annite forms a highly non-ideal solution with respect to the other components and may be represented by a regular solution model. Wones and Eugster also drew a number of secondary conclusions which they attempted to apply to natural biotites. They suggested for example that the markedly non-ideal character of the biotite solution found by them would require that the distribution coefficient with respect to certain coexisting ferromagnesian silicates vary from less than unity to greater than unity as Fe/Mg increased. They referred to the rocks of the Southern California batholith (Larsen and Drasin, 1948) as illustrating this effect. They also suggested that the ratio $\text{Fe}/(\text{Fe} + \text{Mg})$ in biotites increased from gabbro to granites because 1) it is a bulk compositional effect, or 2) Mg -rich biotites are more stable than Fe -rich biotites at high temperatures. They also favored the idea that the iron enrichment of biotite in granites of the gabbro-granite sequence was due to a buffering effect by associated "anhedral mineral assemblages."

The broad outlines of the stability field of the phlogopite-annite series as determined by Wones and Eugster are consistent with the general aspects of natural biotites and with other ferromagnesian minerals. However, there are serious disagreements in detail between several of the points listed above and the observed features of natural

assemblages. Although Wones and Eugster inferred oxybiotite concentrations as high as 19 percent they still assumed that the solution could be treated as a quasibinary regular solution. However, there are in existence appropriate ternary models for the regular solution. The model presented by Prigogine and Defay (1951) indicates that in such solutions one interaction coefficient is inadequate and that it is necessary also to introduce additional coefficients which take into account the interaction between all three components. This does not of course preclude treatment of the system as quasibinary as long as Fe^{3+} is in low concentration.

The activity—composition relations deduced by Wones and Eugster indicate very large deviations from ideality as defined by the Fe_3 model and that this deviation increases greatly as the phlogopite and oxybiotite components increase. Furthermore, the deviation from ideality is still very large when defined with respect to the Fe_1 model. It is probable that some of this inferred deviation from the quasibinary ideal models is simply due to Fe^{3+} in high concentration on the Fe_2O_3 - Fe_3O_4 buffer curve. However, it must also be considered that much of the deviation may be due to systematic errors between the oxygen fugacities determined through different buffer systems. This is particularly true of the Fe_2O_3 - Fe_3O_4 and Fe_2SiO_4 - SiO_2 - Fe_3O_4 systems which have very large uncertainties attached to them. Indeed the great difference between fugacity values determined by mass spectrometer and thermochemical methods for the system Fe_2O_3 - Fe_3O_4 have been discussed by Wones and Eugster (1965).

The very small fugacity coefficients deduced by Wones and Eugster (1965) for annite are clearly out of harmony with the distribution data previously discussed. Also since many of these data incorporate several percent Fe_2O_3 there is no evidence that this component perturbs the distributions greatly at the concentrations which usually prevail in natural biotite. In addition, it should be pointed out that even if Wones and Eugster had found ideal behavior with respect to the Fe_3 model, the resulting equilibrium distribution curves corresponding to Figures 1 to 4 should have been of a much more complex character than those actually determined. With large deviations from ideality the complexity should be even greater, as previous calculations have shown (Mueller, 1964). The fortuitous cancellation of these effects between coexisting minerals may be virtually excluded when the distribution coefficients deviate from unity (Mueller, 1961). Furthermore, the use of the data of Larsen and Draisin (1948) for the precise determination of distribution coefficients is not advisable because several

coexisting minerals show evidence of disequilibrium magmatic processes (Mueller, 1963).

Although one may concur with Wones and Eugster that the iron enrichment of biotites in granites is related to both the stability of iron biotite and to bulk composition effects, the same might be said for all the ferromagnesian silicates. However, the enrichment of iron in ferromagnesian minerals is not a necessary consequence of crystallization differentiation but is highly dependent on the oxygen and water fugacities. It has been shown elsewhere (Mueller, 1969) that such iron enrichment demands a large and systematic decrease in oxygen fugacity as differentiation proceeds from gabbro to granite. If this does not occur the late ferromagnesian minerals will be enriched in magnesium as is observed in certain acidic volcanic rocks. It is important to realize that such a decrease is consistent with a constant activity ratio a_{H_2O}/a_H in the melt so that it may occur even if the concentration of water increases with differentiation (Mueller, 1969).

THERMODYNAMICS OF BIOTITE SOLUTION

In the treatment of complex multi-component equilibria, it has been the practice, whenever possible, to represent activities of mineral components by simple compositional parameters such as the mole fraction of a given end member. In case of non-ideal behavior, an activity coefficient in which other compositional parameters enter is also introduced. Thus the activity of the component $\frac{1}{3} KFe_3AlSi_3O_{10}(OH)_2$ (annite) may be represented by

$$a_{Fe^{bi}} = X_{Fe^{bi}} f_{Fe^{bi}},$$

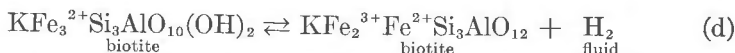
in which $f_{Fe^{bi}}$ is the activity coefficient. As we have seen considerable complication is introduced when $X_{Fe^{bi}}$ is taken to represent $KFe_3AlSi_3O_{10}(OH)_2$ since under these circumstances $f_{Fe^{bi}}$ may diverge greatly from unity.

It is possible to represent complex components by another method in which the expression for the activity contains as factors the atomic fractions of the different kinds of ions present in the end member utilized. When sufficient information is available each atomic fraction may refer to a nonequivalent lattice site, but this is not necessary. This "geometrical" model was applied by Kretz (1961) in his treatment of heterogeneous distributions among complex silicates. Analogous expressions for the activities of Mg and Fe components were also employed to account for the distribution of these ions between nonequivalent lattice sites in pyroxenes and amphiboles (Mueller, 1962). Recently also, Saxena and Ghose (1971) have generalized this method

Equation (4) reduces to (5) for any set of biotite end members utilized in reaction (c).

Now the factor $f_{\text{Fe}^{2+}}^{\text{op}}/f_{\text{Mg}}^{\text{op}}$ may be taken into account through the analysis of Saxena and Ghose (1971), but depending on the compositional details of the orthopyroxenes. The factor $f_{\text{Mg}}^{\text{bi}}/f_{\text{Fe}}^{\text{bi}}$ incorporates not only the mixing properties of Mg^{2+} and Fe^{2+} but also the effect of the variations in the Al/Si ratio (as well as other effects) on the exchange of Mg^{2+} and Fe^{2+} . The fact that there is only small deviation from the ideal distribution curve in the granulite facies rocks represented by Figures 1-4 is consistent with the small deviation from ideality in orthopyroxene (Saxena and Ghose, 1971) and with the general data for biotite which indicates a similar situation for this mineral as previously discussed. The same data also indicate a small perturbation effect of Al^{3+} , Fe^{3+} , and Si^{4+} .

The relation between the hydrogen fugacity, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, and the OH/O ratio (where O refers to oxygen in the OH position) in biotite may also be clarified by the method of partial activities. If we consider the oxidation of the annite component we have the reaction



If we note that the partial activities of Al and Si cancel, we have the following equation of equilibrium

$$K_d = \frac{P_{\text{H}_2}(X_{\text{Fe}^{3+}}^{\text{bi}})^2 X_{\text{Fe}^{2+}}^{\text{bi}} (X_{\text{O}}^{\text{bi}})^2}{(X_{\text{Fe}^{2+}}^{\text{bi}})^3 (X_{\text{OH}}^{\text{bi}})^2} \phi, \quad (7)$$

in which all the partial activity coefficients are incorporated into ϕ . Equation (7) then reduces to

$$K_d = P_{\text{H}_2} \left(\frac{X_{\text{Fe}^{3+}}^{\text{bi}}}{X_{\text{Fe}^{2+}}^{\text{bi}}} \right)^2 \left(\frac{X_{\text{O}}^{\text{bi}}}{X_{\text{OH}}^{\text{bi}}} \right)^2 \phi, \quad (8)$$

and where

$$\phi = \left(\frac{f_{\text{Fe}^{3+}}^{\text{bi}} f_{\text{O}}^{\text{bi}}}{f_{\text{Fe}^{2+}}^{\text{bi}} f_{\text{OH}}^{\text{bi}}} \right)^2. \quad (9)$$

If ϕ does not vary greatly, it may be seen how the ratios $X_{\text{Fe}^{3+}}^{\text{bi}}/X_{\text{Fe}^{2+}}^{\text{bi}}$, and $X_{\text{O}}^{\text{bi}}/X_{\text{OH}}^{\text{bi}}$ increase with decreasing values of P_{H_2} , corresponding to increased oxidation. In general, however, it will be necessary to deduce the values or functional form of the ϕ factors so that non-ideal behavior on the individual sites as well as perturbations of ions on other sites may be taken into account.

SOME PETROLOGIC INFERENCES

As was recognized by Wones and Eugster (1965) biotites are important potential indicators of intensive variables such as temperature, oxygen fugacity and water fugacity during petrogenesis. Indeed Wones and Eugster attempted to estimate P_{O_2} and P_{H_2O} for a number of igneous and metamorphic rocks. It is important to consider how such estimates depend on uncertainties in the measured values of the biotite compositions and on the estimates of the biotite component activities as a function of these compositions. One of the most important reactions in this regard is the following:



The general equilibrium constant for this reaction may be written as

$$K_e = \frac{a_K^{fs} a_{Fe}^{Mt} P_{H_2O}}{(a_{Fe}^{bi})^3 P_{O_2}^{1/2}} \quad (10)$$

where a_K^{fs} , a_{Fe}^{Mt} and a_{Fe}^{bi} are the activities of $KAISi_3O_8$, Fe_3O_4 , and of $\frac{1}{3} KFe_3AlSi_3O_{10}(OH)_2$ in feldspar, magnetite and biotite respectively. For purposes of illustration we assume that a_K^{fs} and a_{Fe}^{Mt} are unity, corresponding to pure potassium feldspar and magnetite. Then the logarithmic form of (10) becomes

$$\log K_e = \log P_{H_2O} - \frac{1}{2} \log P_{O_2} - 3 \log a_{Fe}^{bi} \quad (11)$$

If, as we have every reason to believe, biotite does not deviate greatly from ideality we may write (11) as

$$\log K_e = \log P_{H_2O} - \frac{1}{2} \log P_{O_2} - 3 \log X_{Fe}^{bi} \quad (12)$$

where X_{Fe}^{bi} is the mole fraction of $\frac{1}{3} KFe_3AlSi_3O_{10}(OH)_3$.

What is apparent from equations (11) and (12) is that while a_{Fe}^{bi} and X_{Fe}^{bi} are quite insensitive to variations in P_{O_2} estimates, P_{O_2} and P_{H_2O} are very sensitive to estimates of a_{Fe}^{bi} and X_{Fe}^{bi} . Although P_{H_2O} is not as sensitive as P_{O_2} , larger constraints are placed on P_{H_2O} in a practical sense. For example, if X_{Fe}^{bi} varies from 1 to 0.1 at constant T and P_{O_2} , P_{H_2O} must respond by varying by a factor of 10^3 . Thus estimates of P_{H_2O} in rocks are highly sensitive to any errors in a_{Fe}^{bi} . We have already seen that a_{Fe}^{bi} estimates by Wones and Eugster appears to be too small by many factors. Although these authors did not utilize the model which is represented by equations (11) and (12), the values of a_{Fe}^{bi} obtained by them fall well below those obtained from this

model. The end result is the same as if they had utilized this model with a large uncertainty in X_{Fe}^{bi} . It is likely that this result led them to infer consistently low values for the water fugacities of the rocks they studied.

In addition to leading to serious errors in the estimates of intensive parameters during petrogenesis, errors in the activities can also give false impressions of the state of equilibrium. Thus inferred great deviations from ideality might lead to the conclusion that Mg-rich biotites in certain acidic lavas were in equilibrium with much more iron rich phenocrysts of other ferromagnesian minerals, when as a matter of fact the late stage biotites are a response to late stage oxidation of iron.

In summary we might conclude that estimates of the conditions of petrogenesis are highly dependent on details of the biotite compositions and an estimate of activities and the solution models upon which these estimates depend. At the present time the weight of theory and data from natural assemblages greatly favors a model for biotite in which the activity a_{Fe}^{bi} of the component $\frac{1}{3} KFe_3AlSi_3O_{10}(OH)_2$ is close to the mole fraction X_{Fe}^{bi} .

REFERENCES

- ALBEE, A. L., E. BINGHAM, A. A. CHODOS, AND A. D. MAYNES (1965) Phase equilibria in three assemblages of kyanite-zone pelitic schists, Lincoln Mountain Quadrangle, Central Vermont. *J. Petrology* 6, 246-301.
- ANNERSTEN, HANS (1968) A mineral chemical study of a metamorphosed iron formation in Northern Sweden. *Lithos* 1, 374-397.
- CHINNER, G. A. (1960) Pelitic gneisses with varying ferrous/ferric ratios from Glen Clova, Angus, Scotland. *J. Petrology* 1, 178-217.
- DODGE, F. C. W., V. C. SMITH, AND R. E. MAYS (1969) Biotites from granitic rocks of the central Sierra Nevada batholith, California. *J. Petrology* 10, 250-271.
- EUGSTER, H. P., AND D. R. WONES (1962), Stability relations of ferruginous biotite, annite. *J. Petrology* 3, 82-125.
- HOUNSLOW, A. W., AND J. M. MOORE, JR. (1967) Chemical petrology of Grenville schists near Fernleigh, Ontario. *J. Petrology* 8, 1-28.
- KRETZ, RALPH (1959) Chemical study of garnet, biotite, and hornblende from gneisses of southwestern Quebec, with emphasis on distribution of elements in coexisting minerals. *J. Geol.* 67, 371-402.
- (1961) Some applications of thermodynamics to existing minerals of variable composition. Examples: orthopyroxene-clinopyroxene and orthopyroxene-garnet. *J. Geol.* 69, 361-386.
- (1960) The distribution of certain elements among coexisting calcic pyroxenes, calcic amphiboles and biotites in skarns. *Geochim. Cosmochim. Acta* 20, 161-191.

- LARSEN, E. S. JR., AND W. M. DRAISIN (1948) Composition of the minerals in the rocks of the Southern California batholith. *Internat. Geol. Cong. Rep. 18th Session, Great Britain* 2, 66-79.
- MUELLER, R. F. (1961), Analysis of relations among Mg, Fe and Mn in certain metamorphic minerals. *Geochim. Cosmochim. Acta* 25, 267-296.
- (1962), Energetics of certain silicate solid solutions. *Geochim. Cosmochim. Acta* 26, 581-598.
- (1969) Hydration, oxidation and the origin of the calc-alkali series. *NASA TN D-5400*.
- (1963) Interaction of chemistry and mechanics in magmatism. *J. Geol.* 71, 759-772.
- (1964) Theory of immiscibility in mineral systems. *Mineral. Mag.* 33, 1015-1023.
- PRIGOGINE, I., AND R. DEFAY (1951) *Chemical Thermodynamics* (English Translation by D. H. Everett, 1954). Longmans Green, London.
- SAXENA, S. K. (1968a) Distribution of elements between coexisting minerals and the nature of solid solution in garnet. *Amer. Mineral.* 53, 994-1014.
- (1968b) Chemical study of phase equilibria in charnockites, Varberg, Sweden. *Amer. Mineral.* 53, 1674-1695.
- , AND SUBRATA GHOSE (1971) Mg^{2+} - Fe^{2+} order-disorder and the thermodynamics of the orthopyroxene crystalline solution. *Amer. Mineral.* 56, 532-559.
- SEN, S. K., AND K. R. CHAKRABORTY (1968) Magnesium-iron exchange equilibria in garnet-biotite and metamorphic grade. *Neues Jahrb. Mineral.* 108, 181-207.
- STEINFINK, H. (1962) The crystal structure a trioctohedral mica phlogopite. *Amer. Mineral.* 47, 886-
- WONES, D. R., AND H. P. EUGSTER (1965) Stability of biotite: experiment, theory and application. *Amer. Mineral.* 50, 1228-1272.

American Mineralogist
Vol. 57, pp. 316-317 (1972)

STABILITY OF BIOTITE: A REPLY

DAVID R. WONES¹, *Department of Earth and Planetary Sciences,
Massachusetts Institute of Technology, Cambridge,
Massachusetts 02139*

Mueller's (1972) proposed for an ideal solution model for biotite stabilities is sound, and his model is correct for biotites with low Fe^{3+} contents. Wones, Burns, and Carroll (1971) redetermined the stability of the end member, annite, $KFe_3AlSi_3O_{10}(OH)_2$. New data on Ni-NiO (Huebner and Sato, 1970) and Fe_2SiO_5 - SiO_2 - Fe_3O_4 (Wones and Gilbert, 1969) are also available. This led to a correction of the so-called