Compositional variation of muscovite in medium- to high-grade metapelites of northwestern Maine

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Abstract

Detailed chemical analyses of muscovite from high-Al metapelites of lower garnet zone to upper sillimanite zone show a number of systematic changes with metamorphic grade. However, the pattern of changes for several elements in muscovite from the lower garnet zone to upper staurolite zone is markedly different from that for the upper staurolite zone to upper sillimanite zone. Although Si decreases and Ti increases across the whole metamorphic spectrum, in the upper staurolite zone Al^{VI}, ΣAl, and $Na/(Na + K)$ attain maxima and Fe, Mg, and $\Sigma(Mg + Fe)$ attain minima.

In the garnet and staurolite zone rocks, the systematic variations in the composition of the tetrahedral and octahedral sites of muscovite can be attributed to T-controlled continuous reactions which cause a decrease in the celadonite content of muscovite. A secondary control is a small expansion of the Ti saturation limit of muscovite.

In the range from upper staurolite zone to upper sillimanite zone, the celadonite content of muscovite seems little affected by increase of T, primarily because the presence of sillimanite results in Al-saturated muscovite. However the Ti saturation limit in muscovite expands markedly over this metamorphic range, and the requirement of charge balance for the Ti^{4+} cation appears to control the other tetrahedral and octahedral cation changes.

Introduction

In order to understand the details of metamorphic reactions, petrologists have shown considerable interest in the compositional variation of solid-solution minerals. In a previous paper (Guidotti, 1973), the writer discussed compositional variation of muscovite in upper staurolite to upper sillimanite zone pelitic schists in northwestern Maine. This paper extends the range of continuously covered grades down to the lower part of the garnet zone.

The new analyses discussed in this study and those previously reported were all done in the same laboratory by the same method and by the same analyst (C. V. G.). This is an important factor, as some of the observed compositional trends involve only small changes. Guidotti and Sassi (1976) have noted the problems encountered in trying to integrate analytical data obtained in different laboratories when only small variations occur in the compositional variable [*e.g.* $\Sigma(Mg + Fe)$].

This paper will emphasize cation variation in the octahedral and tetrahedral sites of muscovite as a function of metamorphic grade. Aspects such as the $Na/(Na + K)$ ratio have already been discussed in Guidotti and Sassi (1976).

Metamorphic environment of specimens

The upper staurolite zone considered by Guidotti (1973) is identical with that of this paper. Figure 1 shows the distribution of grades below the upper staurolite zone. Only two distinct mineral facies are shown: garnet zone and staurolite zone. Based on the change in the AFM diagram (Thompson, 1957) showing the mineral compatibilities in each zone (Guidotti, 1970a), the two zones are related by the discontinuous reaction:
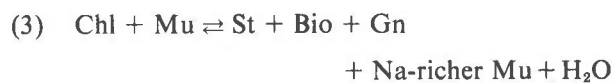
(1) $Mg-Chl^1 + Gn + Mu \rightleftarrows St + Bio + Qz$

$$+ \text{Na-richer Mu} + H_2O$$

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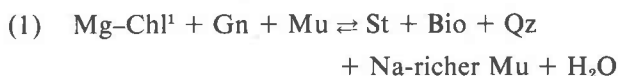
[1] Mu = muscovite; Qz = quartz; Bio = biotite; St = staurolite; Si = sillimanite; Gn = garnet; Pl = plagioclase; Chl = chlorite; Il = ilmenite; Gr = graphite; Po = pyrrhotite.

By also considering continuous reactions as reflected by changes in the composition of solid-solution phases in limiting assemblages (and also to some extent modal changes), it has been possible to contour the progressive increase in metamorphism *within* each grade. Figure 1 shows the garnet zone subdivided into a lower, middle, and upper garnet zone, and the staurolite zone into a lower and upper portion. The continuous reactions are:

Garnet zone: in the AFM assemblage Gn + Bio + Chl:

(2) Chl + Mu ⇌ Gn + Bio + Na-richer Mu + H₂O

Staurolite zone: in the AFM assemblage St + Bio + Chl + Gn:

(3) Chl + Mu ⇌ St + Bio + Gn

+ Na-richer Mu + H₂O

As discussed in Thompson (1957, 1972) these reactions should cause Mg-enrichment of the ferromagnesian phases participating in the reactions.

In the garnet zone the following observations reflect reaction (2) and provide the basis for the contours shown in the garnet zone on Figure 1 (see Guidotti, 1970a for details).

(a) In the upper garnet zone chlorite becomes Mg-richer as indicated by its birefringence colors (Albee, 1962). Moreover, it decreases modally.

(b) Biotite increases modally and becomes Mg-richer (Guidotti and Cheney, in preparation).

(c) Based on chemical analyses and a large number of d(002) measurements, muscovite becomes progressively Na-richer.

In the staurolite zone continuous reaction (3) is reflected by the following:

(a) Chlorite decreases modally and, based on changes in birefringence colors, becomes Mg-richer.

(b) Biotite increases modally and becomes Mg-richer.

(c) Based on chemical analyses and many d(002) measurements, muscovite continues to become Na-richer.

(d) Staurolite increases modally.

The contour dividing the staurolite zone into an upper and lower portion is based mainly on changes in the muscovite Na/(Na+K) ratio. However, the other changes would have been equally applicable.

Guidotti and Sassi (1976) have reviewed the difficulties of comparing muscovite data from specimens with non-equivalent assemblages. They note that bulk Al₂O₃ is an important control on muscovite
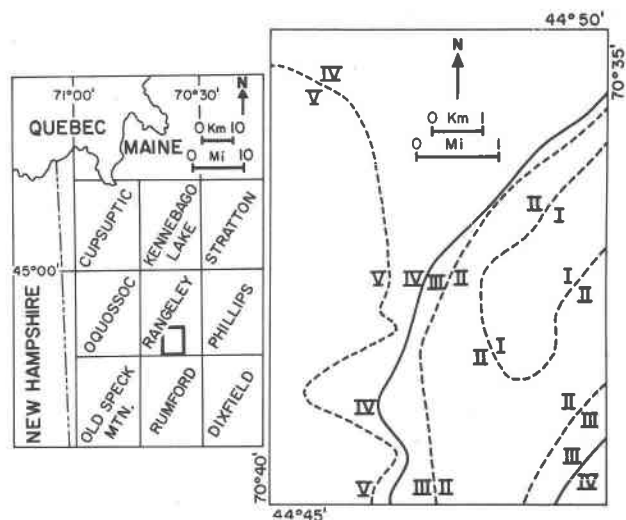

Fig. 1. Distribution of metamorphic grades in the south–central 1/9th of the Rangeley 15' quadrangle, Maine. Zones I, II, and III are lower, middle, and upper garnet zones respectively. Similarly, zones IV and V are lower and upper staurolite zones. See text for definition of these zones.

composition when the muscovite is from a non-limiting AKNa assemblage, *e.g.* muscovite + plagioclase as in the garnet and staurolite zones of this report (see Thompson, 1961 for a discussion of the AKNa system). In such cases compositional variables such as Na/(Na+K), ΣAl, *etc.* are not rigorously a function of metamorphic grade. Nonetheless, as shown by Guidotti (1973) and Guidotti and Sassi (1976), in non-limiting assemblage rocks with relatively high bulk Al₂O₃, muscovite compositions are quite close to being a function of grade.

Although there is some variation of assemblages in the garnet and staurolite zones, all of the new specimens considered in this study are relatively high-aluminum types, as indicated by the presence of garnet and/or staurolite (see above for assemblages) and abundant muscovite. Moreover, in the sillimanite zone these same rocks have sillimanite present as a coexisting phase. Thus the muscovite from the garnet and staurolite grade rocks is close to being Al-saturated. In terms of the muscovite + plagioclase assemblage of an AKNa diagram, these specimens plot near the tie line forming the upper boundary of the two-phase field (see Fig. 2B of Guidotti, 1973).

In view of the high Al₂O₃ in all rocks of this study, the writer concludes that one is justified in comparing the compositions of the muscovites in them as a function of grade. Moreover, the systematic results discussed below certainly support such a proposition.

Because much of the discussion also involves the effects of variation of Ti content in muscovite, it is important to note that all specimens contain ilmenite. Hence, all of the silicate phases should be Ti-saturated. Furthermore, because graphite is present in most specimens, and hematite and magnetite are absent, it can be assumed that the amount of Fe^{3+} will be low and uniform relative to Fe^{2+}.

Analytical data

All analyses were carried out by electron microprobe, using the same instrument, procedures, and standards as used for the muscovite anlayses reported in Guidotti (1973). The analyses presented in Tables 1A–1E[2] are estimated to have an analytical error of about two percent for elements amounting to more than about two percent of the sample. The relative amounts of elements analyzed together (*e.g.* Fe, Ti, Mg) have a similar error, even for lower concentrations (Albee, 1972). The anhydrous analytical totals in Tables 1A–1E are grouped near 95 to 96 percent, so that addition of 4 to 5 percent H_2O produces analytical totals near 100 percent.

Figure 2 summarizes the data according to metamorphic intensity for the lower garnet through upper staurolite zones. Especially notable is the relative uniformity of the data for a given cation within a given metamorphic grade. Comparison of the data for the upper staurolite zone on Figure 2 with that for the

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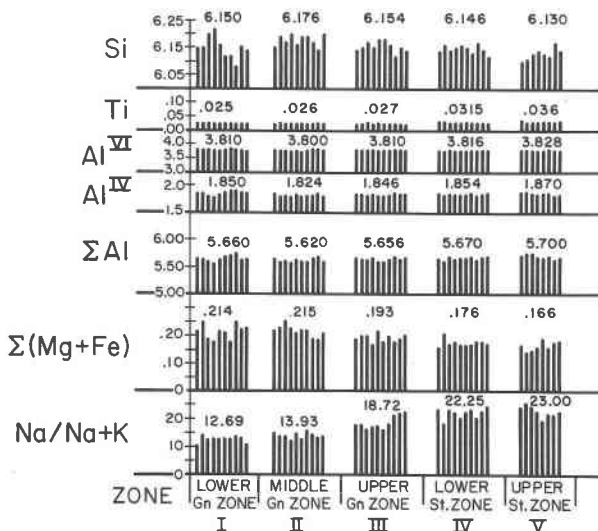
[2] Tables 1A–1E are on file with ASIS/NAPS.

Fig. 2. Summary of muscovite analytical data (zones I–V) based on formula proportions. Each bar represents one specimen. Number above bars is the average for the group.

same zone presented by Guidotti (1973, Fig. 3) shows that the average values are quite similar for both data sets. Thus, one is justified in combining the two sets of data and considering the compositional variation of muscovite, grade by grade, from lower garnet zone (Zone I) through upper sillimanite zone (Zone VIII). Table 2 gives the average formulas of the muscovites over this range of metamorphism, and Figure 3 shows graphically the average values of several of the compositional variables. As seen by the error bars on Figure 3, with the exception of a few cases in Zone I and some of the ΣVI values, the data variations are quite uniform from zone to zone. In Figure 3 and Table 2 the upper staurolite zone values represent a combination of data from this study and that of Guidotti (1973).

Discussion of analytical results

Interesting compositional trends for muscovite shown on Table 2 and Figure 3 are:

(1) Si^{4+} decreases (hence, Al^{IV} increases) fairly systematically with increase in grade—especially if one considers the range from Zone II to VIII.

(2) Al^{VI} increases systematically from Zone II to V and then decreases quite distinctly from Zone V to VIII.

(3) Mg^{VI}, Fe^{VI}, and $\Sigma(Mg+Fe)$ pass through minima in Zone V, but the effect is less pronounced for Mg^{VI}. Concomitantly, the Mg/Fe ratio goes through a broad maximum. This latter trend is largely a reflection of a similar trend for the Mg/Fe ratio of biotite (Guidotti and Cheney, in preparation).

(4) Ti^{VI} increases very slightly from Zones I to IV but then increases more rapidly in a regular fashion through Zone VIII.

(5) The number of occupied octahedral sites decreases fairly sharply from Zone I to V and then may increase a small amount progressively from Zone V to VIII. In contrast, the number of occupied alkali sites may rise slightly from Zone I to VIII.

(6) The sum of $(Al^{IV} + Al^{VI})$ passes through a moderate maximum in Zone V, especially if we disregard the average value for Zone I.

(7) The ratio Na/(Na+K) increases up to Zone V and then decreases. Aspects of this pattern have been discussed in some detail by Guidotti (1970b, 1974) and Guidotti and Sassi (1976).

It should be noted that the values given for Zone I and II could have been combined, because the difference in metamorphic grade between these two zones is quite small. Such a combination would further emphasize most of the trends discussed above.

Table 2. Summary of average muscovite formulas (based on 22 oxygen) for lower garnet zone through upper sillimanite zone in northwestern Maine

ZONE[1]	I	II	III	IV	V	VI	VII	VII'	VIII
Si^{IV}	6.150	6.176	6.154	6.146	6.135	6.142	6.123	6.135	6.118
Al^{IV}	1.850	1.824	1.846	1.854	1.865	1.858	1.877	1.865	1.882
Al^{VI}	3.810	3.800	3.810	3.816	3.825	3.804	3.791	3.778	3.755
Fe	.110	.110	.092	.081	.074	.081	.081	.095	.098
Mg	.104	.103	.101	.095	.088	.0975	.103	.0983	.108
Mn	.0016	.0016	.0014	.0011	.0012	.0015	.0018	.0014	.002
Ti	.025	.026	.027	.0315	.036	.042	.051	.055	.068
Σ	4.051	4.041	4.031	4.025	4.024	4.026	4.028	4.028	4.031
K	1.644	1.616	1.537	1.478	1.453	1.501	1.551	1.535	1.630
Na	.239	.263	.354	.423	.447	.404	.363	.375	.270
Ba	.010	.010	.010	.010	.010	.010	.010	.001	.014
Σ	1.893	1.889	1.901	1.911	1.910	1.915	1.924	1.920	1.914
Σ Al	5.660	5.620	5.656	5.670	5.690	5.662	5.668	5.643	5.637
Na/Na + K	12.69	13.93	18.72	22.25	23.52	21.20	18.96	19.63	14.20
Σ Mg + Fe	.214	.215	.193	.176	.162	.179	.184	.193	.206
Mg/Fe[2]	.926	.912	1.101	1.182	1.196	1.208	1.270	1.035	1.102

The patterns of element variation shown on Figure 3 suggest that some of the mutual substitutions of cations are quite systematic. Hence, one may try tentatively to identify and understand these substitutions. The shapes of several of the trends shown on Figure 3 are marked by maxima or minima in Zone V. Moreover, it is in Zone V that Ti starts to show a marked increase. These features suggest that the mutual cation substitution schemes for I to V and V to VIII are different.

The substitution models suggested below are only the more obvious major trends, in that they take into account most of the observed cation changes shown on Figure 3. That they cannot account for all of the variations suggests that additional, smaller-magnitude cation substitutions are present and superimposed on the more readily recognized major trends. Because these small-scale variations are probably in-terrelated with each other as well as with the major trends, they will be quite complicated and obscure.

Several additional factors which add to the difficulty of determining the small-scale trends and even the major trends include: (1) the variations shown in Table 2 and on Figure 3 involve quite small numbers, [see also Fig. 2 and Guidotti (1973, Fig. 3)]; (2) extraneous components (*e.g.* Zn, Li, *etc.*) may be present in small amounts and would influence the details of any charge-balance considerations; (3) the possible presence of some Fe^{3+} would also influence charge-balance aspects of the major and minor substitution trends. Although arguments were presented above suggesting low and uniform amounts of Fe^{3+} relative to Fe^{2+}, this has not been demonstrated by means of chemical analyses; (4) the observed variation in the number of occupied VI sites also increases the complexity of the possible substitution models.

Table 2. (continued)

(1) Summary of Zones

    I.   Lower garnet zone - 9 specimens with the AFM assemblage
          Gn + Bio + Chl and 1 specimen with Bio + Chl.

    II.   Middle garnet zone - 8 specimens with the AFM assemblage
          Gn + Bio + Chl and 2 specimens with Bio + Chl.

    III. Upper garnet zone - 10 specimens with the AFM assemblage
          Gn + Bio + Chl.

    IV.   Lower staurolite zone - 10 specimens with the AFM
          assemblage St + Gn + Bio + Chl.

    V.   Upper staurolite zone - 13 specimens with the AFM
          assemblage St + Gn + Bio + Chl; 8 specimens from this
          study and 5 from Guidotti (1973).

    VI.   Transition zone - from Guidotti (1973): 8 specimens with
          the AFM assemblage Si + St + Gn + Bio $\pm$ Chl.

    VII. Lower sillimanite zone, Rangeley area; from Guidotti
          (1973): 7 specimens with the AFM assemblage Si + St
          + Gn + Bio.

    VII'. Lower sillimanite zone, Oquossoc area; from Guidotti
          (1973): 6 specimens with the AFM assemblage Si + St +
          Gn + Bio.

    VIII. Upper sillimanite zone, Oquossoc area; from Guidotti
          (1973): 6 specimens with the AFM assemblage Si + Gn
          + Bio.

(2) Omitting the Bio + Chl assemblages in Zones I and II for the
    Mg/Fe ratio.

Substitution model for Zones I to V

Despite the difficulties listed above, a consideration of Table 3 and Figure 3 suggests that the observed changes from Zone I to V are largely due to decrease in the celadonite content of the muscovite. Such a change would be a function of increased grade (*i.e. T*) and occur by the substitution $Si^{IV}Mg^{VI} \rightleftarrows Al^{IV}Al^{VI}$. Decrease of celadonite content in muscovite as a function of increased T (or decreased P) has long been recognized (*e.g.* see Ernst, 1963) and has recently been reviewed in some detail by Guidotti and Sassi (1976).

In the context of the celadonite substitution equation given above, it should be noted that the increase of Al^{VI} numerically balances the decrease of Si^{IV}. Furthermore, as developed by Guidotti (1974) and Guidotti and Sassi (1976), continuous reactions such as (2) and (3) produce a celadonite-poorer muscovite, because in effect they transfer Al_2O_3 from the phases making up the assemblage of the AFM system into the muscovite + plagioclase assemblage of the AKNa system. Moreover, this effect should produce an increase in the Na/(Na+K) ratio of the muscovite—

which is in fact observed. Thus, decrease of the celadonite content of muscovite from Zone I to V is consistent with the expected effects of continuous reactions (2) and (3), which are based on observational data and theoretical predictions.
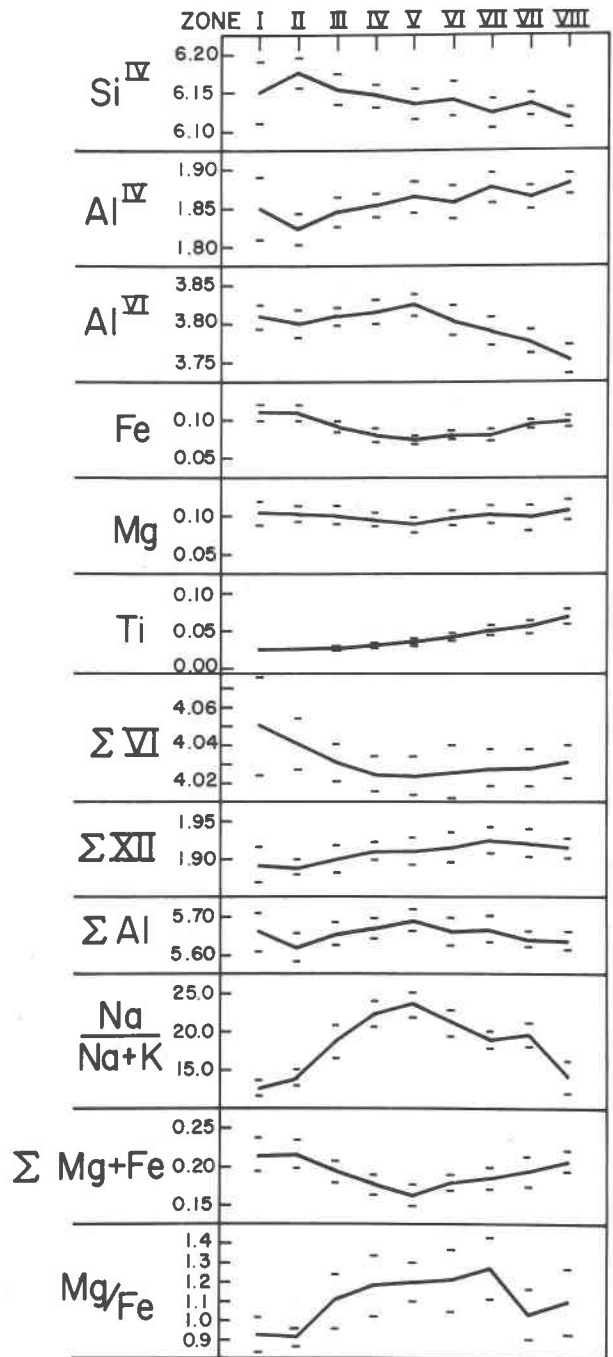

Fig. 3. Variation of average muscovite composition in high-Al specimens as a function of metamorphic grade (zones I–VIII). Data points from Table 2. Error brackets indicate one standard deviation for the given group.

However, decrease in celadonite content of muscovite accounts for only 0.015 of the 0.052 decrease in the $\Sigma(Mg+Fe)$. An additional 0.022 decrease in the $\Sigma(Mg+Fe)$ would seem, for charge-balance reasons, to be in response to the 0.011 increase of Ti^{4+}. Presumably Ti substitutes for Mg and Fe *via* $2(Mg,Fe) \rightleftharpoons Ti,vacancy$. This suggestion is at least qualitatively consistent with the observed 0.027 decrease in the number of occupied VI sites (*i.e.* a closer approach to a purely dioctahedral mica).

The two substitutions discussed above appear to be the most important ones for muscovite over the range from Zone I to V. Moreover, they are readily attributable to petrologic factors such as increase of T which drives reactions (2) and (3) to the right, thereby producing a celadonite-poorer muscovite. Increase of the Ti saturation limit of muscovite can readily be attributed to change of T also.

Substitution model for Zones V to VIII

At first impression, the increase of $\Sigma(Mg+Fe)$ and decrease of Al^{VI} (see Table 3 and Fig. 3) would seem to imply an increase in the celadonite content of muscovite from Zone V to VIII. In fact, however, Si^{IV} decreases instead of showing the increase expected *via* the celadonite substitution, $Mg^{VI}Si^{IV} \rightleftharpoons Al^{VI}Al^{IV}$. Thus, if celadonite content of muscovite is defined (as commonly done) in terms of the amount by which the Si^{IV}/Al^{IV} ratio exceeds 3, then there is a decrease in the celadonite content of muscovite from Zone V to VIII. Guidotti (1973) and Cheney (1975) have discussed some aspects of the substitutions occurring from Zones V to VIII.

From the data given in Table 3 it would appear that because of charge-balance requirements, increase of Ti^{4+} in VI sites controls most of the other observed cation changes. One substitution would be $Ti^{VI},(Mg,Fe)^{VI} \rightleftharpoons 2Al^{VI}$, and the other would be $Ti^{VI} Al^{IV} \rightleftharpoons Al^{VI}Si^{IV}$. Concomitant operation of these two substitutions seems to account for much of the observed variation in the tetrahedral and octahedral sites of muscovite from Zone V to VIII. Because only an irregular low decrease is shown by the Si^{IV} curve on Figure 3 for Zone V to VIII, the first of these two substitutions is probably the more important one.

In either case it seems that a rapidly expanding saturation limit for Ti in muscovite from Zone V to VIII is the most important control on the cation changes in the octahedral and tetrahedral sites. The marked increase of Ti in muscovite from Zone V to VIII is mirrored by an even more pronounced increase of Ti in the coexisting biotite. Details of the

Table 3. Changes in octahedral and tetrahedral site occupancy for muscovite in (A) zones I to V and (B) V to VIII

	(A) Zones I to V.	(B) Zones V to VIII.
Si^{IV}	−0.015	−0.017
Al^{IV}	+0.015	+0.017
Al^{VI}	+0.015	−0.070
$\Sigma(Mg+Fe)^{VI}$	−0.052	+0.044
Ti^{VI}	+0.011	+0.032
# of filled VI Sites	−0.027	+0.007

distribution of Ti between coexisting muscovite and biotite have been discussed by Guidotti *et al.* (1977).

Summary

This paper has extended the range of coverage of detailed muscovite analyses in northwestern Maine in a downgrade direction to the lower-grade portion of the garnet zone. This extension of coverage enables consideration of muscovite compositional variation over a wide spectrum of metamorphic grades—lower garnet zone to upper sillimanite zone.

The pattern of tetrahedral and octahedral cation variation from Zone I to V is quite different from that of Zone V to VIII. From Zones I to V continuous reactions (2) and (3), which proceed to the right with increase of T and cause a decrease in the celadonite content of muscovite, seem to be the main controls on the observed changes of muscovite composition. A secondary control appears to be a small increase in the Ti saturation limit of muscovite.

Above Zone V sillimanite is present, and thus the coexisting muscovite is then truly Al-saturated. As a result, the celadonite content of muscovite changes little with further rise of T. Instead the controlling factor on the mutual cation substitutions appears to be the *marked* increase in the Ti saturation limit of muscovite as a function of increased T.

The substitution models suggested above explain the maxima and minima shown on Figure 3 for some of the cations in muscovite over the range from lower garnet zone to upper sillimanite zone.

Acknowledgments

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