Chemical formulae and activity models for biotite, muscovite, and chlorite applicable to pelitic metamorphic rocks

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Abstract

For several reasons, the use of simple formulae for phyllosilicates involved in medium- and high-grade metamorphism of pelites leads to problems: (1) such formulae are not accurate representations of natural minerals; (2) they may lead to errors and inconsistencies in calculating thermodynamic quantities; (3) they do not adequately express the nature of experimental equilibria; and (4) in addition to varying with the nature of coexisting minerals, formulae of the phyllosilicates vary with metamorphic grade. In an effort to reduce these problems, analyses of natural minerals have been used to determine realistic "end-member" formulae for phyllosilicates occurring in pelitic rocks saturated with Al and Si. The formulae are: (1) biotite, $K_{0.91}Fe_{2.42}Al_{1.83}Si_{2.69}O_{10}(OH)_2$; (2) muscovite, $K_{0.95}Fe_{0.08}Al_{2.91}Si_{3.04}O_{10}(OH)_2$; and (3) chlorite, $Fe_{4.54}Al_{2.92}Si_{2.54}O_{10}(OH)_8$. It is concluded that activity models for these minerals should be based on solid-solution-free end members, and activity corrections should be made on both experimental and naturally occurring phyllosilicates. In cases of pelitic experimental equilibria where product compositions have not been measured, the above formulae may be used to determine activities of the pure end-member components in experimental product minerals.

Introduction

In the quantitative study of pelitic mineral reactions, the phyllosilicates biotite, muscovite, and chlorite pose problems because of their variable compositions both in nature and in experimental systems. In addition to Mg/Fe substitution all three minerals are variable in Al/(Fe+Mg) and the micas have octahedral and probably 12-fold site deficiencies. The Fe or Mg end members of these phases in pelitic rocks cannot be expressed in simple formulae (Thompson, 1976; Holdaway and Lee, 1977). It follows that equations for chemical equilibria in pelitic rocks do not have whole-member coefficients if they are based on accurate phyllosilicate compositions.

In writing equations to describe experimental equilibria, generate secondary thermodynamic data, or describe model reactions in pelitic metamorphic rocks, some workers have used simple end-member formulae for biotite, muscovite, and chlorite. Such an approach is valid if care is taken to properly evaluate the activity of each simple component in both experimental and natural systems. Nevertheless, several problems can arise.

First, end-member compositions of minerals relating to experimental and natural equilibria may differ. This leads to different coefficients for experimental and natural equilibria involving the same set of minerals. Evaluating equilibrium constants becomes a problem because the two versions of the same equilibrium relation lead to different formulations. Some of the compositional differences between natural and experimental analogs may not be real, but may only exist because of the difficulty of measuring experimental product compositions.

A second and more serious problem is that unknown experimental end-member compositions, or end-member compositions which vary depending on the particular reaction involved, may produce errors in the retrieval of thermodynamic quantities for minerals. Helgeson *et al.* (1978) have used four reactions involving various combinations of phlogopite, chlorite, cordierite, muscovite, Al silicate, forsterite, spinel, and enstatite to retrieve standard free energies
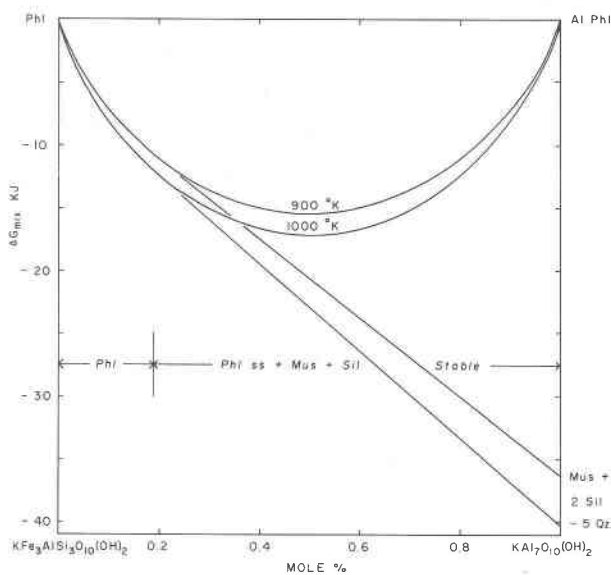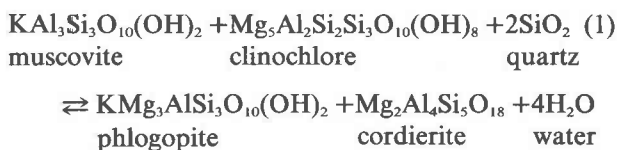
Fig. 1. Free energy of mixing diagram for phlogopite in a pelitic rock system based on three-site ideal solution model. In pelitic rocks the stable Al phlogopite would have about 19% replacement of Mg and Si by Al as shown by results of this paper.

Mineral abbreviations for Figs. 1 and 3: Phl = phlogopite, Mus = muscovite, Sil = sillimanite, Ann = annite, Alm = almandine, Qz = quartz.

for cordierite, spinel, chlorite, and phlogopite. Phlogopite in their balanced equations contained 1 Al and chlorite contained 2 Al. Of the four reactions two were saturated with Al silicate and quartz and two were saturated with cordierite and forsterite. The Al/Mg and Al/Si ratios in phlogopite and chlorite are expected to be higher in the first two reactions than in the last two. If we consider only the two reactions involving Al silicate and quartz, the phlogopite probably contained about 1.8 Al instead of 1 Al and the chlorite contained about 2.9 Al instead of 2 Al, as shown later in this report. Figure 1 illustrates a possible G–X configuration for phlogopite coexisting with Al silicate, muscovite, and quartz, which assumes a 3-site ideal mixing model. Although the use of an incorrect formula simply means that the true composition is expressed as a mixture of phlogopite, muscovite, and Al silicate, this approach does not account for up to 12 kJ free energy of mixing in phlogopite solid solution. For the first two reactions, if all the other free energies are internally consistent, the calculations will lead to a free energy 5 kJ too negative for simple phlogopite. On the other hand the last two equilibrium relations should involve nearly pure phlogopite, whose free energy should be about 5 kJ less negative than that determined from

the last two reactions. Similar arguments may be made for chlorite. The net effect is that the four free energies obtained from these equilibria are in some doubt. The problem could be resolved by estimating compositions of the experimental phlogopite and chlorite for each equation and calculating activities for each to relate to the simple end-member formulae. Note that when the thermodynamic results of Helgeson et al. were tested on several other experimental reactions, most of the calculated curves did not fit the experimental curves. As discussed by them (p. 175) there are also several other possible reasons for this failure.

A third and closely related problem is that even though an experimentalist may begin with simple biotite or chlorite compositions, the effective reaction being studied probably involves mineral compositions more like the stable compositions than the starting ones. Consider the reaction

$$KAl_3Si_3O_{10}(OH)_2 + Mg_5Al_2Si_3O_{10}(OH)_8 + 2SiO_2 \quad (1)$$
muscovite   clinochlore   quartz

$$\rightleftarrows KMg_3AlSi_3O_{10}(OH)_2 + Mg_2Al_4Si_5O_{18} + 4H_2O$$
phlogopite   cordierite   water

studied by Seifert (1970). As phlogopite grew in its stability field, it was saturated in Al and Si from coexisting cordierite and quartz. Similarly, the chlorite must have been Al-rich as it grew in experiments in the chlorite stability field. When the initial chlorite was in the chlorite stability field it must have started changing composition by diffusion of ions into the rims of mineral grains. Under conditions close to the equilibrium for the reaction, the compositional changes in chlorite and phlogopite probably proceeded faster, promoted by larger free energy differences, than the growth of products or reactants. Two conclusions may be drawn: (1) The compositions of phases involved in experimental reactions are likely to be closer to the stable compositions than to the initial compositions. (2) One should be somewhat skeptical of experimental work in which initial compositions were far from the stable compositions.

A fourth problem is that minerals such as those being discussed here have compositions which depend not only on the coexisting minerals but also on metamorphic grade. For Fe or Mg end members of biotite, muscovite, and chlorite, these effects appear to be somewhat smaller than effects due to the mineral assemblage.

Some of these problems could be resolved by determining Fe or Mg "end-member" compositions for

biotite, muscovite, and chlorite applicable to pelitic mineral assemblages. These may then be related to simple end members through activity relationships. In order to obtain these "end-member" compositions the following procedures were used. (1) From chemical analyses compositions were expressed in terms of the major components K_2O, FeO, Al_2O_3, SiO_2, and H_2O. Each element which proxies for a major element was replaced by the same amount of the major element. Replacement of Fe by Mg yields the appropriate Mg "end member." (2) Microprobe analyses were taken of phyllosilicates from medium- and high-grade pelitic rocks. Thus muscovites with considerable phengitic component were ruled out as well as possible low-grade variations of Al/(Fe+Mg) in biotite and chlorite. (3) All chemical analyses were selected from rocks containing quartz, ilmenite, muscovite or K feldspar, and staurolite, cordierite, or Al silicate. Such assemblages are typical of many pelitic rocks and of experimentally determined mineral equilibria. Many such rocks contain graphite, but rocks containing magnetite, hematite, or abundant sulfides were excluded. This assured saturation with Si, Al, and Ti, and minimized Fe_2O_3. The resultant formulae are most applicable to rocks with Fe/Mg near one, but Fe-rich and Mg-rich rocks and mineral equilibria should be compatible with the formulae because the effect of Mg/Fe ratio on Al content of these minerals is negligible (Guidotti et al., 1975; this study). (4) The compositions of calculated "end members" were not allowed to vary with grade. A single average composition was assumed for each. Much of the variation which occurs with grade is in Ti content and K/Na ratio, which are adequately handled by the activity model. (5) Finally, it was as-

sumed that H^+ does not replace K^+ in 12-fold sites of micas. This assumption is necessitated by the absence of evidence to the contrary. Saturation with Al and Si consistently produces excess charge in the combined octahedral and tetrahedral sites of micas which necessitates small 12-fold site deficiencies. Such deficiencies are minor or absent in micas from rocks which are not Al-saturated. Part or all of this 12-fold site deficiency could be a function of analytical procedures e.g. Na, K volatilization or choice of standards. Because it occurs in both micas it partly cancels out in equilibrium calculations.

Chemical formulae

The analyses used are all recent electron microprobe analyses from pelitic rocks of New England, made by several investigators using different microprobes, standards, and data reduction schemes.

Biotite

For biotite composition, chemical analyses with atomic Mg/(Mg+Fe) between 0.40 and 0.55 were taken from Guidotti et al. (1975), Holdaway and Novak (in preparation), and Tracy (1978). The analyses of Guidotti et al. are from the staurolite and sillimanite zones of the Rangeley and Old Speck Mountain Quadrangles in western Maine. The rocks studied by Holdaway and Novak are from the staurolite, sillimanite, and K feldspar–sillimanite zones in the region between Augusta, Rumford, and Phillips in west-central Maine. All these rocks contain muscovite. The analyses of Tracy are from the K feldspar–sillimanite zone in the Quabbin Reservoir area in west-central Massachusetts; about two thirds of the rocks contain muscovite. These rocks appear to

Table 1. Average and standard deviation for biotite compositions from three metamorphic regions, in order of increasing average grade*

| Composition category	Guidotti, Cheney, Conatore, 1975 16 analyses	Holdaway, Novak, in preparation 15 analyses	Tracy, 1978 16 analyses
Si^{iv}	5.368 ± 0.042	5.383 ± 0.046	5.373 ± 0.086
Al^{iv}	2.632 ± 0.042	2.617 ± 0.046	2.627 ± 0.086
$(Al+Cr)^{vi}$	0.917 ± 0.042	0.876 ± 0.063	0.760 ± 0.074
Ti^{vi}	0.188 ± 0.012	0.248 ± 0.070	0.382 ± 0.037
$(Fe+Mg+Mn+Zn)^{vi}$	4.728 ± 0.073	4.541 ± 0.123	4.472 ± 0.126
$(K+Na+2Ca+2Ba)^{xii}$	1.702 ± 0.029	1.855 ± 0.080	1.852 ± 0.070

* Based on 22 oxygens per formula unit.

Table 2. Linear regression of 47 biotite analyses on Ti*

Composition category	Average composition	Composition at Ti = 0	Slope	Correlation coefficient	Accepted formula
Si^{iv}	5.371	5.359	0.038	0.06	5.38
Al^{iv}	2.629	2.641	-0.038	-0.06	2.62
$(Al+Cr)^{vi}$	0.839	1.042	-0.721	-0.74	1.04
Ti^{vi}	0.281	0	-	-	0
$(Fe+Mg+Mn+Zn)^{vi}$	4.570	4.926	-1.264	-0.74	4.84
$(K+Na+2Ca+2Ba)^{xii}$	1.808	1.662	0.512	0.54	1.82

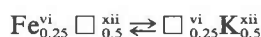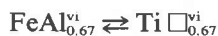*Accepted formula is $K_{0.91}Fe_{2.42}Al_{0.52}Al_{1.31}Si_{2.69}O_{10}(OH)_2$ on 11 oxygen basis.

have crystallized at higher pressures and temperatures than the Maine rocks, as suggested by presence of kyanite at lower grades and the lack of muscovite in several of the rocks.

Average analyses and standard deviations for each group are given in Table 1. With the exception of Ti^{vi}, each compositional category becomes a part of the "end-member" biotite formula. Ti is not grouped with one of the other categories because its solid-solution role is not obvious. Contents of Ti increase with average grade while Al^{vi} and $(Fe+Mg+Mn)^{vi}$ decrease with grade. Because Ti is not a part of the model system, it must be replaced with ions which proxy for it. In attempting to eliminate Ti from the pelitic biotite formula, Holdaway and Lee (1977) replaced Ti with 2 Fe. Dymek and Albee (1977) proposed the same relation. Table 1 shows that this is probably not a good assumption. A linear least-squares regression on all 47 analyses (Table 2) suggests a more accurate substitution. A relationship which closely matches the regression data is

$$Fe_{1.25}Al^{vi}_{0.67}\square^{xii}_{0.5} \rightleftarrows Ti\square^{vi}_{0.92}K^{xii}_{0.5}$$
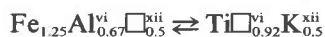
This gives a slope of -0.67 for Al^{vi}, -1.25 for $(Fe+Mg+Mn)^{vi}$, and 0.5 for $(K+Na)^{xii}$.

However, I believe that the regression actually represents two independent substitutions, both of which are a function of grade.

$$FeAl^{vi}_{0.67} \rightleftarrows Ti\,\square^{vi}_{0.67}$$

$$Fe^{vi}_{0.25}\square^{xii}_{0.5} \rightleftarrows \square^{vi}_{0.25}K^{xii}_{0.5}$$

There is no apparent reason besides metamorphic grade for these substitutions to be coupled. Since Ti content of pelitic biotites which occur with ilmenite is clearly a function of grade (Guidotti et al., 1977), the increase in 12-fold site population is probably also a function of grade. Because this second substitution is minor in amount and leads to compositional variation of the "end member" with metamorphic grade, we will ignore it and simply use the average 12-fold site population.

The accepted formula (Table 2) represents the average Si^{iv} and $(K+Na)^{xii}$, the average Al^{vi} regressed to zero Ti with a -0.67 slope, and the average $(Fe+Mg+Mn)^{vi}$ regressed to zero Ti with a -1 slope. The values were then adjusted slightly to give charge balance and a formula rounded off to the nearest hundredth on the basis of 11 oxygens. The regression lines, average compositions from the three regions, and "end-member" composition are illustrated for octahedral sites in Figure 2A. Note that the octahedral sites for Ti-free biotite are 98% full and that octahedral vacancies increase with Ti. Replacing each Ti with 2Fe would have produced 99% filled octahedral sites. The Al^{vi} in the "end member" is larger than $Al^{iv}-1$, the excess charge of 0.21 being compensated partly by octahedral site deficiency (0.12) and partly by 12-fold site deficiency (0.09).

The ionic substitution model proposed here for Ti in biotite does not conflict with the model proposed by Guidotti et al. (1977). These authors deal with the reduction of Ti solubility in Mg-rich biotites and propose a substitution model for biotites saturated in Ti, Al, and Si as Mg/Fe increases at constant grade. We are restricting Mg/Fe ratio and considering the substitution model which results as temperature increases. Note that the two models are quite different and equally defensible, but the Guidotti et al. model applies only to the actual decrease in Ti as Mg increases.
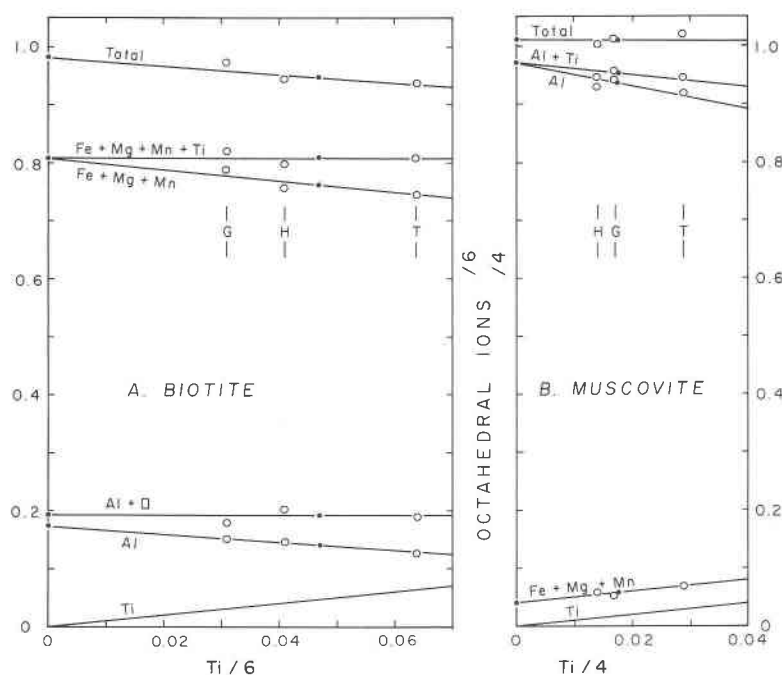
Fig. 2. Site occupancy of octahedral ions in biotite (A) and muscovite (B) plotted against Ti content. Circles represent average values from the three regions represented: G—Guidotti and coworkers, H—Holdaway and Novak (in preparation), T—Tracy (1978). Dots represent the overall average composition and those compositions adjusted to zero Ti according to the accepted solid-solution models.

The present formula for "end-member" biotite is most correct for composition ranges near $Mg/Fe = 1$. Other things being equal, Al content of biotite decreases very slightly with increasing Mg/Fe (Guidotti *et al.*, 1975). Because the formula is based on mid-range compositions, deviations at Fe- or Mg-rich compositions will not be large. The present composition is the best *single* biotite end-member composition for medium- to high-grade pelitic rocks saturated in Si and Al.

Muscovite

In the analysis of muscovite "end-member" composition, chemical analyses with $Mg/(Mg+Fe)$ between 0.38 and 0.60 were accepted. Analyses were taken from Holdaway and Novak (in preparation),

Table 3. Average and standard deviation for muscovite compositions from three metamorphic regions, in order of increasing average grade*

Composition category	Holdaway, Novak, in preparation 15 analyses	Guidotti and coworkers 60 analyses	Tracy, 1978 10 analyses
Si^{iv}	6.135 ± 0.045	6.056 ± 0.039	6.132 ± 0.068
Al^{iv}	1.865 ± 0.045	1.944 ± 0.039	1.868 ± 0.068
$(Al+Cr)^{vi}$	3.725 ± 0.058	3.765 ± 0.080	3.673 ± 0.033
Ti^{vi}	0.056 ± 0.024	0.067 ± 0.029	0.117 ± 0.029
$(Fe+Mg+Mn+Zn)^{vi}$	0.230 ± 0.035	0.211 ± 0.047	0.280 ± 0.020
$(K+Na+2Ca+2Ba)^{xii}$	1.950 ± 0.037	1.902 ± 0.046	1.821 ± 0.045

* Based on 22 oxygens per formula unit.

Table 4. Linear regression of 85 muscovite analyses on Ti*

Composition category	Average composition	Composition at Ti = 0	Slope	Correlation coefficient	Accepted formula
Si^{iv}	6.079	6.072	0.076	0.28	6.08
Al^{iv}	1.921	1.928	-0.076	-0.28	1.92
$(Al+Cr)^{vi}$	3.746	3.890	-2.015	-0.83	3.90
Ti^{vi}	0.071	0	-	-	0
$(Fe+Mg+Mn+Zn)^{vi}$	0.225	0.152	0.977	0.64	0.16
$(K+Na+2Ca+2Ba)^{xii}$	1.902	1.916	-0.210	-0.12	1.90

*Accepted formula is $K_{0.95}Fe_{0.08}Al_{1.95}Al_{0.96}Si_{3.04}O_{10}(OH)_2$ on 11 oxygen basis.

Evans and Guidotti (1966), Guidotti (1970, 1973, 1974), and Tracy (1978). The analyses of Holdaway and Novak are from the region between Augusta, Lewiston, Rumford, and Phillips, Maine, and the analyses of Guidotti and coworkers are from Bryant Pond, Rumford, Oquossoc, and Rangeley Quadrangles, Maine. Both suites of samples represent the staurolite, sillimanite, and K feldspar–sillimanite zones, with muscovite stable in all rocks. The Tracy analyses are from the Quabbin Reservoir area, Massachusetts, and represent the K feldspar–sillimanite zone with muscovite only barely stable in the rocks. Average compositions and standard deviations for muscovite from each of the three groups are given in Table 3. As is the case for biotites, increase in Ti appears to be a reflection of increasing grade, and the effect of Ti is largely compensated within the octahedral layers.

For muscovite, linear regression of 85 analyses on Ti nicely illustrates the coupled substitution suggested by Guidotti (1973) and Tracy (1978):

$$Al^{vi} \rightleftharpoons Ti_{0.5}Fe^{vi}_{0.5}$$

This can be seen as slopes near −2 for Al^{vi} and near 1 for $(Fe+Mg)^{vi}$ (Table 4). The variability in 12-fold site population does not correlate significantly with Ti content, but site occupancy may decrease somewhat with grade. If we assume the above substitution to be correct, adjustment of the average values gives a muscovite "end-member" composition of $K_{0.95}$ $Fe_{0.08}Al_{1.95}Al_{0.96}Si_{3.04}O_{10}(OH)_2$. Figure 2B illustrates the regression lines drawn through the group averages to show the Ti-free composition.

This formula leaves the octahedral sites overfilled

by 1.5%. Each average value (Table 3) also shows overfilled sites. No effort was made to rectify the problem; it may result from minor Al in the third site or from choice of Al standards in microprobe analyses. The discrepancy is not significantly different from the limit of precision of the microprobe. Guidotti et al. (1977) pointed out that increasing Mg/Fe reduces Ti in biotite at constant grade but slightly increases Ti in muscovite, provided the micas are saturated with Ti. This observation is consistent with the conclusion that the substitution mechanisms are different for Ti in the two minerals.

Chlorite

Very few microprobe analyses of chlorite meet the criteria discussed above. Analyses chosen for the study are from the Augusta Quadrangle, Maine (Novak and Holdaway, 1980, 3 analyses; Holdaway and Novak, in preparation, 1 analysis) and the Rangeley Quadrangle, Maine (Guidotti, 1974, 5 analyses). All are from the staurolite zone and have Mg/(Mg+Fe) between 0.45 and 0.62.

Fortunately the small number of analyses poses no serious problem because Ti contents are 0.12% or less and there are no 12-fold sites. The Guidotti analyses (Table 5) show octahedral and tetrahedral Al nearly the same, while the Holdaway and Novak analyses show an average of 0.15 more Al^{vi} than Al^{iv} (28-oxygen basis) and no structural reason for the difference. This is almost certainly due to an error in Si standardization. From the limited data, it seems best to assume $Al^{iv} = Al^{vi}$. The average value of $Al/(Al+Fe+Mg+Mn+2Ti)$ is very nearly constant for all analyses at 0.392 ± 0.006. There is no significant cor-

Table 5. Average and standard deviation for chlorite compositions from two metamorphic areas*

Composition category	Holdaway, Novak 4 analyses	Guidotti, 1974 5 analyses	Accepted formula
Si^{iv}	5.240 ± 0.067	5.056 ± 0.017	5.08
Al^{iv}	2.760 ± 0.067	2.944 ± 0.017	2.92
Al^{vi}	2.908 ± 0.068	2.956 ± 0.039	2.92
Ti^{vi}	0.007 ± 0.005	0.016 ± 0.002	0
$(Fe+Mg+Mn)^{vi}$	8.954 ± 0.096	9.005 ± 0.060	9.08
$Al/Al+Fe+Mg+Mn+2Ti$	0.388 ± 0.006	0.395 ± 0.003	0.391

*Based on 28 oxygens per formula unit. Accepted formula is $Fe_{4.54}Al_{1.46}Al_{1.46}Si_{2.54}O_{10}(OH)_8$ on 14 oxygen basis.

relation between Al content and Mg/Fe ratio. The "end-member" composition of chlorite in pelitic rocks is thus $Fe_{4.54}Al_{1.46}Al_{1.46}Si_{2.54}O_{10}(OH)_8$.

This chlorite composition should be applicable to reactions involving cordierite, staurolite, or Al silicate, but not those involving olivine or orthopyroxene since these minerals control activity of Fe+Mg at values higher than in typical pelites. The composition may be applicable to low-grade reaction of chlorite to garnet when chloritoid is present, but more analyses of such chlorites are required to establish this. Note that Mg-rich chlorites from aluminous hematite-bearing rocks (Grambling, manuscript in preparation) have almost exactly the same Al/(Al+Fe+Mg+Mn+2Ti) ratio, which implies that Fe^{3+} may not enter such chlorite in significant amounts. The "end-member" chlorite has about the same Al/(Al+Fe+Mg+Mn) ratio (0.4) as almandine.

Activity models

In relating these formulae to the chemical equilibria of experiments or nature it is necessary to use an activity model for each mineral. There are two possible approaches: (1) The "end-member" formulae, which involve solid solution on several sites, could be used as the basis for activity models. This method has the advantage that non-ideality in Al/Si and Al/(Fe+Mg) solid solution may be ignored, because the "end members," experimental minerals, and natural minerals have similar Al content in pelitic systems. A decided disadvantage is that the activity models are very complex and must involve approximations. Choosing end members which themselves have solid solution can lead to difficulty when formulating thermodynamic models for mixing relations. (2) An alternative approach is to use the solid-solution-free end member closest to the composition of the formula determined here. Then the activity can be viewed as being composed of two parts: the Al change which results from the shift to an idealized pelitic "end member," and the Mg, Mn, and Ti dilution in a natural mineral. The first step could be non-ideal, while the second may be nearly ideal. However, this apparent difficulty is overcome by the fact that any non-ideality in going from the true end-member formulae to the idealized pelitic system is cancelled out if natural pelitic systems are based on experimental pelitic systems. If pure end-member thermodynamic quantities are calculated from pelitic experimental data, it must be clearly understood that these numbers can only be used in natural pelitic systems. The free energy for annite applicable to pelitic systems need not be the same as for annite in non-pelitic systems, because the former free energy also takes account of any non-ideality in the Al solid solution. After considerable reflection I have chosen the pure end-member approach.

The activity models given in Table 6 reflect the following assumptions: (1) 12-fold sites and biotite octahedral sites are not necessarily filled, (2) muscovite and chlorite octahedral sites are filled, (3) solid solution on tetrahedral sites may be ignored because it is spacially coupled to adjacent octahedral and 12-fold sites, (4) there is no spacial coupling between 12-fold and octahedral sites. Table 6 also gives activities of ideal annite, muscovite, and Al-free chlorite in the

Table 6. Activity models for biotite, muscovite, and chlorite based on solid-solution-free end members

Mineral	Activity model*	Solid solutions	Activity in pelitic "end member"
Biotite	$\bar{X}_K^{xii} \bar{X}_{Fe}^{vi3}$	$K^{xii} \rightleftarrows Na^{xii}$ $Fe^{vi}Si^{iv} \rightleftarrows Al^{vi}Al^{iv}$ $FeAl_{0.67}^{vi} \rightleftarrows Ti\square_{0.67}^{vi}$ $Fe_{0.25}^{vi}\square_{0.5}^{xii} \rightleftarrows \square_{0.25}^{vi}K_{0.5}^{xii}$ $Fe^{vi} \rightleftarrows (Mg,Mn)^{vi}$	0.478
Muscovite	$\bar{X}_K^{xii} X_{Al}^{vi2}$	$K^{xii} \rightleftarrows Na^{xii}$ $Al^{vi} \rightleftarrows Ti_{0.5}Fe_{0.5}^{vi}$	0.877
Chlorite	X_{Fe}^{vi6}	$Fe^{vi}Si^{iv} \rightleftarrows Al^{vi}Al^{iv}$ $Fe^{vi} \rightleftarrows (Mg,Mn)^{vi}$	0.188

*Ideal solid solution is assumed. X - mole fraction of filled site, $\bar{X}$ - site occupancy of partially vacant site. See text for additional assumptions.

pelitic "end members." Al-rich end members for biotite and chlorite could also be formulated, but such end members would either involve solid solution on several sites or be quite far from the composition limits of these minerals in nature (Fig. 1).

The mole fractions given in the models relate to ideal solid solution. Activity coefficients should be included for K in muscovite and biotite. Until there is better understanding of the Al solid solution, ideality and equal partitioning must be assumed in the octahedral sites. As stated above, this may lead to mineral free energies applicable only to pelitic rocks.

Application

There are several important applications for the "end-member" formulae determined here. (1) They can be used as the most probable formulae for previous experimental studies involving quartz and an Al-rich mineral. (2) They can be used as the best starting material for future experimental studies of pelitic mineral equilibria. (3) The "end members" apply to formulating Fe–Mg phase diagrams from experiments. Such diagrams are directly applicable to natural pelitic mineral equilibria. It is hoped that careful microprobe analyses of experimental product minerals can be used to confirm or modify these formulae.

As an example of the application of the "end-member" formulae and activity models we will consider a single pelitic rock (specimen 107, Novak and Holdaway, 1980) from the southwest part of the Augusta Quadrangle, Maine. The specimen contains sillimanite, biotite, almandine, staurolite, quartz, and ilmenite. Textural evidence shows that garnet is partly replaced by biotite and sillimanite. The equilibrium can be expressed as:

$$KAl_3Si_3O_{10}(OH)_2 + Fe_3Al_2Si_2O_{12} \rightleftarrows \qquad (2)$$
muscovite ss   almandine ss

$$2Al_2SiO_5 + KFe_3AlSi_3O_{10}(OH)_2 + SiO_2$$
sillimanite   biotite ss   quartz

The reaction has a ΔV of 2.1163 J/bar. Garnet–biotite geothermometry indicates that the garnet cores equilibrated with biotite at about 550°C (Ferry and Spear, 1978) and Novak and Holdaway estimate the pressure at 4±1 kbar. Chemical analyses of biotite indicate $\bar{X}_K^{xii} = 0.888$ and $\bar{X}_{Fe}^{vi} = 0.379$, giving an activity of 0.048; muscovite has $\bar{X}_K^{xii} = 0.818$ and $X_{Al}^{vi} = 0.936$, giving an activity of 0.716; and garnet has $X_{Fe}^{viii} = 0.665$, giving an activity of 0.294. Dividing products by reactants gives an activity quotient Q of
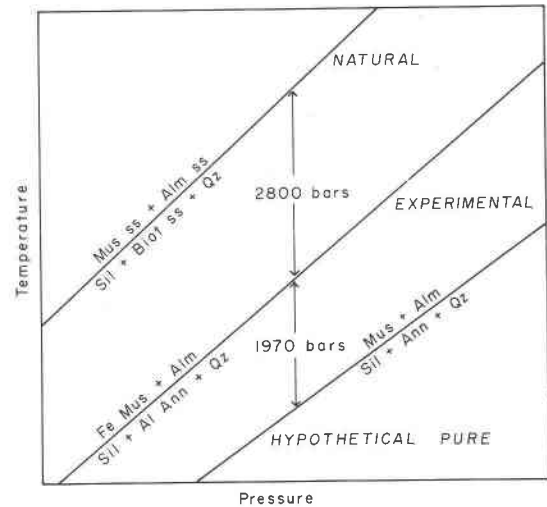

Fig. 3. Comparison of *PT* position of equilibrium 2 between a natural occurrence, an experimental system, and the hypothetical system with pure solid-solution-free minerals. See caption of Fig. 1 for mineral abbreviations.

0.229. The pressure difference between the hypothetical pure end-member equilibrium 2 (P_1) and the equilibrium as it occurs in the rock (P_2) is

$$(P_2 - P_1) = -\frac{RT\ln Q}{\Delta V} \qquad (3)$$

The rock crystallized at a pressure about 4770 bars above that of the pure end-member reaction (Fig. 3).

The Fe "end-member" reaction involving Al biotite and Fe muscovite is being determined in our laboratory. Using relation 3 and the activities given in Table 6, the experimental curve is 1970 bars above the hypothetical pure end-member equilibrium and thus 2800 bars below the pressure of formation of the naturally occurring specimen (Fig. 3).

Conclusions

1. The best single composition of biotite to relate to natural and experimental equilibria in pelitic compositions is $K_{0.91}Fe_{2.42}Al_{1.83}Si_{2.69}O_{10}(OH)_2$. The activity of pure annite in this formula is 0.478.

2. The best composition of muscovite to relate to such equilibria is $K_{0.95}Fe_{0.08}Al_{2.91}Si_{3.04}O_{10}(OH)_2$. The activity of pure muscovite in this formula is 0.877.

3. From more limited data, chlorite with formula $Fe_{4.54}Al_{2.92}Si_{2.54}O_{10}(OH)_8$ may be used to relate to equilibria in medium-grade rocks. The activity of Al-free chlorite in this formula is 0.188.

4. It is probably wisest to relate all equilibria and pelitic "end-member" formulae to solid-solution-free

end members. This approach simplifies activity models but could lead to the ultimate result that calculated free energies of these minerals based on pelitic experimental data can only be used on other pelitic equilibria.

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