The Systematics of Trace-Element Partitioning Between Coexisting Muscovite and Biotite in Metamorphic Rocks from the Black-Hills, South-Dakota, USA

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The systematics of trace-element partitioning between coexisting muscovite and biotite in metamorphic rocks from the Black Hills, South Dakota, USA

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Abstract—Coexisting muscovite and biotite in forty-nine staurolite- and sillimanite-zone schists from the southern Black Hills, South Dakota, USA, have been analyzed by ICP spectrometry for major and selected trace elements. This study represents the first comprehensive effort to document and explain trace-element partitioning behavior between coexisting micas in metamorphic rocks. Overall, the data reveal systematic element distributions across a wide thermal-compositional range. Mean Henry’s Law partition coefficients \( K_D^* \) (bio/mus) are as follows: Mn (14 ± 6 (1σ)), Ni (13 ± 6), Zn (13 ± 8), Li (4.0 ± 1.1), Ti (2.9 ± 0.7), Co (2.6 ± 1.6), Yb (2.0 ± 1.7), Cu (1.9 ± 1.7), Y (1.5 ± 1.5), Be (1.1 ± 1.5), Cr (1.0 ± 0.2), La (0.8 ± 0.7), V (0.7 ± 0.1), Zr (0.6 ± 0.2), Ba (0.5 ± 0.3), Sc (0.4 ± 0.1), Sr (0.4 ± 0.4), and Na (0.2 ± 0.1). This sequence is governed largely by the crystal structure of the micas and their major-element compositions.

Several structural effects on \( K_D^* \) have been identified. First, the observed \( K_D^* \) sequences Cr\(^{3+} \) > V\(^{3+} \) > Sc\(^{3+} \) and Ni\(^{3+} \) > Co\(^{2+} \) > Cu\(^{2+} \) are just as predicted from relative octahedral site preference energies, indicating that crystal-field effects influence the partitioning behavior of transition-metal cations. Second, the presence of smaller (i.e., more collapsed) interlayer sites in muscovite (relative to biotite) favors substitution in muscovite of cations smaller than K\(^+\), namely, Na\(^+\), Sr\(^2+\), Ba\(^2+\), and La\(^3+\). Likewise, interlayer cations larger than K\(^+\) (e.g., H\(_2\)O\(^+\), Rb\(^+\), and Cs\(^+\)) are predicted to substitute preferentially into biotite. Third, tetrahedral Fe\(^{3+} \) is predicted to favor biotite over muscovite because of larger tetrahedral sheets in biotite (due, in turn, to more Al and less Si). Fourth, the occurrence of heterovalent interlayer cations in micas suggests that their partitioning behavior is partly governed by charge-balance reactions.

As a general compositional effect on \( K_D^* \), the preferences exhibited by biotite for Li\(^+\) and divalent cations of first-row transition elements reflect its high abundance of comparably sized (Mg, Fe\(^{2+} \)) relative to coexisting muscovite. Likewise, relatively strong affinities of muscovite for Cr\(^{3+} \), V\(^{3+} \), and Sc\(^{3+} \) abundance. Element-specific compositional effects on \( K_D^* \) are less evident; but there are indications that Mg\(^{2+} \) partitioning affects that of Li\(^+\), Ni\(^{3+} \), and Mn\(^{3+} \).

Temperatures inferred from Mg-Tschermak (MgSiAl\(_2\)) exchange between coexisting muscovite and biotite (Hösch, 1989) provide a convenient datum by which to evaluate the thermal behavior of analogous vector components involving trace elements. Several of these components appear to possess exchange potentials (\( \Delta G_{\text{ex}} \)) sufficiently large so that respective equilibrium constants approach unity with temperature increase. These components include the following: NiSiAl\(_2\), MgSiCr\(_{1-x}\)Al\(_x\), MgSiV\(_{1-x}\)Al\(_x\), MgSiSc\(_{1-x}\)Al\(_x\), CrAl\(_x\), Va\(_x\), and Li\(_2\)Si "Al\(_{1-x}\)" Mo\(_{1-x}\)"Al\(_x\)". In contrast, any thermal sensitivity of other such components is masked by analytical scatter.

INTRODUCTION

UNDERSTANDING TRACE-ELEMENT partitioning among metamorphic phases is important for at least four reasons. First, equilibrium trace-element distributions have the potential to reflect metamorphic P-T conditions, according to the thermodynamic laws of Henry-ion behavior (Kretz, 1961; Saxena, 1973). However, two fundamental obstacles to trace-element geothermometry are evident from the more studied igneous systems. These include the sensitivity of partition coefficients to both major-element composition (e.g., Yoder, 1989) and crystalline structure (e.g., Speer, 1984), the latter encompassing crystal-field effects, intracrystalline distortions, and coupled ionic substitutions (to maintain charge balance). Second, distributions of trace elements can influence mineral P-T stabilities to the extent that partition coefficients govern how elements are concentrated and depleted in minerals during metamorphic reactions. As an example, Dutrow et al. (1986) showed that Li is favorably partitioned into staurolite and demonstrated the effect of elevated Li abundance in staurolite on its P-T stability. Third, trace-element zoning profiles preserved in metamorphic minerals appear to monitor open-system behavior during metamorphism, and with greater sensitivity than major elements, as shown by Hickmott et al. (1987), who studied element zoning in garnet. If the open-system behavior preserved by their garnet can be attributed to breakdown of adjacent trace-element-bearing phases in the same rock (as they suggest), then it follows that qualitative and quantitative efforts to decipher reaction histories of metamorphic assemblages would benefit greatly from knowledge of trace-element partition coefficients among coexisting minerals. Fourth, the partitioning behavior of trace elements and their relative mobilities in minerals are inevitably linked to similar aspects of crystal-chemistry and mineral structure. Understanding how these factors influence partitioning behavior may ultimately lead us, therefore, to an improved understanding of how they also affect diffusion rates of chemical species in minerals. Diffusion rates, in turn, govern closure temperatures upon cooling (Dodson, 1973), and knowledge of closure temper-
atures is a key element of modern thermochronologic modeling of orogenic cooling histories. It follows that refined closure temperature estimates (e.g., for K, Ar, Rb, and Sr) that account for crystal-chemical and structural effects could potentially improve the resolution of thermochronologic models.

To date, trace elements have not fulfilled their petrologic potential in metamorphism, despite rigorous thermodynamic treatments of their partitioning behavior (e.g., MCKINTIRE, 1963; BURNS and FYFE, 1966; WHITTAKER, 1967). One reason for this is the lack of thermodynamic data for most trace-element analogues of common metamorphic minerals, without which the thermal behavior of major-element-trace-element exchange between coexisting minerals cannot be predicted. Another reason is the relative paucity of experimental and/or natural assemblage studies dealing with trace-element partitioning behavior in metamorphic systems, as compared to a voluminous literature pertaining to igneous crystal-melt systems. It is clear that deciphering the structural-compositional-thermal effects on trace-element partitioning between coexisting metamorphic minerals will require experimental work and study of natural samples paralleling the numerous published studies of major-element partitioning. At present, however, there are relatively few published trace-element partitioning studies in metamorphic systems (e.g., NICKEL, 1954; DEVORE, 1955; KRETZ, 1959; TUREKIAN and PHINNEY, 1962; MONHAM, 1965; ENGEL and ENGOEL, 1960; SCHWARZ, 1967; ANNERSTEN and ECKSTROM, 1971; KORSMAN, 1975; DUPuy et al., 1980; PAPEK et al., 1984; DUTROW et al., 1986; SHEarer et al., 1986; HENDRICKS and DAHL, 1987; Hervig and Peacock, 1989; etc.), and only a few of these studies specifically address trace-element partitioning between muscovite and biotite. The special significance we attribute to these micas stems from their overall usefulness in both petrogenetic (GUIDOTTI, 1984) and geochronologic studies, coupled with their abundance and widespread coexistence in metapelitic and related rocks.

This is the first of three papers dealing with the geochemistry of coexisting biotites and muscovites in staurolite- and sillimanite-zone rocks from the Black Hills, South Dakota, USA. In one paper, we critically evaluate the two-mica geothermometer of HOISCH (1989), based upon comparison of muscovite- and garnet-biotite temperature maps for the southern Black Hills (P. S. Dahl et al., unpubl. microprobe data). In the second paper (P. S. Dahl et al., unpubl. data), we interpret maps of regional thermal-chemical patterns in micas in terms of lithology and assemblage, mineral reactions, hydrothermal fluid infiltration, and metamorphic grade. In this paper, however, we focus specifically on the systematics of trace-element partitioning between coexisting muscovite and biotite, although some reference is made to the other aspects of the work, as appropriate. Our principal goals here are to establish and explain the following: (1) trace-elemental abundances and preferences in coexisting micas, (2) relative elemental ordering of $K_{bio/mus}^*$ values for mica pairs, and (3) structural-compositional-thermal effects on the partitioning behavior of selected elements. Other papers have presented analytical data on some of the constituents in micas that we consider here. However, we know of no comparable study reported previously in which the systematics of trace-element partitioning in coexisting biotite and muscovite in metamorphic rocks is comprehensively documented and interpreted.

**GEOLOGIC SETTING**

The Black Hills constitute an elongate Laramide dome with a Precambrian core flanked by Paleozoic and younger sedimentary rocks. Core lithologies consist primarily of Early Proterozoic metasedimentary, metavolcanic, and intrusive rocks (REDDEN et al., 1990). The metasedimentary rocks (originally shales, graywackes, quartz sandstones, and iron formations) were deposited unconformably on Archean basement near the eastern edge of the Wyoming craton during Early Proterozoic rifting of the Black Hills basin (Gosselin et al., 1988). They were then subjected to intense deformation and low- to medium-grade regional metamorphism, probably during convergence of the Wyoming and Superior cratons between 1.88 and 1.72 Ga (REDDEN et al., 1990). Subsequent emplacement of the Harney Peak granite (Fig. 1) and associated pegmatite bodies at approximately 1.715–1.680 Ga (Riley, 1970; R. E. Zartman in Ratté, 1986) caused doming and superimposed an extensive high-temperature metamorphic aureole on the country rocks (REDDEN et al., 1990). To a first approximation, the areal extent of fluid-rock interaction associated with this event correlates with the envelope of pegmatite activity, as mapped by Norton and Redden (1990). This envelope (not shown in Fig. 1) surrounds the main mass of Harney Peak granite. Its outer boundary nearly coincides with the western exposure of the sillimanite isograd, extends northeast to the staurolite isograd near Hill City, and trends southeast to Keystone, then northeast again toward Rockerville. Gravity modeling by Duke et al. (1990) suggests that (Harney Peak?) granite underlies metamorphic rocks in the vicinity of Custer, Hill City, Keystone, and the Archean rocks in the west of the map area (Fig. 1). Vertical infiltration of exsolved hydrothermal fluids from these granite bodies and satellite pegmatites may account for the extensive metamorphic aureole developed in the southern Black Hills (Dahl et al., 1992; P. S. Dahl et al., unpubl. data).

Mineral isograds in the Black Hills have been mapped in metapelites, metagraywackes, and metabasalts by Redden (1963, 1968), Ratté and Wayland (1969), Powell et al. (1973), Ratté (1986), and Helms and Labotka (1991). Redden et al. (1990) and Terry and Friberg (1990) indicate that the regional metamorphism was responsible for the present distribution of the biotite and garnet isograds. However, they indicate that the first and second sillimanite isograds and probably the staurolite isograd resulted from the high-temperature metamatism associated with the Harney Peak intrusive event. The resulting subconcentric pattern of the staurolite and sillimanite isograds about the Harney Peak granite is shown in Fig. 1. The petrologic study by Helms and Labotka (1991) of metapelitic rocks from largely within the pegmatite envelope mapped by Norton and Redden (1990) summarizes AFM reactions, net isograd reactions, and regional $PT_i$ evolution associated with the Harney Peak intrusive event. Although pre-Harney Peak metapelitic assemblages and mineral compositions are largely overprinted by hydrothermal activity within the pegmatite
SAMPLE LOCATIONS & GENERAL GEOLOGY OF HARNEY PEAK AREA

FIG. 1. Generalized geologic map of the southern Black Hills, South Dakota, showing locations of the forty-nine samples included in this study (after HELMS and LABOTKA, 1991). The Grand Junction, Burnt Fork, Hill City, and Empire Mine faults (see text) are indicated as G.J.F., B.F.F., H.C.F., and E.M.F., respectively. Geology from DEWITT et al. (1989).

envelope (J. A. Redden, L. M. Friberg, pers. commun.), rocks outside the envelope may preserve evidence of both of the 1.88-1.72- and 1.71-Ga events (e.g., TERRY and FRIBERG, 1990).

For further geologic details, the reader is referred to recent syntheses of Precambrian tectonothermal evolution of the Black Hills by DEWITT et al. (1986, 1989), GOSSELIN et al. (1988), DUKE et al. (1990), NORTON and REDDEN (1990), REDDEN et al. (1990), TERRY and FRIBERG (1990), HELMS and LABOTKA (1991), and NABELEK et al. (1992).

SAMPLE DESCRIPTION AND ANALYTICAL METHODS

The forty-nine fine- to medium-grained metapelitic schists chosen for study include thirty-one rocks from the staurolite zone and eighteen from the two sillimanite zones (Fig. 1). Most rocks exhibit a well-defined biotite-muscovite foliation associated with F2 folding (1.88-1.72 Ga); those within 2-3 km of the Harney Peak granite also preserve a weak F3 foliation associated with doming during granite emplacement. The Proterozoic rocks sampled between the Grand Junction and Hill City faults (plus samples St-29, -60, -61, and -70; see shaded areas in Fig. 1) are mapped as mica (either biotite- or muscovite-rich) schists by DEWITT et al. (1989), whereas those from elsewhere in the region represent metagraywacke. Also, the rocks are predominantly from within the pegmatite envelope mapped by NORTON and REDDEN (1990), except for staurolite-zone mica-schists west of the Hill City fault (Fig. 1).

All selected rocks are well foliated and are composed primarily (40-70 modal%) of biotite and muscovite, with quartz, lesser oligoclase, and (in the sillimanite zones) minor microcline constituting the remainder. Thin-section analysis reveals that the micas are typically fresh in appearance, with only occasional, minor hematite or

[Diagram showing geologic map with sample locations and geological contacts]
chlorite alteration of biotite. Accessory tourmaline, zircon, garnet, and late chlorite (roseties) are present in the rocks; extensive tourmalinization is only evident near pegmatites and plutonic margins. Also, the muscovite-rich schists (metamorphosed tuffaceous shales) typically contain accessory magnetite and ilmenite; in contrast, the biotite-rich schists (metamorphosed Carbonaceous shales) and meta-graywackes typically contain ilmenite and graphite and ilmenite, respectively. Accessory, post-F2 cordierite porphyroblasts are found in some muscovite-rich schists and appear to occur exclusively within them. Post-F2 stage accessory porphyroblasts (e.g., Lawsonite, muscovite, stilpnomelane) are rare within the sample suite (and garnet is accessory), but only because sampling was selective for high modal mica abundance. Likewise, sampling was selective against post-F2 muscovite porphyroblasts, although the finer-grained ones could not be completely avoided in the subsequent separates. Fortunately, microprobe analyses reveal that they are chemically homogeneous and indistinguishable from the predominant F2 muscovites (L. M. Friberg, pers. commun.), so they present no complication in this study. A likely explanation for the chemical similarity (following Essene, 1982) is that F2 micas were chemically reset by diffusion without necessarily recrystallizing during the Harvey Peak intrusive event that produced the porphyroblasts. The overall absence of zoning in these micas suggests subsequent rapid cooling through their diffusion closure temperatures, but other explanations under the retrograde metamorphism are not similarly constrained.

Mineral assemblages, textures, and reactions in metapelitic rocks of the southern Black Hills are considered in further detail elsewhere (e.g., Redden, 1963, 1968; Emadian, 1981; Vogel, 1985; Shearer et al., 1986; Terry, 1990; and Helms and Labotka, 1991).

A Franz isodynamic separator was used to separate biotite and muscovite fractions from crushed and sieved hand samples. High magnetic field strength was then applied to all mica separates to remove any grains containing ilmenite or magnetite inclusions. All mica separates were then riffled on paper to roll off most remaining grains of quartz, plagioclase, and garnet. Finally, all separates were handpicked. For all biotites and many muscovites, purity of approximately 99% was obtained by this procedure, as evidenced by petrographic examination and confirmed stoichiometrically after ICP analysis. Particularly among staurolite-zone rocks, however, muscovite separates completely free of quartz ± oligoclase grains were not always attainable, necessitating generally small corrections to the analytical data, as described later in this section. The difficulty here stemmed from similarities in magnetic properties, color, and specific gravity among the three minerals, coupled with the finer grain size typical of the staurolite-zone rocks. Other impurities consisted of minor (but ubiquitous) inclusions of zircon.

Two solutions were prepared from each oven-dried and weighed mica separate, for subsequent elemental analysis. Lithium-borate fusions dissolved in 5% (v/v) HNO3 were prepared for major-element analysis, and 1% (v/v) HCl (Langmyhr and Sveen, 1965) were prepared for trace-element work. Dissolution by these methods effectively diluted the original separates by factors of 1:5000 and 1:100, respectively.

All chemical analyses were performed on an Instrumentation Laboratory Plasma-200 ICP spectrometer. USGS rock standards AGV-1, BCR-1, and W-1 were used to calibrate the ICP for major elements, using accepted oxide concentrations tabulated in ABBEY (1983); W-1 was used for calibration of all trace elements except Y and Yb, which were calibrated with aqueous standards. Repeated analyses of standards during all ICP runs provided independent calibration cross-checks for all major and trace elements. Where necessary, elemental calibration corrections were applied to the ICP results. Where applicable, the zircon microprobe analyses of TERRY (1990) and (3) reduced scatter on Nd and Sr distribution diagrams. Microprobe analysis directly and independently confirmed this; spot checks of ten of our muscovites agreed with the major-element abundances we report to within ±1-4% (relative). Similar agreement was obtained in microprobe spot checks of biotite.

Estimated analytical accuracy for major-element abundances is within 2.5% relative, as determined from repeated analysis of the thousand USGS rock standards as samples during each ICP run. Likewise, trace-element concentrations (reported in ppm) are generally accurate to within 1-9% relative, depending on the element; Ba, V, Cr, Sc, and Mn are accurate to within 5% (and Li, Be, Zr, and La to within 9%) in both micas. Accuracy is somewhat poorer than the 9% figure only when ICP detection limits were approached (i.e., for Zn, Cu, Co, Ni, Y, and Yb in many muscovites). Further details of the analytical intercorrelation of major- and trace-element abundances among the three standards are given by WENH (1987).

Results of analysis of rock standards during each ICP run yielded estimates of long-term analytical precision within ±3% for each element in each standard after linear drift-correction was performed. Precision of sample preparation procedures was within ±3% for all elements, based upon splits of a biotite separate dissolved and analyzed in triplicate. However, degraded precision was determined for Zr ±7.4%, Y (±3.8%), Yb (±8.3%), and La (±24%), probably reflecting irreproducible partitioning of zircon inclusions in the mica separates during HF-perchloric acid digestion.

Impurities and inclusions in some of our micas were unavoidable, as noted above; but synthesis of the data both with and without appropriate corrections revealed that they have little or no bearing on the main conclusions presented in this paper. Nevertheless, some amplification is appropriate on this point. First, the ubiquity of minor zircon inclusions coupled with inherently low Zr abundances in micas resulted in imprecise characterization of Zr partitioning. Partitioning data for the REE and Y are likewise somewhat suspect, since these elements readily substitute for Zr in zircon. Positive correlations between REE and Zr in both our muscovites and biotites are consistent with this effect. There was no practical approach to correcting mica analyses for the presence of zircon; for this reason, the partitioning behavior of Zr, Yb, and La in micas earlier in this study is mentioned only briefly in subsequent discussion of possible interlayer substitutions. Second, quartz ± oligoclase impurities in the 1-5% range occurred in most of the staurolite-zone muscovites. Muscovites with quartz impurity were easily recognized by their anomalously high SiO2 and low Al2O3 abundances, coupled with inferior stoichiometries. Likewise, oligoclase contamination in muscovite was evidenced by somewhat elevated CaO abundance relative to electron microprobe analyses of typical metapelitic micas from the literature (including some from the staurolite zone in the Black Hills).

Muscovite analyses were stripped of the effects of quartz and plagioclase contamination, as necessary, using published microprobe analyses of muscovite to constrain the correction procedure. The quartz correction assumed a true SiO2 abundance of 46.79 wt%, which represents the mean value for seventeen southern Black Hills muscovites analyzed by electron microprobe (TERRY, 1990); SHEARER et al. (1986) reported similar SiO2 results. Corrections (typically for 2-3 modal% quartz) were applied to twenty-two of thirty-one staurolite-zone muscovites, improving stoichiometry in every case and reducing the overall scatter on element distribution diagrams. Corrections for oligoclase assumed a mean composition of staurolite-zone oligoclases from the southern Hills, as estimated from seven electron microprobe analyses presented by TERRY (1990); mean Sr abundance (587 ppm) was calculated from data presented by SHEARER et al. (1986). The amount of correction needed was inferred from the extent to which SiO2 abundance in the oligoclase fraction is a 0.03 wt% maximum evident in seventy microprobe analyses of muscovite from the literature. This correction (amounting generally to 1-2% oligoclase) was applied to twenty-eight of the thirty-one staurolite-zone muscovites. Evidence that the correction was effective includes (1) improved muscovite stoichiometries, (2) K/Na mas ratios that agree with the microprobe analyses of TERRY (1990), and (3) reduced scatter on Na and Sr distribution diagrams. Microprobe analysis directly and independently confirmed this; spot checks of ten of our muscovites agreed with the major-element abundances we report to within ±1-4% (relative). Similar agreement was obtained in microprobe spot checks of biotite.

The Range of Coexisting Mica Compositions

ICP analyses of the forty-nine biotites and coexisting muscovites from the staurolite and sillimanite zones are presented...
Table 1. Compositions of silemmite-zone biotites

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Table 2. Compositions of sillimmite-zone biotites

| Sample # | S1-12 | S1-23 | S1-25 | S1-29 | S1-30 | S1-31 | S1-32 | S1-33 | S1-34 | S1-35 | S1-36 | S1-37 | S1-38 | S1-42 | S1-43 | S1-44 | S1-45 | S1-46 | S1-47 | S1-48 | S1-49 | S1-50 | S1-51 | S1-52 | S1-53 | S1-56 | S1-61 | S1-62 | S1-63 | S1-68 |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| wt%       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Na2O      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Al2O3     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| FeO*      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Fe2O3     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| MgO       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| CaO       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| MnO       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| FeO        |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Total     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
### Table 3. Compositions of stauralite-zone muscovites

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<th>St 32</th>
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<th>St 55</th>
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<th>St 78</th>
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### Table 4. Compositions of stauralite-zone muscovites

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in Tables 1–4. Corresponding mica stoichiometries are given in Tables 5–8, respectively, wherein cation site-occupancies were assigned on the basis of ionic radii (from Shannon, 1976). Stoichiometric data were used to calculate Henry’s Law partition coefficients, $K_D$, for sixteen trace elements (plus Ti and Na) in the forty-nine mica pairs (Table 9). As noted by Dutrow et al. (1986), such coefficients are especially useful for evaluating trace-element partitioning. $K_D$ is defined here as follows:

$$K_D = \frac{(X_{bio})}{(X_m)^{m+s}}$$  

(1)

where $X_i$ is the mole fraction of component $i$. Mole fractions were computed on the basis of two interlayer sites, eight tetrahedral sites, and either six octahedral sites (biotite) or four (muscovite). Elements are listed in Table 9 in order of decreasing mean $K_D$. Standard deviations and $K_D$ ranges are also tabulated for each element; the relative standard deviation of a typical mean $K_D$ ranges from 25–50%, depending upon the element. Relative trace-cation occupancies in M1/M2 sites of biotite could not be evaluated. Consequently, any cation ordering on these sites is not considered in the $K_D$ values presented in Table 9, despite new evidence for ordering (of at least Fe$^{2+}$) on these sites in biotite (Guidotti and Dyar, 1991). Metamorphic temperature estimates for the forty-nine rocks, inferred from the empirical muscovite-biotite geothermometer of Hovischi (1989), are also given in Table 9.

Compositional variation among our biotites with the idealized annite-phlogopite-siderophyllite-eastonite plane is illustrated in Fig. 2, based upon data from Tables 5–6. Also included for reference are biotites adjacent to Black Hills pegmatites (microprobe analyses of Shearer et al., 1986). Because our biotites all coexist with muscovite, ilmenite, and quartz, they are saturated with respect to Al, Ti, and Si, respectively. Five staurolite-zone biotites (St-61, -103, -106, -107, and -112), exhibiting among the highest Mg/Fe...
explains why regional cordierite occurrences are restricted biotite in this unit served to accentuate this effect. The 
rocks by its magnetic nature distinguished geophysically from surrounding micaceous 
dances are generally used to demonstrate diadochy (e.g., DUTROW et al., 1991) account for most trace-element deviations from the 
tion of diadochy with major elements. 
element abundances in our biotites preclude direct verifica-
Table 6. Stoichiometries of sillimanite-zone biotites

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Notes: See Fig. 1 for sample locations. Stoichiometries are based on \( \text{O}_2 \) and site occupancies were assigned on the basis of similar analyses and bulk compositions. *Total sample not detected.

+ \( \text{Mg}_2 \), all occur in the muscovite-rich schist unit, which is distinguished geographically from surrounding micaceous rocks by its magnetic nature (KLEINKOPF and REDDEN, 1983). Evidently, magnetite growth depleted the rock reservoir of Fe (particularly \( \text{Fe}^{3+} \)), resulting in the relatively high \( \text{Mg}/(\text{Fe}^3 + \text{Mg}) \) ratios. Relatively low amounts of biotite in this unit served to accentuate this effect. The reservoir \( \text{Mg}/(\text{Fe}^3 + \text{Mg}) \) ratio was likewise elevated, which probably explains why regional cordierite occurrences are restricted to this lithology (YARDLE, 1989; J. A. Redden, pers. comm.).

Presumably, the eleven exchange vectors listed by TRACY (1991) account for most trace-element deviations from the tricticadoma mica plane shown in Fig. 2. (The concept of exchange vectors was introduced by THOMPSON, 1982.) Inverse linear correlations of major- vs. trace-element abundances are generally used to demonstrate diadochy (e.g., DUTROW et al., 1986; TRACY, 1991), but this is feasible only in micas containing unusually high concentrations of the trace element in question. In contrast, the relatively lower trace-element abundances in our biotites preclude direct verification of diadochy with major elements.

Coexisting muscovites deviate from the idealized additive component, \( \text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 \), in terms of paragonite, celadonite, and \( \text{Fe}^{3+}\text{Al}^{3+} \) substitutions (GUIDOTTI, 1984). In describing composition space for barian muscovites, TRACY (1991) presented seven exchange vector components in addition to the additive component \( \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 \). These components probably also describe compositional space for our muscovites. We would modify his list by the following:

1) adding \( \text{RMg}_2 \), to account for minor substitutions of di-
valent cations of transition metals;
2) adding \( (\text{K}^+ \text{Na}^+\text{H}_2\text{O})_\text{M} \), to account for possible inter-
layer hydronium-ion substitutions (LOUCKS, 1991); and
3) generalizing the \( \text{CrAl}_3 \) component to \( \text{(Cr,V,Sc)Al}_3 \).

The second exchange component may account partially for the apparent interlayer site deficiencies evident in our micas (Tables 5-8) and published microprobe analyses of micas in general (see also DYAR, 1988; HERVIG and PEACOCK, 1989; and GUIDOTTI and DYAR, 1991).

We have not yet distinguished \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) in our mica analyses, which prevents us from fully characterizing the extent and any crystal-chemical aspects of mica compositional variation involving iron. However, DYAR (1990) reported that metapelitic biotites of metamorphic grade similar to ours have mean octahedral \( \text{Fe}^{3+} \) contents of 4 and 12% of total iron, respectively, in ilmenite/graphite-bearing and magnete-bearing assemblages. We assume here that the results of DYAR (1990) extend directly to the biotites in our metagraywackes/biotite-schists and muscovite-schists. This assumption is consistent with the widespread occurrence of graphite + ilmenite in the biotite-rich schists, which probably kept \( f_{\text{O}_2} \) at fairly low values during metamorphism; in contrast, the presence of magnetite in the adjacent muscovite-rich schist unit is probably indicative of a relatively higher \( f_{\text{O}_2} \). DYAR (1990) also reported a mean 8% of total iron occurring as tetrahedral \( \text{Fe}^{3+} \), regardless of oxidation state of the rock, which we assume also extends to our biotites. Judging from published analyses of micas, it is very likely that the overall \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratios of our muscovites exceed those of the coexisting biotites. Ultimately, muscovites may prove to exhibit baseline behavior of tetrahedral \( \text{Fe}^{3+} \) similar to that reported by DYAR (1990) for biotites. As yet, however, there exists no definitive study on oxidation states of iron in muscovites.
Trace-element partitioning between muscovite and biotite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti</th>
<th>La</th>
<th>Sc</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Zn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>St-7</td>
<td>1.261</td>
<td>1.097</td>
<td>1.821</td>
<td>1.895</td>
<td>1.795</td>
<td>1.717</td>
<td>1.851</td>
<td>1.891</td>
<td>1.988</td>
</tr>
<tr>
<td>St-10</td>
<td>1.508</td>
<td>3.462</td>
<td>2.741</td>
<td>2.760</td>
<td>2.756</td>
<td>2.960</td>
<td>3.135</td>
<td>3.208</td>
<td>2.961</td>
</tr>
<tr>
<td>St-11</td>
<td>1.508</td>
<td>3.462</td>
<td>2.741</td>
<td>2.760</td>
<td>2.756</td>
<td>2.960</td>
<td>3.135</td>
<td>3.208</td>
<td>2.961</td>
</tr>
</tbody>
</table>
the range of element abundances exhibited in Figs. 3–4 partly signifies variable fluid-rock interaction among the forty-nine biotite-muscovite pairs.

Element Partitioning Behavior

For the trace elements, it is evident from Fig. 3 and Table 9 that (1) Zn, Ni, Mn, Li, Co, and Cu prefer biotite over muscovite; (2) Cr and V partition nearly equally between the micas; and (3) Be, Sc, La, Ba, and Sr favor muscovite. Among the major elements, Ti, Fe, Mg, and "Al invariably prefer biotite; whereas Na and Sr prefer muscovite (Fig. 4; Tables 5–8). These results are all consistent with published analyses of coexisting biotite and muscovite (e.g., LAMBERT, 1959; BUTLER, 1967; MOORBATH et al., 1968; DE ALBUQUERQUE, 1973, 1975; BAADSGAARD et al., 1976; ZEN, 1981; PAPIKE et al., 1984; DUTROW et al., 1986; SHEARER et al., 1986; WANG and BANNO, 1987; HERVIG and PEACOCK, 1989; TERRY, 1990; and HARLOW, 1991).

We can infer that tetrahedral Fe\(^{3+}\) is probably favored in biotite over muscovite from inspection of our analyses (Tables 5–8) in view of the determination of DYAR (1990) that 8% of total Fe in biotite occurs as tetrahedral Fe\(^{3+}\); for even if all the Fe in our muscovites were to occupy tetrahedral sites (as Fe\(^{3+}\)), most coexisting biotites would still contain more tetrahedral Fe\(^{3+}\), according to the 8% baseline estimate. Moreover, the preference of tetrahedral Fe\(^{3+}\) (0.49 Å) we infer for biotite is consistent with its larger average tetrahedral layer (relative to muscovite), which derives from its higher tetrahedral Al\(^{3+}\) (0.39 Å) and lower Si\(^{4+}\) (0.26 Å) abundances compared to muscovite (ionic radii from SHANNON, 1976). Other structural controls on element partitioning are considered in the forthcoming Discussion section.

Many trace elements we studied exhibit systematic linear distribution between muscovite and biotite (e.g., Fig. 3a–h) across the entire range of pre-metamorphic bulk-rock composition and fluid-rock interaction represented by the sample suite. Moreover, the available data from other terrains (cited above) also plot on or very close to our trends. The linearity seen in most distribution diagrams is consistent with Henry's Law behavior; there is no evidence that any of the trace elements reached their limits of solubility in muscovite or biotite.

Valid petrogenic conclusions from trace-element distribution data are predicated upon attainment of chemical equilibrium in the sample set. VOGEL (1985) found no violations of the Gibbs Phase Rule and observed systematic Fe-Mg distributions between rims of coexisting garnets and biotites, with few crossing tie lines on an AFM diagram. Likewise, a close approach to chemical equilibrium between coexisting minerals is suggested by a linear cluster of element distribution on a ternary or pseudoternary diagram. The linearity of element behavior of certain first-series transition metals between coexisting minerals is also plotted on or very close to our trends. This linearity is well demonstrated for Ba, Zr, and V in Fig. 3a–b. Analytical data and VOGEL (1985) found no violations of the Gibbs Phase Rule and observed systematic behavior of certain first-series transition metals between coexisting minerals.

Likewise, a close approach to chemical equilibrium between coexisting minerals is suggested by a linear cluster of element distribution plots. The linearity is well demonstrated for Ba, Zr, and V in Fig. 3a–b. Analytical data and VOGEL (1985) found no violations of the Gibbs Phase Rule and observed systematic behavior of certain first-series transition metals between coexisting minerals.

DISCUSSION

Structural Controls on Trace-element Partitioning

Crystal-field effects appear to influence the partitioning behavior of certain first-series transition metals between coexisting muscovite and biotite, whereas various other struc-
Table 1. Sample low partition coefficients and eclogitization temperatures for metabasaltic biotite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>No.</th>
<th>Mg/(Fe+Mg)</th>
<th>Si</th>
<th>Al</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>V</th>
<th>Co</th>
<th>Ni</th>
<th>Mg</th>
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</thead>
<tbody>
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<td>HN</td>
<td>1</td>
<td>0.50</td>
<td>1.81</td>
<td>0.59</td>
<td>0.34</td>
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<td>0.04</td>
<td>0.01</td>
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<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
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<td>0.02</td>
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<td>0.03</td>
</tr>
<tr>
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<td>0.57</td>
<td>0.31</td>
<td>0.13</td>
<td>0.02</td>
<td>0.02</td>
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</tr>
<tr>
<td>4</td>
<td>0.45</td>
<td>1.71</td>
<td>0.52</td>
<td>0.27</td>
<td>0.08</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
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</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>1.81</td>
<td>0.60</td>
<td>0.36</td>
<td>0.18</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>6</td>
<td>0.49</td>
<td>1.78</td>
<td>0.59</td>
<td>0.33</td>
<td>0.16</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
<td>7</td>
<td>0.47</td>
<td>1.74</td>
<td>0.57</td>
<td>0.31</td>
<td>0.13</td>
<td>0.02</td>
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<td>0.02</td>
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<tr>
<td>8</td>
<td>0.43</td>
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<td>0.27</td>
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<td>0.01</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
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</tr>
</tbody>
</table>

*Note: Ratios are calculated from partition coefficients. Magnetic powders of the sample are not constrained by the Websterite (1980) method.*

**Mg/(Fe+Mg) non-determination of partition coefficient in biotite at 1 GPa.**

**Table 2.** Compositional variation among metapelitic biotites in the southern Black Hills, South Dakota, as projected onto part of the siderophylite-eatonite-annee-phlogopite "ideal biotite" plane (see inset for complete quadrilateral). Solid and open circles represent staurolite- and sillimanite-zone biotites, respectively (see Tables 5 and 6). Open triangles represent biotites in schists adjacent to pegmatites, from SHEARER et al. (1986).

**Fig. 2.** Compositional variation among metapelitic biotites in the southern Black Hills, South Dakota, as projected onto part of the siderophylite-eatonite-annee-phlogopite "ideal biotite" plane (see inset for complete quadrilateral). Solid and open circles represent staurolite- and sillimanite-zone biotites, respectively (see Tables 5 and 6). Open triangles represent biotites in schists adjacent to pegmatites, from SHEARER et al. (1986).

Natural effects account largely for the partitioning behavior of alkaline and alkali earths.

**Crystal-field effects**

McClure (1957) and Dunitz and Orgel (1957) showed that crystal-field theory could account for intracrystalline partitioning of transition-metal ions in spinels. Schwarck (1967) demonstrated that crystal-field stabilization is more important than ionic radii in accounting for the distribution of certain transition-metal ions among coexisting metamorphic minerals, a conclusion confirmed by other workers (e.g., Annersten and Ekstrom, 1971; Dupuy et al., 1980; Hendricks and Dahi, 1987). We now apply crystal-field theory to explain the systemsatics of transition-metal partitioning among our forty-nine metamorphic muscovite-biotite pairs. For a thorough discussion of crystal-field effects and their potential role in transition-metal ion partitioning, the reader should consult Burns (1970).

The crystal-field splitting parameter, $\Delta$, for a metal ion depends on the $(l)$ ionic charge ($Q$) and $d$-orbital radius ($r$):
FIG. 3. Distribution diagrams illustrating the partitioning of Ba (a), V (b), Cr (c), Sc (d), Mn (e), Ni (f), Li (g), and Cu (h) between coexisting muscovite and biotite. Solid and open circles represent staurolite- and sillimanite-zone mica pairs, respectively (see Tables 1–4). Open triangles represent mica pairs in schists adjacent to pegmatites, from SHEARER et al. (1986). Regressions are computed for all data, except for (e) and (f), in which only the sillimanite-zone data were used. Labeled data points are discussed in the text.
Trace-element partitioning between muscovite and biotite

0.10
0.08
0.06
0.04
0.02
0.00

0.0 0.1 0.2 0.3 0.4

Muscovite

r = 0.86

Na

0.6

0.4

0.2

0.0

0.00 0.04 0.08 0.12 0.16

Biotite

r = 0.83

Mg

1.9

1.7

1.5

1.3

1.1

0.9

0.7

0.5

0.3

1.8

1.7

1.6

1.5

1.4

1.3

1.2

1.1

1.0

0.9

0.8

0.7

0.6

0.5

0.4

0.3

0.2

0.1

0.0

0.0 0.1 0.2 0.3 0.4

Biotite

FIG. 4. Distribution diagrams illustrating the partitioning of Ti (a), K (b), Na (c), and Mg (d) between coexisting muscovite and biotite. Cations per twenty-two oxygens are plotted on each diagram. Solid and open circles represent staurolite- and sillimanite-zone mica pairs, respectively (see Tables 5-8). Open triangles represent mica pairs in schists adjacent to pegmatites, from SHEARER et al. (1986). Labeled data points are discussed in the text.

(2) identity and symmetry of coordinated ligands; and (3) interatomic distance (R) between metal ion and ligand, as indicated by

\[ \Delta = Q(r^4/R^2) \]  

(see BURNS, 1970). The octahedral sites in biotites and muscovites are virtually identical with respect to two of these parameters, namely, the nature of ligand (i.e., oxygen and hydroxyl) and ligand symmetry. However, the metal-ligand interatomic distance differs significantly between the minerals. Tabulations of structural parameters in micas by BAILEY (1984) indicate that, among the most common mica polytypes, the occupied M2 site of muscovite (2M1) has a longer mean octahedral metal-oxygen bond length [2.236 ± 0.021 Å (1σ)] than the M1-M2 sites of 1 M biotite [2.093 ± 0.027 Å (1σ)]. This difference is statistically significant at the 1% level. Thus, for cations exhibiting crystal-field effects, the 6.4% shorter octahedral cation-oxygen bond length in biotite should correspond to an octahedral splitting parameter (\( \Delta_0 \)) that is 28% higher in value than that for muscovite, according to Eqn. 2. As a result, these cations should gain more crystal-field stabilization energy (CFSE) by entering a biotite than by a coexisting muscovite. Indeed, except for V\(^{3+} \), the other cations susceptible to crystal-field effects, namely, Ti\(^{4+} \), Cr\(^{3+} \), Co\(^{2+} \), Ni\(^{2+} \), and Cu\(^{2+} \), do favor biotite, as indicated by their \( K_p^* \) (bio/mus) values (Table 9).

The most compelling evidence for crystal-field influence on partitioning of transition-metal cations is that the relative magnitudes of \( K_p^* \) (bio/mus) values observed for these ions (Table 9; Fig. 5a,b) are just as predicted from their CFSE values (given in BURNS, 1970), in conjunction with the higher \( \Delta_0 \) inferred above for biotite relative to muscovite. Within each sequence below, the predicted relative \( K_p^* \) values reflect decreasing octahedral site preference energies (OSPE) in biotite (relative to coexisting muscovite), as follows: for divalent cations,

\[ \text{Ni > Co > Cu > Mn > Zn} \]

and for trivalent cations,

\[ \text{Cr > V > Sc} \]

For trivalent ions, the observed \( K_p^* \) sequence follows crystal-field predictions exactly (Sc\(^{3+} \) gains no CFSE because of its 3d\(^0 \) d-orbital configuration). Both mean \( K_p^* \) values (Table 9) and individual values within each mica pair (Fig. 5) follow this sequence. Figure 5a shows that \( K_p^* \text{Cr} \) is higher than the corresponding \( K_p^* \text{V} \) value in all samples; in turn, \( K_p^* \text{V} \) is invariably higher than the corresponding \( K_p^* \text{Sc} \) (Fig. 5b).

Among divalent ions, only Ni\(^{2+} \), Co\(^{2+} \), and Cu\(^{2+} \) follow the predicted sequence (see Table 9). \( K_p^* \text{Ni} \) exceeds the corresponding \( K_p^* \text{Co} \) in all samples, and \( K_p^* \text{Co} \) exceeds \( K_p^* \text{Cu} \) in all but nine samples. Analytical uncertainty involving Co
and Cu abundances in muscovite, mentioned earlier, may account for some of this discrepancy. Mn$^{2+}$ and Zn$^{2+}$ do not follow the predicted sequence; but neither do they gain any CFSE, due to the electronic configuration of their d-orbitals ($3d^4$ and $3d^{10}$, respectively). Were CFSE effects exerting the only control on partitioning, $K_d^*$ values for these cations would be the lowest among the divalent ions; yet they are among the highest (Table 9). In the absence of crystal-field effects, it is likely that major-element composition exerts the controlling influence on the partitioning behavior of these cations.

**The effect of interlayer structure**

Our calculated $K_d^*$ values (Table 9) indicate that interlayer Ba$^{2+}$, Sr$^{2+}$, La$^{3+}$, and Na$^+$ are preferentially incorporated into muscovite relative to coexisting biotite (see also Figs. 3 and 4). In contrast, K$^+$ partitions nearly equally between the micas, although a slight preference for biotite is common (Fig. 4b). This behavior can be rationalized in crystal-chemical terms. The substitution of $''$(Mg, Fe$^{2+}$) in biotite laterally extends the octahedral sheet (GUIDOTTI, 1984), resulting in relatively less tetrahedral-octahedral misfit than for a coexisting muscovite. In accommodating its T-O misfit, therefore, biotite should require less tetrahedral rotation than muscovite. Indeed, BAILEY (1984) noted that the tetrahedral rotation angle ($\alpha$) for trioctahedral micas (1.4°-11.0°) is less than for dioctahedral micas (6.0°-19.1°). MOLOSHAG and TEREMETSKAYA (1975) showed that the interlayer K$^+$-O bond length for biotite exceeds that of muscovite. Together, these results indicate a more open interlayer structure in biotite relative to muscovite, as also indicated by PAPIKE et al. (1984) and SHEARER et al. (1986). Coupled with ionic radii for twelvefold coordination, this difference accounts quite well for the relative partitioning behavior of most interlayer cations in coexisting muscovites. Thus, the cations Ba$^{2+}$ (1.61 Å), Sr$^{2+}$ (1.44 Å), La$^{3+}$ (1.36 Å), and Na$^+$ (1.39 Å) (ionic radii from SHANNON, 1976) favor muscovite with its somewhat collapsed interlayer site, whereas the larger K$^+$ (1.64 Å) favors biotite slightly, due to its relatively more open structure. In contrast, cations that are even larger than K$^+$, namely, Rb$^+$ (1.72 Å) and Cs$^+$ (1.88 Å), favor the more open structure of biotite (PAPIKE et al., 1984, and SHEARER et al., 1986). Moreover, the relative ionic radii of Rb$^+$ and Cs$^+$ lead to the prediction that $K_d^*$(Cs$^+$) exceeds $K_d^*$(Rb$^+$). This prediction is borne out by the experimental work of VOLFINGER (1976).

The likely existence of interlayer H$_2$O and/or H$_3$O$^+$ (hydrogen ion) in biotite and muscovite has received renewed attention in recent literature (e.g., DYAR, 1988; HERVIG and PEACOCK, 1989; GUIDOTTI and DYAR, 1991; FORTIER and GILETTI, 1991; and LOUCKS, 1991). Understanding the partitioning of these species in coexisting micas is especially important if they ultimately prove to affect diffusion rates and closure temperatures of radiogenic Ar and Sr, which, like H$_2$O and/or H$_3$O$^+$, also reside in the interlayer cavities of micas (also see GUIDOTTI and DYAR, 1991; and LOUCKS, 1991).

The structural argument advanced above for interlayer trace-element partitioning can be extended to include H$_2$O$^+$ and H$_2$O. The ionic radius of H$_3$O$^+$ is about 5% greater than that of K$^+$ (LOUCKS, 1991), whereas the radius of H$_2$O (1.5 Å, KRYNICKI et al., 1979) is smaller than that of K$^+$. Thus, we predict that H$_2$O$^+$ (if present) should prefer the relatively open interlayer sites of biotite; conversely, H$_2$O (if present) ought to favor the more collapsed interlayer sites of muscovite. Our ICP analyses (Tables 1–8) are not of sufficient quality to test these predictions directly, and even if our data were completely free of error from impurity phases, we would still be missing the analyses for H, O, F, Cl, Fe$^{2+}$, and Fe$^{3+}$ necessary for direct stoichiometric inference of interlayer water in our micas. The importance of complete mica analyses in this regard has recently been underscored both for biotite (DYAR, 1990; DYAR et al., 1991; GUIDOTTI and DYAR, 1991) and for muscovite (LOUCKS, 1991).

In forty-seven of our forty-nine mica pairs, biotite exhibits the higher abundance of apparent interlayer vacancies (relative to muscovite), as inferred from its lower interlayer cation sums, $\Sigma$(K + Na + Ca + Ba + La + Sr) (see Tables 5–8). Among the thirty-one staurolite-zone rocks, $\Sigma$(K + Na + Ca + Ba + La + Sr) for biotite averages 1.71 ± 0.09 cations per twenty-two oxygens compared to 1.84 ± 0.04 for coexisting muscovite; our sillimanite-zone values are somewhat higher, possibly reflecting grade-related dehydration of interlayer sites (see also GUIDOTTI and DYAR, 1991). Results
identical to these are also evident from microprobe analyses of coexisting biotite-muscovite pairs we have examined from the literature (e.g., DUTROW et al., 1986; SHEARER et al., 1986; and the forty-three analyses compiled by HOISCH, 1989). The best-fit site-occupancy model of LOUKCKS (1991) considers that apparent interlayer site vacancies in white micas are all occupied by a combination of H2O and H3O. If this holds true for biotite as well, then it follows from the relative interlayer cation sums discussed previously that biotite potentially houses more (H2O, H3O)++ than coexisting muscovite.

It is tempting to consider that (H2O, H3O)++ content affects the diffusion rates (and thus the closure temperatures) of Ar and Sr typically inferred for micas from thermochronologic studies. Instead, however, we believe that both interlayer water contents and isotopic closure temperatures are governed by the interlayer "ionic porosity" (DOWTY, 1980; FORTIER and GILLETI, 1989), which is dictated, in turn, by the density of vacancies remaining after substitution of "(K, Na)+. Thus, in explaining the partitioning behavior of these and other interlayer cations, we have also identified some of the crystal-chemical and structural reasons why a biotite may (1) exhibit lower interlayer ionic porosity, (2) contain higher (H2O, H3O)++ content, and (3) preserve lower closure temperature (for a given radiogenic isotope), compared to the coexisting muscovite.

The effect of coupled substitution

The crystal-chemical arguments advanced above are not fully satisfactory in accounting for observed Ba2+ partitioning (Table 9) because its ionic radius in twelve-coordinated sites is only slightly less than that of K+, yet the partitioning behavior observed for these cations is clearly very different. To put the issue in perspective, we must explain why muscovite will accommodate five to ten cations of Ba2+ per 1000 interlayer sites, whereas the coexisting biotite will accept only two to four (data from Tables 5–8). In both these, it seems logical that the answer might involve only occasional distortions of interlayer sites that render the local-scale structural environment quite different from the average, gross-scale structure. Consequently, arguments based upon the average interlayer structure may not be entirely adequate.

Clearly, however, the occurrence of Ba2+ in a mica necessitates some sort of coupled substitution mechanism to maintain charge balance, and numerous schemes have been suggested (e.g., WENDLANDT, 1977; MANKSISH et al., 1979; DYMIEK, 1983; GUIDOTTI, 1984; RAASE et al., 1983; GUO and GREEN, 1990; HARLOW, 1991; and TRACY, 1991). GUIDOTTI (1984) has commented on the difficulty of identifying substitution schemes in micas from natural samples. Among our micas, for example, the relatively small changes in Ba2+ are masked by analytical fluctuations of K+ and other major cations. Despite being unable to pinpoint the precise exchange mechanism(s) by which Ba2+ substitution actually occurred in our micas, we can still consider the possible consequence of different mechanisms operating simultaneously in coexisting biotite and muscovite on Ba2+ partitioning behavior. Mica-fluid exchange may favor substitutions involving only one type of site (SHEARER et al., 1986). Thus, for example, were K-Ba substitution in muscovite to involve an interlayer-scheme (e.g., Ba4K7 K–, as one mechanism proposed by GUIDOTTI, 1984), but an interlayer-octahedral or -tetrahedral scheme (as generally supposed) in coexisting biotite, the expected result would be preference of Ba2+ for muscovite over biotite, all other being factors equal, as shown unequivocally in Fig. 3a.

Compositional Controls on Trace-element Partitioning

As a general compositional effect, the preference exhibited by biotite for Li+ and divalent cations of transition elements (Table 9) reflects the high abundance of comparably sized "Fe2+ and "Mg2+ in biotite (relative to coexisting muscovite). Consistent with this view is the successful synthesis of trioctahedral mica endmembers involving some of these trace cations (HAZEN and WONES, 1972). Likewise, strong affinities of muscovite for Cr3+, V3+, and Sc3+ are due to its relatively high stoichiometric [(Al,Fe2+)] abundance. Support for this argument comes from FRONDEL (1970), who showed that Sc3+ forms a solid solution with Fe3+ in muscovite, but only to a very limited extent with Fe2+. In addition, Cr3+ and V3+ exhibit solid solution with Al3+, as indicated by natural occurrences of fuchsite and roscoelite, respectively.

A possible example of an element-specific compositional effect involves Mn. The partitioning of Mn between coexisting micas exhibits Henry's Law behavior, but the scatter in Fig. 3e is surprising given that Mn is analytically very sensitive in both micas. Muscovites in samples St-103, -106, and -112 in particular contain anomalously high levels of Mn compared to coexisting biotites. This Mn-deviance may reflect the relative Fe2+ and Mg contents of micas in these rocks. The three samples are all from the muscovite-rietite unit (Fig. 1), in which (as noted above) biotites have relatively high Mg/Fe2+ ratios in keeping with the presence of magnetite ± cordierite. Thus, barring disequilibrium, the Mn-deviance in Fig. 3e can be interpreted on an ionic size basis, whereby relative exclusion of Mn3+ (0.83 Å) occurs in biotites having high Mg2+ (0.72 Å) and/or low Fe2+ (0.78 Å) (ionic radii from SHANNON, 1976). Alternately, some of the Mn in these samples may exist as Mn3+ (0.645 Å), consistent with the more oxidized nature of the magnetite-bearing muscovite-rietite unit. Significant levels of Mn2+ are known to occur both in trioctahedral manganophyllite (coexisting with pie-montite; BURNS, 1970) and dioctahedral alurgite (coexisting with viridine; GUIDOTTI, 1984). Because Mn3+ (0.645 Å) is far more likely than Mn2+ (0.83 Å) to substitute for octahedral Al3+ (0.535 Å) in muscovite, its presence may contribute to the Mn-deviance of the three samples observed in Fig. 3e, as well as the overall scatter exhibited by the other samples.

Other element-specific compositional effects are harder to infer unequivocally. Among the thirty-one staurolite-zone biotites, for example, positive correlations (cf. Figs. 3f and 4d) for Mg2+ (0.72 Å) vs. Ni2+ (0.69 Å), Co2+ (0.745Å), and Zn2+ (0.74 Å) (radii from SHANNON, 1976) suggest that Mg2+ partly controls partitioning of the trace elements. (Such correlations are absent in coexisting muscovite, reflecting the analytical imprecision attendant to relatively low trace-element abundances.) However, these correlations could just as easily represent pre-metamorphic geochemical affinities. Moreover, it is actually (Mg + Fe2+)00 that potentially affects
these elements, not just Mg\(^{2+}\) alone; yet the uncertainty in Fe\(^{3+}\) abundances precludes consideration of this parameter.

**Thermal Effects on Trace-element Partitioning**

Given the excellent ICP analytical sensitivity and freedom from spectral interference exhibited by Mg, it is highly unlikely that analytical error is significantly involved in the scatter observed in Fig. 4d. Nor are disequilibrium or impurities likely sources of scatter, for reasons discussed earlier. Instead, the scatter is interpreted to represent widely variable equilibration temperatures among the sixty-nine mica pairs (this total includes samples from Shearer et al., 1986). This interpretation is based upon the known temperature-dependence of MgSi\(_{w}\) (Mg-Tschermak) exchange between coexisting muscovite and biotite (Hoisch, 1989). The labeled points clustered on the far right side of Fig. 4d represent the lowest muscovite-biotite temperatures (cf. Table 9), whereas samples plotting in the upper left represent the highest temperatures (generally near exposures of granite or pegmatite). Intermediate temperatures are inferred for points plotting between these extremes.

The implications of temperature with respect to the partitioning behavior of trace elements that substitute for Mg and Al are plainly evident. Specifically, the ionic radii and/or valences of cations like Li\(^{+}\), Ni\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\), and Cu\(^{2+}\) facilitate their substitution for Mg\(^{2+}\). Likewise, Cr\(^{3+}\), V\(^{3+}\), and perhaps Sc\(^{3+}\) are potentially controlled by "Al\(^{3+}\). Even the substitutional behavior of interlayer cations in muscovites potentially is affected by temperature (albeit indirectly) to the extent that celadonite content exerts a structural control on the K/[(Na + K)] ratio (Guidotti, 1984). Support for this idea among our forty-nine muscovites is provided by the strong positive correlation between octahedral Mg\(^{2+}\) and K/[(Na + K)] ratios (not shown).

Hoisch (1989) based an empirical geothermometer upon thermodynamic treatment of the Mg-Tschermak exchange reaction between iron-free micas, as follows:

\[
KMg_3(AlSi_3)O_{10}(OH)_2 + KAl_2(AlSi_3)O_{10}(OH)_2 \rightarrow K(Mg,Al)(Al_2Si_2)O_{10}(OH)_2 + K(MgAl)SiO_2(OH)_2,
\]

for which he inferred the ideal equilibrium constant,

\[
K_Mg-Al = 27\left[\frac{(Mg/"Al")_{muscovite}}{(Mg/"Al")_{celadonite}}\right].
\] (3)

As yet, no experimental or field-based evaluation of this geothermometer has been published, but preliminary evidence from our data indicates that the method has considerable promise. First, a regional map of some sixty-nine biotite-muscovite temperatures across the southern Black Hills qualitatively resembles a garnet (rim)-biotite thermal map of Frifberg and I. M. Frifberg et al. (unpubl. data) for the same area and Proterozoic time frame. Thermal
contour lines on both maps delineate (1) a partial "bullseye" associated with the main mass of Harney Peak granite, (2) a prominent N-S thermal "trough" coincident with the Thompson Draw synform (axial trace shown in Fig. 1), and (3) localized thermal highs just south of Custer and adjacent to Archean rocks (Fig. 1), presumably associated with unexposed granitic plutons. Second, muscovite- and garnet-biotite temperature estimates from nearby samples agree to within 50°C (or better), with the latter tending to be the lower of the two, across the approximately 250°C range inherent in the two southern Black Hills sample sets. Third, the samples yielding the highest muscovite-biotite temperatures (>660°C; analytical data from Table 9 and from SHEAKER et al., 1986) were sampled immediately adjacent to granitic or pegmatitic heat sources, where relatively rapid cooling rates may have resulted in closure of Mg-Tschermak exchange at higher temperatures than elsewhere. Given these lines of evidence, we believe that the muscovite-biotite temperatures presented in Table 9 are valid. Electron microprobe analysis of all our micas is underway to fully verify this conclusion.

The scatter in Mg distributions between muscovite and biotite (Fig. 4d) is significantly reduced by normalizing stoichiometric Mg in Tables 5–8 to the corresponding Li abundances. This behavior is shown in Fig. 6a. The range in Li/Mg values preserved in the micas presumably reflects variable (Li/Mg)fluid among the samples during metamorphism, and the positive linear trend indicates that both biotite-fluid and muscovite-fluid Li-Mg exchange were systematic. The slope of the trend is KLi_Mg, defined analogously to KMsAl (Eqn. 3) as

$$K_{Li-Mg} = (Li/Mg)_{mica}/(Li/Mg)_{biotite}. \quad (4)$$

KLi_Mg is constant to a first approximation, by inspection of Fig. 6a. By rearranging terms in Eqn. 4, it is evident that maintaining constant KLi_Mg requires covariance of Li_Mus/Li_Bio and Mg_Mus/Mg_Bio. However, Mg_Mus/Mg_Bio depends on temperature according to Eqn. 10 of HOISCH (1989), coupled with Eqn. 3. It follows from the trend in Fig. 6a that Li-Al exchange is itself either temperature-sensitive or compositionally controlled by the Mg-Al exchange. Ni2+ appears to behave much like Li+ in resolving the scatter of the Mg2+ distribution, as shown in Fig. 6b, which likewise implies that the exchange vector NiSiAl2 is either directly temperature-sensitive or indirectly so by virtue of compositional control by the component MgSiAl2. Similarities in the partitioning of Mg2+, Li+, and Ni2+ are not unexpected in that their octahedral ionic radii are similar (0.72, 0.76, and 0.69 Å, respectively; SHANNON, 1976).

Temperatures inferred from Mg-Tschermak (MgSiAl2) exchange between coexisting muscovite and biotite (HOISCH, 1989) provide a convenient datum by which to evaluate the thermal behavior of analogous vector components involving trace elements. Several of these components appear to possess exchange potentials (ΔGrea) sufficiently large that the respective equilibrium constants K (analogous to KMsAl; Eqn. 3) approach unity with temperature increase. These components include NiSiAl2, MgSiCr2Al1, MgSiV-Al1, MgSiSe-Al1, CrAl1, Val1, and Li2 Si "Al2 ∑1 "Al1. Plots of KLi_Mg and KmSc vs. temperature are shown in Fig. 7a,b. Although modest, the trends in Fig. 7 are consistent with the suggestion that Li-Al and Mg-Se partitioning are temperature-dependent; experimental work is needed to verify this idea, however. In contrast, any apparent thermal sensitivity of other exchange vector components is masked by analytical scatter.

It should be emphasized that the axes used in Fig. 7 are not entirely independent since "Al and Mg partitioning are inherent in the muscovite-biotite temperature equation (see HOISCH, 1989). However, we note that a plot of ("Al)Musc/("Al)Biot vs. mica temperature is highly scattered and shows no trend whatsoever.) Nevertheless, circular reasoning can be entirely avoided if garnet-biotite (instead of muscovite-biotite) temperature is plotted on the x-axes. Conceptually, this axis translation should not change the apparent thermal responses of K shown in Fig. 7 because of the overall similarity of garnet-biotite and muscovite-biotite thermal patterns across the southern Black Hills (indicated earlier in this section and discussed by P. S. Dahl et al., unpubl. data).

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