American Mineralogist, Volume 71, pages 1126–1128, 1986

Limitations on the interpretation of biotite substitutions from chemical analyses of natural samples

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Abstract

Biotites, as well as other phases, are sufficiently complex chemically that there are numerous sets of linearly independent exchange components with which to describe the composition of a naturally occurring crystal. Even after complete chemical analysis, this leads to ambiguities in the correlation of exchange components with valid substitution mechanisms in complex phases. The best means of identifying valid substitutions are by the observation of simple endmember compositions, the investigation of compositional changes in zoned crystals or petrogenetic sequences, and by direct experimental synthesis.

Introduction

Studies of the crystal chemistry of biotite, particularly those investigating the substitution of Ti, frequently try to define individual substitutions as important in producing the chemical composition of particular phases. This has led to disagreement among various researchers as to which substitutions are important and how the compositions of biotite should be expressed in terms of endmembers.

The purpose of this paper is to present an analysis of biotite compositions using the methods presented by Thompson (1982) applied along the lines of a similar treatment of biotites by Labotka (1983). We will show again that any common biotite can be represented in terms of an additive component and a limited number of linearly independent exchange components. Furthermore, there are numerous sets of viable exchange components that can be used, and the substitutions touted will depend on the particular choice of exchange vectors. Finally, although it has been widely understood that incomplete analyses—especially those neglecting Fe_2O_3 and H_2O—will lead to ambiguities regarding biotite substitutions, it can also be demonstrated that even with complete biotite analyses we are unable to make unique substitution models.

Biotite components

Based on crystallographic information, summarized most recently by Hazen and Burnham (1973) and Bailey (1984), the structural formula for biotite, normalized to 24 anions and including the commonly discussed substitutions, can be expressed as shown in Table 1.

Altogether these amount to 18 components. By analogy with the phase rule, the variance of the system equals the number of variables minus the number of equations relating those variables: Therefore, we must place 18 restrictions on the system in order to define the composition of the phase in this structural arrangement. As pointed out by Thompson (1982) and Labotka (1983), there are numerous ways of expressing these restrictions. The standard structural formula gives the number of moles of each of the 18 components in such a way that charge balance and the crystal-chemical integrity of the biotite are maintained. A more useful approach, because we are trying to simplify our expression of the biotite composition, is to define one set of equations basic to the crystal chemistry of biotite and then a smaller set of exchange components with which to describe the composition of the phase (Thompson, 1982; Labotka, 1983).

The first group of equations defining the biotite structure for these 18 components is

$$\mathrm{K} + \mathrm{Na} + \mathrm{Ca} + \square(\mathrm{XII}) = 2 \qquad (1)$$

$$\mathrm{Mg} + \mathrm{Fe}^{2+} + \mathrm{Mn}^{2+} + \mathrm{Fe}^{+3}(\mathrm{VI}) + \mathrm{Al(VI)} + \mathrm{Ti} + \square(\mathrm{VI}) = 6 \qquad (2)$$

$$\mathrm{Si} + \mathrm{Al(IV)} + \mathrm{Fe}^{3+}(\mathrm{IV}) = 8 \qquad (3)$$

$$\mathrm{O} + \mathrm{OH} + \mathrm{F} + \mathrm{Cl} = 24 \qquad (4)$$

$$\Sigma\ \text{positive charges} = \Sigma\ \text{negative charges} \qquad (5)$$

Labotka (1983) shows that using a single additive component, such as phlogopite, is equivalent to these first five equations as long as the additional exchange components are charge-balanced. Therefore, we need to define only 13 exchange components: The choice of these 13 is arbitrary,

Table 1. Common components in biotite

Two interlayer sites	Six octahedral sites	Eight tetrahedral sites	Twenty-four anions
K	Mg	Si	O
Na	Fe^{2+}	Al(IV)	OH
Ca	Fe^{3+}(VI)	Fe^{3+}(IV)	F
□(XII)	Al(VI)		Cl
	Ti		
	Mn		
	□(VI)		

Note: □*n* refers to a vacancy of coordination number *n*.

0003-004X/86/0910-1126$02.00

but all of the original 18 components must be included and the exchanges must be linearly independent and charge-balanced. The first group of these can be expressed as simple two-element exchanges:

$\mathrm{NaK_{-1}}$ (6)
$\mathrm{FeMg_{-1}}$ (7)
$\mathrm{MnMg_{-1}}$ (8)
$\mathrm{Fe^{3+}Al(IV)_{-1}}$ (9)
$\mathrm{FOH_{-1}}$ (10)
$\mathrm{ClOH_{-1}}$ (11)

The choice of the remaining components is not so well defined. There are many possibilities, and the particular choice that is made will influence any interpretation on substitutions that might be attempted. In our comparison we will use two very similar sets of exchanges, both containing only commonly quoted mica substitutions (given in parentheses in the following lists). Even though more divergent sets can easily be constructed, the minor differences between these two sets are sufficient to yield significantly different results when applied to natural biotites.

Exchange Set I

$\mathrm{CaAl(IV)K_{-1}Si_{-1}}$	(Clintonite)	(12)
$\mathrm{Si\square(XII)K_{-1}Al(IV)_{-1}}$	(Talc)	(13)
$\mathrm{Al(IV)Al(VI)Fe_{-1}Si_{-1}}$	(Al-Tschermak's)	(14)
$\mathrm{Fe^{3+}(VI)OFe_{-1}OH_{-1}}$	(Fe oxy-annite)	(15)
$\mathrm{Ti\square(VI)Fe_{-2}}$	(Ti-vacancy)	(16)
$\mathrm{Al(IV)_2TiFe_{-1}Si_{-2}}$	(Ti-Tschermak's)	(17)
$\mathrm{TiO_2Fe_{-1}OH_{-2}}$	(Ti oxy-annite)	(18)

Exchange Set II

$\mathrm{CaAl(IV)K_{-1}Si_{-1}}$	(Clintonite)	(12)
$\mathrm{Si\square(XII)K_{-1}Al(IV)_{-1}}$	(Talc)	(13)
$\mathrm{Al(IV)_2TiFe_{-1}Si_{-2}}$	(Al-Tschermak's)	(14)
$\mathrm{Fe^{3+}(VI)OFe_{-1}OH_{-1}}$	(Fe oxy-annite)	(15)
$\mathrm{Al(VI)_2\square(VI)Fe_{-3}}$	(Muscovite)	(16)
$\mathrm{Al(IV)_2TiFe_{-1}Si_{-2}}$	(Ti-Tschermak's)	(17)
$\mathrm{Al(VI)OFe_{-1}OH_{-1}}$	(Al oxy-annite)	(18)

APPLICATION TO NATURAL BIOTITES

How do these different sets of equations describe the compositions of natural biotites? Both work equally well and are accurate to the degree that the original analyses are accurate. If they are applied to incomplete analyses, particularly those neglecting Fe_2O_3, H_2O, F, and Cl, some coefficients of the exchange vectors must be falsely set to zero, and the results obtained are questionable at best. Clever treatment of the data and choices of the exchange components can alleviate some of the problems, but the coefficients of the vectors chosen can only be reliable for the part of the biotite analyzed and not for the whole.

Table 2. Calculated biotite formulae

	FD-12*	Au Sable**
Si	5.42	5.587
Al(IV)	2.58	2.413
Al(VI)	0.67	0.243
Ti	0.35	0.636
Fe^{3+}	0.44	0.000
Fe^{2+}	2.78	2.786
Mg	1.22	2.321
Mn	0.14	0.015
□(VI)	0.40	−0.001
Ca	0.00	0.005
Na	0.15	0.040
K	1.86	1.971
□(XII)	−0.01	−0.016
Cl	0.02	0.275
F	0.39	0.165
OH	3.17	2.435
O†	20.42	21.125

* Dodge et al. (1969).
** Bohlen et al. (1980).
† Calculated by difference based on 24 anions.

We will compare these sets of equations for two natural biotites that have been analyzed for all the elements in our original list except oxygen. Table 2 lists the structural formulae for both biotites calculated on the basis of 24 anions. The first is an analysis (FD-12) of a biotite from the Taft Granite in the Sierra Nevada reported by Dodge et al. (1969). The second is an analysis of a granulite-facies metamorphic biotite from the Adirondacks (Au Sable) for which Bohlen et al. (1980) have reported both a complete chemical analysis and structural determination.

Table 3 compares the vector coefficients necessary to describe the biotites with the two different sets of exchanges using phlogopite (24 anions) as the additive component. The first eight exchanges need not be compared because they are the same and yield identical results for both sets. Even though there are only two differences in the last five exchange components, there are significant differences in the apparent substitutions. Looking at sample FD-12, just three exchanges out of the last five in Set I account for most of the necessary changes in composition. Those substitutions are the Al-Tschermak's, Ti-vacancy, and Fe oxy-annite exchanges, all of which have been shown to be important substitutions by experimental synthesis and/or have been commonly proposed as major substitutions in biotite (Rutherford, 1973; Forbes and Flower, 1974; Wones, 1963). Using Exchange Set II we see that the same material is equally well expressed by major amounts of Ti-Tschermak's, muscovite, and Fe oxy-annite exchanges with a small negative amount of Al-Tschermak's substitution. These too are well-accepted mica substitutions and give an equally good description of the biotite; however, we get a very different view of the importance of particular substitutions than we got with Exchange Set I.

A similar result is obtained when we look at the data for the Au Sable biotite. This has been cited as a biotite demonstrating the importance of the Ti oxy-annite sub-

Table 3. Vector coefficients from phlogopite

Set I	FD-12	Au Sable	Set II	FD-12	Au Sable
NaK$_{-1}$	0.15	0.040	NaK$_{-1}$	0.15	0.040
FeMg$_{-1}$	4.64	3.664	FeMg$_{-1}$	4.64	3.664
MnMg$_{-1}$	0.14	0.015	MnMg$_{-1}$	0.14	0.015
Fe^{3+}Al(IV)$_{-1}$	0.00	0.000	Fe^{3+}Al(IV)$_{-1}$	0.00	0.000
FOH$_{-1}$	0.39	0.165	FOH$_{-1}$	0.39	0.165
ClOH$_{-1}$	0.02	0.275	ClOH$_{-1}$	0.02	0.275
Clintonite	0.00	0.005	Clintonite	0.00	0.005
Talc	−0.01	−0.016	Talc	−0.01	−0.016
Al-Tschermak's	0.67	0.243	Al-Tschermak's	−0.11	−0.880
Fe oxy-annite	0.44	0.000	Fe oxy-annite	0.44	0.000
Ti-vacancy	0.40	−0.001	Muscovite	0.40	−0.001
Ti-Tschermak's	−0.04	0.074	Ti-Tschermak's	0.35	0.636
Ti oxy-annite	−0.01	0.563	Al oxy-annite	−0.02	1.125

stitution, although Bohlen et al. (1980) only refer to it as one of the substitutions that might be considered. The vector coefficients in Table 3 using the Set I exchange components give very similar results to those in Table 7 of the Bohlen et al. (1980) paper. However, an equally good representation of the Au Sable biotite is given without any Ti oxy-annite substitution by using the exchange components in Set II. Here the Al oxy-annite substitution replaces the Ti oxy-annite substitution; we see no reason why the latter substitution should be any more or less valid than the former. No experimental or observational data are currently available to give preference to either substitution.

DISCUSSION

Thompson (1982) has demonstrated the vector approach to compositional analysis of minerals and has made it clear that there are many combinations of exchange vectors that lead to the same composition. Whether or not particular vectors correspond to crystal-chemically valid substitutions may be an important question, but it is usually not answerable by analysis of complex natural phases. Other criteria must be used to determine an independent set of important substitutions. Three kinds of data seem most likely to yield this information. First, the natural occurrence of compositions related to a principal additive component by a single "simple" exchange vector. The occurrences of these endmember phases provide valuable information on the validity of particular vectors as substitutions, although any single substitution may be a combination of two or more other substitutions. It seems reasonable, however, that we should choose the set of substitutions that represents the least common denominators. Second, changes in compositions of phases that occur as zoned crystals or in petrogenetic sequence can be directly related to appropriate substitutions. In these samples there is the added advantage of being able to define initial and final compositions and therefore the vectors that relate them. This allows us to examine more complex phase compositions, but we should still search for simple changes in composition if we want to identify the most fundamental substitutions. Finally, experimental methods can be useful in establishing substitutions. The 100% synthesis and persistence of a phase on the composition of a particular substitution are compelling evidence for its validity. With less than 100% synthesis, accurate microanalysis is a necessity and often shows the phase composition located off the planned substitution vector. It has been our experience that this is especially true for biotites and that often there is no unique set of simple vectors leading to the measured composition in these multiphase experiments (Abrecht and Hewitt, in prep.).

In summary it must be remembered that there is no generally valid correlation between exchange components and substitution mechanisms. For complex phases, multiple equivalent sets of exchange components are available to describe the phase compositions. Additional information must be obtained in order to choose a set or sets of exchange components that are also valid substitutions for the phase in question.

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MANUSCRIPT RECEIVED OCTOBER 2, 1985
MANUSCRIPT ACCEPTED MAY 16, 1986