

Analysis of the compositional variations of biotite in pelitic hornfelses from northeastern Minnesota

THEODORE C. LABOTKA

Department of Geological Sciences
University of Tennessee, Knoxville, Tennessee 37996

Abstract

Biotite from pelitic hornfelses, northeastern Minnesota, shows a wide compositional range, from $Mg/(Mg + Fe) = 0.35$ to 0.95 . Strong correlations among Mg, Fe, Ti, ^{VI}Al , and ^{IV}Al are observed, and the technique of principal components analyses is used to extract independent biotite components. The dependence of composition on assemblage is exemplified by biotite from the assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite with compositions that contain more dioctahedral component and less Ti than biotite from a similar, but muscovite-free assemblage. Principal components analysis shows that 98% of the total variance in compositions of biotite from the muscovite-bearing assemblage can be ascribed to two substitutions with *phlogopite*: the substitution $^{IV}Al_{0.45} + Fe_{2.29} + ^{VI}Al_{0.21} + Ti_{0.31} + ^{VI}\square_{0.19} \rightleftharpoons Si_{0.45} + Mg_{3.0}$, and the substitution $Ti_{1.5} + ^{IV}\square_{0.5} \rightleftharpoons ^{VI}Al_2$. The analysis indicates that although biotite is rigorously a six- or more-component mineral, three components are sufficient to describe the bulk of its compositional range. These three components are used to calculate the possible range in biotite compositions for the muscovite-bearing assemblage using ideal-mixing activity models. The calculated range is very similar to the observed range; however, the absolute value of K_D (Mg/Fe, Cord/bio) is underestimated. In addition, the amounts of octahedral Al, Ti, and vacancies are poorly estimated, especially for Mg-rich biotite. These faults are probably the result of treating biotite as a three-component rather than a six-component phase. The observed cation correlations are believed to result from crystal chemical constraints on the volume of the biotite unit cell. It is proposed that biotite compositions from a particular assemblage might be sensitive indicators of the thermal gradient.

Introduction

Biotite occurs in a great variety of rock types and has a structure that can accommodate most of the abundant elements. The large range in composition of natural biotite makes it a valuable source of information regarding equilibrium conditions. The composition of biotite depends principally on the bulk composition and the extents of the various continuous reactions among the minerals in the rock. The latter dependence can be used to deduce the prevailing conditions during equilibration of the mineral assemblage. For example, the partitioning of Fe and Mg between biotite and garnet can be used to determine temperature (Goldman and Albee, 1977, Ferry and Spear, 1978), and the $Fe/(Fe+Mg)$ value of biotite coexisting with magnetite and sanadine can be used to determine the value of fH_2O/fO_2 (Wones and Eugster, 1965). The composition of biotite in these examples is governed by the progress of the continuous reactions that involve biotite end-members like *phlogopite* and *annite*. In order to obtain the values of the desired intensive parameters, the activities of the end-member components

must be determined. Previous workers have expressed the activity of the end-member component using the ionic model of Kerrick and Darken (1975). For example, Ghent *et al.* (1979) expressed the activity of *phlogopite* as $(X_K)(X_{Mg})^3(X_{OH})^2$ in which X refers to the mol fraction of the cation or anion in the appropriate crystallographic site. Thompson (1976) used the activity model $(X_K)(X_{Fe})^3$ for *annite* in his calculations of continuous and discontinuous mineral equilibria during progressive metamorphism of pelitic schists. In this type of model cations and anions are presumed to substitute on their respective sites independently.

Holdaway (1980) addressed the problem of picking end-member biotite compositions to use in thermodynamic calculations involving natural or experimental systems. Holdaway determined an iron end-member composition for biotite from pelitic schists by linear regression of the various cations or groups of similar cations like $^{VI}(Al+Cr)$ against Ti. The end-member biotite is given by Holdaway as the composition at $Ti = 0$, determined by the regression coefficients.

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APPENDIX II: Biotite analyses from muscovite + Kfeldspar - bearing assemblages

ANALYSIS	039A1B10 102	039A1B10 201	039A2B10 101	039A2B10 301	039A2B10 401	039A2B10 401	039A2B11 401	035F2B10 201	035F2B10 301	035F2B10 401	035F1B10 101
SEQ #	5	6	7	9	10	11	23	24	25	34	
REF #	0	0	0	0	0	0	0	0	0	0	0
SI02	35.71	36.85	38.71	38.54	38.16	37.34	36.22	35.60	36.47	35.62	
AL203	19.60	17.46	18.37	18.36	17.93	17.61	18.10	18.44	18.84	18.63	
FEO	18.72	18.68	18.57	18.58	19.10	18.88	21.90	21.80	21.60	22.34	
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
MGO	10.47	9.18	9.45	9.24	9.33	9.14	6.34	6.68	6.59	6.96	
MNO	.02	.02	.04	.05	.03	.00	.03	.04	.03	.03	
TI02	1.62	4.29	2.96	3.54	3.84	3.99	3.92	3.91	3.49	3.79	
CR203	.03	.44	.34	.42	.47	.43	.23	.27	.22	.29	
CAO	.02	.04	.06	.03	.04	.04	.03	.03	.02	.05	
NA20	.00	.00	.20	.00	.00	.00	.00	.00	.00	.00	
K20	8.92	9.23	8.96	9.27	9.14	9.47	9.63	10.25	10.05	9.84	
SUM	95.11	96.19	97.66	98.03	98.04	96.90	96.40	97.02	97.31	97.55	
FEO	18.72	18.68	18.57	18.58	19.10	18.88	21.90	21.80	21.60	22.34	
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
SI	2.70	2.76	2.83	2.81	2.80	2.78	2.76	2.70	2.75	2.69	
AL	1.75	1.54	1.58	1.58	1.55	1.55	1.62	1.65	1.67	1.66	
FE2+	1.18	1.17	1.14	1.13	1.17	1.17	1.39	1.39	1.36	1.41	
FE3+	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
MG	1.18	1.03	1.03	1.00	1.02	1.01	.72	.76	.74	.78	
MN	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
TI	.09	.24	.16	.19	.21	.22	.22	.22	.20	.21	
CR	.00	.03	.02	.02	.03	.02	.01	.02	.01	.02	
CA	.00	.00	.01	.00	.00	.00	.00	.00	.00	.00	
NA	.00	.00	.03	.00	.00	.00	.00	.00	.00	.00	
K	.86	.88	.84	.86	.85	.90	.94	.99	.97	.95	

REF #	35	36	45	46	47	48	49	50	51	52
035FIBRIO 201	0	0	0	0	0	0	0	0	0	0
035FIBRIO 301	0	0	0	0	0	0	0	0	0	0
035RIBRIO 401	0	0	0	0	0	0	0	0	0	0
035RIBRIO 501	0	0	0	0	0	0	0	0	0	0
035RIBRIO 601	0	0	0	0	0	0	0	0	0	0
039CIBRIO 201	0	0	0	0	0	0	0	0	0	0
039CIBRIO 301	0	0	0	0	0	0	0	0	0	0
039CIBRIO 401	0	0	0	0	0	0	0	0	0	0
039FIBRIO 401	0	0	0	0	0	0	0	0	0	0
039FIBRIO 501	0	0	0	0	0	0	0	0	0	0
SI02	35.57	35.81	35.45	35.26	34.76	36.21	36.45	36.12	35.80	35.51
AL203	18.55	18.96	21.50	18.98	19.01	18.20	18.06	18.08	19.49	19.23
FEO	22.52	22.32	18.63	21.12	21.08	18.33	18.39	18.42	18.64	17.78
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
MG0	6.67	6.66	10.00	7.51	7.39	9.28	9.05	8.65	10.09	10.36
MNO	.02	.03	.04	.03	.05	.00	.04	.00	.04	.06
TI02	3.83	3.80	.07	3.93	4.02	3.44	3.51	3.62	1.76	1.60
CR203	.33	.29	.04	.29	.25	.36	.36	.29	.06	.00
CA0	.05	.05	.02	.01	.04	.01	.02	.02	.08	.01
NA20	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
K20	9.94	9.70	9.54	9.46	9.53	9.50	9.64	9.52	9.09	9.39
SUM	97.48	97.62	95.29	96.59	96.13	95.33	95.52	94.72	95.05	93.94
FEO	22.52	22.32	18.63	21.12	21.08	18.33	18.39	18.42	18.64	17.78
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
SI	2.69	2.70	2.68	2.67	2.65	2.74	2.75	2.75	2.71	2.72
AL	1.66	1.68	1.91	1.69	1.71	1.62	1.61	1.62	1.74	1.73
FE2+	1.43	1.41	1.18	1.34	1.34	1.16	1.16	1.17	1.18	1.14
FE3+	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
MG	.75	.75	1.12	.85	.84	1.05	1.02	.98	1.14	1.18
MN	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
TI	.22	.21	.00	.22	.23	.20	.20	.21	.10	.09
CR	.02	.02	.00	.02	.02	.02	.02	.02	.00	.00
CA	.00	.00	.00	.00	.00	.00	.00	.00	.01	.00
NA	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
K	.96	.93	.92	.91	.93	.92	.93	.92	.88	.92

ANALYSIS	039R1R10	039R1R10	039R1R10	039R1R11	048F1R10	048F1R10	048F1R10	048F1R10	048F1R10	048F2R10	048F2R10
	601	101	201	101	201	301	701	801	201	501	
SEQ #	53	41	42	43	57	58	59	60	61	62	
REF #	0	0	0	0	0	0	0	0	0	0	
SI02	36.31	35.98	35.90	36.14	41.38	41.50	41.00	41.26	40.71	40.97	
AL203	19.74	20.01	19.70	19.89	15.80	15.43	16.05	15.92	16.14	16.71	
FEO	17.31	19.38	18.65	19.13	3.03	2.85	2.96	2.84	3.07	3.23	
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
MGO	10.47	8.90	8.98	9.44	22.51	22.68	22.64	22.80	21.71	22.16	
MNO	.04	.02	.05	.03	.00	.01	.00	.00	.00	.00	
TI02	1.47	2.50	2.70	2.34	.64	.71	.70	.76	.77	.85	
CR203	.01	.29	.30	.24	.09	.06	.11	.10	.20	.16	
CAO	.01	.03	.01	.03	.00	.00	.00	.00	.02	.00	
NA20	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
K20	9.36	9.41	9.31	9.38	9.84	10.11	10.16	9.95	9.51	9.88	
SUM	94.72	96.52	95.60	96.62	93.29	93.35	93.62	93.63	92.13	93.96	
FEO	17.31	19.38	18.65	19.13	3.03	2.85	2.96	2.84	3.07	3.23	
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
SI	2.74	2.69	2.70	2.70	2.95	2.96	2.92	2.94	2.94	2.91	
AL	1.75	1.77	1.75	1.75	1.33	1.30	1.35	1.33	1.37	1.40	
FE2+	1.09	1.21	1.17	1.19	.18	.17	.18	.17	.19	.19	
FE3+	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
MG	1.18	.99	1.01	1.05	2.39	2.41	2.41	2.42	2.34	2.34	
MN	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
TI	.08	.14	.15	.13	.03	.04	.04	.04	.04	.04	
CR	.00	.02	.02	.01	.01	.00	.01	.01	.01	.01	
CA	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
NA	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
K	.90	.90	.90	.89	.90	.92	.92	.90	.88	.90	

ANALYSIS	048F2R11	039DOR10	039DOR10	039DOR10	039DIR10	018A1R10	018A1R10	018A1R10	022A1R10	022A1R10	022A1R10
	101	201	301	301	101	201	301	201	301	201	401
SER #	63	70	71	72	90	91	92	78	79	80	
REF #	0	0	0	0	0	0	0	0	0	0	0
SI02	40.79	36.03	36.68	36.37	34.45	34.40	34.73	35.04	35.23	35.22	
AL203	16.36	18.33	18.89	18.60	18.61	18.96	19.66	19.40	19.14	19.79	
FEO	3.22	17.51	17.98	17.98	21.87	22.03	21.28	16.27	16.61	16.11	
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
MGO	22.09	9.30	9.10	8.58	6.87	6.76	6.68	9.53	9.75	10.05	
MND	.00	.03	.03	.03	.01	.00	.00	.03	.02	.07	
TI02	.90	3.15	3.06	3.29	3.91	3.74	3.51	2.40	1.92	2.07	
CR203	.31	.23	.31	.34	.16	.16	.22	.16	.14	.11	
CA0	.01	.00	.03	.03	.02	.01	.00	.03	.02	.04	
NA20	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
K20	9.82	8.92	9.15	9.72	9.42	9.46	9.11	9.47	9.33	9.30	
SUM	93.50	93.50	95.23	94.94	95.32	95.52	95.19	92.33	92.16	92.77	
FE0	3.22	17.51	17.98	17.98	21.87	22.03	21.28	16.27	16.61	16.11	
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
SI	2.91	2.76	2.76	2.76	2.66	2.65	2.66	2.71	2.73	2.71	
AL	1.38	1.65	1.67	1.66	1.69	1.72	1.78	1.77	1.75	1.79	
FE2+	.19	1.12	1.13	1.14	1.41	1.42	1.37	1.05	1.08	1.03	
FE3+	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
MG	2.35	1.06	1.02	.97	.79	.78	.76	1.10	1.13	1.15	
MN	.00	.00	.00	.00	.00	.00	.00	.00	.00	.01	
TI	.05	.18	.17	.19	.23	.22	.20	.14	.11	.12	
CR	.02	.01	.02	.02	.01	.01	.01	.01	.01	.01	
CA	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
NA	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
K	.89	.87	.88	.94	.93	.93	.89	.94	.92	.91	

ANALYSIS 041E0B11 043D0B10 043D0B10 0032B102 0032B103 0031B106
 001 601 701 01 01 01

SEQ #	REF #	56	84	85	13	14	18
SI02		35.48	34.59	36.10	35.90	35.90	37.87
AL203		18.85	18.27	18.19	19.10	19.28	20.63
FEO		20.55	17.74	18.27	17.28	17.06	16.60
FE203		.00	.00	.00	.00	.00	.00
M60		7.95	9.97	9.49	9.77	9.68	10.63
MND		.03	.11	.11	.09	.11	.07
TI02		1.57	2.23	1.97	1.53	1.57	1.57
CR203		.17	.03	.03	.11	.12	.06
CAG		.05	.16	.07	.06	.03	.04
NA20		.00	.00	.00	.00	.00	.00
K20		9.43	8.14	8.81	8.53	9.20	8.47
SUM		94.08	91.24	93.04	92.37	92.91	95.94
FEO		20.55	17.74	18.27	17.28	17.06	16.60
FE203		.00	.00	.00	.00	.00	.00
SI		2.75	2.72	2.78	2.77	2.76	2.78
AL		1.72	1.69	1.65	1.74	1.75	1.78
FE2+		1.33	1.17	1.18	1.11	1.10	1.02
FE3+		.00	.00	.00	.00	.00	.00
HG		.92	1.17	1.09	1.12	1.11	1.16
MN		.00	.01	.01	.01	.01	.00
TI		.09	.13	.11	.09	.09	.09
CR		.01	.00	.00	.01	.01	.00
CA		.00	.01	.01	.01	.00	.00
NA		.00	.00	.00	.00	.00	.00
K		.93	.82	.87	.84	.90	.79

ANALYSIS	022H1B10 301	043F3B10 101	043F3B10 201	043F1B10 201	043F1B10 501	043F3B10 102
SEQ #	83	64	65	66	68	69
REF #	0	0	0	0	0	0
SI02	36.34	41.05	39.97	35.95	36.72	39.27
AL203	14.52	12.69	14.83	16.57	15.56	13.73
FEO	23.39	11.88	12.22	16.09	16.27	12.11
FE203	.00	.00	.00	.00	.00	.00
MGD	9.80	19.03	18.18	14.69	13.61	18.58
MNO	.06	.13	.18	.17	.12	.13
TI02	2.71	.59	.75	1.30	1.83	.53
CR203	.11	.03	.00	.03	.03	.00
CAO	.30	.09	.07	.19	.23	.05
NA20	.00	.00	.00	.06	.00	.00
K20	8.17	9.38	9.28	8.15	9.51	9.61
SUM	95.40	94.87	95.48	93.20	93.88	94.01
FEO	23.39	11.88	12.22	16.09	16.27	12.11
FE203	.00	.00	.00	.00	.00	.00
SI	2.81	3.01	2.92	2.74	2.80	2.92
AL	1.32	1.10	1.28	1.49	1.40	1.20
FE2+	1.51	.73	.75	1.03	1.04	.75
FE3+	.00	.00	.00	.00	.00	.00
MG	1.13	2.08	1.98	1.67	1.55	2.06
MN	.00	.01	.01	.01	.01	.01
TI	.16	.03	.04	.08	.11	.03
CR	.01	.00	.00	.00	.00	.00
CA	.02	.01	.01	.02	.02	.00
NA	.00	.00	.00	.01	.00	.00
K	.81	.88	.86	.79	.93	.91

ANALYSIS	018E1R10 401	018B0R10 301	016I1R10 301	016I1R10 401	039M3R10 101	039I0R10 201	039I0R10 401	039I1R10 101	039I1R10 201	039I1R10 301
SEQ #	88	89	94	95	12	13	14	15	16	17
REF #	0	0	0	0	0	0	0	0	0	0
S102	41.39	36.83	39.31	39.23	37.87	36.14	36.62	36.44	36.18	35.83
AL203	14.74	14.83	14.94	14.90	16.11	15.93	16.10	16.22	15.95	16.18
FED	2.73	16.22	10.04	10.01	17.69	18.78	19.43	19.17	18.61	18.78
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
MG0	23.96	14.22	17.53	17.85	13.85	11.07	11.57	11.23	11.36	11.51
MND	.02	.04	.12	.12	.02	.02	.06	.08	.00	.05
T102	2.22	3.59	3.35	3.26	2.51	3.25	3.54	3.26	2.93	2.66
CR203	.15	.14	.04	.01	.12	.10	.12	.12	.11	.12
CA0	.04	.09	.02	.00	.14	.12	.10	.10	.07	.11
NA20	.00	.00	.00	.00	.09	.07	.04	.05	.05	.03
K20	9.56	8.67	8.82	8.92	8.24	9.28	9.04	8.92	8.78	8.70
SUM	94.81	94.63	94.17	94.30	96.64	94.76	96.62	95.63	94.04	93.97
FED	2.73	16.22	10.04	10.01	17.69	18.78	19.43	19.17	18.61	18.78
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
SI	2.91	2.78	2.87	2.87	2.79	2.76	2.75	2.76	2.78	2.76
AL	1.22	1.32	1.29	1.28	1.40	1.44	1.42	1.45	1.44	1.47
FE2+	.16	1.02	.61	.61	1.09	1.20	1.22	1.21	1.19	1.21
FE3+	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
MG	2.51	1.60	1.91	1.94	1.52	1.26	1.29	1.27	1.30	1.32
MN	.00	.00	.01	.01	.00	.00	.00	.01	.00	.00
TI	.12	.20	.18	.18	.14	.19	.20	.19	.17	.15
CR	.01	.01	.00	.00	.01	.01	.01	.01	.01	.01
CA	.00	.01	.00	.00	.01	.01	.01	.01	.01	.01
NA	.00	.00	.00	.00	.01	.01	.01	.01	.01	.00
K	.86	.83	.82	.83	.78	.91	.87	.86	.86	.85

ANALYSIS	0391B10	039M2B10	039M2B10	039M2B10	039M2B10	035A2B10	035A2B10	035A2B10	022B1B10	022B1B10
	401	201	301	401	501	501	601	701	101	201
SEQ #	18	19	20	21	22	31	32	33	81	82
REF #	0	0	0	0	0	0	0	0	0	0
SI02	36.26	36.98	38.08	38.28	37.99	34.40	34.55	35.53	35.98	35.78
AL203	16.14	16.80	16.48	16.60	16.22	16.00	14.79	15.60	14.93	14.53
FEO	19.16	17.33	16.72	15.57	16.23	25.63	24.02	24.28	22.97	23.24
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
MG0	11.25	14.23	14.89	13.52	14.61	8.25	8.24	8.60	.00	.00
MNO	.04	.03	.04	.02	.00	.11	.08	.10	.64	9.40
TI02	3.39	1.82	2.45	2.19	2.28	3.25	3.59	3.83	.09	.08
CR203	.09	.11	.09	.09	.11	.00	.02	.03	.11	2.73
CAO	.10	.20	.15	1.61	.16	.44	.66	.13	.11	.09
NA20	.04	.04	.06	.04	.03	.00	.00	.00	.11	.15
K20	8.87	8.22	7.51	8.13	8.20	9.10	8.90	9.26	.00	.00
SUM	95.34	95.76	96.47	96.05	95.83	97.18	94.85	97.36	8.70	8.51
FEO	19.16	17.33	16.72	15.57	16.23	25.63	24.02	24.28	22.97	23.24
FE203	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
SI	2.75	2.75	2.79	2.82	2.81	2.66	2.72	2.72	.00	.00
AL	1.44	1.47	1.42	1.44	1.41	1.46	1.37	1.41	2.79	2.80
FE2+	1.22	1.08	1.02	.96	1.00	1.66	1.58	1.55	1.36	1.34
FE3+	.00	.00	.00	.00	.00	.00	.00	.00	1.49	1.52
MG	1.27	1.58	1.62	1.48	1.61	.95	.97	.98	.00	.00
MN	.00	.00	.00	.00	.00	.01	.01	.01	1.11	1.10
TI	.19	.10	.13	.12	.13	.19	.21	.22	.01	.01
CR	.01	.01	.01	.01	.01	.00	.00	.00	.16	.16
CA	.01	.02	.01	.13	.01	.04	.06	.01	.01	.01
NA	.01	.01	.01	.01	.00	.00	.00	.00	.01	.01
K	.86	.78	.70	.76	.77	.90	.90	.90	.00	.00