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Crystal chemistry of a metamorphic biotite and its significance in water barometry[1]

STEVEN R. BOHLEN,[2] DONALD R. PEACOR AND ERIC J. ESSENE

Department of Geology and Mineralogy, The University of Michigan
Ann Arbor, Michigan 48109

Abstract

The crystal structure of a metamorphic biotite from Au Sable Forks, New York (northeast Adirondacks) has been refined to an unweighted R value of 4.2%. The Au Sable biotite is a $2M_1$ mica with space group symmetry $C2/c$. Although the biotite equilibrated near and cooled slowly from $T = 700° \pm 50°C$, octahedral and tetrahedral cations are apparently disordered. There are few, if any, octahedral and interlayer cation site deficiencies. Average bond lengths are M1–O 2.106, M2–O 2.086, T1–O 1.657, T2–O 1.661, inner K–O 3.046, outer K–O 3.289A. The tetrahedral rotation angle (α) is 5.3°. The Au Sable biotite structure is nearly identical to the igneous $2M_1$ biotite of similar composition refined by Takeda and Ross (1975).

The Au Sable biotite coexists with magnetite (Usp_{32}), ilmenite (Hm_5), perthite (Or_{68}), and plagioclase (An_{22}). This assemblage fixes T (700°C), f_{O_2} ($10^{-17.2}$), and f_{H_2O} (10^2–10^3) for metamorphic pressure of 7±1 kbar. Metamorphism of orthogneisses in the Au Sable area of the Adirondacks took place under quite dry ($P_{H_2O} \ll P_{solid}$) conditions.

Introduction

Although the basic mica crystal structure was solved in the early 1930's, in the past fifteen years the knowledge of the details of mica crystal chemistry has been significantly increased through numerous structure refinements. Muscovite polytypes $2M_1$ and 3T have been refined by Burnham and Radoslovich (1964), Güven (1967), and Güven and Burnham (1967). $2M_1$ paragonite and $2M_1$ phengite have been investigated by Burnham and Radoslovich (1964) and Güven (1967) respectively. Brittle micas of various compositions have been studied by Takéuchi (1964), and Guggenheim and Bailey (1975) have discussed the details of margarite crystal structure. Lithium micas such as fluor-polylithionite (Takeda and Burnham, 1969) and $2M_1$ and 1M lepidolites (Takeda *et al.*, 1971) have also been refined.

In comparison to the numerous crystal structure refinements of these dioctahedral calcium and lithium micas, trioctahedral micas have received somewhat less attention. Steinfink (1962), Hazen and Burnham (1973), McCauley *et al.* (1973), and Takeda and Ross (1975) have refined various phlogopites, biotites, or annites. Of these micas only one, a nearly end-member phlogopite, was obtained from a metamorphic rock. Refinements of igneous biotite suggest that the octahedral and tetrahedral cations are disordered, a result which might have been predicted from our understanding of cation order–disorder in minerals equilibrating at igneous temperatures.

There may be a good reason why no refinements of metamorphic biotites have been attempted to date. Due to the nature of the rocks in which metamorphic biotites occur, it is difficult to obtain an undeformed mica sample acceptable for crystal structure analysis. Nevertheless, phlogopite and biotite are found in many metamorphic rock types and are involved in numerous important metamorphic reactions. Because mica-bearing reaction equilibria can be profoundly affected by mica cation ordering, which reduces configurational entropy, the assumption of an igneous structure model for metamorphic biotites may lead to systematic errors in calculated equilibria.

In addition to their importance in isogradic reactions, micas along the phlogopite–annite join have been used to infer equilibrium water fugacities when

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[1] Contribution No. 350 from the Mineralogical Laboratory, Department of Geology and Mineralogy, The University of Michigan, Ann Arbor, Michigan 48109.

[2] Present address: Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California, 90024.

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the mica coexists with magnetite and K-feldspar (Wones and Eugster, 1965; Wones, 1972). This requires an estimation of the activity of the annite component in micas of intermediate composition. However, again, the details of metamorphic mica crystal structure may be important in utilizing these equilibria to infer f_{H_2O}. Calculation of annite component will depend on (1) cation ordering, (2) octahedral and interlayer cation site deficiencies, and (3) substitution of cations not on the phlogopite–annite join. Two of the three cannot be obtained from electron microprobe analyses, and consequently biotite structure refinements are necessary to confirm or deny previous assumptions concerning site occupancy variables. One would hope that a mica structure refinement is not necessary every time one wishes to infer P–T–X from reactions involving biotite, and, indeed, this may be the case. Before one accepts the necessary simplifying assumptions, more must be known about metamorphic biotites, however.

We chose a biotite from Au Sable Forks, New York, because it is similar in composition to a $2M_1$ biotite from a rhyodacite lava flow whose structure has been refined (Takeda and Ross, 1975). Comparison of these two structures should define the nature of fundamental differences (or similarities) between the igneous and metamorphic biotites. The Au Sable biotite is also significant in that it coexists with magnetite, ilmenite, and alkali feldspar. This assemblage fixes f_{O_2}–T (Buddington and Lindsley, 1964; Lindsley, 1977) and allows estimation of f_{H_2O} if the activity of the annite component can be identified (Wones and Eugster, 1965; Wones, 1972). Therefore, the Au Sable biotite is of particular interest for a fuller understanding of the nature and significance of metamorphic fluids in this area of the Adirondacks.

Analytical techniques

The mica crystal used for refinement was obtained from broken fragments of an orthogneiss containing biotite, magnetite, ilmenite, alkali feldspar, sodic plagioclase, clinopyroxene, quartz, with minor (late?) garnet, amphibole, apatite, and zircon. The rock was taken from outcrops along the north edge of the Au Sable River approximately one mile ENE of the town of Au Sable Forks, New York. Samples of the biotite are on deposit in the Mineralogical Collection, the Department of Geology and Mineralogy, The University of Michigan.

After exhaustive searching through thousands of mica cleavage fragments and examination of many by 0-level Weissenberg or precession photography, we selected one mica crystal which was suitable for determination of intensity data. The cleavage fragment was mounted along the *b* axis and measured 0.42 × 0.36 × 0.08 mm. The calculated density is 3.33 g/cm^3, and the linear absorption coefficient for Mo$K\alpha$ ($\lambda = 0.7107$) radiation is 37.1 cm^{-1}. Intensity data were measured using the Supper-Pace automated system which employs measurement of background on both sides of a peak scan. The direct Mo$K\alpha$ X-ray beam was monochromated with a flat crystal of pyrolytic graphite, and intensities were detected with a scintillation counter. The crystal was examined using 0 and 1st level Weissenberg photographs, which confirmed the diffraction symbol as $2/mC\text{-}/c$ and confirmed the lack of twinning.

A total of 1130 hkl and $\bar{h}kl$ intensities were measured. These were corrected for absorption and Lorentz-polarization factors, the polarization correction being modified for the polarization of the direct beam. Minimum observable intensity values were assigned to weak reflections on the basis of standard counting statistics. Despite care in crystal selection, reflections were quite broad, requiring scan widths of up to 8°. Because of this wide scan width, background for a given reflection was sometimes counted on the edge of another reflection. For these reflections, backgrounds were estimated from backgrounds of other reflections. A few reflections (6) were deleted from the data set where peak profiles actually overlapped.

The full-matrix least-squares refinement program RFINE (Finger, 1969) was employed under the following conditions; (1) The initial structure parameters were those obtained from Takeda and Ross (1975). (2) Form factors were obtained from Doyle and Turner (1968). The form factors for octahedral cations $Fe^{2+} + Mn^{2+} + Ti^{4+}$ were approximated as $\Sigma\ Fe^{2+} + Mn^{2+} + Ti^{4+} = Fe^{2+}$ and $\Sigma\ Mg^{2+} + Al^{3+}$ was approximated as Mg^{2+}. (3) The weighting scheme devised by Cruickshank (1965) was used, except that all reflections with intensity values less than minimum observable values were rejected. (4) Refinement of variables was carried out in the general sequence of the scale factor and atomic coodinates, isotropic temperature factors, site occupancies, and anisotropic temperature factors. Refinement was completed with cycles during which all coordinates and anisotropic temperature factors were allowed to vary. The final unweighted R value for all reflections is 8.7%; for unrejected reflections (787 of 1125) the final R value is

4.2%. Final observed and calculated structure factor data are compiled in Table 1.[3]

Electron microprobe analyses of the Au Sable biotite and other minerals with which it coexists (Table 2) were obtained using an ARL-EMX electron microprobe analyzer with wavelength-dispersive PET, LiF, and TAP crystal spectrometers. Spectrometer data were corrected for atomic number, fluorescence, absorption, continuous background, and machine drift effects with the Fortran program EMPADR (Rucklidge and Gasparrini, 1969). Microprobe analyses of several biotite grains in the rock from which the biotite crystal was taken for structure refinement indicate remarkable inter- and intra-grain chemical homogeneity. For complete details of microprobe analysis techniques see Bohlen and Essene (1977). The lack of Li in the mica was established by atomic absorption spectrophotometry. OH was determined by weighing hydrogen yield from weighed mineral separates. The technique is used for hydrogen extraction for isotopic analysis and is described by Friedman (1953) and Godfrey (1962). Ferric iron in the biotite was determined by the titration method of Wilson (1955). Ferric iron in spinel was inferred from stoichiometric considerations (see Bohlen and Essene, 1977).

Table 2. Chemical analyses of Ruiz Peak biotite and coexisting minerals from Au Sable Forks

	Ruiz Peak Biotite	Au Sable Biotite	Au Sable Magnetite	Au Sable Ilmenite	Au Sable K-Spar	Au Sable Plag
SiO_2	37.79	35.73	0.00	0.00	65.11	62.79
TiO_2	6.05	5.40	10.70	50.01	nd	nd
Al_2O_3	14.92	14.41	1.04	0.01	20.36	23.48
Fe_2O_3	3.25	0.00	46.26	4.95	0.00	0.06
FeO	11.25	21.30	41.27	43.98	0.00	0.00
MnO	0.16	0.11	0.03	0.81	nd	nd
MgO	14.87	9.95	0.00	0.12	0.00	0.00
CaO	0.00	0.02	nd	nd	0.32	4.68
Na_2O	1.10	0.14	nd	nd	3.48	8.31
K_2O	8.05	9.88	nd	nd	11.31	0.21
F	0.71	0.33	nd	nd	nd	nd
Cl	0.00	1.03	nd	nd	nd	nd
H_2O^+	1.41	2.19	nd	nd	nd	nd
	100.30	100.49	99.30	99.98	100.58	99.53
O≡F,Cl	0.30	0.37	0.00	0.00	0.00	0.00
Total	100.00*	100.12	99.30**	99.98**	100.58	99.53
Si	5.714	5.587	0.000	0.000	3.000	2.779
Al	2.286	2.413	---	---	1.000	1.219
Al	0.372	0.243	0.048	0.000	---	---
Ti	0.688	0.636	0.313	0.952	---	---
Fe^{3+}	0.370	0.000	1.326	0.097	---	0.002
Fe^{2+}	1.422	2.786	1.313	0.930	---	---
Mn	0.020	0.015	0.000	0.017	---	---
Mg	3.352	2.321	0.000	0.004	0.000	0.000
Ca	0.000	0.005	---	---	0.016	0.221
Na	0.324	0.040	---	---	0.311	0.710
K	1.554	1.971	---	---	0.673	0.012
F	0.338	0.165	---	---	---	---
Cl	0.000	0.275	---	---	---	---
OH	1.422	2.435	---	---	---	---
O	22.240	21.125	4.000	3.000	8.000	8.000

*Analysis of Ruiz Peak Biotite (Takeda and Ross, 1975), calculated from stoichiometry.

**Ferric iron calculated from stoichiometry.

Structure refinement

Unit-cell parameters, atomic coordinates and anisotropic temperature factors, and bond lengths for tetrahedral, octahedral, and interlayer sites are given in Tables 3, 4, and 5 respectively. In these tables equivalent data are also given for the hydrogenated Ruiz Peak biotite (Takeda and Ross, 1975). Both biotites have very similar structures, predictable from their similar chemical compositions. Both show similar deviations from the ideal mica structure outlined by Pabst (1955). The tetrahedral rotation angle, α, is 5.3° for the Au Sable biotite and 7.6° for the Ruiz Peak biotite. These values are different due to the slightly larger average octahedral cation radius (Shannon, 1976) (due to higher Fe^{2+} and lower Fe^{3+} and Ti^{4+}) in the Au Sable biotite. The rotation angles for both micas are in good agreement with predicted values (Hazen and Wones, 1972). The micas also show similar distortions of the octahedral layer. As opposed to octahedral flattening which is typically observed in micas (Donnay *et al.*, 1964), the Au Sable and Ruiz Peak biotite octahedra show distortion wherein the upper triad of oxygens (O31–O32–O4) shifts as a unit along the *b* axis and the symmetrically-equivalent lower triad shifts in the opposite direction. This causes four of twelve M–O bond distances to become shortened, four to become lengthened, and four to remain similar to equivalent bonds in 1M structures (Takeda and Ross, 1975;

Table 3. Comparison of unit-cell parameters for the Au Sable and Ruiz Peak biotites

Biotite	a(Å)	b(Å)	c(Å)	β
Au Sable ($2M_1$)*	5.357(6)	9.245(5)	20.234(5)	94.978(4)
Ruiz Peak ($2M_1$)**	5.329(2)	9.234(3)	20.098(7)	95.09(3)

*Debye-Scherrer and X-ray powder data.

**Data for hydrogenated Ruiz Peak biotite taken from Takeda and Ross (1975).

Values in parentheses represent the estimated standard deviation (esd) in terms of least units cited for the value to the immediate left, thus 5.376(6) indicates an esd of 0.006.

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[3] To receive a copy of this material, order Document AM-79-121 from the Business Office, Mineralogical Society of America, 2000 Florida Ave., N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

Table 4. Atomic coordinates, anisotropic temperature factors and equivalent isotropic temperature factors

Atom	X	Y	Z	B	β_{11}*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au Sable Biotite										
M1	3/4	1/4	0	0.83(3)	0.0072(6)	0.0019(2)	0.0006(3)	-0.0007(3)	0.0006(1)	-0.0001(1)
M2	0.2480(2)**	0.0826(2)	0.0000(1)	0.99(2)	0.0092(1)	0.0022(4)	0.0006(2)	-0.0004(3)	0.0005(1)	-0.0000(1)
K	0	0.0844(3)	1/4	2.47(5)	0.0232(8)	0.0071(3)	0.0016(1)	0	0.0007(2)	0
T1	0.4625(3)	0.2508(2)	0.1373(1)	0.62(3)	0.0066(5)	0.0019(1)	0.0003(1)	-0.0002(3)	0.0005(1)	0.0001(1)
T2	0.9630(3)	0.4175(2)	0.1375(1)	0.70(3)	0.0071(5)	0.0020(1)	0.0005(1)	-0.0001(3)	0.0005(1)	-0.0000(1)
011	0.7341(10)	0.3201(5)	0.1656(2)	1.48(9)	0.0133(18)	0.0075(6)	0.0006(1)	-0.0041(8)	0.0005(3)	0.0003(2)
021	0.2368(9)	0.3476(5)	0.1659(2)	1.52(9)	0.0147(19)	0.0064(6)	0.0007(1)	0.0030(9)	0.0000(2)	-0.0002(2)
022	0.4459(8)	0.0836(5)	0.1660(2)	1.47(8)	0.0237(16)	0.0030(4)	0.0007(1)	0.0012(9)	0.0014(3)	0.0001(2)
031	0.4323(6)	0.2395(5)	0.0544(2)	0.83(7)	0.0080(17)	0.0011(4)	0.0008(1)	-0.0020(7)	0.0004(3)	0.0002(2)
032	0.9361(7)	0.4073(6)	0.0545(2)	0.88(7)	0.0113(15)	0.0016(4)	0.0004(1)	-0.0006(1)	0.0005(2)	0.0003(2)
04	0.9367(7)	0.0709(5)	0.0537(2)	1.58(8)	0.0136(15)	0.0002(4)	0.0019(1)	0.0002(7)	0.0012(3)	0.0004(2)
Ruiz Peak Biotite (Takeda and Ross, 1975)										
M1	3/4	1/4	0	0.85(4)	0.0055(7)	0.0025(2)	0.0007(1)	0	0.0003(1)	0
M2	0.2406(3)	0.0802(2)	-0.00004(8)	1.05(3)	0.0110(5)	0.0026(2)	0.0006(3)	0.0020(4)	0.0002(1)	0.0002(1)
K	0	0.0840(3)	1/4	2.21(4)	0.0182(8)	0.0065(3)	0.0014(1)	0	0.0003(2)	0
T1	0.4621(3)	0.2498(2)	0.13798(9)	0.70(3)	0.0052(5)	0.0023(2)	0.0005(1)	0.0003(3)	0.0001(1)	0.0001(1)
T2	0.9635(3)	0.4169(2)	0.13799(9)	0.71(2)	0.0053(5)	0.0022(2)	0.0005(1)	-0.0006(3)	0.0002(1)	-0.0002(1)
011	0.7410(8)	0.3140(5)	0.1662(3)	1.54(8)	0.0136(17)	0.0054(6)	0.0008(1)	-0.0019(8)	0.0000(4)	0.0001(2)
021	0.2430(8)	0.3532(5)	0.1672(3)	1.53(8)	0.0108(16)	0.0060(6)	0.0008(1)	0.0025(8)	0.0000(4)	-0.0002(2)
022	0.4337(8)	0.0840(5)	0.1666(2)	1.48(7)	0.0181(16)	0.0038(5)	0.0007(1)	0.0003(9)	0.0004(3)	-0.0000(3)
031	0.4314(7)	0.2406(5)	0.0545(2)	0.57(6)	0.0047(12)	0.0007(4)	0.0006(1)	0.0001(7)	0.0003(3)	0.0004(3)
032	0.9375(7)	0.4090(6)	0.0547(2)	0.69(6)	0.0070(12)	0.0014(4)	0.0005(1)	0.0001(1)	0.0002(3)	0.0005(3)
04	0.9348(7)	0.0739(5)	0.0508(2)	0.80(6)	0.0088(13)	0.0011(4)	0.0006(1)	0.0009(8)	0.0000(3)	-0.0000(3)

* β_{ij} is in the expression $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}2hk + \beta_{13}2\ell h + \beta_{23}2k\ell)$.

** Values in parentheses represent estimated standard deviations (esd) in terms of the least units cited for the value to the immediate left, thus 0.2480(2) indicates an esd of 0.0002.

Hazen and Burnham, 1973). Similarly, the shared edges of the octahedra also shift, two becoming longer, two shorter, and two remaining roughly the same as in equivalent 1M structures. For a complete discussion the reader is referred to Takeda and Ross (1975).

Table 5. Comparison of interatomic distances between the Ruiz Peak and Au Sable biotite

	Au Sable Biotite	Ruiz Peak* Biotite		Au Sable Biotite	Ruiz Peak* Biotite
Bond	Length (Å)	Length (Å)	Bond	Length (Å)	Length (Å)
T1-011	1.647(7)	1.649(4)	T2-011	1.662(7)	1.659(4)
T1-021	1.649(7)	1.656(4)	T2-021	1.660(8)	1.656(4)
T1-022	1.656(5)	1.644(5)	T2-022	1.646(7)	1.662(4)
T1-031	1.675(5)	1.675(4)	T2-032	1.674(4)	1.674(4)
Mean	1.657	1.656	Mean	1.661	1.663
M1-032[2]	2.033(7)	2.034(4)	M2-031	2.025(7)	2.054(5)
M1-031[2]	2.109(9)	2.104(4)	M2-032	2.103(9)	2.124(4)
M1-04[2]	2.176(7)	2.120(4)	M2-031'	2.161(7)	2.146(4)
			M2-032'	2.159(7)	2.147(5)
			M2-04	1.998(7)	1.934(5)
			M2-04'	2.069(9)	1.999(4)
Mean	2.106	2.086	Mean	2.086	2.067
(inner)			(outer)		
K-011[2]	3.042(9)	2.975(5)	K-021[2]	3.290(8)	3.329(5)
K-021[2]	3.042(9)	2.971(5)	K-021[2]	3.285(9)	3.313(5)
K-022[2]	3.049(4)	2.971(4)	K-022[2]	3.290(9)	3.322(4)
Mean	3.046	2.972	Mean	3.289	3.321

*Data for Ruiz Peak Biotite taken from Takeda and Ross, 1975. Values in parentheses represent the estimated standard deviation (esd) in terms of the least units cited for the value to the immediate left, thus 1.647(7) indicates an esd of 0.007. Bracked values indicate bond multiplicity.

Octahedral site occupancies were refined using an initial model: M1 = ($Fe^{2+}_{1-x}Mg_x$) and M2 = ($Fe^{2+}_{1-y}Mg_y$) where x ≡ y = 0.43. Subsequent refinement cycles indicate that y is slightly greater than x ($x = 0.40$, $y = 0.46$), suggesting a slight preference of Fe^{2+} for the M1 site. This is consistent with the slightly larger M1–O mean bond distance (2.106A) as compared to M2–O (2.086A). However, the difference in mean M–O bond distances (0.02A) is the same in other micas where no cation ordering was inferred (Hazen and Burnham, 1973). A 0.02A difference in mean M–O bond distances is also observed in the Ruiz Peak biotite, even though site occupancy refinement suggests that Mg may have a very slight preference for M1 (Takeda and Ross, 1975). Unfortunately, because of errors in the chemical analyses and errors due to the approximation of scattering factors, these small apparent site occupancy preferences in the Au Sable and Ruiz Peak biotites may not be significant. These biotites have essentially disordered octahedral sites, although limited ordering cannot be ruled out.

The existence of tetrahedral cation ordering depends on the presence or lack of a center of symmetry in the biotite structure. Guggenheim and Bailey

(1975) have shown through least-squares refinement that margarite shows Al–Si ordering, reducing the symmetry from *C2/c* to *Cc*. Using similar techniques Guggenheim and Bailey also found that a $2M_1$ muscovite apparently showed no tetrahedral ordering of Al–Si which indicates that the true space group of $2M_1$ muscovite is *C2/c*. Using optical secondary harmonics Bish and Horsey (1978) found no evidence to indicate the lack of inversion-symmetry in phlogopite, muscovite, and biotite, suggesting a lack of Al–Si ordering of the type found in margarite. Margarite on the other hand exhibits the absence of inversion centers, again confirming Al–Si ordering in agreement with structure refinements. Our data are consequently consistent with little or no tetrahedral ordering in muscovites and biotites. In the Au Sable biotite average T1–O and T2–O bond distances are identical within error (Table 5), consistent with no Al–Si ordering. However limited ordering within domain structure cannot be entirely ruled out. For the Au Sable biotite the average T–O bond distance (1.659A) agrees extremely well with the predicted value (1.657A) (Hazen and Burnham, 1973) for a tetrahedral composition of $Al_{2.286}Si_{5.714}$. Similarly the Ruiz Peak biotite shows excellent agreement between predicted and observed values.

Table 6. Magnitudes and orientations of thermal ellipsoids

Atom	Axis	rms(Å) Displacement	Angle with respect to: a(°)	b(°)	c*(°)
M_1	r_1	0.085(5)*	60(18)	30(16)	89(14)
	r_2	0.094(4)	47(15)	112(20)	129(7)
	r_3	0.119(3)	57(6)	109(6)	39(7)
M_2	r_1	0.096(3)	105(11)	15(12)	90(12)
	r_2	0.110(2)	52(9)	80(15)	140(7)
	r_3	0.122(2)	42(7)	79(7)	50(7)
K	r_1	0.176(3)	90	0	90
	r_2	0.178(3)	51(20)	90	141(20)
	r_3	0.185(3)	39(20)	90	51(20)
T_1	r_1	0.073(4)	119(6)	106(10)	34(80
	r_2	0.091(4)	85(17)	163(11)	106(14)
	r_3	0.104(3)	29(7)	94(19)	61(8)
T_2	r_1	0.090(4)	132(13)	102(84)	45(25)
	r_2	0.093(3)	85(56)	167(80)	102(63)
	r_3	0.108(3)	43(9)	95(14)	47(9)
O_{11}	r_1	0.103(9)	126(17)	112(7)	44(20)
	r_2	0.126(8)	131(16)	107(9)	134(20)
	r_3	0.196(8)	118(5)	29(5)	85(4)
O_{21}	r_1	0.118(9)	86(30)	83(20)	8(6)
	r_2	0.128(10)	33(8)	123(9)	89(35)
	r_3	0.183(8)	57(7)	34(7)	98(5)
O_{22}	r_1	0.110(9)	98(44)	130	41
	r_2	0.113(9)	73(23)	139	126
	r_3	0.189(6)	19(4)	82(6)	73(4)
O_{31}	r_1	0.039(22)	62(7)	30(7)	99(6)
	r_2	0.119(11)	152(7)	62(9)	94(27)
	r_3	0.131(7)	89(24)	80(14)	10(13)
O_{32}	r_1	0.069(13)	103(8)	142(12)	56(12)
	r_2	0.105(9)	83(15)	127(12)	142(13)
	r_3	0.129(7)	15(8)	96(13)	76(12)
O_4	r_1	0.020(40)	89(5)	6(3)	96(3)
	r_2	0.136(8)	172(4)	89(5)	82(4)
	r_3	0.199(6)	82(4)	84(3)	10(4)

*Values in parentheses represent the estimated standard deviation (esd) in terms of the least units cited for the value to the immediate left, thus 0.085(5) indicates an esd of 0.005.

The magnitudes of the isotropic temperature factors are given in Table 4. The bridging oxygens O11, O21, and O22 have isotropic temperature factors which are unusually large compared with other silicates (Burnham, 1965), and have nearly twice the magnitude of the non-bridging O31, O32, and O4 oxygens. Hazen and Burnham (1973) suggested that these large isotropic temperature factors may not be due solely to thermal motion but may also include a component due to tetrahedral positional disorder. Furthermore the anisotropic temperature factors for the bridging oxygens are unusual in their magnitude (Table 4) and orientations (Table 6). The bridging oxygens, O11, O21, O22, have one very large thermal ellipsoid axis oriented in the plane of closest packing, nearly perpendicular to the T–O bond. The orientations of these ellipsoids are consistent with tetrahedral rotation about an axis perpendicular to the plane of closest packing or tetrahedral tilting. The thermal ellipsoids of the non-bridging oxygens are also unusual. O4 (hydroxyl position), for instance, shows one very small ellipsoid axis nearly parallel to *c**, hence appears to be vibrating parallel to the plane of the closest-packed layers. Ordinarily one might reject these thermal ellipsoids (Table 6) as being unusual artifacts of this particular data set. However, we have calculated the magnitude and orientations of the anisotropic thermal ellipsoids for the Ruiz Peak biotite and obtain magnitudes and orientations nearly identical to those of the Au Sable biotite. This suggests that these unusual thermal ellipsoids obtained from two completely different data sets may be characteristic of micas with compositions similar to the Ruiz Peak and Au Sable $2M_1$ biotites. Presumably the unusually large magnitudes and unusual orientations of the thermal ellipsoids reflect tetrahedral positional disorder in addition to thermal vibration. Exactly how the positional disorder affects the non-bridging oxygens is not yet fully understood.

A more fundamental problem is that of determining precisely the chemical composition of natural biotites. A complete microprobe analysis does not unambiguously fix the biotite formula because compositions obtained by microprobe analysis lack data

Table 7. Substitutions in Au Sable biotite

	Component	Substitution
.276	$K_2(Fe,Mg)_4Ti_2(Al_2Si_6)O_{20}O_4$	$Ti^* + 2O = R^{2+} + 2(OH)$
.042	$K_2(Fe,Mg)_4Ti_2(Al_6Si_2O_{20}(OH)_4$	$Ti + 2Al = 2Si + R^{2+}$
.121	$K_2(Fe,Mg)_4Al_2(Al_4Si_4)O_{20}(OH)_4$	$2Al = R^{2+} + Si$
.561	$K_2(Fe,Mg)_6(Al_2Si_6)O_{20}(OH)_4$	

Minor substitutions:

$Mn^* = (MgFe)$ $(Cl,F) = (OH)$ $Na = K$

*Ti and Mn are assumed to be Ti^{4+} and Mn^{2+}, respectively

for Li, H, and Fe^{2+}/Fe^{3+} (all of which must be determined by alternative techniques). Without these data it is simply impossible to normalize a biotite formula correctly. The potentials for interlayer cation and octahedral site deficiencies are additional uncertainties which must be considered in normalization procedures. In this study microprobe analyses and direct determination of Li, Fe^{2+}/Fe^{3+}, and H unambiguously fix the Au Sable biotite composition as $(K_{1.971}Na_{0.040}Ca_{0.005})$ $(Fe^{2+}_{2.786}Mg_{2.321}Mn_{0.015}Ti_{0.636}Fe^{3+}_{0.000}Li_{0.000}Al_{0.243})$ $(Al_{2.413}Si_{5.587})$ $(O_{21.125}OH_{2.435}F_{0.165}Cl_{0.275})$, which indicates a lack of significant amounts of interlayer cation or octahedral site deficiencies, a result which is confirmed by the least-square refinement of single-crystal intensity data. In addition, the electron density calculated from the refined occupancies for octahedral sites agrees extremely well with the electron density calculated from the chemical analyses, further corroborating the chemical data.

Having fully characterized the crystal chemistry of the Au Sable biotite, we now may use these results in applying phase equilibria to the biotite assemblage of Au Sable Forks (following section). While our conclusion concerning the lack of site deficiencies in the Au Sable biotite may not apply to all metamorphic biotites, our tentative conclusions regarding octahedral and tetrahedral cation ordering are applicable to many micas from high-grade metamorphic terranes. Biotites forming or equilibrating at low metamorphic grades (lower amphibolite facies) might possibly show some significant cation ordering, and for this reason a refinement of such a biotite is warranted. For the moment, however, assumptions concerning the lack of cation ordering in metamorphic biotites appear to be well-founded. Nevertheless, all variables, including complete chemical characterization and potential for order–disorder, must be considered and evaluated before experimental phase equilibria can be applied to natural assemblages. Because of the extreme complexities and uncertainties noted above, this is particularly true for biotites.

Water barometry

Ever since Wones and Eugster's (1965) pioneering work on experimental calibration of biotite stability as a function of P–T–f_{O_2}–f_{H_2O}, the assemblage biotite–magnetite–alkali feldspar has been used to infer water fugacity in numerous field areas. Inference of f_{H_2O} depends on relatively accurate determinations of T and f_{O_2}, which allow f_{H_2O} to be constrained significantly. Frequently T and/or f_{O_2} cannot be adequately evaluated, and in addition biotite compositions are rarely unambiguously determined. Because of these difficulties f_{H_2O} can often only be approximately limited. Unfortunately, however, even if T, f_{O_2}, and a proper biotite formula can be accurately determined, water fugacity fixed by coexisting biotite–magnetite–alkali feldspar can still only be approximated, due to a fundamental lack in present understanding of biotite solution models.

In their original work Wones and Eugster argued that neither a molecular model, assuming $a_{\text{annite}} = Fe^{2+}/(Fe^{2+} + Mg)$, nor an ionic model, assuming $a_{\text{annite}} = [Fe^{2+}/(Fe^{2+} + Mg)]^3$, fits the experimental data for biotites in the phlogopite–annite–oxybiotite ternary. They concluded that the solution of phlogopite–annite was non-ideal, with estimated activity coefficients as small as 10^{-3}. Mueller (1972) disputed this conclusion, based on Mg–Fe^{2+} partitioning data between biotite and other coexisting silicates such as garnet, ortho- and clinopyroxene. He suggested that biotites low in Fe^{3+} on or near the phlogopite–annite join were very nearly ideal, and that an ionic model, $a_{\text{annite}} = (X_{Fe^{2+}})^3$, might well be used to describe them. In reply Wones (1972) indicated that adjustments in annite stability equilibria (Wones *et al.*, 1971) and the FMQ buffer (Wones and Gilbert, 1969) have since led to changes in the standard state on which Wones and Eugster (1965) had originally based their solution model. In light of these more recent data Wones agreed that an ionic model, $a_{\text{annite}} = (X_{Fe^{2+}})^3$, was reasonable for biotites on the phlogopite–annite join. More recently Czamanske and Wones (1973) have proposed that F, Cl, and O in the (OH) site could be accounted for as an ideal solution yielding an annite component: $a_{\text{annite}} = (X_{Fe^{2+}})^3 (X_{OH})^2$. Unfortunately, biotites have many additional substitutions, and it is not obvious how best to deal with them when attempting to calculate an annite component. For instance, the biotite of interest in this paper might be considered as being composed of components (Table 7) which involve the substitutions Ti + 2O = (Mg,Fe) + 2OH, Ti + 2Al = 2Si + (Mg,Fe), 2Al = (Mg,Fe) + Si, Mn = (Mg,Fe), Na = K, and (Cl,F) = OH. In addition, analyses of other biotites require substitutions which involve interlayer cation and octahedral site deficiencies [for example, $\square^{VI}$ + 2(Al,Fe^{3+}) = 3(Mg,Fe^{2+}), $\square^{XII}$ + Si = Al + K^{XII}, $\square^{VI}$ + Ti = 2(Mg,Fe^{2+})], dioctahedral mica substitution involving an octahedral vacancy ordered on M1 site, the oxybiotite substitution ($Fe^{2+} + OH^- = Fe^{3+} + O^{2-}$), in addition to substitutions involving Ca, Li, and Cr, *etc*. The complexities of biotite solutions are not well modeled by simple solution theories, which makes exact calculation of annite activity impossible. Because of these complexities one must resort to limiting f_{H_2O} by choosing models which yield high and low annite activities, which in turn give upper and lower limiting water fugacity estimates for biotite–magnetite–alkali feldspar assemblages. An upper annite activity can be calculated as $a_{\text{annite}} = Fe^{2+}/(Fe^{2+} + Mg)$, where components not on the phlogopite–annite join are ignored. Although this model is most likely incorrect, since it disagrees with the experimental data, it establishes an upper limit of f_{H_2O}. A lower f_{H_2O} limit can be obtained by choosing a completely ionic model of the sort:

$$\frac{(X_K)(X_{Fe^{2+}})^3(X_{Al})(X_{Si})^3(X_{OH})^2}{(X^0_{Al})(X^0_{Si})^3} = a_{\text{annite}}$$

where X^0 = the mole fractions of the given component in pure annite. This model assumes ideal mixing of the additional components, but treats them as diluents, diminishing the annite component and yielding a lower limiting f_{H_2O}. Although these models are by no means the only two that could be chosen, they serve a useful purpose in providing reasonable limits of f_{H_2O}.

The rock from which our biotite crystal was obtained also contains magnetite (Usp_{32}), ilmenite (Hm_5), microcline perthite (Or_{68}), and plagioclase (An_{22}) (see Table 2 for analyses). Application of feldspar (Stormer, 1975; Whitney and Stormer, 1977) and iron–titanium oxide thermometry (Buddington and Lindsley, 1964; Lindsley and Rumble, 1977) fixes $T = 700° \pm 50°C$ and $f_{O_2} = 10^{-17.2\pm0.4}$ for an estimated metamorphic pressure of 7±1 kbar. Knowledge of P, T, and f_{O_2} allows calculation of f_{H_2O}. The upper water fugacity estimate calculated for this assemblage is $10^{3.3\pm0.2}$ bars ($\simeq$ 2000 bars), assuming $a_{\text{annite}} = Fe^{2+}/(Fe^{2+} + Mg)$. Using the ionic model the lower f_{H_2O} estimate is calculated to be 10^2. Choosing the model suggested by Mueller (1972) and Wones (1972), *i.e.* $a_{\text{annite}} = (X_{Fe^{2+}})^3$, f_{H_2O} is calculated to be $10^{2.8}$ ($\simeq$ 630 bars). These calculations assume that $a = X$ for feldspar and magnetite solid solutions. Consideration of experimentally-determined activities for alkali feldspars (Thompson and Waldbaum, 1969) and magnetites (Katsura *et al.*, 1975) produces negligible differences in the calculated water fugacities.

The data indicate that the Au Sable biotite assemblage equilibrated at quite low water fugacity, suggesting low water pressures ($P_{H_2O} < 0.25\ P_{\text{total}}$) for orthogneisses in the Au Sable area. Similar low water fugacity has been estimated for gneisses in the Blue Mountain Lake Quadrangle, central Adirondacks Highlands (Boone, 1978), and it appears that $P_{H_2O} \ll P_{\text{total}}$ for at least a few areas, if not the entire Adirondacks Highlands region. A number of mechanisms resulting in low water fugacities in metamorphic rocks have been proposed, among them: (1) progressive dehydration with upward movement of volatiles; (2) localized partial melting with partitioning of volatiles into the melt and subsequent intrusion to higher levels; (3) dilution of H_2O-rich fluid phase by other volatiles; (4) metamorphism of rocks with inherited low f_{H_2O}. Igneous pyroxene data from Adirondack orthogneisses (Bohlen and Essene, 1978), the presence of granite gneisses with bulk compositions near the granite minimum, and general lack of well-developed migmatites suggest that the inherited f_{H_2O} of most orthogneisses was sufficiently low to inhibit partial melting at Adirondack Highlands T–P (750°±50°C and 8±1 kbar). We cannot rule out the possibility that the metamorphic fluid phase coexisting with Highlands orthogneisses was rich in volatiles other than H_2O. However, if the original fluid composition was water-rich, the diluting components cannot have originated from decarbonation reactions in nearby marbles, as the fluid composition in equilibrium with the marbles is itself water-rich (Essene *et al.*, 1977).

Based on these data and the results from this paper, our present model for Adirondack Highlands metamorphism is that orthogneisses crystallized from relatively dry magmas pre- or syn-tectonically, and maintained their initial low f_{H_2O} during the regional metamorphism. We suggest that for most orthogneisses in the Highlands $P_{H_2O} \ll P_{\text{total}}$ and that $P_{\text{fluid}} \ll P_{\text{total}}$.

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