

PHYSICAL PROPERTIES OF SYNTHETIC BIOTITES ON THE JOIN PHLOGOPITE-ANNITE¹

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ABSTRACT

Indices of refraction, α , γ , n (average of an aggregation); d_{060} ; and unit-cell parameters have been measured for synthetic biotites on the join phlogopite-annite, which have been synthesized and annealed at a variety of pressures, temperatures, and oxygen fugacities. Regression coefficients relating physical properties to $Fe/(Fe+Mg)$ have been computed for biotites annealed at oxygen fugacities defined by the assemblages $Fe_{1-x}O-Fe_3O_4$, $Fe_2SiO_4-SiO_2-Fe_3O_4$, $Ni-NiO$, and $Fe_3O_4-Fe_2O_3$. Systematic variations in the physical properties are observed with changes in both $Fe/(Fe+Mg)$ and oxygen (hydrogen) fugacities. These variations are attributed to the presence of "oxyannite" $KFe^{2+}Fe^{3+}AlSi_3O_{12}$ molecule in the biotite solid solutions.

INTRODUCTION

The relationship existing between the chemical composition and the physical properties of biotites has been the subject of several investigations, the most recent compilations being prepared by Deer *et al.* (1962) and Radoslovich (1962). In a study concerning the phase equilibria of synthetic biotites intermediate to phlogopite [$KMg_3AlSi_3O_{10}(OH)_2$] and annite [$KFe_3AlSi_3O_{10}(OH)_2$] it was found necessary to determine $Fe/(Fe+Mg)$ ratios of fine-grained biotites (1–50 microns) coexisting with sanidine and magnetite by means of optical and x-ray measurements. This paper summarizes the results of measurements in graphic and analytic expressions relating indices of refraction, d_{060} , and unit-cell parameters with the $Fe/(Fe+Mg)$ ratio of biotites synthesized and "annealed" under given conditions of pressure, temperature, and oxygen (hydrogen) fugacity.

The term "annealed" describes the process of subjecting a synthetic biotite to a given temperature, total pressure and oxygen fugacity for a given length of time. This process differs from synthesis in which the biotite is crystallized from a mixture of other phases.

SYNTHESIS: CONTROL OF VARIABLES

The biotites prepared for this study were synthesized by the techniques described by Eugster and Wones (1962) in their study of annite. K_2O and SiO_2 were weighed as potassium silicate glass of the composition $K_2O \cdot 6SiO_2$, prepared and crystallized using the technique of Schairer and Bowen (1955) and under Schairer's direction. Iron was weighed as Fe_2O_3 (J. T. Baker Lot No. 4137) or as $FeC_2O_4 \cdot 2H_2O$ (Fisher Lot No. 541312). The oxalate was analyzed by E. G. Zies and

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found to contain, by weight, Fe, 30.54 per cent; Mg, 0.21; Mn, 0.07; Na, 0.13; Ca, 0.04; and C_2O_4 , 49.04. MgO was weighed as periclase (J. T. Baker Lot No. 82735). Al_2O_3 was prepared as γ -alumina by heating $AlCl_3 \cdot 6H_2O$ at $700^\circ C$. for one hour (see for example, Stirland, *et al.* 1958). The γ -alumina was examined by x -ray diffraction techniques and also found to be optically homogeneous.

The mixtures of reagents were weighed out in a ratio corresponding to $K_2O \cdot Al_2O_3 \cdot 6SiO_2 \cdot 6(FeO + MgO)$. These mixtures were then ground in an agate mortar under acetone for one hour. For producing bulk quantities of biotites, oxalate mix was placed in an unsealed silver capsule which in turn was placed in a sealed platinum tube containing water and oxalate mix. The oxygen fugacity (or perhaps more important, hydrogen fugacity) was controlled by diffusion of hydrogen through the platinum tube (Eugster and Wones, 1962). When gold tubes were used in conjunction with oxalate mixes, the slower rate of hydrogen diffusion maintained highly reducing conditions and graphite crystals were observed in the products of the experiments. Preliminary synthesis was carried out at $500^\circ C$. 2070 bars (30,000 psi) for a period of 48 hours. The resultant biotites were dried at $120^\circ C$. for about 10 minutes and then "annealed" under buffered conditions in order to determine the physical properties as a function of the $Fe/(Fe + Mg)$ ratio and the oxygen (or hydrogen) fugacities of the experiment. The biotites synthesized without buffers (at the oxygen fugacity controlled by the pressure vessel) have low indices of refraction, and yield x -ray diffraction patterns with diffuse reflections, as compared to the "annealed" biotites. This phenomenon is similar to that observed by Yoder and Eugster (1954, 1955) for poorly crystallized micas in their studies of synthetic muscovite and phlogopite.

The buffers used are listed in Table 1 which is from the compilation of Eugster and Wones (1962). As the oxygen fugacities are calculated from gas equilibria measurements or thermodynamic data, they are referred to as fugacities rather than pressures.

An experimental difficulty was to keep the iron content of the charge constant, as iron alloys with platinum under the more reducing conditions of the experiments buffered by $Fe_{1-x}O$ - Fe_3O_4 assemblages. Silver foil capsules were used in the center of the charge (Eugster and Wones, 1962) so that only in the portions of the charge adjacent to the platinum tube did leaching occur. The material within the silver capsule was used for the measurements. Results of these experiments were identical to those obtained from experiments in which the silver-palladium tubes, as suggested by Muan (1962), were used.

The values of $Fe/(Fe + Mg)$ [0.169, 0.352, 0.550, 0.765, 0.880, 0.939] correspond to values of weight per cent annite [20, 40, 60, 80, 90, 95].

TABLE 1. OXYGEN FUGACITIES OF OXYGEN BUFFERS (EUGSTER AND WONES, 1962)

Buffer	$\text{Log } f_{\text{O}_2} = -\frac{A}{T} + B + C\frac{(P-1)}{T}$		
	A	B	C
$\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$	24912	14.41	0.019
$\text{Fe}_3\text{O}_4\text{-Fe}_{1-x}\text{O}$	32730	13.12	0.023
$\text{Fe}_{1-x}\text{O-Fe}$	27215	6.57	0.055
NiO-Ni	24709	8.94	0.046
$\text{SiO}_2\text{-Fe}_2\text{SiO}_4\text{-Fe}_3\text{O}_4$	27300	10.30	0.092

As the data are more useful in terms of atomic ratios, they have been recast in that form.

OPTICAL PROPERTIES

Indices of refraction were measured by oil immersion techniques using white light and oils calibrated at the time of measurement with a sodium vapor light source on an Abbé refractometer. The measurements were usually made to ± 0.002 to ± 0.003 , and very rarely to ± 0.001 . Dispersion did not interfere with these determinations.

The index of refraction, γ , is readily measured, and in all of these synthetic biotites $\beta \approx \gamma$, so that a pseudo-uniaxial indicatrix is observed. Because the biotites are very fine grained ($< 50 \mu$) and oil wet, they float in the immersion oil with the {001} cleavage parallel to the vertical. Hence, the measurement of α is greatly facilitated. Finally, for these biotites, an index of refraction n could be obtained for aggregates at low magnification. This value is surprisingly close to the index calculated from either the formula

$$\bar{n} = \frac{\alpha + 2\gamma}{3} \quad \text{or} \quad \bar{n} = \sqrt[3]{\alpha\gamma^2}$$

(Larsen and Berman, 1934).

The data are presented in graphic form in Figs. 1, 2 and 3, and the regression coefficients, listed in Table 2, are of the form $y = A + Bx$ where y is the particular physical parameter, x the $\text{Fe}/(\text{Fe} + \text{Mg})$ ratio of the biotite and A and B the regression coefficients. The individual sample data are presented in the appendix. The appendix includes data for phlogopite as well.

Regression coefficients were calculated for linear, quadratic and cubic expressions. The quadratic equations provided a slightly better fit than the linear. The cubic equations gave very poor results.

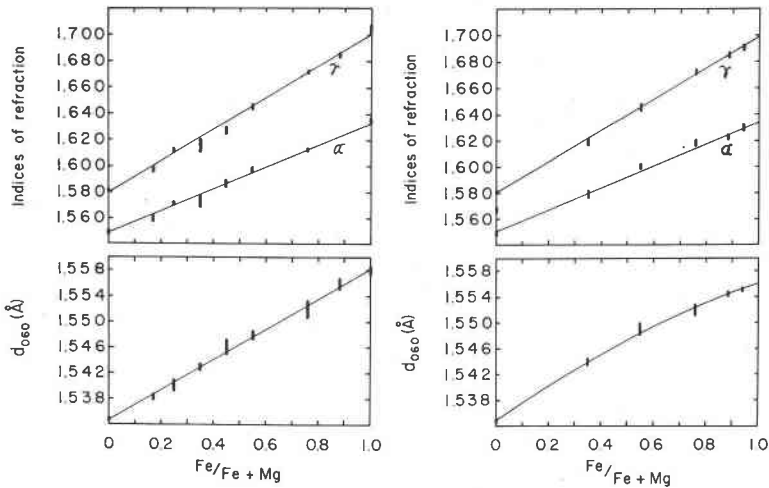


FIG. 1. Values of the indices of refraction and d_{060} x-ray reflection for biotites on the join phlogopite-annite. Light lines indicate regression equations of the form $y=A+Bx$, where x is the ratio $Fe/Fe+Mg$ and y is the property in question; heavy lines indicate the experimental values and limits of error: a) biotites annealed at oxygen fugacities defined by wustite-magnetite assemblages; b) biotites annealed at oxygen fugacities defined by fayalite-quartz-magnetite assemblages.

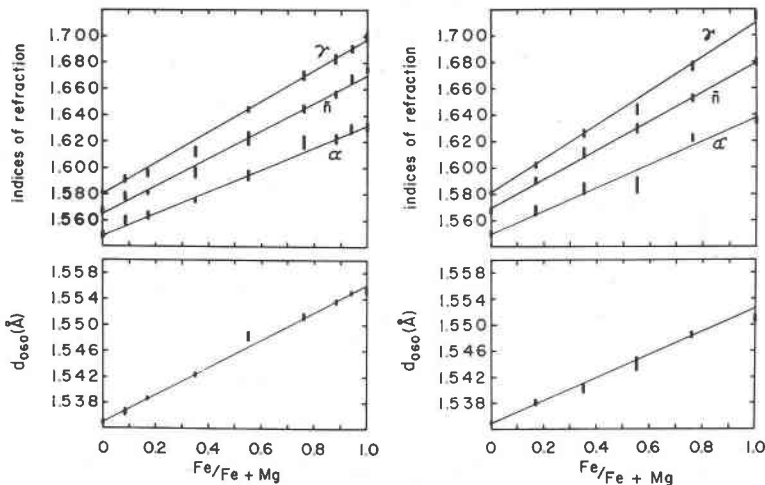


FIG. 2. Values of the indices of refraction and d_{060} x-ray reflection for biotites on the join phlogopite-annite. Solid lines indicate regression equations of the form $y=A+Bx$ where x is the ratio $Fe/Fe+Mg$ and y is the property in question; heavy lines indicate the experimental values and limits of error: a) biotites annealed at oxygen fugacities defined by nickel-nickel oxide assemblages; b) biotites annealed at oxygen fugacities defined by magnetite-hematite assemblages.

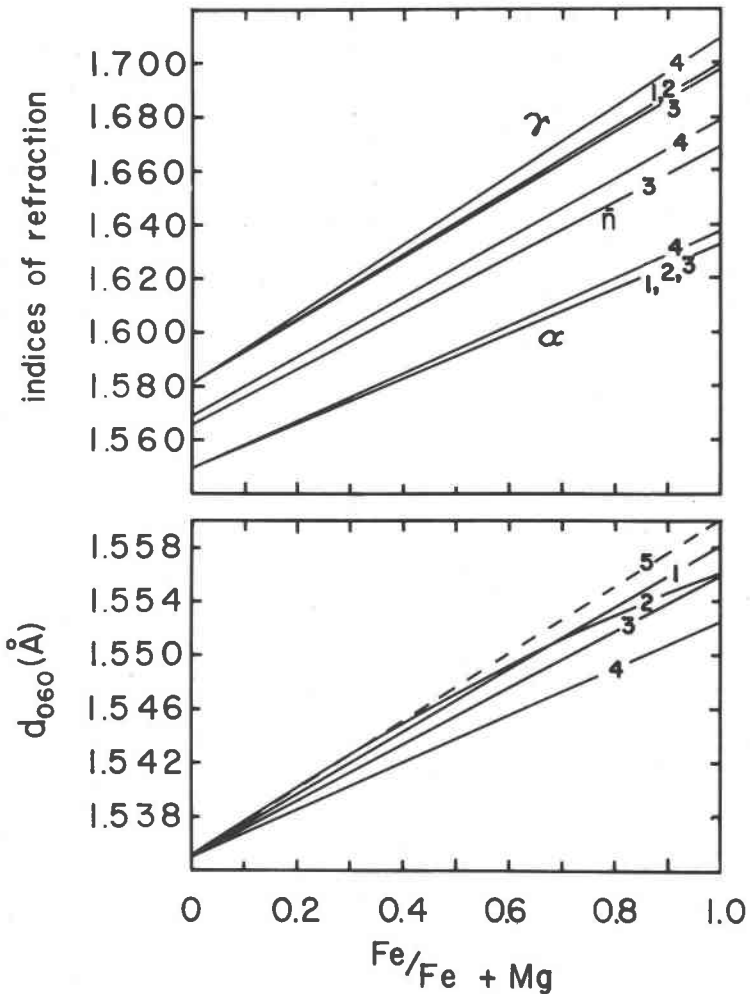


FIG. 3. Plot of regression equations for biotites on the join phlogopite-annite comparing results from differing conditions of annealing. Oxygen fugacities defined by the following assemblages: 1) $\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$; 2) $\text{Fe}_2\text{SiO}_4-\text{SiO}_2-\text{Fe}_3\text{O}_4$; 3) Ni-NiO; 4) $\text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3$; 5) Prediction by Radoslovich (1962).

The regression coefficients for the optical properties are essentially equivalent for biotites annealed at oxygen fugacities defined by $\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$, $\text{Fe}_2\text{SiO}_4-\text{SiO}_2-\text{Fe}_3\text{O}_4$, and Ni-NiO buffers. However, the coefficient B, for biotites annealed at oxygen fugacities equivalent to $\text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3$ assemblages is considerably larger than for the biotites annealed at more reducing conditions. The maximum birefringence

$(\gamma - \alpha)$ is greater for the iron-rich biotites, than for the magnesium rich ones, and an expression for $(\gamma - \alpha)$ can be readily obtained by subtracting the expression for α from that for γ .

X-RAY POWDER DATA

All x -ray diffraction patterns were obtained by powder techniques, using glass slide mounts with Norelco diffractometers. Films were used to observe weak reflections, but all data used in computing unit-cell parameters were obtained by measurement on a diffractometer with a silicon ($a = 5.4307 \text{ \AA}$) internal standard. Measurements consisted of at least two oscillations between the 2θ values of the standard and unknown peaks. The uncertainties listed for d_{060} values in the appendix are the standard deviations determined from four or more measurements.

Malcolm Ross (pers. comm.) has pointed out to the author that the d_{060} may well be a doublet involving the $(\bar{3}31)$ reflection as well as (060) . This fact will tend to decrease the reliability of the (060) as a measure of b , but the shift with composition has relatively little scatter as is seen by the errors quoted in Table 2. Hence the d_{060} has value as a measure of annite content in this solid solution series. The accuracy is also dependent on the true value of the cell parameters of the internal standard and the instrumental errors. The temperatures of the laboratories where the data were collected were in the range of 23° – 28° C. Both $\text{FeK}\alpha$ and $\text{CuK}\alpha$ radiations were used in these measurements.

The unit-cell parameters were determined by a least-squares refinement of the x -ray powder data. The computations were carried out on the Burroughs 220 computer programmed by D. S. Handwerker, H. T. Evans, Jr. and D. E. Appleman of the U. S. Geological Survey. The basic problem in determining unit-cell parameters lies in establishing accurate values for a sufficient number of independent reflections. The majority of peaks in biotite powder patterns represent the superposition of several reflections. For this study the (003) , $(\bar{1}13)$, (004) , $(\bar{1}32)$, (005) and $(060)/\bar{3}31$ reflections were measured for a majority, and with some samples the (110) , $(200)/(\bar{1}31)$, $(\bar{1}33)/(202)$, (006) , $(\bar{1}35)$ and (204) reflections were also measured. The d -spacings selected for determination of the unit-cell parameters of biotites are given in Table 3. The occurrence of doublets: $(200)/(\bar{1}31)$; $(\bar{1}33)/(202)$; $(060)/\bar{3}31$; also increases the uncertainties. Table 4 lists the unit-cell parameters for 14 synthetic biotites.

The $(060)/\bar{3}31$ reflection demonstrated the greatest shift with changing $\text{Fe}/(\text{Fe} + \text{Mg})$, and the position of this reflection was measured for most of the biotites. The regression coefficients for d_{060} are given in Table 2, and the relationship of d_{060} to $\text{Fe}/(\text{Fe} + \text{Mg})$ is plotted in Figs. 1, 2

TABLE 2. REGRESSION COEFFICIENTS FOR THE INDICES OF REFRACTION, α γ n
 (AGGREGATE) d_{060} X-RAY REFLECTION (\AA) AND UNIT-CELL PARAMETERS
 a , b , c AND β (\AA) FOR BIOTITES ON THE JOIN PHLOGOPITE+ANNITE¹

	Property	Buffer	A	B	C	Std. Error
Optical	α	$\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$	1.5492	0.0829	0.0037	0.0031
			1.5497	0.0795		0.0029
	γ	$\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$	1.5800	0.1196	0.0142	0.0054
			1.5808	0.1076		0.0053
x-ray	d_{060}	$\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$	1.5348	0.0234	-0.0003	0.0002
			1.5348	0.0236		0.0002
			5.320	0.0742		0.006
	a	$\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$	5.328	0.025	0.048	0.004
			9.209	0.139		0.003
	b	$\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$	9.209	0.142	-0.004	0.003
			10.309	-0.006		0.010
	c	$\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$	10.312	-0.029	+0.023	0.010
			99.897	0.143		0.160
	β	$\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$	100.073	-0.069	+0.011	0.131
Optical	α	$\text{Fe}_2\text{SiO}_4-\text{SiO}_2-\text{Fe}_3\text{O}_4$	1.5514	0.0814	-0.0198	0.0036
			1.5497	0.1001		0.0027
			1.5808	0.1174		0.0019
	γ	$\text{Fe}_2\text{SiO}_4-\text{SiO}_2-\text{Fe}_3\text{O}_4$	1.5809	0.1132	0.0050	0.0020
x-ray	d_{060}	$\text{Fe}_2\text{SiO}_4-\text{SiO}_2-\text{Fe}_3\text{O}_4$	1.5348	0.0222	0.0068	0.0005
			1.5348	0.0281		0.0003
Optical	α	Ni-NiO	1.5502	0.0845	0.0186	0.0046
			1.5502	0.0672		0.0042
			1.5800	0.1170		0.0037
	γ	Ni-NiO	1.5808	0.1005	0.0187	0.0030
			1.5642	0.1053		0.0037
n	Ni-NiO	1.5671	0.0803	0.0253	0.0030	

¹Regression equations are of the form $y = A + Bx + Cx^2$, where $x = \text{Fe}/(\text{Fe} + \text{Mg})$ and y is the particular property.

TABLE 2—(continued)

	Property	Buffer	A	B	C	Std. Error
x-ray	d_{060}	Ni-NiO	1.5348	0.0213		0.0007
			1.5348	0.0256	-0.0048	0.0004
Optical	α	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$	1.5506	0.0878		0.0052
			1.5492	0.1116	-0.0247	0.0047
			1.5806	0.1295		0.0039
	γ	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$	1.5813	0.1123	0.0197	0.0031
			1.5689	0.1097		0.0022
	n	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$	1.5678	0.1211	-0.0115	0.0017
x-ray	d_{060}	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$	1.5348	0.0176		0.0004
			1.5348	0.0190	-0.0017	0.0005
	a	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$	5.325	0.045		0.006
			5.327	0.029	0.017	0.006
	b	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$	9.210	0.098		0.004
			9.209	0.110	-0.012	0.004
	c	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$	10.307	-0.040		0.005
			10.307	-0.039	-0.001	0.006
	β	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$	99.97°	0.045		0.153
			100.05°	-0.596	0.692	0.153

and 3. Except for biotites annealed at oxygen fugacities defined by the fayalite-quartz-magnetite assemblage, a linear expression fits the data just as well as a quadratic expression. There is a systematic increase in d_{060} with increase of $\text{Fe}/(\text{Fe}+\text{Mg})$ for a given "buffer series," and a systematic decrease in d_{060} at constant $\text{Fe}/(\text{Fe}+\text{Mg})$ as oxygen fugacity increases.

Two relationships characterize the unit-cell parameters. For a given buffer series the a and b axes increase with increasing Fe content, and a , b and c all decrease with increasing oxygen fugacities at a constant value of $\text{Fe}/(\text{Fe}+\text{Mg})$. The optical data show an increase in the indicet of refraction with the increase in oxygen fugacity as well as the increase in Fe content. These results are fully reversible, biotites originally annealed at either reduced ($\text{Fe}_{1-x}\text{O-Fe}_3\text{O}_4$; Ni-NiO) or oxidized

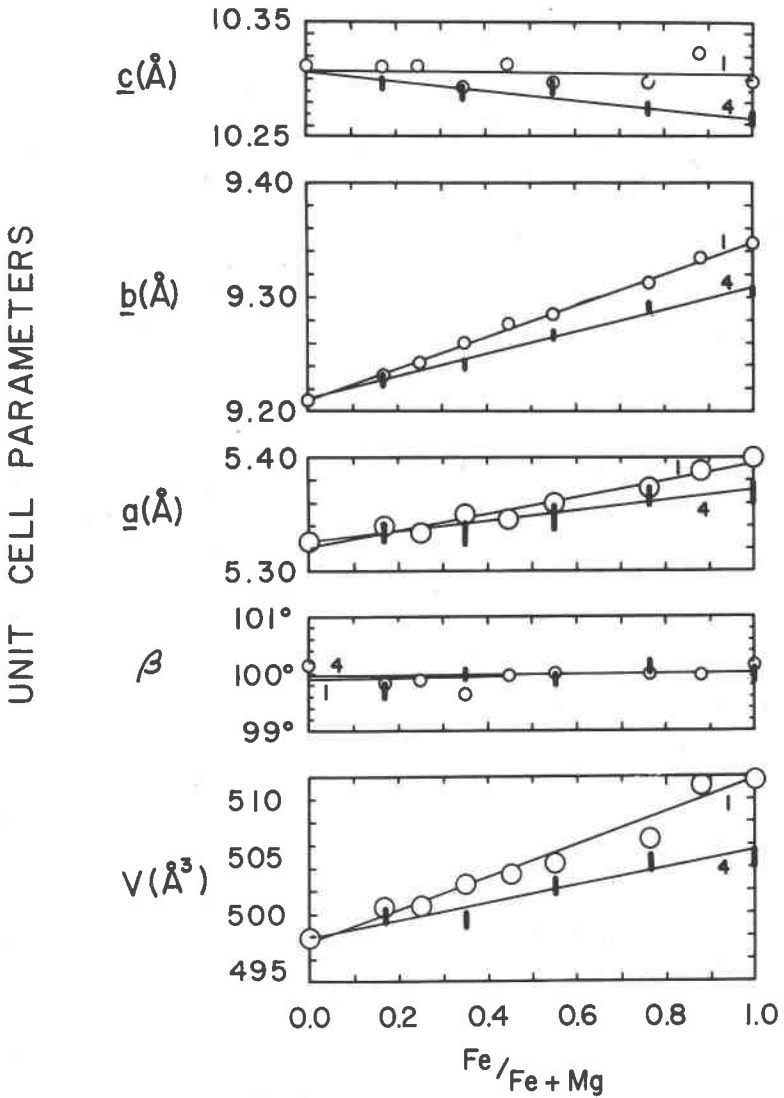


FIG. 4. Unit-cell parameters of biotites on the join phlogopite-annite. Open circles are those annealed at oxygen fugacities defined by $\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$ assemblages; bars are those annealed at oxygen fugacities defined by $\text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3$ assemblages. Solid lines are regression equations given in Table 1.

($\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$) conditions change their properties apropos to the new conditions at which they are annealed a second or third time.

No attempt was made to investigate Gower's (1957) method of determining Fe contents by measuring the ratio of the intensities of the (004) and (005) reflections. In general, the intensity of (005) for iron-rich micas was so weak that the peak could not be observed in many cases. As the (004) coincides with the (113) reflection of magnetite, the method would not be useful for determining the composition of biotites intimately mixed with magnetite. As this was the case in the phase equilibria studies, Gower's method was not investigated for the synthetic biotites.

PROPERTIES OF PHLOGOPITE

The values of α , γ and d_{060} were determined for two phlogopites synthesized during this study and for eight synthetic phlogopites supplied by H. S. Yoder, Jr., and H. P. Eugster. In addition, the unit cell was redetermined by a least-squares analysis of the x -ray powder diffraction data. The results are slightly different from those reported by Yoder and Eugster (1954). The individual data are listed in the Appendix and the average values are compared with the values of Yoder and Eugster:

	Wones	Yoder and Eugster
α	1.550 ± 0.002	1.548 ± 0.003
γ	1.581 ± 0.001	1.588 ± 0.003
a	$5.326 \pm 0.01 \text{ \AA}$	$5.314 \pm 0.01 \text{ \AA}$
b	$9.210 \pm 0.01 \text{ \AA}$	$9.204 \pm 0.02 \text{ \AA}$
c	$10.311 \pm 0.01 \text{ \AA}$	$10.314 \pm 0.005 \text{ \AA}$
β	$100^\circ 10' \pm 8'$	$99^\circ 54' \pm 5'$
\bar{n} (average)	1.571	1.575
\bar{n} (Gladstone and Dale)	1.575	1.576

The phlogopite cell as determined in this study does not meet the exact requirements for transformation to a hexagonal cell (Smith and Yoder, 1956, p. 231). The ratio b/a is 1.729 rather than $\sqrt{3}$, and $\cos^{-1} a_M/3c_M = 99^\circ 54'$ rather than the value of $100^\circ 10'$ found in this study.

THE OXYBIOTITE PROBLEM

The observed variations in the indices of refraction and the x -ray powder data are readily explained by the dehydrogenation of the biotites to form "oxybiotites." Barnes (1930) conclusively proved this to be the case for the "basaltic hornblendes," or "oxyhornblendes." An excellent review of this concept is given by Deer *et al.* (1963). This concept was first demonstrated experimentally for biotites by Rinne (1925) and by Larsen *et al.*, (1937) for the biotite phenocrysts in the San Juan region, Colorado. Eugster and Wones (1962), in a study of annite, demonstrated

TABLE 3 d-SPACINGS OF BIOTITES SELECTED FOR DETERMINATION OF UNIT-CELL PARAMETERS

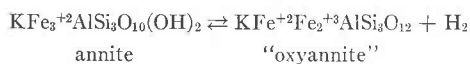
	Phlogopite	Fe/(Fe+Mg) of biotites buffered by Fe _{1-x} O-Fe ₃ O ₄ assemblages					Fe/(Fe+Mg) of biotites buffered by Fe ₃ O ₄ -Fe ₃ O ₃ assemblages							
<i>hkl</i> ¹		0.169	0.250	0.352	0.450	0.550	0.765	0.880	1.000	0.169	0.352	0.550	0.765	1.000
002	0.000									0.169	0.352	0.550	0.765	1.000
110	5.071													
112	4.589													
022	3.371	3.681	3.385	3.417	3.386	3.424	3.381	3.387	3.388	3.381	3.377	3.377	3.372	3.367
112			3.168	3.171	3.172	3.176	3.185							
113			2.938	2.939	2.941	2.942	2.946	2.950	2.961				2.942	
023			2.729	2.732	2.729	2.733	2.731							
200	2.621			2.631		2.639		2.654	2.656			2.634	2.641	2.644
131		2.626								2.624				
004	2.540	2.540		2.538	2.538	2.537		2.543	2.535	2.532	2.532			
202	2.514													
132	2.436	2.441		2.447	2.451	2.452		2.458	2.467	2.440	2.441	2.448	2.455	2.456
201				2.367										
114														
040														
221										2.303	2.308			
133										2.182			2.192	2.193
202	2.180								2.201					
221				2.170										
042														
005	2.032	2.031	2.030	2.032	2.032			2.023		2.030	2.027	2.029	2.011	
204														
006	1.694													
135	1.684													
204	1.678													
060	1.5349	1.5383	1.5404	1.5433	1.5460	1.5475	1.5522	1.5558	1.5579	1.5380	1.5403	1.5443	1.5484	1.5506

¹ For unit-cell parameters, see Table 4.

TABLE 4. UNIT-CELL PARAMETERS OF SELECTED BIOTITES

Fe/(Fe+Mg)	a	b	c	β	V(Å ³)
Phlogopite					
0.000	5.326 ± .006	9.210 ± .009	10.311 ± .009	100°10' ± 8'	497.77
Biotites annealed at oxygen fugacities defined by Fe ₃ O ₄ -Fe ₂ O ₃					
0.169	5.339 ± .003	9.228 ± .001	10.295 ± .003	99°45' ± 5'	499.9
0.352	5.333 ± .003	9.241 ± .001	10.288 ± .004	99°59' ± 5'	499.4
0.550	5.347 ± .01	9.266 ± .003	10.293 ± .007	99°54' ± 10'	502.4
0.765	5.377 ± .002	9.291 ± .001	10.275 ± .006	100°8' ± 14'	504.2
1.000	5.369 ± .005	9.304 ± .001	10.264 ± .001	100°0' ± 10'	504.7
Biotites annealed at oxygen fugacities defined by Fe _{1-x} O-Fe ₃ O ₄					
0.169	5.339 ± .006	9.230 ± .001	10.311 ± .002	99°50' ± 4'	500.6
0.250	5.333 ± .002	9.242 ± .001	10.312 ± .001	99°56' ± 1'	500.6
0.352	5.349 ± .005	9.260 ± .002	10.293 ± .006	99°38' ± 6'	502.6
0.450	5.343 ± .007	9.276 ± .001	10.312 ± .003	99°57' ± 4'	503.4
0.550	5.358 ± .003	9.285 ± .003	10.297 ± .002	100°0' ± 1'	504.5
0.765	5.373 ± .01	9.312 ± .003	10.297 ± .009	100°3' ± 6'	507.3
0.880	5.389 ± .003	9.335 ± .002	10.322 ± .004	99°58' ± 4'	511.4
1.000	5.401 ± .01	9.347 ± .005	10.297 ± .01	100°10' ± 12'	511.7

a relationship between the physical properties of annite and the conditions of "annealing," and suggested the variations were due to the reaction:



Several lines of evidence indicate that this is the case.

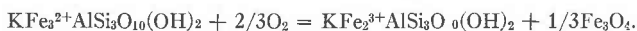
First of all, the variations are correlated with buffers, rather than with temperature and oxygen fugacities. As Eugster and Wones (1962) demonstrated, the hydrogen fugacities associated with each buffer are more or less independent of temperature and are constant for a constant total pressure.

Secondly, biotites synthesized from oxalate mix *in buffered runs* are at hydrogen fugacities, but not oxygen fugacities, equivalent to the hydrogen fugacities of biotites annealed in buffered runs. For example, a biotite with Fe/(Fe+Mg) of 0.169 held at 700° C., 2000 bars, with an Fe₃O₄-Fe₂O₃ buffer, had a value of $\gamma = 1.608 \pm .003$ in an H₂+H₂O atmosphere, and a value of $1.609 \pm .003$ in an H₂+H₂O+CO+CO₂ atmosphere. Another biotite with Fe/(Fe+Mg) of 0.550 held at 800° C., 2000 bars, buffered by Fe₂SiO₄-SiO₂-Fe₃O₄, had values of $1.645 \pm .003$ and $1.644 \pm .003$ for the respective types of gas phases.

The changes in properties are completely reversible; biotites annealed at conditions of high or low hydrogen fugacities readily change their properties when annealed again at different hydrogen fugacities.

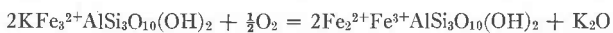
Finally, all runs used in this tabulation contain 99+ per cent biotite (by volume). If the cationic content varied from that prepared in the starting material, such phases as iron oxides, iron silicates, or feldspars should appear. The only additional phase encountered was sanidine, and it was readily attributed to loss of iron to the platinum container (Eugster and Wones, 1962), and such material was not used in this compilation.

The "ferrimuscovite," $\text{KFe}_2^{3+}\text{AlSi}_3\text{O}_{10}(\text{OH})_2$, molecule might be formed from a reaction such as the following:



This is considered very unlikely as no synthesis or annealing experiments were carried out in which iron oxides were observed without equivalent amounts of sanidine also being present.

Another possible reaction would be the following:



In order to test this hypothesis annite was annealed at 2000 bars total pressure, 375° C. in a 2 molar KCl solution for one week, buffered by an Fe_3O_4 - Fe_2O_3 assemblage. The mean index of refraction n is 1.680, and the unit-cell parameters are $a = 5.351 \pm 0.01 \text{ \AA}$, $b = 9.297 \pm 0.005 \text{ \AA}$, $c = 10.266 \pm 0.02 \text{ \AA}$, $\beta = 99^\circ 45' \pm 20'$. These values, sufficiently close to those listed in Table 3 for an annite annealed in distilled water, indicate that the above reaction is improbable for these experimental conditions.

Estimating the mol fractions of phlogopite, annite and "oxyannite" presents another problem. Three methods have been used to estimate "oxyannite" contents: 1) partial chemical analyses, 2) comparison of the b unit-cell edge with the regression coefficients of Radoslovich (1962) and 3) application of the rule of Gladstone and Dale to the synthetic biotites.

As reported by Eugster and Wones (1962), Dr. Graham Chinner performed a partial microanalysis of a 60 mg synthetic annite sample containing about 1 volume per cent sanidine. Chinner reported 36.4 weight per cent FeO and 4.7 per cent Fe_2O_3 . Converting to atomic ratios, 10.4 per cent of total iron is ferric. This corresponds to 15.6 mol per cent "oxyannite."

Radoslovich (1962) has determined regression coefficients for the b axis of micas as a function of cations present in the structure. Using Chinner's partial analysis, and assuming no vacancies in the octahedral layer, Radoslovich's regression technique predicts a b axis of 9.336 \AA for oxyan-

nite, 9.372 Å for annite, 9.210 Å for phlogopite, and 9.367 Å for the annite analyzed by Chinner. The phlogopite value is in exact agreement with the values determined in this study in (Table 4), but the other values seem to be quite far from the value of 9.334 Å determined for the annite analyzed by Chinner, and even farther from the values determined for more oxidized annites. The suggestion is that Radoslovich's values for the iron coefficients are not as good as those for the other constituents. Radoslovich does quote an error of ± 0.03 in his analysis, which just covers the deviations between these data and his regression predictions. The possibility of octahedral "vacancies" ("ferrimuscovite" solid solutions) would resolve some of this problem, but for reasons stated earlier, it seems unlikely that this is the case.

An attempt at a quantitative determination of the oxybiotite contents by means of the rule of Gladstone and Dale was made. Defining the mean index of refraction \bar{n} , the mol per cent m , the refractivity k , molecular weight w , of the components phlogopite, annite, and oxyannite by the respective subscripts 1, 2, 3, the following expression for the mol per cent of oxyannite in the iron end member ($Fe/Fe+Mg=1.00$) can be obtained:

$$m^3 = \frac{(\frac{1}{2}\bar{n} - 1)VA - 102.492}{13.297}$$

when V is the volume of the unit cell, and A is Avogadro's number (6.0247×10^{23}). The values obtained using this relation are listed in Table 5 for three synthetic annites and the regression equations of Table 2. The uncertainties (± 0.013) are derived by standard propagation of error technique assuming uncertainties of 0.003 in \bar{n} , and 1 Å³ in V . The regression data indicate an orderly progression from reduced conditions to oxidized conditions, but the data on individual samples are more

TABLE 5. COMPARISON OF ESTIMATES OF MOLAR CONCENTRATION OF "OXYANNITE" IN SYNTHETIC ANNITES BY MEANS OF THE RULE OF GLADSTONE AND DALE (LARSEN AND BERMAN, 1934)

Conditions of Synthesis	Buffer	\bar{n}	V (Å ³)	Mol % "oxyannite"
Regression, Table 2	Fe _{1-x} O-Fe ₃ O ₄	1.6687	511.7	4.4
Regression, Table 2	Fe ₃ O ₄ -Fe ₂ O ₃	1.6752	505.5	2.4
800° C., 72 hrs.	Fe _{1-x} O-Fe ₃ O ₄	1.681	511.7	18.6
400° C., 163 hrs.	Fe ₃ O ₄ -Fe ₂ O ₃	1.688	504.7	15.9
600° C., 212 hrs.	Ni-NiO	1.681	509.8	15.7
Analysis, Chinner, of above sample (Ni-NiO)		—	—	15.5

scattered. However, all indicate oxyannite contents of about 15–19 mol per cent, which correspond to $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$ ratios of about 0.04–0.05, and are in excellent agreement with the analysis by Dr. Chinner.

Unfortunately, when the rule of Gladstone and Dale is applied to the phlogopite end member, a mean index of refraction of 1.575 is derived as opposed to the value of 1.571 derived from the measurements. However, when applied to the annite analyzed by Chinner, the agreement was almost exact. The problem lies in the “ $\bar{n} - 1$ ”V” term of the above expression, where the increase of \bar{n} is matched by a decrease in V.

The determination of the concentration of “oxyannite” molecule in synthetic biotites, and the correlation of that concentration with variations in temperature, pressure and gas composition will require careful synthesis and analytical work before it is completely resolved.

APPLICATION TO NATURAL BIOTITES

These data do not apply directly to natural biotites except as defining properties of the end members. However, it does indicate that the $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio may serve as an indicator of variations in the oxygen fugacity of the environment in which a biotite crystallizes. Chinner's (1960) work on the pelitic gneisses of Glen Clova provides an excellent example of how the $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ content of biotite increases as the oxygen content (or perhaps fugacity) increases. Chinner was able to demonstrate such a change in the coexisting iron oxides (ilmenite, magnetite and hematite) as well, so that the biotite data as such is redundant. However, in assemblages lacking iron oxides the biotites could be used to define variations in the fugacities of oxygen or hydrogen.

The data of Larsen *et al.* (1937) on the biotite phenocrysts of the volcanic rocks of the San Juan Mountains, Colorado, clearly demonstrate the formation of oxybiotite through rapid “dehydrogenation” of lava upon extrusion.

Hellner and Euler (1957) treated biotites from the Albtal granite (Black Forest) hydrothermally and found that hematite flakes formed, and the indices of refraction increased. It seems apparent that they formed oxybiotite in their experiments. As such effects are due primarily to variations of oxygen fugacities, the value of knowing oxybiotite contents is more important as a hydrogen barometer rather than as the thermometer suggested by Hellner and Euler.

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Appendix. PROPERTIES OF SYNTHETIC BIOTITES ANNEALED AT VARIOUS CONDITIONS OF TEMPERATURE, PRESSURE, AND OXYGEN FUGACITY

Fe/Fe+Mg	Temp (° C.)	Time (hrs.)	Pressure (bars)	Buffer	α	γ	μ	$d_{(060)}$
0.169	800	166	2000	"FeO"-Fe ₃ O ₄	1.560 ± .003	1.597 ± .002	n.d.	1.5383 ± .0005
0.250	800	118	2000	"FeO"-Fe ₃ O ₄	1.571 ± .002	1.612 ± .002	n.d.	1.5402 ± .0010
0.352	700	120	2000	"FeO"-Fe ₃ O ₄	1.573 ± .005	1.615 ± .005	n.d.	1.5430 ± .0005
0.450	700	215	2000	"FeO"-Fe ₃ O ₄	1.586 ± .003	1.622 ± .001	n.d.	1.5460 ± .0012
0.550	850	69	1035	"FeO"-Fe ₃ O ₄	1.597 ± .002	1.645 ± .002	n.d.	1.5488 ± .0008
0.550	850	177	1035	"FeO"-Fe ₃ O ₄	1.597 ± .002	1.646 ± .001	n.d.	1.5475 ± .0002
0.765	700	160	2000	"FeO"-Fe ₃ O ₄	1.611 ± .002	1.671 ± .003	n.d.	1.5520 ± .0010
0.765	820	69	1035	"FeO"-Fe ₃ O ₄	1.612 ± .004	1.673 ± .002	n.d.	1.5505 ± .0011
0.765	800	51	1035	"FeO"-Fe ₃ O ₄	1.612 ± .002	1.671 ± .003	n.d.	1.5520 ± .0012
0.880	800	73	2000	"FeO"-Fe ₃ O ₄	n.d.	1.684 ± .002	n.d.	1.5558 ± .0010
1.000	700	72	2000	"FeO"-Fe ₃ O ₄	1.634 ± .001	1.704 ± .003	n.d.	1.5580 ± .0005
0.352	825	118	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.580 ± .003	1.620 ± .002	n.d.	1.5442 ± .0003
0.352	800	89	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.578 ± .005	1.617 ± .002	n.d.	1.5432 ± .0002
0.352	700	92	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.575 ± .003	1.616 ± .003	n.d.	1.5435 ± .0003
0.352	850	94	1035	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.581 ± .003	1.622 ± .003	n.d.	1.5445 ± .0005
0.550	800	122	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.600 ± .003	1.648 ± .002	n.d.	n.d.
0.550	790	47	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.600 ± .003	1.644 ± .003	n.d.	n.d.
0.550	760	92	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.600 ± .002	1.647 ± .002	n.d.	1.5498 ± .0006
0.550	750	89	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.597 ± .002	1.643 ± .004	n.d.	1.5489 ± .0002
0.550	750	89	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.600 ± .002	1.644 ± .002	n.d.	1.5491 ± .0006
0.550	740	92	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.601 ± .003	1.644 ± .002	n.d.	1.5493 ± .0008
0.550	740	80	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.601 ± .003	1.651 ± .002	n.d.	1.5475 ± .0007
0.550	700	150	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.597 ± .003	1.644 ± .003	n.d.	1.5478 ± .0006
0.550	720	141	1035	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.600 ± .003	1.647 ± .002	n.d.	1.5483 ± .0007
0.550	720	64	1035	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	n.d.	1.639 ± .004	n.d.	1.5496 ± .0016
0.550	700	142	1035	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.606 ± .003	1.645 ± .003	n.d.	1.5507 ± .0004

¹ Specimens supplied by H. S. Yoder, Jr. and H. P. Eugster.

Appendix (continued)

Fe/Fe+Mg	Temp (° C.)	Time (hrs.)	Pressure (bars)	Buffer	α	γ	η	d_{660}
0.765	760	74	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.617 ± .003	1.670 ± .003	n.d.	1.5513 ± .0003
0.765	730	167	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.618 ± .003	1.677 ± .001	n.d.	1.5509 ± .0010
0.765	720	69	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.617 ± .003	1.670 ± .003	n.d.	n.d.
0.765	715	92	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.617 ± .002	1.675 ± .002	n.d.	n.d.
0.765	705	449	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.613 ± .002	1.670 ± .002	n.d.	1.5514 ± .0014
0.765	705	118	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.617 ± .002	1.671 ± .002	n.d.	1.5526 ± .0003
0.765	700	92	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.617 ± .002	1.670 ± .002	n.d.	1.5514 ± .0002
0.765	700	84	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.618 ± .003	1.676 ± .003	n.d.	1.5510 ± .0010
0.765	690	189	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.617 ± .003	1.670 ± .003	n.d.	1.5528 ± .0003
0.765	680	169	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.613 ± .003	1.674 ± .002	n.d.	n.d.
0.765	525	68	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	n.d.	1.670 ± .003	n.d.	n.d.
0.765	500	48	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	n.d.	n.d.	n.d.	1.5515 ± .0008
0.765	700	48	1035	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.617 ± .003	1.671 ± .002	n.d.	n.d.
0.765	660	209	1035	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.618 ± .003	1.670 ± .003	n.d.	1.5515 ± .0004
0.765	600	162	1035	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	n.d.	1.670 ± .003	n.d.	1.5515 ± .0002
0.880	715	113	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.623 ± .002	1.684 ± .002	n.d.	1.5546 ± .0006
0.880	715	92	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.623 ± .002	1.682 ± .003	n.d.	1.5542 ± .0002
0.880	705	113	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.623 ± .003	1.684 ± .003	n.d.	1.5546 ± .0004
0.880	705	113	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.620 ± .002	1.682 ± .002	n.d.	1.5544 ± .0006
0.880	700	48	2070	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.623 ± .002	1.686 ± .003	n.d.	1.5542 ± .0004
0.939	700	140	2000	Fe ₃ SiO ₄ -SiO ₂ -Fe ₃ O ₄	1.629 ± .003	1.690 ± .002	n.d.	1.5550 ± .0003
0.083	700	132	2000	Ni-NiO	1.560 ± .003	1.591 ± .003	1.577 ± .003	1.5362 ± .0002

Appendix (continued)

Fe/Fe+Mg	Temp (° C.)	Time (hrs.)	Pressure (bars)	Buffer	α	γ	η	d_{1000}
0.169	800	118	2070	Ni-NiO	1.564 ± .005	1.597 ± .002	1.581 ± .003	1.5387 ± .0010
0.169	800	92	2070	Ni-NiO	1.564 ± .003	1.597 ± .002	1.581 ± .003	1.5385 ± .0006
0.169	700	139	2070	Ni-NiO	1.564 ± .003	1.597 ± .002	1.580 ± .003	1.5385 ± .0006
0.169	700	117	2070	Ni-NiO	1.561 ± .003	1.595 ± .004	1.581 ± .003	1.5390 ± .0003
0.169	600	138	2070	Ni-NiO	1.557 ± .003	1.592 ± .003	1.581 ± .003	1.5385 ± .0006
0.169	600	107	2070	Ni-NiO	1.566 ± .003	1.589 ± .006	1.581 ± .003	1.5384 ± .0004
0.250	700	138	2000	Ni-NiO	1.577 ± .003	1.608 ± .002	1.597 ± .003	1.5412 ± .0009
0.352	800	121	2070	Ni-NiO	1.575 ± .003	1.612 ± .002	1.593 ± .005	1.5440 ± .0010
0.352	700	139	2070	Ni-NiO	1.575 ± .003	1.616 ± .003	1.595 ± .004	1.5410 ± .0010
0.352	700	117	2070	Ni-NiO	1.575 ± .003	1.616 ± .002	1.602 ± .002	1.5434 ± .0009
0.352	700	113	2070	Ni-NiO	1.575 ± .003	1.612 ± .002	1.598 ± .004	1.5415 ± .0006
0.352	600	107	2070	Ni-NiO	1.575 ± .003	1.605 ± .003	1.592 ± .004	1.5429 ± .0003
0.352	600	92	2070	Ni-NiO	n.d.	1.612 ± .005	1.594 ± .004	1.5415 ± .0004
0.550	800	168	2070	Ni-NiO	1.599 ± .002	1.643 ± .002	n.d.	1.5479 ± .0009
0.550	800	168	2070	Ni-NiO	n.d.	1.646 ± .005	n.d.	n.d.
0.550	700	179	2070	Ni-NiO	1.595 ± .005	1.645 ± .002	1.622 ± .003	1.5475 ± .0003
0.550	700	118	2070	Ni-NiO	1.591 ± .003	1.645 ± .003	1.616 ± .003	1.5475 ± .0009
0.550	600	115	2070	Ni-NiO	1.592 ± .002	1.641 ± .003	1.610 ± .003	1.5476 ± .0010
0.765	700	160	2070	Ni-NiO	1.620 ± .003	1.673 ± .002	1.645 ± .004	1.5518 ± .0003
0.765	700	148	2070	Ni-NiO	1.616 ± .002	1.666 ± .002	1.640 ± .003	1.5516 ± .0004
0.765	650	89	2070	Ni-NiO	n.d.	1.673 ± .004	1.650 ± .003	1.5511 ± .0008
0.765	600	165	2070	Ni-NiO	n.d.	n.d.	1.640 ± .003	1.5513 ± .0003
0.765	600	92	2070	Ni-NiO	1.623 ± .003	1.668 ± .002	1.645 ± .004	1.5519 ± .0002
0.880	600	139	2070	Ni-NiO	n.d.	n.d.	1.657 ± .003	1.5536 ± .0009
0.880	600	132	2070	Ni-NiO	1.622 ± .003	1.681 ± .003	1.654 ± .002	1.5534 ± .0009

Appendix (continued)

Fe/Fe+Mg	Temp (° C.)	Time (hrs.)	Pressure (bars)	Buffer	α	γ	n	d_{980}
0.939	600	166	2000	Ni-NiO	n.d.	1.694 ± .003	1.672 ± .005	1.5548 ± .0004
0.939	600	140	2000	Ni-NiO	1.628 ± .003	1.690 ± .003	1.664 ± .003	1.5549 ± .0009
0.169	700	47	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.571 ± .003	1.605 ± .002	1.591 ± .003	1.5375 ± .0007
0.169	600	115	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.569 ± .003	1.603 ± .002	1.591 ± .003	1.5374 ± .0002
0.169	600	41	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.566 ± .003	1.602 ± .001	1.586 ± .003	1.5381 ± .0005
0.169	800	66	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.571 ± .002	1.602 ± .002	1.586 ± .003	1.5379 ± .0004
0.169	700	64	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.566 ± .003	1.600 ± .002	1.586 ± .003	1.5380 ± .0006
0.169	600	63	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.561 ± .002	1.600 ± .003	1.591 ± .003	1.5384 ± .0003
0.352	700	122	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.581 ± .002	1.628 ± .002	1.612 ± .003	1.5399 ± .0008
0.352	700	29	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.591 ± .003	1.630 ± .002	1.612 ± .003	1.5401 ± .0007
0.352	600	73	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.576 ± .003	1.623 ± .003	1.607 ± .003	1.5397 ± .0001
0.352	760	67	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.586 ± .003	1.625 ± .001	1.613 ± .003	1.5409 ± .0006
0.352	750	70	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.586 ± .003	1.627 ± .003	1.617 ± .003	1.5397 ± .0007
0.352	600	139	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.582 ± .003	1.621 ± .002	1.607 ± .003	1.5411 ± .0004
0.550	650	94	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.596 ± .002	1.651 ± .002	1.635 ± .003	1.5430 ± .0002
0.550	600	94	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.591 ± .003	1.645 ± .002	1.630 ± .004	1.5426 ± .0006
0.550	582	89	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.591 ± .003	1.648 ± .001	1.630 ± .004	1.5450 ± .0007
0.550	550	140	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.586 ± .003	1.646 ± .002	1.630 ± .003	1.5432 ± .0006
0.550	545	157	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.586 ± .003	1.641 ± .002	1.630 ± .004	1.5431 ± .0005
0.550	520	96	2070	Fe ₃ O ₄ -Fe ₂ O ₃	1.592 ± .003	1.643 ± .001	1.630 ± .004	1.5441 ± .0004
0.550	520	192	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.576 ± .003	1.635 ± .001	1.625 ± .002	1.5450 ± .0010
0.550	510	159	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.576 ± .003	1.635 ± .001	1.623 ± .005	1.5431 ± .0006
0.550	500	64	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.576 ± .003	1.641 ± .002	1.626 ± .004	1.5455 ± .0004

Appendix (continued)

Fe/Fe+Mg	Temp (° C.)	Time (hrs.)	Pressure (bars)	Buffer	α	γ	n	d_{900}
0.765	500	83	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.621 ± .002	1.673 ± .002	1.652 ± .003	1.5486 ± .0007
0.765	485	42	1035	Fe ₃ O ₄ -Fe ₂ O ₃	1.625 ± .001	1.679 ± .003	1.655 ± .003	1.5484 ± .0010
1.000	400	240	2000	Fe ₃ O ₄ -Fe ₂ O ₃	n.d.	n.d.	1.680 ± .005	n.d.
1.000	400	165	2000	Fe ₃ O ₄ -Fe ₂ O ₃	n.d.	n.d.	1.677 ± .003	n.d.
1.000	400	163	2000	Fe ₃ O ₄ -Fe ₂ O ₃	1.635 ± .002	1.715 ± .003	n.d.	1.5508 ± .0008
1.000	400	140	2000	Fe ₃ O ₄ -Fe ₂ O ₃	n.d.	n.d.	1.677 ± .003	n.d.
<i>Data for phlogopite</i>								
.000 ¹	1000	5	5175	—	1.550 ± .002	1.581 ± .002	n.d.	1.5348 ± .0003
.000 ¹	1160	5	2070	—	1.550 ± .003	1.581 ± .002	n.d.	n.d.
.000 ¹	1080	5	2070	—	1.545 ± .002	1.580 ± .002	n.d.	n.d.
.000 ¹	800	826	2070	—	1.548 ± .003	1.581 ± .002	n.d.	1.5348 ± .0004
.000 ¹	800	502	2070	—	1.549 ± .003	1.581 ± .003	n.d.	n.d.
.000 ¹	800	130	2070	—	1.551 ± .002	1.581 ± .002	n.d.	n.d.
.000	800	48	2070	—	1.552 ± .003	1.582 ± .002	1.567 ± .002	1.5349 ± .0006
.000	925	5	1035	—	1.551 ± .003	1.578 ± .005	n.d.	n.d.
.000 ¹	350	2208	1035	—	n.d.	n.d.	n.d.	1.5349 ± .0003
.000 ¹	900	330	340	—	1.533 ± .003	1.580 ± .002	n.d.	n.d.