

## Synthetic biotite oxidation under hydrothermal conditions

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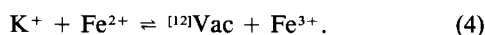
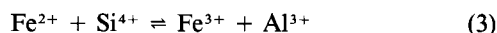
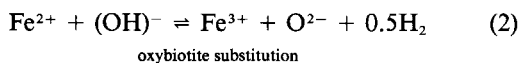
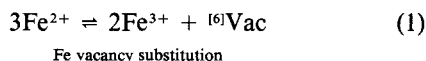
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### ABSTRACT

The oxidation of synthetic ferruginous biotite in hydrothermal systems was studied for two ideal compositions, annite,  $\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ , and siderophyllite,  $\text{KFe}_{2.5}\text{Al}_2\text{Si}_{2.5}\text{O}_{10}(\text{OH})_2$ . These biotite samples were annealed in Shaw-type vessels under controlled  $f_{\text{H}_2}$  at a total pressure of 1 kbar. The ratio of  $\text{Fe}^{2+}$  to total Fe, determined by wet-chemical analysis, is directly proportional to the  $f_{\text{H}_2}$ , regardless of temperature variations. For  $f_{\text{H}_2}$  values of < 1 bar to 102 bars, this ratio varies from 0.72 to 0.90 for annite and from 0.76 to 0.96 for siderophyllite. The H contents of the biotite do not vary with  $\text{Fe}^{3+}$  content for either composition and result in 94 and 100% of the OH sites being occupied in annite and siderophyllite, respectively. A consistent decrease in total octahedral cation content with increasing  $\text{Fe}^{3+}$  content for both annite and siderophyllite suggests that the Fe-vacancy substitution  $3\text{Fe}^{2+} \rightleftharpoons 2\text{Fe}^{3+} + {}^{16}\text{Vac}$  plays a dominant role in the oxidation of these synthetic biotite samples.

### INTRODUCTION

Biotite is among the most common rock-forming minerals and is found in assemblages of diverse bulk compositions and origins. Its chemical complexity is manifested by a wide range of both cationic and anionic substitutions (e.g., Deer et al., 1962; Guidotti, 1984). Such variability in biotite chemistry accommodates a number of possible mechanisms that can account for any observed compositional change. Even for the limited compositions of ideal annite,  $\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ , and siderophyllite,  $\text{KFe}_{2.5}\text{Al}_2\text{Si}_{2.5}\text{O}_{10}(\text{OH})_2$ , where Fe may occur in both the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states, many substitutions have been proposed to explain the oxidation of the Fe. Among the suggested substitutions are the following:



Two factors make it difficult to evaluate the relative roles of the different substitutions on the basis of available analytical data. First, electron microprobe analyses do not determine either the proportions of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  or the concentrations of H. Second, the chemical complexities

of natural biotite make the unique determination of a set of substitutions difficult or impossible (Hewitt and Abrecht, 1986). Efforts to understand the  $\text{Fe}^{3+}$  substitution in biotite that circumvent one or the other or both of these issues have resulted in limited success.

Studies by Eugster and Wones (1962), Wones (1963a, 1963b), and Wones and Eugster (1965) suggested that the amount of  $\text{Fe}^{3+}$  in ferruginous biotite may be an indicator of the temperature and  $f_{\text{H}_2}$  under which the biotite crystallized. They proposed that oxidation occurs by the oxybiotite substitution. Wones and Eugster (1965) showed that the amount of  $\text{Fe}^{3+}$  increases with  $f_{\text{O}_2}$  at constant  $f_{\text{H}_2\text{O}}$ . Other studies using the Mössbauer effect for both synthetic (Wones et al., 1971; Ferrow and Annersten, 1984) and natural micas (Dyar, 1990; Guidotti and Dyar, 1991) have correlated an increase in  $\text{Fe}^{3+}$  with  $f_{\text{O}_2}$ .

The thermal oxidation of biotite in air and vacuum has been fairly well characterized by many workers (e.g., Vedder and Wilkins, 1969; Rimsaite, 1970; Hogg and Meads, 1975; Takeda and Ross, 1975; Bagin et al., 1980; Sanz et al., 1983; Ferrow, 1987a; Güttler et al., 1989; Tikhomirova et al., 1989) using a range of analytical tools including infrared spectroscopy, X-ray diffraction, differential thermal analysis, thermogravimetry, Mössbauer spectroscopy, EXAFS and XANES spectroscopies, and gas chromatography. From these studies there is a general consensus that biotite oxidizes by the oxybiotite substitution. Heating in vacuo does not change the mechanism, but it may delay oxidation until higher temperatures are reached (Sanz et al., 1983).

The substitution mechanisms for biotite oxidized by

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TABLE 1. Experimental conditions and wet-chemistry results

Expt.*	P (bars)	T (°C)	$f_{H_2}$ (bars)	$\frac{Fe^{2+}}{Fe^{2+} + Fe^{3+}}$	H <sub>2</sub> O (wt%)
<b>Annite</b>					
CR-41	1000	750	102.4	0.892	
DW-A34	1000	791	101.6	0.894	
DAH-92E4	1000	740	52.8	—	3.2–3.3
EP-182;282;7a82	1000	750	51.9	0.890	
DH-8-80	1000	750	51.9	0.886	
CR-10/11	1000	749	51.7	0.890	
CR-19/20	1000	640	51.7	0.900	
EP-14a83	1000	710	26.1	0.897	
EP-14b;15a	1000	700	26.1	0.844	
DAH-92E9	1000	602	10.0	—	3.3
CR-15/16	1000	640	10.0	0.828	
CR-23/24	1000	550	10.0	0.830	
EP-11a82;12a82;14a82;15a82	1000	615	6.0	0.814	
EP-2383 (NNO)	2000	600	4.0	0.769	
DAH-92E8	1000	519	1.0	—	3.3
CR-31;39	1000	520	1.0	0.765	
DW-A30 (HM)	2000	399	0.004	0.718	
<b>Siderophyllite</b>					
CR-17 (CCH <sub>4</sub> )	1000	801	143.0	0.954	
DAH-93E12	830	741	104.5	—	3.7
CR-26/30	1000	748	102.4	0.955	
DAH-93E6	1000	742	52.8	—	3.7
EP-3283	1000	750	51.9	0.971	
CR-6ACDE	1000	750	51.7	0.945	
CR-7BC	1000	669	51.7	0.940	
CR-13/22	1000	549	51.7	0.950	
EP-3083;21a83	1000	700	26.1	0.950	
DAH-93E7	1000	636	10.0	—	3.7
CR-3A/7A	1000	671	10.0	0.916	
CR-28/29	1000	581	10.0	0.913	
EP-3183;11a83	1000	615	6.0	0.895	
EP-2583 (NNO)	2000	600	4.0	0.829	
DAH-93E10	1000	517	1.0	—	3.7
CR-35/36	1000	520	1.0	0.861	
EP-1783 (HM)	2000	400	0.004	0.765	

\* Data are averaged for experiments separated by semicolons. Solid buffer experiments are indicated: CCH<sub>4</sub> = graphite + methane; NNO = nickel + nickel oxide; HM = hematite + magnetite.

various chemical treatments have also been determined. Farmer et al. (1971) vermiculitized natural biotite, which resulted in a small degree of oxidation. Treatment with N<sub>2</sub>H<sub>4</sub> reversed the changes completely. This result suggested that oxidation was accompanied by the release of protons, in accord with Reaction 2. More vigorous oxidation of the biotite by either H<sub>2</sub>O<sub>2</sub> or a Br-saturated solution was not reversible and resulted in the formation of octahedral vacancies (Reaction 1). Similar experiments were carried out by Gilkes et al. (1972), who also found the dominant mechanism of oxidation to be the depletion of <sup>65</sup>Fe. This was accompanied by a small loss in inter-layer atoms (Reaction 4).

All the above studies involved biotite subjected to conditions well outside its stability field. Ferrow and Annersten (1984), Redhammer et al. (1993), and Rancourt et al. (1994) investigated synthetic ferruginous biotite that had been either synthesized or annealed using the solid O<sub>2</sub> buffer technique. All three studies used Mössbauer spectroscopy to characterize the oxidation state of the micas, and none of them determined the H<sub>2</sub>O content of the biotite samples. Ferrow and Annersten (1984) con-

cluded that the oxybiotite substitution was the operative mechanism. Analyses of infrared spectra in the other two studies resulted in conflicting interpretations for the oxidation of Fe in annite: Redhammer et al. (1993) favored the <sup>65</sup>Fe vacancy substitution, and Rancourt et al. (1994) the oxybiotite substitution.

Geometric considerations of the mica structure impose further constraints on the amount of Fe<sup>3+</sup> in biotite. In an ideal end-member annite, with all the Fe in the Fe<sup>2+</sup> state, the tetrahedral sheet is smaller than the octahedral sheet. Substitution of cations smaller than Fe<sup>2+</sup>, such as Al<sup>3+</sup>, Mg<sup>2+</sup>, or Fe<sup>3+</sup>, into the octahedral sheet or substitution of cations larger than Si<sup>4+</sup> into the tetrahedral sheet tends to stabilize the structure. Thus, Hazen and Wones (1972, 1978) predicted that Fe<sup>3+</sup> occupies approximately 12 mol% of the octahedral sites or 7 mol% of the tetrahedral sites in annite. Studies by Wones et al. (1971), Partin (1984), Rebbert and Hewitt (1986), and Redhammer et al. (1993) have supported this prediction.

The purpose of this study is to investigate the relationships among  $f_{H_2}$ , structural H, and the oxidation state of Fe in synthetic biotite under equilibrium conditions.

### EXPERIMENTAL METHODS AND ANALYTICAL TECHNIQUES

Biotite was synthesized from oxide mixes that had been reduced in a  $H_2$  atmosphere at 500 °C for 1 h. Standard hydrothermal techniques were used for synthesis. The samples were encapsulated with excess distilled  $H_2O$  in either  $Ag_{70}Pd_{30}$  or Au and held at a pressure of 4 kbar and temperatures between 400 and 600 °C in cold-seal pressure vessels (Tuttle, 1949). After 3–6 d the experimental products were examined optically with the polarizing microscope, and those with at least 98% biotite were utilized. Impurities identified include magnetite, fayalite, and sanidine. Most biotite specimens were then sealed in  $Ag_{70}Pd_{30}$  capsules and annealed using Shaw vessel techniques for controlling  $f_{H_2}$  (Shaw, 1967; Hewitt, 1977). A few experiments were carried out using the solid  $O_2$  buffering methods developed by Eugster (1957). Temperatures were measured with chromel-alumel thermocouples calibrated against the melting points of LiCl and KCl and found accurate to within  $\pm 3$  °C. Pressures were measured with Heise Bourdon-type gauges. One experiment was made with the graphite +  $CH_4$  buffer (French and Eugster, 1965; Jacobs and Kerrick, 1981).

The annealed experiment products were examined optically, with most yields estimated by comparison with standard mixtures of synthetic fayalite in synthetic phlogopite (see Appendix A of Rebbert, 1986). Weight percent  $Fe^{2+}$  was determined by the wet-chemical technique outlined by Whipple (1974), and the stoichiometry of the biotite was checked by an ARL-SEMQ microprobe. Because of the fine-grained nature of the crystals, the analytical methods and graphical procedures developed by Solberg et al. (1981) were employed. Only experiments where the percentage of biotite in the final product was >93% are reported in Table 1.

H contents of several synthetic annite and siderophyllite samples were determined by a procedure developed by Hewitt (in preparation). Dried samples of biotite weighing 5–10 mg are melted at 900 °C with an anhydrous  $Na_2B_4O_7$  flux in open Pt capsules that are sealed together with Zn in evacuated  $SiO_2$  glass tubes. The  $H_2$  and  $H_2O$  released during melting is totally reduced to  $H_2$  by the Zn in the system. The  $SiO_2$  glass tube is then broken in an evacuated constant volume system, and the resulting pressure generated by the released  $H_2$  is measured. Blanks are analyzed with every batch of samples, and the system is calibrated with a talc standard. Analysis of the standard talc by thermal decomposition yielded 4.76(3) wt%  $H_2O$ . Interlaboratory comparisons with D. Virgo and R. Popp at the Geophysical Laboratory showed excellent agreement on the  $H_2O$  contents of this standard material. The accuracy of the method is better than  $\pm 2\%$  of the amount of  $H_2O$  present for the sample sizes and  $H_2O$  contents of the biotite analyzed in this study.

The X-ray diffraction patterns of the biotite samples were obtained from an automated Philips diffractometer

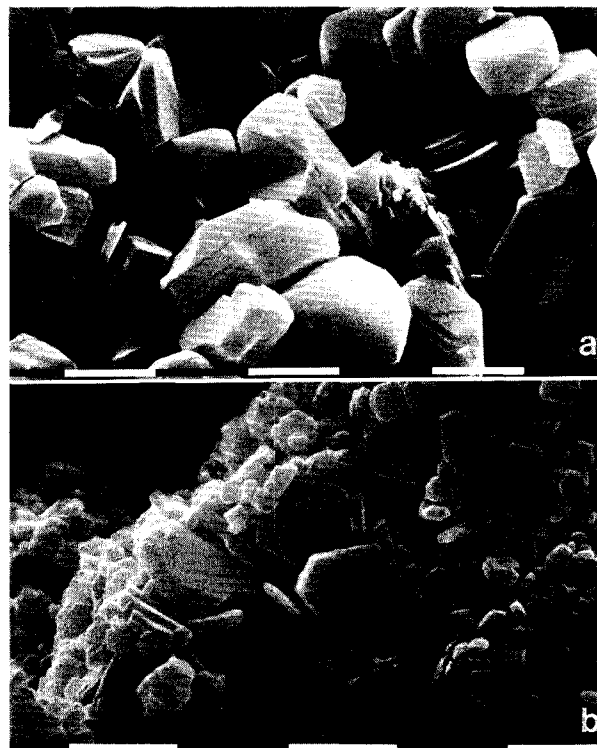


Fig. 1. SEM photomicrographs. (a) CR-10/11. (b) CR-35/36. Scale bar represents 1  $\mu m$ .

using  $CuK\alpha$  radiation. Fluorite,  $CaF_2$  ( $a = 5.4633 \pm 0.0005$  Å), served as an internal standard. Unit-cell dimensions were obtained by the refinement of 10–20 reflections for each sample (Appleman and Evans, 1973).

## RESULTS

### Optical examination

All the annealed experiment products were examined optically, and some were observed by SEM (Fig. 1). The biotite specimens are in general well-crystallized, with clean, smooth edges. Each experiment includes a wide range of crystal sizes, but low-temperature experiments have a smaller average size than higher temperature experiments, and siderophyllite specimens form smaller, thinner platelets (0.35–2  $\mu m$  wide, <0.5  $\mu m$  thick) than the annite specimens (0.5–2  $\mu m$ , 0.25–1  $\mu m$  thick) under similar high-temperature conditions. The siderophyllite is a bluish green color, whereas the annite is a darker olive drab, and both show a faint pink to green normal pleochroism. All experiments include a small percentage of sanidine and magnetite or fayalite (or both) as impurity phases. They constitute 2–5% (by volume) of the siderophyllite samples and 4–7% of the annite samples.

### Chemical analysis

The wet-chemical analyses show a positive correlation between the percentage of  $Fe^{2+}$  and  $f_{H_2}$  (Table 1, Fig. 2).

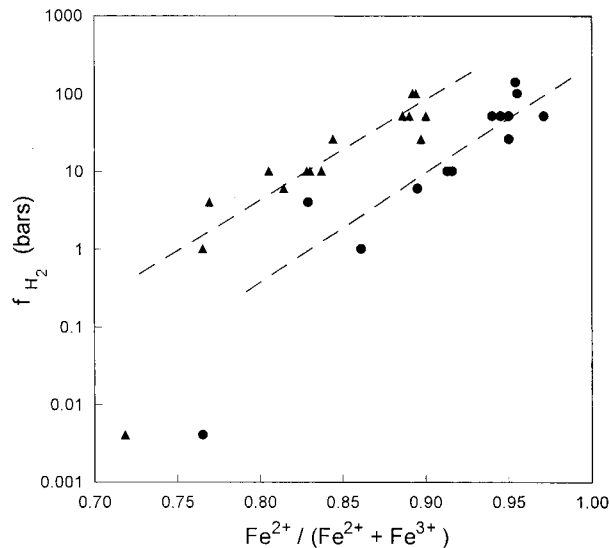


Fig. 2. Hydrogen fugacity vs.  $\text{Fe}^{2+}$  content for the synthetic biotite samples in Table 1. Triangles represent annite data, circles the siderophyllite data. Errors related to the  $\text{Fe}^{2+}$  determination are within the size of the symbols.

The annite contains 5–9 mol% more  $\text{Fe}^{3+}$  than siderophyllite annealed under similar conditions. The data in Table 1 indicate that the amount of  $\text{Fe}^{3+}$  is constant [ $\pm 0.001$ – $0.03 \text{ Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ] for a given  $f_{\text{H}_2}$  regardless of temperature variations of up to 200 °C. This agrees well with the results of Wones (1963b), who showed that biotite samples synthesized at the same temperature and total pressure and similar  $f_{\text{H}_2}$ , but at different values of  $f_{\text{O}_2}$  as a result of a different C-O-H fluid, had essentially identical  $\gamma$  refractive indices. The refractive index was shown to be inversely related to  $f_{\text{H}_2}$  and therefore to  $\text{Fe}^{2+}$  content.

Electron microanalysis of some of the biotite specimens indicates that their stoichiometry agrees well with that of the two ideal end-member compositions (Table 2). The annite specimens tend to be slightly deficient in

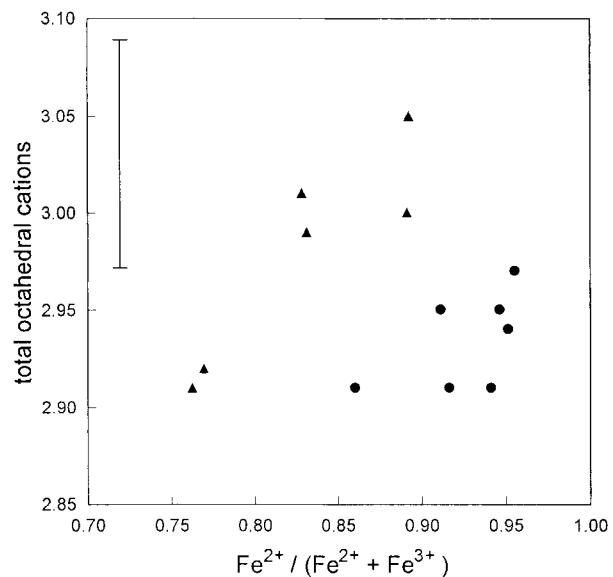


Fig. 3. Octahedral occupancies vs.  $X_{\text{Fe}^{2+}}$ . Symbols as in Fig. 2; error bar represents  $2\sigma$ .

$\text{SiO}_2$  and  $\text{H}_2\text{O}$ , and both compositions have about 10% interlayer vacancies. All the siderophyllite samples have octahedral vacancies, whereas both octahedral vacancies and filled sites occur in annite. There is a general trend of decreasing total octahedral cation content with increasing  $\text{Fe}^{3+}$  that is especially apparent for the annite experiments (Fig. 3).

Foster (1960) assumed that  $^{49}\text{Fe}^{3+}$  is present in trioctahedral mica compositions with insufficient Si and Al to fill the site. Since that time, Annersten (1975), Dyar and Burns (1986), Dyar (1987), and Rancourt et al. (1992) have verified its existence by means of Mössbauer spectroscopy. On the basis of the calculated cation occupancies, we expect to see  $^{49}\text{Fe}^{3+}$  in annite, since the sum of Si and Al cations in all cases is  $< 4$ . Siderophyllite, on the other hand, has sufficient Si and Al to completely fill the tetrahedral site.

TABLE 2. Chemical composition of synthetic biotite as weight percent oxides and numbers of cations based on 12 anions

Sample*	41	10/11	15/16	23/24	31	39	17	26/30	6ACDE	7BC	13/22	3A/7A	28/29	35/36
$\text{SiO}_2$	33.6	34.2	32.9	33.8	34.0	34.1	30.3	30.9	31.2	31.8	30.6	31.4	30.6	30.2
$\text{Al}_2\text{O}_3$	10.6	10.6	10.1	9.9	9.8	10.2	21.0	20.5	20.7	20.5	20.6	20.8	20.6	21.1
$\text{Fe}_2\text{O}_3$	5.3	5.2	8.5	8.3	11.2	11.4	1.8	1.8	2.2	2.3	2.0	3.3	3.5	5.5
FeO	39.2	38.2	36.8	36.6	33.6	32.8	34.3	34.4	33.6	32.8	33.9	32.0	33.0	30.8
$\text{K}_2\text{O}$	8.1	8.5	8.4	8.1	8.1	8.2	8.9	8.6	8.5	8.7	9.2	8.8	8.6	8.7
$\text{H}_2\text{O}$	3.3	3.3	3.3	3.3	3.3	3.3	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7
Total	100.1	100.0	100.0	100.0	100.0	100.0	100.0	99.9	99.9	99.8	100.0	100.0	100.0	100.0
Si	2.86	2.90	2.81	2.87	2.87	2.87	2.48	2.53	2.54	2.58	2.51	2.55	2.50	2.46
Al	1.06	1.06	1.02	0.99	0.97	1.01	2.03	1.98	1.99	1.96	1.99	1.99	1.98	2.02
$\text{Fe}^{3+}$	0.34	0.33	0.55	0.53	0.71	0.72	0.11	0.11	0.13	0.14	0.12	0.20	0.22	0.34
$\text{Fe}^{2+}$	2.79	2.71	2.63	2.60	2.37	2.31	2.35	2.35	2.29	2.23	2.32	2.17	2.25	2.09
$\Sigma \text{oct}$	3.05	3.00	3.01	2.99	2.92	2.91	2.97	2.97	2.95	2.91	2.94	2.91	2.95	2.91
K	0.88	0.92	0.92	0.88	0.87	0.88	0.93	0.90	0.88	0.90	0.96	0.91	0.90	0.90
OH	1.88	1.87	1.88	1.87	1.86	1.85	2.02	2.02	2.01	2.00	2.02	2.00	2.01	2.01
O	10.12	10.13	10.12	10.13	10.14	10.15	9.98	9.98	9.99	10.00	9.98	10.00	9.99	9.99

\* All sample numbers preceded by CR-.

The H<sub>2</sub>O contents of biotite synthesized and annealed under conditions identical to those for the determination of Fe<sup>3+</sup> contents are all very consistent (Table 1). The annite samples average 3.3(1) wt% H<sub>2</sub>O and show no regular variation with Fe<sup>3+</sup> contents. Similarly, the siderophyllite samples average 3.70(5) wt% H<sub>2</sub>O and also show no regular variation with Fe<sup>3+</sup> contents. By comparison with the ideal of 3.52 wt% H<sub>2</sub>O in annite and 3.63 wt% H<sub>2</sub>O in siderophyllite, it is apparent that there is a small deficiency (~6%) in the annite and a stoichiometric amount or possibly a slight excess (~1%) of H<sub>2</sub>O in the siderophyllite. What is most important for understanding the Fe<sup>3+</sup> substitution in biotite is that the data demonstrate no correlation between the Fe<sup>3+</sup> and the H contents of these synthetic biotite specimens.

#### X-ray data

Results from the X-ray data refinements are shown in Figure 4. There are good correlations between the mole fraction of Fe<sup>2+</sup> and the *b*-cell dimension, the *c*-cell dimension, and the unit-cell volume. Other workers demonstrated similar trends (Eugster and Wones, 1962; Wones, 1963b; Rutherford, 1973; Ohta et al., 1982; Ferron and Annersten, 1984). Gilkes et al. (1972) demonstrated that *c* remained constant with increasing oxidation of mica. However, their starting mica is fairly Mg-rich, and Wones (1963b) showed that the progressive change in cell dimensions with oxidation is much less for magnesian biotite. The absolute values for the cell edges and unit-cell volumes of our biotite specimens are similar to those from the above studies, excluding the natural biotite of Ohta et al. (1982), which has a very different composition.

#### Errors in Fe<sup>2+</sup> and Fe<sup>3+</sup> determinations

The errors introduced in calculating the mole fraction of Fe<sup>2+</sup> are difficult to determine. The precision of the titrations is quite good, with replicate determinations agreeing to within 0.1–0.3% (relative). If all impurities present are taken to be Fe-bearing phases, then absolute maximum errors can be calculated. The presence of 3 wt% fayalite leads to overestimation of the Fe<sup>2+</sup> content of the biotite, but because the weight percent FeO is similar in fayalite and iron biotite, this amounts to a maximum correction of 0.2–0.4 mol% of Fe<sup>2+</sup>. If instead there were 3 wt% of magnetite present, the Fe<sup>2+</sup> content would be underestimated by a maximum of 2.5 mol%. The presence of sanidine decreases the correction, since it suggests that the sum of the impurities has a stoichiometry equivalent to that of the biotite. On the basis of the optical examination of these experiments, magnetite constitutes at most 2%, but usually <1%, of the total weight of material. This corresponds to underestimating the Fe<sup>2+</sup> content by a maximum of 1 mol%.

Errors based on the linear regression statistics from the microprobe analyses were also determined for CR-17. The sample variance of the mean elemental weight percent for a given total weight percent was calculated. Weight

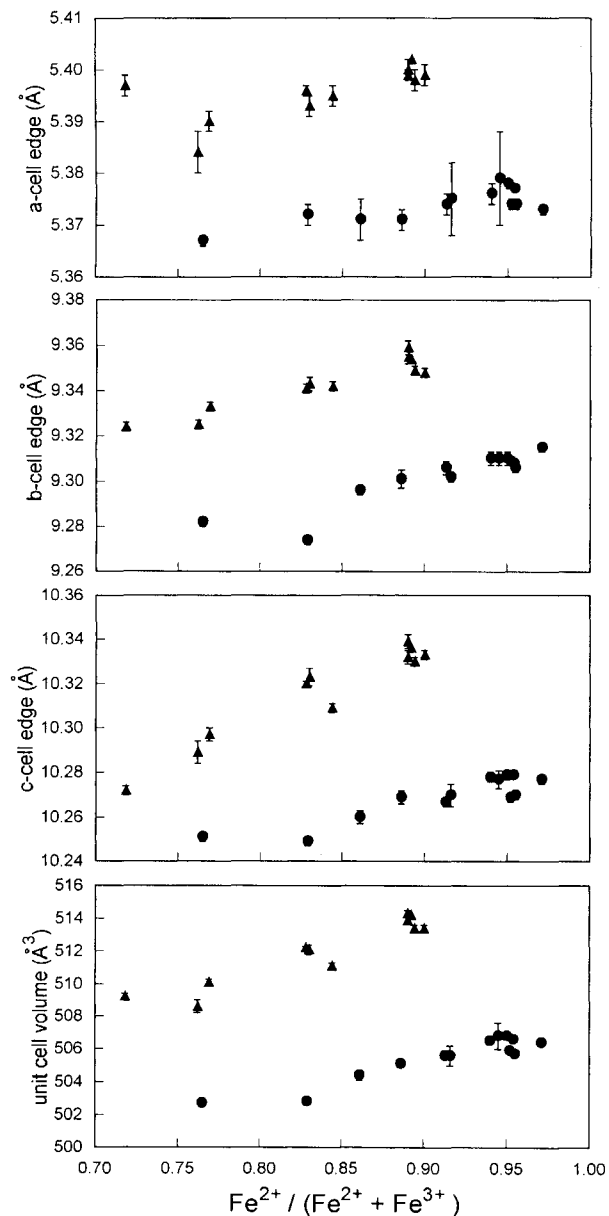


Fig. 4. X-ray data vs.  $X_{Fe^{2+}}$ . Symbols as in Fig. 2.

percent FeO was adjusted to account for the presence of Fe<sub>2</sub>O<sub>3</sub>, and the errors were propagated through this calculation. The standard deviation for each oxide was used to generate a random set of 100 oxide weight percents with a normal distribution about the mean. These in turn were used to calculate mineral formulas whose mean and standard deviation were determined. The error on Fe<sup>2+</sup> is ±0.05 cations and on Fe<sup>3+</sup> is ±0.02 cations.

#### DISCUSSION

##### The variation of Fe<sup>2+</sup> with $f_{H_2}$

The Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratios of annite and siderophyllite specimens as a function of  $f_{H_2}$  are shown in Fig-

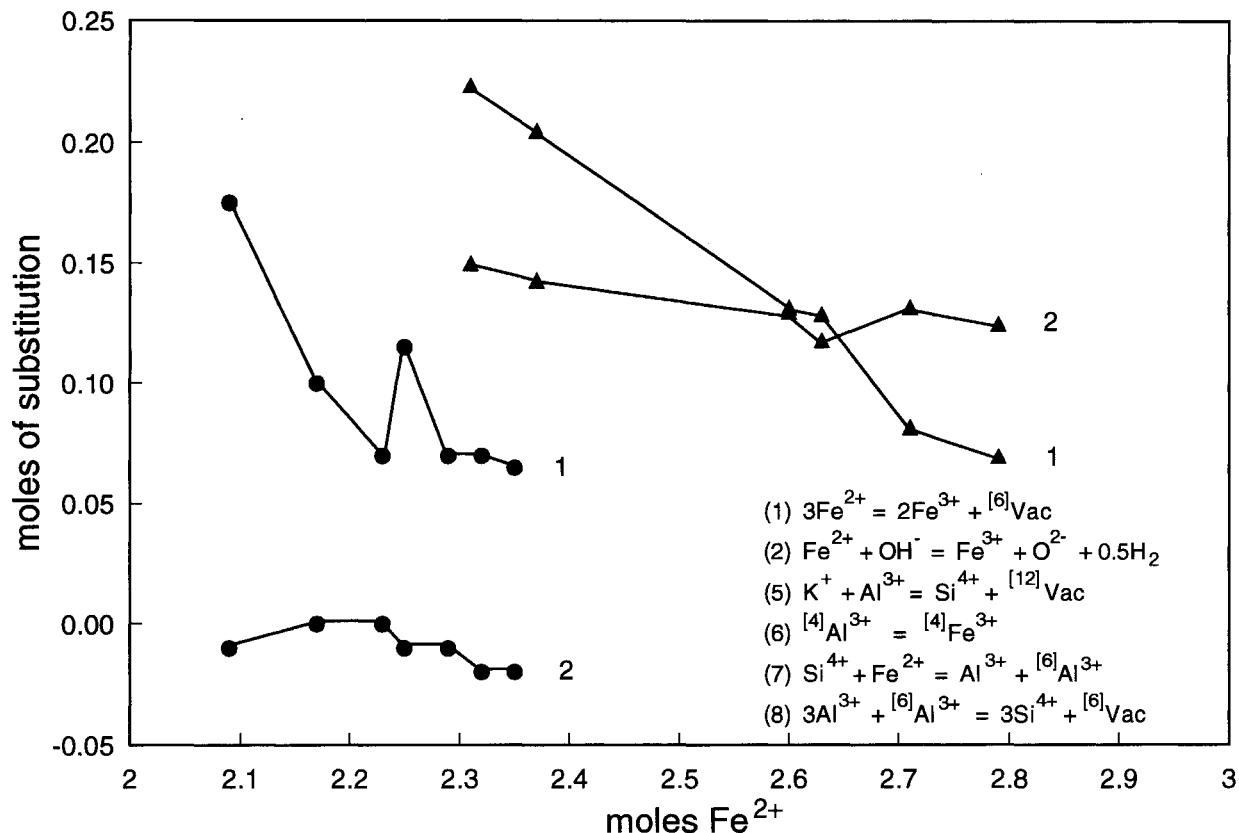


Fig. 5. Moles of substitutions 1 and 2 required to account for differences in composition between the two ideal end-members and the synthetic biotite samples as a function of total number of Fe<sup>2+</sup>. Symbols as in Fig. 2. The other four substitutions (5–8) used to describe the synthetic biotite compositions are listed as well.

ure 2. For annite, the maximum attainable Fe<sup>2+</sup> content is 0.90 mole fraction. This value is reached at a  $f_{\text{H}_2}$  of 50 bars and does not increase at  $f_{\text{H}_2}$  values up to 102 bars. There is a regular decrease in the amount of Fe<sup>2+</sup> at lower  $f_{\text{H}_2}$ , with the lowest value of  $X_{\text{Fe}^{2+}} = 0.72$  at the HM buffer. It should be noted that the data are not isothermal, with temperatures ranging from approximately 800 °C at the highest  $f_{\text{H}_2}$  values to 400 °C at the HM buffer. Most experiments were carried out near the upper thermal stability for biotite at the various oxidation conditions. However, there are numerous examples in Table 1 (e.g., compare CR-10/11 and CR-19/20, CR-15/16 and CR-23/24, and CR-6ACDE, CR-7BC and CR-13/22), demonstrating that the Fe<sup>2+</sup> content does not change with temperature, and therefore  $f_{\text{O}_2}$ , under conditions of constant  $f_{\text{H}_2}$ . Significant differences in Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratios are generated only by differences in bulk composition and differences in  $f_{\text{H}_2}$ .

The data for annite support the predictions of Hazen and Wones (1972, 1978) with regard to the structural limitation on the maximum amount of Fe<sup>2+</sup> allowable for a fit between the tetrahedral and octahedral sheets. In addition, they clearly demonstrate the existence of a significant variation in Fe<sup>2+</sup> content with  $f_{\text{H}_2}$ . The trend for

siderophyllite is similar, except that the maximum Fe<sup>2+</sup> content is approximately 0.96 mole fraction Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>). Because Tschermak's substitution (Fig. 5, Reaction 7) increases the lateral dimension of the tetrahedral sheet and decreases that of the octahedral sheet, this higher limit for the Fe<sup>2+</sup> content provides further support for the Hazen and Wones's (1972, 1978) arguments. Simple calculations on the size changes for the tetrahedral and octahedral sheets with Tschermak's substitution indicate that the siderophyllite composition should have no required Fe<sup>3+</sup> caused by size limitations. Whether the 0.04 mole fraction Fe<sup>3+</sup> in the siderophyllite samples synthesized at very reducing conditions is present because of a lack of analytical accuracy, or whether it represents <sup>149</sup>Fe<sup>3+</sup>, or whether it is simply the result of not having a sufficiently high  $f_{\text{H}_2}$  is not known. However, the consistently higher Fe<sup>2+</sup> content of siderophyllite is a strong argument for the Hazen and Wones (1972, 1978) model.

Within the limits of the data, the slopes of the variation of Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) vs.  $f_{\text{H}_2}$  are similar, if not identical, for annite and siderophyllite (Fig. 2). This suggests that the same oxidation-substitution mechanism is active for both compositions. Although there is no a priori reason that the variation be linear, and clearly it cannot be so at

the  $\text{Fe}^{2+}$  end-member for annite if the structural model is correct, there is some reason to doubt the values determined at the hematite + magnetite (HM) buffer. These experiments were carried out at low temperature by means of the solid  $\text{O}_2$  buffering technique (Eugster, 1957). Hewitt (1985) and Chou and Cygan (1990) have raised questions about the  $f_{\text{H}_2}$  in these types of experiments. Equilibration of  $f_{\text{H}_2}$  at low temperatures or for a sluggish reaction, such as quartz + fayalite + magnetite (QFM), may be slower than the diffusion of  $\text{H}_2$  through the capsule walls. Because most hydrothermal experiments are performed in René 41 vessels, the  $f_{\text{H}_2}$  in the vessel is fixed at nearly the value of the nickel + nickel oxide (NNO) buffer. This means that experiments with solid buffers more reducing than NNO may actually be exposed to a  $f_{\text{H}_2}$  lower than expected, and experiments with more oxidizing buffers may be exposed to a  $f_{\text{H}_2}$  higher than expected. On the basis of this hypothesis, the actual  $f_{\text{H}_2}$  for the two HM buffer experiments probably was higher than the equilibrium value and therefore more consistent with the linear trends in Figure 2.

### Substitution models

Since the work of Wones and Eugster (1965), it has been commonly assumed that biotite oxidation is accompanied by a loss of protons (Reaction 2). Low OH occupancies are common in natural trioctahedral micas (Foster, 1964; Rimsaite, 1970; Forbes, 1972; Dyar et al., 1991). However, Foster (1964), Rimsaite (1970), and Dyar et al. (1993) noted that OH deficiencies are not necessarily correlated to  $\text{Fe}^{3+}$  contents. The synthetic annite and siderophyllite specimens in this study have essentially constant and stoichiometric amounts of  $\text{H}_2\text{O}$ , despite a significant range of  $\text{Fe}^{3+}$  contents. The data on natural biotite are inconclusive because its compositional complexity allows equivalent explanations for a variety of additional substitutions, but the data presented here on the synthetic iron biotite specimens rule out the oxybiotite substitution as the fundamental mechanism for biotite oxidation in these end-member systems.

What then, is the controlling reaction for oxidation of these ferruginous biotite samples? The data in Figure 3 indicate a correlation between  $\text{Fe}^{2+}$  content and octahedral occupancies (Reaction 1), but there is scatter in the data, especially for siderophyllite. For this composition, no completely consistent trend is obvious from the mineral formulas (Table 2), and yet cation contents had to adjust in order to balance the positive charges introduced by increasing amounts of  $\text{Fe}^{3+}$ . However, there is no requirement that the adjustment scheme be simple or constant, and, as pointed out by Forbes (1972), "charge imbalance, caused by cationic substitutions in biotites . . . , can be balanced in a variety of ways." Hewitt and Abrecht (1986) argue that it is difficult or impossible to uniquely specify the substitutions that are occurring in complex biotites. Different sets of substitutions are equivalent in their ability to represent the compositional variability of a mineral and are therefore all equally good. Following

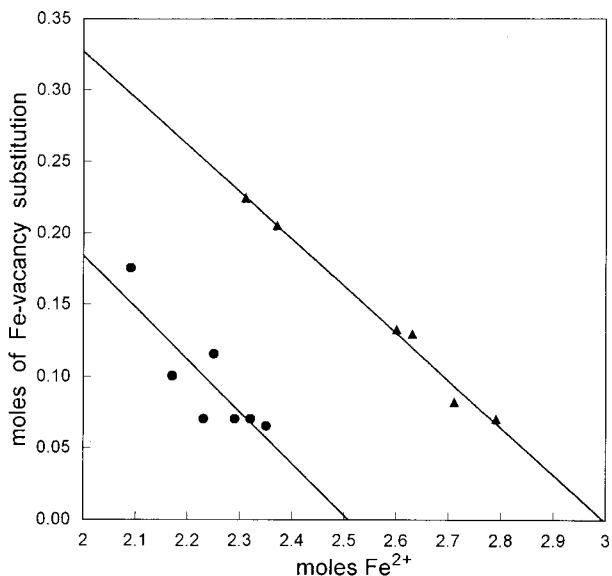


Fig. 6. Required moles of the Fe vacancy reaction vs. moles of  $\text{Fe}^{2+}$  in the synthetic biotite formulas. Symbols as in Fig. 2.

their methods, we postulate one possible, but not unique, set of six substitutions to describe the biotite compositions in this study (Fig. 5). For each sample, the degree to which each of the reactions is responsible for the difference between the analyzed mica composition and that of ideal annite or siderophyllite was calculated, and the results for Reactions 1 and 2 are illustrated in Figure 5. The oxybiotite substitution is insignificant for the siderophyllite, but does account for a certain amount of the  $\text{Fe}^{3+}$  content in annite; however, the amount of this substitution that is required remains constant over the range of  $\text{Fe}^{3+}$  contents. For both compositions, the amount of Fe vacancy substitution shows a significant increase as the concentration of  $\text{Fe}^{3+}$  increases and thus may play an important role in the oxidation of biotite. Note that this result is indistinguishable from an anion excess model, but the results of Dyar et al. (1991) do not support the presence of many extra anions in the structure, and experiments that we have carried out to test for variable numbers of anions in biotite have all yielded negative results.

Several additional lines of evidence support Reaction 1 as an important mechanism for  $\text{Fe}^{3+}$  substitution in biotite. Figure 6 demonstrates the correlation between the required amount of Fe vacancy substitution and the number of moles of  $\text{Fe}^{2+}$  in the structure. As expected, the regression lines extrapolate to end-members with 2.5 and 3.0 moles of  $\text{Fe}^{2+}$  for siderophyllite and annite, respectively. More importantly, both lines have slopes of approximately  $-0.33$ , which suggests that the change in the  $\text{Fe}^{2+}$  content between samples is largely attributable to Reaction 1. Also, on the basis of her exhaustive analysis of natural biotite compositions, Foster (1960) sug-

gested two main substitutions to accommodate trivalent octahedral cations: (a)  $Al^{3+} + R^{3+} \rightleftharpoons Si^{4+} + R^{2+}$  and (b)  $3R^{2+} \rightleftharpoons 2R^{3+} + {}^{16}Vac$ , which corresponds to the Fe vacancy reaction. Most natural biotite specimens require both substitutions to be operative, but Foster (1960) demonstrated that the relative importance of Reaction a diminishes with increasing Fe content. The synthetic mica data support that conclusion because when they are fitted to a different set of substitutions that includes Foster's Reaction a, they show only a weak correlation between the amount of Reaction a required and the degree of oxidation. Furthermore, the Fe vacancy substitution is consistent with the results and conclusions of both the hydrothermal study of Redhammer et al. (1993) and the two studies that treated biotite with chemical oxidants, Farmer et al. (1971) and Gilkes et al. (1972).

Finally, Hazen and Wones (1972) and Ferrow (1987b) found that while octahedral cation substitutions have a dramatic effect on the *b*-cell dimension, they have virtually no effect on *c*. The Fe vacancy substitution involves only octahedral sites, and so it is expected that *c* will remain constant. Yet Wones (1963b), Rutherford (1973), Ferrow and Annersten (1984), Redhammer et al. (1993), and our data all demonstrate a decrease in *c* with hydrothermal oxidation of biotite (Fig. 4). A possible explanation for this observation lies in the orientation of the OH dipole. Sanz et al. (1984) demonstrated that OH bonds near octahedral vacancies are inclined away from the *c* axis. This inclination diminishes the repulsion between the positive K and H ions and is used by Gilkes et al. (1972) to explain the increased stability of K in oxidized biotites. This should result in diminishing the K-O bond length and thereby decreasing the *c*-cell dimension.

The Fe vacancy reaction does not directly explain the pronounced correlation between  $f_{H_2}$  and the mole fraction of  $Fe^{2+}$  (Fig. 2), and so far we have not explained why the results from our hydrothermal experiments are so disparate from the numerous thermal oxidation experiments that support an oxybiotite substitution. This behavior is irreconcilable if only the biotite is considered. However, the hydrothermal experiments involve the system biotite- $H_2O$ , and the thermal oxidation experiments take place in the system biotite-air. From an energetic point of view, there is probably little alternative to an oxybiotite substitution when biotite is heated under disequilibrium conditions in the presence of air ( $\sim 0.2$  bars  $f_{O_2}$ ) or even in the presence of a modest vacuum, where the partial pressure of  $O_2$  might be on the order of  $10^{-7}$  bars. In the hydrothermal system biotite- $H_2O$ , a variety of oxidation reactions involving the two phases could easily occur. Even more are possible if we expand the system to include the capsule or other solid phases. One simple reaction for the biotite- $H_2O$  system that is consistent with both the Fe vacancy substitution and the inverse dependence between  $Fe^{3+}$  in biotite and  $f_{H_2}$  is the following:  $3Fe_{(o)}^{2+} + H_2O_{(f)} \rightleftharpoons 2Fe_{(o)}^{3+} + Fe_{(f)}^{2+} + O_{(f)}^{2-} + H_{2(f)}$ . Here, a decrease in  $f_{H_2}$  drives the reaction to the right and thus to more  $Fe^{3+}$ -rich compositions in the biotite. Our data

are insufficient to verify its occurrence, but they are at least consistent with a reaction of this sort.

We propose that the mechanism of oxidation in Fe-bearing silicates is linked both to environmental conditions and to crystal chemical considerations. Certain natural biotite specimens have been shown to oxidize, at least in part, by the oxybiotite substitution. Takeda and Ross (1975) described the occurrence of biotite from the top of a series of rhyodacite flows in which 53% of the OH deficiency can be attributed to the oxybiotite reaction in a highly oxidized and probably nearly anhydrous environment. Feldstein et al. (1993) correlated  $Fe^{3+}$  with H contents in phlogopite from a variety of mantle-derived melts, but these biotites represent compositions and have formed under conditions far different from those for our experiments. The current data supporting the vacancy substitution are for iron biotite synthesized under conditions of high  $f_{H_2O}$  (400–1000 bars).

Amphiboles have long been assumed to oxidize by the equivalent oxyamphibole substitution (e.g., Clowe et al., 1988). Investigations by Popp et al. (1993) and Phillips et al. (1993) have demonstrated clearly that this assumption is well founded for experiments carried out under both hydrothermal and atmospheric conditions. The significant difference in oxidation behavior between biotite and amphibole must be related to the common tendency for octahedral vacancy formation in the micas compared with the rare occurrence of substitutions in the amphiboles that generate octahedral vacancies.

The jump from understanding the  $Fe^{3+}$ - $Fe^{2+}$  substitutions in synthetic iron biotite to dealing with the complex compositions of natural biotite is a significant one. The following observations are based on the extensive amount of analytical data in the literature for the compositions of natural biotite: (1)  $Fe^{3+}$ - $Fe^{2+}$  ratios and total Fe contents vary widely. (2) Octahedral vacancies are common and variable in amount. (3) The OH contents are often less than the ideal amount. (4) Ti is frequently present as a minor or major element. (5) K and Na contents are commonly insufficient to fill the interlayer site. (6) The Si-Al ratio is highly variable. The  $Fe^{3+}$  variation that is observed in natural and synthetic biotite can legitimately be related to substitutions involving any of the constituents in the final five observations. That we have been able to eliminate the oxybiotite substitution and demonstrate the importance of the  ${}^{16}Fe$  vacancy substitution to account for the variation of  $Fe^{3+}$  in some simple synthetic systems is significant. To generalize very far from that success is not well justified. Similarly, to find a correlation between  $Fe^{3+}$  and OH content in a suite of natural biotite samples is interesting but does not establish the oxybiotite substitution as generally important and, depending on the other compositional variations in the same samples, might not even establish it as important in the samples described. It is apparent that the  $Fe^{3+}$  substitutions in biotite depend on the composition of the biotite as well as the intensive parameters of the environment. We suggest that additional experimental and crystal-



chemical studies on synthetic or generally less compositionally complex natural biotite specimens must be undertaken to understand these relationships further.

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