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Experimental investigation of the effect of oxygen fugacity on ferric-ferrous ratios and unit-cell parameters of four natural clinoamphiboles

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ABSTRACT

To investigate the relation between oxygen fugacity, ferric-ferrous ratio (*R*), and unit-cell parameters, four natural clinoamphiboles (grunerite, tschermakitic hornblende, magnesio-hornblende, and a riebeckite-arfvedsonite solid solution) were reacted at 650°C, 1 kbar at oxygen fugacities defined by several solid oxygen-buffer assemblages. In order to produce more highly oxidized samples, heating in air at 700 °C was also carried out. Variation in *R* is accomplished mainly by the oxidation-dehydrogenation equilibrium

$$Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + \frac{1}{2}H_2,$$

but the results suggest that other mechanisms may also be involved. All four amphiboles exhibited systematically higher ferric-ferrous ratios with increasing f_{O_2} of equilibration. Equilibrium *R* values were achieved relatively rapidly and could be readily restored to original values by treatment at the appropriate buffer. In some cases, a metastable equilibrium of ferric-ferrous ratio was achieved before the amphibole decomposed to other Fe^{3+}-bearing phases.

Of the four amphiboles, grunerite is apparently the least able to accommodate Fe^{3+} within its crystal structure and decomposes at relatively higher oxygen fugacities.

The value of $a \sin \beta$ decreases systematically uniformly as the Fe^{3+} content of tschermakitic hornblende, magnesio-hornblende, and riebeckite increases, reflecting increasing Fe^{3+} in the octahedral cation sites. The variation in $a \sin \beta$ of grunerite is significantly less than for the other three amphiboles. The variation in *b* for the two hornblendes suggests that Fe^{3+} produced by oxidation is not strongly ordered into the M(2) site.

INTRODUCTION

Amphiboles are the most chemically complex of the major rock-forming mineral groups. This complexity arises from the wide variation of unique structural sites available for cations. Fe is a major component in many naturally occurring amphibole solid solutions, but the factors that control the proportions of Fe^{3+} and Fe^{2+} in any given amphibole are still very poorly understood quantitatively.

Two types of experiments have been carried out in attempts to produce variation in the ferric-ferrous ratios in amphiboles: heating of amphiboles in air, and hydrothermal synthesis and/or treatment of amphiboles at oxygen fugacities defined by the standard solid oxygen buffers. The earlier air-heating studies were carried out mainly on abestiform amphiboles, but more recently, nonasbestiform varieties have been so-treated (see Hawthorne, 1981, 1983, for reviews). Hydrothermal studies to delimit physical properties and the pressure–temperature–oxygen fugacity stability have been carried out on a wide variety of bulk compositions representing the major chemical groups of amphiboles (e.g., Gilbert et al., 1982).

The results of the existing experimental studies have shown that changes in chemical compositions and physical properties occur as a function of oxygen fugacity and temperature. Oxidation of Fe in an amphibole results initially from the formation of oxy-amphibole component by a dehydrogenation reaction of the type

$$Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + \frac{1}{2}H_2, \qquad (1)$$

in which O^{2-} replaces OH^- in the O(3) anion site of the amphibole. This process, first suggested by the results of Barnes (1930), has also been proposed to be operative in other hydrous minerals such as the micas (e.g., Wones, 1963; Vedder and Wilkins, 1969). Most studies in synthetic systems are complicated by the fact that 100% yields of amphibole are not achieved. Therefore, changes in either the proportions or compositions of the nonamphibole phases may cause variations in amphibole compositions. That is, changes observed in physical properties may result from changes in amphibole bulk composition

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TABLE 1. Compositions of starting amphiboles

	Grunerite	Tschermakitic hornblende	Magnesio-hornblende	Riebeckite
SiO_2	49.19	43.44	47.05	51.39
TiO_2	0.03	0.60	0.31	0.78
Al_2O_3	0.51	13.82	10.24	0.80
FeO	44.30	12.53	12.54	21.67
Fe_2O_3	N.D.	3.70	1.05	11.85
MnO	0.66	0.25	0.74	0.71
MgO	3.21	9.80	12.24	0.25
CaO	0.32	11.57	11.93	0.15
Na_2O	0.04	1.45	1.13	8.87
K_2O	N.D.	0.51	0.59	1.54
F	0.17	0.13	0.72	1.97
Cl	0.12	N.D.	N.D.	N.D.
Sum	98.55	97.80	98.54	99.98
Si	7.94	6.41	6.87	8.00
^{IV}Al	0.06	1.59	1.13	
^{VI}Al	0.04	0.83	0.64	0.15
Ti	0.01	0.07	0.04	0.09
Fe^{2+}	5.99	1.54	1.54	2.83
Fe^{3+}		0.42	0.12	1.40
Mn	0.09	0.04	0.09	0.09
Mg	0.78	2.16	2.67	0.06
Ca	0.06	1.83	1.87	0.03
Na	0.10	0.41	0.32	2.68
K		0.09	0.11	0.30
Cl	0.01			
F	0.09	0.06	0.33	0.98
O	23.00	23.00	23.00	23.00
		Grain size (mm)		
Max.	1.0 × 0.025	0.19 × 0.025	0.5 × 0.1	0.15 × 0.05
Min.	0.1 × 0.025	0.075 × 0.075	0.1 × 0.2	0.1 × 0.02

Note: N.D. = not detected. Chemical compositions (in wt% oxides and as atoms per 23 oxygens) and grain sizes of amphiboles used in experiments. Chemical compositions were determined by electron microprobe. Ferric-ferrous ratio determined by wet-chemical analysis. Amphibole compositions were normalized to 23 oxygens because of unknown oxy-amphibole content.

as oxygen fugacity varies, rather than solely from changes in the ferric-ferrous ratio. For most synthetic hydrothermal studies, precise chemical compositions and, more importantly, ferric-ferrous ratios of the amphiboles have not been determined routinely.

This study reports the results of experiments designed to elucidate further ferric-ferrous equilibrium in amphiboles. Four natural amphiboles were annealed over a range of oxygen fugacities at constant temperature and pressure to determine the variation in Fe^{3+} content and in unit-cell parameters. Natural amphiboles were chosen in order to avoid the complication of less than 100% yields in synthetic systems and also to provide crystals large enough for single-crystal structure refinements. Results that describe the variation of optical properties as a function of ferric-ferrous ratio and the results of crystal-structure refinements have been presented elsewhere (Phillips et al., 1986; Clowe and Popp, 1987; Phillips et al., 1988).

EXPERIMENTAL METHODS

Four natural clinoamphiboles representing the three major amphibole chemical groups (iron-magnesium, calcic, and sodic amphiboles) were selected for the study. These amphiboles include a grunerite from metamorphosed iron formation (sample 1, Klein, 1964); a tschermakitic hornblende from a kyanite-staurolite grade amphibolite (sample 73-31B, Spear, 1982); a magnesio-hornblende from Strickland quarry, Portland, Vermont, for which petrologic information has not been published (National Museum of Natural History specimen 146169); and a riebeckite-arfvedsonite solid solution, hereafter referred to as riebeckite, from a granitic pegmatite (Scofield and Gilbert, 1982).

Separation techniques

In order to ensure close to 100% purity in the starting materials, each amphibole sample was subjected to a variety of separation techniques. All samples were disaggregated, washed in acid, subjected to isodynamic magnetic and heavy-liquid separation techniques, and hand picked to produce 99–100% purity. Additional details of the separation techniques are given in Clowe (1987). The final grain sizes of samples are reported in Table 1. With the exception of a small proportion of crushed grains, there was no change in amphibole grain size during runs.

Phase identification and characterization

Electron-microprobe analysis of the starting materials and selected run products was carried out using the ARL instrument in the Department of Geological Sciences at Virginia Tech, Blacksburg, Virginia. The analytical procedures and operating conditions were essentially identical to those described by Solberg and Speer (1982).

Fe^{3+}/Fe^{2+} ratios were determined using a single-dissolution technique applicable to small sample sizes (Fritz and Popp, 1985). Sample aliquots ranging from 0.95 to 11.96 mg were digested with HF and H_2SO_4 in the presence of *o*-phenanthroline, after which Na-citrate and boric acid solutions were added. The solutions were then analyzed colorimetrically for FeO. Total Fe as Fe_2O_3 was determined by atomic absorption spectrophotometry after further dilution of the samples with the quartz blank used in the FeO determination. Duplicate solutions were made for each sample in the colorimetric analysis for FeO, and each of those solutions was diluted and analyzed twice for Fe_2O_3. Ferric-ferrous ratios, reported as molar $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ and abbreviated *R*, are considered to be precise to ±0.01 (Fritz and Popp, 1985).

A complication arises in electron-microprobe analyses of phases that contain oxy-amphibole component because total Fe is generally reported as FeO and the formulas are normalized to 23 oxygens. For an end-member grunerite, for example, this procedure is equivalent to expressing the chemical formula in terms of oxides with one molecule of water present in the stucture, i.e.,

$$Fe_7Si_8O_{22}(OH)_2 = 7FeO \cdot 8SiO_2 \cdot H_2O.$$

The formulas are normalized to 23 oxygens because the electron microprobe cannot analyze for H, and therefore, the amount of oxygen necessary to form "hydrogen oxide" is not included in the normalized formula. In the case of a totally dehydrogenated grunerite, it is necessary to normalize microprobe analyses to 24 rather than 23 oxygens, i.e.,

$$Fe_5^{2+}Fe_2^{3+}Si_8O_{24} = 5FeO \cdot Fe_2O_3 \cdot 8SiO_2.$$

Thus, normalization of the formula of an amphibole containing a significant oxy-component to 23 oxygens results in a total oxide weight percent that is too low by a factor that represents the additional oxygen present as Fe_2O_3 rather than as FeO. To correct an analysis based on 23 oxygens to the proper number of oxygens, (1) the total elemental weight percent of Fe is multiplied by the ferric-ferrous ratio (*R*) to determine the absolute elemental weight percent of Fe in each valence state, (2) the elemental

TABLE 2. Compositions of amphibole run products

	AOE 3A G	AEO 3A G	AOE 24	AOE 11A	AEO 11A	AOE 14	AOE 19	AOE 32	AOE 32	AOE 31
SiO_2	49.26		49.91	43.70		44.12	47.59	51.01		50.05
TiO_2	0.02		0.05	0.59		0.66	0.29	0.94		0.87
Al_2O_3	0.46		0.14	13.64		13.18	8.23	1.05		0.71
FeO	36.99		44.06	11.03		12.33	12.82	14.37		23.92
Fe_2O_3	7.82		N.D.	5.50		3.86	N.A.	20.30		9.33
MnO	0.64		0.67	0.28		0.32	0.79	0.70		0.70
MgO	3.21		3.22	10.00		10.33	12.81	0.22		0.21
CaO	0.33		0.32	11.61		11.73	11.86	0.15		0.18
Na_2O	0.07		0.06	1.40		1.24	0.88	8.87		8.64
K_2O	N.D.		0.01	0.51		0.47	0.47	1.46		1.35
F	0.17		0.08	0.18		0.47	0.62	2.00		1.98
Cl	0.11		0.11	N.D.		N.D.	0.01	N.D.		N.D.
Sum	99.08		98.63	98.44		98.31	96.37	101.08		97.94
Si	7.82	7.98	8.04	6.40	6.43	6.46	7.09	7.78	7.94	8.02
^{IV}Al	0.10	0.02		1.60	1.57	1.54	0.91	0.19	0.06	
^{VI}Al		0.07	0.03	0.76	0.80	0.75	0.54		0.14	0.14
Ti	0.01	0.01	0.01	0.07	0.07	0.08	0.03	0.11	0.11	0.11
Fe^{2+}	4.91	5.01	5.94	1.36	1.36	1.51	1.59	1.83	1.87	3.21
Fe^{3+}	0.94	0.96		0.61	0.61	0.43		2.34	2.39	1.13
Mn	0.09	0.09	0.09	0.04	0.04	0.04	0.10	0.09	0.09	0.10
Mg	0.76	0.78	0.78	2.18	2.19	2.25	2.85	0.05	0.05	0.05
Ca	0.06	0.06	0.06	1.82	1.83	1.84	1.89	0.03	0.03	0.03
Na	0.02	0.02	0.02	0.41	0.41	0.35	0.25	2.62	2.68	2.68
K				0.09	0.09	0.09	0.09	0.29	0.30	0.27
Cl	0.03	0.03	0.03				0.01			
F	0.09	0.09	0.04	0.09	0.09	0.03	0.62	1.00	1.00	0.97
O	23.00	23.48	23.00	23.00	23.10	23.00	23.00	23.00	23.49	23.00

Note: N.D. = not detected; N.A. = not available. Chemical compositions (in wt% oxides and in atoms per formula unit normalized to given number of oxygens) of selected run products (see Table 3 for details). Samples with >10% oxy-amphibole component have been normalized to the appropriate number of oyxgens per formula unit (see text for discussion).

weight percents are converted to oxide weight percents by multiplication by the proper conversion factor, (3) the oxide weight percents are converted to moles, and (4) the formula is normalized to the required number of oxygens (23 plus one-half the number of Fe^{3+} ions present as oxy-amphibole component per formula unit). The effect of the correction for grunerite is shown in the two columns labeled AOE 3A G in Table 2. The grunerite, which originally contained no Fe^{3+}, was oxidized in air, but there was no evidence for decomposition to secondary phases. Thus, its chemical composition should remain constant except for loss of H and oxidation of a portion of the Fe^{2+}. The corrected formula of the oxidized grunerite based on 23.48 oxygens is virtually identical to that of the unoxidized starting material (Table 1), whereas the formula normalized to 23.00 oxygens contains overall lower atomic amounts. It is important to note that this method of correcting chemical formulas presumes knowledge of the amount of Fe^{3+} present as oxy-amphibole component. Because Fe^{3+} can enter the amphibole structure by processes other than the formation of oxy-amphibole component (see Discussion), the amount of oxy-amphibole component is not necessarily the same as the number of ferric irons per formula unit. For example, in the case of the tschermakitic hornblende starting material, which originally contained Fe^{3+} (Table 1), the chemical formula was based on 23 oxygens because the amount of oxy-amphibole was unknown. However, when the tschermakitic hornblende was oxidized without decomposing, the chemical formula could be corrected to the increased number of oxygens that represents the increase in Fe^{3+} as oxy-amphibole component (columns labeled AOE 11A, Table 3).

Chemical analyses of the amphiboles used in the experiments are given in Table 1. Chemical zoning and significant impurities both within and between grains were not observed. Agreement between these analyses and those reported previously in the literature is excellent. Previous analysis for the magnesio-hornblende has not been reported. The analysis of riebeckite-arfvedsonite reported in Scofield and Gilbert (1982) contains 0.3 Li per formula unit, which is not analyzed by the electron microprobe and, therefore, is not included in the table. The formulas in Table 1 have been corrected to 23 oxygens, because the percent oxy-component is unknown. As discussed below, the presence of Fe^{3+} in an amphibole does not necessarily imply the presence of oxy-component.

Phase identification and unit-cell parameters were determined using a Philips X-ray diffractometer with Ni-filtered CuK_α radiation. Peak locations used to calculate unit-cell parameters were collected from four scans (two oscillations) collected at 0.5°/min using synthetic calcium fluoride as an internal standard, except in the case of riebeckite, for which synthetic $MgAl_2O_4$ spinel was used in order to avoid significant overlap of peaks. Centers of peaks were located at ⅔ peak height. Reflections were indexed in comparison to the calculated powder patterns in Borg and Smith (1969). Unit-cell parameters, reported in Table 3, were obtained by least-squares refinement (Evans et al., 1963), weighting all peaks equally.

Apparatus

Hydrothermal runs were carried out in horizontally mounted Rene-41 pressure vessels (e.g., Ernst, 1968, Fig. 6) using either Ar or methane as the pressure medium. Pressures were generally maintained within ±10 bars, with a maximum variation of 30 bars recorded. Temperature gradients within the vessels were calibrated previously at elevated temperature and pressure, and are 3° or less over a 2.54-cm capsule. Temperature variations in most runs were ±1 °C, with a maximum variation of ±4 °C.

The 1-atm runs were made in a Lindberg muffle furnace that

TABLE 3. Run results

	Run	Starting material	Run duration	Buffer	Run products	*R* (±0.01)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å^3)	*a* sin *β*
Grunerite		UNOX				−0.01	9.556(2)	18.397(4)	5.347(7)	101.904(35)	919.855(961)	9.350(7)
	AOE 3A/3B*	UNOX	0.5 h	Air	A	0.16	9.566(3)	18.382(12)	5.332(4)	101.928(40)	917.447(543)	9.359(4)
	AOE 12A	UNOX	2.0 h	Air	A	0.27	9.505(18)	18.379(16)	5.274(43)	99.895(547)	907.615(7.188)	9.364(33)
	AOE 12	UNOX	4.5 h	Air	A	0.31						
	AOE 10 G	UNOX	4 d	MH	A-M-H-LCRIS		9.556(5)	18.320(33)	5.376(26)	101.717(129)	921.554(314)	
	AOE 11	UNOX	2 d	MH	A-M-Q							
	AOE 24*	UNOX	4 d	NNO	A-OP	−0.02						
	AOE 6 G	UNOX	4 d	CCH$_4$	A-OL	0.00	9.568(3)	18.369(18)	5.370(16)	101.867(76)	923.662(2.052)	9.364(3)
	AOE 5 G	UNOX	8 d	CCH$_4$	A	0.01	9.565(4)	18.398(30)	5.347(23)	101.715(80)	921.372(2.733)	9.366(6)
	AOE 7A G	AOE 3A G	4 d	CCH$_4$	A	0.02	9.563(2)	18.405(5)	5.331(7)	101.866(42)	918.120(102)	9.359(7)
Tschermakitic hornblende		UNOX				0.21	9.782(10)	18.030(15)	5.343(10)	104.762(130)	911.221(1.707)	9.459(31)
	AOE 3A/3B T	UNOX	0.5 h	Air	A	0.47	9.786(8)	18.091(28)	5.316(8)	104.904(94)	909.458(1.334)	9.457(12)
	AOE 10 T	UNOX	4 d	MH	A	0.30	9.811(2)	18.069(4)	5.320(1)	104.994(19)	910.948(224)	9.477(3)
	AOE 11A*	UNOX	8 d	MH	A	0.31	9.813(2)	18.068(5)	5.320(2)	105.042(25)	910.958(355)	9.477(3)
	AOE 21	AOE 3B T	4 d	MH	A-H-Q							
	AOE 17	AOE 5 T	8 d	MH	A	0.30						
	AOE 23	UNOX	4 d	NNO	A	0.19						
	AOE 14*	UNOX	8 d	NNO	A-Q	0.22						
	AOE 13	UNOX	12 d	FMQ	A	0.18	9.836(2)	18.070(4)	5.319(1)	105.033(23)	913.106(268)	9.500(3)
	AOE 6 T	UNOX	4 d	CCH$_4$	A	0.16	9.846(2)	18.055(7)	5.315(2)	105.043(19)	912.443(355)	9.509(3)
	AOE 5 T	UNOX	8 d	CCH$_4$	A	0.15	9.848(4)	18.044(13)	5.315(2)	105.034(36)	912.133(537)	9.511(5)
	AOE 7A T	AOE 3A T	4 d	CCH$_4$	A	0.14	9.841(3)	18.066(11)	5.312(2)	105.043(42)	912.102(436)	9.504(5)
Magnesio-hornblende		UNOX				0.07	9.843(4)	18.072(9)	5.315(5)	104.574(46)	913.901(871)	9.526(8)
	AOE 18B	UNOX	0.5 h	Air	A-(OP)	0.31	9.838(12)	18.116(27)	5.281(7)	105.044(92)	908.862(1.240)	9.501(16)
	AOE 18	UNOX	1.5 h	Air	A	0.50	9.820(6)	18.064(11)	5.284(5)	105.014(45)	905.274(926)	9.485(8)
	AOE 19*	UNOX	8 d	MH	A-PYX-SP		9.847(3)	18.085(11)	5.303(3)	105.001(21)	912.236(523)	
	AOE 26	UNOX	8 d	NNO	A	0.11						
	AOE 37	UNOX	8 d	FMQ	A	0.12						
	AOE 25	UNOX	8 d	CCH$_4$	A	0.00	9.859(3)	18.079(7)	5.300(8)	104.591(37)	912.861(1.110)	9.541(5)
	AOE 27	AOE 18B	8 d	CCH$_4$	A-(OP)	0.09	9.855(9)	18.077(15)	5.315(22)	105.003(111)	914.636(3.476)	9.519(14)
Riebeckite		UNOX				0.33	9.816(18)	18.054(52)	5.323(16)	103.207(113)	917.969(2.505)	9.556(23)
	AOE 32*	UNOX	0.5 h	Air	A-Q	0.56	9.781(46)	18.078(116)	5.349(66)	103.604(430)	918.119(8.876)	9.507(62)
	AOE 30	UNOX	8 d	MH	A-M-H-Q-AC							
	AOE 34	UNOX	8 d	FMQ	A	0.28						
	AOE 31*	UNOX	8 d	CCH$_4$	A	0.26	9.836(10)	18.035(37)	5.322(11)	103.216(62)	918.592(1.679)	9.575(12)

Note: Atmospheric runs were conducted at 700 °C. Hydrothermal runs were conducted at 650 °C and 1 kbar. Abbreviations: h = hours, d = days, A = amphibole, H = hematite, M = magnetite, OP = opaque minerals, Q = quartz, LCRIS = low cristobalite, OL = olivine, PYX = pyroxene, SP = spinel, AC = acmite, (OP) = trace opaque minerals. *R* = molar $Fe^{3+}/(Fe^{3+} + Fe^{2+})$.

* Analyzed by microprobe.

was calibrated with the same temperature-measuring system used in the hydrothermal runs.

Oxygen fugacity in the hydrothermal runs was controlled using the standard solid buffer techniques (e.g., Huebner, 1971). The magnetite-hematite (MH), nickel–nickel oxide (NNO), fayalite-magnetite-quartz (FMQ), and graphite-methane (CCH_4) buffers were used. In addition, some samples were heated in air to achieve a much more highly oxidizing atmosphere than MH. A few runs were made at the more reducing iron-wüstite buffer, but that approach was abandoned because of the rapid loss of H_2 gas from the capsules. In runs as short as one day at 650 °C and 1 kbar, H_2 diffusion resulted in the complete loss of water from the buffer assemblage, even when the graphic-methane system was used as the pressure medium.

In hydrothermal runs, the amphibole charges (approximately 0.10 g) plus a measured amount of distilled-deionized water (approximately 20 μL) were sealed into an inner $Ag_{70}Pd_{30}$ capsule (2.54 cm × 3.0 mm outside diameter × 2.4 mm inside diameter) or into a Pt capsule (2.54 cm × 3.0 mm outside diameter × 2.6 mm inside diameter) in the case of runs made at the NNO buffer. The inner capsule was sealed into an outer Au capsule (3.81 cm × 4.75 mm outside diameter × 4.0 mm inside diameter) containing approximately 0.25 g of the buffer assemblage, and 50- to 75-μL distilled-deionized water. For runs made at the graphite-methane buffer, the sealed Ag-Pd capsule was loaded directly into the bomb with a small graphite filler rod, and the system was pressurized with methane. For samples heated in air, approximately 0.15 g of charge was loaded into a small Au boat, which was placed in the preheated muffle furnace.

Upon completion of hydrothermal runs, the vessels were removed from the furnaces and initially quenched in a stream of compressed air and then immersed in water. Using this procedure, the vessels reached a temperature of less than 50 °C in less than 5 min. After opening the capsules, the presence of water in both the buffer and charge was verified by heating each of the capsules in a small bottle on a hot plate and noting the condensation on the upper walls of the bottle. The 1-atm runs were simply removed from the furnace and allowed to cool to room temperature.

In attempts to demonstrate steady-state conditions and the approach to equilibrium, run times were varied from 1 to 12 d for the hydrothermal runs, and from 0.5 to 4.75 h for the runs in air. In addition, products of some experiments were re-run at different conditions in order to reverse the effects of oxidation or reduction.

RESULTS

Results of experiments are presented in Table 3, which gives experimental run conditions, a description of run products, R = molar $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ values, and unit-cell parameters of selected amphiboles. Chemical compositions of amphiboles from selected runs are given in Table 2.

Except for the air-annealing experiments, which were run at 700 °C, all experiments were carried out at 1 kbar and 650 °C. Temperature was not varied in this series of experiments in order to avoid the complication produced by variation in oxygen fugacity of the buffers with changing temperature. As a result, because of the different thermal stabilities of the four amphiboles, decomposition of amphibole was observed in a number of cases. Treatment of two amphiboles at the same buffer but at two different temperatures, so that each mineral lies within its own stability field, would result in a different oxygen fugacity in each run. Thus, an additional variable would be added to the interpretation of results, as compared to isothermal experiments.

Ferric-ferrous ratios and phase relations

Grunerite. As expected, air treatment produced the most highly oxidized grunerite, with R increasing from zero in the starting material to 0.16, 0.27, and 0.31 after treatment for 0.5, 2.0, and 4.75 h, respectively. These values represent O^{2-} occupancy of 48, 81, and 93 mol% of the O(3) site, respectively, assuming that only the dehydrogenation mechanism (Eq. 1) is operative. X-ray and optical analysis of run products indicate no decomposition to secondary phases, even though the grunerite, as a hydrous phase, is clearly unstable in air at elevated temperature. Peak broadening was observed in the X-ray pattern of the 4.75-h run, which may represent the initial stages of decomposition. The chemical composition of the amphibole in 0.5-h run (AOE3AG, Table 2) is virtually identical with that of the starting material, except for R, after the analysis is corrected for the presence of oxy-component.

In runs made at the MH buffer, the sample decomposed to a presumably Mg-enriched amphibole + iron oxides + silica, behavior that is consistent with previous experimental studies in Fe-Mg amphibole systems (Forbes, 1977; Popp et al., 1977). Ferric-ferrous ratios were not determined for these runs because of the contaminating effect of additional Fe-bearing phases on the analytical technique.

A small amount (<2%) of opaque phases was observed optically in the 4-d run at the NNO buffer. Previous studies of phase relations (e.g., Gilbert et al., 1982) indicate that Fe-rich amphiboles should decompose to Mg-enriched amphibole containing approximately 60% grunerite component by the liberation of magnetite and quartz at the conditions employed here. It is concluded that the amphibole was in the incipient stages of decomposition, but that the 4-d run time was not sufficient for a significant extent of reaction (Popp et al., 1977). The relatively small extent of decomposition results in both a ferric-ferrous ratio (Table 3) and a chemical composition (AOE24, Table 2) that are not significantly different from those of the starting material.

Runs carried out at the CCH_4 buffer resulted in no change in R as compared to the unoxidized starting material. Within the precision of measurement, no Fe^{3+} was detected. A weak olivine reflection was observed in products of one of the runs, but decomposition of the amphibole to small amounts of olivine is not unexpected (Gilbert et al., 1982). Starting material for one of the CCH_4 runs was the 0.5-h air-oxidized material (R = 0.16). Restoration of the ferric-ferrous ratio to essentially zero, within error of measurement, in 4 d demonstrates that the formation of oxy-amphibole component is easily reversible.

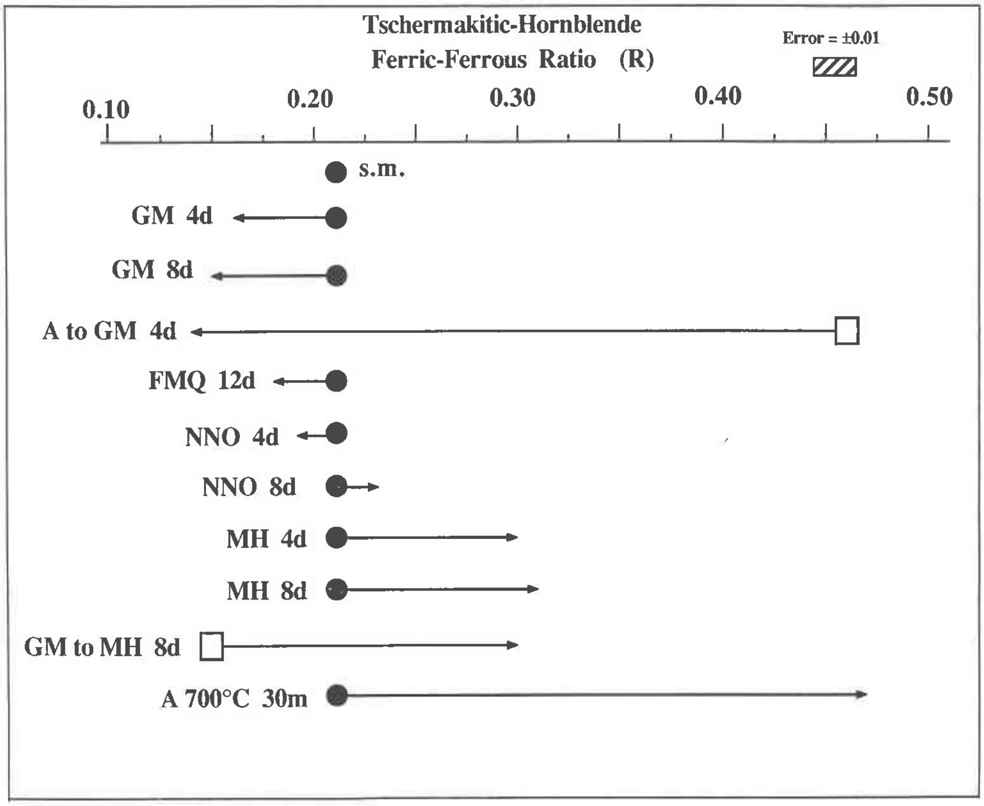

Fig. 1. Results of experiments on tschermakitic hornblende. Circles represent ferric-ferrous ratio of unaltered starting material. Tips of arrows indicate ferric-ferrous ratio in run products; precision of measurement is ±0.01. Boxes represent runs in which starting materials were products of previous experiments. Abbreviations: s.m. = unaltered starting material; GM = graphite-methane; FMQ = fayalite-magnetite-quartz; NNO = nickel–nickel oxide; MH = magnetite-hematite; A = air; d = days; m = minutes.

In the products of the air and NNO runs, some grunerite grains were observed to exhibit small, widely spaced, dark striations perpendicular to the long axis of the crystal when viewed optically before crushing. Optical examination was unable to reveal whether the features were fractures or inclusions, but electron-microprobe analysis, including dot maps, indicated no compositional variations. This phenomenon was also observed in riebeckite treated at the graphite-methane buffer.

Tschermakitic hornblende. The tschermakitic hornblende exhibited continuous variation in ferric-ferrous ratio as a function of increasing oxygen fugacity. Run results are shown graphically in Figure 1. Air oxidation for 0.5 h produced an increase in R from 0.21 in the untreated sample to 0.47, which represents oxidation of 0.52 Fe per formula unit. The 4- and 8-d runs at the f_{O_2} of the MH buffer resulted in statistically identical R values of 0.30 and 0.31, respectively, with no evidence for decomposition. The composition of the amphibole in the 8-d run did not change, except for R, after correction for the increased oxy-amphibole component (AOE 11A, Table 2).

Samples treated at the NNO buffer for 4 d ($R = 0.19$) and 8 d ($R = 0.22$), and at the FMQ buffer for 12 d ($R = 0.18$) resulted in little change in ferric-ferrous ratio relative to the starting material. A small amount of quartz (<3%) was detected optically in the 8-d NNO run, but the chemical composition of the amphibole (AOE 14, Table 2) did not change significantly. Whether the presence of quartz indicates an original quartz impurity or actual decomposition is unclear. In an experimental investigation at pressures above 7 kbar, Oba (1978) observed quartz, clinopyroxene, and garnet in the dehydration assemblage of tschermakite. However, data on the stability relations in the temperature-pressure range of this study are not available.

Treatment of tschermakitic hornblende at the CCH_4 buffer produced the somewhat reduced ferric-ferrous ratios of 0.16 after 4 d, and 0.15 after 8 d.

Treatment of the air-oxidized sample at the CCH_4 buffer for 4 d reduced R from 0.47 to 0.14, which agrees well with the values of 0.15 and 0.16 obtained using unoxidized starting material. Re-annealing the amphibole from a CCH_4 run at the MH buffer for 4 d resulted in a value of $R = 0.30$, which is identical with that obtained by starting with the original amphibole. In contrast, treatment of the air-oxidized sample at MH for 4 d resulted in partial decomposition of the amphibole to liberate approximately 10% hematite and quartz.

Magnesio-hornblende. The magnesio-hornblende is somewhat similar in composition to the tschermakitic hornblende, containing 1.66 vs. 1.96 total Fe per formula unit, respectively. However, the magnesio-hornblende contains 0.65 fewer Al per formula unit, and has a lower initial ferric-ferrous ratio of 0.07 vs. 0.21. As with the tschermakitic hornblende, a systematic variation in *R* was observed over the range of oxygen fugacities employed (Table 3).

The most highly oxidized amphibole was obtained by air-heating: $R = 0.31$ after 0.5 h, $R = 0.50$ after 1.5 h. Very small amounts of opaques (<1%), presumably iron oxide, were observed optically in the air-heated runs. Treatment at the MH buffer for 8 d resulted in the formation of pyroxene and a spinel phase in the charge, as identified by X-ray diffraction. Electron-microprobe analysis (AOE 19, Table 2) reveals that the oxidized amphibole is somewhat depleted in Al and Fe, and enriched in Si and Mg relative to the starting material. Whether this amphibole composition represents an equilibrium value is unknown; treatment for longer times could result in further decomposition and changes in composition.

As with the tschermakitic hornblende, runs of 8 d at the NNO and FMQ buffers produced little change in *R*. The resulting amphiboles are slightly more oxidized as compared to the ferric-ferrous ratio of 0.07 in the starting material, i.e., $R = 0.11$ for NNO, and $R = 0.12$ for FMQ.

Treatment of the original sample at the CCH_4 buffer for 8 d resulted in total reduction ($R = 0.00$) of the Fe in the amphibole. Treatment of the air-heated sample at the same conditions resulted in run products with $R = 0.09$, but the small amount of opaque phases present in the air-heated sample was not resorbed during the run at lower oxygen fugacity. The presence of 1% magnetite in the sample would increase *R* of the bulk sample by 0.025. Thus, subtraction of the effect of the magnetite results in an amphibole with *R* in the range 0.06 to 0.07, as compared to the value of 0.00 obtained from treatment of the original starting material at the CCH_4 buffer.

Riebeckite. The riebeckite-arfvedsonite solid solution had an initial *R* value of 0.33 as compared to 0.20 for ideal arfvedsonite and 0.40 for ideal riebeckite. In addition, it contained 0.98 F per formula unit, so that the maximum possible amount of dehydrogenation is limited relative to the other three amphiboles studied here.

Treatment of the original sample in air for 0.5 h resulted in the liberation of a small amount of free quartz (<2%). The resulting amphibole may be slightly silica deficient (AOE 32, Table 2), but the difference is at the level of detection. Because the analytical technique for ferric-ferrous ratio is not affected by the presence of additional non-Fe-bearing phases (Fritz and Popp, 1985), a value of *R* can be determined for the oxidized riebeckite. The resulting value of *R* (0.56) requires that 0.97 atoms of Fe^{2+} were oxidized. That is, of the 1.02 atoms of OH^- available per formula unit, nearly all were converted to O^{2-}.

In an 8-d run at the MH buffer, riebeckite decomposed nearly completely to hematite, magnetite, quartz, and acmite. These results are in agreement with those observed in the synthetic system (Ernst, 1962), in which riebeckite-arfvedsonite solid solutions are unstable down to temperatures as low as 500 °C at the oxygen fugacity defined by the MH buffer.

Runs carried out at the FMQ and CCH_4 buffers for 8 d resulted in slightly reduced ferric-ferrous ratios of 0.28 and 0.26, respectively, with no optical or X-ray evidence for decomposition. Based on the results of Ernst (1962), the amphibole should lie within its stability field at these conditions. In contrast to the results of Ernst, Owen (1985) reported arfvedsonitic amphibole to be unstable at 750 °C, 1 kbar, and f_{O_2} defined by the FMQ buffer, but the results cannot be directly compared to those obtained here at 650 °C. The most reduced of the riebeckites requires reduction of 0.27 Fe^{3+} per formula unit relative to the starting material.

Unit-cell parameters

Unit-cell parameters of selected amphibole run products determined from powder X-ray diffraction are given in Table 3. The numbers in parentheses in the table represent one-standard-error values calculated by the least-squares computer program. The relatively larger standard-error values for the air-treated samples probably are due to the fact that the crystallinity of those samples has been affected by incipient stages of decomposition.

As a simple test for precision, unit-cell parameters for the grunerite, as determined by several different techniques and by several different individuals, are compared in Table 4. The grunerite used for this study was obtained as a hand sample of schist from C. Klein, who has made the amphibole available to workers for a variety of different kinds of analyses (e.g., Finger, 1969; Dyar, 1984). Shown in Table 4 are five different determinations, two obtained by different individuals using a powder diffractometer as described above, two obtained from powder photographs utilizing an internal standard, and one obtained from an automated single-crystal diffractometer. In general, the agreement among the values in Table 4 is good, but the data suggest that doubling of the standard-error values, a practice advocated by some researchers, gives better agreement for comparing the results of the different analysts.

DISCUSSION

In the discussion that follows, it is assumed that the reader is familiar with the basic features of the amphibole crystal structure, the nomenclature for cation and anion sites, and the general scheme of partitioning of cations among the sites according to size and valence. Excellent reviews of the subject are given in Ernst (1968), Cameron and Papike (1979), and Hawthorne (1981, 1983).

TABLE 4. Comparison of unit-cell parameters

Analyst	Method of X-ray diffraction	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å³)
C. A. Clowe*	diffractometer	9.556(2)	18.397(4)	5.347(7)	101.904(35)	919.855(961)
M. W. Phillips (pers. comm.)	single crystal	9.570(2)	18.397(3)	5.342(2)	101.94(3)	920.2(8)
Klein (1964)	powder photo	9.562(2)	18.380(7)	5.338(4)	101.86(3)	918.2(7)
Finger (1969)	powder photo	9.5642(7)	18.393(2)	5.3388(3)	101.892(3)	919.0(2)
M. A. Cusimano (pers. comm.)	diffractometer	9.568(5)	18.374(17)	5.335(16)	101.828(48)	918.067(2.058)

Note: Comparison of unit-cell parameters of grunerite (Klein, sample 1, 1964) determined by several different methods and experimenters.
* Values as given in Table 3.

Ferric-ferrous ratios and phase relations

Because no single value of *R* has been approached from opposite directions, the strict reversal of equilibrium has not been documented in any of the runs in this study. However, the relatively rapid changes in *R*, the time independence of final *R* values in the hydrothermal runs, and the fact that *R* values can be restored after having been altered (Fig. 1) lend support to the assumption that an approach to equilibrium has been obtained.

Clearly, there are differences in the behavior of the four different amphiboles. Air oxidation produces the most highly oxidized samples in all four minerals. As hydrous phases, amphiboles are unstable in air at 700 °C. The slight, but still significant broadening of peaks in the X-ray patterns, particularly in runs longer than 0.5 h, may represent incipient stages of decomposition. Longer-term air-heating runs described elsewhere (Hodgson et al., 1965; Patterson and O'Connor, 1966) have resulted in decomposition. It is, thus, concluded that equilibrium is not approached in any of the air-heating runs. The Fe^{3+} content of the amphiboles should increase with longer run times until complete dehydrogenation occurs, complete oxidation of Fe is achieved, or the amphibole decomposes. Therefore, differences in *R* values of the four amphiboles heated in air are most likely related to kinetic factors and to their different initial Fe^{2+} contents.

At the oxygen fugacity of the MH buffer, all the amphiboles except tschermakitic hornblende decomposed to assemblages containing Fe^{3+}-bearing oxides, or in the case of riebeckite, Fe^{3+}-bearing pyroxene. The original tschermakitic hornblende ($R = 0.21$) did not decompose in runs of up to 8 d, but treatment of the more highly oxidized air-heated sample ($R = 0.47$) at MH did result in decomposition to an assemblage containing iron oxides. These results suggest that the amount of Fe^{3+} required in amphibole by this relatively high oxygen fugacity cannot be accommodated within the crystal structure, and decomposition to other Fe^{3+}-bearing phases results. The attainment of an apparent metastable equilibrium in tschermakitic hornblende indicates that the equilibrium ferric-ferrous ratio is achieved more rapidly than the rate at which decomposition reactions occur. The fact that decomposition is not observed in the more highly oxidized air-heated samples is considered to be a result of the significantly shorter run times and the fluxing effect of water in the hydrothermal runs.

The NNO and FMQ buffers produce little, or only slight, variation in ferric-ferrous ratio relative to all four starting materials. Most significant is the fact that grunerite, unlike the other three varieties, contains no Fe^{3+} at the f_{O_2} defined by NNO.

The different behavior of the four amphiboles may be related partially to the two mechanisms by which Fe^{3+} is accommodated within the amphibole crystal structure. In the first mechanism, formation of oxy-amphibole component by oxidation-dehydrogenation (Eq. 1), the increased charge that results from oxidation of Fe^{2+} to Fe^{3+} is compensated by replacement of the same number of univalent hydroxyls by divalent oxygens. As discussed in detail elsewhere (Phillips et al., 1988), dehydrogenation produces significant underbonding at the O(3) site, which in turn, induces compensational mechanisms to offset the underbonding. For example, changes in octahedral occupancies, shortening of M–O bond lengths, displacement of univalent cations from M(4) to the A site, and increased interaction of A-site cations with O(3) accompany oxidation-dehydrogenation.

In the second mechanism, herein termed Al substitution, Fe^{3+} behaves analogously to Al^{3+} in octahedral cation sites. Octahedral Al^{3+} is accommodated in amphiboles either (1) by a coupled tschermakitic-type substitution in which replacement of divalent cations by Al^{3+} in octahedral sites is coupled with substitution of Al^{3+} for Si^{4+} in the tetrahedral sites or (2) by a substitution in which replacement of Ca^{2+} by a univalent cation in the M(4) sites is coupled with substitution of Al for divalent cations in the octahedral sites, as in the case of glaucophane ($Na_2Mg_3Al_2Si_8O_{22}(OH)_2$) or alumino-winchite ($NaCaMg_4AlSi_8O_{22}(OH)_2$). The extent to which each of the two mechanisms determines the Fe^{3+} content of any given natural amphibole is unknown, but published chemical analyses of amphiboles suggest that both processes are involved in many natural samples (Popp and Phillips, 1987).

Reduction of Fe^{3+} present as oxy-component in an amphibole can be accomplished by a hydrogenation reaction; that is, the reverse of Equation 1. The extent to which Fe^{3+} that is present as a result of Al substitution can be reduced is less well known. Semet (1973) documented the complete reduction of Fe in magnesio-hastingsite ($NaCa_2Mg_4Fe^{3+}Al_2Si_6O_{22}(OH)_2$) to 100% Fe^{2+} and concluded that one excess H was present in the structure in order to produce the required charge balance. The presence of excess OH has also been reported in synthetic amphiboles (Witte et al., 1969; Maresch and Langer, 1976), as well as in natural calcic and subcalcic varieties (Leake, 1968).

Some conclusions can be made based on the two different mechanisms for incorporation of Fe^{3+} into amphiboles. The experimental results indicate that grunerite can contain a considerable amount of Fe^{3+} under short-term, nonequilibrium conditions (i.e., the air-heated samples), but can accommodate only a very limited amount of Fe^{3+} under equilibrium conditions. No Fe^{3+} was observed to be present in any of the hydrothermal runs made in this study, although analysis of amphibole Fe^{3+} content of runs made at the MH buffer was not possible. Because grunerites, in general, contain only small amounts of Na and Al, the Al substitution mechanism cannot produce a significant Fe^{3+} content. The extent to which oxy-amphibole component can form in grunerite may also be limited. If the presence of A-site cations is required to relieve a portion of the imbalance of bond strengths caused by O^{2-} in the O(3) site, the relative absence of Na in this and most naturally occurring grunerites may severely limit the amount of oxy-component that can form. The result of the local charge imbalance may be that grunerites either resist oxidation of Fe^{2+}, as observed in the NNO run, or at higher oxygen fugacities, decompose to Fe^{3+}-bearing oxides so that the Fe^{3+} in the system is accommodated in oxides rather than in the amphibole. Previous experimental studies (e.g., Popp et al., 1977) have documented that Fe-Mg amphiboles are restricted to very Mg-rich compositions at the oxygen fugacity defined by the MH buffer, which is likely to be related to the inability of this group of amphiboles to accommodate Fe^{3+}. Low Fe^{3+} contents are also observed in naturally occurring Fe-Mg amphiboles (Fig. 2 in Robinson et al., 1982; Deer et al., 1963).

The magnesio-hornblende is more reduced than the tschermakitic hornblende for all the buffer conditions and is totally reduced ($R = 0.00$) at the CCH_4 buffer as compared to the value of $R = 0.15$ obtained for the tschermakitic hornblende. These results suggest that the original Fe^{3+} content of the magnesio-hornblende may have been virtually all oxy-component, whereas that of the tschermakitic hornblende may have been due to both oxy-component and Al substitution.

A simple comparative thermodynamic analysis can provide some information regarding the comparative behavior of the two hornblendes. The log form of the equilibrium constant for Equation 1 is

$$\log K = \log a_{\mathrm{Fe}^{3+}} + \log a_{\mathrm{oxy}} + \tfrac{1}{2}\log f_{\mathrm{H}_2 - \log} a_{\mathrm{Fe}^{2+}} \\ - \log a_{\mathrm{hydroxy}}, \quad (2)$$

where f_{H_2} is the fugacity of H_2 in the system, and the terms a_i represent the activities of the appropriate components in the amphibole solid solution ($a_{\mathrm{Fe}^{3+}}$, the activity of Fe^{3+} component; a_{oxy}, oxy-amphibole component; $a_{\mathrm{Fe}^{2+}}$, Fe^{2+} component; and a_{hydroxy}, hydroxy-amphibole component). Because the values of f_{H_2} for the buffer assemblages can be calculated, Equation 2 can be used to compare calculated and observed compositions for a single amphibole treated over a range of buffers, or two different amphiboles treated at the same buffer, provided activity-composition relations for the amphiboles are known. The major compositional differences between the two hornblendes are that the magnesio-hornblende (1) contains a larger amount of F in O(3) (0.33 vs. 0.06 per formula unit), and (2) contains a smaller amount of octahedral Al (0.64 vs. 0.83 pfu). Given these compositional differences, some semiquantitative conclusions can be made, provided that the activity coefficients for the two minerals are unity or are assumed to be similar. For unit activity coefficients, the activity of hydroxy-amphibole component can be expressed as

$$a_{\mathrm{hydroxy}} = X^2_{\mathrm{OH}}, \quad (3)$$

where X is the mole fraction of OH in the O(3) site. Therefore, from Equations 2 and 3, for two amphiboles equilibrated at the same buffer, the lower activity of hydroxy-component in the magnesio-hornblende requires a lower ferric-ferrous ratio at constant activity of oxy-component. That is, if the activity of oxy-component is the same in the two minerals, the lower activity of hydroxy-component requires a lower ferric-ferrous ratio. The activities of Fe^{3+} and Fe^{2+} can be expressed as

$$a_{\mathrm{Fe}^{3+}} = X^2_{\mathrm{Fe}^{3+}(\mathrm{M}(1))} X^2_{\mathrm{Fe}^{3+}(\mathrm{M}(2))} X_{\mathrm{Fe}^{3+}(\mathrm{M}(3))} \quad (4)$$

$$a_{\mathrm{Fe}^{2+}} = X^2_{\mathrm{Fe}^{2+}(\mathrm{M}(1))} X^2_{\mathrm{Fe}^{2+}(\mathrm{M}(2))} X_{\mathrm{Fe}^{2+}(\mathrm{M}(3))}, \quad (5)$$

where the X terms refer to the mole fraction of the ions in the individual cation sites. Fe^{3+} and Al are strongly partitioned into the M(2) site in amphiboles (e.g., Hawthorne, 1983), and thus effectively reduce the number of sites on which Fe^{2+} can mix. For example, if M(2) were totally occupied by Al and Fe^{3+}, Fe^{2+} could mix on only three rather than five sites, whereas Fe^{3+} could still mix on all five. A consequence of mixing on fewer sites is an increase in activity, i.e., the mole fraction is raised to a lower power. Therefore, if two amphiboles contained identical amounts of Fe^{2+}, that with the higher Al content would have a higher activity of Fe^{2+}. From Equation 2, a higher activity of Fe^{2+} requires a higher activity of Fe^{3+} at constant a_{hydroxy}, a_{oxy}, and f_{H_2}. Thus, increased Al content favors a higher ferric-ferrous ratio, given that all other variables are constant.

It can be concluded that the higher OH and Al contents of the tschermakitic hornblende are consistent, in a semiquantitative sense, with its higher ferric-ferrous ratios relative to magnesio-hornblende. Without knowledge of the actual site populations of the cations, more rigorous analysis is not warranted.

The fact that the air-oxidized magnesio-hornblende cannot be totally reduced, whereas the unoxidized magnesio-hornblende can, is considered to be related to the presence of the iron oxides in the air-heated sample. The presence of oxides suggests that mechanisms other than solely oxidation-dehydrogenation may have been operative (e.g., Addison et al., 1962a, b; Hodgson et al., 1965). The possibility and identity of such mechanisms are the subject of continued investigation.

The results of the riebeckite experiments are more difficult to explain in some respects. The ferric-ferrous ratio of the air-oxidized sample ($R = 0.56$) requires loss of 0.97 OH from the starting amphibole composition. Given the original F content of 0.98 F pfu (Table 1), the maximum original oxy-component can be no greater than 0.05 oxygen pfu. The problem arises in that the riebeckite treated at the FMQ and CCH_4 buffers is significantly reduced relative to the starting material. For example, the most reduced riebeckite ($R = 0.26$) requires 0.30 O^{2-} to be converted to OH^-. However, this number of oxygens is significantly larger than the number present in the chemical formula.

Two possible mechanisms could be responsible for the apparent "over-reduction" of Fe^{3+} in riebeckite. The presence of excess H in the form of OH within the amphibole as proposed elsewhere (Leake, 1968; Witte et al., 1969; Semet, 1973; Maresch and Langer, 1976) would permit the existence of excess Fe^{2+}. The likelihood of this being the actual mechanism cannot be evaluated without quantitative analyses of water contents or without the application of techniques such as infrared spectroscopy or single-crystal structure analyses. Alternatively, Rebbert and Hewitt (1986) reported results of a similar experimental study of the variation of ferric-ferrous ratios in synthetic biotites in response to changes in controlled f_{H_2}. Based on the direct measurement of H content of the run products, they concluded that anion vacancies were present in the more reduced samples. The presence of such vacancies in amphiboles would allow for excess reduction of Fe^{3+} over that present as oxy-component, but in the absence of H analyses, such an explanation is also totally speculative.

Unit-cell parameters

Changes in unit-cell parameters with changing ferric-ferrous ratio should be related to the size difference between Fe^{2+} and Fe^{3+}, as well as to changes in cation site occupancies. The observed variations in unit-cell parameters can be interpreted to some extent based on the results of Colville et al. (1966), who investigated the relation between unit-cell parameters, bulk chemical composition, and site occupancies in synthetic and natural clinoamphiboles. They concluded that the size of the *b* unit-cell edge is related to the lateral linking of the tetrahedral chains by the cations occupying the M(4) and M(2) sites. In the case of the calcic and sodic amphiboles, in which M(4) is occupied mainly by Ca and Na, the occupancy of M(2) exerts the major control on *b*. In the Fe-Mg amphiboles, however, the proportions of Fe and Mg in M(4) also exert control on *b*. The size of $a \sin \beta$ is related to the unit repeat across facing double chains. Given constant thickness of the tetrahedral chains (i.e., constant tetrahedral occupancy), $a \sin \beta$ is related to the thickness of the octahedral strip. For constant M(4) content, the occupancy of the M(1), M(2), and M(3) sites determines the size of $a \sin \beta$. The *c* unit-cell edge is a measure of the unit repeat parallel to the tetrahedral chains. Its size is apparently controlled by complex interactions of the cations occupying all of the M sites, as well as the Si:Al ratio. Finally, β is determined mainly by the occupancy of cations in M(4). These controls on unit-cell parameters describe the general trends observed, but in some cases, the variations in unit-cell parameters calculated strictly on the size differences between cations in specific sites are significantly smaller than, or even opposite to, those observed in the actual amphiboles (e.g., Table 4 in Colville et al., 1966). Such observations suggest that other crystal-chemical factors contribute to variations in amphibole unit-cell parameters.

Given the variations in unit-cell parameters (Table 3), some interpretations can be made, but the interpretation is complicated somewhat by the relatively large standard errors in the unit-cell refinement for the air-heated samples when the standard statistical test for significance at the two-standard-error level is used.

***a* sin *β*.** Figure 2 shows the variation in $a \sin \beta$ of the amphiboles normalized to the change in number of ferric irons per formula unit. Positive values represent increased amounts of Fe^{3+}, whereas negative values represent reduction of Fe^{3+} relative to the unaltered starting material. The similar slopes for tschermakitic hornblende, magnesio-hornblende, and riebeckite (0.084, 0.062, and 0.060 Å per atom of Fe^{3+}, respectively) suggest that the expansion or contraction in the direction perpendicular to the chains is approximately the same in all three crystal structures as the amount of Fe^{3+} changes. Assuming that the Fe content of the M(4) site is negligible for these three amphiboles, the changes in Fe^{3+} content must be accommodated in the M(1), M(2), and M(3) sites, which is then reflected in the size of $a \sin \beta$.

The response of $a \sin \beta$ to changing Fe^{3+} content is distinctly different for grunerite. The least-squares curve through the data points shows essentially no change over the range of compositions obtained in the experiments. It is difficult to envision a mechanism by which replacement of a larger cation by a smaller one would result in no change or an increase, but given the very large relative error for the most oxidized air-treated run, a decrease in $a \sin \beta$ with increasing Fe^{3+} content is certainly possible. Part of the difference between grunerite and the other three minerals may be due to the fact that in grunerite, there is occupancy of Fe in the M(4) site, and thus the occupancy of M(4) is involved in controlling $a \sin \beta$. Klein and Waldbaum (1967) calibrated the variation in unit-cell parameters as a function of Fe-Mg ratio for the cummingtonite-grunerite series. The dashed line in Figure 2 shows the variation in $a \sin \beta$ calculated from the equa-

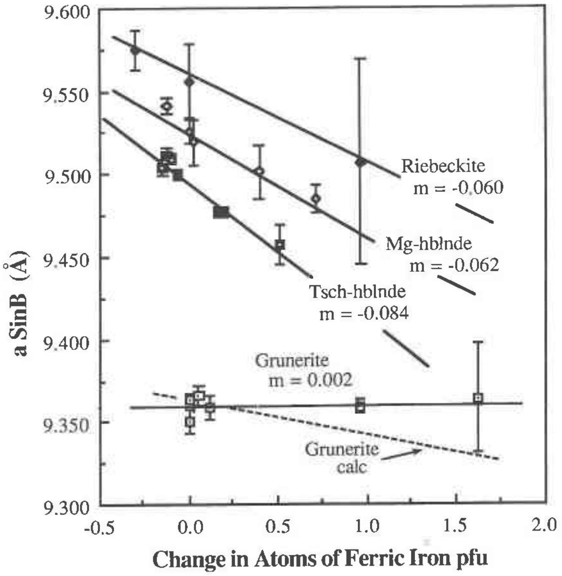

Fig. 2. Variation in $a \sin \beta$ of the amphiboles as a function of the change in the number of ferric irons per formula unit. The value 0.0 on the abscissa represents the original starting material. Positive values indicate increase in Fe^{3+} content, whereas negative values represent reduction of Fe^{3+}, relative to the starting material. Slopes (m) are in Å/atom of Fe^{3+}. The dashed line for grunerite shows the change in $a \sin \beta$ that would result from substitution of an equivalent amount of Mg for Fe^{2+}, rather than Fe^{3+} for Fe^{2+}. See text for details.

tion of Klein and Waldbaum for replacement of Fe^{2+} by Mg. The variation observed for grunerite is in better agreement with the calculated curve than with the curves for the other three amphiboles, but the analogous behavior of Fe^{3+} and Mg^{2+} is questionable. Colville et al. (1966) were able to explain observed variations in unit-cell parameters with the assumption that the two cations are similar in radius. However, in more recent compilations of ionic radii (Shannon and Prewitt, 1969), the radius of Fe^{3+} is approximately 10% smaller than that of Mg. Ideal ⟨M–O⟩ bond lengths in amphiboles (Table 15, Hawthorne, 1981) also reflect the smaller radius of Fe^{3+} relative to Mg. Increasing Mg content in the natural cummingtonites-grunerites is strongly partitioned into the M(1), M(2), and M(3) sites, whereas changes in site occupancies in the oxidized grunerites are unknown. The significantly smaller response of $a \sin \beta$ relative to Fe^{3+} as compared to Mg may indicate that oxidation occurs with little repartitioning of Fe within the cation sites. In summary, the observed behavior of $a \sin \beta$ in grunerite is considerably different from that of the three amphiboles with negligible Fe content in M(4), but an explanation for the difference cannot be verified without data on site populations.

***b* unit-cell edge.** The data for grunerite (Table 3) suggest a decrease in b as R increases. Such a decrease is to be expected because, in grunerite, there is significant Fe^{2+} content in both M(2) and M(4), which, presumably, is oxidized to the smaller Fe^{3+}. As was the case for $a \sin \beta$, the observed change in b is considerably less than that observed for an analogous amount of replacement of Fe^{2+} by magnesium. The observed decrease of 0.020 Å for replacement of the 1.62 atoms per formula unit compares to the value of 0.120 Å for replacement of 1.62 atoms in the Fe-Mg system (Klein and Waldbaum, 1967). In the natural cummingtonites-grunerites, the increased Mg partitions very strongly into M(2); thus, the smaller change in b observed here could be explained if Fe^{3+} is not strongly partitioned into the M(2) site.

In the two hornblendes, there is no evidence for a change in b. For both amphiboles, all values of b except the two extremes are equal within one standard error, and those of the extremes are the same well-within two standard errors. In general, it has been observed that Fe^{3+} partitions strongly into the M(2) site in hornblendes (Cameron and Papike, 1979; Hawthorne, 1981, 1983). The constancy of b observed here is interpreted to indicate that Fe^{3+} is not strongly partitioned into that site in the oxidized hornblendes. This conclusion is confirmed by Phillips et al. (1988), who have shown that both total Fe content and Fe^{3+} content of the M(2) site decrease in the oxidized tschermakitic hornblendes of this study.

Given the large magnitude of the errors, there is no significant change in b for the riebeckite, but Ernst and Wai (1970) have documented a general decrease in b of sodic amphiboles with an increase in oxidation-dehydrogenation.

***c* unit-cell edge.** The factors that control the variation in c are understood more poorly on a crystal-chemical basis than for the other two unit-cell edges (Colville et al., 1966), so that interpretation of the results may be less meaningful than for the other parameters. In addition, the data for the c unit-cell edge are considered to be of lesser quality because the least-squares refinement of c is based on a relatively small number of peaks as compared to a and b. A decrease in c with increasing Fe^{3+} content should be expected in grunerite, based on the behavior of Fe-Mg substitutions (Klein and Waldbaum, 1967), but the observed difference is several times larger than that in the Fe-Mg system. The relatively imprecise value for the most oxidized sample may contribute to the difference.

There is no evidence for variation of the c unit-cell edge of the tschermakitic hornblende, but that of the magnesio-hornblende apparently decreases with increasing Fe^{3+} content. Given the similarities in compositions of the two amphiboles, significant differences would not be expected. Explanation of the behavior, if not related to the precision of measurement, awaits further crystallographic investigation.

Within the standard errors of the unit-cell refinement, c of riebeckite does not vary with R.

β angle. With the exception of grunerite, the value of the interaxial angle β does not vary significantly for the amphiboles (Table 3). This observation is consistent with the results of Colville et al. (1966), who concluded that β

is determined mainly by the identity of the cation in the M(4) site, Ca vs. Na vs. Fe-Mg.

Unit-cell volume. The unit-cell volume is the product of the other parameters, and thus reflects the variations of the individual unit-cell parameters discussed above. Except for riebeckite, for which the standard errors are very large, unit-cell volumes of all the amphiboles decrease with increasing content of the smaller Fe^{3+}.

CONCLUSIONS

Based on the results obtained in this study, the following conclusions can be made.

1. Significant variation in Fe^{3+} content can be achieved in amphiboles by variation in oxygen fugacity. Oxidation-dehydrogenation equilibrium as described in Equation 1 can account for most, but not all of the observed behavior.
2. Steady-state values of ferric-ferrous ratio, which are presumed to approach equilibrium, are attained relatively rapidly as compared to rates of decomposition reactions. In some cases, metastable Fe^{3+}-Fe^{2+} equilibrium is achieved prior to decomposition.
3. The Fe^{3+} content of the magnesio-hornblende is present mainly as oxy-amphibole component, whereas that of the tschermakitic hornblende is present as both oxy-component and as the result of Al substitution. The possible reduction of Fe^{3+} either by the presence of excess H over two atoms per formula unit or by the formation of anionic vacancies is possible, but cannot be evaluated from the results obtained here.
4. Under equilibrium conditions, grunerite is inherently less able to accommodate Fe^{3+} than are the other three amphiboles. Grunerite responds to increased oxygen fugacity by either resisting oxidation, or by expelling the oxidized Fe from its crystal structure.
5. Unit-cell parameters respond to changes in ferric-ferrous ratio, but the large errors of refinement of some samples limit crystal-chemical interpretation. The most significant change observed is a decrease in $a \sin \beta$ of the two hornblendes and riebeckite with increasing R, which represents increasing overall content of Fe^{3+} in M(1),M(2), and M(3). The variation of $a \sin \beta$ with R in grunerite is significantly different from that of the other three amphiboles. There is no strong evidence for partitioning of Fe^{3+} into the M(2) site of the oxidized amphiboles, based on the variation in b.

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