Complete chemical analyses of metamorphic hornblendes: implications for normalizations, calculated H_2O activities, and thermobarometry *

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Abstract. Twenty-two hornblendes separated from amphibolites and granulites of the Grenville Orogen of Ontario have been quantitatively analyzed for major and minor elements by electron microprobe, for FeO/Fe_2O_3 by wet chemistry, and for H_2O by manometric measurement as H_2. Hornblende formulae were calculated on the basis of $24\ O + OH + Cl + F$. Most samples are magnesio-hornblendes, ferroan pargasitic hornblendes and ferroan hastingsitic hornblendes, with weight fractions of $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ranging from 0.15 to 0.50. An oxy-amphibole component of 0–25 mol%, with an average value of 17 mol%, is obtained for these complete analyses. When compared with structural formulae determined solely from microprobe data, normalization based on $13 = Si + Ti + Al + Fe + Mn + Mg$ cations provides the best approximation to hornblende formulae calculated from the complete analyses. Less satisfactory agreement is obtained from a normalization scheme based on $15 = Si + Ti + Al + Fe + Mn + Mg + Ca$, while worst agreement is obtained from normalization to 23 oxygens assuming all Fe is Fe^{2+}. No normalization scheme based on microprobe data alone consistently replicates the measured FeO, Fe_2O_3, and H_2O; accurate determination of these values requires complete chemical analyses. Ionic solution models previously have been proposed to evaluate the activity of $Ca_2Mg_5Si_8O_{22}(OH)_2$ (a_{Trem}) in hornblende for use in equilibria that constrain the activity of H_2O (a_{H_2O}) in igneous and metamorphic rocks. Application of ionic models to typical hornblendes produces low a_{Trem} (usually <0.01), consequently yielding extremely low a_{H_2O}. If an oxy-amphibole component is present, the calculated a_{Trem} and H_2O is further reduced. An oxy-amphibole component of 25% reduces the calculated H_2O activity and that of *any* hydroxyl-amphibole component by 50% below that calculated with simplified assumptions regarding X_{OH} in the hydroxyl site (i.e., $X_{OH} = 1$, or $X_{OH} = 1 - X_{Cl} - X_F$). Thus, methods of amphibole normalizations appear to have a substantial effect on calculated amphibole and H_2O activites. Before *quantitative* hornblende thermobarometry can be calibrated and applied, the amounts of FeO, Fe_2O_3 and H_2O must be measured in order to fully characterize hornblende solid solutions.

Introduction

Hornblende is commonly present in many high-grade metamorphic rocks, including mafic to felsic granulites which are generally thought to have equilibrated under conditions of $P_{H_2O} < P_{total}$ (e.g., Bohlen et al. 1980; Valley et al. 1983, 1990; Edwards and Essene 1988; Lamb and Valley 1988). The composition of hornblende may ultimately be used to constrain the metamorphic P_{H_2O} if accurate formulae and activity-composition $(a - X)$ relations are available for hornblende solid solutions. While realistic $a - X$ models for complex minerals such as hornblende have yet to be developed, it is possible to determine accurate hornblende formulae if complete chemical analyses are available. However, most petrologic studies that include hornblende in calculations of phase equilibria are based on hornblende formulae derived from incomplete electron-microprobe analyses.

Because hornblendes usually contain some ferric iron, as well as ferrous iron and hydroxyl ion, accurate hornblende formulae require accurate measurements or reliable estimates of these ions (Leake 1968). Before electron-microprobe analyses became commonplace, hornblende compositions were determined by a variety of wet chemical techniques on mineral separates that usually included measurement of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O and H_2O, in addition to measurements of Cl_2 and F_2 (e.g., Leake 1968). Such analyses of hornblende usually accounted for the significant cations and anions, and a formula was calcu-

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lated on the basis of $24 = O + OH + Cl + F$ (e.g., Deer et al. 1963). With the advent of modern electron microprobes, wet chemical analyses of mineral separates have become exceedingly rare, as data can be obtained rapidly with much less effort; nearly all recent studies report hornblende formulae estimated from electron-microprobe data alone. A serious shortcoming of the electron microprobe when used to analyze complex OH- and iron-bearing minerals, such as hornblende, is its inability to measure H_2O and to discern Fe^{2+} from Fe^{3+}. Nevertheless, most electron-microprobe analyses of hornblende continue to be published with structural formulae reported on the basis of 23 oxygens assuming that all Fe is Fe^{2+} (for careful discussions of the limitations of this method, cf. Stout 1972; Robinson et al. 1982).

In a recent experimental study, Clowe et al. (1988) measured the Fe_2O_3/FeO ratio of natural amphiboles annealed at 750° C in air and 650° C at 1 kbar, showing that this ratio varies with the f_{O_2} of the experiment and is experimentally reversible. The well known reaction is:

$$2\ Fe^{2+}(OH)_2\ \text{(in amphibole)} =$$
$$2\ Fe^{3+}O(OH)\ \text{(in amphibole)} + H_2,$$
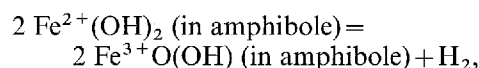
which is a measure of f_{O_2} only at fixed f_{H_2O}. Although Clowe et al. (1988) did not determine directly the H_2O contents of their amphiboles, variation in Fe_2O_3/FeO is related to concomitant variation in O/OH by the above reaction. However, the OH estimated in their amphiboles is likely to have systematic errors as the starting materials were assumed to carry stoichiometric amounts of OH, and the amounts of OH in the run products were calculated relative to the assumed OH in the starting materials. As yet the Fe_2O_3/FeO ratio in natural amphiboles cannot be related to the f_{H_2}/T at the time of last equilibration without a direct determination of O/OH and a comprehensive mixing model.

We report complete chemical analyses of 22 metamorphic hornblendes that were separated from amphibolites and tonalitic gneisses. The hornblende formulae determined on the basis of $24 = O + OH + Cl + F$ are compared to formulae calculated using electron-microprobe data alone. The common method of normalizing microprobe data to 23 oxygens while assuming that all Fe is Fe^{2+} is shown to have large systematic errors, and more reliable cation normalization schemes are suggested. Moreover, based on the inferred OH, F, Cl, and O occupancies in the OH sites of the hornblendes, we conclude that H_2O activities calculated from hornblende equilibria may be grossly in error even if the accuracies of the solution models for hornblendes can otherwise be improved.

Analytical techniques

The hornblendes examined in this study initially were purified for a geochronological investigation using organic heavy-liquid, magnetic-separation, and hand-picking techniques (Cosca et al. 1991). Based on optical evaluation, the purity of the mineral separates was judged to be >99%. In a few samples, mineral inclusions of quartz, plagioclase or ilmenite were identified with the aid of

backscattered electron imaging, but they constitute <1% of the total volume of sample.

Electron-microprobe analyses

Quantitative electron-microprobe analyses were performed on polished grain mounts of the separated hornblendes. Wavelength-dispersive analyses were obtained using the Cameca CAMEBAX electron microprobe at the University of Michigan. Standard operating conditions consisted of a focused electron beam, an accelerating potential of 15 kV, and a sample current of 10 nA. the following well-characterized standards were used for the analyses: fluor-topaz (F), Irving Kakanui hornblende (Na and Mg), Ingamells almandine (Al and Si), synthetic alforsite (Cl), Gotthard adularia (K), ANU wollastonite (Ca), synthetic geikielite (Ti), ANU rhodonite (Mn) and synthetic ferrosilite (Fe). Counting times were set to 30 s for major elements, and up to 50 s for minor elements. Raw data were corrected for atomic number, absorption, and fluorescence using Cameca (PAP) software.

Analyses of ferric iron contents

The Fe^{2+}/Fe^{3+} ratios were determined for the hornblende separates following the procedures of Wilson (1955). Ammonium metavanadate was added to the hornblende to oxidize all FeO to Fe_2O_3, and the amount of FeO in the sample was determined indirectly by measuring the amount of oxidant reduced. Approximately 0.1 g of NH_4VO_3 was added to 0.2 g of hornblende and dissolved overnight in approximately 10 ml of concentrated HF. To this solution 30 ml of 10 N H_2SO_4, 10 ml of Ba-diphenylaminesulphonate indicator, and approximately 250 ml of saturated H_3BO_3 solution were added. The amount of V^{5+} remaining in solution was determined by titrating this solution with a calibrated solution of ferrous ammonium sulphate, and the amount of FeO in the hornblende was calculated from mass balance. The amount of Fe_2O_3 was calculated from the difference between the total iron as determined on the electron microprobe and the FeO as determined by wet chemical methods. Replicate analyses of FeO were perforemd on all samples with a precision of ± 2–5% of the amount present.

Alternatively, the amounts of Fe^{2+} and Fe^{3+} could have been obtained on bulk samples of hornblende with Mossbauer spectroscopy (e.g., Hawthorne 1983). Spear (1982) gave comparisons of FeO and Fe_2O_3 obtained by Mossbauer methods and stoichiometric estimates that are in fair agreement. Unfortunately, given the multiplicity of possible sites containing Fe^{2+} and Fe^{3+}, and the serious overlaps among the Mossbauer absorption peaks, hornblende is not an ideal mineral for Mossbauer measurements. Additional tests of independently analyzed hornblendes are needed before Mossbauer spectroscopy should be accepted as yielding accurate measurements of total FeO and Fe_2O_3 in hornblende.

Water and D/H determinations

The H_2O content and δD value of each hornblende was determined using a hydrogen-isotope-extraction line at the University of Utah following the general technique of Friedman (1953). A small amount of hornblende (ca. 0.1 g) was first dried under vacuum at 100° C to remove adsorbed (non-structural) water, and then it was fused under vacuum to liberate all structural water. The structural water was collected and reduced to H_2 over uranium metal at approximately 800° C (Bigeleisen et al. 1952). The amount of H_2 was measured with a standardized Hg manometer and the D/H ratios measured by standard mass-sepctrometry techniques. The precision of H_2O determinations for this study, based on replicate analyses, is ± 2%. This method is greatly preferred over the traditional method of analysis which involves fusion and trapping of released H_2O (Penfield 1894), because part of the OH released from hornblende upon heating is driven off as H_2. The H_2 would not be trapped unless first thoroughly oxidized by a flux such as PbO or $PbCrO_4$, but such oxidants are not always used even

Table 1. Hornblende analyses including measured FeO, Fe_2O_3, H_2O and D/H ratios

	FA86-1	FA8610	FA86-3	FA86-6	FKL-6	HL8610	HL8611	HL862C	HL86-3	HL86-6	MIN863
SiO_2	40.94	44.60	41.70	41.45	41.79	40.88	42.37	42.80	45.18	44.85	43.67
TiO_2	2.69	0.62	1.43	2.56	2.00	1.05	0.97	0.59	0.74	0.33	1.00
Al_2O_3	13.28	11.58	10.07	11.56	12.87	11.34	11.76	11.80	9.63	11.38	11.02
Fe_2O_3	3.14	3.83	5.65	3.19	3.89	6.61	5.66	6.74	4.84	5.96	3.79
FeO	13.14	14.62	15.13	14.74	12.99	18.11	11.44	11.24	12.51	9.68	14.24
MnO	0.27	0.29	0.31	0.18	0.15	0.59	0.32	0.72	0.38	0.34	0.35
MgO	10.01	9.03	8.38	8.92	10.17	5.23	10.30	10.07	10.90	11.45	9.27
CaO	10.57	11.77	11.74	11.50	11.28	10.95	11.30	11.69	11.41	11.61	11.79
Na_2O	3.12	1.34	1.61	1.53	2.06	1.68	2.09	1.49	1.52	1.40	1.37
K_2O	1.04	0.11	1.66	1.88	1.31	1.35	1.22	1.12	0.42	0.25	1.52
H_2O	1.43	1.87	1.46	1.45	1.43	1.69	1.74	1.88	2.02	1.98	1.71
F_2	0.05	0.08	0.35	0.40	0.18	0.12	0.35	0.18	0.05	0.22	0.31
Cl_2	0.46	0.06	0.52	0.27	0.02	0.01	0.31	0.02	0.01	0.01	0.13
$O = F_2$	0.02	0.03	0.15	0.17	0.07	0.05	0.15	0.07	0.02	0.09	0.13
$O = Cl_2$	0.10	0.01	0.12	0.06	0.00	0.00	0.07	0.00	0.00	0.00	0.03
Sum	100.01	99.75	99.75	99.41	100.06	99.55	99.60	100.26	99.58	99.35	100.01
$\delta^2 H_{SMOW}$	-96	-80	-102	-86	-65	-95	-95	-86	-84	-81	-80

Table 1 (continued)

	MIN864	MR86-1	MR865A	MR86-8	PSM4-1	SSA-10	SAS-13	SSA-4	SSA-5	SSA-7	SSA-8
SiO_2	44.53	41.07	38.71	42.90	44.17	42.84	42.65	42.38	41.95	42.46	42.08
TiO_2	0.91	2.17	0.99	0.64	1.11	1.80	1.41	0.75	0.72	1.04	1.93
Al_2O_3	10.15	12.96	10.43	11.52	11.45	11.25	12.69	14.41	11.59	13.12	12.10
Fe_2O_3	6.10	3.99	7.49	8.14	3.88	4.15	5.26	4.10	6.41	4.96	4.25
FeO	11.31	14.88	23.83	9.14	12.92	12.63	8.83	12.29	14.16	11.36	14.55
MnO	0.33	0.09	0.62	0.40	0.26	0.26	0.31	0.26	0.47	0.25	0.17
MgO	10.40	8.16	1.09	10.60	10.15	10.49	12.26	9.60	8.49	9.92	8.76
CaO	11.59	11.62	10.28	11.52	11.11	11.65	11.63	11.99	11.46	11.53	11.42
Na_2O	1.48	1.63	1.83	1.70	1.80	1.52	1.57	1.30	1.65	1.27	1.51
K_2O	1.21	1.87	1.96	1.46	0.43	1.48	1.73	1.21	1.59	1.06	1.69
H_2O	1.78	1.49	1.78	2.11	1.64	1.44	1.41	1.88	1.68	1.86	1.49
F_{22}	0.15	0.08	0.33	0.16	0.05	0.29	1.04	0.14	0.42	0.16	0.25
Cl_2	0.08	0.02	0.15	0.08	0.47	0.15	0.02	0.11	0.02	0.04	0.03
$O = F_2$	0.06	0.03	0.14	0.07	0.02	0.12	0.44	0.06	0.18	0.07	0.11
$O = Cl_2$	0.02	0.00	0.03	0.02	0.11	0.03	0.00	0.02	0.00	0.01	0.01
Sum	99.92	99.99	99.35	100.29	99.31	99.80	100.36	100.33	100.44	98.95	100.11
$\delta^2 H_{SMOW}$	-59	-88	-83	-82	-84	-88	-68	-58	-63	-62	-94

in modifications of the Penfield method (Fairbairn 1951; Shapiro and Brannock 1956). Furthermore, the Penfield method requires 2 gm of sample, which increases the likelihood of analyzing an impure separate. Other comparisons with the techniques used here suggest that the Penfield method is far less precise (JR O'Neil personal communication 1990).

Analytical results

Chemical and isotopic analyses of the hornblendes including measured FeO, Fe_2O_3, H_2O, and D/H ratios are shown in Table 1. The electron-microprobe data represent average compositions based on at least ten individual analyses. The amphibole formulae in Tables 2–5 were generated with the Minfile program of Afifi and Essene (1989). There is no significant compositional variation between cores and rims of these hornblendes

based on electron-microprobe analyses of elements with $Z > 8$. The formulae in Table 2 were normalized on the basis of $24 = O + OH + Cl + F$ using the measured FeO, Fe_2O_3 and H_2O. Following the terminology of Leake (1978) most of the hornblendes are magnesio-hornblendes, ferroan hastingsitic hornblendes, and ferroan pargasitic hornblendes; their weight fractions of $Fe_2O_3/$ $(FeO + Fe_2O_3)$ range from 0.15 to 0.50, revealing that ferric iron is indeed at significant levels in these hornblendes (Fig. 1). A considerable oxy-hornblende component is present in some of the hornblendes, where as much as 25% of the OH site is occupied by O (Table 2). While the possibility of grain to grain variations or zoning in the oxy-amphibole content of an individual hornblende sample cannot be tested with bulk analytical techniques, the optical properties of oxy-amphibole are significantly at variance with the equivalent unoxidized and

Table 2. Structural formulae calculated on the basis of $O+OH+Cl+F=24$; includes measured FeO, Fe_2O_3 and H_2O

	FA86-1	FA8610	FA86-3	FA86-6	FKL-6	HL8610	HL8611	HL862C	HL86-3	HL86-6	MIN863
T sites											
Si	6.17	6.64	6.41	6.32	6.27	6.36	6.35	6.37	6.70	6.59	6.56
Al	1.83	1.36	1.59	1.68	1.73	1.64	1.65	1.63	1.30	1.41	1.44
M1, 2, 3 sites											
Al	0.52	0.67	0.23	0.40	0.55	0.44	0.43	0.44	0.39	0.56	0.51
Ti	0.30	0.07	0.17	0.29	0.23	0.12	0.11	0.07	0.08	0.04	0.11
Fe^{3+}	0.36	0.43	0.65	0.37	0.44	0.77	0.64	0.75	0.54	0.66	0.43
Fe^{2+}	1.54	1.79	1.94	1.88	1.49	2.36	1.43	1.40	1.53	1.19	1.79
Mn	0.03	0.04	0.04	0.02	0.02	0.08	0.04	0.09	0.05	0.04	0.04
Mg	2.24	2.00	1.92	2.03	2.28	1.21	2.30	2.24	2.41	2.51	2.07
Ca	0.00	0.00	0.05	0.00	0.00	0.02	0.05	0.01	0.00	0.01	0.05
M4 site											
Fe	0.12	0.03	0.00	0.00	0.14	0.00	0.00	0.00	0.02	0.00	0.00
Ca	1.71	1.88	1.93	1.88	1.81	1.82	1.82	1.87	1.81	1.83	1.90
Na	0.17	0.10	0.07	0.12	0.04	0.18	0.18	0.13	0.17	0.17	0.10
A site											
Na	0.74	0.29	0.41	0.33	0.56	0.33	0.42	0.30	0.27	0.22	0.29
K	0.20	0.02	0.33	0.37	0.25	0.27	0.23	0.21	0.08	0.05	0.29
Sum	0.94	0.31	0.74	0.70	0.81	0.60	0.65	0.51	0.35	0.27	0.58
Anion sites											
O	22.42	22.09	22.20	22.26	22.48	22.19	22.02	22.05	21.98	21.95	22.11
OH	1.43	1.85	1.50	1.48	1.43	1.75	1.73	1.87	2.00	1.95	1.71
F	0.03	0.04	0.17	0.19	0.08	0.06	0.17	0.08	0.02	0.10	0.15
Cl	0.12	0.02	0.13	0.07	0.01	0.00	0.08	0.00	0.00	0.00	0.03

Table 2 (continued)

	MIN864	MR86-1	MR865A	MR86-8	PSM4-1	SSA-10	SAS-13	SSA-4	SSA-5	SSA-7	SSA-8
T sites											
Si	6.62	6.24	6.26	6.34	6.60	6.44	6.27	6.27	6.34	6.35	6.36
Al	1.38	1.76	1.74	1.66	1.40	1.56	1.73	1.73	1.66	1.65	1.64
M1, 2, 3 sites											
Al	0.40	0.57	0.24	0.35	0.61	0.43	0.47	0.78	0.41	0.66	0.52
Ti	0.10	0.25	0.12	0.07	0.12	0.20	0.16	0.08	0.08	0.12	0.22
Fe^{3+}	0.68	0.46	0.91	0.91	0.44	0.47	0.58	0.46	0.73	0.56	0.48
Fe^{2+}	1.41	1.87	3.22	1.13	1.54	1.51	1.06	1.52	1.79	1.42	1.79
Mn	0.04	0.01	0.08	0.05	0.03	0.03	0.04	0.03	0.06	0.03	0.02
Mg	2.31	1.85	0.26	2.34	2.26	2.35	2.69	2.12	1.91	2.21	1.97
Ca	0.06	0.00	0.16	0.16	0.00	0.00	0.00	0.01	0.02	0.00	0.00
M4 site											
Fe	0.00	0.02	0.00	0.00	0.08	0.07	0.03	0.00	0.00	0.00	0.05
Ca	1.85	1.89	1.78	1.82	1.78	1.88	1.83	1.90	1.86	1.85	1.85
Na	0.15	0.08	0.22	0.18	0.14	0.05	0.14	0.10	0.14	0.15	0.10
A site											
Na	0.27	0.40	0.35	0.31	0.38	0.39	0.31	0.27	0.34	0.21	0.34
K	0.23	0.36	0.41	0.28	0.08	0.28	0.33	0.23	0.31	0.20	0.33
Sum	0.50	0.76	0.76	0.59	0.46	0.67	0.64	0.50	0.65	0.41	0.67
Anion sites											
O	22.14	22.45	21.87	21.82	22.22	22.38	22.13	22.05	22.10	22.06	22.37
OH	1.77	1.51	1.92	2.08	1.64	1.44	1.39	1.86	1.70	1.85	1.50
F	0.07	0.04	0.17	0.08	0.02	0.14	0.48	0.06	0.20	0.08	0.12
Cl	0.02	0.00	0.04	0.02	0.12	0.04	0.00	0.03	0.00	0.01	0.01

Table 3. Structural formulae calculated on the basis of 23 O − 0.5 (F + Cl)

	FA86-1	FA8610	FA86-3	FA86-6	FKL-6	HL8610	HL8611	HL862C	HL86-3	HL86-6	MIN863
Calculated Fe_2O_3, FeO^a, H_2O^b, and adjusted total											
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	15.97	18.06	20.21	17.61	16.50	24.06	16.53	17.31	16.86	15.03	17.65
H_2O	1.85	1.95	1.64	1.70	1.91	1.84	1.73	1.89	1.97	1.90	1.80
Total	100.12	99.44	99.35	99.35	100.16	99.04	99.02	99.60	99.04	98.67	99.72
T sites											
Si	6.16	6.69	6.47	6.34	6.27	6.44	6.44	6.47	6.79	6.69	6.60
Al	1.84	1.31	1.53	1.66	1.73	1.56	1.56	1.53	1.21	1.31	1.40
M1, 2, 3 sites											
Al	0.51	0.73	0.31	0.42	0.54	0.54	0.55	0.57	0.49	0.69	0.57
Ti	0.30	0.07	0.17	0.29	0.23	0.12	0.11	0.07	0.08	0.04	0.11
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{2+}	1.91	2.14	2.54	2.23	1.94	3.02	1.97	2.00	1.94	1.69	2.19
Mn	0.03	0.04	0.04	0.02	0.02	0.08	0.04	0.09	0.05	0.04	0.04
Mg	2.24	3.02	1.94	1.97	2.27	1.23	2.36	2.27	2.44	2.55	2.09
M4 site											
Fe	0.10	0.13	0.08	0.03	0.13	0.15	0.13	0.19	0.18	0.19	0.04
Ca	1.70	1.88	1.92	1.88	1.81	1.85	1.84	1.81	1.82	1.81	1.91
Na	0.19	0.00	0.00	0.09	0.06	0.01	0.03	0.00	0.00	0.00	0.04
A site											
Ca	0.00	0.01	0.04	0.00	0.00	0.00	0.00	0.08	0.02	0.05	0.00
Na	0.72	0.39	0.48	0.37	0.54	0.50	0.59	0.44	0.44	0.40	0.36
K	0.20	0.02	0.33	0.37	0.25	0.27	0.24	0.22	0.08	0.05	0.29
Sum	0.92	0.42	0.85	0.74	0.79	0.77	0.83	0.74	0.54	0.50	0.35
Anion sites											
O	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00
OH	1.85	1.94	1.69	1.74	1.91	1.94	1.75	1.92	1.98	1.89	1.82
F	0.03	0.04	0.17	0.19	0.08	0.06	0.17	0.08	0.02	0.11	0.15
Cl	0.12	0.02	0.14	0.07	0.01	0.00	0.08	0.00	0.00	0.00	0.03

[a] All Fe assumed as FeO
[b] Calculated from normalized formula

hydrated amphibole (Deer et al. 1963). The failure to detect obvious variations in the extinction angle and in pleochroism is therefore consistent with little zoning in the oxy-amphibole content. The oxy-hornblende contents in different hornblendes appear to reflect original variations in the oxidation environment in which these various hornblendes equilibrated during metamorphism. The amount of oxy-hornblende component present in these samples suggests that the significant oxy-hornblende substitutions observed and/or expected in extrusive environments (Popp et al. 1990) also occur in metamorphic environments.

The δD values of the hornblendes, expressed relative to Standard Mean Ocean Water (Craig 1951) vary between −58‰ to −119‰. However, the two samples with the lowest δD values, FA86-3 (−102) and MR86-5A (−119) have significantly higher total-iron contents and Fe/Mg ratios than the average, suggesting that their significantly lower δD values result from fractionation effects associated with Fe for Mg substitutions. The δD values of the remaining samples range from −58‰ to −96‰, typical of metamorphic hornblendes. There is no hydrogen isotopic evidence for post-metamorphic ex-

change with D-depleted meteoric waters that could have modified the Fe^{3+}/Fe^{2+} and water contents of these hornblendes.

Hornblende normalization schemes

The task of generating a mineral formula from an electron-microprobe analysis of hornblende is complicated by at least two unknowns, the H_2O content and the FeO/Fe_2O_3 ratio. Most hornblende analyses determined by electron microprobe are reported on an anhydrous basis with all iron as FeO. Corresponding mineral formulae usually are presented on a basis of 23 oxygens, although this calculation ignores the known substitutions of O for OH and of Fe^{3+} for Fe^{2+} in hornblende (Robinson et al. 1982). Some estimate of FeO, Fe_2O_3 and H_2O must be made if accurate hornblende formulae are to be obtained.

In order to test the validity of the normalization of hornblende to 23 oxygens we have recalculated the formulae from the data in Table 1 on the basis of 23 oxygens [−1/2(F + Cl)] assuming all Fe as Fe^{2+} (Table 3).

Table 3 (continued)

	MIN864	MR86-1	MR865A	MR86-8	PSM4-1	SSA-10	SSA-13	SSA-4	SSA-5	SSA-7	SSA-8
Calculated Fe_2O_3, FeO^a, H_2O^b, and adjusted total											
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	16.80	18.47	30.56	16.46	16.41	16.36	13.56	15.98	19.93	15.82	18.37
H_2O	1.90	1.93	1.62	1.88	1.86	1.81	1.52	1.92	1.75	1.90	1.85
Total	99.43	100.04	98.40	99.24	99.14	99.76	99.94	99.96	99.87	98.49	100.04
T sites											
Si	6.70	6.25	6.40	6.49	6.63	6.45	6.34	6.32	6.43	6.42	6.38
Al	1.30	1.75	1.60	1.51	1.37	1.55	1.66	1.68	1.57	1.58	1.62
M1, 2, 3 sites											
Al	0.50	0.57	0.43	0.55	0.65	0.45	0.56	0.86	0.52	0.76	0.54
Ti	0.10	0.25	0.12	0.07	0.13	0.20	0.16	0.08	0.08	0.12	0.22
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{2+}	2.02	2.32	4.22	2.09	2.16	2.06	1.69	1.99	2.56	2.00	2.32
Mn	0.04	0.01	0.09	0.05	0.03	0.03	0.04	0.03	0.06	0.03	0.02
Mg	2.33	1.85	0.13	2.14	2.13	2.26	2.56	2.03	1.78	2.10	1.90
M4 site											
Fe	0.09	0.03	0.14	0.15	0.14	0.10	0.16	0.10	0.16	0.14	0.08
Ca	1.87	1.89	1.82	1.85	1.79	1.88	1.85	1.90	1.84	1.86	1.85
Na	0.04	0.08	0.04	0.00	0.07	0.02	0.00	0.00	0.00	0.00	0.06
A site											
Ca	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.02	0.04	0.01	0.00
Na	0.39	0.40	0.55	0.50	0.45	0.43	0.45	0.38	0.49	0.37	0.38
K	0.23	0.36	0.41	0.28	0.08	0.28	0.33	0.23	0.31	0.20	0.33
Sum	0.62	0.76	0.96	0.80	0.53	0.71	0.79	0.63	0.85	0.58	0.71
Anion sites											
O	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00
OH	1.91	1.96	1.79	1.90	1.86	1.82	1.51	1.91	1.80	1.91	1.87
F	0.07	0.04	0.17	0.08	0.02	0.14	0.49	0.06	0.20	0.08	0.12
Cl	0.02	0.00	0.04	0.02	0.12	0.04	0.00	0.03	0.00	0.01	0.01

[a] All Fe assumed as FeO
[b] Calculated from normalized formula

The H_2O contents of hornblendes presented in Table 3 were calculated assuming $OH = 2 - F - Cl$. When comparing the formulae presented in Tables 2 and 3, the amount of ferrous iron is overestimated on a 23 anion basis by 21–85%, which produces serious errors in the calculated Mg/Fe^{2+} ratios. Many of these hornblendes have excess oxygen in the OH site, requiring normalization to more than 23 oxygens if anion normalization is used. Once electron-microprobe analyses of amphiboles are normalized to 23 oxygens, there is no unique method to estimate the FeO/Fe_2O_3 ratio, as conversion of FeO to Fe_2O_3 increases the moles of oxygen by half of the moles of Fe^{3+} that are inferred to be present. The resultant inaccuracies will preclude accurate calculations of K_D relations involving Mg/Fe^{2+} between hornblende and other ferromagnesian silicates using electron-microprobe analyses alone (cf. Graham and Powell 1984). In order to obtain a more accurate estimate of Fe^{2+}/Fe^{3+} ratios in hornblende, two alternative cation-normalization schemes have been considered.

One approach to calculating hornblende formulae from electron-microprobe data is based on a fixed sum of cations (e.g. Stout 1972; Robinson et al. 1982). With this technique it is assumed that a specified number of cations are stoichiometric for a given mineral; this procedure is widely used today for normalizing mineral formulae from electron-microprobe data for many minerals including garnets, clinopyroxenes, feldspars and magnetites. For hornblendes, the crystallographic site preferences for most common elements have been determined by X-ray structure refinements, which indicate site preferences of $Si > Al > Fe^{3+} > Ti$ in tetrahedral sites, $Al > Ti > Fe^{3+} > Fe^{2+} > Mg > Mn > Ca$ in the M1, M2, and M3 sites, $Ca > Na > Fe^{2+}$ in the M4 site, and $K > Na$ in the A site (cf. Hawthorne 1983). Because X-ray data indicate that the tetrahedral and M1, M2, M3 and usually the M4 sites in hornblendes are filled (i.e., have no vacancies) a mineral formula may be calculated based on fixed-cation occupancies in these sites. Normalization of calcium amphiboles on the basis of a fixed number of octahedral and tetrahedral cations satisfies most crystal-chemical relations.

Hornblende formulae normalized to $13 = Si + Ti + Al + Fe + Mn + Mg$ in the T, M1, M2 and M3 sites are shown in Table 4. This procedure necessarily excludes any Fe^{2+}, Mn or Mg from the M4 site and any Ca

Table 4. Structural formulae calculated on the basis of $Si+Ti+Al+ +Fe+Mn+Mg=13$

	FA86-1	FA8610	FA86-3	FA86-6	FKL-6	HL8610	HL8611	HL862C	HL86-3	HL86-6	MIN863
Calculated[a] Fe_2O_3, FeO, H_2O, and adjusted total											
Fe_2O_3	3.25	3.87	2.51	0.87	4.10	4.32	4.05	5.93	5.69	6.07	1.43
FeO	13.05	14.58	17.96	16.83	12.80	20.17	12.89	11.97	11.74	9.57	16.36
H_2O	1.87	1.96	1.65	1.71	1.93	1.87	1.75	1.92	2.00	1.93	1.81
Total	100.46	99.85	99.62	99.44	100.59	99.50	99.45	100.23	99.64	99.31	99.87
T sites											
Si	6.11	6.62	6.43	6.33	6.21	6.37	6.38	6.38	6.69	6.59	6.58
Al	1.89	1.38	1.57	1.67	1.79	1.63	1.62	1.62	1.31	1.41	1.42
M1, 2, 3 sites											
Al	0.45	0.65	0.26	0.41	0.46	0.45	0.46	0.45	0.37	0.56	0.54
Ti	0.30	0.07	0.17	0.29	0.22	0.12	0.11	0.07	0.08	0.04	0.11
Fe^{3+}	0.46	0.43	0.25	0.10	0.46	0.51	0.46	0.66	0.63	0.67	0.16
Fe^{2+}	1.53	1.81	2.36	2.15	1.59	2.63	1.62	1.49	1.45	1.18	2.06
Mn	0.03	0.04	0.04	0.02	0.02	0.08	0.04	0.09	0.05	0.04	0.04
Mg	2.23	2.00	1.93	2.03	2.25	1.21	2.31	2.24	2.41	2.51	2.08
M4 site											
Ca	1.69	1.87	1.94	1.88	1.79	1.83	1.82	1.87	1.81	1.83	1.90
Na	0.31	0.13	0.06	0.12	0.21	0.17	0.18	0.13	0.19	0.17	0.10
A site											
Na	0.59	0.26	0.42	0.33	0.39	0.33	0.43	0.30	0.25	0.23	0.30
K	0.20	0.02	0.33	0.37	0.25	0.27	0.23	0.21	0.08	0.05	0.29
Sum	0.79	0.28	0.75	0.70	0.64	0.70	0.66	0.51	0.33	0.28	0.59
Anion sites											
O	21.95	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00
OH	1.85	1.94	1.70	1.74	1.91	1.94	1.75	1.92	1.98	1.90	1.82
F	0.03	0.04	0.17	0.19	0.08	0.06	0.17	0.08	0.02	0.10	0.15
Cl	0.12	0.02	0.13	0.07	0.01	0.00	0.08	0.00	0.00	0.00	0.03

Table 4 (continued)

	MIN864	MR86-1	MR865A	MR86-8	PSM4-1	SSA-10	SSA-13	SSA-4	SSA-5	SSA-7	SSA-8
Calculated[a] Fe_2O_3, FeO, H_2O, and adjusted total											
Fe_2O_3	2.96	0.89	3.94	4.60	4.46	3.20	4.89	3.29	4.87	4.37	2.66
FeO	14.13	17.67	27.02	12.33	12.40	13.48	9.16	13.02	15.55	11.89	15.98
H_2O	1.92	1.93	1.64	1.91	1.88	1.83	1.55	1.93	1.78	1.92	1.86
Total	99.74	100.13	98.82	99.73	99.61	100.09	100.46	100.30	100.38	98.95	100.32
T sites											
Si	6.65	6.23	6.33	6.42	6.56	6.40	6.26	6.27	6.35	6.35	6.33
Al	1.35	1.77	1.67	1.58	1.44	1.60	1.74	1.73	1.65	1.65	1.67
M1, 2, 3 sites											
Al	0.44	0.55	0.34	0.45	0.56	0.38	0.46	0.79	0.42	0.66	0.48
Ti	0.10	0.25	0.12	0.07	0.12	0.20	0.16	0.08	0.08	0.12	0.22
Fe^{3+}	0.33	0.10	0.51	0.52	0.50	0.36	0.54	0.37	0.55	0.49	0.30
Fe^{2+}	1.77	2.24	3.68	1.54	1.54	1.69	1.12	1.61	1.97	1.49	2.01
Mn	0.04	0.01	0.09	0.05	0.03	0.03	0.04	0.03	0.06	0.03	0.02
Mg	2.32	1.85	0.27	2.37	2.25	2.34	2.68	2.12	1.92	2.21	1.97
M4 site											
Ca	1.86	1.89	1.80	1.85	1.77	1.86	1.83	1.90	1.86	1.85	1.84
Na	0.14	0.11	0.20	0.15	0.23	0.14	0.17	0.10	0.14	0.15	0.16
A site											
Na	0.28	0.37	0.38	0.34	0.29	0.30	0.28	0.27	0.34	0.21	0.28
K	0.23	0.36	0.41	0.28	0.08	0.28	0.32	0.23	0.31	0.20	0.32
Sum	0.51	0.73	0.79	0.62	0.37	0.58	0.60	0.50	0.65	0.41	0.60
Anion sites											
O	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00
OH	1.91	1.96	1.79	1.90	1.86	1.82	1.52	1.91	1.80	1.91	1.87
Fc	0.07	0.04	0.17	0.08	0.02	0.14	0.48	0.06	0.20	0.08	0.12
Cl	0.02	0.00	0.04	0.02	0.12	0.04	0.00	0.03	0.00	0.01	0.01

[a] Calculated from normalized formula

**Table 5.** Structural formulae calculated on the basis of $Si + Ti + Al + Fe + Mn + Mg + Ca = 15$

	FA86-1	FA8610	FA86-3	FA86-6	FKL-6	HL8610	HL8611	HL862C	HL86-3	HL86-6	MIN863
Calculated[a] Fe_2O_3, FeO, H_2O, and adjusted total											
Fe_2O_3	0.00	0.40	0.92	0.00	0.00	0.00	0.00	2.29	0.47	1.30	0.00
FeO	15.97	17.70	19.38	17.61	16.50	24.06	16.53	15.25	16.44	13.87	17.65
H_2O	1.53	1.95	1.64	1.56	1.82	1.83	1.68	1.91	1.97	1.91	1.73
Total	99.79	99.48	99.45	99.20	100.07	99.03	98.98	99.84	99.09	98.81	99.64
T sites											
Si	6.24	6.68	6.46	6.38	6.29	6.44	6.45	6.43	6.78	6.67	6.62
Al	1.76	1.32	1.54	1.62	1.71	1.56	1.55	1.57	1.22	1.33	1.38
M1, 2, 3 sites											
Al	0.62	0.73	0.29	0.47	0.58	0.55	0.56	0.52	0.48	0.66	0.59
Ti	0.31	0.07	0.17	0.30	0.23	0.12	0.11	0.07	0.08	0.04	0.11
Fe^{3+}	0.00	0.05	0.11	0.00	0.00	0.00	0.00	0.26	0.05	0.15	0.00
Fe^{2+}	1.76	2.10	2.46	2.16	1.90	3.02	1.95	1.80	2.24	1.58	2.15
Mn	0.03	0.04	0.04	0.02	0.02	0.08	0.04	0.09	0.05	0.04	0.05
Mg	2.27	2.02	1.94	2.05	2.28	1.23	2.34	2.26	2.44	2.54	2.10
M4 site											
Fe	0.27	0.11	0.05	0.10	0.18	0.15	0.16	0.11	0.17	0.15	0.09
Ca	1.73	1.89	1.95	1.90	1.82	1.85	1.84	1.89	1.83	1.85	1.91
A site											
Na	0.92	0.39	0.48	0.46	0.60	0.51	0.62	0.44	0.44	0.40	0.40
K	0.20	0.02	0.33	0.37	0.25	0.27	0.24	0.21	0.08	0.05	0.29
Sum	1.12	0.41	0.81	0.83	0.85	0.78	0.86	0.65	0.52	0.45	0.69
Anion sites											
O	22.44	22.00	22.00	22.21	22.14	22.01	22.07	22.00	22.00	22.00	22.10
OH	1.55	1.94	1.69	1.61	1.83	1.93	1.71	1.92	1.98	1.89	1.75
F	0.03	0.04	0.17	0.19	0.08	0.06	0.17	0.08	0.02	0.11	0.15
Cl	0.12	0.02	0.14	0.07	0.01	0.00	0.08	0.00	0.00	0.00	0.03

Table 5 (continued)

	MIN864	MR861A	MR865A	MR868A	PSM4-1	SSA-10	SSA-13	SSA-4	SSA-5	SSA-7	SSA-8
Calculated[a] Fe_2O_3, FeO, H_2O, and adjusted total											
Fe_2O_3	0.00	0.00	0.00	0.44	0.00	0.00	0.16	0.58	1.08	0.20	0.00
FeO	16.80	18.47	30.56	16.07	16.41	16.36	13.42	15.46	18.96	15.65	18.37
H_2O	1.85	1.80	1.57	1.89	1.74	1.78	1.52	1.92	1.76	1.90	1.75
Total	99.37	99.91	98.35	99.29	99.02	99.72	99.96	100.02	99.98	98.51	99.94
T sites											
Si	6.72	6.28	6.42	6.49	6.66	6.46	6.33	6.32	6.41	6.42	6.40
Al	1.28	1.72	1.58	1.51	1.34	1.54	1.67	1.68	1.59	1.58	1.60
M1, 2, 3 sites											
Al	0.52	0.61	0.46	0.54	0.70	0.46	0.55	0.85	0.50	0.75	0.57
Ti	0.10	0.25	0.12	0.07	0.13	0.20	0.16	0.08	0.08	0.12	0.22
Fe^{3+}	0.00	0.00	0.00	0.05	0.00	0.00	0.02	0.06	0.12	0.02	0.00
Fe^{2+}	1.99	2.27	4.06	1.90	1.87	1.95	1.52	1.84	2.30	1.84	2.20
Mn	0.04	0.01	0.09	0.05	0.03	0.03	0.04	0.03	0.06	0.03	0.02
Mg	2.34	1.86	0.27	2.39	2.28	2.36	2.72	1.97	1.93	2.23	1.99
M4 site											
Fe	0.13	0.09	0.18	0.13	0.20	0.11	0.15	0.08	0.12	0.13	0.14
Ca	1.87	1.91	1.82	1.87	1.80	1.89	1.85	1.92	1.88	1.87	1.86
A site											
Na	0.43	0.48	0.59	0.50	0.53	0.44	0.45	0.38	0.49	0.37	0.45
K	0.23	0.36	0.42	0.28	0.08	0.28	0.33	0.23	0.31	0.20	0.33
Sum	0.66	0.84	1.01	0.78	0.61	0.72	0.78	0.61	0.80	0.57	0.78
Anion sites											
O	22.08	22.18	22.06	22.00	22.00	22.03	22.00	22.00	22.00	22.00	22.09
OH	1.86	1.84	1.73	1.90	1.76	1.79	1.51	1.91	1.80	1.91	1.78
F	0.07	0.04	0.17	0.08	0.02	0.14	0.49	0.06	0.20	0.08	0.12
Cl	0.02	0.00	0.04	0.02	0.12	0.04	0.00	0.03	0.00	0.01	0.01

[a] Calculated from normalized formula
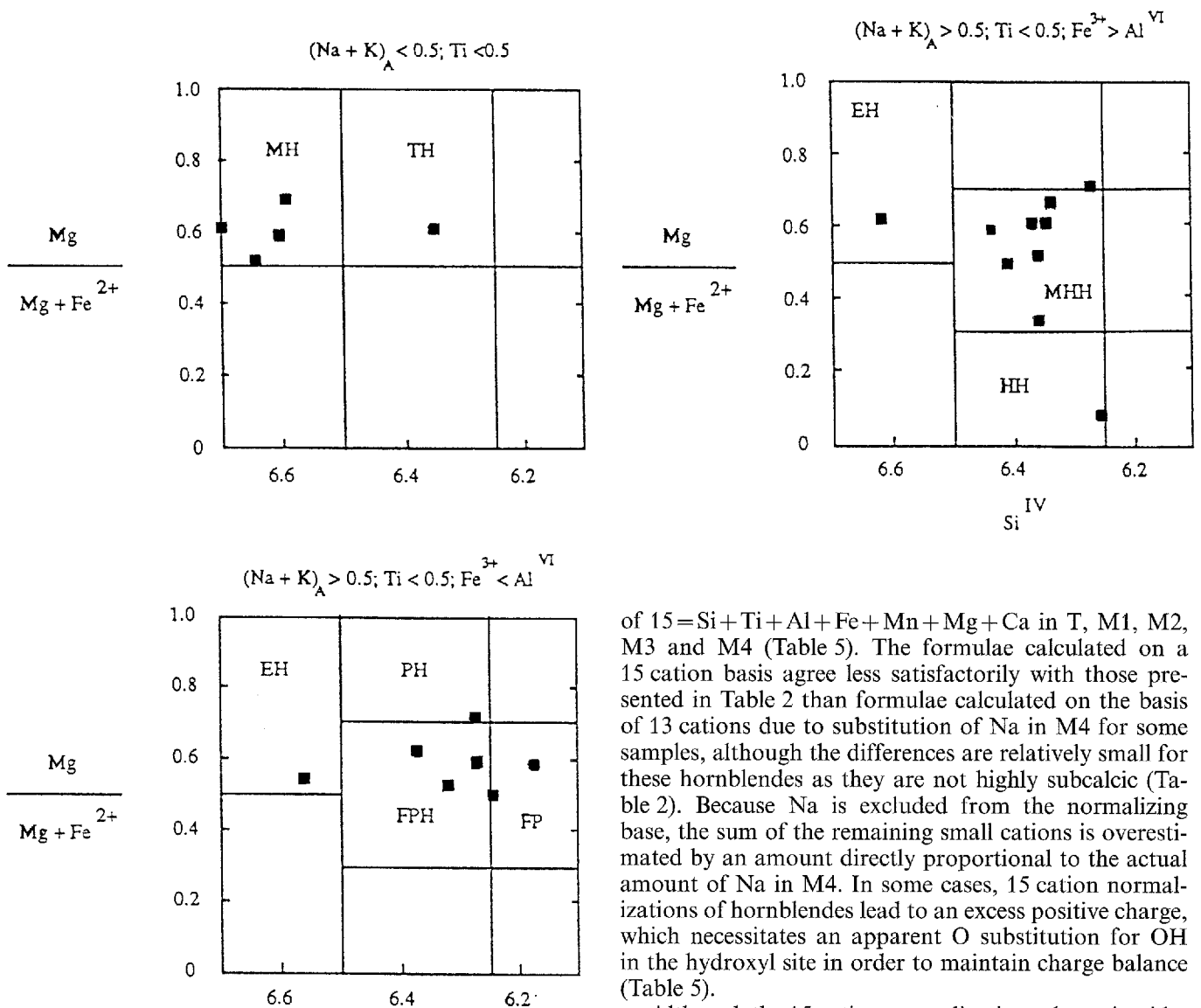
Fig. 1. Plots of amphiboles analyzed for this study on the diagram of Leake (1978). *MH*, magnesio-hornblende; *TH*, tschermakitic hornblende; *EH*, edenitic hornblende; *PH*, pargasitic hornblende; *FPH*, ferroan pargasitic hornblende; *FP*, ferroan pargasite; *MHH*, magnesian hastingsitic hornblende; *HH*, hastingsitic hornblende

from the M1, M2, or M3 sites. The molecular proportions of OH and the equivalent weight percent H_2O were calculated assuming $OH = 2 - Cl - F$, and the Fe^{2+}/Fe^{3+} ratios were estimated from charge balance. Comparison of these formulae with those presented in Table 2 indicates good agreement in measured vs calculated FeO and in the distributions of elements, but poor agreement in measured vs estimated H_2O. The differences between the formulae in Tables 2 and 4 are due mainly to excess O inferred to occupy the OH sites in some samples. The 13 cation normalization procedure excludes the possibility of Fe^{2+} substitution in M4, which may be significant in highly subcalcic hornblendes that coexist with cummingtonite or hypersthene.

An alternative normalization procedure was performed with the electron-microprobe data on the basis of $15 = Si + Ti + Al + Fe + Mn + Mg + Ca$ in T, M1, M2, M3 and M4 (Table 5). The formulae calculated on a 15 cation basis agree less satisfactorily with those presented in Table 2 than formulae calculated on the basis of 13 cations due to substitution of Na in M4 for some samples, although the differences are relatively small for these hornblendes as they are not highly subcalcic (Table 2). Because Na is excluded from the normalizing base, the sum of the remaining small cations is overestimated by an amount directly proportional to the actual amount of Na in M4. In some cases, 15 cation normalizations of hornblendes lead to an excess positive charge, which necessitates an apparent O substitution for OH in the hydroxyl site in order to maintain charge balance (Table 5).

Although the 15 cation normalization scheme is widely thought to provide an upper limit to the amount of ferric iron (Stout 1972; Robinson et al. 1982; Spear 1982), this cannot be the case when a significant oxyamphibole component substitutes in hornblende. No cation-based scheme can be used to detect the difference between $Fe^{2+}OH$ and $Fe^{3+}O$ in hornblende, because the amount of iron and the total charge is the same in both cases. The only limit that can be placed on ferric iron is when no hydroxyl ion is left to be converted to oxygen or when all ferrous iron is oxidized to ferric iron. This little-appreciated inference is equally applicable to cation normalizations of other amphiboles, allanites, chlorites, clay minerals, hoegbomites, illites, micas, pumpellyites, staurolites, vesuvianites, i.e., all hydroxyl-bearing minerals that may contain both ferric and ferrous iron.

The differences between normalization schemes can be viewed by comparison with the formulae presented in Table 2. For elements other than Fe, the cation-site assignments from the various normalization schemes yield relatively small differences. However, significant differences in the estimated Fe^{2+}/Fe^{3+} ratios are obtained in the different procedures. Figure 2 is a plot of
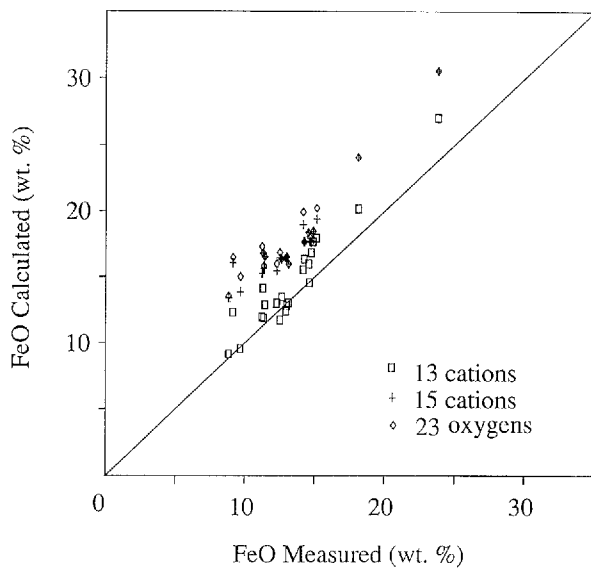
Fig. 2. Plot of measured vs calcualted FeO for hornblendes investigated in this study. Normalization schemes described in text
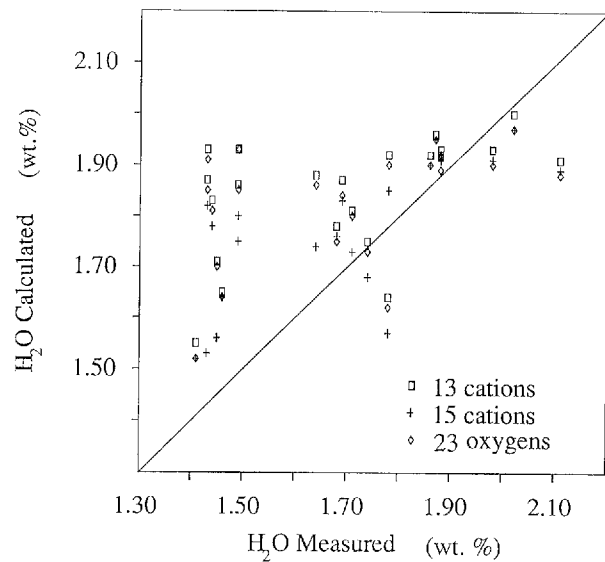

Fig. 4. Plot of measured vs calculated H_2O for hornblendes investigated in this study. Normalization schemes described in text
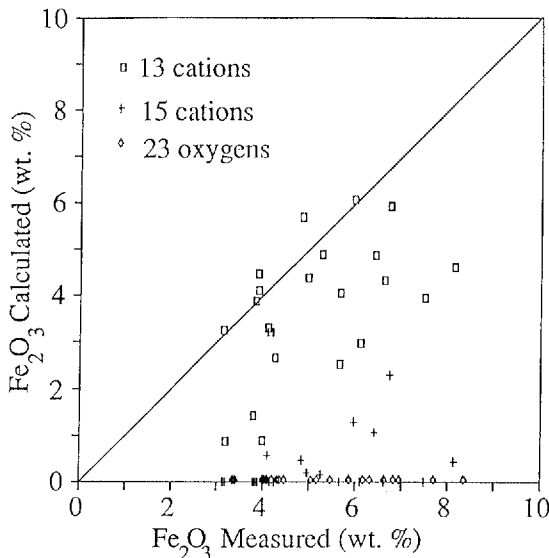

Fig. 3. Plot of measured vs calculated Fe_2O_3 for hornblendes investigated in this study. Normalization schemes described in text
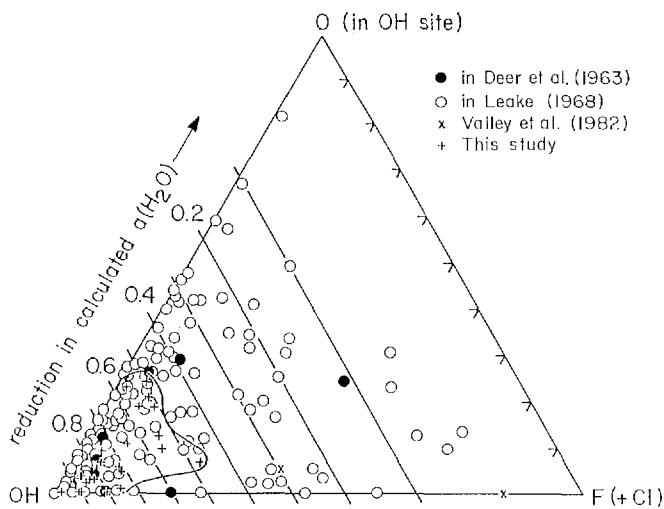
poor agreement suggests that H_2O contents of hornblendes should not be estimated from electron-microprobe data alone even if F_2 and Cl_2 are analyzed and that the H_2O content of hornblende should only be determined by direct measurement.

Effects on a_{H_2O} calculations

Hornblende should be useful in constraining the a_{H_2O} especially in rocks metamorphosed to the granulite facies, which are generally believed to have formed under relatively "dry" (i.e., $P_{H_2O} < P_{solid}$) and fluid-absent (i.e., $P_{fluid} < P_{solid}$) conditions. However, the occurrence in many granulites of OH-, F-, and/or Cl-bearing minerals, such as hornblende or biotite, indicates the presence of some fluid components locked up in the solids during metamorphism. The activities of fluid components buffered by the coexisting solids are essential in constraining the former presence or absence of a fluid phase and the formation of a melt phase in granulites. Unfortunately, accurate estimates of the activities of major fluid species are difficult to obtain in most igneous or metamorphic rocks.

Investigations aimed at constraining fluid compositions in high-grade rocks have relied on phase equilibria involving biotite (e.g., Bohlen et al. 1980; Phillips 1980; Edwards and Essene 1988) or amphibole (e.g., Phillips 1980; Valley et al. 1982; Ghent 1988; Lamb and Valley 1988). For granulite facies assemblages containing tremolitic amphiboles, several reactions have been applied that constrain H_2O activity during metamorphism (e.g., Valley et al. 1982, 1983, 1990; Ghent 1988; Lamb and Valley 1988). However, for granulites containing hornblende rather than tremolite, a reduced $Ca_2Mg_5Si_8O_{22}(OH)_2$ activity (a_{Trem}) must be calculated from a hornblende analysis if the same equilibria are to be applied. Unfortunately, no measured $a - X$ relations are

the amount of FeO determined by titration vs the amount of FeO calculated from each of the normalization schemes outlined above. Similarly, a plot of measured vs calculated Fe_2O_3 is presented in Fig. 3. Although not in perfect agreement, the results presented in Figs. 2 and 3 indicate that fairly reasonable estimates of FeO and Fe_2O_3 may be obtained after normalization on the basis of 13 small cations. All normalizations tend to underestimate the amount of Fe_2O_3 and to overestimate the amount of FeO (Figs. 2, 3), but the best normalization scheme for estimating Fe^{2+}/Fe^{3+} ratios of these amphiboles is based on 13 small cations (Fig. 4). In contrast, there is no systematic reltionship between measured and calculated H_2O contents from the different normalization schemes, although the estimates of H_2O are generally higher than measured values. The

Fig. 5. Plot of hydroxyl site occupancy of amphiboles from this study together with data from other workers. Also shown are lines of reduced H_2O (and hydroxyl-amphibole) activity assuming an ionic solution model on the hydroxyl site

as yet available for calcic amphiboles, and the ionic models that have thus far been proposed are extremely sensitive to composition (Ghent 1988). As a result, attempts to constrain H_2O activities using equilibria applied to most natural assemblages with hornblende yield unreasonably low values and highly imprecise results (e.g., Phillips 1980; Ghent 1988; Lamb and Valley 1988; Valley et al. 1990). Ionic solution models applied to hornblende compositions are, in addition, highly sensitive to F, Cl, and O substitutions in the OH site. For instance, if an ionic solution model of the form $a_{Trem} = (X_\square^A) (X_{Ca}^{M4})^2 (X_{Mg}^{M1,2,3})^5 (X_{Si}^T)^8 (X_{OH})^2$ (e.g., Powell 1975) or if a locally charge balanced model such as $(X_\square^A)$ $(X_{Ca}^{M4})^2 (X_{Mg}^{M1,3})^3 (X_{Mg}^{M2})^2 (X_{OH})^2$ (e.g., Essene 1989) is used for hornblende, substitution of F, Cl, and O in the hydroxyl site may significantly reduce the calculated a_{Trem} and a_{H_2O}. To illustrate these effects and their influence on calculated H_2O activity based on an ideal ionic solution model of OH – F – Cl – O exchange for hornblende (and biotite), the measured hydroxyl-site occupancies of hornblendes from this study are plotted for hornblende together in Fig. 5 with similarly characterized hornblendes from the literature. Substitution of 25 mol% O and/or F for OH is common in hornblende (Fig. 5). For an ideal OH-site mixing model, substitution of 25% F + Cl + O for OH decreases the calculated H_2O activity by 50%. Substitution of greater O for OH (Fig. 5) may indicate lower H_2O activity, although late oxidation of hornblende will also decrease the H_2O content and increase the Fe_2O_3/FeO ratio concomitantly (Deer et al. 1963). Conversely, inclusion of more hydrous alteration products such as chlorite will increase the apparent H_2O content of an impure separate. Quantitative microanalytical techniques such as ion-microprobe or laser-Raman analysis on a more routine basis could minimize such problems and could also be used to evaluate zoning of OH. Nonetheless, determination of such substitutions in optically pure bulk samples is still important especial-

ly if hornblendes are seen to be unzoned by optical and microprobe observations.

Substitutions of F and Cl in hornblendes may be evaluated by electron-microprobe analysis, but the H_2O content is generally estimated by assuming that OH (+ F + Cl) fully occupies the hydroxyl site. The substitution of O for OH is difficult to evaluate without direct measurements of H_2O, FeO, and Fe_2O_3 contents. Therefore, even when reliable solution models eventually become available for hornblendes, direct determination of H_2O will still be necessary to document the presence of oxygen in the hydroxyl site if hornblende is to be used for precise calculations of H_2O and hydroxyl-amphibole activities.

Implications for hornblende thermobarometry

Hammarstrom and Zen (1986) proposed an empirically derived barometer involving the Al content of hornblende solid solutions, which has recently become widely used in studies of granitic rocks (e.g., Hollister et al. 1987; Ague and Brimhall 1988; Anderson 1988; Barton et al. 1988). Hollister et al. (1987) empirically recalibrated this barometer based on additional comparisons with other field-based barometers. Johnson and Rutherford (1989) and Rutter et al. (1989) measured the pressure dependence of the Al content in hornblendes with experimental calibrations, which yield somewhat different pressures than the empirically based equations of Hammarstrom and Zen (1986) and of Hollister et al. (1987). Blundy and Holland (1990) sharply criticize the hornblende barometer suggesting that the emperical correlations between total aluminum in igneous hornblende and pressure may instead reflect variations in granitoid solidus temperatures with pressure. Because none of the above calibrations of the "hornblende barometer" are thermodynamically based, the possible effects of variable ferric iron and/or oxy-substitutions in hornblendes for this barometer are difficult to evaluate. If the serious shortcomings of the hornblende barometer (e.g., Blundy and Holland 1990) can be overcome, the levels of Fe^{3+}/Fe^{2+} and O/OH should be estimated or measured in the natural and synthetic hornblendes on which the barometers are based so that variations in these substitutions can be incorporated in the barometric calibrations. Hornblende barometry is related to the tschermakite exchange, which has been approximated by the total aluminum in hornblende (Hollister et al. 1987). As a first-order approximation, ferric iron could be added to total aluminum or tetrahedral Al alone could be used, assuming that ferri-tschermakite would have the same effect as tschermakite. In addition, the effects of variable P_{H_2O} and of solid solutions in the coexisting minerals (especially biotite and K-feldspar) should be explicitly considered for this barometer. Hornblende barometry needs to be reevaluated using a specific solid-solid reaction while including complete chemical analyses of participating phases and realistic mixing models for hornblendes (and biotites or other hydrous phases if used

in such calculations). These will not be easy tasks to accomplish.

Graham and Powell (1984), Nabelek and Lindsley (1985), Kohn and Spear (1989, 1990) and Blundy and Holland (1990) evaluated various other hornblende-bearing equilibria as potential thermometers and/or barometers. These empirical calibrations yield reasonable apparent temperatures and pressures over restricted $P - T$ ranges of application. However, in none of the hornblende thermobarometers was the effect of the "hidden" substitutions involving Fe^{3+}/Fe^{2+} and O/OH evaluated in hornblende (and biotite). In addition to the serious difficulties currently engendered by inadequate solution models, *any thermobarometry involving complex hydroxyl-bearing silicates, such as hornblende and biotite, cannot be viewed as fully quantitative until such substitutions are measured and their effects evaluated.*

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