

MAGNESIAN HORNBLende FROM A METAMORPHOSED ULTRAMAFIC BODY IN SOUTHWESTERN FINLAND: CRYSTAL CHEMISTRY AND PETROLOGICAL IMPLICATIONS

FRANCO MANCINI¹

Geologian ja Mineralogian Laitos, Turun Yliopisto, FIN 20014, Turku, Finland

REIJO SILLANPÄÄ

Kemian Laitos, Epäörganinen Kemian Laboratorio, Turun Yliopisto, FIN 20014, Turku, Finland

BRIAN MARSHALL

Department of Applied Geology, University of Technology, Sydney, Australia 2007

HEIKKI PAPUNEN

Geologian ja Mineralogian Laitos, Turun Yliopisto, FIN 20014, Turku, Finland

ABSTRACT

A synkinematic sample of magnesian hornblende from a Svecofennian ultramafic body in southwestern Finland, metamorphosed under conditions of the upper amphibolite – lower granulite facies, has been structurally refined to $R = 0.027$ for 1082 reflections. The distribution of cations in $M(1)$, $M(2)$ and $M(3)$ is inferred from site-scattering refinement and the relations between mean bond-length and ionic radius. The Fe^{2+} -ordering pattern is $M(1) > M(3) \gg M(2)$. Fe^{2+} -Mg partitioning between the $M(1)$ and $M(3)$ sites ($K_D^{M(1)-M(3)} = 0.85$) is consistent with high-temperature hornblende ($800^\circ < T < 900^\circ\text{C}$), whereas Fe^{2+} -Mg distribution between the $M(1)$ and $M(2)$ sites ($K_D^{M(1)-M(2)} = 0.45$) is in better agreement with a lower inferred peak of metamorphism ($T = 700^\circ\text{C}$). Owing to uncertainties in the Mg($M4$) estimates, the Fe^{2+} -Mg partitioning between $M(2)$ and $M(4)$, ($K_D^{M(2)-M(4)} = 4.7 \cdot 10^{-2}$) corresponds to an unrealistically high temperature of equilibration ($800^\circ < T < 900^\circ\text{C}$). Compared with other structurally refined calcic amphiboles from ultramafic parageneses, the extent of solid solution toward cummingtonite, 9.8%, is consistent with pressure and temperature being the main controlling parameters. The refined distribution of cations correlates with the physicochemical conditions of peak and post-peak metamorphic equilibration. Thus: (1) the low contents of ^{23}Na and Al_T , which indicate a low pressure (<3 kbar), combined with the high temperatures ($680^\circ < T < 720^\circ\text{C}$) required by the amphibole-plagioclase exchange equilibrium, are consistent with a period of decompression and uplift accompanied by heating; (2) the low oxidation ratio, the absence of detectable Cl, and the limited extent of F-for-OH substitution, imply that hydration of the ultramafic body resulted from hydrothermal fluids of low $f(\text{O}_2)$, near the magnetite-wüstite buffer, and low fugacity of halogens, and was therefore likely unrelated to dehydration of a downgoing slab.

Keywords: ultramafic rocks, metamorphism, magnesian hornblende, structural refinement, degree of Fe-Mg order, site occupancies, pressure, temperature, Finland.

SOMMAIRE

Nous avons affiné la structure d'un échantillon syn-cinématique de hornblende magnésienne provenant d'un massif ultramafique du sud-ouest de la Finlande, équilibré dans les conditions du faciès amphibolite supérieur à granulite inférieur, ceci jusqu'à un résidu R de 0.027 en utilisant 1082 réflexions. La distribution des cations dans les sites $M(1)$, $M(2)$ et $M(3)$ découle de l'affinement de l'occupation des sites, et des relations entre longueur moyenne de liaison et rayon ionique. Le Fe^{2+} est réparti selon le schéma $M(1) > M(3) \gg M(2)$. La distribution de Fe^{2+} et de Mg sur les sites $M(1)$ et $M(3)$ ($K_D^{M(1)-M(3)} = 0.85$) concorde avec ce qui caractérise la hornblende de température élevée ($800^\circ < T < 900^\circ\text{C}$), tandis que leur distribution entre les sites $M(1)$ et $M(2)$ ($K_D^{M(1)-M(2)} = 0.45$) concorde mieux avec une température plus faible de métamorphisme ($T = 700^\circ\text{C}$). A cause d'une incertitude dans le contenu du site $M(4)$ en Mg, la répartition de Fe^{2+} et Mg entre $M(2)$ et $M(4)$, ($K_D^{M(2)-M(4)} = 4.7 \cdot 10^{-2}$) indique une température d'équilibration trop élevée, et jugée invraisemblable ($800^\circ < T < 900^\circ\text{C}$). En comparaison avec d'autres exemples d'amphibole calcique provenant de milieux ultramafiques, dont la structure a été affinée, l'écart de cette

¹ E-mail address: fmancini@utu.fi

solution solide vers le pôle cummingtonite concorde avec l'hypothèse que la température et pression ont été les contrôles importants de la composition de la hornblende. Le schéma de distribution des cations concorde avec les conditions physicochimiques pendant le paroxysme métamorphique et au cours du refroidissement et de la décompression régionales. La faible teneur de ^{24}Na et de Al_T , qui indiquerait une faible pression (<3 kbar), en même temps que la température élevée ($680^\circ < T < 720^\circ\text{C}$) nécessaire pour expliquer l'équilibre d'échange entre amphibole et plagioclase, semblent indiquer une période de décompression et de soulèvement régional avec réchauffement. Le faible taux d'oxydation, l'absence de Cl, et l'insignifiance du taux de substitution de F pour OH font penser que l'hydratation du massif ultramafique a impliqué une phase fluide hydrothermale de faible fugacité d'oxygène, en équilibre avec l'assemblage magnétite-wüstite, et de halogènes, et donc probablement sans relation à la déshydratation d'un socle en subduction.

(Traduit par la Rédaction)

Mots-clés: roches ultramafiques, métamorphisme, hornblende magnésienne, affinement structural, degré d'ordre Fe-Mg, occupation des sites, pression, température, Finlande.

INTRODUCTION

Calcic amphibole is an important rock-forming mineral in hydrous metamorphic rocks. It is stable from the greenschist to granulite facies, and its compositional trends vary with host-rock composition, oxygen fugacity, pressure and temperature (Spear 1981a, Robinson *et al.* 1982, Holland & Blundy 1994, Anderson & Smith 1995). Although great care must be invested in defining the system, the distribution of cations in calcic amphiboles may have geothermometric (Cameron 1975, Spear 1981a, Holland & Blundy 1994) and geobarometric applications (Raase 1974, Cameron 1975, Brown 1977, Hammarstrom & Zen 1986, Anderson & Smith 1995). Calcic amphibole is the principal constituent of the 1.9-Ga polymetamorphic Ni-bearing ultramafic bodies in southwestern Finland (Peltonen & Korsman 1990, Marshall & Mancini 1994, Peltonen 1995, Mancini *et al.* 1996). Its role in prograde reactions accompanying peak metamorphism has been discussed by Mancini *et al.* (1996), but because the compositions determined by electron-microprobe analysis lack structural data, details of its crystal chemistry remain obscure. Our purpose in this paper is to document the mineral chemistry of a synkinematic calcic amphibole from the Sääksjärvi area of southwestern Finland and to examine the metamorphic implications of the site occupancies.

PETROGRAPHY OF THE INTRUSIVE BODIES AND OCCURRENCE OF MAGNESIAN HORNBLLENDE

Metaperidotite, metadunite and metapyroxenite form the principal rock-types of the intrusive bodies of the Proterozoic (1.8–2.0 Ga old) Vammala Nickel Belt in southwestern Finland (Mäkinen 1987, Peltonen 1995, Mancini *et al.* 1996). These cumulate bodies relate to the volcanic arc magmatism that developed above a subduction zone, at the margin of the Archean Karelian continent (Mäkinen 1987, Peltonen 1995). The metadunite and metaperidotite (olivine – calcic amphibole – pyroxene are dominant) are low in aluminum and typically lack plagioclase, the latter

instead found as accessory phase in hornblende (metapyroxenite) and in less common metagabbro (Mancini *et al.* 1996). Although principally metamorphic, relict cumulate-textured olivine, pyroxene and chromite have been reported (Marshall & Mancini 1994, Peltonen 1995). Magnesian hornblende is found in all the assemblages formed at the peak of metamorphism in the upper amphibolite facies: i) Hbl + Ol (Fo_{78-83}) + Chr; ii) Hbl + Ol + Opx \pm Phl; iii) Hbl + Ol + Cpx + Opx; iv) Hbl + Pl (An_{42-60}) + Cum + Cpx + Ti-Fe oxides \pm Phl. Accessory phases are serpentine, chromian spinel, graphite, carbonate, Fe-Ti oxide and Ni-Cu-Fe sulfides. The polymetamorphic history of the ultramafic rocks is reflected by a second generation of calcic amphibole and the common replacement textures associated with amphibolitization and phlogopitization, indicative of chemical transfer from the country rocks. Prograde synkinematic magnesian hornblende is porphyroblastic in metaperidotite, whereas it is idioblastic and prismatic in hornblende and in the rare metagabbro. Retrograde tremolite is either nematoblastic and overprints other phases, or it overgrows coexisting minerals and is equigranular. Aluminum- and alkali-rich tschermakitic hornblende occurs in certain examples of metapicrite of the Vammala area (Peltonen 1995), but the paragenesis is uncertain.

On the basis of textural relationships, peak metamorphic temperatures in the upper amphibolite or even lower granulite facies (T in the range $700\text{--}720^\circ\text{C}$) have been inferred from the chlorite-out and the orthopyroxene-in isograds (Mancini *et al.* 1996), the latter presumably involving high levels of cummingtonite solid-solution (*e.g.*, Robinson *et al.* 1982). In some cases, calcic amphibole contains cusped inclusions of augite (Fig. 1a) interpreted to indicate the breakdown of amphibole to clinopyroxene which, in the presence of plagioclase and Fe-Ti-oxides, corresponds with a temperature in the range $700\text{--}750^\circ\text{C}$ (Spear 1981a). Other grains contain saussuritized blebs of plagioclase (Fig. 1b) similar to those described by Blundy & Holland (1990), indicating an amphibole – plagioclase reaction. Later retrogression to the upper greenschist or lower amphibolite facies is supported by geothermo-

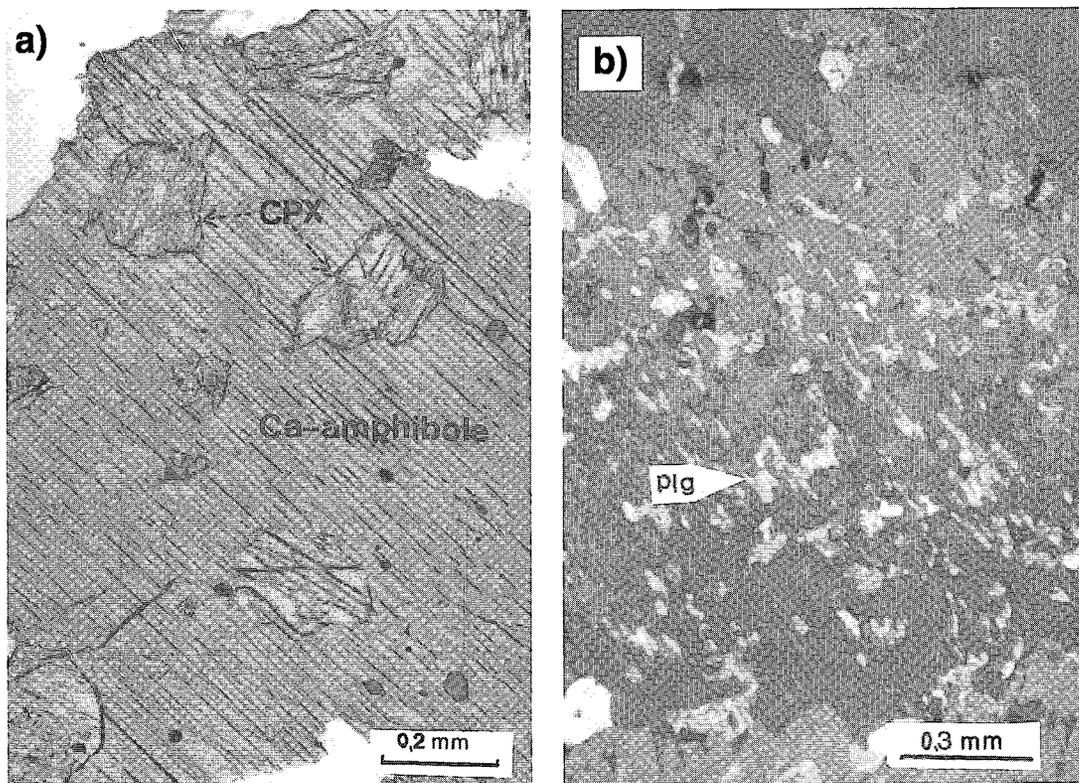


FIG. 1. Microphotograph of magnesian hornblende from the Sääksjärvi intrusive body containing: A) cusped and lobate inclusions of augite, and B) exsolution blebs of plagioclase (saussuritized). Crossed nicols.

metry based on olivine – chromian spinel (580–640°C) and pyroxene (600–700°C) (Peltonen 1995, Mancini *et al.* 1996), formation of “ferrit-chromit” (Peltonen & Korsman 1990), of (100) exsolution lamellae of augite in orthopyroxene, and of (100) and (101) lamellae of cummingtonite in calcic amphibole (Mancini *et al.* 1996). A suitable paragenesis for geobarometry does not exist in these ultramafic rocks, but pressure estimates from the mineral assemblages in the country rocks indicate a pressure in the range 4–5 kbar (Peltonen & Korsman 1990, Kilpeläinen & Rastas 1992), consistent with low pressure – high temperature (LP-HT) metamorphism.

EXPERIMENTAL PROCEDURES

The magnesian hornblende used in this structural refinement was taken from a drill-core sample of hornblende (metapyroxenite) from the Sääksjärvi ultramafic body. The mineral assemblage comprises magnesian hornblende (85–90%), plagioclase (An_{48-52} ; 5–8%), augite + olivine (1–2%), and accessory albite + cummingtonite + ilmenite + titaniferous magnetite. In thin section, magnesian hornblende is pleochroic

(*X* pale tan, *Y* brownish green, *Z* pale green), with colorless (100) and (101) lamellae of cummingtonite. The straight intergrain boundaries of amphibole against sporadic plagioclase are consistent with equilibrium crystallization. The crystal was selected on the basis of optical clarity and freedom from inclusions.

Electron-microprobe data

The chemical composition of the magnesian hornblende was determined with a JEOL electron microprobe and an energy-dispersion detector. Operating parameters were: 15 kV, a 20-nA current beam, and a beam diameter of 20 μm . Silicates and oxides were employed as standards. The composition quoted in Table 1 is the average of six points. The concentrations Na and K were particularly checked to evaluate degree of evaporation, but this yielded negative results.

Collection of X-ray data and structure refinement

X-ray data were collected with a Rigaku AFC5S automatic four-circle diffractometer (graphite-

TABLE 1. CHEMICAL COMPOSITION OF MAGNESIAN HORNBLLENDE FROM SÄÄKSJÄRVÄ*

OXIDES	wt %	atoms per 23 O	
SiO ₂	50.16	Si	7.269
TiO ₂	0.49	IVAl	0.704
Al ₂ O ₃	5.85	Σ[VI]	8.000
FeO _T	10.55	VIAl	0.301
MgO	16.42	Fe ²⁺	1.197
MnO	0.23	Mg	3.450
CaO	10.88	Ti	0.054
K ₂ O	0.01	Σ[C]	5.000
Na ₂ O	1.59	Fe ²⁺	0.087
Cl	<0.01	Mn	0.029
F	0.03	Mg	0.110
Total	96.21	Ca	1.696
		Na	0.080
		Σ[B]	2.000
		K	0.011
		Na	0.369

Chemical composition determined by electron-microprobe analysis. *Average of six points.

TABLE 2. CRYSTAL DATA* AND REFINEMENT INFORMATION

a (Å)	9.857(1)
b (Å)	18.112(1)
c (Å)	5.309(1)
β (°)	104.81(1)
V (Å ³)	916.40
Scan mode	2θ-ω
2θ _{max} (°)	55
Refl. (total)	1142
Refl. (unique)	1083
Refl. (suppr.)	1
F ₀ > 4σ	988
wR (F ₀ ²)	0.0689
R = Σ F ₀ - F _{calc} / Σ F ₀	0.0275

*Space group: C2/m.

TABLE 3. ATOMIC COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS OF MAGNESIAN HORNBLLENDE FROM SÄÄKSJÄRVÄ

Site	x	y	z	U _{eq} (x 10 ⁵)*
T(1)	0.28043(7)	0.08473(3)	0.29766(12)	39(2)
T(2)	0.28980(6)	0.17165(3)	0.80710(12)	44(3)
M(1)	0	0.08867(4)	1/2	72(2)
M(2)	0	0.17758(4)	0	50(3)
M(3)	0	0	0	64(3)
M(4)	0	0.27859(15)	1/2	102(14)
M(4')	0	0.25303(237)	1/2	141(65)
O(1)	0.10972(17)	0.08803(9)	0.21450(32)	122(3)
O(2)	0.11919(17)	0.17282(9)	0.72856(31)	116(3)
O(3)	0.11049(25)	0	0.71371(45)	120(7)
O(4)	0.36759(18)	0.24858(10)	0.79144(32)	141(3)
O(5)	0.34774(17)	0.13612(10)	0.10242(30)	139(3)
O(6)	0.34322(17)	0.11856(9)	0.59259(31)	133(3)
O(7)	0.33548(26)	0	0.28790(48)	147(5)
A(2/m)	0	1/2	0	463(149)
A(2)	0	0.51594(471)	0	627(256)
H	0.20245(583)	0	0.77002(955)	117 (86)

*U_{eq} = 1/6σ²Σ_iU_{ij} a_j · a_j

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN MAGNESIAN HORNBLLENDE FROM SÄÄKSJÄRVÄ

T(1)-O(1)	1.627(1)	M(4)-O(2) × 2	2.406(4)
-O(5)	1.653(2)	-O(4) × 2	2.316(2)
-O(6)	1.647(2)	-O(5) × 2	2.733(3)
-O(7)	1.633(1)	-O(6) × 2	2.547(4)
-T(1)-O>	1.640	<M(4)-O>	2.501
T(2)-O(2)	1.627(2)	M(4)-O(2) × 2	2.057(7)
-O(4)	1.603(9)	-O(4) × 2	2.264(1)
-O(5)	1.655(3)	-O(5) × 2	3.019(6)
-O(6)	1.675(9)	-O(6) × 2	2.903(1)
<T(2)-O>	1.639	<M(4)-O>	2.561
M(1)-O(1) × 2	2.074(1)	M(4)-M(4)'	0.463(1)
-O(2) × 2	2.108(7)	A(2/m)-O(5) × 4	3.007(1)
-O(3) × 2	2.101(1)	-O(6) × 4	3.157(1)
<M(1)-O>	2.094	-O(7) × 2	3.713(1)
M(2)-O(1) × 2	2.113(2)	-O(7) × 2	2.496(2)
-O(2) × 2	2.080(2)	<A(2/m)-O>	3.089
-O(4) × 2	1.995(2)	A(2)-O(5) × 2	2.775(1)
<M(2)-O>	2.063	-O(5) × 2	3.248(1)
M(3)-O(1) × 4	2.092(2)	-O(6) × 2	2.968(1)
-O(3) × 2	2.083(3)	-O(6) × 2	3.360(1)
<M(3)-O>	2.090	-O(7) × 2	2.512(2)
		-O(7) × 2	3.724(1)
		<A(2)-O>	3.098

monochromatized MoKα radiation). Unit cell dimensions (Table 2) were determined by least-squares refinement of 20 automatically centered reflections. Intensity data were collected over the 2θ range 0–55° and scanned through 1.63°, at a scan-speed of 4° 2θ/min. These data were then corrected for Lorentz-polarization and absorption effects and averaged. One thousand and eighty-two unique reflections were used in the refinement, and 988 of these had a F₀ (structure factor) greater than 4σ(F₀).

Structural refinement was performed using the SHELXL-93 program (Sheldrick 1993), and ionized

TABLE 8. SITE OCCUPANCIES AND OBSERVED (SREF) AND CALCULATED (EMPA) SCATTERINGS (epfu) IN MAGNESIAN HORNBLLENDE FROM SÄÄKSJÄRVÄ*

SITE	ATOM	OCCUPANCY	SREF	EMPA
T(1)	Si	0.82		
	Al	0.18		
T(2)	Si	1.00		
	Al	0.00		
M(1)	Mg	0.71	32.12	
	Fe ²⁺	0.29		
M(2)	Mg	0.69	29.06	
	Fe ²⁺	0.13		
	Al	0.14		
	Ti	0.03		
M(3)	Fe ³⁺	0.02		
	Mg	0.67	16.51	
	Fe ²⁺	0.33		
M(1-2-3)			77.69	77.61
M(4)	Fe ²⁺	0.06	38.84	39.10
	Mn	0.01		
	Na	0.08		
	Ca	0.83		
	Mg	0.01		
A	Na	0.31	3.39	4.15
	K	0.01		
O(3)	O	0.90	32.54	32.18
	F	0.10		

epfu: electrons per formula unit. *Occupancy expressed in atoms per formula unit.

TABLE 9. EMPIRICAL BOND-VALENCES (v.u.) FOR MAGNESIAN HORNBLENDE FROM SÄÄKSJÄRVI

	M(1)	M(2)	M(3)	M(4)	T(1)	T(2)	Σ
O(1)	0.364	0.331	0.344 ²		0.984		2.023
O(2)	0.338	0.355		0.258		0.987	1.938
O(3)	0.343 ²		0.351				1.037
O(4)		0.413		0.330		1.052	1.794
O(5)				0.136	0.922	0.917	1.975
O(6)				0.215	0.936	0.871	2.023
O(7)					0.971 ²		1.943
Σ	2.091	2.197	2.091	1.897	3.814	3.827	

scattering factors. The following scattering curves were utilized: (Na + □) (□:vacancy) for the A(2m) and A(2) subsites, (Na + Ca) for M(4), (Fe + □) for M(4)' subsite, (Fe + Mg) for M(1) and M(3), (Fe + Mg + Al) for M(2), (Al + Si) for T(1) and T(2) and (O¹⁻ + F) for O(3), with O half-ionized. The position of H atoms, initially detected on a Fourier-difference map, was refined according to the procedure of Oberti *et al.* (1993), in that the occupancy was fixed and the positional parameters and U were allowed to vary. Data concerning the structural refinement are given in Table 2, the atomic coordinates and isotropic displacement parameters in Table 3, the anisotropic displacement parameters in Table 4 (deposited), selected bond-lengths in Table 5, bond angles in Table 6 (deposited), the observed and calculated structure-factors in Table 7 (deposited), the site-scattering powers in Table 8, and selected bond-valences in Table 9. Copies of Tables 4, 6 and 7 may be obtained from CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

THE SITE OCCUPANCIES

T1 and T2 sites

The results of the electron-microprobe analysis (EMPA) show relatively low levels of [4]-coordinated Al (Table 1). The T(1) and T(2) occupancies, separately derived from $\langle T(1)-O \rangle$ and $\langle T(2)-O \rangle$ distances using various relationships (*e.g.*, Hawthorne 1983) indicated that ⁴¹Al is strongly ordered in T(1). The Oberti *et al.* (1995a) relationships $^{71}\text{Al} = \langle T(1)-O \rangle - 1.6187 \cdot 33.205$ and $^{72}\text{Al} = \text{Al}_T$ (EMPA) - ^{71}Al , that here constrain all Al in T(1), show the best agreement with EMPA, yielding total ⁴¹Al = 0.72 atoms per formula unit, *apfu* (Table 8) (only 0.02 *apfu* disagreement: *cf.* Table 1).

The M(1), M(2) and M(3) octahedral sites

The relatively long $\langle M(1)-O \rangle$ and $\langle M(3)-O \rangle$ distances, 2.094 and 2.090 Å, respectively, suggest that the smaller trivalent and tetravalent cations should be

TABLE 10. OBSERVED AND CALCULATED MEAN BOND-LENGTHS (Å) OF THE OCTAHEDRAL SITES

	distance	observed	calculated*
$\langle M(1)-O \rangle$		2.094	2.091
$\langle M(2)-O \rangle$		2.063	2.065
$\langle M(3)-O \rangle$		2.090	2.085
$\langle M-O \rangle$		2.082	2.080

*calculated from Hawthorne's (1983) equations, assuming O(3)=OH.

excluded from the M(1) and M(3) sites, and that the iron is here overwhelmingly divalent. On the other hand, the shorter $\langle M(2)-O \rangle$ length (2.064 Å) indicates that the smaller trivalent and tetravalent cations, Al, Ti and possibly also a little Fe³⁺, are ordered in the M(2) site.

Following Ungaretti *et al.* (1981), Hawthorne (1983) and Makino & Tomita (1989), cations have been assigned to the M(1) and M(3) sites by converting the respective refined site-scatterings to Mg and Fe²⁺ occupancies. The calculated $\langle M(1)-O \rangle$ and $\langle M(3)-O \rangle$ distances, interpreted using relationships between the mean bond-length and the ionic radius of the constituent cations (Hawthorne 1981, 1983), agree with the observed values (0.04% maximum disagreement: Table 10).

In calcic amphiboles, the linear relationship between the mean bond-length and the mean ionic radius holds very well for M(2) (Hawthorne 1981, 1983). The cation distribution at the M(2) site of the Säksjärvi magnesian hornblende has therefore been calculated by taking into account i) the full occupancy, ii) the observed $\langle M(2)-O \rangle$ distance, iii) the refined site-scattering value at the M(2) site, and iv) the overall charge neutrality (Ungaretti *et al.* 1981, Hawthorne *et al.* 1993, Oberti *et al.* 1993). The fractions of Mg, Fe²⁺, Al, Ti and Fe³⁺ at the M(2) site have been derived by solving a system of four linear equations, constraining Ti-content from EMPA results. Calculated (EMPA) and refined (SREF) total scattering at the octahedral site are in good agreement (0.08 *e* disagreement: Table 8) (see also below).

The M(4) polyhedron

The unit formula derived from EMPA indicates an excess of C-group cations. Thus, in addition to Ca and small amounts of Na (*e.g.*, Hawthorne 1983), Fe²⁺, Mn and Mg also enter M(4). Refinement of the scattering power at M(4) was performed assuming full site-occupancy, and Ca and Na as the scattering species (*i.e.*, $X_{\text{Na}} + X_{\text{Ca}} = 1$). The smaller C-group cations tend to order into an extra M(4)' site (*e.g.*, Bocchio *et al.* 1978, Ungaretti *et al.* 1981, Phillips *et al.* 1989);

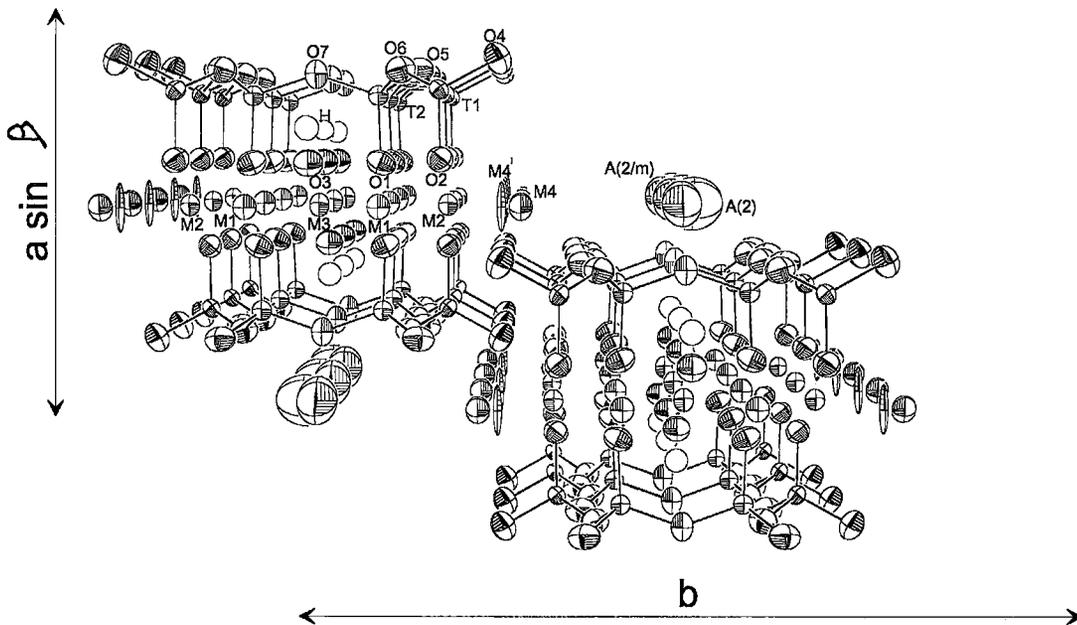


FIG. 2. ORTEP drawing of the Sääksjärvi magnesian hornblende projected down (001), showing the split A and M4 sites (see text).

because Mn and Fe^{2+} have a stronger site-preference for $M(4)$ than Mg (*e.g.*, Hawthorne *et al.* 1980, Hawthorne 1983, Oberti *et al.* 1995a), the site-scattering refinement of the split $M(4)'$ position was carried out using the scattering curves for Fe and vacancy ($X_{\text{Fe}} + X_{\square} = 1$). The total scattering is given by $M(4) + M(4)'$ scatterings and, following Oberti *et al.* (1995), the cations Mn, Fe^{2+} and Mg were partitioned between the C and B groups with the constrain that the calculated scattering powers at $M1 + M2 + M3$ and $M4$ should be coincident with the respective observed values; the best agreement is shown in Table 8. A view down [001] of the refined structure, showing the split $M4$ and $M4'$ positions, is shown in Figure 2.

The A site

The A site was evaluated with the site empty by means of various difference-Fourier maps. This revealed a major peak at $2/m$ and a minor peak shifted by about 0.2 Å along y . In view of the obvious positional disorder, different split-atom models were tested, using various combinations of $A(2/m)$, $A(m)$ and $A(2)$ subsites. Ultimately, $A(2/m)$ and $A(2)$ were refined (Fig. 2). The scattering species Na and vacancy ($X_{\text{Na}} + X_{\square} = 1$) were assumed at both subsites. On completion of the refinement, the disagreement between the refined (SREF) and the calculated (EMPA) site scatterings is small, $-0.66 e$ (Table 8).

The O3 site

The absence of significant oxy-anion substitution ($\text{O}^{2-} \equiv \text{OH}$) at O(3) is indicated by i) the long $M(1)$ – and $M(3)$ –O(3) distances, ii) the lack of trivalent and tetravalent cations at $M(1)$ and $M(3)$, and iii) the bond-valences sum at O(3), 1.037 valence units (Table 9). This finding reflects negligible dehydrogenation. The long $M(1)$ and $M(3)$ distances to O(3) (Table 5) also are consistent with the low F-content indicated by EMPA (< 0.01 ppm F). Hawthorne *et al.* (1993) have shown that small amounts of F at O(3) can be quantitatively estimated with sufficient accuracy by means of site-scattering refinement. We have therefore set $X_{\text{F}} + X_{\text{O}} = 1$, and refined F against O. The result (Table 8) indicates 0.1 F *apfu*.

Fe^{2+} ORDERING

Degree of order in $M(1)$ – $M(2)$ – $M(3)$

The Fe^{2+} –Mg distribution among the $M(1)$, $M(2)$ and $M(3)$ octahedral sites of hornblende is temperature-dependent (Makino & Tomita 1989); hornblende samples equilibrated at $600 \leq T \leq 800^\circ\text{C}$ have an Fe^{2+} –Mg distribution in which $M(3) > M(1) \gg M(2)$, whereas at a T of approximately 900°C , the site-population of these octahedra becomes practically indistinguishable. The Fe^{2+} –Mg distribution coeffi-

cient between the $M1$ and $M3$ octahedral sites is defined as $K_D^{M(1)-M(3)} = (X_{Mg}/X_{Fe})_{M(3)}/(X_{Mg}/X_{Fe})_{M(1)}$ where X is the mole fraction. In the refined magnesian hornblende, the value of $K_D^{M(1)-M(3)}$ is 0.85, which corresponds with the values of Makino & Tomita (1989) for a disordered Fe^{2+} -Mg distribution, consistent with a T of approximately 900°C. On the other hand, the Mg- Fe^{2+} distribution coefficient between the $M(2)$ and the $M(1)$ sites, defined as $K_D^{M(1)-M(2)} = (X_{Mg}/X_{Fe})_{M(1)}/(X_{Mg}/X_{Fe})_{M(2)}$, is 0.45, and intermediate between values typical of high- and low-temperature hornblendes; it is, therefore, consistent with 650° ≤ T ≤ 850°C. If allowance is made for the small amount of Fe^{3+} in $M(2)$, there is negligible change in the distribution coefficient: $K_D^{M(1)-M(2)} = 0.46$.

Degree of order in $M(4)$

In calcic amphibole, there is an increase of Mg in the $M(4)$ and Fe^{2+} in the $M(2)$ positions with increasing temperature (Skogby & Annersten 1985, Skogby 1987). Using the experimental calibration of the Fe^{2+} -Mg exchange between the $M(4)$ and $M(2)$ positions (Skogby 1987) which is: $T(K) = 9.2 (\pm 1.5)/[1.9(\pm 1.7) - \ln K_D]$, where $K_D = X_{Mg}/X_{Fe})_{M(4)}/(X_{Mg}/X_{Fe})_{M(2)}$, the magnesian hornblende refined here, with a $K_D = 4.7 \cdot 10^{-2}$, yields an apparent equilibrium temperature in the range 850–900°C. However, as Skogby (1987) emphasized, the uncertainty in the derived temperature is high, owing to the high levels of uncertainty in the estimates of $[M4]Mg$.

DISCUSSION

Pressure and temperature

The coexistence of magnesian hornblende, plagioclase (X_{Ab} in the range 0.38–0.42) and quartz permits the use of amphibole-plagioclase geothermometry. Two equations describe the amphibole-plagioclase exchange equilibria (e.g., Spear 1981a, b, Holland & Blundy 1994): (i) albite + tremolite = edenite + quartz, represented by the vector $[Al]Na^{[T]}Al = ([Al]_{\square}^{[T]}Si)_{-1}$, and (ii) albite + tschermakite = anorthite + glaucophane, represented by the vector $[M4]Na^{[T]}Si = ([M4]Ca^{[T]}Al)_{-1}$. Having determined Na in $M(4)$ from the structure refinement, both equilibria can be applied. The calibration of Holland & Blundy (1994) yields $T = 699 \pm 30^\circ C$ for equilibrium (i) and $T = 745 \pm 50^\circ C$ for equilibrium (ii) at $P = 2$ –3 kbar (see below). This temperature range is consistent with that required by isogradic reactions for peak metamorphic assemblages (Peltonen & Korsman 1990, Mancini *et al.* 1996) and also in accord with the approximate temperature, 700°C, for equilibrium (i) obtained from Spear's (1981b) graphical thermometer. The consistency of the temperatures constitutes an independent check on

the correct assignment of $[M4]Na$.

The $[M4]Na$ and $[6]Al + [4]Al$ contents of hornblende are pressure-sensitive and increase with increasing pressure of equilibration (Shidō & Miyashiro 1959, Brown 1977, Spear 1981a, Hammarstrom & Zen 1986, Anderson & Smith 1995). The $[M2]Al$ content alone can also constitute a geobarometer, on the basis of Hawthorne's (1983) suggestion that Al partitions in $M(2)$ with increasing pressure. Application of Brown's (1977) graphical $[M4]Na$ geobarometer to the Sääksjärvi magnesian hornblende, in which $[M4]Na = 0.16$ apfu, indicates $2 < P < 3$ kbar. A plot of Al_T versus P (Fig. 3) using the calibration of the Al-in-hornblende barometer corrected for the effect of temperature of Anderson & Smith (1995), is consistent with equilibration at approximately 2 kbar. This lies within the pressure range $0.6 < P < 2.20$ kbar defined by the chemically determined (EMPA) Al_T in other amphiboles from the same intrusive body (data from Mancini *et al.* 1996). In addition to pressure and temperature, $f(O_2)$ exerts a major control on the Al-in-amphibole barometer (Hammarstrom & Zen 1986, Anderson & Smith 1995). In the refined magnesian hornblende, however, the low $f(O_2)$ of equilibration (see below) indicates that pressure estimates obtained from Al_T are maximal, on the basis of the inverse relationship $Al_T - f(O_2)$ (Anderson & Smith 1995). A low pressure also is required by the low $[M2]Al$ content (0.242 apfu), which compares with amphiboles that have equilibrated at $P \ll 5$ kbar (e.g., Stephenson 1977). These pressure estimates are consistently lower than those in the range 4–5 kbar, indicated by the country-rock assemblages (Peltonen & Korsman 1990,

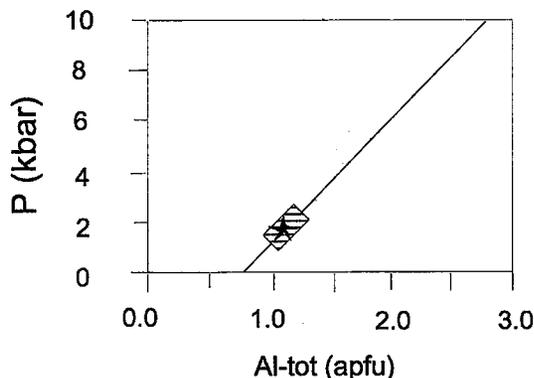


Fig. 3. Plot of Al_T against P (calibration of Anderson & Smith 1995; T : 700°C). Symbols: star: refined magnesian hornblende, shaded area: other calcic amphiboles from the same intrusive body, determined by EMPA (data from Mancini *et al.* 1996).

Kiipeläinen & Rastas 1992); this probably reflects re-equilibration by Al loss during regional uplift and exhumation.

Variations of Mg + Fe + Mn in M(4) with grade of metamorphism: comparison with other case studies

In the magnesian hornblende refined here, $^{[M4]}(\text{Mg} + \text{Fe}^{2+} + \text{Mn})$, which indicates the extent of solid solution toward cummingtonite (Hafner & Ghose 1971,

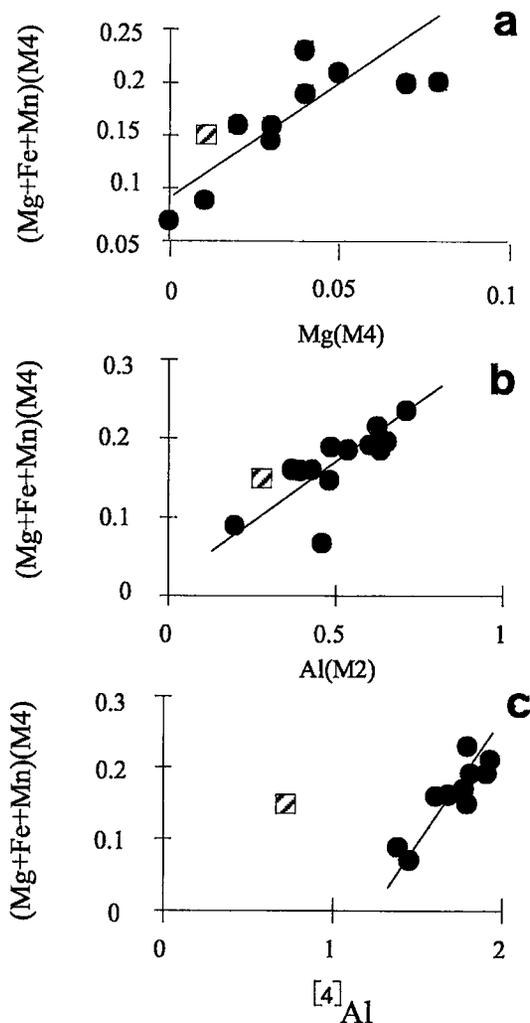


FIG. 4. $^{[M4]}[\text{Mg}/(\text{Mg} + \text{Fe} + \text{Mn})]$ population of magnesian hornblende (this study) compared with structurally refined samples of pargasitic amphibole equilibrated at higher pressure and temperatures (taken from the Finero massif, northwestern Italy; Oberti *et al.* 1995) (see text for discussions). Symbols: square: magnesian hornblende, dots: samples of pargasitic amphibole.

Hawthorne *et al.* 1980) is 9.4 mol.%. It is well established that the extent of solid solution of ferromagnesian amphibole in hornblende reflects metamorphic grade and paragenesis (Cameron 1975, Robinson *et al.* 1982, Oberti *et al.* 1995). In a comparison of our upper-amphibolite-facies magnesian hornblende with pargasitic amphiboles from ultramafic assemblages equilibrated at P–T conditions of the spinel peridotite facies (Oberti *et al.* 1995), thus at a P between 6 and 8 kbar and $T \geq 800^\circ\text{C}$, three characteristics are noted: i) The quantity $^{[M4]}\text{Mg}$ correlates with $^{[M4]}(\text{Mg} + \text{Fe} + \text{Mn})$ (Fig. 4a), supporting the credibility of $^{[M4]}\text{Mg}$ value. ii) The quantity $^{[M4]}(\text{Mg} + \text{Fe} + \text{Mn})$ correlates with $^{[M2]}\text{Al}$ (Fig. 4b); in light of the primary control on $^{[M2]}\text{Al}$ exerted by pressure (Hawthorne 1983, Anderson & Smith 1995), this trend may reflect also an increase in extent of solid solution toward cummingtonite with pressure of equilibration (Cameron 1975, Robinson *et al.* 1982). iii) The quantity $^{[M4]}(\text{Mg} + \text{Fe} + \text{Mn})$ is apparently insensitive to changes in $^{[4]}\text{Al}$ (Fig. 4c); in light of the primary control on extent of $^{[4]}\text{Al}$ exerted by temperature [*i.e.*, through the edenite exchange: $\text{Si} + \square \rightarrow ^{[4]}\text{Al} + ^{[4]}(\text{Na} + \text{K})$; Robinson *et al.* 1982, Anderson & Smith 1995], this finding may result from the fact that the extent of solid solution toward cummingtonite no longer increases with temperature above the orthopyroxene-in isograd (Robinson *et al.* 1982).

Fugacity of oxygen and content of halogens in the fluids at peak metamorphism

The oxidation ratio of amphiboles reflects the oxygen fugacity of equilibration (*e.g.*, Stephenson 1977, Robinson *et al.* 1982, Spear 1981a). The $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ ratio of the Sääksjärvi magnesian hornblende, obtained from structure refinement, is 0.03, and with respect to the ferric iron *versus* oxygen fugacity determinations of Spear (1981a), indicates low redox conditions, near or below the MW (magnetite–wüstite) buffer; these conditions are consistent with the assemblage graphite + ilmenite + titaniferous magnetite, and also with the values determined using the recalculation scheme based on fifteen cations excluding Na and K, and the low oxidation ratio of the prograde metamorphic orthopyroxene and chromian spinel Mancini *et al.* 1996). In fact, despite the documented presence of a CO_2 -bearing metamorphic fluid in areas of medium- to high-grade metamorphism (*e.g.*, Tromsdorff & Skippen 1986), the paucity of CO_3 -bearing phases and the presence of graphite are consistent with the reduction of a CO_2 -rich fluid according to the equation $\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$. Chlorine has not been detected in the magnesian hornblende despite its significant amounts in some bulk-rock compositions (unpubl. data), suggesting that perhaps it was introduced during a later stage of

hydration. On the other hand, the F-for-OH substitution amounts to 0.09 *apfu* and is six times higher than in coexisting disordered $1M_d$ phlogopite [0.015 *apfu* F: F. Mancini, unpubl. data], which contrasts with Sisson's (1987) derived partition coefficient $K_D^{(F-\text{phlog}/F-\text{amph})}$ equal to 1.21; there is thus a suggestion that amphibolitization and biotitization (K-metasomatism) reflect different stages of hydration.

CONCLUSIONS

1. The Fe–Mg distribution among $M1$ – $M3$ and $M1$ – $M2$ octahedral sites of the magnesian hornblende ($K_D^{M(1)-M(3)} = 0.85$ and $K_D^{M(1)-M(2)} = 0.45$) collectively is more disordered than in calcic amphibole equilibrated at 600–650°C. It is comparable to amphiboles equilibrated at $T \geq 700^\circ\text{C}$.
2. SREF and EMPA results indicate considerable ($\text{Fe}^{2+} + \text{Mn} + \text{Mg}$) in $M(4)$, corresponding to 9.8% of ferromagnesian amphibole solid-solution. In the light of the pressure and temperature dependence of this solid solution and in relation to paragenetic amphiboles from ultramafic assemblages, this amount is in accordance with the lower pressure and temperature of equilibration.
3. The $M^{(4)}\text{Na}$, Al_T and $M^{(2)}\text{Al}$ occupancies are consistent with a P of 2–3 kbar. These low pressures, together with a temperatures in the range 700–730°C also required for the exchange equilibrium with plagioclase, suggest a period of decompression and uplift accompanied by heating. The high heat-flux required during the decompression could be achieved in the Svecofennides either by magmatism (Huhma 1986) or by the constrictions of the isotherms during extensional thinning (Pietikäinen 1995).
4. Unlike the hydrous fluids circulating in the wedge of a subduction-zone system (e.g., Arculus 1994), the magnesian hornblende was precipitated from hydrous fluids that were halogen-poor and had a low oxidation potential. We therefore suggest that hydration of the ultramafic body during peak metamorphism progressed owing to hydrous fluids released from the country-rock schist and gneiss undergoing dehydration and anatexis, rather than by fluids that migrated from a dehydrating downgoing slab.

ACKNOWLEDGEMENTS

F.M. acknowledges financial support from the Turun Yliopisto Säätiö (grant No.8363). The authors thank the Partek Oy Mining Company for allowing access to drill core and supplying the sample for this investigation. We are most grateful to F.C. Hawthorne, R. Oberti and M.W. Phillips for suggestions, and to R.F. Martin for editorial comments, which materially improved the manuscript. Prof. C. Ehlers (Åbo Academy) and FL Markku Sundberg (University of Helsinki) read an early version of the manuscript.

REFERENCES

- ANDERSON, J.L. & SMITH, D.R. (1995): The effects of temperature and $f\text{O}_2$ on the Al-in-hornblende barometer. *Am. Mineral.* **80**, 549–559.
- ARCULUS, R.J. (1994): Aspects of magma genesis in arcs. *Lithos* **33**, 189–208.
- BLUNDY, J.D., & HOLLAND, T.J.B. (1990): Calcic amphibole equilibria and a new amphibole – plagioclase geothermometer. *Contrib. Mineral. Petrol.* **104**, 208–224.
- BOCCHIO, R., UNGARETTI, L. & ROSSI, G. (1978): Crystal-chemical study of eclogitic amphiboles from Alpe Arami, Lepontine Alps, southern Switzerland. *Soc. Ital. Mineral. Petrogr. Rend.* **34**, 453–470.
- BROWN, E.H. (1977): The crossite content of Ca-amphibole as a guide to pressure of metamorphism. *J. Petrol.* **18**, 53–72.
- CAMERON, K.L. (1975): An experimental study of actinolite–cummingtonite phase relations with notes on the synthesis Fe-rich anthophyllite. *Am. Mineral.* **60**, 375–390.
- HAFNER, S.S. & GHOSE, S. (1971): Iron–magnesium distribution in cummingtonites $(\text{Fe,Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. *Z. Kristallogr.* **133**, 301–326.
- HAMMARSTROM, J.M. & ZEN, E-AN (1986): Aluminum in hornblende: an empirical igneous geobarometer. *Am. Mineral.* **71**, 1297–1313.
- HAWTHORNE, F.C. (1981): Crystal chemistry of the amphiboles. In *Amphiboles* (D.R. Veblen, ed.). *Rev. Mineral.* **9A**, 1–102.
- _____ (1983): The crystal chemistry of the amphiboles. *Can. Mineral.* **21**, 173–480.
- _____, GRIEP, J.L. & CURTIS, L. (1980): A three-amphibole assemblage from the Tallan Lake Sill, Peterborough County, Ontario. *Can. Mineral.* **18**, 275–284.
- _____, UNGARETTI, L., OBERTI, R., BOTTAZZI, P. & CZAMANSKE, G.K. (1993): Li: an important component in igneous alkali amphiboles. *Am. Mineral.* **78**, 733–745.
- HOLLAND, T. & BLUNDY, J. (1994): Non ideal interactions in calcic amphiboles and their bearing on amphibole plagioclase thermometry. *Contrib. Mineral. Petrol.* **116**, 433–447.
- HUHMA, H. (1986): Sm–Nd, U–Pb and Pb–Pb isotopic evidences for the origin of the early Proterozoic Svecofennian crust in Finland. *Geol. Surv. Finland, Bull.* **337**.
- KILPELÄINEN, T. & RASTAS, J. (1992): Vammalan Stormin Ni malmiympäristön metamorfisista ja rakenne geologista tutkimuksista. *Inst. Geol. Mineral., Univ. of Turku, Publ.* **30**, 1–18.

- MÄKINEN, J. (1987): Geochemical characteristics of Svecofennian mafic-ultramafic intrusions associated with Ni-Cu occurrences in Finland. *Geol. Surv. Finland, Bull.* **342**.
- MAKINO, K. & TOMITA, K. (1989): Cation distribution in the octahedral sites of hornblendes. *Am. Mineral.* **74**, 1097-1105.
- MANCINI, F., MARSHALL, B. & PAPUNEN, H. (1996): Petrography and metamorphism of the Sääksjärvi ultramafic body, southwest Finland. *Mineral. Petrol.* **56**, 185-208.
- MARSHALL, B. & MANCINI, F. (1994): Major- and minor-element mobilization, with implications for Ni-Cu-Fe-sulphide remobilization, during retrograde metasomatism at the Vammala mine, southwest Finland. *Chem. Geol.* **116**, 203-227.
- OBERTI, R., HAWTHORNE, F.C., UNGARETTI, L. & CANNILLO, E. (1995): ^{61}Al disorder in amphiboles from mantle peridotites. *Can. Mineral.* **33**, 867-878.
- _____, UNGARETTI, L., CANNILLO, E. & HAWTHORNE, F.C. (1993): The mechanism of Cl incorporation in amphibole. *Am. Mineral.* **78**, 746-752.
- PELTONEN, P. (1995): *Petrology, Geochemistry and Mineralogy of Ultramafic Rocks and Associated Ni-Cu Deposits in the Vammala Ni-Belt, Southwest Finland*. Ph.D. thesis, Univ. of Turku, Turku, Finland.
- _____, & KORSMAN, K. (1990): Metamorphism of ultramafic rocks in the early Proterozoic Svecofennian nickel province - implications for the timing of emplacement of Ni-Cu ores hosting intrusive bodies. *Abstr. Sect., Baltic Shield Symp.*, 71.
- PIETIKÄINEN, K.J. (1995): *The Geology of the Early Proterozoic Pori Shear Zone, Southwestern Finland, with Special Reference to the Evolution of Veined Gneisses from Tonalitic Protoliths*. Ph.D. thesis, Michigan Tech. Univ., Houghton, Michigan.
- PHILLIPS, M.W., DRAHEIM, J.E., POPP, R.K., CLOWE, C.A. & PINKERTON, A.A. (1989): Effects of oxidation-dehydrogenation in tschermakitic hornblende. *Am. Mineral.* **74**, 764-773.
- RAASE, P. (1974): Al and Ti content of hornblende, indicators of pressure and temperature of regional metamorphism. *Contrib. Mineral. Petrol.* **45**, 231-236.
- ROBINSON, K., GIBBS, G.V., RIBBE, P.H. & HALL, M.R. (1973): Cation distribution in three hornblende. *Am. J. Sci.* **273A**, 522-535.
- ROBINSON, P., SPEAR, F.S., SCHUMACHER, J.C., LAIRD, J., KLEIN, C., EVANS, B.W. & DOOLAN, B.L. (1982): Phase relations of metamorphic amphiboles: natural occurrence and theory. In *Amphiboles* (D.R. Veblen & P.H. Ribbe, eds.). *Rev. Mineral.* **9B**, 1-227.
- SHELDRIK, G. (1993): *SHELXL-93: Program for the Refinement of Crystal Structures*. Inst. für Anorg. Chemie, Univ. of Göttingen, Göttingen, Germany.
- SHIDÓ, F. & MIYASHIRO, A. (1959): Hornblendes of basic metamorphic rocks. *J. Fac. Sci. Tokyo* **12**, 85-102.
- SISSON, V.B. (1987): Halogen chemistry as an indicator of metamorphic fluid interaction with the Ponder pluton, Coast Plutonic Complex, British Columbia, Canada. *Contrib. Mineral. Petrol.* **95**, 123-131.
- SKOGBY, H. (1987): Kinetics of intracrystalline order-disorder reactions in tremolite. *Phys. Chem. Minerals* **14**, 521-526.
- _____, & ANNERSTEN, H. (1985): Temperature dependent Mg-Fe-cation distribution in actinolite-tremolite. *Neues Jahrb. Mineral., Monatsh.*, 193-203.
- SPEAR, F. (1981a): Amphibole-plagioclase equilibria: an empirical model for the relation albite + tremolite = edenite + 4 quartz. *Contrib. Mineral. Petrol.* **77**, 355-364.
- _____, (1981b): An experimental study of hornblende stability and compositional variability in amphibolite. *Am. J. Sci.* **281**, 697-734.
- STEPHENSON, N.C.N. (1977): Coexisting hornblendes and biotites from Precambrian gneiss of the south coast of western Australia. *Lithos* **10**, 9-27.
- TROMMSDORFF, V. & SKIPPEN, G. (1986): Vapour loss ("boiling") as a mechanism for fluid evolution in metamorphic rocks. *Contrib. Mineral. Petrol.* **94**, 317-322.
- UNGARETTI, L., SMITH, D.C. & ROSSI, G. (1981): Crystal-chemistry by X-ray structure refinement and electron microprobe analysis of a series of sodic-calcic to alkali amphiboles from the Nybø eclogite pod, Norway. *Bull. Minéral.* **104**, 400-412.

Received August 23, 1995, revised manuscript accepted January 6, 1996.