Effect of chlorine on the crystal structure of a chlorine-rich hastingsite

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Abstract

The structure refinement of a hastingsite (Cl 0.91 p.f.u.) from West Ongul Island, Lützow–Holm Bay, East Antarctica, has been carried out in order to characterise the effect of Cl on the crystal structure. The composition of the Cl-rich hastingsite is $K_{0.69}Na_{0.26}Ca_{1.99}Mg_{1.09}Fe^{2+}{}_{2.71}Fe^{3+}{}_{0.92}Mn_{0.04}Ti_{0.10}$-$Al_{2.31}Si_{5.83}O_{22}OH_{0.99}Cl_{0.91}F_{0.10}$ with unit cell parameters *a* 9.962(3), *b* 18.283(7), *c* 5.372(1) Å and β 104.87(3)°.

In the Cl-rich hastingsite, Al, Fe^{3+} and Ti occupy only the *M*(2) site, and Fe^{2+} strongly prefers the *M*(1) and *M*(3) sites to the *M*(2) site with respect to Mg. The Mg–Fe^{2+} distribution suggests that the Mg–Cl avoidance is realised in the intracrystalline exchange reaction among the octahedral sites in the Cl-rich hastingsite. The individual position of Cl and OH was refined and the effective ionic radius of Cl in fourfold coordination is determined as 1.79 Å. Substitution of Cl for OH expands the sizes of the *M*(1) and *M*(3) sites and extends the double chains in comparison with hydroxy calcic amphiboles. Cl especially, is close to the O(6) and O(7) oxygens beyond the minimum distance calculated from effective ionic radii. Therefore, the Cl-rich hastingsite is considered to be deformed locally by Cl.

KEYWORDS: Cl-rich hastingsite, structure refinement, chlorine effect, amphibole.

Introduction

CALCIC amphibole with Cl replacing OH occurs in metamorphic, plutonic and volcanic rocks (Suwa *et al.*, 1987). The highest content of Cl recorded so far is 7.24 wt.% in a calcic amphibole from a skarn in Dashkesan (Krutov, 1936). High concentrations (over 3.0 wt.%) of Cl in calcic amphiboles have been reported by Jacobson (1975), Dick and Robinson (1979), Sharma (1981), Kamineni *et al.* (1982), Vanko (1986), and Suwa *et al.* (1987). These Cl-rich calcic amphiboles are high in Fe, and are mostly of hastingsite defined by Leake (1978). Suwa *et al.* (1987) pointed out that the Cl-rich hastingsites are high in Al^{IV} and (Na + K) contents and K/(Na + K) value. The chemical behaviour of Cl-rich amphiboles has been interpreted from a structural point of view by Ito and Anderson (1983), Volfinger *et al.* (1985), Suwa *et al.* (1987), and Yamaguchi (1989).

No structure refinement of Cl-bearing amphiboles, however, has been made with special attention given to the role of Cl in the structure. In this paper, the crystal structure of a Cl-rich hastingsite is described fully and the effect of chlorine on the structure is shown clearly.

Specimen examined

A Cl-rich hastingsite occurs in a calcareous pegmatite within hornblende gneiss on West Ongul Island, Lützow–Holm Bay, East Antarctica.

The calcareous pegmatite was formed during Proterozoic metamorphism, and is composed of Cl-rich hastingsite, scapolite, calcite and actinolite, with accessory analcite, titanite, apatite, quartz and pyrite (Suwa *et al.*, 1987).

Chemical composition and optical properties of the hastingsite were described by Suwa *et al.* (1987). The chemical formula is $(K_{0.69},Na_{0.25})_{\Sigma 0.94}$ $(Ca_{1.99},Na_{0.01})_{\Sigma 2}$ $(Mg_{1.09},\ Fe^{2+}{}_{2.71},\ Fe^{3+}{}_{0.92},Mn_{0.04},Al_{0.14},Ti_{0.10})_{\Sigma 5}$ $(Si_{5.83},Al_{2.17})_{\Sigma 8}$ $O_{22}\ (OH_{0.99},F_{0.10},Cl_{0.91})_{\Sigma 2}$ on the basis of O = 23.

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Table 1. Crystal data for the Cl-rich hastingsite, space group C2/*m*.

Locality	West Ongul, East Antractica		
a(Å)	9.962(3)	Reflections	
b(Å)	18.283(7)	observed	independent
c(Å)	5.372(1)	2233	1924
β(°)	104.87(3)	$-15 \leq h \leq 14$, $0 \leq k \leq 29$, $0 \leq l \leq 8$	
V(Å^3)	945.6(5)	Standard reflections and their variations	
Size(mm)	0.15x0.20x0.38		$\lvert F_o \rvert / < \lvert F_o \rvert >$
Dc(g/cm^3)	3.435	(151)	0.9958–1.0068
μ(cm^{-1})	42.47	(153)	0.9926–1.0098
$R(R_w)$	0.032(0.030)	(310)	0.9938–1.0062
S	20.0		
Maximum Shift(Δ)	0.00006	Maximum Δ/σ	0.09

The hastingsite has high (Na + K) content (0.94), high K/(Na + K) value (0.73), high $Fe^{2+}/(Fe^{2+} + Mg)$ value (0.71), and high Al^{IV} content (2.17). Cl occupies the O(3) site at the rate of 0.45. The Cl-rich hastingsite is observed as being homogeneous by optical microscopy, X-ray photographs and electron microprobe analyses.

Experimental details

Measurement of diffraction intensities. A handpicked {110} cleavage flake with dimensions given in Table 1 was used. The single crystal X-ray photographs showed monoclinic *C*-lattice type and diffraction symmetry 2/*m*, corresponding to space groups *Cm*, *C*2 or *C*2/*m*. Since there was no indication of a non-centric nature from the average intensity distribution test ($<|F_o|>^2/<I_o>$ = 0.570; Wilson, 1949), the space group *C*2/*m* was used in the structure refinement.

The intensity data were collected on a RIGAKU AFC-5UD automatic 4-circle diffractometer. The unit cell parameters were determined by the least-squares method from 15 reflections collected on the 4-circle single crystal diffractometer. Independent reflections within $2\theta = 70°$ were measured with 2θ-ω scan equi-inclination technique using monochromatised Mo-K_α (0.71069 Å) radiation. Absorption effects were corrected by the semi-empirical method of North *et al.* (1968). Intensities less than three times the standard deviation of the observed intensity were rejected in this refinement.

The cell parameters, crystals size, number of independent reflections and the final *R* factor are presented in Table 1.

Refinement procedure. The refinement was carried out by a full matrix least-squares method using computer program RFINE 2 (Finger and Price, 1975) revised by Horiuchi (pers. comm.). The scattering factors for neutral atoms with anomalous dispersion were taken from International Tables for X-ray Crystallography IV (1974). The initial positional parameters and isotropic temperature factors for the present refinement were taken from the Obira hastingsite (Makino and Tomita, 1989).

The Cl-rich hastingsite has complicated chemistry, so that the following simplifying assumptions were employed before refinement of cation occupancies. Since the X-ray scattering power of Mg and Al atoms is indistinguishable, Mg and Al were regarded as one group with one scattering factor (neutral magnesium), and were summed to form Mg* in the atomic fraction. For the same reason, Fe^{2+}, Fe^{3+}, Mn and Ti were assumed to form species, Fe* with the scattering factor of neutral iron. All Ca was assigned to the *M*(4) site, and the rest of this site was filled with Na. Residual Na and K were assigned to the *A* site. The small amount of F, which is similar to O in terms of its scattering factor, was included in O. The conventional O(3) site involves 0.55 O and 0.45 Cl. H accompanied with O in the O(3) was neglected in this refinement.

Assuming random distribution of Al and Si in the tetrahedral sites and of Mg* and Fe* in the octahedral sites, initial site occupancies were determined from the chemical analysis. During all cycles of the refinement, the tetrahedral and octahedral site chemistry was constrained to agree with the chemical analysis. After several cycles of the refinement the O(3) position was divided into O(3*A*) and O(3*B*) positions, referring to the Fourier and difference Fourier sections (Fig. 1). The difference maps show the difference in the electron density between the observed and model at the O(3) under consideration. As the X-ray scattering factor of Cl is about twice the value of that for O, the peak of the electron density in the Fourier map (Fig. 1*b*) may correspond to the position of Cl. Therefore, Cl (0.91 p.f.u.) was assigned to the O(3*B*) site, to match the peak of the electron density on the Fourier maps. The larger residual peak on the difference Fourier map (Fig. 1*c*) may represent the OH position. Therefore, O (1.09 p.f.u.) was assigned to the O(3*A*) site, placed at the position of the residual peak.

The map of electron density shows a peak at the 2/*m* position (1/2, 0, 0) in the *A* site. Assuming the structural model with composite (K, Na) atom at the center of the *A* site (1/2, 0, 0), the difference Fourier map does not show unusually large positive regions near the central location. Thus, a split atom model (Papik *et al.*, 1969; Hawthorne and Grundy, 1973; Makino and Tomita, 1989) was not used in this refinement. After further cycles of the refinement using anisotropic temperature factors, the refinement converged to an *R* factor of 0.032. From the chemical analysis and X-ray refinement, occupancies of Mg* and Fe* in the octahedral sites were determined (Table 5). The final atomic positions and temperature factors are listed in Tables 2 and 3.

Results and discussion

Selected interatomic distances and mean bond lengths given by the refinement are listed in Tables 4 and 5. Features of the individual sites in the Cl-rich hastingsite are now discussed. The ionic radii used throughout, except that for Cl are from Shannon and Prewitt (1969, 1970).

O(3) site. In the Cl-rich hastingsite the O(3) site is split into the O(3*A*) and the O(3*B*). The former site contains 0.55 OH and the latter 0.45 Cl. The position of the O(3*A*) occupied by O with H is comparable with that in hydroxy calcic amphiboles. The O(3*B*) site occupied by Cl is far away from the O(3*A*) site approximately along *a** and

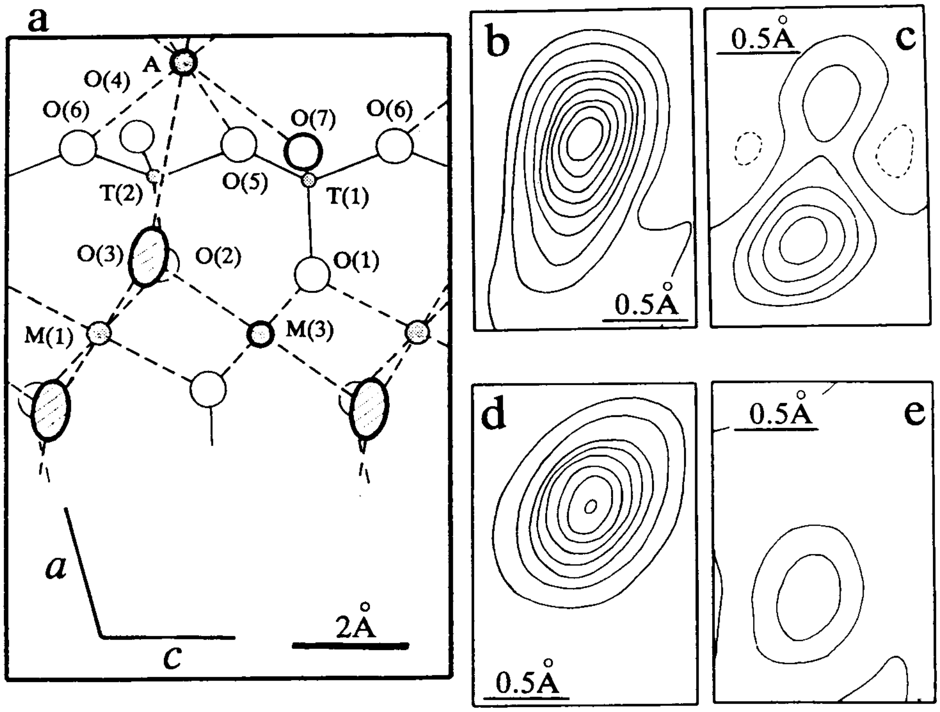

FIG. 1. (*a*) A schematic view of the O(3) site and surrounding oxygens in the Cl-rich hastingsite, projected on the (010) plane. Fourier (*b*) and difference Fourier (*c*, *d* and *e*) sections parallel to (010) at $y = 0$ show the O(3) site. Contour intervals are 2.5 (*b*, *d e*) and 1 $eÅ^{-3}$ (*c*). The *b* and *c* are of O(3) = 0.55 OH + 0.45 Cl. The *d* and *e* sections are obtained, assuming O(3*A*) = 0.55 OH and O(3*B*) and O(3*B*) = empty, and O(3*A*) = empty and O(3*B*) = 0.45 Cl respectively after division of the O(3) site (see text). The residual electron density in the *d* section represents Cl, and that in the e represents OH.

Table 2. Positional parameters and isotropic temperature factorsfors the Cl–rich hastingsite.

Site	*X*	*Y*	*Z*	*B*
T(1)	0.2781(1)	0.0859(1)	0.3013(3)	0.52(2)
T(2)	0.2913(1)	0.1732(1)	0.8116(3)	0.57(2)
M(1)	0.0	0.0945(1)	0.5	0.87(1)
M(2)	0.0	0.1789(1)	0.0	0.60(1)
M(3)	0.0	0.0	0.0	0.82(1)
M(4)	0.0	0.2810(1)	0.5	0.91(1)
A(2/*m*)	0.5	0.0	0.0	4.35(8)
O(1)	0.1040(3)	0.0912(2)	0.2142(7)	0.79(4)
O(2)	0.1216(4)	0.1777(2)	0.7350(7)	0.82(4)
O(3A)	0.1153(10)	0.0	0.7064(20)	0.73(12)
O(3B)	0.1639(4)	0.0	0.7368(8)	0.68(4)
O(4)	0.3692(4)	0.2497(2)	0.7951(7)	0.86(4)
O(5)	0.3476(4)	0.1365(2)	0.1008(7)	0.91(4)
O(6)	0.3427(4)	0.1224(2)	0.5983(7)	0.96(4)
O(7)	0.3333(6)	0.0	0.2990(11)	1.27(7)

Table 3. Anisotropic temperature factors($\times10^5$) for the Cl–rich hastingsite.

Site	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
T(1)	117 (7)	39 (2)	553 (24)	-6 (3)	63 (10)	-1 (6)
T(2)	133 (6)	44 (2)	607 (23)	-3 (3)	102 (10)	4 (5)
M(1)	212 (6)	87 (2)	681 (21)	0	155 (9)	0
M(2)	151 (6)	44 (2)	625 (24)	0	101 (10)	0
M(3)	227 (8)	45 (2)	880 (29)	0	57 (12)	0
M(4)	267 (7)	56 (2)	1087 (27)	0	307 (11)	0
A(2/*m*)	1293 (33)	252 (8)	6371 (146)	0	2554 (61)	0
O(1)	162 (17)	76 (5)	713 (64)	-9 (8)	104 (26)	-11 (15)
O(2)	142 (17)	80 (5)	788 (65)	7 (8)	76 (27)	0 (14)
O(3A)	229 (63)	52 (14)	596 (180)	0	83 (80)	0
O(3B)	120 (21)	60 (5)	733 (66)	0	69 (28)	0
O(4)	247 (18)	54 (5)	972 (67)	-16 (8)	230 (28)	-12 (15)
O(5)	170 (17)	75 (5)	964 (65)	3 (8)	57 (27)	78 (15)
O(6)	186 (18)	73 (5)	1172 (69)	10 (8)	155 (28)	0
O(7)	240 (28)	100 (8)	1612 (118)	0	304 (47)	0

near the *A* site. This is expected for the O(3*B*) site occupied by the larger Cl ions. Interatomic distances between the O(3*A*), O(3*B*) sites and adjacent anion sites are listed in Table 4.

Comparison between observed distances and those calculated from ionic radii is made to examine the geometrical role of Cl in the crystal structure. For a choice of ionic radii from the table proposed by Shannon and Prewitt (1969, 1970), the coordination numbers of the anions are

Table 4. Interaomic distances(Å) between the O(3) site and adajscent oxygen and A site for the Cl-rich hastingsite.

	O(3A): 0.55OH			O(3B): 0.45Cl	
	observed	calculated		observed	calculated
O(1)x2	2.866(10)	2.76	O(1)x2	3.240(5)	3.17
O(1)x2	3.104(10)	2.76	O(1)x2	3.214(5)	3.17
O(1)x2	3.224(10)	2.76	O(1)x2	3.188(5)	3.17
O(2)x2	3.251(4)	2.76	O(2)x2	3.275(4)	3.17
O(3A)	2.753(18)	2.76	O(3B)	3.588(7)	3.59
O(5)x2	3.681(7)	2.76	O(5)x2	3.400(4)	3.17
O(6)x2	3.340(9)	2.76	O(6)x2	3.070(5)	3.17
O(7)	3.456(13)	2.74	O(7)	3.058(6)	3.15
A(2/*m*)	3.751(10)	2.95	A(2/*m*)	3.284(4)	3.36

Ionic radius(Å):*r*(O)=1.38 for fourfold coordination, *r*(O)=1.36 for threeforld coordination, $\langle r\rangle_A=1.57=0.735r(\mathrm{K})+0.265r(\mathrm{Na})$ for the A site (Shannon and Prewitt;1969,1970), *r*(Cl)=1.79 (estimated in this work).

Table 5. Site occupancies and selected interaomic distances (Å) for the Cl-rich hastingsite.

T(1): 0.40(8)Si+0.60Al		M(1): 0.181(6)Mg*+0.819Fe*				M(4): 0.996Ca+0.004Na	
O(1)x1	1.679(4)	O(1)x2	2.062(4)	O(1)x2	2.062(4)	O(2)x2	2.418(4)
O(5)x1	1.696(4)	O(2)x2	2.141(3)	O(2)x2	2.141(3)	O(4)x2	2.364(4)
O(6)x1	1.696(4)	O(3A)x2	2.210(6)	O(3B)x2	2.491(3)	O(5)x2	2.740(4)
O(7)x1	1.665(2)	<M(1)-O>$_A$	2.138	<M(1)-O>$_B$	2.231	O(6)x2	2.504(4)
<T(1)-O>	1.684	<M(1)-O>	2.180			<M(4)-O>	2.507
T(2): 1.00Si+0.00Al		M(2): 0.405(6)Mg*+0.596Fe*				A(2/*m*): 0.247Na+0.685K	
O(2)x1	1.636(4)	O(1)x2	2.087(3)			O(5)x4	3.041(4)
O(4)x1	1.613(4)	O(2)x2	2.093(4)			O(6)x4	3.222(3)
O(5)x1	1.653(4)	O(4)x2	1.969(3)			O(7)x2	2.590(6)
O(6)x1	1.656(4)	<M(2)-O>	2.050			<A(2/*m*)-O>	3.023
<T(2)-O>	1.640						
<T-O>	1.662	M(3): 0.057Mg*+0.943Fe*					
		O(1)x4	2.137(3)	O(1)x4	2.137(3)		
		O(3A)x2	2.177(12)	O(3B)x2	2.418(5)		
		<M(3)-O>$_A$	2.150	<M(3)-O>$_B$	2.231		
		<M(3)-O>	2.186				

<M(1)-O>=0.55<M(1)-O>$_A$+0.45<M(1)-O>$_B$, <M(3)-O>=0.55<M(1)-O>$_A$+0.45<M(1)-O>$_B$
Mg*=Mg+Al, Fe*=Fe^{2+}+Fe^{3+}+Ti

required (Volfinger *et al.*, 1985). O in the O(3*A*) site bonds to cations in three octahedral sites (2*M*(1) and *M*(3)) and to the H cation. Therefore, it is in fourfold coordination. The O(3*B*) site is so close to the *A* site that Cl in the O(3*B*) is considered to interact with K and Na in the *A* site. Therefore, Cl is fourfold coordinated (cations in 2*M*(1), *M*(3) and *A* sites). The observed distance (2.753(18) Å) of the O(3*A*)–O(3*A*) sites in the Cl-rich hastingsite is in good agreement with the calculated value (2.76 Å) from the table by Shannon and Prewitt (1969, 1970). In the same manner, the O(3*B*–O(3*B*) and O(3*B*)–O(3*A*) distances (Table 4) give 1.79 Å as the ionic radius of Cl in fourfold coordination, which is not included in the table.

The distances between Cl in the O(3*B*) and surrounding oxygens are calculated, using estimated (r(Cl) = 1.79 Å and tabulated *r*(O). Provided the calculated distance is the minimum required value, the observed anion–anion distances may be larger than the minimum values (Table 4). Both O(3*B*)–O(6) and O(3*B*)–O(7) distances are less than the required minimum value. Other distances are close to the minimum value or larger. In addition to these facts, temperature factors for the O(6) and O(7) are a little larger and more anisotropic than other oxygens (Tables 2, 3). Thus, the substitution of Cl for OH causes local deformation in the Cl-rich hastingsite such that Cl and adjacent O maintain the required separation at least. Except for the O(3*A*) and O(3*B*), the site positions were refined as the average values of the locally deformed structure. The observed distances between Cl and adjacent O appear to be shorter than the real ones. The positions of the O(6) and O(7) are observed to be strongly affected by the replacement of OH with Cl.

T(1) and T(2) tetrahedral sites. The <*T*–O> length (1.663 Å), an average value of <*T*(1)–O> and <*T*(2)–O> lengths, is comparable with the calculated one (1.660 Å) using the equation of Al^{IV} *vs.* <*T*–O> for hydroxy amphiboles (Hawthorne and Grundy, 1977). The <*T*(1)–O> length is much larger than the <*T*(2)–O> (Table 5). This suggests that Al^{IV} occupies the *T*(1) site in preference to the *T*(2) site in the Cl-rich hastingsite. This preference distribution of Al^{IV} in the tetrahedra is common in most amphiboles.

The double chains are kinked to fit the octahedral strip dimension along *y* and *z* directions. Natural calcic and Mg–Fe–Mn amphiboles show that the kinking angles of the double chains vary with the ratio of the tetrahedral and octahedral sizes as shown in Fig. 2 (Hawthorne, 1983). The O(5)–O(6)–O(5) angle gives a measure of the degree of kinking of the tetrahedral chains.

The O(5)–O(6)–O(5) angle (169°) of the Cl-rich hastingsite indicates that the chains are more extended than in any other hastingsites, which have O(5)–O(6)–O(5) angles of less than 165° (Hawthorne, 1983). Referring to the general trend for natural amphiboles (Fig. 2), the angle can be reconciled with the ratio given of the observed <*T*–O> and <*M*–O> lengths in the Cl-rich hastingsite. The mean <*M*–O> length (2.130 Å) is enlarged remarkably by a large Cl anion, and the existence of Cl therefore contributes to the extension of the double chains (e.g. hastingsite: <*M*–O> = 2.118, 2.065 Å (Makino and Tomita, 1989, and Hawthorne and Grundy, 1977, respectively)).

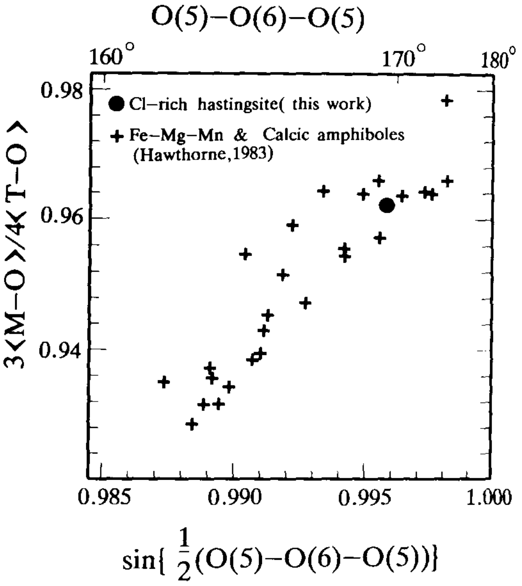

FIG. 2. Variation in the 3 < M–O >/4 < T–O > values with the O(5)–O(6)–O(5) angles.

The M(1), M(2) and M(3) octahedral sites. The site refinement (Table 5) of the Cl-rich hastingsite shows that the *M*(2) site is enriched in Mg* over the *M*(1) and *M*(3) sites, and that the <*M*(1)–O> and <*M*(3)–O> lengths are much larger than the <*M*(2)–O> (Table 5). The Cl-rich hastingsite has larger *M*(1) and *M*(3) sites than any other hornblendes reported by previous authors (e.g. hastingsite; <*M*(1)–O> = 2.146, <*M*(3)–O> = 2.137 Å (Makino and Tomita, 1989), <*M*(1)–O> = 2.116, <*M*(3)–O> = 2.131 Å (Hawthorne and Grundy, 1977).

The chemical complexity of calcic amphiboles makes detailed interpretation of the refined occupancies of the octahedral sites difficult. It was, however, shown by Robinson *et al.* (1973) that the smaller Al, Fe^{3+} and Ti cations are confined in the *M*(2) site of *C2/m* calcic amphiboles. Hawthorne (1983) proposed a linear relationships between the mean bond length and the mean ionic radius of the constituent cations of the individual octahedral site. The ordering of the smaller cations on the *M*(2) site occurs in metamorphic hornblendes but not in volcanic ones (Makino and Tomita, 1989). Thus, Al, Fe^{3+} and Ti in the octahedral sites are assumed to occupy the *M*(2) site in the Cl-rich hastingsite produced by metamorphism. The residual fractions of Mg* and Fe* in the site are Mg and Fe^{2+}, respectively. The refined Mg* and Fe* occupancies in the *M*(1) and *M*(3) sites are believed to be those of Mg and Fe^{2+}.

In Table 5, the observed <M(2)–O> length of the Cl-rich hastingsite is in good agreement with the length calculated from the mean ionic radius using Hawthorne's equation (Hawthorne, 1938). This agreement confirms that the small cations are ordered to the M(2) site, as is the case for metamorphic calcic amphiboles. The cation occupancies of the octahedral sites determined in this way are presented in Table 6.

The Cl-rich hastingsite has the largest M(1) and M(3) sites of any previously reported amphibole. The presence of Cl makes the M(1) and M(3) octahedra expand and deform. When the O(3) site is occupied only by OH, the calculated mean lengths for the octahedral sites can be obtained by Hawthorne's equations (Hawthorne, 1983). The observed and calculated mean lengths disagree with each other for the M(1) and M(3) sites, bonding to the O(3A) and O(3B) (Table 7). Obviously a great amount of Cl in the O(3B) site increases the M(1)–O(3B) and M(3)–O(3B) distances.

Table 6. Site occupancies of M(1), M(2) and M(3) for the Cl-rich hastingsite.

Site	Mg	Fe^{2+}	Al	Fe^{3+}	Ti
M(1)	0.181	0.819			
M(2)	0.333	0.087	0.072	0.460	0.048
M(3)	0.057	0.943			

A little of Mn (0.04pfu) was included in Fe^{2+}.

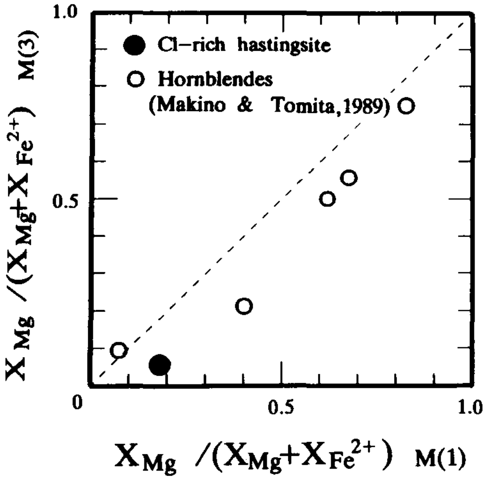

FIG. 3. Mg–Fe^{2+} distribution between the M(1) and M(3) sites in the Cl-rich hastingsite.

In order to examine the sizes of the M(1) and M(3) sites in the hypothetical structure which is free from Cl, both M(1)–O(3B) and M(3)–O(3B) distances were revised in accordance with a difference of ionic radii between Cl and O anions. Such a revision brings close agreement between revised mean bond lengths and those calculated using Hawthorne's equations (Table 7). The agreement for the M(1) and M(3) sites suggests that incorporation of Cl in the O(3B) site has little effect on the M(1)–O(1), O(2) and M(3)–O(1) distances.

In the Table 7, the two revised <M–O> lengths are 2.092 and 2.174 Å for the Cl-free structure and for the OH-free structure, respectively. The structure with these revised <M-O> lengths may appear locally in the Cl-rich hastingsite according to whether Cl or OH occupies the conventional O(3) site. Assuming the relation between the chain angle and the <T–O>/<M–O> ratio is valid locally, the ratio in the local structure require chain angles of 164° for OH and 180° for Cl, estimated roughly from Fig. 2. It, therefore, appears that Cl produces almost complete extension of the tetrahedral chains locally.

Mg–Fe^{2+} distribution among the octahedral sites. The Mg-Fe^{2+} partitioning among the octahedral sites in the Cl-rich hastingsite can be compared with the metamorphic or hydrothermal hornblendes examined by Makino and Tomita (1989).

Fig. 3. is a plot of the Mg/(Mg + Fe^{2+}) values of the M(1) site against that of the M(3) site. The Mg–Fe^{2+} distribution between these sites in the Cl-rich hastingsite is similar to that in ordinary hornblendes.

The Mg–Fe^{2+} distribution between the M(2) and the M(1) sites is shown in Fig. 4. The distribution coefficient between the M(2) and M(1) sites is given by

$$K_D = \left(\frac{x_{Mg}}{x_{Fe^{2+}}}\right)_{M(1)} \Bigg/ \left(\frac{x_{Mg}}{x_{Fe^{2+}}}\right)_{M(2)}, \qquad (1)$$

where x is the atomic fraction in the sites.

The Cl-rich hastingsite deviates from the curve (K_D = 0.3) of ordinary hornblendes, and plots near the curve for K_D = 0.06. This indicates a strong preference for Fe^{2+} on the M(1) and M(3) sites rather than the M(2) site in the Cl-rich hastingsite, whereas Mg prefers the M(2) site against the M(1) and M(3) sites.

The Mg–Cl avoidance rule in mica was proposed. The rule was demonstrated by studies of chemical compositions (Leelanandam, 1970;

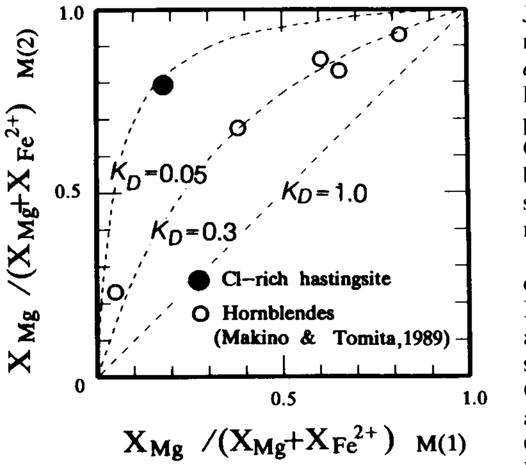

FIG. 4. Mg-Fe^{2+} distribution between the *M*(1) and *M*(2) sites in the Cl-rich hastingsite.

Jacobs and Parry, 1979), and examined experimentally (Munoz and Swenson, 1981, Volfinger *et al.*, 1985). A high Cl-content is observed in Fe^{2+} rich mica (biotite or annite), whereas phlogopite, the Mg end-member, contains little Cl. Volfinger *et al.* (1985) interpreted the relation between Fe^{2+} and the Cl-content in terms of the structural control, and extended the model from micas to amphiboles.

Calcic amphiboles differ from micas in the configuration of (Mg, Fe^{2+}) and (OH, Cl) sites. In calcic amphiboles, Mg and Fe^{2+} cations are accommodated not only in the *M*(1) and *M*(3) sites bonding to the OH and Cl site (conventional O(3)) but also in the *M*(2) site not linked to OH and Cl anions. The Mg–Fe^{2+} partitioning of the Cl-rich hastingsite shows a strong preference of Mg for the *M*(2) site rather than the *M*(1) and *M*(3) sites when compared with hydroxy hornblendes. Thus, it is considered, in the Cl-rich hastingsite, that the Mg–Cl avoidance rule appears to hold in intracrystalline Mg–Fe^{2+}

Table 7. Observed revised and calculated mean lengths(Å) of the octahedral sites in the Cl-rich hastingsite.

	Observed	Revised for OH	Revised for Cl	Calculated for OH
<M(1)-O>	2.176	2.118	2.255	2.125
<M(2)-O>	2.050	2.050	2.050	2.044
<M(3)-O>	2.186	2.124	2.261	2.121
<M-O>	2.130	2.092	2.174	2.092

Revised for OH; mean lengths, presuming the O(3) site occupied only by OH.

$$\langle M(i)\text{-}O\rangle = 0.55\langle M(i)\text{-}O\rangle_A + 0.45[\langle M(i)\text{-}O\rangle_B - \frac{1^{\#}}{3}\{r(Cl) - r(O)\}],\quad i=1,3$$

Revised for OH; mean lengths, presuming the O(3) site occupied only by OH.

$$\langle M(i)\text{-}O\rangle = 0.55[\langle M(i)\text{-}O\rangle_A + \frac{1^{\#}}{3}\{r(Cl) - r(O)\}] + 0.45\langle M(i)\text{-}O\rangle_B,\quad i=1,3$$

Calculated for OH; mean lengths calculated by Hawthorne's equations (Hawthorne; 1983), presuming the O(3) occupied only by OH.

#; Cations in the M(*i*) sites are bonded to 4 oxygens and to 2 anions (O or Cl) in the O(3) site.

exchange reactions. However, it is not known whether the rule is completely realised in the exchange reaction and further examination will be needed to answer this question.

Conclusion

The cation distribution of the octahedral $M(1)$, $M(2)$ and $M(3)$ sites in the Cl-rich hastingsite formed during Proterozoic metamorphism was determined by the structure refinement. The smaller cations such as Al, Fe^{3+} and Ti have been assigned to the $M(2)$ site by analogy with other calcic amphiboles, and the evidence from the $M(2)$–O distance is consistent with this. As regards the Mg–Fe^{2+} distribution (K_D) between the $M(1)$ and $M(2)$ sites, the Cl-rich hastingsite ($K_D = 0.06$) differs from other calcic amphiboles ($K_D = 0.3$). The strong preference of Mg for the $M(2)$ site suggests that the Mg–Cl avoidance is realised in the intracrystalline exchange reaction among the octahedral sites in the Cl-rich hastingsite, because Cl in the O($3B$) site is bonded to the $M(1)$ and $M(3)$ cations and not to the $M(2)$.

OH and Cl occupy distinct sites O($3A$) and O($3B$) whose positions were refined individually. From the O($3B$)–O($3B$) and O($3A$)–O($3B$) distances, the effective ionic radius of Cl is estimated to be 1.79 Å in fourfold coordination. The $M(1)$ and $M(3)$ sites are significantly expanded, in response to the incorporation of large Cl anions. Cl in the O(3) site affects only the $M(1)$–O(3) and $M(3)$–O(3) distances. As a result of the expansion of the $M(1)$ and $M(3)$ octahedra, the incorporation of Cl makes the double chain more extended (O(5)–O(6)–O(5) = 169°). Cl is unusually close to the O(6) and O(7) oxygen, with non-bonded distances less than expected from ionic radii. So, substitution of Cl induces the local deformation in the Cl-rich hastingsite.

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