

Chlorine-rich potassium hastingsite from West Ongul Island, Lützow-Holm Bay, East Antarctica

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Abstract

Chlorine-rich potassium hastingsite occurs in a calcareous pegmatite, a replacement zone and an amphibolite lens within hornblende gneiss on West Ongul Island, Lützow-Holm Bay, East Antarctica. The amphibolite lens and hornblende gneiss were metamorphosed to the kyanite-sillimanite grade of the granulite facies during Proterozoic metamorphism. Chemical analysis (3.27 wt. % Cl), unit cell parameters and optical properties of the Cl-rich potassium hastingsite are given. Cl-rich (> 3 wt. %) calcic amphiboles reported from various rock types are mostly more than 0.9 in (Na+K) content, more than 0.4 in K/(Na+K) ratio, more than 0.75 in $Fe^{2+}/(Fe^{2+} + Mg + Mn)$ ratio and more than 1.9 in Al^{IV} content (total iron as FeO and O = 23). The unit cell volume of Cl-rich hastingsite is distinctly larger than that of Cl-poor hastingsite.

KEYWORDS: Cl-rich calcic amphiboles, hastingsite, West Ongul Island, Antarctica.

Introduction

LARGE concentrations of Cl in calcic amphibole have been reported from various rock types: skarn, calcareous metamorphic rock, calcareous pegmatite, granitic rock, submarine mylonitic gabbro, mylonite, amphibolite, rodingite and charnockitic rock. The Cl content of these amphiboles, however, is usually less than 2 wt. % and rarely exceeds 3 wt. %.

The calcic amphibole reported from a skarn in Dashkesan by Krutov (1936) is the highest in Cl content (7.24 wt. %) so far recorded. Jacobson (1975) reported Cl-rich calcic amphiboles containing 5.34 and 6.51 wt. % Cl respectively from skarn in Dashkesan and mylonite in St. Paul's Rock. Dick and Robinson (1979) reported Cl-rich calcic amphibole containing 3.09 wt. % Cl from a skarn in southern Yukon; Sharma (1981) found similar amphiboles containing 3.6 wt. % Cl in calcareous metamorphic rock in India, and Kamineni *et al.* (1982) reported others containing 4.18 wt. % from charnockitic rock in India. The Cl-rich calcic amphibole from West Ongul Island, the subject of this paper, contains 3.27 wt. % Cl and is one of the Cl-rich calcic amphiboles (Suwa, 1968; this paper). It is noteworthy that these calcic amphiboles containing Cl in sizeable amounts are mostly of

potassian or potassium hastingsites of Leake (1978).

The mineralogical properties and mode of occurrence of the Cl-rich potassium hastingsite and its associated minerals from West Ongul Island are described in this paper.

The rock sample containing Cl-rich potassium hastingsite was collected by the first wintering party of the Japanese Antarctic Research Expedition (JARE) 1956-1958, and was entrusted to one of us (K.S.) for study through Prof. T. Tatsumi, a member of the party.

Geologic setting

Cl-rich potassium hastingsite was found in a calcareous pegmatite, replacement zone and amphibolite lens within hornblende gneiss on the west side of the central ridge of West Ongul Island (lat. 69° 01' 45" S, long. 39° 31' 01" E), 4 km SW of the Syôwa station (69° 00' 20" S, 39° 35' 20" E) of East Ongul Island (Fig. 1). The amphibolite lenses occur within the hornblende gneiss about 100 m thick which strikes north-south and dips eastward at 30-60° on the west side of the central ridge of West Ongul Island (Yanai *et al.*, 1974).

The high-grade metamorphic rocks in the Prince

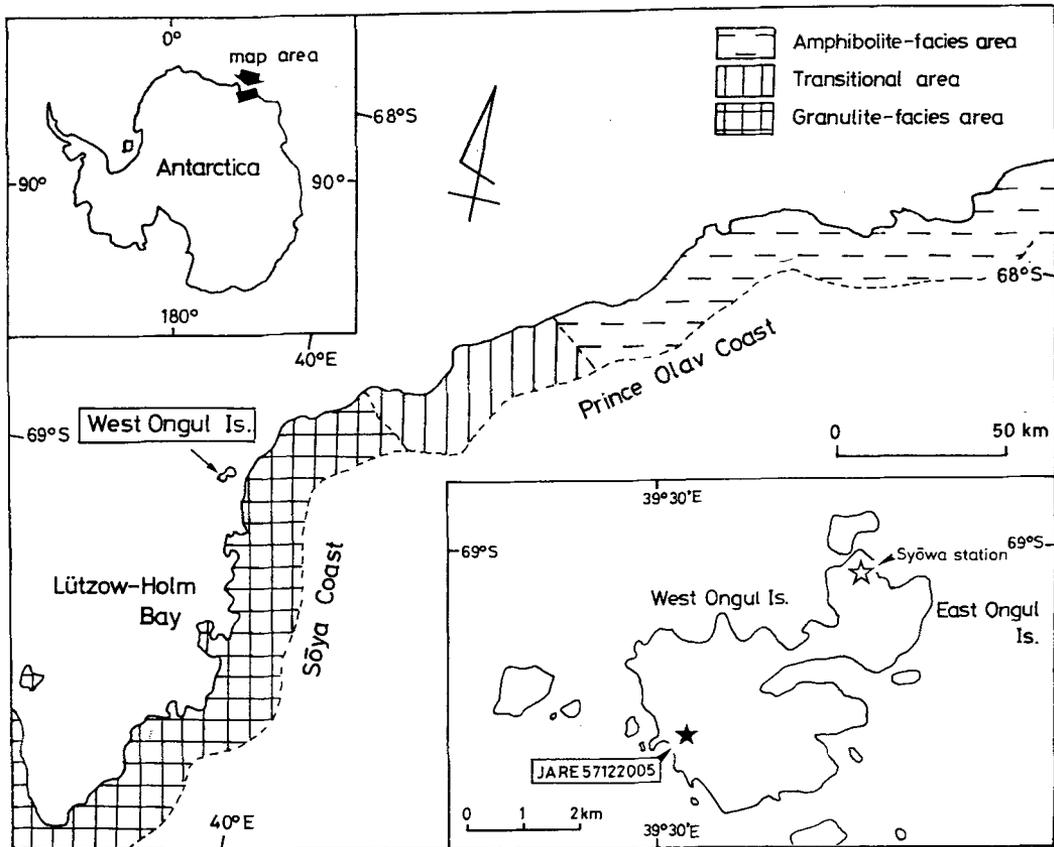


FIG. 1. Geologic setting of West Ongul Island, Lützow-Holm Bay (after Hiroi *et al.*, 1983). SE corner of Fig. 1 shows the locality of Cl-rich potassium hastingsite in West Ongul Island.

Olav and Sōya coasts (68–70° S, 37–45° E) are collectively known as the Lützow-Holm Bay system (Tatsumi and Kizaki, 1969), which is divided into three zones of differing metamorphic grade. Metamorphic grade increases from the amphibolite facies (northeast) to the granulite facies (southwest) through the transitional facies (Hiroi *et al.*, 1983) (Fig. 1). The Sōya coast, including West Ongul Island to the west, forms the granulite facies area characterized by the common occurrence of orthopyroxene and sillimanite. The eastern part of the Prince Olav coast is the amphibolite facies area, characterized by the common occurrence of anthophyllite, gedrite, cummingtonite, kyanite and sillimanite. The regional distribution of sillimanite and kyanite in the Prince Olav and Sōya coasts indicates that the regional metamorphism in the area was of the medium-pressure type.

The K–Ar and Rb–Sr ages of total rocks and of mineral separates concentrate at about 500 Ma, indicating a heating event coeval with Early

Palaeozoic granite and pegmatite activity (Yanai and Ueda, 1974). A few Rb–Sr total rock or mineral ages, however, range from 1000 to 1200 Ma (Maegoya *et al.*, 1968; Shirahata, 1983), dating the regional metamorphism of the Lützow-Holm Bay system.

Petrography

Between the calcareous pegmatite and the amphibolite lens, a replacement zone of a few centimetres width is developed. Melanocratic amphibolite is found locally near the boundary between the amphibolite and the replacement zone (Fig. 2). The calcareous pegmatite consists of Cl-rich potassium hastingsite, scapolite, calcite and actinolite, with accessory analcite, sphene, apatite, quartz and pyrite (Table 1). The Cl-rich potassium hastingsite occurs in euhedral crystals up to 2 cm, scapolite as large euhedral crystals up to 10 cm, and calcite and quartz occur as anhedral crystals.

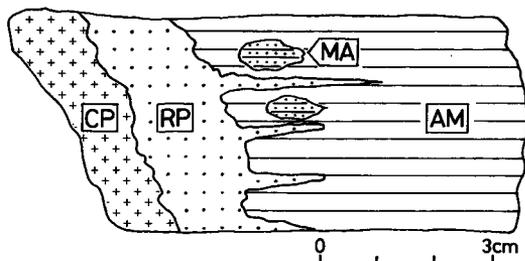


FIG. 2. Relationship between calcareous pegmatite, replacement zone, amphibolite lens and melanocratic amphibolite. Abbreviations: CP: calcareous pegmatite, RP: replacement zone, AM: amphibolite lens, MA: melanocratic amphibolite.

At the boundary between the calcareous pegmatite and the replacement zone, calcite is predominant. The calcite matrix is studded with scapolite, actinolite and sphene. The replacement zone itself consists of scapolite, actinolite, calcite and Cl-rich potassium hastingsite, with accessory quartz, sphene, orthoclase, allanite and pyrite (Table 1).

The amphibolite is made up andesine, scapolite, ferroan pargasitic hornblende, actinolite and salite with accessory biotite, sphene, Cl-rich potassium hastingsite, orthoclase, pyrite, apatite, calcite, zircon and chalcopyrite (Table 1). In the amphibolite, the original mineral assemblage is recognizable as andesine + CaO-rich (12.0 wt. % ±) primary scapolite + ferroan pargasitic hornblende + salite + TiO₂-rich (4.0 wt. % ±) primary biotite. Due to replacement, K and Cl metasomatism, and accompanying injection of the calcareous pegmatite, andesine is partly replaced by secondary scapolite (CaO = 9.7 wt. % ±) and orthoclase. Ferroan pargasitic hornblende and salite are partly replaced

Table 1. Modal compositions (vol. %) of the calcareous pegmatite (CP), replacement zone (RP), amphibolite lens (AM) and melanocratic amphibolite (MA).

	CP	RP	AM	MA
Scapolite	27.8	63.1	25.9*	27.8
Hastingsite	37.9	4.0	0.9	40.4
Actinolite	12.3	15.0	12.1	20.1
Calcite	18.5	10.6	tr	3.3
Plagioclase	0	0	32.2	0
Hornblende	0	0	18.2	0.7
Salite	0	0	6.6	0
Quartz	3.5	3.8	0	0
Orthoclase	0	0.2	0.6	5.5
Sphene	tr	2.3	1.3	1.4
Biotite	0	0	1.3	0
Analcite	tr	0	0	0
Others	0	1.0	1.0	0.7
Total	100.0	100.0	100.1	99.9

* Primary scapolite : 20.4 %,
Secondary scapolite: 5.5 %

Table 2. Chemical composition of the amphibolite lens (AM) (JARE-57122005).

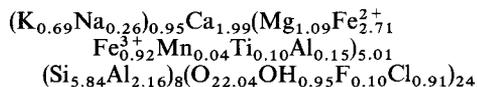
wt. %		Norm	
SiO ₂	48.90	Or	19.3
TiO ₂	0.81	Ab	13.7
Al ₂ O ₃	14.15	An	21.7
Fe ₂ O ₃	2.14	Hl	0.6
FeO	7.04	Di	20.8
MnO	0.21	Wo	10.6
MgO	5.94	En	6.0
CaO	11.04	Fs	4.2
Na ₂ O	1.94	Hy	9.6
K ₂ O	3.27	Fs	3.9
H ₂ O ⁺	1.21	Ol	3.9
H ₂ O ⁻	0.36	Po	2.2
P ₂ O ₅	0.061	Fa	1.7
F	0.192	Mt	3.1
Cl	0.364	Il	1.5
CO ₂	0.92	Ap	0.1
		Fr	0.4
		Cc	2.1
		H ₂ O	1.57
Total	98.547		
		Total	98.37

by Cl-rich potassium hastingsite, actinolite and secondary biotite (TiO₂ = 2.3 wt. % ±). The chemical composition of the amphibolite lens is shown in Table 2.

The melanocratic amphibolite consists of Cl-rich potassium hastingsite, scapolite and actinolite, with accessory orthoclase, calcite, sphene, ferroan pargasitic hornblende, allanite, epidote, apatite, zircon, pyrite and chalcopyrite (Table 1). A sieve texture in the Cl-rich potassium hastingsite is noticeable.

Chlorine-rich potassium hastingsite

Analysis of the Cl-rich potassium hastingsite in the calcareous pegmatite was made using wet chemical methods. Supplementary analyses of the Cl-rich potassium hastingsite and other constituents were made on a JEOL JXA-733 electron-probe microanalyser. Accelerating voltage, specimen current and beam diameter were kept constant at 15 kV, 1.2 × 10⁻⁸ A and 3 μm, respectively. The chemical composition of the Cl-rich potassium hastingsite in the calcareous pegmatite is given in the first column of Table 3 and the empirical formula is



on the basis of (O,OH,F,Cl) = 24. The Cl-rich potassium hastingsite has high (Na + K) content (0.95), high X_K [= K/(Na + K)] value (0.73), high X_{Fe} [= (Fe²⁺ + Fe³⁺)/(Fe²⁺ + Fe³⁺ + Mg + Mn)] value (0.76) and high Al^{IV} content (2.16).

The X-ray powder diffraction data were obtained by a Rigaku RAD-IA X-ray diffractometer (Osaka City University) using Mn-filtered Fe-Kα radiation

Table 3. Chemical compositions of Cl-rich potassium hastingsite (JARE-57122005).

	CP(w)	CP(e)	RP(e)	AM(e)
	n=12		n=8	n=12
SiO ₂	35.52	36.2	37.2	36.3
TiO ₂	0.77	0.52	0.50	0.55
Al ₂ O ₃	11.94	11.2	11.0	11.4
Fe ₂ O ₃	7.44			
FeO	19.73	25.2*	24.6*	25.5*
MnO	0.30	0.34	0.33	0.46
MgO	4.44	4.80	5.35	4.34
CaO	11.32	11.6	11.7	11.5
Na ₂ O	0.80	0.96	0.92	0.79
K ₂ O	3.27	3.12	2.98	3.32
H ₂ O ⁺	0.87			
H ₂ O ⁻	0.14			
F ₂ O ₅	0.01			
F	0.19			
Cl	3.27			3.69
SO ₃	0.02			
CO ₂	0.00			
Total	100.03	93.94	94.58	97.85
O=F,Cl	0.82			0.83
Total	99.21	93.94	94.58	97.02

* Total iron as FeO

n: Number of analytical points

Abbreviations: CP: calcareous pegmatite,

RP: replacement zone, AM: amphibolite

lens, w: wet chemical analysis,

e: electron probe microanalysis,

Table 4. Powder pattern and unit cell parameters of Cl-rich potassium hastingsite (JARE-57122005).

h	k	l	d(Å) _{meas.}	d(Å) _{calc.}	I/I ₀
0	2	0	9.15	9.15	<5
1	1	0	8.52	8.52	100
2	0	0	4.81	4.81	5
0	4	0	4.57	4.57	5
0	4	1	3.432	3.433	10
2	4	0	3.314	3.315	15
3	1	0	3.159	3.159	40
2	2	1	2.978	2.978	10
3	3	0	2.838	2.839	15
-3	3	1	2.770	2.771	5
1	5	1*	2.745	2.744	25
0	6	1*	2.631	2.630	10
-2	0	2*	2.581	2.580	10
3	5	0*	2.411	2.412	10
-3	5	1*	2.370	2.370	10
-4	2	1*	2.354	2.353	5
-1	7	1*	2.332	2.331	5
-3	1	2*	2.315	2.315	5
-2	4	2	2.247	2.247	<5
2	6	1*	2.191	2.191	10
2	0	2*	2.075	2.074	5
3	5	1*	2.042	2.042	5
5	1	0	1.913	1.914	<5
-4	6	1	1.902	1.903	5
5	3	0	1.835	1.835	5
0	10	0	1.830	1.829	5
4	6	1*	1.670	1.670	5
1	11	0*	1.639	1.639	5
-1	5	3*	1.605	1.605	5
4	0	2	1.575	1.575	<5
-3	5	3	1.555	1.557	<5
-2	6	3*	1.539	1.539	<5
0	12	0	1.525	1.525	<5
5	5	1	1.520	1.519	<5
-6	6	1*	1.456	1.456	5

a=9.957(3) Å, b=18.294(4) Å, c=5.377(1) Å,
β=104.90° (4), V=946.5(4) Å³

* Peaks using for calculation of unit cell parameters

(λ = 1.93728 Å): 30 kV, 10 mA, slit 1°-0.3 mm-1° and scanning speed of 0.3°/minute. Silicon was used as an external standard. Peaks were indexed by reference to the calculated powder patterns of hornblende (Borg and Smith, 1969).

The X-ray powder data are summarized in Table 4. The unit cell parameters obtained from the sixteen sharp reflection data with 2θ > 40° (asterisked in Table 4) are as follows: a = 9.957(3), b = 18.294(4), c = 5.377(1) Å, β = 104.90° (4) and V = 946.5(4) Å³. The unit cell volume calculated is similar to that of Cl-bearing (Cl = 2.35 wt. %) potassium hastingsite (V = 943.50 Å³; Dick and Robinson, 1979), and is distinctly larger than that of Cl-poor or Cl-free hastingsite (V = 911.54-922.60 Å³; Shemyakin *et al.*, 1970; Hawthorne and Grundy, 1977).

The Cl-rich potassium hastingsite is biaxial negative with 2V = 19° (3). Refractive indices obtained by the immersion method are: α = 1.712 (1), β = 1.732 (1), γ = 1.734 (1), γ - α = 0.022. Extinction angle is: c ∧ Z = 24°. The optical dispersion is strong with r > v. It is pleochroic with X = light green, Y = green, Z = greenish blue to blue.

Associated minerals

Chemical compositions of associated minerals with Cl-rich potassium hastingsite are shown in Table 5. The average meionite molecules of the primary scapolite in the calcareous pegmatite, replacement zone and amphibolite are 56.7, 53.4 and 48.8%, respectively. Secondary scapolite formed during the replacement stage occurs in the rim of the plagioclase grains. The meionite molecule of secondary scapolite averages 39.1%, and the Na/Ca ratio of secondary scapolite is very similar to that of plagioclase (An₃₅Ab₆₃Or₂). The chemical composition of the secondary scapolite is considered to be controlled by the plagioclase composition.

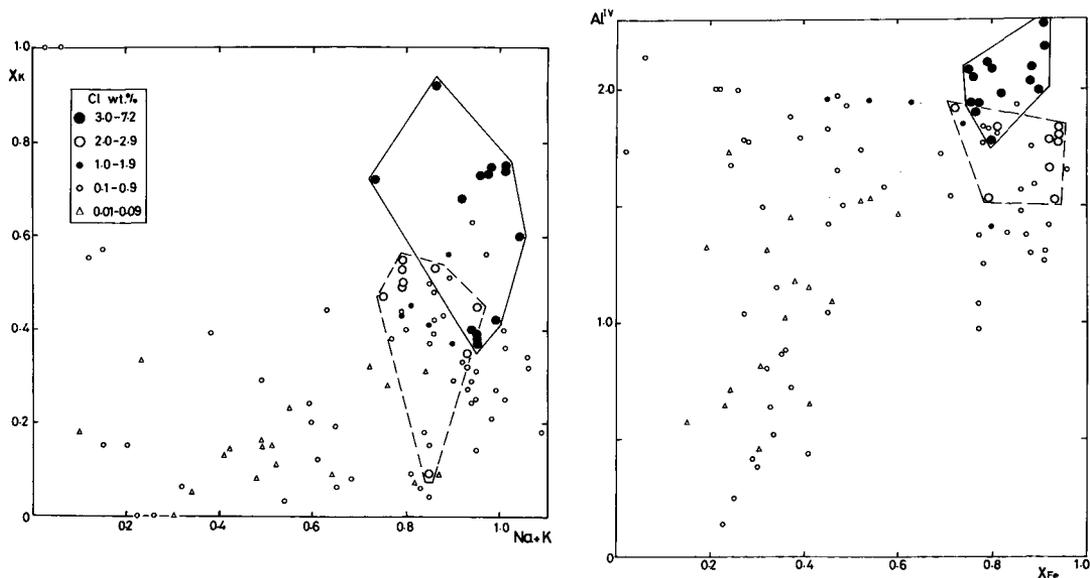
The chemical compositions of primary and secondary biotites are similar, with the exception of TiO₂, FeO and Cl contents: secondary biotite formed during the replacement stage is richer in FeO and Cl content and is poorer in TiO₂ content. The average Cl content of secondary biotite reaches 0.88 wt. %.

Clinopyroxene in the amphibolite lens is salite with average X_{Fe} value of 0.25. Ferroan pargasitic hornblende contains small amounts of chlorine (0.58 wt. % ±), and is considered to have formed during Proterozoic metamorphism. Actinolite in the amphibolite was formed during the replacement stage, and contains a small amount of chlorine (0.07 wt. % ±).

Table 5. Chemical compositions of major constituent minerals.

	CP		RP		AM						
	Sc	Ac	Sc	At	Sc(p)	Sc(s)	Bt(p)	Bt(s)	Sl	Ph	At
	n=13	n=3	n=12	n=7	n=11	n=11	n=7	n=3	n=8	n=12	n=9
SiO ₂	50.5	55.1	51.1	52.1	52.1	54.3	37.5	37.8	53.5	41.4	51.7
TiO ₂	0.00		0.00	0.07	0.00	0.00	4.02	2.26	0.09	1.73	0.24
Al ₂ O ₃	25.2	22.7	25.0	2.66	24.1	23.4	13.3	13.6	0.84	11.3	3.85
FeO*	0.17	0.00	0.12	11.8	0.06	0.05	15.1	16.1	7.73	16.3	11.8
MnO	0.00		0.00	0.30	0.00	0.00	0.20	0.29	0.38	0.25	0.27
MgO	0.00		0.00	15.8	0.00	0.00	14.5	14.8	13.2	10.2	15.4
CaO	13.6	0.11	12.7	12.7	12.0	9.73	0.00	0.00	24.6	11.9	12.7
Na ₂ O	5.00	13.3	5.52	0.28	6.31	7.61	0.04	0.00	0.35	1.51	0.54
K ₂ O	1.11	0.00	1.04	0.25	0.99	1.16	9.68	9.50	0.00	2.09	0.41
Cl							0.35	0.88		0.58	0.07
Total	95.58	91.21	95.48	95.96	95.56	96.25	94.69	95.23	100.69	97.26	96.98

* Total iron as FeO n: Number of analytical points
 Abbreviations: CP: calcareous pegmatite, RP: replacement zone, AM: amphibolite lens,
 Sc(p): primary scapolite, Sc(s): secondary scapolite, Ac: analcite, At: actinolite,
 Bt(p): primary biotite, Bt(s): secondary biotite, Sl: salite, Ph: ferroan pargasitic
 hornblende.



FIGS. 3 and 4. FIG. 3 (left). Relationship between Cl, X_K and (Na + K) values of calcic amphiboles (total iron as FeO and O = 23). The Cl-rich amphiboles are high in both X_K value and (Na + K) content. FIG. 4 (right). Relationship between Cl, Al^{IV} and X_{Fe} values of calcic amphiboles. The Cl-rich amphiboles are high in both Al^{IV} content and X_{Fe} value. The chemical data are based on Borley (1962), Buddington and Leonard (1953), Compton (1958), Czamanske *et al.* (1977), Dick and Robinson (1979), Gulyaeva *et al.* (1986), Honnorez and Kirst (1975), Ito and Anderson (1983), Jacobson (1975), Kamineni *et al.* (1982), Krutov (1936), Krutov and Vinogradova (1966), Leelanandam (1970), Matsubara and Motoyoshi (1985), Matsumoto (1974), Sharma (1981), Suwa *et al.* (this paper) and Vielzeuf (1982).

Discussion

Cl-rich calcic amphiboles containing more than 3 wt. % Cl are mostly potassian or potassium hastingsites of Leake (1978). These are mostly higher than 0.9 in (Na + K) content, 0.37–0.94 in X_K value, higher than 0.75 in X_{Fe} value and 1.8–2.3 in

Al^{IV} content (total iron as FeO and O = 23). Cl-bearing calcic amphiboles containing 2.0–2.9 wt. % Cl are mostly higher than 0.75 in (Na + K) content, 0.35–0.57 in X_K value, higher than 0.75 in X_{Fe} value and 1.5–1.9 in Al^{IV} content. Cl-poor calcic amphiboles containing less than 0.09 wt. % Cl are mostly below 0.8 in (Na + K) content, 0.00–0.33 in

X_K value, below 0.6 in X_{Fe} value and 0.5–1.8 in Al^{IV} content.

These chemical data of Cl-rich, Cl-bearing and Cl-poor calcic amphiboles are plotted in Fig. 3, showing the relationship between Cl content and X_K value, (Na + K) content, and in Fig. 4, showing the relationship between Cl content and Al^{IV} content, X_{Fe} value. These two figures clearly show the positive correlation between Cl content and (Na + K) content, between Cl and X_K , between Cl and X_{Fe} , and between Cl and Al^{IV} in calcic amphiboles.

The unit cell volume of Cl-rich potassium hastingsite (946.5 \AA^3 : 3.27 wt. % Cl and 943.5 \AA^3 : 2.35 wt. % Cl) is distinctly larger than that of Cl-poor or Cl-free hastingsite (911.54 – 922.60 \AA^3). This may indicate that the expansion of calcic amphibole is necessary for the entrance of Cl into the crystal structure of calcic amphibole.

If the entire amphibole chains were expanded, the replacement of OH^- by Cl^- would become easier. The ionic radius of Cl^- (1.81 Å) is 30–35% larger than that of OH^- (1.40 Å) and F^- (1.33 Å). Such expansion may be accomplished if both SiO_4 tetrahedra and octahedral cations are enlarged, i.e. Al into tetrahedral site and Fe into octahedral site. Substitution of Al into the tetrahedral site requires a triply charged cation, Fe^{3+} , in the octahedral site, and/or a singly charged cation, Na or K, in the A site for charge balance (Ito and Anderson, 1983). This expansion scheme may explain the positive correlation between Cl and (Na + K), that between Cl and X_{Fe} , and that between Cl and Al^{IV} in calcic amphiboles.

On the other hand, as regards the crystal-chemical control of the incorporation of chlorine in amphibole, the fundamental role of the local structure of the anion site has been demonstrated by Volfinger *et al.* (1985). In the case of amphiboles, the rotation of tetrahedra controls the dimension of the anionic site (OH, F, and Cl site). The closer the symmetry of the ring of six tetrahedra (in the double chain in amphiboles) is to ideal hexagonal symmetry, the easier the replacement of OH^- by Cl^- . This scheme may explain the positive correlation between Cl and X_K and that between Cl and X_{Fe} in calcic amphiboles. It may not, however, explain the positive correlation between Cl and Al^{IV} in calcic amphibole.

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