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Potassic-ferropargasite, a new member of the amphibole group, from Kabutoichiba, Mie Prefecture, central Japan

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Potassic–ferropargasite, ideally $KCa_2(Fe^{2+}_4Al)Si_6Al_2O_{22}(OH)_2$, is a new member of the amphibole group occurring in a schistose calcareous hornfels from Kabutoichiba, Kameyama, Mie Prefecture, central Japan. The amphibole occurs as black subhedral to anhedral crystals, up to about 700 µm long, associated with calcite, biotite, K–feldspar, plagioclase, scapolite, chlorite and titanite. Potassic–ferropargasite is optically biaxial negative with $\alpha = 1.680(2)$, $\beta = 1.690$ (calc.), $\gamma = 1.698(2)$ and $2V = 80–90°$. The mineral is monoclinic, space group $C2/m$, with refined unit–cell parameters $a = 9.937(5)$, $b = 18.108(5)$, $c = 5.335(4)$ Å, $\beta = 105.30(3)°$, $V = 926.0(9)$ Å^3, $Z = 2$. The three strongest lines in the X–ray powder–diffraction pattern [d in Å (I) hkl] are 2.72 (100) 151, 8.48 (81) 110 and 2.61 (59) 061. Electron–microprobe gave SiO_2 38.08, TiO_2 1.92, Al_2O_3 15.12, Cr_2O_3 0.44, FeO 19.96, MnO 0.22, MgO 6.22, CaO 11.73, Na_2O 1.57, K_2O 2.74, F 0.13, Cl not detected, O = F + Cl –0.05, total 98.08 wt%, corresponding to $(K_{0.54}Na_{0.42})_{\Sigma 0.96}(Ca_{1.95}Na_{0.05})_{\Sigma 2.00}(Fe^{2+}_{2.59}Mg_{1.44}Al_{0.67}Ti_{0.22}Cr_{0.05}Mn_{0.03})_{\Sigma 5.00}(Si_{5.91}Al_{2.09})_{\Sigma 8.00}O_{22}(OH_{1.94}F_{0.06})_{\Sigma 2.00}$ on the basis of O = 23, assuming OH + F + Cl = 2. The crystal structure of the clinoamphibole type was refined to an R of 6.5%.

Keywords: Potassic–ferropargasite, New mineral, Clinoamphibole, Crystal structure, Kabutoichiba, Amphibole group, Potassium

INTRODUCTION

Potassium–dominant ferropargasite was reported from pyroclastic deposits of the Pompeii eruption of Somma–Vesuvias, Italy (Rosi and Santacroce, 1983), thermally metamorphosed rocks in the Nogo–Hakusan area of central Japan (Sawaki, 1989), orthogneisses from the Adirondack Mountains of USA (Morrison, 1991), calc–silicate pods in gneisses from East Antarctica (Shiraishi et al., 1994) and calc–silicate skarns on Kola Peninsula, Russia (Mazdab, 2003). However, these authors who described the K–rich amphibole did not apply for a new mineral species for approval by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association. Therefore the mineral has not been formally described as a species until now (cf., Mazdab, 2003).

Recently, amphibole nomenclature was revised by the Amphibole Subcommittee of CNMMN (Leake et al., 1997, 2004). This nomenclature scheme defines prefixes (e.g., chloro, potassic) that are an essential part of the amphibole name. The prefix “potassic” is related to K > 0.5 atoms per formula unit (apfu) and applies to all amphibole groups (Leake et al., 1997). The amphibole, which has chemical and structural properties that conform to the new nomenclature of potassic–ferropargasite (Leake et al., 1997), was found in a metamorphic rock from Kabutoichiba, Kameyama, Mie Prefecture, central Japan. The mineral data and mineral name have been approved by CNMMN (No. 2007–053). In this paper, we will present a

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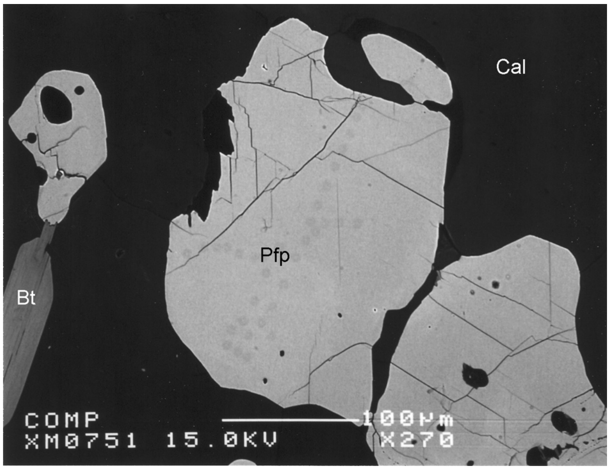

Figure 1. Back-scattered electron image of potassic-ferropargasite. Scale bar is 100 µm. Abbreviations are: Pfp, potassic-ferropargasite; Bt, biotite; Cal, calcite.

description of potassic-ferropargasite from Kabutoichiba. The type specimens of potassic-ferropargasite have been deposited at the Geological Museum, Geological Survey of Japan, AIST, Tsukuba, under the registered number GSJ M38953 and National Museum of Nature and Science, Tokyo, under the catalogue no. NSM-M29296.

GEOLOGICAL SETTING AND PETROGRAPHY

The Kabutoichiba area is underlain mainly by the Cretaceous Kabuto granodiorite and Kanaba tonalite. The Kabuto granodiorite includes many lens-shaped bodies (<about 300 m wide) of the Ryoke metamorphic rocks (Miyamura et al., 1981). These metamorphic rocks are mainly composed of schistose pelitic and psammitic hornfelses with a subordinate amount of schistose calcaleous and basic hornfelses (Miyamura et al., 1981). A potassic-ferropargasite-bearing sample was collected from schistose calcareous hornfels, which occurs as a pod in schistose pelitic hornfels, at a closed quarry in the Kabutoichiba area, Mie Prefecture, central Japan (N 34°51′, E 136°21′). The sample is mainly composed of calcite, biotite, potassic-ferropargasite, K-feldspar, plagioclase, scapolite and titanite with minor chlorite. Potassic-ferropargasite occurs as a rock-forming mineral in the schistose calcareous hornfels, and forms subhedral to anhedral crystals up to 0.7 mm long (Fig. 1). The mineral shows distinct pleochroism (e.g., pale green to bluish green) and frequently includes minute grains of titanite, biotite and feldspar. Biotite is brown and occurs as plates < 1 mm long. K-feldspar and plagioclase are anhedral grains <0.5 mm in size. Scapolite occurs as subhedral grains up to 1 mm in size, and is intimately associated with calcite. Titanite forms euhedral to subhedral crystal <0.5 mm long. Chlorite occurs as flakes in biotite crystals parallel to their (001) plane.

Table 1. Chemical compositions of potassic-ferropargasite

		GSJ M38953	NSM-M29318
SiO_2	(wt%)	38.08	38.45
TiO_2		1.92	1.36
Al_2O_3		15.12	14.58
Cr_2O_3		0.44	0.24
Fe_2O_3*		0.00	0.33
FeO*		19.96	20.13
MnO		0.22	0.24
MgO		6.22	6.37
CaO		11.73	11.91
Na_2O		1.57	1.27
K_2O		2.74	3.18
F		0.13	0.25
Cl		n.d.	n.d.
-O=F+Cl		0.05	0.11
Total		98.08	98.20
H_2O**		1.87	1.81
Total		99.95	100.01
		O = 23, OH+F+Cl = 2**	
Si		5.91	5.98
$^{[4]}$Al		2.09	2.02
ΣT		8.00	8.00
$^{[6]}$Al		0.67	0.65
Ti		0.22	0.16
Cr		0.05	0.03
Fe^{3+}		0.00	0.04
Fe^{2+}		2.59	2.62
Mn		0.03	0.03
Mg		1.44	1.48
ΣC		5.00	5.01
ΣC-5		0.00	0.01
Ca		1.95	1.98
$^{[B]}$Na		0.05	0.01
ΣB		2.00	2.00
$^{[A]}$Na		0.42	0.37
K		0.54	0.63
ΣA		0.96	1.00
Total cations		15.96	16.00
F		0.06	0.12
Cl		n.d.	n.d.
OH		1.94	1.88

* Fe^{3+}/Fe^{2+} calculation based on the minimum ferric estimation (Schumacher, 1997).

** H_2O calculation based on the assumption of OH + F + Cl = 2.0 apfu.

n.d., not detected.

Table 2. Powder X-ray diffraction data for potassic-ferropargasite

$I_{\mathrm{obs.}}$	$d_{\mathrm{obs.}}$	$d_{\mathrm{calc.}}$*	*h k l*
8	9.04	9.05	0 2 0
81	8.48	8.47	1 1 0
10	4.95	4.939	$\bar{1}$ 1 1
8	4.80	4.792	2 0 0
14	4.53	4.527	0 4 0
5	4.01	4.003	1 1 1
7	3.91	3.910	$\bar{1}$ 3 1
51	3.40	3.399	0 4 1
		3.394	1 3 1
25	3.29	3.291	2 4 0
46**	3.15	3.146	3 1 0
41	2.96	2.950	2 2 1
12	2.82	2.824	3 3 0
22	2.77	2.762	$\bar{3}$ 3 1
100	2.72	2.716	1 5 1
59	2.61	2.603	0 6 1
43	2.57	2.573	0 0 2
		2.569	2 4 1
		2.567	$\bar{2}$ 0 2
10	2.40	2.396	3 5 0
		2.396	4 0 0
37	2.36	2.358	$\bar{3}$ 5 1
		2.348	$\bar{4}$ 2 1
17	2.31	2.310	$\bar{1}$ 7 1
		2.307	$\bar{3}$ 1 2
9	2.23	2.237	0 4 2
		2.233	$\bar{2}$ 4 2
39	2.17	2.170	$\bar{3}$ 3 2
		2.169	2 6 1
6	2.15	2.148	$\bar{1}$ 5 2
20	2.05	2.0524	2 0 2
		2.0429	$\bar{4}$ 0 2
20	2.03	2.0241	3 5 1
6	1.895	1.9063	5 1 0
		1.8935	$\bar{4}$ 6 1
11	1.872	1.8733	$\bar{1}$ 9 1
7	1.862	1.8621	$\bar{4}$ 4 2
		1.8570	$\bar{1}$ 7 2
5	1.809	1.8108	0 10 0
5	1.770	1.7699	$\bar{5}$ 1 2
9	1.697	1.7081	0 10 1
		1.6998	$\bar{1}$ 3 3
		1.6977	$\bar{2}$ 8 2
		1.6943	5 5 0
		1.6939	2 10 0
22	1.656	1.6568	$\bar{4}$ 8 1
		1.6563	4 6 1
10	1.622	1.6224	1 11 0
11	1.591	1.5975	6 0 0
		1.5913	$\bar{1}$ 5 3
8	1.560	1.5662	2 10 1
		1.5602	4 0 2
10	1.553	1.5532	$\bar{6}$ 0 2
16	1.526	1.5268	$\bar{2}$ 6 3
		1.5243	1 9 2
10	1.508	1.5090	0 12 0
		1.5082	5 5 1
8	1.477	1.4796	$\bar{2}$ 10 2
		1.4759	1 5 3
		1.4750	4 4 2
5	1.461	1.4634	3 11 0
		1.4616	$\bar{1}$ 7 3
17	1.450	1.4523	$\bar{4}$ 10 1
		1.4506	$\bar{6}$ 6 1
4	1.376	1.3765	$\bar{5}$ 5 3
8	1.369	1.3694	5 1 2
12	1.341	1.3455	1 11 2
		1.3437	$\bar{3}$ 11 2
		1.3394	2 6 3
		1.3391	5 3 2
9	1.319	1.3217	$\bar{7}$ 5 1
		1.3184	$\bar{1}$ 1 4
13	1.301	1.3017	0 12 2
		1.3008	$\bar{2}$ 12 2
3	1.290	1.2913	$\bar{1}$ 3 4
		1.2897	$\bar{3}$ 3 4
6	1.284	1.2865	0 0 4
		1.2833	$\bar{4}$ 0 4
5	1.277	1.2769	4 12 0
7	1.209	1.2081	$\bar{5}$ 11 2

* Calculated from refined cell parameters: $a = 9.937(5)$, $b = 18.108(5)$, $c = 5.335(4)$ Å, $\beta = 105.30(3)°$.

** Estimated from data with the external Si-standard, because of overlap by the diffraction of Si-standard.

PHYSICAL AND OPTICAL PROPERTIES OF POTASSIC-FERROPARGASITE

Potassic-ferropargasite is translucent to nearly opaque and black in color with a vitreous luster under naked eyes. The fracture is uneven and tenacity is brittle. The cleavage is perfect on {110}. The Vickers microhardness is 858-1150 kg/mm^2 (100 g load) corresponding to about 6 on the Mohs scale. The calculated density is 3.34 g/cm^3 based on the empirical formula. The mineral is optically biaxial negative with α 1.680(2), β (calc.) 1.690 for $2V$ of 85°, γ 1.698(2), $2V$ (meas.) > 80° and < 90°; $Z \wedge c$ 20°. It is pleochroic with X = pale green, Y = green and Z = bluish green.

MINERAL CHEMISTRY

Chemical analyses were performed on a JEOL JXA-8800R electron microprobe. Accelerating voltage and specimen current were kept at 15 kV and 12 nA on the Faraday cup, respectively. The beam diameter was 10 μm for the analyses of F and Cl, and 2 μm for the other element. Standards used were quartz (Si), rutile (Ti), corundum (Al), eskolaite (Cr), hematite (Fe), manganosite

Table 3. Crystallographic data and experimental details of a single crystal study on potassic-ferropargasite

a (Å)	9.925(3)
b (Å)	18.102(6)
c (Å)	5.3391(17)
β (°)	105.242(5)
V (Å^3)	925.5(5)
Space group	*C*2/*m*
Z	2
$D_{calc.}$ (g/cm^3)	3.34
μ (cm^{-1})	3.492
Radiation	Mo*K*α
Reflection range	$-12 \leq h \leq 12$
	$-23 \leq k \leq 12$
	$-6 \leq l \leq 5$
No. of measured reflections	2720
No. of unique reflections	1078
No. of observed reflections [$F^2 > 2\sigma(F^2)$]	947
R_{int}	0.0249
Variable parameters	103
$R1$ [$F^2 > 2\sigma(F^2)$], $R1$ (all reflections)	0.0559, 0.0649
w$R2$ (all reflections)	0.1784
Weighting parameters, a, b	0.1, 0
Goodness of Fit	1.324
Final $\Delta\rho_{max}$ (e/Å^3)	0.829
Final $\Delta\rho_{min}$ (e/Å^3)	-1.048

$R1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$.
$wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.
$P = (2F_c^2 + F_o^2)/3$.

(Mn), periclase (Mg), wollastonite (Ca), albite (Na), adularia (K), F-phlogopite (F) and Cl-rich hastingsite (Cl). The Bence and Albee (1968) method was employed for matrix corrections. Detection limits for Cl and F were about 0.02 and 0.08 wt% (3σ level), respectively.

Potassic-ferropargasite

An average of 26 electron microprobe analyses is shown in Table 1. Structural formula was calculated on the basis of O = 23. Chlorine was sought, but not detected. Values of Fe^{3+}/Fe^{2+} were estimated using the minimum ferric method described by Schumacher (1997). The amphibole has a fairly uniform composition (Fig. 1). The average composition shown in Table 1 gives the empirical formula $(K_{0.54}Na_{0.42})_{\Sigma 0.96}(Ca_{1.95}Na_{0.05})_{\Sigma 2.00}(Fe^{2+}_{2.59}Mg_{1.44}Al_{0.67}Ti_{0.22}Cr_{0.05}Mn_{0.03})_{\Sigma 5.00}(Si_{5.91}Al_{2.09})_{\Sigma 8.00}O_{22}(OH_{1.94}F_{0.06})_{\Sigma 2.00}$ on the basis of O = 23 assuming OH + F + Cl = 2, with OH derived by calculation from this constraint. The Gladstone-Dale compatibility index, which indicates a degree of compatibility of the optical data, density and chemical data (Mandarino, 1979, 1981), is -0.011, rated as the superior category. The end-member formula of potassic-ferropargasite is $KCa_2(Fe^{2+}_4Al)Si_6Al_2O_{22}(OH)_2$, which requires: K_2O 4.82, CaO 11.47, FeO 29.38, Al_2O_3 15.64, SiO_2 36.85, H_2O 1.84, Total 100.00 wt%.

Permissible Fe^{3+}/Fe^{2+} ratio can also be calculated by the maximum ferric estimation (Schumacher, 1997). However, despite the applicability of ferric estimation, the range of calculated permissible Fe^{3+}/(total Fe) values is quite small (0-0.008). The formula calculated on the basis of the maximum ferric estimation is $(K_{0.54}Na_{0.42})_{\Sigma 0.96}(Ca_{1.95}Na_{0.05})_{\Sigma 2.00}(Fe^{2+}_{2.57}Mg_{1.44}Al_{0.67}Ti_{0.22}Cr_{0.05}Mn_{0.03}Fe^{3+}_{0.02})_{\Sigma 5.00}(Si_{5.90}Al_{2.10})_{\Sigma 5.00}O_{22}(OH_{1.94}F_{0.06})_{\Sigma 2.00}$. This formula shows also K > 0.5 apfu.

After the approval of potassic-ferropargasite, we found more K-rich potassic-ferropargasite (K = 0.63 apfu) in another sample (NSM-M29318) from the Kabuto-ichiba area. An average of 17 electron microprobe analyses is shown in Table 1.

Other minerals

Biotite has a narrow compositional range with $Mg/(Mg + Fe^{2+})$ = 0.43-0.45 and Si = 2.74-2.75 apfu (O = 11). Its TiO_2 contents are up to 1.77 wt%. The meionite component in scapolite ranges from 75 to 78%. K-feldspar has almost a pure end member composition with Or_{91-93}. Plagioclase shows oscillatory zoning, and its compositional range is $Ab_{32-56}An_{43-67}Or_{0-1}$. Titanite contains up to 3.23 wt% Al_2O_3.

X-RAY CRYSTALLOGRAPHY OF POTASSIC-FERROPARGASITE

A single crystal fragment of potassic-ferropargasite carefully picked from a thin section of GSJ M38953 was used for an X-ray diffraction study. Electron microprobe analyses and X-ray diffraction data were collected using the same fragment.

Powder X-ray diffraction data

The powder X-ray diffraction pattern for potassic-ferropargasite was obtained using a Gandolfi camera with a diameter of 114.6 mm and employing Ni-filtered Cu*K*α radiation. The data were recorded on an imaging plate and processed with a Fuji BAS-2500 bio-image analyzer using a computer program written by Nakamuta (1999). Observed diffraction angles were corrected by the Toraya (1993) method using Si-standard material (NBS, #640b) on the sample fragment. The powder X-ray diffraction data for potassic-ferropargasite is given in Table 2. Potassic-ferropargasite is monoclinic with space group *C*2/*m*. The refined unit-cell parameters are a = 9.937(5), b = 18.108(5), c = 5.335(4) Å, β = 105.30(3)°, V = 926.0(9)

Table 4. Final atomic coordinates, cation occupancies and displacement parameters (Å^2)

Site	Occupancy	x	y	z	U_{eq}
T(1)	0.52Si + 0.48Al	0.27794(15)	0.08616(8)	0.3033(3)	0.0047(4)
T(2)	0.96Si + 0.04Al	0.29118(14)	0.17316(8)	0.8155(3)	0.0045(4)
M(1)	0.318(11)Mg* + 0.682(11)Fe*	0	0.08973(7)	0.5	0.0098(5)
M(2)	0.598(9)Mg* + 0.402(9)Fe*	0	0.17830(9)	0	0.0035(6)
M(3)	0.210(14)Mg* + 0.790(14)Fe*	0	0	0	0.0076(6)
M(4)	0.975Ca + 0.025Na	0	0.28112(8)	0.5	0.0078(4)
A	0.54K + 0.42Na	0	0.5	0	0.079(2)
O(1)	O	0.1044(4)	0.0917(2)	0.2129(8)	0.0100(9)
O(2)	O	0.1209(4)	0.1761(2)	0.7371(7)	0.0088(8)
O(3)	0.97O + 0.03F	0.1096(6)	0	0.7130(11)	0.0109(11)
O(4)	O	0.3692(4)	0.2503(2)	0.7942(7)	0.0073(8)
O(5)	O	0.3498(4)	0.1388(2)	0.1115(7)	0.0091(8)
O(6)	O	0.3423(4)	0.1185(2)	0.6080(7)	0.0106(8)
O(7)	O	0.3331(6)	0	0.2870(11)	0.0136(12)

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
T(1)	0.0057(8)	0.0043(8)	0.0047(8)	-0.0005(5)	0.0024(6)	-0.0018(5)
T(2)	0.0062(7)	0.0027(7)	0.0051(7)	0.0006(5)	0.0023(5)	0.0010(5)
M(1)	0.0125(8)	0.0106(9)	0.0077(8)	0	0.0052(6)	0
M(2)	0.0057(9)	0.0008(9)	0.0047(9)	0	0.0026(6)	0
M(3)	0.0113(10)	0.0034(10)	0.0080(10)	0	0.0024(7)	0
M(4)	0.0104(7)	0.0048(8)	0.0103(8)	0	0.0065(6)	0
A	0.088(4)	0.069(4)	0.116(6)	0	0.092(4)	0
O(1)	0.0099(19)	0.014(2)	0.0075(19)	-0.0007(13)	0.0040(15)	-0.0013(14)
O(2)	0.0062(17)	0.009(2)	0.0112(18)	0.0028(14)	0.0024(14)	0.0009(14)
O(3)	0.011(3)	0.007(3)	0.014(3)	0	0.002(2)	0
O(4)	0.0114(16)	0.0027(18)	0.0108(18)	0.0014(13)	0.0080(15)	-0.0005(14)
O(5)	0.0060(17)	0.013(2)	0.0088(18)	0.0015(14)	0.0022(14)	0.0001(14)
O(6)	0.0095(18)	0.011(2)	0.0119(19)	-0.0051(14)	0.0046(15)	0.0032(15)
O(7)	0.015(3)	0.008(3)	0.017(3)	0	0.004(2)	0

Mg^* = Mg + Al.
Fe^* = Fe^{2+} + Mn + Ti + Cr.

Å^3, $Z = 2$.

Structure refinement

Single crystal diffraction data were obtained using a Bruker SMART APEX CCD area-detector diffractometer with Mo$K\alpha$ radiation. The intensity data were collected using the ω-scan technique. The SAINTPLUS program was used for data reduction and correction for the Lorenz and polarization factors as well as for the background effects. An empirical absorption correction based on symmetrically equivalent reflections was performed with the SADABS software (Sheldrick, 1997). The SHELXL-97 software package (Sheldrick, 1997) was employed to refine the crystal structure. The scattering factors for neutral atoms were taken from the International Tables for Crystallography, Volume C (1992). Full-matrix refinement on F^2 of 1078 independent reflections (R_{int} = 0.0249), of which 947 have criteria to be larger than $2\sigma(I)$, yielded $R1$ = 0.0649 and w$R2$ = 0.1784. The position of the H atom could not be determined in the present analysis.

Potassic-ferropargasite has a complicated chemistry so the following simplifying assumptions were employed for the refinement. Since Mg and Al atoms are indistinguishable with their X-ray scattering powers, they 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+}, Mn, Cr and Ti were assumed to form one species, Fe^*, with the scattering factor of neutral iron. The site occupancies for *T*(1) and *T*(2) were determined from the chemical analysis and equation (3) reported in Oberti et al. (1995) to calculate $^{T(1)}$Al. The site occupancies for *A*, *M*(4) and O(3) were fixed on the basis of the chemical analysis. The result of the refinement was summarized in Table 3. The final atomic coordinates, cation occupancies and displacement parameters were given in Table 4. The selected interatomic distances are in Table 5. The bond valences were calculated from

Table 5. Interatomic distances (Å)

T(1)-O(1)	1.665(4)
O(5)	1.688(4)
O(6)	1.689(4)
O(7)	1.663(2)
<*T*(1)-O>	1.676
T(2)-O(2)	1.632(4)
O(4)	1.616(4)
O(5)	1.655(4)
O(6)	1.661(4)
<*T*(2)-O>	1.641
M(1)-O(1)	2.064(4) ×2
O(2)	2.165(4) ×2
O(3)	2.113(4) ×2
<*M*(1)-O>	2.114
M(2)-O(1)	2.050(4) ×2
O(2)	2.073(4) ×2
O(4)	1.952(4) ×2
<*M*(2)-O>	2.025
M(3)-O(1)	2.122(4) ×4
O(3)	2.100(6) ×2
<*M*(3)-O>	2.115
M(4)-O(2)	2.421(4) ×2
O(4)	2.355(4) ×2
O(5)	2.646(4) ×2
O(6)	2.561(4) ×2
<*M*(4)-O>	2.496
A-O(5)	3.059(4) ×4
O(6)	3.116(4) ×4
O(7)	2.535(6) ×2
<*A*-O>	2.977

the interatomic distances following the procedure of Brown and Altermatt (1985). The values listed in Table 6 are weighted averages according to the occupancies in the final refinement.

Titanium is usually considered as an octahedral cation in most amphiboles, and most structural studies of amphiboles with low Ti contents (<0.20 apfu) have assigned Ti to the *M*(2) site. Recently, Oberti et al. (1992) and Hawthorne et al. (1998) examined the behavior of Ti in sodic-calcic and sodic amphiboles and showed that in these minerals the entry of Ti occurs primarily in substitution, $^{M(1)}(\mathrm{Mg,Fe})^{2+} + 2^{O(3)}\mathrm{OH}^- \rightarrow {}^{M(1)}\mathrm{Ti}^{4+} + 2^{O(3)}\mathrm{O}^{2-}$ and that the *M*(1)-O(3) distance decreases markedly with increasing Ti content in the structure. Sokolova et al. (2000) pointed out that dehydroxylated amphiboles with OH + F < 2 apfu and significant Ti^{4+} and Fe^{3+} at the *M*(1) show *M*(1)-O(3) << <*M*(1)-O>, the mean *M*(1)-O distance. The potassic-ferropargasite in this study shows that the *M*(1)-O(3) distance is similar to <*M*(1)-O>, suggesting that the studied amphibole did not significantly suffer from the above substitution. This interpretation is also supported by the low value of the bond-valence sum for O(3), 1.01 v.u (Table 6).

DISUCUSSION

The majority of calcic amphiboles have relatively small amounts of potassium (Deer et al., 1997). A crystal-chemical control on K content in calcic amphiboles has been previously discussed. Matsubara and Motoyoshi (1985) found potassicpargasite and pargasite showing a positive correlation between their $\mathrm{K}/(\mathrm{K} + {}^{[A]}\mathrm{Na})$ and $\mathrm{Fe}^{2+}/(\mathrm{Fe}^{2+} + \mathrm{Mg})$ values and suggested that the increase in Fe^{2+} serves to stabilize the potassicpargasite. Shimazaki et al. (1984) described potassicsadanagaite and potassic-magnesio-sadanagaite which are characterized by their extremely high $^{[4]}\mathrm{Al}$ (2.76-3.39 apfu) and K (0.62-0.75 apfu) contents and pointed out that substantial replacement of Si by Al in the tetrahedral site might be crystallochemically necessary for the entry of K into the *A* site. Chlorine-bearing K-rich amphiboles have been reported from various rock types (cf., Deer et al., 1997). A crystal-chemical

Table 6. Bond-valence sums weighted on the occupancies for potassic-ferropargasite

	M(1)	*M*(2)	*M*(3)	*M*(4)	*A*	*T*(1)	*T*(2)	Sum
O(1)	$0.38^{x2}\downarrow$	$0.39^{x2}\downarrow$	$0.33^{x4}\downarrow$			0.92		2.02
O(2)	$0.29^{x2}\downarrow$	$0.37^{x2}\downarrow$		$0.29^{x2}\downarrow$			0.98	1.93
O(3)	$0.33^{x2}\downarrow\rightarrow$		$0.35^{x2}\downarrow$					1.01
O(4)		$0.51^{x2}\downarrow$		$0.35^{x2}\downarrow$			1.02	1.88
O(5)				$0.16^{x2}\downarrow$	$0.06^{x4}\downarrow$	0.86	0.92	2.00
O(6)				$0.20^{x2}\downarrow$	$0.05^{x4}\downarrow$	0.86	0.91	2.02
O(7)					$0.24^{x2}\downarrow$	$0.92^{x2}\rightarrow$		2.08
Sum	2.00	2.54	2.02	2.00	0.92	3.56	3.83	

Note: bond-valence parameters are from Allmann (1975), Brown and Altermatt (1985), Brese and O'Keeffe (1991) and Kanowitz and Palenik (1998).

control on Cl content in calcic amphibole has been discussed by many authors (e.g., Suwa et al., 1987; Morrison 1991; Enami et al., 1992; Sato et al., 1997). Makino et al. (1993) and Oberti et al. (1993) revealed the crystal structures of Cl- and K-rich hastingsite and ferropargasite. Based on crystal structure consideration on these amphiboles, they concluded that increasing Cl content in calcic amphiboles crystallochemically requires increasing Fe^{2+}, K and $^{[4]}Al$. Therefore, an important factor regulating K-for-Na substitution is not only the Fe^{2+} and $^{[4]}Al$ contents but also the Cl content. The studied potassic-ferropargasite shows high K contents (0.54–0.63 apfu), but contains a negligible amount of Cl (<0.02 wt%). This amphibole clearly indicates that K-rich calcic amphibole is not always characterized by the substantial replacement of OH by Cl.

Figure 2 summarizes the relationships among K, $X_{Fe^{2+}}$ [= $Fe^{2+}/(Fe^{2+} + Mg)$], $^{[4]}Al$ and Cl of K-rich (≥0.25 apfu) calcic amphiboles with $^{[4]}Al \geq 1.5$ apfu and $^{[A]}(Na + K) \geq 0.5$ apfu in this study and from the literature. Figure 2a shows that K- and Cl-rich (≥3.0 wt% Cl) calcic amphiboles have high $X_{Fe^{2+}}$ values (0.45–0.95). K-rich calcic amphiboles with intermediate content of Cl (1.0–2.9 wt%) extend their compositional range towards lower K than those with high Cl content (3.0–7.2 wt%) (Figs. 2a and 2b). These relationships among Cl, $X_{Fe^{2+}}$ and K are in agreement with the proposed crystal-chemical constraint for Cl incorporation into amphibole by Makino et al. (1993) and Oberti et al. (1993). Figure 2c clearly shows that K-rich and Cl-poor (less than 1.0 wt% Cl) calcic amphiboles extend their compositional range towards lower $X_{Fe^{2+}}$ than K- and Cl-rich calcic amphiboles shown in Figure 2a. This compositional feature implies that Cl-poor calcic amphibole with $X_{Fe^{2+}} \geq$ about 0.2, $^{[4]}Al \geq 1.5$ apfu and $^{[A]}(Na + K) \geq 0.5$ apfu has the capability of accommodating a large amount of K (at least about 0.6 apfu).

Figure 2c also shows that Cl-poor calcic amphiboles with extremely high K (≥0.7 apfu) are sadanagaitic amphibole characterized by a significant amount of $^{[4]}Al$ (2.33–3.39 apfu). However, Hinrichsen and Schürmann (1977) synthesized pure "potassicedenite" [$KCa_2Mg_5Si_7AlO_{22}(OH)_2$] at 750 °C and at 0.5 kbar, suggesting that Cl-poor calcic amphibole with extremely high K (≥0.7 apfu) does not always need unusually high $^{[4]}Al$.

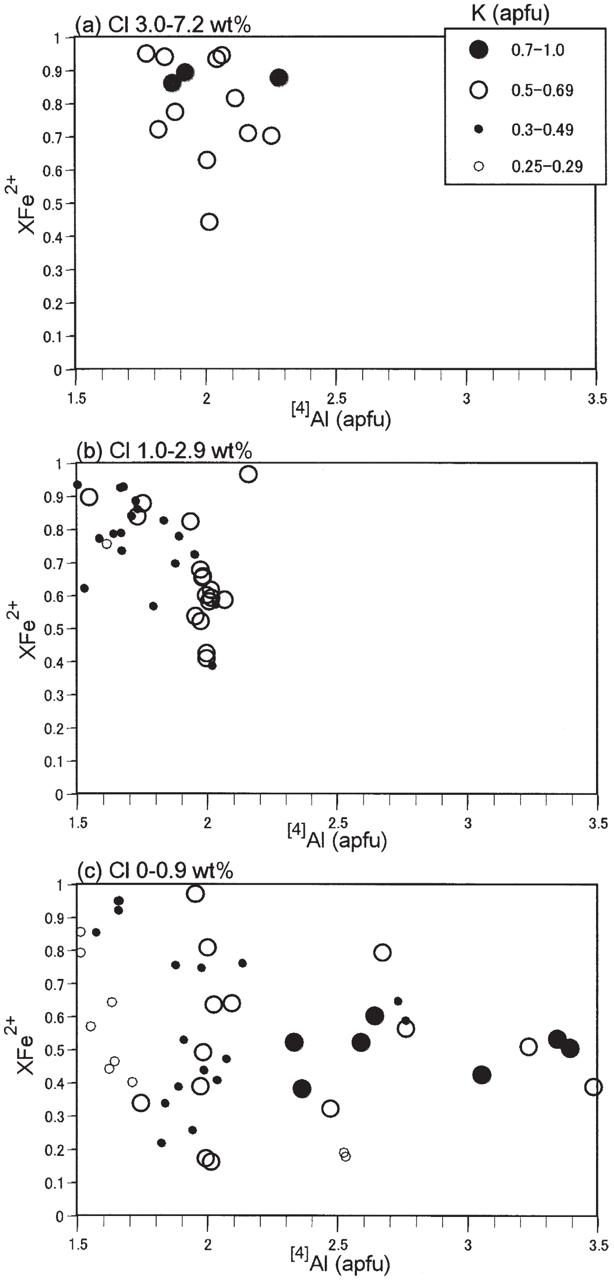

Figure 2. Relationships among K, $X_{Fe^{2+}}$ [= $Fe^{2+}/(Fe^{2+} + Mg)$], $^{[4]}Al$ and Cl of K-rich calcic amphiboles with $^{[4]}Al \geq 1.5$ apfu and $^{[A]}(Na + K) \geq 0.5$ apfu. The chemical data are from Borley (1963), Krutov and Vinogradova (1966), Leelanandam (1970), Czamanske et al. (1977), Hawthorne and Grundy (1977), Dick and Robinson (1979), Sharma (1981), Shimazaki et al. (1984), Matsubara and Motoyoshi (1985), van Marcke de Lummen and Verkaeren (1985), Gulyaeva et al. (1986), Suwa et al. (1987), Sawaki (1989), Morrison (1991), Enami et al. (1992), Oberti et al. (1993), Shiraishi et al. (1994), Deer et al. (1997), Robinson et al. (1997), Sato et al. (1997), Sokolova et al. (2000), Chukanov et al. (2002), Mazdab (2003), Banno et al. (2004), Pekov et al. (2005), Korinevskiy and Korinevskiy (2006), Sautter et al. (2006) and Banno et al. (this study). The Cl contents of K-rich amphiboles described by Shimazaki et al. (1984) and Sawaki (1989) were not given, but they pointed out that qualitative analyses of these amphiboles show no appreciable amount of chlorine. Therefore, it was assumed that their Cl contents are less than 1.0 wt%.

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