Journal of Mineralogical and Petrological Sciences, Volume 97, page 177–184, 2002 Sueno Issue

Potassicleakeite, a New Amphibole from the Tanohata Mine, Iwate Prefecture, Japan

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Potassicleakeite, $KNa_2Mg_2Fe^{3+}{}_2LiSi_8O_{22}(OH)_2$, the K-dominant leakeite, is found in manganese ore deposit at the Tanohata mine, Iwate Prefecture, Japan. It is monoclinic, *C*2/*m*, *a* = 9.922(5), *b* = 17.987(7), *c* = 5.286(2) Å, β = 104.07(3)°, V = 915.1(7) Å^3 and Z = 2. The seven strongest lines in the X-ray powder diffraction pattern are 8.48(67)(110), 4.50(89)(040), 3.40(46)(131), 3.28(45)(240), 3.16(72)(310, 201), 2.83(49)(330), 2.53(100)($\bar{2}$02). Electron microprobe and LAM-ICP-MS analyses gave SiO_2 55.34, TiO_2 0.29, Al_2O_3 0.44, V_2O_3 5.52, Fe_2O_3 9.45, MnO 7.81, MgO 7.23, CaO 0.13, K_2O 3.10, Na_2O 8.73, Li_2O 1.2, H_2O (calc) 2.08, total 100.12 wt. %, corresponding to $(K_{0.57}Na_{0.46})_{\Sigma 1.03}(Na_{1.98}Ca_{0.02})_{\Sigma 2.00}(Mg_{1.29}Mn_{0.65})_{\Sigma 1.94}(Fe^{3+}{}_{1.02}V_{0.64}Mg_{0.26}Al_{0.05}Ti_{0.03})_{\Sigma 2.00}$-$(Li_{0.70}Mn_{0.30})_{\Sigma 1.00}(Si_{7.98}Al_{0.02})_{\Sigma 8.00}O_{22}(OH)_2$ on the basis of O + OH = 24. It is transparent and reddish brown with vitreous luster. The streak is pale brownish yellow and cleavage {110} is perfect. The fracture is uneven and tenacity is brittle. The hardness is VHN_{100} 425 – 572 kg/mm^2 (Mohs ~5). The calculated density is 3.18 g/cm^3. It is distinctly pleochroic from yellowish brown to reddish brown. It is optically biaxial positive with α = 1.672(2), β = 1.680(2), γ = 1.692(2), 2*V*(calc) = 79°, and orientation: *b* = Y, Z^*c* = +35 to 40°. It occurs as prismatic crystals in veinlets composed mainly of quartz, alkali-feldspars, and serandite. The mineral is considered to be formed under the later stage of hydrothermal activities of contact metasomatism.

Introduction

The manganese ore deposit of the Tanohata mine is known for the occurrence of many rare minerals such as kozulite (Nambu et al., 1969a), natronambulite (Matsubara et al., 1985), yoshimuraite (Matsubara, 1985), and Ba-dominant haradaite which was approved as suzukiite later (Watanabe et al., 1973). In autumn of 2000, one of the authors (Y.S.) collected two unfamiliar minerals in quartz-dominant ore at the dump. One of them is a reddish brown prismatic crystal suggesting an amphibole in association with minute aggregate of crystals resembling olivine. X-ray diffraction studies, microprobe and LAM-ICP-MS analyses showed that it is K-dominant leakeite. Leakeite is a Li-bearing amphibole found in the metasediments of the Kajlidongri manganese mine, Jhabua district, India (Hawthorne et al., 1992). K-dominant leakeite is named as potassicleakeite according to the nomenclature of amphiboles (Leake et al., 1997). The mineral data and the name have been approved by the Commission on New Minerals and Mineral Names of IMA (no. 2001-049). The type specimen is deposited at the National Science Museum, Tokyo, under the registered number NSM-M 28188. The other mineral resembling olivine is proved to be V-dominant mangan-neptunite. The mineral also has been approved by the CNMMN of IMA (no. 2001-043), and will be described elsewhere.

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Occurrence

The ore deposit and the surrounding geology of the Tanohata mine were reported by Nambu et al. (1969b). The ores and country rocks of upper Jurassic age are contact metamorphosed and probably metasomatized by the intrusion of Cretaceous granodiorite. Among four ore bodies, the studied material was obtained from No. 3 (Matsumaezawa) Orebody in which pegmatite-like veinlets composed of mainly quartz, K-feldspar and serandite are found. Subordinate constituents of the veinlets are suzukiite, roscoelite, V-bearing aegirine, native copper, chalcopyrite, and yarrowite beside two new minerals. The No. 3 Orebody is characterized by the abundant occurrence of Li-, Na-, and K-rich minerals such as nambulite, natronambulite, kozulite,

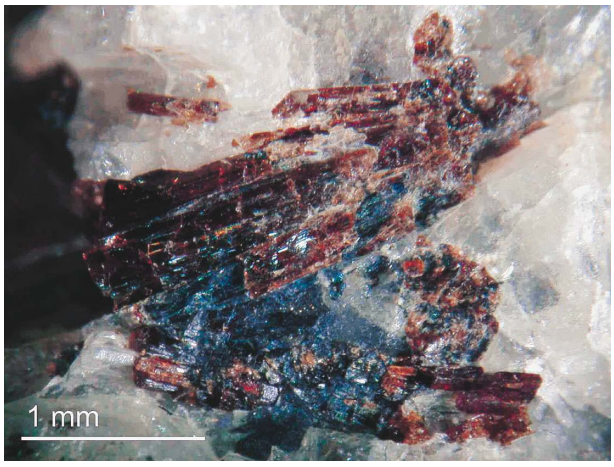

Figure. 1. Photomicrograph of potassicleakeite. The reddish brown elongate crystals of potassicleakeite are associated with yarrowite and quartz.

magnesio-arfvedsonite, aegirine, albite and microcline. Sulfide minerals, pyrrhotite, sphalerite and pyrite, are very common in the ore. It is concluded that the formation of No.3 Orebody was strongly affected by hydrothermal fluid from the intruding granodiorite. Since the pegmatitite-like veinlets containing potassicleakeite cut the thermally metamorphosed manganese ores, the mineral is considered to be formed at the later stage of mineralization.

Potassicleakeite occurs as prismatic crystals elongated along *c*-axis with diamond shaped cross section (Fig. 1) in association with quartz, K-feldspar, V-dominant mangan-neptunite, suzukiite, roscoelite and serandite. The maximum size of crystal reaches 2 mm in length and 0.2 mm in width. It is easily distinguishable from other amphiboles, kozulite and magnesio-arfvedsonite due to the different occurrence and color. Kozulite and magnesio-arfvedsonite occur mostly as banding aggregates in braunite – rhodonite – nambulite ore, and they show brownish black and yellowish orange in color, respectively.

Physical and optical properties

The mineral is transparent and reddish brown in color with vitreous luster. The streak is pale brownish yellow. The fracture is uneven and tenacity is brittle. The cleavage is perfect on {110} like an ordinary amphibole. The Vickers microhardness is 425 – 572 kg/mm^2 (100 g load), corresponding to about 5 on the Mohs scale. The calculated density is 3.18 g/cm^3, using the empirical formula. It is optically biaxial positive with $2V$(calc) = 79°, and orientation is b = Z, X^c = +35 to 40°. The refractive indices are α = 1.672(2), β = 1.680(2), γ = 1.692(2). Pleochroism is distinct; X = yellowish brown, Y = pale brown, Z = reddish brown.

Chemistry

Chemical analyses were made by a laser ablation microprobe – inductively coupled plasma – mass spectrometry (LAM–ICP–MS) for Li and an electron microprobe using energy dispersion methods for the other elements. The LAM–ICP–MS analyses were performed at the Venture Business Laboratory, the University of Tsukuba, using a Perkin-Elmer Sciex ELAN6000 ICP-MS instrument equipped with a frequency quadrupled Nd:YAG laser microprobe (266 nm). The ICP-MS instrument was operated at a RF power of 1050 W, flow rates of the nebulizer gas, auxiliary gas and the plasma gas of 0.72, 1.2 and 15 L/min, respectively. The most abundant nuclides of lithium and magnesium, ^{7}Li and ^{24}Mg, were measured with a dwell time of 10 ms for each element and by using a rapid peak hopping sequence in the pulse-counting mode. The samples were ablated using pulse rate of 10 Hz and beam energies of 0.35 mJ, and the resultant pit diameters by the ablation were 40 μm. Quantification was performed using an external calibration curve method with internal standardization. NIST (National Institute of Standards and Technology) SRM 610 reference material was used as an external calibration standard for the analysis, adopting the preferred element concentrations of Pearce et al. (1997). The major nuclide of magnesium, whose content was determined by electron microprobe analysis, ^{24}Mg, was used as an internal standard to correct the inter-element fractionation and differences in the absolute amount of material that was ablated and transported during an individual analysis. The element, Mg, fulfills the critical requirement in that it has an ablation behavior similar to that of Li being analyzed (Fryer et al., 1995). Data reduction was performed with LAMTRACE (Jackson et al, 1992; Jackson, 1996). Typical run detection limits for the analytical conditions were 0.3 and 0.5 ppm for Li and Mg, respectively. The total analytical error is estimated at less than 10% on the basis of repeated analyses of the standard materials and trace Li determinations of silicate glasses with variable major compositions. Details of the LAM-ICP-MS analytical conditions are presented in Kurosawa et al. (2001). The EDX (Link Systems QX-2000) analysis was carried out with the following standard materials; wollastonite (Si and Ca), TiO_2 (Ti), sillimanite (Al), V (V), Fe_2SiO_4 (Fe), Mn (Mn), Mg_2SiO_4 (Mg), adularia (K), and albite (Na). The details of analytical procedures have been reported by Yokoyama et al. (1993). Fluorine was not detected

Table 1. Chemical compositions of potassicleakeite, leakeite, kornite, kozulite and magnesio-arfvedsonite

wt.%	1	(Range)	2	3	4	5
SiO_2	55.34	54.98 - 55.59	55.80	56.06	51.38	54.71
TiO_2	0.29	0 - 0.68	0.03	n.d.	0	0.24
Al_2O_3	0.44	0.33 - 0.59	1.27	0	1.69	0
V_2O_3	5.52	5.11 - 6.03	n.d.	n.d.	n.d.	0
Fe_2O_3	9.45	9.31 - 9.55	12.23	4.93	2.85	5.80
Mn_2O_3			3.86	13.17		
MnO	7.81	7.40 - 8.16			27.96	13.48
MgO	7.23	6.43 - 7.74	10.96	10.03	2.71	12.87
ZnO	0		n.d.	n.d.	0.03	0
CaO	0.13	0 - 0.30	0.50	0.00	1.12	2.41
K_2O	3.1	2.85 - 3.26	1.12	3.56	1.36	1.68
Na_2O	8.73	8.44 - 8.91	9.69	7.61	8.41	6.09
Li_2O	1.2	1.2 - 1.3	1.42	1.96	n.d.	n.d.
F	0		1.08	n.d.	0.08	n.d.
H_2O	2.08*		1.63	2.68**	2.1	2.05*
O = F			0.45		0.03	
total	100.12		99.14	100	99.72***	99.33
				O+OH+F = 24		
Si	7.98		8.00	7.91	8.01	8.00
Al(IV)	0.02					
Σ	8.00		8.00	7.91	8.01	8.00
Al(VI)	0.05		0.13		0.31	
Ti	0.03		0.41			0.03
Fe	1.02		0.90	0.52	0.33	0.64
Mn	0.95		0.52	1.41	3.69	1.67
Mg	1.55		2.40	2.11	0.63	2.81
V	0.64					
Li	0.70		0.67	1.11		
Σ	4.94		5.02	5.16	4.97	5.15
L-type			[0.02]	[0.16]		[0.15]
Ca	0.02		0.12		0.19	0.38
Na	1.98		1.86	1.84	1.81	1.47
Σ	2.00		2.00	2.00	2.00	2.00
Na	0.46		0.82	0.24	0.73	0.26
K	0.57		0.15	0.64	0.27	0.31
Σ	1.03		0.97	0.88	1.00	0.57

*: calculation
**: difference
***: includes $H_2O(-)$ 0.06 %
1: potassicleakeite (This study).
2: leakeite (Hawthorne et al., 1992).
3: kornite (Armbruster et al., 1993).
4: kozulite (Nambu et al., 1969a).
5: magnesio-arfvedsonite (This study)

by electron microprobe using wavelength dispersion methods, therefore, the amounts of H_2O was calculated according to the ideal number of (OH) = 2 per unit formula of an ordinary amphibole. The average of six measurements by the electron microprobe and three measurements by LAM-ICP-MS leads to the empirical formula, $(K_{0.57}Na_{0.46})_{\Sigma 1.03}(Na_{1.98}Ca_{0.02})_{\Sigma 2.00}(Mg_{1.55}Fe^{3+}{}_{1.02}$-$Mn_{0.95}Li_{0.70}V_{0.64}Al_{0.05}Ti_{0.03})_{\Sigma 4.94}(Si_{7.98}Al_{0.02})_{\Sigma 8.00}O_{22}(OH)_2$ on the basis of O + OH = 24. In Table 1, the average analysis of potassicleakeite is demonstrated together with the analyses of leakeite (Hawthorne et al., 1992), kornite strongly related to leakeite (Armbruster et al., 1993) and also to kozulite and magnesio-arfvedsonite from the Tanohata mine for comparison. The later crystal structure refinement suggests the structural formula, $(K_{0.57}Na_{0.46})_{\Sigma 1.03}(Na_{1.98}Ca_{0.02})_{\Sigma 2.00}(Mg_{1.29}Mn_{0.65})_{\Sigma 1.94}$-$(Fe^{3+}{}_{1.02}V_{0.64}Mg_{0.26}Al_{0.05}Ti_{0.03})_{\Sigma 2.00}(Li_{0.70}Mn_{0.30})_{\Sigma 1.00}$-$(Si_{7.98}Al_{0.02})_{\Sigma 8.00}O_{22}(OH)_2$. Consequently the ideal formula is $KNa_2Mg_2Fe^{3+}{}_2LiSi_8O_{22}(OH)_2$, corresponding to K-dominant analogue of leakeite.

Table 2. Powder X-ray diffraction data of potassicleakeite, and those of leakeite for comparison

	Potassicleakeite Tanohata, Japan (Present study)			Leakeite Madhya Pradesh, India (Hawthorne et al., 1992)			Potassicleakeite Tanohata, Japan (Present study)			Leakeite Madhya Pradesh, India (Hawthorne et al., 1992)	
h k l	*I*	*d*(obs)	*d*(calc)	*I*	*d*(obs)	*h k l*	*I*	*d*(obs)	*d*(calc)	*I*	*d*(obs)
0 2 0	13	9.00	8.99	4	8.926	$\bar{4}$ 4 2			1.840		
1 1 0	67	8.48	8.49	56	8.399	5 3 0	7	1.835	1.833		
1 3 0	28	5.09	5.09	6	5.049	2 8 1			1.830		
$\bar{1}$ 1 1	4	4.86	4.88			4 4 1	3	1.821	1.827		
2 0 0			4.81	5	4.759	1 9 1	21	1.799	1.799		
0 4 0	89	4.50	4.50	13	4.461	0 10 0			1.799		
2 2 0	4	4.25	4.24			$\bar{1}$ 1 3	6	1.750	1.750		
$\bar{2}$ 0 1	18	4.03	4.03	4	4.006	1 7 2	4	1.725	1.730		
1 1 1			4.02	4	4.006	$\bar{2}$ 2 3	4	1.716	1.718		
$\bar{1}$ 3 1	4	3.89	3.87			$\bar{1}$ 3 3	18	1.686	1.687		
$\bar{2}$ 2 1	9	3.67	3.68			$\bar{2}$ 8 2			1.681		
1 3 1	46	3.40	3.40	18	3.383	4 6 1	14	1.664	1.663		
2 4 0	45	3.28	3.29	20	3.254	4 8 0	24 *	1.644	1.643		
3 1 0	72 *	3.16	3.16			1 11 0	32	1.612	1.612		
2 0 1			3.15	100	3.122	6 0 0			1.604		
$\bar{3}$ 1 1	10	3.03	3.03			$\bar{1}$ 5 3	18	1.580	1.580		
2 2 1	12	2.97	2.97	6	2.949	4 0 2			1.574		
$\bar{1}$ 5 1	7 *	2.92	2.93			2 10 1	6	1.560	1.562		
3 3 0	49	2.83	2.83	48	2.798	$\bar{5}$ 7 1			1.561		
$\bar{3}$ 3 1	44	2.74	2.74			$\bar{6}$ 0 2	11	1.540	1.538		
1 5 1	41	2.71	2.71	15	2.696	5 5 1	15	1.516	1.517		
0 6 1	25	2.59	2.59	5	2.573	$\bar{2}$ 6 3			1.512		
$\bar{2}$ 0 2	100	2.53	2.53	5	2.531	0 12 0	26	1.499	1.499		
1 7 0	15	2.48	2.48			2 2 3	5	1.480	1.479		
4 0 0	14	2.40	2.41			3 11 0			1.457		
3 5 0			2.39	6	2.369	$\bar{6}$ 4 2	14	1.456	1.456		
$\bar{3}$ 5 1	38	2.34	2.34			$\bar{1}$ 7 3			1.451		
$\bar{4}$ 2 1			2.33			$\bar{6}$ 6 1	30	1.444	1.445	10	1.431
$\bar{1}$ 7 1	27	2.29	2.29	4	2.274	$\bar{5}$ 3 3	5	1.428	1.425		
3 3 1			2.28			$\bar{3}$ 7 3	4	1.412	1.411		
$\bar{3}$ 1 2	31	2.28	2.27	4	2.274	$\bar{4}$ 6 3	3 *	1.403	1.403		
$\bar{2}$ 4 2	4	2.21	2.21			5 7 1			1.402		
2 6 1	17	2.17	2.17	9	2.154	5 1 2	27 *	1.382	1.382		
$\bar{3}$ 3 2	17	2.14	2.14			$\bar{7}$ 1 0	6 *	1.370	1.371		
2 0 2	18	2.06	2.06	3	2.055	$\bar{5}$ 5 3	7 *	1.357	1.359		
3 5 1	7	2.04	2.03	3	2.013	5 3 2			1.350		
$\bar{4}$ 0 2	12	2.01	2.02			2 6 3	11	1.341	1.341		
1 9 0	28	1.955	1.957			1 11 2			1.340		
4 2 1			1.952			$\bar{3}$ 11 2	5	1.332	1.331		
5 1 0	13 *	1.914	1.914	9	1.891	$\bar{1}$ 9 3			1.320		
$\bar{4}$ 6 1	13	1.880	1.881			$\bar{5}$ 9 2	15	1.319	1.320		
2 4 2			1.876			$\bar{7}$ 5 1			1.318		
$\bar{5}$ 3 1	11	1.860	1.868			$\bar{1}$ 1 4	8	1.310	1.310		
$\bar{1}$ 9 1			1.859			$\bar{2}$ 12 2	11	1.290	1.290	5	1.282

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

X-ray crystallography and crystal structure

The powder X-ray diffraction pattern for potassicleakeite was obtained using a Gandolfi camera of 114.6 mm diameter employing Ni-filtered Cu$K\alpha$ radiation. The data were recorded on an Imaging Plate, and processed with a Fuji BAS-2500 bio-imaging analyzer and with a computer program by Nakamuta (1999). The X-ray diffraction data of potassicleakeite are given in Table 2 with those of leakeite (Hawthorne et al., 1992) for comparison. The unit cell parameters were refined from the powder X-ray diffraction data with internal Si standard (NBS, #640b) using a computer program by Toraya (1993).

The intensity data of single crystal were collected with a Rigaku RASA-7R 4-circle diffractometer using graphite monochromatized Mo$K\alpha$ radiation (56 kV, 270 mA). Experimental details pertaining to collection for single crystal diffraction intensity data with the lattice parameters determined by least-squares refinement of the 2θ values of 25 strong reflections are given Table 3. The data reductions to Fo^2 with corrections for Lorentz,

polarization and absorption (ψ-scan procedure) were made with a computer program written by Dr. Kazumasa Sugiyama of the University of Tokyo (personal communication). The atomic positional parameters of leakeite (Hawthorne et al., 1992) were used as the initial parameters. The computer program, SHELXL-97 (Sheldrick, 1997), was employed for the refinement of crystal structure. Scattering factors for neutral atoms and anomalous dispersion factors were taken from the International Tables for X-ray Crystallography, Volume C (1992). Full-matrix least-squares refinement was performed by refining positional parameters, scale factor, and displacement parameters. The site occupancies for *T*1 and *T*2 sites were fixed to be occupied fully with Si, because of the negligible small amounts of Al (0.07 *apfu*), and the similarity in scattering power between Si and Al. The occupancy parameters for *M*1, *M*2 and *M*3 sites were refined with constraints of Mg + Fe = 1, Fe + Mg = 1, and Li + Mn = 1, respectively. The *M*4 site was assumed to be occupied with Na. The scattering curves for K and Na were introduced to the *A* site. The refinement with anisotropic displacement parameters suggested that the *A* site at the special position, 2*b*, might be split into a *4i* site, the *A*m site. The chemical composition yielded from the refinement was remarkably Mn-poor in comparison with that of chemical analyses (Table 1). Then, Mn atoms were introduced in the *M*1 or *M*2 sites instead of Fe atoms. In the further refinements, the positional parameters and isotropic displacement parameter of H atom, which was observed as the differential Fourier peak with distance of 1.06 Å to the O3 site, were refined with the other parameters. The refinements with Mn atoms in the *M*1 or *M*2 sites converged with comparable *R* factors, *R*1 = 0.0258 and 0.0262 for Mn in the *M*1 and *M*2 sites, respectively. No significant difference was observed in the positional parameters between the two models. The final result of refinement is summarized in Table 3. The final positional parameters and equivalent isotropic displacement parameters are given in Table 4. Table 5 shows anisotropic displacement parameters. The selected interatomic distances are summarized in Table 6.

Table 3. Crystallographic data and experimental details of single crystal study on potassicleakeite

a (Å)	9.932(3)
b (Å)	18.003(5)
c (Å)	5.2893(12)
β (°)	104.04(2)
V (Å^3)	917.5(4)
Space group	*C*2/*m*
Z	2
Formula	(K,Na)Na_2(Mg,Mn,Fe,V)$_2$-(Fe,Mn,V,Mg)$_2$ (Li,Mn)-Si_8O_{22}(OH)
D_{calc} (g/cm^3)	3.158
μ (cm^{-1})	2.668
Crystal dimension (mm)	0.07 x 0.10 x 0.20
Diffractometer	Rigaku AFC-7R
Radiation	Mo*K*α (graphite)
Scan mode, rate (°/ min in ω)	2θ-ω, 4
2θ range	8 – 65
Reflection range	$-7 \le h \le 16$ $0 \le k \le 30$ $-9 \le l \le 8$
No. of measured reflections	2738
No. unique reflections	2468
No. of observed reflections [$I > 2\sigma(I)$]	2114
R_{int}	0.0138
Variable parameters	104
*R*1 [$F_o > 4\sigma(F_o)$]	0.0258
*R*1(all reflections)	0.0350
w*R*2 (all reflections)	0.1133
Weghting parameters, a, b	0.1, 0
Goodness of Fit	0.931
Final $\Delta\rho_{min}$ (e/Å^3)	-0.974
Final $\Delta\rho_{max}$ (e/Å^3)	0.859

$R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \, \Sigma \, |F_o|$

$wR2 = \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2]^{0.5}$

$w = 1 \, / \, [\sigma^2(F_o^2) + (aP)^2 + bP]$

$P = [2F_c^2 + F_o^2] \, / \, 3$

Discussion

It is difficult to determine the valence of Fe, Mn and V in a complex chemical system such as amphiboles showing complicated isomorphous substitutions among heterovalent ions. Manganese is assigned as divalent in the present analyses, but a part of them may be trivalent by calculation from total charge balance. There are four V-rich minerals in the studied ore, that is, potassicleakeite, V-dominant manganese-neptunite, $KNa_2LiMn_2V_2Si_8O_{24}$, suzukiite, $BaVSi_2O_7$, roscoelite, $KV_2AlSi_3O_{10}(OH)_2$ and V-bearing aegirine (up to V_2O_3 8.18 wt.%) (Nakai et al., 1976). It is worth mentioning that high V content of potassicleakeite is extraordinary among hitherto known amphiboles. Coexistence of trivalent and tetravalent V-bearing minerals is not rare in case of metamorphosed manganese ore deposits. For example, haradaite (V^{4+}) – goldmanite (V^{3+}) – roscoelite (V^{3+}) at the Yamato mine, Kagoshima Prefecture, Japan (Momoi, 1964; Watanabe et al., 1982) and suzukiite (V^{4+}) – nagashimalite (V^{3+}) – roscoelite (V^{3+}) at the

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

	x	y	z	U_{eq}	Occ.
*T*1	0.27623(3)	0.08563(2)	0.29408(6)	0.00655(9)	Si
*T*2	0.28677(3)	0.17060(2)	0.80026(6)	0.00675(9)	Si
*M*1	0.0000	0.08743(2)	0.5000	0.01010(13)	0.526(3)Mg + 0.474Mn
*M*2	0.0000	0.181970(16)	0.0000	0.00662(9)	0.761(3)Fe + 0.239Mg
*M*3	0.0000	0.0000	0.0000	0.0120(4)	0.816(3)Li + 0.184Mn
*M*4	0.0000	0.27701(5)	0.5000	0.01668(17)	Na
*A*m	0.0226(5)	0.5000	0.0557(6)	0.0519(12)	0.54K + 0.46Na
O1	0.11031(9)	0.08940(5)	0.21812(19)	0.01041(16)	
O2	0.11877(9)	0.16913(6)	0.72762(18)	0.01100(16)	
O3	0.10916(15)	0.0000	0.7034(3)	0.0154(3)	
O4	0.36144(10)	0.24840(5)	0.79979(19)	0.01296(17)	
O5	0.34511(9)	0.12742(5)	0.08328(15)	0.01053(16)	
O6	0.34121(9)	0.11773(6)	0.58552(16)	0.01111(16)	
O7	0.33149(14)	0.0000	0.2964(3)	0.0133(2)	
H	0.181(7)	0.0000	0.702(14)	0.12(3)*	

* Isotropic displacement parameter.

Table 5. Final anisotropic displacement parameters

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
*T*1	0.00603(14)	0.00672(15)	0.00698(14)	-0.00041(9)	0.00170(10)	-0.00040(9)
*T*2	0.00636(15)	0.00699(15)	0.00717(15)	0.00029(9)	0.00217(10)	-0.00072(9)
*M*1	0.01033(19)	0.01129(19)	0.01025(19)	0.000	0.00559(13)	0.000
*M*2	0.00571(13)	0.00655(13)	0.00783(13)	0.000	0.00207(9)	0.000
*M*3	0.0126(7)	0.0114(7)	0.0116(7)	0.000	0.0023(5)	0.000
*M*4	0.0195(4)	0.0127(3)	0.0226(4)	0.000	0.0142(3)	0.000
*A*m	0.069(3)	0.0307(7)	0.081(3)	0.000	0.066(3)	0.000
O1	0.0068(3)	0.0134(4)	0.0108(3)	-0.0012(3)	0.0018(3)	-0.0011(3)
O2	0.0073(3)	0.0133(4)	0.0118(4)	0.0017(3)	0.0013(3)	0.0006(3)
O3	0.0103(5)	0.0207(7)	0.0142(5)	0.000	0.0012(4)	0.000
O4	0.0163(4)	0.0096(4)	0.0140(3)	-0.0008(3)	0.0055(3)	-0.0044(3)
O5	0.0083(3)	0.0141(4)	0.0095(3)	0.0045(3)	0.0028(3)	0.0000(3)
O6	0.0102(3)	0.0143(4)	0.0086(3)	-0.0036(3)	0.0018(3)	0.0007(3)
O7	0.0128(5)	0.0066(5)	0.0202(6)	0.000	0.0037(4)	0.000

Table 6. Interatomic distances (Å)

*T*1	— O1	1.6001(11)	*T*2	— O4	1.5852(11)			
	— O6	1.6260(9)		— O2	1.6191(11)			
	— O5	1.6271(9)		— O5	1.6614(9)			
	— O7	1.6355(7)		— O6	1.6692(10)			
<*T*1—	O>	1.6222	<*T*2	— O>	1.6337			
*M*1	— O1	2.0536(11)	*M*2	— O4	1.9697(11)	*M*3	— O3	2.1122(16)
	— O1	2.0536(11)		— O4	1.9697(11)		— O3	2.1122(16)
	— O3	2.0602(11)		— O2	2.0845(11)		— O1	2.1234(10)
	— O3	2.0602(11)		— O2	2.0845(11)		— O1	2.1234(10)
	— O2	2.0773(11)		— O1	2.1669(11)		— O1	2.1234(10)
	— O2	2.0773(11)		— O1	2.1669(11)		— O1	2.1234(10)
<*M*1 —	O>	2.0637	<*M*2 —	O>	2.0737	<*M*3 —	O>	2.1197
*M*4	— O4	2.3825(11)	*A*m	— O7	2.529(5)	O3	— H	0.72(7)
	— O4	2.3825(11)		— O7	2.623(4)			
	— O2	2.4340(13)		— O5	2.828(3)			
	— O2	2.4340(13)		— O5	2.828(3)			
	— O6	2.5747(13)		— O5	2.918(3)			
	— O6	2.5747(13)		— O5	2.918(3)			
	— O5	2.9223(12)		— O6	2.946(3)			
	— O5	2.9223(12)		— O6	2.946(3)			
<*M*4 —	$O>_6$	2.4637	<*A*m —	O>	2.817			
<*M*4 —	$O>_8$	2.5784						
			*A*m	— O7	3.381(3)			

Mogurazawa mine, Gumma Prefecture, Japan (Matsubara & Kato, 1980; Matsubara et al., 1982). Also the amphiboles from the Tanohata mine are relatively rich in K; 0.27 *apfu* in kozulite (Nambu et al., 1969a), 0.31 *apfu* in magnesio-arfvedsonite and 0.57 *apfu* in potassicleakeite. Kornite is Mn^{3+}-dominant leakeite found from the Wessels mine, Kalahari, South Africa (Armbruster et al., 1993). It is genetically similar to leakeite and potassicleakeite. It should be remarked that kornite has higher K content (0.64 *apfu.*) than potassic-

Table 7 Comparison of crystallographic data, physical properties and optical properties of potassicleakeite, leakeite and kornite

	potassicleakeite	leakeite	kornite
Ideal formula	$KNa_2Mg_2Fe^{3+}{}_2LiSi_8O_{22}(OH)_2$	$NaNa_2Mg_2Fe^{3+}{}_2LiSi_8O_{22}(OH)_2$	$NaNa_2Mg_2Mn^{3+}{}_2LiSi_8O_{22}(OH_2$
Occurrence	metamorphosed Mn deposit	metamorphosed Mn deposit	metamorphosed Mn deposit
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C2/m*	*C2/m*	$P2_1/m$ or *P2/a*
Cell parameters			
a (Å)	9.922(5)	9.822(3)	9.94(1)
b (Å)	17.987(7)	17.836(6)	17.80(2)
c (Å)	5.286(2)	5.286(2)	5.302(4)
β (°)	104.07(3)	104.37(3)	105.5(2)
V (Å^3)	915.1(7)	897.1(5)	904.0
Z	2	2	2
Color	reddish brown	deep red	brownish lilac to dark red
Hardness (Mohs)	~ 5	~ 6	
D (g/cm^3)	3.18 (calc)	3.11	
Color in thin section	yellowish brown to reddish brown	light pink-red to dark mauve to red	pink, dark red to orange-red
Refractive indices			
α	1.672(2)	1.667(1)	1.654(4)
β	1.680(2)	1.675(1)	1.675(calc)
γ	1.692(2)	1.691(1)	1.696(4)
2*V*	(+) 79°(calc)	(–) 59 ~ 71°	(–,+) 88 ~ 92°
References		Hawthorne et al., 1992	Armbruster et al., 1993

leakeite. This suggests that the name should be changed to potassickornite according to the nomenclature of amphiboles (Leake et al., 1997). The crystal data, physical properties and optical properties of potassicleakeite, leakeite and kornite are compared in Table 7.

Potassicleakeite is isostructural with leakeite (Hawthorne et al., 1992). The refinement of occupancy parameters of potassicleakeite showed that Mg is dominant at the *M*1 site, and that Fe dominates Mg in the *M*2 site, as well as leakeite. The structural formula obtained with the refinement (Table 4), in which scattering curves of Mn and Fe were representatively applied for the transition metals in the *M*1 and *M*2 sites owing to the similarity in their scattering factors, is $(K_{0.54}Na_{0.46})Na_2(Mg_{1.05}Mn_{0.95})(Fe_{1.52}Mg_{0.48})(Li_{0.82}Mn_{0.18})Si_8O_{22}(OH)_2$. The calculation of interatomic distance derived from the site occupancy and the end-member bond lengths according to Hawthorne et al. (1993), "d_{calc}", was applied for potassicleakeite. The values of "d_{calc}" were 2.122, 2.038 and 2.128 Å for <*M*1-O>, <*M*2-O> and <*M*3-O>, respectively. The observed mean *M*1-O distance, "d_{obs}", 2.0637 Å (Table 6), is shorter than the "d_{calc}". The difference between "d_{obs}" and "d_{calc}" suggests that the Mg^{2+} and/or Mn^{2+} cations in the *M*1 site of potassicleakeite should be replaced with the smaller Al^{3+}, Fe^{3+} and V^{3+}. The longer "d_{obs}", 2.0737 Å, in comparison to "d_{calc}", 2.038 Å for the <*M*2-O> shows that the population of cation(s) larger than Mg^{2+} and/or Fe^{3+}, such as Fe^{2+}, Mn^{2+} and V^{3+}, in the *M*2 site of potassicleakeite should be significant. Consequently, some parts of Mg, Mn and Fe in the *M*1 and *M*2 sites can be considered to be replaced with Al, V and Ti, which were detected in the chemical analysis. On the other hand, the "d_{calc}" for <*M*3-O>, 2.128 Å, is comparable to the "d_{obs}", 2.1197 Å. The population of the M3 site, $(Li_{0.82}Mn_{0.18})$, was confirmed by the mean interatomic distances.

No significant differences in the lattice parameters were observed between potassicleakeite and leakeite (Hawthorne et al., 1992), although the larger K atoms constitute potassicleakeite instead of the smaller Na in leakeite. The K atoms in potassicleakeite occupy the *A* sites of amphibole structure. The *A* sites is large enough to accept not only Na atoms, but also K atoms. The mean interatomic distance of 8-coordinated *A*m-polyhedron in potassicleakeite, 2.817 Å, is not longer than the corresponding *A*m-O distance of leakeite, 2.823 Å (Hawthorne et al., 1992). These interatomic distance around 2.8 Å, is much longer than the Na-O distance estimated from the sum of effective ionic radii of Na and O, 2.56 Å (Shannon and Prewitt, 1969), and shorter than the K-O distance, 2.91 Å.

The larger *A* site cations, such as Na, K and Ca, usually occupy the vicinity of *A* site, in addition to or instead of the *A* site at (0, 0.5, 0). Three sites with lower symmetry, *A*2 (0, *y*, 0), *Am* (*x*, 0.5, *z*) and *A*1 (*x*, *y*, *z*) are known as the site for *A* cations in the *C*2/*m* amphiboles (Hawthorne, 1983). The present refinement suggested that the *A* cation split into the *Am* position. This is one

of the most significant difference from the crystal structure of leakeite, in which the *A* cation, Na atoms, are distributed into the *A*, *A*m and *A*2 sites with occupancies of 0.43, 0.37 and 0.05 *apfu*, respectively (Hawthorne et al., 1992). In the present refinement of the crystal structure of potassicleakeite, the maximum residual electron density peak, 0.859 e/Å^3 (Table 3), was observed at the *A*2 position, (0, 0.461, 0). The peak with slight electron density suggests that the *A* cations in potassicleakeite, 0.54K + 0.46Na *apfu*, dominantly occupy the *Am* site among the *A*, *Am* and *A*2 sites, although a part of them is distributed into the *A*2 site. This preference for the *Am* position of the *A* cations in the present K-rich potassicleakeite is the same tendency in distribution of K and Na atoms in the *A* site of *C*2/*m* amphiboles (Hawthorne, 1983).

Acknowledgements

We thank to Dr. K. Yokoyama, Department of Geology, the National Science Museum, for his analysis for F with WDS, and also to Mrs. M. Shigeoka for her preparing the polished thin sections. Special thanks are extended to Prof. Y. Nakamuta of Kyushu University and for Dr. K. Sugiyama of the University of Tokyo for their suggestions on the XRD investigations.

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Manuscript received; 1 March, 2002
Manuscript accepted; 17 July, 2002