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Potassicarfvedsonite, $KNa_2Fe^{2+}{}_4Fe^{3+}Si_8O_{22}(OH)_2$, a K-dominant amphibole of the arfvedsonite series from agpaitic pegmatites – Mineral data, structure refinement and disorder in the *A* site

I. V. Pekov, Moscow, **N. V. Chukanov,** Chernogolovka, **Yu. S. Lebedeva,** Moscow, **D. Yu. Pushcharovsky,** Moscow, **G. Ferraris,** Torino, **A. Gula,** Torino, **A. E. Zadov,** Moscow, **A. A. Novakova,** Moscow, and **O. V. Petersen**, Copenhagen

With 3 figures and 7 tables

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Abstract: Potassicarfvedsonite, a new mineral species of the amphibole group, was found in alkaline pegmatites of three agpaitic complexes: Ilímaussaq in South Greenland (holotype), and Lovozero and Khibiny, both in Kola Peninsula, Russia (cotypes). It is associated with: analcime, sodalite, aegirine, steenstrupine-(Ce), epistolite (Ilímaussaq); sodalite, ussingite, analcime, aegirine, lomonosovite, vuonnemite, serandite, manaksite, villiaumite, natrosilite, sphalerite, *etc.* (Lovozero); microcline, nepheline, aegirine, sodalite, lamprophyllite, eudialyte, rinkite, titanite, fluorapatite, *etc.* (Khibiny). Potassicarfvedsonite forms prismatic to acicular crystals up to 15 cm long. Semitransparent to transparent; black, dark blue-green or blue-grey. The streak is pale greenish-blue and the lustre vitreous. Potassicarfvedsonite shows a {110} perfect cleavage, the fracture is stepped and splintery; it is brittle. Mohs' hardness = 5.5–6. D_{meas} is 3.39(2), D_{calc} is 3.43 g/cm^3. Optically biaxial (–), $2V_{meas} > 60°$, $2V_{calc} = 82°$, $\alpha = 1.683(2)$, $\beta = 1.692(2)$, $\gamma = 1.699(2)$. The dispersion $r > v$ is strong. The pleochroism is strong with X dark blueish-green, Y greyish-green, Z pale greenish-grey to pale greenish-brown. Orientation: Z = *b*; $X \wedge c = 20(10)°$; $Y \wedge a = 30(10)°$. IR and Mössbauer data are given. Electron microprobe, Li by atom emission and H_2O by modified Penfield method gave (sequence:

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Ilímaussaq, Lovozero, Khibiny): Li_2O 0.45, 0.73, not detected; Na_2O 7.01, 7.65, 6.94; K_2O 3.29, 3.76, 3.41; CaO 0.30, 0.09, 1.63; MgO 0.04, 4.80, 7.79; MnO 1.37, 3.26, 1.88; ZnO 0.20, 0.11, 0.06; FeO 24.69, 13.82, 17.53; Fe_2O_3 11.60, 8.50, 4.74; Al_2O_3 0.58, 0.51, 0.58; SiO_2 48.63, 52.82, 51.64; TiO_2 0.43, 0.77, 0.74; H_2O 1.70, 1.38 (calc.), 1.20 (calc.); F 0.36, 1.21, 1.59; $-O = F_2$ 0.15, 0.51, 0.67; Total 100.50, 98.90, 99.06 wt. %. The empirical formula of the Ilímaussaq holotype based on 46 units of charge is: $(K_{0.67}Na_{0.22})_{\Sigma 0.89}(Na_{1.95}Ca_{0.05})_{\Sigma 2.00}(Fe^{2+}{}_{3.29}Fe^{3+}{}_{1.26}Li_{0.29}Mn_{0.19}Ti_{0.05}Zn_{0.02}Mg_{0.01})_{\Sigma 5.11}$ $(Si_{7.76}Fe^{3+}{}_{0.13}Al_{0.11})_{\Sigma 8.00}O_{22}[(OH)_{1.81}F_{0.18}]_{\Sigma 1.99}$; the ideal formula is: $KNa_2Fe^{2+}{}_4Fe^{3+}Si_8O_{22}(OH)_2$. The strongest lines of the X-ray powder pattern [d in Å, $(I)(hkl)$] are: 9.02(28)(020), 8.53(100)(110), 3.303(23)(240); 3.184(40)(310), 2.847(17)(330). Potassicarfvedsonite is monoclinic, $C2/m$; $a = 10.002(2)$, $b = 18.054(3)$, $c = 5.319(1)$ Å, $\beta = 103.90(3)°$, $V = 932.4(3)$ Å^3, $Z = 2$. The crystal structure (Nonius Kappa CCD, λMoK_α radiation) was anisotropically refined to $R(F) = 0.0229$ for 3296 independent reflections with $I_O > 2\sigma(I_O)$. The distribution of the cations over the five independent positions $M1$, $M2$, $M3$, $M4$ and A (split into three subsites) was obtained on the basis of X-ray diffraction analysis and Mössbauer spectroscopy that indicates $Fe^{2+}/Fe^{3+} = 2.61$. The mineral was named as potassium-dominant analogue of arfvedsonite. Mineral and name have been approved by the IMA CNMMN. Type specimens are deposited at the Fersman Mineralogical Museum (Moscow).

Key words: Potassicarfvedsonite, new mineral species, amphibole group, crystal structure, alkaline pegmatites, Ilímaussaq complex, Lovozero massif, Khibiny massif.

Introduction

Sodic amphiboles of the arfvedsonite – magnesio-arfvedsonite series are widespread mafic minerals of the alkaline, especially agpaitic, rocks, pegmatites and metasomatites. Potassium is a typical component of many arfvedsonites; contents of 1–2 wt. % K_2O are often found in these amphiboles (DEER et al. 1997, CHUKHROV 1981, HAWTHORNE 1983). Some samples contain more potassium and their analyses show K > 0.50 atoms per formula unit (*apfu*). In accordance with the nomenclature of amphiboles (LEAKE et al. 1997 and 2003), the latter samples can be defined as individual mineral species. One of these is described in the present paper, the analogue of arfvedsonite, $NaNa_2Fe^{2+}{}_4Fe^{3+}Si_8O_{22}(OH)_2$, with K dominating over Na in the A site; it has been named potassicarfvedsonite. Both the mineral and its name have been approved by the IMA Commission on New

Minerals and Mineral Names 3 November 2003 (IMA 2003–043). Type (#3137/1 from Ilímaussaq) and cotype (#3137/2 from Lovozero) specimens are deposited at the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow.

Actually, potassicarfvedsonite is an “old new mineral”. In fact, analyses of “arfvedsonite” with K > 0.50 *apfu* were published from Ilímaussaq complex, South Greenland (SAHAMA 1956), Red Wine complex, Labrador, Canada (HAWTHORNE 1976), Khibiny massif, Kola Peninsula, Russia (KOSTYLEVA-LABUNTSOVA et al. 1978), and some other alkaline massifs (LITVIN et al. 1976). However, it was never submitted to the CNMMN of IMA and is not part of the present system of nomenclature of amphiboles (LEAKE et al. 1997 and 2003). This paper presents a wide investigation of this amphibole and establishes that it is an important pegmatitic mineral of well-known huge agpaitic complexes: Ilímaussaq in Greenland, and Lovozero and Khibiny in Kola Peninsula. All quantitative data including the crystal structure refinement and Mössbauer spectra were obtained from a specimen from Ilímaussaq; consequently it is the holotype and the analysed Kola specimens are cotypes.

Occurrences and general appearance

Samples from Ilímaussaq and Lovozero alkaline complexes were collected by one of the authors (I. V. P.); additional material from Ilímaussaq was collected at the request (O. V. P.) by K. SECHER in the Summer of 2003; material from Khibiny was provided by amateur collector A. S. PODLESNYI.

The locality of the holotype material is the “Pegmatite Valley”; the small stream in the valley being the lowermost tributary to the Lilleelv river in the Kangerluarsuk area, Southern part of Ilímaussaq complex, altitude about 260 m. Potassicarfvedsonite occurs in one or more pegmatite veinlets more than 20 m long, and up to 0.5 m thick, crosscutting naujaite, on both sides of the stream in the Pegmatite Valley. The pegmatite veinlets mainly consist of white coarse-grained analcime with subordinate amounts of fine-grained sodalite, microcline, aegirine, crude crystals of steenstrupine-(Ce), eudialyte, and epistolite. Potassicarfvedsonite forms well shaped prismatic crystals from a few cm up to 15 × 0.8 cm, showing the {110} and {010} forms, included in an analcime matrix. In other parts of the veinlets, preferably the marginal parts, it occurs as mosaic individuals up to several cm in size, which combine to massive, sometimes divergent and curved, aggregates, constituting up to 30–50 % of the pegmatitic rock.

In Lovozero, potassicarfvedsonite occurs in the Palitra (“Palette”) pegmatite recently uncovered in the underground loparite mine at Mt. Kedykverpakhk. The Palitra is a large (more than 7 × 2 m) pillow-like pegmatite situated in foyaite near its contact with loparite-enriched malignite. The peripheral part of the pegmatite consists of microcline, aegirine, eudialyte, nepheline and arfvedsonite, with subordinate villiaumite, lorenzenite, lomonosovite, and lamprophyllite. In its core, abundant hyperalkaline minerals form nests up to 1 × 0.5 m in size, mainly consisting of sodalite, ussingite, and analcime and containing aegirine, lomonosovite, vuonnemite, serandite, villiaumite, natrolite, kazakovite, chkalovite, steenstrupine-(Ce), phosinaite-(Ce), mangan-neptunite, barytolamprophyllite, sphalerite, löllingite, and the new member of the lovozerite group named kapustinite, $Na_{5.5}Mn_{0.25}ZrSi_6O_{16}(OH)_2$, (Pekov et al. 2003). The latest assemblages are represented by water-free and water-poor minerals: villiaumite, natrosilite (single-crystal blocks up to 30 cm), manaksite (crystals up to 20 cm), nordite-(Ce), ferronordite-(Ce), vitusite-(Ce), belovite-(Ce), the new mineral bario-olgite, $Ba(Na,Sr,\mathit{REE})_2Na[PO_4]_2$ (Pekov et al. 2004), nalipoite, thorosteenstrupine, bartonite, chlorbartonite, serandite and potassicarfvedsonite. The latter forms acicular crystals up to 2 × 0.1 mm in size, usually combined to bunches and hedgehog clusters up to 4 mm; it also occurs as massive nodules up to 1.5 cm across and consisting of thin acicular to fibrous individuals. The potassicarfvedsonite aggregates are situated in ussingite cavities and, together with late Ca-free serandite, inside partially altered crystals of manaksite, $KNa(Mn,Fe)Si_4O_{10}$, whereas earlier large (up to 15 cm long) crystals of arfvedsonite are widespread in the peripheral zone of the Palitra pegmatite.

In Khibiny, potassicarfvedsonite was found in the Hilairitovoye pegmatite (named after the occurrence of nice hilairite crystals) at Kirovskii underground apatite mine, Mt. Kukisvumchorr. Hilairitovoye is an elongated lenticular lode more than 20 m long and up to 1.5 m thick; situated in ijolite-urtite; 77 mineral species were found in this pegmatite (Pekov & Podlesnyi 2004). Potassicarfvedsonite occurs in the peripheral zone of the pegmatite and is closely associated with microcline, nepheline, aegirine, sodalite, lamprophyllite, eudialyte, fersmanite, rinkite, titanite, fluorapatite, natrolite, sphalerite, fluorite, etc. The up to 5 × 1 cm large prismatic crystals of potassicarfvedsonite contain abundant inclusions of green aegirine needles.

Potassicarfvedsonite usually crystallizes later than arfvedsonite, after sufficient accumulation of potassium has been reached during the alkaline pegmatite formation. In potassium-rich complexes (Khibiny), potassicarfvedsonite is an early pegmatitic mineral, unlike in hypersodic complexes (Ilímaussaq and Lovozero), where it was found in paragenesis with late-stage, probably hydrothermal, minerals.

Experimental

Physical, optical and IR data

Potassicarfvedsonite is black (Ilímaussaq; Khibiny) or dark blue-green to blue-grey (Lovozero); it is transparent to semitransparent; the streak is pale-blue. The lustre is vitreous. Potassicarfvedsonite shows {110} perfect

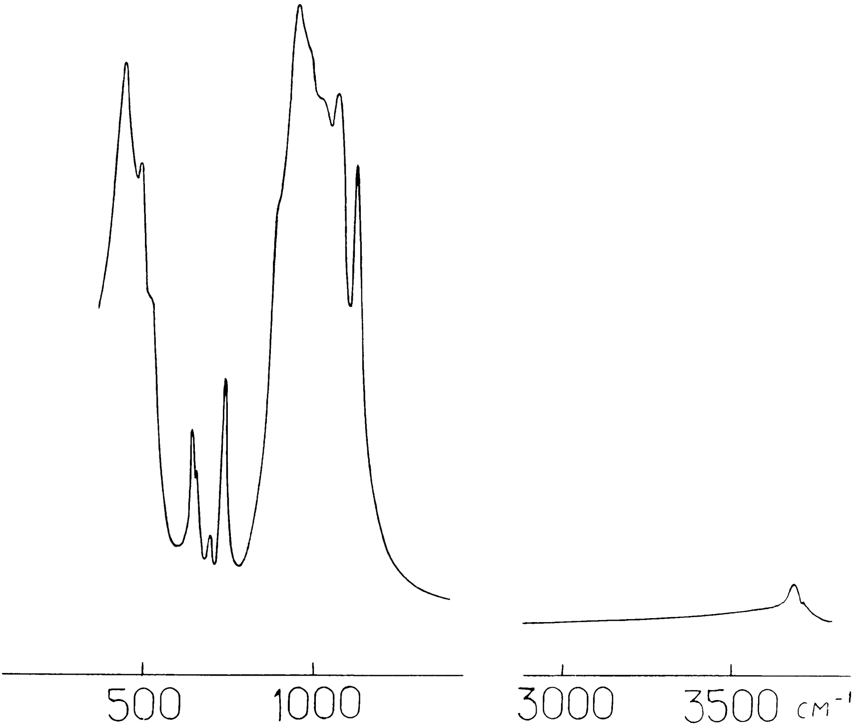

Fig. 1. The IR spectrum of potassicarfvedsonite from Ilímaussaq.

cleavage, the fracture is stepped and splintery. It is brittle, Mohs' hardness is 5.5–6. The density measured using heavy liquids is 3.39(2) g/cm^3, the calculated density is 3.43 g/cm^3 for the holotype.

Optically, potassicarfvedsonite is biaxial (–); $2V_{meas} > 60°$; $2V_{calc} = 82°$; $\alpha = 1.683(2)$, $\beta = 1.692(2)$, $\gamma = 1.699(2)$. The dispersion $r > v$ is strong. The pleochroism is strong: X dark bluish-green, Y greyish-green, Z pale greenish-grey to pale greenish-brown; absorption: X ≥ Y > Z; orientation: Z = *b*; $X \wedge c = 20(10)°$; $Y \wedge a = 30(10)°$.

The IR spectrum of potassicarfvedsonite (Fig. 1) obtained using Specord 75 IR instrument is similar to the spectrum of arfvedsonite (CHUKHROV 1981). Absorption bands (in cm^{-1}, frequencies of the most intensive bands are underlined, sh = shoulder) are: 3700, 3675, $\underline{1134}$, $\underline{1076}$, 1025 sh, 990 sh, $\underline{957}$, 900 sh, 741, 692, 661, 643, 520 sh, 491, $\underline{445}$, 430 sh.

Chemical data

The chemical composition of potassicarfvedsonite (Table 1) was obtained (fluorine and cations except Li) by a Camebax SX50 electron microprobe using an operating voltage of 15 kV and an estimated beam-current of 30 nA. The electron beam was rastered over an area of 10 × 10 μm^2 to minimise sample damage. Standards used were: jadeite (Na), orthoclase (K, Al), amphibole (Ca, Mg, Fe, Si), $MnTiO_3$ (Mn, Ti), ZnSe (Zn), and fluorapatite (F). Li was determined by atom emission using a Carl Zeiss AAS30 spectrophotometer. The water content was determined by the Alimarin method, a modified Penfield, with water absorption by $Mg(ClO_4)_2$. The Fe^{2+}/Fe^{3+} ratio in octahedral sites was calculated from Mössbauer data.

The empirical formula of the holotype from Ilímaussaq, based on 46 units of charge [i. e. formal $O_{22}(OH,F)_2$], is $(K_{0.67}Na_{0.22})_{\Sigma 0.89}(Na_{1.95}Ca_{0.05})_{\Sigma 2.00}(Fe^{2+}_{3.29}Fe^{3+}_{1.26}Li_{0.29}Mn_{0.19}Ti_{0.05}Zn_{0.02}Mg_{0.01})_{\Sigma 5.11}(Si_{7.76}Fe^{3+}_{0.13}Al_{0.11})_{\Sigma 8.00}O_{22}[(OH)_{1.81}F_{0.18}]_{\Sigma 1.99}$. The empirical formulae of Kola samples calculated on the basis of 13 tetrahedral plus octahedral atoms (i. e. Si + Al + Fe + Ti + Mg + Mn + Zn + Li = 13) and 46 units of charge (because of no direct determinations of Fe^{2+} and Fe^{3+}) are $(K_{0.73}Na_{0.27})_{\Sigma 1.00}(Na_{2.00}Ca_{0.01})_{\Sigma 2.01}(Fe^{2+}_{1.77}Mg_{1.10}Fe^{3+}_{0.98}Li_{0.45}Mn_{0.42}Ti_{0.09}Al_{0.09}Zn_{0.01})_{\Sigma 4.91}Si_{8.09}O_{22}[(OH)_{1.41}F_{0.59}]_{\Sigma 2.00}$ (Lovozero) and $(K_{0.67}Na_{0.33})_{\Sigma 1.00}(Na_{1.74}Ca_{0.27})_{\Sigma 2.01}(Fe^{2+}_{2.26}Mg_{1.79}Fe^{3+}_{0.55}Mn_{0.25}Ti_{0.09}Al_{0.05}Zn_{0.01})_{\Sigma 5.00}(Si_{7.94}Al_{0.06})_{\Sigma 8.00}O_{22}[(OH)_{1.23}F_{0.77}]_{\Sigma 2.00}$ (Khibiny). The ideal formula of the Ilímaussaq potassicarfvedsonite is $KNa_2Fe^{2+}_4Fe^{3+}Si_8O_{22}(OH)_2$ and requires: Na_2O 6.36, K_2O 4.83, FeO 29.48, Fe_2O_3 8.19, SiO_2 49.29, H_2O 1.85, total 100.00 wt. %. The potassicarfvedso-

Table 1. Chemical composition of potassicarfvedsonite.

Constituent wt. %	Ilímaussaq (holotype)*	Lovozero	Khibiny
Li_2O	0.45	0.73	not detected
Na_2O	7.01 (6.8–7.4)	7.65	6.94
K_2O	3.29 (3.2–3.4)	3.76	3.41
CaO	0.30 (0.1–0.4)	0.09	1.63
MgO	0.04 (0.02–0.07)	4.80	7.79
MnO	1.37 (1.0–1.9)	3.26	1.88
ZnO	0.20 (0.05–0.3)	0.11	0.06
FeO	24.69	13.82**	17.53**
Fe_2O_3	11.60	8.50**	4.74**
Al_2O_3	0.58 (0.5–0.7)	0.51	0.58
SiO_2	48.63 (48.3–49.0)	52.82	51.64
TiO_2	0.43 (0.3–0.5)	0.77	0.74
H_2O	1.70 (1.58–1.83)	1.38***	1.20***
F	0.36 (0.25–0.45)	1.21	1.59
$-O = F_2$	0.15	0.51	0.67
Total	**100.50**	**98.90**	**99.06**
Fe_{tot}	27.30 (26.4–27.6)	16.69	16.95
Atoms apfu			
K	0.67	0.73	0.67
Na	2.17	2.27	2.07
Ca	0.05	0.01	0.27
Σ (K + Na + Ca)	**2.89**	**3.01**	**3.01**
Li	0.29	0.45	
Mg	0.01	1.10	1.79
Mn	0.19	0.42	0.25
Zn	0.02	0.01	0.01
Fe^{2+}	3.29	1.77**	2.26**
$^{VI}Fe^{3+}$	1.26	0.98**	0.55**
^{VI}Al	–	0.09	0.05
Ti	0.05	0.09	0.09
Σoct.	**5.11**	**4.91**	**5**
$^{IV}Fe^{3+}$	0.13	–	–
^{IV}Al	0.11	–	0.06
Si	7.76	8.09	7.94
Σtetr.	**8**	**8.09**	**8**
O	22.00	22.00	22.00
OH	1.81	1.41***	1.23***
F	0.18	0.59	0.77

* Average of 12 analysis (range in parentheses); the contents of Sr, Ba, Pb, Zr, Nb, Cl are below detection limits.

** Fe_{total} content was determined by electron probe and Fe^{2+}/Fe^{3+} ratio from the charge balance.

*** H_2O content calculated for $(OH, F)_2$.

nite from Ilímaussaq is F-poor and almost Mg-free, unlike that from Lovozero and Khibiny. The potassicarfvedsonite from Lovozero is enriched in Li.

Mössbauer spectroscopy

A Mössbauer spectrum was obtained at room temperature using constant acceleration spectrometer with Co^{57} (Rh) source ($v = \pm 4$ mm/s); its hyperfine parameters (δ – isomer shift, Δ – quadrupole splitting, S – relative area and Γ – line width) were analyzed by means of the programme UNIVEM (Mos Tec, 2002). The complex experimental spectrum was fitted ($\chi^2 = 1.147$) by six doublets (three for Fe^{2+} and three for Fe^{3+}; Table 2 and Fig. 2) indicating that both Fe^{3+} and Fe^{2+} occur in three different sites with an overall Fe^{2+}/Fe^{3+} ratio of about 2.61. According to the isomer shifts (Menil 1985), these sites are octahedral and thus correspond to $M1$, $M2$ and $M3$. The relative area S of the doublets indicates that Fe^{2+} dominates over Fe^{3+} in all three sites. The correspondence between the doublets and the octahedral sites was based on the known crystal-chemical data for amphiboles (Andersen et al. 1975, Hawthorne 1983, Sokolova et al. 2000, Pushcharovskii et al. 2003) and the results of our X-ray diffraction study as discussed below. No signal corresponding to tetrahedral Fe^{3+} was detected.

X-ray diffraction study

The experimental X-ray powder diffraction data (Table 3) of the holotype sample of potassicarfvedsonite from Ilímaussaq were obtained using a DRON UM-1 diffractometer and Fe-filtered CoKα-radiation. The pattern is close to that of arfvedsonite (Chukhrov 1981) and was indexed by comparison with that calculated from the structural data by the XPOW routine

Table 2. Parameters of the doublets* in the Mössbauer spectrum of potassicarfvedsonite.

Site	Fe^{2+}				Fe^{3+}			
	δ, mm/s	Δ, mm/s	Γ, mm/s	S, %	δ, mm/s	Δ, mm/s	Γ, mm/s	S, %
$M1$	1.10(1)	2.96(1)	0.30(1)	31.14	0.41(1)	0.60(1)	0.30(1)	6.66
$M2$	1.09(1)	2.67(1)	0.30(1)	23.52	0.43(1)	0.41(1)	0.30(1)	19.20
$M3$	1.05(1)	1.91(1)	0.30(1)	17.60	0.25(1)	0.31(1)	0.24(1)	1.88

δ – isomer shift (given relative to α-Fe); Δ – quadrupole splitting; Γ – line width and S – relative area.

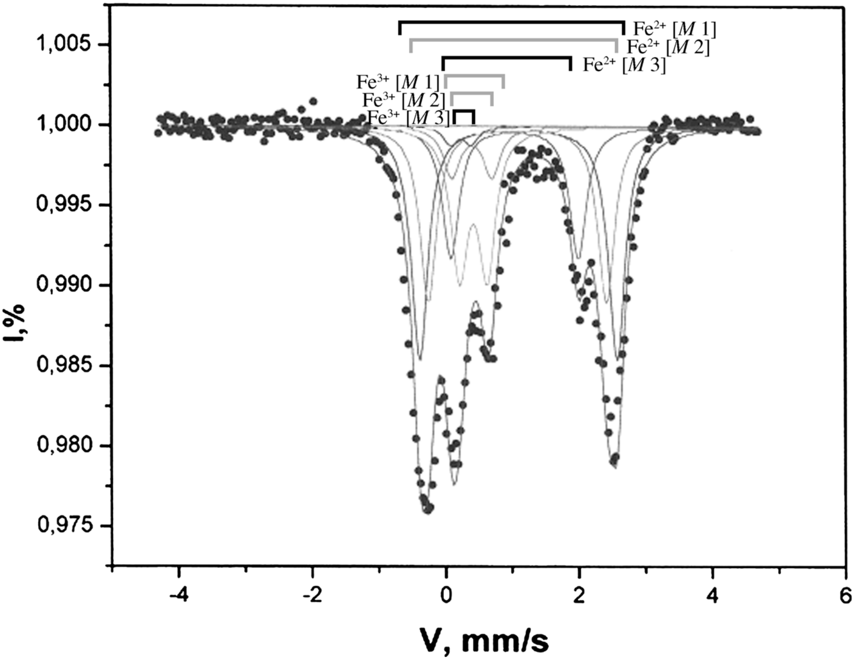

Fig. 2. The Mössbauer spectrum of potassicarfvedsonite showing three Fe^{2+} and three Fe^{3+} doublets and their structural assignment.

(Sheldrick 1997). The poor agreement between I_{meas} and I_{calc} is caused by the strong preferred orientation, related to the perfect {110} cleavage, which leads to overestimate the intensity of the strongest (110) reflection.

Single-crystal diffraction data were collected (Table 4) at room temperature using a Nonius Kappa CCD diffractometer (Institute of Mineralogy and Crystallography, University of Vienna) equipped with a capillary optics collimator and graphite monochromatized MoKα-radiation (λ = 0.71073 Å). A total of 505 frames in several sets of φ- and ω-scans with 2° rotation per frame and 30 mm crystal to detector distance were measured to collect the complete Ewald sphere up to 90.55° 2θ. The extraction of intensity data, including corrections for Lorentz and polarization effects and a pseudo absorption correction by frame scaling, as well as the refinement of lattice parameters from all measured reflections, was performed with the Nonius package DENZO-SMN (Nonius 1998).

Table 3. X-ray powder diffraction data of potassicarfvedsonite from Ilímaussaq.

I_{meas}	I_{calc}	d_{meas}, Å	d_{calc}, Å	h	k	l
28	10	9.02	9.027	0	2	0
100	100	8.53	8.551	1	1	0
2	5	5.117	5.115	1	3	0
8	3	4.855	4.855	2	0	0
6	14	4.509	4.514	0	4	0
7	6	4.048	4.056	1	1	1
12	31	3.419	3.424	1	3	1
23	12	3.303	3.306	2	4	0
40	42	3.184	3.186	3	1	0
4	6	2.993	2.996	2	2	1
17	13	2.847	2.850	3	3	0
5	14	2.753	2.754	3	3	−1
10	66	2.725	2.728	1	5	1
3	28	2.598	2.600	0	6	1
2	42	2.550	2.547	2	0	−2
2	2	2.492	2.493	1	7	0
5	5	2.426	2.427	4	0	0
8	3	2.408	2.410	3	5	0
5	22	2.351	2.351	3	5	−1
6	25	2.181	2.185	2	6	1
3	11	2.047	2.048	3	5	1
2	2	1.968	1.969	4	2	1
4	1	1.930	1.931	5	1	0
2	6	1.893	1.892	4	6	−1
2	1	1.848	1.848	5	3	0
3	8	1.805	1.807, 1.805	1	9	1, 0 10 0
4	18	1.675	1.676	4	6	1
2	4	1.653	1.653	4	8	0
6	12	1.619	1.618, 1.618	1	11	0, 6 0 0
1	16	1.588	1.589	1	5	−3
2	6	1.529	1.530	5	5	1
2	6	1.504	1.505	0	12	0
4	17	1.456	1.455	6	6	−1

The crystal structure was solved by direct methods and refined in the space group *C*2/*m* using 3296 independent reflections with $I_o > 2\sigma(I_o)$ (SHELX-97, Sheldrick 1997). The weighted anisotropic refinement (iso-

Table 4. Experimental and refinement conditions, and crystal data for potassicarfvedsonite.

Chemical formula	$KNa_2Fe^{2+}{}_4Fe^{3+}Si_8O_{22}(OH)_2$
Space group	$C2/m$
a (Å)	10.002(2)
b (Å)	18.054(3)
c (Å)	5.319(1)
β	103.90(3)°
V (Å^3)	932.4(3)
Z	2
Crystal size (mm)	0.11 × 0.08 × 0.34
Absorption coefficient (mm^{-1})	4.97
Dcalc (gcm^{-3})	3.43
$2\theta_{max}$ (°)	90.55
Rotation width [°]	2.0
Collection time per frame [s]	70
Crystal-detector distance [mm]	30
Measured CCD frames	505
Measured reflections	7542
Unique reflections	3893
Independent reflections with $F_o > 4\sigma$ (F_o)	3296
R_{int} (%)	0.02(3)
h_{min}/h_{max}, k_{min}/k_{max}, l_{min}/l_{max}	–19/19, –36/35, –10/10
Number of refined parameters	119
$wR2$ [for all F_o^2]	0.0617
$R1$ [for $F_o > 4\sigma$ (F_o)]	0.0229
$R1$ [for all F_o^2]	0.0308
Goodness of fit	1.052
Weighting* parameters a, b	0.0252, 0.4982
$\Delta\rho_{max/min}$ (e$^-$Å^{-3})	0.69, –0.57

* Weighting scheme:
$w = 1/[s^2(F_o^2) + (aP)^2 + bP]$, $P = \{[\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2\}/3$.

tropic for the hydrogen atom detected from a difference Fourier and two A subsites; Tables 4 and 5) converged to $R(F) = 0.0229$. The electron contents (Table 6) of the $M2$ and $M3$ sites were obtained by refining Fe against Ti and Fe against Li, in the order. To refine the content of the $M1$ site, the scattering curve of Fe was used; the $M4$ site proved to be fully occupied by Na. According to the chemical analysis (Table 1), a deficiency of cations

Table 5. Atom coordinates and isotropic equivalent (*U*eq) displacement parameters in the potassicarfvedsonite structure.

Site	*x*	*y*	*z*	*U*eq (Å^2)
*M*1	0	0.09102 (1)	1/2	0.00873 (5)
*M*2	0	0.18388 (1)	0	0.00721 (4)
*M*3	0	0	0	0.00782 (7)
*M*4	0	0.27795 (3)	1/2	0.0165 (1)
A′m	0.013 (1)	1/2	0.039 (1)	0.038 (3)
A″m	0.067 (3)	1/2	0.121 (3)	0.021 (4)*
*A*2	0	0.472 (2)	0	0.034 (6)*
Si1	0.27470 (2)	0.08610 (1)	0.29088 (4)	0.00669 (5)
Si2	0.28655 (2)	0.17085 (1)	0.79998 (4)	0.00683 (5)
O1	0.10992 (6)	0.09152 (3)	0.2078 (1)	0.0096 (1)
O2	0.12016 (6)	0.17285 (4)	0.7336 (1)	0.0102 (1)
O3	0.1084 (1)	0	0.7081 (2)	0.0124 (2)
O4	0.36430 (7)	0.24753 (4)	0.7991 (1)	0.0130 (1)
O5	0.34497 (6)	0.12684 (4)	0.0802 (1)	0.0107 (1)
O6	0.33740 (6)	0.11819 (4)	0.5814 (1)	0.0115 (1)
O7	0.3271 (1)	0	0.2968 (2)	0.0131 (1)
H	0.223 (4)	0	0.771 (7)	0.07 (1)*

* Isotropic

Table 6. Distribution of the cations over the sites in the potassicarfvedsonite structure. The values of the electron density calculated according to the shown site occupancies (e_{calc}) is compared with those obtained from the refinement (e_{ref}).

Site	e_{ref}	e_{calc}	Site occupancy	Sum of the ionic radii (Å)	Experimental average distance (Å)
*M*1	25.41 (3)	25.90	$0.70Fe^{2+} + 0.20Fe^{3+} + 0.10Mn^{2+}$	2.138	2.115
*M*2	25.4 (1)	25.88	$0.58Fe^{2+} + 0.39Fe^{3+} + 0.03Ti^{4+}$	2.102	2.061
*M*3	19.53 (4)	19.56	$0.63Fe^{2+} + 0.28Li + 0.09Fe^{3+}$	2.142	2.125
A′m + *A″m* + *A*2	7.7 (2)	7.6	(0.67K+0.22Na+0.11□)/2		

occurs at the *A* site together with dominant K and minor Na. This site turned out to be split into three subsites (see discussion below): two on the mirror plane (*A′m* and *A″m*) and one on the twofold axis (*A*2). The scattering factor of K was used for *A′m*, whose electron content converged to

6.5(2), and that of Na for the other two subsites, which show the same electron content of 0.6(1). The refinement of the electron content of the O3 site converged to 8.20(4) electrons corresponding to a 0.8 O + 0.2 F, a value which, taking into account that O and F differ for one electron only, not so badly compares with the value of 0.91 O + 0.09 F given by the chemical analysis (Table 1).

Discussion

Crystal structure

A part the site contents (discussed below), the crystal structure of potassicarfvedsonite (Fig. 3) does not significantly differ from that of arfvedsonite (Kawahara 1963, Hawthorne 1976). Actually, the sample studied by Hawthorne (1976) corresponded to a potassicarfvedsonite, as now defined, with composition $(K_{0.71}Na_{0.29})(Na_{1.84}Ca_{0.16})(Fe^{2+}{}_{3.60}Mg_{0.11}Mn_{0.13}Fe^{3+}{}_{0.92}Ti_{0.09}Al_{0.15})(Si_{7.83}Al_{0.17})O_{22}(OH, F, O)_2$. The localization of the hydrogen atom attached to O3 has been possible, in spite this oxygen is about 10 % substituted by F; that supports absence of de-hydroxylation. As usual in amphiboles, the O3–H = 1.12(4) Å bond develops along [100] (Fig. 3)

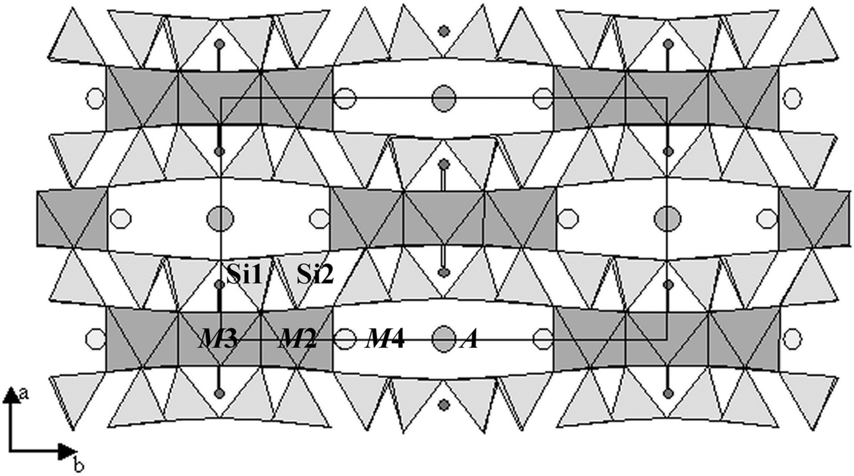

Fig. 3. The potassicarfvedsonite structure projected along [001]. The *M*1 site is not shown because it is behind *M*2 and *M*3. For the splitting of the *A* site see text.

and no hydrogen bond is formed, being O3 not less than 3.3 Å distant from the nearest surrounding oxygen atoms O6 and O7.

The observed average tetrahedral distances $<T1\text{–O}> = 1.627$ Å and $<T2\text{–O}> = 1.636$ Å fall within the range 1.616–1.636 Å typical of the Al-free tetrahedra (HAWTHORNE 1983). From the equation ^{IV}Al (*apfu*) = [16.252 × $<T\text{–O}>$] – 26.434 (HAWTHORNE & GRUNDY 1977) and the value of $<T\text{–O}> = 1.631$ Å, a content of 0.07 Al *apfu* is obtained in good agreement with that of 0.11 *apfu* found by chemical analysis (Table 1). A $<T1\text{–O}>$ distance shorter than $<T2\text{–O}>$ is typical for Al-free alkali amphiboles and, according to HAWTHORNE (1983) and LITVIN (1977), is connected to the presence of Na in the *M*4 site.

Ignoring the little amount of Al mentioned above and other minor cations detected by chemical analysis, the distribution of the cations over the *M*1, *M*2 and *M*3 sites (Table 6) was based on the following constrains. In the order: (i) charge balance, (ii) electron contents of the sites, (iii) chemical analysis, (iv) Fe^{2+}/Fe^{3+} ratio obtained for each site from the relative area of the doublets in the Mössbauer spectrum (Table 2). Comparison of the average interatomic distances obtained as sum of the ionic radii (0.78, 0.645, 0.605, 0.83, 0.76, and 1.38 Å for octahedral Fe^{2+}, Fe^{3+}, Ti^{4+}, Mn^{2+}, Li^{+}, and O^{2-}, in the order; SHANNON 1976), with the experimental ones (Table 6), confirms the reliability of the proposed cation distribution. Even soundly, the reported cation distribution, including the one in the *A* site, leads to a very satisfactory charge distribution calculated according to NESPOLO et al. (1999), i. e. –2.04, –2.00, –1.04 (without the contribution of the H atom), –1.92, –1.98, –2.00, and –2.08 for the oxygen atoms from O1 to O7, in the order. As discussed by NESPOLO et al. (1999), the charge distribution method has advantages compared to the bond-valence distribution, particularly when differently charged cations occupy the same site.

According to HAWTHORNE et al. (1993), the small-size and high-charge cation Ti^{4+} prefers the *M*2 site. Actually, Ti^{4+} has been reported also in *M*1 associated with a de-hydroxylation of O3 that causes a contraction of the *M*1–O3 bond, as shown for richterite (OBERTI et al. 1992) where this distance ranges from 2.071 to 2.087 Å in Ti^{4+}-poor richterites and from 1.998 to 2.025 Å in Ti^{4+}-rich richterites. In contrast, in potassicarfvedsonite the distance *M*1–O3 = 2.128(1) Å is the longest within the *M*1 octahedron. Consequently, even a partial de-hydroxylation of O3 must be excluded, in agreement also with both the chemical analysis (Table 1) and the successful refinement of the atomic position and displacement parameter of the hy-

Table 7. Selected bond lengths (Å) for potassicarfvedsonite. Estimated standard deviations in parentheses.

Si1–	O1	1.604(1)	Si2–	O4	1.588(1)
	O6	1.629(1)		O2	1.617(1)
	O5	1.634(1)		O5	1.666(1)
	O7	1.639(1)		O6	1.673(1)
Average		1.627	Average		1.636
$M1$–	O1 × 2	2.108(1)	$M2$–	O4 × 2	1.955(1)
	O2 × 2	2.110(1)		O2 × 2	2.076(1)
	O3 × 2	2.128(1)		O1 × 2	2.151(1)
Average		2.115	Average		2.061
$M3$–	O3 × 2	2.097(1)	$M4$–	O4 × 2	2.371(1)
	O1 × 4	2.139(1)		O2 × 2	2.423(1)
Average		2.125		O6 × 2	2.586(1)
				O5 × 2	2.947(1)
$A'm$	O7	2.562(9)	Average		2.582
	O7	2.667(8)			
	O5 × 2	2.845(6)	$A''m$–	O7	2.69(3)
	O5 × 2	2.880(7)		O6 × 2	2.69(1)
	O6 × 2	3.070(6)		O5 × 2	2.76(2)
Average		2.852		O7	2.77(3)
				O7	3.02(2)
$A2$–	O5 × 2	2.47(3)		O3 × 2	3.16(3)
	O7 × 2	2.65(1)		O5	3.16(2)
	O6 × 2	2.92(2)	Average		2.89
Average		2.68			

drogen atom. Taking into account the above considerations and that the octahedron centred on $M1$ is larger than that centred on $M2$, Fe and Mn only are assigned to the $M1$ site, even if the refined electron content, 25.41(3) electrons, is the same for the $M1$ and $M2$ sites. As mentioned above, the cation composition of the $M2$ [Fe + Ti; 25.4(1) electrons] and $M3$ [(Fe + Li; 19.53(4) electrons] sites has been determined by refinement. The occurrence of octahedral Li in $M3$ has been shown in about 20 samples of Li-bearing alkali amphiboles, with Li_2O in the range 0.09–1.3 wt.% (Hawthorne et al. 1992, 1993, 1994), in contrast with earlier assignment of Li to the $M4$ site (Litvin 1977, Hawthorne 1976). The incorporation of Li in $M3$ must be compensated by a concomitant increase in charge in other structural positions of the octahedral strip. According to HAWTHORNE et al. (1993), in igneous alkali amphiboles the increase of Li content correlates strongly with the increase of Fe^{3+} content following the substitution $LiFe^{3+} \rightarrow Fe^{2+}Fe^{3+}$ in the $M3$ site, a situation which occurs in the refined potassicarfvedsonite. The presence of Li also correlates with a lack of Al at the tetrahedral positions (HAWTHORNE et al. 1994).

The refinement shows that the $M4$ site is fully occupied by Na. The coordination polyhedron around $M4$ consists of six oxygens in the range 2.371–2.586 Å plus two further oxygens at 2.947 Å (Table 7).

Disorder in the A site

In the alkali monoclinic amphiboles, the A site is within a large cavity, which is sandwiched between two tetrahedral double chains, and is occupied by the large Na and K cations. The cavity is formed by an irregular array of twelve chain-bridging oxygens that, often only in part, are coordinated by the alkalis; deficiency of cations may occur as well (HAWTHORNE & GRUNDY 1972). HAWTHORNE et al. (1996) [see an updating in OBERTI et al. (2003)] emphasized that the alkali amphiboles with a considerable amount of Na in $M4$, tend to disorder in the A site in the following way: (1) with the same probability, Na may be displaced both along the plane, assuming (x, 1/2, z) coordinates, and along the two-fold axis, assuming (0, y, 0) coordinates; (2) the larger K is disordered only within the (010) plane. According to the chemical analysis (Table 1), in the refined sample of potassicarfvedsonite the A site is cation deficient and dominated by K.

In agreement with the pattern of disorder proposed by HAWTHORNE et al. (1996) for the A site, evidence of splitting both within the (010) mirror plane and along the twofold-axis was clearly detected (Tables 5). In the mirror plane, two independent subsites occur: a major one $A'm$, refined as K, and a minor one $A''m$, refined as Na. A third minor subsite $A2$, refined as Na, occurs on the twofold axis. The equal electron content, 0.6(1), of $A''m$ and $A2$ and the conclusion of HAWTHORNE et al. (1996) that Na disorders with the same probability within the mirror plane and along the twofold axis, support the presence of Na only in these two subsites. Thus, $A'm$ must be occupied by K. The proposed distribution of K and Na in the three subsites corresponds to a good agreement between refined and chemically determined contents for the two alkalis (Table 6). The $A'm$, $A''m$ and $A2$ subsites are close each other [$A'm$–$A''m$ = 0.61(3) and 1.02(2) Å; $A'm$–$A2$ = 0.54(3) Å; $A''m$–$A2$ = 0.95(3) Å] and to their symmetry equivalents [$A'm$–

A′m = 0.43(2) Å; *A″m*–*A″m* = 1.62(5) Å; *A*2–*A*2 = 1.00(8) Å], but they show different coordination environments (Table 7). Actually, as discussed by HAWTHORNE et al. (1996), the necessity of establishing different coordination, in order to optimise the bond valence balance, is the force driving the disorder in the *A* site.

The diffraction pattern collected by a CCD diffractometer did not show superstructure diffractions that would be indicative of a long range order of K and Na in the *A* site; thus, the disorder found in the average structure is due to a short range distribution only.

Conclusions

According to the structure refinement and Mössbauer spectrum, the crystal-formula of potassicarfvedsonite can be written as $(K_{0.67}Na_{0.22}\square_{0.11})_{\Sigma 1}Na_2(Fe^{2+}{}_{3.19}Fe^{3+}{}_{1.27}Li_{0.28}Mn^{2+}{}_{0.20}Ti^{4+}{}_{0.06})_{\Sigma 5}Si_8O_{22}(OH_{1.80}F_{0.20})_{\Sigma 2}$. The Fe^{2+}/Fe^{3+} ratio is 2.51 instead of 2.61 as indicated by the Mössbauer spectrum. Taking into account that minor substitutions are ignored and the range of values obtained from the chemical analysis of the holotype potassicarfvedsonite (Table 1), the crystal-chemical formula reasonably fits the chemical data.

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Authors' addresses: I. V. PEKOV, YU. S. LEBEDEVA, D. YU. PUSHCHAROVSKY, Faculty of Geology, Moscow State University, 119899 Moscow, Russia.
N. V. CHUKANOV, Institute of Problems of Chemical Physics, 142432 Chernogolovka, Moscow Oblast, Russia.
G. FERRARIS, A. GULA, Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino, and Istituto di Geoscienze e Georisorse, CNR, Via Valperga Caluso 35, I-10125 Torino, Italy.
A. A. NOVAKOVA, Faculty of Physics, Moscow State University, 119899 Moscow, Russia.
A. E. ZADOV, NPO Regenerator, Skladochnaya ul. 6, 127018 Moscow, Russia.
O. V. PETERSEN, Geological Museum, University of Copenhagen, Øster Voldgade 5–7, DK-1350 Copenhagen, Denmark.
Correspondence author: G. FERRARIS. E-mail: giovanni.ferraris@unito.it