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POTASSIC-CARPHOLITE, A NEW MINERAL SPECIES FROM THE SAWTOOTH BATHOLITH, BOISE COUNTY, IDAHO, U.S.A.

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Abstract

Potassic-carpholite, ideally $(K,\square)\ (Li,Mn^{2+})_2\ Al_4\ Si_4\ O_{12}\ (OH)_4\ (F,OH)_4$, is a new mineral species from the Sawtooth batholith, an anorogenic Tertiary granite pluton near Centerville, Boise County, Idaho, U.S.A. It occurs as irregular tufts (up to 2 mm across) of radiating acicular-to-fibrous crystals in miarolitic cavities in the granite, associated with quartz, microcline, albite, beryl, topaz, bertrandite, hellandite, zinnwaldite, fluorite, hematite and apatite. Individual crystals of potassic-carpholite are white to straw yellow with a white streak and a vitreous luster, and are non-fluorescent in ultraviolet light. Crystals are generally 20–40 μm across and approximately 500 μm long and elongate along [100]. Potassic-carpholite is brittle with an irregular fracture on ends of the acicular crystals, and has a perfect cleavage parallel to {010}. Twinning was not observed. The Mohs hardness is ~5, and the observed and calculated densities are 3.08(2) and 3.06 g/cm^3, respectively. Potassic-carpholite is biaxial negative, with α 1.578, β 1.592, γ 1.598, all ±0.002, 2*V*(obs.) = 57(2)°, 2*V*(calc.) = 66°, weakly pleochroic with *X* pale yellow, $Y = Z$ colorless, with $X > Y, Z$ and $X = b$, $Y = a$ and $Z = c$. Potassic-carpholite is orthorhombic, space group *Ccca*, *a* 13.715(5), *b* 20.302(7), *c* 5.138(3) Å, *V* 1430.6 Å^3, $Z = 4$. The strongest seven lines in the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are as follows: 5.705(100)(220), 2.613(100)(351), 3.048(90)(331), 3.819(80)(221), 3.433(80)(400), 2.744(80)(421), 2.050(80)(621). Chemical analysis by electron microprobe gave SiO_2 36.73, TiO_2 0.10, Al_2O_3 29.38, MnO 13.37, FeO 1.44, MgO 0.04, Na_2O 0.51, Li_2O(calc.) = 1.34, K_2O = 4.07, F 7.47, H_2O (calc.) 7.24, $O \equiv F$ –3.14, sum 98.55 wt.%, where the amount of H_2O was calculated as (8 – F) *apfu*. The resulting empirical formula on the basis of 20 anions (including OH as 8 – F and Li as [2 – {Mn + Fe + Mg}] *apfu* is $(K_{0.56}Na_{0.11}\square_{0.33})\ (Mn^{2+}_{1.26}Fe^{2+}_{0.13}Mg_{0.01}Li_{0.60})\ (Al_{3.85}Si_{0.08})\ Si_4\ O_{12}\ (OH)_4\ (F_{2.63}\{OH\}_{1.37})$. Potassic-carpholite, ideal end-member composition $K\ (Mn^{2+}Li)\ Al_4\ Si_4\ O_{12}\ (OH)_4\ F_4$, is structurally similar to carpholite, $\square\ Mn^{2+}_2\ Al_4\ Si_4\ O_{12}\ (OH)_4\ F_4$, and is related by the substitution $K + Li \rightarrow \square$ (vacancy) + Mn^{2+}.

Keywords: potassic-carpholite, new mineral species, carpholite group, Sawtooth batholith, Idaho.

Sommaire

La potassic-carpholite, dont la formule idéale serait $(K,\square)\ (Li,Mn^{2+})_2\ Al_4\ Si_4\ O_{12}\ (OH)_4\ (F,OH)_4$, est une nouvelle espèce minérale provenant du batholite de Sawtooth, pluton granitique anorogénique tertiaire près de Centerville, comté de Boise, en Idaho, aux Etats-Unis. Elle se présente en touffes irrégulières fibroradiées atteignant 2 mm dans les cavités miarolitiques du granite, associées à quartz, microcline, albite, béryl, topaze, bertrandite, hellandite, zinnwaldite, fluorite, hématite et apatite. Les cristaux individuels de potassic-carpholite sont blancs à jaune paille avec une rayure blanche et un éclat vitreux; ils sont non-fluorescents en lumière ultraviolette. Les cristaux sont généralement entre 20 et 40 μm de diamètre et environ 500 μm en longueur, sur [100]. La potassic-carpholite est cassante, avec une fracture irrégulière aux extrémités des cristaux aciculaires, et possède un clivage parfait parallèle à {010}. Il ne semble y avoir aucun clivage. La dureté de Mohs est ~5, et la densité est 3.08(2) (observée) et 3.06 g/cm^3 (calculée). La potassic-carpholite est biaxe négative, avec α 1.578, β 1.592, γ 1.598, tous ±0.002, 2*V*(obs.) = 57(2)°,

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2*V*(calc.) = 66°, faiblement pléochroïque, avec *X* jaune pâle, *Y* = *Z* incolore, et avec *X* > *Y*, *Z*, et *X* = *b*, *Y* = *a* et *Z* = *c*. La potassic-carpholite est orthorhombique, groupe spatial *Ccca*, *a* 13.715(5), *b* 20.302(7), *c* 5.138(3) Å, *V* 1430.6 $Å^3$, *Z* = 4. Les sept raies les plus intenses du spectre de diffraction X, méthode des poudres [*d* en Å(*I*)(*hkl*)] sont: 5.705(100)(220), 2.613(100)(351), 3.048(90)(331), 3.819(80)(221), 3.433(80)(400), 2.744(80)(421), 2.050(80)(621). Une analyse à la microsonde électronique a donné SiO_2 36.73, TiO_2 0.10, Al_2O_3 29.38, MnO 13.37, FeO 1.44, MgO 0.04, Na_2O 0.51, Li_2O(calc.) = 1.34, K_2O = 4.07, F 7.47, H_2O (calc.) 7.24, O≡F –3.14, somme 98.55% (poids), dans laquelle la quantité de H_2O a été calculée selon (8 – F) *apfu*. La formule empirique qui en résulte, sur une base de 20 anions, y inclus OH égal à 8 – F et Li égal à [2 – {Mn + Fe + Mg}] *apfu*, est $(K_{0.56}Na_{0.11}\square_{0.33})\ (Mn^{2+}{}_{1.26}Fe^{2+}{}_{0.13}Mg_{0.01}Li_{0.60})\ (Al_{3.85}Si_{0.08})\ Si_4\ O_{12}\ (OH)_4\ (F_{2.63}\{OH\}_{1.37})$. La potassic-carpholite, dont la composition du pôle est $K\ (Mn^{2+}Li)\ Al_4\ Si_4\ O_{12}\ (OH)_4\ F_4$, est structuralement semblable à la carpholite, $\square\ Mn^{2+}{}_2\ Al_4\ Si_4\ O_{12}\ (OH)_4\ F_4$, et lui est liée par la substitution $K + Li \rightarrow \square$ (lacune) + Mn^{2+}.

(Traduit par la Rédaction)

Mots-clés: potassic-carpholite, nouvelle espèce minérale, groupe de la carpholite, batholite de Sawtooth, Idaho.

INTRODUCTION

The chemical composition of minerals of the carpholite group can be written as $M_2Al_4Si_4O_{12}(OH)_8$, where *M* = Mn^{2+}, Fe^{2+}, Mg (Ghose *et al.* 1989). Carpholite (*M* = Mn^{2+}, Lindemann *et al.* 1979), ferrocarpholite (*M* = Fe^{2+}, MacGillavry *et al.* 1956) and magnesiocarpholite (*M* = Mg, Viswanathan 1981) are simple homovalent analogues in the carpholite group. However, alkali and alkaline-earth cations can also occur in the carpholite-type structure; for example, balipholite, $Ba\ Mg_2\ Li\ Al_3\ Si_4\ O_{12}\ (OH,F)_8$, has the carpholite structure (Peng *et al.* 1987). The structure of carpholite was solved and refined in the space group *Ccca*, with cell dimensions of $a \approx 13.7$, $b \approx 20.2$, $c \approx 5.1$ Å, but there is evidence in the literature (Mottana & Schreyer 1977, Ferraris *et al.* 1992, Fuchs *et al.* 2001) that the symmetry is lower than *Ccca*. Fuchs *et al.* (2001) reported refinements of two crystals of magnesiocarpholite; one crystal shows strict adherence to *Ccca* symmetry, and the other shows a few reflections that violate the *a*-glide plane (although they do not mention if they checked for double diffraction with regard to these specific reflections). What is clear is that the general topology and state of long-range order conform closely to *Ccca* symmetry.

There are many reports in the literature of K-bearing (and F-bearing) carpholite (Chaska *et al.* 1973, Marchenko & Goncharova 1981, Ghose *et al.* 1989), and inspection of the chemical data presented in these studies indicates that some of these samples deserve recognition as a distinct species within the carpholite group. Accordingly, the new mineral and mineral name (potassic-carpholite) were submitted to and approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA 2002–064). The name denotes the relation of this new species to carpholite: substitution of Li for Mn^{2+}, and substitution of K for $\square$ (vacancy) at the *A*(2) site (Ghose *et al.* 1989). The holotype specimen of potassic-carpholite is stored in the collection of the Canadian Museum of Nature, Ottawa, Ontario (catalogue number CMNMC 83920).

PARAGENESIS

Potassic-carpholite was found in a miarolitic cavity of the Sawtooth batholith near Centerville, Boise County, Idaho, U.S.A. The Sawtooth batholith is an anorogenic Tertiary granite pluton dated at 38–50 Ma by the K–Ar method (Menzies & Boggs 1993). The miarolitic cavities range in size from microscopic to (rarely) more than a meter in all dimensions. Potassic-carpholite is quite rare, having being reported only in two pockets; in the cavities, it is a late-stage mineral coating small crystals of microcline that occur with quartz, microcline, albite, beryl, topaz, bertrandite, hellandite, zinnwaldite, fluorite, hematite and apatite (Ghose *et al.* 1989).

PHYSICAL PROPERTIES

Potassic-carpholite consists of irregular tufts of radiating acicular-to-fibrous needles approximately 2 mm across. The crystals are white to straw yellow; the streak is white, the luster is silky, and crystals do not fluoresce in ultraviolet light. The needles are generally 20–40 μm across and approximately 500 μm long, elongate along [100], with perfect cleavage parallel to {010}. Twinning was not observed. The hardness is difficult to measure accurately because of the minute size of individual crystals, but is ~5 on the Mohs scale. The measured density (by flotation) is 3.08(2) g/cm^3; the calculated density is 3.06 g/cm^3. Optical properties were measured with a Bloss spindle stage for the wavelength 590 nm using a gel filter. The indices of refraction are α 1.578, β 1.592, γ 1.598, all ±0.002 [compatibility index = 0.012 (superior), Mandarino 1981]; 2*V*(obs.) = 57(2)° and 2*V*(calc.) = 66°, *X* = *b*, *Y* = *a*, *Z* = *c*. Pleochroism is weak, *X* pale yellow, *Y* and *Z* colorless, with *X* > *Y*, *Z*.

CHEMICAL COMPOSITION

The crystals were analyzed with a Cameca SX–50 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, and a beam diameter of 5 μm.

The following standards were used: diopside (Si), titanite (Ti), kyanite (Al), arfvedsonite (Fe), spessartine (Mn), forsterite (Mg), albite (Na), orthoclase (K), and a F-dominant analogue of riebeckite (F). Iron was assumed to be in the divalent state, as is the case in ferrocarpholite (Seifert 1979). Ghose *et al.* (1989) reported 1.19 wt.% Li_2O by atomic absorption (0.52 *apfu* Li) on a very inhomogeneous sample. We also calculated Li stoichiometrically as Li = [2 – Mn^{2+} + Fe^{2+} + Mg)] *apfu*. Table 1 gives the chemical composition and formula based on 20 anions *pfu* (per formula unit).

X-Ray Powder Diffraction

The powder-diffraction pattern was recorded with a Gandolfi camera using Cu*K*α X-radiation. Table 2 shows the indexed X-ray powder-diffraction data for potassic-carpholite, together with the refined unit-cell dimensions.

Discussion

The description of potassic-carpholite as a new species, together with the existence of balipholite, suggests that the formula of the carpholite-group minerals should be written more generally to incorporate these species. There are two issues with regard to the formula: (1) addition of two alkali sites (from the structure of potassic-carpholite presented by Ghose *et al.* 1989); (2) the occurrence of F as a dominant constituent at one of the two monovalent-anion sites in potassic-carpholite. Let us use the labels *A* and *B* for the occupants of the two high-coordination sites [$A \equiv A(1) = 8h$, $B \equiv A(2) = 4b$] in channels in the structure. The *B* cation is K in potassic-carpholite, and the *A* group is vacant in the end-member composition; Ghose *et al.* (1989) noted that the *A*(1) site (≡ *A*-group cation) can only be, at most, half-occupied because of steric constraints. Let us use the labels *V* and *W* for the two monovalent-anion sites in the carpholite structure; this is necessary as the occupancies of these two sites may be the same (as in most carpholite-group minerals) or different (as in potassic-carpholite, Ghose *et al.* 1989). Thus we write the formula of the carpholite-group minerals as

$$A_2\ B\ M_2\ Al_4\ Si_4\ O_{12}\ V_4\ W_4$$

where $A = \square \geq$ Na; $B = \square$, K, Ba; $M = Mn^{2+}, Fe^{2+}$, Mg, Li; V = (OH), F; W = (OH), F; all cations and anions listed are dominant in one or more of the constituent minerals, and are listed in the order carpholite, ferrocarpholite, magnesiocarpholite, potassic-carpholite, balipholite. For simplicity, we have assumed that there is no significant substitution for Al or Si in this structure; if such compositional variations were found, modifications to the above formula would be necessary.

Selected properties of the members of the carpholite group are listed in Table 4.

Potassic-carpholite is related to carpholite by the substitution $^{B}K + {}^{M}Li \leftrightarrow {}^{B}\square + {}^{M}Mn^{2+}$. There are many other compositions (see Ghose *et al.* 1989) that seem possible as potential minerals.

TABLE 1. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA* (*apfu*) OF POTASSIC-CARPHOLITE

	Mean	Range	Formula	
SiO_2	36.73	36.52–37.14	K	0.56
TiO_2	0.10	0.00–0.14	Na	0.11
Al_2O_3	29.38	29.08–29.54	□	0.33
FeO	1.44	1.27–1.69		1.00
MnO	13.37	12.01–14.63		
MgO	0.04	0.02–0.05	Mn^{2+}	1.26
Na_2O	0.51	0.36–0.71	Fe^{2+}	0.13
Li_2O	1.34	–	Mg	0.01
K_2O	4.07	3.28–5.19	Li	0.60
F	7.47	6.81–8.43		2.00
H_2O	7.24	–		
–O = F	–3.14		Si	4.08
TOTAL	98.53		Al	3.85
				7.93
			OH^-	4.00
			F^-	2.63
			OH^-	1.37
				4.00

*calculated on the basis of 20 anions, (OH) = (8 – F) *apfu*, Li = [2 – (Mn^{2+} + Fe^{2+} + Mg)] *apfu*.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR POTASSIC-CARPHOLITE

I_{est}	d_{obs}	d_{calc}	*h*	*k*	*l*	I_{est}	d_{obs}	d_{calc}	*h*	*k*	*l*
70	10.250	10.164	0	2	0	20	1.806	1.806	0	8	2
100	5.705	5.688	2	2	0	30	1.770	1.769	7	3	1
70	5.082	5.082	0	4	0	10	1.745	1.747	2	8	2
60	4.679	4.681	1	1	1	50	1.700	1.700	6	8	0
60	4.091	4.084	2	4	0	60	1.670	1.670	7	5	1
80	3.819	3.812	2	2	1	20	1.652	1.652	5	9	1
80	3.433	3.432	4	0	0	40	1.625	1.625	3	11	1
40	3.395	3.388	0	6	0	40	1.601	1.594	0	10	2
30	3.096	3.105	1	5	1	40	1.568	1.567	1	5	3
90	3.048	3.050	3	3	1	30	1.548	1.549	7	7	1
10	2.842	2.844	4	4	0	30	1.518	1.519	7	3	2
80	2.744	2.747	4	2	1	30	1.491	1.492	3	5	3
100	2.613	2.615	3	5	1	80	1.467	1.466	1	7	3
	"	2.615	2	6	1		"	1.469	5	11	1
30	2.505	2.505	1	1	2	80	1.452	1.452	0	14	0
40	2.411	2.411	4	6	0	60	1.424	1.423	7	9	1
40	2.368	2.365	1	3	2	50	1.385	1.385	2	12	2
10	2.290	2.292	0	4	2	60	1.372	1.372	10	0	0
30	2.225	2.226	3	1	2	10	1.358	1.360	10	2	0
70	2.165	2.162	2	8	1	30	1.329	1.329	1	13	2
80	2.050	2.047	6	2	1	50	1.308	1.307	6	10	2
10	1.933	1.933	6	4	1	10	1.288	1.288	9	3	2
70	1.859	1.860	5	7	1						

114.6 mm Debye–Scherrer powder camera with Gandolfi attachment; Cu radiation, Ni filter [λ(Cu*K*α) = 1.54178 Å].
Intensities estimated visually; not corrected for shrinkage and no internal standard.
Indexed with *a* 13.727(3), *b* = 20.329(6), *c* = 5.136(2) Å, *V* = 1433.1(5) $Å^3$

TABLE 3. COMPARISON OF THE PROPERTIES OF THE MINERALS OF THE CARPHOLITE GROUP

	Formula	*a* (Å)	*b* (Å)	*c* (Å)	Space group	*V* (Å³)	*D* (g/cm⁻³)	Cleavage	Hardness	Optics	Ref.
Carpholite	$\square Mn^{2+}{}_2Al_4Si_4O_{12}(OH)_4(OH)_4$	13.718	20.216	5.132	*Ccca*	1423.2	3.071	{010} perfect, {110} indistinct	5–5.5	Biaxial negative	(1)
Potassic-carpholite	$K(Mn^{2+},Li)_2Al_4Si_4O_{12}(OH)_4F_4$	13.715	20.302	5.138	*Ccca*	1430.6	3.08	{010} perfect	5	Biaxial negative	(2)
Ferrocarpholite	$\square(Fe^{2+},Mg)_2Al_4Si_4O_{12}(OH)_4(OH)_4$	13.77	20.18	5.11	*Ccca*	1420.0	3.04	{010} perfect, {110} indistinct	5.5	Biaxial negative	(3)
Magnesiocarpholite	$\square(Mg,Fe^{2+})_2Al_4Si_4O_{12}(OH)_4(OH)_4$	13.694	20.204	5.108	*Ccca*	1413.2	2.82	–	–	Biaxial negative	(4)
Balipholite	$BaMg_2(LiAl_3)(Si_4O_{12})(OH)_4(OH)_4$	13.60	20.24	5.16	*Ccca*	1420.4	3.33–3.35	{010} perfect, {110} distinct	–	Biaxial negative	(5)

(1) Naumova *et al.* (1975); (2) Ghose *et al.* (1989), this study; (3) MacGillavry *et al.* (1956), De Roever (1951); (4) Viswanathan & Seidel (1979), Fuchs *et al.* (2001); (5) Zhizhong *et al.* (1987),Chao (1976)

TABLE 4. POSSIBLE END-MEMBER COMPOSITIONS OF MINERALS OF THE CARPHOLITE GROUP

	A_2	B_2	*M*	*M*	Al_4	T_4	$(OH)_4$	W_4
carpholite	□	□	Mn	Mn	Al	Si	OH	OH
magnesiocarpholite	□	□	Mg	Mg	Al	Si	OH	OH
ferrocarpholite	□	□	Fe	Mg	Al	Si	OH	OH
balipholite	□	Ba	Mg	Li	Al	Si	OH	OH
potassic-carpholite	□	K	Mn	Li	Al	Si	OH	F

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