

Capranicaite, $(K, \square)(Ca, Na)Al_4B_4Si_2O_{18}$: a new inosilicate from Capranica, Italy, with a peculiar topology of the periodic single chain $[Si_2O_6]$

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ABSTRACT

Capranicaite, ideally $(K, \square)(Ca, Na)Al_4B_4Si_2O_{18}$, is a new inosilicate mineral from the Vico volcanic complex collected at Capranica, Viterbo Province, Latium, Italy. It occurs in miarolitic cavities of a feldspathoid-bearing syenite ejectum and formed by late-stage metasomatic processes related to the activity of the Vico volcano.

Capranicaite occurs as thin, tabular crystals no larger than 0.1 mm. Crystals are colourless, with a white streak and a vitreous lustre; they are brittle and their Mohs hardness is certainly <6. Capranicaite is non-fluorescent with good {001} cleavage and no observable parting. The calculated density is 2.41 g/cm³. Crystals are biaxial negative, non pleochroic, with $\alpha = 1.495(1)$, $\beta = 1.543(1)$, $\gamma = 1.544(1)$, $2V_{\text{obs}} = 7.3(2)^\circ$, $2V_{\text{calc}} = 16.0^\circ$.

Capranicaite is monoclinic $P2_1/n$, with $a = 4.8507(2)$, $b = 16.6156(6)$, $c = 20.5445(7)$ Å, $\beta = 90.245(1)^\circ$, $V = 1655.82(17)$ Å³, $Z = 4$. The strongest six X-ray diffraction lines in the simulated powder pattern are [d in Å (hkl):] 3.234 (10) (124; 044), 4.104 (9) ($\bar{1}21$; 121), 3.424 (8) (006), 2.184 (4) (048; $\bar{1}64$), 2.405 (4) (160), 2.425 (3) (200). EMP-WDS analysis gives: SiO₂ 20.70, Al₂O₃ 32.91, B₂O₃ 22.90, K₂O 5.36, CaO 11.04, Na₂O 4.08, Cs₂O 2.20, sum 99.19%; the formula, based on 18 oxygens, is: $(K_{0.69}Cs_{0.10})_{\Sigma 0.79}(Ca_{1.19}Na_{0.80})_{\Sigma 1.99}Al_{3.91}B_{3.99}Si_{2.09}O_{18}$, corresponding to the ideal formula: $(K, \square)(Ca, Na)Al_4B_4Si_2O_{18}$. The crystal structure shows three overlapping layers of polyhedra parallel to (001): (1) the A layer contains periodic single chains formed by Si_2O_6 units with a topology not previously observed; (2) the B layer contains isolated AlO_4 tetrahedra and BO_3 triangles forming a sheet of six-fold rings (3Al + 3B); (3) the C layer contains two octahedral sites: $M(1)$ and $M(2)$, with a mixed (Ca, Na) population. Two B layers and an intermediate A layer are vertex-connected to form a bi-dimensional B-A-B network characterized by large channels not completely populated and accommodating K and minor Cs. Along c from the origin the following layer sequence results: C-[B-A-B]-C-[B-A-B]-C.

KEYWORDS: New mineral, capranicaite, borosilicate, crystal structure, inosilicate.

Introduction

THE Vico volcano complex (Viterbo province, Italy), together with the other latial volcanic complexes (Vulsini, Sabatini and Alban Hills,

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from north to south), is part of the so-called ‘Roman Comagmatic Province’ (Washington, 1906). It is a composite volcano with a summit caldera now occupied by a lake (Lago di Vico). Its evolution can be distinguished in three main phases: (1) a first phase, spanning from 0.8–0.4 m.y. (Sollevanti, 1983), characterized by the emission of predominantly leucitic tephrite to trachyphonolite lavas; (2) an explosive phase during which four pyroclastic units (ignimbrites A to D: Locardi, 1965) were emplaced, lasting up to 0.2 m.y.; and (3) a final explosive phase associated with the caldera collapse occurring ~95,000 y ago (Laurenzi and Villa, 1985).

Among several accessory phases of the syenitic ejecta locally named ‘sanidiniti’, new mineral species were found: vicanite-(Ce) (Maras *et al.*, 1995; Ballirano *et al.*, 2002), peprossiite-(Ce) (Della Ventura *et al.*, 1993; Callegari *et al.*, 2000), stoppaniite (Ferraris *et al.*, 1998; Della Ventura *et al.*, 2000) and piergorite-(Ce) (Boiocchi *et al.*, 2006). Furthermore, some REE-rich hellandite species from these ejecta were studied to clarify the crystal chemical properties of hellandite-type minerals; i.e. hellandite-(Ce) (Oberti *et al.*, 1999, 2002) and ciprianiite (Della Ventura *et al.*, 2002). Other interesting or rare minerals were found and include stillwellite-(Ce) (Callegari *et al.*, 1992; Burns *et al.*, 1993), baddeleyite (Bellatreccia *et al.*, 1998), zirconolite (Bellatreccia *et al.*, 2002), oxycalciobetafite (Caprilli *et al.*, 2006), scheelite and ferberite (Bellatreccia *et al.*, 1999).

A feldspathoid-bearing syenite block collected recently showed the presence of miarolitic cavities containing a few small prismatic crystals similar to the K-feldspar forming the majority of the rock. However, the tabular habit of these crystals attracted attention and suggested further examination. The tabular crystals are the new mineral species described here. The mineral and the name (from the type locality Capranica, Latium, Italy) have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2009-086). Holotype material has been deposited at the Mineralogical Museum of Rome University “La Sapienza”, specimen number MMUR 33036/1.

Occurrence

Capranicaite occurs in miarolitic cavities of a holocrystalline volcanic ejectum enclosed in a pyroclastic deposit (ignimbrite “C”, Locardi,

1965) at Capranica, Viterbo Province, Latium, Italy. The host rock is a feldspathoid-bearing syenite with the groundmass made up of interlocking K-feldspar with minor plagioclase. Other minerals in the host syenite are: andradite, calcic amphibole (hornblende), brown mica (biotite), Fe oxide (magnetite), feldspathoids (of the sodalite-haüyne series) and an as-yet undefined B-Be-Si phase (in the vugs). Titanite, apatite and zircon are accessory phases.

Capranicaite is a B- and Cs-bearing mineral; the paragenesis and relationship between the minerals forming the syenite-containing capranicaite are typical of the Vico volcanic complex and suggest that the syenite formed by late-stage metasomatic processes. In fact, circulation of fluids rich in incompatible and light elements has been assumed to be the reason for metasomatic processes forming many other B- and Cs-bearing minerals (Scherillo, 1940; Della Ventura *et al.*, 2004; Bellatreccia *et al.*, 2006, and references therein) in the volcanic rocks belonging to the Roman Comagmatic Province, which are characterized by very large Cs and B contents (Vasselli and Conticelli, 1990).

Physical and optical properties

Capranicaite occurs as colourless thin tabular crystals with a vitreous lustre and a maximum dimension of no more than 0.1 mm (Fig.1). It has

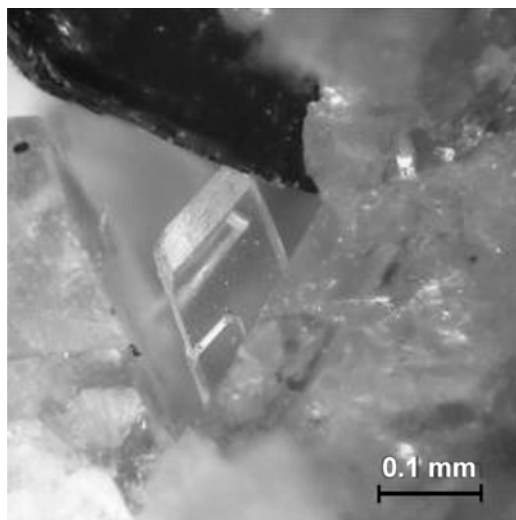


FIG. 1. Tabular crystal of capranicaite in a miarolitic cavity from Capranica (photo: L. Mattei).

a white streak and shows no fluorescence under long-wave or short-wave ultraviolet light. Crystals have good {001} cleavage and a splintery fracture. The hardness could not be measured because of the brittle character and the small size of the crystals. However, it should be less than that of sanidine (<6 on the Mohs scale). The calculated density is 2.41 g/cm³.

The optical data have been measured by means of a micro-refractometer spindle stage using the Lambda-T-variation method after Emmons. The apparatus and procedure were described in detail by Medenbach (1985).

Capranicaite is biaxial negative with indices of refraction $\alpha = 1.495(1)$, $\beta = 1.543(1)$, $\gamma = 1.544(1)$ (for $\lambda = 590$ nm); $2V_{\text{meas}} = 7.3(2)^\circ$, $2V_{\text{calc}} = 16.0^\circ$. Optical orientation is: $\alpha \sim || c$, $\beta \sim || a$, $\gamma || b$ (pseudo-orthorhombic) and the optical plane is (100). Crystals are transparent and vitreous, without dispersion effects or pleochroism.

Chemical composition

Chemical analyses were undertaken using an electron microprobe analyser operating in wavelength-dispersive spectroscopy mode. A serial analysis approach was adopted because of the great difference in atomic number between the boron and other elements; for the former an acceleration voltage of 10 kV and a beam current of 90 nA were used, whereas 15 kV and 9 nA were used for the latter elements (Si, Al, K, Ca, Na, Cs). A probe diameter of 5 μm was used for all the measured elements. The B-K α line was selected with the LDEB crystal and accurately

TABLE 1. Chemical composition (wt.%) and unit formula (a.p.f.u.) for capranicaite on the basis of 18 O.

	Wt. %	Range		a.p.f.u.
SiO ₂	20.70(55)	20.04–21.20	Si	2.09
Al ₂ O ₃	32.91(22)	32.65–33.16	Al	3.91
B ₂ O ₃	22.90(38)	22.54–23.15	B	3.99
K ₂ O	5.36(12)	5.19–5.47		
CaO	11.04(23)	10.81–11.35	Ca	1.19
Na ₂ O	4.08(6)	4.04–4.17	Na	0.80
Cs ₂ O	2.20(53)	1.89–2.98		
Total	99.19		K	0.69
			Cs	0.10

measured for 20 and 10 s, respectively, at the peak and the background position using a gas flow proportional counter. The following primary standards were used: Si, Al, Na – jadeite; K – orthoclase; Ca – wollastonite; Cs – Cs-glass; and B – danburite. Data reduction was undertaken using the ZAF correction method.

The average of four analyses performed on a single grain is given in Table 1. The empirical formula (based on 18 O atoms) is: (K_{0.69}Cs_{0.10}) Σ 0.79(Ca_{1.19}Na_{0.80}) Σ 1.99Al_{3.91}B_{3.99}Si_{2.09}O₁₈. The simplified formula is (K,□)(Ca,Na)Al₄B₄Si₂O₁₈, which corresponds to K₂O 7.88, Na₂O 5.19, CaO 9.39, B₂O₃ 23.30, Al₂O₃ 34.13, SiO₂ 20.11, total 100.00 wt.%.

A Gladstone-Dale calculation gives a compatibility index of –0.059 which is regarded as good (Mandarino, 1981).

FTIR spectroscopy

The single-crystal FTIR spectrum was acquired at the Dipartimento di Scienze Geologiche, Università Roma Tre, with a NicPlan FTIR-microscope equipped with a KBr beamsplitter and an MCT-A nitrogen-cooled detector. Nominal resolution was 4 cm^{–1} and final spectra were the average of 128 scans on both sample and background.

The single-crystal FTIR spectrum (Fig. 2) shows a group of absorptions from 2289 to 2640 cm^{–1} that can be assigned to the overtone of the anti-symmetric stretching (ν_3) vibrations of the BO₃ triangular groups (Grew and

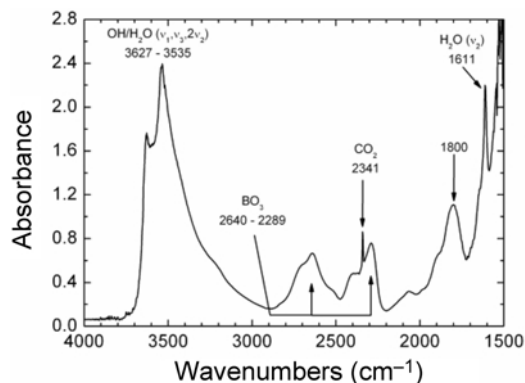


FIG. 2. Single-crystal, unpolarized light FTIR spectrum of capranicaite (thickness ~ 70 μm ; beyond 1500 cm^{–1} the spectrum acquired is completely saturated); see the text for assignment of the absorptions at 1800 cm^{–1}.

Rossman, 1985; Bellatreccia *et al.*, 2005). The broad multi-component absorption from 3627 to 3535 cm^{-1} is due to the stretching modes (ν_1 and ν_3) and the first bending overtone ($2\nu_2$) of the $\text{H}_2\text{O}/\text{OH}$ molecule(s); the absorption at 1611 cm^{-1} is due to the bending mode (ν_2) of H_2O . There is also a small but sharp band at 2341 cm^{-1} assigned to CO_2 molecules ensconced within the mineral structure. The unpolarized spectrum in Fig. 2 does not provide quantitative data; note however that due to the relatively large thickness ($\sim 70 \mu\text{m}$) of the measured crystal, the amount of $\text{H}_2\text{O}/\text{OH}$ and CO_2 should be in the order of hundreds of ppm. Finally, the absorption at 1800 cm^{-1} can be tentatively assigned to the first overtone or combination modes of the $T\text{--O}$ bonds or to the first overtone of the symmetric stretching mode (ν_1) of the BO_3 groups (Ross, 1974).

Single-crystal X-ray diffraction study

Experimental procedures

A platy single crystal was selected for data collection and structure refinement based on optical and diffraction properties. Intensity data were collected on a Bruker AXS three-circle diffractometer equipped with the Smart-Apex CCD detector. Omega rotation frames were processed by the *SAINTE* software (Bruker, 2003) and intensity data were corrected for background, Lorentz and polarization effects. Absorption effects were evaluated by an empirical method (*SADABS*; Sheldrick, 1996) and the absorption correction was applied to the data. Details of the single-crystal diffraction study are reported in Table 2.

Systematic absences were compatible with the $P2_1/n$ space group, and the crystal structure was

TABLE 2. Crystal data for capranicaite.

Crystal size (mm)	0.150 × 0.110 × 0.050
a (Å)	4.8507(2)
b (Å)	16.6156(6)
c (Å)	20.5445(7)
β (°)	90.245(1)
V (Å ³)	1655.82(17)
Z	4
Space group	$P2_1/n$
Detector type	CCD detector
Wavelength Mo- $K\alpha$ (Å)	0.71073
μ Mo- $K\alpha$ (cm^{-1})	12.8
Sample-to-detector distance (mm)	60
Scan mode	ω
Scan width (°)	0.3
Acquisition time (s)	30
No. collected F	14595
No. unique F	4861
No. Obs. F ($I/\sigma(I) \geq 3$)	3399
2θ range (°)	2–60
h range	–6 → 6
k range	–21 → 23
l range	–22 → 28
Completeness (%)	99.9
Mean redundancy	4.03
$F(000)$	1176.7
Largest diff. peak/hole ($\text{e} \text{ \AA}^{-3}$)	1.49/–0.86
No. parameters refined	312
R_{sym} (%)	0.024
R_{obs} (%)	0.050
R_{all} (%)	0.065

CAPRANICAITE, A NEW INOSILICATE

TABLE 3. Fractional atom coordinates, refined site-scattering values (s.s., e.p.f.u.) and site populations (a.p.f.u.), and equivalent isotropic displacement parameters $U_{\text{eq}} \times 10^4 \text{ \AA}^2$; $U_{ij} \times 10^4$ in capranicaite. The atom-displacement parameter is of the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$ (estimated standard deviations in parentheses).

Atom	s.s., e.p.f.u.	x/a	y/b	z/c	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)		0.8024(2)	0.8570(1)	0.2496(1)	160(3)	155(6)	198(6)	126(4)	-27(4)	7(5)	0(5)
Si(2)		0.1980(2)	0.4693(1)	0.2506(1)	151(3)	135(5)	187(6)	129(4)	-15(4)	2(5)	0(5)
Al(1)		0.2517(2)	0.5357(1)	0.3947(1)	99(4)	83(5)	100(7)	115(6)	-1(4)	2(4)	-2(5)
Al(2)		0.2483(2)	0.5357(1)	0.1058(1)	99(4)	80(5)	101(7)	116(6)	-2(4)	1(4)	5(5)
Al(3)		0.7544(2)	0.7945(1)	0.1044(1)	107(4)	116(5)	83(7)	122(6)	-3(4)	5(4)	-3(5)
Al(4)		0.7456(2)	0.7951(1)	0.3954(1)	106(4)	115(5)	83(7)	118(6)	-7(4)	10(4)	3(5)
B(1)		0.2542(9)	0.7072(3)	0.0809(3)	155(14)	67(18)	57(24)	343(30)	-3(15)	2(17)	-11(21)
B(2)		0.2457(9)	0.7074(3)	0.4186(3)	166(15)	51(18)	40(22)	408(34)	12(14)	3(18)	0(21)
B(3)		0.7489(9)	0.4582(3)	0.4295(2)	105(13)	107(18)	111(27)	97(21)	6(15)	2(14)	-8(17)
B(4)		-0.2496(9)	0.4584(3)	0.0703(2)	116(13)	102(19)	103(27)	142(21)	-1(15)	3(15)	4(19)
M(1)	16.40(4)	0.7377(2)	0.6289(1)	0.0037(1)	138(3)	140(5)	131(6)	144(4)	0(4)	2(4)	-1(3)
M(2)	16.49(4)	0.2395(2)	0.3706(1)	0.5038(1)	134(3)	134(5)	125(6)	142(4)	1(4)	-1(4)	-1(3)
A	17.29(5)	0.7125(4)	0.6337(1)	0.2500(2)	600(7)	587(11)	243(7)	970(15)	-56(7)	76(10)	15(10)
O(1)		0.6193(7)	0.9387(2)	0.2484(2)	304(12)	136(16)	288(21)	487(26)	7(13)	11(15)	16(19)
O(2)		1.1196(7)	0.8883(2)	0.2496(2)	309(12)	148(16)	249(20)	529(26)	-20(13)	12(16)	7(19)
O(3)		0.7474(8)	0.8015(3)	0.1873(2)	285(13)	396(21)	323(27)	135(19)	-67(16)	-5(19)	-32(17)
O(4)		0.7459(8)	0.8033(3)	0.3126(2)	290(13)	361(21)	359(28)	149(19)	-67(17)	5(14)	38(17)
O(5)		0.2490(8)	0.5250(3)	0.1883(2)	284(13)	396(22)	322(27)	135(17)	-49(16)	-2(14)	51(16)
O(6)		0.2570(8)	0.5256(3)	0.3121(2)	289(13)	392(22)	343(27)	132(17)	-82(17)	12(14)	-31(17)
O(7)		0.5277(6)	0.7173(2)	0.4212(2)	166(10)	99(14)	113(18)	286(19)	-8(11)	-1(12)	40(14)
O(8)		0.4265(6)	0.7727(2)	0.0724(2)	164(10)	128(14)	118(18)	245(19)	-31(11)	-22(12)	45(14)
O(9)		0.9724(6)	0.7173(2)	0.0774(2)	169(10)	104(14)	105(18)	298(19)	8(11)	-6(12)	-34(14)
O(10)		1.0730(6)	0.7729(2)	0.4273(2)	172(10)	130(14)	127(18)	257(19)	32(11)	-15(12)	-46(14)
O(11)		0.0314(6)	0.4656(2)	0.4312(2)	144(11)	95(13)	113(17)	223(17)	0(11)	6(11)	33(14)
O(12)		-0.0836(6)	0.5250(2)	0.0727(2)	154(10)	107(13)	100(17)	256(19)	-17(11)	-35(12)	25(14)
O(13)		0.4690(6)	0.4660(2)	0.0690(2)	155(10)	90(13)	123(18)	252(17)	5(11)	0(11)	-39(14)
O(14)		0.5844(6)	0.5251(2)	0.4275(2)	160(10)	102(13)	119(18)	259(19)	15(11)	-26(12)	-18(14)
O(15)		0.6346(6)	0.8830(2)	0.4346(2)	169(10)	137(14)	94(17)	276(19)	-16(11)	59(12)	-23(14)
O(16)		0.8666(6)	0.8830(2)	0.0662(2)	162(10)	144(14)	83(17)	259(19)	18(11)	51(12)	15(14)
O(17)		0.1332(6)	0.6311(2)	0.4179(2)	172(10)	115(13)	93(18)	310(19)	-13(11)	25(12)	-10(14)
O(18)		0.3680(6)	0.6313(2)	0.0836(2)	180(10)	115(13)	111(18)	313(21)	4(11)	23(12)	17(14)

Refined site populations: $M(1) = 0.60 \text{ Ca} + 0.40 \text{ Na}$; $M(2) = 0.61 \text{ Ca} + 0.39 \text{ Na}$; $A = 0.72 \text{ K} + 0.07 \text{ Cs}$

TABLE 4. Selected interatomic distances (Å) in capranicaite.

Si(1)–O(1) ¹	1.623(4)	Si(2)–O(1) ¹¹	1.621(4)	Al(1)–O(6) ¹	1.707(4)	Al(2)–O(5) ¹	1.704(4)
Si(1)–O(2) ¹	1.624(4)	Si(2)–O(2) ¹²	1.610(4)	Al(1)–O(11) ¹	1.750(4)	Al(2)–O(12) ¹	1.754(4)
Si(1)–O(3) ¹	1.598(4)	Si(2)–O(5) ¹	1.598(4)	Al(1)–O(14) ¹	1.755(3)	Al(2)–O(13) ¹	1.751(4)
Si(1)–O(4) ¹	1.597(4)	Si(2)–O(6) ¹	1.598(4)	Al(1)–O(17) ¹	1.753(3)	Al(2)–O(18) ¹	1.753(4)
<Si(1)–O>	1.611	<Si(2)–O>	1.607	<Al(1)–O>	1.741	<Al(2)–O>	1.741
Al(3)–O(3) ¹	1.707(4)	Al(4)–O(4) ¹	1.706(4)	B(1)–O(8) ¹	1.385(5)	B(2)–O(7) ¹	1.379(5)
Al(3)–O(8) ¹	1.756(4)	Al(4)–O(7) ¹	1.754(3)	B(1)–O(9) ⁵	1.378(5)	B(2)–O(10) ⁵	1.385(5)
Al(3)–O(9) ¹	1.755(3)	Al(4)–O(10) ¹	1.755(4)	B(1)–O(18) ¹	1.377(6)	B(2)–O(17) ¹	1.381(6)
Al(3)–O(16) ¹	1.754(3)	Al(4)–O(15) ¹	1.754(4)	<B(1)–O>	1.380	<B(2)–O>	1.381
<Al(4)–O>	1.743	<Al(4)–O>	1.742				
B(3)–O(11) ⁴	1.376(5)	M(1)–O(9) ¹	2.393(3)	M(2)–O(7) ¹⁰	2.401	A–O(1) ¹²	3.340(4)
B(3)–O(14) ¹	1.368(6)	M(1)–O(10) ¹³	2.400(3)	M(2)–O(8) ¹¹	2.395	A–O(3) ¹	3.077(4)
B(3)–O(16) ¹²	1.374(6)	M(1)–O(12) ⁴	2.393(3)	M(2)–O(11) ¹	2.393	A–O(4) ¹	3.102(4)
<B(3)–O>	1.372	M(1)–O(13) ⁶	2.390(3)	M(2)–O(14) ¹⁰	2.391	A–O(5) ¹	3.146(4)
		M(1)–O(15) ¹⁴	2.405(3)	M(2)–O(16) ¹²	2.405	A–O(5') ⁴	3.415(4)
B(4)–O(12) ¹	1.369(6)	M(1)–O(18) ¹	2.436(3)	M(2)–O(17) ⁹	2.424	A–O(6) ¹	3.124(4)
B(4)–O(13) ⁵	1.371(5)	<M(1)–O>	2.403	<M(2)–O>	2.402	A–O(6') ⁴	3.435(4)
B(4)–O(15) ¹¹	1.376(6)					<A–O>	3.235
<B(4)–O>	1.372						

Symmetry codes: ¹ x, y, z ; ² $-x+1/2, y+1/2, -z+1/2$; ³ $-x+3/2, y+1/2, -z+1/2$; ⁴ $x+1, y, z$; ⁵ $x-1, y, z$; ⁶ $-x+1, -y+1, -z$; ⁷ $x-1/2, -y+3/2, z+1/2$; ⁸ $x+1/2, -y+3/2, z+1/2$; ⁹ $-x, -y+1, -z+1$; ¹⁰ $-x+1, -y+1, -z+1$; ¹¹ $-x+1/2, y-1/2, -z+1/2$; ¹² $-x+3/2, y-1/2, -z+1/2$; ¹³ $x-1/2, -y+3/2, z-1/2$; ¹⁴ $x+1/2, -y+3/2, z-1/2$

solved by direct methods (*SIR97*; Altomare *et al.*, 1999).

Reflections with $I_o > 3\sigma(I_o)$ were considered as observed during an un-weighted full-matrix least-squares refinement on F undertaken using a locally modified version of the *ORFLS* program (Busing *et al.*, 1962). Scattering curves for fully ionized scattering species were used at sites where chemical substitutions occur [$M(1)$, $M(2)$, A]; neutral vs. ionized scattering curves were used at the tetrahedral sites [Si(1), Si(2), Al(1), Al(2), Al(3), Al(4)] and anion sites, whereas neutral scattering curves were used at B sites [B(1), B(2), B(3), B(4)].

Atomic coordinates and anisotropic displacement parameters are listed in Table 3; selected bond distances and bond angles in Table 4. Observed and calculated structure factors (Table 5) have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat.html.

Sufficient material to collect a powder diffraction pattern was not available. Complete powder X-ray diffraction (XRD) data (Table 6) were

simulated (for Cu-K α X-radiation) combining the integrated intensities from a single-crystal diffraction study at the proper 2θ values, taking multiplicities and Lp factors into account (*XPREP* software, Bruker-AXS Inc.).

Crystal structure

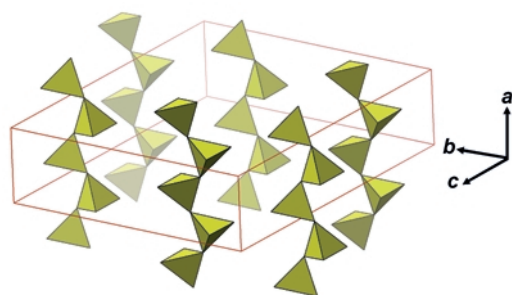
The crystal structure of capranicaite is characterized by three distinct layers overlapping along c : the first layer contains the SiO₄ tetrahedral chains and has been labelled the A layer; the second layer contains BO₃ triangles and AlO₄ tetrahedra and has been labelled the B layer; the third layer contains mixed (Ca,Na)O₆ octahedra and has been labelled the C layer.

The A layer consists of two independent Si tetrahedral sites, Si(1) and Si(2), forming periodic single chains with composition Si₂O₆ extending along a (Fig. 3). The refined bond lengths and bond angles indicate that the tetrahedra are fairly regular and are occupied solely by Si. Even though the repeating unit of the single chains is the same as for pyroxenes, the topology of the tetrahedral couples in capranicaite is quite

CAPRANICAITE, A NEW INOSILICATE

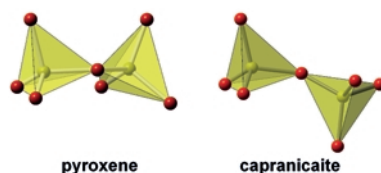
TABLE 6. Complete powder XRD pattern (the intensities of the 10 strongest lines are marked in bold).

<i>I</i>	<i>d</i> _{calc}	<i>hkl</i>	<i>I</i>	<i>d</i> _{calc}	<i>hkl</i>
5.4	8.308	0 2 0	2.1	2.297	0 6 5
14.7	7.702	0 2 1	38.3	2.184	0 4 8
7.0	6.460	0 2 2			1̄ 6 4
8.4	5.284	0 2 3	9.9	2.083	2̄ 4 1
4.6	5.136	0 0 4			2 4 1
3.0	4.723	1̄ 0 1	5.9	2.067	0 8 1
		1 0 1	9.6	2.053	2̄ 4 2
5.7	4.368	0 2 4			2 4 2
14.8	4.187	1 2 0	4.1	2.036	0 8 2
90.1	4.104	1̄ 2 1	7.9	2.001	2 4 3
		1 2 1			0 4 9
3.3	3.955	1 0 3	5.9	1.988	0 8 3
4.8	3.878	1̄ 2 2	7.8	1.966	1 6 6
		1 2 2	11.2	1.938	2̄ 4 4
4.3	3.682	0 2 5			2 4 4
4.8	3.650	1 3 0	8.3	1.926	0 8 4
7.6	3.552	0 4 3	4.7	1.852	0 8 5
82.8	3.424	0 0 6			1̄ 4 9
100.0	3.234	1 2 4	2.4	1.841	0 4 10
		0 4 4	4.5	1.824	2 6 0
32.2	3.119	1̄ 4 1			0 2 11
		1 4 1	1.8	1.791	1̄ 8 4
4.8	3.016	1̄ 4 2	17.4	1.758	2 0 8
		1 4 2			1̄ 6 8
4.8	2.973	1̄ 3 4	2.8	1.731	1̄ 8 5
		1 3 4			1 8 5
22.6	2.922	0 4 5	13.2	1.711	0 0 12
10.0	2.867	1̄ 4 3	12.1	1.704	1 2 11
		1 4 3			0 4 11
5.1	2.769	0 6 0	1.2	1.670	2̄ 6 5
2.7	2.745	0 6 1	1.0	1.656	0 10 1
2.1	2.717	1̄ 5 1	1.2	1.647	2̄ 7 3
		1 5 1			2 7 3
24.3	2.647	1 2 6	0.9	1.626	2̄ 4 8
1.5	2.567	0 6 3	1.5	1.614	0 8 8
1.6	2.544	1 5 3	1.4	1.606	1 4 11
9.0	2.500	1̄ 4 5	9.5	1.582	3̄ 2 1
		1 4 5	29.5	1.564	2 0 10
30.5	2.425	2 0 0			1̄ 6 10
36.8	2.405	1 6 0	8.5	1.536	2 8 3
17.4	2.358	2 0 2			
25.0	2.342	1̄ 6 2			
		1 6 2			

FIG. 3. The A layer formed by chains with periodicity of two Si tetrahedra extending along *a*.

independent B sites: B(1), B(2), B(3) and B(4). These atom sites define isolated AlO_4 tetrahedra and isolated BO_3 triangles connected to form a sheet of six-fold rings ($3\text{Al} + 3\text{B}$; Fig. 5) normal to *c*. The AlO_4 and BO_3 geometrical features are consistent with pure Al- and B-populated polyhedra. Each AlO_4 tetrahedron has three basal oxygens connected to three coplanar BO_3 triangles and an apical O vertex shared with a SiO_4 tetrahedron of an adjacent A layer (Fig. 6). Each SiO_4 tetrahedron shares the two O vertices not involved in the Si_2O_6 structural units with two AlO_4 tetrahedra belonging to two different B layers. The result is a single A layer ‘sandwiched’ between two B layers. This two-dimensional B-A-B network contains seven-fold cavities (*A* sites) incompletely occupied by K and minor Cs (Fig. 6). The small amount of water and CO_2 molecules detected by FTIR could be also located in these cavities.

The C layer consists of two independent atom sites [*M*(1) and *M*(2)] defining isolated octahedra. Direct occupancy refinement suggests that these sites have a mixed (Ca, Na) population. Sharing of all the octahedral vertices with polyhedra belonging to two different B layers allows interconnections among B-A-B two-dimensional networks. Along *c*, the complete sequence of layers results: C-B-A-B-C-B-A-B-C (Fig. 7).

FIG. 4. The topology of the Si_2O_6 unit in pyroxene (left) and capranicaite (right).

peculiar. In fact, in capranicaite the two tetrahedra are significantly kinked around the common O vertex. A comparison between the Si_2O_6 motif in pyroxenes and in capranicaite is shown in Fig. 4.

The B layer is made up of four independent Al sites: Al(1), Al(2), Al(3) and Al(4) and by four

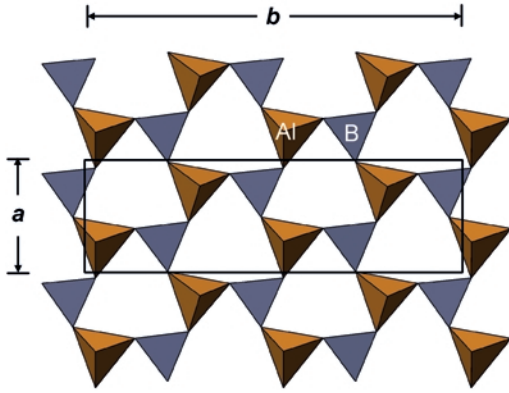


FIG. 5. Projection of the B layer down c showing the six-membered rings formed by 3 Al tetrahedra and 3 B tetrahedra.

Final considerations

The structure refinement of capranicaite allows us to define the crystal-chemical formula of this new mineral: ${}^{[A]}(K_{0.72}Cs_{0.07}\square_{0.21})_{\Sigma=1}{}^{[M1, M2]}(Ca_{1.21}Na_{0.79})_{\Sigma=2}Al_4B_4Si_2O_{18}$. Capranicaite can be placed in the Nickel and Strunz class 09 (silicates), 09.DB (inosilicates with 2-periodic single chains, Si_2O_6 ; pyroxene-related minerals), or in the Dana class 65

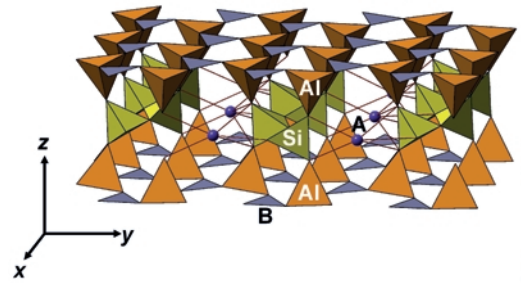


FIG. 6. Sketch of the B-A-B two-dimensional network containing seven-fold coordinated A sites (large sphere). In capranicaite this site hosts alkali species (K and Cs).

(inosilicates), 65.01 (inosilicate single-width unbranched chains, $W = 1$ with chains $P = 2$). However, the crystal structure shows no similarities with other minerals in these groups.

The crystal-chemical study strongly suggests that capranicaite occurs with mixed (Ca, Na)-populated octahedra and with incompletely filled A cavities and this is supported by the bond-valence analysis. In particular, the charge at $M(1)$ and $M(2)$ octahedral sites (1.63 and 1.64 v.u.) is consistent with the value expected from the assigned atom-site population (Table 7). Interestingly, the bond-valence analysis suggests

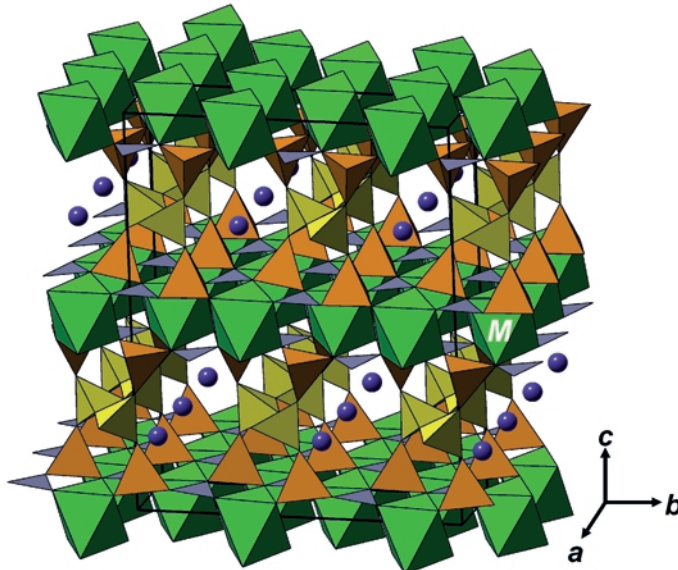


FIG. 7. Simplified sketch of the capranicaite crystal structure. The B-A-B two-dimensional network that contains the A cavities is connected *via* isolated (Ca, Na) octahedra defining the C layer.

CAPRANICAITE, A NEW INOSILICATE

TABLE 7. Bond valence analysis (v.u.) of capranicaite.

Site	Si(1)	Si(2)	Al(1)	Al(2)	Al(3)	Al(4)	B(1)	B(2)	B(3)	B(4)	M(1)	M(2)	A	Total
Atom type	Si	Si	Al	Al	Al	Al	B	B	B	B	Ca _{0.60} Na _{0.40}	Ca _{0.61} Na _{0.39}	K _{0.72} Cs _{0.07}	
Site charge ¹	4	4	3	3	3	3	3	3	3	3	1.60	1.61	0.79	
O(1)	1.00	1.00											0.04	2.04
O(2)	1.00	1.04											0.08	2.04
O(3)	1.07				0.86								0.04	2.01
O(4)	1.07				0.86								0.03	1.97
O(5)		1.07		0.86									0.06	}2.02
O(5) ¹		1.07		0.86									0.03	
O(6)													0.03	}2.03
O(6) ¹													0.07	
O(7)						0.76		0.98				0.27		2.01
O(8)					0.75		0.96					0.28		1.99
O(9)					0.75		0.98				0.28			2.01
O(10)						0.75		0.96			0.27			1.98
O(11)			0.76						0.99			0.28		2.03
O(12)				0.75						1.00	0.28			2.03
O(13)				0.76						1.00	0.28			2.04
O(14)									1.00			0.28		2.03
O(15)			0.75			0.76				0.99	0.27			2.02
O(16)					0.76				0.99			0.27		2.02
O(17)			0.76				0.98	0.97			0.25	0.26		1.99
O(18)							2.92	2.91	2.98	2.99	1.63	1.64	0.35	1.99
Total	4.14	4.18	3.13	3.13	3.12	3.13	2.92	2.91	2.98	2.99	1.63	1.64	0.35	1.99

Note: The valence of each site takes account of the contribution of different atom species; bond valence calculated after Brown and Altermatt (1985) with the parameters given by Bresse and O'Keefe (1991).
¹ calculated from the assigned site population reported in Table 3.

that the *A* site behaves as a cavity providing only very weak charges, thus suggesting that the capranicaite crystal structure is able to form stable phases when the *A* cavity is populated by large monovalent cations, as well as when the *A* cavity is empty. In this latter case, the crystal structure contains structural openwork slabs with channels extending along *a* that can accommodate additional small neutral molecules, as confirmed by our FTIR analysis, which detects a small amount of CO₂ and water.

When this hypothetical mineral (isomorphous to capranicaite and with empty *A* cavities) will be discovered, a new mineral group can be defined following the procedure of Mills *et al.* (2009). According to Dana classification, this still hypothetical ‘capranicaite mineral group’ should have the general formula $^{[A]}(K,Cs)_x^{[M]}(Ca_{2-x}Na_x)Al_4B_4Si_2O_{18}$, with *x* ranging from 0 to 1.

The main isomorphous substitution involves the heterovalent exchange $^{[A]}K^+ + ^{[M]}Na^+ \rightarrow ^{[A]}\square + ^{[M]}Ca^{2+}$ that leads to the two ideal end-members $^{[A]}K^{[M]}(CaNa)Al_4B_4Si_2O_{18}$ and $^{[A]}\square^{[M]}Ca_2Al_4B_4Si_2O_{18}$. The first composition, and in general, all phases of the ‘capranicaite group’ with $x \geq 0.5$, correspond to the capranicaite end-member whereas a different root name must be used for mineral phases with the large alkali sites vacant (i.e. $x < 0.5$). Interestingly, this latter species contains empty ‘zeolitic’ channels and it is potentially suitable to host a significant amount of small neutral molecules.

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