Eur. J. Mineral.
2010, **22**, 113–119
Published online February 2010

Balliranoite, $(Na,K)_6Ca_2(Si_6Al_6O_{24})Cl_2(CO_3)$, a new cancrinite-group mineral from Monte Somma – Vesuvio volcanic complex, Italy

NIKITA V. CHUKANOV[1,*], NATALIA V. ZUBKOVA[2], IGOR V. PEKOV[2], LYUDMILA V. OLYSYCH[2],
ELENA BONACCORSI[3,4] and DMITRY YU. PUSHCHAROVSKY[2]

[1] Institute of Problems of Chemical Physics, Chernogolovka, 142432 Moscow, Russia
*Corresponding author, e-mail: chukanov@icp.ac.ru
[2] Faculty of Geology, Moscow State University, Vorobievy Gory, 119992 Moscow, Russia
[3] Earth Sciences Department, University of Pisa, Via S. Maria 53, 56126 Pisa, Italy
[4] Institute of Geosciences and Georesources, CNR, Via Moruzzi 1, 56126 Pisa, Italy

Abstract: The new cancrinite-group mineral balliranoite was found in a metasomatic rock from Monte Somma – Vesuvio volcanic complex, Campania, Italy. Associated minerals are orthoclase, phlogopite, clinohumite, calcite, diopside, pargasite, haüyne and apatite. The mineral is named for the Italian crystallographer Paolo Ballirano. Balliranoite is transparent, colourless. It occurs in the cavities of the rock as coarse prismatic crystals up to 1 × 1 × 2 mm and as anhedral grains up to 1 cm in the groundmass. The mineral is brittle, with Mohs hardness 5 and perfect cleavage on (10-10). D_{meas} is 2.48(1), D_{calc} is 2.486(12) g/cm^3. Optically, the new mineral is uniaxial (+), $\omega = 1.523(2)$, $\varepsilon = 1.525(2)$. IR spectrum is given. The chemical composition is (mean of 5 analyses, wt%): Na_2O 13.05, K_2O 3.08, CaO 12.70, Al_2O_3 27.28, SiO_2 32.38, SO_3 1.96, Cl 7.43, $-O{=}Cl_2$ -1.68; CO_2 (determined by selective sorption of ignition products) 3.24; H_2O (determined by Penfield method) 0.19; total 99.63. The empirical formula based on 12 (Si + Al) is: $Na_{4.70}Ca_{2.53}K_{0.73}(Si_{6.02}Al_{5.98}O_{23.995})Cl_{2.34}(CO_3)_{0.82}(SO_4)_{0.27}\cdot 0.12H_2O$. The simplified formula is: $Na_5KCa_2(Si_6Al_6O_{24})Cl_2(CO_3)$. The crystal structure was refined ($R = 0.0396$). Balliranoite is hexagonal, $P6_3$; $a = 12.695(2)$ Å, $c = 5.325(1)$ Å, $V = 743.2(2)$ Å^3, $Z = 1$. Balliranoite is an analogue of cancrinite with ...–Ca–Cl–Ca–Cl–... chains in narrow channels instead of ...–Na–H_2O–Na–H_2O–... and an analogue of davyne with prevailing of (CO_3) in the broad channels instead of (SO_4). The strongest lines of the powder diffraction pattern [*d*, Å (*I*, %) (*hkl*)] are: 4.797 (100) (101), 3.669 (57) (300), 3.281 (73) (211), 2.754 (16) (400), 2.662 (58) (002), 2.446 (31) (401), 2.120 (18) (330). The holotype specimen is deposited in Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, Russia, with the registration number 3756/1.

Key-words: balliranoite, new mineral, cancrinite group, crystal structure, Monte Somma – Vesuvio volcanic complex.

1. Introduction

The cancrinite group includes hexagonal and trigonal tecto-aluminosilicates whose frameworks consist of layers containing six-membered rings of Si- and Al-centered tetrahedra. The three possible positions of neighbouring layers in the (*a,b*)-plane are usually denoted by the letters *A*, *B* and *C* (Bonaccorsi & Merlino, 2005). Among about twenty cancrinite-group minerals, five species [cancrinite, hydroxycancrinite, vishnevite, davyne and kyanoxalite (IMA 2008-041; Chukanov *et al.*, in press)] are characterized by a small hexagonal unit cell with the parameters $a \approx$ 12.6–12.8 Å, $c \approx$ 5.1–5.4 Å and by a framework with the simplest stacking sequence *AB* and regular Loewenstein-type alternation of Si and Al atoms in tetrahedral sites (Loewenstein, 1954). The main differences among these minerals consist in the amounts and arrangement of extra-framework anions and cations both in wide channels delimited by 12-membered rings and in narrow channels formed by columns of base-sharing cancrinite cages (Bonaccorsi & Merlino, 2005).

The new mineral balliranoite, recently approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2008-065), is related to davyne being its CO_3-dominant analogue, as well as to cancrinite being its Ca,Cl-dominant analogue (Table 1). It was named in honor of the Italian crystallographer Paolo Ballirano (b. 1964), Department of Earth Sciences, University of Rome ‘‘La Sapienza’’, who has made important contributions to the crystal chemistry of cancrinite-group minerals. In particular, the first structural investigation of a sample very close to the holotype of balliranoite described in this paper was performed by Ballirano *et al.* (1998).

The holotype specimen of balliranoite originates from an old local collection. Its fragment is deposited in the Fersman Mineralogical Museum of Russian Academy

0935-1221/10/0022-1983 $ 3.15
DOI: 10.1127/0935-1221/2010/0022-1983
© 2009 E. Schweizerbart'sche Verlagsbuchhandlung, D-70176 Stuttgart

Table 1. Al,Si-ordered cancrinite-group minerals with the stacking sequence *AB* and unit-cell dimensions $a = 12.6–12.8$ Å, $c = 5.1–5.4$ Å.

Mineral	Space group	Framework	Narrow channels	Wide channels
Cancrinite	$P6_3$	$Si_6Al_6O_{24}$	$Na_2(H_2O)_2$	$(Na,Ca)_6(CO_3)_{1–1.7}$
Vishnevite	$P6_3$	$Si_6Al_6O_{24}$	$Na_2(H_2O)_2$	$(Na,K)_6(SO_4)$
Hydroxycancrinite	$P3$	$Si_6Al_6O_{24}$	$Na_2(H_2O)_2$	$Na_6(OH)_2(H_2O)_n$
Davyne	$P6_3$ or $P6_3/m$	$Si_6Al_6O_{24}$	Ca_2Cl_2	$(Na,K,Ca)_6(SO_4)_{0.5–1}Cl_{1–0}$
Balliranoite	$P6_3$	$Si_6Al_6O_{24}$	Ca_2Cl_2	$(Na,K,Ca)_6(CO_3)$
Kyanoxalite[a]	$P6_3$	$Si_6Al_6O_{24}$	$Na_2(H_2O)_2$	$Na_5(C_2O_4)_{0.5–1}(H_2O)_{3–2}$

[a] References: Chukanov *et al.*, in press; others: Bonaccorsi & Merlino, 2005.

of Sciences, Moscow, Russia, with the registration no. 3756/1.

2. Occurrence, general appearance and physical properties

Balliranoite was discovered at Monte Somma – Vesuvio volcanic complex, Campania, Italy, in an alkaline skarn-like rock formed as a product of metasomatic interaction between the alkaline magma and the limestone. The rock is composed of orthoclase, phlogopite, clinohumite, calcite, diopside, pargasite, haüyne, apatite and balliranoite. All associated minerals have been identified by the combination of IR spectroscopy and electron microprobe analyses. Balliranoite occurs in the cavities of the rock as coarse prismatic crystals up to 1 × 1 × 2 mm and as anhedral grains up to 1 cm in the groundmass. The prismatic faces, probably {10–10}, have a striation parallel to [0001] (Fig. 1).

All data on physical properties (including IR spectrum and optical data), as well as chemical composition, X-ray diffraction and crystal structure of balliranoite have been obtained on the same single-crystal grain.

Balliranoite is transparent, colourless, with vitreous lustre. It is brittle, has Mohs hardness 5, shows perfect cleavage on (10–10) and uneven fracture across the cleavage direction. Fragments of a single-crystal grain are prisms elongated in the [0001] direction. Density measured (D_{meas}) by the method of hydrostatic weighting is 2.48(1) g/cm^3. Calculated density (D_{calc}) is 2.486(12) g/cm^3. Optically, the mineral is uniaxial (+), $\omega = 1.523(2)$, $\varepsilon = 1.525(2)$. Elongation is positive.

3. Chemical data

The electron-microprobe analyses (Table 2) were performed using a fully computer-controlled scanning electron microscope VEGA TS 5130MM equipped with energy dispersive X-ray (EDX) microanalyser with semiconductor Si(Li) detector INCA Energy, at an operating voltage of 15.7 kV and a beam current of 0.5 nA. The electron beam was rastered over an area 16 × 16 μm^2 to minimise sample damage.

CO_2 was determined by selective sorption of CO_2 (on *askarite* sorbent: an asbestiform matter saturated by NaOH) from gaseous products obtained by heating of the

Fig. 1. Crystals of balliranoite.

Table 2. Chemical composition of balliranoite (mean of 5 point analyses).

Constituent	Wt.%	Range	Atoms [on the basis of 12 (Al + Si)]	
Na_2O	13.05	12.80–13.24	Na	4.70
K_2O	3.08	3.01–3.16	K	0.73
CaO	12.70	12.56–12.85	Ca	2.53
Al_2O_3	27.28	27.17–27.42	Al	5.98
SiO_2	32.38	32.23–32.55	Si	6.02
CO_2	3.24	3.18–3.30	C	0.82
SO_3	1.96	1.79–2.10	S	0.27
Cl	7.43	7.20–7.70	Cl	2.34
H_2O	0.19	0.15–0.23	H	0.24
$-O{=}Cl_2$	−1.68			
Total	99.63			

Probe standards are: albite (Na), microcline (K), wollastonite (Ca), Al_2O_3 (Al), SiO_2 (Si), FeS_2 (S), NaCl (Cl). The contents of F, Mg, P, Mn, Fe, Sr, and Ba are below their detection limits.

mineral at 1080 °C in oxygen at 1 atm. H_2O was determined by the modified Penfield method.

The empirical formula of balliranoite based on 12 (Si +Al) is: $Na_{4.70}Ca_{2.53}K_{0.73}(Si_{6.02}Al_{5.98}O_{23.995})Cl_{2.34}(CO_3)_{0.82}(SO_4)_{0.27}\cdot 0.12H_2O$. This formula is not charged that confirms the correctness of the method used by Ballirano *et al.* (1996) for the estimation of weight percent CO_2 necessary to saturate the O excess in electron microprobe analyses. The idealized formula is $(Na,K)_6Ca_2(Si_6Al_6O_{24})Cl_2(CO_3)$.

The Gladstone-Dale compatibility index calculated from the empirical formula is $1 - (K_P/K_c) = 0.012$ with D_{calc}, and 0.010 with D_{meas} (both *superior*).

4. IR spectroscopy

Balliranoite powder was mixed with anhydrous KBr, pelletized, and analysed using a Specord 75 IR spectrophotometer. The IR spectrum of pure KBr-disk was subtracted from the overall spectrum. Polystyrene and gaseous NH_3 were used as frequency standards; the precision of frequency measurement is ± 1 cm^{-1}; the mean resolution for the range 400–1600 cm^{-1} is of 0.8 cm^{-1}.

The IR spectrum of balliranoite is reported in Fig. 2a; wavenumbers of absorption bands and their assignments (cm^{-1}; s – strong band, w – weak band, sh – shoulder) are as follows: 3485w, 3390w (O–H–stretching vibrations of H_2O molecules); 1645w (bending vibrations of H_2O molecules); 1519, 1480sh, 1453w, 1410 (degenerate stretching vibrations of CO_3^{2-} ions); 1125s (Si–O– and probably S–O–stretching vibrations); 1045sh, 1008s, 945sh (stretching vibrations of the tetrahedral framework); 860 (out-of-plane bending vibrations of CO_3^{2-} ions); the absorptions below 700 cm^{--1} are due to the bending vibrations of the tetrahedral framework. Characteristic bands of H_2O molecules are very weak. Although the water content in balliranoite is too low to be detected from structural data, modified Penfield method confirms the presence of H_2O. The band at 1125 cm^{-1} is close (by its position and intensity) to analogous band of typical sulfate-free cancrinite. Unlike SO_4-rich cancrinite-group minerals with the stacking sequence *AB* (*i. e.* davyne and vishnevite), balliranoite does not show absorption maxima in the range 1140–1170 cm^{-1}.

As compared with davyne (Fig. 2b), balliranoite is characterized by the bands of stretching and bending vibrations of CO_3^{2-} anions and shifts of most other bands (see Table 8).

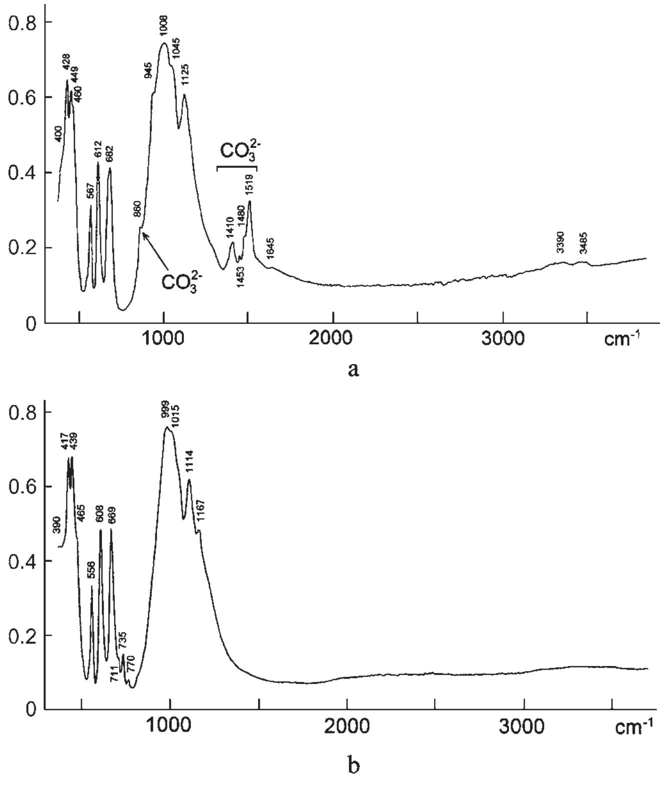

Fig. 2. IR spectra (relative absorption *vs.* wavenumber) of balliranoite (a) and davyne from Sar-e Sang, Afghanistan (b).

5. X-ray crystallography and crystal structure

X-ray powder diffraction data for balliranoite (Table 3) were obtained with STOE STADI MP diffractometer using $CuK\alpha_1$-radiation. The powder-diffraction pattern of the new mineral has been indixed on the basis of the space group $P6_3$ found from the single-crystal XRD data. Unit-cell dimensions of balliranoite refined from powder data are: $a = 12.696(3)$ Å, $c = 5.327(2)$ Å, $V = 743.6(6)$ Å^3, $Z = 1$.

A crystal with approximate dimensions $0.13 \times 0.15 \times 0.30$ mm was used for the structure determination at room temperature. Details of the single-crystal X-ray data collection (Xcalibur S diffractometer equipped with CCD detector operating at 50 kV and 40 mA; absorption correction applied according to the shape of the crystal) and structure refinement of balliranoite are given in Table 4. The measured intensities were corrected for Lorentz, background, polarisation and absorption effects [CrysAlis program (Oxford Diffraction, 2006)]. The refined unit cell parameters are $a = 12.695(2)$ Å, $c = 5.325(1)$ Å. SHELX97 (Sheldrick, 1997) was used for crystal structure refinement (space group $P6_3$) by using 2104 independent reflections ($R_{int} = 0.0407$), of which 1771 reflections have $I > 2\sigma(I)$, up to R-factor 0.0379 (with anisotropic treatment of all atoms except S, C(1), C(2) and corresponding O atoms of sulfate and carbonate groups). Framework atoms of ''carbonate davyne'' (Ballirano *et al.*, 1998) were taken as starting model. All the other atoms were obtained from Fourier syntheses. The studied crystal was found to be twinned racemically; refined twin ratio was 0.52:0.48. Occupancies of both C(1) and C(2) sites and corresponding $O(_C1)$ and $O(_C2)$ sites as well as their z coordinates were constrained to each other; at the last stage of refinement, the occupancies were fixed. The same procedure was

Table 3. X-ray powder diffraction data for balliranoite.

I_{obs}	d_{obs}	I_{calc}	d_{calc}[a]	*hkl*
8	11.02	19	10.994	100
9	6.367	11	6.348	110
100	4.797	88	4.793	101
1	4.162	3	4.155	120
4	3.841	1.5	3.825	201
57	3.669	100	3.665	300
73	3.281	92	3.276	211
3	3.052	7	3.049	310
4	3.018	7	3.019	301
16	2.754	21	2.749	400
58	2.662	45	2.663	002
13	2.648	27	2.646	311
5	2.589	8	2.588	102
31	2.446	43	2.442	401
2	2.400	7	2.399	140
1	2.198	3, 2	2.199, 2.187	500, 411
1	2.157	4	2.154	302
18	2.120	40	2.116	330
6	2.040	11, 3	2.040, 2.032	222, 501
3	2.007	8	2.006	132
1	1.930	1	1.936	241
7	1.913	17	1.912	402
1	1.850	2	1.851	511
11	1.783	27	1.782	142
3	1.753	4	1.752	103
3	1.711	12	1.712	341
4	1.633	9	1.632	123
1	1.586	9	1.587	440
2	1.535	5	1.534	313
3	1.510	5	1.509	602
3	1.506	13	1.506	351
2	1.495	5	1.495	342
4	1.492	10	1.491	403
1	1.464	4	1.466	621
2	1.456	7	1.456	170
10	1.365	17	1.3631	442
3	1.336	7	1.3313	004
7	1.331	15	1.3307	801
1	1.321	1, 2	1.3216, 1.3201	104, 513
1	1.302	2, 1	1.3029, 1.3024	114, 724

[a] Calculated for unit-cell parameters obtained from single-crystal data.

performed for the occupancies of S and corresponding $O(_S1)$ and $O(_S2)$ sites and both Cl and Cl'.

The atomic coordinates, equivalent isotropic displacement parameters and site occupancy factors for balliranoite are presented in Table 5. Selected interatomic distances are given in Table 6. The generalised crystal-chemical formula obtained from structure refinement is $[Na_{4.7}K_{0.7}Ca_{0.5}(CO_3)_{0.9}(SO_4)_{0.3}]$ $[Ca_{2.0}Cl_{2.0}]$ $[Si_6Al_6O_{24}]$.

The crystal structure of balliranoite (Figs. 3, 4) shows a perfect ordering of Si and Al atoms in the tetrahedral sites as typical for cancrinite-group minerals. This is indicated by the ratio of the average bond lengths $\langle$Si-O$\rangle$: $\langle$Al-O$\rangle$ = 0.930 (Hassan & Grundy, 1990). The tetrahedral framework is very close to that found in davyne (Bonaccorsi *et al.*, 1990; Hassan & Grundy, 1990) as well as in the sample studied by Ballirano *et al.* (1998).

Table 4. Crystal data, data collection information and refinement details for balliranoite.

Space group, *Z*	*P*6$_3$ (no. 173), 1
a, *c* (Å)	12.695(2), 5.325(1)
V (Å^3)	743.3(2)
F(000), ρ_{calc} (g·cm^{-3})	548, 2.483
μ (mm^{-1})	1.402
Crystal dimensions (mm)	0.13 × 0.15 × 0.30
Diffractometer	Xcalibur S CCD
λ (Mo*K*α) (Å), *T* (K)	0.71073, 293
Crystal-detector dist. (mm)	45
Total no. of frames	1205
Collection mode, 2θ$_{max}$(°)	(full) sphere, 69.76
h, k, l ranges	−20/20, −20/20, −8/8
Reflections collected	26139
Unique reflections	2104 (R_{int} = 0.0407)
Refinement on	F^2
$R1(F)$, $wR2_{all}(F^2)$[a]	0.0379, 0.1012
'Observed' refls.	1771 [$F_o > 4\sigma(F_o)$]
No. of refined parameters	111
GoF	1.051
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	−0.866, 0.777

Unit-cell parameters were refined from 9345 reflections
* $w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 0.00P]$; $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$.

The calcium cations are located on the three-fold axis in the center of the bases of the cancrinite cages. The Ca^{2+} cations show a hexagonal bipyramidal coordination, forming six bonds with O^{2-} belonging to the base of the cage and two bonds with Cl^- anions, which are placed within the cages above and below the Ca^{2+} cations. Only 58 % of Cl^- anions are located exactly on the three-fold axis whereas the rest 42 % are statistically distributed over three symmetry-related sites slightly offset from the three-fold axis. Taking into account that Cl atoms are characterized by such positional disorder, the alternative Ca-Cl distances are given in Table 6 in square brackets.

The wide channels of the balliranoite crystal structure host six (Na, K, Ca) cations statistically distributed over two independent cationic sites *M* and *M*', as well as 0.9 CO_3 groups distributed in two independent positions and partly substituted by SO_4 groups (0.2 *pfu*).

In the structure of the sample studied by Ballirano *et al.* (1998), three cationic sites *M*(1), *M*(2) and *M*(3) with different values of occupancy factor (0.536, 0.267 and 0.197, respectively) were localized in the wide channel. In the holotype sample of balliranoite studied by us, only two positions are found, namely *M* [close to *M*(1), far from the wall of the channel] and *M*' [close to *M*(3), near to the wall of the channel]. The occupancy factors for these sites were initially refined on the basis of the Ca scattering factor (Table 5); if we assume that the sum of the occupancies of *M* and *M*' is 1, the refined values allow us to calculate the fraction of Na and (Ca, K) in the sites, *i.e.* 0.80 and 0.20, respectively. With these

Table 5. Atomic coordinates, equivalent isotropic displacement parameters (in Å^2) and site occupancy factors (s.o.f.) for balliranoite.

Atom	*x*	*y*	*z*	U_{eq}[a]	s.o.f.
Si	0.32774(4)	0.40839(4)	0.7500	0.00996(11)	1
Al	0.06985(4)	0.40885(4)	0.75030(17)	0.01012(12)	1
Ca	0.6667	0.3333	0.21614(19)	0.0230(2)	1
M	0.1181(2)	0.2424(3)	0.2786(6)	0.0560(7)	0.465(8)[b]
M'	0.1537(10)	0.3136(19)	0.2744(12)	0.073(4)	0.174(7)[b]
O(1)	0.21314(13)	0.42747(14)	0.7131(4)	0.0250(4)	1
O(2)	0.09954(12)	0.55634(11)	0.7423(4)	0.0193(3)	1
O(3)	0.00565(16)	0.32843(15)	0.0267(3)	0.0232(4)	1
O(4)	0.31568(14)	0.33819(14)	0.0107(3)	0.0217(3)	1
Cl	0.3333	0.6667	0.2176(6)	0.082(5)	0.58[c]
Cl'	0.311(2)	0.6326(19)	0.222(3)	0.062(4)	0.14[c]
S	0.0000	0.0000	0.247(3)	0.0416(19)[a]	0.15[c]
O($_S$1)	0.0000	0.0000	0.952(6)	0.046(6)[a]	0.15[b]
O($_S$2)	0.064(3)	0.119(2)	0.387(7)	0.121(10)[a]	0.15[c]
C(1)	0.0000	0.0000	0.1496(18)	0.048(6)[a]	0.30[c]
O($_C$1)	0.1152(8)	0.0606(7)	0.1496(18)	0.0504(18)[a]	0.30[c]
C(2)	0.0000	0.0000	0.333(5)	0.011(4)[a]	0.15[c]
O($_C$2)	0.1152(9)	0.059(2)	0.333(5)	0.106(9)[a]	0.15[c]

[a] U_{eq} as defined by Fischer & Tillmanns 1988.

[b] Refined partial occupancies of the split sites *M* and *M*' by using the scattering factor of Ca: assuming a full occupancy for (*M* + *M*'), a chemical content of 80 % Na and 20 % (Ca, K) was obtained. On the basis of these values, the actual occupancies of *M* and *M*' are 0.73 and 0.27, respectively.

[c] Occupancies fixed on the last stages of the refinement.

Table 6. Selected interatomic distances (Å) in balliranoite.

Si–O(1) 1.602(1)
–O(2) 1.606(1)
–O(3) 1.614(2)
–O(4) 1.615(2)
<Si–O> 1.609

Ca–O(2) 2.576(1) × 3
–O(1) 2.630(2) × 3
–Cl [Cl'] 2.655(3) [2.659(15)]
–Cl [Cl'] 2.670(3) [2.720(15)]

M–O($_C$2) 2.32(3)[a]
–O($_C$2) 2.33(3)[a]
–O($_C$1) 2.391(9)[a]
–O($_C$1) 2.421(10)[a]
–O($_C$1) 2.429(9)[a]
–O(3) 2.567(3)
–O(4) 2.599(3)
–O(3) 2.681(3)
–O(4) 2.691(3)
–O$_C$(2) 2.76(2)[a]

Al–O(2) 1.716(1)
–O(1) 1.725(1)
–O(4) 1.736(2)
–O(3) 1.744(2)
<Al–O> 1.730

S–O($_S$2) 1.504(10) × 3
–O($_S$1) 1.57(3)
C(1)–O($_C$1) 1.267(8) × 3
C(2)–O($_C$2) 1.267(10) × 3

M'–O($_S$2) 2.23(4)[a]
–O(4) 2.379(6)
–O(3) 2.379(6)
–O(3) 2.546(5)
–O(4) 2.578(5)
–O(1) 2.650(9)

[a] The occurrence of these *M*-O bonds depends on the occupancy of the C(1), C(2) and S sites.

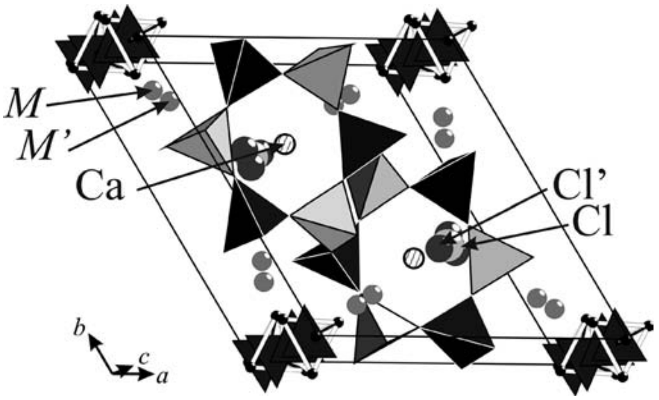

Fig. 3. Crystal structure of balliranoite: general view. SiO$_4$ tetrahedra are grey, AlO$_4$ tetrahedra are black, CO$_3$ triangles are dark grey. S atoms are shown by small white circles, O atoms of the SO$_4$ tetrahedra – by small black circles.

hypothetical chemical contents, the occupancy factors of the sites *M* and *M*' are 0.73 and 0.27, respectively. A different possible interpretation of the refined values is that the *M* sites are preferentially occupied by cations such as K and Ca, whereas the *M*' sites host the light Na cations.

The CO$_3$ groups are distributed in two positions, like the sample investigated by Ballirano *et al.* (1998). The occupancy factors of C atoms in both sites were held fixed during the refinement, and corresponded to 0.30 and 0.15 for the C(1)- and C(2)-sites, respectively. A set of constraints was introduced in the refinement to avoid correlations between parameters. In particular, both CO$_3$ groups were considered to be planar, with the same *z* coordinate of C and O atoms.

A maximum at (0 0 0.26) in the difference Fourier synthesis was attributed to the sulfur atom. Its partial occupancy of 0.15 was fixed in accordance with the results of the chemical analysis and taking into account that very short distances between S and C(1,2) occurs, indicating statistical distribution of these anionic groups. Oxygen atom O($_S$1) of the SO$_4$-tetrahedron was located at distance

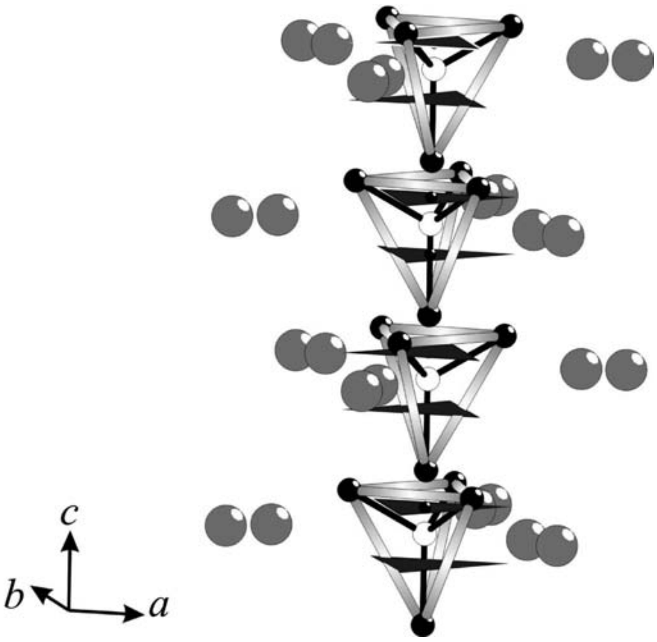

Fig. 4. Contents of wide channels in balliranoite. Black triangles are the CO_3 groups, the sites *M* and *M'* are shown by grey circles, black circles correspond to the vertices of the SO_4 tetrahedron, white circles correspond to S atoms.

of 1.57 Å, with the same occupancy factor of S. In contrast to the sample studied by Ballirano *et al.* (1998), in our case the base of the SO_4-tetrahedron does not coincide with the three oxygen forming CO_3 triangular group. Three additional $O(_S2)$ symmetry equivalent atoms, forming the triangular base of the S-centered tetrahedron, were localized in the wide channels.

The positions of *M* and *M*' cations as well as those of the SO_4 tetrahedra are very close to those found in a phase originally described as 'potassium-rich vishnevite' (Pushcharovskii *et al.*, 1989), and subsequently recognised as 'pitiglianoite'(Bonaccorsi & Merlino, 2005). The sites *M* and *M*' in balliranoite correspond respectively to partially occupied K and Na sites in this phase. Moreover, also the cation distributions in the wide channels of these two minerals are similar, with the occupancy of the *M* site significantly higher than the occupancy of the *M*' site.

6. Discussion and conclusion

Balliranoite belongs to the cancrinite group, characterized by the stacking sequence *AB*, and presenting two kinds of channels running along [001] (Bonaccorsi & Merlino, 2005). Narrow channels are formed by base-sharing cancrinite cages and contain either ...Na–H_2O...Na–H_2O... clusters [in cancrinite, vishnevite, hydroxycancrinite (Khomyakov *et al.*, 1992) and kyanoxalite (IMA 2008-041; Chukanov *et al.*, in press] or infinite chains ...Ca–Cl–Ca–Cl... (in davyne and balliranoite) (Table 1). The most important difference between davyne and balliranoite is the content of the anionic sites in wide channels, with prevalence of SO_4^{2-} anions in davyne and CO_3^{2-} anions in balliranoite. Comparative data for balliranoite, davyne and cancrinite are given in Table 7.

The crystal structure and crystal chemistry of the carbonate analogue of davyne (with CO_3 prevailing over SO_4 in wide channels) have been investigated by Paolo Ballirano with co-authors (Ballirano *et al.*, 1996, 1998) for the first time, on samples from the same locality, Monte Somma. There are some structural differences between holotype sample of balliranoite and the mineral described by Ballirano *et al.* (1998). Unlike the latter mineral, in holotype sample the *Cl* site in the cancrinite cage is split into *Cl* and *Cl*', two (instead of three) *M* sites are present and the basal plane of the SO_4 tetrahedron does not coincide with the plane of CO_3 groups.

Another sample of ''davyne'' from Monte Somma, deposited at the Institut Royal des Sciences Naturelles de Belgique and originally classified as ''nepheline, variété cavolinite'', was studied by Binon *et al.* (2004), and showed 0.9 $(CO_3)^{2-}$ groups *pfu* within the wide channels.

A similar mineral, with the chains ...Ca–Cl–Ca–Cl... in narrow channels and CO_3^{2-} prevailing over other anions in wide channels, was found at the Tultui lazurite deposit, Slyudyanka district, South Baikal area, Siberia, Russia (Sapozhnikov *et al.*, 2006). It belongs to the structural type of cancrinite *s.s.*, with the stacking sequence *AB* and space group $P6_3$. The refinement of its crystal structure resulted in the following crystal-chemical formula: $[Na_{5.5}Ca_{0.5}(CO_3)_{0.66}(SO_4)_{0.34}(S_2)_{0.28}(H_2O)_{0.38}]$ $[Ca_{2.0}Cl_{2.0}][Si_6Al_6O_{24}]$. This mineral can be considered as a SO_4- and S_2-bearing variety of balliranoite.

The content of SO_4 groups *pfu* ($Z = 1$) in davyne typically varies from 0.5 to 0.9 (Bonaccorsi *et al.*, 1990; Hassan & Grundy, 1990; Ballirano *et al.*, 1996; Bonaccorsi & Merlino, 2005), with substitution of $(SO_4)^{2-}$ by Cl^- anions. Recently, the sulfate end-member of the davyne-balliranoite series was discovered in the Sar-e-Sang lazurite deposit, Badakhshan, Afghanistan, and its crystal structure was solved (Rozenberg *et al.*, 2003). The crystal-chemical formula of this mineral is: $[Na_{5.2}K_{0.8}(SO_4)_{1.0}]$ $[Ca_{2.0}Cl_{2.0}]$ $[Si_6Al_6O_{24}]$. A series of davyne-type minerals with variable SO_4:CO_3 ratio (from 0.90:0.12 to 0.19:0.88) was described by Ballirano *et al.* (1996), suggesting that the solid-solution series between the sulfate end-member davyne and balliranoite does exist in nature.

Acknowledgements: We are grateful to A.A. Mukhanova for the electron microprobe study of balliranoite. This work was supported by the Russian Foundation for Basic Research (grants nos. 08-05-00077-a, 09-05-00143-a and 09-05-91330-NNIO_a), grants of the Foundation of the President of the Russian Federation nos. MK-836.2008.5, NSh-2192.2008.5 and NSh-863.2008.5 and a grant from the Russian Science Support Foundation (IVP). F. Bellatreccia and an anonymous reviewer are greatly appreciated for important comments.

Table 7. Comparative data for balliranoite, davyne and cancrinite (all hexagonal with $Z = 1$).

Mineral	Balliranoite	Davyne	Cancrinite
Structural formula			
Narrow channels	$[Ca_2Cl_2]$	$[Ca_2Cl_2]$	$[Na_2(H_2O)_2]$
Wide channels	$[(Na,K,Ca)_6(CO_3)]$	$[(Na,K,Ca)_6(SO_4)_{0.5-1}Cl_{1-0}]$	$[(Na,Ca)_6(CO_3)_{1-1.7}]$
Framework	$[Si_6Al_6O_{24}]$	$[Si_6Al_6O_{24}]$	$[Si_6Al_6O_{24}]$
Space group	$P6_3$	$P6_3$ or $P6_3/m$	$P6_3$
a, Å	12.695	12.71–12.85	12.74
c, Å	5.325	5.33–5.37	5.183
Strong lines of the X-ray powder-diffraction pattern: d, Å (I, %)	4.797 (100), 3.669 (57), 3.281 (73), 2.754 (16), 2.662 (58), 2.446 (31), 2.120 (18)	4.790 (73), 3.658 (100), 3.272 (70), 2.663 (19), 2.438 (22), 2.112 (48), 1.781 (19)	6.43 (25), 4.70 (60), 3.68 (70), 3.26 (100), 2.756 (50), 2.433 (30)
Wavenumbers of strongest bands in IR spectrum, cm^{-1}[a]	1519, 1410, 1125, 1008, 860, 682, 612, 567, 449, 428	1167, 1114, 999, 753, 669, 608, 556, 439, 417	~3600, ~3530, 1630, 1512, 1502, 1480, 1397, 1126, 1036, 995, 942, 859, 685, 621, 577, 498, 458, 422
Optical data			
ω	1.523	1.515–1.526	1.494
ϵ	1.525	1.519–1.532	1.501
Optical sign	+	+	+
Density, g/cm^3	2.486 (calculated) 2.48 (measured)	2.50 (calculated) 2.42–2.53 (measured)	2.26 (calculated) 2.32 (measured)
References	This work	Ballirano *et al.*, 1996, 1997; Bonaccorsi *et al.*, 1990; Bonaccorsi & Merlino, 2005; Hassan & Grundy, 1990; Rozenberg *et al.*, 2003; our data	Khomyakov *et al.*, 1992[b]; our data for IR spectral bands

[a] Shoulders are omitted.

[b] Data for typical cancrinite used by A.P. Khomyakov for comparison with hydroxycancrinite.

References

Ballirano, P., Maras, A., Buseck, P.R. (1996): Crystal chemistry and IR spectroscopy of Cl- and SO_4-bearing cancrinite-like minerals. *Am. Mineral.*, **81**, 1003–1012.

Ballirano, P., Maras, A., Buseck, P.R., Yates, A.M. (1997): Improved powder X-ray data for cancrinites III: Davyne. *Powder Diffraction*, **12**, 2, 99–102.

Ballirano, P., Bonaccorsi, E., Merlino, S., Maras, A. (1998): Carbonate groups in davyne: structural and crystal-chemical considerations. *Can. Mineral.*, **36**, 1285–1292.

Binon, J., Bonaccorsi, E., Bernhardt, H.-J., Fransolet, A.-M. (2004): The mineralogical status of ‘‘cavolinite’’ from Vesuvius, Italy, and crystallochemical data on the davyne subgroup. *Eur. J. Mineral.*, **16**, 511–520.

Bonaccorsi, E., Merlino, S., Pasero, M. (1990): Davyne: its structural relationships with cancrinite and vishnevite. *Neues Jahrb. Mineral.*, Monatsh., **1990**, H. 3, 97–112.

Bonaccorsi, E. & Merlino, S. (2005): Modular microporous minerals: Cancrinite-Davyne Group and C-S-H Phases. *Reviews in Mineralogy and Geochemistry*, **57**, 241–290.

Chukanov N.V., Pekov I.V., Olysych L.V., Massa W., Yakubovich O.V., Zadov A.E., Rastsvetaeva R.K., Vigasina M.F. Kyanoxalite, a new cancrinite-group mineral with oxalate extra-framework anion from the Lovozero alkaline massif, Kola peninsula. *Zapiski Vseross. Mineral. Obshch.* (in press).

Fischer, R.X. & Tillmanns, E. (1988): The equivalent isotropic displacement factor. *Acta Crystallogr.*, **C44**, 775–776.

Hassan, I. & Grundy, H.D. (1990): Structure of davyne and implications for stacking faults. *Can. Mineral.*, **28**, 341–349.

Khomyakov, A.P., Nadezhina, T.N., Rastsvetaeva, R.K., Pobedimskaya, E.A. (1992): Hydroxycancrinite $Na_8[Al_6Si_6O_{24}](OH)_2 \cdot 2H_2O$ – a new mineral. *Zapiski Vses. Mineral. Obshch. (Proc. Russ. Miner. Soc.)*, **121**, 1, 100–105 (in Russian).

Loewenstein, W. (1954): The distribution of aluminum in the tetrahedral of silicates and aluminates. *Am. Mineral.*, **39**, 92–96.

Oxford Diffraction. (2006)CrysAlis. Oxford Diffraction Ltd., Abingdon, Oxford, England.

Pushcharovskii, D.Yu., Yamnova, N.A., Khomyakov, A.P. (1989): Crystal structure of high-potassium vishnevite. *Sov. Phys. Crystal.*, **34**, 37–39.

Rozenberg, K.A., Rastsvetaeva, R.K., Bolotina, N.B., Chukanov N.V. (2003): Crystal-chemical features of a new chloro-sulphate mineral of the cancrinite group, from the locality Sar-e-Sang, Afghanistan. *Abstract of the Anniversary Fedorov Session*, St. Petersburg, Plekhanov Mining Institute, 66–67.

Sapozhnikov, A.N., Chukanov, N.V., Suvorova, L.F., Feoktistova, L.P., Bogdanova, L.A. (2006): Davyne from the Tultui lazurite deposit, Baikal region. *Zapiski RMO (Proc. Russ. Miner. Soc.)*, **135**, 3, 77–84 (in Russian).

Sheldrick, G.M. (1997): SHELXS-97, a program for the solution of crystal structures. University of Göttingen, Germany.

Received 29 April 2009
Modified version received 10 August 2009
Accepted 14 September 2009