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Quadridavyne, $[(Na,K)_6Cl_2][Ca_2Cl_2][Si_6Al_6O_{24}]$, a new feldspathoid mineral from Vesuvius area

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Abstract: A new feldspathoid mineral, quadridavyne, belonging to the davyne group, is described. It was found in the locality Ottaviano, near Napoli, southern Italy, within products of the 1906 volcanic activity of Vesuvius. It occurs as transparent, colorless, prismatic crystals, elongated [001] with hexagonal outline. Twinning $(1\bar{1}00)$ is frequent. The mineral is brittle, with hardness *ca.* 5, $d_{meas} = 2.335(5)$, $d_{calc} = 2.354$ g/cm^3. Optically it is uniaxial (+), with $\omega = 1.529(1)$ and $\varepsilon = 1.532(1)$. Its ideal chemical formula, derived from electron microprobe data, is $[(Na,K)_6Cl_2][Ca_2Cl_2][(Si_6Al_6O_{24})]$. Quadridavyne is hexagonal, space group $P6_3/m$, $a = 25.771(6)$, $c = 5.371(1)$ Å, $Z = 4$. The structure of quadridavyne is topologically identical to that of davyne. The major difference lies in the long-range ordering of alkaline cations (Na^+ and K^+) and chlorine within the open channels running along [001], resulting in the doubling of the *a* parameter.

Key-words: quadridavyne, new mineral, feldspathoids, davyne group, Vesuvius (Italy).

Introduction

Feldspathoids of the cancrinite-davyne group are tectosilicates characterized by an aluminosilicate framework formed by six-membered rings, stacked along [001] according to an AB... sequence (Merlino, 1984). Because of this peculiar stacking sequence the resulting framework presents open channels which run along [001]. A further relevant feature of this framework is the occurrence of undecahedral cages. These feldspathoids are divided in two basic subgroups, those of cancrinite and davyne, depending on the chemical content within the cages: in cancrinite-group minerals the cages host Na^+ and water molecules, whereas the cages host Ca^{2+} and Cl^- in davyne-group minerals.

Since some years, we are involved in a wide project on the crystal-chemistry of davyne-like minerals (Bonaccorsi *et al.*, 1990, 1992; Bonaccorsi, 1993). A major problem within these minerals is lying in the chemical and crystallographic distinction between davyne and microsommite. In fact, incomplete data for these two minerals were given in the literature (for more details on this matter see Bonaccorsi *et al.*, 1990). During routine X-ray diffraction study on feldspathoids from the Vesuvius - Mt.Somma area, some single crystals were found, which presented unique diffraction features, different from those of davyne and microsommite. Careful chemical analyses were carried out, which confirmed the existence of a new mineral species, named quadridavyne. The name comes from the metric relationships with davyne: in fact, the unit-cell volume of quadridavyne is four times that of davyne. Both the mineral and its name were approved by the IMA Commission on New Minerals

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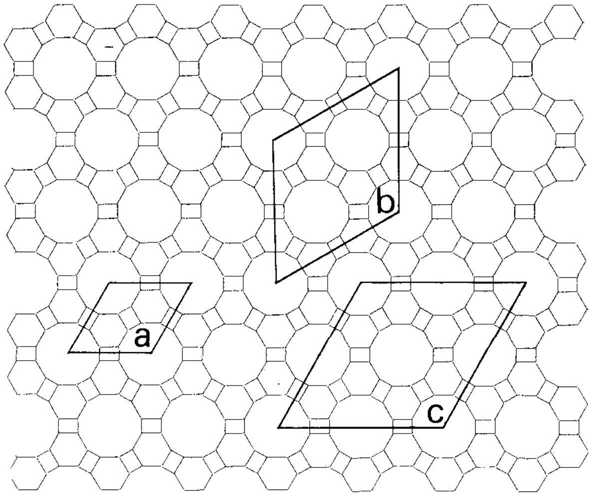

Fig. 1. Schematic drawing of the davyne-type framework, as seen down [001], showing the relationships among the *a* parameters of (a) davyne, (b) microsommite, and (c) quadridavyne.

and Mineral Names. The type specimen has been deposited in the Museo di Storia Naturale e del Territorio, University of Pisa (catalog *no.* 10014).

As stated above, quadridavyne is closely related to davyne and microsommite. All these minerals are characterized by hexagonal unit-cell with a common *c* parameter of ≈ 5.3 Å, which results from the AB.. stacking of layers. The basic *a* parameter of ≈ 12.7 Å is displayed by davyne, whereas microsommite has $a = \sqrt{3} \cdot a_{dav}$, and quadridavyne has $a = 2 \cdot a_{dav}$. In the cancrinite group the basic *a* parameter is displayed by cancrinite (Grundy & Hassan, 1982) and vishnevite (Hassan & Grundy, 1984), the $\sqrt{3} \cdot a$ parameter by pitiglianoite (Merlino *et al.*, 1991). Moreover, a synthetic phase metrically related to microsommite and pitiglianoite, and chemically similar to vishnevite was obtained by Klaska & Jarchow (1977). Fig. 1 shows the metrical relationships among the *a* parameters of davyne, microsommite, and quadridavyne.

Occurrence

Quadridavyne was found in two ash samples preserved in the Museum of Mineralogy, University of Pisa, and catalogued as having been collected at Ottaviano (Napoli, Italy) soon after the eruption of April 1906. These ashes are attributable to the last phases of the volcanic activity of Vesuvius, and contain lithic fragments composed of metasomatized and hydrothermally altered lavas and scoriae, testifying to the involvement of a hydrothermal aquifer (Bertagnini *et al.*, 1991).

Physical properties

Crystals of quadridavyne are transparent, colorless with vitreous lustre, white streak and Mohs' hardness of about 5. The mineral does not fluoresce, is brittle, and presents cleavage {001} perfect, {110} distinct.

Quadridavyne displays a simple morphology: prismatic crystals elongated [001] with hexagonal section, up to 2 mm in length and 0.5 mm in diameter. Dominant forms are {0001} and $\{10\bar{1}0\}$. Twinning $(1\bar{1}00)$ has been frequently observed.

Optically, quadridavyne is uniaxial positive, with $\omega = 1.529(1)$ and $\varepsilon = 1.532(1)$ (in Na light).

The density of 2.335(5) was obtained by sinking method in heavy liquids, to be compared with the calculated value of 2.354. Calculations using the Gladstone-Dale relationships and the constants reported by Mandarino (1981) indicate excellent compatibility: $1 - (K_p/K_c) = -0.031$.

Chemical data

The chemical analysis of quadridavyne was performed with a wavelength dispersive ARL/SEMQ electron microprobe. Operating conditions were 15 kV as accelerating voltage and 20 nA as sample current. Standards used were

Table 1. Electron microprobe analysis (average of 5 points) of quadridavyne.

	wt. %	range	atoms based on (Si + Al) = 12
SiO_2	33.09	32.85 - 33.31	6.049
Al_2O_3	27.62	27.07 - 27.99	5.951
CaO	11.35	11.03 - 11.45	2.223
Na_2O	11.21	10.94 - 11.48	3.973
K_2O	5.93	5.76 - 6.11	1.383
SO_3	1.08	1.03 - 1.12	0.148
Cl	12.13	12.01 - 12.30	3.758
Σ'	102.41		
Cl = O	- 2.74		
Σ	99.67		

albite (for Si, Al, Na), plagioclase-type glass (for Ca), microcline (for K), barite (for S), and sodalite (for Cl). The following formula, recalculated on the basis of 12 (Si + Al), is derived from the analytical data, reported in Table 1:

$Na_{3.97}K_{1.38}Ca_{2.22}Al_{5.95}Si_{6.05}O_{23.90}(SO_4)_{0.15}Cl_{3.76}$

It may be written in simplified form, having regard for the crystal-chemistry of davyne-like minerals, as:

$[(Na,K)_6Cl_2][Ca_2Cl_2][(Si_6Al_6O_{24})]$ (Z = 4)

where the square brackets successively include the chemical content of channels, cages, and framework [1].

It is worth noting that, besides the metrical differences, discriminating chemical differences also exist among davyne, microsommite and quadridavyne, namely in the kind of anion located within the large channels. In davyne both $(SO_4)^{2-}$ and Cl^- occur, whereas quadridavyne and microsommite represent the ideal sulfate-, and chlorine-free end-members, respectively. We carried out several microprobe and SEM-EDS analyses on these minerals which confirmed such a behaviour (Fig. 2).

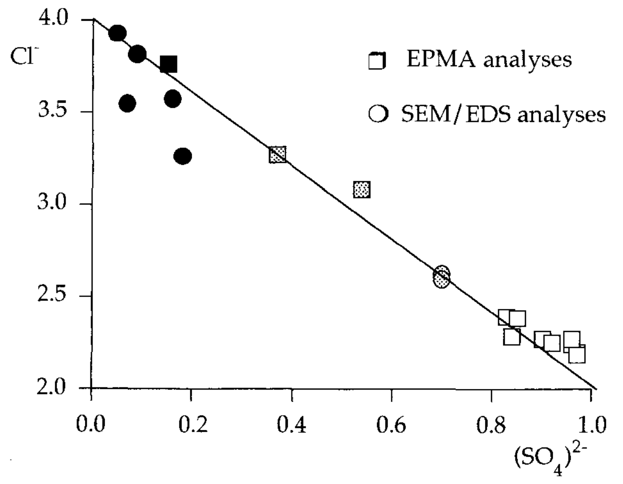

Fig. 2. Plot of Cl *vs.* (SO_4) in atoms per formula unit for selected SEM/EDS and EPMA analyses of quadridavyne (filled), davyne (dotted), and microsommite (open).

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[1] We choose an unusual basis for the recalculation, namely the number of tetrahedral cations, rather than other more common bases, such as total number of oxygens or anions, because of the undefined crystal-chemical role of the complex anion $(SO_4)^{2-}$, which however affects the amount of chlorine within the channels.

X-ray diffraction study

All minerals of both the cancrinite and davyne sub-groups present the same structural topology and a common sub-cell. The multiplication of the unit cells in microsommite, and quadridavyne suggests for these minerals ordering phenomena of cations and anions within the large channels of the structure. This has been confirmed by their thermal behaviour: on progressive heating, the intensity of superstructure reflections continuously decreases and vanishes at temperatures of *ca.* 600°C for quadridavyne and *ca.* 750°C for microsommite, and two davyne-like structures are finally obtained (Bonaccorsi *et al.*, 1993).

As the multiple cells are merely the result of the interrelated ordering of the alkaline cations and chlorine anions within neighboring channels, the intensity of all superstructure reflections in these minerals is weak to very weak. In quadridavyne the superstructure reflections are those with at least one of the *h* and *k* indices odd, whereas in microsommite are those with $h - k \neq 3n$. This is obviously also reflected in the powder pattern of these minerals. The X-ray powder pattern (Gandolfi technique) of quadridavyne is reported (Table 2) only for the sake of completeness in the description of this new minerals, but it seems useful to point out that a reliable crystallographic distinction between quadridavyne and davyne may be performed only with the help of long-exposed single-crystal diffraction photographs.

The following unit-cell parameter were refined through least-square fit of 2θ values of 24 accurately centered reflections (37° < 2θ < 41°): $a = 25.771(6)$, $c = 5.371(1)$ Å.

Structure analysis (preliminary data)

Among a number of crystals previously tested by Weissenberg method, a crystal of quadridavyne, with dimensions of *ca.* 0.3 x 0.3 x 0.8 mm, which presented a higher intensity of superstructure reflections, was chosen for the intensity data collection. The intensity data set was collected with an Ital Structures four-circle diffractometer (graphite monochromated Mo*K*α radiation, $\lambda = 0.71069$ Å, scan mode ω-2θ, scan range 6°-60° in 2θ, scan width 1.2° in θ, minimum scan speed 1.5°/min, proportionally increased on the basis of the intensity of a pre-scan of the peaks). Of the 6503 measurements, only reflections with $I > 3\sigma(I)$ were used in the refinement. The systematic absences indicated both $P6_3$ and $P6_3/m$ as possible space groups for quadridavyne. The latter has been assumed, on the basis of the length of the *c* parameter, which indicated the lack of tetrahedral tilting along [001] (Bonaccorsi, 1993).

A starting structural model for quadridavyne has been built up by means of the Distances Least Square computer program (Baerlocher *et al.*, 1978); the tetrahedral framework was assessed, and calcium and chlorine atoms were located within the undecahedral cages.

To find a plausible ordering scheme of cations and anions within the two channels, we tried to

Table 2. Powder pattern of quadridavyne (Gandolfi camera, Fe*K*α radiation, $\lambda = 1.93728$ Å). 14 more lines were measured with $d < 1.20$ Å. Decreasing scale of intensities: vS, S, m, w, vw.

	d_{meas}	d_{calc}	*hkl*
w	10.98	11.16	200
w	6.43	6.44	220
S	4.85	4.84	201
vS	3.71	3.72	600
vS	3.31	3.32	421
w	3.10	3.09	620
w	3.04	3.06	601
S	2.788	2.790	800
m	2.677	2.685 2.682	002 621
vw	2.514	2.511	730
m	2.474	2.479 2.476	222 801
vw	2.426	2.435 2.420	820 402
vw	2.296	2.301	502
m	2.147	2.148	660
vw	2.099	2.109	840
vw	2.062	2.063	442
vw	2.027	2.028	622
vw	1.961	1.962	841
w	1.933	1.935	802
vw	1.877	1.878	10.2.1
vw	1.834	1.835	860
m	1.804	1.804	822
w	1.735	1.736	861
w	1.609	1.611	880
w	1.529	1.529 1.529	12.0.2 10.6.1
vw	1.505	1.507	803
vw	1.477	1.478	14.2.0
m	1.380	1.381	882
w	1.349	1.350	16.0.1
w	1.293	1.295	14.2.2
vw	1.279	1.281	863
vw	1.268	1.269	16.2.1
w	1.246	1.246	12.6.2
w	1.237	1.238	16.0.2

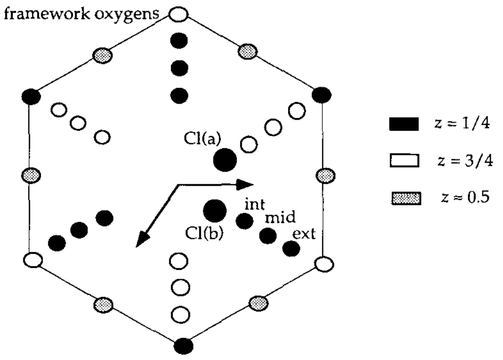

Fig. 3. Schematic cross-section of large channels as seen along [001], featuring the positions of chlorines and alkaline cations. For the sake of simplicity, the equivalent positions for chlorines have been omitted.

refine an average structure. This has been performed in two ways:

a) A refinement of davyne-type structure has been carried out using only a sub-set of reflections, namely those with both *h* and *k* even (halved *a* parameter with new indices $h' = h/2$, $k' = k/2$). The refinement converged to $R = 0.09$.

b) A crystal of quadridavyne has been heated in a furnace up to 600°C for 15 hours and then quenched. A disordered phase with cell parameters $a = 12.750$, $c = 5.383$ Å has been obtained. A new intensity data collection has been carried out on this sulfate-free davyne-like phase. The structural model has been refined to $R = 0.070$, $R_w = 0.063$.

Both refinements provided similar indications. As regards the tetrahedral framework and the contents of the undecahedral cages, no significant differences were observed with respect to the known structural data for related phases.

On the contrary, the alkaline cations unexpectedly seem to distribute among three different neighbour sites (Fig. 3). We shall call them external, middle, and internal sites, on the basis of their distance from the center of the channels. Potassium cations concentrate preferably in the internal sites, at reasonable distances from the oxygen atoms of the channel walls. Chlorine anions can find place in two distinct positions - Cl(a) and Cl(b) sites.

On these arguments, we tried to relate the occupancies of chlorine anions, on one side, and of alkaline cations Na^+ and K^+, on the other side, in the structure of quadridavyne. A sketch of two possible distribution schemes is shown in Fig. 4, in which the mutually exclusive site occupancies, as well as the consistency of the bond distances,

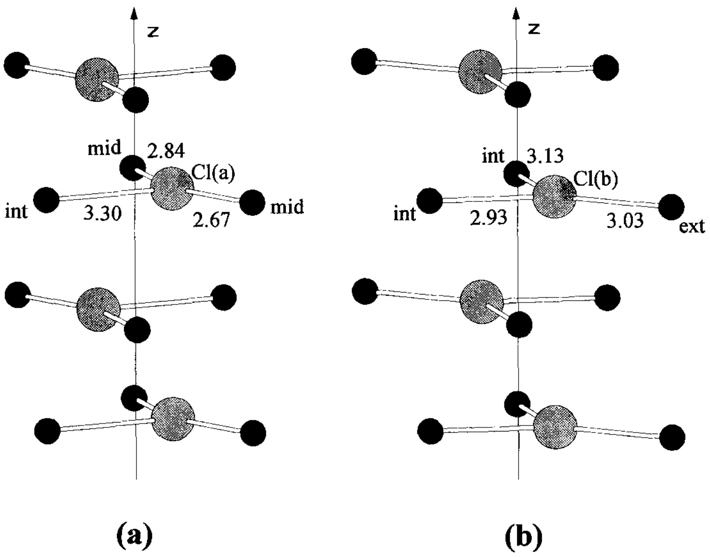

Fig. 4. The two possible distributions of alkaline cations around chlorines. (a): around Cl(a) site; (b): around Cl(b) site. Distances are given in Å.

Table 3. Site occupancies and non-definitive fractional coordinates for quadridavyne. M is the site multiplicity.

Site	M	Occupancy	x	y	z
Si1	1/2	1 Si	0.1615	0.2049	3/4
Si2	1/2	1 Si	0.2921	0.4597	3/4
Si3	1/2	1 Si	0.041	0.335	3/4
Si4	1/2	1 Si	0.2082	0.5408	1/4
Al1	1/2	1 Al	0.0345	0.2082	3/4
Al2	1/2	1 Al	0.299	0.333	3/4
Al3	1/2	1 Al	0.168	0.464	3/4
Al4	1/2	1 Al	0.209	0.6692	1/4
O1	1/2	1 O	0.105	0.215	3/4
O2	1/2	1 O	0.060	0.2844	3/4
O3	1	1 O	0.172	0.002	0.02
O5	1/2	1 O	0.294	0.399	3/4
O6	1/2	1 O	0.211	0.273	3/4
O7	1	1 O	0.667	−0.005	0.021
O8	1	1 O	0.669	0.506	0.508
O9	1/2	1 O	0.106	0.398	3/4
O10	1/2	1 O	0.223	0.445	3/4
O11	1	1 O	0.174	0.511	0.993
O13	1/2	1 O	0.220	0.608	1/4
O14	1/2	1 O	0.276	0.553	1/4
Ca1	1/6	1 Ca	2/3	1/3	3/4
Cl1	1/6	1 Cl	2/3	1/4	1/4
Ca2	1	1/6 Ca	0.334	0.169	1/4
Cl2	1	1/6 Cl	0.3130	0.1561	3/4
int(ab)	1/2	0.28 Na + 0.10 K	0.052	0.106	1/4
mid(ab)	1/2	0.24 Na + 0.12 K	0.068	0.139	1/4
ext(ab)	1/2	0.20 Na + 0.06 K	0.091	0.182	1/4
Cl(a)	1/2	0.1667 Cl	−0.018	0.024	1/4
Cl(b)	1/2	0.1667 Cl	0.029	0.047	1/4
int(c1)	1/2	1 Na	0.391	0.439	1/4
int(c2)	1/2	1 Na	0.587	0.414	1/4
ext(c)	1/2	1 K	0.591	0.683	1/4
Cl(c)	1/2	1 Cl	0.529	0.547	1/4

are considered. For instance, if Cl enters always the Cl(b) site, Na and K could occupy internal and external sites only; however, the occurrence of Cl in the Cl(a) site makes it necessary for Na and K to enter the middle site. Both schemes are compatible with the 2_1 symmetry, which realizes within channels at ($^1/_2$, $^1/_2$, *z*). In these channels the (b) schemes seems to prevail. Contrarily, within the channels at (0, 0, *z*) both (a) and (b) schemes realize; moreover, three statistically equivalent configurations, according to the 6_3 symmetry, may occur for each of them.

The complexity of the real structure of quadridavyne prevented us to refine the model in a satisfactorily way. The best *R* factor is at present 0.14. Provisional fractional coordinates are given in Table 3; however, the structural analysis of quadridavyne is still in progress.

A better knowledge of the ordering schemes within quadridavyne will be possible in one or more of the following ways:

a) By finding a crystal with the highest degree of order, *i.e.* with the maximum intensity of superstructure reflections, and carrying on it a new intensity data collection, possibly using synchrotron radiation.

b) Through the simulation of minimum-energy structures, obtained by the application of mechanical statistics models, and the evaluation of the interaction energies between next-neighbour, and next-nearest-neighbour, channels, in a two-dimensional Ising model (Yeomans, 1988).

c) By increasing the ordering of quadridavyne by means of thermal experiences, namely re-ordering at given temperatures crystals previously disordered at higher temperatures. Such a procedure has been successfully applied to microsommite (Bonaccorsi *et al.*, 1993).

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