# CARBONATE GROUPS IN DAVYNE:
# STRUCTURAL AND CRYSTAL-CHEMICAL CONSIDERATIONS

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ABSTRACT

We have refined the crystal structure of a specimen of davyne from Mt. Vesuvius, Italy, characterized by the presence of a significant amount of carbonate. The crystals have $P6_3$ symmetry, with cell parameters $a$ 12.6916(9), $c$ 5.3333(5) Å. The chemical formula, obtained through electron-microprobe analysis, is $(Na_{4.58}K_{0.67}Ca_{2.56})(Si_{6.06}Al_{5.94}O_{23.94})Cl_{2.35}(CO_3)_{0.88}(SO_4)_{0.19}$. According to its structural and chemical features, it may be classified as carbonate-bearing davyne, as it represents an intermediate phase between davyne *sensu stricto* and a hypothetical $CO_3$ end-member. The carbonate groups are located inside the large channel as in cancrinite *sensu stricto*; their position is influenced by the presence of a limited number of $SO_4$ groups. In fact, the triplets of oxygen atoms of the carbonate groups may alternatively be involved in the tetrahedral coordination of $SO_4$. Because of the short C–C contacts, a deviation from stoichiometry may be expected. This fact, as well as a deficiency of cations, were observed in the structural refinement and confirmed by the electron-microprobe data.

*Keywords*: $CO_3$-bearing davyne, cancrinite-group, feldpathoid, structure refinement.

SOMMAIRE

Nous avons affiné la structure cristalline d'un échantillon de davyne provenant du mont Vésuve, en Italie, dans lequel il se trouve une présence importante de carbonate. Les cristaux possèdent une symétrie $P6_3$, et les paramètres réticulaires $a$ 12.6916(9), $c$ 5.3333(5) Å. La formule chimique, établie à partir des résultats d'analyses chimiques, est $(Na_{4.58}K_{0.67}Ca_{2.56})(Si_{6.06}Al_{5.94}O_{23.94})Cl_{2.35}(CO_3)_{0.88}(SO_4)_{0.19}$. Selon ses attributs structuraux et chimiques, on peut qualifier cet échantillon de davyne carbonatée, ou de membre de la solution solide entre davyne *sensu stricto* et un pôle hypothétique à $CO_3$. Les groupes $CO_3$ occupent un canal spacieux, comme dans la cancrinite *sensu stricto*; leurs positions dépendent de la présence d'un nombre limité de groupes $SO_4$. En fait, les triplets d'atomes d'oxygène des groupes $CO_3$ pourront alternativement être impliqués dans les agencements tétraédriques des groupes $SO_4$. A cause des rapprochements C–C, on peut s'attendre à un écart à la stoechiométrie. Ce phénomène, ainsi qu'un déficit en cations, ont été confirmés lors de l'affinement structural et par les données de microsonde électronique.

(Traduit par la Rédaction)

*Mots-clés*: davyne à $CO_3$, minéral du groupe de la cancrinite, feldpathoïde, affinement de la structure.

## INTRODUCTION

Cancrinite-like minerals are characterized structurally by various cages and channels formed by the stacking along $z$ of layers of six-membered rings of (Si,Al)-tetrahedra. Each ring is linked to three rings in the preceding layer and to three other rings in the succeeding one; if $A$ is considered the position of the starting layer, the successive layer may occupy the positions $B$ or $C$, as schematically illustrated in Figure 1a. The types of stacking sequences have been related to anion contents, and compositional ranges have been predicted for the various members of the family (Ballirano *et al.* 1996). Molecules of $H_2O$ and different anions, most commonly $SO_4$, Cl, $CO_3$, are found within the cages of tetrahedra, and their amount is controlled by geometrical constraints. Because of their relatively low framework density, on the order of 15.5–17 tetrahedra per 1000 Å$^3$, these phases have in the past been included among zeolites (Meier & Olson 1992), although they
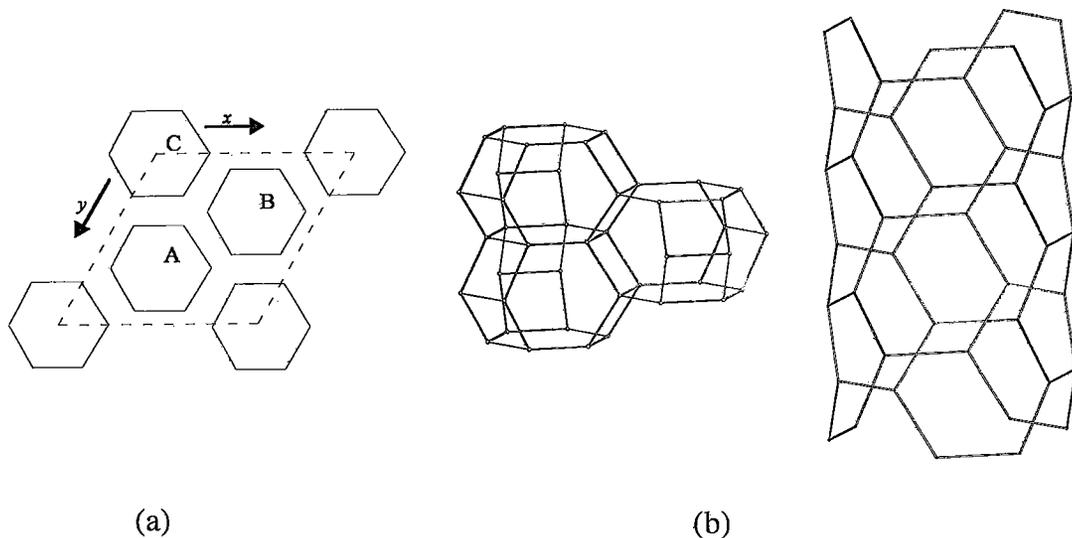
FIG. 1. (a) Schematic [001] drawing of the framework of a cancrinite-like mineral. The three different positions ($A = \frac{1}{3}, \frac{2}{3}, z$; $B = \frac{2}{3}, \frac{1}{3}, z$; $C = 0, 0, z$) occupied by the centers of the six-membered rings of tetrahedra are indicated. (b) Undecahedral cages and free-channel resulting from the $AB...$ stacking sequences.

have been left out of the listing of zeolites in the recent IMA report on zeolite nomenclature (Coombs *et al.* 1997).

Only in the last decade have reliable electron-microprobe analyses of these materials been available, and over the same period, infrared (IR) spectroscopy has become widely used to detect and quantify the proportions of $H_2O$ and $CO_3^{2-}$. The presence of $H_2O$ and $CO_3^{2-}$ in many members of the family, especially those with complex stacking sequences, was uncertain on the basis of the older analytical data. In fact, the very large amount of $H_2O$ and $CO_3^{2-}$ observed by some authors contrasts with the limited volume available inside the framework. This discrepancy has been attributed to the strong tendency of these phases to adsorb moisture, and to the presence of calcite impurities. Calcite as well as dolomite commonly occur associated with cancrinite-like minerals, but their presence may easily be detected by means of IR spectroscopy (Ballirano *et al.* 1996).

All the cancrinite-like minerals with $AB$ stacking sequence are characterized by uninterrupted stacks of "undecahedral cages" (*i.e.*, cages delimited by five six-membered rings plus six four-membered rings of tetrahedra) and by a wide channel running along $z$ (Fig. 1b). The ideal chemical formulae of the known minerals with the $AB$ stacking sequence are reported in Table 1. The $AB$ minerals have been classified into two subgroups: cancrinite-type minerals and davyne-type minerals (Bonaccorsi *et al.* 1990). In the former (cancrinite and vishnevite, which form a solid solution investigated by Hassan & Grundy (1984); pitiglianoite), the base-shar-

ing cages host $Na...H_2O-Na...H_2O-Na$ chains, whereas in davyne-type minerals (davyne, quadridavyne, microsommite...), $Ca-Cl-Ca-Cl-$ chains occur. The remaining extraframework anions and cations are located inside the large channel. If the proportions of the anions occupying the large channels are plotted on a $CO_3-SO_4-Cl$ triangular diagram (Fig. 2), all the known samples of cancrinite-type minerals are located along the $CO_3-SO_4$ join. Only hydroxycancrinite (Nadezhina *et al.* 1991) falls outside this plot because it contains only hydroxyl groups as anions. The channels of the davyne-type minerals, in contrast, contain $(SO_4)^{2-}$ and $Cl^-$ anions (Fig. 2).

TABLE 1. IDEAL CHEMICAL FORMULAE* OF THE MINERALS WITH THE AB... STACKING SEQUENCE

| Cancrinite-Type Minerals | | | |
|---|---|---|---|
| cancrinite | $[(Na,Ca)_{5-6}(CO_3)_{1.2-1.7}]$ | $[Na_2(H_2O)_2]$ | $[Si_6Al_6O_{24}]$ |
| vishnevite | $[(Na,K)_6(SO_4)]$ | $[Na_2(H_2O)_2]$ | $[Si_6Al_6O_{24}]$ |
| hydroxycancrinite | $[(Na,K)_6(OH)_2]$ | $[Na_2(H_2O)_2]$ | $[Si_6Al_6O_{24}]$ |
| pitiglianoite | $[Na_6K_2(SO_4)]$ | $[Na_2(H_2O)_2]$ | $[Si_6Al_6O_{24}]$ |

| Davyne-Type Minerals | | | |
|---|---|---|---|
| microsommite | $[Na_4K_2(SO_4)]$ | $[Ca_2Cl_2]$ | $[Si_6Al_6O_{24}]$ |
| quadridavyne | $[Na_6K_2Cl_2]$ | $[Ca_2Cl_2]$ | $[Si_6Al_6O_{24}]$ |
| davyne | $[Na_6K_2(SO_4)_{0.5}Cl]$ | $[Ca_2Cl_2]$ | $[Si_6Al_6O_{24}]$ |
| $CO_3$-bearing davyne | $[(Na,K,Ca)_{5-6}(CO_3,SO_4,Cl)_{1-2}]$ | $[Ca_2Cl_2]$ | $[Si_6Al_6O_{24}]$ |

* The three distinct structural elements (channel, cages and framework) are emphasized.
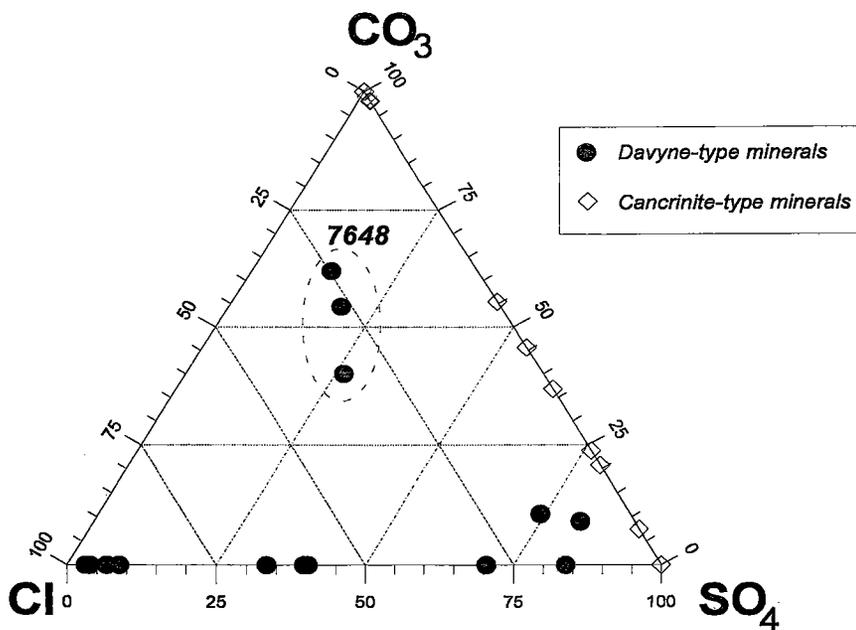
FIG. 2. Anion content of the large channel of the minerals with *AB...* stacking sequence. The dashed line indicates three samples of $CO_3$-bearing davyne, the label "7648" indicates the crystal described in this work. The list of reference data used to derive this graph is available from the authors upon request.

Unlike cancrinite, which generally shows superstructures along the $z$ direction due to ordering of vacancies (Grundy & Hassan 1982, Hassan & Buseck 1992), quadridavyne (the Cl-bearing member) shows a superstructure on the $xy$ plane, which doubles the $a$ cell parameter (Bonaccorsi *et al.* 1994). This superstructure has been interpreted as the result of the ordering of Na and K cations within neighboring channels (Bonaccorsi 1993); this phenomenon also occurs in microsommite, the davyne-related member of the family showing cell parameters $a_{mic} = \sqrt{3}\ a_{dav}$, $c_{mic} = c_{dav}$ (Merlino *et al.* 1991), and in pitiglianoite, the vishnevite-related member, showing cell parameters $a_{pit} = \sqrt{3}\ a_{vis}$, $c_{pit} = c_{vis}$ (Merlino *et al.* 1991).

Ballirano *et al.* (1996) showed, on the basis of IR spectroscopy, that some samples of davyne may contain relatively large amounts of $CO_3$. This fact indicates the possible presence of a further $CO_3$-bearing end-member. Our purpose here is to investigate through single-crystal refinement the role of the carbonate groups in davyne.

### EXPERIMENTAL

A fragment (approximately $0.4 \times 0.5 \times 0.5$ mm) of a crystal of sample MMUR (Mineralogical Museum of the University of Rome) 7648/35 was selected for single-crystal X-ray study. The crystal was found in a cav-

ity of an ejectum, mainly composed of pyroxene and mica, from Mt. Vesuvius (Italy). Miscellaneous data pertaining to the collection of intensity data and the structure refinement are reported in Table 2. The cell parameters $a$ 12.6916(9), $c$ 5.3333(5) Å were derived by a least-square procedure on 36 reflections ($15° < 2\theta < 30°$). A fragment of a different crystal from the same specimen was previously studied by Ballirano *et al.* (1996), and shows slightly different cell parameters [$a$

TABLE 2. MISCELLANEOUS DATA OF THE REFINEMENT OF $CO_3$-BEARING DAVYNE

| | | | |
|---|---|---|---|
| Crystal system | | hexagonal | |
| Space group | | $P6_3$ | |
| $a$ (Å) | 12.6916(9) | $c$ (Å) | 5.3333(5) |
| Diffractometer | | Siemens P4 | |
| Radiation | | Mo$K\alpha$ | |
| Crystal size (mm) | | $0.4 \times 0.5 \times 0.5$ | |
| Scan mode | $\omega$ | Scan speed | 3 – 30°/min* |
| $2\theta_{max}$ | 70° | | |
| Number of measured reflections | | 1315 | |
| Number of independent reflections | | 1187 | |
| Number of observed reflections $F_o > 4\sigma(F_o)$ | | 1114 | |
| $R_{int}$ (%) | 1.04 | | |
| Number of refined parameters | | 117 | |
| $R$ (%) | 3.56 | $wR^2$ (%) | 9.40 |
| Refinement program | | SHELXL-93 | |

*according to reflection intensity estimated by a prescan.

12.6946(7), $c$ 5.3364(4) Å], possibly due to very subtle differences in chemical composition. The sample in the present study was chosen because it contains the largest amount of $CO_3$ among those studied by Ballirano *et al.* (1996).

<center>STRUCTURE REFINEMENT</center>

The structure refinement was carried out in the space group $P6_3$, as indicated by the Laue symmetry $6/m$ of the diffraction pattern and by the systematic absences of the reflections $(00l)$ with $l = 2n + 1$. The space group $P6_3/m$ was discarded, as the observed unit-cell parameter $c$ is too short. In fact, the presence of a horizontal mirror plane implies that one of the edges of the tetrahedra is vertical, and the resulting $c$ parameter has to increase to ~5.4 Å, as happens in davyne from Vesuvius (Bonaccorsi *et al.* 1990) and in heated samples (Bonaccorsi *et al.* 1995).

Starting positional parameters of the atoms of the framework, as well as calcium and chlorine atoms located inside the "undecahedral" cages, were those obtained by Bonaccorsi *et al.* (1992) for the sample of davyne from Zabargad. All the other atoms were located through Fourier syntheses.

The cations of the large channels were found to be distributed over three distinct sites $M1$, $M2$, and $M3$. Partial site-occupancies were refined using the scattering power of Ca; the actual chemical contents were derived by assuming full occupancy of the set of split sites ($M1 + M2 + M3$). We obtained Na (81%) and K + Ca (19%) from the refined partial occupancies.

Two maxima in the electron-density map, located at 0.06, 0.12, 0.17, and 0.06, 0.12, 0.38, were attributed to the oxygen atoms OC(1) and OC(2) belonging to carbonate groups or sulfate groups (or both). Their occupancies were refined as 0.29 and 0.19, respectively. A maximum at 0, 0, 0.28 was assigned to a sulfur atom, and its partial occupancy, 0.09, was fixed in accordance with results of the electron-microprobe analysis. The same occupancy was imposed to the apical oxygen atom OS of the $SO_4$ tetrahedron, located at 0, 0, –0.02. The S–O distances were 1.43 and 1.52 Å, respectively, for the basal OC(2) and apical OS oxygen atoms. A different orientation of the sulfate tetrahedron, involving three OC(1) atoms and the OS. atom located at 0, 0, 0.48, was discarded, because of the short contact-distance between S and OS' (1.14 Å).

In order to reduce the correlations among the various parameters, a set of constraints was introduced at this point of the refinement. Two maxima in the electron density, attributed to carbon atoms C(1) and C(2), were found at the centers of the triplets of oxygen atoms OC(1) and OC(2), respectively. The occupancies of C(1) and OC(1) were constrained to be equal, whereas the occupancy of C(2) was fixed to the calculated value 0.10, as the triplet of oxygen atoms OC(2) may belong both to carbonate and sulfate groups. The

two carbonate groups were considered to be perfectly planar, with the same $z$ coordinate for the oxygen and carbon atoms of a given $CO_3$ group, whereas the displacement parameters of the two carbon atoms and those of the two oxygen atoms were constrained to be equal. At this point of the isotropic refinement, the $R$ agreement index was of the order of 7%. All the atoms, apart from C(1), C(2), S, and OS, were then refined anisotropically, and the $R$ index dropped to 3.7%. A careful scrutiny of the ΔF map revealed a further maximum of electron density located at 0.05, 0.08, 0.13. In keeping with the electron-microprobe results, which gives 0.35 additional chlorine atoms (corresponding to 1.1 wt.%), and with the structure of other samples of davyne (Bonaccorsi *et al.* 1990, 1992), this maximum was attributed to chlorine atom Cl(1), with fractional occupancy. The strong correlation between occupancy and isotropic thermal parameter of Cl(1) led to only a rough estimate of both. Because of this, we preferred to set the isotropic thermal parameter of Cl(1) equal to the refined equivalent $U$ of the chlorine atom Cl, placed within the "undecahedral" cage. The resulting refined occupancy of Cl(1) gave 0.29 additional chlorine atoms per formula unit, in agreement with the value derived from the electron-microprobe data.

The final $R$ index was of 3.56% for 1114 $F_{obs} > 4\sigma$ ($F_{obs}$) and 3.97% for all 1187 data; the $wR^2$ index was 9.40% for 1114 $F_{obs} > 4\sigma$ ($F_{obs}$) and 9.82% for all 1187 data. Fractional coordinates, site multiplicities, occupancies, and equivalent or isotropic thermal parameters are reported in Table 3, anisotropic thermal parameters in Table 4 and relevant bond-distances are listed in

TABLE 3. FRACTIONAL COORDINATES, SITE MULTIPLICITIES, OCCUPANCIES, AND EQUIVALENT OR ISOTROPIC THERMAL PARAMETERS, $CO_3$-BEARING DAVYNE

| Atom | $x$ | $y$ | $z$ | Site multiplicity | Occupancy | $U_{eq}$ ($\times 10^4$) |
|---|---|---|---|---|---|---|
| Si | 0.32745(5) | 0.40795(5) | 0.746(3) | 6 | 1 | 80(1) |
| Al | 0.06911(6) | 0.40807(6) | 0.746(3) | 6 | 1 | 83(2) |
| O1 | 0.2138(2) | 0.4297(2) | 0.717(3) | 6 | 1 | 254(6) |
| O2 | 0.0977(2) | 0.5557(2) | 0.741(3) | 6 | 1 | 168(3) |
| O3 | 0.0030(2) | 0.3254(2) | 0.018(3) | 6 | 1 | 202(5) |
| O4 | 0.3147(2) | 0.3354(2) | 0.001(3) | 6 | 1 | 197(5) |
| Ca | 2/3 | 1/3 | 0.218(3) | 2 | 1 | 184(2) |
| Cl | 0.336(4) | 0.650(2) | 0.221(3) | 6 | 1/3 | 793(38) |
| $M1$ | 0.1179(5) | 0.2459(6) | 0.288(3) | 6 | 0.340(4)* | 314(8) |
| $M2$ | 0.119(1) | 0.234(1) | 0.219(4) | 6 | 0.169(4)* | 398(27) |
| $M3$ | 0.154(1) | 0.316(2) | 0.260(4) | 6 | 0.125(4)* | 707(38) |
| C(1) | 0 | 0 | 0.167(4) | 2 | 0.29(1) | 198(29) |
| OC(1) | 0.114(1) | 0.059(1) | 0.167(4) | 6 | 0.29(1) | 568(50) |
| C(2) | 0 | 0 | 0.380(6) | 2 | 0.10 | 198(29) |
| OC(2) | 0.118(2) | 0.060(2) | 0.380(6) | 6 | 0.19(1) | 568(50) |
| S | 0 | 0 | 0.266(7) | 2 | 0.09 | 261(27) |
| OS | 0 | 0 | 0.98(1) | 2 | 0.09 | 321(94) |
| Cl(1) | 0.014(6) | 0.059(4) | 0.08(1) | 6 | 0.048(5) | 793 |

* Refined partial occupancies of the split $M$ sites by using the scattering factor of Ca. Assuming a full occupancy for ($M1 + M2 + M3$), a chemical content of 81% Na and 19% (Ca+K) was obtained; on the basis of these values, the occupancies become 0.536, 0.267 and 0.197 for $M1$, $M2$ and $M3$, respectively.

Table 5. A table of structure factors is available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

## DESCRIPTION OF THE STRUCTURE

### Framework

The framework of tetrahedra in this variety of davyne differs very little from that in the other davyne-type minerals. The unit cell contains two undecahedral

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS $U_{ij}$ ($\times 10^4$), $CO_3$-BEARING DAVYNE

|  | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Si | 66(2) | 82(2) | 97(3) | 6(3) | 4(3) | 40(2) |
| Al | 77(2) | 84(2) | 95(3) | 4(3) | 3(3) | 47(2) |
| O1 | 117(7) | 267(9) | 437(19) | 108(12) | 44(10) | 140(7) |
| O2 | 195(7) | 103(6) | 225(9) | 0(9) | 1(10) | 89(6) |
| O3 | 274(11) | 201(10) | 193(13) | 85(9) | 139(9) | 164(9) |
| O4 | 183(10) | 204(11) | 160(13) | 72(8) | -50(8) | 64(9) |
| Ca | 148(2) | 148(2) | 256(7) | 0 | 0 | 74(1) |
| Cl | 1357(71) | 1119(79) | 211(14) | -247(48) | -283(54) | 849(61) |
| M1 | 209(13) | 432(17) | 381(23) | -41(19) | 48(16) | 222(13) |
| M2 | 337(37) | 715(71) | 357(48) | -71(43) | 94(37) | 423(46) |
| M3 | 549(58) | 1622(130) | 344(42) | -66(106) | -46(63) | 840(84) |
| OC(1) | 222(30) | 276(32) | 1200(145) | -178(87) | -13(79) | 120(25) |
| OC(2) | 222(30) | 276(32) | 1200(145) | -178(87) | -13(79) | 120(25) |

TABLE 5. RELEVANT BOND-DISTANCES (Å), $CO_3$-BEARING DAVYNE

| Si | – O1 | 1.606(2) | Al | – O1 | 1.723(2) |
|---|---|---|---|---|---|
|  | – O2$^a$ | 1.604(2) |  | – O2 | 1.721(2) |
|  | – O3$^b$ | 1.622(3) |  | – O3$^c$ | 1.736(3) |
|  | – O4$^c$ | 1.607(3) |  | – O4$^d$ | 1.750(3) |
| mean value | | 1.610(7) | mean value | | 1.732(12) |
| | | | | | |
| M1 | – O3 | 2.588(7) | M2 | – O3 | 2.52(1) |
|  | – O3$^b$ | 2.612(6) |  | – O3$^b$ | 2.78(2) |
|  | – O4$^d$ | 2.586(6) |  | – O4 | 2.45(1) |
|  | – O4 | 2.651(6) |  | – O4$^d$ | 2.87(1) |
|  | – OC(1) | 2.43(2) |  | – OC(1) | 2.21(2) |
|  | – OC(1)$^e$ | 2.43(1) |  | – OC(1)$^e$ | 2.29(2) |
|  | – OC(1)$^d$ | 2.49(2) |  | – OC(2) | 2.37(3) |
|  | – OC(2)$^e$ | 2.38(2) |  | – OC(2)$^e$ | 2.41(3) |
|  | – OC(2) | 2.41(3) |  | – OC(2)f | 2.22(3) |
|  | – OC(2)$^f$ | 2.60(3) | | | |
| | | | Ca | – O1$^{g,h,i}$ | 2.605(2) × 3 |
| M3 | – O1 | 2.74(1) |  | – O2$^{g,h,i}$ | 2.594(2) × 3 |
|  | – O3 | 2.36(1) |  | – Cl$^{g,h,i}$ | 2.656(5) |
|  | – O3$^b$ | 2.54(1) |  | – Cl$^{j,k,k}$ | 2.696(6) |
|  | – O4 | 2.37(1) | | | |
|  | – O4$^d$ | 2.55(1) | S | – OC(2)$^{e,l}$ | 1.43(2) × 3 |
|  | – Cl(1) | 2.98(5) |  | – OS$^m$ | 1.52(4) |
| | | | | | |
| C(1)–OC(1)$^{e,l}$ | | 1.25(1) × 3 | C(2)–OC(2)$^{e,l}$ | | 1.29(2) × 3 |

$a = -y+1, x-y+1, z;$    $b = y, -x+y, z+\frac{1}{2};$    $c = x, y, z+1;$
$d = x-y, x, z+\frac{1}{2};$    $e = -y, x-y, z;$    $f = x-y, x, z-\frac{1}{2};$
$g = -x+1, -y+1, z-\frac{1}{2};$    $h = y, -x+y, z-\frac{1}{2};$    $i = x-y+1, x, z-\frac{1}{2};$
$j = -x+1, -y+1, z+\frac{1}{2};$    $k = -x+y-1, x, z+\frac{1}{2};$    $l = -x+y, -x, z;$
$m = x, y, z-1.$
The short distances considered as non occurring, because of partial occupancy, have not been included in the list.

cages, located along $[\frac{1}{3} \frac{2}{3} z]$ and $[\frac{2}{3} \frac{1}{3} z]$, and a large channel along $[0\ 0\ z]$. The structure has a perfect Si–Al order, in keeping with the 1:1 ratio of Al to Si, as indicated by the <Si–O> bond distance of 1.610(7) Å and the <Al–O> bond distance of 1.732(12) Å, leading to a <Si–O>/<Al–O> value of 0.93 (Hassan & Grundy 1990).

### Undecahedral cages

The calcium atoms are located on a three-fold axis, at the center of the bases of the undecahedral cages. The bond distances [Ca–O1 = 2.605(2) Å, Ca–O2 = 2.594(2) Å] with six oxygen atoms at the base of the cage are quite similar. The Cl atom is located near the center of the cage and is disordered over three symmetry-related positions, each with 1/3 occupancy, slightly displaced off-axis. The two Ca–Cl bond distances are similar [2.656(5) Å and 2.696(6) Å] giving rise to an almost perfect hexagonal bipyramidal coordination of Ca, and forming the Ca–Cl chains characteristic of davyne-type minerals.

### Large channel

Differences between this and other davyne-type minerals are revealed by comparing the content of the large channel. The Na,K,Ca cations are disordered over three distinct sites, M1, M2, and M3, each one with a different degree of occupancy (Fig. 3). The M1 site has the
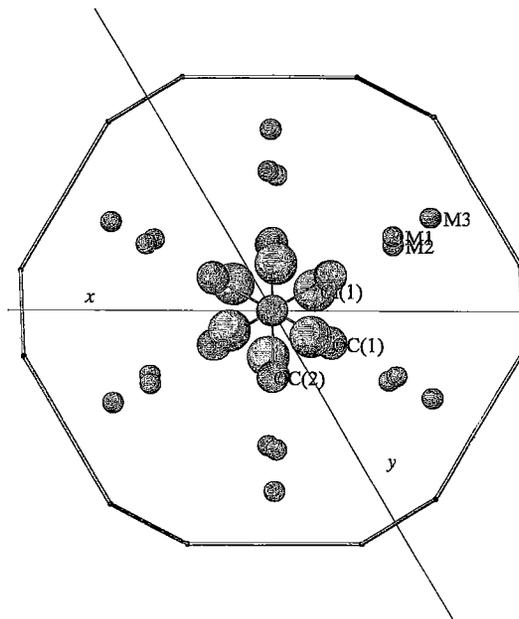


FIG. 3. The distribution of cations and anions inside the large channel, as seen along [001]. The numbering scheme also is indicated.

highest electron density, whereas $M2$ and $M3$ show low and similar values. The cations are located at three distinct $z$ elevations: $M1$ and $M3$ are located almost exactly between the two planes of oxygen atoms of the carbonate group, and their positions roughly correspond, respectively, to the "internal" and "external" cations of Bonaccorsi *et al.* (1990). $M2$ is substantially displaced along $z$, toward the OC(1) oxygen atoms. The total electron-density derived from the occupancy of the cation sites is equal to 12.68 $e^-$, which compares very favorably with the 12.65 $e^-$ inferred from the electron-microprobe results.

The carbonate groups (Figs. 4a, b) are distributed between two nonequivalent positions, C(1) and C(2), respectively, as previously found for cancrinite (Grundy & Hassan 1982). They are separated by 1.13(4) and 1.54(4) Å, compared to 1.23 and 1.33 Å (recalculated) in cancrinite. The C(1) carbonate site has an occupancy three times that of C(2), and their sum accounts for 0.78 carbonate groups per unit cell. The C(1)–OC(1) bond distance is 1.25(1) Å, and the C(2)–OC(2) bond distance is 1.29(2) Å.

The sulfur atom is located exactly midway between the two triplets of oxygen atoms, making favorable bond-distances with OC(2) [1.43(2) Å] and with the OS apical oxygen [1.52(4) Å]. The sulfate group may be present only with the apical oxygen OS pointing down

(Fig. 4a), as the opposite orientation implies a short S–OS contact-distance of 1.14 Å.

As regards the chlorine atom Cl(1) (Figs. 3, 4b), it is bonded to Na,K,Ca cations located in $M$ sites. $M1$ and $M2$ have one "impossible" short contact with it [2.34(5) and 2.08(5) Å, respectively]: the simultaneous occupancy of the sites involved may be easily avoided, owing to partial occupancies, and these "impossible" distances do not actually occur.

The formula derived from the structure refinement, in which the content of the different structural elements (channel, cages, and framework) is reported separately, is: $[Na_{4.88}(K,Ca)_{1.12}Cl_{0.29}(CO_3)_{0.78}(SO_4)_{0.18}]$ $[Ca_2Cl_2]$ $[Si_6Al_6O_{24}]$, in good agreement with $[Na_{4.58}K_{0.67}Ca_{0.56}Cl_{0.35}(CO_3)_{0.88}(SO_4)_{0.19}][Ca_2Cl_2][Si_{6.06}Al_{5.94}O_{23.94}]$ from the electron-microprobe and IR data of Ballirano *et al.* (1996).

## DISCUSSION

As previously stated, the large channel of davyne-type minerals contains large amounts of $SO_4$ and Cl, and it is possible to identify a Cl- and a $SO_4$-bearing end-member (quadridavyne and microsommite, respectively). On the basis of the chemical data of Ballirano *et al.* (1996) and the results of the present refinement, we infer the existence of a $CO_3$-bearing end-member as
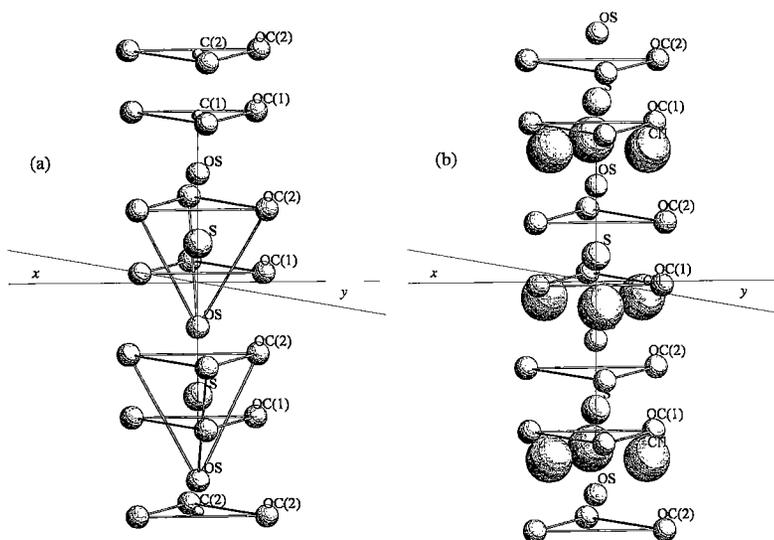


FIG. 4. Schematic drawing of the anionic content of the channel. In (a), the tetrahedral coordination of the sulfur atom is shown in both possible positions; obviously, only one of them may be occupied. The same geometrical constraints exist for the occupancies of C(1) and C(2). In (b), the positions of the chlorine atom Cl(1) are reported as well. Even in this case, the occurrence of a chlorine atom in one of the three symmetry-related positions influences the occupancies of the other anionic sites.

well. Sample 7648 shows an intermediate composition, with more than 50% of the anion content of the channel consisting of $CO_3$ groups. The distribution of the carbonate groups in this structure is very close to that shown by Grundy & Hassan (1982) for cancrinite; in both cases, the anions are split and distributed over four planes. The reported differences in the separation distances between planes may be due to the presence, in our case, of small but significant amounts of S and Cl, which impose geometrical adjustments to the positions of the oxygen atoms. However, despite this chemical and structural similarity to cancrinite, this sample is more properly classified as a $CO_3$-bearing davyne, because it contains ...Ca–Cl–Ca–Cl–Ca... chains running along $z$, a feature distinctive of davyne-type minerals.

The anion content of the free channel of various davyne- and cancrinite-type minerals, obtained from reference data, is represented in Figure 1. Two schemes of substitution have been proposed: (a) $2Cl^- \rightleftharpoons SO_4^{2-}$ (Bonaccorsi et al. 1990), and (b) $2CO_3^{2-} \rightleftharpoons SO_4^{2-}$ (Ballirano et al. 1996). The latter has been already discussed by Hassan & Grundy (1984) in the content of a cancrinite – vishnevite solid solution, and it is obviously

coupled with the compensating cationic substitution $2Ca^{2+} \rightleftharpoons 2Na^+$. In fact, Hassan & Grundy (1984) presented the cancrinite – vishnevite solid solution in terms of the ideal end-members $Ca_2Na_6Al_6Si_6O_{24}(CO_3)_2\bullet 2(H_2O)$ and $Na_8Al_6Si_6O_{24}(SO_4)\bullet 2(H_2O)$, respectively. As regards the chemical composition of the cancrinite end-member, it is worth noting that samples with $2CO_3$ groups per formula unit (pfu) are not known, the carbonate content usually ranging from 1.2 to 1.7 $CO_3$ pfu, as most clearly shown in Figure 5. This point has already been discussed by Hassan & Buseck (1992), who maintained that a $CO_3$ content less than two results in a decrease in the number of short C–C bond distances ($\approx 2.56$ Å), and therefore in a decrease of the structural strain (Hassan & Buseck 1992). Actually, these short distances probably never occur; in fact they are calculated from the average position of the carbonate groups. The relatively high $U_{33}$ displacement parameters of the atoms of the carbonate groups (Grundy & Hassan 1982) may indicate that they assume different positions slightly displaced from the average one, thus allowing more reasonable distances between adjacent $CO_3$ groups. A C–C bond distance of 2.56 Å is substantially
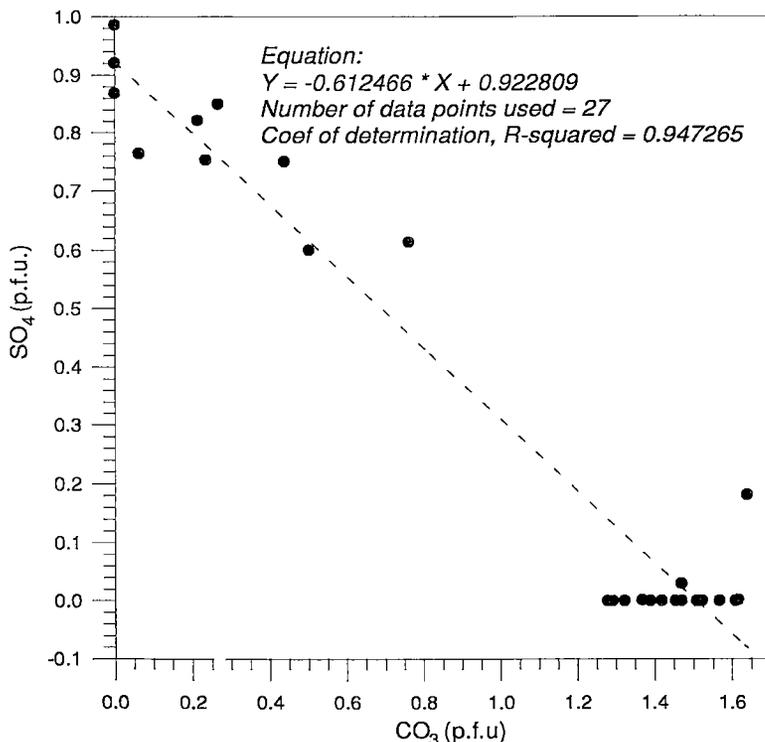


FIG. 5. Plot of proportion of $SO_4$ *versus* that of $CO_3$ in samples of the cancrinite – vishnevite solid- solution series. The list of reference data used to derive this graph is available from the authors upon request.

shorter than that reported by De Villiers (1971) for aragonite, 2.88 Å. If we consider 2.88 Å as the shortest possible C–C contact distance (aragonite forms at relatively high pressure), and assume a $c$ parameter for cancrinite of 5.12 Å, we obtain a maximum content of $CO_3$ for unit cell of the order of ~1.78, which is in close agreement with the data in the literature (Fig. 5). In the case of a hypothetical $CO_3$ end-member davyne, with $c = 5.33$ Å, the maximum number of $CO_3$ groups *pfu* increases to ~1.85, but for intermediate, $SO_4$-, $CO_3$- and Cl-bearing compositions, further geometrical restraints are imposed.

The ordering of $CO_3$ groups and vacancies in cancrinite (Hassan & Buseck 1992) gives rise to satellite reflections that correspond to a superstructure with $c = 8c_{can} \approx 40.9$ Å. In davyne from Zabargad also, superstructure reflections were observed (Bonaccorsi *et al.* 1992) with doubled $a$ and $c$ parameters; such a superstructure may be attributed to the ordering of two differently oriented $SO_4$ tetrahedra within the channel, as well as to correlations of ordered distributions in adjacent channels. To detect possible effects of ordering in our $CO_3$-bearing davyne, we obtained long-exposed photographs with the oscillating-crystal method along [001] and the Weissenberg method, but we did not observe any superstructure reflection. We conclude that there is no evidence of symmetry lowering due to ordering schemes involving $CO_3$, $SO_4$, Cl, and vacancies inside the channel. It seems likely that the activation energy of this ordering process will be higher than for the relatively simple ordering of $CO_3$ and vacancies that takes place in cancrinite (Hassan & Buseck 1992); the diffusion along the channel of anions and anionic groups is probably prevented by their sizes, as well as by the large potassium cations that occupy the $M$ sites and that are absent in cancrinite. As regards the hypothetical $CO_3$ end-member davyne, which is supposed to contain many more than 1.85 carbonate groups per cell, an ordering process could be predicted, with the consequent development of a superstructure along $c$.

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