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The crystal structure of giuseppettite, the 16-layer member of the cancrinite–sodalite group

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Abstract

Giuseppettite, chemical formula $Na_{42}K_{16}Ca_6Si_{48}Al_{48}O_{192}(SO_4)_{10}Cl_2 \cdot 5H_2O$, space group $P31c$, $a = 12.856$, $c = 42.256$ Å, is the 16-layer member of the cancrinite–sodalite group. It is characterised by an ABABABACBABABABC... stacking sequence of layers. The crystal structure of giuseppettite was solved and refined against data collected at the Elettra synchrotron facility, using a $0.3 \times 0.2 \times 0.2$ mm^3 single crystal, twinned on (0 0 1), $\lambda = 0.9989$ Å, $R = 0.074$ for 3769 reflections, $R = 0.073$ for 3706 reflections with $F_o > 4\sigma(F_o)$. The structure contains two big cages ("giuseppettite" cages) along $[0, 0, z]$, and sequences *CCSCCCS* of "cancrinite" (*C*) and "sodalite" cages (*S*) both along $[1/3, 2/3, z]$ and $[2/3, 1/3, z]$. Four sulphate groups surrounded by sodium cations, and alternated with potassium cations, are located within the giuseppettite cages, whereas a partially ordered distribution of sulphate groups and chlorine anions occurs within the sodalite cages. The cancrinite cages host sodium cations and water molecules.

Keywords: Giuseppettite; Cancrinite-sodalite group; Crystal structure; Synchrotron data

1. Introduction

The main features of the cancrinite–sodalite group minerals and a list of them were recently reported elsewhere [1]. They are formed by the three-dimensional stacking of six-membered rings of tetrahedra in which each ring is linked to three other rings both in the preceding and succeeding layers. These minerals constitute a subgroup of the wider ABC-6 family, which includes also phases with double six-membered rings, possibly mixed with layers of single rings [2–4]. Giuseppettite ($a = 12.8$ Å $\approx a_{\text{cancrinite}}$, $c = 42.2$ Å $\approx 8c_{\text{cancrinite}}$) is the 16-layer member of the cancrinite–sodalite group. It was found in volcanic ejected blocks at Sacrofano, Biachella Valley, Latium, Italy [5]. The chemical formula derived from the microprobe analysis in Ref. [5] is $Na_{39.96}K_{14.64}Ca_{7.45}[Si_{47.69}Al_{48.28}Fe^{3+}_{0.03}]_{\Sigma=96}O_{190.97}(SO_4)_{10.68}Cl_{1.90}$, on the basis of $(Si+Al+Fe^{3+}) = 96$. An infra-red absorption spectrum [5] suggested that only traces of water and/or hydroxyl groups were present in the mineral. More recently, the crystal chemistry of giuseppettite, as well as of other minerals of the group, has been revised by Ballirano et al. [6]; their electron microprobe and IR data point to the chemical formula $Na_{39.88}K_{15.15}Ca_{7.13}Si_{48.09}Al_{47.91}O_{190.98}(SO_4)_{10.91}Cl_{1.56}F_{0.05} \cdot 7.3H_2O$.

The observed Laue symmetry and systematic absences [5] pointed to $P6_3/mmc$, $P6_3mc$ or $P\bar{6}2c$ as possible space groups. No structural data were published, even if Mazzi (personal communication, in Ref. [7]) suggested the stacking sequence ABABABACBABABABC..., where A, B, and C stands for the possible positions of the six-membered rings within the layers, following the notation of the close-packed structures. In the Zhdanov's notation [8], that sequence is described by the symbol $|11(4)11|11(4)11|$, whereas it is $(hhhhhccc)_2$ by using the Jagodzinski–Wyckoff notation. The resulting structure has topological symmetry $P6_3/mmc$, and it is formed by a sequence of big cages *G* along $[0, 0, z]$ (hereafter named "giuseppettite" cages, and corresponding to the symbol $[4^6 6^{23}]$ according to the IUPAC nomenclature [9]), whereas sequences of "cancrinite" and "sodalite" cages (corresponding to $[4^6 6^5]$ and $[4^6 6^8]$, respectively [9]) develop along $[1/3, 2/3, z]$ and $[2/3, 1/3, z]$. They form *CCSCCCS* columns (Fig. 1), where *C* and *S* indicate cancrinite and

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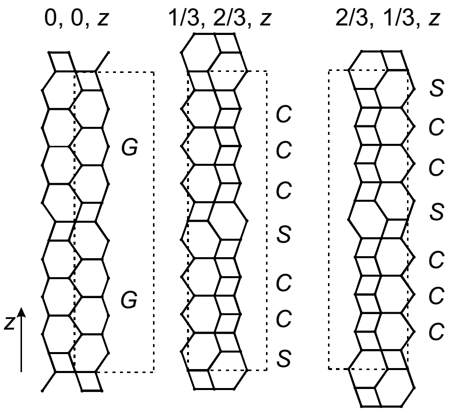


Fig. 1. The cages that built up the framework of giuseppettite: G = giuseppettite cage [$4^6 6^{23}$]; S = sodalite cage [$4^6 6^8$]; C = cancrinite cage [$4^6 6^5$]. The framework is projected along [1 0 0], and the unit cell is outlined. For sake of simplicity, the cages that are superimposed along $[0, 0, z]$, $[1/3, 2/3, z]$, and $[2/3, 1/3, z]$, are shown separately in (a), (b) and (c), respectively.

sodalite cages, respectively [6]. However, the real symmetry of giuseppettite is probably lower than $P6_3/mmc$: for example, the ordering of the Si and Al cations in the tetrahedral sites should reduce it at least to $P\bar{6}2c$, whereas further lowering of symmetry may result as consequence of the ordering of extra-framework ions. Real symmetries lower than the topological and/or topochemical symmetries are frequently observed in the cancrinite–sodalite group of minerals, whenever the extra-framework atoms are ordered in different sites within a given cage, or in different cages. For example, in microsommite [10], pitiglianoite [11] and quadridavyne [12], all of them showing ABAB... sequence of layers, supercells arise for the long-range ordering of Na and K cations as well as of sulphate or chlorine anions within the large channels of the structure. In nosean, showing ABC... stacking of layers, the ordering of $[Na_4(SO_4)]^{2+}$ and $[Na_4(H_2O)]^{4+}$ clusters in the sodalite cages is responsible for the lowering of the symmetry from $P\bar{4}2n$ to $P23$ [13]. In the recently described new mineral marinellite [1], one of the 12-layer members of the group, the observed symmetry $P31c$ is due to the ordering of chlorine anions and sulphate groups within the sodalite cages occurring in the structure.

2. Experimental and structure refinement

A single crystal of giuseppettite (0.3×0.2×0.2 mm^3) was mounted in the beamline 5.2 R-X-ray diffraction, at the Elettra synchrotron facility. The wavelength of the radiation was set to 1 Å; this value was successively checked by means of a powder pattern of silicon ($a = 5.43095$ Å), and scaled to 0.99890 Å. A 165 mm MarCCD detector was placed at 48 mm from the crystal. In this configuration, the resolution is about 1 Å ($2\theta_{max} = 59.8°$). Up to 63 frames with $\Delta\varphi = 3°$ were collected. The recorded images showed sharp reflections, without any streaking, or other indications of stacking disorder.

Table 1
Crystal data and structure refinement for giuseppettite

Space group	$P31c$
Unit cell dimensions	$a = 12.856(2)$ Å $c = 42.256(8)$ Å
Volume	6048.3(17) Å^3
Z	1
Density (calculated)	2.32 g/cm^3
Wavelength	0.99890 Å
$F(000)$	4239
Crystal size	0.3×0.2×0.2 mm^3
θ range for data collection	2.57–29.93°
Index ranges	$-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-36 \leqslant l \leqslant 37$
Reflections collected	23,601
Independent reflections	3769 [$R(\text{int}) = 0.0472$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3769/212/429
Goodness-of-fit on F^2	1.051
Final R indices [$F_o > 4\sigma(F_o)$]	$wR^2 = 0.2159$[a] $R = 0.0733$[b]
R indices (all data)	$wR^2 = 0.2191$[a] $R = 0.0741$[b]

[a] $wR^2 = \sqrt{\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4}$.

[b] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

The frames were processed with the HKL package of programs (XDISP, DENZO and SCALEPACK, [14]). The refined hexagonal unit cell has $a = 12.856(2)$, $c = 42.256(8)$ Å. Information concerning the data collection and refinement are listed in Table 1.

The output file contained 23,601 reflections having positive intensity. The structure was solved in the space group $P6_3/mmc$ by using automatic direct methods, with the program SHELXS-97 [15]. It was possible to locate most of the tetrahedral cations and oxygen atoms, as well as several extra-framework cations and anions. The position of the remaining atoms was obtained through successive Fourier syntheses. The resulting framework was in agreement with the stacking sequence proposed by Mazzi (personal communication, in Ref. [7]). As regards the extra-framework atoms, their nature was obtained from both the total scattering power of the sites and crystal chemical considerations. The isotropic refinement in the space group $P6_3/mmc$ converged to $R = 0.19$ for 1089 unique reflections with $F_o > 4\sigma(F_o)$. The average T–O bond distance was 1.65(2) Å for the five independent tetrahedral sites, and all the extra-framework atoms were split on two or more sites.

As previously suggested, the real symmetry of giuseppettite is lower than $P6_3/mmc$. In fact, the observed Si/Al = 1 ratio [5,6] suggests a regular alternation of Si- and Al-centred tetrahedra, in keeping with the Loewenstein rule. The isotropic refinement in the space group $P\bar{6}2c$, maximal non-isomorphic subgroup of

Table 2
Atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for giuseppettite[a]

A	x	y	z	U_{iso} or U_{eq}
Si1	0.2527(4)	0.0010(4)	−0.0229(3)	0.016(1)
Si2	0.4149(4)	0.0846(3)	−0.7732(4)	0.015(1)
Si3	−0.5829(5)	−0.6642(5)	−0.0856(4)	0.017(1)
Si4	−0.5851(4)	−0.6673(6)	0.5398(4)	0.017(1)
Si5	0.4135(4)	0.0856(4)	0.1025(4)	0.019(1)
Si6	0.4145(4)	0.0836(4)	−0.6484(4)	0.019(1)
Si7	−0.5862(4)	−0.6676(4)	−0.2103(4)	0.016(1)
Si8	−0.5860(4)	−0.6678(4)	0.6647(4)	0.016(1)
Al1	−0.2528(5)	0.0005(5)	−0.0229(4)	0.021(1)
Al2	−0.4157(4)	−0.0745(4)	0.7268(4)	0.021(1)
Al3	0.5842(5)	0.6656(7)	0.0408(4)	0.022(1)
Al4	0.5876(5)	0.6699(6)	−0.5854(4)	0.022(1)
Al5	−0.4164(5)	−0.0756(5)	−0.1482(4)	0.017(1)
Al6	−0.4176(5)	−0.0751(4)	0.6025(3)	0.017(1)
Al7	0.5849(5)	0.6621(5)	0.1653(4)	0.019(1)
Al8	0.5857(5)	0.6623(5)	−0.7103(4)	0.019(1)
O1	0.4058(6)	0.2077(9)	0.2217(4)	0.036(1)
O2	0.4342(9)	0.5526(8)	0.1623(4)	0.031(2)
O3	−0.4473(8)	−0.5663(9)	−0.2123(4)	0.031(2)
O4	0.341(1)	−0.013(1)	0.0756(4)	0.042(3)
O5	−0.353(1)	−0.011(1)	−0.1133(5)	0.041(3)
O6	−0.344(1)	0.012(1)	0.5711(5)	0.041(3)
O7	0.357(1)	0.033(1)	−0.6118(5)	0.042(3)
O8	0.453(1)	0.539(1)	0.0323(4)	0.054(2)
O9	−0.448(2)	−0.551(2)	−0.0811(4)	0.054(2)
O10	0.553(1)	0.1213(8)	0.1025(4)	0.031(1)
O11	−0.5711(9)	−0.1257(8)	−0.1499(4)	0.031(1)
O12	0.1264(9)	−0.1163(9)	−0.0310(4)	0.044(2)
O13	−0.115(1)	0.111(1)	−0.0204(5)	0.044(2)
O14	0.4012(9)	0.2030(8)	0.0985(4)	0.044(2)
O15	−0.4089(9)	−0.2039(9)	−0.1506(4)	0.044(2)
O16	0.557(1)	0.1241(6)	0.2261(5)	0.036(1)
O17	0.303(1)	−0.011(1)	0.0131(5)	0.048(3)
O18	−0.322(1)	0.013(1)	−0.0536(5)	0.052(3)
O19	−0.314(1)	0.011(1)	0.5113(5)	0.052(3)
O20	0.335(1)	−0.021(1)	−0.5472(5)	0.048(3)
O21	0.5969(9)	0.7996(9)	0.1629(4)	0.048(2)
O22	0.4065(9)	0.2054(8)	0.7874(4)	0.048(2)
O23	0.677(1)	0.644(1)	0.1377(4)	0.048(3)
O24	−0.652(1)	−0.664(1)	−0.1784(5)	0.043(3)
O25	−0.662(1)	−0.651(1)	0.6371(4)	0.043(3)
O26	0.653(1)	0.670(1)	−0.6729(5)	0.048(3)
O27	0.645(1)	0.663(1)	0.2019(5)	0.034(3)
O28	−0.661(1)	−0.658(1)	−0.2387(5)	0.055(3)
O29	−0.650(1)	−0.661(1)	0.6964(5)	0.055(3)
O30	0.676(1)	0.642(1)	−0.7374(5)	0.034(3)
O31	0.562(1)	0.7837(9)	0.0420(4)	0.064(2)
O32	−0.569(1)	−0.780(1)	−0.0912(4)	0.064(2)
S1	0	0	0.0557(4)	0.065(3)
OA1	0	0	0.0245(9)	0.101(9)
OB1	−0.058(2)	−0.122(1)	0.0669(5)	0.083(4)
S2	0	0	0.6684(4)	0.057(2)
OA2	0.034(7)	0.084(3)	0.641(1)	0.07(1)
OB2	−0.117(2)	−0.058(3)	0.6780(5)	0.127(6)
S3	0	0	−0.7118(4)	0.064(3)
OA3	0.955(3)	0.879(2)	−0.6953(7)	0.056(7)
OB3	0.110(3)	0.048(5)	−0.7361(8)	0.082(8)
S4	0	0	−0.1013(4)	0.058(2)
OA4	0.079(6)	0.067(7)	−0.071(2)	0.14(2)
OB4	0.076(5)	0.129(3)	−0.1161(7)	0.17(1)
Cl5	0.628(5)	0.333(7)	0.0064(9)	0.11(2)
S5	2/3	1/3	0.024(2)	0.14(2)
OA5	0.604(8)	0.278(7)	−0.009(3)	0.01(1)
OB5	0.531(3)	0.265(5)	0.0301(8)	0.027(7)
Cl6	1/3	2/3	−0.076(2)	0.18(2)
S6	1/3	2/3	−0.057(1)	0.091(5)
OA6	0.398(4)	0.786(3)	−0.0341(8)	0.07(7)
OB6	0.271(7)	0.541(4)	−0.072(1)	0.11(1)
Ca1	0	0	−0.0187(7)	0.024(4)
Ca1b	0	0	−0.0340(6)	0.024(4)
K1	0.1150(5)	−0.1158(5)	0.1072(3)	0.045(2)
K2	0.7709(2)	0.8844(4)	0.2287(4)	0.047(1)
K3	−0.7695(4)	−0.8851(6)	−0.1503(4)	0.066(2)
Na1	−0.3104(6)	−0.1545(7)	0.5433(3)	0.037(2)
Na2	0.8475(7)	0.6912(5)	0.1679(4)	0.037(1)
Na3	0.8490(7)	0.6906(5)	−0.7082(4)	0.034(1)
Na4	0.3160(6)	0.159(1)	−0.5865(4)	0.044(2)
Na4b	0.3970(9)	0.203(2)	−0.5778(4)	0.044(2)
Na5	2/3	1/3	0.2198(6)	0.037(3)
Na5b	2/3	1/3	0.2095(7)	0.037(3)
Na6	2/3	1/3	0.0852(5)	0.072(5)
Na7	1/3	2/3	−0.1318(6)	0.028(3)
Na7b	1/3	2/3	−0.1527(6)	0.028(3)
Na8	2/3	1/3	−0.2234(4)	0.050(3)
Na9	2/3	1/3	−0.0616(5)	0.036(3)
Na9b	2/3	1/3	−0.0920(7)	0.036(3)
Na10	1/3	2/3	0.1487(7)	0.042(4)
Na10b	1/3	2/3	0.1575(8)	0.042(4)
Na11	0.498(1)	0.506(1)	0.9762(4)	0.024(1)
Na11b	0.536(1)	0.464(1)	0.9841(4)	0.024(1)
Na12	1/3	2/3	0.0234(5)	0.038(4)
Na12b	1/3	2/3	0.0066(8)	0.038(4)
W1	2/3	1/3	−0.147(2)	0.10
W2	1/3	2/3	0.103(1)	0.10
W3	2/3	1/3	−0.278(1)	0.10
W4	2/3	1/3	0.293(2)	0.10
W5	1/3	2/3	−0.339(1)	0.10

[a] U_{eq} is defined as one third of the trace of the orthogonalised U^{ij} tensor.

$P6_3/mmc$ allowing the alternation of Si and Al in the tetrahedral sites, resulted in a reliability index of 0.18 for 1947 unique reflections. The 10 independent tetrahedral sites grouped in two sets, the former showing $\langle$T–O$\rangle$ distance of 1.59(4) Å and the latter with $\langle$T–O$\rangle$ = 1.74(3) Å, regularly alternating in the structure. This behaviour indicated that Si and Al were actually ordered in the tetrahedral sites, and that the space group $P6_3/mmc$ can be rejected. However, the high value of R, as well as the statistical distribution of all the extra-framework ions on more sites, suggested that the symmetry of giuseppettite might be actually lower than $P\bar{6}2c$. The introduction of anisotropic displacement parameters at this stage of the refinement lowered the reliability index to 0.13, but resulted in almost all atoms not positively defined, so that it was discarded.

To check the possibility of a lower real symmetry, tentative structural refinements were performed in several subgroups of $P\bar{6}2c$, assuming that the observed higher symmetry depends on the occurrence of twinning. Among them, only the space group $P31c$ is in agreement

Table 3
Selected bond distances (Å) involving the framework oxygen atoms

Si1–O20	1.595(9)	Si2–O27	1.590(8)	Si3–O32	1.598(9)	Si4–O19	1.60(1)
Si1–O13	1.66(2)	Si2–O1	1.66(1)	Si3–O5	1.603(9)	Si4–O6	1.57(1)
Si1–O12	1.606(9)	Si2–O30	1.66(1)	Si3–O18	1.67(1)	Si4–O31	1.60(1)
Si1–O17	1.69(1)	Si2–O16	1.64(1)	Si3–O9	1.63(2)	Si4–O8	1.604(9)
Average	1.64	Average	1.64	Average	1.63	Average	1.59
Si5–O4	1.607(9)	Si6–O15	1.601(9)	Si7–O22	1.592(9)	Si8–O21	1.601(9)
Si5–O10	1.61(1)	Si6–O11	1.602(9)	Si7–O28	1.584(9)	Si8–O29	1.597(9)
Si5–O14	1.604(9)	Si6–O26	1.590(9)	Si7–O24	1.60(1)	Si8–O25	1.601(9)
Si5–O23	1.65(2)	Si6–O7	1.69(1)	Si7–O3	1.602(9)	Si8–O2	1.602(9)
Average	1.62	Average	1.62	Average	1.59	Average	1.60
Al1–O18	1.62(1)	Al2–O29	1.66(1)	Al3–O17	1.65(1)	Al4–O9	1.67(1)
Al1–O13	1.63(1)	Al2–O28	1.73(1)	Al3–O8	1.69(1)	Al4–O32	1.69(1)
Al1–O12	1.73(2)	Al2–O16	1.71(1)	Al3–O4	1.69(1)	Al4–O7	1.74(1)
Al1–O19	1.69(1)	Al2–O1	1.67(1)	Al3–O31	1.68(1)	Al4–O20	1.78(1)
Average	1.67	Average	1.69	Average	1.68	Average	1.72
Al5–O24	1.67(1)	Al6–O6	1.69(1)	Al7–O2	1.74(1)	Al8–O30	1.74(1)
Al5–O15	1.70(2)	Al6–O25	1.70(1)	Al7–O21	1.70(1)	Al8–O3	1.75(1)
Al5–O5	1.69(1)	Al6–O14	1.70(1)	Al7–O27	1.73(1)	Al8–O22	1.71(1)
Al5–O11	1.76(1)	Al6–O10	1.72(1)	Al7–O23	1.76(1)	Al8–O26	1.78(1)
Average	1.71	Average	1.70	Average	1.73	Average	1.75
K1–O4	2.85(1)	K2–O27	2.72(1)	K3–O26	2.57(2)	Na4–O7	2.22(2)
K1–O25	2.89(2)	K2–O29	2.86(2)	K3–O24	2.73(2)	Na4–O5	2.43(2)
K1–O6	2.97(1)	K2–O28	2.89(2)	K3–O5	3.08(2)	Na4–O12	2.48(2)
K1–O23	3.00(2)	K2–O30	3.08(1)			Na4–O18	2.61(2)
K1–O21	3.04(1)			Na3–O30	2.33(2)	Na4–O15	2.90(1)
		Na2–O23	2.34(2)	Na3–O28	2.50(2)	Na4–O20	2.96(2)
Na1–O17	2.46(2)	Na2–O25	2.49(2)	Na3–O24	2.61(2)	Na4b–O7	2.45(2)
Na1–O19	2.54(2)	Na2–O1	2.52(1)	Na3–O15	2.68(1)	Na4b–O5	2.60(2)
Na1–O14	2.54(1)	Na2–O29	2.62(2)	Na3–O26	2.83(2)	Na4b–O12	2.62(2)
Na1–O6	2.66(2)	Na2–O27	2.83(2)			Na4b–O18	2.55(3)
Na1–O4	2.75(2)			Na8–O3	2.434(9)×3	Na4b–O15	3.08(2)
Na1–O13	2.85(1)	Na6–O10	2.47(1)×3	Na8–O22	2.93(1)×3	Na4b–O20	2.88(2)
		Na6–O14	3.01(1)×3				
Na5–O16	2.346(7)×3			Na9–O9	2.69(1)×3	Na10–O2	2.46(1)×3
Na5–O1	2.906(7)×3	Na7–O11	2.44(1)×3	Na9–O32	2.91(2)×3	Na10–O21	3.00(1)×3
Na5b–O16	2.43(1)×3	Na7–O15	2.98(1)×3	Na9b–O9	2.60(1)×3	Na10b–O2	2.404(9)×3
Na5b–O1	2.951(9)×3	Na7b–O11	2.32(1)×3	Na9b–O32	2.63(1)×3	Na10b–O21	2.94(1)×3
		Na7–O15	2.87(1)×3				
				Na11–O20	2.22(2)	Na11b–O20	2.45(2)
Ca1–O13	2.52(1)×3	Na12–O31	2.66(2)×3	Na11–O18	2.57(2)	Na11b–O18	2.80(2)
Ca1–O12	2.75(1)×3	Na12–O8	2.78(1)	Na11–O8	2.53(2)	Na11b–O8	2.69(2)
Ca1b–O13	2.58(1)×3	Na12b–O31	2.95(2)×3	Na11–O9	2.72(2)	Na11b–O9	2.78(2)
Ca1b–O12	2.71(1)×3	Na12b–O8	2.97(2)×3	Na11–O19	2.77(2)	Na11b–O19	2.75(2)
				Na11–O17	2.89(2)	Na11b–O17	2.89(2)

with the observed absences in the X-ray pattern. The isotropic refinement in the space group *P*31*c* resulted in a reliability index of 0.11, which is significantly lower than the value of 0.18 obtained at the end of the isotropic refinement in the space group $P\bar{6}2c$. The Hamilton test [16], applied to our data, indicated that the hypothesis for which the correct space group is $P\bar{6}2c$ can be rejected, as it is under the 0.5% significance level.

Accordingly, the final refinement, introducing anisotropic thermal parameters for the framework oxygen atoms, for the sulphur atoms and for the alkali cations which do not occupy split sites, was carried out in the space group *P*31*c*, and converged to 0.074 for 3769 unique reflections. The refinement was performed assuming that the crystal was twinned with twinning plane (0 0 1), corresponding to the mirror plane that is lost in passing from space group $P\bar{6}2c$ to *P*31*c*. The refined twin fraction was 0.501(6). To avoid correlations among refined parameters, the same displacement parameters were refined for pseudo-symmetrical T and O atoms. Distance restraints were applied to the position of several oxygen atoms to prevent very short Si–O distances ("anti-bumping" restraints [15]). Finally, in order to reduce the ratio between the number of the refined parameters and the number of the data, linear restraints were applied to the anisotropic displacement

Table 4
T–O–T angles in giuseppettite

Si2–O1–Al2	163.3(6)	Si1–O17–Al3	154.2(12)
Si8–O2–Al7	149.0(6)	Si3–O18–Al1	154.9(10)
Si7–O3–Al8	146.6(6)	Si4–O19–Al1	154.8(11)
Si5–O4–Al3	152.1(10)	Si1–O20–Al4	140.8(10)
Si3–O5–Al5	149.0(10)	Si8–O21–Al7	169.3(8)
Si4–O6–Al6	154.9(10)	Si7–O22–Al8	171.0(8)
Si6–O7–Al4	140.5(10)	Si5–O23–Al7	141.3(10)
Si4–O8–Al3	156.2(8)	Si7–O24–Al5	148.3(9)
Si3–O9–Al4	158.7(7)	Si8–O25–Al6	146.5(10)
Si5–O10–Al6	148.4(7)	Si6–O26–Al8	139.9(11)
Si6–O11–Al5	144.1(6)	Si2–O27–Al7	144.8(10)
Si1–O12–Al1	155.0(7)	Si7–O28–Al2	146.9(10)
Si1–O13–Al1	157.6(7)	Si8–O29–Al2	150.8(10)
Si5–O14–Al6	163.9(7)	Si2–O30–Al8	140.4(9)
Si6–O15–Al5	171.7(8)	Si4–O31–Al3	161.6(9)
Si2–O16–Al2	145.6(5)	Si3–O32–Al4	159.0(7)

parameters of the framework oxygen atoms to approximate an isotropic behaviour, allowing the corresponding isotropic U to vary. Such last restraints are commonly applied in refinements of macromolecular structures, and whenever a low data to parameter ratio occurs, and allow to still obtain chemically sensible anisotropic displacement parameters [15]. The refinement converged to $R = 0.074$ for 3769 unique reflections, $R = 0.073$ for 3706 reflections with $F_o > 4\sigma(F_o)$, for 429 refined parameters and 212 restraints.

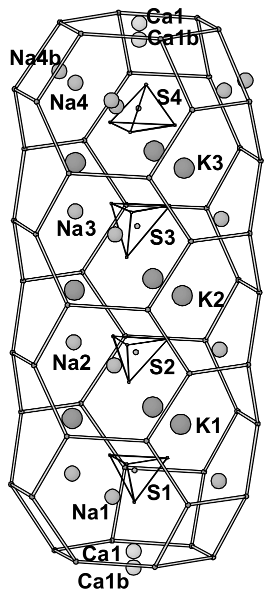
The refined positional and isotropic or equivalent displacement parameters are reported in Table 2, whereas selected bond distances and T–O–T angles are listed in Tables 3 and 4, respectively. Distances involving the extra-framework cations and anions within the different cages are reported directly in the corresponding figures. Additional tables, listing the anisotropic displacement parameters, and the squared F_o and F_c values, respectively, may be obtained from the author upon request.

3. Description of the structure

The stacking sequence of the six-membered rings of tetrahedra (ABABABACBABABABC...) gives rise to the occurrence of two big cages (hereafter denoted as "giuseppettite cages"), as well as of 10 cancrinite cages (or ε cages) and four sodalite cages (β cages) for each unit cell. A schematic drawing of the different parts of the structure is reported in Fig. 1. Silicon and aluminium cations regularly alternate in the tetrahedral sites. The average bond distances in the SiO_4 and AlO_4 tetrahedra are 1.62(3) and 1.71(4) Å, respectively (Table 3); the numbers in parentheses refer in both the cases to the dispersion of the observed values. The T–O–T angles (Table 4) range from 140(1)° to 171.7(8)°, with average value 152(9)°; however, most of them (78%) are comprised between 140° and 160°.

3.1. Giuseppettite cage

The cation distribution within the giuseppettite cage is shown in Fig. 2. Four sulphate groups, centred by S1, S2, S3 and S4 atoms, are surrounded by four groups (Na1, Na2, Na3, Na4) of three sodium cations. In the empty levels between the sulphate groups, triples of K1, K2, and K3 potassium cations occur. A minor substitution by sodium cations is observed in K1 and K3 sites (Table 5). This arrangement is similar to what is realised in davyne [17,18], pitiglianoite [11] and microsommite [10] within the large structural channels, where a regular alternation along c of triples of sodium cations surrounding a sulphate group and of triples of potassium cations (partially substituted by sodium cations and/or vacancies) has been observed. By comparing the refined potassium content in the K sites with the available chemical analyses [5,6] reported in the last rows of Table 5, the hypothesis of a further minor substitution of calcium cations in these sites may be put forward. On the other hand, the Ca content in the giuseppettite structure has to be higher than the refined value 5.33



K1-OB1	2.77(2)	Na1-OB1	2.33(2)
K1-OB1	2.83(3)	Na2-OB2	2.18(2)
K1-OA2	2.59(7)	Na2-OA2	2.74(4)
K1-OA2	2.76(7)	Na3-OA3	2.18(3)
K2-OB3	2.58(5)	Na3-OB3	2.51(3)
K2-OB3	2.75(6)	Na4-OB4	2.43(3)
K2-OB2	3.08(3)	Na4-OA4	2.90(8)
K2-OB2	3.08(3)		
K3-OB4	2.53(4)	Ca1-OA4	2.41(8)
K3-OB4	2.78(4)	Ca1b-OA1	2.47(5)
K3-OA3	2.78(3)		
K3-OA3	3.08(3)		

Fig. 2. The giuseppettite cage and its content. Only one of the three possible orientations of the S2-, S3- and S4-centred tetrahedra, respectively, is shown.

listed in Table 5, in order to obtain a charge balanced formula.

Three of the sulphate groups, centred by the S2, S3, and S4 sulphur atoms, are statistically oriented in three equivalent positions, as their apical oxygen atoms are displaced from the three-fold axis (Fig. 2). On the contrary, the S1 sulphate group is perfectly aligned along the three-fold axis. The cation site on the same level of S4 is split in the two sites Na4 and Na4b, both of them hosting about 70% of calcium and 30% of sodium cations. Therefore, the two ends of the giuseppettite cage show a very different atomic distribution, with the level corresponding to S1 showing a higher degree of positional and chemical order than the level corresponding to S4. These different portions of the cage should be symmetry-equivalent in the space group $P\bar{6}2c$, because of the mirror plane at $z = 1/4$, whereas they are crystallographically distinct in the space group $P31c$.

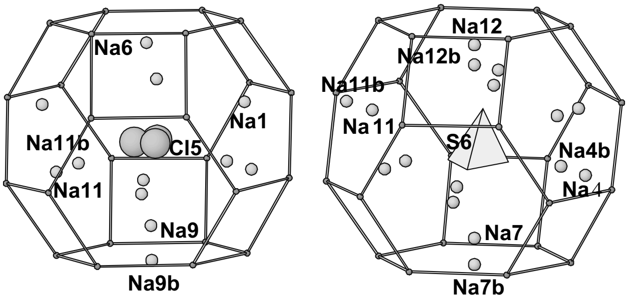
A split cation site (Ca1, Ca1b), near the centre of the cage base, hosts calcium and minor sodium cations, which are bonded to six oxygen atoms of the framework, as well as to one oxygen atom belonging either to the sulphate group S1 or S4, respectively (Fig. 2).

3.2. Sodalite cages

The two groups of symmetrically independent sodalite cages have to host, according to the chemical data [5,6], approximately 2 sulphate groups and 2 chlorine anions. As these anionic species have different charges and sizes, and the framework adapts itself to the different content of the cages, a fully disordered distribution of sulphate and chlorine anions seems to be improbable. Actually, a strong electron density maximum was found in the first group of sodalite cages, corresponding to the slightly off-centred chlorine anion Cl5 (Fig. 3). Within the other sodalite cages, a maximum of electron density surrounded by additional maxima at distances of 1.5–1.6 Å pointed to the occurrence of a sulphate group (S6 in Fig. 3). However, several weaker electron density maxima were found in both the kinds of cages, pointing to a partially disordered distribution of the anionic species: two cages host approximately 2/3 chlorine anions and 1/3 sulphate groups, whereas the opposite situation occurs in the other two sodalite cages.

The S6-centred tetrahedron is very irregular, as the apical oxygen atom is strongly displaced from the three-fold axis. It suggests that different orientations of the tetrahedron may occur, possibly as it happens in franzinite [19].

Near to the centres of each hexagonal face of the sodalite cage, sodium cations, partially substituted by Ca, are located. The displacement parameters of these sodium/calcium cations are strongly anisotropic, and the SHELX-97 program [14] itself suggests that these cationic sites may be split into two, slightly displaced and partially occupied, sites. As a rule, such a hint was followed in the course of the refinement, as a disordered distribution of the extra-framework cation is very common in this group of minerals. Moreover, the actual position of the (Na,Ca) cations in the sodalite cages may depend on the nature of the anion within the cage (either sulphate groups or chlorine anions). The refined occupancies and the calculated content of the cation sites are listed in Table 5.



Na11b-Cl5	2.68(4)
Na9-Cl5	2.92(4)
Na9-OA5	2.34(11)
Na11b-OA5	2.36(8)
Na11b-OA5	2.94(7)
Na1-OB5	2.52(3)
Na6-OB5	2.78(4)
S5-OA5	1.59(11)
S5-OB5	1.53(4)

Na12b-OA6	2.18(4)
Na11-OA6	2.34(3)
Na12-OA6	2.77(4)
Na4-OB6	2.58(4)
Na7-OB6	2.89(5)
Na7-Cl6	2.34(8)
Na4b-Cl6	3.00(1)
S6-OA6	1.65(3)
S6-OB6	1.54(4)

Fig. 3. The two sodalite cages and their content. Only one of the possible orientations of the S6 group is shown. For sake of clarity, the figure shows only the most occupied anionic sites for each of the cages (Cl5 anion and S6 sulphate group, respectively).

3.3. Cancrinite cages

Five symmetrically independent cancrinite cages occur within the framework of giuseppettite. They are grouped in sets of two and three base-sharing cages, respectively, connected through a sodalite cage.

All the cancrinite cages host sodium cations and water molecules (Fig. 4), as it occurs in the minerals of the cancrinite–vishnevite series and in pitiglianoite, which display the simple stacking sequence ABAB..., as well as in franzinite [19] and marinellite [1], 10-layer and 12-layer minerals of the group, respectively. In all the other phases of the group containing cancrinite cages (i.e. davyne, microsommite, quadridavyne, liottite, and afghanite), those cages host calcium cations and chlorine anions.

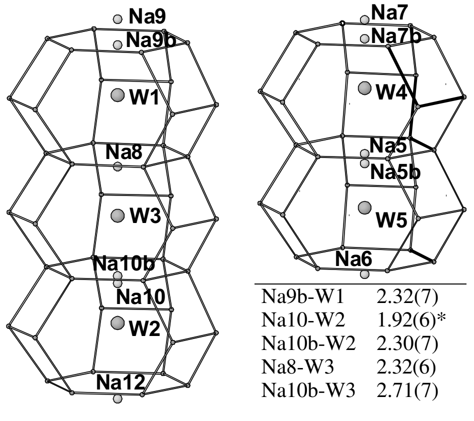
The full occupancy of the H_2O sites, which should give rise to 10 water molecules per unit cell, resulted in very high isotropic displacement parameters. Therefore, the occupancy values for the five sites were refined after fixing

Table 5
Population of the extra-framework cationic sites in giuseppettite

Site	Mult.	Occupancy	% Na	% Ca	% K	Atoms Na	Atoms Ca	Atoms (K,Ca)
Ca1	2	0.361(3)[a]	35	65		0.69	1.31	
Ca1b	2	0.483(4)[a]						
K1	6	0.89(1)[b]	26		74	1.57	–	4.43
K2	6	1.00(1)[b]			100	–	–	6.00
K3	6	0.98(1)[b]	5		95	0.28	–	5.72
Na1	6	1	100			6	–	–
Na2	6	1	100			6	–	–
Na3	6	1	100			6	–	–
Na4	6	0.540(4)[a]	33	67		1.98	4.02	–
Na4b	6	0.31(1)[a]						
Na5	2	0.5	100			2	–	–
Na5b	2	0.5						
Na6	2	1	100			2	–	–
Na7	2	0.5	100			2	–	–
Na7b	2	0.5						
Na8	2	1	100			2	–	–
Na9	2	0.6	100			2	–	–
Na9b	2	0.4						
Na10	2	0.6	100			2	–	–
Na10b	2	0.4						
Na11	6	0.5	100			6	–	–
Na11b	6	0.5						
Na12	2	0.6	100			2	–	–
Na12b	2	0.4						
					$\sum_{\text{atoms}}$	42.52	5.33	16.15
					Chemical content in Ref. [5]	39.96	7.45	14.64
					Chemical content in Ref. [6]	39.88	7.13	15.15

[a] The occupancy of the sites was refined on the basis of the scattering power of Ca. The full occupancy of the sites Ca1/Ca1b would require the presence of only 17.2 electrons, which correspond to 35% Na and 65% Ca. The same calculation for the sites Na4 and Na4b gives 33% Na and 67% Ca.

[b] As above, except that the occupancy of the K sites was refined on the basis of the scattering power of potassium K.



Na9b-W1	2.32(7)
Na10-W2	1.92(6)*
Na10b-W2	2.30(7)
Na8-W3	2.32(6)
Na10b-W3	2.71(7)
Na7b-W4	2.28(8)
Na5b-W5	2.05(6)
Na5-W5	2.48(6)

Fig. 4. The five cancrinite cages and their content. The occurrence of the short distance between Na10 and W2 (*) is actually prevented by the low occupancies of both these sites.

the isotropic displacement parameters of the water molecules to a common sound value. The refined occupancies point to 4.9 H_2O molecules per unit cell, in satisfactory agreement with the most recent available IR data [6].

4. Final remarks

The crystal structure of giuseppettite was solved and refined up to $R = 0.073$, using 3706 X-ray diffraction unique reflections, collected at the Elettra synchrotron radiation source. The experimental results confirmed the stacking sequence of layers proposed by Mazzi, ABABABACBABABABC... (personal communication in Ref. [7]). The symmetry of giuseppettite decreases from $P6_3/mmc$ (topological symmetry) to $P31c$ (real symmetry), because (i) silicon and aluminium are ordered in the tetrahedral sites, and (ii) the distribution of the extra-framework atoms is not compatible with the presence of mirror planes perpendicular to z. However, the strong $P\bar{6}2c$ pseudo-symmetry resulted in high correlations between the z coordinates of pairs of atoms; the occurrence of these high correlations may explain several oddities in the structural results.

The balanced crystal chemical formula of giuseppettite, indicated by the results of the structural refinement, is $[Na_{42}K_{16}Ca_6]_{\Sigma=64}Si_{48}Al_{48}O_{192}(SO_4)_{10}Cl_2 \cdot 5H_2O$.

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