

## Pitiglianoite, a new feldspathoid from southern Tuscany, Italy: Chemical composition and crystal structure

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### ABSTRACT

Pitiglianoite, ideally  $\text{Na}_6\text{K}_2\text{Si}_6\text{Al}_6\text{O}_{24}(\text{SO}_4)\cdot 2\text{H}_2\text{O}$ , is a new aluminosilicate that occurs in ejected blocks near Pitigliano, southern Tuscany, Italy. It is hexagonal, space group  $P6_3$ , with  $a = 22.121(3)$ ,  $c = 5.221(1)$  Å, and  $Z = 3$ . Pitiglianoite is colorless with a vitreous luster;  $D_{\text{meas}} = 2.37(4)$ ,  $D_{\text{calc}} = 2.394$  g/cm<sup>3</sup>. Optically it is uniaxial negative with  $\omega = 1.508(1)$  and  $\epsilon = 1.506(1)$ . Its crystal structure has been refined to  $R = 0.065$  using 2799 reflections obtained with  $\text{MoK}\alpha$  radiation on a four-circle automatic diffractometer. Pitiglianoite belongs to the cancrinite and vishnevite group of minerals, with a three-dimensional framework of alternating  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  tetrahedra with alkali cations,  $\text{H}_2\text{O}$  molecules, and sulphate groups in the channels and in the cages of the structure. The cell parameters of pitiglianoite are nearly identical to those of microsommite. However, the chemical composition of the two minerals is different, according to the coupled substitution  $\text{Na}^+ + \text{H}_2\text{O} = \text{Ca}^{2+} + \text{Cl}^-$  between pitiglianoite and microsommite. The cell volume of pitiglianoite is three times that of vishnevite, which has a very similar chemical composition, because of the ordering of  $\text{Na}^+$  and  $\text{K}^+$  cations and  $(\text{SO}_4)^{2-}$  groups within the channels parallel to the threefold axes.

### INTRODUCTION

A large group of feldspathoids are characterized by the presence of six-membered rings of  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  tetrahedra, linked to give a framework in which each ring is connected to three rings in both the preceding and the succeeding layers, according to an . . .ABC. . . stacking scheme (Merlino and Mellini, 1976; Merlino, 1984). They were named cancrinite-like minerals by Merlino and Mellini (1976), who determined the layer sequence for two of them, liottite (ABABAC) and afghanite (ABA-BACAC). A number of cancrinite-like minerals with complex stacking sequences were found in various localities of Latium and southern Tuscany, Italy (Leoni et al., 1979).

Within the large family of cancrinite-like minerals, the simple sequence (AB) is displayed by the minerals of the cancrinite group: cancrinite, vishnevite, davvne, microsommite.

A new mineral, which has been named pitiglianoite, belonging to this group was found within the geographical area where the minerals with complex sequences of layers have been found. Indeed, it was discovered some years ago and previously designated as "microsommite from Pitigliano" (Leoni et al., 1979). However, new chemical and structural data unequivocally show that pitiglianoite

is not merely a variety of microsommite but a distinct mineralogical species. The name pitiglianoite is from the type locality. Both the mineral and its name were approved by the IMA Commission on New Minerals and Mineral Names. The type material is preserved in the Museo di Storia Naturale e del Territorio, University of Pisa.

### OCCURRENCE

Pitiglianoite was found in a pumice quarry within ejected metasomatic blocks in the locality Casa Collina, near Pitigliano, southern Tuscany, Italy. In the same blocks apatite, diopside, and grossular occur. These ejected blocks may represent the product of the interaction between a trachitic magma and the carbonate and sulphate rocks of the volcanic vent.

### PHYSICAL AND OPTICAL PROPERTIES

Pitiglianoite occurs as well-developed hexagonal prisms up to 4 mm long and 1 mm in diameter. The crystals are elongated parallel to  $[001]$ ; the forms observed are  $\{001\}$  and  $\{100\}$ . Pitiglianoite is transparent and colorless, with a white streak and a vitreous luster. It is brittle, and the fracture is subconchoidal. Hardness is ca. 5. The measured density, obtained by the heavy liquid method, is 2.37(4)

TABLE 1. Chemical analyses of pitiglianoite

	(1)	(2)	(3)
SiO <sub>2</sub>	33.87	34.99	37.69
Al <sub>2</sub> O <sub>3</sub>	26.00	29.05	31.21
CaO	0.09	0.07	—
Na <sub>2</sub> O	15.45	17.10	18.70
K <sub>2</sub> O	9.10	9.41	6.80
SO <sub>3</sub>	7.60	7.58	5.60
Cl	—	0.01	—
H <sub>2</sub> O	—	3.46*	—
Σ	92.11	101.67	100.00
Number of atoms based on 12 (Si + Al)			
Si	6.30	6.07	6.07
Al	5.70	5.93	5.93
Ca	0.02	0.01	—
Na	5.57	5.75	5.84
K	2.16	2.08	1.40
S	1.06	0.99	0.68
Cl	—	0.003	—
H <sub>2</sub> O	—	2.00*	—

Note: The H<sub>2</sub>O content has been recalculated for analysis 2 only. (1) Electron microprobe analysis of pitiglianoite from Leoni et al. (1979). (2) Electron microprobe analysis (average of seven points), this work. Analysis by G. Vezzalini. (3) SEM-EDAX analysis, this work. Analysis by M. Tamponi.

\* The wt% H<sub>2</sub>O is the calculated value corresponding to two H<sub>2</sub>O molecules per formula unit.

g/cm<sup>3</sup>; the calculated value is 2.394 g/cm<sup>3</sup>. Optically, pitiglianoite is uniaxial negative; the refractive indices  $\omega = 1.508(1)$  and  $\epsilon = 1.506(1)$  were measured with light of wavelength 5890 Å.

#### CHEMICAL DATA

Chemical analyses of pitiglianoite were carried out by means of both SEM-EDAX and EPMA techniques. The former was performed with an EDAX device attached to a Philips PW515 scanning electron microscope working at the acceleration voltage of 20 kV and beam current of 10 nA. The latter was performed with an ARL-SEM-Q electron microprobe working at 15 kV and 20 nA. A previous microprobe analysis of pitiglianoite was presented by Leoni et al. (1979). The EDAX data were processed following the method developed by Leoni et al. (1989). Standards used for microprobe analysis were as follows: albite (Si, Al, Na), plagioclase-type glass (Ca), microcline (K), barite (S), and sodalite (Cl). The analyses of pitiglianoite, together with the empirical formulae, are compared in Table 1. Both analyses point to Na<sub>6</sub>K<sub>2</sub>Si<sub>6</sub>-Al<sub>6</sub>O<sub>24</sub>(SO<sub>4</sub>)·2H<sub>2</sub>O as the ideal chemical formula for pitiglianoite. The presence of two H<sub>2</sub>O molecules per formula unit is clearly indicated by the structure analysis and by analogy with cancrinite and vishnevite. A direct evaluation of the H<sub>2</sub>O content was not carried out because of the small amount of material. However, it seems worth noting that pitiglianoite and microsommite, which have the same structure type, were analyzed at the same time with the same microprobe instrument and using the same standards; the sum of the weight percents of oxides was 101.80 for microsommite and 98.21 for pitiglianoite; adding 3.46 wt% H<sub>2</sub>O, corresponding to two H<sub>2</sub>O molecules per formula unit, a total of 101.67 is obtained for

TABLE 2. Powder pattern of pitiglianoite

<i>l</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>l</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>
vw	10.95	11.06	110	vw	1.721	1.719	113
S	6.39	6.39	300			1.717	10, 1, 1
w	5.54	5.53	220	vw	1.680	1.677	931
vS	4.77	4.72	111	vw	1.647	1.650	902
w	4.19	4.18	410	w	1.600	1.605	851
m	3.69	3.69	330			1.596	12, 0, 0
vS	3.27	3.26	411			1.512	771
vw	3.02	3.01	331	w	1.513	1.506	662
vw	2.879	2.873	511			1.466	932
m	2.769	2.765	440	vw	1.467	1.465	960
m	2.650	2.645	521	vw	1.426	1.424	11, 4, 0
			112	w	1.361	1.362	12, 0, 2
vw	2.534	2.537	710	w	1.335	1.337	881
w	2.451	2.444	441	vw	1.309	1.305	004
w	2.288	2.282	711	vw	1.278	1.278	962
vw	2.199	2.191	631	vw	1.256	1.256	10, 7, 1
			332	vw	1.227	1.229	990
w	2.135	2.129	900	vw	1.192	1.195	10, 8, 1
w	1.905	1.898	442	vw	1.170	1.170	773
vw	1.863	1.857	741	vw	1.152	1.151	10, 4, 3
w	1.832	1.818	10, 1, 0	vw	1.083	1.083	883
			632	w	1.025	1.025	16, 4, 1
w	1.779	1.771	930				

Note: Obtained with Gandolf camera; FeK $\alpha$  radiation.

pitiglianoite, close to the value of microsommite. Moreover, the analytical data result in a good compatibility index (Mandarino, 1981).

#### X-RAY CRYSTALLOGRAPHY

The powder diffraction pattern of pitiglianoite has been obtained with a Gandolfi camera (diameter 114.6 mm, FeK $\alpha$  radiation) and is reported in Table 2. The indexing of the various lines has been performed with the help of intensity data measured with a four-circle diffractometer. Preliminary single-crystal Weissenberg photographs indicated that pitiglianoite is hexagonal, space group *P6<sub>3</sub>/m* or *P6<sub>3</sub>*. The following unit-cell parameters were derived through least-squares fit of  $2\theta$  values of 28 reflections ( $12^\circ < \theta < 28^\circ$ ):  $a = 22.121(3)$ ,  $c = 5.221(1)$  Å,  $V = 2212.8(6)$  Å<sup>3</sup>.

#### STRUCTURE ANALYSIS

The crystal structure of pitiglianoite was first solved by two of us (S.M. and M.M.) using intensity data obtained from a partially twinned crystal. The refinement of the structure started using a version of the least-squares program ORFLS (Busing et al., 1962) locally modified to deal with twinned crystals. Initial fractional coordinates were those obtained by Klaska and Jarchow (1977) for "synthetic sulphatic hydrocancrinite," a compound with similar unit-cell parameters and close chemical analogies with pitiglianoite. However, the refinement was not completely satisfactory, probably because of the poor quality of the available crystal. After several trials, a crystal was found that was almost completely unaffected by twinning. On that crystal (dimensions 1.3 × 0.3 × 0.3 mm), new intensity data measurements were carried out using an

**TABLE 3.** Fractional coordinates and equivalent isotropic  $U_{eq}$  or isotropic  $U_{iso}$ \* thermal parameters ( $\text{\AA}^2$ ) for pitiglianoite

Site	Occupancy	x	y	z	$U_{eq}$ or $U_{iso}$
Si1		0.8334(1)	0.2506(1)	0.2864(8)	0.0069(7)
Si2		0.9141(1)	0.4983(1)	0.7875(8)	0.0082(8)
Si3		0.9159(1)	0.7503(1)	0.7865(8)	0.0082(8)
Al1		0.9144(1)	0.1650(1)	0.2858	0.0072(8)
Al2		0.9183(1)	0.4205(1)	0.2876(9)	0.0082(8)
Al3		0.8298(1)	0.5828(1)	0.7891(11)	0.0100(8)
O1		0.8673(3)	0.5334(3)	0.7190(13)	0.014(3)
O2		0.9988(3)	0.7978(3)	0.7183(13)	0.013(2)
O3		0.8694(3)	0.3332(3)	0.2188(13)	0.014(2)
O4		0.8947(3)	0.6691(3)	0.7654(15)	0.021(3)
O5		0.9956(3)	0.5592(3)	0.7669(18)	0.025(3)
O6		0.8939(3)	0.2302(3)	0.2670(15)	0.019(3)
O7		0.7703(4)	0.2090(4)	0.0842(13)	0.019(3)
O8		0.8944(3)	0.4344(3)	0.5875(13)	0.013(3)
O9		0.8977(3)	0.1256(3)	0.5829(14)	0.012(2)
O10		0.8945(4)	0.4639(4)	0.0721(13)	0.017(3)
O11		0.8686(4)	0.0978(3)	0.0701(14)	0.018(3)
O12		0.7995(4)	0.2373(4)	0.5719(14)	0.019(3)
Na		0.3342(3)	0.3334(3)	0.6619(10)	0.037(2)
W1	1/3 O	0.3091(22)	0.3072(22)	0.2324(73)	0.073(11)*
W2	1/3 O	0.3618(13)	0.3290(12)	0.2285(44)	0.035(5)*
W3	1/3 O	0.3373(25)	0.3509(24)	0.2238(86)	0.091(14)*
K1	2/3 K + 1/3 Na	0.7790(1)	0.4461(1)	0.3241(11)	0.032(1)
Na1		0.6660(2)	0.4844(2)	0.8171(13)	0.022(1)
S1		2/3	1/3	0.8207(18)	0.038(1)
OA1	1/3 O	0.7041	0.3444	0.5860	0.20(4)*
OB1		0.7241	0.3319	0.9715	0.095(4)*
K2	2/3 K + 1/3 Na	0.9997(2)	0.1119(2)	0.8286(19)	0.0285(9)*
Na2		0.8495(3)	-0.0001(3)	0.3219(25)	0.0164(12)*
S2	1/2 S	1.0	0.0	0.3375(33)	0.036(3)
OA2	1/3 O	1.0269	0.0387	0.5661	0.13(5)*
OB2	1/3 O	1.0584	0.0569	0.1804	0.104(9)*

Note: The estimated standard deviations are given in parentheses and refer to the last digit. They are missing for the fractional coordinates of the O atoms of the sulphate groups which were held fixed.

Ital Structures four-circle automatic diffractometer, working at 48 kV and 28 mA, with graphite monochromatized  $\text{MoK}\alpha$  radiation. The measurements were performed up to  $2\theta = 60^\circ$  in  $\omega$ -scan mode, scan width  $1.2^\circ$ , scan speed  $2^\circ$  to  $15^\circ/\text{min}$  depending on the intensity of a prescan of the peaks. Of the 4995 measured intensities, 2799 with  $I > 3\sigma(I)$  were considered observed and were used in the least-squares calculations after reduction for Lorentz and polarization factors. The correction for absorption effects was performed through the DIFABS program (Walker and Stuart, 1983). The correction factors were in the range 0.93–1.06.

Some changes were introduced in the starting model, following the indications of Fourier syntheses and chemical analyses. The chemical data indicated that three  $[\text{SO}_4]$  tetrahedra are present in the unit cell of pitiglianoite. Two of them lie on the threefold axes in symmetry-related positions at  $2/3, 1/3, 0.82$  and  $1/3, 2/3, 0.32$ , respectively (S1-centered tetrahedra). The third tetrahedron (S2-centered) was placed on the  $6_3$  axis with half occupancy, as only one of the two equivalent positions at 0, 0, 0.34 and 0, 0, 0.84 is actually occupied. Regarding the O atoms of the sulphate groups, electron density maxima elongated parallel to c were found in positions corresponding to the basal O atoms, whereas a large and weak electron density region was found around the threefold and sixfold axes at levels corresponding to the apical O atoms. The ge-

ometry and location of the sulphate groups were modeled with the help of a DLS program (Baerlocher et al., 1978), starting with ideal S-O and O-O distances (weights 2.0 and 1.25, respectively) and reasonable bond lengths between O atoms of the sulphate groups and the alkali cations of the channels (weight 1.0). The positions of the O atoms of the sulphate groups determined in this way were held fixed in the last refinement cycles, which were carried out with anisotropic thermal parameters for all the atoms apart from the O atoms of the sulphate groups. The  $\text{H}_2\text{O}$  molecules were distributed among three different sites within the undecahedral cages, and the alkali cations were placed, with half occupancy, in the large channels around the sixfold axis. The refinement was carried out in space group  $P6_3$ , using the least-squares program SHELX76 (Sheldrick, 1976), and converged to  $R = 0.065$ .

Careful scrutiny of the intensity data showed that some forbidden  $00l$  reflections with  $l = 2n + 1$  were present, although very weak; this suggested a possible lowering of the space group symmetry from  $P6_3$  to  $P3$ , which could be related to the partial ordering of  $[\text{SO}_4]$  tetrahedra along the  $6_3$  axis, as correlated with ordering of the alkali cations in the same channels. Similar observations were made by Klaska (1977) and by Klaska and Jarchow (1977) in their study of "synthetic sulphatic hydrocancrinite." Final fractional coordinates and equivalent isotropic thermal parameters are reported in Table 3, anisotropic ther-

TABLE 6. Selected bond distances (Å) and angles (°) in pitiglianoite.

Si1-O3	1.626(6)		Si2-O1	1.613(8)		Si3-O2	1.633(6)	
-O6	1.615(8)		-O5	1.632(5)		-O4	1.617(7)	
-O7	1.619(7)		-O8	1.632(7)		-O9 <sup>a</sup>	1.627(8)	
-O12	1.628(8)		-O10 <sup>a</sup>	1.626(8)		-O11 <sup>c</sup>	1.621(9)	
Average	1.622		Average	1.626		Average	1.624	
O3-O6	2.604(11)	107.0(4)°	O1-O5	2.619(10)	107.5(3)°	O2-O4	2.629(7)	108.0(4)°
O3-O7	2.612(8)	107.2(4)°	O1-O8	2.634(11)	108.5(4)°	O2-O9 <sup>b</sup>	2.613(10)	106.6(3)°
O3-O12	2.648(9)	108.9(4)°	O1-O10 <sup>a</sup>	2.655(12)	110.0(4)°	O2-O11 <sup>c</sup>	2.650(10)	109.0(3)°
O6-O7	2.704(11)	113.4(4)°	O5-O8	2.710(8)	112.2(4)°	O4-O9 <sup>b</sup>	2.704(11)	113.0(4)°
O6-O12	2.692(12)	112.2(4)°	O5-O10 <sup>a</sup>	2.699(9)	111.9(4)°	O4-O11 <sup>c</sup>	2.692(11)	112.5(4)°
O7-O12	2.625(10)	107.9(4)°	O8-O10 <sup>a</sup>	2.613(10)	106.6(4)°	O9 <sup>b</sup> -O11 <sup>c</sup>	2.620(10)	107.6(4)°
Average	2.647		Average	2.655		Average	2.651	
Al1-O2 <sup>d</sup>	1.705(6)		A12-O3	1.714(6)		A13-O1	1.711(9)	
-O6	1.717(8)		-O5 <sup>d</sup>	1.721(7)		-O4	1.726(5)	
-O9	1.725(7)		-O8	1.729(8)		-O7 <sup>c</sup>	1.711(9)	
-O11	1.733(6)		-O10	1.722(10)		-O12 <sup>b</sup>	1.738(9)	
Average	1.720		Average	1.721		Average	1.721	
O2 <sup>e</sup> -O6	2.748(11)	106.8(3)°	O3-O5 <sup>d</sup>	2.741(7)	105.8(3)°	O1-O4	2.760(10)	106.9(3)°
O2 <sup>e</sup> -O9	2.803(8)	109.5(3)°	O3-O8	2.790(9)	108.3(3)°	O1-O7 <sup>c</sup>	2.812(12)	110.6(4)°
O2 <sup>e</sup> -O11	2.786(8)	108.3(3)°	O3-O10	2.766(11)	107.1(4)°	O1-O12 <sup>b</sup>	2.797(13)	108.4(4)°
O6-O9	2.876(11)	113.3(3)°	O5 <sup>e</sup> -O8	2.893(11)	113.9(4)°	O4-O7 <sup>c</sup>	2.872(9)	113.3(4)°
O6-O11	2.882(10)	113.4(4)°	O5 <sup>e</sup> -O10	2.900(13)	114.7(4)°	O4-O12 <sup>b</sup>	2.869(8)	111.8(4)°
O9-O11	2.750(10)	105.4(3)°	O8-O10	2.769(10)	106.6(4)°	O7 <sup>c</sup> -O12 <sup>b</sup>	2.749(10)	105.7(5)°
Average	2.807		Average	2.810		Average	2.810	
Si2-O1-Al3	153.2(5)°		Si3-O2-Al1 <sup>e</sup>	153.7(5)°		Si1-O3-Al2	154.1(5)°	
Si3-O4-Al3	147.4(5)°		Si2-O5-Al2 <sup>e</sup>	146.5(4)°		Si1-O6-Al1	146.6(4)°	
Si1-O7-Al3 <sup>f</sup>	141.8(5)°		Si2-O8-Al2	139.5(4)°		Si3 <sup>g</sup> -O9-Al1	141.2(5)°	
Si2 <sup>h</sup> -O10-Al2	140.7(6)°		Si3 <sup>i</sup> -O11-Al1	140.5(4)°		Si1-O12-Al13 <sup>g</sup>	140.7(5)°	
S1-OA1	1.430		S2-OA2	1.417		Na-W	2.33	
-OB1	1.508		-OB2	1.515		-O4 <sup>b</sup>	2.409(9)	
-OB1 <sup>b</sup>	1.508		-OB2 <sup>l</sup>	1.515		-O5 <sup>b</sup>	2.388(10)	
-OB1 <sup>a</sup>	1.508		-OB2 <sup>j</sup>	1.515		-O6 <sup>k</sup>	2.396(6)	
Average	1.488		Average	1.490		-W <sup>i</sup>	3.01	
						-O1 <sup>b</sup>	2.941(6)	
						-O2 <sup>b</sup>	2.937(10)	
						-O3 <sup>k</sup>	2.912(9)	
Na1-O3 <sup>a</sup>	2.386(9)	K1-O1	2.832(7)	Na2-O2 <sup>a</sup>	2.36(1)	K2-O2 <sup>a</sup>	2.84(1)	
-O7 <sup>c</sup>	2.789(9)	-O7 <sup>b</sup>	2.733(10)	-O9 <sup>m</sup>	2.39(1)	-O9	2.74(1)	
-O8 <sup>b</sup>	2.337(7)	-O8	3.022(8)	-O9	2.79(1)	-O9 <sup>b</sup>	2.996(7)	
-O10 <sup>b</sup>	2.833(8)	-O10	2.724(9)	-O11	2.38(1)	-O11 <sup>a</sup>	2.761(8)	
-O12 <sup>b</sup>	2.344(10)	-O12 <sup>b</sup>	3.054(10)	-O11 <sup>n</sup>	2.84(1)	-O11 <sup>a</sup>	3.03(1)	
-OA1 <sup>b</sup>	2.91	-OA1	2.44	-OA2 <sup>l</sup>	2.91	-OA2	2.42	
-OB1 <sup>b</sup>	2.21	-OA1 <sup>a</sup>	2.78	-OB2 <sup>l</sup>	2.18	-OA2 <sup>l</sup>	2.79	
		-OA1 <sup>a</sup>	3.48			-OA2 <sup>l</sup>	3.49	
		-OB1 <sup>n</sup>	2.81			-OB2 <sup>o</sup>	2.80	
		-OB1 <sup>l</sup>	2.86			-OB2	2.85	

Note: The bond distances Na-W and Na-W' are the average of three statistically occurring bonds (Na-W1, Na-W2, Na-W3 and Na-W1<sup>a</sup>, Na-W2<sup>a</sup>, Na-W3<sup>a</sup>, respectively). Within each K polyhedron a single K-OA distance occurs. Symmetry code for equivalent positions are a = x, y, z + 1; b = 1 - y, x - y, z; c = 1 - y, x - y, z + 1; d = 2 - x, 1 - y, z - 1/2; e = 2 - x, 1 - y, z + 1/2; f = 1 - x + y, 1 - x, z - 1; g = 1 - x + y, 1 - x, z; h = x, y, z - 1; i = 1 - y, x - y - 1, z; j = 2 - x + y, 1 - x, z; k = y, 1 - x + y, z + 1/2; l = 1 - y, x - y, z - 1; m = x - y, x - 1, z - 1/2; n = x - y, x - 1, z + 1/2; o = 1 + y, 1 - x + y, z + 1/2; p = 1 - y, x - y - 1, z + 1.

mal parameters in Table 4,<sup>1</sup> and the observed and calculated structure factors in Table 5, whereas bond distances and selected angles are listed in Table 6. Atomic scattering factors ( $f$ ,  $f'$ , and  $f''$ ) were taken from *International Tables for X-Ray Crystallography* (1974).

## DESCRIPTION OF THE STRUCTURE

A schematic drawing of the pitiglianoite structure as seen along [001] is presented in Figure 1. The structure

<sup>1</sup> A copy of Tables 4 and 5 may be ordered as Document AM-91-476 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

of pitiglianoite can be easily described with reference to three distinct structural units:

1. Tetrahedral framework. It is the typical framework of the minerals in the cancrinite group, with a stacking sequence ABAB... of six-membered rings of regularly alternating [SiO<sub>4</sub>] and [AlO<sub>4</sub>] tetrahedra.

2. Undecahedral cages. These base-sharing cages, limited by five six-membered and six four-membered rings of tetrahedra, form columns along the c axis and contain chains of alternating Na<sup>+</sup> cations and H<sub>2</sub>O molecules. The Na<sup>+</sup> cation has four shorter bonds with three O atoms of the framework and an H<sub>2</sub>O molecule and four longer bonds (cf. Table 6) displaying a substantially tetrahedral coordination. The H<sub>2</sub>O molecules statistically occupy one of three positions displaced from the center of the cages.

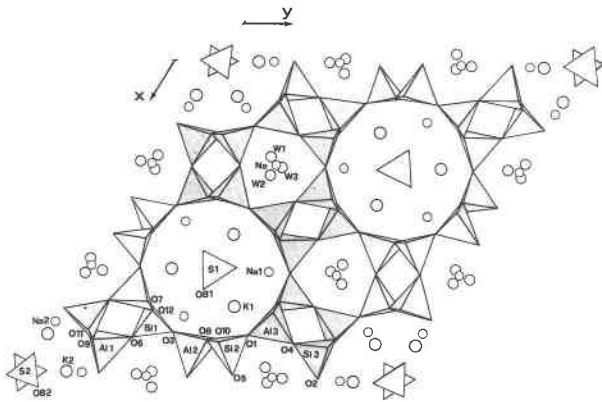


Fig. 1. The crystal structure of pitiglianoite as seen along *c*. The coordinates of the labeled atoms correspond to those reported in Table 3. Smaller and larger circles within the channels indicate Na and K sites, respectively. Within the undecahedral cages, all the three statistically occupied positions for the H<sub>2</sub>O molecules are indicated.

Such a coordination of Na within the undecahedral cages is closely analogous to that found in cancrinite (Jarchow, 1965; Grundy and Hassan, 1982), in vishnevite (Hassan and Grundy, 1984), in high-K vishnevite (Pushcharovskii et al., 1989), and in "synthetic sulphatic hydrocancrinite" (Klaska and Jarchow, 1977).

3. Large channels. Each channel running along *c* around sixfold and threefold axes hosts four Na<sup>+</sup> and two K<sup>+</sup> cations plus a sulphate group. In the channels lying around the threefold axes, substantial ordering on the cation sites occurs. Na1 sites, occupied by the smaller Na<sup>+</sup> cations,

are located at the same level as the (SO<sub>4</sub>)<sup>2-</sup> groups, far from the axes and lying adjacent to the wall of the tetrahedral framework (external sites). K1 sites, predominantly occupied by the large K<sup>+</sup> cations, are located on a level displaced *c*/2 from the preceding one and a short distance from the framework walls (internal sites). One out of the three K1 sites is occupied by Na<sup>+</sup> cations. It is tempting to relate the distribution of Na<sup>+</sup> among the three K1 sites with the displacement of the apical O atom of the sulphate tetrahedron away from the threefold axis: the displacement would bring the apical O atom closer to the position occupied by the Na<sup>+</sup> cation.

Similar ordering in the distribution of alkali cations and [SO<sub>4</sub>] groups occurs around the sixfold axis. However, either of two distributions, symmetry related through the screw axis, may be present, as was found in the study of the structure of davyne (Bonaccorsi et al., 1990), without substantial long-range ordering within the crystal. Actually a limited long-range ordering and consequent lowering of the space group symmetry from *P6<sub>3</sub>* to *P3* was suggested, as stated above, by the occurrence of two forbidden, although very weak, 00*l* reflections (001 and 003).

The structure of pitiglianoite here described is similar to that of microsommite. A chemical and structural study of microsommite from Vesuvius has been recently carried out (Bonaccorsi et al., in preparation). From that study, it appears that microsommite is hexagonal, space group *P6<sub>3</sub>*, *a* = 22.160, *c* = 5.346 Å. Its ideal chemical formula is Na<sub>4</sub>K<sub>2</sub>Ca<sub>2</sub>Si<sub>6</sub>Al<sub>6</sub>O<sub>24</sub>(SO<sub>4</sub>)Cl<sub>2</sub>. The topology of the frameworks of pitiglianoite and microsommite is the same; what neatly differentiates pitiglianoite and microsommite is the kind and the position of the ions and the

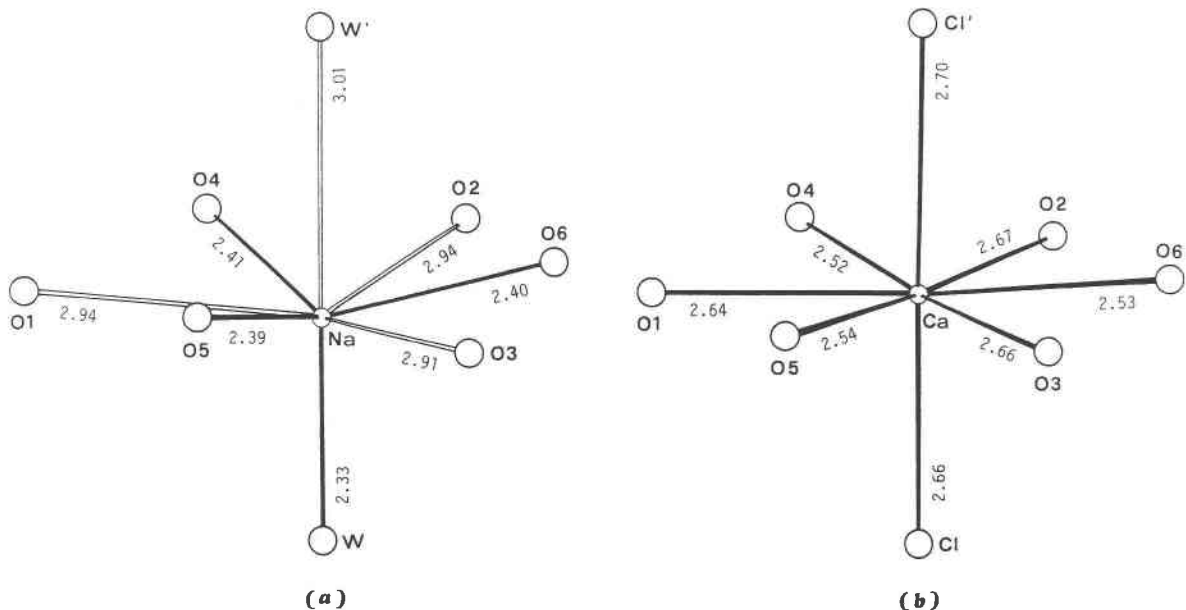


Fig. 2. Schematic drawing of the different coordinations of the cations within the undecahedral cages in (a) pitiglianoite (this work) and (b) microsommite (Bonaccorsi et al., in preparation). In pitiglianoite, Na displays four shorter and four longer bonds (black and white linkages, respectively). For the Na-W and Ca-Cl bonds, the average of three possible distances is reported.

molecules in the undecahedral cages. Within these cages, Na-H<sub>2</sub>O...Na-H<sub>2</sub>O... chains occur in the structure of pitiglianoite, with Na<sup>+</sup> cations in a substantially tetrahedral coordination, whereas Ca-Cl-Ca-Cl- chains occur in the structure of microsommite, with Ca<sup>+</sup> cations in a hexagonal bipyramidal coordination, as shown in Figure 2. Such considerations can be extended to the whole cancrinite group of minerals. If we consider the type of atoms and molecules that occupy the undecahedral cages, we can classify these minerals in two subgroups: cancrinite-type minerals, with Na and H<sub>2</sub>O (cancrinite, vishnevite, pitiglianoite), and davyne-type minerals, with Ca and Cl (davyne, microsommite).

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