

## Dawsonite: new mineralogical data and structure refinement

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With 6 figures and 6 tables in the text

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**Abstract:** Large acicular dawsonite crystals,  $\text{NaAl}(\text{OH})_2\text{CO}_3$ , up to 2 cm in length, were found in vesicles in Permian rhyolitic ignimbrites near Terzano, Bolzano (Italy). In association with dawsonite other minerals occur: quartz, calcite, aragonite, kaolinite, nordstrandite, dolomite, alumohydrocalcite, siderite. Formation of dawsonite is attributed to self-mineralization of ignimbrite by its fluids while releasing them on cooling. The crystal structure of dawsonite was refined to  $R = 0.058$  from 488 automatic diffractometer data (MoK $\alpha$  radiation). The crystals are orthorhombic, space group *Imma*, with  $a = 6.759(1)$ ,  $b = 5.585(1)$ ,  $c = 10.425(1)$  Å;  $D_m = 2.436(4)$  and  $D_x = 2.431$  g cm $^{-3}$  for  $Z = 4$  formula units. Al octahedra are edge-shared along  $b$ ; each  $\text{CO}_3$  group (regular) is attached to two adjacent  $\text{AlO}_2(\text{OH})_4$  octahedra and two  $\text{NaO}_4(\text{OH})_2$  distorted octahedra, in turn edge-shared into chains along  $a$ . H bonding is between the Al chain and the  $\text{CO}_3$  group, strengthening the Al+Na three-dimensional framework.

**Key words:** Dawsonite, refinement, paragenesis, alumohydrocalcite, nordstrandite; Italy (Trentino-Alto-Adige, Terzano).

### 1. Introduction

Though described as a new mineral as early as one century ago by HARRINGTON (1874), just a few findings of dawsonite,  $\text{NaAl}(\text{OH})_2\text{CO}_3$ , were reported until recent years when many authors realized that the mineral can be formed under a wide range of physical and chemical conditions. In all early reports dawsonite, considered a very rare mineral, was found to be always associated with eruptive rocks, generally near the contact with sedimentary rocks. This is true for the findings reported by HARRINGTON (1874), CHAPER (1881), FRIEDEL (1881), CURIE & FLAMAND (1892), LACROIX (1901), HAY (1963), DE MICHELE, MINUTTI & SCAINI (1965), MANDARINO & HARRIS (1965), STEVENSON & STEVENSON (1965), MALESANI & VANNUCCI (1974), HERITSCH (1975). In the occurrences of Komana (PELLOUX, 1932) and of Colorado (SMITH & MILTON, 1966) the sedimentary formations were affected by hydrothermal mineralizations presumably related to magmatic activities. In the Sydney basin instead some dawsonite-bearing formations are clearly sedimentary with absolutely no relationship with magmatic rocks like in the occurrences of the Berry formation (GOLDBERY & LOUGHNAN, 1970; NICHOLAS & OZIMIC, 1970), while in the Greta Coal Measures (LOUGHNAN & SEE, 1967) the sediments contain plenty fragments of volcanic rocks; in the Singleton Coal Measures the bulk of sediments derives from volcanic rocks (LOUGHNAN & GOLDBERY,

1972). At Nefza (DE MICHELE et al., 1965) it is not clear to which rock types the mineral is related.

The evidence of findings is for a widespread mineral occurring in many hydrothermal mineralizations; dawsonite is difficult to recognize because of the un-peculiar habit, of the small size of crystals and aggregates and of its relative abundance. Only in the Green River formation (Colorado) it reaches economic importance; anyway even in this formation dawsonite is so scattered that it is difficult to recognize by the naked eye. The thermal decomposition of dawsonite was studied by HARRIS, ERNST & TENNERY (1971) and by HUGGINGS & GREEN (1973).

Dawsonite exhibits the common habit of radiated needles clustered into rosettes or spherules a few millimeters in diameter, with a white silky luster. The single crystals are very small and brittle, their size making very difficult to take accurate crystallographic measurements. Recently a new finding near Livorno (Italy) was reported (MALESANI & VANNUCCI, 1974) where dawsonite occurs as spherical aggregates with an unusual pink colour. This variety was found together with the white one, the latter occurring in rosettes 8–9 mm approximately in diameter.

As early as 1973 some mineral collectors working in the area of Bolzano raised some doubts about the common identification of the mineral they commonly found in the area as a "zeolite"<sup>1</sup>. Since a preliminary X-ray analysis proved the mineral to be dawsonite the authors made a field trip in July 1973 picking up a large number of samples. From that time on a "dawsonite rush" was started in the area by amateur collectors. Absolutely exceptional is to be considered the finding of dawsonite from Bolzano because of the size and shape of aggregates and especially because of the size of single crystals, sometimes exceeding 20 mm in length and 0.5 mm approximately in cross-section. The samples come from the western slope of Monte Tondo near Terlano, Bolzano (Italy). The new finding of dawsonite in the mineralization at Terlano was reported by EXEL (1974 and 1975), BOSCARDIN & DE MICHELE (1975), EXEL (1976).

Beside giving further informations on the mineralization the present work deals with the crystal structure refinement.

## 2. Occurrence

The rock in which dawsonite occurs is a rhyolitic ignimbrite (lower-middle Permian) containing abundant quartz, sanidine and andesinic plagioclase (35% An) phenocrysts and subordinately biotite. The groundmass, making up to 60% of the rock, is an almost wholly devitrified glass with features typical of ignimbrite (MITTEMPERGHER, 1958).

The rhyolitic ignimbrite formation outcrops in the area as subhorizontal flows, each one tens or even hundreds of meters thick, and it shows a poor vertical fissuration. The ignimbritic character of the formation, containing some tuff and conglomerate intercalations, was demonstrated by GIANNOTTI (1958), MITTEMPERGHER (1958), BRONDI & MITTEMPERGHER (1972). The over-

<sup>1</sup> The authors are greatly indebted to some skilled private collectors: Mr. F. FRANCESCHINI and Mr. E. MARIOTTI who first reported the occurrence of the mineral in the area and helped in the field work, as well as to Rev. T. STOLCIS who supplied some excellent samples.

all thickness of the rhyolitic ignimbrite unit is 300 m approximately; it is overlain by the sedimentary formations of middle Permian sandstones "Arenarie di Val Gardena," by upper Permian limestones and by Werfenian (lowermost Triassic) marls.

The area of Terlano is affected by some volcano-tectonic movements (E–W oriented faults) which can be regarded as a late phase of the hercynian orogenesis, or even post-hercynian. Along these tectonic features, likely to have been related with the effusion of the late volcanic stages in the area, several mineralizations took place, namely a sulfide mineralization near Terlano.

The dawsonite-bearing rhyolite is very massive with little fracturation and a pink to brick-reddish colour. Though appearing fresh and compact the rock is actually altered: the plagioclase and sanidine are commonly transformed into clay minerals and calcite with diffuse iron pigmentation. Vesicular voids are scattered in the massive rock, most of them being just empty bubbles. Dawsonite is found in some of these vesicles, generally more than average in size, associated with other alteration minerals. Even the largest vesicles reaching dimensions of several cm look independent, that is without any apparent relationship with the fractures (where quartz is commonly found in the amethyst variety). The latter feature is seemingly contradictory with the abundance of carbonate phases as cavity-filling material; the apparent absence of a source for carbonate in the bulk of the rock suggests for this mineralization an origin which can be related with solutions derived elsewhere. It looks clear anyway that the mineralization belongs to a low temperature hydrothermal stage which occurred: a) during the late cooling of the thick ignimbrite mass, or b) during a post-depositional tectonic phase which produced the nearby pneumatolitic mineralizations (GIANNOTTI, 1958), or even c) in a low grade regional metamorphism (never observed so far). In the first two cases the age is geologically the same, the tectonic movements being related to the latest effusions.

In view of the lack of evidence for any relationship between mineralized vesicles and fractures or veins of secondary minerals the first hypothesis is preferred, i.e. the self-alteration of ignimbrite by means of its own fluids. Even the uniform alteration of sanidine and plagioclase can favour this choice. The uncertainties of interpretation are due to the abundance of carbonate and to the formation conditions inferred from laboratory studies, as will be discussed in a later paragraph.

## 3. Mineralogy and paragenesis

Dawsonite occurs as perfectly clear orthorhombic crystals rarely terminated and up to some tenths of millimeter in cross dimensions; the length is up to 20 mm, the common size being around 0.2 and 10 mm respectively.

EXEL (1975 and 1976) reported crystals reaching 50 mm in length. The crystals are attached to the vesicle walls and very often they cross the vesicle itself; they normally exhibit the {101} and {001} forms, the elongation being [010]; other forms are unfrequent. Crystals are perfectly transparent and colourless with a vitreous luster; when in aggregates of tiny crystals they look silky white, as well as crystals composed of loose cleavage fibers. The faces are smooth and planar with some faint striations along the elongation axis. At the microscope the only cleavage results to be {101}; the crystals are normally without any termination even if they were grown free-ended, yet in some instances (Figs. 1 and 2) the {010} and {011}; forms can

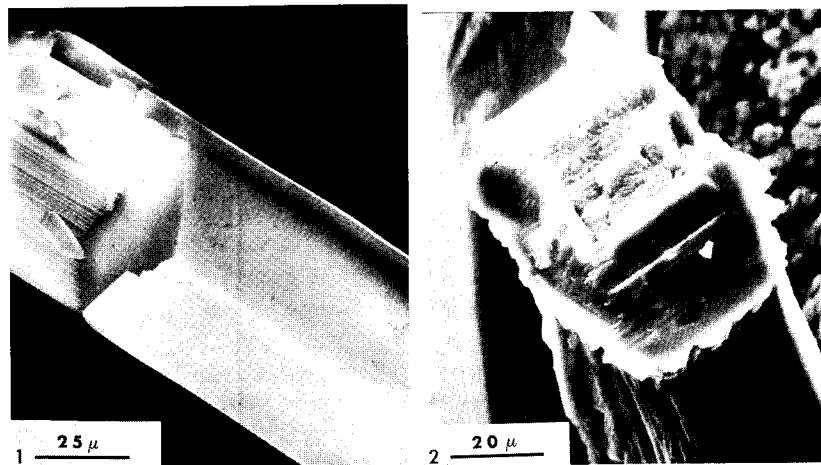


Fig. 1. A crystal of dawsonite showing the {101} prism and cleavage fibers, with {010} termination. JEOL JSM-U3 Scanning Electron Microscope.

Fig. 2. Dawsonite crystal terminated {010} and {011}. On the (011) face a striation is evident, corresponding to the {001} form (dark), while on the (010) face the criss-cross striation corresponds to the {101} cleavage traces. JEOL JSM-U3 SEM.

be observed. In these figures the very easy cleavage can be observed: each single crystal can be regarded as made of isooriented fibers. Two typical clusters of larger dawsonite crystals are shown in Figs. 3 and 4; their appearance looks completely different from the common findings of dawsonite as rosettes or spherules of tiny crystals.

Identification of the mineral was made by means of the X-ray powder pattern which is one of typical dawsonite. In Table 1 the powder pattern of dawsonite from Terlano is given. In this table the relative intensities are taken from single-crystal data in order to eliminate the effect of isoorientation due to the fibrousness of the mineral. Samples were picked up at the microscope from top quality crystals. Experimental conditions were:

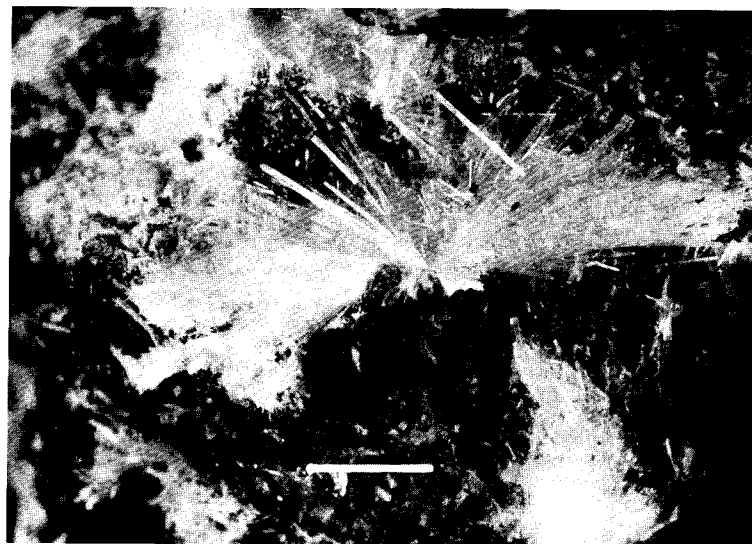


Fig. 3. Radiated dawsonite crystals on a vesicle wall. The scale bar represents 1 cm.

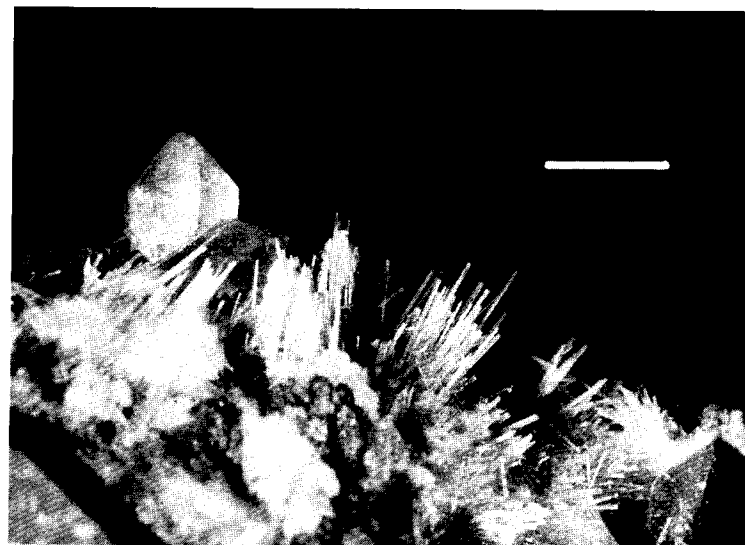


Fig. 4. Cluster of average-sized dawsonite crystals layering the wall of a big vesicle, a small portion of which is visible in the picture. The scale bar represents 1 cm.

Table 1. X-ray powder pattern of dawsonite. For indexing and intensities see text.

hkl	$d_{\text{calc}}$	$d_{\text{obs}}$	I/I <sub>0</sub>	hkl	$d_{\text{calc}}$	$d_{\text{obs}}$	I/I <sub>0</sub>
101	5.671	5.69	68	400	1.690	1.687	100
200	3.380	3.387	31	224	1.660	1.660	28
112	3.320	3.328	5	125	1.622	1.622	7
103	3.090	3.093	9	231	1.6111	1.608	7
202	2.836	2.838	3	116	1.6112		
020	2.793	2.792	59	402	1.6074		
211	2.786						
004	2.606	2.606	65	323	1.5655	1.565	5
121	2.505	2.509	14	206	1.5452	1.545	15
114	2.230	2.231	3	305	1.5303	1.531	8
213	2.223	2.224	3	134	1.4783	1.478	3
220	2.153	2.155	38	026	1.4752	1.474	15
123	2.072	2.074	5	404	1.4178	1.418	5
204	2.064	2.065	5	040	1.3963	1.393	33
105	1.992	1.993	42	422	1.3931		
015	1.953	1.955	25	141	1.3558	1.356	3
303	1.891	1.891	4	226	1.3520	1.352	5
031	1.833	1.834	5	325	1.3420	1.341	11
006	1.738	1.738	12	501	1.3406	1.339	7
321	1.729	1.730	28	008	1.3031	1.303	9
215	1.691	1.691	5	334	1.2572	1.257	4
				044	1.2308	1.230	11

G. E. XRD-5 powder diffractometer, Ni filtered CuK radiation at 45 kV and 15 mA, goniometer speed ( $2\theta$ )  $0.25^\circ \text{ min}^{-1}$ , slit widths  $1^\circ$  and  $0.05^\circ$ . Both Si and NaF were used as calibration standards. The  $d_{\text{calc}}$  are recalculated from the lattice constants determined on a single crystal by Ag calibrated Weissenberg films, this set of constants looking the most accurate one. Indices were attributed on the basis of single crystal data taking into account the single crystal diffractometer intensities. The present pattern compares very well with the previous ones; the aim was to produce a more accurate set of X-ray powder data though limited in  $\theta$  because of the diffractometer geometry and of the numerous coincidences in indexing high angle reflexions.

Another mineral found associated with dawsonite and quite uncommon is nordstrandite, the triclinic polymorph of  $\text{Al}(\text{OH})_3$ . Of the few previous findings the one from Australia (GOLDBERY & LOUGHNAN, 1970) closely resembles the present one because of the association with dawsonite. A detailed description of nordstrandite from Terlano was given by VANNUCCI (1975). A pseudo-hexagonal crystal of nordstrandite lying on a dawsonite crystal is shown in Fig. 5. It is clear that nordstrandite was formed after dawsonite; besides, most sanidine and feldspar crystals in the rock are altered into nordstrandite and a minimal percentage only into kaolinite as perfectly white encrustations; yet nordstrandite was never found in physical

contact with kaolinite. Nordstrandite from Terlano was always found microcrystalline with an earthy appearance or even as crusts and as small stalactitic aggregates.

Quartz occurs very often in vesicles as coatings with very small surfacing crystals and as euhedral crystals up to 10 mm long. Some of the crystals show corrosion effects as irregular pits on the faces. The quartz crystals were grown clearly after dawsonite was crystallized, for there are nice instances of dawsonite needles passing through quartz crystals. Quartz is common also as reddish calcedony encrustations. In the same area quartz crystals with green colour because of chlorite inclusions and especially as the amethyst variety are found very commonly in crevices where dawsonite or other uncommon minerals are missing.

As could be expected, other carbonates are the most common minerals occurring together with dawsonite: aragonite is frequently present as clusters of radiating clear transparent acicular crystals with vitreous luster, generally as needles and sometimes as groups of few roughly grown crystals encrusted with calcite.

Calcite is very common too, the general habit being the rhombohedron. In this case colourless transparent crystals are secondary to the widespread white calcite occurring as spherules and coatings; on the basis of the chemical analysis and of the  $d_{(104)}$  spacing (VANNUCCI, 1975) it resulted to contain 91%  $\text{CaCO}_3$ . Even this "impure" calcite appears to be formed after dawsonite since sometimes it is found as coatings on dawsonite crystals.

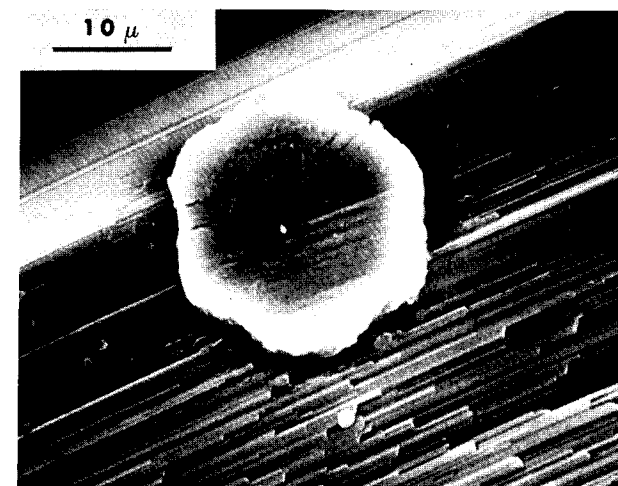


Fig. 5. Pseudo-hexagonal nordstrandite crystal on a dawsonite crystal. On the main face of the latter mineral the {101} cleavage is evident, producing the thin fibers. JEOL JSM-U3 SEM.

A common carbonate exhibiting a typical habit of saddle-shaped white crystals is dolomite; it is evidently secondary to dawsonite since crystals of the latter frequently are found to spear the dolomite ones, while in other instances small dolomite crystals are lying on dawsonite and quartz crystals.

Though not so common as the previous carbonates, siderite rhombohedra are found too in the biggest vesicles. Siderite crystals, often corroded, show a brownish colour with reddish luster and curved faces. Most crystals are actually pseudomorphs after siderite of earthy limonitic materials, more or less amorphous.

Another carbonate, alumohydrocalcite, was found in a few samples as small radiated fibrous spheres white in colour. It was found to be in direct association with dawsonite. This is the first finding of alumohydrocalcite in Italy and one of the few in the world.

Among the many above mentioned minerals dawsonite appears to have formed as the first or at least among the first ones. In fact the depositional succession of siderite and kaolinite with respect to dawsonite is not established, while all other phases crystallized later than dawsonite; besides, dolomite and "impure" calcite belong to a third phase since they were formed after quartz; "pure" calcite belongs to a later phase. The crystallization sequence can be summarized as:

- 1) dawsonite, alumohydrocalcite;
- 2) quartz, aragonite, nordstrandite;
- 3) dolomite, "impure" calcite;
- 4) "pure" calcite.

#### 4. Formation of dawsonite

About the chemical and physical conditions of formation as inferred from the experimental data of synthetic preparations it is not yet clear to what extent extrapolation of laboratory data to a natural environment is legitimate. Most authors who studied the formation conditions for dawsonite in natural environments concluded for decomposition of feldspars as well as of nepheline and analcrite under low temperature hydrothermal conditions or even at normal temperature. While there is a general agreement for a high CO<sub>2</sub> partial pressure, discrepancies arise when the pH conditions are examined. Artificial dawsonite was prepared under different conditions, yet at high pH values that are quite infrequent in natural fluids. Because of the lack of evidence for so high pH values (pH > 12 would be required for the formation of nordstrandite, associated with dawsonite) some authors like LOUGHNAN & SEE (1967), GOLDBERY & LOUGHNAN (1970), LOUGHNAN & GOLDBERY (1972) do not consider a high pH (about 10) to be necessary. On the other hand, other authors conclude for strongly alkaline solutions as resulting from alteration of aluminosilicates, like HAY (1963), SMITH & MIL-

TON (1966), HERITSCH (1975). Other variables not less important than pH, though related to it, are the CO<sub>2</sub> partial pressure and the silica availability (SMITH & MILTON, 1966; COVENEY & KELLY, 1971). BADER (1938) prepared dawsonite from sodium aluminate with a CO<sub>2</sub> excess; his experimental work suggested GOLDBERY & LOUGHNAN (1970) that alteration of aluminosilicates can produce sodium aluminate and this in turn can react with CO<sub>2</sub> rich fluids to yield dawsonite. The problem anyway is the presence of so alkaline solutions deriving from dissolution of aluminosilicates in the presence of high CO<sub>2</sub> concentrations, which in some instances at least looks unlikely. Nordstrandite is considered the obvious daughter of dawsonite (GOLDBERY & LOUGHNAN, 1970) even though experimental data on its synthesis are more stringent for the pH conditions, above 12. The same authors proposed that silicification of nordstrandite can produce kaolinite.

In the mineralization of Terlano the evidence is for a hydrothermalization of the parent rock at low temperature. The present data account for a self-hydrothermalization during the ignimbrite cooling phase which could last tens of years at least, letting the fluid phases react with the rock while escaping. This because no crevices or veins with such mineralizations were found and because of the general kind of alteration of the rock previously described. The presence of high amounts of silica deposited after dawsonite both as corroded euhedral crystals and as calcedony as well as the presence of nordstrandite, deposited after dawsonite too, affords the evidence that high pH values were reached during the formation of dawsonite; yet no zeolites like analcrite so far were found associated with it, but only sanidine and an andesinic plagioclase. The presence of several carbonate minerals accounts for the high CO<sub>2</sub> concentrations, while there is less evidence for the formation of nordstrandite from dawsonite and for the silicification of the former into kaolinite.

The amethyst variety of quartz which is commonly found in crevices scattered in the area and thoroughly searched for appears to be independent from the dawsonite mineralization as if it is related to an independent event.

#### 5. Structure refinement

A crystal structure determination was carried out by FRUEH & GOLIGHTLY (1967) on material from Montreal, Canada. In the present work the crystal structure was refined owing to the good quality of the material available from the Terlano mineralization.

Crystal data are summarized in Table 2. The density was measured by flotation on some perfectly clear crystals. Lattice constants were obtained from Ag-calibrated Weissenberg pictures and refined by least-squares; they are in perfect agreement with the ones obtained from powder patterns and from single crystal diffractometer. Single crystal intensities were measured

Table 2. Crystal data for dawsonite.

Orthorhombic, <i>Imma</i>	NaAl(OH) <sub>2</sub> CO <sub>3</sub>
<i>a</i> = 6.759(1) Å	F.W. 144.0
<i>b</i> = 5.585(1)	<i>D<sub>m</sub></i> = 2.436(4) g cm <sup>-3</sup>
<i>c</i> = 10.425(1)	<i>D<sub>x</sub></i> = 2.431 g cm <sup>-3</sup>
<i>V</i> = 393.53 Å <sup>3</sup>	<i>Z</i> = 4
<i>F</i> (000) = 288	$\mu$ (MoK $\alpha$ ) = 5.50 cm <sup>-1</sup>

by a Philips PW 1100 diffractometer (Istituto di Mineralogia, Università di Perugia, Italy) on a slice approximately equidimensional cut from one of the clearest crystals, 0.3 mm approximately in cross dimensions. The conditions were the following ones:  $\omega - 2\theta$  scan, range  $3^\circ \leq \theta \leq 35^\circ$ , scan speed  $0.05^\circ \text{ s}^{-1}$ , scan range  $1.2^\circ$ , background on both sides of the peak, up to 3 times peak scan, graphite monochromated MoK $\alpha$  radiation, reflexions unobserved if  $I_{\text{peak}} - 2\sqrt{I_{\text{peak}}} \leq I_{\text{back}}$ , observed reflexions: 406, unobserved: 82; no allowance was made for absorption correction; a weight  $1/\sigma$  derived from counting statistics was applied. Systematic absences confirmed the space group found by FRUEH & GOLIGHTLY (1967); the structure solution with the present data confirmed their determination to be correct, adding informations on hydrogen bonding. Atomic scattering factors for all atoms except H were taken from CROMER & WABER (1965), for H from STEWART, DAVIDSON & SIMPSON (1965).

The previous determination by FRUEH & GOLIGHTLY (1967) was the starting step for non-hydrogen atoms; with B factors taken from similar structures it gave after rescaling an  $R = \sum |F_o| - |F_c| / \sum |F_o|$  of 0.12 for measured reflexions, wholly confirming the previous authors' structure. Two full matrix least-squares cycles with isotropic B's gave  $R = 0.103$ . Two more cycles with anisotropic thermal factors except for C gave  $R = 0.075$ ; at this stage the H atom was definitely positioned in a  $\Delta F$  synthesis as a sharp peak. The last two cycles, still full-matrix, using anisotropic thermal factors (isotropic for H) and omitting 10 reflexions evidently affected by secondary extinction, led to the final  $R = 0.058$  for observed reflexions,  $R = 0.082$  including unobserved and extinct ones. The final  $\Delta F$  map shows no relevant residues. Table 3 lists the final positional and thermal parameters; Table 4 is the list of observed and calculated structure factors.

The refinement of the crystal structure of dawsonite yielded a more precise knowledge of bond distances and angles, as well as of the H bonding system.

The structure of dawsonite consists of two kinds of six-fold coordination by Al and Na. The AlO<sub>2</sub>(OH)<sub>4</sub> coordination polyhedron is a fairly regular octahedron, the mean Al-O distance being 1.896 Å. Because of its special position Al coordinates four symmetrical OH groups [O(3) oxygens] form-

ing an almost regular rectangle with edges of 2.841(2) and 2.446(3) Å. Two more symmetrical O(2) oxygen atoms complete the Al coordination as a slightly elongated octahedron. The Na polyhedron NaO<sub>4</sub>(OH)<sub>2</sub> has a mean Na-O distance of 2.440 Å. The Na position being a special one too, there are four symmetrical oxygen atoms O(2) coordinated according to an almost perfect square with edges of 3.642(3) and 3.322(3) Å. Like Al even Na coordinates two more O(3) oxygen atoms (OH groups this time) to complete its sixfold coordination. The resulting polyhedron is a square based oblique bipyramid (the axis is inclined  $57^\circ$ ), slightly flattened. The coordination of C atom is regular: all atoms lie on a mirror plane; the group is also on a twofold axis, so that the O(2) atom is doubled. The mean C-O distance is 1.289 Å, but the C-O(1) distance is remarkably shorter (0.058 Å difference) than the others; the oxygen involved is the one not bound to any cation, but only the acceptor of two symmetrical H bonds [angle O(3)-O(1)-O(3) =  $105.4(1)^\circ$  and angle H-O(1)-H =  $106(1)^\circ$ ]. The hydrogen atom, bound to O(3) at a distance of 0.80(4) Å, connects the donor oxygen to O(1); the donor-acceptor distance is 2.707(3) Å, the hydrogen-acceptor distance is 1.91(4) Å and the donor-hydrogen-acceptor angle is  $180(4)^\circ$ .

The physical characters of dawsonite, especially the {101} perfect cleavage, can be explained in terms of CO<sub>3</sub> group orientation and bonding

Table 3. Final atomic parameters with their standard deviations. Anisotropic thermal parameters ( $\times 10^4$ ) are in the form  $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . B equivalent factors (Å<sup>2</sup>) after HAMILTON (1959). Standard deviations on the last digits are given in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Beq.
Al	.0	.0	.50	0.58
Na	.25	.75	.25	1.55
C	.0	.25	.2526(4)	0.70
O(1)	.0	.25	.1326(3)	1.26
O(2)	.0	.0474(4)	.3156(2)	0.95
O(3)	.1811(3)	.25	.5250(2)	0.74
H	.275(6)	.25	.478(3)	1.18

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Al	52(2)	34(3)	8(1)	0	0	-1(1)
Na	115(5)	110(6)	27(2)	0	26(2)	0
C	39(8)	67(12)	13(3)	0	0	0
O(1)	81(7)	141(11)	12(2)	0	0	0
O(2)	89(5)	52(6)	13(2)	0	0	6(2)
O(3)	50(4)	54(5)	15(2)	0	3(2)	0

Table 4. Observed and calculated structure factors. The asterisk marks unobserved and extinct reflexions.

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
2 0 0*	55.0	60.0	6 6 2*	3.1	4.0	8 1 5*	3.1	-1.0	3 6 7	23.5	-23.2	1 7 10*	3.1	-1					
4 0 0*	91.7	104.9	8 6 2	24.7	19.2	10 1 5*	3.1	2.3	5 6 7	11.0	-10.1	1 0 11	39.1	-41.5					
6 0 0*	52.0	54.8	1 7 2	12.6	12.6	1 2 5	37.6	-36.2	0 7 7	17.9	-15.9	3 0 11	35.1	-36.9					
8 0 0*	28.8	28.8	1 7 2	7.2	6.9	3 2 5	53.0	-52.1	2 7 7	13.5	-11.3	5 0 11	27.3	-29.1					
10 0 0*	20.9	17.9	5 7 2	10.9	10.3	5 2 5	20.5	-19.7	4 7 7	6.5	-2.6	7 0 11	18.6	-20.2					
0 2 0*	37.5	-46.6	0 8 2	16.4	18.7	7 2 5	18.2	-18.1	1 8 7	11.0	-11.1	0 1 11	5.3	5.5					
2 2 0*	77.5	94.0	2 8 2	11.2	14.2	9 2 5	18.2	-17.7	0 0 8	49.6	49.6	2 1 11	4.1	5.0					
4 2 0*	9.9	9.7	4 8 2	4.9	8.6	0 3 5	31.8	-30.9	2 0 8*	3.1	-1.8	4 1 11	7.7	-7.9					
6 2 0*	16.7	16.6	1 0 3	30.2	-30.0	2 3 5	36.8	35.7	4 0 8	50.8	30.8	6 1 11	16.3	17.0					
8 2 0*	15.7	15.7	3 0 3	19.1	18.1	4 3 5	6.5	-5.8	6 0 8	9.4	10.0	8 1 11	8.5	-12.0					
10 2 0*	7.6	10.1	5 0 3	28.2	-29.6	6 3 5	5.3	5.3	8 0 8	13.6	13.1	1 2 11	24.5	-24.7					
0 4 0*	79.7	105.7	7 0 3	7.6	-8.4	8 3 5	5.0	5.4	1 1 8	14.4	-13.9	3 2 11	21.0	-21.3					
2 4 0*	15.2	16.8	9 0 3*	3.1	-1.6	1 4 5	40.6	-41.5	3 1 8	15.9	16.6	5 2 11	16.9	-17.3					
4 4 0*	49.1	53.1	0 1 3	8.6	-8.0	3 4 5	21.3	-20.7	5 1 8	15.9	-16.5	7 2 11	14.1	-13.2					
6 4 0*	32.2	33.0	2 1 3	22.6	23.8	5 4 5	30.2	-30.6	7 1 8*	3.1	1.5	9 3 11	8.6	-7.9					
8 4 0*	16.8	17.0	4 1 3	19.4	-20.0	7 4 5	16.9	-17.9	9 1 8*	3.1	2.9	2 3 11	5.9	-5.9					
0 6 0*	18.1	-21.3	6 1 3	22.1	21.9	9 4 5	8.7	-6.9	0 2 8	33.1	-33.9	4 3 11*	3.1	4.7					
2 6 0*	21.7	25.0	8 1 3	8.9	-8.6	0 5 5	32.3	31.4	2 2 8	12.3	11.9	6 3 11	16.1	-13.4					
4 6 0*	3.1	-1.8	10 1 3	6.7	3.5	2 5 5	11.0	-11.2	4 2 8	15.8	-16.0	1 4 11	23.6	-23.6					
6 6 0*	3.1	-1.1	1 2 3	28.4	25.6	4 5 5	12.4	12.3	6 2 8*	3.1	1.1	3 4 11	22.2	-21.8					
8 6 0*	5.9	-9.0	3 2 3	22.8	-21.4	6 5 5*	3.1	3.7	8 2 8	4.9	-2.6	5 4 11	17.6	-17.8					
0 8 0*	24.7	26.3	5 2 3	12.1	13.5	8 5 5*	3.1	3.2	1 3 8	14.7	14.5	0 5 11	4.9	4.7					
2 8 0*	3.1	-2.3	7 2 3	5.1	-4.9	1 6 5	8.3	-8.3	3 3 8	10.1	-10.5	2 5 11*	3.1	4.4					
4 8 0*	12.3	9.7	9 2 3	7.9	-7.7	3 6 5	17.6	-18.1	5 3 8	15.8	16.1	4 5 11	5.8	-9.0					
6 8 0*	63.5	-73.3	0 3 3	18.4	18.3	5 6 5*	3.1	-3.8	7 3 8*	3.1	4	1 6 11	6.1	-6.3					
8 8 0*	3.1	-1.3	2 3 3	8.9	-8.5	7 6 5	5.7	-6.5	0 4 8	44.5	43.1	3 6 11*	3.1	-5.1					
1 0 1*	42.7	-44.7	4 3 3	21.0	21.1	0 7 5	9.0	-9.0	2 4 8	11.9	10.7	0 0 12	25.3	26.5					
3 0 1*	17.4	-17.4	6 3 3	14.2	-13.9	2 7 5	16.8	16.0	4 4 8	29.1	28.9	2 0 12	11.7	12.9					
5 0 1*	5.2	-4.5	8 3 3	10.1	9.7	4 7 5*	3.1	-1.7	6 4 8	12.4	13.8	4 0 12	23.6	24.8					
7 0 1*	10.8	-10.2	10 3 3	4.7	-1.4	6 7 5*	3.1	-1.5	8 4 8	14.9	10.4	6 0 12	4.9	3.9					
9 0 1*	75.3	-82.1	1 4 3	34.8	-34.5	1 8 5	9.7	-9.5	1 5 8	5.7	-6.0	1 1 12*	3.1	5					
1 1 1*	5.7	-5.8	3 4 3	7.0	-5.6	3 8 5*	3.1	-1.0	3 5 8	12.1	11.5	3 1 12	17.1	18.4					
3 1 1*	26.9	-27.1	5 4 3	29.9	-29.2	0 0 6	48.2	47.7	5 5 8	8.9	-9.6	5 1 12	5.5	-5.5					
5 1 1*	6.0	-5.8	7 4 3	11.1	-11.5	2 0 6	58.4	58.1	7 5 8*	3.1	2.2	7 1 12	5.4	6.5					
7 1 1*	10.5	-6.7	9 4 3*	3.1	-4.2	4 0 6	16.7	17.5	0 6 8*	3.1	-1.9	0 2 12	14.8	14.5					
9 1 1*	43.4	-47.8	0 5 3*	3.1	1.2	6 0 6	40.8	41.8	2 6 8	16.9	17.0	2 2 12	24.2	24.5					
1 2 2*	74.5	-80.8	2 5 3	14.5	15.2	8 0 6*	3.1	4.0	4 6 8*	3.1	3.8	4 2 12	7.6	8.4					
3 2 2*	19.9	-19.8	4 5 3	4.5	-4.7	10 0 6	14.3	16.8	6 6 8	6.6	9.9	6 2 12	18.8	22.2					
5 2 2*	24.4	-24.5	6 5 3	16.2	15.7	1 1 6	11.8	11.3	1 7 8	7.4	6.4	1 3 12	11.8	12.2					
7 2 2*	21.9	-21.8	8 5 3*	3.1	-6.9	3 1 6	34.7	34.4	3 7 8	6.1	-6.6	3 3 12	4.6	-5.0					
9 2 2*	31.5	-34.3	1 6 3	11.4	-12.0	5 1 6*	3.1	.9	1 0 9	12.3	-11.0	5 3 12	14.2	13.5					
1 3 3	22.6	24.8	3 6 3	24.5	-26.5	7 1 6	7.6	7.1	3 0 9	10.7	-9.4	0 4 12	18.8	18.3					
3 3 3	16.1	-16.8	5 6 3*	3.1	-4.5	9 1 6	10.8	10.1	5 0 9	7.7	-8.0	2 4 12	9.9	9.9					
5 3 3	9.0	8.9	7 6 3	10.9	-10.2	0 2 6	58.5	56.7	7 0 9	8.4	-8.9	4 4 12	18.0	14.7					
7 3 3	3.1	-2.5	0 7 3*	3.1	3.7	2 2 6	37.7	37.8	9 0 9*	3.1	-1.8	1 5 12	7.5	7.3					
9 3 3	3.1	-2.6	2 7 3	3.1	-2.4	4 2 6	54.4	54.3	0 1 9	24.3	24.2	3 5 12	19.6	19.9					
1 4 4	50.1	-53.7	4 7 3	6.1	7.4	6 2 6	11.9	11.9	2 1 9	35.6	-36.7	0 6 12	7.6	10.5					
3 4 4	3.4	-1.9	6 7 3	6.8	-3.4	8 2 6	28.5	29.9	4 1 9*	3.1	-1.3	2 6 12	10.4	14.2					
5 4 4	28.3	-28.6	1 8 3	24.1	-24.3	1 3 6	8.3	7.2	6 1 9	3.9	-4.6	1 0 13	6.3	-5.4					
7 4 4	11.2	-11.3	3 8 3	11.0	-11.0	3 3 6	14.7	-14.1	8 1 9	9.2	-6.5	3 0 13	13.4	-13.8					
9 4 4	3.1	-2.1	0 0 4*	91.5	99.6	5 3 6	8.6	8.3	1 2 9	16.7	-16.0	5 0 13*	3.1	-1.3					
0 5 5	9.6	-11.7	2 0 4	28.8	-28.0	7 3 6*	3.1	-1.3	3 2 9	15.6	-15.6	0 1 13	17.4	18.0					
2 5 5	38.9	-43.1	4 0 4	36.9	38.7	9 3 6	5.5	-5.1	5 2 9	12.4	-12.7	2 1 13	14.3	-15.2					
4 5 5	11.2	-12.1	6 0 4	16.0	16.5	0 4 6	21.4	21.1	7 2 9	7.6	-6.9	4 1 13	4.5	3.4					
6 5 5	21.4	-21.6	8 0 4	10.8	10.6	2 4 6	31.2	29.2	0 3 9	5.1	-4.8	6 1 13*	3.1	4.5					
8 5 5	9.5	-6.1	10 0 4	7.7	4.2	4 4 6	7.4	6.8	2 3 9	43.9	43.2	1 2 13	6.7	-7.9					
1 6 6	14.2	-15.2	1 1 4	21.9	-20.1	6 4 6	24.3	25.6	4 3 9	11.8	11.5	3 2 13*	3.1	1.1					
3 6 6	29.2	-31.0	3 1 4	13.6	13.0	8 4 6*	3.1	3.6	6 3 9	11.6	11.4	5 2 13	8.3	-9.8					
5 6 6	5.7	-6.6	5 1 4	15.6	-16.1	1 5 6	10.8	11.0	8 3 9	14.3	10.7	0 3 13	22.8	-22.7					
7 6 6	11.7	-11.8	7 1 4*	3.1	1	3 5 6	23.5	23.4	1 4 9	14.7	-15.0	2 3 13	6.5	6.3					
0 7 7	10.5	-12.1	9 1 4*	3.1	1.1	5 5 6*	3.1	4.1	3 4 9	12.5	-12.4	4 3 13	9.3	-11.7					
2 7 7	7.0	6.2	0 2 4	24.0	-23.1	7 5 6	8.1	7.7	5 4 9	10.0	-10.4	1 4 13	9.1	-8.3					
4 7 7	6.5	-6.8	2 2 4	75.9	76.8	0 6 6	18.9	18.3	7 4 9	8.7	-9.0	3 4 13	15.3	-14.0					
6 7 7	3.1	-1.3	4 2 4	11.6	11.1	2 6 6	13.4	13.3	0 5 9	21.7	21.1	0 5 13	7.4	10.8					
1 8 8	11.0	-11.6	6 2 4	18.9	18.6	4 6 6	21.0	21.7	2 5 9	15.2	-14.2	2 5 13	14.7	-11.4					
3 8 8	3.1	1.7	8 2 4	13.5	13.8	6 6 6*	3.1	-1.7	4 5 9	4.7	4.7	0 0 14	10.1	-10.2					
0 0 2	5.8	5.4	10 2 4	8.1	10.9	1 7 6	5.5	5.6	6 5 9*	3.1	6.3	2 0 14	14.2	14.5					
2 0 2	13.1	-12.6	1 3 4	17.2	-16.1	3 7 6	5.4	-4.9	1 6 9	15.7	-15.5	4 0 14*	3.1	3					
4 0 2	27.1	-26.7	3 3 4	33.2	-32.7	5 7 6	7.1	7.0	3 6 9	15.9	-15.3	6 0 14*	3.1	5.7					
6 0 2	29.7	30.4	5 3 4*	3.1	-2.9	0 8 6*	3.1	7.1	5 6 9	12.0	-12.3	1 1 14*	3.1	8					
8 0 2	14.7	-14.8	7 3 4	9.8	-10.1	2 8 6*	3.1	7.1	0 7 9*	3.1	-1.9	3 1 14	9.9	9.9					
10 0 2	7.9	10.5	9 3 4	8.5	-7.8	1 0 7	14.3	-14.1	2 7 9	24.2	19.3	5 1 14*	3.1	-1.9					
1 1 2*	22.1	-20.1	0 4 4	57.9	59.7	3 0 7*	3.1	2.5	0 0 10	7.5	7.6	0 2 14	18.6	19.8					
3 1 2*	3.1	1.9	2 4 4	5.9	-6.2	5 0 7	15.6	-16.2	2 0 10	33.5	33.6	2 2 14*	3.1	-4.4					
5 1 2	10.3	-10.9	4 4 4	29.7	29.0	7 0 7	4.1	-4.7	4 0 10	5.9	6.2	4 2 14	9.5	6.7					
7 1 2	3.2	-3.2	6 4 4	15.8	15.6	9 0 7*	3.1	-3.0	6 0 10	18.3	19.0	1 3 14	5.9	-4.7					
9 1 2*	3.1	3	8 4 4	9.0	7.2	0 1 7	7.4	7.2	8 0 10	3.8	7.5	3 3 14	14.0	-12.6					
0 2 2	11.3	13.1	1 5 4	19.5	-20.5	2 1 7	13.0	12.8	1 1 10	17.1	-17.5	0 4 14*	3.1	1.7					
2 2 2	23.2	23.7	3 5 4	3.8	-4.4	4 1 7	12.8	-12.5	3 1 10	3.2	3.6	2 4 14	15.0	19.2					
4 2 2	44.8	44.3	5 5 4	17.3	-17.1	6 1 7	22.9	23.9	5 1 10	14.4	-15.2	1 0 15*	3.1	-5.5					
6 2 2	5.7	-6.7	7 5 4	7.2	-5.7	8 1 7	10.0	-9.7	7 1 10	5.8	-5.6	3 0 15	9.8	-12.6					
8 2 2	29.5	29.2	0 6 4*	3.1	-2.7	1 2 7	28.8	-27.3	0 2 10	50.4	50.6	0 1 15	8.1	6.1					
10 2 2*	3.1	-1.3	2 6 4	33.3	33.5	3 2 7	38.7	-38.6	2 2 10	24.0	23.8	2 1 15	8.4	5.5					
1 3 3	36.7	37.3	4 6 4	8.5	8.8	5 2 7	15.4	-15.0	4 2 10	38.7	39.3	4 1 15*	3.1	-3.3					
3 3 3	18.0	18.3	6 6 4	9.2	10.8	7 2 7	16.9	-17.5	6 2 10	17.3	17.0	1 2 15	20.3	-20.1					
5 3 3	20.5	21.0	1 7 4	7.5	-7.2	9 2 7	17.5	-11.9	8 2 10	2									

Table 5. Al-O, Na-O and C-O bond distances (Å) and bond angles (°) in dawsonite. Estimated standard deviations on the last digits are given in parentheses.

Al-O(2)	1.939(2)	Na-O(2)	2.465(2)
Al-O(3)	1.874(2)	Na-O(3)	2.389(2)
O(2)-Al-O(3)	92.06(8)	O(2)-Na-O(2iii)	180
O(2)-Al-O(2i)	180	O(2)-Na-O(3iv)	66.09(6)
O(3)-Al-O(3i)	180	O(2)-Na-O(2v)	84.74(6)
O(3)-Al-O(3ii)	98.55(7)	O(3iv)-Na-O(3vi)	180
C-O(1)	1.250(5)	O(1)-C-O(2)	120.91(18)
C-O(2)	1.308(3)	O(2)-C-O(2)	119.79(34)

Key to symmetry operations:

None	<i>x</i>	<i>y</i>	<i>z</i>
i	- <i>x</i>	- <i>y</i>	1- <i>z</i>
ii	<i>x</i>	- <i>y</i>	1- <i>z</i>
iii	1/2+ <i>x</i>	1/2- <i>y</i>	1/2- <i>z</i>
iv	<i>x</i>	1- <i>y</i>	1- <i>z</i>
v	<i>x</i>	1/2- <i>y</i>	<i>z</i>
vi	1/2- <i>x</i>	1- <i>y</i>	<i>z</i> -1/2

system. Each Al polyhedron shares two opposite edges of its (OH)<sub>4</sub> base with the adjacent Al atoms to build up a chain of octahedra straight along *b*. The Na polyhedra instead, located in the spaces left by the Al chains, make straight chains along *a* by a similar sharing of O<sub>4</sub> basal opposite edges, giving the framework a three-dimensional arrangement. The O(2), O(3) and their symmetrical oxygen atoms belonging to Na and Al polyhedra are shared by both cations, making multiple contacts between the two kinds of perpendicular chains and giving the structure most of its bonds. The CO<sub>3</sub> group is attached to one Al chain and two Na chains providing further three-dimensional bonding. The H bonding system takes place inside an empty channel running at 0 *y* 0. The structure is sketched in Fig. 6. The {101} cleavage can be explained to occur as a rupture of Na chains and hydrogen bonds, thus leaving intact the Al chains with the opposite CO<sub>3</sub> groups attached.

The electrostatic valence balance, given in Table 6, was computed after BROWN & SHANNON (1973) with data from their Table 1 and the hydrogen bond curve by DONNAY & DONNAY (1973) and considering for C four v. u. shared according to the square of the distance.

All calculations were done on a CII 10070 computer using some local programs and ORFLS (BUSING, MARTIN & LEVY, 1962), ORTEP (JOHNSON, 1965), LSQPL and BONDLA from the X-ray System (STEWART, KRUGER, AMMON, DICKINSON & HALL, 1972).

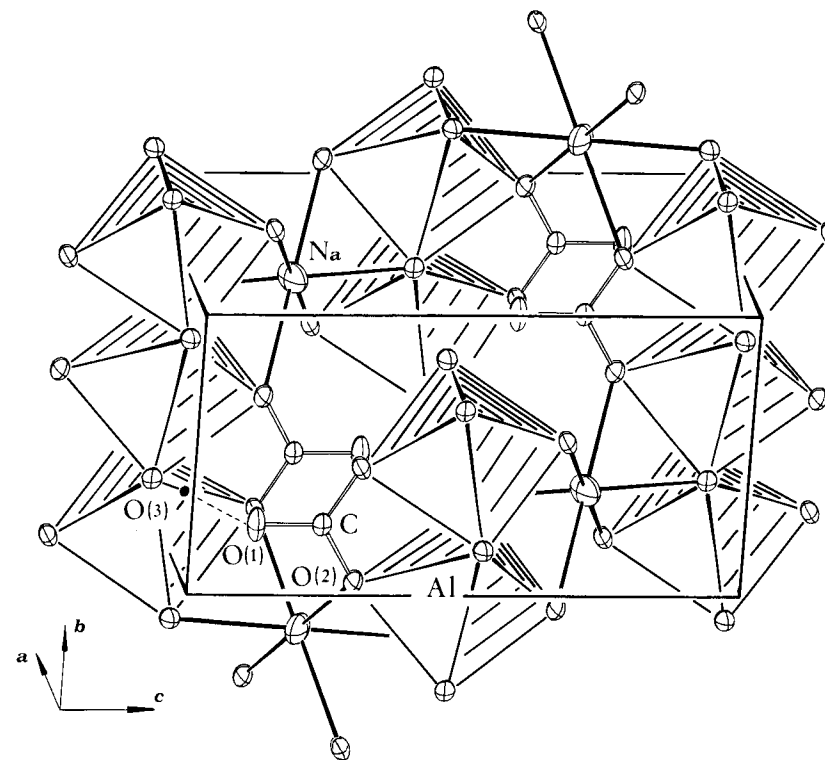


Fig. 6. ORTEP (JOHNSON, 1965) drawing of the structure of dawsonite. The thermal ellipsoids are scaled to include the 50% probability level. Asymmetric atoms are labelled according to Table 3. Al atoms not shown inside their octahedra.

Table 6. Electrostatic valence balance.

Atom	Al	C	Na	H	Tot.
O(1)		1.42		{ 0.17 0.17	1.76
O(2)	0.44	1.29	{ 0.16 0.16		2.05
O(3)	{ 0.53 0.53		0.19	0.83	2.08

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