# THE CRYSTAL STRUCTURE OF DAWSONITE $NaAl(CO_3)(OH)_2$

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## ABSTRACT

The structure of dawsonite was determined from Patterson projections and refined with difference Fourier maps and a least-squares fit of three-dimensional data. The structure consists of an assemblage of distorted $NaO_4(OH)_2$ octahedra, $AlO_2(OH)_4$ octahedra and $CO_3$ groups. Some hydrogen bonding is found to exist.

## INTRODUCTION

A thin, irregular-shaped splinter of dawsonite from the type locality on the McGill University campus in Montreal was used for this determination. A description of this occurrence of dawsonite in veinlets in a feldspathic dike has recently been given by Stevenson & Stevenson (1965) in this journal.

### *Unit cell*

The unit cell constants and space group were originally determined by C. Lauro (1941) on material from Komana, Albania, and are essentially consistent with the following constants determined from the Montreal material:

$$a = 6.710 \pm .006 \text{ Å}$$

$$b = 10.411 \pm .004 \text{ Å}$$

$$c = 5.58 \pm .01 \text{ Å}$$

The $a$ and $b$ parameters were obtained from a zero-level $c$-axis Weissenberg by a least-squares extrapolation to $\theta = 90°$, and the $c$ dimension from zero level $a$- and $b$-axis precession photographs.

The reciprocal lattice showed $mmm$ symmetry and the following systematic extinctions: for $(hkl)$ reflections $h + k + l = 2n$; for $h0l$ reflections, $h = 2n$ and $l = 2n$. This indicates space group $Imam$ which is the $a\bar{c}b$ setting of the space group $Imma$ as listed in the International Tables (1952). The matrix of transformation from the convention of setting used in the International Tables is $100/00\bar{1}/010$.

From the measured density of 2.44 and the formula weight of 143.99 g, the number of formulas per unit cell, $Z$, was determined to be 4. This yielded a calculated density of 2.43.

Powder diffraction data, obtained on a Debye-Scherrer camera (114.7 mm – diameter) using Cu$K\alpha$ radiation, together with calculated $d$ values are listed in Table 1.

Table 1. $X$-ray Powder Diffraction Data of Dawsonite
Observed data taken with Cu$K$ radiation on a Debye-Scherrer camera of 114.7 mm diameter. Calculated values from single crystal data

| $I$ obs. | $d$ obs. | $h$ | $k$ | $l$ | $d$ calc. |
|---|---|---|---|---|---|
| 10 | 5.7 | 1 | 1 | 0 | 5.639 |
| 7 | 3.38 | 2 | 0 | 0 | 3.355 |
| 4 | 3.00 | 1 | 3 | 0 | 3.082 |
| | | 0 | 3 | 1 | 2.946 |
| 9 | 2.79 | 2 | 2 | 0 | 2.819 |
| | | 2 | 1 | 1 | 2.771 |
| | | 0 | 0 | 2 | 2.790 |
| 7 | 2.61 | 0 | 4 | 0 | 2.602 |
| 5 | 2.50 | 1 | 1 | 2 | 2.500 |
| 4 | 2.23 | 2 | 3 | 1 | 2.214 |
| | | 1 | 4 | 1 | 2.225 |
| 6 | 2.15 | 2 | 0 | 2 | 2.145 |
| | | 3 | 1 | 0 | 2.186 |
| 1 | 2.06 | 2 | 4 | 0 | 2.056 |
| 8 | 1.989 | 1 | 5 | 0 | 1.988 |
| | | 2 | 2 | 2 | 1.983 |
| 5 | 1.955 | 0 | 5 | 1 | 1.950 |
| 7 | 1.732 | 0 | 6 | 0 | 1.735 |
| 7 | 1.692 | 1 | 2 | 3 | 1.694 |
| 7 | 1.622 | 4 | 0 | 0 | 1.677 |
| | | 2 | 4 | 2 | 1.655 |
| ½ | 1.619 | 1 | 5 | 2 | 1.619 |
| 2 | 1.551 | 3 | 3 | 2 | 1.559 |
| | | 2 | 6 | 0 | 1.541 |
| 1 | 1.488 | 0 | 6 | 2 | 1.473 |
| | | 2 | 3 | 3 | 1.473 |
| | | 1 | 4 | 3 | 1.476 |
| ½ | 1.422 | 0 | 7 | 1 | 1.436 |
| | | 4 | 0 | 2 | 1.437 |
| 4 | 1.394 | 4 | 4 | 0 | 1.409 |
| | | 4 | 2 | 2 | 1.385 |
| | | 0 | 5 | 3 | 1.387 |
| 4 | 1.341 | 5 | 1 | 0 | 1.330 |
| | | 3 | 6 | 1 | 1.331 |
| | | 3 | 5 | 2 | 1.337 |
| | | 2 | 6 | 2 | 1.349 |
| | | 0 | 2 | 4 | 1.347 |
| 2 | 1.135 | 1 | 9 | 0 | 1.139 |
| | | 0 | 9 | 1 | 1.132 |
| | | 3 | 7 | 2 | 1.131 |
| 1 | 1.113 | 6 | 0 | 0 | 1.118 |
| | | 2 | 8 | 2 | 1.112 |
| 1 | 1.097 | 6 | 2 | 0 | 1.093 |
| | | 6 | 1 | 1 | 1.090 |
| | | 4 | 7 | 1 | 1.091 |
| | | 3 | 8 | 1 | 1.102 |
| | | 2 | 7 | 3 | 1.097 |
| ½ | 1.076 | 2 | 9 | 1 | 1.073 |
| | | 4 | 0 | 4 | 1.072 |
| ½ | 1.053 | 1 | 9 | 2 | 1.055 |
| | | 1 | 8 | 3 | 1.053 |
| | | 4 | 2 | 4 | 1.050 |
| ½ | 1.032 | 2 | 6 | 4 | 1.034 |
| | | 3 | 5 | 4 | 1.028 |

### *Atomic positions*

Intensities were gathered from the 0, 1st, 2nd, and 3rd level of the $c$ axis by a single-crystal Geiger counter goniometer using Cu$K\alpha$ by recording the peaks on a chart recorder and determining the area under the recorded curves with a planimeter. These intensities were corrected for Lorentz and polarization factors. The fragment of a crystal broken from a platy rosette was very irregular in shape and no attempt was made to correct for absorption. The linear absorption coefficient $U = 42.8\ \text{cm}^{-1}$ for the very small crystal would involve only a small correction.

Patterson projections were computed on the $(0kl)$ and $(hk0)$ faces. These were interpreted by means of minimum function maps. The structure was confirmed and refined by electron density projections and sections. Final refinement was done by least squares until the residual factor was reduced to $R = .17$ for all non-zero reflections. The temperature factor was $B = .03\ \text{Å}^2$. The final parameters were as follows:

(to each of the parameters below add 1/2, 1/2, 1/2).

4 Na in 4 (*c*) 1/4, 3/4, 1/4; 1/4, 1/4, 3/4.

4 Al in 4 (*b*) 0, 1/2, 0; 0, 1/2, 1/2.

4 C in 4 (*e*) 0, .254, 1/4; 0, .746, 3/4.

4 $O_I$ in 4 (*e*) 0, .133, 1/4; 0, .867, 3/4.

8 $O_{II}$ in 8 (*h*) 0, .315, .052; 0, .685, .948; 0, .685, .552; 0, .315, .448.

8 (OH) in 8 (*i*) .18, .525, 1/4; .82, .525, 1/4; .32; .975, 1/4; .68, .975, 1/4.

*Crystal chemistry*

The crystal structure of dawsonite is illustrated in Fig. 1.

As might be expected, the carbonate groups are planar triangular groups. Two oxygens are at 1.27 Å from the carbon and one is at 1.26 Å. The O—C—O bond angles are one of 120.2° and two of 119.9°. Sodium is surrounded by four oxygens and two hydroxyl ions in a octahedral configuration with considerable trigonal distortion. The four sodium-oxygen distances are 2.47 Å, and both the sodium-hydroxyl distances are 2.39 Å.

Aluminum is octahedrally coordinated to four hydroxyl ions at 1.86 Å and to two oxygens at 1.95 Å. The four hydroxyl ions are in a rectangular rather than square array, with the OH═OH distance being 2.84 Å along one edge and 3.72 Å along the other.

Although most of the oxygen-oxygen and oxygen-hydroxyl distances are 2.73 Å or greater, one of the oxygens of each carbonate group is 2.66 Å from a hydroxyl ion, suggesting a possible hydrogen bond. The infrared absorption spectrum of dawsonite (Fig. 2) shows two bands related to hydrogen. The OH stretching fundamental is a broad band centred at $3{,}280\ \text{cm}^{-1}$, and is thus shifted by $370\ \text{cm}^{-1}$ from that of free $OH^-$. It is thus typical of multiple non-equivalent hydrogen bonds (Cross, 1960). The band at $\sim 950\ \text{cm}^{-1}$ is probably an O-H—Al bending

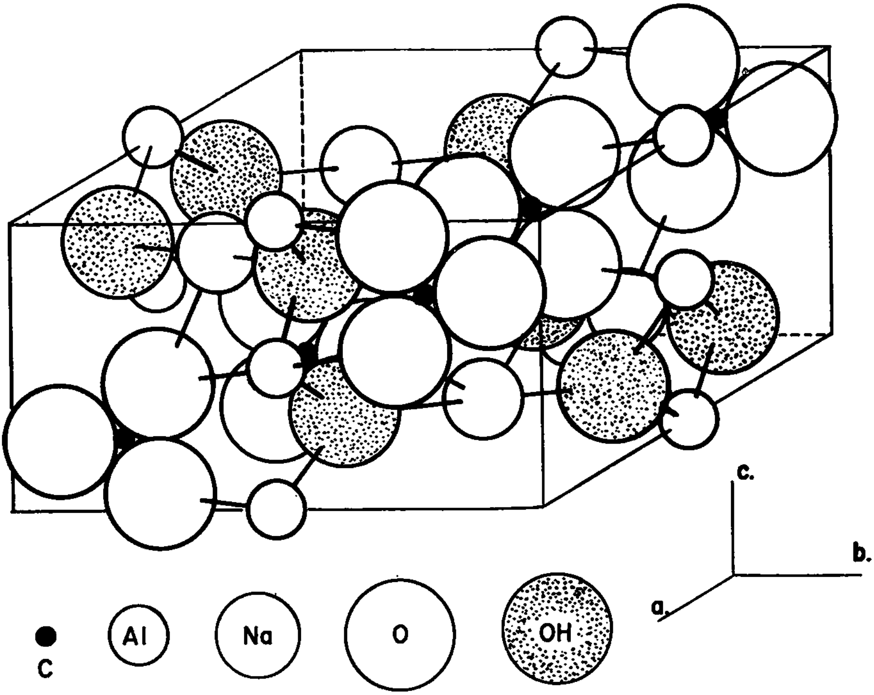

Fig. 1. Crystal structure of dawsonite.

Table 2. The Infrared Absorption Spectrum of Dawsonite

The values were obtained from a higher resolution spectrophotometer than the trace illustrated in figure 2

| Wave number (cm$^{-1}$) | Strength | Assignment |
|---|---|---|
| 3,280 | Strong | OH stretching, multiple hydrogen bonds |
| 2,750 | Weak | |
| 2,470 | " | |
| 1,965 | " | Harmonics, exact origin unknown |
| 1,760 | " | |
| 1,710 | " | |
| 1,550 | Very strong | $CO_3^{--}$ assymetric stretching modes |
| 1,390 | " " | |
| 1,090 | Medium | $CO_3^{--}$ symmetric stretching |
| 950 | Strong | OH—Al bending modes |
| 930 | " | |
| 858 | Medium | $CO_3^{--}$ bending modes |
| 842 | " | |
| 727 | Medium | $CO_3^{--}$ bending modes |
| 690 | Medium strong | |

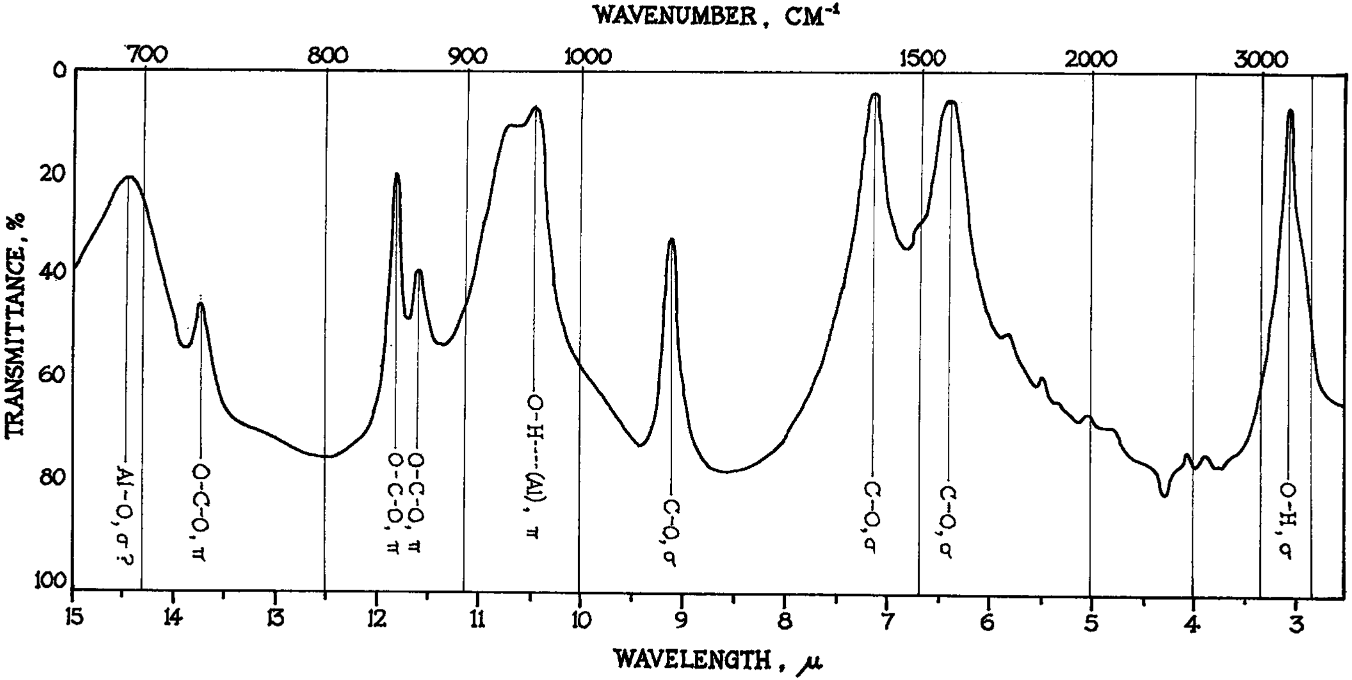

FIG. 2. Infrared absorption spectrum of dawsonite in a KBr pellet. The fundamental vibration bands are assigned with regard to the bond involved and the type of deformation. σ and π are stretching and bending modes respectively.

mode (Stubičan & Roy, 1961). Therefore, some hydrogen bonds at least are directed toward the aluminums.

The remainder of the bands are $CO_3^=$ stretching and bending modes as indicated in Fig. 2 and Table 2. The asymmetric modes are strongly split because the *2mm* symmetry of the crystal field breaks up the two-fold degeneracy of the free ion modes. The great magnitude of the splitting is probably related to the very different environments of $O_I$ and $O_{II}$. The latter is coordinated with one Al and two Na as well as C whereas $O_I$ is coordinated only with C and the two suggested hydrogen bonds. A similar amount of splitting has been observed in the spectra of at least six other hydrated carbonates (Huang & Kerr, 1960).

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