The crystal structure of davreuxite, $MnAl_6Si_4O_{17}(OH)_2$

Kurt Sahl

Institut für Mineralogie
Ruhr-Universität Bochum, BRD

Peter G. Jones and George M. Sheldrick

Institut für Anorganische Chemie der Universität
Göttingen, BRD

Abstract

The structure of davreuxite, $MnAl_6Si_4O_{17}(OH)_2$, (space group $P2_1/m$; $a = 9.518(6)$, $b = 5.753(2)$, $c = 12.04(1)$Å, $\beta = 108.00(5)°$; $Z = 2$) was determined using diffractometer data (1079 unique observed reflections, $R = 0.06$). Davreuxite contains $[SiO_4]$ and $[Si_2O_6(OH)]$ groups and is related to the sorosilicates. The structure consists of double and single chains of alternating vertex-sharing SiO_4 and AlO_4 tetrahedra aligned parallel to [010]. These chains share vertices with parallel chains of vertex-sharing AlO_6 and $AlO_5(OH)$ octahedra. The $Si_2O_6(OH)$ groups and manganese ions (with distorted six-fold coordination) occupy channels between the chains.

Introduction

Davreuxite occurs in the Stavelot Massif, Belgium. It has recently been characterized by Fransolet and Bourguignon (1976), and Fransolet et al. (1984). The crystal structure analysis discussed here was necessary to establish the chemical formula and the structure type.

Experimental and data reduction

Preliminary X-ray investigations with photographic methods showed that davreuxite crystallizes in the monoclinic space group $P2_1/m$ (or $P2_1$) and that crystals are generally of very poor quality. A single crystal was selected for intensity measurements from a fibrous sample obtained from the Institut Royal des Sciences Naturelles (Brussels). It had an irregular lath shape with approximate dimensions $340 \times 50 \times 8$ μm parallel to b, c, and a respectively.

The crystal was oriented on a Syntex-$R\bar{3}$ four-circle diffractometer (MoKα radiation, graphite monochromator). Lattice constants were determined from the angular positions of 20 reflections by least-squares refinement: $a = 9.518(6)$, $b = 5.753(2)$, $c = 12.04(1)$Å, $\beta = 108.00(5)°$. The intensities of 4920 reflections to $\theta_{max} = 30°$ ($\sin \theta/\lambda = 0.7$Å^{-1}) were measured with variable speed ω-scans and scaled by comparison with repeatedly measured standard reflections. After applying Lp and absorption corrections (the latter based on distances between indexed faces), averaging equivalents (merging R-value 0.04) gave 1231 unique reflections, of which 1079 with $F > 4\sigma(F)$ were considered to be observed.

Structure determination and refinement

All calculations were performed with the program system SHELXTL written by G. M. Sheldrick.

The structure was solved in $P2_1/m$ by multisolution direct methods. The best E-map showed the positions of all cations; at this stage, it was not possible to differentiate between Al and Si. After refinement, a difference synthesis showed all the oxygen atoms. Al and Si sites were distinguished by the different M–O bond lengths, and by the temperature factors obtained using neutral Al scattering factors for all the cations. Refinement with anisotropic temperature factors for Al and Si caused all the U_{22} values to become close to zero, presumably due to anisotropic extinction caused by fibrous crystals or residual absorption errors. Refinement (with isotropic temperature factors for the oxygen atoms) proceeded to $R = 0.06$ and $R_w = 0.06$ for all 1079 observed reflections.[1] The final positional and thermal parameters of the metal and oxygen atoms are listed in Table 1.

Determinations of (OH)-groups

The structure determination shows that the cell contains $Mn_2Al_{12}Si_8O_{38}$. Four hydrogen atoms are thus needed for charge balance. Since it was not possible to find the positions of the hydrogen atoms by difference syntheses, the method of Donnay and Allmann (1970) was used to identify O^{2-}, OH^- and H_2O. The structure contains no H_2O but O(5) and O(10) correspond to (OH)-groups. The

[1] To receive a copy of the list of observed and calculated structure amplitudes, order Document AM-84-243 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue N.W., Washington, D.C. 20009. Please remit $5.00 in advance for the microfiche.

Table 1. Davreuxite. Atomic coordinates and thermal parameters. The U_{ij} are defined by the expression for the temperature factor: $T = \exp\,[-2\pi^2(U_{11}h^2a^{*2} + \ldots + U_{12}hka^*b^*)]$. Standard deviation in the last digit in parentheses.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	2e	0.3516(2)	0.25	0.6351(1)	0.015(1)	0.004(1)	0.026(1)	0	0.003(1)	0
Si(1)	2e	0.8115(3)	0.25	0.4796(1)	0.009(1)	0.001(1)	0.013(1)	0	0.002(1)	0
Si(2)	2e	0.4962(3)	0.25	0.3911(2)	0.011(1)	0.002(1)	0.015(1)	0	0.004(1)	0
Si(3)	2e	0.6823(3)	0.25	0.0966(2)	0.008(1)	0.001(1)	0.014(1)	0	0.002(1)	0
Si(4)	2e	0.8992(3)	0.25	0.8574(2)	0.009(1)	0.003(1)	0.014(1)	0	0.002(1)	0
Al(1)	2e	0.3196(3)	0.25	0.9032(2)	0.010(1)	0.004(1)	0.015(1)	0	0.001(1)	0
Al(2)	2e	0.0906(3)	0.25	0.1340(2)	0.009(1)	0.002(1)	0.015(1)	0	0.001(1)	0
Al(3)	4f	0.9387(2)	0.9953(3)	0.3075(2)	0.010(1)	0.000(1)	0.013(1)	0.000(1)	0.003(1)	0.000(1)
Al(4)	4f	0.4026(2)	0.0008(3)	0.1547(2)	0.009(1)	0.001(1)	0.014(1)	0.001(1)	0.002(1)	0.000(1)
O(1)	2e	0.9844(7)	0.25	0.9915(6)	0.015(1)					
O(2)	2e	0.4742(6)	0.25	0.8548(5)	0.010(1)					
O(3)	2e	0.5279(6)	0.25	0.1268(5)	0.011(1)					
O(4)	2e	0.7230(6)	0.25	0.8375(5)	0.010(1)					
OH(5)	2e	0.3656(7)	0.25	0.4535(5)	0.012(1)					
O(6)	2e	0.6499(7)	0.25	0.4992(5)	0.011(1)					
O(7)	2e	0.2786(6)	0.25	0.1501(5)	0.010(1)					
O(8)	2e	0.8290(7)	0.25	0.2097(5)	0.012(1)					
O(9)	2e	0.9432(7)	0.25	0.6047(5)	0.011(1)					
OH(10)	2e	0.0555(6)	0.25	0.3790(5)	0.009(1)					
O(11)	2e	0.1720(6)	0.25	0.7733(5)	0.010(1)					
O(12)	4f	0.8248(4)	0.0158(7)	0.4084(3)	0.009(1)					
O(13)	4f	0.6829(4)	0.0144(7)	0.0223(3)	0.009(1)					
O(14)	4f	0.0593(4)	0.9850(7)	0.2017(3)	0.010(1)					
O(15)	4f	0.4906(4)	0.0209(7)	0.3141(4)	0.011(1)					

valence sum of 1.300 for OH(5) possibly indicates partial substitution of O for OH at this site (see below).

In order to find hydrogen bonds, short oxygen–oxygen distances between coordination polyhedra must be considered. The closest approach between oxygen atoms which do not belong to the same coordination polyhedron is 2.807Å. A linear hydrogen bond would have an estimated bond valence of only 0.162 for this distance (Donnay and Allmann, 1970). This does not allow localization of hydrogen bonding in view of the amplitude of the deviations from charge balance for O(3), OH(5), O(8) and OH(10).

Discussion of the structure

Selected interatomic distances and angles are listed in Table 2. Figure 1 shows a projection of the structure down [010]. Si(4) and Al(2) alternate in double chains of tetrahedra parallel to, and near to, [010]. Si(3) and Al(1) alternate in single chains of tetrahedra also parallel to [010]. Si(1) and Si(2) form Si$_2$O$_6$(OH) groups (see below) near the center of the cell. These structural elements are connected by Mn (which shows distorted 6-fold coordination) and by columns of Al(3) and Al(4) octahedra parallel to [010].

Double chain of tetrahedra

The double chain of tetrahedra [Al(2)$_2$Si(4)$_2$O$_{10}$] consists of two single chains linked via O(1). Silicon and aluminium alternate in each single chain as well as across the O(1)-linkage between chains. The angle Si(4)–O(1)–Al(2) is 175.0°. The tetrahedra in each single chain are

linked through O(14)-atoms with Si(4)–O(14)–Al(2) = 114.2°. The shortest bonding distances in the tetrahedra are Si(4)–O(1) (1.567Å) and Al(2)–O(1) (1.700Å). The longest bonds are Si(4)–O(14) (1.632Å) and Al(2)–O(14) (1.796Å).

Such a double chain of composition [Al$_2$Si$_2$O$_{10}$] was found by Burnham (1963) in sillimanite, Al$_2$SiO$_5$. Al and Si are distributed in the same manner as in davreuxite. The corresponding linkage angles are 171.6° and 114.4°, and the shortest bonds (Si–O 1.564Å, Al–O 1.721Å) involve the oxygen atoms linking the single chains. The deviations from ideal geometry of the tetrahedra in the double chains of sillimanite and davreuxite are thus remarkably similar.

The presence of this double chain in the structure of davreuxite may explain the relationship found by Fransolet and Bourguignon (1976) between the infrared spectra of davreuxite and sillimanite. This applies especially to the intense band at 1200 cm^{-1} which, in sillimanite, is attributed to the nearly linear Si–O–Al bridges between the single chains.

Single chain of tetrahedra

In the single chain [Al(1)Si(3)O$_6$], silicon and aluminium also alternate parallel to [010]; the tetrahedra are linked through O(13). The angle Si(3)–O(13)–Al(1) is 115.8°, slightly larger than the corresponding angle in the double chains of davreuxite and sillimanite. As can be seen from Table 2, the bonding distances in the tetrahedra are closer to the average distances than in the double chains, in which the short bonds to O(1) have to be

Table 2. Davreuxite. Interatomic distances (Å) and angles

Table 2. (continued)

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Double chain [Al(2)₂ Si(4)₂ O₁₀]

Tetrahedron around Si(4)
  Si(4) - O(1)    1.567(6)
  Si(4) - O(4)    1.619(7)
  Si(4) - O(14)   1.632(5)   2x

  O(14) - Si(4) - O(14)   111.9(4)°
  O(14) - Si(4) - O(1)    109.3(2)°   2x
  O(14) - Si(4) - O(4)    108.4(2)°   2x
  O(1)  - Si(4) - O(4)    109.5(4)°

Tetrahedron around Al(2)
  Al(2) - O(1)    1.700(6)
  Al(2) - O(7)    1.739(7)
  Al(2) - O(14)   1.796(5)   2x

  O(14) - Al(2) - O(14)   116.2(3)°
  O(14) - Al(2) - O(1)    109.1(2)°   2x
  O(14) - Al(2) - O(7)    105.0(2)°   2x
  O(1)  - Al(2) - O(7)    112.5(4)°

  Si(4) - O(1)  - Al(2)   175.0(5)°
  Si(4) - O(14) - Al(2)   114.2(3)°

Chain [Al(1) Si(3) O₆]

Tetrahedron around Si(3)
  Si(3) - O(3)    1.619(7)
  Si(3) - O(8)    1.621(5)
  Si(3) - O(13)   1.625(4)   2x

  O(13) - Si(3) - O(13)   113.0(3)°
  O(13) - Si(3) - O(3)    106.4(2)°   2x
  O(13) - Si(3) - O(8)    108.3(2)°   2x
  O(3)  - Si(3) - O(8)    114.7(3)°

Tetrahedron around Al(1)
  Al(1) - O(2)    1.743(7)
  Al(1) - O(11)   1.749(6)
  Al(1) - O(13)   1.770(4)   2x

  O(13) - Al(1) - O(13)   118.5(3)°
  O(13) - Al(1) - O(2)    108.3(2)°   2x
  O(13) - Al(1) - O(11)   108.7(2)°   2x
  O(2)  - Al(1) - O(11)   103.3(3)°

  Si(3) - O(13) - Al(1)   115.8(3)°
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[Si(1) Si(2) O₆ (OH)]  group

Tetrahedron around Si(1)
  Si(1) - O(6)    1.627(7)
  Si(1) - O(9)    1.635(6)
  Si(1) - O(12)   1.623(4)   2x

  O(12) - Si(1) - O(12)   112.3(3)°
  O(12) - Si(1) - O(9)    108.9(2)°   2x
  O(12) - Si(1) - O(6)    108.0(2)°   2x
  O(6)  - Si(1) - O(9)    110.9(4)°

Tetrahedron around Si(2)
  Si(2) - O(6)    1.630(6)
  Si(2) - OH(5)   1.639(8)
  Si(2) - O(15)   1.603(2)   2x

  O(15) - Si(2) - O(15)   110.6(2)°
  O(15) - Si(2) - O(6)    108.8(2)°   2x
  O(15) - Si(2) - OH(5)   111.8(1)°   2x
  O(6)  - Si(2) - OH(5)   104.8(3)°

  Si(1) - O(6)  - Si(2)   122.7(4)°

Polyhedron around Mn
  Mn - O(12)    2.211(4)   (2x)
  Mn - O(15)    2.119(1)   (2x)
  Mn - OH(5)    2.231(7)
  Mn - O(2)     2.538(6)

  O(12)  - Mn - O(12)    87.5(2)°
  O(15)  - Mn - O(15)    94.7(1)°
  O(2)   - Mn - O(12)    108.5(2)°   2x
  O(2)   - Mn - O(15)    69.1(1)°    2x
  O(2)   - Mn - OH(5)    150.8(2)°
  OH(5)  - Mn - O(12)    92.2(2)°    2x
  OH(5)  - Mn - O(15)    91.8(1)°    2x
  O(15)  - Mn - O(12)    88.8(1)°
                         174.6(1)°

Octahedron around Al(4)
  Al(4) - O(2)    1.885(5)
  Al(4) - O(3)    1.959(5)
  Al(4) - O(4)    1.895(5)
  Al(4) - O(7)    1.847(4)
  Al(4) - O(13)   2.033(4)
  Al(4) - O(15)   1.844(2)

  O(2) - Al(4) - O(4)    80.4(2)°
  O(3) - Al(4) - O(7)    81.0(2)°
  O(2) - Al(4) - O(3)    97.3(2)°
  O(4) - Al(4) - O(7)    100.7(2)°

Octahedron around Al(3)
  Al(3) - O(8)     1.966(4)
  Al(3) - O(9)     1.907(4)
  Al(3) - OH(10)   1.880(4)
  Al(3) - O(11)    1.848(4)
  Al(3) - O(12)    1.864(4)
  Al(3) - O(14)    1.962(5)

  O(9)   - Al(3) - O(11)   82.5(2)°
  OH(10) - Al(3) - O(8)    79.8(2)°
  O(8)   - Al(3) . O(11)   98.2(2)°
  OH(10) - Al(3) - O(9)    99.2(2)°
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balanced. The longest bonds in the tetrahedra involve the linking atom parallel to [010] with Si(3)–O(13) 1.625, Al(1)–O(13) 1.770Å.

$Si_2O_6(OH)$ group

A hydroxylated Si_2O_7-group, here [Si(1)Si(2)O_6(OH)], is an unusual feature in silicate chemistry. The tetrahedra around Si(1) and Si(2) in davreuxite are linked by O(6), with Si(1)–O(6)–Si(2) 122.7°. The tetrahedra show no distortions that could be considered typical of an Si_2O_6(OH) group. The distance Si(2)–OH(5) = 1.639Å is not significantly longer than the other bonds in the group. In the structure of pumpellyite (Gottardi, 1965; Galli and Alberti, 1969), a complex mixed-group silicate, an Si_2O_7 group with bond lengths deviating from normal values by up to 0.1Å was found. Allmann and Donnay (1970) showed by valence summation that the structure of pumpellyite contains an Si_2O_6(OH) group. In julgoldite, which is isostructural with pumpellyite, they calculated a valence sum of 1.291 for the hydroxyl group and explain this high value by assuming partial substitution of O for OH. In the carefully refined structure of julgoldite all Si–O distances are in the usual range (Allmann and Donnay, 1973).

Coordination of manganese

The manganese ion is located near the center of a square plane of oxygen atoms with Mn–O(12) 2.211Å (2x) and Mn–O(15) 2.119Å (2x). A further bond is directed perpendicular to this square (Mn–OH(5), 2.231Å), thus completing a slightly distorted tetragonal pyramid. Opposite the base of this pyramid, a further bond (Mn–O(2), 2.538Å) forms angles between 69.1° and 108.5° with the basal bonds (the next closest oxygen atom is O(11) at 2.729Å; this distance is considered to be too large for an Mn–O bond). Distorted five- and six-fold coordinations in the crystal chemistry of manganese are well-known. According to a review by Peacor (1978), Mn^{2+}–O bonds
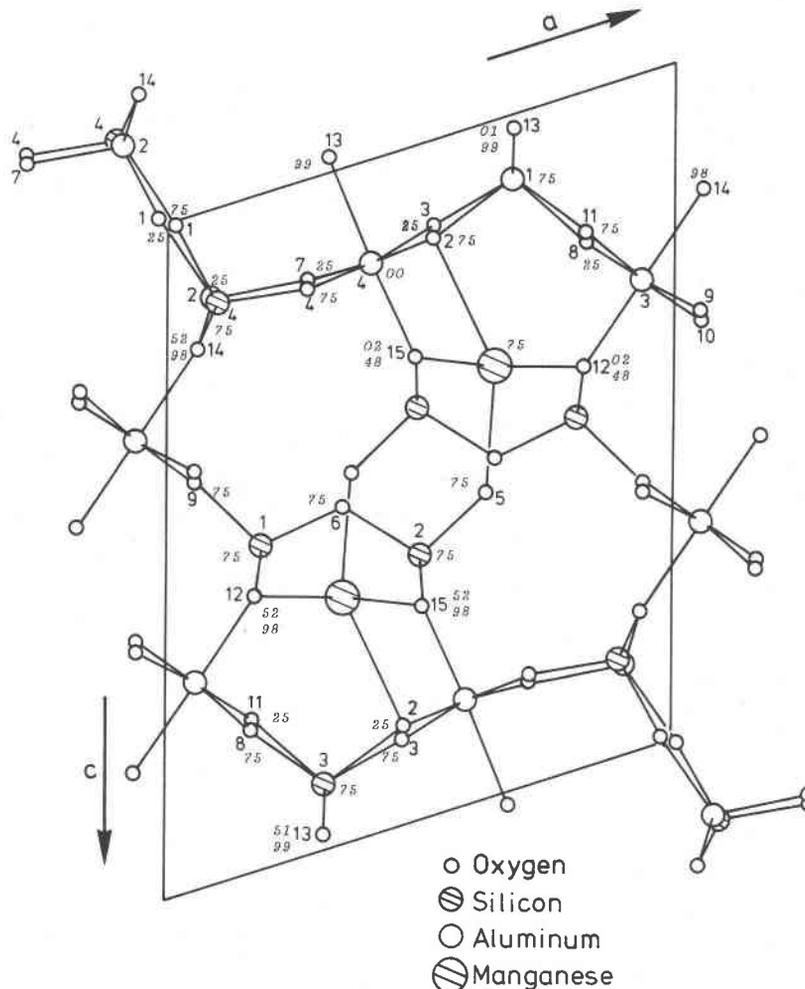
Fig. 1. Davreuxite. Projection of the structure along [010]. The atom numbering corresponds to Table 1 and the text. The figures in italics are y coordinates multiplied by 100.

range from 1.98Å to about 2.50Å, Mn^{2+}–OH bonds from 2.06Å to 2.60Å. Distances between 2.10Å and 2.25Å are most frequent for Mn^{2+}–O bonds (Mn^{3+}–O bonds are as short as 1.90Å).

Al(3) and Al(4) octahedra

Al(4) is octahedrally coordinated by six oxygen atoms, Al(3) by five oxygen atoms and one OH-group (Table 2 and Fig. 1). The bond distances are in the usual range. The octahedra form chains parallel to [010], with shortened common edges.

Conclusions

The crystal chemical formula for davreuxite contains two formula units:
$Mn_2^{[5+1]}Al_8^{[6]}[Al_2^{[4]}Si_2^{[4]}O_{10}][Al^{[4]}Si^{[4]}O_6]_2[Si_2^{[4]}O_6(OH)]_2(OH)_2$. Davreuxite represents a new type of sili-

cate structure. It is a mixed-group silicate with isolated $[SiO_4]$ groups and $[Si_2O_6(OH)]$ groups. Neglecting the distinction between Si and Al, the structure of davreuxite contains an "Einer-Doppelkette" and an "Einer-Einfach-kette" in the terminology of Liebau (1962).

Acknowledgment

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