

Holdawayite, $\text{Mn}_6(\text{CO}_3)_2(\text{OH})_7(\text{Cl},\text{OH})$, a structure containing anions in zeolite-like channels*

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ABSTRACT

The crystal structure of holdawayite, $\text{Mn}_6(\text{CO}_3)_2(\text{OH})_7(\text{Cl},\text{OH})$ [space group $C2/m$, $a = 23.437(5)$, $b = 3.3137(3)$, $c = 16.618(6)$ Å, $\beta = 111.15(2)^\circ$] has been determined and refined to a residual of 0.047. Carbonate groups are linked to five $\text{Mn}(\text{O},\text{OH})_6$ octahedra in planar units, which in turn are linked parallel to \mathbf{b} to form five-octahedron-sided tubes extended parallel to \mathbf{b} , each having a central ribbing of CO_3 groups. Such columns are cross-linked parallel to \mathbf{c} to give slabs parallel to the \mathbf{b} - \mathbf{c} plane. These in turn are cross-linked so that vacant columns occur between slabs. Each column is a channel defined by superimposed eight-membered rings of edge-sharing $\text{Mn}(\text{O},\text{OH})_6$ octahedra. Cl atoms occupy sites along the central axis of these channels and are coordinated only to OH ions through weak hydrogen bonds. The Cl balances the net positive charge of the framework and may give rise to anion exchange or anionic conductivity through the infinitely extended channels. The structure is closely related to that of defernite, $\text{Ca}_3(\text{CO}_3)(\text{OH},\text{Cl})_4$, and differs only in the relative displacements of adjacent slabs of octahedra and CO_3 groups.

INTRODUCTION

Holdawayite has recently been described by Peacor et al. (1988) as a new mineral from the Kombat mine, Namibia, where it occurs locally and abundantly as a primary mineral in low-grade metamorphosed Mn-rich sedimentary rocks intercalated with metasedimentary iron ores. The chemical formula, $\text{Mn}_6(\text{CO}_3)_2(\text{OH})_7(\text{Cl},\text{OH})$, and crystallographic data given by Peacor et al. imply that its crystal structure is closely related to that of the rare mineral defernite, $\text{Ca}_3(\text{CO}_3)(\text{OH})_4 \cdot n\text{H}_2\text{O}$, which perhaps not coincidentally also occurs at the Kombat mine. The structure of defernite was determined by Leibich and Sarp (1985), who showed that it contains sheets of interconnected $\text{Ca}(\text{O},\text{OH})_6$ and CO_3 groups, but with large voids within sheets that form continuous columns oriented normal to the layers. Water molecules partially occupy the channels, which are akin to voids in zeolites and which may thus possess ion-exchange, molecular-sieve, or ionic-conduction properties.

The crystallographic parameters of holdawayite (space group $C2/m$, $a = 23.437(5)$, $b = 3.3137(3)$, $c = 16.618(6)$ Å, $\beta = 111.15(2)^\circ$, $Z = 8$; Peacor et al., 1988) are related to those of defernite (space group $Pnam$, $a = 17.860(5)$, $b = 22.775(6)$, $c = 3.658(1)$ Å; Leibich and Sarp, 1985). These and other data imply that the two minerals may be members of a more extensive family of layered structures, based on simple modules. We therefore undertook a determination of the structure of holdawayite in order to define those relations.

STRUCTURE DETERMINATION

The intensities of 1466 reflections having $\sin \theta \leq 0.46$ were measured using a crystal fragment of dimensions $0.12 \times 0.20 \times 0.27$ mm, graphite-monochromatized $\text{MoK}\alpha$ radiation, and a computer-controlled Supper-Pace diffractometer that uses Weissenberg equi-inclination geometry. Scanning rates were $2^\circ/\text{min}$ or $4^\circ/\text{min}$ with high- and low-side background counts of 25 s. The data were corrected for Lorentz-polarization and absorption effects (Burnham, 1962) ($\mu_1 = 59.4 \text{ cm}^{-1}$), resulting in a final data set of 1436 reflections after symmetry equivalents were removed. Of these, 177 reflections had $|F|_{\text{obs}} < 3\sigma|F|_{\text{obs}}$ and were considered unobserved.

The locations of all atoms, including H, were obtained from a combination of direct methods (Gilmore, 1983), electron density, and difference–electron density syntheses. The structure was refined using the program *SHELX-76* (Sheldrick, 1976), neutral-atom scattering factors, and anomalous dispersion factors (*International Tables for X-Ray Crystallography*, 1974), and the reciprocal variances of the $|F|_{\text{obs}}$ as weights. The E map revealed the locations of all of the metal and C atoms plus 8 of the 13 oxygens. The first Fourier synthesis, calculated when the residual had reached 0.20, revealed the remaining oxygens and three modest peaks at $(0,0,0)$, $(0,0,1/2)$, and $(0,1/2,1/2)$ in the center of the structural channels. A difference synthesis, calculated when the residual had declined to 0.08, yielded two additional occupied channel sites at $(0,0.26,1/2)$ and $(0,0.16,0)$. These five channel sites were initially assumed to be partially occupied O positions but were soon reassigned to Cl, as there were no other peaks in the synthesis that could account for the ca. 2.9 Cl per cell indicated by the chemical analysis, and the channels

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TABLE 1. Positional and anisotropic thermal parameters (both $\times 10^4$)

| | x | y | z | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} | U_{eq} |
|--------|---------|----------|---------|----------|----------|----------|----------|----------|----------|----------|
| Mn(1) | 965(1) | 0 | 2971(1) | 143(7) | 134(7) | 140(6) | 0 | 59(5) | 0 | 0.014 |
| Mn(2) | 4350(1) | 0 | 2229(1) | 146(7) | 88(7) | 157(6) | 0 | 62(5) | 0 | 0.013 |
| Mn(3) | 8440(1) | 0 | 3167(1) | 144(7) | 134(8) | 160(6) | 0 | 62(6) | 0 | 0.015 |
| Mn(4) | 6775(1) | 0 | 1729(1) | 142(8) | 147(8) | 136(7) | 0 | 47(6) | 0 | 0.014 |
| Mn(5) | 6661(1) | 0 | 4915(1) | 209(7) | 127(7) | 126(7) | 0 | 30(5) | 0 | 0.015 |
| Mn(6) | 8374(1) | 0 | 164(1) | 203(7) | 125(7) | 146(7) | 0 | 78(6) | 0 | 0.016 |
| Cl(1) | 7306(3) | 0 | 3650(5) | 157(43) | 97(44) | 168(42) | 0 | 70(35) | 0 | 0.014 |
| Cl(2) | 2858(3) | 0 | 1378(5) | 140(42) | 70(43) | 212(43) | 0 | 90(36) | 0 | 0.014 |
| O(1) | 7463(2) | 0 | 2973(3) | 93(28) | 240(37) | 75(25) | 0 | 52(22) | 0 | 0.014 |
| O(2) | 7721(2) | 0 | 4421(3) | 113(29) | 265(37) | 64(25) | 0 | -12(23) | 0 | 0.015 |
| O(3)* | 9187(2) | 0 | 1312(3) | 115(28) | 146(32) | 108(25) | 0 | 78(22) | 0 | 0.012 |
| O(4)* | 1255(2) | 0 | 1893(3) | 158(29) | 182(33) | 62(25) | 0 | 50(22) | 0 | 0.013 |
| O(5)* | 6311(2) | 0 | 385(3) | 95(27) | 198(33) | 68(25) | 0 | 7(21) | 0 | 0.012 |
| O(6)* | 5353(2) | 0 | 2458(3) | 155(29) | 117(32) | 175(28) | 0 | 23(23) | 0 | 0.015 |
| O(7)* | 3658(2) | 0 | 4023(3) | 43(27) | 197(34) | 101(25) | 0 | 2(21) | 0 | 0.011 |
| O(8) | 2984(3) | 0 | 677(3) | 200(31) | 258(38) | 96(26) | 0 | 94(24) | 0 | 0.018 |
| O(9)* | 9331(2) | 0 | 3058(3) | 43(27) | 168(31) | 96(25) | 0 | 5(21) | 0 | 0.010 |
| O(10)* | 1064(2) | 0 | 4269(3) | 108(27) | 181(34) | 60(25) | 0 | 51(22) | 0 | 0.012 |
| O(11) | 6732(2) | 0 | 3572(3) | 78(28) | 164(33) | 230(30) | 0 | 113(24) | 0 | 0.016 |
| O(12) | 2288(2) | 0 | 1302(3) | 35(27) | 253(37) | 214(29) | 0 | 38(23) | 0 | 0.017 |
| O(13) | 3291(2) | 0 | 2131(3) | 55(27) | 246(36) | 103(27) | 0 | 10(22) | 0 | 0.014 |
| Cl(1) | 0 | 0 | 0 | 313(46) | | | | | | |
| Cl(2) | 0 | 0 | 1/2 | 385(36) | | | | | | |
| Cl(3) | 0 | 1/2 | 1/2 | 306(56) | | | | | | |
| Cl(4) | 0 | 2625(44) | 1/2 | 212(26) | | | | | | |
| Cl(5) | 0 | 1547(48) | 0 | 840(37) | | | | | | |
| H(1) | 9600 | 0 | 3600 | | | | | | | |
| H(2) | 5960 | 0 | 0190 | | | | | | | |
| H(3) | 9430 | 0 | 1060 | | | | | | | |
| H(4) | 4010 | 0 | 4230 | | | | | | | |
| H(5) | 840 | 0 | 4530 | | | | | | | |
| H(6) | 5340 | 0 | 1830 | | | | | | | |
| H(7) | 1090 | 0 | 1480 | | | | | | | |

Note: Esd's are in parentheses. H coordinates are taken from the difference synthesis. Isotropic temperature factors were used for Cl atoms. Asterisks indicate hydroxyl oxygens.

would be the most reasonable locations for a very large anion like Cl⁻. The seven H positions were obtained from a second difference synthesis calculated at a residual of 0.058. These were readily recognized as H from their characteristic distances to O atoms, which were known from their bond-valence sums to be hydroxyl oxygens.

The formula calculated from the chemical analysis suggests solid solution of 21.1 Mn, 2.5 Mg, plus minor Ca and Fe on the 24 octahedral cation sites in the unit cell (Peacor et al., 1988). Refinement of site occupancy factors for Mn(1) to Mn(6) (Table 2) revealed that Mg is

primarily concentrated in Mn(4), as suggested by its lower average Mn-O bond distance (2.18 Å vs. 2.21–2.23 Å for the other Mn sites). The occupancy factors of Cl(1) to Cl(5) were also refined, as these sites were expected on geometrical grounds to be partially vacant. The formula calculated from the chemical analysis further suggests that a fourth atom, probably a hydroxyl oxygen, is also present in one of these partially occupied positions. In some cases, the coordinates of the H atoms refined to give unreasonably short O-H distances. Accordingly, the coordinates of all H atoms were held constant at the values derived from the difference synthesis, with isotropic temperature factors arbitrarily fixed at 0.02 Å². These H positions give O-H distances within the normal range found in X-ray diffraction studies.

Refinement of the structure with isotropic temperature factors converged at an unweighted residual of 0.058. Introduction of anisotropic temperature factors reduced this to the final values of 0.044 (unweighted) and 0.031 (weighted) for the 1259 observed reflections. The final values of the atomic parameters are listed in Table 1, site occupancies in Table 2, the observed and calculated structure factors in Table 3,¹ selected interatomic dis-

TABLE 2. Refined occupancy factors for Mn and Cl sites

| | Equipoint | Mn or Cl occupancy fraction | Site contents |
|-------|-----------|-----------------------------|-------------------------------------|
| Mn(1) | 4i | 0.97(1) | Mn _{3.9} Mg _{0.1} |
| Mn(2) | 4i | 1.01(1) | Mn _{4.00} |
| Mn(3) | 4i | 0.96(1) | Mn _{3.8} Mg _{0.2} |
| Mn(4) | 4i | 0.76(1) | Mn _{3.0} Mg _{1.0} |
| Mn(5) | 4i | 0.96(1) | Mn _{3.9} Mg _{0.1} |
| Mn(6) | 4i | 0.93(1) | Mn _{3.7} Mg _{0.3} |
| Cl(1) | 2a | 0.23(4) | Cl _{0.5} □ _{1.5} |
| Cl(2) | 2c | 0.24(2) | Cl _{0.5} □ _{1.5} |
| Cl(3) | 2d | 0.26(3) | Cl _{0.5} □ _{1.5} |
| Cl(4) | 4h | 0.17(2) | Cl _{0.7} □ _{3.3} |
| Cl(5) | 4g | 0.31(2) | Cl _{1.2} □ _{3.8} |

Note: Esd's are in parentheses.

¹ A copy of Table 3 may be ordered as Document AM-88-379 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

tances and angles in Table 4, and empirical bond valences calculated by the method of Brown and Wu (1976) in Table 5.

STRUCTURE DESCRIPTION

Figure 1 shows the principal features of the structure. All atoms, with the exception of some of the Cl atoms that occupy large zeolite-like cavities, are on mirror planes at $y = 0, 1/2$. Mn atoms are approximately octahedrally coordinated with one of their principal equatorial planes oriented parallel to **b**. These approximately square equatorial planes are defined by two O or OH ions at $y = 0$ (or $1/2$) and two at $y = 1$ (or $-1/2$); apical O or OH ions are at $y = 1/2$ (or 0). All octahedra share two edges of these equatorial planes with octahedra related by $\pm \mathbf{b}$ to form octahedral chains extending parallel to **b**.

Trigonal carbonate groups are planar in (010). The three oxygen atoms of a given CO_3 group are shared with five $\text{Mn}(\text{O},\text{OH})_6$ octahedra. The five octahedra are, in turn, related by edge- and vertex-sharing to form a five-membered ring (Figs. 1 and 2) around each carbonate group. Because each Mn octahedron is part of an infinitely extended chain parallel to **b**, these five-membered rings actually represent a projection of a nearly pentagonal column of octahedra, with CO_3 groups forming an internal ribbing. Because a given octahedral chain may be an edge of two adjacent pentagonal columns, the sequence of parallel columns extending parallel to **c** forms a "wall" or slab of octahedra parallel to (100).

The walls of octahedra are, in turn, cross-linked through vertex-sharing octahedra with O(6) serving as the bridging anion. This results in large voids defined by eight-membered rings of edge-sharing octahedra. Because each octahedron is part of an infinitely extended chain parallel to **b**, these voids are actually infinitely extended octagonal columns or channels parallel to **b**. Figure 1 shows that the channels are effectively ellipsoidal in cross section and are of two types, which differ slightly in shape. The one containing Cl(2), Cl(3), and Cl(4) has free dimensions of ca. $3.3 \times 6.4 \text{ \AA}$, whereas that containing Cl(1) and Cl(5) has dimensions of ca. $3.4 \times 5.1 \text{ \AA}$. These values were estimated graphically from Figure 1 assuming a radius of 1.35 \AA for the three-coordinated OH ions that form the channel walls. The 1.35-\AA value was chosen because it results in contact between adjacent OH ions and because it is the ionic radius of three-coordinated OH^- (Shannon, 1976). From the radii given by Shannon (1976) for six-coordinated OH^- and the halides, it is evident that only OH^- , F^- , and Cl^- (ionic diameters 2.74, 2.66, and 3.62 \AA , respectively) are small enough to be accommodated in the channels of holdawayite and that only Cl^- provides a "close fit" to the minimum channel dimension of ca. 3.3 \AA . All of the qualitative features of the holdawayite structure described here also occur in the structure of defernite (Liebich and Sarp, 1985).

The eight-membered rings of octahedra have Mn atoms that alternate at heights of $y = 0$ and $1/2$ (Figs. 1 and 2). This pattern causes the ligands of the equatorial planes

TABLE 4. Selected interatomic distances (\AA) and angles ($^\circ$)

| $\text{Mn}(\text{O},\text{OH})_6$ octahedra | | | |
|---|---------------------|------------------|---------------------|
| Mn(1)-O(10)* | 2.085(5) | Mn(4)-O(5)* | 2.102(5) |
| -O(4)* | 2.133(6) | -O(1) | 2.114(4) |
| -O(6)* | $2.156(3) \times 2$ | -O(4)* | $2.132(4) \times 2$ |
| -O(11) | $2.383(3) \times 2$ | -O(12) | $2.304(4) \times 2$ |
| Mean | 2.216 | Mean | 2.181 |
| | | -O(11) | 3.100(4) |
| Mn(2)-O(9)* | $2.166(4) \times 2$ | Mn(5)-O(7)* | 2.151(6) |
| -O(3)* | $2.189(3) \times 2$ | -O(10)* | $2.184(3) \times 2$ |
| -O(6)* | 2.242(5) | -O(2) | $2.215(3) \times 2$ |
| -O(13) | 2.428(5) | -O(11) | 2.297(6) |
| Mean | 2.230 | Mean | 2.208 |
| | | -O(2) | 2.884(6) |
| Mn(3)-O(7)* | $2.123(3) \times 2$ | Mn(6)-O(5)* | $2.147(4) \times 2$ |
| -O(9)* | 2.160(6) | -O(3)* | 2.156(4) |
| -O(1) | 2.194(5) | -O(8) | $2.207(4) \times 2$ |
| -O(13) | $2.324(4) \times 2$ | -O(12) | 2.370(4) |
| Mean | 2.208 | Mean | 2.206 |
| -O(2) | 3.117(6) | -O(8) | 2.979(5) |
| Carbonate groups | | | |
| C(1)-O(2) | 1.299(8) | O(2)-C(1)-O(11) | 118.4(8) |
| -O(11) | 1.304(9) | O(1)-C(1)-O(2) | 120.5(6) |
| -O(1) | 1.304(11) | O(1)-C(1)-O(11) | 121.1(6) |
| Mean | 1.302 | Mean | 120.0 |
| C(2)-O(12) | 1.296(9) | O(8)-C(2)-O(12) | 118.2(6) |
| -O(13) | 1.296(8) | O(8)-C(2)-O(13) | 120.9(6) |
| -O(8) | 1.301(11) | O(12)-C(2)-O(13) | 121.0(8) |
| Mean | 1.298 | Mean | 120.0 |
| O(1)-O(2) | 2.260(7) | O(8)-O(12) | 2.228(8) |
| O(1)-O(11) | 2.271(8) | O(8)-O(13) | 2.259(7) |
| O(2)-O(11) | 2.237(6) | O(12)-O(13) | 2.255(6) |
| Hydroxyl groups | | | |
| H(1)-O(9)* | 0.89 | H(5)-O(10)* | 0.79 |
| H(2)-O(5)* | 0.77 | H(6)-O(6)* | 1.03 |
| H(3)-O(3)* | 0.82 | H(7)-O(4)* | 0.66 |
| H(4)-O(7)* | 0.77 | | |
| $(\text{O}-\text{O}) \leq 3.0 \text{ \AA}$ | | | |
| O(5)*-O(12) | $2.792(4) \times 2$ | O(4)*-O(12) | $2.923(8) \times 2$ |
| O(3)*-O(9)* | 2.798(7) | O(7)*-O(13) | 2.945(7) |
| O(10)*-O(11) | 2.801(6) | O(2)-O(2) | $2.993(9) \times 2$ |
| O(5)*-O(8) | 2.819(8) | O(7)*-O(2) | $3.009(6) \times 2$ |
| O(9)*-O(13) | $2.890(5) \times 2$ | O(8)-O(8) | $3.045(7) \times 2$ |
| O(10)*-O(2) | $2.894(6) \times 2$ | O(4)*-O(5)* | $3.046(6) \times 2$ |
| $(\text{Cl}-\text{O}) \leq 3.4 \text{ \AA}$ | | | |
| Cl(3)-O(7)* | $2.974(4) \times 2$ | Cl(4)-O(10)* | $3.261(7) \times 2$ |
| Cl(2)-O(9)* | $3.037(4) \times 2$ | Cl(1)-O(5)* | $3.343(4) \times 4$ |
| Cl(4)-O(7)* | $3.076(6) \times 2$ | Cl(1)-O(3)* | $3.374(6) \times 2$ |
| Cl(5)-O(5)* | $3.121(7) \times 2$ | Cl(2)-O(7)* | $3.404(4) \times 4$ |
| Cl(2)-O(10)* | $3.143(6) \times 2$ | Cl(5)-O(3)* | $3.412(6) \times 2$ |
| Cl(4)-O(9)* | $3.159(6) \times 2$ | Cl(1)-O(4)* | $3.445(4) \times 2$ |
| Shortest distances | | | |
| Mn-Mn | 3.3137(3) | C-O | 1.296(9) |
| Mn-C | 2.979(8) | C-Cl | > 5.0 |
| Mn-O* | 2.085(5) | O-O | 2.228(8) |
| Mn-Cl | 3.822(2) | O*-O | 2.792(4) |
| C-C | 3.3137(3) | O*-Cl | 2.974(4) |

Note: Esd's are in parentheses.

* Hydroxyl oxygens.

to be shared between three octahedra, thus giving rise to ideal (Pauling) bond valences of -1 . The empirical bond valences (Table 5) are also consistent with ligands of charge -1 . These ions must be hydroxyl rather than chloride as shown by the bond distances in Table 4. In addition, it will be seen from Table 4 that atoms Mn(3) to Mn(6) each have one additional long interatomic distance of $2.9\text{--}3.1 \text{ \AA}$ to one of the carbonate oxygens O(2), O(8),

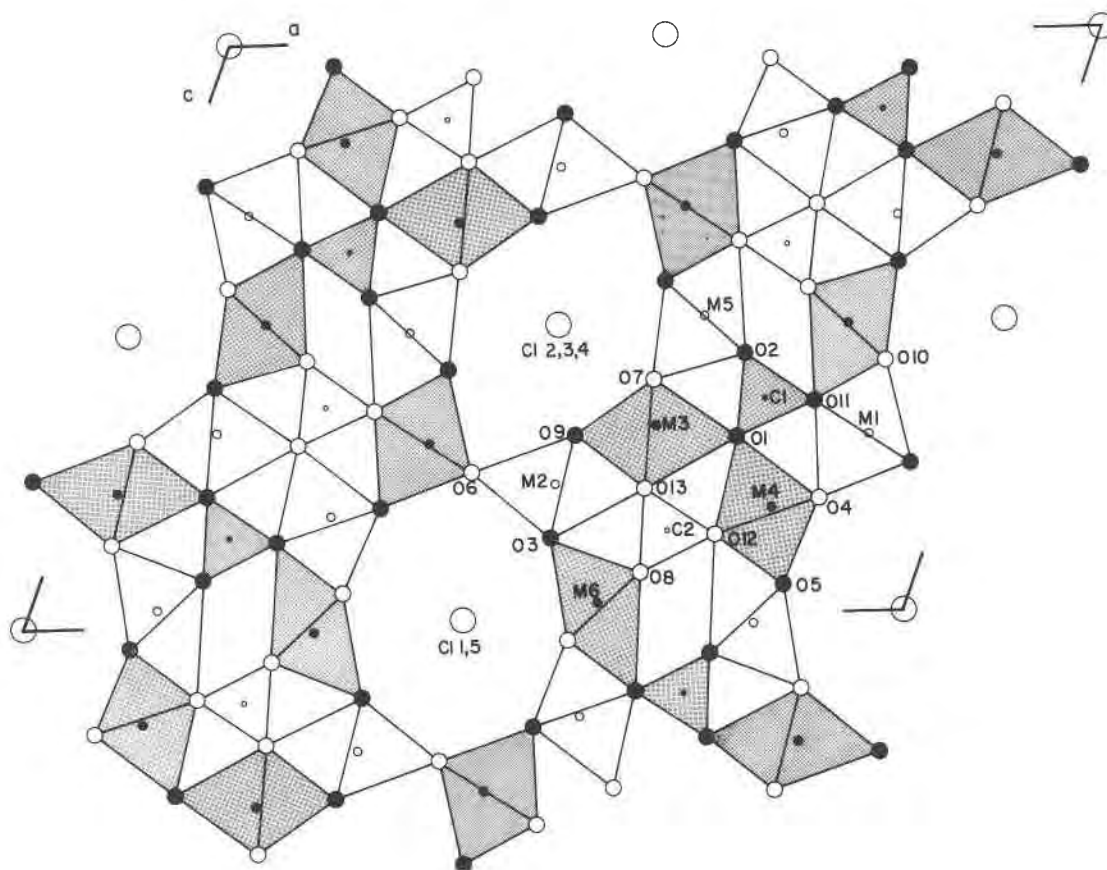


Fig. 1. Projection of the holdawayite structure onto (010). Circles of increasing size represent C, Mn, OH, and Cl. Solid and open circles represent atoms at $y = 0$ and $1/2$, respectively (except for Cl). Polyhedra centered on C or Mn at $y = 0$ are stippled.

and O(11). [The next-shortest Mn–O distance is a long 3.688(4) Å.] Although these distances are outside of the usual range for Mn^{2+} –O bonds, Table 5 shows that their inclusion in the Mn coordination spheres causes the bond-valence sums of Mn(3), Mn(5), Mn(6), O(2), O(8), and O(11) to more nearly approach their ideal values. This suggests that they may represent weak, long-range inter-

actions and that atoms Mn(3), Mn(5), and Mn(6) may each be considered to be coordinated to a seventh ligand. The foregoing hypothesis cannot explain what seems to be a serious undersaturation of Mn(2), however, as the closest additional oxygen is O(8) at 3.308(4) Å, which would contribute only 0.03 v.u. to the sum for Mn(2).

Figure 1 shows that any two eight-membered rings of

TABLE 5. Empirical bond valences (v.u.)

| | Mn(1) | Mn(2) | Mn(3) | Mn(4) | Mn(5) | Mn(6) | C(1) | C(2) | Σv_a |
|--------------|---------------------|---------------------|---------------------|---------------------|----------------------------|----------------------------|------|------|--------------|
| O(1) | — | — | 0.33 | 0.38 | — | — | 1.25 | — | 1.96 |
| O(2) | — | — | (0.05) | — | 0.31 ($\times 2$) (0.07) | — | 1.27 | — | 1.89 (2.01) |
| O(3) | — | 0.33 ($\times 2$) | — | — | — | 0.36 | — | — | 1.02 |
| O(4) | 0.38 | — | — | 0.37 ($\times 2$) | — | — | — | — | 1.12 |
| O(5) | — | — | — | 0.40 | — | 0.37 ($\times 2$) | — | — | 1.14 |
| O(6) | 0.36 ($\times 2$) | 0.29 | — | — | — | — | — | — | 1.01 |
| O(7) | — | — | 0.39 ($\times 2$) | — | 0.37 | — | — | — | 1.15 |
| O(8) | — | — | — | — | — | 0.31 ($\times 2$) (0.06) | — | 1.26 | 1.88 (1.94) |
| O(9) | — | 0.35 ($\times 2$) | 0.36 | — | — | — | — | — | 1.06 |
| O(10) | 0.44 | — | — | — | 0.34 ($\times 2$) | — | — | — | 1.12 |
| O(11) | 0.21 ($\times 2$) | — | — | (0.05) | 0.25 | — | 1.25 | — | 1.92 (1.97) |
| O(12) | — | — | — | 0.24 ($\times 2$) | — | 0.21 | — | 1.28 | 1.97 |
| O(13) | — | 0.19 | 0.24 ($\times 2$) | — | — | — | — | 1.28 | 1.95 |
| Σv_c | 1.96 | 1.84 | 1.95 (2.00) | 2.00 (2.05) | 1.92 (1.99) | 1.93 (1.99) | 3.77 | 3.82 | — |

Note: Valences of M(4) and M(6) are calculated from weighted averages of Mn and Mg. The H atoms were excluded from all calculations. Valences in parentheses are those for Mn–O distances in the 2.9–3.1-Å range (see text).

octahedra that are adjacent parallel to *c* have sequences of Mn atoms with interchanged values of $y = 0$ and $1/2$. The same relation is emphasized in Figure 2a where only the relative positions of the octahedral cations are shown. Figure 2b shows the same feature for the defernite structure. The overall topologies of the structures of defernite and holdawayite are almost identical. Indeed, a slab that extends infinitely parallel to *b* and *c* in holdawayite, and that has a thickness of d_{100} (one unit translation thick), is common to both structures. The structures differ in that alternate slabs in holdawayite may be shifted by $\pm c/2$ ($\pm a/2$ in defernite) to form the defernite structure. This feature resembles a classic unit-cell twinning relationship. It suggests that samples may exist that contain mixtures of the two repeats. Such mixtures could give rise to either ordered or disordered sequences. Accordingly, diffraction patterns of both defernite and holdawayite were examined for evidence of such "stacking faults," but none was observed. It is therefore tempting to consider that the alternate structures are defined by the relative radii of Ca versus Mn, with only one of the two stacking sequences being consistent with one or the other ion; no such relation was discerned. Nevertheless, specimens having compositions intermediate to defernite and holdawayite should be examined for the possibility of alternate stacking sequences as opposed to Ca-Mn solid solution or coexistence of end-member minerals.

An alternative way of visualizing the relationship between the two structures may be obtained by noting that, although the two kinds of eight-membered rings have alternating Mn atoms at different heights ($y = 0, 1/2$ rather than $1/2, 0$), their anions have the same approximate positions. Given this distribution of ligands, an $\text{Mn}(\text{O},\text{OH})_6$ octahedron can be formed by placing an Mn atom either at 0 or $1/2$. The apical ligands for one position (say, $y = 0$) alternatively serve as two of the four ligands of the equatorial plane for the other position (say, $y = 1/2$). Of course, one configuration of anions is extremely distorted relative to the other, but to a first approximation the distributions of anions are the same. The only essential differences in relative atomic positions in defernite and holdawayite, therefore, are the differences in the Mn (or Ca) positions. Alternate slabs of one, as related by $\pm c/2$, have anions approximately invariant to this translation, with only octahedral cations affected.

CHANNEL CONTENTS AND HYDROGEN BONDING

The chemical formula derived from the Mn coordination polyhedra and carbonate groups is $\text{Mn}_{24}(\text{CO}_3)_8(\text{OH})_{28}$, which has an excess of four positive charges assuming that Mn is divalent. The only remaining sources of compensating negative charge are the atoms that lie on special positions in the centers of the octahedral eight-membered rings; i.e., the atoms labeled Cl(1) to Cl(5) in Figure 1. These were refined as anion sites, partially occupied by a total of ca. 3.4 Cl. The latter total is derived from the site-occupancy-factor refinement and is close to the 2.9 Cl per cell derived from the chemical analysis of

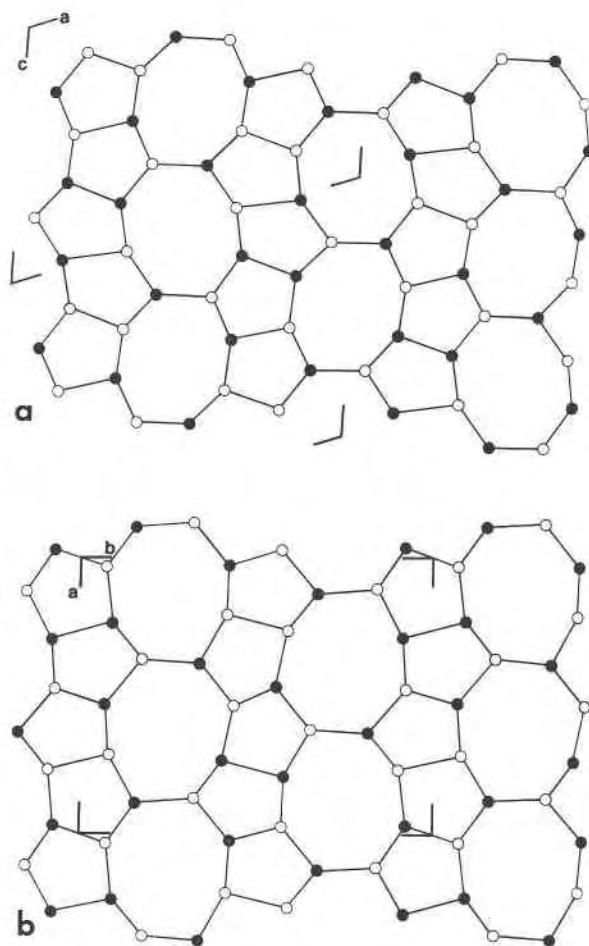


Fig. 2. (a) Patterns of Mn octahedra in holdawayite, projected on (010). Solid and open circles represent Mn at $y = 0$ and $1/2$, respectively. (b) Pattern of Ca octahedra in defernite, projected on (001). A slab of structure with a thickness of d_{100} and infinitely extended parallel to *a* and *c* is common to both holdawayite and defernite. Alternate slabs are related by $\pm a/2$ of holdawayite in the two structures.

Peacor et al. (1988). However, because these provide only 3.4 of the additional negative charges needed, it must be assumed that Cl(1) to Cl(5) also contain a fourth univalent anion, probably $(\text{OH})^-$. The ideal formula of holdawayite is therefore $\text{Mn}_{24}(\text{CO}_3)_8(\text{OH})_{28}(\text{Cl},\text{OH})_4$ or $\text{Mn}_6(\text{CO}_3)_2(\text{OH})_7(\text{Cl},\text{OH})$ with $Z = 4$.

The crystal structure of defernite as determined by Liebich and Sarp (1985) leads to the formula $\text{Ca}_6(\text{CO}_3)_2(\text{OH})_7 \cdot n\text{H}_2\text{O}$, which is based only on the atomic positions and which has excess negative charge. The formula as determined by Sarp et al. (1980) using chemical analyses is $\text{Ca}_6(\text{CO}_3)_2(\text{OH},\text{Cl})_8 \cdot n\text{H}_2\text{O}$. The H_2O derived from the structure analysis corresponds to partially occupied sites in the centers of the eight-membered rings, analogous to the Cl of holdawayite. The equivalent relations for holdawayite suggest that the H_2O of defernite is actually Cl, giving rise to the charge-balanced structural formula

$\text{Ca}_6(\text{CO}_3)_2(\text{OH},\text{Cl})_8$, in agreement with analytical chemical data.

The (Cl,OH) ions present in the channel sites Cl(1) to Cl(5) of holdawayite are coordinated only to the hydroxyl ions that line the channels and to other (Cl,OH) ions of the same set situated above and below them. They are not bonded to any of the octahedral cations, as shown by the fact that the shortest Mn-Cl distance in the structure is 3.822(2) Å (Table 4). On the other hand, there are numerous O-Cl distances less than the sum of the van der Waals radii, 3.3 Å (Alcock, 1972), and the H atoms are located approximately along the lines connecting the OH and Cl sites in the difference map. These relations, plus the absence of any Cl-cation bonds, imply that Cl(1) to Cl(5) are hydrogen-bonded to the hydroxyl oxygens O(3), O(4), O(5), O(7), O(9), and O(10). Their O-Cl distances are all within the 3.0–3.4 Å range given by Baur (1970) for hydrogen-bonded O-H...Cl configurations. Among minerals there is a direct analogy in the structure of zunyite, where each Cl is hydrogen-bonded to six hydroxyl groups, with a Cl-O distance of 3.06 Å (Baur and Ohta, 1982). Atom O(6) is also a hydroxyl oxygen, but the closest channel anions are Cl(5) at 4.030(7) Å and Cl(1) at 4.204(5) Å. It would seem, therefore, that O(6) is the only hydroxyl oxygen that does not participate in the hydrogen-bonding system in holdawayite.

The actual coordination numbers of the Cl atoms are indeterminate because all such sites are partially occupied. Their apparent coordination numbers by OH ions range from two to eight if 3.4 Å is accepted as the maximum bonding distance. However, some of these contacts are necessarily fictitious, as they represent distances between OH and vacant Cl sites.

The system of hydrogen bonds around each Cl acts to distribute its -1 charge over a very large volume and, in fact, represents the sole bonding mechanism for Cl. The weak hydrogen bonding and the continuous columnar nature of the voids parallel to **b** suggest that Cl may be mobile, analogous to cations in zeolites; i.e., the Cl may be exchangeable if holdawayite is placed in solutions even at very low temperatures. The limiting factor may be the OH⁻-halide distance. It is fixed by the dimensions of the eight-membered ring and appears to be inappropriate for other halide ions [but not for (OH)⁻]. The unusual structure type represented by defernite and holdawayite may permit rapid diffusion only of Cl. These compounds may therefore be one-dimensional anion conductors having useful electronic applications.

The occurrence of frameworks with net negative charges, combined with charge-balancing cations in interframework sites is common among minerals. Clay minerals such as smectite and members of the zeolite group are classic

examples. Mineral structures that are based on a framework having a net positive charge, balanced by anions in interframework voids, are rare. There are, to be sure, many examples of tektosilicates containing anions in cavities or channels, e.g., the salt-bearing feldspathoids, but in all such cases the framework is negatively charged. The structure of zunyite (Baur and Ohta, 1982) is an exception in that Cl is hydrogen-bonded to OH, which in turn is part of a tetrahedral-octahedral aluminosilicate framework with an overall positive charge. However, the Cl does not appear to be zeolitic in the sense that it may be mobile or replaceable. The structures of holdawayite and defernite therefore appear to be unique in this respect.

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