Mechanism of the SiO$_4$ for CO$_3$ substitution in defernite, Ca$_6$(CO$_3$)$_{1.58}$(Si$_2$O$_7$)$_{0.21}$(OH)$_7$[Cl$_{0.50}$(OH)$_{0.08}$(H$_2$O)$_{0.42}$]: A single-crystal X-ray study at 100 K

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ABSTRACT

Defernite, Ca$_6$(CO$_3$)$_{1.58}$(Si$_2$O$_7$)$_{0.21}$(OH)$_7$[Cl$_{0.50}$(OH)$_{0.08}$(H$_2$O)$_{0.42}$], is a carbonate mineral [space group *Pnam*; at 100 K: $a = 17.744(2)$, $b = 22.601(4)$, $c = 3.633(1)$ Å, $Z = 4$] with zeolite-like structural channels. The structural framework is formed by edge- and corner-sharing CaO$_{6-7}$ polyhedra, which are additionally linked by CO$_3$ groups aligned parallel to the (001) plane. This framework has channels parallel to the c axis, confined by eight-membered rings of CaO$_{6-7}$ polyhedra. The inner surface of the channels exposes H atoms of OH groups bonded to Ca. The framework carries a positive charge, which is balanced by small anions (mainly Cl) in the structural channels. The crystal structure of defernite from the Kombat mine, Namibia, was refined using 3845 reflections to $R = 2.6\%$ at 100 K. The low but ubiquitous SiO$_2$ concentrations (1–5 wt%) observed in chemical analyses of this mineral were structurally located. Defernite has two symmetrically distinct CO$_3$ groups (C1, C2), which are repeated by a mirror plane parallel to (001). The C2 double layer of CO$_3$ groups is partially replaced by a disilicate Si$_2$O$_7$ unit, where an additional O atom is accommodated between the two O triangles of the former CO$_3$ groups. This substitution is observed only for C2. In addition, all H atoms on the surface of the structural channels were located and refined. Cl in the center of the channel is bonded to six H within 2.8 Å. Defernite may form a solid solution between Ca$_6$(CO$_3$)$_2$(OH)$_7$[Cl,OH] and Ca$_6$(CO$_3$)$_{1.0}$(Si$_2$O$_7$)$_{0.5}$(OH)$_7$, in which the latter end-member is characterized by a neutral framework and structural channels without charged ions.

INTRODUCTION

Defernite (Liebich and Sarp 1985; Peacor et al. 1988b), with the simplified formula Ca$_6$(CO$_3$)$_2$(OH)$_7$[Cl,OH], and holdawayite (Peacor and Rouse 1988), Mn$_6$(CO$_3$)$_2$(OH)$_7$[Cl,OH], comprise a family of rare carbonate minerals with zeolite-like channels. In contrast to ordinary zeolites, the framework carries a positive charge, which is neutralized by small anions within the one-dimensional channels. There is a strong structural relationship between these two minerals. In defernite six CaO$_{6-7}$ and two CO$_3$ units form a framework (Fig. 1). In holdawayite the CaO$_{6-7}$ polyhedra are replaced by MnO$_{6-7}$ polyhedra. However, defernite is orthorhombic [space group *Pnam*, $a = 17.82(2)$, $b = 22.76(2)$, $c = 3.629(4)$ Å, $Z = 4$] with only one type of structural channel parallel to the c axis (Liebich and Sarp 1985; Peacor et al. 1988b), whereas holdawayite is monoclinic [space group *C2/m*, $a = 23.437(5)$, $b = 3.3137(3)$, $c = 16.618(6)$ Å, $\beta = 111.15(2)°$, $Z = 4$] and has two distinct structural channels running parallel to the b axis. The channels in both minerals are confined by eight-membered rings of MO$_{6-7}$ polyhedra from which OH units project into the channels. Peacor and Rouse (1988) discussed the structural similarities and

differences between the two minerals. A slab that extends infinitely parallel to b and c in holdawayite is common to both structures. The structures differ in that alternate slabs in holdawayite are shifted by $\pm c/2$ (corresponding to $\pm a/2$ in defernite) to form the defernite structure. This relationship is characteristic of so called unit-cell twinning. Mixtures of these two structures characterized by alternate ordered or disordered stacking sequences have hitherto not been observed.

Holdawayite is known only from a single occurrence at the Kombat mine, Namibia (Peacor et al. 1988a), where it is found as a primary mineral in low-grade, metamorphosed, Mn-rich sediments intercalated with metasedimentary iron ores. Defernite was described first as an alteration product in a skarn produced by a granitic intrusion in limestone near Güneyce-Ikizdere, Trabzon County, Turkey (Sarp et al. 1980). Associated minerals are vesuvianite, wollastonite, andradite, diopside, calcite, spurrite, rustumite, and hillebrandite. The second occurrence of defernite was reported by Peacor et al. (1988b) at the Kombat mine, Namibia, where it forms idiomorphic laths within massive, unbanded, granular hausmannite. The defernite-bearing (10–40 vol%) hausmannite ore forms a layer from 2 to 4 m in thickness; ~2000 metric
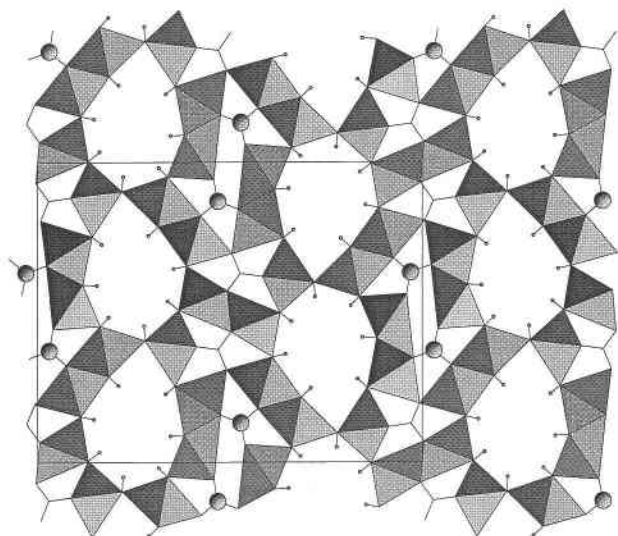
FIGURE 1. Polyhedral model with unit-cell outlines of defernite projected parallel to the *c* axis. H atoms projecting into the channel centers are shown as balls and sticks. The C2 position, which may contain SiO₄, is represented by a shaded sphere. C1 is characterized by three bonds to the neighboring O atoms.

tons of defernite-bearing hausmannite ore were stoped out during mining operation (Peacor et al. 1988b).

One of the peculiarities of defernite is the SiO_2 content in samples from Turkey (Sarp et al. 1980; Liebich and Sarp 1985) and the Kombat mine (Peacor et al. 1988b): (1.2–5.2 and 3.6 wt%, respectively). The crystal structures of samples from both occurrences were refined, but only indirect evidence for the presence of Si in the structure of defernite could be given. Liebich and Sarp (1985) speculated that Si may reside at C2, where they found twice the electron density expected for C, but the crystal studied was of low quality. Peacor et al. (1988b) came to the same conclusion for a crystal from the Kombat mine, but they also found lower than expected electron density for two of the three O atoms surrounding C2. The above authors state: "As unlikely as such a substitution is, it is supported by apparent vacancies for two of the oxygen sites coordinating C2," and later, "nevertheless, we conclude that the data collectively suggest that some Si is essential to defernite."

In a recent study of the structure of twinned sussexite, $MnB_2O_3(OH)_2$ (Hoffmann and Armbruster 1995), we also noticed low, enigmatic SiO_2 concentrations (1 wt%) as analyzed by electron microprobe. At the time we wondered whether SiO_4 could have replaced triangular BO_3 groups, but the SiO_2 concentration was too low for a definitive structural determination. Nevertheless, one of the symmetrically distinct BO_3 units showed a highly significant deviation from planarity, which could be caused by partial SiO_4 substitution. Recently, Reeder et al. (1994) reported an XAFS study indicating that tetrahedral SeO_4^{2-} units substitute in the CO_3 site of calcite grown in

SeO_4^{2-}-bearing aqueous solutions. Furthermore, Sen et al. (1994) established by ¹¹B MAS NMR spectroscopy that BO_4^{5-} tetrahedra substitute for CO_3^{2-} in the aragonite structure. However, the mechanism of this substitution remains unclear.

The aim of the present study is twofold. Because the previous structural studies of defernite (Liebich and Sarp 1985; Peacor et al. 1988b) were not of superior quality, the substitution by SiO_4 could not be explained and the H positions in the framework could not be resolved. In the present investigation, X-ray reflections up to high θ angles at low temperature were used for a structure refinement to elucidate these unanswered questions.

CRYSTAL-STRUCTURE REFINEMENT

A transparent defernite crystal from the Kombat mine, Namibia, with a light rose-brownish hue and dimensions $0.4 \times 0.2 \times 0.15$ mm³, was mounted on a CAD4 single-crystal diffractometer operated with Mo$K\alpha$ X-radiation. A conventional liquid-nitrogen cooling device was used to establish 100 K. Cell dimensions were measured from reflections between $16° < \theta < 23°$ and refined to $a = 17.744(2)$, $b = 22.601(4)$, $c = 3.633(1)$ Å. A total of 8045 reflections were collected using a $(2.0 + 0.35 \tan \theta)°$ ω-scan mode in a half sphere of reciprocal space between 0 and 30° θ and one octant between 30 and 40° θ. An empirical absorption correction was applied using the ψ-scan technique. Averaging symmetry-equivalent reflections (space group *Pnam*) yielded 5238 reflections and an agreement factor of 1.3%. Data reduction, including background and Lorentz and polarization corrections, was performed using the SDP program system (Enraf-Nonius 1983). The structure refinement on the basis of 3845 observations > $3\sigma_I$, weighted $1/\sigma^2$, was performed using the program SHELXTL PC (Siemens 1990) using neutral-atom scattering factors and both real and imaginary anomalous dispersion corrections. As a starting model the coordinates of Peacor et al. (1988b) were used, but a different atom-labeling scheme was preferred. O1, O2, and O3 are bonded to C1; O4S, O5S, O6S, and O7S form a tetrahedron around Si2; O5, O6, and O7 are bonded to C2. O atoms on the channel walls include O8–O14, and the protons completing the corresponding OH groups are labeled H8–H14, respectively. The positions in the structural channel are Ch1 and Ch2–Ch5, where the Ch positions were refined with O scattering factors.

The formula of defernite from the Kombat mine determined by Peacor et al. (1988b) is $(Ca_{23.59}Mn_{0.35}Mg_{0.04}Fe_{0.02})C_{7.53}Si_{1.22}H_{25.95}Cl_{2.02}O_{53.46}$. In the refinement presented in this paper, the Ca populations were allowed to vary but always converged to complete occupancy. Because of the similarity of Ca and Mn scattering factors for X-rays, possible ordering of the low-concentration transition metals could not be resolved.

The major indications of Si on the C2 position are the excess electron density on C2 and the unusual anisotropies of atomic displacement parameters for C2 and the surrounding O atoms. The C2 position exhibits an elon-
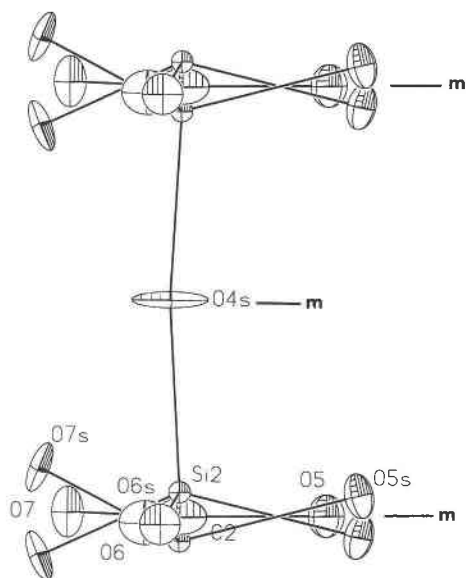
FIGURE 2. Disordered arrangement of O atoms coordinating either Si2 or C2, viewed parallel to the *a* axis with the *c* axis oriented vertically. C2 is coordinated by O5, O6, and O7, all of which reside on a mirror plane. If Si2 is present, then C2, O5, O6, and O7 are empty and O4S, O5S, O6S, and O7S are occupied and disordered about the (001) mirror plane. Ellipsoids are drawn with a 50% probability.

TABLE 1. Atomic coordinates and populations for defernite at 100 K

Atom	Pop.	x/a	y/b	z/c	B_{eq} (Å²)
Ca1		0.71084(2)	0.08323(2)	¼	0.763(4)
Ca2		0.53158(2)	0.42685(1)	¼	0.578(4)
Ca3		0.36989(2)	0.17931(1)	¼	0.736(4)
Ca4		0.62081(2)	0.65941(1)	¼	0.549(4)
Ca5		0.77072(2)	0.90686(2)	¼	0.693(4)
Ca6		0.97448(2)	0.57623(1)	¼	0.702(4)
C1		0.37222(9)	0.47117(7)	¼	0.68(2)
O1		0.56809(7)	0.49527(5)	¾	0.70(2)
O2		0.61760(8)	0.58571(6)	¾	0.96(2)
O3		0.69361(7)	0.50731(6)	¾	1.23(2)
Si2	0.420(2)	0.3693(2)	0.0308(1)	0.307(1)	0.27(6)*
O4S	0.420	0.3480(4)	0.0359(3)	¾	1.4(1)
O5S	0.420	0.3451(7)	−0.0349(3)	0.203(4)	0.8(1)
O6S	0.420	0.4593(2)	0.0342(3)	¼	0.71(6)
O7S	0.420	0.3223(4)	0.0848(3)	0.147(2)	0.82(9)
C2	0.580(2)	0.3691(5)	0.0306(4)	¼	1.2(1)
O5	0.580	0.3444(6)	−0.0227(2)	¼	0.95(7)
O6	0.580	0.4407(2)	0.0404(2)	¼	1.12(5)
O7	0.580	0.3221(3)	0.0744(2)	¼	1.07(7)
O8		0.08948(8)	0.38194(7)	¼	1.16(2)
O9		0.24815(8)	0.85827(6)	¼	0.92(2)
O10		0.04826(7)	0.66228(6)	¼	0.82(2)
O11		0.40225(8)	0.28006(6)	¼	0.85(2)
O12		0.49567(7)	0.63179(6)	¼	0.78(2)
O13		0.15225(7)	0.11250(6)	¼	0.89(2)
O14		0.71552(8)	0.81385(7)	¼	1.11(2)
Cl1	0.249(4)	0.8883(1)	0.75150(7)	0.1149(9)	2.95(5)
Ch2	0.156(6)	0.9238(7)	0.7586(5)	0.569(4)	3.8(3)*
Ch3	0.051(9)	0.8519(5)	0.7457(4)	¾	1.9(2)*
Ch4	0.025(8)	0.930(2)	0.757(1)	¼	3.3(7)*
Ch5	0.031(8)	0.857(2)	0.744(1)	¼	3.95*
H8		0.911(2)	0.655(2)	¾	3.95*
H9		0.775(2)	0.669(1)	¼	3.95*
H10		0.520(2)	0.813(2)	¼	3.95*
H11		0.552(2)	0.724(2)	¾	3.95*
H12		0.466(2)	0.661(2)	¼	3.95*
H13		0.644(2)	0.354(2)	¼	3.95*
H14		0.747(2)	0.788(1)	¼	3.95*

Note: $B_{eq} = \frac{8}{3}\pi^2\Sigma_i[\Sigma_j(U_{ij}a_i^*a_j^*a_ia_j)]$.
* Atoms were refined isotropically; those without standard deviation were isotropically fixed.

gated ellipsoid perpendicular to the CO_3 plane, which is very unusual. Subsequent difference-Fourier maps disclosed a weak but well-defined positive peak (O4S) almost intermediate between two (001) mirror-related CO_3 groups. Bond-distance calculations yielded a strongly distorted Si_2O_7 unit with unreasonable Si-O distances and angles. In addition, the atomic displacement parameters for O5 and O7 were either nonpositive definite or strongly anisotropic. To obtain a reasonable SiO_4 geometry and reliable displacement parameters, the Si-O distances were restrained to 1.61 Å within 0.02 Å. These restrained refinements were successful only if Si, O5S, and O7S of the disilicate unit were removed from the (001) mirror plane. This caused a strongly disordered arrangement (Fig. 2). The CO_3 group consisting of C2, O5, O6, and O7 is fixed on the (001) mirror plane. However, the substituting SiO_4 tetrahedron has O5S and O7S slightly above and Si2 below the mirror plane, with the mirror symmetry repeating these positions on the opposite side of the mirror plane. Only O6S remains on the mirror plane. The O positions (O5, O6, O7) coordinating C2 are a distance of <0.4 Å from those (O5S, O6S, O7S) coordinating Si2. C2 and Si2 are only 0.2 Å apart. This disorder also explains why Peacor et al. (1988b) reported decreased electron density for two O sites of the CO_3 group (type C2) but an excess electron density on C2. For a physically reasonable refinement of the Si_2O_7 unit, the following population constraints were applied: C2 = O5 = O6 = O7 ; pop. (O4S, O5S, O6S, O7S, Si2) = 1 − pop. (C2, O5, O6, O7).

Peacor et al. (1988b) noticed a major concentration of electron density in the structural channel at 0.892, 0.752, ¼. In this study a well-defined double peak was found at 0.888, 0.751, 0.115, which has its (001) mirror image at 0.888, 0.751, 0.385. After refinement of this doublet (named Cl1) with anisotropic displacement parameters, weak peaks (<1.5 e⁻/Å³) remained in subsequent difference-Fourier maps of the channel area. These peaks were refined as disordered, low-populated O positions (Ch2, Ch3, Ch4, Ch5) with isotropic displacement parameters. The Cl population refined to 0.25, and the sum of populations of Ch2, Ch3, Ch4, and Ch5 is 0.25 O atoms. All H positions of the OH groups on the channel walls could be located and refined without restraints but with fixed isotropic displacement parameters (U_{eq} = 0.05 Å²). The final least-squares cycles converged with 203 parameters to R = 2.6%, R_w = 2.7% for 3845 reflections. The strongest positive peaks on difference-Fourier maps are ~0.7e⁻/Å³ and are located ~0.6 Å from Ca positions.

TABLE 2. Anisotropic displacement parameters for defernite at 100 K

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca1	0.0090(1)	0.0140(1)	0.0060(1)	−0.0003(1)	0	0
Ca2	0.0079(1)	0.0086(1)	0.0055(1)	−0.00020(9)	0	0
Ca3	0.0128(1)	0.0092(1)	0.0060(1)	−0.0025(1)	0	0
Ca4	0.0075(1)	0.0079(1)	0.0055(1)	−0.00070(9)	0	0
Ca5	0.0086(1)	0.0109(1)	0.0068(1)	−0.0015(1)	0	0
Ca6	0.0074(1)	0.0098(1)	0.0094(1)	−0.00018(9)	0	0
C1	0.0099(5)	0.0104(6)	0.0055(6)	−0.0007(5)	0	0
O1	0.0079(4)	0.0102(5)	0.0086(5)	−0.0016(4)	0	0
O2	0.0175(6)	0.0082(5)	0.0107(5)	−0.0003(4)	0	0
O3	0.0080(5)	0.0164(6)	0.0224(7)	0.0000(4)	0	0
O4S	0.008(2)	0.042(4)	0.002(2)	0.005(3)	0	0
O5S	0.010(2)	0.006(3)	0.015(6)	0.002(2)	0.000(2)	−0.002(2)
O6S	0.003(2)	0.012(2)	0.012(2)	0.001(1)	0	0
O7S	0.008(2)	0.005(2)	0.018(3)	−0.001(1)	−0.002(2)	0.006(2)
C2	0.016(3)	0.021(3)	0.010(5)	−0.001(1)	0	0
O5	0.014(1)	0.009(2)	0.014(2)	0.004(2)	0	0
O6	0.008(2)	0.020(2)	0.015(1)	−0.001(1)	0	0
O7	0.014(1)	0.007(2)	0.019(3)	0.000(1)	0	0
O8	0.0124(5)	0.0192(6)	0.0123(6)	−0.0021(5)	0	0
O9	0.0119(5)	0.0122(5)	0.0110(5)	0.0004(4)	0	0
O10	0.0107(5)	0.0114(5)	0.0090(5)	−0.0010(4)	0	0
O11	0.0128(5)	0.0098(5)	0.0097(5)	−0.0001(4)	0	0
O12	0.0108(5)	0.0119(5)	0.0069(5)	−0.0008(4)	0	0
O13	0.0097(5)	0.0120(5)	0.0123(6)	−0.0009(4)	0	0
O14	0.0113(5)	0.0180(6)	0.0128(6)	−0.0004(4)	0	0
Cl1	0.027(1)	0.0149(6)	0.070(2)	0.0005(5)	−0.003(1)	−0.0015(8)

Note: Displacement parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

RESULTS

Assuming the position Cl1 represents Cl and Ch2–Ch5 are O atoms of OH groups, defernite has the composition $Ca_6(CO_3)_{1.58}(Si_2O_7)_{0.21}(OH)_7[Cl_{0.50}OH_{0.50}]$, thus yielding 0.42 negative excess charges in the channel. The Cl population is in good agreement with the Cl concentration analyzed by Peacor et al. (1988b). To reconcile this unbalanced formula we suggest that the majority of the OH in the structural channel is actually H_2O, giving rise to the composition $Ca_6(CO_3)_{1.58}(Si_2O_7)_{0.21}(OH)_7[Cl_{0.50}OH_{0.08}$-$(H_2O)_{0.42}]$. Atomic coordinates and populations are summarized in Table 1. Anisotropic displacement parameters are given in Table 2. Table 3 summarizes selected distances and angles, which are different from those in the previous studies (Liebich and Sarp 1985; Peacor et al. 1988b) because of the resolved substitution of Si_2O_7 for two CO_3. In addition, O-H distances and Cl-H bonds are listed (Table 3). Refined O-H distances vary between 0.74 and 0.85 Å, which is rather short in comparison with the common value of 0.96 Å for an O-H bond. However, X-ray data characteristically yield short O-H distances if the proton position is derived from the bonding electron between O and H. Observed and calculated structure factors are listed in Table 4.[1]

The Si_2O_7 unit (Fig. 3) displays an Si2-O4S-Si2 angle of 152.4(5)° and O-Si-O angles between 100 and 119°. The Si2-O4S distance is the longest [1.658(5) Å] within

the tetrahedron because O4S also bonds to Ca5 [2.472(6) Å], increasing the Ca5 coordination from 6 to 7.
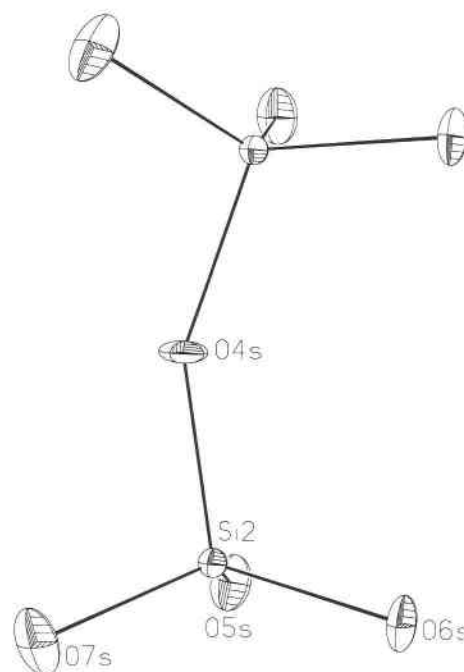
DISCUSSION

Several questions remain to be answered. Why does only the C2 position in defernite have significant Si substitution but not the C1 position, and why is Si not found in the closely related structure of holdawayite (Peacor and Rouse 1988)? To simulate the bridging O atom of a hypothetical Si_2O_7 unit near C1 in defernite, we introduced an additional O position midway between two CO_3 units stacked parallel to (001). This O atom has no short distances other than to the O atoms forming the triangular CO_3 units. The closest Ca position is Ca2, which is sevenfold-coordinated; thus, it could be argued that it is not favorable for Ca2 to bond to an additional O atom. More important, O2 bonded to C1 is the only O position participating in triangular CO_3 groups of defernite that is coordinated by two Ca (all other O atoms are threefold-coordinated), thus O2 requires a high bond strength from the C1-O2 bond [1.33 valence units (vu)] and the contribution of a Si1-O2 bond (1.0 vu) is probably not sufficient. Similar arguments may hold for holdawayite (Peacor and Rouse 1988), in which each triangular CO_3 group around C1 and C2 has one O atom that is only twofold coordinated by Ca (O1 and O8), thus neither triangular configuration is ideal for a SiO_4 substitution. Furthermore, the stacking sequence of CO_3 units in holdawayite is ~3.3 Å in comparison with ~3.6 Å in defernite. This stacking sequence in holdawayite would cause stronger adjustments of the structure for a hypothetical Si_2O_7 substitution.

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[1] A copy of Table 4 may be ordered as Document AM-96-614 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 3. Selected interatomic distances (Å) and angles (°) for defernite

C at C2		Si at C2	
Ca1-O3	2.412(2)	Ca1-O3	2.412(2)
Ca1-O5 × 2	2.476(5)	Ca1-O5S	2.21(1)
Ca1-O8	2.293(2)	Ca1-O5S	2.48(1)
Ca1-O9 × 2	2.362(1)	Ca1-O8	2.293(2)
		Ca1-O9 × 2	2.362(1)
Mean	2.397		2.353
		Ca2-O1	2.472(1)
		Ca2-O1 × 2	2.495(1)
		Ca2-O2	2.662(2)
		Ca2-O12 × 2	2.300(1)
		Ca2-O13	2.318(1)
		Mean	2.431
Ca3-O7	2.519(5)	Ca3-O7S	2.327(7)
Ca3-O11	2.348(2)	Ca3-O11	2.348(2)
Ca3-O10 × 2	2.357(1)	Ca3-O10 × 2	2.357(1)
Ca3-O14 × 2	2.371(1)	Ca3-O14 × 2	2.371(1)
Mean	2.387		2.355
		Ca4-O2 × 2	2.465(1)
		Ca4-O12	2.307(1)
		Ca4-O9	2.295(2)
		Ca4-O11 × 2	2.311(1)
		Mean	2.359
Ca5-O14	2.319(2)	Ca5-O14	2.319(2)
Ca5-O3	2.357(2)	Ca5-O3	2.357(2)
Ca5-O13 × 2	2.315(1)	Ca5-O13 × 2	2.315(1)
Ca5-O7 × 2	2.489(6)	Ca5-O7S	2.200(7)
		Ca5-O7S	2.747(8)
		Ca5-O4S	2.472(7)
Mean	2.381		2.389
Ca6-O5	2.606(9)	Ca6-O5S	2.48(1)
Ca6-O6 × 2	2.494(3)	Ca6-O6S × 2	2.363(3)
Ca6-O6	2.704(5)	Ca6-O6S	2.511(7)
Ca6-O8 × 2	2.341(1)	Ca6-O8 × 2	2.341(1)
Ca6-O10	2.344(1)	Ca6-O10	2.344(1)
Mean	2.475		2.389
		C1-O1	1.303(2)
		C1-O2	1.298(2)
		C1-O3	1.265(2)
		Mean	1.289
C2-O5	1.28(1)	Si2-O4S	1.658(5)
C2-O6	1.29(1)	Si2-O5S	1.590(9)
C2-O7	1.29(1)	Si2-O6S	1.612(5)
		Si2-O7S	1.588(8)
Mean	1.29		1.612
		O4S-Si2-O5S	103.5(6)
		O4S-Si2-O6S	110.3(3)
		O4S-Si2-O7S	100.4(4)
		O5S-Si2-O6S	106.4(6)
		O5S-Si2-O7S	119.3(6)
		O6S-Si2-O7S	115.9(4)
		Si2-O4S-Si2	152.4(5)

O8-H8	0.84(4)	Cl1-H8	2.59(3)	Ch2-H8	2.44(3)
O9-H9	0.78(3)	Cl1-H9	2.78(3)		
O10-H10	0.74(4)	Cl1-H10	2.81(3)	Ch2-H10	2.63(3)
O11-H11	0.83(4)			Ch2-H11	2.39(4)
O12-H12	0.84(3)	Cl1-H12	2.46(3)	Ch2-H12	2.28(3)
O13-H13	0.77(3)	Cl1-H13	2.73(3)	Ch2-H13	2.56(3)
O14-H14	0.80(3)	Cl1-H14	2.69(4)		
Ch3-H8	2.31(4)	Ch4-H10	2.26(4)	Ch5-H9	2.24(4)
Ch3-H14	2.77(3)	Ch4-H12	1.97(4)	Ch5-H14	2.20(4)
Ch3-H13	2.45(4)				

FIGURE 3. Configuration of an Si₂O₇ unit in defernite projected approximately along b with the c axis vertical. Ellipsoids have 80% probability.

be able to accommodate the different bond strength (1.33 vu for C-O vs. 1.0 vu for Si-O). In other words, if one of the O atoms of triangular CO₃ is already underbonded, then an Si substitution is very unlikely. Thus, we can see that a substitution of BO₃ by SiO₄ or CO₃ by SeO₄ (Reeder et al. 1994) is easier to accomplish because the bond-strength requirements are the same. Substitution of PO₄ by CO₃ in apatite (Perdikatsis 1991) involves a bond-strength difference of only 0.083 vu, which is much easier to balance than the 0.333 vu for a CO₃ substitution by SiO₄. A disilicate substitution for two CO₃ groups seems favorable, provided it is spatially feasible, because the additional O atom already has a balanced bond strength.

The channel of defernite has a radius of ~3.4 Å measured from the center to the O atoms of the OH groups on the channel walls. If we assume an O-H distance of ~1 Å with the protons oriented toward the channel center, the radius is reduced to ~2.4 Å. This distance is ideal for Cl⁻-H interactions (Fig. 4). Cl1, with the highest population in the structural channel of defernite, is bonded to six H atoms with distances between 2.5 and 2.8 Å, which are similar to Cl-H distances in H₉O₄⁺Cl⁻·2H₂O (Taesler and Lundgren 1978). Peacor and Rouse (1988) and Peacor et al. (1988b) suggested that in holdawayite and defernite, respectively, Cl⁻ may share the channel with additional OH⁻ groups. To obtain a charge-balanced formula the present study assigned only a very low concentration of channel OH⁻ groups. Thus, the remaining channel occupants are assumed to be H₂O molecules. The H₂O molecules are slightly shifted out of the channel

In general, for a substitution of CO₃ by SiO₄, (1) there must be enough space available to accommodate an additional O atom; (2) the bond strength of the additional O atom must be balanced by additional bonds; (3) charge neutrality must be achieved by an additional substitution; and (4) the O atoms of the triangular CO₃ unit must
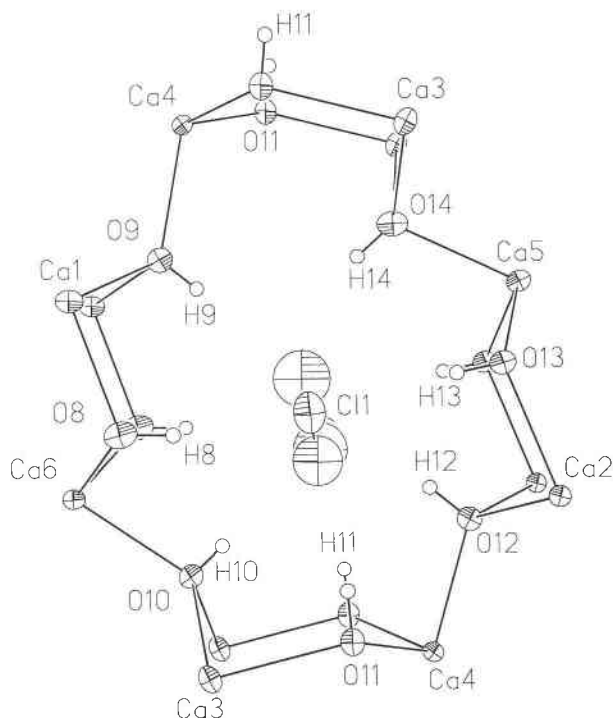
FIGURE 4. Channel environment of defernite projected parallel to the c axis. Low-populated positions of channel anions and H₂O (Ch2–Ch5) are displaced from the channel center and are drawn isotropically. The surface of the channel wall is covered with H atoms (small circles), which are also bonded to Cl1 in the channel center. Ellipsoids have 80% probability.

center to bond within shorter distances (2.0–2.2 Å) to the channel-surface protons. The only argument against channel H₂O, originally suggested by Liebich and Sarp (1985), is the IR powder spectrum mentioned by Peacor et al. (1988b), which allegedly excludes the presence of H₂O. We recollected the IR powder spectrum between 400 and 4000 cm⁻¹ using the KBr-pellet method. The spectrum is characterized by a strong absorption band at 3576 cm⁻¹ with a broad tail toward lower wave numbers representing OH-stretching vibrations of the seven symmetrically distinct OH groups on the channel walls. At ~1780 cm⁻¹ there is a weak absorption on the ascending wing of a very strong triplet with centers at 1542, 1458, and 1412 cm⁻¹. In the range between 400 and 4000 cm⁻¹ the only absorption band that allows a distinction between H₂O and OH is the H₂O bending mode at ~1600 cm⁻¹, which was not observed. However, such a relatively weak absorption band would certainly be masked under the strongly ascending wing of the CO₃ absorptions. For this reason an IR powder spectrum of defernite cannot be used to support or reject the hypothesis of additional channel H₂O.

The ionic radius of Cl⁻ is approximately 1.81 Å (Ahrens 1952; Pauling 1960). If Cl⁻ is the only channel occupant in the hypothetical end-member compositions

$Ca_6(CO_3)_2(OH)_7[Cl]$ (defernite) and $Mn_6(CO_3)_2(OH)_7[Cl]$ (holdawayite), then the 3.6 Å channel length in defernite and the 3.3 Å channel length in holdawayite would yield Cl⁻-Cl⁻ distances that are too short. In this model [assuming one Cl⁻ per formula unit (pfu) in the structural channel], Cl⁻ is bonded only laterally to surrounding OH groups on the channel walls, whereas parallel to the c axis Cl⁻ is not shielded, which should cause strong Cl⁻-Cl⁻ repulsion. Two possibilities seem to exist for the prevention of short Cl⁻-Cl⁻ contacts. (1) The structural framework possesses less than one positive charge (e.g., $Si_2O_7^{6-}$ substitution for two CO_3^{2-} as observed for defernite). In this case Cl⁻ vacancies exist in the structural channel, and Cl⁻ is expected to be disordered as was found in this study. (2) A more ideal configuration can also be obtained (e.g., in holdawayite without replacing $Si_2O_7^{6-}$ units) if Cl⁻ has two H neighbors from additional OH groups or H₂O molecules above and below in channel direction. These channel OH groups and H₂O molecules might have O atoms that are hydrogen-bonded to the channel wall.

Defernite may be regarded as a member of a solid-solution series with end-members in which C2 is completely occupied by C, $Ca_6(CO_3)_2(OH)_7[Cl,OH]$, and by Si, $Ca_6(CO_3)_{1.0}(Si_2O_7)_{0.5}(OH)_7$. The Si end-member must have a doubled c axis to avoid close Si-Si contacts. In other words, an Si₂O₇ unit occurs only in each second 3.6 Å translation unit along the c axis. In addition, the framework of defernite with Si fully substituted in C2 is charge balanced, and thus only neutral molecules may occupy the structural channel.

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