

## Defernite from the Kombat mine, Namibia: A second occurrence, structure refinement, and crystal chemistry

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### ABSTRACT

Discovery of well-crystallized defernite occurring in platy crystals up to 1 cm in diameter in the Kombat mine, Namibia, has led to improved physical and chemical data and refinement of the composition. Crystal-structure analysis ( $R = 7.5\%$ ) implies that  $\text{SiO}_4$  substitutes for  $\text{CO}_3$ . As in the closely related mineral holdawayite,  $\text{Mn}_6(\text{CO}_3)_2(\text{OH})_7(\text{Cl},\text{OH})$ , carbonate groups and octahedrally coordinated cations (principally Ca) define connected slabs having the approximate composition  $\text{Ca}_6(\text{CO}_3)_2(\text{OH})_7$ , and a net positive charge. Zeolite-like channels contain  $(\text{Cl},\text{OH})$  anions which may be mobile and replaceable, but  $\text{H}_2\text{O}$  is apparently absent. Like holdawayite, defernite may have *anion-exchange* properties. The redefined composition is  $\text{Ca}_6(\text{CO}_3)_{2-x}(\text{SiO}_4)_x(\text{OH})_7(\text{Cl},\text{OH})_{1-2x}$ , where  $x \leq 0.5$ .

### INTRODUCTION

A number of new and interesting minerals have been found in the Kombat mine in Namibia in the past ten years. Among these are at least four new species, including holdawayite (Peacor et al., 1988), and a large number of rare minerals, some of which were previously known only from Långban, Sweden, and Franklin and Sterling Hill, New Jersey. Within a suite of carbonate and silicate minerals found in 1976 was a red, platy carbonate that appeared to be related to holdawayite. Our detailed examination of this mineral indicated it is defernite, originally described by Sarp et al. (1980). Its identity as defernite was determined by direct comparison with the type defernite, which occurred in amounts much too small to permit the detailed description we provide here. The described specimen has been deposited in the collections of the Smithsonian Institution with catalogue number NMNH 163802.

Defernite was formerly considered to be  $\text{Ca}_6(\text{CO}_3)_2(\text{OH},\text{Cl})_8 \cdot n\text{H}_2\text{O}$ , with  $n \approx 2$ . The crystal structure was determined by Liebich and Sarp (1985). However, the atom positions that they determined lead to the formula  $\text{Ca}_6(\text{CO}_3)_2(\text{OH},\text{Cl}) \cdot \text{H}_2\text{O}$ , which is deficient in negatively

charged ions. In addition, the structure analysis failed to explain the presence of small quantities ( $\approx 0.1\%$ ) of Si that ubiquitously appeared in electron-microprobe analyses. Lastly, many interatomic distances were outside of commonly accepted limits, and some isotropic temperature factors were unreasonable. The latter factors were attributed to the poor quality of the crystal used as a source of intensity data, as further shown by the high  $R$  factor (12.5%) for observed data. Because the defernite crystals from the Kombat mine appeared to be of high quality, this investigation was carried out in part to clarify the ambiguities in composition and structure.

### OCCURRENCE

This defernite was found in 1976 in the Kombat mine, which is located 37 km east of Otavi, and 49 km south of Tsumeb in Namibia. The geology and mineralogy of this deposit are given by Innes and Chaplin (1985). Most of the rare minerals, including defernite, are found in lenses with Mn-bearing silicates, carbonates, and oxides related to, but not in contact with, the ore body.

Defernite was originally found at the Kombat mine in the W90 stope, 12 level, of the Asis West mining sector on the 1189-m elevation, and was subsequently found up to the 1208-m elevation. The defernite described herein was found in the E15-11 South stope. Defernite typically

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occurs there as idiomorphic "porphyroblastic" laths, distributed through a body of massive, unbanded, granular hausmannite. The ore usually has a decussate texture, and, less frequently, a well-developed tectonic lineation is defined by alignment of the defernite crystal laths. The described specimen (NMNH no. 163802) consists of 1-cm laths of abundant defernite arranged randomly in a matrix of fine- to medium-grained hausmannite. Subhedral grains of brucite fill spaces between, or partially include, hausmannite and hillebrandite. The textures are compatible with equilibrium relations. Small amounts of crednerite are found within the hausmannite. Native copper in a coarse threadlike form, is a ubiquitous associate, with ore grades ranging up to 8% Cu. Granular barite, calcite, and etched crystals of vesuvianite are also common associates. Crednerite, jacobsite, and hematite are less commonly associated. Small grains of cassiterite were found only in separates obtained using heavy liquids. The native copper occasionally forms thin films along multiple cleavage planes in defernite, and appears to have replaced it in part. Rarely, late-stage veins of calcite were observed intergrown with defernite and arborescent growths of native copper.

The defernite-bearing hausmannite ore forms a zone varying from 2 to 4 m in thickness toward the base of a mineralogically layered sequence of manganese ores. It occurs immediately above glaucochroite- and harkerite-bearing zones. Within the defernite zone, defernite typically occupies 10 to 40 vol% of the ore, and it is estimated that ca. 2000 metric tons of defernite-bearing hausmannite ore have been stoped out during mining operations in the W90 stope. Defernite has not been noted in any of the other five manganese ore lenses exposed during mining or in exploration drill holes. Freshly blasted hausmannite-defernite-copper ore is quite spectacular. On exposure, the cleavage surfaces of defernite laths develop a whitish patina.

#### PHYSICAL AND OPTICAL PROPERTIES

Defernite from the Kombat mine is deep red, varying to rose-brown. It is transparent, occurs in anhedral orthorhombic crystals of platy habit,  $2 \times 0.5$  cm in cross section, flattened on {010}. The streak is pink and the luster is vitreous. The cleavage is perfect {010} and distinct {100}; the fracture is conchoidal to splintery. The density, measured using heavy-liquid techniques, is  $2.34 \text{ g/cm}^3$ , compared with the calculated value of  $2.31 \text{ g/cm}^3$ . Defernite dissolves in 1:1 HCl with effervescence. Optically, this defernite is biaxial negative, with  $2V_x = 38(2)^\circ$ ,  $36.2^\circ$  (calc.) and indices of refraction  $\alpha = 1.544$ ,  $\beta = 1.580$ ,  $\gamma = 1.584$  (all  $\pm 0.002$ ). Dispersion is weak,  $r > v$ ; the optical orientation is  $X = c$ ,  $Y = b$ , and  $Z = a$ . Pleochroism is strong in thick section:  $X =$  ochre-brown,  $Y =$  brownish-orange to ochre-brown,  $Z =$  colorless to yellow.

#### CHEMICAL ANALYSIS

Defernite from the Kombat mine was chemically analyzed using the following techniques. Ca and Si were de-

termined by atomic absorption (AA) on 50 mg of carefully purified sample.  $\text{CO}_2$  was determined using a Heraeus CHN analyzer, with rapid combustion of a 20-mg sample. Two separate determinations gave the values 15.91 and 16.75% (mean equals 16.33%). The water content determined by the Penfield method is 11.47%. Combined weight loss of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , measured thermogravimetrically with a Mettler TA1 instrument on a 11.44-mg sample, was approximately 27%. This result is in good agreement with the sum of 27.8% for the separate  $\text{CO}_2$  and  $\text{H}_2\text{O}$  determinations. The absence of molecular  $\text{H}_2\text{O}$  was confirmed by infrared spectra in the range of  $200\text{--}400 \text{ cm}^{-1}$  as obtained on a pellet of 2 mg of sample mixed with 300 mg KBr. Mn, Mg, Fe, Si, and Cl were determined by electron microprobe using many measurements over a broad area of one specimen. In addition, the Ca content as determined by AA was verified. Hornblende was used as a standard. The  $\text{SiO}_2$  content was determined to be 3.6%, with virtually no variation in its concentration over all measurements. This further implies that Si is present in solid solution in defernite.

The resultant analysis, utilizing the preferred values from the data described above, is CaO 65.0 (64–66%), MnO 1.2,  $\text{SiO}_2$  3.6, MgO 0.1, FeO 0.1,  $\text{CO}_2$  16.3,  $\text{H}_2\text{O}$  11.47, Cl 3.5, less O  $\equiv$  Cl 0.8, sum = 100.5 wt%. Because the structure analysis by Liebich and Sarp (1985) indicated that there are 24 octahedrally coordinated cations per unit cell, these data were normalized to  $24(\text{Ca} + \text{Mn} + \text{Mg} + \text{Fe})$  giving rise to the formula  $(\text{Ca}_{23.59}\text{Mn}_{0.35}\text{Mg}_{0.04}\text{Fe}_{0.02})_{24}\text{C}_{7.53}\text{Si}_{1.22}\text{H}_{25.94}\text{Cl}_{2.02}\text{O}_{53.46}$ . This formula is in agreement with the ideal formula  $\text{Ca}_6(\text{CO}_3)_2(\text{OH},\text{Cl})_8 \cdot n\text{H}_2\text{O}$  as determined by Sarp et al. (1980), except that no molecular water is present and Si is implied to occur in solid solution. Because the details of the formula are dependent on the detailed crystal structure, and the latter is in part ill-defined, the final formula is discussed following description of the structure refinement.

#### CRYSTAL-STRUCTURE REFINEMENT

Single-crystal precession and Weissenberg studies showed that defernite from the Kombat mine is orthorhombic with space group  $Pna2_1$ , or  $Pnam$ , in agreement with the results of Sarp et al. (1980) for type defernite. Because Liebich and Sarp (1985) determined the crystal structure using space group  $Pnam$ , this space group was initially chosen; as shown below, refinement of the structure verified that this space group is correct. Unit-cell parameters were determined by least-squares refinement of powder X-ray diffraction data to be  $a = 17.82(2)$ ,  $b = 22.76(2)$ ,  $c = 3.629(4)$  Å,  $V = 1471.9$  Å<sup>3</sup>. The powder data are listed in Table 1 and were obtained using  $\text{CuK}\alpha$  radiation and a Guinier-Hagg camera.

Intensity data were measured using a  $c$ -axis-oriented cleavage fragment measuring approximately  $0.27 \times 0.17 \times 0.28$  mm, mounted on a Supper Weissenberg-geometry diffractometer. The intensities of 1879 reflections with  $\sin \theta \leq 0.46$  corresponding to one asymmetric unit were

TABLE 1. Powder X-ray diffraction data for defernite from the Kombat mine

| <i>hkl</i> | <i>d</i> <sub>calc</sub> | <i>d</i> <sub>obs</sub> | <i>I</i> <sub>visual</sub> | <i>hkl</i> | <i>d</i> <sub>calc</sub> | <i>d</i> <sub>obs</sub> | <i>I</i> <sub>visual</sub> |
|------------|--------------------------|-------------------------|----------------------------|------------|--------------------------|-------------------------|----------------------------|
| 020        | 11.378                   | 11.38                   | 100                        | 710        | 2.529                    |                         |                            |
| 210        | 8.295                    | 8.32                    | 90                         | 511        | 2.527                    |                         |                            |
| 040        | 5.689                    | 5.681                   | 30                         | 441        | 2.522                    | 2.525                   | 5                          |
| 320        | 5.265                    | 5.260                   | <5                         | 261        | 2.515                    |                         |                            |
| 240        | 4.795                    | 4.801                   | <5                         | 720        | 2.484                    | 2.477                   | 5                          |
| 400        | 4.454                    | 4.442                   | <5                         | 521        | 2.481                    |                         |                            |
| 420        | 4.148                    | 4.143                   | 20                         | 570        | 2.402                    | 2.405                   | 10                         |
| 250        | 4.053                    | 4.047                   | 15                         | 451        | 2.393                    | 2.392                   | <5                         |
| 060        | 3.793                    | 3.784                   | <5                         | 740        | 2.323                    |                         |                            |
| 510        | 3.520                    |                         |                            | 541        | 2.321                    | 2.316                   | 5                          |
| 111        | 3.513                    | 3.514                   | <5                         | 371        | 2.242                    | 2.327                   | 5                          |
| 440        | 3.507                    |                         |                            | 181        | 2.221                    |                         |                            |
| 260        | 3.490                    | 3.491                   | 5                          | 551        | 2.220                    | 2.216                   | 10                         |
| 201        | 3.361                    | 3.364                   | 20                         | 810        | 2.216                    |                         |                            |
| 530        | 3.225                    |                         |                            | 281        | 2.171                    | 2.169                   | <5                         |
| 221        | 3.223                    | 3.227                   | 15                         | 840        | 2.074                    |                         |                            |
| 131        | 3.220                    |                         |                            | 590        | 2.062                    | 2.069                   | 10                         |
| 231        | 3.073                    |                         |                            | 191        | 2.061                    |                         |                            |
| 311        | 3.068                    | 3.065                   | 35                         | 1.11.0     | 2.055                    | 2.054                   | <5                         |
| 270        | 3.054                    | 3.048                   | 20                         | 680        | 2.054                    |                         |                            |
| 540        | 3.020                    |                         |                            | 721        | 2.050                    | 2.046                   | <5                         |
| 141        | 3.015                    | 3.013                   | 10                         | 770        | 2.004                    |                         |                            |
| 321        | 2.988                    | 2.985                   | 40                         | 571        | 2.003                    | 2.003                   | 5                          |
| 610        | 2.944                    | 2.930                   | 5                          | 850        |                          |                         |                            |
| 241        | 2.893                    | 2.893                   | 40                         | 481        | 2.000                    |                         |                            |
| 620        | 2.873                    |                         |                            | 741        | 1.957                    |                         |                            |
| 331        | 2.867                    | 2.872                   | <5                         | 3.11.0     | 1.954                    | 1.950                   | 25                         |
| 080        | 2.845                    |                         |                            | 920        | 1.950                    |                         |                            |
| 051        | 2.837                    | 2.837                   | 5                          | 690        | 1.925                    |                         |                            |
| 411        | 2.792                    | 2.787                   | 20                         | 860        | 1.920                    | 1.921                   | 5                          |
| 630        | 2.765                    | 2.754                   | 25                         | 0.12.0     |                          |                         |                            |
| 341        | 2.720                    |                         |                            | 581        | 1.896                    |                         |                            |
| 280        | 2.710                    | 2.716                   | <5                         | 751        | 1.895                    |                         |                            |
| 251        | 2.703                    |                         |                            | 811        | 1.892                    | 1.889                   | 30                         |
| 431        | 2.638                    |                         |                            | 1.12.0     | 1.886                    |                         |                            |
| 640        | 2.632                    | 2.634                   | <5                         | 2.10.1     | 1.884                    |                         |                            |
| 470        | 2.626                    |                         |                            | 3.10.1     | 1.834                    | 1.828                   | 5                          |
| 560        | 2.597                    |                         |                            | 761        | 1.826                    |                         |                            |
| 161        | 2.594                    | 2.590                   | <5                         | 950        |                          |                         |                            |
| 380        | 2.566                    |                         |                            | 002        | 1.815                    |                         |                            |
| 351        | 2.560                    | 2.559                   | <5                         | 3.12.0     | 1.807                    | 1.814                   | 30                         |
|            |                          |                         |                            | 6.10.0     | 1.806                    |                         |                            |

+ twenty weak diffractions

Note: Guinier-Hagg camera;  $\text{CuK}\alpha$  radiation. The pattern is indexed with  $a = 17.82$ ,  $b = 22.76$ ,  $c = 3.629$  Å.

measured using monochromated  $\text{MoK}\alpha$  radiation and background counts of 25 s on both sides of continuous peak scans. Lorentz-polarization factors and absorption ( $\mu_1 = 23 \text{ cm}^{-1}$ ) corrections were applied, giving rise to a data set of 1543 observed reflections.

Refinement was carried out with the program SHELX-76 (Sheldrick, 1976) using anomalous dispersion corrections (Cromer and Liberman, 1970) and weights equal to the reciprocals of the variances of the  $F_0$ . Starting with the structure parameters of Liebich and Sarp (except that  $\text{H}_2\text{O}$  atoms in channels were excluded), with full atom occupancies and isotopic temperature factors, refinement rapidly converged to a conventional  $R$  factor of 12.5%. This structure gives rise to the formula  $\text{Ca}_6(\text{CO}_3)_2(\text{OH})_7$  and lacks charge balance. It does not take into consideration the following factors: (1) the ubiquitous occurrence of minor Si in all analyses (see below), as also noted by Sarp

et al. (1980) for type material; (2) the presence of  $\text{H}_2\text{O}$  in channels of the structure, as noted by Liebich and Sarp (1985) and indicated by the data of the mineral description of Sarp et al. (1980) that gave rise to the formula  $\text{Ca}_6(\text{CO}_3)_2(\text{OH},\text{Cl})_8 \cdot n\text{H}_2\text{O}$  (the water content in the latter formula was determined "by difference," however, and included the 8(OH) required to yield charge balance relative to the 7(OH) as implied by the crystal-structure determination); (3) minor solid solution of Mn for Ca and Cl for OH as implied by the chemical analysis (see below). In addition, the temperature factors of several atoms were not all reasonable in that  $U$  of C(2) was negative, and the temperature factors of several oxygen atoms coordinating C [O(3)C1, O(1)C2, O(2)C2, and O(3)C2] were unusually large (0.03–0.05).

The structure of holdawayite  $\text{Mn}_6(\text{CO}_3)_2(\text{OH})_7(\text{OH},\text{Cl})$  (Peacor and Rouse, 1988) is closely related to that of defernite; indeed, it consists of the same modules but stacked in alternate ways. Peacor and Rouse also found that the structure of holdawayite initially refined in a straightforward way, giving rise to the similarly charge-imbalanced formula  $\text{Mn}_6(\text{CO}_3)_2(\text{OH})_7$ . Further refinement gave rise to definition of (Cl,OH) ions statistically occupying five zeolite-like sites in two channels that accounted for the charge imbalance. An electron-density synthesis was therefore calculated for defernite; it indicated the presence of an atom at only one channel site, which was assumed to be O for purposes of refinement.

The electron-density synthesis also gave rise to an electron density enhanced by approximately 40% for C(2) relative to C(1) and relatively small values for the oxygen atoms coordinating C(2) [O(1)C2, O(2)C2, and O(3)C2]. The latter is consistent with the unreasonable temperature factors, as described above. No peaks were found in the Fourier synthesis corresponding to Si or its coordinating oxygen atoms. However, the data implied the possibility that some  $\text{SiO}_4$  groups substitute for  $\text{CO}_3$ , in that the cation electron density would be enhanced, whereas those of the three ligands would be decreased, owing to vacancies occurring concomitantly with substitution of a Si atom for C(2).

Refinement was therefore continued with a channel anion, OH(8), and with the C(2) scattering factor approximated by those of C and Si. Refinement of the occupancy factor for OH(8) gave rise to the value 0.39(1), and subsequent refinement of the isotropic temperature factor gave rise to a reasonable value, thus confirming its presence. In addition, the occupancy factor for C(2) refined to a value corresponding to 0.74(1)C + 0.26 Si. This compares reasonably well with a value of 0.33 Si as predicted from the chemical analysis and is taken as confirmation of the inferred substitution—especially insofar as there is no other obvious explanation for the enhanced electron density of C(2). The occupancy factors of O(1)C2, O(2)C2, and O(3)C2 refined to values of 1.01(1), 0.88(1), and 0.88(1), respectively. Insofar as vacancies may be coupled with Si substitution, the latter two decreased values are consistent with partial occupancy of these sites.

TABLE 2. Atom coordinates and temperature factors ( $\times 10^4$ ) for defernite

| Atom   | x        | y        | z        | $U_{11}$ | $U_{22}$ | $U_{33}$  | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|--------|----------|----------|----------|----------|----------|-----------|----------|----------|----------|
| Ca(1)  | 7112(1)  | 826(1)   | 1/4      | 165(10)  | 234(10)  | 123(12)   | 0        | 0        | -13(8)   |
| Ca(2)  | 5322(1)  | 4276(1)  | 1/4      | 174(10)  | 179(9)   | 112(11)   | 0        | 0        | -19(8)   |
| Ca(3)  | 3711(1)  | 1788(1)  | 1/4      | 245(11)  | 174(9)   | 100(10)   | 0        | 0        | -19(9)   |
| Ca(4)  | 6214(1)  | 6586(1)  | 1/4      | 172(10)  | 187(9)   | 106(10)   | 0        | 0        | -5(9)    |
| Ca(5)  | 7702(1)  | 9078(1)  | 1/4      | 183(11)  | 226(10)  | 125(12)   | 0        | 0        | -26(8)   |
| Ca(6)  | 9748(1)  | 5756(1)  | 1/4      | 156(10)  | 195(9)   | 130(11)   | 0        | 0        | -1(8)    |
| C(1)   | 3710(5)  | 4712(3)  | 1/4      | 87(43)   | 212(45)  | 76(46)    | 0        | 0        | 89(40)   |
| C(2)   | 8685(3)  | 4689(2)  | 1/4      | 89(28)   | 88(25)   | 334(39)   | 0        | 0        | 37(23)   |
| OH(1)  | 1532(3)  | 1113(3)  | 1/4      | 105(34)  | 403(39)  | 230(50)   | 0        | 0        | 0(29)    |
| OH(2)  | 7162(3)  | 8154(2)  | 1/4      | 228(38)  | 297(35)  | 165(43)   | 0        | 0        | -39(31)  |
| OH(3)  | 0889(3)  | 3840(2)  | 1/4      | 255(38)  | 253(34)  | 95(41)    | 0        | 0        | 39(29)   |
| OH(4)  | 2509(4)  | 8573(2)  | 1/4      | 171(36)  | 298(34)  | 132(40)   | 0        | 0        | -43(28)  |
| OH(5)  | 470(3)   | 6620(2)  | 1/4      | 175(35)  | 233(32)  | 139(40)   | 0        | 0        | -7(28)   |
| OH(6)  | 4021(4)  | 2790(2)  | 1/4      | 342(41)  | 122(29)  | 113(39)   | 0        | 0        | 23(28)   |
| OH(7)  | 4957(3)  | 6310(2)  | 1/4      | 180(36)  | 212(31)  | 96(41)    | 0        | 0        | -21(27)  |
| O(1)C1 | 3811(4)  | 4141(2)  | 1/4      | 394(40)  | 86(29)   | 167(37)   | 0        | 0        | -10(29)  |
| O(2)C1 | 4325(3)  | 5039(3)  | 1/4      | 121(33)  | 279(34)  | 131(40)   | 0        | 0        | -27(28)  |
| O(3)C1 | 3059(4)  | 4931(3)  | 1/4      | 181(39)  | 312(38)  | 573(65)   | 0        | 0        | -27(31)  |
| O(1)C2 | 9477(4)  | 4633(3)  | 1/4      | 351(39)  | 318(33)  | 170(41)   | 0        | 0        | 116(29)  |
| O(2)C2 | 8220(4)  | 4227(3)  | 1/4      | 111(35)  | 151(32)  | 643(65)   | 0        | 0        | 1(30)    |
| O(3)C2 | 8435(4)  | 5267(3)  | 1/4      | 184(37)  | 189(33)  | 177(44)   | 0        | 0        | -16(28)  |
| OH(8)  | 3918(10) | 7484(5)  | 1/4      | 426(74)  | 7(43)    | 3496(267) | 0        | 0        | 24(45)   |
| OH(9)  | 3622(20) | 7499(16) | 571(126) | 338(102) |          |           |          |          |          |
| OH(10) | 1294(64) | 2514(34) | 1/4      | 142(139) |          |           |          |          |          |
| OH(11) | 810(19)  | 2415(12) | 935(106) | 331(80)  |          |           |          |          |          |

Note: Temperature factors are of the form  $\exp[-2\pi^2(U_{11}h^2a^2 + \dots + 2U_{23}klb^*c^*\cos \alpha^*)]$ .

The temperature factors of all atoms became reasonable following these adjustments.

The structure of holdawayite (Peacor and Rouse, 1988) contains five partially occupied channel anion sites that give rise to occupancy of the two kinds of channels. However, the single atom that had been located in the defernite structure [OH(8)] at this stage only provided partial occupancy of one of two channels. In addition, OH(8) did not correspond to either of the positions of the two oxygen channel atoms identified as corresponding to H<sub>2</sub>O by Liebich and Sarp (1985). Therefore, electron-density and difference electron-density syntheses were calculated in order to clarify the channel occupancies. Three peaks, labeled OH(9), OH(10), and OH(11), were located whose heights correspond to the levels of background fluctuations. Nevertheless, their positions and occupancies were refined, with temperature factors held constant at reasonable values ( $U = 0.2$ ), giving rise to occupancies of 0.12(1), 0.08(1), and 0.16(1), respectively. Refinement was concluded by varying all coordinates and temperature factors but with only isotropic temperature factors for OH(9), OH(10), and OH(11) because of the low occupancies and high parameter uncertainties for these channel atoms. An attempt to determine the positions of the H atoms through a difference electron-density synthesis was unsuccessful.

The final  $R$  values are 7.5% (unweighted) and 5.2% (weighted). Final atom parameters are listed in Table 2, cation-anion distances in Table 3, and structure factors in Table 4.<sup>1</sup>

<sup>1</sup> A copy of Table 4 may be ordered as Document AM-88-384 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.

## DISCUSSION

The principal structural units have been described by Liebich and Sarp (1985) for defernite and by Peacor and Rouse (1988) for the closely related mineral holdawayite in relation to defernite and, therefore, will not be described further here. The results of this refinement are compatible with the principal features of the structure determined by Liebich and Sarp, but there are significant detailed differences. These relate to the chemical formula and result in reinterpretations of the chemistry, as described in this section.

TABLE 3. Cation-anion interatomic distances (Å) for defernite

|              |           |              |          |
|--------------|-----------|--------------|----------|
| Ca(1)-OH(3)  | 2.308(6)  | Ca(4)-OH(7)  | 2.326(6) |
| -2OH(4)      | 2.371(4)  | -OH(4)       | 2.336(8) |
| -O(3)C1      | 2.412(8)  | -2OH(6)      | 2.342(4) |
| -2O(3)C2     | 2.421(5)  | -2O(1)C1     | 2.456(4) |
| Avg.         | 2.384     | Avg.         | 2.376    |
| Ca(2)-2OH(7) | 2.306(4)  | Ca(5)-2OH(1) | 2.312(4) |
| -OH(1)       | 2.331(6)  | -OH(2)       | 2.313(6) |
| -2O(2)C1     | 2.474(5)  | -O(3)C1      | 2.344(7) |
| -O(2)C1      | 2.484(7)  | -2O(2)C2     | 2.471(5) |
| -O(1)C1      | 2.710(8)  | Avg.         | 2.371    |
| Avg.*        | 2.396     |              |          |
| Ca(3)-OH(6)  | 2.347(6)  | Ca(6)-2OH(3) | 2.330(4) |
| -2OH(5)      | 2.360(4)  | -OH(5)       | 2.350(6) |
| -2OH(2)      | 2.394(4)  | -2O(1)C2     | 2.446(5) |
| -O(2)C2      | 2.470(8)  | -O(3)C2      | 2.591(8) |
| Avg.         | 2.389     | -O(1)C2      | 2.601(8) |
|              |           | Avg.         | 2.442    |
| C(1)-O(3)C1  | 1.263(11) | C(2)-O(2)C2  | 1.339(9) |
| -O(1)C1      | 1.312(8)  | -O(3)C2      | 1.389(8) |
| -O(2)C1      | 1.325(10) | -O(1)C2      | 1.417(9) |
| Avg.         | 1.300     | Avg.         | 1.381    |

\* Average excludes O(1)C1.

### Si content

The ubiquitous presence of Si in electron-microprobe analyses of defernite from both the Kombat mine and the type locality occurs despite the very different parageneses. It might be argued that material from one locality contains homogeneously distributed grains of a calcium silicate with a size well below that for microprobe resolution. However, the Turkish type defernite occurs as a secondary alteration product of high-temperature calc-silicates, whereas that from the Kombat mine occurs as relatively large, primary, glassy subhedral grains intergrown primarily with hausmannite. In addition, the apparent presence of an atom substituting for C(2) that has an electron density and partial occupancy corresponding approximately to those predicted for Si is also highly suggestive of the presence of Si. As unlikely as such a substitution is, it is supported by apparent vacancies for two of the oxygen sites coordinating C(2). Refinement with no vacancies gives rise to unreasonable temperature factors only for these atoms.

An analogue to the unusual substitution of  $\text{SiO}_4$  for  $\text{CO}_3$  inferred for defernite is found in the apatite group. Young (1975) has reviewed substitution mechanisms in apatite. There are two mechanisms; in one,  $\text{CO}_3$  groups substitute for  $\text{PO}_4$  groups, but such that the plane of the  $\text{CO}_3$  groups is parallel to a face of a  $\text{PO}_4$  group. Speer and Ribbe (1982) and Rouse and Dunn (1982) have reviewed the status of natural apatites that contain essential  $\text{SiO}_4$  and  $\text{SO}_4$  in substitution for  $\text{PO}_4$ . It is thus clear that both  $\text{CO}_3$  and  $\text{SiO}_4$  groups can occur in solid solution in apatite, showing that such substitutions are not unreasonable. The evidence for Si substitution in defernite is still indirect and in part permissive. Nevertheless, we conclude that the data collectively suggest that some Si is essential to defernite.

### Channel contents

Liebich and Sarp concluded that the two kinds of zeolite-like channels each contain  $\text{H}_2\text{O}$  in one partially occupied site in each channel. This conclusion was in part based on the  $\text{H}_2\text{O}$  content that was solely determined by difference and is therefore subject to reinterpretation. Indeed, molecular water is shown to be absent by the infrared analysis of this study. Because the channels are akin to those in zeolites, it was natural to assume that occupied sites correspond to  $\text{H}_2\text{O}$ , but OH could also be inferred for such sites. As noted above, the formula derived from the structure determination has an excess of positive charge, and Peacor and Rouse (1988) showed that the channel atoms in holdawayite are Cl, with some substitution of OH.

Occupancy factors for the four channel atoms were refined using oxygen form factors. The total occupancy summed over all four fractional occupancies corresponds to 5.6 oxygen atoms. By analogy with holdawayite, the 2.02 Cl per cell could therefore preferentially occupy the channel sites. Because Cl has approximately twice the

scattering power of oxygen, the total observed scattering power is consistent with all of the Cl and some OH occupying such sites to provide charge balance for the remainder of the structure.

The standard errors for atom parameters of channel atoms are very high, especially for OH(9), OH(10) and OH(11). This is at least in part due to the very low occupancies and perhaps in part to some positional disorder over these ill-defined channel sites. Lastly, although standard errors for OH(8) are relatively low, in agreement with the fact that it accounts for well over half of the electron density of the channels, its anisotropic temperature factor  $U_{33}$ , parallel to the channel axis, is very large ( $0.35 \text{ \AA}^2$ ), apparently as an expression of positional disorder in that direction. Despite the relatively large uncertainties in the parameters of the channel atoms, their presence is qualitatively consistent with their identification as (Cl,OH) and their satisfaction of the charge imbalance for the remainder of the structure, as was true for holdawayite.

### Chemical formula

The analysis given by Sarp et al. (1980) for type defernite leads to the formula  $\text{Ca}_{24}(\text{CO}_3)_{6.49}(\text{SiO}_4)_{0.4}(\text{OH})_{31.26}\text{Cl}_{2.01} \cdot 7.99\text{H}_2\text{O}$  when normalized to 24 Ca. The data for defernite from the Kombat mine lead to the composition  $(\text{Ca}_{23.59}\text{Mn}_{0.35}\text{Mg}_{0.04}\text{Fe}_{0.02})_{\Sigma 24}(\text{CO}_3)_{7.53}(\text{SiO}_4)_{1.22}(\text{OH})_{25.94}\text{Cl}_{2.02}$ . The deficiency in C in defernite from both localities is compatible with some substitution of Si. However, the Si excess exceeds the C deficiency in the latter case by 0.75 atoms, resulting in some uncertainty about the proposed substitution. The analysis for C in type defernite was by electron microprobe and is therefore of low accuracy.

The Cl is assumed to be ordered in channel sites as opposed to its possible substitution for OH coordinating Ca. Given no substitution of Si, the ideal formula  $\text{Ca}_6(\text{CO}_3)_2(\text{OH},\text{Cl})_8$ ,  $Z = 4$ , requires 4 (Cl,OH) in channel sites per unit cell, or  $(\text{Cl}_{2.02}\text{OH}_{1.98})$ , given the observed Cl value. However, substitution of  $(\text{SiO}_4)^{-4}$  also contributes to balancing the overall charge of the framework,  $(\text{Ca}_6(\text{CO}_3)_2(\text{OH})_7)^+$ , so that the substitution in channels of (Cl,OH) is diminished in proportion to the substitution of  $\text{SiO}_4$ .

Lastly, there is direct evidence for the absence of  $\text{H}_2\text{O}$ , as described above. The channel atoms identified by Liebich and Sarp (1980) as  $\text{H}_2\text{O}$ , are apparently (Cl,OH) as described here. On the basis of these collective relations, the formula of defernite is  $\text{Ca}_6(\text{CO}_3)_{2-x}(\text{SiO}_4)_x(\text{OH})_7(\text{Cl,OH})_{1-2x}$ , where  $x \leq 0.5$ . In the case of type defernite,  $x = 0.1$ , whereas in defernite from the Kombat mine, the average measured value is 0.33. Although the maximum value for  $x$  has been observed to be approximately 0.3, its theoretical maximum is determined by a complete lack of (Cl,OH) in channel sites. We emphasize that the formula is a theoretically derived one. Application to the observed chemical analysis shows that, for example, if the value of  $x$  is chosen as defined by the Si content,

then the predicted values for (Cl + OH) and CO<sub>3</sub> are not identical to the observed values; nevertheless, the agreement is reasonable insofar as the inherent inaccuracies in CO<sub>3</sub> and H analytical values are concerned and serve to support the general form of the proposed substitution mechanisms.

By comparison, holdawayite from the Kombat mine has the ideal formula Mn<sub>6</sub>(CO<sub>3</sub>)<sub>2</sub>OH<sub>7</sub>(Cl,OH) (Peacor et al., 1988) with no substitution of Si having been observed although its presence was sought. Because both the holdawayite and defernite structures consist of the same modules stacked in alternative ways, the lack of analogous Si in holdawayite is surprising, but we have no explanation for the difference.

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