Crystal structure of franklinfurnaceite: A tri-dioctahedral zincosilicate intermediate between chlorite and mica*

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ABSTRACT

Franklinfurnaceite, ideally $Ca_2Fe^{3+}Mn_3^{2+}Mn^{3+}[Zn_2Si_2O_{10}](OH)_8$, has space group $C2$, with $a = 5.483(7)$, $b = 9.39(3)$, $c = 14.51(1)$ Å, $\beta = 97.04(8)°$, and $Z = 2$. The structure has been determined and refined to an unweighted R factor of 3.5%. It is a derivative of the structure of chlorite via substitution of Ca in sites that are ordinarily unoccupied between 2:1 layers and octahedral interlayers. Franklinfurnaceite represents the first example of (1) a type IIa structure (specifically type IIa-1), (2) a tri-dioctahedral chlorite and (3) a structure with Ca occupying octahedral sites between tetrahedral sheets and octahedral interlayers. The structure is intermediate between those of the brittle micas and chlorite, in that it has both interlayer cations and an octahedral interlayer. Alternating Zn and Si are ordered in the tetrahedral sheets.

The octahedral sheet of the 2:1 layer is trioctahedral with ordered Mn^{3+} and divalent cations. The interlayer dioctahedral sheet has ordered divalent cations (principally Mn^{2+}), Fe^{3+}, and vacancies, and it has a net negative charge. Optimum local charge balance is maintained by sandwiching of interlayer octahedral vacancies between opposing Ca sites, Mn^{2+} between Si^{4+} atoms, and Fe^{3+} between two Zn^{2+} atoms. The large tetrahedral Zn permits a large tetrahedral rotation angle, α, of 23.5°, thereby allowing the anions to form a nearly ideal, three-dimensional closest-packing sequence . . . CABABC . . . . Consequently, an octahedrally coordinated site suitable for Ca is formed, and a IIa structure results. Ca repels the H protons so that there is no interlayer hydrogen-bonding system. These structural features imply that Ca substitution in common rock-forming chlorites is unlikely and may occur only if the structure type is IIa, the interlayer is dioctahedral, and if substitutions of substantial Al and/or Fe^{3+} occur in tetrahedral sheets and in the octahedral sheet of the 2:1 layer.

INTRODUCTION

In 1950 N. V. Belov proposed that the vacant octahedral sites between the brucite-like and talc-like layers of the chlorite structure might accommodate Ca^{2+} ions, provided there were concomitant cation vacancies in the brucite-like sheet (Belov, 1950). Evidence from powder X-ray diffraction for the presence of "structural" Ca in some calciferous chlorites was reported (e.g., Makarov, 1971), but these techniques cannot distinguish between structural Ca and that due to contamination by small amounts of Ca-bearing materials, such as a mixed-layer chlorite-smectite component. (The observed CaO values in question are ≤ 5 wt%.) Thus, Brown and Bailey (1963) were unable to locate any Ca in the structure of Ca-bearing kämmererite and ascribed its presence to calcite contamination. Although Drits and Lazarenko (1967) showed minor essential Ca in the formula for donbassite, the presence of Ca was not verified by their structure analysis. Brindley (1961) considered Belov's hypothesis to be an "interesting suggestion" but one that "seems not yet to have any experimental confirmation."

We now report an experimental confirmation of Belov's hypothesis for the special case where there is a large, low-valence substituent for Si^{4+} (in this case Zn^{2+}) in the 2:1 (talc-like) layers of the chlorite structure. This occurs in the natural layer zincosilicate mineral franklinfurnaceite, recently reported from Franklin, New Jersey (Dunn et al., 1987).

Dunn et al. (1987), gave the ideal formula for franklinfurnaceite as $Ca_2Fe^{3+}Mn_3^{2+}Mn^{3+}Si_2Zn_2O_{10}(OH)_8$, in part on the basis of the initial results of a structure analysis, the details of which are reported here. The physical and optical data of Dunn et al. (1987) implied that franklin-

furnaceite is a phyllosilicate with a unit cell, space group, and diffraction intensities consistent with those of a monoclinic, one-layer chlorite. The 22 cations per cell, however, exceed the 20 required by a trioctahedral chlorite, implying that the structure is different from that of common chlorite. Moreover, the chemical analysis showed the presence of 4 Ca per cell, and Ca is generally assumed to be too large for substitution into the octahedral sites of either the 2:1 or interlayer octahedral sheets.

The structure analysis has verified that franklinfurnaceite is indeed isotypic with chlorite but with a unique combination of (1) a trioctahedral 2:1 layer combined with a dioctahedral interlayer, (2) ordering of Zn and Si in the tetrahedral sites, and (3) Ca occupying octahedral sites between the tetrahedral sheets and the interlayer sheets. This last feature establishes the structure as a link between those of micas and chlorites.
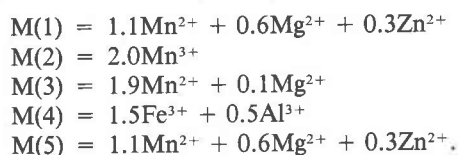
STRUCTURE SOLUTION AND REFINEMENT

The structure analysis was carried out using crystals from cotype specimen JEM 1093 from Franklin, New Jersey. The same material was studied by Dunn et al. (1987), who reported a chemical analysis, space group $C2$, Cm, or $C2/m$, and unit-cell parameters $a = 5.483(7)$ $b = 9.39(3)$, $c = 14.51(1)$Å, $\beta = 97.04(8)°$, $Z = 2$. Using the measured density of 3.66 g/cm³ and the water content of the type specimen (C6309), the calculated unit-cell contents for sample JEM 1093 are $Ca_{4.2}Mn_{5.9}Mg_{1.5}$-$Fe_{1.9}Al_{0.3}Zn_{4.6}Si_{3.9}O_{34.8}H_{15.2}$. As the equipoint ranks in $C2$, Cm, and $C2/m$ are multiples of two, the formula may be simplified to $Ca_2(Mn,Mg,Zn)_4(Fe,Al)Zn_2Si_2O_{10}(OH)_8$ with $Z = 2$. A microchemical test by Dunn et al. showed the Fe to be Fe^{3+}, and the results of the structure refinement are consistent with a $Mn^{2+}:Mn^{3+}$ ratio of 2:1.

The intensity data, consisting of 948 reflections with $\sin \theta \leq 0.460$, were obtained from an irregular cleavage fragment of approximate dimensions 0.22 × 0.31 × 0.19 mm using a computer-controlled Supper-Pace diffractometer system, graphite-monochromatized MoKα radiation, and scanning rates of 2° or 4°/min. The intensities were corrected for Lorentz-polarization and absorption effects ($\mu_l = 85$ cm^{-1}) and then averaged with the program SHELX-76 (Sheldrick, 1976) to remove symmetry-equivalent reflections ($R_{int} = 0.019$). The final data set contained 920 reflections, of which the 16 having $|F|_{obs} < 3\sigma(|F|_{obs})$ were considered to be unobserved. The structure refinement was carried out with SHELX-76, using neutral-atom scattering factors (Doyle and Turner, 1968), anomalous scattering corrections (Cromer and Liberman, 1970), and the reciprocal variances of the $|F|_{obs}$ as weights. Figures were drawn with ORTEP-II (Johnson, 1976).

The crystal structure was solved using the direct methods program MITHRIL (Gilmore, 1983), supplemented with electron-density and difference electron-density syntheses, which were interpreted in the light of the proposed isotypic relationship to chlorite. Intensity statistics produced by MITHRIL favored space group $C2/m$, which is the symmetry of the "ideal" chlorite structure IIa-1.

However, the chlorite-like model produced by MITHRIL in this space group required four Zn and four Si atoms to be disordered over a single 8-fold equipoint, and the model would not refine below a residual of 0.13. Likewise, an attempt to refine the model in Cm failed, as the residual would not decrease below 0.11 and the tetrahedral cations were ordered in an improbable fashion, i.e., into separate sheets of ZnO_4 and SiO_4 6-membered rings. A refinement in space group $C2$, which allows ordering of the tetrahedral cations into alternating sites in the same 6-ring, was successful, converging to a residual of 0.039 with isotropic temperature factors.

Inspection of the octahedral cation–oxygen bond distances, site-occupancy refinements, and bond-valence sum calculations (Brown and Wu, 1976) produced the following octahedral cation (M-site) ordering scheme:

$$M(1) = 1.1Mn^{2+} + 0.6Mg^{2+} + 0.3Zn^{2+}$$
$$M(2) = 2.0Mn^{3+}$$
$$M(3) = 1.9Mn^{2+} + 0.1Mg^{2+}$$
$$M(4) = 1.5Fe^{3+} + 0.5Al^{3+}$$
$$M(5) = 1.1Mn^{2+} + 0.6Mg^{2+} + 0.3Zn^{2+}.$$

With the cations so ordered, introduction of anisotropic temperature factors gave rise to residuals of 0.035 (unweighted) and 0.028 (weighted) for all 920 reflections and the same values for the 904 observed reflections. An attempt was then made to locate the H atoms of the hydroxyl groups (which had been identified as such by their bond-valence sums) from the final difference electron-density synthesis, but this was unsuccessful. The refined M-site occupancy factors, neglecting Zn and utilizing Fe and Al form factors for M(4) and Mn and Mg form factors for M(1) to M(3) and M(5), are $Mn_{1.673(5)}Mg_{0.327}$, $Mn_{2.032(1)}Mg_{-0.032}$, $Mn_{1.940(6)}Mg_{0.060}$, $Fe_{1.530(6)}Al_{0.470}$, and $Mn_{1.640(7)}Mg_{0.358}$ for M(1) to M(5), respectively.

Table 1 contains the refined positional and thermal parameters of franklinfurnaceite; Table 2,[1] the observed and calculated structure factors; Table 3, selected interatomic distances and angles; and Table 4, the empirical bond-valence sums. The standard deviations in Tables 1 and 3 are rather high in view of the very low value of the final unweighted residual (0.035). This is attributed to the $C2/m$ pseudosymmetry of the structure, which results in strong parameter interactions between atoms related by the pseudo–mirror plane. Correlation coefficients in such cases were typically in the range 0.6 to 0.8.

DESCRIPTION OF THE STRUCTURE

Overview of structure topology

The crystal structure (Figs. 1 and 2) is closely related to that of chlorite in that 2:1 layers alternate with octahedral interlayers. However, Ca atoms are ordered in octahedrally coordinated sites between the 2:1 layers and
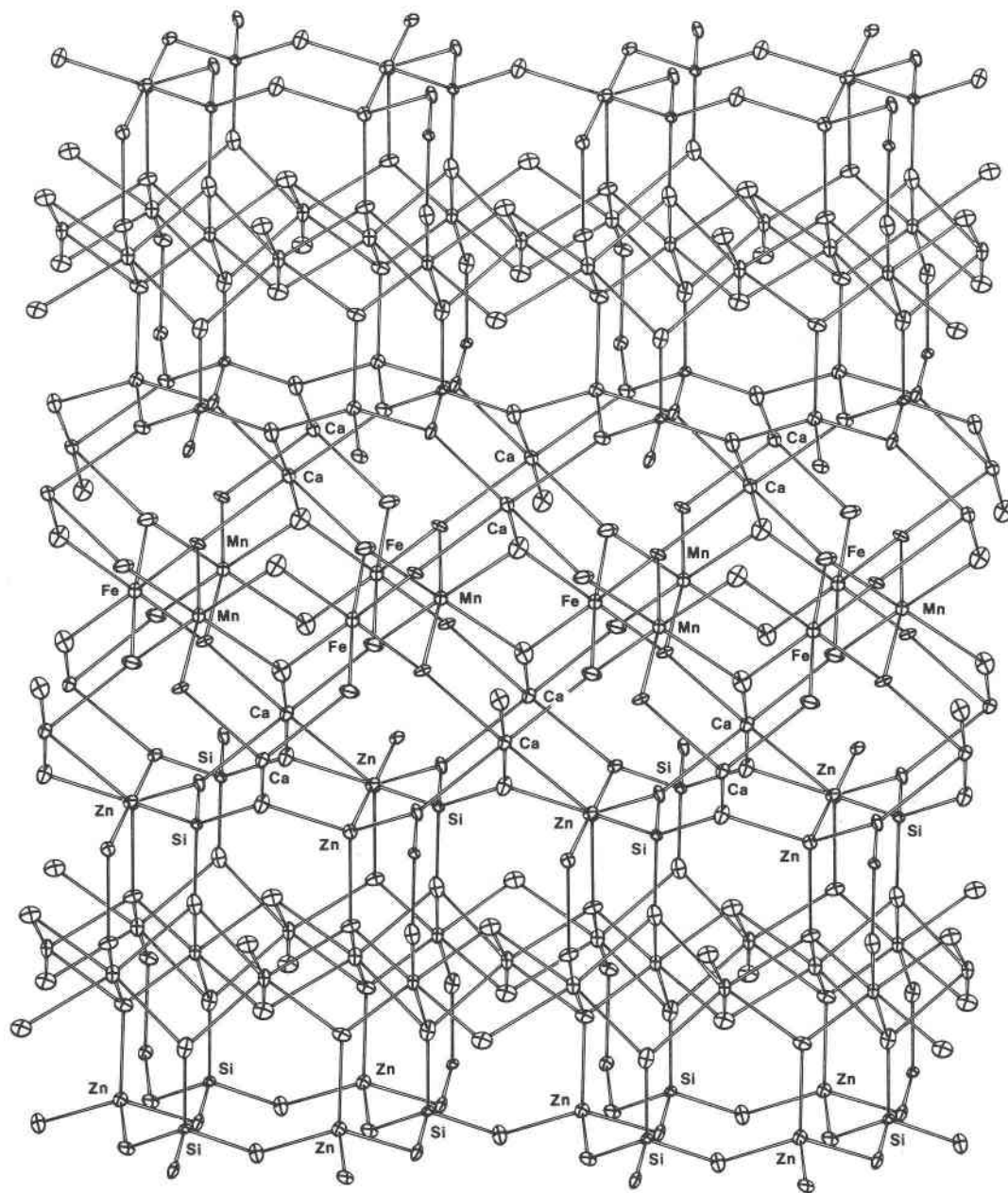
Fig. 1.   Projection of the franklinfurnaceite structure on a plane 17° from (100).

the octahedral interlayers, with Ca articulated to the bases of the tetrahedral 6-rings with a geometry similar to that for Ca in the brittle micas. The structure is thus also akin to that of the micas; in that sense, it represents a link between the mica and chlorite groups. For purposes of discussion, we shall consider it to be isotypic with chlorite, as it can be derived formally from chlorite as a stuffed derivative structure by the insertion of Ca between the 2:1 layers and the octahedral sheets, with concomitant substitutions and distortions described in detail below. In subsequent discussion, units of structure may be referred

to as having heights "above" or "below" other units. The sense of height refers to the translation **c** in such cases.

Considered as a chlorite, the structure has several unique features, not heretofore observed. These include the following: (1) The octahedral sheet of the 2:1 layer is trioctahedral, whereas the interlayer sheet is dioctahedral. (2) The structure is of the IIa-1 type in the terminology of Bailey and Brown (1962). (3) Ca occupies sites between the 2:1 layers and the octahedral interlayer. (4) The tetrahedrally coordinated cations (Zn and Si) are fully ordered. (5) Both octahedral sheets contain ordered di- and

trivalent cations. (6) No interlayer hydrogen-bonding system can be discerned. All of these features are interrelated and a consequence of the $+2$ charge of the tetrahedrally coordinated Zn. No other chlorite has substantial tetrahedral Zn, although the species baileychlore has been described by Rule and Radke (1988) as a trioctahedral chlorite in which Zn is the dominant octahedral cation.

Octahedral sheets

The octahedral sheet within the 2:1 layer (Fig. 3) is trioctahedral and is occupied by the cations M(1), M(2), and M(3). All Mn^{3+} is ordered in M(2) and although there is preferential substitution of Mg and Zn into M(1), both M(1) and M(3) are occupied entirely by divalent cations, chiefly Mn^{2+}. The M(2) octahedron is severely distorted with two *trans* ligands [O(1)] at long bond distances (2.29 Å) relative to those in the equatorial plane (2×1.88 and 2×1.98 Å). This is the usual kind of distortion expected for octahedrally coordinated Mn^{3+} due to the Jahn-Teller effect.

Atom O(2) is coordinated (e.g., Table 4) to M(1), M(2), and M(3) of the 2:1 octahedral sheet and also serves as an apical tetrahedral oxygen for the Zn tetrahedron. Because of the low charge on the tetrahedrally coordinated Zn^{2+}, the apical oxygen O(2) would be undersaturated (1.5 v.u.) with respect to positive charge if M(1), M(2), and M(3) contained only cations of charge $2+$. Even occupancy of M(2) by trivalent Mn^{3+} is sufficient only to raise the sum to 1.67 v.u. However, the Jahn-Teller distortion leads, in part, to a very short M(2)–O(2) bond, thereby increasing the empirical bond strength (Brown and Wu, 1976) to a reasonable 2.08 v.u. for O(2), as shown in Table 4. The unusual compositional features of franklinfurnaceite (Mn^{3+} in the octahedral sheet of the 2:1 layer; Zn^{2+} in the tetrahedral sheets) thus compensate for one another.

The interlayer (dioctahedral) sheet (Fig. 4) has three different octahedral sites. These are (1) M(5), which is occupied by Mn^{2+} and lesser amounts of Mg and Zn; (2)
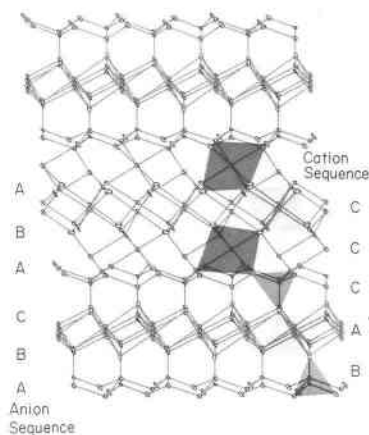

Fig. 2. Projection of the franklinfurnaceite structure on a plane 5° from (010), showing the anion- and cation-stacking sequences.

M(4), which is occupied by trivalent cations ($1.5Fe^{3+}$ + $0.5Al$) and (3) vacant sites, which are sandwiched between occupied Ca sites. The Ca occupies sites (Figs. 4 and 5) between the plane of the tetrahedron basal oxygens and the interlayer that are vacant in ideal chlorite. There are two Ca atoms for each vacant interlayer octahedral site, explaining the excess in the total of 22 cations per cell over the 20 of an ideal chlorite, in partial compensation for the divalent Zn in tetrahedral coordination. The distribution of occupied sites in the interlayer minimizes charge repulsion with tetrahedral cations. Although interlayer cations project directly onto Si and Zn in the adjacent tetrahedral sheet (*a*-type superposition), the divalent cations in M(5) superimpose on Si^{4+}, and trivalent cations superimpose on Zn^{2+} in accord with similar observations by Rule and Bailey (1987). The sandwiching of the octahedral vacancies between Ca atoms likewise minimizes cation-cation repulsion.

The oxygen atoms O(3), O(4), and O(5) that form the bases of tetrahedra are severely underbonded as shown

TABLE 1. Atomic coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$) for franklinfurnaceite

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca	4462(3)	0087(6)	3309(1)	7(1)	8(1)	9(1)	1(1)	−1(1)	0(1)	0.008
M(1)	0	0000	0	5(1)	6(1)	13(1)	0	0(1)	0	0.008
M(2)	0	3230(5)	0	7(1)	5(1)	10(1)	0	0(1)	0	0.008
M(3)	0	6707(6)	0	5(1)	7(1)	13(1)	0	−2(1)	0	0.008
M(4)	0	1757(6)	½	6(1)	8(1)	10(1)	0	−2(1)	0	0.008
M(5)	0	8412(5)	½	7(2)	7(2)	9(2)	0	−1(1)	0	0.008
Zn	9041(3)	1742(5)	1993(1)	7(1)	8(1)	9(1)	−1(1)	−1(1)	0(1)	0.008
Si	9066(7)	8404(6)	2043(2)	5(2)	6(2)	4(2)	−1(1)	−1(1)	1(1)	0.005
O(1)	3726(17)	3381(13)	0907(7)	6(4)	10(5)	18(5)	−2(4)	2(3)	1(3)	0.011
O(2)	3617(13)	6779(16)	0661(5)	5(3)	15(4)	6(3)	2(5)	−3(3)	−3(4)	0.009
O(3)	1382(14)	3309(11)	2440(7)	10(4)	6(4)	11(4)	−3(3)	−2(3)	0(4)	0.009
O(4)	0820(14)	7054(10)	2446(6)	9(4)	11(5)	7(4)	3(3)	1(3)	7(3)	0.009
O(5)	0439(12)	−0110(11)	2442(5)	9(3)	9(5)	13(3)	2(4)	−7(3)	−3(4)	0.010
OH(1)	2764(15)	1861(16)	4184(6)	19(4)	18(6)	8(4)	−2(5)	2(3)	4(5)	0.015
OH(2)	3021(16)	8199(14)	4190(7)	6(4)	11(5)	5(4)	3(5)	0(3)	−2(4)	0.008
OH(3)	3711(14)	−0190(11)	0701(5)	7(3)	19(6)	10(4)	0(4)	−9(3)	−1(3)	0.012
OH(4)	8441(13)	0154(17)	4167(5)	6(3)	16(5)	16(4)	−2(5)	−8(3)	5(5)	0.013

Note: Temperature factors are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \cdots + 2hka^*b^*U_{12})]$. Esd's are in parentheses.

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

Octahedral sites			
Ca–OH(1)	2.355(14)	M(1)–O(2)	2.113(13) ×2
–OH(4)	2.376(7)	–OH(3)	2.167(8) ×2
–OH(2)	2.377(13)	–O(1)	2.181(12) ×2
–O(4)	2.401(11)	Mean	2.154
–O(5)	2.408(7)		
–O(3)	2.411(11)		
Mean	2.388		
M(2)–O(2)	1.879(13) ×2	M(3)–O(2)	2.095(7) ×2
–OH(3)	1.978(11) ×2	–OH(3)	2.210(11) ×2
–O(1)	2.294(9) ×2	–O(1)	2.217(13) ×2
Mean	2.050	Mean	2.174
M(4)–OH(2)	2.020(12) ×2	M(5)–OH(4)	2.148(14) ×2
–OH(1)	2.037(9) ×2	–OH(2)	2.155(10) ×2
–OH(4)	2.050(14) ×2	–OH(1)	2.161(12) ×2
Mean	2.036	Mean	2.155
Tetrahedral sites			
Zn–O(2)	1.918(8)	O(2)–Zn–O(3)	107.8(5)
–O(5)	1.978(12)	O(2)–Zn–O(4)	109.2(3)
–O(4)	1.980(9)	O(3)–Zn–O(5)	109.4(4)
–O(3)	2.007(10)	O(2)–Zn–O(5)	110.0(5)
Mean	1.971	O(3)–Zn–O(4)	110.2(4)
		O(4)–Zn–O(5)	110.2(4)
		Mean	109.5
Si–O(1)	1.636(11)	O(4)–Si–O(5)	107.6(5)
–O(3)	1.647(10)	O(3)–Si–O(5)	108.1(5)
–O(4)	1.654(10)	O(1)–Si–O(4)	109.6(6)
–O(5)	1.656(11)	O(3)–Si–O(4)	109.9(5)
Mean	1.648	O(1)–Si–O(5)	110.7(6)
		O(1)–Si–O(3)	110.8(5)
		Mean	109.5
Si–O(3)–Zn	119.3(6)		
Si–O(4)–Zn	120.0(5)		
Si–O(5)–Zn	119.0(4)		
OH–O and OH–OH ≤ 3.0 Å			
OH(3)–OH(3)	2.62(2)	OH(3)–O(1)	2.87(1)
OH(1)–OH(2)	2.75(2)	OH(1)–OH(2)	2.89(1)
OH(4)–OH(4)	2.78(1)	OH(1)–O(3)	2.89(1)
OH(3)–O(2)	2.85(2)	OH(3)–O(2)	2.89(1)
OH(1)–OH(4)	2.86(2)	OH(2)–OH(2)	3.00(2)
OH(4)–O(5)	2.86(1)	OH(1)–OH(4)	3.02(2)
OH(2)–OH(4)	2.87(2)	OH(3)–O(1)	3.04(1)
OH(2)–O(4)	2.87(1)		
O–O ≤ 3.0 Å			
O(2)–O(2)	2.59(2)	O(1)–O(4)	2.69(1)
O(3)–O(5)	2.67(1)	O(3)–O(4)	2.70(1)
O(4)–O(5)	2.67(2)	O(1)–O(5)	2.71(1)
O(1)–O(3)	2.70(1)	O(1)–O(2)	2.89(1)
Cation-Cation ≤ 3.2 Å			
M(1)–M(2)	3.033(11)	M(4)–M(5)	3.141(5)
M(1)–M(3)	3.092(11)	M(4)–M(5)	3.151(5)
M(2)–M(3)	3.092(5)	Zn–Si	3.151(6)
Zn–Si	3.136(12)	Zn–Si	3.160(6)
M(4)–M(5)	3.141(12)	M(1)–M(3)	3.176(5)

Note: Esd's are in parentheses. Octahedral site occupancies are M(1) and M(5) = (Mn$_{1.1}^{2+}$Mg$_{0.6}$Zn$_{0.3}$), M(2) = 2 (Mn^{3+}), M(3) = (Mn$_{1.9}^{2+}$Mg$_{0.1}$), and M(4) = (Fe$_{1.5}^{3+}$Al$_{0.5}$).

in Table 4. In contrast, the hydroxyl ions OH(1), OH(2), and OH(4) in the adjacent octahedral interlayer are slightly overbonded, suggestive of hydrogen-bond interactions between the oxygen and hydroxyl anions, as is usual in phyllosilicates. However, as noted above, the positions of the H atoms could not be found experimentally, as they might be if a well-defined system of hydrogen bonds existed. The shortest OH-O interlayer approaches [OH(1)–

O(3) = 2.89, OH(2)–O(4) = 2.87, OH(4)–O(5) = 2.86 Å] are between the only atoms that can be involved in a hydrogen-bonding system. Because Ca occupies sites between the OH and O planes, it is likely that the H protons are repelled by the Ca ions, so that the shortest OH-O distances are not part of a hydrogen-bonding system. In addition, it is probable that the protons are repelled by the M(4) and M(5) cations of the interlayer. These relations imply that the protons are directed away from their normal basal oxygen acceptors and into the interlayer sheet toward the vacancies, resulting in the absence of a hydrogen-bonding system and further accentuating the role played by Ca in bonding the 2:1 layer with the interlayer.

Oxygen closest packing and tetrahedron rotation

Bailey (1984) has summarized the relations between the dimensions of the octahedral sheet and the rotation angle, α, which reduces the lateral dimensions of the tetrahedral sheet. Substitution of a larger ion (e.g., Al^{3+} or Zn^{2+}) for Si^{4+} increases the dimensions of the tetrahedral sheet. The tetrahedral vertices must articulate to the octahedral sheet and, if the radii of the octahedral cations cause the dimensions of the octahedral sheet to be smaller than those of the tetrahedral sheet, then in-phase rotation of tetrahedra may reduce the "misfit" and permit articulation.

The tetrahedral sheet in franklinfurnaceite (Fig. 5) consists of alternating Zn and Si tetrahedra. The average Zn–O distance (1.97Å) is similar to other tetrahedral Zn–O distances, but the average Si–O distance (1.65 Å) is larger than is typical of phyllosilicates. During the final stages of refinement, the occupancy factors for the Si and Zn sites were allowed to vary, with both Si and Zn form factors assigned to each site. The occupancy factor for the Si site refined to 1.03 Si and −0.03 Zn, implying that no Zn occupies the site. Indeed, the small variation from 1.0 is consistent with occupancy only by Si. Because the chemical analysis indicated the presence of sufficient Si (3.9) per cell to provide for full occupancy of the Si site by Si within analytical error and because the occupancy factor for the tetrahedral Zn site [1.0030(4) Zn] was consistent with occupancy only by Zn, the data imply complete ordering of Si and Zn. The large average Si–O distance can therefore not be explained as a consequence of (Si,Zn) solid solution.

The unusual role of Zn as a tetrahedrally coordinated cation sharing bridging oxygen atoms with Si might conceivably lead to anomalous Si–O bond parameters, but Liebau (1985) has found no such relationship in the effects of non-Si tetrahedral atoms on Si–O distances. However, Hill and Gibbs (1979) showed that T–O distances increase with decreasing T–O–T angles. In franklinfurnaceite, the large tetrahedral rotation angle (see below) results in unusually small Si–O–Zn angles of 119.0 to 120.0°. As shown in Table 3, the three bridging oxygen atoms O(3), O(4), and O(5) have the largest Si–O and

TABLE 4. Empirical bond valence sums (v.u.) for franklinfurnaceite

	Ca	M(1)	M(2)	M(3)	M(4)	M(5)	Zn	Si	Σv
O(1)		0.31	0.24	0.31				0.97	1.83
		0.31	0.24	0.31					
O(2)		0.37	0.72	0.42			0.57		2.08
		0.37	0.72	0.42					
O(3)	0.28						0.43	0.93	1.64
O(4)	0.29						0.47	0.92	1.68
O(5)	0.29						0.47	0.92	1.68
OH(1)	0.32				0.44	0.32			1.08
					0.44	0.32			
OH(2)	0.31				0.46	0.33			1.10
					0.46	0.33			
OH(3)		0.32	0.54	0.31					1.17
		0.32	0.54	0.31					
OH(4)	0.31				0.43	0.33			1.07
					0.43	0.33			
Σv	1.80	2.00	3.00	2.08	2.66	1.96	1.94	3.74	

Note: Bond valences for M(1), M(4), and M(5) are calculated from weighted averages for Mn^{2+}, Mg, Zn, Fe^{3+}, and Al.

Zn–O distances for each tetrahedron, in agreement with Hill and Gibbs.

The unusually long bond distances from Si to O(3), O(4), and O(5) might be expected to be coupled with and compensated by a shorter bond for the apical oxygen atom O(1). However, the Si–O(1) distance (1.636 Å) is not unusually short. The latter distance apparently results as an adjustment to accommodate articulation of the tetrahedral and octahedral sheets. The Zn tetrahedra are flattened ($\tau = 109.0°$, relative to the ideal value of 109°47′), and the Si tetrahedra are elongate ($\tau = 110.4°$), as is the case in phyllosilicates with ordered Al and Si. The long Zn–O apical bond and the short Si–O(1) bond result in an unusually large corrugation ($\Delta z = 0.325$ Å) of the articulated anion plane. A shorter Si–O(1) bond would result in even longer bonds from O(1) to M(1)–M(3), and these are already the longest within each octahedron. The result is therefore a compromise that avoids extremes in shapes and sizes of the tetrahedral and octahedra.

Because of the large radius of Zn^{2+} [0.74 Å according to Shannon (1976)], the average tetrahedral cation radius is among the largest in layer silicates, with only that of cronstedtite being nearly as large. The resulting misfit is compensated partially by the radii of the cations M(1), M(2), and M(3), which also are unusually large for a chlorite or mica structure. (The Mn^{2+} and Mn^{3+} are the dominant cations in these sites.) In general, it is not possible to articulate the conventional Si,Al tetrahedral sheet to such an octahedral sheet, as the large octahedral cation radii require that the tetrahedral sheet exceed its maximum permissible dimensions, corresponding to $\alpha = 0°$. As a result, layer silicates with octahedral Mn tend to have tetrahedral sheets with unusual features that compensate for the misfit, as in pyrosmalite (Takéuchi et al., 1969), caryopilite, and a variety of other minerals (Guggenheim et al., 1982). In contrast, however, the large average tetrahedral cation radius in franklinfurnaceite causes the lateral dimensions of the undistorted tetrahedral sheet to be greater than those of the large octahedral sheet.

As a result, rotation of tetrahedra by $\alpha = 23.5°$ occurs. This value is among the largest in all phyllosilicates and underscores the effect of tetrahedral cation radius on the geometry of articulated sheets.

There are two limiting geometries for tetrahedral sheets corresponding to rotations (α) of 0° and 30°. [See Guggenheim (1984) for diagrams of relevant geometries.] The relationship of the tetrahedral rotations to closest packing of the anions has been reviewed by Zvyagin (1967). For $\alpha = 0°$, the 6-rings are hexagonal. Coplanar basal oxygen atoms occupy sites with a two-dimensional *geometry*; however, alternate rows of oxygen atoms have vacancies at alternate sites so that such planes of anions are not closest-packed, sensu strictu. Thus one-quarter of the oxygen atoms are missing as compared with a complete closest-packed sheet of oxygens, with these sites corresponding, in projection, to the centers of the 6-rings. However, a rotation of $\alpha = +30°$ or $-30°$ (defined as toward or away from, respectively, the octahedral cations of the 2:1 layer) is defined by a shift of the oxygen atoms to positions that reduce the symmetry of the 6-rings to ditrigonal. The arrangement of oxygen atoms in the basal plane of tetrahedra becomes ideally closest-packed, with no anion vacancies. The center of a 6-ring corresponds, in projection, to the center of a triad of basal oxygen atoms. Each of the oxygen atoms is an alternate bridging site of a 6-ring.

Tetrahedral sheets with $\alpha = 0°$ have a geometry preventing three-dimensional closest-packing of opposing basal planes if adjacent sheets are constrained so that vacancies superimpose, as in a mica structure. Basal oxygen atoms directly oppose one another, rather than being in a closest-packed geometry, producing large interlayer separations of approximately of 3.2 Å (Bailey, 1984). However, the oxygen-vacancy-free, ideal anion packing that corresponds to $\alpha = 30°$ permits three-dimensional closest packing.

The franklinfurnaceite structure provides a unique opportunity for analyzing this relationship, which is ordi-
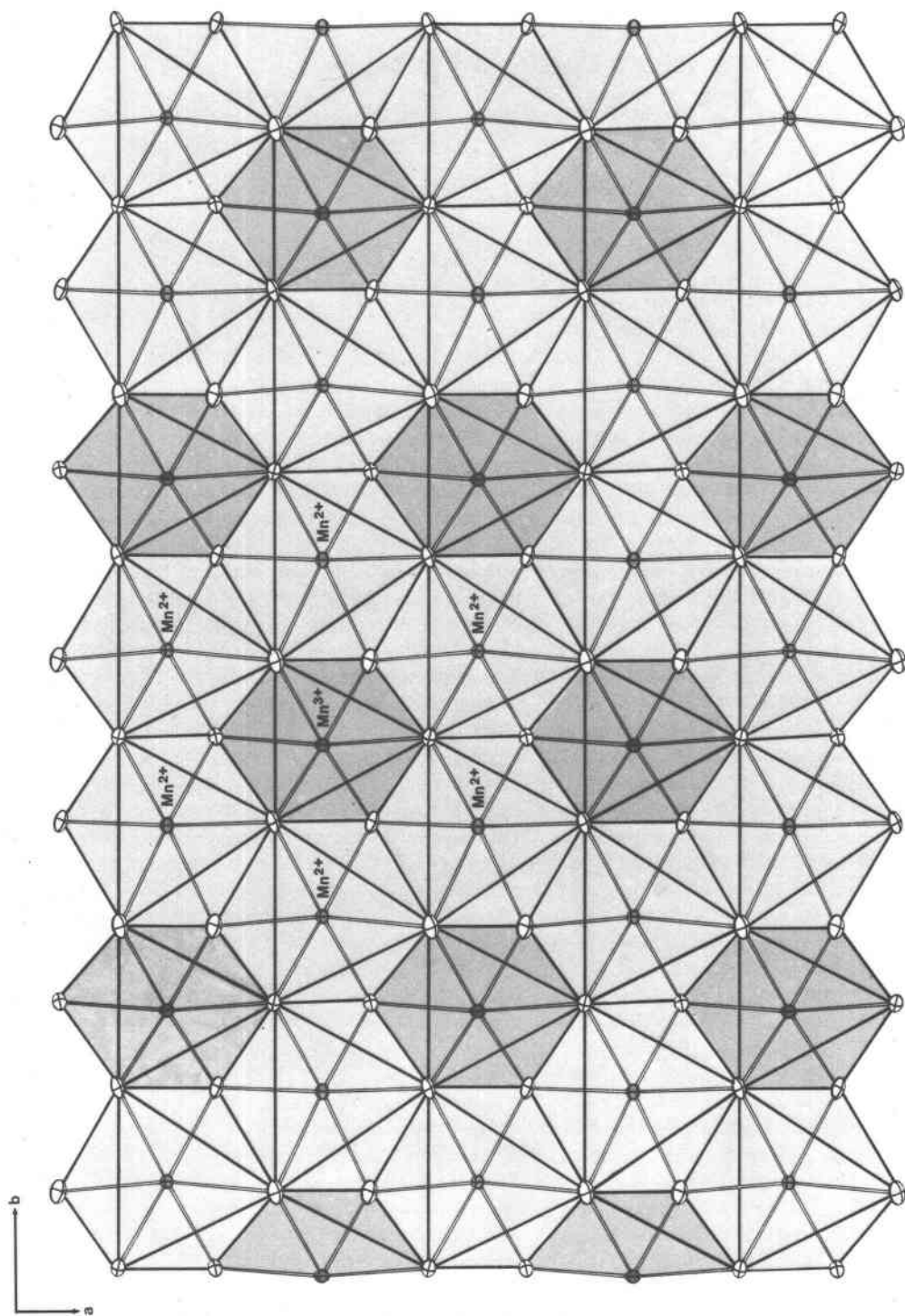
Fig. 3.   Projection of the octahedral sheet of the 2:1 layer of franklinfurnaceite on (001), showing the ordering of $Mn^{2+}(O,OH)_6$ and $Mn^{3+}(O,OH)_6$ octahedra. The Mn^{2+} sites contain minor Mg and Zn.
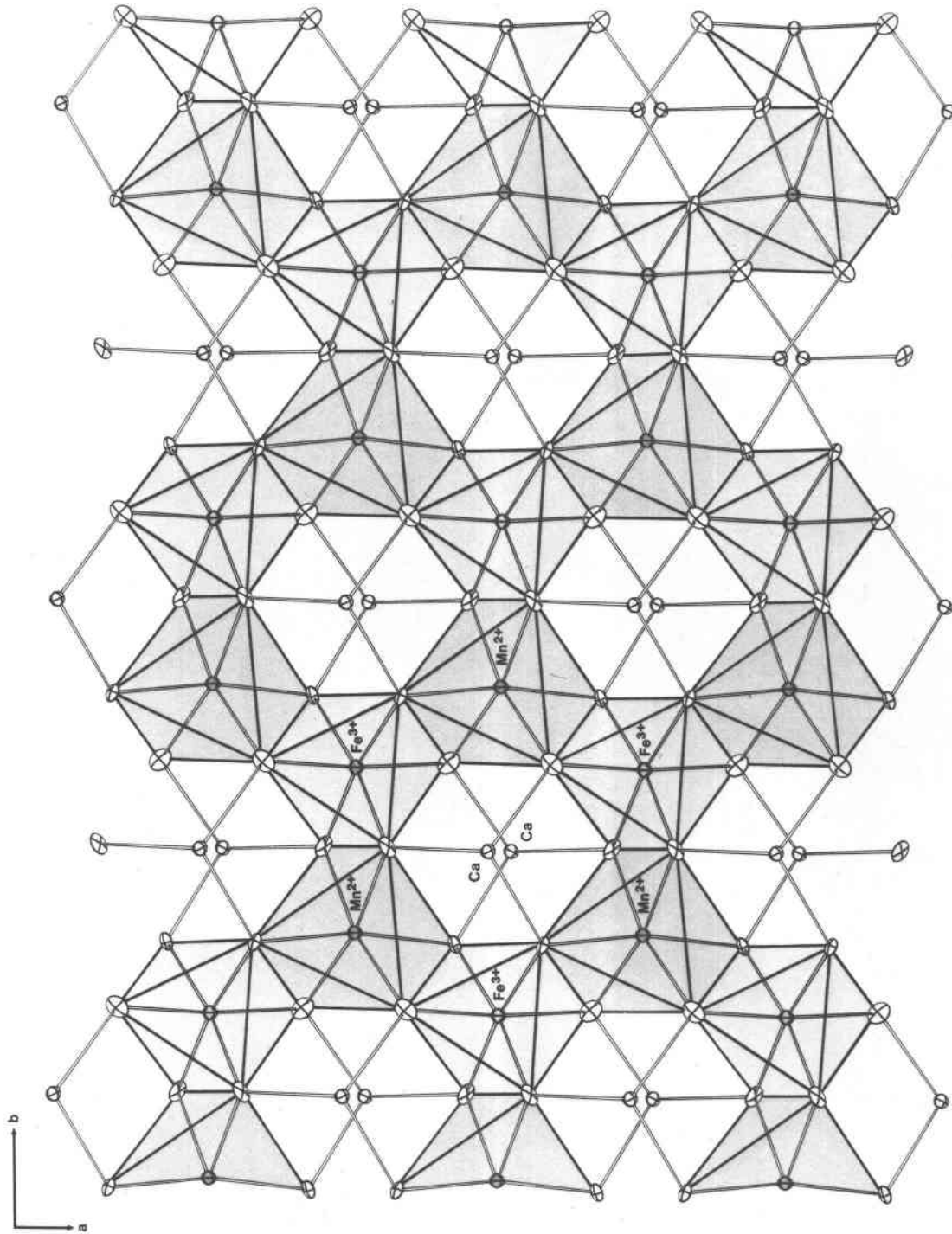
Fig. 4. Projection of the dioctahedral interlayer of franklinfurnaceite on a plane rotated by 5° from (001), showing the rings of alternating $Mn^{2+}(OH)_6$ and $Fe^{3+}(OH)_6$ octahedra and the Ca atoms situated above and below vacant octahedral sites. Only three of the six Ca–O bonds are shown. The Mn^{2+} sites contain minor Mg and Zn and the Fe^{3+} sites contain minor Al.
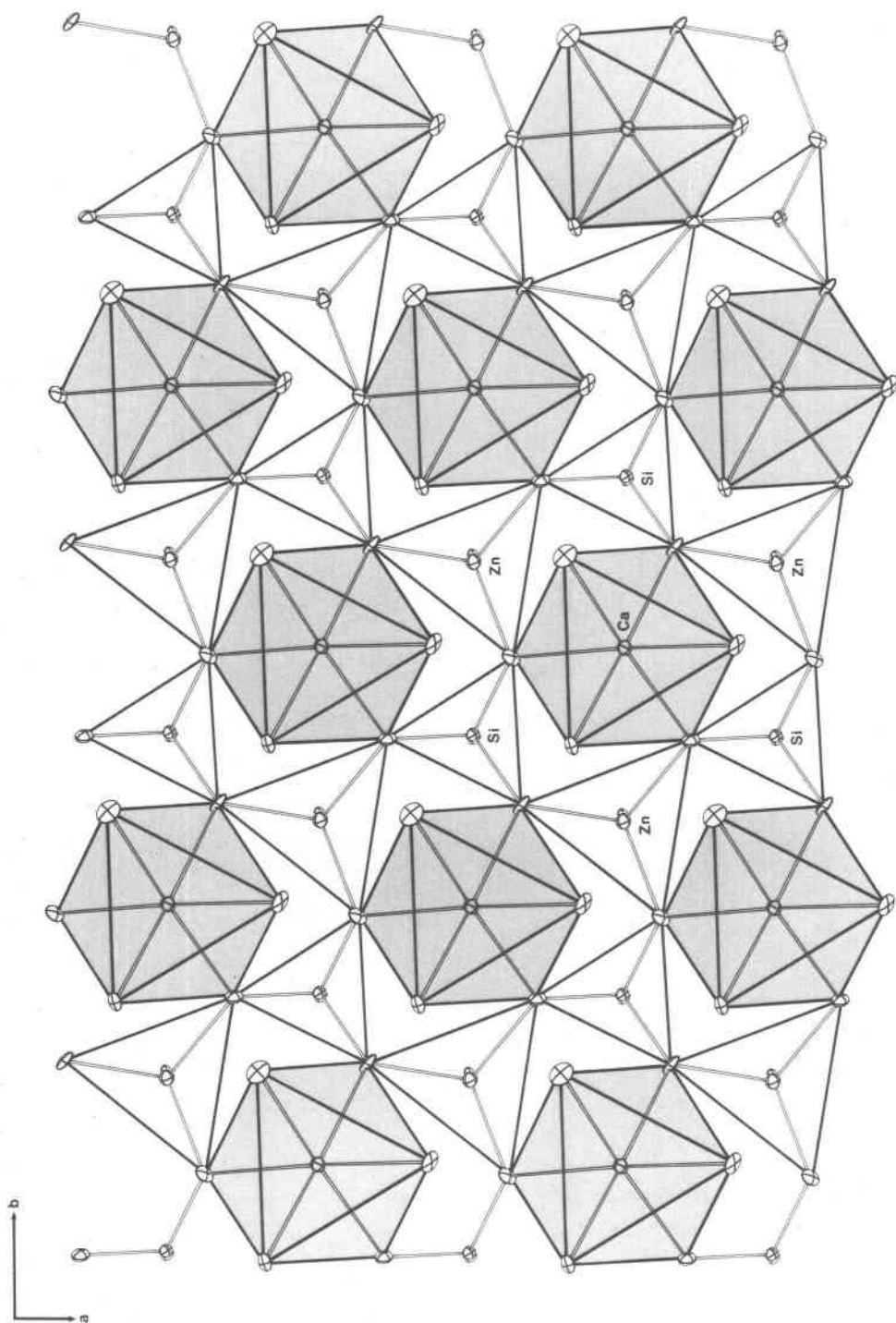
Fig. 5. Projection of the upper tetrahedral sheet of the 2:1 layer of franklinfurnaceite on (001), showing the ditrigonal 6-rings of alternating ZnO$_4$ and SiO$_4$ tetrahedra and the overlying Ca(O,OH)$_6$ octahedra.

narily obscured by distortions in chlorites or micas. Starting with the anion plane at $z = 0.07$, the sequence of anion planes (Fig. 2) is CABABCABCBC . . . . The symbols for planes in the second cell (planes 7–12) are different than those for the first unit cell (planes 1–6) even though they are translation-equivalent, because the angle α causes **c** to be offset along **a** by $a/3$ (the closest-packing nomenclature is referred to orthohexagonal axes). The translation $a/3$ causes the sites CAB of the first cell to be labeled ABC, respectively, in the second cell, BCA in the third cell, and so on. The sequence of both cations and anions is given in Table 5. The franklinfurnaceite structure can therefore be considered to be three-dimensionally closest-packed, with only small distortions relative to ideal geometry. There is a unit of six cubic closest-packed anion planes centered about the origin. The coordination polyhedra of all cations, including Ca, are well-defined octahedra or tetrahedra in accordance with the requirements of such packing, vis-a-vis the larger coordination numbers of cations such as K^+ and Na^+ in micas, where α is generally small. The anion closest-packed planes therefore can articulate closely to one another along **c**, as anions of the interlayer fit neatly into "valleys" in the centers of triangles of anions in layers below. As a result, the separation between the plane of basal tetrahedral oxygen atoms and the bottom of the octahedral interlayer (Ca is between these planes as shown in Fig. 5) is an unusually small 2.502 Å, as opposed to typical values of approximately 3.2 Å (Bailey, 1984) in micas and 2.8 Å in brittle micas (Guggenheim, 1984). Electrostatic attraction between Ca and coordinating oxygens produces, in part, the small interlayer separation. The Ca is essential to the structure because it links together two negatively charged units, the 2:1 layer and the interlayer. In true chlorites the interlayer has a positive charge.

DISCUSSION

Relation of the IIa structure type to Ca occupancy

Bailey and Brown (1962) showed that chlorites can be classified as type I if the octahedra in the 2:1 layer and interlayer have the same slant, or type II if the slants are opposite. These may, in turn, be subdivided into layer-interlayer superpositions of types a or b. In type a structures, octahedrally coordinated cations of the interlayer project along c^* onto tetrahedral cations in the layer immediately below; in type b structures, they do not. Lastly, the position of the 2:1 layer above the interlayer is further specified by numbers 1–6. The specific value is defined by one of the six possible positions that the center of the 6-rings of the bottom tetrahedral sheet may take relative to the upper anion plane of the interlayer. In this nomenclature, franklinfurnaceite has the type IIa-1 structure (the opposite slants of octahedra can be seen in Fig. 2). We also note that the differences in types may be ascribed to differences in the sequences of closest packing, for which franklinfurnaceite has only one of several possible sequences.

Bailey and Brown (1962) and Shirozu and Bailey (1965)

TABLE 5. Anion and cation positions in closest-packing terminology for one-half cell ($z = 0$ to 0.5)

Level (z)	Symbol		Atoms
0.00		A	M(1), M(2), M(3)
0.07	C		O(1), O(2), OH(3)
0.20		C	Si, Zn
0.24	A		O(3), O(4), O(5)
0.33		C	Ca
0.42	B		OH(1), OH(2), OH(4)
0.50		C	M(4), M(5), (vacancies)

concluded that repulsion between superimposed octahedral and tetrahedral cations should cause the Ia and IIa structures to be less stable than Ib and IIb structures. In addition, Bailey and Brown (1962) showed that these relations are compatible with the frequency of occurrences of each form, with IIb being common, Ib uncommon, Ia rare, and IIa unknown. There is now an exception to this rule, as franklinfurnaceite is the first example of a IIa structure.

The type of structural unit (IIa) in franklinfurnaceite is determined by the tetrahedral rotations in the tetrahedral sheet. This rotation causes the three basal oxygen atoms, O(3), O(4), and O(5), to form a triangle of anions suitable for coordinating Ca, which occupies a site that projects along c^* onto the center of the trigonally distorted 6-ring (Fig. 5). In order for the Ca to be octahedrally coordinated, the three ligands forming the upper triangular face [OH(1), OH(2), and OH(4)] at the base of the interlayer sheet must have positions that are uniquely defined; i.e., the positions of all anions in the lower plane of anions of the interlayer are determined relative to the position of the Ca atom. Using closest-packing nomenclature, if those anions are designated B, and Ca atoms C, then octahedral cations in the interlayer can be A or C (Table 5). However, in order to maximize Ca-cation distances and to minimize the repulsions, only positions of type C may be occupied by octahedrally coordinated interlayer cations. These conditions occur because interlayer octahedral vacancies (C) superimpose directly over Ca atoms (C). This defines the structure as superposition type a. In addition, the positions of the atoms in the upper plane of anions of the dioctahedral interlayer must be of type A in order to complete octahedral coordination, defining the slant of the octahedra as opposite to those in the 2:1 layer. The structure is therefore required to be of type IIa by the restrictions precisely controlled by the presence of Ca.

However, there are two possible IIa structures, each having the same cation positions as given in Table 5, but differing in the rotation direction and thus in the notation of anion closest-packing. Starting with the octahedral cation plane at $z = 0$ and arbitrarily labeling it as a plane of type A, the anion layer at 0.07 can be labeled as B or C and is arbitrarily labeled as C. Because these anions serve as lower vertices of Zn and Si tetrahedra, the Zn and Si atoms must also be of type C. Anions at $z = 0.24$ may then be of type A or B. Positions of type A (as is the case in franklinfurnaceite) define tetrahedron rotations of

$+23.5°$. Alternating, bridging, basal oxygen atoms of a given 6-ring (Fig. 5) appear to have rotated to positions that lie directly above cations (A) in the adjacent octahedral sheet of the 2:1 layer and away from the projected positions of the OH groups (B) of the overlying octahedral interlayer at $z = 0.42$. If the bases of the tetrahedra are defined instead by B anion positions, however, the tetrahedra appear to have rotated by $-23.5°$, to form a ring of ditrigonal symmetry identical to that for a rotation of $+23.5°$. The bridging oxygen atoms in this case appear to have rotated away from cations in the underlying 2:1 layer (A), however, and toward the projected positions of OH groups (B) in the adjacent interlayer. Applying the relations described in the preceding paragraph to develop the remainder of the structure leads to two structure possibilities, both of type II*a*, and having (ideally) identical cation positions but different closest-packed anion sequences. They are II*a*-1 structures with opposite directions of tetrahedral rotation.

In all other chlorites and 1:1 structures in which O and OH surfaces are in contact and for which good refinements are available, tetrahedral rotations cause basal oxygen atoms to shift toward the nearest OH group of the adjacent interlayer. This minimizes O–OH distances and promotes formation of a well-defined set of hydrogen bonds that compensates for charge imbalances, as described above. This direction of shift may also be toward underlying cations in some chlorite-structure types.

The only other one-layer chlorite in which adjacent 2:1 layers have the mica configuration is I*a*-2. This has the same structure as II*a*-1 except that the upper and lower OH planes of the interlayer are interchanged. Consequently, in normal projection, the lower OH ions superimpose on octahedral cations in the 2:1 sheet for the I*a*-2 structure. Upon tetrahedral rotation, the basal oxygens can shift in response to both attractive forces at an intermediate z level. This should be a more stable structure for a normal chlorite than II*a*-1, in which the two attractive forces compete for the basal oxygen. In franklinfurnaceite the hydrogen-bonding system is inoperative, and the $+23.5°$ rotation is the only possible choice in the II*a*-1 structure. The I*a*-2 structure is not adopted because the lower OH ions of the interlayer sterically impede such a large rotation and resultant closest-packing of the anions.

Essential Ca in common rock-forming chlorites

The critical factor in the introduction of Ca into the chlorite structure is that it requires octahedral coordination. As shown above, such coordination requires a large rotation angle, α. This in turn defines the octahedral interlayer as dioctahedral with vacant sites superimposing on Ca atoms and occupied sites superimposing on tetrahedral sites, in order to minimize repulsion between Ca and interlayer cations (i.e., the structure must locally be of type *a*). Charges on tetrahedral and octahedral cations are in turn restricted because repulsion between superimposed interlayer octahedral and tetrahedral cations must be minimized. As implied by the superpositions of

Fe^{3+} on Zn^{2+} and Mn^{2+} on Si^{4+} in franklinfurnaceite and assuming that at least 50% of the tetrahedral sites are occupied by Al (see below for further requirements for the composition of the tetrahedral sheet), only a divalent cation (say Mg) may superimpose on Si^{4+} and either a divalent or trivalent cation on Al^{3+}.

The required large tetrahedral rotation causes the lateral dimensions of the tetrahedral sheet to decrease. This shrinkage has consequences for the misfit between, and articulation of the tetrahedral and octahedral sheets within, the 2:1 layer. Comparison of the relative dimensions of tetrahedral and octahedral sheets in micas (Bailey, 1984) and in brittle micas (Guggenheim, 1984) shows that, among micas with common cations such as Mg, Al, etc., dioctahedral, Al-containing sheets of 2:1 layers have minimum dimensions. However, misfit is minimized and articulation of the tetrahedral and octahedral sheets occurs when the tetrahedral sheet has a large value of α (decreasing lateral dimensions) and approximately 50% occupancy by Al (increasing the dimensions). The composition of the octahedral sheet of the 2:1 layer is therefore indirectly coupled to Ca occupancy.

The necessity for charge balance further constrains the sheet compositions described above. Assuming 50% occupancy of tetrahedral sites by Al gives rise to a dioctahedral 2:1 layer with Al^{3+} and a negatively charged dioctahedral interlayer with only $+2$ cations. The overall formula is implied to be $Ca_2Al_2Mg_2[Si_2Al_2]O_{10}(OH)_8$. Variations on this theme might involve substitution of Fe^{3+} for Al and divalent cations such as Fe^{2+} for Mg in the octahedral interlayer.

One other major variant of this theme is possible. In clintonite, a large rotation angle, α, and increase in dimensions of the tetrahedral sheet caused by substitution of Al to approximately 75%, are coupled with an increase in the dimensions of the octahedral sheet. It becomes a trioctahedral sheet of cation composition Mg_2Al_1. The coupled substitutions give rise to the balanced formula $Ca_2(AlMg_2)Mg_2[SiAl_3]O_{10}(OH)_8$.

Significant features of the above two hypothetical endmember formulae include (1) $\geq 50\%$ substitution of Al in tetrahedral sites, (2) a negatively charged dioctahedral interlayer with divalent cations, (3) essential Al in the octahedral sheet of the 2:1 layer, and (4) a structure of type II*a*. The latter would appear to be the Achilles heel of such a structure. As noted above, structures of type *a* are rare, with franklinfurnaceite as the only known representative of type II*a*—a circumstance ascribable to the unusual occurrence of a cation of charge $+2$ (Zn) in tetrahedral sites.

Although the occurrence of minerals having the hypothetical formula given above cannot be entirely ruled out, they must be considered relative to more stable alternatives. Alternatives to such hypothetical chlorites are either margarite or clintonite brittle micas, plus (Mg,Ca)(OH)$_2$. The former structures clearly are stable over a wide range of *P, T,* and composition. Given the unusual features of the hypothetical Ca-containing chlorite struc-

tures, they must be considered to be unstable relative to the brittle micas. If such chlorite units do exist, they are most likely to occur as intercalations within brittle micas that coexist with chlorites. Such phases should be carefully studied TEM for such a possibility.

On the other hand, it is well-known that layer silicates that form at low temperatures under conditions of diagenesis may be inherently unstable phases that give way, through further diagenesis, to less unstable phases in sequences of Ostwald-step-rule-like reactions (Lee et al., 1985). This is especially true when reactions occur where reactant phases have structures that are in part inherited from pre-existing unstable, detrital phases. For example, mixed-layer chlorite/smectite phases are not uncommon in the sedimentary environment, and the diagenesis that gives rise to reactions involving smectite layers might conceivably give rise to locally intercalated (Ca,Al)-rich chlorite layers.

It is also well-known that disparate phyllosilicate layers of various kinds may be interlayered with layers of a second kind at a scale detectable only by transmission electron microscopy (e.g., Ahn and Peacor, 1985). Where chemical analytical data show measurable amounts of Ca in chlorite, it is therefore much more likely that small numbers of randomly intercalated layers of such phases as Ca-smectite, margarite or clintonite occur, as opposed to the inherently unlikely Ca-substituted aluminosilicate chlorite.

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