A Re-investigation of the Crystal Structures of Chevkinite and Perrierite

CRISPIN CALVO, AND R. FAGGIANI

Institute for Materials Research, McMaster University, Hamilton, Ontario

Abstract

Synthetically prepared chevkinite and perrierite are both monoclinic with space group $P2_1/a$. Perrierite, $2[Mg_2La_4Ti_3Si_4O_{22}]$, has unit cell parameters a = 13.818(4), b = 5.677(2), c = 11.787(6) Å, and $\beta = 113.85(3)^{\circ}$. This structure was refined by full-matrix methods to R = 0.046. The structures of two crystals of chevkinite were refined. The one with composition $2[Mg_2Nd_4Ti_3Si_4O_{22}]$ has lattice parameters a = 13.328(10), b = 5.727(4), c = 10.971(8) Å, $\beta = 100.91(6)^{\circ}$ and refined to R = 0.043. The second with composition $2[Co_2Nd_4Ti_3Si_4O_{22}]$ has lattice parameters a = 13.328(10), b = 5.727(4), c = 10.971(8) Å, $\beta = 100.82$ (6)°, and refined to R = 0.050. Both structures have disilicate ions, Si_2O_7 , with nearly eclipsed configurations; Si-O-Si bond angles are 157.5° and 157.3° in the two chevkinites and 165.4° in perrierite. Two Mg(Co) ions per unit cell are octahedrally coordinated to oxygen atoms which are shared with six disilicate ions. The remaining cations of small radii, six Ti and two Mg(Co) ions per unit cell, are distributed non-randomly in sheets among sites with distorted octahedral coordination. The distribution of Ti and Mg(Co) among the available sites differs between perrierite and the chevkinite.

Introduction

The structures of naturally occurring chevkinite (Pen and Pan, 1964) and perrierite (Gottardi, 1960) were refind in space group C2/m and were shown to be similar. Ito and Arem (1971) confirmed the suspicion of Bonatti (1959) that perrierite has a primitive cell, and indexed the powder patterns of synthetic preparations of each mineral in space group $P2_1/a$. The unit cells of these minerals are related as proposed by Bonatti and Gottardi (1966), and the similarity in their structures makes it difficult to rationalize their relative stability. Ito and Arem (1971) suggested that these minerals can be represented as $A^{3+}_{4}B^{2+}C^{3+}_{2}Ti^{4+}O_{8}(Si_{2}O_{7})_{2}$ and that synthetic chevkinite is stabilized, relative to perrierite, by high temperature, by A ions with smaller radii, and by B and C ions of larger radii. An accurate refinement of these structures was needed to pursue the question of the distribution of ions of various sizes and their rôle in the stabilization of these phases.

Experiments

Crystals of chevkinite and perrierite were obtained from Ito (see Ito and Arem, 1971, for analyses and conditions of synthesis). Accurate cell parameters were determined from the same crystals used to collect the intensity data. The crystals were roughly spherical in shape, with mean radii of 0.062 mm for perrierite and 0.10 mm for both Mg- and Co-chevkinite. Graphite monochromatized MoK α radiation ($\lambda = 0.71069$ Å) was used in conjunction with a Syntex PI automatic diffractometer. These parameters listed with other crystal data were obtained by least-squares methods using the angular coordinates for 15 well-centered reflections (Table 1).

For perierite and Mg-chevkinite $(\sin \theta/\lambda)_{max} = 0.70$, and for Co-chevkinite $(\sin \theta/\lambda)_{max} = 0.59$. Peaks were scanned at rates determined by the peak intensity, and backgrounds were measured at either side of the peak. Intensities greater than 3σ , where σ is determined from the counting statistics, were considered "observed." The remaining reflections of positive measure were considered "unobserved" and given zero weight in the refinement, unless $F_e > F_o$. The data were corrected for Lorentz, polarization effects, and absorption.

The structure of perrierite was refined in space group C2/m from parameters reported by Gottardi (1960), and the atoms were allowed to assume positions consistent with space group $P2_1/a$. Initial coordinates for the atoms in both chevkinites were

| | Perrierite* | Mg-chevkinite** | Co-chevkinite** |
|-------------|---|--|---|
| | Mg ₂ La ₄ Ti ₃ Si ₄ 0 ₂₂ | ^{Mg} 2 Nd 4 ^{Ti3^{Si}4⁰22} | Co ₂ Nd ₄ Ti ₃ Si ₄ O ₂₂ |
| space group | P21/a | P21/a | P21/a |
| a(Å) | 13.818(4) | 13.328(10) | 13.325(4) |
| b(Å) | 5.677(2) | 5.727(4) | 5.706(2) |
| c(Å) | 11.787(6) | 10.971(8) | 10.998(2) |
| β(°) | 113.85(3) | 100.91(6) | 100.82(6) |
| Ζ | 2 | 2 | 2 |
| ρ | 4.94 | 4.98 | 5.27 |
| fw | 1212.31 | 1233.60 | 1302.8 |

 TABLE 1. Crystal Data for Synthetic Perrierite, Mg-Chevkinite, and Co-Chevkinite

those obtained for the perrierite refinement. These structures were refined by full-matrix least-squares methods using a program written by J. S. Stephens and varying a parameter allowing for the effects of extinction, following the method of Larson (1967). Scattering factors, corrected for dispersion, were obtained from Cromer and Waber (1967) and Cromer (1965).

When the refinements converged, it was apparent that the Ti and Mg were partially disordered amongst the octahedrally coordinated sites. Both the magnitudes of the thermal parameters and the mean bond lengths to the six nearest oxygen atoms indicated partial ordering. The occupancies of these sites were assigned initially on the basis of a linear plot of the expected mean Ti-O and Mg-O bond lengths versus composition. In the case of site C(2) in perrierite, the large distortion and short C(2)-O(5) bond length indicated that the site was almost completely occupied by Ti. A lowering of the R value when this model was refined suggested that the assigned compositions were approximately correct. The final site occupancies were determined with the RFINE program (Finger, 1969), which allows the site occupancies to vary within the restriction of a total composition corresponding to that given by Ito (1967). The cation sites were assumed to be fully occupied. The compositions of all the octahedral sites were varied, but only those designated as C(n)showed mixed composition. The atomic and siteoccupancy parameters at convergence, when all the shifts-to-errors were less than 0.15, are shown in Tables 2, 3, and 4. Observed and calculated structure factors are compared in Tables 9a, 9b, and 9c.

Description of the Structure

The gross structural features of the two minerals are essentially the same, consisting of sheets of octahedrally coordinated C(n) atoms with n = 1,2 in perrierite and 1,2A and 2B in chevkinite, sites running parallel to the (001) plane and separated by the *c*-axis translation (Fig. 1). These sheets have configurations much like the (10) planes in rutile (Fig. 2). These sheets are interleaved with a layer consisting of a double thickness of Si₂O₇ groups and MgO₆ or CoO₆ octahedra. For convenience Mg and Co will be designated as *B* ions. Each disilicate group is joined to six MgO₆ octahedra, forming a layer with the composition $n[Mg(Si_2O_7)_2]$. The rare earth ions lie between the disilicate ions and the sheet of octahedra.

The disilicate ions in the two structures are bent significantly at the bridging oxygen atom (Table 5), which shows the highest thermal parameters in each of the three refinements. The anions have nearly msymmetry. The pseudo-mirror plane is defined by the two silicon ions, and O(6), O(7), and O(8). The individual Si-O bonds show the same trends in each structure although some of the distances differ by more than 2σ . In particular, for each anion the bonds in the pseudo-mirror plane are shorter than the remaining ones. The bridging oxygen atom is shared with RE(1) in each structure.

The bond lengths between the rare-earth (RE) ion and the oxygen atoms are given in Table 6. In perrierite La(1) has eight oxygen atoms within 3.0 Å, while in chevkinite Nd(1) has nine oxygen atoms, including O(5), within a similar sphere.

TABLE 2. Atomic Parameters for Synthetic Perrierite, Mg₄La₈Ti₆Si₈O₄₄ (standard errors in parentheses)

| atom | x | у | z | U(Å ²) |
|----------------------|------------------------------|------------------------|-----------------------|-------------------------------------|
| La(1) | 0.23756(5) | 0.0198(1) | 0.26687(6) | 0.0078(3) |
| La(2) | 0.04897(5) | 0.0265(1) | 0.7432(6) | 0.0087(3) |
| Si(1) | 0.4123(2) | -0.0001(5) | 0.7322(3) | 0.0057(6) |
| Si(2) | 0.1624(2) | 0.0027(5) | 0.5489(3) | 0.0069(6) |
| O(1) | 0.0794(6) | -0.2597(14) | 0.1864(7) | 0.0091(14) |
| 0(11) | 0.0652(6) | 0.2556(14) | 0.1858(7) | 0.0103(14) |
| 0(2) | 0.2899(6) | 0.2606(15) | 0.1229(7) | 0.0128(15) |
| 0(21) | 0.2875(6) | -0.2401(14) | 0.1225(7) | 0.0105(15) |
| 0(3) | 0.3736(6) | -0.2511(14) | 0.4058(7) | 0.0123(15) |
| 0(31) | 0.3920(6) | 0.2862(15) | 0.4066(8) | 0.0139(15) |
| 0(4) | 0.0957(7) | 0.0077(14) | 0.9894(8) | 0.0114(15) |
| 0(5) | 0.4067(7) | -0.0041(14) | 0.0089(8) | 0.0110(15) |
| 0(6) | 0.4932(7) | 0.0328(15) | 0.6667(8) | 0.0150(16) |
| 0(7) | 0.2884(7) | -0.0337(16) | 0.6366(8) | 0.0176(17) |
| 0(8) | 0.1384(6) | -0.0036(14) | 0.4042(7) | 0.0115(15) |
| Mg C(1)* C(2)* | 0 -0.0039(2) 0.2749(2) | 0.2385(6) 0.0071(4) | 0.0004(3) 0.017(2) | 0.0047(9) 0.0105(6) 0.0068(4) |

Site C(1) contains 0.616(6) Ti and 0.384 Mg and C(2) contains 0.884 Ti and 0.116 Mg.All atoms are in sites of type 4e except Mg which lies in a site of type 2c.

| . | (standard errors in parentheses) | | | | | | |
|------------------------------|----------------------------------|--------------------------------|-------------------------|--|--|--|--|
| atom | x | у | z | U(Å ²) | | | |
| Nd(1) | 0.35442(4) | 0.02260(7) | 0.23312(4) | 0.0095(1) | | | |
| Nd(2) | 0.07127(4) | -0.03662(7) | 0.24017(4) | 0.0094(2) | | | |
| Si(1) | 0.2015(2) | 0.4972(3) | 0.2306(2) | 0.0069(4) | | | |
| Si(2) | 0.3596(2) | 0.5019(3) | 0.0470(2) | 0.0076(4) | | | |
| O(1) | 0.2393(5) | -0.2098(9) | 0.3133(5) | 0.0075(10) | | | |
| 0(11) | 0.2170(5) | 0.2527(9) | 0.3130(5) | 0.0081(10) | | | |
| 0(2) | -0.0247(5) | -0.2527(9) | 0.3742(5) | 0.0085(10) | | | |
| 0(21) | -0.0214(5) | 0.2448(10) | 0.3736(5) | 0.0093(10) | | | |
| 0(3) | 0.4131(5) | -0.2493(10) | 0.0946(5) | 0.0093(10) | | | |
| 0(31) | 0.4437(5) | 0.2947(10) | 0.0931(5) | 0.0107(11) | | | |
| 0(4) | 0.1457(6) | -0.0104(10) | 0.4757(5) | 0.0106(11) | | | |
| 0(5) | 0.1511(6) | 0.5044(10) | 0.5099(5) | 0.0105(11) | | | |
| 0(6) | 0.0866(6) | 0.5469(10) | 0.1686(5) | 0.0113(11) | | | |
| 0(7) | 0.2741(6) | 0.4477(10) | 0.1307(6) | 0.0151(12) | | | |
| 0(8) | 0.3132(6) | 0.4892(9) | 0.0985(5) | 0.0074(10) | | | |
| Mg C(1) C(2A) C(2B) | 0.2434(2) 0 1/2 | 1/2 0.2466(3) 1/2 1/2 | 0.5000(2) 1/2 1/2 | 0.0078(7) 0.0082(3) 0.0111(5) 0.0093(4) | | | |

TABLE 3. Atomic Parameters for Mg-Chevkinite, Mg₄Nd₅Ti₆Si₅O₄₄

Mg, C(2A) and C(2B) lie in sites 2d, 2b and 2b respectively. C(2A) contains 0.807(7) Ti and C(2B) contains 0.834(9) Ti, with the remainder being Mg. Site C(1) contains 0.680 Ti and 0.320 Mg.

Since C(2) in perierite is strongly bonded to O(5), with an interatomic distance of 1.789 Å (Table 6), the very long RE(1) to O(5) distance of 3.452 Å, in compensation, is not unexpected. RE(2) is coordinated to nine oxygen atoms in each structure with all the RE(2)-O bonds lying between 2.470 and 2.711 Å in perrierite and 2.391 and 2.688 Å in Mg-chevkinite with a somewhat smaller range in Cochevkinite.

Each structure has a B ion on a center of symmetry with average B-O bond lengths of 2.124 Å in perrierite and of 2.133 and 2.151 Å in Mg and Co

TABLE 4. Atomic Parameters for Co-Chevkinite, Co4NdsTisSisO14 (standard errors in parentheses)

| atom | × | У | z | U(Å ²) |
|--|---|--|---|--|
| Nd(1) Nd(2) Si(1) Si(2) O(1) | 0.35651(5) 0.06955(5) 0.2003(3) 0.3584(3) 0.2384(6) | 0.01889(12) -0.03317(13) 0.4974(5) 0.4993(6) -0.2725(15) | 0.23426(7) 0.24116(6) 0.2298(3) 0.0464(3) 0.3137(8) | 0.0099(3) 0.0089(3) 0.0053(7) 0.0063(7) 0.007(2) |
| 0(11) 0(21) 0(2) 0(3) 0(31) | 0,2183(6) -0.0254(7) -0.0241(7) 0,4134(7) 0,4402(7) | 0.2595(15) 0.2515(15) -0.2575(16) -0.2550(16) 0.2880(17) | 0.3126(8) 0.3721(8) 0.3697(8) 0.0957(8) 0.0954(9) | 0.007(2) 0.008(2) 0.012(2) 0.012(2) 0.012(2) 0.013(2) |
| 0(5) 0(4) 0(6) 0(7) 0(8) | 0.1516(7) 0.1450(7) 0.0833(7) 0.2705(7) 0.3149(7) | 0.4959(15) -0.0121(15) 0.5434(16) 0.4515(17) -0.0097(15) | 0.5092(8) 0.4752(9) 0.1737(9) 0.1247(9) -0.0992(9) | 0.008(2) 0.007(2) 0.010(2) 0.013(2) 0.011(2) |
| Co C(1) C(2A) C(2B) | 0.2447(2) 0 1/2 | 1/2 0.2456(6) 1/2 1/2 | 0 0.5003(3) 1/2 1/2 | 0.0093(6) 0.0106(8) 0.0119(2) 0.0129(9) |

to, t(ZA) and C(2B) lie in sites of type 2d, 2b and 2b respectively. C(1 contains 0.68(1) Ti, C(2A) contains 0.82(1) Ti and C(2B) contains 0.82 Ti with the remainder being Co.



Fig. 1a. The 010 projection of the structure of perrierite. The circles represent oxygen atoms, rare-earth ions, divalent metal ions, and silicon atoms as their sizes decrease. The broken circles represent superimposed atoms.

chevkinite respectively. The octahedra show a large tetragonal distortion with the B-O(6) bond lengths contracted by more than 0.15 Å. The individual bond lengths for these octahedrally coordinated cations are given in Table 7. The Mg and Ti are non-randomly distributed among the remaining cation sites. Site C(2) has 0.884 Ti in perierite and shows high distortion with O(4) and O(5) separated by



FIG. 1b. The 010 projection of the structure of chevkinite. The circles represent atoms as in Figure 1a. The relationship between the two structures is most clearly seen by superposing the origin of this figure, after reflection in the plane of the diagram, on the x = 1, $z = \frac{1}{2}$ position of Figure 1a.



FIG. 2. A superposition of the octahedral sheets in perrierite (left hand side) and chevkinite (right hand side). The two structures have been superimposed as suggested in Figure 1b to emphasize their structural similarity. Note the reversal in the direction of the a axis and the positions of the two-fold screw axes in the two phases.

1.789 and 2.421 Å from the cation and with an O(4)-C(2)-O(5) angle of 178°. Adjacent $C(2)O_6$ octahedra are generated by the 2_1 axis, and the C(2) octahedra share edges which are nearly normal to the

TABLE 5. Bond Lengths and Angles in Perrierite and Chevkinite

| bond | perrierite | Mg-chevkinite | Co-chevkinite | | | | |
|--|-------------|---------------|---------------|--|--|--|--|
| | distance(Å) | distance(Å) | distance(Å) | | | | |
| Si(1)-0(1) | 1.645 | 1.639 | 1.626 | | | | |
| -0(11) | 1.646 | 1.636 | 1.628 | | | | |
| -0(6) | 1.605 | 1.580 | 1.594 | | | | |
| -0(7) | 1.636 | 1.618 | 1.634 | | | | |
| Si(2)-0(7) | 1.639 | 1.623 | 1.634 | | | | |
| -0(8) | 1.601 | 1.602 | 1.598 | | | | |
| -0(31) | 1.635 | 1.644 | 1.647 | | | | |
| -0(3) | 1.643 | 1.633 | 1.628 | | | | |
| <si-0></si-0> | 1.642 | 1.629 | 1.632 | | | | |
| angle | (degrees) | (degrees) | · (degrees) | | | | |
| $\begin{array}{c} 0(1)-Si(1)-0(11) \\ -0(6) \\ -0(7) \\ 0(11)0(6) \\ -0(7) \\ 0(6)0(7) \end{array}$ | 113.9 | 112.6 | 111.1 | | | | |
| | 106.6 | 105.3 | 105.1 | | | | |
| | 107.7 | 110.9 | 112.1 | | | | |
| | 112.2 | 113.6 | 112.4 | | | | |
| | 101.7 | 101.4 | 102.8 | | | | |
| | 114.9 | 113.3 | 113.6 | | | | |
| $\begin{array}{c} 0(8) - \text{Si}(2) - 0(31) \\ & -0(3) \\ & -0(7) \\ 0(31) - & -0(3) \\ & -0(7) \\ 0(3) - & -0(7) \\ \text{Si}(1) - 0(7) - \text{Si}(2) \end{array}$ | 113.7 | 112.7 | 113.4 | | | | |
| | 113.9 | 114.9 | 114.7 | | | | |
| | 112.9 | 112.0 | 111.6 | | | | |
| | 107.3 | 107.5 | 107.0 | | | | |
| | 102.3 | 101.5 | 101.8 | | | | |
| | 106.6 | 107.3 | 107.3 | | | | |
| | 165.6 | 157.4 | 157.3 | | | | |
| Si(1)-O(7)-Si(2) 165.6 157.4 157.3 The standard errors on the bond lengths and bond angles are 0.010A or less and 0.8° or less. | | | | | | | |

 TABLE 6. Bond Lengths around the Rare Earth Ions in Perrierite and Chevkinite

| | perrierite | Mg-chevkinite | Co-chevkinite |
|---|---|---|--|
| bond | distance (Å) | distance (Å) | distance (Å) |
| RE(1)-0(11) -0(21) -0(31) -0(5) -0(7) -0(1) -0(2) | 2.556 2.549 2.591 3.452 2.860 2.553 2.503 | 2.557 2.434 2.627 2.836 2.807 2.538 2.537 | 2.571 2.492 2.564 2.845 2.887 2.554 2.492 |
| -0(3) -0(8) | 2.468 2.511 | 2.407 2.441 | 2.403 2.485 |
| RE(2)-0(1) -0(11) -0(2) -0(21) -0(3) -0(3) -0(3) -0(4) -0(6) -0(8) | 2.603 2.612 2.624 2.544 2.711 2.610 2.707 2.666 2.470 | 2.600 2.581 2.459 2.636 2.688 2.525 2.591 2.531 2.391 | 2.625 2.598 2.581 2.430 2.664 2.541 2.585 2.545 2.545 2.394 |

Bond length errors are of the order of 0.007Å.

a axis. Analogous to that of C(2) in perrierite are the C(2A) and C(2B) octahedral sites in chevkinite, each of which has $\overline{1}$ site symmetry and contains 0.81 and 0.83 mole per cent Ti, respectively. These octahedra are substantially more regular than in perrierite, since the latter has a long C(2)-O(4) bond and a short C(2)-O(5) bond. The C(n)-C(n) distance is 2.863 Å in Mg-chevkinite compared with 2.917 Å in perrierite. O(2) and O(21) are shared by the C(n) cations and the rare earth ions only. The C(1) site in perrierite contains 0.62 mole per cent Ti and in Mg-chevkinite 0.68 mole per cent Ti. Here the oxygen atoms which are not bonded to cations in the octahedral layer are bonded to Si in

 TABLE 7.
 Selected Bond Lengths in Perrierite and Chevkinite

| | perrierite distance(Å) | Mg-chevkini te distance(Å) | | Co-chevkinite distance (Å) |
|--------------|---------------------------|--------------------------------------|-------|-------------------------------|
| B-0(31) (2x) | 2.179 | 2.216 | | 2.239 |
| -0(3) (2x) | 2.179 | 2.177 | | 2.180 |
| -0(6) (2x) | 2.014 | 2.003 | | 2.036 |
| C(1)-O(1) | 2.023 | 2.020 | | 2.018 |
| -O(11) | 2.002 | 2.015 | | 2.029 |
| -O(4) | 1.942 | 2.009 | | 1.998 |
| -O(4) | 1.924 | 1.951 | | 1.966 |
| -O(5) | 2.018 | 1.992 | | 1.967 |
| -O(5)' | 1.978 | 1.938 | | 1.942 |
| C(2)-0(2) | 1.979 | C(2A)-O(2) (2x) | 1.961 | 1.974 |
| -0(2) | 1.963 | -O(21)(2x) | 1.997 | 1.993 |
| -0(21) | 1.956 | -O(5) (2x) | 1.998 | 2.003 |
| -0(21)' | 1.982 | C(2B)-O(2) (2x) | 1.984 | 2.035 |
| -0(4) | 2.421 | -O(21)(2x) | 1.955 | 1.981 |
| -0(5) | 1.789 | -O(4) (2x) | 2.011 | 2.004 |

the disilicate ions. Co-chevkinite differs insignificantly from the Mg-containing member.

Discussion

The structures of perrierite and chevkinite (Fig. 1a, 1b) show these minerals to be related as proposed by Bonatti and Gottardi (1966)-that is, with the a axes antiparallel and the c axis of chevkinite parallel to the a + 2c direction of perrierite. If the origin of the mirror image of Figure 1b is superimposed upon the x = 1, z = 1/2 position of Figure 1a, the structures nearly superimpose. Besides the fact that the individual bond lengths are more nearly equal, the coordination number of the rare earth ions is now nine for the two sites rather than ten as assigned by Bonatti and Gottardi (1966) for the minerals. This requires that RE(1)-O(4)at 3.059 Å be in the coordination sphere for perrierite. One important difference is that the overbonded oxygen, 0(7), has only one moderately strong bond with a rare-earth ion rather than the two reported for the mineral. The most striking difference between perrierite and chevkinite is the strong C(2)-O(5) interaction (1.789 Å) and the weak trans interaction, C(2)-O(4) = 2.421 Å, in the former compound. This strong interaction in perrierite results in a broken RE(1)-O(5) bond. Distorted environments, such as that of C(2) in perrierite, are not uncommon for Ti and thus the higher preference of Ti for this site is not unexpected. Five-fold coordination for Co and Mg with oxygen atoms are known (Calvo, 1967; Krishnamachari and Calvo, 1972), but the appearance of one very strong bond is unusual. Contrary to the results of Ito (1967), the perrierite structure would seem to be stable for small RE ions in the presence of ion supportive of five-fold coordination at the C(2)site.

Bonatti and Gottardi (1966) and Ito (1967) have speculated that the distribution of the cations in the structure can be represented as $[A^{3+}_{4}B^{2+}C^{3+}_{2}\text{Ti}^{4+}_{2}\text{O}_{8-}(\text{Si}_{2}\text{O}_{7})_{2}]$. In terms of the present structure, A represents the rare-earth ion, $B = Mg^{2+}$ or Co^{2+} lying between the cation sheets, C = C(1). The other octahedral site [C(2) or C(2A), C(2B)] is occupied by Ti. The average ionic charges in the synthetic systems differ from those represented by this formula. In perrierite the average charges at C(1) and C(2)are 3.23 and 3.77. In Mg-chevkinite C(1) has an average charge of 3.30 with values of 3.67 and 3.61 at C(2A) and C(2B) respectively. The electrostatic valency (Pauling, 1960) for some of the oxygen atoms are compared in Table 8. The charged distributions proposed for the mineral chevkinite (ordered chevkinite) and that for a random distribution of cations in the octahedral sheet in this phase are included. For perrierite, C(2) is taken as having six-fold coordination, but the C(2)-O(5) and C(2)-O(4) bonds are given weights of 3/2 and 1/2 respectively. This is consistent with the bond strengths calculated as suggested by Brown and Shannon (1973). The sum of squares of the deviations from 2 is smallest for the ordered chevkinite. In fact, a solution for the charge distribution by least-squares methods yields charges of 3.30 and 3.70 for C(1) and C(2) in periorite, under the assumption that the disorder is restricted to the octahedral sheet. For chevkinite the solutions are 2.86 for C(1) and 4.14 for C(2A) and C(2B).

Thus, the disorder in the perierite is predicted on the basis that the energy is minimized when the bond strengths are nearest their ideal value. On the other hand, it would appear that chevkinite might be stabilized relative to perierite by an entropy contribution involving configurational terms. Furthermore these calculations indicate that some pentavalent substitution in C(2A) and C(2B) would enhance the chance for the appearance of chevkinite. However, in general these structure studies have not provided a basis for an understanding of the role of the ionic radius in perierite-chevkinite stability.

TABLE 8. Selected Anionic Electrostatic Valencies

| | | 1 | | Cati | ons | | | |
|----------------------------------|--|---|----------------------------------|----------------------------|-------------------------|-------------------------|------------------------------|--------------------------------------|
| anion | model | RE | C(1) | C(2) | C(2A) | C(2B) | Si | Σ2 |
| 0(1), 0(11) | a b c d | 0.708 0.667 0.667 0.667 | 0.535 0.550 0.500 0.583 | | | | 1.00 1.00 1.00 1.00 | +0.243 +0.217 +1.167 +0.250 |
| 0(2), 0(21) | a b c d | 0.708 0.667 0.667 0.667 | | 1.257 | 0.607 0.500 0.583 | 0.607 0.500 0.583 | | -0.035 -0.109 -0.000 -0.156 |
| 0(4) | a b c d | 0.333 0.333 0.333 0.333 0.333 | 1.070 1.100 1.333 1.166 | 0.314 | | 0.617 0.500 0.483 | | -0.283 +0.050 +0.000 +0.082 |
| 0(5) | a b c d | 0.333 0.333 0.333 | 1.070 1.100 1.333 1.16 | 0.943 | 0.607 0.500 0.58 | | | +0.013 +0.040 +0.000 +0.033 |
| | | | m | ean charg | je | | | |
| | model | | site | <u>C(1)</u> | C(2) | C(2A) | C(2B) | |
| a) pe b) ch c) or d) ra | rrierit evkinit dered c ndom ch | e e hevkinit evkinite | e | 3.23 3.30 3.0 3.5 | 3.77 | 3.67 4.0 3.5 | 3,61 4.0 3,5 | |

C. CALVO, AND R. FAGGIANI

| | TABLE 9a. Observed and Calculated Structure Factors for Synthetic Perrierite, Mg ₄ La ₈ Ti ₆ Si ₈ O ₄₄ * |
|---------------|--|
| BSECCO | |
| re ≉ | |
| | 96699699999999944444444444444444444444 |
| FCLG | |
| F085 | |
| | |
| 51 C | an anna a' na sharan a sharan a sharan a sharan a annaish tasa a sharan a |
| FORSIF | |
| - | |
| | |
| BALFCLC | |
| E G | |
| | |
| Ford | |
| F085 | |
| | |
| رم | |
| 093 1560 | |
| - | |
| | ###################################### |
| FCLC | 2 |
| 1 €088 | |
| | |
| cra | ಜೆ ಎಲ್ಲ್ಲೇನಿ ನಿಲ್ಲಿ ವೇಷೆ ಕಾರ್ಯಕ್ರಿ ಗ್ರಾಮದ ಸಾರ್ಥಿಕ್ರ ಕ್ರಿಯಾ ಕ್ರಮದ ಸ್ವಾಮದ ಸ್ವಾಮದ ಸ್ವಾಮಿಸಿ ಸ್ವಾಮದ ಸಂಭಾಗ ಸಾಯದ ಸಂಭಾಗ ಸಾಹಿತ ಸ್ವಾಮದ ಸಂಭಾಗ ಸಾಹಿತ ಸ್ವಾಯದ ಸಂಭಾಗ ಸಹಿತ ಸ್ವಾಯದ ಸಂಭಾಗ ಸಹಿತ ಸ್ವಾಯದ ಸಂಭಾಗ ಸಹಿತ ಸ್ವಾಯದ ಸಂಭಾಗ ಸಾಹಿತ ಸ್ವಾಯದ ಸಂಭಾಗ ಸಾಹಿತ ಸ್ವಾಯದ ಸಹಿತ ಸ್ವಾಯದ ಸಹಿ |
| FOBS F | |
| | |
| 5 | |
| BSERCE | |
| je o | |
| | nn nn 133333333333333333333333333333333 |
| LCLC | |
| F083 | |
| | |
| גם | |
| FOBS F | |
| - | |
| | |
| ist frond | |
| F OB | อากับเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเป็นสายเ |
| | |

* Unobserved reflections are indicated with *.

CRYSTAL STRUCTURES OF CHEVKINITE AND PERRIERITE

TABLE 9b. Observed and Calculated Structure Factors for Synthetic Chevkinite, Mg₄Nd₈Ti₆Si₈O₄* 🖞 STINGERERETANDERETANDERETA 🖞 VERTERENTING 🕺 VERTERETANDERETA 🖞 VERTERETAND 🚊 3...THEMBAT METAL M 🖞 Raparanan ara 🖞 raparanananananananananananananana arana a ಕ್ಷೆ ಸೋಚಾನವಾಗ 🖕 ನಾಡುಗಳಲ್ಲಿ ಸಂಪಾಧವಾಗಿ ಸಂಶ್ವಾಮ ಪ್ರಮಾನವಾಗ ಪ್ರಮಾನವಾಗ ಪ್ರಮಾನವಾಗ 👔 ಸೇವಿ ಸಂಪಾಧ ಪ್ರಮಾನವಾಗ 🖉 ಪ್ರಾಣ್ಣ ಸಂಪರ್ಧ ಪ್ರಮುಖ ಪ್ರಮಾನವಾಗ ಪ್ರಮ ಪ್ರಮಾನವಾಗ ಪ a han was not a stand and the second of the ä seratasianen serationen s B HALLORD A BRABAN FARMARENDER STRATER S a stantin fan stanten san าะระบระบบสามารรณรารระบบสามารรรรณราช เป็นการระบบสามารรรฐสามารรรฐสามารรรฐสามารรรณราช (1977) and a second rest of the second s 5 21-20. addression and 20 million researched and a stratter an ន្និ 🕷 🖕 រណានរាលនាក់រំហើកនេះក្រោមនេះលោកនាក់អាមមេស លោក ប្រមានអនុមរណ៍នេះ និងនៅលើកែវាទទនរបស់និង ដឹងដឹង កែងដែលពីដីក្រោមនាយស សេរ 🕯 ជើងជាតិ 🖉 🖓 🖓 🕺 * Unobserved reflections are indicated with*.

| k Pobe Foste | k / Food Can | * Fanne Fonte | k Fand Fand | k i Rinn Peale | k i Finn faild | k [obs] cost | k 1 obs Calc |
|--|---|---|--|--|--|---|---|
| h = 0 | 5 -4 83 86 5 5 103 103 5 -5 • 11 15 5 5 40 41 5 -6 20 22 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 3 1 33 34 3 1 8 3 9 3 2 70 70 3 2 74 42 3 3 35 | 0 1 253 257 0 1 267 245 0 1 267 245 9 2 215 199 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 22 -6 44 41 -6 69 59 22 -7 69 59 22 -7 8 25 26 | 3 |
| 0 1 49 50 0 2 178 191 0 3 200 211 0 4 431 423 | 5 7 70 64 5 7 83 5 8 42 33 5 8 42 33 5 8 42 33 | 1 -7 325 334 1 8 227 225 1 9 50 48 | 73737 - 4451 - 4451 - 4451 - 4451 - 4451 - 4451 - 55 - 65 - 65 - 7 | 0 3 25 223 0 4 25 223 0 4 25 11 0 4 15 11 | 4 -2 16 16 4 3 32 33 4 -3 37 39 4 -3 37 39 -4 -4 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 | 2 -8 62 64 2 -9 55 55 2 -10 55 55 2 -11 20 16 3 -11 68 | 3 -7 56 54 3 -8 145 151 3 -9 47 41 4 0 48 54 |
| 0 5 40 38 0 6 144 145 0 7 292 293 0 8 356 345 0 9 108 111 | 5 1 121 130 6 -1 111 113 6 2 22 19 6 3 112 121 121 | 1 - 3 248 254 1 19 206 196 1 -10 27 32 1 11 34 31 1 -11 24 31 | 3 6 31 37 - 3 - 6 87 85 - 7 7 34 34 - 7 12 11 | U = -5 306 307 0 6 41 43 0 -6 177 180 0 7 92 67 U = 7 144 146 | 4 - 19 27 55 5261 4 - 65 53 38 | 3 -1 87 87 3 -2 20 27 3 -2 16 157 3 -2 16 157 | 4 -1 47 $444 -2$ 38 $434 -2$ 54 $564 -3$ 31 37 |
| 0 10 59 6) 0 11 735 229 0 12 185 174 1 1 2 21 1 2 8 | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 3 -8 68 167 3 -9 212 18 3 10 27 28 | 0 8 97 92 0 8 89 87 0 9 81 79 0 9 114 112 0 10 92 92 | 4 -7 42 48 4 -8 14 8 4 -9 - 27 - 28 5 0 123 125 5 1 17 18 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 4 - 5 - 5 - 7 - 2 - 5 - 7 - 2 - 5 - 5 |
| 1 3 19 19 1 5 18 17 1 5 18 17 | 6 - 3 31 33 | 2 2 47 45 2 36 38 2 3 23 23 21 2 3 23 21 2 3 4 9 3 2 4 69 64 | 3 + 11 + 3 + 1 4 + 10 + 16 + 15 4 + 1 + 74 + 188 4 + 1 + 74 + 188 | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 5 -1 14 15 5 2 106 106 5 -2 110 110 5 -3 21 18 5 -3 40 35 | 3 -6 56 53 3 7 20 16 3 -7 33 31 3 -8 127 128 | h = 12 |
| | h = 2 | 2 - 4 52 52 2 - 5 16 16 2 - 5 17 17 2 - 6 45 57 2 - 6 33 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1 -1 94 96 1 2 8 8 6 1 3 43 41 1 -3 44 44 1 -3 14 | 5 + 124 - 24 - 5 - 4 + 136 + 113 5 - 5 + 4 + 46 5 - 5 + 55 5 - 6 - 71 - 73 | 3 -10 57 55 4 0 89 925 4 1 87 85 4 -1 55 59 | |
| 1 367 399 1 127 125 2 2 25 2 1 126 2 16 1 16 1 16 1 16 1 16 1 16 1 | 0 1 59 59 0 -1 22 15 0 2 50 51 4 -2 43 47 0 3 107 11 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 4 -4 58 76 4 -5 207 195 4 -5 140 128 4 -6 140 128 | 1 - 4 25 25 1 1 - 5 30 322 1 - 5 37 35 1 - 6 37 35 | 5 -7 37 40 6 0 16 21 6 1 22 24 6 -1 17 14 6 -2 13 17 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 0 3 66 66 0 -3 66 66 0 4 103 105 0 -9 176 102 |
| 2 5 184 165 2 6 241 2223 7 235 1227 | n →3 + 7 7 9 0 4 76 76 0 -4 13 10 0 5 146 143 7 -5 86 77 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 4 -7 87 862 4 -7 42 42 4 -8 44 40 4 -8 32 19 4 9 156 153 | 1 7 31 27 1 -7 17 10 1 8 22 19 1 -8 18 13 1 9 6 6 | 6 -3 34 40 h = 8 | 4 -5 199 189 4 -5 19 18 4 -6 19 18 4 -6 115 115 | 0 -5 22 15 0 6 26 20 0 -6 116 112 0 -7 80 73 |
| 2 10 161 163 2 11 164 165 2 12 111 109 3 1 37 41 3 2 11 5 | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 2 -12 14 16 3 94 107 3 1 238 249 3 -1 125 138 3 2 280 267 | 4 - 10 163 187 5 - 10 160 76 5 - 12 25 23 5 - 13 36 33 | 1 -9 29 23 1 -10 27 22 1 -10 5 15 2 -12 15 15 | u 0 72 79 0 1 133 136 0 1 369 311 | 4 -8 111 113 5 0 53 51 5 1 79 81 5 -1 23 20 | 0 +9 51 48 0 -10 115 115 1 0 31 33 1 1 5 7 1 -1 58 58 |
| 5 5 55 + 9 5 4 10 9 5 5 58 37 3 6 7 5 6 7 7 10 | 0 -6 134 129 0 -9 13 7 0 -9 12 7 0 10 + 11 7 0 -10 72 74 | 3 -2 196 216 3 -3 46 3 -3 268 203 3 4 220 205 3 -4 220 205 | 22 23 24 23 24 24 25 25 25 25 25 25 25 25 25 25 25 25 25 | 2 1 281 273 2 -1 158 173 2 2 155 1444 2 -2 251 259 2 3 88 89 | 5 2 210 205 u -2 253 233 0 3 194 198 0 -3 163 155 | -2 175 44 -5 -3 -95 -45 -5 -3 -95 -95 -5 -4 -97 | |
| 3 8 * 6 13 3 9 29 27 3 10 * 8 3 3 11 38 36 5 0 51 677 | 0 11 93 88 0 -11 42 45 0 12 35 30 0 -12 90 88 0 -13 81 73 | 3 ~5 108 101 3 ~5 218 297 3 6 206 192 3 ≁6 95 93 3 ≁6 51 | 55555555555555555555555555555555555555 | 2 -3 236 236 2 4 195 172 2 -4 96 87 2 5 303 277 2 -5 80 79 | 0 -4 123 118 0 5 31 83 J -3 218 216 0 5 303 295 | 5 -6 28 29 h = 10 | 1 -5 - 26 - 25 1 -5 - 26 - 35 1 -5 - 5 - 5 - 5 1 -5 - 5 - 5 - 5 - 5 1 -5 - 5 - 5 - 5 - 5 - 5 1 -5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 |
| 4 1 43 35 4 2 81 87 4 3 102 104 4 3 22 307 | 1 0 +8 52 1 1 51 47 1 -1 25 27 1 -2 53 47 1 +2 55 65 | 3 -7 271 273 3 8 202 183 3 -8 9 9 3 -8 9 9 3 9 34 30 7 -9 191 199 | 25 - 7 * 3 + 3 + 3 + 3 + 3 + 3 + 3 + 3 + 3 + 3 | 2 6 13 16 2 -6 284 281 2 -7 60 59 2 -7 252 253 2 8 140 134 | 0 7 124 118 0 -7 47 47 0 8 43 41 0 -8 104 107 | 0 0 134 156 0 1 207 210 | 1 -7 - 12 14 1 -9 31 29 1 -10 13 13 2 0 32 38 2 1 44 53 |
| 4 7 204 194 4 7 204 194 4 8 242 225 4 9 61 63 | 1 3 57 52 1 -3 12 11 1 4 29 20 1 -4 63 62 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 6 -7 57 55 6 -3 13 14 | 2 -8 52 53 2 9 136 132 2 -9 97 132 2 10 40 35 2 -10 233 233 | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 0 -2 105 155 0 -2 100 91 0 -3 215 203 0 -3 215 203 | 2 -1 65 70 -2 -2 + 10 12 -2 + 10 12 -2 + 10 12 |
| 5 2 5 29 33 5 4 10 30 | +5 * 8 7 1 5 28 29 1 5 44 47 1 7 35 37 | 2 -1 17 19 | 6 4 56 52 6 4 44 43 6 5 41 40 | 2 -11 151 153 2 -12 48 52 3 0 16 15 3 1 107 110 3 -1 78 85 | 1 -2 22 24 | 0 -4 12 76 0 5 123 124 0 -5 158 155 0 5 194 195 | 2202200 44 5 44 5 44 5 44 5 44 5 44 5 44 5 45 5 44 5 45 5 46 |
| 5 6 8 1 5 7 33 32 5 8 2 1 5 9 1 5 | 1 -7 10 6 1 9 21 23 | 4 | h = 5 | 3 2 19 15 3 2 7 3 3 3 113 108 3 - 3 107 113 3 4 55 4 3 | 1 -3 47 50 1 -3 47 50 1 -4 36 34 1 -4 17 14 1 -5 54 54 | 0 -7 252 255 0 -7 252 255 0 -8 110 107 0 -8 180 126 | 2 -7 29 31 2 -8 20 15 2 -9 15 10 3 0 94 100 |
| 6 2 71 71 6 3 28 31 6 4 153 166 6 7 J | 1 9 40 38 1 10 9 16 1 11 42 41 1 11 28 27 | 4 5 4 6 3 4 -5 51 54 4 6 93 86 4 -9 46 51 | 1 0 104 113 1 40 36 1 -1 81 80 | 3 -4 35 35 3 5 105 98 3 -5 73 75 3 5 42 33 3 -6 51 51 | 1 6 17 1E 1 6 23 25 1 7 12 12 1 -7 56 56 | 0 -10 137 136 D -11 212 211 1 D 36 35 1 .123 19 | 3 -1 22 20 3 2 84 79 |
| | 1 -12 25 26 2 0 125 141 2 1 125 124 2 -1 98 111 2 -1 98 111 2 2 52 50 | 4 -7 27 27 4 8 74 72 4 8 27 27 4 9 15 10 4 9 77 30 | 1 2 19 23 1 3 69 64 1 3 49 34 1 4 266 213 | 3 7 74 73 37 57 56 33 8 59 426 3 8 18 167 | 1 - 3 = 10 1 - 3 = 20 20 - 26 1 - 9 - 37 - 37 1 - 10 - 34 - 33 1 - 10 - 34 - 32 | | 3 -4 123 117 3 -5 52 53 3 -6 79 75 3 -7 76 75 |
| n = 1 1 0 20 27 | 2 -2 20 20 - 2 3 110 100 2 -3 11 11 2 -3 259 240 2 -4 250 239 | -4 = 10 $31 = -365 0$ 76 $785 1$ 137 $1485 -1$ 69 $735 -1$ 157 | -4 67 87 60 75 11 -5 54 54 -54 -371 -55 - 371 | 5 -10 31 33 3 -11 51 53 4 0 47 47 4 1 128 139 | 1 -12 * 7 2 2 0 21 21 2 1 210 198 2 -1 91 101 2 -1 91 101 | 1 5 13 12 -5 4 A 2 1 6 13 6 1 7 4 8 2 1 -7 38 39 | 3 - 3 - 73 - 71 4 1 66 65 4 -1 4 3 72 4 -2 110 122 |
| 1 ~1 153 162 1 2 45 34 1 -2 60 57 1 3 207 191 | 2 -5 42 37 2 -5 120 122 2 -6 207 183 2 -6 74 68 | 5 -2 166 170 5 -3 175 194 5 -4 - 120 121 | 1 -7 31 16 1 -8 159 168 1 -8 70 60 | 4 -1 + 174 + 175 + 14 - 6 + 14 - 6 + 14 - 6 + 14 - 6 + 14 - 6 + 14 - 153 + 153 + 14 - 3 + 153 | 22 41 - 40 2 - 3 - 130 - 122 2 -3 - 179 - 184 2 - 4 - 76 - 69 2 - 4 - 46 - 45 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 4 -3 60 61 4 -4 58 63 |
| 1 4 90 85 1 4 82 76 1 5 246 231 1 -5 95 100 1 6 1,0 142 | 2 -7 62 61 2 8 109 99 2 -8 86 87 2 9 54 44 2 9 57 64 | 6 5 54 53 5 5 103 116 5 6 134 127 5 6 6 6 6 5 6 4 | 1 10 107 55 1 10 107 10 1 11 67 67 1 11 64 9 | 4 -4 21 13 4 -5 91 92 4 -5 199 24 4 -5 199 24 4 -6 44 192 | 2 5 183 174 2 -9 174 175 2 6 154 152 2 6 26 29 | 2 0 51 52 2 1 121 159 2 -1 219 243 2 -2 256 246 2 -2 117 119 | h = 13 1 ⊓ 19 17 |
| 1 -6 77 71 1 7 114 117 1 -7 167 170 1 8 131 127 1 -8 193 105 | 2 10 114 111 2 11 52 449 2 -11 75 73 2 -12 177 177 3 149 165 | 5 -7 147 152 5 -8 19 5 6 0 52 67 6 1 48 48 5 +1 36 29 | 2 D 89 56 2 1 20 21 2 2 3 91 58 2 2 2 91 58 | | 2 -7 131 130 2 8 99 93 2 -8 35 41 2 9 77 71 2 -9 84 85 | 2 -3 164 149 120 149 22 -4 32 359 22 -5 59 | 1 -1 109 137 1 -2 139 137 1 -2 49 49 1 -2 139 137 |
| 9 127 125 -9 53 55 1 14 146 133 1 ~10 32 25 1 11 35 37 | 3 1 98 102 3 -1 69 77 3 2 95 95 3 -2 132 149 3 3 117 107 | 6 2 580 627 6 23 29 27 6 3 29 27 6 4 3 29 27 6 4 3 29 27 | 22 - 45 - 542 - | 4 + 1 105 1242 - + 1 105 142 1 105 142 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 2 -5 241 237 2 5 297 390 2 -6 155 156 2 -7 66 55 2 -7 141 138 | 1 -4 -31 -41 1 -4 -31 -41 1 -5 -72 -67 1 -5 -115 -115 |
| 1 ~11 89 82 1 12 81 79 1 -12 63 67 2 1 9 95 | 3 -3 21 21 5 4 87 95 5 -4 125 131 5 88 81 7 -5 21 24 | 6 -4 44 55 6 5 31 28 6 -5 29 29 6 -6 32 37 | 2-55 665 85 -5-57 70 74 -7-77 72 74 | 5 3 118 124 5 -3 108 114 5 -4 19 118 5 -4 46 47 5 -4 107 103 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 2 -9 160 154 2 -10 63 60 3 -1 33 35 3 -1 39 32 | 1 -7 85 67 1 -8 91 85 1 -9 96 95 2 0 13 15 |
| 2 41 62 63 2 4 6 4 2 -2 19 8 3 104 97 2 -3 94 97 | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | h = 4 | 7 8 72 73 2 -8 46 47 2 9 11 12 2 -9 78 80 2 -9 78 80 | 5 -5 91 99 5 -6 68 91 5 -6 11 31 5 -7 62 65 5 -8 46 5 | 3 - 4 + 4 - 3 3 - 5 + 6 + 4 3 - 5 + 12 + 13 3 - 6 - 34 - 35 3 - 6 - 17 + 10 | 3 7 5 5 7 7 5 7 7 5 7 7 5 7 7 5 7 7 5 7 7 5 7 | 45 4 |
| 4 40 37 -4 10 70 5 76 70 22 -5 10 100 22 -5 19 15 | 3 9 7 7 7 7 7 7 7 7 7 | | 2 -10 14 27 7 -11 57 56 2 -12 * 5 9 3 0 78 84 3 1 * 10 11 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 3 -7 77 79 | | 2 -4 - 4 2 -5 -44 -44 2 -5 -22 -17 2 -7 -39 -44 2 -7 -39 -44 |
| -7 725 46 | 4 0 22 25 4 1 62 61 | 0 - 2 7040 2 20 0 - 3 240 2 20 0 - 3 240 2 20 0 - 4 196 | 3 -1 E3 57 3 -2 31 35 | 5 -3 + 10 + 12 5 -4 - 79 = 87 | 4 -1 193 207 4 -1 193 145 | 3 -8 21 20 3 -9 21 21 4 0 21 24 4 1 115 124 | 3 0 17 7 3 1 87 82 3 -1 105 107 3 -2 43 44 |
| 2 4 5° 54 2 - 4 30 51 | 4 -1 -27 -14 4 -2 -48 -47 4 -2 -11 -11 4 -3 -38 -40 4 -3 -36 -32 | 0 5 319 323 0 -5 65 65 0 6 177 172 0 -6 361 363 0 7 157 159 | 7 4 198 180 3 -4 40 40 3 -5 60 56 3 -5 68 65 3 -5 68 67 | 1 9 274 285 | 4 3 135 129 4 -3 76 84 4 4 54 51 - 4 55 57 5 5 57 | 4 2 93 97 4 2 57 61 4 3 42 38 4 -3 112 120 4 -3 113 15 | 3 -7 104 106 3 -4 50 56 3 -5 94 93 3 -6 65 66 |
| 2 10 33 31 2 10 46 45 11 26 29 2 11 42 43 2 12 17 36 | 4 4 22 20 4 44 12 7 4 5 103 91 4 -5 10 8 4 p 5754 | 0 -7 79 79 8 63 57 .0 -82047. n 9 255 240 8 9 51 47 | 3 -7 26 13 3 -7 26 323 3 -7 132 12 3 -7 132 12 3 -7 132 | 1 -1 17 10 1 -2 246 237 1 -2 292 287 1 -3 28 2 -2 292 287 1 -3 28 2 -1 -3 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 | 4 -5 134 142 4 -5 205 194 4 -6 40 41 4 -7 16 20 4 -8 92 92 | $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$ | h = 14 |
| 2 - 12 40 38 19 13 1 164 175 3 - 1 13 125 1 2 30 | 4 -7 - 6 - 64 - 65 4 -7 - 32 - 30 4 -8 - 44 - 4 4 -8 - 79 - 77 | 0 10 93 87 0 10 284 274 0 11 165 161 0 11 65 161 0 12 61 63 | 3 -9 44 44 3 10 52 49 3 -10 7 4 4 0 129 135 | 1 4. 260 252 1 -4 262 264 1 5 90 87 1 -5 1J5 104 1 6 199 195 | 4 -9 133 132 5 0 26 25 5 1 119 125 5 -1 191 108 5 2 28 25 | 5 1 + 28 28 5 - 1 + 28 31 5 - 1 - 28 31 5 - 1 - 28 31 | 0 0 223 260 0 1 87 92 0 -1 * 11 6 0 2 152 146 0 -2 179 170 |
| 3 -2 30 33 3 -3 145 138 3 -3 130 139 3 -4 43 48 3 -4 50 48 3 -4 50 48 | 4 - 7 - 14 - 17 - 44 - 7 - 14 - 11 - 44 - 10 42 - 44 - 44 - 5 - 0 - 140 - 150 - 5 - 1 - 107 - 107 - 5 - 1 - 107 - 107 - 5 - 1 - 107 | 0 - 13 22 25 1 0 48 52 1 1 11 5 1 - 1 9 9 1 2 59 50 | 4 -1 61 65 4 -2 137 140 4 -2 118 129 4 -3 35 30 4 -3 85 91 | 1 -6 180 188 1 7 80 74 1 -7 71 75 1 8 214 212 . 1 -9 242 248 | 5 -3 10A 116 5 -3 10A 116 5 -4 63 57 5 -4 03 57 | 5 -4 48 53 | 0 3 54 52 0 -7 27 13 0 -4 271 260 7 -5 58 56 9 -6 180 174 |
| 5 -5 b7 56 5 -6 80 74 3 -6 54 45 3 -7 105 978 3 -7 105 978 | 5 -2 112 121 5 -2 157 166 5 -3 112 116 5 -3 31 35 | 1 -2 + 5 - 8 1 -3 - 37 - 24 1 -3 -27 - 24 1 -3 -27 - 24 1 -4 -28 - 27 1 +4 - 44 - 43 | 4 4 143 137 4 -4 112 121 4 -5 19 21 4 -5 98 100 | 1 9 165 154 1 9 170 174 1 10 89 85 1 -10 19 85 1 -11 97 99 | 5 -6 37 37 5 -7 121 126 | | |
| 3 -5 90 86 3 -5 99 103 3 -7 14 105 3 -9 21 20 3 10 121 115 | 5 -4 137 152 5 5 121 116 5 -5 10 9 5 6 92 80 5 -6 121 129 | | 4 -6 83 88 6 -7 105 113 6 -8 115 113 6 -8 105 15 6 -9 105 15 6 -9 | 12 130 130 15 16 16 16 17 16 16 17 16 17 16 17 16 19 16 1 | 5 = 9 1 1 104 103 | | -3 26 26 -4 10 2 1 -5 5 7 1 -7 36 35 |
| 3 -10 26 19 3 11 28 23 3 +11 54 63 4 0 12 13 4 1 20 129 | 5 7 122 117 5 7 8 8 8 5 8. 59. 59. 5 8 112 120 6 9 51 51 | | 4 -10 34 74 5 0 61 66 5 1 31 27 5 -1 78 79 5 2 6 13 | 2 - 3 34 37 2 - 3 36 36 2 - 4 • 9 1 2 - 4 • 10 9 | 1 -1 106 96 1 -1 18 17 1 -2 40 40 1 -2 42 42 1 -2 51 49 | 1 -5 164 166 1 -6 189 191 1 -6 189 195 1 -7 209 195 1 -7 79 75 | 2 1 * 10 15 22 -1 62 62 22 -2 102 102 22 -2 102 102 |
| -1 127 140 -2 27 25 -2 4 3 -3 115 116 -3 131 119 | 6 -1 83 829 6 -2 61 65 6 -3 * 10 6 | 1 - 12 32 355 2 3 220 245 2 1 285 187 2 -1 285 187 2 -1 285 1824 | 25555555555555555555555555555555555555 | 2 -5 30 29 2 -6 8 7 2 -6 12 7 2 -7 19 17 3 -7 35 37 | 1 -3 120 119 1 4 13 7 1 -4 187 192 -1 -5 53 57 - 1 -5 24 22 | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 2 -4 274 269 2 -6 69 70 3 4 23 21 3 -1 34 31 3 -2 24 30 |
| 4 4 26 26 4 -4 20 20 4 5 368 149 4 -5 147 43 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | | 5 -6 12 10 5 -7 35 31 5 -8 77 14 | 2 -9 22 $222 -10 - 10$ $52 -11 - 27$ $232 -12 - 12 - 4$ | 1 -6 13 149 1 -6 819 120 1 -7 120 1 -7 120 | | 3 -3 * 11 °2 3 -4 16 10 |
| 6 40 41 4 7 93 93 4 -7 117 119 4 8 56 48 4 -8 78 79 | h = 3 | 2 -5 180 165 2 -5 131 129 2 -6 38 33 2 -6 177 181 2 7 259 248 | 6 -1 35 38 6 -1 81 83 6 -2 131 135 6 -2 131 135 | 3 0 195 212 3 1 21 21 3 2 184 183 3 -2 207 229 3 3 4 10 5 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 147 147 147 147 147 147 147 147 147 147 | 4 • 15 |
| 9 69 70 4 10 54 559 4 10 58 59 5 15 11 | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 2 -7 15 10 2 8 17 10 2 -8 17 10 2 -8 17 10 2 -9 122 122 2 -9 104 98 | 6 +3 84 87 6 -4 98 100 6 -5 99 105 | s -3 47 209 3 4 209 3 -4 205 209 3 -5 85 88 | C U 61 648 22 -1 651 649 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 - | 2 - 5 5 5 5 2 - 7 - 5 5 5 2 - 10 3 - 10 | 1 1 96 96 77 77 70 70 70 70 70 70 70 70 70 70 70 |
| 2 1 54 55 14 55 17 55 17 55 17 51 16 16 16 16 16 | 1 2 356 316 1 2 167 152 1 3 167 152 1 3 77 366 1 4 272 255 | 2 10 29 20 2 10 162 164 2 11 204 191 2 11 77 80 | h = 6 | 3 -6 129 131 3 -6 129 131 3 -7 -62 -56 | 1001148 0355848 0356453 0356453 0356453 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ |

 $T_{ABLE} \ 9c. \ Observed \ and \ Calculated \ Structure \ Factors \ for \ Synthetic \ Chevkinite, \ Co_4Nd_8Ti_6Si_8O_{44}.$

* Unobserved reflections are indicated with*.

Acknowledgments

The authors wish to express their gratitude to Dr. Jun Ito for supplying the crystals and to the National Research Council of Canada for a grant in support of this research.

References

- BONATTI, S. (1959) Chevkinite, perrierite, and epidotes. Am. Mineral. 44, 145-149.
- AND G. GOTTARDI (1966) Un caso di polimorfisma a strati in sorosilicate perrierite and chevkinite. *Period. Mineral.* **35**, 69–91.
- BROWN, I. D., AND R. D. SHANNON (1973) Empirical bond-strength bond-length curves for oxides. Acta Crystallogr. A29, 266–282.
- CALVO, C. (1967) The crystal structure of α Mg₂P₂O₇. Acta Crystallogr. 23, 289–295.
- CROMER, D. T. (1965) Anomalous dispersion corrections computed from self-consistent field relativistic Dirac-Slater wave functions. Acta Crystallogr. 18, 17-23.
- , AND J. T. WABER (1965) Scattering factors computed from relativistic Dirac-Slater wave functions. *Acta Crystallogr.* 18, 104–109.

- FINGER, L. (1969) An improved method of treating dependent parameters in least-squares refinement. Program Abstr., Am. Crystallogr. Assoc. Winter Meet., p. 54.
- GOTTARDI, G. (1960) Crystal structure of perrierite. Am. Mineral. 45, 1-14.
- ITO, J. (1967) A study of chevkinite and perrierite. Am. Mineral. 52, 1094-1104.
- -----, AND J. E. AREM (1971) Chevkinite and pertierite; synthesis, crystal growth, and polymorphism. Am. Mineral. 56, 307-319.
- KRISHNAMACHARI, N., AND C. CALVO (1972) The crystal structure of alpha cobalt diphosphate. Acta Crystallogr. **B28**, 2883-2885.
- LARSON, A. C. (1967) Inclusion of secondary extinction in least-squares calculations. Acta Crystallogr. 23, 664-665.
- PAULING, L. (1960) The Nature of the Chemical Bond, 3rd ed. Cornell University Press, Ithaca.
- PEN, CHEEJEE-CHORY'OUN AND CHEEJAS-LAU PAN (1964) The crystal structure of chevkinite. *Sci. Sinica*, **13**, 1539– 1545.
 - Manuscript received, November 19, 1973; accepted for publication, May 17, 1974.