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

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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 $\beta = 113.85(3)°$. 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, $\beta = 100.91(6)°$ 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 $A^{3+}{}_4B^{2+}C^{3+}{}_2Ti^{4+}O_8(Si_2O_7)_2$ 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 Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) was used in conjunction with a Syntex $P\bar{1}$ 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 perrierite 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 $F_c > F_o$. 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

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

	Perrierite* $Mg_2La_4Ti_3Si_4O_{22}$	Mg-chevkinite** $Mg_2Nd_4Ti_3Si_4O_{22}$	Co-chevkinite*** $Co_2Nd_4Ti_3Si_4O_{22}$
space group	$P2_1/a$	$P2_1/a$	$P2_1/a$
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)
Z	2	2	2
ρ	4.94	4.98	5.27
fw	1212.31	1233.60	1302.8

* 1878 reflections of positive measure used in the refinement.
** 1913 reflections of positive measure used in the refinement
***1414 reflections of positive measure used in the refinement.

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 site-occupancy 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 Si_2O_7 groups and MgO_6 or CoO_6 octahedra. For convenience Mg and Co will be designated as B ions. Each disilicate group is joined to six MgO_6 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 m symmetry. 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, $Mg_4La_8Ti_6Si_8O_{44}$
(standard errors in parentheses)

atom	x	y	z	U(Å²)
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)
O(11)	0.0652(6)	0.2556(14)	0.1858(7)	0.0103(14)
O(2)	0.2899(6)	0.2606(15)	0.1229(7)	0.0128(15)
O(21)	0.2875(6)	-0.2401(14)	0.1225(7)	0.0105(15)
O(3)	0.3736(6)	-0.2511(14)	0.4058(7)	0.0123(15)
O(31)	0.3920(6)	0.2862(15)	0.4066(8)	0.0139(15)
O(4)	0.0957(7)	0.0077(14)	0.9894(8)	0.0114(15)
O(5)	0.4067(7)	-0.0041(14)	0.0089(8)	0.0110(15)
O(6)	0.4932(7)	0.0328(15)	0.6667(8)	0.0150(16)
O(7)	0.2884(7)	-0.0337(16)	0.6366(8)	0.0176(17)
O(8)	0.1384(6)	-0.0036(14)	0.4042(7)	0.0115(15)
Mg	0	½	½	0.0047(9)
C(1)*	-0.0039(2)	0.2365(6)	0.0004(3)	0.0105(6)
C(2)*	0.2749(2)	0.0071(4)	0.017(2)	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.

TABLE 3. Atomic Parameters for Mg-Chevkinite, $Mg_4Nd_8Ti_6Si_8O_{44}$
(standard errors in parentheses)

atom	x	y	z	U(Å²)
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)
O(11)	0.2170(5)	0.2527(9)	0.3130(5)	0.0081(10)
O(2)	-0.0247(5)	-0.2527(9)	0.3742(5)	0.0085(10)
O(21)	-0.0214(5)	0.2448(10)	0.3736(5)	0.0093(10)
O(3)	0.4131(5)	-0.2493(10)	0.0946(5)	0.0093(10)
O(31)	0.4437(5)	0.2947(10)	0.0931(5)	0.0107(11)
O(4)	0.1457(6)	-0.0104(10)	0.4757(5)	0.0106(11)
O(5)	0.1511(6)	0.5044(10)	0.5099(5)	0.0105(11)
O(6)	0.0866(6)	0.5469(10)	0.1686(5)	0.0113(11)
O(7)	0.2741(6)	0.4477(10)	0.1307(6)	0.0151(12)
O(8)	0.3132(6)	0.4892(9)	0.0985(5)	0.0074(10)
Mg	0	1/2	0	0.0078(7)
C(1)	0.2434(2)	0.2466(3)	0.5000(2)	0.0082(3)
C(2A)	0	1/2	1/2	0.0111(5)
C(2B)	1/2	1/2	1/2	0.0093(4)

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.

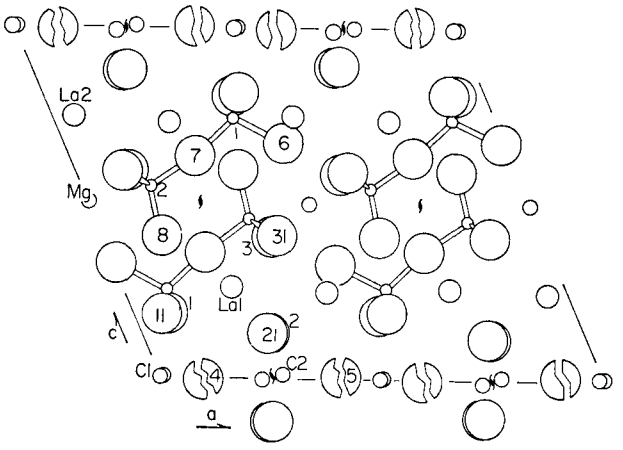


FIG. 1a. The 010 projection of the structure of perrierite. The circles represent oxygen atoms, rare-earth ions, divalent metal ions, and silicon atoms as their sizes decrease. The broken circles represent superimposed atoms.

Since $C(2)$ in perrierite 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 Co-chevkinite.

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 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 nonrandomly distributed among the remaining cation sites. Site $C(2)$ has 0.884 Ti in perrierite and shows high distortion with O(4) and O(5) separated by

TABLE 4. Atomic Parameters for Co-Chevkinite, $Co_4Nd_8Ti_6Si_8O_{44}$
(standard errors in parentheses)

atom	x	y	z	U(Å²)
Nd(1)	0.35651(5)	0.01889(12)	0.23426(7)	0.0099(3)
Nd(2)	0.06955(5)	-0.03317(13)	0.24116(6)	0.0089(3)
Si(1)	0.2008(3)	0.4974(5)	0.2298(3)	0.0053(7)
Si(2)	0.3584(3)	0.4993(6)	0.0464(3)	0.0063(7)
O(1)	0.2384(6)	-0.2725(15)	0.3137(8)	0.007(2)
O(11)	0.2183(6)	0.2595(15)	0.3126(8)	0.007(2)
O(21)	-0.0254(7)	0.2515(15)	0.3721(8)	0.008(2)
O(2)	-0.0241(7)	-0.2575(16)	0.3697(8)	0.012(2)
O(3)	0.4134(7)	-0.2550(16)	0.0957(8)	0.012(2)
O(31)	0.4402(7)	0.2880(17)	0.0954(9)	0.013(2)
O(5)	0.1516(7)	0.4959(15)	0.5092(8)	0.008(2)
O(4)	0.1450(7)	-0.0121(15)	0.4752(9)	0.007(2)
O(6)	0.0833(7)	0.5434(16)	0.1737(9)	0.010(2)
O(7)	0.2705(7)	0.4515(17)	0.1247(9)	0.013(2)
O(8)	0.3149(7)	-0.0097(15)	-0.0992(9)	0.011(2)
Co	0	1/2	0	0.0093(6)
C(1)	0.2447(2)	0.2456(6)	0.5003(3)	0.0106(8)
C(2A)	0	1/2	1/2	0.0119(2)
C(2B)	1/2	1/2	1/2	0.0129(9)

Co, C(2A) 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.

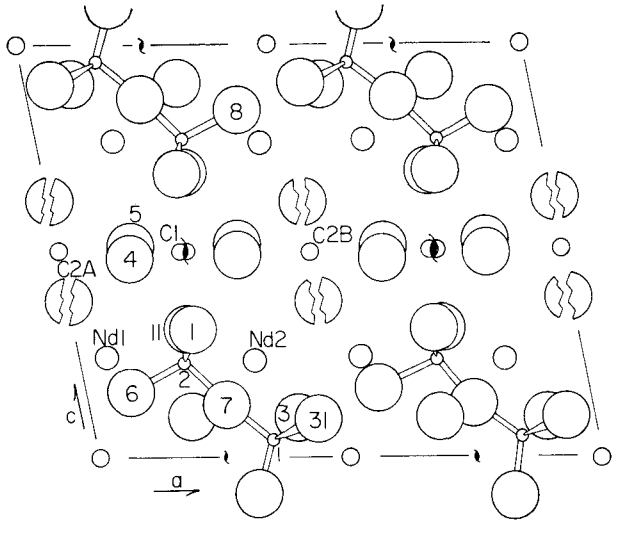


FIG. 1b. The 010 projection of the structure of chevkinite. The circles represent atoms as in Figure 1a. The relationship between the two structures is most clearly seen by superposing the origin of this figure, after reflection in the plane of the diagram, on the $x = 1$, $z = \frac{1}{2}$ position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

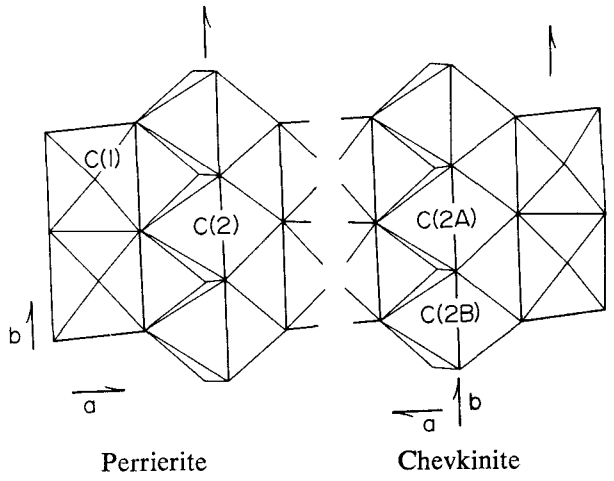


FIG. 2. A superposition of the octahedral sheets in perrierite (left hand side) and chevkinite (right hand side). The two structures have been superimposed as suggested in Figure 1b to emphasize their structural similarity. Note the reversal in the direction of the *a* axis and the positions of the two-fold 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 *a* axis. Analogous to that of *C*(2) in perrierite are the *C*(2*A*) and *C*(2*B*) octahedral sites in chevkinite, each of which has $\bar{1}$ 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 5. Bond Lengths and Angles in Perrierite and Chevkinite

bond	perrierite distance(Å)	Mg-chevkinite distance(Å)	Co-chevkinite distance(Å)
Si(1)-O(1)	1.645	1.639	1.626
-O(11)	1.646	1.636	1.628
-O(6)	1.605	1.580	1.594
-O(7)	1.636	1.618	1.634
Si(2)-O(7)	1.639	1.623	1.634
-O(8)	1.601	1.602	1.598
-O(31)	1.635	1.644	1.647
-O(3)	1.643	1.633	1.628
<Si-O>	1.642	1.629	1.632
angle	**(degrees)**	**(degrees)**	**(degrees)**
O(1)-Si(1)-O(11)	113.9	112.6	111.1
-O(6)	106.6	105.3	105.1
-O(7)	107.7	110.9	112.1
O(11)- -O(6)	112.2	113.6	112.4
-O(7)	101.7	101.4	102.8
O(6)- -O(7)	114.9	113.3	113.6
O(8)-Si(2)-O(31)	113.7	112.7	113.4
-O(3)	113.9	114.9	114.7
-O(7)	112.9	112.0	111.6
O(31)- -O(3)	107.3	107.5	107.0
-O(7)	102.3	101.5	101.8
O(3)- -O(7)	106.6	107.3	107.3
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

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

Bond length errors are of the order of 0.007Å.

TABLE 7. Selected Bond Lengths in Perrierite and Chevkinite

	perrierite distance(Å)	Mg-chevkinite distance(Å)		Co-chevkinite distance (Å)
B-O(31) (2x)	2.179	2.216		2.239
-O(3) (2x)	2.179	2.177		2.180
-O(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)-O(2)	1.979	C(2A)-O(2) (2x)	1.961	1.974
-O(2)'	1.963	-O(21)(2x)	1.997	1.993
-O(21)	1.956	-O(5) (2x)	1.998	2.003
-O(21)'	1.982	C(2B)-O(2) (2x)	1.984	2.035
-O(4)	2.421	-O(21)(2x)	1.955	1.981
-O(5)	1.789	-O(4) (2x)	2.011	2.004

The standard errors are of the order of 0.008Å.

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, O(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 $[A^{3+}{}_4B^{2+}C^{3+}{}_2Ti^{4+}{}_2O_8(Si_2O_7)_2]$. 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 perrierite, 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 perrierite 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 perrierite 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 perrierite-chevkinite stability.

TABLE 8. Selected Anionic Electrostatic Valencies

		Cations						
anion	model	RE	C(1)	C(2)	C(2A)	C(2B)	Si	$\sum$ -2
O(1), O(11)	a	0.708	0.535				1.00	+0.243
	b	0.667	0.550				1.00	+0.217
	c	0.667	0.500				1.00	+1.167
	d	0.667	0.583				1.00	+0.250
O(2), O(21)	a	0.708		1.257				-0.035
	b	0.667			0.607	0.607		-0.109
	c	0.667			0.500	0.500		-0.000
	d	0.667			0.583	0.583		-0.156
O(4)	a	0.333	1.070	0.314				-0.283
	b	0.333	1.100			0.617		+0.050
	c	0.333	1.333			0.500		+0.000
	d	0.333	1.166			0.483		+0.082
O(5)	a		1.070	0.943				+0.013
	b	0.333	1.100		0.607			+0.040
	c	0.333	1.333		0.500			+0.000
	d	0.333	1.16		0.58			+0.033

	mean charge			
model	site	C(1)	C(2)	C(2A) C(2B)
a) perrierite		3.23	3.77	
b) chevkinite		3.30		3.67 3.61
c) ordered chevkinite		3.0		4.0 4.0
d) random chevkinite		3.5		3.5 3.5

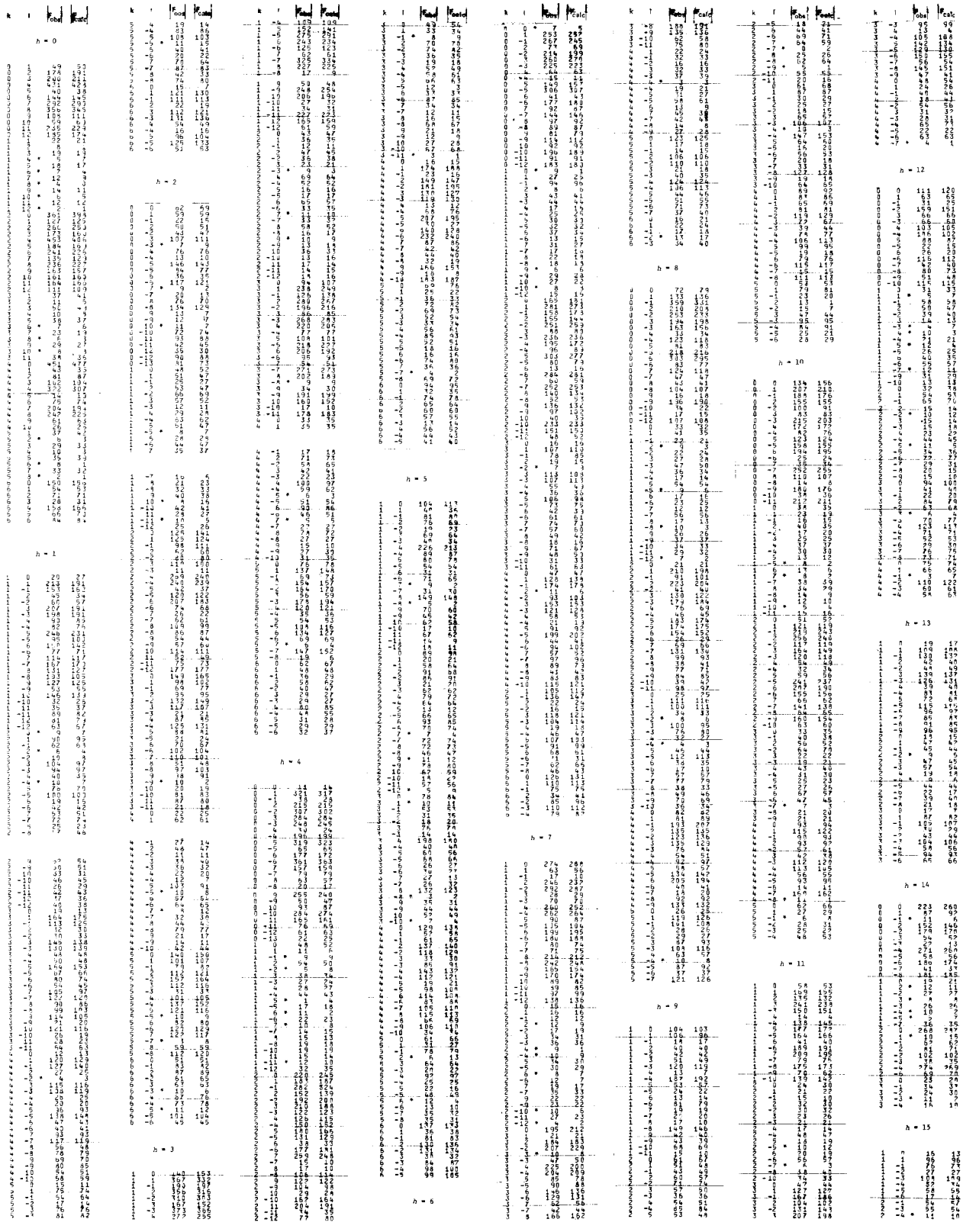
TABLE 9a. Observed and Calculated Structure Factors for Synthetic Perrierite, $Mg_4La_8Ti_6Si_8O_{44}$*

* *Unobserved reflections are indicated with *.*

TABLE 9b. Observed and Calculated Structure Factors for Synthetic Chevkinite, $Mg_4Nd_8Ti_6Si_8O_{44}$*

* *Unobserved reflections are indicated with*.*

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



** Unobserved reflections are indicated with*.*

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