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, \( 2[\text{Mg,La,Ti}\text{Si}_2\text{O}_8] \), has unit cell parameters \( a = 13.818(4) \) \( \text{Å} \), \( b = 5.677(2) \) \( \text{Å} \), \( c = 11.787(6) \) \( \text{Å} \), 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 \( 2[\text{Mg,Nd,Ti}\text{Si}_2\text{O}_8] \) has lattice parameters \( a = 13.328(10) \) \( \text{Å} \), \( b = 5.727(4) \) \( \text{Å} \), \( c = 10.971(8) \) \( \text{Å} \), \( \beta = 100.91(6)^\circ \) and refined to \( R = 0.043 \). The second with composition \( 2[\text{Co,Nd,Ti}\text{Si}_2\text{O}_8] \) has lattice parameters \( a = 13.328(10) \) \( \text{Å} \), \( b = 5.727(4) \) \( \text{Å} \), \( c = 10.971(8) \) \( \text{Å} \), \( \beta = 100.82(6)^\circ \), and refined to \( R = 0.050 \). Both structures have disilicate ions, \( \text{Si}_2\text{O}_5^- \), with nearly eclipsed configurations; \( \text{Si-O-Si} \) bond angles are 157.5° and 157.3° in the two chevkinites and 165.4° in perrierite. Two \( \text{Mg(Co)} \) ions per unit cell are octahedrally coordinated to oxygen atoms which are shared with six disilicate ions. The remaining cations of small radii, six \( \text{Ti} \) and two \( \text{Mg(Co)} \) ions per unit cell, are distributed non-randomly in sheets among sites with distorted octahedral coordination. The distribution of \( \text{Ti} \) and \( \text{Mg(Co)} \) 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 refined 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 \( A_3^+B_4^+C_2^+\text{Si}_2^+\text{O}_8(\text{Si}_2\text{O}_7)_2 \) 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 role 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\( \alpha \) radiation (\( \lambda = 0.71069 \) \( \text{Å} \)) was used in conjunction with a Syntex P\( \text{T1} \) 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 3\( \sigma \), where \( \sigma \) 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 \( F_o > F_c \). 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
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). The atomic and site-to-errors were less than 0.15, arcs were 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 $n[Mg(Si_2O_7)]$. 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 A, while in chevkinite $Nd(1)$ has nine oxygen atoms, including $O(5)$, within a similar sphere.

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

<table>
<thead>
<tr>
<th>Space group</th>
<th>$P2_1/a$</th>
<th>$P2_1/a$</th>
<th>$P2_1/a$</th>
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</thead>
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<tr>
<td>$a(\AA)$</td>
<td>13.816(4)</td>
<td>13.326(10)</td>
<td>13.325(4)</td>
</tr>
<tr>
<td>$b(\AA)$</td>
<td>5.677(2)</td>
<td>5.727(4)</td>
<td>5.706(2)</td>
</tr>
<tr>
<td>$c(\AA)$</td>
<td>11.787(6)</td>
<td>10.971(6)</td>
<td>10.998(6)</td>
</tr>
<tr>
<td>$\beta(\degree)$</td>
<td>90.000</td>
<td>90.000</td>
<td>90.000</td>
</tr>
</tbody>
</table>

* 1878 reflections of positive measure used in the refinement.
** 1913 reflections of positive measure used in the refinement.
*** 1914 reflections of positive measure used in the refinement.

### Table 2. Atomic Parameters for Synthetic Perrierite, Mg$_2$La$_4$Ti$_4$Si$_4$O$_{22}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U^{eq}$ ($\AA^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La$</td>
<td>0.23756(5)</td>
<td>0.01948(5)</td>
<td>0.26668(6)</td>
<td>0.00783(3)</td>
</tr>
<tr>
<td>$La$</td>
<td>0.04897(5)</td>
<td>0.02655(7)</td>
<td>0.0746(3)</td>
<td>0.0087(3)</td>
</tr>
<tr>
<td>$Si$</td>
<td>0.4123(2)</td>
<td>-0.0001(5)</td>
<td>0.7322(3)</td>
<td>0.0057(6)</td>
</tr>
<tr>
<td>$Si$</td>
<td>0.1624(2)</td>
<td>0.0027(5)</td>
<td>0.5630(3)</td>
<td>0.0069(3)</td>
</tr>
<tr>
<td>$O(1)$</td>
<td>0.0794(4)</td>
<td>-0.2597(4)</td>
<td>0.1864(7)</td>
<td>0.0091(14)</td>
</tr>
<tr>
<td>$O(2)$</td>
<td>0.0652(4)</td>
<td>0.2566(14)</td>
<td>0.1858(7)</td>
<td>0.0103(14)</td>
</tr>
<tr>
<td>$O(3)$</td>
<td>0.2899(6)</td>
<td>0.2606(15)</td>
<td>0.1225(7)</td>
<td>0.0128(15)</td>
</tr>
<tr>
<td>$O(4)$</td>
<td>0.2875(6)</td>
<td>-0.2407(14)</td>
<td>0.1225(7)</td>
<td>0.0128(15)</td>
</tr>
<tr>
<td>$O(5)$</td>
<td>0.3736(6)</td>
<td>-0.2511(14)</td>
<td>0.4058(7)</td>
<td>0.0123(15)</td>
</tr>
<tr>
<td>$O(6)$</td>
<td>0.3920(6)</td>
<td>0.2862(14)</td>
<td>0.4066(6)</td>
<td>0.0139(15)</td>
</tr>
<tr>
<td>$O(7)$</td>
<td>0.0597(5)</td>
<td>0.0014(5)</td>
<td>0.9904(6)</td>
<td>0.0174(15)</td>
</tr>
<tr>
<td>$O(8)$</td>
<td>0.4893(7)</td>
<td>-0.0328(5)</td>
<td>0.6667(6)</td>
<td>0.0150(16)</td>
</tr>
<tr>
<td>$O(9)$</td>
<td>0.2884(7)</td>
<td>-0.0337(6)</td>
<td>0.6667(6)</td>
<td>0.0150(16)</td>
</tr>
<tr>
<td>$O(10)$</td>
<td>0.1384(6)</td>
<td>-0.0336(4)</td>
<td>0.4047(6)</td>
<td>0.0115(16)</td>
</tr>
<tr>
<td>$Mg$</td>
<td>0.0047(9)</td>
<td>0.2385(6)</td>
<td>0.0004(3)</td>
<td>0.0105(6)</td>
</tr>
<tr>
<td>$Co$</td>
<td>0.2749(2)</td>
<td>0.0071(6)</td>
<td>0.0172(4)</td>
<td>0.0060(4)</td>
</tr>
</tbody>
</table>

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.
CRYSTAL STRUCTURES OF CHEVKNITE AND PERRIERITE

Table 3. Atomic Parameters for Mg-Chevkinite, MgNd,TiSiO₄
(standard errors in parentheses)

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>u²(Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(1)</td>
<td>0.35442(4)</td>
<td>0.022600(7)</td>
<td>0.23312(4)</td>
<td>0.0095(1)</td>
</tr>
<tr>
<td>Nd(2)</td>
<td>0.07127(4)</td>
<td>-0.03562(7)</td>
<td>0.24071(4)</td>
<td>0.0094(2)</td>
</tr>
<tr>
<td>Si(1)</td>
<td>0.2019(2)</td>
<td>0.4973(5)</td>
<td>0.2508(2)</td>
<td>0.0052(4)</td>
</tr>
<tr>
<td>Si(2)</td>
<td>0.3566(2)</td>
<td>0.5019(3)</td>
<td>0.0470(2)</td>
<td>0.0076(4)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.2393(5)</td>
<td>-0.2096(9)</td>
<td>0.3133(5)</td>
<td>0.0075(10)</td>
</tr>
<tr>
<td>O(11)</td>
<td>0.2175(5)</td>
<td>0.2527(19)</td>
<td>0.3130(5)</td>
<td>0.0081(10)</td>
</tr>
<tr>
<td>O(2)</td>
<td>-0.0271(6)</td>
<td>0.2472(5)</td>
<td>0.3745(5)</td>
<td>0.0098(10)</td>
</tr>
<tr>
<td>O(21)</td>
<td>-0.3241(5)</td>
<td>0.2484(10)</td>
<td>0.3736(5)</td>
<td>0.0093(10)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.4131(5)</td>
<td>-0.2544(15)</td>
<td>0.0495(5)</td>
<td>0.0093(10)</td>
</tr>
<tr>
<td>O(31)</td>
<td>0.4437(5)</td>
<td>0.2947(10)</td>
<td>0.0935(5)</td>
<td>0.0075(11)</td>
</tr>
<tr>
<td>O(4)</td>
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<td>-0.0104(10)</td>
<td>0.4755(5)</td>
<td>0.0106(11)</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.1611(6)</td>
<td>0.5044(10)</td>
<td>0.5099(5)</td>
<td>0.0105(11)</td>
</tr>
<tr>
<td>O(6)</td>
<td>0.0866(6)</td>
<td>0.5464(10)</td>
<td>0.1665(5)</td>
<td>0.0113(11)</td>
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<tr>
<td>O(7)</td>
<td>0.2741(6)</td>
<td>0.4577(10)</td>
<td>0.1307(5)</td>
<td>0.0151(12)</td>
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<tr>
<td>O(8)</td>
<td>0.3132(6)</td>
<td>0.4892(9)</td>
<td>0.0985(5)</td>
<td>0.0074(10)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(1)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mg(2)</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>Co(1)</td>
<td>0</td>
<td>1/2</td>
</tr>
<tr>
<td>Co(2)</td>
<td>1/2</td>
<td>1/2</td>
</tr>
</tbody>
</table>

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 Hg.

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 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 non-randomly 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, CoNd,TiSiO₄
(standard errors in parentheses)

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>u²(Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(1)</td>
<td>0.3555(5)</td>
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<td>0.0099(5)</td>
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<tr>
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<td>Si(1)</td>
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<td>0.2298(3)</td>
<td>0.0053(7)</td>
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<tr>
<td>Si(2)</td>
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<td>0.4992(6)</td>
<td>0.0464(3)</td>
<td>0.0057(7)</td>
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<tr>
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</tr>
<tr>
<td>O(11)</td>
<td>0.2183(6)</td>
<td>0.2595(15)</td>
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<tr>
<td>O(2)</td>
<td>-0.0254(7)</td>
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<td>O(21)</td>
<td>-0.0241(7)</td>
<td>-0.2575(16)</td>
<td>0.3697(6)</td>
<td>0.0122(2)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.4134(7)</td>
<td>-0.2550(16)</td>
<td>0.0997(6)</td>
<td>0.0122(2)</td>
</tr>
<tr>
<td>O(31)</td>
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<tr>
<td>O(4)</td>
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<tr>
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<tr>
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<tr>
<td>O(8)</td>
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</tr>
<tr>
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<td>0</td>
<td>0.0003(6)</td>
</tr>
<tr>
<td>Co(2)</td>
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<td>0.5002(13)</td>
<td>0.0106(6)</td>
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<tr>
<td>Co(3)</td>
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<td>0.0192(9)</td>
<td>0</td>
<td>0.0192(9)</td>
</tr>
</tbody>
</table>

Co, C(2A) and C(2B) lie in sites of type 2d, 2b and 2b, respectively. C(1) contains 0.807(7) Ti, C(2A) contains 0.834(9) Ti and C(2B) contains 0.884 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.

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 = 1/2 position of Figure 1a.
1.789 and 2.421 Å from the cation and with an O(4)-C(2)-O(5) angle of 178°. Adjacent C(2)O₆ octahedra are generated by the 2₁ 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(2A) and C(2B) octahedral sites in chevkinite, each of which has 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 6. Bond Lengths around the Rare Earth Ions in Perrierite and Chevkinite

<table>
<thead>
<tr>
<th>Bond</th>
<th>Perrierite Distance (Å)</th>
<th>Mg-Chevkinite Distance (Å)</th>
<th>Co-Chevkinite Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE₁(1)-O₁(1)</td>
<td>2.556</td>
<td>2.557</td>
<td>2.571</td>
</tr>
<tr>
<td>RE₁(1)-O₁(2)</td>
<td>2.549</td>
<td>2.434</td>
<td>2.492</td>
</tr>
<tr>
<td>RE₁(3)-O₁(3)</td>
<td>2.591</td>
<td>2.627</td>
<td>2.564</td>
</tr>
<tr>
<td>RE₁(3)-O₁(4)</td>
<td>2.636</td>
<td>2.836</td>
<td>2.495</td>
</tr>
<tr>
<td>RE₁(5)-O₁(5)</td>
<td>2.860</td>
<td>2.807</td>
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<tr>
<td>RE₁(8)-O₁(8)</td>
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<td>2.537</td>
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<tr>
<td>RE₂(1)-O₁(1)</td>
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<td>2.600</td>
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<tr>
<td>RE₂(1)-O₁(2)</td>
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<td>2.581</td>
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<tr>
<td>RE₂(3)-O₁(3)</td>
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Bond length errors are of the order of 0.007 Å.

### Table 7. Selected Bond Lengths in Perrierite and Chevkinite

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<tr>
<th>Bond</th>
<th>Perrierite Distance (Å)</th>
<th>Mg-Chevkinite Distance (Å)</th>
<th>Co-Chevkinite Distance (Å)</th>
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<tr>
<td>O₁(1)-O₁(11)</td>
<td>2.179</td>
<td>2.216</td>
<td>2.239</td>
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<td>O₁(2)-O₁(12)</td>
<td>2.179</td>
<td>2.177</td>
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<tr>
<td>O₁(3)-O₁(13)</td>
<td>2.014</td>
<td>2.003</td>
<td>2.036</td>
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<tr>
<td>C₁₁(1)-O₁(1)</td>
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<td>2.020</td>
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<td>C₁₁(2)-O₁(12)</td>
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<td>2.016</td>
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<td>1.924</td>
<td>1.951</td>
<td>1.996</td>
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<tr>
<td>C₁₁(5)-O₁(15)</td>
<td>2.014</td>
<td>1.992</td>
<td>1.995</td>
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<tr>
<td>C₁₁(6)-O₁(16)</td>
<td>1.978</td>
<td>1.938</td>
<td>1.942</td>
</tr>
<tr>
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<td>1.961</td>
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<td>C₁₁(8)-O₁(18)</td>
<td>1.961</td>
<td>1.961</td>
<td>1.974</td>
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The standard errors are of the order of 0.008 Å.
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 bonded 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 [A₄ textured BₓCₓ₂Tiₓ₂O₈₋₆(Si₄O₁₂)₉]. In terms of the present structure, A represents the rare-earth ion, B = Mg²⁺ or Co³⁺ 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>
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<tr>
<th>Anion</th>
<th>Model</th>
<th>Cations</th>
<th>C(1)</th>
<th>C(2)</th>
<th>C(2A)</th>
<th>C(2B)</th>
<th>Sr</th>
<th>( \sum -z )</th>
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<td>0.500</td>
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<tr>
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<td>c</td>
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<td>0.500</td>
<td>1.00</td>
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Table 8. Selected Anionic Electrostatic Valencies

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<th>Anion</th>
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<th>Cations</th>
<th>C(1)</th>
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Table 8. Selected Anionic Electrostatic Valencies
Table 9a. Observed and Calculated Structure Factors for Synthetic Perrierite, Mg$_2$La$_3$Ti$_6$Si$_3$O$_{18}$

* Unobserved reflections are indicated with *
TABLE 9b. Observed and Calculated Structure Factors for Synthetic Chevkinite, Mg$_6$Nd$_4$Ti$_8$Si$_6$O$_{44}$*

* Unobserved reflections are indicated with *.
**Table 9c. Observed and Calculated Structure Factors for Synthetic Chevkinite, Co\textsubscript{5}Nd\textsubscript{2}Tl\textsubscript{3}Si\textsubscript{3}O\textsubscript{14}**

*Unobserved reflections are indicated with*. 

---

*Table content*
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References


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