The Physical Properties of the Mg-Fe Richterites

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Abstract

Six compositions of amphiboles along the join Na₂CaMg₅Si₅O₁₆(OH)₆-Na₂CaFe₄Si₅O₁₆(OH)₆ have been synthesized, and the physical properties studied with respect to Pₒ₀, T, and fₒ． The fₒ was controlled by standard oxygen buffering techniques. The unit cell data for the compositions studied on the iron-wüstite buffer are:

<table>
<thead>
<tr>
<th>Composition</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>β</th>
<th>V(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₅Fe</td>
<td>9.902(1)*</td>
<td>17.980(4)</td>
<td>5.269(1)</td>
<td>104°13'(1)</td>
<td>909.4(3)</td>
</tr>
<tr>
<td>Mg₅Fe₁</td>
<td>9.917(2)</td>
<td>18.020(5)</td>
<td>5.277(1)</td>
<td>104°8'(3)</td>
<td>914.5(3)</td>
</tr>
<tr>
<td>Mg₅Fe₂</td>
<td>9.935(4)</td>
<td>18.063(3)</td>
<td>5.284(2)</td>
<td>104°5'(3)</td>
<td>919.6(6)</td>
</tr>
<tr>
<td>Mg₅Fe₃</td>
<td>9.962(5)</td>
<td>18.122(6)</td>
<td>5.292(2)</td>
<td>104°4'(2)</td>
<td>926.7(3)</td>
</tr>
<tr>
<td>Mg₅Fe₄</td>
<td>9.980(7)</td>
<td>18.180(7)</td>
<td>5.297(5)</td>
<td>103°58'(2)</td>
<td>932.7(9)</td>
</tr>
<tr>
<td>Fe₅</td>
<td>9.982(7)</td>
<td>18.223(6)</td>
<td>5.298(5)</td>
<td>103°44'(7)</td>
<td>936.2(1.0)</td>
</tr>
</tbody>
</table>

* Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 9.902(1) indicates an esd of 0.001.

Refractive indices increase linearly from α = 1.604(4) and γ = 1.622(3) at Mg₅ to α = 1.690(5) and γ = 1.710(4) at Fe₅. Experiments on buffers above iron-wüstite (I-W) yielded large amounts of clinopyroxene in addition to amphibole.

Mössbauer studies indicate Fe⁺⁺ is present in all cases. This fact is explained by structural and local charge balance considerations. It is concluded that Na in the M(4) site produces a local charge imbalance, which is corrected by placing Fe⁺⁺ in the neighboring M(2) site. Na is lost from the A site to maintain charge balance.

Introduction

Richterites are monoclinic amphiboles having high sodium, moderate calcium, and low alumina contents and lying between the calcic and sodic amphiboles of Ernst (1968). The ideal formula is

Na₂Ca(Fe, Mg)₅Si₅O₁₆(OH)₆,

but substitutions of K⁺ for Na⁺ and F⁻ for OH⁻ are common in nature. The amphibole structure consists of double chains of silicon tetrahedra linked by the M(1), M(2), and M(3) octahedra of 6-fold coordination and by the larger, 6- to 8-fold M(4) sites (Papike, Ross, and Clarke, 1969). The still larger, 8- to 12-fold A site completes this linking strip of cations. In richterite the A site is 8-fold and contains Na, whereas the M(4) site, also 8-fold, contains equal amounts of Na and Ca. The Fe and Mg are distributed between the remaining M sites, and OH⁻ occupies the O(3) sites.

Richterite is an uncommon alkali amphibole but is found in varied environments. Occurrences range from alkaline and peralkaline basalts to gneisses and impure metamorphosed limestones and meteorites. Analyses compiled by Deer, Howie, and Zussman (1963, pp. 352-358) indicate that most natural samples are relatively iron-free, or, when containing iron, much of it is in the ferric state. Richteritic amphibole has also been reported in an iron meteorite (Olsen, 1967) and in an enstatite chondrite (Douglas and Plant, 1968). Both of these examples contain significant amounts of F⁻ replacing OH⁻.

Natural examples of ferrous richterites, though few in number, are known. The lunar basalts have yielded one richterite of composition

(K₀.₂₈Na₂.₄₇Ca₀.₃₃)(Mg₃.₆₇Fe₁.₅₀Al₀.₁₉)

(Si₇.₉₉Al₀.₀₁)O₂₅(OH, F)₂

(Gay, Bancroft, and Bown, 1970). All Fe was assumed
to be ferrous. Compared with the fluororichterite synthesized by Huebner and Papike (1970) and the hydrous ferrous richterites presented here, the fluorine content of the lunar amphibole was probably high. Ferrorichterite has been reported by Nicholls and Carmichael (1969) from a Kenya pantellerite, both in phenocrysts,

\[
(K_{0.28}Na_{1.82}Ca_{0.77})(Fe_{4.68}Ti_{0.20}Mn_{0.13}Mg_{0.33})
\]

\[
(Si_{7.76}Al_{0.11})O_{20}(OH_{1.28}F_{0.01}),
\]

and as microlites in the glass,

\[
(K_{0.81}Na_{2.09}Ca_{0.70})(Fe_{4.72}Ti_{0.10}Mn_{0.13}Mg_{0.17})
\]

\[
(Si_{7.78}Al_{0.11})O_{20}(OH_{1.28}F_{0.02}).
\]

**Previous Investigations**

Experimental work has been confined primarily to the magnesian end member. The fluorine analogue was first synthesized by Eitel (1954) and Comeforo and Kohn (1955), whereas hydrous richterite was synthesized by Phillips and Rowbotham (1968). Huebner and Papike (1970) studied the effect of potassium substitution in richterite, and the stability field of richterite was first defined by Forbes (1971).

Work on the ferrous compositions has been limited to a study of the stability of the hydrogous analogue of a lunar richterite (Charles, Hewitt, and Wones, 1971), the synthesis of a potassic ferrorichterite by Huebner and Papike (1970), and the synthesis of a fluor iron-bearing richterite by Cameron and Gibbs (1971). In Table 1 the cell parameters obtained by previous investigators are compared with the results of this study.

The molecule \(Na_2Mg_5Si_8O_{22}(OH)_2\), "magnesi richterite," was first prepared by Iiyama (1963); and Gibbs, Miller, and Shell (1962) determined the cell constants of its fluorine analogue. In this study magnesi richterite refers to the composition \(Na_2CaMg_5Si_8O_{22}(OH)_2\) and should not be confused with the calcium-free compositions.

**Experimental Procedure**

Oxide mixes were prepared for six compositions at equally spaced points on the join

\[Na_2CaMg_5Si_8O_{22}(OH)_2-Na_2CaFe_5Si_8O_{22}(OH)_2.\]

Iron was introduced as hematite, and portions of each mix were heated under \(H_2\) to reduce the iron to the native state. Results were consistent regardless of the initial oxidation state of the iron. Oxygen fugacities were buffered using the following techniques: (1) solid oxygen buffers (Eugster, 1957); (2) hydrogen diffusion membrane (Shaw, 1967); (3) graphite-methane buffer (Eugster and Skippen, 1967). The charges and buffers were sealed in precious metal capsules and subjected to pressure and temperature in standard hydrothermal apparatus.

**Description of Phases**

Microscopic examination reveals that 2-day experiments at 800°C and 1 kbar produced 98–100 percent magnesi richterite. The amphibole consisted of elongate euhedral grains, some occurring in a felty mass. Amphibole containing iron was grown most readily on the iron-wüstite (I-W) buffer. Compositions containing more iron than \(Fe_2Mg_3\) invariably produced 20–30 percent clinopyroxene in addition to amphibole on buffers more oxidizing than iron-wüstite. At more oxidizing buffers than C-CH₄ only the \(FeMg_4\) composition could be grown at greater than 95 percent purity. However, even \(FeMg_4\) yielded significant amounts of clinopyroxene (>10 percent) on the hematite-magnetite (H-Mt) buffer. High purity is important because the pyroxene grown on H-Mt is acmite, judging from the powder X-ray diffraction pattern. If the clinopyroxene exceeds a
few percent, the resulting amphibole is nonstoichiometric, as shown by the lattice parameters for Mg₃Fe on various buffers. Small amounts (<5 percent) of pyroxene, olivine, and glass were assumed to be roughly equal to the bulk composition of the mix. For such a small amount of pyroxene the partitioning of Fe and Mg between pyroxene and amphibole was ignored. The effect of the introduction of pyroxene to the products is shown in Figure 1 and Table 2 for results on quartz-fayalite-magnetite (QFM). Between Mg₆Fe and Mg₃Fe₂ pyroxene appears, and on Mg₆Fe₂ equals about 10–15 percent of the products. The cell volume for Mg₆Fe₂ approximately equals that for Mg₃Fe. Pyroxene increases in abundance until 30–40 percent of the charge is pyroxene at Feₛ. Attempts to produce ferrorichterite on the QFM buffer yielded a very dark green amphibole plus about 40 percent pyroxene. Presumably, the color indicates the increased content of ferric iron in the amphibole.

The amphibole changed greatly in optical character along the magnesiorichterite-ferrorichterite join. Figure 2 and Table 3 display the change in refractive indices on the I-W buffer. The extinction angle (γ = Z) increases from roughly 5°–10° for the magnesian compositions to 10°–15° for the iron-rich varieties. Color varies from white to green across the compositional field. The pleochroism—X-green; Y-yellow-green; Z-green—is most easily seen in the more ferrous amphiboles.

Experiments conducted on I-W at low temperatures (500°–550°C) produced a finely crystalline mass containing >95 percent amphibole with subordinate pyroxene, olivine, and clear glass for the compositions Mg₆Fe through Mg₆Fe₂. Most of the crystals, regardless of composition, were <5 μm in greatest dimension. The Mg₆Fe₂ richterite was difficult to grow at less than 5 kbar. Almost invariably, charges of this composition contained >10 percent pyroxene at low pressures. The Mg₆Fe₂ amphibole was always very hard and brittle whereas all other compositions were soft and fibrous.

Ferrorichterite can be characterized as a short prismatic green amphibole with nₓ = 1.710(3) and nᵧ = 1.690(5). Two varieties were synthesized. Shorter synthesis experiments (<10 days) at higher temperatures (600°–700°C) resulted in a coarse amphibole accompanied by about 10 percent clinopyroxene, fayalite, and a trace of glass. Longer experiments (22–30 days) at lower temperatures (500°–530°C) yielded fine-grained amphibole (>95 percent) plus a few percent clinopyroxene, olivine, and clear glass. The pyroxene was a striking bright green with refractive index around 1.730. Fayalite appeared as roughly equant grains with a light brown color. It is important to point out that less ferrous compositions yielded only one variety of amphibole regardless of the synthesis time.

For the series in general, clinopyroxene, olivine, and glass were always less than 5 percent for compositions Mg₃ through Mg₆Fe₂ and for long experiments on Feₛ. Short experiments on Feₛ and low-pressure experiments on Mg₆Fe₂ (<5 kbar) yielded 10 percent or more clinopyroxene, olivine, and glass. Long experiments on Feₛ contained more glass than those on any other bulk composition; however, the amount was only 2–3 percent.

**X-Ray Determinations**

The unit cell parameters were determined using a Norelco powder X-ray diffraction goniometer. Scans of 1/2° per minute at a strip chart recorder rate of 1/2 in. per minute were satisfactory to fix the peak positions of amphibole to ±0.01°, standardized against BaF₂ (a = 6.1971 ± 0.0002 Å). BaF₂ in turn was standardized against diamond (a = 3.56703 ± 0.00018 Å) and has four usable reflections between 24° and 49°. The 220 reflection of BaF₂ at 41.164°
<table>
<thead>
<tr>
<th>Composition</th>
<th>T (°C)</th>
<th>P (kbar)</th>
<th>Duration (hr)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>a sin β (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂Ca₂Mg₂Si₄O₂₂(OH)₂ + Px</td>
<td>850</td>
<td>1</td>
<td>48</td>
<td>9.903(1)*</td>
<td>17.982(2)</td>
<td>5.267(1)</td>
<td>104°14'(1°)</td>
<td>909.2(1)</td>
<td></td>
</tr>
<tr>
<td>Na₂Ca₂Mg₂Si₄O₂₂(OH)₂</td>
<td>850</td>
<td>1</td>
<td>96</td>
<td>9.903(3)</td>
<td>17.976(2)</td>
<td>5.270(2)</td>
<td>104°13'(1°)</td>
<td>909.4(3)</td>
<td></td>
</tr>
<tr>
<td>Na₂Ca₂Mg₂Si₄O₂₂(OH)₂</td>
<td>800</td>
<td>1</td>
<td>48</td>
<td>9.901(2)</td>
<td>17.976(2)</td>
<td>5.270(1)</td>
<td>104°12'(1°)</td>
<td>909.3(2)</td>
<td></td>
</tr>
<tr>
<td>Na₂Ca₂Mg₂Si₄O₂₂(OH)₂</td>
<td>800</td>
<td>1</td>
<td>96</td>
<td>9.902(1)</td>
<td>17.980(4)</td>
<td>5.269(1)</td>
<td>104°13'(1°)</td>
<td>909.3(4)</td>
<td></td>
</tr>
</tbody>
</table>

*Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 9.903(1) indicates an esd of 0.001.
Fig. 2. Alpha and gamma refractive indices for the amphibole series grown on the I-W buffer. Mg$_3$Fe$_2$ and Mg$_5$Fe$_3$ yielded only bulk indices.

could not be used for compositions more iron-rich than Mg$_3$Fe$_2$ owing to overlap of the 261 reflection of the richterites. The richterites were indexed and cell parameters calculated using a program developed by Evans, Appleman, and Handwerker (1963). Twenty-four reflections for magnesiorichterite were unambiguously indexed using the cell refinements of Huebner and Papike (1970). The number of usable reflections decreases to sixteen for ferrorichterite. Some peaks, for example 020, decrease in intensity; others are broadened by poorer crystallinity; and one, 261, interferes with a standard peak.

A continuous shift in peak position toward lower angles and changes in intensity of a given reflection occur with addition of iron. Sample results are reproduced in Table 4 for magnesiorichterite and ferrorichterite. All cell dimension data with buffer and P-T conditions are listed in Table 2.

The uniformity of cell parameters on I-W in P-T space is shown in Figure 3 for Mg$_4$Fe, Mg$_5$Fe$_2$, and Mg$_5$Fe$_5$. The cell volumes of quench phases remain essentially constant in the pressure range 1 to 10 kbar and temperature range 500° to 650°C.

Mg-richerite has a rather low stability limit with respect to pressure, as indicated by the experiments listed in Table 5. Changes in cell dimensions occurred between 2 and 7 kbar even though the charge was > 95 percent amphibole. Experiments of 6 days at 7 kbar and 600°C using an oxide mix yielded quartz in addition to amphibole. Quartz is gradually resorbed and after 20 days is absent. At 10 kbar and 510°C, experiments of 25 days’ duration produced persistent quartz plus an amphibole with a powder pattern not unlike that of tremolite. The cell parameters do show some trend toward tremolite with increasing P. Most striking is the distinct trend of $a$ sin $\beta$ and $b$.

Addition of Fe to richterite apparently stabilized the structure to higher P because all experiments at high P containing iron show no variation in cell parameters. Greater iron concentrations (i.e., Mg$_4$Fe$_2$ and Fe$_5$) were not plotted because the number of experiments is insufficient to show any trend in cell volume with P and T.

The uniformity of cell volume on a given buffer is shown in Figure 4 for Mg$_4$Fe at a $P_{\text{total}}$ of 1 kbar. Two points should be noted here. First, the uniformity of the amphibole cell volume even in the presence of large amounts (>10 percent) of pyroxene on H-Mt is evident. [The pyroxene will be completely characterized in a later paper on a study of the phase equilibria of the richterites. Preliminary examination of its cell constants indicates it is an acmite diopside.] Second, the apparent constancy of the cell volume along the C-CH$_4$ buffer is unexpected. Because the C-CH$_4$ buffer does not parallel the other buffer curves, the volume should increase at higher temperatures. This effect, however, is not recognized for so small a concentration of iron. Other compositions of amphibole on buffer curves more oxidizing than I-W will be examined closely in the phase equilibrium studies for uniformity with P and T.

Figure 5 exhibits the variation in cell volume and $a$ sin $\beta$ with oxygen fugacity at $P_{\text{total}}$ = 1 kbar, $T$ = 650°C, and constant composition (Mg$_4$Fe). Cell volume and $a$ sin $\beta$ are largest for the iron-wüstite (I-W) buffer but are roughly equal for fugacities

Table 3. Optical Properties

<table>
<thead>
<tr>
<th>Composition</th>
<th>Buffer</th>
<th>$\alpha$</th>
<th>$\gamma$</th>
<th>Mean R.I.</th>
<th>Maximum Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_5$</td>
<td>I-W</td>
<td>1.604(5)</td>
<td>1.622(3)</td>
<td>25 x 5</td>
<td></td>
</tr>
<tr>
<td>Mg$_5$Fe</td>
<td>I-W</td>
<td>1.623(3)</td>
<td>1.636(3)</td>
<td>15 x 3</td>
<td></td>
</tr>
<tr>
<td>Mg$_5$Fe$_2$</td>
<td>I-W</td>
<td>1.640(5)</td>
<td>1.653(5)</td>
<td>10 x 2</td>
<td></td>
</tr>
<tr>
<td>Mg$_5$Fe$_5$</td>
<td>I-W</td>
<td>1.668(5)</td>
<td>1.680(5)</td>
<td>30 x 10</td>
<td></td>
</tr>
<tr>
<td>Fe$_5$</td>
<td>I-W</td>
<td>1.690(5)</td>
<td>1.710(5)</td>
<td>10 x 2</td>
<td></td>
</tr>
</tbody>
</table>

*Parenthesized figures represent the estimated standard deviation (r.s.d.) in terms of least units cited for the value to their immediate left, thus 1.604(5) indicates an r.s.d. of 0.005.
between the C-CH₄ and nickel-nickel oxide (N-NO) buffers. At fₒ, higher than the N-NO buffer, pyroxene appears in increasing amounts, causing the unit cell volume of the amphibole to drop off rapidly. The trend in lattice parameters is generally toward magnesioriebeckite.

Because the I-W buffer produced the highest yields of amphibole, the cell parameters calculated from these run products must be examined very closely to interpret the variations in these parameters in light of the richterite structure. The data plotted in Figure 6 are taken from Table 2. Both ferrorichteritic amphiboles are plotted, with experiments of lower yield plotted in parentheses. The parameters a, c, and a sin β increase almost linearly from Mg₂ to MgFe; for more iron-rich compositions, however, the curves for all parameters appear to branch. The values for b are slightly below the line for the compositions Mg₆Fe, Mg₆Fe₂, and Mg₆Fe₅, whereas β decreases monotonically. The volume of mixing for the compositions Mg₆Fe and Mg₆Fe₂ is slightly negative. Ideal mixing, of course, would be linear. Only some of these observations are statistically real. These observations and structural arguments will be applied to show that the less statistically accurate deviations from linearity are also real.

Each straight line and dashed extension in Figure 6
was drawn not as a least-squares fit but with these considerations in mind: (1) the Mg$_6$ composition yields correct parameters; (2) it is assumed that $A$ and $M(4)$ are uniformly occupied by the same cations throughout, and all other $M$ sites are the same size with no preferred ordering of cations. Obviously, (2) is not true and deviations from linearity will be discussed on such a basis.

Preliminary results from Mössbauer work by D. Virgo (personal communication, 1972) indicate roughly 5 percent ferric iron is present in the amphibole at Fe$_5$ that is on the linear trend shown in the cell parameter diagrams. The purest ferr richterite, however, contains noticeably more (>10 percent) ferric iron and deviates from this trend. At least four mechanisms of incorporation of ferric iron into the amphibole structure relevant here are possible. First, ferric iron commonly can be explained by assuming that Fe$^{3+}$ and O$^{2-}$ replace Fe$^{2+}$ and OH$^{-}$ to produce oxyamphibole. Effectively, hydrogen is removed from the structure and iron is oxidized to Fe$^{3+}$. Second, H$_2$O may leach Na from the amphibole so that Fe$^{3+}$ and a vacancy substitute for Fe$^{2+}$ and Na. Third, either of these could be accomplished if there is a structural limitation on the amount of ferrous iron in the five $M(1), M(2),$ and $M(3)$ sites in the unit cell. Bancroft and Burns (1969), Wilkins (1970), and Mitchell, Bloss, and Gibbs (1970) indicate that the $M(2)$ site is smaller in hydrous amphiboles and generally accepts magnesium or ferric iron instead of the larger ferrous iron. This may not be true for fluoroamphiboles (Cameron and Gibbs, 1971) because iron does not coordinate well with fluorine. The only $M$ sites not coordinated with fluorine in O$_2$ are the two $M(2)$ sites. Fourth, Ghose (1966) and Whittaker (1949, 1960) postulated that, if Na occupies the $M(4)$ site, a local charge imbalance will result since the Na is coordinated with six oxygens. Such an imbalance would be corrected by addition of ferric iron into the $M(2)$ site because $M(2)$ lies closest to $M(4)$ (Papike, Ross, and Clarke, 1969). To complete charge balance in richterites, either Na$^+$ or H$^+$ must

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**Table 5. Mg-Richterite at Increasing Pressure**

<table>
<thead>
<tr>
<th>$P$ (bars)</th>
<th>$T$ ($^\circ$C)</th>
<th>Duration (hr)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$</th>
<th>$V$ (Å$^3$)</th>
<th>$\Delta\ln V$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>700</td>
<td>72</td>
<td>9.901(2)$^*$</td>
<td>17.976(4)</td>
<td>5.270(1)</td>
<td>104.712' (1')</td>
<td>909.4(0.3)</td>
<td>9.599</td>
</tr>
<tr>
<td>2000</td>
<td>800</td>
<td>48</td>
<td>9.903(1)</td>
<td>17.982(2)</td>
<td>5.287(1)</td>
<td>104.716' (1')</td>
<td>909.7(0.1)</td>
<td>9.599</td>
</tr>
<tr>
<td>5000</td>
<td>700</td>
<td>119</td>
<td>9.884(7)</td>
<td>17.984(7)</td>
<td>5.268(3)</td>
<td>104.849' (3')</td>
<td>907.7(0.6)</td>
<td>9.587</td>
</tr>
<tr>
<td>7000</td>
<td>600</td>
<td>456</td>
<td>9.893(3)</td>
<td>18.003(8)</td>
<td>5.286(2)</td>
<td>105.166' (2')</td>
<td>909.5(0.4)</td>
<td>9.589</td>
</tr>
<tr>
<td>10,000</td>
<td>510</td>
<td>600</td>
<td>9.896(7)</td>
<td>18.001(9)</td>
<td>5.270(3)</td>
<td>104.202' (3')</td>
<td>906.6(0.6)</td>
<td>9.588</td>
</tr>
<tr>
<td>Tremolite</td>
<td>(Papike et al., 1969)</td>
<td>9.818(5)</td>
<td>18.047(8)</td>
<td>5.273(3)</td>
<td>104.399' (3')</td>
<td>904.2(0.6)</td>
<td>9.499</td>
<td></td>
</tr>
</tbody>
</table>

*Parenthesized figures represent the estimated standard deviation (e.s.d.) in terms of least units cited for the value to their immediate left, thus 9.901(2) indicates an e.s.d. of 0.002.

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**Fig. 4. Uniformity of cell volume along a given buffer for Mg$_6$Fe$_4$ at $P_{total} = 1$ kbar.**

1 For potassic richterite: $M(2)$-$M(4) = 3.182$ Å; $M(1)$-$M(4) = 3.410$ Å.
be removed elsewhere. Burns and Prentice (1968) support the charge balance theory by reporting the preferential positioning of Fe$^{3+}$ in M(2) in riebeckites (Na$_3$Fe$^{2+}$_xFe$^{3+}$ySi$_8$O$_{22}$(OH)$_2$), which necessarily have Fe$^{3+}$ in their structural formula.

**Discussion**

The key to the interpretation appears to be that (1) all experiments on I-W contain a trace amount of glass, and (2) the long syntheses of ferrorichterite (22–30 days) contain a larger amount of glass. Production of an oxyamphibole would yield no glass. The H$_2$O leaching of Na and Si should have caused more scatter in the data points depending upon time and the amount of H$_2$O in the experiments. In addition, leaching would not have preferentially occurred in long syntheses of just ferrorichterite composition. Syntheses of equal or longer duration were performed on Fe$_5$Mg$_3$ and Fe$_3$Mg with no such branching of the cell parameters. Any explanation such as alloying of iron in the A$_{89}$C$_{21}$O$_{32}$ fails for the same reason. One is left with the conclusion that five ferrous irons may just be too large to fit in the amphibole structure, especially in close proximity to Na in M(4). Because all experiments on I-W started with a reduced mix containing native iron, short experiments on this buffer may have metastably yielded a ferrous amphibole whose ferrorichterite composition agrees with the extrapolated cell parameter curves. This amphibole, presumably not the stable form, is more nearly a completely ferrous amphibole. Preliminary Mössbauer results indicate that the Fe$^{3+}$/Fe$^{2+}$ ratio for this phase is less than that for Mg$_5$Fe$_3$. 

![Figure 5](image1.png)  

**FIG. 5.** Variation of cell volume with log $f_2$ for Mg$_4$Fe at $T = 650^\circ$C, $P_{\text{total}} = 1$ kbar.

![Figure 6](image2.png)  

**FIG. 6.** Variation of unit cell parameters for the amphibole series grown on I-W. Both Fe$_5$ varieties are plotted.
Using these interpretations, the observed lattice constants can be explained completely. The parameter \(a\) depends upon the mean size of the cations in the linking cation strip (Ernst, 1968; Huebner and Papike, 1970). It should be a linear function if the incremental change in cation size remains constant as one proceeds across the series. Beyond MgFe\(_2\), the mean size of the cations increases at a smaller rate because of sodium loss and the introduction of more ferric iron.

The parameter \(b\) is influenced most by the occupancy of the \(M(4)\) and \(M(2)\) sites, which actually link the double chains of silicon tetrahedra (Colville, Ernst, and Gilbert, 1966; Ernst, 1968). The \(M(4)\) site is occupied by Na and Ca in all these amphiboles. Of secondary importance are the other \(M\) sites. Although not actually linking the double chains, they may cause some increase in the \(b\) dimension when occupied by larger cations. The diagram presented here clearly shows that, while the two \(M(1)\) and \(M(3)\) sites are filling preferentially with ferrous iron (Mg,Fe to Mg,Fe), the observed points drop below the line representing uniform, totally disordered filling of the \(M\) sites. Complete ordering is not observed from the Mössbauer spectra. More will be stated on this point when all the Mössbauer data are analyzed. The deviation at Fe\(_2\) is small. Only 10 percent ferric iron apparently has little effect on the \(b\) dimension.

The parameter \(c\), or chain length, is controlled by (1) the size of cations in the \(M(1)\) and \(M(3)\) sites (Colville, Ernst, and Gilbert, 1966) and/or (2) the size of the tetrahedral cations (Ernst, 1968). In spite of the great difference in size between Fe\(^{3+}\) and Si in 4-fold coordination, 0.40 Å vs 0.63 Å (Shannon and Prewitt, 1969), local charge imbalance may require some Fe\(^{3+}\) to enter and lengthen the chain to balance the Na in the \(A\) site. Judging from the structure, large cations in \(M(2)\) should also affect the chain length. Once again an essentially uniform linear trend is observed until more ferric iron is present, causing a much smaller stretching of the chain. If the increased Fe\(^{3+}\) goes into \(M(2)\) instead of a tetrahedral site, less expansion occurs along \(c\), as is observed.

Huebner and Papike (1970) show clearly that the \(A\) site controls angle \(\beta\) as well as influencing \(a\). Addition of larger cations to \(A\) causes \(\beta\) to increase. In sodic richterite the \(A\) is uniformly filled with Na, but as one proceeds from Mg\(_2\) to Fe\(_2\), the structure expands around the Na to produce an effect equivalent to placing a relatively smaller cation in the \(A\) site. Consequently, \(\beta\) decreases. Near Fe\(_2\), it decreases more sharply owing to not only Fe\(^{3+}\) but actual Na loss.

The parameter \(a\) sin \(\beta\) reflects the mean size of the cations in the linking cation layer more clearly than does \(a\) because this dimension is perpendicular to the layer of \(M\) sites. The \(M(1)\) sites project more into the rings formed by the double chains and have less influence than the other \(M\) sites. Also, a larger portion of the iron in lower iron compositions is Fe\(^{3+}\) owing to Na in \(M(4)\). The effect is small, but it can be seen in the compositions Mg\(_2 Fe\) and Mg,Fe\(_2\), which fall below the linear curve. Loss of Na and oxidation of Fe\(^{2+}\) cause a small decrease at Fe\(_2\).

Combining the effects of all other cell parameters, the cell volume shows a slightly negative volume of mixing on the low-iron compositions and a slightly positive volume of mixing on the high-iron compositions.

Using these physical properties, ferrorichterite can be compared with the other iron-bearing amphiboles. The stability of ferropargasite (NaCa\(_2 Fe^{2+}_4 AlSi\(_8\) Al\(_2\)O\(_{22}(OH)\(_2\)\)), ferrotremolite (Ca\(_2 Fe\)\(_2\)Si\(_8\)O\(_22\) (OH)\(_2\)\)), and riebeckite-arfvedsonite (Na\(_2 Fe^{2+}_4 Fe^{3+}_1 Si\(_7\)Fe\(^{3+}\)\(_{0.3}\) (OH)\(_2\)\)) have been experimentally defined by Gilbert (1966), Ernst (1966), and Ernst (1962), respectively. Table 6 and Figure 7 show pertinent data regarding their upper stability limits. The decomposition curve of ferrorichterite has been added. Its phase equilibria will be covered in more detail in a later paper. When these results are compared, calcium vs sodium should have little effect on the stability limit (Ernst, 1968).

Ferropargasite, which shows the greatest stability, has Al and Fe\(^{2+}\) in the \(M(2)\) sites and Al in the double chains. Ferropargasite is stable to a much higher \(f\(_{O_2}\)\), owing principally to the lack of Na in \(M(4)\). At lower \(f\(_{O_2}\)\) (QF1), this amphibole becomes less stable with respect to temperature because of the great decrease

### Table 6. Ferrous Amphibole Stabilities on I-W Buffer

<table>
<thead>
<tr>
<th>Phase and Composition</th>
<th>Stability Limit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T) (kbar)</td>
<td>(T) (°C)</td>
</tr>
<tr>
<td>Ferrotremolite</td>
<td>500</td>
<td>437</td>
</tr>
<tr>
<td>Ca(_2 Fe^{2+}<em>5 Si_8 O</em>{22}(OH)(_2))</td>
<td>1000</td>
<td>465</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>485</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>506</td>
</tr>
<tr>
<td>Riebeckite-arfvedsonite</td>
<td>500</td>
<td>670</td>
</tr>
<tr>
<td>Na(_2 Fe^{2+}_4 Fe^{3+}_1 Si_7 Fe^{3+}<em>1 O</em>{22}(OH)(_2))</td>
<td>1000</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>735</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>770</td>
</tr>
<tr>
<td>Ferrorichterite</td>
<td>500</td>
<td>690</td>
</tr>
<tr>
<td>NaCa(_2 Fe^{2+}<em>4 AlSi_5 O</em>{22}(OH)(_2))</td>
<td>1000</td>
<td>715</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>2000</td>
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</tr>
<tr>
<td>Ferropargasite</td>
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<td>1500</td>
<td>835</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>850</td>
</tr>
</tbody>
</table>
in activity of $H_2O$ under these conditions, a factor unrelated to the ferrous-ferric problem.

Ferro tremolite has complete local charge balance. Consequently, five ferrous irons are placed into the five available $M$ sites. The predicted increase in $b$ for the conversion of tremolite to ferrotremolite is calculated as 0.32 Å (Colville, Ernst, and Gilbert, 1966). Colville et al experimentally observed an increase of 0.29 Å, which was considered within the error of the calculation. On this basis all iron is thought to be ferrous. Most of the decreased stability of ferrotremolite compared with other ferrous amphiboles is attributable to the vacant $A$ site (Ernst, 1968). The decreasing linking caused by the ferrous iron also adds to the comparative instability of this amphibole. Riebeckite, which also has a vacant $A$ site, is slightly more stable, probably because of the two ferric irons in $M(2)$.

The riebeckite-arfvedsonite synthesized by Ernst (1962) on the bulk composition riebeckite comes close to ferrotremolite in stability. Some vacancy in the $A$ site as well as some local charge imbalance would account for its lowered stability.

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FIG. 7. Comparison of the thermal stability limits of ferrotremolite (Ernst, 1966), riebeckite (Ernst, 1962), riebeckite-arfvedsonite (Ernst, 1962), ferri richterite (this paper), and ferropargasite (Gilbert, 1966). Oxygen fugacities are defined by the labeled buffer systems.


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