A Crystal-Chemical Study of Synthetic Magnesiohastingsite

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Abstract

Mössbauer and infrared spectra of synthetic magnesiohastingsite (Mh), NaCa$_2$Mg$_4$Fe$_{10}$Si$_6$Al$_2$O$_{22}$ (OH)$_2$, indicate that, except at high values of $f_{O_2}$, Fe occurs both as Fe$^{2+}$ and Fe$^{3+}$ contrary to the ideal formula. The amount of Fe$^{3+}$ produced is a function of the oxygen fugacity of synthesis. Oxidation and reduction of Fe may be carried out reversibly under hydrothermal conditions at relatively fast rates. Apparently this does not involve gain or loss of O(3)-H hydroxyls contrary to the case of Fe$^{2+}$ bearing sodic amphiboles. Octahedrally coordinated cations are significantly ordered among the M(1), M(2), and M(3) sites in agreement with recent crystal-structure determinations. The distribution scheme is dependent on the amount of Fe$^{2+}$ and Fe$^{3+}$ present. Refractive indices ($c = 1.642-1.657$, $c = 1.653-1.672$), color, and unit-cell parameters ($a = 9.928-9.933$ Å; $b = 18.015-18.029$ Å; $c = 5.282-5.297$ Å; $V = 105.43-105.46$) also reflect the $f_{O_2}$ of synthesis. Physical properties agree well with a sample of natural Mh similar to U-1236 of Larsen (1942). The experimental data suggest a mechanism to produce Fe$^{3+}$ in synthetic Mh which involves an excess of two protons (and/or anionic defects at low $f_{O_2}$) per unit formula.

Introduction

As a preliminary step in the study of the phase relations of the calcic amphibole end-member magnesiohastingsite,$^2$ (NaCa$_2$Mg$_4$Fe$^{2+}$Si$_6$Al$_2$O$_{22}$ (OH)$_2$), amphiboles of this bulk composition were synthesized hydrothermally at a variety of temperatures, pressures, and oxygen fugacities. Significant and systematic variation in physical properties of the amphiboles produced led to a detailed investigation of the influence of the intensive variables (mostly oxygen fugacity) on the chemistry of the synthetic minerals.

During the last decade the applications of infrared absorption and Mössbauer spectral techniques (e.g., Burns and Strens, 1966; Whitfield and Freeman, 1967; Bancroft et al, 1967a, b; Bancroft and Burns, 1969; Ernst and Wai, 1970; Burns and Greaves, 1971), coupled with precise three-dimensional crystal structure determinations of the clino-amphiboles (e.g., Papke et al, 1969, to whom the reader is referred for site nomenclature), have added greatly to our understanding of one of the most complex mineral series. Before the advent of such techniques the intracrystalline chemical behavior of synthetic amphiboles could be delineated only by physical measurements relatively insensitive to order-disorder or other phenomena at the nuclear or atomic level (Colville et al, 1966).

Mössbauer and infra-red spectra of synthetic magnesiohastingsites reveal that Fe occurs as Fe$^{2+}$ and Fe$^{3+}$ in variable proportions according to experimental conditions. The mere existence of Fe$^{2+}$ ions in the structure suggested that a mechanism, as yet poorly known, might be operative in the production of "reduced magnesiohastingsite."

This study presents an attempt at correlating physico-chemical changes in synthetic amphiboles with the variable crystallization environment, and an attempt at resolving the nature of the changes.

Experimental and Analytical Techniques$^3$

Hydrothermal runs. Synthesis of magnesiohastingsite was carried out using conventional hydrothermal apparatus, and the oxygen buffer technique (e.g., Eugster and Wones, 1962). Abbreviations for the buffers are listed in Table 1, and the necessary thermodynamic data in Table 2. Pt sample capsules were used with the NNO buffer and Ag-Pd capsules with the other buffers. Pressures were measured with calibrated Bourdon tube gauges, temperatures with chromel-alumel thermocouples. Presumed accuracy is ± 10 bars, and ±6°C, respectively. Starting material consisted of mixtures of reagent grade oxides, hydroxides, and carbonates in the stoichiometric proportions for Mh.

Optical and X-ray measurements. Optical properties were obtained on a flat stage petrographic microscope using refractive-index oils of .002 interval. Average values of several

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$^2$ End-members nomenclature follows Ernst (1968).

$^3$ Detailed description of the experimental apparatus and the analytical techniques are presented in Semet (1972).
determinations are presented in Table 3. The results are in accord with an earlier determination by Colville et al. (1966).

Refined cell parameters were computed from powder diffraction data (Cu-Kα radiation) by a least-square program (Burnham, 1962) using Si (a = 5.43054 Å) as an internal standard. Indexing was done by comparison with single crystal (U-1236) intensity data and by using the Fortran IV program of Evans et al. (1963). Typical powder data are presented in Table 4. Average unit-cell dimensions obtained for the synthetic Mh at various °/n, and sample U-1236 are listed in Table 5.

Mössbauer spectra. Data collection was done on a conventional loudspeaker drive spectrometer (Kündig et al., 1966). Sample preparation and analysis of the spectra follow procedures outlined by Ernst and Wai (1970). More recently, computer processing of the data was accomplished utilizing a Fortran IV least-square curve fitting program (Dollase, 1972). All isomer-shifts are quoted relative to 0 mm/sec for Fe⁴⁺ in metallic iron.

Infrared spectra. A Perkin-Elmer model 421 was used in obtaining the infrared spectra of the amphiboles by the KBr pellet method. The fundamental O-H stretching region (3800–3600 cm⁻¹) was covered in more detail with the abscissa expanded 2x, 5x, and 10x. High resolution spectra were obtained on carefully dried specimens and show very little absorption due to absorbed H₂O.

Electron microprobe analysis. Chemical compositions of selected samples of synthetic Mh and sample U-1236 were obtained on an ARL-EMX electron microprobe. Analyzed hornblende was used as standards. Empirical correction factors (Bence and Albee, 1968) and a Fortran IV program provided the refined analyses presented in Table 6. Accuracy is considered to be better than 3 percent of the amount present for sample U-1236, and approximately 7 percent (due to relatively large count rate variation on the minute synthetic crystals) for the other samples.

Synthesis of Magnesiohastingsite

Magnesiohastingsite can be readily synthesized at a variety of experimental conditions from a number

Table 1. Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Oxygen fugacity buffers</th>
<th>Other symbols</th>
</tr>
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<tbody>
<tr>
<td>IOF 2Fe₁₀Si₅O₂₂ + 30₂ = Fe₂SiO₄</td>
<td>n Refractive Index</td>
</tr>
<tr>
<td>FMQ 3Fe₂SiO₄ + 20₂ = 2Fe₂O₃ + 3SiO₂</td>
<td></td>
</tr>
<tr>
<td>NNO 2MnO₂ = 2MnO₄</td>
<td></td>
</tr>
<tr>
<td>MMO 0NiO + 0₂ = 2MnO₄</td>
<td></td>
</tr>
<tr>
<td>CCO 4CuO = 2CuO</td>
<td></td>
</tr>
<tr>
<td>HM 4Fe₂O₄ + 0₂ = 6Fe₂O₃</td>
<td></td>
</tr>
<tr>
<td>CT 2CuO + 0₂ = 4CuO</td>
<td></td>
</tr>
</tbody>
</table>

* Numbers in parentheses in tables and figures represent one standard deviation unless otherwise stated and applied to the last significant digit. Example: 2.35(9) = 2.35 ± 0.09, or 1.996(12) = 1.966 ± 0.012.

of starting materials (Semet, 1972). Yields of 90–100 percent are common on initial synthesis. At low oxygen fugacities, however, significant amounts (up to 10 percent vol.) of the high temperature assemblage of equivalent bulk composition (clinopyroxene + olivine + nepheline + spinel = melilitite) always appear on first synthesis; repeated grinding and recrystallization yield a product which contains virtually only amphibole. The amphibole synthesized from an oxide mix is always very fine grained (10 x 5 x 5 μm) and it is only run time does not bring about significant growth. Crystals of a larger size (100 x 20 x 20 μm) can be obtained when amphibole is synthesized from the high temperature assemblage of equivalent bulk composition. The amphibole presumably nucleates very easily from the highly unstable oxide mix, whereas it does not from the metastable high temperature assemblage. In the latter case the clinopyroxene crystallites, because of their similar atomic configuration, may serve as nucleus centers for the growth of the amphibole (e.g., see Greenwood, 1963).

A temperature of approximately 850°C, and a pressure of 2000 bars, were found to be the experi-

Table 2. Thermodynamic Data on the Oxygen Fugacity Buffers

<table>
<thead>
<tr>
<th>Buffer</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IOF</td>
<td>29382</td>
<td>7.51</td>
<td>0.050</td>
<td>Eugster and Wones, 1962</td>
</tr>
<tr>
<td>FMQ</td>
<td>25650</td>
<td>8.92</td>
<td>0.092</td>
<td>Wones and Gilbert, 1969</td>
</tr>
<tr>
<td>NNO</td>
<td>24709</td>
<td>8.94</td>
<td>0.046</td>
<td>Eugster and Wones, 1962</td>
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<tr>
<td>MMO</td>
<td>25880</td>
<td>13.38</td>
<td>0.0007</td>
<td>Huebner and Sato, 1970</td>
</tr>
<tr>
<td>CCO</td>
<td>17050</td>
<td>6.85</td>
<td>0.096</td>
<td>Semet, manuscript</td>
</tr>
<tr>
<td>HM</td>
<td>29102</td>
<td>14.41</td>
<td>0.019</td>
<td>Eugster and Wones, 1962</td>
</tr>
<tr>
<td>CT</td>
<td>13928</td>
<td>10.34</td>
<td>0.0015</td>
<td>Semet, manuscript</td>
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</table>

* T is the temperature in °K; P is the total pressure in bars

Table 3. Optical Properties of Synthetic Magnesiohastingsite

<table>
<thead>
<tr>
<th>Buffer</th>
<th>10⁻⁴fO₂</th>
<th>a</th>
<th>γ</th>
<th>Z Xc</th>
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</thead>
<tbody>
<tr>
<td>IOF</td>
<td>18.56</td>
<td>1.624(4)</td>
<td>1.653(4)</td>
<td>24°</td>
</tr>
<tr>
<td>FMQ</td>
<td>13.76</td>
<td>1.650(5)</td>
<td>1.662(4)</td>
<td>26°</td>
</tr>
<tr>
<td>NNO</td>
<td>12.90</td>
<td>1.637(6)</td>
<td>1.649(6)**</td>
<td>23°</td>
</tr>
<tr>
<td>U</td>
<td>10.90</td>
<td>1.653(8)</td>
<td>1.668(8)</td>
<td>25°</td>
</tr>
<tr>
<td>MMO</td>
<td>7.74</td>
<td>1.654(4)</td>
<td>1.669(4)</td>
<td>25°</td>
</tr>
<tr>
<td>CT</td>
<td>2.03</td>
<td>1.657(3)</td>
<td>1.672(4)</td>
<td>25°</td>
</tr>
</tbody>
</table>

* Samples synthesized at 850°C, 2000 bars.
** The anomalously low indices are due to Fe loss to the Pt sample capsule.
Table 4. X-ray Powder Data for Synthetic and Natural Magnesiohastingsite

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>d_{calc}</th>
<th>d_{obs}</th>
<th>Intensity</th>
<th>d_{calc}</th>
<th>d_{obs}</th>
<th>Intensity</th>
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</thead>
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<tr>
<td>0</td>
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<td>2.68</td>
<td>2.68</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2.72</td>
<td>2.73</td>
<td>100</td>
<td>2.72</td>
<td>2.73</td>
<td>100</td>
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Table 5. Cell Parameters of Synthetic* and Natural** Magnesiohastingsite

<table>
<thead>
<tr>
<th>Buffer</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>β (degrees)</th>
<th>V [Å³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF</td>
<td>8.920(2)</td>
<td>18.015(9)</td>
<td>5.282(3)</td>
<td>105.43(4)</td>
<td>910.7(8)</td>
</tr>
<tr>
<td>WM</td>
<td>9.930(5)</td>
<td>18.025(9)</td>
<td>5.290(4)</td>
<td>105.43(4)</td>
<td>912.0(10)</td>
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<tr>
<td>PMQ</td>
<td>9.933(2)</td>
<td>18.029(4)</td>
<td>5.293(11)</td>
<td>105.43(11)</td>
<td>910.6(5)</td>
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<tr>
<td>NMO</td>
<td>9.932(1)</td>
<td>18.015(4)</td>
<td>5.289(11)</td>
<td>105.43(2)</td>
<td>912.2(3)</td>
</tr>
<tr>
<td>NH</td>
<td>9.933(1)</td>
<td>18.028(3)</td>
<td>5.297(1)</td>
<td>105.44(2)</td>
<td>914.3(3)</td>
</tr>
<tr>
<td>CT</td>
<td>9.926(5)</td>
<td>18.029(9)</td>
<td>5.297(4)</td>
<td>105.46(5)</td>
<td>913.7(8)</td>
</tr>
<tr>
<td>Nat. Mn</td>
<td>9.940(3)</td>
<td>18.050(4)</td>
<td>5.310(4)</td>
<td>105.45(4)</td>
<td>918.4(4)</td>
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</tbody>
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* Samples synthesized at 850°C, 2000 bars.
** Iron Hill, Colorado.

Table 6. Chemical Composition of Synthetic and Natural Magnesiohastingsite

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>42.08</td>
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<td></td>
<td></td>
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<tr>
<td>Al₂O₃</td>
<td>11.90</td>
<td>12.85</td>
<td>12.1</td>
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<tr>
<td>TiO₂</td>
<td></td>
<td>0.58</td>
<td></td>
<td>11.6</td>
</tr>
<tr>
<td>FeO</td>
<td>8.39</td>
<td>10.57</td>
<td>8.4</td>
<td>8.5</td>
</tr>
<tr>
<td>MgO</td>
<td>18.82</td>
<td>16.01</td>
<td>19.1</td>
<td>18.5</td>
</tr>
<tr>
<td>CaO</td>
<td>13.09</td>
<td>12.93</td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.62</td>
<td>2.59</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td>1.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total: 100.00 100.2 98.2

1. Theoretical magnesiohastingsite, Fe recalculated as FeO.
2. U-1236, see Larsen (1942); the structural formula recalculated on the basis of 15.51 Al, 1 Ti, Fe, Mg, Ca, and Mn, the Fe/F Mn/Si ratio given by Mössbauer spectra, and (OH)⁺ as required to compensate for total cationic charge gives:

K₂₂Mo₇Si₃₀O₇(OH)⁺₄, 2H₂O


* Hyd by difference.
** Theoretical Hyd from column 1.
boile is pale golden yellow. The colors referred to here were observed with a hand-lens on a sample of the charge; under the microscope the small crystals are only very faintly colored or colorless. At intermediate oxygen fugacities (HM, NNO, FMQ buffers), the color ranges from pale yellowish green to pale blue-green from higher to lower fugacities; at low oxygen fugacity (IQF buffer), it is very pale grayish green to white.

Studies of a number of synthetic iron-bearing hydroxylated silicates have consistently shown a regular variation of refractive indices with oxygen fugacity (e.g., Ernst, 1960, 1962; Eugster and Wones, 1962; Wones, 1963; Forbes, 1969). This variation, also observed in this study (Table 3), has been variously interpreted as representing solid solution with other end-members of the series or the production of oxypheases. However, the specific refractive energy for FeO being larger than for FeO$_2$ (Larsen and Berman, 1934, pp. 30–31), oxidation of iron in a crystal concomitant with minor changes in the structure due to the redistribution of electrical charges could account for the whole effect (or part of it).

The variability of both color (e.g., Burns, 1970, pp. 63–75) and refractive indices with oxygen fugacity, which presumably indicates a change in the valence state of iron in magnesiohastingsite, prompted a detailed investigation of the synthetic products to determine quantitatively the nature of the variation.

**Interpretation of the Spectra**

**Mössbauer spectra of magnesiohastingsite**

The parameters which can be obtained from a Mössbauer spectrum of an iron-bearing paramagnetic compound are: the isomer shift (I.S.), the quadrupole splitting (Q.S.), the width (at half height) or the half width at half height (HWHH), and the ratios of the areas of the contributing peaks (or dips). Both I.S. and Q.S. are sensitive to the valence state of the Fe ion and, to a lesser degree, to the crystal-chemical character of the site. The observed half-width of the spectrum lines always departs significantly from the theoretical 0.105 mm/sec because of thickness broadening, and/or scatter of the electric field gradients at the different nuclear sites, and/or diffusional effects. The values of I.S., Q.S., and HWHH are generally given in units of mm/sec (1 mm/sec = 7.694 x 10$^{-8}$ ergs). Finally, the ratios of the peak areas in a multisite compound are, in general, directly proportional to the absolute numbers of contributing Fe$^{57}$ nuclei. To be rigorous, the ratio of the recoil-free fractions $f^5$ of Fe$^{57}$ at the different sites should also be taken into account; however, this ratio does not, in general, depart significantly from unity. Detailed discussion of the principles involved is readily available in the literature (e.g., Wertheim, 1964; Goldanskii and Herber, 1968).

The amount of Fe entering either the eightfold-coordinated M(4) site and the Si I and Si II tetrahedral sites in magnesiohastingsite appears to be negligible. If enough Ca is present to fill the M(4) site, solid solution toward cummingtonite-grunerite should be non-existent, as disordering of Ca and Fe$^{2+}$ between M(4) and M(1) + M(2) + M(3) has not proven significant in the recent crystal structure determination of C$_2$/$m$ amphiboles (Papike et al., 1969). Similarly, when enough Al is present to preserve the electrical neutrality of the structure by substituting for Si in the tetrahedral sites, it does so preferentially to Fe$^{3+}$. Ernst and Wai (1970) have reported a case (sample C-4980) where Fe$^{3+}$ proxying for Si seemed to be required on the basis of the chemical analysis. Mössbauer spectra of this sample of magnesioriebeckite and its heat-treated products to determine quantitatively the nature of the change.

**Table 7. Experimental Run Conditions for Selected Samples of Synthetic Magnesiohastingsite**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starting material</th>
<th>Buffer</th>
<th>$-\log f_2$</th>
<th>T (°C)</th>
<th>Time (h)</th>
</tr>
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<tbody>
<tr>
<td>IQF-A3</td>
<td>Oxide mix</td>
<td>IQF</td>
<td>10.52</td>
<td>850</td>
<td>50</td>
</tr>
<tr>
<td>CT to IQF</td>
<td>Oxide mix</td>
<td>CT</td>
<td>7.36</td>
<td>850</td>
<td>28</td>
</tr>
<tr>
<td>IQF-A2</td>
<td>Oxide mix</td>
<td>IQF</td>
<td>10.52</td>
<td>850</td>
<td>50</td>
</tr>
<tr>
<td>CT-A2</td>
<td>Oxide mix</td>
<td>CT</td>
<td>7.36</td>
<td>850</td>
<td>28</td>
</tr>
<tr>
<td>CT to IQF</td>
<td>Oxide mix</td>
<td>CT</td>
<td>7.36</td>
<td>850</td>
<td>28</td>
</tr>
<tr>
<td>IQF to CT</td>
<td>Oxide mix</td>
<td>CT</td>
<td>7.36</td>
<td>850</td>
<td>28</td>
</tr>
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<td>Oxide mix</td>
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<td>850</td>
<td>50</td>
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<td>COO</td>
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<td>150</td>
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<td>850</td>
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<td>AAR-12T</td>
<td>Oxide mix</td>
<td>CT</td>
<td>7.36</td>
<td>850</td>
<td>42</td>
</tr>
</tbody>
</table>

* Total pressure was maintained at 2000 bars + 10 bars for all runs.

...
of what is required to fill the Si I and Si II sites, randomization of Al and Fe$^{3+}$ among the M(2) and tetrahedral sites could occur at high temperatures, but to the author’s knowledge such an occurrence has not yet been documented. In the general case, then, the Mössbauer spectrum of calcic amphiboles containing both Fe$^{2+}$ and Fe$^{3+}$ would consist of absorption peaks contributed by six different octahedrally coordinated Fe “species,” namely Fe$^{2+}$ and Fe$^{3+}$ in M(1), M(2), and M(3). Greaves et al (1971) and Burns and Greaves (1971) have, for instance, resolved the Fe$^{2+}$ spectrum of actinolites into three quadrupole split doublets, the contributions arising from Fe$^{2+}$ in M(1), M(2), and M(3). It is, however, very difficult if not impossible to resolve the Fe$^{3+}$ spectra into three different doublets because of the smaller splittings and the similarity of the M sites. Greaves et al (1971) and Burns and Greaves (1971) observed the Fe$^{3+}$ spectrum of actinolites to consist of a single broad doublet.

The Mössbauer spectrum (Fig. 1) of magnesiohastingsite (OA5-19-71U) synthesized at an intermediate oxygen fugacity (log $f_{O_2}$ = -10.36) reveals that more than one Fe “species” contribute to the spectrum. A shoulder on the low velocity side of dip C' clearly indicates that it is overlapped by a second, less intense dip (D'). It is not obvious, however, that the Fe$^{3+}$ absorption areas represent overlapping of at least two dips (AA' and BB'). This conclusion was arrived at by comparing the spectra of magnesiohastingsite synthesized at higher oxygen fugacity (sample CT-A2, CT buffer) where the overlap is more easily perceived (Fig. 2). Furthermore, the availability of spectra of amphiboles synthesized at a variety of $f_{O_2}$ values has led to an unambiguous identification and assignment of the peaks. The peak locations do not vary greatly in the series, so that the complex spectrum presented in Figure 1 can be fitted to overlapping doublets with reasonable confidence. Even then convergence and a reasonable $\chi$ resulted only after several computer runs that released one by one the positions, approximate area ratios, and half-width constraints. The values of the Mössbauer parameters of sample OA5-19-71U are compared in Table 7 with those obtained from selected spectra of natural magnesiohastingsite and of amphiboles synthesized at different oxygen fugacities. The isomer shifts and quadrupole splittings are typical of Fe$^{2+}$ and Fe$^{3+}$ in distorted octahedral sites (Bancroft et al, 1967a; Dollase, personal communication). Table 7 summarizes the experimental conditions of synthesis for the specimens.

![Fig. 1. Mössbauer spectrum of sample OA5-19-71U (‘annealed Mh, 707°C, 2000 bars, cco buffer). 0 mm/sec corresponds to the isomer shift of metallic Fe$^{57}$.](image-url)
The spectra of the IQF-buffered Mh (labeled IQF in Table 8) were fitted to three quadrupole split doublets, with widths constrained to be equal. The parameters deduced from the spectra did not differ from the average more than two standard deviations. The same procedure was followed for the FMQ-A2 spectrum. Two resolved Fe\(^{3+}\) doublets with unequal widths gave the best \(\chi\) for sample CT-A2.\(^6\) When the same spectrum was fitted with two doublets of equal widths (Kündig's 1969 program), the same peak positions resulted (\(\chi = 1.15\), but the area ratio differed significantly, being 1.78 instead of 1.17; however, 1.17 is considered more reliable. The spectrum refinement for sample CT to IQF converged only when the three doublets were constrained to be of equal width. The IQF to CT spectrum was also resolved into two Fe\(^{3+}\) doublets of unequal half-widths. Except for the area ratios, which reflect different experimental conditions, the parameters agree well with those obtained for CT-A2. The same spectrum (IQF to CT) was also fitted with two doublets of equal half-widths (Kündig's program) but gave a much less satisfactory \(\chi\) (1.49), although the other parameters were within one standard deviation of the values reported in Table 8. Attempts to fit the natural magnesiohastingsite spectrum to two Fe\(^{3+}\) doublets did not result in convergence, indicating that if more than one Fe\(^{3+}\) "species" existed, it must be only minor. The three quadrupole doublets fitted with equal Fe\(^{3+}\) half-widths and an independent Fe\(^{3+}\) half-width gave a good resulting \(\chi\). It is apparent from the table that, in general, the peak positions agree well. The Fe\(^{3+}\) quadrupole splitting in samples FMQ-A2 and CT to IQF are, however, slightly larger than the average. This may be due to an unresolved contribution of a second Fe\(^{3+}\) "species."

On the basis of the foregoing discussion of independent crystal-chemical evidence (e.g., Ghose, 1965; Ernst, 1968; Papike et al, 1969) and of published spectra of calcic amphiboles (Bancroft et al, 1967a; Greaves et al, 1971; Burns and Greaves, 1971), the following peak assignment has been made. Doublet AA' (Figs. 1 and 2) is attributed to Fe\(^{3+}\) in the \(M(2)\) site; it represents the major contribution of Fe\(^{3+}\) to the total absorption and confirms the gen-
eraly accepted view that trivalent $M$ cations present
in clinocarnes are concentrated in this site. The
remaining $Fe^{3+}$ doublet $BB'$ is attributed to unres-
solved absorption from $Fe^{3+}$ in the $M(1)$ and $M(3)$
sites. The fact that the width of the latter doublet is
larger in those spectra where the equal width con-
traint was not applied (ct-A2 and IQF to CT) also
seems to favor such an assignment. The two $Fe^{2+}$
doublets $CC'$ and $DD'$ are very similar to those found
in actinolite (Bancroft et al., 1967a; Greaves et al.,
1971). The outer doublet $CC'$, which is also the most
intense, is due to $Fe^{2+}$ in $M(1)$ and $M(3)$ (unresol-
ved); the inner doublet $DD'$ represents $Fe^{2+}$ in $M(2)$. Assuming that $Fe^{2+}$
was randomly distributed among the $M$ sites, and
that the recoil-free fraction $f'$ is the same for all sites,
the area ratio should be

$$\frac{2M(1) + M(3)}{2M(2)} = \frac{3}{2};$$

this clearly is not the case for most of the specimens
studied. For $Fe^{3+}$, this ratio differs even more from
that calculated for random distribution.

Additional spectra not reported in Table 8 were
taken on samples synthesized employing the NNO
and H2O buffers to determine the $Fe^{3+}/Fe^{2+}$ ratios.
Table 9 presents the pertinent data for those samples
and a summary of the data of Table 8.

Infrared spectra of magnesiohastingsite

The investigation of infrared absorption of mineral-
ogically important compounds has proven useful in
characterizing structural units and in quantitative
studies of solid-solution series or mineral mixtures
(e.g., Lyon, 1967). In particular, studies of hy-
droxy-stretching absorption in minerals of the talc
and mica groups (e.g., Farmer and Russel, 1964,
1967; Vedder, 1964; Jørgensen, 1966; Wilkins and
Ito, 1967; Vedder and Wilkins, 1969) are directly
applicable to amphiboles in view of the close simi-
larity of their proton environment (e.g., Burns and
Strens, 1966; Burns and Prentice, 1968; Ernst and
Wai, 1970). In amphiboles the hydroxyl is directly
coordinated to two $M(1)$ and one $M(3)$ cations,
the proton extending toward the tetrahedral chain
cavity (Papik et al., 1969). Combinations of ca-
tions with different electronegativities and/or polariz-
abilities (mostly Mg, $Fe^{2+}$, $Fe^{3+}$, Al) in $M(1)$ and
$M(3)$ influence the bond-strength of the hydroxyl
ion. This, in turn, is reflected by slightly different i.r.
absorption frequencies. In the talc-minnesotaite series
(Wilkins and Ito, 1967) and in the tremolite-actino-
liste series (Burns and Strens, 1966; Wilkins, 1970;
Burns and Greaves, 1971), the OH stretching fre-
quencies corresponding to MgMgMg, MgMgFe2+,
MgFe2+Fe2+, Fe2+Fe2+Fe2+ groups coordinated to the
hydroxyl are equal within a few cm$^{-1}$. Here, the
proton is vibrating in a cavity closed by SiO4 rings.
In trioctahedral micas of the phlogopite-biotite series,
however, the O-H bonding is perturbed by the Al-
for-Si substitution in the tetrahedral layer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$-log f_{O_2}$</th>
<th>$Fe^{3+}$ Percent</th>
<th>$Fe^{2+}$ Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>IQF***</td>
<td>18.56</td>
<td>13</td>
<td>87</td>
</tr>
<tr>
<td>NNO-A1</td>
<td>13.76</td>
<td>54</td>
<td>48</td>
</tr>
<tr>
<td>H2O</td>
<td>12.98</td>
<td>57</td>
<td>43</td>
</tr>
<tr>
<td>CT to IQF</td>
<td>2.03</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>IQF to CT</td>
<td>2.03</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

* Ratio of the Mössbauer absorption area due to $Fe^{3+}$ nuclei
to the total absorption expressed in percent.
** 100 - $Fe^{3+}$.
*** Average of two.
A similar situation occurs in synthetic magnesio-
hastingsite where the Al for Si substitution in the
tetrahedral chains parallels that of the phlogopite-
biotite series and where the A site, sandwiched be-
tween opposite tetrahedral chains, is occupied by Na.
Spectra of the synthetic amphiboles are compared
with a spectrum of natural magnesiohastingsite (U-
1236) in Figure 3a and b (abscissa expanded 2x,
no special precautions regarding H₂O). Selected
spectra taken at higher resolution (abscissa expanded
10x, dried specimens) are compared in Figure 4 to
a spectrum of synthetic pargasite (NaCa₃Mg₄AlSi₆-
Al₉O₂₂(OH)₂, synthesized hydrothermally at 800°C,
2000 bar). The spectra are seen to consist of two
major bands and several minor peaks and shoulders.
The major bands at 3705, 3675, and/or 3660 cm⁻¹
can be assigned with reasonable confidence to OH
ions bonded to MgMgMg, MgMgFe²⁺, and/or
MgMgFe³⁺ (MgMgAl for synthetic pargasite) groups
in the 2M(1) + M(3) sites. The minor peaks
around 3645-3620 cm⁻¹ most probably represent
MgFe²⁺Fe³⁺-OH, MgFe²⁺Fe³⁺-OH, and MgFe³⁺-OH
(MgAlAl-OH) groups. The observed frequencies for
those groupings are similar to what is observed in
phlogopite-biotite micas, although the assignment dif-
fers somewhat from those of Jørgensen (1966) and
Wilkins (1967). The limited substitution of Fe (or
Al) for Mg in magnesiohastingsite (or pargasite)
precluded observation of bands corresponding to
FeFeFe-OH (AlAlAl-OH). The significance of the
shoulders in the spectra of the oxidized and reduced
samples (cr to iqf, iqf to cr) as well as the broad,
almost featureless spectrum of the natural sample is
less clear. In sample cr to iqf, where significant Fe²⁺
and Fe³⁺ occur, the broadening of the band at 3670-
3660 cm⁻¹ may arise from MgFe³⁺Fe³⁺-OH and/or
MgFe²⁺Fe³⁺-OH groups; in sample iqf to cr, where
only Fe³⁺ was detected in the Mössbauer spectra, the
3660 cm⁻¹ shoulder is of unknown origin (Si-Al
ordering in the tetrahedral chains may cause such a
splitting). The spectrum of the natural specimen
(U-1236) most probably represents a combination
of several bands arising from the complex substitu-
tion of different cation species (Mg, Fe²⁺, Fe³⁺, Ti⁴⁺,
Al) among the M sites as well as the influence of
Al-substitution in the tetrahedral chains and of in-
complete occupancy of the A site.

Where ordering among the three cations coordi-
nated to the hydroxyl in binary solid-solutions does
not occur, the intensities of the absorption bands
corresponding to the possible groupings are in the

$$\frac{3x}{1-x} : 3\left(\frac{x}{1-x}\right)^2 : \left(\frac{x}{1-x}\right)^3$$

(Vedder, 1964), where x is the concentration of the
substituting ion. Spectra of synthetic magnesio-
hastingsite taken at high resolution have been fitted
by hand to Gaussian-like curves after normalization.
of the non-uniform background; then the ratios of width-at-half-height × peak-height products have been calculated. The results obtained are presented in Table 10 and compared with the same ratios obtained from Mössbauer spectra where available. When allowance is made for the uncertainty in background position and the strong peak overlap, the agreement is rather good. The observed ratios for samples A9-11T and A9-12T, synthesized under reducing conditions (IQF buffer) and rerun under oxidizing conditions (CT buffer, 850°C, 2000 bars) for 19 and 42 hours respectively, do not differ significantly from each other; neither do they differ from the ratios obtained from the Mössbauer spectrum of sample IA9 to CT (10 hours), indicating that no substantial cation migration has taken place in the longer runs. Using samples prepared as for the high resolution spectra, repeated spectra of magnesiohastingsite synthesized at low oxygen fugacity (IQF buffer) or synthesized at high fo, but reduced at low fo, consistently showed a broad, flat, and featureless absorption band developed between 3640 and 3540 cm⁻¹. The possible significance of this feature will be discussed below.

Comparison of band intensities in the spectrum of synthetic pargasite (Fig. 4) indicates that Mg and Al apparently are randomly distributed among the M(1), M(2) and M(3) sites.

**Discussion**

**Optical properties.** Variations in refractive indices of magnesiohastingsite synthesized directly from an oxide mix (Table 3) have been plotted (Fig. 5) against the Fe³⁺/(Fe³⁺ + Fe²⁺) ratios calculated from Mössbauer spectra (Table 9) of the same or similar material. Also included in Figure 5 are the data for sample OA5-19-71U, which was synthesized at lower temperature and for which \( \alpha = 1.653, \gamma = 1.668, \frac{\text{Fe}^{3+}}{\text{Fe}^{2+} + \text{Fe}^{3+}} = 76 \text{ percent}. \) Except for samples synthesized under NNO buffer conditions, which show anomalously low indices (probably because of significant loss of Fe to the Pt sample capsule used

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**Table 10. Ratios of Band Areas in the Infrared Spectra of Synthetic Magnesiohastingsite**

<table>
<thead>
<tr>
<th>Sample</th>
<th>1 : 1.83 : 0.20</th>
<th>1 : 0.80 : 0.21</th>
</tr>
</thead>
<tbody>
<tr>
<td>IQF-A3</td>
<td>Observed</td>
<td>Calculated**</td>
</tr>
<tr>
<td>CT-A2</td>
<td>1 : 0.46 : 0.10</td>
<td>1 : 0.54 : 0.10</td>
</tr>
<tr>
<td>A9-11T</td>
<td>1 : 0.80 : 0.19</td>
<td>1 : 0.85 : 0.24***</td>
</tr>
<tr>
<td>A9-12T</td>
<td>1 : 0.87 : 0.22</td>
<td>1 : 0.85 : 0.24***</td>
</tr>
</tbody>
</table>

* \( x = \) mole fraction of Fe in the M(1), M(3) sites.
** Calculated from data of Mössbauer spectra.
*** Calculated for Sample IQF to CT.

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**Fig. 4. Infrared spectra of synthetic magnesiohastingsite and pargasite (high resolution).**

**Fig. 5. Variation of refractive indices of synthetic magnesiohastingsite with oxidation ratio. The size of the symbols indicates the probable error (a different symbol has been used for NNO samples because they are depleted in Fe).**
in conjunction with NNO buffer), a regular variation of refractive indices is apparent. A linear fit to the data indicates an increase of both \(a\) and \(\gamma\) with the oxidation ratio. As pointed out earlier, such a relation would obtain where the rule of Gladstone and Dale is followed and the specific refractive energy for \(\text{Fe}_2\text{O}_3\) is larger than for \(\text{FeO}\) (Larsen and Bereman, 1934, pp. 30–31). The systematic change in color also follows directly the variation in \(\text{Fe}^{3+}\) proportion. The refractive indices for sample IQF to CT and CT to IQF—\(\alpha = 1.651(4)\), \(\gamma = 1.669(5)\), \(\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = 100\%\), and \(\alpha = 1.640(5)\), \(\gamma = 1.660(6)\), \(\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = 35\%\) respectively—are also in good agreement with the values obtained for direct synthesis. This indicates that the observed variation can be attributed primarily to changes in \(\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})\).

**Distribution of octahedral cations in synthetic Mh.** Recent crystal-structure determinations (for a review see Papike et al., 1969), infrared and Mössbauer studies (Bancroft et al., 1967a; Burns and Prentice, 1968; Bancroft and Burns, 1969; Ernst and Wai, 1970; Wilkins, 1970; Buckley and Wilkins, 1971; Burns and Greaves, 1971) have demonstrated that extensive cation ordering occurs in natural clino-amphiboles. Ordering in synthetic clino-amphiboles, however, has not been conclusively documented previously. Ernst (1963) has suggested that a second order polymorphic transition involving Al ordering in the \(M(2)\) site occurs in synthetic members of the glaucoephane series. Attempts at disordering natural sodic amphiboles (Ernst and Wai, 1970) by one atmosphere and hydrothermal heat-treatment resulted in oxidation of \(\text{Fe}^{3+}\) ions and concomitant loss of \(\text{H}_2\text{O}\) and/or \(\text{H}_2\text{O}\). Significant octahedral cation migration occurred in runs of 94 hours at 700°C and atmospheric pressure. A two year long hydrothermal heat-treatment of a natural iron-bearing glaucoephane produced a partly oxidized amphibole “anhydride” which was interpreted as being the disordered equivalent of the starting material.

The cation occupancy of the \(M(1)\), \(M(2)\), and \(M(3)\) sites in synthetic magnesiohastingsites produced in this study has been deduced from the Mössbauer data of Table 8 (assuming \(4\text{Mg} + \text{Fe}\) per \(2M(1) + 2M(2) + M(3)\) sites) and is presented in Table 11. The results for natural magnesiohastingsite based on the new microprobe analysis (Table 12) and the Mössbauer spectra, assuming \(\text{Ti}^{4+}\) and \(\text{Al}^{3+}\) to be concentrated in \(M(2)\), are included for comparison.

### Table 11. Octahedral Site Occupancy in Synthetic and Natural Magnesiohastingsite

<table>
<thead>
<tr>
<th>Sample*</th>
<th>(M(1)), (M(3))</th>
<th>(M(2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>IQF (avg)</td>
<td>(\text{Mg} = 0.79) (\text{Fe}^{2+} = 0.21)</td>
<td>(\text{Fe}^{3+} = 0.07)</td>
</tr>
<tr>
<td>CT-4</td>
<td>(\text{Mg} = 0.87) (\text{Fe}^{2+} = 0.06)</td>
<td>(\text{Fe}^{3+} = 0.07)</td>
</tr>
<tr>
<td>CT-4</td>
<td>(\text{Mg} = 0.85) (\text{Fe}^{2+} = 0.15)</td>
<td>(\text{Fe}^{3+} = 0.73)</td>
</tr>
</tbody>
</table>

* Sample identities: (1) magnesiohastingsite synthesized at low oxygen fugacity (IQF buffer) and rerun at high oxygen fugacity (average of 4); (2) magnesiohastingsite synthesized at high oxygen fugacity (CT buffer) and rerun at low oxygen fugacity (average of 2).

In magnesiohastingsite directly synthesized from an oxide mix, the number of \(\text{Fe}^{2+}\), \(\text{Fe}^{3+}\), and \(\text{Mg}\) ions per site clearly does not reflect random distribution of these ions (0.20Fe + 0.80Mg per site if random). Evidently \(\text{Fe}^{3+}\) has a strong preference for the \(M(2)\) site over \(M(1)\) and \(M(3)\), whereas \(\text{Fe}^{2+}\) is less strongly concentrated in \(M(1)\) and \(M(3)\). Although the observed cation distribution may be different from the equilibrium distribution at the conditions of synthesis, the ordering scheme observed compares favorably with the results obtained for sample U-1236. For this sample \(\text{Fe}^{3+}\) seems to be restricted to \(M(2)\), whereas \(\text{Fe}^{2+}\) occupies all octahedral sites but is relatively concentrated in \(M(1)\) and \(M(3)\). The cation distribution scheme observed is also in agreement with the crystal-chemical behavior of other natural calcic amphiboles (Zussman, 1955; Ghose, 1965; Ernst, 1968; Papike et al., 1969).

In pargasite synthesized at similar pressure and temperature conditions, Al occupancy of \(M(1)\) and \(M(3)\) deduced from the i.r. spectrum is 0.23 ± 0.05 ions per site and thus undistinguishable from random distribution. Apparently ionic size differences between \(\text{Fe}^{3+}\) and Al play a lesser role in the octahedral ordering process than the higher electronegativity of the former ion over the latter. The process presumably involves the rectification of...
charge imbalance caused by Al for Si substitution in the tetrahedral chains. If similar considerations (here the local charge imbalance may be caused by the more or less complete occupancy of the “A” site by monovalent ions and/or the occupancy of the M(4) site by monovalent ions) can be extended to the glaucophane-magnesioriebeckite series, then the lack of polymorphism in the iron-rich portion, noted by Ernst (1963), could be explained by the fact that Fe$^{4+}$ is already concentrated in M(2) for all pressure, temperature conditions investigated.

When compared to their initial values, the site occupancies of the oxidized and reduced samples (IQF to CT and CT to IQF, respectively, Table 11) are seen to remain essentially unchanged except for in situ oxidation or reduction of Fe ions. Furthermore, it appears that Fe ions in M(1) and M(3) are preferentially reduced (in the reduced sample) but that Fe ions in M(2) are also affected. Similar relations are also suggested by the infrared spectra of samples hydrothermally oxidized for longer times (AA9-11T and AA9-12T, Tables 7 and 10). Redox reactions apparently occur at least an order of magnitude faster than octahedral cation rearrangements at these temperatures.

Mechanism of Fe$^{3+}$ reduction in synthetic Mh.

The structural formula of the end-member magnesiohastingsite, NaCa$_2$Mg$_4$Fe$_3$Si$_6$Al$_2$O$_{22}$ (OH)$_2$, in which all sites are filled, does not theoretically allow for the occurrence of Fe$^{2+}$ ions without the addition of positive ions or the subtraction of anions. Three mechanisms that would produce the observed effects have been considered:

1. The amphiboles synthesized are not “on composition,” or the composition varies as a function of run conditions.
2. The structure allows anion vacancies when exposed to low oxygen fugacity.
3. Protons in excess of two per unit formula can be accommodated in the structure at low values of $f_{\text{O}_2}$, ($= \text{high } f_{\text{O}_2}$).

Each involves the diffusion of some species in or out of the amphibole structure. A model where no diffusion occurs but charge balance is attained by the change in valence of ions other than Fe seems to be out of the question.

If the proportions of oxides in the starting material were not equal to what is required for magnesiohastingsite synthesis, solid solution with other end-members could have produced variations in Fe$^{3+}$/\(\text{Fe}^{3+} + \text{Fe}^{2+}\) ratio with run conditions. To test this hypothesis two amphiboles synthesized at high (CT buffer) and low (IQF buffer) oxygen fugacity have been analyzed with an electron microprobe. The data presented in Table 6 show that the oxide percentages are equal, within experimental errors, to those of the ideal end-member. This seems to rule out the possibility of significant compositional variation. Furthermore, refractive indices and cell parameters presented in this work were obtained from specimens synthesized from three batches of oxide mixes prepared at several months’ interval. No systematic differences in those properties were observed, indicating that errors in starting material preparation were probably kept to a minimum. Solid-solution with other amphibole end-members (mostly ferropargasite and/or ferroedenite) to produce the observed high Fe$^{2+}$ proportion at low oxygen fugacity (IQF buffer) would require that at least 10 percent by volume of other phases be present in the synthetic products. Such phases (clinopyroxene, olivine, plagioclase, etc.) would most certainly have been detected with the petrographic microscope or by X-ray powder diffraction. Variations or systematic deviations from the ideal bulk composition may still account for a minor part of the redox phenomenon but are certainly not the major factor in this effect.

The feasibility of the second mechanism proposed is very difficult to assess by direct analytical means because of the lack of reliable oxygen determination methods. Anion vacancies, especially at low oxygen fugacities (IQF buffer) could conceivably establish electrical neutrality in reduced magnesiohastingsite. If, however, this mechanism were solely responsible it would require that close to one oxygen position per unit cell (on the average) be vacant \((\text{Na}_{32}\text{Ca}_{4}\text{Mg}_{8}\text{Fe}_{2}^{2+}\text{Si}_{12}\text{Al}_{4}\text{O}_{48}\square(\text{OH})_{4})\); such a structure would most probably be quite unstable. Moreover, the oxidation of Fe$^{2+}$ (sample IQF to CT) without concomitant diffusion of oxygen into the vacant anion position should lead to a loss of positive charge (presumably mostly H$^+$ or Na$^+$); no evidence for such a loss has been obtained. On the other hand, if rapid (less than a few hours) O$^{2-}$ diffusion on oxidation or reduction were possible, it would likely involve cation rearrangement toward the more stable distribution (Fe$^{3+}$ in M(1) and M(3), Fe$^{2+}$ in M(2)). Such cation redistributions were not observed in samples IQF to CT and CT to IQF.

A model involving the reduction of “theoretical magnesiohastingsite” by the formation of hydroxyl
groups in excess of two per unit formula was tested with the available data. From the equilibrium constant for the reaction:

\[ 2 \text{NaCa}_2\text{Mg}_2\text{Fe}^3\text{Si}_8\text{Al}_2\text{O}_{22}(\text{OH})_2 + \text{H}_2 \rightleftharpoons 2 \text{NaCa}_2\text{Mg}_2\text{Fe}^3\text{Si}_6\text{Al}_2\text{O}_{22}\text{H}(\text{OH})_2 \]

we obtain:

\[ RT \ln f_{\text{H}_2} = 2(\mu_{\text{Fe}^3\text{+}} - \mu_{\text{Fe}^3\text{+o}}) \]

where \(f_{\text{H}_2}\) is the hydrogen fugacity in the gas phase, \(\mu_{\text{Fe}^3\text{+}}\) and \(\mu_{\text{Fe}^3\text{+o}}\) are the standard chemical potential of the reduced and "ideal" magnesiohastingsite respectively, and \(a_{\text{Fe}^3\text{+}}\) and \(a_{\text{Fe}^3\text{+o}}\) are the activities of the "end members" in the amphibole solid solution. For an ideal solid-solution (the data do not warrant a more rigorous treatment), the activity \(a_{\text{Fe}^3\text{+}}\) of ideal magnesiohastingsite in the solid-solution is equal to \(x_{\text{Fe}^3\text{+}}\) (hereafter denoted \(x\)), the molar concentration. \(a_{\text{Fe}^3\text{+}}\) is also equal to the molar concentration of the "reduced end-member" and to \(1 - x\). Then for the equation above

\[ \log f_{\text{H}_2} = 2 \log \frac{1 - x}{x} + \text{constant}. \]

Hydrogen fugacity in the gas phase may be calculated as a function of total pressure, temperature, and oxygen fugacity, as defined by the different buffers (Eugster and Wones, 1962):

\[ f_{\text{H}_2} = \frac{P_{\text{H}_2} \gamma_{\text{H}_2} \gamma_{\text{H}_2\text{o}}}{K_{\text{W}} f_{\text{o}_2}^{1/2} \gamma_{\text{H}_2} \gamma_{\text{H}_2\text{o}}} \]

where \(P\) is the total pressure, \(K_{\text{W}}\) is the equilibrium constant for H\(_2\)O dissociation, \(f_{\text{H}_2}\), \(f_{\text{o}_2}\) are the \(\text{H}_2\) and \(\text{O}_2\) fugacities, and \(\gamma_{\text{H}_2}\), \(\gamma_{\text{H}_2\text{o}}\) are the fugacity coefficients for \(\text{H}_2\) and \(\text{H}_2\text{o}\). At 850°C, 2000 bars total pressure, the following values obtain: \(K_{\text{W}} = 4.387 \times 10^8\) (JANAF Tables, 1965); \(\gamma_{\text{H}_2} = 1.403\) (Shaw and Wones, 1964); \(\gamma_{\text{H}_2\text{o}} = 0.8760\) (Burnham et al, 1969); and

\[ f_{\text{H}_2} = \frac{2806}{7.026 \times 10^8 \times f_{\text{o}_2}^{1/2} + 1} \]

The values obtained for \(\log f_{\text{H}_2}\) and \(\log (1 - x)/x\) for the amphiboles directly synthesized from an oxide mix are presented in Figure 6; the size of the symbols represents the estimated accuracy based on \(5 \pm 0.05\) for \(x\), and \(6^\circ\text{C}\) from the nominal 850°C. A straight line has been fitted visually to the data points; the slope obtained \((2.5 \pm 0.4)\) is consistent with (but far from proving) the model proposed which requires a slope of 2. Other aspects of the redox process make the latter model particularly attractive. The fast diffusion rates would be in accordance with a mechanism first proposed by Brindley and Youell (1953) for chamosite. They showed that for this structure the reaction:

\[ \text{Fe}^{2+} + \text{OH}^- \rightleftharpoons \text{Fe}^{3+} + \text{O}^{2-} + \text{H}^+ + e^- \]

That is, oxidation or reduction of Fe occurs by the break or formation of OH bonds from or to Fe ions (by diffusion of H*, e− pairs) and provides an easily reversible process even at rather low temperatures. An identical mechanism has since been invoked to account for similar phenomena in micas and amphiboles (Addison et al, 1962a; Addison et al, 1962b; Eugster and Wones, 1962; Wones, 1963; Newman and Brown, 1966; Patterson and O’Connor, 1966; Vedder and Wilkins, 1969; Ernst and Wai, 1970). Wilkins and Vedder (1969) present a review of the phenomenon for micas and amphiboles. Furthermore, Newman and Brown (1966) and Newman (1967, 1970) have presented evidence which strongly

![Fig. 6. Hydrogen fugacity of the gas phase coexisting with "magnesiohastingsite solid-solution" containing \(x\) (mole fraction) ideal Mh and 1 - \(x\) reduced Mh. The size of the symbols indicates the estimated accuracy. Value for CT extends to \(-\infty\).]
suggests protonation of oxygens in the tetrahedral sheets of artificially altered micas. During heat-treatment in H₂ of experimentally oxidized or outgassed crocidolites, Addison and Sharp (1962) produced strongly reduced amphiboles. At a relatively low temperature (415°C), the structure is not destroyed and the measured intake of H₂ led the authors to postulate proton fixation by oxygens coordinated to the tetrahedral chains. The oxygen O(4) is a likely candidate for protonation due to its strong underbonding (loc.cit.; Brown and Gibbs, 1969). The presence of hydroxyls in excess of two per formula unit is also suggested by a number of amphibole analyses (Zussman, 1955; Gillberg, 1964; Leake, 1968; Witte et al., 1969) and may not all be due to inaccurate H₂O determination. The broad absorption band in the i.r. spectra of the Fe²⁺-rich synthetic magnesiohastingsites in the OH-stretching region may be attributed to extra hydroxyl ions (protons coordinated to oxygens of the tetrahedral chains). In this case oxidation would only involve the diffusion of the extra protons and would not require the loss of normal O(3)-H hydroxyls coordinated to the octahedral cations, in agreement with the major features of the i.r. spectra.

Most of the experimental data suggest that redox in magnesiohastingsite involves the protonation of oxygens belonging to the tetrahedral chains, but this may not be the only mechanism responsible. For instance, it is not clear why magnesiohastingsite with Fe²⁺/(Fe²⁺ + Fe³⁺) = 87 percent can be synthesized directly from an oxide mix at low oxygen fugacity, whereas the reduction of a previously synthesized Fe³⁺ amphibole cannot be carried further than Fe²⁺/(Fe²⁺ + Fe³⁺) = 65 percent under the same conditions. Furthermore, the variation of cell parameters with the proportions of Fe²⁺ and Fe³⁺ are not always in the expected direction. For example, the relationship of the b cell dimension with the mean radius of cations occupying M(2), as observed by Colville et al. (1966), does not seem to hold in detail for the amphiboles produced in this study. A small proportion of anion vacancies compensated by Fe reduction (in addition to OH) may explain the relatively shorter a and b parameters in samples synthesized at low oxygen fugacity (Table 5). If such vacancies were retained on oxidation (they are, then, no longer compensated by a neighboring Fe²⁺ ion but by some other process), the slightly enlarged a repeat in oxidized samples (Table 13) could be attributed to a small dilation of the structure across the tetrahedral chains and octahedral strips by cation-cation repulsion. In contrast to this, comparisons of the b parameter in the Fe³⁺ samples (CT buffer, Table 5) and in the reduced samples (Table 13) show a normal trend, b being enlarged when some Fe²⁺ in M(2) is reduced to the larger Fe²⁺ ion, while the other dimensions remain constant.

Conclusions

Saxena and Ekström (1970) have shown that the variability of (OH) content in amphiboles is a significant parameter of this mineral group's crystal-chemistry. Inaccurate H₂O analysis, however, has a notable influence on the computation of structural formulae (Leake, 1968), particularly the distribution of tetrahedral and octahedral cations. As this study suggests, computation of structural formulae on the basis of 23 anions or 24 (O, OH, F, Cl) may not always be appropriate. However, this may be the only alternative in the absence of accurate density and cell parameter measurements, and of accurate chemical analyses that include oxidation ratios for elements with variable valence.

Although it is not known whether “reduced magnesiohastingsite” would be stable in systems differing chemically from its own bulk composition, this amphibole could indicate the existence of a stability field for similar hornblendes occurring in igneous or metamorphic rocks. Natural and synthetic amphiboles experimentally studied so far have indicated that redox reactions occur in them at a very fast rate due to the high mobility of protons and electrons. It is, therefore, unlikely that the measured oxidation ratios in metamorphic and igneous hornblendes will reflect the redox potential at the time of crystallization. They will instead carry the imprint of conditions existing at some late cooling stage. Within certain limits, compositional variations in natural amphiboles may not significantly affect the oxidation ratios (the other variables being held constant). This is suggested by the behavior of the iron-depleted samples (NNO buffer). The distribution of the absolute amounts of Fe ions per site is a function of the intensive parameter controlling crystallization, especially oxygen fugacity. Therefore,
the accurate determination of site occupancy for Fe ions could, in principle, serve as an intensive variable indicator (mostly \( f_o \), sensitive), providing the Fe distribution has not changed on cooling.

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