

## A Crystal-Chemical Study of Synthetic Magnesiohastingsite

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### Abstract

Mössbauer and infrared spectra of synthetic magnesiohastingsite (Mh),  $\text{NaCa}_2\text{Mg}_4\text{Fe}^{3+}\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$ , indicate that, except at high values of  $f_{\text{O}_2}$ , Fe occurs both as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  contrary to the ideal formula. The amount of  $\text{Fe}^{2+}$  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  $\text{Fe}^{2+}$  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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  present. Refractive indices ( $\alpha = 1.642\text{--}1.657$ ;  $\gamma = 1.653\text{--}1.672$ ), color, and unit-cell parameters ( $a = 9.928\text{--}9.933 \text{ \AA}$ ;  $b = 18.015\text{--}18.029 \text{ \AA}$ ;  $c = 5.282\text{--}5.297 \text{ \AA}$ ;  $\beta = 105.43\text{--}105.46^\circ$ ) also reflect the  $f_{\text{O}_2}$  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  $\text{Fe}^{2+}$  in synthetic Mh which involves an excess of two protons (and/or anionic defects at low  $f_{\text{O}_2}$ ) per unit formula.

### Introduction

As a preliminary step in the study of the phase relations of the calcic amphibole end-member magnesiohastingsite,<sup>2</sup> ( $\text{NaCa}_2\text{Mg}_4\text{Fe}^{3+}\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$ ), 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.*, Papike *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  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in variable proportions according to experimental conditions. The mere existence of  $\text{Fe}^{2+}$  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<sup>3</sup>

*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  $\pm 10$  bars, and  $\pm 6^\circ\text{C}$ , 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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<sup>2</sup> End-members nomenclature follows Ernst (1968).

<sup>3</sup> Detailed description of the experimental apparatus and the analytical techniques are presented in Semet (1972).

TABLE 1. Abbreviations and Symbols\*

Oxygen fugacity buffers		Other symbols	
IQF	$2\text{Fe}+\text{SiO}_2+\text{O}_2 = \text{Fe}_2\text{SiO}_4$	n	Refractive index
FMQ	$3\text{Fe}_2\text{SiO}_4+\text{O}_2 = 2\text{Fe}_3\text{O}_4+3\text{SiO}_2$	Mh	Magnesiohastingsite
NNO	$2\text{Ni}+\text{O}_2 = 2\text{NiO}$	$f_{\text{O}_2}$	Oxygen fugacity
MMO	$6\text{MnO}+\text{O}_2 = 2\text{Mn}_3\text{O}_4$		
CCO	$4\text{Cu}+\text{O}_2 = 2\text{Cu}_2\text{O}$		
HM	$4\text{Fe}_3\text{O}_4+\text{O}_2 = 6\text{Fe}_2\text{O}_3$		
CT	$2\text{Cu}_2\text{O}+\text{O}_2 = 4\text{CuO}$		

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

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-K $\alpha$  radiation) by a least-square program (Burnham, 1962) using Si ( $a = 5.43054 \text{ \AA}$ ) as an internal standard. Indexing was done by comparison with single crystal (U-1236)<sup>4</sup> 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  $f_{\text{O}_2}$  and sample U-1236 are listed in Table 5.

*Mössbauer spectra.* Data collection was done on a conventional loud-speaker 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 Fe<sup>57</sup> 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  $\text{cm}^{-1}$ ) was covered in more detail with the abscissa expanded 2 $\times$ , 5 $\times$ , and 10 $\times$ . High resolution spectra were obtained on carefully dried specimens and show very little absorption due to absorbed H<sub>2</sub>O.

*Electron microprobe analysis.* Chemical compositions of selected samples of synthetic Mh and sample U-1236 were obtained on an ARL-EMX electron microprobe. Analyzed hornblends were 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

<sup>4</sup> The sample referred to as U-1236 was collected by the author from the same site (Iron Hill, Gunnison Co., Colo.) as U-1236 from Larsen (1942). A new microprobe analysis is presented in Table 6.

TABLE 2. Thermodynamic Data on the Oxygen Fugacity Buffers

Buffer	$\text{Log } f_{\text{O}_2} = -\frac{A}{T} + B + \frac{C(P-1)}{T} *$			Reference
	A	B	C	
IQF	29382.	7.51	.050	Eugster and Wones, 1962
FMQ	25660.	8.92	.092	Wones and Gilbert, 1969
NNO	24709.	8.94	.046	Eugster and Wones, 1962
MMO	25680.	13.38	.0807	Huebner and Sato, 1970
CCO	17050.	6.85	.096	Semet, manuscript
HM	24912.	14.41	.019	Eugster and Wones, 1962
CT	13928.	10.34	.0105	Semet, manuscript

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

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  $\pm$  melilite) 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 ( $10 \times 5 \times 5 \mu\text{m}$ ) and prolonged run time does not bring about significant growth. Crystals of a larger size ( $100 \times 20 \times 20 \mu\text{m}$ ) 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 nucleation 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 3. Optical Properties of Synthetic Magnesiohastingsite\*

Buffer	$-\log f_{\text{O}_2}$	$\alpha$	$\gamma$	ZAC
IQF	18.56	1.642(4)	1.653(4)	24°
FMQ	13.76	1.650(5)	1.662(4)	26°
NNO	12.98	1.637(6)**	1.649(6)**	23°
U	$\sim 10.50$	1.653(8)	1.668(8)	25°
HM	7.74	1.654(4)	1.669(4)	25°
CT	2.03	1.657(3)	1.672(4)	25°

\* 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

			A3-11T			Natural Magnesiohastingsite Iron Hill, Colorado		
h	k	l	d <sub>calc</sub>	d <sub>obs</sub>	I/I <sub>0</sub>	d <sub>calc</sub>	d <sub>obs</sub>	I/I <sub>0</sub>
0	2	0	9.01	9.00	2	9.03	9.05	4
1	1	0	8.45	8.40	20	8.47	8.46	33
1	3	0	5.09	5.06	1			
-1	1	1	4.91	4.87	2			
0	4	0	4.51	4.49	5	4.51	4.51	9
2	2	0	4.22	4.22	3	4.23	4.24	2
1	1	1	3.975	3.978	2			
-1	3	1	3.891	3.883	3			
1	3	1	3.372	3.369	31	3.379	3.378	21
2	4	0	3.279	3.273	33	3.286	3.283	32
3	1	0	3.138	3.133	100	3.147	3.144	>100
-3	1	1	3.056	3.050	2			
2	2	1	2.933	2.932	37	2.939	2.940	18
3	3	0	2.815	2.811	16	2.822	2.820	26
-3	3	1	2.755	2.752	23	2.761	2.759	15
1	5	1	2.700	2.696	48	2.705	2.704	28
-1	1	2	2.621	2.626	2			
0	6	1	2.589	2.586	31	2.593	2.592	15
-2	0	2	2.553	2.548	35	2.558	2.559	11
0	0	2	2.553			2.558		
-2	2	2	2.456	2.450	3			
-2	6	1	2.418	2.410	4			
3	5	0	2.387	2.387	7	2.393	2.393	9
-3	5	1	3.251	2.344	39	2.355	2.353	28
-4	2	1	2.344			2.350		
-1	7	1	2.299	2.295	14	2.303	2.302	7
3	3	1	2.251	2.250	3			
-2	4	2	2.221	2.219	6			
2	6	1	2.158	2.156	30	2.162	2.162	20
-4	0	2	2.037			2.042		
2	0	2	2.037	2.035	24	2.042	2.042	9
3	5	1	2.014	2.012	13	2.018	2.017	8
3	7	0	2.003	2.002	2	2.007	2.009	3
1	9	0	1.9599	1.9564	2	1.9632	1.9611	3
5	1	0	1.9015	1.9012	10	1.9068	1.9062	15
-4	6	1	1.8882	1.8876	3	1.8923	1.8947	2
-1	9	1	1.8643					
-4	4	2	1.8563	1.8581	5			
2	4	2	1.8565					
-1	7	2	1.8465					
5	3	0	1.8221	1.8210	3	1.8270	1.8264	4
0	10	0	1.8022	1.7998	2	1.8051	1.8039	3
-5	1	2	1.7661	1.7648	3			
-1	1	3	1.7506	1.7499	2			
0	10	1	1.6995					
0	0	3	1.7023	1.7017	3			
3	9	0	1.6956					
-3	1	3	1.6947					
-2	8	2	1.6893	1.6874	8			
-1	3	3	1.6880					
0	2	3	1.6727	1.6741	3			
4	6	1	1.6486	1.6476	19	1.6524	1.6529	12
4	8	0	1.6394	1.6401	1	1.6429	1.6428	2
1	11	0	1.6149	1.6140	7	1.6175	1.6171	5
6	0	0	1.5035	1.5926	5	1.5979	1.5978	8
-1	5	3	1.5808	1.5780	7			
4	0	2	1.5507	1.5490	13	1.5543	1.5538	7
-6	0	2	1.5505			1.5542		
1	9	2	1.5152	1.5153	13	1.5202	1.5197	4
0	12	0	1.5019	1.5022	11	1.5043	1.5043	9
-2	12	2	1.4724	1.4762	2			
-6	4	2	1.4661	1.4683	1			
4	4	2	1.4663					
1	5	3	1.4652	1.4641	1			
2	2	3	1.4637					
3	11	0	1.4571	1.4565	1	1.4598	1.4615	2
-6	6	1	1.4473	1.4467	26	1.4508	1.4509	28
4	10	0	1.4390	1.4391	1			
-5	3	3	1.4400	1.4213	1			
-3	7	3	1.4199					
-4	6	3	1.4146	1.4128	1			
6	6	0	1.4077	1.4072	1			
6	2	1	1.4002	1.4030	1			
-5	5	3	1.3716	1.3717	2			
7	1	0	1.3619	1.3621	10	1.3651	1.3655	8
5	1	2	1.3617			1.3657		

TABLE 5. Cell Parameters of Synthetic\* and Natural\*\* Magnesiohastingsite

Buffer	a Å	b Å	c Å	β (degrees)	V Å <sup>3</sup>
IQF avg of 8	9.928(2)	18.015(9)	5.282(3)	105.43(4)	910.7(8)
WM avg of 5	9.930(5)	18.025(8)	5.290(4)	105.43(4)	912.0(10)
FMQ avg of 10	9.933(2)	18.029(4)	5.293(1)	105.43(1)	913.0(5)
NNO avg of 3	9.932(2)	18.015(4)	5.289(1)	105.43(2)	912.2(3)
MH avg of 6	9.933(1)	18.028(3)	5.297(1)	105.44(2)	914.3(3)
CT avg of 12	9.926(5)	18.029(9)	5.297(4)	105.46(5)	913.7(8)
Nat. Mn.**	9.940(3)	18.050(4)	5.310(4)	105.45(4)	918.4(4)

\* Samples synthesized at 850°C, 2000 bars.

\*\* Iron Hill, Colorado.

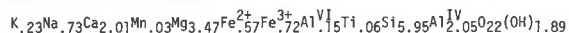
mental conditions combining a fast recrystallization of the starting material to an amphibole, a high yield (close to 100 percent), and a good crystallinity. Run conditions for synthesis of the samples cited in the text are presented in Table 7.

Oxygen fugacity has a pronounced effect on the color of synthetic magnesiohastingsite. At high oxygen fugacity (CT buffer) the color of the amphi-

TABLE 6. Chemical Composition of Synthetic and Natural Magnesiohastingsite

	1	2	3	4
SiO <sub>2</sub>	42.08	40.94	41.8	41.2
Al <sub>2</sub> O <sub>3</sub>	11.90	12.85	12.1	11.6
TiO <sub>2</sub>	-	0.58	-	-
FeO	8.39	10.57	8.4	8.5
MgO	18.82	16.01	19.1	18.5
CaO	13.09	12.93	13.2	12.9
MnO	-	0.26	-	-
Na <sub>2</sub> O	3.62	2.59	3.5	3.5
K <sub>2</sub> O	-	1.24	-	-
H <sub>2</sub> O	2.10	2.03*	2.1**	2.1**
Total	100.00	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 Si, Al, Ti, Fe, Mg, Ca, and Mn, the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio given by Mössbauer spectra, and (OH)<sup>-</sup> as required to compensate for total cationic charge gives:

3. A3-11T, synthetic magnesiohastingsite, 850°C, 2000 bars, CT buffer.

4. A4-11C, synthetic magnesiohastingsite, 850°C, 2000 bars, IQF buffer.

\* H<sub>2</sub>O by difference.\*\* Theoretical H<sub>2</sub>O from column 1.

bole 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 oxyphases. However, the specific refractive energy for  $\text{Fe}_2\text{O}_3$  being larger than for  $\text{FeO}$  (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 =  $7.694 \times 10^{-20}$  ergs). Finally, the

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

Sample	Starting material	Buffer	$-\log f_{\text{O}_2}$	T (°C)	Time (h)
IQF-A3	Oxide mix	IQF	18.56	850	50
OX to IQF	Oxide mix	IQF	18.56	850	28
FMQ-A2	Oxide mix	FMQ	13.76	850	46
CT-A2	Oxide mix	CT	2.03	850	26
CT to IQF	Mh (CT buffer)	IQF	18.56	850	10
IQF to CT	Mh (IQF buffer)	CT	2.03	850	10
NNO-A1	Oxide mix	NNO	12.98	850	50
HM-A2	Oxide mix	HM	7.74	850	50
OA5-19-71U	Mh (unbuffered)	CCO	10.36	707	150
AA9-11T	Mh (IQF buffer)	CT	2.03	850	19
AA9-12T	Mh (IQF buffer)	CT	2.03	850	42

\* Total pressure was maintained at 2000 bars  $\pm$  10 bars for all runs.

ratios of the peak areas in a multisite compound are, in general, directly proportional to the absolute numbers of contributing  $\text{Fe}^{57}$  nuclei. To be rigorous, the ratio of the recoil-free fractions  $f^{\text{R}}$  of  $\text{Fe}^{57}$  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  $\text{Fe}^{2+}$  between  $M(4)$  and  $M(1) + M(2) + M(3)$  has not proven significant in the recent crystal structure determination of  $C2/m$  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  $\text{Fe}^{3+}$ . Ernst and Wai (1970) have reported a case (sample C-4980) where  $\text{Fe}^{3+}$  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 equivalents show absorption attributable to  $\text{Fe}^{3+}$  in tetrahedral sites. Furthermore, synthetic studies have shown that significant  $\text{Fe}^{3+}$  can enter the tetrahedral site in the related diopside structure (Huckenholz *et al.*, 1969; Hafner and Huckenholz, 1971). It is thus possible that, even when Al is present in excess

<sup>5</sup>  $f^{\text{R}}$  is the fraction of  $\text{Fe}^{57}$  nuclei which absorb the  $\gamma$  ray resonantly without recoil. It is dependent on temperature and on the vibrational spectrum at each iron site in the structure.

of what is required to fill the Si I and Si II sites, randomization of Al and  $\text{Fe}^{3+}$  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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  would consist of absorption peaks contributed by six different octahedrally coordinated Fe "species," namely  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in  $M(1)$ ,  $M(2)$ , and  $M(3)$ . Greaves *et al* (1971) and Burns and Greaves (1971) have, for instance, resolved the  $\text{Fe}^{2+}$  spectrum of actinolites into three quadrupole split doublets, the contributions arising from  $\text{Fe}^{2+}$  in  $M(1)$ ,  $M(2)$ , and  $M(3)$ . It is, however, very difficult if not impossible to resolve the  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  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 ( $\log f_{\text{O}_2} = -10.36$ ) 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  $\text{Fe}^{3+}$  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  $f_{\text{O}_2}$  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 8 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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in distorted octahedral sites (Bancroft *et al*, 1967a; Dollase, personal communication). Table 7 summarizes the experimental conditions of synthesis for the specimens.

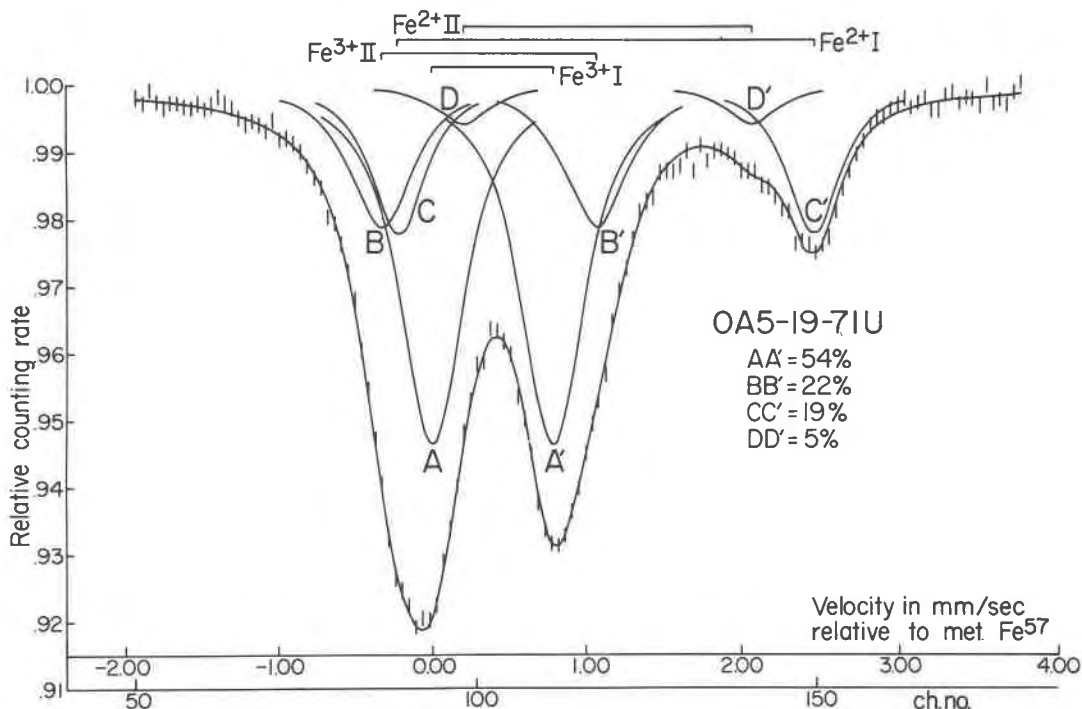


FIG. 1. Mössbauer spectrum of sample OA5-19-71U ("annealed Mh, 707°C, 2000 bars, cco buffer). 0 mm/sec corresponds to the isomer shift of metallic  $\text{Fe}^{57}$ .

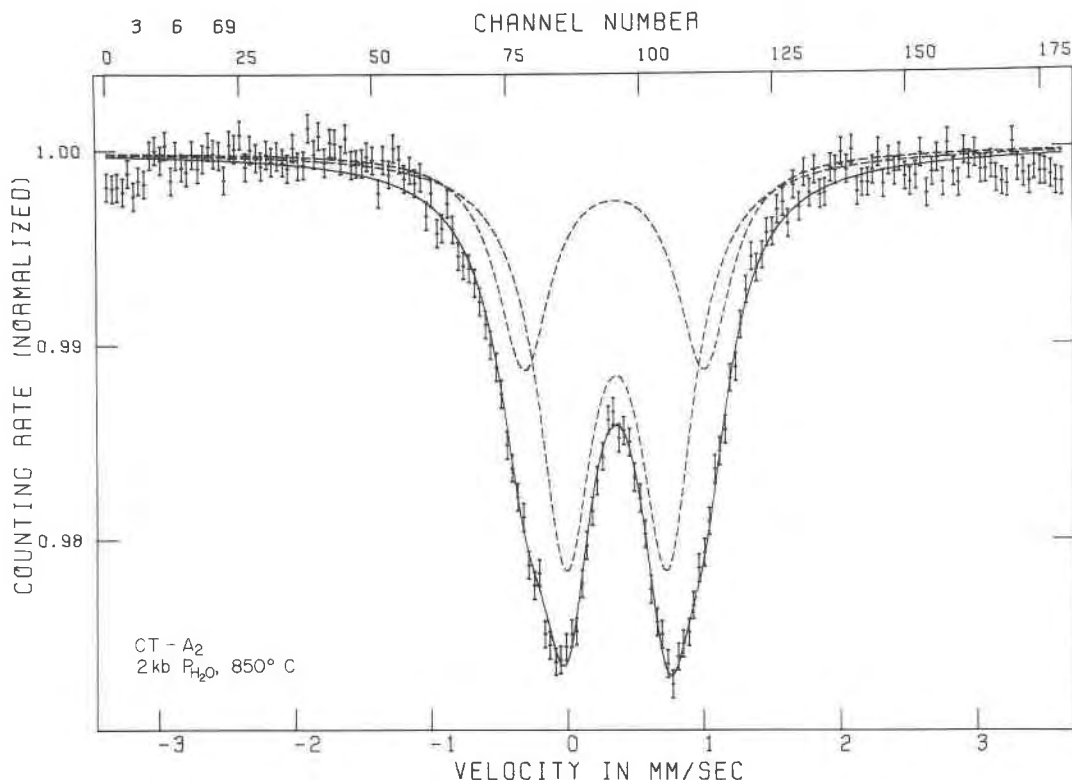


FIG. 2. Computer plotted Mössbauer spectrum of sample CT-A2. 0 mm/sec corresponds to the isomer shift of metallic Fe<sup>57</sup>.

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<sup>3+</sup> doublets with unequal widths gave the best  $\chi$  for sample CT-A2.<sup>6</sup> 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<sup>3+</sup> 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<sup>3+</sup> doublets did not result in convergence, indicating that if more than one Fe<sup>3+</sup> "species" existed, it must be only minor. The three quadrupole doublets fitted with equal Fe<sup>2+</sup> half-widths and an independent Fe<sup>3+</sup> half-width gave a good resulting  $\chi$ . It is apparent from the table that, in general, the peak positions agree well. The Fe<sup>3+</sup> 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<sup>3+</sup> "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<sup>3+</sup> in the M(2) site; it represents the major contribution of Fe<sup>3+</sup> to the total absorption and confirms the gen-

<sup>6</sup> A value of  $\chi$  less than 1.00 means that the *rms* deviation per channel is less than the variance at a single channel but is a statistically acceptable value if the observations consist of a limited number of channels.

TABLE 8. Mössbauer Parameters of Synthetic and Natural Magnesiohastingsite\*

Sample	Outer Fe <sup>2+</sup> Doublet				Inner Fe <sup>2+</sup> Doublet				Outer Fe <sup>3+</sup> Doublet				Inner Fe <sup>3+</sup> Doublet				X
	I.S.**	Q.S.	HWHH	%	I.S.	Q.S.	HWHH	%	I.S.	Q.S.	HWHH	%	I.S.	Q.S.	HWHH	%	
IQF avg of 2	1.13(1)	2.73(2)	.19(1)	63(3)	1.14(2)	2.11(3)	.19(1)	24(3)					.26(9)	.79(6)	.19(1)	13(1)	1.55
FMQ-A2	1.10(1)	2.74(2)	.19(1)	37(2)	1.15(2)	1.92(4)	.19(1)	17(2)					.36(1)	.84(1)	.19(1)	46(1)	1.36
CT-A2									.35(3)	1.28(7)	.31(2)	46(2)	.36(1)	.73(3)	.25(1)	54(2)	.90
OA5-19-71U	1.12(1)	2.67(2)	.23(1)	19(1)	1.13(3)	1.87(7)	.23(1)	5(1)	.37(2)	1.39(3)	.26(1)	22(2)	.39(1)	.79(1)	.26(1)	54(2)	.94
CT to IQF	1.12(1)	2.71(2)	.21(1)	47(2)	1.17(2)	2.01(4)	.21(1)	18(3)					.37(2)	.85(2)	.21(1)	35(1)	1.08
IQF to CT									.37(2)	1.23(4)	.34(1)	66(3)	.37(1)	.79(2)	.24(1)	34(2)	1.13
Nat. Mh. Colorado	1.12(1)	2.64(1)	.21(1)	37(1)	1.10(3)	2.01(6)	.21(1)	7(1)					.39(1)	.80(1)	.25(1)	56(1)	1.05

\* All Isomer Shifts are quoted relative to Fe<sup>57</sup> in metallic iron.

\*\*All Isomer Shifts, Quadrupole Splittings, and Half Widths at Half Height are quoted in mm/sec.

Numbers in parentheses indicate precision on the last digit; accuracy may be significantly lower for strongly overlapping peaks.

erally accepted view that trivalent *M* cations present in clin amphiboles are concentrated in this site. The remaining Fe<sup>3+</sup> doublet BB' is attributed to unresolved absorption from Fe<sup>3+</sup> 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 constraint was not applied (CT-A2 and IQF to CT) also seems to favor such an assignment. The two Fe<sup>2+</sup> doublets CC' and DD' are very similar to those found in actinolite (Bancroft *et al.*, 1967a; Greaves *et al.*, 1971; Burns and Greaves, 1971). The outer doublet CC', which is also the most intense, is due to Fe<sup>2+</sup> in *M*(1) and *M*(3) (unresolved); the inner doublet DD' represents Fe<sup>2+</sup> in *M*(2). Assuming that Fe<sup>2+</sup> 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<sup>3+</sup>, 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 HM buffers to determine the Fe<sup>3+</sup>/Fe<sup>2+</sup> 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 mineralogically 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 hydroxyl-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 similarity 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 (Papike *et al.*, 1969). Combinations of cations with different electronegativities and/or polarizabilities (mostly Mg, Fe<sup>2+</sup>, Fe<sup>3+</sup>, 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-actinolite series (Burns and Strens, 1966; Wilkins, 1970; Burns and Greaves, 1971), the OH stretching frequencies corresponding to MgMgMg, MgMgFe<sup>2+</sup>, MgFe<sup>2+</sup>Fe<sup>2+</sup>, Fe<sup>2+</sup>Fe<sup>2+</sup>Fe<sup>2+</sup> groups coordinated to the hydroxyl are equal within a few cm<sup>-1</sup>. Here, the proton is vibrating in a cavity closed by Si<sub>6</sub>O<sub>24</sub> 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 9. Oxidation Ratios in Synthetic Magnesiohastingsite

Sample	-log <i>f</i> <sub>02</sub>	Fe <sup>3+</sup> * Percent	Fe <sup>2+</sup> ** Percent
IQF***	18.56	13	87
FMQ-A2	13.76	46	54
NNO-A1	12.98	57	43
OA5-19-71U	10.36	76	24
HM-A2	7.74	89	11
CT-A2	2.03	100	-
CT to IQF	18.56	35	65
IQF to CT	2.03	100	-

\* Ratio of the Mössbauer absorption area due to Fe<sup>3+</sup> nuclei to the total absorption expressed in percent.

\*\* 100 - Fe<sup>3+</sup>.

\*\*\* Average of two.



A similar situation occurs in synthetic magnesiohastingsite where the Al for Si substitution in the tetrahedral chains parallels that of the phlogopite-biotite series and where the *A* site, sandwiched between 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 2×, no special precautions regarding H<sub>2</sub>O). Selected spectra taken at higher resolution (abscissa expanded 10×, dried specimens) are compared in Figure 4 to a spectrum of synthetic pargasite (NaCa<sub>2</sub>Mg<sub>4</sub>AlSi<sub>6</sub>Al<sub>2</sub>O<sub>22</sub>(OH)<sub>2</sub>, 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<sup>-1</sup> can be assigned with reasonable confidence to OH ions bonded to MgMgMg, MgMgFe<sup>2+</sup>, and/or MgMgFe<sup>3+</sup> (MgMgAl for synthetic pargasite) groups in the 2*M*(1) + *M*(3) sites. The minor peaks around 3645-3620 cm<sup>-1</sup> most probably represent MgFe<sup>2+</sup>Fe<sup>2+</sup>-OH, MgFe<sup>2+</sup>Fe<sup>3+</sup>-OH, and MgFe<sup>3+</sup>-OH (MgAlAl-OH) groups. The observed frequencies for those groupings are similar to what is observed in phlogopite-biotite micas, although the assignment differs 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 (CT to IQF, IQF to CT) as well as the broad, almost featureless spectrum of the natural sample is less clear. In sample CT to IQF, where significant Fe<sup>2+</sup> and Fe<sup>3+</sup> occur, the broadening of the band at 3670-3660 cm<sup>-1</sup> may arise from MgFe<sup>3+</sup>Fe<sup>3+</sup>-OH and/or MgFe<sup>2+</sup>Fe<sup>3+</sup>-OH groups; in sample IQF to CT, where only Fe<sup>3+</sup> was detected in the Mössbauer spectra, the 3660 cm<sup>-1</sup> 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 substitution of different cation species (Mg, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ti<sup>4+</sup>, Al) among the *M* sites as well as the influence of Al-substitution in the tetrahedral chains and of incomplete occupancy of the *A* site.

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

ratio

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

(Vedder, 1964), where *x* is the concentration of the substituting ion. Spectra of synthetic magnesiohastingsite taken at high resolution have been fitted by hand to Gaussian-like curves after normalization

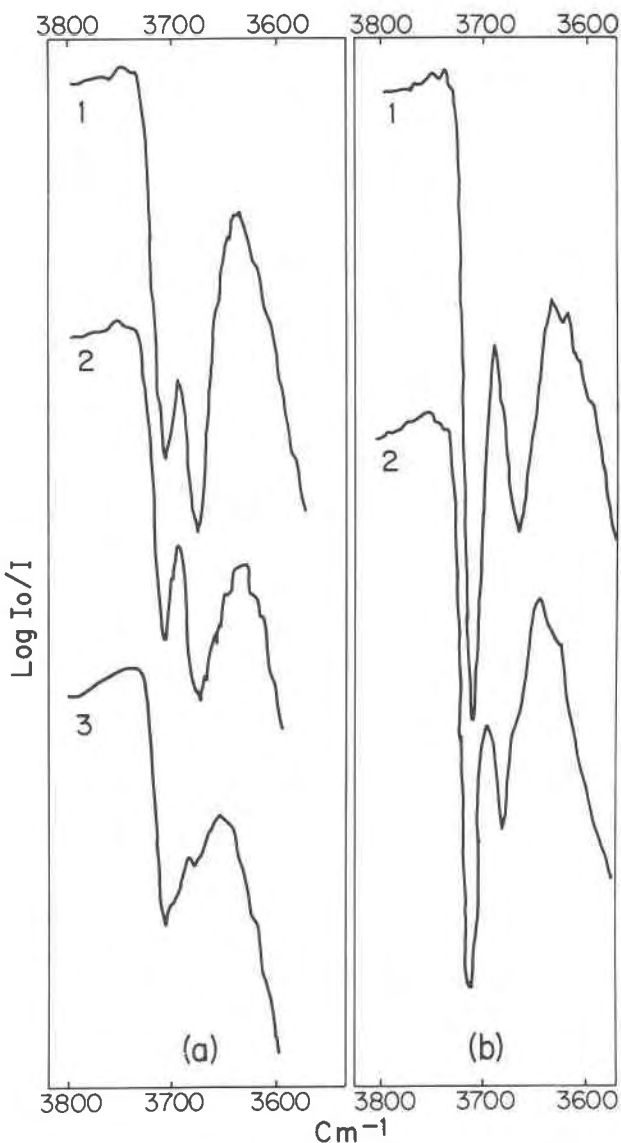


FIG. 3. Infrared spectra of synthetic and natural magnesiohastingsite

- (a) 1. ox to IQF (IQF buffer)
- 2. CT to IQF (reduced Mh)
- 3. U-1236 (natural Mh)
- (b) 1. ox to CT (CT buffer)
- 2. IQF to CT (oxidized Mh)



of the non-uniform background; then the ratios of width-at-half-height  $\times$  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 AA9-11T and AA9-12T, 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 IQF 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  $f_{O_2}$ , but reduced at low  $f_{O_2}$ , consistently showed a broad, flat, and featureless absorption band developed between 3640 and 3540  $\text{cm}^{-1}$ . 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  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  ratios calculated from Mössbauer spectra (Table 9) of the same or similar material. Also included in Figure 5 are the data for

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

Sample	$1 : \frac{3x}{1-x} : 3 \left  \frac{x}{1-x} \right ^2$ *	
	Observed	Calculated**
IQF-A3	1 : .83 : .20	1 : .80 : .21
CT-A2	1 : .46 : .10	1 : .54 : .10
AA9-11T	1 : .80 : .19	1 : .85 : .24***
AA9-12T	1 : .87 : .22	1 : .85 : .24***

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

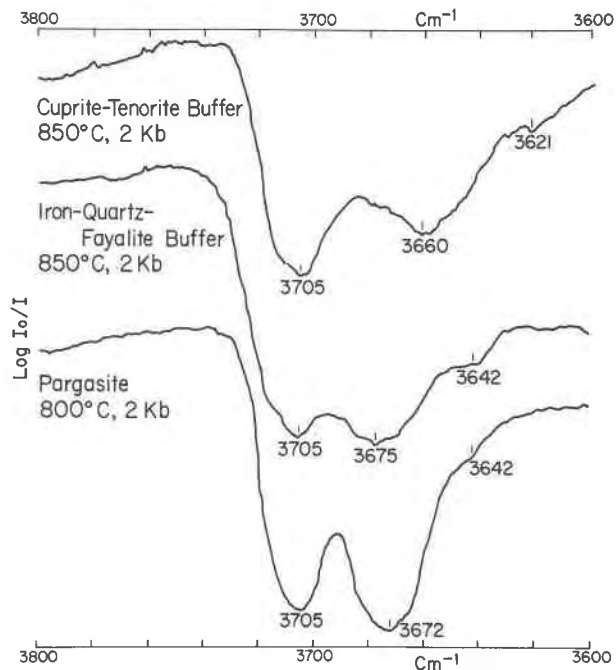


FIG. 4. Infrared spectra of synthetic magnesiohastingsite and pargasite (high resolution).

sample OA5-19-71U, which was synthesized at lower temperature and for which  $\alpha = 1.653$ ,  $\gamma = 1.668$ ,  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = 76$  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

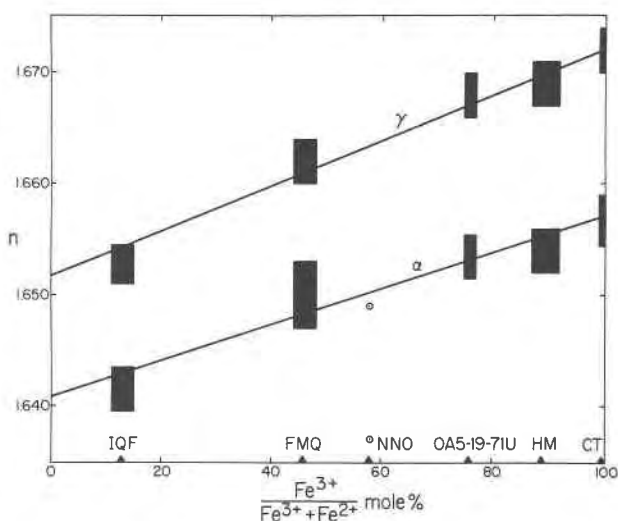


FIG. 5. Variation of refractive indices of synthetic magnesiohastingsite with oxidation ratio. The size of the symbols indicates the probable error (a different symbol has been used for NNO samples because they are depleted in Fe).

in conjunction with NNO buffer), a regular variation of refractive indices is apparent. A linear fit to the data indicates an increase of both  $\alpha$  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 Berman, 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— $\alpha = 1.651(4)$ ,  $\gamma = 1.669(5)$ ,  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = 100$  percent, and  $\alpha = 1.640(5)$ ,  $\gamma = 1.660(6)$ ,  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = 35$  percent respectively—also are 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 clin amphiboles. Ordering in synthetic clin 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 glaucophane series. Attempts at disordering natural sodic amphiboles (Ernst and Wai, 1970) by one atmosphere and hydrothermal heat-treatment resulted in oxidation of  $\text{Fe}^{2+}$  ions and concomitant loss of  $\text{H}_2$  and/or  $\text{H}_2\text{O}$ . Significant octahedral cation migration occurred in runs of 94 hours at  $700^\circ\text{C}$  and atmospheric pressure. A two year long hydrothermal heat-treatment of a natural iron-bearing glaucophane 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

Sample	M(1), M(3)			M(2)		
	Mg	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$	Mg	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$
IQF (avg)	.79	.21	-	.81	.12	.07
QA5-19-71U	.87	.06	.07	.70	.03	.27
CT-A2	.85	-	.15	.73	-	.27
IQF to CT	.78	-	.22	.83	-	.17
CT to IQF	.84	.16	-	.73	.09	.17
U-1236	.86	.14	-	.46	.07	.36*

\* .08 Al + .04 Ti not included.

In magnesiohastingsite directly synthesized from an oxide mix, the number of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and Mg ions per site clearly does not reflect random distribution of these ions ( $0.20\text{Fe} + 0.80\text{Mg}$  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  $0.23 \pm 0.05$  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

TABLE 12. Cell Parameters of Oxidized and Reduced Magnesiohastingsite

Sample*	a Å	b Å	c Å	$\beta$ (degrees)	V Å <sup>3</sup>
1	9.980(4)	18.011(9)	5.287(2)	105.40(4)	908.0(7)
2	9.955(2)	18.053(5)	5.293(1)	105.46(3)	916.8(4)

\* Identities of samples: (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).

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  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  reduction in synthetic Mh.* The structural formula of the end-member magnesiohastingsite,  $\text{NaCa}_2\text{Mg}_4\text{Fe}^{3+}\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$ , in which all sites are filled, does not theoretically allow for the occurrence of  $\text{Fe}^{2+}$  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  $f_{\text{O}_2}$  (= high  $f_{\text{H}_2}$ ).

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.

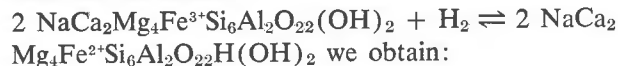
If the proportions of oxides in the starting material were not equal to what is required for magnesiohastingsite synthesis, solid solution with other end-members could have produced variations

in  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  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  $\text{Fe}^{2+}$  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 ( $\text{Na}_2\text{Ca}_4\text{Mg}_8\text{Fe}^{2+}\text{Si}_{12}\text{Al}_4\text{O}_{43}\square(\text{OH})_4$ ); such a structure would most probably be quite unstable. Moreover, the oxidation of  $\text{Fe}^{2+}$  (sample IQF to CT) without concomitant diffusion of oxygen into the vacant anion position should lead to a loss of positive charge (presumably mostly  $\text{H}^+$  or  $\text{Na}^+$ ); no evidence for such a loss has been obtained. On the other hand, if rapid (less than a few hours)  $\text{O}^{2-}$  diffusion on oxidation or reduction were possible, it would likely involve cation rearrangement toward the more stable distribution ( $\text{Fe}^{2+}$  in  $M(1)$  and  $M(3)$ ,  $\text{Fe}^{3+}$  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:



$$RT \ln f_{\text{H}_2} = 2(\mu_{\text{Fe}^{2+}}^\circ - \mu_{\text{Fe}^{3+}}^\circ) + 2RT \ln a_{\text{Fe}^{2+}} - 2RT \ln a_{\text{Fe}^{3+}}$$

where  $f_{\text{H}_2}$  is the hydrogen fugacity in the gas phase,  $\mu_{\text{Fe}^{2+}}^\circ$ ,  $\mu_{\text{Fe}^{3+}}^\circ$  are the standard chemical potential of the reduced and "ideal" magnesiohastingsite respectively, and  $a_{\text{Fe}^{2+}}$ ,  $a_{\text{Fe}^{3+}}$  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  $a_{\text{Fe}^{2+}}$  of ideal magnesiohastingsite in the solid-solution is equal to  $x_{\text{Fe}^{2+}}$  (hereafter denoted  $x$ ), the molar concentration.  $a_{\text{Fe}^{3+}}$  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):

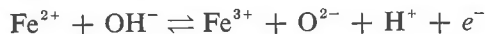
$$f_{\text{H}_2} = \frac{P_t \gamma_{\text{H}_2} \gamma_{\text{H}_2\text{O}}}{K_w f_{\text{O}_2}^{1/2} \gamma_{\text{H}_2} + \gamma_{\text{H}_2\text{O}}}$$

where  $P_t$  is the total pressure,  $K_w$  is the equilibrium constant for  $\text{H}_2\text{O}$  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  $850^\circ\text{C}$ , 2000 bars total pressure, the following values obtain:  $K_w = 4.387 \times 10^8$  (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  $\pm 6^\circ\text{C}$  from the nominal  $850^\circ\text{C}$ . A straight line has been fitted visually to the data points; the slope obtained ( $2.5 \pm .4$ ) 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:



That is, oxidation or reduction of Fe occurs by the break or formation of OH bonds from or to Fe ions (by diffusion of  $\text{H}^+$ ,  $e^-$  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

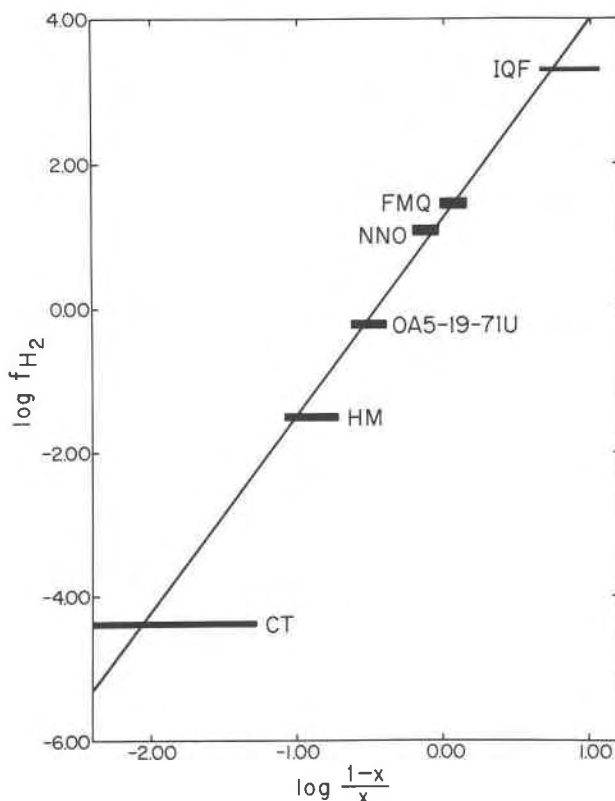


FIG. 6. Hydrogen fugacity of the gas phase coexisting with "magnesiohastingsite solid-solution" containing  $x$  (mole fraction) ideal Mh and  $1 - x$  reduced Mh. The size of the symbols indicates the estimated accuracy. Value for CT extends to  $-\infty$ .

suggests protonation of oxygens in the tetrahedral sheets of artificially altered micas. During heat-treatment in  $H_2$  of experimentally oxidized or outgassed crocidolites, Addison and Sharp (1962) produced strongly reduced amphiboles. At a relatively low temperature ( $415^\circ C$ ), the structure is not destroyed and the measured intake of  $H_2$  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  $H_2O$  determination. The broad absorption band in the *i.r.* spectra of the  $Fe^{2+}$ -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,<sup>7</sup> but this may not be the only mechanism responsible. For instance, it is not clear why magnesiohastingsite with  $Fe^{2+}/(Fe^{2+} + Fe^{3+}) = 87$  percent can be synthesized directly from an oxide mix at low oxygen fugacity, whereas the reduction of a previously synthesized  $Fe^{3+}$  amphibole cannot be carried further than  $Fe^{2+}/(Fe^{2+} + Fe^{3+}) = 65$  percent under the same conditions. Furthermore, the variation of cell parameters with the proportions of  $Fe^{2+}$  and  $Fe^{3+}$  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  $Fe^{2+}$  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  $Fe^{3+}$  samples (CT buffer, Table 5) and in the reduced samples (Table 13) show a normal trend, *b* being enlarged when some  $Fe^{3+}$  in *M*(2) is reduced to the larger  $Fe^{2+}$  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  $H_2O$  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,

<sup>7</sup> Volumetric  $H_2$  analyses kindly performed by H. Taylor (California Institute of Technology) on synthetic samples definitely prove that Mh annealed at low  $f_{O_2}$  contains H in amounts greater than 2 per unit formula and sufficient to account for  $Fe^{2+}$  charge imbalance.

the accurate determination of site occupancy for Fe ions could, in principle, serve as an intensive variable indicator (mostly  $f_{O_2}$  sensitive), providing the Fe distribution has not changed on cooling.

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