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CATION ORDERING IN SYNTHETIC MG-FE-MN OLIVINE

CATION ORDERING IN SYNTHETIC MG-FE-MN OLIVINE OF INTERMEDIATE COMPOSITION

BY

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ABSTRACT

An olivine of the intermediate composition (Mg.33, Fe.33, Mn.33)2SiO4, along with the olivine end members forsterite, Mg2SiO4, fayalite, Fe2SiO4, and tephroite, Mn2SiO4, were synthesized to a fair degree of purity, and the cation ordering of the intermediate composition determined. Neutron diffraction was carried out on the end members for calibration, and a combination of x-ray and neutron diffraction was done on the intermediate olivine, using the Rietveld refinement method. The divalent Mn ion was found to be preferentially ordered in the larger M2 site, while the divalent Fe and Mg ions showed no preference for either site. This confirms other studies which indicate a preference of Mn for the M2 site and an absence of preference of Mg or Fe for either site in a variety of different olivine compositions between forsterite, fayalite, and tephroite. Since only the Mn has a preference for a certain site, and because the Mn is not totally ordered, one application of these results is the use of intermediate olivines as geothermometers.

ACKNOWLEDGEMENTS

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CHAPTER ONE

INTRODUCTION

NATURAL OCCURRENCE OF OLIVINES:

Olivines are rock-forming minerals that occur chiefly in basic and ultrabasic igneous rocks. Mg, Fe, Mn and Ca varieties exist. It is believed that complete solid solution exists between the Mg end member (forsterite), the Fe end member (fayalite), and the Mn end member (tephroite) (figure 1). The most common olivines are in the Fo - Fa series; tephroite is rare.

Forsterite occurs in meteorites, basalts, dolerites, gabbros and trachytes. It is found in thermally metamorphosed impure limestones as a product of dedolomotization.

Fayalite occurs in syenites, dolerites, gabbros, and cavities in obsidian, rhyolites and pegmatites. It exists in metamorphosed iron-rich sedimentary ores and furnace slags.

Tephroite is found in metamorphic rocks, such as skarns associated with iron-manganese ore deposits. It also exists in massive hydrothermal replacement deposits.

THE STRUCTURE OF OLIVINES:

The olivines are a group of orthosilicate minerals with a structure consisting of unpolymerized (isolated SiO_4) tetrahedra linked by divalent metal ions surrounded by oxygen octahedra (Deer et al., 1962). Oxygens form sheets oriented along the (100) direction and exist in a hexagonal closest packed array that is slightly distorted.

The SiO4 tetrahedra point alternately along both x and y directions by virtue of the orthorhombic symmetry.

Half of the cations are located at centres of symmetry (they have 2 associated oxygens from 2 tetrahedra); the other half are located on mirror planes (they have 2 associated oxygens from 1 tetrahedron). The former cation sites are designated M1, the latter as designated M2 (figure 2). The larger size of the M2 site relative to the M1 site gives rise to ordering in olivines.

The ionic sizes (figure 3) are similar enough to allow substitution in the sites, yet different enough to allow ordering. Ordering determination studies on samples of various compositions between forsterite, fayalite and tephroite have indicated this.

PREVIOUS RESEARCH ON ORDER-DISORDER OF OLIVINES:

Mg-Fe olivines, the most common type, have been the most studied (Teeter, 1988).

In the forsterite - fayalite series, the Mg and Fe ions are randomly distributed over the M1 and M2 sites, with a possible slight enrichment of Fe in the M2 position in some cases (Burns, 1970), and a slight enrichment of Fe in the M1 position at high temperatures (Aikawa et al., 1985;

Princivalle, 1990). No significant ordering occurs in Mg - Fe olivines at room temperature, however.

Studies of Mg - Mn and Fe - Mn olivines indicate a definite partial ordering with the Mn cations favouring the M2 site relative to both Mg and Fe (Burns, 1970; Huggins, 1973; Burns et al., 1972; Annersten, 1984; Teeter, 1988).

In Fe - Mn olivines, the ordering decreases with increasing quenching temperature (Annersten et al., 1988), Mg - Mn olivines also become less ordered with increasing temperature (Akamatsu et al., 1988). These results are consistent with an increase in configurational entropy with increasing temperature.

The behaviour of the divalent Fe ions in the Mg - Fe olivines is complicated by the Crystal Field Stabilization Energy (CFSE) of the Fe: The 3d orbitals of the ferrous ion can split into 2 energy levels; the greater the distortion of the site, the greater the energy difference between the levels and the greater the stability of the cation. The M1 site may be more distorted than the M2 site, resulting in a more stable configuration when Fe is in the M1 site (Burns, 1970). The divalent Mg and Mn ions have no CFSE.

Many researchers point to the opposite effects of ion size and CFSE; the larger size of the ferrous ion causes it to prefer the larger M2 site, yet the increased stability of the ion in the M1 site due to CFSE causes it to favour the M1 site (Lumpkin and Ribbe, 1983).

Most of the natural olivines studied in terms of ordering have been of compositions rich in two metal cation types (ie Mg - Fe, Fe - Mn or Mg - Mn olivines) with minor amounts of the third. The purpose of this project is to determine the cation ordering of an olivine with significant quantities of all three elements, Mg. Fe, and Mn; the rarity of these olivines in nature required the use of synthetic minerals. An olivine with the composition (Mg.33, Fe.33, Mn.33)2SiO4 was synthesized, and end members with the compositions Mg2SiO4, Fe2SiO4 and Mn2SiO4 were also synthesized for calibration purposes.

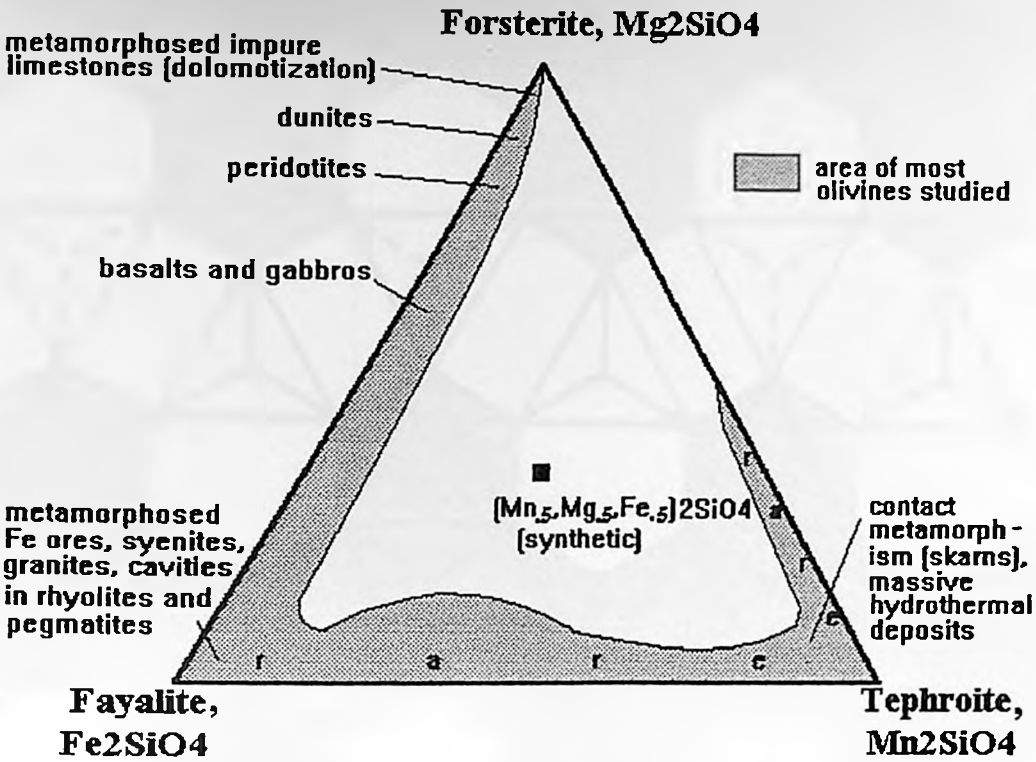

Figure 1: Olivine Solid Solution

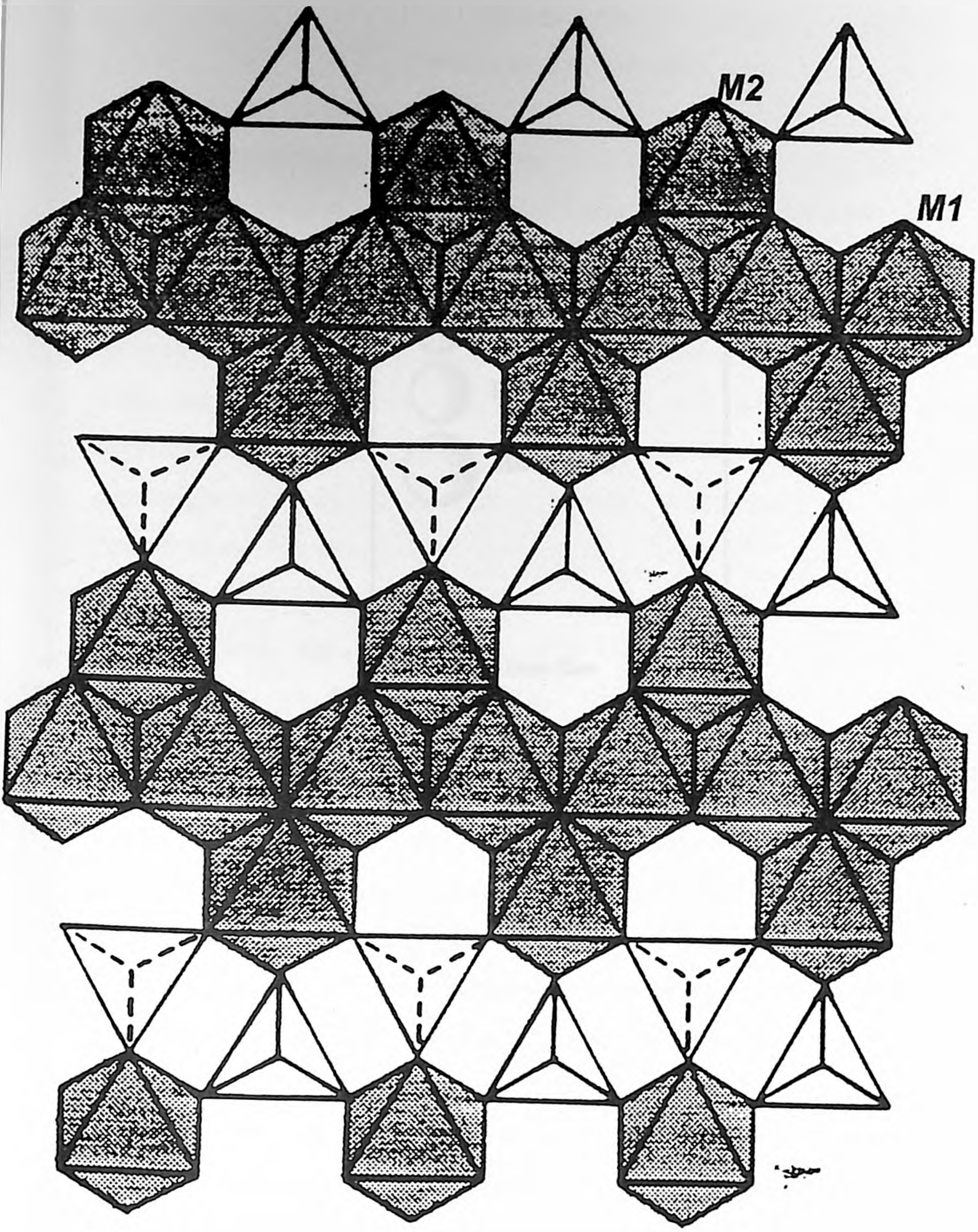

Fig. 2 Olivine structure in (001) plane showing the [SiO4] tetrahedra and octahedra occupied by divalent ions. M2 sites are larger than M1.

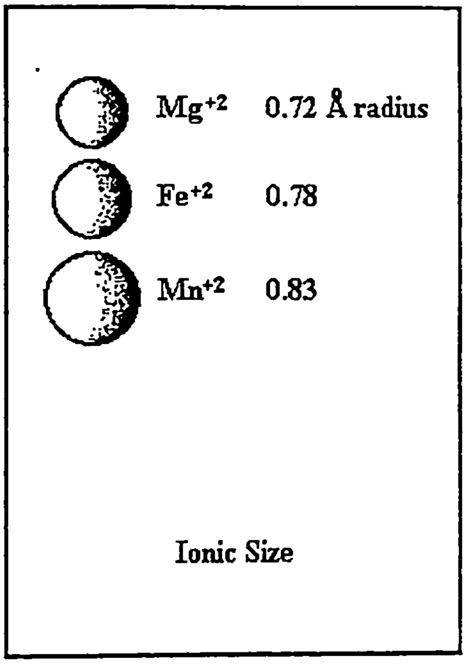

Figure 3

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CHAPTER TWO

SYNTHESIS OF OLIVINES

PREPARATION OF SAMPLES:

SYNTHESIS OF FORSTERITE:

Silica gel and magnesium carbonate were combined in a 1 : 2 molar ratio. The materials were ground, pelleted, and heated at 800 deg. C for 24 hours. The material was then heated to 1300 deg. for 24 hrs, 1525 deg. for 24 hrs, and 1550 deg. for 24 hrs, with grinding and pelleting between each heating. A large volume decrease occurred initially, corresponding to a loss of CO_2 gas. The result was a hard colourless solid.

SYNTHESIS OF FAYALITE:

Silica gel, iron metal, and ferric oxide were combined in 1 : 2/3 : 2/3 molar ratio, ground, pelleted, and heated from 1110 to 1125 deg. C over a period of 7 hrs in a tube furnace in an argon atmosphere. The alumina boat was lined with a steel boat. The mass of ferric oxide was multiplied by 0.9 and the mass of iron metal was multiplied by 1.1 to compensate for any initial oxidation of the iron.

The tube furnace with argon was chosen to prevent the iron from oxidizing into a ferric form or reducing into a metal form. The result was a hard, yellow-brown solid.

SYNTHESIS OF TEPHROITE:

Silica gel and manganous carbonate were combined in a 1 : 2 molar ratio. The materials were ground, pelleted, and heated in a tube furnace in an argon atmosphere at 1050 deg. C for 15 hrs, then at 1200 deg. for 8 hrs, with grinding and pelleting in between. Once again, the inert atmosphere was required, as the manganic form of Mn was not desired. The result was a hard, olive green solid.

SYNTHESIS OF INTERMEDIATE OLIVINE:

Silica gel, iron metal, ferric oxide, magnesium carbonate and manganous carbonate were combined in a 1 : 2/9 : 2/9 : 2/3 : 2/3 molar ratio. The mass of ferric oxide was multiplied by 0.85 and the mass of iron metal was multiplied by 1.15 to compensate for any initial oxidation of the iron. The material was ground, pelleted and heated from 1110 to 1125 deg. C over a period of 7 hrs. Once again, a tube furnace with an argon atmosphere was used. The result was a hard, ginger brown solid.

PURITY OF SAMPLES:

The samples were analyzed for purity at the Institute for Materials Research (IMR) at McMaster. X-ray powder diffraction was used and the JCPDS-ICDD (1990) files, with peaks listed for known minerals, provided the standards with which to compare the samples (fig. 8). A Phillips $\theta 2\theta$ powder diffractometer with a graphite monochromator and copper $k\alpha$ radiation was used. The effective scan speed was 1 degree per minute. The samples were fairly pure, but were determined to contain both crystalline and amorphous impurities in small amounts. After heat treatment, the

Table 1: Results of Olivine Synthesis

SAMPLE	REAGENTS	ATMOSPHERE	TEMPERATURE AND TIME OF REACTION	COLOUR OF PRODUCT
Mg2SiO4	1SiO2 + 2MgCO3	air	800 deg C 24 h 1300 deg 24 h 1525 deg 24 h 1550 deg 24 h	colourless
Fe2SiO4	1SiO2 + 2/3Fe + 2/3Fe2O3	argon	1110-1125 deg 7h	light brown
Mn2SiO4	1SiO2 + 2MnCO3	argon	1050 degC 15 h 1200 degC 8 h	olive green
(Mg.33, Fe.33, Mn.33)2SiO4	1SiO2 + 2/9Fe + 2/9Fe2O3 + 2/3MnCO3 + 2/3MgCO3	argon	1110-1125 deg 7hrs	ginger-brown

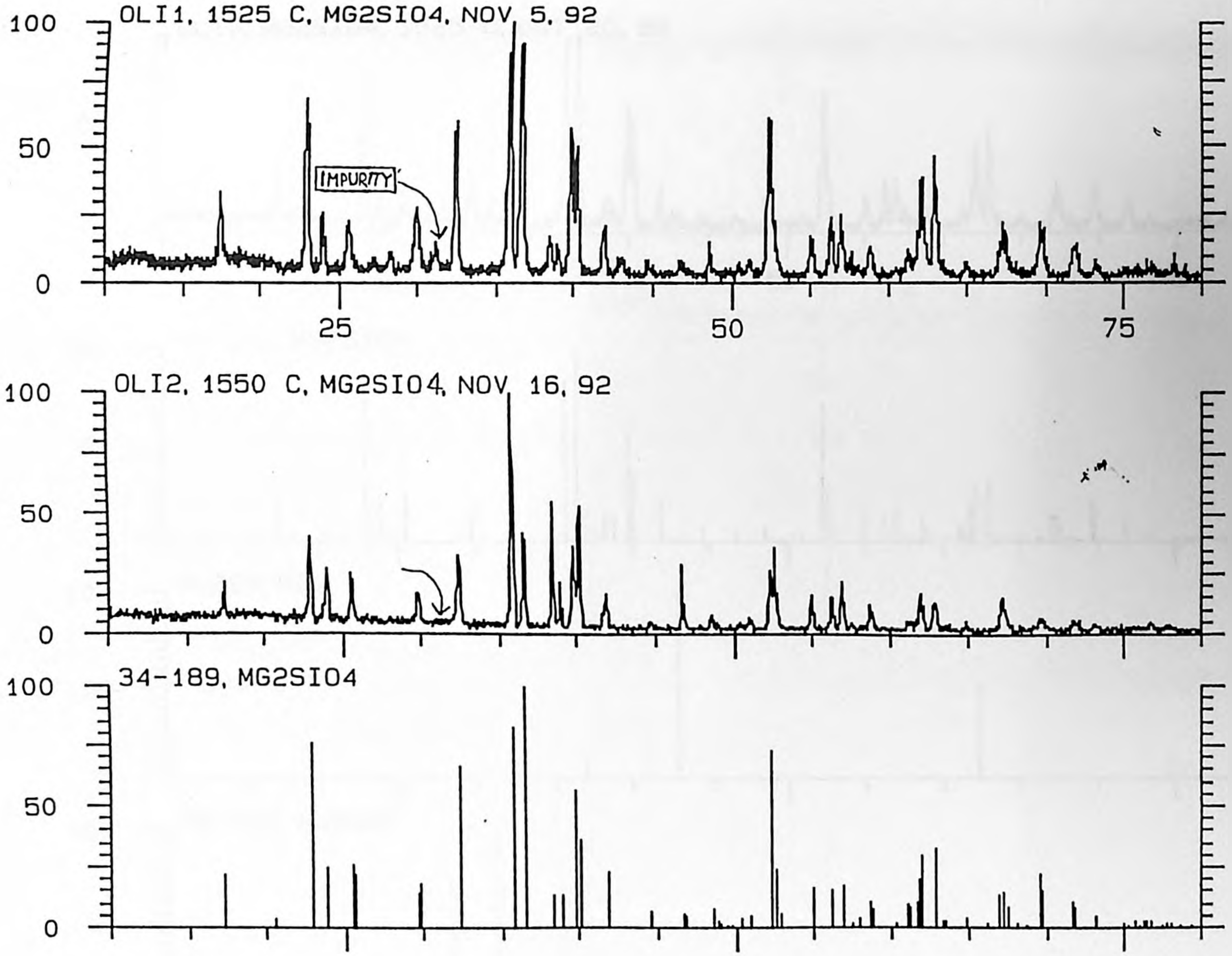


Figure 4:   Use of PDF File   in Forsterite Synthesis

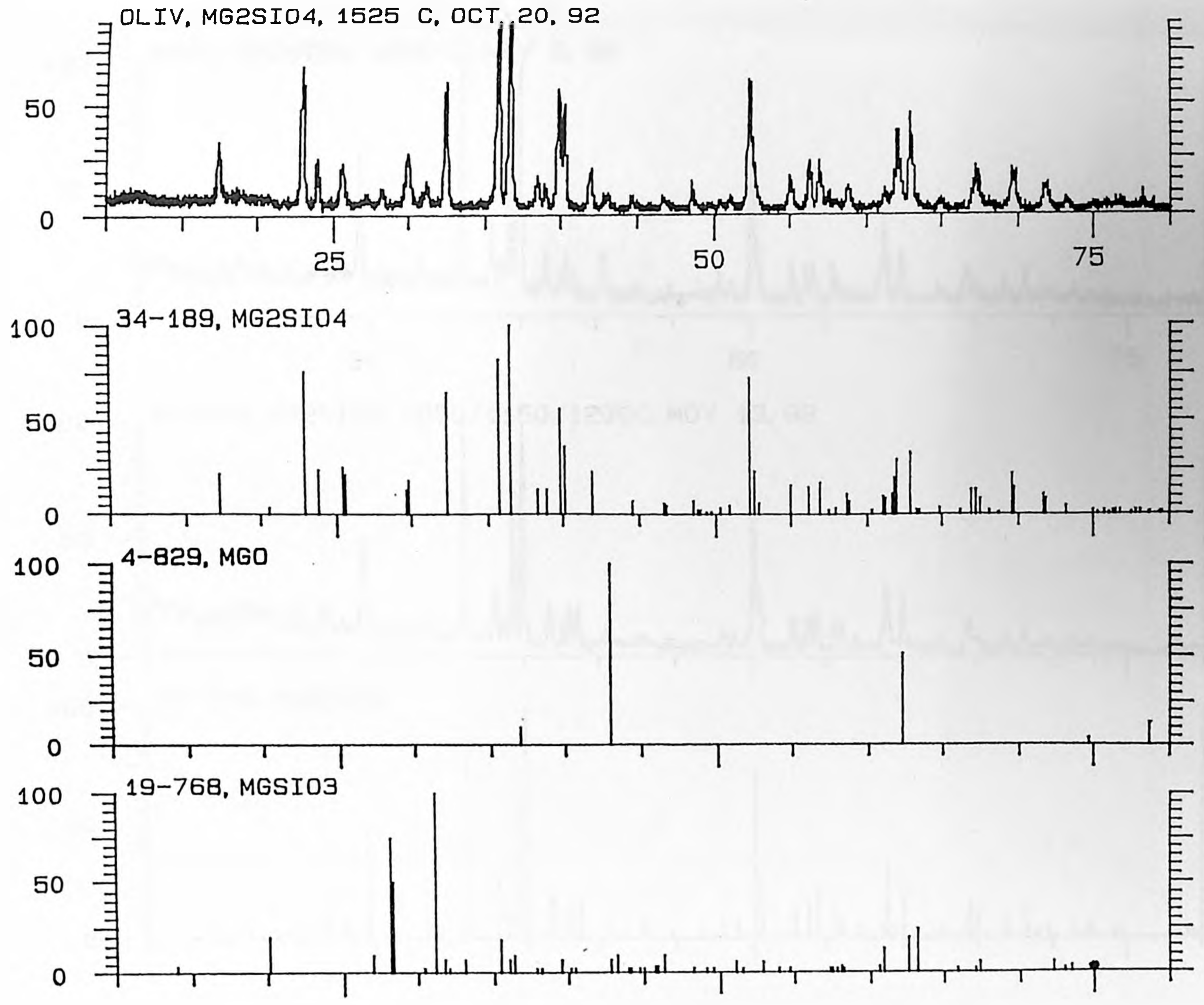


Figure 5: Use of PDF Files in Forsterite Synthesis

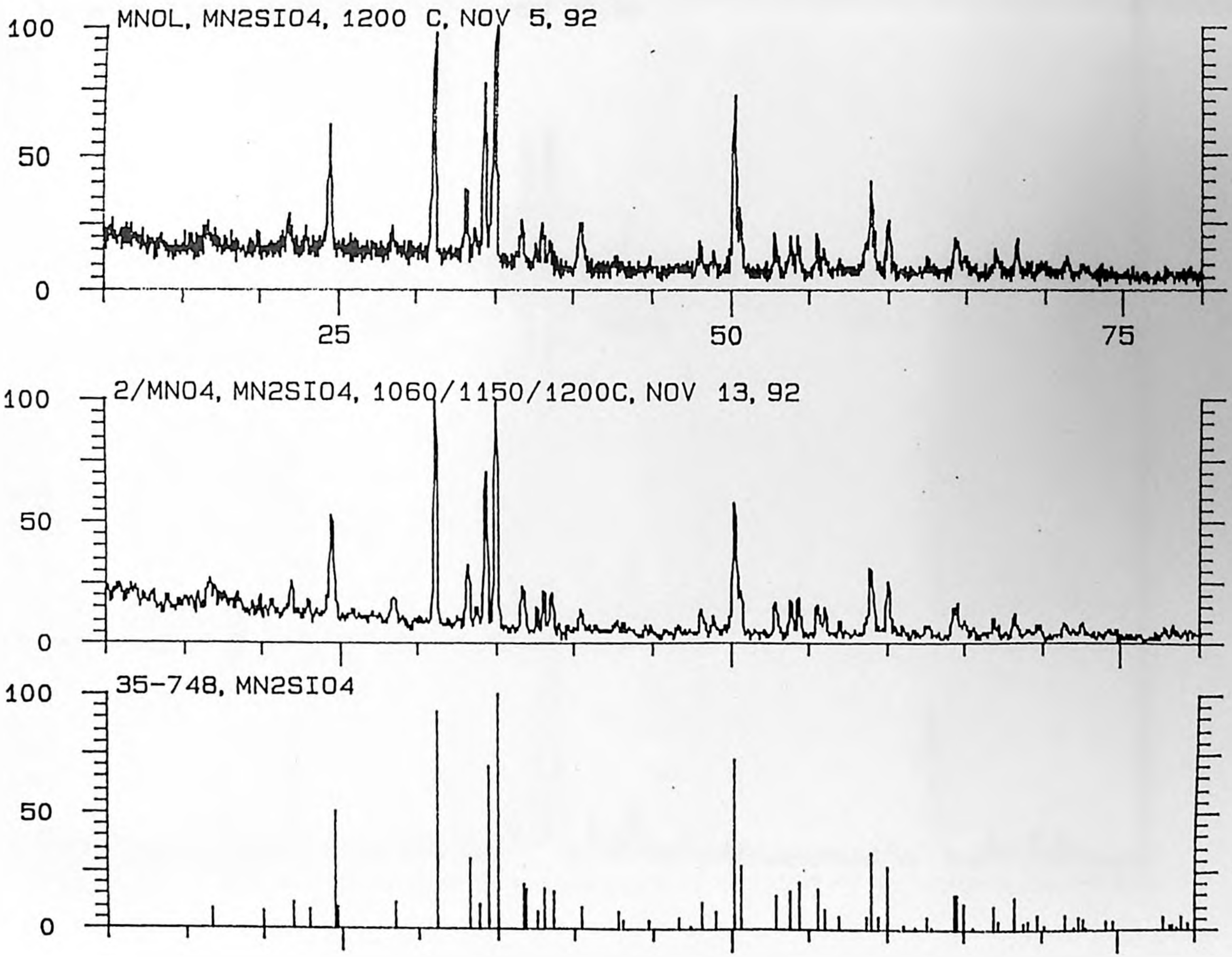


Figure 6: Use of PDF File in Tephroite Synthesis

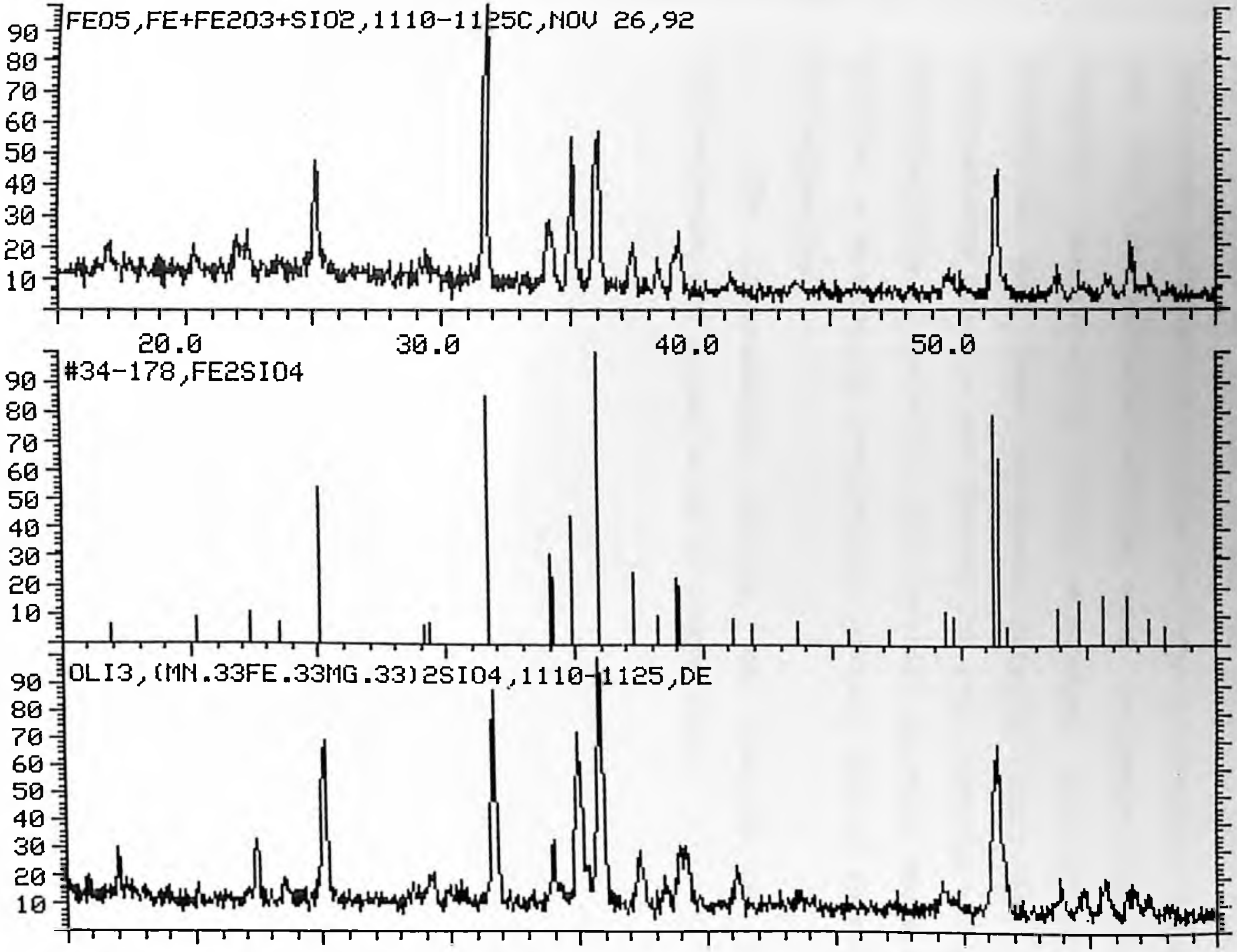


Figure 7: Fayalite PDF File vs. Synthetic Fayalite (top) and Intermediate Olivine (bottom)

impurities were reduced (fig. 4). Figure 5 shows the experimental forsterite profile compared to the determined peak locations of forsterite and two possible impurities. In the x-ray powder diffraction patterns of fayalite, tephroite and the intermediate olivine, much amorphous material was observed (indicated by a high background; figs. 6-7). The forsterite had less amorphous material (fig. 4). The intermediate olivine was checked for peak locations using the fayalite file (figure 7). The fayalite structure was assumed to have a d-spacing intermediate between that of forsterite and tephroite.

The intermediate olivine was analyzed by x-ray fluorescence and found to be on composition.

CHAPTER THREE

ANALYSIS OF SAMPLES

METHODS USED:

Most studies on cation ordering in olivines involve the use of x-ray diffraction. Other common methods used include the Mossbauer technique (nuclear gamma resonance), and crystal field spectra measurements. Neutron diffraction is a method that is rarer, owing to the small number of locations having high intensity neutron sources (Von Dreele, 1989).

X-RAY VS. NEUTRON DIFFRACTION:

Neutron and x-ray diffraction rely on the principal that monochromatic particles in a beam will be diffracted by parts of the atoms forming the lattice. The particles that are diffracted are detected if they obey Bragg's Law ($\lambda = 2d\sin\theta$, where λ is the wavelength of the incident beam, d is the interplanar spacing, and θ is the glancing angle of the beam.

The x-ray diffraction technique for cation ordering determination relies on scattering that is proportional to the number of electrons surrounding the atom. Neutron scattering lengths are proportional to the number of nuclear particles (potential scattering) and the absorption of neutrons by the nucleus (resonance scattering). X-ray scattering factors therefore increase with increasing atomic number, while neutron scattering lengths show no correlation

ode
?E
11
5P4
93

with atomic number (Von Dreele, 1989).

Also, the x-ray scattering power decreases as the angle increases. The scattering factors of neutrons are not affected by the angle increase, because the scattering is created by nuclei (point sources).

X-ray diffraction is an effective way to distinguish between Mg and Fe site occupancy, as the electronic configurations are very different; Mg has an atomic number of 12 while Fe has an atomic number 26. The elements Mn and Fe are numbers 25 and 26, respectively, on the periodic table. The similar electronic configurations make the distinction of the site occupancy of these atoms difficult. The erratic scattering length variation of elements across the periodic table makes neutron diffraction effective method of ordering determination when dealing with many adjacent pairs of elements (Von Dreele, 1989). This is the case with Fe and Mn; the scattering lengths of Mg, Fe and Mn are .538, .954 and -.373, respectively.

The method used in this study of Mg - Fe - Mn olivines was a combination of x-ray and neutron diffraction. The X-ray diffraction allowed distinction between the presence of Mg ions and Fe/Mn ions in a site, while the neutron diffraction allowed the distinction between Fe and Mn.

USE OF THE NEUTRON POWDER DIFFRACTOMETER:

This study makes use of a neutron powder diffractometer at McMaster University.

Neutron powder diffraction was chosen rather than neutron single-crystal diffraction because the crystal required for the latter would be too large (several mm) to synthesize.

The powder diffraction relies on the random orientation of the tiny grains that make up the powder; some of the crystallites have the necessary orientation for scattering. No preferred orientation is assumed for olivine, although it has weak cleavage.

In neutron diffraction, neutrons created by fission in the reactor are directed through a beam port, where the shielding of the core is penetrated. The neutron beam is filtered through a sapphire plug.

The instrument used was a constant-wavelength (CW) neutron powder diffractometer, in which the angle of the neutron beam is varied. A monochromating crystal creates the diffraction necessary to create a constant-wavelength beam. The diffractometer used in this project utilizes a copper monochromating crystal. The machine used was custom-built for the reactor at the University.

A small volume (corresponding to 5-10 grams) of the olivine sample is placed in a cylindrical vanadium vessel (vanadium has essentially no neutron scattering power). Three tubes, containing helium-3, make up a linear position-sensitive detector. A collimator exists between the sample and detector to lower the level of background. Four to five frames of 32 degrees 2 each, with overlap, are collected for the sample. Each frame is collected over a period of at least eight hours; the counting statistics separation improves with time, the final error about ±1%.

THE RIETVELD METHOD FOR CRYSTAL STRUCTURE DERIVATION:

The Rietveld method of crystal structure determination utilizes a starting model provided by the researcher (initial parameters from Teeter, 1988). The model has profile and structural parameters which can be modified until the difference between the experimental and modelled powder diffraction profiles is minimized (by least squares procedures).

The program used is DBWS-9006 (1990). It was written in FORTRAN/ANSI 77. Several, usually interdependent parameters can be modified, in this study, the following were important:

* Regions could be excluded.

* The background can be made linear, parabolic, etc.

* The scale factor can be modified

* The site occupancies can be allowed to vary

* the profile parameters can be allowed to vary (the profile used in this project is Gaussian)

- the cell parameters (dimensions and angles) can be varied
- the fractional atomic coordinates can be allowed to vary

The program was run through 4 cycles in this study. As the minimization was non-linear, the amount of variation of the parameters was continually adjusted until the minimum was found. The best fit was obtained after variance of the appropriate parameters reduced the difference between the observed and calculated profiles (fig. 9)

REITVELD REFINEMENT OF Mg, Fe, AND Mn OLIVINES:

The refinement of the forsterite, fayalite and tephroite was accomplished varying the parameters noted above. Peaks representing crystalline impurities were removed. The fractional atomic coordinates, are located in table 2.

COMBINATION OF NEUTRON, X-RAY DIFFRACTION DATA FOR MgFeMn OLIVINE:

The neutron and x-ray data were combined to discover the ordering in the intermediate olivine. Once again, the parameters were allowed to vary. the background, scale factors, and cell parameters were changed. The atomic positions were allowed to vary. X-ray data was collected at 1/4 degree per minute scan speed on a Phillips $\theta 2\theta$ powder diffractometer between 10 deg. and 70 deg. 2θ, using copper $K\alpha$ radiation. A Rietveld refinement was used (the only x-ray Rietveld refinement in the project). The neutron fractional

Fig. 8: MgFeMn Olivine X-ray Data

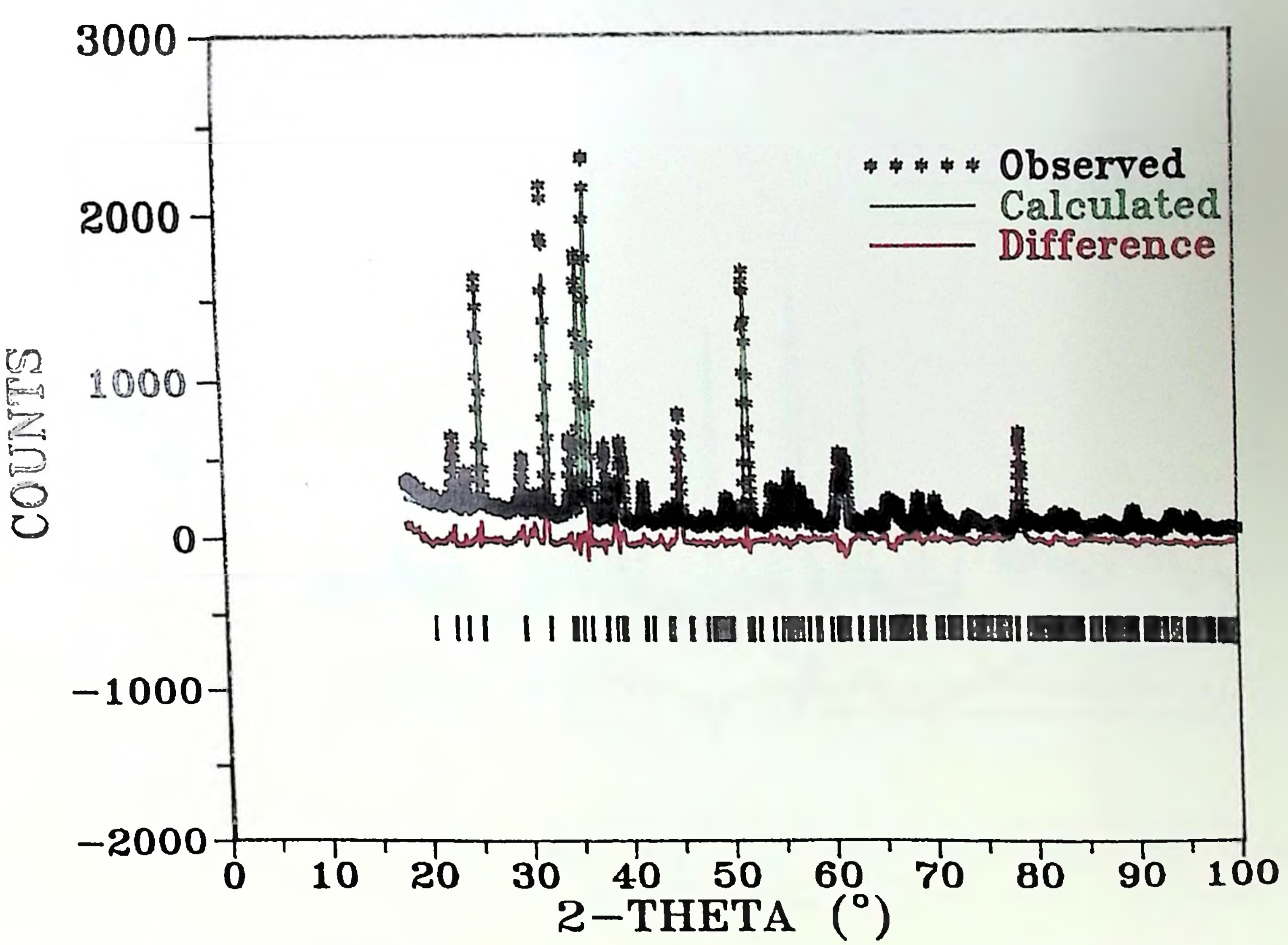
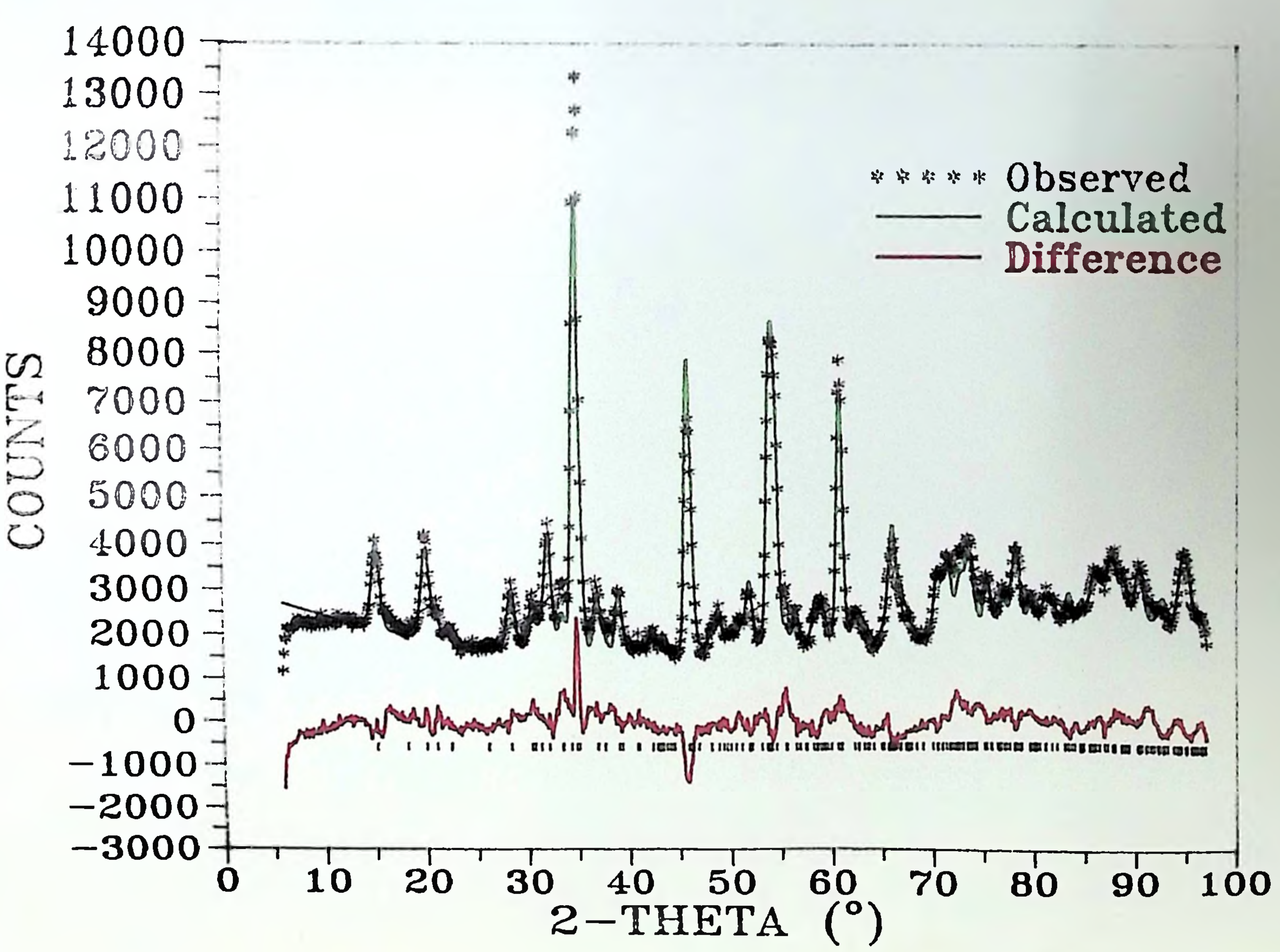


Fig. 9: MgFeMn Olivine Neutron Data



fractional atomic coordinates were carried into the x-ray Rietveld refinement. The positions of the Fe + Mn (they are treated the same in the x-ray refinement because of the similar electronic configurations) were found (relative proportions in the M1 and M2 sites). This x-ray data (fig. 8) provided the site occupancies of the Mg atoms vs. the Fe + Mn atoms collectively. The final neutron refinement used the x-ray site occupancies, adjusted for the scattering power, in terms of Mg vs. Fe + Mn positioning; since the Mg ordering had already been determined, only the ordering of the Fe relative to the Mn had to be determined.

TABLE 2: FRACTIONAL ATOMIC COORDINATES

SAMPLE	ATOM	x	y	z
Mg2SiO4	O1 O	.76650	.09281	.25000
	O2 O	.21757	.44709	.25000
	O3 O	.27542	.16110	.03175
	SI SI	.42779	.09299	.25000
	MG1 MG	.00000	.00000	.00000
Fe2SiO4	O1 O	.75802	.09436	.25000
	O2 O	.19690	.45864	.25000
	O3 O	.28859	.16260	.03746
	SI SI	.42837	.09621	.25000
	FE1 FE	.00000	.00000	.00000
	FE2 FE	.99063	.28096	.25000
Mn2SiO4	O1 O	.75798	.09344	.25000
	O2 O	.20431	.45720	.25000
	O3 O	.28461	.16283	.04053
	SI SI	.42895	.09312	.25000
	MN1 MN	.00000	.00000	.00000
	MN2 MN	.99762	.28671	.25000
(Mg.33, Fe.33, Mn.33)2SiO4	O1 O	.76049	.09213	.25000
	O2 O	.20680	.45584	.25000
	O3 O	.27999	.15874	.03714
	SI SI	.43847	.09172	.25000
	MG1 MG	.00000	.00000	.00000
	MG1 FE	.00000	.00000	.00000
	MG1 MN	.00000	.00000	.00000
	MG2 MG	.99892	.27659	.25000
	MG2 FE	.99892	.27659	.25000
	MG2 MN	.99892	.27659	.25000

CHAPTER FOUR

RESULTS AND DISCUSSION

The final results showed M1/M2 ratios for the Mg, Fe and Mn atoms to be 21/12, 22/11, and 7/27 respectively. Thus, a preference of Mn ions for the M2 site in olivines in intermediate composition between forsterite, fayalite, and tephroite exists. Mg and Fe ions demonstrate a random site distribution. The combination of x-ray and neutron data in this study, coupled with the intermediate composition of the synthetic olivine provides a good basis for applications of this result to all olivines of intermediate composition. The x-ray work effectively distinguished between Mg and Fe + Mn atom positions, while the neutron work distinguished between Fe and Mn. Lattice parameters are in table 3.

It appears that the Mn can exist in both sites, but is more readily taken into the M2 site upon olivine formation. It is expected that at higher quenching temperatures, the Mn would be less ordered due to the higher configurational entropy.

The Fe is taken up by both sites in equal amounts in intermediate olivines, although the reason is unclear. As was mentioned in Chapter 1, the reason may be due to a compromise between the extra stability of the iron in the M1 site due to the Crystal Field Stabilization Energy (not present in Mg or Mn), and the preference of the iron for the M2 position. This is only one theory, however.

TABLE 3: LATTICE PARAMETERS

*RELAXATION FACTOR=.90Å

SAMPLE	CELL LENGTH a *	CELL LENGTH b *	CELL LENGTH c *
Mg2SiO4	4.7534 Å	10.1977 Å	5.9826 Å
Fe2SiO4	4.8217	10.4875	6.0983
Mn2SiO4	4.9009	10.5994	6.2529
(Mg.33, Fe.33, Mn.33)2SiO4 (neutron diffr.)	4.8237	10.4801	6.1218
(Mg.33, Fe.33, Mn.33)2SiO4 (x-ray diffr.)	4.8238	10.4795	6.1223

Th
(
3°
.04
19
c.

Comparison with FeMn Olivine Results

SAMPLE	PRESENT STUDY	K. TEETER* #21267	K. TEETER* #85542	K. TEETER* #5387
OLIVINE COMP.	XFe = .33	.47	.53	.69
	XMn = .33	.46	.47	.28
	XMg = .33	.08	.02	.05
SITE DISTRIB.	M1:mol Fe:.22	.64	.77	.86
	Mn:.07	.20	.21	.06
	Mg:.21	.16	.02	.08
	M2:mol Fe:.11	.20	.26	.52
	Mn:.26	.80	.74	.48
	Mg:.12	—	—	—

* From Teeter, 1988.

Table 4

An study by Teeter (1988) on Fe - Mn olivines with small Mg contents (table 4) indicated a the Mg to be entirely in the M1 site. This result is from Mossbauer spectroscopy, and contradicts the results of this study. This study, however, more effectively dealt with the problem of the ordering of the three divalent cations Mg, Fe, and Mn in intermediate olivines, because of its use of the two methods of structure derivation, x-ray and neutron diffraction, and its use of a synthetic olivine at the centre of the forsterite - fayalite - tephroite composition diagram.

This study confirms previous research indicating ordering of Mn, with a preference in the M2 site, and an absence of preference of Mg and Fe in various olivine compositions in the forsterite - fayalite - tephroite solid solution.

CHAPTER 5

CONCLUSIONS

In olivines of equal forsterite, fayalite, and tephroite compositions, the Mn cations occur preferentially in the larger M2 positions, while the Fe and Mn ions show no preference for either the M1 or M2 sites.

The use of x-ray diffraction, to distinguish between Mg and Fe + Mn atom occupancy of the sites, and neutron diffraction, to distinguish between Fe and Mn atom occupancy, is an effective method of determining cation ordering in Mg - Fe - Mn olivines.

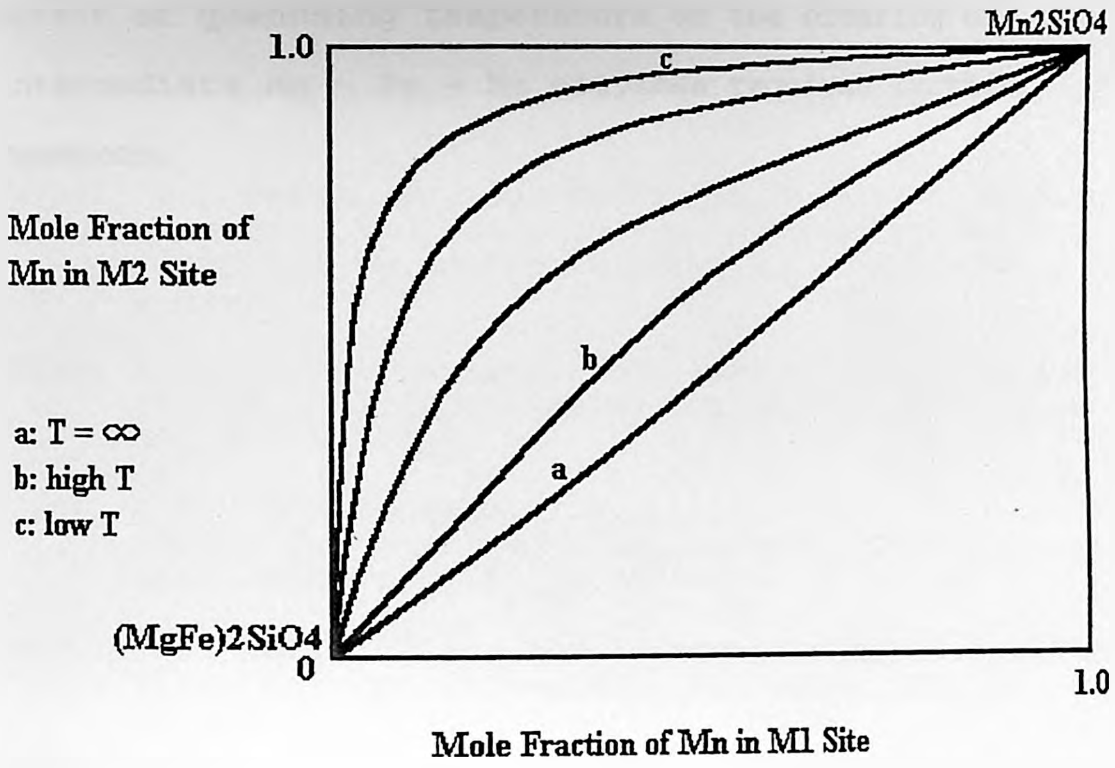
The olivines studied, the three end members and the intermediate olivine, were synthesized to a high degree of purity, enough for effective results of diffraction studies on ordering. Other methods, however, such as reaction in a solution could have produced purer olivines. As heat treating the samples in this project improved their purity, additional heating could have reduced the impurities further.

FUTURE CONSIDERATIONS:

As the Mn is preferentially, but not entirely ordered in the M2 site, Mg - Fe - Mn olivines could be used as geothermometers. The idea that Mn ordering can be used as a geothermometer (ie. it can indicate thermal history) has been proposed by many researchers (eg. Akamatsu, et al., 1988). The mole fraction of Mn in the M2 site would be plotted vs. the mole fraction of Mn in the M1 site (fig. 10). A straight

Figure 10

Location of Mn in MgFeMn Olivines as Geothermometer



diagonal line would represent complete disorder; the more cyrved a line that resulted, the lower the quenching temperature.

$$k = \frac{X1(1 - X2)}{X2(1 - X1)},$$

where k is the equilibrium constant for the ideal solution model, and X1 and X2 are site occupancy numbers. The effect of quenching temperature on the ordering of intermediate Mg - Fe - Mn olivines requires further research.

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