MÖSSBAUER EFFECT: INVESTIGATIONS
OF
CERTAIN IRON BEARING
MINERALS AND ROCKS

INAAM Y. ELADAS

A Thesis
in
The Department
of
Physics

Presented in Partial Fulfillment of the Requirements
for the Degree of Master of Science at,
Concordia University
Montreal, Quebec, Canada

AUGUST 1981

© INAAM Y. ELADAS, 1981
ABSTRACT

MÖSSBAUER EFFECT: INVESTIGATIONS OF
CERTAIN IRON BEARING MINERALS AND ROCKS

Inaan Y. Eladas

The Mössbauer spectra of three bulk rocks, four orthopyroxenes, six clinopyroxenes, two pyrites and six samples taken from a calcareous formation adjacent to the Copper mountain plug of the Gaspe Copper mines (Quebec), have been recorded at room temperature. The spectra were computer fitted to Lorentzian line shapes and the component peaks of each spectrum were assigned to particular positions of Fe$^{2+}$ and Fe$^{3+}$ in the various minerals.

Andradite and hedenbergite were identified as the main Fe containing minerals in the samples taken from the Gaspe Copper mines. It was found that the percentages of andradite and hedenbergite, vary linearly with the iron contents of the samples. An attempt was made to relate the variation in iron contents to the distance from the Copper mountain plug; no unique conclusion could be drawn. In ortho and clinopyroxenes, the variation in the quadrupole splitting was related to the variation of the ratio Fe/(Fe+Mg).

It is concluded that the Mössbauer effect can be used as a fingerprint technique in mineral studies.
ACKNOWLEDGEMENTS

The author would like to thank Dr. S.K. Misra for suggesting this work and for his continued interest and advice.

He is also grateful to Dr. S. Kumarapeli, Professor J.T. Jenkins and Professor E. Procyshyn of the Geology Department, for the supply of samples and for many helpful discussions.

Special thanks are due to Dr. N. Eddy for assistance and help during the whole experimental work, and to Pawel Mikolajczak for the encouragement and help during the early stages of this work.

Financial assistance came from Dr. Misra's NSERC Grant Number A4485.

This thesis was typed by Marie Berryman.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>chapter/section</th>
<th>title</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td></td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td></td>
<td>vi</td>
</tr>
<tr>
<td>CHAPTER I</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER II</td>
<td>THEORY</td>
<td>3</td>
</tr>
<tr>
<td>2.1</td>
<td>Resonance – Rotol Free Emission</td>
<td>3</td>
</tr>
<tr>
<td>2.2</td>
<td>Hyperfine Structure</td>
<td>5</td>
</tr>
<tr>
<td>2.2.a</td>
<td>Isomer Shift</td>
<td>6</td>
</tr>
<tr>
<td>2.2.b</td>
<td>Quadrupole Splitting</td>
<td>9</td>
</tr>
<tr>
<td>2.2.c</td>
<td>Magnetic Splitting</td>
<td>13</td>
</tr>
<tr>
<td>CHAPTER III</td>
<td>EXPERIMENTAL</td>
<td>15</td>
</tr>
<tr>
<td>3.1</td>
<td>Method</td>
<td>15</td>
</tr>
<tr>
<td>3.2</td>
<td>Source</td>
<td>17</td>
</tr>
<tr>
<td>3.3</td>
<td>Driving Unit</td>
<td>20</td>
</tr>
<tr>
<td>3.4</td>
<td>Multichannel Analyzer</td>
<td>22</td>
</tr>
<tr>
<td>3.5</td>
<td>Detector – Amplification System</td>
<td>23</td>
</tr>
<tr>
<td>3.6</td>
<td>Calibration</td>
<td>23</td>
</tr>
<tr>
<td>3.7</td>
<td>Data Transfer</td>
<td>24</td>
</tr>
<tr>
<td>CHAPTER IV</td>
<td>IRON IN MINERALS</td>
<td>29</td>
</tr>
<tr>
<td>4.1</td>
<td>Characterization of the Oxidation State</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>of Iron – Coordination Number</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Correlation of the Quadrupole Splitting</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>with Structural Variation</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER V  ANALYSIS OF SPECTRA ........................................ 36
  5.1  Computer Analysis - Method ........................................ 36
  5.2  Line Shapes - Mineral Spectra ..................................... 37
  5.3  Estimation of Percentage Composition ............................. 39

CHAPTER VI  RESULTS AND INTERPRETATIONS - PART I .............. 42
  6.1  Estimation of Iron Sites in Bulk Samples ......................... 42
  6.2  Pyroxene Structure ................................................ 47
  6.3  Orthopyroxenes .................................................. 50
  6.4  Clinopyroxenes ................................................... 59
  6.5  Pyrites .......................................................... 69

CHAPTER VII  RESULTS AND INTERPRETATIONS - PART II .......... 72
  7.1  Introduction ..................................................... 72
  7.2  The Formation and the Samples ................................... 73
  7.3  Absorbers Preparation Results ................................... 74
  7.4  Interpretation of Results ........................................ 84
  7.5  Discussion of Results ............................................ 88

CHAPTER VIII  CONCLUSION ............................................. 89

APPENDIX A  Description of Samples ................................... 91

APPENDIX B  Programme MOSSBR ........................................ 93

APPENDIX C  Data Transfer - Programmes and Steps ................... 108

APPENDIX D  Published Data on Orthopyroxenes, Clinopyroxenes, and Pyrites ........................................ 120

LIST OF REFERENCES .................................................. 124
**LIST OF TABLES**

<table>
<thead>
<tr>
<th></th>
<th>Title</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Electron Densities at the Iron Nucleus for Different Configurations</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Properties and Parameters of the 14.4kev Gamma Rays</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>Isomer Shift Scales</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Isomer Shifts for High Spin Iron</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>$\delta$ Values for Various Electronic States and Coordination Numbers</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>Parameters of Bulk Samples</td>
<td>46</td>
</tr>
<tr>
<td>7</td>
<td>Calculated Parameters of Orthopyroxenes</td>
<td>51</td>
</tr>
<tr>
<td>8</td>
<td>Calculated Parameters of Clinopyroxenes</td>
<td>67</td>
</tr>
<tr>
<td>9</td>
<td>Calculated Parameters of Pyrite</td>
<td>69</td>
</tr>
<tr>
<td>10</td>
<td>Calculated Parameters of Gaspé Copper Mines Samples</td>
<td>83</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Classical Emission of Gamma Rays</td>
<td>3</td>
</tr>
<tr>
<td>2.</td>
<td>Nuclear Energy Levels and the Isomer Shift</td>
<td>7</td>
</tr>
<tr>
<td>3.</td>
<td>Quadrupole Splitting and the Resultant Mössbauer Spectrum</td>
<td>12</td>
</tr>
<tr>
<td>4.</td>
<td>Magnetic Splitting in $^{57}$Fe</td>
<td>14</td>
</tr>
<tr>
<td>5.</td>
<td>Block Diagram of the Mössbauer Experiment</td>
<td>16</td>
</tr>
<tr>
<td>6.</td>
<td>Decay Scheme of $^{57}$Co</td>
<td>18</td>
</tr>
<tr>
<td>7.</td>
<td>Drive Velocity Waveform, the Corresponding Channel Advance and Absorption Spectrum</td>
<td>21</td>
</tr>
<tr>
<td>8.</td>
<td>Positions and Splitting in an Iron Foil Spectrum</td>
<td>24</td>
</tr>
<tr>
<td>9.</td>
<td>Iron Foil Spectrum at a Velocity of 10mm/sec</td>
<td>25</td>
</tr>
<tr>
<td>10.</td>
<td>Iron Foil Spectrum at a Velocity of 4mm/sec</td>
<td>26</td>
</tr>
<tr>
<td>11.</td>
<td>Schematic of Data Transfer Arrangement (6809)</td>
<td>27</td>
</tr>
<tr>
<td>12.</td>
<td>Schematic of Data Transfer Arrangement (6800)</td>
<td>28</td>
</tr>
<tr>
<td>13.</td>
<td>$^{57}$Fe Isomer Shift Data in Various States</td>
<td>29</td>
</tr>
<tr>
<td>14.</td>
<td>Variation in Quadrupole Splitting versus Coordination Number</td>
<td>33</td>
</tr>
<tr>
<td>15.</td>
<td>Qualitative Relative Distortion from Octahedral Symmetry versus $\Delta$ in Silicates</td>
<td>34</td>
</tr>
<tr>
<td>16.</td>
<td>Absorption Spectrum of Sample E288.c</td>
<td>43</td>
</tr>
<tr>
<td>17.</td>
<td>Absorption Spectrum of Sample E282.b</td>
<td>44</td>
</tr>
<tr>
<td>18.</td>
<td>Absorption Spectrum of Sample E294</td>
<td>45</td>
</tr>
<tr>
<td>19.</td>
<td>Pyroxenes in the System (Ca-Fe-Mg)</td>
<td>47</td>
</tr>
<tr>
<td>20.</td>
<td>Idealized Illustration of a Single Pyroxene Chain</td>
<td>48</td>
</tr>
<tr>
<td>21.</td>
<td>Crystal Structure of Diopside</td>
<td>49</td>
</tr>
<tr>
<td>22.</td>
<td>Absorption Spectrum of CGWL</td>
<td>52</td>
</tr>
<tr>
<td>Page</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>23.</td>
<td>Absorption Spectrum of CG3</td>
<td>53</td>
</tr>
<tr>
<td>24.</td>
<td>Absorption Spectrum of CG5</td>
<td>54</td>
</tr>
<tr>
<td>25.</td>
<td>Absorption Spectrum of CG12</td>
<td>55</td>
</tr>
<tr>
<td>26.</td>
<td>Quadrupole Splitting versus the Ratio Fe/(Fe+Mg) in Orthopyroxenes</td>
<td>57</td>
</tr>
<tr>
<td>27.</td>
<td>Fe$^{2+}$ site Occupancy at M$_1$ against M$_2$ of Natural Orthopyroxenes</td>
<td>59</td>
</tr>
<tr>
<td>28.</td>
<td>Absorption Spectrum of CG1</td>
<td>60</td>
</tr>
<tr>
<td>29.</td>
<td>Absorption Spectrum of CG6</td>
<td>61</td>
</tr>
<tr>
<td>30.</td>
<td>Absorption Spectrum of CG8</td>
<td>62</td>
</tr>
<tr>
<td>31.</td>
<td>Absorption Spectrum of CG11</td>
<td>63</td>
</tr>
<tr>
<td>32.</td>
<td>Absorption Spectrum of CG14</td>
<td>64</td>
</tr>
<tr>
<td>33.</td>
<td>Absorption Spectrum of CGM3</td>
<td>65</td>
</tr>
<tr>
<td>34.</td>
<td>Variation of $\Delta M_1$ against Fe/(Fe+Mg) in Diopside-Hedenbergite</td>
<td>68</td>
</tr>
<tr>
<td>35.</td>
<td>Absorption Spectrum of Pyrite SS7P</td>
<td>70</td>
</tr>
<tr>
<td>36.</td>
<td>Absorption Spectrum of Pyrite SS8P</td>
<td>71</td>
</tr>
<tr>
<td>37.</td>
<td>Geological Map of the Gaspé Copper Mines Area</td>
<td>73</td>
</tr>
<tr>
<td>38.</td>
<td>Cross Section Through the Copper Mountain Plug</td>
<td>75</td>
</tr>
<tr>
<td>39.</td>
<td>Drill Holes and Variation of Thickness in the Cap Bon Ami Formation</td>
<td>76</td>
</tr>
<tr>
<td>40.</td>
<td>Absorption Spectrum of Sample A (S675-2612)</td>
<td>77</td>
</tr>
<tr>
<td>41.</td>
<td>Absorption Spectrum of Sample B (S678-2761)</td>
<td>78</td>
</tr>
<tr>
<td>42.</td>
<td>Absorption Spectrum of Sample C (S258-2027)</td>
<td>79</td>
</tr>
<tr>
<td>43.</td>
<td>Absorption Spectrum of Sample D (U3587-1552.5)</td>
<td>80</td>
</tr>
<tr>
<td>44.</td>
<td>Absorption Spectrum of Sample E (U1467-240)</td>
<td>81</td>
</tr>
<tr>
<td>45.</td>
<td>Absorption Spectrum of Sample F (S674-2313)</td>
<td>82</td>
</tr>
</tbody>
</table>
46. The Copper Mountain Plug and Metamorphic Zones  84
47. Variation of Fe$^{3+}$ Against Absorption  85
48. Fe$^{3+}$ versus Distance from Center of Plug  86
49. Fe$^{3+}$ versus Distance from Plug Boundary  87
CHAPTER I

INTRODUCTION

The first studies of geologically important minerals using gamma ray resonant absorption were performed shortly after the discovery of the Mössbauer effect. They were concerned with the quadrupole perturbed magnetic hyperfine interaction of $^{57}$Fe in hematite ($\alpha$ - $Fe_2O_3$) by Kistner and Sunyar in 1960, and the effect of the Verwey transition ($Fe^{2+}$ $\rightarrow$ $Fe^{3+}$) on the internal magnetic fields in magnetite ($Fe_3O_4$) by Bauminger et al. in 1961. The aims in the early period were primarily directed towards the properties of nuclear states (low energy nuclear physics). General interest in its applications to mineralogy, geology and crystallography developed a few years later, where attention was focused on $^{57}$Fe resonance in minerals, while little work has been performed on other Mössbauer nuclei.

Former applications in mineralogy and geology, cover mainly the following areas, (i) the analysis of the oxidation states of iron at different crystal sites (ii) The assignment of distinct hyperfine patterns to non equivalent lattice positions which leads to the determination of the $Fe^{2+}$, $Fe^{3+}$ site preference. (iii) The study of area ratios of distinct hyperfine patterns, which leads to the determination of certain thermodynamical parameters, like the exchange energies of chemical reactions between non-equivalent lattice sites, activation energies, order-disorder phenomena, etc... (iv) The identification of iron minerals using the fingerprint technique (comparing observed parameters, with previously published data on refined minerals). This technique is followed mainly in the analysis of bulk rock, meteorites and lunar soils.

The main objectives behind this work are:
A - To investigate the possible use of Mossbauer spectroscopy as a geochemical prospecting technique: firstly, in rapid semiquantitative analysis of fine grained rocks (e.g. alteration products around certain ore deposits), and secondly, for the detection of very small amounts of iron minerals formed at a considerable distance from an actual ore body but which are by products of the same ore forming process. The possible use of Mossbauer spectroscopy in geochemical prospecting, was suggested by Bancroft 3 in 1973. Our investigation is carried on the Gaspé Copper mines in the Gaspé Peninsula of Quebec by studying samples belonging to specific formations of the area and others which are picked randomly.

B - To reinvestigate previously proposed relations concerning the variation of the quadrupole splitting of iron in certain minerals with the variation of iron contents or the iron ratio in pyroxenes (Bancroft 1967) 13.

The theory of the Mössbauer effect is presented in Chapter 2, while the Mössbauer experimental technique is presented in Chapter 3. Chapter 4 constitutes the background on iron minerals. The method of analysis and description of the Computer programme used, are given in Chapter 5. A brief presentation on the pyroxene crystal structure is followed by the results and interpretations in the study of the bulk samples, the orthopyroxenes and the clinopyroxenes, in Chapter 6. The potential use of Mossbauer spectroscopy in studying alteration patterns related to ore forming processes is illustrated by the results of six samples taken from a formation adjacent to the Copper Mountain plug at Gaspe Copper mines in the Gaspé peninsula of Québec, in Chapter 7. Chapter 8 is a conclusion.
CHAPTER II
THEORY

2.1 RESONANCE-RECOIL FREE EMISSION.

According to the laws of conservation of energy and momentum, the emission of a gamma ray by a nucleus of a free atom (moving in the X-direction with a velocity $V_x$) due to its transition from an excited state $E_e$ to a ground state $E_g$; subjects the nucleus to have a total momentum $MV$ before and after emission, i.e. the momentum of the emitted gamma ray ($E/\gamma$) is balanced by a change in the velocity of the nucleus, Figure 1. The difference between the nuclear transition energy $E_0$ and the gamma ray energy $E_\gamma$ is given by equation 1.

$$\delta E = E_0 - E_\gamma = E_R + E_D$$  \hspace{1cm} (1)

![Figure 1](image-url)

CLASSICAL EMISSION OF GAMMA RAYS

$\delta E$ is the sum of two factors: a) the recoil energy $E_R = \frac{1}{2} M v_R^2$ where $v_R$ is the recoil velocity and $M$ the mass of the nucleus, b) a Doppler term $E_D = M v_R V_x$ because the energy of a gamma ray emitted by a nucleus
moving with a velocity \( V \) along the gamma ray propagation is shifted by a first order Doppler term. \( \delta E \) is very small compared to \( E_{\gamma} \) but it is significant if we consider the line width \( \Gamma \) of the gamma ray. This is an aspect of Heisenberg's uncertainty principle which for energy and time is given by equation 2:

\[
\Delta E \cdot \Delta t \geq \frac{h}{\pi}
\]

\( h \) is Planck's constant; \( \Delta E \) is associated with the line width \( \Gamma \) of a gamma ray and \( \Delta t \) with the mean life \( \tau \) of the excited state. The least uncertainty in such a case is \( \Gamma = h/\pi \) or \( \Delta E = \Gamma = h/\pi \).

The natural line width \( \Gamma \) is defined as the full width at half maximum of an emission curve, and is very small when compared to the recoil energy of the nucleus, i.e. \( \delta E \) is greater than the line width. Absorption of gamma quanta could not be observed in systems of similar transition energies because emission and absorption profiles do not overlap.

Mössbauer discovered while studying the scattering of gamma rays of \(^{191}\text{Ir}\) by \( \text{Ir} \) and \( \text{Pt} \) that for some low energy gamma rays \( \delta E \) is negligible, and that emission and absorption profiles overlap.

Mössbauer interpreted the situation by postulating that a fraction of the gamma rays emitted by solid sources are without recoil. His interpretation viewed a crystal lattice as a quantized system (electrons and nuclei) where it cannot be excited in any fashion but as a simple Einstein model of a solid, it needs an energy of \( \pm 2h\nu \) to be excited; i.e. the recoil energy \( E_R \) of a nucleus must be
equal to or greater than $\hbar \nu$ to excite the lattice to its lowest states. If $E_R$ is less than $\hbar \nu$, the lattice is not excited and the emitting atom does not recoil but the whole crystal lattice mass takes up the recoil energy. In such a case $E_R$ and $E_D$ are small compared to $E_Y$, and resonance or overlapping of emission and absorption profiles takes place.

Due to the comparable magnitudes of the recoil energy and the lattice excitation energy, only a fraction of the gamma rays is emitted without recoil. This fraction is known as Mössbauer fraction and is given by equation 3.

$$f = \exp \left[ -\frac{4\pi^2}{\lambda^2} <X^2> \right]$$

$\lambda$ stands for the wavelength of the gamma quanta and $<X^2>$ is the component of the mean square vibrational amplitude of the emitting nucleus in the direction of the gamma ray.

2.2 HYPERFINE STRUCTURE

Prior to Mössbauer discovery, the ability to resolve hyperfine interactions by observing the transitions of gamma rays was discounted, although a less direct measure of quadrupole and magnetic splitting could be obtained from gamma-gamma directional correlation\(^1\). These interactions are attributed to the nuclear charge distribution and the extra-nuclear electric and magnetic fields. There are three main hyperfine interactions corresponding to the nuclear moments determining the nuclear levels:

A. Electric Monopole Interaction ($E_0$) - Isomer Shift
B. Electric Quadrupole Interaction (\(E_2\)) - Quadrupole Splitting

C. Magnetic Dipole Interaction (\(M_1\)) - Nuclear Zeeman Effect

2.2.a ISOMER SHIFT

A nucleus occupies a finite volume. The s-electrons have the ability to penetrate the nucleus and spend a fraction of time inside the nuclear region. The p, d, and f electrons do not possess this ability except in the case of relativistic effects where the electrons can spend a very small fraction of time inside the nucleus. Due to the electrostatic interaction between the nuclear charge and the s-electron charge, the nuclear energy levels are shifted by a small amount \(\delta\). This shift \(\delta\) (known as the Isomer, chemical or central shift), was computed classically by Wertheim², assuming that the nucleus is a uniformly charged sphere of radius \(R\), where the electron cloud is uniformly distributed over the nuclear range. \(\delta\) then represents the energy difference between the electrostatic interaction of a point nucleus and one with radius \(R\), having the same charge \(Ze\). The derived expression of \(\delta\) is given by equation 4 where \(-e\left|\psi_{(0)}\right|^2\) is the electronic charge density.

\[
\delta = \frac{2\pi}{5} Ze^2 R^2 \left|\psi_{(0)}\right|^2
\]  

(4)

The energy difference between the ground state \(g\) and an excited state \(e\) of the nucleus is given by equation 5:

\[
\delta = (\delta E)_e - (\delta E)_g = \frac{2\pi}{5} Ze^2 \left( R^2_e - R^2_g \right) \left|\psi_{(0)}\right|^2
\]  

(5)
In a Mössbauer experiment, we actually observe the difference of the electrostatic shift between a source and an absorber of different electrostatic environments, where the electron density is different from source to absorber. Equation 6:

\[
\delta = \frac{4\pi}{5} \frac{Ze^2}{R^2} \left( \frac{5R}{R} \right) |\psi_0^{(o)}|^2_A - |\psi_0^{(o)}|^2_S.
\]  

\( \delta R \) stands for the difference between the radii of the excited and ground states. The corresponding resonant Doppler velocity in an experiment is given by equation 7:

\[
V = \left( \frac{4\pi e}{5eY} \right) \frac{Ze^2}{R^2} \frac{\delta R}{R} |\psi_0^{(o)}|^2_A - |\psi_0^{(o)}|^2_S
\]  

\( \delta \) then is the distance of the center of gravity of the absorption peak or peaks from the zero Doppler velocity Figure 2.

---

(a) SOURCE AND ABSORBER NUCLEAR ENERGY LEVELS
(b) RESULTANT ISOMER SHIFT

Figure 2
From the previous expression of the Isomer shift, it is noticed that \( \delta \) is dependent mainly on two factors, \( |\psi_{(o)}|^2 \) and \( R \). The ratio \( \frac{\delta R}{R} \) is known but not to a great accuracy\(^7\) while the electron density is dominated by the s-electrons which can be assumed as being composed of two contributions. The direct s-density contributions and the indirect s-changes caused by the shielding of the outer s-electrons from the nucleus by the charge densities of the p, d, and f electrons. Changes in the valence shell structure influence the s-electron density directly by altering the s-electron population where increasing s-density will increase \( |\psi_{(o)}|^2 \) and shielding s-electrons by p, d, and f electrons, i.e. increasing the density of p, d, and f respectively will cause s-electrons cloud to expand\(^2,4\) and thus decrease \( |\psi_{(o)}|^2 \).

The Isomer shift between Fe\(^{2+}\)(3d\(^5\)) and Fe\(^{3+}\)(3d\(^5\)) is a direct illustration of the facts mentioned above. 3d has no charge density at the nucleus and this suggests no shifts, however, the behaviour of the 3s and 4s electrons in iron depends on the number of 3d electrons where an added 3d electron partially screens the nuclear potential seen by the 3s electrons leading to a larger average radius and a lower \( |\psi_{(o)}|^2 \).

Table 1 shows electron densities at the iron nucleus for different configurations.

### Table 1

**Electron Densities at the Iron Nucleus for Different Configurations**

<table>
<thead>
<tr>
<th>Configuration</th>
<th>3d(^8)</th>
<th>3d(^7)</th>
<th>3d(^6)</th>
<th>3d(^5)</th>
<th>3d(^6) 4s(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 electron in 1s</td>
<td>5378.005</td>
<td>5377.973</td>
<td>5377.840</td>
<td>5377.625</td>
<td>5377.873</td>
</tr>
<tr>
<td>1 electron in 2s</td>
<td>493.953</td>
<td>493.873</td>
<td>493.796</td>
<td>493.793</td>
<td>493.968</td>
</tr>
<tr>
<td>1 electron in 3s</td>
<td>67.524</td>
<td>67.764</td>
<td>68.274</td>
<td>69.433</td>
<td>68.028</td>
</tr>
<tr>
<td>1 electron in 4s</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\( |\psi_{(o)}|^2 \) = 11878.9, 11870.2, 11879.8, 11881.7, 11885.8

(in atomic units: electrons per cubic Bohr radius)
Other expressions for the isomer shift have been derived taking into account relativistic self-consistent fields of electrons. One of these expressions is equation 8. Its derivation assumes that the difference in electron density for two different states can be expressed as a change in the electron density alone and that the radial coefficients $a_2$ and $a_4$ depend only on the nuclear charge $\Sigma$.

$$\delta = \frac{2}{3} \pi \Sigma^2 \Delta \rho_e (o) \left[ \Delta \rho^2 < r^2 > - b^4 < r^4 > + b^6 < r^6 > \ldots \right]$$  \hspace{1cm} (8)

where

$$\Delta \rho (r) = \Delta \rho (o) \left[ 1 - a_2 (z) r^2 + a_4 (z) r^4 \ldots \right]$$

$$b^4 = \frac{3}{10} a_2 ; b^6 = \frac{1}{2} a_4$$

2.2.3 Quadrupole Splitting

The derivation of the isomer shift expression by Wertheim assumes the nucleus to be uniformly charged and spherically symmetrical. However, in reality a nucleus is more or less charged ellipsoidal. This deviation is given by the electric quadrupole moment $\hat{Q}$ which is a tensor. A nuclear state with $I > 1/2$ has a non-zero quadrupole moment that interacts with the electric field gradient EFG at the nucleus. This interaction results in a splitting of the nuclear energy levels and is known as the electric quadrupole interaction expressed in the general form by the Hamiltonian of equation 9.

$$H = \hat{Q} \cdot (\hat{\mathbf{E}})$$ \hspace{1cm} (9)

$\hat{Q}$ denotes the operator of the nuclear electric quadrupole moment and $(\hat{\mathbf{E}})$ the EFG tensor operator. $Q$ is a constant for a given Mossbauer
nuclide in different compounds, and the changes in quadrupole interaction arises only from changes of the EFG expressed as equation (10).

\[
\begin{vmatrix}
V_{xx} & V_{xy} & V_{xz} \\
V_{yx} & V_{yy} & V_{yz} \\
V_{zx} & V_{zy} & V_{zz}
\end{vmatrix}
\]

\begin{equation}
\text{EFG} = \nabla \varepsilon = -\varepsilon \nabla \varepsilon = -\begin{vmatrix}
V_{xx} & V_{xy} & V_{xz} \\
V_{yx} & V_{yy} & V_{yz} \\
V_{zx} & V_{zy} & V_{zz}
\end{vmatrix}
\end{equation}

(10)

where

\[
V_{ij} = \frac{\partial \varepsilon}{\partial \varepsilon_i \varepsilon_j}; \quad (V_i, V_j = x, y, z)
\]

The EFG, which is a 3x3 tensor, can be reduced to diagonal form in the proper coordinate system so that it could be specified by the three diagonal components only. These components obey Laplace's equation in a region where the charge density vanishes.

\[
V_{xx} + V_{yy} + V_{zz} = 0
\]

(11)

In such a case, there remains only two independent parameters normally chosen to be \( V_{zz} \) and \( \eta \) the assymmetry parameter defined as equation 12.

\[
\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}
\]

(12)

The EFG axis are chosen such that; the off-diagonal components are zero and \( |V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \). This constrains \( \eta \) to have values between zero and one. If the off-diagonal elements are non-zero, then the tensor must be diagonalized before the diagonal elements are chosen as above. Further more, two mutually perpendicular axis of three fold or
higher symmetry give rise to a vanishing EFG\(^9\).

In general there are two fundamental sources which can contribute to the total EFG\(^3\). a - charges on distant atoms or ions surrounding the Mössbauer atom in non-cubic symmetry, usually called the ligand-lattice contributions. b - non-cubic electron distribution in partially filled valence orbitals of the Mössbauer atom usually denoted as the valence electron contribution. In the simple case where \( \eta \) is zero \( Q \) is expressed as equation (13).

\[
Q = (1 - \gamma_\infty) Q_{lattice} + (1 - R) Q_{valence}
\]  

(13)

\( R \) and \( \gamma_\infty \) are respectively the Sternheimer anti shielding factors, \( Q_{lattice} \) is the contribution from external Ligand Charges, whereas \( Q_{valence} \) is the Contribution from the valence electrons.

The Hamiltonian representing the interaction between the nuclear quadrupole moment and the electric field gradient with its eigenvalues are given below by equations (14) and (15) respectively. Where \( I \) is the nuclear spin, \( \hat{I} \) the nuclear spin operator, \( \hat{I}_+ \) and \( \hat{I}_- \) the raising and lowering operators respectively. \( M_I \) is the nuclear magnetic spin quantum number.

\[
K = \frac{e^2 QV_{zz}}{4I(2I-1)} [3I_z^2 - \hat{I}^2 + \frac{\eta}{2} (\hat{I}_+^2 + \hat{I}_-^2)]
\]  

(14)

\[
F_Q = \frac{e^2 QV_{zz}}{4I(2I-1)} [3M_I^2 - I(I+1)](1 + \frac{\eta^2}{2})^4
\]  

(15)

The splitting of the nuclear energy levels by the electric quadrupole interaction are illustrated by the \(^{57}\text{Fe}\) case where the excited state
has \( I = \frac{3}{2} \) and the ground state has \( I = \frac{1}{2} \). The excited state splits into two \( (M_I = \pm \frac{3}{2}; \pm \frac{1}{2}) \) while the ground state is not split because its quadrupole moment vanishes. Both transitions are allowed and the spectrum observed is a two line spectrum. In Figure 3, the separation of the peaks is the quadrupole splitting \( \Delta \) and the center of the two peaks relative to the source is the isomer shift (\( \delta \)).

![Diagram]

**Figure 3**

(a) Quadrupole Splitting  (b) Resultant Mössbauer spectrum
2.2.c MAGNETIC SPLITTING

A nucleus with a non-zero spin has a magnetic dipole moment $\mu$ which can interact with local or applied magnetic fields at the nucleus. The Hamiltonian of the interaction is given by equation 16 where $g_n$ is the gyromagnetic ratio (nuclear $g$-factor) and $\beta_n = e\hbar/2mc$ is the nuclear Bohr magneton.

$$\mathcal{H}(M_1) = -\mu \cdot H = -g_n \beta_n \mathbf{I} \cdot \mathbf{H}$$

(16)

The eigenvalues of $\mathcal{H}$ that are obtained using the first-order perturbation theory are given by equation 17.

$$E_m (M_1) = -\mu \cdot H M_1/I = -g_n \beta_n H M_1$$

(17)

Due to the magnetic interaction, a nuclear level with a spin $I$ is split into $2I + 1$ equally spaced sublevels. These sublevels are characterized by the nuclear magnetic spin quantum number $M_1$, $M_1 = I, I-1, \ldots, -I$. For $^{57}\text{Fe}$, the excited and ground states have $I_e = \frac{3}{2}$ and $I_g = \frac{1}{2}$ respectively. Both states have magnetic dipole moments and are split by magnetic interaction. The Selection rule $\Delta I = 1; \Delta M = 0, \pm 1$ gives rise to a symmetric six lines spectrum as shown in Figures 4 and 10.

The isomer shift $\delta$ is given by the center of gravity of the six lines; these have in general equal line widths but different intensities, the intensities are given as:

$$I_1 = I_6 = 3(1 + \cos^2 \Theta)$$

$$I_2 = -I_5 = 4 \sin^2 \Theta$$
$I_3 = I_4 = 1 + \cos^2 \theta$

$\theta$ is the angle between the direction of radiation and the effective magnetic field $H$.

Except for metallic iron, pure nuclear magnetic dipole interactions are not encountered, but frequently the nucleus experiences both magnetic and quadrupole interactions. As a result, for the case of $^{57}\text{Fe}$ the sublevels of $I = \frac{3}{2}$ state are no longer equal and the spectrum is not symmetric. Many cases arise. One case is when the EFG tensor is axially symmetric and its principle axis make an angle $\beta$ with the axis of the magnetic field. First order perturbation theory yields equation 18 as the general expression for the eigenvalues:

$$E = -g_n \beta_n H \mathcal{M}_I + (-1)^I \frac{|\mathcal{M}_I|+1}{2} eQ \frac{V_{zz}}{8} (3 \cos^2 \beta - 1)$$

$E = -g_n \beta_n H \mathcal{M}_I + (-1)^I \frac{|\mathcal{M}_I|+1}{2} eQ \frac{V_{zz}}{8} (3 \cos^2 \beta - 1)$

Figure 4

MAGNETIC SPLITTING IN $^{57}\text{Fe}$
CHAPTER III
EXPERIMENTAL

3.1 METHOD

A Doppler Velocity $V$ is applied to a source (Section 3.2) mounted on a transducer driven by a Velocity driver (Section 3.3). The applied velocity shifts the initial energy $E_0$ of the emitted gamma rays by a value $dE$ (the Doppler Velocity is considered positive when the Source moves towards the absorber and negative when it moves away). Some gamma rays are resonantly absorbed by an absorber placed in between the Source and the detector (whenever the energy of the emitted gamma rays equals the excitation energy of the nuclei of the absorber). The gamma rays which are transmitted through the absorber are transformed into pulses proportional to their energies by a detector and an amplification system consisting of a pre-amplifier and an amplifier. A single channel analyzer (Section 3.5) selects the 14.4 kev gamma rays only. The resulting pulses are fed into a 512 multi-channel analyzer (Section 3.4). A time-base generator opens one channel after the other with constant intervals of time; each channel corresponds to a certain velocity of the source. The acquired spectrum, stored by the memory of the MCA, as displayed on a cathode ray oscilloscope, consists of two parts, one being the mirror image of the other. This is because of the particular driving signal used. Figure 5 represents a block diagram of the experiment.

The spectra so obtained, may consist of one or more absorption peaks, these peaks are defined by their heights, half-widths, positions and areas. A good spectrum is characterized by having minimal errors
in the calculated and observed spectrum. Errors in position of the peaks mainly arise from the non-linearity of the waveform that drives the source. Several methods have been described in different texts to eliminate this error. The well known positions of the six peaks of an iron foil are used for Velocity Calibration (Section 2.6).

The data stored by the memory unit of the MCA is transferred to the main CDC computer where it is analyzed. The transfer procedure and the system carrying the operation is described in Section 2.7. While description of the Computer Programme and analysis is discussed in Chapter 4.

3.2 SOURCE

The most commonly used isotope in Mössbauer experiments is $^{57}$Fe. Besides the great abundance of systems containing iron, the $^{57}$Fe nuclear parameters are very favorable. It has relatively low energy gamma transitions, a large recoilless fraction at room temperature. A long lived parent nucleus, little interference from other gamma rays and x-rays, and a relatively narrow line.

The source used is $^{57}$Co in a Pd matrix of few millicurie strength. The decay scheme of $^{57}$Co is shown in Figure 6 and the parameters of the 14.4 Kev gamma transition are given in Table 2. The source lattice should have a high Debye temperature and a symmetric structure so that the gamma rays are not modified by either electric quadrupole or magnetic dipole interactions. The effective temperature of a Mössbauer nucleus introduced as an impurity in a host lattice is given by equation 19 where $M_{host}$ and $M_{imp}$ are the masses of the host and impurity atoms respectively, and $\Theta$ the Debye temperature of the lattice.
Because of the host matrix, the 14.4 Kev gamma ray undergoes an isomer shift. Isomer shifts for $^{57}$Fe 14.4 kev relative to sodium nitro prusside at room temperature are given in Table 3. (All isomer shift values reported in this thesis are expressed relative to sodium nitro prusside).

Figure 6

DECAY SCHEME OF $^{57}$Co
**Table 2**

**PRINCIPAL PROPERTIES AND PARAMETERS**

- $E_Y$ : $14.41125 \pm 0.0006$ keV
- Half life time $\frac{1}{2}(\gamma_m)$ : $97.7 \pm 0.2 \times 10^{-19}$ sec
- Total internal conversion coefficient $\alpha(r_m)$ : $8.18 \pm 0.16$
- Natural isotopic abundance : $2.19\%$
- Magnetic moment of the ground state : $+0.0904206 \pm 0.00000012$ nm
- Magnetic moment of the first excited state : $-0.15463 \pm 0.0002$ nm
- Quadrupole moment of the first excited state : $+0.196 \pm 0.008$ b
- Cross Section $\sigma_0$ : $2.569 \times 10^{-18}$ cm$^2$
- Natural line width $\Gamma$ : $4.670 \times 10^{-9}$ eV
- Observable line width $W_0$ : $0.1943$ mm/sec
- Free atom recoil energy : $1.958 \times 10^{-3}$ ev

**Table 3**

**ISOMER SHIFT SCALE**

<table>
<thead>
<tr>
<th>Material</th>
<th>$\delta$(mmsec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$Fe(CN)$_5$NO H$_2$O</td>
<td>$0^+$</td>
</tr>
<tr>
<td>Cr</td>
<td>$0.106 \pm 0.009$</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>$0.17 \pm 0.02$</td>
</tr>
<tr>
<td>$\alpha$-Iron</td>
<td>$0.260 \pm 0.002$</td>
</tr>
<tr>
<td>Pd</td>
<td>$0.437 \pm 0.002$</td>
</tr>
<tr>
<td>Cu</td>
<td>$0.485 \pm 0.002$</td>
</tr>
<tr>
<td>Pt</td>
<td>$0.609 \pm 0.006$</td>
</tr>
</tbody>
</table>

$\delta$ - RELATIVE TO SODIUM NITRO PURRISSIDE AT 300°K
3.3 **DRIVING UNIT**

The Mössbauer effect Spectrometer is an apparatus which imparts a Doppler Velocity or motion to the source. It also coordinates the counting rate at the detector so that the spectrum channel number will be a function of the Source Velocity.

The spectrometer used is the model AM-1, manufactured by Nuclear Science and Engineering Corporation. It consists of three parts:

1. **The Base Plate** - a solid aluminium plate on which the transducer, the source and the absorber holder are mounted.

2. **The Transducer** - a precision electromechanical unit which provides a forward and retrograde motion to the source with constant acceleration. The operating frequency range is 15 - 50 cps and the velocity range is 0 - 60 cm/sec. The linearity precision of the triangular waveform is about 1% over 95% of the half period of the velocity waveform.

3. **The Control Unit** - a solid state electronic unit which accepts a square wave signal from the address register of a multi channel analyzer. It contains input signal idealizing circuitry, triangular function generating circuitry and the necessary servo and D.C. power amplifier required to drive the transducer. In Figure 7, the drive velocity waveform, the corresponding channel advance, and an absorption spectrum for a single line source and absorber, are displayed.
FIGURE 7

(a) DRIVE VELOCITY WAVE FORM,
(b) CORRESPONDING CHANNEL ADVANCE
(c) ABSORPTION SPECTRUM FOR A SINGLE LINE SOURCE AND ABSORBER
3.4 MULTICHANNEL ANALYZER (MCA)

The MCA used is the Series 2200 - NUCLEAR DATA System Analyzer. It consists of four units.

1 - ADC - Analog to digital Converter: Is designed primarily for the processing of amplitude modulated signal pulses such as encountered in pulse height analysis. Data acquisition efficiency is enhanced by a 30 megahertz digitizing rate.

2 - Master Control - it contains facilities for establishing the primary operating modes (data acquisition, display, read in, read out) and all the data handling functions of the system. Analysis data may be added to or subtracted from data previously stored in the system memory. After data has been acquired it can be subjected to operations such as transfer from one selected memory group to another. Front panel controls enable digital selection of memory groups for data storage, display, processing and read out.

3 - Read in/out Display - it incorporates those features necessary for selection of a particular read out (print, plot, type) or control of the appropriate device. This unit is capable of driving high speed digital printers and x-y plotters.

4 - System Memory - it is divided into three modules: the memory scalar module, the memory drivers module and the memory array module. The memory scalar module contains the memory address scalar and register which allows the content of a single channel to be transferred back into the identical channel location of the memory. The memory Drivers module consists of all the driving and sensing circuits for the memory array module which permits proper handling of the data being stored. The memory array
module is designed in a manner that allows expansion up to the maximum of 24-bit, 4096 channels where each channel can store up to 1 million counts.

3.5 DETECTOR - AMPLIFICATION SYSTEM

The detector used is a Si (Li) drift solid state detector, manufactured by Simtec Ltd.; model K-036 used with a Simtec P-11 HR/CN preamplifier and a Simtec M-31 linear amplifier. The detector area is 50 \text{ mm}^2 and the window is Beryllium oxide of 250\mu thickness. The Simtec model P-11 HR/CN pre-amplifier is a cooled N-channel FET optimized for Simtec ultra high resolution silicon and germanium photon spectrometer elements with capacity less than 10 picofarads. The detector and the FET preamplifier are kept at temperature of liquid nitrogen. This requires low pressure in the cryostat, which is attained by a mechanical diffusion pump and monitored by an ion appendage pump control. The 14.4 keV gamma rays are selected by a Hewlett-Packard 5583A - Single channel analyzer.

3.6 CALIBRATION

The well known positions of the six lines of a natural iron foil were used to calibrate the velocity scan of the Mossbauer spectrometer. This is needed to eliminate any error in the position of the absorption peaks of the different absorbers studied. Figure 8 shows the splitting between the three doublets of an iron foil spectrum and the corresponding velocities for a $^{57}$Co source in a Pd matrix.
Figure 8
SPECTRUM OF AN IRON FOIL

The use of an iron foil for calibration is justified by the velocity ranges during the experiment (4 - 10 mm/sec) and the assignment of the above velocities for the peaks obtained in our experiment insures the elimination of any error in position and the parameters derived, such as the isomer shift and the quadrupole splitting. Figures 9 and 10 show the iron spectra obtained at 10 and 4 mm respectively.

3.7 DATA TRANSFER

Analysis of the absorption spectra by programme MOSSBR and the University Computer facilities, is outlined in Chapter 5. Transfer of the data stored by the memory unit of the multi-channel analyzer to the university main computer (CYBER), was carried through two Computer Systems via the two main steps as outlined below.
FIGURE 10.

MÖSSBAUER SPECTRUM OF AN IRON FOIL ($4\text{mm/sec}$).
A. LOADING OF DATA ON MAGNETIC TAPES

The ability of the "read in/out - display" unit of the multi-channel analyzer to drive plotters and fast printers, has been explained in Section 3.4. Figure 11 shows the set up for the 6809 Computer System (Southwest Technical Prod. Corp.) which was assembled and programmed with the aid of the expertise available in the Physics department of Concordia University.

![Diagram showing T. REC., 6809, MCA, and TTY connected in series]

**FIGURE 11**

SCHEMATIC OF DATA-TRANSFER ARRANGEMENT (6809)

The 6809 is linked to the MCA, Teletype and tape recorder by an MP-LA parallel interface board and two MP-S Serial interface boards respectively. The Commands that drive the System are given through the teletype. The data is read to the memory of the 6809 from the MCA, and then recorded on magnetic tapes by a tape recorder (relevant programmes and steps are listed in Appendix C).
B. LOADING OF DATA ON CYBER

The procedure followed is similar to that of the previous step A. The data is read from a magnetic tape to the memory of the MSI 6800 Computer System (Midwest Scientific Instruments) and then from the 6800 to the Concordia CYBER. The set up is illustrated in Figure 12, the Commands are given through a teletype or a video, while the Programmes that drive the system and perform various operations are stored on discs; the disc drives are shown in Figure 12 also (Programmes and steps are listed in Appendix C).

![Diagram](https://example.com/diagram.png)

**FIGURE 12**

SCHEMATIC OF DATA-TRANSFER ARRANGEMENT (6800)
CHAPTER IV
IRON IN MINERALS

4.1 CHARACTERIZATION OF THE OXIDATION STATE OF IRON-
COORDINATION NUMBER

Since the early investigations of iron compounds, a correlation
of the isomer shift $\delta$ with the formal oxidation state of iron was
established. The isomer shift is sensitive to the spin state of iron
in a complex compound. As a result, the $\delta$-values of high spin iron
($S = 2$) appear in a region well separated from the $\delta$-values of low
spin iron ($S = 0$). Where $S$ is the spin quantum number. Figure 13.

![Graph showing Fe isomer shift data in various ionization states indicated by bars, and in highly covalent materials indicated by shaded areas.](image)

Figure 13

Fe isomer shift data in various ionization states indicated by bars, and in highly covalent materials indicated by shaded areas.

57
Table 4 below shows that for ionic iron (high spin) the $\delta$-values become more positive with decreasing oxidation states, and the $\delta$-ranges for different oxidation states of high spin iron hardly overlap.

**TABLE 4**

**ISOMER SHIFT ($\delta$) - FOR HIGH SPIN IRON**

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>+1</th>
<th>+2</th>
<th>+3</th>
<th>+4</th>
<th>+6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomer shift (mm sec$^{-1}$)</td>
<td>$\sim$+2.2</td>
<td>$\sim$+1.4</td>
<td>$\sim$+0.7</td>
<td>$\sim$+0.2</td>
<td>$\sim$0.6</td>
</tr>
</tbody>
</table>

For low spin iron II and iron III the $\delta$-values do overlap and it is very difficult to distinguish compounds using $\delta$-values only. However, in this case the quadrupole splitting $\Delta$-values which range from 0 to +0.8 mm/sec for low spin iron II and from +0.7 to +1.7 mm/sec for low spin iron III can be very useful.

The dependence of the isomer shift on the electron configuration was discussed before in section 2.2a. Table 1 showed that the s-orbitals are the main contributors and that the difference in densities originates from changes in the 3s shell. The removal of 3d electrons leads to an increase in the electron density at the nucleus due to the shielding of the 3s electrons from the nuclear charge by 3d electrons. While adding 4s electrons increases the electron density at the nucleus and causes the isomer shift to become more negative ($\frac{5R}{R}$ is negative for Fe$^{57}$). The widespread ranges of the $\delta$-values for each oxidation state is a direct consequence of the nature of the chemical bond and the capabilities of the ligands to donate or accept electrons from the iron metal via
σ-bonding or π-bonding respectively.

In minerals, iron is conclusively ferrous and ferric. The δ-values for these two high spin states vary around the mean values 1.4 mm/sec and 0.7 mm/sec respectively. The variation depends on the coordination number, site symmetry and type of ligand. In Mössbauer analysis the determination of the oxidation state is valuable because of the certainty it provides over other techniques such as x-ray or chemical analysis. However, in few minerals the oxidation state cannot be assigned readily, e.g. pentlandite (Ni, Fe₉) S₈ which has two quadrupole doublets of isomer shifts 0.83 and 0.62 mm/sec. These values have been attributed to electron exchange where the oxidation state is in between Fe²⁺ and Fe³⁺. Table 5 shows how the isomer shift is correlated to the coordination number in minerals. The fact that the δ-values generally increase with increasing coordination number is very useful in assigning the structure of iron in a certain species, but the limited variation of δ and the anomalous behaviour in some minerals makes it necessary to use extra information available from Mössbauer analysis and from other techniques.


<table>
<thead>
<tr>
<th>Mineral or Species</th>
<th>Type of Iron</th>
<th>$\delta$ mmsec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Almandine garnet</td>
<td>8 coordinate Fe$^{2+}$</td>
<td>1.56</td>
</tr>
<tr>
<td>Silicates</td>
<td>6 coordinate Fe$^{2+}$</td>
<td>1.30 - 1.43</td>
</tr>
<tr>
<td>Staurdite</td>
<td>4 coordinate Fe$^{2+}$</td>
<td>1.22</td>
</tr>
<tr>
<td>Spinel</td>
<td>4 coordinate Fe$^{2+}$</td>
<td>1.07</td>
</tr>
<tr>
<td>Gillespite</td>
<td>4 coordinate Fe$^{2+}$</td>
<td>1.01</td>
</tr>
<tr>
<td>(square planar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epidote</td>
<td>6 coordinate Fe$^{3+}$</td>
<td>0.61</td>
</tr>
<tr>
<td>Amphiboles</td>
<td>6 coordinate Fe$^{3+}$</td>
<td>0.65</td>
</tr>
<tr>
<td>Iron orthoclase</td>
<td>4 coordinate Fe$^{3+}$</td>
<td>0.72</td>
</tr>
</tbody>
</table>

4.2 CORRELATION OF THE QUADRUPOLE SPLITTING WITH STRUCTURAL VARIATIONS

Figure 14 shows the variation in the quadrupole splitting $\Delta$ against coordination number. Variations in $\Delta$-values are related to structural effects by consideration of the field gradient expressed earlier by equation 13 of Chapter 2.
For ferric iron in minerals, we suppose $Q_{\text{valence}}$ is zero and the quadrupole splitting observed is due to $Q_{\text{lattice}}$ only. The ferric quadrupole splitting is expected to increase as the distortion from octahedral symmetry about Fe$^{3+}$ increases. Ferrous iron gives rise to a large $Q_{\text{valence}}$ term, the distortion from octahedral symmetry being small, a very large $\Delta$ results. Broadly the $\Delta$-values decrease as the distortion increases, Figure 15.
The above distortion theory is very useful for the assignment of ferrous positions in silicates for instance, the ferrous iron of the pyroxene $M_2$ and the amphibole $M_4$ Crystal sites give a smaller $\Delta$ than the Pyroxene $M_1$ and Amphibole $M_{123}$ less distorted sites respectively as expected. However, the distortion treatment cannot be applied conclusively because of many deviations such as, the Pyroxene $M_1$ and
the Amphibole $M_2$ Crystal sites. Where the variation in distortion is weak but $\Delta$ may vary up to 1 mm/sec and 0.4 mm/sec in the above sites respectively.

The large variations are attributed to the contribution to the $Q_{\text{lattice}}$ by the other factors such as the effective charges on the oxygen atoms, the symmetry and charge on the neighbouring cations, silicons and oxygens as in the substitution of $\text{Ca}^{2+}$ for $\text{Fe}^{2+}$ in the orthopyroxene $M_2$ and the cummingtonite $M_4$ which influences $\Delta$ markedly. Contributions by other factors are usually difficult to estimate and the distortion criteria is useful which applied with caution.
CHAPTER V

ANALYSIS OF SPECTRA

5.1 COMPUTER ANALYSIS — METHOD

The absorption line shapes of minerals using sources with narrow lines, such as $^{57}$Co embedded in Pd matrix, have been found to be ideal Lorentzians. The intensity of a Lorentzian-shape transmitted gamma beam, as a function of its energy, has the form of equation 20

$$I(v) = b - \frac{I(0)}{1 + \left(\frac{V - V(0)}{\Gamma/2}\right)^2} \quad (20)$$

$I(0)$ is the intensity at the resonance velocity $V(0)$, $\Gamma$ the full width at half height of the absorption line, and $b$ is the background or baseline intensity.

For $n$ lines, the above function is represented by equation 21.

$$I(v) = b - \sum_i \frac{I(0)_i}{1 + \left(\frac{V - V(0)_i}{\Gamma/2}_i\right)^2} \quad (21)$$

The $n$ line spectrum is a function of $3n+2$ parameters; position, width, and intensity of each line, plus the background and slope of the background. The best fit ideally should correspond to the minimum weighted sum of squares $X^2$, as given by equation 22.

$$X^2 = \sum_{c=1}^{n} W_c \left[I_c - I(\dot{V}_c/q_i)\right]^2 \quad (22)$$
where \( n \) is the number of channels fit; \( I_c \) the observed count at channel \( C \); \( I(V/c_q) \) is the transmission function; \( q_1 \) denotes the \( 3n+2 \) parameters, and \( W_c \) is the inverse of the variance for Channel \( C \).

Initial estimates are chosen for the \( 3n+2 \) parameters, and using \( \frac{dx^2}{dq_i} = 0 \) for each \( q_i \), corrections are determined for each \( q_i \) such that \( x^2 \) is minimized. The procedure is repeated using the corrected estimates from the previous iteration, until \( x^2 \) reaches a minimum.

The fitting mentioned above is carried through the programme MOSSBR (Appendix B). MOSSBR consists of a main block and several subroutines. The main block reads in the data, applies corrections to it and prints the results. Subroutine FUNC calculates the function derivatives; subroutine CURFIT carries the least square fitting; subroutine MATINEV is for matrix inversion and accompanying solution of linear equations; subroutine JACOBI is for matrix diagonalization through successive rotations, subroutine EXAM applies corrections to the eigenvalues if any is zero or negative otherwise the fitting will diverge, while subroutine PLOTB plots the raw and calculated spectra.

5.2 LINE SHAPES - MINERAL SPECTRA

The spectral shape of an emission line centered at an energy \( E_s \) with a natural width \( \Gamma_0 \), when a Doppler velocity \( V \) is applied; is given by the distribution of equation 23; known as Breit-Wigner, or Lorentzian distribution:

\[
I(E,V) = \frac{\Gamma_0}{2\pi} \left[ \frac{1}{E-E_s-E(Y(V/c_q) + (\frac{\Gamma_0}{2}))^2} \right] \quad (23)
\]
If the emission line is broadened, it is sufficient to replace $\Gamma_0$ in equation 23 by an effective line width $\Gamma_s^{3.6}$. The experimentally determined full width at half height $\Gamma_{ex}$ is usually expressed as equation 24.

$$\Gamma_{ex} = \Gamma_a + \Gamma_s + 0.27 \frac{\Gamma_s X}{n}$$

(24)

$\Gamma_n$ is the natural line width as determined by the lifetime of the excited state, while $X$ is given by equation 25.

$$X = n f_a \sigma_o$$

(25)

$n$ is the number of atoms of the Mössbauer isotope per cm$^2$; $f_a$ the recoil free fraction of the absorber, and $\sigma_o$ is the maximum cross section as given by equation 26.

$$\sigma_o = \frac{\lambda^2}{2\pi} \frac{2I_e + 1}{2I_g + 1} \frac{1}{\alpha_t + 1}$$

(26)

$I_e$ and $I_g$ are the nuclear spins of the excited and ground states respectively; $\alpha_t$ is the total internal conversion coefficient.

In order to get symmetrical Lorentzian lines, very thin absorbers must be used (not exceeding 10 mg per cm$^2$ in the case of iron). If this is obeyed, the last term in equation 24 is minimal when compared to $\Gamma_a$ and $\Gamma_s^{3}$. Otherwise the shoulders of a line may deviate from the Lorentzian shape. A line can also be broadened by the cosine angle effect, when the source is too close to the detector. This depends on the areas of the source, the detector and the distance separating them from the absorber. However, this effect is easily minimized by applying corrections to the
spectra or by collimation of the gamma beam.

Mineral spectra are often characterized by the presence of two or more quadrupole doublets with close absorption peaks; i.e. an absorption envelope may consist of several lines, non-resolved visually, and a fit may diverge if the initial guess of the number of lines, or the values of the parameters are far from their true values. To overcome the fitting difficulties, the use of constraints (such as assigning the intensities or the widths of a doublet to be the same) was justified, and the weighted sum of squares ($X^2$) value was regarded as an indicator to the goodness of a fit \(^3\),\(^11\),\(^12\). An acceptable $X^2$ value should lie within a 5% difference from the total number of degrees of freedom of a certain fit where the number of degrees of freedom is the number of fitted channels and parameters. However, the $X^2$ value is sometimes misleading, since it may drop when the number of fitted lines is increased, and the best fit does not always correspond to a minimum of $X^2$. In such a case the parameter values are taken as a guide; for instance, the line width and the intensities of a doublet are expected to be very close when the resolution of a spectrum is satisfactory and the baseline is linear.

The use of constraints is helpful when the number of absorption peaks in a certain envelope is high, or when a certain quadrupole doublet, overlapping another doublet, accounts to less than ten percent of the total absorption. It should be mentioned also that it is very difficult to resolve peaks contributing to less than 5 percent of the total intensity\(^13\).

5.3 **ESTIMATION OF PERCENTAGE COMPOSITION**

For non-overlapping Lorentzians, area ratios for thin absorbers can be expressed as equation \(^2\),\(^1\),\(^4\)
\[
\frac{A_A}{A_B} = C \frac{N_A}{N_B}
\]  

(27)

where \(A_A\) and \(A_B\) are the areas of lines A and B respectively; \(C\) a constant given by equation 28; \(N_A\) and \(N_B\) are the numbers of Iron atoms at sites A and B respectively.

\[
C = \frac{\Gamma_A}{\Gamma_B} \frac{G(x_A)}{G(x_B)} \frac{f_a}{f_b}
\]  

(28)

In equation 28; \(\Gamma\) is the line width, \(G(x)\) represents saturation corrections depending on the thickness of absorbers; where for very thin absorbers \(G(x)\) approaches unity. \(f_a\) and \(f_b\) are the recoil free fractions for A and B.

For silicates \(C\) is almost unity or very close to it\(^3\), implying equal line widths, no isotope fractionation between sites and that the \(f\)-factors are identical for each iron atom in every mineral. However, the usual overlap of lines in silicates (Pyroxenes) makes it difficult to apply the method quantitatively.

An alternative method derives the fractions from intensity ratios directly. As is the case in estimating fractions of iron of the \(M_1\) and \(M_2\) sites in orthopyroxenes, where the widths are in general equal\(^15\). The standard error \(\Delta \Gamma / \Gamma\) of the line width is about 10-15 times larger than the standard error \(\Delta I / I\) of the corresponding peak heights. The areas of Lorentzians, being proportional to the product \(I \Delta \Gamma\); the relative line errors in widths and areas are due to the strong overlap of Lorentzian tails, even when the peaks are well separated\(^16\). The relations given by equation 29 are for a two doublets fit, where \(I\) refers to the intensity,
A and B are the two doublets, where the subscripts 1 and 2 refer to the low and high velocity peaks respectively; \( T(M_1) \) and \( T(M_2) \) are the fractions of iron at sites \( M_1 \) and \( M_2 \) respectively.

\[
T(M_1) = \frac{I(A_1) + I(B_1)}{I(A_1) + I(B_1) + I(A_2) + I(B_2)}
\]

\[
T(M_2) = \frac{I(A_2) + I(B_2)}{I(A_1) + I(B_1) + I(A_2) + I(B_2)}
\]

(29)

In Chapter 6, explanations are provided, as to which method is used for the estimation of iron sites.
CHAPTER VI

RESULTS AND INTERPRETATIONS - PART I

6.1 ESTIMATION OF IRON SITES IN BULK SAMPLES

The samples studied are E288.C, E282.b, and E294 (for samples description see Appendix A). Each sample was crushed and then powdered. Absorbers were prepared by enclosing an amount of powder (100mg) between two circular plastic sections of diameter close to an inch. The absorption spectra for the above three samples are shown in Figures 16, 17 and 18 respectively. The results obtained by computer analysis are listed in Table 6.

Initial spectra of these samples revealed the presence of magnetite in small amounts; the magnetite lines were very weak to analyze. For later runs, the magnetite was removed by means of a hand magnet. No absorption lines due to any magnetite left appeared.

Sample E282.b gave a single doublet spectrum. The quadrupole splitting and the isomer shift of this doublet are characteristic of ferrous iron in pyroxenes. The width of the lines is more than expected from a single mineral (using $^{57}$Co in a Pd matrix, silicates line widths are up to 0.35 mm/sec), especially the low velocity peak. However, due to the very weak absorption (1.2%), trials to resolve the other lines failed.
FIGURE 17
WÖSSBAUER SPECTRUM OF SAMPLE Z82.6

VELOCITY (mm/sec)

ABSORPTION %

0.24  0.48  0.72  0.96
MÖSSBAUER SPECTRUM OF SAMPLE E294

FIGURE 18

VELOCITY (mm/sec)

% ABSORPTION

0.88  1.76  2.64  3.52
TABLE 6

CALCULATED PARAMETERS OF THE BULK SAMPLES (Δ, δ and Γ ARE IN MM/SEC. NUMBERS IN PARENTHESES ARE ERRORS TO THE LAST DIGIT. ERROR IN IRON RATIOS IS UP TO 5%)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>E282.b</th>
<th>E288.c</th>
<th>E294</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ(11')</td>
<td>1.98(2)</td>
<td>1.99(2)</td>
<td>2.03(2)</td>
</tr>
<tr>
<td>δ(11')</td>
<td>1.43(2)</td>
<td>1.46(2)</td>
<td>1.46(2)</td>
</tr>
<tr>
<td>Δ(22')</td>
<td>0.65(4)</td>
<td>0.56(2)</td>
<td>0.66(2)</td>
</tr>
<tr>
<td>δ(22')</td>
<td>0.53(4)</td>
<td>0.66(2)</td>
<td>1.44(4)</td>
</tr>
<tr>
<td>Δ(33')</td>
<td></td>
<td></td>
<td>2.66(4)</td>
</tr>
<tr>
<td>δ(33')</td>
<td></td>
<td></td>
<td>1.44(4)</td>
</tr>
<tr>
<td>Γ1, Γ1'</td>
<td>0.45, 0.39(2)</td>
<td>0.35, 0.35(2)</td>
<td>0.31, 0.31(2)</td>
</tr>
<tr>
<td>Γ2, Γ2'</td>
<td></td>
<td>0.39, 0.39(4)</td>
<td>0.32, 0.32(2)</td>
</tr>
<tr>
<td>Γ3, Γ3'</td>
<td></td>
<td></td>
<td>0.27, 0.27(4)</td>
</tr>
<tr>
<td>Fe(11')/Fe</td>
<td>100</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>Fe(22')/Fe</td>
<td></td>
<td>25</td>
<td>68</td>
</tr>
<tr>
<td>Fe(33')/Fe</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>X²</td>
<td>309</td>
<td>219</td>
<td>268</td>
</tr>
<tr>
<td>max ab.</td>
<td>1.2%</td>
<td>2%</td>
<td>4%</td>
</tr>
</tbody>
</table>

The spectrum of the sample E288.c was resolved into two quadrupole doublets. The isomer shift and the quadrupole splitting of the doublet labelled 11' are close to that of sample E282.b i.e. it is assigned to ferrous iron in pyroxenes. The weaker doublet 22' has its parameters close to the published parameters of pyrite.¹⁷,¹⁸ (Section 6.5).
The two outer doublets 11' and 33' of the three doublet spectrum of sample E294 were assigned to ferrous iron in pyroxenes, while the intense doublet 22' was assigned to ferric iron entering the silicate structure (see Chapter 7).

The percentage composition of the different iron sites was derived using area ratios.

6.2 PYROXENES – STRUCTURE

Pyroxenes are an important group of the rock-forming ferromagnesium silicates, which have a wide abundance in nature. The majority of the pyroxenes present in igneous and metamorphic rocks can be considered as members of the system shown in Figure 19.

FIGURE 19

PYROXENES IN THE SYSTEM CaFeSi$_2$O$_6$ - CaMgSi$_2$O$_6$ - Mg$_2$Si$_2$O$_6$ - Fe$_2$Si$_2$O$_6$
The pyroxene crystal structure is roughly divided into two groups—a structure close to the diopside-Hedenbergite structure (clinopyroxenes) and a structure characteristic of pyroxenes lying on the Enstatite-Ferrosilite line (Orthopyroxenes).

The characteristic pyroxene structure, is the linkage of $\text{SiO}_4$ tetrahedra by sharing two out of four corners to form continuous chains of composition $(\text{SiO}_3)_n$; see Figure 20. The chains are linked laterally by cations (Ca, Mg, Fe, ... ) but may have relative disposition; different arrangement of chains lead to the main subdivision of pyroxenes (monoclinic, orthorhombic)$^{19}$.

![Diagram of pyroxene structure](image)

**FIGURE 20**

IDEALIZED ILLUSTRATION OF A SINGLE PYROXENE CHAIN $(\text{SiO}_3)_n$ AS SEEN IN THREE PROJECTIONS (a) on (100), (b) ALONG THE z DIRECTION, (c) ALONG THE y DIRECTION, AND (d) IN PERSPECTIVE$^{19}$. 
FIGURE 21

CRYSTAL STRUCTURE OF DIOPSIDE, \( \text{CaMgSi}_2\text{O}_6 \), VIEWED ALONG THE \( a \) AXIS.

\( M_1 = \text{Mg} \), \( M_2 = \text{Ca} \).

A general chemical formula for the pyroxene group, proposed by Bermann (1937) and later slightly modified by Hess (1949) may be expressed as

\[(W)_{1-p}(X,Y)_{1+p}Z_2\text{O}_6\]

where

\( W = \text{Ca,Na}; \quad X = \text{Mg,Fe}^{2+}, \text{Mn,Ni,Li}; \)

\( Y = \text{Al,Fe}^{3+}, \text{Cr,Ti}, \) and \( Z = \text{Si,Al}, \)

In the orthopyroxene series, \( P = 1 \) and the content of \( Y \) ions is small.

In the clinopyroxene series, \( P \) varies from zero (e.g. diopside; where \( y \)
is small, and Aegerine - Jadite in which X is small) to 1 (eg. Spodumene). Normally, there are two crystallographically distinct positions in the pyroxene structure labeled $M_1$ and $M_2$. In the orthopyroxene structure, cations in the $M_1$ position are coordinated to six oxygen ions, each linked to one silicon atom in a nearly regular octahedron (six coordinates site), same as in the clinopyroxene diopside structure; see Figure 21. However, the $M_1$ octahedron in diopside is more distorted than in orthopyroxenes. The $M_2$ position in the clinopyroxene diopside structure is an eight coordinated site occupied usually by $\text{Ca}^{2+}$ ions, while in the orthopyroxene hypersthene structure $M_2$ is a six coordinated site and may be a five coordinated one, same as that occurs in synthetic orthoferrosilite.

Though many pyroxenes have only one structural type, the space group changes from $\text{Pbca}$ for orthopyroxenes to $\text{P21/c}$ for Pigeonite to $\text{C2/c}$ for diopside hedenbergite. In clinopyroxenes, the type of structure is determined by the charge and the size of cations entering the $M_2$ position. Large univalent ($\text{Na}^+$) or bivalent ($\text{Ca}^{2+}$) cations are responsible for the diopside type structure (space group $\text{C2/c}$), small univalent cations ($\text{Li}^+$) are responsible for spodumene type structure (space group $\text{C2}$) and small bivalent cations ($\text{Mg}^{2+}$) for the clinoenstatite type structure (space group $\text{P21/c}$).

In the next two sections determination of iron ions entering the different sites is discussed in detail.

6.3 ORTHOPYROXENES $(\text{Mg, Fe})_2\text{Si}_2\text{O}_6$

Four orthopyroxene samples were studied. They are labelled CGW1; CG3; CG5 and CG12; (for sample description see Appendix A). Absorption
spectra are shown in Figure 22, 23, 24, and 25 for the above four samples respectively. The calculated parameters are listed in Table 7. Preparation of the absorbers followed the same procedure outlined in Section 6.1. However, the orthopyroxene samples were considered to be pure crystals; this was confirmed by their absorption spectra, which showed that the absorption peaks are due to one structural type only.

**TABLE 7**

CALCULATED PARAMETERS OF THE ORTHOPYROXENES (\(\Delta, \delta\) and \(\Gamma\) ARE GIVEN IN MM/SEC. THE NUMBERS IN PARANTheses ARE ERRORS IN THE LAST DIGIT. ERROR IN PERCENTAGE COMPOSITION IS ± 3%).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>SGW1</th>
<th>CG3</th>
<th>CG5</th>
<th>CG12</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta(11'))</td>
<td>2.50(5)</td>
<td>2.44(5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\delta(11'))</td>
<td>1.37(3)</td>
<td>1.40(3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\Gamma(1,1'))</td>
<td>0.31(2)</td>
<td>0.28(2)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\Delta(22'))</td>
<td>2.11(2)</td>
<td>2.09(2)</td>
<td>2.11(2)</td>
<td>2.13(2)</td>
</tr>
<tr>
<td>(\delta(22'))</td>
<td>1.34(2)</td>
<td>1.34(2)</td>
<td>1.34(2)</td>
<td>1.35(2)</td>
</tr>
<tr>
<td>(\Gamma(2,2'))</td>
<td>0.33(1)</td>
<td>0.31(1)</td>
<td>0.36(1)</td>
<td>0.35(1)</td>
</tr>
<tr>
<td>(\Delta(33'))</td>
<td>0.49(5)</td>
<td>0.34(5)</td>
<td>0.35(5)</td>
<td>0.55(5)</td>
</tr>
<tr>
<td>(\delta(33'))</td>
<td>0.69(5)</td>
<td>0.68(5)</td>
<td>0.65(5)</td>
<td>0.74(5)</td>
</tr>
<tr>
<td>(\Gamma(3,3'))</td>
<td>0.31(2)</td>
<td>0.32(2)</td>
<td>0.27(2)</td>
<td>0.35(2)</td>
</tr>
<tr>
<td>(Fe^{2+}/Fe^{2+})</td>
<td>8.6%</td>
<td>10.5%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Fe^{2+}/Fe^{2+})</td>
<td>91.4%</td>
<td>89.5%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>(Fe^{2+}/Fe^{2+})</td>
<td>94%</td>
<td>96%</td>
<td>96%</td>
<td>95%</td>
</tr>
<tr>
<td>(Fe^{2+}/Fe^{2+})</td>
<td>6%</td>
<td>4%</td>
<td>4%</td>
<td>5%</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>209</td>
<td>250</td>
<td>257</td>
<td>286</td>
</tr>
<tr>
<td>max. abs.</td>
<td>9%</td>
<td>9%</td>
<td>8%</td>
<td>9%</td>
</tr>
</tbody>
</table>
FIGURE 23

MÖSSBAUER SPECTRUM OF ORTHOPYROXENE CG3
MÖSSBAUER SPECTRUM OF ORTHOPYROXENE CG5
The assignment of the orthopyroxene spectra follows the interpretation of Evans (1967). Fe\(^{3+}\) free orthopyroxenes give rise to two quadrupole doublets at most. One doublet due to ferrous iron entering the M\(_2\) site while the other is due to ferrous iron entering the M\(_1\) site. Our samples showed a weak doublet assigned to Fe\(^{3+}\) in the M\(_1\) or M\(_2\) sites, however, ferric iron accounted to no more than 6% of the total iron present (see Table 7). The intense doublet of the ferrous ions is assigned to the M\(_2\) position because according to the preference criteria Mg preferably fills the M\(_1\) crystal site. While iron enters the more distorted M\(_2\) site. Since the quadrupole splitting decreases as the distortion from octahedral symmetry increases, the doublet due to the M\(_2\) site has a smaller \(\Delta\). Similar and varying explanations were given to the larger \(\Delta\) of the M\(_1\) site. Virgo and Hafner (1972) interpreted the situation as "crystal site with the larger radial distortion index generally exhibits the smaller splitting". Greenwood and Gibb (1971) interpretation is "at M\(_2\) presumably there is a larger lattice term in the electric field gradient which partly cancels the contribution from the valence electrons".

The works of Nozik and Kaplan (1967) showed that lattice contribution for Fe\(^{2+}\) is usually negligible or, in extreme cases, amounts to only 15% of the total quadrupole splitting, the major contribution being that of the ground state electron configuration.

Walsh and Donnay (1974) dismissed the above explanations as not satisfactory; basing their argument on Nozik and Kaplan results concluded that "Since the ground orbital states at M\(_2\) is different from that of M\(_1\), the quadrupole splitting will also be different. The type of distortion controls the resulting ground orbital state and the
magnitude of distortion determines the temperature at which the excited orbital states becomes populated and the quadrupole splitting starts to decrease. So predictions about the ratio of the quadrupole splittings cannot be made without investigating the electronic states at $M_1$ and $M_2$.

Though there are many different arguments but the assignments of the quadrupole doublets has been agreed on by all previous works.

Figure 26 shows the variation of $\Delta$ at $M_1$ and $M_2$ against the ratio $\text{Fe}/(\text{Fe+Mg})$. The variation of $\Delta(M_2)$ is found to be a linear one. This was noticed by Bancroft (1967)\textsuperscript{13}. Though Bancroft suggested that $\Delta(M_1)$ follows a similar trend, but Figure 26 dismisses such a relation. However the values of $\Delta(M_1)$ usually have a much larger error than $\Delta(M_2)$ due to the difficulty in resolving its less intense doublet overlapping the $M_2$. 

**Figure 26**

QUADRUPOLE SPLITTING AT $M_1$ AND $M_2$ VERSUS THE RATIO $\text{Fe}/(\text{Fe+Mg})$ IN ORTHOPYROXENES (VALUES ARE LISTED IN APPENDIX D)
doublet, especially when the ratio Fe/(Fe+Mg) is less than one half. This is the case in the samples CG5 and CG12 where the doublet at $M_1$ could not be resolved, though the slightly larger line widths of the doublet due to $M_2$ in these samples suggest that a very small percentage of Fe$^{2+}$ enters the $M_1$ site.

The distribution of iron at the $M_1$ and $M_2$ crystal sites in orthopyroxenes with a varying ratio Fe/(Fe+Mg) was studied in details by Virgo and Hafner (1979, 1970) (fractions of iron at the $M_1$ and $M_2$ sites for different iron ratios as derived from Mossbauer analysis at liquid nitrogen temperature, are listed in Appendix D). Their analysis shows that site $M_1$ has usually less than 12% of total iron in orthopyroxenes where Fe/(Fe+Mg) is less than one half. As Fe/(Fe+Mg) decreases the ratio of iron in the site $M_1$ decreases; it becomes very difficult to resolve that doublet, especially at room temperature. The isotherms derived from heating experiments on natural orthopyroxene crystals in the range 500-1000°C are shown in Figure 27. Virgo and Hafner found that an Fe$^{2+}$,Mg distribution is close to ideal (ordered) in the region $0 < x < 0.6$ where $x = Fe^{2+}/(Fe^{2+} + Mg)$. Figure 27 shows that orthopyroxenes from granulites and plutonic rocks have an equilibrium temperature of 480°C while volcanic pyroxenes show a disordered Fe$^{2+}$, Mg distribution of 500°C - 600°C equilibrium temperature.
FIGURE 27

PLOT OF $\text{Fe}^{2+}$ SITE OCCUPANCY AT $M_1$ AGAINST $M_2$ OF NATURAL ORTHOPYROXENES. THE SOLID LINES REFER TO EXPERIMENTALLY DETERMINED Isotherms AT THE INDICATED TEMPERATURES; ●-ORTHOPYROXENES FROM METAMORPHIC IRON FORMATIONS IN QUEBEC; ●-FROM GRANULITES IN CEYLON AND MADRAS AREA; ○ - FROM GRANULITES; X - FROM VOLCANIC ROCKS.

The $M_1$, $M_2$ distribution in the four samples studied suggest that their (Fe/Fe+Mg) is less than 30% and are ordered in the range 400°C-500°C.

6.4 CLINOPYROXENES

Six clino pyroxene samples labelled CG1; CG6; CG8; CG11; CG14; CGW3 (See Appendix A) were studied. Their absorption spectra are shown in Figures 28, 29, 30, 31, 32 and 33 respectively. While the calculated
FIGURE 29
MÖSSBAUER SPECTRUM OF CLINOPIROXENE CC6

VELOCITY (mm/sec)

ABSORPTION
Figure 30
Mössbauer Spectrum of Clinoptilolite CS8

Absorption

1.74  3.48  5.52  6.96

Velocity (mm/sec)
FIGURE 31.
MOSSBAUER SPECTRUM OF CLINOPLYXENITE CS11

VELOCITY (mm/sec)

1.54  3.08  4.62  6.16

% ABSORPTION
parameters are listed in Table 3.

Unlike the orthopyroxene series, where structural changes are due to variation in the Fe/(Fe+Mg) ratio, clinopyroxenes usually have other numerous substitutions. In calcic clinopyroxenes (diopside-hedenbergite line), only the ratio of iron to magnesium is variable. The spectra obtained are analyzed easily because iron is expected to occupy the $M_1$ site. Since site $M_2$ is filled by calcium, and if there is no calcium deficiency, the spectra should consist of one doublet due to Fe$^{2+}$ present at site $M_1$. This has been affirmed in natural samples very close to the diopside-hedenbergite line and in synthetic pure samples. If there is no calcium deficiency and more than one quadrupole doublet is present – one doublet must be due to impurities. Figure 34 shows the variation in $\Delta(M_1)$ against the ratio Fe/(Fe+Mg) (Sources of data are listed in Appendix D). The variation is noticed to be linear, the non-smoothness of the curve is attributed to the effects of different cations especially in natural samples on the quadrupole splitting.

Sample CGW$_3$ spectrum was resolved into one doublet only. It is due to ferric iron in the $M_1$ site as expected from the chemical structure of aegerine (acmite), NaFe$^{3+}$Si$_2$O$_6$. The parameters are analogous to those given by Angelis and Sgarlata (1979) in their study of pyroxenes from central Sweden, where it is reported that ferric iron enters the $M_1$ position only in the crystal structure, which is similar to the diopside structure.
**TABLE 8**

CLINOPYROXENES CALCULATED PARAMETERS (Δ, δ AND Γ ARE IN MM/SEC, VALUES IN PARENTHESES ARE ERRORS IN THE LAST DIGIT, ERRORS IN IRON RATIOS ARE UP TO 5%)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>CG11</th>
<th>CG6</th>
<th>CG14</th>
<th>CG8</th>
<th>CG1</th>
<th>CGW³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ(11')</td>
<td>2.15(2)</td>
<td>2.47(2)</td>
<td>2.80(2)</td>
<td>2.62(2)</td>
<td>2.75(2)</td>
<td></td>
</tr>
<tr>
<td>δ(11')</td>
<td>1.38(2)</td>
<td>1.46(2)</td>
<td>1.40(4)</td>
<td>1.38(2)</td>
<td>1.40(3)</td>
<td></td>
</tr>
<tr>
<td>Γ(1,1')</td>
<td>0.36(2)</td>
<td>0.36(2)</td>
<td>0.27(2)</td>
<td>0.29(2)</td>
<td>0.35(2)</td>
<td></td>
</tr>
<tr>
<td>Δ(22')</td>
<td>2.72(2)</td>
<td>1.93(2)</td>
<td>2.40(2)</td>
<td>2.18(2)</td>
<td>2.46(2)</td>
<td></td>
</tr>
<tr>
<td>δ(22')</td>
<td>1.36(2)</td>
<td>1.40(2)</td>
<td>1.35(2)</td>
<td>1.39(2)</td>
<td>1.35(2)</td>
<td></td>
</tr>
<tr>
<td>Γ(22')</td>
<td>0.28(2)</td>
<td>0.37(2)</td>
<td>0.30(2)</td>
<td>0.34(2)</td>
<td>0.35(2)</td>
<td></td>
</tr>
<tr>
<td>Δ(33')</td>
<td>1.99(2)</td>
<td>1.85(2)</td>
<td>2.01(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ(33')</td>
<td>1.33(2)</td>
<td>1.38(2)</td>
<td>1.37(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Γ(2'2)</td>
<td>0.32(2)</td>
<td>0.34(2)</td>
<td>0.33(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ(44')</td>
<td>0.48(3)</td>
<td>0.54(4)</td>
<td>0.43(4)</td>
<td>0.55(3)</td>
<td>0.35(2)</td>
<td></td>
</tr>
<tr>
<td>δ(44')</td>
<td>0.71(3)</td>
<td>0.74(4)</td>
<td>0.62(4)</td>
<td>0.71(3)</td>
<td>0.63(2)</td>
<td></td>
</tr>
<tr>
<td>Γ(2'2)</td>
<td>0.38(3)</td>
<td>0.32(2)</td>
<td>0.36(2)</td>
<td>0.35(3)</td>
<td>0.40(2)</td>
<td></td>
</tr>
<tr>
<td>Fe(11')/Fe²⁺</td>
<td>76%</td>
<td>22%</td>
<td>10%</td>
<td>13.2%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Fe(22')/Fe²⁺</td>
<td>24%</td>
<td>78%</td>
<td>20%</td>
<td>63.4%</td>
<td>45%</td>
<td></td>
</tr>
<tr>
<td>Fe(33')/Fe²⁺</td>
<td>19%</td>
<td>70%</td>
<td>23.4%</td>
<td>45%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe³⁺/Fe</td>
<td>81%</td>
<td>90%</td>
<td>71%</td>
<td>100%</td>
<td>68%</td>
<td></td>
</tr>
<tr>
<td>Fe²⁺/Fe</td>
<td>19%</td>
<td>10%</td>
<td>29%</td>
<td>32%</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>X²</td>
<td>272</td>
<td>238</td>
<td>249</td>
<td>252</td>
<td>286</td>
<td>330</td>
</tr>
<tr>
<td>max a.b.</td>
<td>7.7</td>
<td>7.3</td>
<td>7.1</td>
<td>8.7</td>
<td>3.6</td>
<td>11.5</td>
</tr>
</tbody>
</table>
VARIATION OF $\Delta(M_1)$ AGAINST Fe/(Fe+Mg) IN DIOPSIDE-HEDENBERGITE

In subcalcic pyroxenes, (Ca/(Fe+Mg)<1), the assignment of Mossbauer spectra has followed different explanations, confusion is mostly due to comparison with orthopyroxenes and calcic clinopyroxenes assignments. It is also due to the supposition that Mg is favorable to fill the calcium deficiency at the $M_2$ site$^{29,31}$. However, studies on calcium-poor pyroxenes by Walsh et al. (1974)$^{22}$ showed that Fe$^{2+}$ is more likely to fill the calcium deficiency at the more distorted site $M_2$.

The spectra of samples CG6, CG8 and CG14 is assigned in a similar way to the assignment of the spectra of augites in 1971 by Williams et al.$^{32}$. The inner doublet (smaller $\Delta$) is assigned to ferrous iron at site $M_2$; the outer doublet (less intense) to ferrous iron at site $M_1$. 
The weak doublet (11') in CG14 is assigned to impurities, while CG8 spectrum, one different from other augites and clinopyroxenes; (since there is no detected presence of ferric iron also the high velocity peak is almost more intense than the low velocity one), has two doublets of quadrupole splitting 1.85 and 2.18 mmsec$^{-1}$ assigned to the $M_2$ site. An anomalous behaviour attributed to a fine domain structure of pyroxenes close to the composition Ca$_{0.8}$Fe$_x$Mg$_{1-x}$Si$_2$O$_6$ (0 < x < 1.2)$^{32}$. Sample CG1 spectrum is very close to that of ordered omphacites, where ferrous iron enters four $M_1$ positions$^{33}$. Though only three ferrous doublets were resolved, the similarity of the spectra and the large percentage of ferric iron (32%) present allows the suggestion that CG1 is an ordered omphacite where the structure space group is P2.

6.5 PYRITES

Two naturally occurring pyrite sample labelled SS7P and SS8P were studied (see Appendix A). Their absorption spectra are shown in Figures 35 and 36 respectively, while the parameters are listed in Table 9. Sample SS7P consisted of small cubic crystals (~ 3mm edge) that were separated from a host rock. Sample SS8 had no specific shape. The two samples yielded almost identical isomer shifts and quadrupole splitting, which are consistent with those previously published (see Appendix D). The $\Delta$ and $\delta$ values are characteristic of low spin iron II.

<table>
<thead>
<tr>
<th>TABLE 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>CALCULATED PARAMETERS OF PYRITE SAMPLES</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>SS7P</td>
</tr>
<tr>
<td>SS8P</td>
</tr>
</tbody>
</table>
CHAPTER VII
MÖSSBAUER SPECTROSCOPY AS A GEOCHEMICAL
PROSPECTING TECHNIQUE - STUDY OF SOME SAMPLES
FROM GASPE COPPER MINES

7.1 INTRODUCTION

The possible use of Mössbauer spectroscopy as a geochemical pros-
ppecting technique for ore deposits was suggested by Bancroft in 1973.
Since then, the only published works related to the subject are by
Amirkhanov et al. in 1974-75, where tracing some thermodynamic condi-
tions of the ore-forming process and estimation of the potential of ore
zones, were deduced from a proposed relation between the absolute age of iron
containing rocks and mudstones and the corresponding quadrupole splitting.

The results presented earlier in Chapter 6, and Mössbauer data from
various references on silicate minerals, correlate mostly the variation in
the quadrupole splitting of a specific mineral to the variation in the
contents of iron or other ions; as in the diopside - hedenbergite line,
where the quadrupole splitting is found to increase linearly as the ratio
Fe/(Fe+Mg) increases, in both synthetic and natural samples.

In this chapter, an investigation of the possible use of Mössbauer
spectroscopy in geochemical prospecting is carried out by studying six
samples from specific locations in the Gaspe Copper mines area, the approach
is outlined in Chapter 1. Information on the different formations in the
area is given in Figure 37. A previous geological study of the area by
J. Allcock is used as a guide and a background for this study.
FIGURE 37

GEOLOGICAL MAP OF THE GASPE COPPER MINES AREA

7.2 THE FORMATION AND THE SAMPLES

A cross section of the Copper mountain plug is shown in Figure 38 with the distribution of metamorphic zones and iron metasomatism. As is clear from the Figure, the Cap Bon Ami formation is divided into several units \((Q_1, T_1, \ldots)\) which differ in general composition. The
Ll unit, to which the samples belong, refer to a calcareous layer that is mostly formed of an intergrowth of grossular and diopside with minor idocrase and wollastonite. The samples are specified as follows, (see also Appendix A).

A - S675 - 2612
B - S678 - 2761
C - S258 - 2027
D - U3587 - 1552.5
E - U1467 - 240
F - S674 - 2313

A, B, ..., F refer to the sample number, the second part of each label refer to the drill hole position, whereas the last part refer to the depth in feet from the surface. The drill holes mentioned are shown in Figure 39.

7.3 ABSORBERS PREPARATION - RESULTS

Polished thin sections were prepared from the six samples and were studied under a microscope (to help in identifying the minerals present and their proportions). The absorbers were prepared by crushing each piece of rock (Sample) to a coarse grain; grains free of pyrite were only picked (Pyrite is easily detected by its glitter, it is present in the samples in very small quantities). The picked grains were ground and then freed from magnetite by use of a hand magnet (magnetite showed a very weak presence < 0.001% wt. also). Thereafter, each sample was powdered, absorbers were then made by enclosing about 100mg of powder between two thin circular plastic discs of an inch diameter. The thickness of absorbers was about 0.2 mm except that for sample F, for which it was 0.4mm.
FIGURE 38
CROSS SECTION THROUGH THE COPPER MOUNTAIN PLUG ON 25400E SHOWING DISTRIBUTION OF METAMORPHIC ZONES AND IRON METASOMATISM.

The absorption spectra of the samples are shown in Figures 40-45; Table 10 gives the calculated parameters. The main feature of the absorption spectra of the six samples, is that they are composed of two quadrupole doublets in varying proportions (see absorption spectra). The doublet labelled 11' of δ around 0.53 mm/sec and δ = 0.63 mm/sec is assigned to ferric iron entering the structure of the garnet andradite of chemical composition Ca₂(Fe³⁺,Al)₂Si₃O₁₂. The garnet structure consists of independent SiO₄ tetrahedra linked by trivalent ions in octahedral coordination and divalent ions in eightfold coordination. The octahedron of one Fe and 60 atoms is reported to be regular in andradite and the
parameters are consistent with Fe$^{3+}$ being in a slightly distorted octahedral configuration. The doublet labelled (2') in the absorption spectra is assigned to ferrous iron of the hedenbergite structure of chemical composition Ca(Fe$^{2+}$,Mg)Si$_2$O$_6$. The hedenbergite structure is similar to
MÖSSBAUER SPECTRUM OF SAMPLE E(U1467-240)
that of diposite (see Section 6.2, Figure 21). The extra ferrous doublet (33') in the spectrum of Sample A (S675-2612) is probably due to an impurity of another pyroxene or silicate mineral. The percentages of ferrous and ferric iron, as calculated from area ratios (Section 5.3), the percentage absorption calculated using the formula

\[
\text{Absorption} = \frac{\text{peak height (counts)}}{\text{background (counts)}},
\]

and the total absorption, calculated using the formula,

\[
\text{Total absorption} = \frac{\text{absorption area}}{\text{background area}}
\]

are given in Table 10 along with the \(X^2\) values.

### Table 10

CALCULATED PARAMETERS OF THE GASPE COPPER MINES SAMPLES (NUMBERS IN PARANThESes REPRESENT THE MAXIMUM EXPERIMENTAL ERROR, \(\Delta\) AND \(\delta\) ARE GIVEN IN mm/sec)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta(11'))</td>
<td>0.53(3)</td>
<td>0.54(3)</td>
<td>0.52(3)</td>
<td>0.54(3)</td>
<td>0.54(3)</td>
<td>-</td>
</tr>
<tr>
<td>(\delta(11'))</td>
<td>0.63(3)</td>
<td>0.63(3)</td>
<td>0.63(3)</td>
<td>0.63(3)</td>
<td>0.63(3)</td>
<td>-</td>
</tr>
<tr>
<td>(\Delta(22'))</td>
<td>2.00(3)</td>
<td>2.03(3)</td>
<td>2.06(3)</td>
<td>2.02(3)</td>
<td>2.05(3)</td>
<td>2.02(3)</td>
</tr>
<tr>
<td>(\delta(22'))</td>
<td>1.40(3)</td>
<td>1.40(3)</td>
<td>1.40(3)</td>
<td>1.40(3)</td>
<td>1.40(3)</td>
<td>1.40(3)</td>
</tr>
<tr>
<td>(\Delta(33'))</td>
<td>2.50(3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\delta(33'))</td>
<td>1.35(3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\Sigma\text{Fe}^{2+}/\Sigma\text{Fe})</td>
<td>42(5)</td>
<td>29(5)</td>
<td>60(5)</td>
<td>14(5)</td>
<td>54(5)</td>
<td>100(5)</td>
</tr>
<tr>
<td>(\Sigma\text{Fe}^{3+}/\Sigma\text{Fe})</td>
<td>58(5)</td>
<td>71(5)</td>
<td>40(5)</td>
<td>86(5)</td>
<td>46(5)</td>
<td>0(5)</td>
</tr>
<tr>
<td>max. abs.%</td>
<td>7.64</td>
<td>8.88</td>
<td>7.17</td>
<td>9.40</td>
<td>4.18</td>
<td>5.24</td>
</tr>
<tr>
<td>Total abs.(\times 10^3)</td>
<td>7.88</td>
<td>8.93</td>
<td>7.31</td>
<td>8.78</td>
<td>4.26</td>
<td>5.97</td>
</tr>
<tr>
<td>(X^2)</td>
<td>247</td>
<td>247</td>
<td>271</td>
<td>300</td>
<td>262</td>
<td>256</td>
</tr>
</tbody>
</table>
7.4 INTERPRETATION OF RESULTS

Hedenbergite and andradite in the inner calcic-silicate zone and in veins and crackles extending into the outer calcic-silicate zone (Figure 46), were formed by iron metasomatism (caused by the emplacement of the plug in its present position). Introduction of iron to diopside and grossular, the main constituents of the calcic-silicate zone formed hedenbergite and andradite as follows:

FIGURE 46
THE COPPER MOUNTAIN PLUG AND METASEDIMENTS, CONTOURS DRAWN ON UPPER SURFACE OF THE CAP BON AMI FORMATION. OUTLINE OF COPPER MOUNTAIN PLUG AT 500 FEET A.S.L. METAMORPHIC ZONES AT 1200-1500 FEET A.S.L.
CaMgSi₂O₆ (diopside) + Fe → Ca(Fe²⁺,Mg)Si₂O₆ (hedenbergite)
Ca₃Al₂Si₃O₁₂ (gроссular) + Fe → Ca₃(Fe³⁺,Al)₂Si₃O₁₂ (andradite)

There is no consensus upon the origin of iron and other metals (Cu, Mo, ...) According to one argument "it has been leached from a large volume of surrounding rocks and redeposited by a circulating hydrothermal system". While according to another one it is due to "similar hydrothermal systems that occurred during the emplacement of the igneous rocks".

Figure 47
VARIATION OF THE RATIO \( \frac{Fe^{3+}}{\Sigma Fe} \) AGAINST TOTAL ABSORPTION \( \frac{Ap}{Ab} \times 100 \).

Figure 47 represents the variation of andradite in the samples, with the total absorptions (the increase in the resonant absorption, is a
direct consequence of the increase in the iron contents). As the contents of iron increase in the rocks, a higher andradite content is noticed, while hedenbergite follows a reverse trend. Sample E (U1467 - 240) is not included in Figure 47 because its location is far away from the rest (Figure 39), and its thin section revealed that it is mostly formed of calcite while the others are mostly intergrowths of diopside and grossular.

The result of Figure 47 is a direct consequence of one fact; the andradite zone is closer to the mountain plug, i.e. the andradite ratio decreases as one moves toward the outer calcic-silicate zone, where the iron content fall rapidly (neglecting the veinlets and crackles).

![Graph](image)

**FIGURE 48**

Fe$^{3+}$ VERSUS DISTANCE FROM CENTER OF PLUG (THEORETICAL), SHOWN IN FIGURE 39 AS A CROSSED CIRCLE (°).
**FIGURE 49**

$\text{Fe}^{3+}$ VERSUS DISTANCE FROM BOUNDARY OF MOUNTAIN PLUG (FIGURE 39).

Figures 48 and 49, are two attempts to correlate the variation of $\text{Fe}^{3+}$ with the distance from the mountain plug. In the first the center of the plug is taken outside the given boundaries of Figure 39 and this hypothetical center gives somewhat a close to linear variation of $\text{Fe}^{3+}$ with distance. In Figure 49 the distance of the drill holes (Figure 39) to the nearest boundary of the plug is taken, the points are scattered in a similar manner if the center of the plug is taken anywhere inside the boundaries.
7.5 DISCUSSION OF RESULTS

In the previous Section (7.4), the trials done to correlate the variation of \( \text{Fe}^{3+} \) (which is also an indicator to the variation of iron contents as a whole) with distance, were not successful, due to two factors:

1 - The lack of precise shape of the plug in three dimensions, which prevented the estimation of the distance separating the samples from the plug.

2 - Since the Mössbauer spectroscopy deals with samples on a very small scale, studied samples should represent to a good degree the location, the layer or the formation to which they belong. Taking into consideration the inhomogeneity of geological formations, a larger number of samples would yield more detailed results.
CHAPTER VIII

CONCLUSION

8.1 CONCLUSION

The valuable use of the Mössbauer effect in semiquantitative analysis, is illustrated by the results of the study on bulk rocks and the Gaspe Copper Mines samples, where the identification of iron bearing minerals and their proportions (using the fingerprint technique and area ratios) is successful.

In studying the bulk rocks, though the iron contents were minimal and the absorption very weak, peaks accounting to less than ten percent of the total absorption were solved.

In studying the orthoand clinopyroxenes, the Mössbauer spectra obtained and the parameters derived from computer analysis, indicate to a good degree the purity and uniformity of their structure. Predictions about the iron contents (Fe/(Fe+Mg)) could be made only qualitatively, due to the limited variation of the quadrupole splitting.

The results derived from samples of Gaspe Copper Mines (Chapter 7) where a linear relation was found to hold between the ferric or ferrous iron proportions and the total iron contents, is a basic step toward the study of better chosen samples, other locations and reaction aureoles. There is a good degree of evidence in the derived results (Chapter 7), that Mössbauer spectroscopy will prove to be valuable and useful in geochemical prospecting.
8.2 RECOMMENDATION FOR FUTURE WORK IN GASPE COPPER MINES AREA

1. independent checks of results (chemical, X-ray analysis etc.)

2. closer representative sampling

3. better controlled sample preparation (using more advanced techniques in the separation of Fe containing minerals, present in the samples studied but regarded as impurities).
APPENDIX A

SAMPLES DESCRIPTION

1. E288.c  Diopside Límy quartzite, Gaspé Copper Mines, Quebec, Ref. A.
2. E282.b  Porcellenite, Gaspé Copper Mines, Quebec, Ref. A.
3. E294  Chalcopyrite in altered límy quartzite, Gaspé Copper Mines, Quebec, Ref. A.
4. CGW1  Bronzite (St. Agathe), Ref. B.
5. CG3  Enstatite, Ref. C.
6. CG5  Bronzite, (MRD-606), Ref. C.
7. CG12  Enstatite (St. Set. 131B), Ref. C.
8. CG1  Clinopyroxene (from Alaska), Ref. C.
9. CG6  Augite (MRD-608), Ref. C.
10. CG8  Augite (MRD-614), Ref. C.
11. CG11  Hedenbergite (MRD-622), Ref. C.
12. CG14  Augite (St. Set. 134B.), Ref. C.
13. CGW2  Aegerine, Ref. C.
14. SS7P  Pyrite, Eastern Townships, Quebec, Ref. D.
15. SS8P  Pyrite, Eastern Townships, Quebec, Ref. D.
16. Samples from Gaspé Copper Mines (S675-2612; S678-2761; S258-2027; 43587-1552.5; U1467-240; S674-2313), Ref. E.
References:

A. P.S. Kumarapeli, Department of Geology, Concordia University, Montreal, Quebec.

B. E. Prochshin, Department of Geology, Concordia University, Sir George Williams Campus, Montreal, Quebec.

C. J.T. Jenkins, Department of Geology, Concordia University, Loyola Campus, Montreal, Quebec.

D. I.Y. Elad.

E. Kevin Shelton, Department of Geology and Geophysics, Yale University, New Haven, Connecticut.
THE FOLLOWING FOR REMOVING ANY DATA POINTS THAT WERE NOT READ.

LET X = 3, 512
LET Y = FLATA(X-1) * 1.2
FLATA(X) = FLATA(X-1) / 2.

继续

IF (FLATA(J) .LT. 111) THEN.
FLATA(J) = FLATA(J-1) + FLATA(J-2) / 2.
END IF.

FUNCTION = 5X .* ENHANCED CHANNEL CORRECTED AGAIN.

LET Y = 54

继续

FUNCTION = 52

FUNCTION = 51

FUNCTION = 50

FUNCTION = 49

FUNCTION = 48

FUNCTION = 47

FUNCTION = 46

FUNCTION = 45

FUNCTION = 44

FUNCTION = 43

FUNCTION = 42

FUNCTION = 41

FUNCTION = 40

FUNCTION = 39

FUNCTION = 38

FUNCTION = 37

FUNCTION = 36

FUNCTION = 35

FUNCTION = 34

FUNCTION = 33

FUNCTION = 32

FUNCTION = 31

FUNCTION = 30

FUNCTION = 29

FUNCTION = 28

FUNCTION = 27

FUNCTION = 26

FUNCTION = 25

FUNCTION = 24

FUNCTION = 23

FUNCTION = 22

FUNCTION = 21

FUNCTION = 20

FUNCTION = 19

FUNCTION = 18

FUNCTION = 17

FUNCTION = 16

FUNCTION = 15

FUNCTION = 14

FUNCTION = 13

FUNCTION = 12

FUNCTION = 11

FUNCTION = 10
\text{LINE} \text{LINE} \text{LINE} \text{LINE} \text{LINE} \text{LINE} \text{LINE} \text{LINE} \text{LINE}
2.1 FORMAT (1X,15I: LINE POSITIONS, 6X, 7H ERRORS/
WHITE (/,6,202) (F(J),F(I),J=1,N)
262 FORMAT (3X,IF 10.5,6X,IF 11.6/)
WHITE (/,6,263)
263 FORMAT (/,1X,13H LINE HEIGHTS, 6A, 7H ERRORS/)
WHITE (/,6,264) (H(J),F(I),J=1,N)
264 FORMAT (2X,FL,3,1LX,FL,4/)
WHITE (/,6,265)
265 FORMAT (/,3X,14L FWHM LF LINE5,7A, 7H ERRORS/)
WHITE (/,6,266) (F(J),FL,(11),J=1,N)
266 FORMAT (/,3X,16L,6A, IF 11.7/)
WHITE (/,6,267)
267 FORMAT (/,5X,11L LINE AREA, L:, 7H ERRORS/)
WHITE (/,6,268) (A(J),AL(J),J=1,N)
268 FORMAT (/,1X,IF 16.6,2A, IF 16.6/)
WHITE (/,6,270)
CALL FLTLE(NA,N,FL,FI.)
NA=N
DL 4L kk=1,NA
FL(kk)=FL(kk)*LLLL
FI(kk)=FI(kk)*LLLL
41 CONTINUE
WHITE(6,168)
WHITE(6,3135) (FI(kJ),kJ=1,NA)
WHITE(6,3135) (FL(kJ),kJ=1,NA)
WHITE(6,3135) (FL(kJ),kJ=1,NA)
WHITE(6,3135) (FL(kJ),kJ=1,NA)
WHITE(6,3135) (FL(kJ),kJ=1,NA)
933 FUnHet(5X,11F7.6)
9461 FUnHet (5I,15I,51I/*NA,15,15I/*)
16 FUnHet (11)
STOP
END
SUBRoutines: DATA
EXTENSION, ILATA(5I2), LL(2L), ILATA(5I2), LL(2L), ILATA(5I2)
SAMPLE(5), THI(5), NUMW(5), SAM(5), THI(5), HUN(5)
COMMON LC
EQUIVALENCE (ILATA, LL(2L)), (LL, LL(17C)), (L2, LL(1705)),
(1(N, LL(17L1)), (K2, LL(212L)), (L4, LL(17L3)), (L, LL(17L9)),
(2(N, LL(272L)), (J, LL(272)), (SAMPLE, LL(272L)), (THI, LL(272L)),
(3(HUN, LL(273L))
REAL (5, 115L) (ILATA(1), I=1, 5I2)
DL 145 k3=1,512
ILATA(k3)=ILATA(k3)
145 ILATINE
1150 FUnHet(6,517)
DATA (NUM(3), J=1,2)/0.0185, 0.02, TH. 2L, 1977/
DATA (SAH(J), J=1,2)/100.0-575000, 1Ld/.
DATA THI(1)/0.0185, 1Ld/
DATA (L(T), T=1,11)/
5-.10000, 4, 127, -5000, 4, 130, -6500, 4, 170,
524000, 4, 0001/
SUBROUTINE CLHFIT

END

SUBROUTINE CLHFIT

LJAN

CALL Z(256),FL(256),EF(256),EL(256),D(256),
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
LJL,CLJL,CLZL,CL2L,CL1L,CL2L,CL1L,CL2L,CL1L,
162    GHOE=U.H=U.H+U(I)*U2
      WRITE(6,243)SA,UC,UC
243    FORMAT(1X,20H*INITIAL VALUE SUM U=SU.E=13.5, 20X,17H.*SU. HLL OF GR
      1AL=E13.5)
      WRITE(6,1751)
1751   FORMAT(14H*DERIVATIVES-)
      WRITE(6,246)(B1(J),J=1,16)
246   FORMAT(15X,5(I13.5,5X))
      IF (SA = 41) 110, 110, 260
110   LE = 1
      GO TO 606
260   S = 0.5
      G6L = 0.5
      H6L = 0.5
      PH6L = 0.5
      A2=ALL(1)
      LE 460 J = 1, 16
          Li(J) = B6L
      LE 461 K = 1, 16
      460   U2(J,K) = B6L
        GO 220 JJ = 1, 16
        LE J =1
            Li=J
        CALL FUNC(J)
        LF(JJ) = F(JJ)
      220   962 J = 1, 16
          Li(J) = B6L - (2.0*LF(JJ)*U1(J))/X(JJ)
      962   963   K = 1, 16
      240   U2(J,K) = B6(J,K) - (2.0*LF(JJ)*U2(J,K) + B1(J)*B1(K))/X(JJ)
      250   964 J = 1, 16
      260   965   J = 1, 16
        CALL EXAH(2,J,LB,LF)
      LF(LF) 250, 250, 305
      250   231 966 J = 1, 16
      231   231   JJ = 1, 16
        CALL JACUL(1,L3,1,4,62)
      HHL=H
      U2 235 967 J = 1, 16
      235   968   JJ = 1, 16
      235   969   J = 1, 16
        A2=ALL(2)
      260   U1(J) = 0.5
        LA 276 J = 1, 16
        LA 276 K = 1, 16
      276   U1(J) = B1(J) + B2(J,K)*GNAL(J)
      276   972 J = 1, 16
        IF (U1(J)) 260, 290, 295
      295   U1(J) = 0.5

285 DI(J) = BL(J)/BL(J)
290 LU TL 275
295 BL(J) = 0.0
275 CONTINUE
295 BL(J) = 0.0
300 LU 360 J = 1, NN
305 LU 360 K = 1, NN
310 LU BL(J) = BL(J) + B2(J,K)*DL(K)
315 LU 310 J=1,1,
315 LU LL = LL + LL*GAL(J)**2
315 LU LL = LL + LL*BL(J)**2
320 IF (LHLL(42) .LT. 2) 315, 315, 320
315 LE = 4
320 LU TL 666
320 LU C=PHLL/SWAT(LL,LL*GAL(L))
320 IF (L) 335, 335, 666
335 LU = 4
335 LU TL 666
400 LL = C
400 L3 = 6
410 LU 410 J = 1, NN
415 LU GAL(J) = B(J) - BL(J)
450 LU 420 II = 1, NN
450 LE = 2
460 LE = 11
460 CALL FMIN (J)
460 IF (II) .EQ. FF(II) - FC(II)
465 S = S + DF(II)**2/X(II)
465 IF (SA - S) 435, 546, 566
435 LL = LL + 1
435 LU 446 J = 1, NN
435 LU BL(J) = BL(J)/2.C
445 LU GAL(J) = B(J) - BL(J)
445 S = C.0
445 LU L3 = L3 + 1
445 IF (L3 - 256) 450, 466, 466
460 LE = 5
460 LU TL 666
500 IF (LL) 515, 505, 505
505 LL = C
505 LU TL 436
505 LU 510 J = 1, NN
510 LU B(J) = GAL(J)
510 SA = S
510 IF (SA - 41) 567, 507, 530
567 LE = 1
567 LU TL 666
530 IF (L4) 260, 270, 560
560. WHATEVER (0, Z, L), L1, L2, L3, L4L6, (L(J), J=1,7)
920. ESHAT(/, 15), arrange AU=15, 10X, 43h
TRANSFORMATION NALE TO PR
INCLIPAL AXES = H(Y, 10X), 10H, LINARY CHAP USEL=13,6h TIMES/1X, 27h w
2L. UGEL 51X, UF SQUARES = E14, 7, 25h, 32h SQUARE MODULS OF GRADIENT
       3T = (E14, 7, 25h, 32h), PARAMETERS L(J) = (E17, E2)/
IF (L1 = L4) 260, 51O, 51O
51O. L(J) = 0
       GO TO 71O
71O. UG 71O J=1, 11
       L(J) = U(J)
       UG 72O K=1, 11
72O. L(J) = L(J, K) = (E2, UF(J, J, K) - L(J)*L(J) - L(K)*L(K))/L(J, K)
CALL MAINTAIN(Z:2, H, 1, L1, 1, L1)
       L1 73O J=1, 11
       IF (L2(J, J)) 261, 261, 262
261. U(J) = -SHAT(-LZ(J, J))
       UG TL 73O
262. L(J) = SHAT(LZ(J, J))
73O. CONTINUE
       UG 74O J=1, 11
       UG 74O K=1, 11
74O. L(J, K) = L(J, K)/(L(J)*L(K))
WHILE (6, 51O) L(J, K)
91O. END/13, EXIT NQALF: K=13, 2O, 2St WEIGHTED SUN OF SQUARES=1, 15, L
RETURN
END
60 FL(1)=FL(1) + L(3*J-2,L)/(L(3*J-1,L))**2 + b(3*J-1,L)**2
110 IF(LX-1)=11L,11G,12L
120 LI(I-1)=1,L
130 LI(I)=LI(I)
140 XL=U(1)-L(3*J,L)**2
150 ETA=L(3*J-1,L)**2
160 LEN=K+LTA
170 LI(3*J-L)=1,L/LE
180 LI(3*J-1)=2,L*LI(3*J-1,L)*L(3*J-2,L)/LEN**2
190 LI(3*J)=L*LI(3*J-1,L)*L(3*J-2,L)/LEN**2
200 UZ(3*J-1,3*J-2)=L*LI(3*J-1,L)/LEN**2
210 UZ(3*J-2,3*J-1)=UZ(3*J-1,3*J-2)
220 UZ(3*J,3*J-2)=L*LI(3*J-1,L)/LEN**2
230 UZ(J,J)=LI(3*J-1,3*J-2)
240 UZ(3*J-1,3*J-2)=L*LI(3*J-2,L)*(LI-3,L*ETA/LEN**2)
250 UZ(3*J-2,3*J-1)=L*LI(3*J-2,L)*(LI-3,L*ETA/L**2)
260 UZ(3*J,3*J-1)=L*LI(3*J-2,L)**3
270 UZ(3*J,3*J-1)=L*LI(3*J-2,L)**3
100 CONTINUE
110 END
555 L=1,5
145 S=S-A(L,J)*A(L,K)
120 A(J,H)=S/A(J,J)
406 b(1)=b(1)/A(1,1)
IF(T=-1)420,420,405
405 LU 410 J=2,1
  S=b(J)
  J=J-1
LU 415 L=1,31
415 S=S-A((L,J)*L(L)
410 L(J)=S/A(J,J)
420 L(T)=b(1)/A(T,H)
  J=J-1
435 IF(J=450,450,425
425 S=b(J)
  J2=J+1
LU 430 L=J2,H
430 S=S-A((J1,L)*L(L)
  L(J)=S/A(J,J)
  J=J-1
LU TL 435
450 LF=1
LU TL 460
200 LF=0
LU TL 460
300 LF=1
460 LU 465 J=1,H
  A(J,J)=L(J)
  IF(J H)440,475,475
475 J2=J+1
LU 465 H=J2,K
465 A(J,K)=A(J,K)
475 RETURN
END

SUBPROGRAM LATINV(A,N,L,N,DETERM)
SUBPROGRAM LATINV
C MATRIX INVERSION WITH ACCOMPANYING SOLUTION OF LINEAR EQUATIONS
DIMENSION IPIVOT(2L),A(2L,2L),B(2L,1),INDEX(2L,2),P(2L)
EQUIVALENCE (INDEX,IPIVOT),(ICLUEO,ICLUEO),(ALAX,1,SHAPE)
DETERM=1,L
LU 20 J=1,N
20 IPIVOT(J)=L
  LU 555 L=1,N
  AIX=0,L
LU 105 J=1,N
IF(IPIVOT(J)=L)60,105,60
60 LU 150 K=1,N
IF(IPIVOT(K)=L)60,100,746
60 IF(AUX(ALAX)-AUX(A(J,K)))=0,100,100

65 1thh=j
ICLULU=k
ARhx=A(j,k)
100 CONTINUE
105 CONTINUE
 1P1VLT(1CLULU)=1P1VLT(1CLULU)+1
 1F (1thh-1CLULU)=146,266,146
146 1L1L1L1:=L1L1L1
 1U 2CL L=1,N
 1S1A1F=A(1thh,L)
 1A(1thh,L)=A(ICLULU,L)
 2CL A(ICLULU,L)=SHAF
 1F (1)ZCL,ZCL,ZCL
210 1U 256 L=1,N
 1S1A1F=A(1thh,L)
 1L(1thh,L)1=C(1CLULU,L)
 256 B(1CLULU,L)=SHAF
260 1INEX(1,1)=1thh
 1INEX(1,2)=1CLULU
 1P1VLT(1)=A(1CLULU,1CLULU)
 1L1L1L1:=L1L1L1+P1VLT(1)
 1A(1CLULU,1CLULU)=1.0
 1U 256 L=1,N
350 A(1CLULU,L)=A(1ICLULU,L)/P1VLT(1)
 1F (1)ZCL,ZCL,ZCL
360 1U 256 L=1,N
370 B(1CLULU,L)=A(1ICLULU,L)/P1VLT(1)
380 1U 556 L=1,N
 1F (L1-1CLULU)=466,556,466
460 1Tm(L1,1CLULU)
 1A(L1,1CLULU)=0.0
 1U 456 L=1,N
450 A(L1,L)=m(L1,L)-A(L1,L)*T
 1F (1)556,556,466
460 1U 556 L=1,N
550 1L(L1,L)=L(L1,L)-L(1CLULU,L)*T
550 CONTINUE
 1U 71L L=1,N
 1L=K+1
 1F (INEX(L,1)=INEX(L,2))630,710,636
630 mth=mINEX(L,1)
 1JCLULU=1NEX(L,2)
 1U 765 h=1,N
 1S1A1F=A(h,mth)
 1A(h,mth)=A(h,JCLULU)
 1A(h,JCLULU)=SHAF
705 CONTINUE
 710 CONTINUE
 740 RETURN
END
SUBROUTINE ELUTL (N, K, A, L)

SUBROUTINE FLT U

A = LARGEST IF FL AND FR, L = SMALLEST

CALL STA x(1L), A, (512), LL(512), Y(4), A(L)(Z)

CALL LSTAX (ALL=2INL, 3INL), (Y=1H, 1HL, 1H*, 1HH)

A = AA(1).

UL 5UL 1=1, K

IF (AA(1)-A) $05, 505, 510

UL A = AA(1)

UL IF (LL(1)-U) $15, 515, 52L

UL A = EL(1)

UL IF (AA(1)-L) $3L, 525, 925

UL L = AA(1)

UL IF (LL(1)-L) $3L5, 5CL, 9CL

UL U = EL(1)

UL CONTINUE

FACTUL = 1.T

UL IF (A - 1.L - L.L - L.L - L.L) $5L, 51L, 51L

UL A = 2.L*A

UL U = 2.L*U

FACTUL = 2.L*FACTUL

UL TO 520

UL KB = (A - B)/112.0 + 1.C

UL KS = UL 1X(L) / 2*KB

UL IF (A = 1.L) (L = 1.L) 1

UL IF (L - 0.L) 12L, 13L, 12L

UL X(L) = Y(3)

UL TO 125

UL X(L) = Y(4)

UL ING = L + NL - 1

UL WRITE (6, 56) ING, X

UL FORMAT (1X13, 116A1)

UL END

SUBROUTINE JACUL (N, K, A, N, V)

SUBROUTINE FCALU FOR LARGESTIZATION OF MATRIX L BY SUCCESSIVE ROTATIONS.

DIMENSION U(2L, 2L), V(2L, 2L), X(2L), IN(2L)
NEXT 6 STATEMENTS FOR SETTING INITIAL VALUES OF MATRIX V

10   IF (J+I.C) 16,15,16
11   L9 14 T=1,N
12   L9 14 J=1,N
13   IF (I-J) 12,11,12
14   V(I,J)=1.0
15   L9 14
16   L9 14

NEXT 6 STATEMENTS SCAN FOR LARGEST OFF DIAG. ELEMENT IN EACH ROW
X(I) CONTAINS LARGEST ELEMENT IN ITH ROW
H(I) HOLDS COLUMN SUBSCRIPT DEFINING POSITION OF ELEMENT

17   H(I)=N-1
18   L9 30 I=1,N
19   L9 30 J=I,N
20   H(I)=I+1
21   L9 30 L=J,N
22   IF (X(I)-ABS(L(I,J))) ZL,ZL,ZL
23   X(1)=ABS(L(I,J))
24   H(I)=J
25   ZL L9 30

NEXT 7 STATEMENTS FIND MAXIMUM OF X(1)S FOR PIVOT ELEMENT

26   L9 30 I=1,N
27   IF (I-1) ZL,ZL,ZL
28   L9 30 X(IMAX)=X(I)
29   H(I)=1
30   J=H(I)
31   L9 30

NEXT 2 STATEMENTS TEST FOR XM, IF LESS THAN 1.E-6, LL TO ICCCC

32   EPSL=1.E-6
33   IF (XMAX-EPSL) ICCCC, ICCCC, ICCCC
34   L9 14
35   H(I)=I+1

NEXT 11 STATEMENTS FOR COMPUTING TAN, SIN, COS, V(I, J), V(J, J)

36   IF (L(IP, IP)-L(JP, JP)) 150,161,151
37   TANG =Z.*L(IP, IP)/(ABS(L(IP, IP)-L(JP, JP))+SQRT(L(IP, IP)-L(JP, JP))**2)
38   L9 160
40   COS =1.0/SQRT(1.0+TANG**2)
\[
\sin = \tan \times \cos
\]
\[
\theta = \cos^{-1}(\sin)\\
\]
\[
\sin^2 + \tan^2 + \cos^2 = 1
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
\]
\[
\theta = \cos^{-1}(\sin)
\]
\[
\sin = \sin^{-1}(\sin)
37L IF (1, LP) 37L, 53L, 42L
37L TEMP=5L
37L U(LP, 1)=U(L, LP)+SIN*U(L, JP)
37L IF (X(LP)-ALS(U(LP, 1))) 38L, 39L, 390
38L X(LP)=ALS(U(LP, 1))
38L IF (L(1, LP)=1)
39L U(L, 1)=U(L, LP)+SIN*TEMP+U(L, JP)
39L IF (X(L)-ALS(U(L, JP))) 40L, 53L, 53L
40L X(L)=ALS(U(L, JP))
40L IF (L(1, JP)=1)
40L U(L, JP)=U(L, JP)+SIN*TEMP+U(L, JP)
40L IF (X(L)-ALS(U(L, JP))) 41L, 53L, 53L
41L TEP=U(LP, 1)
41L U(LP, 1)=U(LP, 1)+SIN*U(JP, 1)
41L IF (X(LP)-ALS(U(LP, 1))) 42L, 53L, 53L
42L X(LP)=ALS(U(LP, 1))
42L IF (L(LP)=1)
43L U(JP, 1)=U(JP, 1)+SIN*TEMP+U(JP, 1)
43L IF (X(JP)-ALS(U(JP, 1))) 44L, 53L, 53L
44L X(JP)=ALS(U(JP, 1))
44L IF (L(JP)=1)
45L CONTINUE

NEXT 6 STATEMENTS TEST FOR COMPUTATION OF EIGENVECTORS

54L IF (UE<0) 54L, 46L, 54L
54L U<550 L=1, 46L
54L TEP=1(L, LP)
54L V(L, LP)=U(L, LP)+SIN*V(L, JP)
55L V(L, JP)=U(JP, 1)+SIN*TEMP+U(JP, 1)
55L TC 46
55L RETURN
55L END
COMPUTER SYSTEM CLOCK TRANSFER PROGRAMS

PROGRAM SCAREAD

6E 0C36   LDAA $F036
6F 01     CLH 1,
6F 03     CLX 2,
10        POP B
18 4C5C   LDY $EC5C
10        STA ,Y++
10        FUI TO LDA, CA INTO CBA
10        FUI TO LDX, CA INTO CBL
18 63     LDA ,X++
18 63     READ PIA0 TO CLEAR INTERRUPTS
18 63     LIKENSIE FOR PIA0, X HOL=$EC36
18 6C     LDY $EC6C
18 70      LDY $70
17 62     STA ,X,
18 66     LDX $66
24 READ
04        PULS E
26 10     LDA $10
12        NOP
5A DELAY
20 FD     DEC DELAY
35        RETRIEVE DIGIT COUNTER
04        WAIT FOR ICA TO PRESENT DATA
18 54     LDA ,X
14 6F     ADD $6F
1A 36     ORA $36
17 6A     STA ,Y+1
16        STORE DIGIT2 AND INCREMENT Y BY 1
18 6C     LDY $EC6C
27 11     LDC 0
27 11     (ALL READ PAST ENDA TO GENERATE ENDA WHICH SETS ICA FOR "DISPLAY")
5A DELE REDY 2
27 4D     CALL OUT NEXT CHANNEL AFTER 6 DIGITS
26 4C     LDY $4C
17 02     STA ,X,
18 02     CLX ,X
18 02     STA ,X,
18 60     LDA $60
18 02     STA ,X,
20 67     BBA READ
3F STOP
55        READY2 =$10
54 67     SHFT ,$20
36        SP =$40
PROGRAM PUNCH

6E 6024  LDX #PORTB  =6E024
B6 63  LDA #3  BASTEK RESET
A7 84  STA ,X
B6 11  LDA #0C01 0001 & LIT ,NO PAR ,2 STOP BITS-NUST
ERROR FREE
A7 84  STA ,X  WRITT PORMAT (2 SL HELP LOCATE
6L GG1D  LDX #ENTRY  FOLLOWING START BITS )
PLACE RE-ENTRY PC OR STACK TO BE
PULLED BY RTS AT END OF SLUG
PUNCH ROUTINE

54 10  PSHS ,X  FOLLOWING SLUG
6F.E2  CLH ,5
6D FD20  JSR UEADH  INPUT BEGA,ENDS,SAVE ON STACK
C6 24  LDH 224  LSLYTE OF PORTB
1F BFE1  STL CPOR1+1  I/O NOW VTA POR T2B (TAPE RECORDER)
7E FCO9  JNP FOB  ENTER SLUG PUNCH ROUTINE AFTER
LDA'S  ACCEPTING REGA,ENDS FROM PORT B
80 53  (EGOO = TTY)
LL FLDF  JSR OUTCH  WRITE 54 (TAPE EOF)
66 39  LDA 'Y'
6B FLDF  JSR OUTCH
7E F814  JNP HOUTCH  RETURN I/O TO CONSOLE

PROGRAM LOAD

6E 6024  LDX #PORTB  =6E024
B6 63  LDA #3
A7 84  STA ,X
B6 01  LDA #1
A7 84  STA ,X
BE BEEC  STX CPOR T
6D FCO9  JSH LOAD  NO KEYP ENTRY, SO ENTR SLUG
LOAD ROUTINE OR
72 F814  JNP HOUTCH  RETURN I/O TO CONSOLE
46EB 9D E015  JSK  OUTCH  
46EB 96 0A   LDA A $90A  
46ED 9D E015  JSK  OUTCH  
40F4 A6 0A READ  LDA A $A  
40F2 81 0A  CMP A $A  
40F1 21 41  BEQ RETURN  
40F6 7A 4140  DEC DIGI  
40F9 21 0E  BEQ DASKET  
40FB BD E015  JSK  OUTCH  
40FE FF 414A  STA A  
4111 DB 22  INA  
4102 BD 0100  GBA  MASN  
410C 27 30  BEQ RETURN  IF LAST CHANNEL SENT  
4101 21 17  BRA READ  
4109 FF 414D DASKET  STA C DIGI  
4106 86 00  LDA A $920  
410C 86 00  LDA A $900  
4111 7A 414D  DEC CHAN  
4114 27 0E  BEQ LINEL  
4116 20 0B  BRA READ  
411A CA 04 LINEL  LDA A $90A  LINE LENGTH = 10 CHAN.  
411A FF 414D  STA C CHAN  
4116 86 01  LDA B $901  
411F BD 00  LDA A $900  
4121 BD E075  JSK  OUTCH  
4124 BD 0A  LDA A $90A  
4126 40 04/5 LINEL  JSK  OUTCH  OUTPUT LF  
4129 FF 4006  STA CURRA  
412C CC 1000  LDA $81000  DELAY FOR MUGUMP  
412F 89  DELYM DEA  
4133 8F FD  BNE DELYM  
4132 FE 1006  LDA CURRA  
4133 20  BY  BRA READ  
4137 CE F500 RETURN  LDA A $AC1ACC  
413A FF FF12  STA OUIADD  
413D CE 414E  LDA MSG  
4140 BD E01E  JSK  PDATA1  
4143 FE 414A  LDA A  
4144 BD E01E  JSK  OUI4MS  
4149 89  R1S  
414A 8002  XI  RMA  2  
414C 0A  CHAN FCH $0A  
414D 01  DIGI C8 $01  
414E 4C  MSG FCH /LAST DATA LOCATION (ENDA)=/  
4165 20  FCH $20-$2A-$4  

*ENTER MSG/M1EAL IN10 MEMORY A1  
*BEGA - ENDA, TERMINATE #110 IN0*  

4168 0F  MIEAL SEI  
416C CE 420B  LDA #6F1  
416F BD 001E  JSK PDATA1  
4172 BD E0CC  JSK OUTS  
4175 CE 41FE  LDA #10
TRANSFER

436B 3H  SWI
436C 01  NOP
436D 0D 4000 DATA  JSR  INTR
4370 0F  SEI
4371 8D 4386  JSR  LOGIN
4373 0D 4341 IN1  JSR  INP
4375 81 0A  CMP A #50A
4379 26 89  BNE  INP
437B 0D 4386  JSR  LOGIN
437F 0D 4341 INK  JSR  INP
4381 81 11  CMP A #511
4383 26 89  BNE  INK
4385 7F F01A  CLR  OUTS
4386 CE 5000  LDX #5F500
4388 FF F016  SIA  OUTADD
438E CE 4412  LDX #MSG9
4391 0D 4D7E  JSR  MDATA1
4394 7E 431D  JMP SEND
4397 CE 5528 U211  LDA #ACIAMC
439A FF F01B  SIA  OUTADD
439D 0D 4D75  JSR  OUTCH
439E 39  RTS
439F CE 5528 INP  LDA #ACIAMC
43A4 FF F016  SIA  INADD
43A7 0D 4D7B  JSR  INCH
43AA 54 7F  AND A #57F
43AC FF F002  LDX BEGA
43AF 07 00  SIA A #A
43B1 08  INA
43B2 FF F002  SIA BEGA
43B5 39  RTS
43B6 7F F01A LOGIN  CLR  OUTSW  ECHO ON FOR OUTPUT
43C9 CE 0000  LDA #0
43CC 08  DELAY  INA
43D3 8C 0000  CPA #FE000
43D6 26 FA  BNE DELAY
43C2 FF F022 MSG  LDX MESS
43C5 A6 00  LDA A 0, A
43C7 IN  INA
43C8 FF F022  SIA MESS
43CB 81 04  CMP A #544
43D0 27 07  BEU RESTOR
43D0 FF 01  NOP
43D1 01  NOP
43D2 00 C3  BSA UIT
43D4 20 EC  BRA MESS
43D6 7C F01A RESTOR  INC OUTSW  ECHO OFF FOR INPUT
43D9 39  RTS

43DA 0D  MSG1  FCB $0D,$0A,$0A
43DD 45  MSG2  FCB $0D,$0A,$4
43E9 00  FCB $0D,$0A,$4
43EC 52  MSG3  FCB *REC*
TRANSFER

43EF 00  FCH  $0D,$0A,$4
43F2 54  MSG  FCH  *IMP*  
43F6 00  FCH  $0D,$0A,$4
43F9 4E  MSG  FCH  *NEW*  
43FE 00  FCH  $0D,$0A,$4
4461 54  MSG  FCH  *MSG*  
4467 00  FCH  $0D,$0A,$4
446A 00  MSG  FCH  $0D,$0A,$4
446D 00  MSG  FCH  *PACK*  
446F 00  FCH  $0D,$0A,$4
4473 44  MSG  FCH  *DATA TRANSFER INTO FILE "A"*  
4477 54  FCH  *TYPE "LNA" TO VERIFY DATA*  
447B 00  FCH  $0D,$0A,$4
447F 54  FCH  *TYPE TO HALT UNLESS*  
4482 00  FCH  $0D,$0A,$4
4486 54  FCH  *THEN TYPE 6 2010 TO REBOOT PLUS,*  
448A 41  FCH  *AND THEN "SEND" TO SEND*  
448E 4A  FCH  *NEXT COMMAND (SAVE, S=FILENAME)*  
4493 00  FCH  $0D,$0A,$4

END