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PARTITIONING OF FLUORINE BETWEEN
TREMOLITE, TALC AND PHLOGOPITE

by Hugh James Abercrombie, B.Sc (Honours)

A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Master of Science

Carleton University
Ottawa Ontario
December 1983

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ABSTRACT

The distribution of F between tremolite, talc and phlogopite has been determined in siliceous carbonates of the Central Metasedimentary Belt (CMB) of the Grenville Province. Fluorine distribution is consistent with ideal solution behaviour in F-OH tremolite and phlogopite mixtures and nonideal asymmetric solution behaviour in F-OH talc mixtures. Activity-composition relations for each mineral are derived from the solution models.

Using the calculated activities, the effects of F-OH substitution are modelled in $T-X_{CO_2}$ and P-T space. With increasing F content, the stabilities of assemblages containing tremolite, talc, and especially phlogopite, are enhanced. At high F substitution levels, the topology of the KA1O2-present system is rendered invalid in $T-X_{CO_2}$ space.

Calculations show that with increasing F content, the upper stability limit of the assemblage talc-calcite enters the sillimanite stability field. However, this occurs only over restricted pressures suggesting that F substitution can only partly explain the existence of talc within the mapped sillimanite zone of the CMB.
ACKNOWLEDGMENTS

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I thank Mr. P. Jones for instruction and assistance in the use of the electron microprobe and, for carrying out electron microprobe analyses at BRGM-CNRS, Orleans, France, I thank Dr. D.H. Watkinson.

I greatfully acknowledge the assistance of Dr. R. Thomas in diagnosing the inherent problems in linear regression estimation of excess parameters and for providing a solution through nonlinear regression.

Research was supported through a Carleton University Graduate Scholarship and through Natural Sciences and Engineering Research Council grant number A4253 awarded to Dr. G.B. Skippen. I also express my gratitude to the Ministry of Natural Resources, Kemptville, Ontario, for their financial and logistical support early in this study.

And lastly, I want to thank my wife Sandi for her love, patient understanding and especially for her ability to see beyond this work, even when I could not.
# TABLE OF CONTENTS

Abstract \( \text{iii} \)
Acknowledgments \( \text{iv} \)
Table of Contents \( \text{v} \)
List of Figures \( \text{viii} \)
List of Tables \( \text{ix} \)
List of Plates \( \text{x} \)

## I INTRODUCTION

- Introduction \( \text{1} \)
- Symbols, Units and Abbreviations \( \text{3} \)
- Previous Work \( \text{3} \)
- F-OH Exchange \( \text{3} \)
- Phase Relations \( \text{7} \)
- Field Research \( \text{8} \)

## II GEOLOGICAL SETTING

- Regional Geology \( \text{13} \)
- Regional Metamorphism \( \text{15} \)
- Talc Occurrences \( \text{19} \)

## III SOLUTION MODELLING

- Observed Behaviour \( \text{23} \)
- Talc-Tremolite \( \text{23} \)
- Phlogopite-Tremolite \( \text{29} \)
- F-OH Exchange Equilibria \( \text{31} \)
**TABLE OF CONTENTS**

Solution Models

- Symmetric Solution Model 33
- Asymmetric Solution Model 35

Calculation of the Model

- Linear Regression 36
  - Method 36
  - Applications 38
- Nonlinear Regression 40
  - Method 40
  - Applications 45

Effects of Temperature and Pressure 46

Activity-Composition Relations 47

**IV DISCUSSION AND CONCLUSIONS**

Petrological Effects of F-OH Substitution 52

- T-X CO₂ Space 52
  - Fluorine-free system 54
  - Fluorine-present system 55
- P-T Space 57

Implications of F-OH substitution 62

- Field Mapping 62
- Mineral Exploration 63

Conclusions 64

Recommendations for Further Research 67

References 69
TABLE OF CONTENTS

APPENDIX I  T-\(X_{CO_2}\) Diagrams 77

APPENDIX II Petrography, Electron Microprobe Analyses
     Mineral Chemistries 94

APPENDIX III Computer Programs 141

APPENDIX IV Nonlinear Regression Methods 150

LIST OF FIGURES

Figure 1. Distribution of marbles in the Central Metasedimentary Belt 9

Figure 2. Sample locations. 12

Figure 3. Lithostructural subdivisions of the Central Metasedimentary Belt. 14

Figure 4. Metamorphic zones of the Central Metasedimentary Belt. 14

Figure 5. Metamorphic conditions in the Elzevir Terrane. 18

Figure 6. Talc occurrences in marbles of the Central Metasedimentary Belt. 20

Figure 7. Schematic isobaric T-\(X_{CO_2}\) section for the system CaO-MgO-SiO_2-H_2O-CO_2. 21

Figure 8. Distribution of F between coexisting talc and tremolite. 24

Figure 9. Distribution of F between coexisting phlogopite and tremolite. 30

Figure 10. Fe distribution between cummingtonite and actinolite; linear regression curve of Saxena (1973) and nonlinear regression line shown. 39
LIST OF FIGURES

Figure 11a. Predicted F distribution between tremolite and talc using an asymmetric model for both; linear and nonlinear curves shown. 39

Figure 11b. Predicted F distribution between tremolite and phlogopite using an asymmetric model for both; linear and nonlinear curves shown. 39

Figure 12. Activity-composition relations for OH and F tremolite and phlogopite components calculated using the ideal solution model. 39

Figure 13. Estimated temperatures of metamorphism from calcite-dolomite geothermometry by Ewert (1977). 48

Figure 14. Activity-composition relations for F and OH talc components. 50

Figure 15. Fluorine substitution levels referred to in the text. 53

Figure 16. Summary of the petrological effects of F-OH substitution in P-T space. 58

Figure 17. Mineral zones and isograds of Alpine metamorphism. 61

Figure I.1a T-X_{CO_2} diagram at 100 MPa; F-free. 88
Figure I.1b T-X_{CO_2} diagram at 100 MPa; \( X_F(1) \). 88
Figure I.1c T-X_{CO_2} diagram at 100 MPa; \( X_F(2) \). 89
Figure I.1d T-X_{CO_2} diagram at 100 MPa; \( X_F(3) \). 89
Figure I.2a T-X_{CO_2} diagram at 200 MPa; F-free. 90
Figure I.2b T-X_{CO_2} diagram at 200 MPa; \( X_F(1) \). 90
Figure I.2c T-X_{CO_2} diagram at 200 MPa; \( X_F(2) \). 91
Figure I.2d T-X_{CO_2} diagram at 200 MPa; \( X_F(3) \). 91
Figure I.3a T-X_{CO_2} diagram at 500 MPa; F-free. 92
Figure I.3b T-X_{CO_2} diagram at 500 MPa; \( X_F(1) \). 92
LIST OF FIGURES

Figure I.3c  $T-x_{CO_2}$ diagram at 500 MPa; $x_F(2)$. 93

Figure I.3d  $T-x_{CO_2}$ diagram at 500 MPa; $x_F(3)$. 93

Figure II.1  Mg/Mg+Fe versus Si in tremolites. 112

Figure II.2  Cation and anion distribution in tremolite. 112

Figure II.3  Mg/Mg+Fe versus $x_F$ in tremolite. 115

Figure II.4  Cation and anion distribution in talc. 115

Figure II.5  Mg/Mg+Fe versus octahedral Al in phlogopite. 120

Figure II.6  Cation and anion distribution in phlogopite. 120

Figure II.7  $x_F$ versus total Fe in phlogopite. 122

LIST OF TABLES

Table 1. Symbols, units and abbreviations. 4

Table 2. Fluorine distribution data. 25

Table I.1  Estimated 2-sigma error for electron microprobe analyses. 79

Table I.2  Stable reactions in the system CaO-MgO-SiO$_2$-KAlO$_2$-H$_2$O-CO$_2$. 81

Table I.3  Thermodynamic data. 83

Table I.4  Data used to calculate reactions in the F-free system and at $x_F(1)$, $x_F(2)$ and $x_F(3)$. 85

Table II.1 Standards and lower limits of detection. 106

Table II.2  Estimated 2-sigma error for electron microprobe analyses. 108
LIST OF PLATES

PLATE II.1 Photomicrographs - coexisting tremolite, talc and phlogopite. 97

PLATE II.2 Photomicrographs - coexisting tremolite, talc and phlogopite; includes reflected light photomicrographs of talc. 98
CHAPTER I INTRODUCTION

INTRODUCTION

The substitution of F for OH in hydrous minerals occurs in a variety of geological environments and is well known in amphiboles and micas of metamorphic origin. The hydrous silicate minerals, tremolite, talc and phlogopite, are widely found in metamorphosed siliceous carbonates where they commonly exhibit varying degrees of F-OH substitution. The highest reported F content for a natural talc, \( X_F = 0.45 \), has been identified in this study in a sample from a locality near Tatlock, Lanark County, Ontario. Fluortremolite (\( X_F = 0.82 \)) and fluorphlogopite (\( X_F = 0.96 \)) have been documented in Grenville marbles found near Balmat, New York (Petersen et al., 1982).

Fluorine has long been known to increase the thermal stability of hydrous silicate minerals (Munoz and Eugster, 1969, citing Van Valkenburg and Pike, 1952). However, the effects of F on the stabilities of mineral assemblages that contain hydrous silicate minerals is not known with certainty. The partitioning of F between tremolite, talc and phlogopite has been studied in natural talc-tremolite pairs (Allen, 1976; Mercolli, 1980; Walther, in press) and from field (eg. Rice, 1977) and experimental studies of phlogopite-tremolite pairs (eg. Westrich, 1981). These studies show F to be partitioned such that \( X_F \)-phlogopite > \( X_F \)-tremolite > \( X_F \)-talc at constant HF fugacity.
The present study was undertaken to evaluate the importance of F in controlling the stability of mineral assemblages containing tremolite, talc or phlogopite in metamorphosed siliceous carbonates. The Central Metasedimentary Belt (CMB; Wynne-Edwards, 1972) of the Grenville Province is ideally suited for this study. Mid-greenschist through amphibolite to granulite grade regional metamorphism within the CMB has produced abundant occurrences of these minerals in siliceous carbonates. As well, F has been documented in tremolites, talcs and phlogopites of the CMB (Allen, 1976; G.B. Skippen, pers. comm., 1981).

Samples containing coexisting, texturally stable tremolite and talc or phlogopite, have been analyzed by wavelength-dispersive electron microprobe techniques and the pattern of F partitioning between these minerals has been established. Solution theory provides the necessary theoretical framework for relating F partitioning between hydrous silicate minerals to the activity-composition relations of the solution components of each F-OH solid solution. Using ideal and nonideal solution models and a new nonlinear regression technique developed herein, activity-composition relations for F and OH end-members of tremolite, talc and phlogopite solid solutions and excess free energies of mixing for F and OH talc components have been derived. The calculated activity-composition relations are used to model the effects of F on the stability of mineral assemblages that contain tremolite, talc or phlogopite.
SYMBOLS, UNITS AND ABBREVIATIONS

The symbols used are those common in geological literature. In particular, notation used in solution modelling is similar to that of Thompson (1967). Units are standard SI units. Symbols and corresponding units, and abbreviations, are given in Table 1. Mineral formulas and component compositions are given in Appendix I.

PREVIOUS WORK

F-OH Exchange

Experimental investigation of F-OH exchange in tremolite was carried out by Troll and Gilbert (1972). The lack of significant structural differences between the F and OH tremolite end-members led Cameron and Gibbs (1973) to relate the increase in the thermal stability of fluortremolite over tremolite to stronger Mg-F bonds in fluortremolite. Munoz and Eugster (1969) and Munoz and Ludington (1974, 1977) have experimentally investigated F-OH exchange in phlogopite and have related the presence of significant amounts of F in phlogopite to HF fugacities on the order of 0.1 MPa in fluids composed predominantly of H₂O. Similar studies on F-OH exchange in talc are lacking, probably because of the difficulty in synthesizing pure fluortalc (Troll and Gilbert, 1972). In both amphiboles and micas, increasing F contents have been correlated with decreasing Fe²⁺ contents; this is termed Fe-F avoidance (Rosenberg and Poit, 1977).
Table 1. Symbols, units and abbreviations.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Activity</td>
</tr>
<tr>
<td>f</td>
<td>Fugacity</td>
</tr>
<tr>
<td>$H_f^0$</td>
<td>Standard molal enthalpy of formation from the elements</td>
</tr>
<tr>
<td>$\Delta H_{Tr,Pr}$</td>
<td>Standard molal enthalpy of reaction at Tr,Pr</td>
</tr>
<tr>
<td>i, j</td>
<td>Subscripts indicate components</td>
</tr>
<tr>
<td>$K_{(n)}$</td>
<td>Equilibrium constant; reaction n</td>
</tr>
<tr>
<td>$K_D_{(n)}$</td>
<td>Distribution coefficient; reaction n</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$S_f^0$</td>
<td>Standard molal entropy of formation from the elements</td>
</tr>
<tr>
<td>$\Delta S_{Tr,Pr}$</td>
<td>Standard molal entropy of reaction at Tr,Pr</td>
</tr>
<tr>
<td>Tr, Pr</td>
<td>Reference temperature and pressure; 298.15 K, 0.1 MPa (25 °C, 1 bar)</td>
</tr>
<tr>
<td>$V_f^0$</td>
<td>Standard molal volume of solids</td>
</tr>
<tr>
<td>$\Delta G_{Mg_2SiO_4(OH)_{2}}$</td>
<td>Excess partial molal free energy at infinite dilution of subscripted component</td>
</tr>
<tr>
<td>X, X_F</td>
<td>Mole fraction; mole fraction F in talc</td>
</tr>
<tr>
<td>X_F(1)</td>
<td>Fluorine substitution level (1)</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>Activity coefficient for component i</td>
</tr>
<tr>
<td>$v_{i,TC}$</td>
<td>Reaction coefficient for component i or subscripted phase</td>
</tr>
</tbody>
</table>
Table 1. Continued

<table>
<thead>
<tr>
<th>Units</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>dm</td>
<td>Decimetre</td>
</tr>
<tr>
<td>j</td>
<td>Joule</td>
</tr>
<tr>
<td>K</td>
<td>Degrees Kelvin</td>
</tr>
<tr>
<td>mol</td>
<td>Mole</td>
</tr>
<tr>
<td>MPa</td>
<td>Megapascal (100 MPa = 1.0 Kb)</td>
</tr>
<tr>
<td>nA</td>
<td>Nanoampere</td>
</tr>
<tr>
<td>um</td>
<td>Micrometre</td>
</tr>
</tbody>
</table>

Abbreviations

- CMB: Central Metasedimentary Belt
- EDS: Energy dispersive spectrometry
- NTS: National Topographic Survey
- UTM: Universal Transverse Mercator
- WDS: Wavelength dispersive spectrometry

Normalization Schemes:

- 7eCNK: 7 cations except for Ca, Na and K
- 13eCNK: 13 cations except for Ca, Na and K
- 15eNK: 15 cations except for Na and K
- 15eK: 15 cations except for K

Mineral abbreviations given in Appendix I
Exchange equilibria involving F-OH substitutions in co-existing hydrous silicate minerals have been investigated experimentally and by observation of natural mineral assemblages. Multiphase equilibria in the system MgO-MgF₂-SiO₂-H₂O were experimentally studied by Duffy (1977) and Duffy and Greenwood (1979) who reported nonideal asymmetric solution behavior in F-OH talc mixtures and gave values for free energies of formation and excess free energies of mixing for talc and fluortalc at 750 °C and 0.1 MPa. Exchange equilibria involving F distribution between phlogopite-tremolite and phlogopite-pargasite were experimentally determined at 750 °C and 850 °C and 50 MPa by Westrich (1981) who modelled F-OH tremolite and phlogopite mixtures as ideal solutions.

Exchange equilibria in natural talc-amphibole pairs were studied in two rocks from the Grenville Province by Allen (1976) and in rocks from the Campolungo area, Lepontine Alps, Switzerland, by Mercolli (1980) and Walther (in press). All studies show F preferentially incorporated into tremolite over talc and model F-OH talc and tremolite mixtures as ideal solutions.

Results of studies on F-OH substitution in natural phlogopite-amphibole pairs are reported in Ekstrom (1972), Allen (1976), Zaw and Clark (1978), Kearns and Kite (1980), Rice (1980), Valley and Essene (1980), Petersen et al. (1982), and Walther (in press, 1983). These studies are in accord with preferential incorporation of F into phlogopite over tremolite, and, in general, support the view of Valley et al. (1982) that
the distribution of F between natural micas and amphiboles is less a function of metamorphic grade than compositional variations dominated by cation substitutions.

Phase Relations

Phase relations among silicate and carbonate minerals present during the metamorphism of siliceous carbonates have been studied in the field (e.g. Carmichael, 1970; Trommsdorff, 1972) and experimentally (e.g. Metz and Trommsdorff, 1968; Skippen, 1971, 1974; Hoschek, 1973; Slaughter, Kerrick and Wall, 1975; Hewitt, 1975; Puhan, 1978). Thermodynamic data obtained from these experiments have been combined with equations of state for \( \text{H}_2\text{O}-\text{CO}_2 \) mixtures (e.g. Kerrick and Jacobs, 1981) to position, in isobaric \( T-X_{\text{CO}_2} \) space, univariant equilibria which, taken together, define the stability fields of mineral assemblages in the system \( \text{CaO}-\text{MgO}-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2 (-\text{KAIO}_2) \) (e.g. Skippen, 1971, 1974; Slaughter, Kerrick and Wall, 1975). Following the lead of Trommsdorff (1972), Flowers and Helgeson (1983) have used the thermodynamic data of Helgeson et al. (1978) to position stable reaction equilibria in polybaric \( T-X_{\text{CO}_2} \) space. This method has the advantage of graphically portraying the phase relations along a unique \( P-T \) trajectory that corresponds to a particular metamorphic terrane.

The calculated positions of reaction equilibria that limit the stability fields of mineral assemblages commonly observed in metamorphosed siliceous carbonates may, in some cases, not be
reconciled with field observations. Skippen (1974) drew attention to discrepancies between observed and calculated phase relations for the assemblage talc-calcite and suggested that F-OH substitution in natural talc and tremolite might complicate experimentally determined phase relations. Using measured F contents in talc and tremolite, Rice (1976) suggested that the stability field of talc-calcite could be increased by as much as 200 K. Based on ideal solution models for F-OH talc and tremolite solid solutions, Mergoli (1980) also showed an increased stability field for the assemblage talc-calcite upon incorporation of F into talc and tremolite. Holloway (1977) calculated that temperature of the thermal decomposition of tremolite to diopside, enstatite and H₂O, could be increased by as much as 275 K at 500 MPa by F-OH substitution in tremolite.

FIELD RESEARCH

Abundant outcrops of metamorphosed siliceous carbonates in the Ontario part of the CMB of the Grenville Province, shown in Figure 1, provide an easily accessible source of tremolite, talc and phlogopite-bearing marbles. Because of the near ubiquitous distribution of phlogopite and the widespread distribution of tremolite in siliceous carbonates, the most consuming task of field research was the discovery of talc-bearing marbles. This was accomplished in three ways: by field-checking known talc occurrences, by identification and subsequent sampling of talc-bearing marbles that were identified by examination of about 190
Figure 1. Distribution of marbles in the Central Metasedimentary Belt. Areas underlain by marbles are indicated in the rectangular pattern and the diagonal lines represent areas underlain by Paleozoic strata. The location of Figure 2 is outlined.
thin sections of rocks obtained by G. B. Skippen, and by exploration for new talc occurrences in areas where metamorphic P-T-X conditions were thought to be suitable for the formation of talc.

During the summer of 1981, field research consisted of location and examination of talc occurrences known in the CMB from the work of: Allen (1976), Ewert (1977), Hewitt (1957, 1972), Laakso (1968), Lumbers (1968), McKinstry (1977), Spence (1940), Thomson (1943), and van Haaften et al. (1980). In all, twelve known talc occurrences were field-checked; two reported occurrences could not be located.

During the fall of 1981, field research consisted of checking of roadside outcrops in the Carleton Place 1:50,000 scale map sheet (NTS 31F/1), specifically in areas of siliceous carbonate exposure where Ewert (1977) positioned regional isograds which correspond to the first appearance of the mineral assemblage tremolite-calcite. Isobaric T-X_CO2 diagrams for siliceous carbonates (e.g. Skippen, 1974) predict that the assemblage talc-calcite should first appear at lower X_CO2 than the first appearance of the assemblage tremolite-calcite. Thus, by following the isograd which records the first appearance of tremolite-calcite into areas where, locally, X_CO2 may have been low, it is theoretically possible to locate metamorphosed siliceous carbonates that contain the assemblage talc-calcite.

This method proved successful in locating previously unknown talc occurrences.
During the summer of 1982, field research consisted of examination and sampling of tremolite and talc or phlogopite-bearing siliceous carbonates that had been identified, in a reconnaissance F survey (Appendix II), to contain significant amounts of F. The field area for this phase of research is outlined in Figure 1; twenty localities were visited. In addition, several new occurrences of talc-bearing siliceous carbonates were discovered.

The sample locations of rocks used in studying the distribution of F between coexisting tremolite and talc or phlogopite are given in Figure 2. All samples but one (M869012), were collected by the author in 1981 and 1982. Samples are identified by the year of collection followed by a string of six numerals that are the UTM (Universal Transverse Mercator) coordinates of the sample site given to the nearest 100 m.

Field research in the CMB of the Grenville Province was supplemented by sampling of talc and tremolite-bearing siliceous carbonates in the Campolungo area, Lepontine Alps, Switzerland. Talc and tremolite from this area are known to have high F contents (Skippen, 1974) and the distribution of F between hydrous silicate minerals of the Campolungo region has been studied by Mercolli (1980) and Walther (in press, 1983). Approximately forty samples were collected in areas known to be enriched in F (pers. comm., V. Trommsdorff, 1981), during two visits made to Campolungo in the summer of 1981. Talc and tremolite-bearing marbles from Val Sissone (Chissone?), Italy, were also sampled.
Figure 2. Sample locations; year of collection and UTM coordinates of each locality are given. Map symbols as for Figure 1.
CHAPTER II  GEOLOGICAL SETTING

REGIONAL GEOLOGY

Field study was carried out in metamorphosed siliceous carbonates of the Grenville Supergroup in the Ontario part of the CMB. The Grenville Supergroup, as defined by Moore and Thompson (1980), comprises a succession of metamorphosed miogeoclinal carbonate and clastic sedimentary rocks of Neohelikian age. Metavolcanic rocks including submarine basalts and andesites, with subordinate dacites and rhyolites, are known in the central part of the CMB. The volcanics are included in the Grenville Supergroup and are interpreted to be of continental arc or island arc affinity (Brown et al., 1975; Moore and Condie, 1977). An angular unconformity of regional extent separates rocks of the Grenville Supergroup from overlying carbonate and clastic metasediments of the Flinton Group, also of Neohelikian age.

Metasedimentary and metavolcanic rocks of the Grenville Supergroup have been intruded by a diverse suite of plutonic rocks that are predominantly granitic to tonalitic in composition. Polyphase deformation and low to high grade regional metamorphism have obscured geological relationships throughout most of the CMB, except in areas of lowest strain.

Supracrustal rocks of the Grenville Supergroup have been subjected to two orogenic events which together are referred to as the Grenville orogenic cycle (Moore and Thompson, 1980). The earliest, the Elzevirian orogeny (ca. 1.2-1.1 Ga; Brock and
Figure 3. Lithostructural subdivisions of the Central Metasedimentary Belt; after Brock and Moore (1983). Dashed line indicates possible southeastern boundary of the Elzevir Terrane (pers. comm., B. Brock, 1983). Solid line indicates the northeaster boundary of the CMB.

Figure 4. Metamorphic zones of the Central Metasedimentary Belt; (pers. comm., J.M. Moore, 1983) after Carmichael et al. (1978). Boundaries between metamorphic zones are indicated by solid lines (dashed where uncertain); where indicated, symbols are on the upgrade side. Lithostructural subdivisions are indicated by finely broken lines. CH - chlorite; GT - garnet; ST - staurolite; KY - kyanite; SI - sillimanite; KF - potassium feldspar; OP - orthopyroxene; CP - clinopyroxene; CD - cordierite.
Moore, 1983), is associated with major arc-type volcanic and plutonic activity which produced local contact metamorphism of metasediments of the Grenville Supergroup. The second event, the Ottawa orogeny (ca. 1.0-1.15 Ga; Brock and Moore, 1983), postdates deposition of the Flinton Group and is characterized by polyphase deformation and regional metamorphism.

Moore (1983a, b) and Brock and Moore (1983) propose that the CMB is an assemblage of allochthonous, fault-bounded, lithologically and structurally distinct terranes which have been tectonically transported from the southeast to their present positions. Davidson et al. (1981, 1982) have proposed similar origins for high grade gneissic terranes which exist to the northwest in the Parry Sound area. The distribution and boundaries of each lithostructural terrane within the CMB are shown in Figure 3. The Bancroft, Elzevir and Frontenac Terranes roughly correspond to zones IVa, IVb (the "Hastings Basin"), and IVc respectively of Wynne-Edwards (1972). The CMB is bounded to the northwest and southeast by high-grade gneissic terranes, the Algòquin and the Adirondack Terranes respectively.

**REGIONAL METAMORPHISM**

Regional metamorphism associated with the Ottawa orogeny has overprinted all supracrustal rocks of the CMB. The regional isograd distribution is shown in Figure 4 (pers. comm., J.M. Moore, 1983), which is modified from Carmichael et al. (1978). Metamorphic grade is lowest in the southwestern part of the
Elzevir Terrane. In this region, Carmichael (1970), Moore and Thompson (1980) and Bartlett (1983) have mapped chlorite and biotite zone rocks of medium to upper greenschist grade and iso-grads corresponding to the transition between greenschist and amphibolite grade.

Metamorphic grade increases northwestwards to the biotite-sillimanite-K-feldspar zone of amphibolite grade in the Bancroft Terrane (Carmichael et al., 1978); locally andalusite is reported. Regional metamorphic grade rises similarly to the northeast, but decreases in the Lanark-Carleton Place region where lower grade is inferred on the basis of the work of Ewert (1977). Within the Frontenac Terrane, metamorphic grade reaches its culmination in the cordierite-hypersthen-K-feldspar zone of upper granulite grade (Carmichael et al., 1978). Southeastwards grade decreases from granulite to amphibolite grade in the Adirondack lowlands, but again rises sharply to granulite grade in the Adirondack highlands.

Chesworth (1972) proposed that the regional distribution of metamorphic grade within the CMB is not related to a continuous gradient in P-T space, but is better explained by juxtapositioning, by faulting, of diverse metamorphic terranes. The coincidence of abrupt increases in metamorphic grade with the boundaries between lithostructural terranes proposed by Moore (1983a, b) and Brock and Moore (1983) is consistent with the existence of such terranes. An apparent example of this can be seen at the boundary between the Elzevir and Frontenac Terranes shown in Figure 4. Here, metamorphic grade increases from the
sillimanite zone of the amphibolite facies to the two-pyroxene zone of the granulite facies along a narrow zone paralleling the proposed intert errane boundary. The rapid change in metamorphic grade along this zone argues favourably for the presence of a metamorphic discontinuity coincident with the proposed lithostructural boundary.

The possibility of "stacking" of lithostructural terranes with differing metamorphic histories precludes the analysis of P-T conditions for the CMB in its entirety. On the basis of mineral assemblage data, Sethuraman and Moore (1973) concluded that the P-T conditions in a part of the central Elzevir Terrane were analogous to an intermediate pressure "Idahoan" metamorphic field gradient. A P-T trajectory equivalent to the proposed metamorphic field gradient and consistent with data from the southwestern part of the Elzevir Terrane is given in Figure 5. Also shown on Figure 5 are, using thermodynamic data of Helgeson et al. (1978), the calculated positions, in P-T space, of the three invariant points in the system CaO-MgO-SiO₂-H₂O-CO₂ (subvolume CaCO₃-CaMg(CO₃)₂-SiO₂) which control the first appearances of tremolite, diopside and forsterite respectively. Isobaric T-XCO₂ sections at 100, 200 and 500 MPa are included in Appendix I. In the model system, the first invariant point also corresponds to the upper stability limit of the assemblage talc-calcite.
Figure 5. Metamorphic conditions in the Elzevir Terrane.
The P-T trajectory is consistent with the "Idahoan" field gradient of Sethuraman and Moore (1973) and with metamorphic conditions throughout most of the Elzevir Terrane. Also shown are the P-T traces of invariant points, which, in the model system, correspond to the upper stability of the assemblage talc-calcite (dot-dash), the first appearance of diopside (dotted), and the first appearance of forsterite (short dash); invariant points are positioned using the data of Helgeson et al. (1978). Aluminosilicate triple point from Holdaway (1971); other reactions from Turner (1981). AN - andalusite; QZ - quartz; MU - muscovite; als - aluminosilicate.
TALC OCCURRENCES

The locations of known talc occurrences in siliceous carbonates of the CMB are shown, with regional metamorphic isograds and lithostructural subdivisions, in Figure 6. The locations are from published and unpublished sources and from work carried out as part of this research. All talc occurrences lie within the Elzevir Terrane as defined by Brock and Moore (1983). As shown in Figure 6, talc is apparently not confined to areas of low metamorphic grade, but persists into the sillimanite and staurolite zones of amphibolite grade.

The existence of talc within the sillimanite zone is not possible in the model system. Phase relations predicted using thermodynamic data of Helgeson et al. (1978) are illustrated schematically in Figure 7 and show the position of invariant point I to limit the upper stability of talc in siliceous carbonates. As seen in Figure 5, the plot of invariant point I does not intersect the sillimanite stability field.

Several possible explanations may account for the apparent inconsistency between experimental models and field data. Among these is the possibility that the sillimanite and staurolite isograds have been incorrectly positioned. A related possibility is that the northeastern part of the Elzevir Terrane, where the majority of talc occurrences within the sillimanite zone exist, may be part of an unrecognized low grade terrane located between the Frontenac and Elzevir Terranes. Ewert (1977) has reported low grade assemblages from part of the study area.
Figure 6. Talc occurrences in marbles of the CMB; talc occurrences are indicated by solid circles. Lithostructural subdivisions and metamorphic zones are as for Figure 4.
Figure 7. Schematic isobaric T-X\textsubscript{CO2} diagram; this diagram has been constructed using data of Helgeson et al. (1978). Heavy lines outline stability fields discussed in text; TC-CC - talc-calcite; TR-CC - tremolite-calcite; DI-DL - diopside-dolomite. Numbered reactions are given in Appendix I.
Alternative possibilities for the persistence of talc to high grade are: incorrect positioning of the aluminosilicate triple point; inaccuracies in the thermodynamic data used in calculating the P-T trace of invariant point I; or, increased stability of assemblages containing F-bearing talc. An objective of this thesis then, at least in a Grenville context, is to evaluate whether or not F-OH substitution in talc and tremolite, can influence the stability of talc-bearing assemblages to account for the existence of talc within the sillimanite field.
III SOLUTION MODELLING

OBSERVED BEHAVIOR

Talc-Tremolite

The distribution of F between coexisting talc and tremolite from the CMB, investigated in this study and by Allen (1976), is shown in Figure 8; data for this figure are given in Table 2. Complete chemical analyses for each tremolite and talc are given in Appendix III. The maximum F content of coexisting talc and tremolite from the CMB is \( X_F = 0.45 \) in talc and \( X_F = 0.46 \) in tremolite (82-854041-1A, pair 03; Appendix II).

Below F contents in tremolite of about \( X_F = 0.35 \), the distribution coefficients \( K_D = \left( X_F^{Tc} X_{OH}^{TR} / X_F^{TR} X_{OH}^{Tc} \right) \) are in agreement with Allen (1976), Mercolli (1980) and Walther (in press), with typical \( K_D \) values near 0.5. These workers have modelled talc and tremolite as ideal F-OH mixtures. However, as seen in Figure 8, the upward deflection of the distribution curve near \( X_F^{TR} = 0.35 \) is incompatible with ideal solution behavior of one or both of the F-OH talc or tremolite mixtures.

The shape of the talc-tremolite F distribution curve is consistent with ideal solution behaviour in tremolite and nonideal solution behaviour in talc (Saxena, 1973; Figure 12). This is in agreement with experimental studies reported by Duffy (1977) and Duffy and Greenwood (1980), where the binary F-OH talc solid solution is modelled using a nonideal solution model.
Figure 8. Distribution of F between coexisting talc and tremolite. The outlined area corresponds to estimated analytical error and the distribution curve has been calculated using a nonideal asymmetric solution model for OH and F talc components and an ideal solution model for OH and F tremolite components. Data for the diagram are given in Table 2; data includes two points from Allen (1976).
Table 2a. Fluorine distribution data: talc - tremolite.

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**Table 2b.** Fluorine distribution data; phlogopite - tremolite.
Table 2b. Continued.

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* - sample from Allen (1976)
** - sample from Petersen et al. (1982)
Analysis of two talc and tremolite-bearing siliceous carbonates from Campolungo, Switzerland, has been carried out and results are included in Appendix II. These analyses are in agreement with Mercolli (1980) and Walther (in press), confirming a $K_w = 0.5$ between talc and tremolite from this area. The $F$ contents of tremolite from the Campolungo area range from $X_F = 0.11$ (Figure 9, Walther; in press) to $X_F = 0.49$ (CAM81-04, pair 01; Appendix II).

**Phlogopite-Tremolite**

The distribution of $F$ between coexisting phlogopite and tremolite in siliceous carbonates of the CMB, determined in this study and by Allen (1976) and Petersen et al. (1982), is shown in Figure 9. The $F$ contents of coexisting tremolite and phlogopite pairs are given in Table 2 and the compositions of each phlogopite and tremolite, determined by electron microprobe analysis, are given in Appendix II. The $F$ distribution curve for phlogopite-tremolite is less precisely defined than for talc-tremolite. This may partly be explained by the high correlations in phlogopite between $F$ and other elements such as: Si, Al$^v$, Al$^vi$, Ti, Fe, Mg and possibly Ca and K, reported in Appendix II. This suggests a relatively higher control of $F$ content by mineral chemistry in phlogopite than in tremolite or talc.

The convex upwards shape of the phlogopite-tremolite $F$ distribution, shown in Figure 9, is in agreement with earlier workers (e.g., Allen, 1976; Westrich, 1981). Within the error limits, both phlogopite and tremolite are most simply modelled as
Figure 9. Distribution of P between coexisting phlogopite and tremolite. The outlined area corresponds to analytical error and the distribution curve represents an average $K_0=3.4$. Data for the diagram are given in Table 2; data includes points from Allen (1976); the most P-rich point is from Petersen et al. (1982).
ideal F-OH solutions. Using this model, the average distribution coefficient \( K_D = \frac{X_F^{TC} X_{OH}^{TR}}{X_{OH}^{TC} X_F^{TR}} \) is \( K_D = 3.4 \). This is in excellent agreement with the data of Walther (in press) from the Campolungo area, which give an average \( K_D = 3.33 \).

**F-OH EXCHANGE EQUILIBRIA**

The exchange of F and OH between talc and tremolite (similarly for phlogopite and tremolite) is described by the equilibrium,

\[
\begin{align*}
\text{Mg}_1.5\text{Si}_2\text{O}_5(\text{OH}) + \text{CaMg}_{2.5}\text{Si}_4\text{O}_{11}(\text{F}) & \rightleftharpoons \\
\text{TC}(\text{OH}) + \text{TR}(\text{F}) & \\
\text{Mg}_1.5\text{Si}_2\text{O}_5(\text{F}) + \text{CaMg}_{2.5}\text{Si}_4\text{O}_{11}(\text{OH}) & \\
\text{TC}(\text{F}) + \text{TR}(\text{OH}) & \\
\end{align*}
\]

(1)

The equilibrium constant, \( K_{(1)} \), is

\[
K_{(1)} = \frac{[a_{\text{Mg}_1.5\text{Si}_2\text{O}_5(\text{F})}] [a_{\text{CaMg}_{2.5}\text{Si}_4\text{O}_{11}(\text{OH})}]}{[a_{\text{Mg}_1.5\text{Si}_2\text{O}_5(\text{OH})}] [a_{\text{CaMg}_{2.5}\text{Si}_4\text{O}_{11}(\text{F})}]} \tag{2}
\]

where activity for exchange component 'i' is defined as

\[
a_i = x_i \gamma_i \tag{3}
\]

In equation 3, \( x_i \) is the mole fraction of exchange component 'i' and \( \gamma_i \) is the activity coefficient. The distribution coefficient, \( K_{D(1)} \), is defined as

\[
K_{D(1)} = \frac{(X_F^{TC})(X_{OH}^{TR})}{(X_{OH}^{TC})(X_F^{TR})} \tag{4}
\]
Substituting equations (3) and (4) into equation (2) and taking the logarithm gives

$$\ln K(1) = \ln K_D(1) + \ln [\gamma_{M_{81.5}Si_{2}O_{5}}(F)]$$

$$+ \ln [\gamma_{Ca_{82.5}Si_{4}O_{11}}(OH)]$$

$$- \ln [\gamma_{M_{81.5}Si_{2}O_{5}}(OH)]$$

$$- \ln [\gamma_{Ca_{82.5}Si_{4}O_{11}}(F)]$$

(5)

It is common to adopt a standard state of unit activity for a pure component at all temperatures and pressures; such a standard state is here used for all silicate components (Appendix I). This choice of standard states requires unit value for the activity coefficient of each exchange component in an ideal solution, hence the equilibrium constant equals the distribution coefficient. For an F-OH exchange equilibrium involving two ideal mixtures, the distribution coefficient is independent of composition and is equal to the equilibrium constant.

In a nonideal mixture, the activity coefficients of each exchangeable component are free to vary with solution composition. To fully describe an F-OH exchange equilibrium between two solid solutions, one or both of which are nonideal, an expression for the activity coefficient as a function of composition must be derived. Solution modelling provides the necessary theoretical framework by relating activity coefficients to the distribution of exchangeable components between coexisting solid solutions.
SOLUTION MODELS

Solutions may be classified by the symmetry of the variation of the activity coefficients of each exchange component with composition or, equally, by the number of constants necessary to model this variation in a power series expansion (Froese, 1976). An ideal solution requires no such constants; the activity coefficient of each component is independent of composition. In nonideal solutions, however, the variation of the activity coefficients can be described by symmetrical (one constant) or asymmetrical (two constant) solution models.

Many authors including Guggenheim (1967), Thompson (1967), Saxena (1973), Froese (1976), Grover (1976) and Brown (1978), have presented, discussed and shown examples of the use of various solution models which trace their origins to the original power series expansions of Margules (1895). Brown (1978) derives the equations for nonideal solutions, demonstrating how the resulting solution models are consistent with Henry's and Raoult's Laws, which state that solution behavior becomes ideal as \( X_1 \) approaches zero and \( X_1 \) approaches one, respectively.

**Symmetric Solution Model**

Although the specific form of the symmetric or one constant Margules solution model may vary depending on the writer, all symmetrical solution models described by the authors above are based on a second order power series which expresses a particular excess parameter in terms of solution composition. The form
given by Guggenheim (1967) and Froese (1976) is adopted here. For an F-OH talc mixture the symmetric model is

\[ \ln \left( \gamma_{\text{Mg}_{81.5} \text{Si}_{2} \text{O}_{5}(\text{OH})} \right) = \left[ \gamma_{\text{Mg}_{81.5} \text{Si}_{2} \text{O}_{5}(\text{OH},F)} \right] \left( 1 - x_{\text{OH}}^{\text{TC}} \right)^2 \] (6a)

\[ \ln \left( \gamma_{\text{Mg}_{81.5} \text{Si}_{2} \text{O}_{5}(F)} \right) = \left[ \gamma_{\text{Mg}_{81.5} \text{Si}_{2} \text{O}_{5}(\text{OH},F)} \right] \left( 1 - x_{\text{F}}^{\text{TC}} \right)^2 \] (6b)

Analogous equations may be written for tremolite. The term \[ \gamma_{\text{Mg}_{81.5} \text{Si}_{2} \text{O}_{5}(\text{OH},F)} \]
is here the excess partial molar free energy at infinite dilution for talc and is identical to \( \gamma_{G} \) of Thompson (1967). \( \gamma_{G} \) is often referred to as the Margules parameter. Solutions that conform to the symmetric solution model are termed "simple mixtures" by Guggenheim (1957), however, Froese (1976) points out that such solutions are referred to as "regular" by some authors.

For F-OH talc mixtures

\[ x_{\text{OH}}^{\text{TC}} = (1 - x_{\text{F}}^{\text{TC}}) \] (7)

Combining equations (5), (6a), (6b) and (7), and their analogues for tremolite, yields an expression relating the equilibrium constant to measured compositions of talc and tremolite:

\[ \ln K(1) = \ln K(0) + \left[ \gamma_{\text{Mg}_{81.5} \text{Si}_{2} \text{O}_{5}(\text{OH},F)} / \text{RT} \right] \left( 1 - 2 x_{\text{F}}^{\text{TC}} \right) \]

\[ - \left[ \gamma_{\text{CaMg}_{2.5} \text{Si}_{4} \text{O}_{11}(\text{OH},F)} / \text{RT} \right] \left( 1 - 2 x_{\text{F}}^{\text{TR}} \right) \] (8)
Asymmetric Solution Model

The asymmetric solution model results when a third order power series is used to express the variation of an excess parameter in terms of solution composition. The form of the asymmetric model adopted here is from Thompson (1967). For an F-OH talc mixture, the relationship between the activity coefficient and solution composition is given by the asymmetric solution model as

\[
\ln \gamma_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})} = (x_{\text{T}C})^2 \left( \left( \frac{w_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}}{RT} \right) \right) + \\
2(x_{\text{T}C}) \left( \left( \frac{w_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}}{RT} \right) - \left( \frac{w_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}}{RT} \right) \right) \\
\ln \gamma_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})} = (x_{\text{OH}}) \left( \left( \frac{w_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}}{RT} \right) \right) + \\
2(x_{\text{OH}}) \left( \left( \frac{w_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}}{RT} \right) - \left( \frac{w_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}}{RT} \right) \right)
\]

(9a)

(9b)

The Margules parameters for the OH and F talc exchange components,

\[w_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}\] and \[w_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}\]

are equivalent to \[w_1\] and \[w_2\] of Thompson (1967). The symmetric model is a special case of the asymmetric model, where these two parameters are constrained to be equal.

If the solution behaviour of talc and tremolite are modelled with the asymmetric solution model, equations (9a) and (9b) and their analogues for tremolite, are combined with equations (5) and (7) giving.
\[ \ln K_1 = \ln K_D(1) \]
\[ = - (W_{MB_{1.5}Si_2O_5(OH)/RT}) [3(x_F^{TC})^2 - 2(x_F^{TC})] \]
\[ + (W_{MB_{1.5}Si_2O_5(F)/RT}) [3(x_F^{TR})^2 - 4(x_F^{TR}) + 1] \]
\[ + (W_{CaMB_{2.5}Si_4O_{11}(OH)/RT}) [3(x_F^{TR})^2 - 2(x_F^{TR})] \]
\[ - (W_{CaMB_{2.5}Si_4O_{11}(F)/RT}) [3(x_F^{TR})^2 - 4(x_F^{TR}) + 1] \]

\[ \text{(10)} \]

**Calculation of the Model**

**Linear Regression**

**Method**

Calculation of the optimum values for the unknowns \( \ln K_1 \) and the two (or four) Margules parameters in equations (8) and (10) has, in the past, been carried out using least squares linear regression optimization (e.g., Saxena, 1973; Froese and Gordon, 1974). This is accomplished by rearranging equations (8) and (10) into regression-compatible form. Thus equation (10) is rewritten,

\[ \ln K_D(1) = \ln K_1 \]
\[ + (W_{MB_{1.5}Si_2O_5(OH)/RT}) [3(x_F^{TC})^2 - 2(x_F^{TC})] \]
\[ - (W_{MB_{1.5}Si_2O_5(F)/RT}) [3(x_F^{TC})^2 - 4(x_F^{TC}) + 1] \]
\[ - (W_{CaMB_{2.5}Si_4O_{11}(OH)/RT}) [3(x_F^{TR})^2 - 2(x_F^{TR})] \]
\[ + (W_{CaMB_{2.5}Si_4O_{11}(F)/RT}) [3(x_F^{TR})^2 - 4(x_F^{TR}) + 1] \]

\[ \text{(11)} \]
For each analyzed talc-tremolite pair, values for $X_F^{TC}$ and $X_F^{TR}$ are known and $\ln K_D(1)$ can be calculated with equation (4). The linear regression is carried out by defining $\ln K_D(1)$ to be the dependent variable and defining the independent variables to be:

i) \[ 3(X_F^{TC})^2 - 2(X_F^{TC}) \]

ii) \[ -(3(X_F^{TC})^2 - 4(X_F^{TC}) + 1) \]

iii) \[ -(3(X_F^{TR})^2 - 2(X_F^{TR})) \]

iv) \[ 3(X_F^{TR})^2 - 4(X_F^{TR}) + 1 \]

Using linear regression, values for $\ln K(1)$ (the regression intercept) and the four regression coefficients:

i) \( \frac{W_{Mg1.5Si2O5(OH)}}{RT} \)

ii) \( \frac{W_{Mg1.5Si2O5(F)}}{RT} \)

iii) \( \frac{W_{CaMg2.5Si4O11(OH)}}{RT} \)

iv) \( \frac{W_{CaMg2.5Si4O11(F)}}{RT} \)

can be calculated once the compositions of a minimum of five talc-tremolite pairs, and preferably, ten times this number, are known. If one of the two F-OH mixtures (i.e., talc or tremolite) are instead modelled using a symmetrical or ideal solution model, the number of terms in equation (11) will be reduced by one or two respectively.

Linear regression is efficiently carried out by computer using standard linear regression programs such as BMDP program 9R, "All Possible Subsets Regression," described in Dixon and Brown (1979), or program REGSOL1 given in Saxena (1973).
Calculated values for \( \ln K_{(1)} \) and the four (or less) Margules parameters can be verified by reintroducing them into equation (11) to determine whether they are capable of reproducing the measured \( F \) distribution. A program, SOLCRV, written by the author and included in Appendix II, has been used to calculate the predicted distribution curve. At constant \( X_P^{TR} \), SOLCRV calculates predicted values for \( X_P^{TC} \) using an interval halving technique. If the predicted curve successfully reproduces the observed distribution data, the set of calculated regression coefficients are judged to be correct.

**Applications**

Least squares linear regression has been used by Saxena (1973) to calculate Margules parameters for Fe-Mg exchange between coexisting cummingtonite and actinolite. Both minerals were modelled as binary, asymmetric Fe-Mg mixtures using two constant solution models of Guggenheim (1937; in Saxena, 1973). Several problems become evident upon detailed examination of the values reported by Saxena: First, only six data points are used to calculate five unknowns: \( \ln K_{(1)} \) and the four Margules parameters. This is statistically unsound and, as noted by Saxena (1973), the results of the regression can only be used qualitatively.

The most serious deficiency is evident when the values for \( \ln K \) and the four Margules parameters are reintroduced into the regression equation. The distribution curve predicted from the values of Saxena (1973) is shown in Figure 10. This curve does
Figure 10. Fe distribution between cummingtonite and actinolite. Linear regression curve of Saxena (1973) shown as dashed line; nonlinear regression fit to the same data shown as solid line.

Figure 11a. Predicted F distribution between tremolite and talc using an asymmetric model for both. Linear fit shown as dashed line; nonlinear as solid line.

Figure 11b. Predicted F distribution between tremolite and phlogopite using an asymmetric model for both. Linear fit shown as dashed line; nonlinear as solid line.

Figure 12. Activity-composition relations for OH and F tremolite and phlogopite components (2-site) calculated using the ideal solution model.
not adequately reproduce the observed distribution of Fe and Mg between coexisting cummingtonite and actinolite and reflects erroneous excess parameter values given by Saxena (1973).

Using linear regression, an attempt was made to calculate Margules parameters for binary F-OH tremolite, talc and phlogopite mixtures from F distribution data for coexisting talc-tremolite and phlogopite-tremolite pairs from the CMB. Each mineral was initially assumed to require a nonideal asymmetric solution model. Regression equations similar to equation (11) were used to calculate the Margules parameters for each exchange component. Although the assumption of nonideal solution behaviour in tremolite and phlogopite is unsupported by F distribution data, the calculated Margules parameters must, if the regression is successful, reproduce the observed distribution when reintroduced into the regression equation.

The inability of linear regression to calculate meaningful values for \( \ln K_D^{(1)} \) and the Margules parameters is illustrated in Figures 11a and 11b. The most serious deficiency in the application of linear regression to distribution data is found in equation (11), which only implicitly defines the regression. That is, the linear regression minimizes the sum of squares of the dependent variable \( \ln K_D^{(1)} \), not the directly measured variables, i.e. \( X_F^{TR}, X_F^{TC} \) or \( X_F^{PH} \). To successfully carry out a linear regression, the model must be explicitly defined; i.e. for one mineral, \( X_F \) must be expressed in terms of \( X_F \) in the other mineral and the Margules parameters for each exchange component.
NONLINEAR REGRESSION

Method

Linearization of equation (11), whereby $X_F$ for one mineral is isolated and expressed in terms of all other variables, is extremely difficult, if not impossible. The problem is therefore nonlinear and is better solved using nonlinear regression.

Nonlinear regression requires: i) a mathematical model consisting of a dependent, and one or more independent variables and regression parameters, ii) initial estimates for each of the parameters, and iii) a minimum of $n$ values for the dependent and independent variables, where $n$ is the number of parameters to be estimated. The mathematical model defines the regression and is used to return a value for the dependent variable at fixed values of the independent variables and parameters. Because equation (11) can not be rearranged to explicitly define the regression, an alternate method, such as the Newton-Raphson iterative convergence technique (Dorn and McCracken, 1972) must be used to return a value for the dependent variable.

Equation (11) can be combined with equation (4) and rewritten,

$$f(X_F^C, X_F^R, (W_{Mg1.5Si2O5(OH)/RT}), (W_{Mg1.5Si2O5}(F)/RT),$$

$$(W_{CaMg2.5Si4O11(OH)/RT}), (W_{CaMg2.5Si4O11}(F)/RT), \ln k(1) \}$$

$$- \ln \{X_F^C(1-X_F^R)/(X_F^R(1-X_F^C))\} - \ln k(1)$$

$$- (W_{Mg1.5Si2O5(OH)/RT}) [3(X_F^C)^2 - 2(X_F^C)]$$
\[ + [\frac{W_{CaMg_{2.5}Si_{4}O_{11}(OH)}}{RT}] \left[ 3(x_{F}^{TR})^2 - 2(x_{F}^{TR}) \right] \]
\[ - [\frac{W_{CaMg_{2.5}Si_{4}O_{11}(F)}}{RT}] \left[ 3(x_{F}^{TR})^2 - 4(x_{F}^{TR}) + 1 \right] \]
\[ = 0 \] (12)

The Newton-Raphson iteration scheme is given by,

\[ (x_{F}^{TC})_{n+1} = (x_{F}^{TC})_{n} + \frac{f(x_{F}^{TC}; x_{F}^{TR}, \ldots)}{f'(x_{F}^{TC}; x_{F}^{TR}, \ldots)} \] (13)

where \( f(x_{F}^{TR}; x_{F}^{TR}, \ldots) \) indicates the value of function \( f \) at a given value for \( x_{F}^{TC} \) and constant values of \( x_{F}^{TR}, \ln K(1) \) and the four Margules parameters; similarly for its derivative with respect to \( x_{F}^{TC} \), \( f'(x_{F}^{TC}; x_{F}^{TR}, \ldots) \). The derivative of (12) with respect to \( x_{F}^{TC} \) is

\[ f'(x_{F}^{TC}; x_{F}^{TR}, \ldots) = \frac{1}{X_{F}^{TC}} + \frac{1}{1-X_{F}^{TC}} \]
\[ - [\frac{W_{Mg_{1.5}Si_{2}O_{5}(OH)}}{RT}] \left[ 6(x_{F}^{TC}) - 2 \right] \]
\[ + [\frac{W_{Mg_{1.5}Si_{2}O_{5}(F)}}{RT}] \left[ 6(x_{F}^{TC}) - 4 \right] \] (14)

Substituting equations (12) and (14) into (13) defines the iterative convergence scheme. Using the measured value for \( x_{F}^{TR} \) and the values for \( \ln K(1) \) and the four Margules parameters, which are set first by initial approximation and subsequently by the nonlinear regression program, a predicted value for \( x_{F}^{TC} \) can be calculated once an initial approximation for \( x_{F}^{TC} \) is introduced.
into equation (14).

Predicted values for $X^T_C$ are compared with the observed values of $X^T_C$ and a sum of the square of the differences between them is computed. Using mathematical convergence techniques, new values for the Margules parameters and for $\ln K(1)$ are generated and a new sum of squares is computed. The optimum values for $\ln K(1)$ and the Margules parameters are those which minimize the sum of squares.

Initial approximations for $\ln K(1)$ and the Margules parameters were made using a linear regression program, BMDP program 9R, "All Possible Subsets Regression," (Dixon and Brown, 1979), to estimate the necessary values. The linear regression-derived parameter values can be considered as first approximations and they are often sufficiently close to the real values to be of use. If linear regression cannot provide adequate approximations, nonlinear regression can be simplified by holding some, but not all parameters constant and, with each successive run, allowing more parameters to vary until a unique solution is achieved.

An initial approximation for $X^T_C$ is made using the measured value of $X^T_C$ at $X^T_F$. If this estimate is not sufficiently close to a "best-fit" distribution curve, a polynomial expression may be fitted to the distribution data to provide an initial value for $X^T_C$. The choice of initial approximations for $X^T_C$ may be complicated by the existence of several solutions for equation (13) at constant $X^T_R$ over the range $X^T_C = 0.00$ to $1.00$. Depending on the initial approximations made, differing values for $X^T_C$ may
be converged upon. Since only one value can be returned by the mathematical model, a criterion for selecting the correct value for \( X^T_{TP} \) must be used.

The procedure adopted in this study was to introduce successive initial approximations for \( X^T_{TP} \) from 0.05 to 0.95, in 0.05 increments, into equation (13). If more than one root was found over this range, the root closest to the initial (measured) value of \( X^T_{TP} \) was chosen.

The nonlinear regression was carried out using BMDP program AR, "Derivative Free Nonlinear Regression," (Dixon and Brown, 1979), available on-line at Carleton University. Control statements for BMDP program AR are given in Appendix IV. Included in Appendix IV is a methodology for calculating \( \ln K \) and Margules parameters using, as an example, data from Saxena (1973). The results of nonlinear regression of Saxena's data are shown in Figure 10.

The utility and statistical validity of nonlinear regression is illustrated in Figures 11a and 11b, where the calc-tremolite and phlogopite-tremolite F distribution curves have been successfully reproduced. Although, as previously discussed, the assumption of asymmetric solution behaviour in phlogopite and tremolite, implied in Figures 11a and 11b, is unwarranted, nonlinear regression is here demonstrated to be capable of returning useful values for \( \ln K \) and the Margules parameters.
Applications

The nonlinear regression method has been used to calculate values for lnK and Margules parameters for F distribution between talc and tremolite. Because the distribution of F between tremolite and phlogopite is consistent with ideal solution behaviour in both minerals, tremolite and phlogopite are modelled as ideal solutions. Distribution of F between tremolite and talc is indicative of nonideal behaviour in talc; an asymmetric solution model has been adopted for talc. If the calculated Margules parameters for the F and OH talc exchange components were equal, the assumption that talc is an asymmetric solution is invalid and a symmetric model would instead be applied.

The modified form of equation (12) used to calculate lnK(1) and Margules parameters for F and OH talc exchange components involved in exchange reaction (1), assuming ideal solution behavior for the F-OH tremolite mixture, is

\[ \ln K(1) = \]
\[ \ln [x_{TC}^{TC}(1-x_{TR}^{TR})/x_{TP}^{TR}(1-x_{TP}^{TC})] - \ln K(1) \]
\[ - (w_{Mg_{1.5}Si_{2}O_{5}(OH)}/RT) \left[ 3(x_{TP}^{TC})^2 - 2(x_{TP}^{TC}) \right] \]
\[ + (w_{Mg_{1.5}Si_{2}O_{5}(F)}/RT) \left[ 3(x_{TP}^{TC})^2 - 4(x_{TP}^{TC}) + 1 \right] \]
\[ = 0 \]  \hspace{1cm} (15)  

and its derivative with respect to \( x_{TP}^{TC} \) is given by equation (14).
Nonlinear regression analysis is carried out using equations (14) and (15) and the iterative convergence scheme defined by equation (13). Using the talc-tremolite F distribution data given in Table 2, the values calculated by nonlinear regression are:

\[ \ln K_{(1)} = 0.458764 \]
\[ \frac{W_{81.5S_i2O_5(OH)}}{RT} = 2.49479 \]
\[ \frac{W_{81.5S_i2O_5(F)}}{RT} = 0.940213 \]

Using these values, program SOLCRV has been used to generate the F distribution curve between talc and tremolite shown in Figure 8.

**EFFECTS OF TEMPERATURE AND PRESSURE**

In the absence values for \( W_{cp} \), the excess partial molar heat capacity at infinite dilution, the approximation \( W_{cp} = 0 \) is generally made. This in turn implies that \( W_H \) and \( W_S \), the excess partial molar enthalpy and entropy at infinite dilution, are constant. By analogy with partial molar quantities, the variation of \( W_G \), the excess partial molar free energy at infinite dilution, with temperature is given by (e.g. Brown, 1978),

\[ \left( \frac{\delta W_G}{\delta T} \right)_P = -W_S \quad (16) \]

and, with pressure, by

\[ \left( \frac{\delta W_G}{\delta P} \right)_T = W_V \quad (17) \]

where \( W_V \) is the excess partial molar volume at infinite dilution. If excess partial molar entropies and volumes at infinite dilution are assumed to be zero, equations (16) and (17) require \( W_G \).
to be independent of temperature and pressure.

**ACTIVITY-COMPOSITION RELATIONS**

**Tremolite and Phlogopite**

For tremolite and phlogopite, both modelled as ideal solutions, the activity of each exchange component is its mole fraction. In the chemical formulas for tremolite and phlogopite adopted in this study there are two exchangeable anions per formula unit. Thus, the variation of activity for the tremolite and phlogopite OH exchange components are:

\[
\ln(a_{Ca_2Mg_5Si_8O_{22}(OH)_2}) = 2\ln(x_{OH}^{TR}) \quad (18a)
\]

\[
\ln(a_{KMg_3AlSi_3O_{10}(OH)_2}) = 2\ln(x_{OH}^{PH}) \quad (18b)
\]

Activity-composition relations for tremolite and phlogopite, calculated using equations (18a) and (18b), are shown in Figure 12.

**Talc**

If the temperature of equilibrium is known for all talc-tremolite pairs, the values of

\[
\bar{w}_{Mg_{1.5}Si_2O_5(OH)}/RT \quad \text{and} \quad \bar{w}_{Mg_{1.5}Si_2O_5(F)}/RT
\]

calculated by nonlinear regression, can be multiplied by T, and substituted into equations of the form

\[
\ln\gamma_i = (1/T)(x_j)^2[(\bar{w}_i/R) + 2(x_i)((\bar{w}_j/R) - (\bar{w}_i/R))] \quad (19)
\]
for component i, or by interchanging i and j, component j. Equation (19) can be used to calculate the activity coefficient as a function of both temperature and composition, but requires the assumption that \( W_{CP} = W_S = W_V = 0 \). The assumption that \( W_S = 0 \) is commonly made; solutions exhibiting such behaviour are termed regular solutions. Based on X-ray volume measurements, Duffy (1977) reported \( W_V = 0 \) for F-OH talc mixtures.

Metamorphic temperatures in parts of the study area have been estimated by Ewert (1977) using the calcite-dolomite geothermometer; these are shown in Figure 13. Because many of the samples in this study originated west of Clayton Lake (Figure 13), in an area where temperatures are about 425 °C, this value is accepted as the average temperature of equilibration for all talc-tremolite pairs. In the model system, the temperature is consistent with the existence of talc in siliceous carbonates under H₂O-rich conditions. However, considering the limitations of calcite-dolomite thermometry (eg. Espene, 1982), this estimate is likely to be a minimum value.

Using 425 °C (698 K) as the average temperature of equilibrium allows an estimate of the excess free energies for OH and F talc to be made:

\[
W_{Mg_{1.5}Si_2O_5(OH)}/RT = 1741.36 \, K
\]

\[
W_{Mg_{1.5}Si_2O_5(OH)} = 14.478 \, Kj \, mol^{-1}
\]

\[
W_{Mg_{1.5}Si_2O_5(F)/RT} = 656.27 \, K
\]

\[
W_{Mg_{1.5}Si_2O_5(F)} = 5.456 \, Kj \, mol^{-1}
\]
Figure 14. Activity-composition relations for OH and F talc components (2-site); the heavy line is calculated using the asymmetric solution model. For reference, the lighter line is calculated using the ideal solution model.
The magnitude of uncertainty associated with each value is difficult to estimate. Less than ten percent analytical error and unknown errors introduced in the nonlinear regression analysis, plus error associated with the temperature estimate suggest that a reasonable error is 15 to 20 percent.

The activity-composition relations for talc with two exchangeable anions per formula unit are given by

\[
\ln(a_{\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2}) = 2\ln(x^{\text{TC}}) + \left[\frac{1}{T}(x^{\text{TC}})^2\right] \left(3483 - \frac{4340(x^{\text{TC}})}{\text{Oh}}\right) \quad (20a)
\]

\[
\ln(a_{\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{F})_2}) = 2\ln(x^{\text{TC}}) + \left[\frac{1}{T}(x^{\text{TC}})^2\right] \left(1313 + \frac{4340(x^{\text{TC}})}{\text{F}}\right) \quad (20b)
\]

The activity-composition relations for F and OH talc are illustrated in Figure 14, which is calculated at 425 °C, the assumed average equilibrium temperature for talc-tremolite pairs. Because the values for W_i/R given above and used in equations (20a) and (20b) are calculated by multiplying the calculated values for W_i/RT by 698 K (425 °C), multiplying by 1/T in equations (20a) and (20b) means that the activity-composition relations depicted in Figure 14 are independent of the temperature estimate. Thus, Figure 14 represents the activity-composition relations for the average temperature of equilibrium, regardless of whether this figure is 425 °C, or not.
IV DISCUSSION AND CONCLUSIONS

PETROLOGICAL EFFECTS OF F-OH SUBSTITUTION

T-X_{CO_2} SPACE

The petrological effects of F-OH substitution in tremolite, talc and phlogopite in siliceous carbonates can be modelled using the calculated activity expressions for the OH exchange component of each mineral. Equations necessary for calculating equilibrium conditions for mixed volatile equilibria are given by Skippen and Carmichael (1978). These equations are easily modified to accept expressions relating the activity of each component to its abundance in a solid solution (e.g. Skippen and Trommsdorff, 1975).

Isobaric T-X_{CO_2} diagrams have been constructed for pressures of 100 MPa, 200 MPa and 500 MPa (1Kb, 2Kb and 5Kb), for the F-free system and at three arbitrarily set levels of F-OH substitution in each mineral. The three levels, X_F(1), X_F(2) and X_F(3), correspond to F contents in tremolite of X_F^{TR}=0.05, 0.30 and 0.47. X_F values for talc and phlogopite are taken from the calculated distribution curves shown in Figures 8 and 9 and are shown together in Figure 15. The three levels represent low, moderate and high F contents; an average level of F-OH substitution in tremolite, talc and phlogopite of the CMB is intermediate between X_F(1) and X_F(2). T-X_{CO_2} diagrams and all information necessary for their construction are given in Appendix I.
Figure 15. Fluorine substitution levels referred to in the text.
Figure 16. Summary of the petrological effects of F-OH substitution in P-T space; the diagram is calculated using activity models developed in text and thermodynamic data of Helgeson et al. (1978). The number beside the P-T traces of invariant points refers to the F substitution level; (0) refers to the F-free system. Dot-dash is the upper stability of calcite; dotted and short dashed lines are the first appearance of diopside and forsterite respectively.
aureole, can be explained, as will later be shown, by the presence of up to 2.0 weight percent F in phlogopites of the Marysvale Aureole (Rice, 1977b).

With increasing pressure, the calcite field diminishes significantly in size and invariant point I is restricted to increasingly lower $X_{CO_2}$ values. The expanded field for phlogopite-quartz with increased pressure, reported by Flowers and Helgeson (1983), has not been reproduced; the position of invariant point II migrates to slightly lower $X_{CO_2}$ values with increasing pressure. Of possible importance to field mapping is the increase in size, with rising pressure, of the diopside-dolomite stability field, which is limited by reactions 8, 11 and 14 and invariant points III and IV.

Fluorine-Present Systems

Isobaric $T-X_{CO_2}$ diagrams for each level of F-OH substitution are given at 100 MPa, 200 MPa and 500 MPa in Figures 1.1b-d, 1.2b-d and 1.3b-d in Appendix I. The predicted petrological effects of F-OH substitution are most significant in phlogopite, into which F is preferentially partitioned. Less affected are talc and, lastly, tremolite. In all minerals, the effect of increased F content is most pronounced at higher pressure.

At low F-OH substitution levels, $X_F(1)$, which corresponds to $X_F = 0.05, 0.03$ and 0.15 in tremolite, talc and phlogopite respectively, the only significant change in the $T-X_{CO_2}$ diagram is the expansion of the phlogopite-quartz field and the migration to higher $X_{CO_2}$ values of invariant point II. This is accompanied,
at 100 MPa, by the shifting of reaction 1, the lower limit for phlogopite-quartz, to lower temperatures than reaction 3, which limits the lower temperature of occurrence of talc-calcite. This is illustrated in Figure 1.1b, which is representative of the conditions reported in the Marysvale Aureole by Rice (1977b) and explains the occurrence of phlogopite, and not talc, at lowest grade in the contact aureole.

At moderate F-OH substitution levels, \( X_F(2) \), which corresponds to \( X_F \) values of 0.30, 0.20 and 0.59 in tremolite, talc and phlogopite respectively, the effects of F on phase relations are again most pronounced on the stability field of the assemblage phlogopite-quartz. At 200 MPa, the upper temperature limit for this assemblage increases from 470 °C in the F-free system to 540 °C at \( X_F(2) \). At low pressure, the talc-calcite stability field is not significantly affected. However, at 500 MPa the talc-calcite stability field has expanded to about three times its F-free size and the position of invariant point I has shifted to \( X_{CO_2} = 0.40 \) from \( X_{CO_2} = 0.20 \).

At 500 MPa and substitution level \( X_F(2) \) a change in topology within the system CaO-MgO-SiO_2-KAlO_2-H_2O-CO_2 is indicated by the interchange in position of reactions 7 and 8 and the down-temperature migration of the position of invariant point III past invariant point II. The topology change is encountered only at 500 MPa at \( X_F(2) \), but is encountered at all pressures at \( X_F(3) \). At pressures and F-OH substitution levels exceeding conditions necessary to cause the topology change, reactions involving potassium-bearing phases have been excluded. The resulting T-
$X_{CO_2}$ diagrams thus represent stable phase relations in the system CaO-MgO-SiO$_2$-H$_2$O-CO$_2$.

At high levels of F-OH substitution, $X_F(3)$, which corresponds to F contents of $X_F=0.46$ and $X_F=0.50$ in tremolite and talc respectively, the stability field for talc-calcite is again expanded, most significantly at higher pressures. The stability field for tremolite-calcite (Figure 7), is also expanded. Of possible petrological importance at high $X_F$ levels, is the diminution of the diopside-dolomite field.

In summary, increasing F content in each of tremolite, talc and phlogopite, leads to enhanced stabilities of assemblages containing these minerals. For each mineral this is accomplished by a downward shift in the lower temperature limit accompanied by an upward shift in the upper stability limit. Accompanying the expansion of the stability fields is a general migration of invariant points to increased $X_{CO_2}$ positions which leads to diminishing stability fields for assemblages present only in CO$_2$-rich fluids.

**P-T SPACE**

The effects of F on the stability of mineral assemblages containing tremolite and talc are summarized in Figure 16. Here, the calculated positions of the upper stability limit of the assemblage talc-calcite and invariant points III and V, which correspond to the first appearance of diopside and forsterite respectively, are traced through P-T space at the three F-OH
Figure 16. Summary of the petrological effects of F-OH substitution in P-T space; the diagram is calculated using activity models developed in text and thermodynamic data of Helgeson et al. (1978). The number beside the P-T traces of invariant points refers to the F substitution level; (0) refers to the F-free system. Dot-dash is the upper stability of talc-calcite; dotted and short dashed lines are the first appearance of diopside and forsterite respectively.
substitution levels. In general, calculated $T-X_{CO_2}^S$ sections predict the trace of the upper stability limit for talc-calcite to be equivalent to the trace of invariant point I, except at high F-OH$_{sub}$ substitution levels. At $X_F(3)$ the maxima in reaction 5 is located up to twenty degrees above invariant point I at 100 MPa; this decreases to about ten degrees at 500 MPa. Invariant points II, IV and VI, which involve phases in the KAlO$_2$-present system, have not been shown because of the topology change discovered in this system.

With increasing F-OH substitution, the upper stability of talc-calcite and the traces of invariant points II and V shown on Figure 23, are deflected to higher temperatures. The displacement is most pronounced for the upper limit of talc-calcite, and is less for invariant point V and least for invariant point III. The most significant increase in the upper limit of talc-calcite is between $X_F(2)$ and $X_F(3)$, which corresponds to the interval $X_{TC}^S=0.2$ to $X_{TC}^S=0.5$, where upward deflection of the talc-tremolite F distribution curve occurs (Figure 8).

In the F-free system, thermodynamic data of Helgeson et al. (1978) place the upper stability of talc-calcite at slightly lower temperatures than the aluminosilicate triple point of Holdaway (1971) adopted here and shown in Figure 16. With increasing F contents, the upper stability limit of the assemblage talc-calcite enters the sillimanite stability field. At moderate F contents ($X_F(2); X_{TC}^S=0.2$), the trace of the upper limit of talc-calcite intersects the sillimanite stability field between 360 MPa and 400 MPa. At high F contents ($X_F(3); X_{TC}^S=0.5$)
this occurs between 330 MPa and 500 MPa (Figure 23).

Analyzed talcs from the area west of Bennett Lake (Figure 2) originate from well within the sillimanite zone shown in Figure 4 and contain F in amounts approximately equal to or less than \( X_F \). Using the calculated model, the existence of talc in the sillimanite zone is possible at this substitution level, but only between 360 MPa and 400 MPa. Ewert (1977) estimated pressure in the study area to be near 300 MPa, while the assumed "Idahoan" metamorphic field gradient predicts pressure to be above 450 MPa. At either pressure, talc-calcite can not exist within the sillimanite zone at \( X_F \). The possibility remains, however, that this area was metamorphosed between pressures of 360 MPa and 400 MPa.

Although the model for F-OH substitution in talc partly explains the enhanced stability of the assemblage talc-calcite, it is likely that other factors are important for the apparent existence of talc within the sillimanite zone. The position of the aluminosilicate triple point of Holdaway (1971) is consistent with field data (e.g. Hodges and Spear, 1982) and will be assumed to be applicable to the study area.

Field evidence from the Lepontine Alps, Switzerland, is inconsistent with phase relations predicted from the data of Helgeson et al. (1978) (pers. comm. G. B. Skippen, 1982). The distribution of regional Alpine metamorphic zones is given in Figure 17. As seen in this figure, the assemblage diopside-dolomite first appears below the regional sillimanite isostrad. In the model system, invariant point III records the first
Figure 17. Mineral zones and isograds of Alpine metamorphism; from Trommsdorff (1980).
appearance of diopside-calcite. As shown in Figure 16, the thermodynamic data predict invariant point III to be within the sillimanite zone, not, as field evidence suggests, within the kyanite zone. This indicates inaccuracies in the thermodynamic data set which may also affect the positioning of equilibria involving talc.

Alternative possibilities for the apparent persistence of talc to high grade may be related to the existence of a previously unrecognized low grade metamorphic terrane between the Elzevir and Frontenac Terranes. The proposed pressure of 300 MPa for this region (Ewert, 1977), and the existence of talc in siliceous carbonates are incompatible with pressures and temperatures of the sillimanite zone. Data from this area suggest lower grade than is indicated by the present isograd distribution.

**IMPLICATIONS OF F-OH SUBSTITUTION**

**Field Mapping**

As recognized by Skippen (1974), F-OH substitution will complicate field relations in areas containing F-bearing hydrous silicate minerals. This is most significant for phlogopite-bearing rocks, but, as has been shown, is also important for talc and, to a lesser degree, tremolite-bearing rocks. The distribution of F in siliceous carbonates, however, is usually inhomogeneous and, if in any one area, $X_F$ in these minerals is known to be high, it is a good probable that samples with low $X_F$ will also be found nearby. This has been noted in the Alps by
Mercolli (1980) and in the Adirondacks by Valley et al. (1982). In areas where F is known to be high, or where data are lacking, F analyses must be routinely carried out and the F-OH substitution level for all samples determined.

As seen in Figure 16, the position of invariant point III, which corresponds to the first occurrence of diopside in the model system, is least affected by F-OH substitution. Up to pressures of 500 MPa its calculated position varies only five degrees between the F-free system and high F substitution levels \(x_F(3); x_T^{TR}=0.47, x_T^{TC}=0.5\). The model suggests that the first appearance of diopside will be relatively insensitive to variations in F contents in hydrous silicate minerals. This implies that the mapped trace of invariant point III may be used as an isothermal datum against which the effects of F-OH substitutions on other equilibria and invariant points could be measured.

**Mineral Exploration**

F-OH substitution has been shown to increase the stability of the assemblage talc-calcite, but, paradoxically, talc deposits within the CMB contain little F. Talc analyses reported by Ross et al. (1968) from Canada Talc mine, Madoc, Ontario, give 0.18 weight percent F \(x_T^{TC}=0.02, \) approx. and from the Gouverneur talc district, New York, give 0.48 weight percent F \(x_T^{TC}=0.05, \) approx. Talc from the Eldorado talc mine near Eldorado, Ontario, reported in this study (Appendix III; sample 81-979413-2) averages \(x_T^{TC}=0.05.\)
Theoretically, in rocks of appropriate bulk composition, the formation of talc should be enhanced by F-OH substitution. This does not appear to be a controlling factor in the localization of known talc deposits and indicates that other factors such as bulk rock and fluid compositions, fluid source and metamorphic grade are of greater importance. Highest priority should be given to areas where the bulk rock compositions are known to be SiO$_2$-rich and KA1O$_2$-poor. Exploration for talc deposits would be most successful in low-grade terranes, but talc stability extends to at least 500 MPa and, with moderate amounts of F, talc is stabilized to higher pressures. The presence of F in siliceous carbonates is an encouraging sign, especially at higher grades, but is by no means a "pathfinder" for talc occurrences, regardless of grade.

CONCLUSIONS

Field research conducted in metamorphosed siliceous carbonates of the CMB of the Grenville Province has demonstrated the widespread occurrence of talc of prograde metamorphic origin in the eastern part of the Elzevir Terrane of Brock and Moore (1983). Talc is one of the least abundant minerals in the rocks studied; phlogopite and tremolite are widespread.

Much of the tremolite, talc and phlogopite of the study area contains significant amounts of F. The maximum F content in talc 82-854041-1A, pair 03, $x^T_C=0.45$, has been confirmed at BRGM-CNRS, Orleans, France, and is the highest reported F content for a
naturally occurring talc. High $X_F$ values in tremolite, talc and phlogopite and abundant outcrops of talc-bearing marbles are known from the Indian River area in the northwest corner of the Carleton Place 1:50,000 map sheet (NTS 31F/1), where the above talc sample originated.

The distribution of $F$ between tremolite, talc and phlogopite has been determined by wavelength dispersive electron microprobe analysis of samples of siliceous carbonates containing appropriate minerals which have, on textural criteria, been demonstrated to coexist in chemical equilibrium. Solution modelling has been used to model binary $F$-OH tremolite, talc and phlogopite mixtures. The distribution of $F$ between phlogopite and tremolite is consistent with ideal solution behaviour in both minerals and gives an average $K_D = 3.4$; $F$ is preferentially partitioned into phlogopite. Distribution of $F$ between talc and tremolite is indicative of nonideal solution behaviour in talc. Below $X_F^{TR} = 0.35$ and $X_F^{TC} = 0.24$, $F$ distribution is consistent with earlier workers with $K_D = 0.5$. With increasing $F$ contents, the talc-tremolite distribution curve is deflected upwards and $K_D$ values approach unity.

Activity-composition relations have been calculated for $F$ and OH tremolite and phlogopite using an ideal solution model. Activity-composition relations and the excess free energy of mixing for the $F$ and OH talc exchange components have been calculated using a newly developed nonlinear regression technique. Talc is modelled as an asymmetric $F$-OH solution.
Calculation of excess functions by linear regression has been shown to be inaccurate because the regression equation cannot explicitly be defined in either of the measured values, $X_F^{TC}$ or $X_F^{TR}$, but is implicitly defined through $\ln K_D$. The nonlinear regression technique uses an iterative Newton-Raphson convergence scheme to explicitly define the regression in terms of $X_F^{TC}$ or $X_F^{TR}$. This new method has been used to estimate excess partial molar free energies at infinite dilution for OH and F talc; these are:

\[
\begin{align*}
W_{Mg_3Si_4O_{10}(OH)_{2}} &= 28.956 \text{ Kj/mol} \\
W_{Mg_3Si_4O_{10}(F)_{2}} &= 10.912 \text{ Kj/mol}
\end{align*}
\]

with an estimated error of 20 percent.

The petrological effects of F-OH substitution in siliceous carbonates are greatest for the assemblage phlogopite-quartz; its stability is greatly enhanced, even at low F-OH substitution levels. At moderate to high $X_F$ levels in phlogopite, the topology of the KAlO$_2$-present system in T-XCO$_2$ space is rendered invalid. The stability fields for talc-calcite and tremolite-calcite are also increased with increasing $X_F$ levels. The stability field for diopside-dolomite decreases with increasing F contents, especially at high pressure.

The calculated effects of F-OH substitution on the KAlO$_2$-absent system in P-T space are most significant for the assemblage talc-calcite. In the F-free system, the P-T trace of the upper temperature limit for this assemblage does not intersect the sillimanite field. With increasing F contents, the trace of
containing these minerals. The effect of reduced activities of F-bearing silicates on geothermometers involving hydrous silicate minerals should also be investigated.
containing these minerals. The effect of reduced activities of F-bearing silicates on geothermometers involving hydrous silicate minerals should also be investigated.
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APPENDIX I

T-χ_{CO2} DIAGRAMS

1.1 Calculation of the T-χ_{CO2} Diagram

Table 1.1 Mineral and component compositions and standard states.

Table 1.2 Stable reactions and equilibria in the system CaO-MgO-SiO₂-KAlO₂-H₂O-CO₂.

Table 1.3 Thermodynamic data.

Table 1.4 Data used to calculate reactions in the F-free system and at X_F(1), X_F(2) and X_F(3).

1.2 T-χ_{CO2} Diagrams

Figure 1.1a 100 MPa: F-free.
.1b : X_F(1)
.1c : X_F(2)
.1d : X_F(3)

Figure 1.2a 200 MPa: F-free
.2b : X_F(1)
.2c : X_F(2)
.2d : X_F(3)

Figure 1.3a 500 MPa: F-free
.3b : X_F(1)
.3c : X_F(2)
.3d : X_F(3)
APPENDIX I

$T-X_{CO_2}$ DIAGRAMS

1.1 Calculation of the $T-X_{CO_2}$ Diagram

A general equation for the free energy change of a devolatization reaction as a function of temperature, pressure, and fluid composition is given in Skippen and Carmichael (1978, equation 8.15). At equilibrium the free energy of reaction is zero and the general equation can be rewritten

$$\ln K = A/T + B + C(P-1)/T - DELA/T + DELB/T$$
$$+ DELC/T - DELD/T$$

(I.1)

where:

$$A = [-\Delta H_{Tr,Pr}/R]$$
$$B = [\Delta S_{Tr,Pr}/R]$$
$$C = [-\Delta V_s/R]$$

and, using the fourth order polynomial of Holland (1981) to express the variation of heat capacity with T,

$$DELA = (\Delta a/R)[T-Tr-T\ln(T/Tr)]$$
$$DELB = (\Delta b/R)[(T^2)/2+(Tr^2)/2-Tr]$$
$$DELC = (\Delta c/R)[(T^{-1})/2-(Tr^{-1})+T(Tr^{-2}y)/2]$$
$$DELD = (\Delta d/R)[2(2T^{-5}-(Tr^{-5})-T(Tr^{-5}))]$$
Table I.1 - Minerals, Components, Compositions and Standard States

<table>
<thead>
<tr>
<th>PHASES</th>
<th>COMPONENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>QZ Quartz</td>
<td>qz SiO₂</td>
</tr>
<tr>
<td>CC Calcite</td>
<td>cc CaCO₃</td>
</tr>
<tr>
<td>DL Dolomite</td>
<td>dl CaMg(CO₃)₂</td>
</tr>
<tr>
<td>TC Talc</td>
<td>tc Mg₃Si₄O₁₀(OH)₂</td>
</tr>
<tr>
<td>TR Tremolite</td>
<td>tr Ca₂Mg₅Si₈O₂₂(OH)₂</td>
</tr>
<tr>
<td>DI Diopside</td>
<td>di CaMgSi₂O₆</td>
</tr>
<tr>
<td>FO Forsterite</td>
<td>fo Mg₂SiO₄</td>
</tr>
<tr>
<td>PH Phlogopite</td>
<td>ph KMg₃AlSi₃O₁₀(OH)₂</td>
</tr>
<tr>
<td>KF Potassium feldspar</td>
<td>kf KAlSi₃O₈</td>
</tr>
<tr>
<td>(magnesite)</td>
<td>mg MgCO₃</td>
</tr>
</tbody>
</table>

STANDARD STATES

Silicate minerals: Unit activity of the component which is compositionally equivalent to the stable form of the pure mineral at the temperature and pressure of interest.

Carbonate minerals: Unit activity of pure CaCO₃ and MgCO₃ at the temperature and pressure of interest.

Fluid phase: Unit fugacity for H₂O and CO₂ at 0.1 MPa (1 bar) and the temperature of interest.
Activities of less than one for solid solution exchange components involved in reaction are accounted for by separating and subtracting $\ln(a_i)$, where $a_i$ is the activity of each exchange component $i$, from $\ln K$. Reactions involving dolomite have been recast as equilibria involving the pure components $\text{MgCO}_3$ and $\text{CaCO}_3$. The activities of the components $\text{MgCO}_3$ and $\text{CaCO}_3$ are not independent, but are related through the Gibbs-Duhem equation and are accounted for using the equations given by Skippen and Hutcheon (1974). The activities of OH tremolite and phlogopite components are given by equations (18a and b) and the activity of the OH talc component is calculated with equation (20a). Using these activity models equation 1.1 is rewritten,

$$
\nu_{\text{CO}_2} \ln(f_{\text{CO}_2}) + \nu_{\text{H}_2\text{O}} \ln(f_{\text{H}_2\text{O}}) = A/T + B + C(P-1)/T
$$

- $\text{DELA}/T + \text{DELB}/T + \text{DELC}/T - \text{DELD}/T$  \hspace{1cm} (I.2)

with new A and B terms defined by,

$$
A = -[\frac{\Delta H_{\text{Tr},Pr}}{R} - \nu_{\text{mg}}(1683) + \nu_{\text{cc}}(157) + \nu_{\text{TC}}(3483 - 4340(\text{X}_{\text{TC}}))]
$$

$$
B = [\frac{\Delta S_{\text{Tr},Pr}}{R} - \nu_{\text{mg}}(1.1177) + \nu_{\text{cc}}(0.253) - 2 \nu_{\text{TC}} \ln(\text{X}_{\text{OH}}^{\text{TC}}) - 2 \nu_{\text{TR}} \ln(\text{X}_{\text{OH}}^{\text{TR}}) - 2 \nu_{\text{PH}}(\text{X}_{\text{OH}}^{\text{PH}})]
$$

The C term and the four heat capacity terms DELA, DELB, DELC, and DELD remain unchanged.

Fluids present during the metamorphism of siliceous carbonates are assumed to be $H_2O-CO_2$ mixtures with $X_{H_2O} + X_{CO_2} = 1$; additional fluid phases have not been considered. At fixed
APPENDIX II

PETROGRAPHY, ELECTRON MICROPROBE
ANALYSIS AND MINERAL CHEMISTRY

II.1 Petrography

The primary objectives of petrographic study were: i) identification of samples containing coexisting tremolite and talc or phlogopite, and ii) evaluation of textural relationships among coexisting minerals, particularly talc, tremolite and phlogopite. Petrographic examination was carried out on all samples suspected of containing F-bearing silicate minerals. Only contiguous mineral pairs exhibiting unaltered mineral boundaries were selected for further study. This constraint was also imposed upon tremolite-phlogopite pairs, with the exception of section 82-871841 which contains acceptable talc-tremolite pairs, individual unreacted phlogopite grains, but no tremolite-phlogopite pairs in direct contact.

Textures consistent with chemical equilibrium among contiguous minerals include triple-point grain contacts and the absence of replacement or reaction textures at shared boundaries, along cleavages in grain interiors, or around grain perimeters. All samples analyzed by electron microprobe showed clearly defined boundaries between mineral grains without evidence of retrograde reactions. Examples of equilibrium textures between
<table>
<thead>
<tr>
<th>REACTIONS</th>
<th>EQUILIBRIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 3DL + KF + H₂O = PH + 3CC + 3CO₂</td>
<td>3mg + kcf + H₂O = ph + 3CO₂</td>
</tr>
<tr>
<td>2. 8QZ + 5DL + H₂O = TR + 3CC + 7CO₂</td>
<td>8qz + 5mg + 2cc + H₂O = tr + 7CO₂</td>
</tr>
<tr>
<td>3. 3DL + 4QZ + H₂O = TC + 3CC + 3CO₂</td>
<td>3mg + 4qz + H₂O = tc + 3CO₂</td>
</tr>
<tr>
<td>4. 5TC + 6CC + 4QZ = 3TR + 2H₂O + 6CO₂</td>
<td>5tc + 6cc + 4qz = 3tr + 2H₂O + 6CO₂</td>
</tr>
<tr>
<td>5. 2TC + 3CC = TR + DL + H₂O + CO₂</td>
<td>2tc + 2cc = tr + mg + H₂O + CO₂</td>
</tr>
<tr>
<td>6. 5PH + 6CC + 24QZ = 3TR + 5KF + 2H₂O + 6CO₂</td>
<td>5ph + 6cc + 24qz = 3tr + 5kf + 2H₂O + 6CO₂</td>
</tr>
<tr>
<td>7. PH + 2DL + 8QZ = TR + KF + 4CO₂</td>
<td>ph + 2mg + 2cc + 8qz = tr + kf + 4CO₂</td>
</tr>
<tr>
<td>8. DL + 2QZ = DI + 2CO₂</td>
<td>mg + cc + 2qz = di + 2CO₂</td>
</tr>
<tr>
<td>9. TR + 3CC + 2QZ = 5DI + H₂O + 3CO₂</td>
<td>tr + 3cc + 2qz = 5di + H₂O + 3CO₂</td>
</tr>
<tr>
<td>10. 3TR + 6CC + KF = PH + 12DI + 2H₂O + 6CO₂</td>
<td>3tr + 6cc + kf = ph + 12di + 2H₂O + 6CO₂</td>
</tr>
<tr>
<td>11. TR + 3CC = 4DI + DL + H₂O + CO₂</td>
<td>tr + 2cc = 4di + mg + H₂O + CO₂</td>
</tr>
<tr>
<td>12. TR + 11DL = 8FO + 13CC + H₂O + 9CO₂</td>
<td>tr + 11mg = 8fo + 2cc + H₂O + 9CO₂</td>
</tr>
<tr>
<td>13. 3TR + 5CC = 11DI + 2FO + 3H₂O + 5CO₂</td>
<td>3tr + 5cc = 11di + 2fo + 3H₂O + 5CO₂</td>
</tr>
<tr>
<td>14. DI + 3DL = 2FO + 4CC + 2CO₂</td>
<td>di + 3mg = 2fo + cc + 2CO₂</td>
</tr>
<tr>
<td>15. 2FO + CC + KF + H₂O = DI + PH + CO₂</td>
<td>2fo + cc + kf + H₂O = di + ph + CO₂</td>
</tr>
</tbody>
</table>
pressure, temperature and \( X_F \) in all \( F \)-bearing hydrous silicate minerals, all terms of equation 1.2, except those that involve the fugacities of \( H_2O \) and \( CO_2 \), are independent of fluid composition (\( X_{CO_2} \)). Under these conditions, values for \( X_{CO_2} \) (hence \( X_{H_2O} \)) can be selected and, utilizing a modified Redlich-Kwong (MRK) equation of state for \( H_2O-CO_2 \) mixtures (e.g., Kerrick and Jacobs, 1981; Flowers, 1979), \( \ln(f_{CO_2}) \) and \( \ln(f_{H_2O}) \) can be calculated. By iteratively solving equation 1.2 for equilibrium \( X_{CO_2} \) at various temperatures under isobaric and fixed \( X_F \) conditions, each reaction can be positioned in \( T-X_{CO_2} \) space.

Using computer programs ONEMAX, OPPMAX and XCDMAX written by G.B. Skippen, stable reactions involving quartz, calcite, dolomite, talc, tremolite, diopside, forsterite, potassium feldspar, phlogopite and an \( H_2O-CO_2 \) fluid phase have been positioned in \( T-X_{CO_2} \) space. Fugacities of \( H_2O \) and \( CO_2 \) have been calculated using the MRK equation of Kerrick and Jacobs (1981) by incorporating several subroutines from the program FLUIDS of Jacobs and Kerrick (1981) into programs ONEMAX, OPPMAX and XCDMAX.

Within the system \( CaO-MgO-SiO_2-KAlO_2-H_2O-CO_2 \), Flowers and Helgeson (1983) have identified fifteen stable reactions that affect bulk compositions within the chemographic subvolume \( CaCO_3-CaMg(CO_3)_2-SiO_2-KAlO_2-H_2O-CO_2 \); these are given in Table I.2. Reactions are accompanied by corresponding equilibria which are consistent with standard states given in Table I.1. Each reaction is expressed in terms of components which, except for carbonate minerals, are compositionally identical to the pure mineral and fluid phases.
<table>
<thead>
<tr>
<th>Phase</th>
<th>$H^0_F$</th>
<th>$S^0_{ii}$</th>
<th>$V^0_{iii}$</th>
<th>$V_a^{iv}$</th>
<th>$b(\times 10^{-3})^{iv}$</th>
<th>$c(\times 10^5)^v$</th>
<th>$d^{vi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc</td>
<td>-5903.289</td>
<td>260.83</td>
<td>13.6252</td>
<td>534.30</td>
<td>37.416</td>
<td>-88.052</td>
<td>-2153.2</td>
</tr>
<tr>
<td>Tremolite</td>
<td>-12319.696</td>
<td>548.90</td>
<td>27.2927</td>
<td>1214.40</td>
<td>26.528</td>
<td>-123.62</td>
<td>-7388.5</td>
</tr>
<tr>
<td>Calcite</td>
<td>-1208.222</td>
<td>92.66</td>
<td>3.6935</td>
<td>142.20</td>
<td>27.307</td>
<td>1.454</td>
<td>-1182.7</td>
</tr>
<tr>
<td>Diopside</td>
<td>-3203.262</td>
<td>143.09</td>
<td>6.6107</td>
<td>328.19</td>
<td>1.8881</td>
<td>-14.430</td>
<td>-2519.2</td>
</tr>
<tr>
<td>Quartz ( )</td>
<td>-910.648</td>
<td>41.34</td>
<td>2.2689</td>
<td>104.35</td>
<td>6.070</td>
<td>0.342</td>
<td>-1070</td>
</tr>
<tr>
<td>Magnesite</td>
<td>-1111.396</td>
<td>15.70</td>
<td>2.8109</td>
<td>82.55</td>
<td>52.463</td>
<td>-19.865</td>
<td>0</td>
</tr>
<tr>
<td>Forsterite</td>
<td>-2175.680</td>
<td>95.19</td>
<td>4.3806</td>
<td>149.83</td>
<td>27.36</td>
<td>-35.648</td>
<td>0</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>-6226.072</td>
<td>318.40</td>
<td>14.9662</td>
<td>420.95</td>
<td>120.4</td>
<td>-89.956</td>
<td>0</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>-3971.403</td>
<td>213.93</td>
<td>10.8872</td>
<td>320.57</td>
<td>18.03</td>
<td>-125.29</td>
<td>0</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>-393.52</td>
<td>213.69</td>
<td>—</td>
<td>44.22</td>
<td>8.78</td>
<td>-8.619</td>
<td>0</td>
</tr>
<tr>
<td>$H_2O$ (steam)</td>
<td>-241.82</td>
<td>188.72</td>
<td>—</td>
<td>30.54</td>
<td>10.29</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

i. Kj mol$^{-1}$  
ii. j mol$^{-1}$ K$^{-1}$  
iii. j mol$^{-1}$ bar  
iv. j mol$^{-1}$ K$^{-2}$  
v. j K mol$^{-1}$  
vi. j mol$^{-1}$ K$^{-0.5}$
Enthalpies and entropies of reaction at reference temperature and pressure (298.15 K; 0.1 MPa), $\Delta H_{Tr,Pr}$ and $\Delta S_{Tr,Pr}$, are calculated from standard molal enthalpies of formation and standard molal entropies tabulated by Helgeson et al. (1978). The volume change of solid phases during reaction was calculated from standard molal volumes given by Helgeson et al. (1978). Equilibrium states of order/disorder in potassium-feldspar are accounted for by using thermodynamic data from this data set.

Heat capacity polynomials for quartz, calcite, talc, tremolite, and diopside were taken from Holland (1981). Heat capacity polynomials for magnesite, forsterite, phlogopite, potassium-feldspar, and $H_2O$ (steam) and $CO_2$ were taken from Helgeson et al. (1978). Enthalpy, entropy, volume, and heat capacity data for all phases considered are given in Table I.3.

Data necessary for the solution of equation I.2 for the fifteen reactions considered, are given in Table I.4. Each reaction has been calculated on a F-free basis and at substitution levels $X_F(1)$, $X_F(2)$ and $X_F(3)$ in tremolite, talc and phlogopite. The effects of F-OH substitution in talc is reflected in adjustment of both the A and B reaction parameters due to the nonideal model adopted for F-OH mixing in talc. The ideal mixing of F-OH tremolite and phlogopite enables activity-composition relations for these minerals to be accommodated solely by adjustment of the B reaction parameter.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>DELA</th>
<th>DELB</th>
<th>DELC</th>
<th>DELD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>21980</td>
<td>46.622</td>
<td>-0.5204</td>
<td>-5.4298</td>
<td>-4.684</td>
<td>8.3078</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>59347</td>
<td>126.74</td>
<td>-1.4739</td>
<td>-4.6393</td>
<td>-34.610</td>
<td>-10.857</td>
<td>425.25</td>
</tr>
<tr>
<td>3.</td>
<td>21255</td>
<td>45.540</td>
<td>-0.4638</td>
<td>-3.4436</td>
<td>-15.418</td>
<td>-6.6969</td>
<td>255.73</td>
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<tr>
<td>4.</td>
<td>71765</td>
<td>152.52</td>
<td>-2.1029</td>
<td>3.3002</td>
<td>-26.740</td>
<td>0.9133</td>
<td>-2.884</td>
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<td>5.</td>
<td>16837</td>
<td>35.659</td>
<td>-0.5464</td>
<td>2.2479</td>
<td>-3.774</td>
<td>2.5368</td>
<td>-86.203</td>
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<td>6.</td>
<td>61840</td>
<td>147.11</td>
<td>-1.1898</td>
<td>13.231</td>
<td>-80.410</td>
<td>-74.110</td>
<td>1275.74</td>
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<tr>
<td>7.</td>
<td>37367</td>
<td>80.116</td>
<td>-0.9535</td>
<td>0.7906</td>
<td>-29.926</td>
<td>-19.165</td>
<td>425.25</td>
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<tr>
<td>8.</td>
<td>19640</td>
<td>40.486</td>
<td>-0.5319</td>
<td>-2.0225</td>
<td>-8.714</td>
<td>-1.6767</td>
<td>96.605</td>
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<tr>
<td>9.</td>
<td>38854</td>
<td>75.691</td>
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<td>-5.4731</td>
<td>-8.960</td>
<td>2.4736</td>
<td>57.776</td>
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<td>11.</td>
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<td>-3.4506</td>
<td>-0.246</td>
<td>4.1503</td>
<td>-38.829</td>
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<td>14.</td>
<td>28157</td>
<td>48.139</td>
<td>-0.3081</td>
<td>-5.4776</td>
<td>-7.177</td>
<td>-1.5699</td>
<td>160.746</td>
</tr>
<tr>
<td>15.</td>
<td>-6177</td>
<td>-1.5171</td>
<td>-0.2123</td>
<td>0.04781</td>
<td>2.493</td>
<td>9.8777</td>
<td>-160.746</td>
</tr>
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</table>

Table 1.4 - Data used to calculate reactions in the F-free system and at X_F(1), X_F(2) and X_F(3)
Table I.4 - continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( X_f(1) )</th>
<th>( X_f(2) )</th>
<th>( X_f(3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A )</td>
<td>( B )</td>
<td>( A )</td>
</tr>
<tr>
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<td>21980</td>
<td>46.947</td>
<td>21980</td>
</tr>
<tr>
<td>2.</td>
<td>59347</td>
<td>126.84</td>
<td>59347</td>
</tr>
<tr>
<td>3.</td>
<td>21254</td>
<td>45.600</td>
<td>21255</td>
</tr>
<tr>
<td>4.</td>
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<td>71763</td>
</tr>
<tr>
<td>5.</td>
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<td>16836</td>
</tr>
<tr>
<td>6.</td>
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<td>145.79</td>
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<td>7.</td>
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<td>79.894</td>
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<td>8.</td>
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<td>40.486</td>
<td>19640</td>
</tr>
<tr>
<td>9.</td>
<td>38854</td>
<td>75.388</td>
<td>38854</td>
</tr>
<tr>
<td>10.</td>
<td>79622</td>
<td>152.26</td>
<td>79622</td>
</tr>
<tr>
<td>11.</td>
<td>19214</td>
<td>35.103</td>
<td>19214</td>
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<td>12.</td>
<td>131843</td>
<td>227.66</td>
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</tr>
<tr>
<td>13.</td>
<td>85799</td>
<td>158.45</td>
<td>85799</td>
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<tr>
<td>14.</td>
<td>28157</td>
<td>48.139</td>
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<tr>
<td>15.</td>
<td>-6177</td>
<td>-1.192</td>
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</table>
1.2 $T-X_{CO_2}$ Diagrams
Figure 1.1c T-XCO₂ diagram at 100 MPa
Figure I.2b T-X CO\textsubscript{2} diagram at 200 MPa

Figure I.2a T-X CO\textsubscript{2} diagram at 200 MPa
Figure I.2c  $T$-$X_{CO_2}$ diagram at 200 MPa; $X_p(2)$

Figure I.2d  $T$-$X_{CO_2}$ diagram at 200 MPa; $X_p(3)$
Figure I.3c  T-X CO₂ diagram at 500 MPa; $X_P(2)$

Figure I.3d  T-X CO₂ diagram at 500 MPa; $X_P(3)$
APPENDIX II

PETROGRAPHY, ELECTRON MICROPROBE ANALYSIS AND MINERAL CHEMISTRY

II.1 Petrography

Plate II.1
Plate II.2

II.2 Electron Microprobe Analysis

Table II.1 Standards and lower limits of detection.
Table II.2 Estimated 2-sigma error for electron microprobe analysis.

II.3 Mineral Chemistry

Figure II.1 Mg/Mg+Fe versus Si in tremolite.
Figure II.2 Cation and anion distribution in tremolite.
Figure II.3 Mg/Mg+Fe versus X_F in tremolite.
Figure II.4 Cation and anion distribution in talc.
Figure II.5 Mg/Mg+Fe versus octahedral Al in phlogopite.
Figure II.6 Cation and anion distribution in phlogopite.
Figure II.7 X_F versus total Fe in phlogopite.

II.4 Electron Microprobe Analyses
APPENDIX II

PETROGRAPHY, ELECTRON MICROPROBE ANALYSIS AND MINERAL CHEMISTRY

II.1 Petrography

The primary objectives of petrographic study were: i) identification of samples containing coexisting tremolite and talc or phlogopite, and ii) evaluation of textural relationships among coexisting minerals, particularly talc, tremolite and phlogopite. Petrographic examination was carried out on all samples suspected of containing F-bearing silicate minerals. Only contiguous mineral pairs exhibiting unaltered mineral boundaries were selected for further study. This constraint was also imposed upon tremolite-phlogopite pairs, with the exception of section 82-871841 which contains acceptable talc-tremolite pairs, individual unreacted phlogopite grains, but no tremolite-phlogopite pairs in direct contact.

Textures consistent with chemical equilibrium among contiguous minerals include triple-point grain contacts and the absence of replacement or reaction textures at shared boundaries, along cleavages in grain interiors, or around grain perimeters. All samples analyzed by electron microprobe showed clearly defined boundaries between mineral grains without evidence of retrograde reactions. Examples of equilibrium textures between
tremolite, talc and phlogopite in siliceous carbonates of the Grenville Province are shown in Plates II.1 and II.2. Thin sections containing serpentine were not used in this study as further petrographic studies are needed to establish the textural relationships of retrograde and prograde serpentine in siliceous carbonates of the CMB.

The principal minerals present in samples collected from siliceous carbonates of the CMB are, in decreasing order of abundance: calcite, dolomite, tremolite, phlogopite, and talc. Other minerals identified in these samples include quartz, muscovite, chlorite, apatite, titanite (sphene), serpentine, possible fluorite, graphite, pyrite and associated goethite, and Ti-bearing tourmaline which was identified by quantitative electron microprobe analysis. Minerals present in siliceous carbonates collected at Campolungo, Switzerland, are, in decreasing order of abundance: calcite, tremolite, talc, quartz, phlogopite, pyrite, and malachite.

II.1a Tremolite

In the majority of samples examined, tremolite is the most abundant silicate mineral present. Tremolite generally occurs in needle-like or tabulate crystals arranged in elongate to radiating aggregates which, at hand specimen or outcrop scale, often impart a foliation to the rock. Tremolite is usually white, but is also found to be clear or light grey. Individual crystals vary from mm to dm scale, but most commonly they are a
II.1A Section 82-854041-1B. Coexisting, texturally stable tremolite, talc and phlogopite with calcite; plane polarized light; scale bar is 0.25 mm.

II.1B Section 82-854041-1B. Coexisting, texturally stable tremolite and talc, with calcite. Note unreacted grain boundaries; plane polarized light; scale bar is 0.25 mm.

II.1C Section 82-871841. Coexisting, texturally stable tremolite and talc; plane polarized light; scale bar is 0.25 mm.

II.1D Section 82-871841. Coexisting talc, tremolite with calcite. Note mosaic textures and unreacted talc-tremolite pair near the center of the photomicrograph; plane polarized light; scale bar 0.25 mm.

II.1E Section 82-779694. Coexisting tremolite and talc in weathered carbonate matrix; plane polarized light; scale bar 0.25 mm.

II.1F Section 82-779694. Coexisting, texturally stable tremolite and talc with calcite and dolomite. Note mosaic textures and unreacted talc-tremolite boundaries; plane polarized light; scale bar 0.50 mm.
PLATE II.2

11.2A Section 82-815834-1. Coexisting phlogopite and tremolite with calcite. Note unreacted grain boundaries; plane polarized light; scale bar is 0.25 mm.

11.2B Section 82-815834-1. Coexisting tremolite and phlogopite with dolomite and calcite. Dark, high relief mineral is titanite (sphene, "TI"); plane polarized light; scale bar is 0.25 mm.

11.2C Section 82-854853-1. Tremolite and talc interpreted to be in textural equilibrium. Note sharp, unreacted boundaries between talc and tremolite; plane polarized light; scale bar 0.25 mm.

11.2D Section 82-849047. Reflected light photomicrograph showing polished surfaces on talc and tremolite in carbonate matrix; plane polarized light; scale bar 0.25 mm.

11.2E Section 81-979413-2. Reflected light photomicrograph of talc with quartz and calcite in a sample from the Eldorado talc mine, Eldorado, Ontario. Note well polished talc surface; plane polarized light; scale bar 0.50 mm.
few mm to cm in length. Decimetre-scale tremolite occurs most commonly in veins in siliceous carbonates. With talc and other silicate minerals, tremolite crystals stand out in relief on weathered marble surfaces. Tremolite is distinguished from other silicate minerals commonly found in marbles by its elongate habit, hardness and cleavage. In some localities, talc forms pseudomorphs after tremolite.

In thin section tremolite appears colourless and is distinguished by the characteristic twinning of amphiboles, low to medium birefringence, and the interference figure which gives a negative sign and a large 2V angle. In samples containing evenly distributed talc and tremolite, tremolite generally occurs in solitary crystals, although some contiguous talc-tremolite pairs are almost invariably present. When tremolite, talc and phlogopite are present, talc is generally subordinate in abundance and therefore fewer talc-tremolite than phlogopite-tremolite pairs have been observed.

11.1b Talc

With few exceptions, talc is the least abundant hydrous silicate mineral present in samples collected from the Grenville Province. Talc is often present at the trace to 1 percent level and rarely exceeds 10 percent by volume. For this reason, tremolite or tremolite-phlogopite bearing marbles often contain talc that is virtually impossible to detect by non-microscopic methods.
Talc is most commonly found in 0.5 to 2 mm flakes or thin books, although it may occur in larger flakes up to 1 cm in size. The larger talc grains are restricted to talc occurrences in veins where it is often found as large aggregates of cm-sized crystals. Talc is usually clear and colourless, but may be very light green. Talc commonly stands out in relief on weathered surfaces where it can readily be recognized by its white colour, characteristic softness, greasy feel, and undulating cleavage surfaces. On fresh surfaces talc appears similar to muscovite or colourless phlogopite, but exhibits a diffuse surface sheen. Talc is also seen in finely crystalline masses as a retrograde alteration product of tremolite and, less commonly, diopside.

In thin section talc may be confused with high-Mg chlorite or phlogopite, especially when the latter mineral exhibits little or no pleochroism. Talc is most easily distinguished from chlorite by its high birefringence and from phlogopite in optic axis or bisectrix figures where its optic sign and 2V, which can be as high as 30°, are easily observed. The basal cleavage is usually better developed in talc than in phlogopite, giving talc a more fibrous appearance in random sections. Identification of talc is most difficult when it is present in low amounts. Under these circumstances, X-ray or qualitative electron microprobe analyses are useful for talc identification.
11.1c Phlogopite

Phlogopite is virtually ubiquitous in siliceous carbonates of the CMB. After tremolite it was the second most abundant hydrous silicate mineral encountered and was present in nearly every thin section examined in the course of this study. In hand specimen phlogopite generally forms equant, 1 to 3 mm books which are commonly light brown in colour and stand out on weathered surfaces. Phlogopite rarely occurs in crystals exceeding 5 mm in length and is only rarely seen as finely crystalline masses. Schistose siliceous carbonates may contain larger phlogopite crystals that are oriented such that their c-axes are perpendicular to foliation. Phlogopite is often associated with pyrite and the majority of thin sections containing phlogopite also contain pyrite.

In thin section, phlogopites exhibiting little or no pleochroism are almost indistinguishable from talc. Because of the contrasting 2V angles for phlogopite and talc (a maximum of 5° and 30° respectively), basal sections most easily serve to distinguish between these two minerals. Phlogopite usually occurs as equant to elongate, subhedral to euhedral crystals with less prominent development of basal cleavage. In the samples examined, phlogopite shows few signs of textural disequilibrium, although it may appear somewhat iron-stained due to oxidization of nearby pyrite.

As previously described, tremolite and phlogopite are often found in contact where they generally do not exhibit textures
indicative of chemical disequilibrium. Phlogopite, however, is only rarely seen in contact with talc. When talc is found in contact with phlogopite, talc usually shows no signs of disequilibrium.

II.2 Electron Microprobe Analysis

Thin sections satisfying mineralogical and textural criteria were chosen for further study utilizing energy dispersive spectrometer (EDS) and quantitative wavelength dispersive spectrometer (WDS) electron microprobe techniques. Qualitative EDS analyses were carried out on selected polished thin sections to confirm optical mineral identification and to aid in identifying unknown minerals. The EDS was also used to identify anomalously Ba-rich phlogopites present in thin section 82-756694-3. Semi-quantitative and quantitative analyses of tremolite, talc and phlogopite were carried out using WDS electron microprobe techniques.

All sections were polished in several stages to ensure a high quality surface for electron microprobe analysis. Initially each sample was impregnated with Araldite polyester resin prior to being bonded with the same material to a glass slide. After trimming, the sample was reduced to 50 μm with an automated grinder, hand ground in water with 400 to 3200 μm carborundum grit to a thickness of about 34 μm, and polished with an automated polisher, first using a 6 μm diamond paste in a kerosene and paraffin oil mixture and finally with 0.3 μm alpha
alumina powder in water to a final thickness of 30 um.

Previous workers (Moore and Kerrick, 1976) reported difficulties in obtaining smooth surfaces on talc grains due to the softness of this mineral. Although talc did not accept as high a polish as tremolite, it is evident in Plate II.2 that the method described produced talc grains that are polished to an acceptable degree. Inspection of talc analyses given in this appendix show that analyzed talc grains are polished sufficiently well to give reproduceable values for all elements analyzed and, assuming stochiometric values for (OH+F), sum to give percentage totals close to 100 percent.

II.2a Reconnaissance Fluorine Survey

Semi-quantitative WDS electron microprobe analyses were carried out as part of a reconnaissance F survey that was designed to locate areas with F-bearing hydrous silicate minerals. During this survey, 190 uncovered, unpolished (beyond normal thin section standards) thin sections of Grenville marbles which had previously been obtained by B. McKinstry, were examined. Quantitative F analysis of the uncovered thin sections was impossible because most thin sections were too thin (30 um) to accept sufficient polishing for quantitative analysis, and rock samples corresponding to the thin sections were unavailable. One exception is section 4869012 which was successfully polished and has been used in the study of F partitioning.
Uncovered thin sections identified by optical methods to contain tremolite, talc or phlogopite were polished by hand with 0.3 μm alpha alumina powder in water until a moderate polish was achieved. The thin sections were then carbon-coated and semi-quantitative WDS analysis was carried out. The survey resulted in the identification of twenty areas found to contain F-bearing tremolite with talc or phlogopite.

11.2b Quantitative Mineral Analyses

Specimens chosen for quantitative WDS electron microprobe analysis on the basis of textural relationships, were analyzed using a Cambridge Microscan 5 electron microprobe with two spectrometers and a take-off angle of 75 degrees. Operating conditions were: 15 kV accelerating potential, specimen current of 5 nA as measured on pure Fe, and a beam diameter of 2 to 3 μm.

The elements K, Ca, Fe and Ti were analyzed using a quartz diffracting crystal and a flow proportional counter with a mylar window. Lighter elements, F, Si, Mg, Al and Na were analyzed using a KAP diffracting crystal and a light-element LAN flow proportional counter fitted with an ultra-thin collodion window. All elements were counted for 30 seconds, with the exception of F and K, which were counted for 100 seconds.

X-ray counts were reduced to oxide weight percents using the program EMPADR of Rucklidge and Gasparini (1969). Oxide weight percent data were used to calculate the chemical formula of each analyzed mineral using a program, MINCAL, written by the author.
A listing of MINCAL is given in Appendix IV.

Analyses labelled "BRGM" were carried out by D.H. Watkinson at BRGM-CNRS, Orleans, France, on a CAMBAX electron microprobe. Operating conditions were: an accelerating potential of 25 kV, a specimen current of 30 nA and a beam diameter of 0.4 microns. Raw data were reduced on-line using a correction program based on atomic number, absorption and fluorescence (ZAF) correction factors to give oxide weight percents. The author's program MINCAL was used to calculate the chemical formula of each analyzed mineral, oxide percentage totals, and normalized mineral formulas.

All minerals were analyzed for nine elements: Si, Al, Ti, Fe, Mg, Ca, Na, K and F. During the initial stages of research, all minerals were routinely analyzed for these nine elements plus Cl and Mn. Analyses for Cl and Mn were abandoned after analyses of approximately thirty tremolite, talc and phlogopite grains indicated that the largest quantities of Cl and Mn present were 0.02 and 0.06 weight percent respectively. Analyses for Cr and Zn were not routinely made. Two tremolites that were analyzed contained 0.05 and 0.04 weight percent Cr and Zn respectively. One phlogopite sample that was identified by qualitative EDS electron microprobe analysis to contain significant amounts of Ba, was subsequently analyzed for Ba by WDS electron microprobe analysis.

In order to minimize ZAF correction factors applied to raw X-ray data, all standards used were chosen to be as close in composition to the mineral analyzed as possible. Both synthetic
Figure II.1 Mg/Mg+Fe versus Si in tremolite. Named fields from Robinson et al. (1982).

Figure II.2 Cation and anion distribution in tremolite. Unshaded areas represent the frequency of occurrence of each element in the site; the shaded areas represent the average proportion of the site occupied.
and natural standards were used. These are listed for each element and mineral in Table II.1.

Estimates of the lower limit of detection (LLD) for each element have been calculated using equations given by Jenkins and Devries (1969) and are listed for each element and mineral in Table II.1. The equations relate peak and background counting rates with counting time; a higher peak-to-background ratio and a longer counting time will result in a lower LLD. Because of the low peak-to-background ratio for F, approximately 4, an increased counting time of 100 seconds was chosen for this element. An increase in counting time from 30 to 100 seconds for F (and for K which was analyzed concurrently) resulted in a one-half decrease in the LLD for fluorine.

Estimates of analytical error based on counting statistics have also been calculated using equations given by Jenkins and Devries (1969). The equations used relate standard deviation of each element analyzed to peak and background counting rates and counting time. Additional sources of error such as variation of carbon coating thickness, surface irregularities, and transient variations in operating conditions have been considered in addition to the equations of Jenkins and Devries in setting the estimates of error for each element given in Table II.2.

Results of electron microprobe analyses are given in section II.4. Reported compositions are not averages, but represent the composition measured at a single a single point on a mineral grain. Each pair of analyses reported are from the rim
Table 11.2 Estimated 2-sigma error for electron microprobe analyses.

<table>
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<th>Element</th>
<th>Concentration (wt. percent)</th>
<th>Estimated Error (percent)</th>
</tr>
</thead>
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<tr>
<td>all</td>
<td>10</td>
<td>+/- 2</td>
</tr>
<tr>
<td>all</td>
<td>3-10</td>
<td>+/- 5</td>
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<tr>
<td>F</td>
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<tr>
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</tr>
<tr>
<td>all</td>
<td>0.5</td>
<td>+/- 20</td>
</tr>
</tbody>
</table>
of grains near the boundary between contiguous mineral pairs. Pairs are identified by number; letters following a pair number indicate multiple analyses at one spot. Mineral analyses were accepted if the sum of measured and calculated oxide weight percents was between 98.0 percent and 102.0 percent.

In general, agreement is very good between analyses of mineral pairs within a single thin section. With few exceptions, agreement is within the error limits given in Table II.2. In addition, agreement is good between analyses done at Carleton University and at BRGM-CNRS, France.

II.3 Mineral Chemistry

II.3a Tremolite

II.3a.1 Normalization Schemes

The number of cations in the chemical formula of each analyzed tremolite is calculated on the basis of 23 oxygens and is then normalized using procedures outlined by Laird and Albee (1981) and Robinson et al. (1982). Three normalization schemes have been considered. These are:

i) 13 cations except for Ca, Na and K (13eCNK);
   \[ \text{Total Cations} - (\text{Ca} + \text{Na} + \text{K}) = 13.000. \]

ii) 15 cations except for Na and K (15eNK);
   \[ \text{Total Cations} - (\text{Na} + \text{K}) = 15.000. \]

iii) 15 cations except for K (15eK);
    \[ \text{Total Cations} - (\text{K}) = 15.000. \]
Ideally, the normalization scheme chosen for any particular tremolite analysis is the one which gives the value for the total number of oxygens associated with all cations (cation-associated oxygen total) nearest to, but less than, the ideal total of 23. Detailed discussion of the merits and shortcomings of each scheme is given by Robinson et al. (1982) and will not be discussed here.

As noted by Robinson et al. (1982), difficulties arise when attempting to generate cation site distributions for near end-member amphiboles. This is because there are limited amounts of non-stoichiometric components available to substitute into unfilled site in near end-member amphiboles. For example, if normalized cation totals yield less than the ideal 23 cation-associated oxygens, Fe$^{2+}$ (FeO) can theoretically be converted to Fe$^{3+}$ (Fe$_2$O$_3$) to make up the missing oxygen. In this manner an estimate of Fe$^{3+}$ can be made. However, for the majority of tremolites analyzed in this study, the normalization scheme which gives a cation-associated oxygen total of less than 23 requires more Fe$^{3+}$ than total Fe to achieve this ideal sum. For this reason, the normalization scheme chosen for each tremolite analyzed is the one which gives the cation-associated oxygen total nearest to 23, regardless of whether the total is above or below this value.

Using this criterion, the most commonly used normalization scheme for tremolite is 15eNK which does not allow Ca to enter the A-site unless (Si+Al) total less than 8.000. This restricts Ca to the B-site (M4), or if present in excess of 2.000, to the
C-site (M1, M2, M3). The next most commonly used normalization scheme is 13eCNK which allows the questionable assignment of Ca to the A-site (Robinson et al., 1982). Lastly, the 15eK scheme is required for only two tremolites. This scheme allows only K to be assigned to the A-site. A minority of tremolites were not normalized because calculation of the number of cations based on 23 oxygens gave the cation-associated oxygen total nearest to 23.

Direct determination of Fe$^{2+}$ and Fe$^{3+}$ is not possible with the electron microprobe. Utilizing the method outlined above it is possible to obtain estimates of Fe$^{3+}$. However, this estimate is dependent on the normalization scheme used. Allen (1976) has shown that the presence of graphite in siliceous marbles from the Beaver Creek area is indicative of low oxygen fugacities and is consistent with the predominance of Fe$^{2+}$ over Fe$^{3+}$. The presence of graphite in many of the samples considered in this study is indicative of the predominance of Fe$^{2+}$ over Fe$^{3+}$ in these samples. Because of the low Fe contents present in samples analyzed in this study and inherent problems in estimating Fe$^{3+}$, no estimates of Fe$^{3+}$ have been made and Fe is reported in Appendix II as FeO.

II.3a.2 Cation Distribution

A plot of Mg/Mg+Fe against Si for all analyzed tremolites from the CMB is given in Figure II.1. All tremolites are uniformly Mg-rich; Mg/Mg+Fe ranges from 0.975 to 1.000 with a mean value of 0.988. Less consistency is seen in Si values
Figure II.1 Mg/Mg+Fe versus Si in tremolite. Named fields from Robinson et al. (1982).

Figure II.2 Cation and anion distribution in tremolite. Unshaded areas represent the frequency of occurrence of each element in the site; the shaded areas represent the average proportion of the site occupied.
which vary from 7.406 to 7.994 with a mean value of 7.748. Because in all analyses Ti is less than 0.50 (maximum value 0.022), and Na+K sum to less than 0.50 (maximum value 0.402), all analyzed amphiboles but two are true tremolites as defined by Leake (1978) and Robinson et al. (1982).

The remaining two amphiboles lie within the more aluminous tremolitic hornblende field. Because of the predominance of tremolite over tremolitic hornblende, all analyzed amphiboles will collectively be termed tremolite. The implicit assumption that Fe is present solely in the ferrous state has the effect of maximizing the calculated amount of Si in the mineral formula. In most cases this effect is not significant because of the low amounts of Fe in the tremolites analyzed.

The chemistries of analyzed tremolites from the CMB is shown in Figure II.2. For each element the frequency of its occurrence in each site (unshaded area), and the relative proportion of the site occupied (shaded area) are shown.

The two tetrahedrally coordinated sites in the tremolite structure (T1, T2) are together termed the T-site and are here assumed to contain only Si and Al. In most tremolites analyzed, the T-site is completely filled to its theoretical limit of 8.000; in no cases did Si exceed this amount. The T-site, on average comprises about 97 percent Si and 3 percent Al in tremolites from the Grenville Province. In a minority of analyses, (Si+Al) totalled less than 8.000; the minimum value was 7.927. Although theoretically possible, no Fe²⁺ or Ti⁴⁺ is assigned to
the T-site.

The three pseudo-octahedrally coordinated sites in the tremolite structure (M1, M2, M3) are collectively termed the C-site. Excess Al and Ti, Fe and Mg are assigned to this site and, if the total of these elements is less than 5.000, Ca is added to reach this amount. In all cases the C-site cation total is 5.000. In analyzed tremolites, Mg occupies an average of slightly more than 97 percent of the C-site; Al and Fe account for about 1 percent each and Ca generally accounts for the balance. Ti is negligible in all analyzed tremolites.

The eight-coordinated B-site is assigned excess Fe and Mg from the C-site, Ca, and Na if it is needed to reach the theoretical B-site limit of 2.000. The B-sites of analyzed tremolites comprise an average of 99 percent Ca and less than 1 percent combined Na, Mg and Fe. In only one analysis is the B-site total less than 2.000.

Excess Ca from the B-site, Na and K are assigned to the ideally unfilled tremolite A-site. This site is variably filled, with a mean value of 0.174 and ranges from 0.000 to 0.402. Figure 9 indicates that Na and K are present in the A-sites of over 96 percent of analyzed tremolites while Ca is present in slightly under 44 percent. Na is generally more abundant than either Ca or K; on average it occupies about 12 percent of the tremolite A-site.
**Figure II.3 Mg/Mg+Fe versus X_F in tremolite.**

**TALC: Mg_3Si_4O_10(OH)_2**

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<th>Min.</th>
<th>Mean</th>
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**Figure II.4 Cation and anion distribution in talc. Unshaded and shaded areas as for tremolite.**
II.3a.3 Anion Distribution

The H₂O content and the number of OH and F ions in the chemical formula for each analyzed tremolite is calculated on the basis of 24 oxygens using the procedure outlined by Deer, Howie and Zussman (1966). Using this method, OH and F are assumed to sum to 2.000; OH (and hence H₂O) is calculated by differences. The substitution of Cl for OH has been found to be insignificant in tremolites from siliceous carbonates of the CMB.

The magnitude of F-OH substitution varies significantly in tremolites analyzed in this study and elsewhere. Tremolite with up to \( X_F = 0.82 \) (Petersen et al., 1982) is known from the Balmat area, New York; the most F-rich tremolite identified in this study has F content \( X_F = 0.57 \). Anion distribution in tremolites from the CMB is shown in Figure II.2. Although the tremolites analyzed are not representative of tremolite in general, the large number of tremolites that exhibit significant F-OH substitution indicate that this is the most important deviation from ideal stoichiometry. Only one analyzed tremolite from the CMB contains no detectable F.

Previous studies including Allen (1976), Zaw and Clark (1978), and Valley and Essene (1980) have demonstrated an antithetic relationship between Fe and F. This has been termed Fe-F avoidance and has been explained in terms of increased strength of Mg-F bonds over Fe²⁺-F bonds by Ramberg (1952) and in terms of crystal field theory by Rosenberg and Foit (1977) (Valley et al., 1982). Examination of Figure II.3, a plot of Mg/Mg+Fe versus \( X_F \),
suggests that a weakly negative correlation with Mg/Mg+Fe exists. This is contrary to the Fe-F avoidance theory and indicates that this theory is incompatible with analyzed tremolites with high Mg/Mg+Fe ratios. This result is in agreement with Valley et al. (1982).

II.3b Talc

II.3b.1 Cation Distribution

The chemical formula for each analyzed talc is calculated on the basis of 11 oxygens and is then normalized such that: (Total Cations) - (Ca+Na+K) = 7,000. This method is termed the 7eCNK normalization scheme and assumes that within the tetrahedral and octahedral sheets of talc there are no large-radius sites capable of accepting Ca, Na or K. These ions are therefore assigned to interlayer positions as suggested by Deer et al. (1965) or can be considered as impurities within the talc crystal (C.Y. Chao, pers. comm., 1983).

The 7eCNK normalization scheme consistently yields cation-associated oxygen totals closer to the ideal value of 11 than the unnormalized calculation based on 11 oxygens. The result of the 7eCNK scheme is that, except where (Si+Al) sum to less than 4,000, all tetrahedral and octahedral sites are filled by Si, Al, Ti, Fe and Mg. Ca, Na and K are unconstrained, but are confined to the interlayer position.

Figure II.4 illustrates the mineral chemistry of analyzed talcs from the Grenville Province. All talcs are uniformly Si-
and Mg-rich. In the tetrahedral coordinated Z-site, Al substitutes for Si in slightly less than 92 percent of all talcs. On average, the Z-site comprises 99 percent Si with Al making up the remainder. In the octahedral Y-site Mg accounts for an average 99 percent of the site while Al, Ti and Fe together occupy the remaining sites. The "interlayer" site ranges from a minimum of 0.010 to a maximum of 0.108 with a mean value of 0.046. Na accounts for the majority of the ions present in this site.

II.3b.2 Anion Distribution

The amount of H₂O and the number of OH and F ions in the chemical formula for each talc analyzed are calculated on the basis of twelve oxygens; (OH+F) is assumed to equal 2.000. The distribution of OH and F in analyzed talcs from the CMB is shown in Figure 11. All talcs contain detectable quantities of F. The minimum F content is 0.071 (Xₖ=0.036) and the maximum is 0.905 (Xₖ=0.453) which is the highest F content known to exist in naturally occurring talc. Duffy (1977) and Duffy and Greenwood (1979, Figure 3) report the existence of synthetic talc with Xₖ equal to about 0.6 coexisting with F-rich norbergite.

Allen (1976) reported that higher F contents in talc corresponded to lower Fe contents. In the present study, F-content cannot be shown to vary systematically with Fe-content. Because of the high Mg/Mg+Fe ratios for analyzed talcs (minimum Mg/Mg+Fe = 0.983), this data should not be taken as negative evidence for the Fe-F avoidance theory (e.g. Rosenberg and Foit, 1977).
II.3c Phlogopite

II.3c.1 Cation Distribution

The number of cations in the chemical formula for each analyzed phlogopite is calculated on the basis of 11 oxygens and is then normalized using the 7eCNK normalization scheme (Normalization scheme "A" of Dymek, 1983). The 7eCNK normalization scheme results in complete filling of both the tetrahedral and octahedral sites and excludes Ca, Na and K from the normalization. These elements are together assigned to the phlogopite interlayer site. In all analyzed phlogopites, the 7eCNK scheme gives cation-associated oxygen totals superior to the unnormalized calculation based on 11 oxygens. An alternative normalization scheme proposed by Dymek (1983) was not used because of insignificant amounts of Al and Ti assigned to the octahedral phlogopite Y-site in phlogopites of the CMB.

Various authors have set arbitrary limits on the composition of phlogopite. Bailey (1980) set the minimum Mg/Mg+Fe ratio at 0.70 for phlogopite while Deer et al. (1966) set this value at 0.67. A plot of Mg/Mg+Fe versus octahedral Al is given in Figure 11.5. Both Fe and octahedral Al are very low in these phlogopites; all Mg/Mg+Fe ratios are above 0.96 and octahedral Al is in all cases less than 0.20; only in one sample (four analyses) was octahedral Al greater than 0.10. The name phlogopite is therefore justified and will be used for all such micas analyzed in this study.
Figure II.5  Mg/Mg+Fe versus octahedral Al in phlogopite. Named fields from Bailey (1980).

PHLOGOPITE:  $K_2Mg_3Al_3Si_3O_{10}(OH)_2$

<table>
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<tr>
<th>Site</th>
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Figure II.6  Cation and anion distribution in phlogopite. Unshaded and shaded areas as for tremolite and talc.
In phlogopites from all but one sample, the tetrahedrally coordinated Z-site is completely filled such that (Si+Al) sum to 4.000. The proportions of Si to Al in the Z-site are shown in Figure II.6, which shows Si and Al occupying 75 and 23 percent of this site respectively. This is almost exactly the stoichiometric ratio of three Si to one Al. Although Ti$^{4+}$ and Fe$^{3+}$ may occupy a part of the Z-site, this substitution has not been considered due to low total Ti and Fe values and to large uncertainties involved in determining cation valency distribution from electron microprobe data.

Excess Al, Ti, Fe and Mg were assigned to the octahedrally coordinated Y-site. Mg, Al and Fe are present in all phlogopites; Mg accounts for 96 percent of the Y-site and Al and Fe for slightly less than 2 percent each. Ti is present in most analyzed phlogopites, but accounts for less than 0.5 percent of the Y-site.

All Ca, Na and K are assumed to occupy the interlayer X-site in phlogopite. K occupies an average of 87 percent of this site while Na and Ca occupy an average of 6 and 1 percent respectively. The X-site is completely filled in only one analyzed phlogopite. X-site totals range from 0.794 to 1.012 with a mean value of 0.938, or about 94 percent.

II.3c.2 Anion Distribution

The $\text{H}_2\text{O}$ content and the number of OH and F ions in the chemical formula of each analyzed phlogopite is calculated on the
Figure II.7 Mole fraction $F$ versus total Fe in phlogopite.
basis of twelve oxygens; (OH+F) is assumed to equal 2.000. Of the three minerals analyzed, phlogopite exhibits the greatest range of F-OH substitution. The distribution of F and OH in analyzed phlogopites from the CMB is shown in Figure 11.6. In these phlogopites the minimum measured F-content was 0.233 (X_f=0.117) and the highest was 1.560 (X_f=0.780). Naturally occurring phlogopite of up to X_f=0.96 have been reported in the Balmat area, New York, by Petersen et al. (1982).

In contrast to tremolite and talc, phlogopite does show an antithetic relationship between F and Fe contents, consistent with Fe-F avoidance. Figure 11.7, a plot of X_f versus Fe for phlogopites indicates a negative correlation between Fe and F (R=-0.6397). Phlogopite also exhibits clearly defined correlations between F-content and other elements. Si, Mg, Na and, with less certainty, Ca, show positive correlation with X_f while Al^IV, Al^VI, Ti, Fe and, with less certainty, K, show negative correlation. These interrelationships require further investigation, but the documented correlations suggest coupled substitutions involving both cation and anion components.
11.4 Electron Microprobe Analyses
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| Ti | 7.976 | 7.976 | 7.976 | 7.976 | 7.976 | 7.976 | 7.976 | 7.976 |
| Fe | 006   | 006   | 006   | 006   | 006   | 006   | 006   | 006   |
| Na | 013   | 013   | 013   | 013   | 013   | 013   | 013   | 013   |
| Fe | 006   | 006   | 006   | 006   | 006   | 006   | 006   | 006   |
| Mg | 006   | 006   | 006   | 006   | 006   | 006   | 006   | 006   |
| Ca | 2.064 | 2.064 | 2.064 | 2.064 | 2.064 | 2.064 | 2.064 | 2.064 |
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| K  | 0.14  | 0.14  | 0.14  | 0.14  | 0.14  | 0.14  | 0.14  | 0.14  |
| OH | 1.255 | 1.255 | 1.255 | 1.255 | 1.255 | 1.255 | 1.255 | 1.255 |
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## Calculated Formulas

- **SiO2**
- **Al2O3**
- **TiO2**
- **Fe2O3**
- **MgO**
- **CaO**
- **Na2O**
- **K2O**
- **OH**
- **F**

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### Notes

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- **Al2O3**
- **TiO2**
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- **MgO**
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### Notes

- The table above shows the composition of the samples expressed as weight percentages.
- The calculated formulas are based on the stoichiometric ratios of the elements present.\n
---

### Additional Data

- The table includes columns for Si, Al, Ti, Fe, Mg, Ca, Na, K, and Total.
- The values are given in weight percentages for each element.

---

### Conclusion

The data presented above provide a detailed analysis of the composition of the samples, allowing for a comprehensive understanding of their chemical makeup.
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**CALCULATED FORMULAS**

- **Si**: 3.91
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- **Ti**: 0.12
- **Fe**: 0.12
- **Mg**: 0.26
- **Ca**: 0.11
- **Na**: 0.06
- **K**: 0.43
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**CALCULATED FORMULAS**

- **Si**
- **Al**
- **Ca**
- **Na**
- **K**
- **Mg**

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*Note: The table contains mineral compositions and calculated formulas for various samples.*
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APPENDIX III

COMPUTER PROGRAMS

III.1 MINCAL

III.2 SOLCRV
142

PROGRAM MINDX

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59  57,000  END IF
60  61,000  WPOX(15)=0.
61  61,000  READ(106,15) (EL(IA),IA=1,12)
62  62,000  FORMAT(12(2X,A2))
63  63,000  DO 10 IR=1,12
64  64,000  IF(EL(IR).EQ.'AL') NAL=1B
65  65,000  IF(EL(IR).EQ.'CA') NCA=IR
66  66,000  IF(EL(IR).EQ.'CL') NCL=1B
67  67,000  IF(EL(IR).EQ.'F') NF=1B
68  68,000  IF(EL(IR).EQ.'FE') NFE=1B
69  69,000  IF(EL(IR).EQ.'K') NK=1B
70  70,000  IF(EL(IR).EQ.'AG') NAG=1B
71  71,000  IF(EL(IR).EQ.'MN') NM=1B
72  72,000  IF(EL(IR).EQ.'NA') NNA=1B
73  73,000  IF(EL(IR).EQ.'AS') NSA=1B
74  74,000  IF(EL(IR).EQ.'I') NI=1B
75  75,000  IF(EL(IR).EQ.'CA') NC(1)=0 DO 10
76  76,000  10 CONTINUE
77  77,000  17 NEL=IB-1
78  78,000  DO 20 IC=1,CCO
79  79,000  READ (106,25)END=97) SL PR M
80  80,000  FORMAT (A11,'A2')
81  81,000  READ (106,35) (UPOX IE),IE=1, NEL)
82  82,000  FORMAT (15F5.2)
83  83,000  IF (MIN.EQ.'CH') GO TO 20
84  84,000  WRITE (107,'(52)
85  85,000  65,000  125 FORMAT (//11X,'76(=',:))
86  86,000  137 DO 30 ID=1,15
87  87,000  127 MODPR(ID)=0.
88  88,000  186 APOX(ID)=0.
89  89,000  189 FORAM1(ID)=0.
90  90,000  189 FORAM2(ID)=0.
91  91,000  189 FORAM3(ID)=0.
92  92,000  189 CONTINUE
93  93,000  30 TOTAL=0.
94  94,000  30 APOX=0.
95  95,000  30 DO 40 IF=1, NEL
96  96,000  40 TOTAL=TOTAL+WPOX(IF)
97  97,000  40 CONTINUE
98  98,000  40 MODFCL=(WPOX(NF)*MWD/(2.0*MMF)+WPOX(NCL)*MWD/(2.0*MMCL))
99  99,000  40 CONTINUE
100  100,000  100 TOTAL=TOTAL-MODFCL
101  101,000  100 MODPR(1)=WPOX(NST)/MMST
102  102,000  100 MODPR(2)=WPOX(NAL)/MMAL
103  103,000  100 MODPR(3)=WPOX(NNI)/MMNI
104  104,000  100 MODPR(4)=WPOX(NFE)/MMFE
105  105,000  100 MODPR(5)=WPOX(NAG)/MMAG
106  106,000  100 MODPR(6)=WPOX(NNA)/MNNA
107  107,000  100 MODPR(7)=WPOX(NCA)/MNCAX
108  108,000  100 MODPR(8)=WPOX(NCA)/MNCA
109  109,000  100 MODPR(9)=WPOX(NCA)/MNCA
110  110,000  100 MODPR(10)=WPOX(NCC)/MNCC
111  111,000  100 MODPR(11)=WPOX(NCL)/MNCL
112  112,000  100 APOX(1)=2.0 MODPR(1)
113  113,000  100 APOX(2)=6.0 MODPR(2)
114  114,000  100 APOX(3)=2.0 MODPR(3)
115  115,000  DO 50 IG=4,12
116  116,000  50 CONTINUE
117  117,000  50 APOX(16)=MODPR(16)
DO 50 IH=1,M
120 APOXI=APOXI+APOX(IH)
121 CONTINUE
122 APOXT=APOXT-0.5*HMLPR(I1)+HMLPR(I2)
123 IF (MIN.EQ. 'TR') THEN
124   OXY=24.
125   OH=2.
126   TET=8.
127 ELSE IF (MIN.EQ. 'TC' .OR. MIN.EQ. 'PH') THEN
128   OXY=12.
129   OH=2.
130   TET=4.
131 ELSE IF (MIN.EQ. 'OH') THEN
132   OXY=18.
133   OH=8.
134   TET=4.
135 ELSE
136   WRITE (106,45)
137   FORMAT (11G4.5)
138   STOP
139 END IF
140 APOX(10)=(OXY*(APOXI+APOX(12)))-OHX*(AROXT+APOX(11))
141 APOX(12))/(OH-2.*OXY)
142 WPX2=(APOXI+WPX2)
143 HMLR(10)=APOX(10)
144 HMLR(12)=APOX(12)
145 T=OXY-1.*/APOXI
146 46.000 C
147 WTPC(1)=WPOX(NT)
148 WTPC(2)=WPOX(NL)
149 WTPC(3)=WPOX(NM)
150 WTPC(4)=WPOX(NH)
151 WTPC(5)=WPOX(NO)
152 WTPC(6)=WPOX(NP)
153 WTPC(7)=WPOX(NA)
154 WTPC(8)=WPOX(NN)
155 WTPC(9)=WPOX(NK)
156 WTPC(10)=WPX2
157 WTPC(11)=WPOX(NF)
158 WTPC(12)=WPOX(NH)
159 WTPC(13)=WPOX(NI)
160 WTPC(14)=WPOX(NH)
161 WTPC(15)=WPOX(NH)
163 MULT=1.0
164 NIT=0
165 TET=OXY*(APOXI+APOX(10)+APOX(12))+HMLR(11)
166 CALL FORMCAL (FORAMA, APOXI, TET, TET, OH, MULT-1.0, MIN)
167 CALL NUMBERS (FORAMA, OXY, CAT1, CAT2, CAT3, MULT, MIN)
168 IF (MIN.EQ. 'TR') THEN
169 MULT=13./CAT1
170 MULT=15./CAT2
171 MULT=15./CAT3
172 ELSE IF (MIN.EQ. 'TC') THEN
173 MULT=17./CAT1
174 MULT=17./CAT2
175 ELSE IF (MIN.EQ. 'PH') THEN
176 MULT=17./CAT1
177 MULT=8./CAT2
178 END IF
126  =  179.000
128  =  184.000
129  =  185.000
130  =  186.000
132  =  188.000
133  =  189.000
137  =  190.000
138  =  192.000
143  =  194.000
144  =  195.000
146  =  196.000
147  =  197.000
149  =  198.000
152  =  199.000
153  =  200.000
155  =  201.000
156  =  202.000
158  =  203.000
160  =  204.000
162  =  205.000
164  =  206.000
165  =  207.000
167  =  208.000
168  =  209.000
170  =  210.000
172  =  211.000
173  =  212.000
174  =  213.000
176  =  214.000
178  =  215.000
180  =  216.000
181  =  217.000
182  =  218.000
183  =  219.000
184  =  220.000
186  =  221.000
187  =  222.000
188  =  223.000
189  =  224.000
191  =  225.000
192  =  226.000
193  =  227.000
194  =  228.000
195  =  229.000
196  =  230.000
197  =  231.000
198  =  232.000
199  =  233.000
201  =  234.000
202  =  235.000
203  =  236.000
204  =  237.000
205  =  238.000

180   CALL FORMCAL (FORAM2APC4X1TEETE1H+MULTYNTITMIN)
182   CALL NUMBERS (FORAM2TOXYL1CAT20C5CAT3MIN)
183   IF (MINMAXTC) THEN
184   NIT=
185   CALL FORMCAL (FORAM3APX0X1TEETE0HMULTYNTIMIN)
186   CALL NUMBERS (FORAM3TOXYL1CAT20C5CAT3MIN)
187   IF (MINMAXPH) THEN
188   NIT=3
189   CALL FORMCAL (FORAM4APX0X1TEETE0HMULT11MIN)
190   CALL NUMBERS (FORAM4TOXYL1CAT20C5CAT3MIN)
191   END IF
192   END IF
193   WRITE (107,55) SLPRMIN
194   WRITE (107,55) ANALYSIS: 61,2X+2X+1X+?2
195   WRITE (107,55) (MINEQTR) WRITE (107,55)
197   FORMAT (12X,0X14X,11X,1X,ENK,10X,1SEK)
198   IF (MINEQTC) WRITE (107,175)
200   FORMAT (12X,0X14X,11X,1X,ENK)
201   IF (MINEQPH) WRITE (107,185)
202   FORMAT (12X,0X14X,11X,1X,ENK)
209   DO 70 J=1,14
210   IF (IIJEOEQ6, AND, NMEQ15) GO TO 70
211   IF (IIJEOEQ12, AND, NMEQ15) GO TO 70
212   WRITE (107,55) TITL4(IIJ), WTP(IIJ)
213   IF (MINEQTC) WRITE (107,225) TITL4(IIJ), WTP(IIJ)
214   IF (MINEQPH) WRITE (107,235) TITL4(IIJ), WTP(IIJ)
215   FORMAT (12X,0X14X,11X,1X,ENK)
216   FORMAT (12X,0X14X,11X,1X,ENK)
217   CONTINUE
218   IF (MINEQTR) WRITE (107,95) TOXYL1TOXYL2TOXY3TOXY4
219   IF (MINEQTC) WRITE (107,95) TOXYL1TOXY2
220   IF (MINEQPH) WRITE (107,95) TOXYL1TOXY2
221   FORMAT (22X,OXYGENS,11X,FL7,0,8X)
222   IF (OUTEQYF) THEN
223   MIN='1'
224   WRITE (109,135) SLPRMINFORAM2(I), IT1=1,13,TOXY
225   WRITE (110,135) SLPRMINFORAM3(I), IT1=1,13,TOXY
226   WRITE (111,35) SLPRMINFORAM4(I), IT1=1,13,TOXY
227   FORMAT (12X,15X,5X,2X,13F6,3,F7,3)
228   ELSE IF (MINEQTC) THEN
229   MIN='2'
230   WRITE (113,135) SLPRMINFORAM2(IV), IV=1,13,TOXY2
231   ELSE IF (MINEQPH) THEN
232   MIN='3'
233   WRITE (114,135) SLPRMINFORAM1(IV), IT1=1,13,TOXY2
234   END IF
235   CONTINUE
236   CONTINUE
237   STOP
238   END
SUBROUTINE FORMCAL (FORAM,APOX,T,TEE,1ET,OH,MULT,M1,M2)

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

CHARACTER MINT

DIMENSION FORAM(15),APOX(15)

FORAM(1)=APOX(1)*MULT/2,

FORAM(2)=APOX(2)*MULT/3,

FORAM(3)=0.

IF ((FORAM(1)+FORAM(2)) .GT. TET) THEN

FORAM(2)=10-FORAM(1)

IF (FORAM(2) .LE. 2.) FORAM(2)=0.

FORAM(3)=APOX(2)*MULT/3-MULT/3.

END IF

FORAM(4)=APOX(3)*MULT/2.

FORAM(5)=APOX(4)*MULT.

FORAM(6)=APOX(5)*MULT.

FORAM(7)=APOX(6)*MULT.

FORAM(8)=APOX(7)*MULT.

FORAM(9)=APOX(8)*MULT.

FORAM(10)=APOX(9)*MULT.

FORAM(11)=APOX(10)*TEE.

FORAM(12)=APOX(12)*TEE.

FORAM(13)=APOX(13)*TEE.

FORAM(14)=FORAM(13)/OH.

IF (MIN.EQ.'TR') THEN

FORAM(10)=FORAM(10)/MULT.

IF (N1.NE.0 .OR. N1.EQ.2) FORAM(1)=FORAM(9)/MULT.

IF (N1.EQ.1) FORAM(9)=FORAM(8)/MULT.

ELSE IF ('(M1.EQ.'TH') .AND. N1.EQ.1 .OR. (MIN.EQ.'TC') THEN

FORAM(10)=FORAM(10)/MULT.

FORAM(9)=FORAM(9)/MULT.

FORAM(8)=FORAM(8)/MULT.

END IF

RETURN

END
III.2 SOLCRV
**Program SOLCRV**

**Purpose:** A program to calculate non-ideal solution distribution curves for one- or two-constant Margules solution model

**Variables:**
- M: Molar quantity of component 1
- N: Molar quantity of component 2
- X: Mole fraction of component 1
- Y: Mole fraction of component 2
- H: Molar enthalpy of solution
- S: Molar entropy of solution
- V: Molar volume of solution
- A: Activity coefficient of component 1
- B: Activity coefficient of component 2

**Constants:**
- R: Gas constant
- T: Temperature

**Equations:**
- Gibbs-Duhem equation
- Margules equation

**Subroutines:**
- CHECK1
- CHECK2

**Data Input:**
- LNK: Link to equilibrium constant

**Output:**
- Results of calculated distribution curves

**Implementation:**
- Input data: M, N, X, Y
- Compute H, S, V
- Calculate A, B
- Solve Gibbs-Duhem and Margules equations
- Print results
59 59.000 55
60 60.000 66
61 61.000 66
62 62.000 66
63 63.000 66
64 64.000 66
65 65.000 66
66 66.000 66
67 67.000 66
68 68.000 66
69 69.000 66
70 70.000 66
71 71.000 66
72 72.000 66
73 73.000 66
74 74.000 66
75 75.000 66
76 76.000 66
77 77.000 66
78 78.000 66
79 79.000 66
80 80.000 66
81 81.000 66
82 82.000 66
83 83.000 66
84 84.000 66
85 85.000 66
86 86.000 66
87 87.000 66
88 88.000 66
89 89.000 66
90 90.000 66
91 91.000 66
92 92.000 66
93 93.000 66
94 94.000 66
95 95.000 66
96 96.000 66
97 97.000 66
98 98.000 66
99 99.000 66
100 100.000 66
101 101.000 66
102 102.000 66
103 103.000 66
104 104.000 66
105 105.000 66
106 106.000 66
107 107.000 66
108 108.000 66
109 109.000 66
110 110.000 66

FORMAT (5F10.5)
WRITE (106, 65) LEXP(LNK), LNK, M1, M2, H1, H2
FORMAT (5F10.5)
WRITE (106, 65) C1, C2, C3, C4, C5, C6, C7, C8
ENDIF
ELSE
WRITE (108, 75) SOLTY
FORMAT ('**', A3, ' UNRECOGNIZED AS SOLUTION MODEL TYPE
**')
STOP
END IF
DO 20 IT=1,19
YB=DFLDAT(IK)*.05
XAPR=XAI
IF (IX.EQ.1.OR.ITER.GT.99) THEN
XAI=.001
XAPR=XAI
ENDIF
DO 30 IER=1,100
XAI=(XAI+XAPR)/2
IF (SOLTY.EQ.‘ONE’) THEN
CK=CHECK1(LNK, M1, M2, H1, H2, XAI, XB)
IF (DABS(CK).LT.10) GO TO 17
ENDIF
ELSE IF (SOLTY.EQ.‘TWO’) THEN
CK=CHECK2(LNK, M1, M2, H1, H2, XAI, XB)
IF (DABS(CK).LT.10) GO TO 17
ENDIF
CONTINUE
WRITE (108, 85) XB, XAI, CK, IER
FORMAT (5X-F10.3, T23, 'XAI NOT FOUND AFTER 100 ITERATIONS')
GO TO 20
END IF
CONTINUE
WRITE (108, 95) XB, XAI, CK, IER
FORMAT (5X-F10.3, 5X-D12.5, 6X-D12.5)
XAI=XAI-(XAI-XAPR)/2
IF (XAI.LE.0.) XAI=0.001
IF (XAI.GE.1.) XAI=0.999
CONTINUE
APPENDIX IV

NONLINEAR REGRESSION

METHODS

IV.1 BMDP control program for talc-tremolite
distribution data

IV.2 Nonlinear regression using data of Saxena (1973)
14:30 Dec 96 '83 Stats20.PJ020148

1 1.000 IE=0 NAME=NOLIN20
2 2.000 IE=2 NAME=MOMENT=250,TIME=5:100
3 3.000 IE=2 SET 2 GRCTER=3045041
4 4.000 IE=2 BEMED PROG=DF;#X=.133;#Y=4;#F=REFS20
5 5.000 IE=2 YFWU
6 6.000 IE=2 DIMENSNC 100 ROOT(1)
7 7.000 IE=2 TOL=1.0E-6
8 8.000 IE=2 WEST=X
9 9.000 IE=2 NWROT=0
10 10.000 IE=2 DO 100 WN=0.05,0.95,0.95
11 11.000 IE=2 W=WN
12 12.000 IE=2 IF 100 IC=15
13 13.000 IE=2 WN=0.05*W/(W-1, X(2))/X(1)*X(2)*X(1, W-1)) - P(1)
14 14.000 IE=2 $ 4F(5)*3.3*NF2-4.3*W11, W11
15 15.000 IE=2 $ -F(3)*3.3*NF2-2.6*N
16 16.000 IE=2 FPWU=1.0/UN+1.(1-WN+1.2*X(2, W-1)) * P(3)*X(2)*X(2, W-1))
17 17.000 IE=2 WN=UN-FWU/FPWU
18 18.000 IE=2 IF (NP1<0.01) OR (WN=1.0E-4) GO TO 100
19 19.000 IE=2 E-DAUB(NP1-UN)
20 20.000 IE=2 IF (E.LT.10) THEN
21 21.000 IE=2 WROT=NP1+1.
22 22.000 IE=2 ROOT(NROOT)=NP1
23 23.000 IE=2 NROOT=NROOT+1.
24 24.000 IE=2 GO TO 100
25 25.000 IE=2 END IF
26 26.000 IE=2 UN=NP1
27 27.000 IE=2 CONTINUE
28 28.000 IE=2 CONTINUE
29 29.000 IE=2 IF (WROT.EQ.0) THEN
30 30.000 IE=2 PRINT 105
31 31.000 IE=2 PRINT 105 , WROT(1),WROT(2),WROT(3),WROT(4),WROT(5),WROT(6)
32 32.000 IE=2 FORMAT ('W10.5','W10.5','W10.5','W10.5','W10.5','W10.5')
33 33.000 IE=2 STOP
34 34.000 IE=2 END IF
35 35.000 IE=2 IF (DIFF 101.1) THEN
36 36.000 IE=2 IF (DIFF.EQ.1.0) THEN
37 37.000 IE=2 DO 120 K=1,NROOT
38 38.000 IE=2 DIFF2=DAUB(Root(K)-WROT)
39 39.000 IE=2 IF (DIFF2.LT.1.0E-6) F=ROOT(K)
40 40.000 IE=2 CONTINUE
41 41.000 IE=2 ZERD
42 42.000 IE=2 TITLE IS TALE - 2KI TREM - IDEAL; NONLINEAR; GRCTER
43 43.000 IE=2 INPUT VARIOUS ARE 0.
44 44.000 IE=2 FORMAT IS 210.31.
45 45.000 IE=2 UNIT IS 5.
46 46.000 IE=2 VARIABLES ARE XFB, XFT.
47 47.000 IE=2 DEPENDENT IS XFT.
48 48.000 IE=2 PARAMETERS ARE 3.
49 49.000 IE=2 MAXIMUM ARE -3.043.0,3.0.
50 50.000 IE=2 MINIMUM ARE -3.0,-3.0,-3.0.
51 51.000 IE=2 END

IV.2a Data (from Saxena, 1973)

<table>
<thead>
<tr>
<th>$x_{cum}^{Fe}$</th>
<th>$x_{act}^{Fe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.783</td>
<td>0.714</td>
</tr>
<tr>
<td>0.668</td>
<td>0.560</td>
</tr>
<tr>
<td>0.652</td>
<td>0.547</td>
</tr>
<tr>
<td>0.580</td>
<td>0.427</td>
</tr>
<tr>
<td>0.457</td>
<td>0.307</td>
</tr>
<tr>
<td>0.230</td>
<td>0.129</td>
</tr>
</tbody>
</table>

IV.2b Nonlinear regression

The control program for BMDP program AR, "Derivative-Free Nonlinear Regression," described in Dixon and Brown (1979), is given on the following page. In the FORTRAN subprogram inserted by the user,

\[
P(1) = \ln K
\]
\[
P(2) = w_{cum}^{Fe}/RT
\]
\[
P(3) = w_{cum}^{Mg}/RT
\]
\[
P(4) = w_{act}^{Fe}/RT
\]
\[
P(5) = w_{act}^{Mg}/RT
\]

IV.2c Results of nonlinear regression

The calculated values for $\ln K$ and the four Margules parameters are:

\[
\ln K = 0.229316
\]
\[
w_{cum}^{Fe}/RT = 1.30490
\]
\[
w_{cum}^{Mg}/RT = 2.08520
\]
\[
w_{act}^{Fe}/RT = 1.88131
\]
\[
w_{act}^{Mg}/RT = 1.95152
\]

These values have been used to reproduce the Fe distribution curve between cummingtonite (cum) and actinolite (act) shown in Figure 10.
1.000 JOB NAME=SAXSTATS
2.000 RESOURCE MEMORY=250; TIME=5:00
3.000 SET 3 SAXMAYT
4.000 BIMETH 1=PROG=AR; XMEM=123; OUT=RES20
5.000 XFUN
6.000 DIMENSION ROOT(10)
7.000 TOL=1.0E-07
8.000 WEST=X(1)
9.000 NROOT=0
10.000 DO 100 WIN=0.05,0.95,0.05
11.000 WN=WN+
12.000 DO 110 J=1,15
13.000 FWN=ILN(WN)+(1.-X(2))/'(X(2)**1/(1.-WIN));-P(1)
14.000 IF (WN**3.25)**2.4-WN**2.4+1.)
15.000 & 4.0
16.000 & (X(3)**2.0)**2.0+5.0*X(4-1.1)
17.000 & (X(5)**2.0)**2.0+5.0*(X(2)**2.0)**2.0
18.000 & FPWN=1./WN+1./WIN+P(2)**2.0-4.0*WN**4.0-P(3)**2.0*6.0*WN**2.0
19.000 IF (FPWN.LT.TOL) THEN
20.000 IP=IP+1.
21.000 DO 250 WN=WN-1.0
22.000 IF (E(WN).LT.E(0.0)) GO TO 100
23.000 GO TO 250
24.000 RC=R(C)R(WN)=1.0
25.000 GO TO 250
26.000 END IF
27.000 WN=WN1
28.000 110 CONTINUE
29.000 100 CONTINUE
30.000 IF (NROOT.EQ.0) THEN
31.000 PRINT 105
32.000 FORMAT ('NO CONVERGENCE NOT ACHIEVED')
33.000 PRINT 105, (X(N),W(N)=1.2)*(PLI)**1.3
34.000 FORMAT ('U: Y: P(XZ,2FB.3)'/P(1) TO P(3)'/4FB.4.
35.000 100(I)
36.000 STOP
37.000 END IF
38.000 105 DO 250 WN=WN+1.0
39.000 IF (WN.LT.WN1) GO TO 100
40.000 IF (DIFF2.LT.DIFF1) F=ROOT(K)
41.000 GO TO 100
42.000 CONTINUE
43.000 ZEDB
44.000 /PROBLEM TITLE IS 'NONLINEAR REGRESSION FOR FE EXCHANGE BETWEEN'
45.000 CUMMINGTONITE AND ACTINOLITE DATA OF SAXENA
46.000 (1973)
47.000 /INPUT
48.000 VARIABLES ARE 2.
49.000 FORMAT IS ('2F10.3').
50.000 UNIT IS 5.
51.000 VARIABLES ARE XFECUM, XFECT.
52.000 /REDRESS DEPENDENT IS XFECUM.
53.000 PARAMETERS ARE 5.
54.000 /PARAMETER醫NALS ARE 1.0,0.1,0.1,0.1,0.1.
55.000 /END
56.000
END

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FIN