1

National Library
of Canada

Bibliothèque nationale
du Canada

Canadian Theses Service Services des thèses canadiennes

Ottawa, Canada
K1A 0N4

CANADIAN THESES

THÈSES CANADIENNES

NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

Les documents qui ont déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

**THIS DISSERTATION
HAS BEEN MICROFILMED
EXACTLY AS RECEIVED**

**LA THÈSE A ÉTÉ
MICROFILMÉE TELLE QUE
NOUS L'AVONS REÇUE**

National Library
of CanadaBibliothèque nationale
du Canada

Canadian Theses Division

Division des thèses canadiennes

Ottawa, Canada
K1A 0N4**PERMISSION TO MICROFILM — AUTORISATION DE MICROFILMER**

• Please print or type — Écrire en lettres moulées ou dactylographier

Full Name of Author — Nom complet de l'auteur

HUGH JAMES ABERCROMBIE

Date of Birth — Date de naissance

12 November, 1956

Country of Birth — Lieu de naissance

CANADA

Permanent Address — Résidence fixe

250^W Rockland Road, North Vancouver, British Columbia V7N 2W3

Title of Thesis — Titre de la thèse

Partitioning of Fluorine Between Tremolite, Talc and Phlogopite.

University — Université

Carleton University

Degree for which thesis was presented — Grade pour lequel cette thèse fut présentée

MSc.

Year this degree conferred — Année d'obtention de ce grade

1984

Name of Supervisor — Nom du directeur de thèse

Dr. G.B. Skippen

Permission is hereby granted to the NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission

L'autorisation est, par la présente, accordée à la BIBLIOTHÈQUE NATIONALE DU CANADA de microfilmer cette thèse et de prêter ou de vendre des exemplaires du film

L'auteur se réserve les autres droits de publication, ni la thèse ni de longs extraits de celle-ci ne doivent être imprimés ou autrement reproduits sans l'autorisation écrite de l'auteur.

Date

January 31, 1984

Signature

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

Copyright 1983

The undersigned hereby recommend to the Faculty of Graduate Studies, acceptance of this thesis submitted by Hugh James Abercrombie, B.Sc. (Honours), in partial fulfilment of the requirements for the degree of Master of Science.

A handwritten signature in dark ink, appearing to read "J.B. Kipper", is written over a horizontal line.

Thesis Supervisor

A handwritten signature in dark ink, appearing to read "J.E. Donaldson", is written over a horizontal line.

Chairman, Department of Geology

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_{CO₂} 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 KAlO₂-present system is rendered invalid in T-X_{CO₂} 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

I would like to thank Dr. G.B. Skippen for initially proposing this research, for his support throughout its growth and for his perceptive criticisms in its final stages. I also thank Drs. G.B. Skippen and V. Trommsdorff for giving me the opportunity to experience Alpine geology first hand.

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 greatly 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	iii
Acknowledgments	iv
Table of Contents	v
List of Figures	viii
List of Tables	ix
List of Plates	x
 I INTRODUCTION	 1
Introduction	1
Symbols, Units and Abbreviations	3
Previous Work	3
F-OH Exchange	3
Phase Relations	7
Field Research	8
 II GEOLOGICAL SETTING	 13
Regional Geology	13
Regional Metamorphism	15
Talc Occurrences	19
 III SOLUTION MODELLING	 23
Observed Behaviour	23
Talc-Tremolite	23
Phlogopite-Tremolite	29
F-OH Exchange Equilibria	31

TABLE OF CONTENTS

Solution Models	33
Symmetric Solution Model	33
Asymmetric Solution Model	35
Calculation of the Model	36
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 _{CO₂} 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 _{CO₂} section for the system CaO-MgO-SiO ₂ -H ₂ O-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 $X_F\text{-phlogopite} > X_F\text{-tremolite} > X_F\text{-talc}$ 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 S.I. 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 Foit, 1977).

Table 1. Symbols, units and abbreviations.

Symbols	
a	Activity
f	Fugacity
H_f^0	Standard molal enthalpy of formation from the elements
$\Delta H_{Tr,Pr}$	Standard molal enthalpy of reaction at Tr, Pr
i, j	Subscripts indicate components
$K(n)$	Equilibrium constant; reaction n
$K_D(n)$	Distribution coefficient; reaction n
R	Gas constant
S^0	Standard molal entropy of formation from the elements
$\Delta S_{Tr,Pr}$	Standard molal entropy of reaction at Tr, Pr
Tr, Pr	Reference temperature and pressure; 298.15 K, 0.1 MPa (25 °C, 1 bar)
V_s^0	Standard molal volume of solids
$W_{Mg_3Si_4O_{10}(OH)_2}$	Excess partial molar free energy at infinite dilution of subscripted component
x, x_F^{TC}	Mole fraction; mole fraction F in talc
$x_F(1)$	Fluorine substitution level (1)
γ_i	Activity coefficient for component i
$\nu_{i,TC}$	Reaction coefficient for component i or subscripted phase

Table 1. Continued

Units	
°C	Degrees Celsius
dm	Decimetre
j	Joule
K	Degrees Kelvin
mol	Mole
MPa	Megapascal (100 MPa = 1.0 Kb)
nA	Nanoampere
um	Micrometre

Abbreviations

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

Normalization Schemes: 5

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 $\text{MgO-MgF}_2\text{-SiO}_2\text{-H}_2\text{O}$ 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 (eg. Carmichael, 1970; Trommsdorff, 1972) and experimentally (eg. Metz and Trommsdorff, 1968; Skippen, 1971, 1974; Hoschek, 1973; Slaughter, Kerrick and Wall, 1975; Hewitt, 1975; Puhon, 1978). Thermodynamic data obtained from these experiments have been combined with equations of state for H_2O - CO_2 mixtures (eg. Kerrick and Jacobs, 1981) to position, in isobaric $T-X_{CO_2}$ space, univariant equilibria which, taken together, define the stability fields of mineral assemblages in the system $CaO-MgO-SiO_2-H_2O-CO_2$ ($-KAlO_2$) (eg. 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 $T-X_{CO_2}$ 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, Mercolli (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 H_2O , 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_{CO_2} diagrams for siliceous carbonates (eg. Skippen, 1974) predict that the assemblage talc-calcite should first appear at lower X_{CO_2} 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_{CO_2} 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 meta-sediments 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. 1.2-1.3 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 northwestern 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 Algonquin 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 isograds 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-hypersthene-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 interterrane boundary. The rapid change in metamorphic grade along this zone argues favourably for the presence of a metamorphic discontinuity coincident with the proposed litho-structural 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 analagous 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 $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O-CO}_2$ (sub-volume $\text{CaCO}_3\text{-CaMg}(\text{CO}_3)_2\text{-SiO}_2$) which control the first appearances of tremolite, diopside and forsterite respectively. Isobaric T-X_{CO_2} 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. Litho-structural subdivisions and metamorphic zones are as for Figure 4.

Figure 7. Schematic isobaric T - X_{CO_2} 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 ($K_D = [X_F^{TC} X_{OH}^{TR}] / [X_F^{TR} X_{OH}^{TC}]$) 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.

Section	Pair	X _P ^{TC}	X _P ^{TR}	Section	Pair	X _P ^{TC}	X _P ^{TR}
82-854041-1A	01	.437	.456	82-854043	01	.167	.226
82-854041-1A	02	.396	.449	82-854043	02	.148	.229
82-854041-1A	03	.453	.464	82-849047	01	.049	.069
82-871841	01	.068	.116	82-849047	02	.036	.074
82-871841	02	.066	.129	M869012	01	.300	.393
82-871841	03	.091	.142	M869012	02	.312	.402
82-871841	04	.105	.107	M869012	03	.310	.406
82-871841	05	.064	.137	82-851046	01	.266	.329
82-779694	01	.214	.335	82-851046	02	.255	.345
82-779694	02	.197	.325	82-854041-1B	01A	.296	.414
81-756694-1	01	.159	.285	82-854041-1B	01B	.321	.403
81-756694-1	02	.168	.281	82-854041-1B	02A	.338	.408

Table 2a. Continued

Section	Pair	X_P^{TC}	
82-854041-1b	02B	.342	.434
82-755740-2	01	.204	.314
82-755740-2	02	.195	.304
82-755740-2	04	.177	.249
82-755740	05	.175	.256
82-832748	03	.124	.190
82-832748	04	.149	.284
82-832748	05	.099	.231
14	*	.043	.070
17	*	.060	.103

* - Sample from Allen (1976)

Table 2b. Fluorine distribution data: phlogopite - tremolite.

Section	Pair	x_P^{PH}	x_P^{TR}	Section	Pair	x_P^{PH}	x_P^{TR}
82-854041-1A	04	.774	.455	82-755740-2	03B	.596	.244
82-854041-1A	05	.780	.477	82-755740-2	05	.584	.256
82-854041-1A	06	.656	.462	82-756694-3	01A	.117	.019
M869012	04	.748	.413	82-756694-3	01B	.138	.097
M869012	05	.734	.404	82-756694-3	02B	.118	.017
82-815834-1	01	.512	.386	82-832748	01A	.501	.298
82-815834-1	02	.508	.288	82-832748	01B	.468	.310
82-815834-1	03	.498	.266	82-832748	02A	.495	.246
82-851046	av	.590	.337	82-832748	02B	.502	.238
82-854041-1B	02	.778	.421	82-849047	02	.287	.074
82-854041-1B	03	.761	.379	82-849047	av	.277	.072
82-755740-2	03A	.584	.276	82-854043	01	.532	.226

av - average value

Table 2b. Continued.

Section	Pair	x_P^{PH}	x_P^{TR}
82-854043	02	.508	.229
12	*	.225	.143
13	*	.170	.076
14	*	.136	.070
15	*	.271	.203
16	*	.054	.046
18	*	.198	.110
19	*	.079	.063
BMT-1	~	.96	.82

* - 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 $K_D = 0.5$ between talc and tremolite from this area. The F contents of tremolite from the Campolungo area range from X_F of about 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^{IV} , 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 (eg. Allen, 1976; Westrich, 1981). Within the error limits, both phlogopite and tremolite are most simply modelled as

Figure 9. Distribution of F between coexisting phlogopite and tremolite. The outlined area corresponds to analytical error and the distribution curve represents an average $K_D=3.4$. Data for the diagram are given in Table 2; data includes points from Allen (1976); the most F-rich point is from Petersen et al. (1982).

ideal F-OH solutions. Using this model, the average distribution coefficient ($K_D = [X_F^{TC} X_{OH}^{TR} / X_{OH}^{PH} X_F^{TR}]$) 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,

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

$$K_{(1)} = \frac{[a_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}] [a_{\text{CaMg}_{2.5}\text{Si}_4\text{O}_{11}(\text{OH})}]}{[a_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}] [a_{\text{CaMg}_{2.5}\text{Si}_4\text{O}_{11}(\text{F})}]} \quad (2)$$

where activity for exchange component 'i' is defined as

$$a_i = X_i \gamma_i \quad (3)$$

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

$$K_{D(1)} = \frac{(X_F^{TC}) (X_{OH}^{TR})}{(X_{OH}^{TC}) (X_F^{TR})} \quad (4)$$

Substituting equations (3) and (4) into equation (2) and taking the logarithm gives

$$\begin{aligned} \ln K_{(1)} &= \ln K_{D(1)} + \ln [\gamma_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}] \\ &\quad + \ln [\gamma_{\text{CaMg}_{2.5}\text{Si}_4\text{O}_{11}(\text{OH})}] \\ &\quad - \ln [\gamma_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}] \\ &\quad - \ln [\gamma_{\text{CaMg}_{2.5}\text{Si}_5\text{O}_{11}(\text{F})}] \end{aligned} \quad (5)$$

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

$$\ln[\gamma_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}] = [W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH},\text{F})}] (1-x_{\text{OH}}^{\text{TC}})^2 \quad (6a)$$

$$\ln[\gamma_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}] = [W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH},\text{F})}] (1-x_{\text{F}}^{\text{TC}})^2 \quad (6b)$$

Analogous equations may be written for tremolite. The term

$$W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH},\text{F})}$$

is here the excess partial molar free energy at infinite dilution for talc and is identical to W_G of Thompson (1967). W_G is often referred to as the Margules parameter. Solutions that conform to the symmetric solution model are termed "simple mixtures" by Guggenheim (1967), however, Froese (1976) points out that such solutions are referred to as "regular" by some authors.

For F-OH talc mixtures

$$x_{\text{OH}}^{\text{TC}} = (1-x_{\text{F}}^{\text{TC}}) \quad (7)$$

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;

$$\begin{aligned} \ln K(1) = & \ln K_D(1) + [W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH},\text{F})}/RT] (1-2x_{\text{F}}^{\text{TC}}) \\ & - [W_{\text{CaMg}_{2.5}\text{Si}_4\text{O}_{11}(\text{OH},\text{F})}/RT] (1-2x_{\text{F}}^{\text{TR}}) \end{aligned} \quad (8)$$

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

$$\begin{aligned} \ln \gamma_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})} = & (x_{\text{F}}^{\text{TC}})^2 [(W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}/RT) + \\ & 2(x_{\text{OH}}^{\text{TC}})((W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}/RT) - (W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}/RT))] \end{aligned} \quad (9a)$$

$$\begin{aligned} \ln \gamma_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})} = & (x_{\text{OH}}^{\text{TC}})^2 [(W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}/RT) + \\ & 2(x_{\text{F}}^{\text{TC}})((W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}/RT) - (W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}/RT))] \end{aligned} \quad (9b)$$

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

$$W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})} \quad \text{and} \quad W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}$$

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

$$\begin{aligned}
\ln K_{(1)} = & \ln K_{D(1)} \\
& - (W_{Mg_{1.5}Si_2O_5(OH)}/RT) [3(x_F^{TC})^2 - 2(x_F^{TC})] \\
& + (W_{Mg_{1.5}Si_2O_5(F)}/RT) [3(x_F^{TC})^2 - 4(x_F^{TC}) + 1] \\
& + (W_{CaMg_{2.5}Si_4O_{11}(OH)}/RT) [3(x_F^{TR})^2 - 2(x_F^{TR})] \\
& - (W_{CaMg_{2.5}Si_4O_{11}(F)}/RT) [3(x_F^{TR})^2 - 4(x_F^{TR}) + 1]
\end{aligned} \tag{10}$$

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 (eg. Saxena, 1973; Froese and Gordon, 1974). This is accomplished by rearranging equations (8) and (10) into regression-compatible form. Thus equation (10) is rewritten,

$$\begin{aligned}
\ln K_{D(1)} = & \ln K_{(1)} \\
& + (W_{Mg_{1.5}Si_2O_5(OH)}/RT) [3(x_F^{TC})^2 - 2(x_F^{TC})] \\
& - (W_{Mg_{1.5}Si_2O_5(F)}/RT) [3(x_F^{TC})^2 - 4(x_F^{TC}) + 1] \\
& - (W_{CaMg_{2.5}Si_4O_{11}(OH)}/RT) [3(x_F^{TR})^2 - 2(x_F^{TR})] \\
& + (W_{CaMg_{2.5}Si_4O_{11}(F)}/RT) [3(x_F^{TR})^2 - 4(x_F^{TR}) + 1]
\end{aligned} \tag{11}$$

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) $(W_{Mg_{1.5}Si_2O_5(OH)}/RT)$
- ii) $(W_{Mg_{1.5}Si_2O_5(F)}/RT)$
- iii) $(W_{CaMg_{2.5}Si_4O_{11}(OH)}/RT)$
- iv) $(W_{CaMg_{2.5}Si_4O_{11}(F)}/RT)$

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 (ie. 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_F^{TR} , SOLCRV calculates predicted values for X_F^{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 $\ln K_{(1)}$ 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, ie. X_F^{TR} , X_F^{TC} or X_F^{PH} . To successfully carry out a linear regression, the model must be explicitly defined; ie. 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,

$$\begin{aligned} f(x_F^{TC}, x_F^{TR}, (w_{Mg_{1.5}Si_2O_5(OH)}/RT), (w_{Mg_{1.5}Si_2O_5(F)}/RT), \\ (w_{CaMg_{2.5}Si_4O_{11}(OH)}/RT), (w_{CaMg_{2.5}Si_4O_{11}(F)}/RT), \ln K_{(1)}) \\ = \ln[x_F^{TC}(1-x_F^{TR})/(x_F^{TR}(1-x_F^{TC}))] - \ln K_{(1)} \\ - (w_{Mg_{1.5}Si_2O_5(OH)}/RT) [3(x_F^{TC})^2 - 2(x_F^{TC})] \end{aligned}$$

$$\begin{aligned}
& + (W_{Mg_{1.5}Si_2O_5}(F)/RT) [3(X_F^{TC})^2 - 4(X_F^{TC}) + 1] \\
& + (W_{CaMg_{2.5}Si_4O_{11}}(OH)/RT) [3(X_F^{TR})^2 - 2(X_F^{TR})] \\
& - (W_{CaMg_{2.5}Si_4O_{11}}(F)/RT) [3(X_F^{TR})^2 - 4(X_F^{TR}) + 1] \\
& = 0
\end{aligned} \tag{12}$$

The Newton-Raphson iteration scheme is given by,

$$(X_F^{TC})_{n+1} = (X_F^{TC})_n + \frac{f(X_F^{TC}; X_F^{TR}, \dots)}{f'(X_F^{TC}; X_F^{TR}, \dots)} \tag{13}$$

where $f(X_F^{TR}; X_F^{TR}, \dots)$ 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} , $f'(X_F^{TC}; X_F^{TR}, \dots)$. The derivative of (12) with respect to X_F^{TC} is

$$\begin{aligned}
f'(X_F^{TC}; X_F^{TR}, \dots) &= \frac{1}{X_F^{TC}} + \frac{1}{(1-X_F^{TC})} \\
&- (W_{Mg_{1.5}Si_2O_5}(OH)/RT) [6(X_F^{TC}) - 2] \\
&+ (W_{Mg_{1.5}Si_2O_5}(F)/RT) [6(X_F^{TC}) - 4]
\end{aligned} \tag{14}$$

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_F^{TC} are compared with the observed values of x_F^{TC} 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 can not 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_F^{TC} is made using the measured value of x_F^{TC} at x_F^{TR} . 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_F^{TC} . The choice of initial approximations for x_F^{TC} may be complicated by the existence of several solutions for equation (13) at constant x_F^{TR} over the range $x_F^{TC} = 0.00$ to 1.00. Depending on the initial approximations made, differing values for x_F^{TC} may

be converged upon. Since only one value can be returned by the mathematical model, a criterion for selecting the correct value for X_F^{TC} must be used.

The procedure adopted in this study was to introduce successive initial approximations for X_F^{TC} 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_F^{TC} 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 talc-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 $\ln K$ 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 $\ln K_{(1)}$ 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

$$\begin{aligned}
 f[X_F^{TC}, X_F^{TR}, (W_{Mg_{1.5}Si_2O_5(OH)}/RT), (W_{Mg_{1.5}Si_2O_5(F)}/RT), \\
 \ln K_{(1)}] = \\
 \ln[X_F^{TC}(1-X_F^{TR})/(X_F^{TR}(1-X_F^{TC}))] - \ln K_{(1)} \\
 - (W_{Mg_{1.5}Si_2O_5(OH)}/RT) [3(X_F^{TC})^2 - 2(X_F^{TC})] \\
 + (W_{Mg_{1.5}Si_2O_5(F)}/RT) [3(X_F^{TC})^2 - 4(X_F^{TC}) + 1] \\
 = 0 \qquad (15)
 \end{aligned}$$

and its derivative with respect to X_F^{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:

$$\ln K_{(1)} = 0.458764$$

$$W_{Mg_{1.5}Si_2O_5(OH)}/RT = 2.49479$$

$$W_{Mg_{1.5}Si_2O_5(F)}/RT = 0.940213$$

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 (eg. Brown, 1978),

$$[\delta W_G / \delta T]_P = -W_S \quad (16)$$

and, with pressure, by

$$[\delta W_G / \delta P]_T = W_V \quad (17)$$

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:

$$\ln(a_{\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2}) = 2\ln(X_{\text{OH}}^{\text{TR}}) \quad (18a)$$

$$\ln(a_{\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2}) = 2\ln(X_{\text{OH}}^{\text{PH}}) \quad (18b)$$

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

$$W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{OH})}/RT \quad \text{and} \quad W_{\text{Mg}_{1.5}\text{Si}_2\text{O}_5(\text{F})}/RT$$

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

$$\ln \gamma_i = (1/T)(X_j)^2[(W_i/R) + 2(X_i)((W_j/R) - (W_i/R))] \quad (19)$$

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

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, this temperature is consistent with the existence of talc in siliceous carbonates under H₂O-rich conditions. However, considering the limitations of calcite-dolomite thermometry (eg. Essene, 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:

$$W_{Mg_{1.5}Si_2O_5(OH)}/RT = 1741.36 \text{ K}$$

$$W_{Mg_{1.5}Si_2O_5(OH)} = 14.478 \text{ KJ mol}^{-1}$$

$$W_{Mg_{1.5}Si_2O_5(F)}/RT = 656.27 \text{ K}$$

$$W_{Mg_{1.5}Si_2O_5(F)} = 5.456 \text{ KJ mol}^{-1}$$

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 error 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

$$\ln(a_{\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2}) = 2\ln(x_{\text{OH}}^{\text{TC}}) + [(1/T)(x_{\text{F}}^{\text{TC}})^2(3483 - 4340(x_{\text{OH}}^{\text{TC}}))] \quad (20a)$$

$$\ln(a_{\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{F})_2}) = 2\ln(x_{\text{F}}^{\text{TC}}) + [(1/T)(x_{\text{OH}}^{\text{TC}})^2(1313 + 4340(x_{\text{F}}^{\text{TC}}))] \quad (20b)$$

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_{CO₂} 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 (eg. Skippen and Trommsdorf, 1975).

Isobaric T-X_{CO₂} 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_{CO₂} 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 talc-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 Marysville Aureole (Rice, 1977b).

With increasing pressure, the talc-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 I.1b-d, I.2b-d and I.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.b, which is representative of the conditions reported in the Marysville 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 $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O-CO}_2$.

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 $T-X_{\text{CO}_2}$ 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 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 $X_F^{\text{TC}}=0.2$ to $X_F^{\text{TC}}=0.5$, 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 ($X_F(2)$; $X_F^{\text{TC}}=0.2$), the trace of the upper limit of talc-calcite intersects the sillimanite stability field between 360 MPa and 400 MPa. At high F contents ($X_F(3)$; $X_F^{\text{TC}}=0.5$)

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 $X_F(2)$. 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 $X_F(2)$. 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 (eg. 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 isograd. 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 ($X_F(3)$; $X_F^{TR}=0.47$, $X_F^{TC}=0.5$). 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 ($X_F^{TC}=0.02$, approx.) and from the Gouverneur talc district, New York, give 0.48 weight percent F ($X_F^{TC}=0.05$, approx.). Talc from the Eldorado talc mine near Eldorado, Ontario, reported in this study (Appendix III; sample 81-979413-2) averages $X_F^{TC}=0.05$.

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 KAlO_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, $X_F^{\text{TC}}=0.45$, 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 can not 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:

$$W_{Mg_3Si_4O_{10}(OH)_2} = 28.956 \text{ Kj/mol}$$

$$W_{Mg_3Si_4O_{10}(F)_2} = 10.912 \text{ Kj/mol}$$

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 $T-X_{CO_2}$ 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.

REFERENCES

- Allen, J., 1976: Silicate-carbonate equilibria in calcareous meta-sediments of the Tudor Township area, Ontario; Ph.D. Thesis, Queens University, Kingston, Ontario, 227 p.
- 1978: F-OH distribution among minerals in marbles and implications for the stability of talc-calcite; Geological Association of Canada - Mineralogical Association of Canada, Abstracts with Programs, V. 3, p. 358.
- Bailey, S.W., 1980: Structures of layer silicates; in Crystal Structures of Clay Minerals and their Identification, G.W. Brindley and G. Brown editors, Mineralogical Society, Monograph Number 5.
- Bartlett, J.R., 1983: Stratigraphy, physical volcanology, and geochemistry of the Belmont Lake Metavolcanic Complex, Southeastern Ontario; MSc. Thesis, Carleton University, Ottawa, Ontario.
- Brock, B.S. and Moore, J.M., Jr., 1983: Chronology, chemistry, and tectonics of igneous rock in terranes of the Grenville Province, Canada [abstract]; Geological Society of America, Program with Programs, V. 15, p. 533
- Brown, R.L., Chappel, J.F., Moore, J.M., Jr., and Thompson, P.H., 1975: An ensimatic island arc and ocean closure in the Grenville Province of southeastern Ontario, Canada; Geoscience Canada, V. 2, p. 141-144.
- Brown, T.H., 1978: Introduction to nonideal and complex solutions; in Application of Thermodynamics to Mineral Deposits, H.J. Greenwood, ed., Mineralogical Association of Canada, Short Course Handbook, V. 2, p. 126-135.
- Cameron, M. and Gibbs, G.V., 1973: The crystal structure and bonding of fluor-tremolite: a comparison with hydroxyl tremolite; American Mineralogist, V. 58, p. 879-888.
- Carmichael, D.M., 1970: Intersecting isograds in the Whetstone Lake area, Ontario; Journal of Petrology, V. 11, Part 1, p. 147-181.
- Carmichael, D.M., Moore, J.M., Jr., and Skippen, G.B., 1978: Isograds around the Hastings metamorphic "low"; in Field Trips Guidebook, Toronto '78, eds. A.L. Currie and W.O. MacKasey, Geological Association of Canada, Annual Meeting, 1978.

- Chesworth, W., 1972: Metamorphic facies series in the Grenville Province of Ontario; *Tectonophysics*, V. 14, p. 71-78.
- Condie, K.C. and Moore, J.M., Jr., 1977: Geochemistry of Proterozoic volcanic rocks from the Grenville Province, eastern Ontario; in, *Volcanic Regimes in Canada*, W.R.A. Baragar, L.C. Colman, and J.M. Hall, eds., Geological Association of Canada, Special Paper Number 46.
- Davidson, A. and Morgan, W.C., 1981: Preliminary notes on the geology east of Georgian Bay, Grenville Structural Province, Ontario; *Current Research, Part A*, Geological Survey of Canada, Paper 81-1A, p. 291-298.
- Davidson, A., Cuthshaw, N.G., Nadeau, L., 1982: A tectono-metamorphic framework for part of the Grenville Province, Parry Sound Region, Ontario; *Current Research, Part A*, Geological Survey of Canada, Paper 82-1A, p. 175-190.
- Deer, W.A., Howie, R.A., and Zussman, J., 1966: *An Introduction to Rock Forming Minerals*; Longman Group, London, 528 p.
- Dibble, W.E. and Dickson, F.W., 1978: The influence of fluorine on the thermodynamic stability of sheet silicates [abstract]; EOS, American Geophysical Union, Transactions, V. 59, Number 12, p. 1218.
- Dixon, W.J. and Brown, M.B., eds., 1979: BMDP-79; Biomedical Computer Programs P-Series; University of California Press, Berkeley, 880 p.
- Dorn, W.S. and McCracken, D.D., 1972: *Numerical Methods with Fortran IV Case Studies*, John Wiley & Sons, Inc., New York, 447 p.
- Duffy, C.J., 1977: Phase equilibria in the system $\text{MgO-MgF}_2\text{-SiO}_2\text{-H}_2\text{O}$; Ph.D. Thesis, University of British Columbia, Vancouver, British Columbia, 70 p.
- Duffy, C.J. and Greenwood, H.J., 1979: Phase equilibria in the system $\text{MgO-MgF}_2\text{-SiO}_2\text{-H}_2\text{O}$; *American Mineralogist*, V. 64, p. 1156-1174.
- Dymek, R.F., 1983: Titanium, aluminum and interlayer cation substitutions in biotite from high-grade gneisses, West Greenland; *American Mineralogist*, V. 68, p. 880-899.
- Ekstrom, T.K., 1972: The distribution of fluorine among some coexisting minerals; *Contributions to Mineralogy and Petrology*, V. 34, p. 192-200.

- Essene, E.J., 1982: Geologic thermometry and barometry; in, Characterization of Metamorphism through Mineral Equilibria, J.M. Ferry, ed., Mineralogical Society of America, Reviews in Mineralogy, Volume 10, p. 153-206.
- Ewert, W.D., 1977: Metamorphism of siliceous carbonate rocks in the Grenville Province of southeastern Ontario; PhD. Thesis, Carleton University, Ottawa, Ontario, 276 p.
- Flowers G.C., 1979: Correction of Holloway's (1977) adaption of the modified Redlich-Kwong equation of state for calculation of the fugacities of molecular species in supercritical fluids of geologic interest; Contributions to Mineralogy and Petrology, V. 315-318.
- Flowers, G.C. and Helgeson, H.C.: Equilibrium and mass transfer during progressive metamorphism of siliceous dolomites; American Journal of Science, V. 283, p. 239-286.
- Froese, E., 1976: Applications of thermodynamics in metamorphic petrology; Geological Survey of Canada, Paper 75-43.
- Froese, E. and Gordon, T.M., 1974: Activity coefficients of coexisting pyroxenes; American Mineralogist, V. 59, p. 204-205.
- Gordon, T.M. and Greenwood, H.J., 1970: The reaction: dolomite + quartz + water = talc + calcite + carbon dioxide; American Journal of Science, V. 268, p. 225-242.
- Grover, J., 1976: Chemical mixing in multicomponent solutions: An introduction to the use of Margules and other thermodynamic excess functions to represent nonideal solution behavior; in Thermodynamics in Geology, D.G. Fraser editor, D. Reidel Publishing Company, Boston, 410 p.
- Guggenheim, E.A., 1967: Thermodynamics, fifth revised edition; North-Holland Publishing Company, Amsterdam, 390 p.
- Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K., 1978: Summary and critique of the thermodynamic properties of rock-forming minerals; American Journal of Science, V. 278-A, 229 p.
- Hewitt, D.A., 1975: Stability of the assemblage phlogopite-calcite-quartz; American Mineralogist, V. 60, p. 391-397.
- Hewitt, D.F., 1957: Geology of Cardiff and Faraday Townships, Haliburton and Hastings Counties, Ontario; Ontario Department of Mines, Annual Report, V. 6, Part 3, including Colmap 1957-1.

- Hewitt, D.F., 1972: Talc in Ontario; Ontario Department of Mines and Northern Affairs, Industrial Minerals Report 40.
- Hodges, K.V. and Spear, F.S., 1982: Geothermometry, geobarometry and the Al_2SiO_5 triple point at Mt. Moosilauke, New Hampshire; *American Mineralogist*, V. 67, p. 1118-1134.
- Holdaway, M.J., 1971: Stability of andalusite and the aluminum silicate phase diagram; *American Journal of Science*, V. 271, p. 97-131.
- Holland, T.J.B., 1981: Thermodynamic analysis of simple mineral systems; in *Thermodynamics of Minerals and Melts*, K.C. Newton, A. Navrotsky, and B.J. Wood editors, *Advances in Physical Geochemistry*, Springer-Verlag, V. 1, 304 p.
- Holloway, J.R., 1977: The effect of fluorine in dehydration equilibria [abstract]; *Geological Society of America, Abstracts with Programs*, V. 9, p. 1021.
- Hoschek, G., 1973: Die Reaktion Phlogopit + Calcit + Quarz = Tremolit + Kalifeldspat + H_2O + CO_2 ; *Contributions to Mineralogy and Petrology*, V. 39, p. 231-237.
- Jacobs, G.K. and Kerrick, D.M., 1981: APL and FORTRAN programs for a new equation of state for H_2O , CO_2 , and their mixtures at supercritical conditions; *Computers & Geosciences*, V. 7, p. 131-143.
- Jenkins, R. and de Vries, C., 1970: Worked examples in X-ray spectrometry; The MacMillan Press Limited, London, 129 p.
- Kearns, L.E., Kite, L.E., Leavens, P.B., and Nelen, J.A., 1980: Fluorine distribution in the hydrous silicate minerals of the Franklin Marble, Orange County, New York; *American Mineralogist*, V. 65, p. 557-562.
- Kerrick, D.M. and Jacobs, G.K., 1981: A modified Redlich-Kwong equation for H_2O , CO_2 , and $\text{H}_2\text{O}-\text{CO}_2$ mixtures at elevated pressures and temperatures; *American Journal of Science*, V. 281, p. 735-767.
- Laakso, R.K., 1968: Geology of Lake Township, Hastings County, Ontario; Ontario Department of Mines, Geological Report 54, including Colmap 2106.
- Laird, J. and Albee, L.A., 1981: High pressure metamorphism in mafic schist from northern Vermont; *American Journal of Science*, V. 281, p. 97-126.
- Leake, B.E., 1978: Nomenclature of amphiboles; *Canadian Mineralogist*, V. 16, p. 501-520.

- Lumbers, S.B., 1968: Geology of Cashel Township, Hastings County, Ontario; Ontario Department of Mines, Geological Report 71, including Colmap 2142.
- Margules, M., 1895: Über die Zusammensetzung der gesättigten Dämpfe von Mischungen; Sitzungsber. Akad. Wiss. Wien, V. 104, p. 1243-1278.
- McKinstry, B., 1977: The wollastonite occurrence near Tatlock, Ontario; Unpublished report, Carleton University, Ottawa, Ontario.
- Metz, P. and Trommsdorf, V., 1968: On phase equilibria in metamorphosed siliceous dolomites; Contributions to Mineralogy and Petrology, V. 18, p. 305-309.
- Mercolli, I., 1980: Fluor-Verteilung in Tremolit und Talk in den metamorphen Dolomiten des Campolungo (Tessin) und ihre phasenpetrologische Bedeutung; Schweiz. mineral. petrog. Mitt., V. 60, p. 31-44.
- Moore, J.M., Jr., 1983a: Evolution of the Central Metasedimentary Belt, Grenville Province in eastern Ontario; unpublished abstract, Ottawa-Carleton Centre for Geoscience Studies, Geoscience Seminar.
- 1983b: The Grenvillian and Cordilleran Orogens: Comparisons and contrasts [abstract]; Geological Association of Canada, Program with Abstracts, Victoria, 1983, p. A48.
- Moore, J.M., Jr. and Thompson, P.H., 1980: The Flinton Group: a late Precambrian metasedimentary succession in the Grenville Province of eastern Ontario; Canadian Journal of Earth Sciences, V. 17, p. 1685-1707.
- Moore, J.N. and Kerrick, D.M., 1976: Equilibria in siliceous dolomites of the Alta Aureole, Utah; American Journal of Science, V. 276, p. 502-524.
- Munoz, J.L. and Eugster, H.P., 1969: Experimental control of fluorine reactions in hydrothermal systems; American Mineralogist, V. 54, p. 943-959.
- Munoz, J.L. and Ludington, S.D., 1974: Fluoride-hydroxyl exchange in biotite; American Journal of Science, V. 274, p. 396-413.
- Munoz, J.L. and Ludington, S.D., 1977: Fluorine-hydroxyl exchange in synthetic muscovite and its application to muscovite-biotite assemblages; American Mineralogist, V. 62, p. 304-308.
- Petersen, E.U., Essene, E.J. and Peacor, D.R., 1982: Fluorine end-member micas and amphiboles; American Mineralogist, V. 67, p. 538-544.

Puhan, D. and Hoffer, E., 1973: Phase relations of talc and tremolite in metamorphic calcite-dolomite sediments of the Damara Belt (South West Africa); Contributions to Mineralogy and Petrology, V. 40, p. 207-214.

Puhan, D., 1978: Experimental study of the reaction: dolomite + K-feldspar + H_2O = phlogopite + calcite + CO_2 at the total gas pressures of 4000 and 6000 bars; Neues Jahrbuch für Mineralogie Monatshefte, p. 117-127.

Ramberg, H., 1952: Chemical bonds and distribution of cations in silicates; Journal of Geology, V. 60, p. 331-355.

Rice, J.M., 1976: The influence of OH-F substitution on the stability of talc in metamorphosed siliceous dolomite [abstract]; EOS, American Geophysical Union, Transactions, V. 57, Number 4, p. 338.

_____ 1977a: Contact metamorphism of impure dolomitic limestone in the Boulder Aureole, Montana; Contributions to Mineralogy and Petrology, V. 59, p. 237-259.

_____ 1977b: Progressive metamorphism of impure dolomitic limestone in the Marysville Aureole, Montana; American Journal of Science, V. 277, p. 1-24.

_____ 1980: Phase equilibria involving humite minerals in impure dolomitic limestones, Part I. Calculated stability of clinohumite; Contributions to Mineralogy and Petrology, V. 71, p. 219-235.

Robinson, P., Spear, F.S., Schumacher, J.C., Laird, J., Klein, C., Evans, B.W., and Doolan, B.L., 1981: Phase relations of metamorphic amphiboles: natural occurrence and theory; in Amphiboles: Petrology and experimental phase relations, D.R. Veblen and P.H. Ribbe, eds., Mineralogical Society of America, Reviews in Mineralogy, V. 9B, p.1

Rosenberg, P.E. and Foit, F.F., Jr., 1977: Fe^{2+} -F avoidance in silicates; Geochemica et Cosmochemica Acta, V. 41, p. 345-346.

Ross, M., Smith, W.L. and Ashton, W.H., 1968: Triclinic talc and associated amphiboles from Gouverneur Mining District, New York; American Mineralogist, V. 53, p. 751-769.

Rucklidge, J. and Gasparrini, E.L., 1969: Specifications of a computer program for processing electron microprobe analytical data. EMPADR VII. Department of Geology, University of Toronto, Toronto, Ontario.

Saxena, S.K., 1973: Thermodynamics of Rock-Forming Crystalline Solutions, Springer-Verlag, New York, 188 p.

Sethuraman, K. and Moore, J.M., Jr., 1973: Petrology of metavolcanic rocks in the Bishops Corners - Donaldson area, Grenville Province, Ontario, Canadian Journal of Earth Sciences, V. 10, p. 589-614.

Skippen, G.B., 1971: Experimental data for reactions in siliceous marbles; Journal of Geology, V. 79, p. 457-481.

——— 1974: An experimental model for low pressure metamorphism of siliceous dolomitic marble; American Journal of Science, V. 274, p. 487-509.

——— 1977: Dehydration and decarbonation equilibria; in Application of Thermodynamics to Mineral Deposits, Mineralogical Association of Canada, Short Course Handbook, V. 2, p. 66-83.

Skippen, G.B. and Carmichael, D.M., 1977: Mixed-volatile equilibria; in Application of Thermodynamics to Mineral Deposits, Mineralogical Association of Canada, Short Course Handbook, V. 2, p. 109-125.

Skippen, G.B. and Hutcheon, I., 1974: The experimental calibration of continuous reactions in siliceous carbonate rocks; Canadian Mineralogist, V. 12, p. 327-333.

Skippen, G.B. and Trommsdorff, V., 1975: Invariant phase relations among minerals on T-X_{fluid} diagrams; American Journal of Science, V. 275, p. 561-572.

Slaughter, J., Kerrick, D.M., and Wall, V.J., 1975: Experimental and thermodynamic study of equilibria in the system CaO-MgO-SiO₂-H₂O-CO₂; American Journal of Science, V. 275, p. 143-162.

Spence, H.W., 1940: Talc, steatite and soapstone; pyrophyllite; Canada Department of Mines and Resources, Report Number 803.

Thomson, J.E., 1943: Mineral occurrences in the north Hastings area; Ontario Department of Mines, Annual Report, V. 52, Part 3.

Thompson, J.B., Jr., 1967: Thermodynamic properties of simple solutions; in Researches in Geochemistry II, P.H. Abelson editor, John Wiley and Sons, New York.

Troll, G. and Gilbert, M.C., 1972: Fluorine-hydroxyl substitution in tremolite; American Mineralogist, V. 57, p. 1386-1403.

Trommsdorff, V., 1980: Alpine metamorphism and Alpine intrusions; in, Switzerland: An outline of the Geology of Switzerland, R. Trumphy, ed., 26th International Geological Congress, Guidebook 10, p. 82-93.

- Trommsdorff, V., 1972: Change in T-X during metamorphism of siliceous dolomitic rocks of the central Alps; Schweiz. Mineral. Petrog. Mitteil., V. 52, p. 1-4.
- Turner, F.J., 1981: Metamorphic Petrology; McGraw-Hill Book Company, New York, 524 p.
- Valley, J.W. and Essene, E.J., 1980: Calc-silicate reactions in Adirondack marbles: The role of fluids and solid solutions; Geological Society of America Bulletin, V. 91, Part I (summary), p. 114-117, Part II, p. 720-815.
- Valley, J.W., Petersen, E.U., Essene, E.J., and Bowman, J.R., 1982: Fluorophlogopite and fluortremolite in Adirondack marbles and calculated C-O-H-F fluid compositions; American Mineralogist, V. 67, p. 545-557.
- van Haafden, S., Young, A.F. and Kingston, P.W., 1980: An evaluation of talc occurrences in eastern Ontario; Unpublished Report, Mines Branch, Ontario Ministry of Natural Resources, Kemptville, Ontario.
- Walther, J.V., (in press): Description and interpretation of metasomatic phase relations at high pressures and temperatures: 2. Metasomatic reactions between quartz and dolomite at Campolungo, Switzerland; American Journal of Science.
- Westrich, H.R., 1977: F-Oh exchange equilibria in several hydrous minerals [abstract]; EOS, American Geophysical Union, Transactions, V. 58, p. 1243.
- Westrich, H.R., 1981: F-OH exchange equilibria between mica-amphibole mineral pairs; Contributions to Mineralogy and Petrology, V. 78, p. 318-323.
- Westrich, H.R. and Navrotsky, A., 1981: Some thermodynamic properties of fluorapatite, fluorparagasite, and fluorophlogopite; American Journal of Science, V. 281, p. 1091-1103.
- Wynne-Edwards, H.R., 1972: The Grenville Province; in Variations in Tectonic Styles in Canada, R.A. Price and R.J.W. Douglas, eds., Geological Association of Canada, Special Paper Number 11, p. 264-334.
- Zaw, U.K. and Clark, A.H., 1978: Fluoride-hydroxyl ratios of skarn silicates, Cantung E-zone scheelite orebody, Tungsten, Northwest Territories; Canadian Mineralogist, V. 16, p. 207-221.

APPENDIX I

T-X_{CO₂} DIAGRAMS

I.1 Calculation of the T-X_{CO₂} Diagram

Table I.1 Mineral and component compositions and standard states.

Table I.2 Stable reactions and equilibria in the system CaO-MgO-SiO₂-KAlO₂-H₂O-CO₂.

Table I.3 Thermodynamic data.

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

I.2 T-X_{CO₂} Diagrams

Figure I.1a 100 MPa: F-free.

.1b : $X_F(1)$

.1c : $X_F(2)$

.1d : $X_F(3)$

Figure I.2a 200 MPa: F-free

.2b : $X_F(1)$

.2c : $X_F(2)$

.2d : $X_F(3)$

Figure I.3a 500 MPa: F-free

.3b : $X_F(1)$

.3c : $X_F(2)$

.3d : $X_F(3)$

APPENDIX I

T-X_{CO₂} DIAGRAMS1.1 Calculation of the T-X_{CO₂} Diagram

A general equation for the free energy change of a devolatilization 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

$$\begin{aligned} \ln K = & A/T + B + C(P-1)/T - \text{DELA}/T + \text{DELB}/T \\ & + \text{DELC}/T - \text{DELD}/T \end{aligned} \quad (1.1)$$

where:

$$A = [-\Delta H_{\text{Tr,Pr}}/R]$$

$$B = [\Delta S_{\text{Tr,Pr}}/R]$$

$$C = [-\Delta V_s/R]$$

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

$$\text{DELA} = (\Delta a/R)[T - T_r - T \ln(T/T_r)]$$

$$\text{DELB} = (\Delta b/R)[(T^2)/2 + (T_r^2)/2 - TT_r]$$

$$\text{DELC} = (\Delta c/R)[(T^{-1})/2 - (T_r^{-1}) + T(T_r^{-2})/2]$$

$$\text{DELD} = (\Delta d/R)[2(2(T \cdot^5) - (T_r \cdot^5) - T(T_r \cdot^{-5}))]$$

Table I.1 - Minerals, Components, Compositions and Standard States

PHASES		COMPONENTS	
QZ	Quartz ( )	qz	SiO_2
CC	Calcite	cc	CaCO_3
DL	Dolomite	dl	$\text{CaMg}(\text{CO}_3)_2$
TC	Talc	tc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
TR	Tremolite	tr	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
DI	Diopside	di	$\text{CaMgSi}_2\text{O}_6$
FO	Forsterite	fo	Mg_2SiO_4
PH	Phlogopite	ph	$\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
KF	Potassium feldspar	kf	KAlSi_3O_8
	(magnesite)	mg	MgCO_3

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 CaCO_3 and MgCO_3 at the temperature and pressure of interest.

Fluid phase: Unit fugacity for H_2O and CO_2 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 MgCO_3 and CaCO_3 . The activities of the components MgCO_3 and 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 I.1 is rewritten,

$$\begin{aligned} \nu_{\text{CO}_2} \ln(f_{\text{CO}_2}) + \nu_{\text{H}_2\text{O}} \ln(f_{\text{H}_2\text{O}}) = & A/T + B + C(P-1)/T \\ & - \text{DELA}/T + \text{DELB}/T + \text{DELC}/T - \text{DELD}/T \end{aligned} \quad (\text{I.2})$$

with new A and B terms defined by,

$$\begin{aligned} A = & - [(\Delta H_{\text{Tr,Pr}})/R - \nu_{\text{mg}}(1683) + \nu_{\text{cc}}(157) \\ & + \nu_{\text{TC}}(x_{\text{F}}^{\text{TC}})^2(3483 - 4340(x_{\text{OH}}^{\text{TC}}))] \\ B = & [(\Delta S_{\text{Tr,Pr}})/R - \nu_{\text{mg}}(1.1177) + \nu_{\text{cc}}(0.253) \\ & - 2 \nu_{\text{TC}} \ln(x_{\text{OH}}^{\text{TC}}) - 2 \nu_{\text{TR}} \ln(x_{\text{OH}}^{\text{TR}}) - 2 \nu_{\text{PH}}(x_{\text{OH}}^{\text{PH}})] \end{aligned}$$

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 $\text{H}_2\text{O}-\text{CO}_2$ mixtures with $x_{\text{H}_2\text{O}} + x_{\text{CO}_2} = 1$; 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 I.2 - Stable Reactions in the System CaO-MgO-SiO₂-KAlO₂-H₂O-CO₂

REACTIONS	EQUILIBRIA
1. 3DL + KF + H ₂ O = PH + 3CC + 3CO ₂	3mg + kf + H ₂ O = ph + 3CO ₂
2. 8QZ + 5DL + H ₂ O = TR + 3CC + 7CO ₂	8qz + 5mg + 2cc + H ₂ O = tr + 7CO ₂
3. 3DL + 4QZ + H ₂ O = TC + 3CC + 3CO ₂	3mg + 4qz + H ₂ O = tc + 3CO ₂
4. 5TC + 6CC + 4QZ = 3TR + 2H ₂ O + 6CO ₂	5tc + 6cc + 4qz = 3tr + 2H ₂ O + 6CO ₂
5. 2TC + 3CC = TR + DL + H ₂ O + CO ₂	2tc + 2cc = tr + mg + H ₂ O + CO ₂
6. 5PH + 6CC + 24QZ = 3TR + 5KF + 2H ₂ O + 6CO ₂	5ph + 6cc + 24qz = 3tr + 5kf + 2H ₂ O + 6CO ₂
7. PH + 2DL + 8QZ = TR + KF + 4CO ₂	ph + 2mg + 2cc + 8qz = tr + kf + 4CO ₂
8. DL + 2QZ = DI + 2CO ₂	mg + cc + 2qz = di + 2CO ₂
9. TR + 3CC + 2QZ = 5DI + H ₂ O + 3CO ₂	tr + 3cc + 2qz = 5di + H ₂ O + 3CO ₂
10. 3TR + 6CC + KF = PH + 12DI + 2H ₂ O + 6CO ₂	3tr + 6cc + kf = ph + 12di + 2H ₂ O + 6CO ₂
11. TR + 3CC = 4DI + DL + H ₂ O + CO ₂	tr + 2cc = 4di + mg + H ₂ O + CO ₂
12. TR + 11DL = 8FO + 13CC + H ₂ O + 9CO ₂	tr + 11mg = 8fo + 2cc + H ₂ O + 9CO ₂
13. 3TR + 5CC = 11DI + 2FO + 3H ₂ O + 5CO ₂	3tr + 5cc = 11di + 2fo + 3H ₂ O + 5CO ₂
14. DI + 3DL = 2FO + 4CC + 2CO ₂	di + 3mg = 2fo + cc + 2CO ₂
15. 2FO + CC + KF + H ₂ O = DI + PH + CO ₂	2fo + cc + kf + H ₂ O = di + ph + CO ₂

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 (eg. 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 1.3 - Thermodynamic data

Phase	i H_f°	ii S°	iii V_g°	ii a	iv $b(\times 10^{-3})$	v $c(\times 10^5)$	vi d
Talc	-5903.289	260.83	13.6252	534.30	37.416	-88.052	-2153.2
Tremolite	-12319.696	548.90	27.2927	1214.40	26.528	-123.62	-7388.5
Calcite	-1208.222	92.66	3.6935	142.20	27.307	1.454	-1182.7
Diopside	-3203.262	143.09	6.6107	328.19	1.8881	-14.430	-2519.2
Quartz ( )	-910.648	41.34	2.2689	104.35	6.070	0.342	-1070
Magnesite	-1111.396	15.70	2.8109	82.55	52.463	-19.865	0
Forsterite	-2175.680	95.19	4.3806	149.83	27.36	-35.648	0
Phlogopite	-6226.072	318.40	14.9662	420.95	120.4	-89.956	0
K-feldspar	-3971.403	213.93	10.8872	320.57	18.03	-125.29	0
CO ₂	-393.52	213.69	—	44.22	8.78	-8.619	0
H ₂ O (steam)	-241.82	188.72	—	30.54	10.29	0	0
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 ⁻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 is 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 I.4 - Data used to calculate reactions in the F-free system and at $X_F(1)$, $X_F(2)$ and $X_F(3)$

Reaction	A	B	C	DELA	DELB	DELC	DELD
1.	21980	46.622	-0.5204	-5.4298	-4.684	8.3078	0
2.	59347	126.74	-1.4739	-4.6393	-34.610	-10.857	425.25
3.	21255	45.540	-0.4638	-3.4436	-15.418	-6.6969	255.73
4.	71765	152.52	-2.1029	3.3002	-26.740	0.9133	-2.884
5.	16837	35.659	-0.5464	2.2479	-3.774	2.5368	-86.203
6.	61840	147.11	-1.1898	13.231	-80.410	-74.110	1275.74
7.	37367	80.116	-0.9535	0.7906	-29.926	-19.165	425.25
8.	19640	40.486	-0.5319	-2.0225	-8.714	-1.6767	96.605
9.	38854	75.691	-1.1856	-5.4731	-8.960	2.4736	57.776
10.	79622	152.24	-2.4814	-15.782	-5.422	20.7587	-116.487
11.	19214	35.206	-0.6537	-3.4506	-0.246	4.1503	-38.829
12.	131843	227.761	-1.8860	-25.3612	-28.954	-2.1291	604.156
13.	85799	153.76	-2.2691	-15.830	-7.915	10.881	44.259
14.	28157	48.139	-0.3081	-5.4776	-7.177	-1.5699	160.746
15.	-6177	-1.5171	-0.2123	0.04781	2.493	9.8777	-160.746

Table I.4 - continued

Reaction	$X_F(1)$		$X_F(2)$		$X_F(3)$	
	A	B	A	B	A	B
1.	21980	46.947	21980	48.405	21980	49.394
2.	59347	126.84	59347	127.45	59347	128.01
3.	21254	45.600	21255	45.986	21583	46.926
4.	71768	152.52	71763	152.42	70124	149.39
5.	16838	35.640	16836	35.480	16181	34.156
6.	68140	145.79	68140	140.33	68140	137.05
7.	37367	79.894	37367	79.046	37367	78.613
8.	19640	40.486	19640	40.486	19640	40.486
9.	38854	75.588	38854	74.978	38854	74.421
10.	79622	152.26	79622	151.88	79622	151.20
11.	19214	35.103	19214	34.493	19214	33.936
12.	131843	227.66	131843	227.05	131843	226.49
13.	85799	158.45	85799	151.62	85799	149.95
14.	28157	48.139	28157	48.139	28157	48.139
15.	-6177	-1.192	-6177	0.2661	-6177	1.256

1.2 T- X_{CO_2} Diagrams

Figure 1.1a T- X_{CO_2} diagram at 100 MPa;
F-free

Figure 1.1b T- X_{CO_2} diagram at 100 MPa;
 $X_F(1)$

Figure I.1c T- X_{CO_2} diagram at 100 MPa;
 $x_F(2)$

Figure I.1d T- X_{CO_2} diagram at 100 MPa;
 $x_F(3)$

Figure 1.2a T- X_{CO_2} diagram at 200 MPa;
F-free

Figure 1.2b T- X_{CO_2} diagram at 200 MPa;
 $X_F(1)$

Figure I.2d T- X_{CO_2} diagram at 200 MPa;
 $x_F(3)$

Figure I.2c T- X_{CO_2} diagram at 200 MPa;
 $x_F(2)$

Figure I.3a T- X_{CO_2} diagram at 500 MPa;
F-free

Figure I.3b T- X_{CO_2} diagram at 500 MPa;
 $X_F(2)$

Figure I.3c T- X_{CO_2} diagram at 500 MPa;
 $X_F(2)$

Figure I.3d T- X_{CO_2} diagram at 500 MPa;
 $X_F(3)$

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 F-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

PLATE II.1

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 1

A

B

C

D

E

F

PLATE II.2

II.2A Section 82-815834-1. Coexisting phlogopite and tremolite with calcite. Note unreacted grain boundaries; plane polarized light; scale bar is 0.25 mm.

II.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.

II.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.

II.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.

II.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.

PLATE 2

A

B

C

D

E

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.

II.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.

II.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 blocks 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.

11.2 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 μm .

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 reproducible values for all elements analyzed and, assuming stoichiometric 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 μm) to accept sufficient polishing for quantitative analysis, and rock samples corresponding to the thin sections were unavailable. One exception is section M869012 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.

II.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 Gasparrini (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 CAMEBAX 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 point on a mineral grain. Each pair of analyses reported are from the rim

Table II.2 Estimated 2-sigma error for electron microprobe analyses.

Element	Concentration (wt. percent)	Estimated Error (percent)
all	10	+/- 2
all	3-10	+/- 5
F	3-10	+/- 10
all	0.5-3	+/- 10
all	0.5	+/- 20

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);
(Total Cations - (Ca+Na+K) = 13.000).
- ii) 15 cations except for Na and K (15eNK);
(Total Cations - (Na+K) = 15.000).
- iii) 15 cations except for K (15eK);
(Total Cations - (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 sites 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_2O_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 $\text{Mg}/\text{Mg}+\text{Fe}$ against Si for all analyzed tremolites from the CMB is given in Figure II.1. All tremolites are uniformly Mg-rich; $\text{Mg}/\text{Mg}+\text{Fe}$ ranges from 0.975 to 1.000 with an 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.

TREMOLITE: $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$

Site	El.	Frequency %				Min.	Mean	Max.	El.
		20	40	60	80				
T	Si	100				7.406	7.748	7.994	Si
	Al	100				.006	.238	.593	Al
C	Al	75				.000	.059	.161	Al
	Ti	75				.000	.005	.022	Ti
	Fe	80				.000	.048	.096	Fe
	Mg	100				4.727	4.863	5.000	Mg
B	Ca	60				.000	.024	.122	Ca
	Fe	20				.000	.011	.072	Fe
	Mg	10				.000	.001	.029	Mg
	Ca	100				1.875	1.984	2.000	Ca
A	Na	10				.000	.004	.082	Na
	Ca	40				.000	.036	.224	Ca
	Na	80				.000	.120	.301	Na
	K	80				.000	.019	.103	K
OH	OH	80				.866	1.414	2.000	OH
	F	60				.000	.586	1.134	F

which vary from of 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 11.2. 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 Fe^{2+} or Ti^{4+} 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^{TR} in tremolite.

TALC: $Mg_3Si_4O_{10}(OH)_2$

Site	El.	Frequency %	Min.	Mean	Max.	El.
		20 40 60 80				
Z	Si		3.873	3.964	4.027	Si
	Al		.000	.032	.127	Al
Y	Al		.000	.014	.068	Al
	Ti		.000	.000	.002	Ti
	Fe		.000	.021	.050	Fe
	Mg		2.912	2.969	3.026	Mg
Int.	Ca		.001	.015	.033	Ca
	Na		.000	.028	.084	Na
	K		.000	.002	.012	K
'OH'	OH		1.095	1.605	1.929	OH
	F		.071	.398	.905	F

Figure II.4 Cation and anion distribution in talc. Unshaded and shaded areas as for tremolite.

II.3a.3 Anion Distribution

The H_2O 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 H_2O) 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 anti-thetic 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 Fe^{2+} -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. (1969) or can be considered as impurities within the talc crystal (G.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 tetrahedrally 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.

11.3b.2 Anion Distribution

The amount of H_2O 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 ($X_F=0.036$) and the maximum is 0.905 ($X_F=0.453$) 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 X_F 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 can not 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 (eg. 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 II.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: $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$

Site	El.	Frequency %				Min.	Mean	Max.	El.
		20	40	60	80				
Z	Si	[shaded bar]				2.861	3.015	3.141	Si
	Al	[unshaded bar]				.859	.985	1.139	Al
Y	Al	[unshaded bar]				.000	.053	.184	Al
	Ti	[unshaded bar]				.000	.013	.036	Ti
	Fe	[unshaded bar]				.018	.050	.086	Fe
	Mg	[shaded bar]				2.720	2.884	2.964	Mg
X	Ca	[unshaded bar]				.001	.007	.023	Ca
	Na	[unshaded bar]				.008	.061	.144	Na
	K	[shaded bar]				.772	.866	.958	K
OH	OH	[shaded bar]				.440	.985	1.767	OH
	F	[unshaded bar]				.233	1.015	1.560	F

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 H_2O 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 II.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 II.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

TRIPOLITE. CMB

SAMPLE	H67012	82-815834-1	83-815834-1	82-815834-1	82-815834-1	82-815846	82-854041-1B	83-854041-1B	81-854041-1B	82-854041-1B	SAMPLE
Pt Norm	O5 ISOEX	81 ISOCHX	82 ISOCHX	83 ISOCHX	82 ISOCHX	82 ISOCHX	OJA ISOCHX	DIB ISOCHX	OJA ISOCHX	OJB ISOCHX	Pt Norm
SiO2	55.39	54.81	53.91	55.13	55.61	56.98	55.74	54.20	55.18	55.41	SiO2
Al2O3	3.97	3.51	3.66	2.58	1.01	1.19	2.19	2.42	3.16	2.54	Al2O3
TiO2	.88	14	18	12	.08	.03	.00	.00	.00	.00	TiO2
FeO	38	42	36	37	56	56	58	56	74	72	FeO
MgO	23.42	23.81	24.13	24.53	23.99	23.87	23.58	23.34	23.19	23.12	MgO
CaO	14.21	14.86	14.11	14.19	14.27	14.33	14.16	14.53	14.25	14.19	CaO
Mn2O	59	56	84	59	77	41	42	27	46	55	Mn2O
K2O	.69	23	23	13	.02	.02	.09	.84	.13	.28	K2O
H2O	1.32	1.33	1.55	1.41	1.44	1.43	1.27	1.31	1.29	1.23	H2O
F	1.88	1.74	1.32	1.23	1.49	1.59	1.98	1.86	1.87	1.99	F
-O=F	79	74	56	52	63	67	80	78	79	84	-O=F
Total	180.74	99.88	99.74	100.13	98.16	99.64	99.35	99.94	99.42	99.31	Total

SINCE 1913

82-454041-1B	01-854041-1B	01-854041-1B	02-854041-1B
01A 13cMK	01B 15cMK	01A 13cMK	02B 15cMK
55 74	54 20	55 10	55 41
2 17	2 42	3 16	2 54
00	00	00	00
00	00	00	00
60	76	76	72
23 58	23 34	23 19	23 12
14 16	14 53	14 25	14 19
42	27	46	55
09	64	13	28
1 27	1 31	1 29	1 23
1 90	1 84	1 87	1 99
60	78	79	84
99 35	99 94	99 42	99 31

CALCULATED FORMULAS

	7 527	7 462	7 486	7 534	7 773	7 779	7 697	7 661	7 418	7 662
SI	473	538	593	416	166	192	303	339	392	338
AI	8 000	8 000	7 999	7 950	7 939	7 971	8 000	8 000	8 000	8 000
AL	161	834	880	880	880	880	833	849	133	874
TL	808	815	819	812	800	803	800	808	808	808
Fe	848	848	840	808	802	864	891	887	888	883
MG	4 727	4 983	4 941	4 982	4 998	4 853	4 779	4 742	4 748	4 748
CA	861	888	880	880	880	869	881	122	888	895
	5 000	5 000	5 000	5 000	5 000	5 000	5 000	5 000	5 000	5 000
Fe	880	881	883	841	851	880	880	880	880	886
MG	880	880	889	880	880	880	880	880	880	888
CA	2 000	1 999	1 977	1 958	1 939	2 000	2 000	2 000	2 000	2 000
MA	880	880	880	880	880	880	880	880	880	880
	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000
CA	904	123	113	157	224	879	129	880	143	880
MA	158	153	227	207	112	185	114	873	125	158
K	816	840	841	823	804	804	816	807	823	834
	174	316	381	387	360	138	359	880	291	186
OR	1 193	1 229	1 425	1 467	1 343	1 310	1 172	1 194	1 184	1 131
F	807	771	575	533	437	670	828	886	816	819
	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000
IF	484	386	288	266	329	345	414	403	488	434

III

SAMPLE	82-850403	82-849047	82-849047	82-756694-3	82-756694-3	82-756694-3	82-756694-3	82-756694-3	82-837748	82-837748
Pr Norm	02 15eNK	01 15eNK	02 15eNK	01A 15eNK	01B 15eNK	02A 23(O)	02B 23(O)	01A 15eNK	01A 15eNK	02A 15eNK
S102	57.42	58.11	57.90	55.85	55.85	56.93	57.44	54.54	54.54	54.55
A1203	1.34	20	38	1.66	3.83	1.66	2.05	1.73	1.73	1.14
T102	1.34	84	83	84	13	85	89	13	13	86
F80	1.04	55	52	39	38	39	38	61	67	70
H90	23.84	24.16	24.32	23.84	23.56	23.97	24.14	23.51	23.58	24.24
C40	13.45	13.75	13.14	14.03	13.72	13.99	14.32	13.75	13.55	13.58
M20	18	89	88	81	99	36	36	1.12	1.11	55
X20	19	64	82	83	17	83	12	53	58	11
H20	1.69	2.84	2.82	2.16	1.98	2.19	2.19	1.54	1.51	1.44
F	1.06	31	34	69	45	86	88	1.38	1.43	1.13
-O=F	45	13	14	84	19	00	83	58	48	48
Total	99.87	99.13	98.58	100.18	100.07	99.51	101.24	100.46	100.52	99.15

STANDARD LIGHT BOX

4-3	63-75694-3	61-632748	62-632748	62-833748
02B	23(0)	01A 15eHK	01B 15eHK	02A 13eCHK
	57 44	54 54	55 08	56 35
	2 05	1 73	3 28	1 14
	88	13	21	86
	30	61	67	70
	24 14	23 51	23 58	24 34
	14 22	13 75	13 55	13 58
	36	1 12	1 11	35
	12	53	58	11
	2 19	1 54	1 51	1 44
	68	1 38	1 43	1 13
	03	58	60	48
	101 24	108 46	100 52	99 15

5710003 0319195193

Symbol	7 838	7 756	7 742	7 811	7 756	7 786	7 759	7 772	7 552	7 767
Si	162	332	338	186	340	214	241	220	448	185
Al	8 000	8 000	8 000	8 000	8 000	8 000	8 000	8 000	8 000	7 952
Al	853	888	910	878	129	844	884	852	869	880
Al	810	884	883	884	813	885	813	885	822	886
Fe	887	868	882	846	843	885	843	893	891	881
Mg	4 850	4 931	4 985	4 838	4 804	4 886	4 883	4 817	4 816	4 962
Ca	886	885	880	844	811	820	821	825	888	888
Ca	5 000	5 000	5 000	5 000	5 000	5 000	5 000	5 000	5 000	5 000
Fe	822	888	861	886	888	888	888	888	889	816
Mg	888	888	888	888	888	888	888	888	888	888
Ca	1 767	2 000	2 000	2 000	2 000	2 000	2 000	2 000	1 952	1 952
Mn	881	880	880	880	880	880	880	880	880	880
Ca	2 888	2 888	2 888	2 888	2 888	2 888	2 888	2 888	2 888	2 888
Ca	888	812	888	888	888	838	830	888	888	862
Mn	887	884	821	110	243	895	894	301	299	148
K	833	887	884	885	838	885	821	894	183	828
OH	1 542	1 461	1 852	1 941	1 804	2 008	1 946	1 483	1 381	1 508
F	458	137	148	839	194	888	834	597	619	492
Y	2 000	2 008	2 080	2 080	2 080	2 080	2 000	2 000	2 000	2 000
Y	229	869	874	819	887	888	817	298	310	246

TEMPERATURE: CMB OXIDE WEIGHT PERCENTS

SAMPLE	02-032746	02-032746	02-032746	02-032746	02-032746	SAMPLE
Pr Norm	020 156K	03 136CHK	04 136CHK	05 156K	05 156K	Pr Norm
SiO2	56.46	56.31	54.13	56.78	56.78	SiO2
Al2O3	2.27	34	1.58	1.81	1.81	Al2O3
TiO2	14	.02	.07	.11	.11	TiO2
FeO	80	.73	.91	.88	.88	FeO
MgO	23.78	24.78	23.87	24.22	24.22	MgO
CaO	13.18	13.75	13.24	13.45	13.45	CaO
Mn2O	42	.38	.31	.46	.46	Mn2O
K2O	13	.14	.48	.13	.13	K2O
H2O	1.67	1.79	1.56	1.69	1.69	H2O
F	1.59	.89	1.38	1.87	1.87	F
-O-F	46	37	.55	.45	.45	-O-F
Total	99.63	100.76	99.34	100.09	100.09	Total

CALCULATED FORMULAS

Si	7.757	7.874	7.732	7.721	7.721	Si
Al	.243	.854	.256	.278	.278	Al
Al	8.000	7.938	7.986	8.000	8.000	Al
Ti	.123	.000	.000	.013	.013	Ti
Fe	.016	.002	.007	.013	.013	Fe
Fe	.025	.010	.024	.055	.055	Fe
Mg	4.836	4.988	4.899	4.921	4.921	Mg
Ca	.000	.000	.000	.000	.000	Ca
Fe	.067	.071	.011	.036	.036	Fe
Mg	.888	.888	.000	.000	.000	Mg
Ca	6.753	1.928	1.981	1.964	1.964	Ca
Mn	.000	.000	.000	.000	.000	Mn
Ca	2.000	2.000	2.000	2.000	2.000	Ca
Ca	.000	.002	.000	.000	.000	Ca
Mn	.113	.101	.211	.168	.168	Mn
K	.023	.024	.071	.023	.023	K
OH	1.524	1.619	1.493	1.538	1.538	OH
F	.476	.381	.578	.462	.462	F
I	2.000	2.000	2.000	2.000	2.000	I
F	.238	.190	.285	.231	.231	F

TALC CMB

SAMPLE		OXIDE WEIGHT PERCENTS										SAMPLE	
Pr	Norm	81-756694-1	81-756694-1	81-756694-1	81-756694-1	81-756694-1	81-756694-1	81-756694-1	81-756694-1	81-756694-1	81-756694-1	Pr	Norm
		01 %CNK	02 %CNK	01 %CNK	02 %CNK	01 %CNK	02 %CNK	01 %CNK	02 %CNK	01 %CNK	02 %CNK		
SiO ₂	41.74	62.34	62.31	62.26	60.95	60.95	62.26	62.31	62.34	61.57	60.39	SiO ₂	62.49
Al ₂ O ₃	1	56	51	50	1.71	1.71	50	51	56	1.33	89	Al ₂ O ₃	44
FeO	37	41	36	19	38	38	19	36	41	00	83	FeO	00
MgO	30.88	30.86	31.28	31.10	31.45	31.45	31.10	31.28	30.86	31.15	31.34	MgO	31.00
CaO	09	21	02	03	29	29	03	02	21	28	47	CaO	25
MnO	21	24	09	07	66	66	07	09	24	59	51	MnO	09
K ₂ O	04	04	04	04	05	05	04	04	04	01	01	K ₂ O	00
H ₂ O	3.94	3.92	4.42	4.48	3.25	3.25	4.48	4.42	3.94	3.46	3.46	H ₂ O	3.31
F	1.57	1.67	48	42	2.99	2.99	42	48	1.57	2.43	2.50	F	2.95
-O=F	1.70	1.70	20	18	1.26	1.26	18	20	1.70	1.11	1.05	-O=F	1.24
Total	99.19	99.67	99.15	98.72	100.52	100.52	98.72	99.15	99.67	99.54	99.09	Total	99.98

CALCULATED FORMULAS

[illegible]

OXIDE WEIGHT PERCENTS

[illegible]

CALCULATED FORMULAS

3 991	3 989	3 981	3 932	3 950	3 927	3 934	3 950	3 904	3 925	3 976
009	011	019	054	050	053	046	050	060	021	024
4 000	4 000	4 000	4 000	4 000	3 980	3 980	3 980	3 964	3 994	4 000
013	045	039	000	012	000	000	000	000	000	009
000	000	000	000	000	000	000	000	000	001	002
005	015	024	013	011	014	014	013	017	049	047
2 912	2 930	2 937	3 001	2 977	3 006	3 016	3 013	3 013	2 954	2 943
3 000	3 000	3 000	3 014	3 000	3 010	3 010	3 010	3 004	3 000	3 000
021	013	013	032	022	019	011	011	010	008	011
013	013	024	058	041	038	041	041	041	043	046
000	004	003	003	003	005	003	003	003	002	006
843	050	040	093	064	072	064	064	064	062	067
3 359	3 324	3 314	3 291	3 310	3 347	3 350	3 343	3 343	3 367	3 371
641	678	684	609	390	353	350	347	347	333	346
2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000
321	318	342	204	195	177	175	167	169	162	148

OXIDE WEIGHT PERCENTS

TALC CNB		OXIDE WEIGHT PERCENTS			
SAMPLE	42-889047	81-849047	62-83748	82-83748	82-832748
Pt Norm	01.76CNK	02.76CNK	03.76CNK	04.76CNK	05.76CNK
SiO ₂	62.27	61.71	62.66	62.24	62.06
Al ₂ O ₃	06	08	15	00	13
TiO ₂	02	00	00	00	00
FeO	59	54	93	72	77
MgO	31.27	31.06	31.01	30.88	31.04
CaO	13	13	20	09	42
Mn ₂ O	00	03	00	08	02
K ₂ O	01	03	00	01	14
H ₂ O	4.46	4.48	4.13	3.98	4.22
F	40	35	1.33	1.47	98
-O=F	20	15	52	62	41
Total	99.09	98.38	99.79	99.05	99.39

CALCULATED FORMULAS

Si	3 982	3 980	3 993	3 993	3 982	Si
Al	005	006	007	007	010	Al
	3 987	3 986	4 000	4 000	3 992	
Al	000	000	004	008	000	Al
Al	001	000	000	000	000	Al
Ti	001	000	000	000	000	Ti
Fe	032	029	050	039	041	Fe
	2 980	2 985	2 946	2 953	2 967	
Mg	3 013	3 014	3 000	3 000	3 008	Mg
	009	016	014	006	029	
Ca	000	004	000	010	003	Ca
Na	001	002	000	001	012	Na
K	010	027	014	017	044	K
	1 903	1 929	1 752	1 702	1 802	
OH	097	071	248	298	198	OH
F	2 800	2 000	2 000	2 000	2 000	F
	049	036	124	149	99	
I						I
F						F

OXIDE WEIGHT PERCENTS

CALCULATED FORMULAS

	3 049	3 022	3 092	3 059	3 007	3 064	1 910	2 945	2 947	3 047
Si	951	978	908	941	993	936	1 010	1 035	1 053	950
Al	4 000	4 000	4 000	4 000	4 000	4 000	4 000	4 000	4 000	4 000
Al	040	044	041	030	019	076	000	003	034	058
Ti	002	002	000	000	003	003	000	006	005	005
Fe	017	038	036	026	018	024	016	027	017	046
Mg	2 913	2 916	2 923	2 944	2 910	2 897	2 819	2 964	2 993	1 891
-	3 000	3 000	3 000	3 000	3 000	3 000	3 000	3 000	3 000	3 000
Ca	008	023	001	003	012	010	004	011	004	010
Mn	007	095	090	078	088	098	088	081	088	009
K	857	855	784	775	777	772	819	860	840	851
OH	451	440	687	642	505	532	576	985	1 003	794
F	1 549	1 560	1 313	1 358	1 495	1 468	1 044	1 015	977	1 006
1	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000
1	774	780	656	679	748	734	512	508	498	603

PHILOSCOPITE CMB

SAMPLE	82-851046	82-851046	82-851046	80-858441-1B	82-854041-1B	82-854041-1B	82-854041-1B	81-755740-1	82-755740-1	82-755740-1	SAMPLE
Pt. Name	04 TeCNK	05 TeCNK	06 TeCNK	02 TeCNK	03 TeCNK	04 TeCNK	06 TeCNK	03A TeCNK	03B TeCNK	05 TeCNK	Pt. Name
S101	43 59	43 88	43 71	43 54	43 72	45 10	44 54	44 12	45 17	43 85	S101
A1203	12 27	13 34	12 19	11 72	11 59	11 45	11 99	11 37	11 02	11 94	A1203
Ti02	08	16	09	02	02	00	00	03	03	01	Ti02
F80	76	79	75	59	57	56	57	31	31	37	F80
MgO	27 96	27 49	27 80	28 33	28 41	28 53	28 40	28 16	28 37	28 33	MgO
CaO	15	16	26	05	05	08	09	11	10	1	CaO
Mn2O	48	1 01	48	70	63	61	57	62	58	62	Mn2O
K2O	8 88	9 14	8 99	9 03	8 86	8 78	9 05	9 21	8 78	9 27	K2O
H2O	1 71	1 77	1 87	1 85	1 82	1 16	1 17	1 79	1 75	1 59	H2O
F	5 45	5 39	5 12	7 02	6 87	6 86	5 44	5 29	5 44	5 31	F
-3-F	2 29	2 27	2 36	2 96	1 89	2 90	2 82	2 33	2 29	2 24	-3-F
Total	98 94	108 06	99 21	98 89	98 85	100 39	100 29	99 01	99 26	99 51	Total

OXIDE WEIGHT PERCENTS

1-18	82-054041-15	82-755740-1	82-755740-1	82-755740-1
Q	038 7eCMX	03A 7eCMX	03B 7eCMX	05 7eCMX
	44 54	44 12	45 17	43 45
	11 99	11 37	11 03	11 94
	83	13	13	12
	57	33	31	37
	28 40	28 16	18 17	28 33
	09	12	10	4
	57	62	58	62
	9 05	9 21	8 28	9 22
	1 17	1 79	1 75	1 79
	6 70	5 29	5 44	5 31
	2 82	2 23	2 28	2 24
	100 19	99 01	99 24	96 51

CALCULATED FORMULAS

	3 035	2 999	3 031	3 050	3 054	3 100	3 072	3 088	3 141	3 053	55
Al	965	1 001	949	958	946	900	918	912	859	94	Al
Al	4 000	4 000	4 000	4 000	4 000	4 000	4 000	4 000	4 000	4 000	Al
Al	944	993	954	917	908	944	916	926	945	932	Al
Ti	004	000	000	001	001	000	000	007	007	006	Ti
Fe	044	086	048	035	033	032	032	019	018	022	Fe
Mg	2 908	2 853	2 873	2 947	2 958	2 924	2 899	2 948	2 936	2 940	Mg
	3 000	3 000	3 000	3 000	3 000	3 000	3 000	3 000	3 000	3 000	
Ca	012	013	012	004	004	006	017	009	008	017	Ca
Na	069	164	088	102	092	087	082	080	082	081	Na
K	837	855	843	869	850	816	823	866	821	848	K
	918	1 012	933	975	946	919	942	964	911	949	
OH	796	818	821	443	479	505	539	832	807	832	OH
F	1 204	1 182	1 139	1 557	1 521	1 495	1 481	1 168	1 163	1 46	F
	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	
I	602	591	585	778	761	748	730	584	594	584	I

OXIDE WEIGHT PERCENTS

[illegible]

CALCULATED FORMULAS

Si	3 041	3 046	3 052	3 049	3 053	3 057	3 060	3 061	3 062	3 063	3 064	3 065	3 066	3 067	3 068	3 069	3 070	3 071	3 072	3 073	3 074	3 075	3 076	3 077	3 078	3 079	3 080	3 081	3 082	3 083	3 084	3 085	3 086	3 087	3 088	3 089	3 090	3 091	3 092	3 093	3 094	3 095	3 096	3 097	3 098	3 099	3 100	3 101	3 102	3 103	3 104	3 105	3 106	3 107	3 108	3 109	3 110	3 111	3 112	3 113	3 114	3 115	3 116	3 117	3 118	3 119	3 120	3 121	3 122	3 123	3 124	3 125	3 126	3 127	3 128	3 129	3 130	3 131	3 132	3 133	3 134	3 135	3 136	3 137	3 138	3 139	3 140	3 141	3 142	3 143	3 144	3 145	3 146	3 147	3 148	3 149	3 150	3 151	3 152	3 153	3 154	3 155	3 156	3 157	3 158	3 159	3 160	3 161	3 162	3 163	3 164	3 165	3 166	3 167	3 168	3 169	3 170	3 171	3 172	3 173	3 174	3 175	3 176	3 177	3 178	3 179	3 180	3 181	3 182	3 183	3 184	3 185	3 186	3 187	3 188	3 189	3 190	3 191	3 192	3 193	3 194	3 195	3 196	3 197	3 198	3 199	3 200	3 201	3 202	3 203	3 204	3 205	3 206	3 207	3 208	3 209	3 210	3 211	3 212	3 213	3 214	3 215	3 216	3 217	3 218	3 219	3 220	3 221	3 222	3 223	3 224	3 225	3 226	3 227	3 228	3 229	3 230	3 231	3 232	3 233	3 234	3 235	3 236	3 237	3 238	3 239	3 240	3 241	3 242	3 243	3 244	3 245	3 246	3 247	3 248	3 249	3 250	3 251	3 252	3 253	3 254	3 255	3 256	3 257	3 258	3 259	3 260	3 261	3 262	3 263	3 264	3 265	3 266	3 267	3 268	3 269	3 270	3 271	3 272	3 273	3 274	3 275	3 276	3 277	3 278	3 279	3 280	3 281	3 282	3 283	3 284	3 285	3 286	3 287	3 288	3 289	3 290	3 291	3 292	3 293	3 294	3 295	3 296	3 297	3 298	3 299	3 300	3 301	3 302	3 303	3 304	3 305	3 306	3 307	3 308	3 309	3 310	3 311	3 312	3 313	3 314	3 315	3 316	3 317	3 318	3 319	3 320	3 321	3 322	3 323	3 324	3 325	3 326	3 327	3 328	3 329	3 330	3 331	3 332	3 333	3 334	3 335	3 336	3 337	3 338	3 339	3 340	3 341	3 342	3 343	3 344	3 345	3 346	3 347	3 348	3 349	3 350	3 351	3 352	3 353	3 354	3 355	3 356	3 357	3 358	3 359	3 360	3 361	3 362	3 363	3 364	3 365	3 366	3 367	3 368	3 369	3 370	3 371	3 372	3 373	3 374	3 375	3 376	3 377	3 378	3 379	3 380	3 381	3 382	3 383	3 384	3 385	3 386	3 387	3 388	3 389	3 390	3 391	3 392	3 393	3 394	3 395	3 396	3 397	3 398	3 399	3 400	3 401	3 402	3 403	3 404	3 405	3 406	3 407	3 408	3 409	3 410	3 411	3 412	3 413	3 414	3 415	3 416	3 417	3 418	3 419	3 420	3 421	3 422	3 423	3 424	3 425	3 426	3 427	3 428	3 429	3 430	3 431	3 432	3 433	3 434	3 435	3 436	3 437	3 438	3 439	3 440	3 441	3 442	3 443	3 444	3 445	3 446	3 447	3 448	3 449	3 450	3 451	3 452	3 453	3 454	3 455	3 456	3 457	3 458	3 459	3 460	3 461	3 462	3 463	3 464	3 465	3 466	3 467	3 468	3 469	3 470	3 471	3 472	3 473	3 474	3 475	3 476	3 477	3 478	3 479	3 480	3 481	3 482	3 483	3 484	3 485	3 486	3 487	3 488	3 489	3 490	3 491	3 492	3 493	3 494	3 495	3 496	3 497	3 498	3 499	3 500	3 501	3 502	3 503	3 504	3 505	3 506	3 507	3 508	3 509	3 510	3 511	3 512	3 513	3 514	3 515	3 516	3 517	3 518	3 519	3 520	3 521	3 522	3 523	3 524	3 525	3 526	3 527	3 528	3 529	3 530	3 531	3 532	3 533	3 534	3 535	3 536	3 537	3 538	3 539	3 540	3 541	3 542	3 543	3 544	3 545	3 546	3 547	3 548	3 549	3 550	3 551	3 552	3 553	3 554	3 555	3 556	3 557	3 558	3 559	3 560	3 561	3 562	3 563	3 564	3 565	3 566	3 567	3 568	3 569	3 570	3 571	3 572	3 573	3 574	3 575	3 576	3 577	3 578	3 579	3 580	3 581	3 582	3 583	3 584	3 585	3 586	3 587	3 588	3 589	3 590	3 591	3 592	3 593	3 594	3 595	3 596	3 597	3 598	3 599	3 600	3 601	3 602	3 603	3 604	3 605	3 606	3 607	3 608	3 609	3 610	3 611	3 612	3 613	3 614	3 615	3 616	3 617	3 618	3 619	3 620	3 621	3 622	3 623	3 624	3 625	3 626	3 627	3 628	3 629	3 630	3 631	3 632	3 633	3 634	3 635	3 636	3 637	3 638	3 639	3 640	3 641	3 642	3 643	3 644	3 645	3 646	3 647	3 648	3 649	3 650	3 651	3 652	3 653	3 654	3 655	3 656	3 657	3 658	3 659	3 660	3 661	3 662	3 663	3 664	3 665	3 666	3 667	3 668	3 669	3 670	3 671	3 672	3 673	3 674	3 675	3 676	3 677	3 678	3 679	3 680	3 681	3 682	3 683	3 684	3 685	3 686	3 687	3 688	3 689	3 690	3 691	3 692	3 693	3 694	3 695	3 696	3 697	3 698	3 699	3 700	3 701	3 702	3 703	3 704	3 705	3 706	3 707	3 708	3 709	3 710	3 711	3 712	3 713	3 714	3 715	3 716	3 717	3 718	3 719	3 720	3 721	3 722	3 723	3 724	3 725	3 726	3 727	3 728	3 729	3 730	3 731	3 732	3 733	3 734	3 735	3 736	3 737	3 738	3 739	3 740	3 741	3 742	3 743	3 744	3 745	3 746	3 747	3 748	3 749	3 750	3 751	3 752	3 753	3 754	3 755	3 756	3 757	3 758	3 759	3 760	3 761	3 762	3 763	3 764	3 765	3 766	3 767	3 768	3 769	3 770	3 771	3 772	3 773	3 774	3 775	3 776	3 777	3 778	3 779	3 780	3 781	3 782	3 783	3 784	3 785	3 786	3 787	3 788	3 789	3 790	3 791	3 792	3 793	3 794	3 795	3 796	3 797	3 798	3 799	3 800	3 801	3 802	3 803	3 804	3 805	3 806	3 807	3 808	3 809	3 810	3 811	3 812	3 813	3 814	3 815	3 816	3 817	3 818	3 819	3 820	3 821	3 822	3 823	3 824	3 825	3 826	3 827	3 828	3 829	3 830	3 831	3 832	3 833	3 834	3 835	3 836	3 837	3 838	3 839	3 840	3 841	3 842	3 843	3 844	3 845	3 846	3 847	3 848	3 849	3 850	3 851	3 852	3 853	3 854	3 855	3 856	3 857	3 858	3 859	3 860	3 861	3 862	3 863	3 864	3 865	3 866	3 867	3 868	3 869	3 870	3 871	3 872	3 873	3 874	3 875	3 876	3 877	3 878	3 879	3 880	3 881	3 882	3 883	3 884	3 885	3 886	3 887	3 888	3 889	3 890	3 891	3 892	3 893	3 894	3 895	3 896	3 897	3 898	3 899	3 900	3 901	3 902	3 903	3 904	3 905	3 906	3 907	3 908	3 909	3 910	3 911	3 912	3 913	3 914	3 915	3 916	3 917	3 918	3 919	3 920	3 921	3 922	3 923	3 924	3 925	3 926	3 927	3 928	3 929	3 930	3 931	3 932	3 933	3 934	3 935	3 936	3 937	3 938	3 939	3 940	3 941	3 942	3 943	3 944	3 945	3 946	3 947	3 948	3 949	3 950	3 951	3 952	3 953	3 954	3 955	3 956	3 957	3 958	3 959	3 960	3 961	3 962	3 963	3 964	3 965	3 966	3 967	3 968	3 969	3 970	3 971	3 972	3 973	3 974	3 975	3 976	3 977	3 978	3 979	3 980	3 981	3 982	3 983	3 984	3 985	3 986	3 987	3 988	3 989	3 990	3 991	3 992	3 993	3 994	3 995	3 996	3 997	3 998	3 999	4 000	4 001	4 002	4 003	4 004	4 005	4 006	4 007	4 008	4 009	4 010	4 011	4 012	4 013	4 014	4 015	4 016	4 017	4 018	4 019	4 020	4 021	4 022	4 023	4 024	4 025	4 026	4 027	4 028	4 029	4 030	4 031	4 032	4 033	4 034	4 035	4 036	4 037	4 038	4 039	4 040	4 041	4 042	4 043	4 044	4 045	4 046	4 047	4 048	4 049	4 050	4 051	4 052	4 053	4 054	4 055	4 056	4 057	4 058	4 059	4 060	4 061	4 062	4 063	4 064	4 065	4 066	4 067	4 068	4 069	4 070	4 071	4 072	4 073	4 074	4 075	4 076	4 077	4 078	4 079	4 080	4 081	4 082	4 083	4 084	4 085	4 086	4 087	4 088	4 089	4 090	4 091	4 092	4 093	4 094	4 095	4 096	4 097	4 098	4 099	4 100	4 101	4 102	4 103	4 104	4 105	4 106	4 107	4 108	4 109	4 110	4 111	4 112	4 113	4 114	4 115	4 116	4 117	4 118	4 119	4 120	4 121	4 122	4 123	4 124	4 125	4 126	4 127	4 128	4 129	4 130	4 131	4 132	4 133	4 134	4 135	4 136	4 137	4 138	4 139	4 140	4 141	4 142	4 143	4 144	4 145	4 146	4 147	4 148	4 149	4 150	4 151	4 152	4 153	4 154	4 155	4 156	4 157	4 158	4 159	4 160	4 161	4 162	4 163	4 164	4 165	4 166	4 167	4 168	4 169	4 170	4 171	4 172	4 173	4 174	4 175	4 176	4 177	4 178	4 179	4 180	4 181	4 182	4 183	4 184	4 185	4 186	4 187	4 188	4 189	4 190	4 191	4 192	4 193	4 194	4 195	4 196	4 197	4 198	4 199	4 200	4 201	4 202	4 203	4 204	4 205	4 206	4 207	4 208	4 209	4 210	4 211	4 212	4 213	4 214	4 215	4 216	4 217	4 218	4 219	4 220	4 221	4 222	4 223	4 224	4 225	4 226	4 227	4 228	4 229	4 230	4 231	4 232	4 233	4 234	4 235	4 236	4 237	4 238	4 239	4 240	4 241	4 242	4 243	4 244	4 245	4 246	4 247	4 248	4 249	4 250	4 251	4 252	4 253	4 254	4 255	4 256	4 257	4 258	4 259	4 260	4 261	4 262	4 263	4 264	4 265	4 266	4 267	4 268	4 269	4 270	4 271	4 272	4 273	4 274	4 275	4 276	4 277	4 278	4 279	4 280	4 281	4 282	4 283	4 284	4 285	4 286	4 287	4 288	4 289	4 290	4

PHLOGOPHILE CMS

OXIDE WEIGHT PERCENTS

SAMPLE	82-849847	82-849847	82-756694-3	82-756694-3	82-756694-3	82-756694-3	82-831748	82-832748	82-832748	82-832748	SAMPLE
Pr Norm	05A 7eCNK	05B 7eCNK	01A 7eCNK	01B 7eCNK	02A 7eCNK	01B 7eCNK	01A 7eCNK	02A 7eCNK	01B 7eCNK	02A 7eCNK	Pr Norm
SiO2	41.93	41.91	40.85	40.18	40.43	40.84	42.48	42.65	42.40	43.03	SiO2
Al2O3	13.31	13.59	15.12	15.54	15.44	15.23	12.11	12.01	11.16	11.85	Al2O3
TiO2	38	31	57	54	58	50	40	34	33	34	TiO2
FeO	1.13	1.11	1.08	1.20	1.10	1.45	94	91	93	93	FeO
MgO	26.75	26.98	25.77	25.78	25.49	25.78	27.99	28.08	27.59	28.07	MgO
CaO	07	05	09	11	05	06	04	08	04	09	CaO
MnO	09	08	1.61	1.72	1.54	1.42	18	15	14	14	MnO
K2O	9.48	9.49	9.17	8.92	9.24	9.34	10.15	10.05	10.20	10.81	K2O
H2O	3.85	3.85	3.75	3.64	3.62	3.75	2.12	2.15	2.16	2.13	H2O
F	2.61	2.53	1.04	1.22	1.30	1.05	4.50	4.45	4.20	4.52	F
-O-F	1.10	1.07	44	51	55	44	1.89	1.87	1.77	1.90	-O-F
Total	98.90	98.44	98.96	98.65	99.00	99.33	99.82	98.95	98.81	99.12	Total

CALCULATED FORMULAS

Si	3.009	2.950	2.905	2.861	2.872	2.894	2.987	2.998	2.982	3.018	Si
Al	991	1.050	1.095	1.139	1.128	1.104	1.004	990	993	980	Al
Al	109	077	173	165	184	164	080	000	014	000	Al
Ti	831	017	031	029	031	016	011	019	028	014	Ti
Fe	064	065	044	071	045	086	055	054	053	055	Fe
Mg	2.794	2.831	2.732	2.735	2.720	2.722	2.933	2.933	2.903	2.933	Mg
Ca	005	004	007	009	004	005	003	006	002	007	Ca
Ba	013	011	045	048	044	039	016	021	020	020	Ba
Mn	869	894	836	819	847	804	956	945	958	940	Mn
K	887	909	936	919	940	922	998	981	972	967	K
OH	1.423	1.436	1.747	1.726	1.709	1.765	1.062	1.009	1.063	1.004	OH
F	577	564	233	274	291	235	937	991	937	1.004	F
X F	2.808	2.000	2.000	2.000	2.000	1.000	1.000	2.000	2.000	2.000	X F
X F	289	282	117	137	144	118	501	495	488	502	X F

APPENDIX III

COMPUTER PROGRAMS

III.1 MINCAL

III.2 SOLCRV

12:70 DEC 06 19 MINERAL 1002148

```

1 - 1.000 C*****
2 - 2.000 C
3 - 3.000 C      PROGRAM MINCON
4 - 4.000 C
5 - 5.000 C*****
6 - 6.000 C
7 - 7.000 C SET 104 INPUT DATA FROM EMPAGE
8 - 8.000 C SET 107 OUTPUT FILE TO CONTAIN TOTALS AND ALL NORMALIZATION
9 - 9.000 C      FOR EACH ANALYSIS
10 - 10.000 C SET 109 BMDP-COMPATIBLE FILE: TW13CNK
11 - 11.000 C SET 110      : TR15EN
12 - 12.000 C SET 111      : TR15E
13 - 13.000 C SET 113      : TC2ECN
14 - 14.000 C SET 114      : PH2ECN
15 - 15.000 C
16 - 16.000 C*****
17 - 17.000 C
18 - 18.000 C      IMPLICIT DOUBLE PRECISION (A-H,M,O-Z)
19 - 19.000 C      CHARACTER EL*2,SL*11,MIN*2,TITL1*7,TITL2*6,PH*1,PH2*1
20 - 20.000 C      DIMENSION EL(12),WPOX(15),TITL1(14),TITL2(14),MU(16),
21 - 21.000 C      &      WTRCT(14),FORAM1(15),FORAM2(15),FORAM3(15),FORAM4(15),
22 - 22.000 C      &      APOX(15)
23 - 23.000 C
24 - 24.000 C      DATA MWAL/26.9815/,MWCA/40.08/,MWFE/18.9984/,MWFL/55.847/
25 - 25.000 C      DATA MWH/1.00797/,MWK/39.102/,MWMG/24.312/,MWHN/54.9366/
26 - 26.000 C      DATA MWNA/22.98983/,MWQ/15.9994/,MWSI/28.086/,MWTI/42.9/
27 - 27.000 C      DATA MWCL/35.453/,MWALX/101.9612/,MWCAV/56.0794/,MWFI/11.2141/
28 - 28.000 C      DATA MWH20/18.01534/,MWKX/94.2034/,MWMGY/40.3114/
29 - 29.000 C      DATA MWMNX/70.9374/,MWNAX/61.97906/,MWSIX/60.0848/
30 - 30.000 C      DATA MWTIX/72.8998/
31 - 31.000 C      DATA NAL/15/,NCA/15/,NCL/15/,NFE/15/,NFE/15/,NN/15/,NMG/15/
32 - 32.000 C      DATA NMN/15/,NNA/15/,NSI/15/,NTI/15/
33 - 33.000 C      DATA TITL1(1)/// SI02//,TITL1(2)/// AL2O3//,TITL1(3)/// TiO2//
34 - 34.000 C      DATA TITL1(4)/// FeO//,TITL1(5)/// MgO//,TITL1(6)/// MnO//
35 - 35.000 C      DATA TITL1(7)/// CaO//,TITL1(8)/// Na2O//,TITL1(9)/// K2O//
36 - 36.000 C      DATA TITL1(10)/// H2O//,TITL1(11)/// F//,TITL1(12)/// CO2//
37 - 37.000 C      DATA TITL1(13)///-D=F,CL//,TITL1(14)/// TOTAL//
38 - 38.000 C      DATA TITL2(1)///SI//,TITL2(2)///AL//,TITL2(3)///AL//,TITL2(4)///Ti//
39 - 39.000 C      DATA TITL2(5)///Fe//,TITL2(6)///Mn//,TITL2(7)///Mg//,TITL2(8)///Ca//
40 - 40.000 C      DATA TITL2(9)///Na//,TITL2(10)///K//,TITL2(11)///OH//
41 - 41.000 C      DATA TITL2(12)///CL//,TITL2(13)///F//,TITL2(14)///YF//
42 - 42.000 C
43 - 43.000 C      WRITE (108,105)
44 - 44.000 105  FORMAT (' CREATE BMDP-COMPATABLE FILES FOR CALCULATION',
45 - 45.000 C      &      ' FORMULAS? (Y/N)')
46 - 46.000 C      READ (105,115) OUTOP
47 - 47.000 115  FORMAT (A1)
48 - 48.000 C      IF (OUTOP.EQ.'Y') THEN
49 - 49.000 C          WRITE (109,145)
50 - 50.000 145  FORMAT (' RESULTS FOR TR - 13eCNK:')
51 - 51.000 C          WRITE (110,155)
52 - 52.000 155  FORMAT (' RESULTS FOR TR - 15eCNK:')
53 - 53.000 C          WRITE (111,165)
54 - 54.000 165  FORMAT (' RESULTS FOR IR - 15eK:')
55 - 55.000 C          WRITE (113,245)
56 - 56.000 245  FORMAT (' RESULTS FOR TC - 7eCNK:')
57 - 57.000 C          WRITE (114,205)
58 - 58.000 205  FORMAT (' RESULTS FOR PH - 7eCNK:')

```

```

59 - 59.000      END IF
60 - 60.000      WPOX(15)=0.
61 - 61.000      READ(106,15) (EL(IA),IA=1,12)
62 - 62.000 15   FORMAT(12(2X,A2))
63 - 63.000      DO 10 IB=1,12
64 - 64.000          IF(EL(IB).EQ.'AL') NAL=IB
65 - 65.000          IF(EL(IB).EQ.'CA') NCA=IB
66 - 66.000          IF(EL(IB).EQ.'CL') NCL=IB
67 - 67.000          IF(EL(IB).EQ.'F') NF=IB
68 - 68.000          IF(EL(IB).EQ.'FE') NFE=IB
69 - 69.000          IF(EL(IB).EQ.'K') NK=IB
70 - 70.000          IF(EL(IB).EQ.'MG') NMG=IB
71 - 71.000          IF(EL(IB).EQ.'MN') NMN=IB
72 - 72.000          IF(EL(IB).EQ.'NA') NNA=IB
73 - 73.000          IF(EL(IB).EQ.'SI') NSI=IB
74 - 74.000          IF(EL(IB).EQ.'TI') NTI=IB
75 - 75.000          IF(EL(IB).EQ.'') RD TO
76 - 76.000 10   CONTINUE
77 - 77.000 17   NEL=IB-1
78 - 78.000 C
79 - 79.000      DO 20 IC=1,200
80 - 80.000          READ(106,25,END=97) SL,PR,M1N
81 - 81.000 25   FORMAT(A11,2A2)
82 - 82.000          READ(106,35) (WPOX(IE),IE=1,NEL)
83 - 83.000 35   FORMAT(15F5,2)
84 - 84.000          IF(M1N.EQ.'CH') GO TO 20
85 - 85.000          WRITE(107,125)
86 - 86.000 125  FORMAT(//,11X,76('='))
87 - 87.000 27   DO 30 ID=1,15
88 - 88.000          MOLPR(ID)=0.
89 - 89.000          APOX(ID)=0.
90 - 90.000          FORAM1(ID)=0.
91 - 91.000          FORAM2(ID)=0.
92 - 92.000          FORAM3(ID)=0.
93 - 93.000 30   CONTINUE
94 - 94.000          TOTAL=0.
95 - 95.000          APOXT=0.
96 - 96.000          DO 40 IF=1,NEL
97 - 97.000              TOTAL=TOTAL+WPOX(IF)
98 - 98.000 40   CONTINUE
99 - 99.000          MOEFCL=(WPOX(NF)*MWD/(2.*MWF))+(WPOX(NCL)*MWD/(2.*MWCL))
100 - 100.000      TOTAL=TOTAL-MOEFCL
101 - 101.000      MOLPR(1)=WPOX(NSI)/MWSTX
102 - 102.000      MOLPR(2)=WPOX(NAL)/MWALX
103 - 103.000      MOLPR(3)=WPOX(NTI)/MWITX
104 - 104.000      MOLPR(4)=WPOX(NFE)/MWFEX
105 - 105.000      MOLPR(5)=WPOX(NMG)/MWMGX
106 - 106.000      MOLPR(6)=WPOX(NMN)/MWMNX
107 - 107.000      MOLPR(7)=WPOX(NCA)/MWCAX
108 - 108.000      MOLPR(8)=WPOX(NNA)/MWNAX
109 - 109.000      MOLPR(9)=WPOX(NK)/MWKX
110 - 110.000      MOLPR(11)=WPOX(NF)/MWF
111 - 111.000      MOLPR(12)=WPOX(NCL)/MWCL
112 - 112.000 C
113 - 113.000      APOX(1)=2.*MOLPR(1)
114 - 114.000      APOX(2)=3.*MOLPR(2)
115 - 115.000      APOX(3)=2.*MOLPR(3)
116 - 116.000      DO 50 IG=4,12
117 - 117.000          APOX(IG)=MOLPR(IG)
118 - 118.000 50   CONTINUE

```

```

119 - 119.000
120 - 120.000
121 - 121.000
122 - 122.000
123 - 123.000
124 - 124.000
125 - 125.000
126 - 126.000
127 - 127.000
128 - 128.000
129 - 129.000
130 - 130.000
131 - 131.000
132 - 132.000
133 - 133.000
134 - 134.000
135 - 135.000
136 - 136.000
137 - 137.000
138 - 138.000
139 - 139.000
140 - 140.000
141 - 141.000
142 - 142.000
143 - 143.000
144 - 144.000
145 - 145.000
146 - 146.000
147 - 147.000
148 - 148.000
149 - 149.000
150 - 150.000
151 - 151.000
152 - 152.000
153 - 153.000
154 - 154.000
155 - 155.000
156 - 156.000
157 - 157.000
158 - 158.000
159 - 159.000
160 - 160.000
161 - 161.000
162 - 162.000
163 - 163.000
164 - 164.000
165 - 165.000
166 - 166.000
167 - 167.000
168 - 168.000
169 - 169.000
170 - 170.000
171 - 171.000
172 - 172.000
173 - 173.000
174 - 174.000
175 - 175.000
176 - 176.000
177 - 177.000
178 - 178.000

```

```

DO 50 IH=1,9
  APOXT=APOXT+APOX(IH)
CONTINUE
APOXT=APOXT-0.5*(MOLPR(11)+MOLPR(12))
IF (MIN.EQ.'TR') THEN
  OXY=24.
  OH=2.
  TET=8.
ELSE IF (MIN.EQ.'TC'.OR.'PH') THEN
  OXY=12.
  OH=2.
  TET=4.
ELSE IF (MIN.EQ.'CH') THEN
  OXY=18.
  OH=8.
  TET=4.
ELSE
  WRITE (108,45)
  FORMAT ('** LEGAL MINERALS ARE TR,TC,PH AND CH **')
  STOP
END IF

APOX(10)=(OXY*(APOX(11)+APOX(12))-OH*(APOXT+APOX(11)+
  APOX(12)))/(OH-2.*OXY)
WPH20=APOX(10)*MWH20
MOLPR(10)=APOX(10)
T=(OXY-1.)/APOXT

WTPCT(1)=WPOX(NSI)
WTPCT(2)=WPOX(NAL)
WTPCT(3)=WPOX(NTI)
WTPCT(4)=WPOX(NFE)
WTPCT(5)=WPOX(NMG)
WTPCT(6)=WPOX(NMN)
WTPCT(7)=WPOX(NCA)
WTPCT(8)=WPOX(NNA)
WTPCT(9)=WPOX(NK)
WTPCT(10)=WPH20
WTPCT(11)=WPOX(NF)
WTPCT(12)=WPOX(NCL)
WTPCT(13)=MOEFCL
WTPCT(14)=TOTAL+WPH20
IF (WTPCT(14).LT.98..OR..WTPCT(14).GT.101.99) GO TO 20.

MULT=1.0
NIT=0
TEE=OXY/(APOXT+APOX(10)+APOX(11)+APOX(12))
CALL FORNCL (FORAM1,APOX,T,TEE,TET,OH,MULT,NIT,MIN)
CALL NUMBERS (FORAM1,TOXY1,CAT1,CAT2,CAT3,MIN)

IF (MIN.EQ.'TR') THEN
  MULT1=13./CAT1
  MULT2=15./CAT2
  MULT3=15./CAT3
ELSE IF (MIN.EQ.'TC') THEN
  MULT1=7./CAT1
ELSE IF (MIN.EQ.'PH') THEN
  MULT1=7./CAT1
  MULT2=8./CAT2
END IF

```

```

175 - 179.000 2
180 - 180.000
181 - 181.000
182 - 182.000
183 - 183.000
184 - 184.000
185 - 185.000
186 - 186.000
187 - 187.000
188 - 188.000
189 - 189.000
190 - 190.000
191 - 191.000
192 - 192.000
193 - 193.000 C
194 - 194.000
195 - 195.000 55
196 - 196.000
197 - 197.000 75
198 - 198.000
199 - 199.000
200 - 200.000 175
201 - 201.000
202 - 202.000 185
203 - 203.000
204 - 204.000
205 - 205.000
206 - 206.000
207 - 207.000
208 - 208.000
209 - 209.000 85
210 - 210.000
211 - 211.000
212 - 212.000 225
213 - 213.000
214 - 214.000
215 - 215.000 235
216 - 216.000 70
217 - 217.000
218 - 218.000
219 - 219.000
220 - 220.000 95
221 - 221.000
222 - 222.000
223 - 223.000
224 - 224.000
225 - 225.000
226 - 226.000
227 - 227.000 135
228 - 228.000
229 - 229.000
230 - 230.000
231 - 231.000
232 - 232.000
233 - 233.000
234 - 234.000
235 - 235.000
236 - 236.000 20
237 - 237.000 97
238 - 238.000

      NIT=1
      CALL FORMCAL (FORAM2, APOX, T, TEE, TET, OH, MUL, NIT, MIN)
      CALL NUMBERS (FORAM2, TOXY2, CAT1, CAT2, CAT3, MIN)
      IF (MIN.EQ. 'TC') THEN
        NIT=2
        CALL FORMCAL (FORAM3, APOY, T, TEE, TET, OH, MUL, NIT, MIN)
        CALL NUMBERS (FORAM3, TOXY3, CAT1, CAT2, CAT3, MIN)
        IF (MIN.EQ. 'PH') THEN
          NIT=3
          CALL FORMCAL (FORAM4, APOX, T, TEE, TET, OH, MUL, NIT, MIN)
          CALL NUMBERS (FORAM4, TOXY4, CAT1, CAT2, CAT3, MIN)
        END IF
      END IF

      WRITE (107,55) SL,PR,MIN
      FORMAT (///, ' ANALYSIS: ', A11, 2X, A2, 1X, A2)
      IF (MIN.EQ. 'TR') WRITE (107,75)
      FORMAT (12X, 'OXIDE %', 14X, '23(0)', 11X, '1X=CNK', 10X, '15eWK',
             11X, '15eK')
      IF (MIN.EQ. 'TC') WRITE (107,175)
      FORMAT (12X, 'OXIDE %', 14X, '11(0)', 11X, '7eCNK')
      IF (MIN.EQ. 'PH') WRITE (107,185)
      FORMAT (12X, 'OXIDE %', 14X, '11(0)', 11X, '7eCNK')
      DO 70 IJ=1,14
        IF (IJ.EQ.6 .AND. MIN.EQ.15) GO TO 70
        IF (IJ.EQ.12 .AND. MIN.EQ.15) GO TO 70
        IF (MIN.EQ. 'TR') WRITE (107,85) TITL1(IJ), WTPCT(IJ),
             TITL2(IJ), FORAM1(IJ), FORAM2(IJ), FORAM3(IJ), FORAM4(IJ),
             TITL2(IJ)
        IF (MIN.EQ. 'TC') WRITE (107,225) TITL1(IJ), WTPCT(IJ),
             TITL2(IJ), FORAM1(IJ), FORAM2(IJ), TITL2(IJ)
        IF (MIN.EQ. 'PH') WRITE (107,235) TITL1(IJ), WTPCT(IJ),
             TITL2(IJ), FORAM1(IJ), FORAM2(IJ), TITL2(IJ)
        FORMAT (1X, A7, F10.2, 10X, A2, F8.3, F16.3, 4X, A2)
      CONTINUE
      IF (MIN.EQ. 'TR') WRITE (107,95) TOXY1, TOXY2, TOXY3, TOXY4
      IF (MIN.EQ. 'TC') WRITE (107,95) TOXY1, TOXY2
      IF (MIN.EQ. 'PH') WRITE (107,95) TOXY1, TOXY2
      FORMAT (22X, 'OXYGENS: ', 4(F8.3, BX))
      IF (OUTOP.EQ. 'Y') THEN
        IF (MIN.EQ. 'TR') THEN
          MIN= '1'
          WRITE (109,135) SL,PR,MIN, (FORAM2(IJ), IJ=1,13), TOXY2
          WRITE (110,135) SL,PR,MIN, (FORAM3(IJ), IJ=1,13), TOXY3
          WRITE (111,135) SL,PR,MIN, (FORAM4(IJ), IJ=1,13), TOXY4
          FORMAT (1X, A11, 5X, 2A2, 2X, 13F6.3, F7.3)
        ELSE IF (MIN.EQ. 'TC') THEN
          MIN= '2'
          WRITE (113,135) SL,PR,MIN, (FORAM2(IJ), IJ=1,13), TOXY2
        ELSE IF (MIN.EQ. 'PH') THEN
          MIN= '3'
          WRITE (114,135) SL,PR,MIN, (FORAM2(IJ), IJ=1,13), TOXY2
        END IF
      END IF
      CONTINUE
      STOP
      END

```

```

239 - 239.000 C
240 - 240.000 C
241 - 241.000
242 - 242.000
243 - 243.000
244 - 244.000
245 - 245.000
246 - 246.000
247 - 247.000
248 - 248.000
249 - 249.000
250 - 250.000
251 - 251.000
252 - 252.000
253 - 253.000
254 - 254.000
255 - 255.000
256 - 256.000
257 - 257.000
258 - 258.000
259 - 259.000
260 - 260.000
261 - 261.000
262 - 262.000
263 - 263.000
264 - 264.000
265 - 265.000
266 - 266.000
267 - 267.000
268 - 268.000
269 - 269.000
270 - 270.000
271 - 271.000
272 - 272.000
273 - 273.000
274 - 274.000
275 - 275.000 C
276 - 276.000
277 - 277.000
278 - 278.000
279 - 279.000
280 - 280.000
281 - 281.000
282 - 282.000
283 - 283.000
284 - 284.000
285 - 285.000 300
286 - 286.000
287 - 287.000
288 - 288.000
289 - 289.000
290 - 290.000
291 - 291.000
292 - 292.000

SUBROUTINE FORMCAL (FORAM,APOX,T,TEE,TET,OH,MULT,NIT,MIN)
IMPLICIT DOUBLE PRECISION (A-H,M,O-Z)
CHARACTER MIN*2
DIMENSION FORAM(15),APOX(15)
FORAM(1)=APOX(1)*T*MULT/2.
FORAM(2)=APOX(2)*T*2.*MULT/3.
FORAM(3)=0.
IF ((FORAM(1)+FORAM(2)).GT.TET) THEN
  FORAM(2)=TET-FORAM(1)
  IF (FORAM(2).LT.0.) FORAM(2)=0.
  FORAM(3)=APOX(2)*T*2.*MULT/3.-FORAM(2)
END IF
FORAM(4)=APOX(3)*MULT*T/2.
FORAM(5)=APOX(4)*T*MULT
FORAM(6)=APOX(6)*T*MULT
FORAM(7)=APOX(5)*T*MULT
FORAM(8)=APOX(7)*T*MULT
FORAM(9)=APOX(8)*2.*T*MULT
FORAM(10)=APOX(9)*2.*T*MULT
FORAM(11)=APOX(10)*2.*TEE
FORAM(12)=APOX(12)*TEE
FORAM(13)=APOX(11)*TEE
FORAM(14)=FORAM(13)/OH
IF (MIN.EQ.'TR') THEN
  FORAM(10)=FORAM(10)/MULT
  IF (NIT.EQ.1.OR.NIT.EQ.2) FORAM(9)=FORAM(9)/MULT
  IF (NIT.EQ.1) FORAM(8)=FORAM(8)/MULT
ELSE IF ((MIN.EQ.'PH').AND.(NIT.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

SUBROUTINE NUMBERS (FORAM,TOXY,CAT1,CAT2,CAT3,MIN)
IMPLICIT DOUBLE PRECISION (A-H,M,O-Z)
CHARACTER MIN*2
DIMENSION FORAM(15)
CAT1=0.
TOXY=2.*(FORAM(1)+FORAM(4))+1.5*(FORAM(2)+FORAM(3))+FORAM(5)
+FORAM(6)+FORAM(7)+FORAM(8)+0.5*(FORAM(9)+FORAM(10))
DO 300 II=1,7
  CAT1=CAT1+FORAM(II)
CONTINUE
IF (MIN.EQ.'TR') THEN
  CAT2=CAT1+FORAM(8)
  CAT3=CAT2+FORAM(9)
END IF
IF (MIN.EQ.'PH') CAT2=CAT1+FORAM(8)+FORAM(9)+FORAM(10)
RETURN
END

```


III.2 SOLCRV

14:30 DEC 06 '83 SOLCRV.FJ092148

```

1 - 1.000 C*****
2 - 2.000 C*****
3 - 3.000 C
4 - 4.000 C PROGRAM SOLCRV
5 - 5.000 C
6 - 6.000 C*****
7 - 7.000 C*****
8 - 8.000 C
9 - 9.000 C SOLCRV : A PROGRAM TO CALCULATE NON-IDEAL SOLUTION DISTRIBUTION
10 - 10.000 C CURVES ONE- OR TWO-CONSTANT MARGULES 'SOLUTION' MODEL
11 - 11.000 C PARAMETERS
12 - 12.000 C
13 - 13.000 C*****
14 - 14.000 C
15 - 15.000 C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
16 - 16.000 C DOUBLE PRECISION LNK,M,N,M1,M2,N1,N2
17 - 17.000 C CHARACTER SOLTYP*3,TITLE*80
18 - 18.000 C CHECK1(LNK,M,N,XA,XB)=LNK-DLOG(XA*(1.-XB)/(XB*(1.-XA)))
19 - 19.000 C * -M*(1.-2.*XA)+N*(1.-2.*XB)
20 - 20.000 C CHECK2(LNK,M1,M2,N1,N2,XA,XB)=LNK-DLOG(XA*(1.-XB)/(XB*(1.-XB)))
21 - 21.000 C * +M1*(-3.*(XA**2)+4.*XA-1.)
22 - 22.000 C * +M2*(3.*(XA**2)-2.*XA)
23 - 23.000 C * +N1*(3.*(XB**2)-4.*XB+1.)
24 - 24.000 C * +N2*(-3.*(XB**2)+2.*XB)
25 - 25.000 C TOL=1.0E-04
26 - 26.000 C DO 10 I=1,10
27 - 27.000 C
28 - 28.000 C*****
29 - 29.000 C
30 - 30.000 C INPUT DATA : LNK = LN(EQUILIBRIUM CONSTANT)
31 - 31.000 C M = W-A/RT M1=Wb-A/RT
32 - 32.000 C N = W-B/RT M2=Wb-A/RT
33 - 33.000 C N1=Wb-B/RT
34 - 34.000 C N2=Wb-B/RT
35 - 35.000 C
36 - 36.000 C*****
37 - 37.000 C
38 - 38.000 C WRITE (108,5)
39 - 39.000 5 FORMAT (' ENTER SOLUTION TYPE [ONE] or [TWO] AND TITLE: ',/
40 - 40.000 C * , FORMAT IS (A3/A80)')
41 - 41.000 C READ (105,15,END=37) SOLTYP,TITLE
42 - 42.000 15 FORMAT (A3//,A80)
43 - 43.000 C WRITE (108,25) SOLTYP,TITLE
44 - 44.000 25 FORMAT (1X,A3,'-CONSTANT MARGULES SOLUTION MODEL',/,1X,A80)
45 - 45.000 C IF (SOLTYP.EQ.'ONE') THEN
46 - 46.000 C WRITE (108,125)
47 - 47.000 125 FORMAT (' ENTER LNK, M, N: ',/,2X,3('-----'))
48 - 48.000 C READ (105,35) LNK,M,N
49 - 49.000 35 FORMAT (3F10,5)
50 - 50.000 C WRITE (108,45) DEXP(LNK),LNK,M,N
51 - 51.000 45 FORMAT (T5,'K = ',F8,4,5X,'LNK = ',F8,4,5X,'M = ',
52 - 52.000 C * F8,4,5X,'N = ',F8,4,5X,'T13, 'XAR',T23,'XAR',
53 - 53.000 C * T33,'R88105,T48, 'ITER',/)
54 - 54.000 C ELSE IF (SOLTYP.EQ.'TWO' .OR. SOLTYP.EQ.'T62') THEN
55 - 55.000 C WRITE (108,135)
56 - 56.000 135 FORMAT (' ENTER LNK, M1, M2, N1, N2: ',/,2X,
57 - 57.000 C * 5('-----'))
58 - 58.000 C READ (105,55) LNK,M1,M2,N1,N2

```

```

59 - 59.000 55
60 - 60.000
61 - 61.000 65
62 - 62.000
63 - 63.000
64 - 64.000
65 - 65.000
66 - 66.000
67 - 67.000 75
68 - 68.000
69 - 69.000
70 - 70.000
71 - 71.000
72 - 72.000
73 - 73.000
74 - 74.000
75 - 75.000
76 - 76.000
77 - 77.000
78 - 78.000
79 - 79.000
80 - 80.000
81 - 81.000
82 - 82.000
83 - 83.000
84 - 84.000
85 - 85.000
86 - 86.000
87 - 87.000
88 - 88.000
89 - 89.000
90 - 90.000
91 - 91.000
92 - 92.000
93 - 93.000
94 - 94.000
95 - 95.000
96 - 96.000 85
97 - 97.000
98 - 98.000
99 - 99.000
100 - 100.000 30
101 - 101.000 17
102 - 102.000 95
103 - 103.000 27
104 - 104.000
105 - 105.000
106 - 106.000
107 - 107.000 20
108 - 108.000 10
109 - 109.000 37
110 - 110.000

FORMAT (5F10.5)
WRITE (108,85) DEXP(LNK),LNK,M1,M2,N1,N2
FORMAT (T5,'K = ',F8.4,5X,'LNK = ',F8.4,'/T5,M1 = ',
      F8.4,5X,'M2 = ',F8.4,5X,'N1 = ',F8.4,5X,'N2 = ',
      F8.4,'/T13,'XAA',T23,'XAB',T33,'RESID',T48,
      'ITER',/)
ELSE
  WRITE (108,75) SOLTYP
  FORMAT ('**',A3,' UNRECOGNIZED AS SOLUTION MODEL TYPE',
        '**')
  STOP
END IF
DO 30 JY=1,19
  YR=IFLOAT(IX)*0.05
  XAPR=XAI
  IF (IX.EQ.1.OR.ITER.GT.99) THEN
    XA1=.001
    XA2=.999
    XAPR=XAI
  END IF
  DO 30 ITER=1,100
    XAI=(XA1+XA2)/2.
    IF (SOLTYP.EQ.'ONE') THEN
      CK=CHECK1(LNK,M,N,XAI,XR)
      IF (DABS(CK).LT.TOL) GO TO 17
      CK1=CHECK1(LNK,M,N,XA1,XR)
      CK2=CHECK1(LNK,M,N,XA2,XR)
    ELSE IF (SOLTYP.EQ.'TWO') THEN
      CK=CHECK2(LNK,M1,M2,N1,N2,XAI,XR)
      IF (DABS(CK).LT.TOL) GO TO 17
      CK1=CHECK2(LNK,M1,M2,N1,N2,XA1,XR)
      CK2=CHECK2(LNK,M1,M2,N1,N2,XA2,XR)
    END IF
    IF ((CK*CK1).GT.0.) XAI=XAI
    IF ((CK*CK2).GT.0.) XA2=XAI
    IF (ITER.EQ.100) THEN
      WRITE (108,85) XB
      FORMAT (5X,F10.3,T23,'XAA NOT FOUND AFTER 100',
            'ITERATIONS')
      GO TO 20
    END IF
  CONTINUE
  WRITE (108,95) XB,XAI,CK,ITER
  FORMAT (5X,2F10.3,5X,D12.5,6X,I2)
  XAI=XAI-(XAI-XAPR)
  XA2=XAI+(5.*(XAI-XAPR))
  IF (XAI.LT.0.) XAI=0.001
  IF (XAI.GE.1.) XA2=0.999
  CONTINUE
  STOP
END

```

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 06 '83 STATS20.PJ02148

```

1 - 1.000 1J01 NAME=NONLIN20
2 - 2.000 1RESOURCE MEMORY=250,TIME=5:00
3 - 3.000 1SET 7 GRTCTR=0J045042
4 - 4.000 1BINEDT PROG=AF,XMEM=123,OUT=RES20
5 - 5.000 XFUN
6 - 6.000 DIMENSION ROOT(10)
7 - 7.000 TOL=1.0E-07
8 - 8.000 WEST=X(1)
9 - 9.000 NROOT=0
10 - 10.000 DO 100 WLN=0.05,0.95,0.05
11 - 11.000 WN=WIN
12 - 12.000 RO 110 J=1.15
13 - 13.000 FUN=BL0K(WN*(1.-X(2))/(X(2)*(1.-WN)))-P(1)
14 - 14.000 +P(2)*(3.*WN**2-4.*WN+1.)
15 - 15.000 -P(3)*(3.*WN**2-2.*WN)
16 - 16.000 FPN=1./WN+1./(1.-WN)+P(2)*(6.*WN-4.)-P(3)*(6.*WN-2.)
17 - 17.000 WNP1=WN-FUN/FPN
18 - 18.000 IF (WNP1.GE.1. OR. WNP1.LE.0.) GO TO 100
19 - 19.000 E=DABS(WNP1-WN)
20 - 20.000 IF (E.LT.TOL) THEN
21 - 21.000 NROOT=NROOT+1
22 - 22.000 ROOT(NROOT)=WNP1
23 - 23.000 GO TO 100
24 - 24.000 END IF
25 - 25.000 WN=WNP1
26 - 26.000 110 CONTINUE
27 - 27.000 100 CONTINUE
28 - 28.000 IF (NROOT.EQ.0) THEN
29 - 29.000 PRINT 105
30 - 30.000 105 FORMAT (/,100(' '),/, ' CONVERGENCE NOT ACHIEVED')
31 - 31.000 PRINT 106, (X(N),N=1,2),(P(L),L=1,3)
32 - 32.000 106 FORMAT (' W, Y: ',9X,2F8.3,/, ' P(1) TO P(3): ',4F8.4,
33 - 33.000 & /,100(' '))
34 - 34.000 STOP
35 - 35.000 END IF
36 - 36.000 DIFF1=1.0
37 - 37.000 DO 120 K=1,NROOT
38 - 38.000 DIFF2=DABS(ROOT(K)-WEST)
39 - 39.000 IF (DIFF2.LT.DIFF1) F=ROOT(K)
40 - 40.000 120 CONTINUE
41 - 41.000 ZERR
42 - 42.000 /PROBLEM TITLE IS 'TALC - 2K; TREM - IDEAL; NONLINEAR; GRTCTR'.
43 - 43.000 /INPUT VARIABLES ARE 2.
44 - 44.000 FORMAT IS '(2F10.3)'.
45 - 45.000 UNIT IS 3.
46 - 46.000 /VARIABLE NAMES ARE XFTC,XFTR.
47 - 47.000 /REGRESS DEPENDENT IS XFTR.
48 - 48.000 PARAMETERS ARE 3.
49 - 49.000 HALTING=20.
50 - 50.000 /PARAMETER INITIAL ARE .459,1.024,2.449.
51 - 51.000 MAXIMUM ARE 3.0,3.0,3.0.
52 - 52.000 MINIMUM ARE -3.0,-3.0,-3.0.
53 - 53.000 NAMES ARE LNK,WFTC,WQHTC.
54 - 54.000 /END

```

IV.2 Nonlinear regression using data of Saxena (1973).

IV.2a Data (from Saxena, 1973)

x_{Fe}^{cum}	x_{Fe}^{act}
0.783	0.714
0.668	0.560
0.652	0.547
0.580	0.427
0.457	0.307
0.230	0.129

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,

$$P(1) = \ln K$$

$$P(2) = w_{Fe}^{cum}/RT$$

$$P(3) = w_{Mg}^{cum}/RT$$

$$P(4) = w_{Fe}^{act}/RT$$

$$P(5) = w_{Mg}^{act}/RT$$

IV.2c Results of nonlinear regression

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

$$\ln K = 0.229316$$

$$w_{Fe}^{cum}/RT = 1.30490$$

$$w_{Fe}^{act}/RT = 1.88131$$

$$w_{Mg}^{cum}/RT = 2.08520$$

$$w_{Mg}^{act}/RT = 1.95152$$

These values have been used to reproduce the Fe distribution curve between cummingtonite (cum) and actinolite (act) shown in Figure 10.

14:30 DEC 06 '83 SAXSTATS.PJ092148

```

1 - 1.000 JOB NAME=SAXSTATS
2 - 2.000 RESOURCE MEMORY=250, TIME=5:00
3 - 3.000 SET 3 SAXUAT
4 - 4.000 BIMEIT PROG=AR, XMEM=123, OUT=RES20
5 - 5.000 XFUN
6 - 6.000 DIMENSION ROOT(10)
7 - 7.000 TOL=1.0E-07
8 - 8.000 WEST=X(1)
9 - 9.000 NROOT=0
10 - 10.000 DO 100 WIN=0.05,0.95,0.05
11 - 11.000 WN=WIN
12 - 12.000 DO 110 J=1,15
13 - 13.000 FWN=DLOG(WN*(1.+X(2))/(X(2)*(1.-WN)))-P(1)
14 - 14.000 +P(2)*(3.*WN**2-4.*WN+1.)
15 - 15.000 -P(3)*(3.*WN**2-2.*WN)
16 - 16.000 -P(4)*(3.*X(2)**2-4.*X(2)+1.)
17 - 17.000 +P(5)*(3.*X(2)**2-2.*X(2))
18 - 18.000 FFWN=1./WN+1./(1.-WN)+P(2)*(6.*WN-4.)-P(3)*(6.*WN-2.)
19 - 19.000 WNP1=WN-FWN/FFWN
20 - 20.000 IF (WNP1.GE.1. .OR. WNP1.LE.0.) GO TO 100
21 - 21.000 E=DABS(WNP1-WN)
22 - 22.000 IF (E.LT.TOL) THEN
23 - 23.000 NROOT=NROOT+1
24 - 24.000 ROOT(NROOT)=WNP1
25 - 25.000 GO TO 100
26 - 26.000 END IF
27 - 27.000 WN=WNP1
28 - 28.000 110 CONTINUE
29 - 29.000 100 CONTINUE
30 - 30.000 IF (NROOT.EQ.0) THEN
31 - 31.000 PRINT 105
32 - 32.000 105 FORMAT (/,100(' '),/, ' CONVERGENCE NOT ACHIEVED')
33 - 33.000 PRINT 106, (X(N), N=1,2), (P(L), L=1,3)
34 - 34.000 106 FORMAT (' W: Y: ',9X,2F8.3,/, ' P(1) TO P(3): ',4F8.4,
35 - 35.000 /,100(' '))
36 - 36.000 STOP
37 - 37.000 END IF
38 - 38.000 DIFF1=1.0
39 - 39.000 DO 120 K=1,NROOT
40 - 40.000 DIFF2=DABS(ROOT(K)-WEST)
41 - 41.000 IF (DIFF2.LT.DIFF1) F=ROOT(K)
42 - 42.000 120 CONTINUE
43 - 43.000 XEOD
44 - 44.000 /PROBLEM TITLE IS NONLINEAR REGRESSION FOR FE EXCHANGE BETWEEN
45 - 45.000 CUMMINGTONE AND ACTINOLITE; DATA OF SAXENA
46 - 46.000 (1973)
47 - 47.000 /INPUT VARIABLES ARE 2.
48 - 48.000 FORMAT IS '(2F10.3)'
49 - 49.000 UNIT IS 3.
50 - 50.000 /VARIABLE NAMES ARE XFECUM,XFEACT.
51 - 51.000 /REGRESS DEPENDENT IS XFECUM.
52 - 52.000 PARAMETERS ARE 5.
53 - 53.000 HALVING=20.
54 - 54.000 /PARAMETER INITIAL ARE 1.0,1.0,1.0,1.0,1.0.
55 - 55.000 NAMES ARE LNK,XFECUM,XHOCUM,XFEACT,XHGAET.
56 - 56.000 /END

```

END

09-06-86

FIN