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**Scapolite phase equilibria and carbon isotope variations in high  
grade rocks: Tests of the CO<sub>2</sub>-flooding hypothesis of granulite  
genesis**

**Moecher, David Paul, Ph.D.**

**The University of Michigan, 1988**

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**SCAPOLITE PHASE EQUILIBRIA AND CARBON ISOTOPE VARIATIONS  
IN HIGH GRADE ROCKS: TESTS OF THE CO<sub>2</sub>-FLOODING HYPOTHESIS  
OF GRANULITE GENESIS**

by

David Paul Moecher

A dissertation submitted in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy  
(Geology)  
in The University of Michigan  
1988

**Doctoral Committee:**

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To Amy Elizabeth Luchsinger



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## CHAPTER I

### INTRODUCTION

The granulite facies is distinguished from other metamorphic facies by its relatively anhydrous nature (low water activities) compared to lower grade equivalents. Although Eskola (1939) originally defined the granulite facies based on the absence of hydrous minerals, it was later redefined to include rocks that contained primarily anhydrous minerals but that may contain amphibolite or mica, depending on bulk composition. How granulites attain this relatively anhydrous state has developed into a point of contention among many workers in this field. This dissertation was designed to evaluate one of the hypotheses that attempts to account for the development of low water activities ( $a_{\text{H}_2\text{O}}$ ) in granulites, that of  $\text{CO}_2$  flooding or carbonic metamorphism. Originally, Touret (1971) noted that fluid inclusions in granulites were generally high density,  $\text{CO}_2$ -rich inclusions while those in amphibolite facies equivalents were  $\text{H}_2\text{O}$ -rich inclusions. The  $\text{CO}_2$  inclusions were interpreted to have been entrapped at or near the thermal peak of metamorphism and reflect the composition of the fluid with which the minerals equilibrated. Subsequent studies have corroborated Touret's observations (see refs. Chap 4), although the interpretation that these inclusions represent peak fluid compositions has been questioned (Lamb et al. 1987). Thus,  $\text{CO}_2$  was implicated as the diluent of the granulite facies fluid phase, and  $\text{CO}_2$  flooding or carbonic metamorphism was proposed as a mechanism to account for the regional metamorphic scale of this phenomenon (Janardhan et al. 1979, Newton et al. 1980, Newton 1987). Initially, it was proposed that  $\text{CO}_2$  derived from the mantle, mantle-derived basalt ponded at the base of the crust, or  $\text{CO}_2$  dissolved in tonalitic

melts emplaced during crustal accretion, copiously pervaded the crust driving out the H<sub>2</sub>O. The resulting anhydrous fluid would stabilize orthopyroxene relative to amphibole or biotite. The dehydration of the system via this mechanism was also used to account for the variable LIL element depletion of some granulites. Later modifications of the model proposed that CO<sub>2</sub> could be derived from subducted or underthrust carbonates in orogenic zones (Newton 1987), from decarbonation of high grade carbonate units in the lower crust during high grade metamorphism (Glassley 1983) or decarbonation in response to melting of lithologies enclosing marble or calc-silicate units at high temperatures brought on by basaltic underplating (Wickham 1988).

Where carbonic fluid inclusions have been recorded, CO<sub>2</sub>-flooding has often been the accepted mechanism to account for their formation (e.g., Santosh, 1985), and a CO<sub>2</sub>-rich or pure CO<sub>2</sub> fluid phase has been proposed to be the peak metamorphic fluid (e.g., Rudnick et al. 1984). However, there are few quantitative constraints or direct tests of the model (c.f., Lamb and Valley 1984, Vry et al. 1988, Baker 1988). The available fluid inclusion, LIL element, and textural evidence (Janardhan et al. 1979) for CO<sub>2</sub> streaming is mostly consistent with such a process and do not prove or directly test its implications. If rocks have been infiltrated on a grain boundary scale by a free, CO<sub>2</sub>-rich fluid, one would expect this process to be recorded mineralogically. The mineral assemblages and compositions should reflect a CO<sub>2</sub>-rich fluid composition. One would also expect to see homogenization of fluid compositions. Carbonate or graphite mineral equilibria could be used to constrain high grade fluid compositions (Lamb et al. 1987). Unfortunately, most granulite facies orthogneisses do not contain a primary carbonate phase. Scapolite, a carbonate-bearing silicate, is reported in some high-grade rocks from a variety of metamorphic terranes, and by virtue of the CO<sub>3</sub>, Cl, and SO<sub>4</sub> groups is potentially a sensor of fluid composition and fluid source. In addition, if the mantle, subducted carbonate and organic matter, or high grade calc-silicate gneisses were the dominant source of the CO<sub>2</sub> leading to dehydration, it should have a distinct carbon isotopic signature or a limited range of  $\delta^{13}\text{C}$  that

would be recorded in carbon bearing species in the rocks. One would also predict homogenization of regional carbon isotopic compositions and swamping of isotopic gradients. The present work will use scapolite in this role to determine whether the granulite facies fluid is rich in CO<sub>2</sub>, whether there is a free fluid phase in high grade rocks, and to use the carbon isotopic compositions to constrain potential fluid sources.

In order to perform calculations of fluid composition in high grade rocks, a number of data are required. There are no accurate geobarometers for many scapolite-bearing assemblages, and regional metamorphic pressures are not known in some terranes that contain scapolite-bearing gneisses. The assemblage clinopyroxene-garnet-plagioclase-quartz was found to occur in many of the scapolite gneisses investigated for this study. In Chapter II of this thesis I describe the thermodynamic calculation and evaluation of geobarometers based on the reactions  $3Hd + 3An = 2Gr + Alm + 3Qz$  and  $3Di + 3An = 2Gr + Py + 3Qz$ . In the absence of regional thermometry, the assemblage also allows metamorphic temperatures to be calculated using the garnet-clinopyroxene thermometer. Many of the samples for this study were collected in the Central Gneiss Belt of the southwestern Grenville Province where regional thermobarometric work has been performed (Anovitz 1987). However many of the Grenville samples were collected in ductile shears or settings that may postdate the peak of granulite facies metamorphism, or are samples from other terranes and crustal xenoliths for which P-T data have not been estimated. These barometers and the garnet-clinopyroxene thermometer allow calculation of P and T in most of the samples analyzed for this study.

In Chapter III, a discussion is presented of the derivation of thermodynamic data needed to calculate fluid composition in scapolite-bearing assemblages. Thermodynamic data for melonite scapolite are derived from a number of sources and constrained by experiments on scapolite stability. An internally consistent thermodynamic data set is derived for phases in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O

(CASCH) system, constrained by available experimental equilibria in CASCH. Quantitative phase equilibria for this system, including melonite-bearing reactions, are calculated at 5 and 10 kbar. Finally, activity-composition relations for carbonate scapolite solid solutions are calculated from data on natural scapolite-plagioclase-calcite assemblages. These data allow calculation of  $\text{CO}_2$  activities in scapolite-bearing granulites, amphibolites, mafic gneisses, meta-anorthosite, and calc-silicates from the Grenville Province and other granulite terranes, the subject of Chapter III. Scapolite-plagioclase-garnet-quartz assemblages are common in scapolite gneisses and buffer the activity of  $\text{CO}_2$  ( $a_{\text{CO}_2}$ ) by the reaction  $2\text{Me} + \text{Qz} = 5\text{An} + \text{Gr} + 2\text{CO}_2$ . This reaction was used to calculate  $a_{\text{CO}_2}$  in the above lithologies.

In Chapter IV the carbon isotope systematics of scapolite are presented. Carefully characterized scapolite mineral separates are used to evaluate quantitative extraction of the  $\text{CO}_3$  group of scapolite by standard phosphoric acid techniques at 25 and 75°C, and by combustion at high temperature. The fractionation of  $^{13}\text{C}$  between scapolite and calcite was measured on natural scapolite-calcite pairs, in order to constrain the carbon isotope composition of the fluid phase inferred to have formed scapolite. These techniques are tested where scapolite is developed in a meta-anorthosite adjacent to marble to determine if scapolite accurately records the carbon isotope composition of the source marble. They were applied to high grade gneisses from the Grenville Province in order to determine carbon sources and extent of homogeneity on a regional scale.

If  $\text{CO}_2$ -flooding is a pervasive and significant process, it should be recorded in scapolite gneisses as uniformly high values of  $a_{\text{CO}_2}$  and as uniform values of  $\delta^{13}\text{C}$  for the Central Gneiss Belt of Ontario (assuming no retrograde exchange of carbon). These constraints on fluid composition in high grade rocks are preferred over indirect evidence such as fluid inclusions, whose entrapment history may not record conditions at or near the peak of metamorphism.

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## CHAPTER II

### CALCULATION OF CLINOPYROXENE-GARNET-PLAGIOCLASE-QUARTZ GEOBAROMETERS: EVALUATION AND APPLICATION TO HIGH GRADE METAMORPHIC ROCKS

#### Introduction

Major advances in the accuracy and precision of geobarometers have been made in the last decade, in part a result of careful experimental reversal of pressure dependent equilibria (Bohlen et al. 1980; Bohlen and Boettcher 1982; Bohlen et al. 1983a 1983b; Gasparik 1984a, 1984b; Gasparik and Newton 1984; Bohlen and Liotta 1986; Koziol and Newton 1986), more precise thermodynamic data (e.g. Haselton and Newton 1980; Metz et al. 1983; Bohlen et al. 1983; Robie and Hemingway 1984; Haselton et al. 1987; Robie et al. 1987), and more accurate modeling of activity-composition relations for mineral phases involved in geobarometric equilibria (e.g., Newton et al. 1980; Newton and Haselton 1981; Ganguly and Saxena 1984; Davidson and Lindsley 1985; Anovitz and Essene 1987a). Reasonably accurate and precise geobarometers now exist for most granulite facies metabasites, charnockites and high grade metapelites, and for some upper amphibolite facies metabasites and metapelites. The above experiments also serve as important constraints on thermodynamic data for mineral phases involved in the particular reaction. In concert with precise thermodynamic data for other phases, the experimentally constrained thermodynamic data may be used to calculate geobarometers that are not easily reversed experimentally. Using this approach we have calculated the location of the pressure dependent reactions





the "Hedenbergite (HD) barometer") and,



(the "Diopside (DI) barometer"), in order to expand the range of assemblages for which there exist reasonably precise geobarometers. Because garnet, plagioclase and quartz are phases common to both barometers we have chosen to distinguish them on the basis of the particular pyroxene present. Reaction 2 was previously calculated by Newton and Perkins (1982) based on the best available thermochemical data. Their version of Reaction 2 typically underestimated pressure by an average of 2.2 kbar relative to their orthopyroxene geobarometer (Newton and Perkins 1982), which was ascribed to imprecise thermodynamic data (Newton and Perkins 1982).

This paper presents calculations of new calibrations for clinopyroxene - garnet - plagioclase - quartz geobarometers in the system  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{FeO} - \text{MgO} - \text{SiO}_2$ , based on thermodynamic data derived from a number of sources and constrained by a variety of experimental equilibria. The precision and accuracy of these calibrations are tested by comparing pressures obtained for Reactions 1 and 2 against the equilibrium



(the "Ferrosilite (FS) barometer"), and the location of the polymorphic transition



(Richardson et al. 1968, Holdaway 1971, Robie and Hemingway 1984). Reaction 3 is derived by addition of the experimentally reversed reactions



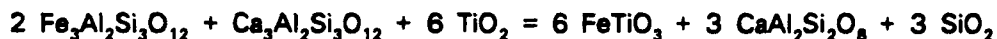
(Bohlen et al. 1980) and



(where SS is a 2/3 almandine + 1/3 grossular solid solution produced in the experiments, Bohlen et al. 1983a), and has proven to be an extremely useful geobarometer for granulites. Calculations of Reaction 3 as a geobarometer have been presented by Bohlen et al. (1983a), Perkins and Chipera (1985), and Anovitz and Essene (1987a) that differ in the choice of thermodynamic data and garnet mixing model used to calculate the position of the end member reaction (Reaction 3). For these purposes we have used the garnet mixing model of Ganguly and Saxena (1984) with Ca-Fe mixing parameters derived by Anovitz and Essene (1987a). Sources of thermodynamic data are discussed in detail in the following sections.

#### Thermodynamic data

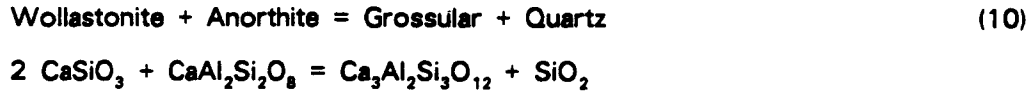
A variety of sources and experimental studies were used in the compilation of thermodynamic data for the present study. Carefully reversed experiments on Reactions 5, 6 and the reactions



(Bohlen et al. 1983b, 1983c, Bohlen and Liotta 1986)



(Koziol and Newton 1988) and



(Newton 1966, Hays 1967, Boettcher 1970, Huckenholz et al. 1975) combined with heat capacity functions and volume data serve to constrain the 1 bar Gibbs free energy ( $\Delta G_{298}^\circ$ ) of fayalite, ferrosilite, kyanite, grossular, almandine and anorthite. The latter data were compiled by Anovitz and Essene (1987a; Table 1) from a number of sources and comprise part of an internally consistent thermodynamic data set for selected phases in the system CaO-FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> (Table 1 and 2). Thermodynamic data for diopside (Tables 1 and 2) have been compiled and evaluated by Sharp et al. (1986) from various sources and experiments in the system CaO-MgO-SiO<sub>2</sub>-CO<sub>2</sub>. The reader is referred to these sources for a detailed discussion of the methods used in deriving the respective data. Thermodynamic data for enstatite are taken from Robinson et al. (1982), and derivation of thermodynamic data for pyrope and hedenbergite is described below.

There has been considerable discussion concerning the presence of Al-Si disorder in synthetic anorthite produced in phase equilibrium experiments such as Reaction 9, and the necessity of adding a configurational entropy term to  $S_{298}^\circ$  of anorthite in order to fit the experimental reversals (e.g., Gasparik 1984a, Wood & Holloway 1984, Koziol & Newton 1986). Anovitz & Essene (1987a) also address this problem, concluding that use of different values for  $S_{298}^\circ$  of grossular, and lack of application of thermal expansion and compressibility in phase equilibrium calculations may require an  $S_\phi$  term for anorthite in order to fit the reversals. However, the thermodynamic data set derived by Anovitz & Essene (1987a: Tables 1 and 2 of this study) uses an alternative  $S_{298}^\circ$  for grossular and includes the effects of expansivity and compressibility of solids, providing an adequate fit to the reversals for Reaction 9 and other equilibria. Following their conclusion we do not believe a configurational entropy term is warranted for anorthite.

TABLE 1. Molar volume, entropy, entropy coefficients, and Gibbs free energies (relative to oxides) of phases involved in thermodynamic calculations.

PHASE	$V_{298}^0$ cc/mol	ref	$S_{298}^0$ J/mol K	A	B	C	D	ref	$\Delta G_{298}^0$ kJ/mol	ref
M1	6.59	1	29.87	29.397	4.410	1.473	-187.3	1	0	-
M10	10.97	1	37.99	41.060	11.707	5.954	-234.2	1	-211.6	17
$\alpha$ -Quartz	22.89	1	41.46	73.488	0.782	15.376	-436.1	11	-856.3	2
$\beta$ -Quartz	22.30	2	41.46	70.601	4.265	32.715	-421.1	11	-853.2	18
Corundum	26.57	1	50.92	116.336	11.983	19.514	-688.3	1	-1562.2	1
Hematite	30.28	2	87.49	84.429	92.839	1.987	-511.0	2	-745.3	2
Magnetite	44.52	2	160.33	376.660	-139.903	122.478	-2242.1	2	-1017.5	2
Kyanite	44.21	3	82.42	177.000	24.849	29.564	-1049.1	3	-2445.8	4
Sillimanite	50.02	3	95.77	169.439	28.903	25.623	-1002.8	3	-2440.7	4
Wollastonite	39.79	2	81.67	102.236	28.447	13.443	-605.9	2	-1549.2	2
Enstatite	31.35	2	66.32	118.248	11.159	20.280	-699.6	1	-1457.4	2
Ferrosillite	32.99	4	95.82	116.495	15.201	16.159	-686.3	12	-1116.2	18
Fayalite	46.15	5	152.13	156.620	35.066	15.619	-920.4	2	-1377.1	18
Diopside	66.11	6	142.72	230.948	22.916	34.840	-1361.3	13	-3026.0	19
Hedenbergite	67.85	7	173.59	214.116	48.359	24.698	-1262.0	14,15	-2678.8	20
Anorthite	100.79	2	199.28	263.705	62.848	31.468	-1556.7	2	-4010.9	18
Grossular	126.30	2	255.98	494.298	7.895	83.893	-2912.6	4	-6282.3	18
Andradite	131.67	8	316.82	470.395	46.903	63.743	-2765.6	16	-5413.2	20
Almandine	115.11	9	342.63	429.345	90.458	53.133	-2532.8	9	-4940.8	18
Pyrope	113.27	10	266.27	452.332	44.807	65.538	-2664.2	10	-5936.4	20

$$S_T^0 = S_{298}^0 + A \ln(T) + B 10^{-3} T + C 10^{-5} T^2 + D$$

- 1: Robie et al. 1979; 2: Robinson et al. 1982; 3: Robie and Hemingway 1984; 4: Anovitz and Essene 1987b; 5: Essene unpubl.; 6: Levien and Provit 1981; 7: Caseron et al. 1973; 8: Huckenholz et al. 1974; 9: Metz et al. 1983; 10: Haselton and Newton 1980; 11: Hemingway 1987; 12: Bohlen et al. 1983c; 14: Krupka et al. 1986a, 1986b; 14: Bennington et al. 1984; 15: Haselton et al. 1987; 16: Robie et al. 1987; 17: Holmes et al. 1986; 18: Anovitz and Essene 1987; 19: Sharp et al. 1986; 20: this study

TABLE 2. Compressibility and thermal expansion data used in thermodynamic calculations

PHASE	a	b	ref.	c	d	e	f	ref.
Mt	0.535	0.900	21	1.092E-01	4.207E-03	1.663E-06	-5.866E-10	30
MtO	0.600	1.000	22	-3.570E-02	1.347E-03	-2.206E-08	-1.056E-10	31
$\alpha$ -Quartz	4.300	24.000	17	1.944E-03	3.274E-03	2.876E-06	6.922E-10	2
$\beta$ -Quartz	0	0	17	3.861E-01	1.983E-02	2.562E-05	1.044E-08	2
Corundum	0.380	0	21	-7.528E-02	2.034E-03	0.876E-06	-3.160E-10	30
hematite	0.509	0.454	2	9.682E-02	3.870E-03	1.056E-09	-1.402E-12	2
Magnetite	0.560	0	2	-6.156E-02	2.320E-03	3.481E-06	-1.496E-09	2
Kyanite	0.790	5.000	23	5.427E-02	2.144E-03	8.101E-10	-3.208E-10	32
Sillimanite	0.788	4.810	23	1.904E-02	7.618E-04	1.478E-06	-7.665E-10	32
Wollastonite	1.465	9.819	2	1.118E-01	5.008E-03	-4.169E-06	1.554E-09	2
Enstatite	1.010	0	2	4.569E-03	-3.292E-04	5.928E-06	-2.534E-09	2
Ferrosillite	0.990	0	24	9.500E-02	3.822E-03	5.737E-11	2.778E-13	4
Fayalite	0.767	0.978	2	-2.810E-01	1.017E-03	3.881E-06	-1.672E-09	2
Diopside	1.108	11.020	6,21,25	9.535E-02	4.005E-03	-1.420E-06	7.625E-10	7
Hedenbergite	2.117	31.313	26	-5.224E-02	4.148E-03	-4.245E-06	2.909E-09	7
Anorthite	1.087	0	27	1.566E-01	1.311E-03	-8.876E-06	2.075E-10	2
Grossular	0.721	3.200	2	-4.468E-02	1.761E-03	9.401E-07	2.674E-10	2
Andradite	0.725	0	28	-4.731E-02	2.107E-03	5.732E-07	7.252E-01	30
Almandine	0.571	0	4	4.541E-02	1.654E-03	1.231E-06	-3.023E-10	4
Pyrope	0.137	2.650	29	4.876E-02	2.084E-03	8.206E-07	-2.678E-10	30

$$V_{T,0}^* = V_{T,0}^* (1 - aP^{10^3} + bP^2 \cdot 10^6), P \text{ kbar}$$

$$V_T^* = V_{T,0}^* + V_{T,0}^* / 100 [c + dT + eT^2 + fT^3], T^\circ C$$

2, 4, 6, 7: Table 1; 21: Birch 1966; 22: Hazen and Prewitt 1977; 23: Brace et al. 1969;  
 24: Bans and Weidner 1984; 25: Hazen and Finger 1981; 26: Vaidya et al. 1978;  
 27: Liebermann and Ringwood 1976; 28: Babaska et al. 1978; 29: Hazen and Finger 1978;  
 30: Skinner 1966; 31: Nielson and Leisold 1965; 32: Winter and Ghose 1979

The loci of relevant equilibria were calculated with a computer program (EQUILI, Wall and Essene unpubl) that solves the relation

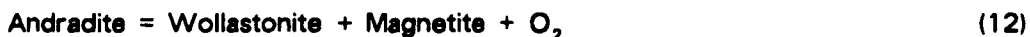
$$\Delta G_{T_2}^{P_2} - \Delta G_{T_1}^{P_1} = \int_{P_1}^{P_2} \Delta V dP - \int_{T_1}^{T_2} \Delta S dT$$

with an experimental reversal or a known Gibbs free energy of reaction as the starting point for the calculation. Using EQUILI, reactions are then calculated at 1 bar, 298 K in order to obtain the Gibbs free energy ( $\Delta G_{298}^{\circ}$ ) of each reaction. Algebraic combinations of the reactions allows calculation of the  $\Delta G_{298}^{\circ}$  of each phase assuming that the  $\Delta G_{298}^{\circ}$  of quartz and other simple phases (e.g., hematite, magnetite, wollastonite) are known (Robie et al. 1979, Robinson et al. 1982). Equilibria for which there are no experimental reversals can then be calculated at high P and T using the 1 bar, 298 K data as a starting point.

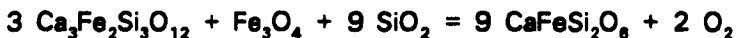
Thermodynamic data for hedenbergite (Tables 1, 2) are constrained by the following experiments in the system Ca-Fe-Si-O:



(Huckenholz et al. 1974, Suwa et al. 1976),



(Gustafson 1974),



(Burton et al. 1982), and,



(Liou 1974).

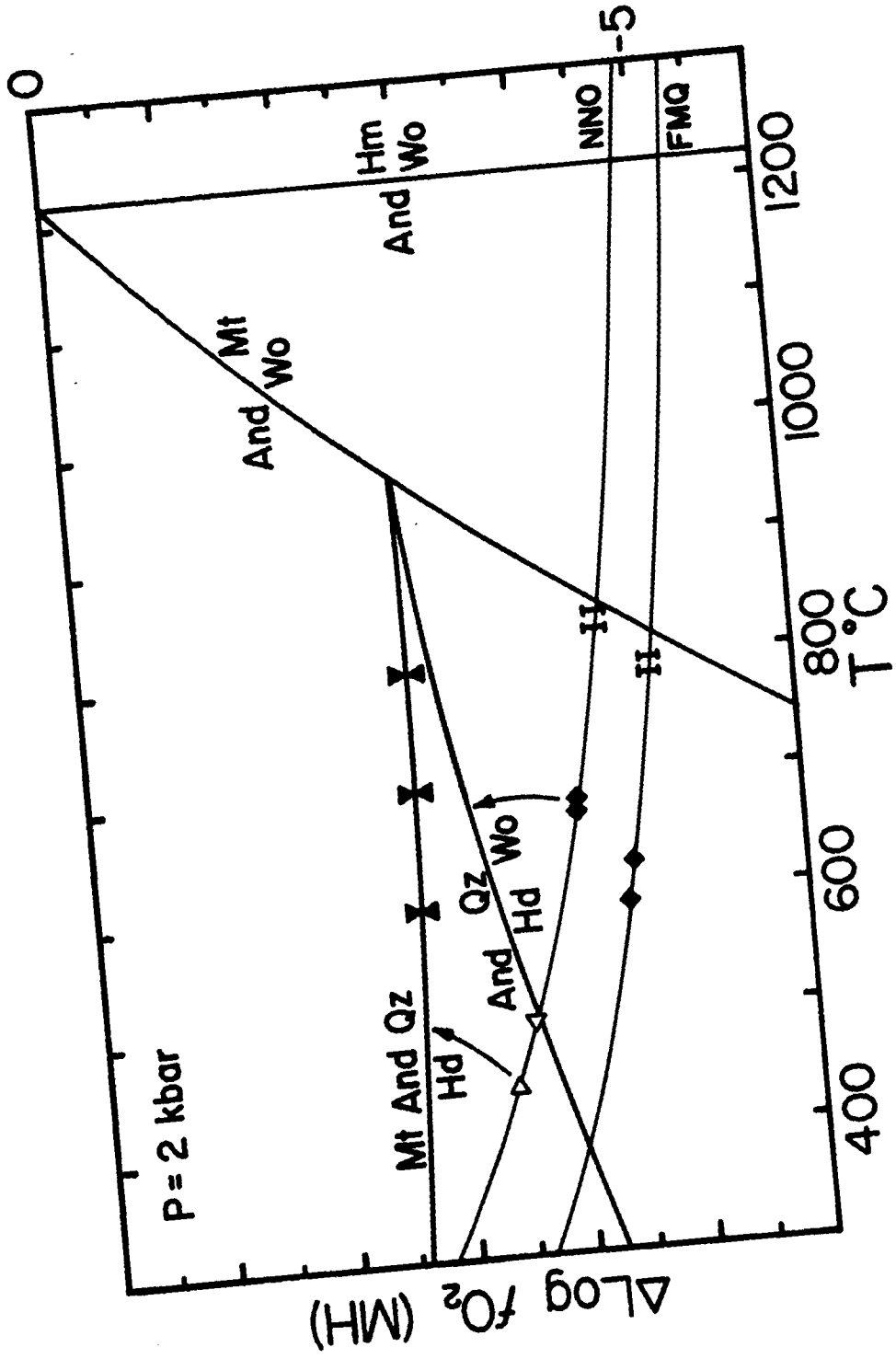
The calculated position of these reactions in  $f\text{O}_2$ -T space at 2 kbar (relative to MH) are shown in Fig. 1, along with the calculated position of the NNO and QFM buffers. The HM and QFM buffers are calculated from data in Robinson et al. (1982, Table 1), and the NNO buffer is calculated from the solid state electrochemical measurements of Holmes et al. (1986, Table 1). All buffers were corrected for pressure and temperature using the expansivity and compressibility data in Table 2.

Thermodynamic data for hematite, magnetite, and wollastonite are taken from Robinson et al. (1982), and data for andradite and hedenbergite are compiled from sources listed in Table 2. The  $\Delta G_{298}^\circ$  for andradite was calculated from Reaction 11 using the experimental reversal of Huckenholz et al. (1974) (1 bar,  $1137 \pm 5^\circ\text{C}$ ) as a starting point, yielding  $\Delta G_{298}^\circ (\text{And}) = -5413.2 \text{ kJ/mol}$ . If the reversal of Suwa et al. (1976: 1bar,  $1165^\circ\text{C}$ ) is used as a starting point, the free energy of andradite changes by  $-0.3 \text{ kJ}$ . Use of the latter value for  $\Delta G_{298}^\circ (\text{And})$  shifts Reaction 12 to higher temperature, increasing the discrepancy between the experimental reversal for Reaction 12 and its calculated position (Fig 1). Therefore, we have used the reversal of Huckenholz et al. (1975) as the reference point for  $\Delta G_{298}^\circ (\text{And})$ .

The experimental reversal at  $800^\circ\text{C}$  of Burton et al. (1982) for Reaction 13 was selected as the starting point for the calculation of  $\Delta G_{298}^\circ (\text{Hd})$ , and the calculated position of Reaction 13 is in good agreement with the reversals at  $600$  and  $700^\circ\text{C}$  (Fig 1). The position of Reaction 14 was calculated using the  $\Delta G_{298}^\circ (\text{Hd})$  ( $-2677.7 \text{ kJ/mol}$ ) determined from these latter experimental constraints. Assuming that the reversals of Burton et al. (1982) are reliable, there is a discrepancy of 1.5 log units between the calculated position of Reaction 14 and the experimental reversals of Liou (1974) (Fig. 1) that is not ascribable to errors in the thermodynamic data. The direction of the shift suggests that the synthetic andradite used in the experiments of Liou (1974) may not be stoichiometric andradite with

**Figure 1.**  $fO_2$ -T equilibria at 2 kbar in the system Fe-Si-Ca-O (relative to MH buffer) that constrain  $\Delta G_{298}^\circ$  of hedenbergite and andradite. Vertical bars: reversals of Gustafson (1974) for  $\text{And} = \text{Wo} + \text{Mt} + \text{O}_2$ ; diamonds: reversals of Liou (1974) for  $\text{Hd} + \text{Wo} = \text{And} + \text{Qz} + 2\text{O}_2$ ; triangles: reversals of Burton et al. (1982) for  $\text{Mt} + \text{And} + \text{Qz} = \text{Hd} + \text{O}_2$ . Note disparity between calculated and experimental positions of the latter reactions as denoted by arrows between reversals and reactions to which they correspond.





possible substitutions of the nature  $\text{Fe}^{+2}\text{Fe}^{+3}-\text{CaFe}^{+2}$  or  $(\text{OH})_4^{4-}-(\text{SiO}_4^{4-})$ . The reactants used in the experiments of Burton et al. (1982) were stoichiometric, but analyses of run products for Reaction 13 are not given. More thorough characterization of the run products for all experiments or new experiments in the Ca-Fe-Si-O system are required in order to resolve the discrepancy. Further calculation of reactions involving hedenbergite rest on the assumption of the choice of experimental constraints used here.

Using a slightly different experimental and thermodynamic data base, Robie et al. (1987) obtained values for  $\Delta G_{298}^\circ$  (And) =  $-5414.8 \pm 5.5$  and  $\Delta G_{298}^\circ$  (Hd) of  $-2674.3 \pm 5.8$  kJ/mole. The values differ somewhat from ours because we have included the effects of thermal expansion and compressibility in our calculation, and have started with a different thermodynamic data base. Helgeson et al. (1978) report values of  $\Delta G_{298}^\circ$  (And) =  $-5428.7$  kJ/mol and  $\Delta G_{298}^\circ$  (Hd) =  $-2674.5$  kJ/mol.

Volume and entropy data for pyrope are taken from Haselton and Westrum (1980) and Haselton and Newton (1980). The Gibbs free energy of pyrope was calculated from experimental data on the reaction



(Gasparik and Newton 1984), using thermodynamic data for enstatite from Robinson et al. (1982) and data for corundum from Robie et al. (1979). In the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (MAS), enstatite contains significant solid solution of Mg-Tschermak's component ( $\text{Mg}_{0.5}\text{AlSi}_{0.5}\text{O}_3$ ) (Boyd and England 1964, Hensen and Essene 1971, Anastasiou and Seifert 1972, MacGregor 1974, Danckwerth and Newton 1978, Lane and Ganguly 1980, Perkins and Newton 1980, Perkins et al. 1981, Perkins 1983). In order to calculate the location of the end member Reaction (15) one must correct for the reduction in enstatite activity. Aranovich and Kosyakova (1987) have recently published activity-composition relations for orthopyroxene that are based on experimental equilibria in the MAS and FMAS systems. For the range of aluminum

contents encountered in the above experimental studies the model of Aranovich and Kosyakova (1987) yields activity coefficients for the  $\text{MgSiO}_3$  component in enstatite-Mg-Tschermak's solid solutions ( $\gamma_{\text{MgSiO}_3}^{\text{Opx}}$ ) that are slightly less than one, suggesting only slight departures from ideality. However, the difference between the ideal model and the model of Aranovich and Kosyakova (1987) may yield significant differences in the Gibbs energy of pyrope because reactions involving pyrope and enstatite are extremely sensitive to changes in pressure. We have employed the latter model in the calculations to follow.

Using the midpoint of the reversal for Reaction 15 (Gasparik and Newton 1984, 850°C and  $16.25 \pm 0.25$  kbar,  $X_{\text{MgTs}}^{\text{En}} = 0.06$ ) as a starting point for the calculation, the shift in position of Reaction 15 due to orthopyroxene solid solution was calculated from the relation

$$RT \ln(K_2/K_1) = \int_{P_1}^{P_2} \Delta V dP$$

where  $K_2 = 1$  for the position of the corrected reversal,

$$K_1 = (1/a_{\text{MgSiO}_3}^{\text{Opx}})^3,$$

and pyrope, sillimanite and quartz are assumed to be pure phases. For these calculations we have followed the convention of Hensen and Essene (1971) and Aranovich and Kosyakova (1987) by writing the formula of enstatite and Mg-Tschermak based on 2 cations (see Appendix I). The location of Reaction 15, adjusted to pure enstatite, is at 12.7 kbar, 850°C, and serves as the starting point for calculation of the Gibbs free energy of pyrope. The calculated value of  $\Delta G_{298}^{\circ}$  (Reaction 15) is 18.1 kJ/mol, yielding  $\Delta G_{298}^{\circ}$  (Py) = -5936.4 kJ/mol. As in deriving the Gibbs energy of hedenbergite, the Gibbs energy for pyrope is dependent on our choice of experiments and Gibbs free energies for enstatite and corundum.

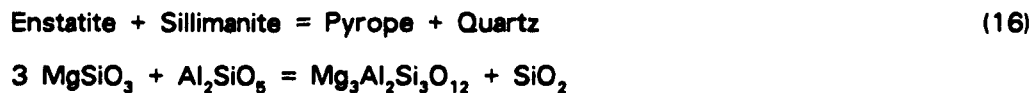
Wood and Holloway (1984) present an analysis of equilibria in the CMAS system, deriving an  $\Delta H_{1000}^{\circ}$  for pyrope (relative to oxides) of -84.9 kJ/mol ( $S_{1000 \text{ K}} =$

777.8 J/mol, Haselton and Newton 1980). Using enthalpy and entropy data for the oxides (Robie et al. 1979), this yields  $\Delta G_{1000}^{\circ}$  (Py) for the study of Wood and Holloway of  $-87.8$  kJ/mol, in fair agreement with the value derived in this study ( $\Delta G_{1000}^{\circ} = -83.4$  kJ/mol,  $\Delta H_{1000}^{\circ} = -79.3$  kJ/mol).

Newton (1987) has re-evaluated experiments in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  that constrain  $\Delta H_{298}^{\circ}$  and  $\Delta G_{298}^{\circ}$  of pyrope and enstatite. Based on analysis of the available experimental and thermochemical data base Newton (1987) obtains values for  $\Delta H_{298}^{\circ}$  (Py) and  $\Delta H_{298}^{\circ}$  (En) (relative to oxides) of  $-74.2$  and  $-32.7$  kJ/mol, respectively. Combined with entropy data for these phases the calculated values of  $\Delta G_{298}^{\circ}$  (oxides) are  $-77.2$  and  $-32.1$ , respectively. Our values of  $\Delta G_{298}^{\circ}$  are in very good agreement with those of Newton (1987):  $-77.7$  and  $-31.9$  for pyrope and enstatite, respectively. The same experimental data base was used in both studies, but different values of  $S_{298}^{\circ}$  for enstatite were used and the mechanics of calculating the location of the equilibria using EQUILI differ slightly from the method used by Newton (1987).

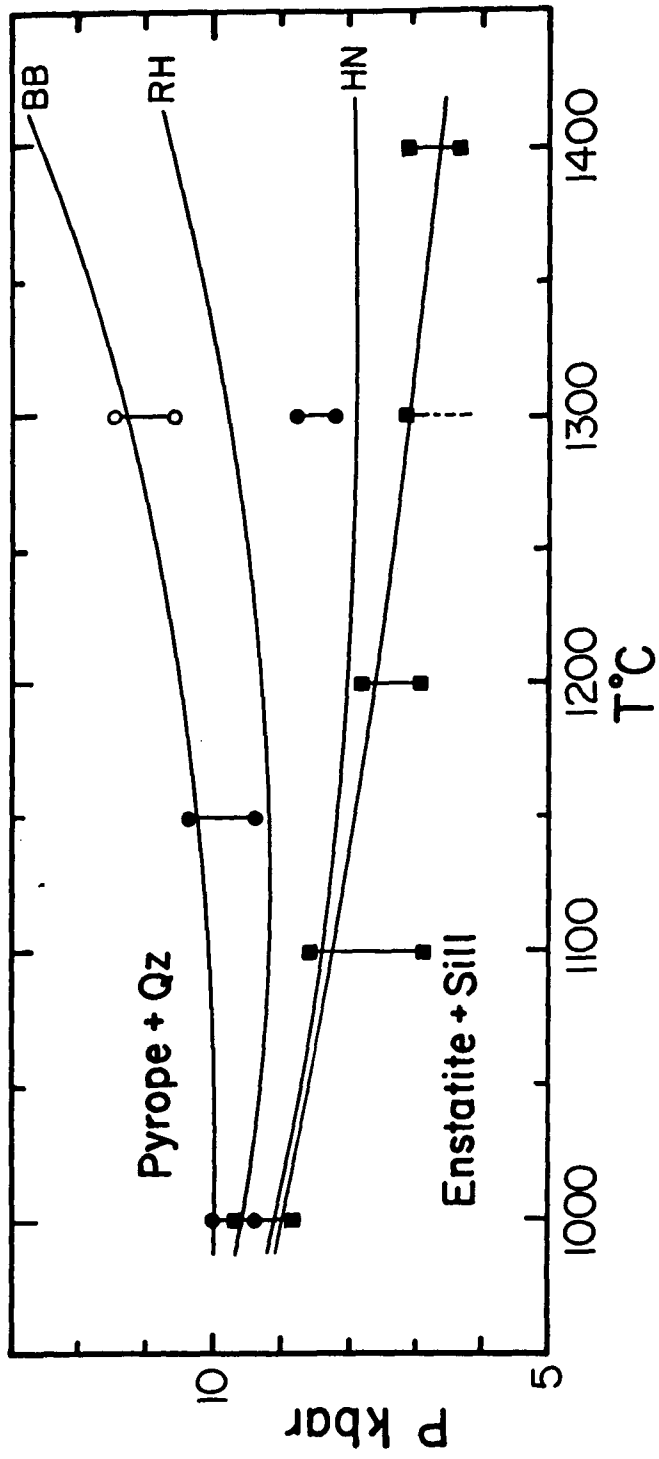
Other thermodynamic compilations yield Gibbs free energies for enstatite that are in good agreement with the values used in this study. Berman et al. (1986) give a value for  $\Delta G_{298}^{\circ}$  (En) =  $-1458.5$  kJ/mol, and Helgeson et al. (1978) report a value of  $-1459.9$  kJ/mol.

The free energies of pyrope and enstatite have also been evaluated using the experimentally reversed equilibrium



(Hensen and Essene 1971; Perkins 1983), with various estimates of the high temperature heat capacity of pyrope. There are some significant disparities between the experiments of Hensen and Essene (1971) and Perkins (1983) on Reaction 16, and among the possible high temperature extrapolations for the entropy of pyrope in the temperature range of the available experiments (Haselton and Newton 1980;

**Figure 2.** Experimental constraints on  $S_{298}^{\circ}$  and  $\Delta G_{298}^{\circ}$  for pyrope. Filled squares: adjusted reversals of Hensen and Essene (1971: HE); open circles: adjusted reversals of Perkins (1983) using quoted  $Al_2O_3$ ; filled circles: adjusted reversals of Perkins (1983) using  $Al_2O_3$  contents of Hensen and Essene (1971) for that temperature. Lines represent position of Reaction 16 using different extrapolations of high temperature heat capacity for pyrope. BB: Berman and Brown (1985); RH: Robinson and Hass (1983); HN: Haselton and Newton. Lowest line is 0.3% increase in HN extrapolation.



Robinson and Haas 1983; Berman and Brown 1985). However, both experimental data sets (adjusted for the Al content of the orthopyroxene using the methods discussed above) and the various heat capacity expressions converge at 1000°C. The thermodynamic data used in the present study for pyrope (with the heat capacity of pyrope from Haselton and Newton 1980) and enstatite are in very good agreement with both sets of experiments at 1000°C.

The experimental reversals for Reaction 16 lie outside of the temperature range for heat capacity data on pyrope (greater than 1200 K: Haselton and Newton 1980). The high temperature end of the heat capacity expression of Haselton and Newton (1980) is based on an arbitrary extrapolation (Haselton, pers comm 1987), but a thermodynamically based extrapolation is preferred. Robinson and Haas (1983) present an empirical estimation scheme for calculating heat capacities and entropies based on the relative contribution of various oxides in different crystal chemical coordinations within a lattice. However, constraints on the lattice contribution to heat capacity from Mg in 8-coordination as in garnet are derived solely from Haselton's (1979) data and should not be extrapolated above 1200 K. Berman and Brown (1985) present an alternative method of extrapolating  $C_p$  data. We have tested the effect of each of these extrapolation methods against the original heat capacity expression of Haselton and Newton (1980) on the shift in the location of Reaction 16 (Fig. 2).

Experimental reversals for Reaction 16 were adjusted for MgTs component in a manner similar to Reaction 15. We have used the analyzed MgTs contents for the aluminous enstatite produced in the experiments of Hensen and Essene (1971) to correct the positions of Perkins' (1983) reversals at 1000° and 1150°C, as these latter pyroxenes produced in the experiments were not analyzed. The location of the adjusted experimental reversals are presented in Fig. 2, along with the calculated position of Reaction 16 based on the heat capacity expressions of Haselton and Newton (1980; HN), and extrapolations based on Robinson and Haas (1983; RH) and Berman and Brown (1985; BB). The differences in calculated entropy at 1600 K

between the RH, and RH and BB extrapolations is only +0.6 and 0.9% of the HN value, respectively. Above approximately 1000°C these apparently small differences produce a significant change in sign and magnitude of the slope of Reaction 16. The heat capacity expression of HN approaches the adjusted position of the reversals of Hensen and Essene (1971) and the BB extrapolation gives a reasonably good fit to the adjusted reversals of Perkins (1983). Increasing the entropy at 1800 K obtained from the HN expression by 0.3%, and smoothing the entropy data by eye to 1400 K yields a reasonable fit to the adjusted experiments of Hensen and Essene (1971: Fig. 2).

The apparent discrepancy in the experimental data base for Reaction 16 makes the choice of high temperature values for the entropy of pyrope rather subjective. Both the experiments and entropy data converge near the lower temperature range of the experiments where the original data for pyrope were obtained and where the data will be applied to granulites. Therefore, we retain the heat capacity expression of Haselton and Newton (1980). Because the calculations tend to converge in the temperature range of the reversal for Reaction 15, the various heat capacity expressions change the Gibbs free energy of pyrope by less than 1.5 kJ. Clearly, more complete characterization of synthetic reactants and experimental products for Reaction 15, or high temperature (> 1200 K) calorimetry on pyrope are needed in order to resolve the discrepancy.

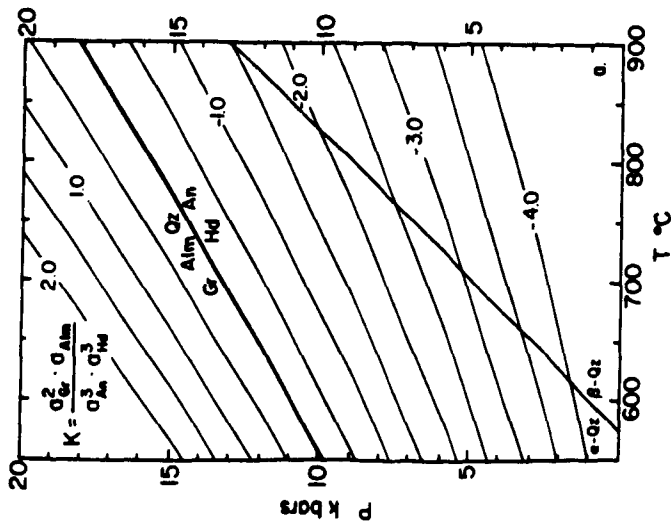
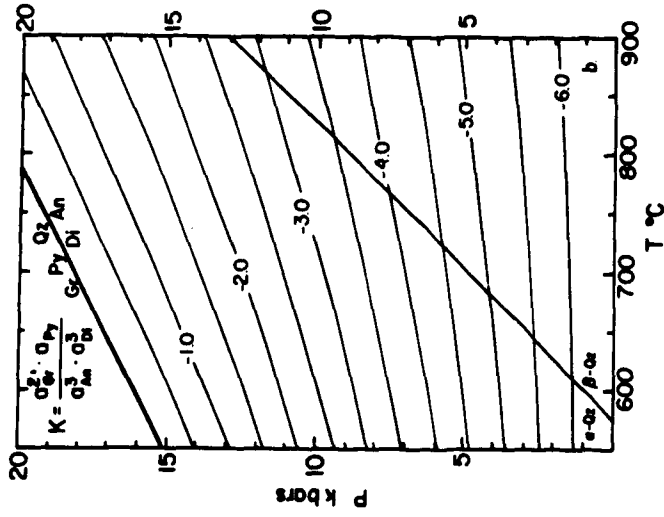
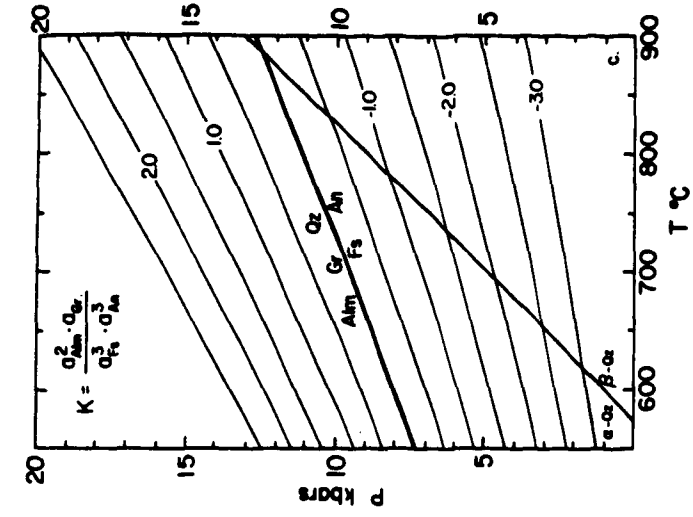
### Geobarometry

#### Clinopyroxene Barometers

The positions of Reactions 1, 2, and 3 were calculated using 1 bar, 298 K as a starting point (Figs. 3a – 3c). The clinopyroxene reactions have average slopes ( $\Delta P/\Delta T$ ) of 23 (HD) and 20 bar/°C (DI). These slopes are not as low as Reaction 3 (14.5 bar/°C), but are still useful for geobarometry, with the HD barometer having the greatest temperature dependency of the three barometers. The calculated slopes become less steep at lower pressure and more negative values of  $\log_{10}K$ .



**Figure 3a-c.** Calculated position and values of  $\log_{10}K$  for Reactions 1 through 3. a: HD barometer; b: DI barometer; c: FS barometer.



(Fig. 3), particularly for the FS and DI barometers. An uncertainty of 5 kJ in the value of  $\Delta G_{298}^{\circ}$  (rxn) results in an uncertainty of approximately 0.7 kbar for both Reactions 1 and 2. Uncertainties of 5 kJ in the  $\Delta G_{298}^{\circ}$  for any phase involved in the reaction will yield an uncertainty of 0.7 kbar per mole of that phase in Reactions 1 and 2.

### Activity Models

Application of these equilibria to natural systems requires consideration of the reduction in activity of end member components due to solid solutions in plagioclase, garnet, orthopyroxene, and clinopyroxene. Included in Figs. 3a, 3b, and 3c are the calculated positions for values of  $\log_{10}$  of the equilibrium constant K for each reaction. For example K is defined for Reaction 1 by the relation:

$$K = \left\{ \left( \frac{a_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}}}{a_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}}} \right)^2 \left( \frac{a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{Pg}}}{a_{\text{CaFeSi}_2\text{O}_8}^{\text{Cpx}}} \right) \right\}^3$$

Variations in  $\log_{10}K$  with pressure were calculated from the relation:

$$RT \ln(K_2/K_1) = \Delta G_{T_2}^{P_2} - \Delta G_{T_2}^{P_1} = \int_{P_1}^{P_2} \Delta V dP$$

Given appropriate activity models for plagioclase, garnet, and pyroxene, the equilibrium constant can be calculated from analyses of the coexisting phases, and with an estimate of temperature the pressure can be read from Figure 3.

The activity models for plagioclase, garnet, or pyroxene will ultimately limit the accuracy and precision of a geobarometer. The models of Newton et al. (1980) or Orville (1972) for plagioclase, Perkins (1979), Newton and Haselton (1981), or Ganguly and Saxena (1984) for garnet, and an ideal two site approximation (e.g., Wood and Banno, 1973) for pyroxenes are typically selected by most workers. For this study the plagioclase activity model of Newton et al. (1980) (Appendix 4) was used in evaluation of the geobarometers. At 700°C and constant garnet and pyroxene activities, this latter plagioclase activity model yields slightly lower pressures (on the order of 0.1 kbar) than that of Orville (1972).

The quaternary garnet mixing model of Ganguly and Saxena (1984) with modified values for Ca-Fe mixing parameters (Anovitz and Essene, 1987a) was used to calculate the activity of  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ,  $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ , and  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  in garnet, and to calculate the position of the FS reaction (Reaction 3). The derivation of these parameters are discussed by Anovitz and Essene (1987a), and analytical expressions for calculating activities are outlined in Appendix 4. The model used here typically yields  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  and  $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  activities 1 to 5% greater than values obtained from the original formulation of Ganguly and Saxena (1984).

Activity coefficients for  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  in garnet ( $\gamma_{\text{Mg}}^{\text{Gt}}$ ) obtained from the model of Ganguly and Saxena (1984: GS) are significantly greater than those obtained from the model of Haselton and Newton (1980: HN). For a garnet of composition  $\text{Alm}_{50}\text{Py}_{25}\text{Gr}_{25}$  at 700°C,  $\gamma_{\text{Mg}}^{\text{Gt}}$  (GS) = 1.7 and  $\gamma_{\text{Mg}}^{\text{Gt}}$  (HN) = 1.3. This difference is due to the sign for the ternary constants as discussed by Ganguly and Saxena (1984, p 94, eq 16). If the sign of the ternary constant in the expression for  $\gamma_{\text{Mg}}^{\text{Gt}}$  is changed from that given in Ganguly and Saxena (1984), one obtains similar values for  $\gamma_{\text{Mg}}^{\text{Gt}}$  for the two models. This discrepancy needs further evaluation. In general, use of the GS model as it now stands yields significantly greater pressures than the HN model for the DI barometer, all other factors being equal.

Chatillon-Colinet et al. (1983) proposed that an ideal mixing approximation for Mg-Fe orthopyroxenes is consistent with solution calorimetric data on orthopyroxene solid solutions. Therefore the activity of  $\text{FeSiO}_3$  in orthopyroxene was calculated using the ideal model of Wood and Banno (1973) (Appendix II). Davidson and Lindsley (1985) have modeled the phase equilibria of quadrilateral pyroxenes in order to derive a pyroxene activity model. Although Davidson and Lindsley do not present an explicit analytical formulation for activity coefficients similar to garnet and plagioclase, we obtained a computer program (PM Davidson pers comm 1987) that calculates activities of  $\text{Fe}_2\text{Si}_2\text{O}_6$ ,  $\text{Mg}_2\text{Si}_2\text{O}_6$ ,  $\text{CaFeSi}_2\text{O}_6$ , and  $\text{CaMgSi}_2\text{O}_6$  for quadrilateral pyroxene. The pyroxene projection scheme of Lindsley (1983) was used to calculate mole fractions of Wo, En, and Fs, the components

upon which the activity model of Davidson and Lindsley (1985) is calculated. The pyroxene activity model of Davidson and Lindsley (1985) yields activities of  $a_{\text{Fe}_2\text{Si}_2\text{O}_6}^{\text{Ppx}}$  that are similar to or only slightly less than ideal two site activities calculated with the Wood and Banno (1973) model (Fig. 4a).

Activities of  $\text{CaFeSi}_2\text{O}_6$  and  $\text{CaMgSi}_2\text{O}_6$  were also calculated using a modified ideal model, in comparison with the model of Davidson and Lindsley (1985). Ideal  $\text{CaFeSi}_2\text{O}_6$  activities were approximated by the relationship

$$a_{\text{CaFeSi}_2\text{O}_6}^{\text{Cpx}} = [X_{\text{Ca}}^{\text{M}2}][X_{\text{Fe}^{2+}}^{\text{M}1}] \quad (17)$$

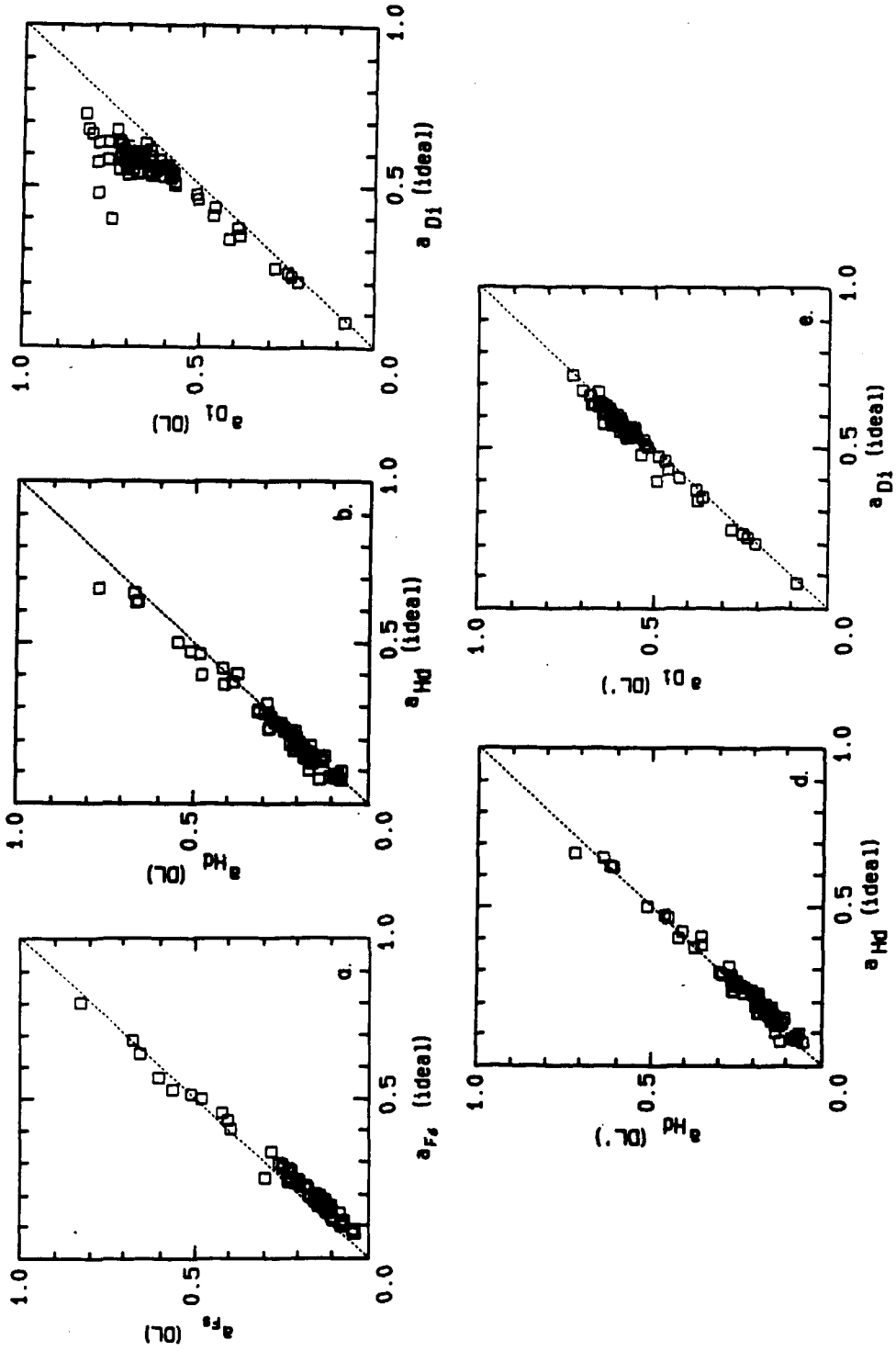
where  $X_{\text{Fe}^{2+}}^{\text{M}1} = \text{Fe}^{2+} - (1 - \text{Ca} - \text{Na} - \text{Mn})$ ,  $X_{\text{Ca}}^{\text{M}2} = \text{Ca}$ , and Ca, Na, Mn, and  $\text{Fe}^{2+}$  are the number of atoms of the respective cations. Pyroxene analyses taken from the literature are re-normalized to four cations, and values of ferric and ferrous iron were calculated from charge balance and stoichiometry. Analyses taken from the literature were of varying quality, and not all of these pyroxenes were analyzed for Na, which usually occurs in significant quantities in high grade clinopyroxenes. Failure to analyze for Na will affect the calculation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and ultimately the value of  $X_{\text{Fe}^{2+}}^{\text{M}1}$ . Ideal  $\text{CaMgSi}_2\text{O}_6$  activities were calculated as

$$a_{\text{CaMgSi}_2\text{O}_6}^{\text{Cpx}} = [X_{\text{Ca}}^{\text{M}2}][X_{\text{Mg}}^{\text{M}1}] \quad (18)$$

where  $X_{\text{Ca}}^{\text{M}2} = \text{Ca}$  and  $X_{\text{Mg}}^{\text{M}1} = \text{Mg}$ , based on a 4-cation pyroxene formula. The clinopyroxene model is based on crystal chemical observations on igneous pyroxenes that iron and magnesium do not mix ideally on the M1 and M2 sites, with iron showing a greater tendency relative to magnesium to partition into the M2 site (Cameron and Papike 1980, Dal Negro et al. 1982). Although there are no cation partitioning data on granulite facies augites, one might predict that the ordering would be even more pronounced in granulite facies augites compared to igneous augites, as temperatures are lower and cooling histories are likely to be slower for the former. Single crystal refinements and Mossbauer studies of homogeneous natural pyroxenes from the granulite facies are needed to evaluate this assumption.

**Figure 4a-c.** Ideal activities of ferrosilite, hedenbergite, and diopside (e.g.,  $a_{\text{Hd}}$  ideal) versus activities calculated using model of Davidson and Lindsley (1985).

**Figure 4d, 4e** Ideal activities of hedenbergite and diopside versus Davidson and Lindsley activities adjusted for non-quadrilateral components (DL').



Activities of  $\text{CaFeSi}_2\text{O}_6$  in Cpx ( $a_{\text{CaFeSi}_2\text{O}_6}^{\text{Cpx}}$ ) calculated with the model of Davidson and Lindsley (1985) yield  $a_{\text{CaFeSi}_2\text{O}_6}^{\text{Cpx}}$  that are usually similar to or slightly greater than values obtained using the ideal approximation (Fig. 4b). The values for  $a_{\text{CaMgSi}_2\text{O}_6}^{\text{Cpx}}$  calculated from the model of Davidson and Lindsley (1985) are generally greater than ideal activities (Fig. 4c). The scatter in  $a_{\text{CaMgSi}_2\text{O}_6}^{\text{Cpx}}$  is an artifact of the projection scheme used to correct natural compositions to those appropriate for the activity model. The effect of subtracting non-quadrilateral components (mainly Al, Na, and  $\text{Fe}^{3+}$  in granulite facies pyroxenes) in the projection scheme is to overestimate the amount of quadrilateral pyroxene components, and this projection scheme is not strictly valid for clinopyroxenes with a large fraction of non-quadrilateral components (Lindsley 1983). The greatest departure from quadrilateral space is for aluminous and sodic pyroxenes in granulites from Doubtful Sound, N.Z., in granulite xenoliths from Lesotho, and from the Westchester Prong, PA, granulites. When the Davidson and Lindsley (1985) activities are reduced by an amount equal to the mole fraction of non-quadrilateral components ( $1 - \text{Al}^{\text{vi}} - 2\text{Ti} - \text{Fe}^{3+} - \text{Mn}$ ), the degree of scatter is significantly reduced (Figs. 4d, 4e).

#### Evaluation of Barometers

Pressures were calculated using the Gt-Cpx-Pg-Qz (HD, DI) barometers (Reactions 1 and 2) and the Gt-Opx-Pg-Qz (FS) geobarometer (Reaction 3) for 68 samples with Gt-Cpx-Opx-Pg-Qz assemblages (Tables 3 and 4). Widespread application of the FS barometer in the Central Gneiss Belt of the Grenville Province of Ontario has yielded pressures that are in good agreement with aluminosilicate occurrences and other geobarometers (Anovitz and Essene, 1987b). The FS barometer also yields pressures that are consistent with reported aluminosilicate occurrences for the terranes studied here (Table 3) and previous estimates of pressure for other terranes (Table 4).



**Figure 5a.** Pressure obtained for FS barometer with ideal fs activities ( $P_{Fs,ideal}$ ) versus pressure obtained with model of Davidson and Lindsley ( $P_{Fs,DL}$ ).

**Figure 5b.** Pressure obtained for HD barometer vs. those for FS barometer, both with ideal approximation for pyroxene activities.

**Figure 5c.** Pressure obtained for DI barometer vs. those for FS barometer, both with ideal approximation for pyroxene activities.

**Figure 5d.** Pressure obtained for HD barometer vs. those for FS barometer, with HD activities adjusted for non-quad components (DL') and ideal ferrosilite activities

**Figure 5e.** Pressure obtained for DI barometer vs. those for FS barometer, with DI activities adjusted for non-quad components (HD') and ideal diopside activities.

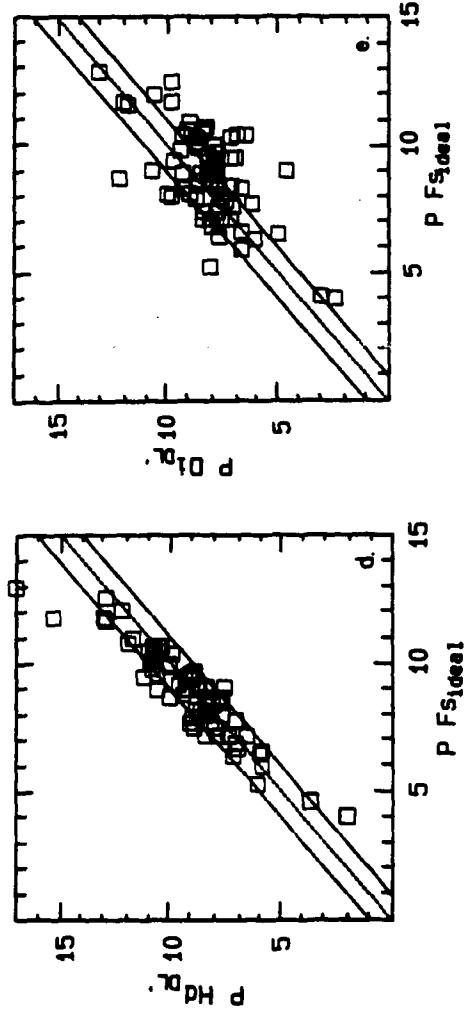
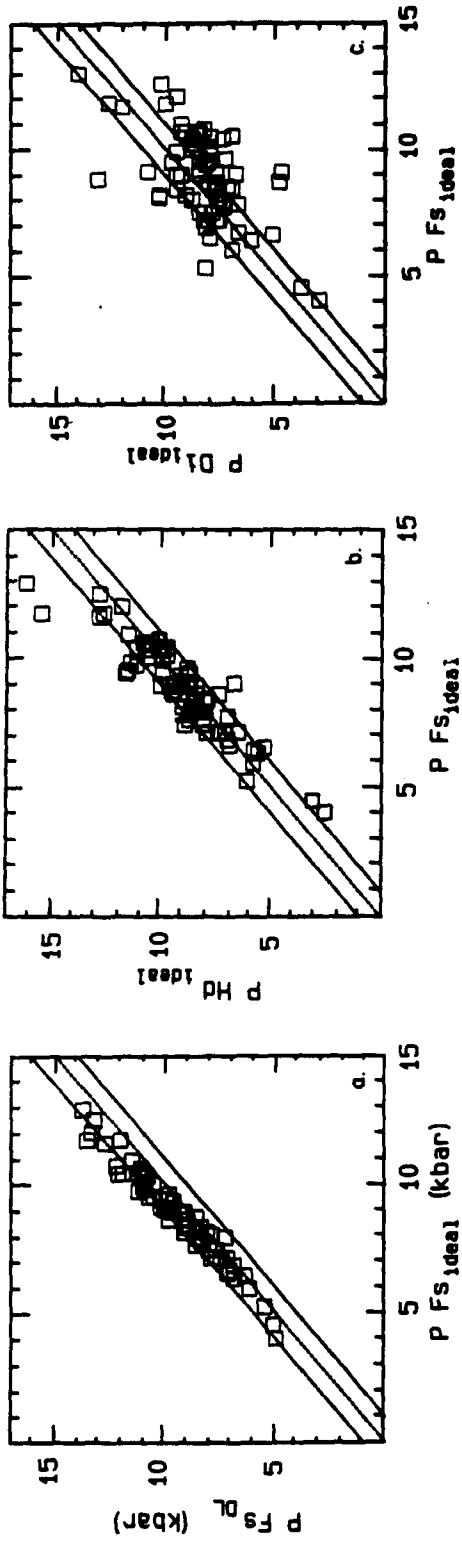


TABLE 3. Sources of analytical data on Gt-Cpx-Opx-Pg-Qz assemblages and quoted aluminosilicate occurrences used to evaluate geobarometers of this study.

TERRANE	SAMPLES	REF	ALS <sup>1</sup>	T°C/P kbar <sup>2</sup>
Grenville Province				
Parry Sound ONT	S3B O15B S10B M65 S32 S86E33	1	Sil	800/<9.8
Otter Lake QUE	A12 DL2	2	Sil	700/<7.8
Adirondack Mts NY				
Highlands	BM2 BM13 ET15 ET24 LL6 MM4 MM18 PH4 SL5 SL26 SR31 W9	3	Sil	800/<9.8
Lowlands	74C248B	4	Sil	700/<7.8
Pikwitonei Belt MAN	A41 C104 D50 D110 E18	5	Sil	800/<9.8
India				
Sargur Belt	S33	6	-	
	S3 S4	7	Ky/Sil	700/<7.8
Karnataka	113E GH4A	8	-	
	DT MB GV2	9	-	
Nilgiri Hills	332 352 690	10	Sil	750/<8.8
Mysore	K21	11	-	
Bengal	SM4B SM44B	12	Sil	700/<7.8
Furua Complex TANZ	MF283.3 MF268.1 WE322.3 ZC.8 DMA40 C247.1 C311.1 C352.2	13	Ky/Sil	800/9.8
Westchester PA	74-67 -71 -207A -322C	14	Ky	650/>6.8
Wind R. Range WY	A22	15	Sil	700/<7.8
SW Minnesota	DN4C2	16	Sil	700/<7.8
Lesotho	LT2	17	-	
Oaxacan Complex	16076 25277 169076	18	Sil	730/<8.3
West Greenland				
Buksefjorden	174087	19	Sil	800/<9.8
	174102		Ky/Sil	600/6.3
Isortoq	88589 91141	20	-	
Finnish Lapland	47III 66II	21	Sil	750/<8.8
Doubtful Sound NZ	36461 36468	22	-	
Broken Hill	911 10770	23	Sil	800/<9.8

1: ALS = aluminosilicate; Ky = kyanite, Sil = sillimanite. 2: Quoted T with P constraint.  
 1: Moecher (1988); 2: Perkins (1979); 3: Bohlen (1979); 4: Stoddard (1976);  
 5: Paktunc and Baer (1986); 6: Janardhan and Gopalakrishna (1983); 7: Srikantappa et al. (1985);  
 8: Janardhan et al. (1982); 9: Hansen et al. (1984); 10: Harris et al. (1982);  
 11: Devaraju and Coolen (1983); 12: Bhattacharya and Mukherjee (1987); 13: Coolen (1980);  
 14: Wagner and Srogi (1987); 15: Sharp (1988); 16: Moecher (1984); 17: Griffen et al. (1979);  
 18: Mora and Valley (1985); 19: Wells (1977); 20: Glascoley and Sorensen (1980);  
 21: Hornmann et al. (1980); 22: Oliver (1977); 23: Phillips (1980).

TABLE 4. Comparison of quoted pressures from other Opx-Pg-Gt-Qz barometers with orthopyroxene and clinopyroxene barometers of this study (using ideal pyroxene activities). References as in Table 3. nd = pressure not determined.

LOCALITY	REF	BWB-FS	PC-FS	MAE-FS	NP-EN	PC-EN	MAE-HD	MAE-DI
Parry Sound	1	nd	nd	7.5 - 11.7	nd	nd	8.1 - 12.8	8.2 - 12.0
Otter Lake	2	8.1, <8.4	8.0, <7.5	8.4, <8.5	6.6, <8.1	9.7, <9.1	8.5, <7.9	7.8, <7.2
Adir. High.	3	7.1 - 8.2	7.1 - 8.6	6.5 - 8.8	8.5 - 9.9	10.4 - 11.5	5.8 - 9.5	7.4 - 13.1
Adir. Low.	4	6.6	nd	6.4	6.1	nd	5.6	6.1
Pikwitonei*	5	6.6 - 9.2	7.9 - 11.7	6.6 - 9.1	7.1 - 9.5	11.1 - 12.8	5.3 - 9.4	4.7 - 8.3
Sargur*	6	nd	nd	9.0	9.0	nd	10.1	8.3
	7	nd	nd	10.5, 10.5	9.1, 9.1	nd	9.7, 10.1	7.0, 7.1
Karnataka*	8	9.0, 9.2	10.0, 9.5	9.5, 10.4	8.3, 9.5	9.4, 9.8	8.7, 10.7	8.1, 8.8
	9	nd	nd	8.4 - 9.1	9.1, 9.1	nd	8.0 - 8.7	7.0 - 7.7
Milgiri*	10	nd	nd	9.0 - 10.2	6.9 - 8.8	nd	9.1 - 10.0	8.5 - 9.5
Mysore*	11	nd	nd	12.1	9.9	nd	11.8	9.5
Bengal*	12	nd	nd	7.5, 7.2	6.2, 6.3	nd	8.9, 7.9	7.9, 7.6
Furua Complex	13	9.6 - 11.4	9.9 - 12.1	10.1-12.6	9.4 - 12.7	9.8 - 11.6	9.9 - 12.8	7.4 - 10.2
Westchester*	14	8.9 - 9.6	9.8 - 10.8	9.6 - 10.0	5.6 - 9.4	9.1 - 12.3	9.9 - 11.5	7.3 - 8.8
Wind R Range*	15	5.0	nd	5.3	nd	nd	6.1	8.2
Minn R Valley*	16	nd	nd	6.0	nd	nd	5.8	7.0
Lesotho	17	nd	nd	11.8	10.1	nd	12.6	10.0
Oaxaca Complex*	18	6.3 - 7.3	nd	7.3 - 8.0	7.5 - 7.8	nd	7.0 - 8.0	6.7 - 8.0
Baksefjorden	19	8.3, 7.4	9.3, 8.5	9.5, 8.7	7.6, 7.5	9.2, 8.6	11.6, 7.4	9.1, 4.8
Isortoq	20	nd	nd	7.7, 7.7	7.6, 8.3	nd	8.1, 8.7	7.4, 7.6
Finnish Lapland	21	7.6, nd	7.9, 8.0	9.0, 9.0	7.3, nd	9.1, 9.1	8.8, 9.6	8.5, 9.2
Doubtful Sound	22	11.2, 9.6	11.2, 12.7	13.0, 11.8	12.1	12.5, 12.7	16.1, 15.4	14.0, 12.6
Broken Hill	23	nd	nd	4.5, 4.0	nd	nd	3.0, 2.5	3.8, 3.0

\*: pressure quoted by reference for a particular locality otherwise pressure quoted by authors of calibration.

NP: Newton & Perkins (1982) Mg-opx + Pg = Gt + Qz barometer

BWB: Bohlen, Wall and Boettcher (1983a) Fe-opx + Pg = Gt + Qz barometer

PC: Perkins and Chipera (1985) Fe-opx and Mg-opx + Pg = Gt + Qz barometer

MAE: Moecher, Anovitz and Essene, this study. FS, HD, and DI barometers

Shown in Fig. 5a are pressures obtained from the FS barometer as calculated for the different models for  $a_{\text{Fe}_2\text{Si}_2\text{O}_6}^{\text{Opx}}$ . Using the Davidson and Lindsley (1985: DL) model one obtains slightly greater pressures than with the ideal model, with the greatest departures being at high pressures (low  $a_{\text{Fe}_2\text{Si}_2\text{O}_6}^{\text{Opx}}$ ). The pressure difference between the two models is well within a liberal estimate of precision for the FS barometer of  $\pm 1$  kbar. If the DL ferrosilite activities are adjusted for non-quadrilateral components in a manner similar to clinopyroxene activities, the pressure difference does not change or increases on the order of only 0.1 kbar, because of the lower amount of non-quadrilateral components in Opx relative to Cpx. For convenience we will compare the HD and DI barometers using ideal ferrosilite activities for the FS barometer.

Pressures obtained for the HD and DI barometers are plotted against pressures obtained for the FS barometer in Figs. 5c and 5d, using ideal activities for clinopyroxene and orthopyroxene. There is a significant difference between the two clinopyroxene barometers relative to the orthopyroxene barometer in terms of apparent relative pressure differences and apparent precision. Some 53 of the 68 pressures obtained for the HD barometer fall within 1 kbar of equal pressure, with an average pressure difference ( $P_{\text{FS}} - P_{\text{HD}}$ ) of  $-0.2 \pm 1.0$  kbar. For the DI barometer 28 of the 68 samples fall within 1 kbar of the values obtained from the orthopyroxene barometer, and the average pressure difference ( $P_{\text{FS}} - P_{\text{DI}}$ ) is  $0.6 \pm 1.6$  kbar. The same general distribution of pressures with slightly less scatter is observed if clinopyroxene component activities are calculated using the model of Davidson and Lindsley (1985), corrected for non-quadrilateral components (Figs. 5d and 5e).

We have also evaluated the HD and DI barometers by comparison with pressure constraints from reported aluminosilicate occurrences in high grade terranes (Table 4). For this purpose pyroxene activities were calculated using the ideal model. In general the HD barometer is consistent with aluminosilicate constraints when a reasonable temperature uncertainty is included, although pressures are

overestimated for some samples from Parry Sound, Ontario, Canada, the Sargur Belt, India and the Furua Complex, Tanzania. The DI barometer yields pressures consistent with aluminosilicates, but pressures are lower than both the FS and HD barometers.

To a first approximation, the HD and DI barometers yield reasonable estimates of pressure for most garnet two-pyroxene granulites, assuming the FS barometer is recording accurate pressures. Considering the possible sources of error in deriving the thermodynamic data, the agreement with FS pressures is satisfying. The HD barometer shows a slight tendency to overestimate pressure relative to the FS barometer for some samples, and the DI barometer shows an opposite trend. In testing the barometers it was generally observed that the greatest pressure discrepancies using the HD barometer were for pyroxenes with a high Mg number ( $100 \text{ Mg}/(\text{Mg}+\text{Fe}^{2+})$ ), e.g., Doubtful Sound, NZ, sample 36461. In general pyroxenes in the assemblage Gt-Cpx-Opx-Pg-Qz become more magnesian and aluminous with increasing pressure. Therefore, higher pressures are accompanied by greater extrapolations from the end member Fe system and the pressures will be less reliable. Aside from the general tendency for the DI barometer to underestimate pressure, the DI barometer overestimates pressure in Fe-rich systems such as high grade banded iron formation from the Wind River Range and samples of Fe-rich metabasites from the Adirondack Highlands and Minnesota River Valley. This accounts for the samples that fall 3 to 4 kbar above the line of equal pressure in Figs. 5c and 5e. Conversely, Mg-rich samples with Fe-poor Opx yield high FS pressures causing the largest excursions below the line of equal pressure (Fig 5c, 5e). The apparent disagreement between the DI and FS barometers is in part an artifact of the comparison scheme and is not seen when comparing the HD and FS barometers (Fig 5b, 5d), because in Mg-rich rocks both  $X_{\text{CaFeSi}_2\text{O}_6}^{\text{Cpx}}$  and  $X_{\text{FeSiO}_3}^{\text{Opx}}$  will be low, yielding high pressures for both HD and FS. Therefore the highest pressures in Figs. 5b and 5d are likely to be overestimates of pressure. The data are consistent with a pressure dependence for some compositions, and in application of these barometers one should be aware of the possible errors involved

in extrapolation of the HD barometer to Mg-rich systems, and the DI barometer to Fe-rich systems.

The observed pressure difference for the DI barometer relative to the FS barometer cannot be a result of the clinopyroxene barometers equilibrating at lower pressure relative to the FS barometer. If the agreement in pressure between the HD and FS barometers is real, it suggests that the DI barometer is yielding lower pressures as a result of errors in thermodynamic data and/or activity models. The difference ( $P_{FS} - P_{DI}$ ) is well within a reasonable error in  $\Delta G_{298}^{\circ}$  for any of the phases involved in the reaction, and we cannot identify any one phase as having an erroneous  $\Delta G_{298}^{\circ}$ . We believe the pressure discrepancy can be tied to ideal diopside activities. By assigning all the Mg to the M1 site, the ideal model for diopside (Eq. 18) may overestimate the activity of diopside, as some of the Mg is likely to partition into the M2 site (Cameron and Papike 1980, Dal Negro et al. 1983). This will tend to lower the  $X_{Mg}^{M1}$ , decreasing the  $a_{CaMgSi_2O_6}^{Cpx}$  and raising the pressure calculated from Reaction 2. For example, diopside activities calculated using the Wood and Banno (1973) approximation (in which Mg and Fe<sup>2+</sup> are equipartitioned between the M1 and M2 sites) raises pressures by 0.1 to 0.6 kbars, with the greatest pressure increase being for the most Mg-rich clinopyroxenes.

The temperature dependence of the HD and DI barometers has been evaluated by carrying through a  $\pm 50^{\circ}\text{C}$  temperature uncertainty in the calculation of  $\log_{10}K$  and pressure. For this temperature range the value of  $\log_{10}K$  changes by only 1 to 2%, but pressure varies by  $\pm 1.0$  and  $\pm 0.3$  kbar for the HD and DI barometers respectively. The former is a relatively high temperature dependence for a barometer and illustrates the need for reasonably precise temperatures ( $\pm 30^{\circ}\text{C}$ ) when applying the HD barometer. Compositional variations on the order of 1 mol% anorthite in plagioclase, hedenbergite and diopside in clinopyroxene, and almandine and pyrope in garnet correspond to pressure variations on the order of 0.1 kbar. A compositional variation of 1 mol% grossular has approximately twice the effect as

other components, as grossular activities are raised to a higher exponent in the expression for  $\log_{10}K$ .

#### Application of Barometers

Orthopyroxene barometry is the preferred technique for calculating pressure in Gt-Opx-Cpx-Pg-Qz granulites. The available FS geobarometers have a sound experimental and thermodynamic basis, and modeling of  $a-X$  relations for orthopyroxene is relatively straightforward. However, clinopyroxene barometry is required for rocks containing Gt-Cpx-Pg-Qz assemblages without orthopyroxene. To evaluate the utility of the clinopyroxene barometers we have applied them to Gt-Cpx-Pg-Qz assemblages in rocks from several high grade metamorphic terranes.

The Whitestone Anorthosite (WSA) is a 170 km<sup>2</sup> gabbroic anorthosite metamorphosed to granulite facies in the western Grenville Province of Ontario (Thompson 1983). Gt-Cpx-Pg-Qz assemblages occur within the main body of the anorthosite and within segments of the WSA intersected by the Parry Sound Shear Zone (PSSZ), a high grade ductile shear zone separating a predominantly amphibolite facies tectonic domain from one at granulite facies (Davidson 1984, 1986). Calculation of pressure (using ideal activities) for samples within the main body of the WSA average 9.8 (HD) and 9.5 (DI) kbar (at 750°C, Gt-Cpx thermometry), identical to regional metamorphic pressures deduced from a variety of geobarometers ( $10 \pm 1.0$  kbar, Anovitz 1987). In comparison, pressures from assemblages within the PSSZ average 10.8 (HD) and 11.4 kbar (DI) at 700°C (Gt-Cpx thermometry), or essentially the same as the regional data considering a 1 kbar pressure uncertainty. The pressures are consistent with the occurrence of kyanite in pelitic gneisses within the PSSZ ( $P > 7.8 \pm 1.0$  kbar at  $700 \pm 50^\circ\text{C}$ ), and indicate that ductile shearing occurred in a deep crustal setting.

Gt-Cpx-Pg-Qz-( $\pm\text{Wo}\pm\text{Cc}\pm\text{Scap}$ ) assemblages are also common in calc-silicate rocks from the western Grenville Province. The primary compositional difference between calc-silicate and mafic granulite assemblages is that garnet in the calc-silicates has higher  $X_{\text{Gt}}^{\text{Fe}}$ , and lower  $X_{\text{Fe}}^{\text{Mg}}$  and  $X_{\text{Mg}}^{\text{Fe}}$  than in mafic rocks.



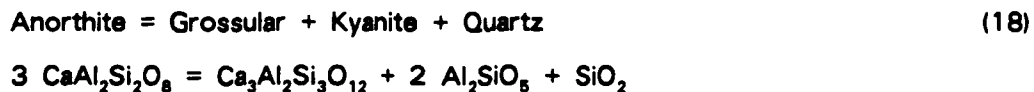
Clinopyroxene is typically a diopside-hedenbergite solid solution with minor Al, Fe<sup>3+</sup> and Na, and plagioclase shows the same range of composition as in samples of mafic granulite. Calc-silicate assemblages from the Parry Sound-Muskoka area of Ontario (Moecher, unpubl data) with high  $X_{Ca}^{Gt}$  (> 0.90) yield unrealistic pressures (13 to 15 kbar) using the HD barometer and low pressures using the DI barometer (5 - 6 kbar), with pressure varying widely with slight variations in  $X_{Fe^{2+}}^{Gt}$  and  $X_{Mg}^{Gt}$ . It is likely that the garnet activity model used here is not accurate at such extreme garnet compositions, and in garnet with large amounts of andradite component. However some calc-silicate samples with intermediate garnet compositions (e.g.,  $X_{Ca}^{Gt} = 0.35$  to 0.40,  $X_{Fe^{2+}}^{Gt} = 0.45$  to 0.55) yield pressures (8.9 (DI) to 11.9 kbar (HD)) that are consistent with regional pressure estimates (Anovitz and Essene 1987b). To avoid the subjective choice of which samples yield accurate pressure, calculations based on Reaction 10 would be more appropriate for high grade calc-silicate rocks.

Percival (1983) describes Gt-Cpx-Pg-Qz-(±Hbl±Ilm±Ti) assemblages in mafic gneisses from the Chapleau-Foley area of the Wawa Belt of western Ontario, which are regarded as a cross section of deep crust upthrust along the Kapuskasing Structural Zone (Percival and McGrath 1986). Sillimanite is the only aluminosilicate found and is reported in one sample from this terrane. Application of the DI barometer of Newton and Perkins (1982) yields pressures in the range 3.9 to 8.3 kbar, with an average of 6.3 kbar for peak temperatures of 800°C (Percival 1983). These values do not include the +1.6 kbar correction suggested by Newton and Perkins (1982), which would raise the average pressure to approximately 7.9 kbar. Gt-Opx-Pg-Qz barometry by Percival and McGrath (1986) yield pressures that average 9.4 kbar (at 800°C) using the FS barometers of Bohlen et al. (1983a) and Perkins and Chipera (1985). The FS barometry indicates that the DI barometer of Newton and Perkins (1982) underestimates pressure by 3.1 kbar for these samples. We have applied the present clinopyroxene barometers to 27 samples of Gt-Cpx-Pg-Qz metabasites from this terrane, obtaining pressures from the HD and DI barometers that average  $9.6 \pm 1.3$  kbars (HD, 1 $\sigma$ ) and  $8.9 \pm 1.4$  kbar (DI). Some of the pressure variation may be real variations in regional pressure. The pressures are

consistent with a maximum pressure of approximately 10 kbar imposed by the occurrence of sillimanite at 800°C, and are in excellent agreement with the orthopyroxene barometry.

Tella and Eade (1986) report Gt-Cpx-Pg-Qz assemblages in fragments of mafic gneisses entrained within the Tulemalu fault zone, a high grade ductile shear zone in the Northwest Territories, Canada. The samples are interpreted as deep crustal relics brought to the surface in granitic melts along the shear zone during ductile displacements. At temperatures of  $750 \pm 50^\circ\text{C}$ , the DI barometer of Newton and Perkins (1982) yielded pressures that average 10.9 kbar (unadjusted for the 1.6 kbar pressure correction). The clinopyroxene barometers of this study yield 12.9 (HD) and 11.7 (DI) kbar. It is difficult to evaluate the accuracy of these values without other petrologic constraints on pressure.

Ghent et al. (1983) have mapped a prograde Gt-Cpx isograd in sillimanite zone metabasites (Hbl-Pg-Ilm±Qz±Gt±Cpx±Cc±Ti) from Mica Creek, British Columbia. The Gt-Cpx isograd nearly coincides with a kyanite-sillimanite isograd, placing excellent constraints on maximum pressure of  $7.8 \pm 1$  kbar at an upper temperature limit of  $700^\circ\text{C}$  (based on Gt-Cpx thermometry). The DI barometer of Newton and Perkins (with correction) yields pressures of  $7.2 \pm 0.3$  kbar at  $650^\circ\text{C}$  (Ghent et al. 1983, 8 samples). In lower grade rocks containing kyanite, Ghent et al. (1979) and Newton and Haselton (1981) quote pressures of 6.6 to 8.9 kbar at approximately  $575 \pm 50^\circ\text{C}$  using the reaction



(Ghent 1976). The clinopyroxene barometers of the present study yield apparently high values of  $9.8 \pm 0.9$  (HD) and  $10.5 \pm 0.6$  (DI) kbar at  $650^\circ\text{C}$ . The reason for this discrepancy is not immediately apparent. Ghent et al. (1983) see no structural evidence for an increase in pressure for the higher grade rocks near the sillimanite isograd, relative to lower grade rocks below the Ky=Sill isograd and that yield

pressures approaching those calculated for the mafic gneisses. It appears for these rocks that the clinopyroxene barometers overestimate pressure by about 1 kbar, although the upper limit of pressure obtained from Reaction 18 overlaps the lower limit of pressure for the clinopyroxene barometers assuming an error estimate of about 1 kbar.

Sanders et al. (1987) describe high pressure granulite facies gneisses from the Northeast Ox Inlier of northwestern Ireland. Gt-Cpx-Pg-Qz-Ilm-Ru metabasites interpreted as decompressed eclogites occur with metapelites, metapsammites, and ultramafites. Sieve-texture intergrowths of clinopyroxene and plagioclase are interpreted to be a result of exsolution of an original omphacitic clinopyroxene. As with the Doubtful Sound, NZ samples, the presently preserved clinopyroxenes are magnesian ( $X_{\text{Di}}^{\text{Cpx}} = 0.03$  to 0.10) and relatively high in  $\text{Al}_2\text{O}_3$  (up to 8 wt %  $\text{Al}_2\text{O}_3$ ). Peak temperatures are estimated at 850 - 900°C, based on Gt-Cpx thermometry and the presence of mesoperthite, and the occurrence of kyanite in pelites (Gt-Ky-Pg-Kfs-Qz-Ru) places a minimum constraint on pressure of 10.8 to 11.8 kbar at 850 - 900°C. Pressure estimates for the metabasites from Gt-Cpx core compositions range from 19 (HD) to 15 (DI) kbar, and 16 (HD) to 13 (DI) kbar for rim compositions. In view of the tendency of HD barometer to overestimate pressure for Mg-rich clinopyroxenes, the HD values are likely to be upper limits on pressure. However, pressures calculated from Reaction 18 for the Gt-Ky-Pg-Qz assemblage reported by Sanders et al. (1987), using the calibration of Newton and Haselton (1981) and Essene (1988), are also in excess of 15 kbars (at 800°C), in agreement with the DI barometer. Pressures calculated from Gt-Pg-Ilm-Ru-Qz assemblages in the metabasite (Reaction 8: Anovitz and Essene 1987a) yield minimum pressure estimates of 12 to 13 kbar (assuming  $a_{\text{Fe}^{2+}\text{TlO}_3}^{\text{Ilm}} = 1$ ). If equilibrium can be demonstrated for the sieve texture clinopyroxenes then the pressures indicated by the geobarometry are consistent as a whole with the extremely deep crustal history for these samples suggested by Sanders et al. (1987).

Wood (1975) presents analyses for coexisting garnet, clinopyroxene inclusions within garnet, and plagioclase from metagabbros from the South Harris, Scotland, Igneous Complex. The presence of kyanite in metapelites associated with the meta-igneous lithologies places a lower limit on pressure of 9 kbar. Pressures were estimated to range from 10 to 13 kbar at 800 to 860°C (two-pyroxene and Gt-Cpx thermometry), based on constraints from Gt-Ol-Pg and Gt-Opx-Pg-Qz barometry. We have recalculated the Gt-Cpx temperatures to be 750°C using the Ellis and Green (1979) thermometer, and these are likely to be lower limits on temperature as garnet and clinopyroxene in contact with one another tend to re-equilibrate with falling temperature after the peak of metamorphism (Johnson et al. 1983, Moecher et al. 1986). Pressures for three samples average 12.3 (HD) and 10.6 (DI) kbar. One sample with  $X_{\text{Di}}^{\text{Cpx}} = 0.07$  yields the highest pressure, and as with the samples from Doubtful Sound, NZ and the Northeast Ox Inlier, Ireland, this is likely to yield an overestimate of pressure. Excluding this sample the average HD pressure is 11.3 kbar. Metamorphic pressure for the South Harris area is likely to be  $11 \pm 1$  kbar, essentially that predicted by Wood's earlier analysis.

Evaluation of the HD and DI barometers in previous sections indicated that the DI barometer tended to yield somewhat lower and more scattered pressures than the HD and FS barometers. The results from the six areas above indicate that the two clinopyroxene barometers are in better agreement with one another. This is not inconsistent with the former observation, as some of the garnet two-pyroxene granulites yield similar pressures for all three barometers. From the foregoing applications it is apparent that the clinopyroxene barometers of this study can yield reasonable pressures for most Gt-Cpx-Pg-Qz assemblages. In the absence of assemblages for which experimentally determined geobarometers are available, the HD and DI barometers can be applied with reasonable precision in the granulite facies. However, the thermodynamic, temperature, and compositional dependencies of these barometers, and the inherently less precise nature of empirical calibrations must be kept in mind when applying the barometers in natural settings. More accurate calibrations of these barometers will require careful experiments on

Reactions 1 and 2, or on the reactions that constrain the  $\Delta G_{.298}^{\circ}$  of hedenbergite and pyrope.

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## CHAPTER III

### SCAPOLITE PHASE EQUILIBRIA I: QUANTITATIVE PHASE RELATIONS IN THE SYSTEM $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CO}_2-\text{H}_2\text{O}$ (CASCH)

#### Introduction

Scapolite solid solutions involving marialite ( $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$ ), meionite ( $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$ ), and sulfate meionite ( $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$ ) are potential sensors of fluid composition in a wide variety of geologic environments. Provided that thermodynamic and thermobarometric data were available, one may calculate or limit the activities of NaCl,  $\text{CO}_2$ , and/or  $\text{SO}_2$  in scapolite-bearing calc-pelites (Hietanen, 1967; Frank, 1983; Tuisku, 1985; Mora & Valley, 1988), hydrothermally metamorphosed metabasites (Vanko & Bishop, 1982), calc-silicate skarns, gneisses, and marbles (Shaw *et al.*, 1963a, 1963b; Misch, 1964; Trommsdorff, 1966; Kerrick *et al.*, 1973; Rollinson, 1980; Oterdoom & Wenk, 1983; Shenk, 1984; Perchuk *et al.*, 1985; Warren *et al.*, 1987), amphibolites (Kwak, 1977; Oliver & Wall, 1987), and mafic granulites and deep crustal xenoliths (von Knorring & Kennedy, 1958; Lovering & White, 1964; Wilkinson, 1974; Devaraju & Gowd Reddy, 1976; Edwards *et al.*, 1979; Okrusch *et al.*, 1979; Coolen, 1980; Boivin & Camus, 1981; Devaraju & Coolen, 1983; Jones *et al.*, 1983; Austreim & Griffen, 1985; Srikantappa *et al.*, 1985; Thomas & Nixon, 1987; Stolz, 1987). This would provide a powerful tool in evaluating the presence and activity (fugacity) of some fluid species other than  $\text{H}_2\text{O}$  in metamorphic rocks.

The experiments of Ellis (1978) and Vanko & Bishop (1980) on sodic scapolite suggest that Na- and Cl-rich scapolites are indicative of highly saline metamorphic fluids. The high P-T stability of CO<sub>2</sub> and SO<sub>4</sub>-rich calcic scapolites led Goldsmith (1976) to propose that scapolite would be a significant phase in lower crustal lithologies, being stabilized relative to plagioclase in the presence of CO<sub>2</sub> and SO<sub>2</sub>. However, these hypotheses have yet to be quantitatively tested in natural systems by phase equilibrium calculations. As a result of calorimetric measurements on the scapolite solid solution series (Komada *et al.*, 1988) some of these calculations are now more feasible. Using the relevant experimental data on meionite and other phases as constraints, we have generated quantitative P-T and T-X equilibria for scapolite (meionite) phase relations in the system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O (CASCH). Work in the Grenville Province of southwestern Ontario (Chapter IV) and a survey of the literature reveal that scapolite often occurs in calc-silicate assemblages with quartz, calcite, wollastonite, clinopyroxene, plagioclase, garnet, and/or clinozoisite, and in metabasites and meta-anorthosite with garnet, plagioclase, quartz, amphibole, clinopyroxene, and orthopyroxene. Reactions involving quartz, calcite, wollastonite, anorthite, grossular, clinozoisite, meionite, and to a lesser extent corundum and gehlenite, were chosen as the most practical in evaluating fluid composition in natural systems. For these phase relations to be of practical significance, activity-composition (a-X) relations for the meionite component in scapolite were calculated based on natural scapolite-plagioclase-calcite assemblages. In a later publication we will discuss the application of these phase equilibrium and a-X relations to the calculation of CO<sub>2</sub> activities in high grade scapolite-bearing lithologies from a number of localities and in different geologic settings.

#### Re-examination of Al-Si and Anion Ordering in Scapolite

Application of new entropy data for the scapolite solid solution series (Komada *et al.* 1988) in phase equilibrium calculations on natural systems is limited by accurate estimates of the configurational entropy (S<sub>g</sub>) of end-member meionite.

Contributions from Al-Si disorder and CO<sub>3</sub> and SO<sub>4</sub>-group disorder potentially comprise up to 12% of the total molar entropy of meionite at 298 K. Uncertainties of this magnitude in molar entropy may have serious consequences for calculation of reliable phase equilibria in this system. Therefore, a re-examination of available data that constrain S<sub>0</sub> is warranted.

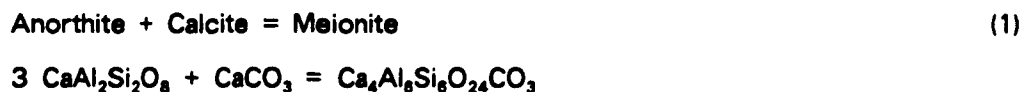
#### Crystal Chemical and Experimental Constraints

The scapolite crystal structure is comprised of two types of four-membered Si-Al tetrahedral rings oriented perpendicular to the c axis: two T<sub>2</sub>-T<sub>3</sub> rings and one T<sub>1</sub> ring per formula unit (Z = 2) which links every second and third T<sub>2</sub>-T<sub>3</sub> ring along c (Papike & Zoltai, 1965; Papike & Stephenson, 1966; Lin & Burley, 1972, 1973a, 1973b, 1973c, 1975; Ulbrich, 1973a; Levien & Papike, 1976; Peterson *et al.*, 1979; Aitken *et al.*, 1984). This linking of the tetrahedra in T<sub>2</sub>-T<sub>3</sub> rings by T<sub>1</sub> tetrahedra results in five-membered tetrahedral rings oriented parallel to C and perpendicular to a. The Cl, CO<sub>3</sub> and SO<sub>4</sub> anions are centered immediately between successive T<sub>1</sub> rings, in cages formed by the Al-Si tetrahedra.

Single crystal X-ray diffraction studies of calcic scapolites have shown that the CO<sub>3</sub> and SO<sub>4</sub> groups are disordered over at least four and two orientations in the anion site, respectively (Papike & Stephenson, 1966; Peterson *et al.*, 1979). This would contribute 11.5 (Rln4) and 5.8 (Rln2) J/mol K to S<sub>0</sub> for meionite and sulfate meionite. More recently Aitken *et al.* (1984) have refined a calcic, carbonate scapolite (Me<sub>84</sub>: %Me = 100Ca/(Ca+Na+K)) with the carbonate group disordered over eight orientations in the anion site. This would contribute 17.3 (Rln8) J/molK to S<sub>0</sub>. The positional disorder of anions within the scapolite structure is required by symmetry constraints on the trigonal carbonate and tetragonal sulfate radical. We have assumed a model of long range disorder over eight and two positions respectively for the CO<sub>3</sub> and SO<sub>4</sub> groups in the meionite structure, consistent with the most recent single crystal refinements.



Oterdoom & Wenk (1983) summarized the available single-crystal XRD, TEM, and experimental data relative to Al-Si ordering, and concluded that ordering in scapolites is a function of composition, with  $Me_{33-37}$  ( $EqAn = 100[(Al-3)/3] = 33$ ) being the only composition for which complete long range Al-Si order is possible. The Al and Si are interpreted to be disordered over the  $T_2$  and  $T_3$  sites in marialite. With increasing substitution of the meionite component into marialite, Al partitions into the  $T_2$  site until, at a composition of approximately  $Me_{33}$ , Al and Si alternate in an ordered arrangement in the  $T_2(Al)-T_3(Si)$  ring. From  $Me_{37}$  to  $Me_{90\pm 2}$  (the most calcic scapolite studied) Al enters the  $T_1$  ring. Between  $Me_{37}$  to  $Me_{90}$  the presence of five-membered tetrahedral rings makes it impossible to maintain an ordered Al-Si distribution without forming Al-O-Al bonds. Such bonds are generally unstable in silicate structures (Lowenstein, 1954) and have been shown to control Al-Si ordering in plagioclase (Ribbe, 1983) and cordierite (Gibbs, 1966; Putnis & Bish, 1983). The increase in meionite content is also accompanied by a change in the refined space group from  $P4_2/n$  for  $Me_{37}$  to  $I4/m$  for samples of  $Me_{90-90}$ . This has been interpreted to reflect a change in the degree of Al-Si disorder and/or the extent of  $Cl-CO_3$  substitution in the anion site. As the end members are approached the degree of Al-Si disorder increases until, presumably, complete disorder is attained for end-member meionite. This would result in maximum separation of Al-O-Al bonds throughout the structure. However, Oterdoom and Wenk concluded that natural scapolites are as ordered as is possible up to 1000°C, the onset of Al-Si disorder proposed by Levien & Papike (1976) in a single crystal study of scapolite ( $Me_{37}$ ) at elevated temperature, and that the available single crystal data are not inconsistent with a short range ordered domain structure. Oterdoom and Wenk (1983) further concluded that synthetic meionite is metastably and completely disordered in terms of Al-Si, and that the reaction



has a positive slope in the range 850 to 875°C and 1 to 18 kbar. A positive slope for Reaction 1 necessitates a very high (nearly vertical)  $dP/dT$  in order to fit the experimental reversals of Goldsmith & Newton (Fig. 1). This in turn requires  $S_0^\circ$  to be that for completely disordered meionite, or 80.8 J/mol·K, corresponding to complete Al-Si disorder over twelve sites and carbonate group disorder over four sites (Goldsmith & Newton, 1977; Oterdoom & Wenk, 1983, pg. 339).

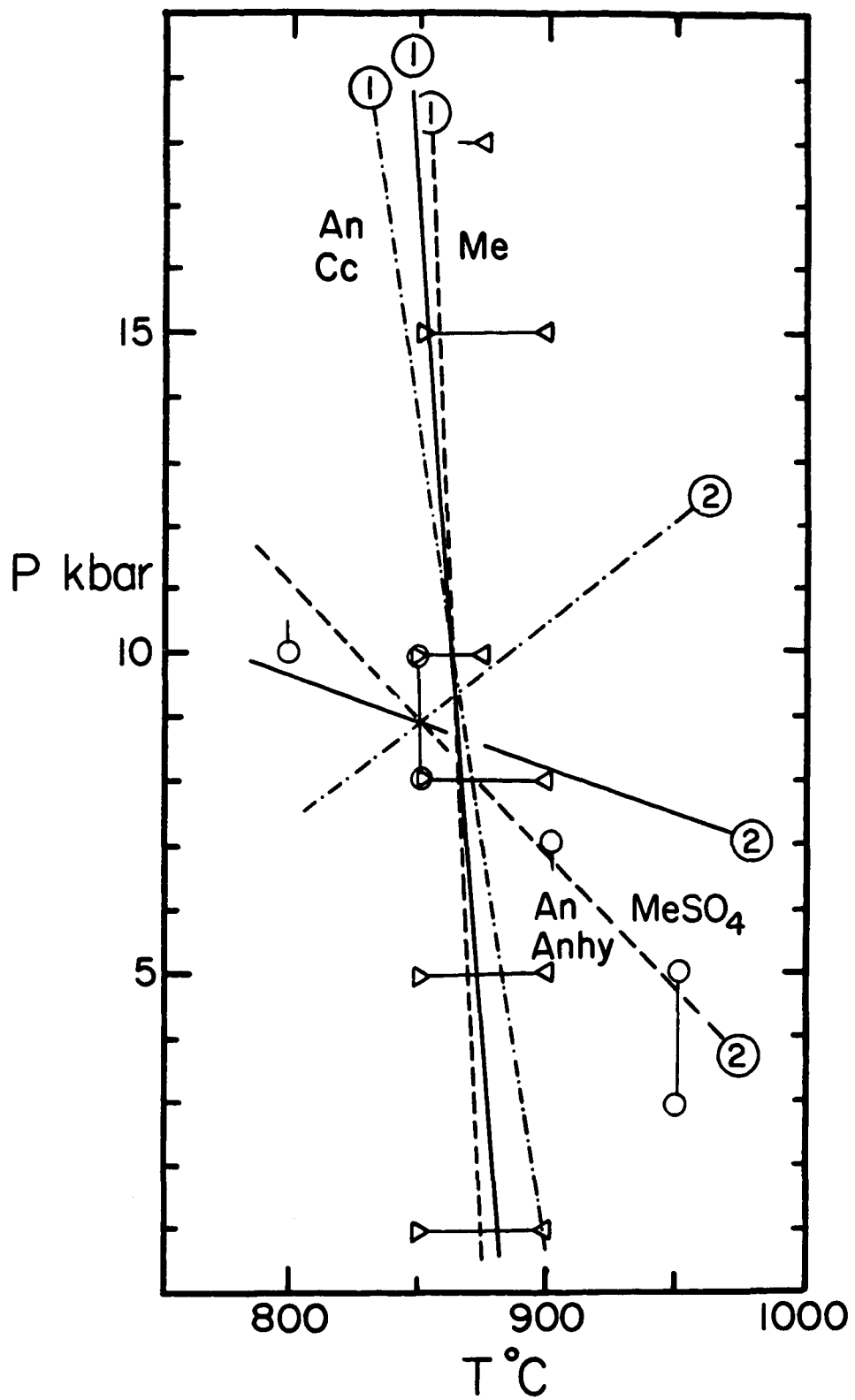
Oterdoom & Wenk's conclusion of complete disorder in synthetic end-member meionite rests in part on the assumption of a positive slope for Reaction 1. Their analysis is based on the expansivity of a scapolite of composition  $Me_{37}$  (Levien & Papike, 1976). However, the expansivity data of Grazziani & Lucchessi (1982) for sodic scapolites yield a much higher  $dV/dT$  than calcic scapolites. If  $\Delta V_0^\circ$  for Reaction 1 were calculated using the  $dV/dT$  of a sodic scapolite one would indeed obtain a positive slope. Use of the measured expansivity for a scapolite of composition  $Me_{88}$  (Grazziani & Lucchessi, 1982) in the calculation of Reaction 1 yields a negative slope for all values of  $S_0^\circ$  (meionite) over the temperature interval 850–875°C. The experimental reversals for Reaction 1 suggest a negative slope is entirely consistent with the experimental data (Fig. 1). In reality the reversals do not constrain the ordering state of meionite; the reaction can be made to fit the experimental reversals assuming a wide range of Al-Si disorder.

Experimental reversals for the reaction



provide additional constraints on the configurational entropy of end member meionite, as sulfate-meionite was synthesized under conditions similar to those for meionite (Fig. 1: Goldsmith & Newton, 1977). The  $S_{298}^\circ - S_0^\circ$  estimated for sulfate meionite (Komada *et al.*, 1988) is 703.7 J/mol·K, and  $S_{298}^\circ$  is 778.6 J/mol·K for completely disordered sulfate-meionite (Al-Si and  $\text{SO}_4$  group disorder over twelve and two sites, respectively). It was assumed that the heat-capacity function for

**Figure 1.** Experimental reversals and calculated position of Reactions 1 (  $\triangleleft$  ) and 2 (  $\circ$  ) (Goldsmith & Newton, 1977) assuming complete Al-Si order (dashed-dot lines), complete disorder (dashed lines), and intermediate ordering state ( $-6R \ln 2$  for Al-Si, solid lines). The slope of Reaction 2 changes from positive to negative with increasing degrees of Al-Si disorder. A range of Al-Si disorder is allowed by the reversals for Reaction 1 ( $3 \text{ An} + \text{Cc} = \text{Me}$ ), but a high degree of disorder is required for Reaction 2 ( $3 \text{ An} + \text{Anhy} = \text{Me-SO}_4$ ).



meionite adequately describes that of sulfate meionite. The reversals require a high degree of Al-Si and  $\text{SO}_4$  disorder to adequately fit the reversals (Goldsmith & Newton, 1977) (Fig. 1), but not necessarily complete Al-Si disorder. If this analysis were performed assuming  $\Delta S_{298}^{\circ} = \Delta S_{\text{T}}^{\circ}$  for Reaction 2, one would reach the erroneous conclusion that a wider range of intermediate ordering states would be possible, with completely ordered and completely disordered sulfate meionite being prohibited by the reversals for Reaction 2.

#### MASNMR Constraints

Recent MASNMR (magic angle spinning nuclear magnetic resonance) spectroscopic methods are an additional means of evaluating the Al-Si ordering state of scapolite (Sheriff *et al.*, 1987; see Klinowski *et al.*, 1981; Putnis & Angel, 1985; Yang *et al.*, 1986; and references therein for MASNMR theory and application). Sheriff *et al.* (1987) analyzed an extensive set of  $^{29}\text{Si}$  MASNMR spectra for natural scapolites, including the samples used by Komada *et al.* (1988) in their heat capacity measurements. Systematic changes are evident in the spectra of the scapolite solid solution series as a function of composition. Sheriff *et al.* (1987) interpreted the spectra in terms of a model based on predictions of tetrahedral occupancies from the single crystal XRD data base, electrostatic energy considerations that are consistent with cation-anion ordering in  $\text{Me}_{33}$  (Chamberlain *et al.*, 1985), and  $^{29}\text{Si}$  peak assignments based on previous empirical studies (Janes & Oldfield, 1985). The latter assumptions preclude a unique solution for the ordering state of scapolites. The spectra and models of Sheriff *et al.* (1987) are in good agreement with the prediction of Al-Si order in samples of  $\text{Me}_{33}$  for which the predicted and observed tetrahedral structural formula are  $[\text{Si}_4]_{\text{T}^1}[\text{Al}_4]_{\text{T}^2}[\text{Si}_4]_{\text{T}^3}$ . For  $\text{Me}_{70}$  the model predicts  $[\text{Si}_{3.2}\text{Al}_{0.8}]_{\text{T}^1}[\text{Al}_4]_{\text{T}^2}[\text{Si}_{4.0}]_{\text{T}^3}$ , while the observed site occupancies from the deconvoluted NMR spectra are  $[\text{Si}_{3.2}\text{Al}_{0.8}]_{\text{T}^1}[\text{Al}_4]_{\text{T}^2}[\text{Si}_{3.8}\text{Al}_{0.2}]_{\text{T}^3}$ , in good agreement considering the imprecision in measuring peak intensities of complex spectra consisting of several overlapping peaks (Sheriff *et al.*, 1987, Fig.

10). However, there are significant differences between the predicted and observed site occupancies for more calcic scapolites. For example, the model of Sheriff *et al.* predicts occupancies for a sample of  $Me_{91}$  to be  $[Si_{0.8}Al_{3.2}]^{T_1}[Si_{0.3}Al_{3.7}]^{T_2}[Si_{3.8}Al_{0.2}]^{T_3}$ , while the observed NMR occupancies are  $[Si_{0.8}Al_{3.2}]^{T_1}[Si_{1.5}Al_{2.5}]^{T_2}[Si_{4.0}]^{T_3}$ . Aside from the observation that the two occupancies are rather different, both indicate that the  $T_1$  tetrahedral ring contains excess Al and the  $T_2$ - $T_3$  ring is Al deficient, relative to the commonly assumed distribution where  $T_2$ - $T_3$  cannot have more than four Si and four Al. Tetrahedral site occupancies for  $Me_{93}$ , calculated from mean T-O bond distances, are consistent with equal amounts (approximately 50%) of Al and Si in the  $T_2$ - $T_3$  ring, and 21 to 34% Al in the  $T_1$  ring (Lin & Burley, 1973a; Ulbrich, 1973a). It is likely that the peak assignments are not valid for the more calcic scapolites. Sheriff *et al.* (1988, in press) report revised values of peak positions for a large number of silicates, and this may eventually change the interpretation of the spectra for more calcic scapolites (Sheriff pers. comm., 1988).

For intermediate scapolite ( $Me_{33}$  to  $Me_{78}$ ) it appears that Al and Si are ordered in the tetrahedral framework, but more work is needed on the most calcic samples in order to constrain Al-Si disorder. Disorder that is not resolvable by MASNMR methods may still be present in calcic scapolite and MASNMR methods may not be sufficiently precise at present to calculate the amount of Al-Si disorder and configurational entropy in silicates, even for minerals less complex than scapolite (e.g., low and high albite, W.-H. Yang, 1987, writ. comm.). Small degrees of Al-Si disorder can contribute significant amounts of configurational entropy because of the rapid increase of  $S_0^\ddagger$  at small degrees of disorder. In addition, the ordering state of scapolite at the elevated temperatures where natural scapolites form still needs to be evaluated, by collecting MASNMR spectra on quenched samples heated to approximately 600-900°C. The presence of domains imaged by TEM methods in natural scapolites ranging in composition from  $Me_{33}$  to  $Me_{78}$  (Phakey & Ghose, 1972; Oterdoom & Wenk, 1983; Hassan & Buseck, 1988) is consistent with the development of ordering upon cooling, and scapolites may

possess either cation or anion disorder at metamorphic temperatures. In addition, any Al-Si disorder indicated by NMR may be a result of disorder at domain boundaries in a short range-ordered structure (depending on the size of domains).

Based on the preceding discussion, natural scapolite solid solutions, particularly the intermediate compositions, appear to be ordered at room temperature. Hassan & Buseck (1988) reached a similar conclusion based on HRTEM analysis of two intermediate natural scapolites. They deduced coupled ordering of Na-Ca with Si-Al and Cl-CO<sub>3</sub>, producing compositional domains of marialite and meionite-rich components. This information places important constraints on ordering in scapolite solid solutions, however it will not have a similar bearing on end member meionite, nor does it provide information on the ordering state of scapolite at high temperature. The exact ordering state of *synthetic* scapolite remains unresolved, although the experiments are consistent with intermediate to high degrees of Al-Si disorder (Goldsmith & Newton, 1977, p.1076). Until MASNMR spectra on synthetic end-members are collected and tighter experimental reversals for Reactions 1 and 2 are obtained, one can only assume a particular ordering state consistent with the experiments and X-ray diffraction data on synthetic samples. We have assumed a model of partial Al-Si disorder (6Rln2 or one-half of total Al-Si disorder) for synthetic meionite as this is consistent with the experimental reversals for Reactions 1 and 2, and with the refined space group I4/m of synthetic scapolite (Me<sub>85</sub>: I4/M, Aitken *et al.* 1984). The implication of this assumption and the effect of varying degrees of Al-Si disorder on scapolite phase equilibrium relations will be discussed in following sections.

#### Thermodynamic and Experimental Data Base

Low temperature (10-350 K) adiabatic calorimetry and high temperature (300 - 1000 K) DSC data for five natural scapolites ranging in composition from Me<sub>28</sub> to Me<sub>88</sub> are presented in Komada *et al.* (1988). These data were used to calculate

the lattice contribution to  $S_{298}^{\circ}$  ( $S_{298}^{\circ} - S_0^{\circ}$ ) for four scapolite end members: marialite ( $\text{Na}_4\text{Al}_3\text{Si}_5\text{O}_{24}\text{Cl}$ ), an intermediate composition commonly referred to as mizzonite ( $\text{Ca}_3\text{NaAl}_5\text{Si}_7\text{O}_{24}\text{CO}_3$ ), meionite, and sulfate-meionite ( $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$ ). The reader is referred to Komada *et al.* (1987) for a summary of the calorimetric data and the methods used to correct data on natural samples to the end-members. A value for  $S_{298}^{\circ} - S_0^{\circ}$  of 697.9 J/mol·K was calculated for end-member meionite. Including  $6R\ln 2$  for Al-Si and  $R\ln 8$  for  $\text{CO}_3$  disorder,  $S_{298}^{\circ}$  for meionite is 749.8 J/mol·K. High temperature DSC data for  $\text{Me}_{88}$  from Komada *et al.*, adjusted to end-member meionite, were fit with a Meier-Kelley polynomial expansion yielding the coefficients in Table 2. Extrapolation of entropy above 1000 K was calculated from the method of Robinson & Haas (1982).

Because of the relatively steep slope of Reaction 1 in P-T space (due to a small  $\Delta V_r$ ), small variations in the volume of the anorthite and meionite will affect the interpretation of the experimental data. The value of  $V_{298}^{\circ}$  for end-member meionite was obtained from a linear regression of molar volume versus percent Me for natural scapolite (Ulbrich, 1973). The value of  $V_{298}^{\circ}$  calculated from this relation ( $340.36 \text{ cm}^3$ ) is nearly identical to that measured by Goldsmith & Newton (1977) for synthetic end-member meionite ( $340.39 \text{ cm}^3$ ). Thermal expansion for meionite (Table 2) was calculated from expansivity data on a sample of Monte Somma meionite (Grazziani & Lucchessi, 1982). The compressibility of meionite (Table 2) is that measured for a sample of Monte Somma meionite by the diamond anvil technique in the pressure range 1 bar to 30 kbar (Hazen & Sharp, 1988).

Values of  $V_{298}^{\circ}$  and  $V_r^{\circ}$  for anorthite are taken from Robie *et al.* (1978) and Skinner (1966), and the compressibility of anorthite was taken from Liebermann & Ringwood (1976) and Angel *et al.* (1988). The compressibility of anorthite should be used in calculations, rather than that of labradorite (Birch, 1966), as only slight variations in the volume of anorthite will change the calculated slope of Reaction 1 and affect the interpretation of the degree of Al-Si disorder in synthetic meionite.



TABLE 1. Entropy and Gibbs free energies (relative to elements) for phases used in thermodynamic calculations.

PHASE	$S_{298}^0$ J/mol K	ref.	A	B	C	D	ref.	$\Delta G_{298}^0$ kJ/mol	ref.
Quartz ( $\alpha$ )	41.5	1	55.414	18.863	7.141	-329.4	2	-856.3	1
Quartz ( $\beta$ )	47.3	2	65.616	6.074	14.665	-391.9	4,2	-854.4	2
Corundum	50.9	3	116.336	11.983	19.514	-688.3	3	-1582.2	3
Calcite	91.8	3	88.884	45.256	9.492	-530.6	3	-1131.2	3
Anhydrite	106.7	1	72.170	97.206	0.846	441.1	1	-1321.7	1
Wollastonite	81.7	3	102.238	28.446	13.444	-605.9	3	-1549.2	3
Kyanite	82.4	4	177.002	24.849	29.564	-1049.1	4	-2445.8	2
Ca-Tschemarkite	141.1	3	232.052	24.860	35.780	-1369.5	3	-3127.1	2
Anorthite	199.3	3	278.255	47.694	38.295	-1642.6	3	-4010.9	2
Gehlenite	210.0	5	274.530	28.577	38.343	-1615.5	3	-3782.1	2
Zoisite	295.4	3	398.825	171.962	44.865	-2374.1	3	-6509.1	2
Clinzoisite	297.1	2	398.825	171.962	44.865	-2374.1	3	-6506.5	2
Grossular	256.3	3	463.212	463.212	70.651	-2731.3	3	-6282.3	7
Meionite(ord)	709.3	2	959.108	158.200	144.418	-5673.2	6		2
Meionite(int)	749.8	2	959.108	158.200	144.418	-5673.2	6	-13115.4	2
Meionite(dis)	778.3	2	959.108	158.200	144.418	-5673.2	6		2
SO <sub>4</sub> meionite	778.2	2	959.108	158.200	144.418	-5673.2	6	-13108.8	2
$S_{298}^0 + \text{AlInT} + \text{B}10^{-3}\text{T} + \text{C}10^5/\text{T}^2 + \text{D}$									

1: Robie et al. 1978; 2: this study; 3: Robinson et al. 1982; 4: Robie & Hemingway 1984  
 5: Hemingway & Robie 1984; 6: Komada et al. 1988; 7: Anovitz and Essene 1987

TABLE 2. Molar volume, compressibility, and expansivity for phases used in thermodynamic calculations

PHASE	$V_{298}^0$ $\text{cm}^3$	ref.	a	b	ref.	cE-02	dE-03	eE-07	fE-10	ref.
			mbar <sup>-1</sup>	mbar <sup>-2</sup>						
Quartz ( $\alpha$ )	22.69	1	2.76	24.00	11	11.414	4.877	-25.192	9.984	17
Quartz ( $\beta$ )	23.79	2	1.78	0.00	11	1.392	-0.452	-1.352	0.617	17
Corundum	25.57	3	0.38	0.00	11	-7.526	2.034	-8.758	-3.150	17
Calcite	36.92	3	1.37	3.90	11	-3.912	1.244	19.108	0.000	18
Anhydrite	45.94	1	1.84	0.00	11	-11.657	4.690	-11.271	14.033	19
Wollastonite	39.79	3	1.47	9.82	3	11.177	5.009	-41.664	15.535	3
Kyanite	64.21	4	0.79	5.00	12	5.427	2.144	8.100	-3.296	20
Ca-Tschermakite	63.58	3	0.78	1.38	3	-5.531	2.162	7.709	-2.334	3
Anorthite	100.79	1	1.11	2.48	13,14	-5.030	2.055	-17.795	12.376	17
Gehlenite	90.25	3	0.46	1.01	3	-6.947	2.753	0.043	0.020	3
Zoisite	135.80	5,6	1.13	0.00	3	-6.248	4.117	-7.597	3.295	3
Clinozoisite	136.45	7,8	1.13	0.00	3	-6.248	4.117	-7.597	3.295	3
Grossular	125.30	3	0.74	4.47	15	-4.359	1.721	9.114	-1.866	17
Meionite	340.36	9	1.14	2.07	16	-3.720	1.529	-16.389	9.631	21
SO <sub>4</sub> meionite	340.39	10	1.14	2.07	2	-3.720	1.529	-16.389	9.631	2

$$V_{298}^0 = V_{298}^0[\text{aP} - \text{bP}^2], \text{ P in mbars}$$

$$V_{\text{P}}^0 = V_{298}^0 + V_{298}^0/100[\text{c} + \text{dP} + \text{eP}^2 + \text{fP}^3], \text{ P in } ^\circ\text{C}$$

1:Robie et al. 1978; 2:this study; 3:Robinson et al. 1982; 4:Robie & Hemingway 1984;

5:Perkins et al. 1980; 6:Dollase 1968; 7:Seki 1959; 8:Myer 1966; 9:Ulbrich 1973b;

10:Goldsmith & Newton 1977; 11: Birch 1966; 12: Bass & Weidner 1984; 13: Liebermann & Ringwood 1975;

14: Angell et al. 1988; 15: Hazen & Finger 1978; 16: Hazen & Sharp 1988; 17: Skinner 1966;

18: Markgraf & Reeder 1985; 19: Evans 1979; 20: Winter & Ghose; 21: Grazziani & Lucchessi 1983

The expansivity of anorthite is from Skinner (1966). The sources of the remaining thermodynamic data are listed in Tables 1 and 2.

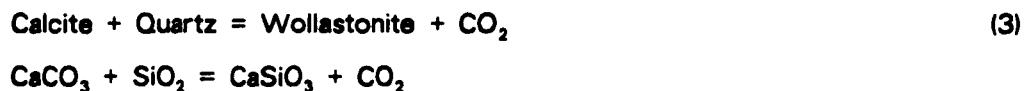
Thermodynamic calculations were performed with a computer program (EQUILI, Wall & Essene unpubl.) that solves the relation

$$\Delta G_{T_2}^{P_2} - \Delta G_{T_1}^{P_1} = \int_{P_1}^{P_2} \Delta V_s dP - \int_{T_1}^{T_2} \Delta S_s dT + \Delta G_f(P_2, T_2, X_{H_2O}, X_{CO_2}) - \Delta G_f(P_1, T_1, X_{H_2O}, X_{CO_2})$$

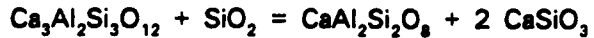
using available standard volume, entropy, expansivity, compressibility and free energy data. Equilibria are adjusted to fit experimental reversals in order to obtain internally consistent values for free energy ( $\Delta G_{298}^{\circ}$ , Table 1). Additional equilibria can then be calculated at any P and T using 1 bar, 298 K as a starting point. Mixed volatile equilibria were calculated using the modified MRK equation of state for H<sub>2</sub>O-CO<sub>2</sub> mixtures of Kerrick & Jacobs (1981).

The  $\alpha$ - $\beta$  quartz transition is involved in the location of reactions 3, 4, 5, and 6. Entropy and expansivity data for  $\beta$ -quartz from Hemingway (1987) and Skinner (1966) are valid only above the  $\alpha$ - $\beta$  quartz transition, but were empirically extrapolated to 298 K and 1 bar to yield fictive values of  $S_{298}^{\circ}$  and  $V_{298}^{\circ}$  for the purposes of calculation. Using the compressibility for  $\beta$ -quartz in Birch (1966), the  $V_T^{\circ}$  of  $\alpha$ -quartz from Skinner (1966) empirically extrapolated above 844 K, and the compressibility of  $\alpha$ -quartz from Birch (1966), the value of  $S_T^{\circ}$  for  $\alpha$ -quartz was obtained at  $T > 844$  K by solving the first derivative of the equation for the  $\alpha$ - $\beta$  transition (Mirwald & Massone 1980) to obtain  $\Delta S_T^{\circ} / \Delta V_T^{\circ}$  at a series of temperatures from 1 to 20 kbar. Using the above data and  $S_T^{\circ}$  obtained from this calculation, the transition can be fit to within  $\pm 15^{\circ}\text{C}$  in the range of 1 to 20 kbar.

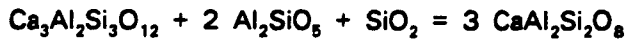
In addition to Reaction 1 the following experimentally reversed equilibria were selected as constraints on the Gibbs free energy of relevant phases:



(Harker & Tuttle, 1956; Jacobs & Kerrick, 1981);



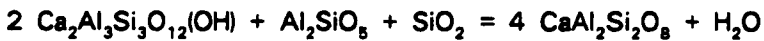
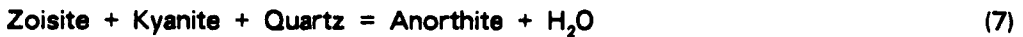
(Newton, 1966; Boettcher, 1970; Huckenholz *et al.*, 1975);



(Goldsmith, 1980; Gasparik, 1984b; Koziol & Newton, 1988)



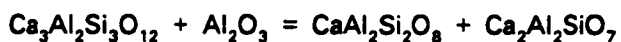
(Newton, 1966; Boettcher, 1970; Chatterjee *et al.*, 1984);



(Newton & Kennedy, 1963; Goldsmith, 1981; Chatterjee *et al.*; 1984, Jenkins *et al.* 1985);



(Newton, 1965; Boettcher, 1970; Chatterjee *et al.*, 1984)



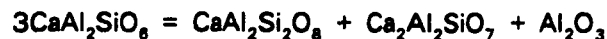
(Boettcher, 1970; Huckenholz *et al.*, 1975)



(Boettcher, 1970, Huckenholz *et al.*, 1975);



(Gasparik 1981, 1984b);



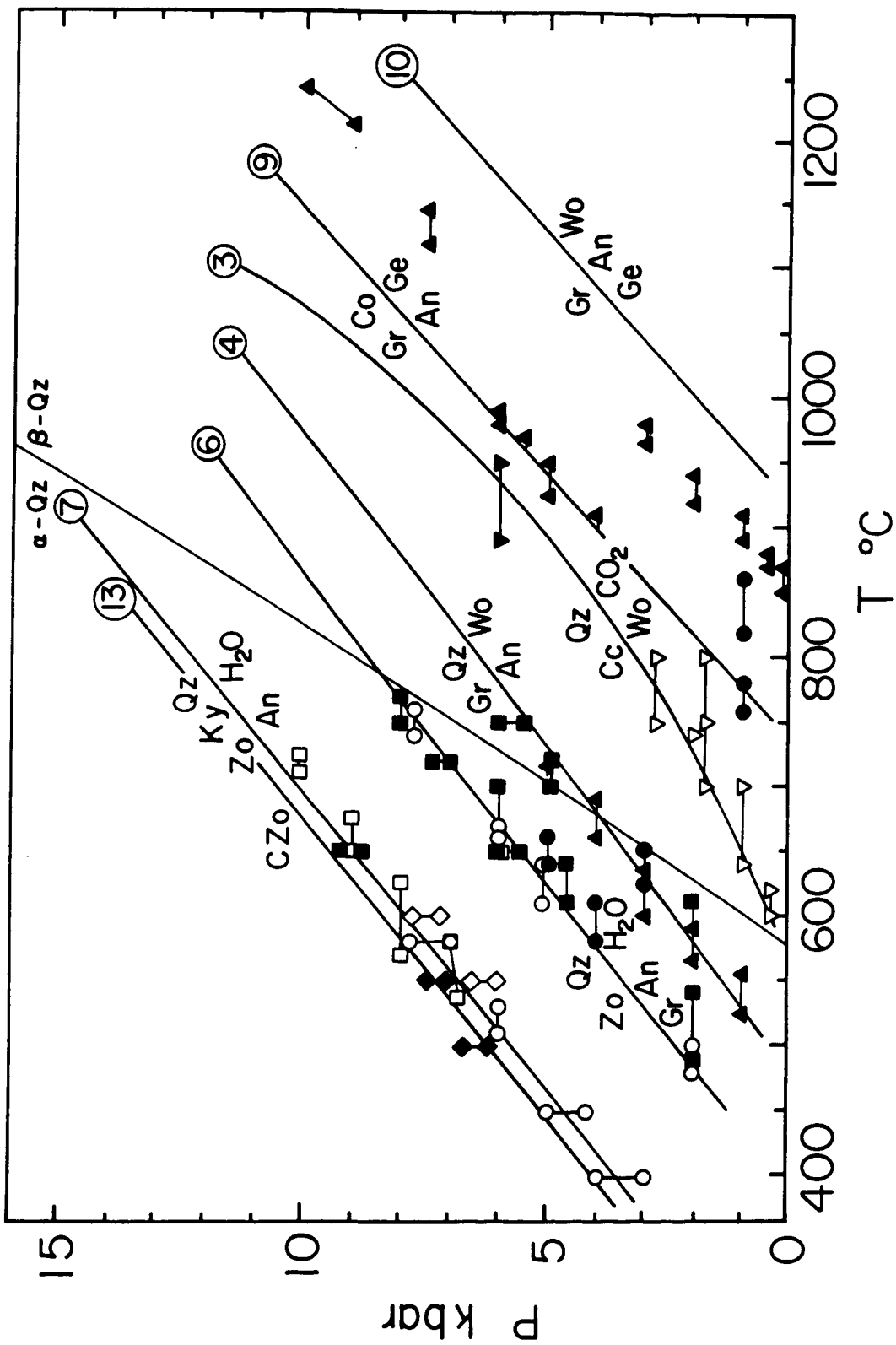
(Hays 1967).

Most of the resultant Gibbs energies were adjusted only slightly from Robinson *et al.* (1982), which is a statistical least squares fit of available experimental data. The experimental reversals and our calculated fits are shown in Figs. 2, 3, and 4. A reasonable fit to most of the reversals can be attained with our thermodynamic data set. However, there is an inconsistency between the calculated and experimental position for Reactions 9 and 10. Assuming a set of free energies that are consistent with Reactions 1 through 8, 11, and 12, one cannot simultaneously fit both sets of reversals for Reactions 9 and 10 (Chatterjee *et al.*, 1984). On the other hand, Robinson *et al.* (1982) derived a set of Gibbs energies consistent with reactions 9 and 10 that was inconsistent with the available reversals for Reaction 5. We have placed more weight on Reaction 5 because its location is now well established, and it appears that one of the gehlenite reactions is incorrectly located. There is considerable disagreement between the reversals of Boettcher (1970) and Huckenholz *et al.* (1975) for Reaction 10. The slope of Reaction 9 is consistent with a considerable amount of Al-Si disorder in gehlenite ( $2R\ln 2 = 11.5 \text{ J/mol}\cdot\text{K}$ , Ulbrich & Waldbaum, 1976), whereas the high temperature reversals of Huckenholz *et al.* (1975) for Reaction 10 suggest a greater slope than that calculated for Reaction 10. We have chosen to fit Reaction 9, because it is most consistent with the location of Reaction 12, which is derived from the intersection of Reactions 9 and 11, and our phase equilibrium analysis to follow rests on this assumption. Re-evaluation of the gehlenite equilibria are necessary in order to resolve the discrepancy.

The  $\Delta G_{298}^\circ$  of partially disordered meionite used in this study was calculated from  $\Delta G_{298}^\circ$  for Reaction 1, and  $\Delta G_{298}^\circ$  for anorthite and calcite:

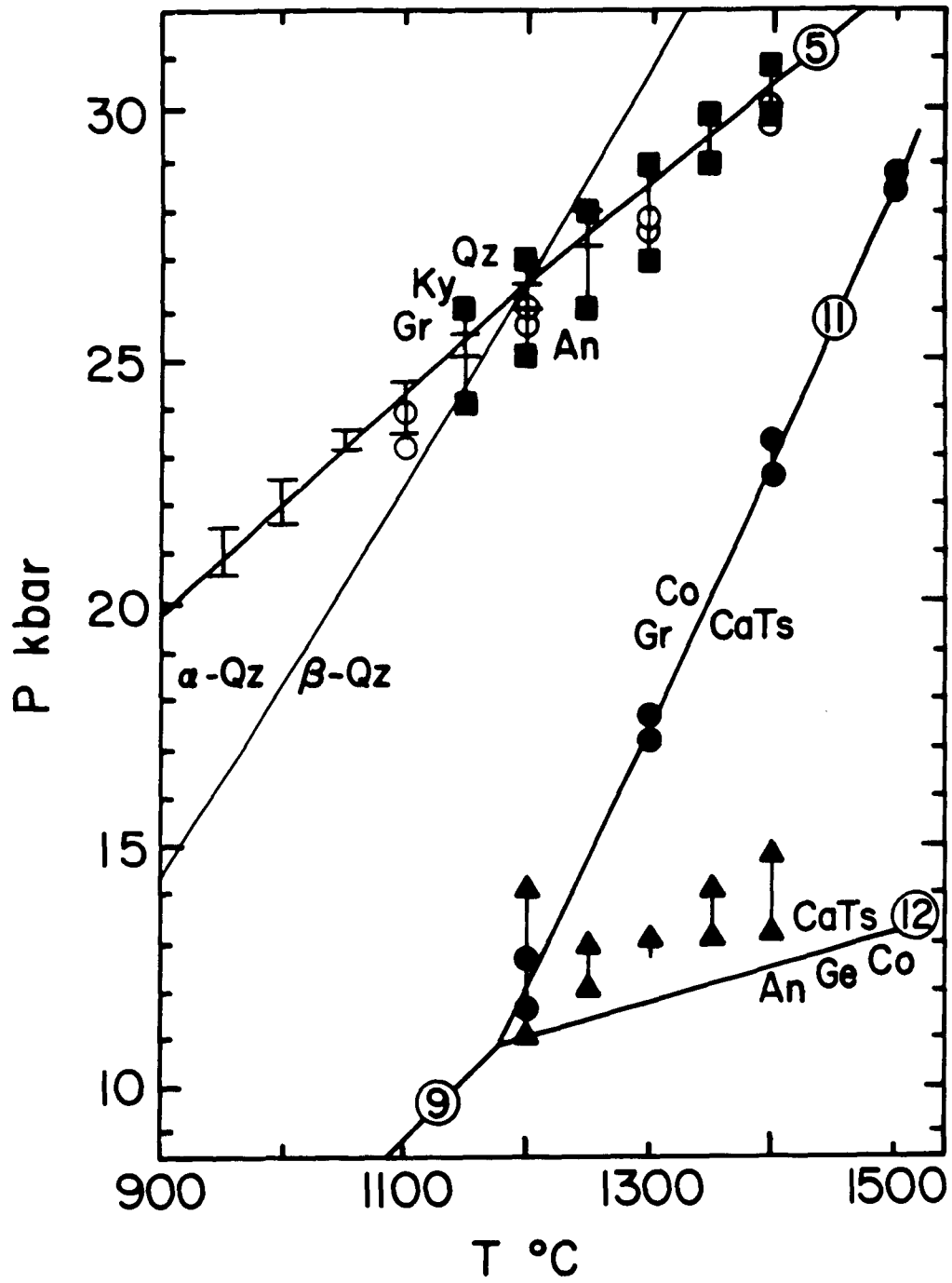
$$\Delta G_{298}^\circ (\text{Me}) = \Delta G_{298}^\circ (\text{Reaction 1}) + 3\Delta G_{298}^\circ (\text{An}) + \Delta G_{298}^\circ (\text{Cc})$$

**Figure 2.** Experimental constraints and calculated position of Reactions 3, 4, 6, 7, 9, 10 and 13, used to constrain thermodynamic data in Tables 1 and 2. The location of Reaction 10 ( $\text{Gr} = \text{An} + \text{Ge} + \text{Wo}$ ), was calculated from the thermodynamic data assuming a fit to Reaction 9 ( $\text{Gr} + \text{Co} = \text{An} + \text{Ge}$ ). The reversals for Reaction 10 are at a lower temperature than its calculated position. Symbols:  $\nabla$ : Harker & Tuttle, 1956;  $\blacksquare$ : Newton, 1966;  $\bullet$ : Boettcher, 1970;  $\blacktriangle$ : Huckenholz *et al.*, 1975;  $\square$ : Goldsmith, 1981;  $\nabla$ : Jacobs & Kerrick, 1981;  $\circ$ : Chatterjee *et al.*, 1984;  $\diamond$  (Reaction 7), and  $\blacklozenge$  (Reaction 13): Jenkins *et al.*, 1985.



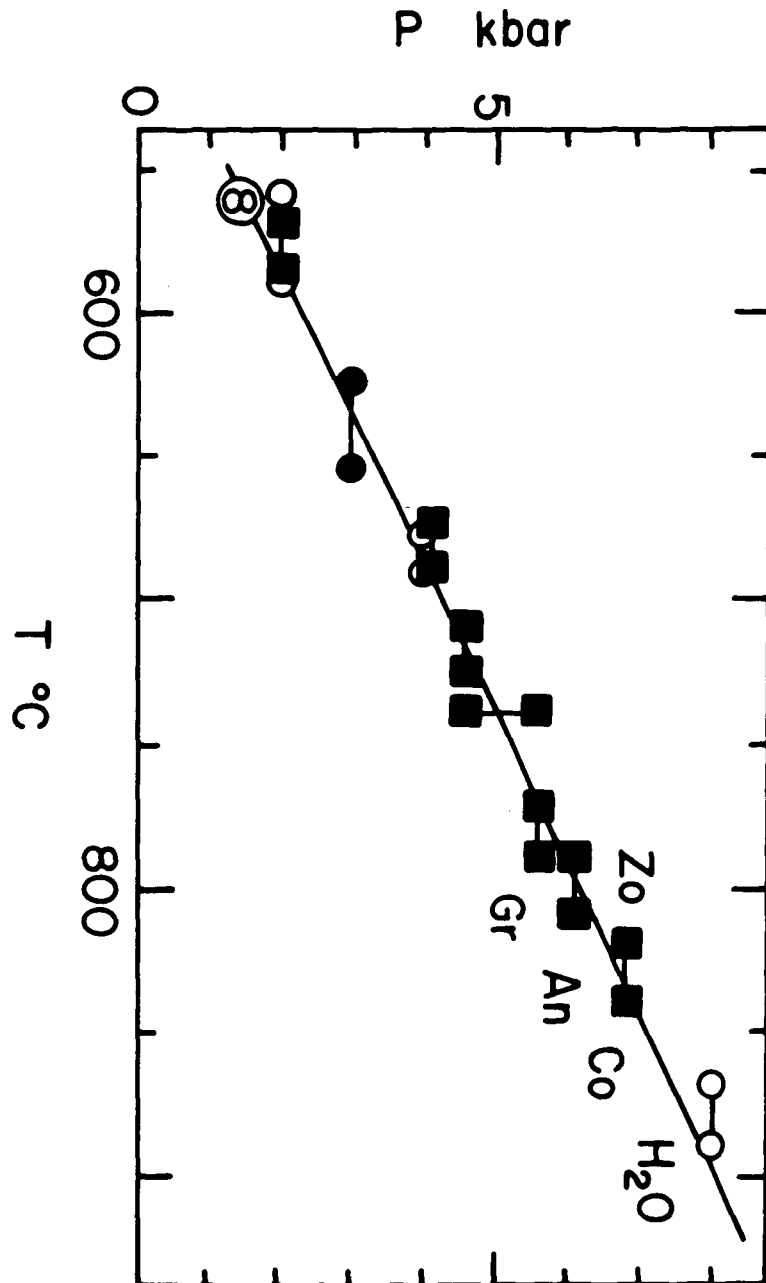
**Figure 3.** Experimental constraints and calculated positions of Reactions 5, 11, and 12. Symbols: ▲ : Hays, 1965; ■ : Goldsmith, 1980; ○ : Gasparik, 1984a; ● : Gasparik, 1984b; I : Koziol & Newton, 1986. The disagreement between the calculated and experimental locations of Reaction 12 may be related to systematic errors in pressure corrections of the piston cylinder.





4. Experimental constraints and calculated positions of Reaction 8. Symbols: ■ :  
Newton, 1965; ● : Boettcher, 1970; ○ : Chatterjee *et al.* 1984.

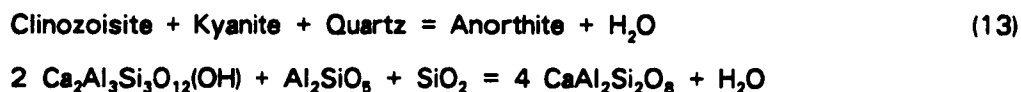
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The  $\Delta G_{298}^{\circ}$  (Reaction 1) was calculated using the midpoint of the reversal at 10 kbar (863°C) as a starting point. The  $\Delta G_{298}^{\circ}$  for meionite with the intermediate disordering state assumed here is -13,115.4 kJ/mol. Also tabulated are the Gibbs energies for completely disordered and ordered meionite calculate relative to the ordering state assumed for this study. The reversals correspond to only one ordering state, and if the partially disordered state is the correct ordering state for the experiments, then the ordered reaction would lie at higher temperatures and the disordered reaction at lower temperature relative to the present reversals.

The thermodynamic data set derived here assumes that anorthite is ordered with respect to its Al-Si distribution. Gasparik (1984b) and Wood & Holloway (1984) concluded that synthetic anorthite may contain small but significant amounts of Al-Si disorder, and a configurational entropy term of approximately three to five J/mol K is required for anorthite in order to fit reversals for Reaction 5. However, Anovitz & Essene (1987) concluded that a satisfactory fit to experiments in the system CaO-FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> can be obtained using alternative entropy data for grossular, and including expansivity and compressibility data in the calculation of the location of Reaction 5. For the present work we have accepted the conclusion of Anovitz & Essene (1987), obtaining a reasonable fit to the CASCH experimental data set. The effect on Reaction 1 of Al-Si disorder in anorthite is the opposite of that of Al-Si disorder in meionite. That is, it causes Reaction 1 to have a lower slope, requiring a greater configurational entropy for meionite to fit the reversals. The ratio of anorthite to meionite in Reaction 1 requires that the meionite entropy increase by 3-fold over the increase in anorthite entropy.

Epidote-group minerals coexisting with scapolite are usually monoclinic, therefore it is more appropriate to use clinzoisite reactions rather than zoisite reactions to model natural systems. Using experimental data for the reaction



(Jenkins *et al.*, 1985), we have calculated  $\Delta G_{298}^{\circ}$  for clinozoisite in the same manner as that for meionite. The  $\Delta G_{298}^{\circ}$  for Reaction 13 was calculated from the mid-point of the experimental reversal at 7.35 kbar, 550°C to 1 bar, 25°C to obtain  $\Delta G_{298}^{\circ}$  (Cz) of -6506.5 kJ/mol. We have assumed the entropy for clinozoisite to be that of zoisite, corrected for a volume difference of 0.65 cm<sup>3</sup> (i.e.,  $S_{298}^{\circ}$  (Cz) =  $S_{298}^{\circ}$  (Zo) + 1.4 J), and that thermal expansion and compressibility are the same for the two polymorphs. The molar volume for natural zoisite of Perkins *et al.* (1980) is consistent with the volume of natural zoisite obtained from Myer (1965, 1966) and that measured by Langar & Lattard (1980) and Chatterjee *et al.* (1984) for synthetic zoisite. The molar volume of clinozoisite was obtained from linear extrapolation of data on natural clinozoisite (Seki, 1959, Myer, 1966, Dollase, 1968) and is in agreement with the data on synthetic clinozoisite (Chatterjee *et al.*, 1984). Clinozoisite will be the polymorph used in the phase equilibrium calculations to follow.

#### Phase Equilibria

Scapolite parageneses from a wide range of metamorphic environments should provide valuable constraints on fluid composition. We have investigated occurrences of calcic, carbonate-rich scapolite in amphibolite and granulite facies gneisses in the Central Gneiss Belt of the southwestern Grenville Province of Ontario in order to constrain fluid compositions in high grade rocks. A detailed description of mineral assemblages and geologic setting of these rocks will be described in Chapters IV and V. Briefly, carbonate-rich calcic scapolite occurs in high grade calc-silicate rocks, marble, garnet amphibolite, and garnet meta-anorthosite. The most common phases coexisting with carbonate scapolite in calc-silicates include grossular-rich garnet, intermediate to calcic plagioclase, salitic clinopyroxene, pistacitic clinozoisite, wollastonite, calcite, and quartz. In contrast, sulfate-bearing carbonate scapolite typically occurs in garnetiferous mafic granulites, amphibolites, and meta-anorthosites.

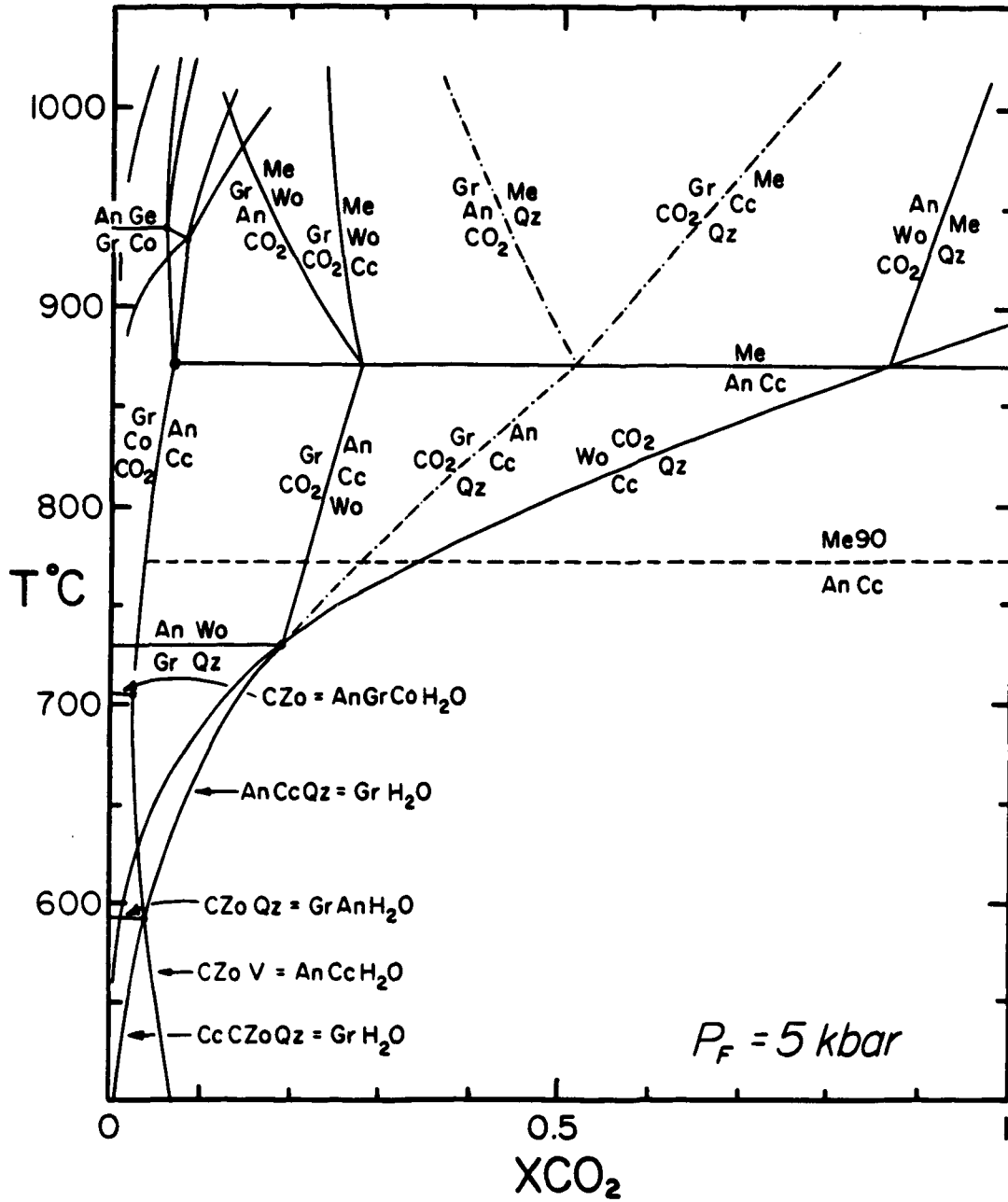
Geobarometric studies indicate the Central Gneiss Belt is a high pressure granulite terrain with peak metamorphic pressures in excess of 10 kbar (Anovitz, 1987). Other high pressure granulite terranes also contain scapolite-bearing granulites (*e.g.*, Furuu Complex, Tanzania: Coolen 1980; Bergen Arcs, Norway: Austrheim & Griffen, 1985; Southern India Archean Terrane: Devaraju & Coolen, 1983; Srikantappa *et al.*, 1985). Scapolite is also widely developed as a prograde index mineral in regional metamorphic terranes at intermediate pressures (*e.g.*, Trommsdorff, 1966; Heitenan, 1967; Kwak 1977). Therefore, scapolite decarbonation equilibria involving the above phases were calculated at 5 and 10 kbar in order to delineate phase relations over a range of crustal conditions and determine the effect of variable fluid pressure and composition on scapolite stability.

Previous studies of the CASCH system are numerous (Boettcher, 1970; Kerrick, 1970; Storre, 1970; Gordon & Greenwood, 1971; Hoschek, 1980; Perkins *et al.*, 1980; Halbach & Chatterjee, 1984; Kerrick & Ghent, 1984), and a number of other studies consider equilibria involving scapolite (Kerrick *et al.*, 1973; Ellis, 1978; Aitken, 1983; Schenk, 1984; Warren *et al.*, 1987). However none of these present a complete *quantitative* analysis of the stability of meionite relative to other CASCH phases. Our study takes the analysis of the CASCH system one step further by placing quantitative constraints on the limits of meionite stability.

At 5 kbar meionite is stable in the absence of quartz to water-rich conditions (Figs. 5a and 5b). The stability of meionite in T- $X_{\text{CO}_2}$  space is delimited by Reaction 1 at 873°C and the reactions  $\text{Me} = \text{Gr} + \text{An} + \text{Co} + \text{CO}_2$  and  $\text{Me} = \text{Gr} + \text{An} + \text{Ge} + \text{CO}_2$  at  $X_{\text{CO}_2} = 0.94 \pm 0.01$ . Therefore, end member meionite has an extremely large stability field at intermediate pressure and high temperature. However, in the presence of quartz the stability of meionite is greatly reduced and is confined to  $X_{\text{CO}_2} \geq 0.9$  at 5 kbar.

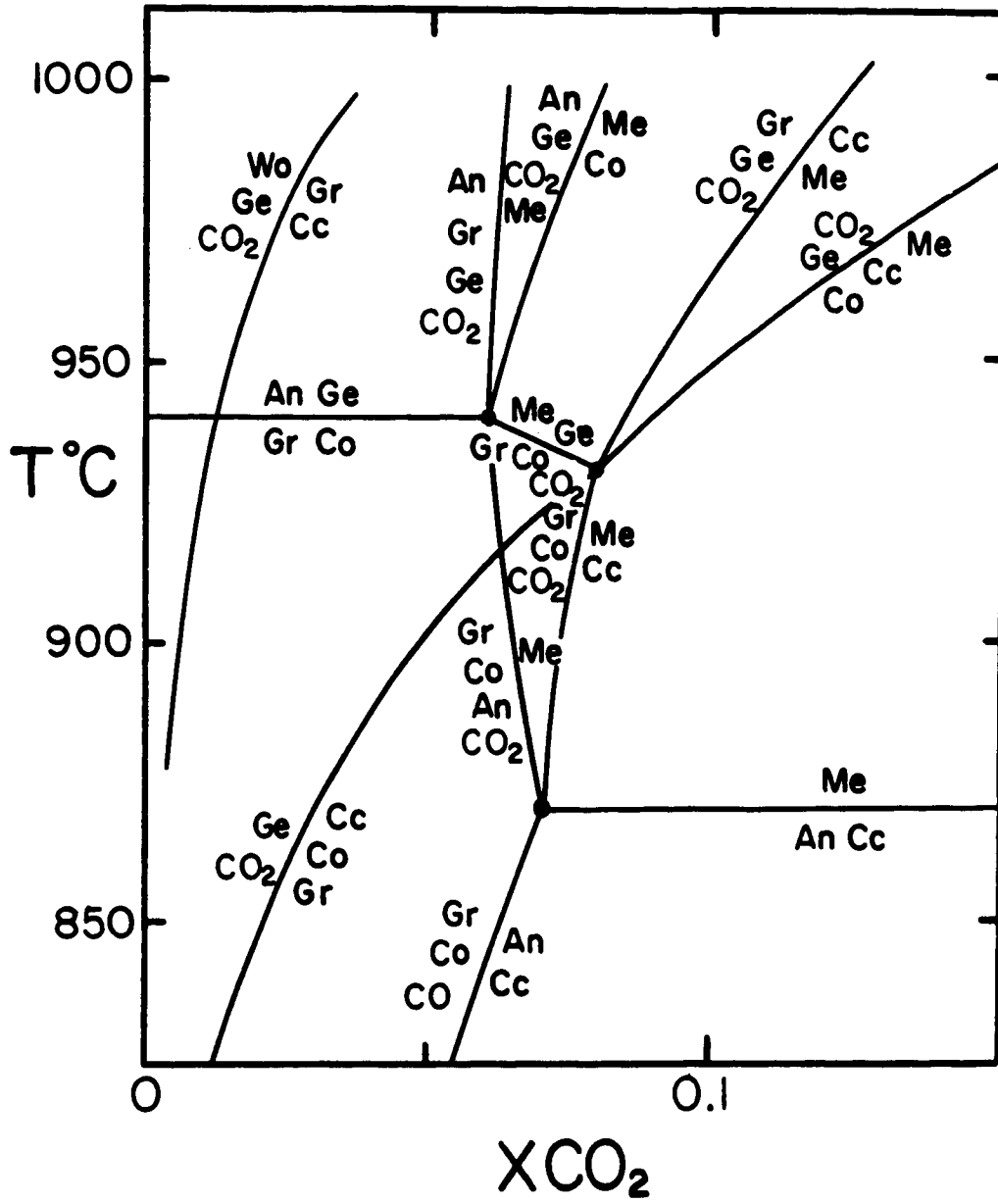
Reaction 1 is virtually independent of pressure, and at 10 kbar all other equilibria shift to higher temperature relative to Reaction 1, yielding a different

**Figure 5a.** Calculated meionite phase equilibria at 5 kbar. Dashed line is stability of  $Me_{90}$  relative to 3 Anorthite + Calcite calculated from assemblage reported by Schenk (1984). Meionite stability is further reduced in temperature for less calcic scapolite coexisting with calcic plagioclase ( $Me_{77}$ ;  $EqAn_{69}$  and  $An_{96}$ ; Table 3). See Fig. 5b for detail of  $H_2O$ -rich region at high temperature.

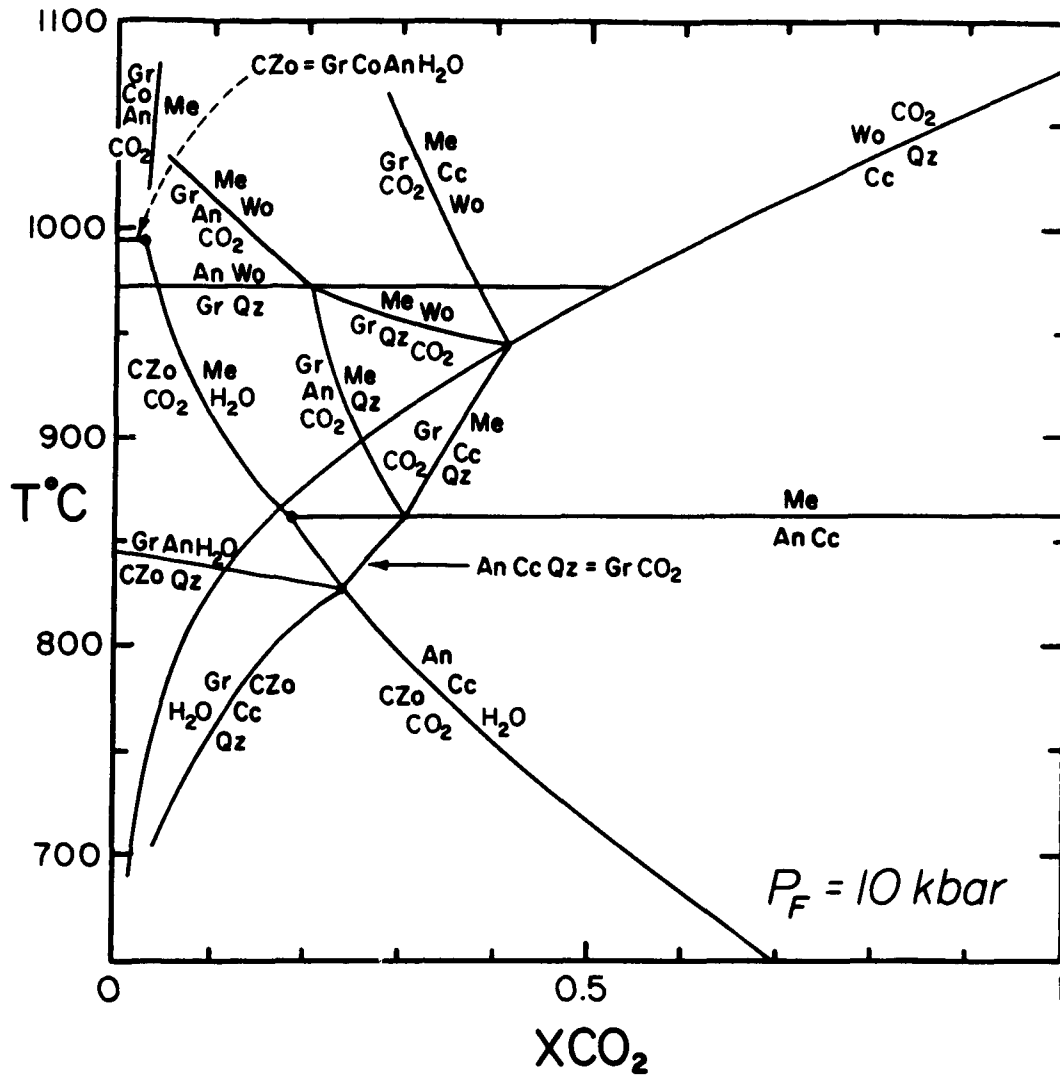




**Figure 5b.** Detail of high temperature, H<sub>2</sub>O-rich area of Fig. 5a. The reaction  $\text{Me} + \text{Ge} = \text{Gr} + \text{Co} + \text{CO}_2$  is an example of a decarbonation reaction with a negative T-XCO<sub>2</sub> slope. This results from the assemblage Me + Ge having a higher entropy than the volatile-bearing assemblage.



**Figure 6.** Calculated meionite phase equilibria at 10 kbar. All equilibria shift to higher temperature relative to  $3 \text{ Anorthite} + \text{Calcite} = \text{Meionite}$ . Terminal meionite reaction as a function of fluid composition is  $\text{Me} + \text{H}_2\text{O} = \text{Czo} + \text{CO}_2$ . The effect of increasing pressure on the phase relations is essentially the same as solid solutions in meionite.



topology (Fig. 6). The stability field of Me + Qz assemblages expands to much more water rich conditions, and meionite alone reacts to clinozoisite at  $X_{\text{CO}_2} < 0.2$  and 865 to 1000°C. Reactions that were metastable at 5 kbar (e.g.,  $\text{An} + \text{Cc} + \text{Qz} = \text{Gr} + \text{CO}_2$ ,  $\text{Me} + \text{Qz} = \text{Gr} + \text{An} + \text{CO}_2$ ) become stable at 10 kbar.

Ellis (1978) was the first to present a complete, detailed, qualitative topology of the same reactions shown in Figs. 5 and 6. Schenk (1984) deduced a phase diagram for selected meionite T-X equilibria at 6 kbar in the CASCH system that is similar to our T-X diagram (Fig. 5a). However, Ellis (1978) implied a much more restricted range of T- $X_{\text{CO}_2}$  stability for meionite than that calculated here. In addition, previous topologies were drawn with the meionite decarbonation equilibria as all having positive T- $X_{\text{CO}_2}$  slopes (relative to the common T-X diagram with  $X_{\text{CO}_2}$  increasing to the right, Figs. 5 and 6). Based on the model for Al-Si disorder assumed here, many of the meionite reactions have negative slopes in T-X space, and in P-T space. That is, meionite decarbonation reactions have negative slopes with meionite on the *high* temperature side of the reaction. The reaction



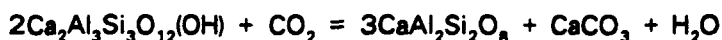
is used in Chapter IV to calculate  $\text{CO}_2$  activities in high grade gneisses. This is unusual for decarbonation reactions, reactions that characteristically involve high volume and entropy changes, but a necessary consequence of the disordering model. A completely ordered model yields a slight positive slope, and an entropy of approximately 728 j/mol K (configurational entropy of 19 j/mol K) yields a slope of 0.

The phase relations depicted in Figs. 5 and 6 are essentially the same (with regard to locations of reactions in T- $X_{\text{CO}_2}$  space) if one assumes an alternative ordering state for synthetic meionite. Phase relations were calculated for the hypothetical case of meionite with completely ordered and disordered Al-Si distribution, and although the slopes of meionite volatilization equilibria change, the

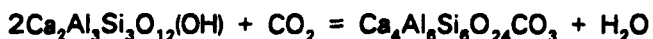
invariant points out of which the meionite reactions emanate do not change, as they are controlled by equilibria such as Reactions 1, 3 and 4.

#### Effects of Solid Solutions

The phase relations in Figs. 5 and 6 indicate that the stability of end-member meionite is restricted to unusually high temperatures for regional metamorphism (Goldsmith, 1976), and it would only be found in high temperature contact metamorphism of pure calc-silicates (Na and Cl free) adjacent to mafic or intermediate intrusions, or in high temperature granulite terranes. The tendency of scapolite to preferentially partition Na relative to plagioclase (Orville, 1974; Goldsmith & Newton, 1977) would further restrict the occurrence of meionite to an extremely pure protolith. In order to account for the common occurrence of calcic carbonate scapolite in quartz-bearing assemblages in metamorphic rocks, solid solutions are required as an alternative to the high pressures discussed above, in order to bring the stability of scapolite into the temperature and pressure range of the amphibolite and granulite facies. The effect of solid solutions on meionite phase relations is essentially identical to the shift observed with increasing pressure (i.e., Reaction 1 shifts to lower T relative to other equilibria; Ellis, 1978), with the ultimate stability of meionite limited by the intersection of Reaction 1 with



to yield the equilibrium



(Kerrick *et al.*, 1973; Aitken, 1983) (Fig. 6). With increasing solid solution of Na, Cl, or  $\text{SO}_4$  in scapolite, Reaction 1 will track along Reaction 14 to higher  $X_{\text{CO}_2}$  and lower temperature. For example, scapolite of composition  $\text{Me}_{90}$  (EqAn = 85) is the most calcic natural scapolite known (Shaw, 1960; Schenk, 1985; Perchuk *et al.*,

1985). The occurrence of nearly pure anorthite ( $An_{97.5}$ ) with scapolite ( $Me_{90}$ ) and calcite at 6 kbar and 750°C (Schenk, 1984: Table 3) defines the position of Reaction 1 for the most calcic scapolite known.  $Me_{90}$  would break down to grossular + anorthite + corundum +  $CO_2$  at  $X_{CO_2} < 0.1$ , and the absence of scapolite-gehlenite assemblages may be due to the relative instability of end member meionite (Fig. 5a). The stability field of meionite + quartz is also greatly expanded with dilutions of meionite compared to the end member system in which a limited stability field for meionite is predicted in the presence of quartz at 5 kbar. Further dilution of the meionite component (e.g., assemblages reported by Oterdoom & Gunter, 1983; Table 3: Sc ( $Me_{80}$ ) + Pg ( $An_{90}$ ) + Cc) shifts the locus of the end member reaction to even lower temperature. Meionite alone would then break down to clinozoisite, and in the presence of quartz would break down to grossular at nearly the same  $X_{CO_2}$ .

An example of the effect of solid solutions in scapolite *and* coexisting phases on the location of scapolite reactions is exemplified by the assemblage Sc ( $Me_{73}$ ) + Pg ( $An_{42}$ ) + Gt ( $Gr_{37}Py_5Alm_{55}Sp_3$ ) + Ep ( $Ps_{21}$ ) + Cc + Qz + Hbl (Table 3, PS86E-31), found in a sheared meta-anorthosite in the southwestern Grenville Province of Ontario (Chapter IV). This is an invariant assemblage formed by the intersection of Reaction 1 with Reactions 7, 14, and 15. At 10 kbar and 700°C,  $a_{CO_2}$  was calculated using the equilibrium



to be 0.38, corresponding to  $X_{CO_2}$  of approximately 0.30 to 0.35 assuming  $P_{fluid} = P_{total}$  (anorthite activity calculated from Newton *et al.*, 1980 (Table 3), and grossular activity from Anovitz & Essene, 1987). Because the activity of meionite is fixed by the presence of plagioclase and calcite in this assemblage, and the free energy of meionite is calculated relative to anorthite + calcite, one obtains the same value of

TABLE 3. Data used in calculation of activity-composition relations for carbonate scapolite. K is equilibrium constant for Reaction 1 defined in text.

REFERENCE	P kbar	T°C	K	Plagioclase		Scapolite		$\gamma_{Me}$
				XAn	aAn	EqAn	aMe	
Frank 1983 Grevola, Switz.	7	600	0.0923	0.50	0.743	0.71	0.441	0.6211
Ferry 1976 Maine, U.S.A.	3.5	600	0.0913	0.34	0.569	0.65	0.360	0.5538
Oterdoom & Gunter 1983	3	600	0.0912	0.94	0.940	0.73	0.525	0.7192
Val Schiesone, Switz.	3	600	0.0912	0.91	0.910	0.74	0.512	0.6919
Hayob, pers. comm Idaho, U.S.A.	7	600	0.0923	0.98	0.960	0.69	0.535	0.7754
Thompson, quoted in Oterdoom & Gunter E. Conn., U.S.A.	6	675	0.2037	0.96	0.950	0.74	0.646	0.8730
Mezger & Okrusch 1985 Samos, Greece	5	700	0.2570	0.59	0.720	0.64	0.556	0.8688
Moecher 1988 Parry Sound, Ont. Canada	10 10	700 700	0.2655 0.2655	0.42 0.65	0.598 0.740	0.62 0.69	0.488 0.573	0.7871 0.8304
Ellis 1978 experiments	4 4	750 750	0.3963 0.3963	0.92 0.50	0.920 0.642	0.82 0.53	0.745 0.569	0.9085 1.0736
Glassley 1983 W. Greenland	6	750	0.4027	0.83	0.830	0.67	0.693	1.0343
Schenk 1984 S. Calabria, Italy	6	750	0.4027	0.98	0.980	0.85	0.785	0.9235



$a_{\text{CO}_2}$  for this sample from Reaction 16 if  $a_{\text{CO}_2}$  is calculated using meionite decarbonation equilibria such as Reaction 14. Therefore, in scapolite-calcite-bearing calc-silicates, meionite equilibria will not provide additional information with regard to fluid composition. It is in scapolite-bearing calc-silicates, orthogneisses and metabasites devoid of calcite that meionite equilibria will prove most useful in constraining fluid composition.

#### Activity-Composition (a-X) Relations

A reduction in activity of the meionite component in scapolite may arise from substitution of NaCl and  $\text{CaSO}_4$  for  $\text{CaCO}_3$ , and NaSi for CaAl. The various substitutions are related as a result of local charge balance constraints (Chamberlain *et al.*, 1985; Hassan & Buseck, 1988), and complete modeling of activity-composition (a-X) relations for all scapolite solid solutions is likely to be extremely complex, and perhaps more realistically treated as mixing of marialite-mizzonite and mizzonite-meionite. Here, we will attempt to model only the NaSi-CaAl exchange for application to carbonate-rich scapolites. Oterdoom & Gunter (1983) have performed similar calculations based on the model for completely disordered end-member meionite of Oterdoom & Wenk (1983). The results of our calculations are similar to the model of Oterdoom & Gunter (1983), in that both models predict negative departures from ideality.

Natural scapolite-plagioclase-calcite assemblages buffer the activity of Me in scapolite ( $a_{\text{Me}}^{\text{Sc}}$ ) according to Reaction 1. Knowing the pressure and temperature of equilibration of such an assemblage, the value of  $\ln K (= -\Delta G^\circ/RT)$  for the shift in Reaction 1 at this P and T can be calculated using EQUILI. Assuming an activity model for anorthite in plagioclase, one can then calculate the activity of meionite in natural scapolite (Oterdoom & Gunter, p. 983). For pure calcite, K for Reaction 1 reduces to

$$K = a_{\text{Me}}^{\text{Sc}} / (a_{\text{Al}}^{\text{Pl}})^3.$$

For carbonate scapolite, mixing of Ca and Na occurs on four equivalent cation sites. Therefore, the activity of meionite based on mixing of one cation is obtained from the relation

$$a_{Me}^{Sc} = [K \cdot (a_{An}^{Pg})^3]^{0.25}$$

One parameter is not sufficient to describe the composition of natural scapolite that may contain Cl in addition to CO<sub>3</sub>, and the mole fraction of meionite calculated above (Me = Ca/(Ca+Na+K)) takes into account only the NaSi-CaAl solid solution. However, the mole fraction of meionite in pure carbonate scapolite is adequately described by the equivalent anorthite content (Orville, 1974; Ellis, 1978), or EqAn = 100[(Al-3)/3] for the meionite formula based on Si + Al = 12 (Shaw, 1960; Evans *et al.*, 1969). This convention will be used for calculating the mole fraction of meionite for the purposes of modeling a-X relations. The two end members are taken to be meionite (Ca<sub>4</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>CO<sub>3</sub>, EqAn = 100) and the hypothetical composition CaNa<sub>3</sub>Al<sub>3</sub>Si<sub>9</sub>O<sub>24</sub>CO<sub>3</sub> (EqAn = 0).

In the absence of experiments aimed at directly modeling a-X relations, one would ideally use well-characterized scapolite-plagioclase-calcite assemblages from a single regional metamorphic terrane for which there exists good temperature control and a wide range of scapolite and plagioclase compositions. Sc-Pg-Cc assemblages are reported from a number of metamorphic settings, however mineral chemistries are not always reported, analyses may be of questionable quality or are incomplete, or textural relations make identification of equilibrium equivocal. Using a variety of sources that do not all provide detailed petrographic and compositional data, and for which well calibrated geothermobarometers are not used, certainly introduces errors in the activity model. However, the data provide insight into the mixing properties of calcic carbonate-scapolites and allow a provisional model to be developed for the purposes of calculating CO<sub>2</sub> activities in scapolite-bearing gneisses.

Thermobarometric and compositional data compiled for natural scapolite-plagioclase-calcite assemblages, along with the calculated  $a_{Me}^{Sc}$  and  $\gamma_{Me}^{Sc}$  are summarized in Table 3. Activities of anorthite in plagioclase for  $X_{An} < 0.80$  were calculated using the model of Newton *et al.* (1980). For  $X_{An} > 0.80$  the latter model predicts  $\gamma_{An} < 1$ . However, ion exchange experiments on the plagioclase solid solution series predict  $\gamma_{An}$  equal to or slightly greater than 1 (Orville, 1972; Blencoe *et al.* 1982). For these anorthite rich plagioclases we have assumed  $\gamma_{An} = 1$ . A  $\pm 25^\circ\text{C}$  temperature uncertainty was included in the calculation of  $a_{Me}^{Sc}$  as temperature is the greatest source of uncertainty in the data on natural assemblages. An asymmetric regular solution was used to model the activity-composition relations, with the constraint that  $a_{Me}^{Sc} = 1$  at  $X_{Me}^{Sc} = 1$  and  $a_{Me}^{Sc} = 0$  at  $X_{Me}^{Sc} = 0$ . Based on a least squares fit of the  $a$ - $X$  data to the relation

$$RT \ln \gamma_{Me}^{Sc} = (1 - X_{Me}^{Sc})^2 [W_{GM_e} + 2X_{Me}^{Sc} (W_{GM_a} - W_{GM_e})]$$

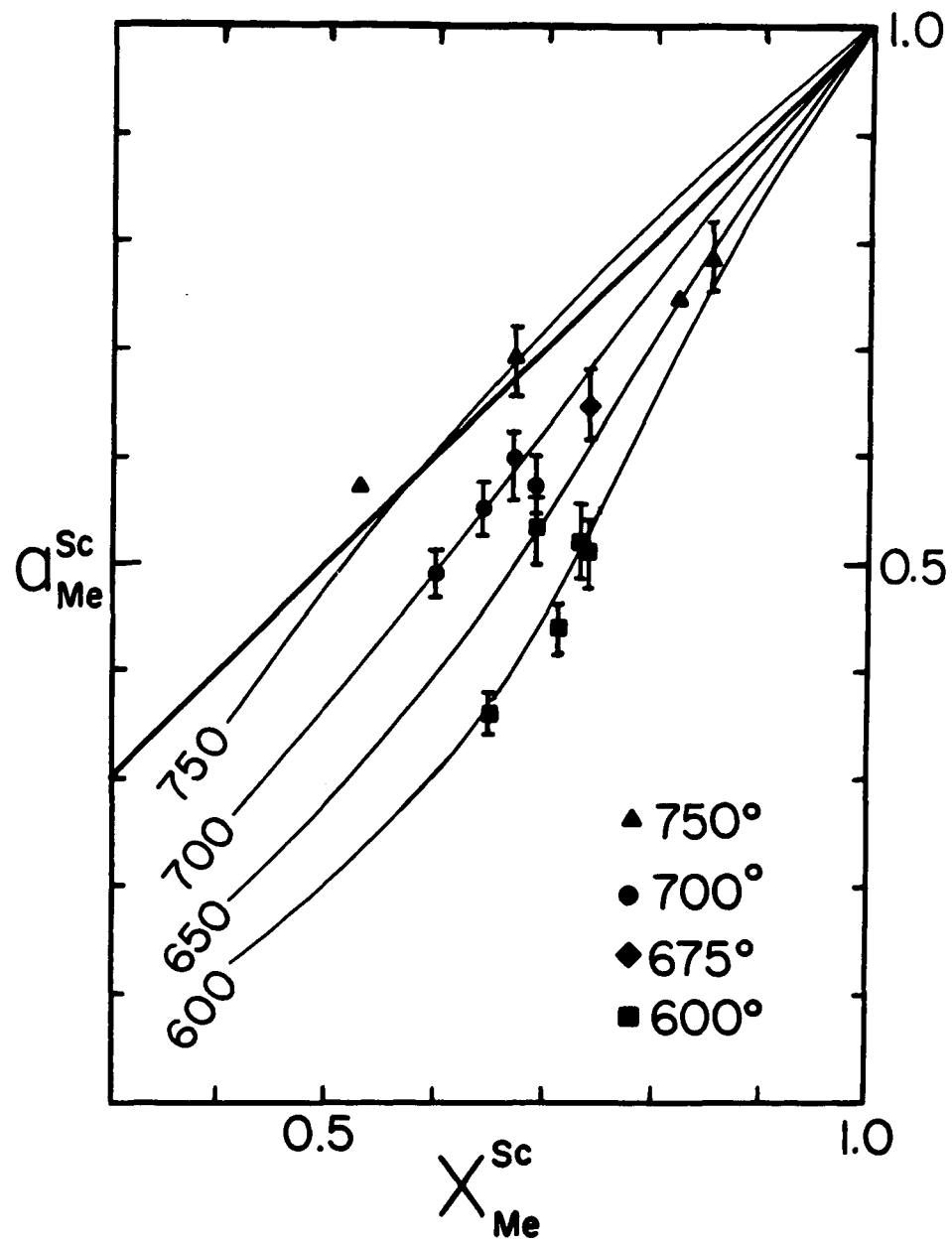
the following values are obtained for  $W_{GM_e}$  and  $W_{GM_a}$ , where Me is the  $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$  end member, Ma is the hypothetical  $\text{CaNa}_3\text{Al}_3\text{Si}_9\text{O}_{24}\text{CO}_3$  end member ("carbonate marialite"), and  $W_G = W_H - TW_S$ :

$$W_{GM_e} = 21,761 - 33T(\text{K}) \text{ J/mol-cation, and}$$

$$W_{GM_a} = -176,314 + 171T(\text{K}) \text{ J/mol-cation.}$$

These values were used to calculate the distribution of isotherms in Fig. 7. The calculated activities are generally in good agreement with the observed activities except for the two  $750^\circ\text{C}$  samples at EqAn 82 and 85. This discrepancy may result from the assumption that for all temperatures  $a_{Me}^{Sc} = 1$  at  $X_{Me}^{Sc} = 1$ , with the real mixing relations being more complex. It is evident that at  $750^\circ\text{C}$ , mixing is essentially ideal. Extrapolation to temperatures greater than  $750^\circ\text{C}$  indicates a marked positive deviation from ideality, consistent with the experiments of Goldsmith & Newton (1977) at  $1100^\circ\text{C}$ . Additional data on scapolite more calcic than EqAn = 0.75 in the temperature range 600 to  $800^\circ\text{C}$  are required in order to determine how  $a$ - $X$  relations vary in this  $T$ - $X$  field. The  $a$ - $X$  relations are valid for

**Figure 7.** Activity–composition relations for carbonate scapolite. Vertical bars are variation in  $a_{M_0}^{Sc}$  produced by a  $\pm 25^\circ\text{C}$  variation in reported equilibration temperature. Symbols without bars are experimental data points of Ellis (1978), all others based on natural assemblages tabulated in Table 3.



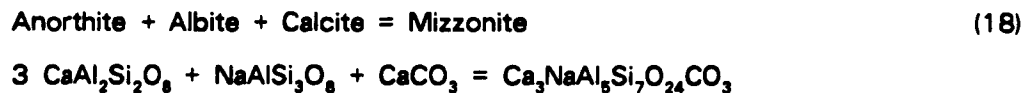
carbonate scapolite only in the temperature and composition range of the data in Fig. 7 and Table 3, and should not be extrapolated outside this region.

The negative values of  $W_H$  and  $W_S$  obtained for Ma component are consistent with observations on the stability of intermediate scapolite solid solutions relative to the isostructural, partly disordered end member standard state assumed here. The scapolite solid solutions are much more stable than the end members, consistent with the lack of reported occurrences of meionite, marialite, or sulfate meionite in nature. Scapolites with compositions centered around mizzonite are an unusually common intermediate composition (Evans *et al.*, 1969; Orville, 1974; Aitken, 1983; Oterdoom & Gunter, 1983; Chapter 3), and mizzonitic scapolite with a limited compositional range in terms of EqAn and  $CO_3/(CO_3+Cl)$  often coexists with an extremely wide range of plagioclase compositions (e.g., Frank, 1983). The stability of mizzonite is manifest by the relatively high molar entropy compared to more meionite and marialite-rich compositions, and its high heat of solution relative to oxide mixes (Komada *et al.* 1988). If the a-X relations are calculated assuming a less disordered end member than that used here, one obtains slightly less non-ideal behavior, and a completely disordered end member yields greater departures from ideality, particularly for the 600 and 700°C samples. Therefore, the mixing effects observed here are in part dependent on the modeling assumptions, but may have some physical basis in reality.

The activity of meionite calculated in this manner is directly dependent on the activity of anorthite, and therefore on the choice of anorthite activity model. The degree of model dependency was evaluated by comparing meionite activities obtained above with those calculated using the anorthite models of Orville (1972) and Blencoe *et al.* (1982) at 700°C. The calculated meionite activities are only slightly different from those obtained using the activity model of Newton *et al.* (1980) and yield a smaller variation than that produced by a  $\pm 25^\circ C$  variation in temperature for any of the models. However, there is no means of evaluating the isotherms at 600, 650, or 750°C for our scapolite model. The model for the

activity of anorthite in plagioclase of Newton *et al.* can be used to calculate anorthite activities at temperatures other than those at which the solution calorimetry was performed (970 K; Newton *et al.* 1980), but there is only one additional thermodynamic constraint on the calculated activities for the model of Newton *et al.* This limits the general validity of the meionite activity model developed here, and more reliable modeling of a-X relations in scapolite will depend on a more carefully calibrated activity model for anorthite in plagioclase and meionite in scapolite.

An artifact of the empirical method of calculating meionite activities based on anorthite activities from coexisting plagioclase is that its application to phase equilibrium calculations for systems based on alternative thermodynamic data will lead to erroneous conclusions involving the activity of meionite. For example, application of the activity model derived above (or that of Oterdoom & Wenk 1983) in the calculation of CO<sub>2</sub> activities using the thermodynamic data base of Berman *et al.* (1986), for example, will yield values that may be highly disparate and inaccurate. Both our model and that of Oterdoom and Gunter (1983) are based on different assumptions concerning the standard state of end member meionite, activity models for anorthite, and thermodynamic data for anorthite, calcite, and meionite. Future work should be directed at direct experimental determination of a-X relations for plagioclase and carbonate scapolite over a wide temperature range, and at obtaining better constraints on the ordering state of synthetic scapolites. It may prove more useful to experimentally constrain the stability of mizzonite (Me<sub>75</sub>)



as it appears to be a relatively stable and common intermediate composition.

The presence of carbonate rich scapolite in calc-silicate assemblages has been inferred to indicate high CO<sub>2</sub> partial pressures in high grade calc-silicates (*e.g.*, Kumar & Chacko, 1986). Based on the phase relations quantified above, this is not

necessarily the case, and melonite is stable over virtually the entire range of fluid compositions. Intermediate scapolite solid solutions may eventually be found to be consistent with high  $\text{CO}_2$  activities (e.g., Aitken 1983; Chapter IV). Clearly, the exact fluid composition will depend on temperature, pressure, and activities of components in the solid phases. In Chapter IV the thermodynamic data base and scapolite mixing model derived here will be applied to evaluation of the effects of solid solutions in scapolite and coexisting phases on fluid composition in upper amphibolite and granulite facies calc-silicates, garnet amphibolites, meta-anorthosites, and metabasites.



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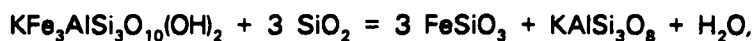
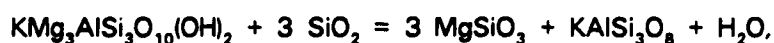


## CHAPTER IV

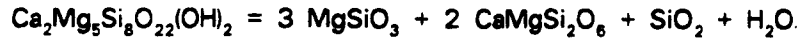
### SCAPOLITE PHASE EQUILIBRIA. II: CO<sub>2</sub> ACTIVITIES IN HIGH GRADE ROCKS

#### Introduction

The role of fluids in the petrogenesis of high grade rocks and the granulite facies in particular has received considerable attention during the last decade. Although long recognized as the distinguishing feature of granulites (e.g., Eskola 1939), it has become increasingly apparent, based on quantitative petrologic, phase equilibrium and stable isotopic studies, that the granulite facies is characterized by its relatively anhydrous nature relative to lower grade equivalents. The role of a fluid phase in high grade metamorphism can be distilled into two salient questions: 1) is a free fluid phase actually present during high grade metamorphism?; and, 2) is the low H<sub>2</sub>O activity ( $a_{\text{H}_2\text{O}}$ ) commonly calculated for high grade rocks necessarily balanced by a high CO<sub>2</sub> activity ( $a_{\text{CO}_2}$ ) in order to maintain  $P_{\text{fluid}} = P_{\text{total}}$ ? In order to address these questions one needs to know the activities of the dominant fluid species typically assumed to be present during metamorphism of high grade rocks (H<sub>2</sub>O and CO<sub>2</sub>). The  $a_{\text{H}_2\text{O}}$  in high grade rocks is usually calculated from biotite (phlogopite or annite) or amphibole (tremolite) dehydration equilibria such as



or



In most cases the  $a_{\text{H}_2\text{O}}$  has been shown to be considerably less than unity in natural assemblages, and often in the range 0.1 to 0.3 (Wells, 1979; Bohlen *et al.*, 1980; Phillips, 1980; Percival, 1983; Valley *et al.*, 1983; Bhattacharya & Sen, 1986; Aranovich *et al.*, 1987; Hansen *et al.*, 1987; Edwards & Essene, 1988; Lamb & Valley, in press). Except in the unusual occurrence of nearly pure end-member phases (*e.g.*, Valley *et al.*, 1983), application of these equilibria is generally complicated by strong dilutions of the end-member hydrous phase. Lack of a realistic solution model for the mixing relations, and a poorly constrained correspondence between the material on which the experimental or thermodynamic data were collected and the natural phase (*c.f.* Clemens *et al.*, 1987), complicate the issue. Although the precision of such calculations may be low, the general pattern of low  $a_{\text{H}_2\text{O}}$  is consistent with the interpretation that granulites represent relatively dry lithologies, and this has become an established tenet of metamorphic petrology.

The implication of  $a_{\text{H}_2\text{O}} < 1$  has usually been interpreted as resulting from either 1) the presence of some other fluid species with dilution of  $\text{H}_2\text{O}$ , but maintaining  $P_{\text{Fluid}} = P_{\text{Total}}$  and leading to low  $\text{H}_2\text{O}$  activities; or 2) low volatile contents *before* the high grade metamorphism, either as inherently dry igneous protoliths or as rocks having experienced multiple or protracted metamorphic events. In support of 1), fluid inclusion studies of granulites have demonstrated that  $\text{CO}_2$ -rich inclusions are characteristic of many granulite facies gneisses relative to their lower grade equivalents, which commonly have  $\text{H}_2\text{O}$ -rich inclusions (Touret, 1971; Coolen, 1982; Schreurs, 1984; Hansen *et al.*, 1984; Rudnick *et al.*, 1985; Santosh, 1986). Thus the logical conclusion has been that  $\text{CO}_2$  is the major diluent in the granulite facies fluid. This then implies that either the  $\text{CO}_2$  was preferentially left behind in the rock during prograde dehydration or by partitioning of  $\text{H}_2\text{O}$  into a granitic partial melt, or that the  $\text{CO}_2$  was introduced from an external source.

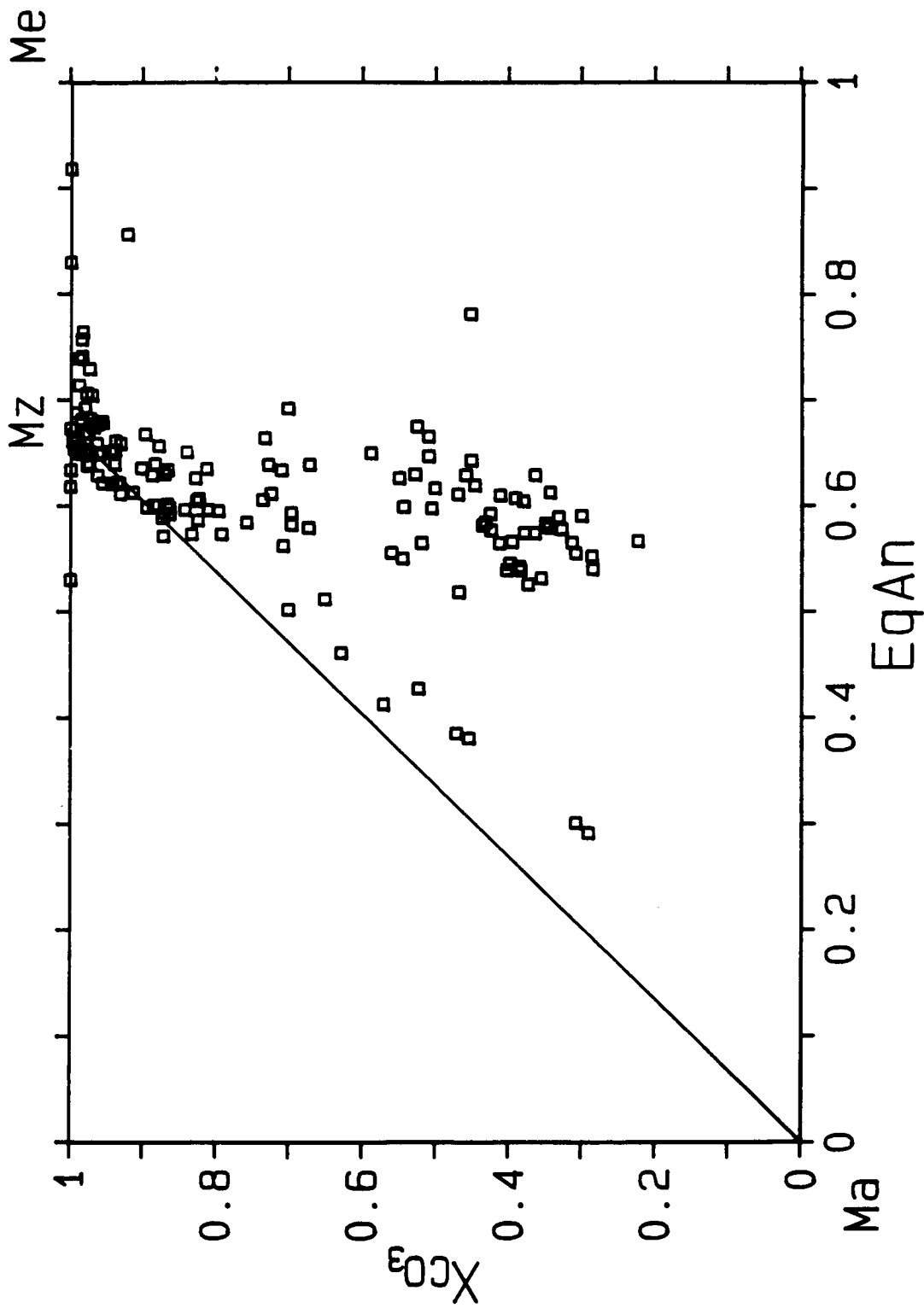
Recent studies have attempted to evaluate quantitatively the hypothesis that  $\text{CO}_2$  is the dominant component of the fluid phase in the granulite facies, and some conflicting evidence has been presented. For example, Lamb & Valley (1985) emphasized that the stability of  $\text{CO}_2$  is restricted to rocks with  $f_{\text{O}_2}$  greater than that corresponding to the FMQ buffer, and that  $\text{CO}_2$  cannot be a major fluid component in some rocks with low  $a_{\text{H}_2\text{O}}$ , implying fluid absent metamorphism. Lamb *et al.* (1987) demonstrated that  $\text{CO}_2$ -rich fluid inclusions in granulite facies calc-silicates are often inconsistent with peak metamorphic fluid compositions calculated from wollastonite-calcite-quartz equilibria or from constraints on  $f_{\text{CO}_2}$  based on calculations of fluid speciation in the C-O-H system. This would imply late entrapment of a  $\text{CO}_2$ -rich fluid phase for these rocks, or post-metamorphic modification of fluid inclusions. Vry *et al.* (1988) have shown by carbon isotope measurements and calculations of fluid-rock ratios that many cordierite-bearing gneisses could not have experienced interaction with a  $\text{CO}_2$ -rich fluid phase possessing a heavy carbon isotopic signature (greater than or equal to the assumed average upper mantle value of approximately -6 per mil), or resetting of the cordierite carbon isotope compositions to the heavier values would have occurred at the fluid-rock ratios required by models of large-scale  $\text{CO}_2$  infiltration (e.g., Touret, 1971; Newton *et al.*, 1980).

The purpose of the present study is to extend the quantitative evaluation of fluid compositions in high grade rocks, by applying a reasonably well constrained scapolite decarbonation equilibrium to directly calculate  $a_{\text{CO}_2}$ . An analysis of the thermodynamics, phase equilibria, and mixing relations of calcic, carbonate scapolite (meionite) were presented in Chapter III. This chapter is an application of these relations to natural systems. Although the intent is not to evaluate mechanisms for the generation of low  $\text{H}_2\text{O}$  activities in high grade rocks, the results presented here have important implications for models of granulite genesis that invoke open system interaction via a  $\text{CO}_2$ -rich fluid as the means of reducing the  $a_{\text{H}_2\text{O}}$ .

### Scapolite Compositions in High Grade Settings

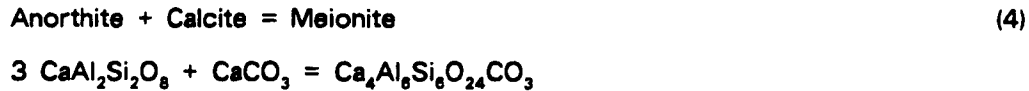
Shaw (1960) reviewed the chemical variation of scapolite in metamorphic rocks, and included available analyses of scapolite from high grade terranes (*e.g.*, von Knorring & Kennedy, 1958). Numerous studies since then have demonstrated that scapolite from the upper amphibolite and some granulite facies occurrences tends to be more calcic and carbonate-rich than that from lower grade settings, the latter tending to be more sodic and chlorine-rich (*e.g.*, Hietanen, 1967; Kwak, 1977; Tuisku, 1985). Furthermore, scapolite in the granulite facies proper, *i.e.*, coexisting with orthopyroxene, has been shown to be sulfate-rich ( $SO_4/(SO_4+CO_3+Cl)$  in the anion site = 0.25 to 0.75) as is scapolite in garnet-clinopyroxene granulite facies gneisses and deep-crustal xenoliths (von Knorring & Kennedy, 1958; Lovering & White, 1964; Wilkinson, 1974; Devaraju & Gowd Reddy, 1976; Edwards *et al.*, 1979; Okrusch *et al.*, 1979; Coolen, 1980; Devaraju & Coolen, 1982; Jones *et al.*, 1983; Austreim & Griffin, 1985; Srikantappa *et al.*, 1985; Stolz, 1987; Thomas & Nixon, 1987). These observations are consistent with the relatively high temperature and pressure stability of calcic, sulfate-carbonate scapolite solid solutions (Goldsmith & Newton, 1977). The most prolific occurrence of sulfate rich scapolite is in the Furuu Granulite Complex of Tanzania (Coolen, 1980), where scapolite with  $SO_4/(SO_4+CO_3)$  ranging from 0.27 to 0.77 is encountered. A characteristic feature of the Furuu Complex is the widespread development of sulfate-rich scapolite in all calcium-rich lithologies (calc-silicates, amphibolites, felsic to mafic granulites). Scapolite-bearing lithologies in the Central Gneiss Belt (CGB) of the Grenville Province of Ontario and other localities were investigated for the present study. A wide range of scapolite compositions were encountered, with the same general pattern observed above. The range of anion and cation compositional variation of scapolite in high grade lithologies from this and other studies is summarized in Fig. 1. Scapolite compositions approaching mizzonite ( $EqAn = 100(Al-3)/3 = 67$ ,  $CO_3/(SO_4+CO_3+Cl) = 1$ ) are very common in these occurrences. This intermediate member of the scapolite solid solution series has been inferred to be stable relative

**Figure 1.** Compositional range of natural scapolites expressed in terms of EqAn ( $100(\text{Al}-3)/3$ ) and anion site composition  $X_{\text{CO}_3}$  ( $\text{CO}_3/[\text{CO}_3+\text{SO}_2+\text{Cl}]$ ). Samples falling along the trend between Mz (mizzonite,  $\text{NaCa}_3\text{Al}_5\text{Si}_7\text{O}_{24}\text{CO}_3$ ) and Ma (marialite,  $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$ ) are  $\text{CO}_3$ -Cl solid solutions. Field of points between Mz field and EqAn 55 at intermediate  $X_{\text{CO}_3}$  are sulfate-rich scapolites from granulites and high grade gneisses.

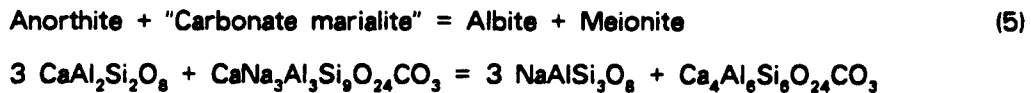


to other scapolite compositions, probably as a result of Al-Si ordering within the silicate framework (Oterdoom & Gunter, 1983; Oterdoom & Wenk, 1983; Komada *et al.*, 1988; Chapter III). Sulfate-bearing scapolite tends to be slightly less calcic than mizzonite, but these compositions also cluster within a limited compositional range (Fig. 1). This study will deal with carbonate and sulfate solid solutions in the upper amphibolite and granulite facies. Chlorine-carbonate solid solutions, and constraints they place on fluid composition are discussed in various detail by Hietanen (1967), Ellis (1977), Kwak (1977), Vanko & Bishop (1982), and Mora & Valley (1988).

The partitioning of Ca and Na between scapolite and plagioclase has been proposed as a geothermometer (Goldsmith & Newton, 1977) for calcic plagioclase-scapolite assemblages. The reaction



has a large  $dP/dT$  (Goldsmith & Newton, 1977; Chapter III), making it a potentially ideal geothermometer. A provisional experimental calibration was presented by Goldsmith & Newton (1977). However, application of the thermometer to natural assemblages has yielded mixed results, in some cases giving temperatures consistent with other thermometers, and in others often resulting in erroneously high temperatures (Goldsmith & Newton, 1977; Rollinson, 1980). A reason for this may be seen in the  $K_{D_{\text{Sc-Pg}}}^{\text{Ca-Na}}$  relationship for naturally occurring scapolite and plagioclase pairs. For carbonate and/or sulfate-bearing scapolite, the relevant exchange reaction is essentially:

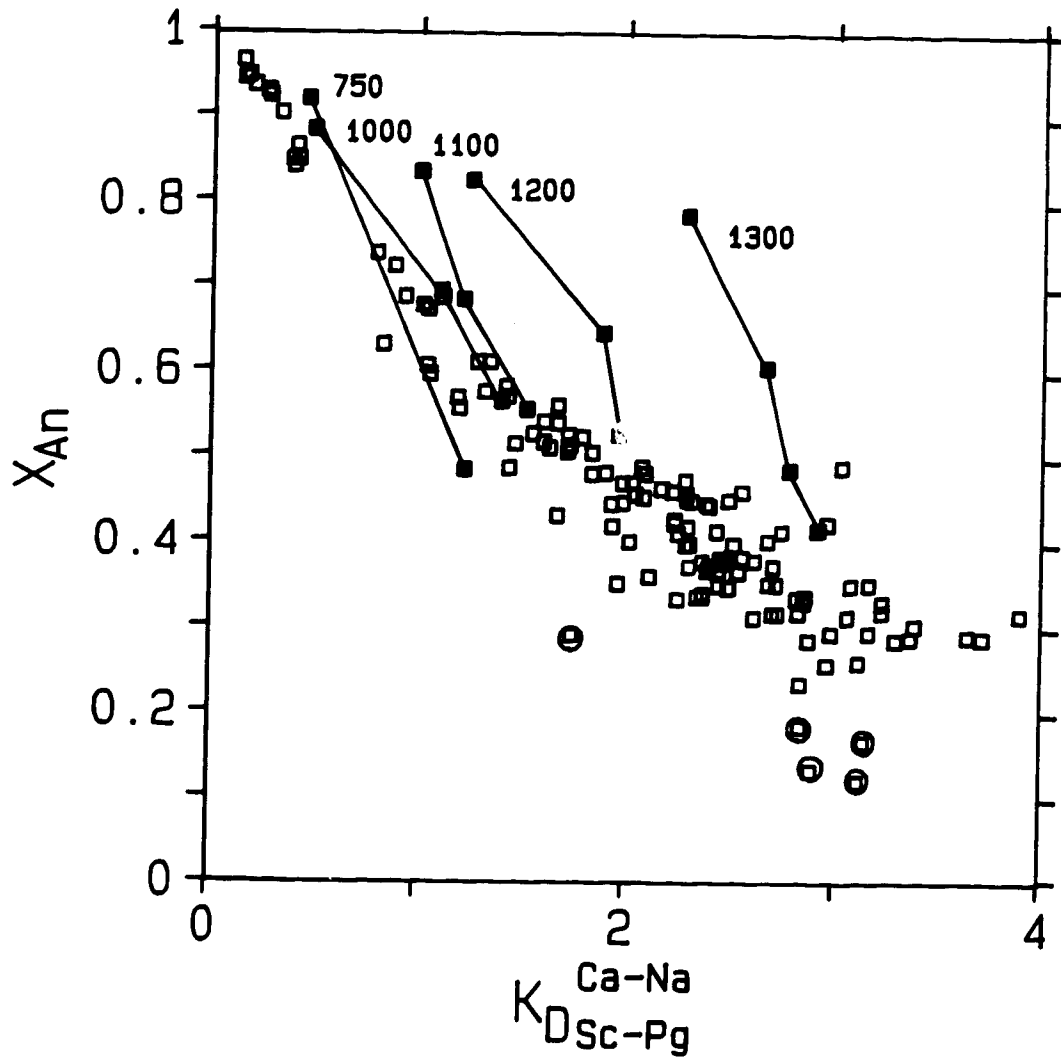


where carbonate marialite is a hypothetical endmember, and  $K_{D_{\text{Sc-Pg}}}^{\text{Ca-Na}}$  was calculated as

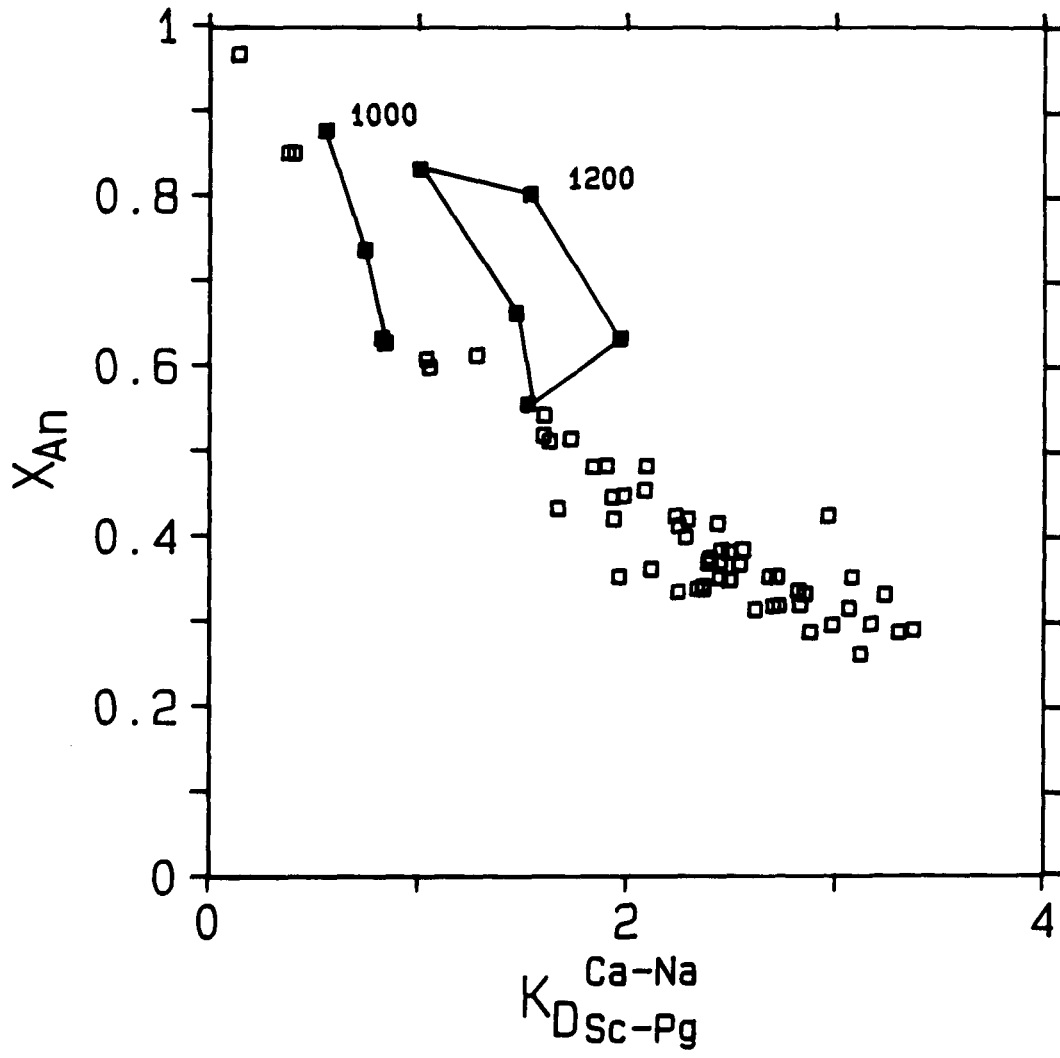
$$K_{D_{\text{Sc-Pg}}}^{\text{Ca-Na}} = \frac{[X_{\text{Ca}}^{\text{Sc}}/X_{\text{Na}}^{\text{Sc}}]/[X_{\text{Ca}}^{\text{Pg}}/X_{\text{Na}}^{\text{Pg}}]}{1} \quad (6)$$

**Figure 2a.**  $K_{D_{Sc-Pg}}^{Ca-Na}$  vs.  $X_{An}$  content of plagioclase for coexisting scapolite-plagioclase in high grade gneisses (this study) and data compiled from literature. Data are plotted irrespective of anion site composition. Open symbols: natural parageneses; filled symbols: experimental scapolite-plagioclase pairs at quoted temperatures (Goldsmith & Newton, 1977; Ellis, 1978). Range of  $K_{D_{Sc-Pg}}^{Ca-Na}$  at a given  $X_{An}$  content is due in part to compositional variability of plagioclase coexisting with scapolite and to disequilibrium partitioning between scapolite and plagioclase. Points falling below trend at  $X_{An} < 0.20$  are chlorine-rich scapolites from amphibolite facies calc-silicates and amphibolites encountered in the southwestern Grenville Province.





**Figure 2b.**  $K_{\text{D}_{\text{Sc-Pg}}^{\text{Ca-Na}}}$  vs  $X_{\text{An}}$  content for scapolite with  $X_{\text{SO}_4} \geq 0.10$  in the anion site. Symbols as in Fig. 2a. The field of these samples is indistinguishable from that of all available scapolites compiled in 2a.



where  $X_{Ca}^{Sc}$  is defined as the EqAn content of scapolite,  $X_{Na}^{Sc}$  is 1-EqAn of scapolite, and  $X_{Ca}^{Pg}$  and  $X_{Na}^{Pg}$  are the anorthite and albite contents of plagioclase (abbreviations in Appendix 5). Fig. 2 was compiled from data in Appendix 3, and includes samples from the present study and available literature sources. The analyses mainly represent coexisting carbonate/sulfate scapolite and plagioclase from calc-silicate and mafic gneisses that are estimated to have equilibrated in the temperature range 550 to 800°C. Some samples coexist with calcite, and some contain up to 15 mol % Cl in the anion site. Experimental data points for carbonate/sulfate scapolite are also included for comparison. For the natural assemblages, there is a distinct curvilinear relationship within a restricted range between  $K_{D_{Sc-Pg}}^{Ca-Na}$  and plagioclase composition (a best fit line,  $K_D = 4.923 - 7.363 X_{An} + 2.507 X_{An}^2$ , with  $R^2 = 0.83$  and standard error = 0.37, was calculated for the distribution) indicating that the composition of scapolite is primarily dependent on the plagioclase composition, and that  $K_{D_{Sc-Pg}}^{Ca-Na}$  is only slightly dependent on temperature.  $An_{27}$  is the approximate lower limit for which coexisting carbonate-sulfate scapolite has been reported, and  $An_{65}$  is the composition at which the scapolite EqAn composition is the same as the anorthite content of the coexisting plagioclase. The experimental data of Goldsmith & Newton (1977) are consistent with a marked temperature-dependent fractionation at temperatures greater than 1000°C, but apparently not in the temperature range of high grade regional metamorphism where the 1000°C isotherm of Goldsmith & Newton merges with the natural assemblages (Fig 2). Unfortunately, the data are not consistent with coexisting scapolite and plagioclase being a reliable geothermometer. Goldsmith & Newton (1977) inferred that this may be due to ordering of natural scapolite relative to the experimental phases. Based on a thermodynamic analysis, ordering of intermediate compositions relative to the end members is highly likely (Oterdoom and Wenk 1983; Oterdoom & Gunter 1983; Chapter III).

The analyses plotted in Fig. 2a represent all available scapolite solid solutions. Of these the sulfate-rich scapolites are indistinguishable from the other scapolite samples (mainly  $CO_3$  scapolites) in terms of  $X_{An}$  versus  $K_D$  (Fig. 2b), consistent with

nearly ideal mixing of carbonate and sulfate anions in the scapolite structure. A limited number of points for chlorine-rich scapolite coexisting with sodic plagioclase fall well below the trend for calcic scapolite-plagioclase pairs, possibly as a result of disequilibrium, lower temperature, and/or a different equilibrium partitioning relation (Fig. 2a). Despite the lack of direct useful thermometric information, analysis of scapolite-bearing assemblages can provide important constraints on  $a_{\text{CO}_2}$ , given reliable temperatures obtained from other equilibria.

### Calculation of $\text{CO}_2$ Activities

#### Thermodynamic Data and Activity Models

Thermodynamic data and activity-composition ( $a$ -X) relations for scapolite are necessary in order to calculate  $a_{\text{CO}_2}$  in high grade rocks using scapolite equilibria. An internally consistent thermodynamic data set for meionite and other calc-silicate phases in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$  (CASCH) has been derived based on recently acquired thermodynamic data for scapolite and published experiments in the CASCH system. The  $a$ -X relations for carbonate scapolite were calculated from natural scapolite-plagioclase-calcite assemblages. The reader is referred to Chapter III for the details of these calculations. Briefly, the  $a$ -X relations for meionite in scapolite approach ideality at 750°C and exhibit increasingly negative departures from ideality below 750°C. The only constraints above 750°C are the experiments of Goldsmith & Newton (1977) which indicate positive departures from ideality at 1000 to 1300°C, consistent with our model.

Assumptions concerning the mixing of carbonate and sulfate in the anion site need to be made in order to apply the scapolite  $a$ -X relations based on pure carbonate scapolite to natural carbonate-sulfate-chlorine solid solutions. Based on the  $K_D$  relations discussed above, it appears that the carbonate and sulfate groups mix ideally in the anion site in calcic scapolite. In addition, Ellis (1977) presented evidence for ideal mixing between  $\text{CO}_3$  and Cl in the anion site for intermediate carbonate-chlorine solid solutions. Therefore the activity of carbonate meionite in a

carbonate-sulfate solid solution with less than 10 mol percent Cl in the anion site will be calculated from the mixing relations for carbonate scapolite presented in Chapter III, but reduced by the factor  $X_{\text{CO}_3} = \text{CO}_3 / (\text{CO}_3 + \text{SO}_4 + \text{Cl})$  for that particular scapolite.

Thermodynamic data for anorthite, grossular, and quartz comprise part of the internally consistent data set used in the derivation of scapolite phase equilibria in the CASCH system (Chapter III). The equation of state for  $\text{CO}_2$  by Shmonov & Shmulovich (1974) was used to calculate end member decarbonation equilibria. The data of Burnham *et al.* (1969) was used to calculate end member dehydration equilibria. Thermodynamic calculations were performed with a computer program (EQUILI, Wall & Essene, unpublished) that solves the relation

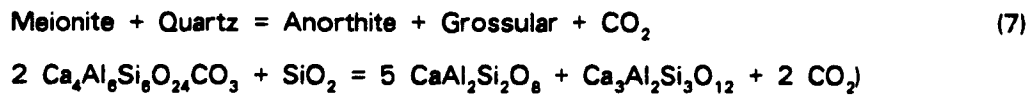
$$\Delta G_{T_2}^{P_2} - \Delta G_{T_1}^{P_1} = \int_{P_1}^{P_2} \Delta V_s dP - \int_{T_1}^{T_2} \Delta S_s dT + \Delta G(P, T, X)_{\text{H}_2\text{O}} + \Delta G(P, T, X)_{\text{CO}_2}$$

using available volume, entropy, expansivity and compressibility data.

In the calculations to follow, anorthite activities were calculated using the plagioclase activity model of Newton *et al.* (1980). The same model was used in the derivation of meionite activities from natural Sc-Pg-Cc assemblages (Chapter III), and is used here in order to maintain internal consistency. The model of Newton *et al.* (1980) predicts that the activity coefficient ( $\gamma$ ) for anorthite becomes less than one at compositions more calcic than  $\text{An}_{80}$ . In fact, based on a comparison of various studies of plagioclase mixing, it is unlikely that activity coefficients are less than one for these compositions (see Carpenter & Ferry (1984) for a critique and summary of available constraints on plagioclase mixing). For plagioclase with compositions more calcic than  $\text{An}_{80}$  we have assumed ideal mixing, that is  $\gamma = 1$ . Grossular activities for quaternary Gr-Py-Alm-Sp garnets were calculated using the quaternary mixing model of Anovitz & Essene (1987) which is a modification of the model of Ganguly & Saxena (1984), and incorporates updated mixing parameters for the grossular-almandine exchange. Explicit analytical expressions for calculating activity coefficients for the garnet components are presented in Appendix 4.

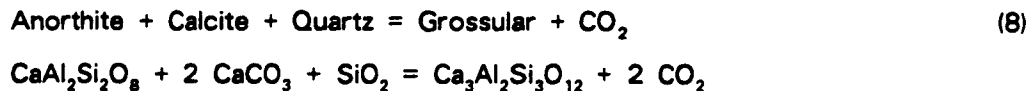
## Volatile Equilibria

A number of scapolite equilibria are potential CO<sub>2</sub>-barometers, particularly for calc-silicate lithologies (e.g., Jones *et al.*, 1983; Chapter III). A survey of the reported scapolite-bearing assemblages and our investigation in the CGB of Ontario reveal that the sub-assemblage scapolite-plagioclase-garnet-quartz is common to the range of bulk compositions discussed above. This assemblage monitors  $a_{\text{CO}_2}$  by the reaction

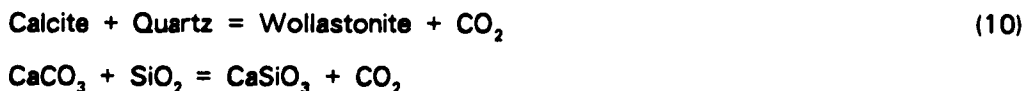
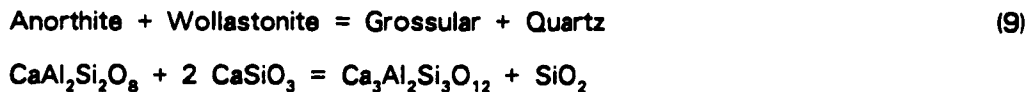


In the absence of quartz in the mineral assemblage, Reaction 7 places an upper limit on  $a_{\text{CO}_2}$ . This allows constraints on  $a_{\text{CO}_2}$  to be placed on many quartz undersaturated lithologies that contain scapolite-garnet-plagioclase, *e.g.*, deep crustal xenoliths.

Although direct experimental studies of Reaction 7 are lacking, constraints on its position are provided by the intersection of Reaction 4 and



whose position in turn is derived from addition of the reactions



for which experimental constraints are available (see Chapter III).

In Chapter III it was seen that the configurational entropy arising from Al-Si disorder in meionite had a marked effect on the  $dP/dT$  slope of Reactions 4 and 7, and on the degree of departure from ideality of  $a$ - $X$  relations for meionite in scapolite. However, if an internally consistent set of data is used to derive the

Gibbs free energy of meionite and to model mixing relations of meionite (defined by Reaction 4), the same value of  $a_{\text{CO}_2}$  is obtained for a given sample no matter what value of configurational entropy one allows for meionite, as long as the entropy of meionite is consistent with experimental constraints on Reaction 7. In addition to using Reaction 7,  $a_{\text{CO}_2}$  was calculated for calcite-bearing meta-anorthosite and mafic gneisses using Reaction 8. In rocks that contain the assemblage Sc-Pg-Gt-Cc-Qz, one may calculate  $a_{\text{CO}_2}$  from both Reactions 7 and 8, however the same value of  $a_{\text{CO}_2}$  should be obtained from each reaction for a given Sc-Pg-Gt-Qz-Cc assemblage because of the dependence of the Gibbs free energy and mixing relations for meionite on thermodynamic data for calcite and anorthite. This was found to be the case in all samples for which this calculation was performed (see following sections and Table 2).

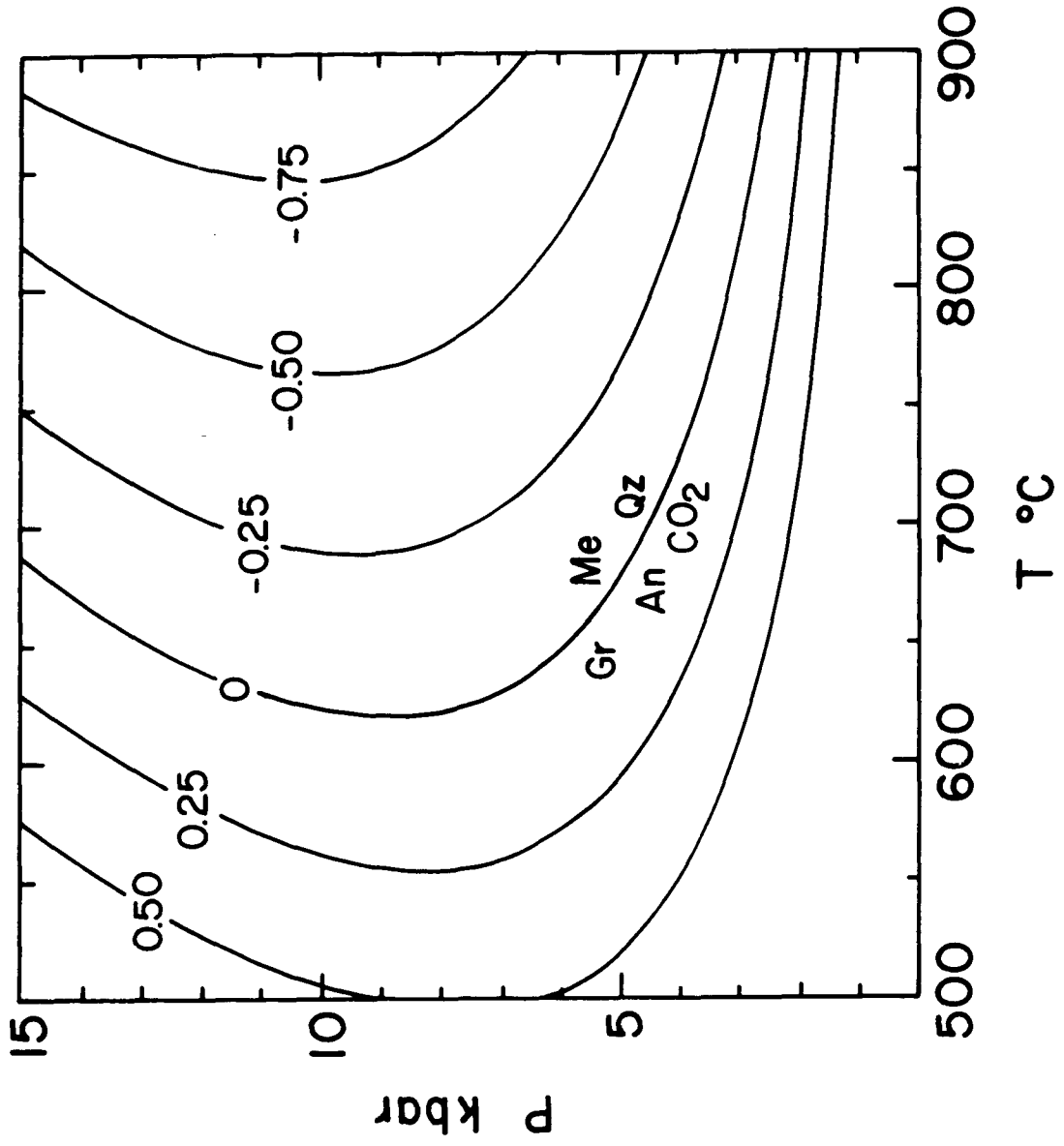
The locus of Reaction 7 in P-T space is displayed in Fig. 3. The unusual orientation of this reaction, that is, the negative slope with meionite on the high T side and CO<sub>2</sub> on the low T side of the reaction, is due to the high entropy of meionite. In contrast to other volatilization reactions, in which the energetics of the reaction are dominated by the higher entropy and volume of the volatile-bearing assemblage, Reaction 7 is dominated by the entropy contribution from a phase with a large number of atoms that also has a significant configurational entropy, and that produces a relatively low mole fraction of CO<sub>2</sub> per formula weight of the carbonate-bearing silicate phase. This is in contrast to calcite, which has a large mole fraction of CO<sub>2</sub> per mole of a carbonate-bearing phase with few atoms. By comparison, Reaction 10 is a reaction dominated by the energetics of the high entropy and molar volume of CO<sub>2</sub>.

Based on Reaction 7 values of  $\log_{10}K$  were calculated at various P and T using EQUILI (Fig. 3), and the expression

$$K = [(a_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}}) \cdot (a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{Pg}})^5 \cdot (a_{\text{CO}_2})^2] / (a_{\text{Ca}_4\text{Al}_6\text{Si}_8\text{O}_{24}\text{CO}_3}^{\text{Sc}})^2 \quad (11)$$



**Figure 3.** Locus and values of  $\log_{10}K$  for Reaction 7. See text for discussion.



was solved for  $a_{\text{CO}_2}$  using the appropriate activity models. Explicit expressions for calculating the activity of grossular and meionite are outlined in Appendix 5 and Chapter III, respectively.

The  $a_{\text{CO}_2}$  calculated in the above manner is relative to a standard state of pure  $\text{CO}_2$  at the pressure and temperature of interest. An  $a_{\text{CO}_2}$  of unity implies a pure  $\text{CO}_2$  fluid phase with  $P_{\text{Fluid}} = P_{\text{Total}}$  at the equilibrium P and T. An  $a_{\text{CO}_2}$  less than one results from either a mixed  $\text{H}_2\text{O}-\text{CO}_2$  fluid with  $P_{\text{Fluid}} = P_{\text{Total}}$  or fluid absence ( $P_{\text{Fluid}} < P_{\text{Total}}$ ). Alternatively, the fugacity of  $\text{CO}_2$  may be calculated using a 1 bar, T standard state and thermodynamic data. From this a partial pressure of  $\text{CO}_2$  is determined from  $P_{\text{CO}_2} = f_{\text{CO}_2}/\gamma_{\text{CO}_2}$ , where  $\gamma_{\text{CO}_2}$  is the fugacity coefficient of  $\text{CO}_2$  obtained from the data of Shmulovich & Shmonov (1975). Where possible, calculation of the partial pressures of all gas species allows evaluation of fluid absence or fluid presence.

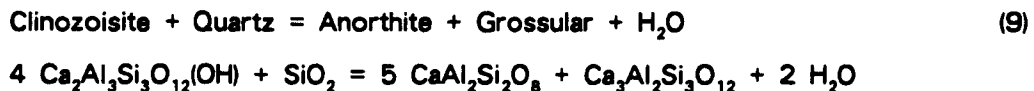
The final data required to calculate  $a_{\text{CO}_2}$  are accurate P-T estimates for the conditions of equilibration of the scapolite-bearing assemblage. Initial calculations showed that temperature is the most critical factor in obtaining precise values of  $a_{\text{CO}_2}$ . Typically, a temperature variation of  $\pm 50^\circ\text{C}$ , a commonly quoted estimate of precision for geothermometry, will double or halve the resultant value of  $a_{\text{CO}_2}$ . This is less of a problem when working with samples that equilibrated at apparently low  $a_{\text{CO}_2}$  (e.g.,  $a_{\text{CO}_2} \leq 0.2$ ). For intermediate fluid activities it means the difference between realistic ( $a_{\text{CO}_2} \leq 1.0$ ) and erroneous ( $a_{\text{CO}_2} \geq 1.0$ ) estimates of  $a_{\text{CO}_2}$ . Therefore the most precise value of temperature possible is necessary for accurate  $\text{CO}_2$  barometry. The  $a_{\text{CO}_2}$  was calculated over a range of T for all settings to evaluate the effect of T on  $a_{\text{CO}_2}$ . Values of  $a_{\text{CO}_2}$  are quoted to two decimal places for rounding purposes. However, the precision of the values may approach  $+100\%/-50\%$  of the calculated value for  $+50/-50^\circ\text{C}$  temperature difference.

The temperature sensitivity of Reaction 7 arises primarily from two factors. First, the activity of meionite increases rapidly from 650 to 800°C, while the

activities of anorthite and grossular decrease with increasing temperature, though not as markedly as that of meionite. This results in rapid changes in calculated  $K$  (Eq. 11) with changing  $T$ , compared to using an ideal model for all species that would result in little variation of  $K$  (and therefore  $a_{\text{CO}_2}$ ) with  $T$  (e.g., Reaction 1). In the calculation of meionite and grossular activities, mole fractions are raised to the 8th, and 3rd powers, and anorthite activities are raised to the 5th power, accentuating even small shifts in composition of these phases. Secondly, the free energy of Reaction 7 does not change markedly with temperature (Fig. 3), so that small shifts in the composition or activity of any component will result in major shifts in  $a_{\text{CO}_2}$  of the magnitude quoted above. Therefore the calculation of  $a_{\text{CO}_2}$  using Reaction 7 is highly model dependent.

The effect of overestimating the equilibrium temperature is to yield erroneously high values of  $a_{\text{CO}_2}$  such as  $a_{\text{CO}_2}$  greater than unity, which implies  $P_{\text{CO}_2} > P_{\text{Total}}$ , a structurally unsustainable condition in rocks. The temperature may be overestimated as a result of retrograde metamorphism in which the scapolite assemblage is secondary after and replaces a higher grade assemblage. Examples of such a condition will be noted in later sections. Pressure, which is presently more accurately determined than temperature (Essene, 1988), has much less of an effect on  $a_{\text{CO}_2}$  than temperature, and precision of  $\pm 1$  kbar results in only a  $\pm 2\%$  variation in  $a_{\text{CO}_2}$ . However, partial pressures are more sensitive to total pressure as the fugacity coefficient of  $\text{CO}_2$  is highly pressure dependent.

The  $a_{\text{H}_2\text{O}}$  was calculated for selected scapolite-bearing samples when appropriate mineral assemblages are present. The reaction



is applicable to many calc-silicates and some scapolite-bearing meta-anorthosite for calculating  $a_{\text{H}_2\text{O}}$ . Reaction 1 was also used to calculate  $a_{\text{H}_2\text{O}}$ . Thermodynamic data for clinozoisite are compiled in Chapter III. The activity model of Bird & Helgeson

(1980) was used to calculate the activity of clinozoisite in epidote solid solutions. For the epidotes encountered in this study the activity model of Bird & Helgeson (1980) yields ideal activities, that is  $a_{\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})}^{\text{Ep}} = X_{\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})}$ .

### Microprobe Analyses

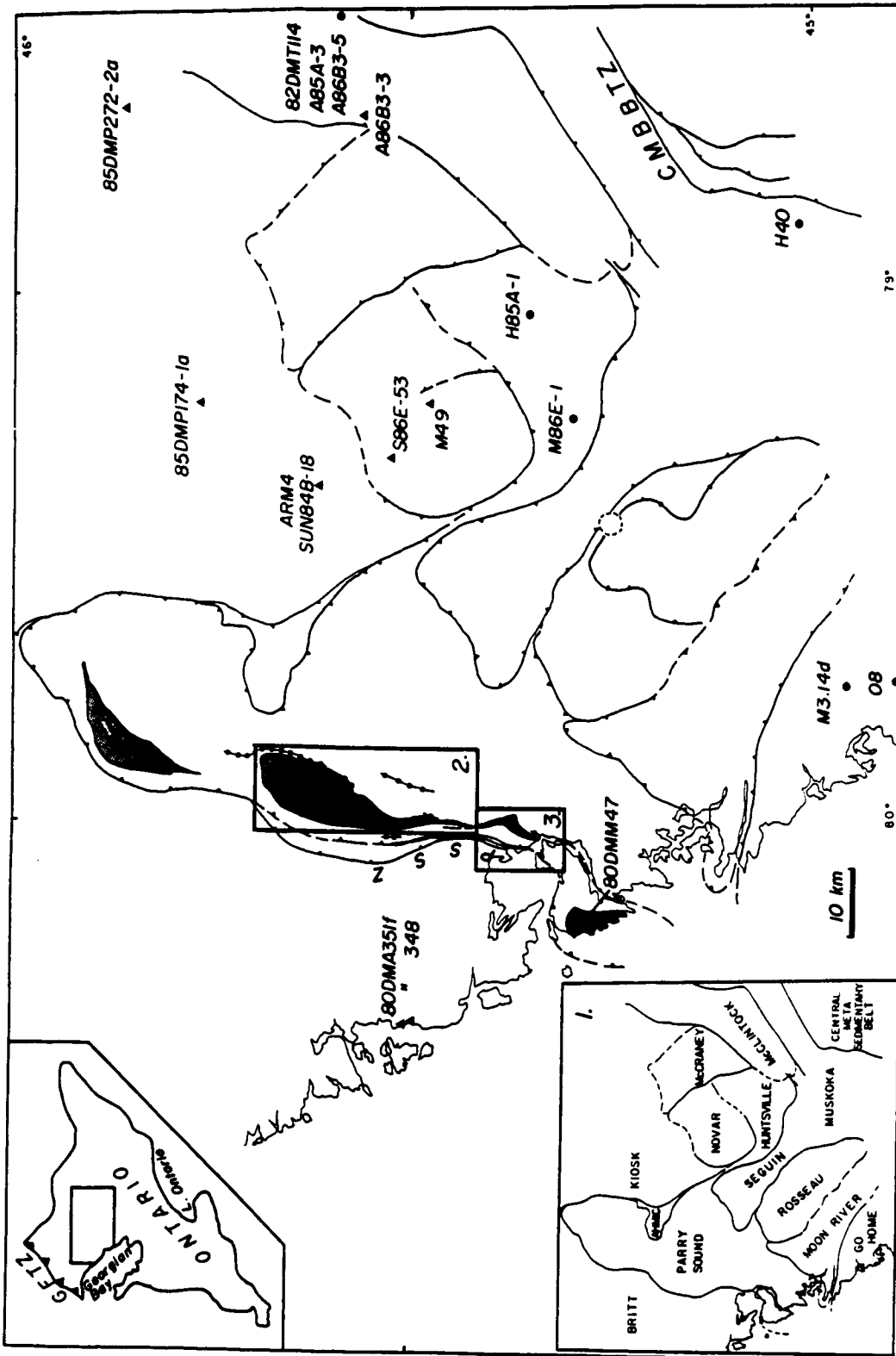
Microprobe analyses of phases for  $\text{CO}_2$  barometry and P-T calculations were obtained on a Cameca CAMEBAX microprobe. All phases were analyzed at an accelerating potential of 15 kV and sample current of 10 nA, using natural or synthetic silicates and oxides. A slightly defocussed or rastered beam was used to analyze plagioclase and scapolite to prevent Na and volatile loss. Core compositions were generally used in the calculation of  $a_{\text{CO}_2}$ , although core and rim analyses were commonly collected to evaluate compositional zonation and its effect on  $a_{\text{CO}_2}$ . Mineral formulae were calculated on the basis of 8 (garnet and epidote), 5 (plagioclase), or 4 (pyroxene) cations, and  $\text{Fe}^{3+}$  was calculated for garnet and pyroxene on the basis of charge balance and stoichiometry. Scapolite formulae were calculated on the basis of  $\text{Si} + \text{Al} = 12$  (Evans *et al.* 1969), and  $\text{CO}_3 + \text{Cl} + \text{SO}_4 = 1.00$ . Mineral analyses are compiled in Appendix 2.

## Application and Interpretation

### Sample Localities and Description

The majority of samples for this study were collected in upper amphibolite to granulite facies gneisses from the Central Gneiss Belt (CGB) of Ontario, a major section of the Grenville Province bounded by the Grenville Front Tectonic Zone (GFTZ) to the northwest and the Central Metasedimentary Belt Boundary Tectonic Zone (CMBBTZ) to the southeast (Figs. 4 and 5). The CGB is comprised of distinct lithotectonic domains which are bounded by km-wide to 100's km long zones of high strain and ductile shearing (Davidson, 1984a, 1984b; Davidson *et al.*, 1979, 1982). The ductile shearing has been dated to have been syn- to slightly post peak-metamorphic (van Breemen *et al.*, 1986). The domains are interpreted to

**Figure 4. Sample localities and lithotectonic domains (inset 1) for southwestern Grenville Province, Ontario. Boxes 2 and 3 outline area of Whitestone Anorthosite (shaded) detailed in Figs. 5 through 7. PSSZ = Parry Sound shear zone.**



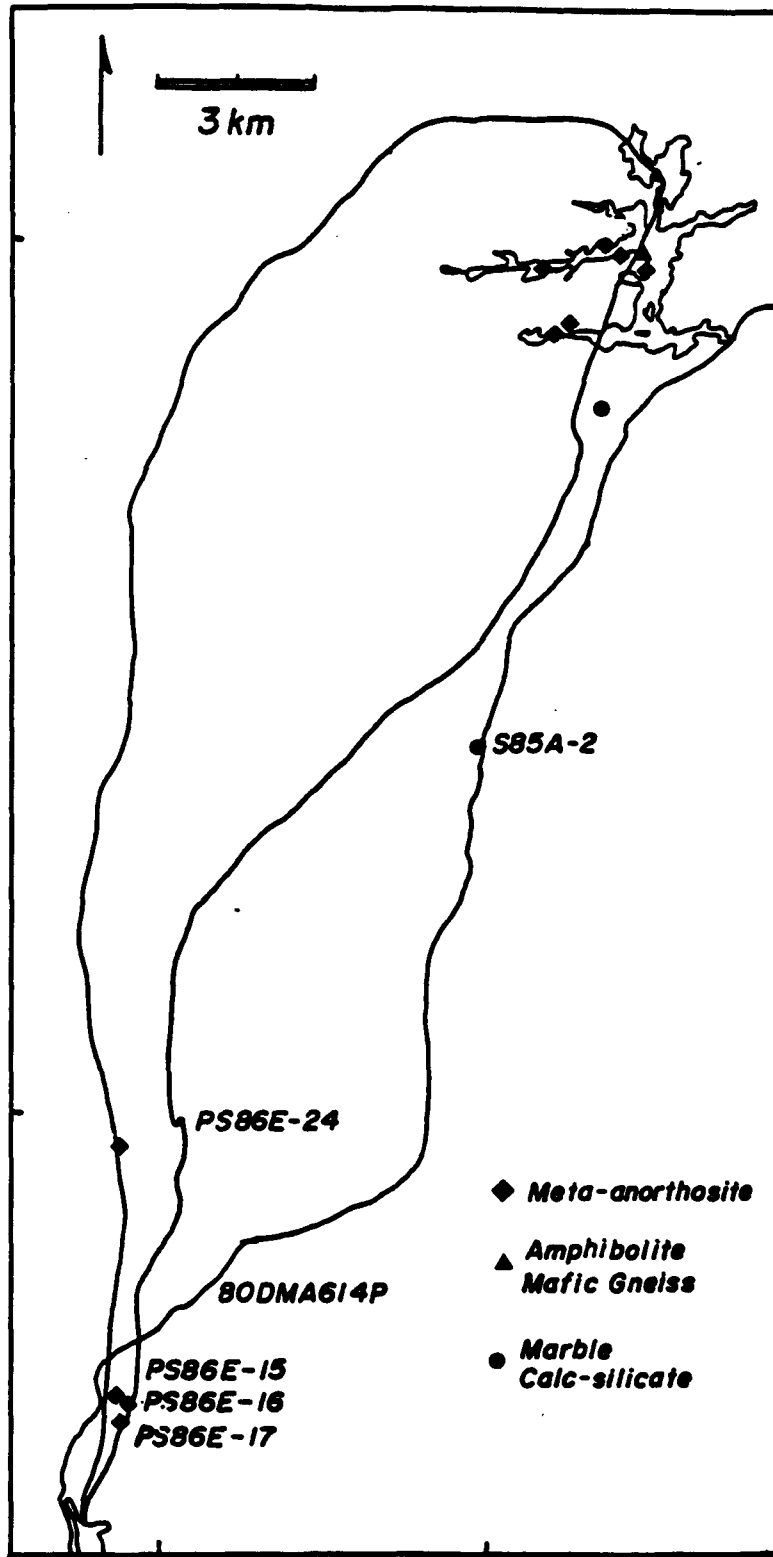
represent large scale segments of deep crust, transported via thrusting toward the northwest during the Grenville Orogeny. Each domain is characteristically of a single, consistent metamorphic grade and each is underlain by lithologies distinct from neighboring domains. Thermobarometric studies have outlined a wide expanse of high pressure rocks within the CGB, with pressures approaching 11 kbar toward the GFTZ and decreasing to 7 kbar toward the CMBBTZ (Anovitz, 1987). Peak temperatures are in excess of 800°C in the vicinity of Parry Sound and decrease to 700°C near the CMBBTZ. The scapolite-bearing lithologies sampled for this study are primarily in granulite facies Parry Sound and McCraney domains of the CGB, (Figs. 4 through 7).

Within the Parry Sound Domain (PSD), scapolite is widely developed in the Whitestone Anorthosite (WSA), a 170 km<sup>2</sup> leucocratic gabbroic anorthosite to anorthositic gabbro sill (Mason, 1969; Nadeau, 1983; Thompson, 1983; Bright, 1987) that was emplaced at approximately 1.35 Ga and underwent granulite facies metamorphism within Parry Sound Domain at approximately 1.15 Ga (van Breemen *et al.*, 1986). Contemporaneous with the waning stages of Grenville metamorphism, the WSA experienced a protracted episode of ductile shearing that was most pervasive within the Parry Sound Shear Zone (PSSZ), which delineates the western boundary of the PSD (Fig. 4). Detailed descriptions of the development of scapolite within the WSA and PSSZ are presented by Mason (1969), Nadeau (1983), and Thompson (1983). An upper amphibolite facies metamorphic aureole is developed within the outer 75% of the WSA, characterized by a modal increase in scapolite, hornblende, epidote and garnet toward the pluton margin. The aureole is developed around a core of relict granulite facies Cpx-Gt-Opx meta-anorthosite. Toward the center of the aureole, where relict igneous textures are preserved (Mason, 1969), scapolite and hornblende are seen to replace and mantle plagioclase and clinopyroxene, and garnet porphyroblasts are commonly embayed and resorbed. In contrast to the core of the WSA, the margin exhibits a foliation concordant to enclosing lithologies, and

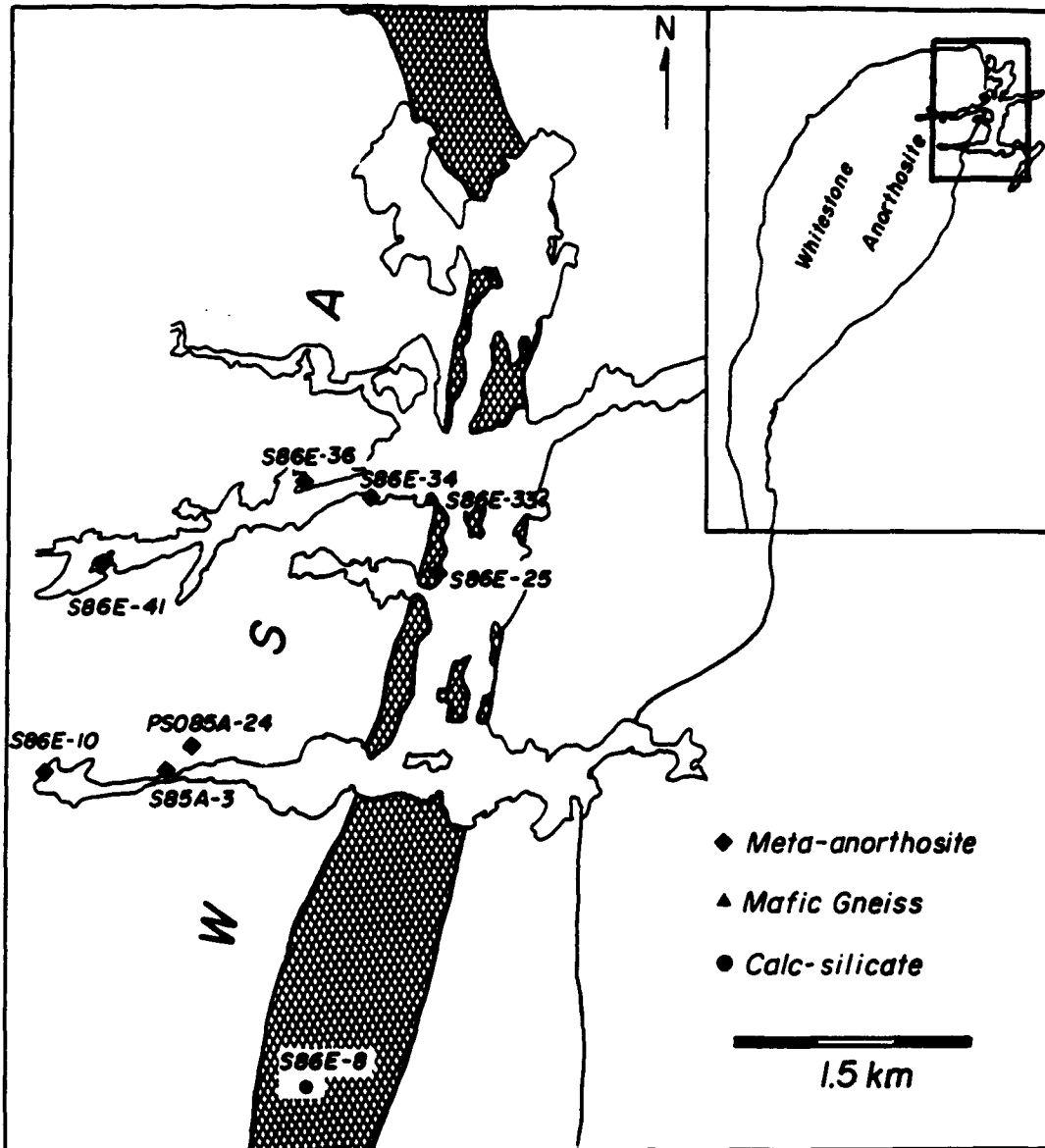


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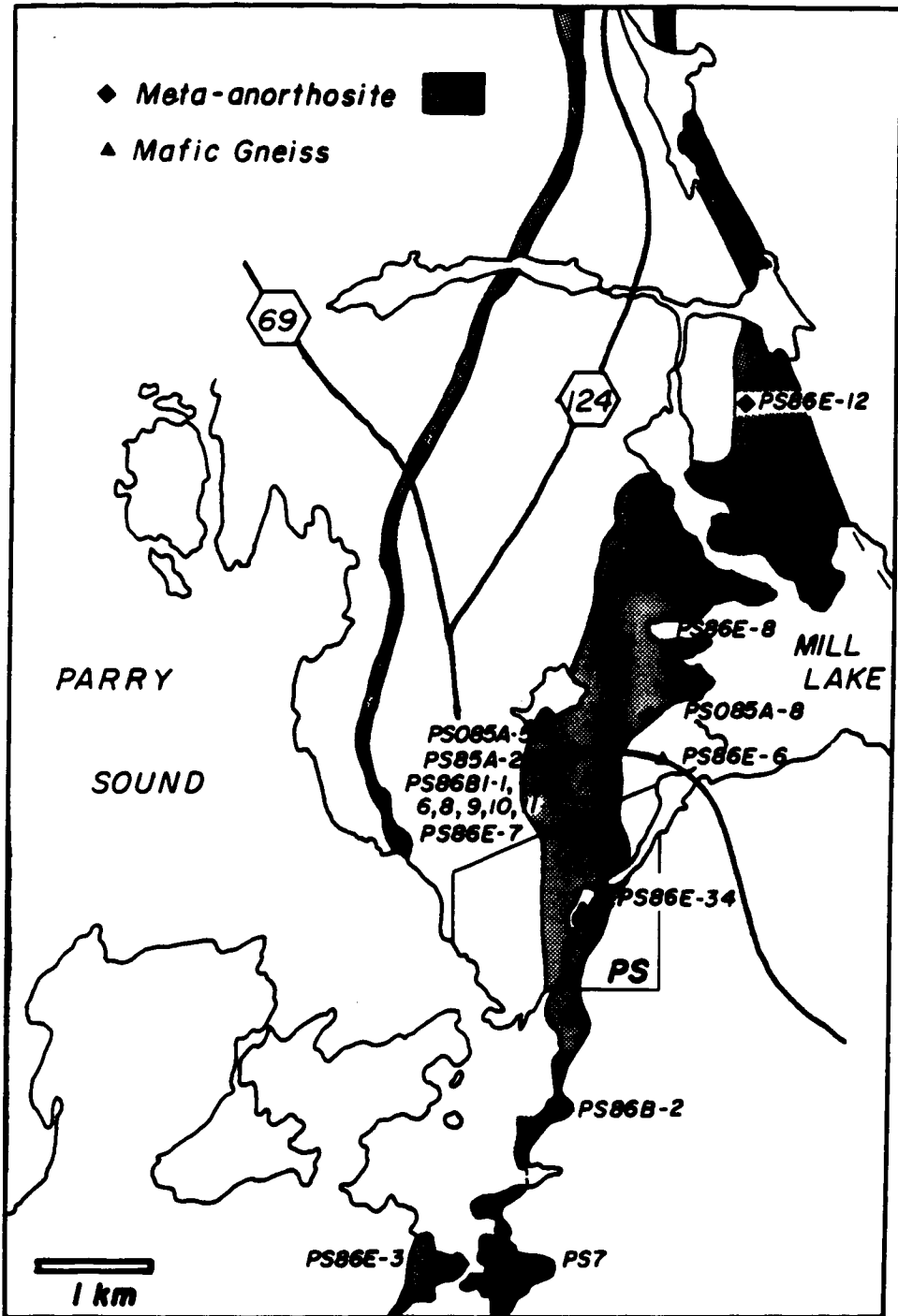
**Figure 5.** Location of samples from main body and southern extension of WSA.



**Figure 6. Detail of sample localities along east margin of WSA adjacent to marble breccia (hatched), in vicinity of Whitestone Lake. Inset outlines area shown in Figure 6.**



**Figure 7.** Detail of sample localities in WSA in vicinity of Parry Sound Shear Zone.  
PS: town of Parry Sound.



Sc-Hbl-Pg-Cpx-Gt mineral assemblages exhibit granuloblastic equilibrium textures. The WSA is in tectonic contact with a marble tectonite breccia on the east, and Gt-Cpx amphibolite on the west. In the southern extension of the WSA where it is intersected by the PSSZ, mineral assemblages are identical to those in the aureole of the anorthosite.

Regional metamorphic temperature for the peak of granulite facies metamorphism in PSD is in excess of 800°C (including Gt-Cpx thermometry, (Anovitz, 1987). However, Gt-Cpx temperatures for gneisses in the aureole, for Gt-Cpx amphibolites along the western margin of the WSA and that bound the PSSZ, and for sheared meta-anorthosite in the PSSZ, range from 650 to 750°C, consistent with movement of the PSSZ and WSA during cooling of the PSD.

Fluid composition was calculated for Sc-Gt-Pg-Qz±Ep±Cc assemblages along the entire length of the WSA, from the eastern margin of the main body to the PSSZ. The range of temperatures calculated from lithologies within the variably tectonized western margin of PSD make precise CO<sub>2</sub> barometry difficult for this area. The western PSD was probably a dynamic system during scapolite formation in the WSA. As ductile shearing proceeded during cooling of the PSD, it is likely that retrograde diffusion continued to varying degrees, which would account for the range of Gt-Cpx temperatures calculated for this area.

Sulfate-bearing carbonate scapolite was identified in mafic garnet-clinopyroxene gneisses, mafic garnet granulites *sensu strictu* (containing orthopyroxene and generally with clinopyroxene), and garnet-amphibolites from Algonquin and Parry Sound Domains of the CGB. The amphibolites are distinguished from the mafic gneisses by the preponderance of hornblende over other mafic phases, and often by the presence of biotite. The mafic gneisses are generally Pg-Cpx-Gt-Sc assemblages with 5 to 10% hornblende and lacking biotite.

Carbonate-rich scapolite with up to 20 mol% Cl occurs in high grade calc-silicates with any or all of grossular-rich garnet, calcic plagioclase, salitic

clinopyroxene, epidote, wollastonite, quartz, titanite, and calcite. Calc-silicate lithologies usually occur as conformable units interlayered with pelitic or mafic gneisses. Equilibrium textures and equilibrium compositional relations are common among the phases in such units.

Samples of scapolite-bearing granulites and mafic gneisses, collected and donated by other workers or taken from the literature, were also analyzed. Microprobe analyses of samples donated for CO<sub>2</sub> barometry and thermobarometry were obtained at the University of Michigan. Samples usually contained mineral assemblages that allowed calculation of P and T using Gt-Cpx thermometry and Cpx-Opx-Gt-Pg-Qz barometry.

## Grenville Province

### Granulites, Mafic Gneisses and Amphibolites

Values of  $a_{\text{CO}_2}$  average range 0.09 to 0.68 (Table 1, Fig. 8) for the granulites and mafic gneisses. The garnet amphibolites are from widely separated localities and yield a range of values: 0.05 to 0.97. ARM 4 and SUN84B-18 are two samples from the same outcrop in the Kiosk domain that yield essentially the same  $a_{\text{CO}_2}$  (average 0.85), high values for a lithology that might be expected to be relatively hydrous. Unfortunately the samples do not contain mineral assemblages for which  $a_{\text{H}_2\text{O}}$  could be calculated. The third sample is from Parry Sound Domain, and in contrast to the previous amphibolites, yields comparatively low  $a_{\text{CO}_2}$  (0.09).

For the granulites it would appear that  $P_{\text{Fluid}} < P_{\text{Total}}$  if  $a_{\text{H}_2\text{O}}$  is correspondingly low, as has been calculated for many granulites and charnockites. Although CO<sub>2</sub> may have a finite activity in these samples, it certainly does not have a high enough activity to yield a partial pressure that would be equal to  $P_{\text{Total}} - p_{\text{H}_2\text{O}}$  assuming  $a_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}$  is low (approximately less than 0.5)



TABLE 1. P, T, Mineral compositions, calculated component activities, and CO<sub>2</sub> activities for granulites and gneisses calculated from Reaction 7. 1: equilibrium constant for Reaction 7 relative to standard state for CO<sub>2</sub> at P and T of interest, used to calculate aCO<sub>2</sub>. 2: equilibrium constant for Reaction 7 relative to 1 bar, T standard state used to calculate fCO<sub>2</sub>. 3: activity of meionite calculated from scapolite activity model in Chapter III, reduced by factor I<sub>CO<sub>3</sub></sub> (see text). \* = grain to grain variability in any one or all of plagioclase, scapolite, or garnet.

SAMPLE	P	T°C	K <sup>1</sup>	logK <sub>f</sub> <sup>2</sup>	I <sub>An</sub>	Eq <sub>An</sub>	I <sub>CO<sub>3</sub></sub>	I <sub>Gr</sub>	a <sub>An</sub>	a <sub>Me</sub>	a <sub>Me</sub> <sup>3</sup>	a <sub>Gr</sub>	a <sub>CO<sub>2</sub></sub>	logfCO <sub>2</sub>	P	CO <sub>2</sub>
Southwestern Grenville Province																
Granulites (G), Mafic Gneisses (M), Amphibolites (A)																
80DMA614p(G)	10	800	0.2455	5.076	0.510	0.643	0.45	0.187	0.628	0.775	0.351	0.220	0.23	4.749	2314	
85DMP272-2a(G)	11	800	0.2489	5.245	0.415	0.619	0.45	0.208	0.540	0.753	0.338	0.263	0.22	4.898	3031	
85DMP174-1a(M)	11	800	0.2544	5.245	0.314	0.565	0.52	0.201	0.409	0.695	0.362	0.243	0.68	5.373	9053	
S86E-53a(M)	10	800	0.2455	5.076	0.394	0.597	0.51	0.275	0.515	0.731	0.371	0.327	0.26	4.801	2608	
A86B3-3B-3(G)	10	800	0.2455	5.076	0.443	0.612	0.34	0.129	0.570	0.747	0.256	0.156	0.14	4.530	1397	
M49(M)	10	800	0.2455	5.076	0.419	0.617	0.50	0.440	0.544	0.751	0.377	0.483	0.14	4.516	1353	
80DMA348c(A)	10	800	0.2455	5.076	0.407	0.607	0.39	0.288	0.531	0.741	0.291	0.337	0.09	4.325	872	
ARM4(A)	10	800	0.2455	5.076	0.413	0.579	0.68	0.254	0.537	0.711	0.480	0.305	0.74	5.249	7317	
SUN64B-18(A)	10	750	0.3532	5.206	0.365	0.584	0.76	0.239	0.504	0.591	0.449	0.267	0.97	5.417	9594	
Calc-silicates																
A85A-3b	10	800	0.2455	5.076	0.713	0.694	0.980	0.372	0.733	0.814	0.798	0.444	1.47	5.549	13559	
A85A-3a*	10	800	0.2455	5.076	0.680	0.669	0.980	0.355	0.720	0.798	0.780	0.433	1.47	5.548	13526	
	10	800	0.2455	5.076	0.840	0.669	0.980	0.355	0.840	0.798	0.780	0.433	1.00	5.380	9185	

TABLE 1, continued

SAMPLE	P	T°C	K <sup>1</sup>	logK <sub>f</sub> <sup>2</sup>	I <sub>An</sub>	EqAn	I <sub>CO<sub>3</sub></sub>	I <sub>Gr</sub>	a <sub>An</sub>	a <sub>Me</sub>	a <sub>Me</sub> <sup>3</sup>	a <sub>Gr</sub>	a <sub>CO<sub>2</sub></sub>	logf <sub>CO<sub>2</sub></sub>	P <sub>CO<sub>2</sub></sub>
H85A-1b	10	750	0.3532	5.208	0.724	0.686	0.989	0.710	0.750	0.709	0.701	0.617	0.61	5.216	6040
H85A-1d-1	10	750	0.3532	5.208	0.676	0.708	0.978	0.833	0.733	0.730	0.714	0.741	0.53	5.153	5224
H85A-1e(2)	10	750	0.3532	5.208	0.513	0.659	0.964	0.817	0.654	0.679	0.655	0.771	0.47	5.099	4613
H85A-1e(1)	10	750	0.3532	5.208	0.441	0.649	0.988	0.809	0.593	0.668	0.660	0.639	0.82	5.344	8110
M86E-1c-2	10	750	0.3532	5.208	0.280	0.598	0.885	0.984	0.378	0.608	0.526	0.930	0.58	5.192	5715
M86E-1b	10	750	0.3532	5.208	0.253	0.502	0.702	0.972	0.335	0.483	0.339	0.921	0.14	4.571	1368
O8e	10	750	0.3532	5.208	0.513	0.661	0.906	0.838	0.654	0.682	0.618	0.816	0.34	4.962	3365
S85A-2a	10	750	0.3532	5.208	0.390	0.621	0.933	0.946	0.536	0.636	0.593	0.846	0.45	5.084	4457
S85A-2b	10	750	0.3532	5.208	0.285	0.596	0.844	0.952	0.386	0.606	0.511	0.871	0.54	5.163	5346
S85A-2d	10	750	0.3532	5.208	0.395	0.601	0.868	0.925	0.542	0.612	0.531	0.862	0.27	4.867	2704
S86E-8c	10	700	0.5200	5.344	0.315	0.598	0.895	0.542	0.459	0.495	0.443	0.650	0.37	4.767	4188
Meta-anorthosite															
PS7a	10	700	0.5200	5.344	0.485	0.661	0.939	0.324	0.662	0.579	0.544	0.396	0.71	5.338	7051
PS7b	10	700	0.5200	5.344	0.440	0.668	0.898	0.340	0.622	0.589	0.529	0.435	0.65	5.296	6401
PS7c	10	700	0.5200	5.344	0.433	0.653	0.979	0.340	0.615	0.569	0.557	0.433	0.82	5.404	8208
PS85A-2c	10	700	0.5200	5.344	0.573	0.638	0.977	0.340	0.714	0.548	0.536	0.417	0.51	5.195	5073
PS085A-5*	10	700	0.5200	5.344	0.363	0.568	0.834	0.267	0.530	0.456	0.381	0.317	0.41	5.102	4095
	10	700	0.5200	5.344	0.363	0.612	0.914	0.267	0.530	0.514	0.470	0.317	0.96	5.468	9511

TABLE 1, continued

SAMPLE	P	T°C	K <sup>1</sup>	logK <sub>f</sub> <sup>2</sup>	I <sub>An</sub>	EqAn	I <sub>CO<sub>3</sub></sub>	I <sub>Gr</sub>	a <sub>An</sub>	a <sub>Me</sub>	a <sub>Me</sub> <sup>3</sup>	a <sub>Gr</sub>	a <sub>CO<sub>2</sub></sub>	logf <sub>CO<sub>2</sub></sub>	P <sub>CO<sub>2</sub></sub>
PS865A-8b	10	700	0.5200	5.344	0.466	0.639	0.884	0.328	0.646	0.550	0.486	0.395	0.48	5.170	4789
PS865A-13	10	700	0.5200	5.344	0.410	0.656	0.988	0.365	0.590	0.573	0.566	0.443	0.94	5.458	9294
PS865A-24	10	700	0.5200	5.344	0.538	0.651	0.841	0.252	0.697	0.565	0.476	0.310	0.53	5.209	5239
PS86B1-1	10	700	0.5200	5.344	0.375	0.611	0.932	0.339	0.546	0.513	0.478	0.430	0.60	5.267	5987
PS86B1-11''	10	700	0.5200	5.344	0.502	0.649	0.961	0.286	0.674	0.563	0.541	0.343	0.82	5.402	8170
PS86B2-1	10	700	0.5200	5.344	0.397	0.571	0.873	0.339	0.575	0.460	0.402	0.419	0.28	4.928	2743
PS86B2-3	10	700	0.5200	5.344	0.466	0.634	0.867	0.325	0.646	0.543	0.471	0.399	0.42	5.108	4152
PS86E-7e	10	700	0.5200	5.344	0.445	0.650	0.963	0.356	0.627	0.565	0.544	0.439	0.70	5.329	6906
PS86E-8	10	700	0.5200	5.344	0.478	0.657	0.879	0.351	0.656	0.574	0.504	0.422	0.49	5.174	4833
PS86E-15	10	700	0.5200	5.344	0.510	0.605	0.828	0.310	0.680	0.505	0.418	0.373	0.25	4.890	2513
PS86E-16a	10	700	0.5200	5.344	0.536	0.659	0.932	0.295	0.696	0.576	0.537	0.358	0.69	5.327	6874
PS86E-24f	10	700	0.5200	5.344	0.478	0.635	0.814	0.323	0.656	0.544	0.443	0.396	0.32	4.991	3171
PS86E-31	10	700	0.5200	5.344	0.424	0.621	0.956	0.367	0.605	0.526	0.503	0.465	0.51	5.193	5049
PS86E-34	10	700	0.5200	5.344	0.374	0.586	0.826	0.285	0.545	0.480	0.396	0.340	0.41	5.096	4039
S85A-3a(C)	10	700	0.5200	5.344	0.594	0.607	0.825	0.150	0.723	0.507	0.418	0.211	0.51	5.196	5084
S85A-3a(R)	10	700	0.5200	5.344	0.566	0.606	0.837	0.204	0.711	0.506	0.423	0.278	0.37	5.053	3658
S85A-3b(C)	10	700	0.5200	5.344	0.560	0.651	0.976	0.259	0.708	0.566	0.553	0.317	0.89	5.437	8856
S85A-3b(R)	10	700	0.5200	5.344	0.560	0.651	0.976	0.304	0.708	0.566	0.553	0.374	0.70	5.329	6906

TABLE 1, continued

SAMPLE	P	T°C	K <sup>1</sup>	logK <sub>f</sub> <sup>2</sup>	X <sub>An</sub>	EqAn	X <sub>CO3</sub>	X <sub>Gr</sub>	a <sub>An</sub>	a <sub>Me</sub>	a <sub>Me</sub> <sup>3</sup>	a <sub>Gr</sub>	a <sub>CO2</sub>	logf CO <sub>2</sub>	P CO <sub>2</sub>
S85A-3c-1(C)	10	700	0.5200	5.344	0.557	0.677	0.968	0.175	0.707	0.601	0.582	0.215	1.97	5.781	19553
S85A-3c-1(R)	10	700	0.5200	5.344	0.557	0.677	0.968	0.232	0.707	0.601	0.582	0.279	1.33	5.611	13220
S86E-25a	10	700	0.5200	5.344	0.522	0.652	0.940	0.311	0.688	0.567	0.533	0.374	0.65	5.299	6445
S86E-25c(C)	10	700	0.5200	5.344	0.456	0.651	0.946	0.304	0.637	0.566	0.535	0.368	0.82	5.399	8114
S86E-34	10	700	0.5200	5.344	0.472	0.626	0.829	0.292	0.651	0.532	0.441	0.558	0.19	4.769	1902
S86E-36b	10	700	0.5200	5.344	0.496	0.635	0.903	0.288	0.670	0.544	0.492	0.346	0.56	5.237	5588
S86E-41	10	700	0.5200	5.344	0.573	0.661	0.997	0.221	0.714	0.579	0.578	0.272	1.31	5.605	13038

Furua Complex, Tanzania (Coolen, 1983). All granulites except 1 = calc-silicate and 2 = amphibolite.

MF-283.2	10	800	0.2455	5.076	0.323	0.583	0.35	0.174	0.422	0.716	0.251	0.207	0.18	4.637	1788
MF-288.1	10	800	0.2455	5.076	0.322	0.581	0.44	0.171	0.420	0.714	0.312	0.206	0.44	5.024	4358
MF-283.1	10	800	0.2455	5.076	0.339	0.589	0.33	0.174	0.444	0.722	0.240	0.209	0.13	4.497	1295
WE-322.3	10	800	0.2455	5.076	0.405	0.629	0.46	0.174	0.528	0.762	0.351	0.212	0.38	4.960	3761
ZC-8	10	800	0.2455	5.076	0.340	0.564	0.41	0.176	0.446	0.694	0.287	0.214	0.26	4.791	2549
MF-266.3	10	800	0.2455	5.076	0.306	0.552	0.29	0.163	0.397	0.679	0.195	0.196	0.08	4.301	825
C-247.1	10	800	0.2455	5.076	0.327	0.542	0.39	0.173	0.427	0.667	0.258	0.196	0.21	4.707	2101
C-112	10	800	0.2455	5.076	0.327	0.539	0.40	0.179	0.427	0.663	0.268	0.213	0.22	4.719	2159
C-311.1	10	800	0.2455	5.076	0.352	0.578	0.33	0.177	0.462	0.710	0.233	0.213	0.10	4.393	1019

TABLE 1. continued

SAMPLE	P	T°C	K <sup>1</sup>	logK <sub>f</sub> <sup>2</sup>	$\lambda_{An}$	EqAn	$\lambda_{CO_3}$	$\lambda_{Gr}$	aAn	aMe	aMe <sup>3</sup>	aGr	aCO <sub>2</sub>	logfCO <sub>2</sub>	P CO <sub>2</sub>
SC-157	10	800	0.2455	5.076	0.330	0.545	0.40	0.171	0.432	0.670	0.268	0.217	0.21	4.697	2053
C-54.1	10	800	0.2455	5.076	0.277	0.531	0.36	0.170	0.353	0.652	0.232	0.213	0.20	4.675	1951
C-52.2	10	800	0.2455	5.076	0.276	0.565	0.31	0.186	0.352	0.695	0.218	0.211	0.16	4.579	1564
SC-156.1	10	800	0.2455	5.076	0.304	0.579	0.35	0.198	0.394	0.711	0.246	0.224	0.18	4.626	1743
C-57	10	800	0.2455	5.076	0.351	0.540	0.29	0.181	0.461	0.664	0.190	0.249	0.04	3.937	357
C-217	10	800	0.2455	5.076	0.286	0.566	0.40	0.188	0.367	0.696	0.276	0.236	0.31	4.872	3071
C-180.1	10	800	0.2455	5.076	0.334	0.557	0.37	0.166	0.438	0.687	0.254	0.207	0.16	4.590	1604
ZC-6.2 <sup>1</sup>	10	800	0.2455	5.076	0.337	0.567	0.22	0.844	0.441	0.697	0.156	0.220	0.02	3.726	219
MF-274.2 <sup>1</sup>	10	800	0.2455	5.076	0.981	0.781	0.45	0.848	0.961	0.864	0.392	0.695	0.02	3.732	222
C-42.1 <sup>2</sup>	10	700	0.5200	5.076	0.425	0.555	0.56	0.223	0.606	0.440	0.247	0.268	0.07	4.049	429

BERGEN ARCS, NORWAY (Austreim, pers. comm., 1987) All granulite facies meta-anorthosite.

HA10/83 11.5 900 0.1253 5.069 0.502 0.626 0.551 0.150 0.582 1.020 0.562 0.233 1.22 5.606 12017

HA54/83 12 900 0.1268 5.146 0.500 0.629 0.365 0.173 0.580 1.021 0.373 0.242 0.22 4.946 2295

HA46/85 14.5 900 0.1536 5.526 0.322 0.525 0.375 0.154 0.383 0.953 0.357 0.205 0.76 5.813 10780

HA53/80 14.5 900 0.1536 5.526 0.307 0.555 0.309 0.150 0.362 0.984 0.304 0.204 0.46 5.596 6535

SARGUR TERRANE, INDIA (Devaraju, pers. comm., 1987) Granulites (33A, 39) and calc-silicates (5, 25)

TC033A 10 800 0.2455 5.076 0.369 0.584 0.433 0.173 0.485 0.717 0.311 0.217 0.28 4.828 2775

TC039 10 800 0.2455 5.076 0.379 0.610 0.413 0.169 0.497 0.744 0.307 0.217 0.25 4.781 2491

TABLE 1, continued

SAMPLE	P	T°C	K <sup>1</sup>	logK <sub>f</sub> <sup>2</sup>	X <sub>An</sub>	EqAn	X <sub>CO3</sub>	X <sub>Gr</sub>	a <sub>An</sub>	a <sub>Me</sub>	a <sub>Me</sub> <sup>3</sup>	a <sub>Gr</sub>	a <sub>CO2</sub>	logf <sub>CO2</sub>	P <sub>CO2</sub>
TCD5	10	800	0.2455	5.076	0.945	0.739	0.989	0.894	0.945	0.842	0.833	0.596	0.60	5.157	5920
TCD25	10	800	0.2455	5.076	0.927	0.764	0.983	0.902	0.927	0.856	0.841	0.612	0.63	5.179	6228
Devaraju & Coolen (1983) Granulite															
K21	10	800	0.2455	5.076	0.386	0.601	0.342	0.168	0.506	0.735	0.251	0.216	0.11	4.417	1077
Srikantappa (pers. comm., 1988) Granulite															
285	10	800	0.2455	5.076	0.380	0.574	0.38	0.158	0.498	0.706	0.268	0.209	0.15	4.566	1518
New South Wales (Wilkinson, 1973) Gt-Cpx-Pg-Hbl-Sc xenolith															
R30241	14	850	0.2109	5.594	0.378	0.599	0.545	0.243	0.474	0.868	0.473	0.298	0.92	5.894	12880
LASHAINE, TANZANIA (Jones et al., 1983) GA = Gt anorthosite, GPC = Gt-Pg-clinopyroxenite															
533 GA	14	800	0.3119	5.7485	0.419	0.681	0.985	0.307	0.544	0.805	0.793	0.370	4.50	6.655	48402
526 GPC	14	800	0.3119	5.7485	0.290	0.550	0.546	0.233	0.374	0.677	0.370	0.321	0.67	5.828	7215
528* GPC	14	800	0.3119	5.7485	0.326	0.611	0.611	0.275	0.426	0.745	0.455	0.352	0.97	5.987	10385
727a GPC	14	800	0.3119	5.7485	0.480	0.611	0.611	0.275	0.604	0.745	0.455	0.352	0.40	5.608	4345
798* GPC	14	800	0.3119	5.7485	0.347	0.621	0.944	0.227	0.455	0.755	0.712	0.304	6.14	6.790	66008
	14	800	0.3119	5.7485	0.347	0.608	0.778	0.227	0.455	0.740	0.576	0.304	2.62	6.420	28188
EIFEL, W. GERMANY (Okrusch et al. 1979) Granulite															
AS-K-3	10	850	0.1741	4.9545	0.702	0.718	0.592	0.196	0.717	0.919	0.544	0.243	0.70	5.178	6913
	10	850	0.1741	4.9545	0.537	0.718	0.592	0.196	0.627	0.919	0.544	0.243	0.98	5.324	9676

TABLE 1. continued

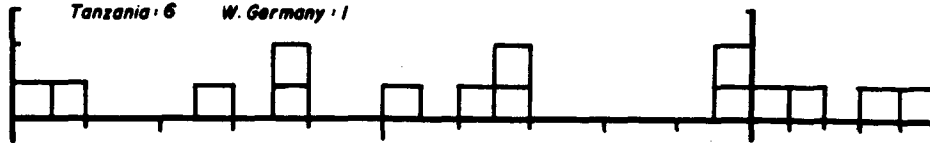
SAMPLE	P	T°C	K <sup>1</sup>	logK <sub>f</sub> <sup>2</sup>	X <sub>An</sub>	EqAn	X <sub>CO<sub>3</sub></sub>	X <sub>Gr</sub>	a <sub>An</sub>	a <sub>Me</sub>	a <sub>Me</sub> <sup>3</sup>	a <sub>Gr</sub>	a <sub>CO<sub>2</sub></sub>	logf <sub>CO<sub>2</sub></sub>	P	f <sub>CO<sub>2</sub></sub>
LESOITHO (Griffin et al.), 1978) All granulites or mafic gneisses																
K-2	10	800	0.2455	5.076	0.200	0.627	0.604	0.213	0.234	0.760	0.459	0.310	4.82	6.064	47789	
PHN2852	10	800	0.2455	5.076	0.190	0.568	0.443	0.165	0.219	0.698	0.309	0.244	1.68	5.606	16647	
PHN1670	10	800	0.2455	5.076	0.230	0.459	0.428	0.166	0.281	0.546	0.234	0.264	0.26	4.798	2590	
PHN3017	10	800	0.2455	5.076	0.270	0.408	0.176	0.233	0.343	0.461	0.081	0.295	0.00	2.672	19	
L-12A	10	800	0.2455	5.076	0.190	0.392	0.352	0.199	0.219	0.434	0.153	0.283	0.08	4.284	793	
LQ-2	10	800	0.2455	5.076	0.320	0.533	0.55	0.174	0.417	0.654	0.360	0.275	0.51	5.090	5074	
LT-2	10	800	0.2455	5.076	0.270	0.506	0.443	0.163	0.343	0.618	0.274	0.218	0.40	4.982	3967	

**Figure 8.** Histogram summarizing results of calculations of  $a_{\text{CO}_2}$  as a function of lithology and setting, including values that exceed unity.



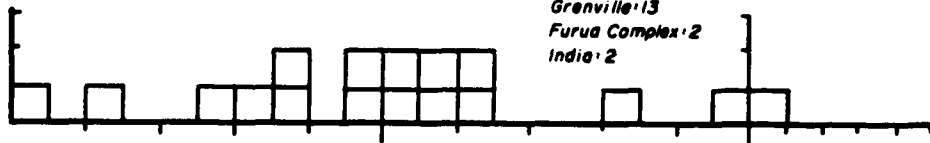
**Xenoliths**

Lesotho: 7      New S. Wales: 1  
Tanzania: 6      W. Germany: 1



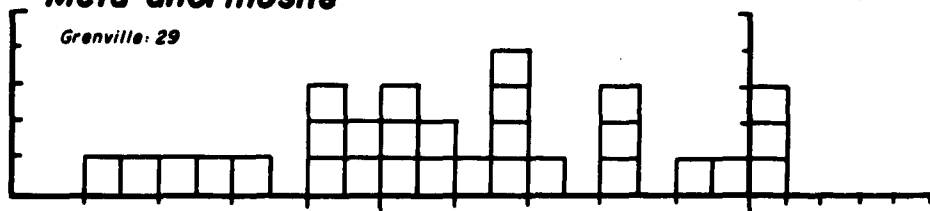
**Calc-silicate**

Grenville: 13  
Furua Complex: 2  
India: 2



**Meta-anorthosite**

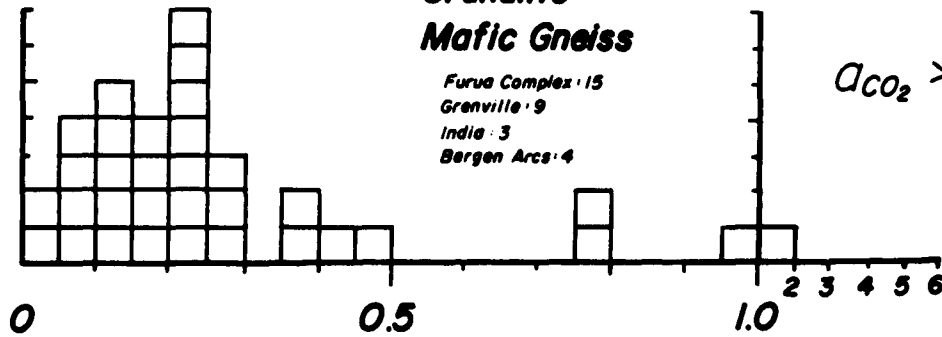
Grenville: 29



**Granulite  
Mafic Gneiss**

Furua Complex: 15  
Grenville: 9  
India: 3  
Bergen Arcs: 4

$a_{CO_2} > 1$



No. Observations

0      0.5      1.0      2      3      4      5      6  
 $a_{CO_2}$

## Whitestone meta-anorthosite

The calculation of  $a_{\text{CO}_2}$  for scapolite bearing samples of the WSA was done at 650, 700, and 750°C. Most of the temperatures are in the range 675 to 700°C, and therefore only the results of calculations at 700°C are summarized in Table 1. For some of these samples, an  $a_{\text{CO}_2} > 1.0$  was obtained at temperatures above 700°C. The highest value of  $a_{\text{CO}_2}$  was calculated for sample S86E-41 (1.3), in which secondary scapolite and hornblende after plagioclase, clinopyroxene, and garnet are extensively developed. As with other samples of WSA with late scapolite, garnet in this sample is depleted in grossular component relative to those exhibiting equilibrium textures and values of  $a_{\text{CO}_2} < 1.0$  (Table 1). The high  $a_{\text{CO}_2}$  is a manifestation of the retrograde disequilibrium. The results at 700°C are considered the most reasonable estimates of fluid activity for the aureole of the WSA and WSA in the PSSZ. Geobarometry in the same area indicates that pressure was  $10 \pm 1$  kbar during ductile shearing and tectonic displacement (Chapter II), essentially the same as peak regional P.

In general, Sc-Gt-Pg-Qz equilibria indicate that  $a_{\text{CO}_2}$  was in the range 0.2 to 0.8 in the WSA aureole and in sheared WSA (Table 1, Fig. 8), with the majority of samples exceeding 0.5. Using Reaction 8 calculation of  $a_{\text{CO}_2}$  for samples that are primarily from the PSSZ yields a similar range (Table 2). The samples of WSA represent a suite of lithologically similar rocks with limited mineral chemistry from the same tectonic setting. The range of activities and partial pressures is likely to mainly represent inherent imprecision in the calculation due to the limited chemical variation. Temperature imprecision is also a likely source for the range of  $a_{\text{CO}_2}$ . Where appropriate mineral assemblages were present, calculations of  $a_{\text{H}_2\text{O}}$  (Table 3) were performed using Reaction 9. A range of  $a_{\text{H}_2\text{O}}$  are obtained and indicate local fluid-present conditions, and that the fluid was a mixed H<sub>2</sub>O-CO<sub>2</sub> fluid with CO<sub>2</sub> the dominant fluid component in the scapolite-bearing meta-anorthosite. Although the

TABLE 2. CO<sub>2</sub> activities for calc-silicate (C), meta-anorthosite (MA) and mafic gneisses (MG) from Parry Sound Domain calculated from Reaction 8 (An + 2Cc + Qz = Gr + 2CO<sub>2</sub>).

SAMPLE	P	T°C	logK <sup>1</sup>	logK <sub>f</sub> <sup>2</sup>	I <sub>An</sub>	I <sub>Gr</sub>	a <sub>An</sub>	a <sub>Gr</sub>	a <sub>CO<sub>2</sub></sub>	logf <sub>CO<sub>2</sub></sub>	P <sub>CO<sub>2</sub></sub>
M86E-1c-2 (C)	10	750	-1.212	9.650	0.280	0.964	0.378	0.930	0.17	4.661	1683
M86E-1b (C)	10	750	-1.212	9.650	0.253	0.972	0.335	0.921	0.16	4.641	1607
08e (C)	10	750	-1.212	9.650	0.513	0.838	0.654	0.816	0.27	4.865	2693
S86E-8c (C)	10	700	-1.437	9.536	0.315	0.542	0.459	0.650	0.25	4.880	2456
PS86B1-6 (MA)	10	700	-1.437	9.536	0.151	0.280	0.182	0.397	0.33	5.000	3238
PS86B1-9b (MA)	10	700	-1.437	9.536	0.156	0.280	0.190	0.345	0.41	5.101	4055
PS86B1-8 (MA)	10	700	-1.437	9.536	0.151	0.280	0.182	0.264	0.60	5.266	5973
PS86E-6b (MG)	10	700	-1.437	9.536	0.331	0.333	0.484	0.404	0.52	5.200	5131
PS86E-31 (MA)	10	700	-1.437	9.536	0.424	0.367	0.605	0.465	0.47	5.157	4648
S86E-33 (MA)	10	700	-1.437	9.536	0.152	0.205	0.184	0.226	0.77	5.370	7590

1: log<sub>10</sub>K relative to standard state of CO<sub>2</sub> at P and T of interest, used to calculate a<sub>H<sub>2</sub>O</sub>.

2: log<sub>10</sub>K relative to standard state of CO<sub>2</sub> at 1 bar, T, used to calculate f<sub>H<sub>2</sub>O</sub>.

TABLE 3.  $H_2O$  activities and fugacities for meta-anorthosite calculated from Reaction 9  
( $4Czo + Qz = 5An + Gr + H_2O$ ).

Sample	P	T°C	$\log K^1$	$\log K_f^2$	$X_{An}$	$X_{Ps}$	$X_{Gr}$	$a_{An}$	$a_{Czo}$	$a_{Gr}$	$a_{H_2O}$	$\log f_{H_2O}$	$P_{H_2O}$
PS85A-2c	10	700	-1.425	6.887	0.573	0.195	0.340	0.714	0.415	0.417	0.29	3.614	2871
PS86B1-11''	10	700	-1.425	6.887	0.502	0.200	0.286	0.674	0.399	0.343	0.41	3.770	4112
PS86E-7e	10	700	-1.425	6.887	0.445	0.201	0.356	0.627	0.397	0.439	0.34	3.685	3381
PS86E-8	10	700	-1.425	6.887	0.478	0.218	0.351	0.656	0.346	0.422	0.24	3.542	2433
PS86E-12	10	700	-1.425	6.887	0.492	0.199	0.381	0.667	0.402	0.404	0.33	3.681	3350
PS86E-15	10	700	-1.425	6.887	0.510	0.193	0.310	0.680	0.420	0.373	0.40	3.753	3794
PS86E-16a	10	700	-1.425	6.887	0.536	0.215	0.295	0.696	0.357	0.358	0.28	3.610	2845
PS86E-17	11	700	-2.051	6.600	0.545	0.210	0.335	0.701	0.370	0.456	0.10	3.333	1277
PS86E-24f	10	700	-1.425	6.887	0.478	0.193	0.323	0.656	0.420	0.396	0.39	3.751	3936
S86E-25a	10	700	-1.425	6.887	0.522	0.169	0.311	0.688	0.493	0.374	0.53	3.877	5261
PS86E-31	10	700	-1.425	6.887	0.424	0.214	0.367	0.605	0.358	0.465	0.27	3.595	2748

1:  $\log_{10}K$  relative to standard state of  $H_2O$  at P and T of interest.

2:  $\log_{10}K$  relative to standard state of  $H_2O$  at 1 bar, T.

precision of these calculations are low, fluid present conditions are likely in some of the samples (Table 4), where  $P_{\text{CO}_2} + P_{\text{H}_2\text{O}}$  is within 1 kbar of  $P_{\text{Total}}$  at 700°C.

#### Calc-silicates

The calc-silicates generally yield intermediate to high  $a_{\text{CO}_2}$  (Table 1). Four samples from a two meter thick calc-silicate lens in which the scapolite, plagioclase, and garnet exhibit variable composition (H85A-1 sample series) shows the range of values obtained as a result of variable mineral chemistry at constant P and T (0.47 to 0.82). The values of  $a_{\text{CO}_2}$  for this occurrence indicate either a CO<sub>2</sub>-rich mixed CO<sub>2</sub>-H<sub>2</sub>O fluid, or fluid absent metamorphism. Other calc-silicates yield similar results except for the A85A-3 samples. At the temperature inferred for the McCraney domain, where the A85A-3 samples were collected (800°C)  $a_{\text{CO}_2} = 1.47$ , another example of either overestimating T or retrograde equilibration of the mineral assemblage. Petrographic examination of the samples indicated no textural evidence of retrogression. However, the plagioclase compositions were found to be highly variable within sample A85A-3a (not uncommon in scapolite-bearing rocks, *c.f.* Frank 1985). Based on the  $K_D$  relations discussed above, the samples that yield  $a_{\text{CO}_2} > 1$  contain plagioclase that is less calcic than the scapolite (in terms of An content), and these samples are likely to represent disequilibrium resetting of the plagioclase composition. The most calcic plagioclase in this sample, one that is consistent with the  $K_D$  relations, yields  $a_{\text{CO}_2}$  of 1.0 at the equilibrium P and T, consistent with a pure CO<sub>2</sub> fluid phase and essentially  $P_{\text{Fluid}} = P_{\text{Total}}$  for this sample. It would be interesting to compare the calculated fluid composition with that determined from fluid inclusion analysis.

TABLE 4. Comparison of activities and partial pressures of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  for samples of Whitestone Anorthosite at  $700^\circ\text{C}$  and 10,000 bars total pressure. Pressure in bars.

SAMPLE	$a_{\text{CO}_2}$	$P_{\text{CO}_2}$	$a_{\text{H}_2\text{O}}$	$P_{\text{H}_2\text{O}}$	$P_{\text{Total}}$
PS85A-2c	0.51	5073	0.29	2871	7944
PS86E-7e	0.70	6906	0.34	3381	10287
PS86E-8	0.49	4833	0.24	2433	7266
PS86E-11"	0.82	8170	0.41	4112	12282
PS86E-15	0.25	2513	0.40	3794	6307
PS86E-16a	0.69	6874	0.53	2845	9719
PS86E-24f	0.32	3171	0.39	3936	7107
S86E-25a	0.65	6445	0.53	5261	11706
PS86E-31	0.51	5049	0.27	2748	7797

## Other Granulite Terranes

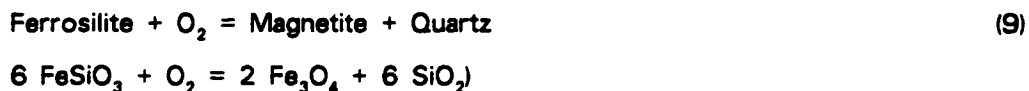
### Furua Complex, Tanzania

Coolen (1980) presented a detailed discussion of the petrology and geochemistry of the Furua Complex, a 700 km<sup>2</sup> granulite terrane in the Pan-African Mozambique Belt of Tanzania. Sulfate scapolite occurs in quartz-bearing felsic to mafic two-pyroxene garnet granulites, garnet-clinopyroxene granulites, calc-silicate gneisses, and garnet-clinopyroxene amphibolites. P and T estimates for the granulite metamorphism cluster tightly around 10 kbar and 800°C (Coolen, 1980). We have recalculated P and T from Coolen's data using the pyroxene-garnet-plagioclase-quartz geobarometers of Chapter II and the garnet-clinopyroxene geothermometer of Ellis & Green (1979) and Pattison & Newton (1988), obtaining precisely the values determined by Coolen. As a result of the good control and limited variability in P and T, the Furua Complex provides a good opportunity to evaluate fluid composition in a well constrained setting, and to estimate precision based on compositional variation within this setting.

The  $a_{\text{CO}_2}$  was calculated for 15 samples of garnet two-pyroxene and clinopyroxene-garnet granulites from throughout the complex, two calc-silicate gneisses, and one garnet-clinopyroxene amphibolite. The  $a_{\text{CO}_2}$  ranges from 0.02 to 0.44 for the Furua granulites (Table 1). Values of 0.02 to 0.10 were obtained for the calc-silicates, and 0.07 for the amphibolite.

Several of the scapolite-bearing granulites from the Furua Complex also contain the assemblage  $\text{Phl-Kfs-Opx-Qz}$  which were used to evaluate  $a_{\text{H}_2\text{O}}$  by Reaction 1. The experimental reversal for Reaction 1 of Bohlen *et al.* (1983) (5 kbar, 790°C, and  $X_{\text{H}_2\text{O}} = 0.35$ ) was used as a starting point for the calculation of  $a_{\text{H}_2\text{O}}$ . Entropy and volume data for phlogopite are from Robie and Hemingway (1984) and Hewitt and Wones (1975), respectively. Complete Al-Si disorder was assumed for phlogopite (Clemens *et al.*, 1987). Thermodynamic data for sanidine are

from Robie *et al.* (1978), and data for enstatite and quartz are from a number of sources summarized in Chapter II. The position of the pure H<sub>2</sub>O reaction was determined using the activity coefficient for H<sub>2</sub>O at X<sub>H<sub>2</sub>O</sub> = 0.35 calculated from the MRK equation of state of Kerrick & Jacobs (1981). Ideal mixing models were used for enstatite (Wood & Banno 1973) and phlogopite (Bohlen *et al.*, 1980). Biotite in the Furua Complex granulites was not analyzed for F or Cl, so calculation of a<sub>H<sub>2</sub>O</sub> will be an upper limit as F or Cl would reduce the activity of phlogopite and therefore reducing the a<sub>H<sub>2</sub>O</sub>. The a<sub>H<sub>2</sub>O</sub> and p<sub>H<sub>2</sub>O</sub> of four samples are uniformly low (0.14 to 0.18, Table 5). The results of the calculations indicate that p<sub>CO<sub>2</sub></sub> is less than p<sub>H<sub>2</sub>O</sub>, and the two gases do not sum to P<sub>Total</sub>. The presence of magnetite and pyrite in these samples allows calculation of fO<sub>2</sub> and fS<sub>2</sub> by the reactions



and from these values the fugacities of various fluid species in the C-O-H-S system can be calculated (French, 1966; Eugster, 1977; Holloway, 1977; Ohmoto & Kerrick, 1977; Lamb & Valley, 1985). Thermodynamic data for the various gases are taken from Robie *et al.* (1978). These calculations show that at the fO<sub>2</sub>-fS<sub>2</sub> calculated for these four samples, most other gas species have low fugacities, and CO<sub>2</sub> and H<sub>2</sub>O are the dominant gases (Table 5). SO<sub>2</sub> and H<sub>2</sub>S have the next highest fugacities. Based on fugacity coefficients for H<sub>2</sub>S and SO<sub>2</sub> calculated from the data of Ryzhenko & Volkov (1971), the two species have partial pressures on the order of 10 and 150 bars, respectively. The results for these samples from the Furua complex are consistent with fluid absent metamorphism. The limited range of mineral compositions determined for these lithologies suggests that this conclusion will hold for other samples in the Furua Complex once further characterization of the samples is performed.



TABLE 5. Activities and fugacities ( $\log_{10}$ ) of gas species, and activity ( $\log_{10}$ ) of graphite activity in C-O-H-S system for Furua Complex granulites at 800°C and 10 kbar.  $a_{\text{H}_2\text{O}}$  calculated from Reaction 1,  $a_{\text{CO}_2}$  calculated from Reaction 7.

SAMPLE	$a_{\text{CO}_2}$	$f_{\text{CO}_2}$	$P_{\text{CO}_2}$	$a_{\text{H}_2\text{O}}$	$f_{\text{H}_2\text{O}}$	$P_{\text{H}_2\text{O}}$	$f_{\text{O}_2}$	$f_{\text{H}_2}$	$a_{\text{C}}$	$f_{\text{CO}}$	$f_{\text{CH}_4}$	$f_{\text{S}_2}$	$f_{\text{H}_2\text{S}}$	$f_{\text{SO}_2}$	$f_{\text{SO}_3}$
MF-283.2	0.18	4.64	1788	0.18	3.86	4407	-11.13	0.25	-3.76	-1.00	-4.34	1.29	2.70	3.24	-2.36
MF-268.1	0.44	5.02	4358	0.17	3.84	4268	-11.18	0.25	-3.33	-1.26	-3.92	1.26	2.68	3.20	-2.42
MF-283.1	0.13	4.50	1295	0.17	3.83	4171	-11.11	0.20	-3.92	-0.85	-4.59	1.30	2.66	3.27	-2.32
ZC-8	0.26	4.79	2649	0.14	3.73	3313	-11.07	0.09	-3.66	-1.12	-4.57	1.33	2.56	3.32	-2.25
C-180.1	0.16	4.59	1604	0.14	3.76	3550	-10.80	-0.05	-4.15	-1.80	-5.32	1.51	2.52	3.69	-1.75

Coolen (1982) performed a fluid inclusion study of a mafic gneiss from the Furua Complex (sample C-180.1), documenting CO<sub>2</sub>-rich fluid inclusions in quartz, plagioclase, and garnet. The calculated fluid compositions for this sample are not consistent with the presence of a pure CO<sub>2</sub> or CO<sub>2</sub>-rich fluid inclusions. The pressure determined by Coolen from the CO<sub>2</sub> isochore and inferred metamorphic temperature was lower than that calculated from mineral equilibria. This is consistent with the interpretation that the fluid inclusions were trapped or modified after the peak of metamorphism and the fluid they contain does not represent that of peak metamorphism.

The results from the Furua Complex are intriguing with regard to the consistency of mineral compositions and calculated fluid activities, origin of the scapolite, and the geologic setting of the Complex in East Africa. The presence of scapolite in a wide range of differing bulk compositions, many that are not likely to contain significant pre-metamorphic carbon, might be taken as evidence that at some stage in the history of the complex there occurred an episode of fluid infiltration and interaction with the gneisses. The calculated fluid compositions are consistent with fluid absent metamorphism, indicating this infiltration would had to have occurred before the peak of granulite facies metamorphism. Although the scapolite is a mixed sulfate-carbonate variety, both volatile components need not both be externally derived. Based on geochemical data, Coolen (1980) proposes that the protoliths for the complex were sulfide-rich felsic to mafic volcanics and sediments. Stable S and C isotope analysis of the scapolite is consistent with an igneous source for the sulfur (Hoefs *et al.*, 1981), but the source of the carbon is equivocal (Hoefs *et al.*, 1981; Chapter V). Therefore the sulfur could have been a component of the sulfides in the igneous protoliths of the felsic to mafic gneisses and amphibolites, later oxidized by infiltrating CO<sub>2</sub>-bearing fluids (Coolen, 1980). The area of East Africa is rich with active carbonic volcanism and scapolite-bearing deep crustal xenoliths are common. The Furua Complex and other granulite complexes of

Tanzania and East Africa deserve further study. If a case can be made for carbonic metamorphism, this would be the area in which it should be evaluated.

#### Bergen Arcs, Norway

Sulfate-rich scapolite is reported in coronitic granulite facies meta-anorthosite of the Bergen Arcs, Norway (Griffin, 1972; Austrheim & Griffin, 1985; Austrheim, 1987), which was locally subjected to ductile shearing under eclogite facies conditions. Using Gt-Cpx geothermometry (Ellis & Green 1979) and Gt-Opx geobarometry (Harley & Green, 1982), Austrheim & Griffin (1985) report equilibration conditions of 775 to 850°C and  $P = 7.8$  to 9.4 kbar for the granulites from the Bergen Arcs. In contrast, coronitic gneisses from the Bergen Arcs yield consistently higher temperatures (875 to 1015°C) and pressures (8.6 to 12.4 kbar; Austrheim & Griffin, 1985). Four samples of the Sc-Gt±Cpx±Opx granulites and meta-anorthosites obtained from Austrheim (pers. comm., 1988) were analyzed for this study. Pressures were recalculated to be  $13 \pm 1.5$  kbar using Cpx-Opx-Gt-Pg barometry, which are maximum pressure limits as quartz is absent in these lithologies. Values of  $a_{\text{CO}_2}$  were calculated at 800 and 900°C (Table 1). At 900°C one sample yields  $a_{\text{CO}_2} = 1.2$  while the other three range from 0.2 to 0.8. At 850°C the four samples yield  $a_{\text{CO}_2}$  of 0.1 to 0.6.

#### South India

Scapolite granulites and calc-silicates are reported from a number of localities in Archean terranes of southern India (Devaraju & Gowd Reddy, 1976; Devaraju & Coolen, 1983; Srikantappa *et al.*, 1985; Kumar & Chacko, 1986; Mukherjee *et al.*, 1986). This area has been proposed as an example where the granulite facies fluid phase has been diluted by  $\text{CO}_2$  influx and where the presence of scapolite has been taken to indicate high  $\text{CO}_2$  partial pressures (Srikantappa *et al.*, 1985). Four mafic granulites from the Sargur area yield consistently low  $a_{\text{CO}_2}$  (0.11 to 0.28, Table 1). If  $a_{\text{H}_2\text{O}}$  is as low in these mafic granulites as it is in charnockites, for which  $a_{\text{H}_2\text{O}}$  is

usually much less than 0.5, and if other gas species are of minor importance, the results of our calculations argue for fluid absent metamorphism. Two calc-silicates from this area yield intermediate values of  $a_{\text{CO}_2}$  and  $P_{\text{CO}_2} < P_{\text{Total}}$  ( $a_{\text{CO}_2} = 0.6$ ), similar to the Grenville samples, and consistent with fluid absence or a mixed  $\text{CO}_2\text{-H}_2\text{O}$  fluid. The calc-silicates we evaluated contain no hydrous phases and  $a_{\text{H}_2\text{O}}$  cannot be evaluated from mineral equilibria.

### Crustal Xenoliths

Sulfate-carbonate scapolite has been found to be a common phase in deep-crustal granulite facies xenoliths (see previous section on Scapolite Compositions). Calculation of precise fluid activities in crustal xenoliths is hampered by equivocal estimates of metamorphic temperature, more so than in a regional metamorphic setting. The requisite assemblage for geothermometry is often present in the scapolite xenoliths, however a suite of xenoliths may or may not represent a single metamorphic event, with the xenoliths being a sample from a range of levels in the crust or of different metamorphic events. Retrograde resetting of temperatures may also occur under static conditions in the deep crust, so that peak metamorphic temperatures are not preserved. However, a suite of xenoliths from a single volcanic vent may represent a coherent group of rocks sampled from the same crustal level. With this caveat in mind we have calculated  $a_{\text{CO}_2}$  in xenoliths from four settings (Table 1, Fig 8). We have recalculated P and T for most of these samples using Gt-Cpx thermometry (Ellis & Green, 1979; Pattison & Newton, 1988) and Cpx-Gt-Pg-Qz geobarometry (Chapter II).

Mineral analyses are reported for the requisite assemblage in single xenoliths from each of the occurrences at New South Wales, Australia (Wilkinson 1973) and Eifel, West Germany (Okrusch *et al.* 1979). These samples yield high  $a_{\text{CO}_2}$  ( $\leq 0.83$  and  $\leq 0.79$ , respectively, quartz absent) at the inferred temperatures.

A suite of crustal xenoliths from Lashaine, Tanzania (Jones *et al.*, 1983) were interpreted to represent a relict suite of mafic igneous rocks metamorphosed to

granulite facies, and include a sample of meta-anorthosite (533, Table 1). The samples yield a range of Gt-Cpx temperatures (610–1035°C), and variably high values of  $a_{\text{CO}_2}$  with several exceeding 1.0. It is possible that there has been considerable resetting of mineral compositions at lower temperatures, resulting in the unrealistic values of  $a_{\text{CO}_2} > 1.0$ . However, considering even a 100°C decrease in estimated T the results are consistent with a CO<sub>2</sub>-rich fluid phase if  $P_{\text{Fluid}} = P_{\text{Total}}$ .

A suite of xenoliths from the Kaapvaal Craton in Lesotho were analyzed by Griffin *et al.* (1978). Temperatures for all but one sample (1098°C) ranged from 650 to 770°C. Values of  $a_{\text{CO}_2}$  were calculated at 50° intervals between 650 and 800°C, with the 800°C values reported in Table 1. The values of  $a_{\text{CO}_2}$  are uniformly low, except for K-2 and PHN2852, which yield  $a_{\text{CO}_2} > 1.0$  even at 700°C. Sample PHN3017 yields the lowest  $a_{\text{CO}_2}$  calculated for this study (<0.0), a result of the extremely sulfate rich scapolite. This is the most sulfate-rich natural scapolite that has been described to date.

### Discussion

The results presented above indicate that scapolite mineral assemblages may be used to obtain reasonable estimates of  $a_{\text{CO}_2}$ . Improvements in the precision of the calculations are certainly possible, particularly in the experiments on scapolite stability and in the scapolite a-X relations. Variations on the order of 0.1 to 0.3 in  $a_{\text{CO}_2}$  for a given locality are likely to be due to the sensitivity of the calculations to local variations in mineral composition or resetting of equilibria. The results also illustrate a number of features of the mechanics of calculating fluid composition in high grade settings and the uncertainties inherent its calculation. There is a critical need for accurate geothermometry and determination of metamorphic conditions that correspond to the equilibration of fluid with solid phases. The erroneous conclusion that  $P_{\text{Fluid}}$  is less than  $P_{\text{Total}}$  may be reached if peak temperature is actually greater than that where thermometric equilibria are "frozen-in" (Pattison & Newton, 1988).

The equilibrium used here (Reaction 7) demonstrates that the presence of scapolite in a mineral assemblage may indicate a range of fluid composition. High  $a_{\text{CO}_2}$  is characteristic of carbonate-rich scapolite assemblages in meta-anorthosite and some calc-silicates and sulfate-rich scapolite assemblages in xenoliths, whereas low  $a_{\text{CO}_2}$  was calculated for most granulites and mafic gneisses. However, the results are equally sensitive to the anorthite content of plagioclase and grossular content of garnet. Higher grossular and anorthite contents will yield lower  $a_{\text{CO}_2}$  by Reaction 7, for a constant scapolite composition. The point to be made is that the entire mineral assemblage monitors the fluid composition, and that the presence of scapolite alone does not correlate with  $\text{CO}_2$ -rich fluid composition. Similarly, the presence of amphibole, biotite, or calcite in any other mineral assemblage does not by itself imply  $\text{H}_2\text{O}$  or  $\text{CO}_2$ -rich fluid composition.

If even moderate or low  $a_{\text{CO}_2}$  are recorded by scapolite equilibria in meta-anorthosite and granulites, one might consider what implications the *absence* of scapolite has in these same lithologies in other high grade settings. In response to influx of a  $\text{CO}_2$ -rich fluid phase during post-granulite facies ductile shearing, a scapolite-bearing metamorphic aureole (up to 4 km wide) developed around the Whitestone Anorthosite. If other occurrences of anorthosite experienced the same processes, why should they not also develop scapolite-bearing mineral assemblages? Anorthosite massifs that have experienced granulite facies metamorphism are characteristic features of the Grenville Province, and smaller masses similar to the WSA have been reported in other high grade terrains. By analogy with the WSA, these intrusions should be the locus of scapolite formation if anorthosite-fluid interaction has occurred within the stability field of scapolite. For example Subramaniam (1956a) describes the occurrence of scapolite in meta-anorthosite of the Sittampundi Complex, an arcuate mafic layered intrusion in the Salem district, Madras, India. The highly aluminous composition of the anorthosite is reflected in the anorthite-rich plagioclase ( $\text{An}_{70}$  to  $\text{An}_{100}$ ), grossular-rich garnet, clinozoisite-rich epidote, and the presence of corundum. Scapolite in the meta-anorthosite was not analyzed, however refractive indices correspond to values approaching EqAn 60.

Subramaniam (1956b) also describes a smaller metamorphosed anorthosite-gabbro mass from Kadavur, Madras, with mineralogic variation and structure remarkably similar to the WSA. Modal scapolite content increases from 0.5% in the core to 5% in the periphery of the body. Manna & Sen (1974) also report scapolite in the Bengal granulite-anorthosite complex at Saltora, W. Bengal, India (the complex is also described by Bhattacharyya & Mukherjee (1987) but they do not describe scapolite occurrences). These occurrences of scapolite merit further investigation as to fluid composition and the source of carbon in scapolite. In contrast to these latter two occurrences, the Bolangir granulite facies anorthosite massif and related mafic granulite gneisses near Orissa, eastern Ghats Belt, India have no reported scapolite (Mukherjee *et al.*, 1986). Except for the marginal facies and demonstrably retrograde occurrences (Valley *et al.*, 1978; Morrison, 1988), primary high grade scapolite is noticeably absent from the Adirondack (Buddington, 1939), and the Morin anorthosite massif of Quebec (Martignole & Schrijver, 1971), both massifs metamorphosed under granulite facies conditions.

As with calculations of  $a_{\text{H}_2\text{O}}$  based on hydrous phase equilibria (Reactions 1 to 3), scapolite equilibria are potentially a powerful tool in recording peak fluid compositions in a wide range of geologic settings and rock types. This would be preferred to using fluid inclusions in high grade rocks which require interpretation as to what fluids they have trapped, and often yield equivocal results. Perhaps as important, scapolite equilibria allow a means of evaluating the critical assumption of  $P_{\text{Fluid}} = P_{\text{Total}}$  in high grade settings.

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## CHAPTER V

### THE CARBON ISOTOPE SYSTEMATICS OF HIGH-GRADE SCAPOLITE: CONSTRAINTS ON FLUID SOURCES IN GRENVILLE GNEISSES

#### Introduction

Scapolite is unique among the more common rock-forming silicates because it may contain one or all of the volatile species Cl, CO<sub>2</sub>, and SO<sub>2</sub> (marialite: Na<sub>4</sub>Al<sub>3</sub>Si<sub>9</sub>O<sub>24</sub>Cl; meionite: Ca<sub>4</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>CO<sub>3</sub>; sulfate meionite: Ca<sub>4</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>SO<sub>4</sub>). As such it is potentially a sensor of fluid source and composition in a variety of rocks. Scapolite from the upper amphibolite and granulite facies is typically Ca<sub>4</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>CO<sub>3</sub>/Ca<sub>4</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>SO<sub>4</sub> solid solutions (*e.g.*, von Knorring and Kennedy, 1958; Lovering and White, 1964; Wilkinson, 1974; Coolen, 1980; Devaraju and Coolen, 1983; Srikantappa *et al.*, 1985), whereas those from the greenschist and amphibolite facies are usually Na<sub>4</sub>Al<sub>3</sub>Si<sub>9</sub>O<sub>24</sub>Cl/Ca<sub>4</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>CO<sub>3</sub> solid solutions (Shaw, 1960; Hietanen, 1967; Kwak, 1977; Vanko and Bishop, 1982; Frank, 1983; Tuisku, 1985; Oliver and Wall, 1987). Many lithologies containing scapolite would not be expected to have significant quantities of pre-metamorphic carbon, sulfur, or chlorine, and therefore fluid interaction or metasomatic introduction of volatile species may often be inferred from the presence of scapolite-bearing rocks. Massive introduction of fluid may be inferred from heavily scapolitized rocks that are virtually monomineralic scapolite rock, or a bimineralic scapolite-diopside or scapolite-biotite skarn. More subtle evidence of fluid interaction is indicated by granulite facies meta-anorthosites, metabasites, calc-silicates, and amphibolites that contain up to 40 modal percent CO<sub>2</sub> and SO<sub>4</sub> scapolite (*e.g.*, Mason, 1969; Coolen, 1980). Alternatively, many occurrences of scapolite are more realistically interpreted

in terms of isochemical metamorphism of an evaporitic protolith, without significant fluid-rock interaction (*e.g.*, Serdyuchenko 1973; Mora and Valley, 1988). Because virtually all scapolite contains some CO<sub>2</sub>, carbon isotope analysis may provide evidence of fluid sources and scales of fluid movement involved in the formation of scapolite-bearing rocks. This would be a particularly useful tool in rocks devoid of another carbonate bearing phase. The carbon isotope data may be used in conjunction with oxygen isotope data to provide additional constraints on the amount and extent of fluid-rock interaction. However, there has been only one attempt to constrain fluid sources using scapolite (Hoefs *et al.*, 1981).

The work presented here is a detailed study of the carbon isotope systematics of scapolite from high grade metamorphic settings. Methods for extracting CO<sub>2</sub> from scapolite were evaluated in order to determine the most accurate and efficient means for extraction and analysis. In addition, the fractionation of <sup>13</sup>C between coexisting scapolite and calcite ( $\Delta^{13}\text{C}_{\text{Sc-Cc}}$ ) was measured in high grade marbles and calc-silicates. Knowledge of the fractionation between scapolite and calcite allows calculation of the fractionation between scapolite and CO<sub>2</sub> ( $\Delta^{13}\text{C}_{\text{Sc-CO}_2}$ ), and in turn constrains the isotopic composition of fluid that led to formation of scapolite. These methods are then applied to scapolite-bearing rocks from the Central Gneiss Belt of the Grenville province of southwestern Ontario, Canada, and other localities. In Ontario, carbonate-rich scapolite occurs in a wide variety of rock types and geologic settings, permitting demonstration of the utility of scapolite as a sensor of fluid sources, and isotopic composition.

#### Experiments on Extraction of CO<sub>2</sub> from Scapolite

Previous study of scapolite carbon isotopes indicated that extraction of CO<sub>2</sub> from scapolite may not be a straightforward procedure (Hoefs *et al.*, 1981). In order to evaluate methods for extraction of CO<sub>2</sub> from scapolite, and to better obtain control on the reaction of scapolite with phosphoric acid, a series of simple experiments were carried out using separates of well characterized scapolite. These

experiments were intended to evaluate the extent of reaction of the carbonate group in scapolite with phosphoric acid as a function of time and temperature. Different methods were used for pretreating the sample in order to remove additional carbon sources such as calcite. Thermal decomposition of scapolite was also evaluated as a means of collecting CO<sub>2</sub>.

Hoefs *et al.* (1981) used phosphoric acid methods to extract CO<sub>2</sub> from scapolite in whole-rock, granulite facies gneisses. Two generations of CO<sub>2</sub> were obtained as a function of temperature. A low temperature generation of CO<sub>2</sub> was interpreted to be a result of reaction with phosphoric acid at 25°C with carbonate inclusions that were assumed to be present in the granulites, but not a result of reaction of phosphoric acid with the carbonate group in scapolite. A second generation of CO<sub>2</sub> was obtained by reaction in 200–400°C phosphoric acid, with the CO<sub>2</sub> produced by this reaction being precipitated as BaCO<sub>3</sub> in Ba(OH)<sub>2</sub> solution, which was then reacted in 25°C phosphoric acid. The second, high temperature, generation was inferred to represent CO<sub>2</sub> obtained from the scapolite. The high temperature fraction of CO<sub>2</sub> was isotopically distinct and lower in δ<sup>13</sup>C relative to the low temperature fraction by up to 11.8‰.

Preliminary analysis of scapolite for this study indicated that the high temperatures used by Hoefs *et al.* (1981) may not be necessary to extract CO<sub>2</sub> from scapolite. Two scapolite mineral samples were chosen to serve as controls on the extraction of CO<sub>2</sub> from scapolite, based on availability of adequate material, purity, and chemical composition. The first scapolite is a coarse-grained aggregate of violet scapolite collected at Bolton, Massachusetts, and donated by Dr. C.A. Francis of the Harvard Mineralogical Museum. The other sample is a 0.5 kg single crystal of gray scapolite collected from a giant scapolite crystal near Ganonogue Park, Quebec, by Dr. D.C. Hogarth of the University of Ottawa. The samples were characterized by optical, X-ray diffraction, back-scattered electron imaging, cathodoluminescence, and microprobe methods in order to determine the composition and homogeneity of the scapolite, and the presence of carbonate



minerals which would contaminate the sample. The theoretical yield of CO<sub>2</sub> for calcite is ten times that of the scapolites used here (approximately 10 vs. 1 μmol CO<sub>2</sub>/mg mineral, respectively). Therefore, small amounts of carbonate contamination could seriously affect analytical results, particularly if the calcite has an isotopic composition significantly different from the host scapolite. In hand sample the two materials appeared inclusion free. However upon closer inspection the Bolton sample ("BOLT") [Na<sub>1.22</sub>Ca<sub>2.79</sub>K<sub>0.02</sub>Si<sub>7.11</sub>Al<sub>4.89</sub>O<sub>24.02</sub>Cl<sub>0.12</sub>(CO<sub>3</sub>)<sub>0.88</sub>] was found to contain 50 to 100 μm-sized inclusions of calcite intergrown with epidote inclusions, and 10 to 100 μm-wide veins of calcite associated with secondary sericitization along fractures (Fig. 1). The Ganonoque sample ("GAN") [Na<sub>0.96</sub>Ca<sub>2.89</sub>K<sub>0.03</sub>Si<sub>7.10</sub>Al<sub>4.90</sub>O<sub>23.95</sub>Cl<sub>0.02</sub>(CO<sub>3</sub>)<sub>0.98</sub>] contained 50 μm inclusions of calcite with epidote, calcite concentrated along planar brittle fractures, 30 μm to mm-sized flakes of graphite, and various silicate inclusions.

Mineral separates of BOLT and GAN were prepared for extraction experiments by crushing and sieving coarse grains to a size range of 75 to 150 μm, followed by a rinse in distilled water. The samples were then immersed in dilute (1 M) hydrochloric acid solution at 23°C for 10 minutes in order to dissolve any calcite. A thin section of the BOLT sample, containing veins and inclusions of calcite as described above, was immersed half-way in 1M HCl to determine if calcite was leached by such a treatment. Cathodoluminescence showed that the calcite was completely dissolved in the immersed half of the thin section, with a sharp interface at the level where the thin section sat in the acid (Fig. 1). Reaction of scapolite in the dilute hydrochloric acid solution is undetectable for this short reaction time. The polished thin section of the coarse, single scapolite crystal showed no indications of etching or dissolution. Following a second elutriation in distilled water, samples were ground to 45μ in order to increase surface area and facilitate reaction of scapolite with acid. The finely ground scapolite powder was then reacted at 25°C or 75°C with 100% phosphoric acid for varying lengths of time in evacuated sidearm flasks. Yields of CO<sub>2</sub> were measured manometrically for all runs. The results of these experiments are compiled in Tables 1 and 2.

**Figure 1.** Cathodoluminescence photomicrographs of scapolite BOLT and GAN, showing nature of included calcite (Cc). Field of view 1.35 mm. a: BOLT with calcite-filled fracture and inclusions of calcite around elliptical epidote inclusion (left); b: HOG with ragged vein-filling calcite (yellow) and scattered calcite inclusions (orange); c: BOLT, calcite inclusions along fracture; d: same as c, showing effect of leaching in 1M HCl. Calcite is entirely dissolved in part of thin section that was immersed in acid (black hole at left in d).



TABLE 1: Experimental data for BOLT scapolite mineral separate.

Scapolite leached in 1M HCl at 23°C for 10 minutes and reacted at 75°C in 100% phosphoric acid.

T°C	%Yield	Time hrs	$\delta^{13}\text{C}$
25	1	12	-6.80
75	35	4	-6.88
75	56	12	-7.01
75	76	34	-6.97
75	82	59	-7.07
75	86	83	-7.02
75	87	115	-7.01
Average	75°C		-6.99

Scapolite treated same as above but without leaching in HCl.

75	41	13	-7.30
75	65	34	-7.40
75	76	59	-7.37
75	84	83	-7.34
75	82	116	-7.34
Average			-7.35

Scapolite finely ground in air without out acid leaching.

75	47	16	-7.59
75	77	90	-7.51
Average			-7.55

Scapolite leached in HCl, ground in distilled water and thermally decomposed at 1050°C

1050	93	0.5	-7.53
1050	97	0.5	-7.59
1050	92	0.5	-7.69
Average			-7.60

TABLE 2: Experimental data for GAN scapolite mineral separate.

Scapolite leached in 1M HCl at 23°C for 10 mins and reacted at 75°C in 100% phosphoric acid

T°C	%Yield	Time hrs	$\delta^{13}\text{C}$
25	9	60	-0.58
75	50	11	-0.47
75	66	18	-0.53
75	40	22	-0.56
75	56	36	-0.58
75	74	41	-0.59
75	84	58	-0.51
75	65	60	-0.56
75	75	82	-0.57
75	81	82	-0.58
75	80	154	-0.54
75	85	203	-0.75
Average 75°C			-0.56

Scapolite leached in 1M HCl, ground in air and thermally decomposed at 1050°C

1050	93	-1.94
1050	91	-1.34

Thermal decomposition of scapolite at 1050°C was evaluated as an alternative method of CO<sub>2</sub> extraction. Measured quantities of the two scapolites with the same grain size and having been leached in dilute hydrochloric acid as above, were finely ground and mixed with CuO in order to prevent reduction of CO<sub>2</sub> to CO during the heating process. Care was taken to hand-pick grains of sample B that were free of visible graphite. The powders were loaded in 1/4"X1" Vycor glass tubes, fused at one end, with a loose plug of silica wool at the other end to prevent sample spillage. Sample tubes were then placed in a 3/4" X 10" quartz tube, evacuated, and heated at 1050°C for 30 minutes. Yields were measured manometrically. Data for the thermal decomposition runs are summarized in Tables 1 and 2.

Results of the extraction experiments on scapolite mineral separates are summarized in Fig. 2, which presents values of  $\delta^{13}\text{C}$  as a function of extraction method and experimental yield. Reaction of scapolite in 25°C phosphoric acid is sluggish compared to that at 75°C. In 25°C phosphoric acid, 60 hours reaction time was required to obtain approximately 10% of expected CO<sub>2</sub>, whereas yields of up to 90% of were obtained in 75°C acid, albeit for longer reaction times. At 75°C yields are higher for longer reaction times and for finer grinding. Values of  $\delta^{13}\text{C}$  are virtually constant as a function of yield, indicating that the reaction of scapolite in phosphoric acid at 75°C is congruent (Fig. 2). Sharma and Clayton (1965) reached the same conclusion concerning  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  for other carbonates that are slow to react at 25°C in phosphoric acid. Values of  $\delta^{13}\text{C}$  obtained for samples reacted in 25°C acid are virtually identical to those for samples reacted in 75°C acid. If  $\delta^{13}\text{C}$  at 75°C is taken as the best representation of the carbon isotope composition of scapolite, it is concluded that structural CO<sub>2</sub> is extractable from scapolite at 25°C, although yields are small.

Values of  $\delta^{13}\text{C}$  for both the BOLT and GAN samples obtained by thermal decomposition are consistently 0.5 to 1‰ lower than those reacted in phosphoric acid (Fig. 2). This is also true for a calcite standard analyzed by acid and thermal decomposition methods, however with a less marked effect (Table 3). The lower

**Figure 2.**  $\delta^{13}\text{C}$  of scapolites BOLT and GAN as a function of temperature and experimental yield of  $\text{CO}_2$  liberated by reaction in phosphoric acid. Data compiled in Table 1. Squares: reaction in 25°C phosphoric acid; circles: reaction in 75°C phosphoric acid; diamonds: thermal decomposition at 1050°C in CuO. For both samples  $\delta^{13}\text{C}$  remains constant at 25 and 75°C as a function of % yield, indicating the reaction of scapolite in phosphoric acid is congruent, and that complete quantitative yields of  $\text{CO}_2$  need not be acquired in order to obtain a precise value for the carbon isotopic composition of scapolite. Lower  $\delta^{13}\text{C}$  values at high yields is interpreted to be due to contamination by carbonate or reduced carbon for BOLT and by graphite for GAN. Dashed lines are averages for BOLT and GAN.

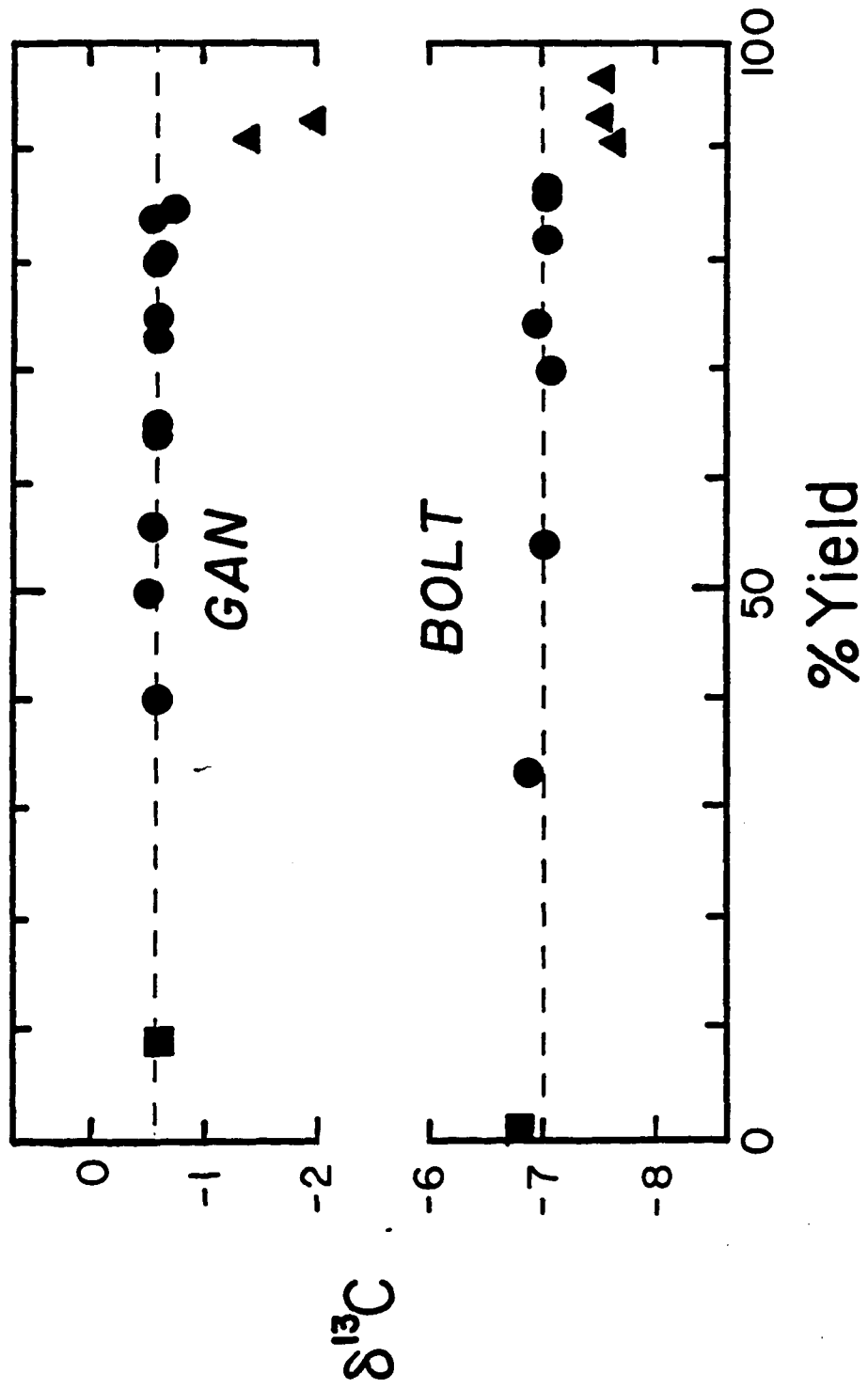




TABLE 3: UW calcite laboratory standard

T°C	%Yield	$\delta^{13}\text{C}$ PDB	$\delta^{18}\text{OCO}_2$ PDB	$\delta^{18}\text{OCc}$ SMOW
Reaction with 100% phosphoric acid				
75	102	-15.95	-3.10	18.98+
75	101	-15.96	-3.13	18.95+
75	100	-15.96	-3.11	18.98+
Average		-15.90	-3.11	18.97
Thermal decomposition				
1050	102	-15.99		na
1050	102	-15.99		na
1050	103	-16.04		na
1050	102	-16.05		na
Average		-15.98		
Reaction with 100% phosphoric acid at 25°C				
25	99	-15.89		18.94
25	99	-15.90		18.99
25	100	-15.88		18.92
25	95	-15.92		19.01
25	98	-15.91		18.91
25	96	-15.96		18.92
25	91	-15.94		18.85
25	96	-15.98		19.07
25	96	-15.99		18.94
25	96	-15.97		18.95
25	95	-15.95		18.94
25	97	-15.96		18.95
Average		-15.93		18.97

na: not applicable due to exchange with CuO.

+: calculated using 75°C acid-Cc  
fractionation factor derived in text

values may result from graphite contamination (*e.g.*, the GAN sample), however graphite was not evident in all the samples. The discrepancy between combustion and phosphoric acid extractions may be due to contamination by a carbon species with low  $\delta^{13}\text{C}$ , either within the sample and not leachable in dilute hydrochloric acid, from extremely light  $\text{CO}_2$  in fluid inclusions, or from  $\text{CO}_2$  adsorbed onto the powdered  $\text{CuO}$  (Hoefs, 1973) and the Vycor reaction tube. The deviation could also be a result of incomplete leaching of extraneous carbonate in the sample preparation. Samples of the BOLT scapolite that were reacted in phosphoric acid, but not leached with dilute hydrochloric acid, have the same lowering of  $\delta^{13}\text{C}$  relative to the leached samples (Table 1). This isotopic pattern is consistent with the existence of secondary calcite in BOLT and GAN that is considerably lighter than the scapolite, as the secondary calcite comprises a small fraction of each sample. Because of the interference of any extraneous carbon, that is exacerbated by the thermal decomposition method which combusts all carbon species in a sample, the preferred method of  $\text{CO}_2$  extraction for this study is reaction in  $75^\circ\text{C}$  phosphoric acid as it provides consistent and precise values of  $\delta^{13}\text{C}$  along with large yields of  $\text{CO}_2$  in a reasonable amount of time. Samples in which secondary carbon sources are absent or thoroughly leached from the rock should yield accurate analysis by the combustion extraction method (Hoefs, 1973). Further tests are required in order to constrain the cause of the isotopic discrepancy for the combustion method.

The results summarized in previous paragraphs permit an alternative interpretation to be made based on the data of Hoefs *et al.* (1981) for extraction of  $\text{CO}_2$  from scapolite. The low temperature generation of  $\text{CO}_2$  that Hoefs *et al.* proposed as being due to carbonate inclusions in the Furuu granulites, could alternatively be derived from partial reaction of scapolite in  $25^\circ\text{C}$  acid. Alternatively, the low temperature generation could be a mixture of gas derived from the carbonate inclusions or other extraneous carbonate as seen in samples examined for this study, with a  $\delta^{13}\text{C}$  near  $0\text{‰}$ , and the lighter carbon derived from the scapolite structure.

### Analytical Methods

In order to extract CO<sub>2</sub> from scapolite in high grade gneisses, whole rock powders (mafic phases removed magnetically) were analyzed. Whole rock samples were utilized because it is extremely difficult to separate scapolite from plagioclase, as the two phases have similar densities and magnetic susceptibilities for the range of compositions studied here. Two size fractions (106 to 150 μm and 150 to 300 μm) from each sample were first treated with dilute hydrochloric acid at 23°C to remove extraneous carbonate. These relatively coarse powders were then ground in air to a 45 to 88 μm grain size, and reacted at 75°C in 100% phosphoric acid for at least 48 to 72 hours. Depending on the modal abundance of scapolite present, up to 5 grams of sample were run in this manner.

High grade gneisses may contain significant secondary calcite along grain boundaries and fractures. This carbonate may not be visible under the polarizing microscope, but is very evident under cathodoluminescence (Morrison and Valley, 1988). Inspection of the samples analyzed for this study revealed variable amounts of secondary calcite. Some samples contained no visible evidence of calcite, whereas others contained pervasive grain boundary calcite and calcite-filled brittle fractures (Fig. 3). Mafic phases such as clinopyroxene and garnet typically contain the most calcite, which is concentrated along fractures, in contrast to plagioclase and quartz which contained few unhealed fractures with calcite. All samples were examined optically and by cathodoluminescence to ascertain approximate modal abundances of scapolite and the presence of secondary calcite. As with the scapolite mineral separates, a mafic gneiss with pervasively developed calcite was immersed in 1M HCl for 10 minutes to demonstrate the efficacy of the leaching process (Fig. 3). Also, samples of scapolite-free gneisses with traces of calcite occurring in a similar mode as in scapolite-bearing gneisses were analyzed as blanks to evaluate the HCl leaching process. The calcite-bearing gneisses that served as blanks yielded either no measurable amounts of CO<sub>2</sub> (PS7g) or only small quantities of gas ( PSB6E-22, 1 μmole CO<sub>2</sub> for three grams of powdered whole rock

**Figure 3.** Cathodoluminescence evaluation of mafic gneiss 85DMP174-1a. Field of view in all photos is 1.35 mm. a: cathodoluminescence photo of secondary calcite concentrated along fractures in clinopyroxene; b: same area, plane light; c: same sample, different area, with left half of sample leached in 1M HCl. Calcite is dissolved from fractures; d: same area, plane light. Abbreviations: hbl: hornblende; cpx; clinopyroxene; gt: garnet; pg: plagioclase; sc: scapolite.



sample). The samples provide a test of the efficacy of hydrochloric acid leaching process, as they initially contained 1 modal % secondary calcite before leaching. The  $\delta^{13}\text{C}$  value of the latter sample is  $-3.3\text{‰}$  identical to values from nearby lithologies with similar occurrences of calcite (see discussion on meta-anorthosite to follow).

Oxygen was extracted from some whole rock samples and converted to  $\text{CO}_2$  for isotopic analysis using the method of Clayton and Mayeda (1963). Analyses of the NBS 28 quartz standard in the University of Wisconsin isotope laboratory average  $9.5\text{‰}$ . Calcite was analyzed according to the method of McCrea (1950).

Isotopic analysis of  $\text{CO}_2$  was performed on a Finnigan/MAT 251, dual inlet, triple collector mass spectrometer at the University of Wisconsin-Madison. Values of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are reported in the standard per mil notation relative to PDB (carbon) and SMOW (oxygen). Analytical precision for a clean sample of  $\text{CO}_2$  and standard gases is typically  $0.01\text{‰}$  for carbon and on the order of  $0.1\text{‰}$  for oxygen. However, reproducibility of  $\delta^{13}\text{C}$  is highly variable for scapolite-bearing whole rock samples. Scapolite mineral separates that yield relatively large volumes of  $\text{CO}_2$  ( $>100 \mu\text{moles}$ ) are reproducible to  $0.1\text{‰}$ . Reaction of whole rock samples with only traces of scapolite often yields smaller volumes of  $\text{CO}_2$  ( $< 10 \mu\text{moles}$ ) and poorer reproducibility ( $\pm 0.5\text{‰}$ ). Scapolite with high Cl and  $\text{SO}_4$  contents ( $> 10 \text{ mol\%}$  in the anion site) typically yield extraneous gas species (HCl and  $\text{SO}_2$ ) that can also lower the reproducibility of a given measurement, and cause systematic lowering of  $\delta^{13}\text{C}$  by up to  $10\text{‰}$ .

Acid extraction of  $\text{SO}_4$ - and Cl-bearing scapolites yields  $\text{SO}_2$  and HCl, which have serious effects on the mass spectrometric analyses, causing systematic errors in  $\delta^{13}\text{C}$ . For example, scapolite with approximately 10% or greater of Cl in the anion site would cause machine errors manifested by drifting sample voltage, and 45/44 mass ratios that systematically increase during the analysis, yielding values that are clearly too high. Routine microprobe analysis of all scapolites for isotopic work

allowed identification of samples for which this may be a problem, and these samples were not analyzed. Gases collected from reaction of  $\text{SO}_4$ -bearing scapolites in 75°C phosphoric acid were scrubbed of  $\text{SO}_2$  by successive distillations in a n-pentane slush. Mass spectrometer scans indicated that significant quantities of  $\text{SO}_2$  can be removed in this manner, yielding clean  $\text{CO}_2$ . Treatment of  $\text{CO}_2$  collected from a calcite standard with the n-pentane slush indicated no fractionation by this distillation. Isotopic analysis of chlorine-rich scapolite using phosphoric acid extraction will require an additional scrubbing step to remove HCl.

#### Fractionation of $^{13}\text{C}$ Between Scapolite and Calcite

The fractionation of  $^{13}\text{C}$  between scapolite and calcite was determined by analyzing the isotopic composition of coexisting scapolite and calcite from high grade marbles, calc-silicates, and skarns. Knowledge of  $\Delta^{13}\text{C}_{\text{Sc-Cc}}$  allows calculation of  $\Delta^{13}\text{C}_{\text{Sc-CO}_2}$ , which constrains the isotopic composition of any fluids.

Based on crystal chemical parameters and fractionations among simple carbonates, one may predict the equilibrium fractionation of  $^{13}\text{C}$  between scapolite and calcite. Table 4 lists coordination numbers (CN), densities, and average M-O bond distances between oxygen atoms in the carbonate group (O) and the cations (M) to which oxygen is coordinated for calcite and aragonite (M = Ca), dolomite (M = Ca and Mg), and a scapolite with the composition  $\text{Me}_{0.4}$  (M = 84% Ca, 16% Na; Aitken *et al.* 1984). The average M-O bond distance for dolomite is less than that for calcite, and the  $\Delta^{13}\text{C}_{\text{Do-Cc}}$  is 2.1 at 25°C and approximately 0.5‰ at  $T > 600^\circ\text{C}$  (Sheppard and Schwarcz, 1970). The average M-O bond length in aragonite is greater than in calcite, but the coordination number and density are higher in aragonite. The fractionation between aragonite and calcite is less than that of dolomite-calcite at 25°C. Estimates of  $\Delta^{13}\text{C}_{\text{Arag-Cc}}$  range from 0.8 (Sommer and Rye, 1978) to 1.8 ‰ (Rubinson and Clayton, 1969). The crystal chemical environment of  $\text{CO}_3$  in scapolite is more similar to aragonite than calcite, and one might predict that the fractionation of  $^{13}\text{C}$  between scapolite and calcite would be similar to that

TABLE 4: Crystal chemical parameters and  $^{13}\text{C}$  fractionations between calcite and aragonite, dolomite, and scapolite.

	Mean M-O		CN	ref.	$\Delta^{13}\text{C}^*$	$\Delta^{13}\text{C}^*$	ref.	Density g/cm <sup>3</sup>	ref
	A				25°C	700°C			
Calcite	2.36		6	1	0	0	-	2.712	6
Aragonite	2.53		9	2	0.8-1.8	na	-	2.930	6
Dolomite	Ca	Mg	6	1	2.1	0.5	4	2.866	6
	2.38	2.08							
Scapolite**	2.47		8	3	-	0.5	5	2.740	3

CN: coordination number;

1: Markgraf and Reeder (1985); 2: de Villiers (1971);

3: Aitken et al. (1984); 4: Sheppard and Schwarcz (1970)

5: this study; 6: Robie et al. (1966).

\*:  $\Delta^{13}\text{C}$  between calcite and mineral at quoted T.

\*\* : Me<sub>84</sub>



TABLE 5: Data relevant to calculation of  $^{13}\text{C}$  fractionation between scapolite and calcite from calc-silicates, marbles, and skarns. All samples are from this study except UK-1 and X27 (D. Mogk, pers. comm. 1987).

SAMPLE	Lith.	X <sub>Ca</sub> Sc	X <sub>CO<sub>3</sub></sub> Sc	$\delta^{13}\text{C}$ Sc	$\delta^{18}\text{O}$ Sc*	$\delta^{13}\text{C}$ Cc	$\delta^{18}\text{O}$ Cc	$\Delta^{13}\text{C}$
A85A-1	M	0.70	0.80	-4.0	9.1	-6.6	9.1	2.6
A85A-3c	CS	0.79	0.98	-8.7	11.9	-8.2	12.8	-0.5
A86B3-5	CS	na	na	-9.5	11.8	-9.9	12.2	0.4
H40d	CS	0.76	0.94	-3.7	11.2	-3.1	11.4	-0.6
M3.14D	SK	0.68	0.85	-8.1	12.3	-8.2	11.8	0.1
M86E-1C-2	CS	0.60	0.87	-1.9	15.4	-3.7	15.1	1.8
O8e	CS	0.74	0.91	-2.6	11.3	-2.2	11.8	-0.4
PS085A-5	MA	0.73	0.90	-0.2	8.9	-1.3	15.1	1.1
PS85A-7	M	0.78	0.98	0.7	15.3	-0.7	15.6	1.4
S4d	SK	0.65	0.86	1.7	20.5	1.4	20.9	0.3
S86E-8c	M	0.69	0.90	0.9	15.4	-0.6	15.9	1.5
S86E-27B	M	0.76	0.93	0.1	17.6	-0.1	17.6	0.2
UK-1	M	0.78	0.98	-1.1	18.9	-1.4	21.1	0.3
X27	M	0.76	0.95	-1.5	15.3	-1.4	17.5	-0.1
82DMT114a	CS	0.79	0.98	-7.9	10.0	-8.1	10.5	0.2

Additional data on scapolite from high-grade calc-silicates in Ontario.

A85A-3d	CS	0.75	0.95	-10.1	12.0			
H85A-1d	CS	0.81	0.98	-9.0	5.2			
M3.14b	SK	0.68	0.82	0.3	16.2			
82DMT114d	CS	na	na	-8.4	9.9			

M: marble; CS: calc-silicate; SK: skarn; MA: meta-anorthosite

\*: see text for assumptions concerning calculation of  $\delta^{18}\text{O}_{\text{SMOW}}$  for scapolite.

for aragonite-calcite. The average  $\Delta^{13}\text{C}_{\text{sc-cc}}$  for 15 scapolite-calcite pairs (Table 5) is  $+0.5 \pm 0.9\text{‰}$  ( $1\sigma$ ), consistent with a small fractionation.

As Na substitutes for Ca in the scapolite structure the density of the scapolite changes (Shaw, 1960), so that  $\Delta^{13}\text{C}_{\text{sc-cc}}$  may be compositionally dependent. Sodic scapolite is less dense than calcic scapolite, and one would predict that scapolite of composition  $\text{Me}_{90}$  (density closer to calcite) would yield higher  $\delta^{13}\text{C}$  than  $\text{Me}_{70}$  for a given calcite composition, and a  $\Delta^{13}\text{C}_{\text{sc-cc}}$  closer to zero than  $\text{Me}_{70}$ -calcite, which should be slightly negative. The spread of values obtained for  $\Delta^{13}\text{C}_{\text{sc-cc}}$  may be due in part to this compositional dependence, as the more sodic and chlorine-rich scapolites tend to yield the greatest fractionation (Table 4). However, the shift in  $\delta^{13}\text{C}$  is opposite to that expected from density considerations, with sodic scapolites yielding more *positive* values of  $\Delta^{13}\text{C}_{\text{sc-cc}}$ . The relative increase in  $\delta^{13}\text{C}$  of these sodic, chlorine-bearing scapolites may instead be an artifact of the contamination by HCl gas, which produces erroneously high values of  $\delta^{13}\text{C}$ . Disregarding samples with  $X_{\text{Cl}} > 0.10$ , in which  $\delta^{13}\text{C}_{\text{scap}}$  is often systematically in error, the fractionation reduces to  $+0.1 \pm 0.6\text{‰}$ . This value is within the analytical precision of many of the analyses performed on scapolite gneisses. Primarily carbonate-rich scapolites will be analyzed for this study, and therefore the latter fractionation is taken as the most appropriate value. For practical purposes the average value of  $\Delta^{13}\text{C}_{\text{sc-cc}}$  will be taken as  $0\text{‰}$ , with the understanding that there is a considerable range in the observed values. Based on this value and  $\Delta^{13}\text{C}_{\text{cc-co}_2} = -2.5\text{‰}$  (Friedman & O'Neil, 1977),  $\Delta^{13}\text{C}_{\text{sc-co}_2}$  is approximately  $-2.5\text{‰}$  in the temperature range 600 to 800°C. Although the equilibrium fractionation of  $^{13}\text{C}$  is small, the secondary carbonate common in many rocks may be much lower in  $\delta^{13}\text{C}$  than the primary scapolite. The experimental data on unleached samples of the BOLT scapolite (Table 1) are consistent with this interpretation, as they yield slightly lighter values than leached samples.

Hoering and Hart (1964) analyzed coexisting scapolite-graphite ( $\Delta^{13}\text{C}_{\text{sc-Gr}} = 5.5\text{‰}$ ) and calcite-graphite ( $\Delta^{13}\text{C}_{\text{cc-Gr}} = 2.2\text{‰}$ ) pairs from two samples of marble

metamorphosed to approximately 750°C in the Adirondack Mts., New York. Coexisting scapolite and calcite samples were not analyzed. From these latter fractionations they calculated  $\Delta^{13}\text{C}_{\text{Sc-Cc}} = +3.3\text{‰}$ , higher than any of the  $\Delta^{13}\text{C}_{\text{Sc-Cc}}$  values measured for this study. We have also analyzed a number of scapolite-calcite pairs from Adirondack marbles, but the scapolite in these samples is Na and Cl-rich, and not amenable to accurate or reliable analysis until the problem with HCl gas contamination is resolved.

#### Oxygen Isotope Composition of $\text{CO}_2$ in Scapolite

The fractionation of  $^{18}\text{O}$  between the framework and carbonate oxygen in scapolite is a potential single mineral geothermometer. Precise estimates of the oxygen isotope composition of the carbonate group extracted from scapolite ( $\delta^{18}\text{O}_{\text{CO}_3}^{\text{Scap}}$ ) cannot be made because the fractionation factor between  $\text{CO}_2$  liberated from the reaction between phosphoric acid and scapolite is not known. However, by assuming that the acid fractionation factor ( $\alpha_{\text{Cc-acid}}$ ) is the same for calcite and scapolite one can obtain *approximate* values for  $\delta^{18}\text{O}_{\text{CO}_3}^{\text{Scap}}$  that can be used on a comparative basis. Sharma and Clayton (1965) showed that this not a valid assumption in precise work for other carbonates, however considerably more work would be required to determine a precise value following the method of Sharma and Clayton (1965), as scapolite has both framework *and* carbonate oxygen. One could combust the scapolite *in vacuo* in the absence of  $\text{CuO}$ , and compare these  $\delta^{18}\text{O}_{\text{CO}_3}^{\text{Scap}}$  values with those obtained in 25°C phosphoric acid. However, reduction of  $\text{CO}_2$  to  $\text{CO}$  and exchange between the carbonate and framework oxygens during the combustion may occur. Most of the scapolite samples were reacted in 75°C acid, and therefore  $\alpha_{\text{acid-Cc}}$  needs to be known at 75°C. The average  $\delta^{18}\text{O}_{\text{PDB}}$  for  $\text{CO}_2$  liberated from the UW calcite laboratory standard at 75°C is -3.11 (Table 3). The fractionation factor at 75°C can be calculated from the relation

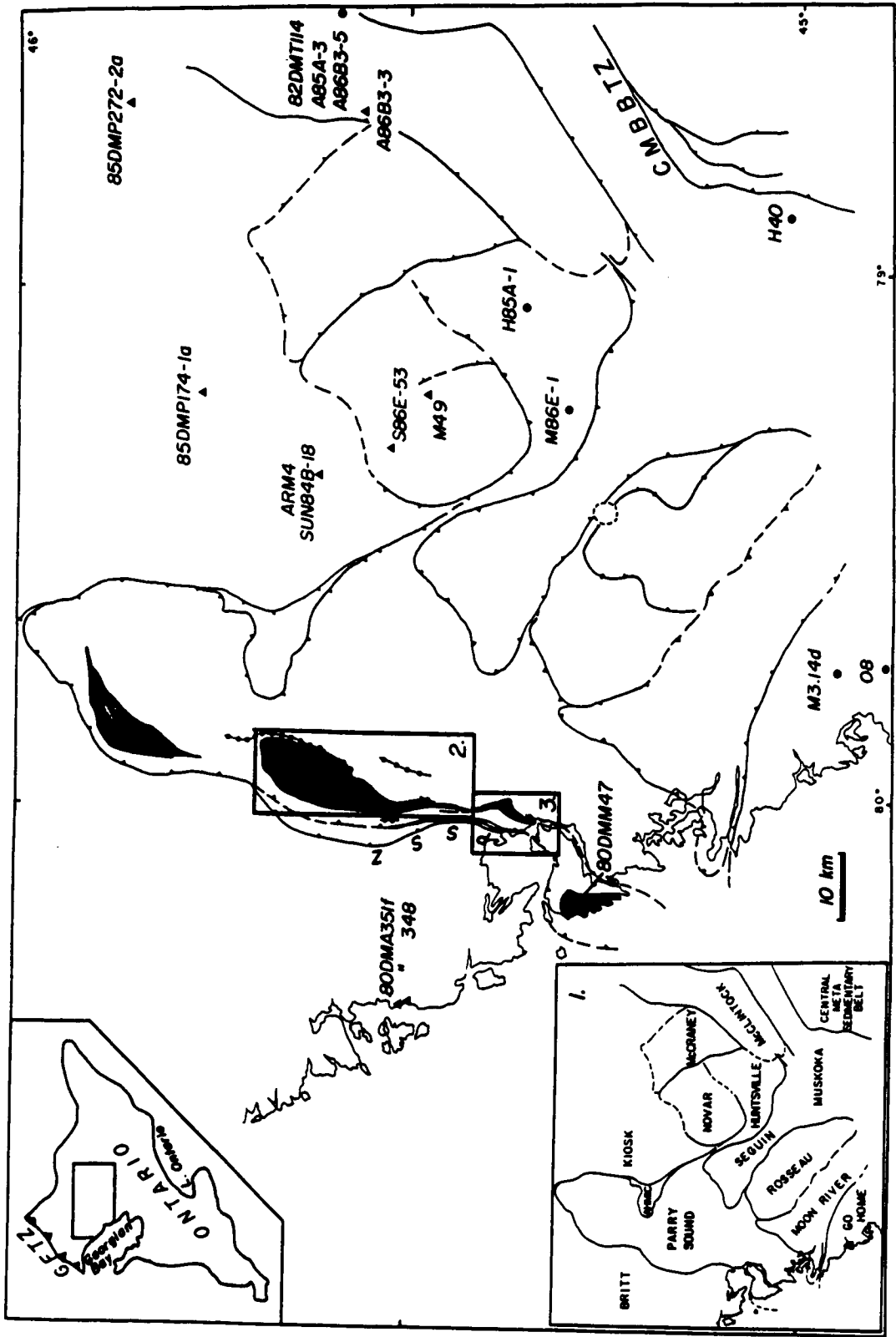
$$[\delta^{18}\text{O}_{\text{PDB}}^{\text{Cc}} + 1000]/[\delta^{18}\text{O}_{\text{PDB}}^{\text{CO}_2} + 1000] = \alpha_{\text{Cc-acid},75^\circ}$$

where  $\delta^{18}\text{O}_{\text{PDB}}^{\text{Cc}}$  is of  $\delta^{18}\text{O}$  for calcite at 25°C relative to the PDB standard. By convention, this is considered the standard oxygen isotope composition of calcite. The relation yields  $\alpha_{\text{Cc-acid},75^\circ}$  of 1.00825. This value was used in calculation of  $\delta^{18}\text{O}_{\text{PDB}}^{\text{Sc}}$  for scapolites analyzed in Tables 5, 6 and 9, from which values were converted to  $\delta^{18}\text{O}_{\text{SMOW}}^{\text{Sc}}$  for the carbonate group in scapolite. The BOLT scapolite sample consistently yields a  $\delta^{18}\text{O}_{\text{SMOW}}^{\text{Sc}} = 11.6\text{‰}$  for the carbonate oxygen when reacted at 75°C in phosphoric acid. A whole mineral oxygen isotope composition of 11.0 ‰ (10.9 when corrected for the fraction of the heavier carbonate oxygen present) was obtained from oxygen extracted by  $\text{BrF}_5$  methods, is consistent with a small, positive fractionation of  $^{18}\text{O}$  between the carbonate group and framework oxygen for this sample. In scapolite gneisses the carbonate oxygen is consistently enriched in  $^{18}\text{O}$  relative to whole rock oxygen (see following section). For the scapolite-calcite samples in Table 5, the scapolite oxygen is the same as or slightly lighter than that in the coexisting calcite, consistent with variable exchange of the carbonate oxygen of scapolite with the framework silicate oxygen upon formation of scapolite from plagioclase and calcite.

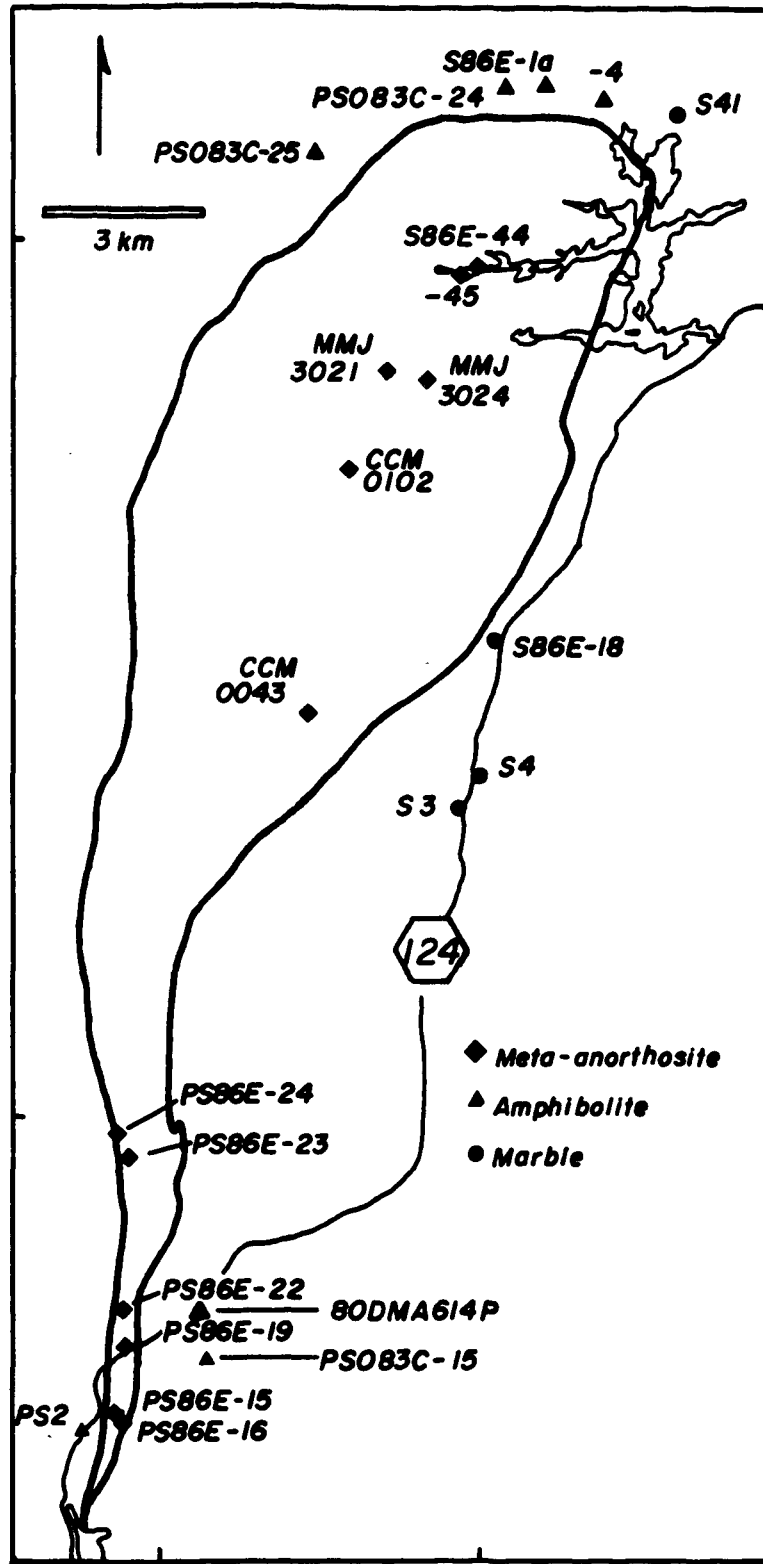
#### Isotopic Analysis of Scapolite Gneisses

Samples of scapolite-bearing gneisses were collected from a variety of localities in the Central Gneiss Belt (CGB) of the southwestern Grenville Province, Ontario, Canada (Fig. 4). Sampling throughout the region allowed delineation of localities and lithologies likely to contain scapolite. A variety of lithologies were found to contain scapolite, and some of these units were sampled on a more detailed scale (Figs. 5, 6, and 7). The tectonic setting of the southwestern Grenville Province is described in Davidson (1984a, 1984b, 1986) and Davidson *et al.* (1979, 1982). Briefly, the region consists of discrete lithotectonic domains separated by km-wide zones of high strain and ductile shearing (Fig. 4). Metamorphic grade is consistent throughout a given domain, but the grade and the dominant lithologies may vary from one domain to another. For example, the Parry Sound Domain, consisting of granulite facies mafic orthogneisses, marble and amphibolite, tectonically overlies

**Figure 4.** Index map for scapolite-bearing gneisses and associated marbles in southwestern Grenville Province of Ontario, showing boundaries between regard to lithotectonic domains mapped by Davidson et al. (1979, 1982) (inset 1). Boxes 2 and 3 outline Whitestone Anorthosite (shaded) detailed in following figures.

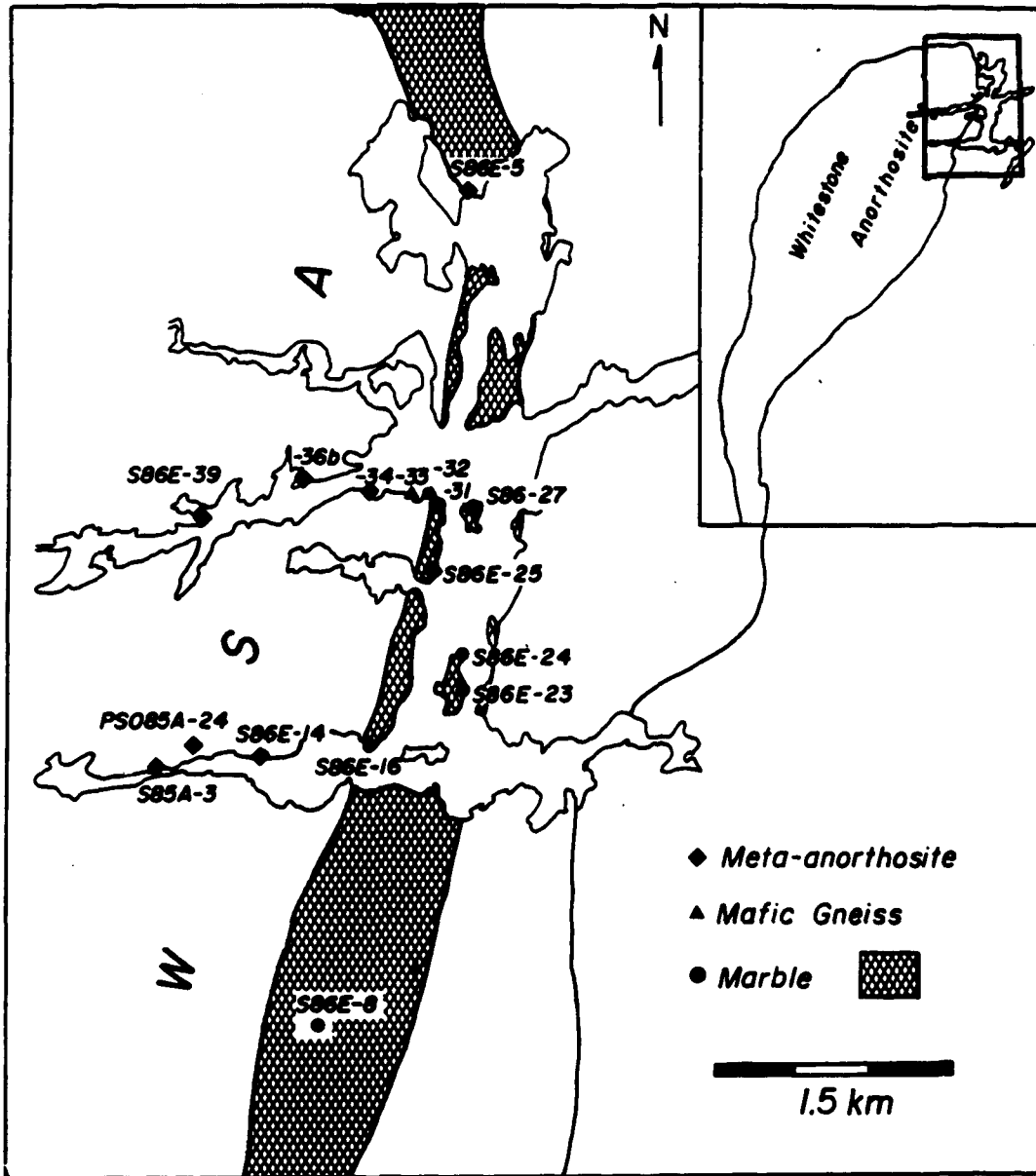


**Figure 5.** Disposition of samples within and around main body of WSA. East margin of Whitestone Anorthosite is detailed in Fig. 6.

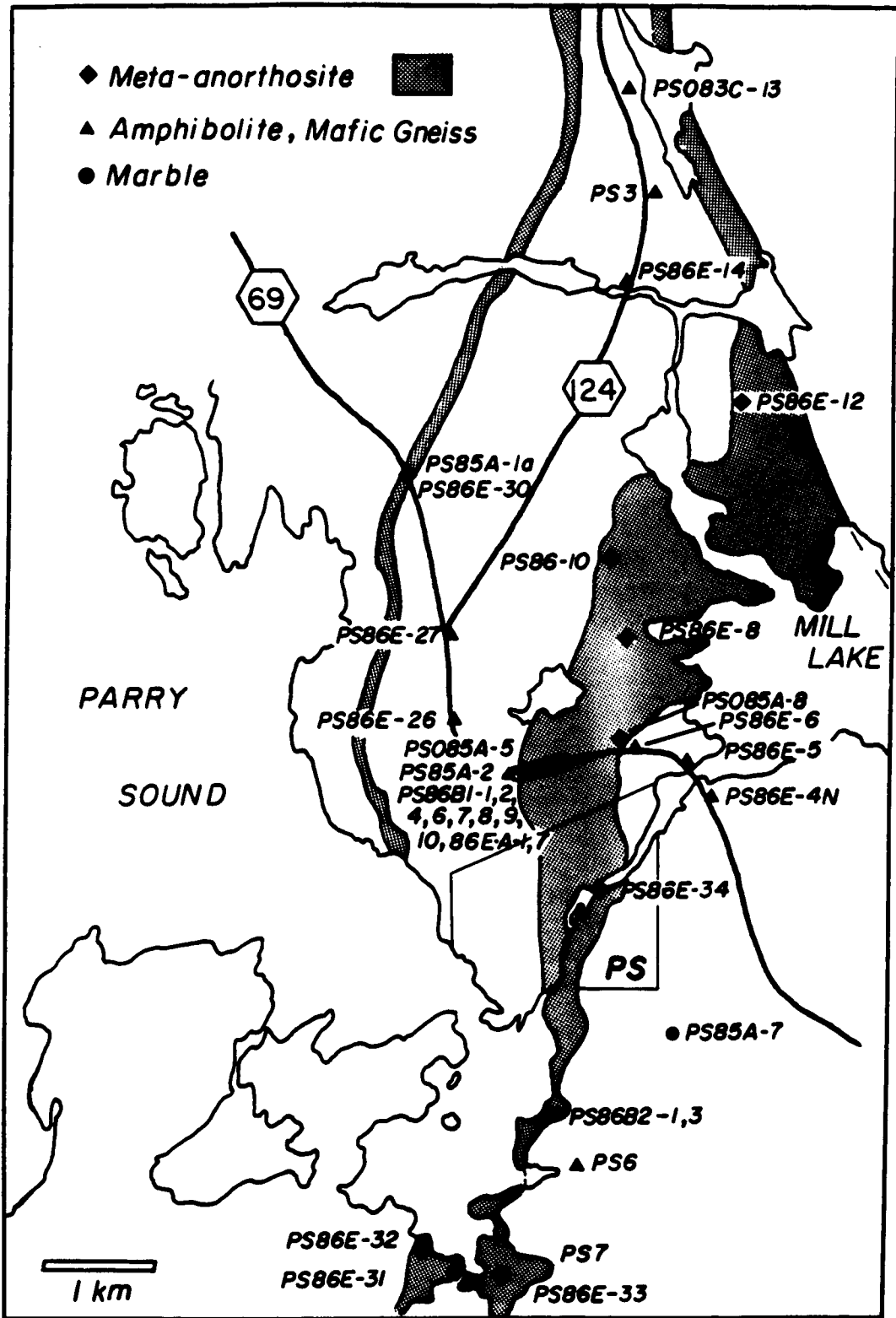




**Figure 6.** Detail of east margin of WSA adjacent to marble breccia in vicinity of Whitestone Lake.



**Figure 7.** Sample localities in vicinity of southern extension of WSA and Parry Sound Shear Zone. PS = town of Parry Sound. Shaded: sheared WSA.



the Britt Domain which consists dominantly of upper amphibolite facies granitic to mafic orthogneisses and pelitic paragneisses. The Moon River Domain is dominantly composed of migmatitic paragneiss juxtaposed against the Parry Sound Domain. Thermobarometric studies indicate that a large part of the CGB of Ontario has experienced metamorphic pressures of at least 10 kbar (Anovitz and Essene, 1988), making it one of the largest known tracts of exposed deep crust in the world.

Shieh and Schwarcz (1974) analyzed orthogneisses, paragneisses, and migmatites collected along a 200 mile traverse across the CGB, from the Grenville Front Tectonic Zone to the Central Metasedimentary Belt. At the time of their study many of the lithologies they studied were interpreted to be migmatitic gneisses. The small range in  $\delta^{18}\text{O}$  they obtained for this large expanse of high grade rocks (80% of their samples were within the range 6.5 to 8.4‰) was interpreted to be due to pervasive exchange on a regional scale with a mafic or ultramafic reservoir via a water rich pore fluid. This process was interpreted to be aided by widespread anatexis. Recently, Wu and Kerrich (1986) performed an extensive isotopic and geochemical study of Grenville granitoid plutons, including two from the CGB. They corroborated the limited range of values observed by Shieh and Schwarcz (1974). However, Wu and Kerrich (1986) concluded that the meta-plutonic rocks retained their primary igneous oxygen isotopic signatures, and that open system exchange with a fluid phase was limited.

#### Calc-silicate Gneisses

In the southwestern Grenville Province calcic scapolite commonly occurs in calc-silicate gneisses, marbles or skarns with quartz, calcite, calcic plagioclase, grossular/andradite garnet, wollastonite, epidote, and salitic/hedenbergitic clinopyroxene. The calc-silicate gneisses themselves usually occur as conformable layers and lenses within upper amphibolite to granulite facies granitic, pelitic, and mafic gneisses. Scapolite and calcite also coexist with the above phases in meta-anorthosite. Samples for this study were collected from the CGB of Ontario, and

represent diverse localities and settings. Because calc-silicates are likely to contain significant quantities of pre-metamorphic carbon within calcite, isotopic analysis of carbon in calc-silicates would likely provide constraints on prograde metamorphic volatilization processes rather than on external carbon sources. However, characterization of the carbon isotopic composition of calcite and scapolite in calc-silicates is necessary to constrain the characteristic carbon isotopic signature of calc-silicates as they may be sources of  $\text{CO}_2$  in high grade terranes (*e.g.*, Glassley, 1983; Kumar and Chacko, 1985), and to determine how well scapolite records the carbon isotopic composition of rocks in which it forms.

Scapolite in calc-silicates, marbles, and skarns ranges widely in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (+1.7 to  $-10.1\text{‰}$ , Table 5), and  $\delta^{13}\text{C}$  are generally very similar to those of the coexisting calcite (see previous section on  $\Delta^{13}\text{C}_{\text{sc-cc}}$ ). Therefore, scapolite is providing a precise record of the isotopic composition of its host lithology, nearly as precisely as calcite. The range of isotopic values for scapolite and calcite in the calc-silicates may be a manifestation of several processes. Many of the samples in Table 5 have  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  characteristic of typical Grenville marbles and calc-silicates, which were interpreted to be indiscernible from primary sedimentary isotopic signatures (Valley and O'Neil, 1984). Therefore, the range of values could be an original bulk chemical effect. For calc-silicate samples that presently lack calcite or graphite and have relatively low  $\delta^{13}\text{C}$  (*e.g.*, A85A-3d ( $-10.1\text{‰}$ ), H85A-1d ( $-9.0\text{‰}$ ), 82DMT114d ( $-8.4\text{‰}$ ); samples that were likely to have contained calcite at lower grades that was consumed in scapolite or grossular-forming reactions) the  $^{13}\text{C}$  depletion may be interpreted in terms of a Rayleigh distillation process whereby  $\text{CO}_2$  evolved during prograde metamorphism left an isotopically light carbon residue that was incorporated in scapolite at high grades. These same samples also have very low  $\delta^{18}\text{O}$  values for calc-silicates (12.0, 5.2, 9.9, respectively), consistent with a Rayleigh process. Alternatively, the pattern could result from varying degrees of interaction with a low  $^{18}\text{O}$ ,  $\text{H}_2\text{O}$ -rich fluid, the influx of which drove decarbonation reactions to completion, yielding an isotopically light carbon residue which was incorporated into scapolite when the latter formed at high grades. The wide

distribution of the samples precludes any detailed analysis of such processes until more detailed and extensive sampling is performed for each locality. An important feature to note from the scapolite data is the heterogeneity of the values, consistent with the lack of regional exchange of a single pervasive and isotopically homogeneous fluid. A second feature of the  $\delta^{13}\text{C}$  values for scapolite is the of the range of low values of  $\delta^{13}\text{C}$  (down to  $-10.1$ ). If the carbonate group of calcite was incorporated directly into scapolite from calcite or  $\text{CO}_2$  without an intervening process such as decarbonation, the range of scapolite  $\delta^{13}\text{C}$  would be expected to overlap with the range of  $\delta^{13}\text{C}$  observed in carbonates from Grenville marbles ( $-7.2$  to  $5.6\text{‰}$ ; Valley, 1986). The observation that the scapolites measured so far are depleted in  $^{13}\text{C}$  is consistent with a relatively complex history leading to the formation of scapolite in calc-silicates.

#### Meta-anorthosite

Carbonate scapolite occurs throughout the Whitestone Anorthosite (WSA), a  $170\text{ km}^2$  gabbroic-anorthosite body found along the western margin of the Parry Sound Domain in the CGB of Ontario (Mason, 1969; Thompson, 1983; Davidson *et al.* 1982; Nadeau 1983) (Fig. 4 through 7). Scapolite is particularly well developed around the margins of the WSA where the anorthosite is in contact with garnet $\pm$ clinopyroxene amphibolite along the west, and marble tectonite breccia, a melange of mafic clasts and boudins entrained within a Cc-Cpx-Hbl $\pm$ Ol $\pm$ Do marble, along its east margin (Mason, 1969; Mummery, 1973; Thompson, 1983). Meta-diorite and mafic granulites occur immediately east of the marble breccia. Mason (1969) delineated a modal increase in scapolite and hornblende from the center of the WSA outward, accompanied by an increase in modal garnet toward the east and north margin, and an increase in modal epidote at the general exclusion of garnet along the west margin. These mineralogic variations exhibit a roughly concentric pattern around the core of the WSA. The WSA provides an opportunity to test the utility of scapolite in sensing fluid sources in a controlled geologic setting where there exists a known source of carbon in the marble breccia. Scapolite is also

found within southern extensions of the WSA where the WSA is cut by the Parry Sound Shear Zone (PSSZ), a high grade ductile shear zone that separates granulite facies rocks of the Parry Sound Domain on the east from upper amphibolite facies assemblages of the Britt Domain to the west (Fig. 4; Davidson *et al.*, 1982; Nadeau, 1983; Davidson, 1984b).

Scapolite may comprise up to 41 modal percent of the meta-anorthosite (Mason, 1969), with the scapolite ranging from 3.5 to 4.7 wt % CO<sub>2</sub> (e.g., sample S86E-25a, Appendix 3). Whole rock analyses range up to 1 wt % CO<sub>2</sub> in the main body of the WSA and 1.6% in the PSSZ (Mason, 1969; Nadeau, 1983), but greater amounts are required by samples with 40 modal percent scapolite having 4 wt % CO<sub>2</sub>. Most anorthosite does not have significant quantities of dissolved CO<sub>2</sub> (Morse, 1982), and the presence of carbonate scapolite in the WSA implies the addition of significant quantities of externally derived fluid as a result of assimilation or fluid interaction. The marbles directly adjacent to the east margin of the WSA are likely sources for this CO<sub>2</sub>, however marbles are rare along the western margin of the WSA and in the PSSZ where scapolite is also developed. The WSA was continuously sampled from the apparent core to the east margin adjacent to marble, in order to test the hypothesis that the marbles were a source for CO<sub>2</sub> leading to the formation of scapolite.

Stable isotopic data were also collected for southern extensions of the WSA where it is intersected by the PSSZ. U-Pb zircon dating of sheared pegmatite dikes within the PSSZ are consistent with syn-metamorphic movement along the PSSZ, relative to the peak of regional metamorphism (van Breemen *et al.*, 1986). Deformation of the WSA within the PSSZ is heterogeneous, with large blocks of less strained gabbroic anorthosite entrained within an anastomosing network of more intensely strained gneiss (Nadeau, 1983). Mineral assemblages within the sheared WSA span the range encountered in the marginal facies of the main body of the WSA, but without the distinct spatial zoning in the latter. Mineral assemblages typically developed in the samples of sheared WSA examined for this study are



subassemblages of Pg-Hbl-Sc-Gt-Qz-Cpx-Ep-Bi-Ti-Ilm. Samples exhibit varying degrees of grain size reduction and recrystallization as a result of ductile shearing. In general, annealed, equilibrium granoblastic textures predominate in the sheared rocks. Other effects developed locally are relict plagioclase phenocrysts in a fine-grained plagioclase-hornblende matrix, neoblast formation around clinopyroxene porphyroclasts, and recrystallization of clinopyroxene to hornblende.

The WSA is bounded on the west (structurally underlain in the shear zone) by amphibolite, and on the east (structurally overlain) by mafic gneiss and granulite that are sheared and retrograded to varying degrees, with local preservation of ductily strained orthopyroxene. The Gt-amphibolite is structurally continuous with that along the west margin of the WSA. Localized masses of marble breccia occur within the overlying mafic gneisses, and coarse marble blocks have been found in sheared anorthosite. The stratigraphy within the PSSZ grossly approximates that for a west to east traverse across the main body of the WSA and enclosing lithologies to the north, but without the large layer of marble breccia occurring east of the WSA.

The margins of the WSA exhibit a marked foliation, manifested by a compositional layering of mafic phases, and locally by evidence of ductile shearing (Mason, 1969). This is in contrast to the center of the WSA where relict igneous textures are often preserved with minor recrystallization (glomeropoikilitic clinopyroxene enclosing relict plagioclase phenocrysts, block structure, igneous layering; Mason, 1969). The core of the WSA also contains orthopyroxene in equilibrium with clinopyroxene, garnet, plagioclase, and traces of sulfate-rich scapolite. The interpretation of equilibrium mineral assemblages in the WSA is complicated by varying textural relations and mineral chemistry. In the marginal facies of the WSA scapolite and hornblende appear to be in textural equilibrium with garnet, plagioclase, and clinopyroxene, exhibiting annealed granoblastic textures. The same phases from the interior of the WSA, between the apparent core and the margins, display varying degrees of replacement textures, with scapolite after plagioclase and hornblende after clinopyroxene (Mason, 1969; Thompson, 1983; this

study). In any one outcrop, equilibrium (i.e., granoblastic) textures may be observed, and in another sample from the same outcrop the scapolite can be seen to embay and replace plagioclase. The volatile composition of scapolite from the two samples may also differ by up to 20 mol% in  $\text{CO}_2/[\text{CO}_2+\text{SO}_2+\text{Cl}]$ . The introduction of fluid components and equilibration of  $\text{Sc-Hbl-Pl-Cpx}\pm\text{Ep}\pm\text{Gt}$  assemblages may not be a single event, being modified by differential pre- to post-peak metamorphic movement, recrystallization, and fluid interaction.

Garnet amphibolites and mafic gneisses ( $\text{Gt-Pg-Hbl-Qz}\pm\text{Bi}\pm\text{Cpx}\pm\text{Opx}$ ) that occur around the margins of the WSA often contain calcite, usually appearing as a secondary phase with ragged grain boundaries but in some cases appearing primary in granoblastic aggregates and having smooth, slightly curved grain boundaries. Whole rock samples of these lithologies were analyzed for  $\delta^{13}\text{C}$  in order to compare it with WSA values.

Carbon isotope analyses of calcite from marbles and scapolite in WSA, and oxygen isotope analyses of calcite from marbles and whole-rock samples of the scapolite-bearing WSA, are presented as a function of distance to the WSA-marble contact (Figs. 8a and 8b), and compared with calcite from marbles and mafic gneisses (Figure 9, Tables 6, 7, and 8). The marbles exhibit a typical Grenville signature for  $\delta^{13}\text{C}$  ( $-0.4\pm 0.3\text{‰}$ ,  $1\sigma$ ,  $n=10$ ) and  $\delta^{18}\text{O}$  ( $+19.4\pm 2.4\text{‰}$ , Table 7). Scapolite from the inner aureole of the anorthosite has a  $\delta^{13}\text{C}$  value of  $-3.4\text{‰}$  and as the marble contact is approached the values become systematically higher, approaching the  $\delta^{13}\text{C}$  of the marble. Calcite in mafic gneisses at the east contact also have values of  $\delta^{13}\text{C}$  approaching marble values (e.g., S86E-5b,  $-14$ ,  $-32$ ,  $-33$ ; Table 6). Whole rock  $\delta^{18}\text{O}$  values of the anorthosite increase from  $6.6\text{‰}$  in the core to  $11.5$  at the marble contact.

Whole rock oxygen isotope analyses of samples at the southwestern margin of the WSA adjacent to garnet amphibolite are more similar to those of the inner aureole of the anorthosite than to values observed along the east margin. The values at the southwest margin range from  $7.3$  to  $7.7\text{‰}$ . Values of  $\delta^{18}\text{O}$  for the

**Figure 8a.**  $\delta^{13}\text{C}$  of scapolite in the Whitestone Anorthosite (WSA) and of calcite in marble breccia as a function of distance to the eastern WSA-marble contact.

**Figure 8b.** Whole rock  $\delta^{18}\text{O}$  values for scapolite-bearing WSA and associated mafic gneisses as a function of distance to the WSA-marble contact.

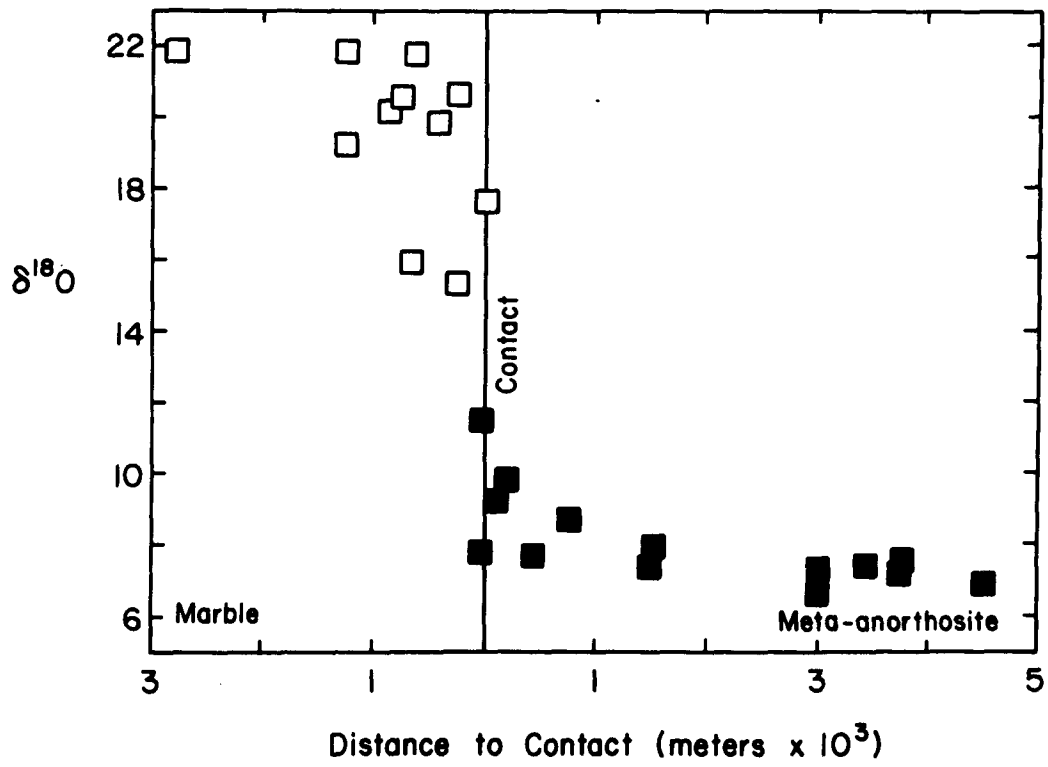
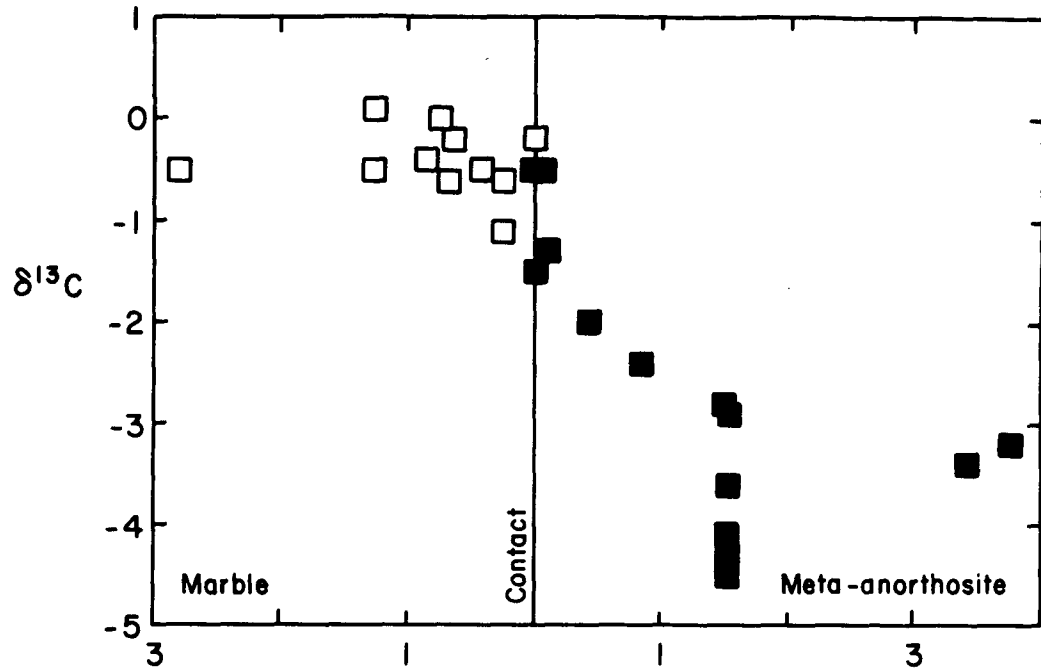


TABLE 6: Carbon and oxygen isotope analyses of scapolite and calcite from WSA and spatially associated garnet amphibolites and mafic gneisses. GA: garnet amphibolite; MA: meta-anorthosite; GMA: garnetiferous meta-anorthostie; EMA: epidote meta-anorthosite; GMG: garnetiferous mafic gneiss; WR: whole-rock silicate analysis.

SAMPLE	ROCK TYPE	PHASE	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$ WR	COMMENTS
PS2	GA	Cc	-7.0	14.4	-	retrograde Cc
PS3	GA	Cc	-2.4	11.0	-	retrograde Cc
PS6	GA	Cc	-2.6	11.2	-	PSSZ
PS7a	GMA	Sc	-1.4	9.6	7.9	sheared WSA, PSSZ
PS7b	GMA	Sc	-1.2	9.9	8.4	sheared WSA, PSSZ
PS7c	GMA	Sc	-1.1	9.6	8.0	sheared WSA, PSSZ
PS7e	GMA	Sc	-1.7	11.9		sheared WSA, PSSZ
PS7g	GMA	-	-	-	8.5	sheared WSA, PSSZ
PS85A-1a	EMA	Sc	-7.5	10.4	-	PSSZ
PS85A-2c	GMA	Sc	-0.1	10.5	-	sheared WSA, PSSZ
PS085A-5	GMA	Sc Cc	-0.2 -1.3	8.9 15.1	-	sheared WSA, PSSZ
PS085A-8	GMA	Sc	-0.5	9.4	8.1	sheared WSA, PSSZ
PS085A-13	GMA	Sc	-1.4	10	-	sheared WSA, PSSZ
PS083C-13	GA	Cc	-4.5	13.7	-	retrograde Cc
PS083C-15	GA	Cc	-4.3	13.8	-	retrograde Cc
PS085A-24	GMA	Sc	-3.6	10.3	-	WSA, retrograde Sc
PS083C-24	GA	Cc	-2.6	10.5	-	retrograde Cc
PS085A-25	GMA	Sc	-4.1	9.9	-	WSA, retro Sc
PS083C-25	GA	Cc	-3.7	10.2	-	retrograde Cc
PS86B1-1	GMA	Sc	-1.2	9.1	-	sheared WSA, PSSZ
PS86B1-2	GA	-	-	-	6.4	PSSZ
PS86B1-4	GMA	-	-	-	7.8	sheared WSA, PSSZ
PS86B1-6	GMA	Cc	-3.0	9.4	8.6	sheared WSA, PSSZ
PS86B1-7	GMA	-	-	-	8.9	sheared WSA, PSSZ
PS86B1-8	GMA	Cc	-3.6	10.0	8.8	sheared WSA, PSSZ

PS86B1-10	GMA	Sc	-1.1	8.8	7.5	sheared WSA, PSSZ
PS86B-11a	GA	-	-	-	6.8	PSSZ
PS86B2-1	GMA	Sc	0.7	9.6	-	sheared WSA, PSSZ
PS86B2-3	GMA	Sc	-0.6	9.6	8.1	sheared WSA, PSSZ
PS86EA-1	GMA	Sc	-0.8	9.1	7.7	sheared WSA, PSSZ
PS86E-4Nd	GA	Cc	-5.1	14	-	sheared, PSSZ
PS86E-5c	GMG	-	-	-	6.8	sheared, PSSZ
PS86E-6a	GMG	Cc	-4.6	9.6	8.0	sheared, PSSZ
PS86E-6b	GA	Cc	-2.3	10.8	8.5	sheared, PSSZ
PS86E-7e	GMA	Sc	-1.7	8.8	-	sheared WSA, PSSZ
PS86E-8	GMA	Sc	-3.7	9.2	-	PSSZ
PS86E-10	GMA	Sc	-3.3	9.4	8.1	PSSZ
PS86E-12	MA	Cc	-4.3	14.1	7.4	retrograde Cc
PS86E-14	GA	Cc	-8.2	10.3	-	retrograde Cc
PS86E-15	GMA	Sc	-2.3	10.2	7.5	"tail of WSA"
PS86E-16a	GMA	Sc	-3.4	9.3	7.4	"tail of WSA"
PS86E-19b	EMA	-	-	-	7.7	"tail of WSA"
		Pg			8.2	
		Ep			6.9	
		Bi			5.0	
PS86E-22	EMA	Cc	-3.3	12.8	-	retrograde Cc, southwest margin WSA
PS86E-23	EMA	Sc	-2.9	9.8	-	southwest margin WSA
PS86E-24a	MA	Sc	-	-	7.6	southwest margin WSA
PS86E-24b	EMA	Sc	-2.4	9.9	-	southwest margin WSA
PS86E-24f	GMA	Sc	-	-	7.7	southwest margin WSA
PS86E-24g	GMA	-	-	-	7.3	southwest margin WSA
PS86E-26c	GA	Cc	-4.6	14.4	6.3	retrograde Cc, PSSZ
PS86E-27	GA	Cc	-8.3	10.7	-	PSSZ
PS86E-30b	EMA	-	-	-	8.5	
PS86E-30c	EMA	Sc	-8.3	12.1	8.8	
PS86E-31	GMA	Cc	-1.0	10.0	-	sheared WSA, PSSZ
PS86E-32	GMA	-	-	-	7.5	sheared WSA, PSSZ

PS86E-33	GMA	Cc	-	-	8.4	sheared WSA, PSSZ
PS86E-34	GMA	Sc	-0.6	9.2	7.5	sheared WSA, PSSZ
S86E-1a	GA	Cc	-3.4	10.1	7.7	
S85A-3a	GMA	Sc	-4.5	9.2	7.9	retrograde Sc
S85A-3b	GMA	Sc	-4.3	9.1	-	retrograde Sc
S85A-3c	GMA	Sc	-2.9	9.1	-	
S86E-4	GA	-	-	-	7.1	
S86E-5b	GMA	Cc	-1.3	10.8	9.2	retrograde Cc
S86E-14	GMA	-	-	-	8.7	
S86E-18b	GMA	Cc	0.7	16.3	-	
S86E-18c	MG	Cc	-1.5	16.9	-	retrograde Cc
S86E-25a	GMA	-	-	-	7.8	east margin WSA
S86E-25c	GMA	Sc	-0.5	10.7	-	east margin WSA
S86E-25i	GMA	-	-	-	11.5	east margin WSA
S86E-25f	GMA	Cc	0.2	15.5	10.8	amphibolite clast in marble breccia
S86E-31c	GMA	Sc	-1.5	10.5	-	east margin WSA
S86E-31e	GMG	-	-	-	8.5	east margin WSA
S86E-32	GMG	Cc	-0.5	12.6	-	east margin WSA
S86E-33	GMG	-	-	-	9.8	east margin WSA
S86E-34	GMA	Sc	-2.0	9.4	7.7	aureole in WSA, retrograde Sc
S86E-36b	GMA	Sc	-2.4	9.6	-	aureole in WSA, retrograde Sc
S86E-39	GMA	Sc	-2.8	9.5	7.4	aureole in WSA, retrograde Sc
S86E-44	MA	Sc	-3.4	9.9	7.4	aureole in WSA
S86E-45	MA	Sc	-3.2	10.2	7.5	aureole in WSA
MMJ3024	MA	-	-	-	7.2	inner aureole of WSA
MMJ3011	MA	-	-	-	7.3	inner aureole of WSA
MMJ0043	MA	-	-	-	6.6	granulite facies core WSA
MMJ0102	MA	-	-	-	6.9	granulite facies core WSA

TABLE 7: Carbon and oxygen isotope composition of calcite in marble and marble breccia along east margin of WSA.

	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
PS85A-7	-0.6	15.7
S3a	-0.5	21.8
S41b	0.1	21.8
S41c	-0.5	19.2
S86E-8c	-0.6	15.9
S86E-16d	-0.6	15.3
S86E-16g	-1.1	20.6
S86E-18a	-0.4	20.1
S86E-23	0.0	20.5
S86E-24c	-0.2	21.7
S86E-27a	-0.5	19.8
S86E-31c	-0.2	17.6
Average	-0.4	19.4



mafic gneisses along the west and east margin of the WSA are similar to those of the WSA, and are not likely to provide constraints for the additional fluid source in the WSA as provided by the carbon isotopic data for scapolite.

The carbon and oxygen isotope data from the WSA and associated mafic gneisses are consistent with a model invoking marble as a local source of high  $^{13}\text{C}$  and  $^{18}\text{O}$  material along the east margin of the WSA.  $\text{CO}_2$  in equilibrium with calcite at  $700^\circ\text{C}$  is enriched in  $^{13}\text{C}$  relative to calcite by approximately  $2.5\text{‰}$ , which would equilibrate with a scapolite that is approximately the same isotopic composition as the calcite from marble (e.g., east margin of WSA). However, the lower values of  $\delta^{13}\text{C}$  recorded in samples of meta-anorthosite from the inner aureole of the WSA argue for a second carbon fluid source, or a much lower temperature for the fluid-rock interaction. The lower values are more similar to  $\delta^{13}\text{C}$  from calcite in the regional country rock garnet amphibolites and mafic gneisses (e.g., PS3, S86E-1a: Table 6). The fractionation of  $^{13}\text{C}$  between  $\text{CO}_2$  and calcite undergoes a crossover at approximately  $190^\circ\text{C}$ , where  $\text{CO}_2$  is lower in  $^{13}\text{C}$  relative to coexisting calcite (Friedman and O'Neil, 1977). Textural relations discussed above are consistent with a syn- to post-peak metamorphic crystallization for the scapolite, but certainly not at temperatures approaching the  $\text{CO}_2$ -calcite crossover. Garnet-clinopyroxene thermometry for the scapolite-bearing WSA yields temperatures in excess of  $650^\circ\text{C}$  (Chapter II). If the  $\text{CO}_2$  is externally derived, the  $\delta^{13}\text{C}$  data for the interior of the WSA require that the  $\text{CO}_2$  be derived from marble with a similar composition to the scapolite, assuming production of  $\text{CO}_2$  from the marble and incorporation into the scapolite occurred at a constant temperature (approximately  $-3$  to  $-4\text{‰}$ ), or an some other source  $2.5\text{‰}$  higher than the scapolite. The data are not consistent with an igneous or mantle source of carbon ( $\text{CO}_2$ ) with  $\delta^{13}\text{C} = -5$  to  $-7\text{‰}$  because of the negative fractionation of  $^{13}\text{C}$  between scapolite and  $\text{CO}_2$ . An igneous or mantle source would produce a scapolite with  $\delta^{13}\text{C}$  of approximately  $-7.5$  to  $-9.5\text{‰}$ .

**Figure 9.** Summary of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  for scapolite WSA, calcite-bearing amphibolites and mafic gneisses, and marbles in vicinity of WSA in Parry Sound Domain.

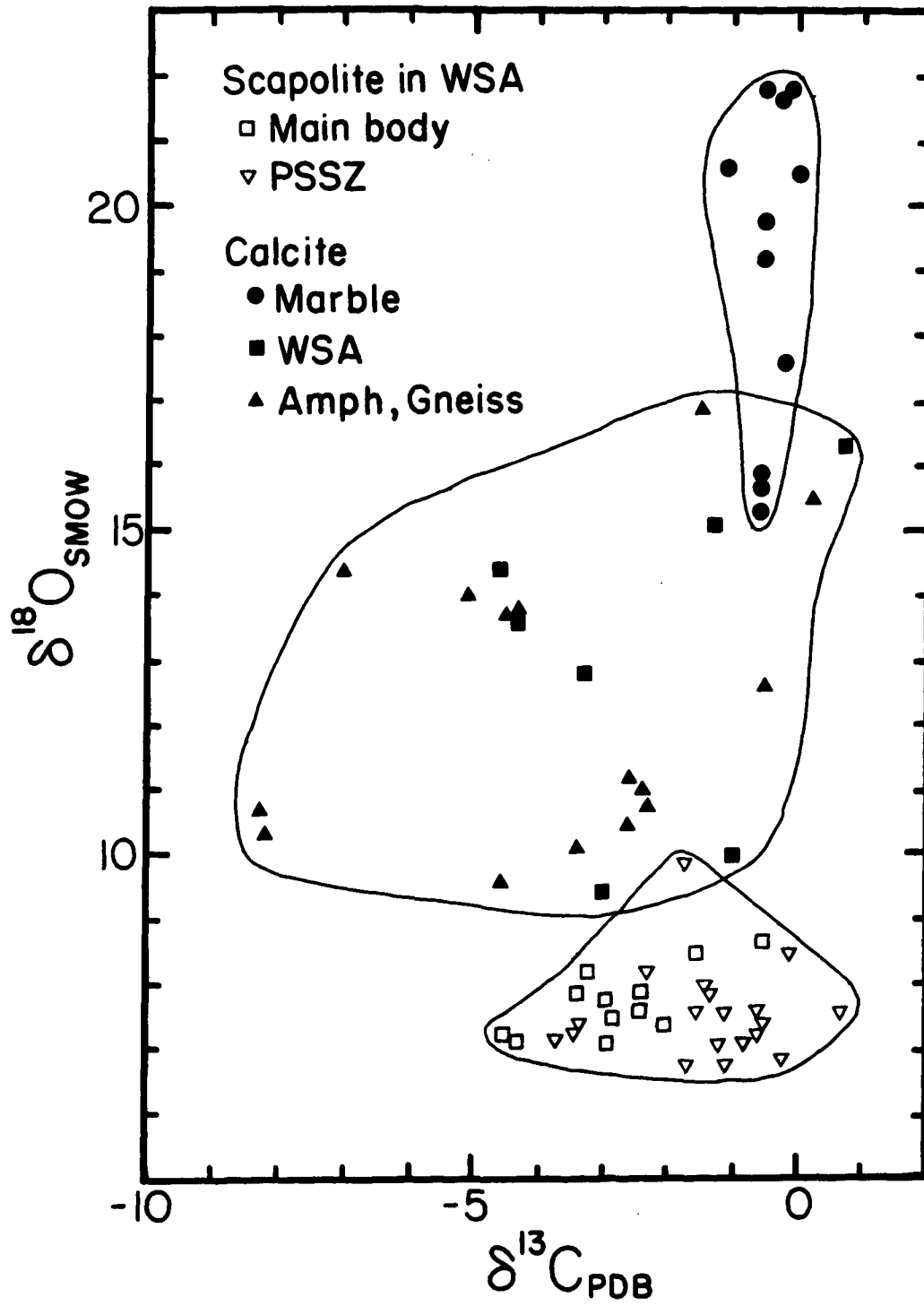


TABLE 8: Carbon isotope analyses of scapolite and calcite, and whole-rock oxygen analyses of WSA as a function of distance from WSA-marble contact. Distance in meters: negative values of distance are for marble samples and for a 1000 X 100 m xenolith of WSA in marble breccia. Scapolite analyzed in samples of GMA, MA, and GMG (see Table 6 for abbreviations), and calcite analyzed in marble samples.

Sample	Lithology	Distance	$\delta^{13}\text{C}$ Sc	$\delta^{18}\text{O}$ WR	Comments
S85A-3A	GMA	1530	-4.5	7.9	retrograde Sc
S85A-3B	GMA	1530	-4.3	-	retrograde Sc
S85A-3C	GMA	1530	-2.9	-	Sc-bearing WSA
PS085A-24a	GMA	1530	-3.6	-	retrograde Sc
PS085A-24b	GMA	1530	-4.1	-	retrograde Sc
S86E-5B	GMG	100	-1.3	9.2	retrograde Cc
S86E-14	GMG	770	-	8.7	retrograde Cc
S86E-25a	GMA	-30	-	7.8	Sc-bearing WSA
-25c	GMA	-30	-0.5	-	Sc in WSA margin
-25i	GMA	-30	-	11.5	Sc-bearing WSA
-31a	MA	0	-1.5	-	Sc-bearing WSA
-32	GMG	66	-0.5	-	Cc-bearing granulite
-33	GMG	200	-	9.8	Cc-bearing granulite
-34	GMA	433	-2.0	7.7	retro Sc
-36B	GMA	850	-2.4	-	retro Sc
-39	GMA	1500	-2.8	7.4	retro Sc
-44	GMA	3430	-3.4	7.4	Sc-bearing WSA
-45	GMA	3770	-3.2	7.5	Sc-bearing WSA
CCM0043	MA	3000	-	6.6	opx-bearing, core facies
CCM0102	MA	4500	-	6.9	core facies
MMJ3011	MA	3000	-	7.3	retro Sc
MMJ3024	MA	3750	-	7.2	retro Sc

Marble samples from east margin of WSA

S3a	-2800	-0.5	21.8
S41b	-1260	0.1	21.8
S41c	-1260	-0.5	19.2
S86E-8c	-670	-0.6	15.9
S86E-16d	-250	-0.6	15.3
S86E-16g	-250	-1.1	20.6
S86E-18a	-850	-0.4	20.1
S86E-23	-750	0.0	20.5
S86E-24c	-640	-0.2	21.7
S86E-27a	-420	-0.5	19.8
S86E-31c	0	-0.2	17.6

The amount of fluid-rock interaction for the east margin of the WSA can be constrained assuming a model of closed system fluid interaction using the relation

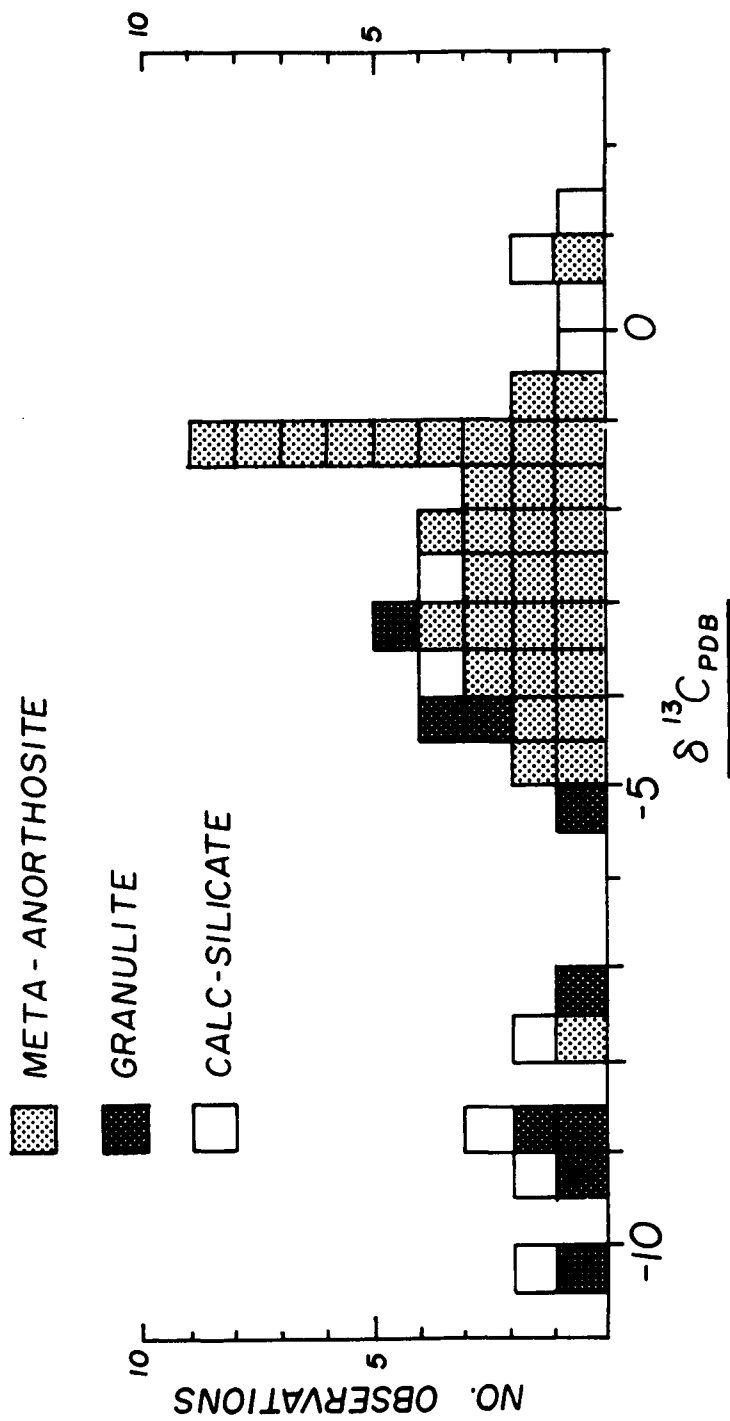
$$F/R = [\delta_R^f - \delta_R^i] / [\delta_F^i - (\delta_R^i - \Delta)]$$

(Taylor, 1977), where f and i are the final and initial isotopic composition of rock (R) and fluid (F), respectively, and  $\Delta$  is the calculated fractionation between rock and fluid. The marbles at the anorthosite margin locally contain the assemblage Cc-Do-Fo-Di. In the absence of tremolite, this restricts the fluid composition derived from marble to approximately  $X_{CO_2} > 0.5$  at 10 kbar (Eggert and Kerrick, 1985).

Scapolite and epidote volatile equilibria for the east margin are consistent with a  $CO_2$ -rich, mixed  $H_2O$ - $CO_2$  vapor phase (Chapter IV). Assuming a fluid of  $X_{CO_2} = 0.5$  in equilibrium with calcite with  $\delta^{18}O = 20.3\text{‰}$ , the initial isotopic composition of the  $CO_2$ - $H_2O$  fluid is  $24.1\text{‰}$ . The initial composition of the gabbroic anorthosite ( $\delta_R^i$ ) is taken as  $6.6\text{‰}$ , the value observed in the WSA core facies. The final rock values ( $\delta_R^f$ ) are taken as the least and most altered values for meta-anorthosite at the east margin ( $7.8$  and  $11.5\text{‰}$ ), allowing a range of fluid/rock values to be calculated relative to the least altered anorthosite. The value of  $\Delta$  was calculated from plagioclase ( $An_{50}$ ) - $H_2O$  and  $H_2O$ - $CO_2$  fractionations at  $700^\circ C$  (Friedman and O'Neil 1977), assuming  $X_{CO_2} = 0.50$ . Based on the above parameters, minimum values of F/R range from 0.1 for the least enriched to 0.3 for the most enriched meta-anorthosite. The same calculations at  $750^\circ C$  and  $X_{CO_2} = 0.75$  do not significantly change the values of F/R. This range of values is for samples in a single outcrop at the east margin of the WSA directly adjacent to marble breccia, indicating varying degrees of fluid interaction on an outcrop scale.

Scapolite from the sheared garnet meta-anorthosite in the PSSZ exhibits a range of  $\delta^{13}C$ , from  $-0.1$  to  $-3.6$ , with a pronounced maximum about  $-1 \pm 1\text{‰}$  (Table 6, Fig. 10). One sample of epidote-scapolite meta-anorthosite from a thin layer approximately 2 km west of the main mass of sheared WSA yields

**Figure 10.** Histogram summarizing carbon isotopic composition of samples for this study.



significantly lighter carbon ( $-8.0\text{‰}$ ). Calcite from meta-anorthosite, mafic gneisses (Pg-Gt-Cpx-Hbl-Cc) and amphibolite (Pg-Hbl-Bi±Gt±Cpx-Cc) overlaps the lower end of the range of scapolite values, but is generally significantly lower ( $\delta^{13}\text{C}_{\text{cc}} = -1.0$  to  $-8.3$ ;  $\delta^{18}\text{O}_{\text{cc}} = 10.2$  to  $16.1$ ). A sample of silicate-rich marble breccia from a 20 m long outcrop east of (structurally above) the axis of the PSSZ has  $\delta^{13}\text{C} = -0.6$  and  $\delta^{18}\text{O} = 15.6\text{‰}$ . Whole rock  $\delta^{18}\text{O}$  values for the sheared WSA span a narrow range from  $7.4$  to  $8.9\text{‰}$ . Garnet amphibolite at the west contact of the WSA has  $\delta^{18}\text{O} = 6.5 - 6.8\text{‰}$ , and  $\delta^{18}\text{O}$  values of mafic gneiss along the east contact range from  $\delta^{18}\text{O} = 5.8 - 8.5\text{‰}$ . On the scale at which we have sampled there does not appear to be any systematic variation of  $\delta^{13}\text{C}$  or  $\delta^{18}\text{O}$  along the length of, or across the WSA in the PSSZ.

The carbon and oxygen isotope data for the PSSZ essentially span the same range of values displayed by the main body of the WSA. The isotopic and mineralogic data for the PSSZ are consistent with the WSA in the PSSZ being the sheared equivalent of the east and west margins of the main body of the WSA, having undergone ductile shearing following fluid-rock interaction to form the scapolite-hornblende-epidote-garnet meta-anorthosite assemblages. The variation of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, and similarity with WSA values, indicate that there has not been significant, additional introduction of fluids through rocks in the PSSZ. This does not preclude the possibility of localized, closed system retrograde hydration, which is evident in both the PSSZ and WSA. The lack of a high fluid flux in the PSSZ is consistent with observations from other ductile shears where stable isotope evidence and mass balance calculations are consistent with low F/R ratios (e.g., Kerrich *et al.*, 1984). The granulite facies, deep crustal environment of the PSSZ and Parry Sound Domain (Anovitz, 1987; Chapter II) would not be a likely source for significant amounts of fluid. Therefore the dry nature of the PSSZ is not surprising considering its geologic setting.



### Mafic Gneisses, Granulites, and Amphibolites

Solid solutions of carbonate-sulfate scapolite occur in amphibolite (Sc+Pg+Hbl+Qz±Gt±Cpx±Bi±Ti±Ilm) and mafic granulite (Sc+Pg+Hbl+Cpx±Gt±Opx±Qz) at a number of localities in the southwestern Grenville Province. The samples are located in four different lithotectonic domains in southwestern Ontario (Davidson *et al.*, 1982) (Fig 4). These occurrences of scapolite-bearing granulites are similar to lithologies and scapolite-bearing assemblages from the Furua Complex in Tanzania (Coolen, 1980) analyzed by Hoefs *et al.* (1981). The igneous protoliths (basalt, diabase) inferred for such lithologies would not be expected to contain significant pre-metamorphic carbon, and as with the meta-anorthosite, the presence of carbonate/sulfate scapolite is consistent with introduction of externally derived C at some point in the rock's history.

$\delta^{13}\text{C}$  values of  $\text{CO}_2$  extracted from scapolite in mafic gneisses are all relatively low, ranging from  $-2.9$  to  $-10.0\text{‰}$  (Table 9). Samples 80DMA614P and 80DMM47b are both from the Parry Sound domain, and have  $\delta^{13}\text{C}$  that are broadly consistent with values from meta-anorthosite (WSA) and mafic gneisses from the same domain (Table 9). The A86B granulite samples occur in the same domain (McCraney) and within 20 km of the A85A and A86B calc-silicate localities (Table 5). Scapolite in the granulites is distinctly enriched in  $^{13}\text{C}$  relative to scapolite and calcite from calc-silicates in this domain. Scapolite derived from a calc-silicate should record the same isotopic composition as the calc-silicate source: the east margin of the WSA is an example of such a process. Therefore, carbon in scapolite from the McCraney domain granulites must record an alternative source or process resulting in the formation of scapolite.

If a simple scenario is adopted to account for the formation of scapolite in these rocks (introduction of  $\text{CO}_2$  into a mafic gneiss without fractionation of carbon during the process of scapolite formation), the data in Table 9 are consistent with a range of sources for the carbon, having distinct isotopic signatures for each domain.

TABLE 9: Carbon and oxygen isotope data for scapolite amphibolite and granulites, southwestern Ontario. Domains as in Fig. 3.

SAMPLE	ASSEMBLAGE	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$ Sc*	$\delta^{18}\text{O}$ WR**	DOMAIN
A86B3-3a	Sc-Pg-Opx-Cpx-Hbl	-8.6	9.1	6.5	McCraney
A86B3-3c'	Sc-Pg-Cpx-Opx-Hbl-Bi-Mt-Ilm-Ap	-7.0	9.3	6.8	McCraney
85DMP272-2a	Sc-Pg-Gt-Cpx-Opx-Hbl-Qz-	-4.0	8.7	-	Kiosk
85DMP174-1a	Sc-Pg-Gt-Cpx-Hbl-Qz-Bi-Mt-Ap	-5.4	10.2	-	Kiosk
80DMA348d	Sc-Pg-Gt-Hbl-Bi-Qz-Ilm-Ap	-8.8	9.7	-	Britt
80DMA351f	Sc-Pg-Cpx-Hbl	-9.4	12.2	-	Britt
S86E-53	Sc-Pg-Gt-Cpx-Hbl-Qz-Bi	-10.0	9.7	6.6	Novar
80DMA614P	Sc-Pg-Gt-Cpx-Opx-Hbl-Ap-Mt-Ilm	-4.1	7.0	-	Parry Sound
80DMP47b	Sc-Pg-Hbl-Bi-Ti	-2.9	9.3	-	Parry Sound

\*:  $\delta^{18}\text{O}$  calculated for  $\text{CO}_2$  extracted from scapolite using fractionation factor for calcite-acid at  $75^\circ\text{C}$ ; see text for discussion.

\*\* : oxygen extracted from whole rock samples using  $\text{BrF}_5$  methods.

Although based on a limited data set, this model precludes large scale pervasive equilibration among the various lithotectonic domains of the Central Gneiss Belt of southwestern Ontario, which would have resulted in homogenization of the scapolite isotopic compositions. This model has implications for carbonic metamorphism (e.g., Touret, 1971; Janardhan *et al.* 1979; Newton *et al.*, 1980) which invokes pervasive infiltration of a CO<sub>2</sub>-rich, mantle derived fluid into high grade terranes, resulting in lowered H<sub>2</sub>O activities and stabilization of granulite facies (Opx-bearing) mineral assemblages. One might predict that if such a pervasive process occurred, scapolite would record the isotopic composition of the fluid with which it equilibrated. Mantle carbon, as recorded in diamonds, carbonatites, and CO<sub>2</sub> in fluid inclusions in basalt glass, has a range of isotopic compositions from -3 to -30‰, with a pronounced mode at approximately -6‰ (Mattey, 1987). A carbonic fluid with  $\delta^{13}\text{C} = -6\text{‰}$  would equilibrate under granulite facies conditions with a scapolite of  $\delta^{13}\text{C} = -8.5\text{‰}$ . Scapolite in the CGB of Ontario spans a wide range from approximately 0 to -11‰. This range is not inconsistent with a mantle or igneous source of carbon for some of the samples, however more than a single source appears to be indicated, or else the mantle below the Grenville Province in Ontario is heterogeneous with respect to its carbon isotopic composition.

The volatile components (C and S) present in the mafic gneisses could have been introduced during an early high temperature alteration event by interaction of mafic protoliths with sea water, resulting in the formation of calcite, sulfides, and/or anhydrite. Such a high temperature process was invoked to account for the anomalously light oxygen isotope composition of granulites from Australia (Wilson and Baksi, 1983). Three mafic scapolite gneisses from this study do not have unusual oxygen isotope compositions, having values approximately 1‰ higher than those for a pristine mafic igneous rock (Table 9). The lack of such <sup>18</sup>O depletions is generally true for all the scapolite gneisses analyzed for this study, consistent with the lack of *extensive* interaction with hot sea water. Lowering of  $\delta^{18}\text{O}$  that would occur during interaction with meteoric water have also not been observed in

the mafic gneisses and WSA. However interaction with seawater could precipitate calcite and elevate the whole-rock  $\delta^{18}\text{O}$  by varying degrees.

Livnat (1983) reports calcite in prehnite/pumpellyite facies metabasalts from the Keweenaw volcanic system, northern Michigan, with  $\delta^{13}\text{C}$  in the range observed for the Grenville gneisses ( $-3.6 \pm 1.6\text{‰}$ ,  $1\sigma$ ). The Keweenaw system has been interpreted to have experienced an episode of hydrothermal interaction with heated seawater that led to extensive Cu mineralization. Thus, carbon in mafic rocks need not be introduced during high grade metamorphism. If basalts that have experienced an early carbon infiltrating event such as the Keweenaw system undergo later high grade metamorphism, this range of carbon compositions in calcite may or may not be later modified to varying degrees by prograde decarbonation reactions.

Application of the carbon isotope systematics of scapolite in high grade settings has been shown to yield reliable estimates of  $\delta^{13}\text{C}$ , particularly in controlled settings such as the Whitestone anorthosite and adjacent marble. However the overlap in isotopic signatures of the various carbon reservoirs makes it difficult to identify carbon sources unequivocally in rocks where there is no immediate source of carbon, such as the scapolite granulites and mafic gneisses investigated here and in the Furuu Complex by Hoefs *et al.* (1981). The pattern of carbon isotope composition of scapolite may be more useful in identifying sources and processes leading to introduction of  $\text{CO}_2$  into a rock and subsequent formation of scapolite. A limited range of  $\delta^{13}\text{C}$  might be expected for models that invoke open system exchange (the system is here defined as the regional metamorphic terrane) and influx of mantle or subcrustally derived  $\text{CO}_2$ . The alternative model would involve decarbonation of crustal calc-silicates or marbles within a given system, having varying isotopic signatures as a result of original isotopic heterogeneity, or from having undergone varying degrees of Rayleigh distillation and depletion of  $^{13}\text{C}$ . This process would be manifested in a wide range of isotopically light carbon values. However both alternatives assume that the gneissic protoliths initially contained no significant pre-metamorphic carbon.

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## CHAPTER VI

### CONCLUSIONS

A systematic analysis of scapolite thermodynamic data, phase equilibria, mixing relations, and carbon isotope systematics has demonstrated the utility of scapolite in sensing fluid composition in a wide range of lithologies in high grade metamorphic settings. In addition to these aspects, which were completely lacking when the work was initiated, I believe the most important conclusions of this dissertation are the constraints placed on  $\text{CO}_2$  activities ( $a_{\text{CO}_2}$ ) in granulites and gneisses, and the scale of carbon isotope heterogeneity in the Central Gneiss Belt of the southwestern Grenville Province.

The calculation of  $a_{\text{CO}_2}$  in regional metamorphic granulites from the Grenville Province, the Furuu Complex of Tanzania, the southern India granulite terrane, and the Bergen Arcs of Norway demonstrate that the  $a_{\text{CO}_2}$  is variable but generally less than 0.5. They are not consistent with a  $\text{CO}_2$ -fluid phase at the inferred peak conditions for granulite facies metamorphism for these terranes. If  $\text{H}_2\text{O}$  activities are correspondingly low, as has been inferred for most granulites, fluid absent metamorphism is likely, or a mixed  $\text{CO}_2$ - $\text{H}_2\text{O}$  fluid is present. Calculation of  $a_{\text{CO}_2}$ ,  $a_{\text{H}_2\text{O}}$ , and fugacities of C-O-H-S fluid species in the Furuu Complex samples makes a strong case for fluid absent metamorphism for this complex, in which scapolite is widely developed, and for which carbonic fluid inclusions are reported. In contrast to these exhumed regional granulite settings, some deep crustal xenoliths from New South Wales, Tanzania, Lesotho, and W. Germany, yield  $a_{\text{CO}_2}$  significantly greater than 0.5, indicating a  $\text{CO}_2$ -rich fluid phase may be present. Likewise,

scapolite-bearing meta-anorthosite adjacent to marble and some scapolite calc-silicate gneisses from the Grenville Province indicate that  $a_{\text{CO}_2}$  was locally high ( $>0.5$ ) and are consistent with the former presence of a  $\text{CO}_2$ -rich fluid. The scapolite-bearing meta-anorthosite may be an example of interaction of anorthosite with a  $\text{CO}_2$ -rich fluid, and small anorthosite plutons similar to the Whitestone Anorthosite should be targets for evaluation of fluid-rock interaction in other terranes. Although scapolite may be present in some granulites, its presence should not be taken as *a priori* evidence that a  $\text{CO}_2$  fluid phase is present at the time of granulite facies metamorphism. As with the presence of biotite or hornblende and their implications for  $a_{\text{H}_2\text{O}}$ , carbonate scapolite requires a finite  $a_{\text{CO}_2}$  but not the presence of a free fluid phase.

The second major contribution of this dissertation is the demonstration of the utility of scapolite in accurately recording  $\delta^{13}\text{C}$ , and the confirmation of previously observed regional carbon isotopic heterogeneity in a high grade terrane. Isotopic analysis of scapolite in meta-anorthosite indicates post-granulite metamorphic gradients in  $\delta^{13}\text{C}$  and identification of mixing between two carbon isotopic reservoirs on a 100 m to km scale. Analysis of regional granulite facies gneisses yields a 10‰ range in  $\delta^{13}\text{C}$  across the Central Gneiss Belt (-1 to -11‰). This range precludes the large scale exchange and homogenization of carbon isotopic values that would be expected if pre-metamorphic fluids were flushed and replaced by an externally derived,  $\text{CO}_2$ -rich fluid. Although the range of values precludes identification of a distinct source of carbon in the gneisses, and determination of the timing for the introduction of carbon, the range of  $\delta^{13}\text{C}$  overlaps that recorded in calc-silicates, marbles, and skarns from the same terrane. Thus, a source of carbon external to the terrane need not be invoked to account for the presence of carbon in these rocks.

Future studies should be directed at refining the thermodynamic calculations and making the isotopic measurements of this study more general. More restrictive experiments on the stability of end member meionite, evaluation of the

effects of Al-Si disorder on meionite stability, and direct experiments on activity-composition relations in carbonate-sulfate scapolites are needed for more accurate calculation of  $a_{\text{CO}_2}$  from scapolite equilibria. The major source of imprecision in the calculation of  $a_{\text{CO}_2}$  is the equilibration temperature of the silicate assemblage. As the activity model and meionite decarbonation reaction are highly temperature sensitive, these aspects should be refined as precisely as possible. More carbon (and sulfur) isotope analyses of scapolite granulites need to be made for the Grenville Province (detailed sampling of known localities and delineation of different occurrences) and from other terranes in order to further evaluate the scale of isotopic heterogeneity. These problems notwithstanding, it is anticipated that the major conclusions of this dissertation will stand.

## APPENDIX 1

### Sample Localities

Sample localities are taken from those plotted on maps published by the Canadian Department of Mines and Technical Surveys, Ottawa, Ontario, and on repository at the University of Michigan. Samples are designated by an upper case letter corresponding to the name of the map sheet used:

#### 1:125,000 map sheets

A Algonquin  
B Bobcaygeon  
BA Bancroft  
BI Byng Inlet  
C Coniston  
GL Golden Lake  
H Huntsville  
M Muskoka  
MA Mattawa  
NB North Bay  
O Orillia  
PS Parry Sound  
S Sundridge  
T Tomika

#### 1:50,000 map sheets

PS Parry Sound  
S Magnetawan (Magnetawan is sub-sheet of Sundridge 1:125,000)

Sample locality numbers without a year designation (e.g., 85A, 86B, 86E) were collected during the 1984 field season. Sample localities are given in terms of latitude and longitude (degrees, minutes ('), seconds (")), if plotted on the 1:125,000 series maps, or the northing-easting metric coordinate system for the 1:50,000 maps and for the Sudbury, Mattawa, and North Bay 1:125,000 maps. If a thin section was cut for the sample it is designated by a "+" in column 2, and mineral assemblages are compiled in Appendix 2. If no thin section was cut a subjective hand sample description of the sample is given. Most samples were collected from outcrops along Ontario highways, with the highway given in column 3. If the sample was collected off a main highway (e.g., along farm or logging roads), this is designated by a "-" sign followed by a brief description of where the road can be found relative to a main highway.

Locality Number	TS or lithology if TS not cut	Hwy	Latitude Northing	Longitude Easting
A1	+	60	45-30'-10"	78-00'-10"
A2	+	"	45-30'-40"	78-16'-00"
A3	+	"	45-33'-30"	78-17'-00"
A4	+	"	45-35'-00"	78-17'-00"
A5	+	"	East end Brewer Lake	
store		"	0.5 km W of road to Opeongo L. dock and	
A6	+	"	45-34'-10"	78-32'-20"
A7	+	"	45-32'-55"	78-39'-05"
B1	+	35	44-39'-20"	78-46'-20"
B2	+	"	Miners Bay road cut	
B3	+	"	44-50'-40"	78-46'-00"
B4	qz-fld gneiss	121	1 km E int Hwys 35 & 121	
B5	+	"	44-59'-50"	78-18'-45"
B6	+	"	44-59'-10"	78-17'-20"
B7	+	503	2.3 km N of Tory Hill	
B8	+	121	44-55'-30"	78-17'-15"
B8-2	hbl meta-anorthosite	503	44-58'-50"	78-37'-40"
B9	calc-silicate	503	44-48'-40"	78-35'-40"
B10	+	"	"Shoe Tree" locality NE Kinmount	
B11	+	121	44-57'-00"	78-40'-00"
B12	+	503	44-49'-00"	78-35'-00"
B13	bi metagabbro	"	44-50'-30"	78-33'-20"
B14	+	"	44-54'-30"	78-23'-40"
B15	calc-silicate	507	1.5 km W. int Hwys 503 & 507	
B16	amphibolite	-	44-53'-55"	78-22'-40"
B17	bi-qz-fld paragneiss	-	44-53'-30"	78-21'-50"
B18	+	503	Side Rd to Trooper Lk.	
B19	Amphibolite	503	44-56'-10"	78-18'-20"
B20	+	648	44-56'-10"	78-18'-20"
B21	calc-silicate	"	44-59'-10"	78-13'-55"
B22	di skarn	"	Int Hwys 648 & 121	
B23	+	"	44-59'-59"	78-13'-45"
B24	+	648	44-57'-40"	78-06'-40"
B25	+	"	44-57'-50"	78-07'-40"
B26	+	"	44-57'-50"	78-07'-40"
B27	+	"	44-58'-40"	78-06'-58"
B28	+	"	44-58'-40"	78-06'-58"
B29	+	"	44-59'-20"	78-06'-50"
B30	actin skarn	121	44-59'-20"	78-07'-30"
B31	+	"	44-59'-20"	78-08'-00"
B32	+	"	44-59'-30"	78-08'-50"
B33	+	"	44-59'-10"	78-11'-45"
		"	44-59'-00"	78-13'-00"
		648	44-59'-00"	78-14'-15"
		"	44-58'-40"	78-14'-30"
		"	44-58'-40"	78-14'-30"
		"	44-58'-43"	78-15'-20"
		"	44-58'-40"	78-15'-20"
		"	44-58'-40"	78-14'-40"
		-	44-58'-00"	78-17'-35"
			Rd W. of 121, N. of McCue Lk.	
B31	+	-	44-57'-30"	78-16'-55"
B32	+	507	44-54'-05"	78-22'-50"
B33	+	"	44-53'-20"	78-22'-50"

B34	calc-silicate	"	44-53'-05"	78-23'-25"
B35	gt-bi meta-pelite, marble, metagabbro	"	44-52'-40"	78-23'-30"
BAcrg	+	-	45-18'-00"	77-35'-50"
			Craigmont Quarry, York R.	
BA1	+	-	45-15'-30"	77-58'-55"
			S. shore Baptiste Lk., NW Bancroft	
BA2	+	127	45-15'-35"	77-56'-00"
BA3	+	"	45-14'-55"	77-56'-50"
BA4	+	523	45-20'-00"	77-56'-35"
BA5	+	"	45-29'-00"	77-56'-20"
BA6	+	-	45-24'-15"	77-35'-50"
BA7	+	62	45-25'-40"	77-39'-55"
BA8	+	"	45-26'-40"	77-39'-55"
BA9	+	"	45-27'-00"	77-40'-20"
BA10	+	"	45-27'-30"	77-40'-00"
BA11	amphibolite		45-20'-00"	77-35'-50"
BA12	syenite		45-23'-15"	77-29'-00"
BA13	qz-fld gneiss		45-23'-15"	77-29'-55"
BA14	+		45-07'-20"	77-52'-00"
BA15	+		45-27'-55"	77-23'-30"
BA16	+		45-27'-05"	77-23'-25"
BA17	+		45-26'-30"	77-22'-25"
BA18	+		45-26'-30"	77-19'-50"
BA19	+		45-19'-00"	77-23'-10"
BA20	+		45-18'-35"	77-30'-00"
BI1	granite orthogneiss		See Tucillo, M.E., M.S. thesis,	
BI2	gt orthogneiss		Univ. Michigan, for locations of BI samples	
BI3	+			
BI4	+			
BI5	grey qz-fld gneiss			
BI6	pink qz-fld gneiss			
BI7	+			
BI8	gt paragneiss			
BI9	gt paragneiss			
BI10	gt paragneiss			
BI11	gt paragneiss			
BI12	gt orthogneiss			
BI13	gt orthogneiss			
BI14	pink qz-feld gneiss			
BI15	grey paragneiss			
BI16	pink qz-feld gneiss			
BI17	pink qz-feld gneiss			
BI18	pink qz-feld gneiss			
BI19	pink qz-feld gneiss			
BI20	pink qz-feld gneiss			
BI21	pink qz-feld gneiss			
BI22	pink qz-feld gneiss			
BI23	pink qz-feld gneiss			
BI24	pink qz-feld gneiss			
BI25	+			
BI26	gt grey paragneiss			
BI27	gt grey paragneiss			

BI28	gt grey paragneiss			
BI29	gt grey paragneiss			
BI30	gt grey paragneiss			
BI32	+			
BI34	+			
BI35	+			
BI36	+			
BI37	gt granulite			
BI38	gt granulite			
BI39	+			
BI40	+			
C1	+	17	5150500	531500
GL1	metagabbro	60	45-30'-35"	77-56'-15"
GL2	gt paragneiss	"	45-31'-30"	77-53'-30"
GL3	+	"	45-31'-35"	77-53'-00"
GL4	gt bi metagabbro	"	45-32'-10"	77-52'-20"
GL5	+	"	45-32'-15"	77-51'-55"
GL6	+	"	45-32'-25"	77-51'-40"
GL7	amphibolite	"	45-32'-15"	77-51'-15"
GL8	+	"	45-30'-15"	77-45'-30"
GL9	amphibolite	"	45-30'-05"	77-43'-50"
GL10	amphibolite	"	45-30'-30"	77-33'-20"
GL11	amphibolite	"	45-30'-00"	77-33'-05"
GL12	amphibolite	"	45-30'-10"	77-31'-40"
GL13	+	62	45-47'-40"	77-11'-00"
GL14	+	"	45-47'-50"	77-10'-15"
GL15	orthogneiss	"	45-47'-50"	77-10'-05"
GL16	+	"	45-47'-05"	77-11'-00"
GL17	granitic orthogneiss	"	45-36'-55"	77-30'-45"
GL18	amphibolite	"	45-37'-15"	77-28'-40"
GL19	orthogneiss	-	45-37'-35"	77-24'-00"
GL20	amphibolite	512	Side Rd off 60 from Deacon 45-37'-15"	77-30'-45"
GL21	+	-	Side Rd off 512 E. of Killaloe Sta. 45-32'-30"	77-30'-45"
GL22	charnockitic gneiss	-	45-32'-35"	77-30'-45"
GL23	calc-silicate	512	45-31'-05"	77-30'-45"
GL24	bi metagabbro	62	45-36'-05"	77-30'-45"
GL25	+	62	45-46'-45"	77-14'-10"
GL26	+	40	45-44'-20"	77-00'-20"
GL27	+	17	45-44'-00"	77-00'-00"
GL28	+	60	Int. 17 and 40	
H1	+	35	45-18'-35"	78-59'-25"
H2	+	"	45-17'-50"	78-58'-35"
H3	amphibolite	"	45-16'-45"	78-53'-40"
H4	+	"	45-15'-10"	78-54'-10"
H5	+	117	Int. 35 and 117 45-15'-10"	78-56'-40"
H6	+	35	45-00'-45"	78-42'-10"
H7	+	118	45-06'-30"	78-35'-55"
H8	gt amphibolite	"	45-06'-00"	78-35'-40"
H9	+	121	45-02'-30"	78-29'-10"

H10	+	"	45-02'-05"	78-27'-30"
H11	+	"	45-01'-35"	78-23'-25"
H12	+	-	45-00'-40"	78-26'-05"
Side rd. off 121 to Blue Hawk Lk.				
H13	+	121	45-02'-05"	78-27'-15"
H14	+	648	45-03'-30"	78-04'-40"
H15	+	127	45-18'-50"	78-02'-30"
H16	+	"	45-21'-25"	78-04'-20"
H17	+	"	45-23'-10"	78-05'-35"
H18	+	"	45-24'-40"	78-07'-58"
H19	+	"	45-26'-30"	78-10'-25"
H20	+	"	45-26'-50"	78-10'-35"
H21	gt paragneiss	"	45-27'-15"	78-11'-05"
H22	+	"	45-27'-35"	78-11'-25"
H23	+	648	45-00'-25"	78-13'-00"
H24	+	"	45-02'-30"	78-13'-50"
H25	sample lost	-	45-05'-40"	78-08'-25"
Side rd. off 648 N. of Mumford				
H26	sample lost	-	45-06'-00"	78-08'-25"
H27	hbl metagabbro	60	45-29'-30"	78-02'-10"
H28	hbl metagabbro	"	45-28'-40"	78-05'-30"
H29	amphibolite	"	45-29'-50"	78-11'-05"
H30	metagabbro	"	45-29'-35"	78-12'-00"
H31	flat charn gneiss	"	45-29'-20"	78-12'-30"
H32	gt paragneiss	"	45-28'-25"	78-46'-30"
H33	flat charn gneiss	"	45-25'-30"	78-50'-15"
H34	flat charn gneiss	"	45-22'-45"	78-55'-05"
H35	flat charn gneiss	"	45-20'-35"	78-56'-25"
H36	calc-sil, amphib	35	45-17'-10"	78-56'-20"
H37	+	"	45-15'-40"	78-53'-50"
H38	calc-silicate	"	45-12'-30"	78-52'-40"
H39	charnockitic gneiss	"	45-07'-50"	78-50'-25"
H40	+	118	45-02'-10"	78-45'-50"
New rd., not on old Haliburton sheet				
NPI	+	-	45-01'-15"	79-45'-40"
M-O	+	-	45-01'-25"	79-46'-50"
Side rd. off 69 to Gibson Ind. Res.				
M1	+	69	45-02'-00"	79-46'-30"
M2	+	"	45-02'-35"	79-46'-45"
M3	+	-	45-03'-45"	79-48'-30"
Side rd. W. off 69 picnic site				
M4	pink qz fld gneiss	69	45-04'-05"	79-46'-55"
M5	gt qz fld migmatite	169	45-06'-05"	79-36'-45"
M6	+	7	45-06'-30"	79-35'-35"
M7	paragneiss	"	45-07'-45"	79-39'-15"
M8	+	"	45-08'-25"	79-40'-00"
M9	+	"	45-10'-25"	79-39'-20"
M10	+	"	45-08'-55"	79-39'-50"
M11	gt migmatite	141	45-16'-10"	79-39'-15"
M12	gt migmatite	"	45-16'-25"	79-40'-15"
M13	+	"	45-16'-30"	79-40'-10"
M14	+	"	45-17'-20"	79-44'-15"
M15	+	"	45-16'-55"	79-45'-45"
M16	gt charnockite	69	45-16'-25"	79-50'-00"
M17	+	"	45-15'-30"	79-49'-35"
M18	+	"	45-17'-25"	79-50'-55"



M19	+	"	45-17'-40"	79-51'-40"
M20	+	"	45-17'-32"	79-51'-50"
M21	metagabbro	"	45-17'-35"	79-52'-00"
M22	+	"	45-17'-55"	79-52'-20"
M23	+	"	45-18'-05"	79-52'-25"
M24	mafic granulite	"	45-18'-25"	79-54'-00"
M25	mafic granulite	"	45-18'-25"	79-57'-45"
M26	mafic granulite	"	45-18'-25"	79-56'-05"
M27	mafic granulite	"	45-18'-40"	79-58'-40"
M28	mafic granulite	"	45-20'-00"	79-59'-30"
M29	gt amphibolite	518	45-20'-00"	79-59'-50"
M30	gt amphibolite	"	45-20'-00"	79-58'-20"
M31	gt amphibolite	"	45-20'-00"	79-57'-55"
M32	+	"	45-20'-20"	79-56'-20"
M33	amphibolite	"	45-20'-25"	79-55'-20"
M34	+	"	45-20'-45"	79-54'-50"
M35	charnockitic gneiss	"	45-21'-45"	79-52'-20"
M36	orthogneiss	"	45-22'-00"	79-51'-15"
M37	gt charnock gneiss	"	45-22'-15"	79-49'-30"
M38	+	-	45-23'-30"	79-47'-00"
Rd. north from Orrville to McKellar				
M39	gt amphibolite	-	45-24'-20"	79-47'-15"
M40	amphibolite	-	45-24'-25"	79-47'-55"
M41	+	-	45-25'-40"	79-48'-30"
M42	gt migmatite	-	45-26'-50"	79-51'-15"
M43	charnockitic gneiss	-	45-27'-30"	79-51'-35"
M44	gt migmatite	-	45-28'-25"	79-51'-50"
M45	+	-	45-29'-30"	79-51'-55"
M46	gt charnock gneiss	-	45-29'-40"	79-52'-00"
M47	gt bi migmat. gneiss	124	45-28'-55"	79-56'-25"
M48	+	"	45-57'-30"	79-47'-15"
M49	bi-gt paragneiss	-	45-27'-05"	79-13'-00"
Side rd off 592 & 11 Novar				
M49a	+	124	45-28'-00"	79-59'-25"
M50	paragneiss	11	45-23'-05"	79-01'-00"
M51	+	"	45-25'-30"	79-14'-15"
M52	gt bi paragneiss	"	45-27'-05"	79-13'-30"
M53	+	"	45-31'-50"	79-19'-10"
On Sundridge 1:125,000 sheet Outcrop S. of MOT garage S. of Emsdale				
M54	+	"	45-33'-10"	79-20'-30"
M55	gt paragneiss	60	45-20'-20"	79-11'-10"
M56	gt bi paragneiss	"	45-20'-30"	79-10'-35"
M57	+	"	45-20'-30"	79-10'-10"
M58	+	"	45-20'-40"	79-09'-30"
M59	gt paragn, calc-sil	"	45-21'-30"	79-08'-15"
M60	gt charnock gneiss	"	45-21'-50"	79-06'-45"
M61	gt charnock gneiss	"	45-21'-20"	79-04'-25"
M62	gt charnock gneiss	"	45-20'-50"	79-20'-20"
M63	gt charnock gneiss	"	45-20'-00"	79-01'-00"
M64	gt charnock gneiss	117	45-12'-30"	79-02'-05"
M65	gt charnock gneiss	"	45-11'-30"	79-04'-15"
M66	gt charnock gneiss	"	45-09'-05"	79-06'-35"
M67	gt charnock gneiss	2	45-16'-20"	79-10'-45"
M68	gt grey paragneiss	"	45-17'-40"	79-12'-00"
M69	gt charnock gneiss	11	45-20'-20"	79-13'-45"

M70	gt charnock gneiss	3	45-17'-20"	79-20'-30"
M71	+	"	45-17'-30"	79-23'-25"
M72	gt granulite	"	45-17'-15"	79-24'-20"
M73	paragneiss	"	45-16'-30"	79-25'-20"
M74	calc-sil, paragneiss	141	45-14'-40"	79-36'-10"
M75	gt bi paragneiss	"	45-13'-20"	79-30'-30"
M76	gt bi paragneiss	"	45-12'-55"	79-30'-15"
M77	pink/grey paragneiss	"	45-13'-20"	79-27'-20"
M78	gt calc-silicate	"	45-10'-50"	79-25'-00"
M79	pink fld hbl gneiss	"	45-10'-50"	79-21'-00"
M80	+	11	45-12'-55"	79-18'-30"
M81	+	"	45-12'-30"	79-18'-25"
M82	gt calc-silicate	"	45-10'-20"	79-18'-45"
M83	charnockitic gneiss	118	45-02'-35"	79-20'-30"
M84	gt charnock gneiss	"	45-03'-30"	79-24'-20"
M85	gt calc-silicate	"	45-03'-30"	79-24'-35"
M86	orthogneiss	"	45-03'-40"	79-26'-10"
M87	granitic orthogneiss	"	45-04'-00"	79-27'-50"
M88	+	"	45-04'-30"	79-28'-30"
M89	+	"	45-50'-25"	79-29'-20"
M90	charn. orthogneiss	"	45-06'-00"	79-30'-20"
M91	granitic orthogneiss	"	45-06'-25"	79-33'-30"
MA-0	+	17	5126000	656100
MA1	gt amphibolite	"	5127600	666100
MA2	gt amphibolite	"	5128200	669600
MA3	+	"	5128300	670000
MA4	+	"	5128500	671050
MA5	orthogneiss, metagab	"	5131300	678100
MA6	amphibolite	"	5130800	684900
MA7	+	"	5128400	691750
MA8	bi hbl orthogneiss	"	5127500	694390
MA9	gt amphibolite	"	5128400	699850
MA10	gt amphib, orthogn	"	5125400	706250
MA11	orthogneiss	533	5132300	676000
MA12	gt amphibolite	"	5142400	660200
MA13	amphibolite	"	5144550	657500
MA14	gt amphibolite	"	5147550	657300
MA15	+	"	5150900	655700
NB1	gt metagabbro	11	5128500	620800
NB2	gt amphibolite	17	5128750	621900
NB3	no sample			
NB4	gt amphibolite	"	5128700	622800
NB5	ep amphibolite	583	5150500	620800
NB6	hbl di mafic gneiss		5135300	628400
Side rd. E. of Feronia				
NB7	amphibolite	17	5127100	628000
NB8	gt amphibolite	17	5126300	631500
NB9	gt amphibolite	17	5126000	632500
NB10	gt amphibolite	17	5125750	633700
NB11	gt orthogneiss	17	5125600	635700
NB12	gt orthogneiss	-	5120300	640600
Rd W. of Bonfield along L. Nosbonsing				
NB13	gt amphibolite	-	5122500	637900
Rd N. of L. Nosbonsing				

NB14	pink gt orthogneiss	17	5126200	632500
NB15	pink gt orthogneiss	-	5127500	633700
Rd N. of Astorville, L. Nosbonsing				
NB16	pink gt orthogneiss	654	5115400	624250
NB17	grey gt orthogneiss	654	5116000	623500
NB18	pink orthogneiss	-	5114700	618000
Rd. off 654 N. to Deepwater Pt.				
NB19	amphibolite	-	5115450	615600
Rd N. of & // to 654				
NB20	pink paragneiss	654	5112500	615400
NB21	amphibolite	654	5110900	616000
NB22	gt orthogneiss	634	5105700	615400
NB23	gt amphibolite	-	5090100	619050
Side Rd E. of Storie				
NB24	cpx gt orthogneiss	-	5106300	630450
Side Rd. NE. of Powasson				
NB25	gt orthogneiss	11	5108100	626350
NB26	gt orthogneiss	"	5100300	628250
NB27	+	"	5121600	625300
NB28	+	"	5112800	626750
NB29	+	"	5111000	626650
NB30	+	-	5104100	631000
Side rd. due E. of Powasson				
NB31	gt orthogneiss	-	5109050	639100
Side rd NE. of Chiswick				
01	granitic orthogneiss	69	44-46'-10"	79-41'-20"
02	granitic orthogneiss	"	44-47'-15"	79-42'-00"
03	grey gneiss	"	44-47'-55"	79-42'-50"
04	granitic orthogneiss	"	44-48'-15"	79-44'-05"
05	pink/grey mig paragn	501	44-48'-30"	79-45'-25"
06	+	69	44-50'-25"	79-44'-20"
07	+	"	44-52'-05"	79-44'-30"
08	+	"	44-52'-30"	79-44'-50"
Rd cut bridge over Go Home Lk				
09	+	-	44-52'-50"	79-41'-50"
Rd E. from 69 to Severn Falls				
010	+	-	44-53'-20"	79-38'-00"
011	+	"	44-58'-20"	79-46'-20"
side rd 0.75 km S. of Gibson R. bridge				
012	na	"	44-58'-00"	79-46'-25"
side rd 1.5 km S. of Gibson R. bridge				
013	+	"	44-57'-10"	79-46'-40"
014	+	"	44-57'-05"	79-46'-20"
015	+	"	44-55'-00"	79-46'-20"
016	+	"	44-55'-30"	79-46'-20"
017	+	"	44-56'-15"	79-46'-20"
PS1	+	124	45-26'-45"	80-01'00"
PS2	+	"	45-26'-20"	80-01'30"
PS3	+	"	45-24'-40"	80-01'15"
PS4	gt amphibolite	69	45-20'-30"	80-00'20"
PS5	+	"	45-20'-40"	80-00'30"
Int. 69 south & 69B				
PS6	+	-	45-19'-25"	80-01'-30"
Rd. from Parry Sound to Parry Is.				

PS7	+	-	45-20'-30"	80-02'-20"
PS8	+	-	45-20'-30"	80-04'-00"
			Rd from mainland to Parry Is. at town of Parry Island (Ind. Res.)	
PS9	+	69	45-21'-30"	80-20'-30"
			Int 69 north & 69B, GAC/MAC trip stop 1-1	
PS10	gt migmatite	69	45-24'-00"	80-03'-45"
PS11	granitic gneiss	"	45-20'-30"	80-06'-50"
			Int. 69 & rd. to Killbear Prov. Pk.	
PS12	granitic gneiss	-	45-26'-50"	80-10'-30"
			Rd. to Killbear Prov. Pk.	
PS13	+	-	45-25'-00"	80-14'-05"
PS14	+	-	45-23'-30"	80-14'-45"
PS15	granitic gneiss	-	45-24'-50"	80-15'-00"
PS16	+		45-28'-30"	80-10'-30"
S1	+	-	45-30'-30"	79-52'-30"
			Side rd. E. of McKellar	
S2	+	124	45-33'-10"	79-55'-20"
S3	+	"	45-33'-30"	79-55'-20"
S4	+	"	45-34'-15"	79-55'-05"
S5	mafic gneiss	"	45-35'-05"	79-54'-20"
S6	mafic gneiss	"	45-35'-20"	79-54'-20"
S7	gt migmatite	"	45-37'-45"	79-52'-45"
S8	gt granite gneiss	"	45-38'-30"	79-51'-40"
S9	pink paragneiss	"	45-36'-20"	79-53'-30"
S10	gt amphib, gt paragn	"	45-48'-30"	79-55'-30"
S11	gt grey gneiss	522	45-55'-05"	79-57'-00"
S12	mylon. gt gneiss	"	45-54'-20"	79-55'-40"
			Side rd. S. from Arnstein	
S13	gt orthogneiss	522	45-58'-30"	79-37'-40"
S14	+	"	45-59'-00"	79-38'-35"
S15	+	"	45-58'-30"	79-39'-30"
S16	gt, ep amphibolite	"	45-55'-05"	79-49'-50"
S17	amphibolite	"	45-57'-00"	79-46'-00"
S18	gt amphibolite	"	45-58'-00"	79-42'-35"
S19	+	"	45-58'-10"	79-42'-10"
S20	+	"	45-58'-50"	79-39'-40"
S21	mafic gneiss	11	45-56'-45"	79-21'-55"
S22	gray orthogneiss	"	45-54'-40"	79-22'-00"
S23	+	"	45-52'-45"	79-22'-30"
S24	bi orthogneiss		45-49'-35"	79-28'-10"
			Rd from S. River to Mikiskew Prov. Pk.	
S25	gt bi orthogneiss	11	45-45'-30"	79-25'-05"
S26	+	"	45-44'-35"	79-26'-25"
S27	gt orthogneiss	"	45-44'-35"	79-26'-10"
S28	calc-sil, paragneiss	"	45-37'-45"	79-24'-50"
S29	+	"	45-36'-00"	79-22'-40"
S30	+	592	45-30'-25"	79-16'-20"
S31	+	518	45-32'-35"	79-15'-35"
			Rd. to Kearyney form 11, Emsdale	
S32	+	"	45-34'-20"	79-09'-45"
S33	gt grey paragneiss	"	45-34'-50"	79-07'-55"
S34	+	"	45-35'-00"	79-07'-45"
S35	gt bi orthogneiss	124	45-43'-15"	79-31'-45"

S36	bi orthogneiss	"	45-42'-30"	79-35'-35"
S37	gt amphibolite	"	45-39'-20"	79-49'-00"
S38	gt meta-anorth	"	45-39'-05"	79-50'-50"
Int. Hwys 124 & 520 E. Dunchurch				
S39	gt orthogn, amphibol	520	45-39'-20"	79-50'-40"
S40	gt metagabbro	"	45-41'-00"	79-51'-15"
S41	+	"	45-41'-30"	79-51'-50"
S42	+	"	45-41'-50"	79-53'-20"
S43	gt metagabbro	"	45-39'-10"	79-50'-00"
SD1	gt orthogneiss	69	5094100	533450
SD2	gt paragneiss	"	5094700	533100
SD3	qz-feld gneiss	-	5093400	530000
Rd W. of 69 Bigwood				
SD4	qz-feld gneiss	-	5093400	529000
SD5	qz-feld gneiss	-	5093400	528800
SD6	qz-feld gneiss	-	5093400	527300
SD7	qz-feld gneiss	-	5093400	528500
SD8	qz-feld gneiss	-	5093300	524800
SD9	gt amphibolite	-	5101600	531500
Rd to Bigwood Bay, S. of 607				
SD10	grey paragneiss	64	5105000	532500
SD11	gt amphibolite	"	5105700	534700
SD12	migmatitic gneiss	"	5106000	543900
SD13	hbl orthogneiss	"	5110900	546400
SD14	amphibolite	-	5111200	546800
Rd to Bear Lk. NW of 64				
SD15	orthogneiss	64	5109900	547900
SD16	amphibolite	535	5118500	543800
SD17	gt amphibolite	"	5126200	543700
SD18	calc-silicate	-	5134300	538100
Rd W. of 535 St. Charles				
SD19	gt amphibolite	-	5134300	534000
SD20	bi amphibolite	17	5144600	544000
SD21	gt amphibolite	"	5146600	537000
SD22	gt metagabbro	"	5147100	535800
SD23	gt amphibolite	"	5146600	516800
SD24	gt amphibolite	537	5139200	517800
SD25	amphibolite	"	5134100	513200
SD26	amphibolite	17	5116900	517500
SD27	gt metagabb, orthogn	64	5112200	551350
SD28	gt hbl meta-anor	-	5113900	556400
Rd. E of N. Monetville				
SD29	hb bi orthogneiss	64	5117900	553100
SD30	gt bi orthogneiss	"	5128300	561100
SD31	amphibolite	"	5128500	559000
SD32	amphibolite	"	5129000	634000
SD33	grey paragneiss	"	5136000	567300
SD34	gt amphibolite	-	5140200	570300
Dirt Rd on farm N. of 17				
SD35	calc-silic, amphib	-	5175100	551000
SD36	grey qz fld gneiss	539	5145200	554150
SD37	meta-ultramafite	"	5148150	555250
SD38	di amphibolite	"	5148400	555300
SD39	bi gt orthogneiss	"	RR cut 1 km SE River Valley	
SD40	orthogneiss	64	between River Valley & Field	

T1	gt metabasite	64	5168600	581950
T2	hbl orthogneiss	11	5171500	594400
T3	bi metasyenite	-	5151000	617750
Rd to Tomiko, NW of Hwy 11				
T4	+	533	5152500	655000
T5	gt amphibolite	"	5153250	645600
T6	gt amph, musc paragn	63	5151950	641650
WSA1	+	-	Same locality as S86E-25 series	

## Sept. 1985 field trip with A. Davidson

A85A-1	+	60	E. boundary of Algonquin park, 2.7 km east of "East Gate".	
A85A-2	+	"	8.7 km east of stop 3-5, GAC/MAC trip	
A85A-3	+	"	Same locality as GAC/MAC trip, stop 3-5.	
H85A-1	+	35	Stop 2-9, GAC/MAC trip: Dragon's Head	
M85A-1	+	11	45-12'-55"	79-18'-30"
Int 11 & 141 W. to Parry Sound				
M85A-2	calc-silicate	118	45-04'-00"	79-27'-50"
M85A-3	+	"	45-06'-20"	79-35'-25"
Int. 118 and Muskoka Rd. 7				
M85A-4	+	M7	Same location as M8	
M85A-5	+	M38	45-01'-00"	79-40'-45"
M85A-6	+	"	45-01'-25"	79-45'-40"
M85A-7	meta-ultramafite	-	45-08'-25"	79-31'-40"
Rt. 25 S. of Windemere on Roseau Lk.				
PS85A-0	+	69	45-18'-35"	79-58'-30"
PS85A-1	+	"	45-23'-20"	80-03'-15"
PS85A-2	+	"	45-21'-30"	80-02'-10"
Hwy 69 road cut N. of Parry Sound				
PS85A-3	+	-	45-21'-45"	80-01'-10"
Stop 1-1, GAC/MAC field trip				
PS85A-4	+	-	45-19'-40"	80-02'-00"
Mill Lake Quarry				
PS85A-5	+	-	45-18'-45"	80-02'-20"
Stop 1-2, GAC/MAC field trip				
PS85A-6	+	-	45-19'-15"	80-01'-50"
PS85A-7	+	-	45-20'-20"	80-01'-00"
PS85A-8	+	-	45-21'-45"	80-01'-10"
Emily St., SE. of Parry Sound				
S85A-1	+	124	45-27'-50"	80-05'-30"
GAC/MAC field trip stop 2-1				
S85A-2	+	"	45-34'-15"	79-55'-00"
S85A-3	+	-	45-38'-50"	79-53'-50"
Farley's side Rd off 124				
S85A-4	+	-	45-39'-40"	79-47'-40"

## May 1986 GAC/MAC granulite field trip. See guidebook for locations.

A86B3-3a	+	60	Day 3, stop 3-3, Hwy 60, Algonquin Park.	
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A86B3-5a	+	"	Day 3, stop 3-5, Hwy 60, Algonquin Park.
H86B2-6	+	11	Day 2, stop 2-6, Hwy 11
PS86B1-1	+		Day 1, stop 1-1, Hwy 69 road cut.
PS86B1-2	+		" "
PS86B1-3	+		" "
PS86B1-4	+		" "
PS86B1-5	+		" "
PS86B1-6	+		" "
PS86B1-7	+		" "
PS86B1-8	+		" "
PS86B1-11	+		" "
PS86B2-1	+		Day 1, stop 1-2, Boat Works, Emily St.
PS86B2-2	+		" "
PS86B2-3	+		" "
PS86B2-4	+		" "

## Sept. 1986 field trip with M.A. Cosca.

M86E-1	+	11	45-18'-20"	79-14'-45"
PS86E-1	gt amphibolite	17	45-14'-35"	79-48'-45"
			Muskoka 1:125,000 map	
PS86E-2	amphib, mafic gran	69	5021500	578850
			Int. 69 S. and 69B.	
PS86E-3	amph, maf & fels gne	"	5022350	577700
			Long outcrop on 69 S. of McDougal St.	
PS86E-4	+	"	5022900	577500
PS86E-5	mafic, gran gneiss	"	5023350	577100
PS86E-6	+	"	5023500	577750
PS86E-7	+	"	5023200	575500
			Series of samples along 69 road cut	
PS86E-8	+	-	5024550	576300
			Mill Rd. betw 69 and 124	
PS86E-9	hbl gt meta-anorth	-	5025050	577450
			Limbert Rd. off Mill Rd.	
PS86E-10	+	-	5025500	576050
			Mill Rd.	
PS86E-11	grey flat paragneiss	-	5026150	576200
			Mill Rd.	
PS86E-12	+	-	5026950	577450
			Burnside Rd. E. off int 124 & Mill Rd.	
PS86E-13	gt ep meta-anorth	-	5026450	526450
			Burnside Rd.	
PS86E-14	gt amphibolite	124	5028150	576300
PS86E-15	+	-	5033050	577200
			Long Lk. Estates Rd.	
PS86E-16	+	-		
			Long Lk. Estates Rd.	
PS86E-17	+	-	5032350	577650
			Long Lk. Estates Rd., Ferguson res.	
PS86E-18	gt cpx amphibolite	124	5033700	576950
PS86E-19	+	"	5034150	577450
PS86E-20	+	-	5075450	577700
			Rd. to Ardberg off 124	

PS86E-21	+	-	5035600	577700
PS86E-22	+	-	5036300	577850
PS86E-23	+	-	5037000	577750
PS86E-24	+	-	5037800	577350
Sample series at W. margin WSA				
PS86E-25	gt amphibolite	-	5038750	576550
PS86E-26	+	69	5023600	574950
PS86E-28	+	"	5025250	574500
PS86E-30	+	"	5026200	574100
PS86E-31	+	"	5027350	573600
PS86E-32	+	-	5018500	574450
Rd. W. of bridge to Parry Is.				
PS86E-33	+	-	5018200	575050
Outcrop just E. of bridge to Parry Is.				
PS86E-34	+	-	5022100	576300
Dam, Sequin R. Cascade St.				
S86E-1	+	520	5061150	585600
S86E-2	gt orthogneiss	"	5060900	586550
S86E-3	gt amphibolite	"	5060900	586500
S86E-4	+	"	5060900	587600
S86E-5	+	-	5059100	587800
Whitestone Lk. Rd., W. off 520				
S86E-7	+	520	5057100	590300
S86E-8	+	-	5053700	585750
W. off 124 on Farley's side road				
S86E-9	gt orthogneiss	-	5053450	587400
10 -17, S. arms of Whitestone Lk.				
S86E-10	+	-	5055100	585200
S86E-11	+	-	5055250	585400
S86E-12	+	-	5055250	585600
S86E-13	+	-	5055400	586250
S86E-14	+	-	5055350	586500
S86E-15	+	-	5055300	586650
S86E-16	+	-	5055300	587200
S86E-17	+	-	5055325	587300
S86E-18	+	124	5043050	583950
S86E-19	+	-	5053450	587400
Int. 124 & Farley side rd.				
S86E-20	+	-	5055400	587875
S86E-21	+	-	5055400	588400
S86E-22	+	-	5055400	588300
S86E-23	+	-	5055750	587850
S86E-24	+	-	5056000	587800
S86E-25	+	-	5056700	587675
S86E-26	+	-	no sample	
S86E-27	+	-	5056900	587900
S86E-28	+	-	5057300	588300
S86E-29	gt metadiorite	-	5057500	588600
S86E-30	cpx metadiorite	-	5057650	588900
S86E-31	+	-	5057000	587650
S86E-32	+	-	5057050	587600
S86E-33	+	-	5057000	587500
S86E-34	+	-	5057000	587250
S86E-35	+	-	5057150	587150
S86E-36	+	-	5057100	586850



S86E-37	+	-	5057050	586750
S86E-38	+	-	5056900	586500
S86E-39	+	-	5056850	586150
S86E-40	+	-	5056000	585800
S86E-41	+	-	5056600	585550
S86E-42	+	-	5056650	585600
S86E-43	+	-	5056650	584800
S86E-44	+	-	5056600	684350
S86E-45	+	-	5056450	584100
S86E-53	+	11	See M53 locality	

## APPENDIX 2

## Mineral Assemblages

Abbreviations		1:125,000 map sheets	
X	Phase present	A	Algonquin
S	Secondary or retrograde	B	Bobcaygeon
Al	Allanite	BI	Byng Inlet
Am	Amphibole (Hornblende unless otherwise noted)	C	Coniston
A	Actinolite	GL	Golden Lake
C	Cummingtonite	H	Huntsville
H	Hornblende	M	Muskoka
Ap	Apatite	MA	Mattawa
Bi	Biotite	NB	North Bay
Cc	Calcite	O	Orillia
Ch	Chlorite	PS	Parry Sound
Cpx	Clinopyroxene	PSO	
Do	Dolomite	S	Sundridge
Ep	Epidote	T	Tomika
Gr	Graphite		
Gt	Garnet		
Kf	K-feldspar		
M	Microcline		
P	Perthite		
Ky	Kyanite		
Mu	Muscovite		
Ne	Nepheline		
Ol	Olivine		
Opx	Orthopyroxene		
Ox	Oxide		
M	Magnetite		PS86E Parry Sound 1:50,000
I	Ilmenite		S86E Magnetawan 1:50,000
Ne	Nepheline		
Pg	Plagioclase		
Qz	Quartz		
Ru	Rutile		
Sc	Scapolite		
Serp	Serpentine		
Sf	Sulfide		
Py	Pyrite		
Po	Pyrrhotite		
Si	Sillimanite		
Sp	Spinel		
Ti	Titanite		
Wo	Wollastonite		
Zc	Zircon		

Sample	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
ARM4	X	X	X	X				X	X	S	X	X		X	
A1a			X	X		X	X	X	X		X			X	
A1b			X					X	X		X				
A2a		X	X	X	M,P	X		X	S					X	
A2b		X	X	X	M	X	X	X	X					X	Zc
A2c		X	X	X	M	X	X	X	X		X			X	
A2d		X	X			X		X	X						
A3a		X	X	X		X	X	X	X					X	
A3b		X	X	X	P				X						
A3c		X	X			X	X				X			X	Zc
A4a		X	X			X	X	X			X			X	
A4a		X	X			X	X	X							
A5a			X	X		X	X	X	X						Ol
A5b			X	X		X	X	X	X		X			X	
A6a		X	X	X		X	X	X	X			Py		X	Ru,Zc
A6b		X	X	X	P	X			S						
A6c		X	X	S	M,P				S		M	Py			
A7a		X	X			X	X	X			X			X	
A85A-1	X	X				X	X			X		Py	X		
A85A-2			X			X		X			X				
A85A-2b		X	X			X	X	X	X						
A85A-3a	X	X	X	X	M		X			X			X		Wo
A85A-3b	X	X	X	X			X			S		Py	X	X	
A85A-3c	X	X	X				X			X			X		Gr
A85A-3d	X	X	X	X			X						X		
A85A-3e	X	X		X			X			X			X		Wo
A86A-3f	X	X	?	X			X			X			X		Wo
A86B3-5a	X	X	X	X			X			X			X		Wo
A86B3-3a	X		X			X	X	X	X					X	
A86B3-3b			X	X		X	X	X	X					X	
A86B3-3c	X		X			X	X	X	S	S	X			X	
B1a									X	X				X	
B1c		X	X		M			X	X				X		
B2b		X	X		M		X			X			X		Zc
B2c		X	X		M	X				S	X		X		
B3a		X	X		M		X			X				X	
B5			X		P		X		X	X					
B6a								X	X	X					
B6b		X	X		M			X	X	X					
B7a	X		X						X	S				X	
B7b	X		X						X					X	
B8b	X		?		X		X			X					
B9a		X	X				X	X					X		
B10	X	X	X		M		X		X	X					Gr
B11	X	X	X		M		X			X					
B12		X	X				X	X							
B14b		X	X		M,P								X	X	
B18a		X	X	X	M				X						Zc
B20			X		M		X	X					X	X	
B20a	X						X	X		X			X		
B22a	X		X				X	X	X				X		
B23b	X		X				X	X	X	S			X		
B23d		X					X		X	X					
B24	X						X		X	X					
B25a,b			X					X	X						
B26a	X	X	X				X	X	X	X			X		
Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other	

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
B26b	X	X	X				X	X	X	X			X		
B27a		X	X		P					S					
B27C	X		X		M		X			X			X		
B27d	X				M		X			X			X		
B29			X		P				X	X	X				
B28a		X	X		P,M				X	X				X	Ne
B31		X	X					X					X		
B32A	X	X	X				X								
B33a		X	X			X	X	H,C	X	X					
BAcrg1															
BAcrg2	X	X	X							S	M				Zc, Mu(S)
BA1a		X	X		M		X		X	X			X	X	
BA1b		X	X		P		X		S				X		
BA2		X	X		P			S	X					X	Ep
BA3		X	X				X	X	S	S			X		
BA4			X				X	X			X		X		
BA5		X	X						X						
BA6a		X	X		M		X	X	X	S	X	X	X		
BA6b		X	X				X	X	S			X			Mu(S)
BA7a		X	X				X	X	X					X	Zc
BA7b		X	X				X	X	X		X			X	Zc
BA7c			X				X	X			X				Zc
BA7d		X	X			X	X	X			X				Zc
BA7-1		X	X				X	X	X	S				X	
BA7-2		X	X				X	S	S		X			X	Mu(S)
BA8		X	X				X	X	X		X	X	X		Gr?
BA9a		X	X	X		X	X	X			X			X	
BA9b		X	X	X	M		X	X	X		X	X			
BA9c		X	X	X		X	X	X			X	X			
BA10		X	X			X	X	X	S		X	X		X	
BA14b			X		M		X						X		Zc
BA14c	X		X				X		X	X			X		Zc
BA15A	X		X				X		X				X		Zc
BA15b	X	X					X		X				X	X	
BA16		X	X		P,M		X		S			X	X		
BA17a	X	X	X		P,M		X		X	X	X	X			Zc
BA17b	X	X	X		P,M		X		X	X			X		Zc
BA18b			X				X		X				X		Zc
BA18c		X	X		M		X				X		X	X	Zc
BA19	X	X							X	X					Zc
BA18a		X	X		P,M		X			S			S	S	Zc
BA20b	X	X	X				X	X			X	X	X		Zc
BA20c		X	X		P			X	X		X	X	X		
BI3c		X	X	X	P			X	X					X	
BI4b		X	X	X				X	X			X	X	X	
BI7		X	X	X			X	X	X		X			X	Zc
BI25a			X	X			X	X	X						
BI31		X	X	X	X		X	X	X						
BI34a			X	X		X	X	X	X		X		X		
BI35		X	X	X			X		X		X	X	X	X	Zc
BI36a		X	X	X				X	X		X			X	
BI36c		X	X	X				X	X		X				Ru
BI49		X	X	X	M			X	X				X		
BI31		X	X	X	P			X	X					X	
C1a		X	X	X					X						Zc
C1b	X	X	X	X			X	X		S			X		Ep
	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
GL3b		X	X	X	P,M		X	X						X	Zc
GL5a		X	X	X	M	X			X		X				
GL6		X	X	X		X	X	X			I,M	Py			
GL8b		X	X	X		X		X	X					X	
GL13a		X	X		P,M			X	X				X	X	
GL14b		X		X				X	X						
GL16a		X	X					X	X						
GL21b		X	X			R		H,C	X					X	Zc
GL25		X	X				X	X	S						
GL26a	X	X	?		?		X			X		X	X		
GL26b	X	X					X			X		X	X		
GL27a	X				X		X			X			X		Zc
GL28b	X		X				X			X			X		Zc
GL28a-1	X		X		M		X			X			X		Ep, Zc
GL28a-2	X				M		X			X			X		Ep
GL28c		X	X		M			X	X				X	X	Gr
GL281										X					
H1		?	X	X		X		X						X	Zc
H2b		X	X	X	P,M				X					X	Zc
H2c		X	X	X					X					X	Zc
H2d			X	X		X	X	X			X			X	
H4		X	X	X	M		?	X	X					X	Ep
H5		X	X	X				X	X					X	Zc
H6		X	X	X				H,C							
H7b		X	X			X			X					X	
H7c		X	X		X							X			Gr
H9a										X					Serp
H9b		X	X				X	X					X	X	
H10b			X		M		X	X		X				X	
H11a		X	X		P,M		X	X	X					X	
H12		X	X		M				X	X	X				
H13	X	X	X				X		X	X			X		
H14	X	X	X		P,M			X	X						
H15a			X					H,C							
H16			X					X	X	S					
H17a		X	X					X	X						
H17c		X	X			X	X	H,C	X						
H18		X	X	X				X							
H19		X	X			X	X	X			X				
H20		X	X			X	X	X	X	S					
H20d		X	X		P,M			X	S		M				Zc
H22		X	X	X		X		X	X		X			X	
H23a	X		X					X	X	X			X		
H24								X	X					X	
H37a		X	X	X		X	X		X					X	
H40a	X	X	X	X			X	X		X			X		Ep
H40b	X			X			X	X		X			X		Ep
H40c-1	X	X		X			X	X		X			X		Ep, Zc
H40c-2	X	X	X	X	M		X	X		X			X		Ep
H40d	X	X	X	X			X	X		X			X		Ep
H40f	X	X	X	X			X	X		X			X		Ep
H85A-1		X	X	X	P			X	X				X		
H85A-1a'		X	X	X		X	X		X					X	
H85A-1a		X	X	X	M			X	X		X				
H85A-1b	X	X	X	X			X						X		
H85A-1d	X	X	X	X									X		
H85A-1e	X	X	X	X			X						X		
	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
H85A-1(3)		X	X	X			X						X		
H85A-3		X	X	X	P,M				X						Mu
H85A-15e			X	X			X	X	X						
H86B2-6a			X	X		X	X	X	X		X			X	
MPIa							X			X					Ol, Gr
MPIb	X		X	X			X	X					X		
MPId	X		X				X	X		X		X	X		
M-0		X		X	X				X						Zc
M1		X	X	X					X						Zc
M2a		X	X	X					X						Zc
M2b		X	X	X			X	X	X				X	X	Zc
M3a			X					X	X				X		Ep(S)
M3b		X	X					X	X	X			X		
M6a			X	X			X	X	X			X		X	
M6b		X	X	X				X	X			X		X	
M8		X	X	X				X	X					X	
M9a		X	X	X			X	X	X						Zc
M10		X	X	X		X	X	X	X		X	X		X	
M13b		X	X	X			X	X	X		X				
M14		X	X	X				X	X		X	X			Ru
M15a			X	X				X	X		X	X	X	X	
M15b		X	X	X				X	X						Ep
M17			X					X	X						
M18a		X	X		M				X						
M18b		X	X	X				X	X				X		Ep
M18c	X	X	X					X	X			Po			
M18d	X	X	X					X	X				X		Ep
M19		X	X					X	X				X	X	Ep
M20b		X	X			X		X	X						
M22a		X	X					X	X					X	
M22b		X	X				X	X	X		X		X		
M22c		X	X				X	X	X		X	X		X	
M23		X	X			X	X	X	X					X	
M32d			X	X		X		X	X		X				
M34a		X	X				X	X	S				X		
M34b			X			X	X	X	S						
M38		X	X	X		X		X	S					S	
M41c		X	X	X	P			X	S						
M45a		X	X	X		X		X	S		X			X	
M45c			X	X		X	X	X			X			X	
M48		?	X	X		X		X	X					X	Zc
M49	X	X	X	X			X	X	X					X	
M51b		X	X	X				X	X		X				
M54b		X	X	X	M				X						Mu
M54b-2		X	X	X					X	S				X	Mu(S)
M57a		X	X	X					X					X	Zc, Ru, Gr
M57b			X	X		X	X	X	X					X	
M57c		X	X	X			X	X	X					X	Zc
M58		X	X	X		X	X	X	S		X			X	
M71b		X	X	X		X	X	X	X		X			X	
M80d		X	X	X	M			X	X					X	Zc
M81			X	X		X	X	X			X				
M88e			X	X	P,M			X	X					X	Zc
M89a		X	X	X		X		X	X					X	
M85A-1			X	X		X	X	X	X		X			X	
M85A-1b	X		X	X			X	X					X		Sp
	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
M85A-3			X	X				X	X		X			X	
M85A-4			X	X				X	X		X			X	Ru
M85A-5a	X	X		X			X			X					Ep(S)
M85A-5c	X	X		X			X			X			X		
M85A-6a		X	X	X						X					Wo
M86E-1a	X		X	X			X					Py	X		
M86E-1b-1	X	X	X	X			X			X			X		Wo
M86E-1b-3	X	X		X			X			X					Wo
M86E-1c-2	X		X	X			X			X			X		Wo
M86E-1d-1	X	X		X			X			X					
M86E-1d-2	X	X	X	X			X						X		Wo
M86E-1e	X	X	X	X			X							X	
MA-0										X					Serp
MA3		X	X	X				X	X				X	X	
MA4b		X	X	X				X	X						
MA7		X	?	X	M		X	H,C	X		X			X	
MA15		X			M										Mu
MA15b		X		X	M										Mu
MAT84B-20		X	X		X					X					Gr
NB27		X	X	X					X				X		
NB28			X	X				X	X		X				
NB29			X	X			X	X	X					X	Zc
NB30		X	X	X	P		X	X	X		X			X	
O6a		X	X	X	M			X	X		X	X			Zc
O6b		X	X	X				X	X						
O6d		X	X	X				X	X					X	Zc
O7a		X		X	P,M			X	X						
O7b		X	X	X				X	X					X	
O8b	X	X		X	M		X			X			X		Zc
O8c	X	X		X			X						X		
O8e	X	X	X	X			X			X		X	X		Ep
O8f	X	X		X	M		X						X		
O9a		X	X	X				X	X						
O9B		X	X	X			X	X	X			X			
O10b		X	X	X	P,M				X						
O11		X		X	P,M				X		X	X		X	Zc
O13a		X	X	X		X	X	X	S		X			X	Zc
O13b			X	X			X	X	S					X	
O13c		X	X	X	X			X	X		X				
O14b		X	X	X				X	X		X			X	Zc
O15a		X	X	X	X			X	X		X			X	Zc
O15b		X	X	X	P	X		X	X					X	
O16		X		X				X	X						
O17		X		X	M		X			X					Zc
PS1a		?	X						X			X	X	X	Ep
PS2		X	X	X				X	X			X	X	X	
PS3		X	X	X				X	X	X		X	X	X	Ru?
PS5			X	X			X	X	X			X			
PS6			X	X			X	X	X				X	X	
PS7a	X	X	X	X				X	X		I	Py	X	X	Zc
PS7b	X	X	X	X				X	X		I	X			
PS7c	X	X	X	X			X	X			X		X	X	
PS7f		X	X	X				X						X	
	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
PS7g		X	X	X			X	X		X	I,M	Py		X	
PS8		X	X	X	P,M				X	S					Mu(S)
PS9a		X	X	X				X	X			X	X	X	
PS9b		X	X		M			X	X			X			Zc
PS13		X	X	X				X	X						
PS14a		X	X		M			X			X				Ep,Zc
PS16		X	X						X			X	X		Ep
PS85A-0a	X	X	X	X	X				X					X	
PS85A-0b		X	X					X	X						
PS85A-1a	X		X					X	X						Ep,Mu(S)
PS85A-2a		X	X					X	X		I		X	X	
PS85A-2c	X	?	X	X				X	X		M			X	Ep
PS85A-2e		X	X					X					X		Ep
PS85A-3d			X					X	X						Ep
PS85A-4			X			X	X	X			I			X	
PS85A-5		X	X	X				X					X		Zc
PS86A-5	X	X	X	X				X		X			X	X	Zc
PS85A-6a		X	X			X	X	S	S						
PS85A-6b		X	X	X		X	X	X	X		X				
PS85A-7	X	X	X	X			X	X		X		X			
PS86A-8a	X	X	X	X			X	X			I		X	X	
PS88TA-8b	X	X	X	X				X	X		X		X	X	
PS86A-8c	X	X	X	X				X	X		I,M	Py	X	X	
PS86A-23		X	X	X			X								Wo
PS86A-24	X	X	X	X			X	X	S				X	X	
PS86A-25	X	X	X	X			X	X	X		X			X	Ru
PS86B1-1	X	X	X	X				X	X	S	X		X	X	
PS86B1-2		X	X	X			X	X			X				
PS86B1-3		X	X	X				X	X				X	X	Zc
PS86B1-4		X	X	X				X			X			X	
PS86B1-5		X	X	X			X	X			X			X	
PS86B1-6		X	X	X				X	X	X	X			X	Zc
PS86B1-7		X	X	X			X	X			X			X	Zc
PS86B1-8		X	X	X			X	X			X			X	Zc
PS86B1-11	X	X	X	X				X	X	S			X	X	Ep
PS86B2-1	X	X	X	X				X	X	X	X		X		
PS86B2-2			X	X		X	X	H,C,A							
PS86B2-3	X	X	X	X				X	X		X		X	X	
PS86B2-4		X	X				X	X	X	X			X	X	Ep
PS86B3-1		X	X	X		X	X	S	S		X		X	X	
PS86E-4Nd		X	X	X				X	X	X	I		S		
PS86E-6a		X	X	X				X	X	X	X		X	X	
PS86E-6b		X	X	X			X	X	X	X			X	X	
PS86E-7e	X	X	X	X				X	X	X			X	X	Ep
PS86E-8	X	X	X	X				X	S		I		X	X	Ep,Mu(S)
PS86E-10	X	X	X	X				X	X	S	X			X	Ep,Mu(S)
PS86E-12		X	X	X				X	X	X			X	X	Ep
PS86E-15	X		X	X				X	X					X	Ep
PS86E-16a	X	X	X	X				X			I		X		Ep
PS86E-17			X	X			X	X			I		X		Ep
PS86E-19b		X	X						X						Ep
PS86E-19c		X	X					X	X	X					Ep,Chl(S)
PS86E-19d		X	X						X	S					Ep,Mu(S)
PS86E-20		X	X					X	X	S					Ep,Mu(S)
PS86E-21			X					X	S						Ep,Mu(S)
PS86E-22			X							X					Ep
PS86E-23	X	X	X					X	X	X			X	X	Ep
PS86E-24a	X	X	X				X	X	X	X					



	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
PS86E-24b	X		X					X							Ep
PS86E-24d	X	X	X	X				X	X	X	I		X		Ep
PS86E-24e	X	X	X	X				X	X				X	X	Ep
PS86E-24f	X	X	X	X				X	X		I		X	X	Ep
PS86E-26c		X	X	X				X	X		I, M	Py, Po		X	
PS86E-28b		X	X	X				X	X	S	X			X	Ru
PS86E-30b			X					X	X				X		Ep, Ru
PS86E-30c	X		X					X	X						Ep, Mu(S)
PS86E-30d		X	X	X	X			X	X			Py			Ky, Gr, Mu, R
PS86E-31	X	X	X	X				X	X	X	I		X	X	Ep
PS86E-32a	X	X	X	X				X	X	X					Ep
PS86E-32b	X	X	X	X				X	X	X	I		X	X	Ep
PS86E-33		X	X	X				X	X					X	Zc
PS86E-34	X	X	X	X				X	X		I		X	X	Zc
S2		X	X	X				X	X						
S2a								X	X						
S2e		X	X	X		X		X		S	Sp				Serp, Ch
S4c		X	X	X			X	X			X				
S11		X	X	X					X						
S14b		X	X	X					X					X	
S14c		X	X	X				X	X				X	X	
S15		X	X	X					X						Ky, Ru
S19a		X	X	X				X	X	S			X	X	Ep
S20a		X	X	X				X	X		I		X		
S23		X	X	X				X	X						
S26		X	X	X				H, C	X						
S29b			X	X				X	X		I		X	X	Zc
S30b		X	X	X		X		X	X				X		Zc
S31b			X	X				X	X					X	
S32		X	X	X		X	X	X	X		X			X	
S34		X	X	X		X	X	X	X		X			X	Zc
S42		?	X	X			X	X	X		X				
S59		X	X	X				X	X						
S85A-1b-1		X	X	X		X	X				M	Py			
S85A-1b-2		X	?	X	X				X						Si
S85A-1b-3		X	X	X	X				X						Si, Ru
S85A-1c		X	X	X					X						Ru
S85A-2		X	X	X	X										
S85A-2a-1	X	X	X	X			X					Py	X	X	
S85A-2a-2		X	X	X			X			S		Py, Cpy	X	X	
S85A-2d		X	X	X			X								
S85A-3a	X	X	X	X			X	X							
S85A-3b	X	X	X	X			X	X	X		I, H				
S85A-3c	X	X	X	X			X	X	X				X		
S85A-4			X	X				X	X						Ep
S85A-4'		X	X	X				X	X	X			X		
S85A-8a	X		X					X	X			Py			Ep, Mu
S85A-8b	X	X	X					X	X			Py	X	X	Ep, Mu(S)
S85A-8c		X	X				X	X	X						
S85A-9a	X	X	X	X			X						X		
S86E-1a		X	X	X			X	X		X	X		X		
S86E-4b		X	X	X			X	X		X	I		X		
S86E-5b		X	X	X			X	X		X	X			X	
S86E-7b			X	X		X	X	X	S		I	Py, Po		X	
S86E-8c-1		X	X	X			X	X		X			X		Wo
S86E-8c-2	X		X	X			X	X		X			X		
	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
S86E-8i		X	X	X		R	X	S	S	S	M	Py,Po		X	
S86E-10	X		X	X			X	X	S		I,M			X	Ep(S)
S86E-11	X		X	X			X	X						X	
S86E-12	X	?	X	X			X	X	S		M			X	
S86E-13b	X	X	X	X			X	X	S	S	I,M		S	X	
S86E-14a-1		X	X	X			X			S	I,M			X	
S86E-14a-2	X	X	X	X			X	S	S					S	
S86E-15		X	X	X			X	X			X			X	
S86E-16e		X		X			X			X					
S86E-16g							X			X	Sp				
S86E-16f-1		X	X	X		X	X	X		S	I,M	Py		X	
S86E-16f-2		X	X	X		X	X	X		S	I	Py		X	
S86E-16f		X	X	X			X	X		S	X				
S86E-17b		X	X	X		X	X	X			X			X	
S86E-18b			X	X			X			X			X	X	
S86E-18c		X	X	X		R	X	X	S	S	S		X		
S86E-20			X	X				X	S	S	I,M			X	Ep
S86E-21a		X	X	X		X	X	X	S	S	I			X	Zc
S86E-22		X	X			R	X	X	X		X				
S86E-23							X	X	X	X			X		Do,Ol
S86E-24a								X	X	X	Sp		X		Do,Ol
S86E-24b		X	X	X		X		X	S		I,M			X	Zc
S86E-25a	X		X	X			X	X	S		X		X	X	Ep
S86E-25b	X		X				X	X	X		I		X	X	Ep
S86E-25c	X	?	X	X			X	X	X		I		X		
S86E-25f		X	X	X			X	X		X	X			X	
S86E-25i	X	X	X				X	X		X	X		X	X	Ep, Zc
S86E-25n	X			X			X			X					Ep
S86E-27a							X		X	X					Ol
S86E-27b	X						X	X	X	X					
S86E-28			X	X		X	X	X			I,M			X	
S86E-31a	X	?	X				X	X		S	I		S		Ru
S86E-31b		X	X	X				H,C,A	X	S	I			S	
S86E-31d-1							X			X	Sp				Ol
S86E-31d-2							X	X	X	X	Sp				Ol
S86E-31d-3		X	X	X		X	X	X	X	X	X	X	X	X	Layered
S86E-32		X	X	X		X	X	X	X	X	I,M			X	
S86E-33		X	X	X		X	X	X	X	X	I	Py		X	Zc
S86E-34	X	X	X	X			X	X	S	S	I		X	X	
S86E-35	X	X	X	X			X	X	S	S	I,M		X	X	
S86E-36b	X	X	X	X			X	X		S	I	Py	X	X	Ep(S), Zc
S86E-37	X	X	X	X			X	X	X	S	I		X	X	Ep(S)
S86E-38a			X	X		X		X	S	S	I			X	
S86E-38b	X		X	X			X	X	S	S	I			X	Ep
S86E-39	X	X	X	X			X	X	S	S	I,M		X	X	Ru
S86E-40	X	X	X	X			X	X	S	S	I,M			X	
S86E-41	X	X	X	X			X	X	S	S	I,M			X	
S86E-42	X		X				X	X	S	S	I,M	Py		X	
S86E-43	X		X				X			S	I,M	X		X	
S86E-44	X	X	X				X	X		S	I,M		X	X	
S86E-45	X		X				X	X			I,M		X		
S86E-53a	X	X	X	X			X	X			X			X	
T46		X	X					X	X		X			X	
WSA1	X	X	X							S					Mu
	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other

Samples contributed by Dr. T.C. Devaraju, Karnatak Univeristy, Dharwad, India.  
 Locality: Sargur Terrane, southern India, mafic granulite and calc-silicate.

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
TCD2		X	X				X			X	I,M		X		
TCD4	X	X	X				X						X	X	
TCD5	X	X	X	X			X						X	X	
TCD8	X	X	X				X						X	X	
TCD18c		X	X				X						X	X	
TCD25	X	X	X	X			X						X		
TCD33a	X		X	X			X	H,C,A			I,M	Py			Ep(S)
TCD33		X	X	X		X	X	X			I,M			X	
TCD34		X	X	X		X	X	H,C		S	I,M	Po			
TCD39	X	X	X	X		X	X	H,C			I,M				Po

Sample contributed by Dr. C. Srikantappa, Dept. Geology, Univ. Mysore, India  
 Locality: Sargur Terrane, southern India, mafic granulite.

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
285	X		X	X		X	X	X			I,M				

Samples contributed by Dr. A.J. Stolz, Univ. Tasmania,  
 Hobart, Tasmania. Locality: New South Wales, xenoliths.

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
32-80	X						X	X			I,M	Py			
32-90	X		X				X	X			I,M	Py			

Samples contributed by Dr. H. Austreim, Mineralogisk-Geologisk  
 Museum, Oslo, Norway. Locality: Bergen Arcs, meta-anorthosite.

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other
HA54/83	X		X	X			X		S						
HA53/80	X		X	X		X	X		S	S	X			X	
HA46/85	X	X	X	X		X	X	X			X				
HA10/83	X		X	X			X	X							

Samples contributed by Dr. A. Davidson, GSC, Ottawa, Canada.  
 Locality: Central Gneiss Belt, southwestern Ontario.

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	
80DMA5a			X	X			X						X		Al
80DMA35c	X		X	X				X			X				
80DMA55h-4	X		X	X				X					X		Ep
80DMA77-5a	X	X	X	X				X	X				X		
80DMA168c	X	X	X				X	X							
80DMA348d	X	X	X	X				X	X		X			X	
80DMA348e	X	X	X	X				X	X		X				Zc,Ep
80DMA351f	X		X				X	X							
80DMA397a	X		X	X				X	X						
80DMA473b	X		X	X		X	X	X	X		X		X		Ru
80DMA614p	X		X	X		X	X	X			X				
80DML214a	X		X	X			X	X							
80DMM47b	X		X					X	X	X			X		
82DMT114a	X		X	X			X			X			X		
82DMT114d	X	X					X			X			X		
83DMP5e	X	X	X	X											Zc,Al
85DM52b				X				X							
85DMP102a		X	X					X	X						Ep
85DMP174-1a	X	X	X	X			X	X	X		X			X	
85DMP272-2a	X	X	X	X		X	X	X							
	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	Other

Samples contributed by C.M. Marmont, Ontario Ministry of Mines and  
 Northern Development. Locality: Central Gneiss Belt, meta-anorthosite.

	Sc	Qz	Pg	Gt	Kf	Opx	Cpx	Am	Bi	Cc	Ox	Sf	Ti	Ap	
CCM 0043			X	X		X	X	X							
CCM 0078			X	X		X	X				I,M			X	
CCM 0102			X	X			X	X			I,M			X	
CCM 0114	X		X	X		X	X	X			I,M			X	
CCM 0118		X	X			X	X	X			I,M				
MMJ 3011	X		X				X	X					X	X	Ep
MMJ 3021			X	X			X	X			X				
MMJ 3023	X		X					X							Ep
MMJ 3024	X	X	X	X					S		I,M		X	X	Ep
MMJ 3041	X	X	X				X				I,M				

## Appendix 3

## Microprobe Analyses

Electron microprobe analyses were obtained on the Cameca CAMEBAX microprobe at the University of Michigan. The microprobe was operated at an accelerating voltage of 15 kV and sample current of 10 nA for all analyses. A focused beam was used for clinopyroxene, garnet, orthopyroxene, and titanite analyses. Either a slightly defocused beam or a rastered beam scanning a  $4\mu$  area were used for epidote, plagioclase, and scapolite analyses, in order to minimize volatilization of light elements. Well characterized natural and synthetic silicates and oxides were used as standards. Analyses were normalized to 3 (titanite), 4 (pyroxene), 5 (plagioclase), and 8 (garnet, epidote) cations. Scapolite formulae were calculated on the basis of  $\text{Si} + \text{Al} = 12$ , and  $\text{Cl} + \text{CO}_3 + \text{SO}_4 = 1$  in the anion site. Wt %  $\text{CO}_2$  was recalculated from this assumption. Fe was calculated as  $\text{Fe}_2\text{O}_3$  for scapolite, plagioclase, and epidote analyses.  $\text{Fe}^{3+}$  for garnet and pyroxene was calculated from charge balance and stoichiometry. In the tabulation of garnet and pyroxene analyses, Fe was analyzed as FeO, but recalculated as  $\text{FeO}^1$  after  $\text{Fe}^{3+}$  and  $\text{Fe}_2\text{O}_3$  were determined. For epidote analyses all iron was calculated as  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}$  was calculated from the assumption of 1.00 molecule of OH.

**Scapolite Analyses**

SAMPLE	ARM4	A85A-1	A85A -3a	A85A -3a	A85A -3b	A85A -3d-1	A85A -3d-2	A86B 3-3a	A86B -3-3b-3	B11
SiO <sub>2</sub>	47.34	47.04	46.07	46.07	46.03	43.83	46.47	45.73	45.28	56.00
Al <sub>2</sub> O <sub>3</sub>	26.19	26.76	27.96	27.96	28.64	28.66	27.38	25.97	25.94	22.89
Fe <sub>2</sub> O <sub>3</sub>	0.28	0.19	0.16	0.16	0.20	0.15	0.22	0.14	0.19	0.03
MnO	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.00
CaO	15.97	16.84	18.69	18.69	18.87	19.92	18.18	16.89	16.81	7.66
Na <sub>2</sub> O	4.41	3.79	3.06	3.06	2.88	2.20	3.26	3.61	3.78	9.31
K <sub>2</sub> O	0.18	0.39	0.09	0.09	0.15	0.22	0.11	0.11	0.07	0.95
Cl	0.34	0.49	0.04	0.04	0.08	0.06	0.10	0.06	0.02	2.80
SO <sub>3</sub>	2.06	0.61	0.09	0.09	0.00	0.00	0.00	5.11	5.48	0.05
CO <sub>2</sub>	3.22	3.85	4.73	4.73	4.77	4.66	4.68	1.77	1.59	1.56
-O=Cl	0.08	0.11	0.01	0.01	0.02	0.01	0.02	0.01	0.00	0.63
TOTAL	99.96	99.85	100.88	100.88	101.60	99.69	100.39	99.40	99.18	100.62
Si	7.263	7.183	6.995	6.995	6.922	6.776	7.081	7.188	7.163	8.098
Al	4.737	4.817	5.005	5.005	5.078	5.224	4.919	4.812	4.837	3.902
Fe	0.032	0.022	0.018	0.018	0.023	0.017	0.025	0.017	0.023	0.003
Mn	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.000
Ca	2.625	2.755	3.040	3.040	3.040	3.299	2.968	2.844	2.849	1.187
Na	1.312	1.122	0.901	0.901	0.840	0.660	0.963	1.100	1.160	2.611
K	0.035	0.076	0.017	0.017	0.029	0.016	0.021	0.022	0.014	0.175
Cl	0.088	0.127	0.010	0.010	0.020	0.016	0.026	0.016	0.005	0.686
SO <sub>4</sub>	0.236	0.070	0.010	0.010	0.000	0.000	0.000	0.603	0.651	0.005
CO <sub>3</sub>	0.675	0.803	0.980	0.980	0.980	0.984	0.974	0.381	0.344	0.308
SAMPLE	B26a	BA20a	C1b	DEB83C -4	GL28a-1	GL28b	H10	H13	H85A -1e(1)	H85A -1e(2)
SiO <sub>2</sub>	46.44	53.38	46.34	45.63	51.15	52.45	53.56	56.16	46.10	45.77
Al <sub>2</sub> O <sub>3</sub>	27.63	23.98	27.70	27.71	24.96	24.68	23.94	22.71	27.44	27.50
Fe <sub>2</sub> O <sub>3</sub>	0.03	0.04	0.07	0.10	0.06	0.03	0.13	0.07	0.06	0.14
MnO	0.00	0.02	0.00	0.01	0.01	0.00	0.00	0.00	0.02	0.00
CaO	18.16	10.14	18.45	19.22	12.94	11.00	10.41	7.69	18.37	18.65
Na <sub>2</sub> O	3.34	7.94	3.36	3.33	6.24	7.66	7.66	10.34	3.09	3.16
K <sub>2</sub> O	0.13	0.82	0.11	0.10	0.46	0.34	0.76	0.94	0.14	0.14
Cl	0.09	2.10	0.02	0.09	1.12	1.82	1.84	2.72	0.04	0.06
SO <sub>3</sub>	0.04	0.04	0.00	0.01	0.79	1.82	0.79	0.39	0.02	0.00
CO <sub>2</sub>	4.69	2.35	4.79	4.66	3.09	2.61	2.27	1.47	4.73	4.60
-O=Cl	0.02	0.47	0.00	0.02	0.25	0.41	0.42	0.61	0.01	0.01
TOTAL	100.53	100.34	100.84	100.84	100.57	102.00	100.94	101.88	100.01	100.01
Si	7.053	7.845	7.039	6.993	7.618	7.718	7.859	8.126	7.052	7.024
Al	4.947	4.155	4.961	5.007	4.382	4.282	4.141	3.874	4.948	4.976
Fe	0.003	0.004	0.008	0.012	0.007	0.003	0.014	0.008	0.007	0.013
Mn	0.000	0.002	0.000	0.010	0.001	0.000	0.000	0.000	0.003	0.000
Ca	2.955	1.597	3.008	2.991	2.065	1.734	1.636	1.192	3.010	3.066
Na	0.984	2.263	0.990	0.990	1.802	2.186	2.180	2.901	0.917	0.940
K	0.025	0.154	0.021	0.012	0.087	0.064	0.142	0.174	0.027	0.027
Cl	0.023	0.523	0.005	0.023	0.283	0.454	0.458	0.667	0.010	0.036
SO <sub>4</sub>	0.005	0.004	0.000	0.001	0.088	0.022	0.087	0.042	0.002	0.000
CO <sub>3</sub>	0.972	0.472	0.995	0.976	0.629	0.524	0.455	0.291	0.988	0.964

SAMPLE	H85A -1d-1	H85A -1b	H85A -1(3)	Mpib	Mpid	M49	M53	M86E -1b	M86E -1C-2	O8e
SiO <sub>2</sub>	44.73	45.65	46.80	48.06	48.04	46.21	45.82	50.33	47.71	46.07
Al <sub>2</sub> O <sub>3</sub>	28.21	28.16	27.26	27.07	26.83	26.58	26.72	25.66	26.91	27.75
Fe <sub>2</sub> O <sub>3</sub>	0.06	0.14	0.25	0.04	0.10	0.22	0.14	0.04	0.02	0.13
MnO	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	19.65	18.91	17.54	16.19	15.73	16.84	17.12	13.63	16.15	18.28
Na <sub>2</sub> O	2.51	2.96	3.36	4.36	4.41	3.78	3.62	5.84	4.32	3.28
K <sub>2</sub> O	0.14	0.06	0.13	0.58	0.34	0.08	0.02	0.57	0.39	0.36
Cl	0.04	0.02	0.12	0.73	0.49	0.05	0.03	1.15	0.51	0.35
SO <sub>3</sub>	0.10	0.00	0.05	0.02	0.01	4.17	3.96	0.07	0.04	0.03
CO <sub>2</sub>	4.65	4.79	4.64	3.96	4.25	2.38	2.50	3.45	4.19	4.36
-O=Cl	0.01	0.00	0.03	0.16	0.11	0.01	0.01	0.26	0.12	0.08
TOTAL	100.08	100.71	100.14	100.85	100.09	100.30	99.92	100.48	100.12	100.53
Si	6.882	6.937	7.115	7.211	7.235	7.150	7.111	7.495	7.207	7.017
Al	5.118	5.063	4.885	4.789	4.765	4.850	4.889	4.505	4.793	6.983
Fe	0.007	0.014	0.029	0.000	0.011	0.028	0.016	0.004	0.002	0.015
Mn	0.000	0.003	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	3.239	3.162	2.857	2.603	2.538	2.792	2.846	2.175	2.614	2.988
Na	0.749	0.842	0.991	1.269	1.288	1.134	1.090	1.687	1.266	0.969
K	0.027	0.014	0.025	0.111	0.065	0.016	0.004	0.108	0.075	0.070
Cl	0.010	0.005	0.031	0.186	0.125	0.013	0.008	0.290	0.131	0.090
SO <sub>4</sub>	0.012	0.002	0.006	0.002	0.001	0.485	0.462	0.008	0.005	0.003
CO <sub>3</sub>	0.978	0.992	0.963	0.812	0.874	0.502	0.530	0.702	0.865	0.906
SAMPLE	PS7a	PS7b	PS7c	PS7e	PS85A -0a	PS85A -1a	PS85A -2c	PS085A -5-1	PS085A -5-12	PS85A -7
SiO <sub>2</sub>	45.45	45.34	46.25	46.62	52.47	46.52	46.54	47.12	47.74	45.84
Al <sub>2</sub> O <sub>3</sub>	27.39	27.50	27.63	27.46	24.30	26.63	27.35	26.99	26.25	28.11
Fe <sub>2</sub> O <sub>3</sub>	0.16	0.21	0.09	0.12	0.07	0.01	0.07	0.24	0.13	0.18
MnO	0.00	0.00	0.00	0.00	0.05	0.00	0.01	0.01	0.09	0.00
CaO	17.62	17.55	18.25	18.04	11.43	16.75	18.15	16.81	15.77	18.59
Na <sub>2</sub> O	3.39	3.42	3.21	3.38	7.00	3.91	3.30	3.87	4.50	2.94
K <sub>2</sub> O	0.18	0.12	0.13	0.19	0.75	0.11	0.11	0.27	0.38	0.20
Cl	0.16	0.05	0.07	0.16	1.54	0.14	0.07	0.33	0.61	0.14
SO <sub>3</sub>	0.33	0.77	0.03	0.10	0.38	2.05	0.04	0.01	0.07	0.03
CO <sub>2</sub>	4.45	4.26	4.71	4.53	2.83	3.45	4.74	4.40	4.00	4.63
-O=Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	99.13	99.22	100.37	100.63	100.83	99.57	100.38	100.15	99.54	100.66
Si	7.016	6.997	7.041	7.082	7.762	7.165	7.086	7.163	7.281	6.964
Al	4.984	5.003	4.959	4.918	4.238	4.835	4.914	4.837	4.719	5.036
Fe	0.019	0.024	0.010	0.014	0.008	0.001	0.010	0.027	0.015	0.021
Mn	0.000	0.000	0.000	0.000	0.006	0.000	0.001	0.001	0.012	0.000
Ca	2.914	2.901	2.976	2.936	1.811	2.764	2.975	2.738	2.576	3.026
Na	1.015	1.024	0.948	0.996	2.008	1.168	0.946	1.141	1.331	0.866
K	0.035	0.024	0.025	0.037	0.142	0.022	0.031	0.052	0.074	0.039
Cl	0.042	0.013	0.018	0.049	0.386	0.037	0.018	0.085	0.158	0.036
SO <sub>4</sub>	0.019	0.089	0.003	0.011	0.042	0.237	0.005	0.001	0.008	0.003
CO <sub>3</sub>	0.939	0.898	0.979	0.940	0.572	0.726	0.977	0.914	0.834	0.961



SAMPLE	PS085A -8b	PS85A -8b	PS085A -13	PS085A -24	PS86B 1-1	PS86B 1-10a	PS86B 1-11"	PS86B 2-1	PS86B 2-3	PS86E -7e
SiO <sub>2</sub>	46.05	47.18	45.85	45.76	47.19	47.35	45.80	47.85	46.13	46.21
Al <sub>2</sub> O <sub>3</sub>	27.13	26.18	27.47	27.27	26.99	26.79	27.24	26.25	27.02	27.51
Fe <sub>2</sub> O <sub>3</sub>	0.13	0.04	0.13	0.10	0.03	0.21	0.07	0.19	0.22	0.08
MnO	0.00	0.03	0.00	0.02	0.05	0.00	0.02	0.00	0.02	0.02
CaO	17.76	16.81	18.54	17.79	16.77	16.11	17.82	16.91	17.53	17.69
Na <sub>2</sub> O	3.38	3.96	3.18	3.39	3.73	3.98	3.28	3.94	3.64	3.46
K <sub>2</sub> O	0.17	0.15	0.05	0.06	0.28	0.31	0.14	0.39	0.25	0.14
Cl	0.08	0.08	0.01	0.02	0.25	0.39	0.07	0.49	0.30	0.10
SO <sub>3</sub>	0.82	2.43	0.08	1.33	0.03	0.12	0.18	0.00	0.48	0.10
CO <sub>2</sub>	4.21	3.32	4.72	4.00	4.49	4.27	4.57	4.20	4.12	4.62
-O=Cl	0.02	0.02	0.00	0.00	0.06	0.09	0.02	0.11	0.07	0.02
TOTAL	99.71	100.16	100.03	99.75	99.75	99.44	99.17	100.11	99.64	99.91
Si	7.082	7.254	7.032	7.048	7.167	7.199	7.054	7.287	7.098	7.051
Al	4.918	4.746	4.968	4.952	4.833	4.801	4.946	4.713	4.902	4.949
Fe	0.015	0.005	0.015	0.012	0.003	0.022	0.008	0.021	0.025	0.009
Mn	0.000	0.000	0.000	0.003	0.006	0.000	0.003	0.000	0.003	0.003
Ca	2.926	2.769	3.046	2.936	2.729	2.624	2.940	2.759	2.890	2.892
Na	1.008	1.181	0.946	1.013	1.099	1.173	0.980	1.164	1.086	1.024
K	0.033	0.029	0.010	0.012	0.054	0.060	0.028	0.076	0.059	0.027
Cl	0.021	0.021	0.003	0.005	0.064	0.101	0.018	0.127	0.078	0.026
SO <sub>4</sub>	0.095	0.281	0.009	0.154	0.003	0.014	0.021	0.000	0.055	0.011
CO <sub>3</sub>	0.884	0.698	0.988	0.841	0.932	0.886	0.961	0.873	0.867	0.963
SAMPLE	PS86E -8	PS86E -10	PS86E -15	PS86E -16a	PS86E -23-1	PS86E -24b	PS86E -24d	PS86E -24f	PS86E -31	PS86E -34
SiO <sub>2</sub>	45.67	46.87	47.20	45.57	47.18	45.83	46.71	46.31	46.87	47.41
Al <sub>2</sub> O <sub>3</sub>	27.39	27.34	26.82	27.38	26.56	27.44	27.21	27.16	27.09	26.42
Fe <sub>2</sub> O <sub>3</sub>	0.10	0.11	0.05	0.05	0.04	0.02	0.06	0.09	0.08	0.11
MnO	0.00	0.04	0.03	0.02	0.03	0.01	0.03	0.00	0.02	0.01
CaO	17.87	17.11	16.05	17.99	16.46	18.05	16.88	17.51	17.58	16.01
Na <sub>2</sub> O	3.39	3.68	4.27	3.36	4.04	3.51	3.88	3.46	3.52	4.37
K <sub>2</sub> O	0.09	0.16	0.24	0.10	0.20	0.12	0.14	0.12	0.11	0.10
Cl	0.06	0.25	0.37	0.06	0.39	0.03	0.31	0.08	0.14	0.55
SO <sub>3</sub>	0.91	0.56	0.67	0.45	0.77	0.02	0.28	1.43	0.07	0.28
CO <sub>2</sub>	4.18	4.21	3.98	4.43	3.88	4.72	4.27	3.89	4.60	3.96
-O=Cl	0.01	0.06	0.08	0.01	0.09	0.01	0.07	0.02	0.03	0.12
TOTAL	99.65	100.27	99.60	99.40	99.46	99.74	99.70	100.03	100.05	99.10
Si	7.030	7.110	7.186	7.024	7.213	7.034	7.114	7.095	7.137	7.242
Al	4.970	4.890	4.814	4.976	4.787	4.965	4.886	4.905	4.863	4.758
Fe	0.012	0.013	0.006	0.006	0.005	0.002	0.007	0.010	0.009	0.013
Mn	0.000	0.005	0.004	0.003	0.004	0.001	0.004	0.000	0.003	0.001
Ca	2.751	2.781	2.618	2.971	2.696	2.968	2.754	2.874	2.868	2.620
Na	1.012	1.083	1.261	1.004	1.198	1.045	1.146	1.028	1.039	1.295
K	0.018	0.015	0.047	0.020	0.039	0.024	0.027	0.023	0.021	0.019
Cl	0.016	0.064	0.096	0.016	0.101	0.008	0.080	0.021	0.036	0.142
SO <sub>4</sub>	0.105	0.064	0.077	0.052	0.088	0.002	0.032	0.165	0.008	0.032
CO <sub>3</sub>	0.879	0.872	0.828	0.932	0.811	0.990	0.888	0.814	0.956	0.826

SAMPLE	S4d	SUN84B -18	S85A -2a	S85A -2b	S85A -2d	S85A -3a(c)	S85A -3a(r)	S85A -3b	S85A -3c	S86E -8c
SiO <sub>2</sub>	47.77	47.47	47.37	47.65	47.65	46.90	47.60	46.25	45.92	47.28
Al <sub>2</sub> O <sub>3</sub>	26.80	26.41	27.37	26.84	26.97	26.67	27.10	27.58	28.12	26.69
Fe <sub>2</sub> O <sub>3</sub>	0.04	0.32	0.06	0.02	0.09	0.33	0.14	0.12	0.08	0.13
MnO	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.02
CaO	16.26	16.38	17.53	16.16	16.40	16.60	16.66	18.36	18.23	16.36
Na <sub>2</sub> O	4.32	4.20	3.72	4.13	3.99	3.83	4.04	3.09	3.12	4.10
K <sub>2</sub> O	0.53	0.20	0.21	0.39	0.53	0.20	0.26	0.14	0.20	0.27
Cl	0.47	0.31	0.26	0.60	0.51	0.43	0.48	0.07	0.12	0.33
SO <sub>3</sub>	0.13	1.40	0.01	0.02	0.01	1.52	0.46	0.05	0.01	0.17
CO <sub>2</sub>	4.19	3.64	4.53	4.08	4.21	3.52	4.00	4.69	4.67	4.30
-O=Cl	0.11	0.07	0.06	0.14	0.12	0.10	0.11	0.02	0.03	0.07
TOTAL	100.40	100.36	101.00	99.75	100.25	99.90	100.63	100.39	100.47	99.58
Si	7.223	7.247	7.137	7.211	7.197	7.183	7.180	7.046	6.969	7.205
Al	4.777	4.753	4.863	4.789	4.803	4.817	4.820	4.954	5.031	4.795
Fe	0.005	0.037	0.007	0.002	0.010	0.038	0.016	0.014	0.009	0.015
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003
Ca	2.634	2.679	2.830	2.620	2.654	2.724	2.692	2.996	2.964	2.671
Na	1.267	1.243	1.087	1.212	1.169	1.138	1.182	0.913	0.918	1.212
K	0.102	0.039	0.040	0.075	0.102	0.039	0.050	0.027	0.039	0.053
Cl	0.120	0.080	0.066	0.154	0.131	0.088	0.123	0.018	0.031	0.085
SO <sub>4</sub>	0.015	0.161	0.001	0.002	0.001	0.175	0.052	0.006	0.001	0.019
CO <sub>3</sub>	0.865	0.759	0.933	0.844	0.868	0.737	0.826	0.976	0.968	0.895
SAMPLE	S86E -10	S86E -25a	S86E -25c	S86E -25i	S86E -25n	S86E -27d	S86E -34	S86E -36b	S86E -41	S86E -45-1
SiO <sub>2</sub>	45.70	46.17	46.10	46.82	45.77	45.23	46.30	46.40	46.07	45.35
Al <sub>2</sub> O <sub>3</sub>	26.91	27.56	27.48	27.09	27.64	28.21	26.90	27.22	27.74	27.41
Fe <sub>2</sub> O <sub>3</sub>	0.09	0.08	0.06	0.08	0.04	0.03	0.10	0.13	0.10	0.09
MnO	0.02	0.03	0.02	0.01	0.02	0.00	0.03	0.03	0.02	0.01
CaO	17.85	18.07	17.91	17.23	17.90	18.44	17.02	17.65	18.33	17.67
Na <sub>2</sub> O	3.40	3.42	3.33	3.68	3.27	3.14	3.70	3.27	3.17	3.38
K <sub>2</sub> O	0.10	0.12	0.21	0.22	0.30	0.08	0.19	0.12	0.10	0.08
Cl	0.02	0.05	0.15	0.14	0.35	0.21	0.16	0.11	0.01	0.02
SO <sub>3</sub>	2.76	0.41	0.13	0.24	0.28	0.13	1.12	0.59	0.00	2.23
CO <sub>2</sub>	3.18	4.51	4.53	4.50	4.19	4.46	3.94	4.33	4.79	3.48
-O=Cl	0.00	0.01	0.03	0.03	0.08	0.05	0.04	0.02	0.00	0.00
TOTAL	100.03	100.41	99.89	99.98	99.68	99.88	99.42	99.83	100.33	99.71
Si	7.083	7.043	7.047	7.134	7.010	6.915	7.122	7.094	7.018	7.007
Al	4.917	4.957	4.953	4.866	4.990	5.085	4.878	4.906	4.982	4.993
Fe	0.010	0.009	0.007	0.009	0.005	0.003	0.010	0.015	0.011	0.010
Mn	0.003	0.004	0.003	0.001	0.003	0.000	0.004	0.000	0.003	0.001
Ca	2.964	2.953	2.933	2.813	2.937	3.020	2.805	2.891	2.991	2.925
Na	1.022	1.012	0.987	1.087	0.971	0.931	1.104	0.970	0.937	1.013
K	0.020	0.023	0.041	0.043	0.059	0.016	0.037	0.023	0.019	0.016
Cl	0.005	0.013	0.039	0.036	0.091	0.054	0.042	0.029	0.003	0.005
SO <sub>4</sub>	0.321	0.047	0.015	0.027	0.032	0.015	0.129	0.068	0.000	0.261
CO <sub>3</sub>	0.673	0.940	0.946	0.936	0.877	0.931	0.829	0.903	0.997	0.734

SAMPLE	S86E -45-2	S86E -53a	80DMA 348c	80DMA 614p	85DMP -174-1a	85DMP 272-2a	CCM 0114	MMJ 3024	MMJ 3011	MMJ 3041
SiO <sub>2</sub>	45.37	46.20	45.60	44.69	46.98	45.57	45.12	46.04	45.35	45.44
Al <sub>2</sub> O <sub>3</sub>	27.72	26.05	25.97	26.42	25.60	26.29	26.79	27.64	27.85	27.05
Fe <sub>2</sub> O <sub>3</sub>	0.14	0.12	0.23	0.09	0.11	0.25	0.19	0.10	0.12	0.14
MnO	0.07	0.00	0.00	0.00	0.00	0.00	0.03	0.05	0.01	0.05
CaO	18.11	16.82	16.36	17.33	15.56	17.19	17.68	17.89	18.73	17.50
Na <sub>2</sub> O	3.06	3.86	3.84	3.58	4.29	3.75	3.27	3.21	2.90	3.38
K <sub>2</sub> O	0.15	0.05	0.11	0.08	0.11	0.04	0.08	0.14	0.08	0.12
Cl	0.12	0.03	0.05	0.07	0.07	0.06	0.02	0.09	0.01	0.04
SO <sub>3</sub>	0.00	4.14	5.03	4.44	3.94	4.55	4.12	0.17	0.34	3.43
CO <sub>2</sub>	4.61	2.38	1.82	2.10	2.45	2.09	2.39	4.53	4.57	2.78
-O=C1	0.03	0.01	0.01	0.02	0.02	0.01	0.00	0.02	0.00	0.01
TOTAL	99.32	99.64	99.00	98.78	99.09	99.78	99.69	99.84	99.96	99.92
Si	6.976	7.208	7.180	7.072	7.306	7.142	7.059	6.963	6.961	7.051
Al	5.024	4.792	4.821	4.928	4.694	4.858	4.941	5.037	5.039	4.949
Fe	0.016	0.014	0.027	0.011	0.012	0.030	0.021	0.012	0.014	0.016
Mn	0.009	0.000	0.000	0.000	0.000	0.000	0.004	0.007	0.001	0.007
Ca	2.983	2.811	2.760	2.938	2.592	2.694	2.963	2.963	3.080	2.909
Na	0.912	1.168	1.173	1.099	1.294	1.100	0.992	0.962	0.863	1.017
K	0.029	0.010	0.022	0.017	0.022	0.008	0.016	0.028	0.016	0.024
Cl	0.031	0.008	0.013	0.019	0.018	0.016	0.005	0.024	0.003	0.011
SO <sub>4</sub>	0.000	0.485	0.595	0.528	0.460	0.536	0.489	0.020	0.039	0.400
CO <sub>3</sub>	0.969	0.507	0.392	0.453	0.521	0.448	0.511	0.957	0.958	0.590
SAMPLE	MMJ 3023	WSA -1Core	WSA -1Rim	BOLT	HOG	DC6	UK-1	X27	TCD 4	TCD 5
SiO <sub>2</sub>	46.28	50.00	50.49	46.64	46.27	47.75	44.51	45.34	43.73	43.73
Al <sub>2</sub> O <sub>3</sub>	27.09	25.38	25.11	27.23	27.08	26.25	27.57	27.69	29.07	28.52
Fe <sub>2</sub> O <sub>3</sub>	0.08	0.11	0.09	0.01	0.07	0.16	0.07	0.11	0.25	0.23
MnO	0.01	0.02	0.03	0.00	0.02	0.00	0.08	0.03	0.02	0.07
CaO	17.33	14.04	13.72	17.04	17.56	16.25	18.50	18.24	20.40	20.40
Na <sub>2</sub> O	3.55	5.44	5.62	4.13	3.21	4.16	2.92	3.19	2.08	2.06
K <sub>2</sub> O	0.29	0.61	0.55	0.12	0.17	0.33	0.10	0.17	0.16	0.10
Cl	0.22	0.96	1.12	0.47	0.07	0.72	0.08	0.19	0.03	0.03
SO <sub>3</sub>	2.01	0.54	0.46	0.03	0.02	0.17	0.00	0.00	0.06	0.03
CO <sub>2</sub>	3.40	3.39	3.24	4.20	4.68	3.81	4.60	4.52	4.69	4.67
-O=C1	0.05	0.22	0.25	0.11	0.02	0.16	0.02	0.04	0.01	0.01
TOTAL	100.21	100.27	100.18	99.76	99.13	99.44	98.41	99.44	100.48	99.83
Si	7.100	7.507	7.565	7.107	7.101	7.281	6.936	6.977	6.728	6.784
Al	4.900	4.493	4.435	4.893	4.899	4.719	5.064	5.023	5.272	5.216
Fe	0.009	0.012	0.010	0.001	0.008	0.018	0.008	0.013	0.029	0.027
Mn	0.001	0.003	0.004	0.000	0.003	0.000	0.011	0.004	0.003	0.009
Ca	2.848	2.258	2.202	2.787	2.887	2.655	3.088	3.007	3.362	3.390
Na	1.056	1.584	1.633	1.220	0.955	1.230	0.882	0.952	0.621	0.620
K	0.057	0.117	0.105	0.023	0.033	0.064	0.020	0.033	0.031	0.020
Cl	0.057	0.244	0.284	0.121	0.018	0.186	0.021	0.050	0.008	0.008
SO <sub>4</sub>	0.232	0.061	0.052	0.003	0.002	0.019	0.000	0.000	0.007	0.003
CO <sub>3</sub>	0.712	0.735	0.664	0.875	0.980	0.794	0.979	0.950	0.985	0.989

SAMPLE	TCD 25	TCD 33A	TCD 39	SRI 285(C)	SRI 285(R)	HA 10/83	HA 46/85	HA 53/80	HA 54/83	STOLZ 32-90
SiO <sub>2</sub>	43.37	46.73	45.94	46.53	46.91	46.06	48.45	47.19	45.69	44.90
Al <sub>2</sub> O <sub>3</sub>	29.03	26.00	26.24	25.61	25.89	26.77	25.33	25.46	26.62	27.17
Fe <sub>2</sub> O <sub>3</sub>	0.22	0.10	0.12	0.16	0.16	0.13	0.11	0.06	0.14	0.33
MnO	0.01	0.03	0.02	0.02	0.00	0.02	0.01	0.02	0.00	0.03
CaO	19.76	16.73	16.84	16.20	16.70	16.75	14.50	15.62	17.12	17.75
Na <sub>2</sub> O	2.17	4.13	4.00	4.15	4.11	3.63	4.85	4.40	3.51	3.25
K <sub>2</sub> O	0.11	0.03	0.03	0.04	0.03	0.18	0.51	0.07	0.08	0.13
Cl	0.05	0.04	0.02	0.02	0.04	0.26	0.54	0.13	0.13	0.02
SO <sub>3</sub>	0.03	4.77	4.96	5.23	4.84	3.28	4.21	5.63	5.14	4.13
CO <sub>2</sub>	4.66	2.04	1.94	1.78	2.01	2.61	1.79	1.45	1.72	2.40
-O=Cl	0.01	0.01	0.00	0.00	0.01	0.06	0.12	0.03	0.03	0.00
TOTAL	99.40	100.59	100.11	99.74	100.68	99.63	100.18	100.00	100.12	100.11
Si	6.707	7.247	7.171	7.278	7.270	7.121	7.424	7.335	7.114	7.004
Al	5.293	4.753	4.829	4.722	4.730	4.879	4.576	4.665	4.886	4.906
Fe	0.026	0.012	0.014	0.019	0.019	0.015	0.013	0.007	0.016	0.039
Mn	0.001	0.004	0.003	0.003	0.000	0.003	0.001	0.003	0.000	0.004
Ca	3.274	2.779	2.816	2.715	2.773	2.774	2.380	2.601	2.856	2.963
Na	0.651	1.242	1.211	1.259	1.235	1.088	1.441	1.326	1.060	0.983
K	0.022	0.006	0.006	0.008	0.006	0.036	0.100	0.014	0.016	0.026
Cl	0.013	0.011	0.005	0.005	0.011	0.068	0.140	0.034	0.034	0.005
SO <sub>4</sub>	0.003	0.556	0.582	0.615	0.563	0.381	0.485	0.657	0.601	0.484
CO <sub>3</sub>	0.983	0.433	0.413	0.380	0.426	0.551	0.375	0.309	0.365	0.511

**Plagioclase Analyses**

SAMPLE	ARM4	A85A -3a-1	A85A -3a-2	A85A -3b	A85A -3d-1	A85A -3d-2	A86B 3-3a	A86B -3-3b-3	B11	B26a
SiO <sub>2</sub>	58.24	51.41	47.52	50.87	56.39	60.73	57.09	56.40	65.48	56.76
Al <sub>2</sub> O <sub>3</sub>	27.39	31.03	33.35	32.31	27.68	24.97	26.89	27.32	21.90	27.76
Fe <sub>2</sub> O <sub>3</sub>	0.04	0.02	0.04	0.10	0.00	0.08	0.07	0.05	0.03	0.03
CaO	8.74	14.09	17.30	14.74	10.24	6.54	9.06	8.93	2.72	9.51
Na <sub>2</sub> O	6.79	3.56	1.85	3.17	5.97	7.95	6.34	6.20	10.14	6.16
K <sub>2</sub> O	0.11	0.13	0.07	0.09	0.13	0.12	0.24	0.21	0.16	0.15
TOTAL	101.31	100.24	100.13	101.28	100.41	100.39	99.69	99.11	100.43	100.37
Si	2.572	2.319	2.263	2.290	2.523	2.692	2.568	2.552	2.869	2.538
Al	1.426	1.674	1.748	1.715	1.460	1.305	1.426	1.457	1.131	1.463
Fe	0.001	0.004	0.001	0.004	0.000	0.003	0.002	0.002	0.001	0.001
Ca	0.413	0.682	0.824	0.710	0.490	0.311	0.437	0.433	0.128	0.455
Na	0.581	0.314	0.159	0.276	0.518	0.683	0.553	0.544	0.862	0.534
K	0.006	0.008	0.004	0.005	0.007	0.007	0.014	0.012	0.009	0.009
SAMPLE	BA20a	C1b	DEB83C -4	GL28a-1	GL28b	H10	H13	H85A -1e(1)	H85A -1e(2)	H85A -1d-1
SiO <sub>2</sub>	63.70	57.33	56.37	62.51	67.78	64.47	66.50	55.93	55.51	51.13
Al <sub>2</sub> O <sub>3</sub>	22.85	27.25	27.88	23.73	20.10	22.83	21.71	26.97	28.76	30.97
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.07	0.00	0.09	0.02	0.09	0.04	0.04	0.10	0.07
CaO	3.72	9.11	9.78	4.80	0.36	3.42	2.42	9.17	10.62	13.91
Na <sub>2</sub> O	9.33	6.61	6.10	8.81	11.54	9.67	10.15	6.25	5.42	3.54
K <sub>2</sub> O	0.31	0.20	0.15	0.22	0.02	0.26	0.23	0.24	0.22	0.22
TOTAL	99.91	100.57	100.28	100.16	99.82	100.74	101.05	98.60	100.63	99.84
Si	2.816	2.551	2.522	2.764	2.966	2.822	2.899	2.542	2.485	2.329
Al	1.191	1.430	1.471	1.237	1.037	1.178	1.116	1.445	1.518	1.664
Fe	0.000	0.002	0.000	0.003	0.001	0.003	0.001	0.001	0.003	0.002
Ca	0.176	0.451	0.469	0.227	0.017	0.160	0.113	0.446	0.509	0.679
Na	0.800	0.570	0.529	0.756	0.979	0.821	0.858	0.551	0.471	0.313
K	0.017	0.011	0.009	0.012	0.001	0.015	0.013	0.014	0.013	0.013
SAMPLE	H85A -1b	H85A -1(3)	Mpib	Mpid	M49	M53	M65	M85A-6a	M86E -1b	M86E -1C-2
SiO <sub>2</sub>	50.12	59.83	59.04	59.94	57.76	56.87	63.59	62.18	62.11	60.79
Al <sub>2</sub> O <sub>3</sub>	32.15	25.60	26.29	25.38	27.00	27.49	22.69	24.13	24.01	24.64
Fe <sub>2</sub> O <sub>3</sub>	0.12	0.05	0.01	0.02	0.16	0.12	0.10	0.03	0.01	0.01
CaO	15.01	7.14	7.81	6.87	8.68	9.24	3.60	5.62	5.27	5.84
Na <sub>2</sub> O	2.97	7.40	7.23	7.60	6.64	6.26	9.37	8.55	8.59	8.09
K <sub>2</sub> O	0.08	0.26	0.28	0.25	0.25	0.14	0.41	0.23	0.23	0.36
TOTAL	100.45	100.28	100.66	100.08	100.49	100.12	99.76	100.74	100.22	99.73
Si	2.277	2.662	2.617	2.534	2.574	2.548	2.814	2.742	2.748	2.708
Al	1.722	1.343	1.374	1.265	1.418	1.452	1.184	1.254	1.252	1.294
Fe	0.004	0.002	0.000	0.001	0.005	0.004	0.003	0.001	0.000	0.000
Ca	0.730	0.340	0.371	0.311	0.414	0.444	0.171	0.265	0.250	0.279
Na	0.262	0.638	0.622	0.623	0.574	0.544	0.804	0.731	0.737	0.699
K	0.005	0.015	0.016	0.014	0.014	0.008	0.023	0.006	0.013	0.020

SAMPLE	08e	015b	PS7a	PS7b	PS7c	PS7g(e) matrix	PS7g(e) porph	PS7g matrix	PS7g porph	PS85A -0a
SiO <sub>2</sub>	55.28	61.25	55.42	56.48	57.67	58.05	53.65	63.85	61.00	61.10
Al <sub>2</sub> O <sub>3</sub>	28.58	24.42	27.89	27.51	26.99	26.45	29.74	22.57	24.27	24.61
Fe <sup>3+</sup>	0.08	0.04	0.11	0.10	0.06	0.05	0.06	0.11	0.03	0.06
CaO	10.87	5.93	9.93	8.98	8.97	8.25	11.96	3.59	5.55	5.94
Na <sub>2</sub> O	5.54	8.20	5.83	6.17	6.33	6.89	4.81	9.53	8.24	8.14
K <sub>2</sub> O	0.24	0.28	0.18	0.25	0.27	0.29	0.20	0.31	0.35	0.43
TOTAL	100.59	100.12	99.36	99.49	100.29	99.98	100.32	99.96	99.44	100.28
Si	2.473	2.718	2.506	2.546	2.580	2.595	2.416	2.819	2.723	2.705
Al	1.508	1.277	1.487	1.462	1.424	1.394	1.579	1.175	1.277	1.285
Fe	0.003	0.001	0.004	0.003	0.002	0.003	0.002	0.004	0.001	0.002
Ca	0.522	0.282	0.481	0.434	0.430	0.395	0.572	0.170	0.265	0.282
Na	0.481	0.706	0.511	0.539	0.549	0.597	0.420	0.816	0.713	0.699
K	0.014	0.016	0.010	0.014	0.015	0.017	0.011	0.017	0.020	0.024
SAMPLE	PS85A -1a	PS85A -2c	PS085A -5-1	PS085A -5-12	PS85A -7	PS085A -8b	PS85A -8b	PS085A -13	PS085A -23	PS085A -24
SiO <sub>2</sub>	52.52	54.24	59.21	59.21	51.69	56.19	52.67	58.03	58.90	54.54
Al <sub>2</sub> O <sub>3</sub>	29.91	29.33	26.34	26.34	31.85	27.60	30.65	26.58	25.90	28.97
Fe <sub>2</sub> O <sub>3</sub>	0.03	0.05	0.04	0.04	0.09	0.08	0.02	0.12	0.03	0.06
CaO	12.15	11.89	7.67	7.67	13.73	9.56	12.95	8.58	7.20	11.09
Na <sub>2</sub> O	4.41	4.90	7.27	7.27	3.74	6.05	4.23	6.82	7.30	5.27
K <sub>2</sub> O	0.06	0.15	0.23	0.23	0.10	0.24	0.06	0.07	0.26	0.15
TOTAL	99.08	100.56	100.76	100.76	101.20	99.72	100.58	100.20	99.59	100.08
Si	2.399	2.437	2.622	2.622	2.320	2.529	2.373	2.591	2.637	2.456
Al	1.611	1.554	1.375	1.375	1.686	1.465	1.628	1.400	1.367	1.538
Fe	0.001	0.002	0.001	0.001	0.003	0.003	0.001	0.004	0.001	0.002
Ca	0.595	0.572	0.364	0.364	0.661	0.461	0.625	0.410	0.345	0.535
Na	0.391	0.427	0.624	0.624	0.325	0.528	0.370	0.591	0.634	0.460
K	0.003	0.009	0.013	0.013	0.005	0.014	0.003	0.004	0.015	0.009
SAMPLE	PS86B 1-1	PS86B 1-6	PS86B 1-7	PS86B 1-8	PS86B 1-9b	PS86B 1-10a	PS86B 1-11"	PS86B 2-1	PS86B 2-3	PS86E -6b
SiO <sub>2</sub>	58.49	61.79	63.95	63.8	63.50	58.18	55.22	58.57	55.21	60.12
Al <sub>2</sub> O <sub>3</sub>	25.95	23.72	22.19	22.39	22.62	26.20	27.65	25.93	27.77	25.31
Fe <sub>2</sub> O <sub>3</sub>	0.03	0.11	0.09	0.03	0.09	0.03	0.08	0.06	0.07	0.04
CaO	7.61	4.56	3.17	3.083	3.27	7.67	9.98	8.04	10.09	6.83
Na <sub>2</sub> O	7.01	8.89	9.81	9.59	9.62	7.03	5.48	6.73	5.86	7.63
K <sub>2</sub> O	0.26	0.26	0.21	0.29	0.20	0.23	0.09	0.26	0.18	0.24
TOTAL	99.35	99.33	99.42	99.18	99.30	99.34	98.50	99.59	99.18	100.19
Si	2.630	2.751	2.833	2.836	2.818	2.615	2.526	2.634	2.500	2.674
Al	1.376	1.245	1.159	1.173	1.184	1.388	1.491	1.375	1.483	1.327
Fe	0.001	0.004	0.003	0.001	0.003	0.001	0.003	0.002	0.002	0.001
Ca	0.367	0.217	0.150	0.147	0.155	0.369	0.489	0.387	0.450	0.325
Na	0.611	0.768	0.843	0.827	0.828	0.613	0.486	0.587	0.515	0.658
K	0.015	0.015	0.012	0.016	0.011	0.013	0.005	0.015	0.010	0.014

SAMPLE	PS86E -7e	PS86E -8	PS86E -10	PS86E -12	PS86E -15	PS86E -16a	PS86E -17	PS86E -23-1	PS86E -24b	PS86E -24d
SiO <sub>2</sub>	56.69	55.30	54.80	53.36	54.92	53.81	54.03	54.51	56.11	56.53
Al <sub>2</sub> O <sub>3</sub>	27.46	27.80	28.85	29.53	28.79	28.73	28.95	29.04	27.51	27.80
Fe <sub>2</sub> O <sub>3</sub>	0.03	0.02	0.08	0.04	0.09	0.04	0.08	0.09	0.05	0.08
CaO	9.25	9.97	10.84	11.80	10.59	11.09	11.24	11.29	9.36	9.34
Na <sub>2</sub> O	6.37	6.02	5.44	4.92	5.58	5.30	5.26	5.04	6.24	6.23
K <sub>2</sub> O	0.14	0.07	0.06	0.05	0.06	0.13	0.04	0.11	0.20	0.06
TOTAL	99.94	99.18	100.07	99.70	100.03	99.10	99.60	100.08	99.47	100.04
Si	2.542	2.502	2.466	2.416	2.470	2.445	2.446	2.459	2.528	2.534
Al	1.451	1.483	1.531	1.576	1.526	1.539	1.544	1.544	1.461	1.469
Fe	0.001	0.001	0.003	0.001	0.003	0.001	0.003	0.003	0.002	0.003
Ca	0.444	0.483	0.523	0.572	0.510	0.540	0.545	0.546	0.452	0.449
Na	0.554	0.528	0.475	0.432	0.487	0.467	0.462	0.441	0.545	0.542
K	0.008	0.004	0.003	0.003	0.003	0.008	0.002	0.006	0.012	0.003
SAMPLE	PS86E -24f	PS86E -31	PS86E -34	S3b	S4d	S10b	S32	SUN84B -18	S85A -2a	S85A -2b
SiO <sub>2</sub>	55.31	57.94	58.25	57.71	60.86	58.89	58.64	59.04	58.80	60.92
Al <sub>2</sub> O <sub>3</sub>	28.20	26.73	26.03	26.97	24.75	26.84	26.42	26.04	26.71	24.38
Fe <sub>2</sub> O <sub>3</sub>	0.07	0.04	0.05	0.07	0.02	0.06	0.12	0.08	0.04	0.01
CaO	9.93	8.71	7.88	8.49	6.04	7.93	7.81	7.62	8.13	5.91
Na <sub>2</sub> O	5.99	6.55	7.28	6.85	7.81	7.15	7.12	7.33	6.89	8.08
K <sub>2</sub> O	0.00	0.13	0.12	0.23	0.65	0.27	0.37	0.14	0.26	0.14
TOTAL	99.50	100.10	99.61	100.32	100.13	101.14	100.48	100.25	100.83	99.44
Si	2.495	2.594	2.608	2.571	2.705	2.599	2.605	2.625	2.608	2.723
Al	1.299	1.411	1.374	1.416	1.297	1.397	1.384	1.365	1.397	1.285
Fe	0.002	0.001	0.002	0.002	0.001	0.002	0.004	0.003	0.001	0.001
Ca	0.480	0.418	0.378	0.405	0.288	0.375	0.372	0.363	0.386	0.283
Na	0.524	0.569	0.632	0.592	0.673	0.612	0.614	0.632	0.593	0.700
K	0.000	0.007	0.007	0.013	0.037	0.015	0.021	0.008	0.015	0.008
SAMPLE	S85A -2d	S85A -3a(c)	S85A -3a(r)	S85A -3b	S85A -3c	S86E -8c	S86E -10	S86E -25a	S86E -25c	S86E -25i
SiO <sub>2</sub>	58.10	53.71	54.22	54.04	54.09	59.66	55.33	54.92	56.48	59.31
Al <sub>2</sub> O <sub>3</sub>	26.76	30.19	29.63	29.01	29.34	25.24	28.28	28.58	27.48	25.60
Fe <sub>2</sub> O <sub>3</sub>	0.01	0.10	0.09	0.08	0.04	0.08	0.06	0.09	0.04	0.04
CaO	8.02	12.24	11.50	11.66	11.47	6.42	10.59	10.60	9.34	7.14
Na <sub>2</sub> O	6.79	4.63	4.88	4.92	5.04	7.71	5.52	5.37	6.15	7.35
K <sub>2</sub> O	0.40	0.08	0.10	0.23	0.18	0.24	0.23	0.18	0.28	0.28
TOTAL	100.08	100.95	100.42	99.94	100.16	99.35	100.01	99.74	99.77	99.72
Si	2.595	2.408	2.440	2.442	2.436	2.672	2.491	2.481	2.540	2.653
Al	1.409	1.595	1.572	1.546	1.558	1.333	1.501	1.522	1.457	1.350
Fe	0.000	0.003	0.003	0.003	0.001	0.003	0.002	0.003	0.001	0.001
Ca	0.384	0.588	0.555	0.565	0.553	0.308	0.511	0.513	0.450	0.342
Na	0.588	0.402	0.426	0.431	0.440	0.670	0.482	0.470	0.536	0.638
K	0.023	0.004	0.005	0.013	0.010	0.014	0.013	0.010	0.016	0.016



SAMPLE	S86E -34	S86E -36b	S86E -41	S86E -45-1	S86E -45-2	S86E -53a	80DMA 348c	80DMA 614p	85DMP -174-1a	85DMP 272-2a
SiO <sub>2</sub>	56.04	55.35	53.47	52.69	52.69	58.14	57.38	54.74	59.79	57.26
Al <sub>2</sub> O <sub>3</sub>	27.73	28.41	29.51	30.32	30.32	26.30	26.33	28.15	25.25	26.81
Fe <sub>2</sub> O <sub>3</sub>	0.05	0.06	0.03	0.12	0.12	0.16	0.11	0.07	0.10	0.04
CaO	9.79	10.28	11.74	12.25	12.25	8.06	8.23	10.49	6.32	8.62
Na <sub>2</sub> O	5.93	5.60	4.71	4.37	4.37	6.85	6.61	5.57	7.62	6.72
K <sub>2</sub> O	0.28	0.25	0.18	0.18	0.18	0.19	0.42	0.19	0.36	0.12
TOTAL	99.82	99.95	99.64	99.93	99.93	99.70	99.08	99.21	99.44	99.57
Si	2.522	2.491	2.425	2.387	2.387	2.609	2.592	2.482	2.678	2.572
Al	1.471	1.508	1.578	1.619	1.619	1.391	1.402	1.505	1.333	1.420
Fe	0.002	0.002	0.001	0.004	0.004	0.005	0.004	0.002	0.003	0.001
Ca	0.471	0.496	0.570	0.595	0.595	0.387	0.398	0.510	0.303	0.415
Na	0.516	0.489	0.414	0.384	0.384	0.596	0.579	0.490	0.662	0.585
K	0.016	0.014	0.010	0.010	0.010	0.011	0.024	0.011	0.021	0.007
SAMPLE	CCM 0114	MMJ 3024	MMJ 3011	MMJ 3011	MMJ 3023	DC6	TCD 4	TCD 5	TCD 25	TCD 33A
SiO <sub>2</sub>	52.30	53.64	53.99	52.70	52.54	56.09	45.37	45.15	44.53	59.12
Al <sub>2</sub> O <sub>3</sub>	30.53	29.80	29.22	30.28	30.27	27.55	35.26	34.92	35.85	26.02
Fe <sub>2</sub> O <sub>3</sub>	0.08	0.06	0.11	0.09	0.07	0.10	0.22	0.17	0.17	0.06
CaO	12.80	11.88	11.53	12.72	12.61	9.84	18.67	19.00	18.65	7.76
Na <sub>2</sub> O	4.09	4.66	4.92	4.12	4.25	5.80	0.89	0.81	0.82	7.33
K <sub>2</sub> O	0.20	0.16	0.24	0.42	0.18	0.11	0.02	0.03	0.03	0.03
TOTAL	100.00	100.20	100.01	100.33	99.92	99.49	100.43	100.08	100.05	100.32
Si	2.372	2.421	2.438	2.382	2.382	2.535	2.084	2.089	2.051	2.630
Al	1.632	1.585	1.555	1.613	1.618	1.468	1.909	1.905	1.947	1.364
Fe	0.003	0.002	0.004	0.003	0.002	0.005	0.008	0.006	0.006	0.002
Ca	0.622	0.574	0.558	0.616	0.613	0.476	0.919	0.942	0.920	0.370
Na	0.360	0.408	0.431	0.361	0.374	0.508	0.079	0.055	0.073	0.632
K	0.012	0.009	0.014	0.024	0.010	0.006	0.001	0.002	0.002	0.002
SAMPLE	TCD 39	SRI 285C	SRI 285(R)	HA 10/83	HA 46/85	HA 53/80	HA 54/83	STOLZ 32-90		
SiO <sub>2</sub>	58.34	58.73	59.00	55.48	59.83	60.95	55.53	55.42		
Al <sub>2</sub> O <sub>3</sub>	26.36	26.16	25.73	28.36	25.35	24.89	28.32	28.06		
Fe <sub>2</sub> O <sub>3</sub>	0.06	0.06	0.11	0.04	0.08	0.05	0.03	0.13		
CaO	7.95	7.80	7.54	10.26	6.67	6.41	10.45	10.19		
Na <sub>2</sub> O	7.18	7.05	7.18	5.51	7.49	7.76	5.46	5.57		
K <sub>2</sub> O	0.04	0.17	0.16	0.19	0.43	0.34	0.48	0.41		
TOTAL	99.93	99.97	99.72	99.84	99.85	100.40	100.27	99.78		
Si	2.605	2.625	2.643	2.502	2.671	2.704	2.493	2.500		
Al	1.388	1.378	1.359	1.508	1.334	1.302	1.499	1.492		
Fe	0.002	0.002	0.004	0.001	0.003	0.002	0.001	0.004		
Ca	0.380	0.374	0.362	0.496	0.319	0.305	0.503	0.492		
Na	0.622	0.611	0.624	0.482	0.648	0.668	0.475	0.487		
K	0.002	0.010	0.009	0.011	0.029	0.019	0.028	0.024		

**Garnet Analyses**

SAMPLE	ARM4	A85A -3a	A85A -3b	A85A -3d	A85A -3f	A86B 3-3b-3	C1b	DEB83C -4	H85A -1b	H85A -1d-1
SiO <sub>2</sub>	38.87	37.99	38.21	39.78	39.17	39.31	38.63	38.14	38.24	39.17
TiO <sub>2</sub>	0.08	0.00	0.07	0.27	0.29	0.00	0.08	0.01	0.14	0.26
Al <sub>2</sub> O <sub>3</sub>	21.30	20.98	20.75	20.87	29.87	21.41	20.81	21.14	15.58	19.21
Cr <sub>2</sub> O <sub>3</sub>	0.06	0.02	0.00	0.05	0.00	0.05	0.00	0.06	0.09	0.05
Fe <sub>2</sub> O <sub>3</sub>	0.72	0.59	0.82	1.15	0.64	0.98	0.00	0.44	8.45	4.02
FeO	23.67	26.01	24.80	3.98	3.94	24.46	20.10	23.84	18.97	5.64
MnO	2.05	1.82	1.36	0.10	0.11	2.57	1.55	1.77	1.24	0.28
MgO	4.85	1.07	1.46	0.22	0.24	7.94	1.49	1.52	0.07	0.02
CaO	9.98	12.47	12.98	34.65	22.72	4.65	16.66	13.50	24.44	34.91
FeO <sup>1</sup>	23.03	25.48	24.07	2.93	3.36	23.58	20.10	23.45	11.38	2.03
Total	100.93	100.22	99.72	100.02	96.40	100.49	99.32	100.03	99.63	99.95
Si	3.003	3.014	3.035	3.017	3.017	3.022	3.046	3.012	3.059	3.000
Ti	0.005	0.000	0.004	0.015	0.017	0.000	0.005	0.001	0.008	0.015
Al	1.940	1.963	1.943	1.866	1.895	1.940	1.935	1.968	1.469	1.735
Cr	0.003	0.002	0.000	0.003	0.000	0.003	0.000	0.004	0.006	0.003
Fe <sup>3+</sup>	0.047	0.035	0.049	0.066	0.037	0.057	0.000	0.026	0.509	0.232
Fe <sup>2+</sup>	1.484	1.692	1.600	0.186	0.217	1.517	1.326	1.550	0.762	0.130
Mn	0.134	0.109	0.091	0.006	0.007	0.167	0.103	0.118	0.084	0.018
Mg	0.559	0.127	0.173	0.025	0.028	0.910	0.175	0.179	0.008	0.002
Ca	0.826	1.060	1.104	2.815	2.782	0.383	1.410	1.142	2.095	2.865

SAMPLE	H85A -1e(1)	H85A -1e(2)	M49	M65	M85A -6a	M86E -1b	M86E -1c-2	O8d	O15b	PS7a
SiO <sub>2</sub>	38.57	38.95	38.87	38.66	39.4	39.47	39.61	39.06	38.45	37.89
TiO <sub>2</sub>	0.30	0.26	0.07	0.05	0.74	0.36	0.32	0.29	0.03	0.02
Al <sub>2</sub> O <sub>3</sub>	15.14	18.73	19.56	21.53	20.66	20.59	21.08	20.28	20.96	20.57
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.05	0.00	0.01	0.03	0.06	0.02	0.00	0.00	0.01
Fe <sub>2</sub> O <sub>3</sub>	9.06	4.23	2.97	0.27	1.97	1.83	1.31	2.76	0.81	1.08
FeO	15.73	11.34	20.89	26.12	2.40	2.55	2.51	5.85	27.41	25.56
MnO	0.82	0.78	4.34	0.88	0.07	0.06	0.17	0.44	3.36	1.97
MgO	0.02	0.03	1.35	5.81	0.12	0.19	0.06	0.02	2.81	2.03
CaO	27.96	29.19	15.36	6.82	36.57	35.89	35.56	33.61	7.74	11.33
FeO <sup>1</sup>	7.58	7.54	18.22	25.88	0.63	0.90	1.33	3.35	26.68	24.59
Total	99.45	99.76	100.74	99.91	100.19	99.35	99.46	99.84	100.84	99.49
Si	3.071	3.033	3.060	3.012	2.976	3.007	3.010	2.988	3.032	3.019
Ti	0.018	0.015	0.004	0.003	0.042	0.021	0.018	0.017	0.002	0.001
Al	1.421	1.719	1.816	1.978	1.839	1.849	1.888	1.830	1.948	1.932
Cr	0.000	0.003	0.000	0.001	0.003	0.004	0.001	0.000	0.000	0.001
Fe <sup>3+</sup>	0.543	0.248	0.176	0.016	0.112	0.105	0.075	0.160	0.048	0.065
Fe <sup>2+</sup>	0.505	0.491	1.201	1.688	0.040	0.058	0.085	0.214	1.761	1.640
Mn	0.055	0.051	0.289	0.058	0.004	0.004	0.004	0.029	0.224	0.133
Mg	0.002	0.003	0.158	0.675	0.014	0.022	0.014	0.002	0.330	0.241
Ca	2.385	2.435	1.246	0.569	2.959	2.929	2.895	2.760	0.654	0.967

SAMPLE	PS7b	PC7c -9	PS7c -15	PS7g(e) w/sc	PS7g(e) w/cpx	PS7g	PS85A -2c	PS085A -5	PS085A -8b	PS085A -13 w/Sc, Pg
SiO <sub>2</sub>	38.10	38.50	39.06	38.38	37.95	37.52	38.27	38.13	38.04	38.79
TiO <sub>2</sub>	0.09	0.05	0.00	0.02	0.04	0.03	0.00	0.00	0.03	0.07
Al <sub>2</sub> O <sub>3</sub>	20.47	21.43	21.31	21.02	20.82	20.44	20.93	20.91	20.68	20.87
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.01	0.09	0.00	0.00	0.00	0.00	0.01
Fe <sub>2</sub> O <sub>3</sub>	0.22	0.39	0.00	1.22	1.12	0.79	0.88	1.25	1.08	1.40
FeO	24.99	23.47	24.50	24.90	23.62	30.46	23.80	26.01	26.02	23.85
MnO	0.51	0.79	0.76	1.27	1.8	1.23	3.81	1.65	0.80	0.82
MgO	2.53	2.49	2.99	2.52	2.31	1.22	1.62	3.14	2.49	3.27
CaO	12.33	13.74	12.31	12.61	13.11	8.78	11.98	10.47	11.53	13.15
FeO <sup>1</sup>	24.79	23.11	24.50	23.80	22.61	27.22	23.02	24.89	25.04	22.59
Total	99.04	100.50	100.93	100.85	99.85	97.23	100.51	100.44	99.69	100.97
Si	3.029	3.003	3.034	3.021	2.995	3.020	3.021	2.995	3.014	3.011
Ti	0.005	0.003	0.000	0.001	0.002	0.002	0.000	0.000	0.002	0.004
Al	1.918	1.971	1.952	1.926	1.937	1.940	1.948	1.936	1.932	1.910
Cr	0.000	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.000	0.001
Fe <sup>3+</sup>	0.013	0.023	0.000	0.071	0.067	0.012	0.052	0.074	0.065	0.082
Fe <sup>2+</sup>	1.650	1.509	1.593	1.548	1.494	1.928	1.521	1.636	1.661	1.468
Mn	0.034	0.052	0.050	0.090	0.12	0.084	0.255	0.110	0.054	0.054
Mg	0.300	0.290	0.346	0.292	0.272	0.146	0.191	0.368	0.294	0.378
Ca	1.050	1.148	1.024	1.050	1.108	0.757	1.013	0.881	0.979	1.093

SAMPLE	PS085A -13 porph	PS085A -13 resorb	PS085A -23	PS085A -24	PS86B 1-1	PS86B 1-6	PS86B 1-7	PS86B 1-8	PS86B 1-9b core	PS86B 1-9b rim
SiO <sub>2</sub>	38.96	38.56	38.87	38.78	38.06	37.76	37.15	37.85	37.70	37.76
TiO <sub>2</sub>	0.08	0.11	0.38	0.04	0.03	0.02	0.04	0.02	0.03	0.06
Al <sub>2</sub> O <sub>3</sub>	20.91	20.79	19.20	21.20	20.83	20.39	20.61	20.48	20.36	20.39
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.05	0.01	0.01	0.02	0.03	0.02	0.01	0.01	0.05
Fe <sub>2</sub> O <sub>3</sub>	1.50	1.52	3.95	1.13	0.60	1.25	0.82	1.07	1.14	1.21
FeO	24.11	24.22	6.64	25.15	25.78	29.51	31.90	31.56	30.37	28.16
MnO	0.60	1.05	0.35	0.80	1.29	1.52	1.51	1.46	2.52	3.22
MgO	3.72	3.97	0.12	5.46	1.56	1.20	1.15	1.08	0.92	0.72
CaO	12.82	11.86	33.69	9.14	11.73	9.73	7.56	8.03	8.44	10.07
FeO <sup>1</sup>	22.76	22.85	3.09	24.13	25.24	28.39	31.17	30.60	29.34	27.07
Total	101.37	100.76	99.66	100.69	99.36	100.29	100.03	100.60	100.46	100.55
Si	3.007	2.996	2.992	2.998	3.037	3.017	2.993	3.017	3.027	3.031
Ti	0.005	0.006	0.022	0.002	0.002	0.001	0.002	0.001	0.002	0.001
Al	1.902	1.904	1.742	1.932	1.959	1.921	1.458	1.933	1.926	1.922
Cr	0.001	0.003	0.001	0.000	0.001	0.002	0.001	0.001	0.001	0.003
Fe <sup>3+</sup>	0.087	0.089	0.229	0.066	0.036	0.075	0.049	0.064	0.069	0.073
Fe <sup>2+</sup>	1.471	1.486	0.199	1.562	1.686	1.899	2.102	2.042	1.972	1.819
Mn	0.039	0.069	0.023	0.052	0.087	0.103	0.103	0.099	0.171	0.218
Mg	0.428	0.460	0.014	0.630	0.186	0.143	0.135	0.129	0.110	0.086
Ca	1.060	0.987	2.778	0.757	1.003	0.833	0.653	0.689	0.726	0.863

SAMPLE	PS86B 1-10a core	PS86B 1-10a rim	PS86B 1-11"	PS86B 2-1	PS86B 2-3 core	PS86B 2-3 rim	PS86E -6B core	PS86E -6B rim	PS86E -7e	PS86E -8
SiO <sub>2</sub>	38.25	38.32	38.00	38.15	38.66	38.51	38.20	38.26	37.94	38.12
TiO <sub>2</sub>	0.06	0.04	0.04	0.04	0.04	0.08	0.07	0.06	0.04	0.04
Al <sub>2</sub> O <sub>3</sub>	20.50	20.87	20.57	20.52	20.72	20.94	20.48	20.48	20.11	20.44
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.01	0.02	0.00	0.02	0.00	0.10	0.02	0.00	0.02
Fe <sub>2</sub> O <sub>3</sub>	1.33	1.00	1.12	1.27	1.34	0.85	1.55	1.50	1.66	1.57
FeO	25.77	26.06	27.72	26.27	25.50	25.75	25.27	25.55	25.95	24.43
MnO	1.15	0.65	1.72	0.80	1.19	0.91	1.09	0.88	1.48	3.13
MgO	2.40	2.75	1.96	2.03	2.82	2.78	3.23	2.78	1.45	1.79
CaO	11.66	11.40	10.00	11.81	11.47	11.29	11.49	11.75	12.33	12.44
FeO <sup>1</sup>	24.57	25.16	26.71	0.01	24.30	24.95	23.88	24.20	24.45	23.02
Total	99.94	100.20	100.14	74.63	100.56	100.31	100.09	99.93	99.48	100.57

Si	3.027	3.015	3.021	3.030	3.033	3.026	3.004	3.019	3.034	3.009
Ti	0.004	0.002	0.002	0.002	0.002	0.005	0.004	0.004	0.002	0.002
Al	1.912	1.936	1.928	1.921	1.916	1.940	1.899	1.905	1.896	1.902
Cr	0.001	0.001	0.001	0.000	0.001	0.000	0.006	0.001	0.000	0.001
Fe <sup>3+</sup>	0.079	0.059	0.067	0.076	0.079	0.050	0.092	0.089	0.100	0.093
Fe <sup>2+</sup>	1.628	1.657	1.778	1.671	1.596	1.641	1.572	1.599	1.637	1.521
Mn	0.077	0.043	0.116	0.054	0.074	0.061	0.073	0.059	0.100	0.209
Mg	0.283	0.323	0.232	0.240	0.330	0.326	0.379	0.327	0.173	0.211
Ca	0.989	0.961	0.852	1.005	0.964	0.950	0.968	0.993	1.056	1.052

SAMPLE	PS86E -12	PS86E -15	PS86E -16a	PS86E -17 w/ep,pg	PS86E -24f	PS86E -31	PS86E -34 core	PS86E -34 rim	S3b	S4c
SiO <sub>2</sub>	38.34	38.58	38.44	38.31	38.65	38.22	38.79	38.91	38.45	38.56
TiO <sub>2</sub>	0.05	0.06	0.04	0.06	0.05	0.06	0.03	0.03	0.03	0.04
Al <sub>2</sub> O <sub>3</sub>	20.39	20.67	20.81	20.58	20.94	20.62	20.78	20.85	20.96	20.83
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.02	0.00	0.01	0.03	0.00	0.01	0.00	0.00	0.00
Fe <sub>2</sub> O <sub>3</sub>	1.72	1.51	1.08	1.30	1.07	1.07	1.41	1.38	0.81	1.29
FeO	24.54	26.04	26.95	24.66	25.96	25.56	26.50	26.83	27.41	28.25
MnO	2.66	1.23	1.04	1.15	1.21	1.56	1.19	0.98	3.36	1.34
MgO	2.05	3.12	2.62	1.85	2.63	1.20	3.35	3.24	2.81	4.30
CaO	12.39	11.07	10.39	13.42	11.50	12.84	10.08	10.19	7.74	7.45
FeO <sup>1</sup>	22.99	24.68	25.98	23.49	25.00	24.59	25.23	25.59	26.68	27.09
Total	100.59	100.94	100.40	100.17	101.08	100.16	100.87	101.17	100.84	100.90

Si	3.020	3.015	3.030	3.023	3.020	3.032	3.032	3.035	3.015	3.015
Ti	0.003	0.004	0.002	0.004	0.003	0.004	1.915	0.002	0.003	0.002
Al	1.894	1.904	1.934	1.915	1.929	1.928	0.001	1.917	1.936	1.920
Cr	0.000	0.001	0.000	0.001	0.002	0.000	0.083	0.000	0.004	0.000
Fe <sup>3+</sup>	0.102	0.089	0.064	0.077	0.063	0.064	0.000	0.081	0.023	0.076
Fe <sup>2+</sup>	1.576	1.614	1.714	1.552	1.635	1.633	1.651	1.671	1.765	1.773
Mn	0.177	0.081	0.069	0.077	0.080	0.105	0.079	0.065	0.069	0.089
Mg	0.241	0.364	0.308	0.218	0.306	0.142	0.391	0.377	0.614	0.501
Ca	1.046	0.927	0.877	1.135	0.963	1.091	0.844	0.851	0.570	0.624

SAMPLE	S4d	S10b	S28c	S32	SUN84B -18 core	SUN84B -18 rim	S85A -2a	S85A -2b	S85A -2d	S85A -3a core
SiO <sub>2</sub>	39.27	38.84	38.68	39.07	37.86	38.45	39.13	39.77	39.43	39.24
TiO <sub>2</sub>	0.34	0.20	0.06	0.02	0.00	0.13	0.11	0.04	0.07	0.05
Al <sub>2</sub> O <sub>3</sub>	20.38	20.83	21.18	21.64	20.88	21.24	20.07	20.16	20.26	22.11
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.00	0.01	0.00	0.00	0.00	0.04	0.02	0.01	0.02
Fe <sub>2</sub> O <sub>3</sub>	2.10	0.50	0.87	0.23	0.71	0.41	3.88	3.12	3.33	1.30
FeO	4.00	27.58	23.3	26.72	23.44	22.83	5.61	4.68	6.00	22.49
MnO	0.24	1.48	0.78	1.15	4.79	1.88	0.24	0.21	0.30	0.83
MgO	0.12	4.95	5.57	5.46	3.69	4.76	0.10	0.07	0.13	8.97
CaO	34.76	7.14	10.01	7.65	8.38	10.08	34.62	34.51	34.09	6.86
FeO <sup>1</sup>	2.11	27.13	22.52	26.01	22.80	22.46	2.12	1.88	3.00	21.32
Total	99.34	101.07	99.68	101.23	99.11	99.41	100.31	99.78	100.62	100.70
Si	3.005	3.019	3.007	3.010	3.010	3.010	2.980	3.037	2.993	2.972
Ti	0.020	0.012	0.004	0.001	0.000	0.008	0.006	0.002	0.004	0.003
Al	1.839	1.909	1.941	1.965	1.957	1.960	1.802	1.815	1.815	1.975
Cr	0.001	0.000	0.001	0.000	0.000	0.000	0.002	0.002	0.001	0.001
Fe <sup>3+</sup>	0.121	0.029	0.051	0.013	0.043	0.024	0.223	0.179	0.190	0.074
Fe <sup>2+</sup>	0.135	1.765	1.465	1.677	1.517	1.472	0.135	0.120	0.191	1.352
Mn	0.016	0.097	0.051	0.075	0.322	0.125	0.015	0.014	0.019	0.053
Mg	0.014	0.574	0.646	0.627	0.437	0.556	0.011	0.008	0.015	1.013
Ca	2.850	0.595	0.834	0.631	0.714	0.845	2.825	2.823	2.772	0.557

SAMPLE	S85A -3a rim	S85A -3b	S85A -3c core	S85A -3c rim	S86E -8c	S86E -8i core	S86E -8i rim	S86E -10	S86E -25a	S86E -25c core
SiO <sub>2</sub>	39.58	38.86	38.92	39.16	38.23	38.81	38.98	38.33	38.67	38.50
TiO <sub>2</sub>	0.10	0.02	0.05	0.05	0.10	0.04	0.06	0.11	0.05	0.07
Al <sub>2</sub> O <sub>3</sub>	22.15	21.09	21.18	21.47	19.46	20.82	20.88	20.60	20.86	21.02
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.00	0.00	0.00	0.03	0.00	0.02	0.01	0.00	0.00
Fe <sub>2</sub> O <sub>3</sub>	0.23	1.22	1.33	1.47	2.87	1.30	1.27	1.18	1.33	1.12
FeO	22.38	25.49	25.78	24.43	20.89	29.34	30.03	24.69	24.32	24.26
MnO	0.55	0.61	0.68	0.55	0.76	0.87	0.96	1.48	1.34	1.31
MgO	8.23	5.13	6.37	5.77	0.86	3.98	3.72	3.10	3.76	4.19
CaO	7.80	9.33	7.75	10.07	19.05	7.11	7.04	11.34	11.26	10.95
FeO <sup>1</sup>	22.17	24.40	24.59	23.10	18.31	28.17	28.89	23.63	23.12	22.40
Total	100.83	100.66	100.87	101.64	99.67	101.10	101.82	99.78	100.39	99.56
Si	2.998	3.011	2.997	2.989	3.025	3.036	3.037	3.024	3.018	2.998
Ti	0.006	0.001	0.003	0.003	0.006	0.002	0.004	0.007	0.003	0.004
Al	1.978	1.927	1.923	1.932	1.816	1.920	1.918	1.916	1.919	1.930
Cr	0.001	0.000	0.000	0.000	0.002	0.000	0.001	0.001	0.000	0.000
Fe <sup>3+</sup>	0.013	0.071	0.077	0.085	0.171	0.076	0.074	0.070	0.078	0.066
Fe <sup>2+</sup>	1.406	1.582	1.585	1.476	1.213	1.845	1.884	1.560	1.511	1.516
Mn	0.035	0.040	0.044	0.036	0.051	0.058	0.063	0.099	0.089	0.086
Mg	0.930	0.593	0.732	0.657	0.101	0.464	0.432	0.365	0.438	0.487
Ca	0.633	0.775	0.639	0.823	1.615	0.596	0.588	0.958	0.941	0.914

SAMPLE	S86E -25c rim	S86E -33	S86E -34 core	S86E -34 rim	S86E -36b	S86E -40	S86E -41 core	S86E -41 rim	S86E -53a core	S86E -53a rim
SiO <sub>2</sub>	38.78	37.46	38.74	38.31	38.35	38.84	38.58	38.60	39.17	38.93
TiO <sub>2</sub>	0.03	0.07	0.08	0.08	0.08	0.04	0.06	0.03	0.06	0.02
Al <sub>2</sub> O <sub>3</sub>	21.05	20.67	20.81	21.02	20.71	20.61	21.06	20.86	21.66	21.77
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.04	0.06	0.02	0.00	0.02	0.02	0.00	0.00
Fe <sub>2</sub> O <sub>3</sub>	1.10	0.95	0.05	0.90	1.33	1.76	1.43	1.41	0.83	0.98
FeO	23.39	32.29	25.90	24.79	26.44	25.33	26.18	25.92	22.18	23.73
MnO	1.45	1.00	0.89	0.69	1.09	0.94	0.63	0.71	0.47	0.99
MgO	3.42	1.76	4.80	4.37	3.48	6.51	6.63	5.90	6.78	6.04
CaO	12.34	7.16	8.61	10.45	10.30	7.33	6.84	7.95	10.05	9.31
FeO <sup>1</sup>	22.40	31.44	25.86	23.98	25.24	23.75	24.89	24.66	21.43	22.85
Total	100.57	100.51	99.88	99.86	100.60	99.78	100.14	100.14	100.45	100.89

Si	3.020	2.994	3.023	2.998	3.004	3.025	2.992	3.003	2.996	2.986
Ti	0.002	0.004	0.005	0.005	0.005	0.002	0.003	0.010	0.003	0.001
Al	1.932	1.947	1.920	1.939	1.912	1.892	1.925	0.157	1.953	1.969
Cr	0.000	0.000	0.002	0.004	0.001	0.000	0.001	0.000	0.000	0.000
Fe <sup>3+</sup>	0.064	0.057	0.068	0.053	0.079	0.103	0.083	0.063	0.048	0.057
Fe <sup>2+</sup>	1.460	2.103	1.629	1.571	1.655	1.548	1.616	0.211	1.372	1.467
Mn	0.096	0.068	0.059	0.046	0.072	0.062	0.041	0.001	0.030	0.064
Mg	0.397	0.210	0.560	0.510	0.406	0.756	0.767	0.682	0.773	0.691
Ca	1.029	0.613	0.722	0.876	0.864	0.612	0.568	0.913	0.824	0.765

SAMPLE	85DMP 174-1a -1	85DMP 174-1a -2	80DMA -614P corona	80DMA -614P porph.	85DMP -272-2a	80DMA -348c core	80DMA -348c rim	SRI 285	TCD 5	TCD 25
SiO <sub>2</sub>	38.92	39.06	38.87	38.98	39.59	38.54	38.49	39.16	37.98	37.89
TiO <sub>2</sub>	0.02	0.02	0.03	0.04	0.01	0.04	0.01	0.30	0.57	0.20
Al <sub>2</sub> O <sub>3</sub>	21.31	21.21	21.19	21.20	21.70	21.45	21.09	21.53	13.55	13.47
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.01	0.03	0.12	0.08	0.00	0.01	0.06	0.12	0.06
Fe <sub>2</sub> O <sub>3</sub>	0.89	1.26	0.82	0.75	0.71	0.51	0.80	0.74	11.21	11.84
FeO	25.16	23.90	24.38	22.72	22.32	23.62	25.09	24.33	14.45	14.67
MnO	1.11	1.08	2.46	3.60	1.03	0.95	1.17	0.77	0.35	0.36
MgO	6.41	5.52	5.76	6.33	7.98	4.89	4.82	8.52	0.08	0.02
CaO	7.17	10.02	7.20	6.66	7.58	10.35	8.78	5.79	32.05	31.71
FeO <sup>1</sup>	24.35	22.77	23.65	22.04	21.66	23.16	24.37	23.66	4.37	4.03
Total	100.19	100.95	100.01	99.72	100.34	99.89	99.54	100.53	100.28	99.58

Si	3.013	3.005	3.028	3.034	3.022	2.999	3.020	2.990	2.999	3.015
Ti	0.001	0.001	0.002	0.002	0.001	0.002	0.001	0.017	0.034	0.012
Al	1.945	1.924	1.946	1.945	1.952	1.968	1.951	1.938	1.261	1.263
Cr	0.001	0.001	0.002	0.007	0.005	0.000	0.001	0.004	0.007	0.004
Fe <sup>3+</sup>	0.052	0.073	0.048	0.044	0.041	0.030	0.047	0.043	0.666	0.709
Fe <sup>2+</sup>	1.556	1.466	1.542	1.436	1.385	1.508	1.601	1.512	0.289	0.268
Mn	0.073	0.070	0.162	0.237	0.067	0.063	0.078	0.050	0.023	0.024
Mg	0.740	0.633	0.669	0.735	0.908	0.567	0.564	0.970	0.009	0.002
Ca	0.595	0.826	0.601	0.555	0.620	0.863	0.738	0.474	2.711	2.703

SAMPLE	TCD 33a	TCD -39	HA 10/83	HA 46/85	HA 53/80	HA 54/83
SiO <sub>2</sub>	39.30	39.57	41.35	40.13	40.15	40.42
TiO <sub>2</sub>	0.02	0.05	0.07	0.12	0.19	0.16
Al <sub>2</sub> O <sub>3</sub>	21.82	22.03	22.74	21.43	21.64	22.42
Cr <sub>2</sub> O <sub>3</sub>	0.04	0.07	0.02	0.00	0.01	0.02
Fe <sub>2</sub> O <sub>3</sub>	1.03	1.10	0.80	1.33	1.12	0.97
FeO	24.19	23.37	13.65	21.15	21.11	17.43
MnO	0.70	0.66	0.18	0.66	0.47	0.28
MgO	8.36	8.90	16.16	10.70	11.20	13.00
CaO	6.33	6.26	5.78	5.64	5.57	6.52
FeO <sup>1</sup>	23.26	22.78	12.93	19.95	20.11	16.56
Total	100.86	101.42	100.03	99.96	100.46	100.35
Si	2.990	2.934	3.004	3.035	3.014	2.988
Ti	0.001	0.003	0.004	0.007	0.011	0.009
Al	1.957	1.959	1.948	1.911	1.915	1.954
Cr	0.002	0.004	0.001	0.000	0.001	0.001
Fe <sup>3+</sup>	0.059	0.062	0.044	0.076	0.063	0.054
Fe <sup>2+</sup>	1.481	1.438	0.786	1.263	1.263	1.024
Mn	0.045	0.042	0.011	0.042	0.030	0.018
Mg	0.948	1.001	1.751	1.207	1.254	1.433
Ca	0.516	0.506	0.450	0.457	0.448	0.516



**Clinopyroxene Analyses**

SAMPLE	A85A -3a	A85A -3b	H85A -1b	H85A -1e(2)	M3.14d	M49	M65	M86E -1b	M86E -1c-2	O8e
SiO <sub>2</sub>	49.85	49.60	48.43	48.15	50.37	49.10	50.62	53.15	53.09	50.96
TiO <sub>2</sub>	0.17	0.24	0.23	0.29	0.07	0.43	0.41	0.04	0.00	0.03
Al <sub>2</sub> O <sub>3</sub>	1.56	1.74	2.10	2.18	1.01	3.95	3.13	1.14	0.99	1.26
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.04	0.02	0.00	0.02	0.03	0.03	0.00	0.01	0.09
Fe <sub>2</sub> O <sub>3</sub>	0.27	3.23	1.22	1.08	1.53	2.74	3.64	0.00	0.00	2.61
FeO	17.67	18.72	24.13	23.72	15.92	15.29	10.76	8.02	9.82	14.18
MnO	0.17	0.27	0.51	0.75	0.33	0.55	0.15	0.06	11.43	0.28
MgO	7.24	7.18	2.59	2.94	8.02	7.66	12.14	12.54	0.08	9.08
CaO	22.81	22.62	21.37	21.14	23.04	22.12	21.92	24.43	24.13	24.34
Na <sub>2</sub> O	1.16	0.35	0.55	0.63	0.34	0.81	0.76	0.35	0.31	0.34
FeO <sup>1</sup>	17.43	15.81	23.03	22.75	14.54	12.78	7.49	8.02	9.82	11.78
Total	100.67	101.08	100.05	99.91	99.27	100.17	100.29	99.73	99.86	100.77

Si	1.955	1.919	1.946	1.947	1.965	1.887	1.895	1.990	2.002	1.948
Ti	0.005	0.007	0.007	0.009	0.002	0.012	0.012	0.001	0.000	0.001
Al	0.072	0.079	0.099	0.104	0.046	0.179	0.138	0.050	0.440	0.051
Cr	0.000	0.001	0.001	0.000	0.001	0.001	0.001	0.000	0.000	0.001
Fe <sup>3+</sup>	0.008	0.094	0.037	0.033	0.045	0.081	0.103	0.000	0.000	0.075
Fe <sup>2+</sup>	0.572	0.512	0.775	0.770	0.475	0.411	0.235	0.251	0.310	0.377
Mn	0.006	0.009	0.017	0.026	0.011	0.018	0.005	0.002	0.003	0.007
Mg	0.423	0.414	0.155	0.147	0.467	0.439	0.678	0.700	0.643	0.517
Ca	0.958	0.938	0.920	0.916	0.963	0.911	0.879	0.980	0.975	0.995
Na	0.088	0.026	0.043	0.049	0.026	0.060	0.055	0.025	0.023	0.027

SAMPLE	O15b	PS7c	PS7g(e)	PS7g	PSO85A -13 porph	PSO85A -13 neo	PS86B1 -7	PS86E -6b core	PS86E -6b rim	PS86E -17
SiO <sub>2</sub>	50.77	50.96	50.33	49.78	49.65	51.57	49.42	49.87	50.70	50.51
TiO <sub>2</sub>	0.15	0.14	0.14	0.10	0.45	0.13	0.01	0.40	0.36	0.26
Al <sub>2</sub> O <sub>3</sub>	1.58	2.27	2.40	1.32	3.53	1.71	1.18	3.82	3.30	3.03
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.00	0.01	0.00	0.03	0.05	0.01	0.03	0.04	0.05
Fe <sub>2</sub> O <sub>3</sub>	4.55	4.67	2.74	3.95	4.28	3.16	2.67	1.32	1.77	1.72
FeO	14.56	11.76	11.41	20.48	12.34	10.81	20.25	12.05	11.62	13.07
MnO	0.58	0.11	0.20	0.21	0.22	0.20	0.23	0.06	0.10	0.14
MgO	10.76	11.36	10.76	6.02	10.81	11.38	5.90	10.29	10.66	9.67
CaO	21.56	23.90	22.56	21.45	22.82	23.90	20.65	21.69	22.18	22.35
Na <sub>2</sub> O	0.64	0.54	0.66	0.96	0.74	0.58	0.87	0.63	0.73	0.72
FeO <sup>1</sup>	10.47	7.56	8.95	16.93	8.49	7.97	17.85	10.86	10.03	11.52
Total	101.08	101.51	98.75	100.72	101.02	100.65	98.79	98.97	99.87	99.97

Si	1.919	1.900	1.927	1.942	1.875	1.934	1.965	1.906	1.917	1.917
Ti	0.004	0.004	0.004	0.003	0.013	0.004	0.000	0.012	0.010	0.016
Al	0.07	0.100	0.108	0.061	0.157	0.076	0.055	0.172	0.147	0.136
Cr	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.001	0.001	0.002
Fe <sup>3+</sup>	0.129	0.131	0.079	0.116	0.122	0.089	0.080	0.038	0.050	0.049
Fe <sup>2+</sup>	0.331	0.236	0.287	0.553	0.268	0.250	0.594	0.348	0.317	0.366
Mn	0.019	0.003	0.006	0.007	0.007	0.006	0.008	0.002	0.003	0.004
Mg	0.607	0.632	0.614	0.350	0.580	0.637	0.350	0.587	0.601	0.547
Ca	0.873	0.955	0.925	0.896	0.923	0.960	0.880	0.888	0.893	0.909
Na	0.047	0.039	0.049	0.073	0.054	0.042	0.067	0.047	0.054	0.053

SAMPLE	S3b	S4c	S10b	S28c	S32	S42	S85A -3a	S85A -3b	S86E -8c	S86E -8i core
SiO <sub>2</sub>	50.37	50.51	50.92	49.59	51.55	50.80	51.44	50.77	49.56	52.08
TiO <sub>2</sub>	0.42	0.22	0.29	0.44	0.18	0.24	0.26	0.26	0.13	0.23
Al <sub>2</sub> O <sub>3</sub>	3.72	2.47	2.84	4.86	2.28	2.61	3.51	3.76	1.95	2.41
Cr <sub>2</sub> O <sub>3</sub>	0.03	0.02	0.00	0.10	0.07	0.03	0.01	0.01	0.04	0.02
Fe <sub>2</sub> O <sub>3</sub>	4.48	5.61	4.06	4.43	2.98	4.24	0.85	4.79	2.97	3.81
FeO	11.87	13.56	12.15	9.86	11.78	10.89	7.53	8.48	18.97	13.39
MnO	0.15	0.29	0.39	0.13	0.17	0.22	0.08	0.07	0.15	0.13
MgO	11.24	11.40	11.27	11.89	12.87	11.77	13.12	12.93	6.03	10.35
CaO	21.15	20.39	21.73	21.95	20.84	22.57	21.98	23.26	21.52	20.76
Na <sub>2</sub> O	1.18	1.15	0.93	0.94	0.62	0.81	0.71	0.83	0.99	1.58
FeO <sup>1</sup>	7.84	8.51	8.50	5.88	9.10	7.07	6.77	4.18	16.30	9.96
Total	100.58	100.57	100.93	100.21	100.66	100.36	98.73	100.86	99.64	101.33
Si	1.885	1.901	1.906	1.851	1.924	1.905	1.929	1.874	1.944	1.944
Ti	0.012	0.006	0.008	0.012	0.005	0.007	0.007	0.007	0.004	0.006
Al	0.164	0.110	0.125	0.214	0.100	0.115	0.155	0.164	0.090	0.106
Cr	0.001	0.001	0.000	0.003	0.002	0.001	0.000	0.000	0.001	0.001
Fe <sup>3+</sup>	0.126	0.159	0.114	0.124	0.084	0.120	0.024	0.133	0.088	0.107
Fe <sup>2+</sup>	0.246	0.268	0.266	0.184	0.284	0.222	0.212	0.129	0.535	0.311
Mn	0.005	0.009	0.012	0.004	0.005	0.007	0.003	0.002	0.005	0.004
Mg	0.627	0.640	0.629	0.662	0.716	0.658	0.734	0.712	0.353	0.576
Ca	0.848	0.822	0.871	0.876	0.833	0.907	0.883	0.920	0.904	0.830
Na	0.086	0.084	0.068	0.068	0.045	0.059	0.051	0.059	0.075	0.114

SAMPLE	S86E -8i rim	S86E -23	S86E 25a	S86E -25c	S86E -33	S86E -34 core	S86E -34 rim	S86E -36b	S86E -40	S86E -41 core
SiO <sub>2</sub>	52.82	54.01	49.51	50.53	50.28	50.73	49.97	49.02	49.78	49.98
TiO <sub>2</sub>	0.11	0.32	0.61	0.41	0.15	0.34	0.28	0.41	0.42	0.43
Al <sub>2</sub> O <sub>3</sub>	1.96	1.49	5.29	4.19	1.77	3.73	3.60	4.40	4.07	4.04
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.00	0.03	0.02	0.05	0.00	0.00	0.02	0.02	0.00
Fe <sub>2</sub> O <sub>3</sub>	2.31	0.13	1.76	2.82	2.35	1.33	2.23	3.39	2.35	2.85
FeO	10.92	1.78	11.65	10.30	18.92	10.50	10.65	13.09	9.29	9.83
MnO	0.07	0.00	0.17	0.11	0.20	0.09	0.04	0.08	0.07	0.07
MgO	11.70	16.99	10.13	11.11	6.85	11.04	11.03	9.51	11.97	11.88
CaO	21.97	25.18	21.14	22.54	19.83	22.17	22.31	21.57	22.08	21.79
Na <sub>2</sub> O	1.15	0.14	0.94	0.91	1.21	0.75	0.66	0.92	0.65	0.80
FeO <sup>1</sup>	8.84	1.67	10.07	7.77	16.81	9.30	8.65	10.04	7.18	7.26
Total	100.95	99.93	99.65	100.41	99.50	99.48	98.77	99.36	98.59	99.10
Si	1.963	1.963	1.874	1.889	1.965	1.916	1.904	1.874	1.887	1.887
Ti	0.003	0.009	0.017	0.012	0.004	0.010	0.008	0.012	0.012	0.012
Al	0.086	0.064	0.236	0.185	0.082	0.166	0.162	0.198	0.182	0.180
Cr	0.001	0.000	0.001	0.001	0.002	0.000	0.000	0.001	0.001	0.000
Fe <sup>3+</sup>	0.065	0.003	0.050	0.079	0.069	0.038	0.064	0.098	0.067	0.081
Fe <sup>2+</sup>	0.275	0.051	0.319	0.243	0.550	0.294	0.276	0.321	0.228	0.230
Mn	0.002	0.000	0.005	0.003	0.007	0.003	0.001	0.003	0.002	0.002
Mg	0.648	0.921	0.572	0.619	0.394	0.622	0.627	0.542	0.677	0.669
Ca	0.875	0.980	0.857	0.903	0.830	0.897	0.910	0.883	0.897	0.881
Na	0.083	0.010	0.069	0.066	0.092	0.055	0.049	0.068	0.048	0.059

SAMPLE	S86E -41 rim	S86E -53a	SODMA -614p core	SODMA -614p rim	S5DMP -174-1a core	S5DMP -174-1a rim	S5DMP -272-2a	TCD 33a	TCD 39	SRI 285
SiO <sub>2</sub>	50.70	51.53	50.90	51.36	50.51	51.91	50.52	51.45	51.73	49.93
TiO <sub>2</sub>	0.35	0.33	0.33	0.33	0.37	0.20	0.46	0.35	0.30	0.45
Al <sub>2</sub> O <sub>3</sub>	3.55	3.41	3.75	3.68	4.29	2.96	4.79	3.60	3.73	4.66
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.04	0.05	0.01	0.03	0.06	0.04	0.03	0.01
Fe <sub>2</sub> O <sub>3</sub>	2.22	1.13	1.51	2.12	2.93	2.69	2.96	2.66	3.33	3.39
FeO	8.71	8.16	9.45	8.40	10.52	8.91	8.33	8.63	7.91	8.45
MnO	0.04	0.10	0.48	0.20	0.19	0.15	0.13	0.08	0.08	0.13
MgO	12.16	12.80	11.89	12.74	11.28	12.66	12.51	12.96	13.31	12.27
CaO	22.65	22.28	21.45	22.06	21.23	22.16	21.66	21.35	22.12	21.61
Na <sub>2</sub> O	0.75	0.71	0.84	0.87	1.15	1.00	1.07	1.04	1.09	1.08
FeO <sup>1</sup>	6.72	7.15	8.09	6.49	7.89	6.49	5.67	6.23	4.91	5.40
Total	99.14	99.44	99.28	99.90	99.85	100.25	99.83	99.76	100.63	98.93

Si	1.907	1.926	1.916	1.911	1.895	1.928	1.878	1.913	1.903	1.875
Ti	0.010	0.009	0.009	0.009	0.010	0.006	0.013	0.010	0.008	0.013
Al	0.157	0.150	0.166	0.162	0.190	0.130	0.21	0.158	0.162	0.206
Cr	0.000	0.000	0.001	0.001	0.000	0.001	0.002	0.001	0.001	0.000
Fe <sup>3+</sup>	0.063	0.032	0.093	0.059	0.083	0.075	0.083	0.075	0.062	0.096
Fe <sup>2+</sup>	0.211	0.224	0.255	0.202	0.248	0.202	0.176	0.194	0.151	0.170
Mn	0.001	0.003	0.015	0.006	0.006	0.005	0.004	0.003	0.002	0.004
Mg	0.682	0.713	0.668	0.707	0.631	0.701	0.694	0.719	0.730	0.687
Ca	0.013	0.892	0.865	0.879	0.853	0.882	0.863	0.850	0.872	0.870
Na	0.055	0.051	0.061	0.063	0.084	0.072	0.077	0.079	0.078	0.074

SAMPLE	HA 10/83	HA 46/85	HA 54/83
SiO <sub>2</sub>	50.63	49.69	49.15
TiO <sub>2</sub>	0.50	0.73	1.10
Al <sub>2</sub> O <sub>3</sub>	6.88	6.77	7.31
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.04	0.00
Fe <sub>2</sub> O <sub>3</sub>	2.16	5.29	1.20
FeO	4.83	9.20	6.55
MnO	0.03	0.16	0.02
MgO	13.43	10.97	12.09
CaO	22.69	20.29	21.62
Na <sub>2</sub> O	1.09	1.86	1.08
FeO <sup>1</sup>	2.89	4.45	5.47
Total	100.31	100.25	99.04

Si	1.847	1.826	1.831
Ti	0.014	0.020	0.031
Al	0.296	0.293	0.321
Cr	0.000	0.001	0.000
Fe <sup>3+</sup>	0.059	0.146	0.034
Fe <sup>2+</sup>	0.088	0.137	0.171
Mn	0.001	0.005	0.001
Mg	0.731	0.601	0.672
Ca	0.887	0.838	0.863
Na	0.077	0.133	0.078

**Orthopyroxene Analyses**

SAMPLE	A86B -3-3b-3	M65	O15b	S3b	S10b	S32	S86E -33	80DMA -614p	85DMP -272-2a	TCD -39
SiO <sub>2</sub>	51.98	51.40	50.25	51.54	51.49	51.37	49.00	51.95	53.04	53.27
TiO <sub>2</sub>	0.08	0.05	0.08	0.04	0.07	0.07	0.08	0.03	0.03	0.00
Al <sub>2</sub> O <sub>3</sub>	2.51	1.02	0.59	1.23	1.36	1.54	0.51	2.04	2.00	2.05
Cr <sub>2</sub> O <sub>3</sub>	0.03	0.01	0.01	0.01	0.00	0.04	0.00	0.02	0.04	0.55
Fe <sub>2</sub> O <sub>3</sub>	1.16	1.64	1.91	1.43	1.03	1.84	0.37	2.12	0.10	2.23
FeO	22.13	28.15	33.93	28.08	27.33	26.67	40.05	23.80	21.39	21.07
MnO	0.79	0.35	1.32	0.28	0.56	0.32	0.42	1.44	0.30	0.16
MgO	22.34	18.94	14.46	18.94	19.07	19.95	9.62	20.23	23.19	24.02
CaO	0.34	0.46	0.51	0.58	0.49	0.43	0.93	0.61	0.33	0.35
Na <sub>2</sub> O	0.01	0.02	0.03	0.01	0.00	0.01	0.03	0.03	0.01	0.02
FeO <sup>1</sup>	21.09	26.67	32.22	26.79	26.41	24.97	39.72	21.89	21.30	19.07
Total	100.33	100.56	101.38	100.85	100.48	100.54	100.68	100.36	100.34	101.72
Si	1.927	1.953	1.957	1.951	1.953	1.937	1.981	1.926	1.954	1.918
Ti	0.002	0.001	0.002	0.001	0.002	0.002	0.002	0.001	0.001	0.000
Al	0.110	0.046	0.027	0.055	0.061	0.068	0.024	0.089	0.087	0.089
Cr	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.001	0.016
Fe <sup>3+</sup>	0.032	0.047	0.056	0.041	0.029	0.054	0.011	0.059	0.003	0.061
Fe <sup>2+</sup>	0.654	0.848	1.050	0.849	0.838	0.788	1.344	0.679	0.657	0.584
Mn	0.025	0.011	0.044	0.009	0.018	0.010	0.014	0.045	0.009	0.005
Mg	1.235	1.073	0.840	1.069	1.079	1.122	0.580	1.174	1.274	1.312
Ca	0.014	0.019	0.021	0.024	0.020	0.017	0.040	0.029	0.013	0.014
Na	0.001	0.001	0.002	0.001	0.000	0.001	0.002	0.002	0.001	0.001

SAMPLE	SRI 285	HA 46/85
SiO <sub>2</sub>	51.77	52.21
TiO <sub>2</sub>	0.07	0.11
Al <sub>2</sub> O <sub>3</sub>	2.75	3.61
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.01
Fe <sub>2</sub> O <sub>3</sub>	0.85	1.15
FeO	22.95	20.42
MnO	0.37	0.27
MgO	21.6	23.54
CaO	0.53	0.54
Na <sub>2</sub> O	0.04	0.04
FeO <sup>1</sup>	22.19	19.38
Total	100.19	100.86
Si	1.927	1.905
Ti	0.002	0.003
Al	0.121	0.155
Cr	0.001	0.000
Fe <sup>3+</sup>	0.024	0.032
Fe <sup>2+</sup>	0.691	0.592
Mn	0.012	0.008
Mg	1.199	1.281
Ca	0.021	0.021
Na	0.003	0.003

**Epidote Analyses**

SAMPLE	C1b core	C1b rim	DEB83C -4	PS85A -1a	PS85A -2c	PS86B 1-11"	PS86E -7e	PS86E -8	PS86E -10	PS86E -12
SiO <sub>2</sub>	39.41	39.27	39.26	38.22	38.71	37.87	37.82	37.95	38.13	38.04
TiO <sub>2</sub>	na	na	na	0.16	na	0.14	0.15	0.20	0.12	0.17
Al <sub>2</sub> O <sub>3</sub>	28.69	28.89	27.71	27.37	26.21	25.93	25.90	25.83	25.78	1.63
Fe <sub>2</sub> O <sub>3</sub>	7.40	6.75	8.10	8.50	9.93	10.17	10.22	10.30	10.85	10.21
MnO	na	na	0.19	0.09	0.02	0.10	0.06	0.08	0.13	0.06
CaO	23.82	24.29	24.03	23.68	23.74	23.35	23.43	23.40	23.40	23.50
H <sub>2</sub> O	1.95	1.96	1.95	1.92	1.92	1.90	1.90	1.90	1.91	1.91
Total	101.27	101.16	101.20	99.94	100.53	99.46	99.48	99.66	100.32	100.05

Si	3.021	3.007	3.020	2.982	3.020	2.991	2.986	2.993	2.990	2.986
Ti	-	-	-	0.009	-	0.006	0.009	0.012	0.007	0.01
Al	2.593	2.608	2.514	2.517	2.410	2.414	2.411	2.401	2.383	2.421
Fe <sup>3+</sup>	0.427	0.389	0.469	0.499	0.583	0.605	0.608	0.612	0.641	0.603
Mn	-	-	0.012	0.006	0.001	0.007	0.004	0.005	0.009	0.004
Ca	1.960	1.996	1.981	1.979	1.984	1.975	1.982	1.977	1.968	1.976

SAMPLE	PS86E -15	PS86E -16a	PS86E -16a porph	PS86E -17	PS86E -23-1	PS86E -24b	PS86E -24d	PS86E -24f	PS86E -31	S86E -25a
SiO <sub>2</sub>	37.97	37.93	38.10	37.99	38.92	37.96	38.14	37.87	38.95	38.53
TiO <sub>2</sub>	0.12	0.13	0.05	0.09	na	0.07	0.16	0.19	na	0.15
Al <sub>2</sub> O <sub>3</sub>	26.21	25.42	26.31	25.78	27.63	27.62	26.26	26.37	25.73	27.22
Fe <sub>2</sub> O <sub>3</sub>	9.83	10.86	9.39	10.74	7.48	8.52	9.95	9.89	10.96	8.57
MnO	0.17	0.03	0.09	0.04	0.06	0.10	0.11	0.03	0.11	0.04
CaO	23.11	23.41	23.34	25.36	23.51	23.74	23.10	23.47	23.27	23.25
H <sub>2</sub> O	1.90	1.90	1.90	1.91	1.92	1.92	1.90	1.90	1.92	1.91
Total	99.31	99.68	99.18	100.11	99.48	99.93	99.62	99.72	100.94	99.67

Si	2.999	2.995	3.007	2.983	3.042	2.962	3.003	2.979	3.038	3.016
Ti	0.007	0.008	0.003	0.005	-	0.004	0.009	0.011	-	0.009
Al	2.441	2.366	2.448	2.387	2.546	2.540	2.437	2.445	2.366	2.512
Fe <sup>3+</sup>	0.585	0.646	0.558	0.635	0.440	0.500	0.590	0.586	0.643	0.507
Mn	0.011	0.002	0.006	0.003	0.006	0.007	0.007	0.002	0.007	0.003
Ca	1.956	1.980	1.973	1.982	1.968	1.984	1.948	1.977	1.944	1.950

SAMPLE S86E  
-25n

SiO <sub>2</sub>	38.97
TiO <sub>2</sub>	0.11
Al <sub>2</sub> O <sub>3</sub>	31.44
Fe <sub>2</sub> O <sub>3</sub>	2.96
MnO	0.00
CaO	24.48
H <sub>2</sub> O	1.96
Total	99.92

Si	2.981
Ti	0.006
Al	2.836
Fe <sup>3+</sup>	0.171
Mn	0.000
Ca	2.006



**Titanite Analyses**

SAMPLE	PS7c	PS085A -8b	PS86B 1-10a
SiO <sub>2</sub>	30.34	30.28	30.01
TiO <sub>2</sub>	37.09	36.57	36.75
Al <sub>2</sub> O <sub>3</sub>	1.55	1.53	1.55
Fe <sub>2</sub> O <sub>3</sub>	0.39	0.56	0.52
MnO	0.02	0.00	0.03
MgO	0.00	0.00	0.00
CaO	28.61	28.91	28.47
Na <sub>2</sub> O	0.02	0.01	0.02
K <sub>2</sub> O	0.01	0.01	0.01
Cl	0.01	0.01	0.00
F	0.72	0.57	0.68
P <sub>2</sub> O <sub>5</sub>	0.07	0.10	0.00
Total	98.83	98.55	98.04
Si	0.999	0.997	0.995
Ti	0.919	0.906	0.916
Al	0.060	0.059	0.061
Fe <sup>3+</sup>	0.010	0.014	0.014
Mn	0.001	0.000	0.001
Mg	0.000	0.000	0.000
Ca	1.009	1.020	1.011
Na	0.001	0.001	0.001
K	0.000	0.000	0.000
Cl	0.001	0.001	0.000
F	0.075	0.059	0.071
P	0.002	0.003	0.000

## Appendix 4

## Activity Models for Chapter II

## Pyroxene

The ideal activity models for clinopyroxene used in this study are summarized in the text, equations 17 and 18 for hedenbergite and diopside, respectively. The model used for orthopyroxene is that of Wood and Banno (1973) in which the activity of ferrosilite is taken as:

$$a_{\text{Fe}_2\text{Si}_2\text{O}_6}^{\text{Opx}} = [X_{\text{Fe}^{2+}}^{\text{M1}}] [X_{\text{Fe}^{2+}}^{\text{M2}}]$$

Pyroxene analyses are normalized to 4 cations and  $\text{Fe}^{3+}$  is calculated from charge balance and stoichiometry. After subtracting the atomic amounts of Ca, Na, and Mn from the M2 site, and subtracting  $\text{Al}^{\text{VI}}$ , Ti, Cr, and  $\text{Fe}^{3+}$  from the M1 site,  $\text{Fe}^{2+}$  is partitioned into each remaining site in the same ratio as  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$  in the mineral.

The equilibrium constant for the FS barometer includes a term for  $a_{\text{Fe}_2\text{Si}_2\text{O}_6}^{\text{Opx}}$  that is raised to the 3rd power. Because the two site model involves the square of  $X_{\text{Fe}}$ , the activity of ferrosilite calculated above is taken to the 3rd power in calculating the equilibrium constant for Reaction 3, although the thermodynamic data for ferrosilite are based on a 2 cation formula (6 moles of Fs for Reaction 3). When calculating the activity of  $\text{FeSiO}_3$  simply as mole fraction of  $\text{Fe}^{2+}$ , the exponent for Fs in Reaction 3 is raised to the 6th power.

## Plagioclase

The activity of anorthite in plagioclase was calculated according to the model of Newton et al. (1980), also given in Newton and Haselton (1981), Newton and Perkins (1982), and Newton (1983). Plagioclase analyses were normalized to 5 cations, and  $X_{\text{An}}^{\text{Pg}} = \text{Ca}/(\text{Ca} + \text{Na})$ . The activity of anorthite is calculated from the following relations:

$$RT \ln \gamma_{\text{An}}^{\text{Pg}} = (X_{\text{An}}^{\text{Pg}})^2 [2050 + 9392 \cdot X_{\text{An}}^{\text{Pg}}]$$

$$a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{Pg}} = \gamma_{\text{An}}^{\text{Pg}} [X_{\text{An}}^{\text{Pg}} \cdot (1 + X_{\text{An}}^{\text{Pg}})^2] / 4$$

## Garnet

Grossular, pyrope, and almandine activities were calculated using the quaternary garnet mixing model of Ganguly and Saxena (1984), with the Ca-Fe mixing parameters for the grossular-almandine join calculated by Anovitz and Essene (1987a). The Ca-Mg, Ca-Mn, Fe-Mg, Fe-Mn, and Mg-Mn mixing parameters are the same as in Ganguly and Saxena (1984). Use of these parameters yields the

following analytical expressions for the activity coefficient of grossular, pyrope, and almandine:

$$\begin{aligned} RT \ln \gamma_{Ca}^{Gt} = & (X_{Mg}^{Gt})^2 (4047 - 1.5T - 6094 X_{Ca}^{Gt}) + (X_{Fe^{2+}}^{Gt})^2 (150 - 1.5T + 7866 X_{Ca}^{Gt}) + \\ & X_{Mg}^{Gt} X_{Fe^{2+}}^{Gt} [3290 - 3.0T + 886 X_{Ca}^{Gt} + 2300 (X_{Mg}^{Gt} - X_{Fe^{2+}}^{Gt}) + 4640 (1 - 2X_{Ca}^{Gt})] + \\ & X_{Fe^{2+}}^{Gt} X_{Mn}^{Gt} [2117 - 1.5T + 3933 X_{Ca}^{Gt} - 1967 (1 - 2X_{Ca}^{Gt})] + \\ & X_{Mg}^{Gt} X_{Mn}^{Gt} [2524 - 1.5T - 3047 X_{Ca}^{Gt} + 1524 (1 - 2X_{Ca}^{Gt})] + \\ & 2300 [X_{Mg}^{Gt} X_{Fe^{2+}}^{Gt} X_{Mn}^{Gt}] \end{aligned}$$

$$\begin{aligned} RT \ln \gamma_{Mg}^{Gt} = & (X_{Ca}^{Gt})^2 (1000 - 1.5T + 6094 X_{Mg}^{Gt}) + (X_{Fe^{2+}}^{Gt})^2 (2500 - 4600 X_{Mg}^{Gt}) + 3000 (X_{Mn}^{Gt})^2 \\ & + X_{Ca}^{Gt} X_{Fe^{2+}}^{Gt} [1757 + 747 X_{Mg}^{Gt} - 3933 (X_{Ca}^{Gt} - X_{Fe^{2+}}^{Gt}) + 4640 (1 - 2X_{Mg}^{Gt})] + \\ & X_{Fe^{2+}}^{Gt} X_{Mn}^{Gt} [4350 - 2300 X_{Mg}^{Gt} + 1150 (1 - 2X_{Mg}^{Gt})] + \\ & X_{Ca}^{Gt} X_{Mn}^{Gt} [5524 + 3047 X_{Mg}^{Gt} - 1524 (1 - 2X_{Mg}^{Gt})] + \\ & 3933 [X_{Ca}^{Gt} X_{Fe^{2+}}^{Gt} X_{Mn}^{Gt}] \end{aligned}$$

$$\begin{aligned} RT \ln \gamma_{Fe^{2+}}^{Gt} = & (X_{Mg}^{Gt})^2 (200 + 4600 X_{Fe^{2+}}^{Gt}) + (X_{Ca}^{Gt})^2 (4083 - 1.5T - 7866 X_{Fe^{2+}}^{Gt}) + \\ & X_{Mg}^{Gt} X_{Ca}^{Gt} [943 - 1633 X_{Fe^{2+}}^{Gt} - 3047 (X_{Mg}^{Gt} - X_{Ca}^{Gt}) - 4640 (1 - 2X_{Fe^{2+}}^{Gt})] + \\ & X_{Ca}^{Gt} X_{Mn}^{Gt} [2117 - 1.5T - 3933 X_{Fe^{2+}}^{Gt} + 1917 (1 - 2X_{Fe^{2+}}^{Gt})] + \\ & X_{Mg}^{Gt} X_{Mn}^{Gt} [-1650 + 2300 X_{Fe^{2+}}^{Gt} - 1150 (1 - 2X_{Fe^{2+}}^{Gt})] + \\ & 3048 [X_{Mg}^{Gt} X_{Ca}^{Gt} X_{Mn}^{Gt}] \end{aligned}$$

Because there are three equivalent 8-coordinated sites in garnet, the activity of  $Ca_3Al_2Si_3O_{12}$ ,  $Mg_3Al_2Si_3O_{12}$ , and  $Fe_3Al_2Si_3O_{12}$  are calculated as

$$a_{Ca_3Al_2Si_3O_{12}}^{Gt} = (X_{Ca}^{Gt} \gamma_{Ca}^{Gt})^3,$$

$$a_{Mg_3Al_2Si_3O_{12}}^{Gt} = (X_{Mg}^{Gt} \gamma_{Mg}^{Gt})^3, \text{ and}$$

$$a_{Fe_3Al_2Si_3O_{12}}^{Gt} = (X_{Fe^{2+}}^{Gt} \gamma_{Fe^{2+}}^{Gt})^3.$$

## APPENDIX 5

Mineral formulae, abbreviations, and symbols.

Albite (Ab):	$\text{NaAlSi}_3\text{O}_8$
Almandine (Alm):	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Andradite (And):	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$
Anhydrite (Anhy):	$\text{CaSO}_4$
Anorthite (An):	$\text{CaAl}_2\text{Si}_2\text{O}_8$
Calcite (Cc):	$\text{CaCO}_3$
Ca-Tschermakite (CaTs):	$\text{CaAl}_2\text{SiO}_6$
Clinozoisite (CZo):	$\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{11}\text{OH}$
Corundum (Cor):	$\text{Al}_2\text{O}_3$
Diopside (Di):	$\text{CaMgSi}_2\text{O}_6$
Enstatite (En):	$\text{MgSiO}_3$
Fayalite (Fa):	$\text{Fe}_2\text{SiO}_4$
Ferrosilite (Fs):	$\text{FeSiO}_3$
Gehlenite (Ge):	$\text{Ca}_2\text{Al}_2\text{SiO}_7$
Grossular (Gr):	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Hematite (Hm):	$\text{Fe}_2\text{O}_3$
Kyanite (Ky):	$\text{Al}_2\text{SiO}_5$
Magnetite (Mt):	$\text{Fe}_3\text{O}_4$
Meionite (Me):	$\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$
Mg-Tschermakite (MgTs):	$\text{Mg}_{0.5}\text{AlSi}_{0.5}\text{O}_3$
Pistacite (Ps):	$\text{Ca}_2\text{Fe}_3^+\text{Si}_3\text{O}_{11}\text{OH}$
Pyrope (Py):	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Quartz (Qz):	$\text{SiO}_2$
Sillimanite (Sill):	$\text{Al}_2\text{SiO}_5$
Sulfate Meionite ( $\text{MeSO}_4$ ):	$\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$
Titanite	$\text{CaTiSiO}_5$
Wollastonite (Wo):	$\text{CaSiO}_3$
Zoisite (Zo):	$\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{11}\text{OH}$

Cc: calcite

Cpx: clinopyroxene

Ep: epidote

Gt: garnet

Hbl: hornblende

Kfs: potassium feldspar

Opx: orthopyroxene

Pg: plagioclase

Sc: scapolite

- $S_0^{\circ}$ : zero-point, configurational entropy,  $\text{J mol}^{-1} \text{K}^{-1}$ .  
 $S_{298}^{\circ}$ : molar entropy at 1 bar, 298 K,  $\text{J mol}^{-1} \text{K}^{-1}$ .  
 $S_T^{\circ}$ : molar entropy at P and T,  $\text{J mol}^{-1} \text{K}^{-1}$ .  
 $V_{298}^{\circ}$ : molar volume at 1 bar, 298 K,  $\text{cm}^3$   
 $V_T^{\circ}$ : molar volume at P and T,  $\text{cm}^3$   
 $\Delta S$ : entropy change of reaction or solid phases  
 $\Delta V$ : volume change of reaction or solid phases  
 $\Delta G_{298}^{\circ}$ : molar Gibbs free energy at 1 bar, 298 K,  $\text{kJ mol}^{-1}$ .  
 $a_j$ : activity of component i in phase j  
 $X_j$ : mole fraction of component i in phase j  
 $\gamma_j$ : activity coefficient of component i in phase j  
 $X_{M_e}^{\text{Ss}}$ :  $\text{Ca}/(\text{Ca}+\text{Na}+\text{K})$ , or  $\text{EqAn } (100[\text{Al}-3]/3)$ , where stated.