

## Experimentally determined activity-composition relations for Ca-rich scapolite in the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-NaAlSi}_3\text{O}_8\text{-CaCO}_3$ at 7 kbar

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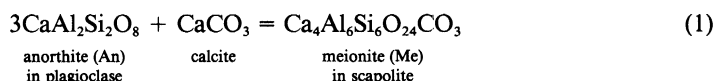
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### ABSTRACT

Equilibrium compositions of coexisting Ca-rich carbonate scapolite and plagioclase in the presence of calcite have been investigated experimentally at 7.0 kbar in the temperature range 775–850 °C. The  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$  univariant reaction is



with  $\text{NaSi}(\text{CaAl})_{-1}$  substitution in both plagioclase and scapolite in the  $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$  divariant assemblage.

The experiments were carried out in a  $\frac{3}{4}$  in. diameter NaCl pressure cell with a hematite + magnetite buffer and a hydrous oxalic acid flux. Starting materials were a natural Cl- and S-free mizzonite ( $\text{Me}_{63}$ ), Baker reagent precipitated calcite, and synthetic meionite and plagioclases of composition  $\text{An}_{100}$  and  $\text{An}_{92}$ . Changes of compositions of the reactants were determined by microprobe analysis.

The experimental results confirm the inferences based on observations in natural assemblages made by earlier workers that Na substitution greatly stabilizes scapolite relative to plagioclase. The marked stabilization of mizzonite to lower temperatures is largely a consequence of the large amounts of atomic mixing possible in the scapolite structure. An activity model for the meionite component in terms of its mole fraction,  $X_{\text{Me}}$ , which involves complete disordering of Ca and Na and, independently, Si and Al, has been derived from the experimental brackets.

$$a_{\text{Me}} = \frac{(1 + X_{\text{Me}})^6(3 - X_{\text{Me}})^6(3X_{\text{Me}} + 1)^4}{4^{10}} \exp\left[\frac{-13450}{T} X_{\text{Me}}(1 - X_{\text{Me}})^2\right].$$

This formula may lose validity in a lower temperature range if scapolite develops greater atomic ordering near the mizzonite composition.

The disordered scapolite model is used to calculate apparent  $\text{CO}_2$  activities for recrystallization of some Grenville granulites studied by Moecher and Essene (1991). We find close agreement with their predicted  $\text{CO}_2$  activities based on scapolite + garnet + plagioclase + quartz equilibrium at 800 °C and 10 kbar, despite the different scapolite activity models used in the two sets of calculations. The simplest explanation of this coincidence is that their empirical scapolite model and the present experimentally based model are both valid, although the latter is restricted to high temperatures (above 750 °C).

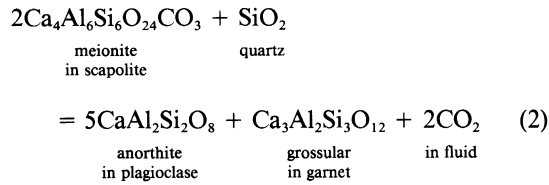
### INTRODUCTION

The mineral scapolite can be chemically represented as a solid solution of four end-members: a calcium carbonate end-member, meionite,  $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$  (Me); a sodium chloride end-member, marialite,  $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$  (Ma); a hypothetical end-member  $\text{Na}_3\text{CaAl}_3\text{Si}_9\text{O}_{24}\text{CO}_3$  (Na-Me); and a calcium sulfate end-member, sulfate meionite,  $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$  ( $\text{SO}_4\text{-Me}$ ). Scapolite rich in the marialite component occurs in high-temperature meta-

somatic settings (e.g., the Idaho Batholith aureole; Hietanen, 1967), whereas scapolite from high-grade metamorphic calc-silicates and mafic gneisses has a composition closer to the meionite and sulfate meionite end-members, with many scapolite grains having close to two-thirds of the meionite component. This particular composition range is termed mizzonite (Shaw, 1960; Evans et al., 1969; Moecher and Essene, 1991).

Carbonate scapolite is unique in being a refractory  $\text{CO}_2$ -bearing phase that can coexist stably with common sili-

cate minerals at elevated temperature conditions. Moecher and Essene (1990, 1991) showed that the reaction



is useful for calculating  $\text{CO}_2$  activities driving recrystallization of high-grade, deep-crustal metamorphic rocks containing the common assemblage scapolite + plagioclase + garnet + quartz, providing a new approach to debate about the role of  $\text{CO}_2$  in the formation of granulite facies terranes (Newton et al., 1980b; Valley et al., 1990; Frost and Frost, 1987; Waters, 1988). However, calculations involving carbonate scapolite require a knowledge of the activity-composition relations along the join from meionite to sodium meionite.

The stability of the scapolite end-member meionite at crustal pressures is limited, at low temperatures, by Reaction 1. Goldsmith and Newton (1977) reported broad reversals of this univariant reaction, and these experiments suggested that meionite is stable relative to anorthite and calcite above 875 °C, almost independently of pressure. Huckenholz and Seiberl (1989) presented a second experimental study of this equilibrium and suggested markedly lower temperature limits for meionite stability and a steep negative  $dP/dT$  slope for the reaction. More recent experiments (Baker and Newton, 1994) favor the results of Goldsmith and Newton (1977) and require a steep positive  $dP/dT$  slope for the univariant reaction.

The incorporation of Na into meionite through a plagioclase substitution,  $\text{NaSi}(\text{CaAl})_{-1}$ , expands the range of conditions over which scapolite is stable. Goldsmith and Newton (1977) found that carbonate scapolite ranging from pure meionite to compositions near  $\text{Me}_{50}$  (or Eq  $\text{An}_{50}$ ) were stable at temperatures above 850 °C. Orville (1975) and Ellis (1978) experimentally determined the stability of mizzonite with respect to plagioclase plus calcite, and both authors found that mizzonite is stable to temperatures at least 100 °C lower than pure meionite. Ellis (1978) found a relatively wide range of solid solution from  $\text{Me}_{53}$  to  $\text{Me}_{83}$  at 750 °C and 4 kbar, whereas Orville (1975) found a much narrower range of solid solution at identical conditions. Observations from natural calcareous assemblages formed at temperatures of 600 °C or below indicate that mizzonite,  $\text{Me}_{67}$ , coexisting with plagioclase of composition  $\text{An}_{44-48}$  or  $\text{An}_{94-95}$ , is the lowest-temperature Na-free scapolite (Oterdoom and Gunter, 1983; Moecher and Essene, 1990).

Estimates of mixing properties along the join from meionite to sodium meionite on the basis of paragenetic analysis have been made by Oterdoom and Gunter (1983) and Moecher and Essene (1990). However, no reversed experimental data describing the compositions of coexisting scapolite and plagioclase have been available here-

fore. The data of Goldsmith and Newton (1977) indicate that the scapolite-plagioclase compositional tie lines are quite temperature dependent, as indicated also by the natural parageneses. They found that the sulfate to carbonate ratio of the synthetic scapolites has a marked effect on the tie lines. However, they were unable to reverse the coexisting compositions in their high-temperature dry experiments. It is the object of the present work to attempt to secure reversals of the temperature dependence of the composition of coexisting carbonate scapolite and plagioclase in the presence of calcite in order to define experimentally the activity-composition relations of calcic carbonate scapolite.

## EXPERIMENTAL METHODS

### Starting materials

Starting material for the present experiments consisted of a nearly Cl- and  $\text{SO}_4$ -free natural mizzonite from Nevada, as well as synthetic meionite, synthetic anorthites of composition  $\text{An}_{100}$  and  $\text{An}_{92}$ , and Baker reagent precipitated calcite.  $\text{An}_{100}$  was prepared from a glass crystallized at 1500 °C and 15 kbar in graphite crucibles in a piston-cylinder apparatus for 2 h.  $\text{An}_{92}$  was crystallized at similar conditions from a homogenized mechanical mixture of anorthite and albite glasses. The synthetic meionite was crystallized in a two-step process. Meionite was synthesized from a mix of synthetic anorthite and calcite seeded with synthetic meionite (crystallized at 1350 °C and 15 kbar from a homogeneous 3:1 molar mix of synthetic anorthite and calcite) at 900–950 °C and 3.5 kbar with an anhydrous oxalic acid flux for 48 h. The result was a nearly complete yield of large (up to 100  $\mu\text{m}$ ) idiomorphic crystals of meionite. Compositions of the synthetic plagioclases and scapolite were checked by microprobe analysis and found to correspond closely to the intended compositions. The Al-Si ratio was taken as the definitive compositional parameter because of Na evaporation from plagioclase and scapolite with the focused electron beam necessary to analyze the fine-grained synthetic materials. Average compositions of the natural and synthetic starting materials are given in Table 1.

Equilibration experiments were made with two kinds of starting mixes. Approach to equilibrium from the Na-rich side was attempted with mixes consisting of 20% 20–50  $\mu\text{m}$  seeds of the natural mizzonite in finely powdered (1–5  $\mu\text{m}$ ) synthetic anorthite and reagent calcite in meionite proportions. Twenty weight percent of hydrous oxalic acid,  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , was added as a flux. Approach to equilibrium from the Ca-rich side was attempted with a mix consisting of a few (<2%) of the synthetic meionite seeds in finely powdered plagioclase  $\text{An}_{92}$  + calcite + hydrous oxalic acid. The charges were sealed in 1.5 mm diameter Pt tube segments. These were packed in 50–80 mg of fine hematite powder + 20 wt%  $\text{H}_2\text{O}$  in sealed Au tube segments of 3 mm diameter and 0.12 mm wall thickness. The double capsules were packed in a mixture of NaCl and hematite within the pressure cell.

**TABLE 1.** Average compositions of natural and synthetic starting materials

	Synthetic meionite*	Synthetic plagioclase An <sub>92</sub>	Natural mizzonite*	Synthetic plagioclase An <sub>100</sub>
SiO <sub>2</sub>	39.0	44.8	46.9	43.6
Al <sub>2</sub> O <sub>3</sub>	32.6	35.1	27.2	37.3
CaO	24.2	18.8	18.0	0.0
Na <sub>2</sub> O	0.0	0.7	3.7	20.2
K <sub>2</sub> O	0.0	0.0	0.2	0.0
Cl <sup>-</sup>	0.0		0.2	
SO <sub>3</sub> <sup>2-</sup>	0		0	
Total	95.8	99.4	96.2	101.1
<b>Cations</b>				
Si	6.0	2.08	7.1	1.99
Al	5.9	1.92	4.9	2.01
Ca	4.0	0.93	2.9	0.99
Na	0.0	0.07	1.1	0.01
K	0.0	0.0	0.0	0.0
Total	16.0	5.00	16.0	5.00
<b>Anions</b>				
Cl <sup>-</sup>	0.0		0.1	
X <sub>Me</sub>	1.0		0.63	
X <sub>An</sub>		0.92		1.0
S	0.0		0.0	

\* Scapolite compositions were recalculated to 16 cations. SO<sub>3</sub><sup>2-</sup> and Cl<sup>-</sup> are calculated assuming 25 O<sup>2-</sup> equivalents per formula unit.

This oxidizing buffer prevented infiltration of H<sub>2</sub> and consequent formation of zoisite during the experiments.

#### Pressure-temperature apparatus

Experiments were made in the piston-cylinder apparatus at 7 kbar with a NaCl pressure-medium. Piston-out conditions were maintained during all experiments. Under these conditions it is well established that the frictional pressure correction for the solid pressure-medium is negligible. Pressures are believed accurate to  $\pm 0.2$  kbar.

Temperature was measured and controlled with chromel-alumel thermocouples in contact with the sample capsules. A thin film of Al<sub>2</sub>O<sub>3</sub> cement protected the thermocouple from contamination by the gold. Temperature control was  $\pm 2$  °C. Charges were quenched to below 100 °C in <10 s by turning off the heating power.

Quenched capsules were inflated with trapped CO<sub>2</sub>, and hematite was always present in the hematite + H<sub>2</sub>O + magnetite buffer after the quench.

#### Analytical techniques

Experimental products were examined by X-ray diffraction and electron microprobe analysis. After confirming that all three principal phases (scapolite, calcite, and plagioclase) were present, the compositions of the recrystallized scapolite and plagioclase in each of the samples were determined using the Cameca electron microprobe in the Department of Geophysical Sciences at the University of Chicago. All elements were analyzed using a WD detector, and synthetic anorthite was the principal standard. An accelerating voltage of 15 kV and a beam current of 0.1  $\mu$ amp were used, with acquisition times of 80 s.

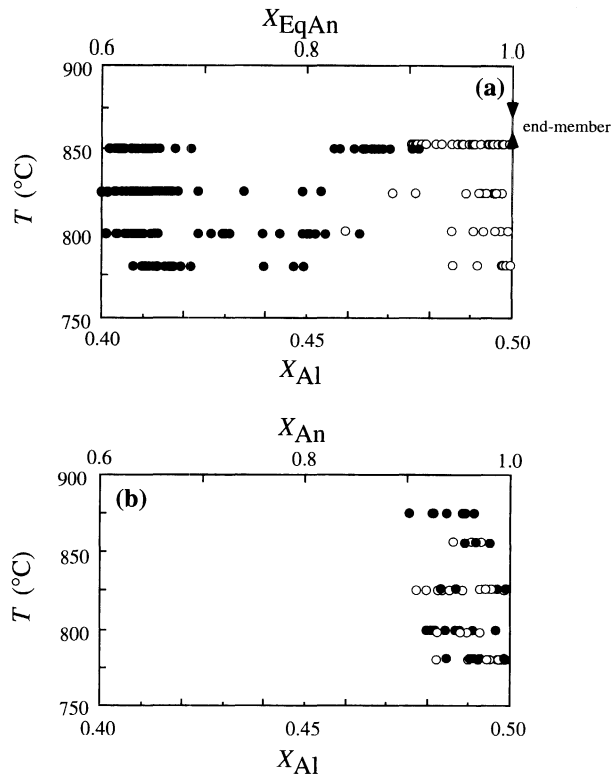


Fig. 1. Compositions of experimentally equilibrated (a) scapolites and (b) plagioclases for experiments at 7.0 kbar, determined by microprobe analysis.  $X_{Al} = Al/(Al + Si)$ . Open circles show compositions from experiments starting with mizzonite + An<sub>100</sub>; solid circles show compositions from experiments starting with meionite + An<sub>92</sub>. The lower temperature stability limit of meionite taken from the experiments of Baker and Newton (1994) is indicated.

#### RESULTS OF EXPERIMENTS

The natural mizzonite starting material was found to have changed composition extensively on the rims and along cleavages in the interiors of the large seed grains. Equilibrated rims as broad as 15  $\mu$ m yielded an array of compositions (Fig. 1) towards the meionite end-member. No evidence was found of any gaps in the spread that could suggest immiscibility. Analyses fulfilled scapolite stoichiometry. Plagioclase was extensively recrystallized to equant 5–10  $\mu$ m untwinned grains of uniform composition. A spread of compositions averaging about An<sub>95</sub> was characteristic of recrystallized plagioclase at all experimental temperatures (Fig. 1 and Table 2). There was no textural evidence of melting in the experiments, and no zoisite formed.

In experiments on the Ca-rich starting material, most of the synthetic meionite grains were recrystallized to compositions with variable Na, the most sodic of which approached the most equilibrated compositions in the experiments with natural mizzonite (Fig. 1 and Table 2). The 850 and 800 °C experiments showed small cross-overs in the equilibrated scapolite compositions.

The anticipated large stabilization of carbonate scapolite to temperatures below the limit of pure meionite is evident in Figure 1. Fifteen mole percent of sodium meionite component stabilizes scapolite by at least 70 °C. The expectation from natural parageneses that these scapolites can coexist with calcite and a plagioclase of composition near  $An_{95}$  is also fulfilled.

### DISCUSSION AND INTERPRETATION

The stabilization of meionite by substitution of Na for Ca and of Si for Al is a consequence of large amounts of atomic mixing and is primarily an entropy effect, as emphasized by Oterdoom and Gunter (1983) and by Moecher and Essene (1990). Unless the solid solution is accompanied by a large positive enthalpy of mixing, the activity of the meionite molecule will be much smaller than its mole fraction in the solid solutions. For a completely disordered solid solution of disordered end-members, with random mixing of Ca and Na on the cation sites and of Al and Si on the tetrahedral sites, and no heat effect of mixing, it may be shown (Appendix 1) that the activity of meionite is given in terms of its mole fraction ( $X_{Me}$ ) by

$$a_{Me}^d = \frac{(X_{Me} + 1)^6(3 - X_{Me})^6(3X_{Me} + 1)^4}{4^{10}} \quad (3)$$

Despite the large amount of atomic mixing implied by Equation 3, additional sources of negative excess Gibbs energy of solid solution are needed to fit the composition brackets in Figure 1 and Table 2. The concept of quasi-compound formation at a certain composition may be useful: an ordering tendency may be present at lower temperatures that would result in greatly reduced meionite activities near this composition. Klee (1974) noted that strict alternation of Al-O and Si-O linkages (Al-avoidance, considered to be the most stable aluminosilicate framework) is not geometrically possible in pure meionite, but that the number of Al-O-Al linkages is substantially reduced in the mizzonite composition range. The analysis based on natural parageneses of Oterdoom and Gunter (1983) emphasizes the special stability of a mizzonite of composition  $Me_{67}$ , but seems unsatisfactory in that the marked stability of this special composition [with  $Ca/(Ca + Na) = 3/4$ ] is attributed to a trade-off between the relatively small amounts of less stable Al-O-Al framework linkages at low  $X_{Me}$  and the increasing size of the cages housing the carbonate groups at higher  $X_{Me}$ . It is not apparent in this hypothesis why any rational composition such as  $Me_{67}$  should exhibit special stability.

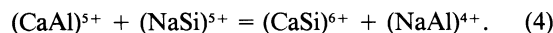
A negative excess enthalpy of solid solution might ensue from preferred grouping of  $Ca^{2+}$  near the anion sites, for better local charge balance, or preferred linkage of  $Ca^{2+}$  with either  $Si^{4+}$  or  $Al^{3+}$  in neighboring tetrahedra, as suggested by Hassan and Buseck (1988). These ordering tendencies might well be expedited by special compositions in which the preferred linkages are more numerous. Incipient clustering might exist without significant

TABLE 2. Reversed experimental brackets of Reaction 1

T (°C)	$X_{Me}$	$X_{An}$
850	0.956–0.904	0.95–0.98
825	0.816–0.884	0.93–0.98
800	0.836–0.852	0.92–0.96
775*	0.796–0.944	0.92–0.98

\* Reaction rates were too slow to produce a tight scapolite composition bracket at 775 °C in two-week experiments.

departure from random configurational entropy. The latter type of association may be formalized by an inter-crystalline exchange reaction (the reciprocal reaction of Wood and Nicholls, 1978):



It may be shown that the number of linkages on the right side of Expression 4 are at a maximum and those of the left side are minimal when  $X_{Me} = 2/3$  (the ideal mizzonite composition), on the basis only of random associations. If the free energy of Reaction 4 is less than zero, the right side assemblage represents energetically preferred linkages, and the  $Me_{67}$  composition may be one of special stability. A large negative  $\Delta G_4$  could result in superstructure formation; this has not been recognized in natural mizzonite. The slight charge segregation suggested by Reaction 4 might be more effective in balancing the charges of the  $CO_3^{2-}$  groups.

The special stability of mizzonite can be expressed, following Oterdoom and Gunter (1983) and Moecher and Essene (1991), in a Margules-type expression for excess free energy of mixing ( $\Delta G_{Ex}$ ):

$$\Delta G_{Ex} = W_1 X_{Me}^2(1 - X_{Me}) + W_2(1 - X_{Me})^2 X_{Me} \quad (5)$$

where  $W_1$  and  $W_2$  are constants. In order for  $\Delta G_{Ex}$  to minimize at the  $Me_{67}$  composition, it must be the case that  $W_2 = 0$  and  $W_1 < 0$ . Decreased free energy of solid solution is given by a factor  $\gamma_{Me}$  on the ideal activity Expression 3:

$$\gamma_{Me} = \exp \left[ \frac{2W_1}{RT} X_{Me}(1 - X_{Me})^2 \right]. \quad (6)$$

This procedure is similar to that used by Oterdoom and Gunter (1983). They evaluated the Margules constant term from compositional data of natural scapolites from the Central Alps, with assumed temperatures of plagioclase + scapolite + calcite recrystallization. In the present work,  $W_1$  is evaluated from the experimental composition bracket at 800 °C and 7 kbar. This is our only reversed bracket with sufficient discrimination to calibrate the excess free energy. Assuming a coexisting plagioclase of  $An_{95}$  and the plagioclase activity model of Newton et al. (1980a), a  $W_1$  of  $-55.92 \pm 12$  kJ results.

Figure 2 shows the calculated equilibrium curve for coexistence of scapolite, plagioclase, and calcite at 7 kbar. Plagioclase compositions of  $An_{97}$  at 850 °C,  $An_{96}$  at 825 °C, and  $An_{95}$  at 800 °C and below were somewhat arbitrarily adopted. All of the experimental brackets are sat-

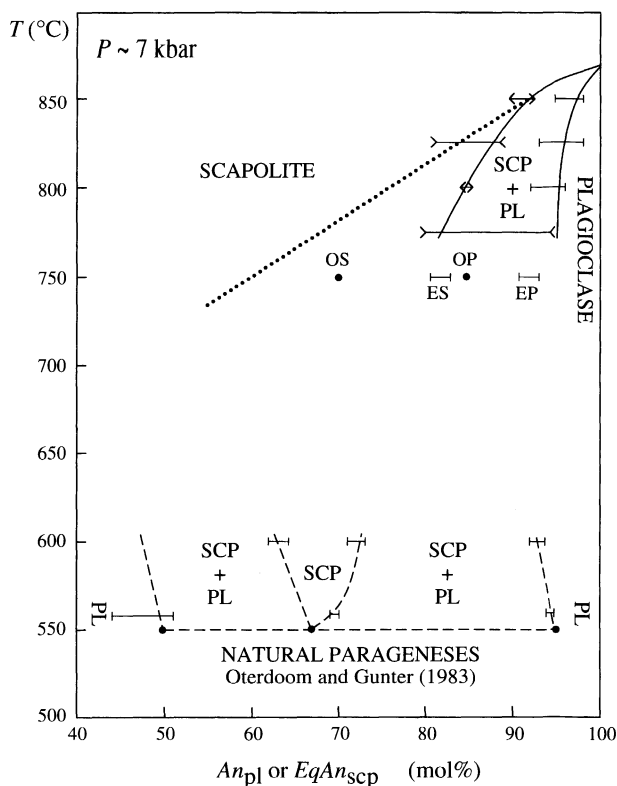


Fig. 2. Preliminary phase equilibria of scapolite, plagioclase, and calcite in the system  $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-NaAlSi}_3\text{O}_8\text{-CaCO}_3$  at 7 kbar and phase relations at 7 kbar suggested by natural parageneses (Oterdoom and Gunter, 1983). All fields contain calcite. Arrowheads denote experimental brackets of scapolite compositions showing direction of approach to equilibrium. Brackets at 750 °C denote experimental compositions of scapolite (ES) and plagioclase (EP) reported by Ellis (1978) at 4 kbar. OS and OP represent the corresponding data of Orville (1975). Dotted line is the calculated phase boundary of scapolite + plagioclase + calcite calculated from an ideal charge-balanced activity model of scapolite ( $a_{\text{Me}} = X_{\text{Me}}^3$ ).

ified. In contrast, a charge-balanced molecular expression  $a_{\text{Me}} = X_{\text{Me}}^3$  results in a much less stable scapolite solid solution, and the calculated three-phase boundary misses the lower temperature brackets by wide margins (Fig. 2). The predicted phase boundaries pass close to the experimental compositions reported by Ellis (1978) in the same system at 750 °C and 4 kbar but differ widely from those reported by Orville (1975) at the same conditions. Extensions of our boundaries calculated from the disordered scapolite model are generally consistent with the paragenetically inferred phase diagram of Oterdoom and Gunter (1983), as shown in Figure 2. A more rigorous comparison cannot be made at present because of the unknown effect of progressive scapolite ordering at lower temperatures, and because calcic plagioclase shows a phase-separation tendency at temperatures below 700 °C, with greater anorthite activities than those given by most

of the activity formulas, as pointed out by Oterdoom and Gunter (1983).

In modeling scapolite solid solutions having significant replacement of  $\text{CO}_3^{2-}$  by  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$ , an additional factor may be included in the activity expression

$$a_{\text{Me}} = a_{\text{Me}}^{\text{id}} \cdot \gamma_{\text{Me}} \cdot X_{\text{CO}_3} \quad (7)$$

where  $X_{\text{CO}_3}$  represents the fraction  $\text{CO}_3^{2-}/(\text{CO}_3^{2-} + \text{SO}_4^{2-} + \text{Cl}^-)$  and  $a_{\text{Me}}^{\text{id}}$  is the disordered activity formula of Equation 3. Such an ideal anion activity factor was used by Moecher and Essene (1991) in their empirical scapolite model. Its validity remains unknown.

An evaluation of the present experimentally based activity model of carbonate scapolite may be made by recalculation of the apparent  $\text{CO}_2$  activities of recrystallization of some of the granulites discussed by Moecher and Essene (1991). Their calculations of  $\text{CO}_2$  activity were based on natural assemblages of scapolite, plagioclase, garnet, and quartz evaluated using Reaction 2. Their calculations incorporated an empirical activity model for scapolite based on Reaction 1 and many compositional data from natural parageneses, as well as corresponding equilibration temperatures calculated from independent geothermometers. Their activity function uses the charge-balanced ideal activity multiplied by an activity coefficient based on a Margules-type expression with logarithmic temperature dependences of the  $W$  parameters. They used a pure meionite standard state from the experiments of Huckenholz and Seiberl (1989) on Reaction 1, which gives a more stable end-member and hence higher activities than if the Baker and Newton (1994) meionite stability curve were used.

In the present calculation, the analytic data given by Moecher and Essene (1991) for six calc-silicate granulites and six mafic granulites from the Central Gneiss Belt of southern Ontario are used. Moecher and Essene's (1991) estimates of 800 °C and 10 kbar for these occurrences are adopted, as well as their calculated values of the anorthite activity of plagioclase and the grossular ( $\text{CaAl}_2\text{SiO}_4$ ) activity of garnet. Their anorthite activities are almost identical to those yielded by the activity model of Newton et al. (1980a), and their grossular activities are close to those yielded by the ternary garnet model of Newton and Perkins (1982). The Moecher and Essene (1991) activities are retained for the sake of a more direct comparison. The Baker and Newton (1994) standard state of meionite is adopted here.

A major uncertainty exists in the standard Gibbs free energy of Reaction 2, if it is compiled from tabulated datasets, because of the accrued uncertainty in the enthalpy of reaction. This uncertainty can be eliminated almost completely by direct use of experimental data for these reactions. Experimental data for Reaction 1 are a major input factor. Baker and Newton (1994) found a 1 bar equilibrium point of 851 °C (1124 K). They derived a  $\Delta S^\circ(1124)$  of 70.4 J/K, which leads to a  $S_{\text{Me}}^\circ(298)$  value of 761 J/K. Because of the lack of published experimental data for the heat capacity of meionite, the approximation

**TABLE 3.** Volumes at 25 °C, 1 bar ( $V^0$ ), thermal expansions ( $\alpha V$ ), and compressibilities ( $\beta V$ ) of pertinent solid phases

	$V^0$	$\alpha V (\times 10^{-5})$	$\beta V (\times 10^{-9})$
Grs	12.535	30.0	7.9
An	10.079	14.3	13.0
Cal	3.769*		5.3
Wo	3.993	9.6	3.6
$\beta$ -Qtz**	2.367	0	2.6
$\alpha$ -Qtz**	2.269	8	5.9
Me	33.985	61.7†	38.0

Note: Grs = grossular,  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ; An = anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ; Cal = calcite,  $\text{CaCO}_3$ ; Wo = wollastonite,  $\text{CaSiO}_3$ ;  $\beta$ -Qtz = beta quartz,  $\text{SiO}_2$ ;  $\alpha$ -Qtz = alpha quartz,  $\text{SiO}_2$ ; Me = meionite,  $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$ . System of units is kilojoules-degrees Celsius-kilobars. Volumes:  $V(T,P) = V^0 + (\alpha V)(T - 25) - (\beta V)P$ . Volume data from Holland and Powell (1990).  $\text{CO}_2$  fugacity (interpolated from Shmulovich and Shmonov, 1978) is 39.09 at 800 °C and 3.69 kbar, and 241.78 at 800 °C and 10.0 kbar.

\* Calcite volume at 800 °C from Dove and Powell (1989).

\*\* The  $\alpha$ - $\beta$  quartz reaction:  $T = 571 \pm 24.04P$  (Cohen and Klement, 1967).

† Thermal expansion of meionite taken from Baker (1994).

that  $\Delta S^0$  does not vary substantially over a short temperature interval around 851 °C must be adopted; this is equivalent to the assumption that the heat capacity of (3 anorthite + calcite) is identical to that of meionite. Using this assumption, the Gibbs free energy of Reaction 1 at 800 °C and 1 bar is  $51 \times 70.4 = 3590$  J. At the same temperature,  $\Delta G^0$  of the reaction



is  $-20.499$  kJ, on the basis of the accurately determined equilibrium pressure of  $6.49 \pm 0.2$  kbar (Huckenholtz et al., 1975) and the thermal expansion and compressibility data of Table 3. Finally,  $\Delta G^0$  of the reaction



at 800 °C is  $-76.825$  kJ, on the basis of the precisely measured equilibrium pressure of  $3.96 \pm 0.07$  kbar (Zhu et al., 1994). The  $\Delta G^0$  at 800 °C of Reaction 2 is then given by

$$\begin{aligned} \Delta G_2^0 &= -2\Delta G_1^0 - \Delta G_8^0 + 2\Delta G_9^0 \\ &= -140.331 \pm 0.7 \text{ kJ.} \end{aligned} \quad (10)$$

The uncertainty in  $\Delta G_2^0$  so calculated is smaller by an order of magnitude than the uncertainties obtained from any of the standard datasets.

The  $f_{\text{CO}_2}$  is obtained from the expression

$$\ln f_{\text{CO}_2} = \left( \frac{-\Delta G_2^0 - P\Delta V_s^*}{2RT} \right) + \frac{1}{2} \ln \left( \frac{a_{\text{Me}}^2}{a_{\text{An}}^5 a_{\text{Grs}}^3} \right) \quad (11)$$

where  $\Delta V_s^*$  is the characteristic solid-volume change  $5V_{\text{An}} + V_{\text{Grs}} - 2V_{\text{Me}} - V_{\text{Qtz}}$  evaluated at  $T$  and  $P/2$ . The first term in parentheses is evaluated as 12.07 from the data in Table 3. The  $\text{CO}_2$  activity is given by dividing the calculated  $f_{\text{CO}_2}$  by the fugacity of pure  $\text{CO}_2$  at 800 °C and 10 kbar. It should be noted that use of the standard meionite entropy of 720 J/K tabulated by Holland and Powell (1990) gives slightly higher  $a_{\text{Me}}$  values from Equation 11, and the  $S_{298}^0$  preferred by Moecher and Essene (1991) of 780 J/K, assuming a completely disordered meionite, gives a somewhat lower  $a_{\text{Me}}$ . Table 3 gives the few data necessary to repeat the preceding calculations.

Calculated fugacities for the 12 Ontario granulites are given in Table 4. Two features of the results are noteworthy. First, the agreement with Moecher and Essene's (1991) calculated fugacities is quite remarkable, especially considering that their meionite activity model was based on empirical deductions from natural parageneses, and that they used a different standard state of meionite. Second, their contention that apparent  $f_{\text{CO}_2}$  of calc-silicates and marbles are characteristically much smaller than those calculated for scapolite-bearing mafic and intermediate

**TABLE 4.**  $\text{CO}_2$  activities ( $a_{\text{CO}_2}$ ) of Central Gneiss Belt (Ontario) calc-silicates and mafic gneisses at 800 °C and 10 kbar from chemical data of Moecher and Essene (1991)

Sample	$X_{\text{Me}}^*$	$X_{\text{CO}_3}$	$a_{\text{Me}}^{**}$	$X_{\text{An}}^*$	$a_{\text{An}}^\dagger$	$a_{\text{Grs}}^\dagger$	$a_{\text{CO}_2}^\ddagger$	$a_{\text{CO}_2}(\text{M} + \text{E})^\ddagger$
<b>Calc-silicates</b>								
H 85A-16	0.69	0.99	0.1153	0.72	0.80	0.61	0.34	0.25
H 85A-1d-1	0.71	0.98	0.1392	0.68	0.77	0.74	0.33	0.23
H 85A-1e(1)	0.65	0.98	0.0782	0.44	0.56	0.64	0.53	0.45
H85A-1e(2)	0.66	0.96	0.0845	0.51	0.64	0.77	0.31	0.30
M 86E-1b	0.50	0.70	0.0124	0.25	0.33	0.92	0.20	0.26
M 86E-1c2	0.60	0.87	0.0422	0.28	0.36	0.93	0.51	0.48
<b>Mafic granulites</b>								
80D MA 614p	0.64	0.45	0.0325	0.51	0.63	0.22	0.82	0.72
85D MP 272-2a	0.62	0.45	0.0267	0.42	0.53	0.26	0.82	0.72
85D MP 174-1a	0.56	0.52	0.0168	0.31	0.41	0.24	1.14	1.28
S86E-53a	0.60	0.51	0.0247	0.39	0.51	0.33	0.59	0.68
A 86B3-3B-3	0.61	0.34	0.0182	0.44	0.57	0.16	0.97	1.00
M49	0.62	0.50	0.0296	0.42	0.54	0.48	0.35	0.31

\* Scapolite ( $X_{\text{Me}} = \text{eq An}$ ;  $X_{\text{CO}_3} = \text{CO}_3/(\text{CO}_3 + \text{SO}_4 + \text{Cl})$ ), Plagioclase ( $X_{\text{An}}$ ) in mole fractions.

\*\* Meionite ( $a_{\text{Me}}$  see text).

† Activities of anorthite ( $a_{\text{An}}$ ) and grossular garnet ( $a_{\text{Grs}}$ ) from Moecher and Essene (1991).

‡ Carbon dioxide activity from present calculations ( $a_{\text{CO}_2}$ ) and from Moecher and Essene (1991)  $a_{\text{CO}_2}(\text{M} + \text{E})$ .

granulites appears to be valid. Harley and Buick (1992) also found that granulite facies calc-silicates from East Antarctica indicate low CO<sub>2</sub> activities.

We tentatively conclude from the agreement of the calculated fugacities that the empirical Me activity model of Moecher and Essene (1991) is accurate, and that the disordered scapolite model of the present study is valid over an extended composition range. If so, this agreement represents a success for the method of paragenetic analysis and vindicates the deduction of Oterdoom and Gunter (1983) of scapolite-plagioclase relations in marbles, shown in Figure 2.

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#### APPENDIX 1.

Expressions for the activities of the components 3CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>·CaCO<sub>3</sub> (Me) and 3NaAlSi<sub>3</sub>O<sub>8</sub>·CaCO<sub>3</sub> (Na-Me) may be formulated assuming that the only contribution to the Gibbs free energy of mixing is the entropy of random mixing of Ca<sup>2+</sup> and Na<sup>+</sup> on the cation sites (site fractions X<sub>Ca</sub> and X<sub>Na</sub>) and independent simultaneous mixing of Si<sup>4+</sup> and Al<sup>3+</sup> on the tetrahedral framework sites (i.e., complete disordering), with site fractions X<sub>Si</sub> and X<sub>Al</sub>. The configurational entropy of mixing of mole fractions X<sub>Me</sub> and 1 - X<sub>Me</sub> is

$$\begin{aligned} \Delta S_{\text{conf}} = & -4R(X_{\text{Ca}} \ln X_{\text{Ca}} + X_{\text{Na}} \ln X_{\text{Na}}) \\ & -12R(X_{\text{Al}} \ln X_{\text{Al}} + X_{\text{Si}} \ln X_{\text{Si}}) \\ & +12R(X_{\text{Me}})(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2}) \\ & +12R(1 - X_{\text{Me}})(\frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4}) \\ & +4R(1 - X_{\text{Me}})(\frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4}). \end{aligned}$$

The first term on the right side expresses the mixing of Na and Ca. The second term accounts for Al and Si mixing. The third term subtracts the Al and Si mixing in the meionite end-member. The fourth term subtracts the Al and Si mixing in the sodium meionite end-member, and the fifth term subtracts the Na and Ca mixing in the sodium meionite end-member.

The site fractions may be converted to functions of the mole fraction of meionite by the following expressions:

$$\begin{aligned} X_{\text{Ca}} &= \frac{3X_{\text{Me}} + 1}{4} \\ X_{\text{Na}} &= \frac{3(1 - X_{\text{Me}})}{4} \\ X_{\text{Al}} &= \frac{X_{\text{Me}} + 1}{4} \\ X_{\text{Si}} &= \frac{3 - X_{\text{Me}}}{4} \end{aligned}$$

If all terms that can be written with a prefix factor  $X_{\text{Me}}$  are segregated from those that can be factored by  $(1 - X_{\text{Me}})$ , the configurational entropy expression becomes

$$\begin{aligned} \Delta S_{\text{conf}} &= -X_{\text{Me}}\text{R} \ln \left[ \left( \frac{3X_{\text{Me}} + 1}{4} \right)^4 \left( \frac{X_{\text{Me}} + 1}{4} \right)^6 \left( \frac{3 - X_{\text{Me}}}{4} \right)^6 \left( \frac{1}{2} \right)^{-12} \right] \\ &- (1 - X_{\text{Me}})\text{R} \ln \left[ \left( \frac{3X_{\text{Me}} + 1}{4} \right) \left( \frac{3 - 3X_{\text{Me}}}{4} \right)^3 \left( \frac{3 - X_{\text{Me}}}{4} \right)^9 \right. \\ &\quad \left. \left( \frac{X_{\text{Me}} + 1}{4} \right)^3 \left( \frac{3}{4} \right)^{-12} \left( \frac{1}{4} \right)^{-4} \right] \end{aligned}$$

The ideal (athermal) Gibbs free energy is therefore

$$\begin{aligned} \Delta G_{\text{conf}} &= -T\Delta S_{\text{conf}} \\ &= \text{RT}(X_{\text{Me}})\ln \left[ \frac{(3X_{\text{Me}} + 1)^4 (X_{\text{Me}} + 1)^6 (3 - X_{\text{Me}})^6}{4^{10}} \right] \\ &+ \text{RT}(1 - X_{\text{Me}})\ln \left[ \frac{(3X_{\text{Me}} + 1)(1 - X_{\text{Me}})^3 (3 - X_{\text{Me}})^9}{3^9} \right] \end{aligned}$$

The first term in square brackets may be identified with the ideal ion-site activity of meionite,  $a_{\text{Me}}^{\text{id}}$ , and the second term in square brackets with  $a_{\text{Na-Me}}^{\text{id}}$ .

An apparent inconsistency in the activity expression for meionite is that the activity does not go to zero when the mole fraction  $X_{\text{Me}}$  is zero but assumes the value 0.0007. This is a consequence of the finite number of Ca-Al and Ca-Si linkages possible in the sodium meionite end-member. In order to satisfy the Gibbs-Duhem equation

$$(X_{\text{Me}}) \frac{d \ln a_{\text{Me}}}{dX_{\text{Me}}} + (1 - X_{\text{Me}}) \frac{d \ln a_{\text{Na-Me}}}{dX_{\text{Me}}} = 0$$

for the composition  $X_{\text{Me}} = 0$ ,  $(d \ln a_{\text{Na-Me}})/(dX_{\text{Me}})$  must go to zero, rather than remain finite, as is normal for end-member compositions. It may be verified that this condition is satisfied by the expression for  $a_{\text{Na-Me}}$ .