The heat capacity of a natural monticellite and phase equilibria in the system CaO-MgO-SiO$_2$-CO$_2$\footnote{Contribution No. 416 from the Thermodynamics Laboratory, Dept. of Chemistry, and the Mineralogical Laboratory, Dept. of Geological Sciences, University of Michigan.}

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Abstract—The heat capacity of a natural monticellite (Ca$_{0.98}$Mg$_{0.02}$Fe$_{0.02}$Mn$_{0.001}$Si$_{6.99}$O$_{18}$) measured between 9.6 and 343 K using intermittent-heating, adiabatic calorimetry yields $C''_p(298)$ and $S''_p$ of 123.64 ± 0.18 and 109.44 ± 0.16 J mol$^{-1}$ K$^{-1}$ respectively. Extrapolation of this entropy value to end-member monticellite results in an $S''_p$ = 108.1 ± 0.2 J mol$^{-1}$ K$^{-1}$. High-temperature heat-capacity data were measured between 340-1000 K with a differential scanning calorimeter. The high-temperature data were combined with the 290-350 K adiabatic values, extrapolated to 1700 K, and integrated to yield the following entropy equation for end-member monticellite (298-1700 K):

$$S''_p (J \text{ mol}^{-1} \text{ K}^{-1}) = S''_{98} + 164.79 \ln T + 15.337 \cdot 10^{-3} T - 22.791 \cdot 10^{-5} T^{-2} - 968.94$$

Phase equilibria in the CaO-MgO-SiO$_2$ system were calculated from 973 to 1673 K and 0 to 12 kbar with these new data combined with existing data for akermanite (Ak), diopside (Di), forsterite (Fo), merwinite (Me) and wollastonite (Wo). The location of the calculated reactions involving the phases Mo and Fo is affected by their mutual solid solution. A best fit of the thermodynamically generated curves to all experiments is made when the $S'_{98}$ of Me is 250.2 J mol$^{-1}$ K$^{-1}$, less than the measured value of 253.2 J mol$^{-1}$ K$^{-1}$. A best fit to the reversals for the solid-solid and decarbonation reactions in the CaO-MgO-SiO$_2$-CO$_2$ system was obtained with the $\Delta G_{98}$ (kJ mol$^{-1}$) for the phases Ak (-3667), Di (-3025), Fo (-2051), Me (-4317) and Mo (-2133). The two invariant points - Wo and -Fo for the solid-solid reactions are located at 1008 ± 5 K and 6.3 ± 0.1 kbar, and 1361 ± 10 K and 10.2 ± 0.2 kbar respectively. The location of the thermodynamically generated curves is in excellent agreement with most experimental data on decarbonation equilibria involving these phases.

INTRODUCTION

Bowen (1940) proposed ten decarbonation reactions in the system CaO-MgO-SiO$_2$-CO$_2$-H$_2$O characteristic of progressive metamorphism, which give rise to a petrogenetic grid in pressure-temperature space. Phase relations in the system CaO-MgO-SiO$_2$-X(CO$_2$) have since been carefully determined by experimental reversals at moderate pressures and temperatures. Unfortunately, efforts to match thermodynamically generated curves for the solid-solid reactions to the experimental reversals have not been entirely successful (Helgeson et al., 1978; Valley and Essene, 1980), and thermodynamic arguments suggest that the experimental reversals for the decarbonation reactions must be in error (Turner, 1968). Valley and Essene (1980) fit thermodynamically derived curves to the experimental reversals for the following reactions:

$$\text{CaMgSi}_2\text{O}_6 + 3\text{CaMgSi}_2\text{O}_4 \rightarrow \text{Ca}_2\text{MgSi}_3\text{O}_8 + \text{MgSi}_2\text{O}_4$$

(1)

$$\text{Ca}_2\text{SiO}_3 + 2\text{CaMgSi}_2\text{O}_4 \rightarrow \text{CaMgSi}_2\text{O}_6 + \text{Ca}_3\text{MgSi}_2\text{O}_8$$

(2)

$$\text{Ca}_2\text{MgSi}_2\text{O}_7 + 3\text{CaMgSi}_2\text{O}_4 \rightarrow \text{CaMgSi}_2\text{O}_6 + \text{Ca}_3\text{MgSi}_2\text{O}_8$$

(3)

$$2\text{CaMgSi}_2\text{O}_7 \rightarrow \text{Ca}_2\text{MgSi}_3\text{O}_8 + \text{MgSi}_2\text{O}_4$$

(4)

$$3\text{CaMgSi}_2\text{O}_4 \rightarrow \text{Ca}_2\text{MgSi}_3\text{O}_8 + \text{MgSi}_2\text{O}_4$$

(5)

Experiments on reactions (2) and (4) could not be fit with available thermodynamic data for the end-member phases. Valley and Essene (1980) and Brousse et al. (1984) concluded that there must be errors in the entropies of monticellite and either merwinite or akermanite, assuming the reversed experiments are valid. At the time of these studies, the heat capacities of merwinite and akermanite had only been measured down to 50 K (Weller and Kelley, 1963), whereas the...
heat capacity of monticellite was unmeasured. VALLEY and ESSENE (1980) used the value \( \frac{1}{2} S(\text{forsterite}) + \frac{1}{2} S(\text{calcium-olivine}) \) as their entropy estimate for monticellite. More recently, the heat capacity of akermanite has been measured between 9 and 1000 K (HEMINGWAY et al., 1986) yielding an entropy 3.4 J mol\(^{-1} \) K\(^{-1} \) higher than WELLER and KELLEY's (1963) estimate at 298 K.

VALLEY and ESSENE analyzed YODER's (1968) run products for reaction (4) in order to evaluate the degree of solid solution and found all phases to be stoichiometric within analytical error. The experiments of SCHAIER et al. (1967) on the binary joins between akermanite and monticellite, forsterite, wollastonite, merwinite and diopside indicate that none of these phases has more than 1% solubility in akermanite. On the other hand, monticellite and forsterite exhibit significant mutual solid solution at high temperatures (BIGGAR and O'HARA, 1969; YANG, 1973; WARNER and LUTH, 1973; ADAMS and BISHOP, 1985), which potentially affects equilibrium reversals involving these phases. In order to refine phase relationships in the system CaO-MgO-SiO\(_2\), the volume and heat capacity of a natural monticellite were measured, and corrected for minor element substitution. The run products of YODER (1968) were analyzed to determine the degree of solid solution in akermanite, diopside, forsterite, merwinite and monticellite. With a measured entropy for monticellite, possible errors in the entropy of merwinite can be evaluated by fitting the thermodynamically generated curves to the experiments corrected for solid solutions.

**MATERIALS**

Ten grams of clear, glassy monticellite from Cascade Slide, NY (VALLEY and ESSENE, 1980) were separated for analysis. Chemical composition was determined with a fully automated CAMECA CAMEBAX microprobe at The University of Michigan (Table 1). The unit-cell volume of the natural material was determined by powder X-ray diffraction at \( \frac{4}{5} \) \(^{2}\theta \) with quartz as an internal standard. A least-squares fit of the observed \( d \) values of unambiguously indexed peaks (Table 2) yielded the lattice parameters given in Table 3. The molar volume of end-member monticellite was calculated assuming a linear variation between the composition and molar volumes for the phases kirschsteinite, calcium olivine and tephroite (Table 4). The monticellite sample was presumed to be free of vacancies (cf. BROWN, 1982) and the analysis was normalized to two octahedral cations. The following equation was solved to obtain the molar volume of pure monticellite:

\[
\text{Ca}_{0.97}\text{Mg}_{0.03}\text{Fe}_{0.02}\text{Mn}_{0.00}\text{SiO}_4 = 0.907\text{CaMgSiO}_4
\]

**HEAT CAPACITY AND ENTROPY OF MONTICELLITE**

The heat capacity of monticellite was measured between 9 and 350 K in the laboratory of E. F. Westrum, Jr. at the University of Michigan with a low-temperature, intermittent-heating, adiabatic calorimeter. Details of the procedure can be found in WESTRUM et al. (1986) and WESTRUM (1984). The data (Table 5) plot as a smooth sigmoid curve with some scatter between 9 and 11 K. The data were extrapolated below 12 K from a \( C_p/T \) vs. \( T^2 \) plot. Any magnetic transitions below 12 K due to Fe and Mn substituting for Mg were not considered. The smoothed and integrated data correspond to an entropy at 298.15 K of 109.44 \( \pm \) 0.16 J mol\(^{-1} \) K\(^{-1} \) (Table 6).
The entropy of end-member monticellite was calculated with a procedure analogous to that for molar volume. Entropy data for kirschsteinite are not available, so the entropy of fayalite and calcium-olivine was substituted for kirschsteinite.

A linear variation in entropy with composition between natural and end-member monticellite and the phases calcium olivine, tephroite, and fayalite was assumed (Table 4). The magnetic entropy contribution to monticellite was smoothed with a procedure analogous to that for molar volume. Entropy data were extended to 1700 K using an equation for the entropy of end-member monticellite as a function of temperature was calculated by the same procedure of HEMINGWAY et al. (1981). The following equations:

\[
C_p(J/mol \cdot K) = 231.404 - 8.53144 \times 10^{-4}T^3
\]

\[
S_{298}^\circ = 108.1 \pm 0.2 \text{ J/mol} \cdot \text{K}
\]

were subtracted from the S's of these phases as the equivalent transition contribution to the entropies of fayalite and tephroite.

For the S's determination, using compatible entropy coefficients for the phases calcium olivine, tephroite and fayalite (Table 4). The following equations:

\[
S(J/mol \cdot K) = 356.9 \text{ J/mol} \cdot \text{K}^{-1}
\]

\[
S(J/mol \cdot K) = 356.9 \text{ J/mol} \cdot \text{K}^{-1}
\]

\[
S(J/mol \cdot K) = 356.9 \text{ J/mol} \cdot \text{K}^{-1}
\]

were fit to the data:

\[
S(J/mol \cdot K) = 356.9 \text{ J/mol} \cdot \text{K}^{-1}
\]

\[
S(J/mol \cdot K) = 356.9 \text{ J/mol} \cdot \text{K}^{-1}
\]

\[
S(J/mol \cdot K) = 356.9 \text{ J/mol} \cdot \text{K}^{-1}
\]

An equation for the entropy of end-member monticellite as a function of temperature was calculated by the same procedure for the S's determination, using compatible entropy coefficients for the phases calcium olivine, tephroite and fayalite (Table 4). Entropy data were extended to 1700 K using the empirical prediction method of ROBINSON and HAAS (1983) constrained by the measured entropy data below 1000 K. High temperature entropy estimates using mineral summation techniques are within 1.5 J/mol \cdot K using the following equations:

\[
S(J/mol \cdot K) = 356.9 \text{ J/mol} \cdot \text{K}^{-1}
\]

\[
S(J/mol \cdot K) = 356.9 \text{ J/mol} \cdot \text{K}^{-1}
\]

\[
S(J/mol \cdot K) = 356.9 \text{ J/mol} \cdot \text{K}^{-1}
\]

With new data on the entropy of monticellite, we attempted to fit the calculated curves for reactions (1-5) and the decarbonation reactions:

\[
MgSiO_4 + 2CaCO_3 + CaMgSiO_4 = 3CaMgSiO_4 + 2CO_2
\]
Table 5. Experimental low temperature molar heat capacity measurements on natural monticellite

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Capacity (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>1.323</td>
</tr>
<tr>
<td>298.25</td>
<td>1.325</td>
</tr>
<tr>
<td>298.35</td>
<td>1.327</td>
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</table>

Table 6. Molar thermodynamic properties of natural monticellite

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Capacity (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>0.349</td>
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<tr>
<td>1201</td>
<td>0.351</td>
</tr>
<tr>
<td>1202</td>
<td>0.353</td>
</tr>
</tbody>
</table>

Table 7. Experimental high temperature molar heat capacity measurements on natural monticellite

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Capacity (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.342</td>
</tr>
<tr>
<td>301</td>
<td>0.344</td>
</tr>
<tr>
<td>302</td>
<td>0.346</td>
</tr>
</tbody>
</table>

Table 8. Experimental high temperature molar heat capacity measurements on natural monticellite

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Capacity (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.342</td>
</tr>
<tr>
<td>301</td>
<td>0.344</td>
</tr>
<tr>
<td>302</td>
<td>0.346</td>
</tr>
</tbody>
</table>

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CaMgSiO₃ + CO₂ = Ca₂MgSi₂O₆ + CO₂

MgSiO₃ + CaCO₃ = CaMgSi₂O₆ + CO₂

Mg₂SiO₄ + CO₂ = CaMgSi₂O₆ + CO₂

to the experimental data. Reactions (2, 5, 11, 13, 14) include the phases forsterite and monticellite which display significant mutual solid solution. The location of the end-member curves determined from the experimental reversals corrected for solid solution can be estimated with the mixing parameters of ADAMS and BISHOP (1985). Their reversed experiments on the join Mg₂SiO₄-CaMgSiO₃ show that the miscibility gap
between forsterite and monticellite is independent of pressure and is asymmetric, with the monticellite limb displaying greater solid solution. Activities of monticellite and forsterite at various temperatures were calculated from the one-site asymmetric solution model of ADAMS and BISHOP (1985). At the temperatures of Yoder's experiments (Fig. 2) for reactions (2) and (5), the amount of solid solution predicted by ADAMS and BISHOP's model (e.g. $\alpha_{MC} = 0.92, \alpha_{Fo} = 0.96$ at 1500 K) shifts the experimental reversals significantly relative to end-member monticellite and forsterite.

The degree of solid solution for the phases akermanite and diopside in the CaO-MgO-SiO$_2$ system should be minimal (KUSHIRO and SCHAIRER, 1964; SCHAIRER et al., 1967; VALLEY and ESSENE, 1980). Since the knowledge of the solid solutions is critical for proper location of the end-member reaction curves, Dr. Yoder has kindly provided the run-products of reactions (2) and (5) for analysis. The X-ray analysis of monticellite synthesized with forsterite at 1350°C and 8 kbar (Table 2) corresponds to a completely ordered olivine of composition $Mg_{89}Fo_{11}$ using the a-b plot for Ca-Mg olivines of LUMPKIN et al. (1983). Compositions of the same sample determined by electron microprobe analyses range from $Mg_{92.85}$ (Table 9). The composition expected from the model of ADAMS and BISHOP (1985) is $Mg_{89}Fo_{11}$, in agreement with the compositions of Yoder's run products. Microprobe analyses of monticellites synthesized at lower temperatures give a much wider range of compositions. A monticellite synthesized at 975°C and 5 kbar by YODER (1968), has an apparent compositional range of $Mg_{6}Fo_{4}$ (Table 9). Back-scattered electron imaging of this monticellite shows it to contain many blebs of forsterite and some akermanite. The most monticellite-rich analysis of this sample ($Mg_{89}Fo_{11}$) corresponds precisely with the composition predicted by the Margules parameters and X-ray determinative methods of
FIG. 2. Pressure-temperature diagram for reactions (1) through (5) for end-member phases. Reversed brackets for reactions (2) and (5) are corrected for solid solution. The univariant points — Fo and — Wo are located at 735°C (1008 K) and 6.3 kbar and 1088°C (1361 K) and 10.2 kbar respectively. Reversals are from the following sources: Wo + Mo = Ak (Harker and Tuttle, 1956; Yoder, 1968); Mo + Di = Fo + Ak (Walter, 1963a; Yoder, 1968); Mo = Me + Fo (Yoder, 1968); Di + Me = Wo + Mo (Yoder, 1968). Abbreviations used (as in all tables) are: Ak = akermanite, Ca = calcite, Di = diopside, Fo = forsterite, Me = merwinite, Mo = monticellite, Pe = periclase, Wo = wollastonite. The reversal directly above the univariant point — Wo is for the reaction Di + Mo = Fo + Ak.

ADAMS and BISHOP (1985). Analyses with greater apparent solid solution are likely due to contamination by the small forsterite inclusions. Alternatively, the variation observed in the microprobe analyses may be caused by metastable reaction products in experiments run at lower temperature and pressure.

YODER (1973, 1975) suggested that akermanite may exhibit solid solution with other phases in the CaO-MgO-SiO$_2$ system. Analyses of akermanite from run products show a consistent enrichment in Mg relative to Ca (Table 9), but a constant (Ca + Mg)/Si ratio of 3/2 indicating no detectable solid solution toward olivine. Merwinite analyses show solid solution toward forsterite with an Mg/(Ca + Mg) ratio of 0.26 (vs. 0.25 for ideal merwinite), but the (Ca + Mg)/Si ratio of 2 suggests that merwinite has no solid solution off the Ca$_2$SiO$_4$-Mg$_2$SiO$_4$ join. Diopside coexisting with forsterite and monticellite may show some solid solution toward enstatite at high temperatures. The diopside analysis (Table 9) is deficient in silica, but monticellite analyzed in the same sample also shows a deficiency in silica, indicating possible analytical errors for silicon. Experiments on the akermanite-diopside join show very slight solid solution of diopside toward akermanite at 1300°C (Kushiro and Schairer, 1964), supported by VALLEY and ESSENE’S (1980) analysis of diopside coexisting with akermanite from the experimental run products of Yoder (1968). This solid solution requires a vacancy related substitution that is not well understood. For the purposes of this paper only the following solid solution effects involving Mg-Ca substitutions will be considered:

1) Monticellite and forsterite exhibit mutual solid solution as defined by ADAMS and BISHOP (1985);
2) Akermanite shows ~2% Mg/Ca enrichment, but maintains a stoichiometric (Ca + Mg)/Si ratio of 3/2;
3) Merwinite shows 3-4% solid solution toward forsterite, but maintains a (Ca + Mg)/Si ratio of 2.
4) Diopside shows slight solid solution toward enstatite [Mg/(Ca + Mg)] and may also lie off the diopside-enstatite join toward akermanite.

For reaction (2) the shift due to solid solution can be evaluated from the equation

$$
\Delta G^\circ_P - \Delta G^\circ_P = \int_{T_1}^{T_2} \frac{\Delta H}{T} dT + R \ln \left( \frac{d_\text{ak}}{d_{\text{fo, ak}}} \right) \left( \frac{d_{\text{fo, mo}}}{d_{\text{mo, ak}}} \right) \ . \ (16)
$$

| reactant | product | reaction
|----------|---------|---------|
| Si | O | SiO$_2$
| Mg | Me | Mg$_2$SiO$_4$
| Ca | Mo | Ca$_2$SiO$_4$
| O | Me | Mg$_2$SiO$_4$

The shift in the other reactions due to solid solution can be estimated with similar equations. Akermanite, merwinite and diopside activities are taken as atom fraction over all octahedral sites. For reactions (2) and (4), the effects of solid solution for akermanite, merwinite and diopside tend to cancel each other and the net shift for both reactions is less than 0.1 kbar. For reaction (5), the solid solution between monticellite, forsterite and merwinite places the theoretical endmember reversal brackets at significantly higher pressures (2 kbar at 1400°C).

The effect of solid solution for the location of the decarbonation reaction reversals is very small at the temperature of the experiments. With the constraints of the reversal brackets corrected for solid solution, the P-T location of reactions (1-5) for the ideal phases was calculated with the aid of the computer program EQUIL1 (WALL and ESSENE, unpublished) from the relation

$$\Delta G_{T1} - \Delta G_{T1} = \int_{T1}^{T2} \Delta V dP - \int_{T1}^{T2} \Delta S dT. \quad (17)$$

Data for all phases are given in Table 10. The two solid-solution invariant points, forsterite-absent (Fo) and wollastonite-absent (Wo) in Fig. 2 are located at 1008 ± 5 K and 6.3 ± 0.1 kbar and 1361 ± 10 K and 10.2 ± 0.2 kbar respectively. The entropies of solid-solid reaction invariant points, forsterite-absent (Fo) and wollastonite-absent (Wo) in Fig. 2 are located at 1008 ± 5 K and 6.3 ± 0.1 kbar and 1361 ± 10 K and 10.2 ± 0.2 kbar respectively. The entropies of all phases considered are now well-known except for merwinite, which has only been measured down to 5 K (WELLER and KELLEY, 1963). The entropy estimate of WELLER and KELLEY for merwinite results in a poor fit of the generated curves to the experimental reversals.

The best fit for reactions (1-5, 11-15) in the experimental reversals and the ΔG°98 of each phase was determined in the following way:

1) The ΔG°98 was calculated for each reaction (1-5, 11-15) from the reversals at high P-T. For the decarbonation reactions, using the modified Redlich-Kwong model of KERRICK and JACOBS (1981) for H2O-CO2 mixing, the experiments with pure CO2 and at low pressures are inconsistent with the experiments with H2O-CO2 mixtures at 1 kbar.

2) Simultaneous calculation does not yield a unique solution for the ΔG°98 of each phase. The ΔG°98 of CO2, calcite, periclase and wollastonite were assumed to be correct (ROBINSON et al., 1982; TREIMAN and ESSENE, 1983), and with these data the ΔG°98 of the remaining phases were calculated.

The best fit for reactions (1-5, 11-15) is shown in Figs. 2-4 using the thermodynamic data in Table 10. The free energy of monticellite (ΔG°98) is calculated as -2133 kJ mol⁻¹, significantly less than previously re-

### Table 10. Thermodynamic data of minerals used in EQUIL1.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Volume and entropy: (V;98 in cm³/mol)</th>
<th>ΔS°98 in J/(mol K)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>ΔG°98 ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Akermanite</td>
<td>92.82 (1)</td>
<td>212.5 242.59 55.184 20.521 -1491.43 (1)</td>
<td>366.7 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>36.42 (18)</td>
<td>91.75 102.91 23.435 12.711 -667.06 (5)</td>
<td>113.2 (20)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forsterite</td>
<td>40.56 (13)</td>
<td>180.17 209.95 32.982 19.643 -361.26 (4)</td>
<td>83.2 (25)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Merwinite</td>
<td>93.46 (7)</td>
<td>250.20 317.06 48.499 31.054 -1798.99 (2)</td>
<td>417 (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monticellite</td>
<td>51.48 (17)</td>
<td>108.31 164.79 15.335 22.791 -605.87 (5)</td>
<td>2133 (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Expansion and Compressibility: (a,b,c) in 10⁻¹⁰ cm²/molecule |
|-----------------|-----------------|-----------------|-----------------|
| a×10⁻¹⁰ | b×10⁻¹⁰ | c×10⁻¹⁰ | a×10⁻¹⁰ ref. |
| Akermanite | -0.639 | 1.221 | -2133.8 | 0.785 | -4316.9 |
| Calcite    | -2.174 | 0.587 | -2133.8 | 1.367 | 3.8 (11) |
| Diopside  | 5.355 | 4.005 | -2133.8 | 1.367 | 3.8 (11) |
| Forsterite | 0.589 | 2.348 | -2133.8 | 1.367 | 3.8 (11) |
| Merwinite | 6.387 | 5.245 | -2133.8 | 1.367 | 3.8 (11) |
| Monticellite | 6.961 | 2.759 | -2133.8 | 1.367 | 3.8 (11) |
| Wollastonite | 11.18 | 5.008 | -2133.8 | 1.367 | 3.8 (11) |

(1) Henningway et al., 1985 (valid above 357.9 K); (2) Hotte et al., 1986; (3) Gareau and Proulx, 1984; (4) Truempy et al., 1986; (5) Roberts et al., 1982; (6) Moore and Araki, 1973; (7) This study; (8) Skinner, 1966; (9) Enthele data from Robinson et al., 1982; (10) Cameron et al., 1975; (11) Birch, 1966; (12) Hase and Finger, 1981; (13) Lager and Weinberg, 1976; (14) 1/2 forsterite, 1/2 calcium-diopside; (15) Nesen, 1976; (16) Hotte et al., 1982b; (17) Vajda et al., 1973; (18) Markgraf and Keeder, 1985; (19) Used value for diopside; (20) Treiman and Essene, 1983.
The apparent reversals for reactions for these curves indicate that reaction (Figs. 2-4) except for reactions (14) and (15) (Fig. 4). lent agreement with all of the experimental reversals yield accurate results. must be combined with the experimental reversals to significant error in the location of a reaction curve. For of just 0.2% in the enthalpy of a phase can result in a solid-solid reactions with enthalpy data alone. An error (5) is located 2.5 kbar higher than the best fit location (at 1200°C using the enthalpy data of BROUSSE ef al. 1984). This illustrates the uncertainties in locating a reaction curve. Reversals are from ZHARIKOV et al. 1977. Reaction numbers are as follows: (2) Di + Mo = Fo + Ak, (11) Fo + Di + Cc = Mo + CO2, (12) Di + Cc = Ak + CO2, (13) Ak + Fo + Cc = Mo + CO2, (14) Fo + Cc = Mo + Pe + CO2, (15) Ak + Cc = Me + CO2. See Fig. 2 for abbreviations.

The locations of the univariant reactions (1-5, 11-15), calculated from the data in Table 10 are in excellent agreement with all of the experimental reversals (Figs. 2-4) except for reactions (14) and (15) (Fig. 4). The apparent reversals for reactions (11-14) (WALTER, 1963a,b) nearly coincide, while the calculated positions for these curves indicate that reaction (14) must lie at higher temperatures than the other three (Fig. 4). This same conclusion was reached by TURNER (1968, p. 135) on the basis of the natural occurrences and thermodynamic calculations.

Phase equilibria in the system CaO-MgO-SiO2-CO2 are pertinent to calc-silicates metamorphosed at high temperatures and low pressures. Monticellite, akermanite, merwinite, and monticellite + periclase are all stable in the pyroxene-hornfels facies. Their stability is controlled primarily by /ICO2) and they provide far better CO2 barometers than thermometers.

Although there are many reports of high-temperature Ca-Mg silicates, few authors have systematically described the sequence of high-temperature assemblages around a contact aureole. JOESTEN (1974, 1976) reports assemblages of Ca- and Ca-Mg silicates in a limestone sequence intruded by a high-level gabbro. He infers temperatures of 900-1000°C based on phase equilibria involving calc-silicates (see also TREIMAN and ESSENE, 1983). JOESTEN (1976) reports a melilite (.A.K)-Cc-Me assemblage which is buffered by reaction (15) for a given a(AK) and f(CO2). He also reports spurrite-rankinite-wollastonite in skarns. These two assemblages may indicate skarn formation at water-rich conditions (X(H2O) = 0.8-0.95) and lower temperatures (850-900°C) than inferred by JOESTEN. These water-rich conditions are also expected for the formation of vesuvianite (VALLEY et al., 1985) which is widespread in the skarn studied by JOESTEN. Independent thermometry is needed before more precise fluid compositions can be reliably obtained.

BOWEN (1940) estimated the relative abundance of phases in the system CaO-MgO-SiO2-CO2 by correlating the abundance of each mineral to its year of discovery. Diopside was named in 1806, wollastonite in 1822, forsterite in 1824, monticellite in 1831, akermanite in 1884 and merwinite in 1921, and the low-temperature enthalpy for each of these phases has to date been measured in the same order. Merwinite was the last named and it remains the only one in this
group that does not have low-temperature calorimetry measurements.

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REFERENCES


BOWEN N. L. (1940) Progressive metamorphism of siliceous limestones and dolomite. J. Geol. 48, 225-274.


ROBIE R. A., HEMINGWAY B. S. and TAKEI H. (1982b) Heat capacities and entropies of Mg$_2$SiO$_4$, Mg$_2$Si$_2$O$_5$, and Co$_2$SiO$_4$ between 5 and 380 K. Amer. Mineral. 67, 470-482.


mophysical properties of selected phases in the MgO-SiO$_2$-H$_2$O-CO$_2$, CaO-Al$_2$O$_3$SiO$_2$-H$_2$O-CO$_2$, and Fe-FeO-Fe$_2$O$_3$-SiO$_2$ chemical systems, with special emphasis on the properties of basahs and their mineral components. U. S. Geol. Surv. Open-File Rept. 83-79, 429 p.


