AN Experimental Model for Low Pressure Metamorphism of Siliceous Dolomitic Marble

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ABSTRACT. Stable phase relations are derived for temperatures from 350° to 650°C and pressures from 500 to 3000 bars among the minerals, quartz, calcite, dolomite, talc, tremolite, diopside, forsterite, enstatite. The following assemblages are stable among these 8 minerals in the system, CaO-MgO-SiO₂-CO₂-H₂O: (1) talc-tremolite-quartz-calcite-dolomite; (2) tremolite-diopside-quartz-calcite-dolomite; (3) forsterite-tremolite-diopside-calcite-dolomite; (4) forsterite-talc-tremolite-calcite-dolomite; (5) enstatite-tremolite-diopside-quartz-dolomite; (6) enstatite-talc-tremolite-quartz-dolomite; (7) enstatite-forsterite-tremolite-diopside-dolomite; (8) enstatite-forsterite-talc-tremolite-dolomite. Assemblage 4 from this list is stable only at very high water fugacities and is not normally encountered in regional metamorphism.

Phase relations affecting bulk compositions in the triangle quartz-calcite-dolomite are shown on T-X_{CO₂} sections with the activities of CaCO₃ and MgCO₃ determined by the calcite-dolomite miscibility gap. The T-X_{CO₂} sections indicate that the Bowen-Tilley sequence of index minerals (that is, talc-tremolite-forsterite-diopside-wollastonite) can develop at pressures above approximately 3 kb in fluids with a high CO₂ content. At pressures less than 3 kb, diopside should normally develop before forsterite.

THE METAMORPHISM OF SILICEOUS DOLOMITIC MARBLE

The first comprehensive study of the metamorphism of siliceous carbonates was undertaken by Bowen (1940), who assumed that the progressive metamorphism of siliceous dolomite is a process of decarbonation. By considering the sequence of joins broken in moving away from the CO₂ apex in the system CaO-MgO-SiO₂-CO₂, he was able to suggest that index minerals should appear in the following sequence:

1. tremolite
2. forsterite
3. diopside
4. periclase
5. wollastonite
6. monticellite
7. akermanite
8. spurrite
9. merwinite
10. larnite

This list was revised by Tilley (1948 and 1951) to include talc as the first mineral formed and tilleyite and rankinite among the higher temperature phases. Korzhinskii (1959) used isothermal, isobaric chemical potential diagrams to describe parageneses in carbonates. This work demonstrated that it was impossible to predict a unique sequence of minerals with increasing metamorphic grade, unless the composition of the fluid was considered in addition to total pressure and temperature.

Wyllie (1962) and Greenwood (1967b) have represented the stability of carbonate assemblages on isobaric plots of temperature against the mole fraction of carbon dioxide in the fluid phase. The gas composition-temperature diagrams have the advantage of displaying simultaneously the effect of temperature and fluid composition on carbonate parageneses.
Metz and Trommsdorff (1968) have considered portions of the T-X_{CO_2} diagrams for carbonates. This paper extends this approach to the seven minerals most frequently encountered in the regional metamorphism of siliceous dolomitic limestone, that is, quartz, calcite, dolomite, talc, tremolite, diopside, forsterite. In addition to these 7 minerals, enstatite is included in the following analysis because some of the experimental data to be used involve enstatite as well as the seven minerals of primary interest. The graphical relationships among the compositions of these eight minerals are shown on figure 1.

**NOTATION AND DEFINITIONS**

\( ^oG \) standard Gibbs free energy of formation  
\( X \) mole fraction  
\( f \) fugacity  
\( a \) activity  
\( \gamma \) activity or fugacity coefficient  
\( R \) gas constant  
\( T \) temperature in degrees Kelvin  
\( P \) pressure in bars  
\( K \) the equilibrium constant  
\( \mu \) the chemical potential  
\( \nu \) the stoichiometric coefficient

Phases are indicated by superscripts, and components by subscripts. Symbols for phases begin with capital letters, and symbols for components with lower case letters.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q α quartz</td>
<td>q SiO(_2)</td>
</tr>
<tr>
<td>Cc calcite</td>
<td>cc CaCO(_3)</td>
</tr>
<tr>
<td>Do dolomite</td>
<td>do CaMg(CO(_3))(_2)</td>
</tr>
<tr>
<td>M magnesite</td>
<td>m MgCO(_3)</td>
</tr>
<tr>
<td>Tc talc</td>
<td>tc Mg(_5)Si(<em>4)O(</em>{10})(OH)(_2)</td>
</tr>
<tr>
<td>Tr tremolite</td>
<td>tr Ca(_2)Mg(_5)Si(<em>6)O(</em>{22})(OH)(_2)</td>
</tr>
<tr>
<td>Di diopside</td>
<td>di CaMgSi(_2)O(_6)</td>
</tr>
<tr>
<td>Fo forsterite</td>
<td>fo Mg(_2)SiO(_4)</td>
</tr>
<tr>
<td>En orthoenstatite</td>
<td>en MgSiO(_3)</td>
</tr>
<tr>
<td>Fl fluid</td>
<td>CO(_2) H(_2)O</td>
</tr>
</tbody>
</table>

Standard states for Gibbs free energy are defined as:

CO\(_2\) and H\(_2\)O: the ideal gas at 1 bar of pressure and the temperature of interest.

Silicates and carbonate: the pure mineral at 2000 bars of pressure and the temperature of interest. The minerals taken to define the standard states are those listed above.

Molar volumes: molar volumes for all phases except orthoenstatite were taken from Robie and Waldbaum (1968). The molar volume of orthoenstatite was taken from Greenwood (1963).
EQUILIBRIA AMONG ASSEMBLAGES OF FIVE MINERAL PHASES

A group of 8 mineral phases can be combined into 56 unique assemblages consisting of five mineral phases. Korzhinskii (1959) has described an analysis of these five-mineral assemblages and the associated three or four-mineral assemblages that can be used to distinguish between stable and metastable equilibria. In the present case, the graphical analysis described by Korzhinskii has been simplified by making use of the degeneracy of certain reactions which involve only solid phases. The reactions used are:

\[
\begin{align*}
2 \text{ enstatite} + 2 \text{ calcite} &= \text{ diopside} + \text{ dolomite} \\
\text{forsterite} + \text{ quartz} &= 2 \text{ enstatite} \\
\text{talc} + 2 \text{ diopside} &= \text{ tremolite}
\end{align*}
\]

These reactions are univariant in the system, CaO–MgO–SiO₂–H₂O–CO₂, and under isobaric conditions, an equilibrium is possible only at a unique temperature. All assemblages that include all phases of a solid-solid equilibrium must also be restricted to the unique temperature at which that solid-solid equilibrium is valid. If temperature and pressure are arbitrarily imposed, then an equilibrium is not, in general, possible, and any assemblage in the system, CaO–MgO–SiO₂–CO₂–H₂O, that contains all the phases of the solid-solid equilibrium is unstable. Under similarly arbitrary conditions, either the assemblage on the left hand side or else the assemblage on the right hand side must be metastable. Any assemblage that includes the metastable group of minerals will also be metastable if at equilibrium. In the present case, it is assumed that the assemblages on the left hand side of each reaction are metastable with respect to the right hand side.

The validity of these assumptions over the metamorphic temperature range is supported by failure to observe the assemblages of the left hand side in the field, by thermochemical data given by Robie and Wald-
baum (1968) and by experimental data described by Skippen (1971, p. 472, 474). Thus, any assemblage that includes enstatite + calcite or forsterite + quartz or talc + diopside is regarded as metastable. The significance of these metastable pairs in reducing the number of possibly stable five-mineral assemblages is most easily understood by labelling each five-mineral assemblage in terms of the three minerals absent rather than those present. Since three minerals must be excluded from each assemblage and there exist three metastable pairs, it is necessary that one mineral from each metastable pair exist in the label.

There are eight combinations that meet this requirement, as listed below:

Combinations involving one mineral from each metastable pair

1. (En, Fo, Di)
2. (En, Fo, Tc)
3. (En, Q, Tc)
4. (En, Q, Di)
5. (Cc, Fo, Tc)
6. (Cc, Fo, Di)
7. (Cc, Q, Tc)
8. (Cc, Q, Di)

Combinations rewritten in terms of minerals present.

1. talc–tremolite–quartz–calcite–dolomite
2. tremolite–diopside–quartz–calcite–dolomite
3. forsterite–tremolite–diopside–calcite–dolomite
4. forsterite–talc–tremolite–calcite–dolomite
5. enstatite–tremolite–diopside–quartz–dolomite
6. enstatite–talc–tremolite–quartz–dolomite
7. enstatite–forsterite–tremolite–diopside–dolomite
8. enstatite–forsterite–talc–tremolite–dolomite

The sequence of paragenesis diagrams about each five-mineral assemblage has been derived by the method of Schreinemakers for the case in which CaO, MgO, and SiO₂ are conserved in the reactions. The results are summarized in figure 2. The mineral reactions between each paragenesis diagram on figure 2 are indicated by numbers referring to the appropriate reaction in table 1. Reaction numbers used by Skippen (1971) are retained.

The position of each five-mineral assemblage on a fugacity plot has been calculated for 500°C and a total pressure of 2000 bars with carbonate activities determined by the calcite-dolomite miscibility gap. The results are shown on figure 3. The position of a point on figure 3 is obtained by simultaneous solution of two equilibrium curves from table 2 that intersect at the point. Those equilibria stable between points are also shown on figure 3. An inspection of figure 3 indicates that all of the eight, five-mineral assemblages are homotypical with regard to stability (see Korzhinskii, 1959, p. 131). If one assemblage is stable, then all must be stable if the system is limited to the minerals under consideration. Conversely, if one assemblage is metastable, then all must be metastable. It should be noted that the term, stable assemblage, refers
only to stability among the minerals under discussion. Consideration of additional minerals such as anthophyllite (Greenwood, 1963), antigorite, or brucite could alter the list of stable assemblages. The configuration of the points on figure 3 indicates that for the conditions of the diagram, all invariant assemblages are stable.

Fig. 2. Sequence of reactions around five-mineral assemblages. Mineral compositions are projected onto the triangle SiO₂–MgO–CaO with the SiO₂ apex at the top, MgO at the lower right, and CaO at the lower left. Those minerals absent from a five-mineral assemblage are indicated in parentheses. The numbers between triangles refer to reactions from table 1 and Skippen (1971).
THE CHOICE OF COMPONENTS

Skippen (1971) expressed equilibria applying to siliceous carbonates in terms of the components, CaCO₃ and CaMg(CO₃)₂. There are, however, reasons for preferring MgCO₃ to CaMg(CO₃)₂ as the magnesium-bearing component. CaMg(CO₃)₂ implies a molecular or coupled substitution of Ca + Mg. Substitution of cations in carbonates is more likely on an atom for atom basis, and activity coefficients will be closer to unity with MgCO₃ chosen as a component. Secondly, the choice of CaCO₃ and CaMg(CO₃)₂ does not permit magnesite to be considered as a possible phase without introducing negative amounts of components. A second set of equilibria can be written with, for example, CaMg(CO₃)₂ and MgCO₃ as components if magnesite is present. Alternatively, the choice of CaCO₃ and MgCO₃ as components allows the single set of equilibria given in table 2 to apply regardless of whether calcite or dolomite or magnesite is a carbonate phase in the rocks or experiments under consideration. Thus, the single set of equilibria makes it easier to compare equilibria observed in carbonate-bearing, metamorphosed ultramafic rocks with equilibria observed in siliceous carbonates and also to compare experimental data measured in the system MgO–SiO₂–H₂O–CO₂ with similar data measured in the system CaO–MgO–SiO₂–H₂O–CO₂. The availability (Gordon and Greenwood, 1970) of activity coefficient data for the component, MgCO₃, rather than CaMg(CO₃)₂ in calcite is

<table>
<thead>
<tr>
<th>Stable reactions among the phases, Fo, Di, Tr, Tc, En, Q, Cc, Do</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Tc = 3En + Q + H₂O</td>
</tr>
<tr>
<td>2. Tc + 3Cc + 2Q = 3Di + 3CO₂ + H₂O</td>
</tr>
<tr>
<td>3. Tr = 2Di + 3En + Q + H₂O</td>
</tr>
<tr>
<td>4. 3Do + 4Q + H₂O = Tc + 3Cc + 3CO₂</td>
</tr>
<tr>
<td>5. 4Tc + 5Do = 5Di + 6Fo + 10CO₂ + 4H₂O</td>
</tr>
<tr>
<td>6. Tr + 3Cc + 2Q = 5Di + 3CO₂ + H₂O</td>
</tr>
<tr>
<td>7. 5Tc + 6Cc + 4Q = 3Tr + 6CO₂ + 2H₂O</td>
</tr>
<tr>
<td>8. Do + 2Q = Di + 2CO₂</td>
</tr>
<tr>
<td>9. 2Tc + 3Cc = Tr + Do + CO₂ + H₂O</td>
</tr>
<tr>
<td>10. Tc + 2Do + 4Q = Tr + 4CO₂</td>
</tr>
<tr>
<td>11. 8Q + 5Do + H₂O = Tr + 3Cc + 7CO₂</td>
</tr>
<tr>
<td>12. Tr + 3Cc = 4Di + Do + CO₂ + H₂O</td>
</tr>
<tr>
<td>13. 5Tc + 2Do = Tr + 12En + 4CO₂ + 4H₂O</td>
</tr>
<tr>
<td>14. 2Do + 5Q + 3En + H₂O = Tr + 4CO₂</td>
</tr>
<tr>
<td>15. 2Tr + Do = 5Di + 6En + 2CO₂ + 2H₂O</td>
</tr>
<tr>
<td>16. Di + 3Do = 2Fo + 4Cc + 2CO₂</td>
</tr>
<tr>
<td>17. Tc + 5Do = 4Fo + 5Cc + 5CO₂ + H₂O</td>
</tr>
<tr>
<td>18. Tr + 11Do = 8Fo + 13Cc + 9CO₂ + H₂O</td>
</tr>
<tr>
<td>19. 5Tr + 5Cc = 11Di + 2Fo + 5CO₂ + 3H₂O</td>
</tr>
<tr>
<td>20. 4Tr + 5Do = 13Di + 6Fo + 10CO₂ + 4H₂O</td>
</tr>
<tr>
<td>21. 11Tc + 10Cc = 5Tr + 4Fo + 10CO₂ + 6H₂O</td>
</tr>
<tr>
<td>22. 6.5Tc + 5Do = 2.5Tr + 6Fo + 10CO₂ + 4H₂O</td>
</tr>
<tr>
<td>23. En + Do = Fo + Cc + CO₂</td>
</tr>
<tr>
<td>24. 13En + 2Do + H₂O = Tr + 5Fo + 4CO₂</td>
</tr>
<tr>
<td>25. Tr + Fo = 5En + 2Di + H₂O</td>
</tr>
<tr>
<td>26. 4En + Do = Di + 2Fo + 2CO₂</td>
</tr>
<tr>
<td>27. Tc + Fo = 5En + H₂O</td>
</tr>
</tbody>
</table>
Fig. 3. Fugacity plot at 500°C and 2000 bars showing the relationship among stable five-mineral assemblages. Numbers in circles refer to: (1) Tc Tr Q Cc Do; (2) Tr Di Q Cc Do; (3) Fo Tr Di Cc Do; (4) Fo Tc Tr Cc Do; (5) En Tr Di Q Do; (6) En Tc Tr Q Do; (7) En Fo Tr Di Do; (8) En Fo Tc Tr Do. Numbered lines refer to equilibria from figure 2 and table 2.

also a factor that encourages a redefinition of components. In the following three sections of the paper, a detailed explanation is given of the method used to recalculate equilibrium constants with CaCO₃ and MgCO₃ as components.

In considering the equilibria discussed subsequently, it is important to keep in mind the distinction between the reactions listed in table 1 and the equilibria listed in table 2. The reactions in table 1 refer to a specific set of phase relations, that is, those illustrated on figure 2, and state a mass balance that must exist if one set of phases with specified composition is to be converted to an alternative set of phases (see, for example, Greenwood, 1967a). The equilibria in table 2 do not refer to a specific set of phase relations but rather to an energy balance among components at equilibrium as expressed by the relationship,

\[ \sum_{i} v_i \mu_i = 0 \]
Table 2  
Equilibrium constants

<table>
<thead>
<tr>
<th>Number</th>
<th>Equilibrium</th>
<th>Equilibrium constant</th>
<th>Upper limit</th>
<th>Lower limit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>$tc = 3\ en + q + H_2O$</td>
<td>-7422</td>
<td>10.540</td>
<td>0.1014</td>
</tr>
<tr>
<td>2</td>
<td>$tc + 3\ cc + 2\ q = 3\ di + 3\ CO_2 + H_2O$</td>
<td>-12931</td>
<td>29.160</td>
<td>0.4918</td>
</tr>
<tr>
<td>3</td>
<td>$3\ m + 3\ q + H_2O = tc + 3\ CO_2$</td>
<td>-9677</td>
<td>9.390</td>
<td>0.1248</td>
</tr>
<tr>
<td>4</td>
<td>$3\ tc + 5\ m + 5\ cc = 5\ di + 6\ fo + 10\ CO_2 + 4\ H_2O$</td>
<td>-11592</td>
<td>24.634</td>
<td>0.2014</td>
</tr>
<tr>
<td>5</td>
<td>$tr + 3\ cc + 2\ q = 5\ di + 3\ CO_2 + H_2O$</td>
<td>-71995</td>
<td>132.405</td>
<td>1.4446</td>
</tr>
<tr>
<td>6</td>
<td>$5\ tc + 6\ cc + 4\ q = 3\ tr + 6\ CO_2 + 2\ H_2O$</td>
<td>-27197</td>
<td>61.950</td>
<td>0.9132</td>
</tr>
<tr>
<td>7</td>
<td>$m + 3\ cc + 2\ q = di + 2\ CO_2$</td>
<td>-5222</td>
<td>12.439</td>
<td>0.2573</td>
</tr>
<tr>
<td>8</td>
<td>$8\ q + 5\ m + 2\ cc + H_2O = tr + 7\ CO_2$</td>
<td>-16754</td>
<td>37.073</td>
<td>0.4587</td>
</tr>
<tr>
<td>9</td>
<td>$tr + 2\ cc = 4\ di + m + CO_2 + H_2O$</td>
<td>-28286</td>
<td>61.707</td>
<td>0.6401</td>
</tr>
<tr>
<td>10</td>
<td>$5\ tc + 2\ m + 2\ cc = tr + 12\ en + 4\ CO_2 + 4\ H_2O$</td>
<td>-46442</td>
<td>79.233</td>
<td>0.8442</td>
</tr>
<tr>
<td>11</td>
<td>$3\ en + 5\ q + 2\ m + 2\ cc + H_2O = tr + 4\ CO_2$</td>
<td>-9332</td>
<td>26.533</td>
<td>0.3573</td>
</tr>
<tr>
<td>12</td>
<td>$2\ tr + m + cc = 5\ di + 6\ en + 2\ CO_2 + 2\ H_2O$</td>
<td>-22108</td>
<td>56.391</td>
<td>0.4807</td>
</tr>
<tr>
<td>13</td>
<td>$di + 3\ m = 2\ fo + cc + 2\ CO_2$</td>
<td>-16792</td>
<td>29.163</td>
<td>0.1339</td>
</tr>
<tr>
<td>14</td>
<td>$tc + 5\ m = 4\ fo + 5\ CO_2 + H_2O$</td>
<td>-4536</td>
<td>69.556</td>
<td>0.5285</td>
</tr>
<tr>
<td>15</td>
<td>$tr + 11\ m = 8\ fo + 2\ cc + 9\ CO_2 + H_2O$</td>
<td>-74850</td>
<td>126.672</td>
<td>0.8197</td>
</tr>
<tr>
<td>16</td>
<td>$3\ tr + 5\ cc = 11\ di + 2\ fo + 5\ CO_2 + 3\ H_2O$</td>
<td>-30624</td>
<td>50.219</td>
<td>0.9864</td>
</tr>
<tr>
<td>17</td>
<td>$4\ tr + 5\ m + 5\ cc = 13\ di + 6\ fo + 10\ CO_2 + 4\ H_2O$</td>
<td>-70215</td>
<td>127.565</td>
<td>1.5384</td>
</tr>
<tr>
<td>18</td>
<td>$11\ tc + 10\ cc = 5\ tr + 4\ fo + 10\ CO_2 + 6\ H_2O$</td>
<td>-59736</td>
<td>118.063</td>
<td>1.6030</td>
</tr>
<tr>
<td>19</td>
<td>$6.5\ tc + 5\ m + 5\ cc = 2.5\ tr + 6\ fo + 10\ CO_2 + 4\ H_2O$</td>
<td>-73107</td>
<td>135.430</td>
<td>1.3860</td>
</tr>
<tr>
<td>20</td>
<td>$en + m = fo + CO_2$</td>
<td>-6573</td>
<td>11.822</td>
<td>0.0815</td>
</tr>
<tr>
<td>21</td>
<td>$13\ en + 2\ m + 2\ cc + H_2O = tr + 5\ fo + 4\ CO_2$</td>
<td>-10611</td>
<td>27.023</td>
<td>0.2405</td>
</tr>
<tr>
<td>22</td>
<td>$tr + fo = 5\ en + 2\ di + H_2O$</td>
<td>-6721</td>
<td>9.292</td>
<td>0.1442</td>
</tr>
<tr>
<td>23</td>
<td>$4\ en + m + cc = di + 2\ fo + 2\ CO_2$</td>
<td>-8666</td>
<td>18.128</td>
<td>0.1923</td>
</tr>
<tr>
<td>24</td>
<td>$tc + fo = 5\ en + H_2O$</td>
<td>-7166</td>
<td>10.442</td>
<td>0.1207</td>
</tr>
</tbody>
</table>

* Constants in an equation of the type $\log K = \frac{A}{T} + B + \frac{C(P_{Total} - 2000)}{T}$.
where $i$ refers to each component in the equilibrium. The criteria for equilibrium require that $\mu_i$ be uniform throughout the system but make no reference to the presence of any particular phase. Thus, the existence of MgCO$_3$ in an equilibrium does not imply the presence of the phase, magnesite, but rather the component, MgCO$_3$, which can be dissolved to a significant extent in calcite, dolomite, or magnesite. The T-X sections presented later in the paper are the unique solutions of the equilibria in table 2 for the case in which CaCO$_3$ and MgCO$_3$ are dissolved in magnesian calcite coexisting with dolomite.

With the definitions of standard states given previously, the measured gas fugacity products for equilibria 1, 2, and 3 from Skippen (1971, eq 7, 8, 9) are equal to the equilibrium constants given in table 2, since all solid phases had the composition of the corresponding component at the beginning and conclusion of experiments. In particular, X-ray diffraction analysis indicated that calcite had not dissolved significant Mg from the silicate phases in equilibrium 2. The gas fugacity product for equilibrium 4, however, was determined in the presence of magnesian calcite coexisting with dolomite. Appropriate activity terms must therefore be considered in calculating the equilibrium constant, as described in the next section. Equilibrium 5 was studied experimentally with pure, stochiometric dolomite as the carbonate phase. With the choice of components and standard states used by Skippen (1971), the equilibrium constant was given by the measured gas fugacity product. With the redefinition of components in the present paper, it is necessary to calculate a new equilibrium constant for equilibrium 5, as discussed in the second section below.

Equilibrium 4.—The formation of talc from quartz and carbonates has usually been considered by the equilibrium,

$$3\text{CaMg(CO}_3\text{)}_2 + 4\text{SiO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 3\text{CaCO}_3 + 3\text{CO}_2$$

[4A]

With MgCO$_3$ chosen as a component in place of CaMg(CO$_3$)$_2$, it is possible to write the following more general equilibrium,

$$3\text{MgCO}_3 + 4\text{SiO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 3\text{CO}_2$$

[4B]

If all components except MgCO$_3$, CO$_2$, and H$_2$O are in the standard state, then the equilibrium constant for 4B is given by,

$$\log K_{4B} = \log \frac{f_{\text{CO}_2}^3}{f_{\text{H}_2\text{O}}} - 3 \log a_{\text{MgCO}_3}$$

(1)

Equation 1 has been used to determine log $K_4$ in table 2 with the terms on the right-hand side evaluated as follows:

$$\log \frac{f_{\text{CO}_2}^3}{f_{\text{H}_2\text{O}}} = - \frac{13725}{T} + 26.09 + \frac{0.1918(P-2000)}{T}$$

(2)

Equation 2 was determined by Skippen (1971, eq 10) by fitting a curve to the experimental data of Metz and Winkler (1963), Gordon and
Greenwood (1970), and Skippen (1971). Equation 2 is consistent with all three sets of experimental data. It is assumed that equation 2 gives the equilibrium gas fugacity product for coexisting calcite and dolomite, even though pure calcite rather than magnesian calcite was used in the starting mixture for experiments by Skippen (1971) and Gordon and Greenwood (1970). Ideally, the two carbonate phases should have been equilibrated along the solvus prior to the beginning of experiments. X-ray diffraction analysis of run products from Skippen (1971) indicated that calcite had dissolved magnesium from dolomite and approached compositions along the solvus at the conclusion of experiments. On the basis of this observation and the agreement among the results from three laboratories, it is assumed that equation 2 is valid for coexisting calcite and dolomite, within the limits of uncertainty given in table 2.

\[
\log a_{\text{MgCO}_3} = -\frac{730.9}{T} + 0.4854
\]  

Equation 3 is taken from Gordon and Greenwood (1970) and gives the activity of MgCO$_3$ in calcite coexisting with dolomite with pure magnesite chosen as the standard state for MgCO$_3$. The effect of total pressure is not given explicitly in equation 3 since Gordon and Greenwood (1970) found that equation 3 could be used to recover the polybaric solvus of Graf and Goldsmith (1958) and Harker and Tuttle (1955) to within 0.01 mole fraction MgCO$_3$ at temperatures less than 704°C.

Equilibrium 4B has been measured experimentally by Johannes (1969) with pure magnesite rather than magnesian calcite as the carbonate phase. The equilibrium constant derived above for 4B can be compared with the data given by Johannes by setting the activity of MgCO$_3$ to unity. The comparison is shown graphically in figure 4 for total pressures of 1000 and 2000 bars. For mole fractions of CO$_2$ greater than 0.2, the two sets of data agree within 15 degrees.

Equilibrium 5.—Experimental data for the following equilibrium were measured by Skippen (1971):

\[
4\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 5\text{CaMg(CO}_3)_2 \rightleftharpoons \\
5\text{CaMgSi}_2\text{O}_6 + 6\text{Mg}_2\text{SiO}_4 + 10\text{CO}_2 + 4\text{H}_2\text{O} \]  

[5A]

Since MgCO$_3$ rather than CaMg(CO$_3$)$_2$ is to be taken as a component in this study, it is necessary to determine the equilibrium constant for an equilibrium written in terms of the components CaCO$_3$ and MgCO$_3$ rather than CaMg(CO$_3$)$_2$.

\[
4\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 5\text{CaCO}_3 + 5\text{MgCO}_3 \rightleftharpoons \\
5\text{CaMgSi}_2\text{O}_6 + 6\text{Mg}_2\text{SiO}_4 + 10\text{CO}_2 + 4\text{H}_2\text{O} \]  

[5B]

The equilibrium constant for 5B can be determined from the equilibrium constant for 5A and thermochemical data by a method analogous
Fig. 4. Comparison of calculated equilibrium data from table 2 with data measured by Johannes (1969) at 1 and 2 kb for the equilibrium, 5MgCO₃ + 4SiO₂ + H₂O = Mg₂Si₂O₇(OH)₂ + 3CO₂. The solid curve was calculated from equilibrium 4 in table 2 by setting the activity of MgCO₃ to unity. The dashed curves indicate upper and lower limits of experimental uncertainty. Vertical bars are equilibrium measurements reported by Johannes.

To that used by Gordon and Greenwood (1970) to calculate the equilibrium constant for 4A from experimental data for 4B. Thus,

\[ \Delta G_{5A}^{\circ} = 5^\circ G_{D_1} + 6^\circ G_{F_0} + 10^\circ G_{CO_2} + 4^\circ G_{H_2O} - 4^\circ G_{T_c} - 5^\circ G_{D_0} \]  

and

\[ \Delta G_{5B}^{\circ} = \Delta G_{5A}^{\circ} + 5(\circ G_{D_0} - \circ G_{C_c} - \circ G_M) \]  

Therefore,

\[ \log K_{5B} = \log K_{5A} - \frac{5(\circ G_{D_0} - \circ G_{C_c} - \circ G_M)}{2.3026 RT} \]  

The equilibrium constant for 5B in table 2 has been determined by equation 6 with the terms on the right hand side given by,

\[ \log K_{5A} = - \frac{75400}{T} + 133.7 + \frac{1.4286(P\cdot2000)}{T} \]  

as determined by Skippen (1971, eq 17) and,

\[ \frac{(\circ G_{D_0} - \circ G_{C_c} - \circ G_M)}{2.3026 RT} = - \frac{681}{T} + 0.259 - \frac{0.0032(P\cdot2000)}{T} \]  

Free energy data in equation 8 were taken from Robie and Waldbaum (1968). The uncertainty in equation 8 is approximately ± 0.3.
CALCULATED EQUILIBRIUM CONSTANTS

Skippen (1971) has shown that only 5 independent equilibria involving a CO₂-H₂O vapor phase exist among the 8 mineral phases under consideration. If the first 5 equilibria in table 2 are chosen to be independent, the remaining dependent equilibria can be derived by algebraic combination, that is

\[ \log K_n = k_1 \log K_1 + k_2 \log K_2 + k_3 \log K_3 + k_4 \log K_4 + k_5 \log K_5 \]  

(9)

where \( n \) is the number of a dependent equilibrium in table 2. Using coefficients \( k_1 \) through \( k_5 \) given by Skippen (1971, table 10) and the values for \( \log K_1 \) to \( \log K_5 \) in table 2, the remainder of the equilibrium constants in table 2 has been derived by equation 9.

The limits of uncertainty in \( \log K \) for equilibria 1 through 5 in table 2 were obtained by fitting a curve to the upper and lower limits of the experimental data given by Skippen (1971). For the remainder of the equilibria in table 2, equation 9 was used. In calculating the upper limit for a dependent reaction, the upper limit of the experimentally measured data was used when the coefficient \( k \) is positive and the lower limit when \( k \) is negative. This procedure was reversed to obtain the lower limit.

The limits of uncertainty are shown graphically in figure 5 for the case in which the activities of CaCO₃ and MgCO₃ are determined by the calcite-dolomite miscibility gap. Figure 5 indicates that the equilibrium constants for equilibria 4, 16, 19, and 32 are reasonably well established. There is, however, considerable uncertainty in the remaining curves and particularly for equilibrium 17 which defines the upper stability field of talc-calcite. This large uncertainty in the position of equilibrium 17 is related to a large uncertainty in the experimental bracketing of equilibrium 1, the talc dehydration reaction, together with a relatively low standard free energy of reaction for equilibrium 17.

It is possible to compare the calculated equilibrium constants for equilibria 28 and 40 from table 2 with other experimental data. Greenwood (1967b) and Johannes (1969) have determined equilibrium 28 with pure magnesite as the carbonate phase. At 2 kb, the temperature maximum on a T-XCO₃ section was found to be between 560° and 586°C by Greenwood and at approximately 560°C by Johannes. The data in table 2 give a temperature of 530 ± 30°C for the same temperature maximum at unit activity of MgCO₃. Similarly for equilibrium 40, Johannes (1969) reports an equilibrium temperature in 2 kb of pure CO₂ of 565° to 575°C. The comparable temperature from the data in table 2 is 525 ± 50°C. Thus, for equilibria involving talc, the calculated data in table 2 give results that decrease the stability field of the talc bearing assemblages relative to experimental measurements in the system MgO–SiO₂–H₂O–CO₂. Some of this disagreement may reflect uncertainty in the activity of MgCO₃ in equation 3.

Slaughter, Kerrick, and Wall (1978) have reported preliminary results of an investigation of equilibria 8, 12, and 16. Their results are as
Fig. 5. Limits of uncertainty in data from table 2 at 2000 bars with activities of CaCO$_3$ and MgCO$_3$ determined by the calcite-dolomite miscibility gap. Curves used to calculate T-X sections in figures 6 through 9 are dashed. The lower limit of uncertainty in equilibrium 17 plots off scale.
follows with the comparable temperature from this paper given in parentheses: For equilibrium 8 at 1 kb, \( X_{\text{CO}_3} = 0.5 \) at 494 ± 15°C (489°C); \( X_{\text{CO}_3} = 0.90 \) at 482 ± 15°C (493°C); for equilibrium 12 at 2 kb, \( X_{\text{CO}_3} = 0.5 \) at 440 ± 10°C (452°C, activity of CaCO\(_3\) = 1); for equilibrium 16 at 1 kb, \( X_{\text{CO}_3} = 0.95 \) at 440 ± 15°C (475°C, activity of CaCO\(_3\) and MgCO\(_3\) specified by calcite-dolomite solvus). The two sets of data are in reasonable agreement.

**Calculation of T-X\(_{\text{CO}_2}\) diagrams for siliceous dolomites**

Inspection of the paragenesis diagrams shown in figure 2 indicates that only four of the sequences affect bulk compositions in the triangle quartz–calcite–dolomite. These are the four sequences in the upper half of figure 2 in which calcite is invariably present and enstatite does not occur. If sedimentary carbonates are assumed to consist initially of quartz, calcite, and dolomite, then it is possible to omit those five-mineral assemblages involving enstatite without affecting parageneses in the resulting marbles. Also, reactions 18, 36, and 39 can be neglected in the sequences involving calcite, since these reactions only affect bulk compositions in the triangle quartz–dolomite–magnesite, as can be seen on figure 2.

For a given total pressure and a specified relationship between \( P_{\text{CO}_2} + P_{\text{H}_2\text{O}} \) and \( P_{\text{Total}} \), equilibrium constants such as listed in table 2 can be used to calculate equilibria as surfaces in the coordinates \( T\cdot X_{\text{CO}_2} - a_{\text{MgCO}_3} - a_{\text{CaCO}_3} \). The activities of silicate components are taken as unity on the assumption that silicate minerals have the composition of the component in many carbonate rocks. In the presence of a carbonate phase consisting only of the components CaCO\(_3\) and MgCO\(_3\), the activities of CaCO\(_3\) and MgCO\(_3\) are related by the Gibbs-Duhem equation and only one activity term is independent. On \( T\cdot X_{\text{CO}_2} \) sections, equilibria involving carbonates can therefore be shown as projected surfaces contoured for carbonate activity.

Gordon and Greenwood (1970) have published an equation giving the activity coefficient for CaCO\(_3\) in calcite as a function of the mole fraction of CaCO\(_3\).

\[
\ln \gamma_{\text{CaCO}_3} = (1 - X_{\text{CaCO}_3})^2 (1.2238 + 1.8960 X_{\text{CaCO}_3})
\]

\[
0 \leq X_{\text{MgCO}_3} \leq 0.18
\]

This equation can be combined with the solvus data of Graf and Goldsmith (1958) and Harker and Tuttle (1955) to produce the following expression for the activity of CaCO\(_3\) in calcite coexisting with dolomite:

\[
\log a_{\text{CaCO}_3} = \frac{68.38}{T} - 0.110
\]

Equation 10 is consistent with equation 3 taken from Gordon and Greenwood (1970). Both equations give the same temperature for a magnesian calcite of specified composition if the activity coefficients given by Gordon and Greenwood are used.
As a first step in calculating a model for siliceous dolomites, it is assumed that the activities of CaCO$_3$ and MgCO$_3$ are determined by the calcite-dolomite miscibility gap. In this way, a single curve, which can be correlated with natural assemblages containing two carbonate phases, is produced.

The derivation of T-X$_{CO_2}$ diagrams from experimental data such as listed in table 2 has been described by Skippen (1971). The T-X$_{CO_2}$ surface is assumed to be given by,

$$ P_{CO_2} + P_{H_2O} = P_{Total} $$

(11)

For a particular equilibrium such as 19,

$$ \log \left[ \frac{(P_{CO_2} \gamma_{CO_2})}{P_{H_2O} \gamma_{H_2O}} \right] = \log K_{19} + 5 \log a_{MgCO_3} + 2 \log a_{CaCO_3} $$

(12)

If the carbonate activities are specified by the calcite-dolomite miscibility gap, then equations 3 and 10 can be used to determine the carbonate activities.

Equations 11 and 12 have been solved by computer (Skippen and Yzerdraat, 1970) at 5 degree intervals for total pressures of 500, 1000, 2000, and 3000 bars. Fugacity coefficients for H$_2$O were taken from Burnham, Holloway, and Davis (1968) and for CO$_2$ from Skippen (1971). The results are shown in figures 6 through 9. Because of the very large experimental uncertainty in the stability field of talc-tremolite-calcite (see fig. 5), the curves bounding this assemblage have been dashed on the T-X$_{CO_2}$ sections.

Equilibria 8, 12, and 35 involve only a single carbonate component, CaCO$_3$, and normally occur with a single carbonate phase present. The activity of CaCO$_3$ is not therefore determined in natural assemblages by the miscibility gap, and equilibria 8, 12, and 35 do not usually plot precisely through invariant points 1, 2, and 3 respectively. Calculation of the equilibrium curves for unit activity of CaCO$_3$ at 3000 bars lowers the temperature maximum for equilibria 8, 12, and 35 by 6, 3, and 6°C respectively. The temperature differences are less at lower pressures. This effect has been neglected in drawing the T-X$_{CO_2}$ sections, and equilibria 8, 12, and 35 are shown as curves passing through the invariant points.

Similarly, equilibrium 16 might be of interest with pure stoichiometric dolomite rather than dolomite in equilibrium with calcite. If CaMg(CO$_3$)$_2$ is retained as a component and an equilibrium constant for 16 calculated using 4A and 5A rather than 4B and 5B in equation 9 (that is, the same method used by Skippen, 1971), then the temperature for equilibrium 16 in pure CO$_2$ is increased by 11°C at 3 kb and 8°C at 500 bars.

DISCUSSION OF T-X SECTIONS

Figures 6 to 9 illustrate the relationships among a number of important equilibria in siliceous carbonates for the case in which $P_{CO_2} +$
Fig. 6. Five hundred bars total pressure. Equilibria affecting bulk compositions in the triangle quartz–calcite–dolomite with the activities of MgCO₃ and CaCO₃ determined by the calcite-dolomite miscibility gap and $P_{\text{CO}_2} + P_{\text{H}_2\text{O}} = P_{\text{Total}}$.

Fig. 7. One thousand bars total pressure. Equilibria affecting bulk compositions in the triangle quartz–calcite–dolomite with the activities of MgCO₃ and CaCO₃ determined by the calcite-dolomite miscibility gap, and $P_{\text{CO}_2} + P_{\text{H}_2\text{O}} = P_{\text{Total}}$. 
Fig. 8. Two thousand bars total pressure. Equilibria affecting bulk compositions in the triangle quartz-calcite-dolomite with the activities of MgCO₃ and CaCO₃ determined by the calcite-dolomite miscibility gap, and P_{CO₂} + P_{H₂O} = P_{Total}. Equilibria 12 and 17 are dashed because of large limits of uncertainty.

Fig. 9. Three thousand bars total pressure. Equilibria affecting bulk compositions in the triangle quartz-calcite-dolomite with the activities of MgCO₃ and CaCO₃ determined by the calcite-dolomite miscibility gap, and P_{CO₂} + P_{H₂O} = P_{Total}. Equilibria 12 and 17 are dashed because of large limits of uncertainty.
If the partial pressures of CO₂ and H₂O sum to less than the total pressure, then the molal free energies of these components are lowered. For all equilibria shown in the figures, this results in a greater decrease in free energy for the high temperature assemblage, and the curves are displaced to lower temperatures. The T-Xₐ₉₀₂ sections shown in figure 6 through 9 therefore indicate the maximum temperature for a particular paragenesis.

Assemblages of 5 minerals are shown as points on the T-Xₐ₉₀₂ sections and have been numbered as follows:

1 and 1'  
1  
2  
3 and 3'  
talc-tremolite-quartz-calcite-dolomite  
tremolite-diopside-quartz-calcite-dolomite  
forsterite-diopside-tremolite-calcite-dolomite.

The uncertainty in the positions of points 2 and 3 on the T-X sections can be estimated graphically from the uncertainty (table 2, fig. 5) in equilibrium curves. The upper limits of uncertainty for curves 8 and 16 intersect 15 degrees above the plotted position of point 2; the minimum intersection for 8 and 16 is 45 degrees lower than the plotted position. Thus, a total temperature uncertainty of 70 degrees exists in the location of point 2, most of this uncertainty lying toward lower temperatures. Similarly, equilibrium 27 and 32 define a maximum temperature for point 3 that is 20 degrees above and 40 degrees below the plotted position.

The T-Xₐ₉₀₂ diagrams are sections through a T-Pₐ₉₀₂-Pₐ₉₀₀ space. In this general space, the 5-mineral assemblages plot along univariant curves. The intersection of these univariant curves with the T-Xₐ₉₀₂ plane can have two, one, or zero solutions: The experimental curves taken from Skippen (1971) result in a duplication of points 2 and 3 for pressures between 500 and 3000 bars, but the temperature of the second intersection for point 2 plots beneath the scales of figures 6 through 9. It is possible to choose equilibrium curves within the wide limits of uncertainty in existing data that do not produce a double intersection for points 2 and 3. The existence of point 3', however, is consistent with field evidence. The repeated occurrence at very low grade of the equilibrium assemblage diopside-dolomite in ophicalcites and metamorphosed ultramafic rocks can only be explained by the stable or metastable existence of 3', that is 3' is possibly metastable with respect to serpentinite-bearing assemblages, which have not been considered in this paper. Thus, the duplication of point 3 as indicated on figures 6 to 9 is consistent with field evidence, although it cannot be proven experimentally due to uncertainties in the existing data.

The limits of error in the equilibria bounding the stability field of talc-calcite are subject to considerable experimental uncertainty. For the actual experimental curves taken from Skippen (1971), point 1 is duplicated on the 2 and 3 kb sections. The temperatures of intersection converge with decreasing pressure until tangency of curves is obtained at a pressure very close to 1 kb. According to this data, talc-calcite is
not stable at very low pressures. If, however, the lower limit of uncertainty for equilibrium 4 at 1 kb is combined with the upper limits of uncertainty for equilibria 12 and 17, then point 1 exists at \( X_{\text{CO}_2} = 0.96 \), and a temperature of 490°C and duplicated point 1' does not exist at 1 kb. Such a wide stability field for talc-calcite would be comparable to that proposed by Metz, Puhan, and Winkler (1968) for a total pressure of 1 kb.

There can be little doubt from field evidence that talc-calcite has a large stability field at relatively high pressure as in the Central Alps (Trommsdorff, 1972) and the Damara Belt of South Africa (Puhan and Hofer, 1973). At low to moderate pressures, the field evidence is less certain. Tilley (1948) has described talc-calcite from a low pressure (1 kb) contact aureole from the Isle of Skye. Guitard (1966) has also described talc-calcite from the Canigou and the Caranca massifs of the eastern Pyrenees. On the other hand, tremolite-calcite is formed rather than talc-calcite in a low pressure, contact aureole in Montana (Melson, 1966) and in marbles from the Grenville Province of Eastern Ontario (Hutcheon and Moore, 1973). Talc-calcite as a pro-grade assemblage has not been described in the low pressure, contact aureole of the Bergell granite in the Swiss Alps (Trommsdorff, 1966), nor in the contact aureole of the Adamello complex in the Italian Alps (E. Callegari, personal commun.), nor in the aureole of the main Donegal granite (Pitcher and Read, 1960).

Factors that may complicate the field evidence with respect to talc-calcite include the substitution of F for OH in both talc and tremolite. Zwart (1953) has suggested that substantial amounts of Si as well as Cl or F have entered dolomitic sediments from adjacent intrusions during the formation of talc schists in the Massif du Saint Barthelemy in the French Pyrenees. Analysis by M. Weibel (personal commun.) of tremolite and talc from Campolungo, Switzerland also indicates high F contents. Since the effect of F on the relative stabilities of talc and tremolite is unknown, the existing experimental data should be applied in the field only where these minerals are free of F.

It is also possible that the fluid phase approaches pure \( \text{CO}_2 \) in some areas due to the production of \( \text{CO}_2 \) during the formation of micas from potash feldspar and dolomite as suggested by Gordon and Greenwood (1970) and Trommsdorff (1972). Fluids extremely rich in \( \text{CO}_2 \) could result in the formation of tremolite-calcite from quartz-dolomite, even if the talc-calcite stability field is relatively large. Field studies that include analysis of fluid inclusions would be helpful in clarifying this possibility.

The assemblage forsterite–talc–tremolite–calcite–dolomite which was previously shown to be stable on figure 3 (that is point 4) fails to intersect the \( T-X_{\text{CO}_2} \) sections up to 3 kb. The absence of an intersection is due to the fact that for all temperatures and pressures considered, the equilibrium \( P_{\text{CO}_2} \) and \( P_{\text{H}_2\text{O}} \) for point 4 sum to more than the total pres-
sure of the T-X sections. An inspection of figure 3 indicates that high water fugacities are required for point 4. An important assemblage that would indicate the existence of point 4 in the field is talc–forsterite–calcite. The fact that talc–forsterite–calcite has not been reported in field studies indicates that the high water fugacities needed for point 4 are not normally produced in siliceous carbonates.

The T-X$_{CO_2}$ sections vary significantly with total pressure. Not only do the temperatures of reaction change substantially, but the relative sizes of the stability fields change. The stability field of talc–calcite appears to increase substantially with pressure as does the stability field of the assemblage tremolite–quartz–calcite. Also significant is the relationship between equilibria 8 and 32. Eight intersects 32 at about 3 kb. Above this total pressure, forsterite + calcite can develop in CO$_2$ rich fluids before tremolite–quartz–calcite must react to form diopside. Thus, the original sequence of minerals predicted by Bowen (1940) in which forsterite was considered to form prior to diopside is possible at higher pressure, whereas in lower pressure environments, diopside forms before forsterite.

It is also possible to compare the T-X$_{CO_2}$ diagrams in figures 6 to 9 with a similar diagram derived by Trommsdorff (1972) for the P-T gradient across the Central Alps. Trommsdorff reports that the total pressure in the Central Alps was at least 5 kb. Due to a lack of fugacity coefficient data for CO$_2$ at high pressures, it is not possible to make a direct comparison of the diagram produced by Trommsdorff and the experimental data. However, the duplication of points 3-3' is confirmed by field evidence, and the appearance of forsterite–calcite at lower grade than the disappearance of tremolite–calcite–quartz in the Central Alps is consistent with the intersection of equilibria 8 and 32 at 3 kb in figure 9.

APPLICATION TO SILICEOUS CARBONATE ROCKS

Examination of the T-X sections indicates the following unique points:

- Five-mineral invariant assemblages: 1', 1, 2, 3', 3
- Maxima in equilibrium curves: 8, 12, 17, 32, 35
- Intersections with X = 1 axis: 16, 27
- Indifferent crossing of equilibrium curves: 8-32

These points are unique both on the T-X diagrams and along a specific P-T gradient. The locus of such points on a map is therefore important in describing the distribution of metamorphic grade in a field area. In most cases, it is not possible to locate these unique points by direct observation. It is necessary to infer their location by mapping the distribution of three and four-mineral assemblages. The critical assemblages for bracketing these points in the field are summarized in table 3. For example, the lowest temperature at which the five-mineral assemblage tremolite–diopside–quartz–calcite–dolomite (point 2) exists is located by the final disappearance of tremolite–calcite–quartz–dolomite (equilibrium
in moving from lower to higher grade. The maximum temperature for point 2 is given by the appearance of diopside-dolomite-calcite in
CO$_2$ rich fluids according to equilibrium 16. The maximum temperature for point 2 is also related to the appearance of diopside-quartz-
calcite and diopside-tremolite-calcite in CO$_2$ rich fluids. There is more
ambiguity in the latter two assemblages due to their existence on both
sides of the maximum in curve 8.

The location of maxima in equilibrium curves is less precise since
only a lower temperature bracket can be located in the field. The like-
lihood of an equilibrium having reached the maximum temperature in
nature is improved if four-mineral assemblages exist with textural rela-
tionships that are compatible with equilibrium (for example, Melson,
1966; Trommsdorff, 1972). Such assemblages over a range of meta-
morphic grade indicate internal buffering of fluid compositions along
equilibrium curves and suggest a mechanism for reaching the tempera-
ture maximum. In some cases, the temperature maximum may lie
on the metastable portion of a curve. The disappearance of a three-mineral
assemblage then occurs at an invariant point rather than a maximum
in an equilibrium curve, as is the case for curve 32 on figure 6.

The indifferent crossing of equilibria such as 8 and 32 can be
located in the field by the simultaneous equilibrium of both four-mineral
assemblages in adjacent samples. The recognition of such crossings there-
fore requires silica-rich and silica-poor bulk compositions to be closely
intermixed.

Table 3
Bracketing of unique points from T-X sections

<p>| Number in | Mineral assemblage at point | Lower bracket (assemblages disappear) | Upper bracket (assemblages appear) |</p>
<table>
<thead>
<tr>
<th>T-X section</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1'</td>
<td>Tc-Tr-Q-Cc-Do</td>
<td>Tr-Do-Q-Cc (19)*</td>
<td>Tc-Do-Cc, Tc-Q-Cc</td>
</tr>
<tr>
<td>1</td>
<td>Tc-Tr-Q-Cc-Do</td>
<td>Tc-Cc-Q-Do (4)</td>
<td>Tr-Do-Q-Cc (19)</td>
</tr>
<tr>
<td>2</td>
<td>Tr-Di-Q-Cc-Do</td>
<td>Tr-Do-Q-Cc (19)</td>
<td>Di-Do-Cc</td>
</tr>
<tr>
<td>3'</td>
<td>Fo-Di-Tr-Cc-Do</td>
<td>Di-Do-Cc</td>
<td>Fo-Tr-Cc</td>
</tr>
<tr>
<td>3</td>
<td>Fo-Di-Tr-Cc-Do</td>
<td>Tr-Cc-Di-Do (20)</td>
<td>Fo-Di-Cc</td>
</tr>
<tr>
<td>8</td>
<td>Tr-Di-Q-Cc</td>
<td>Tr-Q-Cc</td>
<td>—</td>
</tr>
<tr>
<td>12</td>
<td>Tc-Tr-Q-Cc</td>
<td>Tc-Q-Cc</td>
<td>—</td>
</tr>
<tr>
<td>17</td>
<td>Tr-Tc-Do-Cc</td>
<td>Tc-Do-Cc</td>
<td>—</td>
</tr>
<tr>
<td>32</td>
<td>Fo-Tr-Cc-Do</td>
<td>Tr-Do-Cc</td>
<td>—</td>
</tr>
<tr>
<td>35</td>
<td>Fo-Tr-Di-Cc</td>
<td>Fo-Tr-Cc</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>Di-Q-Cc-Do</td>
<td>Q-Cc-Dol.</td>
<td>—</td>
</tr>
<tr>
<td>27</td>
<td>Fo-Di-Cc-Do</td>
<td>Di-Cc-Dol.</td>
<td>—</td>
</tr>
</tbody>
</table>

* Number in parentheses refers to equilibrium on T-X diagrams.

Indifferent crossings

8-32 Di-Tr-Q-Cc
plus
Fo-Tr-Cc-Do
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