SULFIDE–OXIDE–SILICATE EQUILIBRIA; SNOW LAKE, MANITOBA

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ABSTRACT. Examination of sulfide-bearing pelitic rocks shows that the iron content of staurolite, biotite, and chlorite decreases with increasing sulfur fugacity at constant temperature and pressure. A model for end-member equilibria in the system K–Fe–Al–Si–O–H can be developed from published experimental data and applied, with or without the $P_{\text{total}} = P_{\text{fluid}}$ equation, to pyrite–pyrrhotite–magnetite-bearing pelitic rocks using ideal solution models. Simultaneous solutions of silicate equilibria give temperatures of approx 710°C at 7 kb for sillimanite–biotite–muscovite–chlorite–staurolite–sulfide–oxide-bearing pelitic rocks from the Snow Lake area. Simultaneous solution of published annite–muscovite or daphnite equilibria with the equilibrium between pyrite, pyrrhotite, and magnetite yields temperatures of approx 625°C, in better agreement with previous estimates for the Snow Lake area, and suggesting that $P_{\text{fluid}}$ was close to $P_{\text{total}}$. Published staurolite equilibria suggest higher (700°C) temperatures.

Choosing an equilibrium curve closer to the low temperature brackets for one set of staurolite experiments gives temperatures of approx 620°C, in closer agreement with other equilibria and published estimates of metamorphic conditions. In the H–O–S vapor which coexists with pyrite–pyrrhotite–magnetite, pyrrhotite–magnetite, or pyrite–pyrrhotite–biotite–muscovite–sillimanite–staurolite–chlorite, H$_2$O is the dominant species, below 650° to 700°C at 7 kb.

ABBREVIATIONS

al — almandine
an — annite
bi — biotite
ch — chlorite
co — cordierite
cp — chalcopyrite
da — daphnite
gt — garnet
hc — hercynite
Kf — potassium feldspar
ky — kyanite
mt — magnetite
mu — muscovite
pc — plagioclase
po — pyrrhotite
py — pyrite
qz — quartz
si — sillimanite
sp — sphalerite
st — staurolite
$P_t$ — total pressure
$P_f$ — fluid pressure

INTRODUCTION

The Snow Lake area, in Manitoba (fig. 1) offers an excellent opportunity to study the metamorphism of pelitic rocks containing disseminated sulfides and oxides, associated with stratiform volcanogenic massive sulfide ore deposits. Banno and Kanehira (1961), Guidotti (1974), and Bachinski (1975) have described reactions involving sulfides and silicates in pelitic rocks. Hounslow and Moore (1967) have related increasing oxygen fugacity, indicated by oxide assemblages, to iron depletion of co-existing biotite and staurolite. Froese (1971) and Thompson (1972) have shown that sulfides, oxides, and silicates participate in equilibria that control the compositions of the silicate phases and buffer the fugacities of oxygen and sulfur at fixed pressure and temperature. Given the theoretical implication, and the confirmation in natural assemblages, of reactions...
taking place between silicates, sulfides, and oxides, it is useful to develop
a model for the metamorphism of sulfide-bearing pelitic rocks.

Experiments in the systems K–Fe–Al–Si–O–H or K–Fe–Mg–Al–Si–
O–H are often incorrectly applied to observed mineral assemblages in
pelitic rocks. Minerals in pelitic rocks contain other elements in solid
substitution for those listed above, and many pelitic rocks contain sul-
fides, indicating that the H–O–S vapor phase cannot be pure water. In
this study evidence is presented to support the conclusion of previous
authors that the iron content of silicate minerals is a function of sulfur
fugacity at constant pressure and temperature. Equilibrium constants,
applicable to staurolite–biotite–muscovite–sillimanite–chlorite–magnetite
bearing rocks can be derived from published experiments and applied to
natural rocks using ideal solution models.

GEODETICAL SETTING OF SNOW LAKE

The geology of the Snow Lake area and the Stall Lake and Anderson
Lake mines has been described by many authors including Alcock (1917,
1920), Martin (1966), Coates and others (1970), and Moore and Froese
(1972). Snow Lake is located within a 150 km belt of Amisk group meta-
morphosed volcanic rocks 1510 to 1750 m.y. old (Bell, Blenkinsop, and
Moore, 1975) associated with Missi group metasedimentary rocks. The
disseminated and massive sulfide mineralization in the Anderson Lake
and Stall Lake mines is associated with pelitic host rocks which have
been subjected to upper amphibolite facies metamorphism.

Froese and Gasparrini (1975) have defined three mineral reactions
separating the chlorite–biotite–garnet, biotite–chlorite–staurolite, biotite–
staurolite–sillimanite, and biotite–sillimanite–garnet zones. The trace of

Fig. 1. The geology and metamorphic isograds in the Snow Lake area (after Froese
and Gasparrini, 1975).
the mineral reaction (isograd), designated "si-bi" by Froese and Gasparrini:

$$\text{ch + st + mu + qz} \rightarrow \text{bi + si + H}_2\text{O}$$

separating the two intermediate mineral zones, is in the vicinity of the Stall Lake and Anderson Lake mines (fig. 1). From the close spatial relationship of the above mineral reaction and the sillimanite–kyanite transition, Froese and Gasparrini estimate the metamorphic conditions near Stall Lake as 5.5 kb and 600°C. Using the aluminum silicate data of Holdaway (1971) gives 625°C and 6 kb. Scott (1976) and Hutcheon (1978) obtain 7 kb from the composition of sphalerite, coexisting with pyrite and pyrrhotite, at the Stall Lake mine.

**ELEMENT DISTRIBUTION**

Most pelitic rocks from the Anderson and Stall Lake mines contain staurolite, biotite, and chlorite, with muscovite in sufficiently potassic rocks. Nearly all combinations of these minerals plus pyrite, pyrrhotite, and magnetite are present with quartz, ilmenite, clino(pyrite, and sphalerite. Garnet, when present, is rimmed by quartz and plagioclase and has not been observed in contact with chlorite or biotite, except in the iron-rich assemblage garnet–biotite–staurolite. Some samples have, in grain by grain contact, all the minerals present in the mineral reaction that defines the isograd at Stall Lake. The electron microprobe was used to analyze minerals coexisting in rocks from the Stall Lake and Anderson Lake mines. The minerals in these rocks are assumed to have formed at approximately the same temperature and total pressure. Only rocks containing muscovite were included to ensure similar octahedral aluminum content in the layer silicates (Guidotti, Cheney and Conatore, 1975). In figure 2, samples A2, A4, and A7 contain pyrite and pyrrhotite, while A3,

![Diagram](image)

**Fig. 2.** Composition of coexisting staurolite, biotite, and chlorite in muscovite–quartz bearing pelitic rocks from the Anderson Lake (prefix “A”) and Stall Lake (prefix “S”) mines. Samples A2, A4, A7, and S7 contain pyrite and pyrrhotite; samples A3, A8, and S6 contain pyrite as the only iron sulfide phase.
Table 1
Microprobe analyses of minerals (wt percent) with mineral assemblages of analyzed samples

<table>
<thead>
<tr>
<th>CHLORITE</th>
<th>STAUROLITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>A2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>25.14</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.06</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>22.60</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>22.02</td>
</tr>
<tr>
<td>MnO</td>
<td>0.17</td>
</tr>
<tr>
<td>MgO</td>
<td>17.57</td>
</tr>
<tr>
<td>CaO</td>
<td>0.01</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>Total</td>
<td>87.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>BIOTITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>TiO₂</td>
</tr>
<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>MnO</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>K₂O</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

*Calculated from stoichiometry

A8, and S6, with lower iron contents coexist with only pyrite, indicating relatively higher sulfur fugacities at the same temperature and total pressure. While the iron content of the silicates appears to decrease with increasing sulfur fugacity, the oxygen fugacity is not specified by the opaque assemblage since magnetite is not present, and is restricted to values lower than the stability of magnetite. Sample S7 contains pyrite-pyrrhotite-magnetite, indicating a higher oxygen fugacity than the other samples. The analyses in table 1 show that iron is replaced by magnesium in biotite and chlorite, but zinc replaces iron in staurolite. Griffen and Ribbe (1973) report that zinc substitutes in the Fe⁴⁺ site and to a minor extent the Al⁶⁺ site in staurolite. Figure 3 shows iron in chlorite and biotite decreases with increasing zinc in staurolite, in contrast to the observation of Guidotti (1974), who reports that the zinc content of staurolite is independent of the Fe/Mg ratios of biotite coexisting with staurolite.

**Calculated equilibrium data**

It has been observed that the composition of silicates is related to the sulfur fugacity at constant pressure and temperature. To examine this relationship in a quantitative manner it is useful to develop a model for the metamorphism of silicate minerals in the system K–Fe–Al–Si–O–H.
Fig. 3. The mole fractions of magnesium in chlorite ($X^{Mg}_{\text{chlorite}}$) indicated by squares) and biotite (indicated by circles) is directly related to the mole fraction of zinc ($X^{Zn}$) in the coexisting staurolite.

Five algebraically independent equilibria can be used to calculate the equilibrium relationships among the end-member minerals annite, daphnite (chlorite), Fe–staurolite, almandine, sillimanite, quartz, muscovite, and magnetite. Independent equilibria have been recalculated in the form:

$$\text{Fe–aluminous silicate} = \text{magnetite} + \text{sillimanite} + \text{quartz}.$$  

For any equilibrium, the equilibrium constant ($K$) is written in terms of the fugacities of gas species and the activities of solid components. For an equilibrium involving pure phases if the standard state for gases is defined at 1 bar, at equilibrium, the change in free energy ($\Delta G$):

$$\Delta G = \Delta G^\circ + RT \ln K + V_s(P-1) = 0$$

Following Skippen (1975), assuming the change in thermal expansion and isothermal compressibility is negligible (Thompson, 1955; Fisher and Zen, 1971):

$$\log K = \frac{A}{T} + B + \frac{C(P-1)}{T}.$$  

The constants $A$, $B$, and $C$ are related to the change in enthalpy, entropy, and molar volume ($V_s$) of the solids, respectively. If $\log K + \Delta V_s(P-1)/2.3RT$ is plotted against reciprocal temperature for a set of experimental data, then $A$ and $B$ can be determined from the resulting linear relationship. The $C$ constant can be calculated from molar volumes.

**Standard state.**—The standard state for gases is defined at 1 bar. The solid silicate phases are considered to have the standard state defined as
the pure ferrous end-member at the pressure and temperature of interest with the appropriate crystal structure. The compositions of the ideal end-members are shown in table 2.

Activities of solid species.—Most phases to be considered do not have the ideal compositions listed in table 2, either in experiments or in naturally occurring rocks, and activity terms must be included in the equilibrium constant. In the absence of calibrated activity-composition relationships the Temkin (1945) solution model, as described by Ringwood (1958), Oates (1969), or Froese (1976), has been used to calculate activities.

In layer silicates, octahedral and tetrahedral substitutions are coupled and thus not truly random (Wood and Banno, 1973). Calculations include both the assumption of tetrahedral and no tetrahedral site mixing wherever the observed results differ by more than a few degrees. Chlorite contains alternating talc-like and brucite-like layers. The Al for Mg substitution occurs primarily in the brucite layer with one octahedral site in the talc layer usually occupied by Fe²⁺ (Deer, Howie, and Zussmann, 1968). The possible sites that Fe²⁺ may occupy can only be determined by detailed crystal chemical studies, but assuming that mixing is truly random over all six sites seems unrealistic. Therefore calculations involving chlorite have been completed using, in addition to six sites, the extreme case of Fe²⁺ mixing on three sites (substitution on the talc layer only) and adjusting activities in the experiments and natural minerals accordingly.

For staurolite the Fe:Al:Si ratio 4:18:7.5 from Rutherford (ms) and the water content of 2 moles per formula unit (Smith, 1968; Griffen and Ribbe, 1973) are accepted to produce the solution model. Formulae used to calculate activities are given in table 3.

Calculation of independent equilibria.—Experiments with iron-bearing phases employ either solid-phase oxygen buffers or the Shaw hydrogen

<table>
<thead>
<tr>
<th>PHASE</th>
<th>COMPOSITION</th>
<th>VOLUME (cm³/bar)</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>almandine</td>
<td>Fe₄Al₂Si₂O₁₂</td>
<td>2.754</td>
<td>Hsu, 1968</td>
</tr>
<tr>
<td>annite</td>
<td>KFe₃AlSi₃O₁₀(OH)₂</td>
<td>5.688</td>
<td>Robie, Bethke, and Boardsley, 1967</td>
</tr>
<tr>
<td>cordierite</td>
<td>Fe₂Al₂Si₂O₁₂</td>
<td>5.577</td>
<td>Deer, Howie, and Zussmann, 1963</td>
</tr>
<tr>
<td>daphnite</td>
<td>Fe₄Al₂Si₃O₁₂(OH)₈</td>
<td>5.140</td>
<td>McOnie, Faccett, and Jones, 1975</td>
</tr>
<tr>
<td>hereynite</td>
<td>FeAl₂O₄</td>
<td>0.974</td>
<td>Robie and Waldhaun, 1968</td>
</tr>
<tr>
<td>manganite</td>
<td>Fe₄O₆</td>
<td>1.064</td>
<td>Robie and Waldhaun, 1968</td>
</tr>
<tr>
<td>muscovite</td>
<td>KAl₃Si₃O₁₀(OH)₂</td>
<td>3.761</td>
<td>Robie and Waldhaun, 1968</td>
</tr>
<tr>
<td>quartz</td>
<td>SiO₂</td>
<td>0.542</td>
<td>Robie and Waldhaun, 1968</td>
</tr>
<tr>
<td>sanidine</td>
<td>KAlSi₃O₈</td>
<td>2.605</td>
<td>Robie and Waldhaun, 1968</td>
</tr>
<tr>
<td>sillimanite</td>
<td>Al₅SiO₈</td>
<td>1.192</td>
<td>Robie and Waldhaun, 1968</td>
</tr>
<tr>
<td>staurolite</td>
<td>Fe₆Al₃Si₁₃O₈H₈</td>
<td>21.406</td>
<td>Rutherford, ms</td>
</tr>
</tbody>
</table>
Table 3

Formulae used to calculate activities

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td>annite (non-tetrahedral)</td>
<td>( \left( \frac{\text{Fe}^{2+}}{X^{VI}} \right)^3 \cdot \left( \frac{\text{H}}{\text{O}+\text{H}} \right)^2 )</td>
</tr>
<tr>
<td>annite (tetrahedral)</td>
<td>( \left( \frac{\text{Fe}^{2+}}{X^{VI}} \right)^3 \cdot \left( \frac{\text{Si}^{IV}}{0.75(X^{IV})} \right)^3 \cdot \left( \frac{\text{Al}^{IV}}{0.25(X^{IV})} \right) \cdot \left( \frac{\text{H}}{\text{O}+\text{H}} \right)^2 )</td>
</tr>
<tr>
<td>daphnite (non-tetrahedral)</td>
<td>( \left( \frac{\text{Fe}^{2+}}{X^{VI}} \right)^6 \cdot \left( \frac{\text{H}}{\text{O}+\text{H}} \right)^8 )</td>
</tr>
<tr>
<td>daphnite (tetrahedral)</td>
<td>( \left( \frac{\text{Fe}^{2+}}{X^{VI}} \right)^6 \cdot \left( \frac{\text{Si}^{IV}}{0.75(X^{IV})} \right)^3 \cdot \left( \frac{\text{Al}^{IV}}{0.25(X^{IV})} \right) \cdot \left( \frac{\text{H}}{\text{O}+\text{H}} \right)^8 )</td>
</tr>
<tr>
<td>Fe-staurolite</td>
<td>( \left( \frac{\text{Fe}^{2+}}{X} \right)^3 )</td>
</tr>
</tbody>
</table>

Membrane to control the fugacities of species in the system O–H. If solid-phase oxygen buffers are used, the expression:

\[
\log fO_2 = \frac{A}{T} + B + \frac{C(P-1)}{T}
\]

is used to calculate the oxygen fugacities. Table 4 gives the constants used in this study.

For \( P_t < 3 \) kb fugacity coefficients for hydrogen are from Shaw and Wones (1964), for \( P_t > 3 \) kb they are from Ryzenko and Volkov (1971). Fugacity coefficients for water are from Burnham, Holloway, and Davis (1969). The procedure employed to extract the data for each equilibrium is described below.

Daphnite.—The equilibrium used to introduce daphnite in calculated phase relations is:

\[
3\text{da} = 5\text{mt} + 3\text{si} + 6\text{qz} + 7\text{H}_2\text{O} + 5\text{H}_2
\]  

(1)

R. S. James (personal commun.) provided the following data for the

Table 4

<table>
<thead>
<tr>
<th>BUFFER</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NNO</td>
<td>-24930</td>
<td>9.36</td>
<td>0.046</td>
<td>Huebner and Sato (1970)</td>
</tr>
<tr>
<td>QFM</td>
<td>-25287</td>
<td>8.95</td>
<td>0.110</td>
<td>Hewitt (1976)</td>
</tr>
<tr>
<td>MW</td>
<td>-34667</td>
<td>14.45</td>
<td>0.083</td>
<td>Skippen (1967)</td>
</tr>
<tr>
<td>HM</td>
<td>-25773</td>
<td>14.75</td>
<td>0.091</td>
<td>R.E. Beane (personal commun.)</td>
</tr>
<tr>
<td>MI</td>
<td>-29260</td>
<td>8.99</td>
<td>0.061</td>
<td>Norton (1955)</td>
</tr>
<tr>
<td>WI</td>
<td>-27480</td>
<td>6.64</td>
<td>0.056</td>
<td>Robie and Waldbaum (1968)</td>
</tr>
</tbody>
</table>
equilibrium among cordierite, chlorite, magnetite, and quartz at oxygen fugacities specified by the NNO buffer:
\[
\begin{align*}
\text{pH}_2\text{O} &= 2 \text{ kb}; \quad T = 526^\circ\text{C}, \text{ left side of equilibrium stable} \\
T &= 550^\circ\text{C}, \text{ right side of equilibrium stable} \\
\text{pH}_2\text{O} &= 4 \text{ kb}; \quad T = 563^\circ\text{C}, \text{ left side of equilibrium stable} \\
T &= 587^\circ\text{C}, \text{ right side of equilibrium stable}
\end{align*}
\]
These data imply the equilibrium:
\[
6\text{da} = 3\text{co} + 8\text{mt} + 3\text{qz} + 16\text{H}_2\text{O} + 8\text{H}_2. \quad (1A)
\]
The chlorite composition given by James, Turnock, and Fawcett (1976) gives \(a^{da} = 0.0878\) for these experiments, if a 6-site mixing model and tetrahedral mixing are assumed. The authors do not report spinel compositions, but the approximate activity of Fe\(_3\)O\(_4\) from the temperature and \(fO_2\) of the experiments is 0.94, which will decrease \(\log K_{1A}\) by only 0.37 percent. The equilibrium:
\[
2\text{co} + \text{H}_2\text{O} = \text{mt} + \text{hc} + 3\text{si} + 7\text{qz} + \text{H}_2 \quad (1B)
\]
IMPLIED in experiments conducted by Richardson (1968), is used to remove cordierite from equilibrium (1A). The water content of cordierite is a variable function of \(fH_2O\), temperature, and composition (A. Gunter, personal commun.). The necessary cordierite experiments have been completed under different conditions, but, in the absence of published data for hydrous cordierite, it has been assumed that this phase has similar water contents in each set of experiments. Margules parameters given by Froese (1973) are combined with spinel compositions in Richardson (1968) to calculate the activities of Fe\(_3\)O\(_4\) (magnetite) and FeAl\(_2\)O\(_4\) (hercynite) for equilibrium (1B). Combining (1A) and (1B) gives the equilibrium:
\[
6\text{da} = 9.5\text{mt} + 1.5\text{hc} + 4.5\text{si} + 13.5\text{qz} + 14.5\text{H}_2\text{O} + 9.5\text{H}_2 \quad (1C)
\]
The relationships:
\[
\begin{align*}
\Delta H &= \Delta H^o_{(298,1)} + \int_{298}^{T} < C_p dT \\
\Delta S &= \Delta S^o_{(298,1)} + \int_{298}^{T} \frac{\Delta C_p}{T} dT
\end{align*}
\]
\[
\log K_{(1 \text{ atm})} = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R}
\]
can be combined with the thermochemical data in table 5 to calculate the equilibrium:
\[
1.5\text{hc} + 1.5\text{qz} + 0.5\text{H}_2\text{O} = 0.5\text{mt} + 1.5\text{si} + 0.5\text{H}_2 \quad (1D)
\]
Sulfide–oxide–silicate equilibria, Snow Lake, Manitoba

Equilibria (1C) and (1D) may be combined to give:

$$3\text{da} = 5\text{mt} + 3\text{si} + 6\text{qz} + 7\text{H}_2\text{O} + 5\text{H}_2$$

(1)

The A, B, and C constants for (1) are listed in table 6; figure 4 shows the recalculated experimental data points.

*Almandine.*—Hsu (1968) gives brackets for the equilibrium:

$$3\text{al} + 2\text{H}_2\text{O} = 3\text{hc} + 2\text{mt} + 9\text{qz} + 2\text{H}_2$$

(2A)

The activities of coexisting magnetite and hercynite can be calculated from the solvus compositions in Turnock and Eugster (1962) using the Margules solution parameters from Froese (1973). The data in table 5 may be used to calculate the equilibrium:

$$3\text{hc} + 3\text{qz} + \text{H}_2\text{O} = \text{mt} + 3\text{si} + \text{H}_2$$

(2B)

### Table 5

Thermochemical data for components relevant to the equilibrium:

<table>
<thead>
<tr>
<th>Component</th>
<th>$\Delta H^\circ (\text{cal g}^{-1})$</th>
<th>$\Delta S^\circ (\text{cal g}^{-1} \text{K}^{-1})$</th>
<th>a $\times 10^{-3}$</th>
<th>b $\times 10^3$</th>
<th>c $\times 10^5$</th>
<th>$\text{Vcm}^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{hc}$</td>
<td>$-475420. \pm 1160_i$</td>
<td>$25.4 \pm 0.2_i$</td>
<td>$21.57_i$</td>
<td>$26.69_i$</td>
<td>0.0</td>
<td>40.75_i</td>
</tr>
<tr>
<td>$\text{qz}$</td>
<td>$-217650. \pm 400_i$</td>
<td>$9.88 \pm 0.02_i$</td>
<td>$11.22_i$</td>
<td>8.2</td>
<td>$-2.7$</td>
<td>22.69_i</td>
</tr>
<tr>
<td>$\text{mt}$</td>
<td>$-227720.6$</td>
<td>$9.00_i$</td>
<td>$14.4_i$</td>
<td>1.94</td>
<td>0.0</td>
<td>25.72_i</td>
</tr>
<tr>
<td>$\text{qnt}$</td>
<td>$-267250.5$</td>
<td>$34.85_i$</td>
<td>$25.06_i$</td>
<td>$45.11_i$</td>
<td>$-1.45_i$</td>
<td>44.52_i</td>
</tr>
<tr>
<td>$\text{ten}$</td>
<td>$-271720.6$</td>
<td>$20.51_i$</td>
<td>$42.24_i$</td>
<td>2.28</td>
<td>$38.66_i$</td>
<td>44.82_i</td>
</tr>
<tr>
<td>$\text{si}$</td>
<td>$-615099.7$</td>
<td>$23.13_i$</td>
<td>$40.02_i$</td>
<td>7.39</td>
<td>$11.67_i$</td>
<td>49.99_i</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$-57796. \pm 1_i$</td>
<td>$45.1040.010_i$</td>
<td>$7.3_i$</td>
<td>$2.46_i$</td>
<td>0.0</td>
<td>$0_i$</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>0.0</td>
<td>51.2080.010_i</td>
<td>6.52_i</td>
<td>0.78</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>

Calculated constants for an equation of the type:

\[ g \mathcal{K} = \frac{A}{T} + B + \frac{C(P-1)}{T} \]

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3\text{an} + 5\text{mt} + 3\text{si} + 6\text{qz} + 7\text{H}_2\text{O} + 5\text{H}_2 &amp; -101181 \pm 17000 &amp; 144.635 \pm 26.750 &amp; 0.718</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>\text{al} + \text{H}_2\text{O} = \text{mt} + \text{si} + 2\text{qz} + \text{H}_2 &amp; -4301 \pm 2140 &amp; 1.99935 \pm 2.135 &amp; -0.128</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>\text{an} + \text{Kf} + \text{mt} + \text{H}_2 &amp; -5442.8000 &amp; 6.909 \pm 1.000 &amp; 0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>\text{al} + \text{H}_2\text{O} = \text{Kf} + \text{si} + \text{H}_2\text{O} &amp; -4611.8000 &amp; 8.245 \pm 0.900 &amp; 0.025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5\text{an} + 9\text{qz} = 8\text{nt} + 5\text{si} + 4\text{H}_2\text{O} + 8\text{H}_2 &amp; -91376 \pm 13980 &amp; 111.958 \pm 15.451 &amp; -0.828</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5\text{an} + 3\text{qz} = 8\text{nt} + 4\text{si} + 12\text{H}_2\text{O} &amp; -543333 \pm 155600 &amp; 401.583 \pm 161.960 &amp; 0.196</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>\text{an} + \text{si} + \text{H}_2\text{O} = \text{mt} + \text{qz} + \text{H}_2 &amp; -811 &amp; -1.356 &amp; -0.019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3\text{sh} + 3\text{qz} + 4\text{H}_2\text{O} = \text{mt} + 5\text{si} + \text{H}_2 &amp; -377741 &amp; 417.515 &amp; -0.828</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Equilibria (2A) and (2B) can then be combined to give:

\[ \text{al} + \text{H}_2\text{O} = \text{mt} + \text{si} + 2\text{qz} + \text{H}_2 \]

(2)

A, B, and C constants are presented in table 6; figure 5 shows the recalculated data points.

Annite.—The available experimental data for the equilibrium

\[ \text{an} = \text{Kf} + \text{mt} + \text{H}_2 \]

(3)

are published in Wones and Eugster (1965) and Wones, Burns, and Carroll (1971). Of the three data points in Wones, Burns, and Carroll, only one biotite composition is available (Zen, 1973). Since the annite content of biotite is a function of fH2O, only QFM and NNO buffered experiments from Wones and Eugster have been used. The activity of

---

**Fig. 5. Recalculated experimental data for the almandine equilibrium (2).**
Sulfide–oxide–silicate equilibria, Snow Lake, Manitoba

annite in the experiments of Wones and Eugster was obtained from the published compositions and the solution model in table 3. Temperature uncertainties, stated by Wones and Eugster, were used to produce the experimental points on figure 6.

Muscovite.—Chatterjee and Johannes (1974) concluded that the equilibrium conditions for:

\[ \text{mu} + \text{qz} = \text{Kf} + \text{si} + \text{H}_2\text{O} \]  \hspace{1cm} (4)

give the structural state of the potassium feldspar. A, B, and C constants derived from the experiments of Chatterjee and Johannes are given in table 6.

Staurolite.—The equilibrium:

\[ 3\text{st} + 9\text{qz} = 8\text{mt} + 54\text{si} + 4\text{H}_2\text{O} + 8\text{H}_2 \] \hspace{1cm} (5)

is implied by the experiments of Rutherford (1970). The experimental points are shown in figure 7.

Experiments by Richardson (1968) imply the equilibrium:

\[ 3\text{st} + 25\text{qz} = 8\text{al} + 46\text{si} + 12\text{H}_2\text{O} \] \hspace{1cm} (6)

data for which are shown in figure 8. Equilibrium (6), derived from the experiments of Richardson, can be combined with the almandine data for equilibrium (2), obtained from experiments by Hsu (1968), to give a different set of A and B constants for equilibrium (5). These alternate data are listed as equilibrium (8) in table 6.

APPLICATION OF END-MEMBER EQUILIBRIA

Experimentally determined phase relationships can often be applied to observed mineral assemblages for siliceous carbonate rocks because the

![Fig. 6. Recalculated equilibrium data for the annite experiments of Wones and Eugster (1965).](image-url)
minerals approach the ideal compositions of minerals used in experiments. Rice (1977) has used Temkin solution models or experimentally calibrated activities to adjust carbonate equilibria for fluorsilicates and magnesian calcites. Moore (ms) has applied solution models and end-member equilibria to calculate metamorphic conditions in calc-silicate rocks. The equilibria presented in the previous section cannot be applied directly to natural assemblages. The minerals at the Stall and Anderson Lake mines exhibit considerable solid substitution, and the presence of sulfides indicates the vapor phase, assumed to have been present during metamorphism, consisted of species in the system H–O–S, thus pH₂O was not equal to the total pressure (P₁).

Sample S7 (table 1) from the Stall Lake mine, contains coexisting biotite, muscovite, chlorite, staurolite, sillimanite, quartz, pyrite, pyrrhotite, and magnetite in apparent textural equilibrium. The equilibrium constants in table 6 provide independent equilibrium data for daphnite (1), staurolite (5) or (8), and annite-muscovite (7) (derived from (5) and (4)). These data may be expressed as three equations in four unknown quantities, P₁, T, fH₂, and fH₂O, the general form of which is:

\[
\frac{A}{T} + B + \frac{C(P-1)}{T} = \log (fH₂O^w \cdot fH₂O^h \cdot a^s) \tag{9}
\]

where w, h, and s are the stoichiometric coefficients of water, hydrogen, and Fe–Al silicate, respectively. From studies by Scott (1976) and calculations by Hutcheon (1978), it can be assumed that P₁ = 7 ± 1 kb during metamorphism at Stall Lake. For this estimate of P₁, and silicate activities calculated from microprobe analyses, three equations in T, fH₂, and

![Graph](image-url)

Fig. 7. Equilibrium data for the staurolite experiments of Rutherford (1970).
fH$_2$O can be solved simultaneously for both sets of staurolite data (equilibrium (5) derived from Rutherford, 1970; and equilibrium (8) derived from Richardson, 1968, and Hsu, 1968).

Because many natural silicates contain ferric iron, the activities of the ideal ferrous end-members, necessary for these calculations, cannot be obtained from microprobe analyses. Hounslow and Moore (1967) report Fe$^{3+}$/ΣFe averaging 0.13 (from 0.08 to 0.18) for seven biotite analyses from more oxidizing assemblages than those at Stall Lake, therefore Fe$^{3+}$/ΣFe = 0.1 seems a reasonable estimate for the Stall Lake biotites. Subsequent calculations are performed for Fe$^{3+}$/ΣFe ratios of 0.0, 0.1, and 0.2 to display the effects of varying Fe$^{3+}$ content. It has been assumed that chlorite has the same ferric to ferrous iron ratios as biotite. Griffen and Ribbe (1973) could not detect ferric iron in Mossbauer spectra of natural staurolites, therefore staurolite activities are calculated assuming all iron is in the ferrous state. Temperatures obtained are listed in table 7. Employing the staurolite equilibrium (8), derived from the experiments of Hsu (1968) and Richardson (1968), yields temperatures between 700° and 720°C, higher and in poor agreement with the estimates of Froese and Gasparrini (1975). In a general study of pelitic rocks, Thompson (1976) predicts temperatures of approximately 680°C at 5 kb for the reaction:

ch + st + mu + qz → bi + si + H$_2$O

Partial pressures of H$_2$O range from approx 3900 to 10900 bars depending on the ferrous to ferric ratio assigned and, more drastically,
Table 7
Simultaneous solutions of equilibria (1), (7), and (8) compared to solutions for equilibria (1), (5), and (7)

<table>
<thead>
<tr>
<th>Equilibria</th>
<th>$XFe^2+/\Sigma Fe$</th>
<th>$a^{as}=X^a$</th>
<th>$T°C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) (7) (8)</td>
<td>0.0 $X^0$</td>
<td>712</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 $X^0$</td>
<td>707</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2 $X^0$</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0 $X^2$</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 $X^2$</td>
<td>717</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2 $X^2$</td>
<td>712</td>
<td></td>
</tr>
<tr>
<td>(1) (5) (7)</td>
<td>0.0 $X^0$</td>
<td>1194</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 $X^0$</td>
<td>1102</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2 $X^0$</td>
<td>1014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0 $X^3$</td>
<td>1506</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 $X^3$</td>
<td>1412</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2 $X^3$</td>
<td>1319</td>
<td></td>
</tr>
</tbody>
</table>

on the number of sites assigned for $Fe^{2+}$ mixing in chlorite. The two extremes indicate $\text{pH}_2O$, calculated independently of the $P_t = P_t$ equation, may be between one half to one and one half times the total pressure.

SILICATE–SULFIDE–OXIDE EQUILIBRIA

Because S7 contains pyrite, pyrrhotite, and magnetite at fixed temperature and total pressure, the oxygen and sulfur fugacities are specified by the equilibrium:

$$mt + 1.5S_2 = 3po + 2O_2 (\Delta V_s = 0.2408 \text{ cal/bar})$$

The coexistence of pyrite and pyrrhotite allows the calculation of $fS_2$ and the activity of pure $FeS$ in pyrrhotite at any temperature and pressure, as in Hutcheon (1978). The free energy of formation of pyrrhotite is given by Froese (1976). An equation of the form:

$$\Delta G^°f = a + b \ln T + cT$$

which assumes the change in heat capacity ($\Delta C_p$) is constant, was fitted to the data of Haas and Robie (1973) to obtain:

$$\Delta G^°f = -294317. + 5599.739 \ln T + 66.646 T$$

for the free energy of formation of magnetite at 1 atm. This expression gives $\Delta G^°f$ as 0.01 kcal greater, at 900°K, than the value reported by Haas and Robie (a difference of 0.008 in $\log fO_2$). Using the above information $fO_2$ can be calculated at any pressure and temperature for the assemblage pyrite–pyrrhotite–magnetite.

An additional equation, in which the partial pressures of the gas species ($P_i$) sum to the total pressure ($P_t$), is commonly used in petrologic applications. Sulfur bearing species must be present in the vapor phase, and, as in Eugster and Skippen (1967):

$$P_t = \frac{fH_2O}{\gamma H_2O} + \frac{fH_2}{\gamma H_2} + \frac{fH_2S}{\gamma H_2S} + \frac{fSO_2}{\gamma SO_2} + \frac{fS_2}{\gamma S_2}$$

Calculations by Bachinski (1975), LeCheminant (ms), and the author indicate the species in the above equation are the significant species present.
Sulfide-oxide-silicate equilibria, Snow Lake, Manitoba

The fO₂ and fS₂ obtained for the coexistence of pyrite, pyrrhotite, and magnetite may be used with equilibrium constants for H₂O (Zen, 1973), H₂S and SO₂ (Kubachowski, Evans, and Alcock, 1967), and fugacity coefficients to calculate the composition of the H–O–S vapor at 7 kb and any temperature. For H₂ and H₂O, fugacity coefficients were obtained from previously quoted sources, coefficients for S₂ were obtained from the Redlich-Kwong (1949) equation of state, and J. R. Holloway (personal commun.) provided coefficients for H₂S and SO₂ calculated from the modified Redlich-Kwong equation. Representative values at 600°C and 7 kb are:

\[
\begin{align*}
\gamma_{S_2} &= 6.691 \\
\gamma_{SO_2} &= 16.11 \\
\gamma_{H_2S} &= 8.311
\end{align*}
\]

The general form of the equilibrium constant for each of the silicate equilibria in table 6 is given by eq (9). If fH₂O and fH₂ are calculated using the \( P_t = P_f \) equation and the coexistence of pyrite, pyrrhotite, and magnetite, and the activity of the appropriate Fe–Al silicate is calculated from a microprobe analysis, then \( T \) is the only remaining unknown in the equilibrium constant expression for staurolite, daphnite, and annite–muscovite. Figures 9, 10, and 11 show graphically the solutions obtained for the daphnite (1), annite–muscovite (7), and staurolite (5) or (8) equilibria, as applied to sample S7. To account for the possibility that \( P_f < P_t \) gas compositions coexisting with pyrite, pyrrhotite, and magnetite have been calculated at \( P_t = 7 \) kb and allowing \( P_f \) to decrease in 1 kb increments from 7 to 3 kb.

Figure 9 shows that for the daphnite equilibrium (1), increasing \( \text{Fe}^{3+}/\Sigma\text{Fe} \) by 0.1 raises the temperature by 10°C, whereas lowering \( P_f \) by 1 kb decreases the temperature by 10°C.

Fig. 9. The simultaneous solution of the daphnite equilibrium (1), the py–po–mt equilibrium, and the \( P_f \) equation for sample S7, as described in the text. Calculations assume \( \text{Fe}^{3+}/\Sigma\text{Fe} = 0.0, 0.1, \) or 0.2. The long-dashed curves include the assumption of tetrahedral mixing in chlorite; the short dashed curves show the effect of decreasing \( P_f \) at \( P_t = 7000 \) bars. If \( P_f = P_t \) the equilibrium temperature is 625°C.
Figure 10 demonstrates that the equilibrium temperature for annite–muscovite (7), a function of fO₂ only, is very sensitive to the Fe³⁺ to total Fe ratio. Increasing XFe³⁺ by 0.1 increases the temperature by approx 50°C. This equilibrium is unaffected by decreasing Pₜ. Since the Fe³⁺ to total Fe ratio is probably 0.1 or less (biotites in Hounslow and Moore (1967), average 0.13 for the more highly oxidized assemblage hematite–rutile–pyrite), 625°C is a reasonable temperature estimate. To obtain similar temperatures for the daphnite equilibrium requires Pₜ be approximately equal to Pₜ for similar ferric iron contents. Restricting mixing in chlorite to three sites lowers the temperature by 60°C.

Figure 11 shows the data from Rutherford (1970) for the staurolite equilibrium (5) give temperatures of 700°C or higher, greater than any previous estimates. Equilibrium (8), obtained from the data of Richardson (1968) and Hsu (1968), gives temperatures of 670°C to 675°C for staurolite, approx 50°C higher than previous estimates. It is clear from figure 8 that the staurolite data of Richardson (1968) are not tightly constrained. Because the temperatures obtained using the staurolite equilibria are apparently too high, it is possible to choose an equilibrium curve, through the brackets, that will give lower temperatures. This curve is shown in figure 8 by the dashed line. When the new equilibrium constant (A = −2076578., B = 257.669 for equilibrium (6), table 6) is combined with the amandine data from Hsu (1968), a new set of data is obtained for equilibrium (8) (A = −236986., B = 241.738). When the new data is applied to S7 a temperature of approx 630°C, as shown in figure 11, is obtained for the simultaneous solution with the pyrite–pyrrhotite–magnetite equilibrium. The simultaneous solution of the silicate equilibria (equilibria (1) and (7) in table 6 plus the revised data for staurolite) yield temperatures of approximately 610°C and pH₂O approximately 5800 bars (for XFe³⁺ = 0.1, mixing in daphnite on six octahedral sites).

Uncertainties in calculations.—The uncertainties in the experimental data reported in table 6 are large, primarily because of the necessity of combining equilibria, and therefore accumulating errors. These errors

Fig. 10. The simultaneous solution of annite–muscovite (7) and py–po–mt equilibria and the Pₜ = Pₜ equation for sample S7. Calculations assume Fe⁺⁺/ΣFe = 0.0, 0.1 or 0.2; the long-dashed curves display the effect of assuming tetrahedral mixing in biotite. Equilibrium (7) is a function of fO₂, as specified by po–py–mt and independent of the Pₜ = Pₜ equation. Varying Pₜ does not affect equilibrium (7).
alone will encompass the range of geologically reasonable metamorphic conditions. Although the results reported have a large uncertainty, they are consistent internally and with other estimates of metamorphic conditions at Stall Lake (Froese and Gasparrini, 1975), with estimates for the same assemblage in other areas (Guidotti, 1974), and with general estimates for the reaction of chlorite and staurolite to form biotite and sillimanite (Thompson, 1976).

VAPOR COMPOSITION

The equation that sums the partial pressures of the dominant gas species to the total pressure is commonly used in petrologic problems (Engster and Skippen, 1967; Guidotti, 1974; Rice, 1977). Ohmoto and Kerrick (1977) chose $P_t$ as a variable to demonstrate that $pH_2O$ is not equal to $P_t$ (or $P_o$) for graphite-sulfide bearing pelitic rocks. Figure 12 shows that, assuming $P_t = P_o$, the H-O-S fluid coexisting with pyrite-pyrrhotite-magnetite is dominantly $H_2O$ at $T < 675°C$. The surface $pH_2 + pH_2O = P_t$ is shown in figure 13 at a total pressure of 5 kb for all possible two-mineral combinations of pyrite, pyrrhotite, and magnetite. The $pH_2 + pH_2O$ surfaces for pyrite-magnetite and pyrite-pyrrhotite deviate significantly from the $P_t$ surface. The increase in $fS_2$ necessary to bring these assemblages to equilibrium causes an increase in $fSO_2$ and a decrease in $fH_2O$, allowing dehydration equilibria to be stable at lower temperatures. The $pH_2 + pH_2O$ surface for pyrrhotite-magnetite or pyrite-pyrrhotite-magnetite is close to the $P_t$ surface, and the stability of dehydration equilibria should not be affected.

SULFIDE–SILICATE EQUILIBRIA

Sample A7, from the Anderson Lake mine (fig. 1), contains pyrite and pyrrhotite, with no magnetite, in addition to staurolite, sillimanite,
kyanite, chlorite, biotite, muscovite, and quartz. Figure 13 shows that pH₂ + pH₂O is less than P₄ for pyrite-pyrrhotite bearing rocks. The coexistence of pyrite and pyrrhotite fixes fS₂ and a^FeS at any temperature and pressure. The equilibrium:

\[ \text{mt} + 1.5S₂ = 3po + 2O₂ \]  

(10)
can be combined with equilibrium (7) and the dissociation of water (Zen, 1973) to obtain:

\[ \text{an} + \text{si} + 1.5S₂ = \mu = 3po + 1.5O₂ \]
\[ \log K_{11} = 3\log a^\text{FeS} + 1.5\log fO₂ - 1.5\log fS₂ - \log a^\text{an} \]  

(11)
Since \( \log K_{11} \) is known and \( a^\text{FeS} \) and \( fS₂ \) are specified by the coexistence of pyrite and pyrrhotite, if \( a^\text{an} \) is calculated from a microprobe analysis, then \( fO₂ \) can be calculated. This procedure has been applied to sample A7 using the \( P₄ = P₄ \) equation to calculate \( fH₂O \). Equilibria (1) and (8) can be combined to give:

\[ 3\text{da} + 30.75\text{si} = 1.875\text{st} + 11.625\text{qz} + 4.5H₂O \]
\[ \log K_{12} = 4.5 \log fH₂O + 1.875 \log a^\text{st} - 3\log a^\text{da} \]  

(12)
Using microprobe analyses of staurolite and chlorite from sample A7 \( a^{st} \) and \( a^{da} \) can be calculated, and since \( \log K_{12} \) is known another value of \( \log fH₂O \) can be calculated at any pressure and temperature. The simultaneous solutions of equilibria (11) and (12) are shown in figure 14 with the equilibrium curve for the staurolite data for equilibrium (8) calculated as passing through the mid-points of the brackets and, alternately, passing close to the low temperature brackets. Using a six-site solution model for daphnite, temperature estimates are approximately 590°C for the staurolite curve passing through the mid-points of brackets and 625°C, if the staurolite equilibrium curve is placed close to the low tem-
temperature brackets. As shown in figure 14 variations in $P_t$ and $XFe^{3+}$ have a minimal effect on the equilibrium temperature, and the vapor is dominated by $H_2O$.

**SUMMARY AND CONCLUSIONS**

Microprobe analyses of staurolite, biotite, and chlorite indicate these minerals are relatively iron-poor, when they coexist with opaque assemblages stable at relatively high sulfur fugacities. Iron is replaced by magnesium in chlorite and biotite and by zinc in staurolite. Up to 5.2 wt percent ZnO was found in staurolite, and, contrary to the findings of Guidotti (1974), increasing zinc content in staurolite is related to decreasing Fe/Mg ratios of coexisting biotite and chlorite.

**Fig. 14.** The simultaneous solution, for sample A7, of the sulfide-silicate equilibrium (11) for annite-muscovite and the daphnite-staurolite equilibrium (12), with the solid curves displaying the effect of variations in $P_t$. Variation in $Fe^{3+}/\Sigma Fe$ is shown for 0.0 and 0.2. The long-short dashed curves are for the equilibrium curve through the lower temperature side of brackets in experiments by Richardson (1968).
End-member equilibria for daphnite, staurolite, and annite-muscovite, in the system K-Fe-Al-Si-O-H were solved simultaneously using the staurolite data derived from experiments by Rutherford (1970), Richardson (1968), and Hsu (1968). Temperatures obtained using the data of Rutherford are much higher than other estimates derived in this study and estimates by other authors of metamorphic conditions in the same area or for the same assemblage. An equilibrium curve, which passes through the midpoints of brackets in staurolite experiments by Richardson (1968), gives metamorphic temperatures approx 50°C higher than estimates using other equilibria or estimates published by other authors. Selecting an equilibrium curve close to the low temperature brackets in the same experiments produces temperatures of approx 610°C, in better agreement with other results.

The simultaneous solution of the $P_f = P_t$ equation, the pyrite-pyrrhotite-magnetite equilibrium, and each of the silicate equilibria provides a test of the consistency of the silicate data. The annite-muscovite equilibrium predicts temperatures of 600° to 650°C and is very sensitive to changes in $a^m$ but insensitive to $P_t$ changes. Using a six-site solution model the daphnite equilibrium predicts temperatures of approximately 625°C, for $P_f$ approximately equal to $P_t$, and in general agreement with the annite-muscovite equilibrium. Decreasing $P_t$ or using a three-site solution model yields lower temperatures. The staurolite experiments of Rutherford (1970) again give high temperatures (approx. 700°C). Selecting the low temperature equilibrium curve for experiments by Richardson (1968) produces temperatures in agreement with daphnite and annite-muscovite experiments. An equilibrium curve which passes through the midpoints of the brackets in experiments by Richardson gives temperatures of 710°C. These data are still at variance with the annite-muscovite data. Accepting the lower temperature equilibrium curve for staurolite experiments gives results in agreement with annite-muscovite and daphnite equilibria which indicates the temperature during metamorphism at Stall Lake was approximately 625°C and $P_t$ was approximately equal to $P_f$.

Fluids coexisting with pyrite-pyrrhotite-magnetite or pyrrhotite-magnetite are dominated by H$_2$O below 675°C at 7 kb. Fluids coexisting with pyrite-magnetite or pyrite-pyrrhotite may contain much higher amounts of SO$_2$, and H$_2$O may be a minor constituent, depending on the fugacity of sulfur.

Application of sulfide-silicate equilibria to a sample from the Anderson Lake mine which contains pyrite-pyrrhotite, without magnetite, gives temperatures of 620°C and indicates $p$H$_2$O was slightly less than $P_f$, if the lower temperature staurolite data from Richardson (1968) are used.

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