American Journal of Science

JUNE 1973

EQUILIBRIA IN THE SYSTEM Al₂O₃–SiO₂–H₂O
IN INVOLVING THE STABILITY LIMITS OF
PYROPHYLITE, AND THERMODYNAMIC
DATA OF PYROPHYLITE

HERBERT HAAS and M. J. HOLDAWAY
Department of Geological Sciences,
Institute for the Study of Earth and Man,
Southern Methodist University, Dallas, Texas 75275

ABSTRACT. The upper stability limit of pyrophyllite was calculated according to
the two stable reactions:

\[ \text{1 pyrophyllite} + 6 \text{ diaspore} \rightleftharpoons 4 \text{ kyanite} + 4 \text{ water} \]

and

\[ \text{1 pyrophyllite} \rightleftharpoons 1 \text{ kyanite} + 3 \text{ quartz} + 1 \text{ water} \]

For the first reaction with excess alumina the equilibrium curve passes through
the points 2.5 kb at 364°C and 7 kb at 398°C. For the second reaction with excess
silica the equilibrium is at 2.5 kb and 384°C and at 7 kb and 419°C. In this pressure-
temperature range diaspore is the stable form of aluminum oxide. The first step in
this investigation was to determine experimentally pressure-temperature data on the
reactions:

\[ \text{1 pyrophyllite} + 6 \text{ diaspore} \rightleftharpoons 4 \text{ andalusite} + 4 \text{ water} \]

\[ \text{1 pyrophyllite} \rightleftharpoons 1 \text{ andalusite} + 3 \text{ quartz} + 1 \text{ water} \]

in the range of 2.4 to 7 kb and 320° to 460°C. Under these conditions andalusite is
metastable with respect to kyanite, but no difficulties occurred in the use of andalusite
single crystals as reaction detectors.

Thermodynamic data for these experimental equilibrium curves and for pyro-
phyllite in the range of 298° to 800°K were derived. These data allowed calculation
of the stable reaction boundaries involving kyanite.

The stable occurrence of pyrophyllite is limited to aluminous pelitic assemblages
in the lower half of the greenschist facies.

THE PROJECT

The stable occurrence of pyrophyllite is limited on the high temperature side by the following four reactions:

\[ \text{1 pyrophyllite} + 6 \text{ diaspore} \rightleftharpoons 4 \text{ kyanite (or andalusite)} + 4 \text{ water (PDKW or PDAW)} \]

\[ \text{1 pyrophyllite} \rightleftharpoons 1 \text{ kyanite (or andalusite)} + 3 \text{ quartz} + 1 \text{ water (PKQW or PAQW)} \]

Theoretically two more reactions are possible:

\[ \text{1 pyrophyllite} + 3 \text{ corundum} \rightleftharpoons 4 \text{ kyanite (or andalusite)} + 1 \text{ water (PCKW or PCAW)} \]

In nature these last two reactions are not likely to take place, since corundum is metastable and does not occur in the range of pyrophyllite
stability (Haas, 1972).
The abbreviations shown in parentheses will be used in future reference to these reactions. The following mineral formulae apply to the above balanced reactions:

- **Pyrophyllite** \( \text{Al}_2(\text{Si}_4\text{O}_{10})\text{(OH)}_2 \)
- **Andalusite, kyanite** \( \text{Al}_2\text{SiO}_5 \)
- **Diaspore** \( \text{AlO(OH)} \)

The stability field of pyrophyllite has been studied previously with differing results given in several studies. In the following sections a short recapitulation will be given of the more recent reports in which the field of stability of pyrophyllite was the principal subject of investigation. Results, reagents, and techniques used are reported here.

Matsushima and others (1967) determined the pyrophyllite \( \Leftrightarrow \text{sil}-\text{limanite} + \text{quartz} \) equilibrium at 6.5 kb and 535°C and the PCKW equilibrium at 7 kb and 520°C. More equilibrium data at pressures up to 55 kb are also reported. The equipment used was a piston-cylinder apparatus; the runs lasted 10 hours or less. Starting materials were produced by synthesizing the various minerals at high temperatures and pressures.

Althaus (1969) has determined the PAQW equilibrium at 6.9 kb and 513°C and 2 kb and 487°C. He reports the PKQW equilibrium at 7 kb and 512°C. The experiments were performed in a hydrothermal apparatus and lasted between 20 and 70 days. The starting materials were natural minerals which were ground for many hours in a ball mill, in some cases to submicron size. X-ray peak broadening was observed after the intensive grinding. The results were detected by X-ray diffraction techniques.

The PAQW and PKQW equilibrium curves must intersect at the andalusite-kyanite boundary. From data for andalusite and kyanite available in Robie and Waldbaum (1968) one can calculate the difference in slope between the two equilibrium curves, and it is approximately 9° per kilobar in the range between 5 and 7 kb. According to andalusite-kyanite equilibrium data by Althaus (1969), the PAQW and PKQW curves would intersect at 5 kb. More recent studies by Holdaway (1971) would place this intersection nearer to 4 kb. From the above calculation, it follows that at 7 kb the two equilibria, PAQW and PKQW, should be apart by a minimum of 18°, but according to Althaus' data they differ by only about 2°.

Velde and Kornprobst (1969) located the PAQW equilibrium at 1 kb between 486° and 492°C and at 2 kb between 486° and 505°C. A standard hydrothermal apparatus was used with run durations from 46 to 63 days. As starting materials, artificial or natural minerals and precipitated gels were used. Only two of the reported runs initially contained all three mineral phases. The products were examined by X-ray techniques. The authors indicate for several of the experiments that pyrophyllite was affected by small changes only.
Hemley (1967) determined an equilibrium point for the PAQW equilibrium at 1 kb and 400°C. This result was based on aqueous silica concentration measurements. Additional details of technique are not given.

Kerrick (1968) reported two equilibrium points for the PAQW reaction: 430°C at 3.9 kb and 410°C at 1.8 kb. Hydrothermal equipment was used, runs lasted 14 days, starting materials were 43 μm powders and single crystals of andalusite or quartz, the reaction was detected by recording weight changes of these crystals. The reaction could be reversed with both types of crystals, and the two sets of results agreed well.

Most of these studies suffer from one or more experimental inadequacies, for example:

1. Equilibrium was not achieved due to short duration of runs (Matsushima and others, 1967).

2. Unstable reagents were used, such as amorphous oxides and gels, or minerals that were severely ground to powder in μm size or smaller, inducing strain in the grains (Velde and Kornprobst, 1969; Althaus, 1969).

3. Detection of the reaction was based solely on X-ray diffraction techniques which are insensitive and often fallacious for quantitative analysis of sheet silicates (Matsushima and others, 1967; Althaus, 1969; Velde and Kornprobst, 1969).

4. After the experimental work the results were not checked sufficiently to ascertain that they were thermodynamically reasonable (most studies).

In studies subject to criticisms (1) or (2), a synthesis field for pyrophyllite may have been established rather than an equilibrium field.

In the present study the equilibria PDAW and PQAW were experimentally determined. The initial problems presented themselves as follows: (A) It was not known which form of aluminum oxide, diaspore or corundum, is stable in the pressure-temperature range of the study. (B) It is difficult to work with kyanite as a reagent. Kyanite cannot be ground into usable single crystals, and it reacts only very slowly. (C) Andalusite is stable only in the lowermost portion of the pressure-temperature field in which this study was performed.

These difficulties were solved or circumvented as follows:

A. The diaspore-corundum stability field was determined experimentally, and thermodynamic parameters for diaspore were calculated (Haas, 1972). The conclusion is that diaspore is stable in the whole experimental range of the present project.

B. Single crystals of andalusite were used metastably at all experimental pressure and temperature values; that is, in the large region where kyanite is stable. This method was successful since andalusite never reacted to kyanite in any of the experiments.

The reaction PCAW contains, within the experimental range, the metastable minerals andalusite and corundum. Nevertheless, it would be useful to have some equilibrium data on this phase boundary, since
calculations based on this curve can serve as a check on results obtained from other equilibrium curves. A number of experiments were performed on this reaction, but every experiment made within the stability field of diaspare was unsuccessful since the corundum started to convert spontaneously to diaspare; this observation was used in the study on the diaspare-corundum equilibrium (Haas, 1972).

THE EXPERIMENTAL WORK

Equipment used.—The equilibrium temperatures of the reactions studied here were determined experimentally at 2.4, 3.5, 4.8, and 7.0 kb. All experiments were carried out in externally heated rod bombs. At 7.0 kb, pressure was generated with a Harwood 3-stage gas compressor using nitrogen gas. Pressure was monitored continuously with a manganin cell connected to a chart recorder. In addition, the pressure was measured daily with a Harwood compensating bridge. At all other pressures from 2.4 to 4.8 kb, water was used as pressure medium. The desired pressure was generated with hand-operated pumps and a pressure intensifier and was measured with a Bourdon type gauge (Heise, 0-100,000 PSI) connected to the high pressure line. The rod bombs were heated in cylindrical furnaces controlled by Honeywell Versa-Tronik controllers. The tolerances that must be attributed to all pressure and temperature values are as follows: Pressure ± 2 percent, temperature ± 5°C. The temperature gradient within the bombs over the length of the actual charge (crystal + powder + water in silver capsule) is 1° to 2°C depending on the geometry of the bomb used. To obtain the smallest possible temperature error, one rod bomb of each design used in the project was calibrated for its thermal gradient with a matched pair of thermocouples. The thermocouples used for the daily measurements of the bomb temperatures were calibrated against a Leeds and Northrup standard Pt-Pt + 10 percent Rh thermocouple. The bomb calibrations and some of the thermocouple calibrations were repeated by Holdaway giving results within 2° of those made by Haas.

Starting materials and their preparation.—Origins and chemical analyses of the reagents used in this project are given in table 1. The powders of pyrophyllite, diaspare, and quartz were ground to less than 200 or 325 mesh size (74 or 43 µm) and elutriated to remove any ultrafine particles which may stick to the powder grains of the desired size. Andalusite was ground into single crystals weighing about 50 mg. Since andalusite has no prominent cleavage, chipping of the ground crystals during the experiments was rare. However, the grinding process may have caused lattice distortion in the outermost surface layer of the crystal.

This skin of distorted andalusite unit cells seems to be less stable or more reactive than the undisturbed mineral, since every freshly ground crystal showed an initial weight loss that was no longer observed when the freshly ground crystals were etched in dilute HF (20 to 25 percent) until a weight loss of about 200 µg occurred. Later all crystals were routinely etched before being used the first time or before being reused.
Chemical analyses and origins of minerals used in experimental studies

<table>
<thead>
<tr>
<th></th>
<th>Andalusite</th>
<th>Pyrophyllite</th>
<th>Diaspore</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>37.1</td>
<td>63.53*</td>
<td>0.78</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>62.1</td>
<td>27.81*</td>
<td>82.91</td>
</tr>
<tr>
<td>Fe₂O₄**</td>
<td>0.38</td>
<td>0.12</td>
<td>0.43</td>
</tr>
<tr>
<td>CaO</td>
<td>n.a.</td>
<td>0.16</td>
<td>0.35</td>
</tr>
<tr>
<td>Na₂O</td>
<td>n.a.</td>
<td>0.29</td>
<td>0.06</td>
</tr>
<tr>
<td>K₂O</td>
<td>n.a.</td>
<td>0.07</td>
<td>0.13</td>
</tr>
<tr>
<td>MgO</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>—</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Total</td>
<td>99.6</td>
<td>92.00</td>
<td>84.67</td>
</tr>
<tr>
<td>H₂O</td>
<td>—</td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>

* Atomic absorption analyses are 62.12% for SiO₂ and 29% for Al₂O₃. These are probably less accurate than the tabulated X-ray fluorescence values.

** Total Fe calculated as Fe₂O₄.

n.a. = not analyzed

Origins: Andalusite: Minas Gerais, Brazil
Pyrophyllite: Monoclinic Form
Indian Gulch, Calif.
Diaspore: Chester, Mass.
Quartz: Hot Springs, Ark.

Tabulated analyses were made with an atomic absorption spectrophotometer with the exception of SiO₂ and Al₂O₃ data for pyrophyllite, which were obtained with X-ray fluorescence. We consider the analyses to be accurate to ± 1 to 2% of the amount present.

An experimental study made with freshly ground crystals would yield too high an equilibrium temperature.

Demonstration of reliability of experimental results.—In order to demonstrate further that initial weight losses do not occur with etched andalusite crystals, series of experiments were made in which the crystal was removed for reweighing after the following time intervals: 2, 2, 4, 8, and 16 days. These experiments were performed at 410°C and 2.4 kb and included also the minerals pyrophyllite and corundum. At the end of the intervals the following total weight gains were registered: 4, 8, 14, 20, 27, 38 μg. The experimental series was repeated with another andalusite crystal, and matching results were achieved.

In addition to excluding initial weight loss as a limiting factor for the experimental technique, these experimental series also exclude the possibility of a quench product being the source of the weight gains, since the weight increase due to a quench precipitate would not be time dependent. Several crystals were examined under the scanning electron microscope with the expectation that growth of andalusite could be detected on the etch pattern. However, no such growth could be detected with certainty, but at the same time no other foreign matter such as quench precipitates could be observed.

A further check for presence of quench products on crystals that gained weight during a run was made with short duration (10-30 sec) HF etching after the experiment. The small weight loss observed was
compared with the weight loss occurring with similar etching of new crystals. It was the same in both kinds of crystals, indicating that no easily dissolvable coating of the crystals was produced during or at the end of a run. The similarity in solution rate of all crystals strongly suggests that growth was also andalusite.

**Experimental procedure.**—For each experiment the charge consisted of the andalusite crystal plus powders of the other two minerals involved in the reaction under study; that is, for the reaction PDAW, 25 mg pyrophyllite and 25 mg diaspor, and for the reaction PAQW, 35 mg pyrophyllite and 15 mg quartz. The charge was placed in a silver capsule, 50 mg of water was added, and the capsule sealed by fusion welding. In most cases this capsule was placed in a larger silver tube and surrounded with hematite-magnetite buffer. However, later comparisons with results achieved with unbuffered runs showed that the buffer had no influence on the reaction due to the low iron content of the system.

A typical experiment lasted 30 days at pressures of 2.4, 3.5, and 4.8 kb. At 7.0 kb 8 days were sufficient to achieve a significant weight change of the andalusite crystal. Rate and direction of the reaction were determined by weighing the andalusite crystals before and after each experiment. Weighings were performed on a Mettler M-5 microbalance. Each crystal was weighed a minimum of six times in a sequence with reference weights at the upper and lower ends of the optical scale. The average of these weighings was reproducible to within $\pm 2.5$ $\mu$g; this tolerance was established by reweighing reference crystals regularly over the whole duration of the experimental phase of this study.

While the emphasis in this investigation was on gaining equilibrium data with the single crystal method, an attempt was made to confirm the results with a different approach. A number of all-powder runs were made involving reactions PDAW and PDKW. These experiments were run for the same duration as the single crystal runs, and the same powder sizes were used as previously described. In each powder run two phases of the reaction under study made up the bulk of the charge, and the third mineral, diaspor, andalusite, or kyanite, was added in seed quantity; that is, 2 percent if the reaction was to be detected by optical microscopy and 10 percent for detection by X-ray diffraction patterns. The following difficulties were encountered: (1) diaspor, when stable, will nucleate freshly rather than form overgrowth on present seed grains; (2) definite reaction trends can be seen only when the experiment is performed 15$^\circ$ or more from the equilibrium temperature; 3) kyanite reacts too slowly to enable detection of the reaction trend with certainty.

**Results.**—Considering the above restrictions, the results gained with powder experiments can be summed up as follows: the majority of powder runs support the results from the single crystal investigations. Only a few powder results stand in contradiction to all other data and are considered experimental failures, since they may occur in any portion of the temperature-pressure fields and may have been caused by an undetected microleak in the silver capsule. As a final comment to the
powder experiments, it can be said that this method largely supports the single crystal results but is much less precise.

The experimental results by the crystal method are shown in figure 1 for the reaction PDAW and in figure 2 for the reaction PAQW. These figures show for each experimental pressure the weight gains or losses of the andalusite crystals as recorded after each experiment. The weight changes recorded at each pressure can be read from the $\mu g$ scales at the right margin of the figures. The ordinate represents the pressure scale of these pressure-temperature diagrams. Each data point was determined

![Pressure-temperature diagram](image)

**Fig. 1.** Pressure-temperature diagram for the reaction pyrophyllite + diaspore yielding andalusite + water. Equilibrium experimentally determined at 2.4 kb and 366°C, 3.5 kb and 386°C, 4.8 kb and 408°C, 7.0 kb and 445°C. Heavy lines at each pressure represent possible temperature errors based on experimental data. Solid squares indicate weight gains or losses of andalusite single crystals. More details on these are given in the text.
at the pressure signified by the zero weight-change line to which it is connected.

At low pressures and temperatures the reaction rates become very small, and changes in the reagents drop below the detection limit. In the PDW reaction, this is the case for all experiments below 330°C at 2.4 kb. A reaction of unknown nature may have caused the few scattered weight gains. A number of experiments were performed at 1.75 kb, but no meaningful results could be gained from them. In the PAQW reaction, the detection limit is reached at 2.4 kb and 380°C. Again no explanation can be offered for spurious weight gains. In both reactions the equilibrium temperature at 2.4 kb was estimated by ex-

![Pressure-temperature diagram](image)

Fig. 2. Pressure-temperature diagram for the reaction pyrophyllite yielding andalusite + quartz + water. Equilibrium experimentally determined at 2.4 kb and 378°C, 3.5 kb and 398°C, 4.8 kb and 421°C, 7.0 kb and 459°C. Heavy lines at each pressure represent possible temperature errors based on experimental data. Solid squares indicate weight gains or losses of andalusite single crystals. More details on these are given in the text.
tending a line through weight gains at higher temperatures downward to the zero weight-change line. This procedure resulted in the large error fields shown in figures 1 and 2 at 2.4 kb. At higher pressures the zero weight-change line is clearly crossed, demonstrating reversibility of the pyrophyllite stability reactions.

At the end of the experimental work, the writer performed a test experiment with a triclinic pyrophyllite from New Zealand which was kindly furnished by G. W. Brindley and has been described by Brindley and Wardle (1970). This test experiment was performed with the reaction PDAW at 4.8 kb and 409.5°C, and the single crystal of andalusite gained 8.8 μg. In an earlier experiment at 411°C and at the same pressure but with the monoclinic Indian Gulch pyrophyllite in the charge, the andalusite crystal had gained 9.0 μg. Thus the different source for pyrophyllite is most probably not the reason for the scatter of equilibrium temperatures as they were reported by the various workers listed in the introduction of this study. However, the degree of purity of the pyrophyllite used could affect the experimental results. The pyrophyllite used in this study has been purified by numerous heavy-liquid and magnetic separations, and no corundum, quartz, or other aluminum silicate contaminant was present after purification.

THE THERMODYNAMIC DATA FOR PYROPHYLLITE

The results of all calculations are presented in tables 2 and 3. Thermodynamic data for andalusite, quartz, corundum, and water at 1 bar were taken from Robie and Waldbaum (1968), for water at high pressure and temperature from Burnham, Holloway, and Davis (1969) and from Fisher and Zen (1971), for diaspor from Haas (1972). The thermal expansion of the minerals has been considered in the present calculations, and the necessary data for andalusite, corundum, and quartz were taken from tabulations by Skinner (1966), and for pyrophyllite from a report by Taylor and Bell (1969). The thermal expansion of diaspor or similar hydrate minerals for comparison is not known and as a best approximation was assumed in these calculations to be equal to that of corundum. Compressibilities as a function of temperature and pressure are not known for the phases involved, and the changes in ΔV of reactions due to this are ignored.

The entropy for pyrophyllite was obtained from the slopes of the experimentally determined reaction curves PDAW and PAQW using the relation dP/dT = ΔS/ΔV. The two reactions yielded two different sets of entropy values. The first set, calculated from the PDW equilibrium curve, falls close to the entropy calculated by addition of the oxide entropies and is 139.8 cal/deg at 700°C. In this oxide summation the entropy of H₂O was taken as that of ice as plotted by Fye, Turner, and Verhoogen (1958, p. 118). The second set of pyrophyllite entropy values is derived from the PAQW equilibrium and is about 9 cal/deg lower than the first set and falls close to a curve obtained by addition of the oxide entropies minus a correction of 0.6 cal/deg per cm³ volume change.
Table 2
Thermodynamic properties of pyrophyllite Al₂O₃ · 4SiO₂ · H₂O

<table>
<thead>
<tr>
<th>°K</th>
<th>S° cal</th>
<th>ΔG°r kcal*</th>
<th>ΔG°r kcal**</th>
<th>ΔG°r kcal***</th>
<th>ΔH°r kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>61.23 ± 5</td>
<td>-1257.7 ± 0.35</td>
<td>-1259.4 ± 0.35</td>
<td>-1257.4 ± 0.35</td>
<td>-1345.4 ± 2.5</td>
</tr>
<tr>
<td>400</td>
<td>83.41</td>
<td>-1227.5</td>
<td>-1229.1</td>
<td>-1227.1</td>
<td>-1345.8</td>
</tr>
<tr>
<td>500</td>
<td>102.94</td>
<td>-1197.9</td>
<td>-1199.4</td>
<td>-1197.5</td>
<td>-1345.9</td>
</tr>
<tr>
<td>600</td>
<td>120.17</td>
<td>-1168.3</td>
<td>-1169.7</td>
<td>-1167.8</td>
<td>-1345.2</td>
</tr>
<tr>
<td>700</td>
<td>135.10</td>
<td>-1138.6</td>
<td>-1140.1</td>
<td>-1138.2</td>
<td>-1344.5</td>
</tr>
<tr>
<td>800</td>
<td>148.39</td>
<td>-1109.0</td>
<td>-1110.4</td>
<td>-1108.5</td>
<td>-1343.7</td>
</tr>
</tbody>
</table>

S° Third law entropy.
ΔG°r Free energy of formation from the elements
* Based on PAQW experimental results.
** Based on PDGW experimental results.
*** Based on ΔG°r andalusite made less negative by 475 cal (see text, p. 459). Values at 400° to 600° and 800°K obtained by linear interpolation.

ΔH°r Heat of formation from elements, based on data in ΔG°r*** column.
Reference state for ΔG°r and ΔH°r is the elements in their standard state at 1 bar pressure and the stated temperature. Tolerances apply to the results of this study only and do not include the uncertainties of the various mineral and water data.

Table 3
Free energy of pyrophyllite based on the oxides

<table>
<thead>
<tr>
<th>°K</th>
<th>ΔG°r*</th>
<th>ΔG°r**</th>
<th>ΔG°r***</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-6.4 kcal</td>
<td>-8.1</td>
<td>-6.1</td>
</tr>
<tr>
<td>400</td>
<td>-2.6</td>
<td>-4.2</td>
<td>-2.2</td>
</tr>
<tr>
<td>500</td>
<td>-0.7</td>
<td>-0.9</td>
<td>-1.1</td>
</tr>
<tr>
<td>600</td>
<td>+4.2</td>
<td>+2.7</td>
<td>+4.7</td>
</tr>
<tr>
<td>700</td>
<td>+7.9</td>
<td>+6.5</td>
<td>+8.4</td>
</tr>
<tr>
<td>800</td>
<td>+11.7</td>
<td>+10.4</td>
<td>+12.2</td>
</tr>
</tbody>
</table>

* Based on PAQW experimental results.
** Based on PDGW experimental results.
*** Based on ΔG°r andalusite made less negative by 475 cal (see text, p. 459).

for the reaction from the oxides, a procedure suggested by Fyfe, Turner, and Verhoogen (1958, p. 34). This discrepancy of 9 cal/deg is not unrealistic considering possible experimental errors and errors in the entropy of other minerals. Since no experimental or theoretical consideration seems to give a reason for preferring one set of entropy data over the other, the average was assumed to be the best approximation to the true value and was used as a basis for the generation of further thermodynamic data.

Pyrophyllite entropy in the same temperature range may also be calculated from the data of Hemley (1967) and Kerrick (1968). A curve drawn through the equilibrium points given by these authors yielded entropies in the range from 113 to 106 cal/deg decreasing with temperature increase. A flatter equilibrium curve can be drawn within the indicated experimental error range, and the slope of the corresponding entropy-temperature curve becomes positive, but entropy values remain about 17 cal/deg lower than the adopted average value of this report.

The 298°K entropy was estimated previously by Fonarev (1967) and Zen (1969) and was predicted to be 63.3 cal/deg. This estimate was
based on additivity of oxide entropies or on a formula involving the molecular weight of the mineral and on comparison of these parameters with structurally similar minerals such as muscovite and talc. This same analogy is used here, but with the added advantage that the entropy data can now be compared also in the range of temperatures from 600 to 750°K. These oxide entropy summations, including the corrections for the $\Delta V$ of reaction, predict entropies that deviate from the real mineral entropies listed in Robie and Waldbauaum (1968) as follows, shown here as predicted minus real value, in cal/deg:

Muscovite: $-0.38$ at 298°K, $+3.19$ at 700°K

Talc: $+5.03$ at 298°K, $+8.35$ at 700°K

The increase of the deviation from the low to the high temperature comparison is 3.57 cal/deg for muscovite and 3.32 cal/deg for talc. One may assume a similar increase for pyrophyllite and use an estimated value of 3.5 cal/deg. The averaged entropy of pyrophyllite at 700°K is 0.5 cal/deg below the predicted value and will thus be 3.0 cal/deg above the predicted value of 58.2 cal/deg at 298°K. This procedure yields an entropy of 61.2 cal/deg at 298°K.

The $\Delta G^o_f$ of pyrophyllite was calculated from both reactions, PAQW and PDAW, at experimental temperatures and at 298°K, using standard calculations, respectively water data tabulations and equations suggested by Fisher and Zen (1971)$^1$.

Standard pyrophyllite free energy values from the two reactions (table 2) differ from each other by a consistent 1.5 kcal, the PDAW values being more negative. Shifting the two equilibrium curves within experimental error does not bring the $\Delta G^o_f$ values together. Of the phases involved in the reaction, andalusite has the most probability for error. One might make the assumption that the error is caused by an incorrect andalusite free energy and solve the coupling reaction for a new andalusite value. Such a procedure gives an andalusite value that is 475 ± 215 cal$^2$ less negative than that given by Robie and Waldbauaum (1968) and Holdaway (1971). Pyrophyllite free energy values given in table 2, column (3) are based on this less negative andalusite free energy and are consistent with both the PDAW and the PAQW reactions.

The pyrophyllite enthalpy given in table 2 was determined from the free energy of column (3) and the accepted entropy values. Free energy of pyrophyllite from the oxides is given in table 3.

One of the important results of this study is that an andalusite free energy which is significantly lower than that accepted by Robie and Waldbauaum (1968), Holdaway (1971), and Weill (1966) is useful to give internal consistency between the two pyrophyllite stability curves. Table 4 shows several recent determinations of andalusite free energy from the

---

$^1$ The product $\Delta S_{f,3} \cdot \Delta T$ used in the $\Delta G^o_f$ 298° calculation was obtained from a large $\Delta S_{f,3} = f(\gamma)$ plot by integrating its surface.

$^2$ This tolerance includes only experimental errors.
Table 4
Free energy of formation of andalusite from oxides at 298°K based on several methods

<table>
<thead>
<tr>
<th>Source</th>
<th>$\Delta G^\circ$ from oxides, kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovite coupling reaction</td>
<td>1.06 ± 0.60</td>
</tr>
<tr>
<td>Weill (1966), used by Holdaway (1971)</td>
<td>1.42 ± 0.25*</td>
</tr>
<tr>
<td>Robie and Waldbaum (1968)</td>
<td>1.41 ± 0.72</td>
</tr>
<tr>
<td>Shearer and Kleppa (1972)</td>
<td>0.29 ± 0.17</td>
</tr>
<tr>
<td>Pyrophyllite coupling reaction</td>
<td>0.93 ± 0.22</td>
</tr>
</tbody>
</table>

* Estimated error

oxides, all adjusted to 298°K. The calorimetric result of Shearer and Kleppa (in press) on sillimanite has been converted to an equivalent andalusite value using the phase diagram of Holdaway (1971). The muscovite coupling reaction approach is that of Evans (1965), modified by the more recent muscovite-quartz stability data of Althaus and others (1970). In the calculation the separation between the muscovite and muscovite-quartz stability curves was assumed to be 60 ± 35°C, and the $\Delta S$ of the muscovite stability curve was assumed to be 17 cal/deg. The result of the present study agrees well with that determined from the muscovite reactions and is intermediate between the other values given.

The phase diagram shown in figure 3 illustrates mainly the stable phase boundaries PDKW and PKQW. These two curves have been calculated from the $\Delta S$ and $\Delta V$ of reaction and were assumed to intersect the PDAW and PAQW curves on the andalusite-kyanite curve of Holdaway (1971). In order to achieve better consistency within the slope calculations for the silica-rich or the alumina-rich assemblage, each of these calculations has been made with the pyrophyllite entropy data that were derived from the corresponding reaction involving andalusite; that is, the pyrophyllite entropy determined from the PAQW equilibrium was entered into the slope calculation for the PKQW equilibrium. In order to obtain a realistic estimate for the maximum deviation of the PKQW and PDKW curves two more slope calculations were made for each reaction in which the pyrophyllite entropy was allowed to vary to a maximum and to a minimum value consistent with the experimental error range. The averaged entropy corresponds to this maximum value for the PAQW reaction and to the minimum value for the PDAW reaction. For the PKQW curve the following equilibrium points were determined: 2.5 kb and 384°C, 7 kb and 419°C. A calculation made with the averaged entropy for pyrophyllite would shift the equilibrium at 7 kb to 426°C. For the PDKW curve the equilibrium points are at 2 kb and 359°C and at 7 kb and 398°C. Entering the averaged entropy into the calculation would lower the 7 kb equilibrium to 393°C.

At 2.4 kb the experimental error is estimated at ± 7°C for the PAQW reaction and at ± 6°C for the PDAW reaction. A positive tem-
temperature shift in either of these equilibrium points will steepen the PDKW or the PKQW curve and compensate for the temperature shift at about 7 kb. A possible experimental error will not accumulate into an even larger error in the calculated curves. Thus the total temperature error of these curves does not exceed ± 8°.

The PKQW and PDKW curves were also calculated using standard free energy data for pyrophyllite (table 2, column 3) and the standard free energy data of Holdaway (1971) for kyanite made less negative by 475 cal as well as data for the other minerals as given above. The results agree well with the calculations based on ΔS and ΔV.

The diagram (fig. 3) shows metastable equilibria as dashed curves. Two of them are the experimentally determined PDAW and PAQW reactions. Also shown is the PCAW reaction that could not be deter-

![Phase diagram illustrating all reactions described in the text. Abbreviations: And = andalusite, Co = corundum, Dia = diaspore, Ka = kaolinite, Ky = kyanite, Py = pyrophyllite, Qtz = quartz. Heavy lines: stable reactions; dashed lines: metastable reactions; fine lines: reactions determined in other studies cited in the text.](image-url)
mined experimentally due to its metastable character. Therefore, its
slope was calculated at its intersection with the diaspore-corundum
equilibrium. The andalusite-kyanite equilibrium curve was taken from
Holdaway (1971). The curve kaolinite + quartz ⇔ pyrophyllite is
drawn through the three equilibrium points given by Thompson (1970)
and shows a possible lower limit for the pyrophyllite stability field. For
aluminum rich assemblages an additional boundary, kaolinite ⇔ pyro-
phyllite + diaspore, would lie above the kaolinite + quartz boundary.
A stable field for the occurrence of diaspore + pyrophyllite might thus
be nearly or wholly eliminated. Nevertheless the common occurrence
of these two minerals is reported for several locations in the southeastern
states by Espenshade and Potter (1960) and by Zen (1961).

Reed and Hemley (1966) have studied the field relations of kaolinite
and pyrophyllite in northeastern Alaska and have made appropriate
experiments, up to one year in duration, and find the kaolinite +
quartz ⇔ pyrophyllite reaction to occur no higher than 300°C at 1 kb.
In considering all the above evidence, one must conclude that Thomp-
son’s equilibrium curve is probably a little high.

Other field occurrences of pyrophyllite include the assemblage
pyrophyllite, andalusite, and quartz at Bowlings Mountain, Hillsboro,
and Snow Camp, all in North Carolina (Espenshade and Potter, 1960).
Zen (1961) reports the coexistence of diaspore and pyrophyllite in addi-
tion to kaolinite in the Staley pyrophyllite deposit in North Carolina.
At this same location Zen lists another assemblage: andalusite–pyrophy-
llite–quartz. According to figure 3, conditions at such locations and at the
time of metamorphism must have ranged from 340° to 370°C at 1.5 kb,
if the assemblages represent an approach to equilibrium. Occurrences of
pyrophyllite and kyanite, occasionally with diaspore or quartz as a third
phase are more frequently reported: Zen (1961), Hager’s Mountain loca-
tion. J. B. H. Jansen and R. D. Schuiling (in preparation, personal
commun. to Haas) found on the isle of Naxos (Greece), going from south
to north, the following assemblages: kyanite + diaspore + pyrophyllite
(+ chloritoid), chloritoid + diaspore, chloritoid + corundum (+ minor
diaspore), chloritoid + corundum, kyanite + corundum, kyanite + sil-
limanite.

Using the data presented here the stability of pyrophyllite extends
from 345° to 380°C at 2 kb and from 400° to 420°C at 7 kb. Such a nar-
row stability range is suggested by Turner (1968, p. 116) on basis of
restricted field occurrence. The above temperature and pressure range
is reasonable for the chlorite zone in pelitic schists.

Andalusite and kyanite nucleate with difficulty; it is therefore possi-
ble that pyrophyllite has persisted during progressive low grade meta-
morphism during which the temperature reached 440° to 460°C for a
short period. In such a case, pyrophyllite might be found in a mineral
assemblage typical of higher grade subfacies within the greenschist facies.
This possibility must be considered when the presence of pyrophyllite
in a rock is used to establish a temperature range for the observed meta-
morphism, or when the stability limits of pyrophyllite are estimated by field observation.

Tobschall (1969) reports pyrophyllite together with quartz, albite, epidote, biotite and with quartz, muscovite, chlorite, biotite, almandine-spessartine, clinozoisite, albite. Both these assemblages contain albite which, according to Winkler (1967, p. 97) should react to paragonite. Since Tobschall reports the absence of paragonite in the above assemblages, one might assume that complete equilibrium was not achieved in these rocks. In many regions subjected to biotite-zone metamorphism, and where the rocks are aluminous enough, andalusite or kyanite is the stable aluminum silicate. Turner (1968, p. 192 and 280) lists several such assemblages.

After considering the various available field observations, it can be concluded that the pyrophyllite stability relations derived from laboratory studies are in good agreement with the reported natural occurrences.

ACKNOWLEDGMENTS

We thank Dr. D. C. Thorstenson and Dr. C. V. Haynes for critically reviewing the manuscript and for their helpful comments, and the Department of Geological Sciences, the Institute for the Study of Earth and Man, and Southern Methodist University for providing the research equipment. We are grateful to Dr. G. W. Brindley for furnishing a pyrophyllite sample and to the University of Texas at Dallas for the permission to use the scanning electron microscope. This research has been supported by NASA Grant NCR-44-007-006.

REFERENCES

Althaus, Egon, 1969, Das System \( Al_2O_3-SiO_2-H_2O \) Experimentelle Untersuchungen und Folgerungen für die Petrogenese der metamorphen Gesteine, Teil I und II: Neues Jahrb. Mineralogie Abbh., v. 111, p. 74-143.


Haas, Herbert, 1972, Equilibria in the System \( Al_2O_3-SiO_2-H_2O \) involving the stability limits of diaspore and pyrophyllite, and thermodynamic data of these minerals: Am. Mineralogist, v. 57, p. 1375-1388.


Matsushima, Shogo, Kennedy, G. C., Akella, Jagannadhram, and Haygarth, John, 1967, A study of equilibrium relations in the systems $\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3-\text{H}_2\text{O}$: Am. Jour. Sci., v. 265, p. 28-44.


Shearer, T. A., and Kleppa, O. T., in press, The enthalpies of formation of $\text{MgAl}_2\text{O}_4$, $\text{Mg}_2\text{SiO}_4$, $\text{Mg}_2\text{Al}_2\text{O}_4$, and $\text{Al}_2\text{SiO}_4$ by oxide melt solution calorimetry: Jour. Inorganic Nuclear Chemistry.


Zen, E-an, 1961, Mineralogy and petrology of the system $\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ in some pyrophyllite deposits of North Carolina: Am. Mineralogist, v. 46, p. 52-66.