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EXPERIMENTS ON THE UPPER STABILITY LIMIT OF PYROPHYLLITE AT 1.8 KILOBARS AND 3.9 KILOBARS WATER PRESSURE

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ABSTRACT. The reaction pyrophyllite = andalusite + 3 quartz + water, sets a lower limit for the stability of andalusite in quartz-bearing rocks.

With powdered starting materials, complete decomposition of pyrophyllite according to this reaction occurred at 473 ± 7°C and 3.9 kilobars water pressure, 495 ± 7°C and 3.8 to 3.9 kilobars, and 447 ± 7°C at 1.7 to 1.8 kilobars. Partial decomposition of pyrophyllite occurred at 455 ± 7° and 3.8 to 3.9 kilobars.

Experiments involving weighed single crystals of quartz and andalusite suggest equilibrium at 430 ± 15°C at 3.9 kilobars and 410 ± 15°C at 1.8 kilobars. These temperatures are appreciably lower than most previous estimates of the upper stability limit of pyrophyllite.

The present results, considered in relation to recent experimental work on the Al_2SiO_5 polymorphs, allow an appreciable stability field for andalusite and kyanite in quartz-bearing rocks at moderate temperatures, whatever the water pressure.

INTRODUCTION

The reaction:

$$\underset{\text{pyrophyllite}}{Al_2Si_4O_{10}(OH)_2} = \underset{\text{andalusite}}{Al_2SiO_5} + \underset{\text{quartz}}{3\,SiO_2} + H_2O \qquad (1)$$

sets a lower limit for the stability of andalusite in quartz-bearing rocks. There have been several attempts to determine the upper stability limit of pyrophyllite (table 1); in many of these investigations (Roy and Osborn, 1954; Winkler, 1957; Carr and Fyfe, 1960; Carr, 1963; Aramaki and Roy, 1963), reaction reversibility was not demonstrated, and X-andalusite was produced. Althaus (1966a), however, has produced true andalusite; he claims reversibility and suggests equilibrium for reaction (1) at 2 kilobars water pressure and 490 ± 5°C. Hemley (1967), using a method involving determination of aqueous silica concentration, has arrived at a figure of 400 ± 15°C at 1 kilobar water pressure.

For the reaction:

pyrophyllite = sillimanite + 3 quartz + water

Matsushima and others (1967) suggest equilibrium at approximately 505°C and 2.6 kilobars.

EXPERIMENTAL DETAILS

In the present experiments, starting materials consisted of: (1) pyrophyllite from Indian Gulch, California, (2) clear, pink, gem-quality andalusite from Minas Gerais, Brazil, and (3) clear quartz. Electron microprobe analysis shows that the andalusite contains Fe (approximately 0.25 percent) as the only impurity in excess of 0.01 percent; the only detectable impurities in the pyrophyllite are 0.03 percent to 0.23 percent Fe and about 0.02 percent V.

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TABLE 1

Experimental determinations of the upper stability limit of pyrophyllite

Author	Temperature (°C)	Pressure
Roy and Osborn (1954)	580	2 kb
Winkler (1957)	520	2 kb
Carr and Fyfe (1960)	<475	2 kb
Carr (1963)	<513	2 kb
Aramaki and Roy (1963)	565	2 kb
Althaus (1966a)	490	2 kb
Hemley (1967)	400	1 kb

Starting materials were sealed in silver or palladium-silver capsules and placed in cold seal rod bombs. Temperatures were recorded with chromel-alumel thermocouples and a Leeds and Northrup potentiometer (readings were checked against the melting point of LiCl) and corrected for thermal gradients along the length of the capsules. Pressures were measured with an Ashcroft gauge, calibrated with a Heise gauge. The 3.9 kilobar runs were terminated by cooling the bombs with compressed air; the 1.8 kilobar runs ended with a water quench. Capsules were weighed before and after the experiments, and only data from capsules that had undergone little ($\leqq$ 2 mg) or no weight change during the experiments were used in interpreting the results.

EXPERIMENTS WITH ALL-POWDERED STARTING MATERIALS

In these experiments, the starting material consisted of powdered (< 325 mesh) pyrophyllite, andalusite, and quartz (mixed in approximately equal proportions) and 0.1 gram of water. The reaction components were X-rayed before and after the experiments. Results are summarized in figure 1. Complete decomposition of pyrophyllite occurred at: (1) 495 ± 7°C, 3.8 to 3.9 kilobars, (2) 473 ± 7°C, 3.9 kilobars, and (3) 447 ± 7°C, 1.7 to 1.8 kilobars. In the run at 455 ± 7°C and 3.8 to 3.9 kilobars, there was partial decomposition of pyrophyllite. In the starting material and product of this run, 1/4°/minute X-ray scans of ten different mounts were made on the 002 pyrophyllite peak and the 110 andalusite peak. The ratios of the andalusite to pyrophyllite peak intensities averaged 1.4 in the starting material and 2.0 in the product of the run. The differences, according to Student's t test (Chayes, 1966), are significant at the 90 percent level. Thus, it is probable that during this run, pyrophyllite partially decomposed according to reaction (1). Runs at 432 ± 7°C and 3.8 to 3.9 kilobars, 418 ± 7°C and 3.9 kilobars, and 407 ± 7°C and 3.9 kilobars showed no detectable changes in the proportions of the constituents (as determined by repeated 1/4°/minute X-ray scans over major peaks in the starting material and products of the runs).

These results collectively suggest that the upper stability limit of pyrophyllite is below 455 ± 7°C at 3.8 to 3.9 kilobars and 447 ± 7°C at 1.7 to 1.8 kilobars.

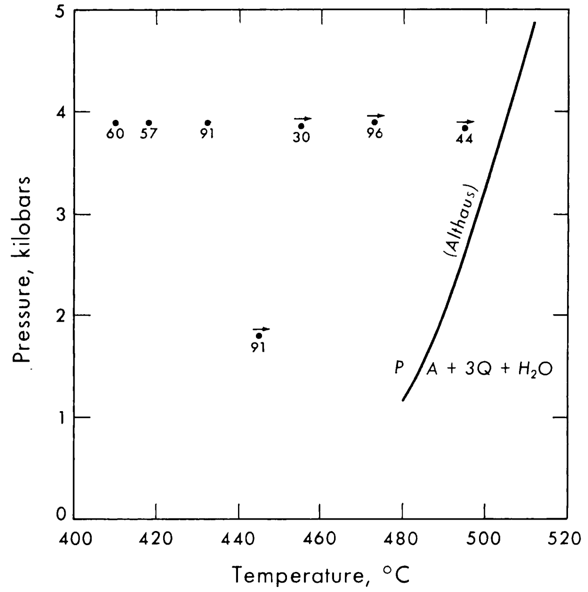

Fig. 1. Pressure-temperature conditions for runs with all-powdered starting materials. Arrows indicate direction of reaction (1) in text. Runs in which no apparent reaction occurred indicated by dots without arrows. Althaus' (1966a) curve for the reaction shown for comparison. Run time (in days) indicated below dots.

SINGLE CRYSTAL EXPERIMENTS

The single crystal method was proposed by Fyfe (1960) and has subsequently been used in several experimental investigations (Weill, 1963; Fyfe and Hollander, 1964; Evans, 1965; Holdaway, 1966). In these experiments, one of the components of the reaction is in the form of a single crystal. Weight changes of this crystal during the run indicate the direction of the reaction, providing that: (1) there are no other reactions contributing to weight change, and (2) allowance is made for solubility of the crystal in the water of the charge. The PT conditions corresponding to zero weight change will be those of univariant equilibrium for the reaction. Two series of runs were carried out at 1.8 kilobars and 3.9 kilobars water pressure. In one series the charge consisted of crystals of andalusite (0.09 g to 0.11 g) with powdered (< 325 mesh) pyrophyllite plus quartz; in the other it was crystals of quartz (0.10 g to 0.15 g) with powdered pyrophyllite and andalusite. Individual crystals were used for several runs. Each crystal was prepared by grinding a small fragment on a lap to an elongated shape fitting 1/8″ diameter capsules. Any chipping during an experiment could be readily identified by subsequent microscopic examination of the initially smoothly-ground faces. The weight of powdered starting material varied somewhat from one capsule to another. Each capsule contained a single crystal along with the powdered mineral components and 0.1 gram of water; each bomb contained two capsules. After each run, the crystals were cleaned with hand rubbing in soapy water, rinsed, dried, and weighed. The single crystals were weighed with a Mettler M5 microbalance under controlled temperature and humidity. The recorded value for each weighing is an average of between five and ten weight measurements.

Results at 1.8 kilobars water pressure are given in figure 2. Weight changes are much greater for quartz crystals than for andalusite crystals; so the quartz data give the clearest indication of the reaction direction. Solubility of the quartz crystals in the water of the charge will lower the position of the zero weight-change line. The solubility has been calculated from the data of Weill and Fyfe (1964), and the lowering is shown as the dashed line in figure 2. However, because of simultaneous solution of powdered pyrophyllite and andalusite, the actual position of the zero weight change line will lie between the dashed and solid zero lines. The temperature of zero weight change (and thus the equilibrium temperature) of the quartz crystals is 410 ± 15°C. The curvature of a line through the quartz crystal data points above the equilibrium point reflects the exponential effect of temperature on reaction rates (Holdaway, 1966).

The data from the andalusite crystal runs at 1.8 kilobars also show weight gains at high temperatures and weight losses at low temperatures. Solubility of the andalusite crystals in the water of the charge is probably negligible, and the line of zero weight change in figure 2 is probably extremely accurate. However, the scatter of the data points is so great that nothing definite can be said as to the equilibrium temperature. It is likely that the scatter is due in part to slight differences in relative amounts of powdered pyrophyllite plus quartz from one run to another; furthermore, since small weight changes are involved, small amounts of contaminant on the crystals (that is, improperly cleaned crystals) could cause significant scatter.

The results of single crystal runs at 3.9 kilobars are shown in figure 3. The equilibrium temperature according to the quartz crystal data is 430 ± 15°C. The andalusite data show some scatter; however, they are compatible with the equilibrium temperature of 430 ± 15°C suggested by the quartz crystal data.

The relatively small change in weight of andalusite crystals suggests that andalusite growth and dissolution is the slow step in the reaction. In the quartz crystal experiments, the large total surface area of andalusite in the powdered form facilitated rapid reaction.

To identify with certainty the nature of the material growing on the crystals, additional experiments to give large weight gains were carried out well above the equilibrium temperatures. Single crystal X-ray photographs were taken by Professor A. Pabst before and after these experiments. In an experiment at 490 ± 7°C and 1.7 to 1.8 kilobars (46 days), a quartz crystal (weighing approximately 0.12 g) in powdered pyrophyllite plus andalusite gained 7594 ± 10 micrograms. Optical and X-ray examination of the powdered components showed significant diminution

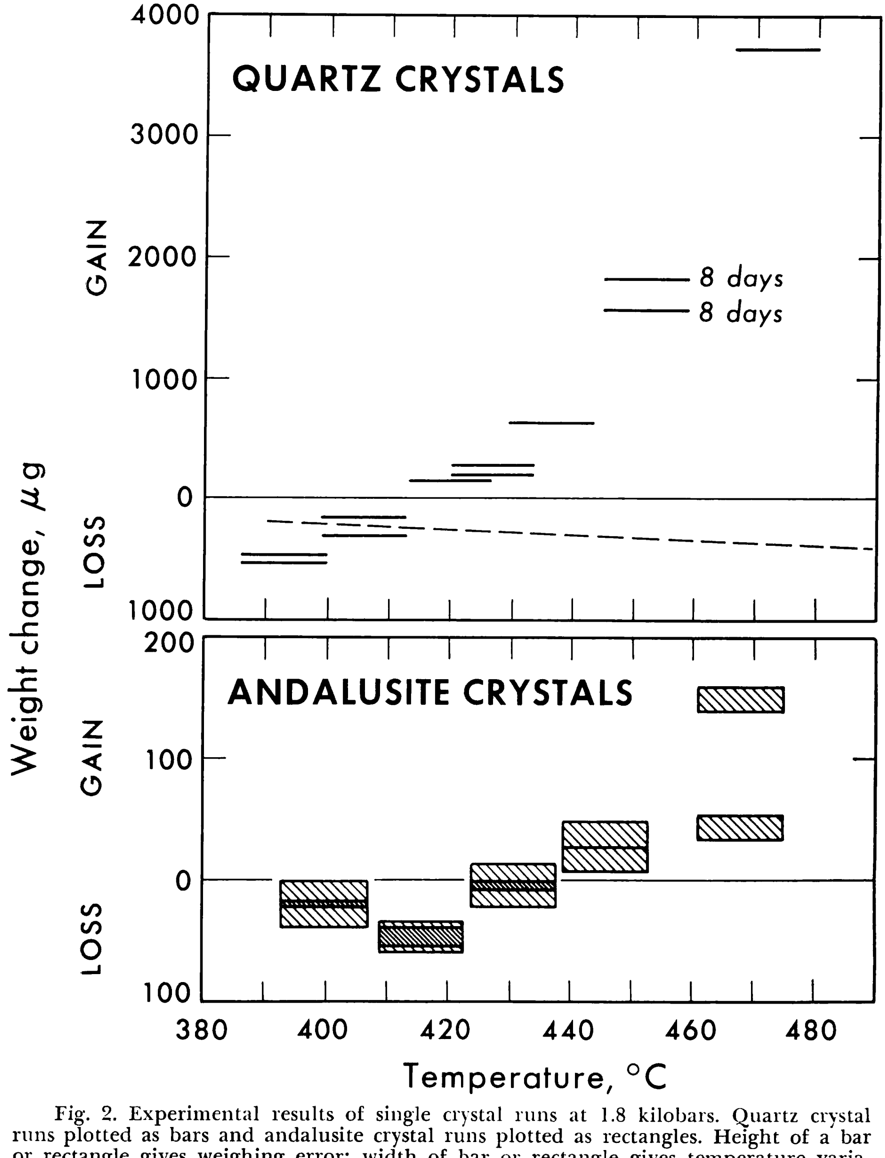

Fig. 2. Experimental results of single crystal runs at 1.8 kilobars. Quartz crystal runs plotted as bars and andalusite crystal runs plotted as rectangles. Height of a bar or rectangle gives weighing error; width of bar or rectangle gives temperature variation plus error during run. Overlap of rectangles indicated by closely-spaced hachures. Duration of runs, 14 days (unless otherwise indicated). Dashed line gives calculated lowering of quartz crystal zero weight change line because of solubility.

in pyrophyllite relative to andalusite. After this run, c-axis rotation photographs made by grazing the X-ray beam along the exterior of the crystal showed rather diffuse powder arcs not corresponding to quartz. Optical examination showed abundant, small, anhedral, moderately birefringent

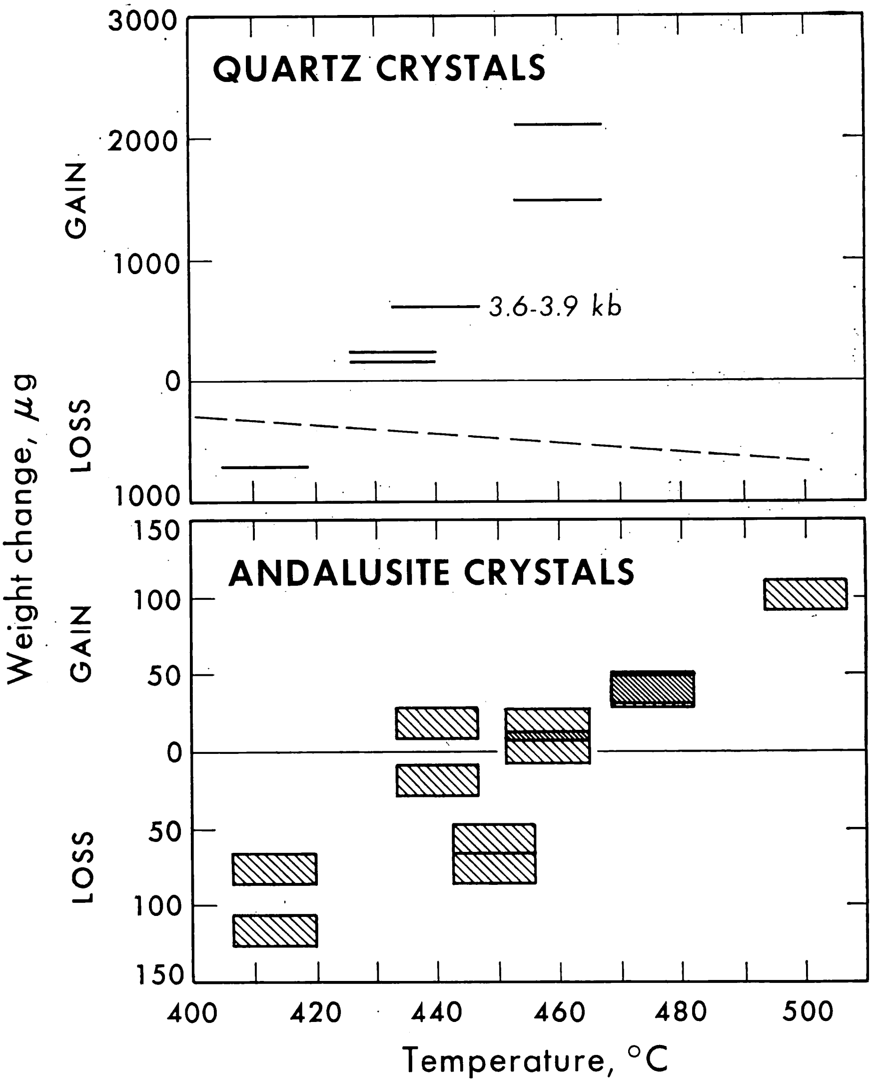

Fig. 3. Experimental results of single crystal runs at 3.9 kilobars. Duration of runs, 14 days. Symbols as for figure 2.

crystallites on the surface of the quartz crystal. Also present are larger, euhedral crystals which resemble quartz prisms and appear to be randomly oriented. Some of the crystallites are completely enclosed in the single crystal; thus, epitaxial growth of the single crystal probably occurred. Two of the smaller crystallites were removed and were found from single crystal patterns to be andalusite (measured cell volume: 342.45 Å^3). A single crystal X-ray pattern of a fragment from one of the larger euhedral crystals showed that they are quartz. It is concluded that the weighed quartz crystal grew by epitaxial growth of quartz and by growth of euhedral quartz in random orientation on its surface; some original powdered andalusite of the charge became attached to, and in some cases incorporated in, the growing quartz crystal.

TABLE 2

Experiments with andalusite single crystals in powdered quartz and 0.1 gram of water. All runs were for 14 days.

T°C	P kb	Weight Change (μg)
402 ± 7	1.7-1.8	+2 ± 10
490 ± 7	1.8	+79 ± 10 and +61 ± 10
395 ± 7	3.9	+12 ± 10 and +5 ± 10
510 ± 7	3.9	+79 ± 10

In an experiment of 36 days duration at 1.8 kilobars and 475 ± 7°C, an andalusite crystal (weighing approximately 0.06 g), with powdered pyrophyllite plus quartz and 0.1 gram of water, gained 85 ± 10 micrograms. Before the experiment, only andalusite spots were present in a c-axis rotation photograph taken with the X-ray beam grazing one end of the elongated crystal fragment; the stronger spots were streaked over a few degrees on "powder" arcs. After the experiment, a c-axis rotation photograph, taken on the same part of the crystal, showed no other phase than andalusite. In a subsequent run with this crystal at 520 ± 7°C and 3.9 kilobars (29 days) the weight gain was 426 ± 10 micrograms. A c-axis rotation photograph taken on the end of the crystal fragment showed a complete quartz powder pattern superposed on the andalusite pattern. After cleaning the crystal in an ultrasonic bath for 1 hour, the crystal was again X-rayed and still showed abundant quartz. A trace of quartz is observed in a rotation photograph on the other end of the crystal; however, a 90° oscillation photograph on the side of the crystal showed no indication of quartz. In this experiment it is possible that the weight gains of the andalusite crystals were produced by quartz grains of the charge adhering to the surface of the crystal or by quartz precipitating out of solution during quenching. To test the magnitude of this effect, experiments were made with andalusite single crystals and powdered quartz. As shown in table 2, the crystals at high temperatures (490-510°C) have undergone weight gains comparable to those obtained at similar PT conditions with andalusite single crystals in powdered pyrophyllite plus quartz. In contrast, the crystals subjected to low temperatures (390-400°C) underwent essentially no weight change. It is possible that the weight gains at high temperatures are produced by quartz precipitating out of solution, as quartz is more soluble at 500°C than at 400°C. Because of the essential agreement between the equilibrium temperatures of the andalusite and quartz single crystals, it is probable that quartz precipita-

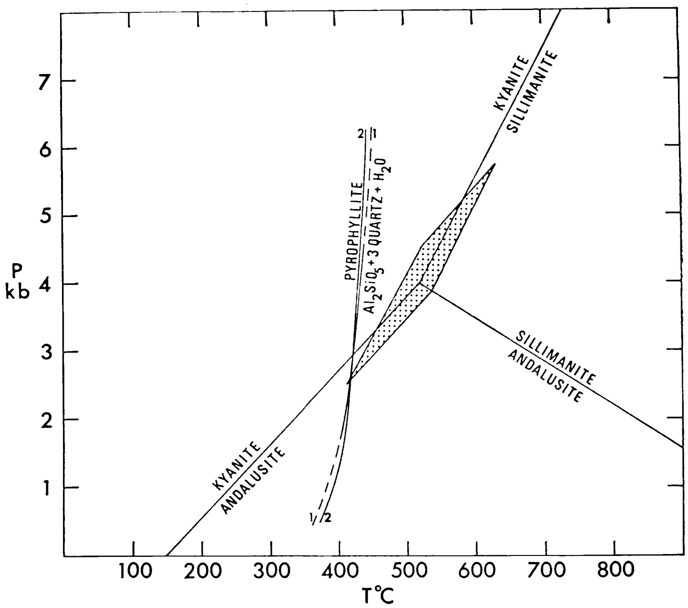

Fig. 4. Equilibrium phase diagram showing relations between aluminosilicate polymorphs and the upper stability limit of pyrophyllite. Aluminosilicate polymorph relationships from Newton (1966). Stippled area represents uncertainty in location of the triple point. Reaction (1) is given in text (dashed portions of this curve are extrapolation from experimental data). Reaction (2) is schematic representation of the reaction:

pyrophyllite = kyanite + 3 quartz + water

tion had a negligible effect on the weight changes of the andalusite single crystals near the equilibrium temperature.

All X-rayed powders of the single crystal runs at 3.9 kilobars showed a small peak at $2\theta = 12.5°$ (CuKα radiation) corresponding to (001) of kaolinite. Collapse of this peak after heat treatment at around 515°C for 9 hours positively identified it as the basal kaolinite peak (Warsaw and Roy, 1961). The intensity of the kaolinite peak is very small compared to the intensities of the major peaks of the other powdered materials. Kaolinite is absent in all the X-ray patterns made from the 1.8 kilobars runs. The runs at 3.9 kilobars were air quenched and thus cooled more slowly than the rapid water quench of the 1.8 kilobars experiments. Therefore, the kaolinite in the experiments at 3.9 kilobars formed during the relatively long quench period, in contrast to the rapid water quench from 1.8 kilobars. Since the amount of kaolinite was always small, its effect on measured weight changes in experiments at 3.9 kilobars is thought to be trivial.

DISCUSSION AND CONCLUSIONS

Data from the single crystal experiments and data from the runs with all-powdered starting materials are mutually compatible and indicate equilibrium conditions for reaction (1) as 430 ± 15°C at 3.9 kilobars and 410 ± 15°C at 1.8 kilobars water pressure. These temperatures are much lower than most previously determined values (table 1). They are in excellent agreement, however, with Hemley's value of 400 ± 15°C at 1 kilobar.[1]

As the experimentally-determined equilibrium temperatures are believed subject to ± 15°C errors, the slope of the equilibrium boundary is somewhat uncertain. From the thermochemical data of Kelley (1960), Kelley and King (1961), Sharp (1962), and Clark (1966), and an estimated value for the entropy of pyrophyllite[2], the calculated slope of the reaction at 410°C and 1.8 kilobars is 37 bars/°C. This value is close to the minimum value of the experimentally-determined slope (40 bars /°C) when account is taken of the estimated temperature error.

The upper stability limit of pyrophyllite, as here presented, when compared with the stability fields of the Al_2SiO_5 polymorphs as determined and estimated by Newton (1966) permits a large field of stability for andalusite plus quartz or kyanite plus quartz even under the condition $P_{H_2O} = P_{total}$ (fig. 4). Transitions between kyanite- and andalusite-bearing assemblages, such as described by Chinner (1966), would be possible under these conditions. If the new data are accepted there is no need to appeal to low ratios of P_{H_2O}/P_{total} to explain some metamorphic assemblages including andalusite or kyanite (Zen, 1961, p. 62; Albee and others, 1965, p. 297).

Althaus (1966b) suggests that a profound lowering of the upper and lower equilibrium temperatures of pyrophyllite occurs with the presence of strong acids, such as HCl and H_2SO_4, in the vapor phase. He suggests (Althaus, 1966c) that high acidities may have been a common feature of fluids during contact metamorphism and that under these conditions, the first appearance of andalusite occurred at much lower temperatures than with pure water as the fluid phase. In his experiments, however, X-andalusite (rather than true andalusite) was produced, and phases such as zunyite and alunite formed in many of the runs; thus, his experiments are not strictly applicable to reaction (1). Such a marked lowering of the equilibrium temperatures cannot be explained on the basis of the lowering of a_{H_2O} as the result of dilution with acid. From the data of Harned and Owen (1958), a_{H_2O} in a 4N H_2SO_4 solution at 60°C is 0.918. Provisionally, using this value and Althaus' (1966a) determination of equilibrium for reaction (1) at 490°C and 2 kilobars (with pure water as the fluid phase), the free energy change of the reaction using the relation:

$$\Delta G = RT \ln a$$

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[1] Production of pyrophyllite from kaolinite plus quartz at 1 kilobar and 300°C by Hemley (*in* Reed and Hemley, 1966) indicates that earlier estimates of the *lower* stability limit of pyrophyllite (governed by the reaction: kaolinite + 2 quartz = pyrophyllite + water) at 390°C to 420°C and 2 kilobars (Althaus, 1966b) may also be too high.

[2] The entropy of pyrophyllite was estimated by adding that of its oxides (Fyfe, Turner, and Verhoogen, 1958), and the estimated high temperature entropy of water in kaolinite (which is structurally similar to pyrophyllite) was used for this calculation.

is −130 calories. From Kelley's (1960) and Kelley and King's (1961) data, ΔS of the reaction at 490°C and 2 kilobars is approximately 18.4 entropy units. According to the relation:

$$\delta \Delta G = - \Delta S \delta T$$

the temperature lowering (ΔT) will be about 7°C. This will be a maximum value for the temperature lowering at these conditions, as the ionization of acids decreases with increasing temperature (Barnes and Ernst, 1963), and thus the activity of water at 400 to 500°C will be greater than at 60°C. The temperature lowering with an equivalent concentration of HCl would be less, as two ions result from the dissociation of HCl, while three result from H_2SO_4 dissociation. Althaus (1966b) suggests that the equilibrium temperature of reaction (1) at 2 kilobars is lowered about 80°C (from 490°C to 410°C) with 4N HCl; thus, the extreme lowering cannot be the result of lowering of a_{H_2O} in solution. Althaus has not conclusively demonstrated reversibility in any of his runs at 2 kilobars. Hence, it is possible that production of X-andalusite at lower temperatures with acid solutions than with pure water largely results from an increase in reaction rates because of the catalytic effect of the acids.

The first appearance of andalusite in quartz-bearing rocks undergoing contact metamorphism indicates temperatures above the upper stability limit of pyrophyllite (410-430°C at 2-4 kb). This is true even though pyrophyllite itself (judging from its rarity in metamorphic rocks) is not one of the reactants involved.

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