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A NOTE ON THE KAOLINITE-PYROPHYLLITE EQUILIBRIUM

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ABSTRACT. An attempt has been made to find the equilibrium conditions for the reaction:

$$\text{Kaolinite} + \text{quartz} = \text{pyrophyllite} + H_2O$$
$$Al_2Si_2O_5(OH)_4 + 2SiO_2 \quad Al_2Si_4O_{10}(OH)_2 + H_2O$$

by studying the weight-change of quartz crystals in the presence of fine-grained powdered kaolinite plus pyrophyllite and excess water. The data suggest equilibrium at 325 ± 20°C at 1 kb, 345 ± 10°C at 2 kb, and 375 ± 15°C at 4 kb (water pressure = total pressure).

INTRODUCTION

There have been several previous attempts to set the upper stability limit of kaolinite in the presence of quartz. As in all such reactions, the stability field of kaolinite alone will be greater than that in the quartz bearing system, and metastable persistence is to be anticipated. Some previous limits (not necessarily considered by their authors to represent equilibrium) are shown in table 1.

EXPERIMENTAL DETAILS

Natural minerals were used in all experiments: (A) analyzed kaolinite (Am. Petroleum Inst. Std 17, from Lewiston, Mont.); (B) clear crystals of low-quartz; (C) commercial pyrophyllite (purity checked with X-ray fluorescence by comparison with kaolinite (see A above); (D) de-ionized water.

METHOD

Powdered kaolinite plus pyrophyllite were ground intimately together in stoichiometric proportions, to size less than 300 mesh. Single crystals were cleaned before and after each experiment, prior to weighing, with hemispherical ends. All crystals were of uniform size (0.25 cm diam × 2 cm long).

Fixed ratios of reagents were used in each case, and the quartz crystals were cleaned before and after each experiment, prior to weighing, in an ultrasonic bath.

The reagents (0.040 g powdered kaolinite plus pyrophyllite and 0.03 g water) were sealed in gold capsules (of constant volume) and placed in cold seal rod bombs. Close checks were kept on the weight-changes of the capsules during the runs. Capsules with less than 1 mg weight-change were considered capable of giving useful data. Likewise, single crystals were weighed under conditions of controlled temperature and humidity. For each set of weighings, comparison with a standard-weight crystal was made, and those showing less than 50 μg change were given less credence than those showing greater weight-change. Two charges were run simultaneously for each temperature and pressure to obtain duplication of weight-change. This approach was found to give good reproducibility of results.

Table 1

Author	Temperature °C (at 2 kb PH_2O, unless otherwise stated)
Roy and Osborn (1954)	405
Winkler (1957)	420
Carr and Fyfe (1960)	420
Carr (1963)	413
Aramaki and Roy (1963)	405
Hemley and Jones (1964)	380 (at 1000 bars PH_2O)
Althaus (1966a)	390 ± 10 (at 2 kb) 405. (at 7 kb)
Velde and Kornprobst (1969)	310
This study	345 ± 10

Note: Reed and Hemley (1966) report a value of approximately 300°C at 1 kb PH_2O.

SINGLE CRYSTAL EXPERIMENTS

The weight-change of quartz crystals is plotted, in figure 1, against temperature for various pressures.

The runs at 2 kb (all pressures refer to water pressure) were conducted for 1 week, and the points follow the curve as indicated. The size of the open boxes shows maximum weight-change and temperature uncertainty. This curve indicates zero weight-change at 345 ± 10°C for 2 kb PH_2O.

Solubility of the phases in the water of the charge will produce the effect of lowering the position of the zero weight-change line.

When pyrophyllite is present in the kaolinite-quartz stability field, the SiO_2 in solution in equilibrium with pyrophyllite will exceed that in equilibrium with quartz. As pyrophyllite and kaolinite are fine grained, it is to be expected that their solution rates will exceed that of a single crystal of quartz; also, that these fine grained materials will first saturate the solution with silica at a level appropriate to their stability.

However, even if all the SiO_2 in solution came from the quartz crystal a consideration of the quartz solubility data of Kennedy (1950) in the P-T region of this study indicates a quartz solubility of 0.1 to 0.2 wt percent. The use of 0.03 g of H_2O in the charge would thus dissolve 30 to 60 μg of quartz. This would tend not to lower the apparent equilibrium temperature of the zero weight-change line more than about 10°C below the true equilibrium temperature. This value of 10°C lowering falls within experimental error.

The shape of the curve for the 2 kb equilibrium was to be compared with the shapes of the curves for 4 kb and 1 kb equilibria. The 1 kb experiments were conducted initially for 1 week to provide closer correlations with the 2 kb data. However, the weight-change of the quartz crystals for runs of 1 week's duration was usually less than 50 μg (see open circles in fig. 1). These weighings did not compare favorably with the weight of the standard, and possibly balance inaccuracies are partly responsible. Runs of much longer duration, ranging from 3 weeks

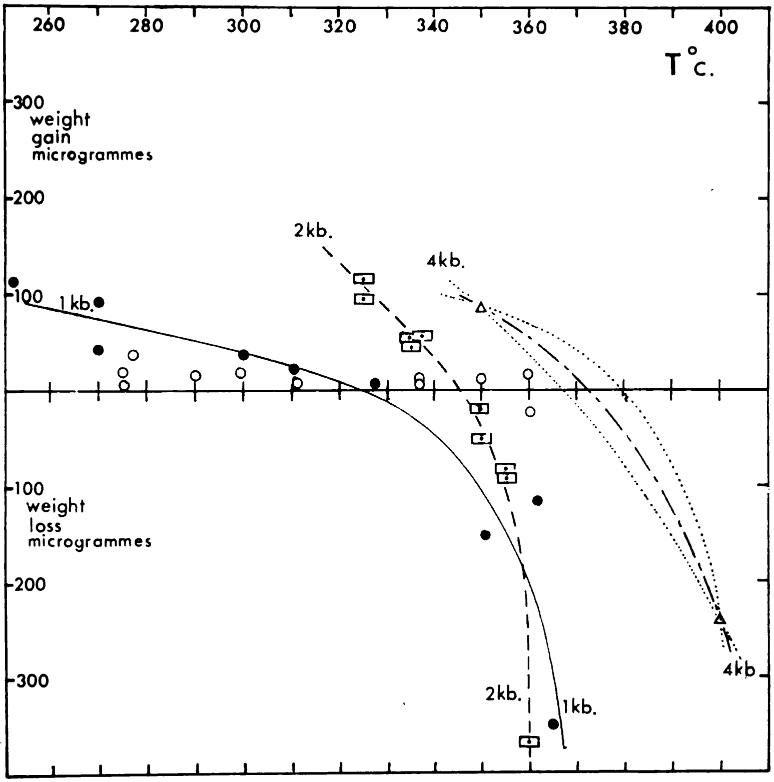

Fig. 1. Plot of weight-change of quartz crystals against temperature for various pressures (PH_2O). The sizes of the open boxes shown for the 2 kb data give the maximum *measured* uncertainty. The indicated curves are the best fits for the observed points. The dotted curves for 4 kb show possible range of error.

Symbols: Closed circles: 1 kb runs of greater than 3 week's duration; open circles: 1 kb runs of 1 week's duration; open boxes: 2 kb runs of 1 week's duration; open triangles: 4 kb runs of 1 week's duration.

to 3 months, but usually 28 days, were conducted at 1 kb, and their results are indicated by solid circles in figure 1. The results at 1 kb are by no means as accurate as those at 2 kb. They indicate a much slower rate of reaction at 1 kb (T range 270-360°C) compared to those at 2 kb (T range 325-360°C). The crossovers obtained from the runs of longer duration indicate an equilibrium value of about 325°C, which should perhaps be considered over a range of ± 20°C (compare 345 ± 10°C at 2 kb).

The runs at 4 kb were conducted for 1 week, and only two sets of runs were conducted to establish the range of the crossover. The crossover is indicated at about 375°C. Curve fitting procedure can allow a range of ± 10°C, at worst a range of ± 15°C.[1]

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[1] Since the completion of the manuscript, additional data were obtained for the 4 kb curve. The data suggest points at −152 ± 5 μg at 390 ± 3°C and +60 ± 5 μg at 360 ± 3°C.

The limitations of the single crystal technique and its advantages have been discussed at length by Evans (1965) and Holdaway (1966) and need no further discussion here. Limitations to the present results must include the use of fine grained materials and possible variation in crystal surface area.

IDENTIFICATION

All powders were examined optically and by X-ray diffraction. In neither of these determinative methods were new phases observed for the studied reaction, although X-ray diffraction is not very sensitive.

THERMODYNAMIC CONSIDERATIONS

As the entropy of pyrophyllite is not know experimentally, it is not possible to compare the experimental and theoretical slopes for the reaction. As the additivity rules for estimating entropies (see Fyfe, Turner, and Verhoogen, 1958) are notoriously inadequate for sheet and chain silicates, no significant estimate is possible.

EXPERIMENTS WITH ACIDS AND ALKALIS

Althaus (1966b, c) suggests that acid solutions lower the temperature of equilibrium by up to 80°C by lowering the a_{H_2O}.

Single crystal runs were conducted as part of this study with 4N.HCl near the newly determined equilibrium boundary. The weight-change of the quartz crystals in these experiments using HCl showed little difference to the weight-change of the crystals when pure water was used under the same experimental conditions. The postulate of Althaus, that the lowering of the a_{H_2O} consequently causing equilibrium to be lowered, was not found. Theoretical considerations of this effect suggest equilibrium could not be lowered by more than 10°C.

Runs with saturated KCl solution produced no new phases on the X-ray pattern, but minute flakes of a micaceous phase were observed microscopically. This is in accord with observations of Hemley and Jones (1964).

Similar runs with 0.51 molal NaOH showed no recognizable change in the X-ray pattern, but minute nucleations of an unidentifiable phase were observed on the kaolinite grains. The amounts of NaOH used are probably insufficient to produce more than trace amounts of albite by reaction with kaolinite.

The phases zunyite and alunite were not observed in the present experiments.

CONCLUSIONS

The results obtained may indicate the maximum stability of kaolinite-quartz assemblages in the system Al_2O_3–SiO_2–H_2O. These results suggest lower equilibrium temperatures for the breakdown of kaolinite plus quartz to pyrophyllite plus water than previously determined. This data, combined with that of Kerrick (1968), can be considered to give new stability limits to the field of pyrophyllite.

It should be mentioned that the phase boundary determined in this study applies to a pyrophyllite/kaolinite mixture of grain size less than 300 mesh. The boundary may not necessarily be exactly applicable where reagents of much larger grain size are used.

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