FORMATION AND STABILITY OF MUSCOVITE IN ACID SOLUTIONS AT ELEVATED TEMPERATURES

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INTRODUCTION

The experiments described below are a few of a larger number undertaken to determine the stability of layer silicates in HCl solutions at temperatures between 300° and 400°C. The present paper is of a preliminary nature only. Enough information has been gathered, however, to be of interest in connection with similar studies by Noll[1] and Norton.[2] Especially Noll's conclusions are significant and have been confirmed by the writer's experiments in most points. It seems, however, that the formation and stability of such minerals as sericite and kaolinite should be greatly affected by the concentration of alkalies, not only in basic solutions, as has been known for many years, but also in acid solutions. The writer found that the concentration of KCl in his experiments with HCl solutions was of great importance in stabilizing muscovite which otherwise would decompose to kaolinite or pyrophyllite.

EXPERIMENTS

As far as the writer knows Schwarz and Trageser[3] are the only ones who have used HCl solutions in bomb experiments at temperatures around 300°C. They speak of steel bombs containing platinum and silver crucibles but do not mention how they protected the steel from the corrosive action of the gases. In the present experiments gold-lined bombs, which have been described a number of times, were used. The bomb has a volume of 50 cc. In all experiments it was filled with 25 cc. of solution. The air above the liquid was displaced by CO_2 (at atmospheric pressure and room temperature), and the bomb was sealed by a sheet of gold which was pressed against the gold flange of the lining. After the experiment a circular hole was cut in the gold sheet. The cooling of the bomb took about 2 hours. The heating of the bomb was carried out in a large oven-like electric furnace controlled by a Leeds and Northrop recording potentiometer. The thermocouple was as close to the

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[1] Noll, W., Über die Bildungsbedingungen von Kaolin, Montmorillonit, Sericit, Pyrophyllit und Analcim: *Mineral. Petrograph. Mitt.*, **48,** 210–247 (1936). This is a summary of several papers on the same subject by Noll.

[2] Norton, F. H., Hydrothermal formation of clay minerals in the laboratory: *Am. Mineral.*, **24,** 1–18 (1939).

[3] Schwarz, R., and Trageser, G., Über die künstliche Unwandlung von Feldspat in Kaolin: *Zeits. anorg. Chem.*, **215,** 190–200 (1933).

bomb as possible. Fluctuations in temperatures of the furnace which amounted to a maximum of 5°C. ± were minimized by the considerable weight of the bomb. The materials used for the experiments were:

Muscovite in large books from the Hugo Mine, Black Hills, South Dakota. The mica was filed to about 200 mesh size.

Kaolinite from Brooklyn, N. Y. The same material was used in the determination of the structure of kaolinite. For its analysis see: Gruner, J. W., *Zeits. Krist.*, **83**, 75 (1932).

Aluminum hydroxide (Merck). This gives an *x*-ray pattern of bayerite and contains 37% H_2O.

"*Silicic acid*" (C. P. Mallinckrodt). It contains 10.36% H_2O = approx. $SiO_2 \cdot \frac{1}{2}H_2O$.

Two hundred milligrams of muscovite and kaolinite were used in each experiment. The amounts of the hydroxides used for synthesis of the minerals are stated for each experiment.

After completion of most experiments, 20 cc. of the filtered solution were titrated with NaOH to find the remaining acidity, and evaporated for SiO_2 analysis by hydrofluorization. The powders were *x*-rayed in precision cameras with radii of 57.3 mm. Unfiltered Fe radiation was used. Very good sharp patterns were obtained in all experiments described. To reproduce the line measurements here would be just a waste of space as none of the diagrams are ambiguous. They seem to be much better than those of Norton,[4] which perhaps is due to more thorough and complete recrystallization in HCl solutions.

Besides the nine experiments listed in Table 1, five others are tabulated in Table 2. The pressures in the bombs were approximately 85 atm. at 300°C. for experiments 106, 111, and 126, and 300–400 atm. in experiment 154 at 400°C. The addition of KCl would cause, however, a lowering of pressures.

Discussion of Results

Experiments 111 and 126 show that muscovite is not stable in HCl solutions at 300°C., provided the concentration of KCl stays below a certain limit. This limit seems to be indicated by the results in 106. Apparently some muscovite changed to kaolinite and when KCl had reached a certain concentration with respect to the concentration of HCl the conversion stopped. The following equation may be written:

$$2[K_2(OH)_4Al_4(Si_6Al_2)O_{20}]+4HCl+6H_2O \rightleftarrows 3[(OH)_8Al_4(Si_4O_{10})]+4KCl$$

Experiments 129, 125, 141, 131, and 147 all indicate that excess of KCl prevents the change of muscovite to kaolinite. On the other hand,

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[4] *Op. cit.*

the reaction will not go from right to left in acid solutions at 300°C. as shown by experiments 130 and 138 even with a very large excess of KCl.

The synthesis of muscovite from the hydroxides does not succeed even though a very large excess of KCl is present as shown by experiment 149 which confirms Noll's[5] contention. On the other hand, at the higher temperature of 400°C. muscovite will form from the hydroxides in acid solutions as shown by experiments 153 and 157. No pyrophyllite was obtained as Noll[6] expects should form under these conditions.

Experiments 153 and 157 differ from each other in the amount of $Al(OH)_3$ used. It was thought at first that an amount of $Al(OH)_3$ sufficient to "neutralize" the HCl in the solution, as well as that formed by the decomposition of KCl, would be necessary to cause the reaction to go in the desired direction. This extra amount caused the formation of boehmite and evidently was not necessary as indicated by experiment 157, in which the weighed-out amounts of the hydroxides correspond to the following equation, the amount of the expected muscovite being about half a gram:

$$\underset{227\text{ mg.}}{3(Al_2O_3\cdot 3H_2O)}+\underset{201\text{ mg.}}{6(SiO_2\cdot \tfrac{1}{2}H_2O)}+\underset{72.3^*}{2KCl}$$
$$\rightleftarrows K_2O\cdot 3Al_2O_3\cdot 6SiO_2\cdot 2H_2O+2HCl+9H_2O$$

It may be of interest to mention that in an experiment such as 149 in which KF was substituted for KCl, leucite was the result. The original acidity in this case was N/0.103, but the solution reacted basic at the end of the experiment. That the reaction can go from right to left in the first equation at 400°C. is definitely established by experiment 155.

It would be of considerable interest to know the temperature–concentration diagram of this reaction more precisely. Since pyrophyllite is not common, it may be assumed that under most natural conditions existing at or above 400°C. the K ion is present in appreciable concentrations in an hydrothermal environment causing sericitization. This probably applies especially to neutral and acid solutions. In basic ones minerals with higher alkali content like the potash feldspars may even predominate. As the temperature decreases, the stability of the potash bearing minerals will depend primarily upon the K ion concentration in the solutions coming in contact with the minerals, and secondarily upon the acidity, or hydrogen ion concentration.

[5] *Op. cit.*, 226.

[6] *Op. cit.*, 227.

* Large excess used.

TABLE 1. HYDROTHERMAL EXPERIMENTS AT 300°C. IN HCl SOLUTIONS
Amount of mineral in each experiment = 200 mg.

No.	Original mineral	Grams of KCl	Original acidity	Resulting acidity	Time in days	SiO_2 in solution	Conversion product
106	muscovite	none	N/0.103	n.d.	10	n.d.	muscovite and some kaolinite
111	muscovite	none	0.350	n.d.	8	n.d.	kaolinite
126	muscovite	none	0.175	0.138	10	920 pt. p.m.	kaolinite
129	muscovite	3.0 g.	0.350	0.264	8	1075 pt. p.m.	muscovite
125	muscovite	1.0 g.	0.350	n.d.	8	n.d.	muscovite
141	muscovite	0.5 g.	0.175	0.138	10	805 pt. p.m.	muscovite
131	muscovite	0.5 g.	0.350	0.269	8	815 pt. p.m.	muscovite
147	muscovite	0.25 g.	0.175	n.d.	14	n.d.	muscovite
130	kaolinite	5.0 g.	0.103	0.085	10	940 pt. p.m.	kaolinite
138	kaolinite	5.0 g.	0.050	0.042	15	950 pt. p.m.	kaolinite and some boehmite

TABLE 2. HYDROTHERMAL EXPERIMENTS AT 300°C. AND 400°C. IN HCl SOLUTIONS

No.	Material placed in bomb	Original acidity	Time in days	Conversion product	Temp.	Remarks
154	200 mg. muscovite	N/0.103	5	muscovite	400°	About half of sol. escaped. Acidity 0.073
153	317 mg. $Al(OH)_3$ 201 mg. $SiO_2 \cdot xH_2O$ 2000 mg. KCl	0.050	5	muscovite and boehmite	400°	Acidity 0.058 $SiO_2 = 570$ pt. p.m.
149	As in 153	0.050	13	kaolinite and boehmite	300°	Acidity 0.039 $SiO_2 = 822$ pt. p.m.
157	227 mg. $Al(OH)_3$ 201 mg. $SiO_2 \cdot xH_2O$ 2000 mg. KCl	0.050	5	muscovite	400°	Sol. lost at end of exp.
155	200 mg. kaolinite 2000 mg. KCl	0.103	5	muscovite	400°	About $\frac{1}{3}$ of sol. recovered.

CONCLUSIONS

Experiments show that the formation of muscovite or sericite does not occur in HCl solutions even in the presence of a large excess of KCl, at temperatures around 300°C. At 400°C. muscovite will form, however, in HCl solutions from aluminum hydroxide, silica and KCl. Also kaolinite will be converted to muscovite at this temperature in the presence of an excess of KCl. The presence of KCl will stabilize muscovite in HCl solutions at temperatures around 300°C. under conditions which do not permit its formation but would ordinarily cause the formation of kaolinite. One may conclude, therefore, that in hydrothermal solutions the concentration of K ions is of primary importance in connection with their reactions upon potash-bearing minerals. Lack of K ions will cause their decomposition; above probably 350° to 375°C. pyrophyllite may form, below this temperature, kaolinite. The upper and lower temperature limits of these minerals are unknown at present.