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## HYDROTHERMAL FORMATION OF CLAY MINERALS IN THE LABORATORY, PART II

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### ABSTRACT

The same materials reported on in the first part of this work were treated under higher pressures of CO<sub>2</sub> and water vapor in order to determine more completely the field of reaction. The results show good agreement with the previous work, but carry the contours up to higher concentrations of CO<sub>2</sub> where the reaction practically ceases. As before, end products were obtained closely approximating, but not exactly identical with, many of the natural clay minerals. The artificial product is less perfectly crystallized and shows some deviation both in x-ray pattern and thermal curve from the natural product. A few runs were made with stronger acids.

### INTRODUCTION

The results presented here are a continuation of the experiments reported in 1939, where a percolating type of reaction chamber was used to break down some of the feldspars.<sup>1</sup> Here the work is continued further by carrying the reactions out under higher pressures of CO<sub>2</sub>, and runs were also made on some additional minerals outside of the feldspar class in order to give a broader picture of the stability relations in these minerals.

It should again be emphasized that the properties of the synthetic clay minerals produced in the laboratory do not in most cases show complete agreement with those of the corresponding natural minerals. The x-ray patterns may show exact agreement except for one or two lines which are weak or absent. The thermal curves of the laboratory product usually have peaks slightly lower in temperature than their natural counterpart. This lack of agreement is not surprising in view of the comparatively short time of formation which produces fine and imperfect crystallization. For these reasons it is difficult to make positive identifications of the end product in many cases, although the type of mineral is quite certain.

<sup>1</sup> Norton, F. H., Hydrothermal formation of clay minerals in the laboratory: *Am. Mineral.*, **24**, 1-17 (1939).

## PREVIOUS WORK

As in the previous paper no detailed mention is made here of the synthesis of the clay minerals, as these can be found in the excellent paper by Morey and Ingerson.<sup>2</sup>

## APPARATUS

The apparatus used here was the same as reported in the previous paper, except that two reaction chambers were made for higher pressure work from chrome-nickel steel. Except for the higher pressures no changes were made in the method of operation. In Table 1 are given the

TABLE 1

CO <sub>2</sub> pressure at room temp.	250°C	275°C	300°C	325°C	350°C
0	560	860	1230	1720	2380
125	775	1087	1467	1967	2638
250	990	1313	1703	2215	2895
375	1205	1540	1940	2460	3154
500	1420	1765	2175	2710	3410
600		2250	2650	3200	
700		2750	3200	3750	
800		3450	3900	4400	
900		4400	4800	5300	

total pressures in the reaction chamber under various initial pressures of CO<sub>2</sub> and temperature. At the higher pressures these values are somewhat variable, and depend on the amount of filling of the chamber.

## RAW MATERIALS

In general, the same raw materials were used as in the previous work, with the exception of the following minerals which were obtained from Ward's Natural Science Establishment and appeared to be of a high grade of purity:

- Analcite, from Table Mountain, Colorado.
- Scolecite, from Teigarhorn, Iceland.

<sup>2</sup> Morey, G. W., and Ingerson, E., The pneumatolytic and hydrothermal alteration and synthesis of silicates: *Paper No. 937, Geophysical Laboratory, Carnegie Inst. of Washington*, (1937).

Volcanic glass, from Wyoming.  
 Diopside, from Templeton, Quebec, Canada.  
 Pyrope (Garnet), from Meronitz, Bohemia.  
 Oligoclase, from Mitchell County, North Carolina.  
 Andesine, from Palmietfontein, Transvaal.  
 Labradorite, from near Nain, Labrador.  
 Bytownite, from Crystal Bay, Minnesota.  
 Anorthite, from Miakejima, Japan.

## RATE OF CONVERSION OF ALBITE

In Table 2 there is shown the test results on the conversion of albite. It will be noticed that this is a comparatively stable mineral, and even under the most favorable conditions the conversion is by no means complete. The previous work is checked fairly closely, although a few small changes have been incorporated into the more recent values.

TABLE 2. CONVERSION OF ALBITE ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ )

Conditions		Product	% Conversion
Temp.	CO <sub>2</sub> Initial Pressure		
250°	250 lbs./in. <sup>2</sup>	Quartz, Montmorillonite or Beidellite	5
250°	500		0
275°	250	Quartz, Montmorillonite or Beidellite	20
300°	250	Montmorillonite or Beidellite	30
300°	500	Quartz, Montmorillonite or Beidellite	20
300°	650	Montmorillonite or Beidellite	10
300°	800		0
300°	925		0
350°	250	Montmorillonite or Beidellite	5
350°	500	Montmorillonite or Beidellite	5

The end product produced by this reaction was previously stated to be beidellite, but our more recent work would indicate that it could also be montmorillonite. In Fig. 1 is shown  $x$ -ray patterns of this end product compared with both beidellite and montmorillonite.

The thermal curves of the end product show a relatively strong double peak at low temperatures, which is characteristic of montmorillonite. The small peak at 550° may be due to a small amount of diasporé which would not show in the  $x$ -ray pattern. In Fig. 2 are shown thermal curves of the end product and the thermal curve of montmorillonite, which unfortunately does not give very characteristic high temperature peaks.

In Fig. 3 are shown the rates of conversion for the various pressure and temperature conditions. It will be seen that the greatest conversion rate occurs at 300° and about 300 pounds initial pressure of CO<sub>2</sub>. At the very

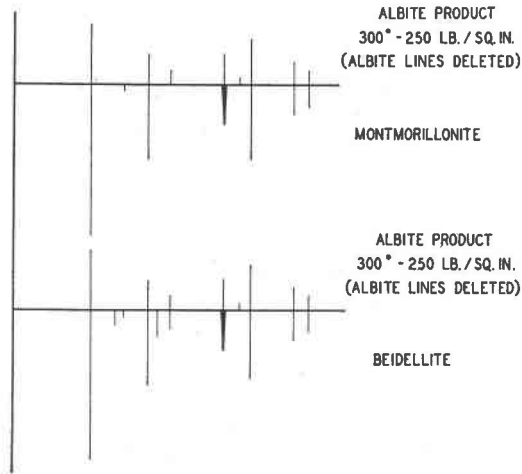


FIG. 1

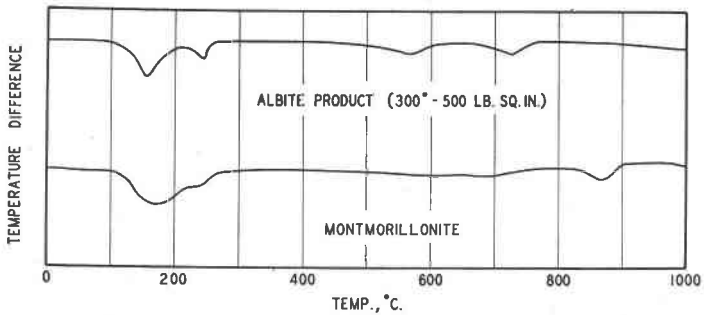


FIG. 2

high CO<sub>2</sub> pressures there was no conversion so that the field of reaction is practically completed.

One run was made on fused albite and the end product seemed to be identical with that resulting from the crystalline material.

## RATE OF CONVERSION OF NEPHELITE

In Table 3 is shown the conversion rates and end products for the various runs made on this material. Nephelite is fairly readily converted into an end product which checks closely with that of sericite, except in

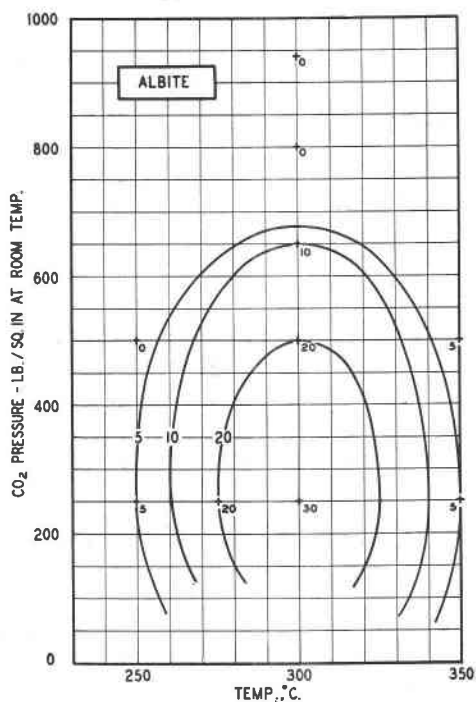


FIG. 3

one case which was noted before, where the mineral gibbsite is indicated by the *x*-ray patterns. In Fig. 4, *x*-ray patterns of the reaction product from the run at 300°C. and a pressure of 375 pounds are compared with the pattern of natural sericite, showing excellent agreement. In Fig. 5 the pattern from the conversion product at 300° Centigrade and 500 pounds pressure is compared with sericite, and in Fig. 6 with gibbsite. It will be seen that both the patterns of sericite and gibbsite are well represented in this pattern.

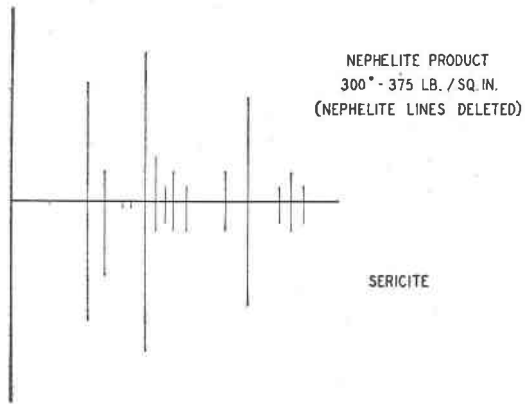


FIG. 4

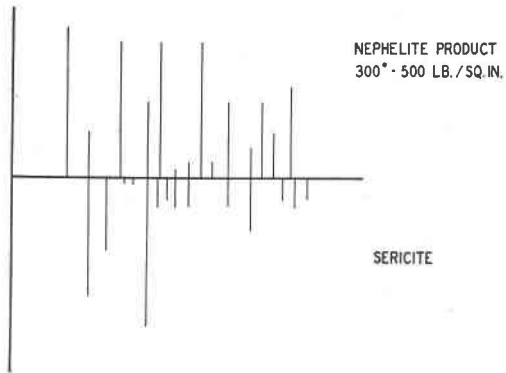


FIG. 5

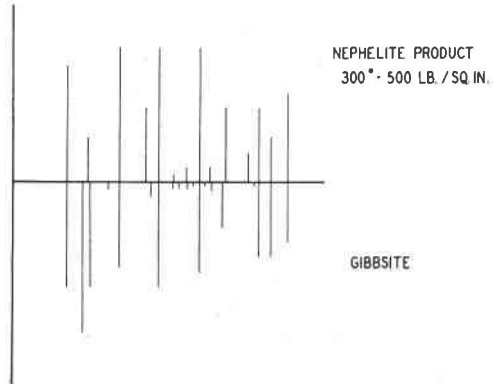


FIG. 6

TABLE 3. CONVERSION OF NEPHELITE ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ )

Conditions		Product	% Conversion
Temp.	CO <sub>2</sub> Pressure		
250°	500 lbs./in. <sup>2</sup>	Sericite	20
275°	500	Sericite	60
275°	650	Sericite	50
300°	250	Sericite	70
300°	375	Sericite	80
300°	500	25% Sericite, 75% Gibbsite	100
300°	650	Sericite	90
300°	850	Sericite	30
300°	950	Sericite	10
325°	500	Sericite	60
325°	850	Sericite	10
350°	250	—	0
350°	500	Sericite	10

The reaction rates for the field studied are shown in Fig. 7, indicating that the conversion curve is of quite large area, but that the limits are well defined. Fused nephelite gave the same end product.

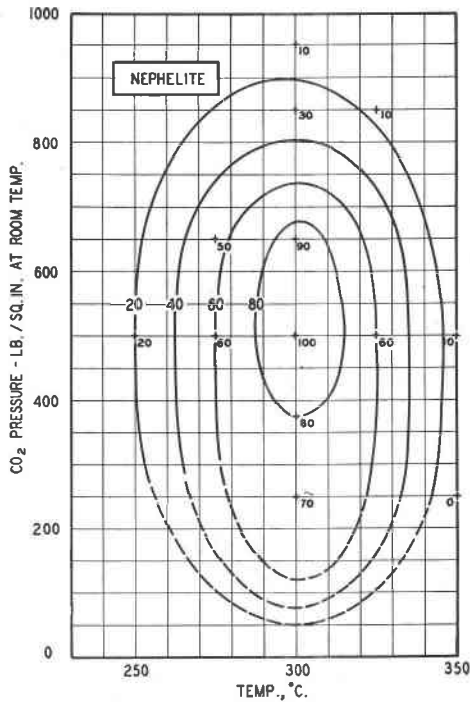


FIG. 7

## RATE OF CONVERSION OF ORTHOCLASE

In Table 4 are shown the various conditions to which this material was subjected. Here again the end product is sericite and the conditions under which the conversion occurs are rather limited. The results check well with our previous experiments, and the runs at higher pressure indicate no conversion. The *x*-ray and thermal curves of the reaction product are identical with the end product from nephelite.

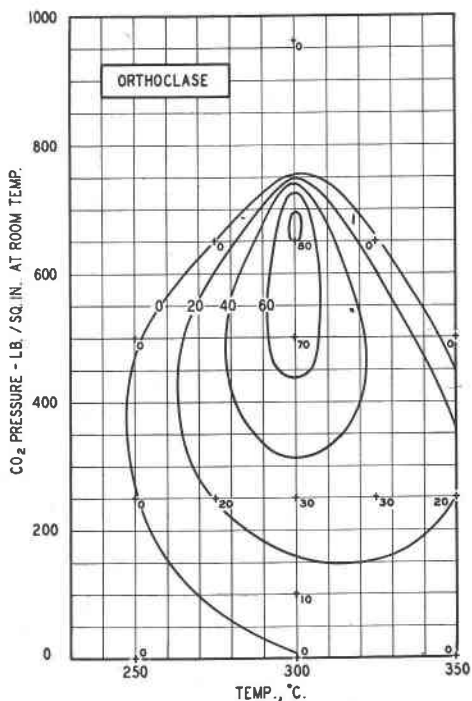


FIG. 8

In Fig. 8 are shown the reaction rates plotted as contours against various pressures and temperatures. It will be noted that the reaction area is comparatively limited.

## RATE OF CONVERSION OF SPODUMENE

In Table 5 are shown the various runs made with this material, which is readily converted. The table is made up somewhat differently from the other minerals in order to show the results obtained from the *x*-ray analysis and also from the thermal analysis. The agreement between the



TABLE 4. CONVERSION OF ORTHOCLASE ( $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ )

Conditions		Product	% Conversion
Temp.	CO <sub>2</sub> Pressure		
250°C	0 lbs./in. <sup>2</sup>	—	0
250°	250	—	0
250°	500	—	0
275°	250	Sericite	20
275°	650	—	0
300°	0	—	0
300°	100	Sericite	10
300°	250	Sericite	30
300°	500	Sericite	70
300°	650	Sericite	80
300°	960	—	0
325°	250	Sericite	30
325°	650	—	0
350°	0	—	0
350°	250	Sericite	20
350°	500	—	0

two methods of analysis is not particularly close because the thermal method does not show inert minerals such as quartz or corundum, nor does it show particularly well montmorillonite or beidellite. On the other hand, the thermal curve shows clearly the relative amounts of kaolin and dickite, which vary in proportion with the various conditions of run. It will be noticed that at the lower temperatures dickite predominates, while at the higher temperatures kaolinite is the dominant material.

In Fig. 9 are shown some thermal curves which clearly indicate the dickite and kaolinite peaks. In Fig. 10 are shown the contours of total

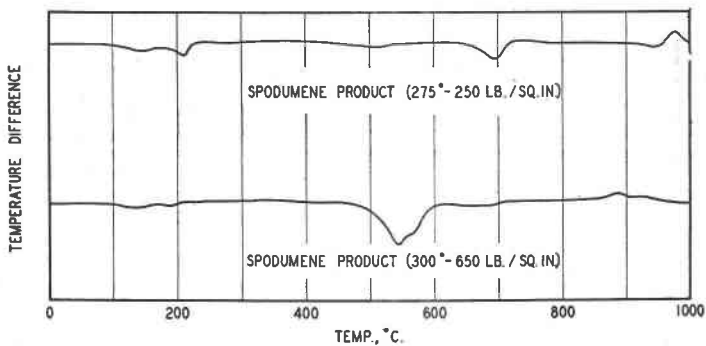


FIG. 9

TABLE 5. CONVERSION OF SPODUMENE ( $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ )

Conditions		Product and Approx. Amount		
Temp.	CO <sub>2</sub> Pressure	X-ray	Thermal Curve	% Total Conversion
250°	500 lbs./in. <sup>2</sup>	Quartz 25% Corundum 15%	Kaolinite 2% Dickite 18%	40
275°	250	Quartz 20% Montmorillonite } Kaolinite } Dickite } 80%	Kaolinite 11% Dickite 24%	100
275°	650	Quartz 25% Montmorillonite } Kaolinite } Dickite } 70%	Kaolinite 58% Dickite 15%	100
275°	850	Quartz 40% Montmorillonite } Kaolinite } Dickite } 60%	Kaolinite 22% Dickite 21%	100
300°	125	Quartz 10% Kaolinite } Dickite } 90%	(No thermal curve)	100
300°	250	Quartz 10% Kaolinite } Dickite } 90%	(No thermal curve)	100
300°	500	Quartz 10% Kaolinite } Dickite } 90%	Kaolinite 113%	100
300°	650	Quartz 15% Montmorillonite } Kaolinite } Dickite } 85%	Kaolinite 82% Dickite 5%	100
300°	950	Quartz 30% Montmorillonite } Beidellite } 70%	Kaolinite 53% Dickite 12%	100
300°	970	?	Kaolinite 27% Dickite 2%	40
325°	250	Quartz 10% Kaolinite 80%	(No thermal curve)	90
325°	650	—	—	0
350°	250	—	(No thermal curve)	0
350°	500	—	(No thermal curve)	0

conversion of spodumene, showing the comparatively large field in which the conversion is complete. In this case the contours are not completely closed at the high pressure side.

Fused spodumene gave the same end product as the original material.

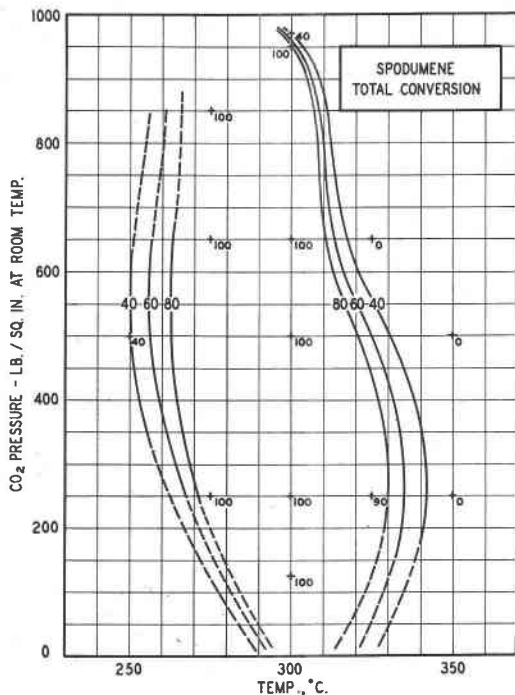


FIG. 10

#### RATE OF CONVERSION OF ANORTHITE

This mineral was checked over carefully, and we have had to come to the conclusion from our latest *x*-ray data that the end product approaches more closely montmorillonite or beidellite than pyrophyllite, which was indicated in the earlier report. The region of rapid conversion is rather narrowly confined as shown in Table 6. In Fig. 11 are shown *x*-ray patterns of the end product compared with beidellite, and the close approximation will be evident. In Fig. 12 are shown contours of conversion rates for the various conditions of pressure and temperature.

TABLE 6. CONVERSION OF ANORTHITE ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ )

Conditions		Product	% Conversion
Temp.	CO <sub>2</sub> Pressure		
250°	250 lbs./in. <sup>2</sup>	Montmorillonite or Beidellite	10
250°	500	Montmorillonite or Beidellite	10
275°	250	?	20
275°	650		0
300°	250	Montmorillonite or Beidellite	30
300°	500	Montmorillonite or Beidellite	70
300°	650		0
300°	850		0
300°	920		0
300°	950		0
325°	250	?	50
325°	650		0
350°	250	Montmorillonite or Beidellite (?)	30
350°	500		0

A sample of anorthite was fused and treated at 300° and 500 pounds of CO<sub>2</sub> pressure. The results indicated a product from the x-ray pattern of 20% kaolinite and 80% gibbsite. The kaolinite lines agree well with

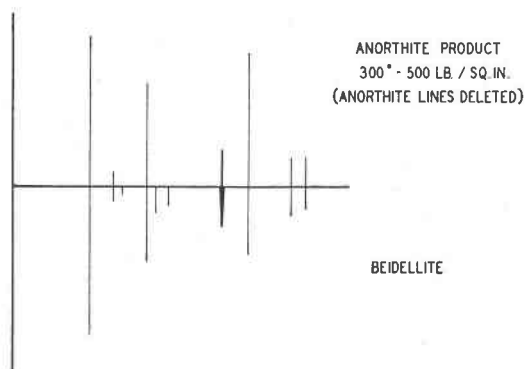


FIG. 11

the standard material, but two strong lines of the gibbsite pattern were weak or missing. The thermal curves indicated dickite with some diaspore, as shown in Fig. 13.

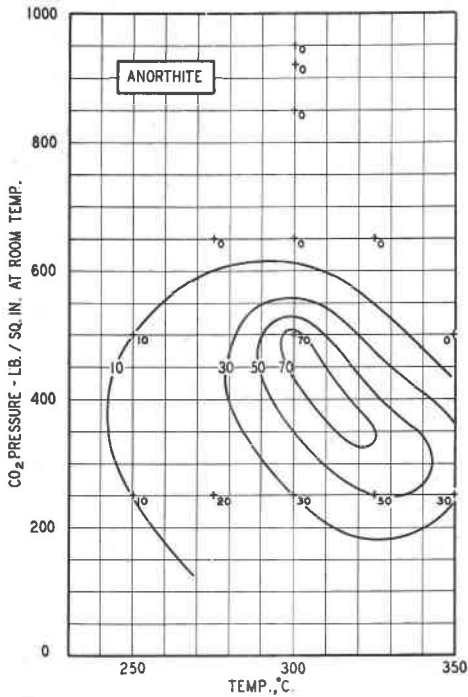


FIG. 12

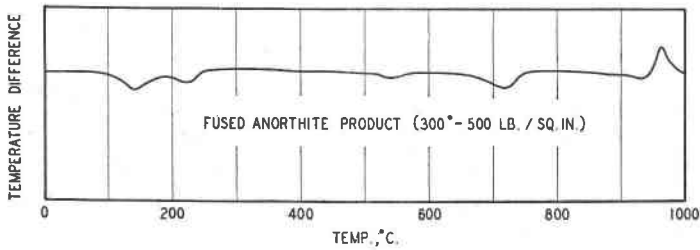


FIG. 13

CONVERSION OF OTHER MINERALS WITH CARBON DIOXIDE

In Table 7 are listed a number of other minerals which have been treated at a temperature and pressure which was believed to give the maximum rate of reaction, but as the general field was not covered we cannot be sure that some other temperature or pressure might not give a greater reaction rate.

The natural volcanic glass seemed to be converted quite readily under these conditions. The analysis of this material is:

SiO <sub>2</sub>	74.7%
Al <sub>2</sub> O <sub>3</sub>	15.2%
K <sub>2</sub> O	4.0 %
Na <sub>2</sub> O	4.0 %
Fe <sub>2</sub> O <sub>3</sub>	1

TABLE 7. CONVERSION OF OTHER MINERALS

Parent Mineral	Formula	End Product	Temp.	Pres.	Conversion in 360 hrs.
Leucite	K <sub>2</sub> O · Al <sub>2</sub> O <sub>3</sub> · 4SiO <sub>2</sub>	Sericite	300°C	500 lbs./in. <sup>2</sup>	80
Petalite	Li <sub>2</sub> O · Al <sub>2</sub> O <sub>3</sub> · 8SiO <sub>2</sub>	Kaolinite	300°	250	100
Petalite	Li <sub>2</sub> O · Al <sub>2</sub> O <sub>3</sub> · 8SiO <sub>2</sub>	Quartz, Montmorillonite	300°	800	60
Lepidolite	Li <sub>2</sub> O · 2Al <sub>2</sub> O <sub>3</sub> · K <sub>2</sub> O · 6SiO <sub>2</sub> · 2H <sub>2</sub> O	Quartz	300°	500	Slight
Beryl	3BeO · Al <sub>2</sub> O <sub>3</sub> · 6SiO <sub>2</sub>	No change	300°	500	0
Pollucite	2Cs <sub>2</sub> O · 2Al <sub>2</sub> O <sub>3</sub> · 9SiO <sub>2</sub> · H <sub>2</sub> O	No change	300°	500	0
Kaolinite	Al <sub>2</sub> O <sub>3</sub> · 2SiO <sub>2</sub> · 2H <sub>2</sub> O	No change	300°	500	0
Analcite	Na <sub>2</sub> O · Al <sub>2</sub> O <sub>3</sub> · 4SiO <sub>2</sub> · 2H <sub>2</sub> O	Kaolinite	300°	500	70
Scolecite	CaO · Al <sub>2</sub> O <sub>3</sub> · 3SiO <sub>2</sub> · 3H <sub>2</sub> O	Quartz, Dickite			
Nat. Volcanic Glass	—	Sericite	300°	500	90
		Sericite	300°	500	50?
		Dickite			

#### TREATMENT WITH STRONGER ACIDS

A few of the minerals were tested in the percolating reaction chamber with stronger acids, as shown in Table 8. It is rather interesting to note that in some cases the conversion with the stronger acids is not as rapid as with the carbon dioxide, a rather interesting fact when considering the formation of clay minerals in nature.

#### CHANGE IN RATE OF ALTERATION WITH DEPTH OF MATERIAL

In all of the preceding work, the sample for analysis of the treated material was taken from the top of the material in the reaction cup. In order to determine the change of the rate of reaction with depth, samples were taken from the top, middle, and bottom portions of the mass and subjected to *x*-ray and thermal analysis. Spodumene treated with water and CO<sub>2</sub> at 300° Centigrade and 650 lbs./in.<sup>2</sup> was chosen for this treatment. The thermal analysis curves of the three parts of the reaction

TABLE 8. CONVERSION IN OTHER ACIDS

Mineral	Acid	Temp.	Product	% Conversion
Anorthite	.3N-HCl	300°C	—	None
Anorthite	.8N-HCl	300°	Montmorillonite	40
Albite	.8N-HCl	250°	—	Slight
Albite	.8N-HCl	300°	10% Quartz, 90% Kaolinite	100
Albite	.8N-HCl	350°	—	Slight
Orthoclase	.02N-HF	300°	—	None
Orthoclase	.01N-HCl	300°	—	None
Orthoclase	.3N-HCl	300°	—	None
Orthoclase	1N-H <sub>2</sub> SO <sub>4</sub>	300°	—	None
Pollucite	.8N-HCl	300°	Montmorillonite or Beidellite	70
Diopside	.8N-HCl	300°	—	None

product show the great difference in alteration between the top, the middle and bottom layers. The large double endothermic peak at 550° in the curve of the top layer is very small in the curve of the middle layer and is almost absent in the curve of the bottom layer. At the same time, the endothermic peak at 700° is barely discernible in the curve of the top layer and is very large in the curves of the middle and bottom layers. Assuming that the peak at 550° is due to kaolinite and that at 700° is due to dickite, the proportions of these minerals present in each layer is given in Table 9.

TABLE 9. SPODUMENE TREATED WITH H<sub>2</sub>O AND CO<sub>2</sub> AT 300°C, 650 LBS./IN.<sup>2</sup>

Position of Sample	Area of Peak at 550°	Area of Peak at 700°	% Kaolinite	% Dickite
Top	.37 in. <sup>2</sup>	.02 in. <sup>2</sup>	82	5
Middle	.05	.13	11	31
Bottom	.02	.15	4	36

Basis: 100% Kaolinite = .45 in.<sup>2</sup>

100% Dickite = .42 in.<sup>2</sup>

The x-ray patterns of the three layers do not show as good correlation as the thermal analysis curves; however they give good evidence that the reaction rate is not the same at all depths. The pattern of the top layer indicates that it is a mixture of quartz and an imperfectly formed kaolinite-dickite-montmorillonite mineral; the pattern of the middle layer corresponds to that of quartz with a small amount of montmorillonite; while the pattern of the bottom layer shows a mixture of 60% quartz

and 40% montmorillonite. It is difficult to understand why the middle and bottom layers give very similar thermal curves yet show such different x-ray patterns.

#### DISCUSSION OF RESULTS

Considering the results obtained in this investigation as a whole, it is evident that the rate of reaction in CO<sub>2</sub> charged water is a maximum in a rather limited region for most of the minerals, centered around 300° Centigrade and 500 pounds CO<sub>2</sub> pressure. Contrary to our original beliefs, the reaction rate in all cases seems to decrease at the very high pressures of CO<sub>2</sub>, and in many cases the reaction becomes substantially zero at the higher acidity. These results, therefore, give us fairly definite limits as to the conditions under which reasonably rapid conversion can take place. However, it should not be concluded that in nature the clay minerals were all formed under these particular conditions as it is quite possible that the changes could go on outside of this region at rates so slow that they could not be detected in our laboratory experiments.

It will also be noted that the stability of the various minerals depends largely on an alkali content; that is, those minerals containing the largest percentage of alkali are the least stable.

There is also more evidence in this investigation than was shown previously that under certain conditions two end products can be formed at the same time. This was noted in the case of nephelite and spodumene, but the relative proportion of these products vary materially with the conditions of treatment.

It is interesting to notice how the reaction varies through the depth of the reacting material. In the one case illustrated there was a decided difference in the alteration product as we went from the top to the bottom of the charge. As might be expected, the amount of quartz was greater in the bottom than in the top, as this material evidently is carried through by the percolating water in the form of more or less colloidal material.

In this investigation some runs were made with stronger acids and in several cases the reaction rate was lower than with CO<sub>2</sub> which indicates that the break up of the original minerals occurred more rapidly in weak acids than in strong ones under these conditions of temperature and pressure. This is a result somewhat contrary to that which we expected. On the other hand, pollucite, which showed no reaction with CO<sub>2</sub> under any conditions, reacted fairly rapidly in strong acid.



## CONCLUSIONS

The conclusions drawn from this work are essentially the same as stated at the end of the previous report.

(1) Under the test conditions where CO<sub>2</sub>-charged water is allowed to percolate through the finely ground mineral, a maximum reaction rate occurs at 300°C. and 500 lbs./sq. in. pressure.

(2) The end products, while similar to the various clay minerals are not identical with them in every respect.

(3) In most cases a single end product is formed, but under a few conditions two end products were formed simultaneously.

(4) In some cases strong acids did not show as high a conversion rate as carbonic acid.

## ACKNOWLEDGMENTS

This work has been made possible by the generosity of The Geological Society of America which has allotted funds to carry out this investigation. The author wishes to express his appreciation for this assistance. The careful laboratory work of Robert L. Green, and J. L. Hall who assisted with this problem, is gratefully acknowledged.