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HYDROTHERMAL FORMATION OF CLAY MINERALS IN THE LABORATORY

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Abstract

A number of feldspars and other alumino-silicate minerals were exposed to CO_2-charged percolating water under high pressures and temperatures in a reaction chamber. A study of the end products indicated that the least stable of these materials readily broke down to form clay minerals, the greatest reaction rate occurring at 300°C. and a maximum CO_2 pressure. It was interesting to notice that the parent minerals were stable at temperatures outside of the range of 250°C. to 350°C. The production of clay minerals similar to, if not identical with, kaolinite, beidellite, sericite, pyrophyllite and gibbsite was accomplished. The resulting end product seems to be determined by the nature of the parent rock as well as by the temperature and acidity during the reaction.

Introduction

This investigation is a continuation of the preliminary work reported last year,[1] where a percolating type of reaction chamber was used to break down the three feldspars, albite, orthoclase and anorthite. In the present investigation the runs on these feldspars were repeated to determine the reaction rates over the complete range of temperature and CO_2 pressure available; and purer samples of the end product were obtained for study. In addition, a number of other minerals containing alumina and silica were studied to see if any light could be shed on the mechanism of formation of the clay minerals under hydrothermal conditions. In other words, what factors cause the formation of kaolinite, for example, rather than sericite? Are they the temperature, acidity, or parent rock? Does the clay mineral serve as the end member of a series of intermediate products, or is it formed directly? While these questions have not been definitely answered, we can begin to see a little further towards the answer than was possible before.

Previous Work

No discussion of the previous work on the synthesis of clay minerals

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[1] Norton, F. H. (1937). The accelerated weathering of feldspars, *Am. Mineral.*, vol. **22**, p. 1.

will be given here because this has been so completely covered by Morey and Ingerson[2] in a recent publication.

APPARATUS

The apparatus was the same as that used in the previous work. Three new units were constructed, making a total of five, which have been running continuously for a year and a half. A special suction pump was used to draw a definite amount of air through the condensing tubes to give, as far as possible, uniform percolation.

During a run the sample was always covered with liquid which slowly flowed down through the mass. However, the reaction started at the upper surface of the specimen and worked down, but seldom more than a few millimeters. All the samples used in the tests were taken from a slice one millimeter thick from the top of the specimen. In many cases the depth of reaction could readily be observed by a change in color and consistency.

The total pressure in the reaction chamber under the various conditions is shown in the table below.

TABLE 1

TOTAL PRESSURE IN REACTION CHAMBER IN LBS./SQ. IN.

CO_2 pressure at room temperature	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

RAW MATERIALS

Albite. This material was the same as used in the previous work.

Nephelite. This is not pure material, as it comes from a syenite rock from Ontario which has been processed to remove the iron minerals. Some albite undoubtedly remains. The approximate composition is:

TABLE 2

SiO_2	51
Al_2O_3	30
Na_2O	13
K_2O	3

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

Orthoclase. This material was the same as that used in the previous work.

Leucite. This material came from large, perfect crystals found at Albano, Italy.

Petalite. This lithium mineral came from West Paris, Maine. Its exact composition is unknown.

Spodumene. This is concentrated material from a deposit near Fitchburg, Mass.

Lepidolite. An apparently pure mineral but its source was unknown.

Anorthite. This is the same material used in the previous investigation.

Beryl. This sample came from a clear crystal found at West Paris, Maine.

Pollucite. This cesium mineral comes from West Paris, Maine. Its purity is unknown.

Kaolinite. A washed English china clay.

RATE OF REACTION AND END PRODUCTS

The materials were ball milled and decanted in water to give a sample having particles all under 1 micron in diameter. The test procedure was the same as previously described, except that the rate of percolation was more carefully controlled.

As the crystal sizes in all cases were too small for petrographic identification, the *x*-ray powder method was used extensively. Patterns of the original mineral and the alteration product were taken in each case. From these it was possible to estimate the amount of conversion by the relative intensity of the lines; a rapid and simple method. However, it should be realized that the determination of the amount of alteration is not better than ±10% and may reach an error in some cases as great as ±20%. Also, it is probable that a mineral mixed with another up to as much as 15% would not be detected by this method. This is sufficiently accurate for our present purpose, although for future work a chemical analysis to supplement the *x*-ray data would be desirable in every case.

The thermal method of analysis was also used in every case where a large enough sample was available. This method has been used extensively to identify the clay minerals, and in general is quite satisfactory.

It is necessary to use the greatest care in making an identification of the clay minerals. The crystal size is so small and the crystallization so imperfect that the *x*-ray diagrams do not have the sharp, distinct lines usually found. Also the background haze is much greater than with more perfectly crystalline materials. Therefore, it is sometimes easy to imagine that an end product coincides with one of the clay minerals, when actually it has real differences. In general the thermal curves show a water loss at lower temperatures for the synthetic mineral than for the natural one, indicating less perfect crystallization. This naturally decreases the usefulness of the thermal curves for identification purposes.

There is reason to believe, and this has been confirmed by other experimenters, that the synthesized minerals may differ slightly from their natural prototypes. Here the lines in the x-ray patterns are sometimes shifted slightly, or even suppressed. This again increases the difficulty of identification. Therefore caution is used here in expressing a definite opinion as to the crystal identity in many cases, although the class of clay mineral to which it belongs is quite certain.

It is thought most convenient to take up each original mineral in turn and discuss the reaction rate and identity of the end product. The rate is expressed as per cent converted, in a run of 320 hours as an average, in the top millimeter of sample.

The amount of conversion is plotted on a pressure-temperature diagram by means of contour lines. That is, the vertical scale expresses acidity of the solution, the horizontal scale the temperature, and each contour represents a zone of equal reaction rate.

ALBITE

This feldspar is a comparatively stable material and shows little conversion under any of the test conditions as shown in Table 3 and Fig. 1. In fact, the conversion is so slow that it was impossible to determine the nature of the end product in these tests until recently. Now it is fairly certain that the new product is beidellite because only a few new lines appear in the x-ray pattern and these correspond to this mineral, as shown in the appendix.

TABLE 3

Conditions		Product	% Conversion
Temperature	CO_2 Pressure		
250°C.	250#	—	0
250°	500#	—	0
275°	250#	Beidellite	5
300°	250#	Beidellite	20
300°	500#	Beidellite	20
350°	250#	—	0
350°	500#	—	0

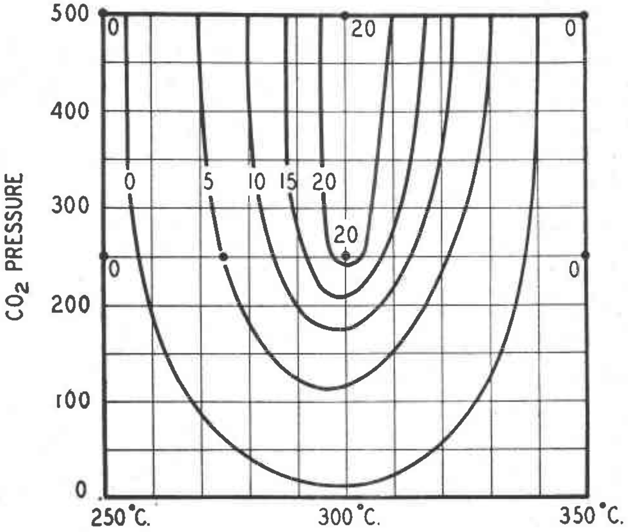

FIG. 1. Conversion of Albite.

NEPHELITE

The rate of conversion of this mineral is shown in Table 4 and Fig. 2. The rate is comparatively rapid over a large area, showing it is readily broken down. It is interesting to note the definite change in end product at different temperature levels.

TABLE 4

Conditions		Product	% Conversion
Temperature	CO_2 Pressure		
250°C.	500#	Sericite	20
275°	500#	Sericite	50
300°	250#	Sericite	20
300°	500#	Gibbsite	80
300°	375#	Sericite	40
325°	500#	Sericite	50
350°	250#	No change	0
350°	500#	No change	0

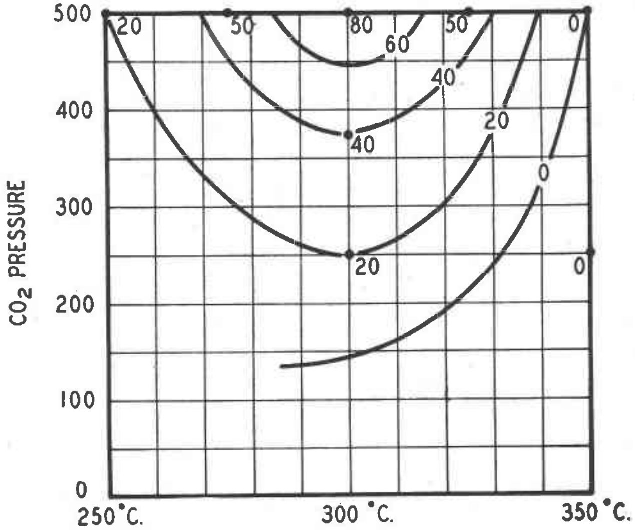

FIG. 2. Conversion of Nephelite.

The x-ray pattern for the 300°C. mineral is similar to that of gibbsite. Yet strangely enough the thermal curve (Fig. 3) is not exactly that of gibbsite, but approaches that of the monohydrate, diaspore. The small peak at 280°C. however corresponds to that of gibbsite.

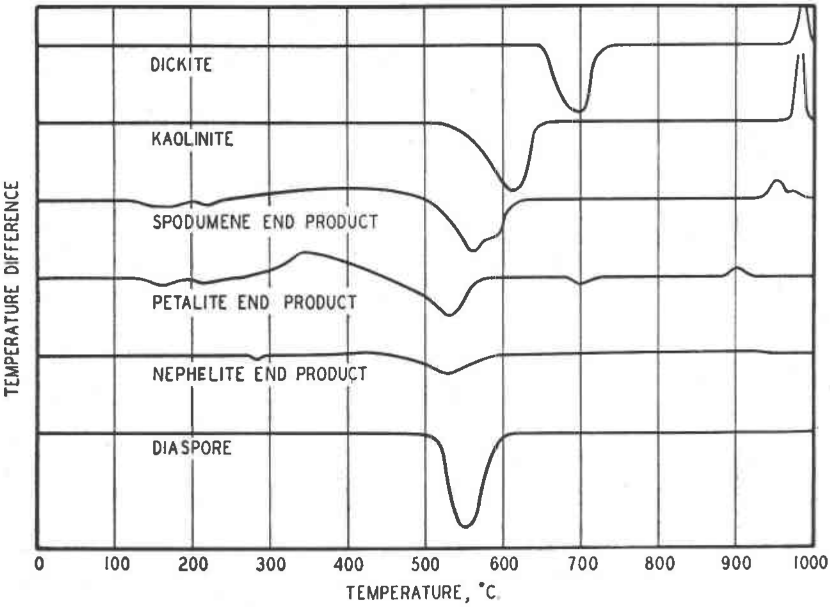

FIG. 3. Differential Thermal Curves.

A rough chemical analysis of this material gave 50% alumina, 22% silica and 22% of combined water, indicating a mixture of gibbsite or diaspore with some other clay mineral. The high alumina and combined water are significant.

Four runs were made on the nephelite at 300°C. and 500 pounds pressure. Two of the runs were carefully controlled so that the temperature never went more than 4°C. from the desired value. The other two runs had temperature variations of ±10°C. Only the carefully controlled runs gave gibbsite; the other gave sericite. This would indicate that we have probably missed other minerals in this investigation by not taking sufficiently close temperature intervals, or maintaining a sufficiently close temperature control.

There was no indication of a mixture of the two minerals; either one or the other was produced in a stable condition. No success was had in breaking up the sericite under hydrothermal conditions.

ORTHOCLASE

The rate of conversion for this mineral is shown in Table 5 and Fig. 4. The maximum rate comes at 300°C. and 500# CO_2 pressure. The equal rate lines go to higher pressures with lower temperatures. In regard to the nature of the end product, the *x*-ray pattern is similar to that of sericite, confirming the earlier results.

TABLE 5

Conditions		Product	% Conversion
Temperature	CO_2 Pressure		
250°C.	0#	—	0
250°	250#	—	0
250°	500#	—	0
275°	250#	—	0
300°	0#	—	0
300°	250#	Sericite	30
300°	500#	Sericite	70
325°	250#	Sericite	30
350°	0#	—	0
350°	250#	Sericite	20
350°	500#	—	0

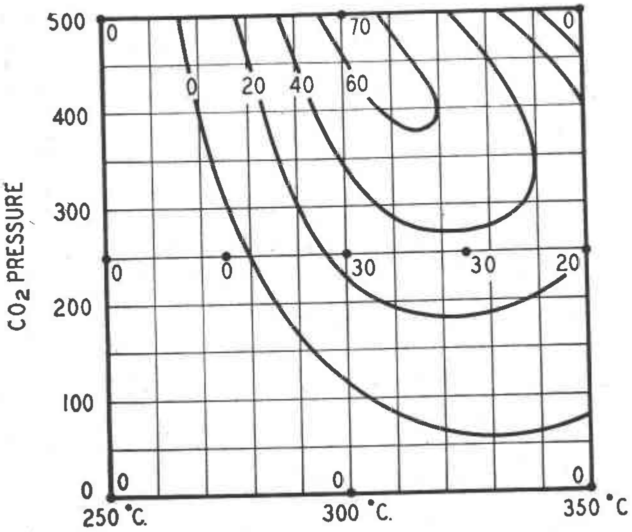

FIG. 4. Conversion of Orthoclase.

LEUCITE

Only one run was made on this mineral at 300°C. and 500#/sq. in. CO_2 pressure, showing 80% conversion. The end product gave an *x*-ray pattern similar to that of sericite.

PETALITE

One run was made on this mineral at 300°C. and 250# CO_2 pressure giving a conversion of 50%. The end product gave an *x*-ray pattern similar to, but not identical with kaolinite. A thermal curve for this mineral (Fig. 3) is somewhat like kaolinite, although the peaks are not as high as for kaolinite because of incomplete conversion. The small endothermic peak at 700°C. indicates that there is about 5% of dickite mixed with the kaolinite, an amount too small to be detected by the *x*-ray method. The irregularities in the initial part of the curve are due to the fine grain sizes, which also causes the low temperature of the exothermic peak.

SPODUMENE

The rate of conversion of this mineral is shown in Table 6 and Fig. 5, indicating a rather wide range of conditions for alteration. The end product gives the *x*-ray pattern of kaolinite. The chemical analysis of the nearly completely converted sample in Table 7 confirms this.

TABLE 6

Conditions		Product	% Conversion
Temperature	CO_2 Pressure		
250°C.	500#	Kaolinite	10
275°	250#	Kaolinite	50
300°	125#	Kaolinite	90
300°	250#	Kaolinite	90
300°	500#	Kaolinite	100
300°	0#	Kaolinite	90
325°	250#	Kaolinite	80
350°	250#	No change	0
350°	500#	No change	0

TABLE 7

Constituent	Spodumene (Thero.)	Kaolinite (Thero.)	End Product
SiO_2	64.5%	46.5%	48.4%
Al_2O_3	27.4	39.6	40.3
H_2O (Combined)	0.0	13.9	11.3
Li_2O	8.4	—	—

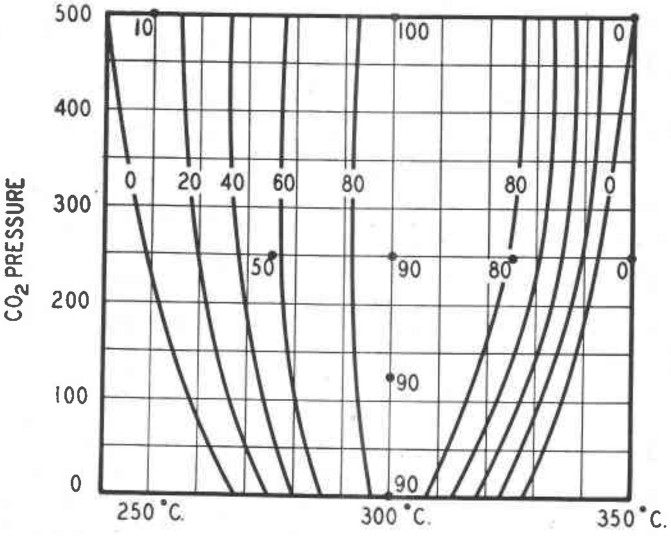

FIG. 5. Conversion of Spodumene.

The thermal curve of the end product (Fig. 3) is quite similar to that of fine grained kaolinite but the double endothermic peak would indicate that some diaspore was mixed with it.

ANORTHITE

The rates of conversion for this mineral are shown in Table 9 and Fig. 6, indicating about the same stability as orthoclase. The *x*-ray analysis shows that the end product consists of a mineral very like pyrophyllite. Unfortunately pyrophyllite does not give a characteristic thermal curve, so it cannot be checked in that way. A chemical analysis of the end product gave the following results.

TABLE 8

Constituent	Anorthite	Pyrophyllite	End Product
SiO_2	43.2%	66.7%	59.1%
Al_2O_3	36.7	28.3	21.9
H_2O	—	5.0	8.3
CaO	20.1	—	11.1

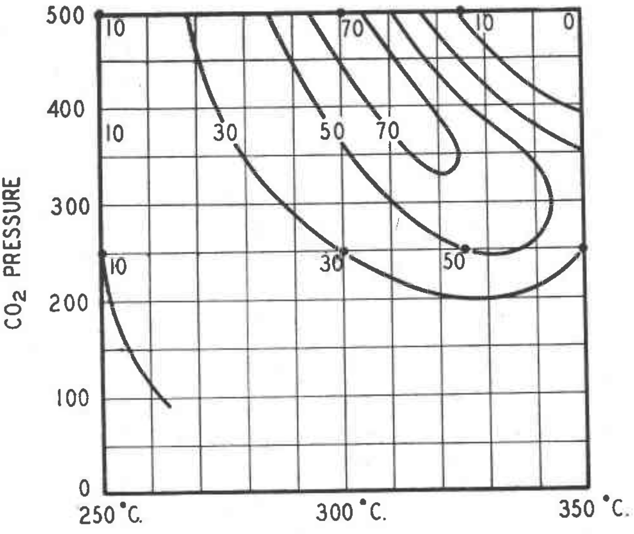

FIG. 6. Conversion of Anorthite.

The lime comes from some undecomposed anorthite and possibly some calcium silicate. In the latter case this would account for the excess silica in the end product.

These results are in agreement with the previous work on this mineral, but it is perhaps not justified in stating that the end product is identical with natural pyrophyllite, although it is very similar to it.

TABLE 9

Conditions		Product	% Conversion
Temperature	CO_2 Pressure		
250°C.	250#	Pyrophyllite	10
250°	500#	Pyrophyllite	10
275°	250#	Pyrophyllite	10
300°	250#	Pyrophyllite	30
300°	500#	Pyrophyllite	90
325°	250#	Pyrophyllite	50
350°	250#	Pyrophyllite	30
350°	500#	No change	0

POLLUCITE

One run was made on this mineral at 500# CO_2 pressure and 300°C. but no change was noted under these particular conditions. Unlike most of the other minerals tested, this one contains a molecule of water which undoubtedly increases its stability.

KAOLINITE

One run was made on this material at 500# CO_2 pressure and 300°C. which indicated no change, a result which would be expected.

LEPIDOLITE

A run at 300°C. and 500# CO_2 pressure gave no change.

BERYL

A run at 300°C. and 500# CO_2 pressure gave no change.

DISCUSSION OF RESULTS

A summary of the results is shown in Table 10 which brings out the fact that under a particular condition of temperature and acidity the end product is determined by the cation or the crystal structure of the original minerals, or some other factor associated with the parent mineral. These end products are not only different minerals, but belong to different groups. While the identity of some of the specific minerals is not too certain, the group to which they belong seems well established.

TABLE 10. SUMMARY OF REACTIONS

Parent Mineral	Formula	End Product	Temp. of Max. rate	Conversion in 320 hrs.
Albite	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	Beidellite	300°C.	25%
Nephelite	$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$	Gibbsite, Sericite	300	80
Orthoclase	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	Sericite	300	75
Leucite	$K_2O \cdot Al_2O_3 \cdot 4SiO_2$	Sericite	300	80

Petalite	$Li_2O \cdot Al_2O_3 \cdot 8SiO_2$	Kaolinite	300	50
Spodumene	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	Kaolinite	300	100
Lepidolite	$Li_2O \cdot 2Al_2O_3 \cdot K_2O \cdot 6SiO_2 \cdot 2H_2O$	No change	—	0
Anorthite	$CaO \cdot Al_2O_3 \cdot 2SiO_2$	Pyrophyllite	300	90
Beryl	$3BeO \cdot Al_2O_3 \cdot 6SiO_2$	No change	—	0
Pollucite	$2Cs_2O \cdot 2Al_2O_3 \cdot 9SiO_2 \cdot H_2O$	No change	—	0
Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	No change	—	0

What are the determining factors that cause a certain clay mineral to form under hydrothermal conditions? There seems to be no evidence in nature that the clay minerals are determined by the cations in the parent rock. Again there is ample evidence of kaolinite forming in nature, for example, from both albite and orthoclase. The answer is that kaolinite when formed from these parent minerals does so under conditions outside of the range of our experiments. These conditions may be at higher pressures and temperatures, or more likely lower temperatures and much longer times; or perhaps with some other acid forming agent such as HCl, F or SO_3.

Much work has been done on the formation of clay minerals from coprecipitated gels where the end product is mainly determined by the temperature and acidity, whereas here there is only one case indicating a change in the end product by varying these factors; and little positive evidence of a mixture of minerals in the end products.

Most geologists consider the formation of the clay minerals as a step by step process such as:

$$\text{orthoclase} \rightarrow \text{sericite} \rightarrow \text{kaolinite} \rightarrow \text{gibbsite}.$$

But here we have no evidence of any intermediate steps. The conversion goes directly to its final, stable state. If kaolinite is the stable end product of spodumene at a certain temperature and acidity, why does leucite go directly to sericite under the same conditions? Does the original mineral break down to silica and alumina gels which recombine to form the clay minerals? If so, why does the cation often seem to govern the final form of the end product?

There is considerable evidence to indicate that the materials with lower total alkali content are more stable. For example albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) is more stable than nephelite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$); and petalite ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$) is more stable than spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$). This is a result which might be expected.

One of the most interesting results is in the case of nephelite which at 500# CO_2 pressure and 300°C. goes almost completely to gibbsite, while at the same pressure and 275°C. or 325°C. the end product is sericite and no gibbsite appears in the *x*-ray pattern. This shows over what a narrow temperature range a particular mineral can form.

CONCLUSIONS

If it is justified to draw any conclusions at this stage of the work, the following tentative statements may be made:

(1) Under the test conditions where CO_2-charged water is allowed to percolate through the finely ground mineral, a maximum reaction rate is observed around 300°C. and at the highest pressure used, that is, 500#/sq. in. for all the parent minerals tried. Below 250°C. and above 350°C. the parent minerals all appeared stable.

(2) The end product, in most of these tests, is not determined solely by the pressure, temperature and acidity, but also by some characteristic of the parent mineral.

(3) The reaction proceeds at once to the final mineral. There is no evidence of any intermediate steps.

(4) There is little evidence to indicate that more than a single clay mineral is in the end product.

FURTHER WORK

Additional work should be carried out on other aluminum silicates to determine the nature of the end product. Some, like celsian, are difficult to obtain pure in nature and will have to be made up from melts. Also, runs should be made on mechanical mixtures of two minerals to see if two end products result. Runs on an isomorphic series of feldspars would also be of interest.

Reaction chambers of high temperatures alloys should be constructed in order to extend the pressure-temperature diagrams to higher values, where other end products may result. Also, other gases such as HCl, F and SO_3 should be tried, as they are believed to cause alteration in nature. Larger quantities of the end products should be prepared so that more positive identification can be made.

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, who assisted with this problem, is gratefully acknowledged.

APPENDIX

The following tables give the spacing of the stronger lines from the *x*-ray patterns. These pictures were taken on a Debeye Scherrer camera of 57.2 cm. diameter with Cu Kα

radiation through an aluminum shield .003 inch thick. The figures are in centimeters on the film, and the numerals after them are the line intensity with 10 the strongest.

TABLE 11. ALBITE CONVERSION

Albite	Conversion Product	Beidellite
	1.01—4	.99—10
1.10—4	1.11—4	
1.28—4	1.28—2	
	1.35—4	1.32—3
1.43—10	1.42—10	
1.55—4	1.54—3	
1.78—2	1.78—4	1.76—5 1.83—2
1.88—2	1.90—2	
2.16—2	2.18—1	
2.54—5	2.53—4	
2.78—2	2.78—2	2.73—2
	3.13—3	3.12—6
3.20—2		
3.31—2	3.30—2	
3.44—2	3.44—3	
3.52—2	3.51—2	
3.77—1	3.75—1	3.70—2
		3.83—2

TABLE 12. NEPHELITE CONVERSION

Nephelite	Conversion Product	Gibbsite
	.69—8	.71—8
	.77—8	.90—10
	1.02—3	1.01—6
1.20—2		
1.41—10	1.43—10	1.41—8
1.54—4		
1.73—2	1.73—5 1.82—5	
1.95—2	1.94—9	1.90—8
2.16		
2.46—2	2.49—10	2.45—8
2.56—3		
2.72—1	2.80—5	2.74—6
2.99—2	3.10—2 3.16—2	3.19—3
3.23—2	3.27—5	3.31—3
3.32—2		
3.43—2	3.42—3	
	3.65—6	3.60—4
3.75		

TABLE 13. ORTHOCLASE CONVERSION

Orthoclase	Conversion Product	Sericite
1.06—1	1.08—2	1.00—8
1.29—½	1.31—2	
1.39—10	1.37—10	1.35—5
	1.42—10	1.39—5
1.55—4		
	1.75—2	1.79—10
	1.88—½	1.91—3
2.11—1	2.13—3	2.14—3
	2.16—½	2.19—2
2.56—5	2.55—5	
	2.57—5	
	2.82—½	2.80—2 2.84—2
	3.10—½	3.08—5
	3.18—1	3.14—5
	3.43—2	
	3.70—½	3.68—3

TABLE 14. LEUCITE CONVERSION

Leucite	Conversion Product	Sericite
	.75—2	
.88—5	.84—2	
.95—1	1.00—7	1.00—8
1.35—10 (V. Broad)	1.35—2	1.35—5
	1.46—2	1.39—5
1.60—8		
1.71—2	1.71—10 1.79—10	1.79—10
	1.88—2	1.91—3
1.94—4		
2.05—3	2.05—2 (V. Broad)	2.14—3
	2.28—2(Broad)	2.19—2
2.60—1		
2.70—1		
2.80—3	2.80—3 (V. Broad)	2.80—2 2.84—2
2.89—1		
2.95—1		
3.05—1	3.09—8	3.08—5
3.16—1	3.15—8	3.14—5
3.45—1	3.50—1 (V. Broad)	
3.60—1		
3.66—1		
	3.70—3	3.68—3
3.85—1	3.85—1	

TABLE 15. PETALITE CONVERSION

Petalite	Conversion Product	Kaolinite
	1.03—6	.98—8 1.03—8
1.22—10	1.30—4	1.23—5
1.34—5	1.38—1	
1.41—5		
1.48—2		
1.58—2	1.62—1	
1.73—1		
1.83—2	1.84—7	1.74—8
1.90—1		
	1.97—3	1.89—10
2.04—1	2.09—1	
2.28—2	2.34—4	2.23—2
		2.52—1
2.60—1	2.61—1	
2.75—1	2.81—3	2.72—7
2.84—1		
2.91—2		
3.09—1		3.06—5
	3.19—9	3.14—1
3.23—2		
3.31—2		
3.42—1		
3.50—2	3.50—1	3.45—1
	3.77—2	3.76—3
3.90—1	3.93—2	3.90—1
3.98—1		
4.04—1		

TABLE 16. SPODUMENE CONVERSION

Spodumene	Conversion Product	Kaolinite
	1.02—8	.98—8 1.03—8
1.30—10	1.30—5	1.23—5
1.42—4		
	1.80—10	1.74—8
2.01—4	1.95—10	1.89—10
2.19—3	2.33—5	2.23—2
2.47—8		2.52—1
2.56—1		
2.84—4	2.80—5	2.72—7
3.06—3	3.02—1	3.06—5
	3.14—10	3.14—1
3.26—2		
3.31—1		
3.39—1		

3.45—2	3.45—½	3.45—1
3.54—1		
3.60—1	3.61—2	3.61—2
3.77—1	3.71—2	3.76—3
3.89—4	3.90—2	3.90—1
3.96—1		
4.07—1		
4.31—1		
4.71—1		
4.86—1	4.90—1	
4.96—1		

TABLE 17. ANORTHITE CONVERSION

Anorthite	Conversion Product	Pyrophyllite
		.73—4
		.82—4
	1.02—8	.98—10
1.34—10		
1.42—2	1.41—5	1.44—8
	1.79—8 (Broad)	1.74—4 1.83—4
	2.03—1	2.07—2
	2.16—2	2.16—2
2.53—3	2.58—2	
	2.76—2	2.75—2
3.03—2	3.06—2	
	3.14—4	3.12—3
3.43—4		
	3.49—4	3.47—2