DECOMPOSITION AND ALTERATION OF FELDSPARS AND SPODUMENE BY WATER

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ABSTRACT

In an attempt to effect considerable decomposition and to produce one of the clay minerals, samples of microcline, albite, and kunzite were reduced to particles less than 0.1 micron in diameter by grinding them for 394 hours and more under water in an agate mortar and pestle. The suspensions produced were electrodialyzed in the mortar, and it was found that all of the constituents of these minerals diffused through the membrane of the dialyzer. This was interpreted as evidence that silica and alumina, as well as the alkalis, were present in solution as ions, indicating that clay minerals may probably form, at least in part, by ionic reactions rather than by colloidal reactions. Over 50 per cent of the alkalis were removed from the feldspars by dialysis; the kunzite lost 44 per cent of its lithia. The decomposed minerals were hydrated. About 50 per cent of the water could not be expelled at 100°C., and some of it still remained at 500°C. Dehydration data suggested that the water was merely adsorbed on the mineral particles. *X*-ray photographs showed that substantial amounts of the minerals were undecomposed and that no detectable new mineral had been formed. After treatment of the decomposed materials in water in a bomb at 300°C., *x*-ray evidence for the formation of quartz and perhaps of kaolinite was found. The particles of the original minerals may also have increased in size during the hydrothermal treatment.

INTRODUCTION

Since several investigators in geology and in soil science have demonstrated that feldspars can be partially decomposed in the laboratory by cold water, this investigation was undertaken for the purpose of determining the amount of decomposition which could be effected by prolonged grinding of feldspars in water. Another purpose was to determine by the powder method of *x*-ray analysis if one of the clay minerals could be produced, either by this method at temperatures normally found in weathering, or by treatment of the material after grinding with water at elevated temperatures.

The counsel of Professor John W. Gruner in connection with the execution of the experimental work and with the preparation of this paper is gratefully acknowledged. The writer is also indebted to Dr. R. B. Ellestad for assistance with the analytical work and for helpful suggestions. This study was made possible by the aid of the Graduate School of the University of Minnesota. The work was completed in December 1937, but due to unforeseen circumstances, it could not be published until now.

WORK OF OTHER INVESTIGATORS

As early as 1848, W. B. and R. E. Rogers[1] found that finely powdered

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[1] Rogers, W. B., and R. E., Decomposition and partial solution of minerals: *Am. Jour. Sci.*, 2d ser., **5,** 401–405 (1848).

feldspars gave an alkaline reaction when moistened with water. Similar experiments on the alkalinity of feldspars were conducted by Kenngott,[2] Clarke,[3] Tamm,[4] and Stevens.[5] Stevens showed that feldspars, spodumene, and numerous other silicates released enough bases when ground in carbon dioxide-free water to give a basic *pH*. Tamm also demonstrated that finely pulverized feldspars have a basic *pH* in water and that they adsorb water, a portion of which can not be eliminated by heating at 110°C. More recently, the work of Correns and v. Engelhardt[6] has indicated that all components of a feldspar go into true ionic solution. After treatment of adularia in water and in weak acid solutions, they found that even silica and alumina diffused through the membrane of an ultrafiltration apparatus.

Except for the experiments of Collins,[7] in which hydrofluoric acid was used, the production of clay minerals by the alteration of feldspars in cold solutions has not been reported in the literature. At elevated temperatures, however, some of the clay minerals have been formed in the laboratory by two methods. First, Badger and Ally,[8] Schwarz and Trageser,[9,10] and Norton[11,12] have altered feldspars with hot carbonated water and weak acid solutions; and secondly, Noll,[13,14,15] Ewell and Insley,[16]

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[2] Kenngott, A., Über die alkalische Reaction einiger Minerale: *Neues Jahrb.*, 778–779 (1867).

[3] Clarke, F. W., Alkaline reaction of some natural silicates: *U. S. Geol. Survey, Bull.* **167,** 156 (1900).

[4] Tamm, O., Experimentelle Studien über die Verwitterung und Tonbildung von Feldspaten: *Chemie der Erde,* **4,** 420–430 (1930).

[5] Stevens, R. E., Studies of the alkalinity of some silicate minerals: *U. S. Geol. Survey, Prof. Paper* **185-A,** 1–13 (1934).

[6] Correns, Carl W., and v. Engelhardt, Wolf, Neue Untersuchungen über die Verwitterung des Kalifeldspats: *Chemie der Erde,* **12,** 1–22 (1938).

[7] Collins, J. H., On the nature and origin of clays: *Min. Mag.*, **7,** 205–214 (1886).

[8] Badger, A. E., and Ally, A., Note on the formation of kaolin minerals from feldspars: *Jour. Geology,* **40,** 745–747 (1932).

[9] Schwarz, R., and Trageser, G., Über die kunstliche Umwandlung von Feldspat in Kaolin: *Zeit. anorg. Chemie,* **215,** 190–200 (1933).

[10] ———, Kunstliche Umwandlung von Feldspaten in Pyrophyllit: *Naturwiss.*, **23,** 512 (1935).

[11] Norton, F. H., Accelerated weathering of feldspars: *Am. Mineral.*, **22,** 1–14 (1937).

[12] ———, Hydrothermal formation of clay minerals in the laboratory: *Am. Mineral.*, **24,** 1–17 (1939).

[13] Noll, W., Hydrothermale Synthese des Kaolins: *Min. pet. Mitt.*, **45,** 175–190 (1934).

[14] ———, Mineralbildung im System $Al_2O_3-SiO_2-H_2O$: *Neues Jahrb.*, **70,** 65–115 (1935).

[15] ———, Über die Bildungsbedingungen von Kaolin, Montmorillonit, Sericit, Pyrophyllit, und Analcim: *Min. pet. Mitt.*, **48,** 210–247 (1936).

[16] Ewell, R. H., and Insley, H., Hydrothermal synthesis of kaolinite, dickite, beidellite, and nontronite: *Jour. Research U. S. Bur. Standards,* **15,** 173–186 (1935).

and Gruner,[17] using co-precipitated silica-alumina gels and mixtures of silica and alumina in various solutions, have synthesized kaolinite and other hydrous compounds of silica and alumina.

EXPERIMENTAL WORK

Apparatus Employed

A machine, consisting essentially of a mechanically rotated agate mortar and pestle, was used for grinding the minerals in distilled water. It was belted to a motor-driven reduction gear in such manner that the pestle revolved about 80 r.p.m. in a clockwise direction while the mortar turned one r.p.m. in the opposite direction.

As the grinding produced suspensions too fine-grained to filter by ordinary methods, an electrodialyzer was used for this process. To eliminate repeated transferences of suspensions from one container to another and to permit the pestle to act as a stirrer, the dialyzer was attached to the grinding machine and designed so that the mortar with its suspension served as the anode compartment. The cathode compartment, consisting of a pyrex glass tube sealed off at one end by a cellophane membrane dipping into the suspension, was continually rinsed by small amounts of distilled water. The electrodes were of platinum. They were connected to a source of 220 volts D.C., and the distance between them was varied to prevent heating of the solutions. Grinding and dialysis were continued until a tiny drop of phenolphthalein introduced into the cathode liquid indicated that bases were no longer being removed from the suspension.

Dehydration of samples of air-dried mineral residues, remaining in the mortar after grinding and dialysis, was carried out in a vacuum apparatus designed very similar to the "tensi-eudiometer" described and successfully used by Calsow[18] in the identification of kaolinite by the shape of its dehydration curve. The portion of the apparatus containing the sample was heated in a small electric furnace maintained to within 3°C. of the desired temperature by a Leed-Northrup thermostatic control.

Small samples of the air-dried residues were treated hydrothermally in a gold-lined, steel bomb with a capacity of 50 cc. The bomb charge consisted only of 20 cc. of distilled water and a half gram of residue; it was maintained at 300°C. in a thermostatically controlled electric furnace.

X-ray powder photographs of the minerals used in the experiments, the residues, and of the hydrothermally treated residues were obtained. All exposures were made in a circular camera with a radius of 57.3 mm. using unfiltered Fe radiation.

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[17] Gruner, J. W., Formation and stability of muscovite in acid solution at elevated termperatures: *Am. Mineral.*, **24**, 524–528 (1939).

[18] Calsow, G., Über das Verhaltnis zwischen Kaolinen und Tonen: *Chemie der Erde*, **2**, 415–441 (1926).

Minerals Used

Two feldspars, microcline and albite, were used in the experiments, and kunzite, a variety of spodumene, was also employed. The compositions of the fresh minerals and of the residues left in the agate mortar after grinding and dialysis are given in Table 1. All analyses were made in the Rock Analysis Laboratory, Department of Geology, University of Minnesota. The methods used were essentially the same as those set forth by Hillebrand and Lundell.[19] Lithium was determined by the procedure described by Wells and Stevens.[20]

TABLE 1. ANALYSES OF MINERALS USED AND OF RESIDUES
(L. C. Armstrong, analyst)

	Microcline		*Albite*		*Kunzite*	
	Fresh	Residue	Fresh	Residue	Fresh	Residue
	%	%	%	%	%	%
SiO_2	65.46	74.35	66.01	69.98	64.20	61.05
Al_2O_3	19.12	8.53	21.40	11.87	28.02	19.37
CaO	nil	nil	1.74	.37	nil	nil
Na_2O	3.51	.64	10.27	2.73	.18	.04
K_2O	11.93	2.26	.56	.23	.05	.04
Li_2O	n.d.	n.d.	n.d.	n.d.	7.62	2.92
Ignition	0.18	14.20	.27	14.76	.05	16.52
Total	100.20	99.98	100.25	99.94	100.12	99.94

Microcline: Locality unknown. Grayish white cleavage fragments. Albite present in perthitic intergrowth; calculation of the norm indicates a composition of 70.6 per cent orthoclase and 29.4 per cent albite.

Albite: Locality unknown. Grayish white moonstone cleavage fragments; calculation of the norm indicates a composition of 86.8 per cent albite, 8.6 per cent anorthite, and 3.1 per cent orthoclase.

Kunzite: From San Diego County, California. Transparent lilac-tinted cleavage fragments.

Decomposition and Hydration Effects

The data relative to grinding and to the amount of material which diffused through the cellophane membrane to the cathode are listed in Table 2. As described in the foregoing, the cathode compartment of the electrodialyzer was continually rinsed by small amounts of distilled water. These cathode solutions, which were clear and free from sediment, were evapo-

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[19] Hillebrand, W. F., and Lundell, G. E., *Applied Inorganic Analysis,* John Wiley and Sons, New York, **1929.**

[20] Wells, R. C., and Stevens, R. E., Determination of the common and rare alkalis in mineral analysis: *Ind. and Eng. Chem.*, **6,** 440 (1934).

rated to dryness in platinum dishes, and the residues were analyzed to determine the number of milligrams of each substance removed in solution. From these weights, the m.e. (milliequivalents—equivalent weights in milligrams) have been calculated to show the relative number of ions of bases removed from each of the three minerals.

TABLE 2. DATA ON GRINDING AND ELECTRODIALYSIS

	Microcline	*Albite*	*Kunzite*
Wt. of sample (gms.)	3	4	4
Time ground (hrs.)	921	876	394
Volume of cathode solution (cc.)	2000	2000	1500

AMOUNT OF MATERIAL IN THE CATHODE SOLUTION

	From Microcline		*From Albite*		*From Kunzite*	
	mgms.	*m.e.*	*mgms.*	*m.e.*	*mgms.*	*m.e.*
SiO_2	16.4		73.5		24.8	
Al	6.4	.71	3.7	.41	5.0	.55
Ca	nil		21.7	1.08	nil	
Na	49.6	2.15	160.2	6.96	n.d.	
K	156.1	3.99	9.6	.24	n.d.	
Li	n.d.		n.d.		59.0	8.50
Total	228.5	6.85	268.7	8.69	88.8	9.05

Calculated on the basis of a four-gram sample, the m.e. of bases removed in solution from the microcline would be 9.13 instead of 6.85 as given in Table 2. It is interesting to note that this figure agrees closely with the m.e. of bases removed from four gram samples of albite and kunzite, indicating that each gram of the three minerals lost about the same number of positively charged ions during the artificial weathering process. However, these data are not strictly comparable. The kunzite was not ground as long as the feldspars, and *x*-ray investigations showed that it was probably the coarsest grained of the three minerals.

As in natural weathering, alumina and silica were the most difficultly soluble. The albite lost considerably more silica than did the other two minerals. This was verified by grinding additional samples of albite and microcline and dialyzing with the current reversed, so that the mineral suspension was in the cathode compartment and the anode was in distilled water. After grinding each sample for 100 hours, the anode solution from albite contained over 50 per cent more silica than that from microcline. Only small traces of alkalis were found in the anode solutions, which excludes the possibility that silica diffused through the membrane as alkali silicate molecules. In an identical experiment conducted with two grams of transparent colorless quartz, the anode solution contained 6.6 milligrams of silica. It seems very probable that some of the silica from the finely ground feldspars and quartz was hydrolyzed to silicic acid and migrated to the anode as negatively charged silicate ions. The presence of silica in the cathode diffusates (Table 2) is more difficult to explain; it may have entered the cathode compartment of the dialyzer as alkali silicate molecules. The bases (Na, K, Ca, Li, and Al) undoubtedly diffused to the cathode as positively charged ions. These data, then, support the observation of Correns and v. Engelhardt[21] that all components of a feldspar go into true ionic solution. This, as they point out, throws new light on the weathering of silicates and the formation of hydrous silicates. It is probable that clay minerals may form, at least in part, by ionic reactions rather than by colloidal reactions as it has been generally believed.

The analyses of the minerals used and those of their respective residues remaining in the mortar after grinding and dialysis are compared in Table 1. The analyses have been recalculated to total 100 per cent in Table 3, and the losses and gains in each constituent have been computed on the assumption of no change in the alumina content. Actually, some alumina was lost by each mineral (see Table 2), but these losses were so small that they do not seriously affect the accuracy of the calculated changes.

Due to wear of the agate mortar and pestle, large amounts of silica were introduced. The microcline, for example, gained 101 per cent of silica by weight from the mortar and pestle. It also gained 31 per cent of water by weight. Since the albite and kunzite did not gain as much silica or as much water as the microcline (Table 3, column D), it seems probable that a part of the water held by the residues may be due to hydration of the silica added from the mortar and pestle.

The microcline lost 59 per cent of its soda and 57 per cent of its potash (Table 3, column F). A greater percentage of soda than of potash was also dissolved from the albite, and the percentage of lime dissolved was larger still. Therefore, if it is assumed that a major portion of the silica removed by dialysis came from the minerals rather than from the agate worn from the mortar and pestle, the rate of solution of the components of the feldspars may be given as follows: $CaO > Na_2O > K_2O > SiO_2$

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[21] Correns and v. Engelhardt, *op. cit.*

TABLE 3. CALCULATION OF LOSSES AND GAINS

	A	B	C	D	E	F
	Microcline					
	%	%	%	%	%	%
SiO_2	65.33	74.37	166.35	+101.02	—	+154.63
Al_2O_3	19.08	8.53	19.08	—	—	—
Na_2O	3.50	.64	1.43	—	−2.07	−59.14
K_2O	11.91	2.26	5.06	—	−6.85	−57.21
H_2O	.18	14.20	31.76	+31.58	—	large gain
Total	100.00	100.00	223.68	+132.60	−8.92	
	Albite					
SiO_2	65.85	70.02	125.83	+59.98	—	+91.09
Al_2O_3	21.35	11.88	21.35	—	—	—
CaO	1.73	.37	.67	—	−1.06	−61.27
Na_2O	10.24	2.73	4.91	—	−5.33	−52.05
K_2O	.56	.23	.41	—	− .15	−26.79
H_2O	.27	14.77	26.54	+26.27	—	large gain
Total	100.00	100.00	179.71	+86.25	−6.54	
	Kunzite					
SiO_2	64.12	61.09	88.23	+24.11	—	+37.60
Al_2O_3	27.99	19.38	27.99	—	—	—
Na_2O	.18	.04	.06	—	− .12	−66.67
K_2O	.05	.04	.06	—	—	—
Li_2O	7.61	2.92	4.22	—	−3.39	−44.55
H_2O	.05	16.53	23.87	+23.82	—	large gain
Total	100.00	100.00	144.43	+47.43	−3.51	

A. Analyses of minerals used recalculated to total 100 per cent.

B. Analyses of residues recalculated to total 100 per cent.

C. Column B recalculated on the assumption of no loss or gain of Al_2O_3. In the case of microcline, for example, the oxides in column B are multiplied by $\frac{19.08}{8.53}$.

D. Gains in parts by weight per 100 parts of the fresh mineral (*C* minus *A*).

E. Losses in parts by weight per 100 parts of the fresh mineral (*C* minus *A*).

F. Losses (−) and gains (+) of each constituent in parts by weight per 100 parts of the constituent in the fresh mineral $\left(\frac{D \text{ or } E}{A}\times 100\right)$.

$>Al_2O_3$. The kunzite was least altered; it lost only 44 per cent of its lithia.

Carbon dioxide was not found in the residues. Therefore, the loss on ignition has been attributed to water. In an attempt to determine if the water was adsorbed or if some of it had become a part of the lattice of a hydrous silicate, the residues were dehydrated at various temperatures. Dehydration curves plotted from these data (Fig. 1) show that approximately one-half of the water could not be expelled by heating the residues at 100° C.; some of it still remained at 500° C. The curves are quite smooth, indicating that the water was held essentially in the same manner at high as at low temperatures.

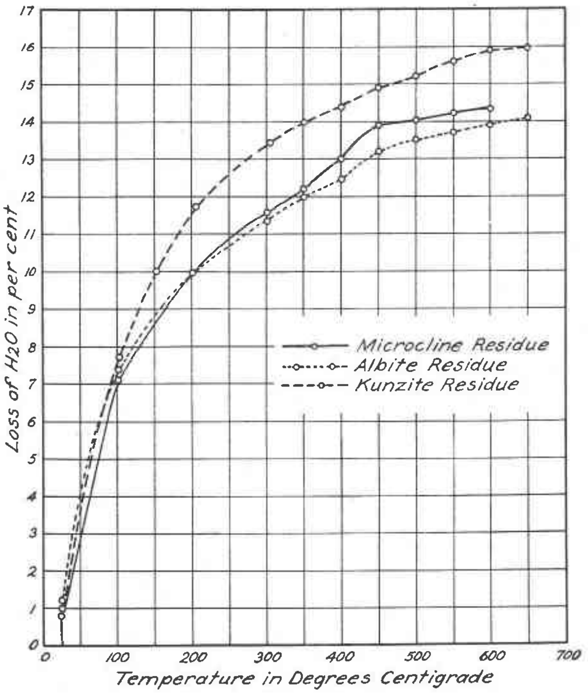

FIG. 1. Dehydration curve of finely ground and electrodialyzed microcline, albite, and kunzite.

Clay minerals, such as kaolinite, have dehydration curves with inflections which show the temperature at which crystal lattice water is liberated. However, as Kelly, et al.[22], have pointed out, these inflections are less pronounced when the clay minerals are finely pulverized. This effect has been ascribed to adsorbed water and to the probability that lattice water is more readily expelled from very tiny particles. Samples of

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[22] Kelly, W. P., Jenny, Hans, and Brown, S. M., Hydration of minerals and soil colloids in relation to crystal structure: *Soil Sci.*, **41,** 259–274 (1936).

Morton kaolinite[23], dehydrated before and after grinding, gave curves (Fig. 2) which agreed closely with the work of these investigators. The shape of the dehydration curve of the kaolinite approached that of the residues as it was ground finer. In view of this fact, the dehydration data are considered to be inconclusive, but it seems probable that most of the water was merely adsorbed on the residue particles.

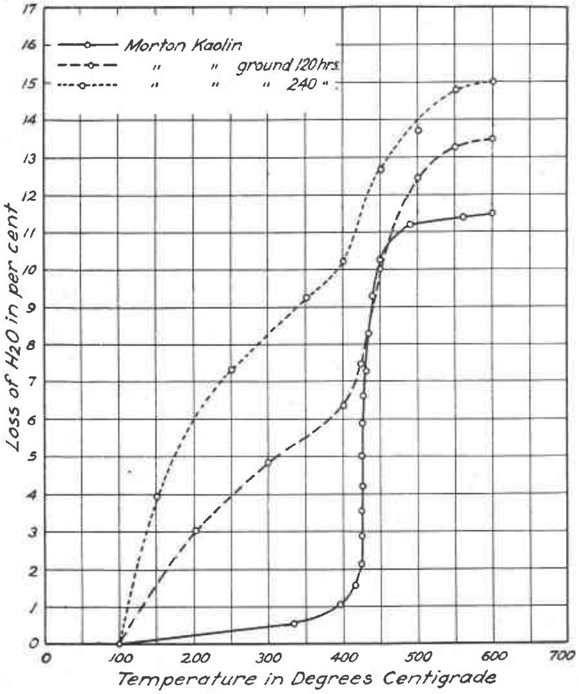

FIG. 2. Dehydration curves of Morton kaolin.

X-RAY DATA

Mineral Residues. X-ray patterns of the microcline, albite, and kunzite residues were essentially the same as those obtained from the fresh minerals, showing that no detectable new mineral had been formed. The lines on the patterns, however, were much broader and more diffuse, and some of the lines from weak reflections in the minerals were entirely lacking in the residue patterns. The broadening of lines on an *x*-ray powder diagram

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[23] For description and analysis of Morton kaolinite see Grout, F. F., and Soper, E. K., Clays and shales of Minnesota: *U. S. Geol. Survey., Bull.* **678,** 219 (1919).

becomes very marked when the mineral particles are approximately 0.01 micron in diameter.[24] From this effect, it was estimated[25] that the residues had a grain size ranging about between 0.1 and 0.02 micron. The kunzite residue was the most coarse-grained; its grain size was probably near the coarser limit of this range. Although large amounts of agate were added to the residues from the mortar and pestle, no quartz lines could be detected in the *x*-ray photographs. It was probably present in particles less than 0.01 micron in diameter, which would be too fine-grained to reflect the *x*-rays.

Bomb-treated Residues. The residues were treated in 20 cc. of distilled water at 300°C. in a gold-lined, steel bomb with a capacity of 50 cc. The new lines, which appeared on the *x*-ray photographs after this treatment, are given in Table 4. The albite and kunzite were subjected to these conditions for 7 and 8 days, respectively, and similar experiments with these materials for 16 days yielded the same results. The line at $d = 3.349$ Å appeared on the microcline residue pattern after hydrothermal treatment for 7 days, but the other two lines did not appear until the residue had been maintained at 300° C. for 18 days. Some of the lines which were missing on the photographs of the residues reappeared after the hydrothermal treatment, and all lines were less diffuse, suggesting that there may have been a small increase in the size of the particles of the original minerals.

TABLE 4. INTERPLANAR DISTANCE, *d*, OF NEW LINES IN THE *X*-RAY PHOTOGRAPHS OF THE RESIDUES AFTER HYDROTHERMAL TREATMENT AT 300°C.

Microcline Residue (18 days)		Albite Residue (7 days)		Kunzite Residue (8 days)	
d in Å	*I**	*d in Å*	*I*	*d in Å*	*I*
4.463	vw	4.457	vw	4.463	vw
3.349	m	3.342	m	3.358	m
				2.555	w
				1.828	w
1.492	m	1.489	m	1.492	m

* I = Intensity; vw—very weak; w—weak; m—moderate.

Since the most intense line of quartz would occur at $d = 3.33$ Å, the line at about that position in the patterns has been assigned to quartz, formed from silica derived either from the minerals or from the agate

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[24] Bragg, W. H., and W. L. *The Crystalline State*, G. Bell and Sons Ltd., London, 188 (**1933**).

[25] Gruner, J. W., Personal communication (1937).

mortar. The other lines agree closely with some of the strong lines of kaolinite. The line at $d=1.49$ Å is particularly characteristic of kaolin minerals and similar layer structures. Two of the most characteristic lines of kaolinite would be produced by reflections from the basal pinacoid and should appear at $d=7.16$ and 3.58 Å. These lines were not detected on the photographs. Somewhat unequal spacings of the layers may be an explanation for the lack of strong reflections from the basal pinacoid.

SUMMARY

Samples of microcline, albite, and kunzite were reduced to particles less than 0.1 micron in diameter by grinding in water in an agate mortar for 394 hours or more. The suspensions produced were electrodialyzed in the mortar to remove bases. It was found that all of the constituents of the minerals diffused through the membrane of the dialyzer. This was interpreted as evidence that all of the constituents were present in solution in the ionic state, and that clay minerals may form, at least in part, by ionic reactions.

The feldspars lost more than 50 per cent of their alkalis. The rate of solution of the components of the feldspars was: $CaO > Na_2O > K_2O > SiO_2 > Al_2O_3$. Silica was dissolved more readily from the albite than from the microcline. The kunzite lost 44 per cent of its lithia and small amounts of silica and alumina.

The decomposed minerals were considerably hydrated. About 50 per cent of the water could not be expelled at 100°C., and a small amount of water was still retained at 500°C. Some of the water may be attributed to hydration of relatively large amounts of silica introduced from the agate mortar and pestle. Dehydration curves of the decomposed minerals were essentially smooth, suggesting that much water was probably present as adsorbed water and not as crystal lattice water.

X-ray investigations revealed that substantial amounts of feldspars and kunzite remained in the residues after grinding and dialysis. No evidence of the formation of a new mineral could be detected in the *x*-ray photographs.

After treatment of the decomposed minerals in water at 300°C., *x*-ray photographs displayed a new line indicating the formation of quartz. Other new lines suggested the formation of kaolinite or of a similar layer structure. The feldspar and kunzite lines were more intense, suggesting that the particles of these minerals increased in size during the hydrothermal treatment.