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The Surface Reactions Of Silicate Minerals

PART II. REACTIONS OF FELDSPAR SURFACES WITH SALT SOLUTIONS.

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The Surface Reactions of Silicate Minerals

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INTRODUCTION

The review of literature cited in Part I of this series indicates that little is known of the interaction of feldspar surfaces with salt solutions. The work of Breazeale and Magistad (1) clearly demonstrated that exchange reactions between potassium and calcium occur in the case of orthoclase surfaces. This is especially interesting because the potash and calcium feldspars belong to different crystal systems. At the same time the structures deduced by X-ray methods make it difficult to visualize how two relatively large K^+ ions can replace one smaller Ca^{++} ion without surface distortion of the silicon-aluminum-oxygen framework.

High cation exchange capacities were attained by Kelley and Jenny (4) in their work on the fine grinding of various silicate minerals, including orthoclase, albite, labradorite, oligoclase and anorthite. However, it was later shown that this type of dry grinding in a ball mill produced amorphous silicate material in many instances. Hence the exchange capacity attained is not primarily due to increase in the specific surface of otherwise unchanged minerals. It was for this reason that grinding in presence of benzene with subsequent fractionation according to particle size was selected in the present work as a means of providing unchanged feldspar of moderate specific surface. Sharp X-ray diffraction patterns were obtained from all these fractions.

Since so little is known of the exchange reactions of feldspar surfaces, the first experiments performed were designed to show whether reasonably constant exchange capacities were attainable, whether the hydrogen ion was a disturbing factor over the middle pH range and whether any relation to chemical composition or to structural features of feldspar surfaces could be detected.

The feldspars contain primarily potassium, calcium and sodium as cations which balance the negative charge on the silicate framework. However, other ions of similar ionic radii are known to fit the feldspar structure. Strontium can substitute for calcium, giving a triclinic strontium anorthite; but barium, which is larger, forms the monoclinic feldspar celsian, isomorphous with orthoclase.

In studying the surface exchange properties of the feldspars, three cations not present appreciably in our natural specimens were employed: ammonium, magnesium and strontium. Ammonium was selected because of its similarity to potassium in respect of ionic size and general exchange properties. Magnesium is a small divalent cation with a coordination number of six. It does not enter into feldspar structures. It was therefore thought that interesting comparisons would be possible between magnesium and strontium, since the latter can proxy for calcium in the anorthite structure.

The feldspar samples and the details of their preparation were the same as described in Part I. (6)

THE INTERACTION OF ALBITE WITH SALT SOLUTIONS

Procedure:

Two grams of unfractionated albite were weighed into a 100-ml. centrifuge tube. All samples were run in duplicate giving a total of six tubes per series. To the first and second tubes 50 ml. of 0.5 N NH_4Cl (pH 4.00) were added; to the third and fourth tubes 50 ml. of 0.5 N NH_4Cl (pH 7.00); and to the fifth and sixth tubes 50 ml. of 0.5 N NH_4Cl (pH 8.62).

These suspensions were well dispersed with a rubber policeman and then shaken by hand intermittently for 30 minutes. The suspensions were then centrifuged at 1500 r.p.m. until the particles settled out. A period of 15 to 20 minutes was usually sufficient for this. The clear supernatant liquid was then siphoned off and used for analysis. Fifty milliliters of absolute methyl alcohol were next added to the residue in the centrifuge tube to wash out the excess ammonium chloride. The suspensions were centrifuged and the alcohol siphoned off. This washing process was repeated five times. A test for the chloride in the wash solution showed this number of washings to be sufficient.

The residue in the centrifuge tubes was then placed on a steam bath until evaporation of the alcohol was complete. The second exchange, namely, by the magnesium cation, was then carried out by adding 50 ml. of 0.5 N $MgCl_2$. The suspension was shaken, centrifuged and the supernatant liquid removed for analysis in the manner outlined for ammonium chloride. The residue was washed again with alcohol, and the exchange series continued next with ammonium chloride. The over-all plan of the experiment can be seen from Experimental Plan I.

EXPERIMENTAL PLAN I

PLAN SHOWING THE SOLUTIONS USED AND ELEMENTS DETERMINED IN MEASURING THE INTERACTION OF SALTS WITH ALBITE*

No.	Solution Used	Elements Determined
	First Exchange	
1	0.5 N NH_4Cl, pH 4.00	Na, Si
2	0.5 N NH_4Cl, pH 7.00	Na, Si
3	0.5 N NH_4Cl, pH 8.62	Na, Si
	Second Exchange	
1	0.5 N $MgCl_2$	Na, NH_4, Al, Si
2	0.5 N $MgCl_2$	Na, NH_4, Al, Si
3	0.5 N $MgCl_2$	Na, NH_4, Al, Si
	Third Exchange	
1	0.5 N NH_4Cl, pH 4.00	Na, Mg, Si
2	0.5 N NH_4Cl, pH 7.00	Na, Mg, Si
3	0.5 N NH_4Cl, pH 8.62	Na, Mg, Si
	Fourth Exchange	
1	0.5 N $MgCl_2$	Na, NH_4, Si
2	0.5 N $MgCl_2$	Na, NH_4, Si
3	0.5 N $MgCl_2$	Na, NH_4, Si
	Fifth Exchange	
1	0.5 N NH_4Cl, pH 4.00	Na, Mg, Si
2	0.5 N NH_4Cl, pH 7.00	Na, Mg, Si
3	0.5 N NH_4Cl, pH 8.62	Na, Mg, Si

*Two grams of albite were treated with 50 ml. of the given solutions.

Results:

The results are shown in Table 1. As a result of the first treatment with the ammonium chloride solutions, about 2.95 m.e. of sodium were released per 100 gm. of feldspar. This represents a replacement of 0.75 percent of the sodium originally present in the mineral. The change in the pH of the salt solutions had no measurable effect on the release of sodium. It appears from this that albite is either not sensitive to changes in hydrogen ion concentration in the range covered, or else the effect of the ammonium chloride was so much greater than that of the hydrogen ion concentration that the former overshadowed any effect due to acidity.

The subsequent exchange with magnesium chloride released ammonium to the extent of 0.27 m.e. per 100 gm. of the feldspar. The magnesium chloride exchange also brought into solution a small amount of sodium, about 0.12 m.e. per 100 gm. This large discrepancy between sodium released by ammonium and ammonium subsequently released by magnesium is later partially accounted for by ammonium fixation.

The first exchange with $MgCl_2$ showed only a small amount of sodium released. This was about 0.12 meq per 100 gm., or only about one-third as much as was released by the following NH_4Cl solutions. There are indications from this that NH_4Cl may be a much better replacer of cations than $MgCl_2$, which is in contradistinction to what would be ex-

TABLE 1 -- SURFACE INTERACTION OF UNFRACTIONATED ALBITE WITH CONSECUTIVE SALT SOLUTIONS

	Extracting Solutions in Order of Extraction				
Element*	NH_4Cl	$MgCl_2$	NH_4Cl	$MgCl_2$	NH_4Cl
		Ammonium Chloride (pH 4.00)			
Na	2.98	0.125	0.360	0.125	0.348
NH_4		0.277		0.263	
Mg			0.839		1.08
Al		0.195			
Si	0.124	0.065	0.027	0.034	0.049
		Ammonium Chloride (pH 7.00)			
Na	2.94	0.122	0.343	0.117	0.350
NH_4		0.278		0.259	
Mg			1.25		0.937
Al		0.206			
Si	0.291	0.067	0.065	0.037	0.032
		Ammonium Chloride (pH 8.62)			
Na	2.92	0.122	0.340	0.109	0.340
NH_4		0.289		0.247	
Mg			3.46		1.42
Al		0.395			
Si	0.071	0.132	0.050	0.055	0.00
	Water				
Na	0.98				
Al	0.538				
Si	0.178				

*M.E. per 100 gm. for Na, NH_4, Mg.
M.Mols. per 100 gm. for Al, Si.

pected for cation exchange in a colloidal system in which the lyotropic series is followed. The point will be tested further later. In all of the subsequent exchanges with NH_4Cl and $MgCl_2$ the amount of sodium released remained about constant, i.e. 0.12 m.e. per 100 gm. for the $MgCl_2$ solutions and 0.36 for the NH_4Cl solution.

The adsorption of magnesium on the feldspar particles was rather erratic. The values varied from 0.839 m.e. per 100 gm. for exchange following the pH 4 NH_4Cl solution to 3.46 m.e. per 100 gm. following the pH 8.62 NH_4Cl solution. This difference may be due to the formation of $Mg(OH)_2$. Since the magnesium, apparently, has little tendency to go into the lattice, the adsorption is probably due entirely to that of the outer surfaces. Possibly it reacts with the hydrogen of the hydroxyl groups of the Si-OH linkage.

The dissolution of silicon by these salt solutions was small. In all cases it was less than that of water alone, indicating that the salts may have a depressing effect on the solubility, or perhaps better, the peptization of silicon. The values in general were erratic and duplication of results was not very good. Since the duplication of the other elements determined was good, it seems that this variation in the silicon values may have been due to silicon coming into solution as fragments of the lattice or perhaps, to polymerization after dissolution. In either case, these units would not be detected by the silicomolydate reduction which was used. It is interesting to note that in the exchange with ammonium solution of pH 8.62 only a trace of silicon came into solution. This is surprising, since it is usually agreed that silicon is more soluble in alkaline solutions than in neutral or acid ones.

Tests were run also for dissolution of aluminum in these samples, but the amount dissolved was too small to be detected with the 8-hydroxyquinoline reagent.

Discussion:

Some peculiar features of exchange reactions are displayed in these results. The first is the variability in the apparent exchange capacity when determined by different methods. If we regard the difference between water-soluble and ammonium chloride-soluble sodium as a measure of exchange capacity we obtain a value of about 2.0 m.e. per 100 gm. Ammonium adsorbed and subsequently released by magnesium chloride treatment gives only 0.28 m.e. Magnesium adsorbed and subsequently released by ammonium chloride gives about 1.0 m.e. for neutral or slightly acidic conditions. Successive cycles give essentially similar values, indicating that there is no pronounced build-up of an exchange layer after the first treatments. Silicon and sodium continue to pass into solution in small amounts throughout, but not by any means in constant proportion. It is evident that ammonium releases sodium much more effectively than does magnesium. This is not in accord with the normal experience of surface exchange reactions. It will be shown later that $NH_4 > Mg$ operates uniformly in release of sodium over the whole concentration range.

THE INTERACTION OF ANORTHITE WITH SALT SOLUTIONS

An experiment using anorthite was conducted to study further the cation exchange reactions of feldspar particles with salt solutions. The experimental procedure was exactly the same as that for albite, save that in this case calcium was used rather than sodium as a measure of the cations released from the minerals. Experimental Plan II shows the experimental arrangement.

There were some differences in the amounts of calcium released by the ammonium chloride solutions at the different pH values in Table 2. The values varied from 2.15 m.e. per 100 gm. for a pH 4.00 solution, to 1.00 for pH 7.00 and 1.72 for a pH of 8.62. These data indicate that the release of calcium from anorthite bears a definite relation to the acidity.

EXPERIMENTAL PLAN II

PLAN SHOWING THE SOLUTIONS USED AND ELEMENTS DETERMINED IN MEASURING THE INTERACTION OF SALTS WITH ANORTHITE*

No.	Solution Used	Elements Determined
	First Exchange	
1	0.5 N NH_4Cl, pH 4.00	Ca, Si
2	0.5 N NH_4Cl, pH 7.00	Ca, Si
3	0.5 N NH_4Cl, pH 8.62	Ca, Si
	Second Exchange	
1	0.5 N $MgCl_2$	Ca, NH_4, Si
2	0.5 N $MgCl_2$	Ca, NH_4, Si
3	0.5 N $MgCl_2$	Ca, NH_4, Si
	Third Exchange	
1	0.5 N NH_4Cl, pH 4.00	Ca, Mg, Si
2	0.5 N NH_4Cl, pH 7.00	Ca, Mg, Si
3	0.5 N NH_4Cl, pH 8.62	Ca, Mg, Si
	Fourth Exchange	
1	0.5 N $MgCl_2$	Ca, NH_4, Si
2	0.5 N $MgCl_2$	Ca, NH_4, Si
3	0.5 N $MgCl_2$	Ca, NH_4, Si
	Fifth Exchange	
1	0.5 N NH_4Cl, pH 4.00	Ca, Mg, Si
2	0.5 N NH_4Cl, pH 7.00	Ca, Mg, Si
3	0.5 N NH_4Cl, pH 8.62	Ca, Mg, Si

*Two grams of anorthite were treated with 50 ml of the indicated solutions.

TABLE 2 -- SURFACE INTERACTION OF UNFRACTIONATED ANORTHITE WITH CONSECUTIVE SALT SOLUTIONS

	Extracting Solutions in Order of Extraction				
Elements*	NH_4Cl	$MgCl_2$	NH_4Cl	$MgCl_2$	NH_4Cl
		Ammonium Chloride (pH 4.00)			
Ca	2.15	0.212	0.280	0.171	0.358
NH_4		0.220		0.120	
Mg			1.06		
Si	0.150	0.062	0.110	0.033	0.090
		Ammonium Chloride (pH 7.00)			
Ca	1.99	0.218	0.187	0.171	0.187
NH_4		0.195		0.130	
Mg			1.03		0.75
Si	0.141	0.062	0.075	0.035	0.095
		Ammonium Chloride (pH 8.62)			
Ca	1.72	0.281	0.121	0.249	0.121
NH4		0.185		0.136	
Mg			1.07		1.06
Si	0.00	0.063	0.0215	0.048	0.00
	Water				
Ca	0.655				

*Elements Ca, NH_4, and Mg are expressed in m.e. per 100 g. Si is expressed as millimols per 100 g.

This effect was not observed in the case of albite. The second and third exchanges with ammonium chloride also showed this relationship of calcium released to acidity, although the actual amounts of calcium released were much less.

As in the case of albite, the apparent exchange capacity varies greatly according to the procedure adopted. If the capacity is taken as the difference between water-soluble and ammonium chloride-soluble calcium, then the value ranges from 1.5 to 1.05 m.e. per 100 gm. Ammonium displaced by magnesium gives about 0.2 m.e. for the first cycle and 0.13 for the second. Magnesium displaced by ammonium gives 1.05 m.e. in the first cycle and values from 0.75 to 1.06 in the second. The same general order is found as in the case of albite. Anorthite shows an additional complication, a variation with pH, which probably reflects its inherent instability in acidic solutions.

In the comparison of the calcium released by the $MgCl_2$ solution and that by the acid NH_4Cl solution following it, there appears to be somewhat greater release of calcium by ammonium than by magnesium. This is in accord with the results for albite. However, for the alkaline solutions the $MgCl_2$ replaced more calcium than the NH_4Cl. Also, there is an increase in the calcium released by the $MgCl_2$ following the alkaline NH_4Cl treatment as compared with that following the acid NH_4Cl solution. It is obvious that the previous treatment of the mineral has some effect on the calcium released. These differences in the effect of magnesium on anorthite as compared with albite indicates that there may be a difference in the mechanism of breakdown.

The adsorption of magnesium was of the same order of magnitude as that of albite. The values varied from 0.75 to 1.13 m.e. per 100 g. There also seemed to be a slightly higher adsorption in the alkaline medium than in the acid medium. This was especially true for the second exchange.

The dissolution of silicon by the NH_4Cl solution followed the same order as the calcium. There was only a trace of silicon found in the pH 8.62 solution, which was similar to the albite results.

RELATIVE EFFECTIVENESS OF AMMONIUM CHLORIDE AND MAGNESIUM CHLORIDE ON THE RELEASE OF SODIUM FROM ALBITE

As pointed out in the previous experiments, there appeared to be a greater amount of sodium released by solutions of NH_4Cl than by $MgCl_2$ of the same normality. An experiment was set up next to measure the sodium released by NH_4Cl and $MgCl_2$ of varying concentrations. A sodium chloride series was also included and soluble silica released was determined in all three salt treatments. It was hoped that from this experiment some additional light might be thrown upon the mechanism of cation exchange in feldspars.

Procedure:

Two grams of oven-dry, unfractioned albite were weighed into a 100-ml. centrifuge tube. To this sample 50 ml. of either NH_4Cl, or $MgCl_2$ solution was added. The concentrations of the solutions varied from 0.0001 N to 0.1. These suspensions were placed on a mechanical shaker and shaken for 8 hours to insure uniform mixing. The suspensions were then centrifuged at 1500 r.p.m. until the supernatant liquid became clear. This required about an hour for the water suspension and the most dilute salt solutions. The supernatant liquid was then siphoned off and used in the analysis for sodium and silicon.

Results:

The results of this experiment, presented graphically in Figure 1, confirm that ammonium is a more effective replacer of sodium than magnesium. The replacement of sodium increased with increasing concentrations of salts up to 0.01 N, then a plateau was reached with little evidence of further sodium release with increasing salt concentrations. These curves resemble the Langmuir adsorption isotherms closely.

The difference in effectiveness of NH_4Cl and $MgCl_2$ in the replacement of sodium may be explained on the basis of size and charge. The ammonium is of proper size and charge to replace the monovalent sodium ion and fit nicely into the lattice. Magnesium, on the other hand, while small enough to fit into the lattice, is divalent and it would be necessary for it to replace two sodium ions. For steric reasons, since it requires 6-fold coordination, this would be difficult without a complete breakdown of the lattice. The high hydration of the magnesium ion may also retard its penetration.

The dissolution of silicon (Figure 2) by the salts bore no relation to the sodium released. The silicon released by the NH_4Cl solution showed a slight increase for the first increments of NH_4Cl. This was probably due to the dispersive effect of the ammonium at low concentrations. Subsequent increases in NH_4Cl concentration showed a decrease in silicon to a constant value of about 0.15 moles per 100 gm. The higher concentrations of NH_4Cl caused a repression of the silicon dissolved.

The silicon dissolved by $MgCl_2$ decreased with the first increments of salt and there was an indication of a minimum solubility at 0.005 N. With increasing concentration above this value there was a slight increase in the amount of silicon dissolved.

The $MgCl_2$ solution was more effective in dissolving silicon than NaCl and NH_4Cl solutions. One might suppose this increased solubility was due to the acidity developed from hydrolysis of the $MgCl_2$; however, the most concentrated solution (0.1 N $MgCl_2$) had a pH of 6.4. Also,

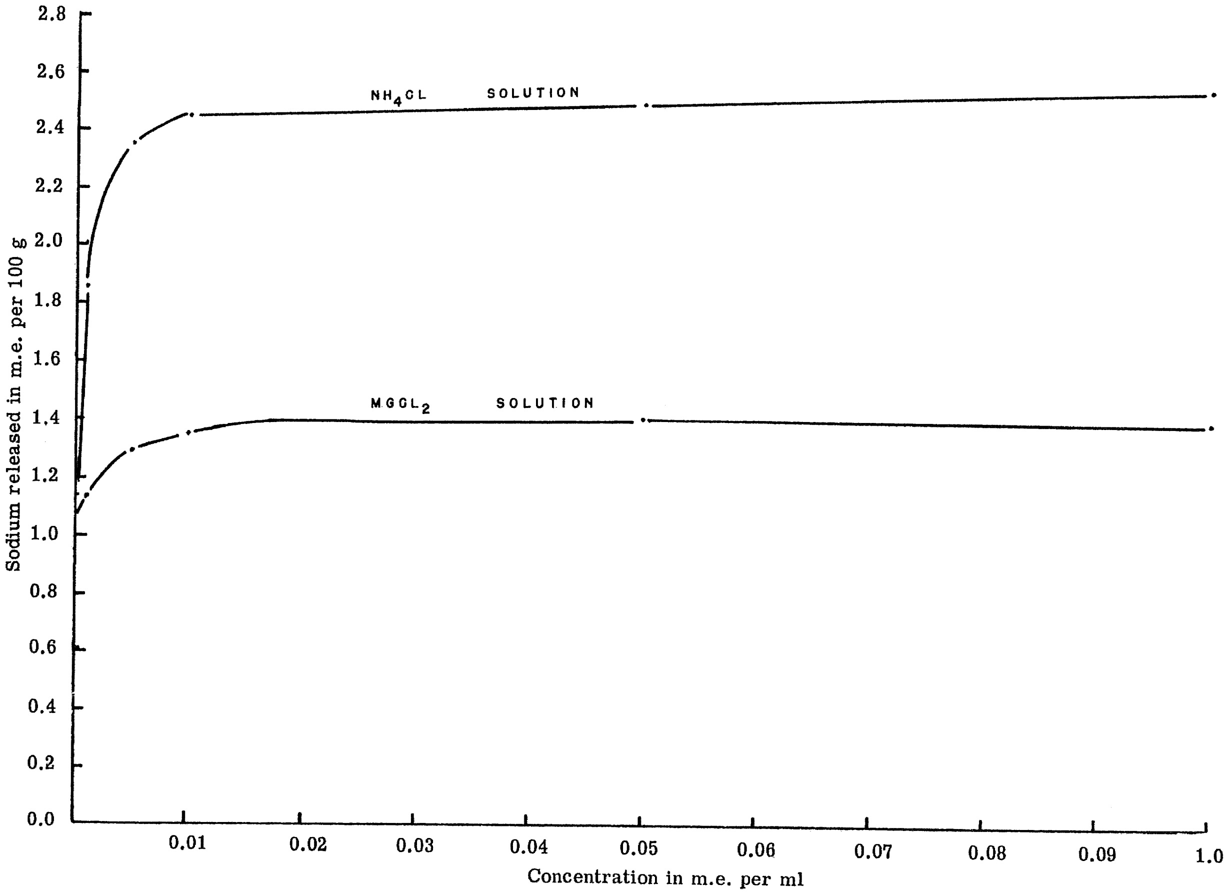

Fig. 1—Sodium released from unfractionated albite by ammonium and magnesium chloride solutions of varying concentration.

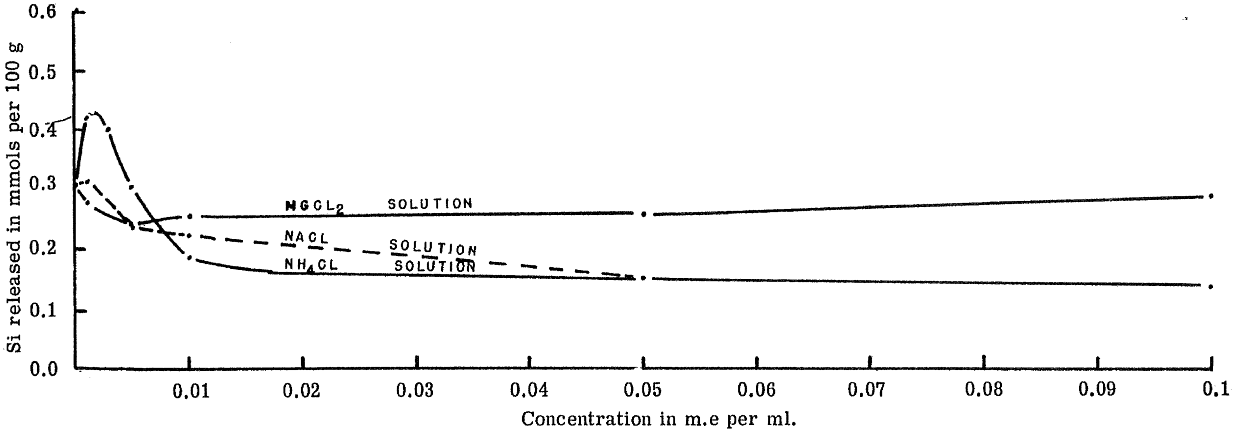

Fig. 2—Silica released from albite by ammonium, magnesium and sodium chloride solutions of varying concentration.

some doubt would remain that the decrease in solubility in the salt solutions, as compared with water, was due to the flocculation of silica. Magnesium is usually considered a better flocculant than ammonium or sodium according to the Hardy-Schulze rule.

The experiment with NaCl was carried out to see if there would be any breakdown at all with sodium. It was thought, since there was sodium in both the lattice and in the solution, there would be little tendency for decomposition. The curves in Figure 2 show that about the same amount of silicon was dissolved by NaCl as by NH_4Cl. This indicates again that the removals of cations and anions are independent processes, at least to a certain extent. Probably a large removal of cations would also cause an increase in the anion release and vice versa.

The order of magnitude of the soluble monomeric silica corresponded roughly to the solubility of quartz of macroscopic crystal size. It was much less than the values given by Iler (2) for amorphous silica. The evidence from solubility thus was decisively against the hypothesis of a surface comprised of mixed gels of silica and alumina.

SURFACE INTERACTION OF ALBITE WITH SALT SOLUTIONS IN METHANOL

In the previous experiments, all exchange reactions were in the presence of water. Since water itself has an appreciable effect on the decomposition of the mineral particles through hydrolysis, an exchange experiment in methyl alcohol was carried out to eliminate this effect. Any replacement of cations in this experiment had to occur through exchange with the salts.

Procedure:

Two-gram samples of unfractionated albite were weighed into 100-ml. conical centrifuge tubes. To these tubes there were added 50-ml. quantities of salt solutions. (The salt solutions used were 0.5 N and were made by dissolving NH_4Cl, $SrCl_2.6H_2O$ and $MgCl_2.6H_2O$ salts in absolute methyl alcohol; the $SrCl_2$ and $MgCl_2$ solutions contained some water but less than 5 percent.)

The suspensions were stirred until good dispersion was obtained. They were then shaken by hand intermittently for 30 minutes. After this, the suspensions were centrifuged at 1500 r.p.m. until a clear supernatant liquid was obtained. This required about 30 minutes. The supernatant liquid was siphoned off and saved for analysis.

The residue in the centrifuged tube was next washed five times with 50 ml. of absolute alcohol to remove the excess salts. The alcohol was then evaporated from the residue and a second salt solution was added with procedures exactly as before. The general plan is outlined in Experimental Plan III.

EXPERIMENTAL PLAN III

THE INTERACTION OF SALTS WITH ALBITE IN METHYL ALCOHOL*

Lab. No.	1st Exchange	2nd Exchange	3rd Exchange	4th, 5th & 6th Exchange
23	NH_4Cl	$MgCl_2$	NH_4Cl	$MgCl_2$
24	NH_4Cl	$SrCl_2$	NH_4Cl	$SrCl_2$
25	$MgCl_2$	NH_4Cl	$MgCl_2$	NH_4Cl
26	$MgCl_2$	$SrCl_2$	$MgCl_2$	$SrCl_2$
27	$SrCl_2$	NH_4Cl	$SrCl_2$	NH_4Cl
28	$SrCl_2$	$MgCl_2$	$SrCl_2$	$MgCl_2$

*Two grams of albite were treated with 50 ml. of the indicated solutions.

For the analytical determination of the ions in the supernatant alcohol, it was necessary to take an aliquot of the alcohol, evaporate it to dryness and make up to volume with water. In the cases where $SrCl_2$ was the extracting salt, it was necessary to remove the strontium before analysis could be made for sodium or magnesium. This was accomplished simply by precipitating the strontium as a sulfate with H_2SO_4 in a 50 percent alcohol solution. The $SrSO_4$ was removed by filtration and the sodium and magnesium were collected in the filtrate. This was evaporated to dryness and made up to volume for analysis..

Results:

The variation in sodium released by treating the feldspars with the different salt solutions for the first exchange is shown in Table 3. Strontium chloride was the most effective replacer of sodium with 1.73 m.e. per 100 gm. This is followed by NH_4Cl with 0.526 and $MgCl_2$ with 0.280 m.e. per 100 gm.

It will be recalled (See Table 1) that this same sample of albite gave 0.89 m.e. Na per 100 gm. in water alone, 2.95 m.e. Na in aqueous ammonium chloride and 0.28 m.e Na in aqueous magnesium chloride. In methyl alcohol, ammonium chloride was much less effective than in water, whereas magnesium chloride released about the same amount of sodium in both solvents.

The subsequent exchanges with salt solutions released much less sodium but in the order that was expected. The $MgCl_2$ solutions, following the NH_4Cl treatments, released only traces of sodium. The second exchanges with NH_4Cl and $SrCl_2$ solution released some additional sodium, the largest amount being released following the $MgCl_2$ exchange. All of the subsequent treatments with NH_4Cl and $SrCl_2$ released some sodium, but $MgCl_2$ released only a trace amount. It is obvious from these

TABLE 3 -- SURFACE INTERACTION OF UNFRACTIONATED ALBITE WITH SALTS IN METHYL ALCOHOL

Lab. No.	Solution Used	Na*	NH_4*	Mg*	Sr*	Si**
		First Exchange				
23	NH_4Cl	0.526				0.019
24	NH_4Cl	0.526				0.033
25	$MgCl_2$	0.290				0.050
26	$MgCl_2$	0.270				0.041
27	$SrCl_2$	1.67				
28	$SrCl_2$	1.79				
		Second Exchange				
23	$MgCl_2$	0.010	0.222			0.021
24	$SrCl_2$	0.328	0.244			
25	NH_4Cl	0.212		0.83		0.039
26	$SrCl_2$	0.645		1.01		
27	NH_4Cl	0.137			1.02	0.029
28	$MgCl_2$	0.050			0.05	0.100
		Third Exchange				
23	NH_4Cl	0.063		0.745		0.033
24	NH_4Cl	0.050			0.815	0.026
25	$MgCl_2$	0.010	0.156			0.038
26	$MgCl_2$	0.020			0.434	0.041
27	$SrCl_2$	0.340	0.208			
28	$SrCl_2$	0.400		0.86		
		Fourth Exchange				
23	$MgCl_2$	0.048	0.164			0.028
24	$SrCl_2$	0.000	0.225			0.176
25	NH_4Cl	0.300		1.44		0.047
26	$SrCl_2$	0.470		1.12		0.030
27	NH_4Cl	0.240			1.81	0.024
28	$MgCl_2$	0.096			0.96	
		Fifth Exchange				
23	$MgCl_2$	0.036	0.062			0.053
24	$SrCl_2$	0.000	0.072			0.113
25	NH_4Cl	0.110		0.338		0.044
26	$SrCl_2$	0.250		0.250		0.011
27	NH_4Cl	0.100			0.60	0.032
28	$MgCl_2$	0.048			0.40	0.183
		Sixth Exchange				
23	$MgCl_2$	0.048	0.075			0.029
24	$SrCl_2$	0.000	0.068			0.046
25	NH_4Cl	0.150		0.46		0.046
26	$SrCl_2$	0.070		0.17		
27	NH_4Cl	0.120			0.48	0.030
28	$MgCl_2$	0.084			0.56	0.030

*m.e./100 gm.
**millimols./100 gm.

facts that the previous history of the sample affects the release of sodium. In general, if the second exchange follows the treatment with a poor replacer of sodium, then more sodium will be replaced than if it follows a good replacer of sodium (compare No. 24 with 26 in second exchange). However, this order of treatment has a profound effect on the sodium released. For instance, in No. 24 the treatments, whose order was ammonium-strontium-ammonium-strontium, released 0.904 m.e. per 100 gm. of sodium, while in No. 27, whose treatment was in the order strontium-ammonium-strontium-ammonium, 2.487 m.e. were released.

The uptake of exchangeable ammonium from the alcoholic solution is only slightly less than that from the aqueous solution. The largest adsorption of ammonium was during the first exchange, and in subsequent exchanges the adsorption capacity decreased. It seems that the previous treatment affects also the amount of ammonium adsorbed. In every case, more ammonium was adsorbed following $SrCl_2$ treatment than when following $MgCl_2$. This might be due to the greater replacing power of strontium compared with that of magnesium. However, in Nos. 23 and 24 there were three consecutive extractions with $MgCl_2$ and $SrCl_2$ and still more ammonium was adsorbed following the $SrCl_2$ exchange than following the $MgCl_2$.

The amounts of magnesium and strontium adsorbed varied somewhat, but they were both of the order of 1 m.e. per 100 gm. The adsorption capacities for these elements seem to increase with successive treatments. This is especially true for those samples following the NH_4Cl exchange. Here again is evidence that the previous history affects the surface properties.

Silicon determinations were made on each of those samples of which there was sufficient material. In all cases only a small amount of silicon was dissolved. The amount of aluminum was not detectable. This shows that even in alcoholic solutions a residual layer composed of silicon and aluminum is formed around the particles.

These experiments in alcoholic solution throw into strong relief the importance of the previous cationic history of the sample. They are more striking here than in water. In the feldspars, cation exchange is anything but a simple reflection of cationic charge and hydration. Specific effects dominate the situation as is most strikingly shown by the dependence of sodium released by ammonium and strontium chlorides upon the order in which successive treatments were given.

EXPERIMENTS ON CATIONIC FIXATION

The extensive release of the native feldspar cations by ammonium and the comparatively small amount of ammonium subsequently released by magnesium chloride solution brought up the possibility of ammonium ion fixation. The following experiments were therefore carried out; in the first series ammonium fixed was determined quantitatively; in the second, evidence was sought on possible strontium or magnesium fixation.

A. Ammonium Fixation.

Procedure: Five-gram samples of unfractionated feldspar, previously ground in benzene and dried, were treated with 75 ml. of 0.5 N neutral ammonium chloride. This quantity of salt corresponds roughly to 75 times the maximum apparent exchange capacity. The mixture was shaken, allowed to react for 1 hour, centrifuged, and the supernatant liquid was analyzed for sodium, calcium, potassium, aluminum and silicon. The feldspar residue was washed five times with methyl alcohol to remove the salt and was then treated with 75 ml. of 0.5 N magnesium chloride solution. The ammonium liberated was determined, then that which still was retained by the feldspar was removed by distillation for 20 minutes from a strongly alkaline solution (1N.NaOH). This was adequate for quantitative removal of the ammonium. All experiments were in duplicate. During the treatment with ammonium chloride all pH values were close to 7.0. The results are presented in Tables 4a and b.

TABLE 4 -- QUANTITATIVE EFFECTS OF AMMONIUM CHLORIDE SOLUTIONS ON FELDSPARS

a. Elements Released

	Cations in m.e./100 gm.				Elements in m.mols/100 gm.	
Feldspar	Calcium	Sodium	Potassium	Total	Aluminum	Silicon
Microcline	0.69	0.54	2.96	4.19	0.022	0.044
Albite	3.97	2.42	0.26	6.64	.032	.039
Oligoclase	1.72	3.68	0.38	5.78	.066	.080
Andesine	2.72	4.15	0.65	7.52	.014	.057
Labradorite	3.57	1.65	0.28	5.51	.030	.057
Bytownite	6.61	2.20	0.25	9.06	.051	.055
Anorthite	2.23	0.41	0.09	2.74	.050	.048

b. Ammonium Exchangeable and Fixed

Feldspar	NH_4 Release by $MgCl_2$ m.e./100 gm.	NH_4 Subsequently Released by Distillation m.e./100 gm.	Ratio $\frac{\text{Total Cations}}{\text{Total } NH_4}$
Microcline	0.85	2.06	1.44
Albite	0.63	1.26	3.51
Oligoclase	1.22	2.57	1.53
Andesine	1.70	2.74	1.69
Labradorite	0.95	1.95	1.90
Bytownite	1.71	2.80	2.01
Anorthite	0.66	0.67	2.06

Discussion. This series clearly indicates that fixation of ammonium is a general effect in the feldspar group. The tenaciously held ammonium exceeds that exchangeable against magnesium chloride solution in all cases; in fact, except for bytownite and anorthite it is more than twice as great. In no case, however, does the sum of the exchangeable and fixed ammonium equal the total cations released in the original ammonium chloride treatment. The discrepancy is particularly marked in the case of albite, as shown by the last column of Table 4b. It is not accounted for in terms of anions released, since the silicon and aluminum were very small in amount throughout. Changes in reaction do not adequately account for it either. For the present it is unexplained.

B. Comparison of Ammonium, Magnesium and Strontium

If the ammonium ion is fixed by feldspars solely in virtue of its size accommodation then the strontium ion might also be fixed, but probably not magnesium. This point was tested in the case of albite.

Duplicate (triplicate in the case of magnesium) 5 gm. samples of unfractionated albite were treated with 7.5 ml. of 0.5 N ammonium chloride, magnesium chloride, or strontium chloride solution. After shaking for 6 hours and centrifuging, the supernatant liquid was removed for analysis. The sodium, calcium, and potassium released were determined. The residual feldspar was shaken for one hour with 50 ml. of 0.5 N magnesium chloride solution in the case of the original ammonium chloride treatment; or with 50 ml. of 0.5 N ammonium chloride solution following the $MgCl_2$ and $SrCl_2$ treatments. The supernatant liquid was separated by centrifuging and removed for analysis. The cations released were determined quantitatively. This treatment was repeated three times, successively, on each sample so that the process of extraction of the ion originally introduced could be followed. Finally, in the case of the original ammonium feldspar the residual ammonium (presumably fixed) was determined by distillation from N sodium hydroxide solution. The results are presented in Table 5.

TABLE 5 -- COMPARISON OF AMMONIUM, MAGNESIUM AND STRONTIUM SATURATED ALBITE IN SUCCESSIVE EXTRACTIONS WITH SALT SOLUTIONS

Exchange Number	Treatment Used	Cations Liberated m.e. per 100 gm.					
		Na	Ca	K	NH_4	Mg	Sr
1 A	NH_4Cl	1.83	2.82	0.19			
1 B	$MgCl_2$	1.09	1.80	0.015			
1 C	$SrCl_2$	N.D.	N.D.	N.D.			
2 A	$MgCl_2$				0.98		
2 B	NH_4Cl					0.94	
2 C	NH_4Cl						1.22
3 A	$MgCl_2$				0.38		
3 B	NH_4Cl					0.10	
3 C	NH_4Cl						0.18
4 A	$MgCl_2$				0.16		
4 B	NH_4Cl					0.08	
4 C	NH_4Cl						0.02
5 A	$MgCl_2$				0.15		
5 B	NH_4Cl					0.07	
5 C	NH_4Cl						0.00
6 A	NaOH Dist.				0.93		

The liberation of ammonium in significant amount continues with successive salt treatments, and finally a large amount is liberated by alkaline distillation. Magnesium and strontium both behave differently. The first treatment with ammonium chloride removes practically the whole Mg or Sr present and further successive treatments after number 3 liberate only insignificant traces. There is thus no evidence of fixation of Mg or Sr by albite.

A parallel experiment using strontium was carried out on unfractionated anorthite. This was of interest since strontium anorthite is isomorphous with anorthite. After saturation of the surface with strontium chloride solution, the first treatment with ammonium chloride liberated 1.25 m.e. strontium per 100 gm. feldspar. The next NH_4Cl treatment brought only 0.01 m.e. into solution and two further successive treatments gave undetectably small amounts. Hence it is clear that strontium is not "fixed" by anorthite.

The fixation of ammonium by feldspars thus stands out by itself and its significance in relation to the structure of feldspar surfaces will be discussed later.

DETAILED EXCHANGE AND ACTIVITY STUDIES WITH INDIVIDUAL FELDSPARS

The experience of the preceding experiments was drawn upon in designing a uniform series of treatments and measurements, carried through with the same size fraction of each feldspar. Three types of information were sought: (a) Evidence on the variation in apparent cation exchange capacity with salt treatment, etc.; (b) evidence on cationic activities in feldspar suspensions, from which mean free bonding energies could be calculated and compared; and (c) evidence from small dilute exchange experiments which could be interpreted through the Donnan theory for comparison with information afforded by (b).

Procedure.

One-gram samples of the (0.5-1) μ fraction of the feldspars were weighed into 100-ml., conical centrifuge tubes. To each was added 25 ml. of the chosen salt solution, either 1N potassium chloride, 1N magnesium chloride, or 1N strontium chloride. The mixture was stirred to break up aggregates and was shaken intermittently by hand for four hours. The suspension was centrifuged and the supernatant liquid siphoned off. A second addition of 25 ml. of the same salt solution was made and the same process was repeated. Owing to the high concentrations of salts used, the cations released from the lattice could not be determined accurately. The residue in the centrifuge tubes was washed five times with absolute methyl alcohol to remove soluble salts. The alcohol was then removed by evaporation on a steam plate.

Ten ml. of water were then added to the dry feldspar and the latter was thoroughly brought into suspension. This suspension was then transferred to a 50 ml. beaker and the activity of the saturating cation was determined, using a calibrated clay membrane—saturated calomel electrode combination (5).

The suspension was then washed back to the centrifuge tube and 25 ml. of 1N ammonium chloride solution were added. The suspension was stirred well and centrifuged. The supernatant liquid was siphoned off. A second treatment with the same amount of ammonium chloride followed. The two supernatant liquids were combined for evaporation to dryness, the residue being taken up in 25 ml. of water for analysis. The cation introduced in the first salt treatment and now displaced by ammonium was determined together with cations liberated from the lattice. The feldspar residue in the centrifuge tube was washed five times with methyl alcohol and finally dried on a steam plate.

This feldspar was next treated twice, successively, with 25 ml. of the same salt as that used originally. Ammonium was determined in the combined centrifugates in addition to Na, Ca, and K originating from the lattice. The feldspar was washed with methyl alcohol as before, evaporated to dryness and taken up in 10 ml. of water for repetition of the cation activity determination. In addition, the pH was determined, using a Beckmann type glass electrode assembly.

After these measurements the suspension was washed back into the centrifuge tube and 1 ml. of 0.01 N ammonium chloride was added. By this means it was hoped to carry out a small dilute exchange. The suspension was centrifuged and the cations in solution (including the ammonium) were determined. From the data the amounts of the two cations on the feldspar surfaces could be calculated. Hence by application of the Donnan relation,

$$\left[\frac{{}^{a}\ \text{potassium}}{{}^{a}\ \text{ammonium}}\right]\ \text{solution} = \left[\frac{\alpha\,\text{potassium}}{\alpha\,\text{ammonium}}\right]\left[\frac{{}^{c}\ \text{potassium}}{{}^{c}\ \text{ammonium}}\right]\text{Feldspar surface}\ ,$$

it was possible to derive $\frac{\alpha K}{\alpha NH_4}$,

i.e. the activity ratio for the dissociating surface.

Finally, the feldspar residue was treated twice successively with 25 ml. of 1 N ammonium chloride and the cations in solution were determined. In this way a second complete cycle of treatments was completed for comparison with the first.

In the following account, each feldspar is considered separately. Finally, comparisons between different feldspars are sought and discussed.

Microcline (Table 6)

Discussion: Detailed analytical figures for the first and second exchange cycles were obtained with potassium and strontium, but not with the magnesium-saturated feldspar surfaces. Ammonium chloride released comparatively large amounts of potassium from this feldspar, even after saturation of the surface with strontium or magnesium. The ratio of sodium to calcium brought into solution by ammonium chloride depends on the cation used for the original saturation of the surface. It is 0.7 to 0.9 for the K saturated feldspar, but only 0.35 to 0.45 for that initially saturated with Sr. The strontium ion seems to displace calcium preferentially.

The apparent exchange capacities as obtained by release of K, Mg, and Sr originally introduced, fall in the order K > Mg > Sr for the first cycle and K > Sr > Mg for the second, the potassium values being almost three times the others. Ammonium released by K, Mg, and Sr is in the order K > Mg > Sr, potassium being much more effective than the other two.

TABLE 6 -- MICROCLINE AS CATION EXCHANGER

a. Cation Exchange Data

(Figures in m.e. per 100 gm.)

Cation Introduced	Ammonium Released	Cations Released From Lattice Na	K	Ca	Introduced Cations Released by NH_4	Total Cations Released
		First Exchange Cycle				
K		0.35		0.40	5.33	6.08
Mg					1.95	
Sr		0.42	2.65	1.00	1.04	5.11
		Second Exchange Cycle				
K	1.76	0.12		0.18	6.48	6.78
Mg	0.90		2.00		1.91	
Sr	0.58	0.17	2.55	0.45	2.14	5.31

b. Cationic Activity Data

Cation Exchange	pH	Activity mols/1.	Concentration mols/1.	Fraction Active	Bonding Energy Calories
		First Exchange Cycle			
K		3.90×10^{-4}	5.33×10^{-3}	.0732	1560
Mg		3.15×10^{-5}	0.97×10^{-3}	.0315	2055
Sr		8.10×10^{-5}	0.52×10^{-3}	.159	1110
		Second Exchange Cycle			
K	7.54	3.28×10^{-4}	6.48×10^{-3}	.0507	1825
Mg	7.26	8.20×10^{-5}	0.96×10^{-3}	.085	1470
Sr	7.30	10.1×10^{-5}	1.07×10^{-3}	.0944	1410

c. Small Dilute Exchange Data

Cation Exchange	Exchanged Cation mols/1.	Ammonium In Soln. mols/1.	Me* Replaced / NH_4 Adsorbed	Percent Cation Displaced	$\alpha K / \alpha NH_4$
K	3.75×10^{-4}	1.12×10^{-4}	2.71	23.1	0.370
Mg	10.78×10^{-5}	0.64×10^{-4}	1.03	41.2	-----
Sr	10.1×10^{-5}	0.95×10^{-4}	1.07	35.9	-----

*Me refers to metal displaced.

This strong predominance of potassium shows itself also in total cation release in the ammonium chloride treatment. The second cycle gives slightly higher figures than the first. The impression throughout is that both K and NH_4 are more powerful displacers than Sr and Mg. The large amount of potassium as compared with ammonium released by these latter cations strongly suggests that while the ammonium ion is extensively and firmly bound, potassium is much less affected by fixation.

The activity data do not show satisfactory agreement between the first and second cycles, but it is nevertheless clear that potassium is held more firmly than strontium. This is the opposite of the expected relationship between the mean free bonding energies of monovalent and divalent cations, which, in absence of specific effects, should be roughly 1:2.

This conclusion is also borne out by the exchange experiments in which only a small amount of ammonium chloride was used. A smaller percentage of potassium was released than of magnesium or strontium, although this figure is affected by the higher apparent exchange capacity toward potassium than toward magnesium or strontium.

Albite (Table 7)

Discussion: In exchanges against ammonium chloride solutions, the amounts of lattice cations released were less than in the case of microcline. Calcium was preferentially released to a large extent, since in the second cycle it equalled the sodium, whereas the feldspar contained only 0.4 percent Ca and 7.8 percent Na. The release of potassium was also greater than that indicated by the potassium content.

The apparent exchange capacity was in the order $K > Mg > Sr$ for the first exchange and $K > Sr > Mg$ for the second. The figures for ammonium released were much smaller, and in relation to the displacing cation fell in the order $K > Sr > Mg$. Since ammonium is partially fixed this indicates that potassium and ammonium are better replacers than strontium or magnesium.

The activity data are not in good agreement as between the first and second cycles but seem to indicate that the mean free bonding energy for strontium is somewhat higher than that for potassium. The magnesium and strontium values are not far apart.

The small dilute exchange indicates that the ammonium ion is able to displace more potassium than magnesium or strontium. This is in agreement with the relative bonding energies of these cations and is the opposite of what was found in the case of microcline. The ammonium ion appears considerably more effective than potassium as an exchanger.

TABLE 7 -- ALBITE AS CATION EXCHANGER
a. Cation Exchanger Data
(Figures in m.e. per 100 gm.)

Cation Introduced	Ammonium Released	Cations Released From Lattice Na	K	Ca	Introduced Cations Released by NH^4	Total Cations Released
		First Exchange Cycle				
K		0.80		0.66	3.46	4.92
Mg					2.91	
Sr		0.96	0.36	0.62	2.74	4.68
		Second Exchange Cycle				
K	1.13	0.21		0.22	4.47	4.99
Mg	0.50		0.30	0.35	2.61	3.26
Sr	0.72	0.38	0.21	0.38	3.02	3.99

b. Cationic Activity Data

Cation Exchange	pH	Activity mols/1	Concentration mols./1	Fraction Active	Bonding Energy Calories
		First Exchange Cycle			
K		2.62x10^{-4}	3.46x10^{-3}	.0759	1537
Mg		3.10x10^{-5}	1.46x10^{-3}	.0213	2290
Sr		3.16x10^{-5}	1.38x10^{-3}	.0229	2246
		Second Exchange Cycle			
K	7.65	4.61x10^{-4}	4.47x10^{-3}	.104	1355
Mg	7.55	8.6 x10^{-5}	1.48x10^{-3}	.0583	1690
Sr	7.44	8.8 x10^{-5}	1.51x10^{-3}	.0536	1860

c. Small Dilute Exchange Data

Cation Exchange	Exchange Cation mols/1	Ammonium In soln. mols/1	Me* Replaced / NH$_4$ Adsorbed	Percent Cation Displaced	$\alpha K/\alpha NH_4$
K	3.67x10^{-4}	0.90x10^{-4}	2.54	34.9	0.863
Mg	7.6 x10^{-5}	0.41x10^{-4}	0.74	23.1	-----
Sr	9.18x10^{-5}	0.84x10^{-4}	0.97	23.8	-----

*Me refers to the metal replaced.

Oligoclase (Table 8)

Discussion: The order of the apparent exchange capacities is K > Mg > Sr for both cycles. In the first cycle the sodium and calcium released from the lattice by ammonium chloride were almost equal; in the second the calcium appreciably exceeded the sodium. In the release of ammonium the order was K > Sr > Mg.

The activity figures clearly indicate that potassium is held less firmly than magnesium and strontium which are closely similar.

The small dilute exchange indicates that the order of displacement by ammonium is K > Mg > Sr. The comparison of potassium and ammonium through the activity coefficient ratio gives $\alpha K/\alpha NH_4 = 1.82$, indicating that ammonium is considerably more tightly bound than potassium.

TABLE 8 -- OLIGOCLASE AS CATION EXCHANGER
a. Cation Exchange Data
(Figures in m.e. per 100 gm.)

Cation Introduced	Ammonium Released	Cations Released From Lattice Na	K	Ca	Introduced Cations Released by NH_4	Total Cations Released
			First Exchange Cycle			
K		0.59		0.64	3.35	4.58
Mg					2.72	
Sr		0.62	0.37	0.57	2.52	4.08
			Second Exchange Cycle			
K	0.97	0.19		0.27	3.65	4.11
Mg	0.45		0.26	0.58	2.09	
Sr	0.60	0.25	0.20	0.35	2.64	3.44

b. Cationic Activity Data

Cation Exchange	pH	Activity mols/1	Concentration mols/1	Fraction Active	Bonding Energy Calories
		First Exchange Cycle			
K		$3.69x10^{-4}$	$3.35x10^{-3}$	.1100	1320
Mg		$5.1\ x10^{-5}$	$1.36x10^{-3}$	.0377	1955
Sr		$4.8\ x10^{-5}$	$1.26x10^{-3}$	.0382	1942
		Second Exchange Cycle			
K	7.70	$5.36x10^{-4}$	$3.65x10^{-3}$	.147	1152
Mg	7.53	$8.0\ x10^{-5}$	$1.35x10^{-3}$	.0593	1680
Sr	7.50	$7.9\ x10^{-5}$	1.32x10-3	.0596	1687

c. Small Dilute Exchange Data

Cation Exchange	Exchange Cation mols/1.	Ammonium In Soln. mols/1	Me* Replaced / NH_4 Adsorbed	Percent Cation Displaced	$\alpha K/\alpha NH_4$
K	$3.9\ x10^{-4}$	$0.73x10^{-4}$	2.22	43.0	1.82
Mg	$8.42x10^{-5}$	$0.92x10^{-4}$	1.28	32.0	----
Sr	$7.22x10^{-5}$	$0.83x10^{-4}$	0.92	24.0	----

*Me refers to the metal being replaced.

Andesine (Table 9)

The order of the apparent exchange capacities is $K > Sr > Mg$ for the first cycle and $K > Mg > Sr$ for the second. Calcium released distinctly exceeds the sodium in both cycles. In spite of the low content of potassium the amount released was equal to that of the sodium. In the release of ammonium the order of effectiveness was $K > Sr > Mg$.

The activity results were consistent in both cycles and indicated that magnesium was held somewhat more firmly than strontium and both considerably more firmly than potassium. The mean free bonding energy for potassium is considerably above half the values for Mg and Sr.

The small dilute exchange indicates that the order of displacement by ammonium is $K > Mg > Sr$. The activity coefficient ratio $\alpha K/\alpha NH_4$ gives 1.70, similar to that for oligoclase.

TABLE 9 -- ANDESINE AS CATION EXCHANGER
a. Cation Exchange Data
(Figures in m.e. per 100 gm.)

Cation Introduced	Ammonium Released	Cations Released From Lattice Na	Cations Released From Lattice K	Cations Released From Lattice Ca	Introduced Cations Released by NH_4	Total Cations Released
		First Exchange Cycle				
K		0.49		0.60	3.93	5.02
Mg					2.75	
Sr		0.44	0.45	0.66	3.26	4.81
		Second Exchange Cycle				
K	1.18	0.18		0.26	4.25	
Mg	0.64		0.26	0.47	3.42	
Sr	0.82	0.22	0.22	0.37	3.40	

b. Cationic Activity Data

Cation Exchange	pH	Activity mols/1	Concentration mols/1	Fraction Active	Bonding Energy Calories
		First Exchange Cycle			
K		3.72×10^{-4}	3.93×10^{-3}	.0950	1410
Mg		4.10×10^{-5}	1.36×10^{-3}	.0301	2060
Sr		7.20×10^{-5}	1.60×10^{-3}	.0432	1870
		Second Exchange Cycle			
K	8.01	4.51×10^{-4}	4.25×10^{-3}	.106	1340
Mg	7.50	6.5×10^{-5}	1.73×10^{-3}	.0374	1950
Sr	7.49	8.2×10^{-5}	1.71×10^{-3}	.0481	1810

c. Small Dilute Exchange Data

Cation Exchange	Exchange Cation mols/1	Ammonium In Soln. mols/1	Me* Replaced / NH_4 Adsorbed	Percent Cation Displaced	$\alpha K/\alpha NH_4$
K	4.17×10^{-4}	0.68×10^{-4}	2.47	40.7	1.70
Mg	10.25×10^{-5}	0.84×10^{-4}	1.19	27.1	----
Sr	8.25×10^{-5}	0.71×10^{-4}	0.87	19.9	----

*Me refers to the metal being displaced.

Labradorite (Table 10)

The apparent exchange capacities fall in the order K $>$ Mg $>$ Sr for the first cycle and K $>$ Sr $>$ Mg for the second. Calcium considerably exceeds the sodium released for both cycles. The potassium released exceeded the sodium. The order of effectiveness in releasing ammonium was K $>$ Sr $>$ Mg.

The activity results were not quite so consistent as with andesine but clearly showed that potassium was held considerably less tightly than Mg and Sr, but more tightly than the ideal valency rule would indicate.

The small dilute exchange gives the order of replacement by ammonium as K $>$ Mg $>$ Sr. The activity coefficient ratio $\alpha K/\alpha NH_4$ is 1.25.

Bytownite (Table 11)

The apparent exchange capacities are considerably higher for bytow-

TABLE 10 -- LABRADORITE AS CATION EXCHANGER
a. Cation Exchange Data
(Figures in m.e. per 100 gm.)

Cation Introduced	Ammonium Released	Cations Released From Lattice			Introduced Cations Released by NH_4	Total Cations Released
		Na	K	Ca		
		First Exchange Cycle				
K		0.30		1.07	4.23	5.60
Mg					3.94	
Sr		0.27	0.43	1.10	3.22	5.01
		Second Exchange Cycle				
K	1.32	0.15		0.39	5.04	5.58
Mg	0.61		0.28	0.70	3.73	
Sr	0.93	0.15	0.19	0.51	3.89	4.74

b. Cationic Activity Data

Cation Exchange	pH	Activity mols/1	Concentration mols/1	Fraction Active	Bonding Energy Calories
		First Exchange Cycle			
K		3.67×10^{-4}	4.23×10^{-3}	.0872	1465
Mg		5.1×10^{-5}	1.97×10^{-3}	.0259	2170
Sr		7.0×10^{-5}	1.61×10^{-3}	.0435	1870
		Second Exchange Cycle			
K	7.85	5.05×10^{-4}	5.04×10^{-3}	.099	1380
Mg	7.61	8.5×10^{-5}	1.87×10^{-3}	.0457	1840
Sr	7.57	7.3×10^{-5}	1.65×10^{-3}	.0447	1850

c. Small Dilute Exchange Data

Cation Exchange	Exchanged Cation mols/1	Ammonium In Soln. mols/1	Me* Replaced / NH_4 Adsorbed	Percent Cation Displaced	$\alpha K/\alpha NH_4$
K	4.52×10^{-4}	0.84×10^{-4}	2.36	34.7	1.25
Mg	8.21×10^{-5}	0.88×10^{-4}	1.16	28.0	----
Sr	8.44×10^{-5}	0.80×10^{-4}	0.94	17.2	----

*Me refers to the metal being replaced.

nite than for the other plagioclase feldspars. In the first cycle they fall in the unusual order Mg $>$ K $>$ Sr, but in the second the order is K$>$Mg $>$ Sr. Calcium considerably exceeds sodium released, the ratio being about the same in both cycles. The absolute amounts are larger than in the case of andesine, indicating greater attack on the lattice. The order of effectiveness in releasing ammonium was K $>$ Sr $>$ Mg.

The activity results varied somewhat as between the first and second cycles. It appears that magnesium is held more strongly than strontium. The bonding energy for potassium is least but is relatively high for a monovalent cation.

The small exchange data give the order of replacement by ammonium as K $>$ Mg $>$ Sr, but the intensity of the ammonium uptake is best seen in the ratio $\alpha K/\alpha NH_4$ which here reaches a value of 7.4, by far the highest found. However, it is in good accord with the extensive and progressive attack on bytownite by ammonium chloride solutions.

TABLE 11 -- BYTOWNITE AS CATION EXCHANGER
a. Cation Exchange Data
(Figures in m.e. per 100 gm.)

Cation Introduced	Ammonium Released	Cations Released From Lattic Na	K	Ca	Introduced Cations Released by NH_4	Total Cations Released
			First Exchange Cycle			
K		0.35		1.83	5.54	7.71
Mg					7.71	
Sr		0.35	0.33	1.93	4.46	7.07
			Second Exchange Cycle			
K	3.24	0.13		0.84	11.93	12.89
Mg	1.10		0.25	0.97	6.62	
Sr	1.41	0.20	0.18	1.14	5.51	7.03

b. Cationic Activity Data

Cation Exchange	pH	Activity mols/1	Concentration mols/1	Fraction Active	Bonding Energy Calories
		First Exchange Cycle			
K		$4.60x10^{-4}$	$5.54x10^{-3}$	.0831	1480
Mg		$5.4\ x10^{-5}$	$3.85x10^{-3}$	.0140	2530
Sr		$8.3\ x10^{-5}$	$2.22x10^{-3}$	.0373	1955
		Second Exchange Cycle			
K	8.12	$5.31x10^{-4}$	$11.93x10^{-3}$	.0445	1850
Mg	7.55	$6.8\ x10^{-5}$	$3.30x10^{-3}$	.0210	2295
Sr	7.33	$7.6\ x10^{-5}$	$2.76x10^{-3}$	.0282	2125

c. Small Dilute Exchange Data

Cation Exchange	Exchanged Cation mols/1	Ammonium In Soln. mols/1	$\frac{Me^*\ Replaced}{NH_4\ Adsorbed}$	Percent Cation Displaced	$\alpha K/\alpha NH_4$
K	$6.5\ x10^{-4}$	$0.093x10^{-4}$	3.00	24.0	7.4
Mg	$8.06x10^{-5}$	$0.72\ x10^{-4}$	1.35	16.0	---
Sr	$9.75x10^{-5}$	$0.81\ x10^{-4}$	1.11	14.8	---

*Me refers to the metal being replaced.

Anorthite (Table 12)

Discussion: The apparent exchange capacities attained are somewhat lower than those of most of the other plagioclase members and considerably lower than those of bytownite. The calcium released by ammonium considerably exceeds the sodium although not so greatly as the composition of the mineral would indicate. The absolute amounts of sodium and calcium released by ammonium are distinctly less than in the case of bytownite. The order of effectiveness in releasing ammonium was K $>$ Sr $>$ Mg.

The cationic bonding energies calculated from activity measurements are lower for K, Mg and Sr than those of bytownite, and in the case of potassium are the lowest of any feldspar.

The small exchange data indicate that potassium and magnesium are replaced more readily than strontium by the ammonium ion. The value of $\alpha K/\alpha NH_4$ is 3.37, indicating strong binding of ammonium as compared with potassium.

TABLE 12 -- ANORTHITE AS CATION EXCHANGER

a. Cation Exchange Data

(Figures in m.e. per 100 gm.)

Cation Introduced	Ammonium Released	Cations Released From Lattice Na	K	Ca	Introduced Cations Released by NH_4	Total Cations Released
		First Exchange Cycle				
K		0.18		1.37	2.03	3.58
Mg					2.29	
Sr		0.11	0.18	1.29	2.78	4.36
		Second Exchange Cycle				
K	0.83	0.13		0.78	3.40	4.31
Mg	0.44		0.24	1.33	1.71	3.27
Sr	0.62	0.07	0.14	0.75	3.06	4.01

b. Cationic Activity Data

Cation Exchange	pH	Activity mols/1	Concentration mols/1	Fraction Active	Bonding Energy Calories
		First Exchange Cycle			
K		3.68×10^{-4}	2.03×10^{-3}	.1810	1020
Mg		6.3×10^{-5}	1.14×10^{-3}	.0547	1735
Sr		10.0×10^{-5}	1.39×10^{-3}	.0723	1565
		Second Exchange Cycle			
K	8.22	4.97×10^{-4}	3.40×10^{-3}	.147	1150
Mg	7.63	10.1×10^{-5}	1.77×10^{-3}	.0583	1690
Sr		8.8×10^{-5}	1.52×10^{-3}	.0576	1705

c. Small Dilute Exchange Data

Cation Exchange	Exchanged Cation mols/1	Ammonium In Soln. mols/1	$\frac{\text{Me* Replaced}}{NH_4 \text{ Adsorbed}}$	Percent Cation Displaced	$\alpha K/\alpha NH_4$
K	3.9×10^{-4}	0.56×10^{-4}	1.98	47.5	3.37
Mg	8.37×10^{-5}	0.77×10^{-4}	1.29	43.5	----
Sr	6.75×10^{-5}	0.73×10^{-4}	1.00	22.8	----

*Me refers to the metal being replaced.

DISCUSSION

When the individual exchange results for different feldspars are compared one with another, certain general regularities clearly emerge.

The magnesium ion throughout shows highly contrasting behavior to potassium. For the release of ammonium we always have K $>$ Mg; in all the plagioclases the order is K $>$ Sr $>$ Mg; in microcline we find K $>$ Mg $>$ Sr. Considering the two cycles of exchanges, the second always gives the greater release of K or Sr by NH_4. Magnesium however shows little variation in amount from the first cycle to the second. We thus gain the impression that magnesium is a non-penetrant exchange ion whereas K and NH_4 are capable of coming to equilibrium with deeper layers. We have already noted from other experiments, two peculiarities of the ammonium ion, namely its tendency to release more lattice cations than correspond to the amount of ammonium entering and its strong fixation.

The apparent exchange capacity as determined by K, Mg or Sr released by ammonium was greater for K than for Mg or Sr, (except in the first cycle with bytownite and anorthite). The mean results for the two cycles combined show that microcline stands somewhat apart from the plagioclase feldspars in this effect, the apparent exchange capacity with K as the saturating cation being three times those obtained when Mg or Sr was the saturating cation. In the plagioclase group the corresponding preponderance did not exceed about 50 percent.

The apparent exchange capacity by release of ammonium was in all cases, much less than that discussed above. Again, however, we found that the highest value was obtained with potassium as the displacing cation and that microcline and bytownite gave high capacities, compared with the other feldspars.

Potassium, whether entering or released, gave exactly the same order for the apparent exchange capacity; namely, bytownite, microcline, labradorite, andesine, albite, oligoclase and anorthite. Strontium also was almost perfectly consistent in the two cases, but the order was slightly different from that for potassium, being: bytownite, labradorite, andesine, albite, anorthite, oligoclase, microcline. The main difference was the changed position of microcline. An identical order was found in the magnesium release experiments except that oligoclase came before anorthite. The ammonium released by magnesium followed the order: bytownite, microcline, andesine, labradorite, albite, oligoclase, anorthite.

The most remarkable feature of these lists is that all treatments place bytownite in first position. Of all the feldspar structures this seems to be the most easily penetrated. Microcline is easily penetrated by ammonium and potassium but not by magnesium or strontium. Anorthite appears to be rather poorly penetrated by potassium and by strontium and even ammonium penetrates only moderately. It will be recalled that strongly acidic solutions attack anorthite the most readily of all the feldspars.

Some of these peculiarities regarding apparent exchange capacity were noted and discussed by Jackson and Truog (3). They ground various minerals, microcline, orthoclase, muscovite, kaolinite tale, quartz and several clays for extended periods in a ball mill in presence of benzene or of water. With the feldspars, extensive changes occurred and apparent exchange capacities from 138-369 m.e. per 100 gm. were obtained, the higher figures representing practically the whole cation content. In the case of clays they found that the apparent exchange capacity was greater toward monovalent than toward divalent cations, ammonium giving the highest value; and that strong fixation effects came into play when attempts were made to displace ammonium or potassium with calcium or lanthamum. They state that "comparable results have been found also in studies of other minerals ground." In the case of microcline, they stated, "the exchange capacity as measured by potassium was distinctly higher than when measured by calcium."

The relative situation between potassium and ammonium can be evaluated through the experiments involving a small dilute exchange. The Donnan condition at equilibrium implies that

$$\left[\frac{a_K}{a_{NH_4}}\right]_{\text{solution}} = \left[\frac{a_K}{a_{NH_4}}\right]_{\text{feldspar surface}}$$

In dilute true solution, $\frac{a_K}{a_{NH_4}} = \frac{c_K}{c_{NH_4}}$

For the feldspar surface $\left[\frac{a_K}{a_{NH_4}}\right]_F$ can be treated as the corresponding product of concentration and activity coefficient. This we can write: $\left[\frac{c_K}{c_{NH_4}}\right]_S = \left[\frac{c_K}{c_{NH_4}}\right]_F \times \left[\frac{\alpha K}{\alpha NH_4}\right]_F$ where the symbol S refers to the equilibrium solution and F refers to the feldspar surface. $\left[\frac{c_K}{c_{NH_4}}\right]_F$ is known from analytical data since it is identical with the ratio of exchangeable potassium/exchangeable ammonium. The values of $\alpha K/\alpha NH_4$ which should display quite sensitively the relative fixation situation as between the two ions are quoted in Tables 6 to 12. For microcline $\alpha K/\alpha NH_4$ is only 0.37, indicating that potassium is more firmly held than ammonium. Albite gives a value just below 1 and labradorite is somewhat above 1. Oligoclase and andesine ranged around 1.7 to 1.8; anorthite gives a higher ratio, 3.37, and bytownite goes the highest of all, 7.4, which indicates a very strong tendency for ammonium to be firmly held. These ratios are not sufficient to characterize the feldspar behavior completely with regard to K and NH_4. Each represents a single point on the complete curve connecting $\alpha K/\alpha NH_4$ with the relative total cation composition of the surface. For complete characterization, small dilute exchanges should be carried out using various surface compositions.

It is interesting to compare the values of $\alpha K/\alpha NH_4$ with $(\Delta F)_K$, values calculated from potassium activity measurements. Microcline shows a high value of $(\Delta F)_K$, combined with a low value of $\alpha K/\alpha NH_4$. On the other hand, bytownite combines a high value of $(\Delta F)_K$ with a high value of $\alpha K/\alpha NH_4$, suggesting that although potassium is strongly held, ammonium is bound even more tightly. Anorthite combines a low bonding energy for potassium with a relatively high $\alpha K/\alpha NH_4$ ratio.

The two quantities thus seem to be affected by different factors. Lattice penetration and bonding by the ammonium ion appear throughout

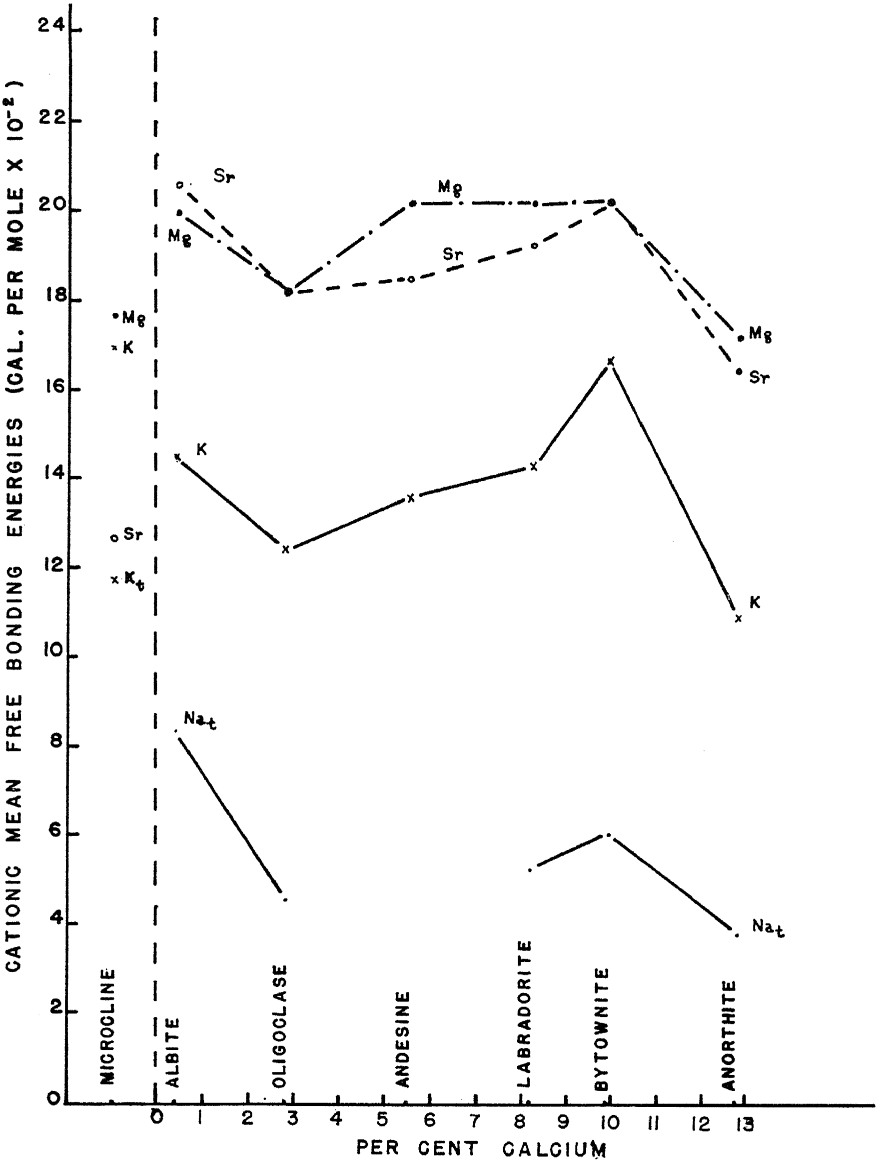

Fig. 3—Cationic mean free bonding energies for surfaces saturated with Mg, Sr, K, and Na, in relation to feldspar composition.

to be a sensitive function of the crystal composition and structure.

Activity measurements on the feldspars saturated with Mg and Sr show similar trends in cationic bonding energy to those displayed by potassium. In Figure 3 the values obtained by titration of the acidic surfaces with KOH (microcline) or NaOH (plagioclases) are included for comparison. The strontium and magnesium values lie close together for the plagioclase members; but in the case of microcline the bonding energy for magnesium is close to that of potassium and both lie considerably above the strontium value. In the plagioclases the variations with composition are roughly in agreement for the three cations, Sr, Mg and K, with albite and bytownite giving the highest values and oligoclase and anorthite the lowest. A similar trend, but at distinctly lower absolute values, was obtained with the sodium ion by titration of acidic feldspar surfaces. It thus appears that acid treatments produce proportionately more exchange sites of low bonding energy than do leachings with neutral salts. This would be expected if acids disrupt the silica-alumina framework with production of a higher proportion of poorly organized material.

Proportions of Cations Released from Feldspars

The analytical data obtained on the release of the native cations of feldspars under different treatments provide interesting comparisons. The potassium/sodium and sodium/calcium ratios are assembled in Table 13.

While the values for water correspond to somewhat alkaline conditions, the salt treatments were close to neutrality and the hydrochloric acid treatments were at pH values slightly above 2.0. The potassium/sodium ratios for microcline indicate that water and acid liberate sodium preferentially over potassium, whereas ammonium and strontium chlorides release potassium preferentially over sodium.

In the plagioclase series the release of sodium is proportionately much greater in water than in acid and in all cases strontium chloride strongly favors the liberation of potassium.

Sodium and calcium are both impurities in microcline. The ratio Na/Ca is a little lower for the water extract than for the original crystal

TABLE 13 -- CATIONIC RATIOS OF FELDSPARS AND OF THEIR AQUEOUS EXTRACTS

Mineral	In Crystal	Water	N/100 HCl	0.4 N.NH_4Cl	N.$SrCl_2$
		K/Na ratios (equivalents)			
Microcline	4.25	2.65	2.00	5.51	6.31
Albite	---	0.027	0.19	0.11	0.38
Oligoclase	---	.025	0.18	.10	.60
Andesine	---	.030	.19	.16	1.00
Labradorite	---	.040	.21	.17	1.61
Bytownite	---	.017	.032	.11	0.96
Anorthite	---	.037	.22	.21	1.65
		Na/Ca ratios (equivalents)			
Microcline	6.2	5.47	0.50	0.77	0.42
Albite	17.0	6.89	.38	.61	1.54
Oligoclase	2.21	---	1.67	2.14	1.08
Andesine	0.77	---	0.94	1.52	0.67
Labradorite	0.34	5.15	.49	0.46	.24
Bytownite	0.18	1.10	1.71	.33	.18
Anorthite	0.014	0.56	.21	.18	.084

but it is very much lower when acids or salts are used.

In albite, with its strong predominance of sodium over calcium, the effect of water is to bring calcium into solution preferentially over sodium and this is greatly accentuated by acid and salt treatments.

Anorthite shows the opposite behavior. It contains much more calcium, but in water, and to a smaller extent in acid and in salt solutions, sodium appears in solution preferentially over calcium. Bytownite and labradorite show the same effects but less strongly. Oligoclase behaves like albite but with a much smaller range of variation of the Na/Ca ratios. Thus at both ends of the plagioclase series, solution of the cation present in smaller amount is favored.

These facts undoubtedly must play a significant part in the reactions of feldspar surfaces with colloidal constituents of soils. The proportions of the cations which are liberated in the early stages may well be quite different from those which prevail under extended attack. How does the feldspar structure adjust itself to a preferential loss of certain cations? Does the framework remain essentially intact or are irreversible structural adjustments necessary? We are not yet in a position to answer these questions, but we can plainly see that the answers will be exceedingly important for the whole conception of rock breakdown and soil formation.

General Discussion

In the preceding experimental work many remarkable features distinguish feldspar surfaces from other types of cation exchanges. Four of the most striking are: (1) The dependence of cation release upon the previous cationic history of the surface; (2) the variability in apparent exchange capacity according to cation; (3) cations released from the lattice are often in excess of those entering; and (4) the ammonium ion in water is extraordinarily effective in causing release of other cations and in its strong fixation at all feldspar surfaces. These facts are not consistent with the concept of a hydrated, gelatinous amorphous layer, which is frequently assumed to exist as the first product of feldspar breakdown. The evidence shows that only a small part of the total possible exchange could be due to such material, in which steric effects would be at a minimum.

The main facts established in the present work can, however, be explained by a radically different concept. Extending from the original unchanged feldspar toward the surface we have first a zone of lattice adjustment or accommodation in which the essential cellular structure of the feldspar is still present although somewhat distorted or loosened. It differs from the unchanged feldspar in that its spatial relationships allow flexibility, so that it can accommodate itself, with greater and greater ease as the external surface is approached, to solvent molecules and to metallic cations. However, it still retains the essential coordination relationships of three-dimensional silicate framework structures and will not accommodate ions such as magnesium with strong sixfold coordination. At and near the surface, which of course must be thought of as highly irregular on a molecular scale, we have a layer of complete accessibility, in which all exchange sites can react freely with external solutions. This is the layer which provides, by dissociation into the solution phase, the cations of the electrical double layer. The solution phase contains, in addition, small amounts of silicic acid. but practically no aluminum.

How can these differing but somewhat interpenetrating zones arise? Vigorous and continued attack by hydrogen ions certainly causes complete lattice disruption, with a loss of considerable material into solution, and a change in the silica:alumina ratio of the undissolved residue as compared with that of the fresh feldspar. This was well demonstrated in the work of Correns and von Engelhardt (Part I Ref.) with orthoclase (sanidine). Under the much milder conditions of our experiments the accessible layer represents mainly the outer surface of the zone of adjustment. It manifests its exchange properties toward cations incompatible with the lattice (e.g. Mg^{++}) equally in aqueous and in alcoholic solutions. However, the disrupting effect of the hydrogen ion still shows itself, namely in the advancing zone of lattice flexibility. This is the zone from which the lattice cations diffuse towards the surface. Their freedom of movement, however, can be drastically altered by framework readjustments which could occur differently for different salt treatments. Some of these may not easily be reversed. In this way it is possible to explain for instance, why the total amount of sodium liberated from albite in the alcoholic ammonium-strontium-ammonium-strontium sequence of treatments is greater than that in the strontium-ammonium-strontium-ammonium sequence. In alcohol these hysteresis effects appear to be more pronounced than in water.

The peculiar effectiveness of the ammonium ion in causing the release of lattice cations and in becoming itself fixed can now be examined. The feldspars are so constituted that there are no unfilled cation positions in the cellular structure and no large channels leading from one cell to another. Only the naked hydrogen ion seems small enough to penetrate freely. Thus, although at the surface hydration undoubtedly accompanies attack by H^+, deep penetration with the breakage of lattice links would seem to be peculiarly a function of H^+. The first step must therefore be

$H_3O^+ = H_2O + H^+$.

This type of reaction is also possible for the ammonium ion, namely

$NH_4^+ = NH_3 + H^+$.

This distinguishes ammonium very sharply from the potassium ion of comparable size. If the ammonia molecule, which is somewhat smaller than water, is strongly adsorbed, then the above reaction would be facilitated. The polar character and small size of the ammonia molecule make a strong adsorption certain. Thus the above reaction would account both for the ready release of lattice cations by ammonium and also for the apparent fixation. Whether the latter is wholly adsorption of NH_3 or also partly anchorage of the ion NH_4^+ remains to be determined. Our experiments do not distinguish between the two mechanisms.

The relationship of external surface and cation exchange capacity affords some guidance in the estimation of the thickness of the surface layers. If we assume, as in orthoclase, that the average cation-cation spacing is just under 7 A , then the cation exchange capacity at the outer surface of cubical 1 μ feldspar particles would be 0.75 m.e./100 gm. For 0.5 μ particles the value would be 1.5 m.e./100 gm. With magnesium as the saturating cation, the apparent exchange capacities of 0.5-1.0 μ fractions range as follows: microcline, 1.95; albite, 2.76; oligoclase, 2.70; andesine, 3.05; labradorite, 3.83; bytownite, 7.16; anorthite, 2.00. These values include, of course, exchange at the exposed ends of silica chains. Such sites would seem especially well suited to the entry and release of magnesium. Taking this into consideration it does not appear that the freely accessible sites range very deeply into the surface layer. They evidently comprise a thickness of no more than three unit cells and more probably only one to two.

It is equally certain that the layer of lattice adjustment cannot be very thick. Considering the extra cations released from the lattice over and above those equivalent to magnesium, a few lattice units only could be involved. A depth of only 2 to 5 unit cells would more than suffice to provide the native cations released by successive salt treatments.

The experiments here reported do not provide a conclusive demonstration of the exact mechanism by which the zone of lattice adjustment acquires its characteristic properties. Penetration by hydrogen ions certainly seems to be important, but physical strains and dislocations caused by the grinding process may also have contributed. It would be extremely interesting to investigate fresh, unground surfaces, but very sensitive methods would have to be employed.

SUMMARY

1. The reaction of mildly ground albite with NH_4Cl solutions at three different pH values, alternating with neutral $MgCl_2$ solutions, indicated that the apparent cation exchange capacities were independent of the pH of the ammonium chloride solutions, but were much greater for ammonium than for magnesium, ammonium being extremely effective in releasing sodium from the lattice.

2. Anorthite gave similar results but showed some variation with pH.

3. The release of sodium from albite is uniformly greater for ammonium chloride than for magnesium chloride solutions over a wide range of concentrations. The release of silicic acid was small near neutrality and varied somewhat with salt concentration. The order of magnitude was similar to that given for quartz. Much higher values are quoted for amorphous silica.

4. The interaction of albite with NH_4Cl, $MgCl_2$ and $SrCl_2$ in methanol gave about the same apparent exchange capacity for magnesium as in water, but the values for strontium were much greater than in water, and those for ammonium were lower.

5. It was shown with microcline, albite, oligoclase, andesine, labradorite, bytownite and anorthite that treatment with ammonium chloride solutions gives both exchangeable and fixed ammonium, the latter being liberated by distillation from alkaline solution.

6. By comparing the behavior of ammonium, magnesium and strontium saturated feldspars upon successive treatments with salt solutions, it was concluded that magnesium and strontium were not fixed.

7. Detailed studies of exchange properties using both small dilute exchanges and total exchanges were carried out on 1 μ -0.5 μ fractions of all the feldspars under experiment. Cation activity measurements of dilute feldspar suspensions, using surfaces saturated with K, Sr and Mg, were also carried out. Bytownite was found to give higher apparent exchange capacities than the other feldspars, a relatively high bonding energy for potassium and an extraordinarily high bonding for ammonium.

8. The proportions of the native cations released from the feldspars by various treatments were found to bear little relation to lattice composition. In the plagioclase series, albite showed a strongly preferential loss of calcium, while anorthite showed a strongly preferential loss of sodium. The proportions varied considerably with the salt or acid treatment employed.

9. In explanation of these results it is suggested that between the external surface and the unchanged feldspar there exists a relatively thin layer of adjustment or accommodation. This consists of a somewhat loosened or modified feldspar framework which does not accommodate the magnesium ion. It apparently fixes ammonium strongly, possibly by strong adsorption of NH_3, thus releasing the hydrogen ion for further penetration.

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