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BASE EXCHANGE IN ORTHOCLASE

J. F. BREAZFALE AND O. C. MAGISTAD

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*In cooperation with the United States Department of Agriculture, Bureau of Plant Industry.

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Errata:

On page 621, line 18,
substitute "arid" for "acid."

On page 623, line 4,
substitute table X for table
VI.

On page 623, lines 7
and 8, omit words "with the
orthoclase solution."

On page 623, line 9,
substitute 38 for 31.

BASE EXCHANGE IN ORTHOCLASE

J. F. BRFAZI VI L AND O. C. MAGISTAD

INTRODUCTION

The objects of the experiments described in this bulletin were to determine the nature of certain colloidal complexes in orthoclase from which potassium may be dissolved, and to correlate the reactions of these complexes with those of the hydrated aluminum-silicates of the soil, that are commonly known as zeolites. While the results may have an immediate bearing upon the many field tests and pot-culture experiments that have been conducted in recent years, looking toward the use of finely ground orthoclase as a fertilizer, such tests will not be considered. The question of availability of potassium must be referred always to the plant, so this phase of the study of orthoclase will be discussed very briefly, and will be taken up in work with plants that is to follow.

This work was not intended, primarily, as a chemical study of base exchange, so, in the replacement of one base for another, no effort was made to obtain theoretical results. Except in a few cases, no attempts were made to get the systems into absolute equilibrium, as this was thought to be unnecessary. In previous work it has been observed often that there are points of similarity between the behavior of finely ground orthoclase and that of soil zeolites, and the work outlined in this bulletin will be confined to these points of similarity.

All samples of orthoclase do not have the same composition, and do not possess the same properties in like degree. During the weathering processes, many changes may have taken place that have altered the properties, and affected the solubilities of orthoclase in certain localities only. The orthoclase that was used in this work was obtained from different points in southern California, and was prepared in separate lots as the work proceeded. The fineness of subdivision also plays an important role in solubility and replacement. An effort was made to have all samples of uniform texture, but this was obviously impossible. The following experiments should not, therefore, be compared with each other, except in a general way.

PREPARATION OF SAMPLES

Potash feldspar occurs as both orthoclase and microcline, but as these rocks have the same composition and differ in crystalline structure only, no distinction will be made between them. Cleavage or massive samples

only were used. All samples were broken into small pieces and ground for several hours in a ball mill. The lighter particles were floated off with water into enameled pans, and the water evaporated off in an air bath at 110°C. The coarser particles were dried, returned to the mill, and ground again.

When dry, the fine particles were passed through a 100-mesh sieve in order to break up any lumps, and the samples were then ready for use. All samples were treated alike, and this treatment gave a very finely divided material.

THE SOLUBILITY OF POTASSIUM IN ORTHOCLASE

When finely ground orthoclase is placed in water, a certain amount of potassium goes into solution and appears partially as the hydroxide. The solubility of potassium in the samples of orthoclase used in these experiments varied from about 60 to about 10 parts per million.

Other investigators have found solubilities both lower and higher than those given above. Thus Haley (2) using 25-gram portions of 200-mesh orthoclase obtained solutions containing 282.2 parts per million of potassium. He did not state the amount of water used. This variation in solubility of different samples of orthoclase is explained by the difference in properties of the original samples, the difference in size of particles, the difference in the ratio of water to solid, and to other factors. Ordinarily, orthoclase, when fused and analyzed, yields about 10 percent of potassium. A very small percentage of this is dissolved by a relatively short digestion in water.

Two 25-gram samples of the orthoclase from Winchester, California, were weighed out. One sample was shaken at intervals with 2,000 cc. of water for 3 days, when the solution was filtered and analyzed for potassium. The other 25-gram sample was placed in a gooch and percolated with small portions of water until the percolate amounted to 2,000 cc. In Table I are given the total amounts of potassium dissolved by 2,000 cc. and also the amounts that were dissolved by the first 900 cc. of the percolate.

TABLE I.—SOLUBILITY OF POTASSIUM IN ORTHOCLASE UNDER DIFFERENT CONDITIONS.

	Grams of K
1. Total in 2000 cc. by percolation	0.0265
2. Total in 2000 cc. by shaking.....	0.0344
3. First 900 cc. percolate	0.0201
4. 900 cc. by shaking	0.0155

It will be noticed that when the orthoclase was shaken with a large amount of water, more potassium was dissolved than when percolated with small successive amounts. However, the first 900 cc. of the percolate showed a greater amount of potassium than did an equal amount of the solution that had been shaken.

The 25 grams orthoclase, when percolated with 900 cc. of water, gave a solution of 22.3 parts per million of potassium. This solution was partially hydrolyzed and gave a strong alkaline reaction.

The subsequent percolation with 1,100 cc. gave a solution of only 5.8 parts per million. This was undoubtedly due to the fact that in the first increments of water used, the ratio of water to replaceable potassium was small and as a result the concentration of potassium in the solution was large. As percolation progressed, with a decrease of replaceable potassium present, the ratio of water to replaceable potassium steadily increased with a rapid decrease in the concentration of the percolate.

Other samples, obtained from Los Angeles and Riverside, California, when treated in this way showed a lower solubility, and less hydrolysis.

EFFECT OF RATIO OF SOLID TO LIQUID

In Table II is shown how the ratio of solid to liquid affects the solubility of potassium, using samples of orthoclase obtained from Los Angeles, California. These samples were treated alike. They were shaken until they had reached approximate equilibrium, allowed to stand until the sediment settled, and the soluble potassium was determined.

TABLE II.—THE SOLUBILITY OF POTASSIUM IN ORTHOCLASE AS AFFECTED BY RATIO OF SOLID TO LIQUID.

	Grams orthoclase	cc. water	Total K dissolved grams	p.p.m. in solution
1	50	500	0.00544	10.9
2	100	500	0.00829	16.6
3	200	500	0.01123	22.4

As the ratio of orthoclase to water was decreased, the concentration of potassium in the solution was increased, not however, in direct proportion to the amount of orthoclase present. The orthoclase was not acting as a solid with a low solubility, gypsum for example, but rather as a zeolite. The potassium was evidently hydrolyzing from some compound in the orthoclase that appeared to possess some of the properties of a zeolite.

As is well known, in ordinary cases of solubility, the concentration of dissolved material in water reaches a constant, and if additional water

is added, tends to maintain this concentration. With zeolites, the concentration of the solution is not a constant, but varies with the ratio of water to zeolite as was determined by Magistad (8). The similarity of the behavior of feldspathic potassium and zeolitic potassium in water is striking. Apparently potassium is not simply dissolved, but is hydrolyzed from the orthoclase in the same general way as from zeolites.

RATIO OF TOTAL POTASSIUM TO POTASSIUM HYDROLYZED AS POTASSIUM HYDROXIDE

Attention has been called already to the fact that hydroxyl ions usually appear in a solution of orthoclase. When potassium zeolite is placed in water and equilibrium is attained, the potassium hydroxide formed by hydrolysis, is largely converted to potassium aluminate. The relation between amount of alumina present as aluminate, and hydroxyl-ion concentration, or pH, is given by Magistad (8) as $\text{Log } X = \text{pH} - 7.20$ where $X = \text{p.p.m. Al}_2\text{O}_3$. Solving this for any particular pH value, such as pH 9.0, for example, we find that 99.2 percent of the potassium is present as aluminate, and the rest as ionized potassium hydroxide. This fraction, from the equation, is constant for all concentrations and pH values of potassium aluminate. Sodium-aluminate solutions are more highly ionized, and with this salt, approximately 1.5 percent of the sodium is present as ionized sodium hydroxide.

The pH values of the three solutions described under Table II were determined by means of the quinhydrone electrode. Calculations then made gave the results given in Table III.

TABLE III.—TOTAL AND ALUMINATE POTASSIUM IN WATER EXTRACTS OF ORTHOCLASE.

Solution no.	pH value	Theoretical amount K as aluminate	Total found by analysis p.p.m. K	Difference p.p.m. K
1	7.10	None	10.9	10.9
	7.12			
2	7.40	1.2 to 1.5	16.6	15
	7.48			
3	7.45	1.4	24.7	23.3
	7.45			

In the foregoing table the amount of potassium present as potassium hydroxide has been omitted. This amount is in the neighborhood of 0.01 part per million according to pH measurements. After calculating the amount of potassium present as aluminate, there is still a large difference found between this figure and the total as determined by very careful gravimetric analysis. This suggests that the remainder of the potassium is combined in some other form, probably as a complex potassium ion.

This potassium, in the regular chlorplatinic-acid method would, of course, become ionized and active after digestion with acid.

Additional data corroborating the data given in Table III are given below in Table IV.

TABLE IV.—THE AMOUNTS OF IONIZED AND ALUMINATE POTASSIUM IN EXTRACTS OF ORTHOCLASE.

Grams orthoclase	cc water	pH value	Amount K in p.p.m.	
			Ionized	As potassium aluminate
25	25	8.90	0.31	38.2
15	25	8.40	0.098	12.1
10	25	8.30	0.078	10.0
10	50	7.63	0.017	2.0
5	25	7.52	0.013	1.6
5	50	7.12	0.005	none

These data indicate clearly that orthoclase in water does not have a constant solubility, but rather that it hydrolyzes in a manner similar to zeolites. If orthoclase had a constant solubility, almost uniform pH values and amounts of ionized potassium, as well as soluble potassium aluminate, would have resulted in all cases.

SOLUBILITY AND AVAILABILITY

It has been shown in a former bulletin of this Station that the potassium that is directly available to plants probably exists in the soil as a hydrated aluminum-silicate, or zeolite. While it may be true that plants depend almost entirely upon the hydrolysis of the zeolite for their potassium, it is true also that the supply of potassium must come ultimately from the orthoclase in the soil. It has been shown by one of the authors, with Dr. L. J. Briggs (1) that the concentration of potassium in a solution of orthoclase is not a measure of its availability to plants. When the soluble potassium in an aqueous solution of orthoclase is low, it is quite probable that at any given time only a small percentage of it is available. In Table III the concentration of total potassium in the solution varied from 10 to 23 parts per million, while the concentration of potassium occurring as ionized potassium hydroxide was about 0.01 part per million. While a plant is able to feed in solutions having a concentration of potassium as low as the latter figure, it is obviously impossible for it to function properly in such solutions. If it is true that the total solubility of potassium in orthoclase is not a measure of its availability, it is probable that the availability would be more accurately represented by the concentration of potassium hydroxide.

There seems to be a distinction between solubility and availability.

A plant food may appear to be in solution and yet not be available to plants. If potassium exists in a solution as a colloid and non-ionized, it is highly probable that it is not available. It is reasonable to assume that, as the plant feeds upon ions, a food element must be ionized properly in order that it may be absorbed. In the opinion of the authors, the absorption of nutrients of a plant is similar to a precipitation in an aqueous solution, in that a rearrangement of the elements is brought about and a new compound is formed. The absorption of an ion is possible, only when that ion fits into some definite chemical compound. If this were not the case, in plant nutrition the nutrient solution and the cell sap would be often out of equilibrium. If the potassium in orthoclase appears in solution yet is not dissociated, it probably is not 100-percent available. This may be explained by assuming that the potassium is present with aluminum as a complex ion.

THE ROLE OF CALCIUM, MAGNESIUM, AND SODIUM ZEOLITES

It is possible that zeolites of calcium, magnesium, and sodium play an important part in plant nutrition by acting as an intermediary between the difficultly available potassium of the orthoclase and the readily available potassium of potassium zeolite. Evidence of this will be shown later.

If zeolites of either calcium, magnesium, or sodium exist in a soil, they must of necessity be in equilibrium with the soil solution, and replace a certain amount of potassium in the orthoclase. This replaced potassium will be in the form of a zeolite which is known to give up its potassium readily to the plant.

BASE EXCHANGE IN ORTHOCLASE

Many determinations of the ability of orthoclase to exchange a part of its potassium for some other base were made upon samples collected at different places, and in every experiment, all samples were found to possess the property of base exchange. Usually only about 0.5 percent of the total potassium in the orthoclase used, was found to be replaceable.

In Table V are shown the results of an experiment upon a sample from Winchester, California.

One hundred grams of the prepared sample were percolated with small amounts of water until the percolate amounted to 1 liter. This solution was evaporated to dryness and the dissolved potassium determined (No. 1).

The orthoclase residue was then percolated with 1 liter of a tenth-normal solution of calcium chloride that had been made alkaline with calcium hydroxide to a pH value of about 8, and this percolate analyzed for potassium also (No. 2).

The orthoclase was then washed free from calcium and chlorine, and the calcium, that had been fixed by the orthoclase, was displaced with a normal solution of potassium chloride and the calcium determined in the percolate (No. 3).

TABLE V.—BASE EXCHANGE IN ORTHOCLASE OF HIGH POTASSIUM SOLUBILITY.

100 grams orthoclase	Grams K
1. K in orthoclase soluble in 1 liter water=	0.0631 or 1.62 M.E
2. K in orthoclase residue soluble in 1 liter n/10 CaCl_2 =	0.0331 or 0.85 M.E
3. Ca fixed by orthoclase = 0.0405 Ca equivalent to	0.0790 or 2.02 M.E

It will be seen that the amount of potassium that was dissolved by the distilled water was relatively high, 63.1 parts per million. However, additional potassium was dissolved when the orthoclase residue was percolated later with alkaline calcium-chloride solution.

The calcium equivalent that was fixed by the orthoclase did not equal the total potassium equivalent that was brought into solution by the water and the calcium-chloride solution. The amount of calcium that was fixed was, however, much greater than the potassium that was liberated by the calcium chloride.

The percolation with water, probably reduced one portion of the zeolite to the hydrogen salt, whose base was replaceable, and possibly broke down another portion of the zeolite into its components Al_2O_3 and SiO_2 , which did not build up 100 percent.

It seems that whenever a zeolite is treated in such a way that the hydrogen-exchange complex is formed, whether by acid salts, electro-dialysis or leaching with water, the greater part of the hydrogen zeolite so formed breaks down. It is not known what the nature of the residue is, whether alumina and silica, or a compound of the two. If one first writes the formula for the hydrogen zeolite as HZ, the hydrogen has the appearance of being replaceable. If the formula is now written $\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_4 \cdot 3\text{SiO}_2$, analogous to $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_4 \cdot 3\text{SiO}_2$, it becomes clear how a shifting of the bonds might change the labile hydrogen into water. Several instances have been observed where acid-reacting hydrogen zeolites have, on standing, become nearly neutral. Apparently this conversion, or zeolite "break-down," takes place under certain conditions.

In the next experiment a different procedure was followed. Two hundred grams of orthoclase, with a lower solubility, were collected from a different locality. This was percolated with small portions of water until the percolate amounted to 500 cc. The percolate was then evaporated to dryness and the potassium determined (No. 1).

The orthoclase residue was then percolated with 500 cc. of a normal solution of potassium chloride to which sodium hydroxide was added

until the mixture was hundredth-normal alkali. The residue was further washed with 100 cc. normal potassium chloride. This percolate gave only a trace of calcium. The orthoclase residue was washed once, percolated with 500 cc. of tenth-normal calcium chloride of pH 7, and washed free from calcium and chlorine. The calcium was then displaced with a normal solution of potassium chloride and the calcium was determined in the percolate (No. 2).

TABLE VI—BASE EXCHANGE IN ORTHOCLASE OF LOW POTASSIUM SOLUBILITY

200 grams orthoclase	Grams K
1. K in orthoclase soluble in 500 cc. water =	0.0154 or 0.39 M.E.
2. Ca fixed by orthoclase = 0.0232, Ca equivalent to	0.0452 or 1.16 M.E.

In general, leaching 200 grams of orthoclase with 500 cc. to 1 liter of water will remove 60 to 90 percent of the total replaceable potassium. The base-exchange capacity of this orthoclase after treatment with an alkaline, calcium-chloride solution, according to Table VI, is 0.0452 gram potassium, or approximately 300 percent of the amount removed by water. It would seem that the alkaline, calcium-chloride solution had caused some "build-up."

Build-up has been observed in the case of soils, synthetic zeolites, ignited zeolites, and even in the case of finely divided silica and alumina gel. It seems perfectly reasonable, therefore, that such a build-up might occur in this orthoclase material. Build-up under such conditions would indicate that zeolites in feldspar behave in every particular like the zeolites in soils. A formation of zeolites from feldspars under somewhat similar conditions was found by Leonard (6). He treated feldspars with alkali, carbonate solutions at atmospheric pressure, and at a pressure of 15 atmospheres, and demonstrated that zeolites had been formed. One of these zeolites, leverrierite, is the zeolite which Kerr (5) found to be present in a Colby silt-loam, and which he believed responsible, in part, for the base-exchange capacity of that soil.

The two experiments just described show that a certain fraction of orthoclase possesses the property of base exchange. They also illustrate the difficulty of obtaining theoretical results. In replacing potassium by calcium, either a break-down or build-up of the zeolite is likely to occur. It is, therefore, difficult to replace potassium with calcium, for example, and have the amount of calcium fixed, exactly balance the amount of potassium liberated.

The dynamic equilibrium which exists in the case of base-exchange compounds is not thoroughly appreciated. Break-down and build-up are apt to occur under most treatments, and the base-exchange capacity is

merely an equilibrium figure under those particular conditions. This viewpoint immediately shows us why various methods for determining the T value will give divergent results, and why barium chloride consistently gives lower results than some other salts when used to determine replaceable hydrogen.

EFFECT OF pH OF SOLUTION UPON BASE EXCHANGE

In a former bulletin of this Station it was shown that the build-up of zeolites depends in large measure upon the pH of the solution. In the two experiments just described, the percolation of at least one salt solution in each case was carried on at a pH of 8 or greater. This pH has been found to be very active in stimulating the formation or build-up of zeolites from these component parts.

In order to permit the reaction $2HZ + CaCl_2 = CaZ + 2 HCl$ to progress to the right and go to completion, the hydrochloric acid must be removed, which can be done by neutralization. When all the hydrogen zeolite initially present has been converted, equilibrium is disturbed and more is probably formed from the components, or zeolite residue from former break-down. The removal of the acid is the factor allowing the above reaction to proceed and for that reason alkaline replacing agents or alkaline solutions stimulate build-up.

BASE EXCHANGE IN AN ACID MEDIUM

In the next experiment the percolation was carried on in an acid medium and the extent of base replacement measured.

One hundred grams of orthoclase were percolated with 1 liter of calcium-chloride solution which had been made fiftieth-normal with hydrochloric acid, and the potassium that was brought into solution determined (No. 1).

The orthoclase residue was washed free from calcium and chlorine, and the calcium that had been fixed was displaced by normal hydrochloric acid and determined in the percolate (No. 2).

The orthoclase residue was then percolated with tenth-normal calcium chloride that had been made alkaline to phenolphthalein with sodium hydroxide to pH 8 or greater, and the fixed calcium replaced by normal potassium chloride (No. 3).

The orthoclase residue was again percolated with tenth-normal calcium chloride that had been made acid to the extent of fiftieth-normal with hydrochloric acid and the fixed calcium replaced by normal potassium chloride and determined (No. 4).

TABLE VII—BASE EXCHANGE IN AN ACID MEDIUM.

100 grams orthoclase		
1. K in orthoclase soluble in acid n/10 CaCl ₂ =	0.0546 or 1.40 M.E.
2. Ca fixed by orthoclase in acid n/10 CaCl ₂ =	0.0079 or 0.39 M.E.
1st percolation.		
3. Ca fixed by orthoclase at pH 8 =	0.0500 or 2.50 M.E.
2nd percolation.		
4. Ca fixed by orthoclase in acid n/10 CaCl ₂ =	0.0048 or 0.24 M.E.
3rd percolation		

It will be noted that there was very little replacement of potassium by calcium in the first percolation, but when the pH was made 8 or above in the second percolation, there was a pronounced exchange of bases. When the residue was finally percolated with an acid solution of calcium chloride very little exchange was noticed.

The treatment of the orthoclase with acidified calcium chloride converted most of the potassium zeolite present into hydrogen zeolite, and probably a large portion of this hydrogen zeolite became inactive. A small amount of potassium zeolite was converted into calcium zeolite, the amount being 0.39 M. E. In acid solutions we should not expect a much greater proportion of calcium absorbed than this, because of the high energy of replacement of hydrogen.

Treatment with an alkaline salt solution converted the hydrogen zeolite back into a sodium or calcium zeolite. If a break-down of the hydrogen zeolite had occurred, this salt was again built up.

Treatment No. 4 with an acid, calcium-chloride solution, a duplication of treatment number two, gave similar results.

EXPERIMENTS WITH IGNITED ORTHOCLASE

It is well known that heating a zeolite will destroy its power of base exchange, so an effort was made to determine the effect of heat upon orthoclase.

One hundred grams of orthoclase with a low, base-replacement capacity was ignited at a bright-red heat for several hours, then cooled, and percolated with 100 cc. of a neutral solution of tenth-normal calcium chloride. The residue was washed, and the fixed calcium replaced by normal sodium chloride (No. 2).

The residue was then washed once and digested for 16 hours at 110°C. in a 20-percent solution of potassium hydroxide in the presence of calcium chloride.

The magma was then neutralized with hydrochloric acid and the orthoclase filtered and washed.

The calcium that had become fixed during this procedure was replaced with tenth-normal barium chloride and determined in the filtrate (No. 3).

As a control, an untreated sample of orthoclase was percolated with neutral tenth-normal solution of calcium chloride, washed, and the fixed calcium displaced by normal potassium chloride and determined in the percolate (No. 1).

TABLE VIII.—BASE EXCHANGE AND BUILD-UP IN IGNITED ORTHOCLASE.

100 grams orthoclase	Grams Ca
1. Replaceable Ca, original sample =	0.0060 or 0.30 M.E.
2. Replaceable Ca, ignited sample =	0.0011 or 0.05 M.E.
3. Replaceable Ca, after treatment with alkali =	0.0372 or 1.86 M.E.

The data in Table VIII show that the base-exchange complex in finely divided orthoclase is rendered inactive by ignition just as are synthetic and soil zeolites. This points to their similarity.

When an ignited and "killed" base-exchange complex, such as a zeolite as it occurs in finely divided orthoclase, is digested with a strong potassium-hydroxide solution, considerable amounts of potassium aluminate and potassium silicate are formed.* If calcium chloride is present considerable amounts of calcium hydroxide and calcium carbonate will be precipitated within the mass. The former can be removed with some difficulty by leaching, but the calcium carbonate cannot be so removed. In order to neutralize the alkali present and to eliminate the carbonate, in these experiments, the whole system was neutralized to about pH 7.0 using hydrochloric acid. In order to detect the end of the reaction, phenolphthalein was used until its endpoint had been passed, then brom thymol blue was added, and the addition of hydrochloric acid continued until the indicator began to lighten in color. Other indicators can well be used and they work well in the presence of colorless or slightly colored magmas which furnish a white background.

By bringing the system to neutrality in the presence of considerable amounts of calcium chloride, the calcium carbonate originally present was converted into the bicarbonate and could be removed by washing. The potassium aluminate and silicate present formed a zeolite, and in the presence of calcium chloride, remained principally as calcium and potassium zeolite. Washing with a calcium-chloride solution then converted all the zeolite into calcium zeolite. In this way very little loss occurred as hydrogen zeolite, or as potassium zeolite at high pH values, and in addition, all the carbonate was removed.

*Since preparing this manuscript it has come to our attention in *Chemical Abstracts*, Vol. 22, p. 2803, that A. Rosenheim has obtained British patent 279,028 for the treatment of various rocks by acid and alkalies, with and without pressure, to make them base-exchange-active or to increase their base exchange capacity.

The very high base-exchange capacity obtained by the alkali treatment, six times as great as the original, must be explained by the formation of new zeolitic material. This was here accomplished by the production of potassium aluminate and potassium silicate, and their interaction to form zeolite.

EXPERIMENT WITH ACID-TREATED ORTHOCLASE

One hundred grams of orthoclase with a low power of base replacement were digested for several hours with a mixture of concentrated nitric acid and hydrochloric acid. The mixture was then diluted, filtered, and washed. The residue was percolated with 1 liter of neutral tenth-normal calcium chloride, washed, and the fixed calcium replaced by sodium chloride and determined (No. 2). The residue was digested 16 hours with 20-percent potassium hydroxide in the presence of an excess of potassium chloride, neutralized, and filtered. It was then percolated with 1 liter of a tenth-normal solution of calcium chloride, washed, and the fixed calcium replaced by normal sodium chloride (No. 4).

In order to determine if the materials that were dissolved by the acid mixture possessed the property of base exchange, the percolate from the acid digestion was neutralized and the precipitate filtered, and washed. The precipitate was percolated with tenth-normal calcium chloride and the amount of calcium that was fixed was determined (No. 3).

TABLE IX.—BASE EXCHANGE AND BUILD-UP IN ACID-TREATED ORTHOCLASE

100 grams orthoclase	Grams Ca
1. Replaceable Ca, original sample =	0.0060 or 0.30 M.E.
2. Replaceable Ca, acid-treated sample =	0.0024 or 0.12 M.E.
3. Replaceable Ca, acid-soluble material =	0.0004 or 0.02 M.E.
4. Replaceable Ca, after treatment with alkali =	0.0172 or 0.86 M.E.

The data in Table IX show that by digesting a zeolite with acid, filtering, and washing, the base-exchange capacity of the residue is reduced. This may have been accomplished in two ways, first, the acid may have dissolved away some of the base-exchanging material, and second, the acid treatment may have produced hydrogen zeolite out of the material previously present. It is the belief of the authors that most of this hydrogen zeolite was broken down, and that a complete build-up did not occur when the material was treated with neutral solutions for the measurement of base-exchange capacity. Either one or both of these processes could account for the low base-exchange capacity of the acid-digested material.

The acid filtrate on neutralization gave a heavy precipitate which after washing and treatment was found to have practically no base exchange.

The small base exchange found might have been caused by absorption on silica or non-zeolitic material. The reason why no appreciable amount of zeolitic material was formed can be explained in two ways. First the acid may not have dissolved any zeolite or zeolitic components so that on neutralization no zeolite could be formed. Secondly, if zeolitic material had been dissolved, neutralization of this material, going from an acid to a neutral solution, resulted in the production of zeolitic material having a low, base-exchange capacity.

Zeolites produced by the author in acid reactions have been found to have only 0 to 10 percent as great a base-exchange capacity, gram for gram, as synthetic zeolites produced in alkaline reactions.

Treatment of the acid residue with alkali, and subsequent digestion resulted in augmented base-exchange capacity, just as the trials reported in Table VIII. Evidently, new zeolitic material had been made. It seems probable that in nature, zeolitic material might be produced in the same way. Some feldspars with water, will give a highly alkaline reaction up to pH 8.5 or 9.0. On drying and digesting, as might occur in our western acid regions, the alkalinity would increase and considerable amounts of potassium aluminate and silicate would be formed. These would react to form a zeolite. We cannot ignore the possibility of such reactions taking place, and the high, base-exchange capacity of our western arid soils could be partially explained on this hypothesis.

EQUILIBRIUM BETWEEN SYNTHETIC ZEOLITES AND SOLUTIONS OF ORTHOCLASE

From all the work that has been described before, it is evident that a certain part of orthoclase acts like a zeolite, that is, it possesses the property of base exchange and has some properties of both solids and liquids.

The property of base exchange is largely a function of the size of the particles. Even in the finely ground material that was used, only a small percentage of the orthoclase possessed this property. Under soil conditions, this percentage is probably even less. At any rate, whenever solid orthoclase occurs there is probably a certain percentage of the compound acting as a zeolite, and if such is the case, this zeolite will tend to maintain equilibrium with the solution in which the solid orthoclase occurs.

In the soil there is a continuous break-down and build-up of zeolites, depending upon the reaction, the salt content of the soil solution, leaching, and the feeding of plants. These zeolites may be derived from other sources than orthoclase. If calcium zeolite, for example, occurs in a soil that also contains orthoclase, the calcium zeolite will be in

equilibrium with the orthoclase. This will entail an exchange of the potassium in the orthoclase solution for the calcium in the zeolite. The tendency to reach equilibrium is inherent in all compounds, and this fact may be of great importance in the nutrition of plants, and the availability of potassium in orthoclase. Such an equilibrium was studied in the following experiments.

Two hundred grams of pulverized orthoclase were percolated with water until the percolate amounted to 500 cc.

One-half gram of synthetic calcium zeolite was then added to the percolate, and it was then filtered through an alundum filter. If any potassium had replaced calcium in the zeolite it should have been held by the filter in the residue, and the calcium that it had replaced should have appeared in solution in the filtrate.

After the filtration, the residue was treated with twentieth-normal hydrochloric acid and the amount of fixed potassium determined (No. 1). The amount of potassium remaining in the filtrate was also determined (No. 2).

TABLE X.—REPLACEMENT OF POTASSIUM BY CALCIUM IN DILUTE EXTRACT OF ORTHOCLASE.

200 grams orthoclase	
1. Potassium fixed by calcium zeolite =	0.0059 or 0.15 M.E.
2. Potassium left in solution =	0.0095 or 0.24 M.E.

It will be seen that 38 percent of the potassium which had gone into solution from the orthoclase was fixed by the calcium zeolite. This represents approximate equilibrium at that concentration.

In the next experiment the same procedure was followed but the concentration of potassium was increased.

A sample of 200 grams of pulverized orthoclase was percolated through a parchment filter with small portions of distilled water until the percolate amounted to 1 liter. The percolate was then evaporated to a volume of 100 cc.

One gram of pure synthetic calcium zeolite was put into an alundum crucible, and the condensed percolate from the orthoclase, was filtered through the crucible containing the zeolite. The zeolite residue was washed once with about 10 cc. of water and the filtrate was evaporated to dryness and analyzed for potassium. The zeolite residue was treated with 100 cc. of twentieth-normal hydrochloric acid, in order to replace any potassium that had been fixed by the zeolite. The hydrochloric acid solution was also analyzed for potassium.

In Table XI is shown the amount of potassium that had been removed from solution and fixed by the zeolite during the filtration, and the amount that remained in solution.

TABLE XI.—REPLACEMENT OF CALCIUM BY POTASSIUM IN CONDENSED EXTRACTS OF ORTHOCLASE.

200 grams orthoclase	Grams K
Total K in 1000 cc. percolate =	0.0276 or 0.71 M.E.
K fixed by calcium zeolite =	0.0188 or 0.48 M.E.
K remaining in solution =	0.0088 or 0.23 M.E.

It will be seen that 68 percent of the potassium was removed from the concentrated solution by the calcium zeolite. This represents approximate equilibrium at the above-noted concentrations. The concentration of the 500 cc. of percolate described under Table VI was 31 parts per million of potassium, while the concentration of the condensed percolate of Table XI was 276 p.p.m. The difference in concentration of the two solutions should have brought about a different equilibrium with the orthoclase solution, and this equilibrium may be roughly represented by the ratio of 31 to 68.

The orthoclase residue described under Table XI, that gave a total base replacement of 0.0276 gram or 0.71 M. E. was percolated with 500 cc. normal potassium chloride that has been made alkaline with sodium hydroxide, then percolated with 500 cc. of tenth-normal calcium chloride and washed free from calcium. The calcium was then replaced by a potassium chloride solution and determined in the percolate.

TABLE XII.—BUILD-UP OF ORTHOCLASE BY POTASSIUM AND CALCIUM CHLORIDE.

	Grams K
Removed by 1000 cc. water =	0.0276 or 0.71 M.E.
Build-up after treatment with alkaline KCl and CaCl ₂ =	0.0394 or 1.01 M.E.

EQUILIBRIUM BETWEEN SYNTHETIC ZEOLITE AND ORTHOCLASE WITH THE SOLID PHASES PRESENT

Two samples of pulverized orthoclase of 200 grams each, were weighed out and one sample percolated with water through a parchment filter until the percolate amounted to 600 cc. To the other 200-gram sample, 2 grams of pure synthetic calcium zeolite were added and mixed. This sample was percolated with water also, until the percolate amounted to 600 cc. Both percolates were then analyzed and the concentration of potassium determined.

TABLE XIII.—EQUILIBRIUM BETWEEN CALCIUM ZEOLITE AND ORTHOCLASE 200 GRAMS ORTHOCLASE

	p.p.m. K
1. Percolate from orthoclase alone =	23.7
2. Percolate from orthoclase mixed with CaZ =	12.8

A control percolate from orthoclase alone contained only a trace of calcium, which indicated that no calcium zeolite, or soluble calcium salts,

occurred in the original orthoclase. The addition of calcium zeolite to the orthoclase brought a replaceable base, calcium, into the system, which came into equilibrium with the potassium as it was dissolved from the orthoclase. It will be noted that under these conditions 48 percent of the soluble potassium was fixed by the calcium zeolite.

If, in the last few experiments, the calcium in the synthetic zeolite had been replaced by potassium alone, and if no break-down or build-up had occurred, the amount of calcium in the percolate should have balanced the amount of potassium that was fixed in the zeolite. This is shown in the following experiment.

Two hundred grams of pulverized orthoclase were percolated with water until the percolate amounted to 100 cc. The percolate was filtered through an alundum crucible containing 1 gram of synthetic calcium zeolite and the filtrate titrated for calcium. The calcium-zeolite residue was percolated with twentieth-normal hydrochloric acid and the potassium determined in the percolate.

TABLE XIV.—REPLACEMENT OF CALCIUM IN CALCIUM ZEOLITE, BY POTASSIUM FROM SOLUTION OF ORTHOCLASE.

200 grams orthoclase	Gram
K that was fixed by Ca Z =	0.0108
K equivalent of Ca in percolate =	0.0103

It was not possible always to obtain results as good as these, as some hydrogen zeolite is often present, and some break-down or build-up is likely to take place. It is evident, however, from all experiments, that calcium in calcium zeolite may be readily replaced by the potassium that is dissolved from orthoclase and that the potassium liberates an equivalent amount of calcium.

It has been shown by one of the authors that an equilibrium exists between the amount of replaceable potassium in the soil and the amount of potassium in the soil solution. Increasing the concentration of potassium in the soil solution shifts this equilibrium, some of the dissolved potassium entering the zeolite, and causing an equivalent outgo of other cations, mainly calcium. This indicates that one of the functions of calcium zeolite is to serve as an elastic reservoir for potassium, doling out potassium slowly to the soil solution as fast as it is taken up by plants or leached away, and removing potassium from solution whenever an excess above equilibrium occurs.

THEORETICAL DISCUSSION

Oden (10) pictures the exchangeable cations held to a particle by electric charges. The cations are not held firmly, some are constantly breaking away and others taking their places. Thus the outer layer of what conforms to Hissink's (3) double layer is in dynamic equilibrium

with the electrical forces in the particle and also with the relatively few ions in the solution. In the classical examples of absorption, increasing the concentration of cations in the solution increases the number of cations held to the particle by the relatively weak electrical bonds, or as some term them, valences. Since there is a definite limit to the electrical forces holding the cations near its surface, there must also be a definite limit to the number of cations so held, or as it is usually termed, there is an absorption maximum for all systems, and when this is reached, increasing the number of cations in the solution cannot increase the number held by the particle in the outer layer.

Hissink (4) states that we look upon absorption as a chemical reaction upon a surface. On subdivision the volume of a sphere decreases as the cube of the radius, while the surface decreases as the square of the radius. With increasing subdivision of a particle, therefore, the ratio of surface to volume increases rapidly until, with particles approaching the size of molecules, almost all the material can be considered as being on the surface. Surface reactions then approach true chemical reactions, following the mass law with which we are all familiar.

Synthetic zeolites apparently approach this condition because all their base can be exchanged for another base, and hence the base originally present must have been on the surface and free to react. This also, explains why, synthetic zeolites take on the properties of solutions as regards the rate and extent of chemical action. The reactions of synthetic zeolites can be considered as taking place on the surface and fit in well with Oden's picture of this process. Thus a zeolite saturated with potassium will maintain a greater number of potassium ions in the adjacent solution than a particle only partially saturated with potassium. The relation between cations on the surface and cations in solution is expressed by the familiar absorption isotherm $X = KC^{1/n}$.

If some other cation is placed into the solution, some of the ions will very soon come within the zone of electrical force. Under the conditions of dynamic equilibrium this new cation will then be attracted and held to the particle, leaving one bond less with which to hold a potassium ion. That particular potassium ion, no longer held by a strong electrical bond, or valance, will then leave the outer layer,—by diffusion and bombardment, and appear in solution. This is the process of base exchange and, exchange of bases necessarily occurs in equivalent quantities. The foregoing views on surface equilibria, according to some of our foremost physical and colloid chemists, hold for strictly chemical reactions as well as the so-called physical adsorption.

The idea of ionic hydration gives us other far-reaching possibilities. Thus Wiegner (11) points out that the strongly hydrated ions such as lithium and sodium cannot get close to the zeolite particle because of the thickness of the water shell. Potassium, for instance, hydrated to a lesser degree, having a thinner water shell, can get closer to the zeolite nucleus and is consequently more firmly held. Among the bivalent ions, barium is hydrated less than calcium, hence it is held more firmly than calcium. Since the bivalent ions are hydrated less than the monovalent ions, and because they are held by two bonds instead of one, fewer of them leave the zeolite nucleus in unit time under the conditions of dynamic equilibrium, than do the monovalent ions. Furthermore, the highly hydrated ions have a large effective radius and consequent slow velocity. This means that, if equal numbers of barium and sodium ions are placed in the neighborhood of a zeolite particle, in a very short time, under the conditions of dynamic equilibrium, far more barium ions will be present in the outer layer than sodium ions.

If we arrange the ions in the order of their hydration and absolute velocity, we also have them in the order of their energy of replacement, the most highly hydrated having the least power of replacement.

Wiegner and Jenny (12) have recently obtained new evidence in favor of their theory. In water solutions the intake of ions is proportional to the hydrodynamic volume, (caesium stronger than rubidium, rubidium stronger than potassium, potassium stronger than sodium, etc.). In alcohol solutions the water of hydration is largely removed and the hydrodynamic volumes of these ions approach their ionic volumes as a limit. Since their ionic volumes are almost proportional to their molecular weights, the intake of lithium may exceed that of sodium, sodium may have a greater energy of replacement than potassium, etc.

From the standpoint of physical absorption and the hypothesis above elaborated, a trivalent ion should be held by a zeolite nucleus even more firmly than bivalent ions. Earlier work by the authors (7) has shown that the trivalent ions iron and aluminum cannot replace. This evidently means that at the point where the electrical forces or valences occur, only two such valences are found. The distance to the next such point is probably too great to allow a cation, such as aluminum, to be held by bonds from both. Or again, the angles between the two sources of origin may be of such a nature that the bonds would be "sprung" in trying to reach a common cation. There are analogous cases in organic chemistry.

In the Oden picture, a portion of the replaceable base is present in the surrounding liquid. The amount present depends on the number of

cations of this kind present on the surface of the particle, the nature of the cation, and the nature of the liquid. Temperature effects, although rather large, are not considered here. A potassium zeolite in water will then maintain a rather definite concentration of potassium ions in the solution surrounding the particle. With a greater ratio of water to zeolite, that is, more water per gram of zeolite, a new equilibrium between the number of potassium ions in solution and on the particle will result. The zeolite will tend to maintain a high concentration of potassium ions in solution, and, with the addition of water, more hydrolysis will take place. At low dilutions, Magistad (8) has found that doubling the amount of water will not reduce the concentration of potassium in the solution 50 percent, but will reduce it only about 30 percent.

Base-exchange capacity depends on two factors at least, chemical nature of material, and state of subdivision. The Oden picture takes into consideration the state of subdivision, but not the chemical composition of the material used. For maximum exchange capacity a bond between the mono- or di-valent base and trivalent element seems necessary. Most active zeolites contain aluminum and substitution of other trivalent metals for aluminum in the nucleus usually results in a very low, base-exchange capacity (9). This lowered, base-exchange capacity is only a few percent of the original, and agrees well with the amount we would have on finely divided silica or other material of equal subdivision.

Taking any specific material, the base-exchange capacity varies with the amount of surface present, or more correctly, with the amount of base present on the surface. Thus finely divided feldspar, on account of its surface, should have a small but significant base-exchange capacity, and act much like a potassium zeolite. With increasing subdivision this exchange capacity should increase. In this respect finely divided feldspar would act like a silica gel. On account of the possibility of direct linkages between base and aluminum in feldspar, it would seem that its base-exchange capacity should be augmented beyond that due to surface alone. It seems possible that, if feldspar were divided as finely as synthetic zeolites are, it would have as great a base-exchange capacity, gram for gram. In experiments reported in the forepart of this paper, phenomena of build-up and break-down occur, which are similar to those occurring in synthetic zeolites. This makes it almost certain that the direct aluminum-to-base linkage occurs in the case of feldspar material. As a result of the numerous tests imposed upon the feldspar material, the authors arrive at the conclusion that the feldspar-base-exchange complex is very similar to that in synthetic zeolites.

SUMMARY

1. The solubility in water of the potassium in orthoclase varies with the origin of the sample, fineness of subdivision, and the ratio of solid to liquid. Investigators have found the solubility to vary from 0 to about 300 parts per million of potassium.
2. A small percentage of potassium in orthoclase hydrolyzes in water forming potassium hydroxide, most of which, in turn, reacts with alumina to form potassium aluminate.
3. All samples of orthoclase examined showed properties of base exchange.
4. Treatment with alkaline salt solutions increased, while acid solutions decreased, the base-exchange capacity of finely ground orthoclase.
5. The base-exchange properties of orthoclase may be destroyed by ignition.
6. Digestion of ignited orthoclase with alkaline solutions, sometimes caused a build-up of the base-exchange capacity beyond that of the non-ignited.
7. When solid orthoclase occurs in the soil in the presence of calcium, magnesium, or sodium zeolites, an equilibrium will exist between the potassium in solution and the zeolites. The plant very probably feeds largely upon hydrolyzed, zeolitic potassium. The zeolites of calcium, magnesium, and sodium may act as stabilizers in that they fix much of the soluble potassium during periods of little plant growth, and slowly liberate this potassium as rapidly as it is absorbed by plants.
8. A theoretical discussion of base exchange is appended.

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