

# POTASSIUM-BEARING MINERALS AS A SOURCE OF POTASSIUM FOR PLANT GROWTH

ERNEST DE TURK

*University of Illinois*

Received for publication October 2, 1919

## I. INTRODUCTION

The necessity of using potassium fertilizers in general agricultural practice is not so vital as the public has been led to believe. The fact that applications of potassium salts have caused increases in crop yields at many of the experiment stations of the United States, together with the propaganda work of the German Kali Syndicate, has led to the popular belief that potassium fertilization is essential for the most profitable crop production on most of our common agricultural soils. As a matter of fact, the majority of soils in the United States contain from 20,000 to more than 60,000 pounds (24) of potassium per acre— $6\frac{2}{3}$  inches (2,000,000 lbs.). While most of this is held in the relatively insoluble form of complex silicates, crop yields as a rule are not limited by deficiencies of available potassium. Furthermore, it is not probable that potassium would become a limiting element under soil treatments that would otherwise produce maximum yields, because those same treatments, such as returning organic manures, improving the physical condition of the soil, and the addition of the usual limiting elements, nitrogen and phosphorus, will tend toward the maintenance of an increasing amount of readily available potassium by the return of this element in residues and manure, by bringing about increased solution of mineral potassium and by increasing the root systems and hence the feeding power of the crops grown. The earth's crust, to a depth of ten miles, has been estimated to contain an average of 2.32 per cent of potassium (66). More recent calculations place the estimate at 2.46 per cent (33, p. 13). This indicates that the problem of potassium for agriculture is ultimately one of liberation rather than of supply for normal agricultural soils and the common farm crops.

Experiments at the Pennsylvania (33, p. 423, 428-431; 36), Ohio (33, p. 442), Illinois (33, p. 466; 34, 35) and other experiment stations indicate that potassium salts are applied, either alone or with other fertilizers, at a loss as a rule, and at best at a very small profit in a few instances.

While the above statements are true for the majority of our farm lands, there are quite large areas in Illinois and other states which are markedly deficient in potassium. These consist mainly of muck and deep peat soils, and light

sandy soils. They contain from practically no potassium to 4000 pounds of potassium per acre—6 $\frac{2}{3}$  inches. In the case of the sandy soils some are actually deficient in total potassium, while others, which respond equally well to potassium fertilization, contain considerable amounts of the element, but the most of it is contained in the coarser particles. Because of the relatively small surface of the sand particles, their potassium can not become available to plants to any appreciable extent. A sample of dune sand, representative of considerable areas in Illinois, was analyzed by the writer. Of the 20,600 pounds of potassium per 2,000,000 pounds which it contained, 94.93 per cent was contained in the combined sands and 5.10 per cent in the silt and clay combined.

On these peaty and sandy soils the use of potassium salts has proved quite profitable, and is in fact absolutely necessary to successful crop production on much of the peat soil. The prohibitive price of potassium fertilizers and their entire withdrawal from the market during the last four or five years has interfered seriously with the profitable cropping of these potassium-poor soils. Soluble potassium salts from any of the several American sources are too high-priced for agricultural use. Potassium-bearing minerals are very abundant in the United States, and are already being produced in commercial quantities in several states for other than agricultural purposes.

Potassium feldspars, orthoclase and microcline ( $\text{KAlSi}_3\text{O}_8$ ) are extremely abundant throughout the United States. Deposits have been extensively developed, however, only in California and some of the eastern states, particularly Maine, Connecticut, Pennsylvania, New York and Maryland (15, 39). The average potassium content is 7 to 11 per cent and the average price per ton in 1914 was \$8.31; in 1915, \$8.33 and in 1916, \$9.30 (15).

The Leucite Hills in Sweetwater County, Wyoming, are the principal source of leucite ( $\text{KAlSi}_2\text{O}_6$ ) in the United States. The area has been carefully studied and mapped by Schultz and Cross (57) who estimate the minimum amount of commercially available potassium at 164,000,000 tons. The scarcity of leucite among igneous rocks is due to the fact that it is formed from the molten magma only when there is a deficiency of silica. Whenever sufficient silica is present orthoclase, which contains 50 per cent more molecules of  $\text{SiO}_2$  than leucite, is formed (57, p. 13).

Alunite is a hydrated basic sulfate of potassium and aluminum ( $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$ ). . . . It is usually contaminated with silica and other impurities and often has a part of its potash replaced by soda. It is widely disseminated through porphyritic volcanic rocks as an alteration product of feldspars, but it usually occurs in such small quantity or is contaminated with so much gangue material that it has no commercial value (26, p. 429).

High-grade alunite is limited in its distribution mainly to certain sections of Utah, Nevada and Colorado. The deposits are easily worked, being near the surface, and according to estimates by Loughlin (45), contain enough recoverable potassium to supply a large part of the American demand. The

ease with which the potassium is completely extracted from alunite as the sulfate (ignition to 750°C. followed by leaching with water) will probably lead to its use almost exclusively for the production of commercial potassium sulfate.

Muscovite ( $\text{KH}_2\text{Al}_3\text{Si}_3\text{O}_{12}$ ) is quite abundant in many parts of the United States and is produced commercially, principally as sheet mica, in twelve states. North Carolina produced in 1916, 63 per cent of the total output of the country; New Hampshire, 14 per cent and South Dakota 13 per cent. Scrap mica, being the clippings from the sheet mica trimming plants, is used, ground, in a number of industries and could be obtained for agricultural use should it prove profitable. The price of scrap mica up to 1913, for the 3000 to 4000 tons produced annually, was \$11 to \$13 a ton, and in 1916, \$16 a ton (55).

Lepidolite is a complex micaceous silicate, in which part of the potassium is replaced by lithium. It is usually a mixture of the pure mineral and mica, and contains 8 to 9 per cent of potassium. It is produced in California, Maine and the Black Hills of South Dakota. It is used mainly as a source of lithium for the preparation of lithium salts, and probably would not be commercially available in large amounts for agricultural purposes. The present cost is \$15 to \$20 a ton (56).

The great drawback to the use of potassium minerals as fertilizers is their low solubility, and hence, comparative unavailability to plants. There have been many attempts to extract soluble potassium salts from minerals by various treatments, and also to subject the minerals to processes which would render the potassium readily available to plants, so that the treated minerals could be used directly upon the soil, thus avoiding the expensive processes of extraction and evaporation. The extent of these efforts is indicated by the fact that the United States Patent Office granted 128 patents for processes of treating silicate rocks for the extraction of potassium between 1904 and 1917 (26). It would seem that the difficulty of the low availability to plants of mineral potassium might be greatly lessened on peat soil, where the decomposition of the large amount of organic matter present, even though slow, should hasten the decomposition of the minerals.

The object of the experiments to be reported in this paper was (a) to determine to what extent the potassium in certain minerals will become available when mixed with peat soil, using both the growth of a crop and chemical analysis as a measure of the amount of soluble potassium, and (b) to determine the effect of certain more active organic materials and soluble salts upon the solubility of the potassium in those minerals.

## II. REVIEW OF PREVIOUS INVESTIGATIONS

A complete review of all the work which has been done concerning the rendering available of soil potassium would obviously be outside the scope of this work. The idea of using powdered minerals, or "stone-meal" as a source of potassium is not new.

In 1848 Magnus (46) grew a barley crop to maturity, and obtained well matured grain in an artificial soil in which powdered feldspar was the sole source of potassium. Since then numerous experiments have been carried out in which the results recorded are more or less contradictory in regard to the potassium absorbed by the plants. The variations are no doubt due to the conditions of the experiments and in a still greater degree to the kinds of minerals, their source and stage of weathering.

Missoux in 1853 (48) noted the beneficial effect upon plant growth of waste rock dust from granite quarries.

H. Hoffman, 1861-1863 (32) conducted wheat culture tests for two years on plats 9 by 50 feet, using ground nephelin-dolerite containing 4.98 per cent of potassium and considerable amounts of calcium, magnesium and phosphorus. The crops on the fertilized plats had a much better appearance during June of each season, but the harvest showed larger yields of grain from the unfertilized plats.

During the next twenty years little was done with silicate minerals as fertilizers, though a great deal of work was reported dealing with their chemical decomposition and the nature of their weathering products.

In 1887 Aitken (1,1a) in Scotland grew peas and turnips on  $\frac{1}{10}$ -acre field plat treated with potassium sulfate and 120-mesh feldspar in comparison. The following yields were obtained from the treatments indicated:

TREATMENT	YIELD OF PEAS	YIELD OF TURNIPS
	<i>pounds</i>	<i>pounds</i>
No potassium.....	96	476
K <sub>2</sub> SO <sub>4</sub> , 3 pounds.....	114	482
Feldspar, 12 pounds.....	102	496

While the feldspar here produced results for peas almost equal to the soluble potassium salt, and a greater yield for turnips, the small percentage increases of both over the yields of the untreated checks, indicate that the soil was not particularly deficient in potassium. Furthermore, the work at the Rothamsted Station indicates that turnips do not respond readily to potassium fertilization. The average turnip yields on the Agdell field were increased by over 13,000 pounds by the use of phosphorus, while a further addition of mineral fertilizers consisting of sodium, potassium and magnesium salts produced no further increase (33, p. 346). On the Barn field, phosphorus and potassium produced no greater increases than phosphorus alone (33, p. 399).

Nilson (50) grew oats on a peat soil in Sweden, comparing feldspar with potassium sulfate, applying 2.5 to 4 times as much potassium in the feldspar as in the soluble salt. Phosphorus and nitrogen were supplied, the latter as crude Chile salt-peter. The yields were as follows, from plats of 100 plants each:

TREATMENT	YIELD OF OATS
	<i>gm.</i>
Nothing.....	17.3
P + K <sub>2</sub> SO <sub>4</sub> .....	394.1
P + Feldspar.....	328.0
P + N.....	439.5
P + N + K <sub>2</sub> SO <sub>4</sub> .....	603.5
P + N + Feldspar.....	463.7

These results indicate large increases where feldspar was used and still larger for K<sub>2</sub>SO<sub>4</sub>, but the experiment does not prove definitely that the increase is caused by the potassium in the mineral. The large yield from phosphorus and nitrogen would indicate either that the soil was not deficient in available potassium, or that potassium was being added in the fertilizer, probably as an impurity in the Chile saltpeter. The high yields from all the plats receiving phosphorus, together with the absence of a plat receiving phosphorus alone, suggests that phosphorus may be the limiting element in that soil and for that crop.

In 1889 Feilitzen (20, 21) grew crops on peat soils, and peat mixed with sand in sunken zinc cylinders, comparing feldspar with kainit as a source of potassium. With oats, equal yields were obtained with feldspar and kainit, but in later experiments, with clover, potatoes and peas, the feldspar jars produced no greater yields than where no feldspar was used. These results as a whole are decidedly unfavorable to the feldspar.

In the same year Ballentine (3) at the Maine Experiment Station reported results of pot experiments with feldspar, in which oats was grown in pure quartz sand. The relative yields from KCl, feldspar and no potassium were 100, 79 and 0, respectively. The author's conclusion was that oats could obtain sufficient potassium from the feldspar used to produce a heavy crop of grain, though the feldspar was inferior to soluble potassium salts.

Headden (29) grew oats to maturity in pure quartz sand and feldspar mixed, the plant-food elements other than potassium being supplied in available form. The feldspar was crushed to 1 mm. and included all the fine material. The crop removed 1.20 gm. K per jar in addition to that contained in the seeds. No comparison was made with other forms of potassium.

The earlier work (1901-1903) of Prianischnikov (52), in which crops of tobacco, buckwheat, flax, peas and millet were grown in acid-washed sand, indicated no benefit from orthoclase and but small benefit from mica. The use of ammonium salts as a source of nitrogen produced much smaller yields than sodium nitrate. The ammonium salts either "exerted no solvent action upon the potassium, or any benefit from such solution was overbalanced by the deleterious effect of acidity produced by the nitrification of the ammonium salts." Somewhat later the same investigator (53) carried out very carefully a series of well-planned experiments upon the sand and peat soils of northern

Russia. The object of the first of these was to determine whether plants can obtain potassium only from secondary minerals in the soil, roughly classed as zeolites, or also from the unweathered primary minerals. Nephelin rock, characterized by easy weathering and a tendency to form zeolites, and containing some zeolites was compared with muscovite and orthoclase in acid-washed sand. Hellriegel's nutrient solution, minus potassium, was supplied to all the jars. The results are reproduced in full:

*Yields*

	KCl	NEPHELIN	MUSCOVITE	ORTHOCLASE	NO K
	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
Mustard.....	13.95	12.68	11.20	5.88	2.77
Buckwheat.....	10.10	14.30	10.90	2.80	4.40
Millet.....	6.90	9.70	7.60	4.40	4.70

*Percentage utilization of the potassium supplied in the mineral*

	NEPHELIN	MUSCOVITE
	<i>per cent</i>	<i>per cent</i>
Mustard.....	25	22
Buckwheat.....	38	30
Millet.....	23	17

Orthoclase here seems to be practically worthless while both nephelin and muscovite are approximately equal to soluble potassium in crop-producing power. The amount of potassium which these last two minerals give up to the crop is exceptionally large. A second experiment involved the use of ten different minerals with five crops. Samples of the minerals were also extracted by shaking with 10 per cent solutions of ammonium chloride and of barium chloride, both with and without boiling. The relative amounts of potassium obtained by these extractions were in harmony with the results of the plant culture experiments. The minerals used were finally classified as a result of these experiments into the following three groups, arranged in order of decreasing availability of the potassium:

1. Nephelin.  
Micas, especially biotite.
2. Phillipsite (a zeolite).  
Muscovite.
3. Eläolith,  
Leucite,  
Apophyllite,  
Sanidin,  
Orthoclase,  
Microcline.

Wotschal (69) reported mica superior to the feldspars.

The investigations of Cushman (15) are not conclusive, because the soils used in greenhouse work as well as in cooperative field tests by farmers, were probably not deficient in potassium, most of them having been heavily "potashed" for tobacco the previous years. In these tests, however, the yields of tobacco were the same whether potassium was supplied in feldspar or in potassium carbonate.

Hartwell and Pember (28) secured increases in yields of wheat and millet of 4 to 18 per cent for feldspar as compared with 130 to 248 per cent increases for potassium sulfate. The soil used had been cropped several years with liberal applications of the other plant-food elements, but no potassium. Fifteen pounds of soil were used in each jar.

Skinner and Jackson (58) increased crop yields by 10 to 20 per cent by applications of raw alunite. The same amounts (25 to 500 pounds  $K_2O$  per acre) of potassium supplied in ignited alunite produced increases of 35 to 43 per cent.

It is a well-known fact that the calcium and sodium feldspars are much more easily weathered than those of potassium. In the sodium-potassium feldspars, the rapidity of weathering should therefore increase with the proportion of sodium present. In 1913 Blanck (8) reported results of an investigation of the availability of the potassium of a series of feldspars decreasing progressively in potassium content, and increasing in sodium. The minerals were applied so that all jars received equal amounts of potassium, and, consequently, increasing amounts of sodium. Crop yields were increased progressively, in accordance with the hypothesis. This led the investigator to suspect that sodium was replacing potassium in its function in the plant. Analysis of the crops, however, proved that the increases in yields were due to potassium. Following is a summary of the results:

	K IN MINERAL	Na IN MINERAL	MINERAL PER JAR	RATIO Na:K IN JAR	YIELD OF OATS	UTILIZATION OF ELEMENT ADDED	
						K	Na
	<i>per cent</i>	<i>per cent</i>	<i>gm.</i>		<i>gm.</i>	<i>per cent</i>	<i>per cent</i>
No K.....					50.6		
Microcline.....	9.47	1.89	14.13	1:5	52.2	1.12	0.13
Orthoclase.....	5.72	2.04	23.40	1:3	53.1	2.23	
Oligoclase.....	0.58	5.47	230.30	10:1	58.7	3.50	
Labradorite.....	0.38	3.49	350.40	10:1	60.3	3.45	
Albite.....	0.11	6.19	620.00*	60:1	61.2	7.07	0.46
$K_2SO_4$ .....					94.5	70.81	

\* One-half as much K as in other applications.

A difficulty in the practical use of the low-potassium feldspars is the obvious impossibility of using the large applications necessary to secure the requisite amount of potassium.

Chirikov (12) found in culture experiments that nepheline, biotite and muscovite were good sources of potassium for plants, but not orthoclase. The ineffectiveness of ammonium salts was also shown.

Miller and Van Natta (47) carried out culture experiments in a mixture of river sand and silt loam in the proportion of 8 : 1. Amounts of feldspar were used ranging from 5700 to 23,000 pounds per acre, and compared to 400 pounds per acre of potassium chloride and sulfate. The cultures were grown in 3-gallon jars, and the yields obtained were 10.2 to 12.6 gm. of barley per jar with the feldspar, 11.7 gm. with KCl and 15.7 gm. with  $K_2SO_4$ . These results are quite favorable to the feldspar. Larger applications prevented germination of the seeds.

Brooks and Gaskill (9) report some results of individual seasons' crops in which feldspar compared favorably with kainit in long continued field plot experiments at the Massachusetts Experiment Station, but state that as an average of 21 years' continuous use of feldspar, no decided increases have been obtained. The soil on which these investigations were conducted is probably well supplied with total potassium.

In addition to plant culture experiments, many investigations have been carried out to study the effects of various chemical compounds upon the solubility of the potassium of silicate minerals, some of which will be discussed later.

### III. SOME CONSIDERATIONS OF THE NATURE AND SIGNIFICANCE OF THE SILICATE MINERALS

#### *Formation, composition and structure*

The silicate minerals are complex compounds, usually considered as salts of the polybasic silicic acids. The more common bases involved are sodium, potassium, calcium, magnesium, aluminum and iron. They are as a class highly insoluble in water. Considered from the standpoint of the molecular proportions of bases and silica, they range from strongly basic to strongly acidic compounds. The proportion of base to acid in the various crystallized minerals depends, of course, upon the proportions in the molten mass in which the crystallization took place.

Primary minerals are to be found quite abundantly in metamorphosed and sedimentary rocks as well as in igneous rocks. Here crystallization has occurred, not in a molten mass, but probably in most cases under the influence of superheated steam at high pressure. The researches of Friedel and Sarasin (25), Daubrée (17), Kuhlmann (41) and others show that many silicate and other minerals may be formed artificially by crystallization in the presence of steam and other gases under pressure. The crystallization occurs at a temperature far below the melting point of the minerals after they are once formed.



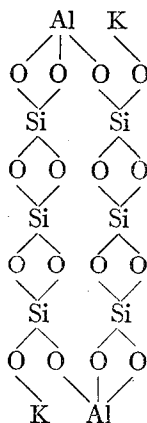
The close chemical relationship between carbon and silicon early led to the assumption that the silicates must be similar in structure to organic carbon compounds. The classical investigations of Lemberg (43, 43a), however, indicate quite clearly that no such analogy exists. It is a noteworthy fact that certain bases are usually associated in the silicate minerals, while certain others are seldom or never found together. Thus sodium-calcium feldspars are quite common, as are also potassium-magnesium silicates, while on the other hand calcium and potassium are seldom found together, and sodium-magnesium minerals are practically unknown. Lemberg found in studying the alterations of these minerals that there is a decided antipathy between certain bases, as a result of which it is extremely difficult to induce a combination of such bases as sodium and magnesium, for example. Potassium and sodium combine indifferently in the silicate molecule, but to such an extent that sodium-potassium silicates are of fairly common occurrence. These may be merely mixtures of complex sodium silicates and potassium silicates in many cases.

The determination of the structure of silicates is very difficult if not impossible, because they do not possess those properties by the use of which molecular weights are ascertained. The structure is therefore not definitely known in many cases. Cameron and Bell (10) suggest four viewpoints from which these minerals may be considered.

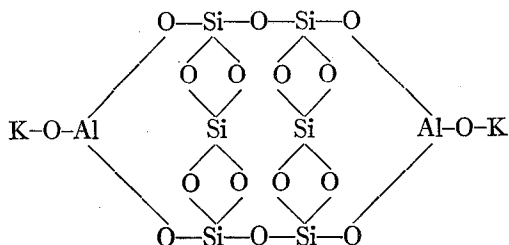
1. They may be considered as combinations of the oxides. Orthoclase, for instance would be  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ . This method of writing the formula, however, gives no clue to the structure of the molecule.

2. They may be molecular compounds, as the alums. But this will not hold for the solution phase; in the solution are found only the simple salts of the various bases.

3. One may consider them double salts of a complex acid, the Si atoms being united through oxygen. Thus orthoclase is a double potassium-aluminum salt of the acid,  $H_4Si_3O_8$ , or  $K_2Al_2(Si_3O_8)_2$ ,



4. Aluminum may be negative, orthoclase being the potassium salt of  $\text{H.AlSi}_3\text{O}_8$  or  $\text{K}_2\text{.(AlSi}_3\text{O}_8)_2$ ,



These last two views seem the most reasonable, and the last is preferable in view of the amphoteric nature of aluminum and the formation of the alkali hydroxide as the principal soluble hydrolysis product of the alkali aluminosilicates.

#### *Chemical properties*

*Reaction with water.* The solubility of the complex silicates in water is very low. Stoddart (60) states, for instance, that orthoclase is soluble in 37,000 parts of water, and in 4,000 parts of carbonated water. As early as 1848 W. B. and R. E. Rogers (54) studied the solubility of fifty-eight different minerals in water and in carbonated water. Among these were sodium, lithium and potassium feldspars, micas and leucite. In most cases the solubility was great enough to give good qualitative tests for the bases, and the solubility was greater, as a rule, in water containing  $\text{CO}_2$  than in pure water. Simple solution of these minerals in water has never been obtained. Being salts of a very weak acid and very strong bases, solution is always accompanied by hydrolytic decomposition. This reaction is usually arrested almost immediately by the gelatinous coating of colloidal silicic acid on the mineral particles, which prevents further action of the solvent. Clarke (13) found that water reacts immediately with rock powders, producing in most cases a reaction alkaline to phenolphthalein, and Cushman (14) states that equilibrium between the rock powder and water is reached in a very few minutes on shaking the two together. This is obviously not a true chemical equilibrium between solid and solvent, but merely the cessation of reaction due to the interference of the colloidal material on the particles. Daubrée in 1867 (18) overcame the interference of the colloidal material by revolving an iron cylinder containing water and pieces of feldspar and quartz. The sliding motion of the fragments kept fresh surfaces exposed so that the decomposing action of the water was progressive. The solution became alkaline and a fine mud (kaolin) was formed as well as considerable soluble and colloidal material and  $\text{FeCO}_3$ . In 8 days he obtained 12.6 gm. of soluble  $\text{K}_2\text{O}$  from 3000 gm. of feldspar in 5 liters of water. The soluble  $\text{K}_2\text{O}$  he reported present mainly as  $\text{K}_2\text{SiO}_3$ . More recently (1905) Cushman (14) obtained similar results by grinding together

powdered feldspar (also powdered glass) and water made up to a thick paste, in a heavy ball mill. By subsequent washing on a filter paper with water, much more sodium and potassium were dissolved out than where the mineral had been ground dry and shaken with water. He assumed that these bases were present as the simple silicates, since the solution obtained was of a glue-like character. In view of the work of Kahlenberg and Lincoln (38) it is not likely that the silicates of potassium or sodium were present to any marked extent as such, prior to evaporation. These investigators, by studying the freezing point and electrical conductivity of solutions of the simple alkali silicates, showed that the hydrolysis into the hydroxide and colloidal silicic acid is practically complete in concentrations up to 1 gram-molecule of the silicate per 48 liters of solution.

*Reaction with carbonic acid.* Silicate decomposition by carbonated water results in the formation, in the main, of the same final products as by reaction with pure water, except that the alkalies and alkaline earth metals appear as the carbonates or bicarbonates. Beginning with the early work of Rogers (54) the majority of investigations indicate a greater degree of solubility of the silicate minerals in water containing  $\text{CO}_2$  than in pure water. With carbonated water, as with pure water, the amount of direct contact of mineral with reagent is of great importance, as is shown by Bassalik's (4, 5) work. Bassalik studied the solvent action upon various minerals of bacterial activity. Pure cultures of many organisms were grown in suspensions of the minerals, after which the filtrates were analyzed. *Bacillus extorquens*, a  $\text{CO}_2$  producer, dissolved from 4 to 40 times as much orthoclase as any other  $\text{CO}_2$  producer studied, although some of the others, including yeast, produced much larger amounts of  $\text{CO}_2$ . This is accounted for by the fact that *B. extorquens* grows directly upon the mineral particles, enclosing the mineral and colony in a zooglear excrecence, thus affording more intimate contact of the  $\text{CO}_2$  and the mineral particles. Van Hise (66), in his comprehensive work upon metamorphism, ascribes by far the largest number of natural alterations of rocks to the action of  $\text{CO}_2$  and water combined.

*Reaction with salts.* This reaction might be expected to effect some solution of the potassium of potassium-containing silicates, through the replacement of the mineral potassium by the basic ion of the soluble salt. Lemberg's (43, 43a) careful researches show that reactions of this character take place most rapidly and go much nearer to completion under fusion conditions. When aqueous solutions and suspensions are used, increasing the temperature accelerates the reactions greatly. Exchange of bases was brought about to a considerable degree in most cases within one month at  $100^\circ\text{C}$ ., but at ordinary temperature the reactions were very incomplete. It may be noted that fusion of silicates with other compounds and also heating such mixtures to varying temperatures with superheated steam under pressure are the bases of many of the patented processes mentioned in another part of this paper. Lemberg also noted that the common bases have different replacing powers, potassium being strongest,

followed by magnesium, sodium and calcium in the order named. Thus it was found much easier to convert a sodium mineral into the corresponding-potassium mineral, than to bring about the reverse reaction. This replacing power holds for the soil mass as well as for the individual minerals, and the point is illustrated by drainage water analyses at Rothamsted (42) and elsewhere, where calcium is present in largest amounts and potassium in the smallest quantities.

All of these observations point to the great difficulty of liberating appreciable quantities of potassium from the primary minerals by means of the so-called exchange of bases, under soil conditions. The liberation in the soil of potassium for plant growth from the primary minerals must be left to the natural process of weathering (19, 31, 61) some of the most important forces of which are the solvent action of water, of  $\text{CO}_2$  and of other products of biological activity. Of the last-named, the nitrous acid formed in nitrification is important (4, 5).

*Secondary minerals and absorption.* When the primary minerals are attacked by various solvent agents the amount of mineral decomposed is greater than would be indicated by the potassium which may be extracted by water (4, 5). This is accounted for as follows. A part of the potassium which is liberated as the hydroxide or carbonate is at once absorbed by the kaolinite formed in the initial reaction (16). This absorption is partly physical, a result of the colloidal nature of the siliceous products of decomposition, but secondary chemical reactions also occur. Similar "absorption-reactions" occur when stable salts of the alkali metals, as the sulfate or chloride, are added to colloidal material. In such cases the metal is usually absorbed as the hydroxide, leaving a pronounced acidity in the solution. While this is the general rule, exceptions occur, depending upon the nature of the colloid and of the salt used (27, 44, 65, 68).

The abundance of colloidal substances and of kaolinite in the average soils makes possible their very great absorptive capacity for potassium. Way (67) was the first to observe the absorption of bases by clay and the practical agricultural application of this phenomenon. Many methods have been devised for determining the so-called "immediately available," "remotely available or reserve" and "unavailable" potassium of soils. These consist for the most part of extraction with water or other solvents such as certain organic and mineral acids of varying concentrations and solutions of various salts. While these methods are purely arbitrary, and for that reason can scarcely be said even to give approximately the availability of soil potassium to the various crops, they do enable one to distinguish roughly the proportions of absorbed potassium, of the potassium of secondary minerals and of that contained in primary minerals in the soil. They are therefore not without value. The work of Fraps and his associates (22, 23) and of Frear and Erb (24) is of interest from this point of view.

The results of chemical researches and of plant culture experiments lead to the conclusions: (a) that the weaker solvents extract the potassium which is contained in the secondary soil minerals and that which may be temporarily held by physical absorption, but only a very small fraction of the potassium of the native minerals; and (b) that while crops may draw upon the unweathered, primary minerals for a portion of their potassium in emergencies, they rely in the main upon the absorbed potassium and secondary minerals for their supply (6, 7, 22, 23, 24, 37, 40, 49, 51, 53, 62, 63).

#### IV. EXPERIMENTAL

##### *General plan of experiments*

The four experiments here reported were carried out for the purpose of obtaining information on the following questions:

1. Will applications of primary potassium-containing minerals to peat soil affect the yield of crops grown therein?
2. To what extent are crops enabled to obtain potassium from those minerals?
3. Is the availability of the mineral potassium for plants affected by the presence of decomposing active organic material, or of magnesium or sodium chloride?
4. What are the effects of decomposing organic material and of magnesium and sodium chlorides upon the amount of potassium which can be extracted by water from these minerals under soil conditions?
5. What effect does decomposing organic matter have upon the solubility of the mineral potassium in the absence of soil?
6. What is the explanation of the low availability of the potassium of dune sand?

##### *Description of materials used*

The soil used was a very loose peaty soil obtained from an area several hundred acres in extent near Manito, Illinois. It was quite free from sand and from roots or other residues of recently grown plants. It had been under cultivation for several years but had not been cropped more than once or twice within the last six or seven years. The last fertilizer treatment it had received was an application of KCl 14 years before the collection of soil for these experiments. The reaction was practically neutral, the lime-requirement as determined by the Hopkins method being 285 pounds  $\text{CaCO}_3$  per acre. It contained 0.411 per cent of total potassium, or 4110 pounds per acre (1 million pounds peat soil assumed as the weight of an acre—6 $\frac{2}{3}$  inches).

The minerals selected for study were orthoclase feldspar from San Diego County, California, microcline from Pennsylvania, leucite rock from the Leucite Hills, Wyoming, alunite from Utah, muscovite from North Carolina and lepidolite from the Black Hills of South Dakota. The impossibility of grind-

ing a large enough amount of muscovite sufficiently fine with the apparatus available necessitated its omission from the experiments. The ignited alunite was prepared by igniting to a bright red heat in a muffle furnace for two hours, until  $\text{SO}_2$  fumes were no longer given off. The minerals used contained the following amounts of total potassium (K).

	per cent		per cent
Orthoclase.....	11.00	Alunite.....	8.32
Microcline.....	11.23	Ignited alunite.....	13.72
Leucite.....	9.49	Lepidolite.....	8.99

The limestone used was high-calcium stone containing 0.21 per cent K and approximately 92 per cent  $\text{CaCO}_3$ .

The organic materials used were: (a) bright clean alfalfa hay, finely ground (legume), (b) clean prairie hay, consisting mainly of blades, finely ground (non-legume) and (c) fresh cow manure, without litter, carefully dried at low temperature and ground. For experiments II and III the manure was used fresh, without drying.

The chemicals were high-grade analyzed chemicals from the laboratory stock.

*Experiment I. Effect of potassium-containing minerals on yield and composition of buckwheat crop*

Six series of plant cultures were grown in 4-gallon glazed earthenware jars provided with drainage outlets. Each jar was filled with peat soil equivalent to 3039 gm. water-free soil. All received limestone, finely ground, at the rate of 1 ton per acre, or 12.5 gm. per jar, based upon the area of the jar. Series 100 was a check series and received no minerals. Series 200 to 600 received orthoclase, microcline, leucite, alunite and lepidolite, respectively, at the rate of 25 gm. per jar, or 2 tons per acre. The only exception to this is that jars 1a and 2a in each series received 125 gm., or 10 tons per acre. Additional treatments were applied to the jars of each of the six series as indicated in the following table:

*Table showing applications to crop culture jars in addition to minerals*

NUMBER OF JAR	SUBSTANCE ADDED	POUNDS PER ACRE	GRAMS PER JAR
1, 2	Nothing		
1a, 2a	Mineral alone, 10 tons	20,000	125.0
1b, 2b	Mineral alone, ignited	2,000	25.0*
3, 4	Alfalfa	6,000	37.5
5, 6	Prairie hay	6,000	37.5
7, 8	Cow manure	3,536	22.1†
9, 10	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	800	5.0
11, 12	$\text{NaCl}$	500	3.1
13, 14	$\text{KCl}$	200	1.25‡

\* Series 500 (alunite) only.

† 22.1 gm. air-dry manure equivalent to 125 gm. fresh manure, or 20,000 pounds per acre.

‡ Series 100 (check) only.

All of the 43 treatments were carried out in duplicate. The jars were planted to buckwheat April 22, 1918, and as soon as the plants were two to three inches high they were thinned to 11 plants per jar. The moisture content was maintained at approximately 160 per cent of the water-free weight of soil. The plants grew vigorously throughout the season, except in series 600, in which they did not thrive as well as in series 100, the next poorest. Numbers 601a and 602a, which received the heavy application of lepidolite were especially stunted, the leaves being small, yellow and curled. Little difference could be observed in the growth of the plants in series 200, 300, 400 and 500.

The crops were harvested on July 25 and preserved in cheesecloth bags until air-dry. They were then weighed, the crops from duplicate jars combined, finely ground, and preserved in tightly stoppered jars for analysis. Table 1 gives the yields from all the jars, the per cent of potassium in the crops, and the amount of potassium removed from each jar.

In experiments II and III the amount of water-soluble potassium which could be extracted from the peat soil by shaking with an excess of water was determined at two different times on aliquots of the same sample, kept under optimum moisture conditions. The water-soluble potassium of the organic materials was determined by the same method. These amounts were:

	<i>Part of total K which is soluble per cent</i>
For peat soil, initial, 37.7 mgm. K per 100 gm. water-free soil.....	9.17
For peat soil 80 days later, 33.9 mgm. K per 100 gm. water-free soil.....	8.25
For alfalfa, 15.4 mgm. K per gram of dry matter.....	96.25
For prairie hay, 8.4 mgm. K per gram of dry matter.....	97.68
For cow manure, 6.6 mgm. K per gram of dry matter.....	100.00

There are three sources of soluble potassium for the crop, which can thus be measured, that in the soil, that in the organic materials added (or KCl in 113 and 114), and that in the seeds planted. The total potassium added per jar in the seeds planted was 2 mgm., all of which is reckoned as available. By difference the potassium obtained by the crop from insoluble sources can be calculated. These amounts are recorded in the last column of table 1 (+) as well as any excess of soluble potassium in the soil which the crop did not take up (-).

#### *Discussion of results*

The relative increases in yield produced by applications of the minerals are quite large, as shown by the percentage calculations recorded in table 2. Lepidolite gives unsatisfactory returns, but with the other four minerals only one case is found in which the yield is less than with the same treatment minus the mineral (jars 209, 210), and here the variation in duplicates is wider than that in the two treatments. That these increases in yield were produced by the mineral rather than by the auxiliary treatment is indicated by table 3.

TABLE 1

*Yield and potassium content of buckwheat in experiment I*

NUMBER OF JAR	YIELD OF CROP	AVERAGE YIELD	K IN CROP	K REMOVED FROM JAR	SOLUBLE K FROM ALL SOURCES	K OBTAINED FROM INSOLUBLE SOURCES
Series 100. Check						
	<i>gm.</i>	<i>gm.</i>	<i>per cent</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
101	52.9					
102	55.3	54.1	1.96	1.060	1.148	-0.088
103	66.5					
104	55.4	60.9	2.07	1.261	1.725	-0.464
105	46.7					
106	40.2	43.4	2.37	1.028	1.463	-0.435
107	44.5					
108	57.8	51.1	2.24	1.146	1.294	-0.148
109	48.8					
110	54.9	51.8	2.21	1.145	1.148	-0.003
111	37.2					
112	50.8	44.0	2.43	1.069	1.148	-0.079
113	59.3					
114	61.9	60.6	1.88	1.140	1.803	-0.663
Series 200. Orthoclase						
201	68.3					
202	76.1	72.2	1.87	1.350	1.148	+0.202
201a	72.1					
202a	66.4	69.2	1.95	1.350	1.148	+0.202
203	65.5					
204	61.8	63.6	2.67	1.698	1.725	-0.027
205	59.7					
206	57.4	58.5	2.23	1.305	1.463	-0.158
207	69.5					
208	71.6	70.5	2.17	1.530	1.294	+0.236
209	42.3					
210	55.1	48.7	2.32	1.130	1.148	-0.018
211	52.6					
212	59.9	56.2	2.34	1.315	1.148	+0.167



TABLE 1—Continued

NUMBER OF JAR	YIELD OF CROP	AVERAGE YIELD	K IN CROP	K REMOVED FROM JAR	SOLUBLE K FROM ALL SOURCES	K OBTAINED FROM INSOLUBLE SOURCES
Series 300. Microcline						
	<i>gm.</i>	<i>gm.</i>	<i>per cent</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
301	76.0					
302	75.6	75.8	1.69	1.281	1.148	+0.133
301a	75.5					
302a	65.0	70.2	1.80	1.264	1.148	+0.116
303	75.2					
304	61.9	68.5	1.90	1.302	1.725	-0.423
305	61.7					
306	57.8	59.7	1.95	1.164	1.463	-0.299
307	77.2					
308	68.0	72.6	2.00	1.452	1.294	+0.158
309	60.5					
310	63.0	61.7	1.78	1.098	1.148	-0.050
311	50.6					
312	53.0*	51.8	1.59	0.855	1.148	-0.293
Series 400. Leucite						
401	71.2					
402	80.3	75.7	1.63	1.234	1.148	+0.086
401a	79.4					
402a	76.4	77.9	1.75	1.363	1.148	+0.215
403	71.2					
404	69.2	70.2	2.32	1.629	1.725	-0.096
405	78.3					
406	56.1	67.2	1.72	1.155	1.463	-0.308
407	74.0					
408	71.8	72.9	1.66	1.210	1.294	-0.084
409	64.9					
410	66.2	65.5	1.86	1.218	1.148	+0.070
411	59.3					
412	61.6	60.4	2.15	1.298	1.148	+0.150

\* Stand of only 2 plants.

TABLE 1—*Concluded*

NUMBER OF JAR	YIELD OF CROP	AVERAGE YIELD	K IN CROP	K REMOVED FROM JAR	SOLUBLE K FROM ALL SOURCES	K OBTAINED FROM INSOLUBLE SOURCES
Series 500. Alunite						
	<i>gm.</i>	<i>gm.</i>	<i>per cent</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
501	74.7					
502	77.9	76.3	1.73	1.320	1.148	+0.172
501a	72.3					
502a	72.4	72.3	1.72	1.244	1.148	+0.096
501b	63.8					
502b	62.4	63.1	2.47	1.559	1.148	{ (-2.999*) } +0.411
503	72.4					
504	66.9	69.6	2.27	1.580	1.725	-0.145
505	62.0					
506	60.1	61.0	1.75	1.068	1.463	-0.395
507	68.7					
508	69.3	69.0	1.92	1.324	1.294	+0.030
509	63.6					
510	72.8	68.2	1.93	1.316	1.148	+0.168
511	67.2					
512	67.0	67.1	1.92	1.288	1.148	+0.140
Series 600. Lepidolite						
601	58.7					
602	60.5	59.6	2.06	1.227	1.148	+0.079
601a	27.9					
602a	33.6	30.7	2.39	0.735	1.148	-0.413
603	60.0					
604	50.4	55.2	2.21	1.220	1.725	-0.505
605	52.6					
606	47.6	50.1	2.60	1.302	1.463	-0.161
607	65.2					
608	63.6	64.4	2.00	1.288	1.294	-0.006
609	45.8					
610	47.5	46.6	1.94	0.903	1.148	-0.245
611	51.9					
612	51.8	51.8	1.95	1.010	1.148	-0.138

\* This value is obtained if the potassium of ignited alunite is considered entirely available.

In this table the relative yields in each series are calculated as percentages of the yield produced by the mineral alone, which is taken as 100. Almost without exception the yield is greater with the mineral alone than where any of the additional treatments were applied.

The value of the decaying organic manures in liberating potassium is unfairly minimized, however, if yields alone are taken as a criterion. The value

TABLE 2  
*Relative yields of buckwheat. Effect of minerals (no mineral = 100)*

JAR NUMBER	AUXILIARY TREATMENT	SERIES 100, NO MINERAL	SERIES 200, ORTHO-CLASE	SERIES 300, MICRO-CLINE	SERIES 400, LEUCITE	SERIES 500, ALUNITE	SERIES 600, LEPID-OLITE
1, 2	None	100	133.5	140.2	139.9	141.0	110.2
1a, 2a	10 tons mineral		127.9	129.7	144.0	133.7	56.7
1b, 2b	Ignition of mineral					116.6	
3, 4	Alfalfa	100	104.4	112.5	115.3	114.3	90.6
5, 6	Prairie hay	100	134.8	137.6	154.8	140.3	115.4
7, 8	Cow manure	100	138.0	142.1	142.7	135.0	126.0
9, 10	MgCl <sub>2</sub> ·6H <sub>2</sub> O	100	94.0	119.1	126.5	131.7	90.0
11, 12	NaCl	100	127.7	122.3	137.3	152.5	117.7
13, 14	KCl	112					
Average.....		100	121.1	128.3	134.8	133.1	107.3

TABLE 3  
*Relative yields of buckwheat. Effect of auxiliary treatment (mineral alone = 100)*

JAR NUMBER	AUXILIARY TREATMENT	SERIES 100, NO MINERAL	SERIES 200, ORTHO-CLASE	SERIES 300, MICRO-CLINE	SERIES 400, LEUCITE	SERIES 500, ALUNITE	SERIES 600, LEPID-OLITE	AVERAGE
1, 2	None	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1a, 2a	10 tons mineral		95.8	92.6	102.9	94.7	51.5	87.5
1b, 2b	Ignition of mineral					82.7		
3, 4	Alfalfa	112.6	88.1	90.4	92.7	91.2	92.6	94.9
5, 6	Prairie hay	80.2	81.0	78.7	88.8	79.9	84.1	82.1
7, 8	Cow manure	94.4	97.7	95.8	96.4	90.4	108.1	97.1
9, 10	MgCl <sub>2</sub> ·6H <sub>2</sub> O	95.7	67.4	81.4	86.5	89.4	78.2	83.1
11, 12	NaCl	81.3	77.8	68.3	79.8	87.9	86.9	80.3
13, 14	KCl	112.0						

of decomposing organic matter in dissolving relatively insoluble mineral plant nutrients is generally ascribed largely to the HNO<sub>2</sub> produced in nitrification, organic acids produced by partial decomposition of non-nitrogenous compounds, and CO<sub>2</sub>. The large excess of limestone applied to all the jars furnished an abundance of readily available base for the neutralization of these acids, thus preventing them from attacking the less soluble potassium silicates. This fact was realized at the beginning of the work, but it was believed that

the beneficial effect of the limestone in the soil to the growing crop would cause sufficiently increased root growth and feeding power of the plant to offset the disadvantage. The data of these experiments furnishes no basis for a comparison of these values. Furthermore, the large amount of organic matter of the peat itself was probably decomposed rapidly enough to affect the minerals to almost if not quite as great an extent as the small amount of organic material added. Indications of considerable nitrification were furnished by the appearance occasionally during the growing season, of a slight white or brownish crust of nitrates and other salts on the surface of the soil in all the jars.

An inventory of the sources of potassium, soluble and insoluble, upon which the crops could draw for their supply indicates that the deficiency of available potassium in this soil is not as great as is to be desired in an experiment of this kind. The soluble potassium in the soil alone, according to the extraction and analysis noted previously, amounts to 1.146 gm. per jar. The amount of soluble potassium added in the organic materials is, for the jars receiving those materials, 0.755 gm. in the alfalfa, 0.315 gm. in the prairie hay and 0.146 gm. in the manure. The 0.002 gm. of potassium added in the seed is considered available, and the sum of these three amounts gives the values recorded in the next to last column of table 1. This leaves insoluble potassium in the soil of each jar, 11.314 gm.; in the limestone added 0.026 gm. and in the minerals added, 2.08 to 2.81 gm. except where the 10-ton applications were made, in which there was five times as much. In calculating the values for the last column of table 1 it was assumed that the crop utilizes all the potassium from the soluble sources named before beginning on the insoluble supply. It may be noted that in 25 of the 43 cultures, a part of the soluble potassium amounting to from 3 to 663 mgm. remained in the jars, unused by the plant, while in only 18 jars the plants utilized a part of the insoluble potassium. These unused reserves of soluble potassium were present mainly in series 100 and 600, where the yields were small, and the crops more or less unthrifty in appearance. In the other four series the unused reserves were found, mainly, in the jars receiving an excess of soluble potassium in the organic manures added.

The percentage of potassium in the crops from the various treatments varies widely. These variations appear to depend as much upon the available supply of potassium as upon the crop yield. The total amount removed per jar, on the other hand, is necessarily dependent upon the yield to a large extent. As a result, the high yields are accompanied by the removal of some potassium from the sources listed as insoluble, except where an abundant supply of soluble potassium has been added in the organic materials. The maximum amount of "insoluble" potassium thus taken up by the plants, was in jars 401a and 402a, where the potassium from insoluble sources constituted 15.8 per cent of the total amount taken up by the crop.

The effect of the minerals upon the amount of potassium utilized by the crop may be shown very clearly by averaging the amounts of potassium removed per jar for each series separately. The following table gives these averages,

as well as the relative amounts removed per jar on a basis of 100 for the series receiving no mineral:

SERIES	K REMOVED PER JAR, AVERAGE OF 14 JARS	RELATIVE AMOUNT OF K REMOVED PER JAR, AVERAGE OF 14 JARS
	gm.	
100, No mineral .....	1.118	100.0
200, Orthoclase .....	1.383	123.7
300, Microcline .....	1.202	107.5
400, Leucite .....	1.301	116.3
500, Alunite .....	1.306*	116.8*
501b, 502b, Ignited alunite .....	1.559	139.5
600, Lepidolite .....	1.098	98.26

\* Average of 16 jars.

Increased amounts of potassium are thus seen to be removed by the crops, amounting to 7.5 to 23.7 per cent where minerals are supplied, if we exclude ignited alunite, which contains much soluble potassium, and lepidolite, which shows unsatisfactory results here as in the yields. This method of averaging is not unfair, because the values averaged are from jars receiving the same supplementary treatments in each series.

These observations lead to the following conclusions:

1. Applications of 25 gm. per jar (approximately 2 tons per acre) of orthoclase, microcline, leucite and alunite increase the yield of buckwheat from 20 to 35 per cent and also enable the crop to utilize all the water-soluble potassium present as well as some of the less available forms. A part of this may come from the minerals applied.
2. On the peat soils used in this experiment the addition of crop residues, manure, or soluble magnesium or sodium salts does not increase the yield of buckwheat or the availability of the potassium of the minerals added.
3. The activities of the root system through contact with the soil or mineral particles, and commonly spoken of as the "feeding power" of plants, is an important factor to be considered in the liberation of relatively insoluble potassium.

*Experiment II. Solubility of the minerals in water as affected by decaying organic materials and soluble salts under soil conditions*

This experiment was carried out in half-gallon Mason jars, loosely covered in order to prevent excessive evaporation and keep out dirt, without excluding air. It was the purpose to follow the general plan of Experiment I as to treatments, but to determine the potassium in a water extract instead of growing a crop in the soil. Since the absorbing power of a soil prevents as complete extraction of the water-soluble potassium as the plant is capable of, a larger proportion of mineral to soil was used than in the culture experiment. The

method of shaking the soil with a large excess of water was chosen in preference to the percolation method of extraction in order to lessen potassium absorption as much as possible.

To each 100 gm. of water-free soil was added enough mineral to carry 1 gm. of potassium. The organic materials were added at the rate of 1 gm. of dry matter per 100 gm. of soil and the soluble salts were added in molecular equivalents of the potassium contained in the mineral. In addition to the auxiliary treatments used in experiment I,  $\text{NH}_4\text{Cl}$  and dextrose were used. Table 4 gives the treatments in detail.

In each case double the amount of soil needed for an extraction was taken. The minerals and other substances were added to the air-dry soil (except soluble salts and dextrose) and well mixed, dry. Enough distilled water was

TABLE 4  
*Soil and treatments used in experiment II*

JAR NUMBER	PEAT SOIL EQUIVALENT TO WATER- FREE SOIL	AUXILIARY TREATMENT		SERIES A, NO MINERAL	SERIES B, ORTHO- CLASE	SERIES C, MICRO- CLINE	SERIES D, LEUCITE	SERIES E, ALUNITE	SERIES F, LEPID- OLITE
		Substance added	Amount						
	gm.		gm.		gm.	gm.	gm.	gm.	gm.
1	200	Nothing			18.32	17.81	21.07	24.04	22.24
2	200	$\text{CaCO}_3$	2.56		18.32	17.81	21.07	24.04	22.24
3	400	Alfalfa	4.26*		36.64	35.62	42.14	48.08	44.48
4	400	Prairie hay	4.29*		36.64	35.62	42.14	48.08	44.48
5	400	Fresh manure	23.91*		36.64	35.62	42.14	48.08	44.48
6	200	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	5.20		18.32	17.81	21.07	24.04	22.24
7	200	$\text{NaCl}$	2.99		18.32	17.81	21.07	24.04	22.24
8	200	$\text{NH}_4\text{Cl}$	2.74		18.32	17.81	21.07	24.04	22.24
9	200	Dextrose	2.00		18.32	17.81	21.07	24.04	22.24
10	200	$\text{KCl}$	3.81						

\* Equivalent to 4.00 gm. dry matter.

added to bring up to optimum (160 per cent) and again very thoroughly mixed. The soluble salts and dextrose were dissolved in the water used for making the soil up to optimum. The entire mass was then weighed, one-half removed for extraction and the other half placed in the Mason jars. The fractions kept in the jars were weighed and brought up to optimum moisture content every few days with distilled water during the period of the experiment. The double amounts of soil prepared in jars 3, 4 and 5 of each series were prepared in order that ammonia and nitrate nitrogen might be determined in the soils receiving organic manures. This might throw some light upon a possible correlation of ammonification, nitrification and solution of the potassium of the minerals used. Unfortunately, the determinations were all ruined by the breaking of a refrigerating machine and consequent flooding of the building with  $\text{NH}_3$  fumes. A few nitrate determinations were saved but the results were not considered of sufficient importance to record.

The method of determining water-soluble potassium was as follows. The moist treated soils were immediately placed in 2½-liter bottles, shaken 5 hours in a mechanical shaker with 1500 cc. distilled water (including the water already contained in the sample) and then allowed to settle 36 hours. The supernatant solution was then filtered through filter paper and placed in glass stoppered bottles with a few drops of chloroform until used. Aliquots of this solution were clarified by shaking with 5 cc. of milk of lime. Aliquots of the

TABLE 5  
*Milligrams of potassium extracted by water from 100 grams of soil*

JAR NUMBER	TREATMENT	A, CHECK NO MINERAL	B, ORTHO- CLASE	C, MICRO- CLINE	D, LEUCITE	E, ALUNITE	F, LEPID- OLITE
		<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
1	Nothing	{ 37.7	26.6	26.6	32.0	28.5	39.8
		{ 33.9	33.5	32.3	37.3	33.7	52.6
2	CaCO <sub>3</sub>	{ 32.9	33.7	32.0	35.3	32.4	46.2
		{ 29.1	33.1	30.1	36.9	33.5	46.1
3	Alfalfa	{ 39.1	40.3	34.6	39.6	35.7	51.9
		{ 41.0	42.6	40.3	45.3	40.6	62.3
4	Prairie hay	{ 31.7	32.8	28.8	30.7	31.4	50.8
		{ 34.4	36.1	33.5	39.6	36.0	49.5
5	Manure	{ 27.7	31.4	27.6	31.2	27.8	48.8
		{ 33.0	36.4	35.0	39.8	35.3	53.1
8	NH <sub>4</sub> Cl	{ 29.8	43.7	41.3	45.9	42.4	62.9
		{ 43.9	44.0	45.2	56.3	46.0	84.4
9	Dextrose	{ 23.6	26.6	26.3	21.2	29.7	49.6
		{ 29.7	31.2	28.1	37.4	31.1	48.4
10	KCl	{ 184.6					
		{ 176.4					

clarified solution were then filtered and taken to dryness in an excess of H<sub>2</sub>SO<sub>4</sub>, ignited to destroy organic matter, taken up in boiling water and thoroughly triturated with an agate pestle. Calcium sulfate was filtered off and washed, the remainder of the calcium was removed as the oxalate, ammonium salts driven off and potassium determined gravimetrically as K<sub>2</sub>PtCl<sub>6</sub>.

At the end of 80 days the second set of moist soil samples was removed from the jars, extracted and the extract analyzed for potassium in the same way. It was impossible in the limited time available to overcome difficulties caused by the interference of the large amounts of magnesium and sodium in numbers 6 and 7. The results are considered untrustworthy and are therefore not presented.

The results of the analyses are recorded in table 5, the figures representing milligrams of K per 100 gm. of water-free soil, or parts per 100,000. The upper row of figures represents the results from the initial water-extraction, and the lower row, results of extraction after 80 days of moist contact of soil and mineral under aerobic conditions.

Subtracting the values given in the check column, A, from those in each of the succeeding columns gives the increase in soluble potassium due to the addition of the minerals. These values are in table 6.

TABLE 6  
*Gains (+) in soluble potassium over check*

JAR NUMBER	TREATMENT	MGM. K PER 100 GM. SOIL				
		B, Orthoclase	C, Microcline	D, Leucite	E, Alunite	F, Lepidolite
1	0	-11.1	-11.1	- 5.7	- 9.2	+ 2.1
		+ 0.4	- 1.6	+ 3.4	- 0.2	+18.7
2	CaCO <sub>3</sub>	+ 0.8	- 0.9	+ 2.4	+ 0.5	+13.3
		+ 4.0	+ 1.0	+ 7.0	+ 4.4	+17.0
3	Alfalfa	+ 1.2	- 4.5	+ 0.5	- 3.4	+12.8
		+ 1.6	- 0.7	+ 4.3	- 0.4	+21.3
4	Prairie hay	+ 1.1	- 2.9	- 1.0	- 0.3	+19.1
		+ 1.7	- 0.9	+ 5.2	+ 1.6	+15.1
5	Manure	+ 3.7	- 0.1	+ 3.5	+ 0.1	+21.1
		+ 3.4	+ 2.0	+ 6.8	+ 2.3	+20.1
8	NH <sub>4</sub> Cl	+ 3.9	+11.5	+16.1	+12.6	+33.1
		+ 0.1	+ 1.3	+12.4	+ 2.1	+40.5
9	Dextrose	+ 3.0	+ 2.7	- 2.4	+ 6.1	+26.0
		+ 1.5	- 1.6	+ 7.7	+ 1.4	+18.7

#### *Discussion of results*

The most striking fact brought out by table 5 is the large amount of soluble potassium in the untreated peat soil. From 8 to 9 per cent of the total potassium in the soil is extracted by shaking with water. This suggests that a considerable proportion of the soil potassium of the peat is held by the organic matter of the soil, since potassium which is bound to the mineral soil constituents is, as a rule, much more firmly held.

An apparent increase in the amount of soluble potassium after 80 days' standing is noted throughout table 5, almost without exception.

The effects of the minerals are most clearly shown in table 6. Three points are conspicuous.



(a) The solubility of lepidolite is very high throughout all the treatments. The solubility of lepidolite is influenced little or not at all by any of the treatments. In view of this result, the stunting of the crop grown in series 600 of experiment I may well be ascribed to the presence of some toxic element dissolved out of the mineral, probably an excess of soluble lithium. The excess of calcium carbonate in the soil, which was already practically neutral makes poisoning by soluble aluminum salts appear improbable.

(b) The addition of the minerals to the untreated soil (no. 1, table 6) caused an immediate disappearance of considerable amounts of potassium from solution which reappeared in the later extraction. This suggests a possible temporary absorbing capacity of the minerals themselves for potassium.

(c) The only evidence of potassium liberation by exchange of bases is furnished by the extraction with  $\text{NH}_4\text{Cl}$ . With the exception of orthoclase there is an increased amount of potassium dissolved to the extent of 11 to 33 mgm. per 100 gm. of soil over that with  $\text{NH}_4\text{Cl}$  alone (no mineral). The increase over the mineral alone is equally marked, as shown in table 5. This is in accord with the findings of André (2), Steiger (59) and Beyer (6). The solubility in all the other treatments is but slight, the values recorded being, for the most part, within the limits of experimental error. Leucite, however, shows distinctly greater solubility than orthoclase, microcline or alunite.

Concerning the auxiliary treatments, nothing can be said in their favor, used under the conditions of this experiment, except for the  $\text{NH}_4\text{Cl}$  already noted. Where the organic manures have been added, there is an increase in potassium extracted, but it should be noted that the increase is not sufficient to cover the amount added in the organic material. In every case the soil-mineral mixture has absorbed half or more of the soluble potassium added in the organic manures. Dextrose has depressed the solution of potassium throughout.  $\text{CaCO}_3$  has had no effect except to decrease slightly the temporary absorption of potassium by the soil-mineral mixture. The absorptive power of the soil is shown in no. 10, table 5. The amounts of soluble potassium found indicate the immediate absorption by the soil of 81.5 per cent of the potassium added as KCl, this being increased to 82.4 per cent during the 80 days.

*Experiment III. Solubility of minerals in water as affected by certain decaying organic materials*

The general plan of experiment III is the same as in experiment II.

In experiment III mixtures of the minerals and the organic materials used in experiment II were allowed to stand moistened, but not saturated with water for 80 days. The method of mixing and of extracting was exactly the same as in experiment II. Each mineral was treated with two different proportions of the organic material. One was the same as in experiment II, namely, 1 gm. dry organic material to 1 gm. total K in mineral, while the other mixture contained 10 times as much organic matter. For the purpose of com-

parison, each of the organic materials and minerals was extracted with water separately. The results of these extractions are given in tables 7, 8, and 9. In table 7 the upper row of figures (a) represents the values obtained at the

TABLE 7  
*Water-soluble potassium in organic matter-mineral mixture*

NUMBER	ORGANIC MATERIALS TAKEN	DRY MATTER	MGM. K PER 1 GM. TOTAL K IN MINERAL a = initial    b = 80 days later (Mineral used = 10 gm. Total K)					
				B, Ortho- clase	C, Micro- cline	D, Leucite	E, Alunite	F, Lepid- olite
		gm.						
10	Alfalfa	10	{ a	17.8	16.5	19.2	16.5	36.0
			{ b	17.0	16.4	19.0	17.7	19.9
11	Alfalfa	100	{ a	139.1	132.1	134.0	129.2	150.0
			{ b	159.6	165.8	159.9	154.7	170.7
12	Prairie hay	10	{ a	11.0	9.5	12.7	9.3	22.5
			{ b	9.7	8.6	11.8	9.8	12.9
13	Prairie hay	100	{ a	72.5	82.1	82.8	85.2	103.7
			{ b	81.5	80.8	85.4	80.5	77.0
14	Manure	10*	{ a	8.0	7.6	10.4	6.9	19.3
			{ b	7.7	8.0	11.0	7.1	13.7
15	Manure	100*	{ a	49.4	30.7	42.3	63.4	78.3
			{ b	57.2	58.4	69.0	68.6	69.7

\* Equivalent amount of fresh manure was used.

TABLE 8  
*Water-soluble potassium in organic materials used*

SUBSTANCE	TOTAL K	WATER-SOLUBLE K	PER CENT OF TOTAL K WHICH IS SOLUBLE
	per cent*	per cent*	
Alfalfa.....	1.60	1.54	96.25
Prairie hay.....	0.86	0.84	97.68
Fresh manure.....	0.66	0.66	100.00

\* Percentage in dry matter.

initial extraction, and the lower row (b) the values obtained 80 days later. In order to show the gain or loss of soluble potassium occasioned by contact of the minerals and organic matter, the sum of the values given in tables 8 and 9 was deducted from those in table 7. Table 10 gives the differences.

*Discussion of results*

An examination of the data in table 10 reveals the following facts. Only where the larger amounts of organic materials are used is there a significant change in the amount of soluble potassium obtained. This is a disappearance of potassium from solution in all the initial extractions and in the later extrac-

TABLE 9  
*Water-soluble K in minerals*

SUBSTANCE	MGM. SOLUBLE K PER 100 GM. MINERAL	MGM. SOLUBLE K PER 1 GM. TOTAL K
Orthoclase.....	11.99	1.1
Microcline.....	11.79	1.0
Leucite.....	42.73	4.5
Alunite.....	11.18	1.3
Lepidolite.....	62.99	7.0

TABLE 10  
*Gain or loss of soluble K occasioned by mixing of organic materials with minerals*

a = initial    b = 80 days later

NUMBER		B, ORTHOCLASE	C, MICROCLINE	D, LEUCITE	E, ALUNITE	F, LEPIDOLITE
		mgm.	mgm.	mgm.	mgm.	mgm.
10	a	+ 1.3	+ 0.1	- 0.7	- 0.2	-13.6*
	b	+ 0.5	0	- 0.9	+ 1.0	- 2.5*
11	a	-16.0*	-13.0*	-24.5*	-26.1*	-11.0*
	b	+ 4.5*	+10.8*	+ 1.4	- 0.6	+ 9.7*
12	a	+ 1.5	+ 0.1	- 0.2	- 0.4	+ 7.1*
	b	+ 0.2	- 0.8	- 1.1	+ 0.1	- 2.5*
13	a	-12.6*	- 2.9*	- 7.7*	- 0.1	+12.7*
	b	- 3.6*	- 4.2*	- 3.1*	- 4.8*	-14.0*
14	a	+ 0.3	0	- 0.7	- 1.0	+ 5.7*
	b	0	+ 0.4	- 0.1	- 0.8	+ 0.1
15	a	-17.7*	-36.3*	-28.2*	- 3.9*	+ 5.3*
	b	- 9.9*	- 8.6*	- 1.5	+ 1.3	- 3.3*

\* The values so marked are the only ones in which the differences are greater than can be accounted for by experimental error.

tions of prairie hay and manure, in amounts up to 55 per cent (C15, initial) of that added in the organic material. Alfalfa during 80 days effected the solution of 4.5 mgm. K per gm. of total K in orthoclase, 10.8 mgm. in microcline and 9.7 mgm. in lepidolite. The greater solvent action of the alfalfa is due in part to the fact that it was decomposed much more rapidly than the other two

organic materials. Four weeks after the beginning of the experiment the alfalfa had broken down to such an extent that none of the plant structure was distinguishable, and the mass resembled the cow manure in appearance. A large proportion of the prairie hay, on the other hand, was but little changed in appearance even at the end of the 80 days. The high proportion of easily decomposable nitrogenous material in the alfalfa may also have been a factor affecting its solvent action. There is a possibility that this factor was really the presence of ammonia, since conditions were more favorable for ammonification than for nitrification.

The high solubility of lepidolite noted in experiment II is further illustrated here, but the potassium dissolved disappears from solution later, as shown by the second extractions. The slow absorption of dissolved potassium suggests

TABLE 11

*Absorption of potassium by minerals. Milligrams of K per gram of total K in mineral*

NUMBER	MINERAL	AMOUNT OF MINERAL USED (= 1 gm. K)	SOLUBLE K ADDED AS KCl	SOLUBLE K IN MINERAL (TABLE 9)	TOTAL SOLUBLE K	SOLUBLE K FOUND	GAIN (+) OR LOSS (-) OF SOLUBLE K
		gm.	mgm.	mgm.	mgm.	mgm.	mgm.
1	Orthoclase	9.16	150	1.1	151.1	144.6	- 6.5
2	Orthoclase	9.16	300	1.1	301.1	290.2	-10.9
3	Orthoclase	9.16	5	1.1	6.1	6.4	+ 0.3
4	Microcline	8.906	150	1.0	151.0	139.7	-11.3
5	Leucite	10.54	150	4.5	154.5	140.3	-14.2
6	Alunite	12.02	150	1.3	151.3	143.6	- 7.7
7	Lepidolite	11.12	150	7.0	157.0	137.1	-19.9
8	Lepidolite	11.12	225	7.0	232.0	210.1	-21.9

chemical reaction with the mineral, possibly a replacement of lithium by potassium.

The disappearance of potassium from solution in this experiment can be accounted for in only two ways. Either the potassium of the organic matter, upon decomposition of the latter, is in part converted into insoluble forms, or it is absorbed by the mineral. In the case of the initial extractions, the disappearance of soluble potassium can be accounted for only by absorption by the minerals (see table 8).

To verify this point the following experiment was carried out. Portions of each of the minerals equivalent to 1 gm. of potassium were weighed out, definite amounts of soluble potassium added as KCl from an accurately made standard solution and made up to a volume such that the proportion of mineral to water was the same as in the extractions of experiment III. These were shaken 5 hours and allowed to stand 36 hours. Suitable aliquots of these extractions were then analyzed.

The results of this experiment are presented in table 11.

The results of this experiment furnish ample verification of the statements made above. The minerals have absorbed potassium in every case, except where the very small amount of potassium was added in no. 3. The amounts may fairly be compared with those in the upper row, a, of no. 11, table 10. Absorption by the mineral thus accounts for a large part of the potassium which disappeared from solution—more than half except for orthoclase and alunite.

*Experiment IV. Availability of Potassium in Sandy Soils*

In another part of this paper certain sandy soils of Illinois containing a large amount of potassium were mentioned as being similar to peat soils in one respect, i.e., in that they are deficient in available potassium. Experiment IV was undertaken in order to determine the reason for the low availability of the potassium in such soils. The cultural treatments consist of (a) whole sand as the cultural medium, (b) coarse separates (sands) and (c) a mixture of the

TABLE 12  
*Total and water-soluble K in the different separates of sandy soil*

SUBSTANCE ANALYZED	TOTAL K	WATER-SOLUBLE K PER 100 GM. SOIL
	<i>per cent</i> *	<i>mgm.</i>
Whole sand, unground.....	1.03	3.5
Coarse separates, 100-mesh .....	1.01	5.9
Fine separates .....	1.59	39.8

\* Samples ground to impalpable powder for total potassium determination.

coarse separates and the same finely ground. Each jar receives a complete nutrient solution minus potassium.<sup>1</sup>

The whole sand and coarse and fine separates were examined in the laboratory as follows. A mechanical analysis showed that the sandy soil used contained 96.7 per cent of coarse separates (sands) and 3.3 per cent of fine separates (silt plus clay). Separations were made by sedimentation in distilled water. Determinations were made in the three materials of total potassium and also of water-soluble potassium. The latter was determined as in the preceding experiments by shaking together 100 gm. of soil and 1500 cc. of distilled water, potassium being determined in an aliquot of the extract. The results are given in table 12.

In view of the fact that the coarse separates were obtained by sedimentation in water, no water-soluble determination was made on this fraction, unground. The large volume of water necessary to wash out all the silt and clay from the sand (approximately 100 liters for the 100 gm. of silt and clay used in the extraction above) would wash out all soluble potassium, which would remain in the silt and clay on evaporation.

<sup>1</sup> The crop is not yet harvested.

The high absorbing power of the fine separates is here illustrated. The 3.5 mgm. of potassium soluble in the whole sand, when concentrated in the fine separates is not extracted, the fine separates from 100 gm. of sand yielding to extraction only 1.31 mgm. of potassium. Grinding the coarse separates liberates some potassium, but not enough to be of any practical value. The grinding of 1 ton of coarse separates to 100-mesh size and down would produce, according to the figures in table 12, 0.114 pound of soluble potassium.

The relatively small surface of the coarse particles of sandy soils of the type used in this experiment readily accounts for the low availability of the potassium in these soils (29).

#### V. SUMMARY

1. The use of finely-ground potassium-bearing minerals increases the yield of buckwheat in peat soil 21 to 34.8 per cent.

2. Lepidolite is detrimental to the growth of buckwheat, especially if present in large amounts.

3. The addition of crop residues, manure, or soluble sodium or magnesium salts to peat soil, together with the minerals used in this experiment, does not increase the yield of crop or the availability of the mineral potassium.

4. The so-called "feeding power" of the plant itself, through the activities of the root system, is an important factor in the utilization of relatively insoluble potassium.

5. The solubility of the minerals used, as determined by extraction with water, is very low, except that of lepidolite. The solubility is increased by ammonium chloride and also by the decomposition of alfalfa. The result in the latter case may be due to ammonification of the nitrogenous compounds in the alfalfa.

6. All the minerals used have the ability to absorb considerable amounts of potassium from solution. The absorption is probably physical to a large extent.

7. The low availability of the potassium of dune sand is due to the fact that most of the potassium is contained in the larger particles. The relatively small surface of the particles is sufficient explanation of the low solubility of the potassium contained in them.

8. The increase in solubility of the potassium in such sands produced by grinding is not sufficient to be of practical value.

9. The results of the crop culture work should not be taken as conclusive. They should be verified by repetition for several seasons with various other farm crops.

#### ACKNOWLEDGMENT

The author takes pleasure in thanking Dr. C. G. Hopkins, Dr. Robert Stewart and Dr. A. L. Whiting for the many helpful suggestions and criticisms which they have so kindly given him.

## REFERENCES

- (1) AITKEN, A. P. 1887 Ground feldspar as a potash manure. *In* Trans. Highland and Agr. Soc. Scot., ser. 4, v. 19, p. 253. *Abs. in* Centbl. Agr. Chem., Bd. 19, p. 410 (1890). Original not seen.
- (1a) AITKEN, A. P. 1889 Finely ground feldspar as a potash manure. *In* Trans. Highland and Agr. Soc. Scot., ser. 5, v. 1, p. 246-251.
- (2) ANDRÉ, G. 1913 Déplacement de la potasse contenue dans certaine roches feldspathique par quelques substances employées comme engrais. *In* Compt. Rend. Acad. Sci. [Paris], t. 157, p. 856.
- (3) BALLENTINE, W. 1889 Experiments with feldspar as a source of potash. *In* Me. Agr. Exp. Sta. Ann. Rpt. 1889, p. 143.
- (4) BASSALIK, K. 1912 Über Silikatzersetzung durch Bodenbakterien. *In* Ztschr. Garüingsphysiol., Bd. 2, p. 1-32.
- (5) BASSALIK, K. 1913. Über Silikatzersetzung durch Bodenbakterien und Hefen. *In* Ztschr. Gährungsphysiol., Bd. 3, p. 15-42.
- (6) BEYER, A. 1871 Über die Zersetzung des Feldspathes unter dem Einfluss von Salzlösungen und einige andere Agentien. *In* Landw. Vers. Stat., Bd. 14, p. 314. See also Campbell (11).
- (7) BLANCK, E. 1912 Gestein und Boden in ihrer Beziehung zur Pflanzenernährung, insbesondere die ernährungsphysiologische Bedeutung der Sandstein-Bindemittel Substanz. *In* Landw. Vers. Stat., Bd. 77, p. 129.
- (8) BLANCK, E. 1913 Die Bedeutung des Kalis in den Feldspathen für den Pflanzen. *In* Jour. Landw., Bd. 61, p. 1-10.
- (9) BROOKS, W. P., AND GASKILL, E. F. 1917 Comparison of potash salts. *In* Mass. Agr. Exp. Sta. 29th Ann. Rpt., p. 50a. See also 27th Ann. Rpt. (1915), p. 33a, and 30th Ann. Rpt. (1918) p. 26a.
- (10) CAMERON, F. K. AND BELL, J. M. 1905 The mineral constituents of the soil solution. U. S. Dept. Agr. Bur. Soils Bul. 30.
- (11) CAMPBELL, F. H. 1907 Einfluss der Chloralkalilösungen auf doppelsilikate des Kalziums und Aluminium. *In* Landw. Vers. Stat., Bd. 65, p. 247.
- (12) CHIRIKOV, F. V. 1914 Biotite, phonolite and similar mineral substances as sources of potash for plants. *In* Iz. Result. Veget. Opytov. Lab. Rabot (Rec. Trav. Lab. Agron.) Moskov. Selsk. Khoz. Inst., v. 10 (1914), p. 366; Izv. Moskov. Selsk Khoz. Inst. (Ann. Inst. Agron. Moscou), v. 22 (1916), p. 126. *Abs. in* Exp. Sta. Rec., v. 36, 1917, p. 728. Original not seen.
- (13) CLARKE, F. W. 1900 The alkaline reaction of some natural silicates. U. S. Geol. Survey Bul. 167, p. 156.
- (14) CUSHMAN, A. S. 1905 Effect of water on rock powders. U. S. Dept. Agr. Bur. Chem. Bul. 92.
- (15) CUSHMAN, A. S. 1907 The use of feldspathic rocks as fertilizers. U. S. Dept. Agr. Bur. Plant Indus. Bul. 104.
- (16) CUSHMAN, A. S., AND HUBBARD, P. A. 1907 Decomposition of the feldspars. U. S. Dept. Agr. Off. Pub. Roads Bul. 28.
- (17) DAUBRÉE, A. 1854 Sur la production artificielle de minéraux de la famille des silicates et des aluminates, par la reaction des vapeurs sur les roches. *In* Compt. Rend. Acad. Sci. [Paris], t. 39, p. 135.
- (18) Daubrée, A. 1857 Recherches experimentales sur les decompositions chimiques des roches produites dans les actions mechaniques. *In* Compt. Rend. Acad. Sci. [Paris], t. 44, p. 997.
- (19) EBELMEN, J. J. 1845 Recherches sur la decomposition des espèces minérales de la famille des silicates. *In* Compt. Rend. Acad. Sci. [Paris], t. 20, p. 1415; t. 26, p. 38 (1848).

- (20) FEILITZEN, C. VON 1891 Kulturversuche des swedischen Moorkulturvereins in Jahre 1890: Düngungswert des Feldspathmehls. *In* Centbl. Agr. Chem., Bd. 20, p. 225.
- (21) FEILITZEN, C. VON 1892 Kulturversuche des schwedeschen Moorkulturvereins im Jahre 1891: Düngungswert des Feldspathmehls. *In* Centbl. Agr. Chem., Bd. 21, p. 506.
- (22) FRAPS, G. S. 1912 Active potash of the soil and its relation to pot experiments. *Tex. Agr. Exp. Sta. Bul.* 145.
- (23) FRAPS, G. S. 1916 Effect of additions on the availability of soil potash, and the preparation of sugar humus. *Tex. Agr. Exp. Sta. Bul.* 190.
- (24) FREAR, WM., AND ERB, E. S. 1918 Condition of fertilizer potash in Hagerstown silty loam soil. *In* Jour. Agr. Res., v. 15, p. 59.
- (25) FRIEDEL, C., AND SARASIN, E. 1881 Sur le reproduction par voie aqueuse du feldspath orthose. *In* Compt. Rend. Acad. Sci. [Paris], t. 92, p. 1374.
- (26) GALE, H. S., AND HICKS, W. B. 1919 Potash in 1917. U. S. Geol. Survey Min. Res. of U. S., 1917, pt. II, p. 397-481.
- (27) HARDY, W. B. 1900 Conditions which determine the stability of irreversible hydrosols. *In* Proc. Roy. Soc. London, v. 66, p. 111.
- (28) HARTWELL, B. L., AND PEMBER, F. R. 1908 Experiments with feldspathic rock as a source of potassium. *R. I. Agr. Exp. Sta. Bul.* 129.
- (29) HEADDEN, W. P. 1901 The soil. *Col. Agr. Exp. Sta. Bul.* 65, p. 7-10, 28-31.
- (30) HILGARD, E. W. 1911 Soils; Their Formation, Properties, Composition, and Relations to Climate and Plant Growth, p. 99. The MacMillan Company, New York.
- (31) HILGER, A., AND LAMPERT, K. 1887 Über Verwitterungsproducte des Granits. *In* Landw. Vers. Stat., Bd. 33, p. 160.
- (32) HOFFMANN, H. 1864 Über Düngung mit Nephelin-Dolerite. *In* Landw. Vers. Stat., Bd. 6 p. 336.
- (33) HOPKINS, C. G. 1911 Soil Fertility and Permanent Agriculture. Ginn & Co., New York.
- (34) HOPKINS, C. G., MOSIER, J. G., PETTIT, J. H., AND FISHER, O. S. 1913 Bond County soils. *Ill. Agr. Exp. Sta. Soil Rpt.* 8 (appendix).
- (35) HOPKINS, C. G., AND PETTIT, J. H. 1908 The fertility in Illinois soils. *Ill. Agr. Exp. Sta. Bul.* 123.
- (36) HUNT, T. F. 1909 Soil fertility. *Pa. Agr. Exp. Sta. Bul.* 90.
- (37) HUSTON, H. A. 1890 The absorptive power of soils. *Ind. Agr. Exp. Sta. Bul.* 33, p. 46.
- (38) KAHLBERG, L., AND LINCOLN, A. T. 1898 Solutions of silicates of the alkalis. *In* Jour. Phys. Chem., v. 2, p. 77.
- (39) KATZ, F. J. 1916 Feldspar in 1916 U. S. Geol. Survey Min. Res. of U. S., 1916, pt. II, p. 173-184.
- (40) KELLNER, O., et al 1887 Quantitative Bestimmung einiger im Boden vorhandenen absorptiv gebundenen Basen, und Versuche über die Frage, ob die Pflanze nur gelöste und absorbierte oder auch stärker gebundene, unlöslichere Nährstoffe aufnehmen kann. *In* Landw. Vers. Stat., Bd. 33, p. 359.
- (41) KUHLMANN, F. 1855 Sur la formation des silicates par voie humide en général. *In* Compt. Rend. Acad. Sci. [Paris], t. 41, p. 1029.
- (42) LAWES, J. B. 1892 Analysis of drainage water from Broadbalk wheat field, Rothamsted. U. S. Dept. Agr. Off. Exp. Sta. Bul. 8.
- (43) LEMBERG, J. 1876 Ueber Silikatumwandlungen. *In* Ztschr. Deut. Geol. Gesell., Bd. 28, p. 519-621.
- (43a) LEMBERG, J. 1883 Zur Kenntniss der Bildung und Umwandlung von Silikaten. *In* Ztschr. Deut. Geol. Gesell., Bd. 35, p. 557-618.



- (44) LINDER, S. E. AND PICTON, H. 1901 Absorption of bases by colloids. *In* Jour. Chem. Soc. London, v. 61, p. 114, 148.
- (45) LOUGHLIN, G. F. 1915 Recent alunite developments near Marysville and Beaver, Utah. U. S. Geol. Survey Bul. 620-K; Contributions to Econ. Geol., 1915, pt. I, p. 237-270.
- (46) MAGNUS, G. 1850 Über die Ernährung der Pflanzen. *In* Jour. Prakt. Chem., Bd. 50, p. 65-75.
- (47) MILLER, M. F., AND VAN NATTA, E. E. 1915 Availability of the potassium in feldspathic fertilizers. *In* Jour. Assoc. Off. Agr. Chem., v. 1, p. 26. 398.
- (48) MISSOUX: 1853-1854 Sur l'emploi de la poudre des roches granitiques comme excitant de la vegetation. *In* Compt. Rend. Acad. Sci. [Paris], t. 36, p. 1136; t. 37, p. 245.
- (49) MORSE, F. W., AND CURRY, B. E. 1909 Availability of potash in clay and clay loam soil. N. H. Agr. Exp. Sta. Bul. 142.
- (50) NILSON, L. F. 1889 Einige Düngungsversuche mit Feldspath, löslichen Kalisalzen und Thomasschlacke. *In* Landtbr. Akad. Handl. öch Tidskr., 1889, p. 1-16, 273-281. *Abs. in* Centbl. Agr. Chem., Bd. 18, p. 608. Original not seen.
- (51) PETERS, C. 1860 Über die Absorption von Kali durch Ackererde. *In* Landw. Vers. Stat., Bd. 2, p. 113.
- (52) PRIANISCHNIKOV, D. 1906 Feldspath und Glimmer als Kaliquellen. *In* Landw. Vers. Stat., Bd. 63, p. 151.
- (53) PRIANISCHNIKOV, D. 1912 Vegetationsversuche mit verschiedenen kalihaltigen Mineralien. *In* Landw. Vers. Stat., Bd. 77, p. 399.
- (54) ROGERS, W. B., AND ROGERS, R. E. 1848 Decomposition of minerals and rocks by water and carbonated water. *In* Amer. Jour. Sci. Arts, ser. 2, v. 5, p. 401.
- (55) SCHALLER, W. T. Mica in the United States, 1916. U. S. Geol. Survey Min. Res. of U. S., 1916, pt. II, p. 291-308.
- (56) SCHALLER, W. T. 1916 Lithium minerals in 1916. U. S. Geol. Survey Min. Res. of U. S., pt. II, p. 7-17.
- (57) SCHULTZ, A. R., AND CROSS, W. 1912 Potash-bearing rocks of the Leucite hills. U. S. Geol. Survey Bul. 512.
- (58) SKINNER, J. J., AND JACKSON, A. M. 1913 Alunite and kelp as potash fertilizers. U. S. Dept. Agr. Bur. Soils Cir. 76.
- (59) STEIGER, GEO. 1915 Note on muscovite. U. S. Geol. Survey Bul. 620-J.
- (60) STODDART, C. W. 1915 Chemistry of Agriculture, p. 168. Lea and Febiger, Philadelphia.
- (61) STOKLASA, J. 1882 Studien über den Verwitterungsprozess von Orthoklas. *In* Landw. Vers. Stat., Bd. 27, p. 197.
- (62) TREUTLER, C. 1869 Einige Versuche über Löslichmachen des im Boden absorbirten Kalis. *In* Landw. Vers. Stat., Bd. 12, p. 184.
- (63) TREUTLER, C. 1872 Weitere Versuche über Löslichmachung des im Boden absorbirten Kalis. *In* Landw. Vers. Stat., Bd. 15, p. 368.
- (64) TRUE, R. H., AND GEISE, F. W. 1915 Greensand as a source of potassium. *In* Jour. Agr. Res., v. 15, p. 483.
- (65) VAN BEMMELEN, J. M. 1900 Die Absorption von Stoffen aus Lösungen. *In* Ztschr. Anorgan. Chem., Bd. 23, p. 358.
- (66) VAN HISE, C. R. 1904 Treatise on metamorphism. U. S. Geol. Survey Mon. 47, p. 333.
- (67) WAY, J. THOS. 1850 On the power of soils to absorb manure. *In* Jour. Roy. Agr. Soc. England, v. 11, p. 313.
- (68) WHITNEY, W. R., AND OBER, J. E. 1901 The precipitation of colloids by electrolytes. *In* Jour. Amer. Chem. Soc., v. 23, p. 842.
- (69) WOTSCHALL 1901 11<sup>te</sup> Versammlung russischer Naturforscher und Artzte in St. Petersburg. Rpt. Dec. 1901.