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J. H. LONGWELL, *Director*

# The Surface Reactions of Silicate Minerals

PART I. THE REACTIONS OF FELDSPAR  
SURFACES WITH ACIDIC SOLUTIONS

V. E. NASH AND C. E. MARSHALL



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## FOREWORD

*Man's historical tendency to concentrate his activities along certain river courses has been a significant factor for his inland survival. The assured supply of water has usually been considered the cause. We have not emphasized the fact that rivers guarantee a food supply of high quality for man by their repeated flood deposits of weatherable minerals which readily develop into highly productive soils.*

*In this respect, attention may well be called to the significance of the Nile for Egypt, the Euphrates and the Tigris for (Mesopotamia) Iraq, the Hwang-Ho or Yellow for China, the Ganges and the Brahmaputra for India, the Indus for Pakistan, the Rhine for the Netherlands, the Danube for Southeastern Europe, the Po for Italy, and others. The sources of these rivers (or tributaries) are at high elevations of significant rainfall or intensive glacial action. These provide both the water and the pulverized rock it carries and deposits for rapid weathering into the productive soil in the streams' flood plains.*

*This series of publications reports on studies of the reactions and rates of decomposition of pulverized minerals common in soil. The studies emphasize the weathering of the minerals in the soil's reserves to furnish active fertility for the growing crops. Thus, soils are productive not only because of their inventory of nutrient elements adsorbed on the clay, but also because their original silicate mineral reserves are being weathered. As the silicates decompose, they enshroud themselves immediately with a surface layer of clay and saturate its exchange capacity with the ionic products made active by the decomposition. Thus the soluble or salt products are already more or less grouped for plant use as an exchangeable ionic suite in this clay layer. Both the clay and the salts result from the decomposition of the complex silicates.*

*Missouri's extensive research on the formation of clay and its properties provided the methods for measuring the surface reactions of the silicate minerals reported in this series of publications. The surface reactions of some of the silicate minerals in contact with (a) water, (b) acids and (c) salt solutions have been investigated so far.*

*The resulting data point out that the weathering processes must still be going on in our productive soils. With erosion exposing previously unweathered minerals to such action, the weathering processes demonstrated in these studies are making the nutrient contents of the primary silicate minerals available for crop production.*

*We have long known that secondary minerals, like limestone and rock phosphate, break down in acidic soils and represent sustaining fertility rather than starter fertilizers. The research reported here suggests that even the primary minerals, like those composing the granite rock, may be put into the same category, though possibly active or available at slower rates. We are gradually comprehending the chemical processes by which rocks form soil to feed our crops which, in turn, feed us.*

Wm. A. Albrecht

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# The Surface Reactions Of Silicate Minerals

## PART I. THE REACTIONS OF FELDSPAR SURFACES WITH ACIDIC SOLUTIONS

V. E. NASH AND C. E. MARSHALL<sup>1</sup>

### INTRODUCTION

Pedology, the science which seeks to describe and evaluate our soils, and geochemistry, the science which treats of the whole earth as a gigantic chemical laboratory, together face the same paradox. It consists of this: In both sciences the reactions by which the greatest quantity of original mineral is transformed to other compounds are the least well known. These reactions, common to both sciences, are the ones responsible for the decomposition of the feldspar minerals which constitute some 60 per cent of the earth's crust. They furnished almost all the sodium now in the oceans, and almost all the calcium now in the limestones. Soils from which feldspars have disappeared by weathering are generally low in the fertility scale and expensive to bring into high production. Soils containing abundant feldspar particles have higher inherent fertility and any deficiencies they may possess are fairly easy to correct.

The feldspars are three dimensional structures in which a strongly linked framework of oxygen, silicon and aluminum atoms carries a negative electric charge, exactly balanced by potassium, calcium or sodium. In primary rocks other minerals are intermingled with the feldspars. The crystallization and solidification of the mass from an originally liquid condition introduces many localized strains and discontinuities. Thus the first stage in rock breakdown involves the movement of water into minute cracks, with physical separation not only of original mineral grains but frequently of still smaller units. The feldspars commonly contain many minute cracks and cleavages, caused in part by local variations in chemical composition and in part by their possible transitions from high to low temperature forms. Thus a major change, at an early stage in rock breakdown, consists of a large increase in the surface exposed by the feldspar. Further processes then involve chemical changes at these surfaces.

Similar considerations, differing somewhat in degree from the case of the feldspars, apply to other mineral constituents of primary rocks. In all cases weathering processes first become apparent at surfaces. Thus the

<sup>1</sup>Instructor and Professor of Soils, respectively.

surface chemistry of minerals is of prime importance, both in the release of elements into solution and in the appearance of new sparingly soluble phases. These two processes are commonly considered together, but there is already evidence that in some cases they may be separated. It seems advisable, therefore, to investigate first, by the methods of colloid chemistry, the properties of comparatively fresh mineral surfaces. Exchange of cations between such surfaces and solutions in contact with them represents a simple chemical reaction of common occurrence. By studying this exchange, investigators can hope to clarify the essential features of the earliest stages in mineral decomposition.

## REVIEW OF LITERATURE

### Crystal Structure of Feldspars

The stability of minerals toward environmental conditions depends to a large degree upon the manner in which the ions are arranged in the crystal. According to Pauling (31) the ions will arrange themselves in a crystal in such a way that the potential energy is a minimum. The particular configuration in which there is a minimum potential energy will depend upon the conditions under which the mineral was formed. When this mineral is brought in contact with atmospheric conditions, it will tend to change in such a way as to be stable under the new conditions. In some cases this may involve complete breakdown of the structure.

Keller (21) has pointed out that the difference in the energies of formation of minerals apparently controls their order of crystallization, their stability, and their susceptibility to weathering. In support of this, he showed that the Goldich (17) stability to weathering series, the Rosenbusch order of crystallization and the Bowen reaction series all follow this order: olivine, pyroxene, amphibole, biotite, alkali-feldspar, alkali-calcic-feldspar, calcic-alkali feldspar, calcic-feldspar, microcline, and quartz. This also follows the classification of silicates by Struntz (39). From these considerations it seemed necessary to consider somewhat the nature of the feldspar structure in any evaluation of chemical decomposition.

The feldspars are divided into groups on the basis of symmetry. Orthoclase and the barium feldspars are monoclinic with cleavage angles along the (001) and (010) planes at 90°. Microcline and the plagioclase feldspars are triclinic with a cleavage angle of about 86°.

The feldspars are further classified on the basis of chemical composition as shown in the following table.

Monoclinic	
Orthoclase .....	$\text{KAlSi}_3\text{O}_8$
Microcline .....	$\text{KAlSi}_3\text{O}_8$ (actually triclinic)
Celsian .....	$\text{BaAl}_2\text{Si}_2\text{O}_8$

## Triclinic-Plagioclase Feldspars

Albite (Ab)*	.....	$\text{NaAlSi}_3\text{O}_8$
Oligoclase	.....	$\text{Ab}_{90}\text{An}_{10}$ to $\text{Ab}_{70}\text{An}_{30}$
Andesine	.....	$\text{Ab}_{70}\text{An}_{30}$ to $\text{Ab}_{50}\text{An}_{50}$
Labradorite	.....	$\text{Ab}_{50}\text{An}_{50}$ to $\text{Ab}_{30}\text{An}_{70}$
Bytownite	.....	$\text{Ab}_{30}\text{An}_{70}$ to $\text{Ab}_{10}\text{An}_{90}$
Anorthite (An)	.....	$\text{CaAl}_2\text{Si}_2\text{O}_8$

A general theory on the structure of the feldspars was first suggested by Machatschki (25) in 1928. He proposed that the structure was based on frameworks of linked  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra with the cation potassium, sodium, calcium, or barium occupying the interstices in the lattice. He also suggested that the difference between monoclinic and triclinic feldspars was due to the difference in the size of the cations in the interstices, the former containing the larger barium and potassium ions and the latter containing the smaller sodium and calcium ions

These suggestions were proved correct by Taylor (44) (45) (46) by his X-ray study on sanidine (variety of orthoclase) and in a more recent and detailed study of orthoclase (8). According to Taylor, the feldspars are a three-dimensional silicon-oxygen-aluminum network consisting of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra linked together into a ring which forms a continuous chain parallel to the a-axis. Four chains lie side by side, the adjacent chains sharing part of their oxygen atoms. This Si-O-Al framework has a negative charge due to replacement of silicon by aluminum in the tetrahedra, which is balanced, in the case of sanidine, by potassium which fits in the cavities between the chains. It should be borne in mind that these chains are not separate as in the pyroxenes and amphiboles but are linked to adjacent chains forming a continuous three-dimensional network. Nevertheless, this chain type of structure results in a certain degree of flexibility which gives rise to overstructures and other complications, making the study of feldspar structures difficult. According to Rankama and Sahama (33), "If along with a given chemical composition, a definite structure is necessary for the definition of a mineral species, the whole classification of the feldspars becomes hazy."

Taylor and Darbyshire (46) showed that the structure of albite is essentially the same tetrahedral framework as sanidine, with the sodium occupying positions similar to those of potassium in sanidine. In albite the tetrahedra chains collapse and rotate slightly so as to permit a closer grouping of oxygen around the smaller sodium ion, sodium being held in 6-coordination compared to a 9-coordination for potassium.

Taylor and Darbyshire also compared the structures of albite and anorthite. The main difference they found was a doubling of the c-axis in anorthite. Albite had a length of  $7.1 \text{ \AA}$  compared to  $14.2 \text{ \AA}$  for anor-

\*In expressing feldspar composition the abbreviations (Ab) for albite and (An) for anorthite are subsequently used.

thite. They speculated that this change occurred at Ab:An ratio equal to 1, and was due to sodium having 6-coordinating oxygens surrounding it compared with a 7- or 8-coordination around calcium. If this is true, then the albite anorthite series must be considered a double isomorphous series.

The structures of these various feldspars are further complicated by the mixing of minerals within a crystal, resulting in a perthitic structure. The perthite structure is lamellar, consisting of interlayers of two different feldspar species. Kozu and Endo (23) showed in 1921 [confirmed by Taylor (44)], that sodium-potassium feldspars did not form homogeneous crystals but consisted of alternate layers of albite and orthoclase. When these crystals were heated they formed a homogeneous solid solution but on cooling they separated out again to the separate species.

The importance of the perthite structure in the stability of feldspar crystals was well demonstrated by Spencer (36; 37; 38). He studied the alteration by weathering of moonstone from Ceylon. The moonstone consisted of inter-laminated layers of albite and orthoclase in the crystal, giving it a "shiller" effect. The "shiller" effect was responsible for the value of the moonstone as a gem stone. He found in the weathered crystals that cleavage was along the "shiller" plane and not along the usual (010) and (001). There was a differential weathering of the crystal, with the albite being converted into kaolin and the orthoclase unchanged. This left a delicate mesh-work of interlacing laminae of orthoclase and kaolin as the final result.

Further studies (37) of thermal stability of these perthite materials have shown that there is a difference in the effect of heat treatment on the "film" and "string" types of perthite of exsolution origin and on coarser "vein" perthite. This agrees with the conclusions of Dittler and Kohler (14) that the fine perthite can be taken into solution much more readily than the "vein" type. Spencer suggests from X-ray studies that the microperthite by exsolution represents a local segregation of the sodium and potassium ions within the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  framework, followed by contraction in the region rich in sodium. This presumably is the reason for abnormal cleavage planes in the perthite crystal. It would also seem to cause a more open structure for penetration of weathering reagents.

The crystal chemistry of the feldspars is further complicated by the order-disorder condition. Order refers to a consistent arrangement of the ions in the lattice. Barth (2) explained the difference in microcline and sanidine on the disorder-order condition of aluminum and silicon, the sanidine being disordered and microcline ordered. The disorder condition in sanidine gives a higher symmetry than microcline. When microcline is heated it is not readily converted to sanidine, presumably due to the

stable aluminum tetrahedron which makes the diffusion of aluminum to a disordered condition difficult. On the other hand, adularia, the low temperature orthoclase, can be readily converted to sanidine by heating. Buerger (5) explains this on the basis of disorder of the alkali rather than silicon-aluminum. Diffusion of potassium and sodium could readily occur through the octagon cavities when heated, thus converting adularia into the high temperature disordered sanidine.

Since the postulation of Tschermak (47) in 1869 that the plagioclase series is an isomorphous mixture of albite and anorthite end-members, this series has been looked upon as the classical example of a perfect solid-solution. This idea is still prevalent even though Taylor (44) showed in 1933 that the structures of albite and anorthite were different.

This whole subject of plagioclase structures has been discussed by Buerger (5) on the basis of the order-disorder phenomena. He concluded that solid solutions of all compositions of albite and anorthite mixtures are stable at high temperatures, but not at low temperatures where order is required for stability. When feldspars are formed at low temperatures, solid solutions are not formed. He states that the ordering of albite  $\text{AlSi}_3$ , is different from the ordering of anorthite,  $\text{Al}_2\text{Si}_2$ , at low temperature. "Albite must, therefore, order as a different phase from anorthite and at different temperature than anorthite, probably at a lower temperature. It is irrational for amounts of aluminum and silicon in the intermediate feldspars to become ordered without splitting of the crystal into two phases."

Buerger's theory postulates three phases of the plagioclase feldspars, namely, that both albite and anorthite have a common high temperature form but two distinct low temperature forms. The stable low temperature state of the intermediate plagioclase is that of a mixture of end-members, not a solid solution. If formed above the ordering temperature, then cooling causes an unmixed aggregate. If formed below the ordering temperature, a stable mixture of intergrowths and overgrowths of end-members results. All of this is further complicated by a second inversion concerned with the ordering of alkali ions.

From this discussion it seems obvious that a knowledge of the structure of the feldspars is necessary in considering the reactions of alteration. Also, the complexity of the study of these structures is apparent, and at this time the incomplete state of our knowledge concerning them is manifest.

### The Process of Alteration of Feldspars

Although literature on the alteration of feldspars or, more correctly, feldspar-containing rocks, is voluminous in terms of stability, rate of



weathering, and end products formed (Goldich, 17; Graham, 20), reports on studies of the actual processes of alteration are scarce. Perhaps one reason for this is the low solubility of the feldspars, making analytical determinations of small amounts of dissolved material difficult. Recent quantitative micro-methods of analysis should now alleviate this problem. One method which has been used to get around this low solubility has been the use of high temperature and pressure bombs (Norton, 31). Whether data from such studies can be applied to atmospheric conditions is uncertain. In this review only those papers that throw some light on the processes of feldspar alteration under atmospheric conditions, excluding the high temperature-pressure work, will be discussed.

One of the earliest attempts to study decomposition was that by Daubr e (13) about 1870. He studied decomposition by grinding orthoclase dry and in water and in various salt solutions. His work indicated that hydrolysis in pure water was very important in decomposition, more so than in a 3 percent sodium chloride solution. In fact, he concluded that the sodium chloride tended to stop the breakdown. Apparently, he based his criterion of breakdown on the increase in alkalinity, but this may not be a true measure. He also emphasized the importance of  $\text{CO}_2$  in decomposition. Grinding in water was much more effective in the decomposition than grinding dry and then placing in water; he thus anticipated the later conclusion that a protective layer is formed around the particles, which slows down decomposition. The present study substantiates the importance of this surface layer.

The work of Daubr e was extended by that of Cushman and Hubbard (12) in which they carried out essentially the same type of grinding experiment with orthoclase. They concluded that during decomposition a new aluminum silicate surface was formed around the particle, thus stopping the reaction. This was based on an electrolysis experiment in which there was a rapid decomposition at first and then a decrease to very low constant value. This initial rapid decomposition could be repeated by grinding the material and presumably removing the outer layer. They also showed that the presence of ammonium chloride greatly enhanced the decomposition.

Beyer (3), experimenting on the solubility of feldspar in water and various salt solutions in about 1866, discovered the surprising fact that there was a differential rate of weathering of the different cations in the feldspar. Sodium went into solution much more readily than potassium, even though the feldspar contained 8.51 percent  $\text{K}_2\text{O}$  and only 3.37 percent  $\text{Na}_2\text{O}$ . He also showed that exchange of cations from the salt solution was important in the release of cations.

One of the first attempts at studying the chemical processes of de-

composition of feldspar was started about 1920 by Tamm (40; 41; 42; 43). Most of his work centered about the reactions of the finely divided feldspars with acids. His most common procedure was to titrate the feldspar particles with HCl and then back-titrate with KOH. From these curves he was able to draw some rather definite conclusions concerning the decomposition process. The acid treatment liberated from the lattice not only alkali ions but also aluminum, as shown by the pronounced buffering effect in the acid region of the titration curve.

For microcline there was a reversible exchange of hydrogen ions in the pH range 10-6 but irreversible in the acid region. For oligoclase there was an irreversible exchange throughout the pH range. This seems to indicate that the first reaction of decomposition is one of cation exchange, with hydrogen replacing the cation of the mineral. The cation exchange, in turn, apparently sets up an unstable situation with a subsequent breakdown of the lattice. Tamm also emphasized the role of hydrolysis of feldspar in the decomposition. When the minerals were placed in pure water the pH rose to 10.7 for microcline and 11.1 for oligoclase.

Perhaps the greatest recent contribution to our knowledge of the decomposition of feldspars (11; 15) and other silicates [i.e., tremolite (48) and leucite (24)] has come out of the Rostock laboratory of Correns and co-workers. Their general approach to the problem has been to leach the minerals continuously by ultrafiltration or dialysis with various alkaline and acid solutions. From the analysis of elements in the ultrafiltrate it has been possible to postulate some of the reactions taking place between the feldspars and the solution.

They concluded from their work that all of the constituents of the feldspar go into solution in the ionic form, although some may be small fragments of the lattice. This confirms a similar conclusion of Armstrong (1) based on the movement of the constituents in an electric field of an electro-dialyser.

Correns and von Engelhardt (11) state that the alkali metal and calcium are first extracted, leaving a thin layer around the particle, rich in aluminum and silicon, that also eventually dissolves. This silica-alumina residue apparently builds up to a constant thickness and thereafter the decomposition depends upon the diffusion of ions through this layer itself. The composition of this layer and its dissolution depend upon the pH of the medium.

It was found that the minimum  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio of 5.70:1 was obtained at a neutral reaction. This was taken by the authors as evidence against the direct formation of kaolin, with a 2:1 ratio, from feldspars by the removal of the bases. They believed that the clay formation was brought about by the recombination of the ionic constituents in the solu-

tion. They also showed that the dissolution of all of the ions was greater in alkaline or acid solution than in pure water, thus refuting the idea that hydrolytic cleavage is the major reaction in the weathering of the feldspars.

Contrary to the idea of Goldich (17) that the role of carbon dioxide is chiefly that of reducing the alkalinity during the hydrolysis rather than performing as a direct chemical action, their data indicate a direct effect, since the alkalinity was reduced in their experiment by continuous replacement of the solvent.

Recently, Frederickson (16) postulated a mechanism of weathering of albite by water. He visualizes an extension of the albite structure by tetrahedral water (ice structure), making it sterically possible for the hydrogen ion to exchange for the sodium ions of the lattice. The 2-coordinate hydrogen taking the place of 6-coordinated sodium would thus set up an unequal strain in the lattice which would be released by breakdown. However, McConnell (30) questions Frederickson's theory on the basis of four assumptions that were made: (1) Whether or not there is an ice structure of the Helmholtz double layer adjacent to the feldspar; (2) if there is an adequate fit between the feldspar and the ice structure; (3) if hydrogen ions would migrate into the feldspar lattice into regions of high sodium ion concentration with a repulsive charge; and (4) if the sodium ion could be expelled through the ice layer.

In summarizing the literature to date, it may be stated that there is still no theory which will adequately explain the processes through which a feldspar goes from its initial decomposition to the formation of ions or clay.

In the present work a high degree of specificity is shown in the cation exchange reactions which represent the very first stage in decomposition.

## MATERIALS AND METHODS

### Material

The feldspar samples used in this work were obtained from the collection of Ward's Natural Science Establishment, Inc., N. Y. The crystals were handpicked to eliminate any observable impurities. A microscopic examination showed that the amount of impurities present was insignificant. These same samples, with the exception of microcline, have been characterized by Graham (20) regarding the sodium and calcium content and their respective refractive indices. His results are given in Table 1. An analysis of microcline was made, using essentially the same method as Graham. The composition of microcline was found to be 12.75 percent

TABLE 1 -- SODIUM AND CALCIUM CONTENTS OF THE PLAGIOCLASE FELDSPARS AND THEIR RESPECTIVE REFRACTIVE INDICES, GRAHAM (20)

Feldspar	Calcium %	Sodium %	Refractive Index		
			Alpha	Beta	Gamma
Albite	0.4	7.8	1.526	1.530	1.537
Oligoclase	2.8	7.1	1.539	1.543	1.547
Andesine	5.5	4.9	1.547	1.551	1.553
Labradorite	8.2	3.2	1.557	1.560	1.565
Bytownite	9.9	2.1	1.565	1.570	1.574
Anorthite	12.8	0.2	1.572	1.579	1.584

$K_2O$ :1.98 percent  $Na_2O$ :0.288 percent  $CaO$ . To permit comparison of this work with that of others on similar material, the location of the source is given below.

Microcline	Near Bathurst, Ontario, Canada
Albite	Amelia Court House, Virginia
Oligoclase	Mitchel County, North Carolina
Andesine	Pamietfontaine, Transvaal
Labradorite	Near Nain, Labrador
Bytownite	Crystal Bay, Minnesota
Anorthite	Makejima, Japan

### Procedures

*Preparation of Samples:* The coarse fragments of the minerals were broken down to particles of about 2 mm. with a mortar and pestle. These particles were ground in a porcelain ball mill in the presence of benzene, using agate balls. This mixture was rotated at 70 r.p.m. for 48 hours. The ground material was dried on a steam hot plate to remove all of the benzene. The dry powder was then dispersed in water for the mechanical separation. For the 1 percent suspension it was not necessary to use a dispersing agent. The materials were separated into five fractions:  $< 0.5\mu$ ,  $(0.5-1)\mu$ ,  $(1-2)\mu$ ,  $(2-5)\mu$ ,  $(5-20)\mu$ . The coarse fractions down to  $2\mu$  were separated by gravity sedimentation using Berzelius beakers. The smaller fractions were separated in 100 ml. centrifuge tubes using the No. 2 International Centrifuge.

*Preparation of Hydrogen-Systems:* Ten grams of H-Amberlite IR 120 were added to 50 ml. of the feldspar suspension. The suspension contained 3-5 percent solid material. This mixture was shaken vigorously for 5 minutes and then intermittently for an hour. The suspension was separated from the coarse Amberlite by decantation. Two 20-ml. aliquots were removed with a pipette for titration with the base. A 5-ml. aliquot was dried at  $110^\circ C$ . to determine the concentration of the suspension.

*Measurement of Cation Activities:* The activities of the cations were determined by use of clay membrane electrodes of the type developed by

Marshall and co-workers (26; 27; 28). The theory and application of these clay membranes to colloidal suspensions have been discussed in detail by Marshall (29). The membranes used in this study were the non-selective type prepared from H-Putnam clay and heated to 615° according to the procedure of Marshall and Krinbill (26).

### Analytical Methods

*Potassium, Sodium, Calcium, and Strontium:* These elements were all determined by standard quantitative methods with the Perkin-Elmer flame photometer. In the solutions that contained more than one element it was necessary to make the appropriate corrections for the interfering one. This was done by adding various amounts of the interfering element to the standard solutions. In cases where calcium was to be determined in solutions of high concentrations of sodium and potassium, the calcium was precipitated with ammonium oxalate. The calcium oxalate was then converted with perchloric acid to the chloride and determined with the flame photometer.

In the cases where  $\text{SrCl}_2$  was used as the extracting agent, it was necessary to remove the strontium in order to determine the other cations. This was accomplished by precipitating the strontium as the sulfate by adding sulfuric acid to the extent of about 10 times the concentration of strontium. To decrease the solubility of  $\text{SrSO}_4$ , sufficient ethyl alcohol was added to give about 50 percent concentration. The precipitate was separated by filtration on a Whatman No. 44 filter and washed with alcohol containing a small amount of sulfuric acid. The filtrate was then taken to dryness on a steam bath and made up to the desired volume with water for analysis.

*Magnesium:* The magnesium was determined volumetrically with EDTA according to the method of Bray (3). Since calcium is also determined by this method, correction had to be made for calcium.

*Silicon:* Silicon was determined colorimetrically by the reduction of the silicomolybdate. Essentially the same procedure was used as given by Snell and Snell (35), with the exception that in this case the reducing agent used was elon.

*Aluminum:* Aluminum was determined colorimetrically by the 8-hydroxyquinoline method given by Sandell (34). In this method the aluminum quinolate complex is extracted from the solution with chloroform and measured, using the 415 lambda filter in the Bausch and Lomb Monochromatic Colorimeter.

## REACTION OF H-FELDSPAR SYSTEMS WITH BASES

In an attempt to learn something about the acidic characteristics of the feldspars, hydrogen-saturated systems were prepared, using H-Amberlite IR-120. These H-systems were titrated with sodium hydroxide, and the changes in pH and sodium activity determined. Results were obtained for the 2-5  $\mu$  and 1-2  $\mu$  fractions. Two determinations were made on each sample. The second one was usually made 3 to 4 hours after the first one.

It is quite apparent from the titration curves that an acid was formed when the feldspar was treated with H-Amberlite. In most cases the suspension showed a pH of 4.5 to 5.0. When this suspension was placed on a filter and washed with distilled water and then redispersed, the pH was found to rise to about 6.5. This decrease in acidity can be due to (1) the removal of a soluble acid which was formed by the decomposition of the feldspar, (2) the hydrolysis of weakly bound hydroxyl groups on the colloidal particle, or (3) the removal of hydrochloric acid which may have been adsorbed molecularly on the feldspar. This third possibility is due to the inability to remove all of the hydrochloric acid from the Amberlite.

To test this third possibility, an experiment that will be described later was set up to see if hydrochloric could be molecularly adsorbed. No chloride was adsorbed at any of the concentrations tested.

Complete titration curves were run on both the 2-5  $\mu$  fractions and the 1-2  $\mu$  fractions. Since the curves for the 2-5  $\mu$  fractions are similar to those for the 1-2  $\mu$  except for the smaller exchange capacity, the coarse sizes will not be discussed in detail.

*Microcline:* The pH titration curve for microcline is shown in Figure 1A. The first addition of KOH causes a rapid rise in pH. The slope of the curve then decreases to a constant value at about pH 5.8 and remains at this slope up to about pH 8. It is obvious from the pH curve that there is a considerable buffer effect throughout the pH range covered.

This buffering effect in the acid range was ascribed by Tamm (43) to aluminum ions. This is probably partially true. However, this explanation would indicate that the potassium added as the hydroxide would remain in solution as the ion. The activity curves show this is not the case.

The decomposition of the feldspar with time is very apparent, not only in the titration curve of the microcline but in all of the feldspars. Within a period of 5½ hours between titrations, the pH rose from 4.45 to 5.28. If this titration were similar to that of an ordinary weak acid, and if this decrease in acidity were due to merely the hydrolysis of potassium from the feldspar, the two curves would be expected to join

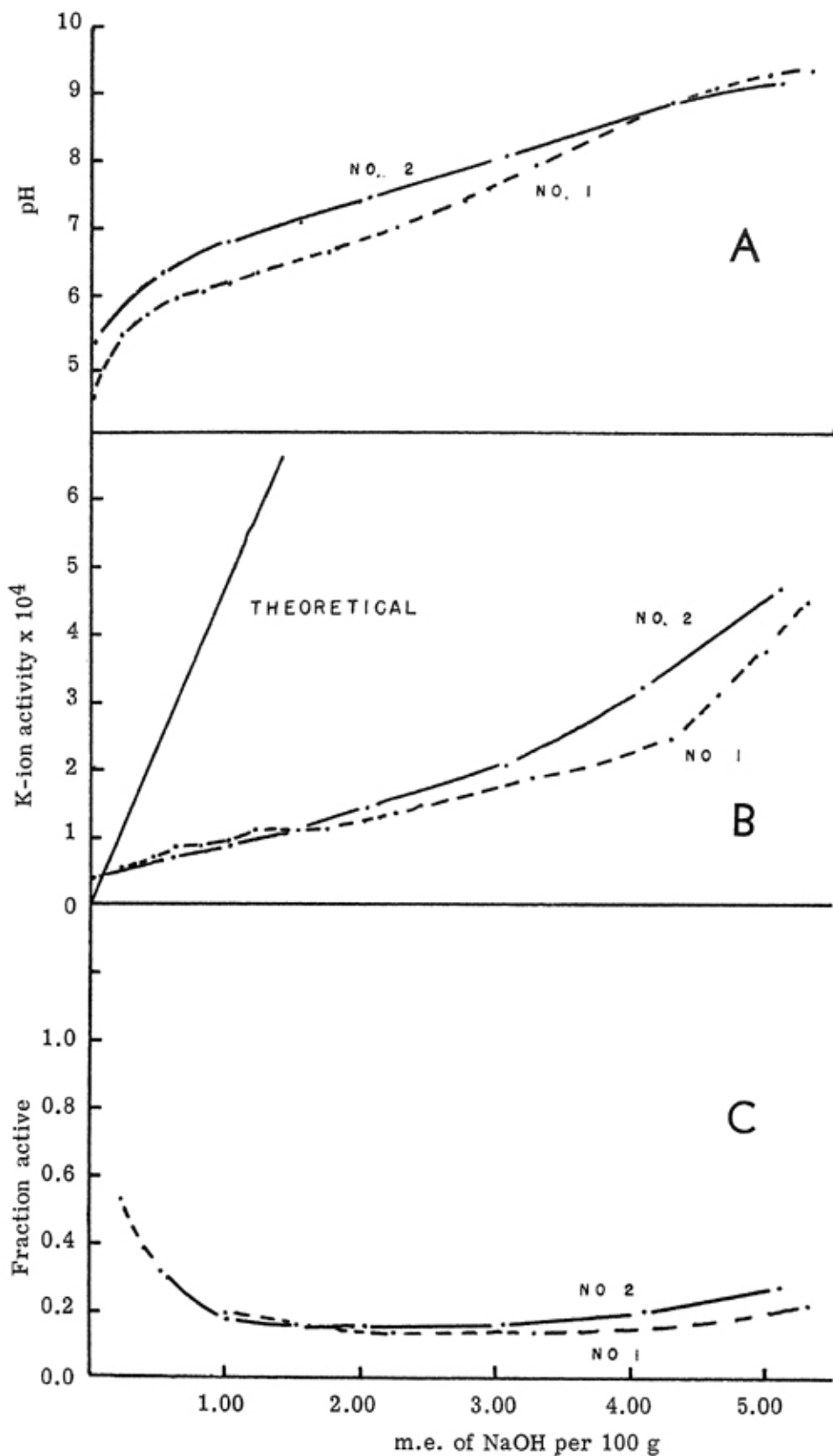


Fig. 1—Titration curves for 4.91 percent microcline, 1 to 2  $\mu$ . Curve No. 2 determined 5½ hours after No. 1.

rapidly and coincide for the remaining part of the curve. This obviously is not the case. The curves remain apart up to pH 8.7

This separation of the curves resembles a strong acid. Again it appears as though we are dealing with a strong acid in solution. It has previously been shown that this could not be molecularly adsorbed hydrochloric acid. Neither could it be hydrochloric acid in solution, since in this case only a small amount of base would be necessary for neutralization. It seems probable from these data that the acid treatment of the feldspar forms soluble, strong, aluminosilicic acid. This acid forms a potassium salt which is only partially dissociated and similar to some colloidal electrolytes.

If the amount of base required to titrate to a pH of 7 is taken as the exchange capacity of the microcline, then there is considerable difference in cation exchange capacity for the two curves. The first curve which was prepared by titrating immediately after treatment with H-Amberlite required 2.25 m.e. of potassium hydroxide per 100 g. to bring the pH to 7.00. The second curve, titrated 5½ hours later, required only 1.5 m.e. per 100 g. to reach pH of 7.0. This means that 0.75 m.e. of hydrogen per 100 g. was consumed in the decomposition process, corresponding to a concentration of  $3.68 \times 10^{-4}$  moles per liter. This is much greater than the amount which corresponds to the decrease in acidity of the suspension. It is conceivable that there was hydrolysis of the potassium and aluminum with a corresponding increase in hydroxyl ions in the solution.

The activity curve for microcline is rather interesting (Fig. 1B). It is readily apparent that much of the potassium is in a non-dissociated state when compared with the theoretical activity curve. This is also apparent from the curve for the fraction active. Most of the fraction active curve showed a dissociation of about 20 percent of the potassium. This seems to offer further proof that the buffering effect is not entirely due to the aluminum, but that an acid substance with a partially dissociated potassium salt is present.

It is interesting to note that although there is a considerable difference in pH values of the two curves at their lower ends, the activities of potassium are about the same. On the other hand, at high pH values, where the two curves come together, the potassium activity for the second titration increases considerably over the first titration. This is probably due to the increased hydrolysis of the silicate at the higher pH, liberating more cations. At the same time there may be an increase in the adsorption of hydroxyl, thus maintaining the pH at about the same value as the previous sample.

The curve for fraction active, or bonding energy (Fig. 1C), shows a high fraction active at the low potassium concentration, or, conversely, the high hydrogen ion concentration. This is what you would expect from



similar data on the clays, where it has been shown that for a small amount of a monovalent cation in the presence of a large amount of hydrogen ions on the exchange complex, the fraction active of the cation is large. As the amount of potassium increases there is an increase in the percentage fixed in a non-dissociated form.

*Albite:* The titration curve for albite is quite similar qualitatively to that for microcline, as shown in Figure 2A, but there are some differences in the details. In this case the base used was NaOH rather than KOH, although Tamm showed that for the pH curve, at least, there was no appreciable difference. The amount of base required to bring the pH up to 7.0, which is considerably less than for microcline, amounts to about 0.82 m.e./100 gm for the first curve and 0.60 m.e. for the second curve.

The activity curves are of about the same order of magnitude as for microcline (Fig. 2B). There is, however, a greater difference in the two activity curves at the lower range than for microcline. This may be due to a greater ease of hydrolysis even at lower pH values than for microcline. At the higher sodium concentration the activity starts to increase more rapidly with increasing base additions.

The fraction active curve (Fig. 2C), indicates that perhaps the sodium complex is more ionized than the corresponding potassium compound from the microcline.

*Oligoclase:* The titration of oligoclase gives a very smooth curve similar to albite, as shown in Figure 3A. It rises rapidly at first (low aluminum), then less rapidly beginning at pH 7.0, and finally approaches a maximum around pH 9.5. The pH curve is similar to that for albite and can probably be interpreted in the same way as the albite curves. It is interesting to note that for quite a few of these minerals there is a crossing of the two curves on the alkaline side. The latter one titrated becomes more acid. This may be due to a greater ease of adsorption of the hydroxyl groups on the surfaces which have been exposed to the solution longest.

The activity curve for sodium (Fig. 3B) is somewhat different from the corresponding curve of albite. Both curves are practically identical except for the most basic end. The activity increases linearly with base added, but not along the same slope as the theoretical curve. Compared with the activity curve of albite, the activity of sodium from oligoclase increases much more rapidly. This could mean that the aluminosilicate formed has a lower bonding energy for sodium, or perhaps less of it formed.

This much greater degree of dissociation for oligoclase is also shown in the curve for the fraction active (Fig. 3C). About 40 percent of the sodium is seen to be active in this case as compared to 20-30 percent for albite.

The cation exchange capacity is about the same as that of albite. The

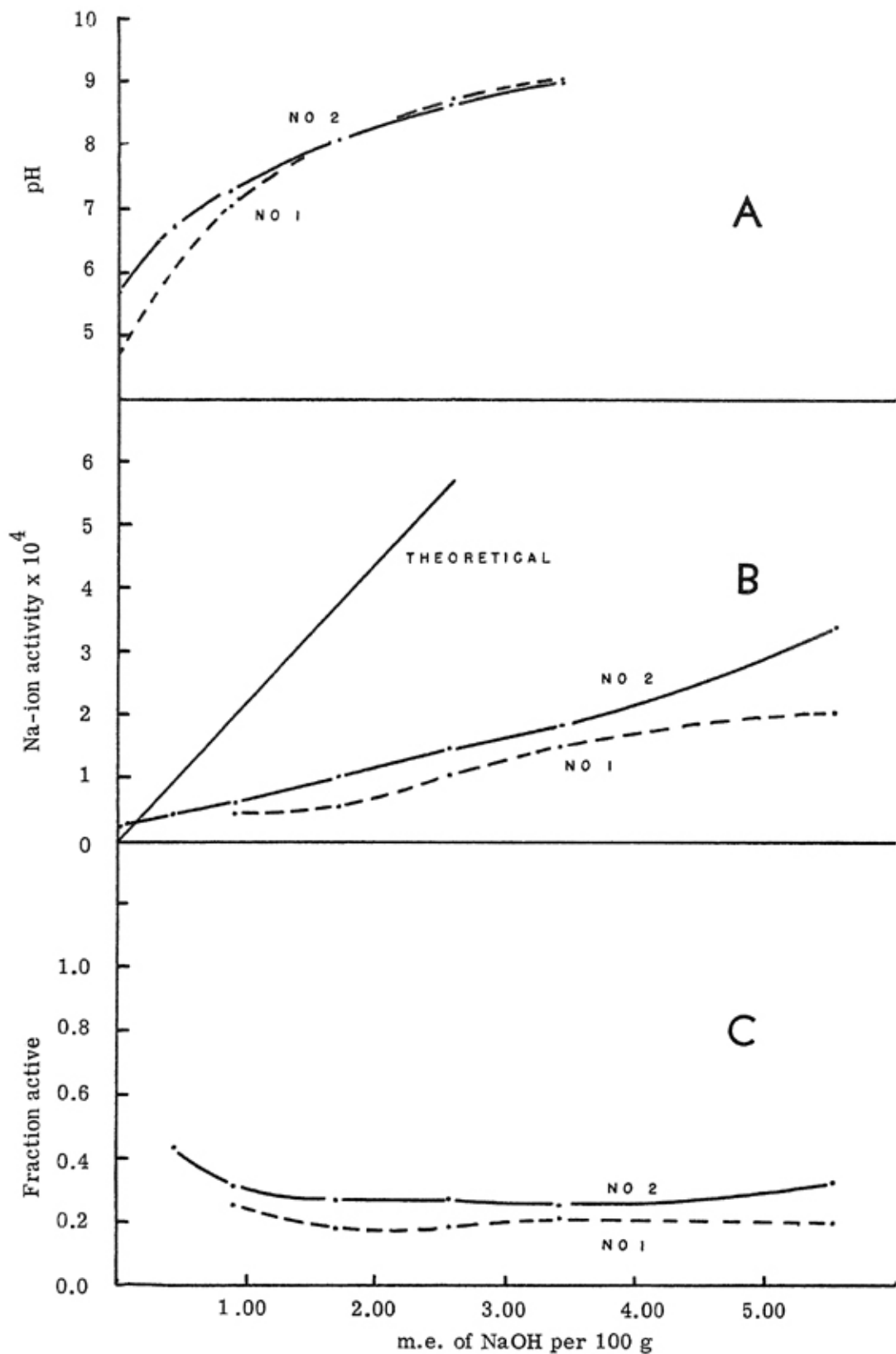


Fig. 2—Titration curves for 2.34 percent albite, 1 to 2  $\mu$ . Curve No. 2 determined 3½ hours after No. 1.

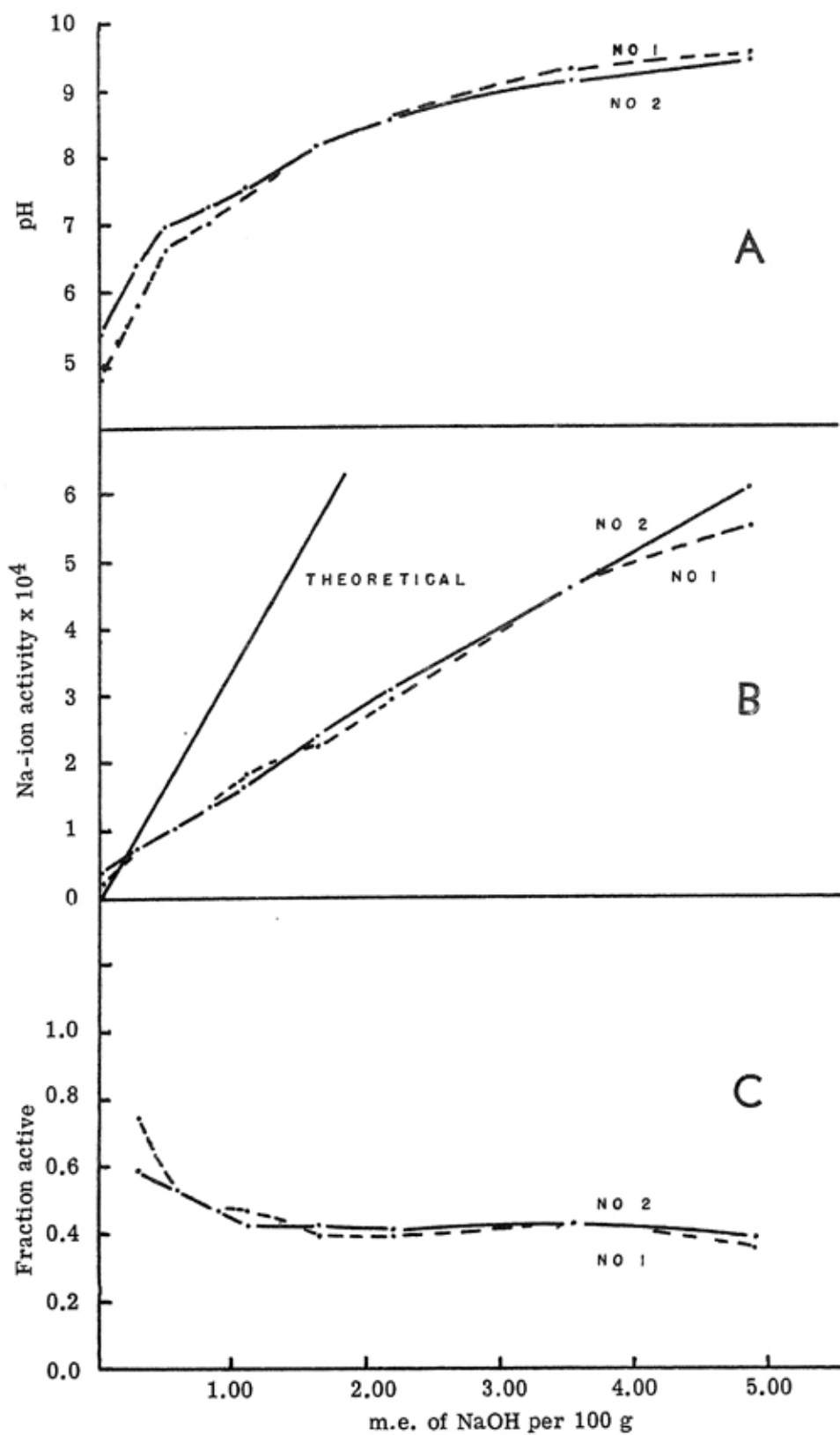


Fig. 3—Titration curves for 3.69 percent oligoclase, 1 to 2  $\mu$ . Curve No. 2 determined 2½ hours after No. 1.

first titration gave a value of 0.80 m.e./100 gm. and the second titration gave about 0.50 m.e./100 gm.

*Labradorite:* The pH titration curve for labradorite (Figure 4A) is very similar to those for albite and oligoclase. It was possible in this case to obtain a more acid suspension, about pH 4. Otherwise, the curve is normal, with a slight indication of an inflection at pH 6.5. The pH rose one unit, from 4.00 to 5.00 in 5 hours, before the second titration. The second curve, as would be expected for a strong acid, remained well separated from the first curve up to pH 9, where the two joined.

The activity curves for the two titrations are nearly identical (Fig. 4B). They are similar in shape and magnitude to those of the oligoclase curve. The activity increases linearly with increasing concentration of base.

The fraction active at the low concentration of base is very high (as in andesine), indicating cations which come readily into solution (Fig. 4C). The fraction active gradually decreases until it reaches a rather constant value of 0.3.

*Bytownite:* The bytownite curve (Figure 5A) again is quite different from the previous curve for labradorite. The initial pH is very low and the change in pH with increasing increments of base is small. The titration curve was not carried out to a pH of 7.00, but it was obvious that it would require about 6.5 to 7.0 m.e. of sodium per 100 g to neutralize the suspension. This is in accord with exchange data which will be presented later showing an exchange capacity for potassium in the order of 6-9 m.e.

The activity curve (Fig. 5B) is also unique in that the initial activity is much greater than for the first increments of base. This indicates an increase in bonding energy of sodium, due to the increase in hydroxyl concentration. The mechanism by which this could happen is not apparent from the data.

The fraction active (Fig. 5C) was similar to those of andesine and labradorite with a very high fraction active at the beginning and then decreasing with addition of base to a rather constant value of 0.38.

*Anorthite:* The titration curve for anorthite (Figure 6A) is very similar to that for albite, oligoclase and some of the other minerals.

The activity curve (Fig. 6B) is normal, increasing rather rapidly with increase in base. The second curve is somewhat higher than the first; this is especially true at the upper range of concentrations.

The curve for the fraction active (Fig. 6C) is not much different from the curves of the other feldspars. Perhaps the most conspicuous difference in these curves is the higher fraction active of sodium, around 0.4 to 0.5. This high value may be due to the larger amount of cations coming into solution from breakdown of anorthite.

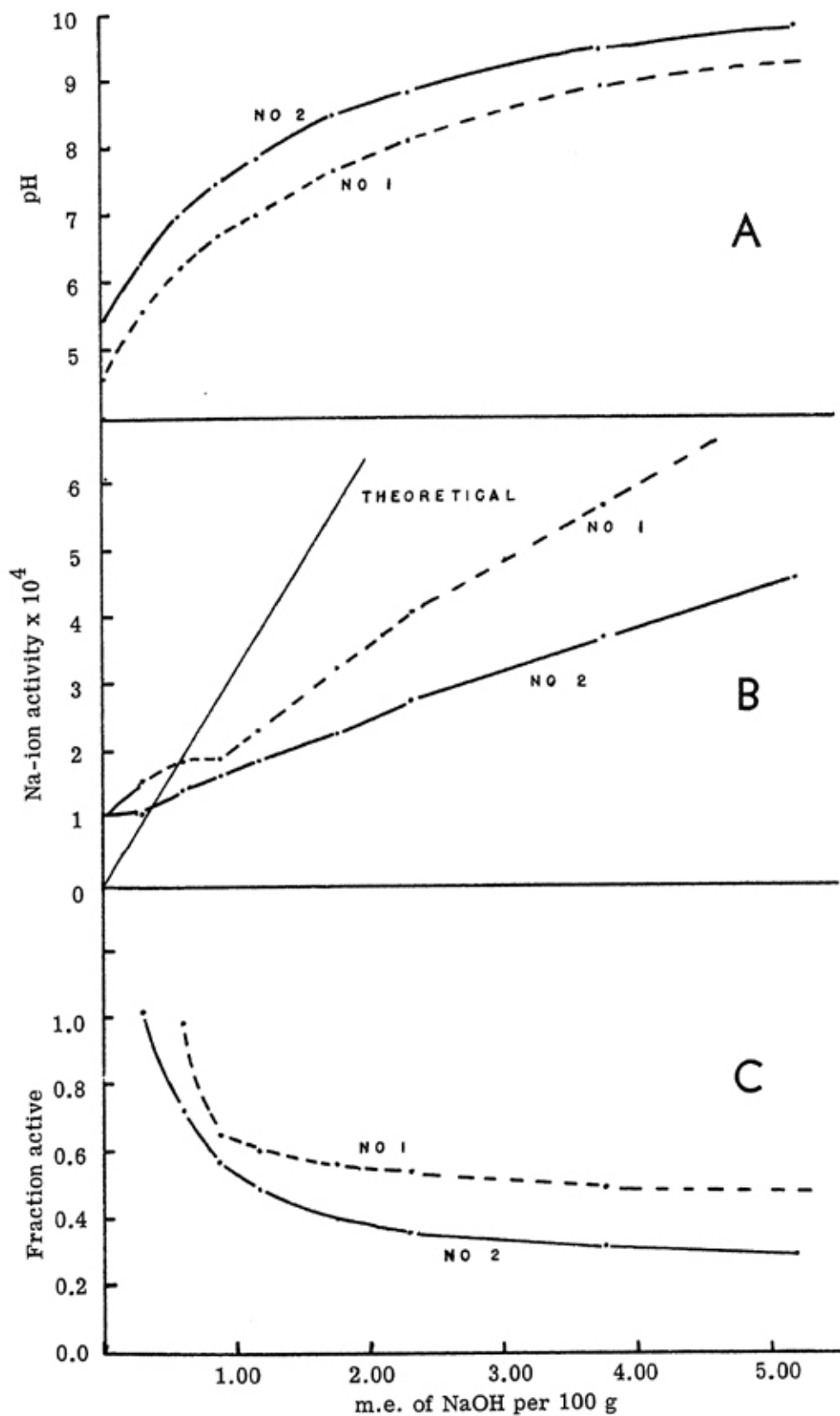


Fig. 4—Titration curves for 3.95 percent labradorite, 1 to 2  $\mu$ . Curve No. 2 determined 5 hours after No. 1.

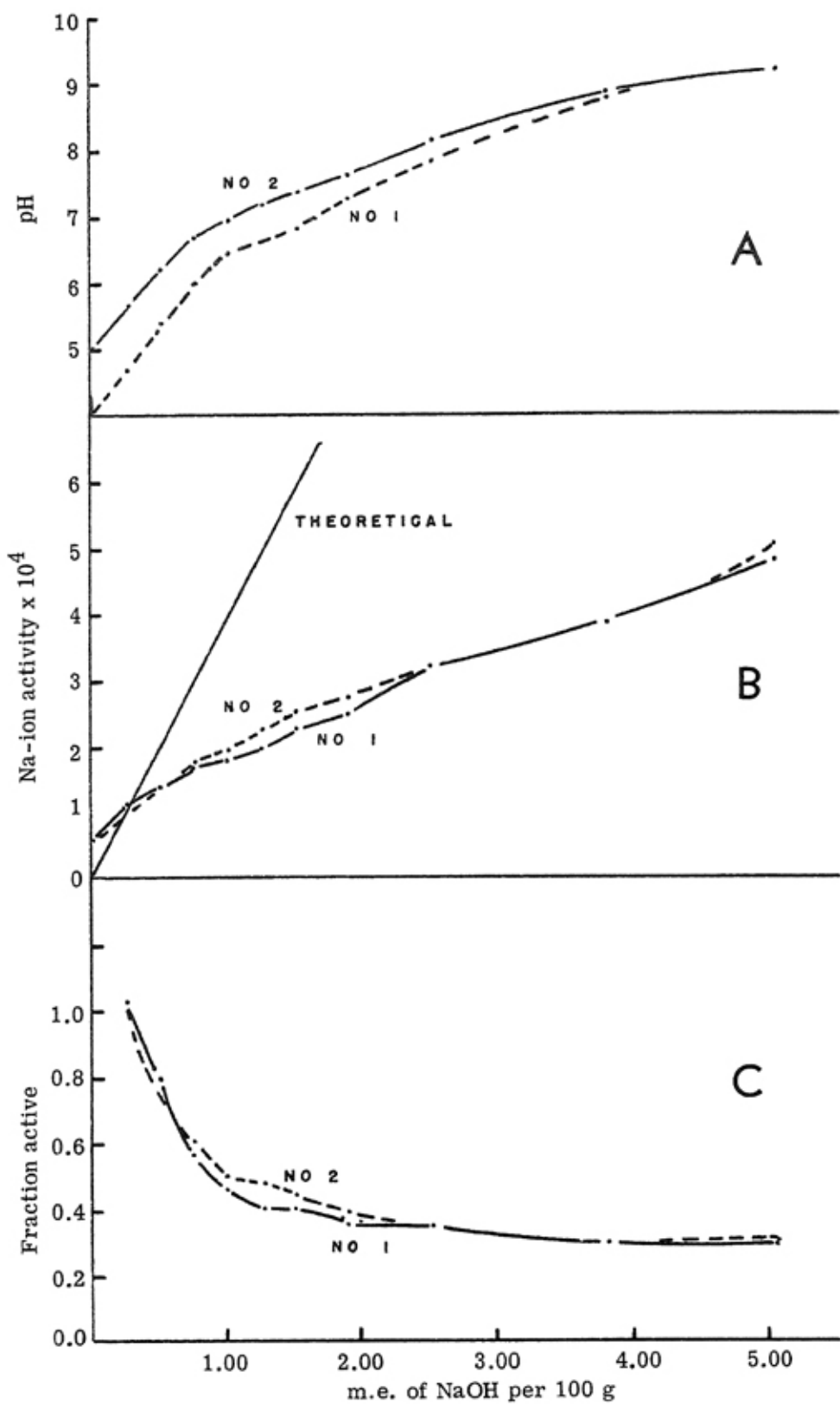


Fig. 5—Titration curves for 2.20 percent bytownite, 1 to 2  $\mu$ . Curve No. 2 determined 3 hours after No. 1.

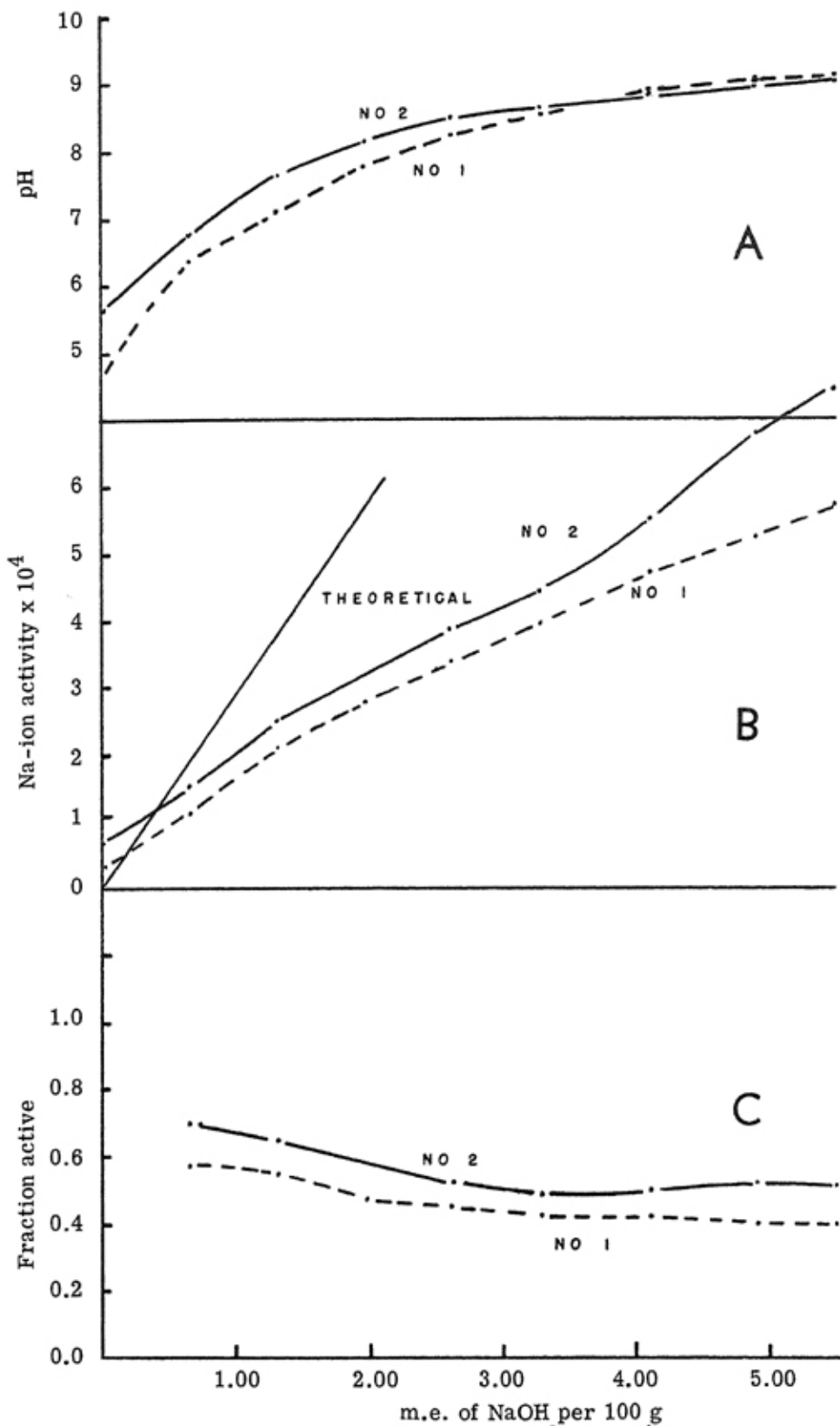


Fig. 6—Titration curves for 3.06 percent anorthite, 1 to 2  $\mu$ . Curve No. 2 determined 3½ hours after No. 1.

# INTERACTION OF FELDSPARS WITH HYDROCHLORIC ACID

## Albite

The following experiment was set up to check the possibility of molecular adsorption of HCl. One gram samples of unfractionated albite were suspended in 100 ml of hydrochloric acid of various concentrations. Measurements were made in the suspension of chloride activity, sodium activity, and pH at periods of 15 minutes, 4 hours, 15 hours, and 63 hours after preparation. The results are in Table 2.

TABLE 2 -- CHLORIDE ADSORPTION AND SODIUM RELEASED FROM ALBITE BY HYDROCHLORIC ACID SOLUTIONS

Initial Solutions						
	Lab. No.	PH	Chloride activity mols/l			
	1	4.32	$8.85 \times 10^{-5}$			
	2	3.33	$4.67 \times 10^{-4}$			
	3	3.02	$9.75 \times 10^{-4}$			
	4	2.31	$4.80 \times 10^{-3}$			
	5	2.00	$9.85 \times 10^{-3}$			
	6	7.00				
After 15 minutes						
Lab. No.	Chloride activity mols/l	Sodium activity mols/l	pH	Chloride activity mols/l	Sodium activity mols/l	pH
1	$1.04 \times 10^{-4}$		8.90	$1.22 \times 10^{-4}$	$2.32 \times 10^{-4}$	8.52
2	$4.58 \times 10^{-4}$		6.68	$4.95 \times 10^{-4}$	$6.35 \times 10^{-4}$	7.48
3	$8.90 \times 10^{-4}$		5.72	$9.40 \times 10^{-4}$	$1.00 \times 10^{-3}$	6.40
4	$4.70 \times 10^{-3}$		2.60	$5.00 \times 10^{-3}$		2.72
5	$9.50 \times 10^{-3}$		2.12	$1.08 \times 10^{-3}$		2.20
6		$1.85 \times 10^{-4}$	9.16			
After 4 hours						
After 15 hours						
1	$1.45 \times 10^{-4}$	$3.40 \times 10^{-4}$	8.73	$1.00 \times 10^{-4}$	$3.90 \times 10^{-4}$	8.38
2	$5.12 \times 10^{-4}$	$6.55 \times 10^{-4}$	7.56	$4.50 \times 10^{-4}$	$6.75 \times 10^{-4}$	7.72
3	$1.08 \times 10^{-3}$	$9.90 \times 10^{-4}$	6.60	$9.30 \times 10^{-4}$	$9.90 \times 10^{-4}$	6.83
4	$5.20 \times 10^{-3}$		2.73	$4.50 \times 10^{-3}$		2.83
5	$1.10 \times 10^{-2}$		2.20	$9.80 \times 10^{-3}$		2.25
6	$3.67 \times 10^{-5}$	$2.85 \times 10^{-4}$	9.26	$2.76 \times 10^{-5}$	$4.18 \times 10^{-4}$	9.12
After 63 hours						

It is immediately evident that there is no adsorption of chloride ions on the feldspar particles. The chloride activity actually increases a little as compared with the initial concentration in the solutions. This may be due to a small amount of chloride in the original mineral or perhaps, more likely, there is negative adsorption. It is also apparent that increasing the concentration of hydrochloric acid did not cause an increase in the chloride adsorption. The data indicate that there is an increase in the chloride activity in the solution up to 15 hours, but at 63 hours it decreases slightly. In a long period of time some of the chloride may diffuse into the particle or amorphous layer and perhaps be adsorbed.

The activity of cations, expressed as sodium, released by the acid solutions was determined for the neutral and alkaline pH values. No at-



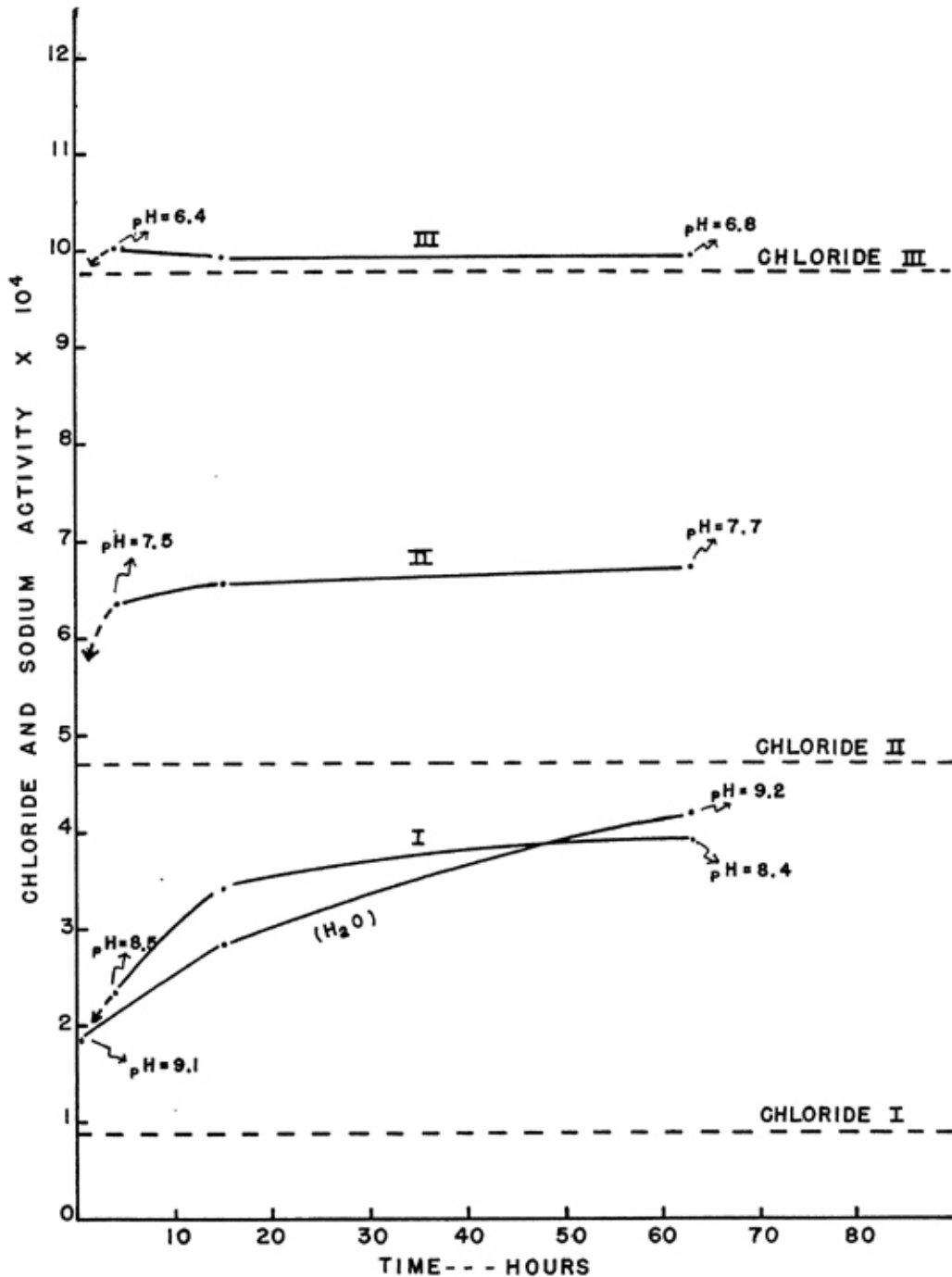


Fig. 7—The release of sodium from albite in water in hydrochloric acid solutions as a function of time.

tempt was made to measure sodium in the acid region because of attack by the acid on the membranes. It is apparent from Table 2 that the ac-

tivity of the sodium released is a direct function of the concentration of the acid. For the acid solutions there was no significant change in the activity of sodium after the first 15 minutes, showing that the reaction is rapid and goes to completion in a short time. The reaction with water alone, however, is somewhat slower. The sodium activity increased from  $1.85 \times 10^{-4}$  moles per L. in 15 minutes to  $4.18 \times 10^{-4}$  per L. in 63 hours. Although the final activity of sodium in the water suspension was slightly higher than in the hydrochloric acid solution which was initially pH 4.32, the latter solution reacted much more rapidly. It seems from this that the rate of release of sodium from the lattice is enhanced by an increase in hydrogen ion concentration, but given sufficient time the equilibrium condition may be the same.

The results of the sodium activity determinations and some of the pH values are given in Figure 7. The three levels of hydrochloric acid and chloride are indicated by horizontal lines across the figure.

### Discussion

The two lowest curves of Figure 7 illustrate the fact that the initial attack on the surface occurs more rapidly in the presence of free acid than in water alone, and that eventually the establishment of alkaline conditions causes greater liberation of sodium in the distilled water treatment than in the most dilute acid used. With larger additions of acid, (curves II and III), the initial attack is rapid, but the sodium activity over and above that equivalent to the chloride becomes much smaller. Thus in III a steady state is reached, slightly on the acid side of neutrality, in which the measured sodium activity is only about 2 percent above that of the chloride. This result suggests strongly that near neutrality, in the presence of salt, the surface structure is stable and that it participates in a reversible reaction between sodium and hydrogen ions. This conclusion is similar to Tamm's for microcline.

### Reaction of Various Feldspars with HCl

To determine further the stability of the various feldspars in an acid medium, the following experiment was conducted. Two-tenths gram of 2 to 5  $\mu$  particles was dispersed in 20 ml. of solution. The series of eight solutions ranged in acid-base contents from 0.1 ml. of 0.1 N NaOH to 1.92 ml. of 0.1 N HCl. All series were run in duplicate. The minerals used in this experiment represent the entire plagioclase series and microcline. The relative decomposition was determined by measuring the pH of the solution with the glass electrode. Each suspension was left seven weeks in an attempt to reach equilibrium before measurements were made.

The results of this experiment are presented in two ways in Figures 8 and 9. Figure 8 shows the pH versus the chemical composition of the

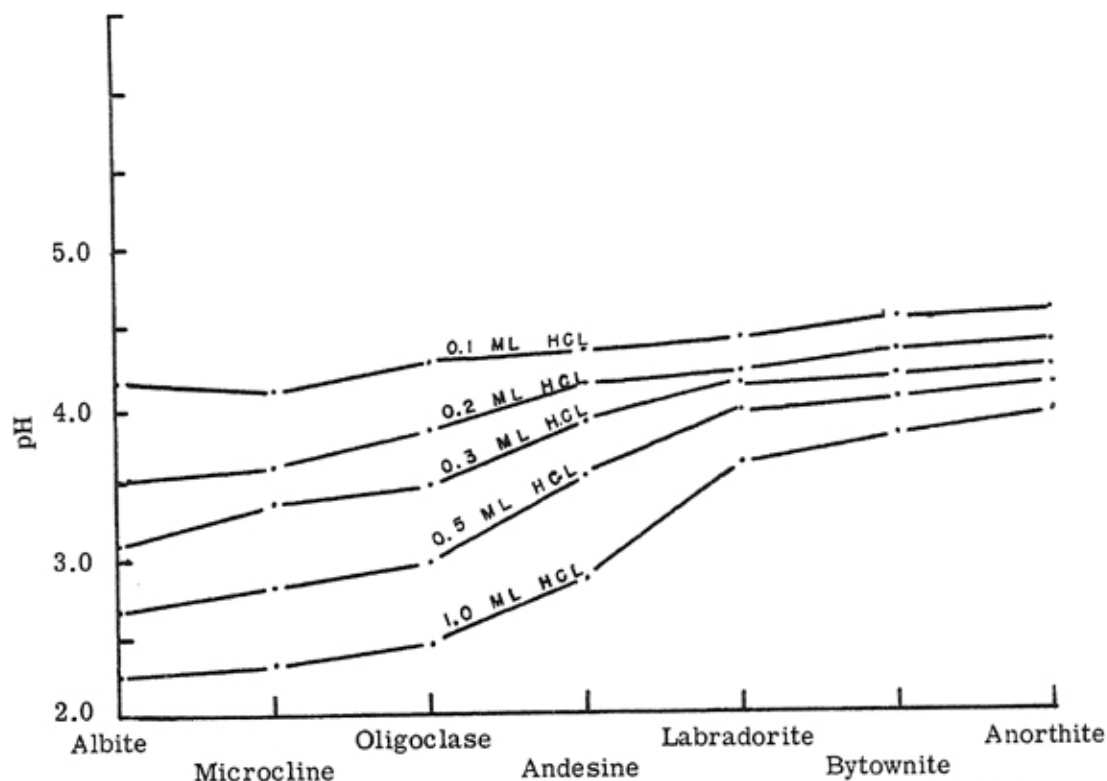


Fig. 8—Curves showing the relative ease of decomposition of the feldspars in hydrochloric acid.

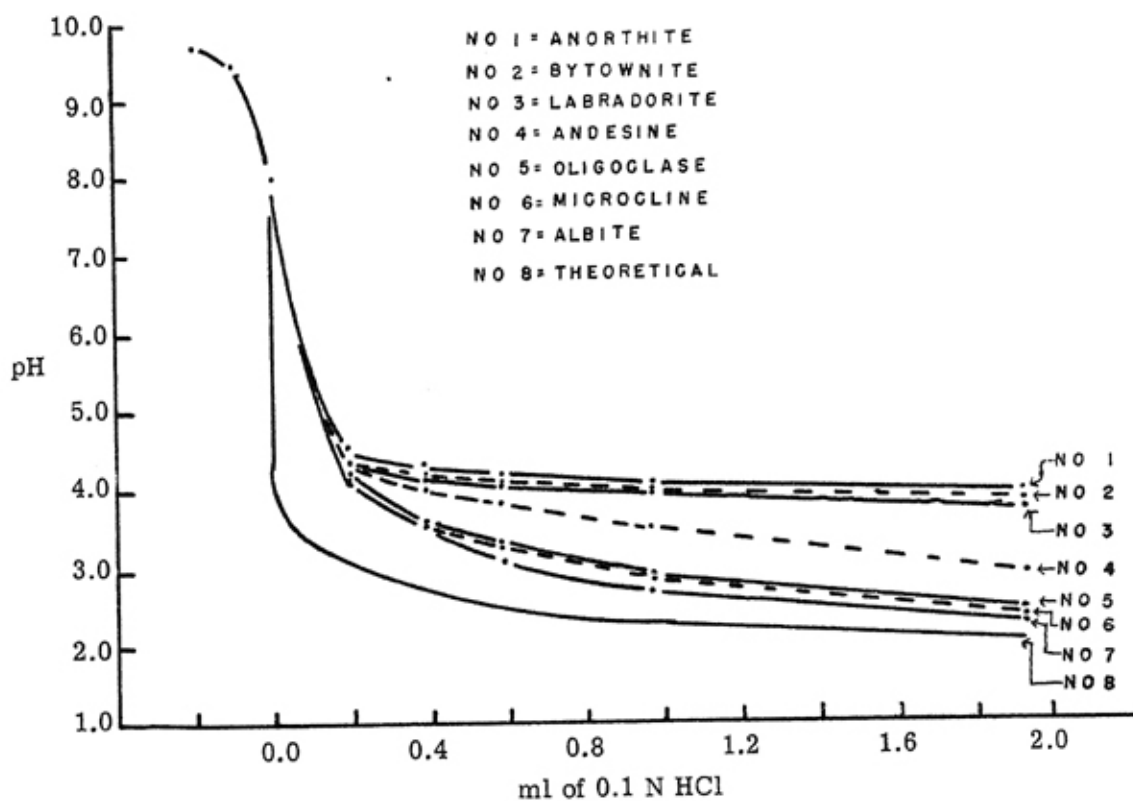


Fig. 9—Titration curves showing the decomposition of the feldspars in hydrochloric acid.

feldspars for the various acid concentrations. The curves show that the calcium-rich feldspars are much more easily broken down than the sodium-potassium members. This is especially apparent for the highly acidic solutions. For the weaker solutions the effect of the chemical composition on the breakdown is not so appreciable, although it is measurable. It seems from this, and from other evidence presented later, that the order of the stability of the feldspars depends to a large degree on the pH of the solution. Anorthite seems to be very sensitive to pH whereas albite is not.

The same data, plotted as the more conventional titration curve, are shown in Figure 9. Here again the buffering effect is quite apparent between pH 4 and 6. This is especially true for microcline, albite, and oligoclase, but is not so noticeable for the calcium-rich members. It is interesting how in an acid medium the curves for microcline, albite, and oligoclase are grouped together, while anorthite, bytownite, and labradorite form another group. Andesine takes an intermediate position between them. These groups may be related to the particular type of structure in the two groups of minerals. The pH values in the alkaline solutions were rather erratic, probably due to carbon dioxide adsorption from the atmosphere. For this reason the values are not considered very reliable.

The suspensions of oligoclase, labradorite, and bytownite were left for seven months, at which time the supernatant liquid was separated by centrifugating and used for the determination of sodium, calcium, and pH. The pH values in all cases increased somewhat during the seven months. Although the change in pH was not great, in some cases it indicated that a long period of time was required to reach an equilibrium between feldspar particles and acid solutions. It is likely that slow breakdown would continue until either all the acid was consumed or the feldspar completely broken down.

The amounts of sodium released are shown in Figure 10 and Table 3. There was an increase in sodium dissolved with increased acidity, as would be expected. In general, the amount released was correlated with chemical composition, save for bytownite. Bytownite always seemed to release a large amount of sodium in spite of its low sodium composition. Apparently sodium in a calcium-rich feldspar is held in a more unstable position than in the corresponding albite structure. There appears to be a minimum in the sodium-release curves for the first increment of acid. However, since this is not true for the calcium curve, this high sodium release for the water suspension is probably due to the hydrolysis of the glass bottle, in this slightly alkaline medium.

The calcium released was about what would be expected as seen in Figure 11 and Table 3. There was a gradual increase in calcium released with increasing acid concentration. Also, the amount released followed the chemical composition of the feldspar closely.

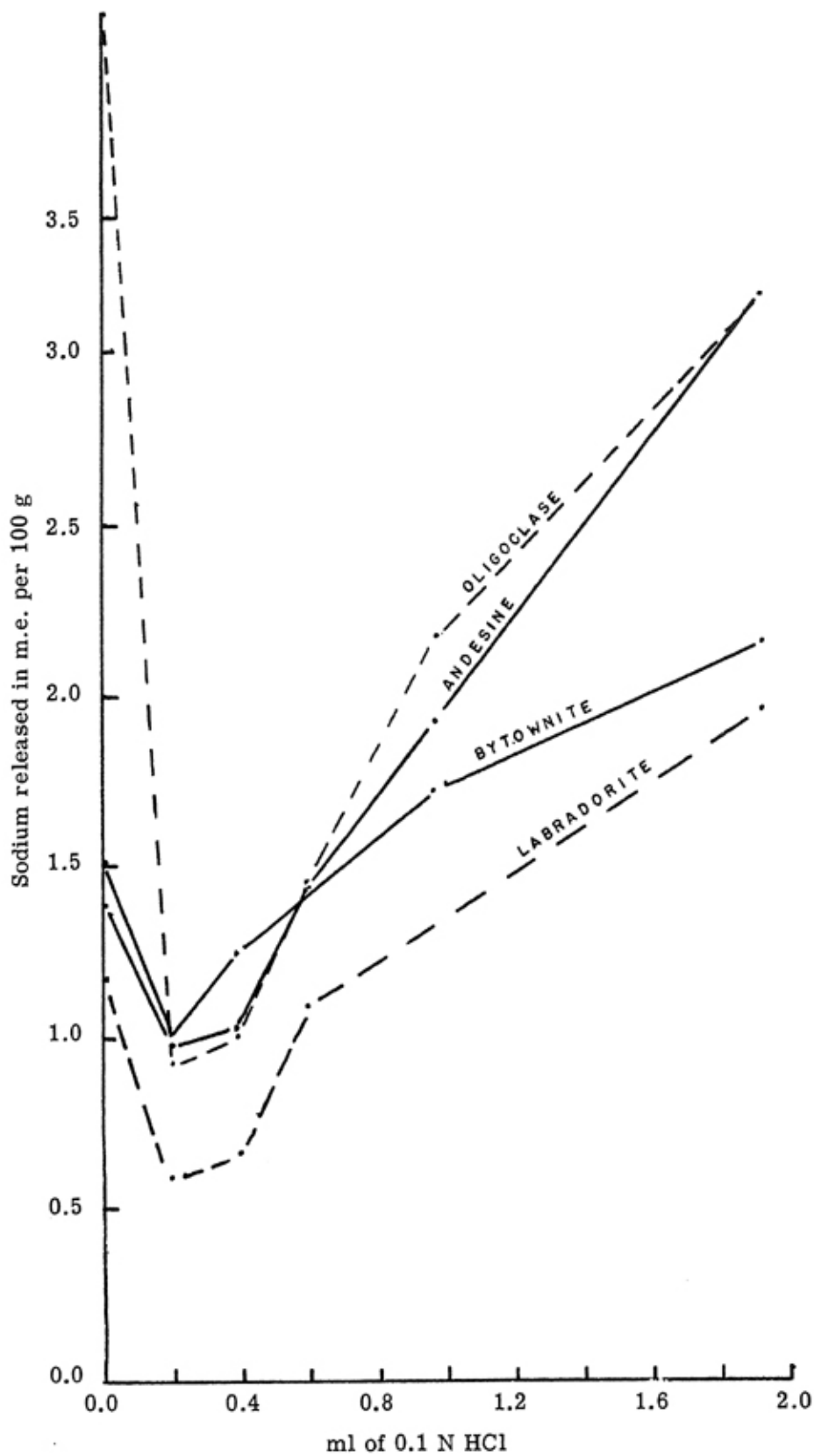


Fig. 10—Curves showing the sodium released by ...ne of the feldspars in hydrochloric acid solutions.

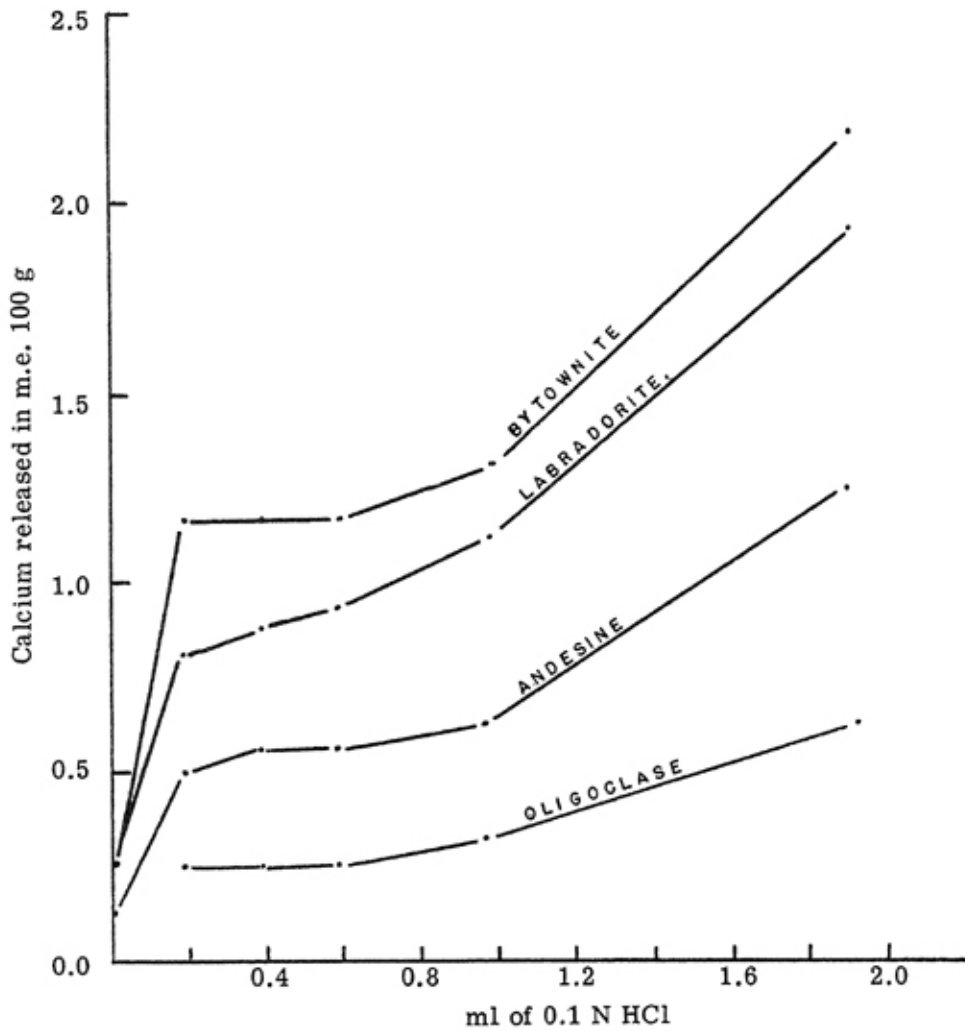


Fig. 11—Curves showing the calcium released by some of the feldspars in hydrochloric acid solutions.

TABLE 3 -- SODIUM AND CALCIUM RELEASED IN DECOMPOSITION OF FELDSPARS IN HYDROCHLORIC ACID

No.	pH		Sodium released m.e./100 gm	Calcium released m.e./100 gm
	HCl solution	Suspension 7 weeks		
Oligoclase				
3	7.00	8.04	7.41	
4	3.17	4.24	4.43	0.93
5	2.71	3.76	4.20	1.01
6	2.54	3.46	4.15	1.46
7	2.32	2.97	3.72	2.17
8	2.17	2.43	2.93	3.17
Andesine				
3	7.00	7.80	7.25	1.39
4	3.17	4.33	4.82	
5	2.71	4.06	4.23	1.09
6	2.54	3.87	4.11	1.44
7	2.32	3.52	3.93	1.92
8	2.17	2.85	3.51	3.18
Labradorite				
3	7.00	7.94	7.38	1.17
4	3.17	4.38	4.74	0.59
5	2.71	4.17	4.30	0.66
6	2.54	4.10	4.18	1.09
7	2.32	3.92	4.04	1.34
8	2.17	3.60	3.85	1.95
Bytownite				
3	7.00	7.86	7.27	1.52
4	3.17	4.51	6.39	1.03
5	2.71	4.30	4.30	1.27
6	2.54	4.14	4.12	1.42
7	2.32	4.00	4.09	1.76
8	2.17	3.75	3.95	2.16

### FELDSPAR DECOMPOSITION IN HCl AND NH<sub>4</sub>Cl SOLUTIONS

In most of the previous studies on the decomposition of the feldspars, acids have been used to a considerable extent as the reagents bringing about the decomposition. To compare these decomposition results from salt solutions with those from acid decomposition, the following experiment was performed. The amounts of calcium, potassium, sodium, silicon, and aluminum released by 0.01 N solutions of HCl, NH<sub>4</sub>Cl, and water were determined for all of the plagioclase series and for microcline. For this study the 5 to 20  $\mu$  fraction was used. This made it possible to compare the results with those obtained by Graham (20) in his weathering study of the same minerals using H-clay systems.

#### Procedure

Two-gram samples of the 5 to 20  $\mu$  fraction of the feldspar were weighed into a 100-ml centrifuge tube. To this was added 50 ml of 0.01 N

$\text{NH}_4\text{Cl}$ , 0.01 N HCl or water. These mixtures were stirred until all the aggregates were broken up. They were then placed on a mechanical shaker and shaken for 24 hours. Next, the suspensions were centrifuged at 1500 r.p.m. until clear. When clear, the supernatant liquid was removed for analysis. The outline of the experiment is shown in Experimental Plan I.

## EXPERIMENTAL PLAN I

OUTLINE OF EXPERIMENT FOR COMPARING THE SURFACE INTERACTIONS  
OF THE FELDSPARS WITH RESPECT TO AMMONIUM CHLORIDE AND  
HYDROCHLORIC ACID

Lab. No.	Mineral	First Exchange Solution	Second Exchange Solution
29	Microcline	0.01 N HCl	0.01 N $\text{NH}_4\text{Cl}$
30	Albite	0.01 N HCl	0.01 N $\text{NH}_4\text{Cl}$
31	Oligoclase	0.01 N HCl	0.01 N $\text{NH}_4\text{Cl}$
32	Andesine	0.01 N HCl	0.01 N $\text{NH}_4\text{Cl}$
33	Labradorite	0.01 N HCl	0.01 N $\text{NH}_4\text{Cl}$
34	Bytownite	0.01 N HCl	0.01 N $\text{NH}_4\text{Cl}$
35	Anorthite	0.01 N HCl	0.01 N $\text{NH}_4\text{Cl}$
36	Microcline	0.01 N $\text{NH}_4\text{Cl}$	0.01 N HCl
37	Albite	0.01 N $\text{NH}_4\text{Cl}$	0.01 N HCl
38	Oligoclase	0.01 N $\text{NH}_4\text{Cl}$	0.01 N HCl
39	Andesine	0.01 N $\text{NH}_4\text{Cl}$	0.01 N HCl
40	Labradorite	0.01 N $\text{NH}_4\text{Cl}$	0.01 N HCl
41	Bytownite	0.01 N $\text{NH}_4\text{Cl}$	0.01 N HCl
42	Anorthite	0.01 N $\text{NH}_4\text{Cl}$	0.01 N HCl
43	Microcline	Water	0.01 N HCl
44	Albite	Water	0.01 N HCl
45	Oligoclase	Water	0.01 N HCl
46	Andesine	Water	0.01 N HCl
47	Labradorite	Water	0.01 N HCl
48	Bytownite	Water	0.01 N HCl
49	Anorthite	Water	0.01 N HCl

Two grams of 5-20  $\mu$  feldspar particles were treated with 50 ml of the indicated solutions.

### Results

According to the results shown in Table 4, perhaps the most obvious difference in reactions of the exchange solutions is the greater amounts of elements released by the HCl solutions. With the exception of anorthite, about two times as much calcium was released by HCl as by  $\text{NH}_4\text{Cl}$  and nearly 10 times as much as by water. The ratio of sodium removed by HCl to that by  $\text{NH}_4\text{Cl}$  varied from 4 to 10, increasing in general, from the sodium-potassium rich feldspar minerals to the calcium-rich minerals.

There seemed to be no consistent order in the release of cations by the different feldspars. There is a different order of release for each of the



TABLE 4 -- SURFACE INTERACTIONS OF THE FELDSPARS WITH RESPECT TO AMMONIUM CHLORIDE AND HYDROCHLORIC ACID

Lab. No.	Mineral	Ca	Na	K	Si	Al	Ca	Na	K	NH <sub>4</sub>	Si	Al
		HCl Treatment					NH <sub>4</sub> Cl Treatment					
29	Microcline	0.20	0.10	0.20	.352		0.08	0.06	0.09		.176	
30	Albite	0.85	0.32	0.06	.600		0.25	0.04	0.03		.144	
31	Oligoclase	0.33	0.55	0.10	.444		0.08	0.06	0.02		.146	
32	Andesine	0.62	0.58	0.11			0.15	0.02	0.03		.230	0.00
33	Labradorite	0.85	0.42	0.09	.773		0.20	0.01	0.02		.170	0.00
34	Bytownite	0.73	1.25	0.04			0.23	0.06	0.02		.173	0.00
35	Anorthite	0.85	0.18	0.02			0.25	0.02	0.01		.132	0.16
		NH <sub>4</sub> Cl Treatment					HCl Treatment					
36	Microcline	0.10	0.02	0.15	.076		0.18	0.09	0.13	.140	.248	
37	Albite	0.33	0.08	0.04	.116	0.0	0.52	0.24	0.03	.226	.392	1.31
38	Oligoclase	0.18	0.12	0.04	.083	0.0	0.15	0.28	0.03	.107	.301	1.39
39	Andesine	0.25	0.08	0.05	.089	0.0	0.40	0.43	0.05	.140	.695	2.90
40	Labradorite	0.30	0.07	0.06	.130		0.48	0.25	0.04	.125	.696	2.46
41	Bytownite	0.52	0.12	0.04	.154		0.57	1.15	0.01	.189	1.16	
42	Anorthite	0.15	0.02	0.02	.308		0.78	0.21	0.01	.078	1.23	
		Water					HCl Treatment					
43	Microcline	0.03	.012	.027	.042		0.20	0.11	0.19		0.30	1.79
44	Albite	0.08	.048	.000	.076	0.00	0.82	0.30	0.03		0.48	
45	Oligoclase	0.05	.072	.007	.052	0.00	0.27	0.36	0.06		0.40	1.80
46	Andesine	0.05	.036	.000	.057	0.00	0.60	0.59	0.09		0.82	3.22
47	Labradorite	0.08	.042	.007	.058	0.00	0.81	0.43	0.08		2.01	3.52
48	Bytownite	0.10	.048	.000	.093	0.00	0.62	1.22	0.03		2.48	
49	Anorthite	0.05	.012	.007	.069		0.82	0.18	0.01		6.32	7.32

Ca, Na, K, and NH<sub>4</sub> are expressed as m.e./100 gm. Al and Si are expressed as mols/100 gm.

solutions used and for each cation displaced. It is usually assumed that calcium-rich minerals are much less stable to weathering than sodium-rich minerals. These data indicate, however, that one must be careful in choosing a criterion of weathering, both with respect to the element released and to the conditions imposed by the environment. In the HCl solutions, just as much calcium was released by albite as by anorthite. Conversely, nearly four times as much sodium was released from bytownite as from albite. There was also less calcium released from anorthite in  $\text{NH}_4\text{Cl}$  and water than from any of the other plagioclase minerals. There seems to be no relationship between the amount of a cation released and the total amount present in the mineral. These anomalies may be explained on the basis of structural intergrowth of crystals. However, even these properties are not refined enough to apply to the results. There are good indications that a small amount of albite dissolved in an anorthite crystal is more subject to decomposition than is pure albite. Similarly, a small amount of anorthite dissolved in albite is also more easily dissolved than is pure anorthite.

The results of the dissolution of aluminum and silicon in HCl solutions are somewhat more in line with the stability studies in acids. Only in the case of HCl solutions was there sufficient aluminum dissolved for determination. The amount of aluminum and silicon dissolved increased with increasing contents of calcium in the minerals. This is somewhat difficult to explain since the other cations bear no simple relation to the composition. Further work will be necessary to clarify these results.

## CONCLUSIONS

The surface chemistry of the plagioclase feldspars included in this study was not in accord with the idea of a uniform change of stability with composition. Losses of sodium and calcium upon treatment with acid showed this clearly. Determinations of pH in feldspar-acid mixtures showed a more regular change with composition, but even here there was evidence that the order of stability varied according to the pH range involved. The same conclusion follows from the comparison of hydrochloric acid, ammonium chloride and water in their release of sodium and calcium. Bytownite appears, then, to be less stable than anorthite; but in respect to silica and alumina released under strongly acidic conditions it appears more stable, which is the normal assumption made by geologists.

Since much of the release of bases by feldspars occurs in soils where the environment is slightly acidic to neutral and since much rock decomposition actually proceeds under alkaline conditions, it is evident that the establishment of the relationships between feldspar composition, de-

tailed crystal structure and stability is a matter of great importance. By combining the highly sensitive colloid-chemical methods with analytical determinations, it should be possible to make rapid progress in this direction. Part II of this series will deal with the cation exchange properties of feldspar surfaces and here again we shall find that reactivities do not follow the order indicated by composition.

## REFERENCES

1. Armstrong, Lee C., "Decomposition and Alteration of Feldspars and Spodumene by Water," *Amer. Min.* 25:810, 1940.
2. Barth, Tom F. W. "Polymorphic Phenomena and Crystal Structure," *Amer. Jour. Sci.*, 27:273, 1934.
3. Beyer, A. "Über die Zersetzung des Feldspathes unter dem Einfluss von Salzlosungen und einigen anderen Agentien," *Land, Ver. Stat.*, 14:314, 1871.
4. Bragg, W. L., *Atomic Structure of Minerals*, Cornell Univ. Press, Ithaca, New York, 1937.
5. Buerger, M. J. "The Role of Temperature in Mineralogy," *Amer. Min.*, 33:101, 1948.
6. Chao, S. H., A. Hargreaves, and W. H. Taylor, "The Structure of Orthoclase," *Min. Mag.*, 25:498, 1940.
7. Chao, S. H., D. L. Smare, and W. H. Taylor, "An X-Ray Examination of some Potash-soda-feldspars," *Min. Mag.*, 25:338, 1940.
8. Chao, S. H. and W. H. Taylor, "The Lamellar Structure of Potash-soda-feldspars," *Proc. of Roy. Soc. A* 174:57, 1940.
9. Cheng, Kuang Lu and Roger H. Bray, "Determination of Calcium and Magnesium in Soil and Plant Material," *Soil Sci.*, 72:449, 1951.
10. Clarke, Frank W., *The Data on Geochemistry*. 5th ed. U.S. Geol. Survey Bul. 770, 1924.
11. Correns, Carl W. und Wolf von Engelhardt, "Neue Untersuchungen über die Verwitterung des Kalifeldspates," *Chemie der Erde*, 12:1, 1939/40.
12. Cushman, Allerton S. and Prevost Hubbard, *The Decomposition of Feldspars*, U. S. D.A. Office of Public Roads, Bul. 28, 1907.
13. Daubrée, A., *Etudes Synthétiques de Géologie Experimental*. Paris, 1879.
14. Dittler and Kohler, *Tschermaks Min. Petr. Mitt.*, 38:229, 1925 (Quoted from Taylor (44) )
15. Engelhardt, Wolf von, "Versuch über die Verwitterung des Feldspates," *Fortschr. Mineral. Krist. Petrog.*, 21:276, 1939.
16. Frederickson, A. E., "Mechanism of Weathering," *Bul. Geol. Soc. Amer.*, 62:221, 1951.
17. Goldich, Samuel S., "A Study in Rock Weathering" *Jour. Geol.*, 46:17, 1938.
18. Graham, E. R., "Colloidal Organic Acids as Factors in the Weathering of Anorthite," *Soil Sci.* 52:291, 1941.
19. Graham, E. R., "Acid Clay—an Agent in Chemical Weathering," *Jour. Geol.* 49:392, 1941.
20. Graham, E. R., "The Plagioclase Feldspars as an Index to Soil Weathering," *Soil Sci. Soc. Amer. Proc.*, 14:300, 1950.
21. Keller, W. D., *The Principles of Chemical Weathering*, Lucas Brothers, Publishers, Columbia, Mo., 1955.

35. Snell, Foster Dee and Cornelia T. Snell, *Colorimetric Methods of Analysis*, 3rd Ed. Vol. II. D. Van Nostrand Company, Inc., New York, 1949.
36. Spencer, Edmondson, "A Contribution to the Study of Moonstone from Ceylon and other Areas and of the Stability-relations of the Alkali-feldspars," *Min. Mag.*, 22:291, 1930.
37. Spencer, Edmondson, "The Potash-soda-feldspars I. Thermal Stability," *Min. Mag.* 24:454, 1937.
38. Spencer, Edmondson, "The Potash-soda-feldspars II. Some Application to Petrogenesis," *Min. Mag.* 25:88, 1938.
39. Strunz, H., *Mineral Tabellen*, 1941 (Quoted from Keller (21) ).
40. Tamm, Olof, "Experimental Studies of Chemical Processes in the Formation of Glacial Clay," *Sveriges Geologiska Undersokning arsbok* 18:5, 1924.
41. Tamm, Olof, "An Experimental Study on Clay Formation and Weathering of Feldspars," *Medd. Statens Skogsforsch sanstalt*, 24:1, 1929.
42. Tamm, Olof, "Experimentalle Studien uber die Verwitterung und Tonbildung von Feldspäten," *Chemie der Erde*, 4:420, 1930.
43. Tamm, Olof, "Experimental Studien uber die Verwitterung von Silikatmineralien," *Arkiv for Kemi, Mineralogi och Geolog*, 11:14, 1934.
44. Taylor, W. H., "The Structure of Sanidine and Other Feldspars." *Zeit. fur Krist.* 85:425, 1933.
45. Taylor, W. H., "The Nature and Properties of Aluminosilicate Framework Structures," *Proc. of the Roy. Soc. A* 145:80, 1934.
46. Taylor, W. H., J. A. Darbyshire, and J. Strunz, "An X-Ray Investigation of the Feldspars," *Zeit. für Krist.*, 87:468, 1933.
47. Tschermak, G., Quoted from Bragg (4).
48. Tunn, Walter, "Untersuchungen uber die Verwitterung des Tremolite." *Chemie der Erde*, 12:275, 1939.
22. Keller, W. D. and A. F. Frederickson, "Role of Plants and Colloidal Acids in the Mechanisms of Weathering," *Amer. Jour. of Sci.* 250:594, 1952.
23. Kozu, S. and Y. Endo, *Sci. Rep. Tohoku Ser. 3*, Nr. 1, 1921 (Quoted from Taylor (46) ).
24. Kruger, Gerhard, "Verwitterungsversche am Leuzit," *Chemie der Erde*, 12:246, 1939.
25. Machatschki, Felix, "Zur Frage der Struktur und Konstitution der Feldspate," *Ctbl. Min.* 3:97, 1928.
26. Marshall, C. E. and C. A. Krinbill, "The Electrochemical Properties of Mineral Membranes V. Beidellite Membranes and the Determination of Sodium," *Jour. Amer. Chem. Soc.*, 64:1814, 1942.
27. Marshall, C. E. and Alvin D. Ayers, "Clay Membrane Electrodes for Determining Calcium Activities," *Soil Sci. Soc. Amer. Proc.*, 11:171, 1946.
28. Marshall, C. E. and L. O. Eime, "The Electrochemical Properties of Mineral Membranes VII. Clay Membranes for the Determination of Magnesium," *Jour. Amer. Chem. Soc.*, 70:1302, 1948.
29. Marshall, C. E., *Colloid Chemistry of Silicate Minerals*, Academic Press, N. Y., 1949.
30. McConnell, Duncan, "Mechanism of Weathering," *Bul. Geol. Soc. Amer.* 62:700, 1951.
31. Norton, F. H. "Hydrothermal Formation of Clay Minerals in the Laboratory. Part II," *Amer. Min.* 26:1, 1941.
32. Pauling, Linus, "The Principles Determining the Structure of Complex Ionic Crystals," *Jour. Amer. Chem. Soc.* 51:1010, 1929.
33. Rankama, Kalervo and Sahama, Th. G., *Geochemistry*, The Univ. of Chicago Press, Chicago, Ill., 1950.
34. Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 2nd Ed., Interscience Publishers Inc., New York, N. Y., 1950.