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EXPERIMENTAL CHEMICAL WEATHERING OF TWO ALKALI FELDSPARS

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I hereby recommend that the thesis prepared under my supervision by Ronald W. Manus

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ABSTRACT

Two perthitic alkali feldspars were experimentally weathered by controlled leaching solutions of pH's within the range of natural waters (4-9). Ground feldspars (200-230 mesh) were contained in plastic columns through which 200 ml of leaching solution, maintained at 40°C, was percolated daily. The duration of leaching was 305 days. Samples of the effluent solutions were collected at 5 day intervals and analyzed for pH, K^+, Na^+ and Si^{+4}. Concentrations ranged from a low of approximately .04 ppm for K^+ late in the experiment to a high of about 4.5 ppm for Si^{+4} early in the experiment. The decomposition products derived from the leaching of the feldspars were analyzed by x-ray diffraction and electron microscopy. The leached feldspars were chemically analyzed and compared to the unleached starting materials. In addition, thin sections were prepared from impregnated samples.

Consideration of the data obtained from the effluent solutions points to the rapid development of a residue product on the feldspar surface which slows down the rate of leaching. The residue product development appears to be characterized by three successive stages: (1) stripping of loosely held ions from the fresh feldspar surface, (2) disorganization and expansion of the surface feldspar lattice and development of a residue product capable of retarding the loss of K^+, (3) further development of the residue material into a near-equilibrium product. The K^+ retarding residue product is shown to be pH indepdendent with respect to time of development. Effluent data indicates that the loss of ions is non-stoichiometric but mutually dependent and variable with time. The solubility of Si^{+4} at pH 4 is greater than at pH 9.

X-ray diffraction of the residue product showed that 7Å, 10Å and 14Å clay-type layer structures were developed. It is suggested that the layer structures resulted from a reorganization of the residue product. Electron micrographs show that the clay-type material is in an incipient stage of development.

Differences between the chemical analyses of the leached and the unleached feldspars are too small to be analytically valid although desilication and loss of bases appears to be exhibited in the case of one of the feldspars.

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INTRODUCTION

This investigation represents the application of detailed physicochemical measurements using highly sensitive analytical procedures to analyze the effect of simulated weathering processes on two different alkali feldspars. Much previous experimental work has been conducted under conditions which do not closely follow those of a weathering environment. A great deal of the work has been conducted at extremes of temperature and/or pH. Experiments which have more closely followed natural weathering conditions have been of relatively short duration or have involved the re-cycling of leaching solutions. This work represents a long duration leaching experiment in which conditions of pH, temperature and drainage were made to more closely approximate those conditions active in a weathering environment.

The rationale upon which the experiment was based is as follows:

(1) A continual supply of fresh solute and a continuous removal of the soluble reaction products as opposed to the re-cycling of leaching solutions would more closely simulate actual weathering conditions in

regions of abundant rainfall.

(2) Leaching solutions of controlled pH, within the range of natural waters (4-9), would provide data relating to the physicochemical equilibria achieved in natural weathering environments including information on rates of chemical weathering and the role of pH as a control in the final decomposition product.

(3) The use of large volumes of feldspar would enhance the collection and detection of materials which had undergone a modification of crystalline structure.

(4) Analysis of effluent leaching solutions sampled throughout the course of the experiment would permit the detection of changes in the feldspar-leaching solution reaction with time.

(5) Analysis of the leached material might provide data relating to the translocation of ions within a vertical column.

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The Feldspar Corporation, Spruce Pine, North Carolina generously provided the bulk feldspars used in the investigation.

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PREVIOUS WORK

General

Many experimental studies of the weathering reactions of feldspars and feldspar bearing rocks have been reported. However, as already noted, most have been of relatively short duration and/or conducted at pH's outside the range of natural waters and/or under experimental conditions which simulated hydrothermal alteration. In considering the literature pertaining to hydrothermal alteration, it must be kept in mind that while the higher temperatures and pressures involved will bring about a more rapid reaction rate, they may also put the reactions taking place in stability fields different from that of the atmospheric conditions encountered in the weathering environment. The writer has, for the purpose of brevity, limited this review mainly to experimental leaching studies. However, some work which may be considered as largely theoretical or, based on field evidence or synthesis of clay minerals using non-crystalline starting materials may also bear strongly on the matters considered in this portion of the report. Discussion of these works where pertinent has been deferred to a later section.

Early Work

Among the very early workers concerned with the effect of solvents upon feldspars were Beyer (1871), Daubree (1879), and Cushman and Hubbard (1907). These early workers recognized or anticipated some of the more significant factors concerning the weathering of feldspars. Daubrée demonstrated that hydrolysis in pure water was an important factor in the decomposition of feldspar. He emphasized the importance of CO_2 in decomposition and noted that grinding in water was more effective in leaching than grinding dry and later placing in water. Beyer noted a differential rate of leaching in orthoclase feldspars. Na^+ went into solution more readily than K^+ even though K^+ was 2 1/2 times more abundant than Na^+ in the unleached feldspar with which he worked. Cushman and Hubbard carried out grinding experiments similar to those of Daubrée and showed a rapid leaching taking place at first, followed by a decrease to a lower constant value. The initial rapid leaching could be repeated by re-grinding the material. From this, they concluded that an aluminosilicate decomposition product was formed around the particles thus slowing the reaction.

The release of ions to a leaching solution and subsequent development of a protective shell around the feldspar grains has since been demonstrated by many other workers.

Soluble Ions

Tamm (1930), Garrels and Howard (1959), and Nash and Marshall (1956a), have demonstrated that the essential reaction in the leaching of ions from a feldspar surface in pure water or acid media is due to the exchange of H^+ for K^+ or Na^+. They have also shown that leaching reactions are pH dependent with greater release of alkalies taking place in the more acid and in the more basic media. Additionally, Nash and Marshall (1956a), Morey and Fournier (1961), and Keller, et al. (1963a), have confirmed the earlier observations of Beyer (1871), that the release of ions from the mineral undergoing leaching is non-stoichiometric. Nash and Marshall (1956a), also point out that while Na^+ was preferentially liberated over K^+ in acid media, the opposite held true when the K^+ and Na^+ were leached out with ammonium and strontium chlorides. They also found, as did Keller, et al. (1963a), that in the plagioclase series, the minor cation displays a tendency to be preferentially removed. Marshall and McDowell (1965) maintain that within wide limits of pH, the release of alkalies is independent of the release of monomeric silica.

Tamm (1930) first demonstrated the solubility of Al^{+3} and Si^{+4} under experimental leaching conditions. Correns (1949) has shown the solubility of Al_2O_3 to be highly dependent upon pH but not within the pH range 4-9 where it displays a uniform low solubility. Pickering (1962), among others, has shown that within the pH range 4-9, Si^{+4} is readily leached from feldspar bearing rocks. Keller, et al. (1963), demonstrated that the amount of Si^{+4} in leaching solutions is lessened with increasing amounts of Al^{+3} as well as Ca^{+2} and Mg^{+2} in solution but is greater with increased amounts of Na^+ and K^+. The ionic as opposed to colloidal state of silica resulting from leaching has been shown by Correns (1963). Pickering has convincingly shown that the leaching of Si^{+4} from silicate rocks by solutions in the pH range 4-9, is greater at the more acid pH's. He ascribes this greater solubility to a weakening of the silicate structure due to more extensive leaching of alkalies in acid media. The lack of a higher solubility of silica in an alkaline solution up to pH 9 is confirmed by the work of Krauskopf (1959) who examined the solubility of amorphous silica in response to various conditions including pH.

Armstrong (1940) and Correns (1961) on the basis of electrodialysis experiments maintain that all the soluble reaction products resulting from silicate leaching are in true ionic solution. On the other hand, Frederickson and Cox (1954) showed by the use of electron microscope examination that the dissolution products occurred both as ions in solution and as silicate fragments.

Keller, et al. (1963), extending the work of Tamm (1930) and Stevens and Carron (1948) showed that when a silicate mineral is ground under water, the pH of the mineral-water slurry rises to a limiting value where it is maintained as long as grinding continues. He regards this abrasion pH as representing the pH of the hydrolysis reaction, i.e., the pH at the interface where the reaction is occurring.

Weathering Shell

There is general agreement on the development of a decomposition product on the surface of feldspars undergoing leaching. The existence of such a decomposition product occurring is evidenced in leaching experiments principally by the reduction in the amount of soluble product with time, even when the mineral undergoing leaching is subject to a continuously renewed supply of solvent (Correns, 1961: Morey and Fournier, (1961). On the other hand, the nature of the decomposition product has not been firmly established. Correns (1961), in reviewing the experimental work done by himself and his collaborators proposes an amorphous gel-like material composed of alumina and silica which achieves and maintains a constant thickness during the leaching process. After development of the protective shell other ions diffuse through the residue at about the same rate as the aluminosilicate residue product itself enters into solution. Nash and Marshall (1956a,b) found that ground feldspar treated with acid behaved temporarily as an acid, i.e., H-feldspar. They observed that surface ions exchanged rapidly but that H ions did not replace those on the interior as rapidly or easily. From this, they suggested that a thin altered layer developed on the surface of the feldspar grains which acted as a zone of accommodation for exchange reactions between the feldspar and the leaching solution. Inward from this outer zone, they propose a less disrupted zone of limited cationic accommodation which, while somewhat distorted or loosened, still maintains the essential feldspar structure. The boundary between the two zones they visualize being transitional. Garrels and Howard (1959) on the basis of detailed experimental work essentially confirm the interpretation of Nash and Marshall, while proposing a K-feldspar→H-feldspar→ K-mica transition taking place on the surface of the feldspar grain.

Feldspar-Clay Transformation

The manner by which a weathered feldspar undergoes the transformation to a crystalline hydrous aluminum silicate has been the subject of considerable speculation and controversy. There are, essentially, two points of view: one of which maintains that the parent mineral must be broken down to a non-crystalline form, either in ionic solution or as an amorphous gel before a clay mineral can form; while the other proposes a direct transformation, in response to the leaching out of certain components, to clay via a rearrangement of the original lattice. Correns (1961, 1963) seems to be the main proponent of the former point of view while Jackson, et al. (1948) and DeVore (1959) among others, support the latter.

Keller (1964) cites abundant evidence which indicates that this neomineralization probably can occur both through a gel phase and by lattice transformation.

MATERIALS, METHODS AND PROCEDURES

Starting Materials

The two alkali feldspars used in the experiment consisted of ground commercial feldspars obtained from the Feldspar Corporation, Spruce Pine, North Carolina. The use of ground commercial feldspars was dictated by the large quantity of material required in the experiment. They were chosen on the basis of their K^+-Na^+ proportions; in which K^+ exceeded Na^+ in one feldspar and in which Na^+ exceeded K^+ in the other. These were designated as feldspars A and B respectively and represented feldspars G-40 and C-20 of the Feldspar Corporation.

X-ray analysis of feldspar A showed it to be an X-ray perthite in which the potassium feldspar predominated over plagioclase. Feldspar B was revealed to also be an X-ray perthite in which, however, plagioclase predominated over potassium feldspar. Relative abundances were based on the relative intensities of the 4.04Å and 3.18Å plagioclase peaks and the 4.23Å and 3.24Å potassium feldspar reflections (Schultz, 1963).

Partial chemical analysis gave the following compositions (Table I).

Table I. Chemical Composition of Feldspars Used in the Experiment.

%	Feldspar A	Feldspar B
SiO_2	68.68	69.51
Al_2O_3	17.48	17.53
K_2O	9.57	4.10
Na_2O	2.94	7.26
CaO	0.88	0.76
MgO	0.10	0.10
FeO	0.10	0.10
TOTAL	99.75	99.36

Preparation of Feldspars

It was decided to use a limited size range of feldspar in order to maintain uniformity between samples and to achieve maximum permeability. To obtain a maximum surface for reaction, the smallest grain size consistent with a suitable quantity available in the bulk material was chosen. This was the fraction between 200 and 230 mesh, U.S. Bureau of Standards (74-62 microns). The ground feldspars were sieved in standard 8 inch sieves and the 100-200 and 200-230 mesh fractions of each were saved. The 100-200 mesh fraction was run through a jaw crusher and re-sieved to obtain additional 200-230 mesh material. This process was repeated several times in order to obtain sufficient amounts of feldspars A and B for the experiment. Including crushing and re-sieving, approximately 450 pounds of feldspar were sieved. The 200-230 mesh fraction was then carefully wet sieved to eliminate fines. Most impurities were then removed by two heavy liquid separations. Finally, the samples were washed with acetone followed by deionized water and dried. Approximately two kilograms of each feldspar was obtained. Optical examination of the prepared feldspar determined an estimated mineralogical purity of 98%. Almost all of the remaining 2% was composed of quartz.

Conduct of the Experiment

Polystyrene tubes 18 inches long by 2 inches in outside diameter with a wall thickness of 1/8 inch were used as leaching columns (Figure 1). One end of each of the tubes was forced into a tight fitting polyethylene buchner funnel, the perforated plate of which was covered with a teflon-impregnated, borosilicate fiber filter paper with a pore size of from 2 to 4 microns. The funnels were connected by polyvinyl chloride flexible tubing to polyethylene containers of 1 liter capacity. The 1 liter containers were used to collect the solution, herein termed the effluent solution, which passed through the column. Polyethylene needle valves were inserted in the flexible tubing to govern the flow rate. The tubes were arranged in two horizontal rows of six

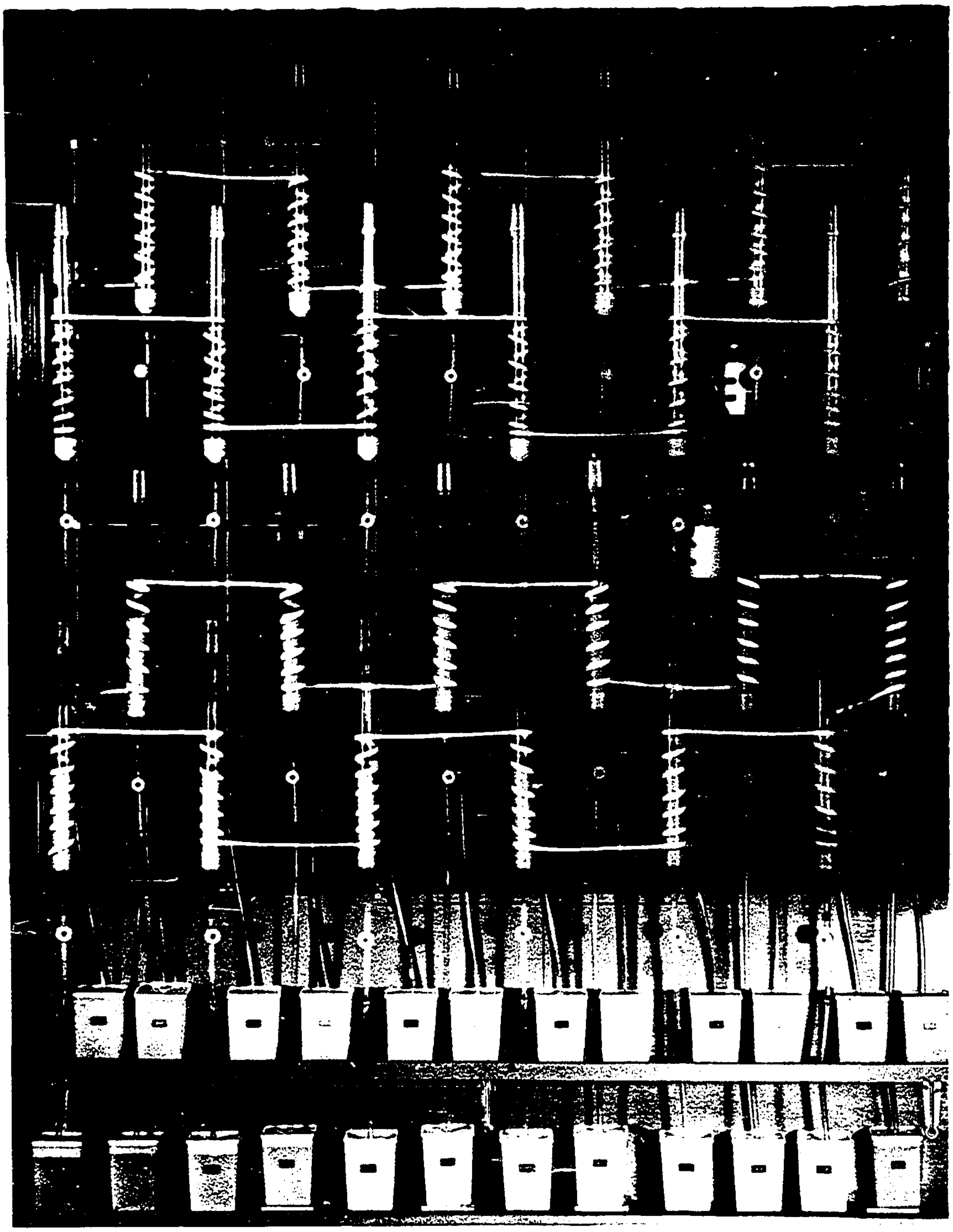

Figure 1. Leaching apparatus. Upper two rows of leaching columns were not used in this experiment.

leaching columns each. One row served to contain samples of feldspar A and the other samples of feldspar B while the individual tubes of each row served to accommodate leaching solutions of different pH (4-9). The leaching columns of each row were numbered 4 through 9 which corresponded to the pH at which the samples were leached. An electrical heating tape was wound about the leaching columns and connected to a thermoregulator placed in a polyvinyl chloride well imbedded in the feldspar in column B-7. Additional thermometers were placed in teflon wells imbedded in the feldspar in columns A-4, A-8, and B-4. The additional thermometers were calibrated against the thermoregulator. The temperature was maintained at 40°C, the ambiency of which was determined to be ± 1°C. To preclude contamination of the leaching solutions, the thermoregulator was coated with an organosilicone compound (Desicote) and the additional thermometers were coated with polyvinyl chloride. After 200 days, the additional thermometers were removed.

Into each leaching column was loaded 290 grams of feldspar. To load the feldspar, a narrower tube open at both ends was inserted into the leaching column. The feldspar was poured into the loading tube which was then withdrawn in one continuous motion. This served to prevent any bedding effects due to loading. When loaded with feldspar, the tubes were only about 40% full. The space above the feldspar served to accommodate the leaching solution. The columns were covered with loose fitting polyethylene cups to prevent airborne contamination. Into each column, 200 ml. of leaching solution, adjusted to the appropriate pH, was poured daily. The leaching solution percolated through the feldspar and into the effluent solution containers. The rate of flow was adjusted by means of the needle valve and approximated 200 ml./24 hrs. Precise adjustment of the flow rate was impossible to maintain but the capillary action of the finely ground feldspar and the hydrophobic tendency of the teflon-impregnated filter paper prevented complete drainage of the leaching columns. At no time did more than the upper 3/4 inch of the feldspar become drained. This was determined by measuring the height above the feldspar required by 200 ml. of solution.

Two aliquot samples of the effluent solution from each column were collected every five days during which time approximately one liter of leaching solution had passed through the leaching column. Each 5 day increment is herein referred to as a period. The duration of the experiment was 61 periods (305 days).

Preparation of Leaching Solutions

The leaching solutions were prepared from water which had been distilled in a Stokes laboratory still with pyrex condenser and then passed very slowly through an Ilco-Way Research Model deionizer. The deionized water was stored in plastic containers and permitted to come into equilibrium with atmospheric CO_2. The adjustment of pH's 4 and 5 was accomplished with HCl. Since deionized water in equilibrium with atmospheric CO_2 has a pH of approximately 5.6, pH's 6-9 were adjusted with NH_4OH. NH_4OH was chosen to adjust pH's 6-9 in the belief that this would avoid the problem of using in the leaching solution a cation already present or possibly present in the feldspar. However, as will be demonstrated, the choice of NH_4^+ was not without its disadvantages.

A special problem presented itself in maintaining leaching solutions of pH 8 and 9, both in storage and in the leaching column in the space above the feldspar. A drop in pH occurred which was attributed to a loss of $NH_3\uparrow$ during storage, during the agitation incurred in measuring and pouring the daily loads, and in the leaching column itself. Apparently the amounts of NH_4OH needed to adjust to pH's 6 and 7 were sufficiently small so as to make the effect of lost $NH_3\uparrow$ negligible. These solutions maintained their pH both in storage and in the leaching column. This condition was first detected during the fourth period. The effective pH of leaching solution pH 8 was at that time approximately 7.5 and that of pH 9 was approximately 8.0 to 8.5. From the beginning of the fifth period, leaching solutions of pH 8 and 9 were mixed daily to values of 8.3 and 9.1 respectively in an attempt to overcome the loss of $NH_3\uparrow$ due to storage and handling. The values to which the solutions were mixed (8.3 and 9.1) were determined by duplicating the manipulations involved in measuring out and pouring the leaching solutions into the column. This procedure was partially successful but a significant drop in pH still occurred over a 24 hour interval in the solution above the feldspar in the column. The necessity for daily mixing was eventually overcome by utilizing completely filled paraffin-lined glass bottles for storage as it was possible to seal these more tightly than regular polyethylene bottles.

By the beginning of the eleventh period, an ammonia-vapor bath system was installed which prevented significant drops in the pH of the leaching solutions in columns 8 and 9 (Figure 2). By trial and error, the optimum NH_4OH concentrations in the ammonia-vapor baths were determined to be 6% and 20% for leaching solutions at pH 8 and 9 respectively. However, it was difficult to maintain optimum concentrations and the final effective leaching pH can only be described as approximately 8 and approximately 9. Periodic pH measurements made directly on the solutions

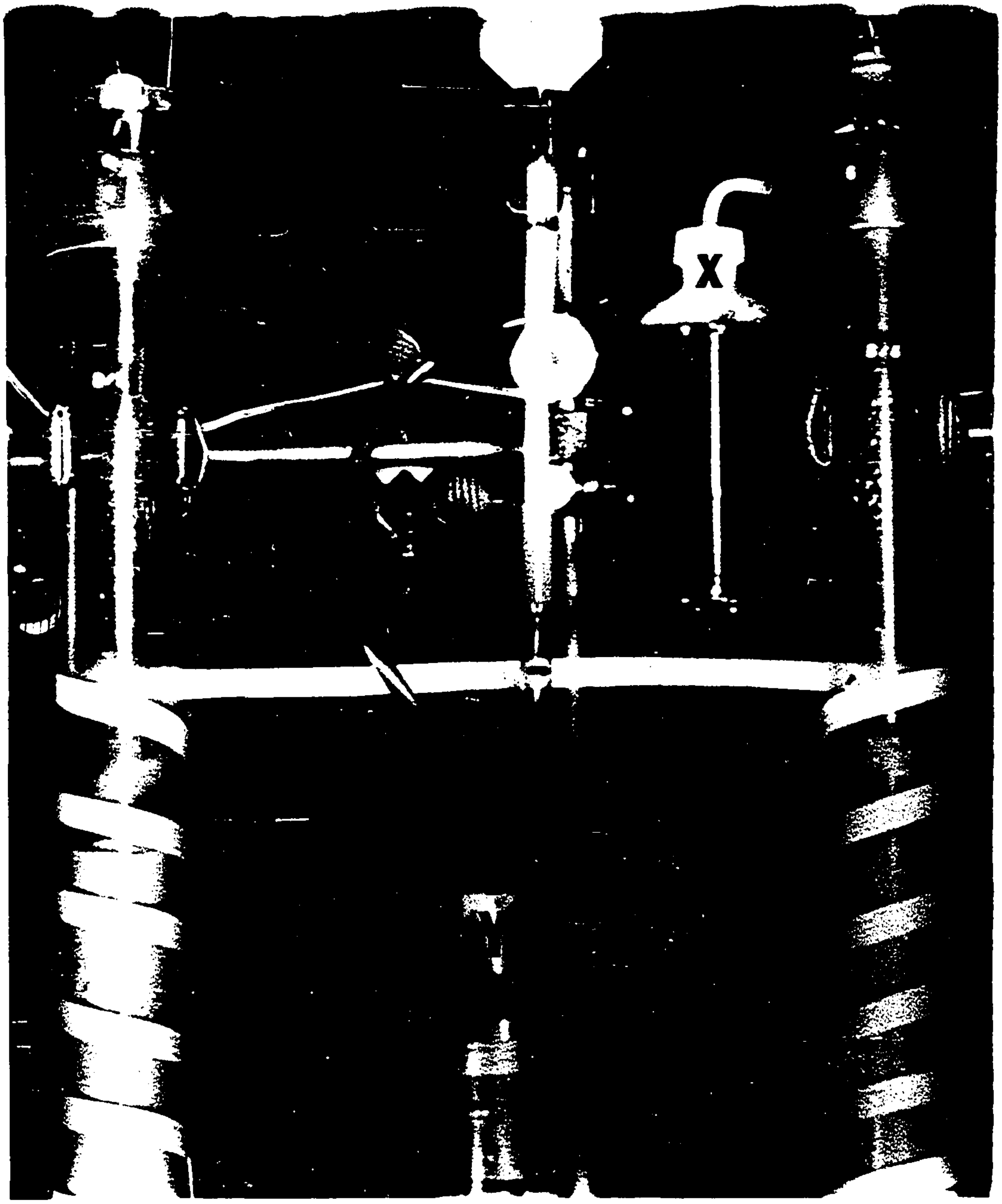

Figure 2. Ammonia-vapor baths. Air entering or leaving tube at Y passes over an NH_4OH solution in plastic bottle at X.

in the columns established that the pH range was 7.6-8.3 for columns A-8 and B-8, and 8.6-9.4 for columns A-9 and B-9. Values higher than pH 8 and 9 occurred only rarely and reflect adjustments in the concentration in the vapor pressure baths. Instances where a relatively high concentration of NH_4OH was present in the leaching solutions for columns 8 and 9 are reflected strongly in the data obtained from the effluent solutions. This is not surprising considering the strong ability of NH_4^+ to displace K^+ from feldspar (Nash and Marshall, 1956).

Effluent Solution Analysis

Two aliquots of effluent solution were collected for each column at the end of each five day period. From one aliquot, the pH of the effluent was determined on either a Beckman Model H pH Meter or a Beckman Model G and then discarded. The second aliquot of about 250 ml. volume was saved in polyethylene bottles for analysis. Effluent samples were numbered according to the feldspar (A or B), the pH of the leaching solution (4-9), and the period represented (1-61). Hence, sample A-6-5 passed through feldspar A at an initial leaching pH of 6 (column A-6) during the fifth period. After the seventh period, analytical samples were combined to represent three periods. Hence, sample B-5-9 is a composite of B-5 samples taken at the end of the eighth, ninth and tenth periods.

During the course of the experiment, every effort was expended to avoid contamination. The materials of which the leaching apparatus was constructed were entirely of plastic. All samples were stored in plastic containers. All plasticware was washed in a high pressure jet of hot tap water and rinsed repetitively with the deionized water previously described. Prior to washing and rinsing as above, all glassware was soaked in a solution of equal parts HNO_3 and H_2SO_4. No soap or detergent was employed at any stage in the experiment as, in the writer's experience, these are virtually impossible to completely remove from glassware. To minimize silica contamination all glassware, with the exception of pipettes, was kept filled with deionized water until used (Govett, 1961).

Analytical Reagent and Primary Standard grade chemicals were used throughout the experiment. All volumetric ware was of Class A accuracy. Wherever possible, plastic pipettes were used. Due to their excellent draining properties, these proved to deliver more repeatable volumes than their glass counterparts.

The chemical analytical methods employed are standard analytical procedures modified to suit the conditions of the experiment. Due to the high dilution of the effluent samples, the most sensitive methods consistent with available equipment and simplicity were chosen. Instrumental operating parameters were optimized for maximum sensitivity for each analytical run.

Concentrations of Si^{+4} in the effluent ranged from 0.3 ppm to 4.5 ppm and were determined colorimetrically on a Beckman Model DU Spectrophotometer using the reduced silicomolybdate complex and measuring the absorption at 820 mu. The procedure is essentially that of Govett (1961) except that the silicomolybdate is reduced with a 1-amino-2-napthol-4-sulfonic acid reducing agent (Talvite and Hyslop, 1958).following adjustment to 2N H_2SO_4 (Charlot, 1964). Concentrations were determined by comparison to known standards prepared by the method of Talvite and Hyslop (1958).

Na^+ ranged from 0.05 to 1.7 ppm and was determined by flame photometry using a Beckman Model DU Spectrophotometer with flame attachment and equipped with a highly sensitive Hamamatsu R-136 photomultiplier photodetector. A hydrogen flame was used and emission was measured at 579 mu. Due to the high dilution of the samples, interference from other ions in solution was negligible. Hence, the samples were analyzed without any prior chemical treatment. Concentrations were determined by comparison to known standards. High sensitivity and increased flame stability was achieved by the fabrication and addition to the standard Beckman Atomizer-Burner of an oxygen sheath with adjustable chimney patterned after Gilbert (1961). To minimize the effect of instrumental drift, standard solutions were run at the beginning of each analytical run, after every 12 samples, and again at the end of the run.

K^+ ranged from 0.03 to 1.7 ppm and was determined in the same way as Na except that emission was measured at 767 mu and better results were obtained by not employing the oxygen sheath.

After concentration by ion exchange, the presence of CA^{+2} in the effluent solutions was detected by flame photometry. However, the concentration was so slight (less than 0.1 ppm) that no quantitative analysis was attempted. After concentration by chloroform extraction using 8-hydroxy-quinoline, Al^{+3} was detected colorometrically but, again, the concentration was inadequate (less than 0.05 ppm) for valid quantitative analysis.

The reliability of the analytical methods employed was tested prior to the analysis of the samples. Testing was accomplished by the preparation and replicate analysis of synthetic samples in the concentration ranges anticipated by approximate analysis of selected effluent samples. Accuracy was checked by comparison with carefully prepared standards and was acceptable. Good precision was evidenced by excellent reproducibility of replicate analysis. Excellent precision was further demonstrated in the case of Si^{+4} where some samples which had been analyzed earlier gave almost identical results when analyzed again several months later. In addition, the consistent trend in the curves obtained from the analytical data (presented in a later section) lend further support to the reliability of the analytical methods.

Sampling of the Leached Feldspar

Upon completion of the 61st leaching period, the feldspar in the leaching column was sampled. This was accomplished by milling two 1/8 inch wide channels almost all the way through the plastic. The channels ran the length of the column and were spaced 180° apart (opposite one another). The columns were then gently squeezed to crack the remaining plastic along the length of the channels. A thin stainless steel spatula was inserted through the column from one channel to the other and worked down the length of the column through the feldspar. In this manner, the column was split lengthwise into two relatively undisturbed main samples. In order to prevent disturbing the samples during the splitting operation, it was necessary to buttress the top and bottom ends of the feldspar. The bottom was supported by removing the column from the buchner funnel and taping a plastic disc over the end of the tube. The top of the feldspar was buttressed by inserting a polyethylene bag into the column and pouring a one inch layer of hot paraffin into the bag on top of the feldspar. Excess tubing above the feldspar was trimmed off. Buttressing the ends of the column also helped to keep the feldspar slightly damp which enhanced its cohesiveness.

One of the main samples was further divided into five sections by cutting across the tube through the feldspar only. These sections represented top, middle, and bottom portions with two one inch divider portions between them. This sample was then cut lengthwise again; one half to be used for chemical analysis, the other for physical analysis. These samples were labeled according to which feldspar they represented, the pH at which they were leached, and the portion of the tube from which they were taken. Hence, sample A-4-T represents the top portion of feldspar A leached at pH 4. The remaining undivided, undisturbed main sample was reserved for thin sectioning.

Sample Impregnation

In order to thin-section the undisturbed but unconsolidated sample, an impregnation technique was employed. The impregnating medium consisted of polystyrene resin, styrene monomer and methyl-ethyl-ketone mixed in the approximate ratio of 100:30:1 by volume. The styrene monomer is used to reduce the viscosity of the resin and the methyl-ethyl-ketone is used to inititate polymerization and, as such, governs the gelation time. The proportions in which the components are mixed can be varied. The ratio used here was the most suitable in this instance.

The sample, still in the halfpiece of tubing, was placed in a suitable tray in a large vacuum chamber. At the same time, a container of polystyrene resin mixture was also placed in the chamber. After evacuating for 15 minutes, the polystyrene resin was poured, by means of a tilting device, into the tray in which the sample lay. The resin was not poured directly onto the sample, but a sufficient volume was used to completely immerse the sample. Evacuation was continued for another 30 minutes before the vacuum was released. Approximately one hour after starting, the resin began to gel and, in an additional one hour, the plastic had hardened. The resultant impregnated sample was suitable for thin sectioning by routine methods. Thin sections were prepared covering the length of the feldspar column from top to bottom.

X-Ray Analysis

Since it was assumed that a decomposition product or weathering shell would mantle each feldspar grain, it was decided to separate this material from the grain for x-ray analysis. The samples reserved for physical analysis were placed in 8 ounce glass jars three-fourths filled with deionized water and tightly capped. The jars were suspended in an ultrasonic vibration bath in order to shake loose the decomposition product from the feldspar grains. By elutriation, the less than 4 micron fraction was separated and then concentrated by centrifugation. This process was repeated several times until sufficient material was obtained. It should be noted that recovery by this method was very slight and that this imposed certain limitations on the extent of physical analysis. Naturally, some finely divided feldspar was also present in the samples. The separated decomposition product was redispersed in the ultrasonic vibration bath and oriented slides prepared of all top, middle and bottom samples. For comparison purposes, slides of crushed, unleached A and B feldspar were also prepared.

X-Ray analysis was performed on a General Electric XRD-5 diffractometer using nickle-filtered CuKα radiation ($\lambda = 1.54050\text{Å}$). The copper x-ray tube was operated at 40kv and 16ma. The counting system used was the Scintillation counter set at 500 cps and at a 4 second time constant. The unit is equipped with a pulse height selector on which the gain was set at 8 and the upper energy (EU) and lower energy (EL) levels were set at 24 volts and 4 volts respectively. The beam slit was used and was set at 1°, the soller slit on medium resolution and the detection slit at 0.2°MR. The linear scale recording chart speed was 2° per minute.

When optimizing the instrument operating parameters for maximum sensitivity, it was discovered that glass slides provided an unsuitable mounting material for the samples. At the high sensitivity used, glass tended to give, between approximately 5 and 15 degrees 2θ, a broad band or hump pattern which obscured the basal clay reflections. A very thin aluminum sheet proved to be a suitable mounting material as it permitted analysis at maximum sensitivity. In addition, the aluminum provided a convenient internal standard. All samples were run between 3 and 45 degrees 2θ. Samples which yielded the appropriate reflections were glycolated and run again. Heat treatments were attempted on some of the samples but it was discovered that at about 200°C, the aluminum mount began to convert to an aluminum oxide which, in turn, produced a band or hump in the pattern which obscured basal clay reflections. By reducing the sensitivity of the instrument and using those samples which gave the most intense reflections, glass slides gave satisfactory results. These samples were subjected to heat treatments at 300° and 550°C.

Electron Microscopy

Selected samples based on their x-ray diffraction patterns were sedimented onto a thin mica substrate. These were then shadowed at a 30° angle with platinum-palladium metal and carbon coated. The replicated sample and substrate were then floated on hydrofluoric acid. After approximately 10 minutes, gentle tapping caused the substrate and sample to separate. The replicated sample was then allowed to float on the hydrofluoric acid an additional 20 minutes to dissolve the sample material. The resultant platinum-palladium replica was then placed on a 200 mesh sample grid for electron microscopy. The electron micrographs were taken on an RCA EMU-2 electron microscope at the Kettering Laboratory, Cincinnati, Ohio.

Chemical Analysis of Leached and Fresh Feldspars

The feldspar samples were put into solution by NaOH fusion (for the determination of SiO_2) and by HF-$HClO_4$ digestion (for all other determinations). In each case, the solution method of Riley (1958) was used.

SiO_2 was determined in the same way as in the effluent solution.

Al_2O_3 was determined colorometrically after complexing and extraction with 8-hydroxyquinoline in chloroform solution. This, too, followed the method of Riley (1958).

Na_2O and K_2O were determined by flame photometry using ammonium sulphate as a radiation buffer. This is essentially the same method as Riley (1958) except that no prior ion exchange separation was made and a didymium filter was used to suppress flame background in the K_2O determination.

CaO and MgO were analyzed by atomic absorption spectrophotometry following the method of Trent and Slavin (1964).

FeO was determined colorometrically using 1, 10-phenanthroline following the method of Shapiro and Brannock (1962).

To check the reliability of the analytical procedures, two feldspars which had been analyzed by C. O. Ingamells at The Pennsyvlania State University were analyzed concomitant with the experiment samples. The values obtained by the methods outlined were comparable to the known compositions.

RESULTS AND DISCUSSION

General

In this section, the results of the chemical analysis of the effluent solutions and of the leached and unleached feldspars are presented. Data obtained from the X-ray analysis and electron microscopy of the residue product, and from thin section analysis of the impregnated samples are given. The possible interpretations derived from a consideration of the results are discussed.

Effluent Samples

In all, 300 samples of effluent solution, 25 samples for each column, were analyzed. These included discrete samples for each of the first seven periods and combined samples representing every three periods thereafter. Effluent samples were analyzed for pH, Si^{+4}, Na^{+} and K^{+} (Tables II-IX, Figures 3-18). As previously noted, Al^{+3} and Ca^{+2} were detected in the effluent solutions but in amounts too small to be quantitatively determined.

The pH of the effluent solutions was measured at the end of each period (Table II, Figures 3-4). The pH data for columns A-8, A-9, B-8, and B-9 strongly reflect, by a rise in the pH, the installation during the eleventh period of the ammonia-vapor baths and also probably reflect later adjustments of the vapor baths. In addition, it was noticed that the effluent pH for columns A-8, A-9, B-8 and

Table II. pH of effluent solutions

Period	1	2	3	4	5	6	7
Column							
A-4	7.30	7.25	6.97	6.68	6.12	4.87	4.55
A-5	7.50	7.41	7.25	7.12	7.05	7.07	6.77
A-6	7.45	7.36	7.19	7.00	6.90	6.90	6.87
A-7	7.39	7.28	6.98	7.07	6.81	6.87	6.82
A-8	7.45	7.38	7.17	7.05	7.05	7.07	6.96
A-9	7.60	7.37	7.22	7.07	7.10	7.07	7.11
B-4	7.57	7.39	7.22	7.11	7.01	7.00	6.66
B-5	7.81	7.61	7.52	7.33	7.24	7.28	7.20
B-6	7.67	7.43	7.32	7.21	7.10	7.10	7.00
B-7	7.40	7.17	7.13	7.03	7.02	6.95	6.95
B-8	7.60	7.28	7.31	7.17	7.18	7.17	7.11
B-9	7.58	7.38	7.30	7.10	7.20	7.20	7.17
Period	8	9	10	11	12	13	14
Column							
A-4	4.52	4.55	4.45	4.45	4.43	4.57	4.43
A-5	6.90	6.85	6.46	6.43	6.53	6.43	6.29
A-6	6.87	6.80	6.58	6.52	6.26	6.27	6.32
A-7	6.85	6.90	6.70	6.72	6.77	6.67	6.73
A-8	6.99	6.85	6.72	6.80	7.39	7.28	7.30
A-9	7.21	7.08	6.92	7.12	7.99	9.39	9.42
B-4	6.08	4.95	4.73	4.62	4.55	4.61	4.43
B-5	6.97	7.03	6.73	6.88	6.85	6.80	6.75
B-6	6.97	6.87	6.69	6.79	6.77	6.70	6.69
B-7	6.92	6.82	6.70	6.72	6.78	6.69	6.70
B-8	7.13	7.00	6.80	9.10	8.23	7.39	7.42
B-9	7.23	7.19	6.97	9.59	9.35	9.12	9.03
Period	15	16	17	18	19	20	21
Column							
A-4	4.37	4.50	4.39	4.36	4.38	4.37	4.45
A-5	6.29	6.27	6.16	5.97	5.93	5.84	5.91
A-6	6.40	6.48	6.41	6.33	6.33	6.19	6.38
A-7	6.71	6.76	6.69	6.57	6.62	6.46	6.69
A-8	7.25	7.32	7.26	7.05	7.14	7.07	7.20
A-9	8.90	8.22	8.86	8.50	8.52	8.57	8.32
B-4	4.43	4.50	4.44	4.37	4.38	4.39	4.49
B-5	6.74	6.68	6.62	6.49	6.54	6.31	6.49
B-6	6.70	6.68	6.56	6.52	6.46	6.41	6.58
B-7	6.79	6.74	6.71	6.55	6.58	6.48	6.63
B-8	7.40	7.54	7.16	7.08	7.20	7.15	7.15
B-9	8.67	9.05	8.59	8.54	8.90	8.61	8.70

Table II. (continued)

Period	22	23	24	25	26	27	28
Column							
A-4	4.44	4.43	4.40	4.40	4.44	4.40	4.45
A-5	5.86	5.82	5.79	5.71	5.64	5.61	5.51
A-6	6.39	6.28	6.31	6.25	6.23	6.20	6.27
A-7	6.67	6.67	6.64	6.61	6.69	6.77	6.75
A-8	7.17	7.25	7.30	7.31	7.44	7.45	7.40
A-9	8.30	8.05	7.88	7.99	8.14	8.12	7.97
B-4	4.40	4.45	4.40	4.47	4.47	4.40	4.47
B-5	6.35	6.33	6.30	6.29	6.27	6.18	6.10
B-6	6.45	6.45	6.42	6.34	6.33	6.32	6.40
B-7	6.58	6.59	6.62	6.57	6.67	6.67	6.65
B-8	7.18	7.23	7.15	7.21	7.27	7.21	7.18
B-9	8.63	8.29	8.68	8.64	8.55	8.90	8.48

Period	29	30	31	32	33	34	35
Column							
A-4	4.47	4.42	4.43	4.41	4.43	4.47	4.39
A-5	5.45	5.44	5.44	5.48	5.44	5.39	5.23
A-6	6.25	6.18	6.10	6.16	6.19	6.17	6.01
A-7	6.62	6.64	6.55	6.60	6.68	6.60	6.55
A-8	7.46	7.36	7.37	7.53	7.49	7.52	7.45
A-9	7.99	8.13	7.95	7.78	7.72	7.72	7.73
B-4	4.50	4.45	4.43	4.44	4.50	4.45	4.41
B-5	6.04	6.10	5.94	6.08	6.03	5.94	5.79
B-6	6.33	6.30	6.23	6.37	6.28	6.29	6.19
B-7	6.50	6.56	6.46	6.65	6.52	6.61	6.51
B-8	7.07	7.06	7.02	7.05	7.10	7.07	7.00
B-9	8.58	8.83	8.50	8.84	8.62	8.64	8.62

Period	36	37	38	39	40	41	42
Column							
A-4	4.44	4.52	4.42	4.41	4.42	4.41	4.41
A-5	5.24	5.38	5.26	5.22	5.23	5.23	5.18
A-6	6.25	6.28	6.17	6.12	6.22	6.14	6.19
A-7	6.71	6.80	6.61	6.51	6.77	6.69	6.74
A-8	7.51	7.50	7.41	7.40	7.37	7.36	7.32
A-9	7.76	7.88	7.77	7.68	7.77	7.76	7.63
B-4	4.45	4.52	4.43	4.41	4.41	4.47	4.44
B-5	5.94	6.13	5.84	5.76	5.79	5.71	5.72
B-6	6.28	6.38	6.25	6.19	6.22	6.28	6.19
B-7	6.51	6.59	6.47	6.49	5.84	6.15	6.27
B-8	7.13	7.18	7.08	7.12	7.10	7.19	7.09
B-9	8.64	8.81	8.52	8.51	8.08	8.10	8.04

Table II. (continued)

Period	43	44	45	46	47	48	49
Column							
A-4	4.38	4.45	4.35	4.33	4.38	4.44	4.31
A-5	5.21	5.25	5.15	5.09	5.21	5.27	5.21
A-6	6.27	6.14	6.20	6.21	6.15	6.10	6.08
A-7	6.67	6.72	6.73	6.75	6.65	6.59	6.49
A-8	7.42	7.40	7.29	7.40	7.44	7.41	7.42
A-9	7.79	8.01	7.59	7.80	7.73	7.85	7.78
B-4	4.41	4.49	4.37	4.35	4.35	4.46	4.33
B-5	5.68	5.65	5.54	5.47	5.37	5.54	5.45
B-6	6.31	6.25	6.24	6.28	6.14	6.14	6.14
B-7	6.58	6.58	6.66	6.54	6.46	6.46	6.36
B-8	7.20	7.18	7.19	7.14	7.10	7.03	7.03
B-9	8.27	8.34	8.16	8.17	8.38	8.16	8.30

Period	50	51	52	53	54	55	56
Column							
A-4	4.25	4.41	4.44	4.41	4.37	4.39	4.36
A-5	5.20	5.25	5.28	5.28	5.23	5.17	5.14
A-6	6.14	6.10	6.15	6.14	6.10	6.13	6.17
A-7	6.38	6.48	6.43	6.32	6.46	6.57	6.69
A-8	7.36	7.33	7.27	7.29	7.28	7.31	7.32
A-9	7.74	7.95	7.82	7.78	7.73	7.68	7.60
B-4	4.35	4.41	4.41	4.42	4.37	4.39	4.39
B-5	5.46	5.51	5.50	5.43	5.45	5.46	5.39
B-6	6.08	6.19	6.20	6.20	6.24	6.24	6.28
B-7	6.34	6.33	6.34	6.30	6.31	6.31	6.37
B-8	6.99	7.03	7.00	7.02	7.06	7.13	7.03
B-9	8.01	8.11	7.93	8.00	8.00	8.21	7.87

Period	57	58	59	60	61		
Column							
A-4	4.35	4.34	4.35	4.35	4.36		
A-5	5.14	5.19	5.13	5.10	5.06		
A-6	6.12	6.16	6.08	6.13	6.05		
A-7	6.71	6.55	6.40	6.46	6.53		
A-8	7.30	7.38	7.24	7.36	7.25		
A-9	7.50	7.52	7.48	7.50	7.40		
B-4	4.40	4.41	4.37	4.34	4.36		
B-5	5.38	5.39	5.33	5.32	5.29		
B-6	6.25	6.27	6.18	6.17	6.17		
B-7	6.28	6.31	6.24	6.28	6.25		
B-8	6.98	7.10	7.08	7.02	7.00		
B-9	7.87	7.92	7.90	7.81	7.68		

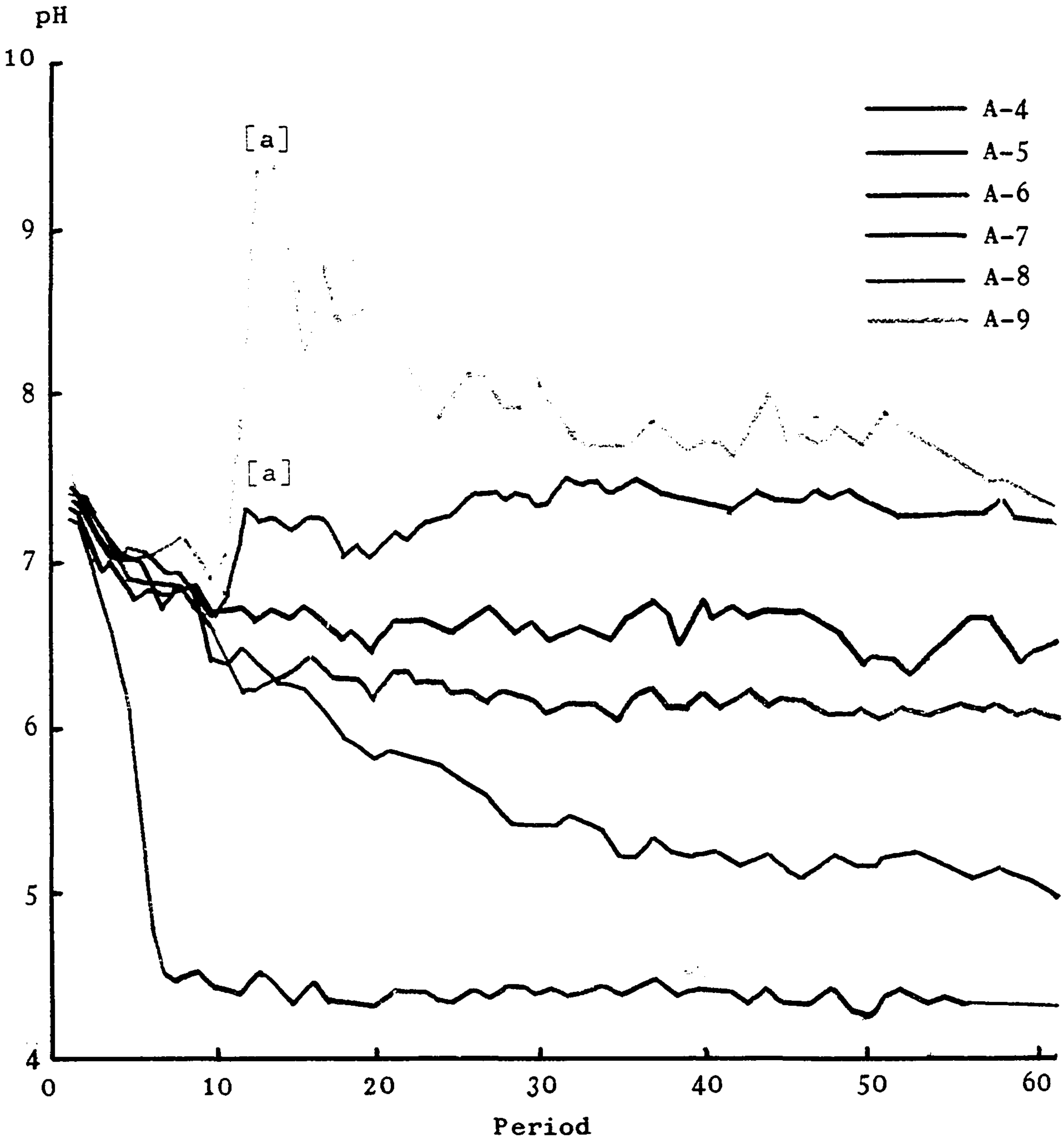

Figure 3. pH of effluent solutions, feldspar A. [a] reflects installation of ammonia-vapor baths, A-8 and A-9 only.

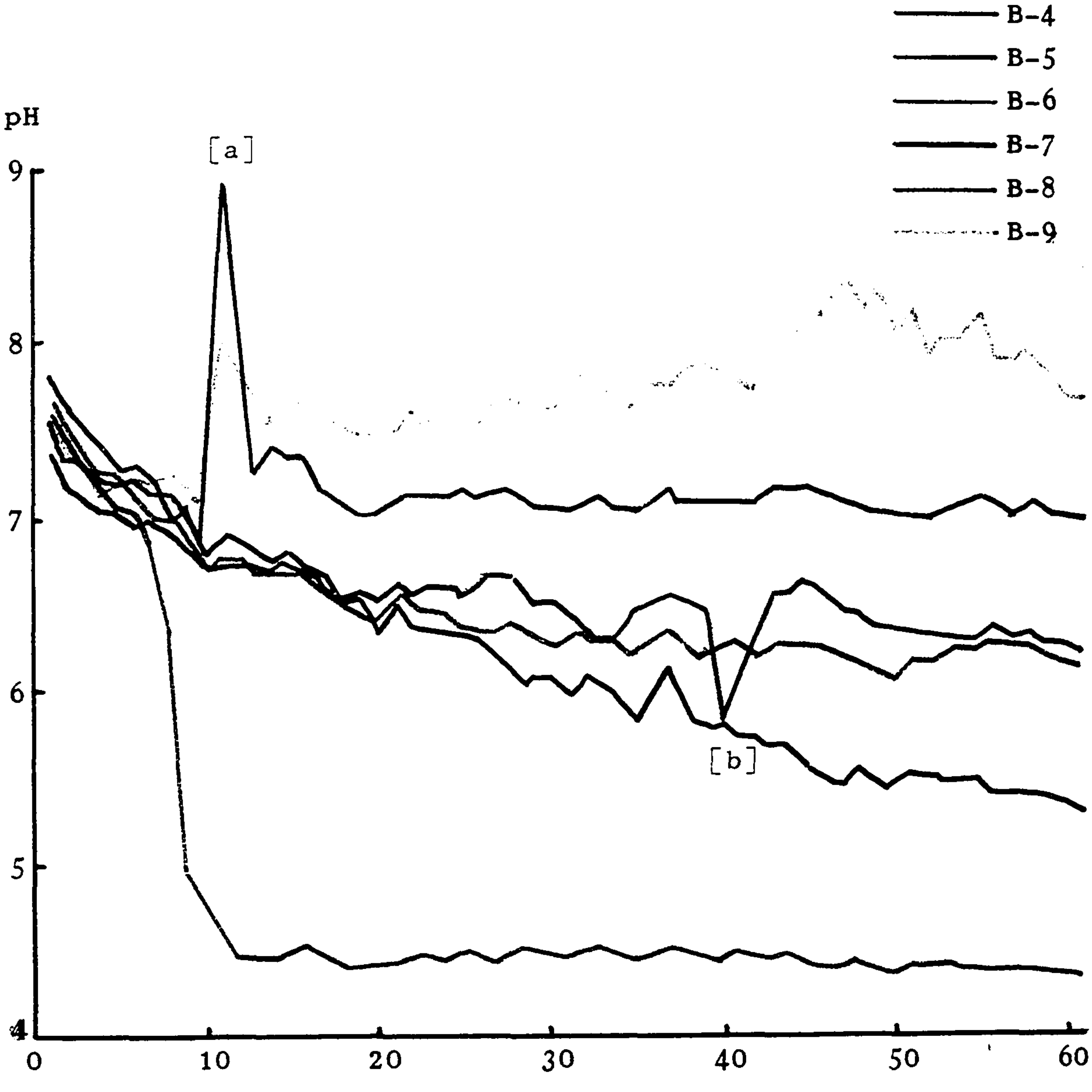

Figure 4. pH of effluent solutions, feldspar B. [a] reflects installation of ammonia-vapor baths, B-8 and B-9 only. [b] reflects documented contamination, B-7 only.

B-9 decreased on standing due probably to a loss of $NH_3\uparrow$ possibly coupled with the absorption of CO_2. Since the flow rates within individual periods varied and since sampling and measuring times also varied, the values obtained for these columns are unavoidably complicated, but they do represent minimum effluent pH values and show trend relations. The effluent pH's for all the other columns show essentially no change on standing. The pH curves for columns A-4 and B-4 show a rather dramatic change with time. From an effluent pH of 7.30 for A-4 and 7.57 for B-4 at the end of the first period, they decrease in relatively few periods to pH's only slightly in excess of the leaching solution pH. This probably reflects the development of a decomposition product on the shell of the feldspar grains which is more nearly in equilibrium with the leaching environment. However, it is obvious that leaching continued to take place although to a lesser degree. While the flattened portion of the curve probably represents a near-equilibrium and a critical thickening of the protective shell, close inspection revealed that the curves continued to decrease. This is possibly due to a continued slight thickening of the residue product. Curves A-5 and B-5 show a more gradual decrease in slope than do A-4 and B-4. This is due to the relative ineffectiveness of the leaching solutions of pH 5 as compared to pH 4. It is somewhat anomalous then, that they do not flatten out more rapidly than the more neutral leaching solutions of pH's 6 and 7. This could be interpreted to indicate that the feldspars are more nearly stable in nearly neutral leaching environments or that the thickness the residue layer attains is somewhat dependent upon the concentration of the leaching solution. The curve for columns 8 and 9 display a similar though less obvious slope relationship. Similar suggestions based on different data have been put forth by Marshall (1964).

Of interest is the effluent pH for all columns of both feldspars (A and B) at the end of the first few periods. Regardless of the pH of the leaching solutions, all effluent pH values are in the range of 7.30 to 7.80. The similarity in pH and the strong parallelism of the curves for the next few periods may represent initial hydration of the fresh feldspar surfaces where many ions of unsatisfied valences would be present. Dipolar water molecules would be attracted to the Si and Al ions. The polarization of the attracted water molecules might be sufficiently strong so that some of the H ions are expelled (Jenny, 1950). These H ions would hydrolyze (exchange for) exposed K^+ and Na^+. In more acid solutions, there would tend to be more hydronium ion (H_3O^{+1}) present which would neither hydrate nor exchange as readily as

H_2O (Marshall, 1964). Hence, the H ions released by hydration in the less acid solutions might tend to equalize the hydrolysis capabilities between less acid and more acid leaching solutions. Once a hydrated surface layer had been formed, this equalization process would tend to be ineffective. It might also be noted here that some of the freed H ions may be attached to exposed oxygen ions converting them to hydroxyl ions. This, plus the HO-Si and HO-Al hydration would tend to surround the surface Si and Al ions with hydroxyls. For Al^{+3} there would be a tendency to achieve a preferred octahedral coordination but Si-OH units in tetrahedral coordination would perhaps tend to be unstable thus causing the solution of Si^{+4} as monosilicic acid, H_4SiO_4.

As in the pH data, Si^{+4} shows a rapid initial leaching followed by a flattening out of the leaching curve thus indicating the development of a near-equilibrium product (Table III and Figures 5-6). The total silica leached over the full term of the experiment shows a pH dependency (Table III). However, the amount of Si^{+4} leached out during the first few periods, with the minor exception of A-4 and B-4 is relatively independent of pH (Figures 5-6). After the first few periods, the effluent Si^{+4} curves begin to reflect the pH dependency. This might be explained as follows: if, as previously contended, hydrolysis is not

Table III. Effluent Si^{+4} in ppm

Period	1	2	3	4	5	6	7	9	12
Column									
A-4	3.96	3.23	3.07	2.95	2.04	1.95	1.38	1.49	1.32
A-5	3.73	3.05	2.90	2.27	1.74	1.69	1.26	1.26	1.03
A-6	3.39	3.00	2.47	2.15	1.52	1.80	1.24	1.15	.88
A-7	3.48	3.00	2.67	2.08	1.90	1.67	1.03	1.00	.70
A-8	3.71	3.23	2.71	2.34	1.52	1.54	1.00	1.00	.80
A-9	3.63	2.98	2.47	2.05	1.56	1.48	1.10	1.08	.89
B-4	4.34	3.50	3.02	2.98	2.83	2.62	1.82	1.73	1.39
B-5	4.56	3.70	3.36	2.67	2.22	2.08	1.55	1.55	1.26
B-6	4.25	3.49	3.21	2.55	2.19	2.00	1.45	1.36	.98
B-7	4.32	3.72	3.08	2.57	2.05	1.88	1.30	1.27	.96
B-8	4.26	3.52	3.10	2.40	2.15	1.95	1.32	1.19	1.14*
B-9	4.52	3.82	3.29	2.88	2.20	1.95	1.31	1.35	1.82*

Period	15	18	21	24	27	30	33	36	39
Column									
A-4	1.31	1.42	1.37	1.36	1.41	1.36	1.33	1.26	1.26
A-5	.89	.84	.80	.78	.69	.63	.58	.56	.56
A-6	.68	.66	.68	.60	.61	.57	.47	.39	.44
A-7	.65	.59	.60	.51	.46	.48	.40	.34	.40
A-8	.68*	.55	.51	.57	.83	.78	.81	.73	.65
A-9	1.39*	1.30	1.51	1.66	1.63	1.52	1.48	1.25	1.19
B-4	1.36	1.50	1.41	1.46	1.33	1.47	1.42	1.44	1.22
B-5	1.07	1.03	.95	.88	.92	.88	.84	.82	.78
B-6	.88	.81	.78	.67	.64	.61	.61	.53	.57
B-7	.79	.75	.75	.62	.61	.58	.57	.50	.54
B-8	.83	.72	.62	.51	.47	.48	.44	.42	.40
B-9	1.46	1.20	1.08	.84	.91	.81	.83	1.00	.98

Period	42	45	48	51	54	57	60	TOTAL
Column								
A-4	1.24	1.34	1.30	1.29	1.24	1.21	1.30	42.39
A-5	.51	.50	.56	.44	.42	.43	.45	29.20
A-6	.39	.38	.40	.36	.34	.36	.36	25.30
A-7	.32	.34	.38	.34	.34	.34	.34	24.36
A-8	.61	.61	.70	.59	.57	.60	.68	28.32
A-9	1.11	1.09	1.02	1.00	.82	.94	.79	36.94
B-4	1.34	1.37	1.41	1.41	1.39	1.35	1.37	46.48
B-5	.78	.73	.70	.70	.67	.63	.63	35.96
B-6	.53	.51	.49	.50	.53	.47	.48	30.17
B-7	.55	.46	.56	.48	.46	.43	.39	30.19
B-8	.38	.41	.43	.39	.37	.33	.34	28.57
B-9	.84	.95	.96	.98	.92	.90	.89	38.69

* Reflects installation of ammonia-vapor bath.

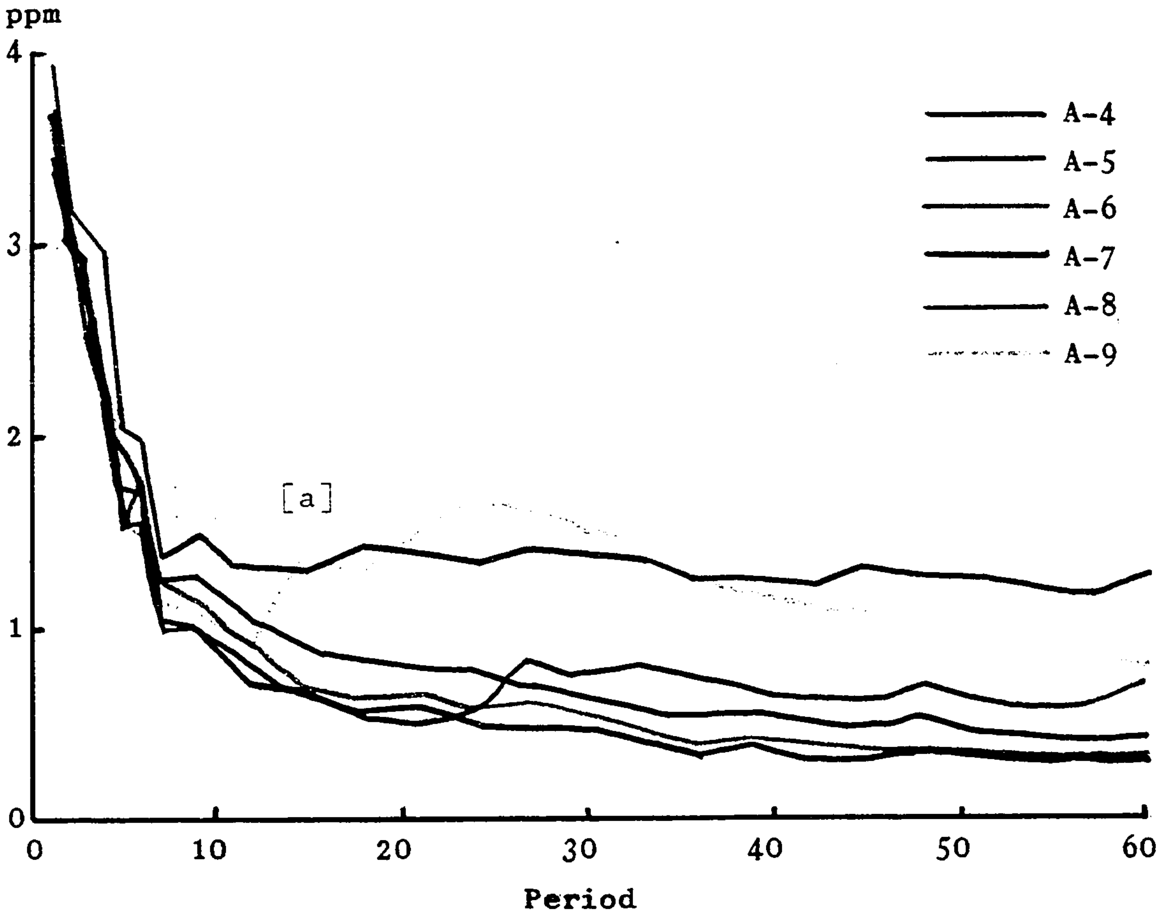

Figure 5.– Effluent Si^{+4} in ppm, feldspar A. [a] reflects installation of ammonia-vapor baths, A-9 only.

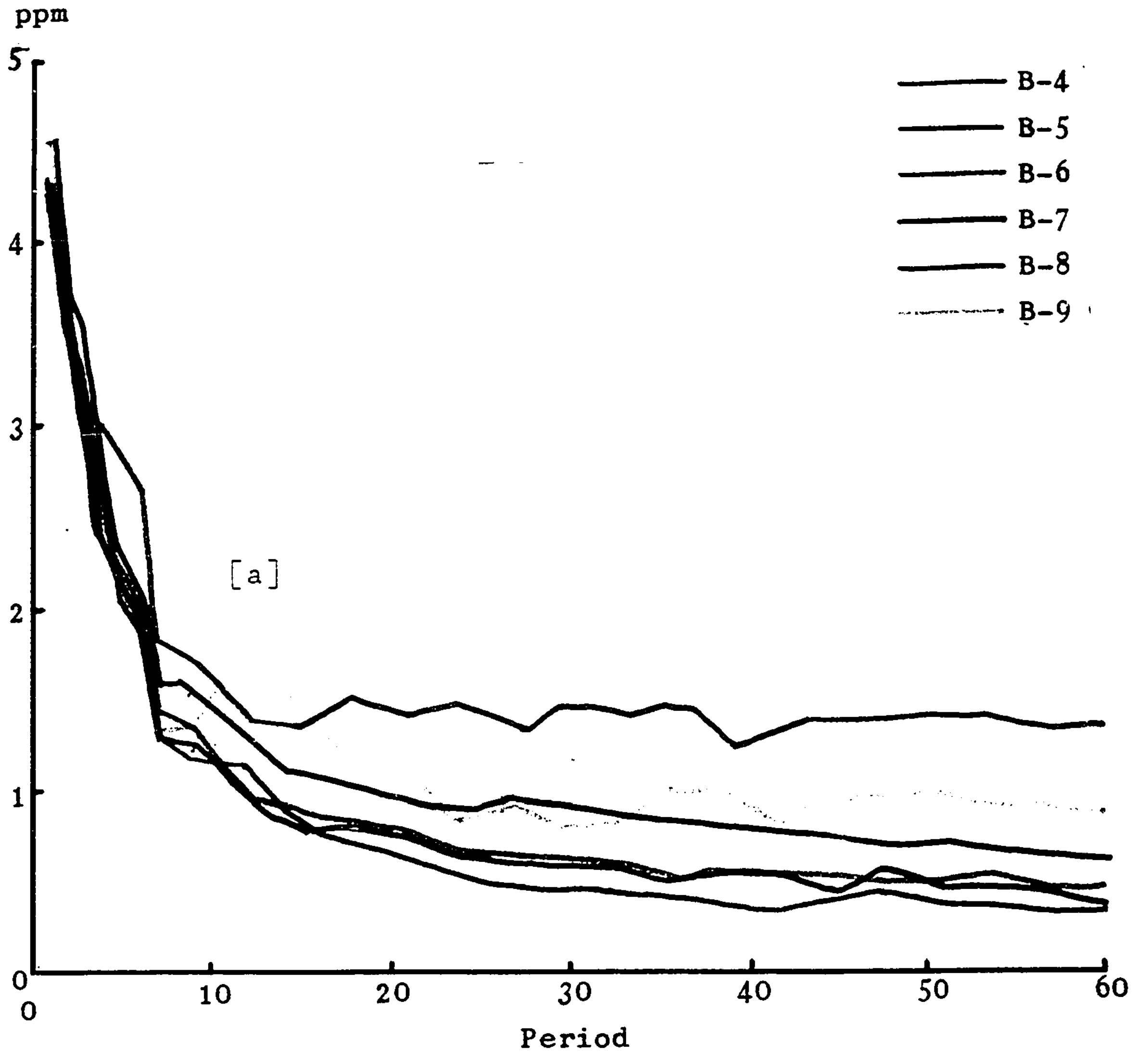

Figure 6. Effluent Si^{+4} in ppm, feldspar B. [a] reflects installation of ammonia-vapor baths, B-9 only.

significantly pH dependent until a residue layer is developed, then the effectiveness of pH in removing Na^+ and K^+ would have to await the development of the residue layer. Once developed, however, a greater H^+ concentration (and also NH_4^+) would cause a greater leaching of Na^+ and K^+. The degree of lattice distortion due to the removal of Na^+ and K^+ would be greater with increased H^+ concentration and, with greater distortion, there would be greater Si^{+4} solubility. The slightly more rapid development of a pH dependency for curves A-4 and B-4 is probably due to a more rapid development of the residue layer.

The data clearly shows that within the pH range of natural waters, Si^{+4} is more soluble in more acid solutions, thus confirming the observations of Pickering (1962) and Woodruff (1954) and the conclusions of Krauskopf (1959) and McKeague and Cline (1963).

The data for effluent Na^+ and K^+ are given in Tables IV-V and Figures 7-10. Effluent Na^+ shows an initial pH independent behavior similar to that shown by Si^{+4} and a later pH dependency. On the other hand, effluent K^+ seems to display a pH dependency right from the start of leaching. In addition, the early behavior of the curves differs markedly from that of Si^{+4} and Na^+. There is an initial drop off in the amount of K^+ leached which probably reflects

Table IV. Effluent Na^+ in ppm

Period	1	2	3	4	5	6	7	9	12
Column									
A-4	1.100	.520	.420	.380	.284	.221	.165	.171	.159
A-5	1.000	.420	.300	.220	.200	.179	.155	.159	.136
A-6	.980	.400	.260	.200	.179	.189	.144	.136	.165*
A-7	.760	.340	.300	.220	.647*	.221	.113	.112	.083*
A-8	1.040	.380	.280	.220	.179	.169	.124	.116	.136*
A-9	.830	.280	.260	.200	.158	.414*	.113	.124	.124
B-4	1.700	1.040	.800	.779	.677	.678	.500	.408	.288
B-5	1.520	.880	.760	.566	.462	.435	.330	.340	.300
B-6	1.460	.920	.680	.545	.462	.435	.309	.319	.242
B-7	1.620	.960	.700	.566	.442	.403	.278	.309	.218*
B-8	1.540	.860	.660	.525	.442	.424	.278	.278	.288**
B-9	1.620	.720	.640	.525	.442	.403	.278	.258	.342*

Period	15	18	21	24	27	30	33	36	39
Column									
A-4	.165	.192	.179	.176	.185	.195	.195	.193	.188
A-5	.112	.124	.102	.095	.095	.024	.084	.086	.106
A-6	.083	.093	.077	.100	.086	.079	.064	.056	.056
A-7	.077	.081	.064	.055	.050	.059	.050	.046	.051
A-8	.059	.062	.051	.079*	.055*	.079	.084	.087	.077
A-9	.077	.136	.141	.181*	.302*	.181	.171	.162	.157
B-4	.267	.304	.262	.282	.272	.287	.302	.285	.292
B-5	.254	.254	.218	.190	.200	.195	.190	.192	.187
B-6	.198	.211	.154	.139	.134	.129	.129	.118	.115
B-7	.180	.186	.147	.124*	.109	.124	.114	.098	.141
B-8	.118	.134	.128	.229**	.050	.090	.084	.087	.089
B-9	.198	.243	.205	.255*	.139	.159	.164	.213	.247

Period	42	45	48	51	54	57	60	TOTAL
Column								
A-4	.192	.213	.208	.204	.204	.200	.198	6.507
A-5	.074	.075	.068	.064	.064	.060	.062	4.120
A-6	.053	.055	.052	.052	.048	.044	.046	3.697
A-7	.048	.045	.044	.048	.048	.044	.043	3.649
A-8	.089	.075	.072	.068	.084	.088	.096	3.773
A-9	.156	.148	.120	.140	.104	.140	.120	4.939
B-4	.298	.292	.314	.290	.294	.290	.278	11.479
B-5	.166	.169	.144	.152	.152	.145	.149	8.450
B-6	.110	.105	.104	.108	.108	.100	.104	7.438
B-7	.100	.085	.120	.104	.100	.088	.096	7.412
B-8	.095	.080	.076	.084	.088	.072	.092	6.891
B-9	.177	.208	.208	.220	.223	.216	.210	8.513

* Documented contamination.

** Reflects installation and adjustment of ammonia-vapor baths.

Table V. Effluent K^+ in ppm

Period	1	2	3	4	5	6	7	9	12
Column									
A-4	1.038	1.187	1.270	1.166	.790	.478	.282	.260	.207
A-5	.770	.603	.645	.603	.562	.499	.396	.418	.319
A-6	.707	.645	.666	.582	.499	.478	.384	.362	.233
A-7	.811	.832	.770	.728	.728	.395	.328	.362	.233*
A-8	1.060	.954	.749	.707	.582	.478	.350	.316	2.030*
A-9	2.109	.624	.478	.437	.395	.333	.305	.339	5.305*
B-4	.437	.374	.475	.565	.542	.531	.429	.241	.302
B-5	.354	.250	.305	.339	.328	.305	.249	.224	.190
B-6	.333	.291	.384	.373	.350	.339	.237	.216	.155
B-7	.478	.520	.509	.509	.396	.305	.215	.216	.134*
B-8	.458	.458	.463	.441	.418	.350	.249	.216	5.200*
B-9	1.124	.437	.362	.350	.305	.283	.215	.172	3.050*

Period	15	18	21	24	27	30	33	36	39
Column									
A-4	.198	.254	.205	.174	.198	.182	.182	.164	.173
A-5	.216	.198	.182	.133	.125	.109	.100	.091	.109
A-6	.181	.182	.198	.149	.141	.127	.109	.091	.082
A-7	.181*	.182	.230	.174*	.166*	.118	.091	.091	.073
A-8	1.206*	.230	.246	.413*	.493*	.264*	.218	.164	.136
A-9	1.186*	.437	.453	.508*	.548*	.506*	.291	.273	.273
B-4	.100	.141	.120	.092	.085	.091	.082	.082	.082
B-5	.134	.141	.120	.092	.085	.073	.064	.064	.064
B-6	.108	.114	.120	.100	.085	.064	.064	.055	.055
B-7	.108*	.125	.182	.125*	.100*	.064	.064	.064	.055
B-8	2.235*	.278	.222	4.785*	.635*	.191	.100	.064	.064
B-9	1.269*	.222	.190	2.840*	.389*	.100	.064	.064	.082

Period	42	45	48	51	54	57	60	TOTAL
Column								
A-4	.179	.187	.178	.170	.158	.158	.169	9.607
A-5	.076	.068	.068	.060	.060	.060	.074	6.544
A-6	.076	.076	.057	.057	.053	.060	.053	6.282
A-7	.076	.060	.040	.040	.053	.047	.047	6.856
A-8	.136	.150	.130	.100	.097	.097	.111	11.317
A-9	.250	.234	.201	.210	.111	.125	.111	16.042
B-4	.092	.068	.083	.076	.067	.082	.074	5.313
B-5	.054	.042	.057	.047	.033	.047	.040	3.701
B-6	.048	.048	.033	.033	.033	.040	.053	3.731
B-7	.048	.036	.033	.027	.033	.033	.033	4.412
B-8	.054	.054	.040	.033	.033	.033	.047	17.121
B-9	.068	.068	.057	.057	.067	.047	.053	11.935

* Reflects installation and adjustment of ammonia-vapor baths.

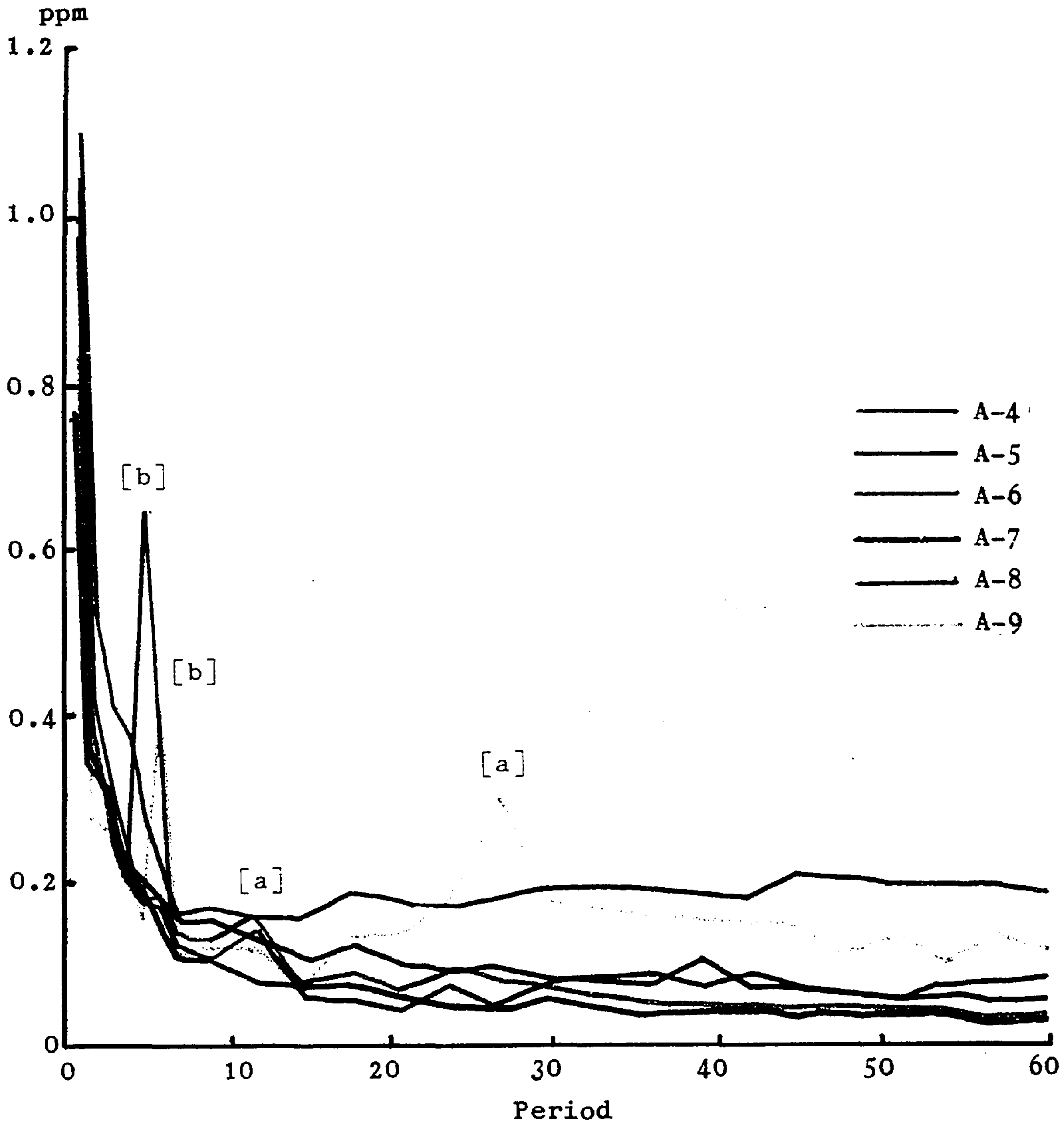

Figure 7. Effluent Na^+ in ppm, feldspar A. [a] reflects installation of ammonia-vapor baths, A-8 and A-9 only. [b] reflects documented contamination, A-7 and A-9 only.

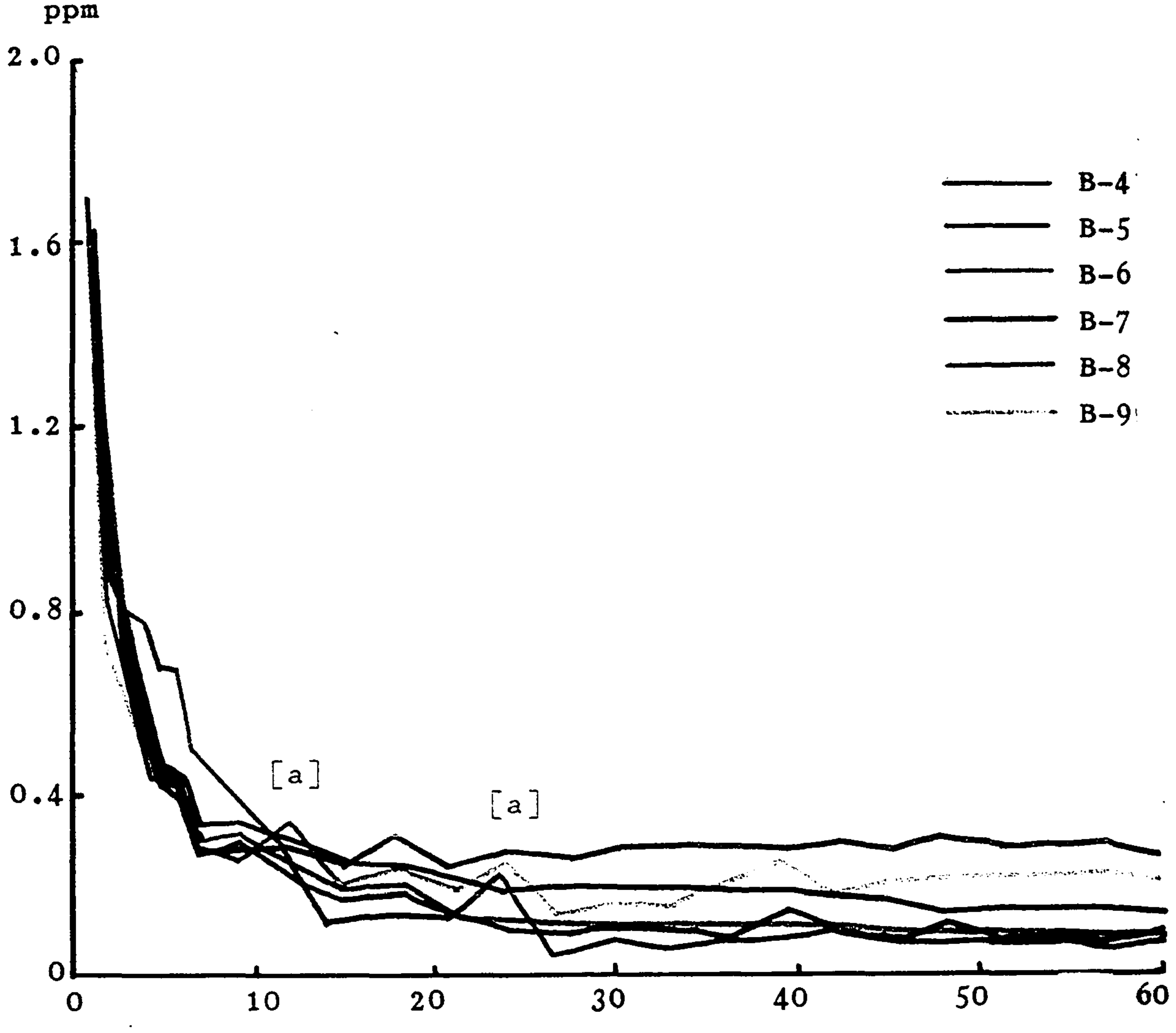

Figure 8. Effluent Na^+ in ppm, feldspar B. [a] reflects installation of ammonia-vapor baths, B-8 and B-9 only.

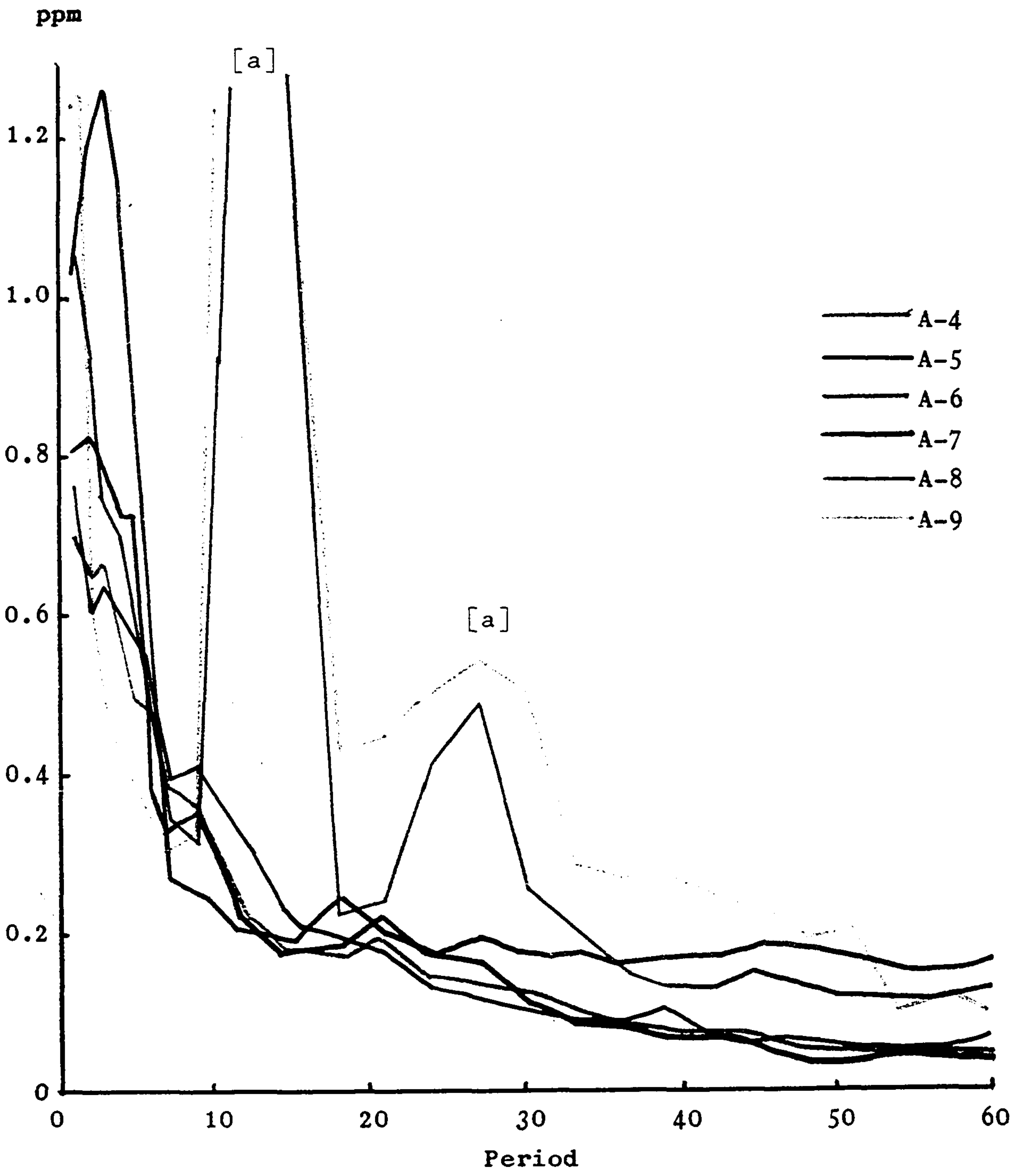

Figure 9. Effluent K^+ in ppm, feldspar A. [a] reflects installation of ammonia-vapor baths, A-8 and A-9 only.

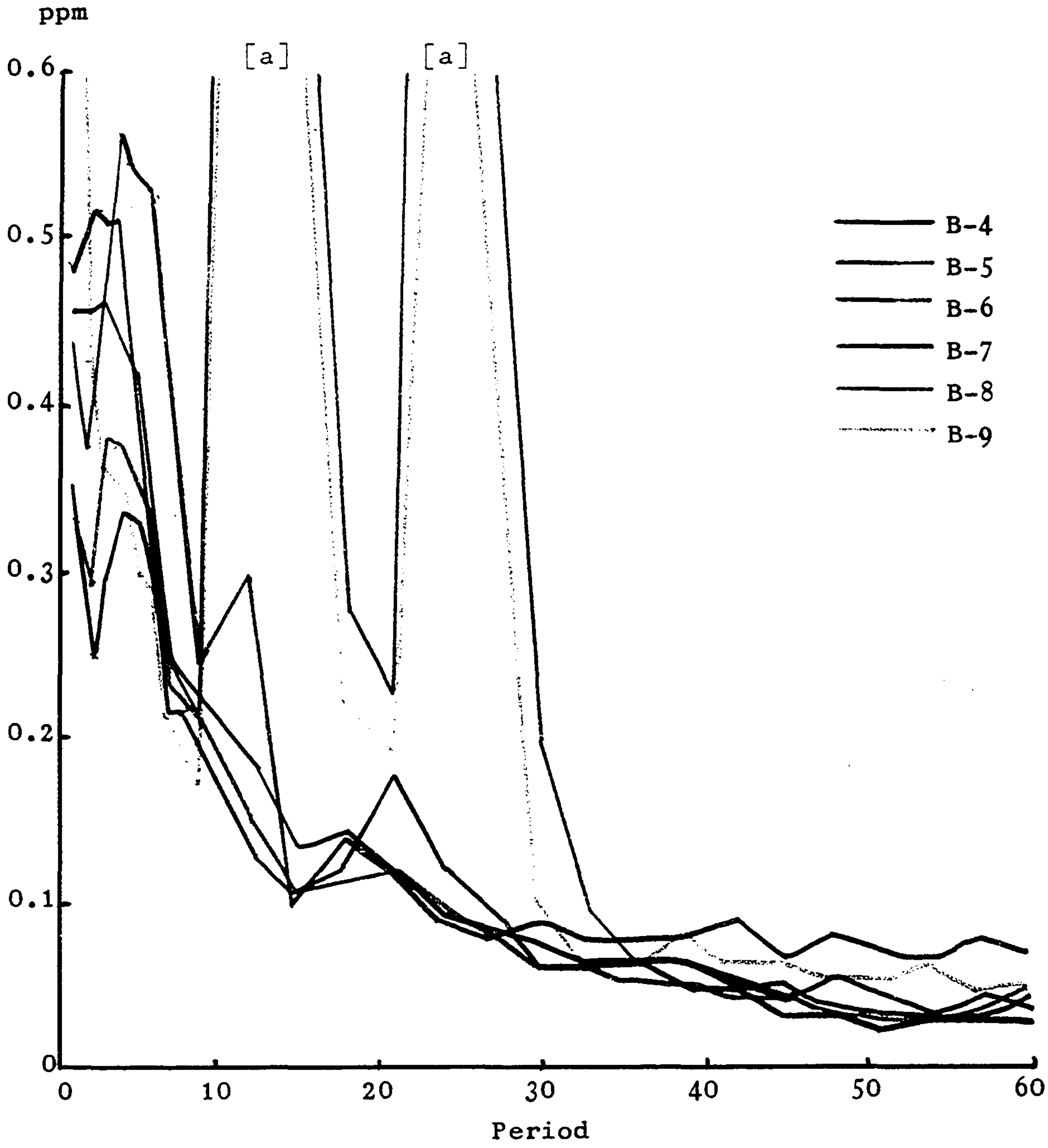

Figure 10. Effluent K^+ in ppm, feldspar B. [a] reflects installation of ammonia-vapor baths, B-8 and B-9 only.

the removal of loose surface K^+. This is followed, in most cases, by a rise in the amount of K^+ leached. The time over which this rise takes place closely corresponds with the interval during which the Si^{+4} curves display their relative independence from pH effects. This rise is interpreted as occurring due to the progressive expansion of the feldspar structure following distortion due to the loss of positive ions. Expansion of the lattice permits K^+ to be more readily removed. Na^+ does not exhibit the same behavior because, due to its smaller size, the lattice expansion would not be as significant a factor. As the residue layer becomes more fully developed, K^+ exhibits a fall off due to the protective effect of the weathering shell. Exceptions to this behavior of the K^+ curve are A-8, A-9, B-8 and B-9. In view of the exceptional ability of NH^{4+} to liberate K^+ from the feldspar structure (Nash and Marshall, 1956) it would seem probable that this speeds up the lattice expansion to the extent that it is not reflected in these K^+ effluent curves. This is further demonstrated by the remarkable increases in the amount of K^+ leached following installation and adjustment of the ammonia-vapor baths. It should be noted that Si^{+4} and Na^+ exhibit this reaction to increased NH_4^+ to a far lesser degree.

The amount of effluent solution which flowed through the columns during each period was recorded (Table VI). For

Table VI. Effluent flow in ml/period (average flow for periods 8-61)

Period	1	2	3	4	5	6	7	9	12
Column									
A-1	1000	1000	1000	1000	1000	1000	1027	989	1003
A-2	1000	1000	1000	1000	1000	1006	994	1000	1000
A-3	1000	1000	1000	1000	1000	1004	996	1000	1001
A-4	1000	1000	1000	1000	1000	1017	983	1006	1003
A-5	1000	1000	1000	1000	1000	1000	1011	1001	995
A-6	1000	1000	1000	1000	1024	976	1000	1001	960
B-1	1000	1000	1000	1027	987	986	1030	1000	1000
B-2	1000	1000	1000	1000	1000	1000	1032	989	1001
B-3	1000	1000	1000	1000	1000	1000	1003	1000	1009
B-4	1000	1000	1000	1000	1000	1000	1009	997	1001
B-5	1000	1000	1000	1006	1016	978	1009	997	1009
B-6	1000	1000	1000	1000	1000	1000	1029	990	1009

Period	15	18	21	24	27	30	33	36	39
Column									
A-1	1008	996	995	1000	999	1000	1001	997	1003
A-2	1000	1010	995	985	1011	992	1017	978	1016
A-3	999	994	986	1012	1007	1010	961	1031	994
A-4	991	996	1004	986	1017	997	1000	1003	994
A-5	1005	995	995	700	485	430	359	383	472
A-6	734	577	457	295	369	238	204	207	230
B-1	990	996	1004	987	1013	1011	992	983	1013
B-2	999	1000	1000	1004	999	1011	991	980	1019
B-3	992	1008	988	996	999	1017	975	1018	990
B-4	999	995	1005	999	1000	1007	993	1011	999
B-5	924	1008	1000	992	1001	989	1001	1017	991
B-6	991	1009	989	1000	999	993	948	700	617

Period	42	45	48	51	54	57	60	TOTAL
Column								
A-1	1006	994	999	1000	1000	1012	988	61,000
A-2	1006	995	995	1004	1006	993	1000	61,011
A-3	991	1018	979	1011	1004	991	1002	60,975
A-4	1012	977	994	1007	969	986	998	60,025
A-5	417	369	358	458	403	328	286	38,215
A-6	218	265	254	279	245	214	238	27,951
B-1	1001	1005	994	1001	999	1015	988	61,000
B-2	998	1001	1000	1000	975	996	977	60,846
B-3	1002	980	994	1027	914	938	909	60,270
B-4	994	996	995	1005	995	999	1009	61,018
B-5	1001	1002	993	1000	998	1002	1004	60,771
B-6	643	524	523	505	488	411	377	47,980

most columns, the flow was approximately one liter per period. However, columns A-8, A-9, and B-9 displayed a marked tendency towards reduced flow. Although not apparent from the data, the writer observed that B-8 also exhibited a tendency towards reduced flow. However, a small break in the filter paper which was discovered on dismantling the column, permitted a normal flow rate for B-5. On sampling the columns, a very fine sludge-like material was found to heavily coat the filter paper of the columns showing diminished flow and it is to the clogging effect of this material to which the reduced flow is attributed. This sludge-like material was also found on the filter paper of columns A-6, A-7, B-6 and B-7 but in less amounts. Much less sludge-like material was found to coat the filter paper from columns A-4, A-5, B-4 and B-5. X-ray analysis of the material recovered from the filter paper leads to the interpretation that it is a highly disorganized form of silicate wreckage (Figure 29). It is unlikely that it represents material precipitated from true ionic solution as it would then be expected to also appear as a coating in the tubing leading to the effluent solution containers. On the other hand, it could represent a rapid precipitation from solution in near proximity to the grains from which the ions were leached. They would then be expected to be washed down the column and retained by the filter paper.

However, there was a positive relationship between the NH_4OH content of the leaching solutions and the amount of sludge-like material recovered and the onset of reduced flow can be equated with the episodes of exceptional K^+ removal which coincided with the installation and adjustment of the ammonia-vapor baths (Figures 11-12). This followed by the rapid reestablishment of equilibrium suggests the partial destruction and removal of the residue product in response to a relatively more alkaline leaching solution.

The values for Si/K and Si/Na were calculated in an attempt to shed more light on the development and nature of the residue layer (Tables VII and VIII, Figures 13-16). Si/K and Si/Na ratios for the feldspars prior to leaching are given in the figure captions. The curves for A-8, A-9, B-8 and B-9 are somewhat subjective as they represent an attempt to correct for the extensive leaching of K^+, and to a lesser degree Na^+, due to the installation and adjustment of the ammonia-vapor baths. In correcting these curves, emphasis was placed on periods 1-7 and 36-60. All the curves have been smoothed for the purpose of clarity. Actual values are given in Tables VII and VIII.

The initial behavior of the Si/K curves shows that an increasing amount of K^+ is released relative to Si^{+4}. This occurs largely over the interval in which absolute K^+ leached increases and Si^{+4} decreases (Figures 5-6, 9-10).

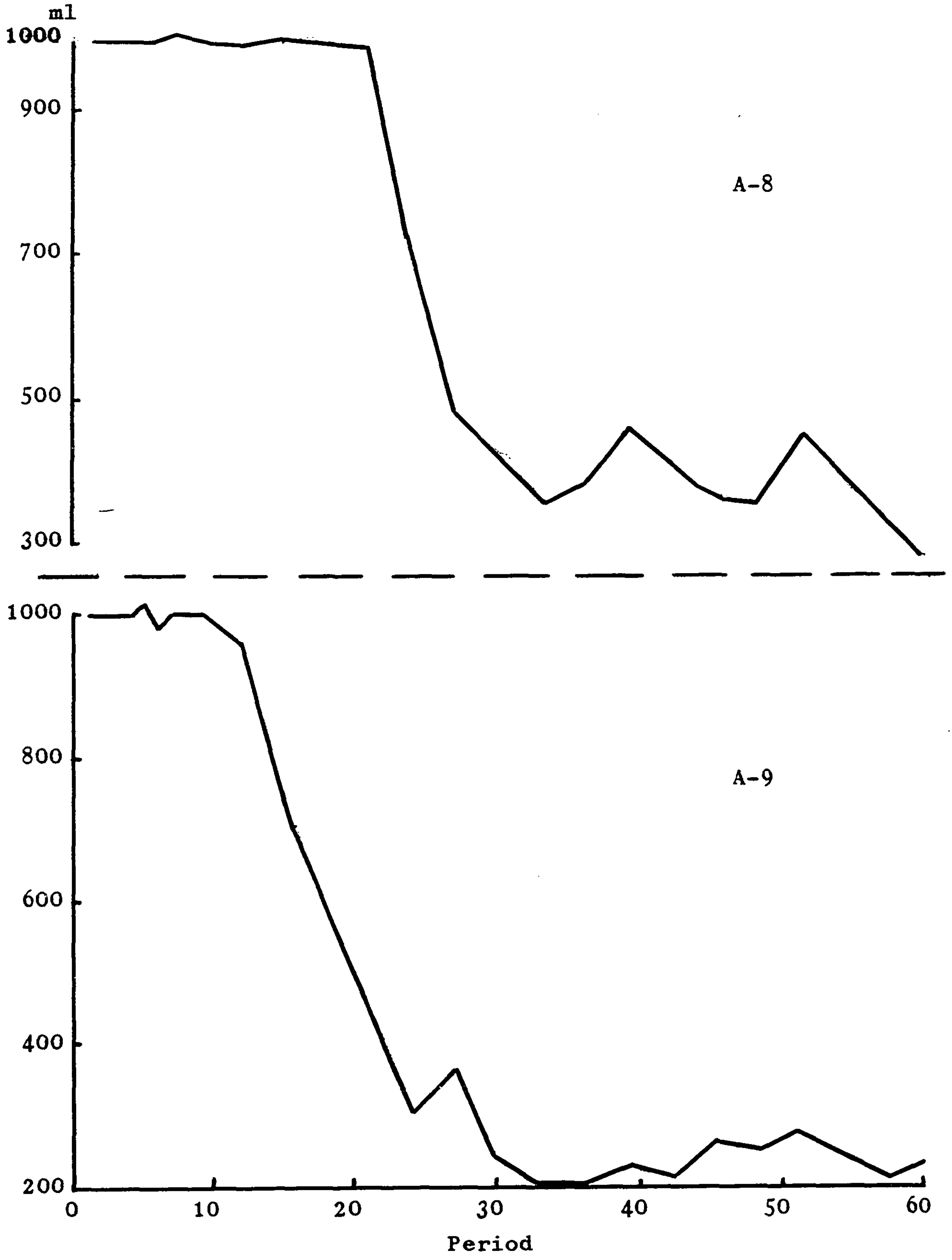

Figure 11. Flow record in ml. per period, A-8 and A-9.

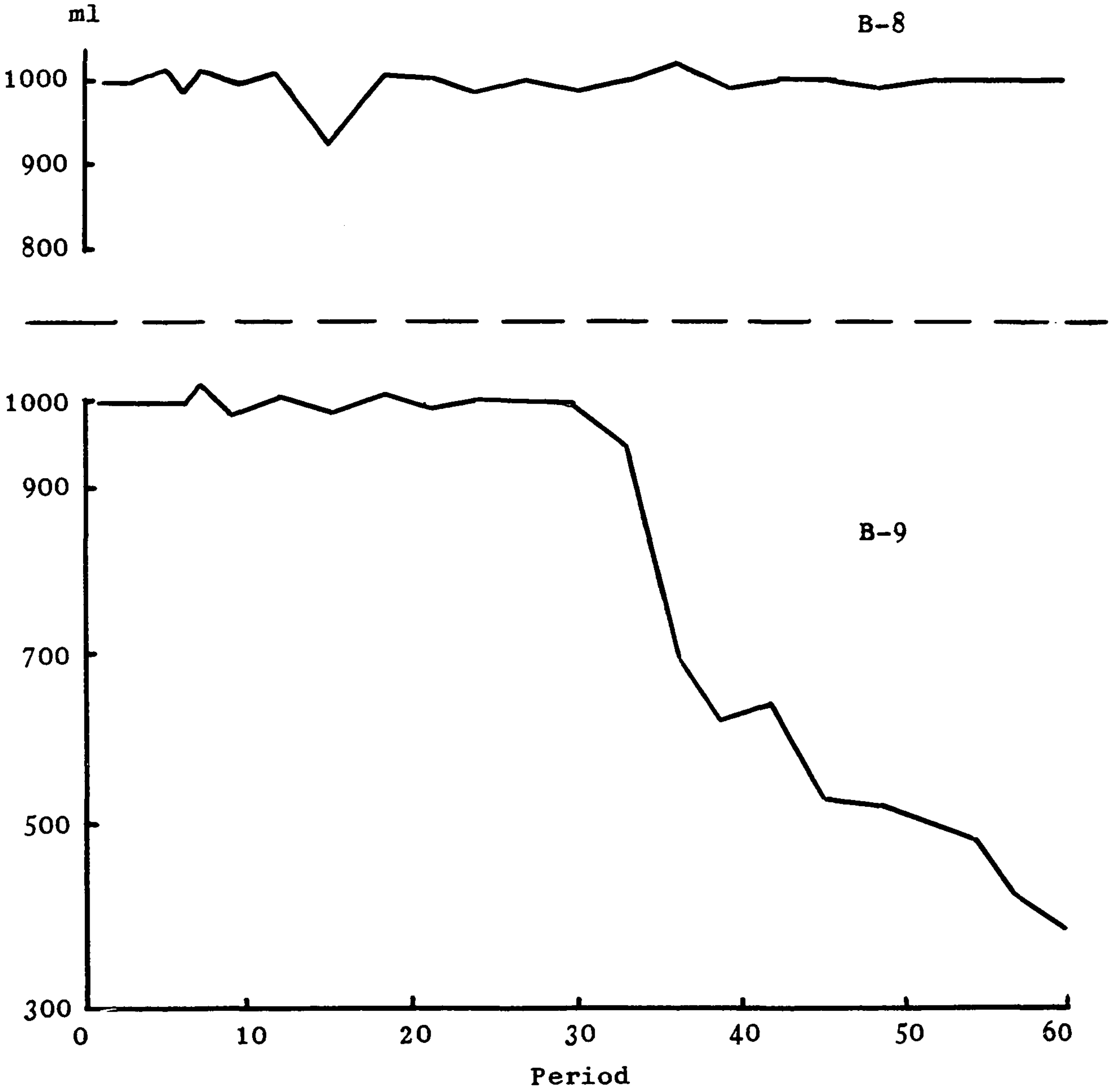

Figure 12. Flow record in ml. per period, B-8 and B-9.

Table VII. Effluent solutions as Si/K in ppm

Period	1	2	3	4	5	6	7	9	12
Column									
A-4	3.82	2.72	2.42	2.53	2.58	4.08	4.89	5.73	6.38
A-5	4.84	5.06	4.50	3.76	3.10	3.39	3.18	3.01	3.23
A-6	4.79	4.65	3.71	3.69	3.05	3.77	3.23	3.18	3.78
A-7	4.29	3.61	3.47	2.86	2.61	4.23	3.14	2.76	3.00*
A-8	3.50	3.39	3.62	3.31	2.61	3.22	2.86	3.16	0.39*
A-9	1.72	4.78	4.18	4.69	3.95	4.44	3.61	3.19	0.17*
B-4	9.93	9.36	6.36	5.27	5.22	4.93	4.24	7.18	4.60
B-5	12.88	14.80	11.02	7.88	6.77	6.82	6.22	6.92	6.63
B-6	12.76	11.99	8.36	6.84	6.26	5.90	6.12	6.30	6.32
B-7	9.04	7.15	6.05	5.05	5.18	4.75	6.05	5.88	7.16*
B-8	9.30	7.69	6.70	5.44	5.14	5.57	5.30	5.51	0.22*
B-9	4.02	8.74	9.09	8.23	7.21	6.89	6.09	7.85	0.60*

Period	15	18	21	24	27	30	33	36	39
Column									
A-4	6.62	5.59	6.68	7.82	7.12	7.47	7.31	7.68	7.28
A-5	4.12	4.24	4.40	5.86	5.52	5.78	5.80	6.15	5.14
A-6	3.76	3.63	3.43	4.03	4.33	4.49	4.31	4.29	5.37
A-7	3.59*	3.24	2.61	2.93*	2.77*	4.07	4.40	3.74	5.48
A-8	0.56*	2.39	2.07	1.38*	1.68*	2.95	3.72	4.45	4.78
A-9	1.17*	2.97	3.33	3.27	2.97	3.00	5.09	4.58	4.36
B-4	13.60	10.64	11.75	15.87	15.65	16.15	17.32	17.56	14.88
B-5	7.99	7.30	7.92	9.57	10.82	12.05	13.13	12.81	12.19
B-6	8.15	7.11	6.50	6.70	7.53	9.53	9.53	9.64	10.36
B-7	7.31*	6.00	4.12	4.96*	6.10*	9.06	8.91	7.81	9.82
B-8	0.37*	2.59	2.79	0.11*	0.74*	2.51	4.40	6.56	6.25
B-9	1.15*	5.41	5.68	0.30*	2.34*	8.10	12.97	15.63	11.95

Period	42	45	48	51	54	57	60		
Column									
A-4	6.93	7.17	7.30	7.59	7.85	7.66	7.69		
A-5	6.71	7.35	8.24	7.33	7.00	7.17	6.09		
A-6	5.13	5.00	7.02	6.32	6.42	6.00	6.79		
A-7	4.21	5.67	9.50	8.50	6.42	7.23	7.23		
A-8	4.49	4.07	5.38	5.90	5.88	6.19	6.13		
A-9	4.44	4.66	5.08	4.76	7.39	7.52	7.12		
B-4	14.57	20.15	16.99	18.55	20.75	16.46	18.51		
B-5	14.44	17.38	12.28	14.89	20.30	13.40	15.75		
B-6	11.04	10.63	14.85	15.15	16.06	11.75	9.06		
B-7	11.46	12.78	16.97	17.78	13.94	13.03	13.03		
B-8	7.04	7.59	10.75	11.82	11.21	10.00	7.23		
B-9	12.35	13.97	16.84	17.19	13.73	19.36	16.79		

* Reflects installation and adjustment of ammonia-vapor baths.

Table VIII. Effluent solutions as Si/Na in ppm

Period	1	2	3	4	5	6	7	9	12
Column									
A-4	3.60	6.21	7.31	7.76	7.18	8.82	8.36	8.71	8.30
A-5	3.73	7.26	9.67	10.32	8.70	9.44	8.13	7.92	7.57
A-6	3.46	7.50	9.50	10.75	8.49	9.52	8.61	8.46	5.33*
A-7	4.58	8.82	8.90	9.45	2.94*	7.56	9.12	8.93	8.43
A-8	3.57	8.50	9.68	10.64	8.49	9.11	8.64	8.93	5.88⁑
A-9	4.37	10.64	9.50	10.25	9.87	3.57*	9.73	8.71	7.18⁑
B-4	2.55	3.37	3.78	3.83	4.18	3.86	3.64	4.24	4.83
B-5	3.00	4.20	4.42	4.72	4.81	4.78	4.70	4.56	4.20
B-6	2.91	3.79	4.72	4.68	4.74	4.60	4.69	4.26	4.05
B-7	2.67	3.88	4.40	4.54	4.64	4.67	4.68	4.11	4.40
B-8	2.78	4.09	4.70	4.57	4.86	4.60	4.75	4.28	3.96⁑
B-9	2.79	5.31	5.14	5.49	4.98	4.84	4.71	5.23	5.32
Period	**15**	**18**	**21**	**24**	**27**	**30**	**33**	**36**	**39**
Column									
A-4	7.94	7.40	7.65	7.73	7.62	6.97	6.82	6.53	6.70
A-5	7.95	6.78	7.84	8.21	7.26	7.50	6.90	6.83	5.28
A-6	8.19	7.10	8.83	6.00	7.10	7.21	7.34	6.96	7.86
A-7	8.44	7.28	9.38	9.27	9.20	8.14	8.00	7.39	7.84
A-8	11.53	8.87	10.00	7.22⁑	15.09	9.87	9.64	8.39	8.44
A-9	18.05	9.56	10.71	9.17	5.40	8.40	8.65	7.72	7.58
B-4	5.09	4.93	5.38	5.18	4.89	5.12	4.70	5.05	4.18
B-5	4.21	4.06	4.36	4.63	4.60	4.51	4.42	4.27	4.17
B-6	4.44	3.84	5.06	4.82	4.78	4.73	4.73	4.49	4.96
B-7	4.39	4.03	5.10	5.00⁑	5.60	4.68	5.00	5.10	3.83
B-8	7.03	5.37	4.84	2.23⁑	9.40	5.33	5.24	4.83	4.49
B-9	7.37	4.94	5.27	3.29⁑	6.55	5.09	5.06	4.69	3.97
Period	**42**	**45**	**48**	**51**	**54**	**57**	**60**		
Column									
A-4	6.46	6.29	6.25	6.32	6.09	6.05	6.57		
A-5	6.89	6.67	8.24	6.88	6.56	7.17	7.26		
A-6	7.36	6.91	7.69	6.92	7.08	8.18	7.83		
A-7	6.67	7.56	8.64	7.08	7.08	7.73	7.91		
A-8	6.85	8.13	9.72	8.68	6.79	6.82	7.08		
A-9	7.12	7.36	8.50	7.14	7.88	6.71	6.58		
B-4	4.50	4.69	4.49	4.86	4.73	4.66	4.93		
B-5	4.70	4.32	4.86	4.61	4.41	4.34	4.23		
B-6	4.82	4.86	4.71	4.63	4.91	4.70	4.62		
B-7	5.50	5.41	4.67	4.62	4.60	4.89	4.06		
B-8	4.00	5.13	5.66	4.64	4.20	4.58	3.70		
B-9	4.75	4.57	4.62	4.45	4.13	4.26	4.24		

* **Documented contamination.**

⁑ **Reflects installation and adjustment of ammonia-vapor baths.**

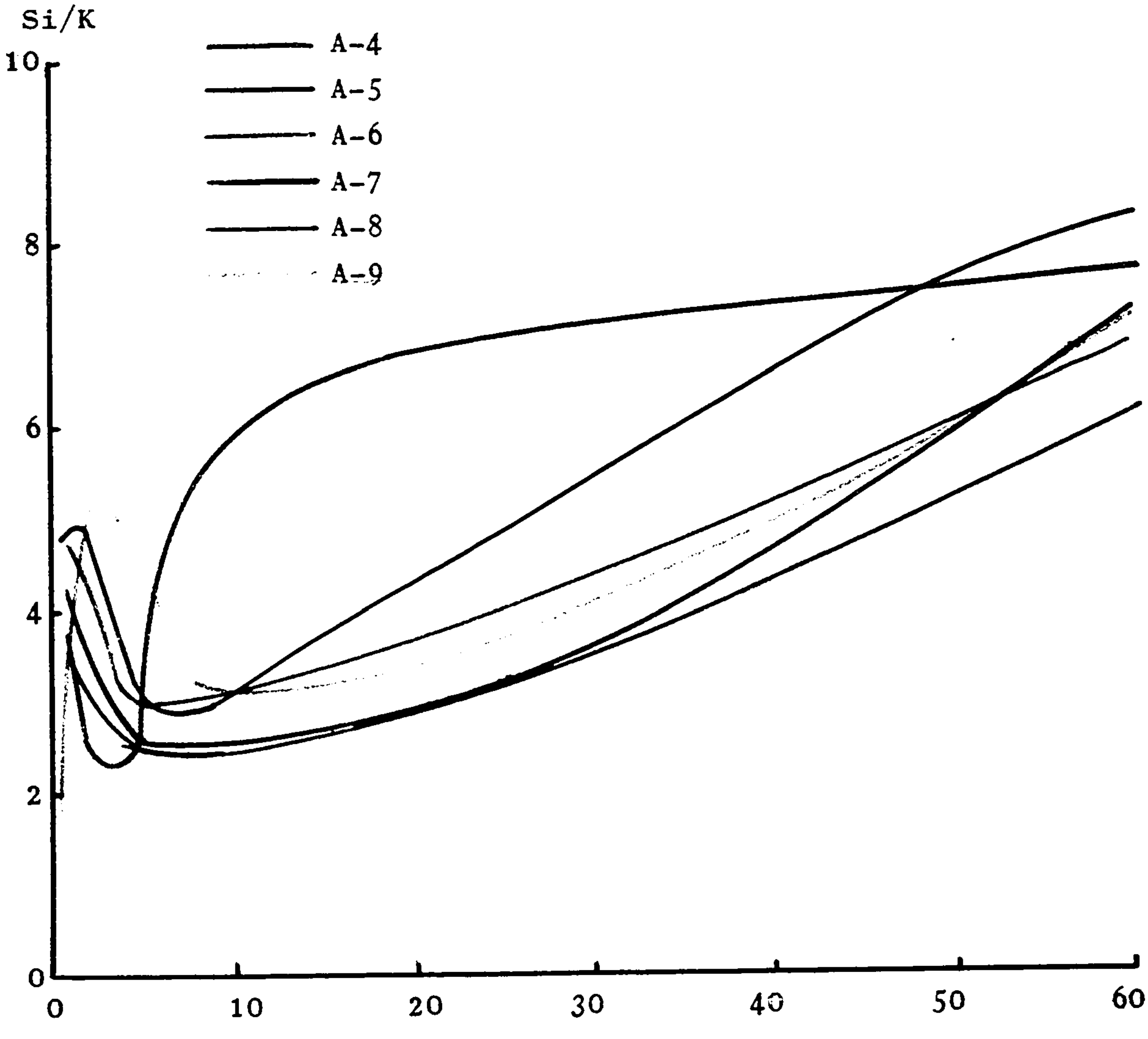

Figure 13. Effluent Si/K, feldspar A. Si/K for unleached feldspar A = 8.12.

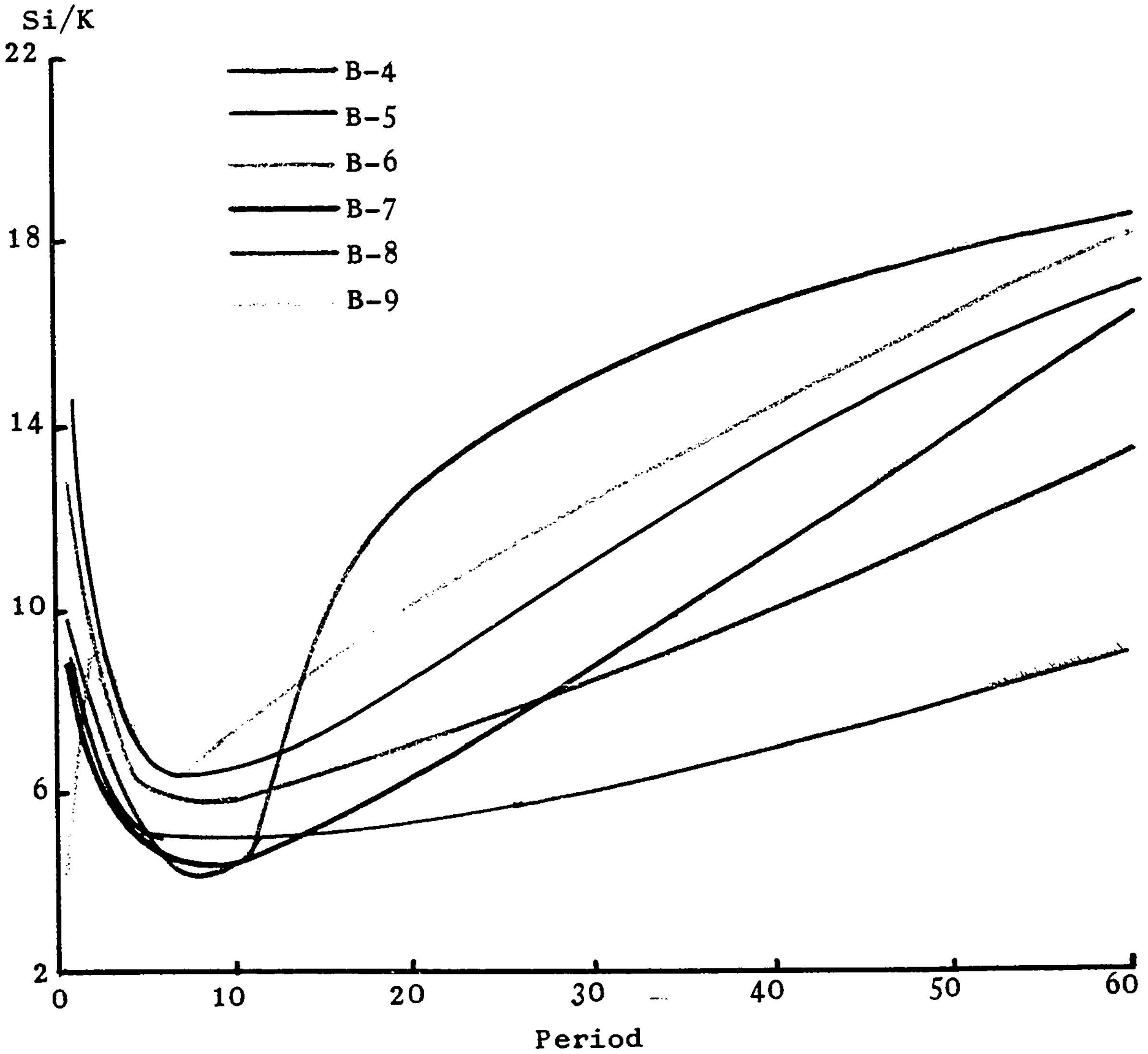

Figure 14. Effluent Si/K, feldspar B. Si/K for unleached feldspar B = 19.1.

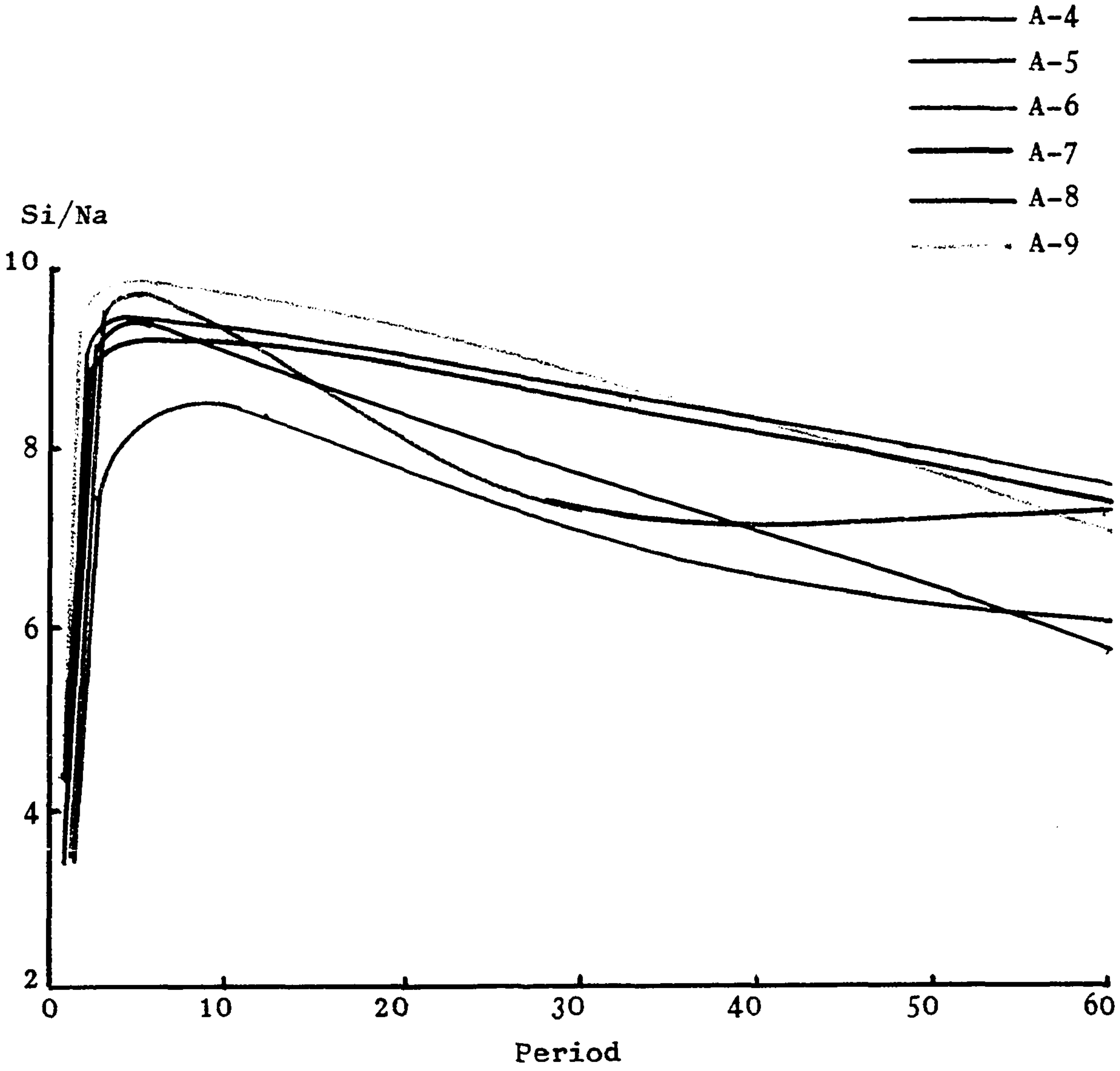

Figure 15. Effluent Si/Na, feldspar A.

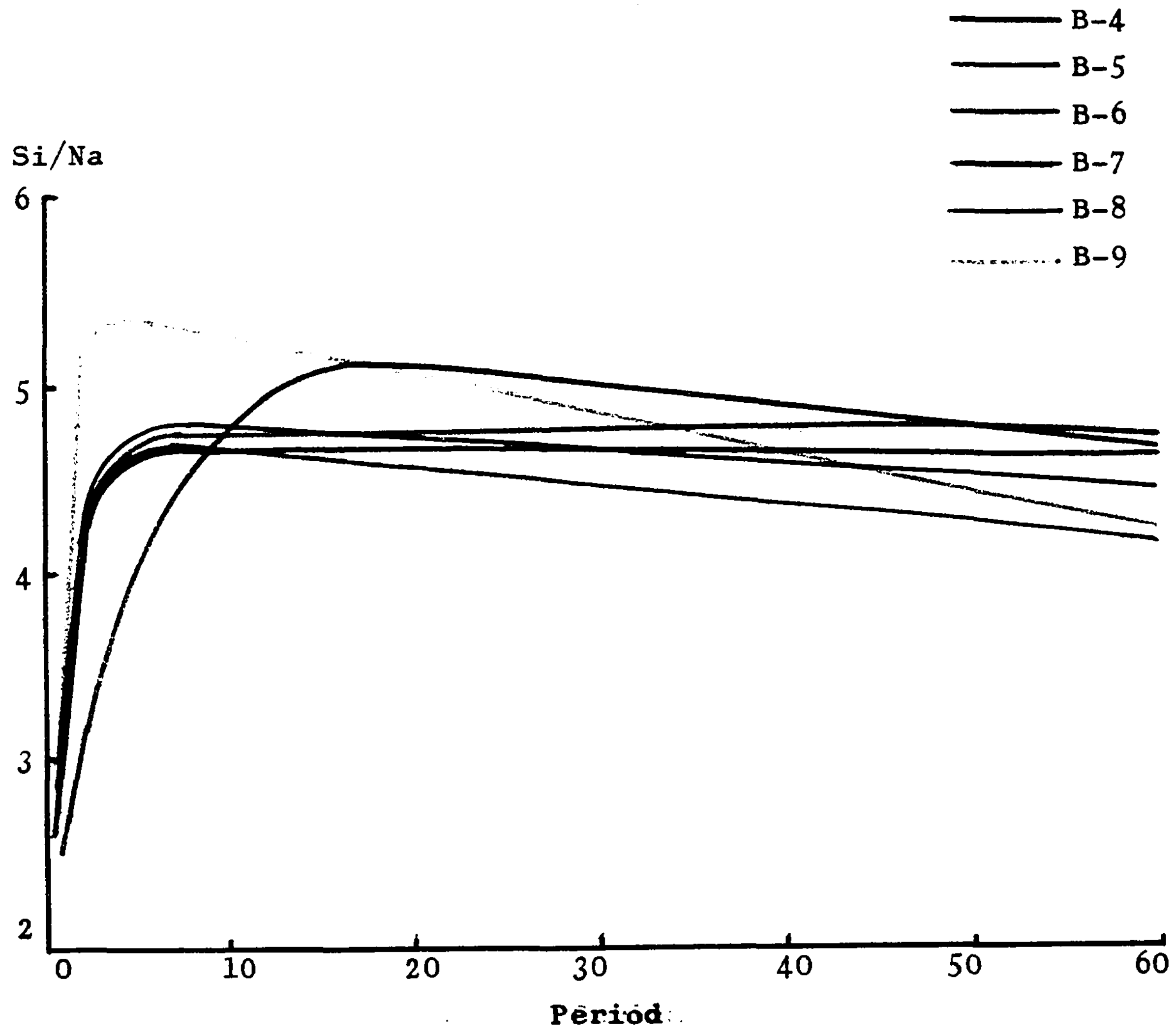

Figure 16. Effluent Si/Na, feldspar B.

This is during the interval of the already discussed lattice expansion. The later behavior of the Si/K curves shows a continuous decrease in the amount of K^+ leached relative to Si^{+4}. It should be noted that at this point the amount of Si^{+4} leached is relatively constant. This change in slope occurs when sufficient residue product has been developed on the feldspar grains to act as a protective weathering shell. Apparently the protective residue product is capable of retarding the loss of K^+, perhaps due to a charge deficiency brought about by the continued loss of Si^{+4} from the residue product. In view of the fact that the curves for absolute Si^{+4} (Figures 5-6) remain fairly constant it is apparent that the ability of the residue product to retard K^+ loss increases.

If the initial negative slope of the Si/K curves was due solely to the stripping off of loose K^+ on the fresh surface of the feldspar and if the later positive slope was due to a progressive thickening of the residue layer the Si/Na curves would be expected to exhibit a similar trend which they clearly do not. In fact, the Si/Na curves display an almost completely opposite behavior (Figures 15-16). The initial positive slope of the Si/Na can be explained by the development of the residue layer. The later occurring negative slope indicates that with time, Na^+ becomes more soluble relative to Si^{+4}. This is probably a direct response to the retardation of K^+ loss.

Effluent K/Na ratios based on the molar proportions are given in Table IX and plotted in Figures 17-18. The curves are all smoothed and those for columns A-8, A-9, B-8 and B-9 are corrected as in the Si/K and Si/Na ratios. Examination of Table IX reveals that there is a rise in the ratio for columns A-6 and A-7 and B-6 and B-7 peaking at period 21. Since this can be equated with a rise in the effluent K^+ (Figures 9-10) and since it is generally confined to those columns in which NH_4^+ was present but not including the columns with ammonia-vapor baths, it probably reflects leaching solutions inadvertently brought to higher NH_4^+ concentration sometime during the periods 20-22. This could have been caused by a failure to properly calibrate the pH meter used in adjusting the leaching solutions. This explanation is offered to support the smoothing of the curves at this point.

The effluent K/Na ratios clearly indicate that after the development of the residue layer, Na^+ is more soluble than K^+ even where K^+ is more abundant in the starting materials, confirming the observations of Beyer (1871) and Morey and Fournier (1961). With one exception, this is also true for the initial period. A consideration of the K/Na ratio for the first period indicates that with sufficient concentration, NH_4^+ tends to be considerably more efficient than H^+ in removing K^+ from the fresh feldspar

Table IX. Effluent solutions as K/Na in molar proportions

Period	1	2	3	4	5	6	7	9	12
Column									
A-4	0.55	1.35	1.78	1.81	1.64	1.27	1.01	0.90	0.77
A-5	0.45	0.85	1.27	1.62	1.66	1.65	1.50	1.55	1.39
A-6	0.42	0.95	1.51	1.72	1.65	1.49	1.58	1.57	0.83*
A-7	0.63	1.45	1.52	1.95	0.68*	1.06	1.71	1.91	1.66*
A-8	0.60	1.48	1.58	1.89	1.91	1.67	1.66	1.66	8.81⁑
A-9	1.50	1.32	1.08	1.29	1.47	0.47*	1.59	1.61	25.24*
B-4	0.15	0.21	0.35	0.43	0.47	0.46	0.51	0.35	0.62
B-5	0.14	0.17	0.24	0.36	0.42	0.41	0.45	0.39	0.37
B-6	0.13	0.19	0.33	0.40	0.45	0.46	0.45	0.40	0.38
B-7	0.17	0.32	0.43	0.53	0.53	0.44	0.46	0.41	0.36*
B-8	0.17	0.31	0.41	0.50	0.56	0.49	0.53	0.46	10.65⁑
B-9	0.41	0.36	0.33	0.39	0.41	0.41	0.46	0.39	5.26*
Period	**15**	**18**	**21**	**24**	**27**	**30**	**33**	**36**	**39**
Column									
A-4	0.71	0.78	0.68	0.58	0.63	0.55	0.55	0.50	0.54
A-5	1.14	0.94	1.05	0.83	0.78	0.77	0.70	0.65	0.61
A-6	1.29	1.16	1.51	0.88	0.97	0.95	1.00	0.96	0.86
A-7	1.39*	1.33	2.19	1.86*	1.96*	1.18	1.07	1.17	0.84
A-8	12.06⁑	2.19	2.84	3.09*	5.29*	1.97	1.53	1.11	1.04
A-9	9.09*	1.89	1.89	1.65	1.07	1.65	1.00	1.00	1.03
B-4	0.22	0.27	0.27	0.19	0.18	0.19	0.16	0.17	0.17
B-5	0.31	0.33	0.32	0.29	0.25	0.22	0.20	0.20	0.20
B-6	0.32	0.32	0.46	0.42	0.37	0.29	0.29	0.27	0.28
B-7	0.35*	0.40	0.73	0.60*	0.54*	0.30	0.33	0.39	0.23
B-8	11.17⁑	1.22	1.02	12.32⁑	7.49*	1.25	0.70	0.43	0.42
B-9	3.78*	0.54	0.55	6.57*	1.65	0.37	0.23	0.18	0.20
Period	**42**	**45**	**48**	**51**	**54**	**57**	**60**		
Column									
A-4	0.55	0.52	0.51	0.49	0.45	0.47	0.50		
A-5	0.61	0.54	0.59	0.55	0.55	0.59	0.70		
A-6	0.84	0.81	0.65	0.65	0.65	0.80	0.68		
A-7	0.93	0.78	0.54	0.49	0.65	0.63	0.64		
A-8	0.90	1.18	1.07	0.87	0.68	0.65	0.68		
A-9	0.94	0.93	0.99	0.89	0.63	0.53	0.55		
B-4	0.18	0.14	0.16	0.15	0.13	0.17	0.16		
B-5	0.19	0.15	0.23	0.18	0.13	0.19	0.16		
B-6	0.26	0.27	0.19	0.18	0.18	0.24	0.30		
B-7	0.28	0.25	0.16	0.15	0.19	0.22	0.20		
B-8	0.33	0.40	0.31	0.23	0.22	0.27	0.30		
B-9	0.23	0.19	0.16	0.15	0.18	0.13	0.15		

* Documented contamination.

⁑ Reflects installation and adjustment of ammonia-vapor baths.

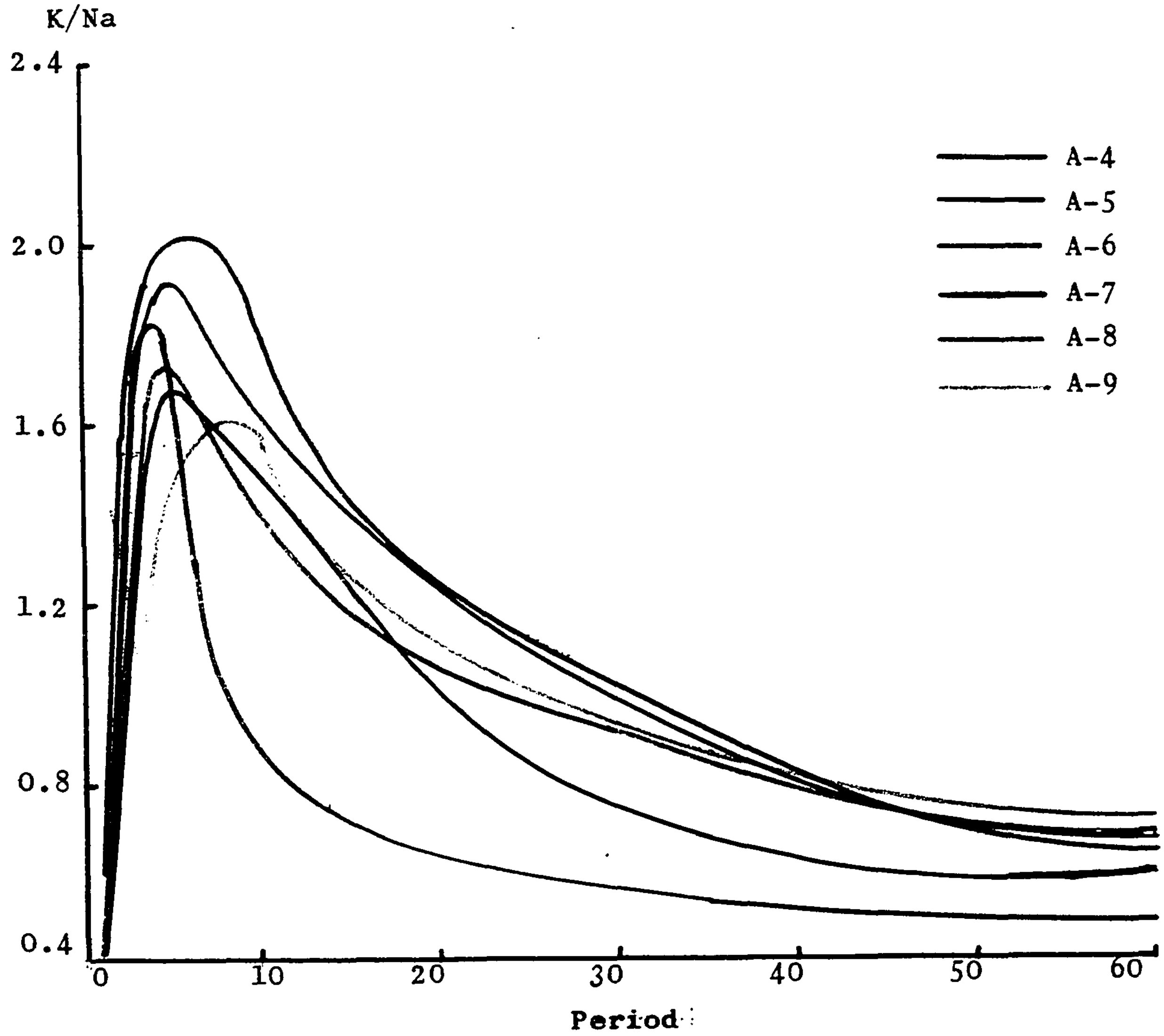

Figure 17. Effluent K/Na, feldspar A.

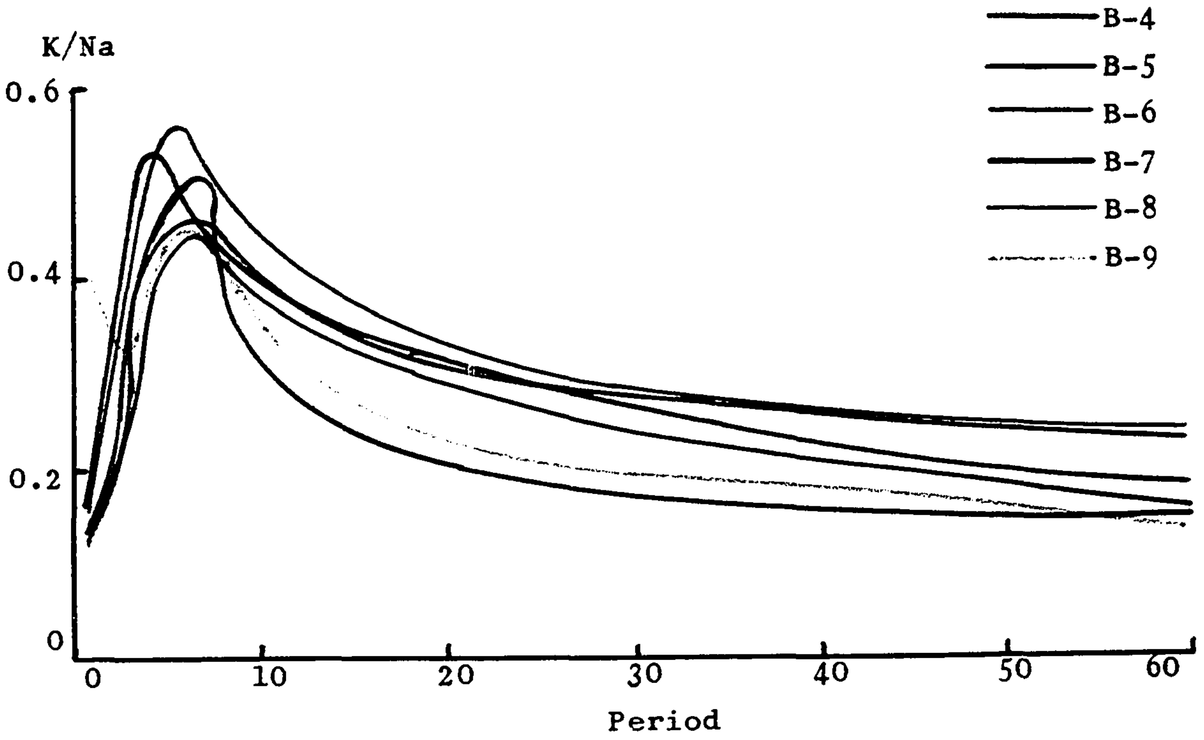

Figure 18. Effluent K/Na, feldspar B.

surface as suggested by Nash and Marshall (1956). However, this tendency seems to be somewhat diminished after development of the residue layer and particularly in the last stages of the total leaching term. The initial rise of the K/Na curves coincides with the interval over which development of the somewhat expanded lattice is postulated and adds validity to the previously suggested reason for the opposite behavior of the Si/Na and Si/K curves during that interval (Figures 13-14, 17-18), i.e., K^+ becomes increasingly more susceptible to leaching during the initial development of the residue product. The later behavior of the Na/K curves shows a trend toward a constant ratio. This is taken to reinforce the reason given for the opposite trends of the Si/Na and Si/K curves in the later stages, i.e., as the retardation of K^+ increases, the loss of Na^+ increases. This may imply the development of a near-equilibrium product with respect to silica and total alkali ions.

The individual total of ions leached are in non-stoichiometric proportion to the starting materials. However, toward the end of the experiment, the effluent Si/K ratios display a trend toward the Si/K ratios in the unleached feldspars. This plus the increasing retardation of K^+ suggests that a reorganization into ordered clay structures possessing Si/K ratios similar to the unleached feldspars occurred. The next section on X-ray data supports this view in that 10Å basal reflections similar to those of muscovite or illite can be recognized.

X-Ray Data

Samples of the decomposition product were obtained in the manner previously described and analyzed by x-ray diffraction. In addition, x-ray diffraction patterns were run on unleached feldspars A and B and on the aluminum slide mount material in order to eliminate from consideration any small peaks in the decomposition product patterns which might possibly be due to the starting materials or the slide mounts. This also served to determine whether there were any clay impurities in the starting materials. Both feldspars A and B exhibited a small broad reflection in the 14Å region which neither expanded with glycolation nor reacted to heat treatments. This raised the possibility of a chlorite impurity in the starting materials. However, owing to the small amount of iron and magnesium present in feldspars A and B, the likelihood of this was considered slight. It was thought that this reflection might be due to a diffuse feldspar reflection somewhat enhanced by a preferred cleavage orientation which occurred when the feldspars were sedimented onto the slides. This possibility was suggested by the 14Å *c*-axis reflection for Anorthite as reported by Chandrasekhar et al. (1961). However, to increase the confidence in this interpretation it was decided to pursue the subject further.

Two rather pure feldspars other than feldspars A and B were selected for further x-ray analysis. One was a potassium feldspar from a pegmatite on the east flank of the Big Horn Mountains and the other was a cleavelandite (variety of albite) from the Hugo pegmatite, Keystone, North Dakota. The specimens were broken and small, clean fragments were hand picked for analysis. These were ground and powder samples were prepared by sedimentation onto a glass slide. In this way, it was expected that a preferred orientation would occur in accordance with the feldspar cleavages. These samples were then x-rayed and the results showed the presence of a small broad reflection in the 14Å region with a possible small repeat at about 7Å (Figure 19). To then determine more certainly whether or not the appearance of the 14Å reflection was a manifestation of preferred orientation clean, thin (001) cleavage flakes were mounted on glass slides and x-ray diffraction patterns obtained. The (001) cleavage was chosen because it appeared that orientation on that cleavage was the most likely to occur. The patterns obtained from x-ray diffraction of these flakes revealed a diffuse but nonetheless distinct reflection at approximately 14Å which was considerably more intense than that of the oriented

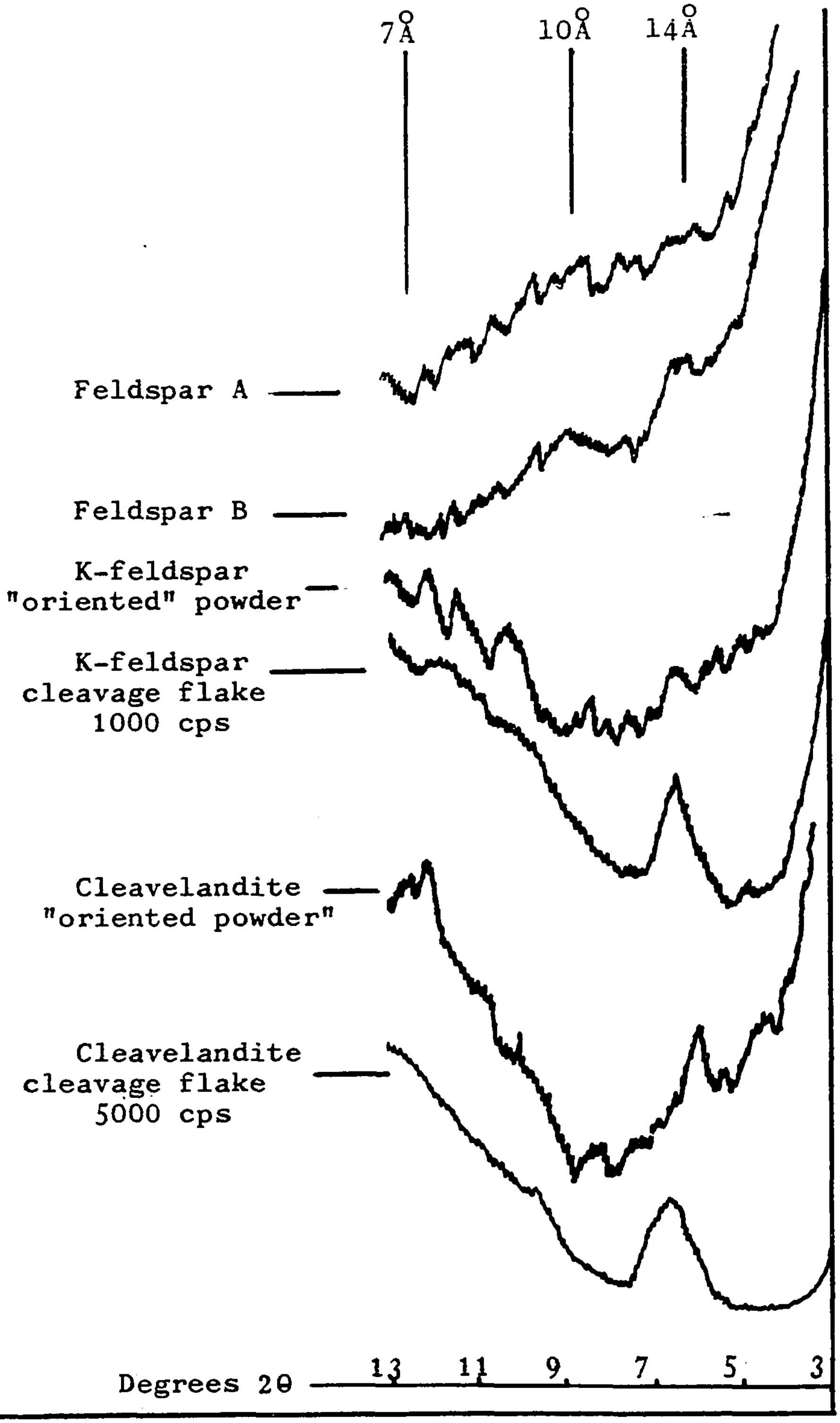

Figure 19. X-ray diffractograms of unleached feldspars A and B compared to feldspars showing effect of cleavage orientation on 14Å reflection.

powder mounts (Figure 19).

X-ray analysis of the decomposition product revealed that there were developed clay-type crystalline structures (Figures 20-25). These clay-type layer structures, as they are herein called, gave reflections of approximately 7Å, 10Å and 14Å.

Glycolation of several samples which yielded relatively good 14Å peaks showed that the 14Å material expands to approximately 17-18Å. The 7Å peak displayed no shift (Figures 26-27).

Selected samples mounted on glass slides were heated to 550°C for approximately 2 hours and dried in a desiccator. X-ray diffractograms of these samples showed the 14Å spacing had collapsed to 10Å and the 7Å spacing had been destroyed in response to the heat treatment (Figure 28). With collapse of the 14Å spacing, the diffuse feldspar reflection previously discussed can be seen.

All of the material derived from feldspar B regardless of the pH of the leaching solution exhibited the three (7Å, 10Å, 14Å) clay-type layer structures although the 14Å peak was far better developed in the material derived from the more alkaline leaching solutions. In addition to the alkaline environment, this may be in part due to the reduced flow to these columns. More residue product formed from feldspar B than from feldspar A which is consistent

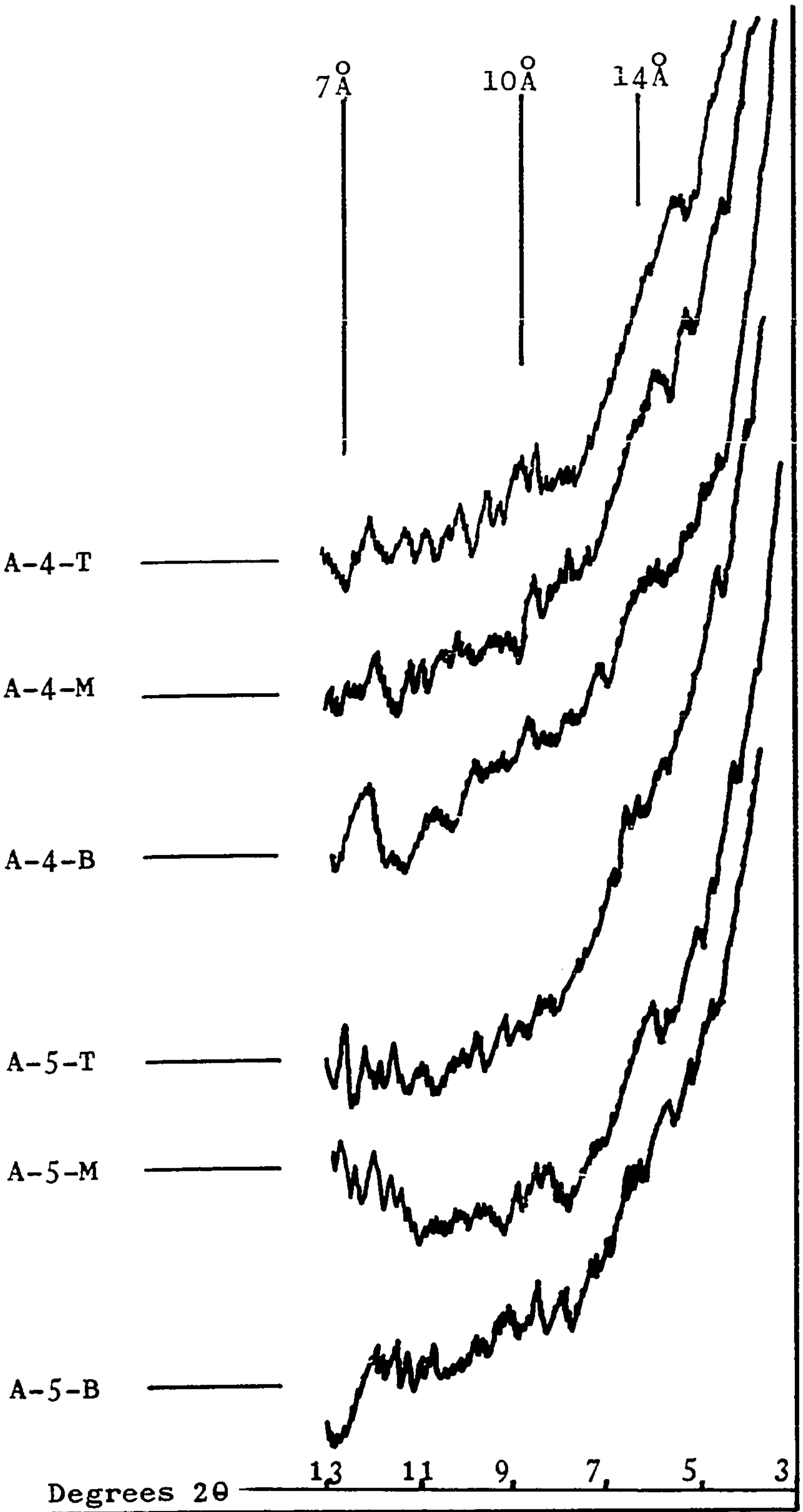

Figure 20. X-ray diffractograms of residue product from columns A-4 and A-5. T-M-B designations refer to top, middle and bottom portions of column.

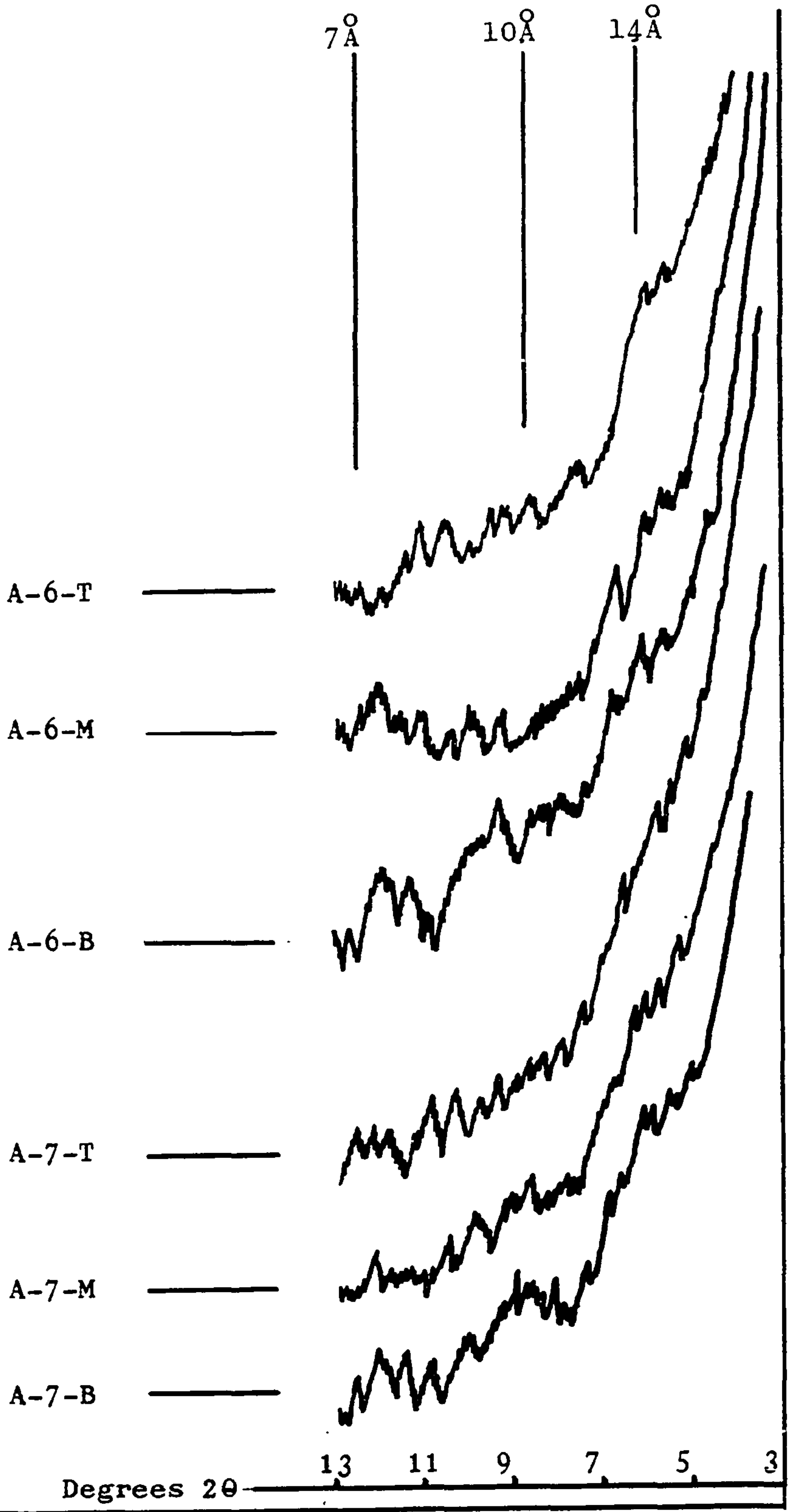

Figure 21. X-ray diffractograms of residue product from columns A-6 and A-7. T-M-B designations refer to top, middle and bottom portions of column.

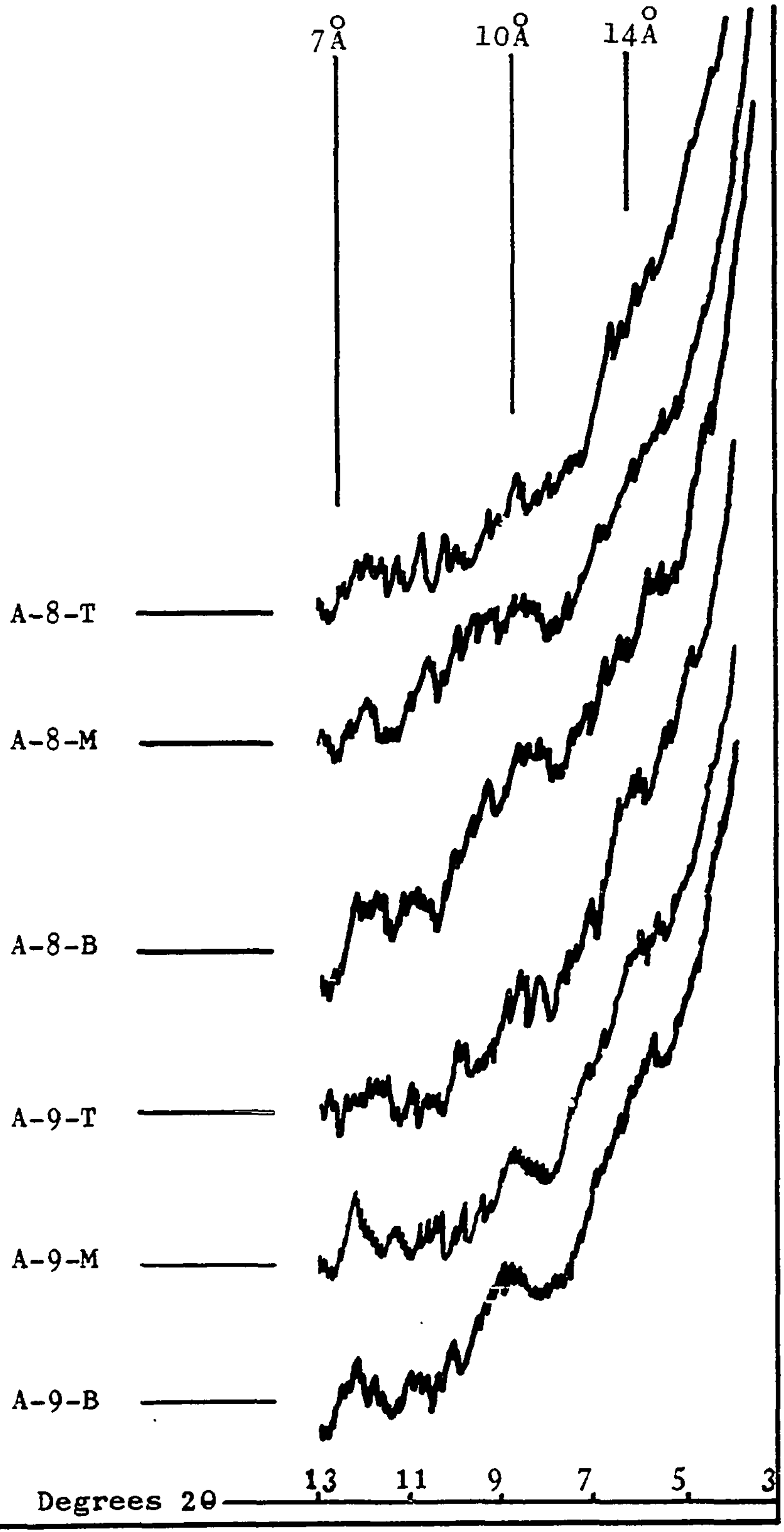

Figure 22. X-ray diffractograms of residue product from columns A-8 and A-9. T-M-B designations refer to top, middle and bottom portions of column.

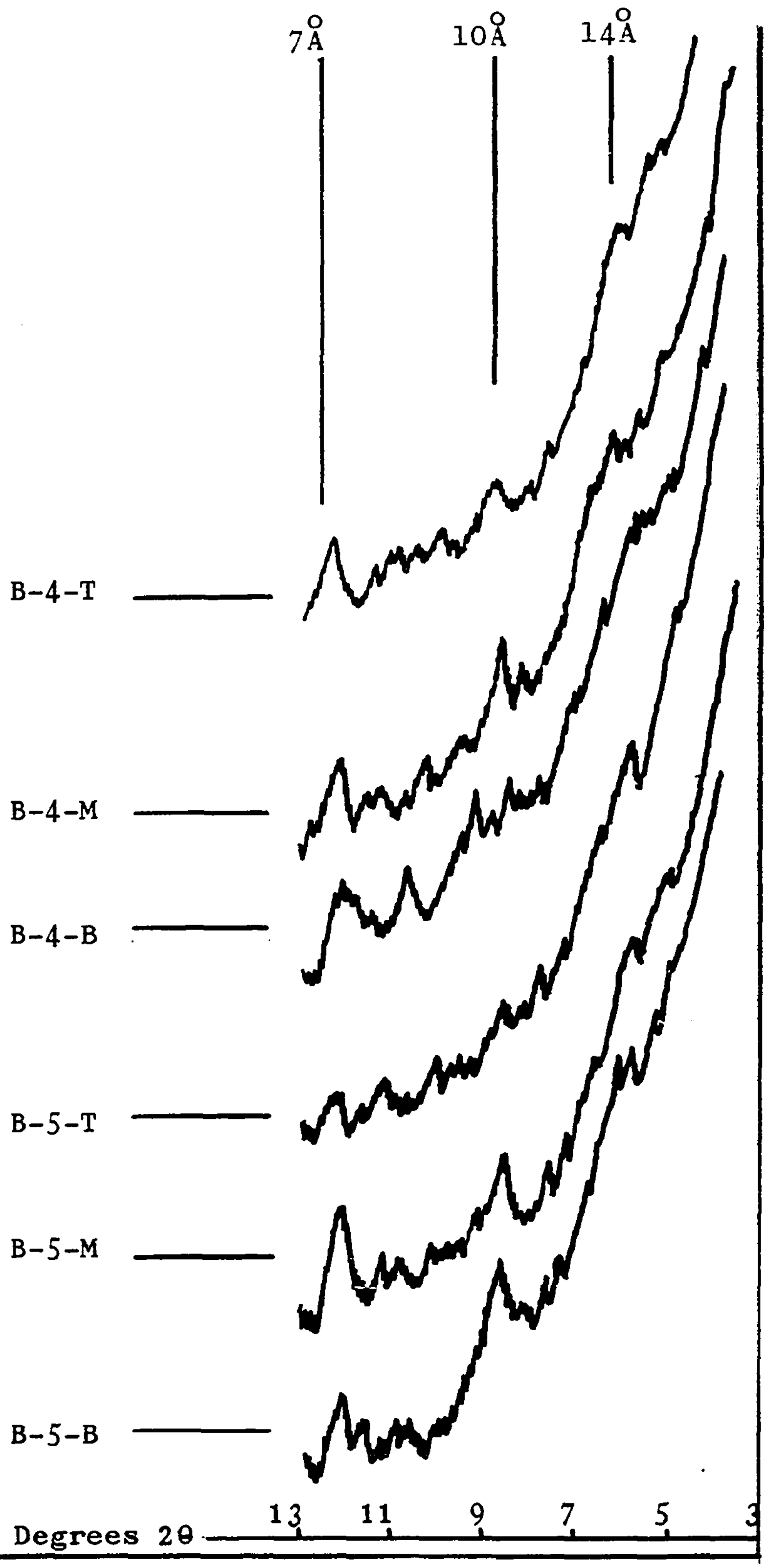

Figure 23. X-ray diffractograms of residue product from columns B-4 and B-5. T-M-B designations refer to top, middle and bottom portions of column.

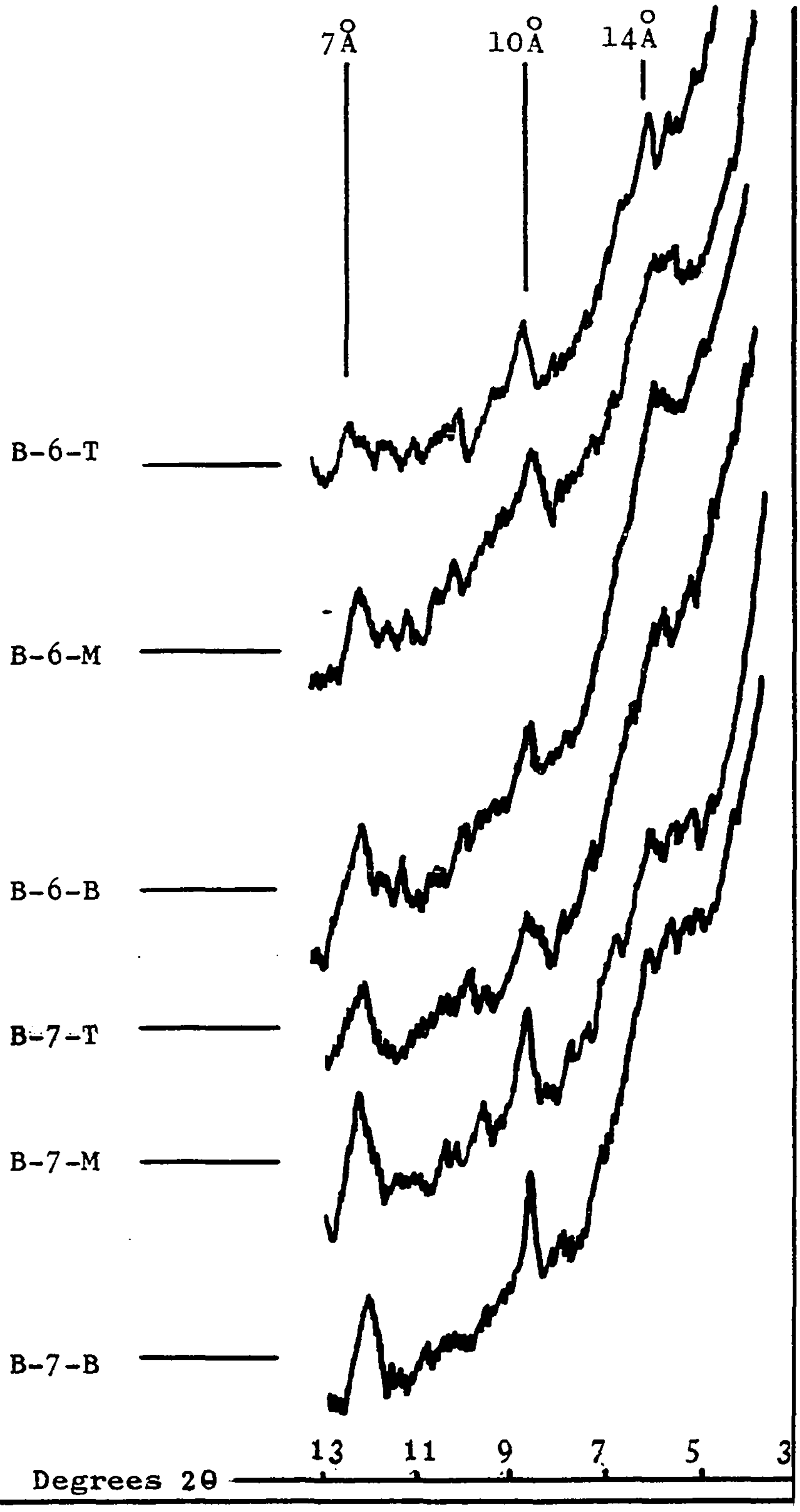

Figure 24. X-ray diffractograms of residue product from columns B-6 and B-7. T-M-B designations refer to top, middle and bottom portions of column.

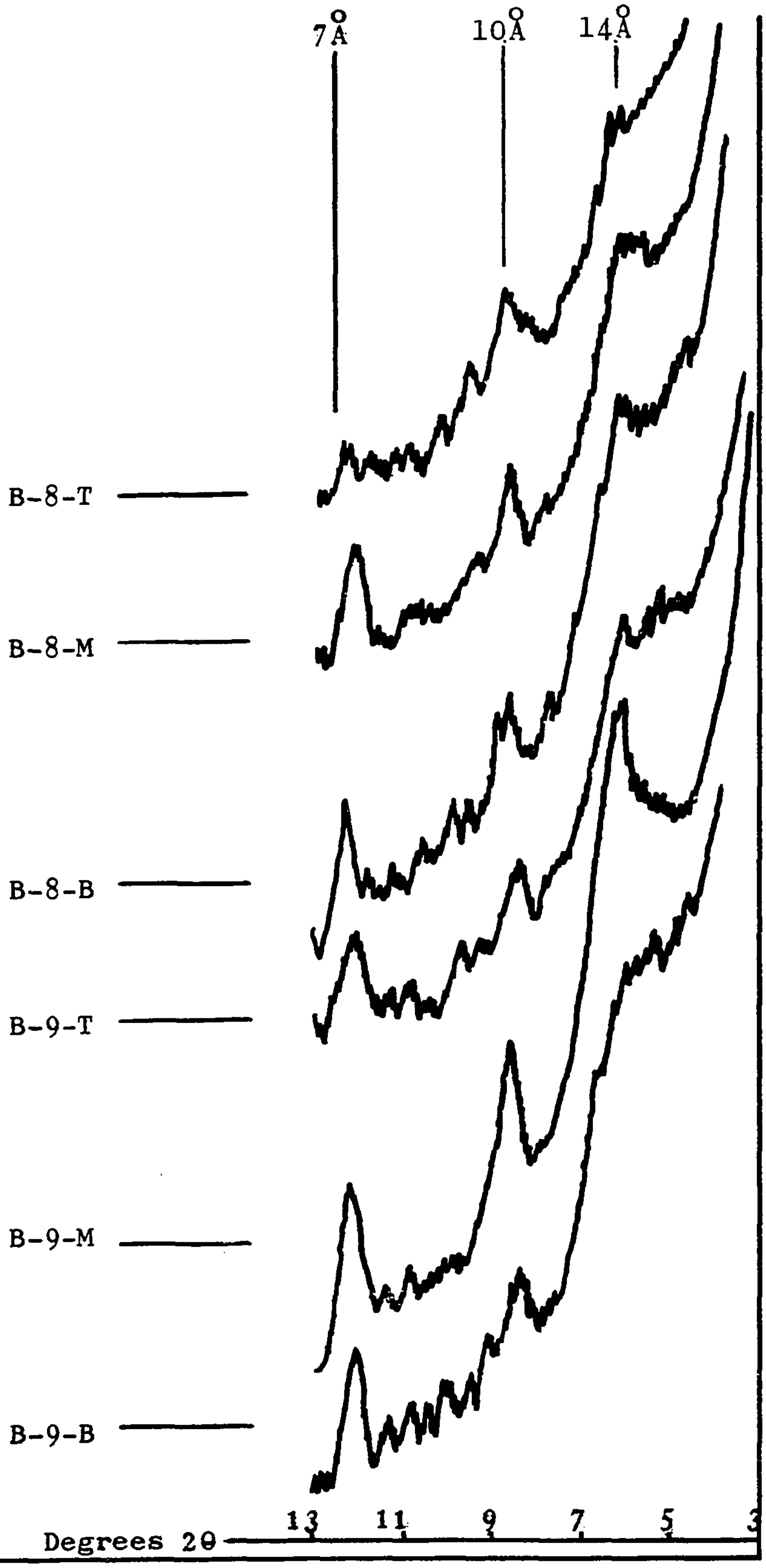

Figure 25. X-ray diffractograms of residue product from columns B-8 and B-9. T-M-B designations refer to top, middle and bottom portions of column.

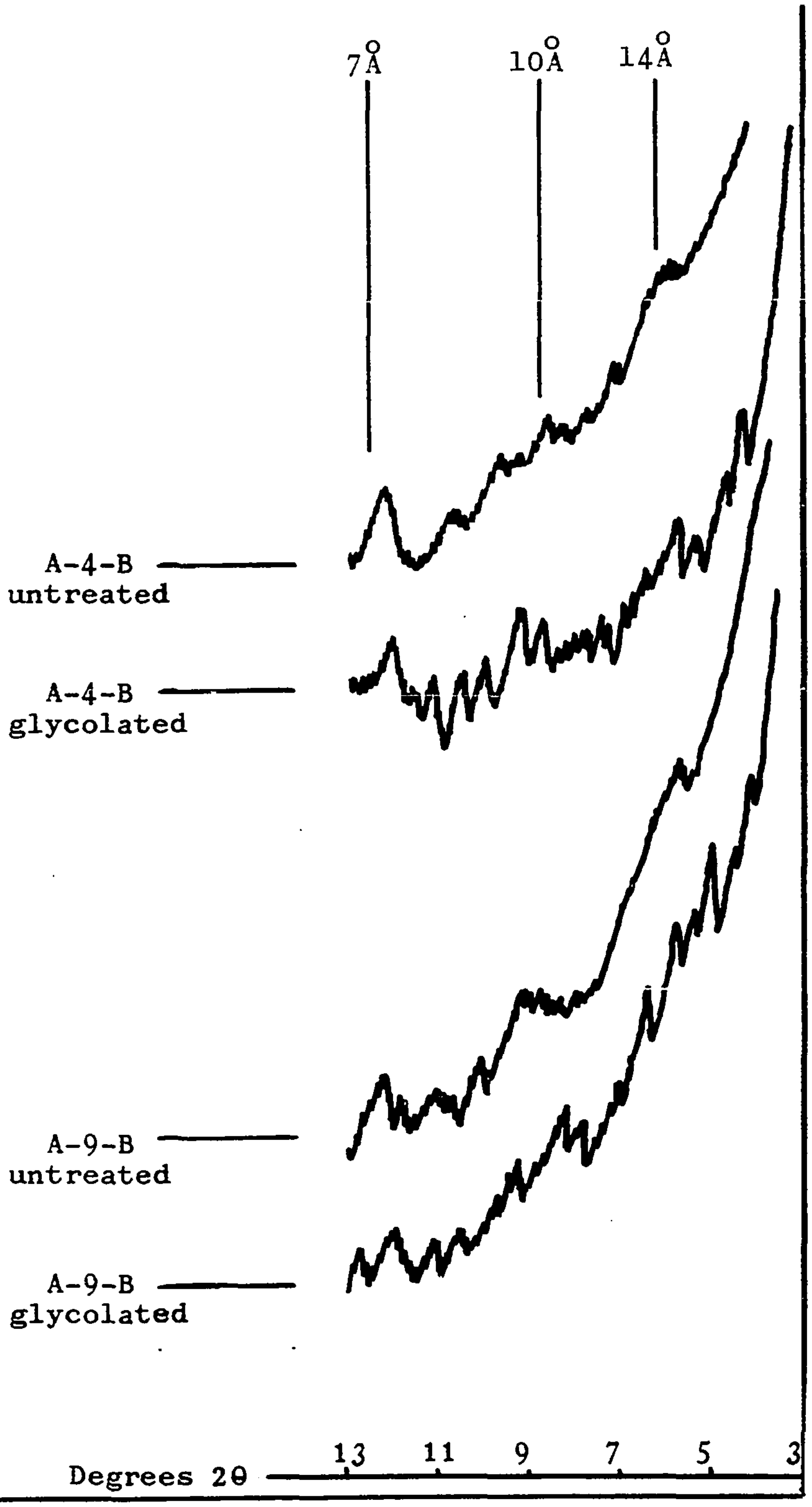

Figure 26. X-ray diffractograms showing effect of glycolation on residue product from columns A-4 and A-9.

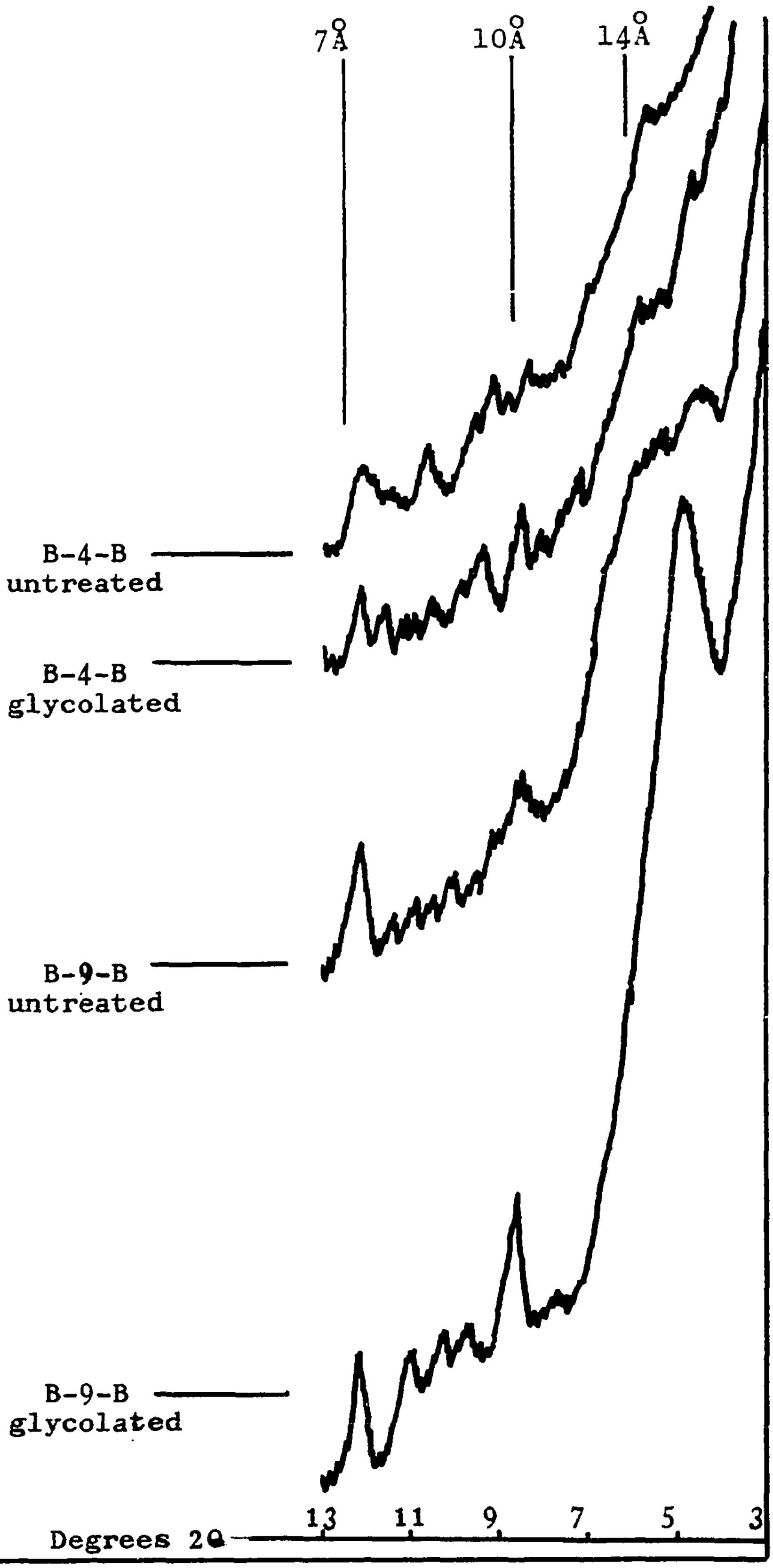

Figure 27. X-ray diffractograms showing effect of glycolation on residue product from columns B-4 and B-9.

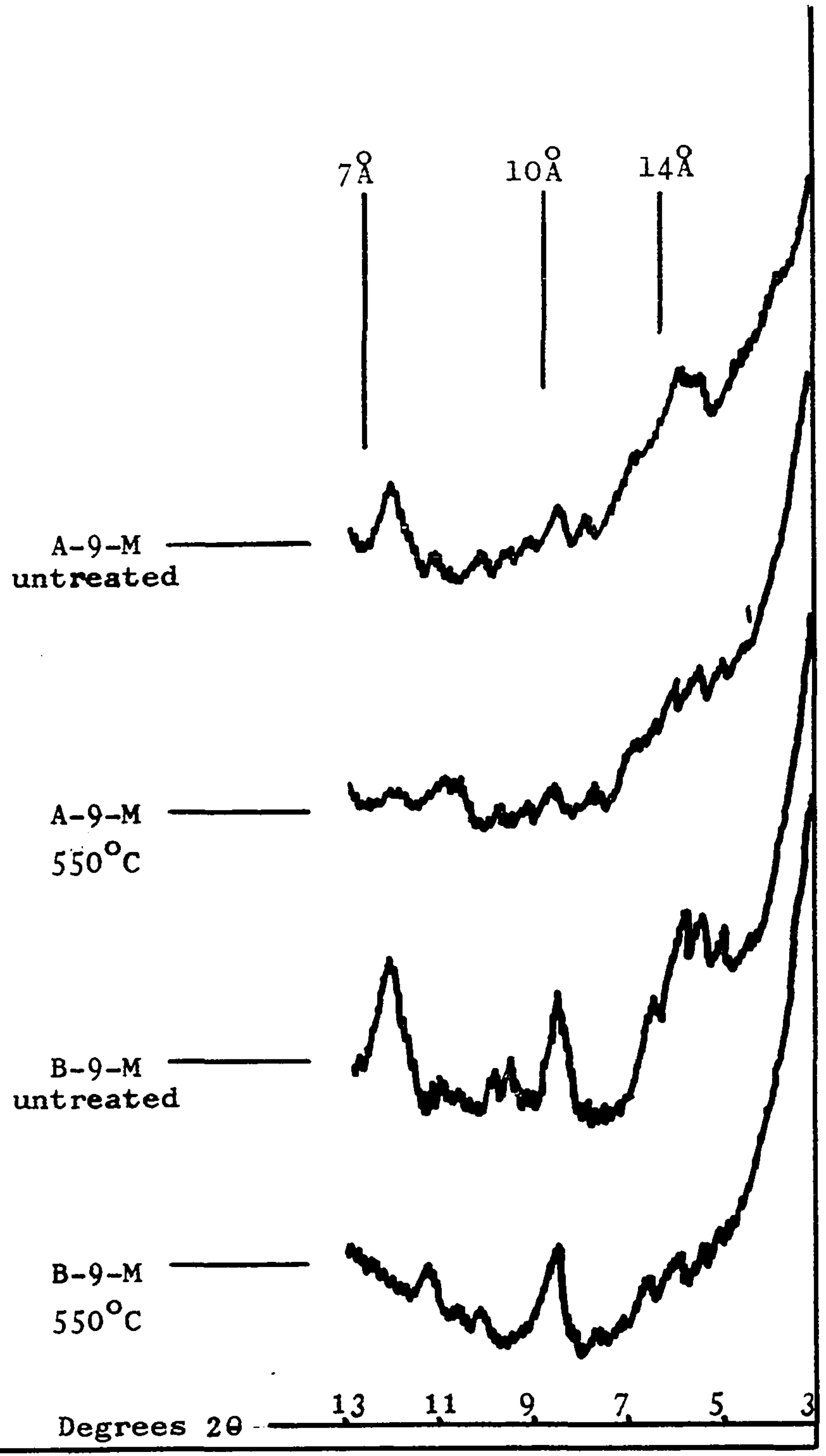

Figure 28. X-ray diffractograms showing effect of heating to 550°C on residue product from columns A-9 and B-9.

with the observation (Sand, 1956 and Hemley, et al., 1961) that plagioclase breaks down more rapidly than potassium feldspar. Clay-type layer structures derived from feldspar A were better developed at pH's 4 and 9 which is where the more extensive leaching took place. The decomposition product samples yielded, in addition to the clay reflections, most of the feldspar peaks found in the fresh feldspar. However, they were of a considerably reduced intensity compared to those of the unleached feldspar. This is at least partially a factor of dilution by the decomposition product. The 3.18Å plagioclase and 3.24Å potassium feldspar peak displayed a variation in intensity grading from least intense in material from the top of the column to most intense, although still less than the fresh feldspar, at the bottom. This might be ascribed to variation in sample thickness and instrumental sensitivity except for the consistency of its occurrence. Variation in intensity occurs in all cases with feldspar A decomposition product and in most cases of the feldspar B decomposition product. This suggests that there is a dilution by the residue product as a coating on the feldspar grains. There did not appear to be any selective diminution of the plagioclase feldspar versus potassium feldspar peaks.

The better developed clay-type layer structure peaks were found in the middle and bottom portions of the feldspar B columns. This trend is not as clear cut as the diminution of the feldspar peaks but it does appear to be consistent. There is no noticeable distinction between the intensity of peaks between the middle and bottom samples. This might be taken to indicate that the clay-type layer structures formed from clusters of colloidal alumino-silicate wreckage and migrated down the tubes, but then it would be expected that the sludge-like material recovered from the filter papers would exhibit a good deal better crystallinity than it does (Figure 29). A relative lack of intensity of the clay-type layer structures obtained from the top portion of the columns may be as readily explained as being due to a physical sloughing off of the clay-type layer structures from the feldspar surfaces and their subsequent migration down the columns.

A number of small peaks between 7Å and 14Å are provocative and may indicate transitional stages in the clay-type layer structure development. However, their small intensity and lack of very consistent appearance casts considerable doubt on their significance.

There is little direct evidence concerning the mechanism by which the clay-type layer structures were developed in the present experiment. The general theories which have been suggested for natural occurrences of feldspar derived clay minerals include: precipitation of

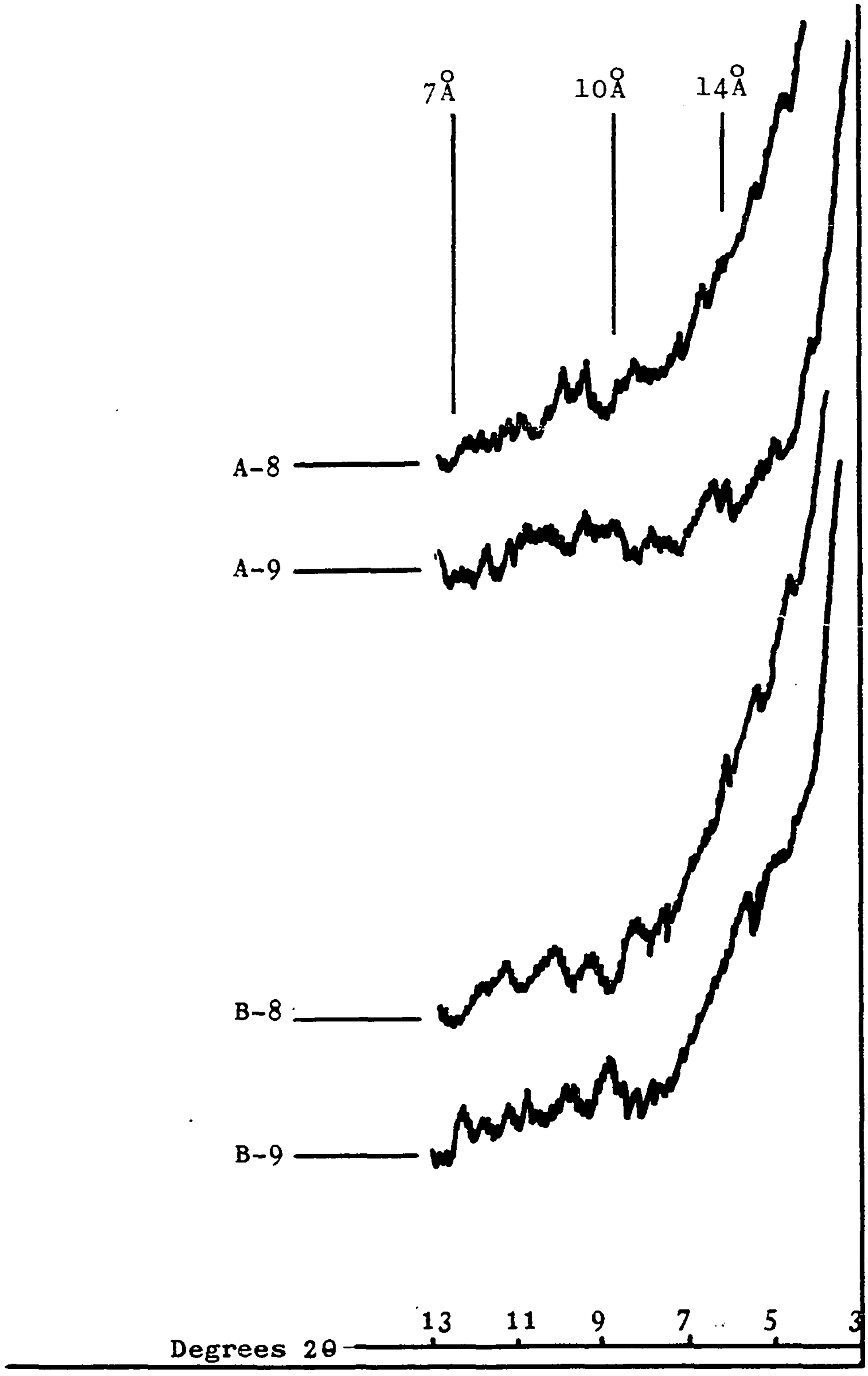

Figure 29. X-ray diffractograms of "sludge" recovered from filter paper of columns A-8, A-9, B-8 and B-9.

Si^{+4} and Al^{+3} from ionic solution to form clay minerals; coagulation of an intermediate alumina-silica colloidal phase from which crystallization proceeds or; a reconstitution of the decomposition product on the surface of the weathered feldspar. The relative merits of these proposals have been reviewed by Van Schuylenborgh (1950), Keller (1957, 1964) and Degens (1965). However, in the present study, the relative rapidity with which clay-type layer structures were derived from the feldspars undergoing leaching and the regularity and rapidity with which K^+ retardation began would seem to imply a reconstitution of the residue material possessing some degree of lattice organization. From a consideration of the effluent solution data, there seems to be little difference between the leaching behavior of feldspars A and B during the development of the residue layer and, since the amount of clay-type layer material predominated in the plagioclase rich feldspar (B), a form of structural control beyond that of simple more rapid decomposition is indicated. This reinforces the idea of the reorganization of the decomposition product into a layer structure.

To account for the development of three different types of layer structures from the same starting material, two possibilities may be considered. First, all three types may form independently in response to different microenvironments. For example, more K^+ or Si^{+4} in one part of the residue layer than in another. The second possibility is a transition from one type to another in response to continued leaching. Garrels and Howard (1959) have proposed a K-feldspar →, H-feldspar →, K-mica transition and Jackson (1948, 1962) has proposed what is essentially a 10Å → 14Å → 7Å transition. Similar transitions have been described in hydrothermal alteration (Schoen and White, 1967).

Chemical Analysis of Leached and Unleached Feldspars

Analysis of the leached feldspars was undertaken in an attempt to determine the displacement of ions both vertically within the columns and according to pH (Table X-XI). Unfortunately, the variations were so small as to be statistically unreliable for this purpose. Comparison of the leached and unleached feldspars showed some interesting differences but, again, these differences are, at best, statistically uncertain. In the case of feldspar B, there is an apparent loss of bases with a concomitant increase in SiO_2 and Al_2O_3. This is what would be expected from a consideration of the effluent data. However, feldspar A displays a gain of K_2O with an accompanying loss of Al_2O_3 while SiO_2, Na_2O and K_2O appear to vary in a random fashion.

Thin Section Analysis

Thin sections of impregnated samples were prepared and examined with the polarizing microscope at approximately

Table X. Chemical analysis of leached feldspar A.

	%	1		2		3		4		5		6		
A-T	SiO_2	68.40	-	69.16	+	68.32	-	68.42	-	67.88	-	68.58	-	
	Al_2O_3	17.32	-	16.49	-	17.20	-	17.37	-	17.41	-	17.19	-	
	K_2O	9.78	+	10.18	+	9.96	+	9.70	+	10.23	+	9.60	+	
	Na_2O	2.91	-	2.94	/	2.94	/	2.94	/	2.95	+	2.97	+	
	CaO	0.85	-	0.87	-	0.85	-	0.87	-	0.86	-	0.88	/	Unleached
	TOTAL	99.26		99.64		99.27		99.30		99.33		99.22		feldspar A
A-M	SiO_2	68.82	+	68.37	-	69.18	+	68.76	+	68.81	+	68.90	+	68.68
	Al_2O_3	16.74	-	16.91	-	17.05	-	17.00	-	17.25	-	17.02	-	17.48
	K_2O	9.83	+	10.04	+	9.81	+	10.03	+	10.20	+	9.72	+	9.57
	Na_2O	2.92	-	2.90	-	2.90	-	2.94	/	2.95	+	2.90	-	2.94
	CaO	0.86	-	0.88	/	0.82	+	0.89	+	0.89	+	0.89	+	0.88
	TOTAL	99.17		99.10		99.83		99.62		100.10		99.43		99.55
A-B	SiO_2	68.87	+	68.64	-	68.75	+	68.42	-	68.43	-	68.65	-	
	Al_2O_3	17.42	-	16.66	-	17.16	-	16.53	-	16.91	-	17.43	-	
	K_2O	9.77	+	9.70	+	9.83	+	9.96	+	9.95	+	9.61	+	
	Na_2O	2.97	+	2.95	+	2.97	+	2.99	+	2.94	/	2.98	+	
	CaO	0.87	-	0.87	-	0.88	/	0.90	/	0.88	/	0.89	+	
	TOTAL	99.90		98.82		99.59		98.80		99.11		99.56		

\+ increase
\- decrease
/ no change

Table XI. Chemical analysis of leached feldspar B.

	%	1		2		3		4		5		6		
B-T	SiO_2	70.00	+	69.80	+	69.63	+	69.78	+	69.79	+	69.47	-	
	Al_2O_3	17.85	+	17.60	+	17.70	+	17.73	+	17.47	-	18.11	+	
	K_2O	3.93	-	4.00	-	3.99	-	3.99	-	3.99	-	4.15	+	
	Na_2O	6.93	-	6.91	-	7.03	-	6.96	-	7.09	-	7.14	-	
	CaO	0.70	-	0.72	-	0.74	-	0.72	-	0.71	-	0.74	-	
	TOTAL	99.41		99.03		99.09		99.18		99.05		99.61		Unleached feldspar B
B-M	SiO_2	69.80	+	69.98	+	70.03	+	70.01	+	70.14	+	70.18	+	
	Al_2O_3	18.08	+	17.74	+	17.77	+	17.84	+	17.75	+	17.42	-	69.51
	K_2O	4.03	-	4.00	-	3.97	-	3.94	-	4.10	/	4.14	+	17.53
	Na_2O	7.21	-	7.08	-	7.47	+	7.18	-	7.08	-	7.24	-	4.10 7.26
	CaO	0.71	-	0.70	-	0.73	-	0.71	-	0.70	-	0.74	-	0.76
	TOTAL	99.83		99.50		99.97		99.68		99.77		99.72		99.16
B-B	SiO_2	70.09	+	70.38	+	70.07	+	70.00	+	70.16	+	69.88	+	
	Al_2O_3	17.22	-	17.67	+	17.48	-	17.57	+	18.08	+	17.62	+	
	K_2O	4.03	-	3.98	-	3.87	-	3.91	-	4.01	-	4.01	-	
	Na_2O	7.26	/	6.89	-	7.04	-	6.70	-	6.27	-	7.27	+	
	CaO	0.72	-	0.71	-	0.75	-	0.71	-	0.64	-	0.72	-	
	TOTAL	99.32		99.63		99.21		98.99		99.16		99.50		

+ increase
- decrease
/ no change

900X using an oil-immersion objective. A very small amount of clayey appearing material was observed to occur both interstitially and along the edges of grains. It could not be determined whether the material along the edges of grains actually was part of the grains or was simply pressed against them. No deterioration effects upon the feldspars were noted.

Electron Micrographs

Electron micrographs of selected samples were prepared at magnifications ranging from 12,000X to 25,000X (Figures 30-33). These yielded little in the way of definitive data except to imply that the clay-type layer structures are in an early stage of clay development. The larger grains appearing in the electron micrographs consist of finely divided feldspar. This is apparent from their well displayed cleavages and from their shadow lengths, which serve as a measure of particle height. Between the feldspars is found a less conspicuous clayey appearing material which is interpreted as the clay-type layer structure constituent. It is similar in appearance to the ultra-fine clay fraction observed in electron micrographs of know clay composition (Huff, 1963). Some of the smaller feldspar particles show deterioration effects and some of the clay-like material shows incipient crystal form. Areas and features of interest are noted on the individual electron micrographs.

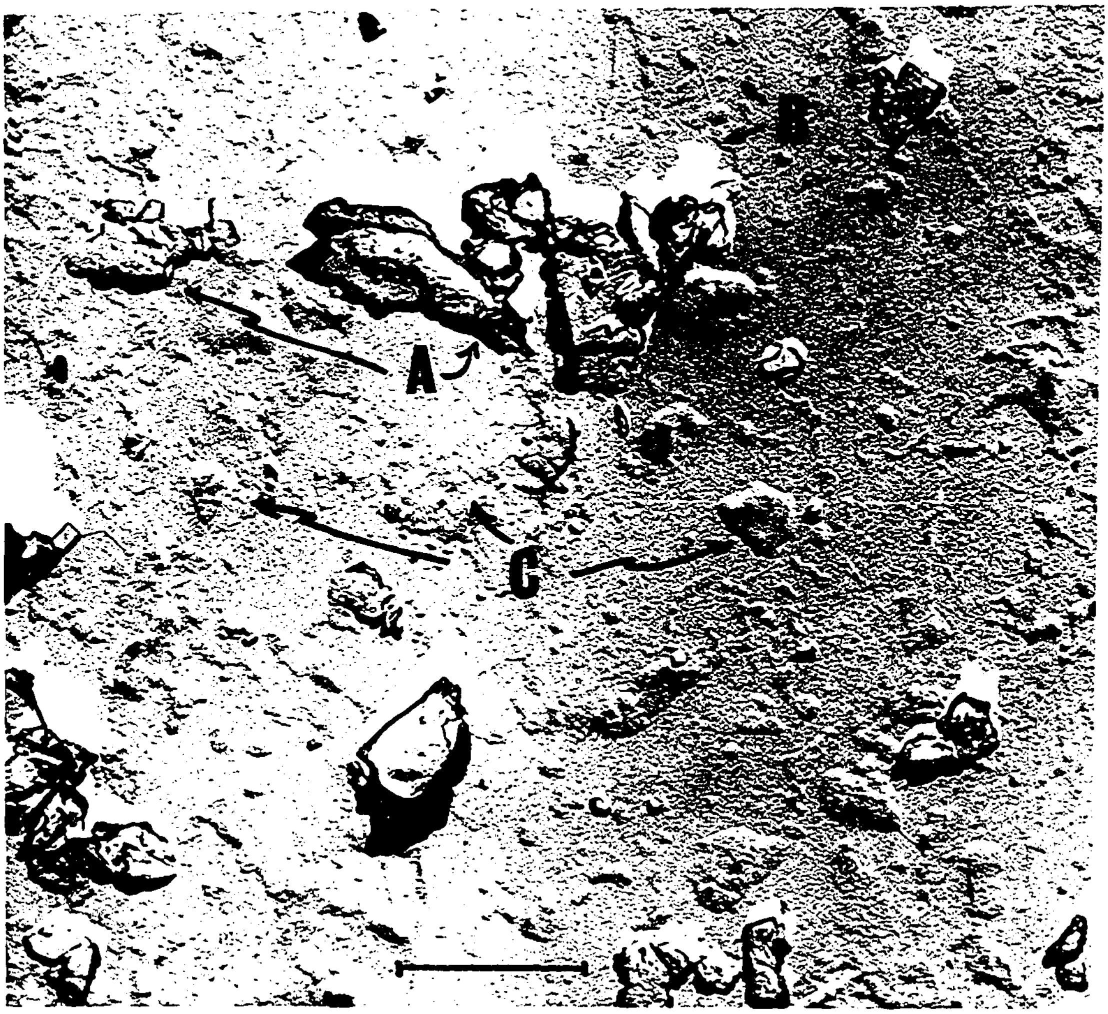

Figure 30. Electron micrograph of residue product from column A-4. Graphic scale represents one micron.

A. Feldspar particles
B. Spherical clusters of fine clay-like material
C. Clay particles with suggestion of regular external morphology

Figure 31. Electron micrograph of residue product from column A-9. Graphic scale represents one micron.

D. Feldspar particles
E. Incipient clay flake development
F. Deteriorated feldspar

Figure 32. Electron micrograph of residue product from column B-4. Graphic scale represents one micron.

G. Feldspar particles
H. Clusters of very fine clay-like material
I. Possible deteriorated feldspar
J. Suggestion of incipient external morphology

Figure 33. Electron micrograph of residue product from column B-9. Graphic scale represents one micron.

K. Feldspar particles
L. Clay-like flakes with incipient regular external morphology
M. Lath shaped clay-like particle

SUMMARY AND CONCLUSIONS

It should be emphasized that, as in any experimental study, to have faithfully reproduced a natural environment would have introduced so many variables as to cause control of the experiment to be lost. Hence, in drawing conclusions from the data obtained it must be kept in mind that they are drawn from a system in which the variables have been selectively limited. Therefore, any significance attached to inferences with respect to natural weathering systems must be considered in light of those variables not studied as well as those included in the experiment.

The data and observations obtained in the experiment are herein summarized and the following conclusions are drawn:

(1) The loss of ions from a feldspar undergoing leaching is non-stoichiometric with respect to the feldspar composition. However, the loss of ions is both mutually dependent and variable with time and a trend toward the Si/K ratios of the unleached feldspars is shown in the effluent solutions.

(2) A greater degree of leaching ability exists for pH's 4 and 9 with pH 4 more effective than pH 9. The overall picture

for the relationship between leaching ability and pH's between 5 and 8 seems to be one of little variation although with sufficient time minor differences may be significant.

(3) The response of a feldspar surface to leaching solutions of pH's within the range of natural waters is characterized by three stages (Figure 34). First, there is an initial stripping of loosely held ions (K^+, Na^+, Si^{+4}) from the fresh feldspar surface. This is followed by a second stage during which the surface feldspar lattice becomes disorganized and expanded permitting K^+ to be more readily leached until a residue product capable of retarding the loss of K^+ develops. The third stage is characterized by the further development of the residue layer to a near-equilibrium product.

(4) The rapidity with which alkali feldspars develop a dissolution retarding residue layer in response to leaching solutions of pH's within the range of natural

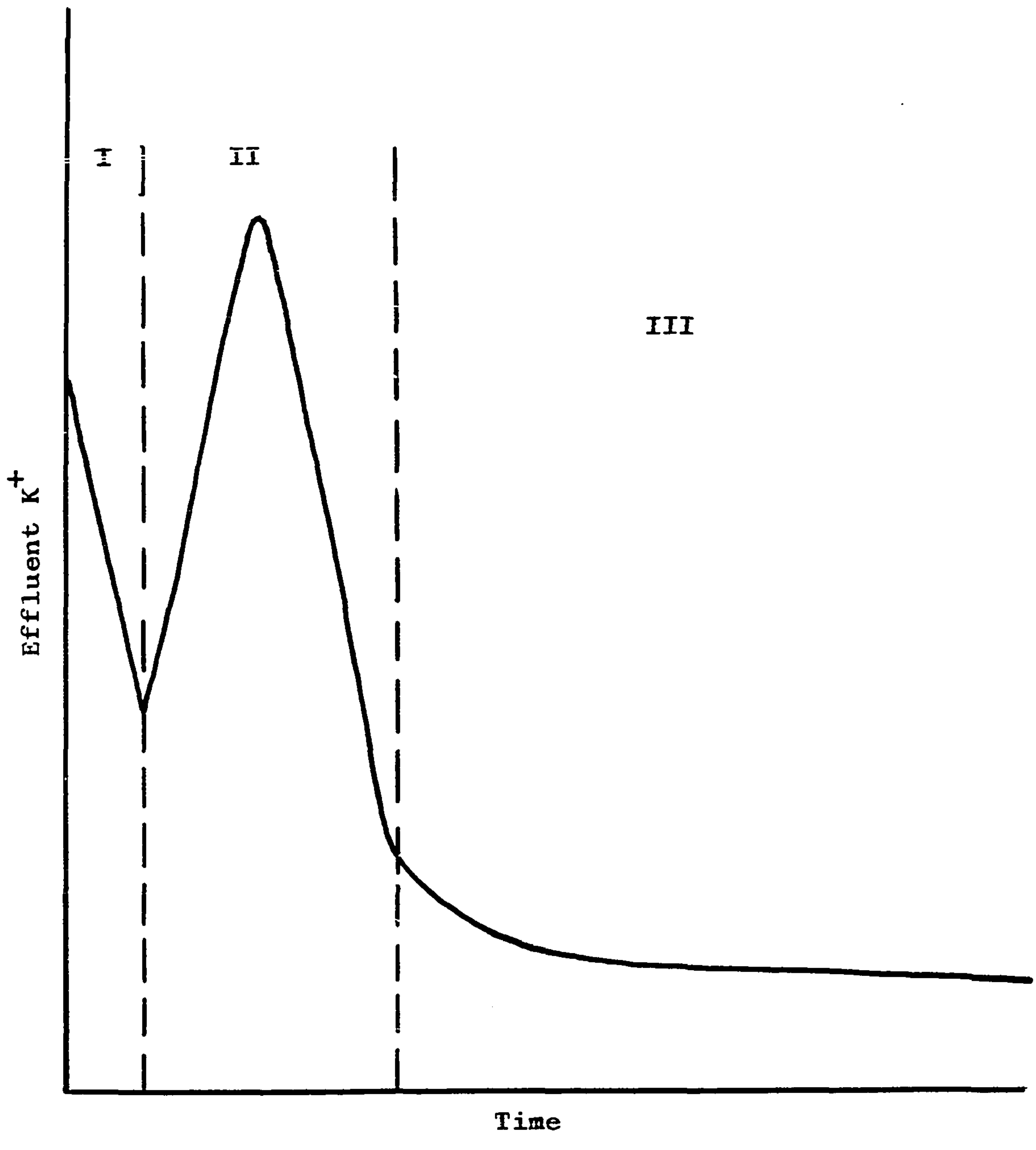

Figure 34. Generalized K^+ effluent curve showing 3 stages of feldspar surface reaction to leaching.

waters has been demonstrated.

(5) The development of a residue product possessing the **capability** of retarding K^+ loss is essentially pH independent with respect to time.

(6) The solubility of Si^{+4} within the pH range of natural waters is greater in the more acid media than in the more alkaline media.

(7) While no definitive evidence can be presented there is a strong implication that the formation of feldspar derived clays is, in this instance, a result of the reorganization of a leaching residue possessing some indeterminate degree of lattice organization.

(8) That three different kinds of clay-type layer structures were formed has been demonstrated and this is interpreted as probably representing a $10\overset{o}{A} \rightarrow 14\overset{o}{A} \rightarrow 7\overset{o}{A}$ transition due to continued leaching.

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