THE SURFACE CHEMISTRY AND GEOCHEMISTRY OF FELDSPAR WEATHERING

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by

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ABSTRACT

In this study the experiments were designed to measure the geochemical and surface charge (zeta potential) changes with time for two crushed samples of feldspar (Na-fs and K-fs) over the pH range of most natural waters (5 to 9). These experiments show:

(a) the importance of adsorption/desorption phenomena in both short-term and long-term feldspar dissolution, and probably for chemical weathering in general;

(b) that the generalized curve which characterizes the geochemical data (an initial rapid rise to a peak followed by a decrease to a lower, either constant or later increasing value) is consistent with a consideration of the adsorption/desorption process (i.e., the formation of the double layer) taking place at the feldspar surface and with the simple dissolution of the mineral;

(c) that the cation-silica ratios (Na_2O/SiO_2, K_2O/SiO_2, CaO/SiO_2) of the solution compared to those in the original feldspar indicate an initially incongruent dissolution which tends towards congruency during the latter part of the experiments.

From information in the literature and the results of these experiments it may be concluded that:

(a) the most important or master variables in chemical weathering are abrasion, minerologic or crystallographic factors such as twinning, exsolution regions, impurities, fractures and grain size, and solution composition and concentration. pH does not appear to be a master variable in most natural waters, especially for long-term weathering, and the chemical composition of the mineral phase is also not a good

criterion for predicting weathering behaviour; and

(b) the most extreme chemical weathering should occur in a high energy environment, either for physical reasons (i.e., high abrasion due to extreme relief) or for chemical reasons (i.e., high rainfall).

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CHAPTER I

INTRODUCTION

Introduction

The feldspar group of minerals is abundant in the rocks of the earth's crust and thus an understanding of their weathering behaviour is an important part of the whole study of rock weathering. It is known that one of the major mechanisms for controlling water composition is silicate mineral weathering (Sillén, 1961). In this mechanism quartz plays a small role and the silica composition of the water is largely determined by the feldspars (Bricker and Garrels, 1967; Garrels and MacKenzie, 1966; Feth, Roberson and Polzer, 1964). Thus to study silicate-water interactions, the best choice would be the feldspars. And, although the feldspars are less reactive than some other silicates, notably olivine, the weathering reaction is very rapid in terms of the rates of most geological processes. That is, the reaction reaches equilibrium in a matter of hours rather than years.

This means that the silicate-water reactions are sufficiently rapid that if the mineral remains in contact with the weathering solution then the solution will always be in equilibrium or near equilibrium with at least one mineral phase (Bricker and Garrels, 1967).

The chemistry of the runoff waters in contact with the feldspars cannot be considered separately from the weathering phenomena, as the two have a strong interrelation. In particular, it should be noted that the weathering of a rock occurs only at interfaces: between solid and liquid, and between solid and gas. Thus, the critical experiments should examine these interfaces and the changes which occur there. This study concentrates on those changes which occur at the solid-liquid boundary, the solid being either albite or orthoclase and the liquid being water at a known initial pH.

The application of principles and techniques of surface chemistry, specifically particle electrophoresis, to a study of weathering phenomena at the feldspar-water interface is a powerful tool in gaining a better understanding of the processes in this complex natural system. The importance of surface chemistry in evaluating mineral alteration can be seen from the recent studies dealing with surface chemistry and particularly surface charge, in connection with geological materials (Parks, 1967; Stumm and Morgan, 1970; Pravdic, 1970; Hem, 1970; Matijevic, 1971; Luce, 1972).

The contribution of surface chemistry is the body of theory dealing with surface effects in solid-liquid systems (see Appendix A) and the techniques which enable the geologist to measure the charge on a mineral surface.

The problem under consideration here is the measurement and interpretation of several variables both geochemical (pH, Na, Ca, K, SiO_2) and surface chemical (specific conductivity, zeta potential) for a semi-closed weathering system of albite or orthoclase and water of known initial pH. In an effort to simulate the natural environment the pH range covered is from 5 to 9 and the experimental containers are agitated periodically to model the suspension-settling processes which occur in a small stream. Published experiments of almost exactly this kind have been done only on the olivine system (Luce _et al_, 1972). The experiments involved shaking 1 g. samples of crushed mineral in 1 ℓ. of pH adjusted water for periods of up to 100 hours and removing aliquots at geometrically increasing intervals for analysis. pH, Mg and SiO_2 were measured in each aliquot and the reaction rates calculated from these results. The present interpretation, therefore, consists of a synthesis of the established surface chemical theory on liquid-solid interfaces and the known theories of weathering as they apply to the feldspar-water system.

Scope

This study will emphasize the relations between particle surface potential (ζ), as determined by particle electrophoresis (zeta potential), and such parameters as pH, composition of the mineral phase, rates of weathering (from the rates of increase of eluted cations in solution) and time. The theories of weathering of feldspars are developed and related to laboratory and field observations. As the experiments presented here deal only with the first stage weathering process, the products of weathering will not be treated in detail.

Conditions

The system dealt with is adiabatic and isobaric, open to the exchange of gases between the system and the atmosphere but closed to all other mass exchange. It is a solid-liquid-gas system in which the solid phase is finely crushed feldspar (albite or orthoclase), the liquid phase is pH adjusted water and the gas is the ambient atmosphere. The small particle size (less than 20 microns) is used to increase the reactive surface area and a low mineral-water ratio (5 g. solids/ℓ. water) is used to increase the chemical potential across the mineral-liquid interface. As the temperature effect over the range considered is likely to be small relative to other changes in the system, it will be ignored. The changes in the composition of the water, which is in equilibrium with the atmosphere, and in the surface composition of the feldspars are due to the competing reactions at the mineral-water interface which remove cations from the mineral structure and form a thin amorphous aluminosilicate coating on the mineral grains which influences all further reactions. It is important to remember that most feldspars are not formed in the pressure-temperature conditions on the earth's surface. Thus, most if not all reactions in which feldspars take part are irreversible. This system is also considered to be free of all other mineral phases. The results of the experiments and their interpretation and implications will be discussed for these conditions.

CHAPTER II

PREVIOUS WORK

CHAPTER II: PREVIOUS WORK

Introduction

The weathering of feldspars has been of interest to earth scientists since the latter part of the 19th century. There have been various approaches to the study of feldspar weathering, which can be broken into 3 basic groups. (1) There have been studies based on the interpretation of observed phenomena in the natural environment. These have been sometimes combined with the second group (2) laboratory studies, which in general have been concerned with fairly simple system modelling. (3) Theoretical studies have grown along with the previous two in an attempt to interpret the results of the laboratory and field studies. These three types of studies have been so interconnected that, although the present study is laboratory oriented, it cannot be discussed without placing it in the context of both field and theoretical studies.

Part A: Field Studies

In the study of feldspar weathering in the field, several approaches have been used. It was recognized very early that a sound knowledge of the mineral phases and chemical composition of the material being weathered was needed. Some studies, particularly since Le Grand (1958), have considered water chemistry as an important part of weathering phenomena. This has been especially true of the classic paper by Feth, Roberson, and Polzer (1964) and similar later studies by Harriss and Adams (1966) and Bricker and Godfrey (1968). Such variables as climate (rainfall, temperature and vegetation), drainage, bedrock type and weathering products have been considered but not always the same variables in different papers so that direct comparison of the results are not always possible. Table II-1 provides a quick summary of the major references and their contributions to weathering.

Probably the best early field study of weathering was done by Tamm (1924) (summary by Keller, 1957), who combined laboratory and field studies to conclude that small silicate particles dissolved incongruently in water to produce a material which had cation exchange properties and an appreciable buffering capacity. The products of weathering (i.e., the clay minerals) were found to be different under different pH and other environmental conditions.

The next major study (Goldich, 1938) dealt with the weathering of a granite gneiss, a diabase and an amphibolite. He was primarily concerned with determining the stability order or "resistance-to-weathering" order of the minerals present in these rocks. The results showed a pattern similar to Bowen's reaction series:

Olivine Ca-feldspar
Augite CaNa-feldspar
Hornblende NaCa-feldspar
Biotite Na-feldspar
K-feldspar
Muscovite
Quartz

↓ stability increasing

Since the parent minerals (quartz, plagioclase, hornblende, biotite, orthoclase) and the product minerals (kaolinite, beidellite) were analyzed, a "profit-and-loss" sheet could be prepared (assuming Al_2O_3 was immobile), showing the relative depletions and enrichments of the major cations. The weathering sequence indicated above is in general still valid with the most reactive minerals at the top and the least reactive minerals at the bottom. Goldich considered the pH a major factor in silicate weathering, particularly with reference to Stevens and Carron (1934) who determined the pH of ground mineral pastes. He believed the reactivity to be mainly controlled by dissolved CO_2 in the water and thus the pH is a useful parameter of weathering behaviour.

Brock (1943) also studied rock weathering and resistance to weathering of various rock constituents. He performed a "Goldich-type" study of a granite, a granodiorite, a syenite and a lamprophyre in the Hong Kong region and found the following decreasing ionic mobility sequence: $Ca > Na > Mg > Si > K$ for all rock types.

The importance of the ionic mobility sequence in weathering is that, for a given pH, it is essentially invariant for all rock types under similar climatic conditions. This means that the process of geochemical segregation due to weathering is not a function of the rock type but of the weathering environment. Thus changes in the ionic mobility sequence can be interpreted broadly as reflecting changes in the weathering environment. The major weathering products he found to be kaolinite and muscovite.

Jackson et al (1948) did an extensive study of soils and sediments to establish a 13-stage weathering sequence. Their study showed that the mineralogy becomes simpler with the progress of weathering and thus the parent material has a small influence on the final products of weathering, and in fact the environment and completeness of decomposition are the major factors. The mineral weathering sequence is characterized by the following minerals: (1) Gypsum, (2) Calcite, (3) Hornblende, (4) Biotite, (5) Albite, (6) Quartz, (7) Ilmenite, (8) Hydrous mica-intermediates, (9) Montmorillonite, (10) Kaolinite, (11) Gibbsite, (12) Hematite, and (13) Anatase. This sequence was derived from colloidal sized particles in soils and sediments. The weathering sequence is not expected to be complete at any one place and minerals may sometimes occur out of sequence due to local climatic and/or topographic conditions. The study put forth the view that to consider weathering as a simple primary mineral to secondary mineral transformation was an oversimplification and that weathering should include the whole range of consecutive and simultaneous processes which are occurring in the system. They presented weathering rate as the product of an intensity factor and a capacity factor, the first being related to the environmental conditions and the second to the nature of the mineral itself.

Frederickson, in 1951, presented a paper on the surface chemistry of silicates, particularly albite. He proposed the theory that the weathering of albite proceeds by the hydration of the fresh mineral surface followed by "base-exchange" reactions of H^+ ions in the water forcing the loosely-held Na^+ ions out of the mineral. This theory included the first mention by a geologist of the Helmholtz double layer and its origin (see Appendix A) and the recognition that the water near the surface of a mineral is structurally altered and behaves quite differently and has a different composition from the bulk water. Frederickson indicated that the substitution of H^+ for Na^+ would cause the surface structure to swell thus making the surface more reactive by increasing its surface area and permitting the exchange and movement of larger ions. Furthermore, he proposed that the strongly adsorbed water had an ice structure which fitted the albite structure closely and assisted in its hydration. Frederickson presented some interesting ideas on weathering but his lack of precision in stating his mechanism and in his terminology led to criticism by McConnell (1951) who objected to the term "base exchange", to the lack of a detailed mechanism for H^+--Na^+ exchange and to the proposed structure of water near the mineral surface. One flaw in Frederickson's theory not pointed out by McConnel is that the weathering of different minerals should involve different structures for the adsorbed water due to differing mineral structures, whereas Frederickson's theory considered the structure of water to be constant.

Butler (1953, 1954) continued studies similar to Goldich and Brock. He compiled a mass of data on the weathering of adamellite, granodiorite gneiss, gabbro, hornblende, schist, serpentine, syenite, monzonite, and olivine diabase in both Cornwall, England and Scandinavia. He concluded that the weathering products (kaolinite, illite, with some mica-intermediate) were more similar to each other than to their respective source rocks. This conclusion emphasized the fact that the geochemical segregation processes are almost completely independent of the parent material.

McLaughlin (1955) studied the weathering of an arkosic sandstone unit from the north to the south of New Zealand and was thus able to show the influence of temperature on the ionic mobilities of the various cation species and on the weathering products. As temperature increased the amount of kaolinite relative to hydromica also increased. This occurred over a range of mean annual temperatures from 9.5°C to 15°C. McLaughlin's paper is a good concise study of a fairly simple system (arkosic sandstone-rainwater) in the humid semi-tropics.

The occurrence of hydrated halloysite and kaolinite as mixtures in residual clay deposits led Sand (1956) to examine the factors which produce and influence this mixture. Working in a granite and pegmatite region of the Southern Appalachians, he found that where a rock was high in mica, weathering tended to produce a kaolinite whereas in a mica-poor region, hydrated halloysite was the more probable product. He also found that the weathering sequence in this region was plagioclase, K-feldspar, mica, and quartz, in increasing order of stability. His explanation for the occurrence of mixtures of hydrated halloysite (secondary mica) and kaolinite was that secondary mica is a necessary intermediate product in the formation of residual kaolinite from feldspar.

A fairly general study of quite a different type was carried out by Le Grand (1958). He analyzed the groundwaters in an area known to be underlain by a granite group and a diorite group and found that water from the granitic region was characterized by its softness, low pH and low dissolved solids, while the water from the dioritic region was hard, had a high pH and high dissolved solids. It was his hope that this method could be used as an exploration and mapping tool where outcrops were scarce. There was no interpretation made of the differences in the ground-water composition.

An interesting "negative experiment" was performed by Kelly and Zumberge (1961), who examined an apparently continuous weathering profile of a quartz diorite in Antarctica. Their location had fresh rock, partially decomposed rock, well decomposed rock and a sand derived from the rock, all of which they found to have essentially the same chemical composition with no evidence of the formation of clay minerals. It was in fact a classical case of purely physical weathering as the plagioclase feldspars in the sand showed no evidence of frosting or alteration at all. These findings may be contrasted to the work of Tamm (1924) previously referred to, in which he found that the hydrolysis of silicate powder took place at 2°C, from which it may be inferred that glacially pulverized rock flour may be hydrolyzed directly in glacier melt water.

More recently Reynolds et al (1972) showed that chemical weathering was a major process in the temperate glacial environment in the North Cascade Mountains. They indicated that the turbulent, well aerated water and the mechanical effects of glaciation were more than sufficient to overcome the expected inhibition due to the low temperatures. The water was kept at a high acid potential and fresh mineral surfaces were constantly being exposed to this "aggressive" water. The explanation of the conflict between Kelly and Zumberge and Reynolds et al may be in the lack of well aerated, aggressive water and freshly exposed rock surfaces in Antarctica due to lower topography and different style of glaciation.

Lazarenko (1961) sampled the sediments of the Dnieper River and examined the mineralogical changes which occurred from the source(s) to the mouth. The major minerals in the sediments were quartz, K-feldspar (orthoclase and micocline) and some plagioclase along with their alteration products kaolinite and sericite. He found that the minerals in the sediments alter very little and that the feldspar weathering in alluvium is determined entirely by the nature of the initial parent material, with the degree of weathering being an inverse function of grain size. These conclusions are somewhat different from those of other workers who emphasized chemical factors and it must be remembered that most other studies have dealt with in situ weathering involved little transport of the solid material, thus the results are not strictly comparable.

Short (1961) examined rock-soil profiles from a granodiorite, a basalt, a granite and a metamorphosed andesite using spectrochemical and mineralogical methods to determine the major and trace element distributions in each size fraction for each layer. Some of his conclusions are already familiar but others are new:

(1) The enrichment or depletion of most trace elements is directly proportional to the amount of clay and silt produced by weathering.

(2) The largest concentration changes occur across the parent rock-soil interface.

(3) Climate appears to be more important than parent rock composition in affecting trace element distributions.

(4) Concentration changes of some elements are related to survival or destruction of certain parent rock minerals.

He also emphasized the effect on rates of weathering of such factors as state of decomposition of the host minerals and the exchange behavior of altered mineral surfaces.

Dennen and Anderson (1962) examined the chemical changes as a mass balance across the fresh rock-weathered rock interface for a great variety of sedimentary, metamorphic and igneous rocks from many parts of the world. They found that chemical changes across the interface were primarily controlled by the local environment and not by the rock type or overall climate. This is similar to Butler's conclusions that the weathering products of diverse rocks bear a closer resemblance to each other than to their parent materials. An implication of this is that the processes which alter the minerals remove the elements according to some fundamental reactions which are little influenced by rock type. For all the rocks examined, the feldspars altered either to chlorite, hydromica or kaolinite and it appears that kaolinite is the most common stable weathering product, a fact that has been substantiated by many other studies.

Also in 1962, Loughnan presented a paper on the role of mineral structures in controlling the hydration and leaching of cations. He pointed out that while olivine, which is made up of isolated SiO_4 tetrahedra, bound by cations, disintegrates easily in water, alkali feldspars having a framework structure dissolve more slowly in spite of having potentially highly mobile cations (i.e., K^+ and Na^+). He related this difference to the fact that the leaching of cations from olivine and substitution of H^+ would cause the structure to break down completely and expose fresh surfaces to attack whereas in the leaching of alkali feldspars Si-O-Al bonds would have to be broken before fresh surfaces could be exposed. Since Al-O bonds are the weakest the Ca plagioclases would appear to be (based on this criteria alone) the least stable of the feldspars in weathering environment. Loughnan noted that the mineral structure is an important factor in controlling the accessibility of soluble cations and thus ultimately the rate of weathering.

However important the consideration of the degree of silica tetrahedra polymerization in determining mineral stability in a weathering environment it is not, and should not be, the sole factor considered. Other important factors are the degree of subdivision of the particles (specific surface area), individual crystal properties (twinning and other structural discontinuities) and the composition of the weathering solution.

Loughnan also mentioned that in a closed system (i.e., non-leaching) the weathering reaction would proceed with the hydration of the mineral surface and exchange of H^+ in solution for cations in the mineral until equilibrium is reached beyond which no further reaction will occur. Upon leaching such a system the cations would be removed and some H^+ ions would be released into solution from the surface and the pH would drop. This is important in understanding the natural water chemistry of intermittent streams and pools and perhaps also tidally isolated systems. The pH-cation relative distribution is closely linked and the factors which influence one influence the other as well. Individual properties of ions must also be considered when accounting for the stability of some phases. For example, the tendency for K^+ to be fixed in soil clay minerals is very important when considering the stability of K containing phases in that environment relative to the statulity of phases containing ions more easily leached (i.e., Na^+, Ca^{+2}). Loughnan's paper was probably the first to give such a comprehensive treatment of the interrelation of mineral structure, ionic mobilities, pH and ion exchange with rates and degrees of weathering.

Perhaps one of the best all-round studies of weathering has been that of Feth, Roberson and Polzer (1964) involving a group of granitic rocks (quartz monzonite and granodiorite), their weathered products and the associated surface and ground waters in the Sierra Nevadas. The range of waters was from "pure" rain (or snow) with very low dissolved solids to hot springs with very high dissolved solids. The major water input to the area is snow and some rain. They examined the mineral content of the water both as a function of season and as a function of distance from input of water. In general the water in the region was low in dissolved solids and could easily be characterized by the cation and bicarbonate content. The silica and common cations were primarily derived from the hydrolysis of feldspar, hornblende and biotite. Consistent with this the pH was relatively low initally but increased as the content of cations increased, indicating the exchange of hydrogen ions for the cations in the mineral lattice. The bicarbonate was found to come partly from CO_2 in the atmosphere and was directly related to the amount of dissolved solids, in agreement with the traditional weathering reaction:

$$\text{cation-aluminosilicate} + H_2O + H + CO_2 = HCO_3 + \text{cations}$$
$$+ \text{(amorphous)aluminosilicate}$$

The ionic mobility sequence of the common cations was found to be Ca > Na > Mg > K > Si > Fe = Al, which in general agrees with that found by others. They concluded that climate as well as lithology exerted a strong influence over water composition, particularly through the extent and kind of precipitation and the depth of weathering. No subsequent paper has been so comprehensive in its coverage of an area and the need for further studies of this kind is very clear. Some of the findings which have particular relevance to this present study are (1) that a major part of the dissolved mineral content of the water is acquired during the first few hours of contact between the water and the lithosphere; (2) that the pH is controlled by CO_2 from the soil atmosphere and not from the free atmosphere; (3) that Al and Fe are immobile elements by virtue of the formation of insoluble hydrous oxides in situ; and (4) that kaolinite seems to be the only thermodynamically stable phase, although montmorillonite, mica and some poorly crystallized clay minerals may persist under some conditions.

Deju and Bhappu, in 1966, placed a great deal of emphasis on the O/Si ratio in silicate groups as a criterion of degree of weathering. This was based on the O-Si bond as being very strong and thus when the O/Si ratio increased the number of O's available for bonding with ions other than Si (i.e., other metal ions) would increase. This would weaken the overall bonding of the mineral. By the nature of an ionic crystal there will be unsatisfied bonds on its surface and due to the predominance of oxygen ions this will produce a negative charge. On being placed in water the H^+ ions in solution, being the most mobile, will most easily satisfy these excess charges. However, the removal of some cations from the crystal (i.e., effectively an ion exchange) is observed and this Deju and Bhappu take to be evidence that simple H^+ ions adsorption is not enough to explain the surface behaviour of the mineral. They propose an ion exchange mechanism which couples the H^+ adsorption to the cation leaching. Surface area seems to also be an important factor, particularly where pH change due to ion exchange is significant. Deju and Bhappu found that the change in pH is related almost linearly to surface area up to a certain limiting value beyond which changes in surface area have virtually no influence on pH. This may be related to the amount of structured versus unstructured or bulk water (see Appendix A) in that as the amount of structured water (i.e., surface area) increases the mobility of the ions decreases and the ability of the surfaces to adsorb more ion decreases since fewer ions are available. Thus, the ability of a surface-water system to adjust its pH decreases as the amount of structured water increases. Deju and Bhappu's emphasis on the minor role of simple physical adsorption compared to ion exchange may be somewhat modified at pH's other than the acid pH's which they considered. That is, the number of H^+ ions available for ion exchange at neutral and basic pH's will be much fewer than at acid pH's and adsorption of OH^- and other ions may become important.

Garrels and MacKenzie (1966) used the data of Feth, Roberson and

Polzer and calculated that these data were consistent with a model of a closed system in which CO_2-rich waters alter the silicates to soil minerals plus a cation-bicarbonate solution. They "back-reacted" the dissolved constituents with the product minerals and found that they could easily form all of the reactant minerals in roughly their proper proportions. This showed that the system was closed. The importance of feldspar weathering in the system was underlined by the fact that 80% of the dissolved constituents could be accounted for by the dissolution of plagioclase alone, and, given that feldspar is the most common of the silicates, the fact that the dissolved silica content of the water could be derived from the feldspar dissolution alone.

A slightly different study, carried out on weathering profiles of granitic rocks by Harriss and Adams (1966) involved the determination of the relative mobilities of several cations in different environments and the soil-water equilibrium relationships. The mineral stability sequence found was, in order of increasing stability, plagioclase feldspar, biotite, K-feldspar, quartz in both the warm humid climate of Georgia and the cooler dryer climate of Oklahoma. The controlling factor of the mobility of Ca, Na, K is the mineralogy, in that the plagioclase feldspars are more resistant and release K later. Some illite and montmorillonite are present in the Oklahoma soils, but kaolinite is the major weathering product, especially in the more mature Georgia soils. The surface water data is consistent with the secondary minerals found, except that illite does not appear to be a stable phase.

Bricker and Godfrey (1967) examined the weathering sequence, rates of reaction, stability relations and chemical balance relations for a small drainage basin in Maryland, underlain by a pelitic schist. This field study combined with a few simple laboratory experiments enabled them to conclude

(1) that silica and the other cations were very rapidly released from the minerals by the surface waters, (2) that the waters were in equilibrium with kaolinite, (3) that the primary source of the dissolved load was from rock weathering, and (4) that Fe and Al are conserved in the weathering system and are therefore immobile. Although illite, vermiculite and gibbsite were found in the region, gibbsite being on the tops of the ridges, they were considered to be intermediate in the reaction to form kaolinite. The laboratory experiments involved passing both distilled water and stream water through columns of soil until equilibrium was established. This occurred very rapidly for the distilled water, which soon reached the composition of the stream water, which did not alter its composition on being circulated through the other column. The rapidity of the mineral-water reaction in this example showed that the rate of removal of material as dissolved load is about five times greater than the rate of mechanical removal. The development of simple chemical relations which would permit the quantification of rock weathering has been the goal of several people.

Ruxton (1968) collected samples of fresh and weathered rocks and using literature data compiled the analyses of these rocks to see what correlations he could find. He had analyses of diorite, granite, granite gneiss, basalt, soreite and dacite with their weathering products, mainly kaolinite. The SiO_2/Al_2O_3 ratio he found to be a primary index which showed a good correlation with silica loss and total element loss which he felt were the indicators of weathering intensity. He did however indicate that the texture of the parent material would have some influence on weathering intensity as evidenced by the different behavior of a rhyolite and a granite in Hong Kong.

Another example of a weathering index is the work of Todd (1968) on two sandstones, in which he tried to establish an index based on the area of grains weathered. The feldspar grains were coated with kaolinite to various degrees and in one case exhibited a reverse weathering sequence (i.e., orthoclase weathered more than andesine). This apparent anomaly was explained by invoking two factors: (1) the structural differences between the feldspars and (2) the weathering environment. Placing emphasis on the latter factor he indicated that a high Na/H relative to K/H of the waters in contact with the minerals would permit the observed weathering order. These conditions would obtain with low relief, high non-seasonal rainfall and subtropical temperatures. He used these results to infer previous climates based on mineralogical evidence, but goes on to say that further study is needed to clarify (1) the influence of structural state on rates of weathering, (2) the inhibiting effects of weathering products on the rates of weathering of the primary minerals and (3) the chemical environment at grain boundaries. The last two are discussed as part of the conclusions in the present study.

Singer (1970) studied the persistence of plagioclase in the rock-soil weathering sequence of a basalt in Galilee. There was a sharp change in the concentration of some of the chemical constituents across the rock-soil boundary as shown by Dennen and Anderson (1962). However, Singer found that halloysite was the major weathering product, gradually changing to meta-halloysite, with some kaolinite. The persistence of plagioclase was explained by its greater stability over the other materials (pyroxene, olivine and apatite). The pH values of the water in the soil and in the weathering crust, and the data of Stevens and Carron (1948) were combined to explain the differences in mobility of the various ions in the soil and in the weathering crust. The high pH of the weathering crust was explained by the hydrolysis of the fresh minerals and the low pH of the soil was explained by the presence of alteration products which are in general much less reactive than the primary minerals.

A recent example of the use of stability diagrams in conjunction with field observations of water composition and weathering products is the paper by Tardy (1971). He used the ratio of the removal of cations to the removal of silica to distinguish between the processes of weathering: allitization, monosiallitization, bisiallitization; these terms having been defined by Pedro (1961). From an examination of the position on the stability diagrams of the water analyses he concluded that the higher the concentration of the solutions the greater the chance for montmorillonite to be formed. This concentration effect in his data corresponded to increasing temperature as one went from Norway to Madagascar (i.e., an evaporative effect). However, this picture was somewhat complicated by the fact that little kaolinite was found at high latitudes. He also found that acidic rocks have a greater tendency to weather to kaolinite than do basic rocks and that temperature and rainfall alter the geochemical processes somewhat. This climatic effect may be responsible for some of the apparent anomalies found in some parts of the world where in fact there may be two different kinds of weathering taking place according to the season. Tardy places special emphasis on the different kinds of micro-environments which occur in the core and boundaries of the minerals and in the circulating, more dilute water. This is in agreement with similar comments by Horne (1970). He uses a geochemical index based on water composition to determine the types of weathering likely to dominate for the system containing those waters. The index is:

$$R_e = \frac{6Na_2O+6K_2O+2CaO-SiO_2}{Na_2O+K_2O+CaO}$$

if $R_e < 0$ allitization

if $R_e > 0, < 2$ monosiallitization

if $R_e > 2$ bisiallitization

This index appears to successfully separate these regimes of weathering, and as a field tool could be quite useful. This paper also provides a fair summary of the extensive French literature on the subject of weathering although the emphasis of most of these papers is on overall changes on a fairly large scale and on the formation of the various clay minerals. There is little consideration given to specific surface chemical effects with the exception of this paper by Tardy.

In summary, the following conclusions can be drawn from these field studies of feldspar weathering.

(1) Where the water is freely circulating and CO_2 charged, the reaction with silicate minerals is initially very rapid, with the reaction reaching equilibrium in a matter of hours.

(2) The factors having the greatest influence on the rate and products of the reaction seem to be the structural and physical state of the mineral, its composition, the composition of the contacting waters, the drainage, the temperature and the biological activity present.

(3) In general, kaolinite is the phase formed from the weathering of feldspars, although illite, montmorillonite, hydromica, halloysite, gibbsite and others are possible intermediates depending upon local conditions.

(4) The most prevalent cation mobility sequence is, in decreasing order, Ca > Na > Mg > K, Si > Fe, Al.

The prevalence of this sequence indicates the uniformity of the geochemical segregation processes and their lack of dependence on mineralogy and pH.

(5) Silica in natural waters comes from the weathering of feldspars and other silicates and not from the breakdown of quartz itself.

The above summary conclusions indicate that the important parameters (mineralogy, time, pH dependence) have been identified and that the experiments carried out here should yield similar results. The experiments carried out here particularly examine the relation between the surface charge on the feldspar grains and the parameters indicated above.

Part B: Experimental Studies

This discussion of previous experimental studies of feldspar weathering will be restricted to those studies with P-T conditions similar to those found in most fresh water lakes and streams. The present work is not concerned either with a hydrothermal system such as that of Manus (1968) or with a saline system such as that of Anderson and Lindqvist (1956).

The history of experimental weathering started with the early work of Daubrée (1879) and Cashman and Hubbard (1907). Daubrée noticed that mineral grinding while wet produced more leaching than dry grinding, indicating the importance of dissolved CO_2 as an agent of decomposition. The work of Cashman and Hubbard was very significant for they found that wet grinding produced rapid leaching which was then followed by a slower leaching of cations. Rapid leaching was re-attained when grinding was repeated. They concluded that the leaching was slowed by the formation of an alteration coating of the feldspar grains. These conclusions have been noted by many other workers since then: Keller (1957), Nash (1955), Garrels and Howard (1957), Correns (1961), Wollast (1967), and Manus (1968).

The work of Tamm (1924, 1929, 1930) indicated that finely ground microcline and oligoclase hydrolyzed in pure water, the cations being replaced by hydrogen ions (i.e., an increase in pH) and silica being released from the structure. His potentiometric titrations showed the reversible nature of K-H exchange reactions for microcline in the pH range 6-10.5 and the decomposition of oligoclase under similar conditions. He noted that these silicates had a buffering effect upon the water they were in contact with and formed a product material which was capable of ion exchange.

Correns (1938, 1940, 1961, 1963) and his co-workers have been consistent in supplying good data and ideas about feldspar weathering. Their experiments use the removal of the solution to prevent its back-reaction and permitting a careful, detailed monitoring of the rate of reaction. They found that stirring increased both the rate of reaction and the thickness of the residual layer for a finely ground albite. The increase in amount of solvent relative to solid also increases the amount of K, Al, and Si released from K-feldspar in a ball-milling experiment at pH 3. Their comments on the complexity of these systems noted that the following additional variables needed to be considered: rate of filtration, type of acid used, type of crushing, particle size, and shaking. It was part of their work which concluded that Al and Si were mobile species in solution although the Al was more likely present as an amphoteric colloid than as an ionic species. As an ionic species they found Al to be immobile in the pH range 4-9. They proposed that the reaction of feldspars with water produced an amorphous coating containing mostly alumina and silica which reaches a constant thickness about the mineral particle and dissolves at a rate roughly equal to the rate of diffusion of cations through the gelatinous layer. They made no direct comment on the relative reaction rates of the silicates because of varying experimental factors, but gave a table (see Correns, 1961, p. 264) which indicates that for acid pH's K-feldspar weathers more, in general, than albite.

Armstrong (1940) ground samples of microcline, albite, and kunzite for about 400 hours in water and electrodialyzed the resulting suspensions. He found that all of the constituents were present in solution and therefore clay minerals may form by ionic reactions. The ions were released from the feldspars in the following decreasing order: Ca > Na > K > Si > Al. Even after this time, some of the original feldspars still remained as indicated by X-ray diffraction and no new minerals were formed. This was in spite of the fact that dialysis could remove over 50% of the alkalis from the feldspars. He found that the residues were considerably hydrated, with water only being released in some cases after heating at 500°C. The dehydration curves were smooth however and thus the water was probably only present as adsorbed water rather than as structural water.

In 1948, Stevens and Carron amassed a great amount of data on "abrasion pH" by grinding about 280 minerals in small amounts of water and measuring the pH of the resulting slurry with pH indicator paper. The feldspars showed pH's from about 8 for anorthite to 10 for albite. This grinding procedure increases the hydrolysis of the mineral as fresh surfaces are constantly exposed to attack. All the feldspars, regardless of composition have a fairly narrow range of abrasion pH's and cannot be easily distinguished by it. In general, Stevens and Carron concluded that this method would be useful in field identification of some minerals although the effects of substitutions would greatly affect the results. They interpreted the pH values to indicate the approximate acid-base strength of the mineral; those minerals having an abrasion pH greater than 7 would be the salts of a strong base and a weak acid.

McClelland (1950) ball-milled samples of olivine, augite, hornblende, albite, labradorite, microcline, anorthoclase, muscovite, phlogopite, and biotite, and separated them into three fractions: course silt (20-50 μ), fine silt (6.5-25 μ) and course clay (0.2-5 μ). Some samples were then electrodialyzed (microcline, muscovite, biotite and olivine) and all were treated with H-bentonite clay to study the removal of bases with time. His conclusions indicate the complex nature of the reactions taking place in a natural system:

(1) The hydrolysis of ground minerals is appreciable, but the extent of hydrolysis of bases varies for the different minerals and for the different ions in the same mineral.

(2) The rate of release of bases from minerals increases with decreasing particle size, but the extent to which particle size influences base release varies with different minerals.

(3) Increasing the ratio of Ca/H on the colloidal complex decreases the rate of base release.

(4) The rate of base release increases with temperature, but the effect of increased temperature decreases with time.

(5) Fresh minerals release bases at a fast rate, but this rate rapidly decreases with time. It appears that residual primary weathering

products retard the release of bases from minerals, presumably by accumulating close to the weathering surface.

(6) Apparently the release of bases from olivine, augite, hornblende, albite, labradorite, microcline, anorthoclase, and phlogopite is accompanied by the breakdown of the crystal lattice of these minerals. The release of K from biotite appears to proceed faster than decomposition of that mineral would indicate.

(7) The minerals tend to weather congruently over a long period of time, particularly with respect to the cations.

(8) The silt and course clay fractions of the K-bearing minerals studied release K at appreciable rates. All of these minerals could be important sources of K if present in soils.

(9) The order with which the minerals studied release bases approximates Goldich's stability series with the exception of muscovite.

Note that these conclusions fit in well with those found from field studies particularly with respect to initial rapid rates of reaction followed by slower ion diffusion and exchange. McClelland indicated that the initial ease of removal of ions from the feldspars was due to the fact that they are held in fairly open channels and are not an integral part of the crystal structure but only serve to balance the negative charges of the silica tetrahedra and alumina octahedra. The substitution of smaller ions (i.e., H^+) into the feldspar structure must cause a great strain on the lattice because of its smaller size and should lead to a collapse of the structure. This would make further exchange more difficult.

The work of Nash (1955) and Nash and Marshall (1956) on seven feldspars spanning the entire K-Na-Ca composition range indicated the nature of the surface reactions of these feldspars with both acids and bases (after conversion to H-feldspars). The samples were ground with benzene in a ball-mill to a small size, dispersed into five fractions in water, and separated by sedimentation and centrifugation. pH and Na were determined on the titrated suspensions as well as the cation exchange capacities for several ions. They found significant changes in the exchange behavior of the suspensions after 3 1/2 hours, indicating the rapidity of the changes taking place in the system with the formation of a silica-alumina layer around the mineral particle. Their conclusions also indicated that Ca-feldspars were less stable (greater change in the pH of the solution) than the Na-feldspars. They noted that when acid concentrations were low the stability of the feldspars became more dependent on impurities and lattice imperfections than on chemical composition alone. The presence of perthitic structures greatly reduces the stability of the minerals concerned because the differential weathering exposes more surface for reaction than would otherwise occur and the structure itself is more open due to the "compromise" nature of the exsolution to accommodate the two different structures. They envisioned the structure of a colloidal feldspar particle as follows:

> First, there is a central nucleus of the original crystal lattice. Around this nucleus there is a porous, amorphous layer, consisting of silica and alumina. Finally, on the outer surface of the silica-alumina layer and penetrating into it there is a diffuse layer of cations.

The order of decreasing release of the cations from the feldspars was as follows: Na > Ca > K where these ions were the major ones present in the mineral. The impurities tended to be released first, presumably because they were less tightly bound. Their experiments were carried out at room temperature.

Devore (1956, 1957) developed a theoretical model of feldspar weathering involving basically the polarizability of the bonds involved in the hydration and ion exchange at the surface. That is since the bonds formed by hydrating Na-O-Si to Na-OH are stronger than those for hydrating K-O-Si to K-OH then albite should more easily release Na^+ than K-feldspar does K^+. This is in contradiction to most observed results and is not a very comprehensive model. For one, it does not consider the structure as a whole having any contribution to weathering rate. That is, bond polarizability is not the only factor governing rate. However, his statement that hydration and/or breaking of the Si-O-Si bonds to Si-OH is probably necessary before K or Na can be released from the mineral is difficult to prove. The opposite order is proposed for the weathering of Ca-plagioclase in that the substitution of H for Ca results in Si-O-Al bond strain such that the bond is broken and hydrated to Si-OH. This two-pronged theory seems to be unnecessary in that the latter theory is more compatible with observed experiments Stevens and Charron (1948) and the former is not. Devore suggested that the alteration of feldspar surfaces produces a surface which has the chemical properties (i.e., exchange capacity) if not the structure of other silicate minerals. The theory of Devore's is possible but it is unnecessary, for two surfaces may have similar properties without their structure and composition being related. That is, there is no reason for the altered surface to have the structure of a particular silicate mineral or even a structure at all. Amorphous material with high specific surface area and cation exchange capacity can account for the same phenomena. In terms of mass the amorphous material may be insignificant but its high reactivity makes it a major component of any chemical system.

In his 1957 paper, Devore examines the necessary surface chemical (i.e., compositional) changes required to form a phyllosilicate from a tectosilicate (albite) in water. He points out that a feldspar crystal will have unsatisfied bonds on 1/2 of the (001) face, 1/3 of the (100) face and 1/4 of the (010) face in that these tetrahedra share only 3 oxygen atoms with other cations. This produces a net negative charge on the surface of the mineral which can be neutralized by the adsorption of H^+ or other cations. Note that the rates of adsorption onto each kind of surface are likely to be different so the rates of alteration will be different and the mineral will differentially weather. In practice the measurement of these different reaction rates would be very difficult and one can only consider the bulk weathering of a mineral. Al-Si disorder in a feldspar could have a large effect on the differential weathering and thus structure is a major factor along with composition in determining rates of weathering. Furthermore, discontinuities of any kind in the crystal would provide locations where differential weathering would rapidly increase the active surface area thus increasing the rate of both mechanical and chemical breakdown.

Garrels and Howard (1957) were interested in the surface reactions of muscovite and K-feldspar, particularly the virtually instantaneous K-H exchange reactions. To study these reactions they produced an H-feldspar and an H-mica by dry grinding their samples and suspending them in water, then "titrating" with KCL. Their summary of previous work points up some interesting features. From Tamm's (1930) data they found a large excess of (K^+, Na^+) over OH^- in the solutions for suspensions of ground microcline, indicating a source of negative charge, either as an ion or as a surface charge. In summary, both K-feldspar and K-mica react rapidly with water to give an alkaline solution, and as the amount of K^+ freed is a function of the total surface exposed, as is the OH^- concentration achieved, suggesting that the water reacts to form at the feldspar or mica surface an insoluble H-Al-silicate which temporarily prevents further reaction. However, this H-Al-silicate which can be visualized simply as an H-feldspar or H-mica, is not stable and breaks down in time to release silica and alumina, at least part of which is in true solution.

For their back-reaction Garrels and Howard proposed the following type of reaction:

$$\mathrm{Kor} + H^+ = \mathrm{Hor} + K^+$$

but found that the equilibrium constant had to be of the form

$$(a_{K^+})/(a_{H^+})(\mathrm{Kor}) = K_{eq}$$

in order to fit the data. This assumes that Hor is an unchanging solid phase of constant activity; that is, the reaction is mainly one of K^+ - H^+ exchange, except at pH's above 10 where OH^--release is less than base release. They also assumed that Kor behaves as a dissolved molecular species whose concentration varies with the concentration of KCl. Their experiments were short term (a few hours) and they interpreted the behavior of the feldspar suspensions with titration to indicate a disordered outer layer on the mineral (of indefinite composition) with an inner layer of H-feldspar which reduces the reactivity of the feldspar and slows further reaction of the grain. This "armouring" by H-feldspar is a slightly different emphasis from other workers who feel that diffusion through the amorphous outer layer and its slow reactivity control the rate of reaction once the amorphous layer has been formed (Correns and von Engelhardt, 1938; Nash and Marshall, 1956). Garrels and Howard found that the formation of H-orthoclase was highly irreversible in spite of high K^+/H^+ ratios in solution, thus indicating that orthoclase is unlikely to form as an authogenic mineral. They also noted that the largest energy change for a weathering reaction occurred with the cation exchange and that energy contributions from other sources is small.

Some experiments by Correns (1961) established the importance of sample preparation on solution rates for K-feldspar. Ball-milling was found to be the most efficient technique but even shaking would increase the solubility over that in a non-agitated system. He interpreted this increased solubility as the result of disordering the surface crystal structure thus permitting K ions to be readily leached from the surface. Based on Krüger's (1939) data, Correns concluded that tectosilicates dissolved as ions and that under some cases a thin layer of amorphous material of constant thickness is formed on the surface of the mineral. This means that clay minerals, either kaolinite or montmorillonite, are not formed by structural reorientation of the mineral surface but by development of new structures from amorphous material. The amorphous layer has no structure and a composition correlated to either kaolinite or montmorillonite.

In 1962, Lerz and Borchert performed some experiments with finely ground microcline under atmospheric P-T conditions to study the process of kaolinitization. Their experiments were long term (1 year) at acid pH's (4.0-5.4) and they found by X-ray diffraction the formation of halloysite and an unidentifiable clay-like phase at all pH's. Their work is also a good summary of previous work in German, particularly with reference to kaolinitization.

Keller et al (1963) and Keller and Reesman (1963) performed some experiments similar to the abrasion pH work of Stevens and Carron (1948). The first paper dealt with the grinding of several silicate minerals both under distilled water (gas-free) and under CO_2-charged water for 1 hour. The distilled water gave pH's of from 8 to 9 whereas the CO_2-rich water gave pH's of from 5.5 to 6.9, and the amount of dissolved material was consistently higher for the latter water. Olivine was the only mineral found to dissolve nearly stoichiometrically in the 1 hour experiments. The results of these experiments confirm the earlier conclusion of Nash (1955) that the impurities are released to solution much more readily than are the essential elements. They also concluded that aluminous minerals did not dissolve stoichiometrically but formed insoluble residues.

When grinding in distilled water, the pH's rose, indicating the removal of H^+ from (or addition of OH^- to) the solution, probably through cation (anion) exchange on the mineral surfaces. The lower pH's for the CO_2-rich water experiments reflect the lower initial pH for the water of around 5.65 (based on CO_2-H_2O equilibrium calculations) which enables the H^+ ions to exchange with the surface cations and still keep the pH below neutral. That is, the distilled water attempts to replace the H^+ ions lost through cation exchange by dissolving more CO_2 from the atmosphere. This is a slow process compared to the reaction rate of the ion exchange and the CO_2-rich waters have an advantage in their "reserve" of H^+ ions.

The latter paper deals with a part field-part laboratory study of glacial milks. The field part consisted of the analysis of the dissolved major ions and amount of suspended load of 17 glacial melts collected from various parts of the world. The experimental part involved pulverizing in a small amount of distilled water samples of the rocks from the glacial moraines to determine their abrasion pH. These values were compared, along with the major ion concentrations, to the field data. They found that in all cases the slurries had higher pH's and higher concentrations of all the major ions, in some cases as much as 40 times as high. The influence of rock type had a large effect on the milk composition, particularly when comparing granitic and carbonate rocks.

Cases (1966) provides the first paper dealing with the electrical properties of the feldspar surface directly, although some work had been done on quartz, glass and amorphous silica. He determined the zero point of charge (ZPC)(see Appendix A) for crushed samples of quartz and three feldspars (microcline, oligoclase and labradorite) and found them to be 1.35±0.1 and 1.5±0.1 respectively. These differ slightly from the values found by Parks (1967) for SiO_2 (1.8) and by Purcell and Bhappu (1966) for albite (2.0) and microcline (2.4), but these differences could be due to differences in method of measurement or in composition of the particular samples. Cases found that treatment with acid had no effect upon the ZPC of the feldspars but did increase the slope of the zeta potential versus pH curve from -8.5 mV/pH unit to -17.6 mV/pH unit for oligoclase and from -7.8 mV/pH unit to -16.3 mV/pH unit for labradorite. The change in slope with acid treatment for microcline was much less--from -10.8 mV/pH unit to -13.3 mV/pH unit. He concluded that the acid leaching removed the cations from the surface, leaving only the silica tetrahedrae, and that the smaller change in slope for microcline indicated its resistance to acid leaching relative to the plagioclases. The source of the surface charge he found to be the adsorbed H^+ and OH^- ions. He was mostly concerned with the floculation of finely divided tectosilicates from the point of view of sedimenting them in a commercial flotation-separation system.

In 1967, Wollast studied the kinetics of K-feldspar alteration in pH buffered solutions with pH's from 4 to 10. The use of buffered pH solutions, while removing pH as an independent variable, adds the influence of the buffering substance to the system as an independent variable whose effect is unknown. He used a finely ground orthoclase and monitored silica and alumina for 25 days during which time the solutions were continuously agitated. He did not measure the cation concentration solution. He does not give any conductivity data, nor does he indicate whether or not the systems were open to the atmosphere. From his data he goes on to propose a model for the weathering behavior and to develop a differential equation for the rate based on this model. The equation is as follows:

$$\frac{dC}{dt} = k_3 t^{1/2} - k_2(C-C_e)$$

where C is the concentration of silica in solution at time t;

C_e is the equilibrium level of concentration of silica based on the reaction

$$H_4SiO_4(\text{solution}) + Al(OH)_3(\text{amorphous}) = \frac{1}{2}(H_4Al_2Si_2O_9)(\text{amorphous}) + 5/2\ H_2O$$

in which the rate of reaction is proportional to the H_4SiO_4 concentration;

k_2 is the equilibrium constant for the above reaction (units time^{-1})

$\frac{dC}{dt} = -k_2(C-C_e)$; and

k_3 is the rate constant for the dissolution of feldspar to yield silica in solution (units time$^{-1\frac{1}{2}}$ x concentration)

This equation is based on a mechanism containing the assumptions that:

(1) the solution is perfectly agitated and the concentrations are uniform throughout;

(2) the alteration layer is thin with respect to the radius of the particle and thus diffusion through the layer is at right angles to the mineral surface;

(3) the amount of silica in solution is equal to that formed by dissolution of the feldspar minus that which reacts with the amorphous layer to form an aluminosilicate;

(4) the rate-determining step for the combination feldspar dissolution-diffusion through the alteration layer is the rate of diffusion. This is indicated by the form of the curves for the release of silica and alumina which are initially steep and straight, but which become less steep and approach a steady-state type of model; and

(5) the initial chemical reaction between fresh feldspar in contact with pure water has a rate equation of the form:

$v_1 = k_1(H^+)^{1/3}$ where $v_1 = dC/dt$ and k_1 is the rate constant.

The above equation was then fitted to the data and the rate constants determined, based on the assumption that $C_e = 5$ mg/ℓ. as SiO_2. The fit obtained was excellent and the model for the alteration is probably a good one, being in line with what is known about the mechanisms of alteration. The weight percent solids in suspension was found to affect the total concentration (as expected--see Deju and Bhappu, 1966) and the thickness of the altered layer decreased with increasing weight percent solids in suspension. The amount of feldspar dissolved and the dissolution rate was greatest for an acid pH and less for pH's 6, 10 and 8 in decreasing order. For dilute (low weight percent solids in suspension) solutions the reaction rate appears to be limited by the thickness of the residual layer. The weathering mechanism he found was only slightly dependent on pH, except that at pH's below 5, the $Al(OH)_3$ layer would be soluble and no amorphous layer would develop. Thus the solution of the $Al(OH)_3$ layer must be slow relative to the reaction to form the amorphous aluminosilicate, since a residual layer is observed.

Huang and Keller (1970) examined the dissolution of finely ground (149-197) micron samples of olivine, augite, muscovite, labradorite, and microcline in a variety of solvents (distilled water, CO_2-rich water, weak acids and strong acids) for 21 days. They centrifuged the suspensions and analyzed them for Si, Al, Fe, Mg, Ca, K, Na, pH and conductivity. In sample preparation the samples were dry ground and washed with distilled water and dried. In the light of previous work on the rapidity of the reactions taking place on the mineral surface, this does not seem to be a good procedure, although their results agree with those of other workers. Their results showed the typical high initial reaction rate for 24 hours followed by a decrease to a nearly constant value after 5 days. Incongruent solution appears to be the rule rather than the exception even with olivine (in the short run), although it approached congruent solution after 21 days. The influence of the solvents was quite marked, particularly in affecting the relative release of ions during dissolution. For example: in organic acids labradorite does not easily release Ca and Na whereas in deionized water or CO_2-rich water these ions are readily removed. The particular solvent, by affecting the ratio of ions released controls the composition of the aluminosilicate surface which is formed. Thus, in the field, the presence of organic acids in the water may lead to the formation of anomalous clay minerals or to an anomalous distribution of several cations.

Recently, Deju (1971) performed experiments passing acid water of known composition through porous beds of known composition. His results indicate that the rate of reaction is initially very fast for the desorption of Na and K from a Na-microcline but it rapidly decreases to a much lower level. Hydrogen adsorption appears to take place only at the beginning of the experiment for Na-microcline indicating the resistance of the framework silicates in general to weathering (see also Loughnan, 1962). The cation desorption was virtually complete in their experiments after 100 minutes and showed a much higher Na/K ratio in solution than in the mineral. This may be a result of several factors, such as greater mobility for Na, K fixation in the mineral surface, Na contamination from fresh glass ware or a combination of the above. Deju does not indicate that he is aware of the very serious Na contamination that can result from the first hydration of new glassware. His approach is quite informative and other experiments of this kind should be carried out with greater attention paid to the structural state of the individual mineral samples involved.

The work of Luce _et al_ (1972), mentioned earlier, indicated that the initial pH of the solutions had a small effect on the reaction rate, increasing for more acid pH's. The experiments showed that the short-term incongruent dissolution and the long-term congruent dissolution observed by others (Loughnan, 1969; Polzer and Hem, 1965) were consistent with a model in which the short-term dissolution was proportional to $t^{\frac{1}{2}}$ and the long-term dissolution proportional to it.

In summary, it is difficult to compare the results of the papers considered here because of the influence of so many factors as pointed out in the papers themselves. However, it is necessary to point out those general factors which have been considered and must be considered correctly to interpret the weathering behavior of minerals *in toto*, i.e., the source minerals, the weathering solution, and the alteration products.

The most important conclusions appear to be the following:

(1) The rate of dissolution of minerals (especially feldspars) is governed by the temperature, the concentration of the weathering solution, the state of subdivision of the mineral, the composition of the weathering solution (with respect to the presence of inorganic and organic materials), the composition and structure of the mineral (particularly with reference to impurities and lattice defects).

(2) In general, the minerals dissolve in a manner compatible with Goldich's stability sequence, modified by some of the factors in (1).

(3) Impurities tend to be released more easily than essential elements from a mineral.

(4) Drainage has an influence on rates of weathering because it affects the amount of fresh water coming in contact with the minerals and the removal of reaction products.

(5) The weathering of feldspar proceeds, in general, by the initial rapid hydration of the fresh mineral surface (in a matter of hours) with the exchange of H^+ for the cations until an amorphous aluminosilicate layer is built up on the surface. Thereafter, the rate of reaction

is controlled by the rate of diffusion of the cations through this layer and the rate of dissolution of this layer, which appear to be about equal and considerably slower than the initial hydration and ion exchange. This aluminosilicate layer, unlike the fresh mineral surface shows considerable reversible ion exchange capacity.

(6) The negative nature of the feldspar surface plays a role in attracting cations and polarizing water molecules and can influence the adsorption and exchange characteristics of the surface. This negative charge appears to persist over the pH range of all natural waters even after considerable acid leaching and alteration. The details of the affect of this surface charge on specific interactions in controlling ion exchanges in the natural environment are unfortunately still lacking.

(7) At the pH's normally encountered for natural waters (6.5 to 8.5), the pH is not a major factor affecting the weathering behavior of feldspars.

The survey of previous work suggests a correlation exists between surface charge and master variables (pH, etc.). This correlation needs to be confirmed by experiment.

TABLE II-1(a)

SUMMARY OF FIELD STUDIES

Reference	Analyses			Type of Study	Comments
	Rock	Weathered Products	Water		
Goldich 1938	yes	yes	no	rock-soil	- first mineral stability sequence established based on persistence in weathering of various rock types.
Brock 1943	yes	yes	no	rock-soil	- found similar mobility trends for different rock types Ca > Na > Mg > Si > K.
Jackson *et al* 1948	no	yes	no	soil-water	- established 13-step mineral weathering sequence based on mineralogy of fines in soils.
Butler 1953,1954	yes	yes	no	rock-soil	- found weathered products more similar to each other than to parent material.
McLaughlin 1955	yes	yes	no		- found kaolinite/hydromica increased with temperature for arkose weathering.
Sand 1956	yes	yes	no	rock-soil	- claimed halloysite was an essential intermediate between mica, feldspar and kaolinite.
Le Grand 1958	no	no	yes	rock-water	- used ground water analyses to infer subsurface geology.
Kelly and Zumberge 1960	yes	yes	no	rock-soil	- no chemical weathering occurred in this Antarctic environment.
Lazarenko 1961	no	yes	no	soil-water	- once sediments enter a river they alter very little, thus sediments are determined by parent rock.

TABLE II-1(b)

Reference	Analyses Rock	 Weathered Products	 Water	Type of Study	Comments
Short 1961	yes	yes	no	rock-soil	- noticed that the greatest changes in composition occurred across the rock-soil interface and that exchange phenomena were important.
Dennen and Anderson 1962	yes	yes	no	rock-soil	- local environment is major factor controlling chemical changes, not climate or rock type.
Feth, Roberson and Polzer 1964	yes	yes	yes	rock-soil-water	- first integrated study of whole mobility - mass balance aspect of weathering. - showed rapidity of weathering reactions.
Harriss and Adams 1966	yes	yes	yes	rock-soil-water	- montmorillonite indicated on immature soil, kaolinite a mature soil.
Bricker and Godfrey 1967	yes	yes	yes	rock-soil-water	- determined weathering sequence, rate of reaction of silicates, chemical mass balance, equilibrium status.
Ruxton 1968	yes	yes	no	rock-soil	- established weathering index - SiO_2/Al_2O_3 decreases with progressive weathering.
Todd 1968	yes	yes	no	rock-soil	- found ortho>plag under some conditions. - set up weathering index from area of grains altered.
Singer 1970	yes	yes	no	rock-soil	- plag persisted with halloysite being the major metastable product mineral formed.
Tardy 1971	no	yes	yes	rock-soil-water	- derived weathering index based on water analyses but pointed out anomalies in dry, hot regions and wet cool regions.

TABLE II-2(a)

SUMMARY OF EXPERIMENTAL STUDIES

Reference	Major Emphasis	Analyses				Primary Mineral	Secondary Mineral	Buffer	Comments
		pH	SiO_2	Al_2O_3	Cations				
Daubree 1879	decomposition with grinding	*				orthoclase		no	- found hydrolysis and CO_2 to be important in the decomposition as well as grinding.
Cushman and Hubbard 1907	electrolysis	alkalinity				orthoclase		no	- very similar to Daubree. - first to note that decomposition was initially rapid and then slower and to postulate the formation of a new aluminosilicate surface.
Tamm 1930	decomposition with titration	*				microcline oligoclase		no	- used the titration curves to show the release of cations and aluminum in the acid pH region. - believed that cation exchange was one of the first reactions with H^+ substituting for M^+ or M^{++} to produce an unstable lattice.
Correns 1940, 1961	decomposition by leaching	*	*	*	*	orthoclase albite		no	- ultrafiltration was used to extract samples for analyses. - found that most constituents go into solution as ions with the metals going first leaving an aluminosilicate residue.

TABLE II-2(b)

Reference	Major Emphasis	Analyses				Primary Mineral	Secondary Mineral	Buffer	Comments
		pH	SiO_2	Al_2O_3	Cations				
Armstrong 1940	grinding and dialysis		*	*	*	macrocline albite		no	- found no new minerals after 400 hours (by X-ray) - altered minerals were hydrated and deficient in cations.
Stevens and Carron 1948	abrasion pH	*				280 minerals		no	- tried to establish a field test for mineral identification by determining the pH of wet ground mineral slurries.
McClelland 1950	soil science and base release				*	albite labradorite microdine anorthoclase		no	- emphasis on factors influencing release of cations, such as particle size, in bentonite-mineral mixtures
Nash and Marshall 1955,1956	reactions at feldspar surfaces	*	*	*	*	microdine albite oligoclase labradorite bytownite		no	- showed the importance of surface composition in rate of alteration and the strong dependence of exchange capacity on the ions involved. - confirmed earlier observations on irreversibility of reactions changes in rate with time and importance of initial pH.
Garrels and Howard 1959	reactions at K-feldspar surface	*				K-feldspar		no	- importance of H^+-M^+ exchange in hydrolyses was emphasized - showed dependence of equilibrium pH on weight percent suspension.

TABLE II-2(c)

		Analyses							
Reference	Major Emphasis	pH	SiO_2	Al_2O_3	Cations	Primary Mineral	Secondary Mineral	Buffer	Comments
Lerz and Borchart 1961	kaolinitization	*				microcline	halloysite kaolinite (X-ray only)	no	- good summary of work on kaolinitization - found clay-like phases formed after weathering the microcline in acid waters.
Pedro 1961	tropical rock weathering					sanidine labradorite andesine	boehmite gibbsite	no	- leached rock samples in a reflux apparatus to show the differences in mineral alteration between the vadose and phreatic zones.
Keller and Reesman 1963	glacial milks	*	*		*	labradorite microcline		no	- compared dissolved products from natural slurries (glacial melts) and laboratory slurries - showed importance of CO_2 in weathering rates - pH's of laboratory slurries were higher than those of natural milks.
Cases 1966	zero point of charge	*				microcline oligoclase labrodorite		no	- first determination of ZPC on natural minerals - showed the importance of the state of the surface in determining ZPC.
Wollost 1967	short-term alteration model	*	*	*		K-feldspar		yes	- produced a model of feldspar weathering based on his experiments with buffered water - a concise presentation of theory and experimental data. - emphasized importance of pH, weight percent suspension, on rates of weathering.

TABLE II-2(d)

		Analyses							
Reference	Major Emphasis	pH	SiO_2	Al_2O_3	Cations	Primary Mineral	Secondary Mineral	Buffer	Comments
Manus 1968	tropical leaching	*	*		*	alkali feldspars	unidentified clay minerals	no	- summarized current theory and previous work with respect to the hydration, alteration and maturation of the feldspar surface - showed the formation of a clay-like mineral.
Huang and Keller 1970	organic acid weathering	*	*	*	*	labrodorite microcline		no	- showed influence of organic acids on congruency of mineral dissolution - this has important implications in soil formation.
Deju and Bhappu 1971	silicate weathering	*		*	*	microcline		no	- proposed a model of silicate bed weathering and tested it. - showed importance of short-term processes such as cation-H^+ exchange. - mineral surface was also important especially with respect to O/Si ratio.
Luce et al 1972	olivine weathering	*	*		*	olivine		no	- results showed short-term incongruent followed by long-term congruent dissolution.

CHAPTER III

EXPERIMENTS

CHAPTER III: EXPERIMENTS

Introduction

In this study the experiments were designed to measure the geochemical and surface charge changes with time for two crushed samples of feldspar (Na-fs and K-fs) over the pH range of most natural waters (5 to 9). To simulate a natural stream the sample flasks containing the pH adjusted water were agitated intermittently for the duration of the experiment. The concentration (as wt. %) of the suspension was determined by the highest concentration which would permit penetration by the light beam of the Zeta Meter. The geochemical variables measured were Na, K, Ca and SiO_2 concentrations along with pH and temperature. The geochemical variables were to give the maximum information concerning the dissolution of the mineral with the most rapid and accurate methods available. Surface charge as Zeta potential was measured along with specific conductivity to determine if the surface charge could be related to the dissolution of the feldspar samples either with regard to reaction rates or kinds of specific surface reactions.

The purpose of these experiments was to provide a body of data to permit those processes which occur at the surface of a mineral during dissolution to be investigated in detail. The experiments are unique in that they are the first combined study of surface charge and geochemical changes as a function of time and pH.

Samples

The samples used in all experiments were U.S. National Bureau of Standards Standard Reference Materials 70a and 99a. These are respectively potash feldspar and soda feldspar, hearafter referred to as K-fs and Na-fs. Their indexed X-ray diffractometer traces are also given (Figures III-1 and

III-2) which show that the feldspars are not pure end members. The X-ray data also indicate that there may be at least 2 structural phases present in the Na-fs. The K-fs, for example, has 24.66 equivalents of Na or, approximately 1/4 of the K^+ sites are filled by Na^+. In the case of the Na-fs, there are also 31.65 equivalents of K and 10.98 equivalents of Ca or, approximately 1/3 of the Na^+ sites are filled by K^+ and slightly more than 1/10 by Ca^+. Their analyses are included with the recalculated analyses as standard feldspars (XYZ_3O_8) in Table III-1.

Recalculation of the analyses as standard feldspars indicate a slight deficiency of cations for both K-fs and Na-fs (7.7 equivalent % and 5.1 equivalent % respectively). This may be the result of pre-treatment of the samples by washing after grinding. K-fs has a higher Si/Al ratio than does Na-fs in keeping with the greater substitution of bivalent for monovalent cations in Na-fs. Plotting the compositions as equivalent % on a ternary diagram indicates that while K-fs is likely to exhibit complete solid solution and can be called an orthoclase, Na-fs is likely to be perthitic, and can be called a potassian oligoclase (Barth, 1969).

The method used to crush these samples was unknown as they arrived pre-crushed to less than 40 microns and the NBS had no record of their method of preparation. In the experiments described below, the samples were not pre-treated in any way, but simply weighed out and added to the reaction vessels. The sample weights are given in Table III-2 as are the factors to be applied to the geochemical data to correct for differences in sample weight. These factors were computed as follows: Sample Weight Correction Factor = 2.5000/sample weight.

Experimental Procedure

Using four liters of room temperature, distilled, deionized water the reaction vessels were organized as follows. Each Erlenmeyer flask contained 500 mls. of water with the pH's adjusted as indicated in Table III-5. One-holed rubber stoppers fitted with 4-inch glass tubes were inserted into the tops of the flasks, which were then fastened securely on the shaker. The shaker was started using a timer, programmed on a 12 hours on - 12 hours off schedule. Accurate 25 ml. aliquots were pipetted from each flask each sampling period according to the timetable in Table III-3. This timetable was designed to give the maximum information during the initial stages of weathering. The aliquots were stored in 30 ml polyethylene bottles and treated as follows:

(1) Temperature and pH were measured immediately.

(2) Zeta potential and conductivity were determined next using a Riddick Zeta Meter.

(3) After Millipore filtration (0.45 microns) and no further reaction can take place, the filtrate is capable of being stored for later analysis of silica and cations by spectrometer and atomic absorption respectively.

(4) The residue was then dried and an X-ray diffractometer trace made of it.

Up to the conclusion of the filtration, the procedure takes about 1 hour and 45 minutes.

Experimental Methods and Equipment

The analytical methods used are given in Table III-4 along with detection limits, sensitivities, and type of instrument employed. All X-ray diffraction traces were made using a Norelco (Phillips) X-ray unit with Cu/Kα radiation and a Ni filter (30 kV and 15 ma), with a chart speed of 1"/min.

Temperature and conductivity were measured but fluctuations in both of these were found to be very small, the temperature ranging from 20.0°C to 23.0°C and the conductivity remaining below 180 μ mhos/cm for the duration of both the experiments. The X-ray diffraction traces did not differ from those of the original samples, thus these results along with the temperature and conductivity measurements are deleted.

Because the shaking was not sufficient to keep all of the feldspar particles in suspension, the removal of a 25 ml. aliquot would reduce the volume without appreciably reducing the reacting mass. Therefore, a correction must be made to the concentration calculations to take the volume change into account. The mass removed per aliquot was much less than 1% of the total reactant mass. Were the aliquot a homogeneous sample of the feldspar-water system at the time of sampling, such a correction would not be necessary.

The experiments were designed to examine the dissolution kinetics of a sodium feldspar and a potassium feldspar in three non-buffered aqueous solutions with initial pH's of 5, 7 and 9. These pH's were adjusted by the addition of HCl and/or NH_4OH to deionized distilled water.

The measurement of zeta potential, (ζ), which is a function of the surface charge on the feldspar particles, was made to determine if the physical (electrical) changes on the surface during weathering were correlated with the chemical changes occurring at the same time.

Figure III-1

X-ray Diffractometer Trace for Na-feldspar (99a).

Na-fs X-ray Diffraction Trace

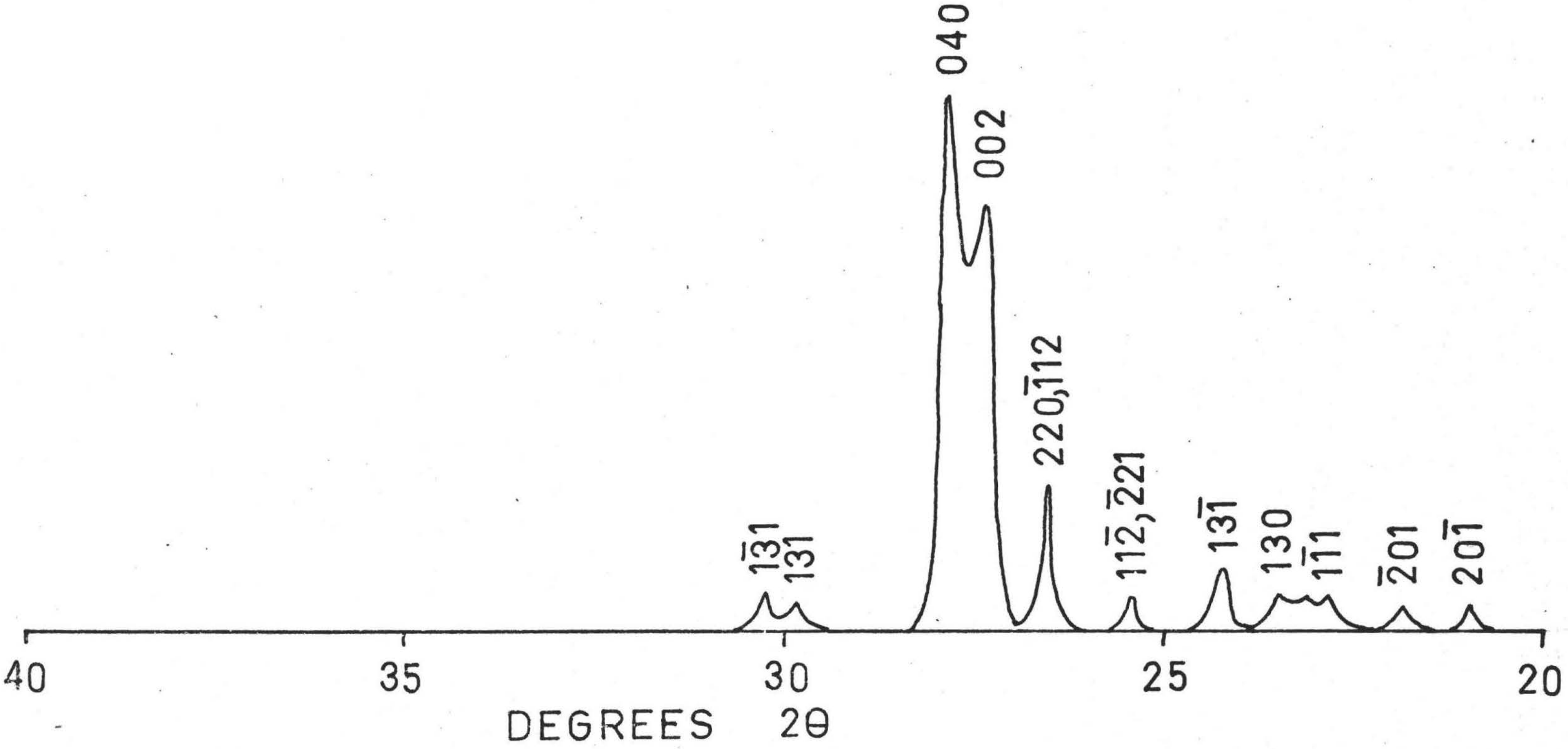


Figure III-2

X-ray Diffractometer Trace for K-feldspar (70a).

K-fs X-ray Diffraction Trace

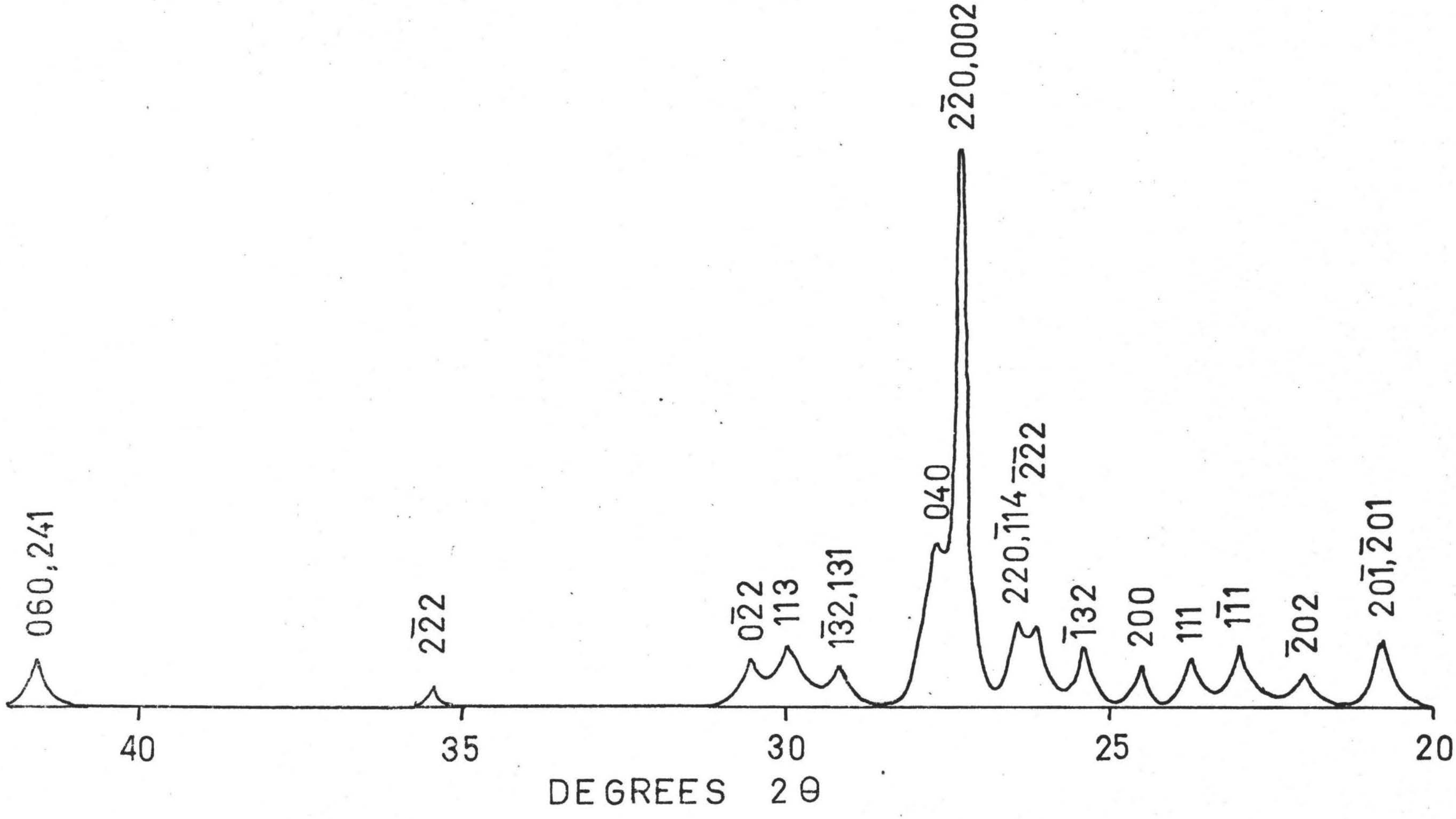


TABLE III-1

Standard Feldspar Compositions

Sodium Feldspar

$(Na_{.54}, K_{.30}, Ca_{.10}, Ba_{.01})_{.95}\ Al_{1.00}\ (Si,Al)_{3.0}\ O_8$

plus trace amounts of Fe, Ti, Mg, P

Potassium Feldspar

$(K_{.68}, Na_{.23}, Ca_{.01}, Al_{.01})_{.93}\ (Al,Si)_{1.00}\ Si_{3.0}\ O_8$

plus trace amounts of Fe, Ti, Ba, Rb

NBS Analysis (weight per cent)

	Na-fs	K-fs
SiO_2	65.2	67.1
Al_2O_3	20.5	17.9
Fe_2O_3	0.065	0.075
TiO_2	0.007	0.01
CaO	2.14	0.11
BaO	0.26	0.02
MgO	0.02	
Na_2O	6.2	2.58
K_2O	5.2	11.8
Rb_2O		0.06
P_2O_5	0.02	
H_2O+	0.26	0.40

TABLE III-2

SAMPLE WEIGHT CORRECTION FACTOR

Flask	Sample Weight (g.)	Correction Factor	
1A	2.5014	0.9994	**Na-feldspar**
1B	2.4914	1.0034	
2A	2.5017	0.9993	
2B	2.4754	1.0099	
3A	2.4904	1.0033	
3B	2.5006	0.9997	
1A	2.5042	0.9983	**K-feldspar**
1B	2.4972	1.0011	
2A	2.5005	0.9999	
2B	2.4978	1.0008	
3A	2.4986	1.0005	
3B	2.5028	0.9989	

TABLE III- 3

SAMPLING TIMETABLE

Sample Period	Time After Start (hours)
1	1
2	2
3	4
4	8
5	12
6	24
7	48
8	120
9	240
10	360
11	480

TABLE III-4

Analytical Instruments, Limits and Sensitivities

Datum	Instrument	Detection Limit	Sensitivity
Na	Atomic Absorption Spectrophotometer	0.02 ppm	0.04 ppm
Ca		0.05 ppm	0.05 ppm
K		0.05 ppm	0.05 ppm
SiO_2	Spectrophotometer	0.4 ppm	0.1 ppm
pH	pH Meter		0.01 units
Specific Conductivity	Zeta Meter	1μmho/cm	0.5μmho/cm
Zeta Potential		5 mv	3 mv

TABLE III-5

Experiment and Sample Organization

Flask No.	Approximate Initial pH	Flask No.	Chemicals Added
1A	5	1B	HCl
2A	7	2B	HCl/NH_4OH
3A	9	3B	NH_4OH
X	6.5	XX	Blanks

CHAPTER IV

RESULTS

CHAPTER IV: RESULTS

Introduction

There were two experiments, one with Na-feldspar and another with K-feldspar in which time was the independent variable and all other parameters were dependent variables. The prime objective was to determine the correlation between the geochemical variables pH, SiO_2, Ca, Na, K and the surface chemical variable, zeta-potential, both as a function of time and as a function of initial mineral composition. The data presented in Tables IV-1(a) and IV-1(b) are the results of these experiments. They have been corrected for blanks, differences in sample weight, volume changes due to removal of aliquots and averaged for duplicate pairs of samples. The raw chemical concentration data for each flask were as follows:

Final Value = (Initial Value-Blank) x (Sample Weight Difference Factor) x (Volume Change Factor).

For the same initial pH conditions these final values were averaged and the results are given in Tables IV-1(a) and IV-1(b). The estimated uncertainty (reproducibility) in these data is given in Table IV-2. The [illegible] [illegible] concentration variables, pH excepted, are given in milliequivalents/litre.

In the figures (IV-1) through IV-11) which follow the tables, the data are presented in graphical form to permit easier interpretation. In all cases the abscissa for the graphs is a non-linear time scale. Table IV-2 gives the maxima, minima, averages and standard deviations for all variables, separated according to sample and initial pH.

Description of the Data

In these experiments we are dealing with a system which is not in equilibrium and thus it would be expected that changes should occur as the system attempts to reach equilibrium. That the system is in fact tending toward equilibrium is indicated by the "congruency" diagrams [Figures IV-8(a), -8(b), -9(a), -9(b), -10(a) and -10(b)] wherein the cation/silica ratios in the solution all converge towards the values in the original mineral.

For all the concentration variables, except pH, there is initially a rapid increase to a high value followed by a slightly slower decrease to a lower, fairly constant value (see Figure IV-12). This is the general pattern and there are exceptions. For example, Ca and SiO_2 [Figures IV-3(a), -3(b), -4(a) and -4(b); also Figure IV-12(b)], both increase again after the "constant" value is reached. The general pattern is most evident for pH 5 and pH 7 with the pattern for pH 9 being an initial rapid increase to a value which is fairly constant for the rest of the experiments [Figure IV-12(a)]. In all cases the values for the concentration variables are in descending order from pH 5 to pH 9. Silica, however, shows little variation with pH, consistent with its nearly constant solubility up to pH 9 (Siever, 1965).

pH itself shows a convergence with time [Figures IV-6(a), -6(b)] to an average value around 7.2, but a detailed pattern is difficult to see. The wide fluctuations in the pH data results from the measurements being taken as the particles settled, in which the measured pH is a weighted average of the bulk water pH and the pH of the adsorbed structured water. An attempt was made to remove this component by taking the measurements 15 sec. after the aliquot was agitated. This was unsuccessful. The aliquots could not be stirred because they were too small (see Chapter III).

Zeta potential shows a pattern which is roundly the inverse of the SiO_2 pattern, especially for the Na-feldspar [Figure IV-5(a)]. There is an initial slow rise to a maximum negative value followed by a rapid decrease. The pattern for K-feldspar is similar but not as well developed [Figure IV-5(b)].

The ΔpH (ΔpH = pH_{sample} - pH_{blank}) data [Figures IV-7(a), -7(b)] shows the convergence with time indicated in the pH data and also the fact that the feldspar-H_2O-CO_2 system seldom deviates more than about 1 pH unit from the pH established by the H_2O-CO_2 system. This means that the deviations are due to feldspar-H_2O reactions and the larger deviations indicate a greater extent of interaction between the feldspar and the water. Compare Figures IV-7(a) and -7(b). Note that while the $CO_2(air) \longleftrightarrow CO_2(water)$ exchange is a factor affecting pH, the mineral-water reactions cannot be ignored, particularly in view of the apparent buffer pH at pH 7, not at 5.45 as would be expected from a simple CO_2-H_2O system.

As indicated above, Figures IV-8(a) through -10(b) show the variation with time of the molar ratios in the solution for Na_2O/SiO_2, K_2O/SiO_2 and CaO/SiO_2 for each mineral and also the values of the same ratios in the original mineral. With the exception of Figure IV-10(a) all the ratios show the same general pattern in which the solution ratios are initially much higher than in the original mineral but decrease and appear to converge towards the original mineral ratio. This phenomena is most pronounced for initial pH's either neutral or acidic [Figures IV-8(a), -8(b), -9(a), -9(b), -10(b)] for both samples and the ratios always decrease from acidic to basic initial pH's. The exceptions are found in the CaO/SiO_2 ratios for both the Na-feldspar and the K-feldspar. In both cases the convergence appears to be complete much earlier and the pH 9 curve shows a trend opposite to that of the other pH's and of the other ratios. There is an excess of silica rather than metal oxide in both cases for initial pH 9. Another anomaly is the behavior of the three curves in Figure IV-10(a) after 24 hours. All other curves continue to converge to the original mineral ratio after this point but these diverge from this point and reach values much higher than the initial solution ratios.

Other ratios of interest are the Na/K and Na/K/Ca ratios. In the original mineral they are 1.8/1 and 5.4/3/1 for the Na-feldspar and 0.34/1 and 23/68/1 for the K-feldspar. For both minerals the Na/K ratios are nearly constant for the duration of the experiments, at 1.47 and 0.31 for Na-fs and K-fs respectively. These values are slightly lower than in the original mineral but close to the stoichiometric ratio indicating that Na and K have similar behavior. Only the Na-fs shows a strong pH dependence for the Na/K values with the ratio increasing from acidic to basic pH's. The Na/K/Ca ratios are difficult to evaluate as the values vary widely and are very dependent on the low Ca values which have the greatest uncertainty. However it is clear that the ratios for the two minerals are converging towards the values in the original minerals.

Figures IV-11(a) and IV-11(b) are the stability diagrams for the Na_2O-H_2O-SiO_2-Al_2O_3 system and the K_2O-H_2O-SiO_2-Al_2O_3 system, respectively. (Data from Garrels and Christ, 1967). All the experimental solution composition data for the appropriate starting mineral are plotted on these diagrams and two facts are immediately clear: (1) the initial composition of the aqueous phase in contact with both minerals lies in the gibbsite field, and (2) only the final composition of the aqueous phase in contact with the K-feldspar lies in the kaolinite field. These figures show the restricted values in final composition of the solution for different initial pH's indicating the weak pH dependence of the reactions. Note also the greater spread of points for the K-feldspar experiment than for the Na-feldspar experiment and the general trends of the solution compositions.

Factor Analysis

Using the BMDO3M Factor Analysis computer program, the data were further analysed as follows: (1) The pH and ΔpH values were deleted from the analysis as being too erratic and unreliable; (2) the remaining variables were scaled by a factor of 10^5 to yield positive real numbers in the range 0.0 to 10,000.0; and (3) the data were subdivided first according to sample, then according to initial pH within samples and finally according to the time of sampling either prior to 24 hours or post 24 hours. This breakdown allowed comparison (a) between samples, (b) between pH's for the same sample, and (c) between initial stages and later stages of weathering for each pH for each sample. Twenty-four hours was chosen as the division point because most variables had reached their "equilibrium" value by then. The variables considered were therefore time (T), zeta-potential (ζ), and concentrations of Na, K, Ca and SiO_2. A summary of the results of these calculations is given in Table IV-4.

The minimum eigenvalue accepted was aribtrarily set at 1.0 but could have been as low as 0.5 in most cases without significantly affecting the results. The number of factors rotated was either 2 or 3, if the factor matrix could be rotated at all, indicating that some of the variables measured were redundant in terms of indicating the trends in the data.

From Table IV-4 it is clear that, in general, Ca and SiO_2 have analogous behavior for both samples as do Na and K. ζ-potential is in general, inversely related to all of the above, plus SiO_2, particularly at basic pH's. At initial pH's 5 and 9, the samples differ in the relations between variables prior to 24 hours, but show similar trends after 24 hours. In fact, after 24 hours the trends between samples are very similar for all initial pH's perhaps reflecting the convergence of the solution pH values. This may also indicate a difference in mechanism or in the rate of a process in the short term, but a long term similarity in mechanism. Considering that the fresh mineral surfaces are quite different (chemically and structurally) it is not surprising that their initial behavior is quite different and the initial reaction(s) influences the ensuing reaction(s) until an altered layer develops. The composition of this altered layer is more a function of initial pH and time than starting mineral composition because the geochemical segregation (weathering) processes which produce the altered layer are not a function of the starting mineral. For the same sample there are significant differences between the trends for all initial pH's prior to 24 hours and post 24 hours. This also suggests a change in the type of alteration process taking place and indicates that this change in process type is not dependent on the feldspar composition or on initial pH.

The general patterns mentioned in the description of the data and generalized in Figure IV-12 are confirmed by the statistics in Table IV-4. For example, the inverse correlation of zeta potential with time (T) and SiO_2, the virtually omnipresent correlation of Ca with SiO_2 and the correlation of Na and K are clearly indicated in the table. The segregation of the data according to initial pH shows that there are differences due to pH but that these differences in most cases are small. The large negative correlations which occur for time and other variables for the prior-to-24-hours data arises because the point (0,0) was not included in the data and thus the peak present in the data does not show up in these statistics.

Interpretation of the Data: Generalizations

The general interpretations from the data are as follows:

(1) Chemical reactions in the feldspar-water system occur initially very rapidly and then slow down after about 24 hours.

(2) The weathering of feldspars proceeds by a two-step process in which the first step is the hydration of the feldspar surface and replacement of the surface metal cations by hydrogen ions and the second step is the formation of an amorphous aluminosilicate coating around the feldspar grain which controls all further reactions. The transition between these two steps occurs at approximately 2 hours after immersion of the feldspar in water.

(3) During the first step of the weathering process the initial minerology, crystallography and solution pH are important but during the second step only the physical and chemical nature of the amorphous coating is important either to the kinds or rates of reactions taking place.

(4) Feldspar weathering reactions tend toward congruency in the long term, but are incongruent in the short term, particularly in neutral and acid waters, the cations going into solution along with silica and the aluminum remaining as a solid phase.

(5) The composition of a solution in contact with a feldspar lies on a stability field diagram [Figures IV-11(a) and IV-11(b)] initially in the gibbsite field but this composition changes with time to plot in the kaolinite field.

(6) For a rapidly weathering feldspar, the amorphous layer is being dissolved at such a rate that the surface properties of the layer are essentially static as the surface has no chance to "age" or alter before it is removed. Thus for a more slowly weathering feldspar the surface properties show a very marked change with time as the surface "ages".

TABLE IV-1(a)

Results of Na-feldspar weathering experiment

Time (hours)	Initial pH	Na	K	Ca	SiO_2	Zeta Potential (mv)	pH	Δ pH
		(meq/l)						
1	5	.075	.078	.007	.008	-56.5	7.09	-1.12
	7	.063	.060	.003	.007	-46.0	7.17	-1.03
	9	.034	.018	.000	.008	-42.3	8.14	-0.06
2	5	.054	.070	.004	.007	-54.5	7.04	-1.23
	7	.034	.033	.001	.006	-48.5	7.26	-1.01
	9	.030	.010	.000	.006	-46.0	7.90	-0.37
4	5	.049	.057	.004	.006	-54.0	7.04	-1.17
	7	.038	.032	.001	.005	-51.0	7.51	-0.70
	9	.027	.012	.001	.006	-47.0	8.14	-0.07
8	5	.059	.055	.004	.005	-55.0	7.23	-1.03
	7	.036	.029	.001	.006	-53.0	7.62	-0.64
	9	.030	.012	.001	.005	-48.0	8.21	-0.05
12	5	.050	.048	.002	.005	-54.5	6.95	-0.45
	7	.025	.018	.001	.005	-51.0	7.00	-0.40
	9	.029	.020	.001	.005	-45.5	7.35	-0.05
24	5	.035	.029	.002	.004	-56.0	6.67	-0.40
	7	.038	.028	.001	.005	-55.5	6.74	-0.33
	9	.024	.013	.001	.005	-46.0	7.25	+0.18
48	5	.041	.045	.003	.005	-58.5	7.18	-0.88
	7	.032	.026	.001	.007	-55.5	7.57	-0.49
	9	.023	.009	.001	.005	-53.0	8.14	+0.08
120	5	.046	.048	.005	.006	-58.0	6.99	-0.51
	7	.035	.025	.002	.006	-48.0	7.41	-0.09
	9	.029	.011	.001	.006	-53.0	7.60	+0.10
240	5	.052	.043	.007	.008	-48.0	7.15	+0.56
	7	.037	.024	.004	.007	-44.0	7.41	+0.82
	9	.033	.011	.002	.006	-46.0	7.30	+0.71
360	5	.047	.055	.010	.009	-45.0	7.22	-0.56
	7	.036	.024	.007	.008	-36.5	7.50	-0.28
	9	.032	.013	.003	.008	-38.0	7.74	-0.04
480	5	.045	.047	.013	.011	-38.8	7.24	+0.81
	7	.034	.028	.012	.010	-30.5	6.86	+0.43
	9	.032	.019	.006	.012	-31.0	6.69	+0.26

TABLE IV-1(b)

Results of K-feldspar weathering experiment

Time	Initial pH	Na	K	Ca	SiO_2	Zeta Potential	pH	ΔpH
(hours)			(meq /l)			(mv)		
1	5	.035	.095	.009	.007	-46.5	5.25	-3.16
	7	.034	.067	.003	.009	-46.5	7.58	-0.51
	9	.017	.036	.001	.015	-46.5	9.68	+1.59
2	5	.022	.090	.005	.007	-48.8	8.50	-0.53
	7	.039	.086	.001	.010	-50.0	8.78	-0.25
	9	.017	.038	.000	.012	-49.3	9.95	+0.92
4	5	.020	.098	.005	.012	-47.5	8.60	-0.68
	7	.038	.080	.005	.008	-46.8	8.95	-0.33
	9	.014	.049	.002	.010	-45.8	9.85	+0.57
8	5	.032	.103	.004	.010	-50.8	7.03	-0.97
	7	.021	.074	.002	.007	-46.8	6.95	-1.05
	9	.014	.040	.001	.012	-44.3	8.91	+0.91
12	5	.022	.097	.003	.007	-47.3	8.24	-0.73
	7	.017	.072	.001	.005	-48.8	8.42	-0.55
	9	.011	.039	.000	.009	-46.5	9.02	+0.05
24	5	.023	.098	.003	.007	-52.5	7.08	-0.70
	7	.024	.068	.002	.006	-50.3	6.84	-0.94
	9	.011	.037	.001	.010	-51.0	8.67	+0.89
48	5	.025	.094	.003	.013	-51.0	7.73	-0.86
	7	.019	.067	.002	.007	-50.5	8.08	-0.51
	9	.013	.042	.001	.017	-48.8	8.78	+0.19
120	5	.024	.096	.003	.010	-49.5	7.68	-0.97
	7	.025	.069	.002	.010	-45.3	6.90	-1.75
	9	.016	.043	.001	.013	-50.0	9.75	+1.10
240	5	.023	.095	.004	.015	-48.0	7.81	-0.84
	7	.021	.069	.004	.016	-41.5	7.68	-0.97
	9	.016	.055	.001	.026	-46.5	8.15	+0.50
360	5	.025	.098	.004	.022	-45.8	7.67	+0.71
	7	.025	.071	.004	.021	-43.5	6.86	-0.10
	9	.034	.058	.002	.039	-43.5	7.18	+0.22
480	5	.017	.078	.005	.032	-48.5	6.36	-0.80
	7	.018	.071	.005	.035	-45.8	6.50	-0.66
	9	.014	.060	.002	.038	-44.3	6.69	-0.47

TABLE IV-2

Maximum, minimum, mean and standard deviation

Variable	Initial pH	Na-feldspar				K-feldspar			
		Max.	Min.	Mean	S.D.	Max.	Min.	Mean	S.D.
Na (meq/l)	5	.075	.035	.050	.010	.053	.017	.024	.005
	7	.063	.025	.037	.009	.039	.017	.026	.008
	9	.034	.023	.029	.003	.034	.011	.016	.006
K (meq/l)	5	.078	.029	.052	.013	.103	.090	.095	.006
	7	.060	.018	.030	.010	.086	.067	.072	.007
	9	.020	.009	.014	.004	.060	.036	.045	.008
Ca (meq/l)	5	.013	.002	.006	.004	.009	.002	.004	.002
	7	.012	.001	.003	.003	.005	.001	.003	.001
	9	.008	.000	.001	.002	.002	.000	.001	.001
SiO_2 (meq/l)	5	.011	.004	.007	.002	.032	.007	.013	.008
	7	.010	.005	.006	.001	.035	.005	.012	.009
	9	.012	.005	.007	.002	.039	.009	.018	.011
Zeta Potential (mv)	5	58.5	38.8	52.6	5.84	52.5	45.8	48.7	1.96
	7	55.5	30.5	47.2	7.43	50.5	41.5	46.9	2.73
	9	53.0	31.0	45.1	6.01	51.0	43.5	46.9	2.39
pH	5	7.24	6.67	7.07	0.16	8.60	5.25	7.45	0.94
	7	7.62	6.74	7.28	0.29	8.95	6.50	7.59	0.82
	9	8.21	6.69	7.68	0.47	9.95	6.69	8.78	1.03

Reproducibility of Duplicates

	Na	K	Ca	SiO_2	Zeta Potential	pH
	±	±	±	±	±	±
Na-fs	.003	.006	.018	.001	1.50	.6
K-fs	.003	.006	.018	.001	1.50	.6

TABLE IV-3

Summary of data trends

Variable	Figure	General Trend with Time
Na	1(a)	-rapid increase, then decrease to a constant value
	(b)	-as above
K	2(a)	-as above
	(b)	-rapid increase to a constant value
Ca	3(a)	-rapid increase, then a decrease to a constant value, followed by a slow increase
	3(b)	-as above
SiO_2	4(a)	-as above
	4(b)	-as above
Zeta Potential	5(a)	-slow increase, then a rapid decrease
	5(b)	-nearly constant value
pH	6(a)	-convergence to about pH 7
	6(b)	-as above, but convergence is less clear
pH	7(a)	-steady increase from below blank to above blank
	7(b)	-irregular convergence to a value slightly below the blank value
Na_2O/SiO_2	8(a)	-initial irregular pattern converges and decreases
	8(b)	-as above
K_2O/SiO_2	9(a)	-as above
	9(b)	-as above
CaO/SiO_2	10(a)	-complex pattern with a late rapid increase
	10(b)	-complex pattern with a late slow decrease

TABLE IV-4(a)

CORRELATION COEFFICIENTS

Na-fs

Conditions	Variables	Correlation Coefficient
All pH's, all times	T, SiO_2	.63
	T, ζ	-.61
All pH's, all times	T, Ca	.76
	T, SiO_2	.81
	T, ζ	-.76
	Na, K	.93
	Ca, SiO_2	.77
	SiO_2, ζ	-.72
pH 5, all times	T, Ca	.89
	T, SiO_2	.84
	T, ζ	-.92
	Na, K	.85
	Ca, SiO_2	.98
	Ca, ζ	-.87
	SiO_2, ζ	-.85
pH 7, all times	T, Ca	.94
	T, SiO_2	.81
	T, ζ	-.91
	Na, K	.95
	Ca, SiO_2	.90
	Ca, ζ	-.96
	SiO_2, ζ	-.87

K-fs

Conditions	Variables	Correlation Coefficient
All pH's, all times	T, SiO_2	.63
	T, ζ	-.61
All pH's, all times	T, SiO_2	.90
	K, Ca	.69
pH 5, all times	T, K	-.60
	T, SiO_2	.94
	K, SiO_2	-.66
pH 7, all times	T, Ca	.64
	T, SiO_2	.94
	T, ζ	-.61
	Na, K	.64
	Ca, SiO_2	.65
	Ca, ζ	-.65
pH 9, all times	T, K	.91
	T, Ca	.68
	T, SiO_2	.96
	Na, SiO_2	.63
	K, Ca	.80
	K, SiO_2	.88
	K, ζ	-.61
	Ca, SiO_2	.76

TABLE IV-4(b)

Conditions	Na-fs Variables	Correlation Coefficient
pH 9, all times	T, Ca	.93
	T, SiO_2	.82
	T, ζ	-.73
	Ca, SiO_2	.88
	Ca, ζ	-.82
	SiO_2, ζ	-.89
	K,	-.64
pH 5, less than 24 hours	T, Na	-.79
	T, K	-.95
	T, Ca	-.76
	T, SiO_2	-.82
	Na, K	.89
	Na, Ca	.91
	Na, SiO_2	.85
	K, Ca	.86
	K, SiO_2	.94
	Ca, SiO_2	.94
pH 7, less than 24 hours (continued)	K, Ca	.96
	K, SiO_2	.87
	K, ζ	-.71
	Ca, SiO_2	.86
	Ca, ζ	-.84
	SiO_2, ζ	-.80

Conditions	K-fs Variables	Correlation Coefficient
pH 5, less than 24 hours	T, Ca	-.68
	T, ζ	.74
pH 7, less than 24 hours	T, Na	-.63
	T, SiO_2	-.81
	Na, SiO_2	.85
	Ca, ζ	-.76
pH 9, less than 24 hours	T, Na	-.86
	Na, SiO_2	.78
	K, Ca	.74
pH 5, greater than 24 hours	T, Na	-.74
	T, K	-.61
	T, Ca	.84
	T, SiO_2	.94
	T, ζ	-.69
	Na, K	.96
	Na, Ca	-.61
	Na, SiO_2	-.79
	K, Ca	-.66
	K, SiO_2	-.78
	Ca, SiO_2	.93

TABLE IV-4(c)

	Na-fs	
Conditions	Variables	Correlation Coefficient
pH 9, less than 24 hours	T, Na	-.77
	T, Ca	.81
	T, SiO_2	-.68
	Na, Ca	-.79
	Na, SiO_2	.75
	Na, ζ	-.62
	K, ζ	-.64
	Ca, SiO_2	-.88
	SiO_2,	-.77
pH 5, greater than 24 hours	T, Ca	.99
	T, SiO_2	.99
	T, ζ	-.98
	Ca, SiO_2	.99
	Ca, ζ	-.97
	SiO_2, ζ	-.97
pH 7, greater than 24 hours	T, Ca	.98
	T, SiO_2	.91
	T, ζ	-.99
	Na, K	-.60
	K, SiO_2	.60
	Ca, SiO_2	.95
	Ca, ζ	-.96
	SiO_2, ζ	-.86
pH 9, greater than 24 hours	T, Na	.74
	T, K	.90
	T, Ca	.94
	T, SiO	.94
	T, ζ	-.99
	Na, ζ	-.63

	K-fs	
Conditions	Variables	Correlation Coefficient
pH 7, greater than 24 hours	T, K	.86
	T, Ca	.88
	T, SiO_2	.97
	K, Ca	.63
	K, SiO_2	.76
	K, ζ	-.74
	Ca, SiO_2	.86
pH 9, greater than 24 hours	T, K	.96
	T, Ca	.75
	T, SiO_2	.93
	T, ζ	-.90
	Na, Ca	.72
	K, Ca	.76
	K, SiO_2	.95
	K, ζ	-.94
	Ca, SiO_2	.92
	Ca, ζ	-.93
	SiO_2, ζ	-.99

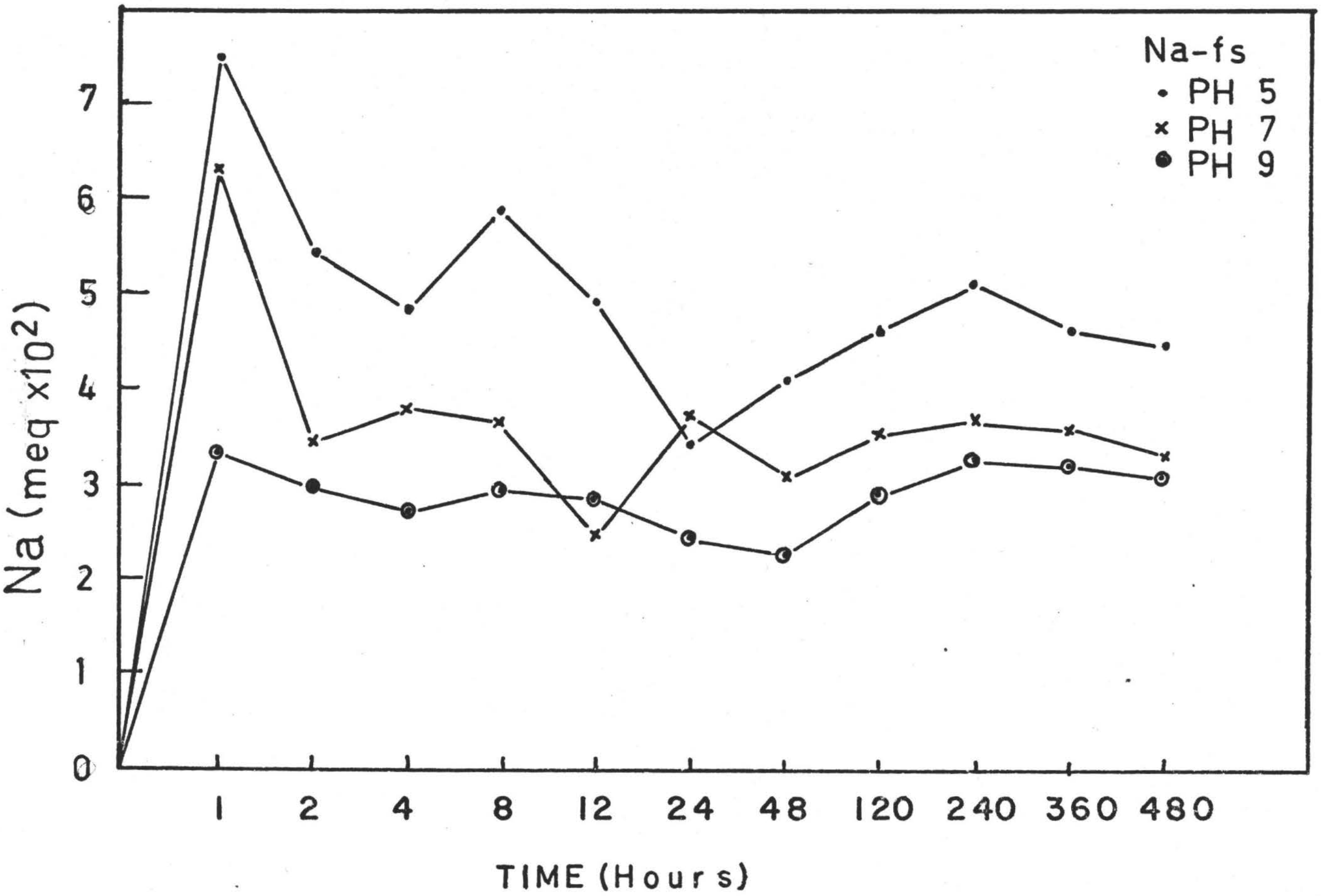
TABLE IV-4(d)

Na-fs			K-fs		
Conditions	Variables	Correlation Coefficient	Conditions	Variables	Correlation Coefficient
pH 9, greater than 24 hours (cont'd.)	K, Ca	.97			
	K, SiO_2	.99			
	K, ζ	-.89			
	Ca, SiO_2	.99			
	Ca, ζ	-.96			
	SiO_2, ζ	-.95			

Figure IV-1

Sodium Concentration vs. Time: (a) Na-fs
(b) K-fs

(a)


Na-fs
• PH 5
× PH 7
● PH 9
Na (meq x10^2)
0
1
2
3
4
5
6
7
1
2
4
8
12
24
48
120
240
360
480
TIME (Hours)

(b)

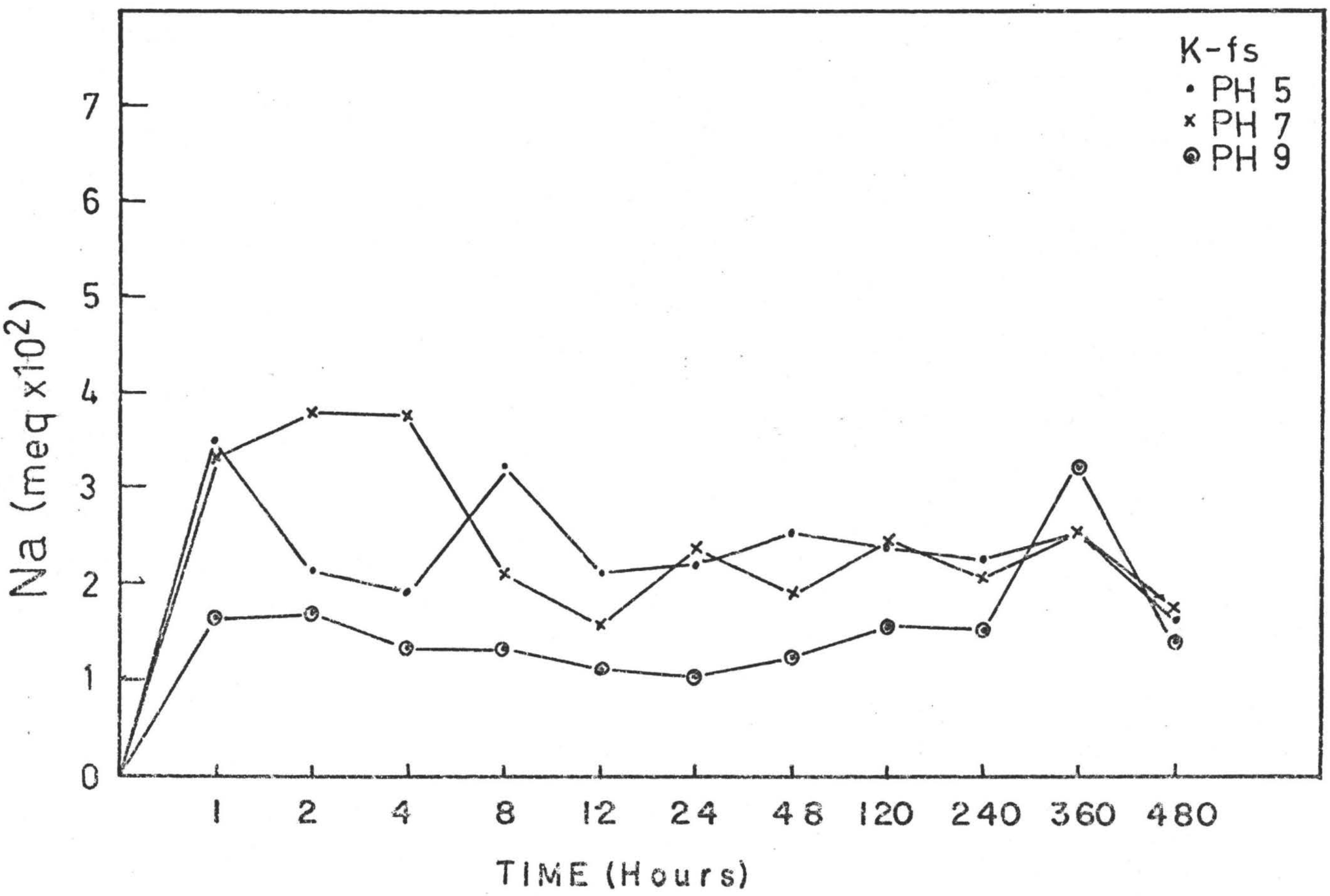
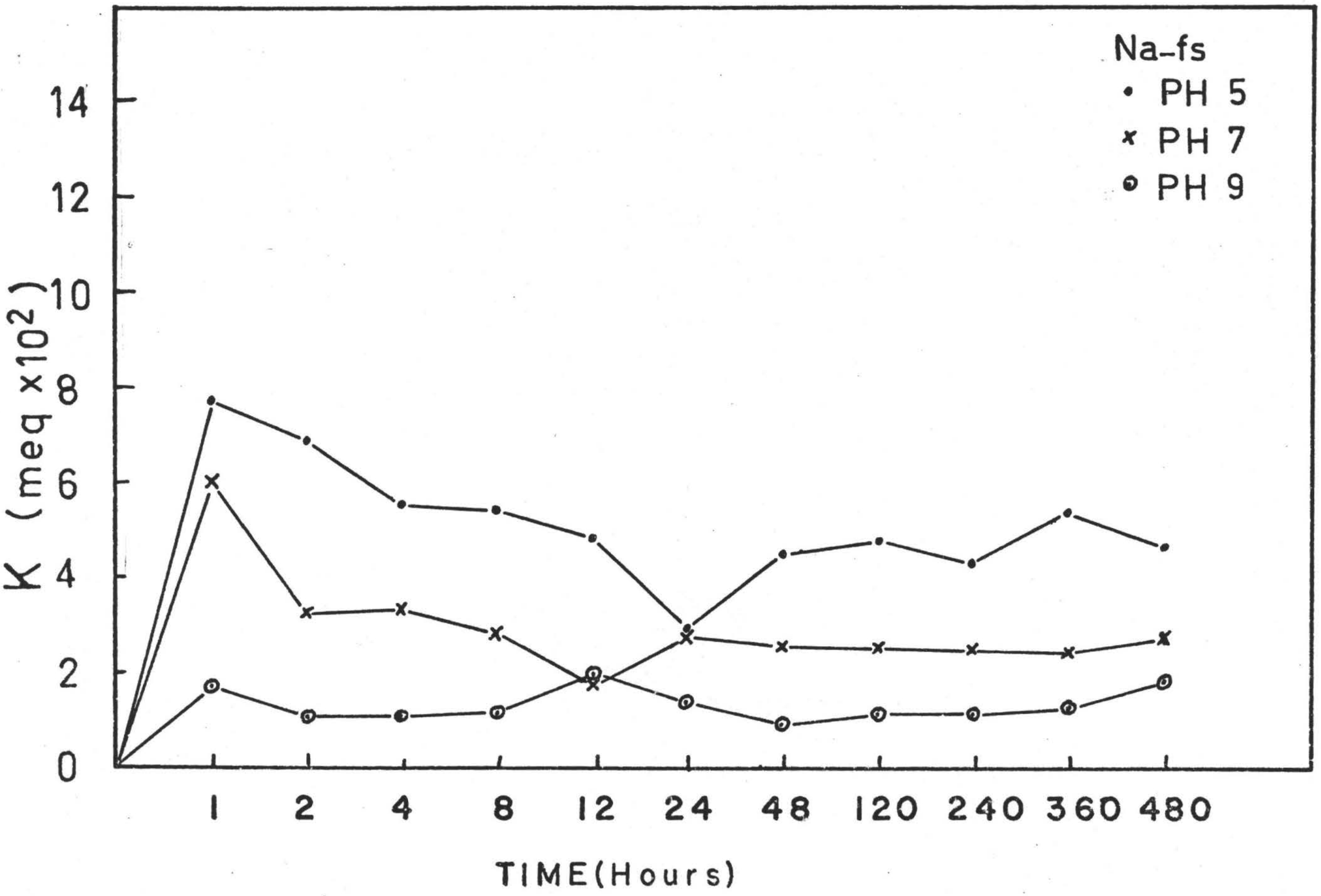

K-fs
• PH 5
× PH 7
◎ PH 9
Na (meq x10^2)
0
1
2
3
4
5
6
7
1
2
4
8
12
24
48
120
240
360
480
TIME (Hours)

Figure IV-2

Potassium Concentration vs. Time: (a) Na-fs

(b) K-fs

(a)


Na-fs
• PH 5
× PH 7
⊙ PH 9
K (meq x10^2)
0
2
4
6
8
10
12
14
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

(b)

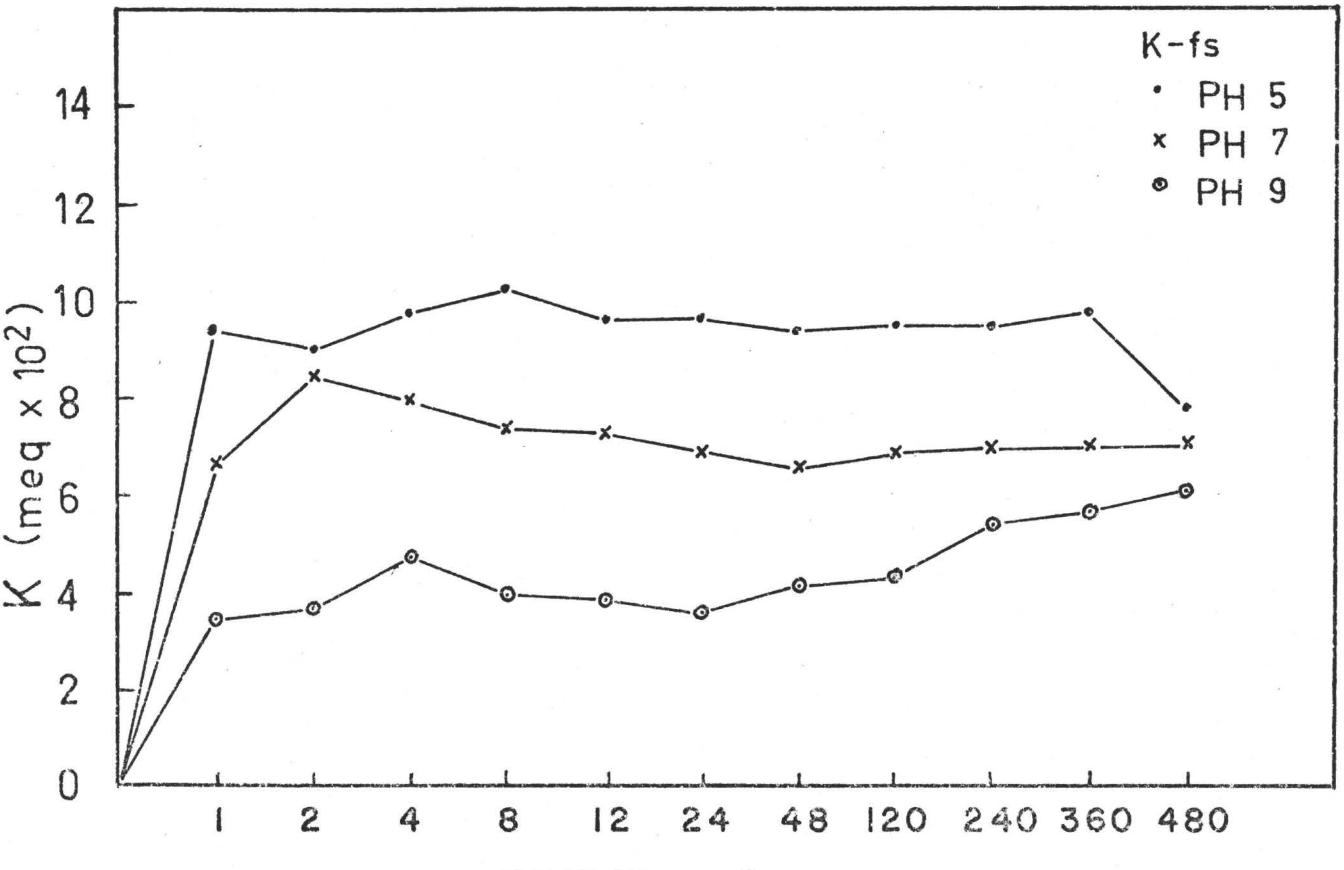
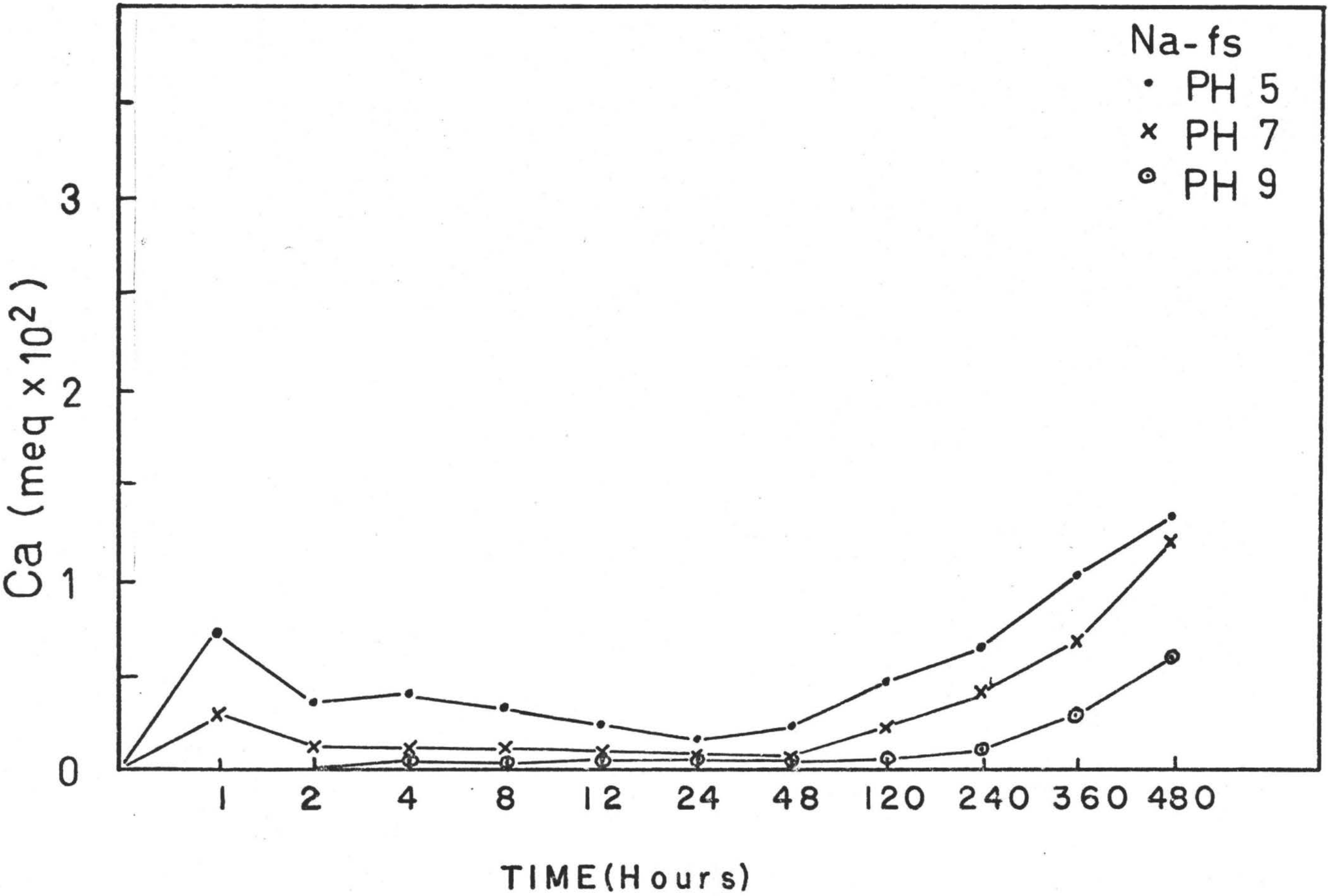

K-fs
• PH 5
× PH 7
⊙ PH 9
K (meq x 10^2)
0
2
4
6
8
10
12
14
1
2
4
8
12
24
48
120
240
360
480
TIME (Hours)

Figure IV-3

Calcium Concentration vs. Time: (a) Na-fs
(b) K-fs

(a)


Na-fs
• PH 5
× PH 7
⊙ PH 9
Ca (meq x 10^2)
0
1
2
3
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

(b)

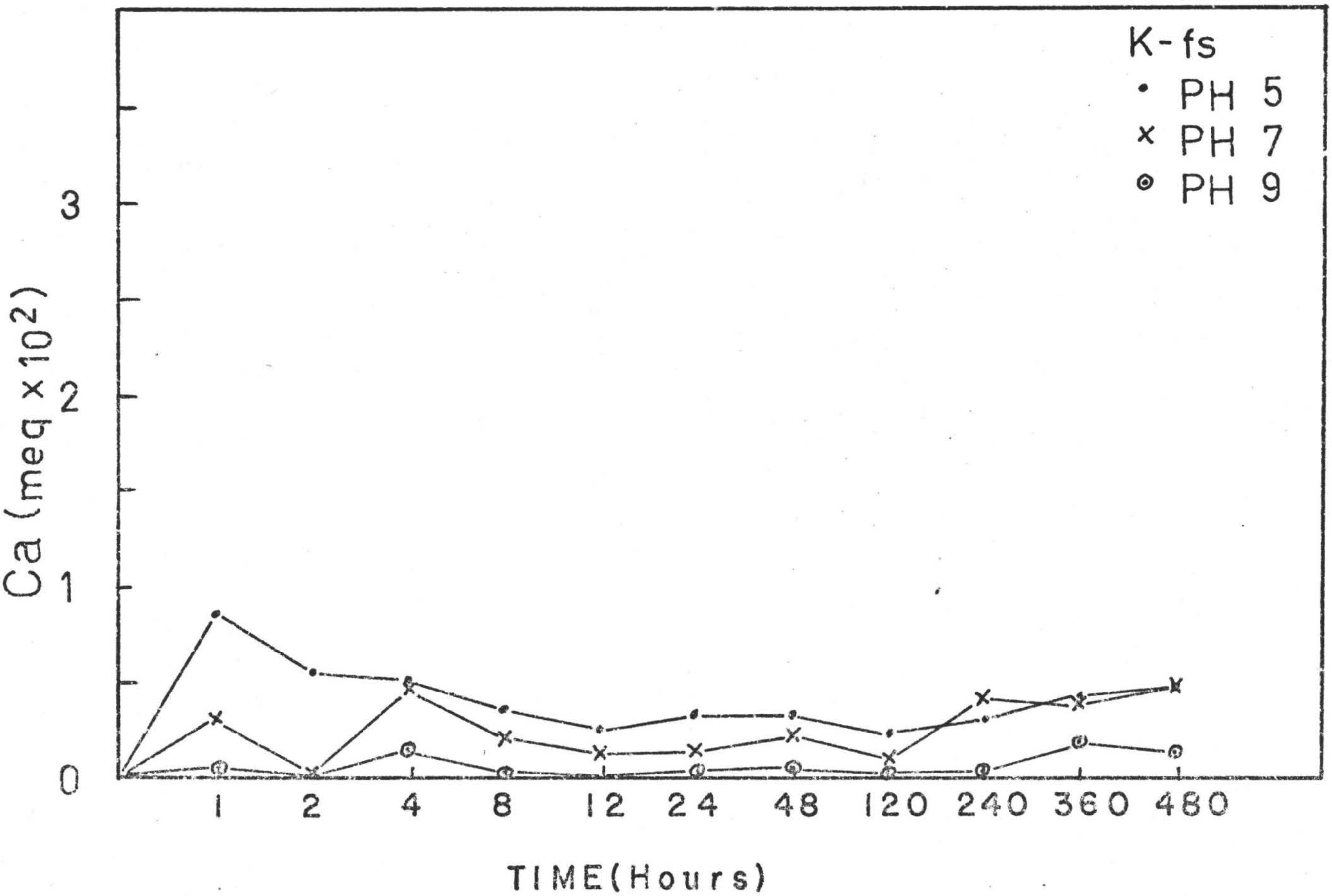

K-fs
• PH 5
× PH 7
⊙ PH 9
Ca (meq x 10^2)
0
1
2
3
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

Figure IV-4

Silica Concentration vs. Time: (a) Na-fs

(b) K-fs

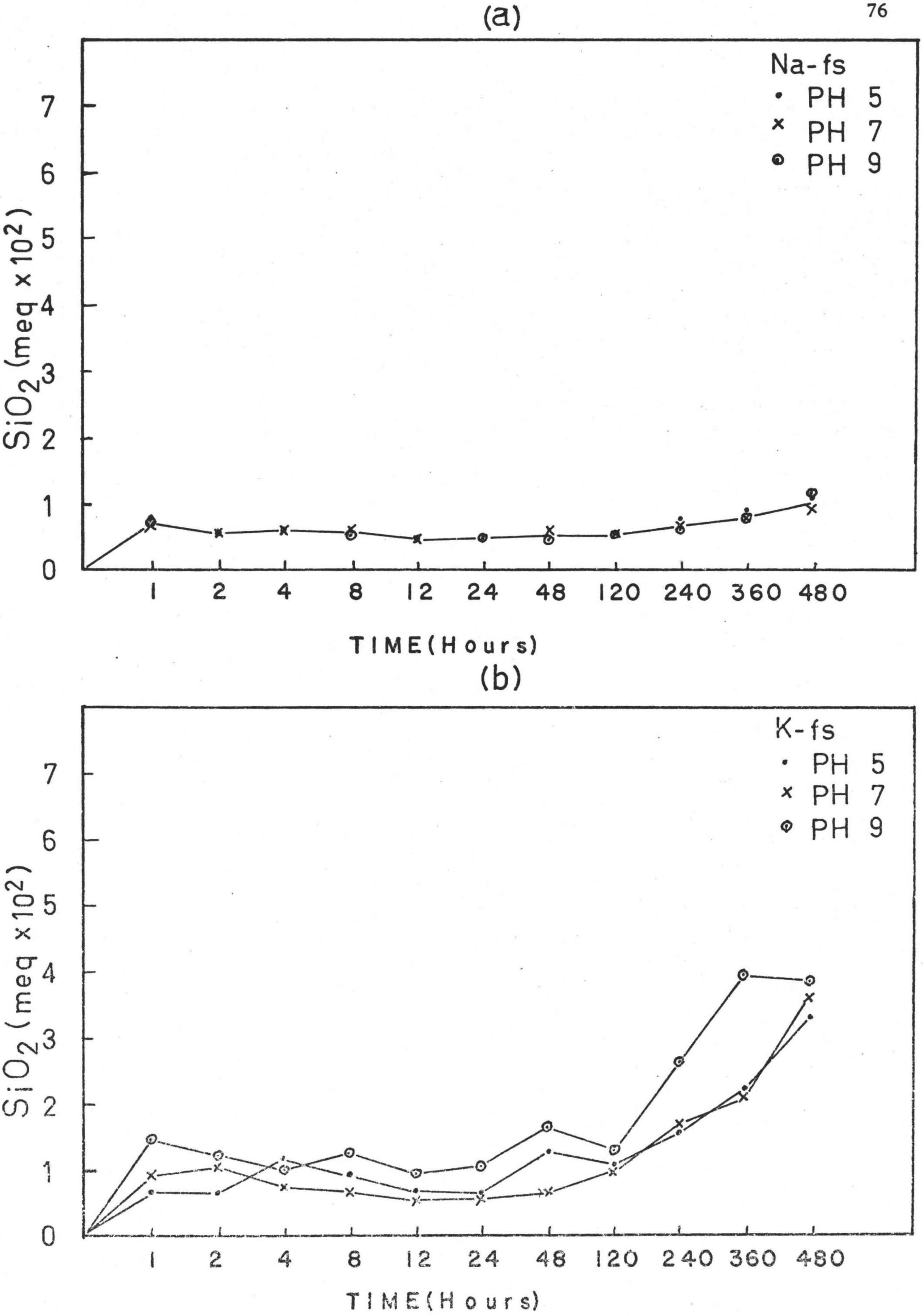
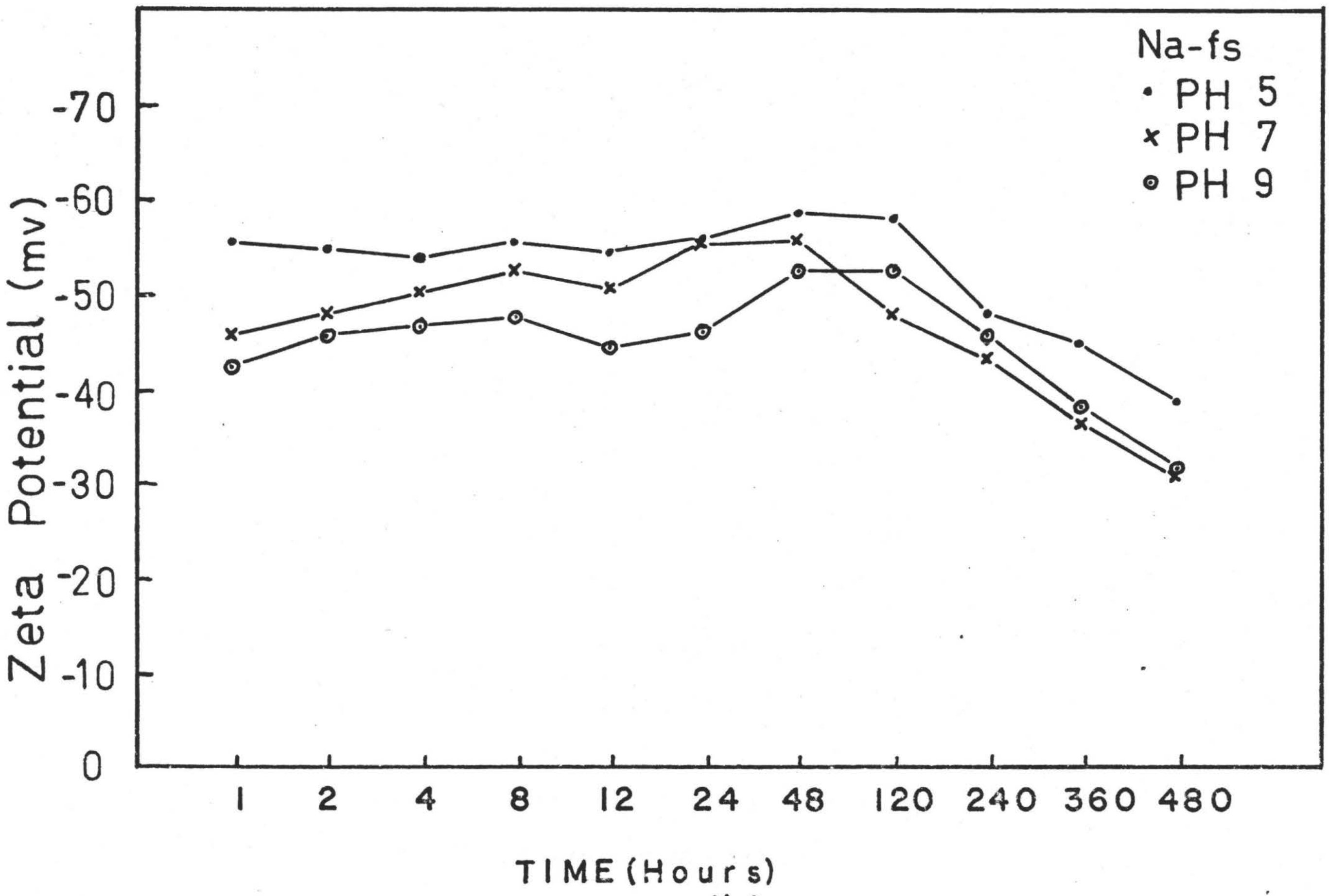

(a)
Na- fs
• PH 5
× PH 7
⊙ PH 9
SiO_2 (meq x 10^2)
0
1
2
3
4
5
6
7
1
2
4
8
12
24
48
120
240
360
480
TIME (Hours)
(b)
K- fs
• PH 5
× PH 7
⊙ PH 9
SiO_2 (meq x 10^2)
0
1
2
3
4
5
6
7
1
2
4
8
12
24
48
120
240
360
480
TIME (Hours)

Figure IV-5

Zeta Potential vs. Time: (a) Na-fs

(b) K-fs

(a)


Na-fs
• PH 5
× PH 7
⊙ PH 9
Zeta Potential (mv)
-70
-60
-50
-40
-30
-20
-10
0
1
2
4
8
12
24
48
120
240
360
480
TIME (Hours)

(b)

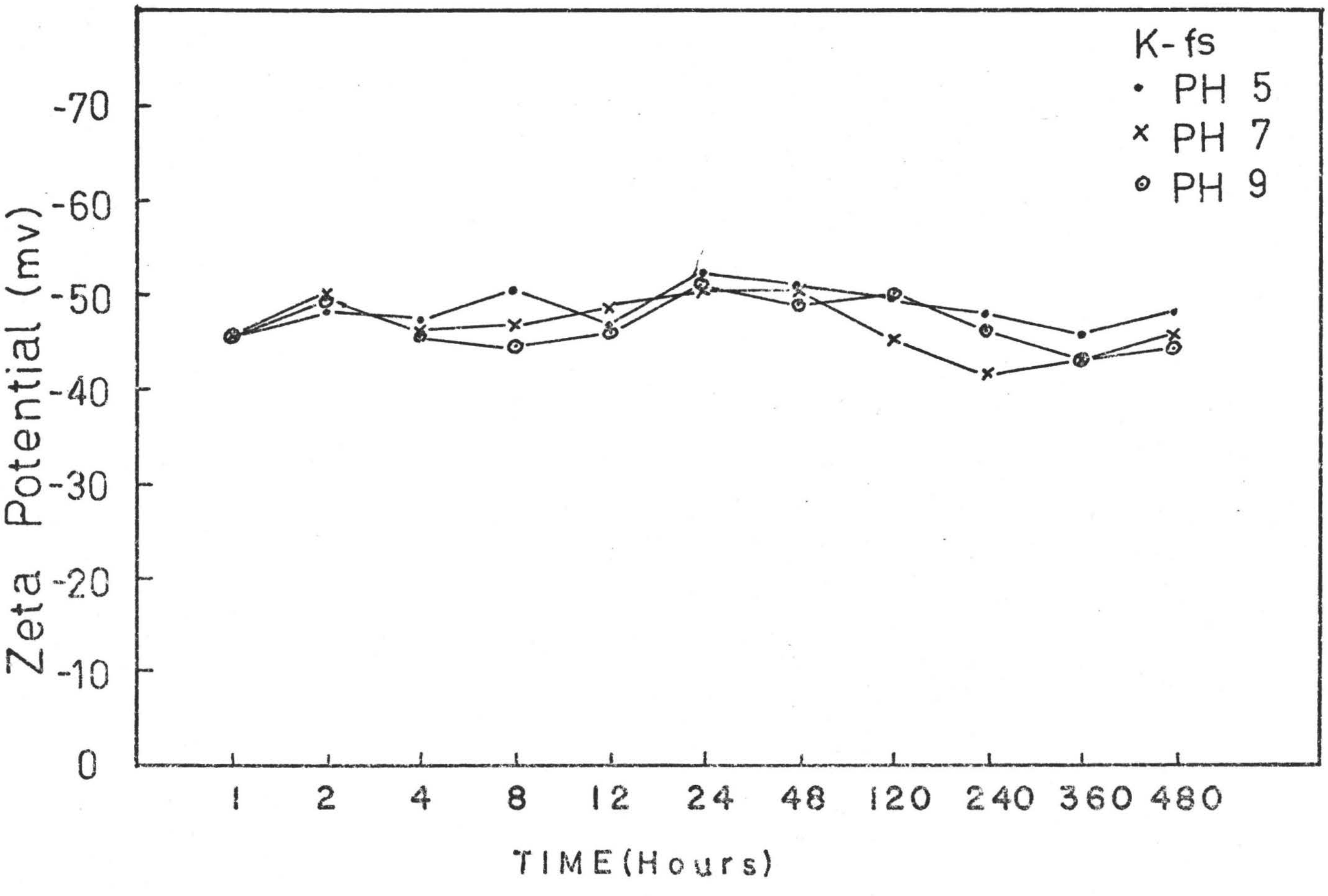
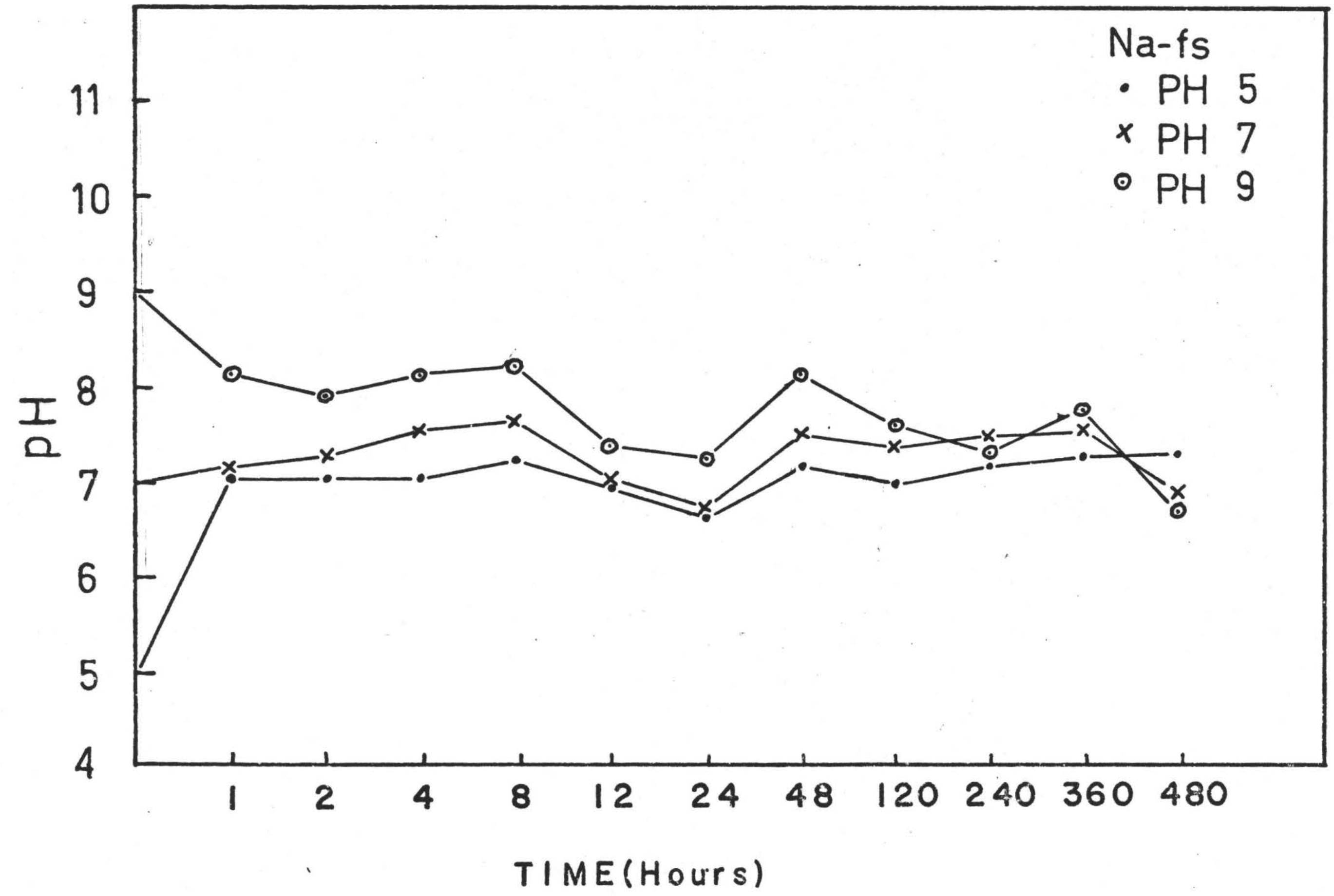

K- fs
• PH 5
× PH 7
⊙ PH 9
Zeta Potential (mv)
-70
-60
-50
-40
-30
-20
-10
0
1
2
4
8
12
24
48
120
240
360
480
TIME (Hours)

Figure IV-6

pH vs. Time: (a) Na-fs

(b) K-fs

(a)


Na-fs
• PH 5
× PH 7
⊙ PH 9
pH
4
5
6
7
8
9
10
11
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

(b)

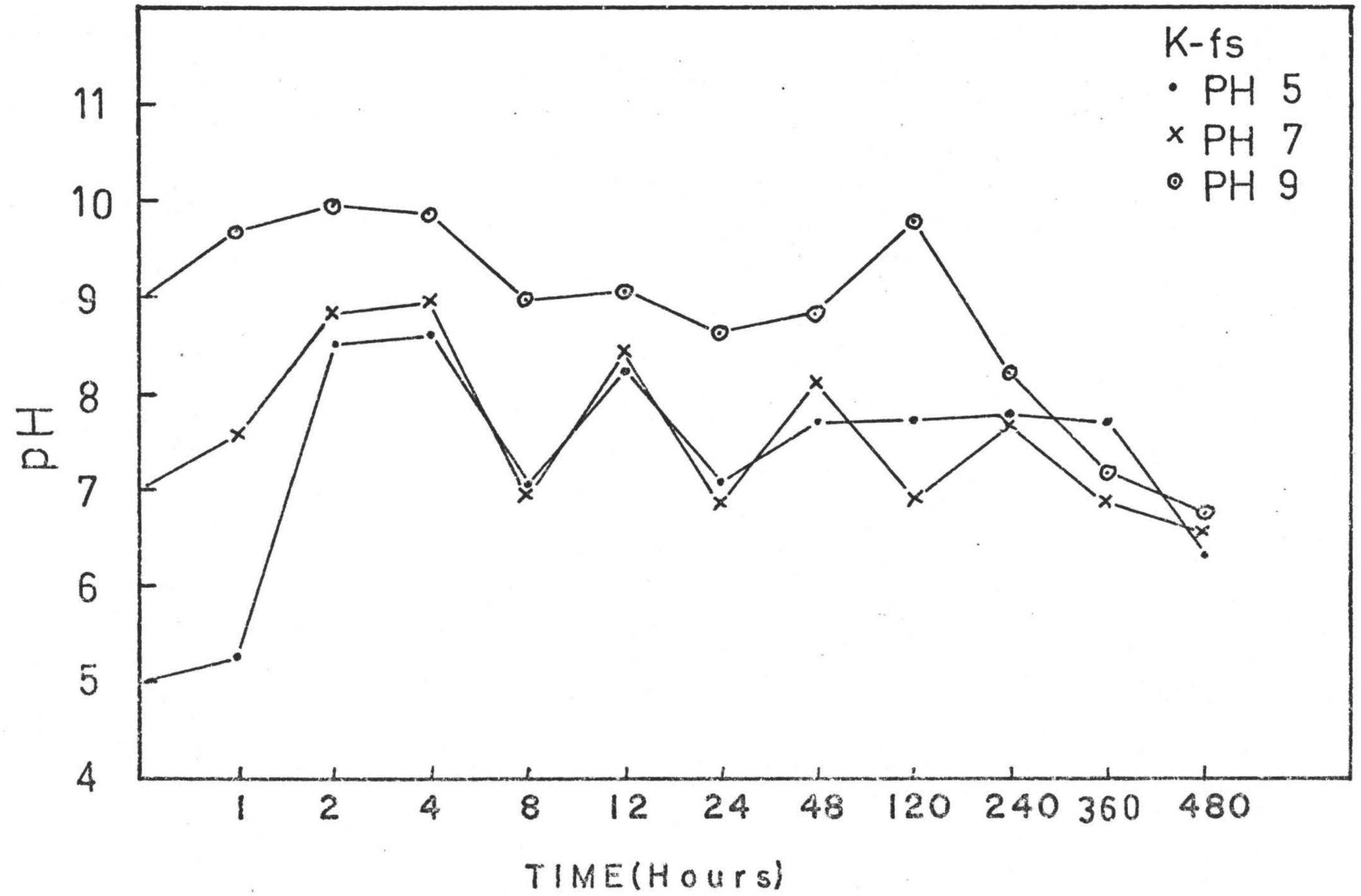
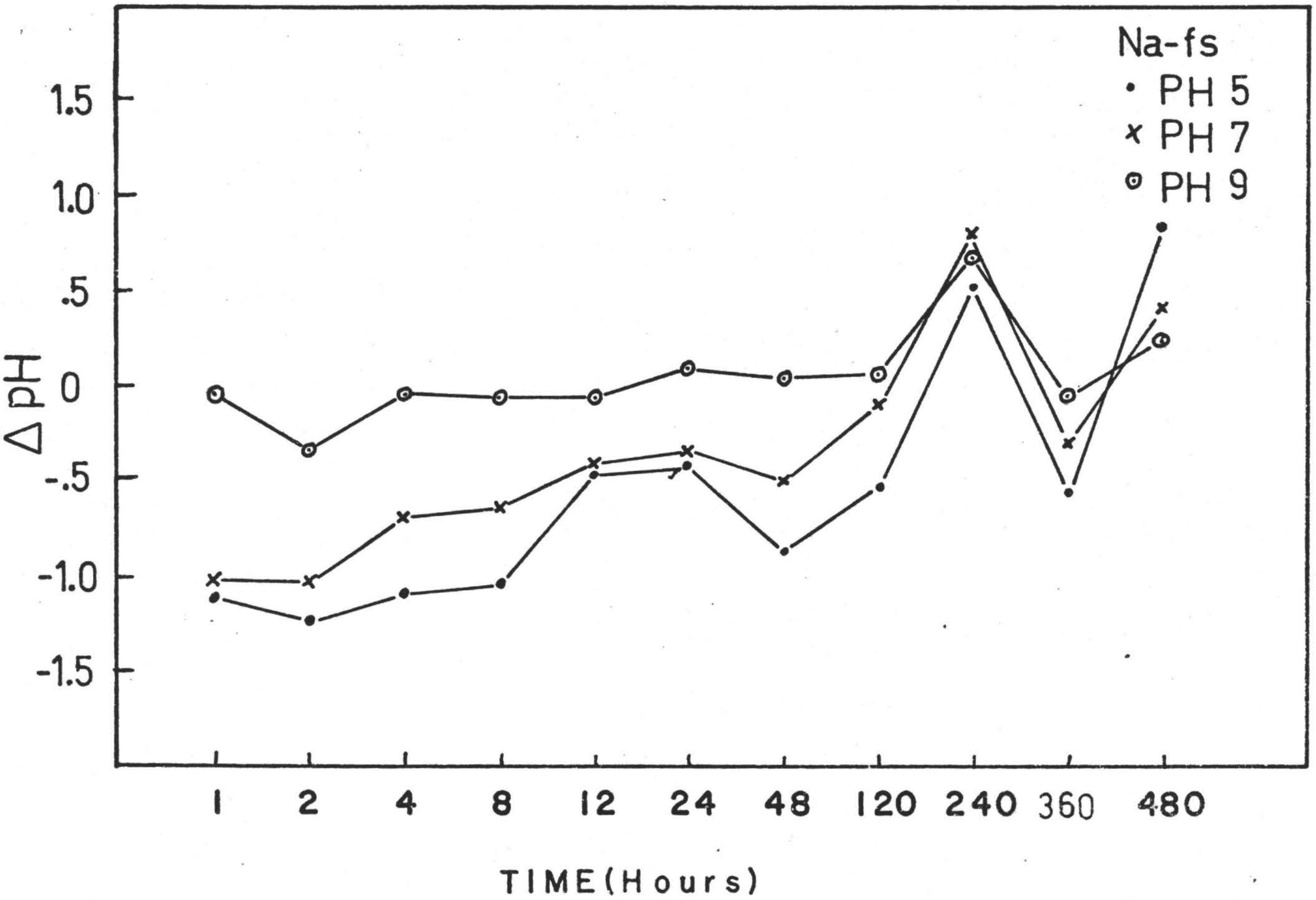

K-fs
• PH 5
× PH 7
⊙ PH 9
pH
4
5
6
7
8
9
10
11
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

Figure IV-7

pH (pH measured - pH blank): (a) Na-fs

(b) K-fs

(a)


Na-fs
• PH 5
× PH 7
⊙ PH 9
1.5
1.0
.5
0
-.5
-1.0
-1.5
ΔpH
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

(b)

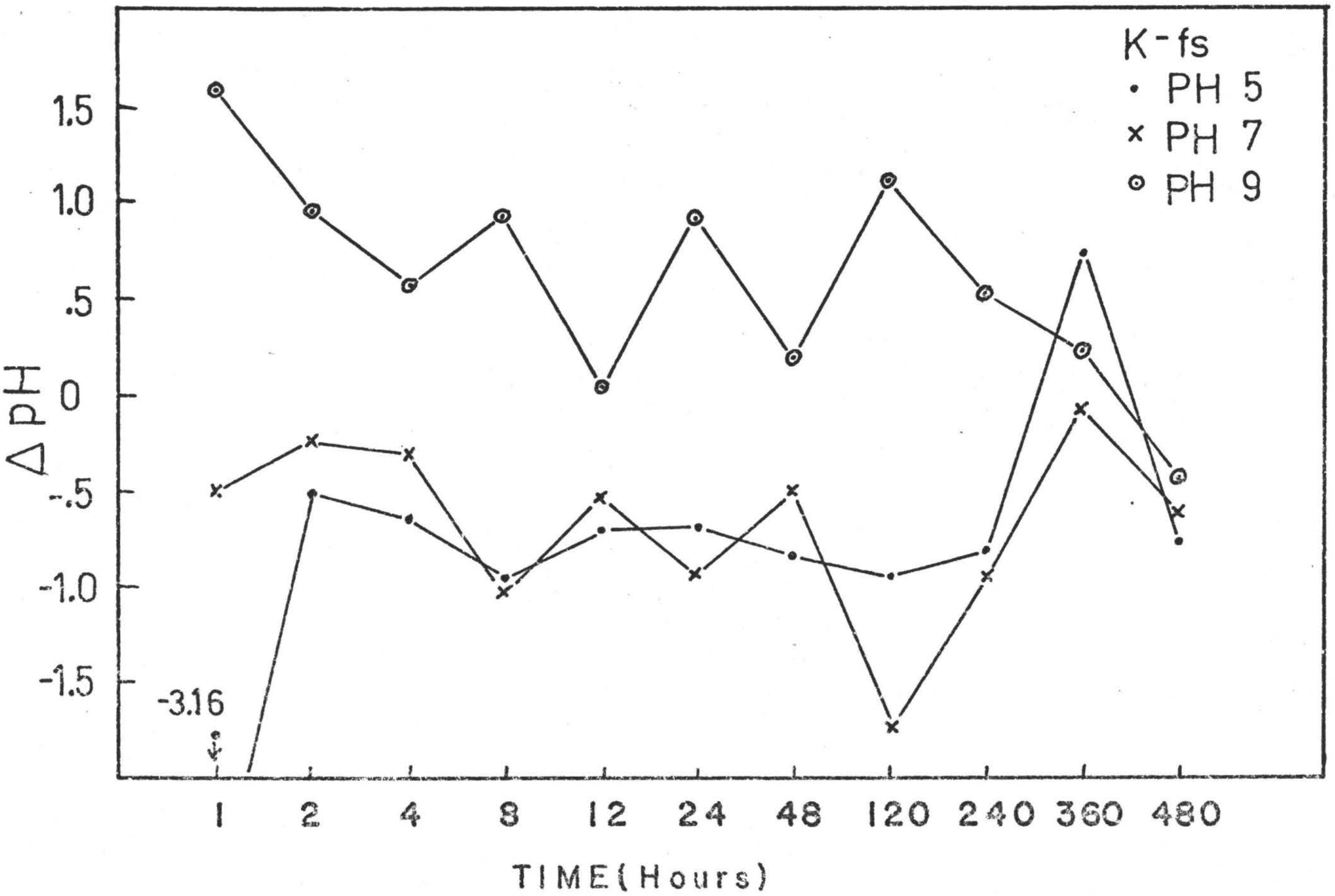

K-fs
• PH 5
× PH 7
⊙ PH 9
1.5
1.0
.5
0
-.5
-1.0
-1.5
-3.16
ΔpH
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

Figure IV-8(a)

Na_2O/SiO_2 in solution vs. Time for Na-fs.

(a)

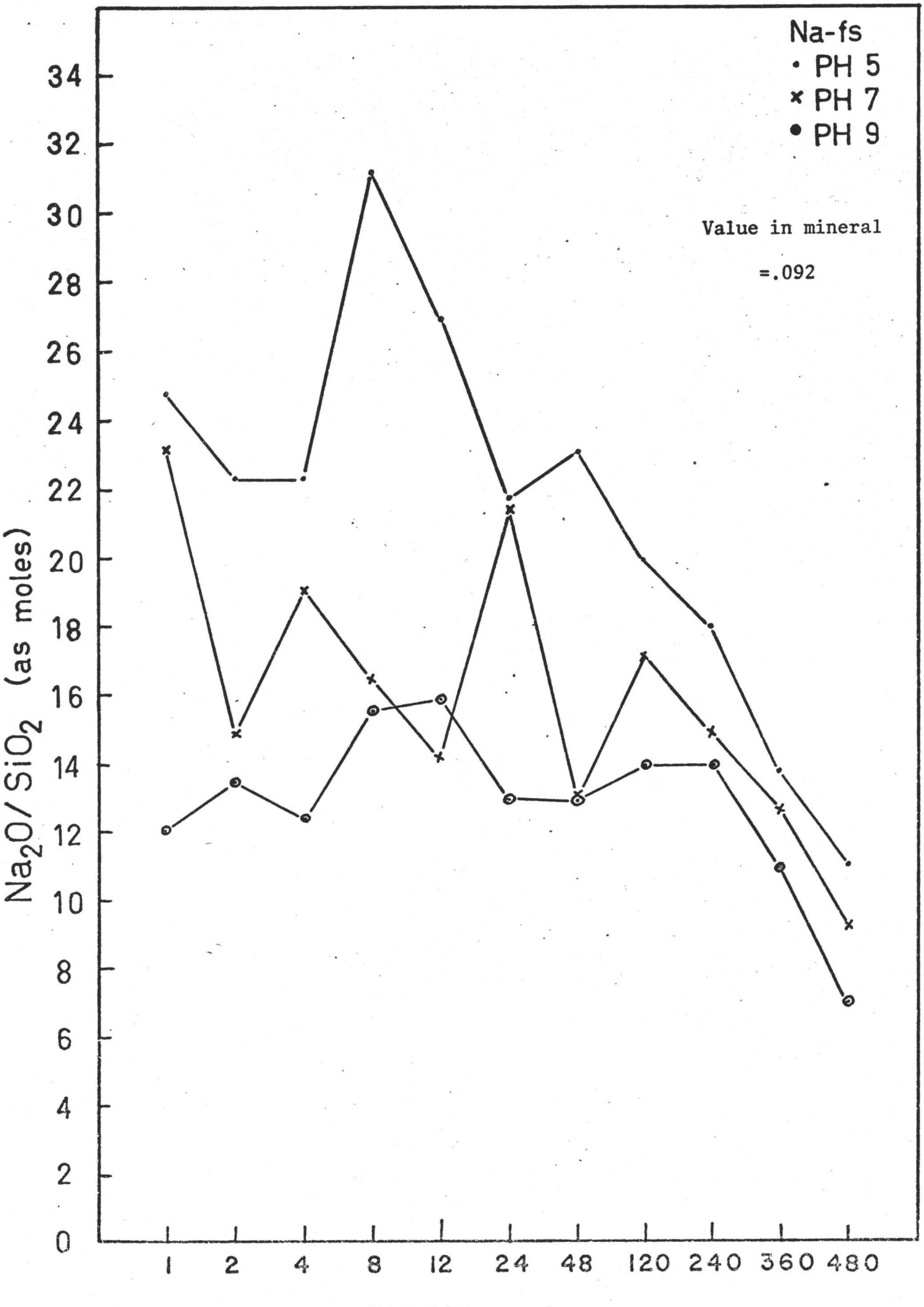

Na-fs
• PH 5
× PH 7
● PH 9
Value in mineral
=.092
Na_2O/SiO_2 (as moles)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

Figure IV-8(b)

Na_2O/SiO_2 in solution vs. Time for K-fs.

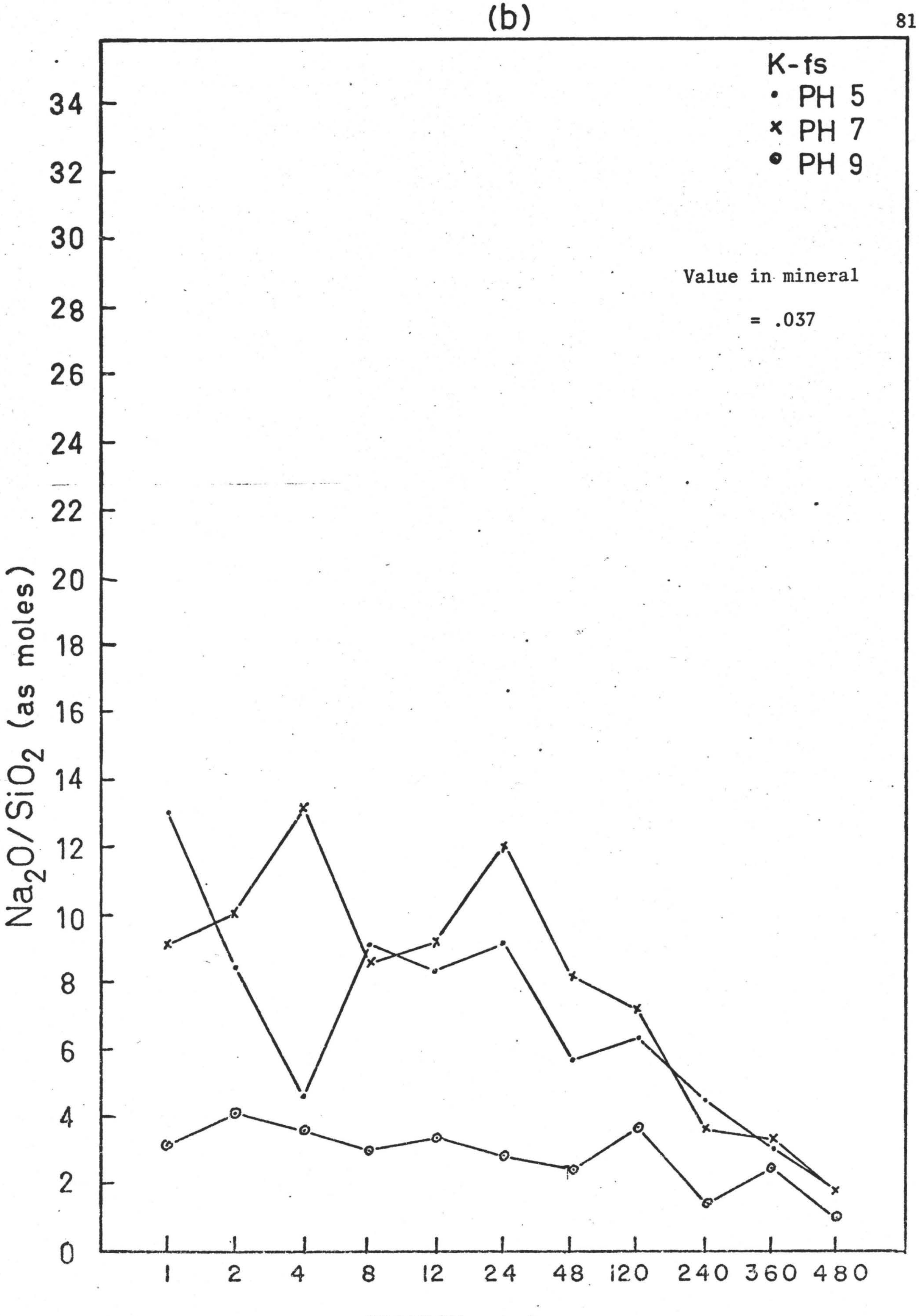

(b)
K-fs
• PH 5
× PH 7
⊙ PH 9
Value in mineral
= .037
Na$_2$O/SiO$_2$ (as moles)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

Figure IV-9(a)

K_2O/SiO_2 in solution vs. Time for Na-fs.

(a)

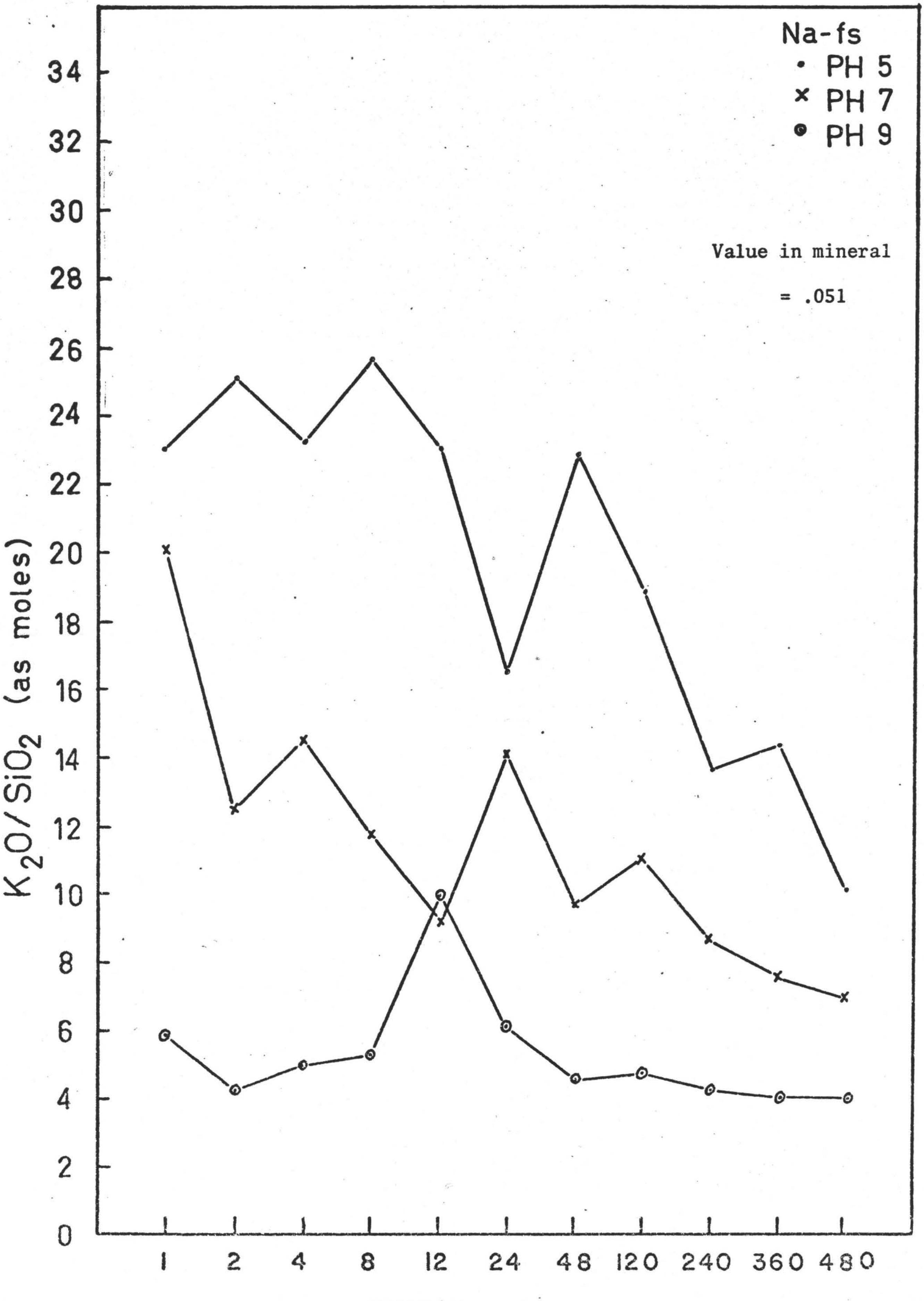

Na-fs
• PH 5
× PH 7
⊙ PH 9
Value in mineral
= .051
K_2O/SiO_2 (as moles)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

Figure IV-9(b)

K_2O/SiO_2 in solution vs. Time for K-fs.

(b)

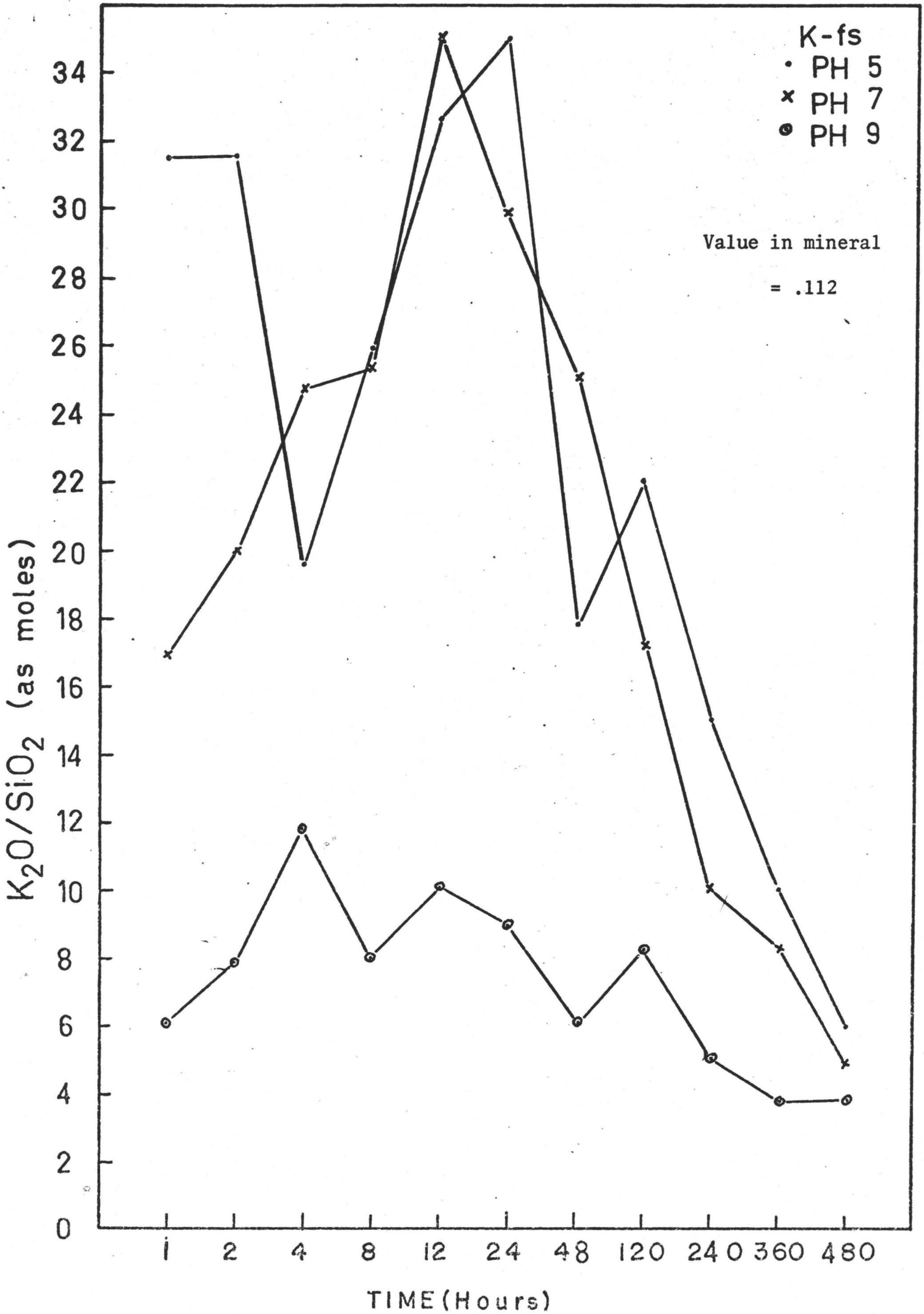

K-fs
• PH 5
× PH 7
◎ PH 9
Value in mineral
= .112
K_2O/SiO_2 (as moles)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
1
2
4
8
12
24
48
120
240
360
480
TIME (Hours)

Figure IV-10(a)

CaO/SiO_2 in solution vs. Time for Na-fs.

(a)


Na-fs
• PH 5
× PH 7
● PH 9
Value in mineral
=.035
CaO/SiO$_2$ (as moles)
0
1
2
3
4
1
2
4
8
12
24
48
120
240
360
480
TIME(Hours)

Figure IV-10(b)

CaO/SiO_2 in solution vs. Time for K-fs.

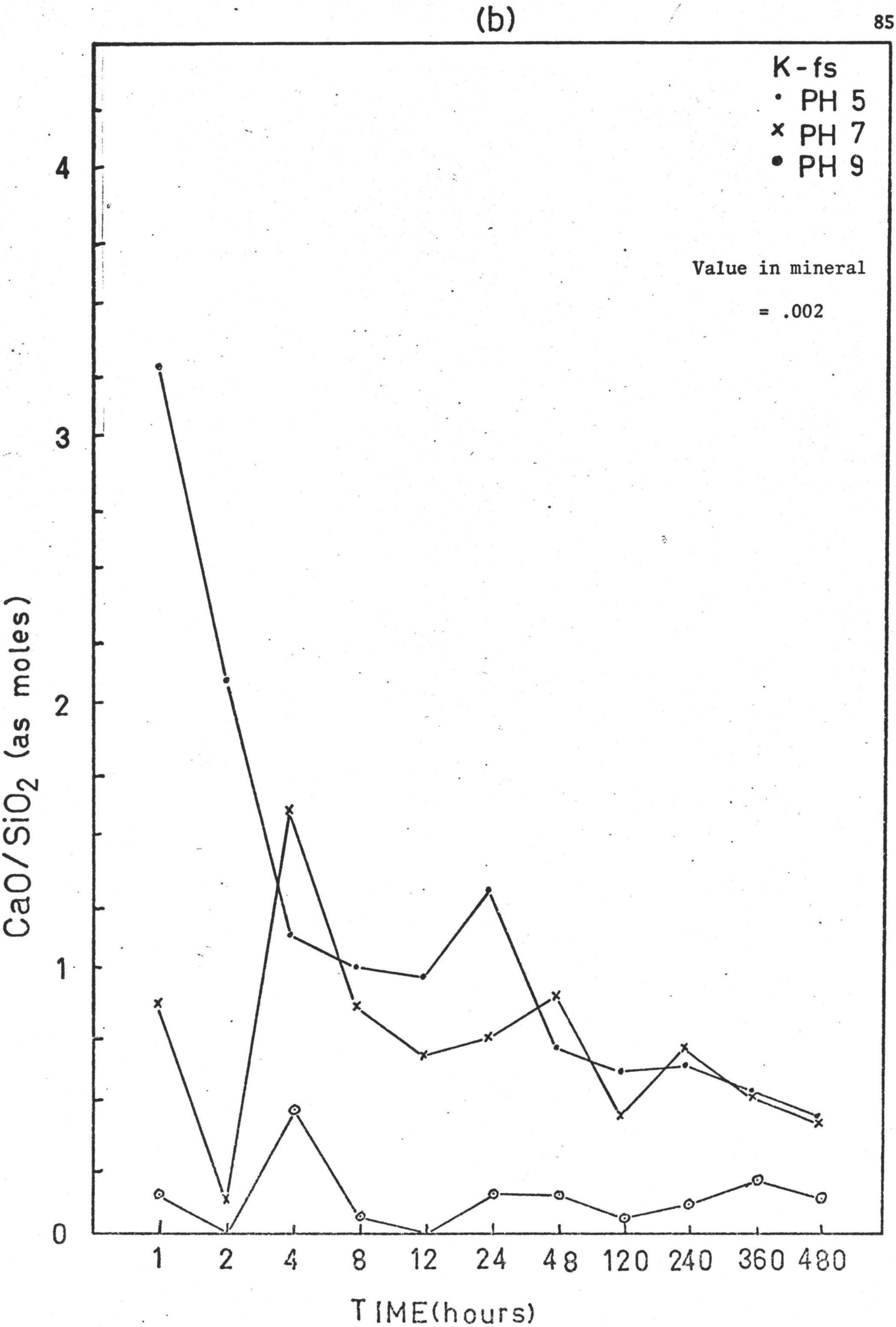

(b)
K-fs
• PH 5
× PH 7
● PH 9
Value in mineral
= .002
CaO/SiO$_2$ (as moles)
0
1
2
3
4
1
2
4
8
12
24
48
120
240
360
480
TIME(hours)

Figure IV-11(a)

Stability Field Diagram for Na-fs.

(a)

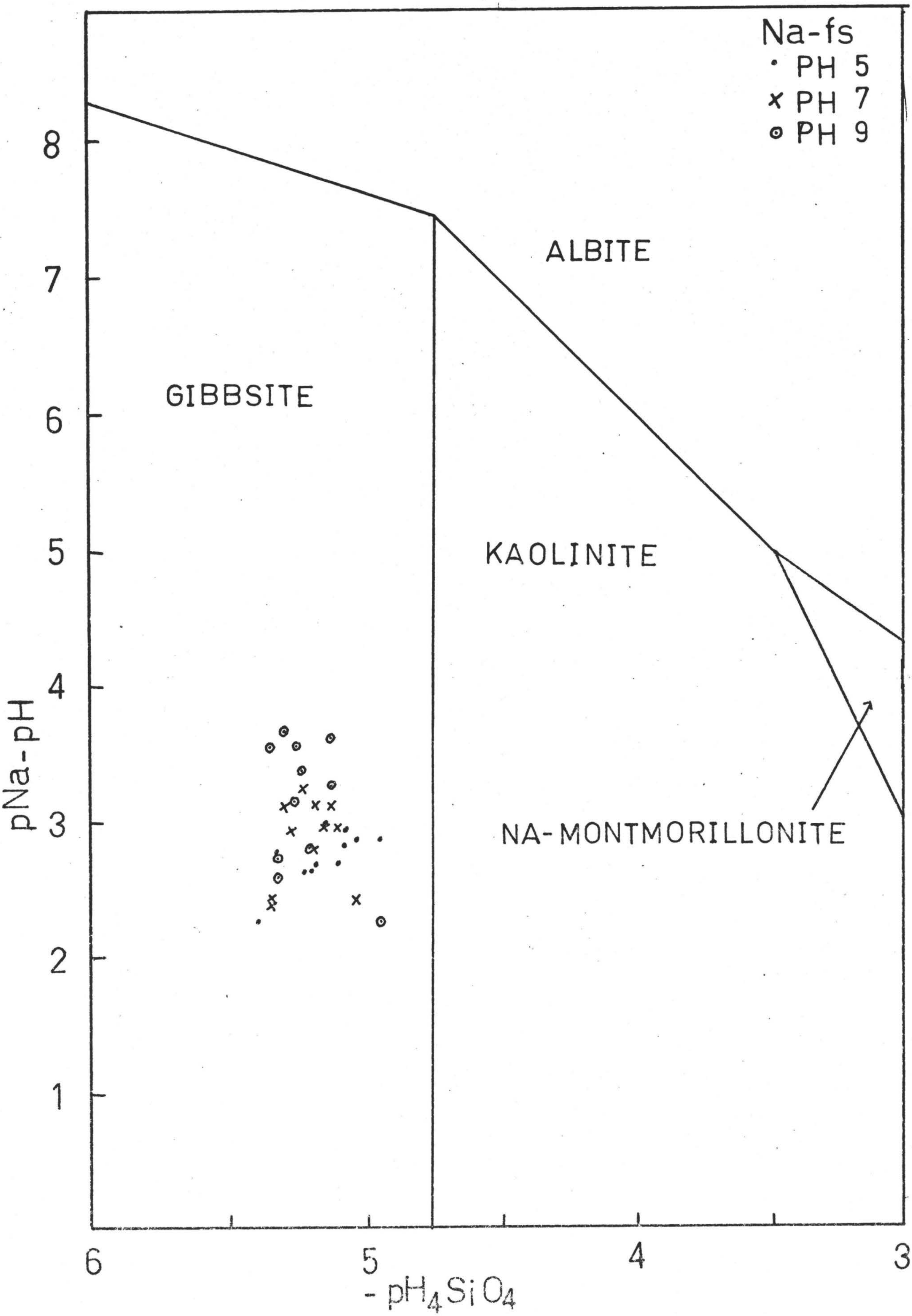

Na-fs
• PH 5
× PH 7
⊙ PH 9
ALBITE
GIBBSITE
KAOLINITE
NA-MONTMORILLONITE
pNa-pH
8
7
6
5
4
3
2
1
6
5
4
3
- pH_4SiO_4

Figure IV-11(b)

Stability Field Diagram for K-fs.

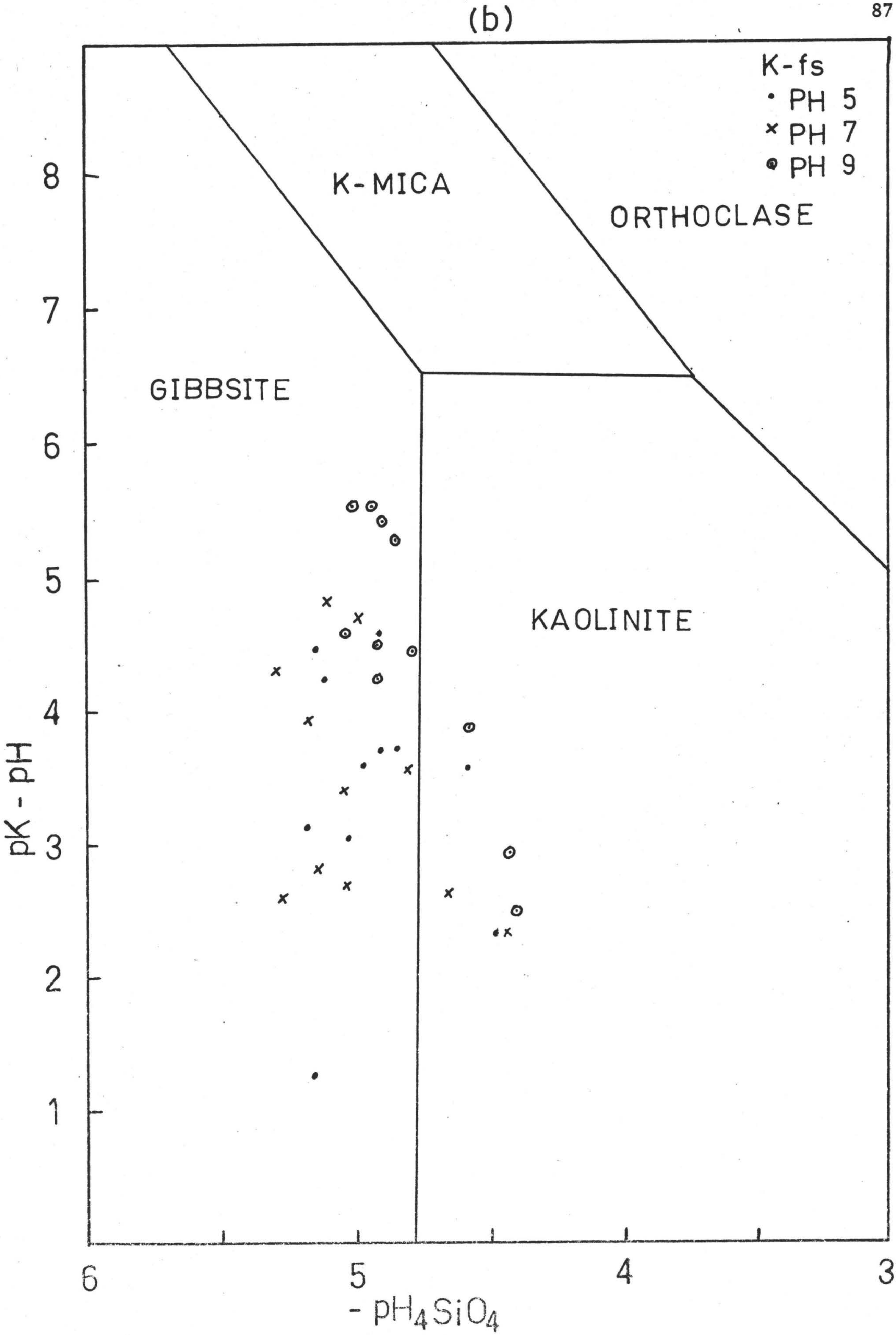
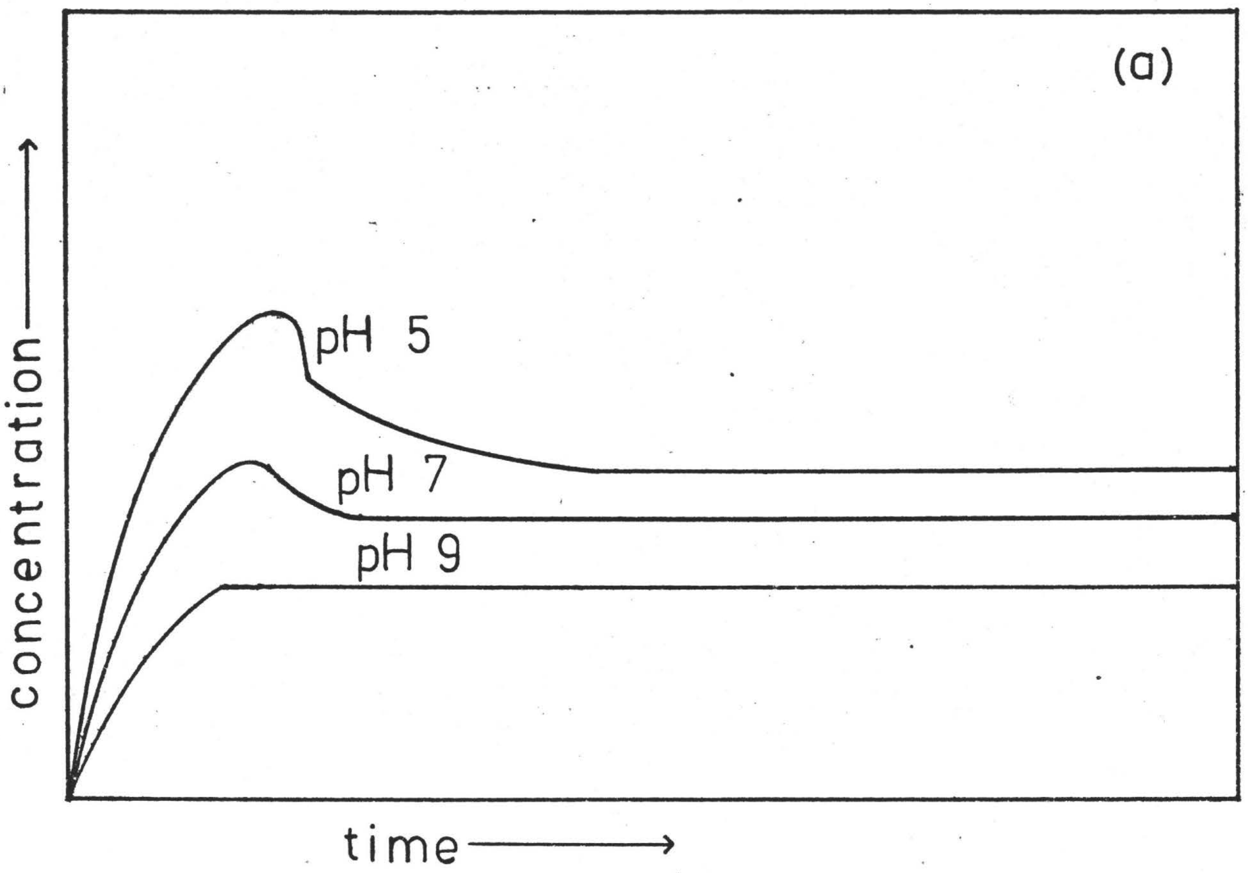

(b)
K-fs
• PH 5
× PH 7
⊚ PH 9
K-MICA
ORTHOCLASE
GIBBSITE
KAOLINITE
pK - pH
8
7
6
5
4
3
2
1
6
5
4
3
- pH4SiO4

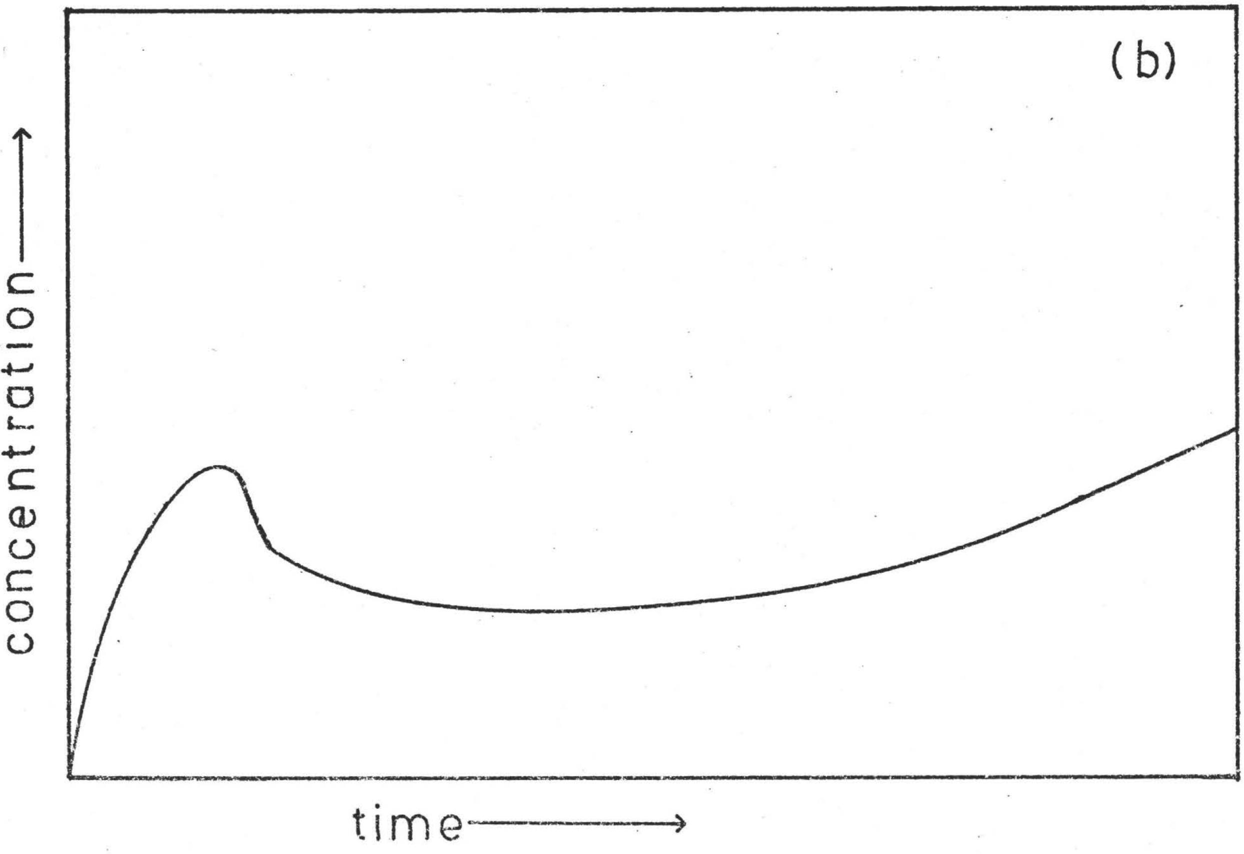
Figure IV-12(a)

Generalized Data Curves as a Function of Time Showing pH Effect.

Figure IV-12(b)

Generalized Data Curve as a Function of Time Showing the Long-Term Behavior of Ca and SiO_2.


(a)
pH 5
pH 7
pH 9
concentration ⟶
time ⟶


(b)
concentration ⟶
time ⟶

CHAPTER V

DISCUSSION

CHAPTER V: DISCUSSION

Introduction

The results presented in Chapter IV provide a set of experimental data which must be interpreted in the light of several factors, namely, the body of established theory concerning weathering processes, other experimental data and also new theories derived as a result of this new body of data. With such a complex system great care must be taken in a comparison with other experimental data to ensure that the systems being compared are in fact sufficiently similar for such comparisons to be valid. The limitations of a given set of experimental data must also be remembered so that unjustified extrapolations to general theories are not made.

Model

A qualitative model can be produced from a consideration of the present experimental data and established surface chemical theory.

As mentioned previously, the dissolution of feldspars is incongruent for a time scale of the order of 24 hours and thereafter tends towards congruency. The initial hydration of the surface and dissolution of surface cations is essentially complete after about 1 hour. These observations are consistent with the following qualitative theory.

The incongruent dissolution of a feldspar is initially very rapid and involves the hydration of an $H^+ - M^+$ exchange on the mineral surface. This means an increase in the concentration of all species in solution. The initial rapid rise in solution concentration slows down as the altered aluminosilicate layer forms and restricts the movement of soluble species into solution. A steady-state condition results when the rate of dissolution of the altered layer equals the rate of migration of the soluble species through the altered layer. The altered layer itself grows until its rate of formation on the mineral side equals its rate of dissolution on the solution side. These processes govern the concentration of a species in solution in the absence of surface chemical effects and are represented by curves like curve B in Figure VI-1 which has an equation of the form:

$$C_s = \frac{k\ t}{1 + t} \qquad \text{(Berner, 1971, p. 35)} \qquad [1]$$

where C_s is the concentration of a species in solution;

k is a constant governing the initial slope of the curve; and

t is time.

The additional consideration of surface chemical effects is important where differences across interfaces are greatest. That is, during the initial hydration of the mineral surface and early formation of the altered layer the surface chemical effects are likely to be most pronounced. The observed "peak" can be explained in terms of this surface chemical process. The adsorption of a species from solution onto a charged surface can be represented by curves like curve A in Figure V-1 which has an equation of the form:

$$C_s = a/t + b$$

where a, b are constants governing the time sensitivity and threshold value of adsorption, respectively. However, the surface chemical forces need material on which to act and the adsorption onto a surface will only be significant when the concentration of a species in solution rises to where the forces of adsorption can act. This is essentially a cross-product of the adsorption and the concentration which follows an equation of the form:

$$C_s = C_s(a/t + b)$$

which reduces to

$$C_s = \frac{1}{1 - a/t - b} = \frac{t}{t(1 - b) - a} \qquad [2]$$

The net result of the two processes can be expressed by the equation which is formed by the difference of the two expressions [1] and [2], i.e.,

$$C_s = \frac{k\,t}{1 + t} - \frac{t}{t(1 - b) - a} \qquad [3]$$

The values of the constants a, b and k would vary depending upon the mineral phase, the composition of the water and the previous history of the mineral surface. It seems unlikely at present that this model can be made more quantitative from purely theoretical considerations. The second term in [3] represents the adsorption from solution of a species onto an active surface and the first term represents the release of a species from a mineral surface by dissolution. Intuitively, one can see certain interesting features of the curve. For example, if a mineral is washed as part of the sample preparation, its surface cations would be removed and this would reduce the surface concentration of such ions. Thus the alteration of the surface would have to precede to some extent before such ions could diffuse from the inner parts of the mineral into solution. This would mean a considerable reduction in the adsorption effect because of lower solution concentrations for the first few hours, and graphically, curve B would most likely represent the experimental results and no maximum would be observed. As another example, consider what happens when all the adsorption sites are filled on a mineral surface. Adsorption stops and the concentration of the solution is entirely controlled by the kinetics of dissolution. In other words, curve D in Figure V-2 would be the likely result of curve A reaching a minimum value A'. In Figure V-2, curve C is the resultant of A and B and can be readily divided into two zones, the dividing line being after the maximum. Prior to the maximum, the system is characterized by high rates of hydration and dissolution of the mineral surface and high rates of adsorption. Much slower rates of all these processes occur after the maximum. Kinetically speaking, the major changes in solution composition occur at very high rates and thus take very little time. Therefore, the mineral-water system adjusts to new physical and chemical conditions very rapidly.

Discussion of the Model

The first example discussed above may be an explanation for the shape of Wollast's (1967) curves for the dissolution of K-feldspar in buffered solutions in which no maximum is observed. The non-observance of the maxima may also be due to the density of sampling points since from the present study the maximum occurs within 1 hour of immersion. Deju and Bhappu's (1966) data on soda microcline seem to fit the model quite well in that a maximum is observed for Na^+, K^+ and Al^{+3}. Their experiments involved non-agitated beds and an open leaching system so that an exact correlation with the model would not be expected.

The model proposed is similar to one proposed by Stöber (1967) for the dissolution of silica phases (see Figure 16, p. 178) in which he proposes that the adsorption of complete molecular layers of SiO_2 from solution inhibits further adsorption onto and dissolution of the solid phase. He emphasized the importance of the unique adsorptive properties of each phase which result in differing dissolution behavior both in degree and kind. His model was particularly applicable to systems with high suspended solid concentrations as would be expected for an adsorption dominated process.

This model is useful in that it enables the results to be explained in a qualitative manner and appears to fit other experimental and field observations. It also permits the rates of weathering of feldspars and perhaps other minerals to be empirically qualified from this and other experiments.

Rate of Reaction

In a discussion of weathering reactions the term "rate of reaction" is often used. A clarification of this term is needed to prevent confusion. Strictly speaking the rate of reaction is the first derivative with time of a reaction product concentration.

e.g., $A + B = C + D$

$$\text{Rate of Reaction} = \frac{d[C]}{dt}$$

Confusion usually arises when attempts are made to compare two systems as to whether they have reached equilibrium, using rates of reaction. That is, it is often assumed that the system with the higher rate of reaction will reach equilibrium first. If one system reaches equilibrium before another then the first system may have a higher rate of reaction than the second or the equilibrium states of the systems may be different. Thus a comparison of whether or not these two systems have reached equilibrium cannot be made on the same time scale alone, but must consider whether the states of equilibrium are the same.

Considering Figures IV-11(a) and -11(b) by themselves it might be concluded that K-feldspar weathers more rapidly (i.e., has a higher rate of reaction) than Na-feldspar since the K-feldspar solution is in equilibrium with kaolinite before the Na-feldspar solution is.

From Figures IV-5(a) and -5(b) it can be seen that the change in the surface charge of Na-feldspar appears to follow some sort of definite decreasing trend with time whereas the K-feldspar surface charge is essentially unchanged. These data are interpreted to mean that the reactions occurring on the surfaces of the two minerals are quite different and that in fact the Na-feldspar does not reach the same equilibrium state that K-feldspar does. Thus to say that K-feldspar weathers more rapidly than Na-feldspar is true only in a kinetic sense (i.e., rate of increase of concentration of a cation in solution) and in terms of changes in the physical (electrical) nature of the surface, Na-feldspar reacts more rapidly (reaches equilibrium sooner) than K-feldspar.

Influence of pH

In the general conclusion (number 3) the influence of pH over the long term was minimized. This is in general true but refers specifically to the final position of the solution composition on a stability diagram. However, as can be seen from the data the initial pH has a significant effect upon the weathering history of a mineral surface with higher cation concentrations being associated with higher initial pH's for Na^+ and K^+. The association is derived from the easy substitution of H^+ for Na^+ and K^+ and the high mobility of the latter two. The lower mobilities of Ca^{+2} and H_4SiO_4 reduces the dependence on pH of their solution concentrations.

Hydration/Diffusion

The transition from surface hydration and H^+ - M^+ exchange to the dissolution of the mineral and diffusion of the dissolution products through the altered surface layer occurs after about 24 hours in these experiments.

This transition is quite clear from all the data except for Na and K and probably marks the point in the reactions where the surface cation sites have become saturated and adsorption from solution, despite the promoting charge difference, stops. However, the dissolution of the whole surface still continues and this process controls the changes in composition which take place after 24 hours. Because of this transition to dissolution diffusion controlled reactions, the values of all solution species are likely to increase in a roughly linear fashion with time if the surface areas of the particles remain constant. The fact that the Na^+ and K^+ data do not show this transition indicates that the $H^+ \longleftrightarrow M^+$ exchange is still taking place. This is probably due to the higher mobilities of Na^+, K^+ and H^+ than for the other solution species (Ca^{+2}, H_4SiO_4).

Surface Charge

The changes in zeta potential which are measures of surface charge show clearly the differences and similarities in weathering behavior of Na-feldspar and K-feldspar. The Na-feldspar curves either remain constant or rise slightly depending upon the initial pH for the first 24 hours. This means that during the hydration and $H^+ - M^+$ exchange the charge on the surface is maintained and in some cases is increased. The chemical forces causing hydration must therefore be greater than the physical forces tending to neutralize the negative charge by positive counter ion adsorption for the first 24 hours. After 24 hours the surface reactions are diffusion controlled by the surface altered layer and the negative surface charge can begin to be neutralized by the adsorption of positive counter ions. This process results in the curves shown in Figure IV-5(a). The apparent convergence of the curves after 24 hours further emphasizes the relatively small part initial pH plays once the altered surface layer is formed.

For K-feldspar a quite different behavior is indicated by the nearly pH-independent curves which show almost no change in surface potential over the time of the experiment. This can be explained if the altered layer is being dissolved fairly rapidly so that a surface of roughly constant surface composition (and thus roughly constant surface potential) is always presented to the solution. That is, the chemical forces involved in hydration and ion exchange are here not diffusion limited but can maintain a balance with the physical adsorption forces to produce a surface of roughly constant potential. This behavior is consistent with the pattern of data points on the stability diagrams [Figures IV-11(a), (b)] and with the consistently stronger convergence to congruent dissolution in Figures IV-10(b).

Comparison with other Data

Only three workers have conducted experiments which can be considered in terms of methodology and materials as even slightly comparable to those discussed here.

Deju and Bhappu (1966) have perhaps done the work most closely resembling this set of experiments in that they dealt with the short term weathering of a soda microcline in a preset but unbuffered pH system. Their results also show the characteristic peak found in the author's data (see Beju and Bhappu, Figure 4). It is significant that their sample treatment involved only dry crushing and sieving and no washing with acid or alkali. The failure to observe the peak mentioned above can be related to the sample treatment (see Discussion of the Model). Their experiments were carried out at an initial pH of 3.00 and thus should probably only be compared to the "initial pH 5" data. Deju and Bhappu noted from the sorption curve (Deju and Bhappu, Figure 3) for soda microcline that sorption occurs only for the initial fresh surface and is not important once the altered layer can reduce the migration of the alkali ions into the solution. Their observations on the higher mobility of Na^+ versus K^+ are borne out in this data for the K-feldspar in which the Na/K ratio is significantly higher in the solution than in the mineral. This is not the case, however, for the Na-feldspar in which the opposite trend is observed, perhaps due to the preferential dissolution of a K-feldspar phase from the mixture or to the presence of K as an impurity in the Na-feldspar and thus allowing it to be more readily leached out.

In 1967, Wollast presented the results on short term weathering of K-feldspar in solutions of buffered pH's at various wt. % solute values. The fact that his experiments were in buffered solutions means that ion exchange reactions ($H^+ \longleftrightarrow M^+$) would be inhibited and thus the results of his experiments may be somewhat different from those presented here. Wollast's solutions were much more concentrated on a wt. % solute basis than for this study and this will have a significant effect upon the mobility of ions in the solution due to the larger active surfaces present and the reduced amount of bulk or unstructured water in the system. The fact that alkali ions were not measured means that only the results for silica can be compared. From Wollast's Figure 10, the expected value of log H_4SiO_4 in solution after 2 hours with a 0.5 wt. % suspension is about 0.8 ppm, a value which is quite close to that found experimentally in this study, indicating that the results are not likely to be too discordant. The dissolution curves are however quite different from those presented here in that they show no early maximum peak and tend to increase for the duration of the experiments except for the pH 8 curve. The lack of a peak may be explained in several ways. If Wollast's samples were washed after crushing (he does not indicate whether or not they were) then the surface ions (including silica) would be rapidly taken into solution, thus later alteration of the washed feldspar would involve almost no real sorption onto the altered surface before the altered layer completely forms. That is, normally the disrupted surface ions are rapidly hydrated and taken into solution. At that point the ions interact with the charged surface and are readsorbed. This produces a peak in the concentration curve. The washing of the samples removes these easily hydrated ions and thus only the dissolution of the altered layer can release the ions to the solution to be readsorbed. However, the dissolution of the altered layer is sufficiently slow that the surface-ion interactions are reduced to an insignificant level. For the surface is no longer the freshly hydrated mineral surface but is an altered layer much more in equilibrium with its environment and much less active. The lack of a peak could also be explained by sampling density in that his data may not be closely enough spaced to detect the peak which occurs within the first 2 hours of immersion. A further consideration is the influence of the buffer which reduces H^+-M^+ exchange and may inhibit the surface-ion interacts described above. Because of the differences in experimental systems, Wollast's numerical model is probably not applicable to the present experiments.

Corren's experimental work, stretching over many years, has employed a fundamentally different system for studying the alteration of minerals. For this reason, while some of the conclusions may be compatible, the data from which they were derived may be quite different. Corren's experiments involved intense leaching and ultrafiltration of suspended samples, not allowing the system to remain closed, consequently his data also show no peak. The pre-treatment of his samples may also contribute to the fact that the "readsorption" peak has not been observed. There are, however, some similarities indicated by Figures IV-8(a) through 10(b) which show the tendency to congruent dissolution over the long-term mentioned by Correns (1961, p. 251-252). This is consistent with a short-term domination of the dissolution by hydration-readsorption processes followed by a long-term domination of the dissolution by diffusion processes.

Aside from this agreement with other workers on somewhat similar experiments there is also confirmation of some of these results by other types of studies. For example, the watershed study of Bricker and Godfrey (1968) found that the dominant secondary mineral on the well drained ridges was gibbsite whereas in the wetter, lower slopes the dominant secondary mineral was kaolinite. With reference to Figures IV-11(a) and 11(b) it can be seen that the faster rate of percolation on the ridges would not permit the weather reaction to proceed as far as on the lower slopes, thus keeping the composition of the percolating waters in the gibbsite field on the ridges. This is in agreement with recent work by Gardner (1972). Another feature of the present study demonstrated by paper was the rapidity with which the alteration reaction reaches equilibrium. By cycling initially distilled water through soil columns, they were able to produce water with the composition of the stream waters. The composition of the latter did not change when the same experiment was performed with it. There is some disagreement with Bricker and Godfrey's weathering sequence in that the weathering of oligoclose should produce gibbsite then kaolinite according to the stability field conditions found in this study. However, the problem may be an artifact in that Bricker and Godfrey's sequence describes what happens in a system where all the silica goes into solution and in fact in the initial stages of weathering very little silica goes into solution thus keeping the solution composition in the gibbsite field. That is, their reaction is the gross overall reaction and this study breaks the reaction down into its constituent steps.

The observation that K-feldspar weathers more rapidly than Na-feldspar, which is in opposition to earlier trends (Goldich, 1938, and others), has some support from a paper by Todd (1968) in which he emphasizes the importance of such factors as crystal structure and water composition on mineral stability. His investigation in central California revealed two sequences: K-feldspar more stable than Na-feldspar and vice versa, which he demonstrated resulted from differences in weathering environment, particularly temperature, topographic and precipitation differences.

Further support for the observed K-feldspar-more-weathered-than-Na-feldspar trend may be derived from Stumm and Morgan (1971, p. 400-402) who calculated the thermodynamic order of weathering to be that found in this study. They also emphasize the importance of a knowledge of all the environmental parameters of both the solution and the mineral in order to predict more accurately the geochemical adjustments of the mineral to the solution with which it is in contact.

The observed weathering rates in the present study are probably the result of differences in crystal structure as the water chemistry is similar in both cases. The presence of a perthitic structure would enhance the reactivity of the K-feldspar by producing structural and chemical discontinuities at the exsolution boundaries.

Significance and Conclusions

The weathering of feldspars is an important part of geochemistry in that feldspars are among the most abundant minerals on the earth and their alteration to secondary minerals and soluble ions determines the nature of soils and many natural waters. Indeed, Sillén (1961) has proposed that silicate- sea-water equilibria may be the mechanism for buffering the pH of the oceans.

The surface charge of a feldspar particle is determined by the nature of the feldspar surface and its interaction with the surrounding solution. Thus the changes in magnitude and sign, if any, of this charge are indicators of reactions between the solution and the surface of the mineral. A combination of both geochemical and surface chemical parameters is therefore necessary and sufficient to characterize the feldspar-water reaction. The surface charge is particularly sensitive to changes at the feldspar-water interface and thus the changes in the composition of the feldspar surface layer. In these experiments therefore, the measurement of surface charge has shown the changes in surface charge with the progress of weathering for two feldspars and through the proposed model has aided the interpretation of the geochemical patterns.

In conclusion, the weathering of feldspars under pH - pCO_2 conditions approximating those in a granitic terrain with moderate rainfall and a temperate climate is an initially very rapid reaction dominated by hydration of the surface and hydrogen-ion-for-cation exchange. As the weathering proceeds the hydrous alumino-silicate residual layer inhibits further exchange by only allowing diffusional movement of cations from the fresh mineral surface to the solution. When the concentration of cations in solution reaches a level where adsorption processes can become significant the existing negatively-charged surface attracts the cations to it. A steady-state balance between adsorption and solution/diffusion results in a nearly constant solution concentration for all cations after the initial hydration. This steady-state situation is disturbed either by agitation of the suspension which results in the abrasion of the surface layer and exposure of new reactive feldspar or by saturation of the adsorption sites. Both of these situations result in higher cation concentrations in solution. (The agitation if only intermittent will result in a "staircase" pattern of cation solution concentration with time whereas a continuous agitation will produce a smooth increase of cation concentration with time. The saturation of the adsorption sites on the hydrous aluminica-silicate surface means that the diffusion/solution process will control the cation concentration and a smooth increase in concentration with time will result.)

The above model and experiments show

(a) the importance of adsorption/desorption phenomena in both short-term and long-term feldspar dissolution, and probably for chemical weathering in general;

(b) that the generalized curve which characterizes the geochemical data (an initial rapid rise to a peak followed by a decrease to a lower, either constant or later increasing, value) is consistent with a consideration of the adsorption/desorption process (i.e., the formation of the double layer) taking place at the feldspar surface and with the simple dissolution of the mineral;

(c) that the cation-silica ratios (Na_2O/SiO_2, K_2O/SiO_2, CaO/SiO_2) of the solution compared to those in the original feldspar indicate an initially incongruent dissolution which tends towards congruency during the latter part of the experiments;

(d) that from these experiments the most important or master variables in chemical weathering are abrasion, mineralogic or crystallographic factors such as twinning, exsolution regions, impurities, fractures and grain size, and solution composition and concentration. pH does not appear to be a master variable in most natural waters, especially for long-term weathering, and the chemical composition of the mineral phase is also not a good criterion for predicting weathering behavior; and

(e) therefore that the most extreme chemical weathering should occur in a high energy environment, either for physical reasons (i.e., high abrasion due to extreme relief) or for chemical reasons (i.e., high rainfall).

Figure V-1(a)

Typical Concentration vs. Time Curve for Adsorption.

Figure V-1(b)

Typical Concentration vs. Time Curve for Dissolution.

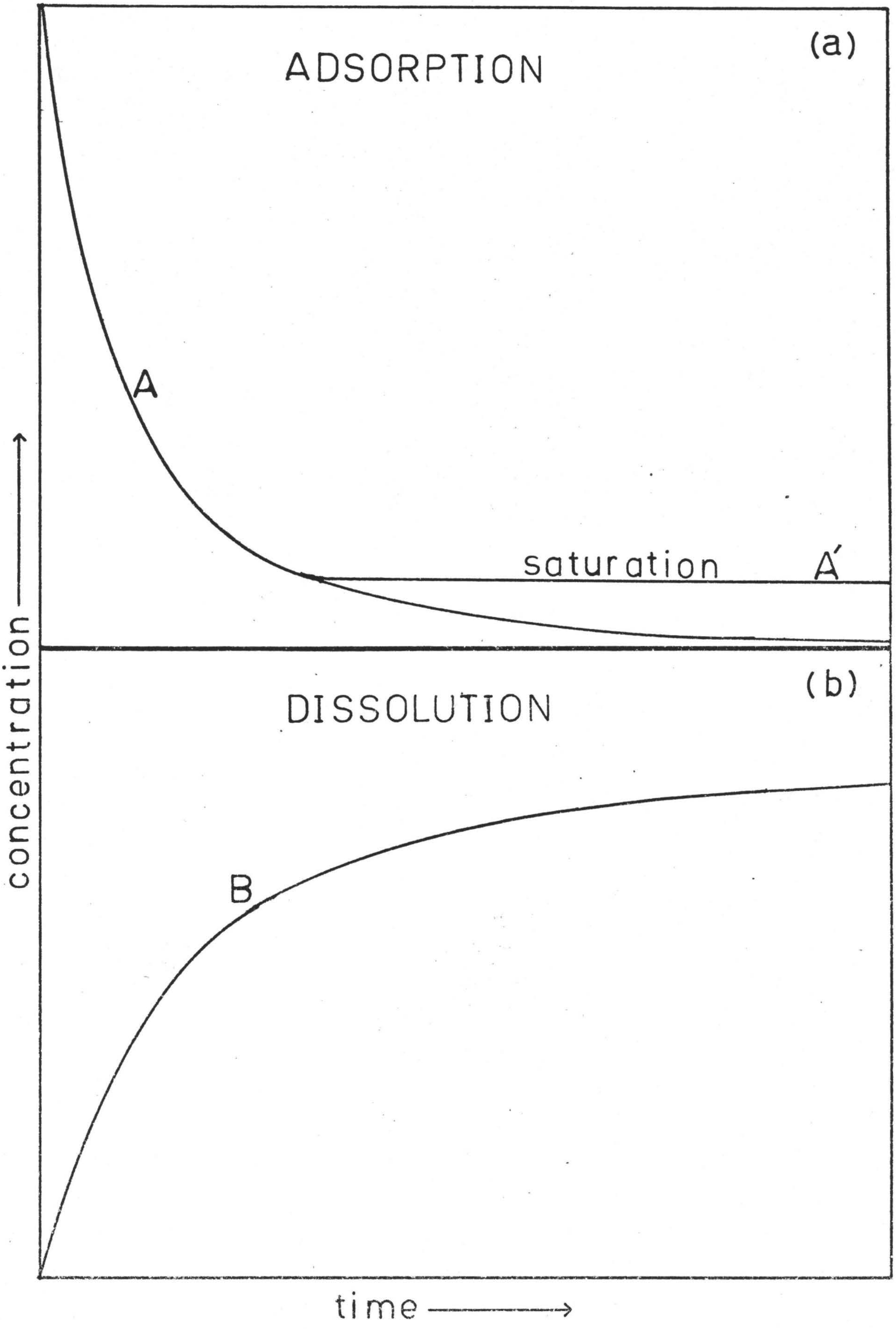
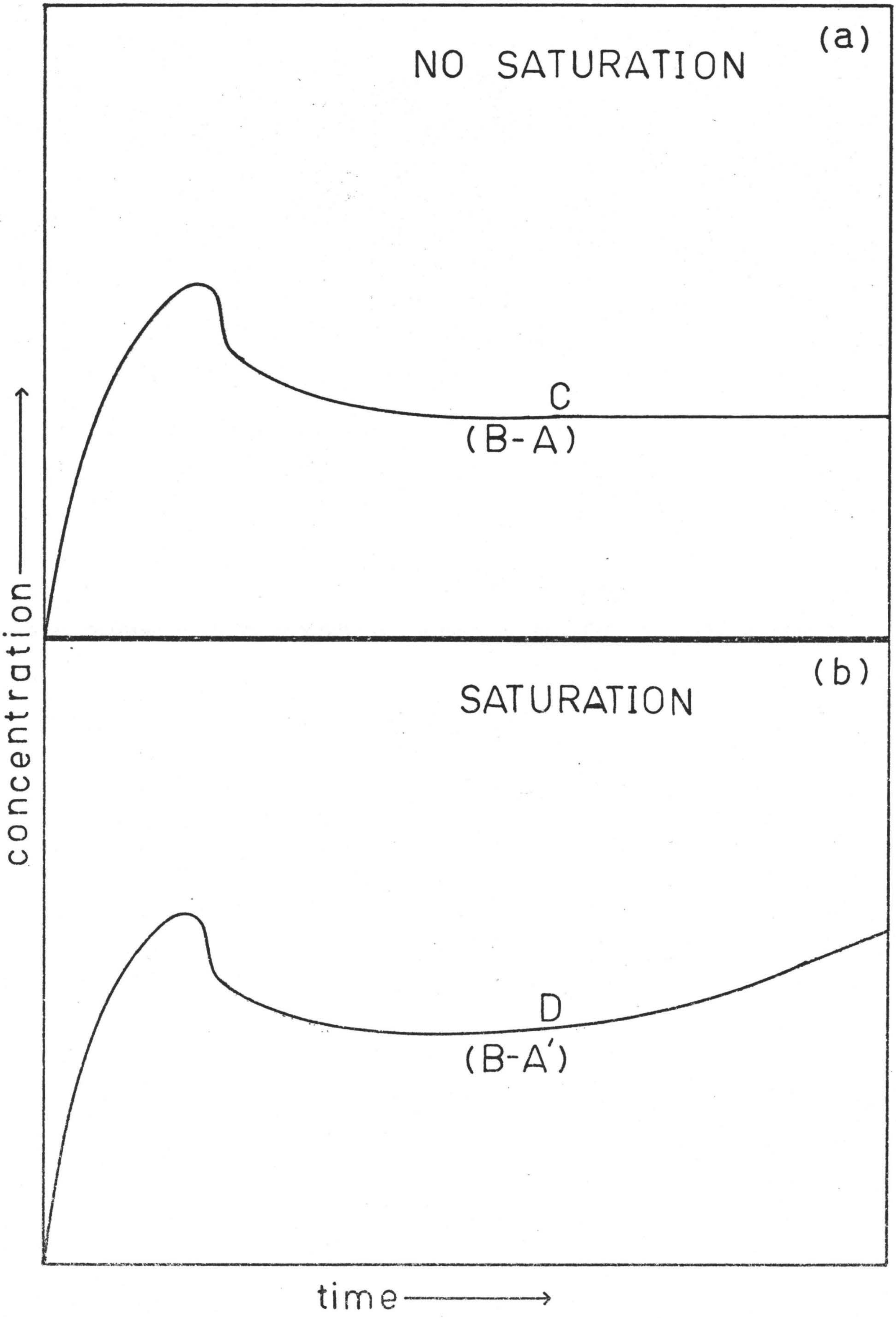

(a)
ADSORPTION
A
saturation
A′
(b)
DISSOLUTION
B
concentration ⟶
time ⟶

Figure V-2(a)

Concentration vs. Time Curve Expected for Mineral Dissolution (with Adsorption not becoming Saturated).

Figure V-2(b)

Concentration vs. Time Curve Expected for Mineral Dissolution (with Adsorption becoming Saturated).


(a)
NO SATURATION
C
(B-A)
(b)
SATURATION
D
(B-A′)
concentration →
time →

APPENDIX A

SURFACE CHEMISTRY THEORY

APPENDIX A: SURFACE CHEMISTRY THEORY

The reactions which occur at interfaces in the mineral weathering process are determined primarily by the nature of the solid surface. The properties of the solid surface are in turn controlled by the previous history of that surface, both in terms of its environment of formation (composition, structure, and metamorphosis) and its environment of alteration (composition of the solvent and temperature). The surface properties thus give important information on the changes at the interface leading to a better understanding of the geochemical weathering process. The significance of the solid-solution interface in natural waters becomes apparent when one considers the state of subdivision of the solid typically present in natural waters. The high specific surface energies of many solid phases mean that substances of high specific surface areas have total surface energies of the order of 10^9 ergs/g. (i.e., 24 cal/g.).

In a natural water system, to attempt to understand the regulatory agents of water composition, it is essential to understand the surface chemical reactions because these, aside from biological reactions, have the most significant effect. The significance of interface effects far overshadows their mass contribution to the system because of the large reactive areas available.

Forces at interfaces are due to the interaction of forces present in the two phases and surface reactions occur because of the imbalance of such forces. In most minerals the forces are largely electrostatic and thus along a cleavage face or other mineral face there will be an imbalance of charges producing a net surface charge. This surface interacts with the polar water molecules to reduce this charge by adsorbing the water (and any dissolved counter ions, i.e., ions whose charge is opposite to that on the surface) onto the surface to form a "double layer" of oppositely charged ions. The size of the electrostatic forces on the mineral surface will be dependent upon substitutions within the crystal structure, lattice defects, and the state of crystallinity of the mineral. However, the potential which exists between the mineral and the solvent also depends upon the nature of the solvent. Thus it is necessary when talking about surface potentials to specify the composition of the solvent phase as well as that of the mineral phase.

Double Layer Theory

The electric double layer refers to the structure and organization of the water and contained ions in the region of the mineral surface. This structuring is due to the distribution of charge (potential) in a double layer. The Gouy-Chapman model considers ions as non-interacting point charges which are affected by the coulombic forces at a charged solid-solution boundary. These ions form a compact double layer at the surface and, because of thermal motion, a more diffuse double layer in the solution. The surface potential (ψ_o) thus decreases as a function of distance from the surface (Stumm and Morgan, 1970, p. 458-9). An application of this theory is in the calculation of ion concentrations close to charged surfaces. For pure water at 20°C the pH at the surface is given by $pH_{surf} = pH_{bulk} + 16.9\ \psi_o$, with a $\psi_o = -50$ mV, $\Delta pH = -0.845$ or nearly a full pH unit difference between the bulk solution and the charged surface. This means that pH measurements of the bulk solution do not tell the true story of the region near the charged surface and only by measuring ψ_o can you get at the pH near the surface. This has tremendous application in measurements of interstitial pH

(Figure A-2). However, because the ions are treated as point charges the calculations tend to overestimate the changes in concentration.

The Stern (1924) theory is a more realistic version of the Gouy-Chapman model and involves two double layers: a compact double layer of adsorbed ions at the surface called the Stern double layer, and a diffuse double layer outside the Stern layer called the Gouy double layer. This model corrects for ion size, shielding effects and specific chemical interaction of ions with the surface. In this model (a double, double-layer) the potential drops from ψ_o, the potential at the surface side of the Stern layer, to ψ_δ, the potential at the solution side of the Stern layer (Figure A-1). This potential ψ_δ is equivalent to the ψ_o of the Gouy-Chapman model. However, specific chemical interaction of an ion with the surface can occur despite an opposing electrostatic force. The free energy of adsorption can be considered as consisting of two parts, one electrostatic, the other chemical. Thus,

$$\Delta G = -\Phi + zF\psi_\delta$$

where ΔG is the total free energy of adsorption;

Φ is the Gibbs free energy due to specific chemical interaction; and

$zF\psi_\delta$ is the electrostatic free energy term

where ψ_δ is the potential which exists between the solvent and the Stern layer, F is the Faraday constant, and z is the charge on the adsorbed ion. Typically, for a potential difference (ψ_δ) of 100 mv the electrostatic term for a monovalent ion adsorbed onto a surface of like charge is 2.3 kcal/mole. The chemical term for a similar adsorption is of the order of -2 to -8 kcal/mole (Stumm and Morgan, 1970, p. 473; Stumm et al, 1970). Therefore, the chemical term can override the electrostatic term, at least with respect to the thermodynamics. This means that in interpreting ion-surface interaction it is difficult to sort out these effects, especially if the surface changes with time. Thus the specific adsorption of an ion, rather than decreasing the surface potential, could in fact increase it. The adsorption of a counter ion will, in general, decrease the surface potential and in the presence of sufficient concentrations will reduce it to zero. Thereafter, in the absence of specific chemical effects, no further net adsorption will take place although ion exchange may occur at some local sites. Table A-1 provides a summary of those factors having the greatest effect upon the double layer. All of the above theory has so far only been applied to simple metals and metal oxides such as MnO_2, TiO_2, SiO_2, and Al_2O_3, whose surfaces do not change significantly with time.

Solid Phase

Most minerals are metal oxides and Parks (1967) has shown that the ZPC of a mineral can be related to a weighted average of the ZPC's of its constituent oxides. Since little work has been done on mineral surfaces it is useful to discuss the nature of the changes on mineral surfaces as if they were composed of separate oxides.

The charge which develops on an oxide surface arises because of a charge transfer reaction:

$$O^{-}(\text{surface}) + H_2O = 2OH^{-}\ (\text{solution}) \qquad \text{Parks and de Bruyn (1961)}$$

This can be seen as a two-step process: the hydration of the oxide surface followed by the dissociation of the surface hydroxide. The hydration step occurs because of the unsatisfied charges on the atoms, both positive and negative, which exist on the oxide surface. The cations attract an OH^- ion or polarize a water molecule to satisfy the charges, whereas the oxygen ions attract a proton from water, producing an OH^- in return. This leaves the oxide surface, once hydrated, with a coating of OH^- ions with the cations underneath. The net charge is thus established by the relative numbers of cationic and anionic sites on the exposed surface and thus will vary from substance to substance. The electronegativity of the sites will modify the sites to give "effective populations" not directly related to their numbers.

Mineral Structure

The influence of mineral structure upon the cleavage and thus upon the proportion of cationic and anionic sites exposed and the surface charge has been considered by Parks (1967). He proposed that the ZPC (zero point of charge - defined later) of a complex mineral can be calculated from the sum of the ZPC's of the component oxides or hydrated oxides, weighted according to the composition of the mineral. This implies that each structural site behaves independently of the other structural sites, while recognizing that lattice defects, surface alteration and specific ion interaction will cause deviation of the observed ZPC from that calculated. For the oxides of transition metals, crystal field effects must also be considered. Considering the fairly simple nature of the calculations, his success in predicting ZPC's is quite good. His calculations involve the following assumptions (Parks, 1967, p. 143):

(1) No ions other than H^+ and OH^- play a potential determining role.

(2) Additivity is on an atomic, not molar, basis and cations alone are counted.

(3) Grinding or abrasion during sample preparation produces a disturbed, disordered or amorphous surface layer which is hydrous. Acid

leaching removes this material.

(4) Precipitates not subsequently dried are hydrous.

(5) The surface composition is the same as the bulk and is given by the idealized chemical formula.

With respect to the weathering behavior of the feldspars, he predicts that a Na-feldspar surface will alter readily as the H^+ will largely substitute for the Na^+ and that this alteration will be less for feldspars with M^{+2} and M^{+3} ions. The dissolution of feldspars will be non-stoichiometric because of the surface alteration by hydration and the H-Na, K substitution mentioned above. This altered surface is much different from that of the unaltered mineral surface and its ZPC is likely to be quite different from that calculated.

Solvent Phase

The behavior of water near a charged surface has been discussed somewhat but there are some other considerations. It is well known that the conductivity of water goes up as the amount of dissolved, dissociated ionic material increases. This can be considered as an increase in "electric activity" in that the water is more receptive to electrical forces. Since these dissolved species are mainly hydrated we can infer some information about the expected behavior of a charged solid surface as the ionic strength goes up. Outside the tightly bound water layer on the oxide surface, the water molecules, while polarized by the charge on the surface, will increasingly be attracted to the solution species as the population of the latter increases. This will in effect decrease the thickness of the double layer and increase the potential between the solid and the solvent (Stumm and Morgan, 1970, Figure 9-3).

The structure of the water adjacent to the surface has the effect of producing a concentration sub-system in which the dissolved ions are excluded from the highly structured water layer to the solvent remote from the surface. This increases the concentration of the ions in the water distant from the interfaces. For example, Horne et al (1968) and Siever et al (1965) found that interstitial water from recent marine muds had higher salinities than the sea water directly above the sediment (see Figure A-2). This implies a loss of water without a loss of dissolved species. The explanation proposed was that the slight compaction forces on the clay were sufficient to squeeze the pure water from the sediment but not the hydrated ions. The structurally altered water extends from the interface outwards about 700 Å according to work by Korringa (1956) with water in capillaries. Both the thickness and nature of this altered layer are a function of the solid phase and the solvent phase, as indicated by Table A-1 (see also Figure A-3).

Zeta Potential

The concept of a potential determining ion is a useful one because it allows prediction, in a qualitative sense, of the effect of changes in concentration of certain ions upon the surface charge. A potential determining ion (p.d.i.) is a species whose concentration controls the potential of the surface, given the reaction the surface takes part in.

E.g., $SiO_2(s) + OH^-(p.d.i.) = SiO_2(OH)^-(surface)$

In fact, the potential difference (ψ_δ or ψ_o) between a solid and a solvent cannot be known but various electrokinetic phenomena permit the measurement of a potential which is related to the surface potential. Electrophoresis refers to the movement of charged particles relative to a stationary solution in an applied potential field. The zeta potential (ζ), which is the charge at a plane of shear between the bulk solution and the adsorbed water layer, can be calculated from the electrophoretic mobility (M_e) of the particles in an applied field and a knowledge of the dielectric constant (ε) and viscosity (η) of the solvent.

$$\zeta = \frac{4\pi\eta}{\varepsilon} \times M_e$$

This function assumes that the particle is an insulator whose radius is large relative to the thickness of the double layer. The zeta potential is in general less than the surface potential because the zeta potential is measured farther from the surface than the double layer thickness and decreases with distance. The position of the shearing plane is not precisely known so that the interpretation of the zeta potential is somewhat qualitative. In the microscopic method for measuring electrophoretic mobility, one must focus on the stationary liquid level (located 0.14% of the diameter of the cell measured from the top of a cylindrical cell). The electrophoretic mobility changes sign near the cell wall and thus there is a large velocity gradient near the depth at which the stationary liquid layer exists. See Figure A-4 for a graphical illustration of the above method of measuring the zeta potential.

Zero Point of Charge

The pH at which the net surface charge of a solid surface is zero is called the zero point of charge. It (ZPC) usually corresponds to the pH of minimum solubility for oxides. The importance of the ZPC lies in its usefulness in predicting the charge dependent behavior of surfaces. Knowing the ZPC of a given substance and having the pH as an independent variable one can determine the probable adsorption-desorption behavior of the surface, in that above the ZPC the surface will be negative and below the ZPC it will be positive. Qualitatively one can also say that near the ZPC small changes in pH can have fairly large effects upon the ion exchanges taking place at the surface due to the "flipping over" of the sign of the charge. It also allows the prediction of dynamic changes resulting from fluctuations in the aqueous medium. For example, $Fe(OH)_3$ is negatively charged at pH's above 8.5 and thus should attract cations in sea water and in fresh water which have pH's above this value. This probably accounts for the scavenging ability of iron-manganese nodules for trace metals. However, should the pH drop below 8.5 the surface becomes positive and desorption (adsorption) of cations (anions) will occur. The surface charge thus has a strong control on water composition and vice versa, the solid surface-water system providing an efficient buffer (because of the large surface areas involved) for not only pH but for cation and anion concentrations. For the sedimentation of colloid sized particles, which are almost invariably charged, the ZPC is also important. At the ZPC the sedimentation rates will be at a maximum for there will be no electrostatic repulsion to prevent coagulation between particles. One obvious implication of this is that sedimentation behavior and water composition is likely to be strongly affected where the transporting medium changes its pH suddenly (i.e., where a river enters into the sea). This will have application to such important parameters as organic nutrients, turbidity, dispersion of and/or concentration of pollutants. In general, below the ZPC the surface is positive and above the ZPC the surface is negative, although some oxides exhibit more than one ZPC. This simple concept allows us to predict, in a semiquantitative way, how a surface of known ZPC is likely to behave given the pH. The ZPC has limitations in that while it tells us where the surface will be neutral but gives no information about the magnitude of the charge away from the ZPC is likely to be and thus what the magnitude of the surface's influence will be.

The ZPC is a function of (a) the composition of the surface itself, (b) the previous "history" of the surface with regard to solutions the surface has been in contact with, (c) the composition of the solution in contact with the surface when the ZPC is measured, and (d) the method of measurement. Therefore, a simple statement of the ZPC for a given surface, say silica, has little value unless the details of sample composition, solution composition, sample preparation and method are given.

TABLE A-1

Factors Influencing the Double Layer Thickness

Factor	Effect
Specific Adsorption	- increases if hydrated ions of similar charge are adsorbed or decreases if hydrated ions of opposite charge are adsorbed, depending in detail upon the nature of the surface and ions
Ionic Strength	- as ionic strength goes up the double layer thickness goes down, since water is removed from the hydration of the ions and the potential is reduced
Nature of Solvent	- increased polarity of solvent increases electric interaction between the surface and ions through ion-dipole forces
Nature of Solid Surface	- state of subdivision affects the surface area available and thus the magnitude of the surface chemical forces in the whole system because with increased area more water is tied up as structurally adsorbed water in the double layer - hydrophilic character of surface determines the extent of interaction with the solvent because of ion-dipole forces between the charged sites and the solvent - fractures, defects, strains affect the concentration and distribution of charged sites providing easily hydrated ions and increasing the available reactive surface area

TABLE A-2

Literature ZPC's

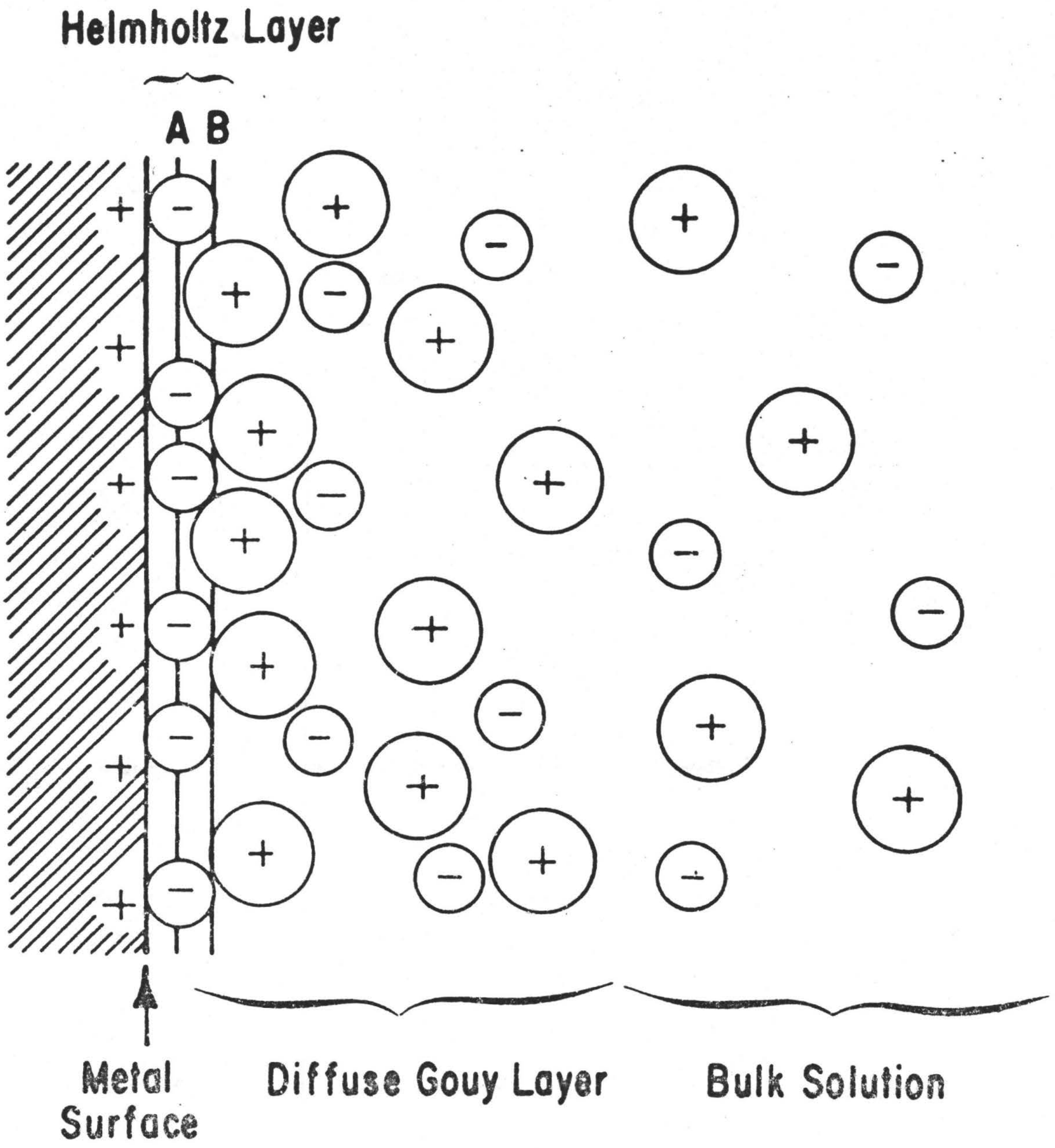
Parks(1967)

Substance	ZPC (observed)	ZPC (observed)
a-Al_2O_3	9.1	---
a-$Al(OH)_3$	5.0	---
SiO_2	2,0	---
Albite	2.0	3.1
Microcline	2,4	3.1
Kaolinite	4.6	5.5
Montmorillonite	2.5	5.3
Augite	4.5	5.5
Spodumene	2.6	4.3
Kyanite	6.2	7.0
Andalusite	5.9	6.6
Sillimanite	5.6	5.9
Olivine	4.1	8.9
Zircon	5.0	6.5
Cases(1966)		
Quartz	1.35	
Microcline	1.49	
Oligoclase	1.45	
Labradorite	1.54	

Figure A-1

The Electric Double Layer for Metals (for Silicates the Signs are Reversed).

(From Horne, Marine Chemistry, 1969, p. 362)



A. Inner Helmholtz or Stern Plane of Anionic Centers

B. Outer Helmholtz or Limiting Gouy Plane of Cationic

Distance of Closest Approach

Figure A-2

Model of Particulate Solids in Aqueous Electrolytic Solution.

(From Horne, Marine Chemistry, 1969, p. 368).

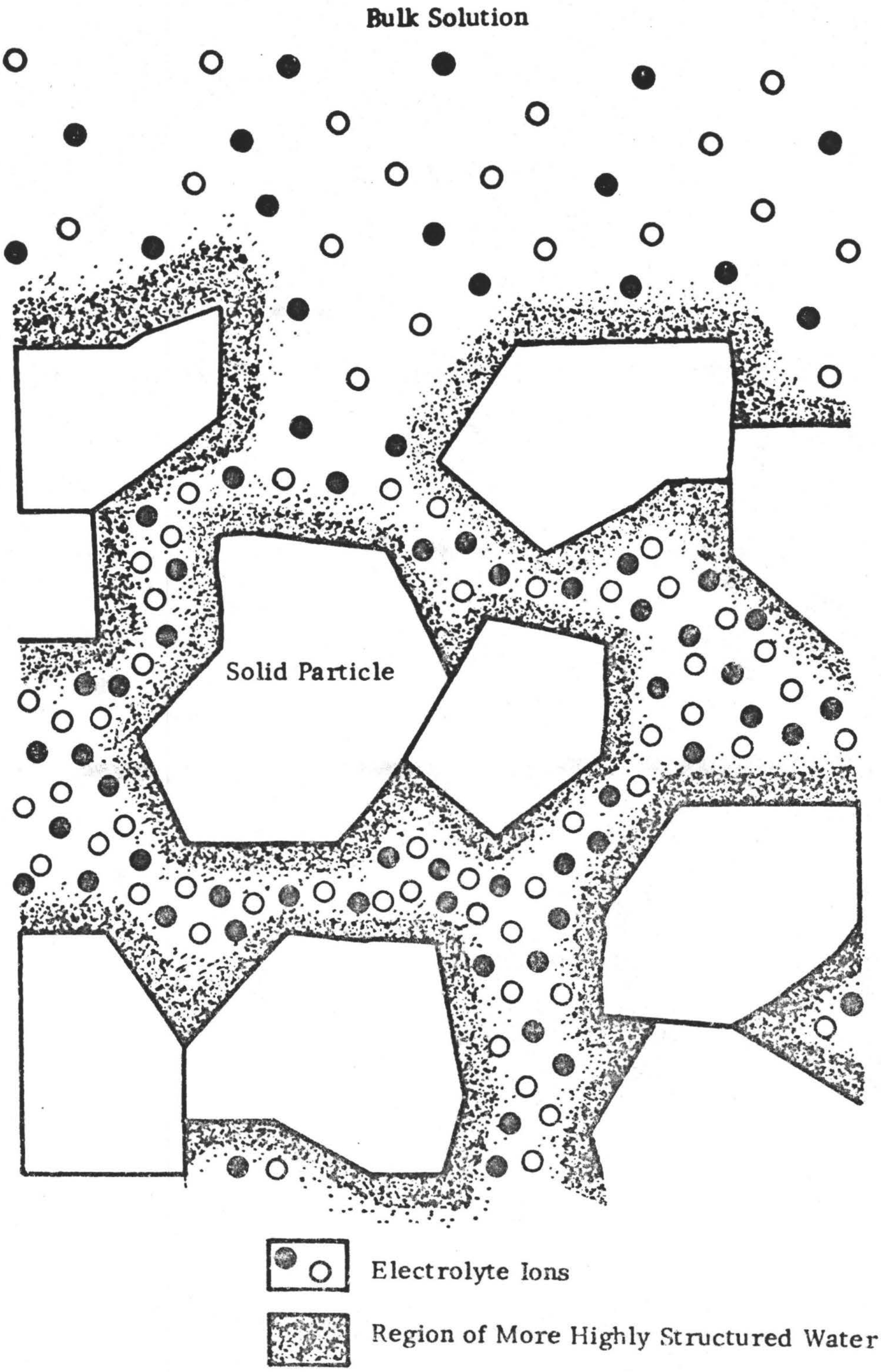

Bulk Solution
Solid Particle
Electrolyte Ions
Region of More Highly Structured Water

Figure A-3

Model for the Position and Orientation of Water Molecules (For Metal read Silicate). (From Horne, Marine Chemistry, 1969, p. 363).

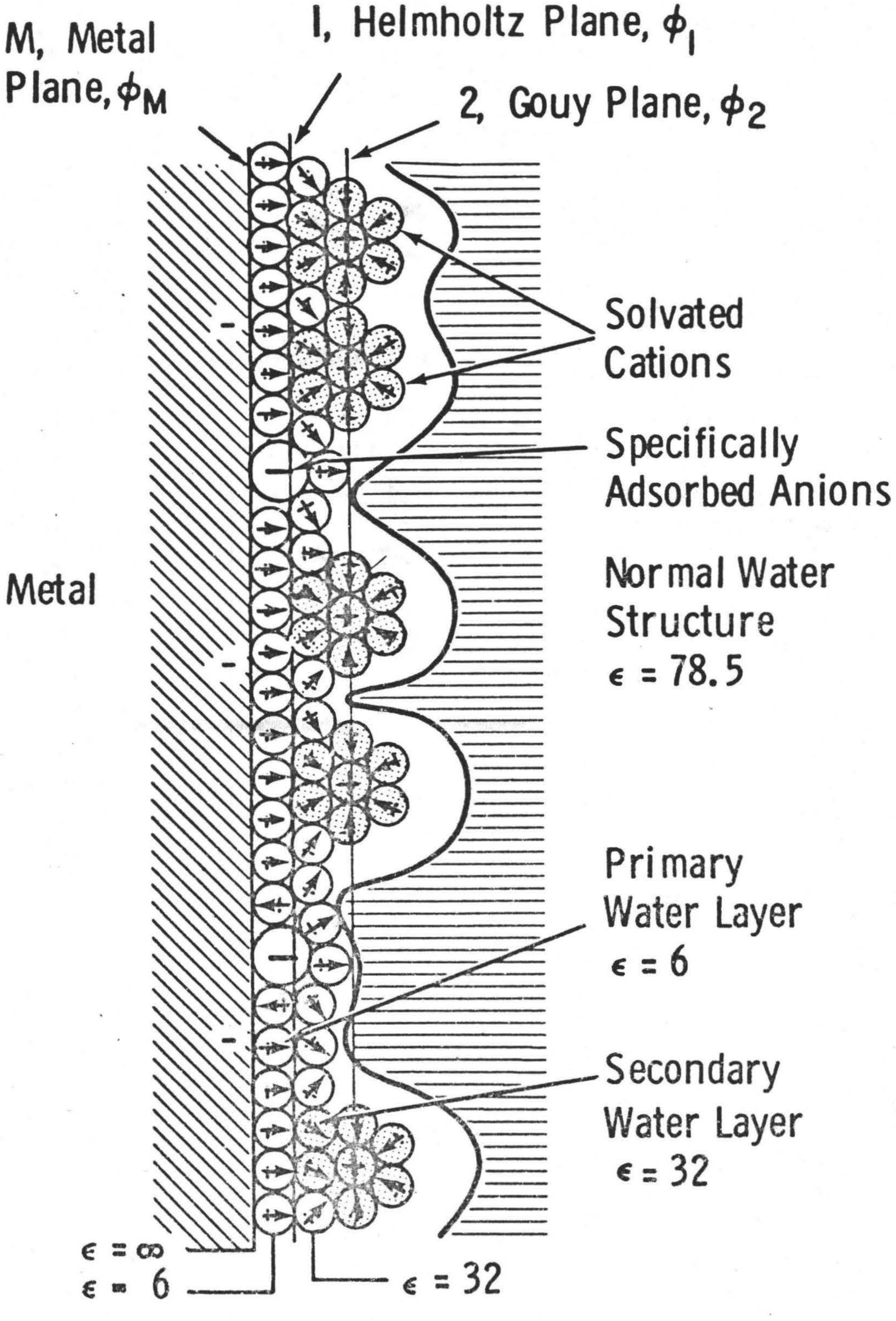
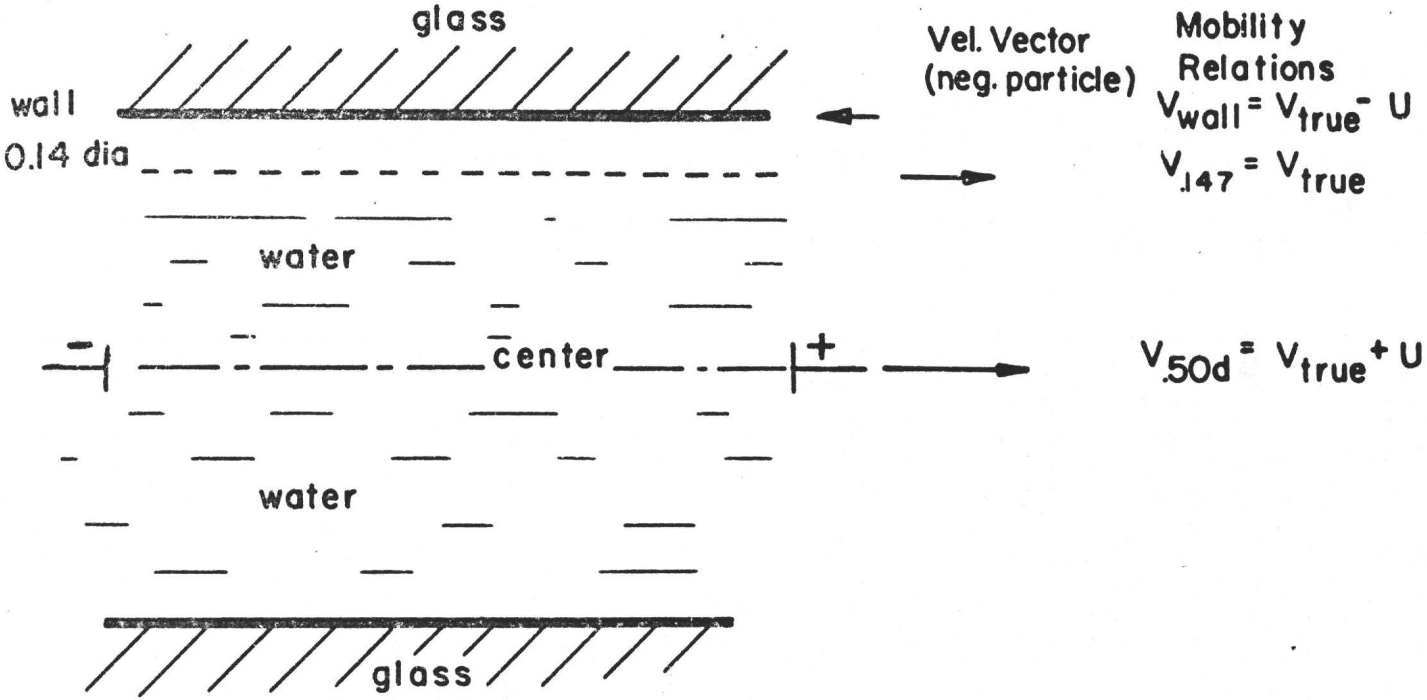

M, Metal
Plane, ϕ_M
I, Helmholtz Plane, ϕ_1
2, Gouy Plane, ϕ_2
Solvated Cations
Specifically Adsorbed Anions
Normal Water Structure
$\epsilon = 78.5$
Metal
Primary Water Layer
$\epsilon = 6$
Secondary Water Layer
$\epsilon = 32$
$\epsilon = \infty$
$\epsilon = 6$
$\epsilon = 32$

Figure A-4

Measurement of Zeta Potential (from Hazel, 1967, p. 311)



MOBILITY-DEPTH RELATIONS, IDEALIZED.
Li = Electroosmotic of water in cell;
V_{wall} = Mobility of particles at wall;
$V_{.147}$ = Mobility of particles at stationary level (After Smoluchowski);
$V_{.50}$ = Mobility of particles at center of cell.

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