

LABORATORY DISSOLUTION OF BASALT IN A
SIMULATED WEATHERING SYSTEM

by

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TABLE OF CONTENTS

	Page
LIST OF TABLES	vi
LIST OF ILLUSTRATIONS	vii
ABSTRACT	ix
INTRODUCTION	1
Experimental Objectives	2
LITERATURE REVIEW	3
Nutrient Cycling	3
Chemical Rock Weathering	5
Parent Material	6
Weathering Solution	8
Artificial Weathering System Designs	14
MATERIALS AND METHODS	17
A HYPOTHETICAL MODEL OF CHANGES IN WEATHERING RATE	22
RESULTS	24
X-Ray Diffraction	25
Rates of Ion Removal as a Measure of Weathering	29
The Main Effects of Treatment and Schedule	29
The Effects of Individual Treatment-Schedule Combinations	43
Interaction of Treatment and Schedule	46
Cumulative Ion Removal	48
The Main Effects of Treatment and Schedule	48
The Effects of Individual Treatment-Schedule Combinations	50
Interaction of Treatment and Schedule	52
The Effect of Treatment and Schedule on Relative Ion Mobility	52
Error Due to Instrument Variation	54

TABLE OF CONTENTS--Continued

	Page
DISCUSSION	55
The Effects of Treatment on α and γ	55
The Effect of Schedule on α and γ	59
The Effects of Schedule and Treatment on Cumulative Weathering	62
Some Thermodynamic Considerations	64
SUMMARY	73
LITERATURE CITED	75

LIST OF TABLES

Table	Page
1. Elemental Analyses and Molar Ratios of Oxides for Fresh and Weathered Basalt Powder	18
2. Average Modal Analysis of Plateau Basalts from Beaver Creek Watersheds 12-2 and 12-3	28
3. Ionic Concentrations of Outgoing Weathering Solutions as a Function of Treatment and Schedule at Selected Times (Combined Means)	30
4. Value of Coefficients, Constants, and r^2 's for Equations 1 and 2 and Significance of Treatment and Schedule Effects	40
5. Values of α , β , and γ Least Significant Differences for Regression Curves of Ion Removal by Individual Treatment-Schedule Combinations	44
6. Cumulative Weight of Ions Removed from Basalt Powder over 28 Weathering Cycles and Significance of Treatment and Schedule Effects	49
7. Cumulative Weight of Ions Removed from Basalt Powder as a Function of Treatment and Schedule and Least Significant Differences among Weights.	51
8. Relative Molar Mobility of Oxides of Ions from Powdered Basalt as a Function of Treatment and Schedule	53
9. Ionic Concentrations of Outgoing Weathering Solutions Natural and Artificial Systems	65

LIST OF ILLUSTRATIONS

Figure	Page
1. Experimental Feldspar Weathering Model of Wollast (1967) after Berner (1971)	11
2. Artificial Weathering Apparatus	19
3. X-Ray Diffraction Patterns for Fresh Powdered Basalt and Weathered Basalt Powder (Cu K α Radiation)	26
4. Mg Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles)	32
5. Na Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles)	33
6. K Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles)	35
7. Ca Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles)	36
8. Fe Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles)	37
9. Al Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles)	38
10. Si Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles)	39
11. Graphs Portraying Treatment-Schedule Interaction for Values of Coefficients and Constants in Equations 1 and 2 (Significant at the 0.05 Level)	47

LIST OF ILLUSTRATIONS--Continued

Figure		Page
12.	Stability Diagram for System $\text{CaO-H}_4\text{SiO}_4\text{-H}_2\text{O-H}^+$ at $\text{pNa} = 4.00$, 1 Atmosphere, 25°C	69
13.	Stability Diagram for System $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 25°C , 1 Atmosphere	71

ABSTRACT

A laboratory weathering system was developed to simulate weathering of basalt rock on a watershed in north central Arizona. Powdered basalt rock was weathered using solutions with pH of 4.5, 5.5, and 7.0 under two conditions: continuous and alternate wetting and drying. Effects of solutions and weathering conditions on rate of weathering were analyzed. Results indicated that weathering rates for Mg, Na, and K (mobile ions) declined over time and approached a relatively stable rate that was not greatly affected by pH differences.

Weathering with alternate wetting and drying showed more cumulative ion removal than continuous weathering for Mg, Na, K, Ca, Fe, and Si. Only Al showed no difference in cumulative weathering due to schedule. The steady-state weathering rate was higher with alternate wetting and drying than continuous weathering. Thus, weathering with intermittent drying resulted in more cumulative ion removal over time than continuous weathering with equal volumes of solution. Intermittent drying appeared to have a greater effect than changes in pH on the steady-state weathering rate. Many of these results are consistent with a weathering mechanism in which a residual layer rich in immobile elements forms on fresh mineral surfaces. The artificial weathering systems were a reasonable simulation of actual field weathering.

INTRODUCTION

Increasing knowledge of nutrient cycling in forest ecosystems has led to speculation that land management techniques could enhance the efficiency of these cycles and possibly increase forage and timber yields over a period of time (Hendricks et al., 1972). The development of effective land treatments depends on a thorough understanding of the substrates and mechanisms involved.

The forest nutrient cycle has been described as an interaction between atmospheric inputs, soil and biological exchange, geologic outputs, and weathering inputs (Ovington, 1958; Bormann and Likens, 1967). Of the above components, the last, nutrient ion inputs from weathering of underlying parent material, presents many problems. Not only is the precise mechanism of chemical weathering still somewhat uncertain, but it is difficult to quantify. The present study considers some of the variables affecting weathering mechanisms and attempts to relate results of laboratory studies to the ecosystems they simulate.

A forest ecosystem is an interaction of myriad elements and forces. Precipitation, vegetation, forest litter, soil, parent material and secondary minerals, and biotic activity are among numerous ecosystem factors affecting each other in dynamic equilibrium. The correlation of laboratory weathering data with field conditions requires contending with many potential variables. As investigators who have conducted laboratory weathering experiments have noted, it is virtually impossible

to perfectly simulate a rock weathering system (Correns, 1961; Huang and Kiang, 1972). Some of the factors that affect the weathering rate on a watershed must be isolated if they are to be quantified and analyzed in a laboratory simulation.

Experimental Objectives

The purpose of this thesis is to measure the effects of changes in pH of the weathering solution and intermittent drying on a simulated basalt weathering environment. These two variables have been isolated for this study as characteristic of changes that are likely to occur in nature. Changes in pH also could be a factor in land management planning.

Changes in weathering rate due to changes in pH and intermittent drying will be measured and used to determine a mathematical model that defines weathering over time. The terms of the model will be used to analyze the effects of the changes in treatment (pH of solution) and weathering schedule (alternate wetting and drying) on rate of weathering and cumulative weathering. Finally, a basis for assuming that the laboratory system is a reasonable simulation of weathering in nature will be developed. Some practical applications will be considered. A watershed at Beaver Creek, south of Flagstaff, Arizona, is the natural system being simulated. Studies in nutrient cycling have been proceeding there for several years.

LITERATURE REVIEW

Nutrient Cycling

The cycling of nutrient ions has long been recognized as essential to the understanding of ecosystem function. One of the early methods of balancing the cation inputs and outputs in a woodland ecosystem was presented by Ovington (1962). He emphasized the cycling of nutrient ions between soil and vegetation, but was unable to quantify inputs to the system by weathering. He did cite a 1956 study by Klausung that proposed a rate of rock weathering higher than expected.

The study of nutrient cycles of whole ecosystems presents several problems of measurement. Materials carried into the system by rain water can be measured. So can materials carried out by stream waters. But cycling between plants and soil, and particularly between minerals and soil, is more difficult to evaluate. Until recently, few efforts have been made to establish the contribution of weathering to nutrient cycles. Some investigators even have questioned if weathering made a significant contribution compared to atmospheric inputs (Deevey, 1970). But other workers have provided increasing evidence that rock weathering by hydrolysis of primary silicate minerals by percolating water is a significant contributor to the available nutrient pool and can be quantified.

Some of the first work to quantify rock weathering in nutrient cycling was begun in 1963 at the Hubbard Brook Experimental Forest in

West Thornton, New Hampshire (Bormann and Likens, 1967; Johnson et al., 1968). The Hubbard Brook workers made two assumptions that are common to nutrient cycling studies. First, in an ecosystem represented by a small watershed, net losses or gains to the whole system were assumed to be the difference between meteorological input (dissolved in rain and snow) and geological output (dissolved in outgoing streams). Second, in an ecosystem having climax vegetation and mature soil colloids, where gains and losses in biomass were minimal, the net gain or loss to the system was considered zero and the system in a steady state. Under these conditions, apparent net losses were assumed to be made up by contributions from weathering rock and soil minerals, and atmospheric input minus geologic output would be a measure of rock weathering in a steady-state ecosystem (where an impermeable layer prevented losses to deep water). Johnson (1971) offered extensive justification for these assumptions. Feth, Robinson, and Polzer (1964), Garrels (1967), Drever (1971), Jacks (1973), and others provided further insight to steady-state conditions by showing that ion concentrations in streams draining mature soils are in dynamic equilibrium with secondary clay minerals of the region.

Further studies of nutrient inputs and outputs were conducted by Cleaves and his associates at Pond Branch in Maryland (Cleaves, Godfrey, and Bricker, 1970; Bricker, Godfrey, and Cleaves, 1968). In their work, nutrient ion concentrations in stream water were correlated with silicate dissolution to make detailed estimates of nutrient balance.

The nutrient cycling study upon which the present laboratory simulation is based began in 1972 as an evaluation of the effects of land treatments on water quality of Beaver Creek, south of Flagstaff, Arizona. The work there was expanded in 1973 to include a comprehensive study of the effects of land treatments and management on nutrient budgets and soil formation. Water-tight bedrock is not present, but the watershed area is underlain by a virtually impermeable B2t layer (Hendricks et al., 1972; Williams and Anderson, 1967). Clay minerals are well developed and the vegetation is climax ponderosa pine forest. The objectives of the Beaver Creek study include the determination of nutrient inputs and transfers within the system, the effect of weathering on release of nutrients, the magnitude of nutrient loss via streamflow, and the rate of soil formation.

Chemical Rock Weathering

Insight to the specific chemical reactions, including rock weathering reactions, that make up broader nutrient cycles, often has been gained by laboratory simulation (Bricker et al., 1968; Roffman, 1973, among others). Artificial weathering simulates natural weathering environments that are far removed from the higher temperatures and pressures in which most primary silicate minerals crystallized. Consequently, the minerals are unstable to varying degrees, and the hydrolysis, ion exchange, chelation, and other important weathering reactions are exothermic and spontaneous. Many of these spontaneous reactions occur simultaneously, involving a broad range of variables. Important independent variables that have been considered in past laboratory

simulations include 1) parent material, 2) weathering solution chemistry (particularly pH, dissolved salts, and organic acids) and weathering solution volume, and 3) design of the weathering system.

Parent Material

Crystal structure of the parent material is one of the overriding factors in determining the rate of ion release during weathering. Positive correlations have been found between mineral resistance to weathering and the number of Si-O-Si bonds (Bowen, 1928). Other studies have shown that minerals with less isomorphic substitution and fewer weak cation bonds tend to be more resistant (Keller, 1954, and others). These long-established relationships have been confirmed or modified only slightly in laboratory studies (Graham, 1950, among others) and field studies (Craig and Loughnan, 1964; Smith, 1962, among others).

Further evidence of the important role of parent material as a determinant of weathering rate is found in numerous studies that have been conducted on the relative mobility of ions out of their mineral lattice. Field studies by Tiller (1958), Feth et al. (1964), Hem (1970), and others, and laboratory studies by Keller, Balgord, and Reesman (1963), Ragland (1975), and others generally have shown that the order of cation mobility is $Ca > Na > Mg > K > Si > Al = Fe$ as originally proposed by Polynov (1937). Anderson and Hawkes (1958) found Mg to be most mobile. Mobility orders may be altered by weathering conditions, such as pH, Eh, or the presence of organic acids, but the influence of parent material on weathering rates is always apparent. Huang and Keller (1970) found that alumino-silicates weather

incongruently so that minerals within a given family with high percentages of mobile ions tended to be less stable than minerals in the same family with less mobile ions. Thus, Ca-feldspar weathered more readily than Na-feldspar (Goldich, 1938; Nash and Marshall, 1956; Burger, 1969). The relatively low position of K in Polynov's mobility series has usually been attributed to the tendency of K to become fixed in secondary minerals such as mica minerals or illite (Pickering, 1962; Loughnan, 1962). The mobility of Mg also can be hindered by fixation, especially in smectites (Hendricks and Whittig, 1968).

Cation concentration in streams also reflects the chemistry of parent material in the region drained. Simonson (1970) noted that most cation losses from a soil profile occur in the region of decomposing rock. He concluded that ions in stream water were derived primarily from parent material rather than soil.

Perhaps the strongest influence of the parent material chemistry is on the nature of the secondary clay minerals. Field work on a wide variety of basalts showed montmorillonite to be an early weathering product (Tiller, 1958; Craig and Loughnan, 1964, and others). Garrels (1967), Drever (1971), Tardy (1971), and others have shown stream chemistry to be related to clay mineralogy. The most widely used method of demonstrating this relationship has been through the application of phase diagrams (Feth et al., 1964, as well as others). Typical phase diagrams have shown equilibria among primary and secondary minerals of a given assemblage (Hess, 1966; Helgeson, Brown, and Leeper, 1969). Each mineral is represented by an area on the diagram in which the mineral is

stable for the corresponding concentrations of the ions being considered. When ion concentrations of stream water are plotted on such a diagram, the concentrations fall in the area of stability for the secondary clay minerals present in the region drained by the stream.

Mg and Fe montmorillonite dominate the clay fraction of Beaver Creek Watershed No. 12. Moderate to small amounts of kaolinite and trace amounts of vermiculite and mica are also present (Hendricks, 1976; Williams and Anderson, 1967). This clay mineral assemblage has been observed after moderate weathering of basic basalts on other sites (Fieldes and Swindale, 1954; Craig and Loughnan, 1964; Wilson, Bain, and McHardy, 1971, and others). However, as Wilson emphasized, there is no fixed order to the development of mineral weathering products. The products invariably depend on prevailing weathering conditions as well as parent material.

Weathering Solution

Weathering Solution Chemistry. The most widely used independent variable in laboratory weathering studies is the chemistry of the weathering solution. Water is the basic solvent for nearly every chemical weathering reaction. It supplies H^+ and OH^- ions in hydrolysis reactions, provides a solvent for organic chelating agents and salts, and carries away dissolved products. Even weathering by oxidation can occur in an aqueous environment (Keller, 1957).

Since most chemical weathering includes some degree of hydrolysis, the hydrogen ion concentration is an important aspect of the weathering solution. Much of the H^+ in the solution is supplied by CO_2

dissolving in rain water and from the soil where it is produced by microflora (Keller, 1957). Besides furnishing H^+ for hydrolysis and cation exchange, carbonic acid further contributes to silicate breakdown by taking Ca^{++} , Mg^{++} , and other ions out of the system in solution or by precipitation as carbonates.

The effects of changes in pH of the weathering environment have been observed in many studies. Nash and Marshall (1956), Correns (1961), Pickering (1962), Keller et al. (1963), Krauskopf (1956), Helgeson (1971), Huang and Keller (1972), and Marion et al., (1976) all observed increased solubility of silicates (congruent or incongruent) with decreasing pH. Keller et al. (1963) pulverized rock-forming silicates in water and CO_2 -charged waters with lower pH. They found that all cation concentrations, except Fe, were higher in solutions charged with CO_2 than in deionized water. Fe was apparently immobilized in a residual ferric oxide. They noted little change in the concentration of Al between water and CO_2 -charged water.

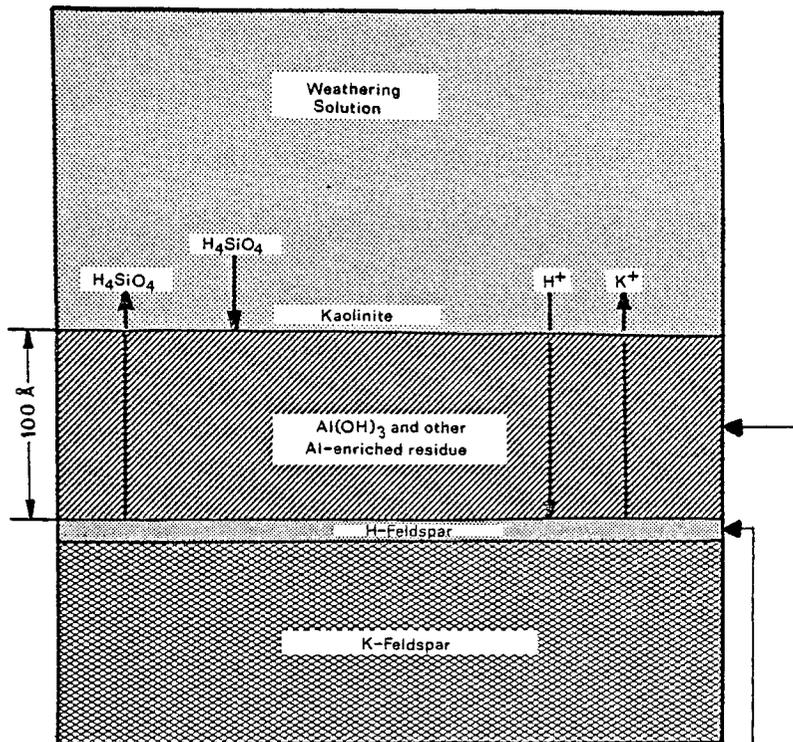
The effect of changes in pH on SiO_2 solubility was uncertain for many years. Krauskopf (1956) confirmed earlier indications that the solubility of amorphous silica does not change appreciably between pH 0 and 9. Al was found to be soluble below pH 4 and above 10. Krauskopf (1956) also showed that the presence of Na or K ions had no effect on Si solubility. Keller et al. (1963), on the other hand, found a slight increase in dissolved Si when Na^+ and K^+ were present.

Although the solubility of amorphous silica is constant as pH's that characterize natural environments, Pickering (1962) emphasized that

the silicate mineral structure is most readily broken down by solutions of low pH. The specific role of H^+ ions in weathering appeared to be in disrupting the silicate lattice by displacing cations and exposing the inner layers of the crystal to further weathering, and by affecting the solution of cations or precipitation of those in solution. The precise mechanism has been the object of long-standing controversy. Early mechanisms of hydrolysis were proposed by Jenny (1950), Fredrickson (1951), DeVore (1959), and Coleman (1962).

Much evidence gathered in artificial weathering experiments supports a hydrolysis reaction in which an Al-enriched surface layer developed (Nash and Marshall, 1956; Correns, 1961; Pickering, 1962). As the removal of soluble cations proceeded on the surface of fresh aluminosilicate minerals, the more immobile ions, particularly Al, were concentrated in a thin, residual surface layer. The mathematics of a diffusion mechanism by which displaced cations are moved into the weathering solution through an Al-enriched layer of increasing thickness were developed by Wollast (1967), Helgeson (1971), Berner (1971), and others. Wollast (1967) predicted and observed a decrease and leveling off of the weathering rate due to the growth of the layer. These observations were consistent with the diffusion model.

Once the displaced ions, including Si^{+4} , were in the weathering solution, they recombined with the $Al(OH)_3$ layer, depending on their concentration (Fig. 1). By continually replacing the ions in solution with fresh water, Berner (1971) observed how an open system would result in the formation of gibbsite from albite. The more slowly the weathering



Weathered zone where H^+ has substituted for K^+ , leaving unstable H-feldspar

Al-enriched zone where some Al precipitates as $Al(OH)_3$, some substitutes for H^+ , and some persists in mineral framework remnants

Fig. 1. Experimental Feldspar Weathering Model of Wollast (1967) after Berner (1971).

solution moved, the more cations were available for recombination in secondary clay minerals. A moderate flow might have produced kaolinite from albite; an even slower rate or stagnant weathering solution might have yielded montmorillonite.

Helgeson (1971) showed that lowering the pH increased the thickness of the Al-enriched layer and, thus, impeded further weathering. Loughnan (1969) agreed that pH played an important role in weathering, but emphasized that H^+ concentration was not an independent variable in natural environments. Rather, it was a function of several interrelated factors that included the chemistry of the parent material, the rate of leaching of the bases, and the cation exchange capacity of the residual mineral products.

Weathering Solution Volume. The volume of weathering solution in contact with parent material is a major factor in affecting weathering rates and secondary mineral genesis as noted above. Most experimental work has been conducted with large volumes of solution. Pedro (1961) passed the equivalent of nearly 40 inches of rainfall per day over parent material for two years. Very little work has been published describing the effects of periodically withdrawing all weathering solution to simulate the inevitable alternations between wetting and drying that occur in natural systems.

Roffman (1973) simulated an arid climate where periodic evaporation occurs by alternate leaching and drying of several silicate minerals. She observed calcite and montmorillonite deposits in pores and along mineral cleavage planes. She concluded that ions dissolved

from rocks where evaporation exceeds precipitation were moved to the outer surfaces by capillary forces in the pores. She also observed formation of some ferric oxyhydroxides. Whether wetting and drying significantly altered weathering rates was not determined.

Experiments in which clay soils were leached and subjected to drying or heating showed definite effects. Coleman (1962) wetted Al-clays with CaCl_2 solution and after repeated cycles of drying and wetting found Ca to be lost from the solution and an equivalent amount of Al moving from exchange sites to Al_2O_3 . This was explained as an Al hydrolysis reaction.

Acquaye and Tinsley (1965) observed an increase in SiO_2 solubility in soils that had been dried before they were leached with water. These soils had been sampled after a warm, wet summer. A second set of soils showed the reverse effect after drying. These soils had been sampled after a long, cold winter. The effects of microorganisms appeared to be the cause of the phenomena.

McKenzie (1963) wetted and heated montmorillonite and observed adsorption of some ions (notably K^+ and Mg^{++}). Entrapment of the ions in surface pores was a possible explanation.

Most observations seemed to indicate that the effects of wetting and drying were either physical in nature or related to organisms. Weathering rates of partially weathered silicates with some clay coating could have been increased by wetting and drying. As Roffman (1973) suggested, wetting and drying could accelerate weathering by oxidation of iron-bearing silicates, especially if appreciable amounts of ferrous

minerals are present. Changes in Eh to create an oxidizing environment were shown to increase the weathering rates of Fe-bearing silicates (Beadle and Burgess, 1953).

Artificial Weathering System Designs

Laboratory experiments that have attempted to simulate silicate mineral weathering have been performed in closed or open systems. In open systems, weathering solutions are percolated through the mineral samples and removed or recycled. Open systems with leaching apparatus have generally been considered more reliable simulations of natural weathering environments than the closed systems in which mineral samples are shaken with a solution in a closed container. The removal of dissolved ions in open systems yields leachates with ion concentrations that more closely approximate the ion concentrations of most natural waters. Also, the ratio of solid to solution has been higher in open systems and in nature than in closed systems (Correns, 1961; Wollast, 1967). There are situations in nature where water movement below the soil is slow or stagnant. Recycling of the weathering solution was used by Carroll and Starkey (1959) to simulate that effect. Pedro (1961) and Parham (1969) used a recycling apparatus and observed halloysite on K-feldspar within five months.

Huang and Kiang (1972) used a closed system, recognizing that it did not simulate the natural environment as well as a leaching-type open system. However, they believed that the micro-environments of the immediate weathered surfaces were essentially a closed system, even in nature. In all closed system experiments, the advantages of accelerating

slow reactions and simpler apparatus have been apparent. Wollast (1967) found the closed system appropriate for studies of equilibrium reactions and diffusion through the residual layers that may develop on the weathering surface. Some questions have been raised whether calculations requiring equilibrium constants are applicable to open systems in a steady state (Marion et al., 1976). Thompson (1970) and Marion et al. (1976) note that under some steady-state conditions equilibrium relationships will apply, particularly if the reactions are fast enough or the time allowed for the reaction is long enough. Johnson (1971) referred to "steady-state" or dynamic equilibrium conditions of the open system as opposed to the true equilibrium of closed systems.

The natural weathering mechanism itself is possibly more closely simulated by an open system. As noted above, a residual layer may develop on the weathering surface and play a role in controlling the rate of release of dissolved ions. Wilson (1975) suggested that the layer may develop differently in nature (if at all) than in the closed systems where it has been most clearly observed. If different mechanisms are involved, the use of open systems may be necessary in experiments where simulation of natural weathering is important. Whether or not the Al-enriched layer forms in open systems and in nature still seems uncertain. Correns (1961) believed an enriched layer does develop in open system weathering. Parham (1969) showed that halloysite developed on K-feldspar in a pattern nearly identical to halloysite

formation in nature. However, the pattern was not entirely consistent with "enriched layer" theory.

All laboratory simulations are implicitly correlated with several features of a specific natural system. But for all of the discussion on the most valid methods of laboratory simulation of rock weathering, relatively few studies have made a concerted effort to correlate field data with laboratory weathering experiments. Tamm's 1924 experiments described by Keller (1957) set up early weathering experiments that were performed under conditions relating to specific field studies of weathering environments and products. Feth et al. (1964), Tardy (1971), and others have correlated thermodynamic data with field observations. Parham (1969) related clay mineral formation in the laboratory with natural weathering processes. Additional work correlating laboratory and field work could help to resolve some of the questions raised recently regarding the mechanism of residual layer formation on weathering feldspar surfaces (Wilson, 1975), as well as establish the validity of certain weathering models.

MATERIALS AND METHODS

The simulated "parent material" in this experiment was prepared from olivine basalt rocks collected at random from Beaver Creek Watershed No. 12 south of Flagstaff, Arizona. The rocks were fractured into small fragments (5-10 mm in diameter) and the weathered surfaces were discarded. The unweathered fragments were ground into a powder in a Spex mixer-mill using tungsten carbide grinding vials. All particles greater than 50 microns in diameter were removed with a 300 mesh screen. Particles less than 10 microns were removed by sedimentation-decantation using methyl alcohol rather than water to avoid weathering during separation. The elemental analysis of the 10-50 micron basalt particles is given in Column A of Table 1.

Forty grams of the basalt powder were placed in Nalgene polypropylene filter funnels (Figure 2) and treated with three weathering solutions of varying pH prepared from deionized water and carbon dioxide. Treatment 1 was deionized water with pH 7.0. Treatment 2 was prepared by bubbling CO₂ through deionized water until the solution was saturated at approximately pH 4.5. Treatment 3 was prepared by bubbling CO₂ through deionized water for brief periods until pH 5.5 was reached.

Each weathering solution was applied to the ground basalt on two different schedules. On Schedule 1, 12 ml of solution (enough to fill all pore spaces in the powder) was added directly to the basalt, which was permitted to soak for 24 hours. The solution was then drawn out of

Table 1. Elemental Analyses and Molar Ratios of Oxides for Fresh and Weathered Basalt Powder.

	Weathered Samples ^b					
	A Fresh Olivine Basalt	B T1S1	C T1S2	D T2S1	E T2S2	F T3S1 G T3S2
	----- (Percent) -----					
SiO ₂	46.9	46.6	46.5	46.1	45.8	46.1
Al ₂ O ₃	14.9	14.4	15.0	15.1	15.6	14.9
Fe ₂ O ₃	3.3	3.4	(10.9) ^c	3.1	3.2	(10.6) ^c
FeO	7.4	7.5	--	7.4	7.0	--
TiO ₂ ^a	1.2	1.2	1.2	1.2	1.2	1.2
CaO	10.1	10.1	9.5	9.6	9.6	9.3
MgO	8.7	9.1	9.2	8.6	8.9	9.0
Na ₂ O	4.1	4.0	4.3	4.0	3.8	4.2
K ₂ O	1.0	1.0	1.0	1.0	0.9	1.1
P ₂ O ₅	0.4	0.4	0.4	0.4	0.5	0.4
H ₂ O	1.1	1.2	1.0	1.1	0.9	1.4
Total	<u>99.1</u>	<u>98.9</u>	<u>99.0</u>	<u>97.6</u>	<u>97.4</u>	<u>98.2</u>
Molar sa ratio	5.34	5.49	5.26	5.18	4.98	5.25
Molar sa ratio weathered samples	--	1.03	0.99	0.97	0.93	0.98
Molar sa ratio basalt						
Molar ba ratio	3.24	3.41	3.25	3.11	3.03	3.21
Molar ba ratio weathered samples	--	1.05	1.00	0.96	0.94	0.99
Molar ba ratio basalt						
						3.27

^aTiO is relatively immobile and assumed constant; chemically analyzed for fresh basalt only.
^bT1 = weathering solution Treatment 1 (pH 7.0); T2 = weathering solution Treatment 2 (pH 4.5); T3 = weathering solution Treatment 3 (pH 5.5); S1 = weathering Schedule 1 (continuous weathering); S2 = weathering Schedule 2 (alternating wetting and drying).
^cTotal Fe as Fe₂O₃.

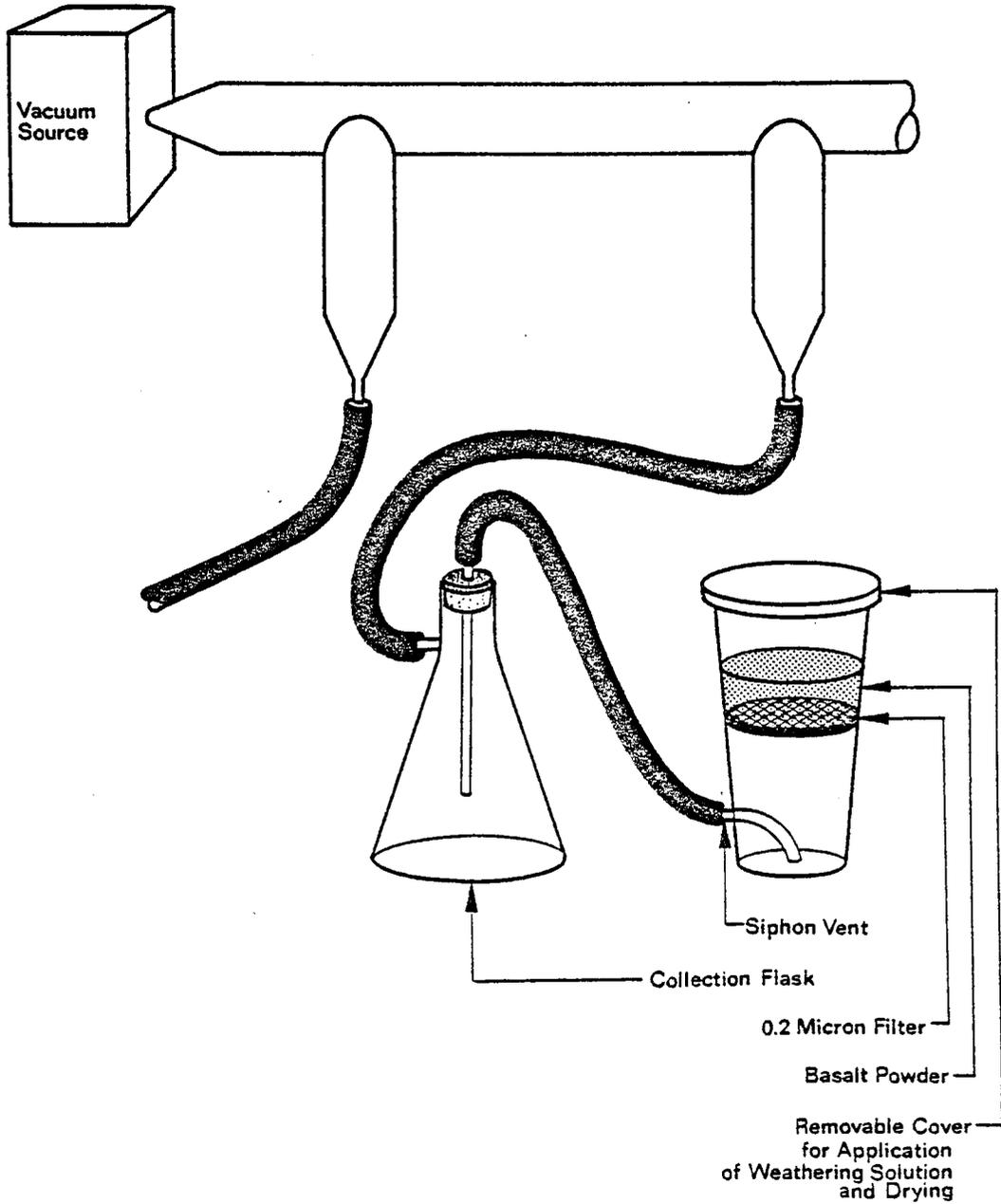


Fig. 2. Artificial Weathering Apparatus.

the filter by a vacuum of 55 mm, reapplied to the basalt powder, which again soaked for 24 hours. After the second 24-hour period, the solution was again withdrawn, reapplied, and permitted to soak the powder for a third 24-hour period. These three 24-hour periods constituted one 72-hour weathering cycle. The 72-hour cycle was used to maximize exposure of the powder to the solution, better simulating the relatively slow water infiltration that characterizes the Beaver Creek environment.

At the end of each 72-hour cycle, the solution was drawn out of the filter and measured for pH and concentration of cations. A fresh 12-ml aliquot was immediately applied, thus initiating the next 72-hour cycle.

Weathering Schedule 2 differed from Schedule 1 only in that the weathering process on Schedule 2 was periodically interrupted by dessication of the basalt powder. After 18 days of continuous weathering (six 72-hour cycles), the filters on Schedule 2 were permitted to air dry for three days before the next aliquots of solution were applied. Both schedules were replicated three times for each treatment.

Leachates from each treatment on both schedules were collected after each 72-hour cycle in polypropylene bottles. The concentration of Ca, Mg, Na, K, and Fe in each leachate and its associated blank were determined by atomic absorption analysis (Angino and Billings, 1967). The concentration of Al and Si (and Ti in the rock analysis) were determined spectrophotometrically as described by Hendricks (1972) and Jackson (1958).

The weathering experiment continued for twenty-eight 3-day cycles. At the end of the experiment, samples of weathered powder from all treatment-schedule combinations, as well as the fresh basalt, were subjected to x-ray diffraction analysis to determine the mineralogical make-up before and after weathering. X-ray diffraction analyses were made with a Phillips diffractometer and Cu K_α radiation. Cu K_β radiation was eliminated and background noise was reduced with a curved crystal (graphite) diffracted beam monochromator. Fresh basalt and weathered residue powders were packed into aluminum sample holders for analysis. An elemental analysis was also made of the fresh and weathered basalt. An NaOH fusion method was used to prepare the Al and Si for colorimetric analysis on a Coleman, Jr., IIA Spectrophotometer. The hydrofluoric-perchloric acid dissolution method was used to prepare the fresh and weathered powders for atomic absorption analysis of Ca, Mg, Na, K, and total Fe concentration (Jeffery, 1970).

Ferrous iron was determined by selectively chelating Fe^{++} and measuring the concentration photometrically (Jeffery, 1970). The Fe^{+++} was determined by subtracting the Fe^{++} from the total iron in the elemental analysis. Phosphorous concentration was also determined spectrophotometrically by the method of John (1970). Loss on ignition was determined by heating the basalt sample at 950°C for two hours. This is reported as the H_2O content in Table 1.

A HYPOTHETICAL MODEL OF CHANGES IN WEATHERING RATE

As artificial weathering proceeds, the concentration of nutrient ions in the outgoing weathering solution is expected to decline. A decrease in concentration is consistent with results of weathering experiments by Burger (1969), Roffman (1973), Huang and Keller (1970), and others. Assuming that the decrease in concentration over time is comparable to similar processes of silicate dissolution in nature, the concentration of ions in the outgoing solution should approach nearly constant, steady-state concentrations. Therefore, the changing ion concentration over time can be theoretically described by an exponential equation in which the asymptote represents the steady-state concentration of a specific ion. Equation (1) is a general regression equation applied to data approaching a lower asymptote (Draper and Smith, 1968):

$$\hat{Y}_i = \alpha + e^{-\gamma t + \beta} \quad (1)$$

where \hat{Y}_i is the concentration of ion i in the outgoing weathering solution at time t , α is the predicted concentration at the steady state, γ is a coefficient of t which determines the rate of decline in concentration of ion i , and β determines the concentration of ion i as weathering begins. The value of $\alpha + e^{\beta}$ represents the y -intercept at time zero. The effect of β declines as t increases. Equation (1) appears to be an appropriate model for weathering rates that approach constant values over time. Its application to the weathering process provides a

convenient means of comparing the effects of pH and intermittent desiccation on the system. Three such comparisons are of particular interest:

1. Changes in the value of γ (steepness of ion concentration curve) as schedule and pH of weathering treatment change.
2. Changes in the value of α with changes in weathering treatments and schedules.
3. Differences in $\sum_{t=1}^f Y_{i,t}$, the cumulative weathering of i during the experiment from time $t=1$ to $t=f$, the final time period.

Assuming a significant correlation between experimental values of i concentration and \hat{Y}_i and assuming that this experimental system at least partially simulates the natural weathering process, a relationship should exist between the experimental values of Y_i at $t=f$, and the actual concentration of i in the streams of the Beaver Creek area. Laboratory formation of secondary clay minerals that also characterize the Beaver Creek Watershed may provide some evidence of this relationship.

RESULTS

The effect of chemical weathering on rock composition is often measured by comparing ratios of relatively mobile ions such as Ca, Na, and even Si to immobile ions such as Al in fresh and weathered rocks. The molar sa ratio and the molar ba ratio are typical of these comparisons (Birkeland, 1974):

$$\text{molar sa ratio} = \frac{\% \text{ SiO}_2 \text{ in sample} \div \text{m.w. SiO}_2}{\% \text{ Al}_2\text{O}_3 \text{ in sample} \div \text{m.w. Al}_2\text{O}_3}$$

$$\text{molar ba ratio} = \frac{\frac{\% \text{ CaO}}{\text{m.w. CaO}} + \frac{\% \text{ MgO}}{\text{m.w. MgO}} + \frac{\% \text{ Na}_2\text{O}}{\text{m.w. Na}_2\text{O}} + \frac{\% \text{ K}_2\text{O}}{\text{m.w. K}_2\text{O}}}{\frac{\% \text{ Al}_2\text{O}_3}{\text{m.w. Al}_2\text{O}_3}}$$

where m.w. is molecular weight. As weathering proceeds, Si and the four bases are removed more readily than Al, so sa and ba ratios generally decline. For example, the sa ratio of a California olivine andesite declined from 5.79 in fresh rock to 3.47 in a slightly weathered saprolite of the andesite (Hendricks and Whittig, 1968). The ratio of the sa value of the slightly weathered saprolite to the sa value of the rock was 0.60. Table 1 gives the elemental analysis and the sa ratios of the Beaver Creek olivine basalt and the artificially weathered samples. Any decline in the sa ratios by virtue of weathering treatments is far less than the decline in even the slightly weathered andesite reported by Hendricks and Whittig (1968).

The molar ba ratio in the California andesite declined 26% in the slightly weathered saprolite. This decline contrasts to the data in Table 1 where, as in the case of sa ratios, there is little or no decline in the ba ratios of the weathered basalt samples. It is difficult to show that there has been any significant chemical weathering based on the results of the elemental analysis. Therefore, the more sensitive methods of x-ray diffraction and direct measurement of rates of ion removal have been applied to determine the extent of weathering occurring before significant changes in sa and ba ratios.

X-Ray Diffraction

Fig. 3a shows the x-ray diffraction patterns for a powdered sample of the unweathered basalt. In the complex combination of minerals, minerals with two or three intense peaks are likely to overlap, making identification difficult. For example, the peak at $d = 2.52 \text{ \AA}$ could indicate either olivine or augite. Both are present according to the microscopic analysis presented in Table 2. D-spacing tables list a fayalite peak (an iron-rich olivine) at $d = 2.51 \text{ \AA}$ and an augite peak of relatively high intensity at $d = 2.53 \text{ \AA}$ (Borg and Smith, 1969). Others are more easily isolated, such as the peak at $d = 3.21 \text{ \AA}$, which most likely corresponds to a plagioclase.

Fig. 3b is the diffraction pattern for basalt weathered continuously for 34 cycles (102 days) with CO_2 -charged water at pH 4.5 (Treatment 2). There are two distinct differences between Figs. 3a and 3b. The two peaks at $d = 2.03 \text{ \AA}$ and 2.35 \AA in Fig. 3a are absent in Fig. 3b. No mineral in the d-spacing tables of Borg and Smith (1969),

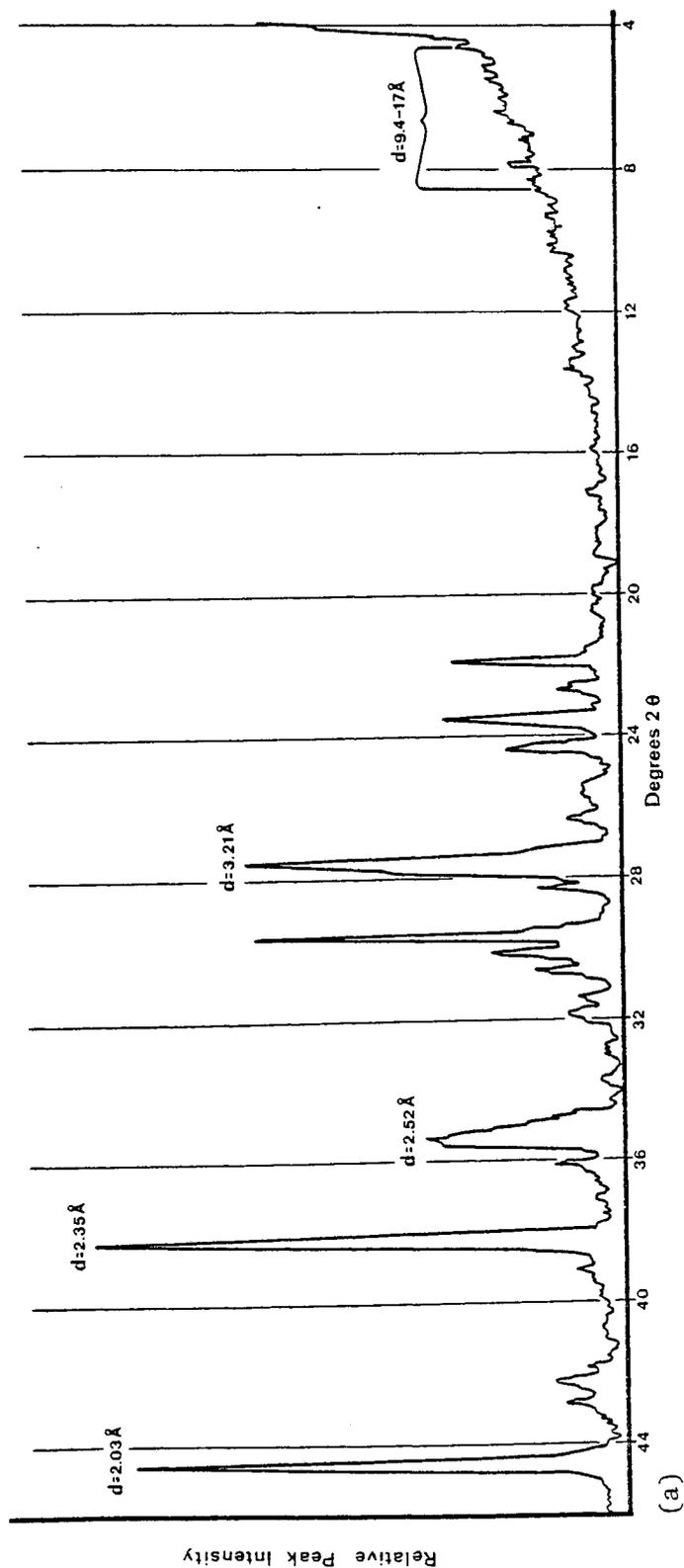


Fig. 3. X-Ray Diffraction Patterns for Fresh Powdered Basalt and Weathered Basalt Powder (Cu $K\alpha$ Radiation). -- θ equals the incident angle of the beam of x-rays with wavelength λ and d equals the distance between planes of atoms in the crystal lattice. θ and d -spacing are related by Bragg's law: $n\lambda = 2d \sin \theta$, where $n =$ the order of the diffraction. Due to the geometry of the goniometer of the diffractometer, the diffractogram is measured in terms of 2θ for convenience.

(a) X-ray diffraction pattern: fresh powdered basalt.

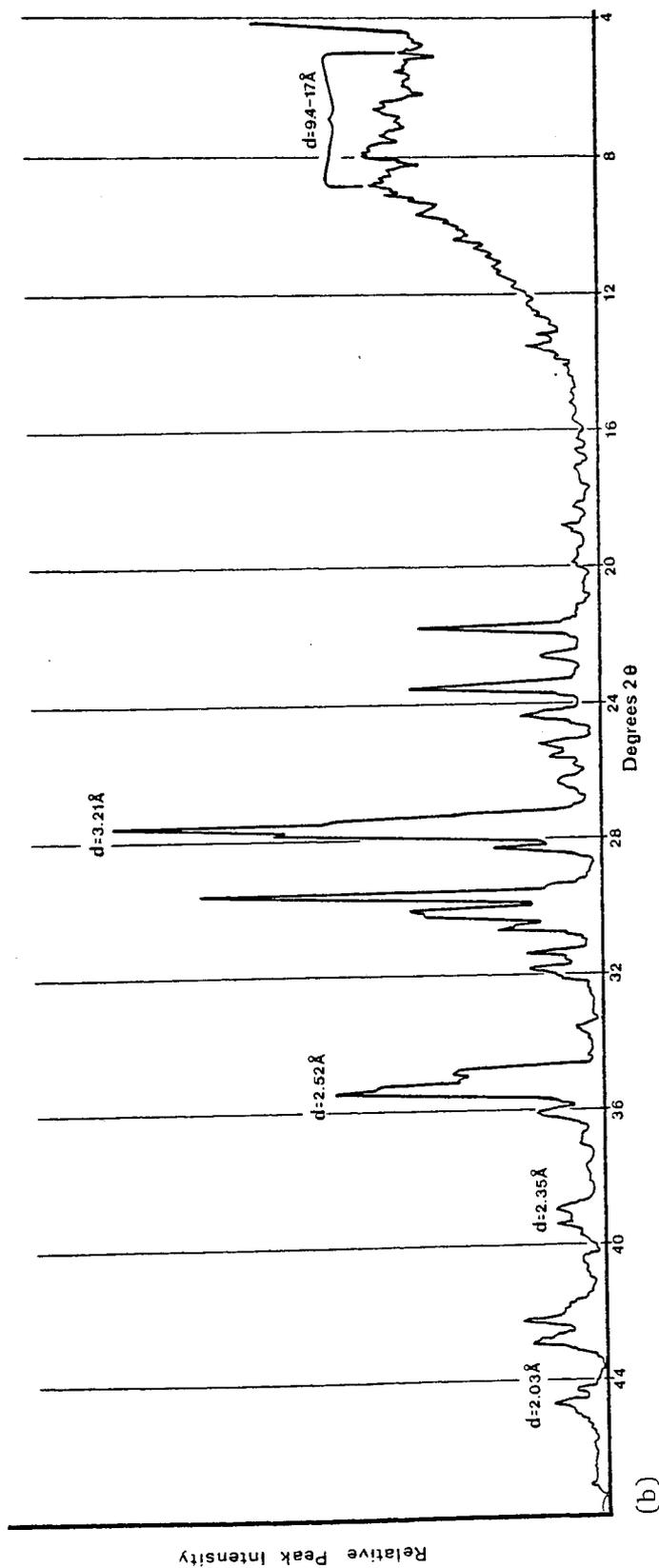


Fig. 3. X-Ray Diffraction Patterns for Fresh Powdered Basalt and Weathered Basalt Powder (Cu K_{α} Radiation). -- Continued.

(b) X-ray diffraction pattern: weathered basalt powder (Treatment 2-Schedule 1).

Table 2. Average Modal Analysis of Plateau Basalts from Beaver Creek Watersheds 12-2 and 12-3. -- From Beus, Rush, and Smouse (1966). Olivine and augite phenocrysts are present.

Mineral	Percent
Labradorite	45
Augite	25
Olivine	15
Magnetite	6
Glass	9

or Deer, Howie, and Zussman (1962) corresponds to those peaks. They may have been impurities, although they appeared consistently in all x-rays of the unweathered basalt.

The second difference is the appearance of several undifferentiated peaks between $d = 9.41 \text{ \AA}$ and $d = 16.99 \text{ \AA}$ of Fig. 3b. These do not occur in the unweathered sample. They are particularly significant because they fall in the range where many of the first-order basal plane diffraction peaks of the secondary clay minerals occur. Air-dried montmorillonite minerals show peaks in the range of $d = 14-15$. X-ray diffraction patterns also were run on samples weathered by solutions of deionized water (Treatment 1) and CO_2 -charged water at pH 5.5 (Treatment 3). The pattern of undifferentiated peaks in the clay range was observed for the pH 5.5 treatment, but not for the samples weathered with the pH 7.0 treatment.

Rates of Ion Removal as a Measure of Weathering

The Main Effects of Treatment and Schedule

Table 3 shows the concentration of seven ions removed from the powdered basalt at selected times during the experiment. The basalt was weathered by three different treatments on two different schedules or six different treatment-schedule combinations. These are:

1. T1S1 Treatment 1 (pH 7.0), Schedule 1 (continuous weathering).
2. T1S2 Treatment 1, Schedule 2 (alternating wetting and drying).
3. T2S1 Treatment 2 (pH 4.5), Schedule 2.
4. T2S2 Treatment 2, Schedule 2.

Table 3. Ionic Concentrations of Outgoing Weathering Solutions as a Function of Treatment and Schedule at Selected Times (Combined Means).^a

Ion	Treatment	Number of Weathering Cycles ^b					
		1	3	5	10	20	28
		(ug per ml)					
Mg	T1	27.1	18.1	10.9	10.1	9.2	9.5
	T2	25.3	24.5	22.2	17.4	11.1	11.1
	T3	24.9	20.4	13.6	10.8	7.9	9.6
Na	T1	--	50.0	30.1	15.9	9.2	7.1
	T2	--	53.6	36.3	16.9	8.8	6.1
	T3	--	52.1	33.4	15.8	8.0	5.8
K	T1	6.0	4.1	2.9	1.8	1.7	1.5
	T2	6.4	4.8	4.1	2.3	1.9	1.6
	T3	6.2	5.1	3.4	2.0	1.6	1.4
Ca	T1	21.7	12.0	8.6	5.7	7.9	9.8
	T2	23.8	23.9	16.8	11.4	9.9	14.1
	T3	20.3	15.7	10.5	8.5	7.4	11.8
Fe	T1	0.9	0.02	0.02	0.0	0.04	-0.1
	T2	1.0	0.0	0.06	0.1	-0.1	0.04
	T3	0.5	1.3	0.1	0.03	-0.2	-0.04
Al	T1	0.1	0.4	0.2	0.0	0.0	0.1
	T2	0.1	0.4	0.3	0.0	0.0	0.2
	T3	0.1	0.4	0.2	0.0	0.0	0.1
Si	T1	2.4	13.1	13.1	12.6	11.8	11.0
	T2	2.6	12.8	11.5	9.6	10.3	12.3
	T3	2.8	13.1	12.4	9.1	9.4	10.4
	Schedule						
Mg	S1	25.7	20.3	17.5	13.1	7.4	10.3
	S2	25.8	21.6	13.6	12.5	10.4	10.5
Na	S1	--	49.2	33.2	17.4	7.5	6.1
	S2	--	54.6	33.3	15.0	9.8	6.6
K	S1	6.0	4.4	3.3	1.8	1.5	1.4
	S2	6.4	4.6	3.6	2.3	1.8	1.5
Ca	S1	22.0	17.8	14.4	9.5	5.9	10.7
	S2	21.9	16.6	9.4	5.9	11.0	13.0
Fe	S1	0.8	-0.03	0.1	0.01	-0.1	-0.1
	S2	0.8	0.03	0.1	0.10	-0.1	0.04
Al	S1	0.2	0.5	0.2	0.0	0.0	0.3
	S2	0.0	0.3	0.3	0.0	0.0	-0.1
Si	S1	2.8	13.6	12.3	13.1	10.9	9.3
	S2	2.4	12.4	11.8	10.0	10.0	13.1

^aTreatments are main treatment effects from combining schedule means (i.e., T1 = mean of T1S1 and T1S2); schedules are main schedule effects from combining treatment means (i.e., S1 = mean of T1S1, T2S1, and T3S1).

^bOne weathering cycle = 72 hours.

5. T3S1 Treatment 3 (pH 5.5), Schedule 1.

6. T3S2 Treatment 3, Schedule 2.

In Table 3, the values of ion concentrations in the six outgoing weathering solutions have been combined to show the main effects of the three treatments and two schedules.

Figs. 4-10 illustrate the changes in rate of removal of the cations from the basalt for each treatment (schedules combined) and schedule (treatments combined). Data representing the removal of Mg, Na, and K as a function of number of weathering cycles (Figs. 4-6, respectively) have been fitted with Equation (1) to produce the regression curves shown. The α , β , and γ values for the curves for each ion are presented in Table 4. An analysis of variance was performed on these values. Significant differences among the α 's, β 's, and γ 's at the 0.05 level are shown in Table 4, as are the r^2 values for the curves. The high r^2 values indicate that Equation (1) was a good predictor of Mg, Na, and K concentrations in the outgoing solutions. No significant regression curves could be drawn through the data points representing removal of Fe, Al, and Si in these weathering experiments (Figs. 8-10).

A rapid decline in the Mg, Na, and K concentrations in the outgoing solutions was observed during the first 10-12 weathering cycles (Figs. 4-6) with all treatments and schedules. This period was followed by a gradual decline in the rate of weathering approaching a relatively constant rate for the duration of the experiment. Whether this constant rate simulates the relatively stable concentration of nutrient cations in stream water observed by Johnson et al. (1968) is uncertain. However,

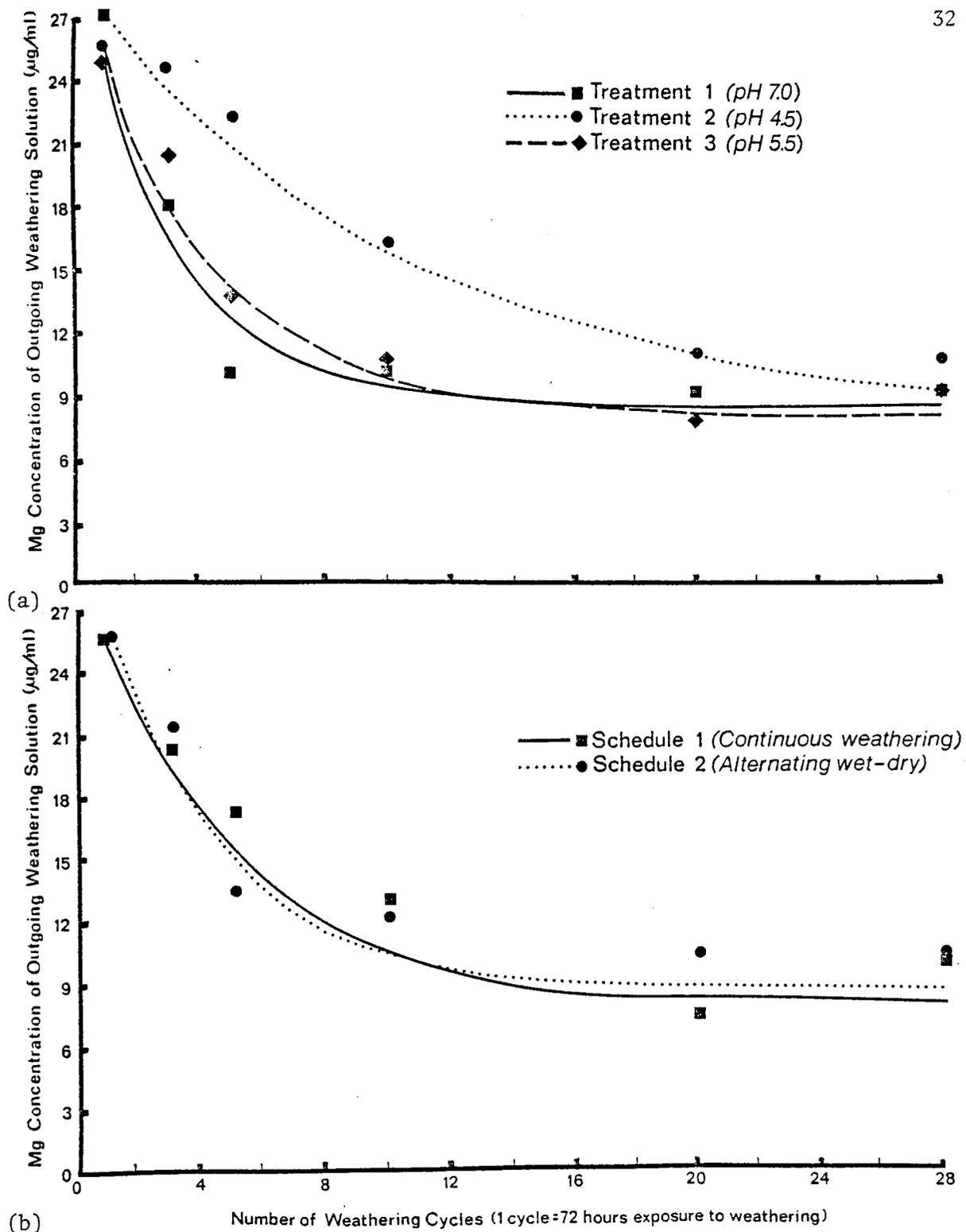


Fig. 4. Mg Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles).

(a) Treatment; (b) schedule.

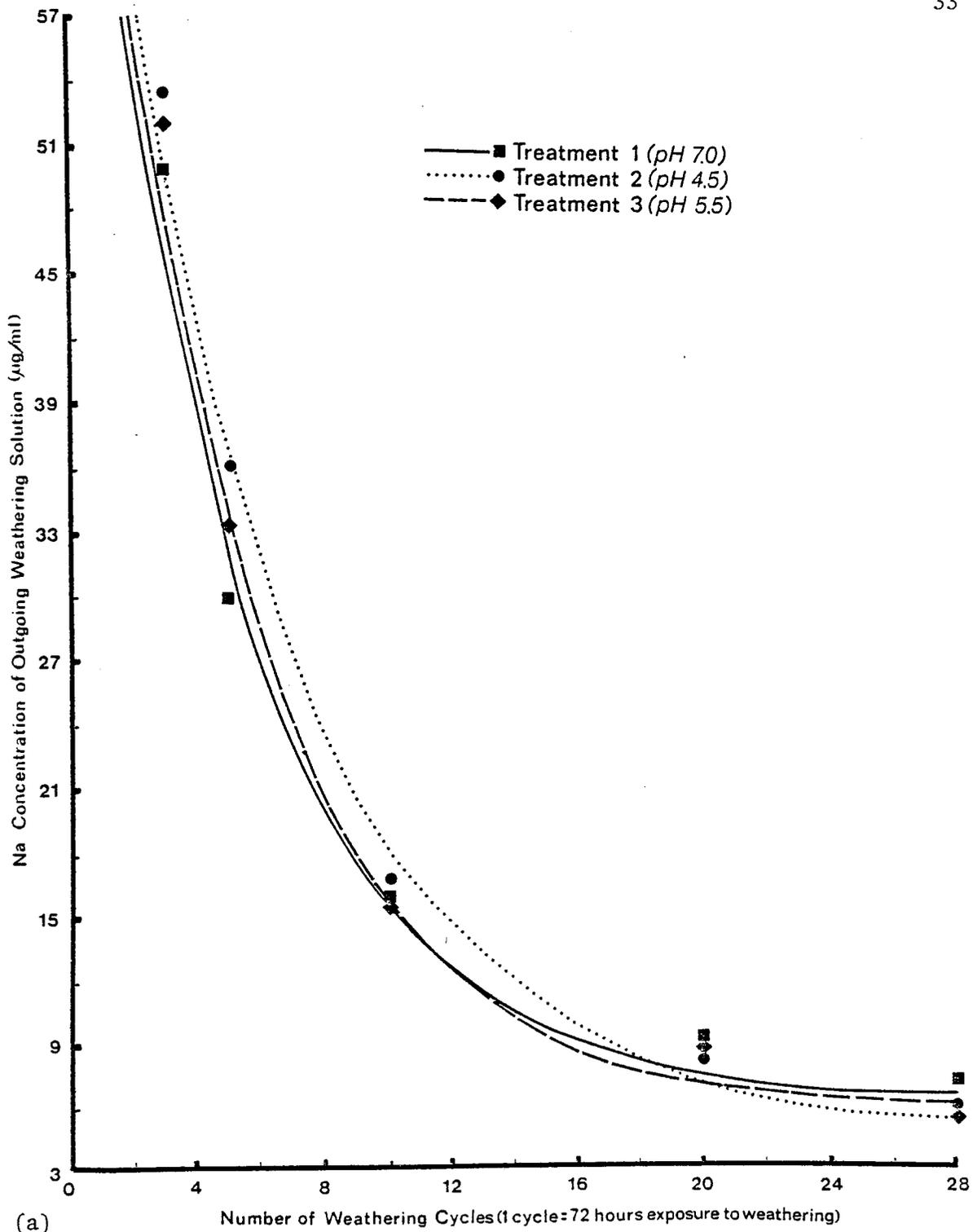


Fig. 5. Na Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles).

(a) Treatment.

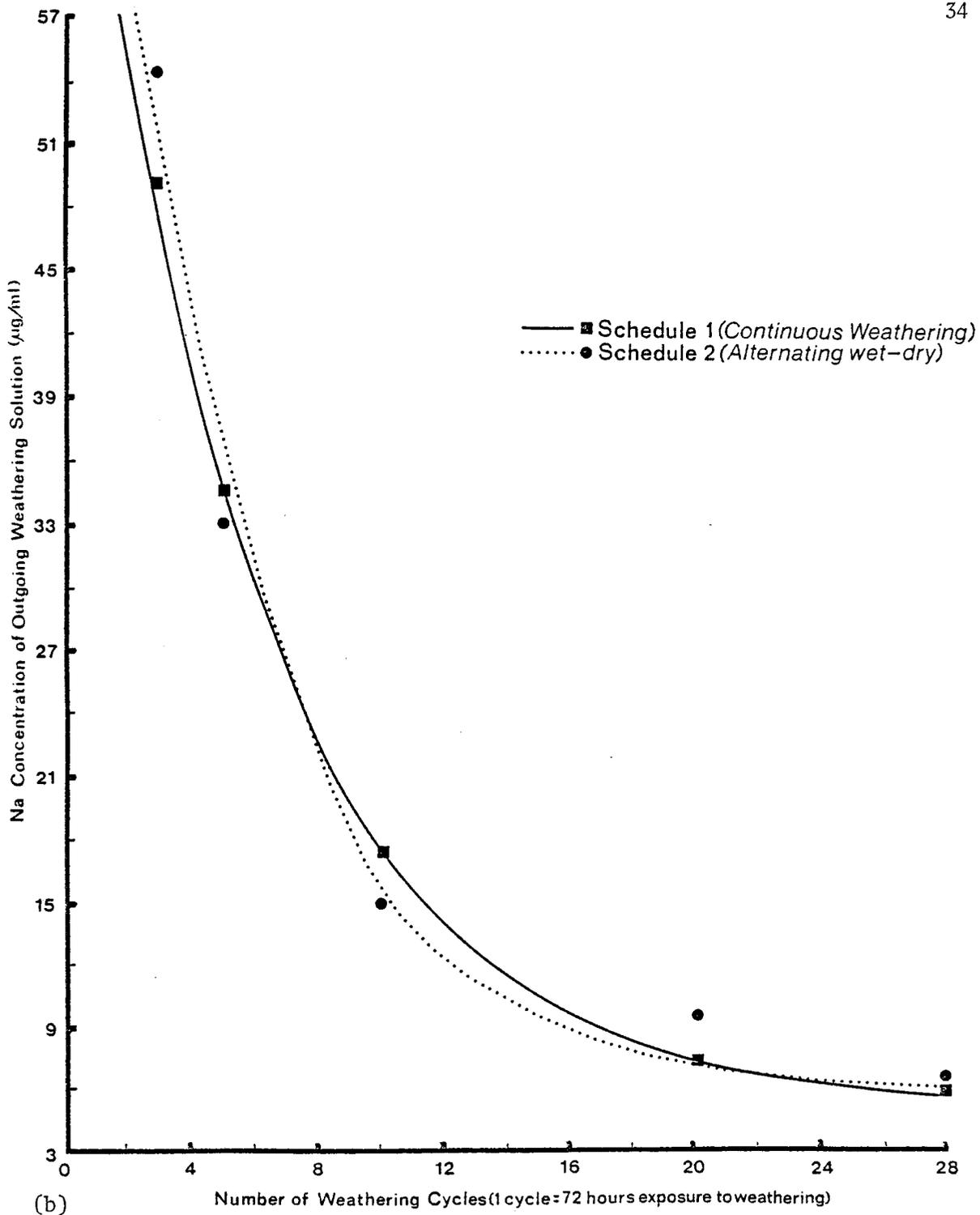


Fig. 5. Na Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles). -- Continued.

(b) Schedule.

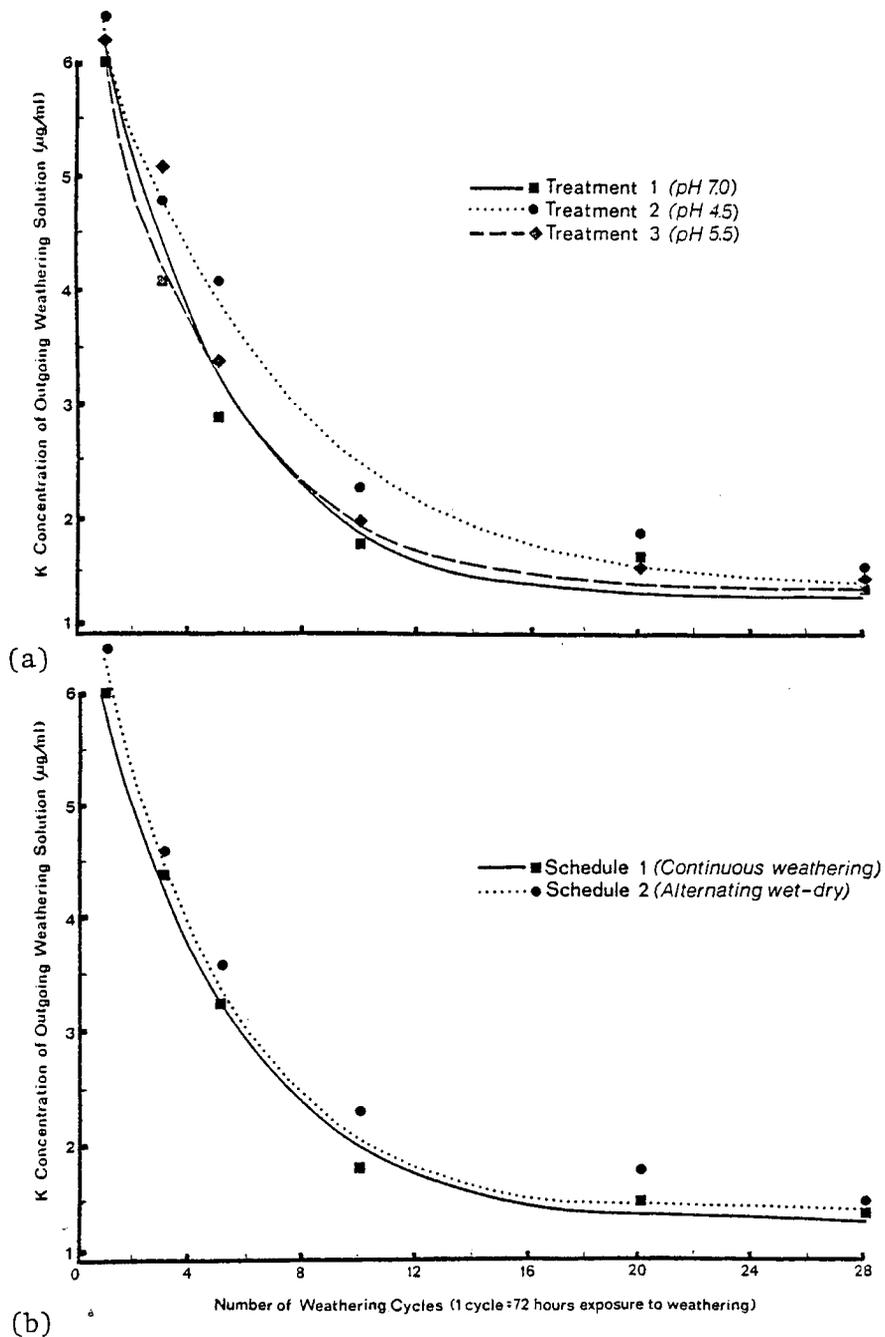


Fig. 6. K Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles).

(a) Treatment; (b) schedule.

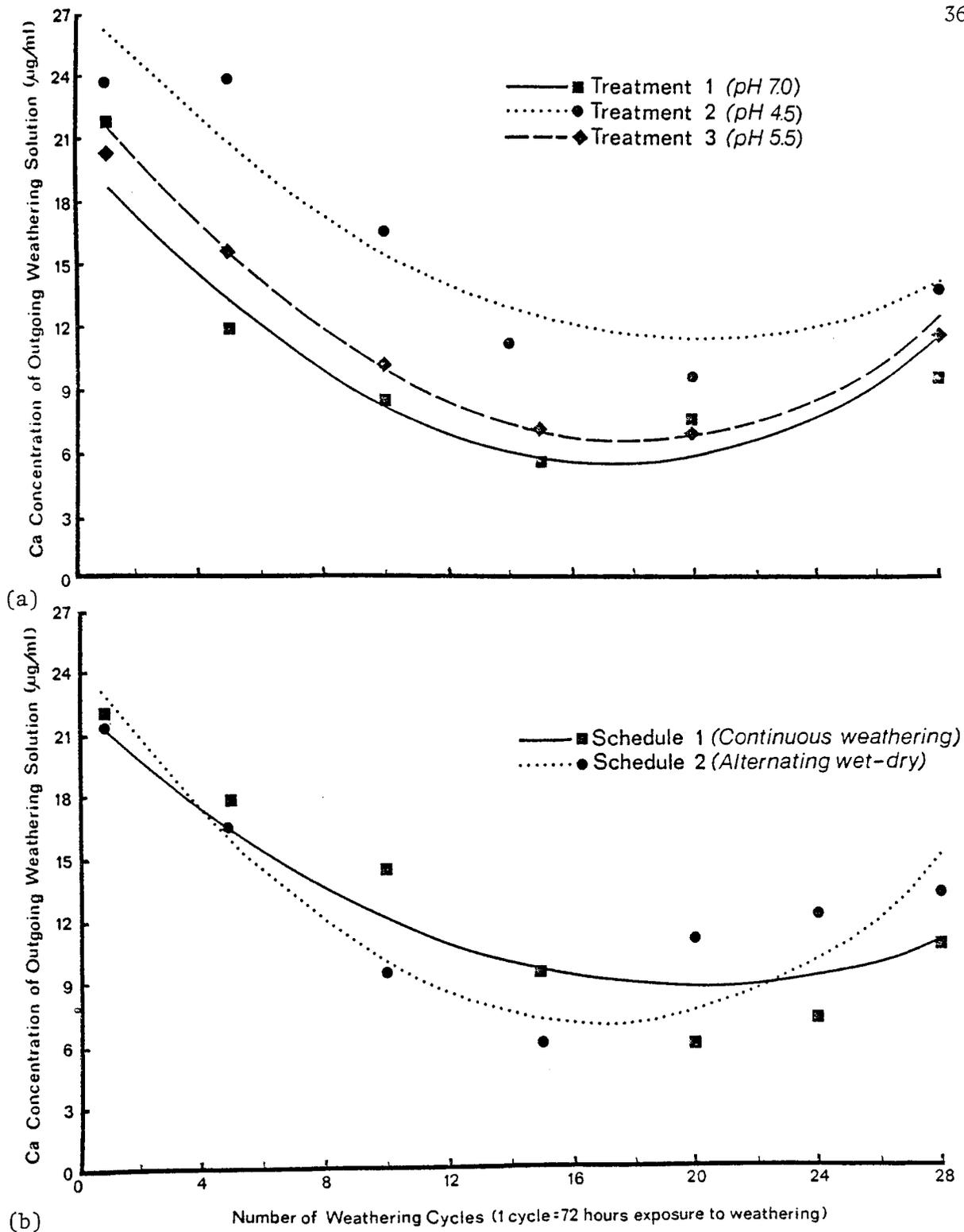


Fig. 7. Ca Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles).

(a) Treatment; (b) schedule.

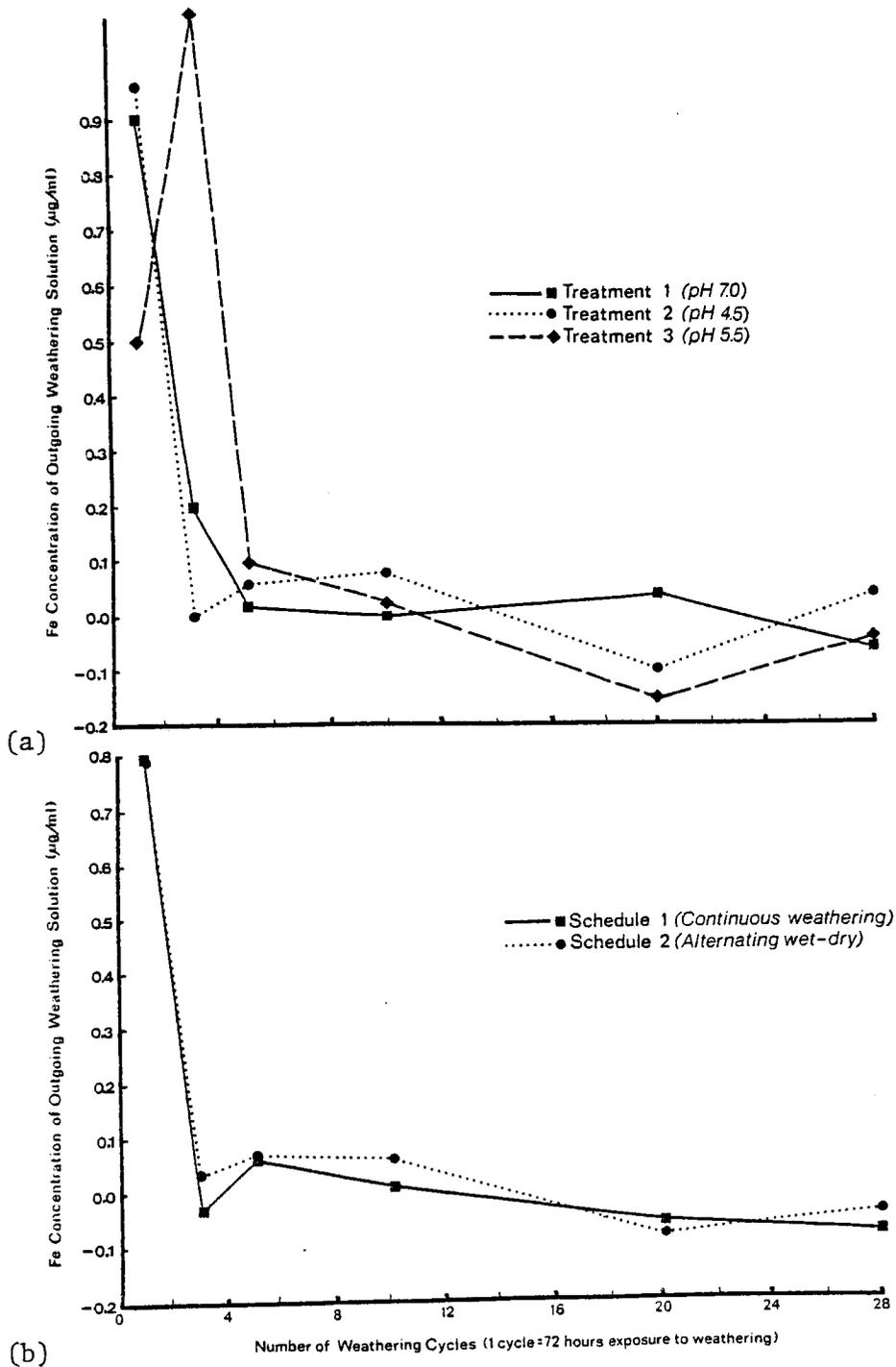


Fig. 8. Fe Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles).

(a) Treatment; (b) schedule.

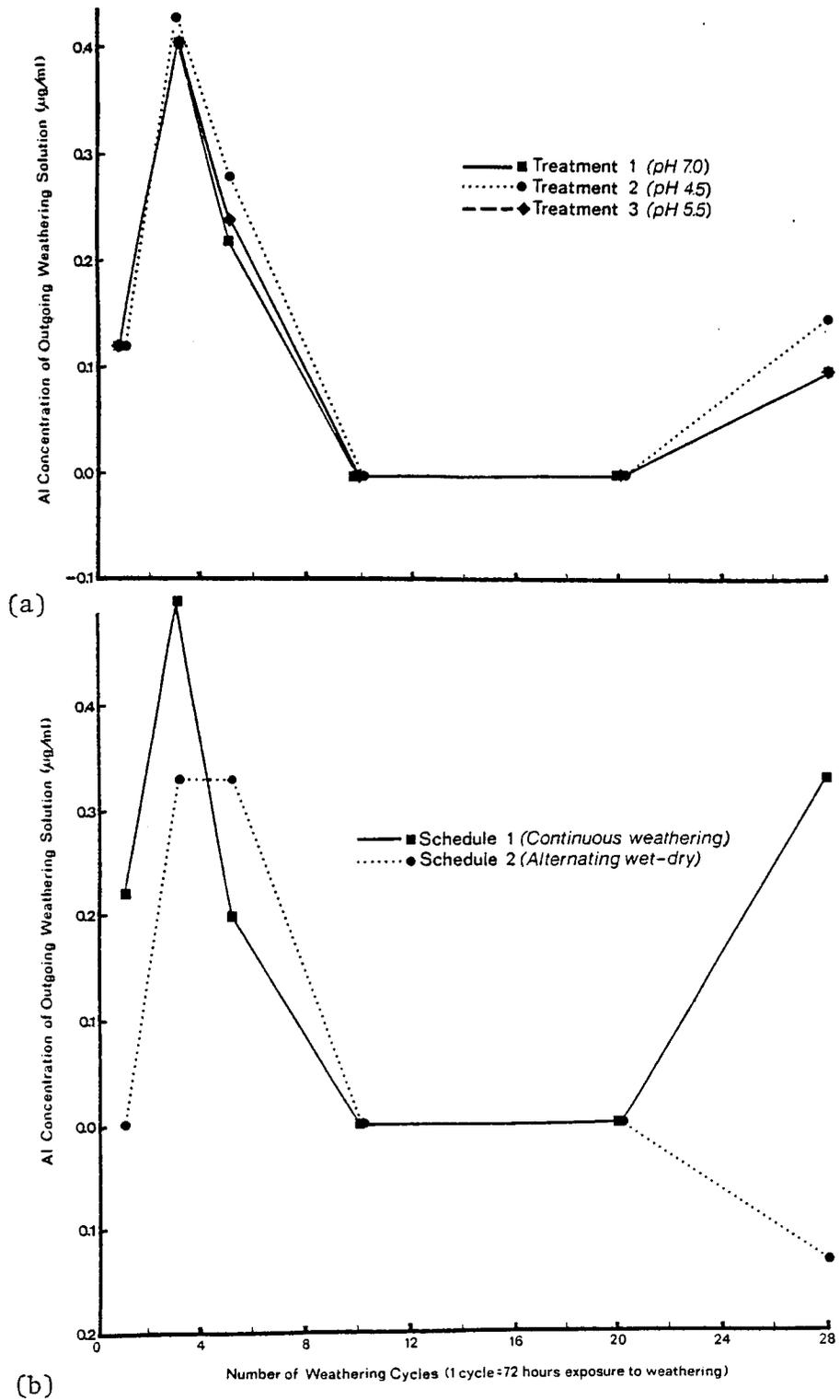


Fig. 9. Al Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles).

(a) Treatment; (b) schedule.

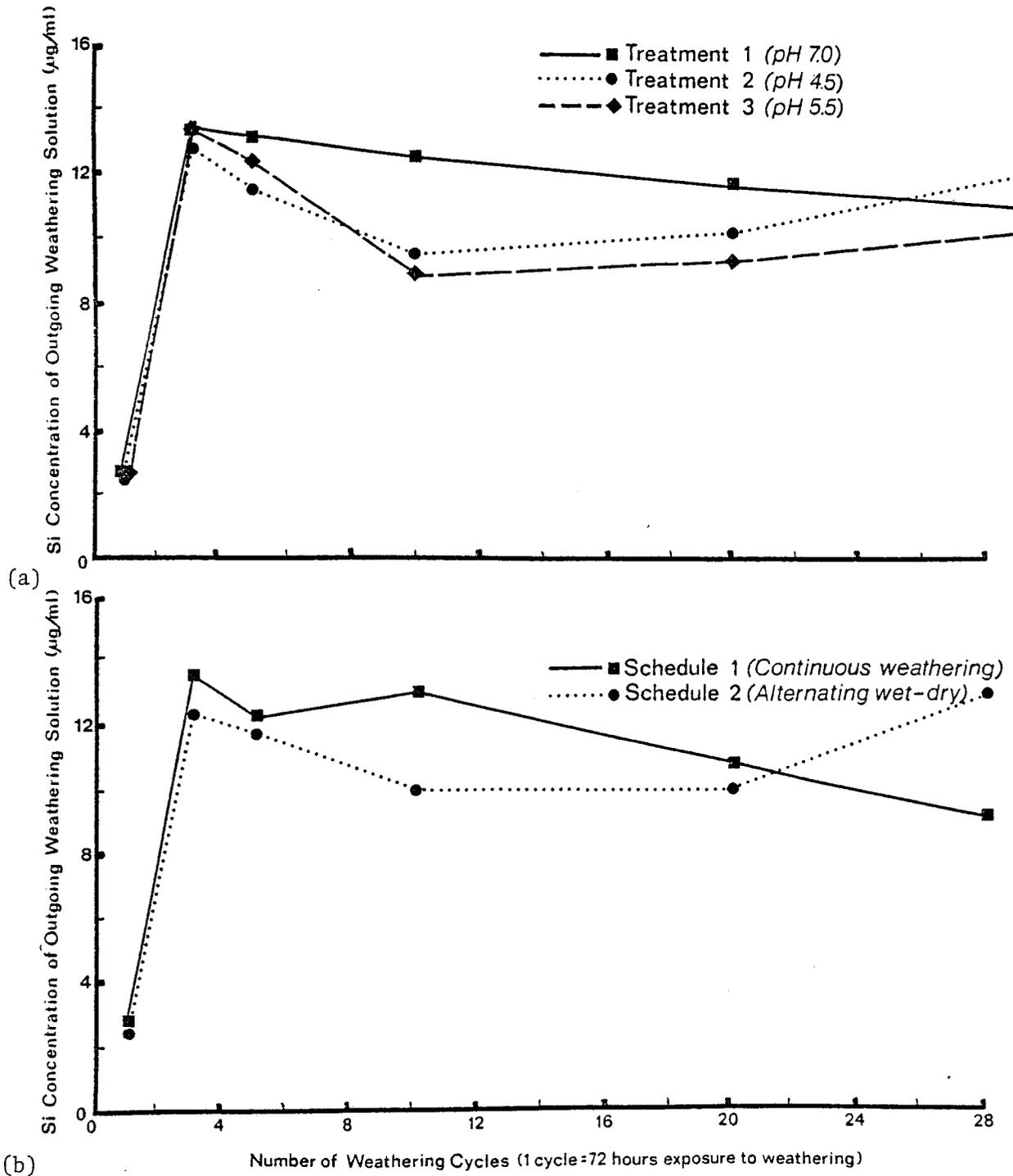


Fig. 10. Si Removal from Powdered Basalt Rock as a Function of Treatment, Schedule, and Time (Number of Weathering Cycles).

(a) Treatment; (b) schedule.

Table 4. Values of Coefficients, Constants, and r^2 's for Equations 1 and 2 and Significance^a of Treatment and Schedule Effects^b.

Ion	Treatment 2 (pH 4.5)		Treatment 3 (pH 5.5)		Treatment 1 (pH 7.0)		Schedule 1 (Continuous Weathering)		Schedule 2 (Alternating Wet and Dry)	
		Sig. Diff. ^c		Sig. Diff.		Sig. Diff.		Sig. Diff.		Sig. Diff.
Mg	α	8.24	=	8.23	=	8.66	8.00	<	8.74	
	β	3.05	=	3.09	<	3.22	3.06	<	3.19	
	γ	0.10	<	0.26	<	0.37	0.21	<	0.27	
	r^2	0.882	N.A. ^d	0.867	N.A.	0.833	0.843	N.A.	0.879	
Na	α	4.80	<	5.76	=	6.12	5.07	<	6.05	
	β	4.36	=	4.41	=	4.32	4.25	<	4.47	
	γ	0.18	<	0.21	=	0.21	0.17	<	0.22	
	r^2	0.984	N.A.	0.980	N.A.	0.975	0.979	N.A.	0.983	
K	α	1.40	=	1.34	=	1.39	1.32	<	1.44	
	β	1.72	=	1.81	=	1.74	1.71	<	1.80	
	γ	0.16	<	0.24	=	0.26	0.21	<	0.23	
	r^2	0.952	N.A.	0.928	N.A.	0.942	0.933	N.A.	0.948	
Ca	β_0	13.32	<	7.44	<	6.15	10.16	>	7.78	
	β_1	-4.11	<	-3.28	<	-2.67	-3.67	<	-3.05	
	β_2	2.90	<	3.97	=	3.77	2.53	<	4.56	
	r^2	0.738	N.A.	0.668	N.A.	0.753	0.626	N.A.	0.813	

^aDifferences among values of α , β , and γ that are significant at the 0.05 level are indicated by inequality signs. Differences that are non-significant are indicated by equal signs.

^b α , β , and γ values are means showing main effects of treatment and schedule.

^cSignificant difference.

^dNot applicable.

a broad analogy between the stable ion concentrations in nature and final experimental ion concentration predicted by α seems reasonable and is further supported by the thermodynamic considerations below.

Figs. 4a-6a show that the decline in removal rate of Mg, Na, and K is significantly (0.05 level) more gradual for Treatment 2 (pH 4.5) than for Treatment 3 (pH 5.5) or Treatment 1 (pH 7.0). This is seen in Table 4 in the lower values of γ for Treatment 2. These results suggest that, at a given moment in the weathering sequence, the ion concentration in the outgoing solution is greatest for Treatment 2. The differences in the decline in removal rate between Treatment 1 and Treatment 3 are smaller. For Mg, the decline in rate of ion removal is more gradual for Treatment 3 than for Treatment 1 (Fig. 4a). For Na and K, differences between rates of ion removal for Treatment 1 and Treatment 3 are not significant (0.05 level).

The effect of treatment appeared smaller on values of α than on values of γ . The analysis of variance indicated no difference due to treatment (at the 0.05 level) between the α values of curves for Mg and K (Figs. 4a and 6a). The results suggest that at least for those two ions changes in pH of the weathering solution do not greatly affect the final, steady-state weathering rate.

The main effects of schedule (continuous weathering versus intermittent drying) are illustrated in the regression lines of Figs. 4b-6b. Although the shapes of the curves for both schedules are similar, the γ values for the continuous weathering schedule are smaller (at the 0.05 level) than those for the intermittent drying schedule. The

continuous weathering schedule also shows significantly lower values of α for Mg, Na, and K. The combination of higher γ values and higher α values for Schedule 2 indicates that intermittent drying causes a more precipitous decline in rate of ion removal, but a higher steady-state rate than continuous weathering.

The β values in Equation (1) (Table 4) are related to the initial concentrations of ions removed, with $\alpha + e^\beta$ representing the y-intercept of the equation (i.e., \hat{Y}_i at time zero). Since the first drying period did not occur until after Weathering Cycle 6 on Schedule 2, the initial stages of the weathering cycles of Schedules 1 and 2 should have been identical and $\alpha + e^\beta$ for Schedule 1 should equal $\alpha + e^\beta$ for Schedule 2. Consequently, since α (the steady-state concentration) for Schedule 2 was greater than α for Schedule 1 for all three ions, β for Schedule 1 should have been greater than β for Schedule 2. Table 4 shows the reverse to be true.

A similar anomalous result is seen in Table 4 for β values of Equation (1) for treatments. Initial ion concentrations appear to be higher for treatments with lower pH for Mg, Na, and K (Figs. 4a-6a). Since there were no significant differences (0.05 level) among the steady-state concentrations (α) for the three treatments (except for the difference between Treatments 2 and 3 for Na), β values for treatments with low pH should be greater than β values for treatments with high pH. Again, Table 4 shows this not to be true. Additional data may be necessary to clarify these inconsistent results for β . Further analysis will not be attempted here.

The analysis of calcium weathering is complicated by an increase in the values of Ca concentration toward the end of the experiment rather than a decline to a constant α value, thus making Equation (1) inappropriate. A quadratic regression equation has been applied to compare treatments and schedules for Ca:

$$\hat{Y}_{Ca} = \beta_0 + \beta_1x + \beta_2x^2 \quad (2)$$

where x is a standardized value for the time in weathering cycles, \hat{Y}_{Ca} is the quantity of Ca removed during a given weathering cycle, and β_0 , β_1 , and β_2 are regression coefficients. The values for these coefficients are given in Table 4. The β 's for Ca in Table 4 are not intended to represent analogs to α , β , and γ . The r^2 values for the Ca regression curves are significant at the 0.05 level and also are presented in Table 4. The coefficients of the quadratic regression line are not readily interpreted in physical terms, as are the α and γ values for Equation (1). However, Figs. 7a and 7b illustrate trends similar to weathering patterns of the other three base ions, particularly in the phase of rapid decline in weathering rate early in the experiment.

The Effects of Individual Treatment-Schedule Combinations

Table 5 gives the values of α , β , and γ for Mg, Na, and K removed by the six combinations of treatment and schedule. Included in the table are the least significant differences (Steel and Torrie, 1960) for the α , β , and γ values at the 0.05 level. The effects due to treatment-schedule combinations were not as apparent as the main effects described above. Combinations with Schedule 2 tended to show

Table 5. Values of α , β , and γ Least Significant Differences^a for Regression Curves of Ion Removal by Individual Treatment-Schedule Combinations.

Ion		Least Significant Difference	Least Significant Differences					
			T1S1	T1S2	T2S1	T2S2	T3S1	T3S2
Mg	α	0.82	8.82	8.51	7.14	9.33	8.04	8.39
	β	0.10	3.10	3.34	3.08	3.02	2.99	3.19
	γ	0.06	0.34	0.40	0.08	0.12	0.22	0.29
Na	α	1.09	5.55	6.68	4.55	5.06	5.11	6.41
	β	0.17	4.14	4.49	4.30	4.43	4.32	4.50
	γ	0.03	0.17	0.24	0.16	0.20	0.19	0.23
K	α	0.13	1.34	1.44	1.37	1.43	1.23	1.45
	β	0.15	1.71	1.77	1.67	1.77	1.74	1.87
	γ	0.03	0.27	0.26	0.15	0.17	0.21	0.27
Ca	β_0	0.35	6.74	5.57	15.23	11.41	8.51	6.36
	β_1	0.83	-2.99	-2.36	-4.08	-4.15	-3.94	-2.63
	β_2	0.56	2.76	4.78	1.80	4.00	3.03	4.91

^aDifferences between values of any two treatment-schedule combinations exceeding the least significant difference indicate significant difference at the 0.05 level.

significantly higher steady-state rates of weathering (α) for Mg, Na, and K. This is consistent with findings in the analysis of main effects. The results suggest that the effects of schedule on α are greater than the effects of treatment. Apparently, in the steady-state condition of weathering, the mineral particles are buffered against changes in pH of the treatment solution. This buffering effect may be disrupted by the drying process in Schedule 2. Further consideration of the mechanism of the effects of schedule on α is presented in the discussion section below.

The effects of treatment-schedule combinations on γ again appear similar to the main effects. The weathering rate of treatment-schedule combinations with Treatment 1 (pH 7.0) tended to decline more rapidly (higher γ values) than combinations with Treatment 2 (pH 4.5). Also, more combinations with Schedule 2 (intermittent drying) had significantly faster declines in weathering rate. When treatments with low pH were combined with intermittent drying, the combination tended to result in a relatively slow decline in weathering rate (low γ values). This tendency was observed most clearly for Mg and K in Table 4. The results suggest that, for at least some of the treatment-schedule combinations, treatment exerts a greater influence on the decline in the rate of ion removal (γ) than schedule. The opposite effect was observed for the effect of treatment and schedule on the steady-state rates of ion removal (α). As in the case of α , these results may be consistent with a buffering mechanism and will be discussed below.

For other treatment-schedule combinations in which treatments characterized by a gradual decline in weathering rate (low γ) are combined with a schedule characterized by a more rapid decline (high γ), the effects appeared to be off-setting.

Interaction of Treatment and Schedule

The analysis of variance of coefficients and constants of Equation (1) for Mg, Na, and K, and Equation (2) for Ca, indicated that significant interaction (0.05 level) occurred between treatment and schedule only for α and β for Mg and for β_0 for Ca. The interactions are plotted in Fig. 11 to provide an indication of the sources of interaction. Where no interaction occurs, the line joining the values of each treatment combined with Schedule 1 should be approximately parallel to the line joining the values of each treatment combined with Schedule 2. For Mg, the effect of Treatment 2-Schedule 2 on the steady-state concentration (α) is greater than expected and the effect of Treatment 2-Schedule 1 is less than expected. Also, the effect of Treatment 1-Schedule 1 on α is greater than expected. For Mg β , the difference between Treatment 2-Schedule 2 is smaller than expected. An explanation for both unexpectedly high steady-state concentrations for Treatment 2-Schedule 2 and Treatment 1-Schedule 1 is difficult to find. Moreover, there is no reason for interaction to occur only in the relatively isolated cases shown in Fig. 11.

For Ca, the value of β_0 represents an approximation of the concentration of the initial ions removed. The treatment-schedule

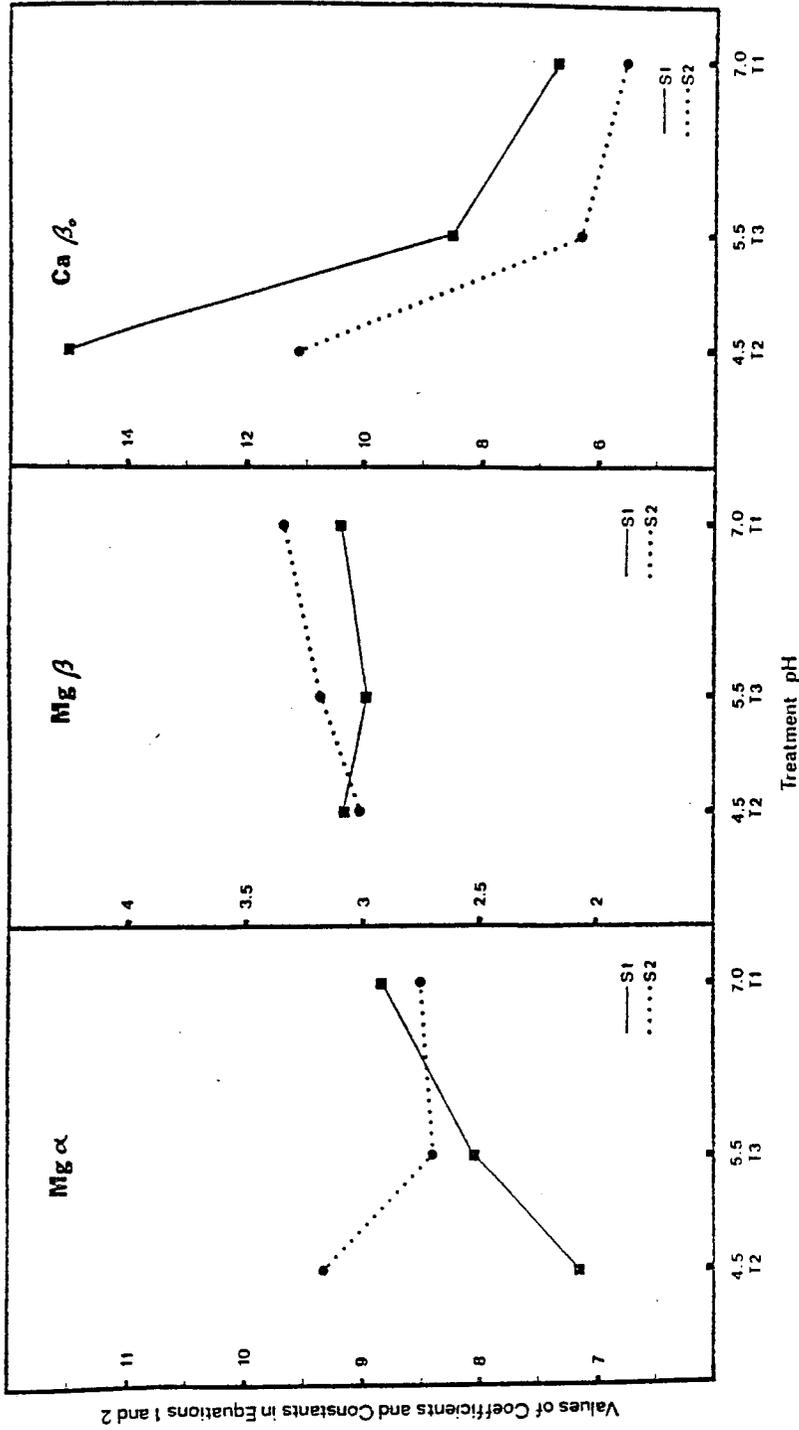


Fig. 11. Graphs Portraying Treatment-Schedule Interaction for Values of Coefficients and Constants in Equations 1 and 2 (Significant at the 0.05 Level).

interaction seems to result because of diminishing differences in the effects of Schedule 1 and Schedule 2 as the treatment pH increases. Interaction between treatment and schedule involving initial weathering rates is anomalous for both Ca and Mg, since no difference between Schedule 1 and Schedule 2 was introduced until six 72-hour cycles were completed.

Cumulative Ion Removal

The Main Effects of Treatment and Schedule

Figs. 8 through 10 illustrate the irregular pattern of weathering of Fe, Al, and Si. The previous analyses of variance of regression curve coefficients and constants were inappropriate for these three ions. This was not unexpected. Fe and Al are relatively immobile in the silicate lattice and their low concentration in the outgoing weathering solutions showed much variability. Si quickly develops relatively stable concentrations in laboratory weathering experiments and in natural river waters (Bricker et al., 1968). This is consistent with general patterns illustrated in Figs. 10a and 10b. A simplified analysis of treatment and schedule effects on rate of removal of Al, Fe, and Si is still possible by considering cumulative weathering -- the total weight of ions removed over the duration of the experiment.

Variance in the cumulative value $(\sum_{t=1}^{28} Y_{i,t})$ may be analyzed for all seven ions whether a regression curve is applicable or not. Table 6 presents the main effects of the three treatments and two schedules on

Table 6. Cumulative Weight of Ions Removed from Basalt Powder over 28 Weathering Cycles and Significance^a of Treatment and Schedule Effects^b.

	Treatment 2 (pH 4.5)	Sig. Diff. ^c	Treatment 3 (pH 5.5)	Sig. Diff.	Treatment 1 (pH 7.0)	Schedule 1 (Continuous Weathering)	Sig. Diff.	Schedule 2 (Alternating Wet and Dry)
					(µg)			
Mg	4050	>	3070	>	2860	3180	<	3470
Na	4450	=	4490	=	4280	4220	<	4590
K	680	>	610	>	566	577	<	661
Ca	4120	>	3050	>	2560	3100	<	3380
Fe	12	>	5	^d	10	6	<	12
Al	38	=	29	=	32	35	=	30
Si	2640	=	2860	=	2740	2580	<	2920

^aSignificant differences at the 0.05 level are indicated by inequality signs; non-significant differences are indicated by equal signs.

^bCombined means showing main effects of treatment and schedule on cumulative weight of ions weathered.

^cSignificant difference.

^dTreatment 2 value > Treatment 3, but Treatment 2 value = Treatment 1 value and Treatment 1 value = Treatment 3 value.

cumulative weathering of the seven ions. Cumulative weathering was significantly greater for Treatment 2 than for Treatment 3, which was greater than Treatment 1 for Mg, K, and Ca (at the 0.05 level). There were no differences in cumulative weathering due to treatments for Na, Al, and Si. Fe weathering was greater with Treatment 2 than Treatment 3, but there was no difference between Treatment 2 and Treatment 1.

Schedule 2 consistently showed significantly higher cumulative weathering than Schedule 1. This result was observed for all ions except Al.

The Effects of Individual Treatment-Schedule Combinations

Table 7 presents the cumulative weight of ions removed from the powdered basalt by each of the six treatment-schedule combinations. As in Table 5, the least significant differences are shown for each ion. The results are consistent with the data in Table 6. The combination of the treatment with the highest cumulative weathering (Treatment 2 in Table 6) and the schedule having the higher cumulative weathering (Schedule 2) was either the combination, or among the combinations that resulted in the highest cumulative weathering for all ions except Si. In a similar manner, Treatment 1-Schedule 1 was the combination or among the combinations resulting in the lowest cumulative weathering for all ions except Si. The results for Si are consistent with Table 6, which shows no significant differences in cumulative Si removal due to treatment. The three treatment-schedule combinations involving Schedule 2

Table 7. Cumulative Weight^a of Ions Removed from Basalt Powder as a Function of Treatment and Schedule and Least Significant Differences^b among Weights.

Ion	Least Significant Difference	T1S1	T1S2	T2S1	T2S2	T3S1	T3S2
Mg	121	2778	2950	3838	4258	2933	3204
Na	211	4104	4447	4216	4677	4341	4632
K	25	530	603	630	731	571	649
Ca	131	2374	2738	3957	4277	2968	3132
Fe	10	2	18	7	17	8	2
Al	- ^c	34	30	41	35	31	26
Si	145	2660	2824	2414	2871	2670	3054

^aCumulative weight over 28 weathering cycles.

^bDifferences between weights of any two treatment-schedule combinations exceeding the least significant difference indicates a significant difference at the 0.05 level.

^cF-test indicates non-significance at the 0.05 level.

all showed higher cumulative Si removal than the combinations with Schedule 1. These results are discussed further below.

Between the two extremes of Treatment 2-Schedule 2 and Treatment 1-Schedule 1, the effects of treatment and schedule were often off-setting. However, there appeared to be a tendency for schedule to have a stronger influence on cumulative weathering than treatment.

Interaction of Treatment and Schedule

Analysis of variance at the 0.05 level indicated that interaction occurred between treatment and schedule for Mg, Fe, and Si. For Mg and Si, possible interaction occurred between treatment and schedule with decreasing pH of the weathering solution (Table 7). In the case of Fe, a strong negative interaction was observed. This resulted from an unexpectedly and inexplicably low value for the cumulative weathering of Treatment 3-Schedule 2.

The Effect of Treatment and Schedule on Relative Ion Mobility

Relative ion mobility was estimated by comparing the ratios for moles of each ion removed from the basalt to moles of each ion present in the fresh basalt. The mobility ratios are given in Table 8 for each treatment-schedule combination. In Table 8, the ions have been listed in descending order of mobility. For each treatment-schedule combination, the order was the same: $Na \geq K \geq Mg \geq Ca \geq Si > Al \geq Fe$. Differences between Ca and Mg and between Al and Fe were extremely small. Different treatment-schedule combinations apparently do not alter the order of ion mobility.

Table 8. Relative Molar Mobility^a of Oxides of Ions from Powdered Basalt as a Function of Treatment and Schedule.

Ion ^b	T1S1	T1S2	T2S1	T2S2	T3S1	T3S2
Na	.025	.027	.026	.029	.027	.028
K	.012	.015	.016	.018	.015	.017
Mg	.008	.008	.011	.012	.008	.009
Ca	.006	.006	.010	.011	.007	.008
Si	.001	.002	.001	.002	.001	.002
Al	.00006	.00005	.00007	.0006	.00005	.00004
Fe	.000005	.00004	.00002	.00004	.00002	.000004

^aRelative molar mobility = $\frac{\text{moles of ion removed in weathering}}{\text{moles of ion in fresh basalt sample}}$

^bIons arranged in order of decreasing mobility. Each treatment-schedule combination produces the same order of mobility.

The order of mobility in the present experiment shows Ca and Mg to be less mobile than Na and K. Previous work has shown Ca and Mg to be among the three most mobile ions. Mg mobility may have been reduced somewhat by incorporation in secondary minerals, but the low relative mobility of Ca is difficult to explain. The present study was not designed to give detailed consideration to relative cation mobility.

Error Due to Instrument Variation

Variation in readings of the spectrophotometers introduced an error of up to 10%. The coefficient of variation was approximately 5% on both the Perkin-Elmer AA Spectrophotometer and the Coleman Jr. II A Linear Absorbance Spectrophotometer when measuring standard solution concentrations. Thus, the probability of a given measurement falling within 10% of the true mean is 0.95.

DISCUSSION

The Effects of Treatment on α and γ

The decline in the rate of ion removal in Figs. 4 through 7 toward relatively stable values is consistent with the weathering patterns observed in the previous work cited above. Burger (1969) referred to the period of declining rate as an "early-weathered" stage and the period of stable rate as a "semi-weathered" stage. He attributed the early higher rates of weathering to the rapid dissolution of soluble carbonates and the "greater weatherability of fresh surfaces. Since there are no carbonates present in the Beaver Creek basalt samples, the "freshness" of the weathering mineral surface is taken to be the major factor in determining weathering rate of the samples in the present experiment. The relatively constant weathering rates (for the more mobile nutrient ions) after 10-12 weathering cycles apparently represents the semi-weathered stage.

The fresh feldspar surfaces probably are slowly altered to an aluminum-enriched layer as more soluble cations are displaced by H^+ . The transitional H^+ -feldspar may be formed by a combination of mechanisms. Stable fragments of the feldspar lattice containing Al may persist on the surface when disruptions in the framework occur at the site where the cations were displaced. Further Al-enrichment of the mineral surface could result from an exchange reaction similar to Coleman's (1962) mechanism for the development of Al-clays. Al ions in

the lattice replace H^+ on the surface. Hydrolysis then leaves additional $Al(OH)_3$ residue. Much of the Al that is released into solution by the breakdown of H^+ -feldspar is probably re-precipitated as additional $Al(OH)_3$ residue (Fig. 1). The concentrations of Ca, Na, and K decline over time as the layer through which they must diffuse grows thicker. A similar process may be slowing the rate of Mg release from the surface of olivine and other mafic minerals. The retarded inward diffusion of H^+ and the recombination of some cations in the developing outer clay layer contribute to the declining rate of weathering. Since the decline in weathering rate will also slow the rate of formation of the layer, the process asymptotically approaches a steady state.

It seems likely that this process also applies to the removal in solution of Ca and Si even though Figs. 7 and 10 do not conform to the steady-state model presented above. The problem of the increase in the Ca concentration toward the end of the experiment as seen in Fig. 7 might be resolved if the weathering process were prolonged until more constant values were obtained. The concentration of Ca probably would not continue to increase during each succeeding weathering cycle as Equation (2) seems to predict. Equation (2) is not intended to represent a model for a complete weathering sequence.

The more rapid weathering of the Mg, Na, K, and Ca during the early weathered stage for samples weathered by Treatment 2 is attributed to the greater effectiveness of higher H^+ concentration. These results are in agreement with all previous work (Correns, 1961; Wollast, 1967; and others). The difference between Treatment 2 at pH 4.5 and

Treatment 3 at pH 5.5 is greater than the difference between Treatments 1 and 3. In fact, Table 4 indicates that there is no significant difference (at 0.05 level) between Treatment 3 and Treatment 1 due to pH for Na or K. This could be due to the effects of mass action (far more H^+ is necessary to decrease pH from 5.5 to 4.5 than from 7.0 to 5.5) or to the increase in Al solubility near pH 4.5. The second factor seems less important since the cumulative weathering of Al was not significantly greater for Treatment 2 than for Treatment 1 (Table 5).

The effect of treatment was not as great on α in Equation (1) as on γ , as seen in Tables 4 and 5. For K and Mg, there is no difference in α regardless of treatment pH. For Na, there was no difference between α 's for Treatment 1 and Treatment 3. α_{Na} for Treatment 2 was actually smaller than for the other treatments. These results suggest that the steady-state concentration is effectively buffered against changes in pH of the weathering solution. The higher weathering rates (lower γ) for Treatment 2 during the early weathered stage indicate that initially more parent material is dissolved by solutions with lower pH. Since Al is equally insoluble and retained in weathering in all treatments, more Al should persist in the Al-enriched layer that may develop in weathering by Treatment 2 than by Treatment 1 or 3. The Al-enriched layer, therefore, should be thicker around feldspar particles weathered by Treatment 2. Differences in layer thickness may account for the stability of α 's with change in pH. Although Treatment 2 provides more H^+ to attack the feldspar, the resultant increase in weathering thickens the Al layer, which in turn reduces the effect of additional H^+ .

Whether these observations may be applied to the natural environment is uncertain. Under most circumstances, long-term changes in pH of a natural system would be very slow, and the question of the immediate effect of pH changes would not arise. As Johnson et al. (1968) observed, the entire watershed is well buffered against changes in stream chemistry by the reservoir of ions in the humus layer. The Hubbard Brook workers showed that stability of stream chemistry was correlated with long residence times of ions in the humus. Bricker et al. (1968) and Davis (1964) noted that the Si concentration of stream water is relatively stable under a wide variety of conditions. To what extent an Al-enriched layer on weathering parent material may contribute to these buffering effects is at best speculative.

The stability of α raises some doubts about the feasibility of modifying nutrient balances by increasing the contribution of the weathering compartment. It is not impossible to apply treatments that could lower the pH of the weathering solution under field conditions. Maintaining a substantial layer of pine litter or other organic matter could contribute organic acids to the weathering solution that could lower the pH somewhat. Direct applications of H_2SO_4 have been effective in lowering soil pH on some basic soils to improve iron and phosphorous availability (Ryan, Stroehlein, and Miyamoto, 1975). Even if treatments to lower pH were conceivable on Beaver Creek where soil pH is near 6.0 (Hendricks, 1976), the stability of α suggests that any increase in rock weathering could be relatively short term.

Likens and Bormann (1974) have cited possible serious consequences of acid rains developing from fallout in some industrial areas. They suggested that declines in soil fertility due to increased leaching of nutrient ions could occur. The results of the present experiment suggest that acid rain might not increase the rate of rock weathering as much as it might increase the leaching of soil nutrients. Whether acid rain could affect the rock weathering contribution of nutrient ions to the soil is unknown and may warrant further investigation.

It is difficult to determine how the short time periods of accelerated laboratory reactions would compare to the time periods of weathering in nature. Over the period of the experiment, the slower decline in weathering rate (smaller γ) at the lowest pH resulted in generally greater cumulative ion removal. For Ca, Mg, and K, Treatment 2 showed the most cumulative weathering. For Na, there were no significant differences among treatments (Table 6). It seems likely that as the period of weathering is increased and weathering proceeds at similar steady states for all treatments, the percentage differences among the cumulative values would diminish.

The Effect of Schedule on α and γ

The curves in Figs. 4 through 7 describing continuous weathering (Schedule 1) appear similar to the curves showing alternating wetting and drying (Schedule 2). However, analysis of variance indicated significant differences (at the 0.05 level) between schedules. For Mg, K, and Na, values of α and γ are greater for Schedule 2. As noted above, this means that when weathering is interrupted by a drying period the

rate of ion removal declines faster, but reaches a steady state in which weathering continues at a higher rate. The effects on cumulative weathering of the larger α 's for Schedule 2 are clearly seen in Table 6. For all ions except the immobile Al, more total weathering has occurred with Schedule 2.

The greater effectiveness of Schedule 2 weathering in ion removal is a somewhat unexpected result. During the drying periods of Schedule 2, the ion concentrations around the weathering minerals are likely to increase, which could cause relatively insoluble hydroxides to precipitate (Keller, 1957). If this process had occurred in Schedule 2, a slightly less soluble layer might have developed on feldspar and other mineral surfaces that could have impeded the weathering process when the treatment solution was reapplied. This hypothesis must be reconsidered in light of the cumulative results and the failure to observe any unusual changes in the weathering rate immediately following the dry periods.

Alternative explanations could include the effects that drying might have on the Al-enriched layer. The drying process may crack the layer, allowing the weathering solution greater access to fresh rock surfaces. The observed interaction between schedule and treatment for cumulative weathering of Mg and Si could arise from the cracking of the Al-enriched layer. Increased differences in cumulative weathering between Schedule 1 and Schedule 2 as pH increased appeared to cause the interaction. If intermittent drying causes cracks in the layer, more fresh mineral surface would be exposed to the weathering solution.

Thus, the buffering effect of the layer would be reduced for Schedule 2 but not for Schedule 1. Weathering under Schedule 2-Treatment 2 would show a higher rate of ion removal than expected had the layer remained intact. This hypothesis may also explain the unexpectedly high values of $Mg\alpha$ for Treatment 2-Schedule 2. The other instances of interactions ($Mg\beta$, $Ca\beta_0$, and cumulative Fe weathering), however, remain unexplained as noted above.

The capillary action suggested by Roffman (1973) also could contribute to higher rates of weathering for Schedule 2 than for Schedule 1 by drawing ions toward the particle surface through pores and along cleavages as the system dries. The cracking and capillary action processes may work together to increase total weathering. Finally, the total time that the parent material was exposed to weathering solution must be considered. The continuously wet system was exposed to solution for exactly 18 days for every six weathering cycles. The wetting and drying system was exposed to the solution for 18 days plus the time it took the system to dry. This additional exposure undoubtedly caused some weakening of the silicate structure that resulted in an increased weathering rate when the system was re-wetted. The effects of this additional weathering time could be minimized in future experiments of this type if the drying process is accelerated by passing clean, dry air through the system while it dries.

The Effects of Schedule and Treatment
on Cumulative Weathering

The effects of treatment and schedule on cumulative weathering for Na, Ca, Mg, and K have been described above. For Fe, Al, and Si, differences in cumulative values appear to be the only way to compare experimental results.

Over the period of the experiment, less Fe was removed by all treatments and schedules than any other ion. The immobility of Fe in silicates is apparent in Table 5. Since much of the Fe present in the parent material is in the more soluble ferrous state, more removal of Fe might have been expected. Schedule 2, with prolonged dry periods, would appear to be a more favorable oxidizing environment, but experimental evidence does not show less Fe removal on Schedule 2. Apparently, the Eh of the weathering system was high enough even under continuous wetting to maintain oxidizing conditions for Fe. Eh is inversely related to pH in natural systems, but the data in Tables 1 and 5 do not give any definite indication that the valance state or cumulative weathering of Fe are affected by the different treatment pH's or schedules. Keller et al. (1963) note that Fe solubility is normally low in CO₂-charged waters.

The variations in cumulative removal of Al due to treatment or schedule were not significant according to the analysis of variance at the 0.05 level. This is consistent with the assumption that Al is retained in a residual layer and is relatively insoluble between pH 4 and 9. The pH of Treatment 2 (4.5) does approach the point of increasing Al solubility, but the analysis of variance did not show increased Al concentration to be significant. The pH of the CO₂-charged weathering

solutions increased during the 3-day cycle due to dissolved bases and volatilization of CO_2 . This would minimize the effect of Treatment 2 on Al solubility.

The cumulative Si weathering did not show significant variation due to treatment. Although a specific steady-state value (α) could not be determined for Si in the present analysis, Si concentrations may reach steady-state levels that are buffered against changes in pH much like Mg, Na, and K. If the buffering process occurs for Si, and if Si quickly approaches a relatively stable concentration, as has been observed under natural and artificial weathering conditions (Bricker et al., 1968), the effects of treatment pH on cumulative weathering also would diminish quickly. This model is supported by the lack of significant differences in cumulative weathering among the three treatments in Table 6. The rapid development of a buffered steady state also could explain the failure of Treatments 1 and 2 to exert their expected influence on cumulative weathering of Si for individual Treatment-Schedule combinations in Table 7. All results are consistent with the conclusion that differences due to treatments in cumulative removal of ions diminish over time. These results do not imply that silicates are not more soluble at lower pH, only that diffusion of dissolved ions through surface layers slows the solution process and minimizes the effects of pH differences over time. This could be particularly true for Si, which is incorporated as an important constituent of secondary minerals forming on weathered surfaces.

Analysis of differences in cumulative Si weathering between Schedule 1 (continuous wetting) and Schedule 2 (alternating wetting and drying) shows results consistent with those of other ions: weathering on Schedule 2 exceeds weathering on Schedule 1 (Table 5). Differences in cumulative weathering due to the two schedules were apparently the result of different steady-state weathering rates, unlike the differences in cumulative weathering due to the three treatments. Over prolonged periods of weathering, cumulative differences between schedules should increase. It seems unlikely that this observation has an application in terms of land management. Alternate wetting and drying is an existing characteristic of most natural environments such as Beaver Creek where long periods without precipitation occur.

Some Thermodynamic Considerations

Stability diagrams are a widely used method of showing the relationship between parent material, secondary clay minerals, and the waters that drain them. It has been emphasized that artificial rock weathering can only simulate isolated elements of natural rock weathering in the Beaver Creek area. Nevertheless, parent material alone is a major influence on stream water chemistry, so it seems reasonable that some similarities would exist between ratios of ions in the natural waters and ratios of ions in the simulated outgoing solutions. Table 9 shows the concentrations of the seven ions in outgoing solutions at the end of 28 cycles of the experiment and the concentrations of three Beaver Creek stream samples.

Table 9. Ionic Concentrations^a of Outgoing Weathering Solutions Natural and Artificial^b Systems.

	Mg		Na		K		Ca		Fe		Al		Si	
	ppm	-Log ppm	ppm	-Log ppm	ppm	-Log ppm	ppm	-Log ppm	ppm	-Log ppm	ppm	-Log ppm	ppm	-Log ppm
<u>Beaver Creek Water</u>														
Woods Canyon ^c	7.3	3.52	3.2	3.86	0.8	4.69	9.5	3.63	0.0	--	0.0	--	7.1	4.13
WS 12 ^d	2.6	3.97	2.3	4.00	0.9	4.64	9.1	3.64	0.3	5.22	0.0	--	8.8	4.04
Bar M ^e	2.1	4.06	3.0	3.88	0.3	5.12	6.0	3.82	0.6	4.97	1.0	5.01	23.2	3.63
<u>Experimental Solutions</u>														
T1S1	9.7	3.40	7.0	3.46	1.6	4.38	8.5	3.67	-1.3	--	0.0	--	11.3	3.93
T2S1	11.4	3.33	5.1	3.65	1.4	4.45	12.4	3.52	0.0	--	0.0	--	10.8	3.94
T3S1	9.6	3.40	5.6	3.61	1.3	4.49	11.1	3.56	-0.1	--	0.0	--	12.0	3.90
T1S2	9.0	3.43	6.1	3.57	1.4	4.45	11.4	3.55	0.0	--	0.3	5.53	12.3	3.89
T2S2	13.0	3.27	6.1	3.57	1.8	4.35	15.7	3.40	0.1	5.79	0.3	5.53	15.0	3.81
T3S2	9.5	3.41	6.0	3.58	1.5	4.42	12.4	3.52	.04	6.14	0.0	--	12.3	3.89

^a(-Log) are taken of the molar concentration presented as ppm.

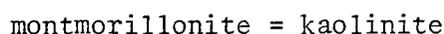
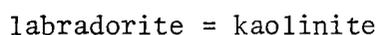
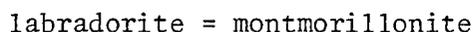
^bSolutions taken from 28th (final) weathering cycle.

^cSampled by J. O. Klemmedson from small, perennial, spring-fed stream, October 1976.

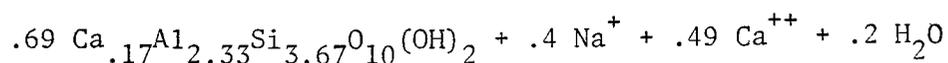
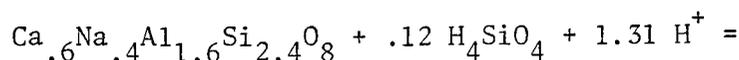
^dForest Service sample, January 1971 (analyzed by U. S. Forest Service).

^eForest Service sample, May 1976 (analyzed by University of Arizona Soil and Water Testing Laboratory). All samples taken from streams draining Broillier or Sponseilior soil with basalt parent material.

A number of assumptions are necessary to reduce these complicated systems, both artificial and natural, to forms that can be applied to stability diagrams. It is assumed that the same basic hydrolysis reaction is weathering the basalt in the laboratory and on Beaver Creek. The parent mineral assemblage includes a variety of silicates (Table 1) which are simultaneously weathering and contributing to the secondary products. Montmorillonite and lesser amounts of kaolinite are known products of the weathering of the Beaver Creek basalt (Hendricks, 1976). Since labradorite is the dominant mineral in the basalt, it is assumed that a simplified stability diagram can be constructed considering three reactions at equilibrium:



Determination of the precise Beaver Creek labradorite and montmorillonite formulas was attempted by the normative methods of Barth (1952) and Van Der Plas and Van Schuylenborgh (1970). The results were uncertain and contradictory. Consequently, reasonable standard formulas were selected for labradorite (Huang and Keller, 1972) and montmorillonite (Helgeson et al., 1969; Hess, 1966). Using these formulas, an equilibrium between labradorite -- $\text{Ca}_{.6}\text{Na}_{.4}\text{Al}_{1.6}\text{Si}_{2.4}\text{O}_8$ -- and montmorillonite -- $\text{Ca}_{.17}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$ -- was established:



(3)

X-ray diffraction analysis of montmorillonite from Beaver Creek indicates that there is some Fe and Mg substitution for Al in the octahedral layer. They are omitted from Equation (3) in order to simplify the equation and to derive an appropriate value for the ΔG of montmorillonite from Hess' (1966) data. An interesting aspect of Equation (3) is the presence of H_4SiO_4 on the left side of the equilibrium. The weathering of labradorite yields insufficient H_4SiO_4 to produce montmorillonite if all Al is assumed to form montmorillonite. Whether this occurs in nature is unknown, although the contribution of additional H_4SiO_4 by the more easily weathered olivine seems feasible. Also, isomorphic substitution of Al for Si in the tetrahedral layer could reduce the amount of Si necessary for the formation of montmorillonite.

From the stability diagrams presented by Hess (1966), an appropriate value for ΔG (free energy of formation) of the montmorillonite in Equation (3) was calculated:

$$\Delta G \text{ montmorillonite} = - 1278 \text{ kcal}$$

This value is consistent with the "activity diagrams" of Helgeson et al. (1969) and Kittrick (1969). The ΔG values for all other reactants and products in Equation (3) are available in Robie and Walbaum (1968). Since $\Delta G \text{ reaction} = \Delta G \text{ products} - \Delta G \text{ reactants}$, a ΔG for Equation (3) may be calculated: $\Delta G (3) = - 13.4 \text{ kcal}$. From the relationship $\Delta G = - RT \ln K$ (Garrels and Christ, 1965), $K_{(3)} = 9.85$.

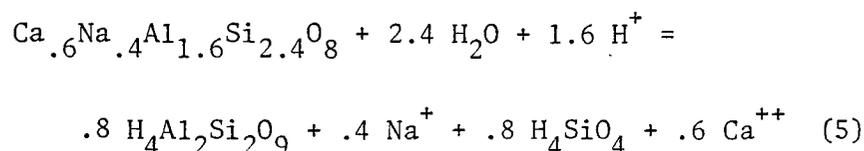
Assuming that the concentration of Na will be in the range found in Beaver Creek waters (approximately 3 ppm), Equation (4) can be derived for the equilibrium between labradorite and montmorillonite:

$$K = \frac{[Ca^{++}]^{.49} [Na^+]^{.4}}{[H_4SiO_4]^{.12} [H]^{1.3}}$$

$$\log \frac{[Ca^{++}]}{[H^+]^{2.67}} = .27 \log [H_4SiO_4] + 23.2 \quad (4)$$

Equation (4) is illustrated as line (4) in Fig. 12.

The same process is applied in developing an equation for the equilibrium between labradorite and kaolinite -- $H_4Al_2Si_2O_9$:

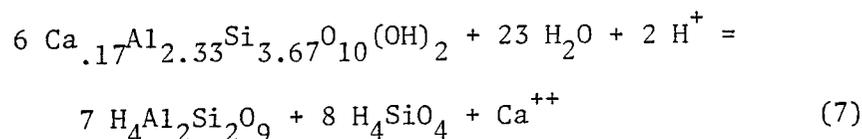


$$K = \frac{[Na^+]^{.4} [H_4SiO_4]^{.8} [Ca^{++}]^{.6}}{[H]^{1.6}}$$

$$\log \frac{[Ca^{++}]}{[H^+]^{2.67}} = - 1.33 \log [H_4SiO_4] + 15.7 \quad (6)$$

Equation (6) is represented as Line (6) in Fig. 12.

Finally, the equation for the equilibrium between montmorillonite and kaolinite is:



$$K = \frac{[H_4SiO_4]^8 [Ca^{++}]}{[H^+]^2}$$

$$\log \frac{[Ca^{++}]}{[H^+]^2} = - 8 \log [H_4SiO_4] - 15.7 \quad (8)$$

Equation (8) is shown in Fig. 12 as Line (8).

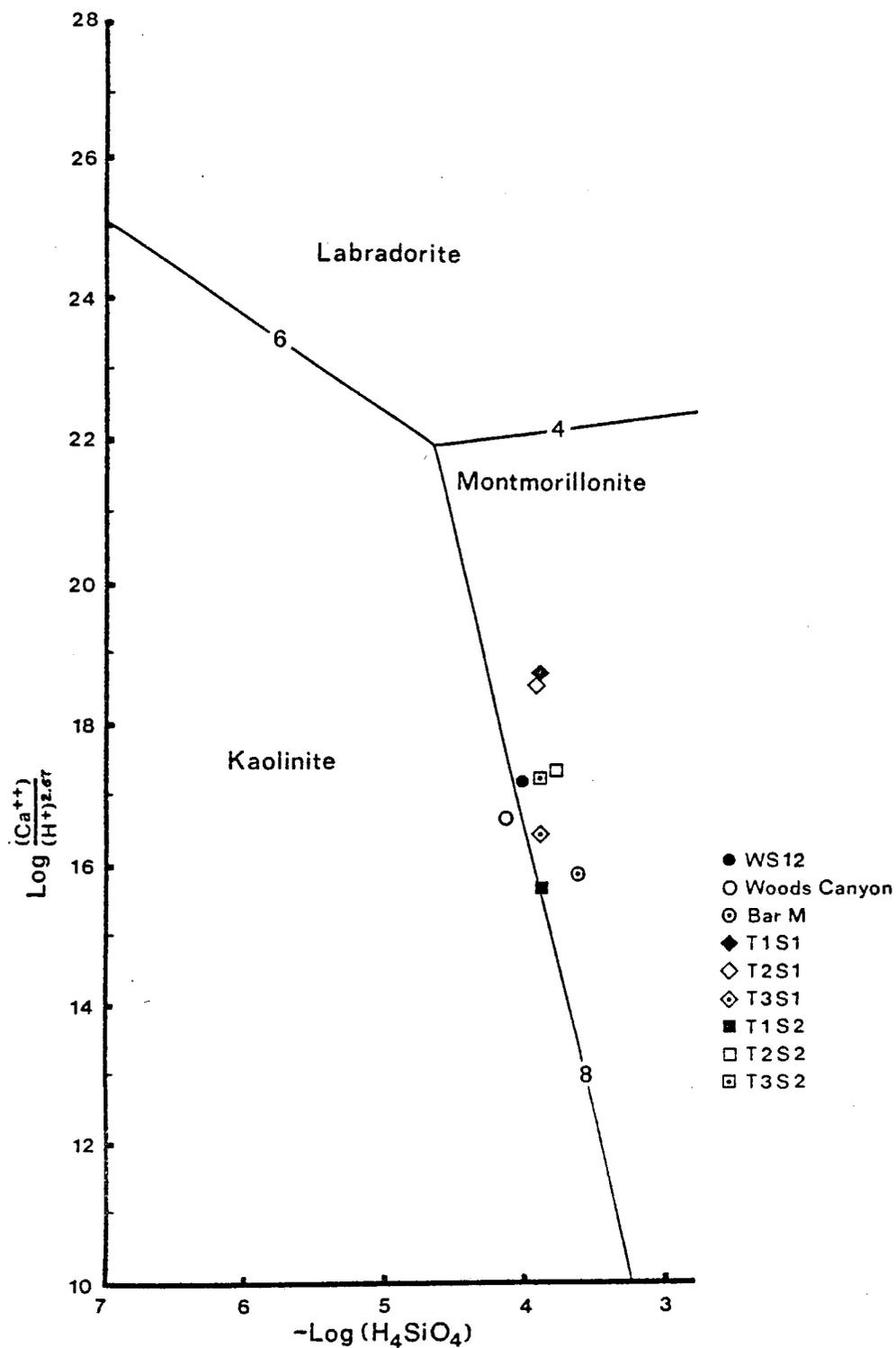


Fig. 12. Stability Diagram for System $\text{CaO-H}_4\text{SiO}_4\text{-H}_2\text{O-H}^+$ at $p_{\text{Na}} = 4.00$, 1 Atmosphere, 25°C .

The x-ray diffraction analysis of clays on Watershed No. 12 from which the basalt for the present experiment was taken, indicates the presence of small amounts of mica as well as montmorillonite and kaolinite. Calculations of equilibrium constants for the reactions of mica with the other three minerals indicate that mica is not forming from the minerals of Equations (3), (5), and (7) under the given conditions.

The negative logarithms of Si concentrations and the logarithms of the ratio of Ca to H^+ concentration are plotted on Fig. 12 for Beaver Creek stream samples and the outgoing weathering solutions from the present experiment. The stream and experimental values fall in the same area of stability near the boundary between montmorillonite and kaolinite. This is consistent with the observations that montmorillonite and kaolinite are both present on Beaver Creek. Intermittent drying and relatively low volumes of weathering solution favor the formation of montmorillonite (Berner, 1971). It is possible that kaolinite could be forming in the same area due to weathering of other minerals not considered in Fig. 12, or due to slight shifts in environmental conditions. An increase in weathering solution volume during periods of rainfall or snowmelt could lower Ca or Si concentrations favoring kaolinite formation.

Concentrations of Si and K are plotted on Fig. 13 in a manner similar to Fig. 12. The phase relationships in Fig. 12 are taken from Helgeson et al. (1969) as modified by Kittrick and Mattigod (Bohn, 1977). Again the points representing the Beaver Creek

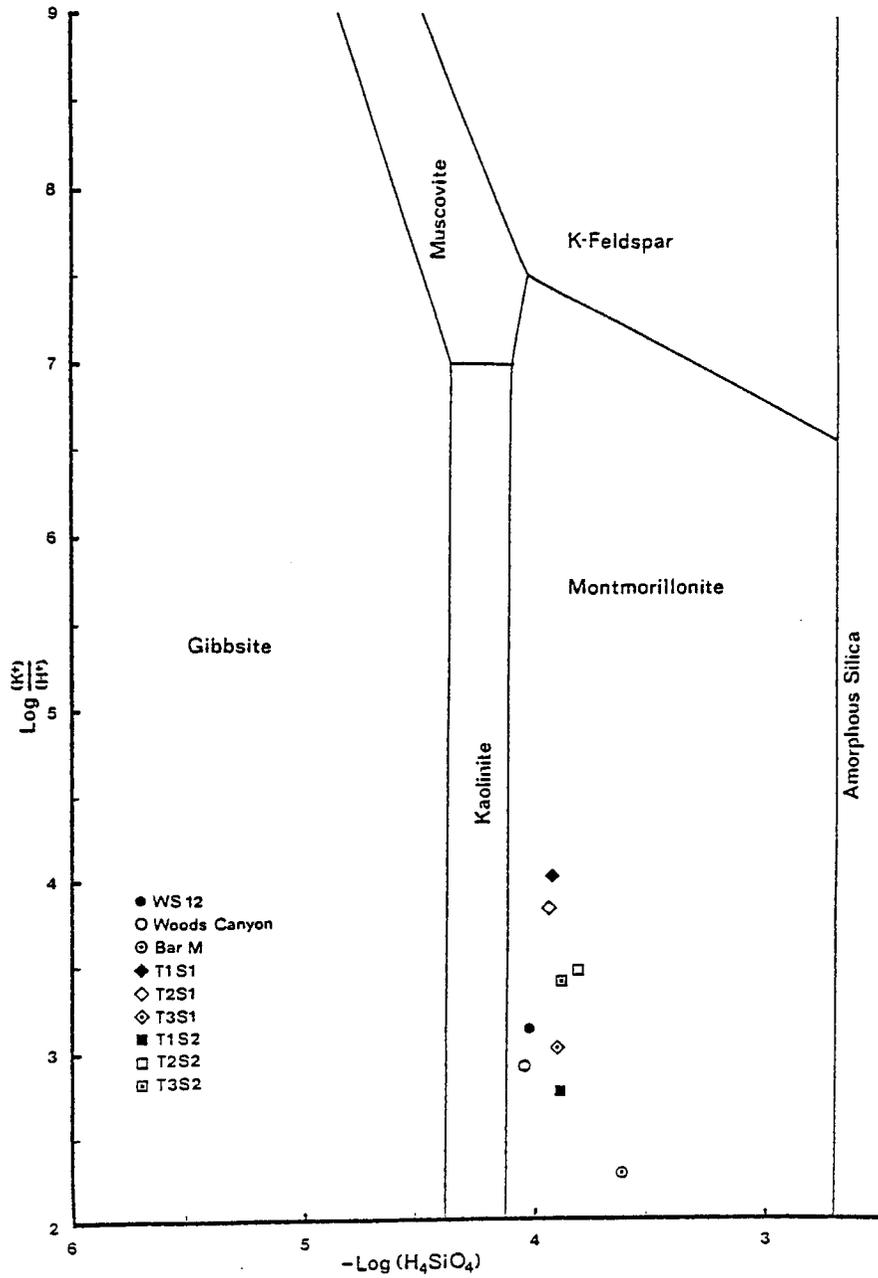


Fig. 13. Stability Diagram for System $K_2O-Al_2O_3-SiO_2-H_2O$ at $25^\circ C$, 1 Atmosphere.

stream chemistry are in the same area of stability as points representing simulated weathering solution chemistry. As in Fig. 12, the points fall in the area representing the dominant clay mineral of the area from which the basalt samples were taken. The kaolinite stability region of Fig. 12 seems small, but Kittrick notes that it is based on reliable field data. If the artificial weathering process is approaching a steady state, Figs. 12 and 13 suggest that the development of secondary clay minerals will follow a direction similar to the natural system. This seems to support the argument that the simulation developed for the present experiment is a reasonable, if broad, approximation of the relationship between parent materials and weathering solutions in the natural environment.

SUMMARY

Recent studies of nutrient cycling on watersheds in steady-state conditions have shown the importance of the contribution of rock weathering to nutrient balance of ecosystems. Increased understanding of rock weathering mechanisms may contribute to effective maintenance of overall nutrient balances on managed watersheds. The present study attempts to isolate and analyze two factors that may influence the rate of rock weathering. By simulating the basalt weathering system on Watershed No. 12 of Beaver Creek, south of Flagstaff, Arizona, the experiment measures the effect of changes in weathering solution pH (treatment) and intermittent drying (schedule) on weathering rate.

The results indicate that treatments with the lowest pH (4.5) show more cumulative weathering due to the effect of pH early in the weathering sequence. However, for three of the mobile nutrient ions analyzed (Na, Mg, and K), weathering rates declined over time, approaching a relatively constant value that was not greatly affected by differences in treatment pH. Weathering rate for Ca also declined but did not reach a definite steady state. Differences in cumulative weathering due to treatments appear to become less important over time.

The weathering schedule with intermittent drying showed more cumulative weathering for all ions (except Al) than the schedule with uninterrupted application of weathering solutions. Since the

intermittent drying schedule developed higher steady-state weathering rates, differences in cumulative weathering due to schedules increase over time.

The experimental results suggest that even if land management could lower the pH of the weathering solution, the long-term effect on weathering rate probably would be minimal. Alternate wetting and drying occurs naturally on Beaver Creek and would not appear to lend itself to practical management.

Comparison of outgoing waters from the Beaver Creek and simulated systems shows ion concentrations that correspond to the same secondary minerals when plotted on stability diagrams. Therefore, the same secondary minerals that are found at Beaver Creek Watershed No. 12 are anticipated after long-term artificial weathering. This is taken as an indication that the artificial system is a reasonable simulation of the relationship between parent materials and weathering solutions in the natural weathering environment.

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