SIMULATED ORGANIC ACID

WEATHERING OF

GRANODIORITE AND BASALT

by

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ABSTRACT

Basalt and granodiorite (medium to fine sand particle size) were leached by three low molecular weight aliphatic organic acids, namely citric, oxalic and acetic acid of .1M concentration. To evaluate the effectiveness of the organic acids in dissolving the rock samples, two control solutions, .005M HCl and distilled water were added to the number of dissolution treatments.

Dissolution of ions from granodiorite, by the leaching treatment shown in parenthesis, decreased in the following order:

Fe(OX) > Al(OX) ~ Si(OX) > Ca(CIT) ~ Mg(OX) ~ K(OX) > Na(OX)

Dissolution of ions from basalt decreased in the following order:

Fe(CIT) > Si(CIT) > Mg(CIT) > Ca(CIT) > Al(OX, ACETIC) > Na(OX) > K(HCl)

Oxalic acid effectively outcompeted citric acid in the weathering of granodiorite in spite of having lower stability constants for certain elements. This was attributed to differences in pH of the solutions (affecting both concentration of H^+ ions and anionic species), ionic competition in solution for ligand sites and geometry and oxidation state of ions in the parent mineral.

There was no conclusive evidence to indicate that chelation of K^+ or $Na+$ took place in any of the experiments.

However, mass balance calculations revealed that oxalic acid extracted approximately 40-50% of the K from granodiorite; citric acid extracted approximately 12%. These levels were significantly higher than those extracted by non-sequestering agents. XRD analysis of granodioritic-oxalate precipitate suggested the possible formation of a K-oxalate salt.

The chelating acids, citric and oxalic, greatly outcompeted acetic acid and HCl of similar pH for multi-valent cations in both basalt and granodiorite. Concentrations of Fe, Al, and Si, in solution were many fold higher than calculated concentrations of those ions in equilibrium with the amorphous oxide in water.

Oxalic acid and citric dissolution curves, determined from 11 weeks of leaching, showed initially increasing rates followed by declining rates which approached steady state towards the eleventh week of the experiment. Declining rates followed by steady-state rates were attributed to the presence of hyperfines the build-up of secondary precipitates, the increase of ions in solutions, and to an eroding leached surface layer.

Non-chelating acids namely acetic acid, HCl and H_2O revealed dissolution curves that were approximately constant (steady-state) throughout the 11 week weathering period.

XRD, XRF, SEM, and EDX analyses of weathered basalt and granodiorite as well as AA spectrophotometric solution analyses provided evidence which indicated incongruent

dissolution of granodiorite and basalt by all 5 leaching treatments.

SEM and XRF analyses indicated that citric acid was less effective than oxalic acid in forming precipitates from granodiorite. EDX revealed that the amorphous precipitate which did form in citric acid consisted primarily of Fe. EDX analyses of inorganic coatings indicated predominantly Si and Fe in 1:1 ratio.

Although citric acid was able to extract greater amounts of Fe from basalt than granodiorite, extractable Fe, Al and Si analysis and SEM detected no organo-amorphous precipitates. Also EDX of inorganic surfaces showed no accumulation of Fe or Al. It was concluded that the Fe extracted from the basalt remained in complexed or soluble form due to the higher pH (3-5) of the basaltic solution.

An amorphous precipitate formed from the leaching of granodiorite with oxalic acid. EDX analysis gave evidence that the precipitate consisted primarily of Si and Fe in a 1:1 ratio. An amorphous precipitate formed also from the leaching of basalt with oxalic acid. EDX analysis gave evidence that the precipitate consisted primarily of Mg and Fe in a 1:1 ratio. Data from molar oxide ratios and mass balance calculations as well as XRD, XRF, extractable Fe, Al and Si analyses were relied upon to determine the possible organic and inorganic components of these precipitates.

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INTRODUCTION

Chemical weathering of rocks and minerals is one of the most important processes by which chemical elements are fractionated at the surface of the earth. Much of the earlier research on the subject of mineral weathering was based on bulk chemistry or mineralogy of vertical profiles as a function of geomorphic or climatic factors. Among the most influential concepts to emerge from the early work were the "weathering series" of Goldich (1938), the "weathering index" of Jackson and co-workers (Jackson et al. 1948), and a variety of elemental mobility indices.

Goldich's weathering series, perhaps the most well known and quoted in many books, is merely the observation that certain minerals weather more rapidly than others. However, numerous attempts to unravel the underlying basis of Goldich's weathering series in terms of thermodynamics (Curtis 1976), or bonding energies in silicate lattices (Keller 1954), have still failed to produce a single unifying theoretical explanation for the stability sequence.

Weathering sequences of secondary minerals (e.g. Jackson et al.) are also based on observation but fail to determine the underlying mineralogical basis for the weathering sequence. The most extreme view holds that the weathering sequence:

Primary silicate ---> smectite ---> kaolinite ---> gibbsite
is in fact a reaction series, brought about by prolonged
leaching with the subsequent removal of cations and then
silica. The duration of leaching dominates this view, with
gibbsite seen as the most advanced product of weathering. In
1963 however, Grant (1963, 1964), showed that there is a
direct transformation of primary feldspars to kaolinite.
Eswaran et al. (1977), discovered formation of gibbsite from
primary minerals and its resilication to kaolinite. Also, as
pointed out by Schwertman and Taylor (1977), reduction or
chelation-solution and oxidation-precipitation reactions make
it difficult to position iron oxides in mineral weathering-
stability sequences. They participate in nearly all stages
of weathering and indicate an advanced stage only if strongly
accumulated under aerobic conditions.

Clearly, confusion has resulted from viewing minerals
outside of their environmental context. Although in 1957
Keller recognized that mineral stability depends on both the
thermodynamic susceptibility of the parent material and the
chemistry of the reactant solution, it is only in the last
decade that research has focused on the importance of aqueous
solution chemistry in the dissolution of primary and secondary
minerals.

The labile aqueous phase undergoes continuous
transformation of dissolved constituents into different
chemical species over a broad range of reaction time scales.

This kinetically complex process is the essential force that drives soil profile development and governs the patterns of chemical weathering (Sposito, 1981). For example, clays, which are non-stoichiometric phases reacting with aqueous solutions cannot be described by one characteristic formula, for their composition may change as a function of the composition of the aqueous phase, during or after their precipitation. Thermodynamic calculations of equilibria between multi-component solid solutions and aqueous solutions are difficult to isolate and understand and a general theory is not yet available. Computer models have, however, recently been developed (e.g. Fritz, 1985) which allow introduction in water-rock interaction modelling of mineral phases which vary with the composition of the solution.

Much remains to be learned regarding the very complex changes in solution chemistry brought about by weathering of minerals in the natural environment. In soils, physical, chemical and biological factors continually interact making it difficult to isolate and quantify the contribution of any one factor at any given time.

It was decided therefore to simplify a weathering environment by artificially leaching crushed basalt and granodiorite with five different extractants comprising both organic and inorganic acids. The focus of the experiment was to study the changes over time in solution chemistry for each leaching treatment. Precipitation products, which formed as

ionic species in solution sought lower free energy levels, were also analyzed. Physical and chemical changes in the weathered basalt and granodiorite were only noted in order to explain certain features of solution-precipitation equilibria.

Accordingly, three main topics for discussion (sections I, II and III in Results and Discussion) were chosen in order to unify the broad scan of information which resulted from the analyses. The first topic considered the chemical composition of the leaching solutions as influenced by parent rock and acid treatment. The second highlighted the kinetic features of dissolution, i.e. the relative rates of change of solution chemistry over time, and the third included a discussion on the formation of organo and amorphous precipitates from solution products.

More specifically the objectives of this study were:

1. To evaluate the effectiveness of two chelating and three non chelating acids in dissolving basalt and granodiorite.

2. To determine whether the extent of dissolution is correlated with stability constants of organic acids, pH of solution, or type of mineral in the parent rock.

3. To trace the changes in rates of dissolution over time (11 weeks) and propose possible explanations for the kinetic behaviour.

4. To ascertain whether dissolution was incongruent or congruent.

5.   To analyze precipitation products formed from solution.

Finally, it was hoped that this experiment would shed light on further research needed to account for differences in the dissolution of minerals by low-molecular-weight aliphatic acids.

MATERIALS AND METHODS

1. EXPERIMENTAL DESIGN

Basaltic and granodioritic samples were collected from the Cheakamus and Cypress Bowl Formations located in the Coastal Mountain Range of British Columbia. The rock samples were then crushed and sieved and the 0.1 mm - 0.5 mm diameter fraction (fine-medium sand) was retained for the experiment. Particles in that size range were considered fine enough to react chemically with aqueous solutions but coarse enough that liquids could be clearly separated from them by gravity and centrifugation. Also particles in that size range preclude the chances of plugging in gravity columns. Samples were mixed thoroughly to achieve maximum homogeneity, then weighed to 100 gms, and leached with 400 mls of acid per day.

In order to compare the relative dissolution powers of organic acids in weathering of minerals, three aliphatic acids were chosen which are characterized by the number of associated carboxyl and hydroxyl groups. Thus, citric acid with one hydroxyl and three carboxyl, oxalic acid with two carboxyl and acetic acid with one carboxyl group were selected. Each acidic solution was brought to .1M concentration (see Table 1).

To further evaluate the effectiveness of the acids in dissolving basalt and granodiorite, two control solutions were

	Citric Acid	Oxalic Acid	Acetic
Chemical Name	2-Hydroxy propane 1,23-tricarboxylic acid	Ethanedioic acid	Ethanoic acid
Chemical Composition	$C_6H_8O_6$	$C_2H_2O_4$	$C_2H_4O_2$
Category	Non-volatile aliphatic	Non-volatile aliphatic	Volatile, aliphatic
Type of Complex	5 and 6 ring	5 ring	Monodentate
pKa	3.14, 4.77, 6.39	1.23, 4.19	4.76
pH of 10^{-1}M solution	2.3	1.6	2.9
Structures			

TABLE 1: CHEMICAL DESCRIPTION OF CITRIC, OXALIC AND ACETIC ACID.

prepared - .004M HCL and distilled water. This concentration of HCL produces approximately the same amount of ionized H in solution (pH = 2.4) as do .1M citric (pH = 2.3) and acetic (pH = 2.9) acids. The pH of .1M oxalic acid was somewhat lower at pH = 1.6 and distilled water much higher at pH = 5.7.

Three replica samples of basalt and granodiorite were leached by the 5 organic and inorganic treatments. Leaching was undertaken by batch and column extraction methods. A summary of the experimental design is as follows:

```
EXPERIMENT                        COLUMN/BATCH
                            ┌──────────────┴──────────────────┐
PARENT MATERIAL          BASALT                        GRANODIORITE
                    ┌──────┴──────┐              ┌──────────┴──────────┐
TREATMENT  Citric Oxalic Acetic HCl   H2O    Citric Oxalic Acetic  HCl    H2O
           ┌─┬─┬─┬─┬─┬─┬─┬─┬─┬─┬─┐     ┌─┬─┬─┬─┬─┬─┬─┬─┬─┬─┬─┐
REPLICAS   1,2,3 1,2,3 1,2,3 1,2,3 1,2,3 1,2,3  1,2,3  1,2,3  1,2,3 1,2,3
```

The column and batch leaching experiments were carried out over two different time periods. In the first, samples were leached for one month followed by destructive analysis of both solutions and weathered material. Fresh samples and solutions were then reassembled and leached for 11 weeks. Solutions were removed and analyzed after week 1, 3, 5, 7, 9, and 11. In this way fresh solutions were introduced into the column and batch experiments every two weeks which not only enhanced the rates of dissolution but enabled calculations of kinetic features of the experiment. At the end of 11 weeks, the mineral samples were air-dried in preparation for further analysis.

2. DESCRIPTION OF COLUMN EXPERIMENTAL APPARATUS AND PROCEDURE

A column extraction procedure was designed which utilized the force of gravity to leach the mineral parent material. From top to bottom the apparatus consisted of the following for each sample:

(a) One litre polyethylene bottle with tubulation in which the extracting solution was placed.

(b) Polyvinylchloride tubing to connect the bottle to the sample column.

(c) Adjustable clamp placed on the tubing to control flow rate.

(d) Rubber stopper inserted into the top of the column. A hole bored into this stopper to direct the PVC tubing into the column.

(e) Acrylic column 25 cm in length and 2.5 cm inner diameter to contain 100 gm of sample.

(f) 2 mm inert glass beads packed to a depth of 2.5 cm into top of column and resting on rock sample to promote even distribution of leachate.

(g) 100 gm of crushed rock sample placed into column.

(h) Whatman ashless No. 41 filter paper beneath rock sample.

(i) Rubber stopper inserted into bottom of column to support sample and filter paper. A hole bored into

this stopper directed an acrylic tube into catchment beaker.

(j) 600 ml catchment beaker with cellophane cover to inhibit evaporation.

The entire assembly was supported on a table in which holes were bored to enable connecting PVC tubing (from the one litre bottle to the column) to pass through. An elastic band was pulled around each sample column and attached to nails inserted on a side panel built on all four sides of the table.

Solutions from each sample were separated from the parent material for further analysis by removing the contents from the 600 ml catch beaker. Recycling of the solution each day was achieved by pouring the solution captured in the 600 ml beaker back into the 1 litre polyethylene bottle resting on the table.

3. DESCRIPTION OF BATCH EXPERIMENTAL APPARATUS AND PROCEDURE

A batch extraction procedure utilized the physical force of shaking sample and solution for 1 hour each day to leach the mineral parent material. An arbitrary time of one hour was chosen to minimize physical or mechanical breakdown of particles.

100 gms of sieved granodiorite and basalt were placed in 500 ml polyethylene bottles with 400 mls of extracting solution and sealed with parafilm and No. 9 rubber stoppers.

Each day the seals were removed so that the extracting

solution could equilibrate with CO_2 in the atmosphere

Solutions from each sample were separated from the parent material by centrifugation at 4200 rpm in order to carry out further analyses.

In batch experiments particle size does not have the potential to interfere with leaching rates as is the case in gravity - column experimental set-ups. It was decided therefore to also study, by batch procedure, the leaching of granodiorite and basalt which were sieved and collected from <.1 mm diameter particles. Samples <.1mm were designated "Granodiorite B" and "Basalt B"; Samples .1 mm - .5 mm were designated "Granodiorite A" and "Basalt A". Furthermore, a crust-like material settled on the top of weathered air-dried batch samples following 11 weeks of leaching. It was thought that this crust-like material might reveal distinctive chemical features and was therefore separated from the bulk of the sample and analyzed. This material was referred to as "crust".

4. ANALYSES OF SOLUTION EXTRACTS AND WEATHERED MINERAL PARTICLES

(a) Solution Extracts

Determination of dissolved Ca, Mg, Na, K, Fe, Al, and Si ions was carried out with a Perkin-Elmer Model 306 atomic absorption spectrophotometer. To overcome possible anionic

interference, a nitrous oxide flame was used in determining levels of Ca, Al and Si. An acetylene flame was used in determining levels Fe, Mg, Na and K. pH of the extracting solutions was determined by an Accumet pH meter, Model 810.

(b) Mineral Residues

Chemical and physical analyses of the unweathered and weathered granodiorite and basalt included the following: X-ray diffraction (XRD), X-ray florescence (XRF), SEM (scanning electron microscopy), light microscopy, EDX (energy dispersive X-ray) CEC (cation exchange capacity), exchangeable bases, surface area, pH and extractable Fe, Al and Si.

Citric and oxalic acid crystals and citrate and oxalate salts of K, Na, Mg, K, Fe, Al and Si were prepared in the laboratory for subsequent XRD analysis. This data was used, in addition to published data of XRD peaks for organo-metallic salts, to assist in the identification of secondary precipitates.

(i) XRD Analysis

Unoriented powder mounts were prepared for XRD examination of the gross mineral distributions. The sediment samples were packed into a standard Philips aluminium sample holder and compressed with a piston and a mechanical press. The determinations were all made with an automated Philips PW 1710 Powder

Diffractometer using CuK & X-radiation with a curved graphite crystal (002) monochromator, and an automatically adjusting divergence slit (goniometer controlled). The unoriented powder and mineral samples were quickly scanned ($.1^{o}2$/sec) from $4.2^{o}\theta$ to $60.2^{o}\theta$.

(ii) **XRF Analysis**

For the major elemental determination by XRF, 36 mm diameter glass discs were prepared by fusing, using 0.4 g of sample and 3.6 g of ultra-pure Spectroflux 105 (Johnson-Matthey Chemicals Ltd.) consisting of $Li_2B_4O_7$, La_2O_3 and Li_2O_3. Before weighing, the flux was dried in a furnace at $500^{o}C$ for one hour to remove absorbed water. The weighed flux and sample were placed into a platinum crucible and fused in a muffle furnace at $1100^{o}C$ for 20 minutes. After cooling the fused samples, the weight loss resulting from the removal of interlayer water, oxidation of organic matter and volatilization of some elements, was made up with Spectroflux 100 which contains only $Li_2B_4O_7$ and thus does not alter the sample/La ratio. La is needed as a heavy absorber in the glass discs to increase the total mass absorption of the glass and thereby minimize matrix absorption effects between different samples. After adding flux 100,

the glass was refused on a Meker burner and poured into an Al-mould on a hotplate set at 400°C. The molten sample was then flattened with a brass plunger, and the resulting disc was later directly presented to the X-ray beam. An automated Philips PW 1400 X-ray florescence in combination with a peripheral digital PDT 11 computer was used for calculating the elemental concentrations. Calibration of the analyses was provided by a large number of international rock standards.

(iii) **SEM and EDX Analysis**

Samples to be microanalyzed by SEM were mounted on scanning electron microscope stubs painted with colloidal graphite in an alcohol base. The mounted particles were then C-coated by a vacuum evaporator and observed using a Hatachi S-570 scanning electron microscope. Polaroid photographs of the electron images were taken at various magnifications and analysis of the sample was carried out with a Kevex 8000 Energy dispersive X-ray spectrometer. Those samples which were not subjected to microanalysis (i.e., EDX) were treated with a Hummer gold sputter coater so as to enhance the quality in the photographic image.

(iv) Photographs of mineral samples were taken with a

Zeiss dissecting microscope at 50 x magnification.

(v) **Surface Area**

Surface area was determined by the ethylene glycol monoethyl ether (EGME) technique (Heilman, M.D; Carter, D.L and Gonzales, C.L. 1965).

(vi) **Chemical Analyses**

Cation exchange capacity and exchangeable cations were measured by the ammonium acetate (pH 7.0) method, following the procedure given by Lavkulich (1981). Iron, aluminum and silicon were extracted by sodium pyrophosphate (pH 10.0) (Bascomb, 1968), acid ammonium oxalate (pH 3.0) (McKeague and Day, 1966) and citrate-bicarbonate solution (pH 7.3) (Weaver et al, 1968; Mehra and Jackson, 1960). The ppm of each element within each extractant was measured using atomic absorption spectrophotometry on a Perkin-Elmer 306 spectrophotometer. These elements were then calculated as a percent of the total sample.

The pH was determined in both water (Peech, 1965) using a 1:1 mineral:water suspension, and in 0.01 M $CaCl_2$ (Peech, 1965) using a 1:2 mineral:0.01M $CaCl_2$ suspension. PH measurements were taken on an Accumet pH meter, Model 810.

LITERATURE REVIEW

A. THE ROLE OF ORGANIC ACIDS IN WEATHERING OF MINERALS

1. Occurence of Natural Organic Acids

Natural organic acids in soils and freshwater environments are derived from plant and animal residues, microbial metabolism and canopy drip (Huang and Violante, 1986). Oxalic and other organic acids can also occur in rainwater in concentrations as high as a few micromolar (10^{-6} M) (Stumm et al., Stumm and Furrer, 1987). In top soils, the presence of water soluble organic acids, such as malic, malonic, citric, oxalic, acetic, succinic, tartaric, vanillic and p-hydroxybenzoic acids may reach concentrations as high as 10^{-5} M to 10^{-3} M, oxalate being the most abundant (Graustein, 1977; Stevenson, 1982). In fungal mats where oxalates are produced, and in the rhizosphere where root exudates are secreted, as well as localized microclimates such as capillary water adjacent to a soil particle, concentrations of organic acids may be even much higher. In one study of a natural environment, the top layer of a forest soil contained an average of 7 mg/g oxalate, with the oxalate crystals adhering to fungal hyphae demonstrating the source of the organic acid (Graustein et al. 1977).

Ca- and Mg-oxalate crystals have also been found in lichen thalli grown on basalt and serpentine (Jones et al.

1980; Wilson et al. 1981). The presence of oxalic and citric acids in the weathering crust of sandstone was demonstrated by thin layer chromatography (Eckhardt 1978).

Stevenson (1967) has reviewed the distribution and pedogenic activity of organic acids in soil. These acids are chemically polyfunctional in that they contain more than one carboxyl group (e.g. oxalic) or carboxyl with one or more hydroxyl groups (e.g. citric) and can form chelates with inorganic ions. A chelate complex forms when two or more coordinate positions about the metal ion are occupied by donor groups of a single ligand to form an internal ring structure. High-molecular-weight organic polymers, such as fulvic and humic acids, although less completely characterized, possess carboxyl, hydroxyl and amide groups and also form chelated complexes with metals (Mortenson, 1963). Konova (1961), Caroll (1970), and McKeague et al. (1986) have discussed the various roles or organic compounds in pedogenesis.

2. Organic Acids and Soil Weathering

The awareness of an interaction between organic and mineral components emerged in the very early years of soil science. Long before Dokuchaiev formulated his pedological concept, soil organic acids, including humic acids, were thought to play an important role in the dissolution of rocks and minerals. Sprengel in 1826 suggested a key role of organic acids in mineral weathering (Tan, 1986), followed by

Kindler in 1836 who reported the bleaching of ferruginous sands around decomposing roots (Bloomfield, 1981). Evidence continues to accumulate to this day indicating that organic acids, both aromatic and aliphatic, accelerate degradation of rocks and minerals due to their inherent acidity as well as chelating capacity (e.g. Huang and Keller, 1970; Huang and Kiang 1972; Boyle et al. 1974; Razzaghe-Karimi 1974; Singer and Navrot 1976; Schnitzer and Kodama, 1976; and Pohlman and McColl 1988).

Debate as to the relative importance of acidity vs. chelation in promoting dissolution of minerals is evident in reviewing the literature of soil science journals. In 1967, Schalsha et al. studied the effect of complexing agents on the solubilization of Fe from granodiorite and postulated that, "the formation of metal complexes may take place simultaneously with acid action, or that chelation may be the sole or major mechanism responsible for some effects theretofore attributed exclusively to H ions." In the same year Boyle et al. (1967) observed that the greater the chelating ability of a biogenic acid the more Fe and Al it removed from biotite. Huang and Kiang (1972) found citric acid to be more effective than other acids in extracting Al and Ca from Ca-rich plagioclase, presumably because of its greater complexing ability. Strongly complexing organic acids increase the total weight of clay minerals dissolved by distilled water by factors of 5 to 75 (Huang and Keller,

1971), and may alter the ratio of Si to other metals, notably Al and Fe, dissolved from some silicate minerals (Huang and Keller, 1970). Indeed, the relative distribution of pH-dependent Al ion species in aqueous solution is markedly altered by Al-Salicylate complexes within the pH range 1.5 to 7.5 (Huang and Keller, 1972).

More recently, Pohlman and McColl (1986) analyzed the moles of metal released from a soil by 10^{-3}M citric acid at pH 3.25 and 5.65. By calculating the ratio of number of moles of cations released to H^+ ions consumed during the leaching process, they concluded that, "the effect of H^+ on the dissolution process was minimal and dissolution of metals from the solid phase was mainly by shift in the anionic species of citric acid." However, Manley and Evans (1986), concluded from their weathering experiments that the amount of Al released from feldspars by the organic acids appeared to be related more to their acidic strengths than to their ability to form complexes. They pointed out that if "complex formation were of paramount importance in dissolution, it would have been expected that protocatechinic, gallic, and, particularly, caffenic acid would have extracted more Al than the observed amounts". Concurrently Tan, (1986), reported that humic acids with both carboxyl and phenolic functional groups affect mineral dissolution by both the acidic effect and complex formation. He maintained, however, that simple aliphatic acids including oxalic acid affect mineral

decomposition "generally more through the acidic (H$^+$ ions) effect". Bloom and Erich (1987) found that the type of anion in solution determined the rate and mechanism of gibbsite dissolution. In solutions containing ions not specifically adsorbed (e.g., NO_3^- and SO_4^{2-}), proton attack of the surface was the rate-determining step. In solutions containing phosphate which forms inner sphere complexes, anion attack predominated and the rate of the reaction was not dependent on pH. Finally, it must be remembered that organic acids may remove metals already released by hydrogen ion attack on silicate minerals thereby providing a sink to keep sparingly soluble metals in solution (Schalscha et al. 1967). In this way the reaction continually shifts to the right of equilibrium and the rate of dissolution is increased over that of a system where precipitation products build up. Also, the domain of congruent dissolution of minerals is extended as higher concentrations of soluble ions can be built up before a new phase is formed.

b. Geochemistry and Weathering

Geochemists have recently begun to apply the principles of chemical kinetics to mineral weathering reactions occurring in soils. Most of the work done has involved feldspars of different composition although pyroxenes, amphiboles, and other minerals have been studied (Berner, 1981; Lasaga, 1981;

Holdren and Speyer, 1985; Chow and Wallast, 1985). In the case of feldspars, many experimental studies of hydrolysis rates have resulted in compilations of rate coefficients for different experimental conditions (Helgeson et al., 1984), yet the actual mechanism of feldspar dissolution is still not clearly defined (Coleman and Dethier, 1986). Some general theories however have arisen from mineral dissolution studies.

In many dissolution experiments the release of silicon and alkali ions are linear functions of the square root of time and this has been characterized as following "parabolic" rate laws. Some researchers have attributed this parabolic behaviour to the diffusion of ions from the fresh mineral through an ever thickening secondary precipitate (Wollast, 1967; Helgeson, 1971), or through a leached layer formed on the parent material (Luce et al., 1972; Paces, 1973; Busenburg and Clemency, 1976).

From the work of Petrovic (1976) and Schott & Berner (1983) it is likely that the structure of a hydrous ferric oxide layer, similar to that of aluminum hydroxides forming on mineral surfaces is not protective towards dissolution. In the leached layer hypothesis, preferential leaching of mobile elements such as alkalis is thought to occur at the mineral surface and leads to the formation of a residual hydrated layer. Diffusion of reactants through this nonstoichiometric residuum then controls the release of exchangeable cations, while the leached silicate or

aluminosilicate framework dismantles at a slower rate. As the layer builds up, the rate of dissolution decreases until a steady state is reached when the rate of removal of silica from the surface keeps pace with the rate of cations from deeper within the solid. Finally, others have argued that the rate-limiting step is, in contrast to diffusion, a surface-controlled reaction (Lagache, 1976; Petrovic et al. 1976; Holdren and Berner, 1979; Holdren, 1983). This theory envisions weathering as a two stage process: a rapid exchange of H^+ for alkalis (Garrels and Howard, 1959) followed by the rate determining step controlled by the detachment of silicate and aluminate units from the crystalline framework (Aagaard and Helgeson, 1982). The rate of dissolution should be constant, as long as parameters such as pH, surface area, ligand concentration do not change (Aagaard and Helgeson, 1982). Schott and Berner (1983) studied the mechanism of iron silicate dissolution during weathering and noted that the hypothetical protonated layer did not continue to grow in thickness during their experiments. They concluded that this was most likely a result of loss by dissolution at the layers outer surface at the same rate that it grew by H^+ attack at its inner surface. Accordingly, the non-linear kinetics at the beginning of most experiments are attributed to the rapid dissolution of hyperfine particles, as it has been observed in experimental systems that Si is released from feldspar in a linear fashion following removal of hyperfines by $HF-H_2-SO_4$

treatment (Holdren and Berner, 1979).

Until very recently the tendency in the literature has been to consider that the rate limiting step during silicate dissolution is related to surface phenomenon, and the hypothesis of diffusion control has been commonly discarded because of the failure to identify a residual layer with the aid of modern spectroscopic methods, such as X-ray photoelectron spectroscopy (XPS) or scanning electron microscopy (SEM). However, as pointed out by Berner et al. (1985), if dissolution occurs along deep cracks, tubes, holes and so on, that intersect only a small portion of the mineral surface, XPS, which samples a large surface area to a small depth, is likely to miss cation depletions on the walls of these etch pits. Hence, the failure to detect cation depletion does not prove absolutely that discontinuous altered layers are not formed. In fact, Petit et al. (1987) have presented the first direct evidence of surficial hydration of silicate minerals using a resonant nuclear reaction (RNR), which allows direct hydrogen profiling. The presence of defects, providing points of access surface energy, would likely facilitate the diffusion of molecular water into the crystal thereby enhancing reactions with the silicate net-work. It should be added that diffusion of molecular water had already been detected during the dissolution of silicate glasses and was invoked by Veblen and Busek (1980) and Eggleton and Boland (1982) as the controlling step for the

weathering of pyroxenes.

It may be summarized that indeed an altered surface layer develops on minerals exposed to solutions. The only question still unanswered concerns the rate-determining step or the kinetics of dissolution.

At any rate, if it is true that for most slightly soluble minerals the rate of dissolution is controlled by reactions at the surface (with or without a leached layer), this rate will depend on the coordinative interactions taking place on these surfaces. Furrer and Stumm (1983) have proposed that reaction rates controlling dissolution of most hydrous oxides and aluminum silicates simply depends on the concentration of species interacting with the surface. Their study showed that the dissolution rate of δ-Al_2O_3 in dilute acids (pH 2.5-6) depended directly on both the extent of surface protonation and on the concentration of surface complexes formed in ·the presence of oxalate, salicylate, citrate and benzoate. Furthermore it was concluded that the effect of the ligand became superimposed on that of surface protonation. The total dissolution rate can therefore be considered to be composed of two or more additive rates:

$R_{TOT} = R_H + R_L$

R = total rate of dissolution in mol m^{-2} h^{-1}

R_H= rate of proton-promoted dissolution

R_L= rate of ligand promoted dissolution

It should be noted that the increase in weathering rate

of δ-Al_2O_3 upon increase in proton concentration was not linear but rather proportional to $[H^+]$ to the 0.4 power. Many other common minerals have also been reported to undergo fractional order dissolution in acids, (eg. K-feldspar $[H^+]^{0.33}$); Wallast, 1967; Grandstaff, 1977, and Schott et al., 1981). Grandstaff (1986) reported that reaction rates for forsteritic olivine are first order with respect to hydrogen activity and approximately proportional to the square root of free-ligand activity. He also comments on the mechanism by which organic ligands may influence the dissolution rate of olivine. According to transition state reaction theory, a reaction or series of reversible reactions occurs, giving rise to an activated complex (Aagaard & Helgeson, 1982). The activated complex of undetermined stoichiometry, may then decompose to yield reactants (reverse reaction) or products dissolved in solution (forward reaction). Organic ligands adsorbed on the surface of the mineral may form metal-organic complexes with ions in the activated complex, destabilizing it and providing an alternative pathway for decomposing the activated complex. The metal-organic complexes then desorb to yield dissolved products.

The concepts given for dissolution of hydrous oxides have been extended to the weathering of kaolinite (Wieland and Stumm, 1987). Hydrogen ions and ligands may associate with the octahedral (Al-bearing) or tetrahedral (Si-bearing) sheets. Wieland and Stumm (1986), found that oxalate and

salicylate accelerated the dissolution reaction of kaolinite through attack of the Al centers. This facilitated the (slower) detachment of the Al species, which is followed by the (faster) detachment of the silica units.

Robert (1970), and Boyle et al. (1974) have shown experimentally the drastic effect of organic complexing agents on micas and micaceous clays. Not only the interlayer and tetrahedral Al, but even a considerable part of the aluminum of the octahedral layer was complexed. The sheet structure was completely destroyed as the constituents became solubilized or amorphous.

Recent work in the field of geochemistry has therefore helped clarify the debate on the relative importance of proton vs. ligand weathering of aluminosilicates. Whether or not the ligand facilitates breakdown through attack of octahedral aluminum or raises the concentrations of complexed ions in solution thereby, extending the domain of congruent dissolution, it seems certain both proton and ligand attack can occur simultaneously and not one exclusive of the other.

B. WEATHERING AND THE FORMATION OF PRECIPITATION PRODUCTS

Weathering of rocks and minerals may result in a vast spectrum of precipitation products as ions brought into solution exceed saturation. These inorganic ions also interact with organic ions and depending on such factors as

charge and molar ratios of the constituent ions, may form solids of varying degree of crystalline order. Much of the research studying these precipitation products has focused on the formation of sesquioxides due to their common occurrence in soils. It was anticipated that due to the high affinity of organic acids for Fe and Al, sesquioxide development might occur in the Batch and Column experiments. A study was undertaken therefore of the literature pertaining to sesquioxide development

1. Forms of Sesquioxides

a) Fe oxides

Fe oxides, oxihydroxides and hydroxides (collectively referred to as Fe oxides) are among the most common minerals formed during rock weathering. They vary in mineral species (goethite, hematite, lepidocrocite, maghemite, ferrihydrite) and, additionally for any mineral, in crystallinity and Al-for Fe substitution in the structure. All the parameters may reflect the weathering environment.

The various Fe oxides with a high specific surface profoundly influence both chemical and physical properties of soils (e.g. bulk density, porosity, structure, surface charge and anion retention) (Jou,1977).In fact, it is now widely believed that oxides of Fe and Al in soils can provide many more sites for adsorption of acidic organic substances than can clays including smectites (Parfitt et al. 1977).

Forms and formation of Fe oxide minerals in natural and synthetic environments have been reviewed by Oades and Townsend (1963), and more recently by Schwertmann and Taylor (1977), and Sposito (1984).

Among the Fe compounds goethite (FeOOH) is most often found in soils as it is the most thermodynamically stable (Sposito, 1984). In the presence of Fe-complexing ligands that inhibit crystallization, however, ferrihydrite ($Fe_2O_3.2FeOOH.2.6H_2O$) may precipitate from soil solution (Sposito, 1984), and even the crystallization of ferrihydrite may be obstructed by the adsorption of soil organic matter on its surface (Schwertmann, 1966).

Clearly the presence of organic ligands in solution directs the transformations of Fe oxides to a remarkable degree. Schwertmann (1966), investigated the effects of a number of low molecular weight aliphatic carboxylic and hydroxy-carboxylic acids on the crystallization of hematite and goethite from freshly precipitated ferrihydrite. The hydroxy-carboxylic (polybasic) compounds (e.g. citric acid) inhibited crystallization whereas the non-hydroxy carboxylic acids (e.g. oxalic acid) did not.

Furthermore, Fischer and Schwertmann (1975), demonstrated that the addition of oxalic acid to an aqueous system containing ferrihydrite (at pH 6 and 70°C) favoured the crystallization of hematite over that of goethite. It was suggested that oxalate accelerated the nucleation of hematite

crystals by acting as a template, with Fe-Fe distances in Fe-oxalate (0.56nm) being similar to those in hematite (0.54 nm). On the other hand, where citric acid provided the organic ligand, oxidation of Fe-citrate yielded pure goethite.

In addition to differences in type of organic ligand, differences in concentration play a key role on determining which iron oxide will form. Schwertmann (1986), concludes, "the higher the concentration of organic compounds compared with the rate of release of Fe from primary silicates, the greater the probability that goethite will be the dominating or only ferric oxide formed." If the rate of Fe supply is high along with higher concentrations of organic matter, ferrihydrite will form. At still higher organic matter content a precursor of ferrihydrite often occurs and can be considered a young metastable Fe-oxide of low structural order and high surface area. Its transformation to more stable forms may be considerably retarded by adsorbed silica and organics (Schwertmann, 1985). Finally, even at higher organic matter content, all the Fe may be organically complexed such as in "O" horizons or in peaty environments and no more Fe oxides will be formed (Schwertmann, 1988).

As a result of such studies the hematite-goethite ratio in soils has been used to discern the C-regime and, in turn, the climate. Figure 1 summarizes the possible pathways of Fe oxide formation under near pedogenic conditions. It should be noted however that amorphous precipitates or gels of Fe, in
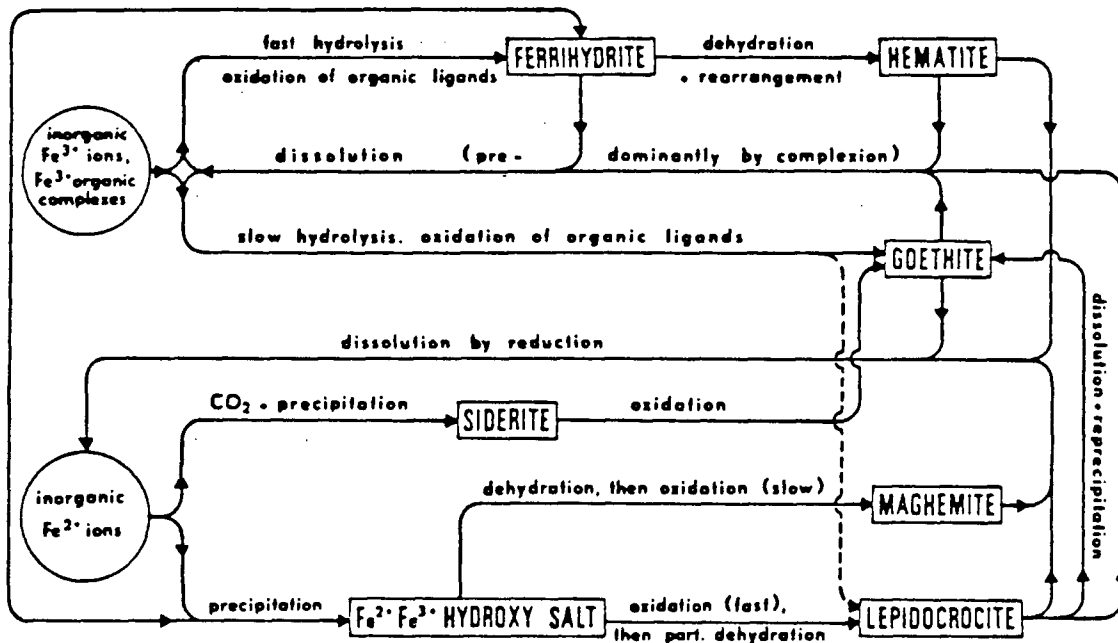
Figure 1: Possible pathways of iron oxide formation under near pedogenic conditions.

Source: Schwertmann, and Taylor, 1977.

Source: Lindsay, 1979.
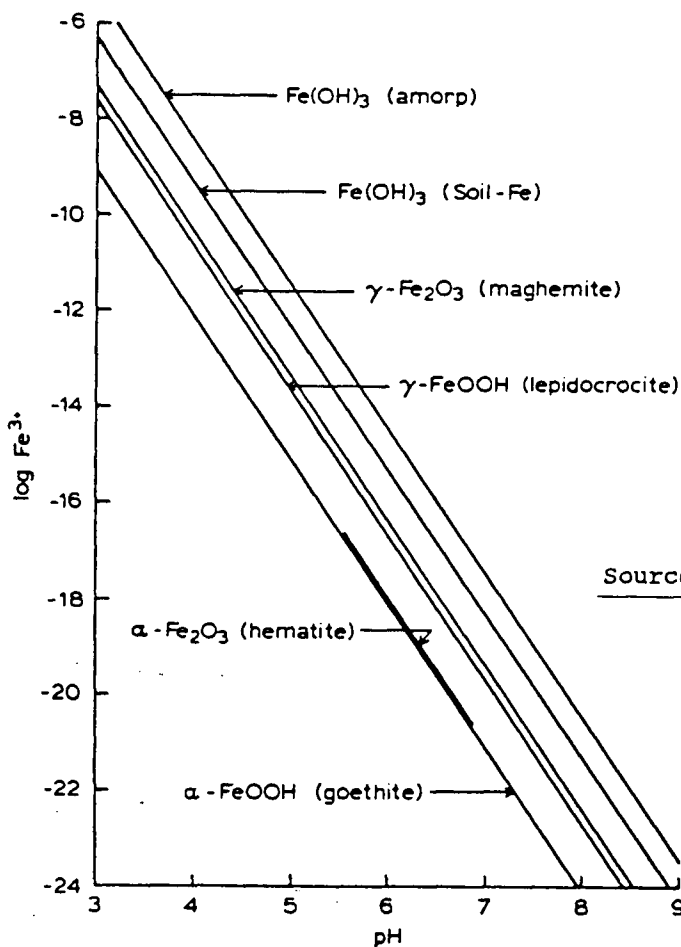
Figure 2: The activity of Fe^{3+} maintained by Fe(III) oxides and soil-Fe.

association with organic and inorganic anions, are not detailed in the diagram. To date there appears to be little base line data in soil science literature chemically characterizing such gels.

b) Al oxides

Al in soil solutions and freshwater undergoes hydrolysis and may give rise to precipitated Al hydroxides (Hsu, 1977). The precipitates may crystallize into 3 polymorphs, namely bayerite, gibbsite or nordstrandite depending on the rate of precipitation, pH of the system, clay surface and nature and concentration of inorganic anions (Hsu, 1977). Also the oxyhydroxides with two polymorphs diaspore and boehmite may form.

The mechanisms governing their development still remain obscure. Al can also enter the structure of Fe^{3+} oxides and replace Fe^{3+}. Substitution of Al for Fe appears to be widespread in soils (Schwertmann and Taylor, 1977).

In the presence of silicic acid which has a strong affinity for Al (Luciak and Huang, 1974), further hydrolysis and polymerization of the OH-Al polymers is retarded. These counter polyvalent anions tend to link OH-Al polymers together but in distorted arrangements.

Similarly, many organic acids promote the formation of precipitation products of Al which are non-crystalline to X-rays (Huang and Violante, 1986). As illustrated in a study

using citric acid (Kwong and Huang, 1975,1977), the occupation of the coordination sites of Al by citrate ions, instead of water molecules, disrupts the hydroxyl bridging mechanism indispensible for the formation of hydroxy-Al polymers. It was found in this study that as little as 1 uM citric acid altered the precipitation behaviour of Al.

Due to steric factors, the perturbing ligands occupying the coordination sites of Al distort the arrangement of the unit sheets normally found in crystalline Al hydroxides as shown below:
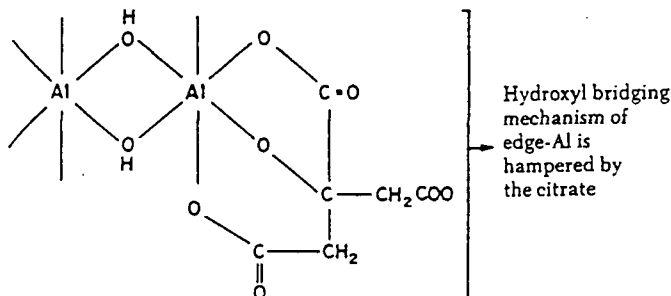
The ability of organic ligands to disrupt hydrolysis of Al is determined largely by the affinity of the acid for Al (reflected in the stability constant) and the organic ligand to Al ratio (determined by the concentration of acid).

2. Evolution of Sesquioxides

Much of the research on formation of sesquioxides has arisen from the study of Podzol development. In particular, debate has centered on whether sesquioxides are transported to the B_2 horizon by complexing organic compounds (Schnitzer and Kodama, 1977; Buurman and Van Reeuwick, 1984), or whether

as short range order silicates upon which organic matter is subsequently precipitated (Farmer, 1981; Farmer et al. 1980; Anderson et al. 1982; Farmer et al. 1985). A summary of these arguments sheds some light on the chemistry of sesquioxide formation from solution, as affected by the presence of organic acids.

a)   Inorganic Fe-Al-Si Sols

During the 1970's, it was apparent that hydroxyaluminum species react with orthosilicic acid at pH< 5 to give stable sols or solutions; the soluble phase was termed proto-imogolite, since its infrared spectrum indicated a close structural relationship to imogolite (Farmer and Fraser, 1978; Farmer et al. 1977,1978,1979). It is proposed that there is ample SiO_2 in most soil solutions (typically 10-40 ppm) to ensure that imogolite rather than aluminum hydroxides form when a reactive aluminum species is liberated by the weathering of minerals (Farmer, 1979).

In 1982, Anderson et al. concluded that imogolite-type materials formed in the B_2 horizons, in the first stage, can be deposited only from solutions containing a positively charged hydroxy-aluminum silicate complex. These solutions cannot, as argued by Farmer et al. (1980) simultaneously transport negatively charged organic matter except as a minor component sorbed on the positive colloid. Iron was stated to be present almost entirely as a separate oxide phase, with

very little of it incorporated into imogolite type phases. The idea that Fe and Al are not combined in a single inorganic complex was based on the findings that although the Al:Fe ratio in B_2 horizons lies between 1.5 and 2.0, acetic acid extracted about 20% of the oxalate-extractable Al, but less than 1% of the oxalate-extractable Fe. Also Kerndoff and Schnitzer (1980), showed that humic acids have a much greater affinity for hydroxy-ferric species than for aluminum ion species in acid solutions,so it was argued that any mechanism that generates ferric species, even in low concentration would likely form ferric organic rather than inorganic species.

However, Farmer and Fraser (1982) succeeded in synthesizing at pH 4.5 and 5.0 a stable $Al_2O_3-Fe_2O_3-SiO_2-H_2O$ sol with Fe:Al molar ratios up to 1.5 (wt/wt) after which stability decined rapidly.These results pointed out that mixed Fe-Al hydroxide sols, with or without incorporated silica, could transport Al and Fe in podzols and account for the constancy in oxalate extracts from podzol B_2 horizons of the Al:Fe ratios of 1.5-2.0.

Hydroxy-Fe species and ortho-silicic acid do not form structures analogous to imogolite (McBride et al, 1984), although Fe^{3+} has been shown to interact with monomeric silicic acid $Si(OH)_4$ in dilute acid aqueous solutions to form relatively stable $FeSiO(OH)_3^{2+}$ complexes (Weber and Stumm, 1965). This complex is monomeric at pH<3.0 and both monomeric and polymeric between between pH 3.0 and 6.0 (Olsen and

Omelia, 1973).The extent of Fe substitution for Al within imogolite/proto-imogolite structures was investigated by McBride et al. 1984. ESR spectra indicated that the non-crystalline precursor of imogolite (i.e. proto-imogolite) can incorporate Fe^{3+}; Fe^{3+} tended, however, not to substitute randomly in the solid but segregated into "clustered" Fe^{3+}-rich phase, even at Al:Fe ratios as high as 40. Segregation was almost complete for Al:Fe ratios of one or less. A mechanism was suggested wherby Al was ejected from an initially Fe-rich polymer, and then reorganized to form an almost Fe-free proto-imogolite allophane. Such a process, therefore, could account for the high colloidal stability of the mixed Al_2O_3-Fe_2O_3-SiO_2-H_2O sols, since the dispersed phase could consist of a ferrihydrite core protected by a proto-imogolite surface structure.

The deposition and precipitation of inorganic sols may occur when the pH rises (>5 for proto-imogolite), or when the positive charges that maintain dispersion at more acid pH values, are neutralized by adsorbed anions, or when these positive colloids encounter negatively charged surfaces (Farmer, 1979).

b) Organic Sesquioxide Interaction

The formation of sesquioxides in the presence of organic substances was studied over half a century ago by Baudisch and Albrecht (1932), who investigated the oxidation of a mixed

solution of ferrous ions and pyridine by air, and by Glesmer (1938), who studied the reaction of $NaNO_2$ precipitating a mixed solution of ferrous ions and hexamethylene tetramine.

In 1964 Van Schuylenborgh reported that one mechanism which could account for the formation of sesquioxides from a metallic organo-complex was that of hydrolysis. Giving an example of a mononuclear complex, the overall equation of such a reaction was presented as:

$$MZ^{n-m} + nOH^- == M(OH)_n + Z^{-m}$$
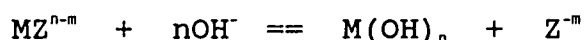
where M represents the metal Fe or Al, n the valency, Z the organic acid with basicity m and MZ^{n-m} the complex. The equilibrium constant for this process is then given by the expression:

$$K= \frac{[\ M(OH)_n\ ]\ [\ Z^{-m}\ ]}{[\ MZ^{n-m}\ ]\ [\ OH^-\ ]^n}$$

As soon as solid $M(OH)_n$ exists in the system, $[M(OH)_n]$ becomes constant and the equilibrium (hydrolysis) constant can then be represented by:

$$K^h= \frac{[\ Z^{-m}\ ]}{[\ MZ^{n-m}\ ]\ [\ OH^-\ ]^n} \qquad \text{and} \qquad \frac{K}{[M(OH)n]} = K_h$$

Thus an increase in hydroxyl ion activity (i.e increase in pH) tends to shift the equilibrium to the right, eventually causing precipitation of the hydroxide. Such precipitation can be counteracted, at least in part, by using an excess of

organic ligand.

In a much later study (Farmer, 1979) reported that fulvic acid, behaving as a strongly complexing acid, could either decompose proto-imogolite to give a soluble Al-fulvate plus silicic acid, or co-precipitate all Al and fulvate from solution, depending on the molar ratio of COOH: metal.

Similarly, Buurman and Van Reeuijk (1984), concluded that metal fulvates remain soluble when undersaturated with metals and become insoluble when the metal/fulvate ratio rises to saturation. The authors also noted that precipitated Al and Fe-saturated organic complexes may be subject to subsequent biodegredation of the organic phase. Thus biological oxidation is another mechanism whereby the inorganic phase is separated from the ligand.

Violante and Huang (1984), suggested that the amounts of organic ligands present in precipitates of Al depend on the nature and initial concentration of the ligands, as well as the aging period. In their experiment more than 70-80% of tartrate, citrate and tannate ligands initially present in solution co-precipitated with Al-oxihydroxides. They also observed that the amount of citrate present in solid phase decreased during the aging period of 30 days. Violante and Huang (1984), conclude that in the case of ligands such as citrate, tannate or tartrate, the anions initially co-precipitated in the non-crystalline Al gel, may be partially liberated upon aging, facilitaing the transformation of the

non-crystalline material into pseudoboehmite. However, the released ligands which have a strong affinity for Al could be readsorbed on the surfaces of the solid phase during aging.

The work of Violante and Huang also supports that of Yoldas (1973), who found that during the formation of pseudoboehmite by hydrolysis of aluminum alkoxides, the initial noncrystalline materials contained considerable -OR groups ($-OC_4H_9$, $-OC_3H_7$, etc.) which were responsible for the structural disorder of the material. During the aging period, the initially noncrystalline materials were converted into pseudoboehmite with a gradual liberation of -OR groups.

3. Extraction of Sesquioxides

The selective removal of naturally occurring sesquioxides from soils and clays represents a serious analytical problem in that many clay minerals are sensitive to attack under the conditions most conducive to dissolution of Fe, Al and Si oxides, namely at low pH. The methods currently in popular use rely upon three extractants, namely a pyrophosphate reagent, an acid-oxalate reagent and a dithionate citrate reagent. Each reagent is thought to extract different forms of Fe, Al and Si. It must be recalled, however, that a continuum of crystalline order exists, ranging from no long-range order to well crystalline, characterized by 3-dimensional periodicity over appreciable distances (Follet, 1965). It is, therefore difficult to assess adequately the portion of this continuum

that is being extracted by any particular reagent.

a) Pyrophosphate Extraction

Pyrophosphate reagent has been used for many years to extract organic compounds from soil (Bremner and Lees, 1949). It is used at neutrality (pH 7) to lessen oxidative breakdown, or at an alkaline pH (pH 10) as organic matter is more soluble, and crystalline inorganic Fe compounds less soluble, at this higher pH (Bascomb, 1968). In recent years, extraction of soils with 0.1M sodium pyrophosphate has been widely used to indicate the amount of Fe and Al associated with organic matter (Farmer et al. 1983) and as a basis of distinguishing spodic and podzolic B horizons from others (McKeague and Schuppli, 1982). Pyrophosphate is specific for Fe-organic complexes and somewhat less specific for Al-organic complexes. The Si levels extracted by prophosphate are usually very low (Parfitt and Childs, 1988).

The original techniques of extracting Fe and Al from soils by McKeague (1966), and Bascomb (1968) differed by using Na- and K-pyrophosphate, respectively. McKeague's method has since been modified by introducing alternative techniques for the clarification of the suspensions, and by requiring the soil to be ground to <150um before analysis (Canada Soil Survey Committee, 1976). In 1982 McKeague and Schuppli reported that centrifugation for longer times or at higher speeds progressively decreased concentrations of Fe and Al

pyrophosphate extracts of soil. They concluded that part of the Fe and Al measured in these extracts was not in dissolved form but present in the structure of suspended minerals thereby overestimating levels at lower centrifugation speeds. This material, amorphous to X-rays, might have been fine particulate amorphous material present in the soil sample, or it might have formed by coagulation of solutes in the pyrophosphate extract. Probably, because of this peptization problem, the precision of replicate determinations by using pyrophosphate reagent has been found to vary (Loveland and Digby, 1984), and comparison of results cannot be made with confidence. The continued use of the reagent has therefore been questioned (Loveland and Digby, 1984; Schuppli et al. 1983).

b) Ammonium Oxalate Extraction

Acid oxalate reagent (Tamm,1922), is ammonium oxalate/ oxalic acid at pH 3 and this, or similar reagents, is an established extractant for soil materials with short-range order. Some laboratories use 4 hour shaking in the dark (McKeague and Day, 1965), and some 2 hour shaking in the dark (Schwertmann et al. 1982).

Borggard (1987), has shown that the reaction involves the formation of soluble complexes of Fe and Al with oxalate. Acid oxalate reagent is known to dissolve, or partly dissolve, allophane, imogolite, ferrihydrite, Fe and Al

associated with humus, lepidocrocite, maghemite, (Borggard, 1982; Farmer et al. 1983), and Al from chloritized vermiculite (Fordham and Norrish, 1983). In particular this reagent is recognized as being fairly specific for estimating ferrihydrite concentrations (Schwertmann et al. 1982). Childs (1985), has proposed that ferrihydrite concentrations (weight %) may be estimated as $Fh_{est} = 1.7 \times Fe\%_{(ox)}$.

A note of caution: this value may be overestimated by the presence of poorly crystalline lepidocrocite, magnetite or organic matter complexes, all of which may be attacked by acid oxalate (Borgarrd, 1987). Also the value may be underestimated where adsorbed species such as silicate inhibit dissolution (Parfitt and Childs, 1988).

The difference between ammonium oxalate and CBD extractable Fe gives a measure of crystalline inorganic Fe. These two extractants are beleived to be less useful in distinguishing forms of Al and Si in soils (Borgaard, 1987), and in fact Wada (1977) reports that non-crystalline silica is not dissolved by ammonium oxalate.

c) Citrate Bicarbonate Dithionate Extraction

The objectives of the CBD method are primarily the determination of free Fe oxides and the removal of amorphous coatings and crystals of free Fe oxide acting as cementing agents, for subsequent physical and chemical analyses of soils, sediments and clay minerals (Mehra and Jackson, 1960).

Prerequisite to a good method for removal of free iron oxides is a reagent with a high oxidation potential (i.e. a good reducing agent). A chelating agent is also required for sequestering Fe^{2+} and Fe^{3+} ions. The CBD system employs sodium citrate as a chelating agent, sodium bicarbonate ($NaHCO_3$, pH 7.3) as a buffer, and sodium dithionate ($Na_2S_2O_4$) for the reduction (Mehra and Jackson, 1960). The reaction is carried out for 15 minutes at 80°C.

It has been claimed that this reagent results in almost complete solution of Fe oxides, including ferrihydrite, without differentiation between various crystal forms (McKeague and Day, 1966). In addition to free Fe oxides, Al-substituted crystalline hematite and goethite are dissolved by this treatment (Norrish and Taylor, 1961; Fey and Le Roux, 1977). Magnetite and ilmenite, however are not extracted by CBD (Walker, 1983). A considerable amount of hydroxy aluminum interlayers of vermiculite chlorite is also extracted, but gibbsite is little effected (Dixon and Jackson, 1962).

RESULTS AND DISCUSSION: SECTION I

A.   Dissolution of Ca, Mg, K, Na, Fe, Al and Si   by 5 Leaching Treatments

The analysis of solution extracts is given in Appendix C and depicted graphically in Appendices B and C.   Mass balance calculations, given in Appendix N, estimate the percentage of each ion from the parent rock brought into solution.   Tables 3 and 4 list the source minerals from which each ion originated.   Table 5 notes the relative changes in XRD peak intensities in basaltic and granodiorite minerals following 11 weeks of weathering.   These Tables have been placed at the end of Results and Discussion Section I for reference.

For the sake of clarity, only the key features of the solution analysis are highlighted in the following discussion.

1.   Iron and Magnesium

The ability of citric acid and oxalic acid to chelate Fe and Mg depended upon the parent material which was subjected to weathering.   The graphs in Appendixes B and C and statistical analysis to the 95% confidence level clearly show that oxalic acid was a more powerful extractant of Fe and Mg from granodiorite than was citric acid.   The complete reversal occurred in the dissolution of basalt.   In this case citric

acid chelated 3-4 times the amount of Fe and Mg than did oxalic acid.

According to stability constants (See Table 2) oxalate is less effective than citrate as an Fe and Mg chelator but it must be remembered that these values are derived for simple nutrient solutions for the specific metal in question. However, the ability of a ligand to chelate Fe or Mg cannot be determined merely by its stability constant for each cation. Differences between this constant and stability constants for competing ions must be considered, along with differences in concentration between Fe^{3+} and competing ions. In addition the pH of the solution will determine the charge of the organic ligand, and therefore the stability of the bond between metal and anion. Finally, the mineralogical makeup of the parent material as well as its active surface area can effect the degree of extraction. Each of these factors will be considered in more detail in the hope of explaining the experimental results.

First of all, reference is made to the fact that at pH of greater than 4.2, Mg can outcompete Fe in solution for the oxalate ligand. This competition is graphically displayed in Figure 3 (Cline et al. 1982). In contrast Fe can outcompete Mg for the citrate ligand up to pH 6.4 (See Figure 3). The pH of the oxalic solution in contact with basalt was, on the average, 4.0 or higher. Under these conditions Mg, which was released from basalt in much greater amounts than from

Log $K^m_{0.01}$

Equilibrium Reaction	Citrate	Oxalate	Source
Ca + L = CaL	4.25	2.64	(3), (4)
Ca + H + L = CaHL	8.71	-	
Ca + 2L = CaL$_2$	7.75	3.15	(2)
		3.09	
		3.40	(3), (4)
CaL + L = CaL$_2$	3.55	-	(2)
	3.50	-	(3)
Mg + L = MgL	4.42	3.26	(2), (4)
	4.0	3.20	(3)
Mg + H + L = MgHL	7.61		(1), (2)
Mg L + H = MgHL	4.2		(3)
Fe + L = FeL	12.62	8.60	(1), (2)
	12.5	8.90	(3)
	11.85	9.4	(4)
Fe + 2L = FeL$_2$		15.07	(4)
Fe + 3L = FeL$_3$		19.06	(2)
Al + L = AlL		7.26	(4)
	9.6	7.30	(3)
AlL + L = AlL$_2$		5.0	(3)

Sources:

(1) Lindsay, W.L. 1979 Chemical Equilibria in sorts John Wiley & Sons, Inc. New York.

(2) Martell, A.E. and Smith, R.M. 1977. Critical stability constants, Vol. 3: other organic ligands. Plenum Press, New York.

(3) Norvell W.A. 1972. In Micronutrients in Agriculture, Ed Mortvedt, J.J. Soil Sci. Soc. of Amer. Madison Wisconson, U.S.A.

(4) Sillan, L.G. and Martell, A.E. 1964 Stability constants of metal-ion complexes. 2nd ed. Spec. Pub. no. 17. The Chemical Society, London.

TABLE 2: STABILITY CONSTANTS OF OXALATE- AND CITRATE-METAL LIGANDS
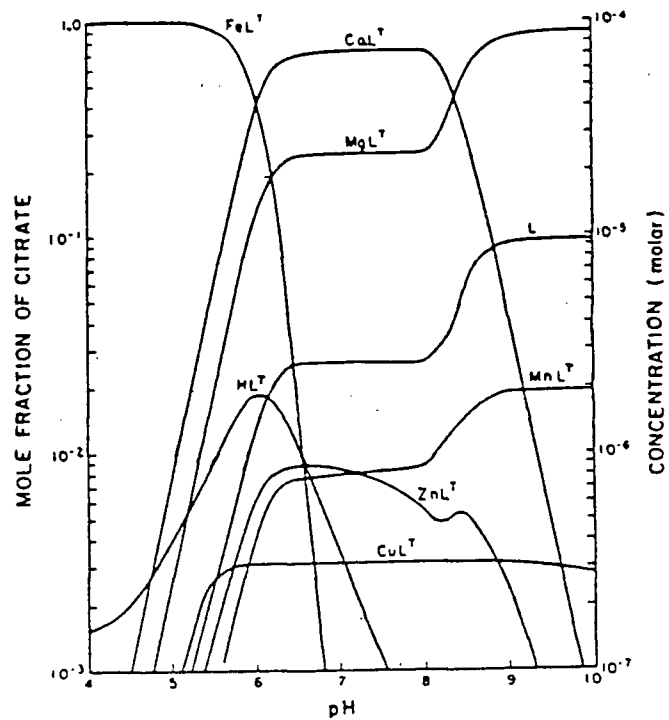
Figure 3: Predicted mole fraction diagrams for citrate and oxalate in a nutrient solution in equilibrium with $Fe(OH)_3$(amorph).
HL^T = sum of all chelated species
L = free ligand

Source: Cline et al., 1982.

granodiorite, could effectively suppress complexation of Fe by oxalate. Conversely, less Mg released from granodiorite could result in less ionic competition between the ions for the oxalate ligand; the complexation of Fe by oxalic acid was therefore "apparently" more effective.

Ionic competition does not explain why citrate outcompeted oxalate in extracting Mg from basalt. One would expect all citrate ligand sites to be taken up by Fe at pH<6.4 leaving little or no Mg-citrate complexes. However, a study by Grandstaff (1986) on the dissolution rate of forsteritic olivine, established that citrate was more effective than oxalate at pH 4.5 in extracting Mg. Although there was no quantitative analysis to determine the percentage of forsterite in the basaltic samples used in the column and batch studies, XRD analysis determined that forsterite was present and could contribute to the Mg released in solution. This could explain in part why the citric acid solution levels of Mg were higher than oxalic acid basaltic extractions. On the other hand, it has been shown by Boyle et al. (1974), that oxalic acid will extract higher levels of Mg from biotite than will citric acid. Biotite was detected in thin section observations of granodiorite and its presence was confirmed by XRD. This could explain why the oxalic acid solution levels of Mg were higher than citric acid granodiorite extractions.

The work of Manley and Evans (1986), studying acid dissolution of feldspars, also demonstrated that the relative extraction powers of citric and oxalic acids depends upon the mineral being attacked. The different reactivity of the chelating agents and minerals may be due at least in part to steric compatibility or incompatibility. Complexes which may be theoretically possible on the basis of strictly chemical considerations may not form because of geometric hindrance. In other words the molecular architecture may prevent ligand groups of a chelating agent from "reaching" metal ions on the surface or within the crystal lattice of the mineral. It may very well be that differences in size and geometry of citric and oxalic acid in addition to crystallographic features of the mineral account for differences in the dissolution of basalt vs. granodiorite.

As yet there appears to be very little information in the soil science literature on chelate formation which connects the crystalline characteristics of the mineral with morphological features of the acid. Analytical methods of sesquioxide determination have revealed that oxalate extracts much of the Fe from magnetite and ilmenite but little from goethite or hematite, while the converse is true of citrate dithionite bicarbonate (McKeague et al. 1971). No mechanistic explanation has been provided.

Work with sesquioxides (McKeague and Schuppli, 1985) has also pointed out that the exactability of Fe from minerals is

strongly dependent on particle size. Citrate failed to dissolve completely crystalline iron oxide particles coarser than 50μm. If citrate is more efficient in attacking finer particles it would also be more effective in dissolving basaltic particles than the coarser granodiorite crystalline particles.

It should also be noted that the valence of Fe in the mineral may influence its interaction with solutions. Schott and Berner (1983), concluded that appreciable Fe-citrate complexes could not have formed in their experiments since only Fe (II) rather than Fe (III) which forms strong citrate complexes was present in solution and on mineral surfaces. Perhaps this partly explains why citrate is successful in sequestering Fe (III) from hematite but not the Fe (II) from ilmenite. At any rate, a quantitative determination of the ratio of Fe (III) to Fe (II) in the basalt and granodiorite parent material might clarify why there was a reversal in extraction powers of the two acids.

Finally, the pH of the extracting solution must be taken into account (See Appendix E). The pH of oxalic acid weathering granodiorite was consistently less than 2 throughout the 11 weeks of the experiment. Citric acid, on the other hand, was consistently greater than pH 2.0. Remembering that the pK for oxalic acid is 1.23, at pH slightly less than 2 approximately 80% of the acid is in the dissociated form HL⁻. The pK, for citric acid is 3.14 and at

pH slightly higher than 2, approximately 99% of the acid is in the undissociated form H_3L. The electrons from the Lewis base of the dissociated oxalic acid are then available for complexation with a metal Lewis acid of the mineral, whereas no such electrons are available from the undissociated citric acid. Weathering will proceed solely by acidolysis in the citric acid solution, and even so, the oxalic acid solution, in addition to complexation, could outcompete citric acid through the action of acidolysis due to the greater number of H^+ ions available in solution at a lower pH.

Furrer and Stumm (1983) conducted a study of the dissolution of $\delta-Al_2O_3$ in dilute acids (pH 2.5-6.0), and their findings support the explanation given above. In the case of citrate, but not oxalate, the rate R_{LIGAND} decreased below pH=4.5. The authors concluded, "most likely this decrease was caused by the presence of protonated surface ligands at lower pH values." In the case of oxalate, over the pH range investigated the deprotonated surface complex prevailed.

Thus, a metal organic complex may have a high stability constant but unlikely to form because the ligand has a greater affinity for H^+ than for the metal ion, and the metal ion may have a greater affinity for OH^- than for the organic ligand.

Finally levels of Fe extracted from basalt and granodiorite reveal for the most part higher levels brought into solution in the batch experiment compared with the column experiment. This result supports the findings of Siever and

Woodford (1979) who observed that the dissolution of mafic minerals in buffered solutions was more rapid when air was excluded. In the more oxidizing environment of the column experiment, dissolution in the presence of oxygen may be slowed by the armoring effect of a Fe (OH)$_3$ precipitate. Also the contribution of physical weathering as a result of shaking cannot be overlooked.

2. Calcium

Mass balance calculations (Appendix N) and AA spectrophotometric analyses for dissolved Ca, depicted in Appendix B and C, point to the ability of citric acid over other acids in extracting Ca, from both basalt and granodiorite. In this case therefore the influence of parent material is overshadowed by other factors which determine the extracting power of the acids. Also the differences in stability constants cannot be used in the case of citric and oxalic acids as the strength of the Ca-ligand complexes are comparable for both (See Table 2). It is more likely that the answer presents itself in the XRD analyses (Appendix K) of the yellow precipitate which formed in the oxalic acid leaching treatments of basalt and granodiorite. The D-spacing peaks of Ca-oxalate appear at 3.19, 2.37 and 1.89 A$^\circ$ confirming the presence of this salt in the precipitate. This salt is highly insoluble and although oxalic acid may have effectively competed with citric acid in detaching Ca from the

mineral much less would remain in soluble form. The formation of a Ca-oxalate precipitate might also explain why the acetic acid solution showed significantly higher levels of dissolved Ca for basaltic column samples even though the stability constant (pK = 1.24) for the Ca-acetic ligand was less than that for the Ca-oxalic ligand (pK = 3.4). At the 95% level there was no significant difference in solubilized Ca from oxalic and acetic acid leachates in the batch experiment.

3. Aluminum

The solubility of Al in equilibrium with aluminum oxide and hydroxide minerals is highly pH dependent, decreasing 1000-fold for each unit. (See Figure 4). Amorphous $Al(OH)_3$ is the most soluble form of aluminum hydroxide expected in soils; when the activity of Al^{3+} is controlled by amorphous $Al(OH)_3$ rather than gibbsite the activity of Al^{3+} is approximately 42 times higher (Lindsay, 1979).

Figure 5 shows the activity of Al^{3+} and its hydrolysis species in equilibrium with gibbsite. The Al^{3+} ion is predominant below pH 4.7 and is octahedrally co-ordinated to six molecules of water forming $Al(H_2O)_6$. $Al(OH)_2+$ is predominant between pH 4.7 and pH 6.5, $Al(OH)_3$ between pH 6.5 and 8, and $Al(OH)_4$ above pH 8.

Activity of Al^{3+} in solution is not predictable from pH alone however. For example, the presence of silica at activities above 10^{-4} decreases the equilibrium of dissolved
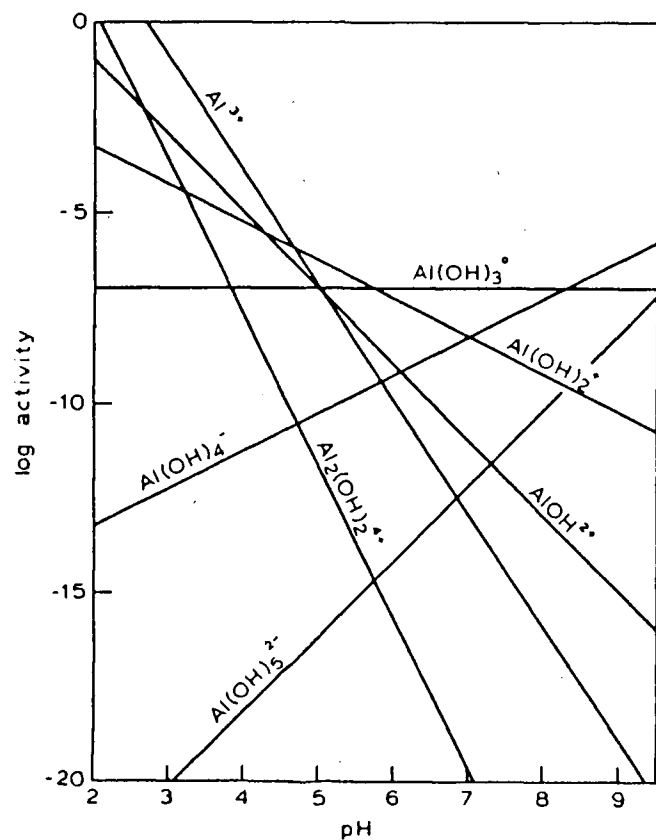
Figure 4: The activity of Al^{3+} and its hydrolysis species in equilibrium with gibbsite.

Source: Lindsay, 1979
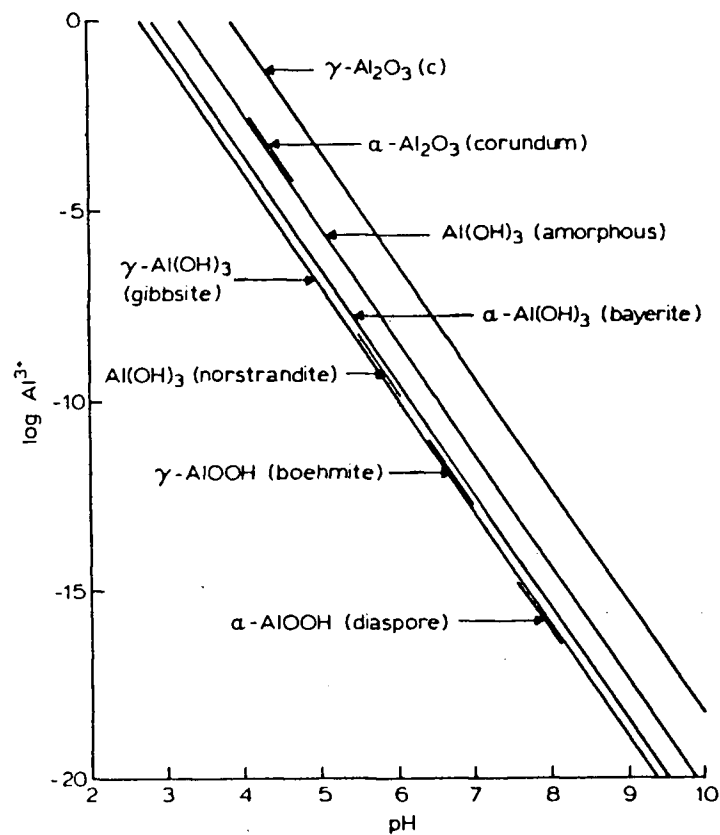
Figure 5: The solubility of various aluminum oxides and hydrides.

Source: Lindsay, 1979

Al activities at all pH values (Drever, 1982). The activity of Al^{3+} in equilibrium with aluminosilicates in water is therefore less than that for aluminum oxides and hydroxides, as a result of Al-silicate bonding. Aluminum has been categorized by geologists as one of the least soluble elements released from aluminous rocks and minerals during weathering. Because of its relative immobility it has been used as a reference "fixed-element" against which the loss and gain of other elements have been compared in studies of rock alteration.

The graphs illustrating the concentration of Al^{3+} in solution (See Appendix B and C) for both batch and column experiments show a fairly linear release of aluminum from basalt and granodiorite as a result of acetic acid, HCl and H_2O extraction. Distilled water was the least effective in dissolving Al^{3+} and supports the findings that dissolved Al in natural water systems is low except in very acid or alkaline conditions. The concentration of Al^{3+} brought into solution by the action of acetic acid and HCl on basalt and granodiorite at pH 4 showed no significant difference at the 95% confidence level and ranged from approximately 3.7 to 7.4 x 10^{-4} M/liter. These levels fall between the activity of Al^{3+} in equilibrium with gibbsite at $10^{-4.96}$ M and amorphous $Al(OH)_3$ at $10^{-3.34}$ M. Mass balance calculations showed that the percentage Al_2O_3 extracted from basaltic and granodioritic parent material was 1% or less for these 3 extractions.

The efficacy of Al extraction from granodiorite was greatly increased when organic chelating solutions acted as weathering agents. According to mass balance calculations, citric acid extracted 4-9% and 7.6% of the granodioritic Al_2O_3 from column and batch experiments respectively. Oxalic acid was even more effective and extracted 13.2% and 15.8% of the granodioritic Al_2O_3 from column and batch experiments respectively. Again the differences in dissolution power may be partly attributed to differences in solution pH of the two acids. The oxalic acid solution (pH<2.0) was slightly less than citric acid (pH 2.2). As noted earlier oxalic acid was 80% dissociated at that pH forming HL^- whereas citric acid was still 99% in undissociated form. Both acidic and chelating factors therefore favored oxalic acid.

In addition the mineralogical make-up of granodiorite must be considered. As noted, Boyle et al. (1974) have shown experimentally the drastic effect of oxalic acid treatment on micas and micaceous clays. The sheet structure was completely destroyed as the constituents became soluble or amorphous and at pH 3, the destruction of biotite was almost total. The greater attack of biotite by oxalic acid relative to that by citric acid was confirmed in XRD analyses (See Appendix K). This could therefore contribute to higher levels of solubilized Al in the oxalic acid leachate.

It is interesting to note that the graphs for Al extraction from **batch** granodiorite show a constant linear

relationship of ion extracted versus time. This suggests that physical weathering from shaking not only broke down a cation depleted layer but opened up new surfaces to further weathering. Also, concentrations of Al^{3+} dissolved in both oxalic and citric acid solutions were in approximately a 1:1 ratio with that of Si extracted by the same acids in the batch experiment.

Al:Si ratios were <1 in the **column** experiment and both oxalic Al and Si curves showed declining rates. Also the levels of Al extracted were lower than that for batch. All three observations suggest that an altered surface was not as easily detached, that precipitates may have formed and remained in localized microenvironments, or that preferred channelling through the column could have contributed to lower and declining rates of dissolution, as well as incongruent weathering.

The efficacy of Al extraction from basalt by citric and oxalic acid exceeded that of the non-chelating acids in the first week of the experiment but quickly dropped off. In fact the graph (Appendix C) showing dissolution of Al from basalt in the batch experiment reveals that acetic acid and HCl were more successful in dissolving Al throughout several weeks. Examination of batch solution pH's (Appendix E) quickly point to the greater acidity of acetic acid and HCl (pH<3.5) in contrast to citric acid (pH=4.0) and oxalic acid (pH 4.5-5.0). Differences in pH however, do not directly explain why the

more alkaline oxalic acid solution extracted higher levels of Al than did the citric acid solution. At the respective pH's, the chelating effect of the oxalic L^{2-} anion could possibly have outcompeted the H_2L- anion of citric acid.

Finally it is important to highlight the fact that soluble Al levels for all treatments were far less in basalt experiments than for granodiorite experiments. This is in spite of the fact that the % Al_2O_3 in basalt as determined by XRF was 15.17%, only slightly less than 16.61% in granodiorite. Again it is to be noted that pH of extracting solutions was much higher after weathering basalt than granodiorite. As pointed out by Manley and Evans (1986), the total amount of Al released from feldspars by different organic acids was significantly correlated (r=.95) with the pH of solutions. Such could be the case in the weathering of mixed minerals. Secondly, very high levels of Si which were not bound up in quartz were released from basalt. The silicate anion as explained earlier could have precipitated any released Al cations thereby suppressing levels of soluble Al. Also at pH < 5 hydroxyaluminum species may react with orthosilicic acid to give stable sols or solutions (proto-imogolite). Thirdly, much of the Al released from granodiorite originated from biotite. The XRD peak intensities for biotite showed the greatest decrease of any mineral subsequent to weathering by citric and oxalic acids. Biotite was therefore less resistant to acid attack than were

any of the Al-bearing minerals comprising the basaltic parent material.

4. Silicon

The solubility of silica minerals in terms of H_4SiO_4 is expected to range from $10^{-2.74}$M (amorphous silica) to 10^{-4}M (quartz) and is determined for equilibrium in water. This corresponds to a range of 6 to 60 ppm. Other minerals have intermediate solubilities including SiO_2 (soil) which has been estimated to have a solubility in water of $10^{-3.10}$M. The levels of silica brought into solution by dissolution of basalt and granodiorite by acetic acid, HCl and H_2O were well below 60 ppm. The solutions were therefore undersaturated with respect to amorphous silica. However, the levels of silica brought into solution as a result of oxalic and citric acid dissolution were exceedingly high. (See Appendix N). For example, basalt leached in the batch experiment by citric acid released approximately 200 x the amount silica in water in equilibrium with amorphous silica. Oxalic acid released a little more than 100 x the amount of silica in equilibrium with amorphous silica in water.

No analyses were carried out to discriminate what percentage of this silica was in either complexed or colloidal form. It is quite likely that colloidal particles contributed to the very high readings. Elgawhary and Lindsay (1972) proposed extracting soils with 0.02 M Ca in order to keep

colloidal silica flocculated during extraction, as well as filtration of samples in which silica is measured. When this procedure was used, they found that measured silica in soil solution corresponded more nearly to the levels of H_4SiO_4 expected from solubility predictions. In the case of the batch and column experiments, filtration of the extraction sample should have been carried out, as a first step in segregating different forms of silica in solution.

If in fact much of the silica detected by AA spectrophotometry was colloidal it may be surmised that these particles were brought into solution subsequent to the extraction of more easily dissolved ions such as Fe, Mg, Na, Ca or K. This unstable cation depleted altered zone, according to Berner and Schott (1982), could then break down as dissolution proceeds releasing the silicate framework. This phenomenon would explain why silica released form basalt was the highest. In the weathering experiments of Smith et al. (1982), the ferromagnesium minerals such as fayalite, forsterite and olivine, having Mg and Fe as the metaloxy groups separating Si-0-tetrahedra, offered least resistance to acid attack and released substantial amounts of monomeric silica. In contrast, much of the silica in the granodiorite samples was bound in the quartz fraction, a tectosilicate highly resistant to weathering.

Again, the possibility of proto-imoqolite existing in solution also cannot be overlooked as this species is soluble

at pH <5.

As discussed earlier, investigations to determine ionic speciation in chelating solutions are still in their infancy. So far, thermodynamic data describing composition and stability of organic complexes in aqueous solution are very scarce in the literature. Henderson and Duff (1963) differentiated 3 different forms of silica released from minerals by the action of an oxalic-producing strain of fungi as follows: ammonium-molybidate-reactive (AMR) silica corresponding to total silica, colloidal polymerized (CP) silica and amorphous silica. Huang and Keller (1971) noted that dissolved Si in .01 M complexing acid solutions exceeded 2-35 times its concentration in distilled water. They did not however determine the various forms of silica brought into solution.

Some final points are worth noting:

(1) Although the curves for basaltic silica extraction by citric and oxalic acid intersected at week 5 in the column experiment, the total amounts of silica extracted in 11 weeks were equal. Mass balance calculations (See Appendix N) indicate that total dissolved silica accounted for 8.52% of the basaltic parent material in **both** citric and oxalic acid treatments.

(2) In the batch experiment citric acid extracted 11.62% and oxalic acid 7.52% silica from basalt. Dissolution of granodiorite showed a reversed trend. Oxalic acid extracted

2.24 and 2.86% of the parent material silica from column and batch respectively. Citric acid on the other hand extracted 0.88% and 1.52% of the parent material silica from column and batch respectively. This reverse trend may be due to differences in pH of the solutions, although generally, Si dissolution is thought to be far less sensitive to pH changes than that for other ions. In fact the log activity of H_4SiO_4 in equilibrium with various forms of SiO_2 is constant in the range pH 2 to pH 9, and only at pH values above 9 does the solubility of silica increase sharply because of the formation of silicate ions (Elgawhary and Lindsay 1972). However, several studies have reported that the release of H_4SiO_4 by soils and many silicate minerals greatly increased as pH changed from 7.0 to 4.0 (McKeague and Cline, 1963; Beckworth and Reeve, 1964; Huang and Jackson, 1968 and Weaver et al., 1968).

5. Sodium and Potassium

Hydrated metal cations such as Na+ and K+ are extremely weak acids (pKa=15) which fail to dissociate a proton from their enveloping sheath of water molecules until extremely high pH values are reached. Because the water molecules of the hydration sheath are doubly protonated at normal soil pH value, there is little tendency for these alkali metal cations to co-ordinate with electrophilic centers on mineral surfaces. Therefore they act as indifferent ions and over the pH range

commonly met in soils, the predominant hydration state of the ions is constant. Thus sodium and potassium are present only as the Na+ and K+ ions in solution.

a) Sodium

It is apparent from the mass balance calculations and the graphs of sodium in solution vs. time (Appendices B and C) that the two chelating acids were at best only slightly more effective in extracting Na from basalt and granodiorite than were acetic acid, HCl or H_2O. In fact at the 95% confidence level there was no significant difference between the concentrations of solubilized Na in the 5 extracting solutions weathering basaltic parent rock. This is in agreement with the finding of Huang and Keller (1970) who reported that the dissolution of alkali ions from muscovite and microcline in organic acids was found to be the same order of magnitude as deionized water or CO_2-charged water. The authors concluded that "it is unlikely that monovalent cation chelates are formed during organic acid dissolution of minerals".

The solution curves also point to a rapid early release of sodium followed by declining rates approaching steady state towards Week 11 of the experiment. This is attributed to either dissolution of hyperfines or to the rapid exchange of H^+ ions for the Na+ ion (hydrolysis). The levels of Na extracted were the highest for citric and oxalic acid –

granodiorite dissolution. At the 95% confidence level citric and oxalic acid dissolved significantly higher levels of Na than did the other acids. This may be due to the fact that citric and oxalic acid were the most effective in attacking hornblende, pyroxene and plagioclase, which served as sources of the Na ion.

b) Potassium

Mass balance calculations and solution graphs of K extracted from **basalt** show similar trends to those noted for Na. First of all, non-chelating acids are as effective in extracting K as the chelating acids. Secondly, there occurred a rapid release of K in the first week followed by sharply declining rates of release until Week 3 of the experiment. Rates then gently increased for 1 to 2 weeks, then decreased until the end of week 11. The curves for all extraction treatments approached 0 at the end of the experiment suggesting that the number of active surface sites of biotite or muscovite were declining. Mass balance calculations show that only a very small percentage (<2%) of the K was removed from the basaltic parent material through leaching. Evidently what remained, likely in the muscovite, was not accessible to further ionic exchange with H^+.

Mass balance calculations and solution graphs of K extracted from **granodiorite** show that oxalic acid was successful in extracting as much as 40% (column) and 50%

(batch) of the K contained in the parent material. In the batch experiment this amounted to approximately 5 times that of acetic acid, 12 times that of HCl, and 29 times that of H_2O. Citric acid extracted 13% (column) and 22% (batch) of the K contained in the parent material, also well ahead of the other three extracting acids. Does this mean that the chelating acids were indeed able to complex K? The XRD analysis of weathered crust material (Appendix K_2) suggests the possibility of a K-oxalate per hydrate salt having formed; however, a more likely clue is given in the X-Ray diffraction analyses (Appendix I) which shows a dramatic drop in intensity for the biotite peak weathered by oxalic and citric acid. As noted earlier, oxalic acid is extremely effective in dissolving biotite through attack of Mg and Fe in the octahedral layer. Subsequent oxidation of octahedral Fe is associated with ejection of octahedral cations, loss of interlayer K, and a contraction of the b-dimension of the biotite sheet (Gilkes, R.J. and Suddhiprakarn, A. 1979). The K detected in AA solution analyses could have been solubilized indirectly following the initial attack of Mg and Fe by the chelating acid.

Ion	Mineral
Calcium	– Hornblende, Pyroxene, Plagioclase
Magnesium	– Olivine, Biotite, Hornblende, Pyroxene
Sodium	– Hornblende, Plagioclase (albite), Pyroxene
Potassium	– Biotite, Muscovite, K-Feldspar
Iron	– Pyroxene (Pigeonite, Augite, Hypersthene) – $Fe(II)$ Hornblende – $Fe(III):Fe(II)$ ratio often high Biotite – $Fe(III):Fe(II)$ ratio approximately equal Olivine – $Fe(II)$ Magnetite – $Fe(III),Fe(II)$; Ilmenite – $Fe(II)$, Hematite – $Fe(II)$
Aluminium	– Feldspars, Pyroxene, Hornblende, Micas
Silicon	– Feldspars, Pyroxene, Hornblende, Quartz, Micas, Olivine

TABLE 3: SOURCE OF IONS FROM BASALTIC AND GRANODIORITIC PARENT MATERIAL

Name	Group	Composition
K-Feldspar (orthoclase, Microcline)	Tectosilicate	$K\ Al\ Si_3O_8$
Plagioclase (oligoclase, Labradorite, anorthite)	Tectosilicate	$(Na,\ Ca)\ Al\ Si_3O_8$
Plagioclase (Albite)	Tectosilicate	$Na\ AlSi_3O_8$
Pyroxene (Pigeonite) (Hypersthene) (Enstatite) (Augite)	Inosilicate Single chain	$(Ca,\ Mg,\ Fe)SiO_3$ $Mg_2\ Si_2\ O_6$ $(Ca,Na)(Mg,Fe,Al,Ti)$ $(SiAl)_2\ O_6$
Hornbelende (amphibole)	Inosilicate Double chain	$(Ca,Na)_{2-3}$ $(Mg,Fe^{2+},Fe^{3+},Al)_5$ $(Al,\ Si)_8\ O_{22}\ (OH)_2$
Olivine (Fayalite) (Forsterite)	Nesosilicate	$(Mg,Fe)_2\ Si\ O_4$ $4\ (Fe_2Si\ O_4)$ $4[(Mg,Fe)_2\ SiO_4]$
Biotite	Phyllosilicate	$K(Mg,Fe^{2+})_3$ $(Al,Fe^{3+})Si_3O_{10}$ $(OH,F)_2$
Muscovite	Phyllosilicate	$K,Al_2(Al\ Si_3)\ O_{10}\ (OH)_2$
Quartz	Tectosilicate	$X-SiO_2$
Ilmenite	Iron Titanate	$FeOTiO_2$
Hematite	Iron Oxide	Fe_2O_3
Magnetite	Iron Oxide	Fe_2O_4
Anatase	Titanium Oxide	$B-TiO_2$
Periclase	Magnesium Oxide	MgO

TABLE 4:   COMPOSITION OF MINERALS IDENTIFIED IN GRANODIORITE & BASALT BY XRD ANALYSES.

A. Granodiorite

	Citric Acid			Oxalic Acid			Acetic & HCl			HOH		
	0	(+)	(−)	0	(+)	(−)	0	(+)	(−)	0	(+)	(−)
K-Feldspar			**			**			*			*
Plagioclase			**			**			*			*
Hornblende			**			***			*			*
Pyroxene	0					***	*				*	
Micas			**			***			**			**
Periclase			**			**			*			*
Ilmenite		*				**	*				*	
Magnetite		*				***	*				*	
Hematite		*				**	*				*	
Quartz		*				*	*			0		

B. Basalt

	Citric Acid			Oxalic Acid			Acetic & HCl			HOH		
	0	(+)	(−)	0	(+)	(−)	0	(+)	(−)	0	(+)	(−)
Plagioclase		***				**			*		*	
Hornblende		***				***			*			*
Pyroxene		***				**			*			*
Fayalite		***				**			*			*
Forsterite		*				*			*			*
Micas	0					*			*			*
Magnetite		*				**	*				*	
Hematite		*				*	*				*	
Quartz	0						*				*	

Note: (0) = No change   (+) = increase   (−) = decrease   * = small change
** = large change   *** = very large change.

TABLE 5: CHANGES IN XRD PEAK INTENSITIES IN BASALTIC & GRANODIORITIC MINERALS FOLLOWING 11 WEEK BATCH DISSOLUTION EXPERIMENT.

RESULTS & DISCUSSION: SECTION II

B.   Dissolution of Basalt and Granodiorite by 5 Leaching Treatments

1.   The Influence of Kinetic Factors on the Dissolution of Basalt and Granodiorite

The distribution for the concentration of ionic species in solution vs. time shown in Appendices B and C reveal several interesting features regarding the kinetics of dissolution in both batch and column experiments. The slopes of each curve indicate immediately whether or not the rate of dissolution is increasing, declining or linear, ie. approaching steady state. On the whole, two tendencies are apparent. Firstly, the curves for citric and oxalic acid extractions for Fe, Mg and K, are characterized by an initial increase in rate, followed by declining rates which approached linearity towards the 11th week. In all other instances, the curves for citric and oxalic acid declined from the start and subsequently levelled out. This is to say that the curves for the two complexing agents suggest rapid, perhaps even parabolic dissolution followed by steady-state dissolution. Secondly, the curves for acetic, HCl and H_2O extractions are linear and approximately constant, with the exception of Na+ and K+ curves, in both basalt and granodiorite. A possible explanation for the constant linear rates over the period of

11 weeks may be found in considering the relative extraction powers of the different acids. It is obvious from the atomic absorption data as well as mass balance calculations and statistical analysis that acetic acid, HCl and H_2O weathered both basalt and granodiorite to a much lesser extent than did the chelating acids. Consequently, maximal concentrations of ions brought into solution were far from reaching a level where precipitates might form. The reactions are far from equilibrium and as such represent an open system where rates of dissolution of elements from minerals have been determined to be linear (Kodama et al. 1983). In contrast, the rate of release of constituent elements in a closed system decreases exponentially with time (Kodama et al. 1983).

Several factors could contribute to the declining rates of ions brought into solution by citric and oxalic acid.

First of all, a cation depleted surface layer may have developed according to the theory mentioned earlier (Correns and von Engelhardt 1938). Accordingly, as this altered layer built up, the rate of dissolution decreased. Eventually, however, the depleted surface layer broke down, being unstable chemically, until it reached an equilibrium thickness, being destroyed at the layer-solution interface at the same rate it was formed at the layer-mineral surface. EDX analysis of weathered surfaces revealed depletion of alkali and alkali earth cations relative to Si. See Figures 16 and 17. Also analysis of the solutions, indicating high levels of cationic

extraction, suggest that such a leached layer possibly developed. The high levels of Si and Al both colloidal and soluble, detected through AA spectrophotometry analysis of the solutions, are consistent with the concept that detachment of silicate and aluminate units from the crystalline framework follows the exchange of H^+ for alkalis (AAgaard and Helgeson, 1982). Interestingly, a comparison of the dissolution graphs for Si and Al in batch and column experiments reveals a fairly linear rate in the batch experiment but declining rates for the column experiment. This suggests that indeed a protective as well as altered layer had built up in the column experiment. In the case of the batch experiment, however, physical grinding, through shaking of samples could continually assist in the breakdown of the chemically unstable surfaces, leading to steady-state dissolution. Where the altered surface is not broken down, as in the column experiment, decreasing rates of dissolution occurred.

There is on the other hand, direct evidence from SEM observations that initial weathering of superfines adhering to the surface of unweathered mineral grains could account for both the rapid rise then fall in rates during the first few weeks of weathering. Figures 6 and 7 show the existence of hyperfine particulate matter, an artifact of grinding, adhering electrostatically to the outer surface of the mineral. After 11 weeks of weathering the surfaces of mineral grains were clean as shown in Figure 8. The dissolution of

006788 20KV X600 50um
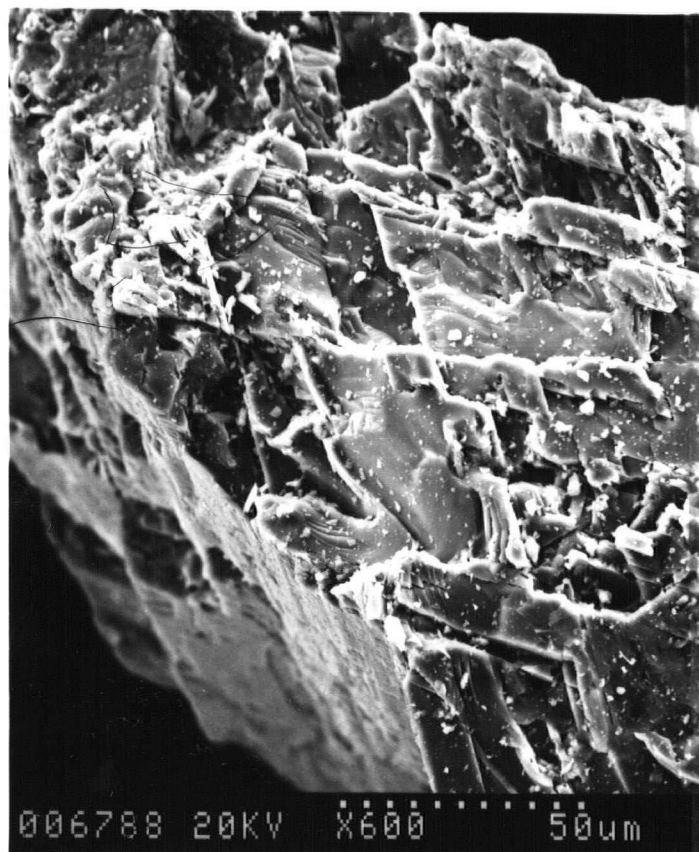
Figure 6: Hyperfines adhering to
granitic surface.
600 x magnification

006791 20KV X600 50um
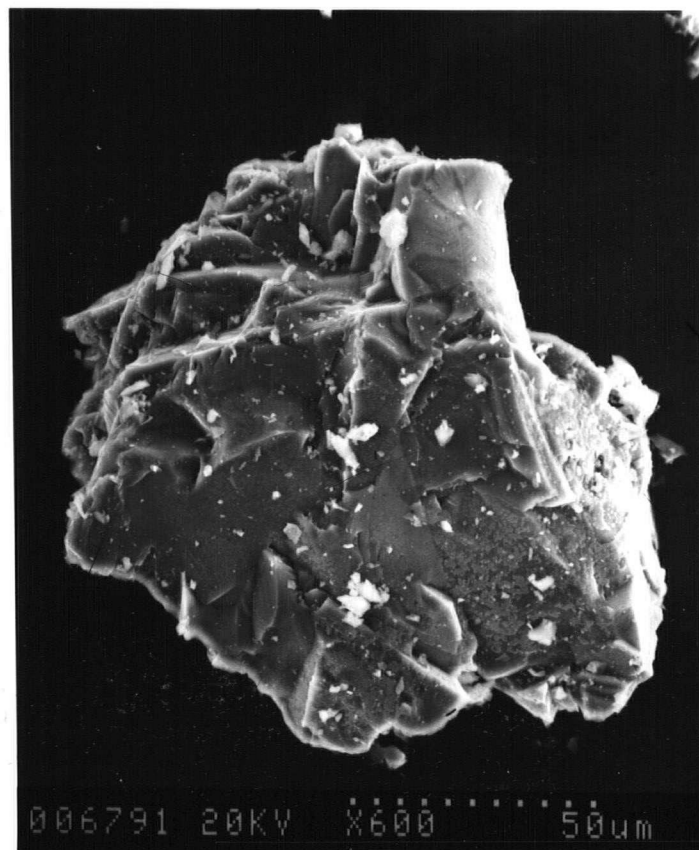
Figure 7: Hyperfines adhering to
basaltic surface.
600 x magnification

Figure 8: Basaltic grain leached by oxalic acid for 11
weeks. Note absence of hyperfines and prominent
etch-pitting.
600 x magnification

these particles occurred more rapidly than that of the bulk mineral due to greater surface area, exposed edges and the large abundance of strained or broken bonds. With time, as the particles were destroyed, the dissolution rate may have tapered off to the linear rate of destruction of the bulk mineral.

Holdren and Berner (1979) demonstrated clearly that adhered fine particles could, in fact, be responsible for the pseudo-parabolic stage of laboratory dissolution experiments. Freshly ground unwashed albite exhibited high initial dissolution rates which did not appear if the fine particles were first removed by $HF-H_2SO_4$.

Similarly, non-linear rates of dissolution may be attributed to the presence of edges, corners, cracks, holes etc. and at a smaller scale, point defects, in boundaries and dislocations (Schott & Petit, 1987). Furrer and Stumm (1983), noted, "If heterogeneities of surface properties (different phases, different particle size, different surface energies) exist, parabolic dissolution rates are typically observed. Linear rate laws are usually obtained if the pretreatment renders the surface properties sufficiently homogenous."

2. Incongruent vs. Congruent Dissolution

Congruent dissolution, or a close approach to it, has been demonstrated in determinations of solubilities from undersaturation of simple silicate minerals in dilute aqueous

solutions at low to moderate temperatures when enough time has passed for equilibrium to be reached. Examples of such studies are: kaolinite $25^{\circ}C$, 2 years (Polzer and Kem, 1965); chrysotile $90^{\circ}C$, 2 months (Hostetler and Christ, 1968) magnesium silicates, 100 hrs. (Luce et al. 1971); and olivine, 2 months (Grandstaff, 1986).

Yet many field studies have shown that silicates weather incongruently in nature (Loughman, 1969). The laboratory dissolution of feldspars by inorganic and organic acids has generally been observed to be incongruent (Correns, 1963; Huang and Keller, 1970 and Gardner, 1983). Usually, alkalis and alkaline earths are released in excess of silica and dissolved alumina is least abundant.

Clearly in a system whereby the parent material such as basalt and granodiorite was comprised of mixed mineral assemblages of undetermined stoichiometry, incongruent weathering was expected to take place. It was impossible to trace the origin of ions brought into solution, so that stoichiometries of ions from mineral to solution could be compared. It was however possible to draw some conclusions indirectly from the experimental data regarding preferential dissolution of certain elements. This data supported the fact that incongruent weathering had indeed taken place.

a) First of all, congruent dissolution may be indicated by constant rates of ion released into solution. For the most part of the experiment, rates of dissolution for the seven

ions measured by spectrophotometry were variable, generally slowing down with time. This behaviour in part reflects the build-up of reaction products which changes the ion activity product of the solution with respect to the parent material. The formation of secondary precipitates of any kind within the system conceals the actual stoichiometry of the dissolution reaction and precludes, by definition, congruent weathering taking place. The presence of both amorphous and crystalline secondary precipitates was revealed by Fe, Al, and Si oxide extraction analysis, scanning electron microscopy and EDX. For example, Figure 9 shows an electron micrograph of granodiorite grains weathered by citric acid. The accompanying EDX graph shows a major peak for Si and a very minor peak for Al suggesting the development of an amorphous silica or alumino-silica surface. Figure 11 features a granodiorite grain weathered by oxalic acid showing a rounding and coalescence of the surface typifying a gel.

b) X-ray fluorescence analysis measuring the percentages of oxides in unweathered and weathered samples may be used to determine chemical losses and gains. In particular, comparison of changes in molar ratios of the oxides, subsequent to leaching over time, provides a strong tool to assess whether weathering has in fact proceeded incongruently.

The following is a summary highlighting key features which became apparent in comparing molar ratios of unweathered to weathered mineral following eleven weeks of leaching. See
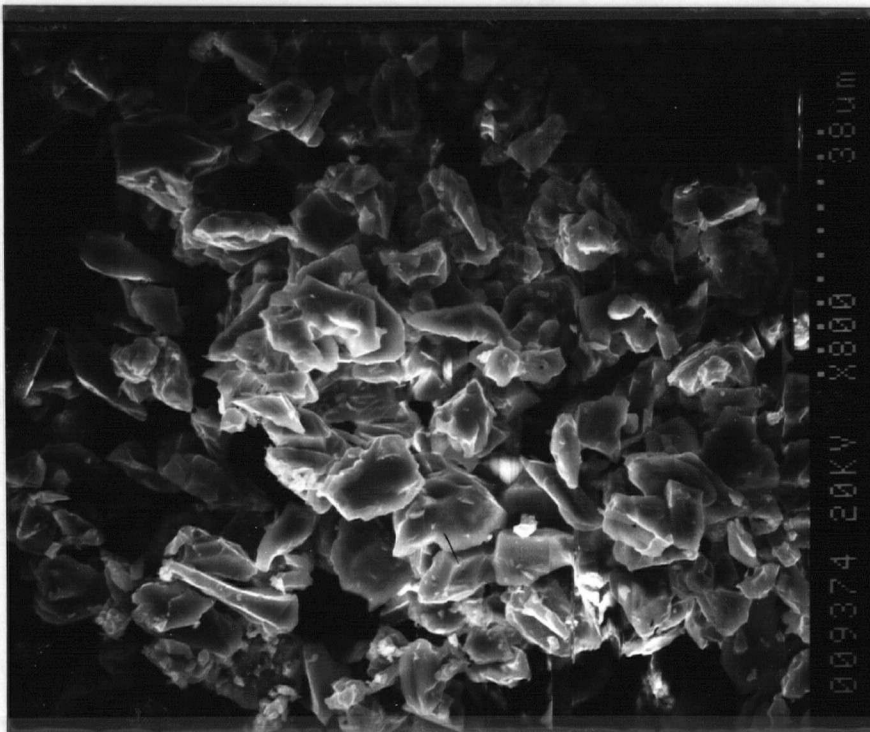
Figure 9: Granodiorite crust materials leached by citric acid for 11 weeks. 800 x magnification
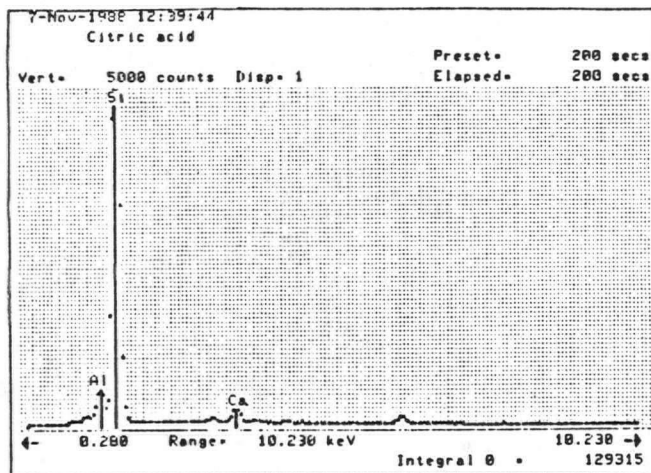
Figure 10: EDX of sample shown in Figure 9 . Note prominent Si peak.
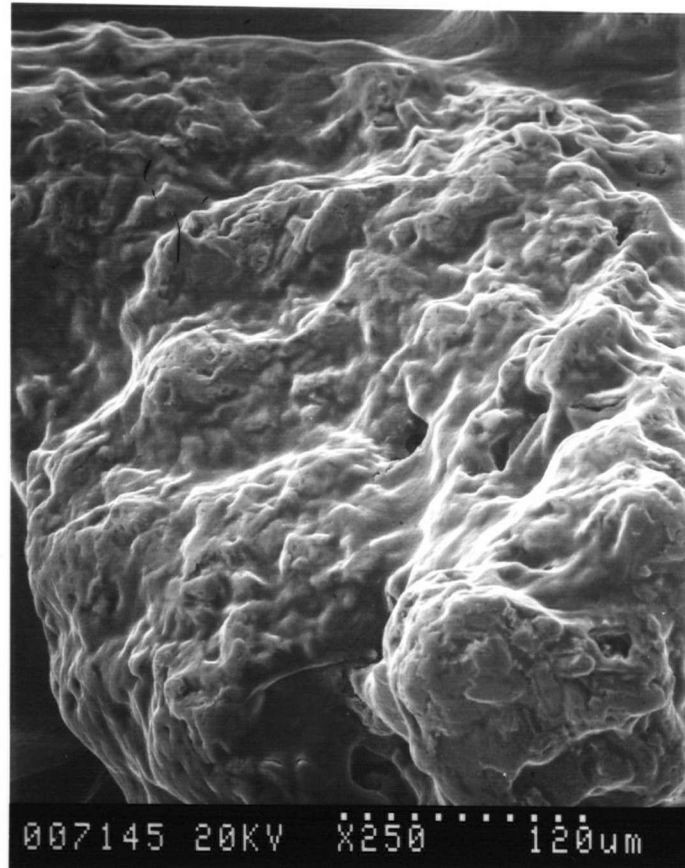
Figure 11: Granodiorite grain weathered by oxalic acid for
11 weeks
Note coalescing surfaces
250 x magnification

tables in Appendix J which give numerical values for calculated molar ratios.

A. Granodiorite 11 weeks - Column and Batch Experiments

1. SiO_2/Al_2O_3 ratios increased slightly for all treatments (Oxalic acid - greatest change)

2. SiO_2/R_2O_3 ratios increased for all treatments (Oxalic acid - greatest change).

3. Al_2O_3/Fe_2O_3 ratios remained the same except for oxalic acid which showed a very high increase.

4. Bases/Al_2O_3 ratios decreased very slightly for all treatments except HCl and H_2O column experiment which showed a slight increase.

5. Bases/SiO_2 ratios remained the same except for oxalic and citric acid which showed slight decrease.

It may therefore be concluded first of all that Fe and Al were removed preferentially to silica. Secondly, except for the oxalic acid treatment Fe and Al were removed in a 1:1 ratio. Oxalic acid extracted Fe to a much greater extent than Al. The removal of the sum of Ca, Mg, K and Na was roughly

equal to that of Al or Si, except for oxalic and citric acid where removal of the bases slightly exceed Al and Si.

B. Basalt - 11 weeks - Column and Batch Experiments

1. SiO_2/Al_2O_3 ratios decreased for citric and oxalic acid and increased for acetic acid, HCl, and H_2O.

2. SiO_2/R_2O_3 ratios increased for all treatments (Citric acid - greatest change).

3. Al_2O_3/Fe_2O_3 ratios increased for all treatments with a very great change shown for citric acid.

4. Bases/Al_2O_3 ratios decreased for all treatments (Citric acid - greatest change).

5. Bases/SiO_2 ratios decreased slightly for all treatments except H_2O (Citric acid - greatest change).

The most apparent feature is that of the extraction power of citric acid in leaching Si, Fe, and Mg. In fact, shifts in weathering ratios for both weathered basalt and granodiorite were greatest for the strongly complexing acids namely oxalic and citric acid. These results support the work of Huang and Keller (1970), who concluded that incongruent

weathering of silicate minerals is brought about through dissolution by chelating acids. The decrease in bases/Al_2O_3 and bases/SiO_2 ratios may be explained either by the greater relative extraction of the bases or by the scavenging of Al and Si by an Fe-oxide coating. However, the Al_2O_3/R_2O_3 and SiO_2/R_2O_3 ratios increased, thus refuting the latter explanation.

c) Incongruent weathering may also arise due to the presence of dislocations commonly manifested by etch pits on reacted mineral grains. Strain energy associated with dislocations may catalyze the breaking of bonds by either a hydronium ion or organic ligand and accelerate formation of the critical activated complex (Aagaard and Helgeson 1982). Also, detachment of the activated complex may occur at different rates in different crystallograhic directions.

Site-selective attack implies a surface-controlled reaction and contradicts the notion of a protective surface layer as a mineral being dissolved by diffusion-controlled reaction should possess smooth, rounded surfaces.

Extensive etch-pitting and site selective dissolution were observed in weathered basaltic and granodioritic grains under the scanning electron microscope. Figures 12 to 14 show increasing magnification of a mica grain leached by oxalic acid for 11 weeks and dramatically illustrate that the grains are anisotropic with respect to dissolution and that
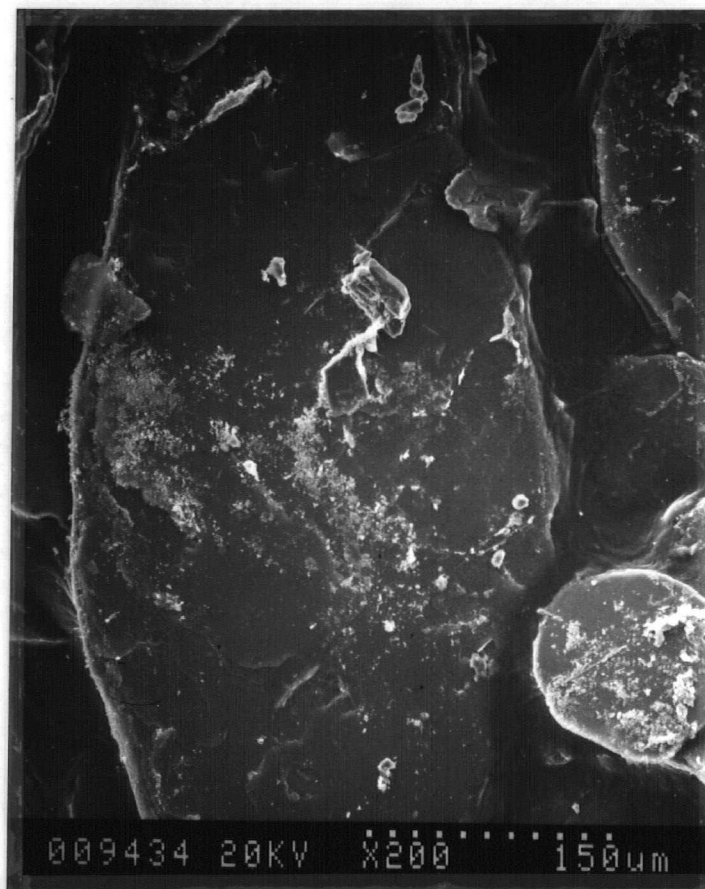
Figure 12: Mica grain leached by oxalic acid - 11 weeks.
200 x magnification
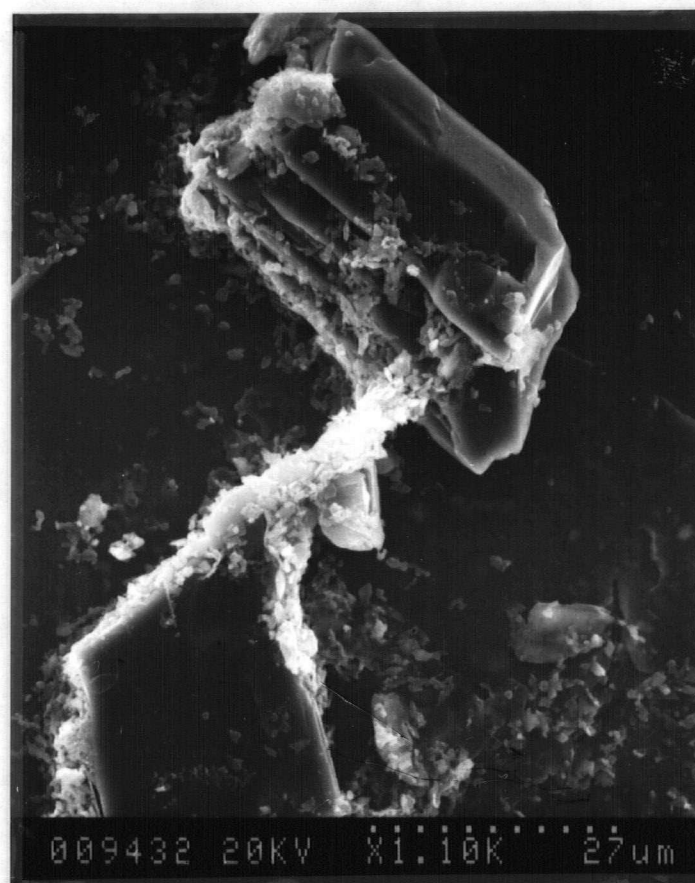
Figure 13: Mica grain leached by oxalic acid - 11 weeks
Note exfoliation.
1100 x magnification
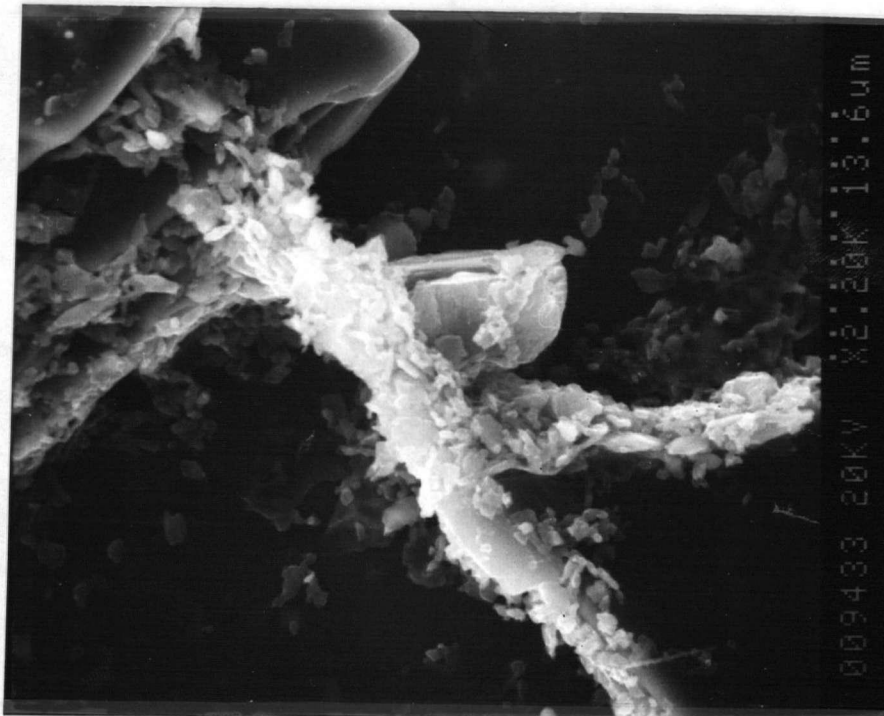
Figure 14: Mica grain leached by oxalic acid 11 weeks
2200 x magnification
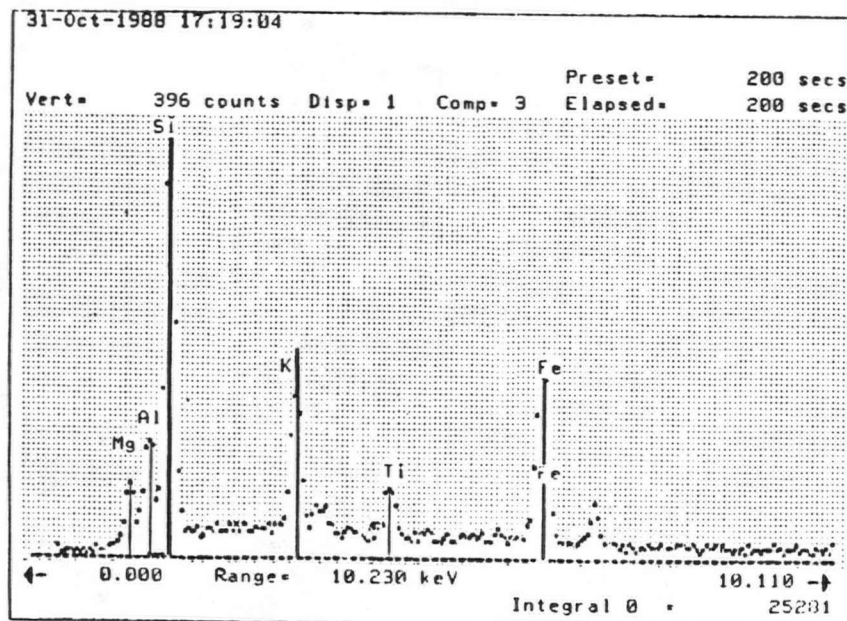
Figure 15: EDX of sample shown in Figure 14.
Note K and Fe peaks.

dissolution occurs at much greater rates on some surfaces than others. The EDX analysis (Figure 15) taken at 2200X magnification suggests the removal of K and Fe from interlamellae regions of the particle, and likely a delayed release of silica. Figure 16 exemplifies more advance etch-pitting of a granodiorite grain also leached by oxalic acid for 11 weeks. The accompanying EDX analysis confirms the incongruent removal of bases leaving a strong silica peak. It is possible that further dissolution could break down the remaining alumino-silicate lattice releasing all constituents to solution. It has been suggested by Holdren and Berner (1979) that this stage of the reaction is most likely congruent for a particular mineral, providing no secondary precipitates on the surface act as a scavenging armour for ions in solution.

It should be further noted that the etch-pitting observed in the micrographs may also be due to differential dissolution of two distinct phases as commonly found, for example, in microperthitic exsolution features of feldspars (Gardner 1983). Gardner (1983) postulated that congruent dissolution of two distinct but intimately intergrown phases at different rates may appear to be incongruent dissolution of the bulk phase.

The presence of etch pits in addition to precipitation of authigenic phases on grain surfaces accounted for the increase in specific surface of the weathered minerals. (See
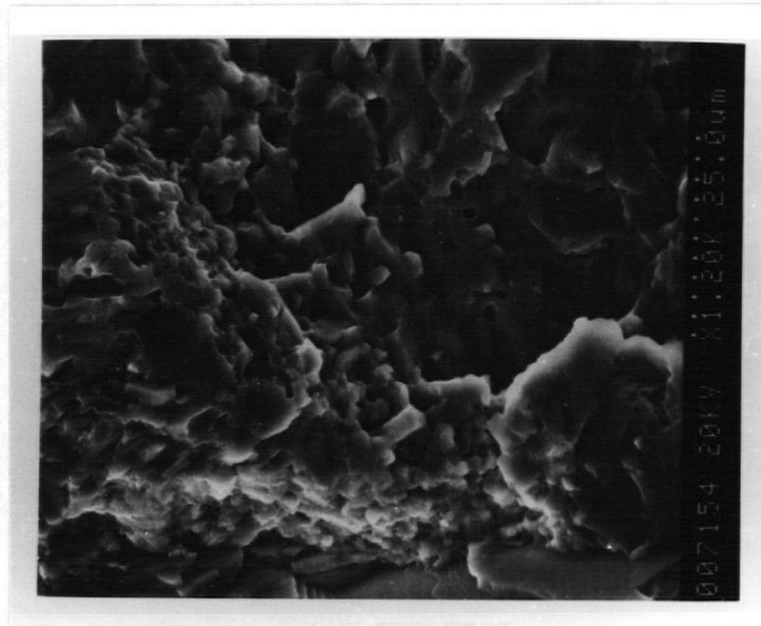
Figure 16: Granodioritic grain leached by oxalic acid 11
weeks.
Note preferential dissolution following
crystallographic features (honeycomb etching)
1200 x magnification
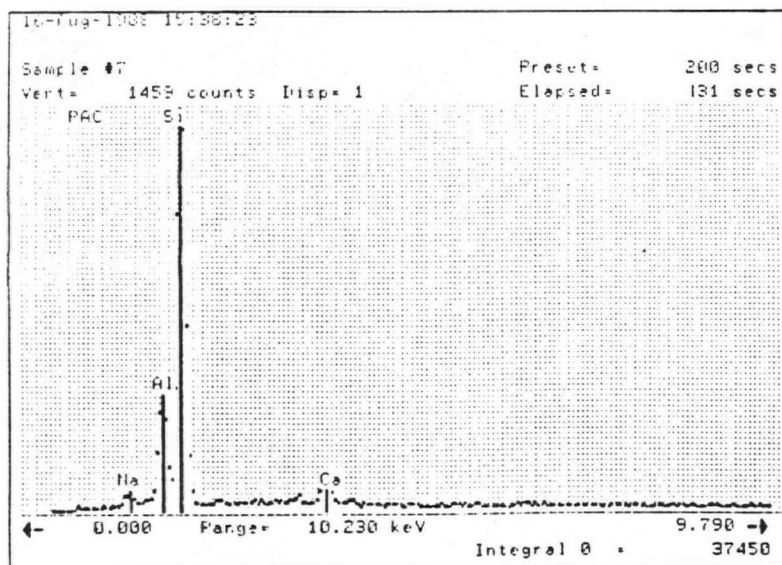
Figure 17: EDX of sample shown in Figure 16.

Appendix L). After 11 weeks, the surface area of granodiorite increased 4-5 fold and that of basalt 4-7 fold. Holdren and Speyer (1986) found in their study of the stoichiometry of alkali feldspars dissolution that as the grain size became smaller, the reaction became more nearly congruent. This could partly explain why dissolution approached linearity towards the end of the 11 week experiment.

Figures 18 to 25 show other types and stages of etch-pitting.
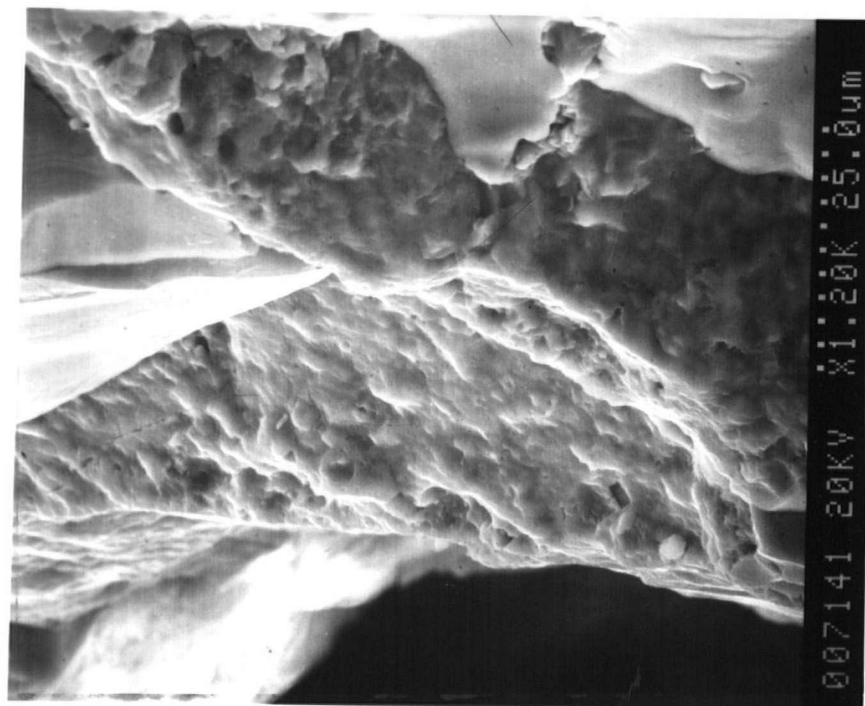
Figure 18: Basaltic grain leached by oxalic acid for 11 weeks
Note smooth vs actively eroding surface
1200 x magnification
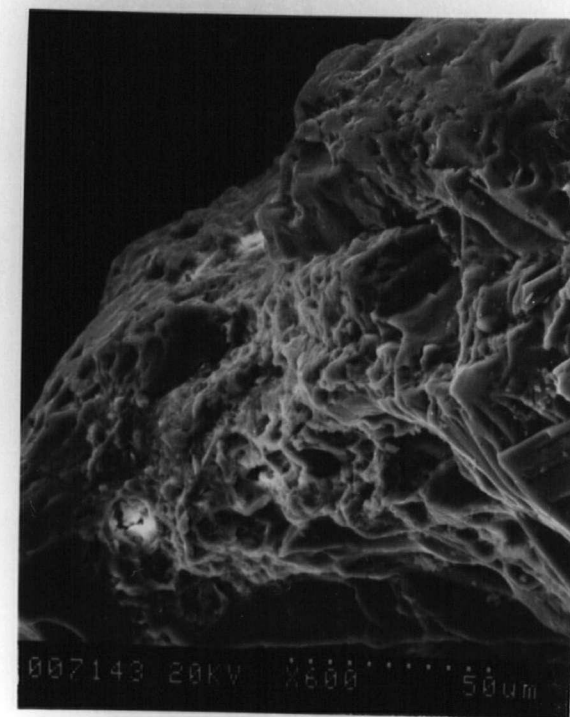
Figure 19: Basaltic grain leached by oxalic acid for 11 weeks
600 x magnification

87
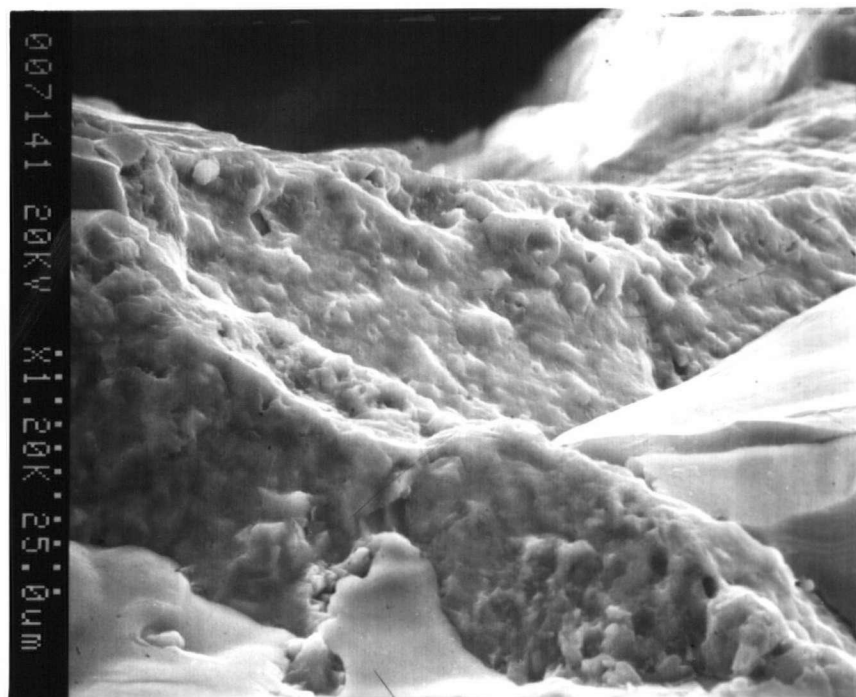
Figure 20: Granodiorite grain leached in oxalic acid for 11
weeks
Note contrast in rough surface features to that
of underlying smooth features
800 x magnification
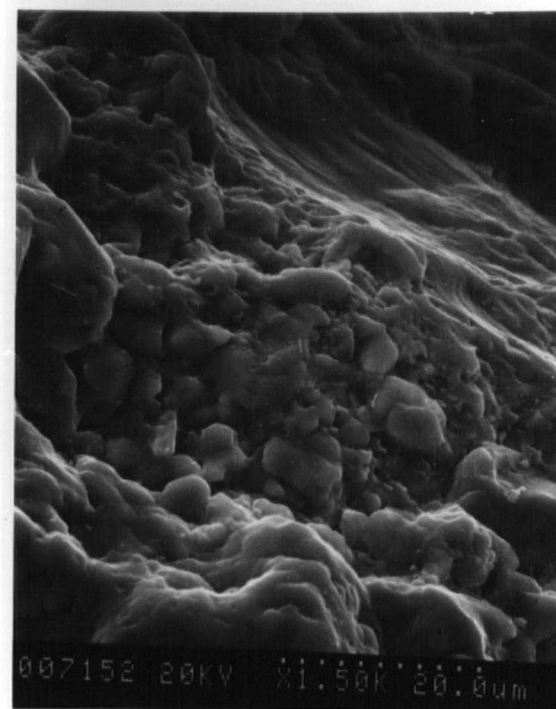
Figure 21: Granodioritic grain leached in oxalic acid for 11
weeks
Note actively eroding surface in foreground
1500 x magnification
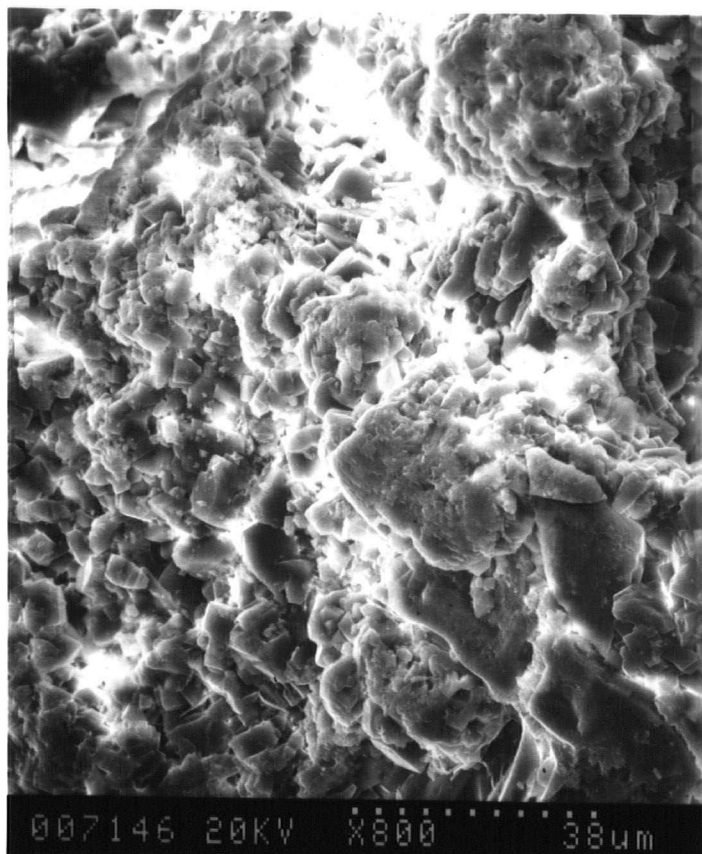
Figure 22: Basaltic grain leached in oxalic acid for 11
weeks.
800 x magnification
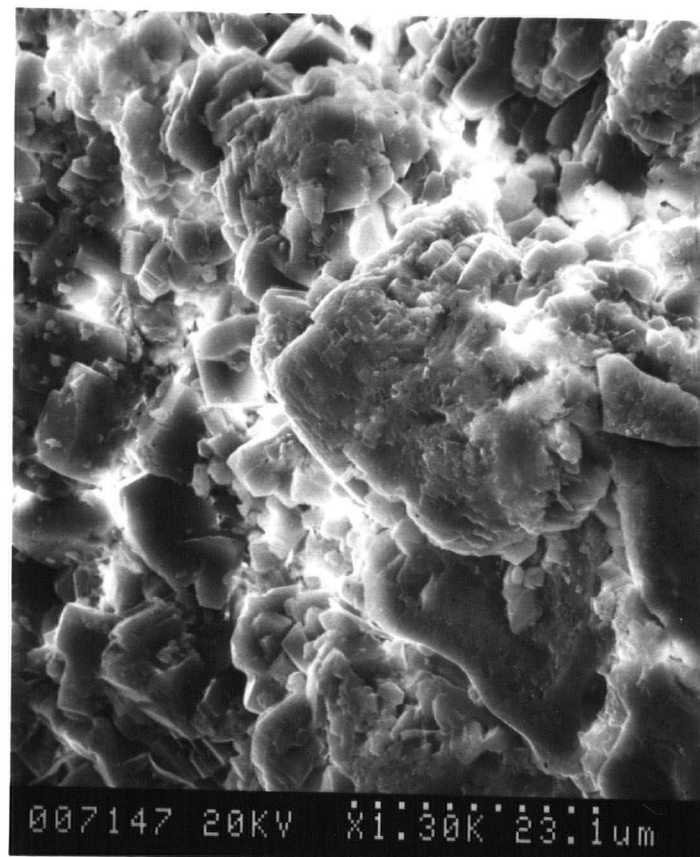
Figure 23: Basaltic grain leached in oxalic acid for 11
weeks.
1300 x magnification
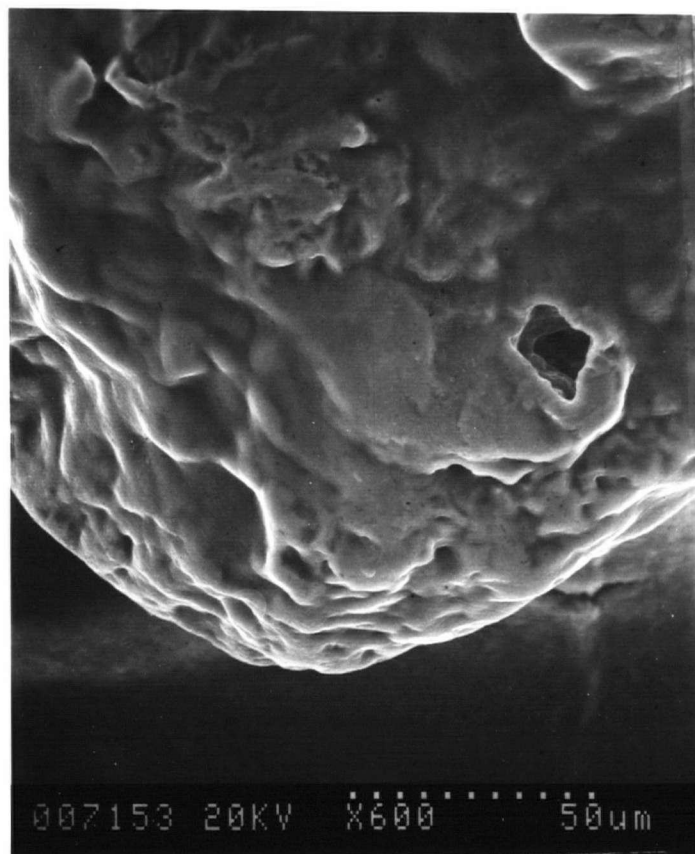
Figure 24: Basaltic grain leached in oxalic acid for 11
weeks.
Note prominent etch pit
600 x magnification
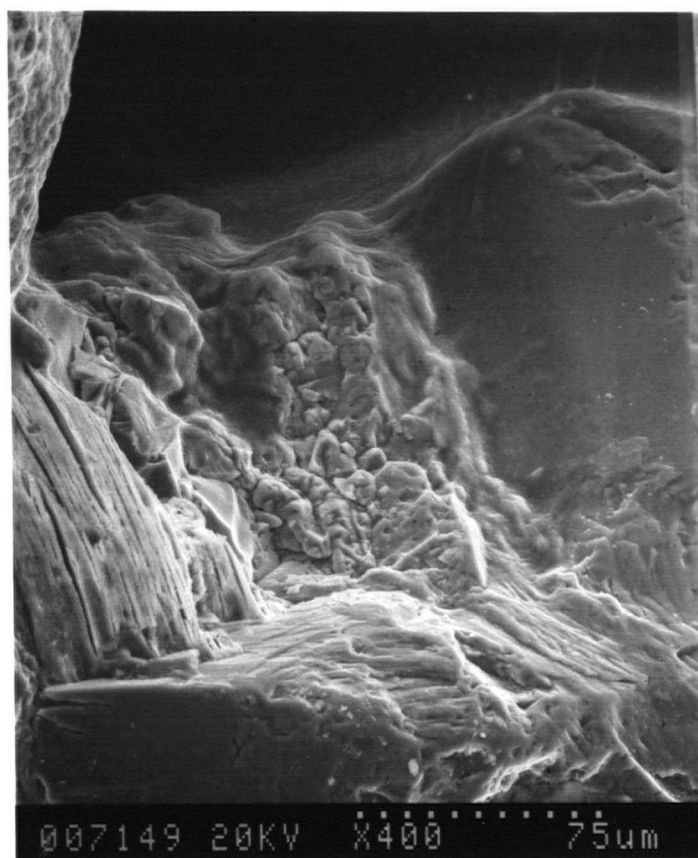
Figure 25: Granodiorite grain leached in oxalic acid for 11
weeks.
Note contrast in actively eroding surface in
centre to smoother striated surfaces in
foreground
400 x magnification

RESULTS AND DISCUSSION: SECTION III

C. Formation of Organo and Amorphous Precipitation Products

The results of the analyses to determine the extent of Fe, Al, and Si oxide formation on the granodioritic and basaltic surfaces is summarized in Appendix A_2. Graphic depiction of this data is shown in Appendix A_1.

It is immediately apparent that the Fe_{PYRO} levels for both basalt and granodiorite leached by oxalic acid are remarkably high. The levels for granodiorite ranged between 2.0-2.4% and for basalt between 4.7-6.5%. To gain an appreciation of the relative magnitude of these levels to those found in soils, it is noted that the percentage of Fe_{PYRO} extracted from an Ortho Humic Ferric Podzol on Vancouver Island reached a maximum of .50% in the B horizon (G. Singleton, 1978).

As noted earlier, research (e.g. Schuppli et al.1983; Loveland and Digby,1984) has given evidence that conventional centrifugation is inadequate to sediment suspended material completely in pyrophosphate extracts at a pH of 10. Jenroy and Guillet (1981), found ferruginous particles >100 nm diameter still present in Na-pyrophosphate solutions centrifuged at RCF 40,000, whilst McKeague and Shuppli (1982), found that stepwise centrifugation up to RCF 120,000 progressively decreased amounts of Fe and Al in solutions.

Name	Formulae	Crystalline Form	Solubility gms/100 g	
			Cold Water	Hot Water
Fe (II) Oxalate	$FeC_2O_4.2H_2O$	pale yellow, rhomb	0.022	0.026
Fe (III) Oxalate	$Fe_2(C_2O_4)_3.5H_2O$	Yellow micro crystalline powder	V.S.	V.S.
Mg oxalate	$MgC_2O_4.2H_2O$	White powder	.07	0.08
Ca Oxalate	CaC_2O_4	Colorless, cubic	0.00067	0.0014
Ca Oxalate hydrate	$CaC_2O_4H_2O$	Colorless, cubic	i	i
Al Oxalate	$Al_2(C_2O_4)_3.4H_2O$	White powder	i	i
Fe (II) citrate	$FeC_6H_6O_7.H_2O$	White micro phomb	sl.s	--
(III)citrate	$FeC_6H_5O_7.5H_2O$	Red-brown scales	sl.s	soluble
Mg.citrate, mono-H	$MgHC_6H_5O_7.5H_2O$	White granular powder	20^{25}	soluble
Ca-citrate	$Ca_3(C_6H_5O_7)_2$ $4H_2O$	White needles	0.085	0.096
Al-citrate	not given	--	--	--

Source: Handbook of Chemistry & Physics, 1984.

TABLE 6: CHEMICAL DESCRIPTION OF CITRATE AND OXALATE SALTS

The laboratories in the soil science department at UBC are not equipped with a high-speed centrifuge (6000-8000 RCF Max.). The Fe measured in the pyrophosphate extracts therefore was not entirely in dissolved form but present also in the strucure of suspended materials, thereby overestimating the values. Mass balance calculations (Appendix N), differentiating % Fe in the unweathered sample v.s. Fe in the dissolved and precipitated form give values which exceeded that of the starting material. Evidently colloidal material was measured in the AA spectrophotometric solution analyses thereby introducing inaccuracy.

It is possible that the source of some of this colloidal material originated from a yellow precipitate which was observed forming in both granodiorite and basalt parent material leached by oxalic acid. These precipitates were examined in more detail with the help of a scanning electron microscope and chemically analyzed by EDX, XRD and XRF. A chemical description of citrate and oxalate salts is given in Table 6 to assist in the identification of the precipitates. A discussion of those findings follows.

1. Granodiorite Oxalic Precipitate

Magnification under the electron microscope revealed 2 distinct components of the precipitate which formed from granodiorite.Firstly, very small (<5 um) fragmented mineral grains were clearly visible. See Figure 27. EDX of these
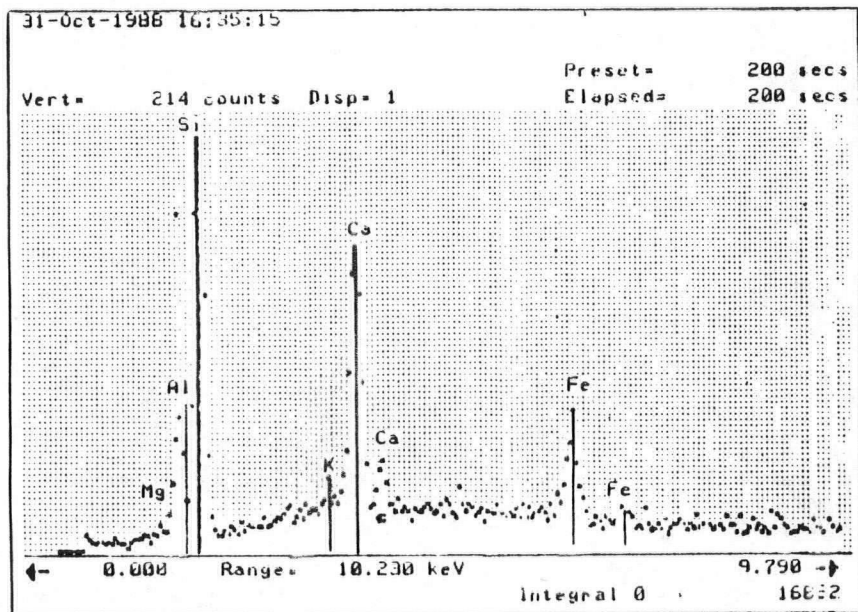
Figure 26: EDX of sample shown in
Figure 27.
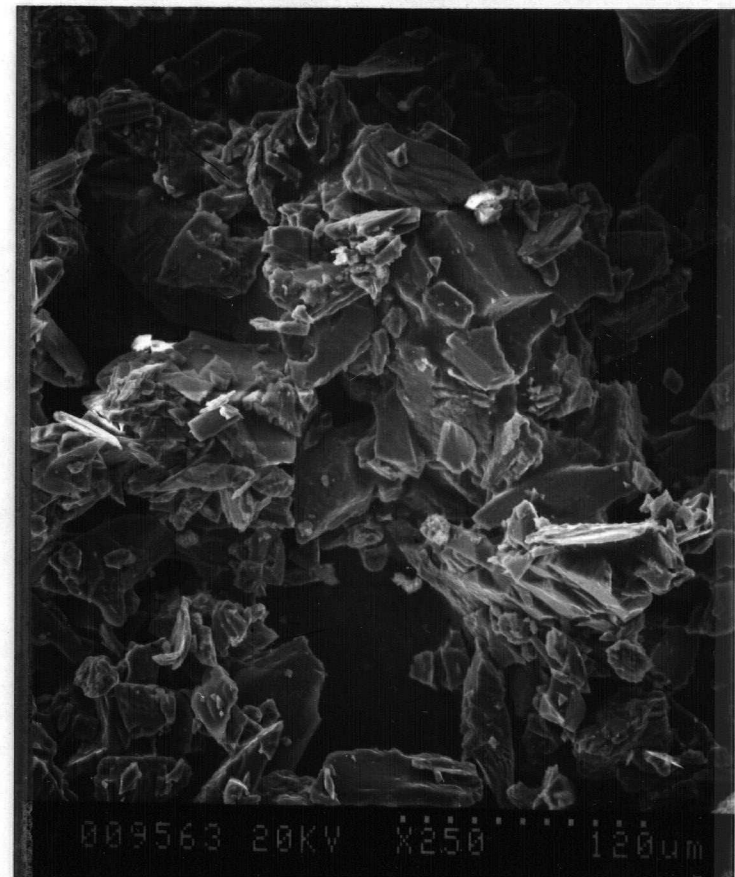
Figure 27: Mineral fragments in
granodioritic crust found
after 11 weeks of leaching in
oxalic acid.
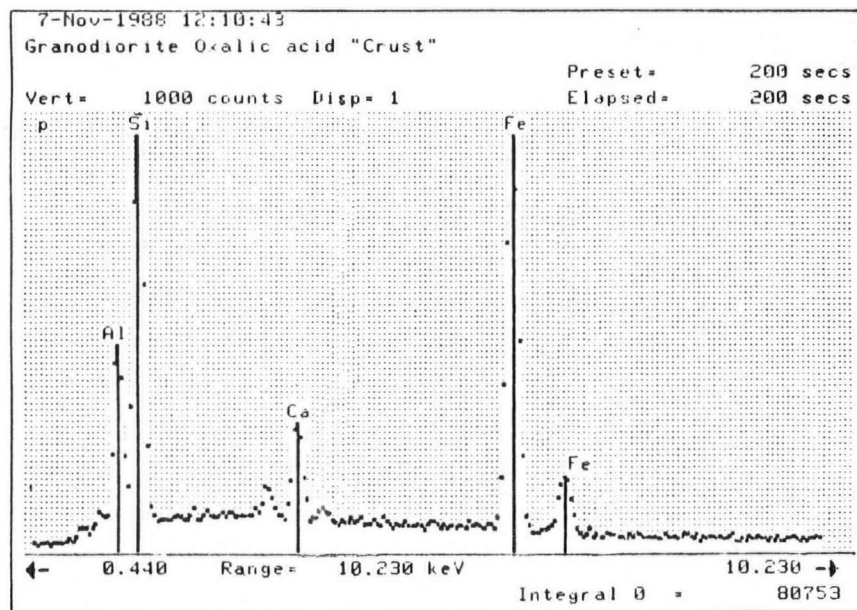
Figure 28: EDX of sample shown in
Figure 29.
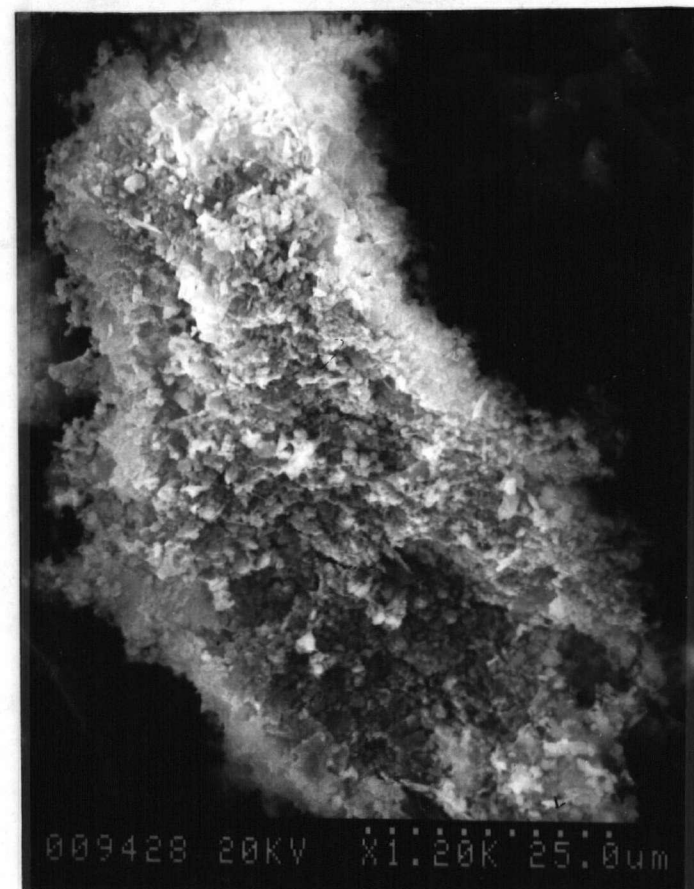
Figure 29: Amorphous precipitate in
granodioritic crust found
after 11 weeks of leaching in
oxalic acid.
1200 x magnification

grains (Figure 26) determined the presence of Si, Al, Ca, Fe and K, indicating a mafic material. XRD of the precipitate confirmed the presence of hornblende as well as plagioclase.

The second component appeared to be a short range ordered "fluffy" precipitate which exhibited very high surface area. (Figure 29). The EDX analyses , (Figure 28), determined the presence of Si and Fe, in approximately 50% ratio, with lesser peaks of Al and Ca. XRD analyses confirmed the presence of Fe-oxalate hydrate, calcium oxalate and oxalic acid.In fact, the yellow colour is indicative of the Fe-oxalate hydrate (Handbook of Chemistry and Physics, 1986).

To date there is neither any reported evidence of a Si-oxalate complex (Drs. Barnes,W. and Clavette,D. pers. comm.), nor any reported stability constants to match. In addition, XRD peak data for such a compound was not found in the literature.

It is likely that in an oxalic acid solution of pH <2, protonation of the granitic surface (and cleavage of the siloxanol bond),took place with subsequent release of $Si(OH)_4$ into solution. With a Saturation Index of greater than 0, precipitates will form, and in fact the fluffy appearance shown in the photograqph (Figure 29), is typical of the metal hydroxide $Si(OH)_4$ (Dr. Orvig, C.E. pers. comm.).

Although no stability constants are to date given in the literaure for a Si-oxalate complex it can be predicted that Fe will effectively compete with the Si for the oxalate anion.

This competition may preclude the chances of Si combining with oxalate.

On the other hand the possibility of a Si-oxalate complex cannot be ruled out (Dr. Clavette,D. pers. comm.). The interaction of silicic acid and silicates with organic components of biological systems is thought to involve several types of chemical bonding such as Si-O-C, Si-N-C, Si-C,as well as hydrogen-bonded complexes (Iler, 1979).Furthermore, not only 4-but also 5- and 6- co-ordinated silicon have been isolated and characterized (Weiss and Herzog, 1978). Weiss and Herzog (1978), were able to precipitate an organic Si-salt, [Si (thpl)$_3$]PF$_6$ by treating finely ground silica (silica gel or quartz), in an aqueous suspension at pH= 3.5 with a tropolone derivative. Tripolones are abundant in higher plants and are similar to oxalic acid in exhibiting bidentate character with a delocalized Pi-system in the anionic form. Subsequent work in Sweden (Sjoberg et. al. 1985), has investigated complex formation of silicic acid and silicates with polyols (mannitol), saccarides (glucose), 1,2- diphenols (pyrocatechol), and tropolones. The authors report ^{29}Si- NMR chemical shift values which showed that, at pH < 3, a hexa-coordinated silicon tropolone (SiL$_3$+) complex was promoted. However, no such complex occured in neutral and alkaline aqueous solutions. But it remains possible that given the low pH conditions of the batch and column experiment, oxalic acid may have formed a complex with silicon similar in nature

to the silicon- tripolone bond.

Finally, an Fe-silicate complex, known to form at low pH's (Dr. Clavette,D. pers. comm.), may have contributed to the observed precipitate. Although the EDX analysis gives no structural information, the height of the peaks in the graph did indicate that Fe and Si were in approximately 1:1 ratio, thereby pointing to the possibility of such a compound existing. XRD peaks for Fe_2SiO_4 did not appear at the diagnostic 2.49 or 1.78 A but the presence of these peaks may have been overshadowed by peaks from other minerals or salts occuring in higher concentration.

The accumulation of Fe in the "fluffy" precipitate is clearly shown from the XRF data, (Appendix I), whereby the levels of Fe_2O_3 rose as high as 16.22% in contrast to 5.21% in the unweathered granodiorite. Also the SiO_2/R_2O_3 and Al_2O_3/Fe_2O_3 ratios (Appendix J) dropped from 5.52 and 5.33 respectively in the unweathered material to 3.26 and 0.90 in the precipitate. It is interesting to note that the SiO_2/R_2O_3 and Al_2O_3/Fe_2O_3 ratios show just the opposite trend for the weathered granodiorite grains which were analyzed separately from the precipitate. These ratios were the highest for all the recorded values for the 5 leaching treatments both in batch and column experiments. This shows a strong depletion of Fe from the parent material. It may be concluded therefore, that Fe leached from the granodiorite into solution is to a large extent reappearing in the precipitate. For this reason,

28-Oct-1988 09:31:59

Basalt Oxalic Crust   Preset=   200 secs
Vert=   2317 counts Disp= 1   Elapsed=   200 secs

Fe

Mg

Si

Na Al   K   Ca Ti   Mn   Fe

,0.000   Range=   10.230 keV   10.110

Integral 0 =   215599
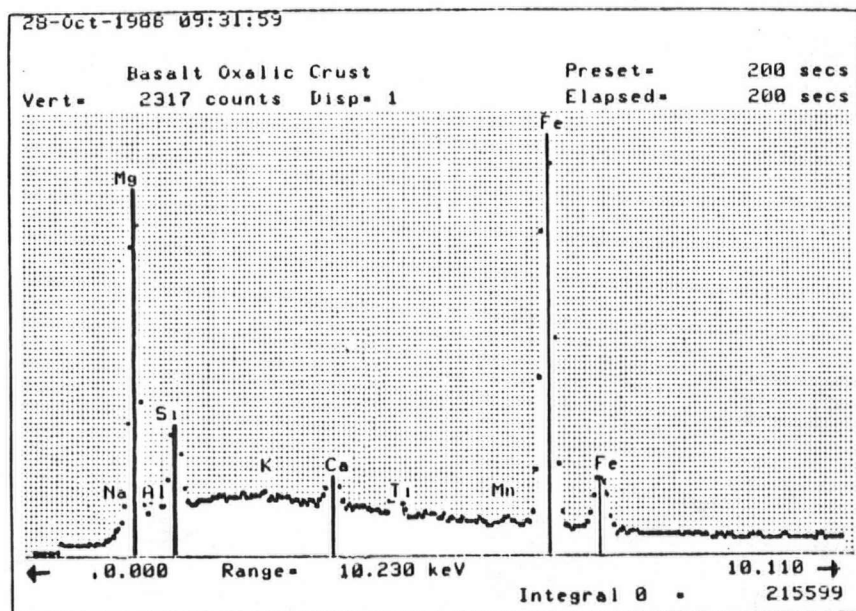
Figure 30: EDX of sample shown in
           Figure 31.

Figure 31: Amorphous precipitate in
           basaltic crust formed after
           11 weeks of leaching in
           oxalic acid.
           1800 x magnification

mass balance calculations (Appendix N) itemizing Fe brought into solution and subsequently precipitated, may total greater than 100% as the Fe extracted is effectively measured twice in two different forms.

2. Basalt Oxalate Precipitate

Magnification under the scanning electron microscope of the precipitate formed from oxalic acid leaching of basalt is shown in Figure 31. EDX analyses produced major peaks for Mg and Fe. XRF analysis (Appendix I) of the precipitate indicated the highest accumulation of Fe_2O_3 (14.63%), of any weathered product under all experimental conditions. Sesquioxide analysis (summarized in the bar graph in Appendix A_1), also show the highest level of extractable Fe_{PYRO} (25%) for any sample and reflects the fact that the Fe is bound in organic complexes with oxalic acid. Surprisingly, the Fe_{CBO} levels (5.5%) are greater than the Fe_{OX} levels (2.0%) pointing to the presence of some crystalline Fe. XRD analysis (Appendix K_2) identified major peaks for Fe-oxalate hydrate, Mg-oxalate hydrate, calcium oxalate, oxalic acid as well as pyroxene and fayalite. Once again, the yellow colour of the precipitate is also indicative of the Fe-oxalate hydrate (Handbook of Physics and Chemistry, 1986).

3a. Granodiorite Citrate Precipitate

The crust-like material which settled out upon drying in the granodiorite batch sample after 11 weeks of weathering was examined under the scanning electron microscope (Figure 33). At 700 and 1100x magnification an amorphous material, "fluffy" in appearance, is seen to adhere to mineral particles. EDX at 8000x magnification, (Figure 32) revealed that the material consisted of Fe and a minor amount of Si. This formation likely accounts for the fact that Fe_{PYRO} levels were slightly higher than other forms of extractable Fe in the crust material (Appendix $A_{1,2}$). XRF analysis of this material showed an accumulation of Fe_2O_3 (6.5%) compared with that of unweathered granodiorite (5.21%). In contrast the precipitate from oxalic acid leaching contained 16.22% Fe_2O_3. Thus the citrate precipitate, although predominantly Fe, developed to a much lesser extent or at a slower rate than that developed under oxalic acid and formed only a small part of the crust. In addition, the XRD analysis did not produce any peaks for cation-citrate complexes which may have existed but were below detectable limits. There was a slight increase in intensity for the hematite peak (Appendix K_2), but the hematite is likely of lithogenic origin and not a secondary product.

3b. Granodiorite Citrate Inorganic Surface Coatings

Coatings on the surface of granodiorite particles weathered by citric acid, differing in appearance from the
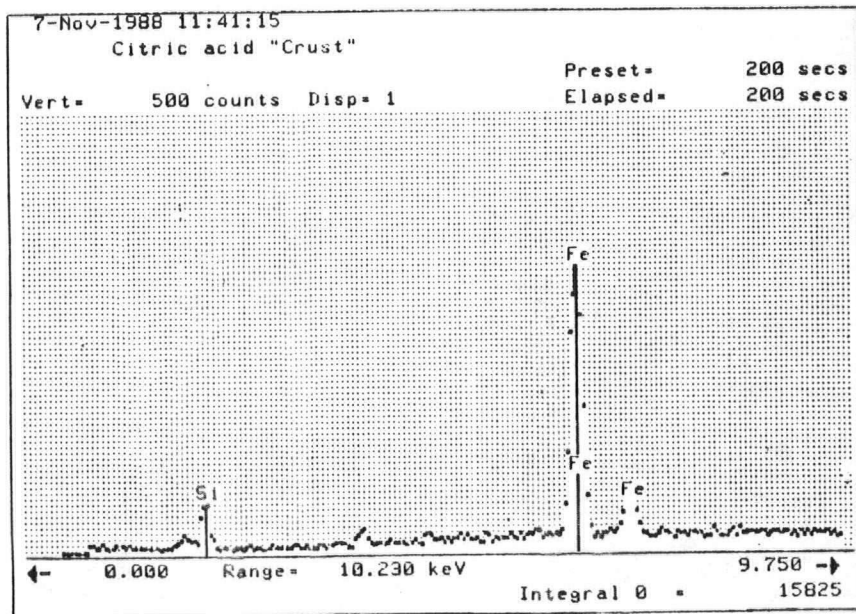
Figure 32: EDX of sample shown in
Figure 33.
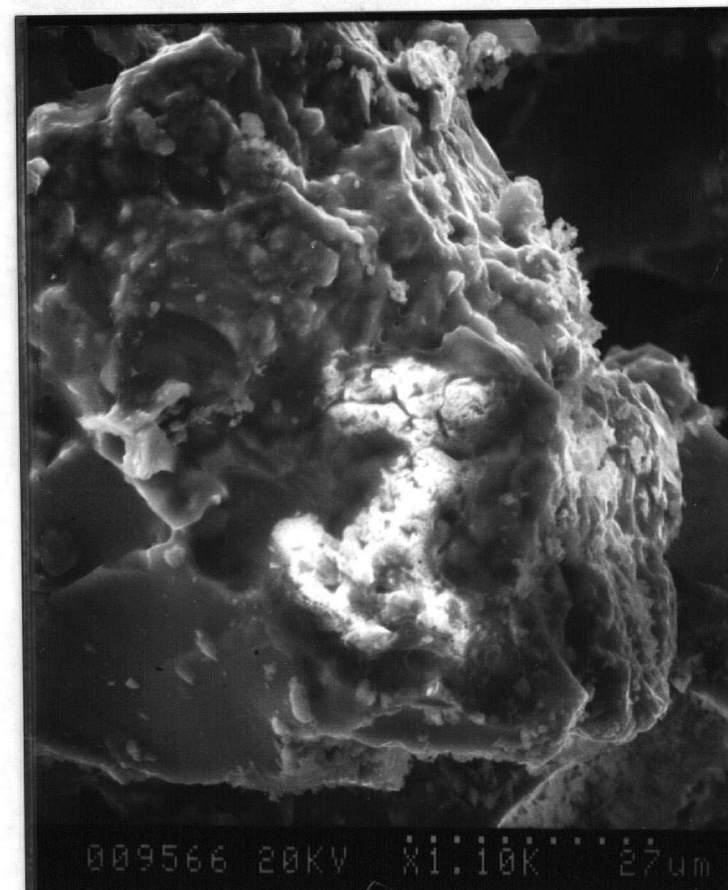
Figure 33: Amorphous precipitate in
granodioritic crust formed
after 11 weeks of leaching in
citric acid.
1100 x magnification

sample noted above, were also observed in the finer "crust" material which settled out upon drying.This second type of coating was photographed under the scanning electron microscope and is shown in Figure 35.

Both 500 and 800x magnification revealed amorphous surface material coalescing between particles. EDX analysis at 800x magnification and penetrating 2um into the surface showed major peaks for Si, Al and Fe. The ratio of Fe:Al as given by the relative heights of the peaks is approximately 1.4. In view of the fact that Farmer and Fraser (1982), were succesful in synthesizing a stable Al_2O_3-Fe_2O_3-SiO_2-H_2O sol (pH 4.5-5.0) with Fe:Al molar ratios up to 1.5, it is possible that the amorphous material (See area A in the photo) could be similar in make-up. As reported however , by McBride et al. (1984), Fe^{3+} tends not to substitute randomly in an Al-Silica gel but rather aggregates into clustered Fe^{3+}-rich phase in the form of ferric oxihydroxide within the gel. The Fe-rich phase forms a precursor to ferrihydrite and the Al-Si rich phase a precusor to proto-imogolite.

The formation of this gel likely occurred subsequent to the removal of the .1M citric acid solution (pH 2.5) from the sample. A small unit of residual citric acid dried on the mineral particles and may be observed in Area B of the photo. At first, the presence of a strong chelator, such as citric acid in such high concentration, would seem to preclude the chances of sesquioxides forming at all. Note that Al in
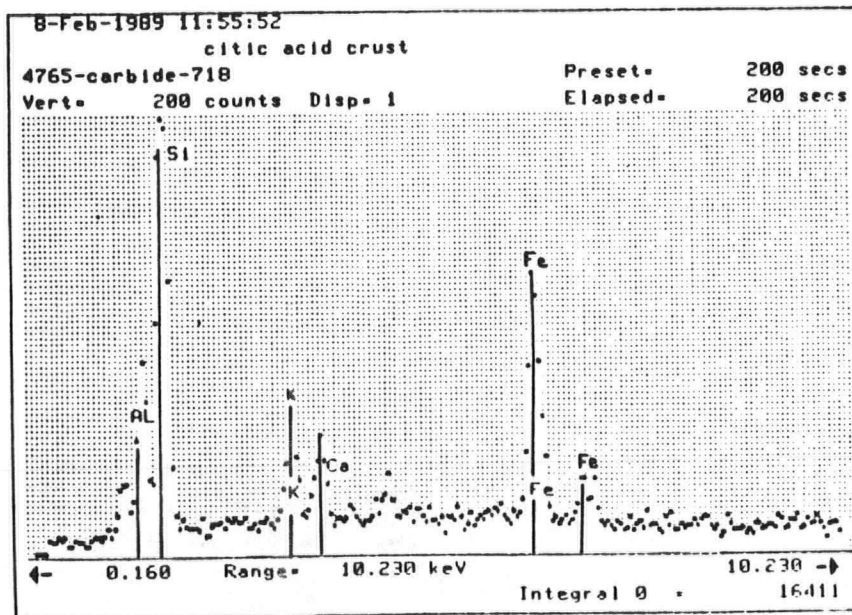
Figure 34: EDX of sample shown in
          Figure 35.
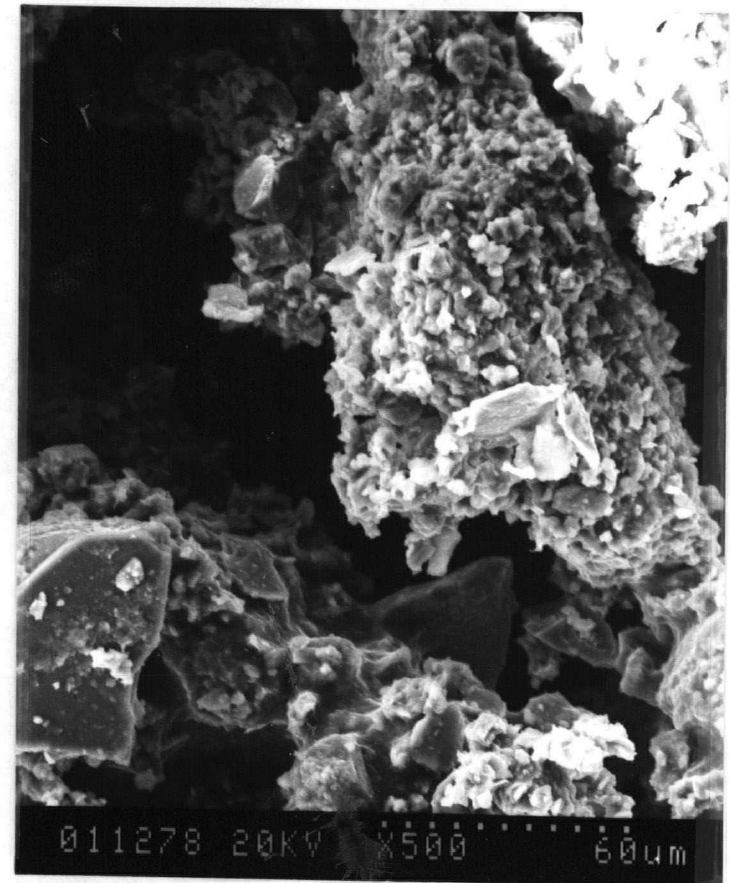
Figure 35: Granodioritic "crust" leached
          in citric acid for 11 weeks.
          500 x magnification

organic complexes, for example, is more stable than in orthosilicate (Buurman and Vav Reeuwijk, 1984). But bearing in mind that most of the solution was removed and the samples were left to air-dry over the course of several weeks, it is possible to trace the formation of these precipitates. As noted by Farmer (1979), metal fulvates remain soluble when undersaturated with metals but become insoluble when the metal:fulvate ratio rises to saturation. Removal of solution through centrifugation followed by air-drying may have effectively separated much of the organic phase from the ligand by reducing the ligand:metal ratio. Secondly, the amount of citrate, at first co-precipitated with a metal, will decrease upon aging (Violante and Huang, 1984). The liberation of the organic anions with time in the laboratory experiments of Violante and Huang (1984), resulted in the formation of an inorganic precipitate. Thirdly, under field conditions, biological oxidation will separate the organic from inorganic phase (Buurman and Van Reeuwijk, 1984). This, of course was not a factor in the batch and column laboratory experiments.

4. Basalt Citrate Precipitate

No "fluffy" precipitate was detected from the weathering of basalt with citric acid under the scanning electron microscope (Figure 37). Rather, the relative EDX analysis of crust material showed an accumulation of silica with only a

28-Oct-1988 10:08:59

Basalt grain under citric acid crust   Preset=   200 secs
Vert=   3605 counts Disp= 1   Elapsed=   200 secs

Si

Al

Ca

Mg

Ti

Fe

MgNa   Fe

◄─   0.600   Range=   10.230 keV   10.230 ─►

Integral 0 =   162562
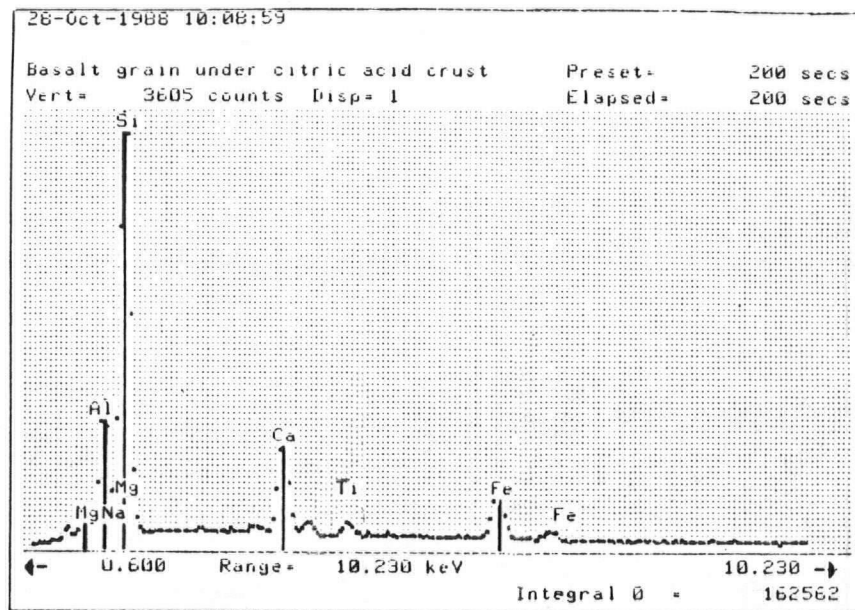
Figure 36: EDX of sample shown in
            Figure 37.

009573 20KV X150   200um
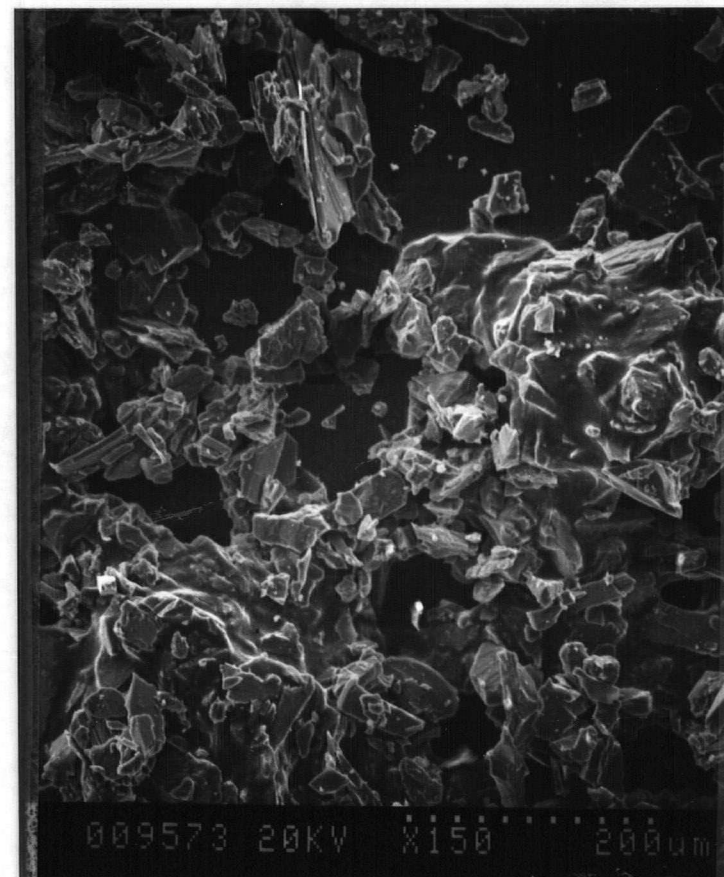
Figure 37: Basaltic grains leached in
            citric acid for 11 weeks.
            150 x magnification

minor Fe peak (Figure 36).The relative accumulation of Si over that of Fe is reflected in the SiO_2/R_2O_3 ratio which increased from 3.61 in the unweathered basalt to 4.05 in the weathered crust.Similarly, Percentage of Fe_2O_3 in weathered crust dropped to 7.04% for Basalt A and even lower to 3.69% for Basalt B, compared with 12.46% for the unweathered basalt. It might be added that the levels of all forms of precipitated Fe as measured in CBD, oxalate, and pyrophosphate extractions, as well as total Fe in the precipitate as measured by XRF were the lowest of all 5 leaching treatments for both column and batch trials. (Conversely, SiO_2/R_2O_3 and Al_2O_3/Fe_2O_3 ratios were the highest.)

The amount of dissolved Fe, on the other hand exceeded all leaching treatments. Clearly, the Fe leached into solution, for the most part, remained in soluble form. The ability of citrate to maintain Fe in solution leached from basalt is far greater than the ability of oxalate of similar molar concentration.

Therefore, although citric acid was able to extract greater amounts of Fe from basalt than from granodiorite the development of precipitates occured only in the granodiorite samples. As citric acid weathered the granodiorite, the pH of the solution rose only to approximately 2.3. At this pH citric acid remains undissociated and dissolution of Fe is brought about more through acidolysis (i.e. H^+ attack) than through chelation. In contrast, as citric acid weathered the

basalt, the pH of the solution rose to approximately 3-5. At these higher pH's the Fe may be complexed to either H_2L^- or to HL^{2-} as each ligand comprises roughly 50% of the citric acid. The complexed Fe therefore remained in soluble form.

5. Granodiorite - Acetic acid, HCl and H_2O Leaching Treatments

Granodiorite leached in acetic and hydrochloric acid as well as distilled water were examined for sesquioxide development. XRF data showed a drop in Fe_2O_3 levels in weathered grains but to a much lesser extent than either citric or oxalic acid treatments. EDX analyses of the crusts resulting from acetic acid and distilled water treatments showed only a minor Fe peak of lesser intensity than those for Si, Al, Ca or K. XRD analyses of crusts from all 3 treatments indicated new peaks appearing at 2.50, 2.21 and $1.96A^o$. These coincide with the peaks of ferrihydrite. It is tempting to conclude that, in the absence of stronger organic acids such as .1M oxalic and citric acids which may inhibit the crystallization of Fe and Al oxides, ferrihydrite could indeed form. However, Schwertmann et al. (1982), reported that because of its poor crystallinity ferrihydrite can only be recognized easily by routine XRD if it is reasonably pure. To identify it in lower concentrations as found in soils or in mixtures with other minerals (e.g. quartz, micas, goethite), special procedures such as DXRD and Mossbauer spectroscopy

must be applied. The authors found that the lower limit of ferrihydrite detection lies somewhere between 13.3% Fe_{OX} and 2.9% Fe_{OX}. Fe_{OX} levels recorded for the weathered residues including crust were appriximately 1% or less for all 3 inorganic treatments.

The photograph in Figure 39, taken under the light microscope, clearly shows some form of Fe oxide development as indicated by the darker orange areas in tha grains of a granodioritic sample leached in water. These coatings were not , however, analyzed in further detail.

6. Basalt - Acetic acid, HCl and H_2O Leaching Treatments

XRF data for basalt leached by the 3 non-chelating acids gave only a slight drop in Fe_2O_3 in the weathered residues. Levels for SiO2 and Al_2O_3 remained about the same following leaching. In addition, XRD analyses did not detect the development of any new peaks.This is consistent with the very low solubility of Fe, Si and Al oxides , even at low pH, in an aquatic environment deplete of strongly complexing organic acids. XRF analyses of the crust material gave a slight increase in % Al_2O_3 and a slight decrease in % Fe_2O_3 compared with both the unweathered and weathered residues.

Data for extractable Fe and Al showed $Fe_{OX,CBD}$ and $Al_{OX,CBD}$ levels higher than those for the citric and oxalic acid treatments. This is surprising in light of the fact that
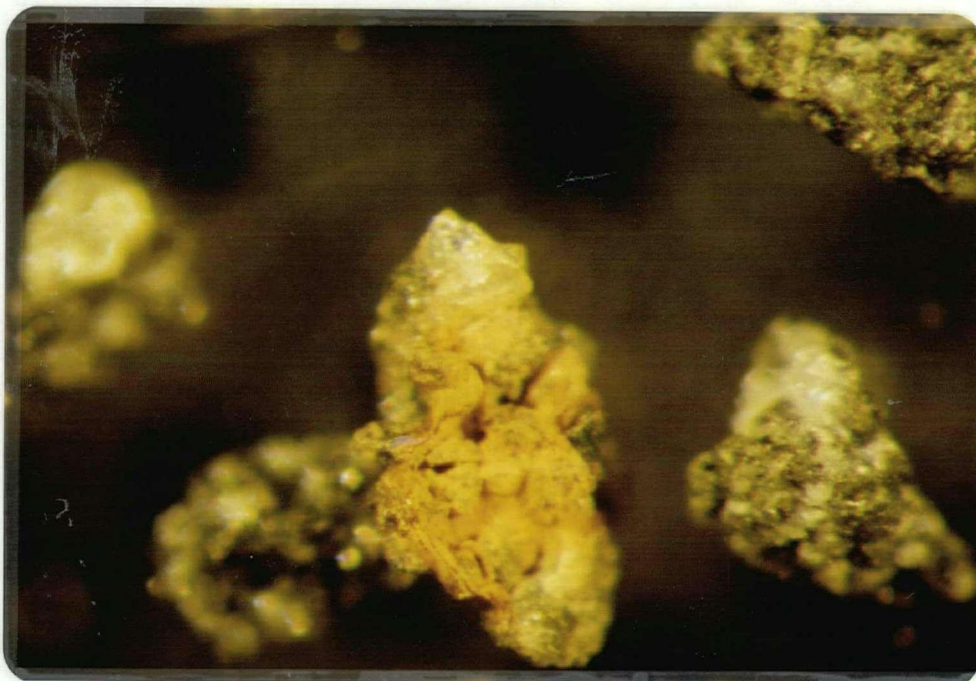
Figure 38: Basaltic grain leached in H_2O for 11 weeks.
Note Fe oxidation in center of photograph
200 x magnification
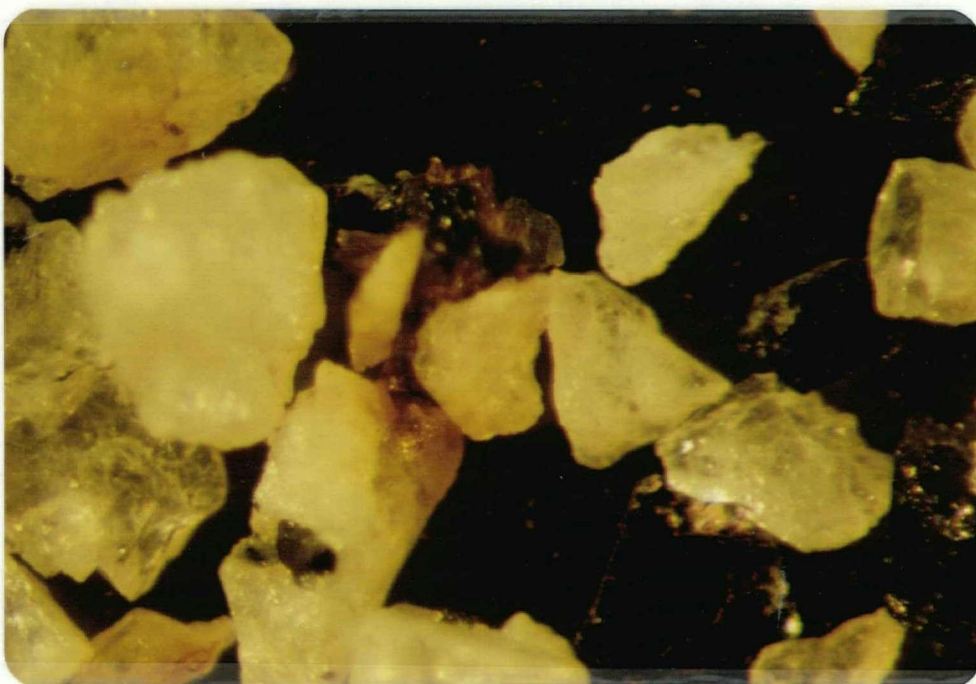
Figure 39: Granodioritic grains leached in H_2O for 11 weeks.
Note Fe oxidation in centre of photograph
200 x magnification

citric and oxalic acid have a much higher extraction capacity for Fe and Al than do acetic acid, HCl and H_2O. These higher than expected values may be due to an error in measurement due to the presence of colloidal particles as discussed earlier. Also, much of the Fe and Al extracted by the chelating acids may be tied up in organic association either in solution as with citric acid or in precipitate as with oxalic acid. On the other hand, any Fe or Al, however little, extracted from non-chelating agents may have adsorbed and oxidized very quickly onto the mineral surface. The photograph in Figure 38 shows areas of dark orange where Fe has oxidized onto the surface of a basaltic grain leached in water.

7. Fe_{OX}: Fe_{CBD} Ratios

The graphic display of data showing the percentage extractable Fe reveals immediately a surprising relationship between Fe_{OX} and Fe_{CBD} levels, for both basalt and granodiorite samples in all 5 leaching treatments: Fe_{OX} levels were higher than Fe_{CBD} levels in the majority of samples. Since CBD removes both poorly and well crystallized Fe oxides, Fe_{OX}:Fe_{CBD} ratios normally should not exceed unity, Data from Mckeague and Day (1966), and Singleton (1978), have revaled typical ranges for the main types of soil horizons between 0 and 1.

Several factors could account for the ratio of Fe_{OX}:Fe_{CBD} exceeding unity in the batch and column weathering experiments. First of all, Fe_{OX}:Fe_{CBD} ratios may be greater

than unity due to the presence of crystalline magnetite. Baril and Bitton (1969), and McKeague et al, (1971a), have shown that ammonium oxalate solution releases Fe from magnetite which is Known to be only sparingly soluble in CBD (Gamble and Daniels, 1972). Results of more recent work by Chao and Zhou (1983), confirmed the observations made by earlier investigators that oxalic acid is particularly effective in bringing magnetites into solution. The inclusion, therefore, of detrital magnetites with amorphous iron oxides could confound the use and interpretation of data on active iron ratios. The presence of magnetite in both basalt and granodiorite was confirmed by XRD analyses.

Secondly, CBD dissolves Fe from fine particles of labile silicates but fails to dissolve completely some crystalline iron oxides particles coarser than approximately 50 um (Pawluk, 1972; McKeague and Schuppli, 1985). For this reason Schwertmann and Taylor suggest that coarse samples may require several treatments of CBD extractant. Considering that samples were leached from crushed basalt and granodiorite whose particle size lay between 100 and 500um it is possible that Fe_{CBD} levels were underestimated.

Thirdly, acid ammonium oxalate can dissolve significant amounts of Fe from organic complexes (McKeague, 1967; McKeague et al. 1971; Schwertmann, 1973). There is, therefore, a tendency for the $Fe_{OX}:Fe_{CBD}$ ratio to increase with increasing C content (Campbell and Schwertmann, 1984). Research has shown

that oxalate-extractable Fe and Al commonly exceed CBD-extractable Fe and Al in B horizons of Orthic Humic Podzols (McKeague and Day, 1966; Singleton, 1978). Accordingly, the presence of metal organic complexes could have weighted the results, in the batch and column experiments, for those samples leached by organic acids in contrast to those samples leached by HCl and H_2O.

A fourth factor to consider is that of time. Aging as an important parameter in the crystallization of sesquioxide compounds has been established by Hsu and Ragone (1972). In a chronological sequence, amorphous forms precede those of more long-range order, and could have accounted, in this experiment, for a large component of the sesquioxides which formed.

In addition, as with other differential dissolution methods used in soils work, both oxalate and CBD methods are largely emperical. In fact, they cannot be expected to separate sharply Fe in iron oxides from Fe in other combinations and particularly amorphous from crystalline forms because they are all part of a continuum. The results, therefore, may not have given a "true " indication of the relative amounts of each Fe form.

Finally, as mentioned previously, the introduction of colloidal material into solution may have overestimated the atomic absorption spectrophotometric readings. It is

recommended therefore that extractants be passed through a 20 um filter paper prior to AA analyses.

8. Additional Notes

a) Sesquioxide formation after 4 weeks of leaching was as high or higher than after 11 weeks of leaching for most samples, basalt and granodiorite, for both column and batch experiments. According to Schwertmann (1973), Fe on freshly ground and exposed surfaces is more easily dissolved than from weathered surfaces commonly present in soils. It appears that the rate of formation decreased with time as the surface became coated with the oxides.

b) It is generally acknowledged that the addition of sesquioxide coatings to a mineral particle will alter the surface charge of that particle. The pH dependent charge developed largely by amorphous coatings may reduce the CEC of the underlying permanent negatively charged surface (Hendershot and Lavkulich, 1983). This phenomena was not apparent in CEC data for basalt and granodiorite which showed a steady increase up to 11 weeks.

c) In the batch and column dissolution studies, granodiorite and basalt of heterogenous mineral composition were leached in solutions whose chemical make-up varied as weathering

proceeded. The formation of amorphous precipitates in this environment could not be modelled in a simple fashion. As pointed out by Holden (1983), the bulk compositions of precipitates formed in simulated mineral dissolution experiments are very complex and continually evolve during the course of a reaction as pH and redox conditions shift. The presence or absence of salt and other nucleation sites on the mineral surface may be important in initiating precipitation and the number of such sites is not fixed over time. Competition between ions for reactive sites or in other words the competition between Lewis acids for Lewis bases and vice versa, further complicates any attempt to model precipitate formation from a very mixed ionic solution. In fact, previous studies of alumino-silicate precipitation which have been used to suggest that precipitates should form with fixed compositions, (Kittrick, 1970;Bussenburg, 1978), or with compositions which are determined solely by the pH of the surrounding medium (Paces, 1978) have been thrown into question in light of Holdren's more recent work. In this current study, further analytical work is needed to first of all determine quantitatively the precise chemical make-up of the precipitates including the molar ratios of each element and organic ligand. Only then can further steps be taken to the solubility product constant which, in addition to the ion activity product (IAP) can be used to formulate the Saturation Index for each compound. This is not such an easy task as

reliable aqueous activities of ions must first be calculated. This involves corrections for ion pairing and complexing as well as activity-coefficient calculations. These corrections can be very difficult, requiring the use of a large computor system.

SUMMARY AND CONCLUSIONS

Two simulated weathering experiments, namely batch (shaking) and column (gravity) were designed to study the dissolution of crushed basalt and granodiorite in the presence of 3 organic and 2 inorganic acids. Chemical and morphological changes in the mineral residues after 4 weeks and 11 weeks of weathering were examined. Changes in both leachate chemistry and rates of dissolution, as revealed by solution analyses were also noted, as well as the formation of precipitation products.

1. Chelation and Stability Constants

First of all, solution analyses show that the dissolution of ions from granodiorite, by the leaching treatment shown in parentheses, decreased in the following order:

Fe(OX) > Al(OX) ~ Si(OX) > Ca(CIT) ~ Mg(OX) ~ K(OX) > Na(OX)

Dissolution of ions from basalt decreased in the following order:

Fe(CIT) > Si(CIT) > Mg(CIT) > Ca(CIT) > Al(OX, ACETIC) > Na(OX) > K(HCl)

In the weathered granodioritic solutions, statistical analysis revealed significant difference, at the 95% confidence level between citric and oxalic acid solutions as well as between the chelating and non-chelating acids for multi-valent solubilized ions. Also levels of solubilized

ions in water were significantly lower than for all other treatments. There was no significant difference between acetic acid HCl treatments for dissolved Ca, Mg, Na, K and Fe.

In the weathered basaltic solutions, there was at the 95% confidence level, significant difference between citric and oxalic acid solutions for Ca, Mg, Fe, Al and Si. In addition significant differences occurred between all 5 leachates for dissolved Fe and Mg. Also there were significant differences between oxalic and acetic acid solutions for dissolved Ca, between oxalic, acetic acid and HCl for dissolved Al and between acetic acid and HCl for dissolved Si. As was the case with granodiorite levels of solubilized ions in water were significantly lower than for all other treatments. There were however insignificant differences for dissolved Na amongst all leachates except water. The same held true for K^+ except in the case of granodiorite where citric and oxalic acid leachates revealed high levels of solubilized K.

Oxalic acid effectively outcompeted citric acid in the weathering of granodiorite in spite of having lower stability constants for most ions. This result was somewhat surprising as many weathering experiments reported in the literature, point to a correlation between the efficacy of an organic acid in extracting ions from a mineral to its stability constant with that ion. A closer inspection of all available data from both batch and column experiments showed that for the two chelating acids, the ability of the acid to extract an ion

ultimately depend on solution pH and on the pKa's of the acids. Formation curves were used in estimating the degree of dissociation (and percentage of each ligand formed) for the pH of the leaching solution. It was shown that at pH of approximately 2.2, citric acid (pK_1 = 3.14) was undissociated. In other words the H^+ ion could outcompete any metal cation from the mineral surfaces for Lewis base citrate ligand. Oxalic acid (pK_1 = 1.23), on the other hand, was approximately 80% dissociated at pH < 2 and the citrate anion was available to form chelates. It is concluded, therefore, that acid dissociation constants may be more important than stability constants per se in determining the relative dissolution power of an organic acid at a particular pH.

Evidence from solution AA analyses and XRD indicated that the effectiveness of oxalic acid in weathering granodiorite might also be explained on the basis of ion competition in solution for ligand sites, geometry and oxidation state of ions in the parent material as well as particle size and active surface area of the parent material.

It is concluded that for any particular weathering environment both the physical and chemical components of the mineral(s) and the chemical make-up of the solution must be scrutinized in order to explain dissolution in the presence of organic acids.

2. Chelation and Alkali Metals

There was no conclusive evidence to indicate that chelation of K^+ or Na^+ took place in any of the experiments. In fact, in the weathering of basalt, HCl extracted more K into solution than did any other leaching treatment. The ability of citric and oxalic acid to extract the highest levels of K from granodiorite was, on the basis of SEM, EDX and AA solution analyses, attributed to the breakdown of biotite initiated by chelation of organic acid to Mg and Fe, with subsequent release of K from the interlayers.

3. Chelation vs. Acid Dissolution

Molar oxide ratios, mass balance calculations, XRF and EDX of unweathered and weathered rock as well as AA solution analyses showed that strongly chelating acids such as citric and oxalic acid greatly outcompeted acetic acid and HCl of similar pH for multi-valent cations. This was particularly evident for Al, Fe and Si whose concentrations in solution were many-fold higher than concentrations in water in equilibrium with the amorphous oxides. This is attributed to the ability of citric and oxalic acids to complex metals and therefore increase the domain of weathering. However, the extent of complexation for any given chelate is also determined by pH. As noted above, depending on the pH of the solution and pKa of the chelating acid both acid attack of a mineral surface through ion exchange and complexation between

mineral and anion may occur concurrently. It is rather simplistic to rely on the use of complexation index as introduced by Razzaghi-Karimi and Robert (1979) whereby values greater than 1 for R

$$R = \frac{\text{Amount of element released by organic acid}}{\text{Amount of element released by HCl}}$$

indicate chelation. There is a need to determine more quantitatively the extent of dissociation of the chelating acid and therefore the extent to which chelation competes with or is superimposed on acidolysis.

4. Kinetics of Dissolution

A study of kinetics of weathering of both basalt and granodiorite showed that oxalic and citric acid dissolution curves were characterized by initially increasing rates followed by declining rates which approached steady state towards the eleventh week of the experiment. Electron microscopic (SEM) evidence of hyperfine particles adhering to mineral surfaces supported the theory that rapid initial rates of weathering were due to the breakdown of these very small artifacts of grinding. Evidence of a leached surface layer, from EDX analyses of basalt and granodiorite, might explain the approach towards steady state kinetics after 11 weeks of dissolution. This cation depleted layer with its imbalance of charge and structural strain may have broken down into solution exposing a fresh surface to repeat the cycle of

events. The very high levels of Si brought into solution by the dissolution of basalt by oxalic and citric acid provide, indirectly, additional evidence to support this theory. Finally the build-up of ions in solution as well as precipitates, is characteristic of a closed weathering system approaching equilibrium with the solid state whereby rates of dissolution decline.

Non-chelating acids such as acetic acid, HCl and H_2O revealed dissolution curves that were approximately constant (steady state) throughout the 11 week weathering experiments. This is characteristic of an open system in which the solution is greatly undersaturated with respect to the solid phase.

5. Incongruent Dissolution

Incongruent dissolution was observed for granodiorite and basalt weathered by all 5 leaching treatments. Incongruent dissolution was noted in particular for citric acid treatments as evidenced by the following:

a)   variable but predominantly declining rates of dissolution (AA solution analysis)

b)   changes in molar ratios of elements from unweathered to weathered sample (from XRF data)

c)   mass balance calculations showing preferential leaching of certain elements by chelating acids (from AA solution analyses)

d)   build up of precipitated reaction products (XRD,

SEM, EDX, XRF and extractable Fe, Al, Si analyses)

e)   leached mineral surface layers with predominantly Si residue (EDX)

f)   etch pits and other discontinuities on mineral surfaces (SEM)

6. The Formation of Precipitation Products

Citric acid was less effective than oxalic acid in forming precipitates from granodiorite. However, EDX analysis of an amorphous (possibly organo) precipitate which did form showed that it consisted of primarily Fe. EDX analysis of a second morphological distinct type of amorphous (likely inorganic) coating indicated predominantly Si and Fe in a 1:1 ratio. Although citric acid was able to extract greater amounts of Fe from basalt than granodiorite and even exceed all extraction treatments no inorganic or organic-amorphous precipitates were detected. In fact extractable Fe, Al and $Si_{(CIT)(PYRO)(OX)}$ were the lowest of all 5 leaching treatments. It is concluded that the Fe extracted remained in complexed or soluble form due to the higher pH (3-5) of the basaltic solution. At the lower pH (2-3) of the granodiorite solution the undissociated citric acid was unable to form Fe-citrate chelates.

What appeared under the scanning electron microscope to be an amorphous precipitate formed from the leaching of granodiorite with oxalic acid. EDX analysis indicated that

it consisted primarily of Si and Fe in a 1:1 ratio. Possible inorganic and organic components of this precipitate were discussed in some detail. An amorphous precipitate also formed from the leaching of basalt with oxalic acid which consisted primarily of Mg and Fe in a 1:1 ratio. Under the experimental conditions given with both batch and column procedures, oxalic acid was more effective than citric acid in promoting the early stages of sesquioxide development.

The dissolution of Fe, Al and Si from basalt and granodiorite by non-chelating agents such as acetic acid, HCl and H_2O was significantly lower (within 95% confidence limits). XRD analysis pointed to the possibility of ferrihydrite having formed on the surfaces of granodiorite, leached with acetic acid, HCl and H_2O.

Finally it was noted that Fe_{OX}/Fe_{CBD} ratios exceeded unity in both batch and column experiments for most samples. Factors which may have contributed to the high Fe_{ox} levels include: a) the presence of magnetite in the parent rocks b) particle-size of sample   c) the presence of organic precipitates d) limited aging period   e) overlap of crystalline and amorphous forms detected by analytical procedures   f) contribution of colloidal matter to the measurements of dissolved elements.

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Appendix A_1:   Extractable Fe and Al from Weathered Basalt and Granodiorite

Extractable Fe and Al

Granodiorite Column – 4 weeks
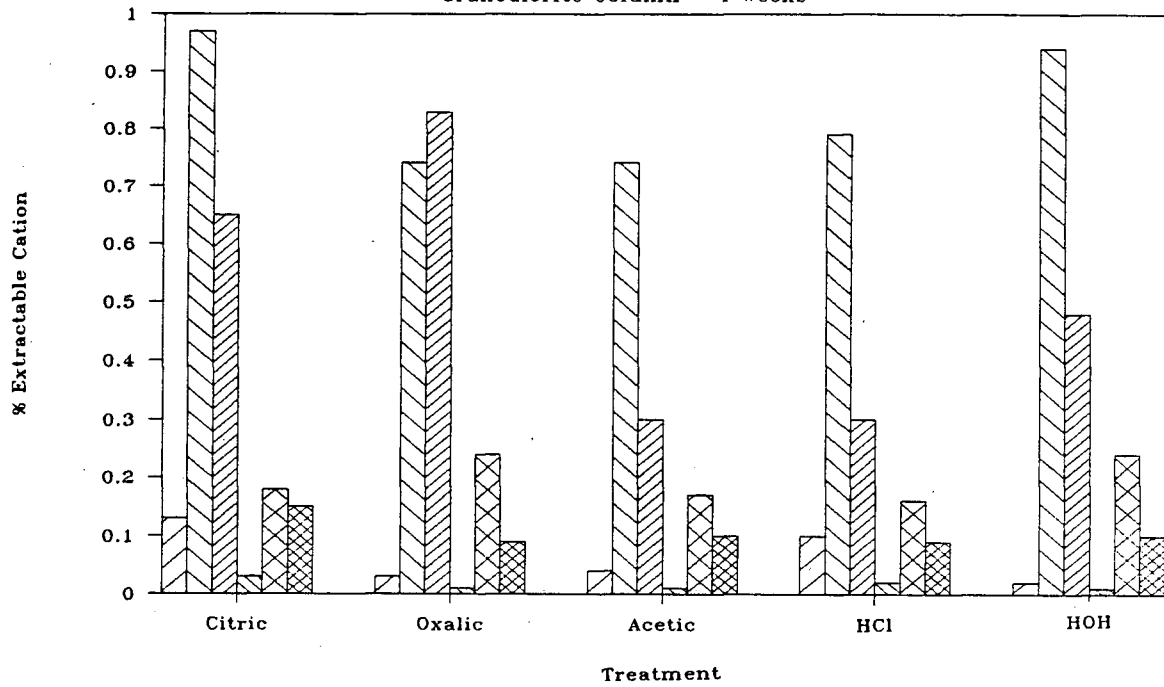
Extractable Fe and Al

Basalt – Column – 4 Weeks

Pyro Fe   Ox Fe   CBD Fe

Pyro Al   Ox Al   CBD Al
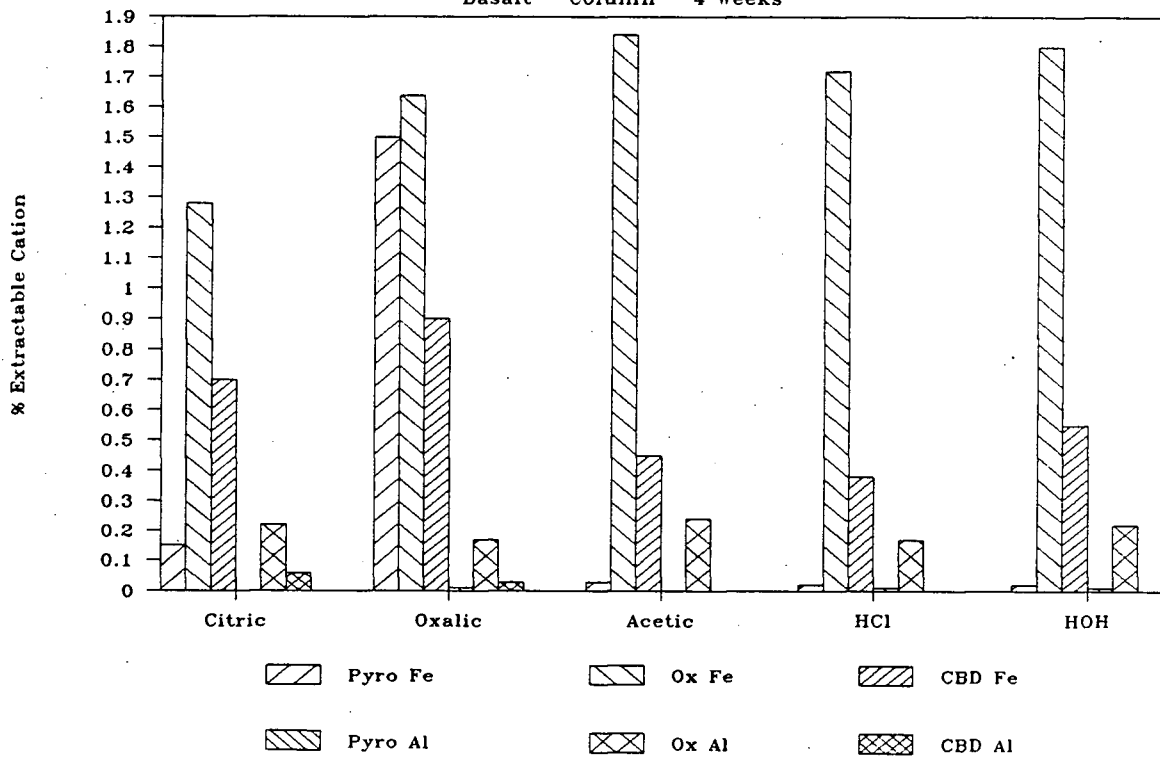
Extractable Fe and Al

Granodiorite – Column – 11 weeks
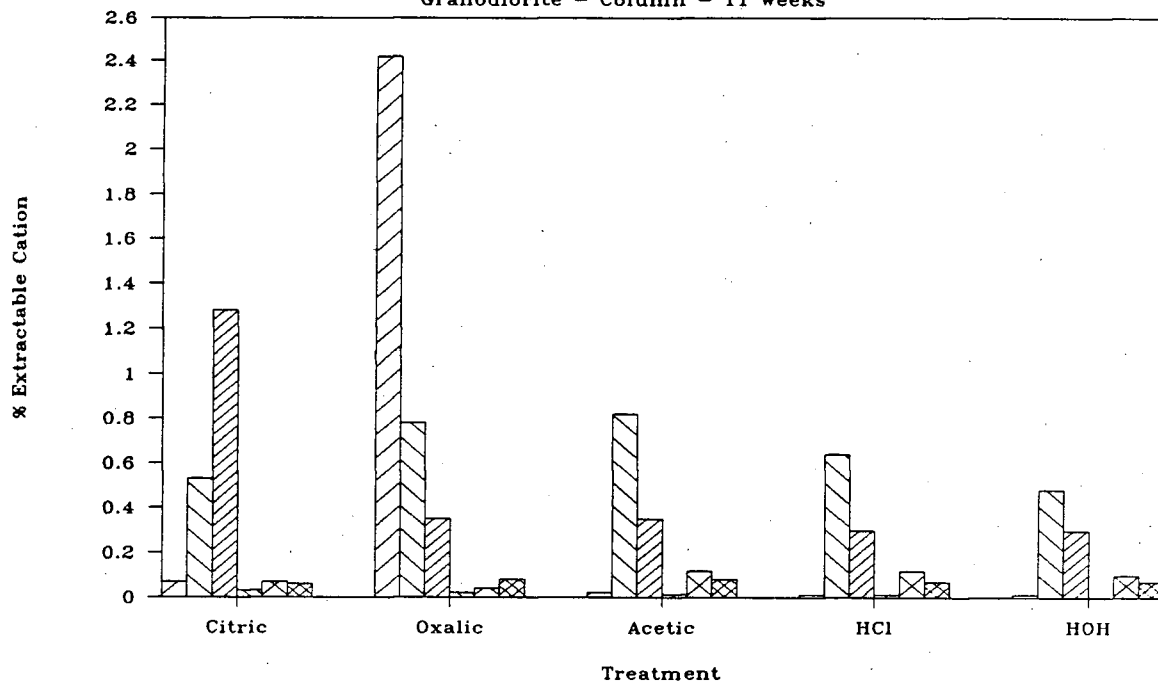
Extractable Fe and Al

Basalt – Column – 11 weeks
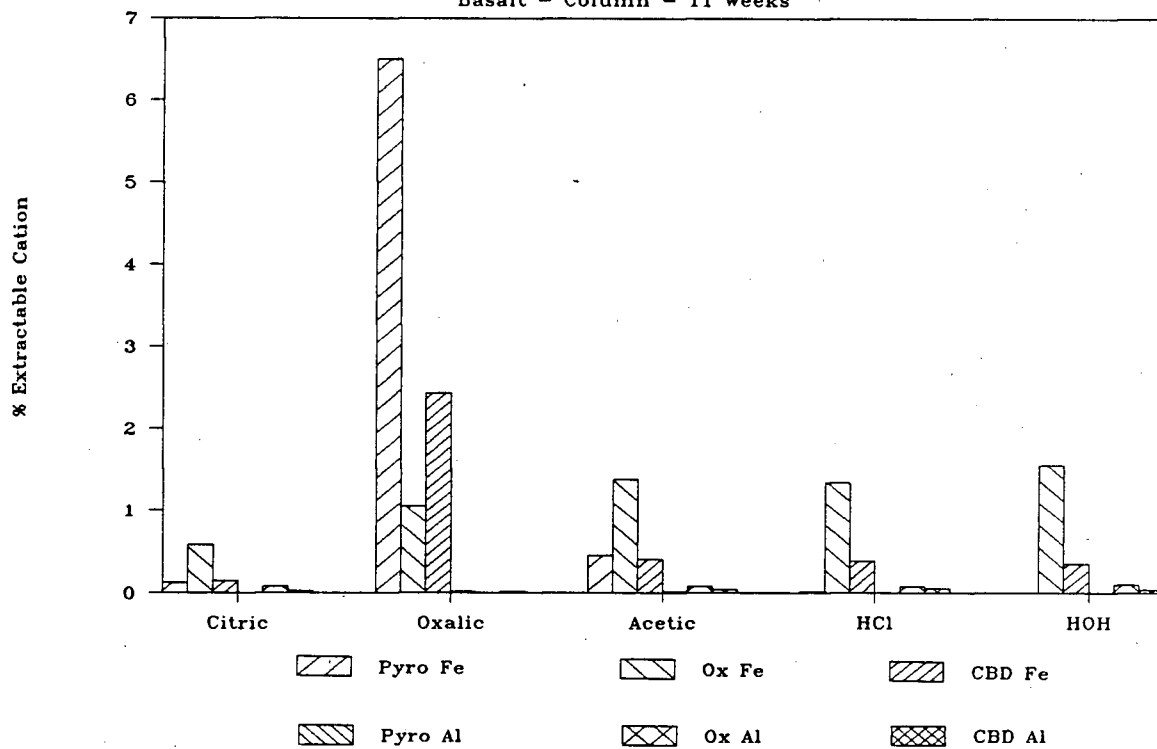
Extractable Fe and Al

Granodiorite – Batch – 4 weeks
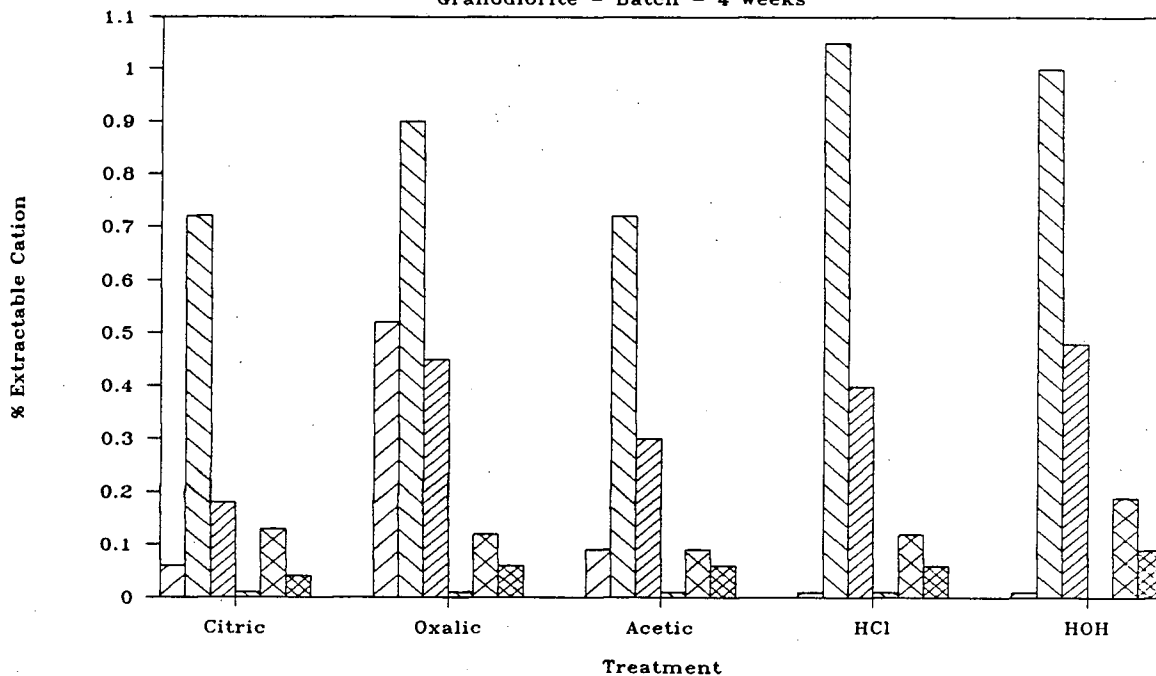
Extractable Fe and Al

Basalt – Batch – 4 weeks

Legend: Pyro Fe, Ox Fe, CBD Fe, Pyro Al, Ox Al, CBD Al

Extractable Fe and Al

Granodiorite — Batch — 11 weeks
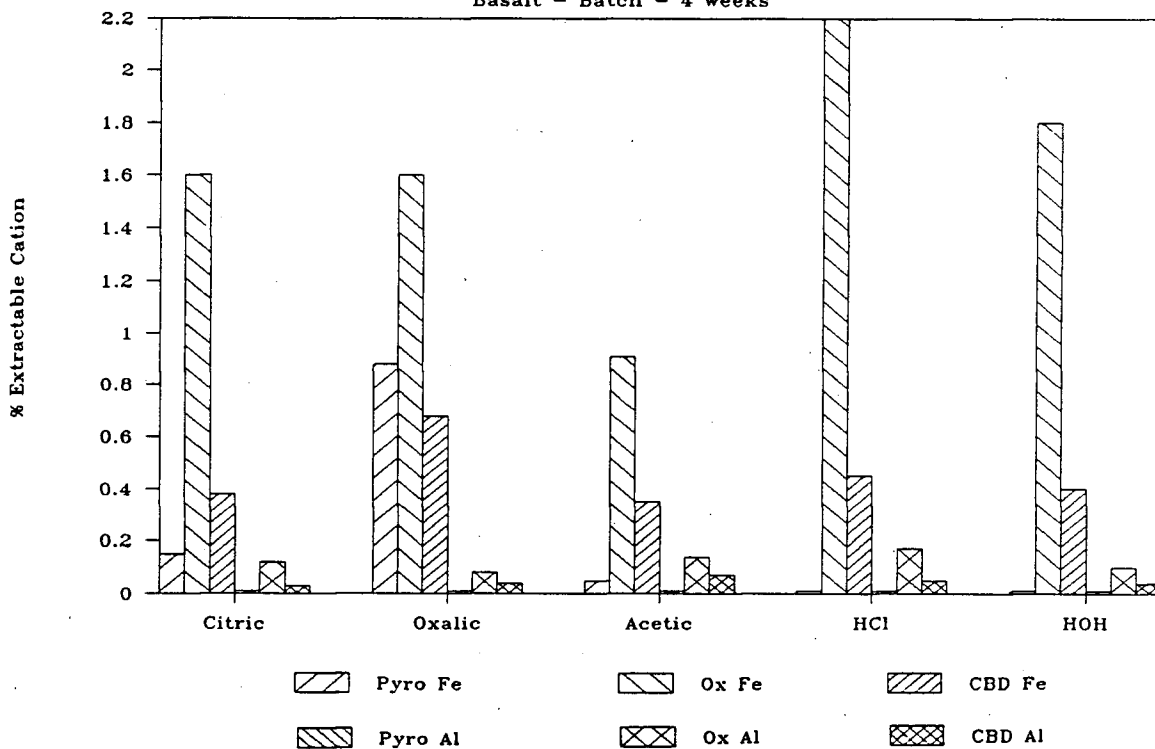
Extractable Fe and Al
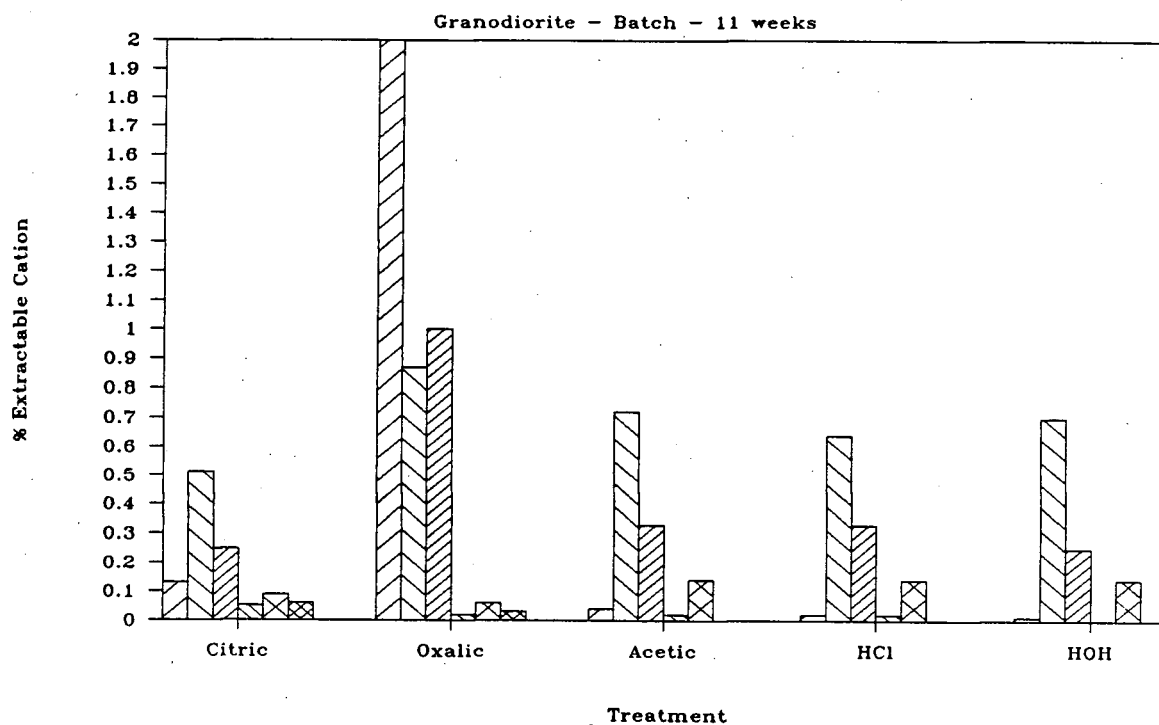
Basalt — Batch — 11 weeks
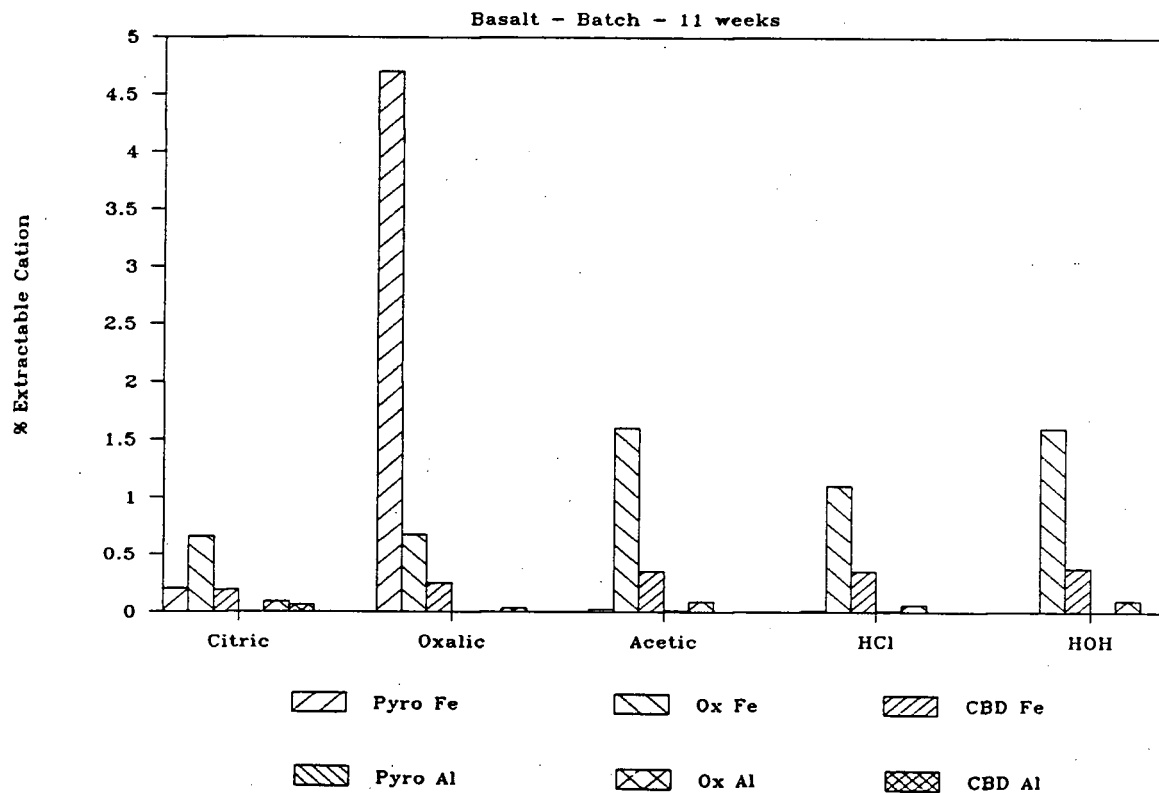
Extractable Fe and Al.

<.1mm Granodiorite − Batch − 11 weeks

Treatment
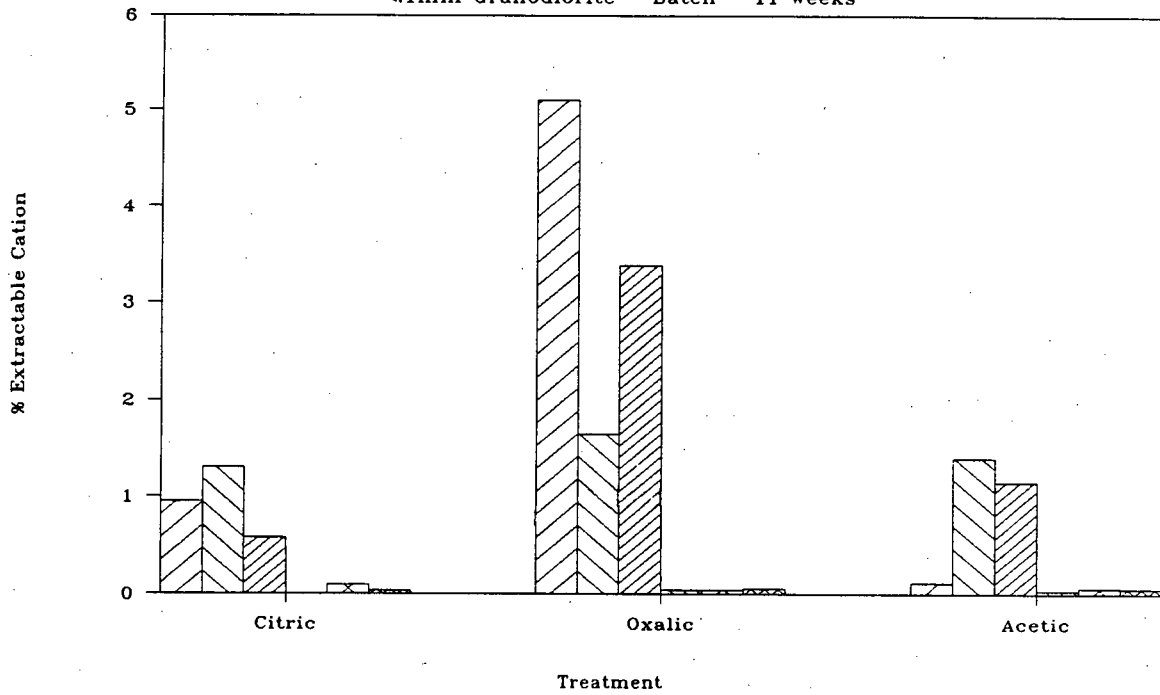
Extractable Fe and Al

<.1mm Basalt Batch−11 weeks

Legend:
- Pyro Fe
- Ox Fe
- CBD Fe
- Pyro Al
- Ox Al
- CBD Al
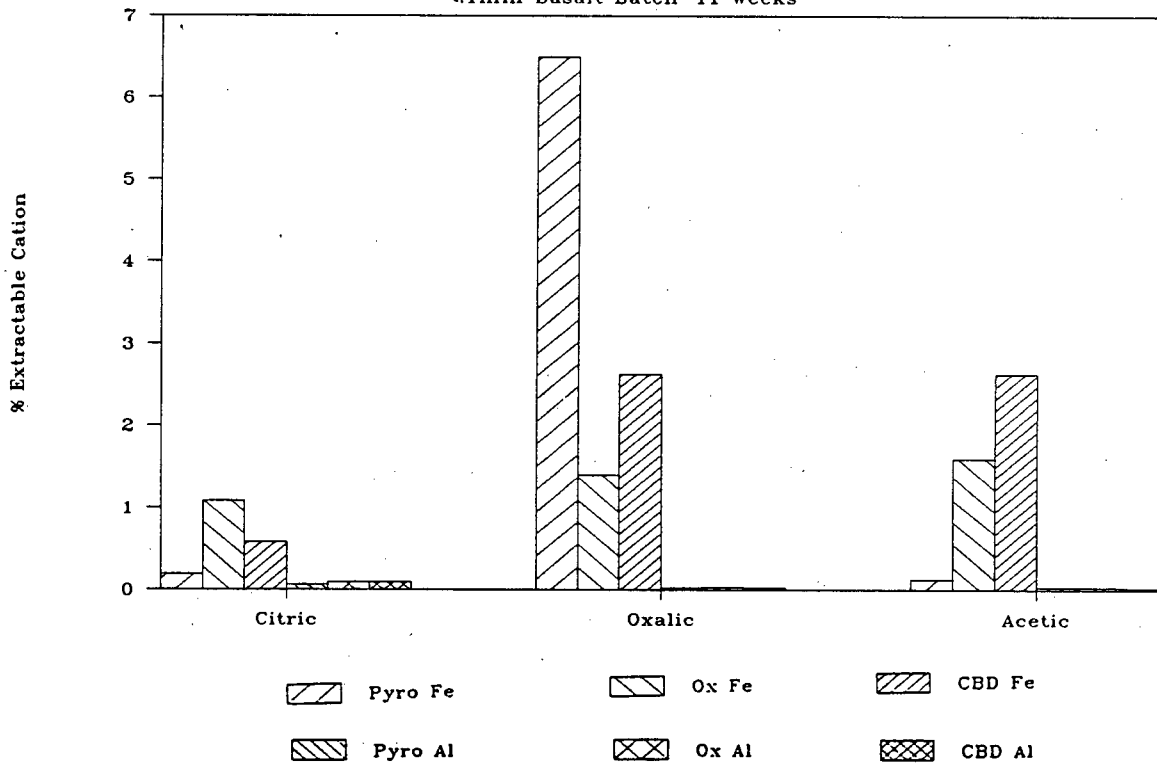
Extractable Fe and Al

Granodiorite Crusts– 11 weeks

Basalt Crusts–11 Weeks

Legend: Pyro Fe, Pyro Al, Ox Fe, Ox Al, CBD Fe, CBD Al
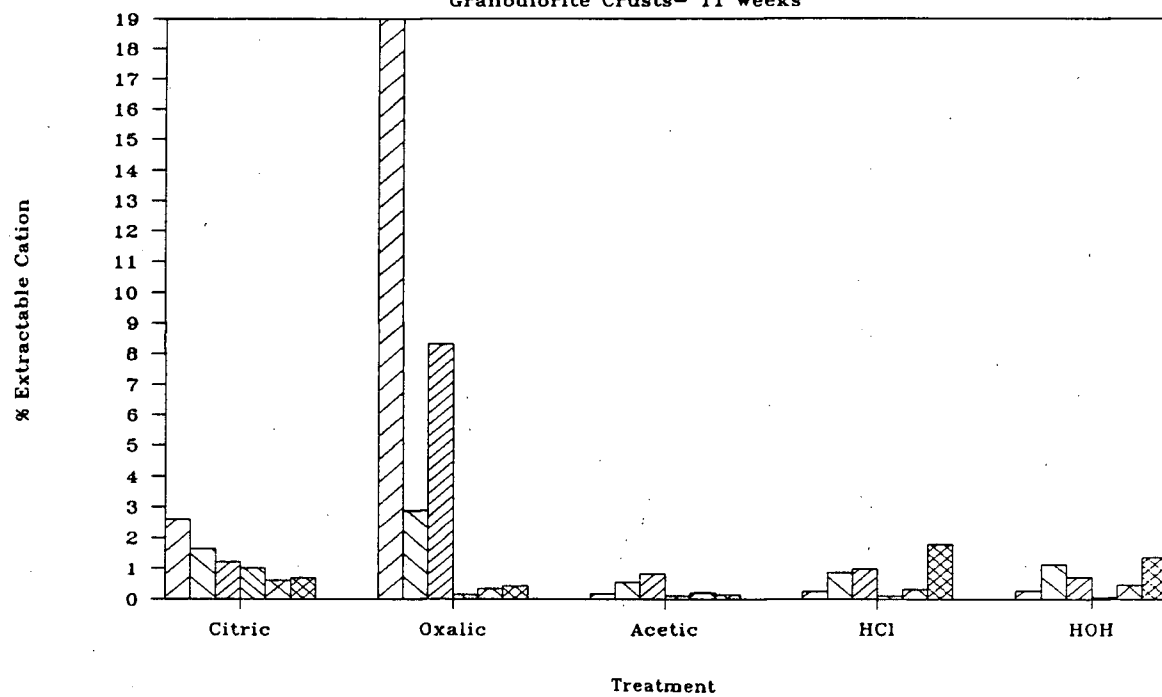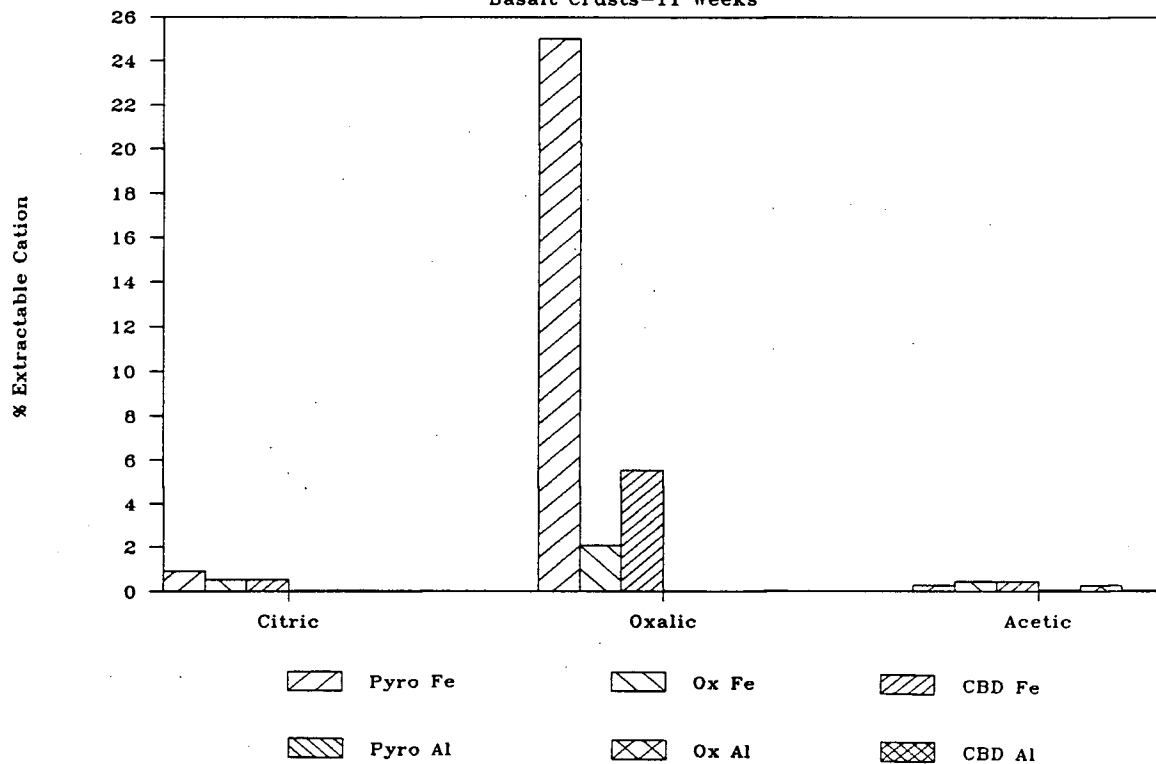
Appendix A$_2$:   Tables of Data from Extractable Fe and Al and Si
                   from Weathered Basalt and Granodiorite

Extractable Iron, Aluminum and Silicon (% by wt.)

PARENT MATERIAL	PYROPHOSPHATE			OXALATE			DITHIONATE		
	Fe	Al	Si	Fe	Al	Si	Fe	Al	Si
Granodiorite A	0.00	0.00	0.00	0.32	0.08	0.00	0.28	0.01	0.00
Granodiorite B	0.00	0.00	0.00	1.32	0.05	0.00	1.38	0.01	0.00
Basalt A	0.00	0.00	0.00	1.31	0.07	0.52	0.18	0.01	0.00
Basalt B	0.00	0.00	0.00	1.92	0.14	0.84	0.61	0.01	0.00
Hawaiin Basalt	0.00	0.00	0.00	0.77	0.24	0.36	0.25	0.00	0.00

*A:.1mm-.5mm
*B:<.1mm

EXPERIMENT 1: COLUMN STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	PYROPHOSPHATE			OXALATE			DITHIONATE		
		Fe	Al	Si	Fe	Al	Si	Fe	Al	Si
GrDio. A	Citric	0.13	0.03	0.11	0.97	0.18	0.00	0.65	0.15	0.20
GrDio. A	Oxalic	0.03	0.01	0.19	0.74	0.24	0.24	0.83	0.09	0.18
GrDio. A	Acetic	0.04	0.01	0.05	0.74	0.17	0.12	0.30	0.10	0.18
GrDio. A	HCl	0.10	0.02	0.07	0.79	0.16	0.12	0.30	0.09	0.10
GrDio. A	HOH	0.02	0.01	0.06	0.94	0.24	0.20	0.48	0.10	0.18
Basalt A	Citric	0.15	0.00	0.30	1.28	0.22	0.52	0.70	0.04	0.28
Basalt A	Oxalic	1.50	0.01	0.32	1.64	0.17	0.92	0.90	0.06	0.25
Basalt A	Acetic	0.03	0.00	0.25	1.84	0.24	1.32	0.45	0.06	0.25
Basalt A	HCl	0.02	0.01	0.15	1.72	0.17	1.00	0.38	0.05	0.25
Basalt A	HOH	0.02	0.01	0.10	1.80	0.22	1.08	0.55	0.05	0.20

EXPERIMENT 2: BATCH STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	PYROPHOSPHATE			OXALATE			DITHIONATE		
		Fe	Al	Si	Fe	Al	Si	Fe	Al	Si
GrDio. A	Citric	0.06	0.01	0.26	0.72	0.13	0.00	0.18	0.04	0.10
GrDio. A	Oxalic	0.52	0.01	0.24	0.90	0.12	0.00	0.45	0.06	0.13
GrDio. A	Acetic	0.09	0.01	0.06	0.72	0.09	0.00	0.30	0.06	0.10
GrDio. A	HCl	0.01	0.01	0.00	1.05	0.12	0.00	0.40	0.06	0.13
GrDio. A	HOH	0.01	0.00	0.00	1.00	0.19	0.24	0.48	0.09	0.10
Basalt A	Citric	0.15	0.01	0.54	1.60	0.12	0.72	0.38	0.03	0.25
Basalt A	Oxalic	0.88	0.01	0.25	1.60	0.08	0.60	0.68	0.04	0.18
Basalt A	Acetic	0.05	0.01	0.07	0.91	0.14	0.00	0.35	0.07	0.10
Basalt A	HCl	0.01	0.01	0.16	2.20	0.17	0.92	0.45	0.05	0.20
Basalt A	HOH	0.01	0.01	0.26	1.80	0.10	0.76	0.40	0.04	0.15

EXPERIMENT 3: COLUMN STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	PYROPHOSPHATE			OXALATE			DITHIONATE		
		Fe	Al	Si	Fe	Al	Si	Fe	Al	Si
GrDio. A	Citric	0.07	0.03	0.18	0.53	0.07	0.00	1.28	0.06	0.18
GrDio. A	Oxalic	2.42	0.02	0.37	0.78	0.04	0.00	0.35	0.08	0.10
GrDio. A	Acetic	0.02	0.01	0.04	0.82	0.12	0.00	0.35	0.08	0.10
GrDio. A	HCl	0.01	0.01	0.00	0.64	0.12	0.00	0.30	0.07	0.08
GrDio. A	HOH	0.01	0.00	0.00	0.48	0.10	0.00	0.30	0.07	0.08
Basalt A	Citric	0.12	0.00	0.47	0.58	0.08	0.00	0.15	0.02	0.18
Basalt A	Oxalic	6.50	0.01	0.45	1.05	0.00	0.00	2.43	0.01	0.20
Basalt A	Acetic	0.45	0.01	0.06	1.39	0.08	0.52	0.40	0.04	0.13
Basalt A	HCl	0.01	0.00	0.04	1.35	0.08	0.52	0.38	0.05	0.13
Basalt A	HOH	0.00	0.00	0.00	1.56	0.10	0.60	0.35	0.04	0.13

EXPERIMENT 4: BATCH STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	PYROPHOSPHATE			OXALATE			DITHIONATE		
		Fe	Al	Si	Fe	Al	Si	Fe	Al	Si
GrDio.A	Citric	0.13	0.05	0.18	0.51	0.09	0.00	0.25	0.07	0.15
GrDio.A	Oxalic	2.00	0.02	0.29	0.87	0.06	0.00	1.00	0.06	0.23
GrDio.A	Acetic	0.04	0.02	0.00	0.72	0.14	0.00	0.33	0.08	0.08
GrDio.A	HCl	0.02	0.02	0.00	0.64	0.14	0.00	0.33	0.08	0.08
GrDio.A	HOH	0.01	0.00	0.00	0.70	0.14	0.00	0.25	0.08	0.05
Basalt A	Citric	0.20	0.00	0.35	0.66	0.09	0.12	0.19	0.02	0.20
Basalt A	Oxalic	4.70	0.00	0.35	0.68	0.00	0.00	0.25	0.05	0.20
Basalt A	Acetic	0.02	0.01	0.00	1.60	0.09	0.68	0.35	0.03	0.13
Basalt A	HCl	0.01	0.01	0.00	1.10	0.06	0.44	0.35	0.04	0.10
Basalt A	HOH	0.00	0.00	0.00	1.60	0.10	0.68	0.38	0.04	0.13
Hawaiin	Citric	0.32	0.01	0.36	1.09	0.23	0.16	0.60	0.06	0.25
Hawaiin	Oxalic	3.00	0.01	0.38	0.88	0.06	0.00	1.43	0.03	0.20

EXPERIMENT 5: BATCH STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	PYROPHOSPHATE			OXALATE			DITHIONATE		
		Fe	AL	Si	Fe	Al	Si	Fe	Al	Si
GrDio.B	Citric	0.95	0.00	0.89	1.30	0.09	0.28	0.58	0.03	0.25
GrDio.B	Oxalic	5.10	0.04	0.43	1.64	0.04	0.00	3.38	0.05	0.23
GrDio.B	Acetic	0.11	0.03	0.07	1.40	0.06	0.00	1.15	0.05	0.08
Basalt B	Citric	0.19	0.06	0.24	1.09	0.09	0.00	0.58	0.09	0.18
Basalt B	Oxalic	6.50	0.02	0.62	1.40	0.03	0.20	2.63	0.02	0.23
Basalt B	Acetic	0.12	0.03	0.08	1.60	0.03	0.28	2.63	0.02	0.20

EXPERIMENT 6: BATCH-11 WEEKS
Analyses of Crust Formations

PARENT MATERIAL	TREATMENT	PYROPHOSPHATE			OXALATE			DITHIONATE		
		Fe	Al	Si	Fe	Al	Si	Fe	Al	Si
GrDio.A	Citric	2.60	1.00	0.70	1.64	0.62	0.00	1.23	0.70	0.28
GrDio.A	Oxalic	19.00	0.14	0.50	2.88	0.33	0.12	8.30	0.42	0.25
GrDio.A	Acetic	0.16	0.11	0.08	0.54	0.20	0.00	0.83	0.14	0.15
GrDio.A	HCl	0.26	0.10	0.07	0.88	0.31	0.20	0.99	1.80	0.19
GrDio.A	HOH	0.28	0.06	0.08	1.14	0.46	0.32	0.72	1.38	0.21
Basalt A	Citric	0.90	0.01	0.61	0.53	0.06	0.16	0.53	0.02	0.25
Basalt A	Oxalic	25.00	0.01	0.54	2.04	0.00	0.24	5.53	0.01	0.33
Basalt A	Acetic	0.25	0.05	0.07	0.42	0.25	0.80	0.43	0.04	0.13
Basalt A	HCl	x	x	x	x	x	x	x	x	x
Basalt A	HOH	x	x	x	x	x	x	x	x	x
Hawaiin	Citric	2.70	0.04	0.86	1.16	0.10	0.24	1.03	0.08	0.30
Hawaiin	Oxalic	25.20	0.03	0.70	2.04	0.00	0.24	4.10	0.05	0.43
GrDio.B	Citric	5.60	0.03	1.52	1.48	0.05	0.28	2.08	0.04	0.45
GrDio.B	Oxalic	31.00	0.03	0.53	2.52	0.07	0.00	11.55	0.09	0.25
GrDio.B	Acetic	0.61	0.11	0.08	8.20	0.42	0.60	0.88	0.05	0.08
Basalt B	Citric	1.38	0.70	0.71	0.92	0.44	0.16	0.90	0.48	0.23
Basalt B	Oxalic	21.00	0.02	1.40	3.20	0.00	0.12	2.53	0.02	0.28
Basalt B	Acetic	0.38	0.03	0.20	2.08	0.24	1.12	0.85	0.07	0.13

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Appendix B: Solution Analyses of 5 Leaching Treatments
                Granodiorite and Basalt Column Study

                *Data is average of 3 replicate samples
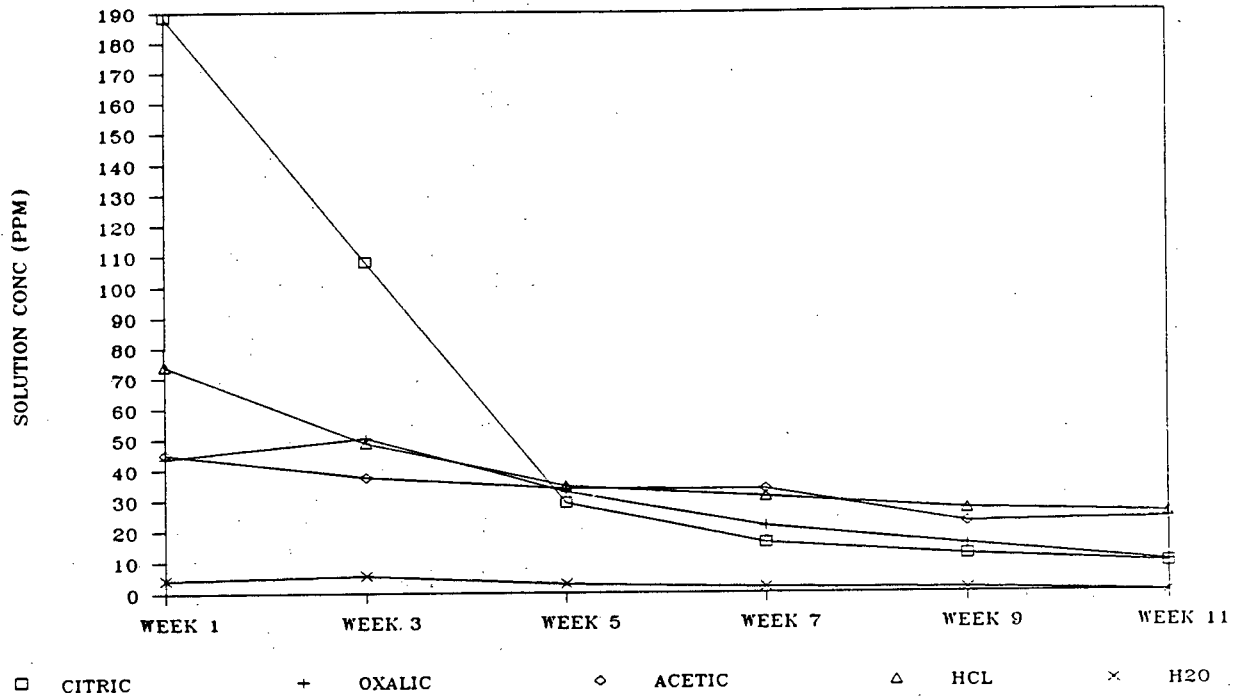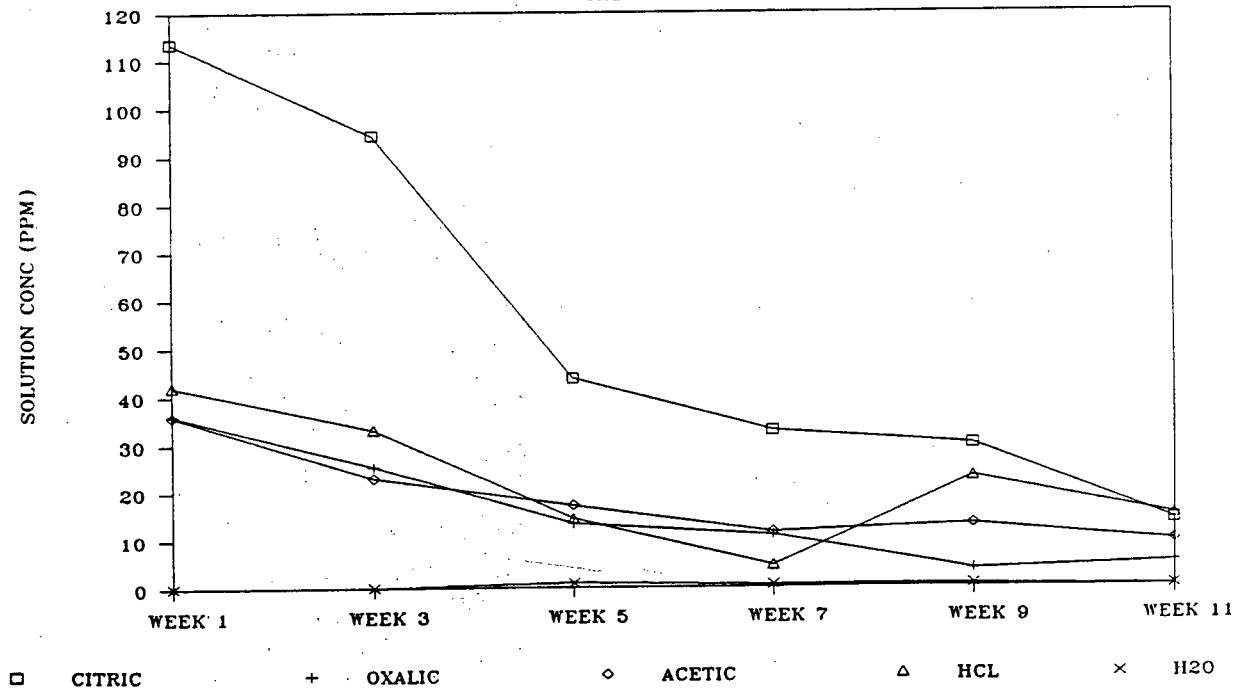
GRANODIORITE

CALCIUM

| ☐ | CITRIC | + | OXALIC | ◇ | ACETIC | △ | HCL | ✕ | H2O |

BASALT

CALCIUM

| ☐ | CITRIC | + | OXALIC | ◇ | ACETIC | △ | HCL | ✕ | H2O |

GRANODIORITE
MAGNESIUM

SOLUTION CONC (PPM)

□ CITRIC   +   OXALIC   ◇   ACETIC   △   HCL   ×   H2O

BASALT
MAGNESIUM

SOLUTION CONC (PPM)
(Thousands)

□ CITRIC   +   OXALIC   ◇   ACETIC   △   HCL   ×   H2O

BASALT
SODIUM

□ CITRIC	+ OXALIC	◊ ACETIC	△ HCL	⨯ H2O

BASALT
SODIUM

□ CITRIC	+ OXALIC	◊ ACETIC	△ HCL	⨯ H2O

GRANODIORITE

POTASSIUM

| □ CITRIC | + OXALIC | ◇ ACETIC | △ HCL | × H20 |

BASALT

POTASSIUM

| □ CITRIC | + OXALIC | ◇ ACETIC | △ HCL | × H20 |

GRANODIORITE
IRON

□ CITRIC	+ OXALIC	◇ ACETIC	△ HCL	× H2O

BASALT
IRON

□ CITRIC	+ OXALIC	◇ ACETIC	△ HCL	× H2O

GRANODIORITE
ALUMINIUM

□ CITRIC   + OXALIC   ◇ ACETIC   △ HCL   × H2O

BASALT
ALUMINIUM

□ CITRIC   + OXALIC   ◇ ACETIC   △ HCL   × H2O
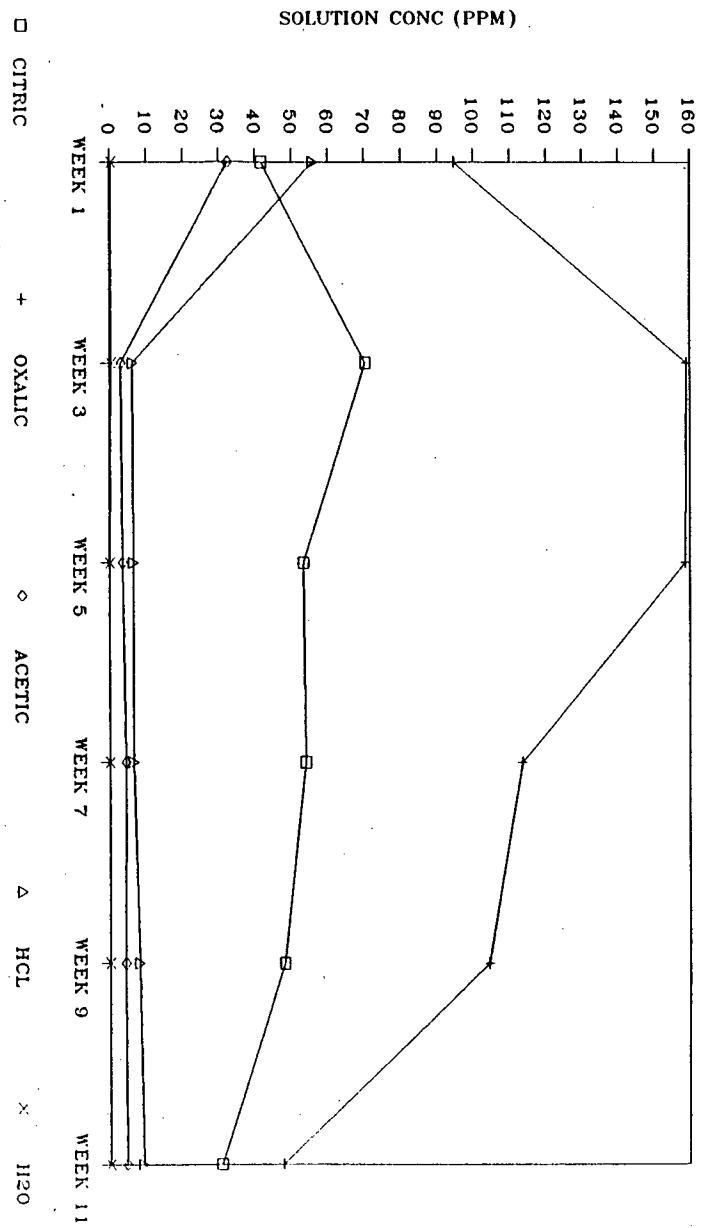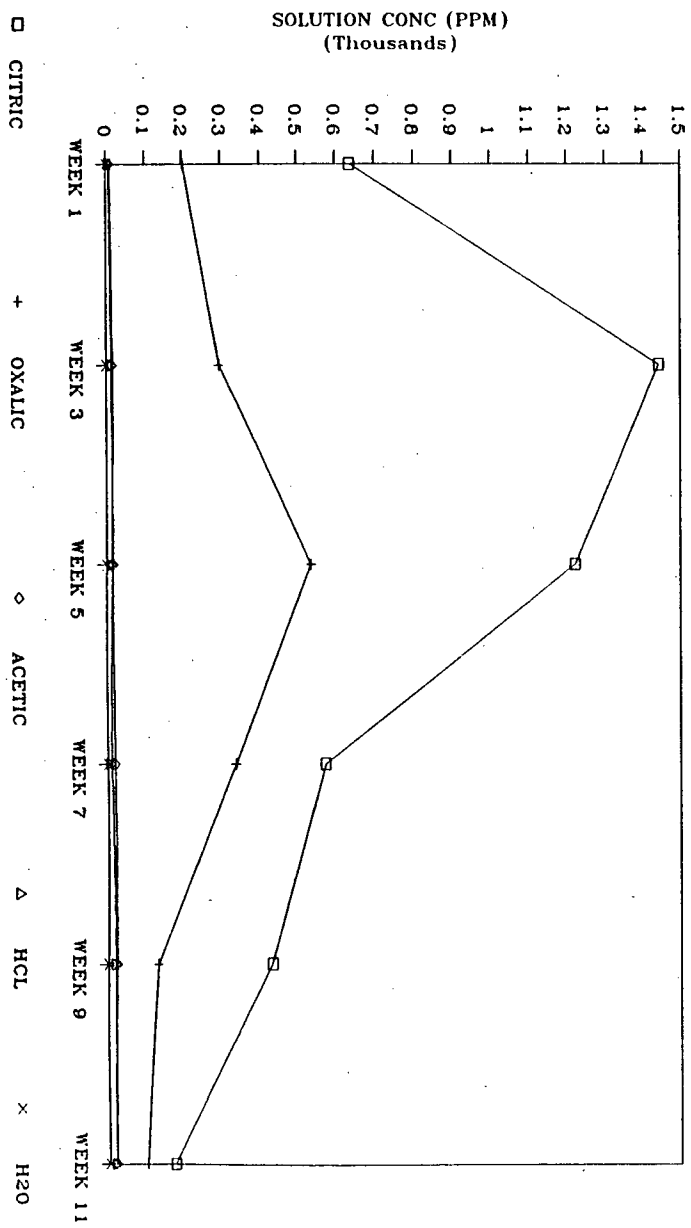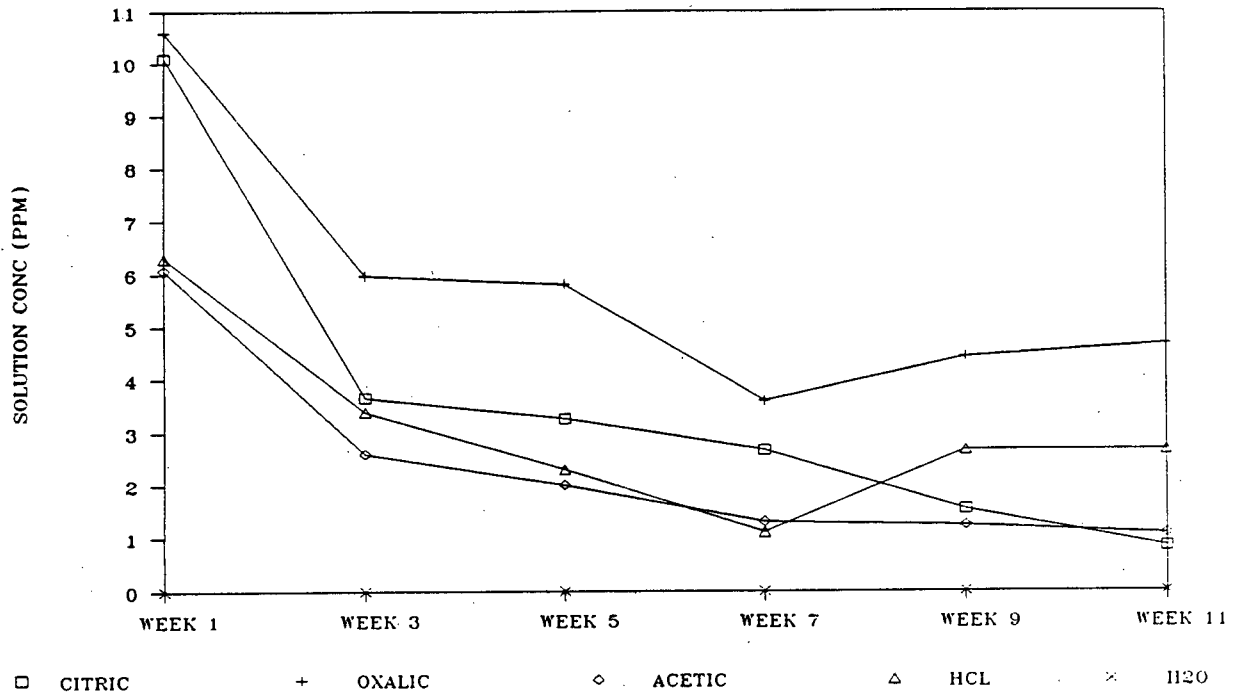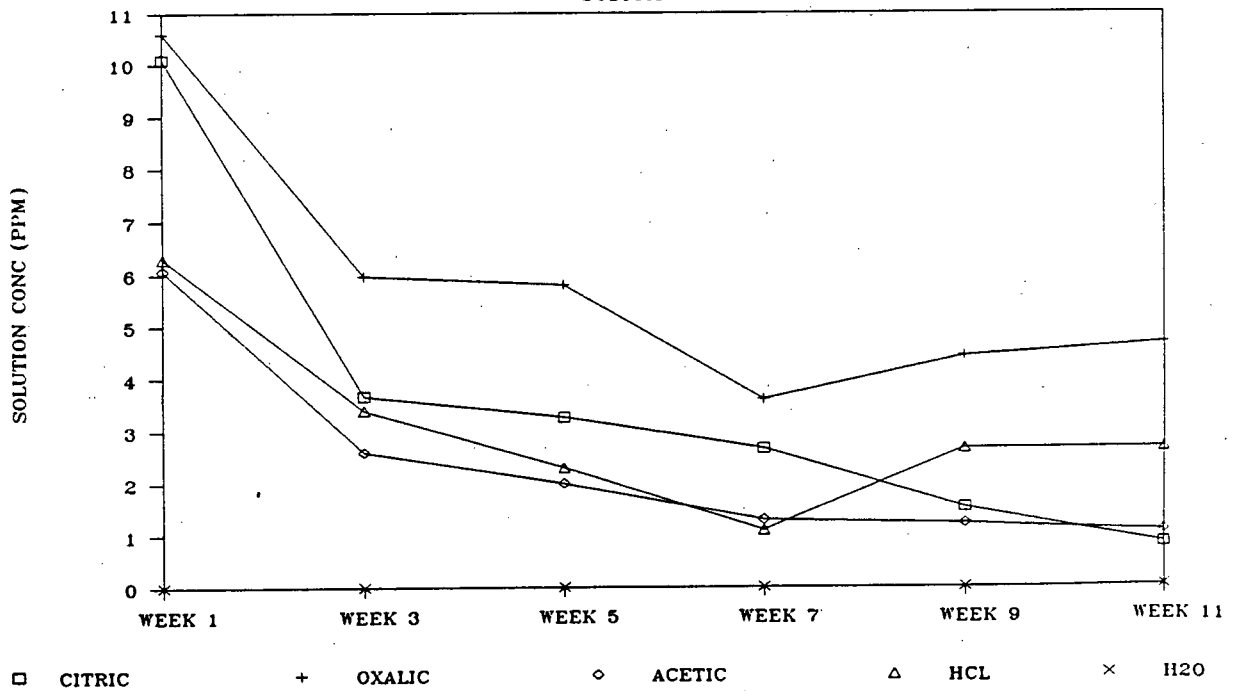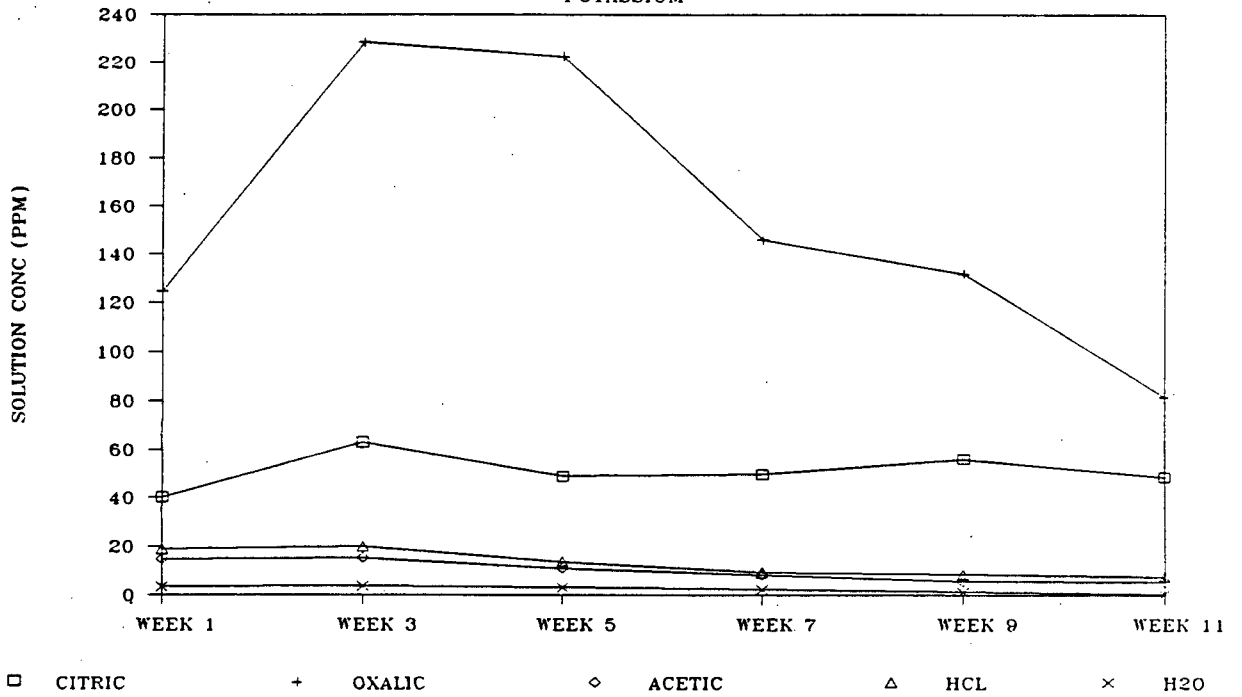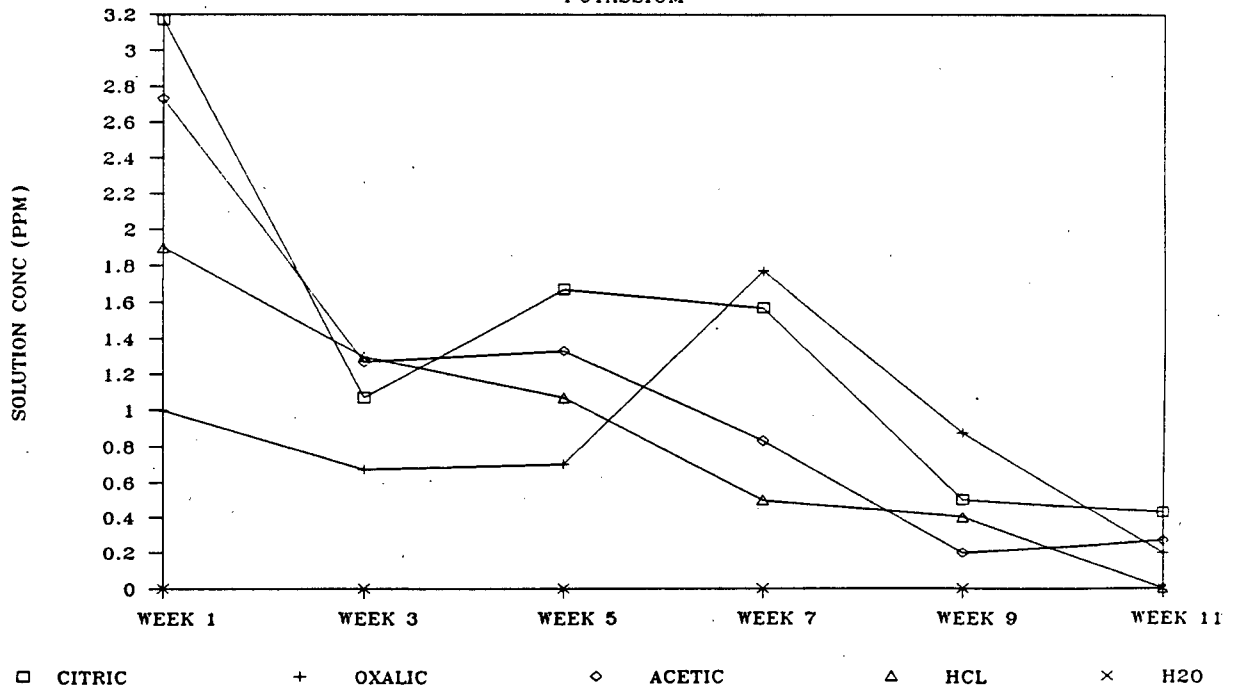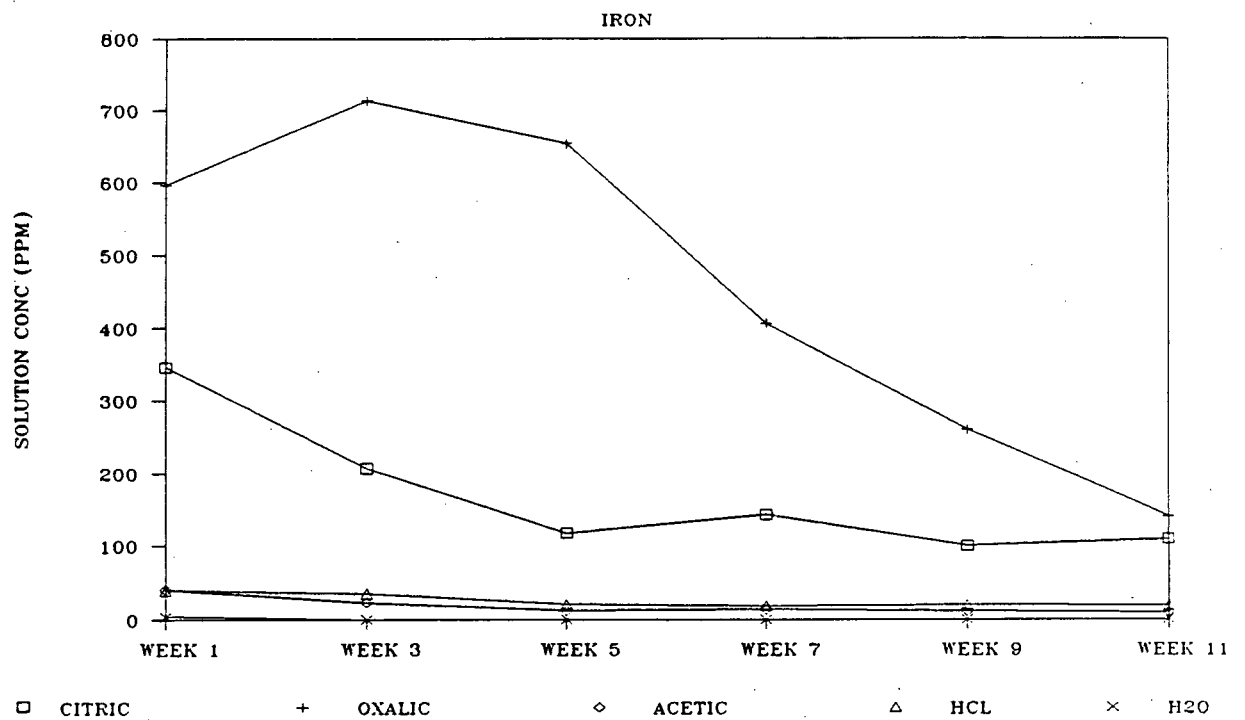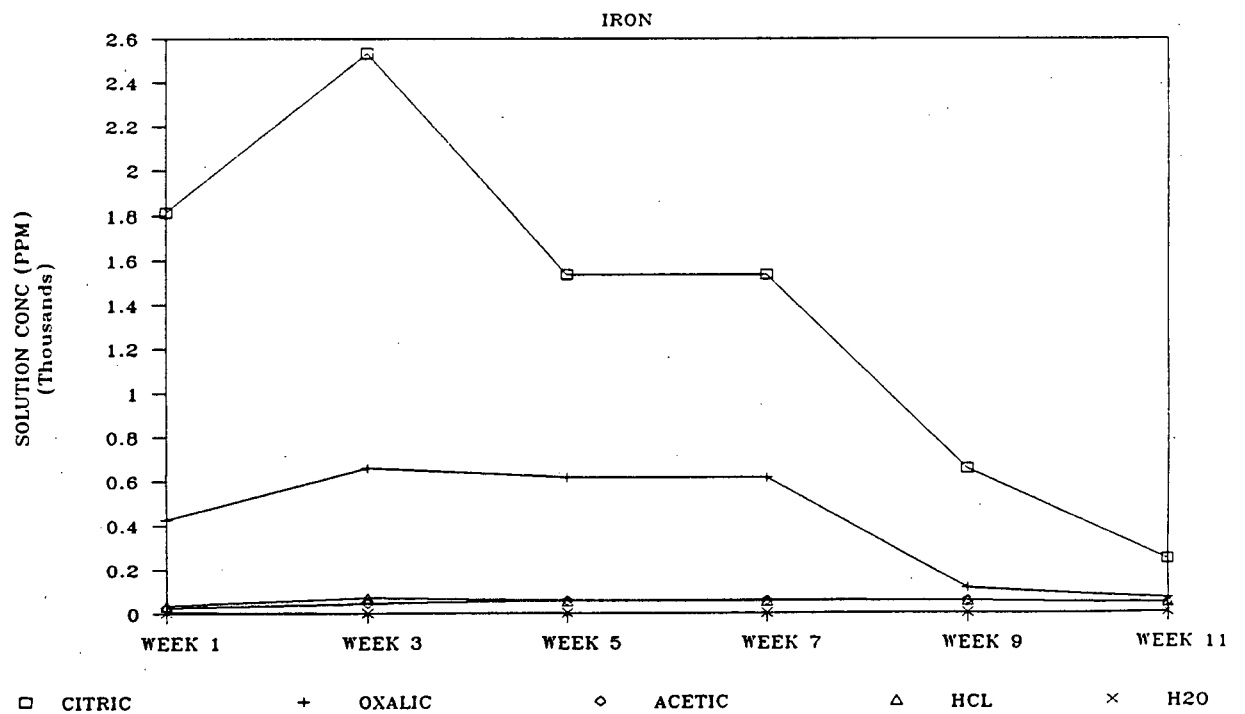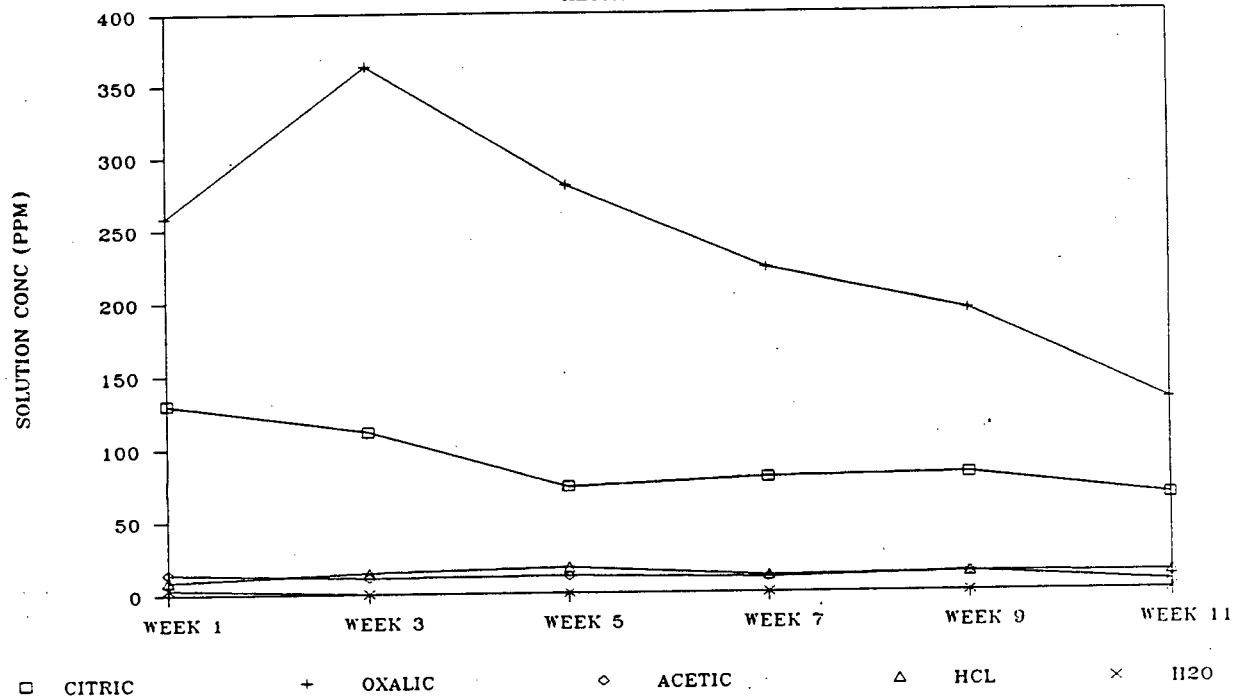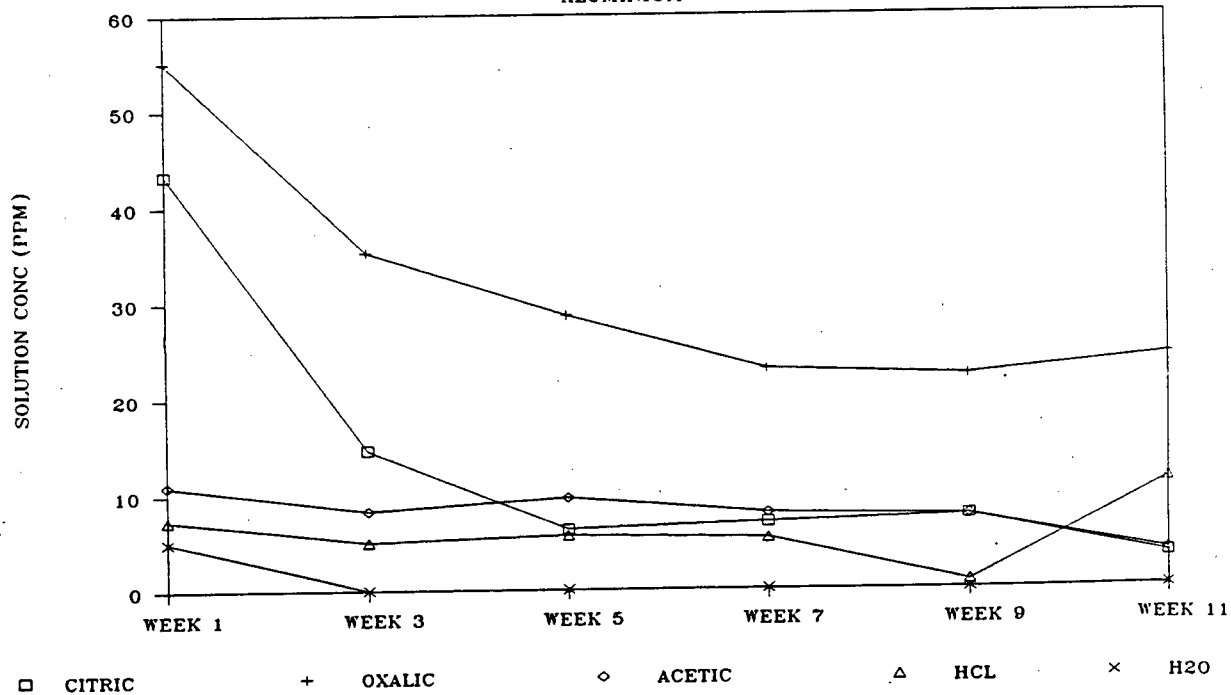
GRANODIORITE
SILICON
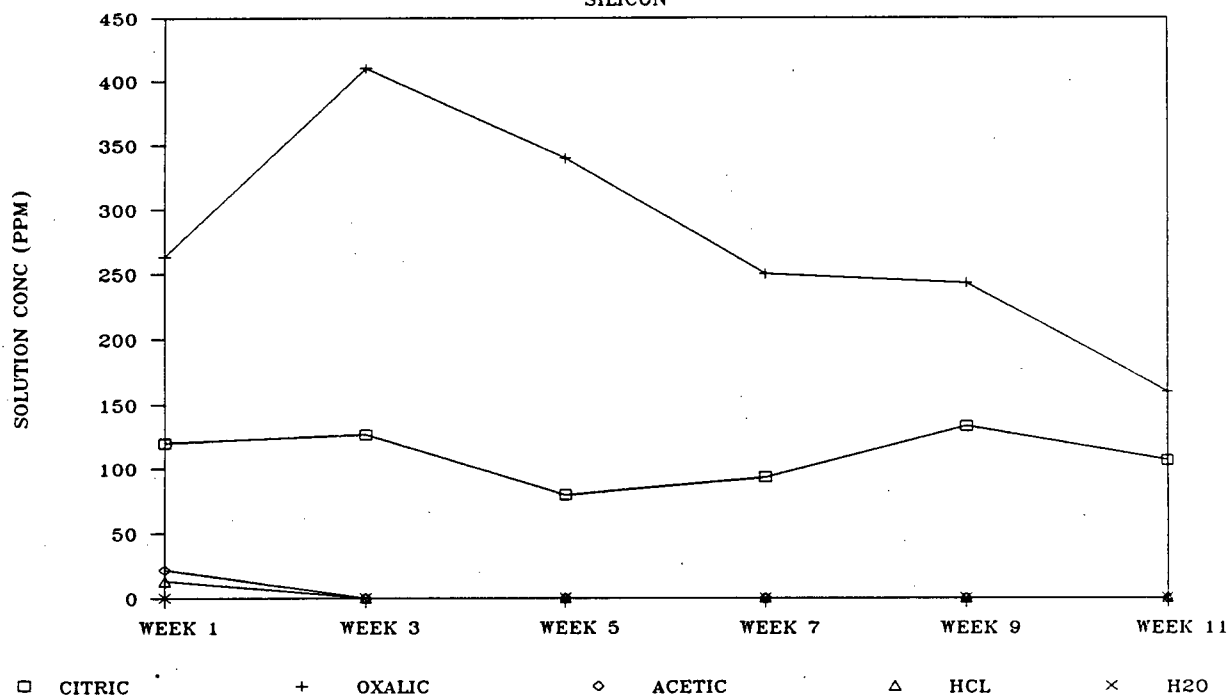
BASALT
SILICON
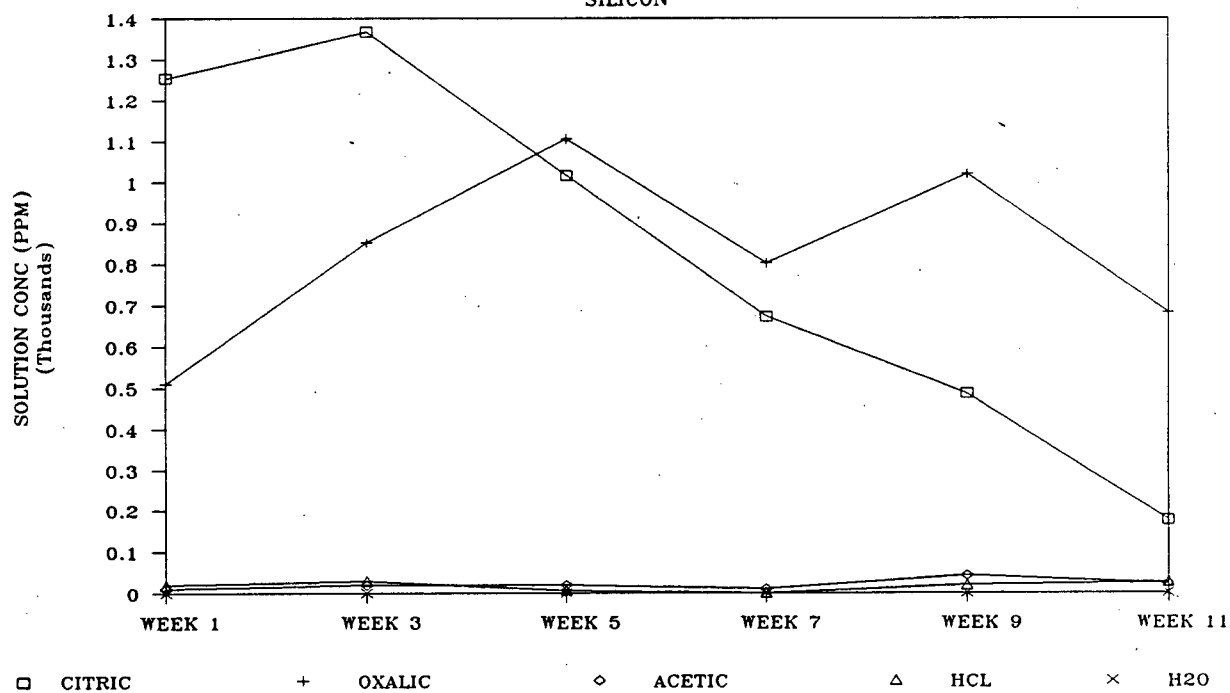
Appendix C: Solution Analyses of 5 Leaching Treatments
               Granodiorite and Basalt Batch Study

               *Data is average of 3 replicate samples

GRANODIORITE

CALCIUM

□ CITRIC	+ OXALIC	◇ ACETIC	△ HCL	× H2O

BASALT

CALCIUM

□ CITRIC	+ OXALIC	◇ ACETIC	△ HCL	× H2O

GRANODIORITE
MAGNESIUM

WEEK 1   WEEK 3   WEEK 5   WEEK 7   WEEK 9   WEEK 11

□ CITRIC   + OXALIC   ◇ ACETIC   △ HCL   × H2O

BASALT
MAGNESIUM

WEEK 1   WEEK 3   WEEK 5   WEEK 7   WEEK 9   WEEK 11

□ CITRIC   + OXALIC   ◇ ACETIC   △ HCL   × H2O

GRANODIORITE

SODIUM

□ CITRIC	+ OXALIC	◇ ACETIC	△ HCL	× H2O

BASALT

SODIUM

□ CITRIC	+ OXALIC	◇ ACETIC	△ HCL	× H2O

GRANODIORITE
POTASSIUM

| □ | CITRIC | + | OXALIC | ◇ | ACETIC | △ | HCL | × | H2O |

BASALT
POTASSIUM

| □ | CITRIC | + | OXALIC | ◇ | ACETIC | △ | HCL | × | H2O |

161
GRANODIORITE
IRON

| □ | CITRIC | + | OXALIC | ◇ | ACETIC | △ | HCL | × | H20 |

BASALT
IRON

| □ | CITRIC | + | OXALIC | ◇ | ACETIC | △ | HCL | × | H2O |

GRANODIORITE

ALUMINIUM

SOLUTION CONC (PPM)

□ CITRIC   + OXALIC   ◇ ACETIC   △ HCL   × H20

BASALT

ALUMINIUM

SOLUTION CONC (PPM)

□ CITRIC   + OXALIC   ◇ ACETIC   △ HCL   × H20

GRANODIORITE

SILICON

| | CITRIC | + | OXALIC | ◇ | ACETIC | △ | HCL | × | H2O |

BASALT

SILICON

| | CITRIC | + | OXALIC | ◇ | ACETIC | △ | HCL | × | H2O |

Appendix D: Solution Analyses of 5 Leaching Treatments
                Granodiorite "B" and Basalt "B" Batch Study

                *Data is average of 2 replicate samples

<.1mm GRANODIORITE

CALCIUM
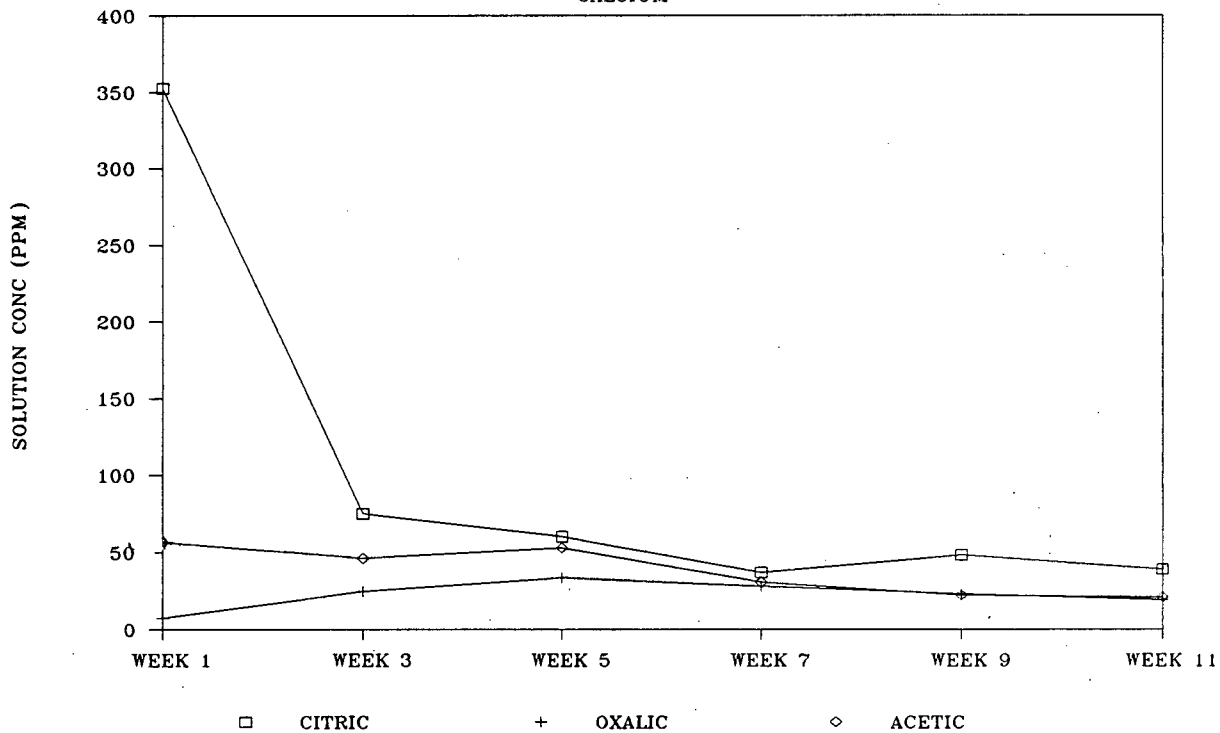
| | CITRIC | + | OXALIC | ◇ | ACETIC |

<.1mm BASALT

CALCIUM
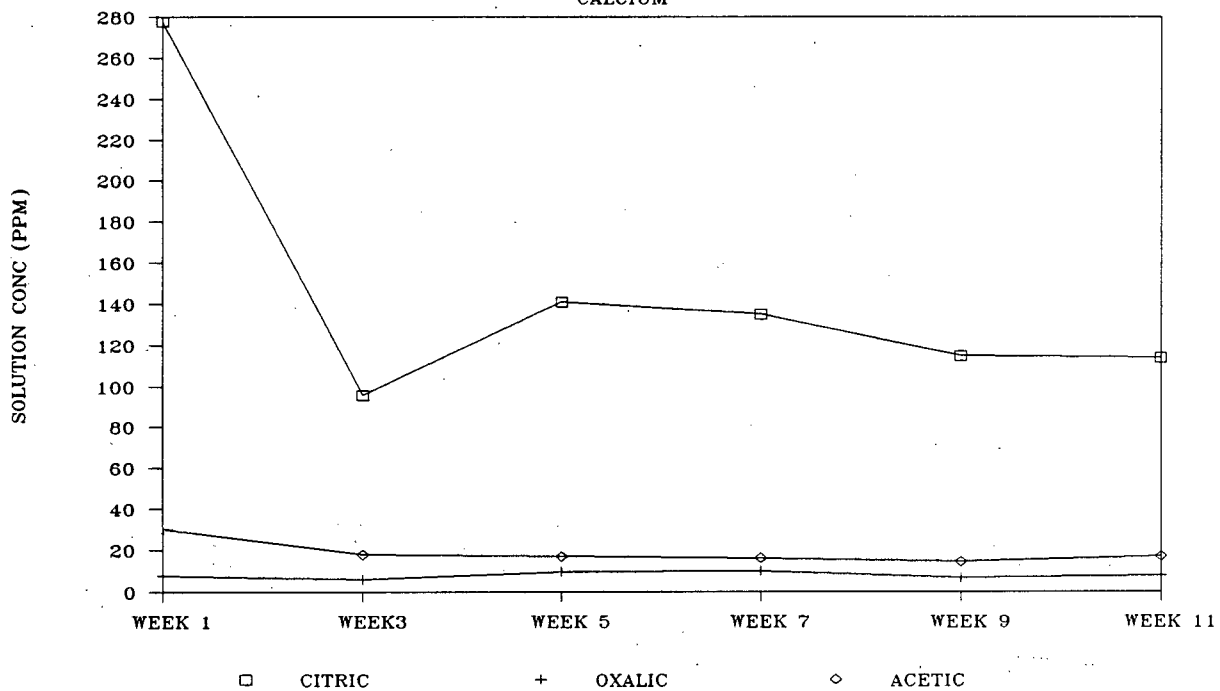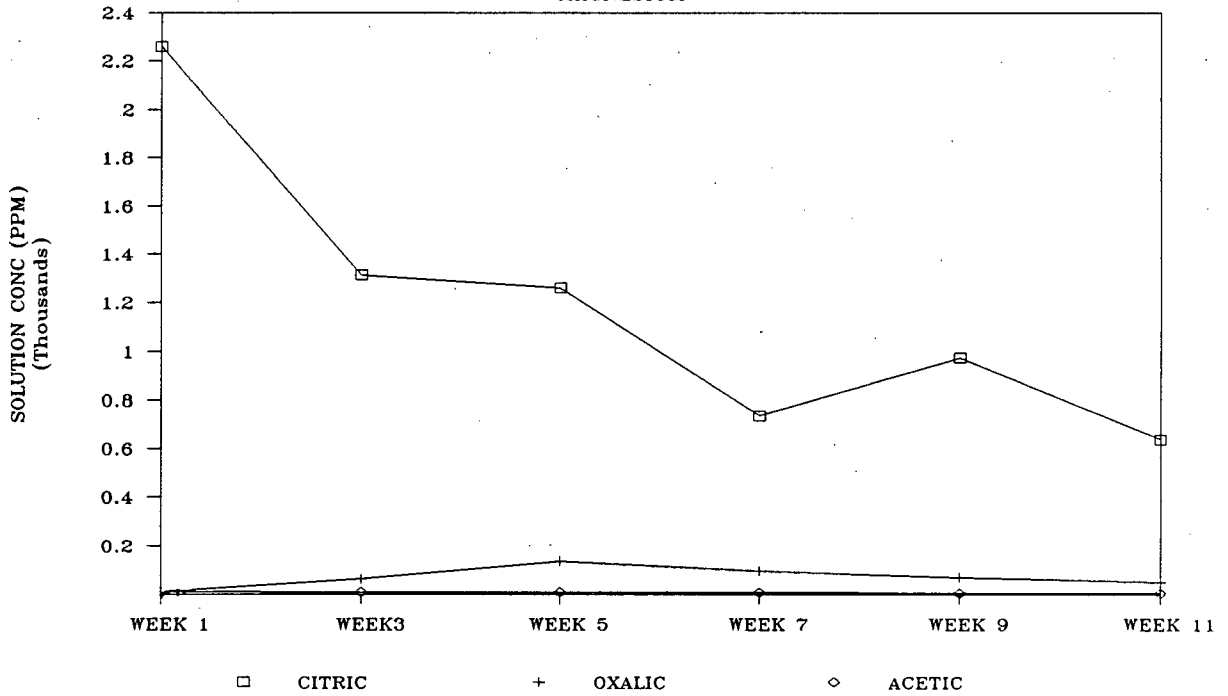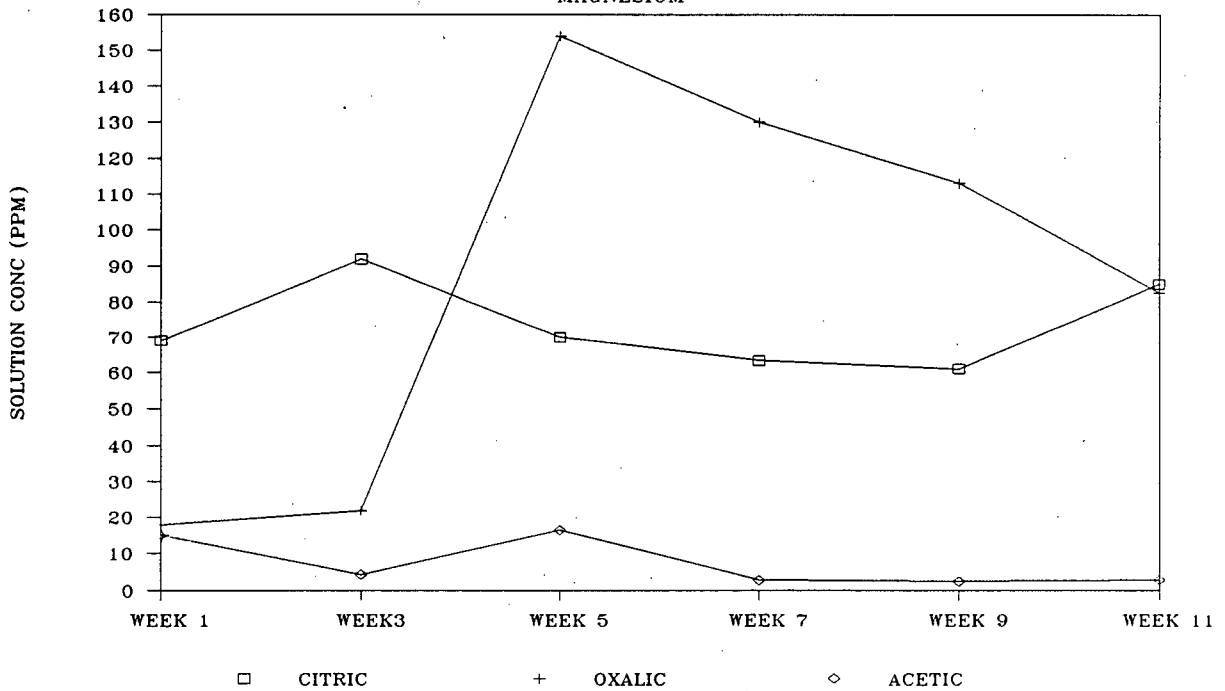
| | CITRIC | + | OXALIC | ◇ | ACETIC |

<.1mm GRANODIORITE

MAGNESIUM

WEEK 1 · WEEK3 · WEEK 5 · WEEK 7 · WEEK 9 · WEEK 11

□ CITRIC   + OXALIC   ◇ ACETIC

<.1mm BASALT

MAGNESIUM

WEEK 1 · WEEK3 · WEEK 5 · WEEK 7 · WEEK 9 · WEEK 11

□ CITRIC   + OXALIC   ◇ ACETIC

<.1mm GRANODIORITE
SODIUM

| | CITRIC | + | OXALIC | ◇ | ACETIC |

<.1mm BASALT
SODIUM

| | CITRIC | + | OXALIC | ◇ | ACETIC |

<.1mm GRANODIORITE

POTASSIUM

WEEK 1   WEEK 3   WEEK 5   WEEK 7   WEEK 9   WEEK 11

□ CITRIC   + OXALIC   ◇ ACETIC

<.1mm BASALT

POTASSIUM

WEEK 1   WEEK 3   WEEK 5   WEEK 7   WEEK 9   WEEK 11

□ CITRIC   + OXALIC   ◇ ACETIC

<.1mm GRANODIORITE
IRON

CITRIC   □   OXALIC   +   ACETIC   ◇

<.1mm BASALT
IRON

CITRIC   □   OXALIC   +   ACETIC   ◇

<.1mm GRANODIORITE

ALUMINIUM

WEEK 1   WEEK 3   WEEK 5   WEEK 7   WEEK 9   WEEK 11

□ CITRIC   + OXALIC   ◇ ACETIC

<.1mm BASALT

ALUMINIUM

WEEK 1   WEEK 3   WEEK 5   WEEK 7   WEEK 9   WEEK 11

□ CITRIC   + OXALIC   ◇ ACETIC

<.1mm GRANODIORITE

SILICON

□ CITRIC   + OXALIC   ◇ ACETIC
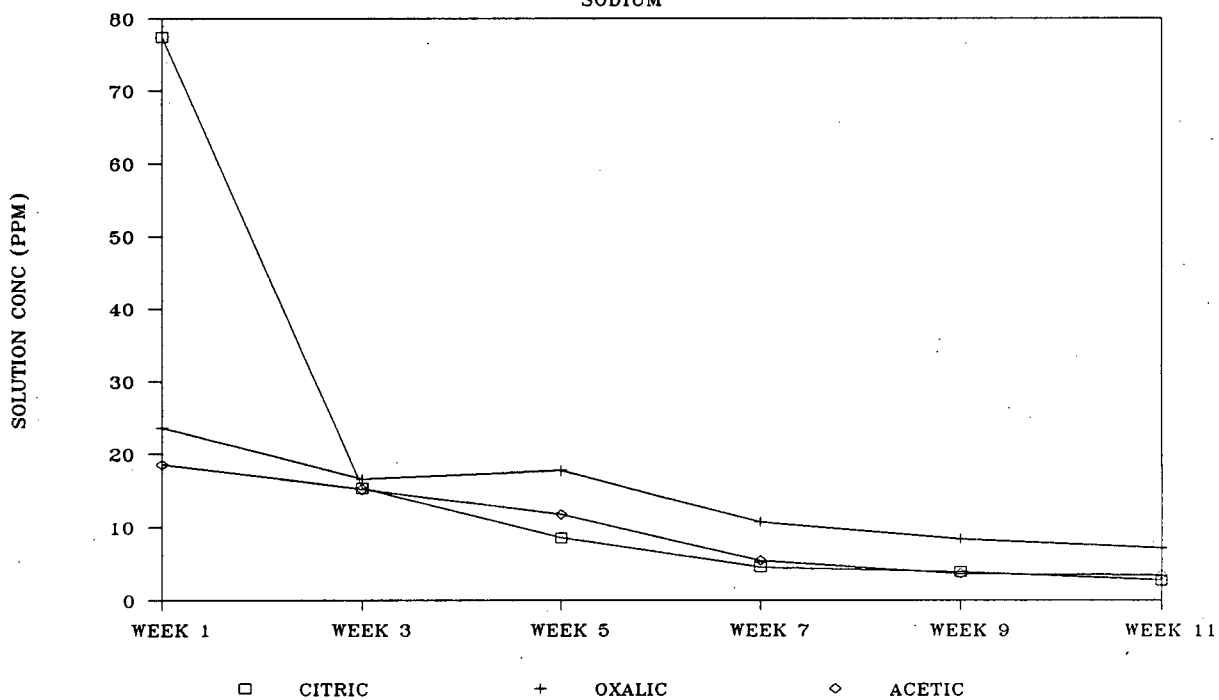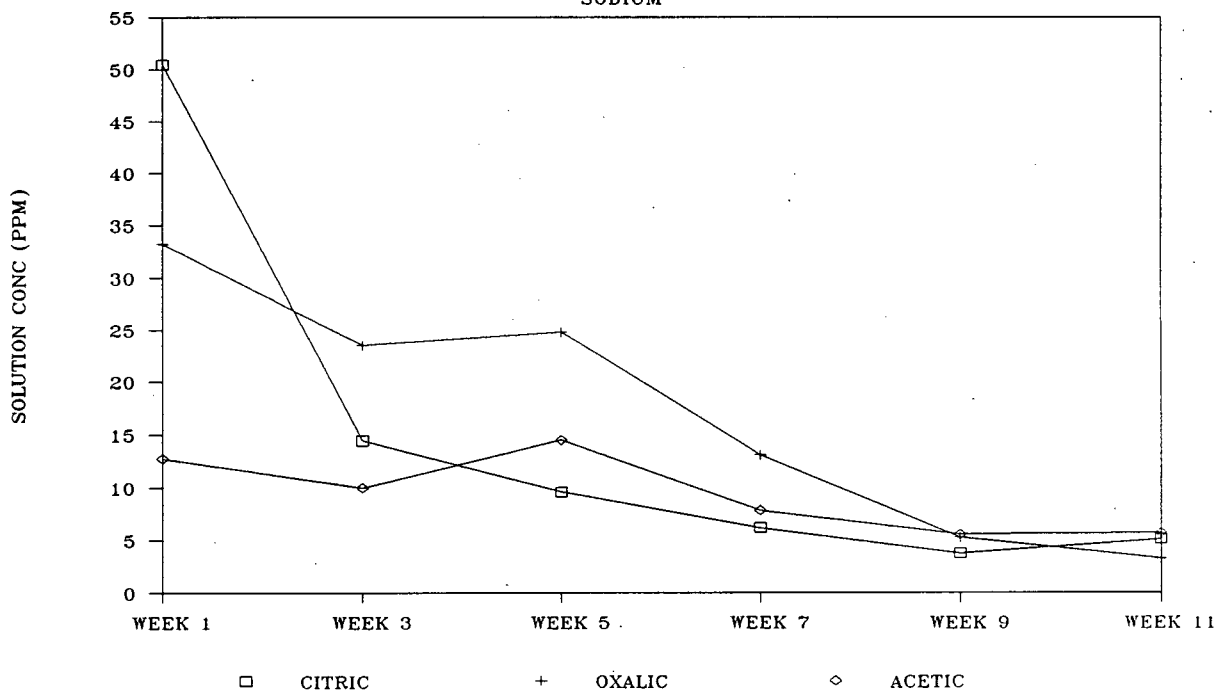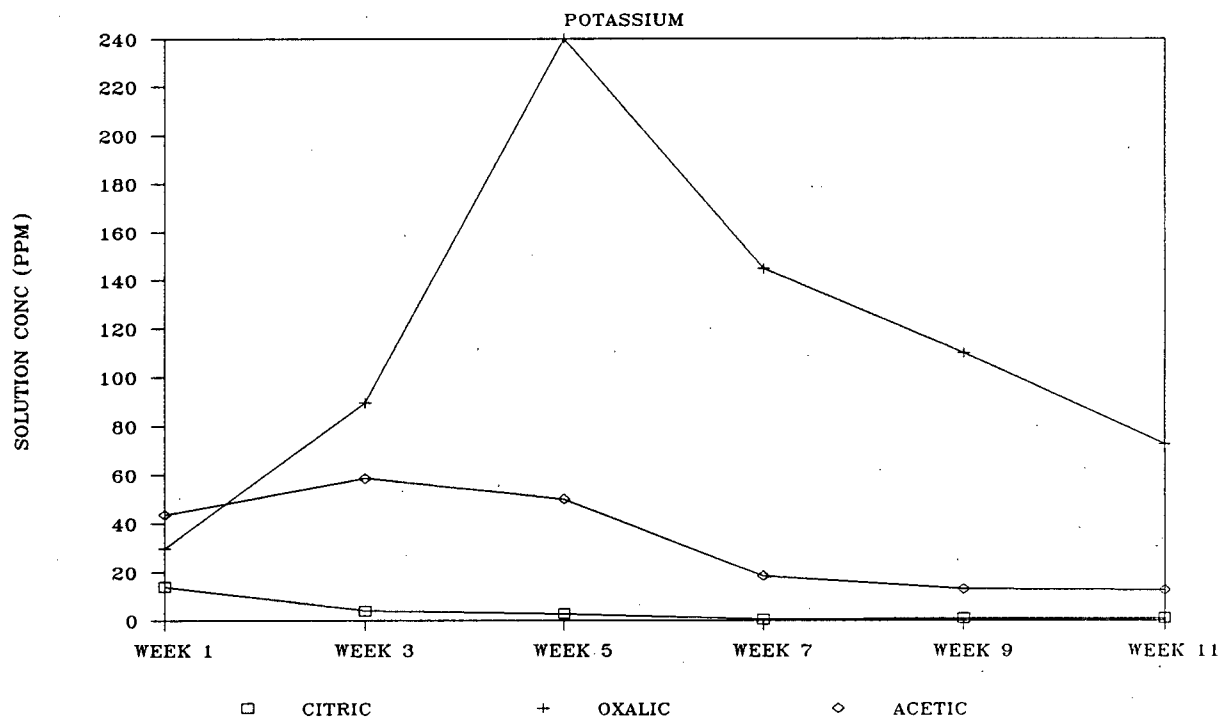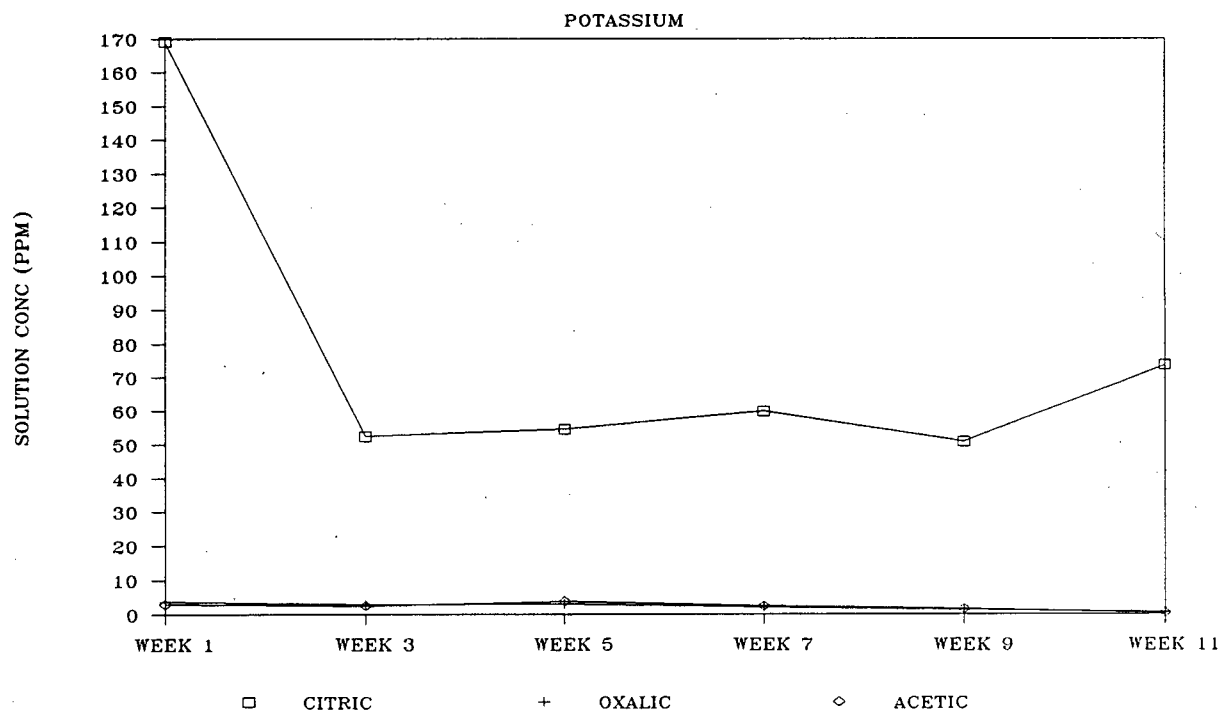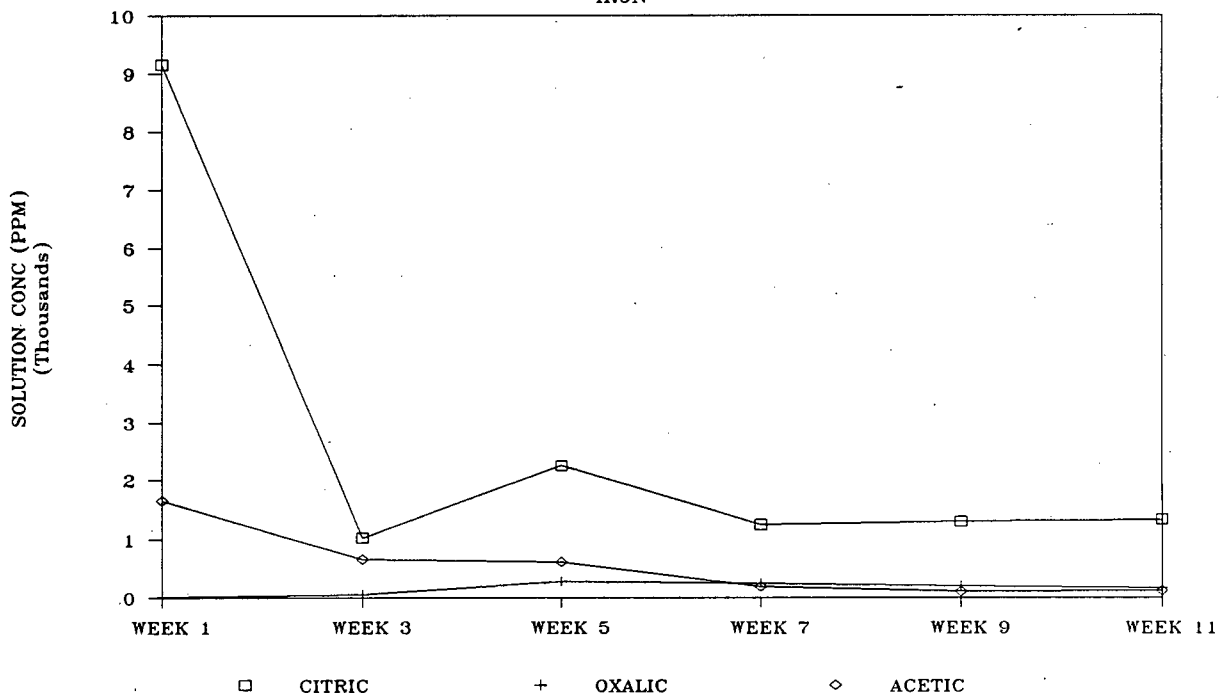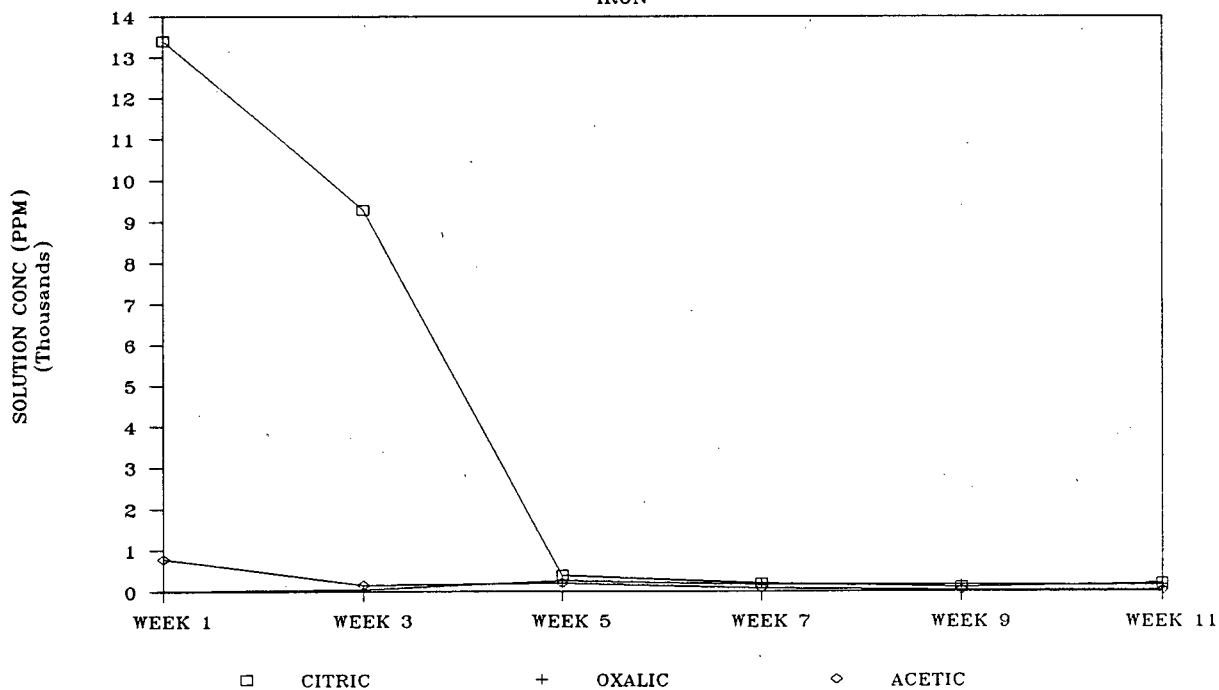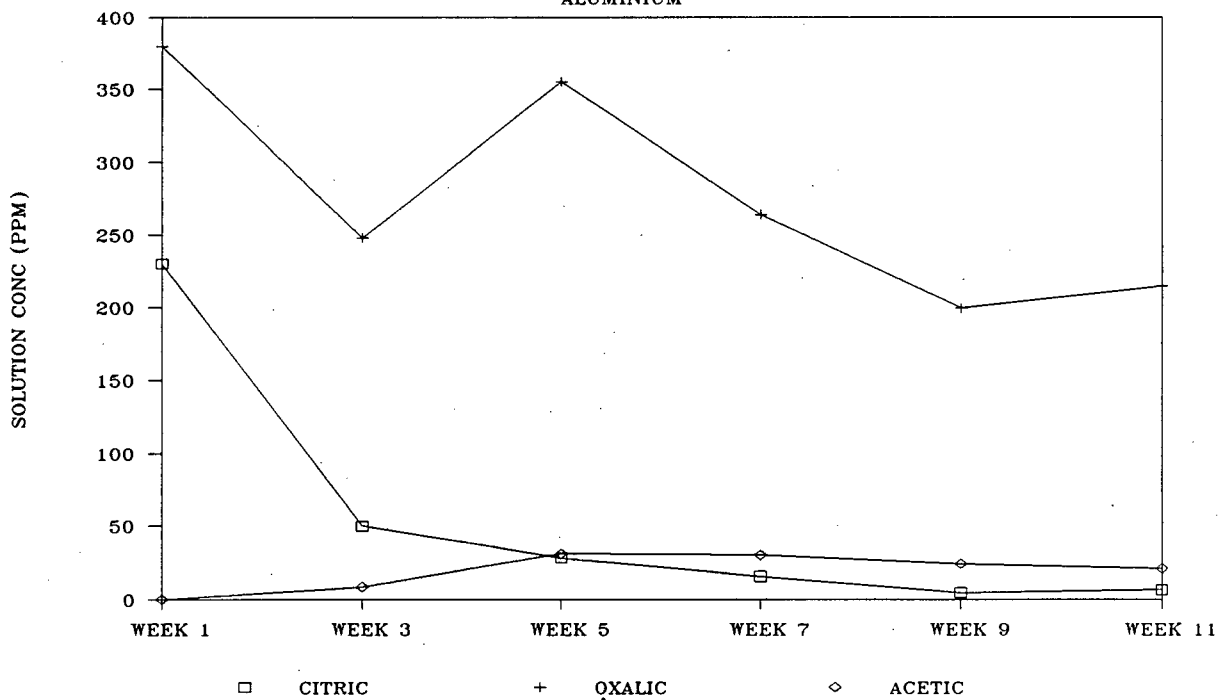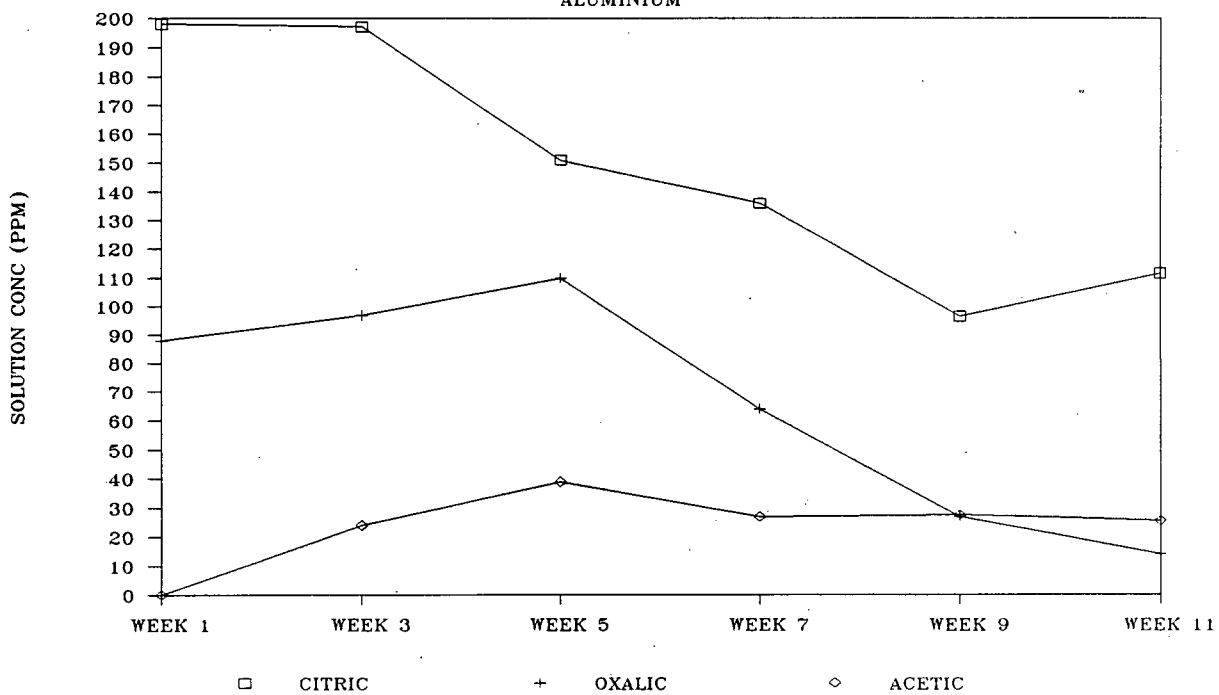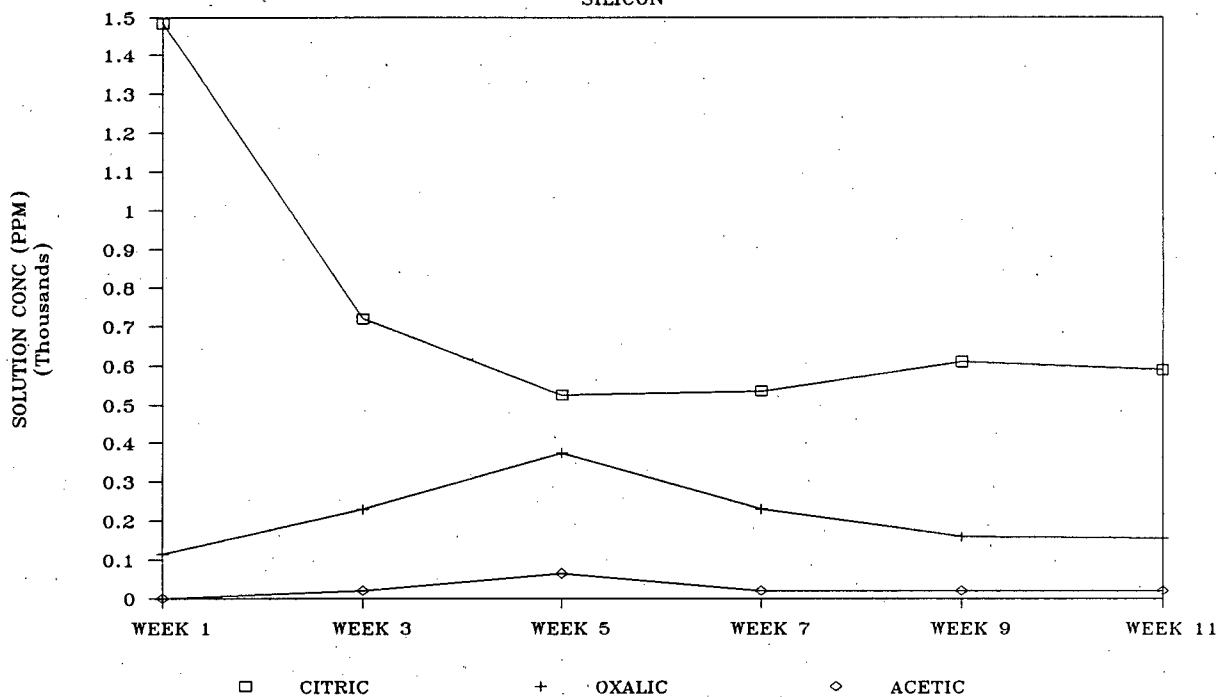
<.1mm BASALT

SILICON

□ CITRIC   + OXALIC   ◇ ACETIC
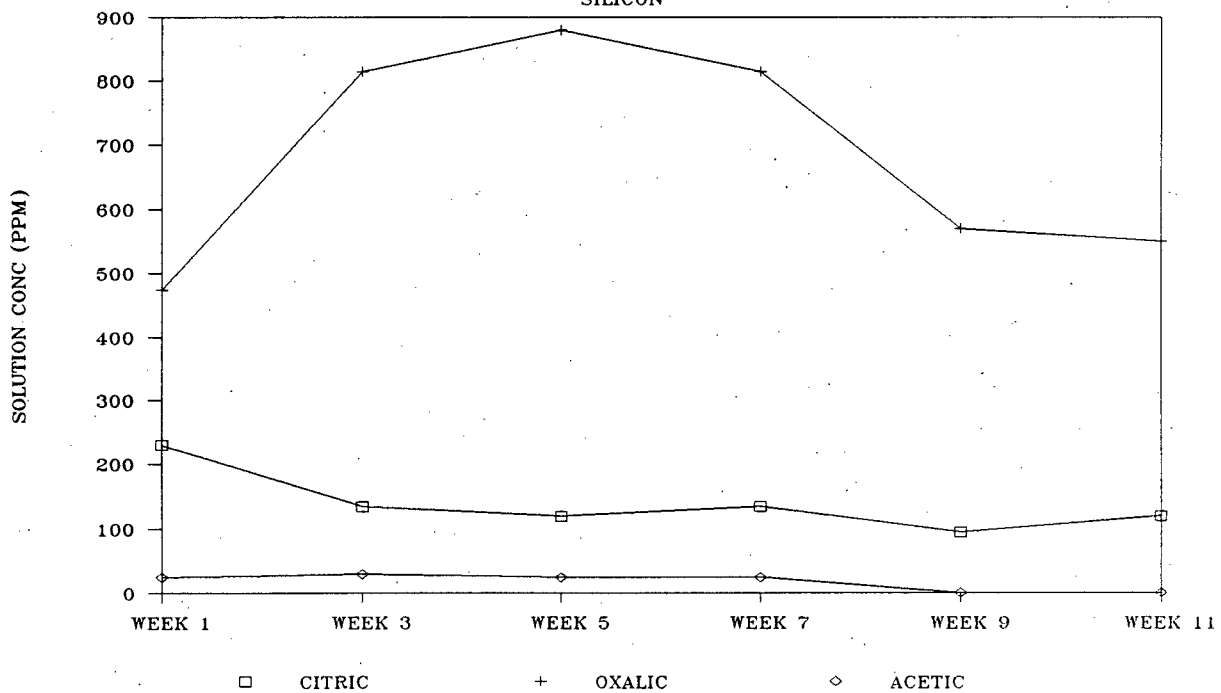
Appendix E: Analyses of Solution pH from 5 Leaching Treatments
                Granodiorite and Basalt-Column and Batch Studies

                *Data is average of 3 replicate samples

Solution pH— 4 Weeks
Batch — Granodiorite

□ Citric	+ Oxalic	◇ Acetic	△ HCl	× HOH	
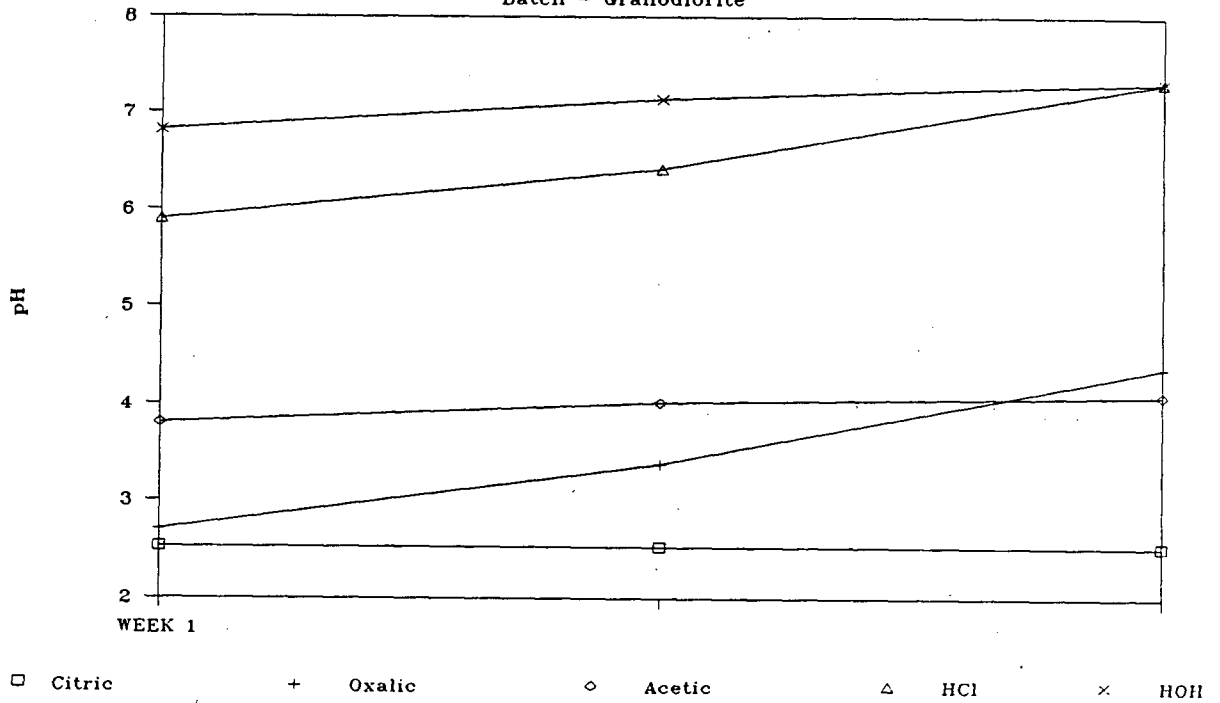
Solution pH— 4 Weeks
Batch — Basalt

□ Citric	+ Oxalic	◇ Acetic	△ HCl	× HOH	

Solution pH
Colomn - Granodiorite

pH

8

7

6

5

4

3

2

1

WEEK 1   WEEK 3   WEEK 5   WEEK 7   WEEK 9   WEEK 11

□ Citric   + Oxalic   ◇ Acetic   △ HCl   × HOH
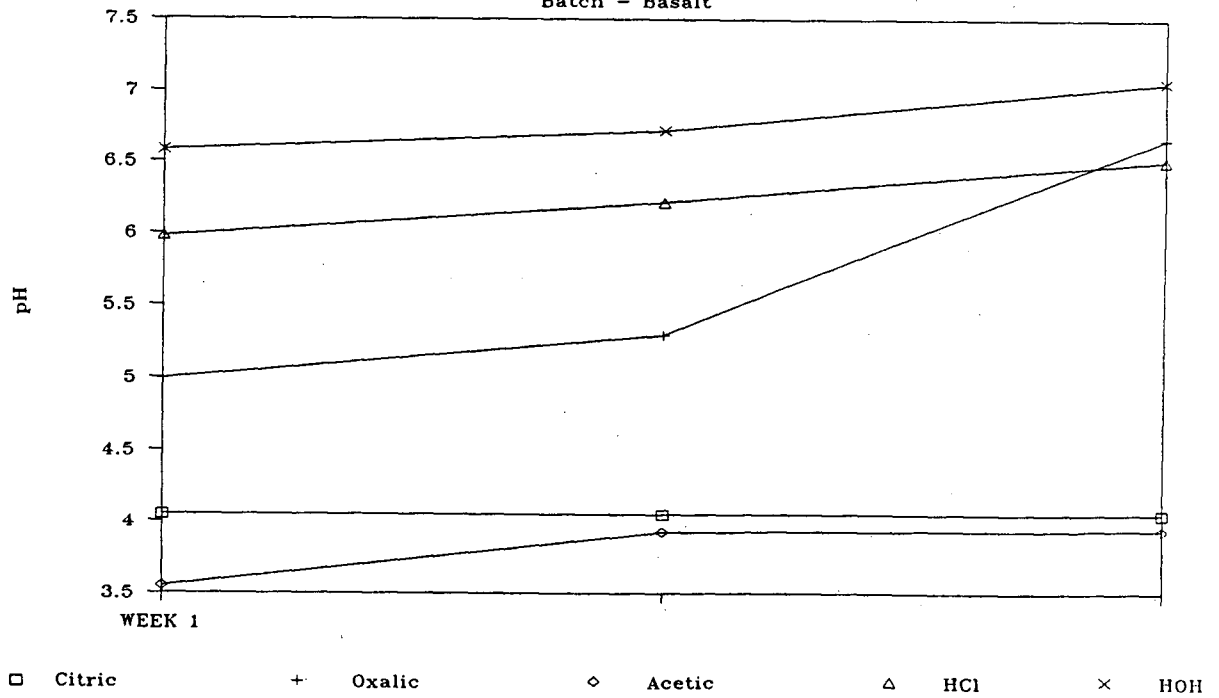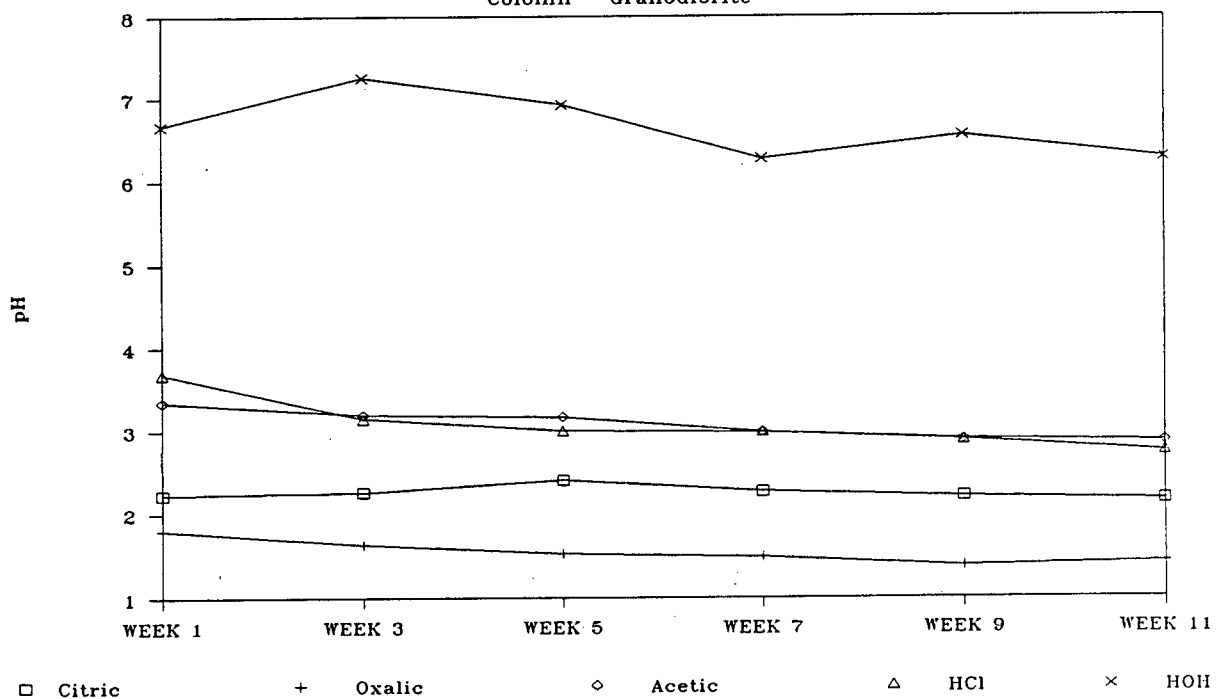
Solution pH
Column - Basalt

pH

7

6

5

4

3

2

1

WEEK 1   WEEK 3   WEEK 5   WEEK 7   WEEK 9   WEEK 11

□ Citric   + Oxalic   ◇ Acetic   △ HCl   × HOH
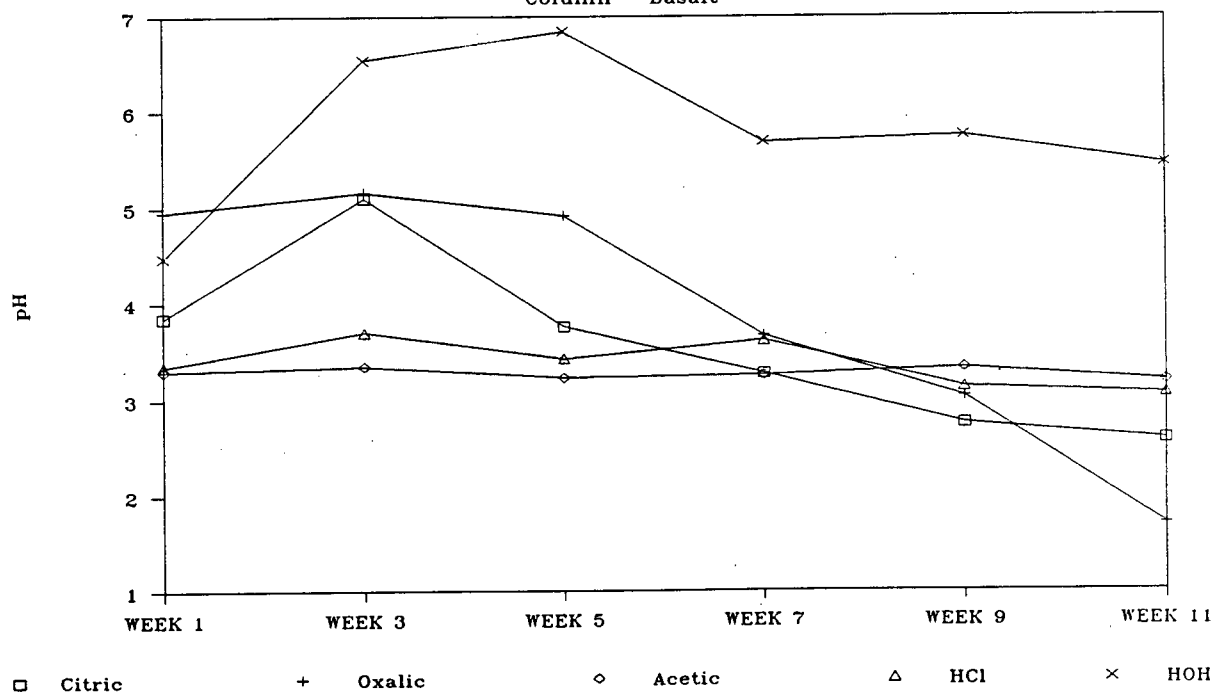
Solution pH
Batch – Granodiorite

□ Citric	+ Oxalic	◇ Acetic	△ HCl	× HOH
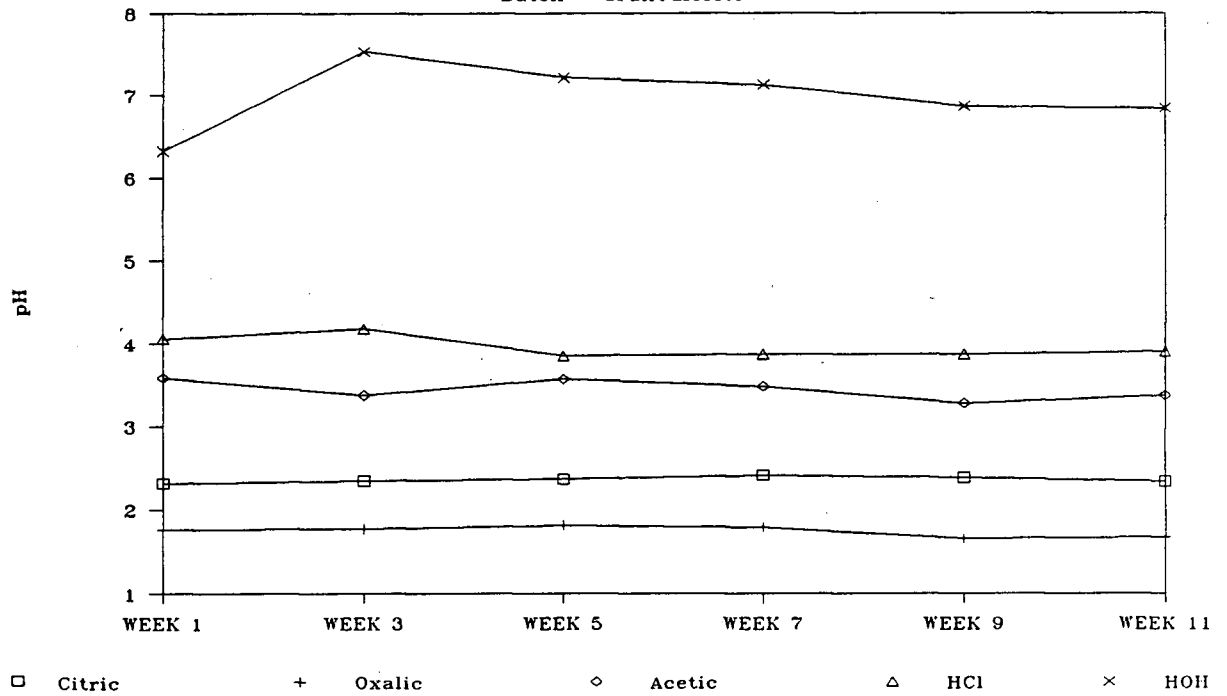
Solution pH
Batch – Basalt

□ Citric	+ Oxalic	◇ Acetic	△ HCl	× HOH
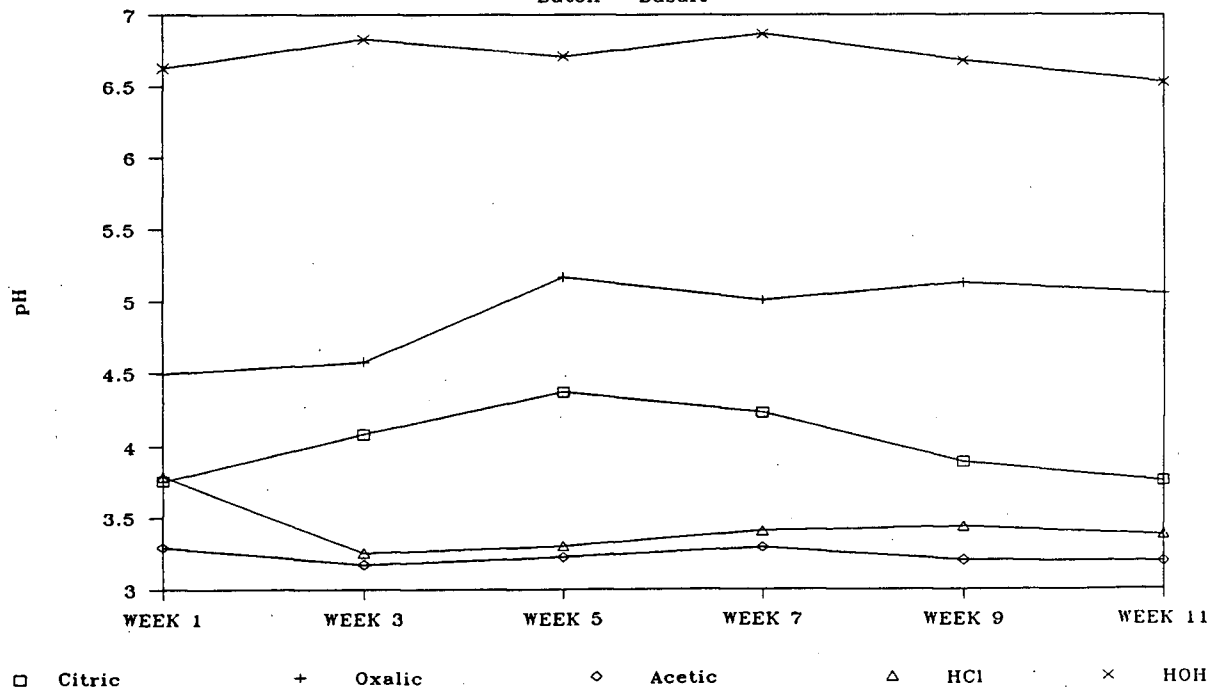
Appendix F: Table of Data from Solution Analyses of 5 Leaching
               Treatments
               Granodiorite and Basalt - Column and Batch 1 Month
               Study

COLUMN STUDY- 4 WEEK WEATHERING EXPERIMENT
ANALYSES OF SOLUTION EXTRACTS (ppm)

PARENT MATERIAL	TREATMENT	Ca	Mg	Na	K	Fe	Al	Si
GRANODIORITE	CITRIC	195.0	106.0	17.2	74.0	860.0	209.0	170.0
GRANODIORITE	CITRIC	206.0	125.0	17.0	85.0	480.0	234.0	190.0
GRANODIORITE	CITRIC	143.0	84.0	16.9	61.0	430.0	216.0	190.0
GRANODIORITE	OXALIC	49.5	159.0	9.7	192.0	310.0	312.0	340.0
GRANODIORITE	OXALIC	40.0	149.0	18.9	162.0	230.0	375.0	340.0
GRANODIORITE	OXALIC	41.0	163.0	19.3	195.0	310.0	370.0	350.0
GRANODIORITE	ACETIC	68.5	4.7	9.3	23.0	250.0	16.0	40.0
GRANODIORITE	ACETIC	65.5	4.4	8.6	27.2	130.0	13.0	30.0
GRANODIORITE	ACETIC	67.0	5.4	8.8	25.5	280.0	12.0	30.0
GRANODIORITE	HCl	89.0	68.0	18.4	62.0	360.0	147.0	140.0
GRANODIORITE	HCl	100.0	44.0	14.9	52.0	370.0	115.0	130.0
GRANODIORITE	HCl	114.0	54.0	12.8	54.5	220.0	112.0	110.0
GRANODIORITE	HOH	10.8	0.9	4.7	6.5	0.0	0.0	0.0
GRANODIORITE	HOH	5.0	0.4	6.5	5.1	0.0	0.0	0.0
GRANODIORITE	HOH	8.2	0.8	4.1	5.6	0.0	0.0	0.0
BASALT	CITRIC	109.0	1180.0	8.3	1.8	2310.0	20.0	100.0
BASALT	CITRIC	75.0	1120.0	11.0	2.4	2100.0	20.0	80.0
BASALT	CITRIC	102.0	1550.0	10.9	2.8	3400.0	30.0	95.0
BASALT	OXALIC	26.5	200.0	10.3	1.0	370.0	44.0	59.0
BASALT	OXALIC	26.5	207.0	10.4	1.2	320.0	41.0	61.0
BASALT	OXALIC	35.3	206.0	10.3	1.4	350.0	44.0	59.0
BASALT	ACETIC	34.0	10.0	5.8	2.3	62.0	12.0	40.0
BASALT	ACETIC	56.0	12.6	9.9	3.2	85.0	11.0	30.0
BASALT	ACETIC	46.0	19.4	10.1	3.6	97.0	13.0	50.0
BASALT	HCl	65.0	375.0	12.9	2.9	520.0	31.0	54.0
BASALT	HCl	48.0	335.0	16.6	5.1	630.0	34.0	58.0
BASALT	HCl	57.0	204.0	14.7	5.0	430.0	35.0	62.0
BASALT	HOH	0.8	0.0	4.2	1.2	0.0	0.0	0.0
BASALT	HOH	0.9	0.0	2.9	0.8	0.0	0.0	0.0
BASALT	HOH	1.6	0.0	3.3	0.8	0.0	0.0	0.0

BATCH STUDY- 4 WEEK WEATHERING EXPERIMENT
ANALYSES OF SOLUTION EXTRACTS (ppm)

PARENT MATERIAL	TREATMENT	Ca	Mg	Na	K	Fe	Al	Si
GRANODIORITE	CITRIC	214.0	142.0	33.5	90.0	930.0	345.0	270.0
GRANODIORITE	CITRIC	192.0	145.0	27.7	92.0	990.0	278.0	240.0
GRANODIORITE	CITRIC	201.0	129.0	34.0	94.0	780.0	359.0	290.0
GRANODIORITE	OXALIC	42.0	193.0	33.2	155.0	147.0	368.0	325.0
GRANODIORITE	OXALIC	34.0	187.0	28.5	145.0	142.0	315.0	350.0
GRANODIORITE	OXALIC	39.5	184.0	33.0	123.0	181.0	379.0	362.0
GRANODIORITE	ACETIC	62.0	17.0	17.5	50.0	310.0	45.0	70.0
GRANODIORITE	ACETIC	51.0	12.0	14.6	45.0	290.0	32.0	40.0
GRANODIORITE	ACETIC	62.9	17.0	19.5	52.0	278.0	38.0	50.0
GRANODIORITE	HCl	120.0	70.0	19.0	64.0	310.0	125.0	125.0
GRANODIORITE	HCl	143.0	75.0	21.0	52.0	325.0	132.0	134.0
GRANODIORITE	HCl	134.0	85.0	24.0	56.0	340.0	128.0	137.0
GRANODIORITE	HOH	7.4	6.8	10.3	14.2	0.0	0.0	0.0
GRANODIORITE	HOH	7.8	6.2	10.3	14.2	0.0	0.0	0.0
GRANODIORITE	HOH	2.0	6.9	10.7	15.0	0.0	0.0	0.0
BASALT	CITRIC	110.0	999.0	25.6	7.0	2710.0	65.0	89.0
BASALT	CITRIC	130.0	1090.0	24.0	8.0	2432.0	49.0	110.0
BASALT	CITRIC	120.0	1020.0	28.0	7.8	2980.0	58.0	98.0
BASALT	OXALIC	30.0	110.0	22.3	2.0	420.0	54.0	70.0
BASALT	OXALIC	28.0	120.0	23.0	1.8	452.0	52.0	50.0
BASALT	OXALIC	29.0	158.0	22.5	2.5	480.0	57.0	54.0
BASALT	ACETIC	55.0	16.0	17.5	47.0	220.0	16.0	45.0
BASALT	ACETIC	86.0	21.0	19.0	61.0	210.0	28.0	42.0
BASALT	ACETIC	75.0	23.0	21.0	58.0	198.0	24.0	42.0
BASALT	HCl	16.4	300.0	11.6	3.7	410.0	35.0	48.0
BASALT	HCl	15.0	320.0	11.8	2.9	390.0	36.0	56.0
BASALT	HCl	18.3	326.0	11.2	2.2	345.0	34.0	57.0
BASALT	HOH	5.5	2.0	13.2	1.0	0.0	0.0	0.0
BASALT	HOH	5.2	2.5	10.5	1.3	0.0	0.0	0.0
BASALT	HOH	6.2	2.1	11.6	1.7	0.0	2.0	0.0

Appendix G: Tables of Data from Solution Analyses of 5
               Leaching Treatments
               Granodiorite and Basalt - Column and Batch 11 Week
               Study

               *Data is average of 3 replicate samples

COLUMN STUDY SOLUTION EXTRACTS (ppm)

|	CALCIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11	MAGNESIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	188.33	108.00	29.00	16.17	12.03	9.33		41.73	70.33	53.33	54.00	48.00	30.67
	OXALIC	43.83	50.30	32.70	21.50	15.33	9.67		94.67	159.00	158.67	113.33	104.33	47.67
	ACETIC	45.17	37.33	33.73	33.47	22.50	23.33		32.33	3.07	3.60	4.47	4.30	4.70
	HCL	74.00	48.83	34.60	31.00	26.83	25.33		56.00	6.27	6.57	6.53	8.13	9.17
	H2O	4.23	5.53	2.80	1.70	1.17	0.00		0.40	0.40	0.00	0.00	0.00	0.00
BASALT	CITRIC	113.67	94.33	43.67	32.67	29.77	14.00		637.67	1443.33	1223.33	573.33	430.00	176.33
	OXALIC	36.00	25.33	13.50	11.00	3.53	5.00		204.33	296.67	536.67	336.67	131.33	100.67
	ACETIC	35.83	23.00	17.23	11.63	13.17	9.67		7.53	13.40	17.00	17.67	21.50	17.37
	HCL	42.01	33.00	14.50	4.43	23.00	15.00		9.67	16.37	14.07	9.47	20.47	18.60
	H2O	0.00	0.00	0.90	0.40	0.43	0.00		0.00	0.00	0.00	0.00	0.00	0.00

	SODIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11	POTASSIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	12.63	4.87	2.70	2.57	2.07	1.93		40.17	62.87	48.80	49.57	56.00	48.37
	OXALIC	16.17	8.97	6.47	5.17	4.37	3.53		124.67	228.67	222.67	146.00	132.00	81.50
	ACETIC	5.67	2.83	1.60	1.20	0.47	0.57		14.70	15.20	11.00	8.37	5.47	5.27
	HCL	6.23	3.03	2.07	1.03	0.77	0.67		18.83	19.93	13.57	9.33	8.43	7.50
	H2O	2.70	1.37	0.80	0.60	0.20	0.07		3.33	3.63	3.07	2.30	1.23	0.33
BASALT	CITRIC	10.10	3.67	3.27	2.67	1.53	0.83		3.17	1.07	1.67	1.57	0.50	0.43
	OXALIC	10.60	5.97	5.80	3.60	4.43	4.67		1.00	0.67	0.70	1.77	0.87	0.20
	ACETIC	6.07	2.60	2.00	1.30	1.23	1.07		2.73	1.27	1.33	0.83	0.20	0.27
	HCL	6.30	3.40	2.30	1.10	2.67	2.67		1.90	1.30	1.07	0.50	0.40	0.00
	H2O	1.83	0.67	0.60	0.13	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00

IRON		WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11		ALUMINIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	346.67	206.67	117.67	143.33	100.00	109.67			130.33	111.33	73.33	79.00	81.00	65.33
	OXALIC	596.67	713.33	653.33	406.67	260.00	141.33			258.67	363.00	280.00	222.67	193.33	131.00
	ACETIC	41.00	23.33	12.33	14.00	11.33	9.33			14.33	11.33	12.00	10.00	13.33	5.67
	HCL	39.67	35.67	21.00	19.00	20.00	19.33			9.00	14.67	17.67	11.67	13.00	12.67
	H2O	4.00	0.00	0.00	0.00	0.00	0.00			3.67	0.00	0.00	0.00	0.00	0.00
BASALT	CITRIC	1813.33	2533.33	1533.33	1533.33	653.33	243.33			43.33	14.67	6.33	7.00	7.67	3.33
	OXALIC	426.67	656.67	613.33	613.33	113.00	64.00			55.00	35.33	28.67	23.00	22.33	24.33
	ACETIC	26.33	44.00	56.67	56.67	55.33	44.33			11.00	8.33	9.67	8.00	7.67	3.67
	HCL	33.00	69.33	54.00	54.00	54.33	44.33			7.33	5.00	5.67	5.33	0.73	11.33
	H2O	3.67	0.00	0.00	0.00	0.00	0.00			5.00	0.00	0.00	0.00	0.00	0.00

SILICON		WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	120.00	126.67	80.00	93.33	133.33	106.67
	OXALIC	263.33	410.00	340.00	250.00	243.33	160.00
	ACETIC	21.67	0.00	0.00	0.00	0.00	0.00
	HCL	13.33	0.00	0.00	0.00	0.00	0.00
	H2O	0.00	0.00	0.00	0.00	0.00	0.00
BASALT	CITRIC	1253.33	1366.67	1016.67	673.33	486.67	176.67
	OXALIC	510.00	853.33	1106.00	803.33	1020.00	683.33
	ACETIC	10.00	20.00	20.00	10.00	43.33	23.33
	HCL	20.00	30.00	6.67	0.00	20.00	26.70
	H2O	0.00	0.00	0.00	0.00	0.00	0.00

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BATCH STUDY SOLUTION EXTRACTS (ppm)

	CALCIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11		MAGNESIUM WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	26.03	183.33	215.00	64.67	39.33	19.26		58.33	96.67	145.33	116.00	97.33	93.67
	OXALIC	45.83	44.67	56.00	43.90	38.17	33.83		157.67	133.33	189.00	175.33	155.33	114.33
	ACETIC	48.17	29.67	18.17	16.47	12.17	12.17		6.33	6.57	7.97	12.67	9.43	9.13
	HCL	25.67	30.00	17.17	14.00	6.43	5.47		4.83	11.60	9.00	10.83	8.03	9.37
	HOH	4.23	4.17	3.73	2.03	3.73	4.17		2.27	3.47	2.83	2.37	2.77	4.60
BASALT	CITRIC	80.50	58.33	49.03	47.93	38.33	34.50		936.67	746.67	1190.00	1300.00	836.67	756.67
	OXALIC	10.53	9.83	11.83	28.50	11.40	23.83		191.00	38.87	140.67	143.00	111.67	139.33
	ACETIC	29.67	13.33	11.83	12.07	10.07	12.50		7.17	3.60	4.40	7.37	7.27	9.77
	HCL	42.20	28.17	18.83	17.17	7.73	10.33		10.00	9.23	9.23	11.23	5.30	8.60
	HOH	1.43	1.90	1.33	1.57	1.53	1.13		0.37	0.00	0.00	0.00	0.40	0.00

SODIUM		WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11		POTASSIUM WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	13.33	9.50	6.80	5.70	5.07	4.40		46.33	81.00	133.67	86.33	95.67	83.67
	OXALIC	17.90	10.50	7.57	8.50	7.67	7.30		146.00	178.33	268.00	239.33	196.33	174.67
	ACETIC	6.50	4.90	2.60	2.67	1.60	1.30		24.17	24.00	20.97	26.03	19.93	15.53
	HCL	3.87	4.03	2.70	1.83	1.07	1.17		12.90	21.50	19.97	21.20	12.97	14.37
	H2O	3.07	2.67	1.47	1.97	0.67	0.83		7.07	8.83	7.20	6.07	5.50	6.87
BASALT	CITRIC	10.57	5.60	4.00	4.27	3.10	2.77		3.33	1.17	1.47	1.53	1.13	0.40
	OXALIC	11.00	7.07	5.20	4.73	3.53	4.10		1.77	0.83	1.13	1.10	0.77	0.20
	ACETIC	8.20	4.10	3.73	4.40	3.50	3.40		4.00	1.17	1.43	1.60	1.00	0.00
	HCL	8.80	5.63	4.43	4.70	2.37	3.17		3.03	1.67	2.00	1.87	0.83	0.00
	H2O	2.43	2.90	1.63	1.60	1.07	0.90		0.53	0.00	0.77	1.13	0.63	0.40

IRON		WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11	ALUMINIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	616.67	336.67	373.33	256.67	270.00	233.33		149.33	169.00	162.33	140.67	154.67	142.33
	OXALIC	683.33	600.00	860.00	740.00	680.00	523.33		323.00	333.33	290.00	338.67	326.67	318.33
	ACETIC	203.00	88.67	58.67	63.33	48.00	37.00		12.00	21.67	18.00	26.00	25.00	18.33
	HCL	31.33	84.33	71.00	54.33	34.33	36.67		0.00	2.67	9.33	10.67	10.33	12.33
	H2O	14.33	28.00	13.33	0.00	9.33	28.67		5.00	9.67	5.67	0.00	6.33	11.00
BASALT	CITRIC	2346.67	1996.67	2666.67	1666.67	1200.00	1113.33		42.33	20.00	13.00	13.00	15.00	12.00
	OXALIC	296.67	173.33	306.67	263.33	193.33	246.67		53.67	30.67	20.33	18.67	21.00	19.67
	ACETIC	36.67	14.00	17.67	20.00	21.67	19.67		12.33	18.33	19.33	19.33	21.33	18.00
	HCL	65.33	50.67	36.00	19.00	13.33	11.67		4.67	22.00	23.00	17.33	15.00	17.33
	H2O	14.67	8.67	2.67	0.00	4.67	1.00		6.67	9.33	5.33	0.00	7.33	0.00

SILICON		WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	140.00	196.70	203.30	206.00	190.00	196.67
	OXALIC	323.33	373.30	350.00	380.00	370.00	336.67
	ACETIC	33.33	50.00	13.30	30.00	26.70	30.00
	HCL	0.00	23.30	0.00	20.00	6.70	13.33
	H2O	16.67	23.30	0.00	0.00	0.00	0.00
BASALT	CITRIC	1113.33	1080.00	1323.30	1346.00	1016.00	903.33
	OXALIC	693.33	643.00	763.30	820.00	753.00	760.00
	ACETIC	26.67	30.00	46.67	40.00	30.00	40.00
	HCL	33.33	36.70	43.30	33.00	0.00	26.00
	H2O	23.33	20.00	3.33	0.00	0.00	0.00

BATCH SOLUTION EXTRACTS (ppm)
Particles <1mm

	CALCIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	330.00	75.00	60.20	37.13	48.50	39.00
	OXALIC	8.00	24.75	33.50	28.25	23.20	19.00
	ACETIC	50.00	46.25	53.00	30.50	22.25	21.00
BASALT	CITRIC	275.00	96.00	141.00	135.00	115.00	114.00
	OXALIC	8.10	6.00	9.75	10.00	6.70	7.75
	ACETIC	31.20	18.00	17.00	16.25	14.50	17.00

	MAGNESIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	2260.00	1315.00	1260.00	735.00	975.00	635.00
	OXALIC	9.80	64.00	136.00	97.50	69.50	51.50
	ACETIC	10.90	8.70	8.20	6.10	3.55	4.15
BASALT	CITRIC	69.00	92.00	70.00	63.50	61.00	85.00
	OXALIC	18.00	21.95	154.00	130.00	113.00	82.50
	ACETIC	15.20	4.30	16.50	2.75	2.40	2.85

	SODIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	77.50	15.35	8.65	4.55	3.90	2.75
	OXALIC	23.50	16.55	17.70	10.80	8.50	7.25
	ACETIC	18.50	15.25	11.80	5.45	3.65	3.50
BASALT	CITRIC	50.50	14.45	9.60	6.20	3.75	5.10
	OXALIC	33.25	23.50	24.80	13.10	5.25	3.20
	ACETIC	12.75	10.00	14.50	7.85	5.55	5.70

	POTASSIUM	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	13.90	3.85	2.65	0.45	0.80	0.80
	OXALIC	29.75	89.50	240.00	145.00	110.00	72.50
	ACETIC	43.75	58.50	50.00	18.45	13.00	12.50
BASALT	CITRIC	169.00	52.45	54.50	59.75	50.70	73.50
	OXALIC	3.75	2.75	3.10	2.10	1.20	0.55
	ACETIC	3.00	2.50	3.85	2.35	1.55	0.35

IRON		WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	9150.00	1030.00	2250.00	1250.00	1300.00	1325.00
	OXALIC	7.50	57.00	280.00	250.00	200.00	170.00
	ACETIC	1650.00	660.00	615.00	190.00	105.00	120.00
BASALT	CITRIC	13400.00	9300.00	390.00	200.00	110.00	200.00
	OXALIC	12.50	39.00	260.00	175.00	175.00	150.00
	ACETIC	790.00	155.00	205.00	76.00	34.00	20.00

SILICON		WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	1485.00	720.00	525.00	535.00	610.00	590.00
	OXALIC	115.00	230.00	375.00	230.00	160.00	155.00
	ACETIC	0.00	20.00	65.00	20.00	20.00	20.00
BASALT	CITRIC	230.00	135.00	120.00	135.00	95.00	120.00
	OXALIC	475.00	815.00	880.00	815.00	570.00	550.00
	ACETIC	25.00	30.00	25.00	25.00	0.00	0.00

ALUMINUM		WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
GRANITE	CITRIC	230.00	50.00	28.00	15.50	4.50	6.50
	OXALIC	380.00	248.00	355.00	264.00	199.50	215.00
	ACETIC	0.00	8.50	31.00	30.00	24.00	21.00
BASALT	CITRIC	198.00	197.00	151.00	136.00	96.50	111.50
	OXALIC	88.00	97.00	110.00	64.00	27.00	14.00
	ACETIC	0.00	24.00	39.00	27.00	27.50	25.50

Appendix H: Tables of Data from pH Analyses of Weathered
Granodiorite and Basaltic Residues and Solution
Extracts

*Data is average of 3 replicate samples

pH OF UNWEATHERED AND WEATHERED RESIDUES

PARENT MATERIALS	HOH	CaCl (.01M)
Granodiorite A	7.10	6.55
Granodiorite B	7.30	5.70
Basalt A	6.60	5.00
Basalt B	7.00	5.83

*A:.1mm − .5mm
*B:<.1mm

EXPERIMENT 1: COLUMN STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	HOH	CaCl(.01M)
GrDio. A	Citric	3.08	2.99
GrDio. A	Oxalic	5.20	4.20
GrDio. A	Acetic	4.83	4.82
GrDio. A	HCL	2.93	3.16
GrDio. A	HOH	5.49	5.80
Basalt A	Citric	5.84	5.70
Basalt A	Oxalic	6.30	4.40
Basalt A	Acetic	4.60	4.18
Basalt A	HCL	3.07	3.34
Basalt A	HOH	4.92	5.47

EXPERIMENT 3: COLUMN STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	HOH	CaCl(.01M)
GrDio. A	Citric	2.94	2.73
GrDio. A	Oxalic	4.50	3.56
GrDio. A	Acetic	4.53	4.06
GrDio. A	HCL	4.00	3.60
GrDio. A	HOH	5.40	5.82
Basalt A	Citric	4.25	3.48
Basalt A	Oxalic	4.81	4.17
Basalt A	Acetic	4.83	4.61
Basalt A	HCL	4.23	3.96
Basalt A	HOH	5.26	5.08

EXPERIMENT 2: BATCH STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	HOH	CaCl(.01M)
GrDio. A	Citric	3.35	3.18
GrDio. A	Oxalic	5.00	4.40
GrDio. A	Acetic	4.45	4.40
GrDio. A	HCL	6.11	6.09
GrDio. A	HOH	6.65	6.40
Basalt A	Citric	5.84	5.80
Basalt A	Oxalic	6.20	5.35
Basalt A	Acetic	4.51	4.30
Basalt A	HCL	5.40	5.02
Basalt A	HOH	5.53	5.72

EXPERIMENT 4: BATCH-11 WEEKS

PARENT MATERIAL	TREATMENT	HOH	CaCl(.01M)
GrDio. A	Citric	2.82	2.88
GrDio. A	Oxalic	4.32	3.84
GrDio. A	Acetic	4.49	4.36
GrDio. A	HCL	3.80	4.26
GrDio. A	HOH	5.35	6.10
Basalt A	Citric	5.57	5.50
Basalt A	Oxalic	5.13	4.42
Basalt A	Acetic	4.51	4.15
Basalt A	HCL	3.50	3.95
Basalt A	HOH	5.50	5.80

BATCH and COLUMN STUDY- 4 WEEK WEATHERING EXPERIMENT
PH ANALYSES OF SOLUTION EXTRACTS (Average of 3 replicates)

COLUMN	TREATMENT	TIME 0	WEEK 1	WEEK 3	WEEK 4
GRANODIORITE	CITRIC	2.2	2.3	2.3	2.3
GRANODIORITE	OXALIC	1.6	1.9	2.8	4.4
GRANODIORITE	ACETIC	2.9	3.1	3.8	3.8
GRANODIORITE	HCl	2.3	2.3	2.4	2.4
GRANODIORITE	HOH	5.8	6.0	7.1	7.2
BASALT	CITRIC	2.2	4.1	5.2	6.4
BASALT	OXALIC	1.6	4.5	5.5	6.7
BASALT	ACETIC	2.9	3.5	3.5	3.5
BASALT	HCl	2.3	2.3	3.0	3.2
BASALT	HOH	5.8	6.7	6.7	6.8

BATCH	TREATMENT	TIME 0	WEEK 1	WEEK 3	WEEK 4
GRANODIORITE	CITRIC	2.2	2.5	2.5	2.6
GRANODIORITE	OXALIC	1.6	2.7	3.4	4.4
GRANODIORITE	ACETIC	2.9	3.8	4.0	4.1
GRANODIORITE	HCl	2.3	2.4	2.5	2.5
GRANODIORITE	HOH	5.8	6.8	7.0	7.2
BASALT	CITRIC	2.2	4.0	4.1	4.1
BASALT	OXALIC	1.6	5.0	5.3	6.6
BASALT	ACETIC	2.9	3.5	3.9	4.0
BASALT	HCl	2.3	2.3	2.4	2.6
BASALT	HOH	5.8	6.6	6.7	7.0

pH OF SOLUTON EXTRACTS

COLUMN EXPERIMENT - 11 WEEKS

PARENT MATERIAL	TREATMENT	TIME 0	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
Gr.Dio. A	Citric	2.2	2.2	2.3	2.4	2.3	2.2	2.2
Gr.Dio. A	Oxalic	1.6	1.8	1.6	1.5	1.5	1.4	1.4
Gr.Dio. A	Acetic	2.9	3.4	3.2	3.2	3.0	2.9	2.9
Gr.Dio. A	HCL	2.3	3.7	3.2	3.0	3.0	2.9	2.8
Gr.Dio. A	HOH	5.8	6.7	7.3	6.9	6.3	6.6	6.3
Basalt A	Citric	2.2	3.9	5.1	3.8	3.3	2.8	2.6
Basalt A	Oxalic	1.6	5.0	5.2	4.9	3.7	3.0	1.7
Basalt A	Acetic	2.9	3.3	3.4	3.2	3.3	3.3	3.2
Basalt A	HCL	2.3	3.4	3.7	3.4	3.6	3.1	3.1
Basalt A	HOH	5.8	4.5	6.5	6.8	5.7	5.8	5.5

BATCH - 11 WEEKS

PARENT MATERIAL	TREATMENT	TIME 0	WEEK 1	WEEK 3	WEEK 5	WEEK 7	WEEK 9	WEEK 11
Gr.Dio. A	Citric	2.2	2.3	2.4	2.4	2.4	2.4	2.3
Gr.Dio. A	Oxalic	1.6	1.8	1.8	1.8	1.8	1.7	1.7
Gr.Dio. A	Acetic	2.9	3.6	3.4	3.6	3.5	3.3	3.4
Gr.Dio. A	HCL	2.3	4.1	4.2	3.9	3.9	3.9	3.9
Gr.Dio. A	HOH	5.8	6.3	7.5	7.2	7.1	6.9	6.8
Basalt A	Citric	2.2	3.8	4.1	4.4	4.2	3.9	3.8
Basalt A	Oxalic	1.6	4.5	4.6	5.2	5.0	5.1	5.1
Basalt A	Acetic	2.9	3.3	3.2	3.2	3.3	3.2	3.2
Basalt A	HCL	2.3	3.8	3.3	3.3	3.4	3.4	3.4
Basalt A	HOH	5.8	6.6	6.8	6.7	6.9	6.7	6.5

Appendix I: Tables of Data from XRF Analyses of Unweathered
               and Weathered Granodiorite and Basalt

XRF DATA FOR MAJOR ELEMENTAL ANALYSIS (expressed as % weight oxide)

PARENT. MATERIALS	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	Na2O	MnO2	TiO2	P2O5	SO2	Total
Granodiorite A	63.80	16.61	5.21	4.93	2.15	2.31	3.77	0.11	0.50	0.11	0.02	99.52
Granodiorite B	63.55	16.43	5.53	4.99	2.27	2.14	3.68	0.13	0.54	0.10	0.02	99.38
Basalt A	49.96	15.17	12.46	8.41	9.04	0.54	3.38	0.16	1.51	0.25	0.02	100.90
Basalt B	51.02	15.41	12.40	8.39	9.13	0.59	3.41	0.18	1.50	0.25	0.02	102.30
Hawaiin Basalt	50.76	12.75	12.92	10.90	10.04	0.45	2.33	0.16	2.38	0.23	0.02	102.94

* A:.1-.5mm

* B:<.1mm

EXPERIMENT 1: COLUMN STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	Na2O	MnO2	TiO2	P2O5	SO2	Total
GrDio.A	Citric	62.13	15.28	4.95	4.66	1.98	2.09	3.76	0.11	0.48	0.06	0.02	95.52
GrDio.A	Oxalic	64.90	16.81	4.42	4.95	1.95	2.21	4.04	0.10	0.51	0.05	0.02	99.96
GrDio.A	Acetic	63.81	16.83	4.88	4.92	2.12	2.33	4.08	0.11	0.52	0.12	0.02	99.74
GrDio.A	HCl	62.18	17.11	4.97	4.82	2.19	2.40	3.93	0.11	0.58	0.08	0.02	98.39
GrDio.A	HOH	62.30	17.22	4.77	4.95	2.09	2.33	3.99	0.10	0.51	0.11	0.02	98.39
Basalt A	Citric	52.24	16.48	9.86	9.23	6.17	0.65	3.72	0.13	1.68	0.22	0.02	100.40
Basalt A	Oxalic	51.06	15.90	11.08	8.82	7.07	0.59	3.60	0.15	1.53	0.20	0.02	100.02
Basalt A	Acetic	50.36	15.36	11.39	8.63	7.20	0.59	3.59	0.15	1.56	0.26	0.02	99.11
Basalt A	HCl	50.00	15.55	11.30	8.75	7.28	0.58	3.47	0.15	1.58	0.26	0.02	98.94
Basalt A	HOH	50.36	15.43	11.71	8.78	7.61	0.60	3.63	0.15	1.56	0.26	0.02	100.11

EXPERIMENT 2: BATCH STUDY - 4 WEEKS

PARENT MATERIAL	TREATMENT	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	Na2O	MnO2	TiO2	P2O5	SO2	Total
GrDio.A	Citric	62.78	17.05	4.28	4.88	1.89	2.28	3.94	0.09	0.48	0.09	0.02	97.78
GrDio.A	Oxalic	62.49	16.51	4.71	4.89	2.13	2.34	3.94	0.09	0.52	0.11	0.02	97.75
GrDio.A	Acetic	65.84	16.84	5.16	4.95	2.20	2.27	4.23	0.11	0.52	0.12	0.02	102.26
GrDio.A	HCl	64.68	16.31	5.37	4.84	2.13	2.24	4.08	0.11	0.50	0.12	0.02	100.40
GrDio.A	HOH	63.42	16.73	4.96	4.85	2.11	2.28	3.91	0.11	0.51	0.11	0.02	99.01
Basalt A	Citric	52.08	16.22	10.49	8.94	7.39	0.59	4.08	0.13	1.54	0.25	0.02	101.73
Basalt A	Oxalic	48.65	15.06	11.41	8.35	7.89	0.56	3.52	0.14	1.48	0.26	0.02	97.34
Basalt A	Acetic	50.32	15.05	11.32	8.63	7.46	0.59	3.46	0.14	1.51	0.26	0.02	99.76
Basalt A	HCl	49.00	14.93	11.22	8.44	7.63	0.56	3.31	0.14	1.51	0.26	0.02	97.02
Basalt A	HOH	50.93	15.73	11.62	8.74	7.49	0.62	3.66	0.15	1.58	0.27	0.02	100.81

EXPERIMENT 3: COLUMN STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	Na2O	MnO2	TiO2	P2O5	SO2	Total
GrDio.A	Citric	64.73	16.75	4.35	4.81	1.73	2.09	3.71	0.09	0.44	0.00	0.02	98.72
GrDio.A	Oxalic	65.11	16.24	3.32	4.94	1.36	1.78	4.06	0.08	0.32	0.04	0.02	97.27
GrDio.A	Acetic	63.81	16.73	4.69	4.83	1.98	2.16	4.04	0.09	0.48	0.07	0.02	98.90
GrDio.A	HCl	63.70	16.71	4.76	4.79	1.91	2.18	4.26	0.11	0.48	0.05	0.02	98.97
GrDio.A	HOH	63.28	16.90	4.78	4.97	2.05	2.29	4.65	0.11	0.49	0.11	0.02	99.65
Basalt A	Citric	54.35	18.11	6.82	9.92	3.11	0.69	4.62	0.10	1.62	0.17	0.02	99.53
Basalt A	Oxalic	45.19	14.69	9.28	8.31	5.34	0.57	3.51	0.13	1.15	0.10	0.02	88.29
Basalt A	Acetic	49.89	15.50	11.26	8.67	7.26	0.56	3.60	0.14	1.57	0.26	0.02	98.73
Basalt A	HCl	50.99	15.63	11.50	8.68	7.63	0.59	3.88	0.15	1.58	0.24	0.02	100.89
Basalt A	HOH	49.73	14.97	11.82	8.44	7.95	0.58	3.55	0.14	1.52	0.26	0.02	98.98

EXPERIMENT 4: BATCH-11 WEEKS

PARENT MATERIAL	TREATMENT	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	Na2O	MnO2	TiO2	P2O5	SO2	Total
GrDio.A	Citric	63.94	16.80	4.15	4.83	1.73	2.08	4.17	0.08	0.44	0.02	0.02	98.26
GrDio.A	Oxalic	61.78	15.64	3.65	4.79	1.28	1.82	4.02	0.08	0.32	0.02	0.02	93.42
GrDio.A	Acetic	63.72	16.77	4.93	4.88	2.08	2.20	4.07	0.10	0.50	0.11	0.02	99.38
GrDio.A	HCl	64.61	17.02	4.65	4.92	1.87	2.23	4.02	0.09	0.45	0.12	0.02	100.00
GrDio.A	HOH	64.05	16.80	4.94	4.87	2.02	2.28	3.95	0.11	0.50	0.12	0.02	99.66
Basalt A	Citric	54.49	17.98	7.50	9.73	4.09	0.64	4.20	0.11	1.64	0.24	0.02	100.64
Basalt A	Oxalic	45.18	14.38	10.54	8.06	7.29	0.51	3.42	0.15	1.31	0.16	0.02	91.02
Basalt A	Acetic	50.93	15.70	11.76	8.65	7.87	0.58	3.57	0.15	1.56	0.26	0.02	101.05
Basalt A	HCl	48.39	14.63	11.25	8.28	7.29	0.56	3.35	0.14	1.46	0.25	0.02	95.62
Basalt A	HOH	50.50	15.63	11.98	8.13	8.13	0.58	3.68	0.15	1.56	0.26	0.02	100.62

EXPERIMENT 5: BATCH STUDY - 11 WEEKS

PARENT MATERIAL	TREATMENT	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	Na2O	MnO2	TiO2	P2O5	SO2	Total
Gr.Dio. B	Citric	62.77	14.15	5.11	4.64	1.87	1.87	6.49	0.10	0.39	0.02	0.02	97.43
Gr.Dio. B	Oxalic	60.12	13.01	7.52	4.64	1.90	1.63	3.20	0.13	0.34	0.01	0.02	92.52
Gr.Dio. B	Acetic	63.90	14.91	6.69	4.96	2.24	2.01	3.72	0.12	0.45	0.21	0.02	99.23
Basalt B	Citric	51.03	15.94	8.08	9.14	5.69	0.53	3.59	0.10	1.43	0.19	0.02	95.74
Basalt B	Oxalic	45.84	14.60	11.17	8.39	7.57	0.47	3.39	0.15	1.20	0.10	0.02	92.90
Basalt B	Acetic	45.06	14.25	11.19	8.29	7.35	0.48	3.13	0.14	1.19	0.11	0.02	91.21
Hawaiin	Citric	52.48	14.08	12.32	11.78	8.83	0.40	2.15	0.17	2.10	0.23	0.02	104.56
Hawaiin	Oxalic	46.25	11.57	11.47	10.10	9.81	0.43	2.06	0.16	1.90	0.17	0.02	93.94

EXPERIMENT 6: CRUST ANALYSES
BATCH EXPERIMENT - 11 WEEKS

PARENT MATERIAL	TREATMENT	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	Na2O	MnO2	TiO2	P2O5	SO2	Total
Gr.Dio. A	Citric	39.97	11.45	6.57	2.58	3.99	3.07	1.87	0.16	1.31	0.02	0.02	71.01
Gr.Dio. A	Oxalic	37.09	9.13	16.22	3.66	2.79	1.97	1.60	0.23	0.97	0.02	0.02	73.70
Gr.Dio. A	Acetic	63.33	16.88	4.79	4.61	2.36	2.44	3.88	0.10	0.63	0.11	0.02	99.15
Gr.Dio. A	HCl	62.70	16.83	5.52	4.61	2.35	2.38	3.70	0.10	0.68	0.14	0.02	99.03
Gr.Dio. A	HOH	63.83	16.81	4.37	4.72	2.05	2.39	3.86	0.10	0.51	0.10	0.02	98.76
Basalt A	Citric	51.33	17.05	7.04	9.31	4.24	0.65	4.29	0.08	1.60	0.23	0.02	95.84
Basalt A	Oxalic	—	—	—	—	—	—	—	—	—	—	—	—
Basalt A	Acetic	50.43	16.08	11.51	8.65	6.46	0.69	3.78	0.15	1.58	0.27	0.02	99.62
Basalt A	HCl	50.65	16.36	10.51	8.98	6.01	0.61	3.95	0.13	1.56	0.27	0.02	99.05
Basalt A	HOH	—	—	—	—	—	—	—	—	—	—	—	—
Gr.Dio. B	Citric	41.63	12.23	6.20	5.43	5.18	0.45	2.82	0.09	0.97	0.08	0.02	75.10
Gr.Dio. B	Oxalic	35.06	8.11	20.21	3.79	1.52	1.27	1.68	0.17	0.41	0.00	0.02	72.24
Gr.Dio. B	Acetic	46.69	11.96	23.17	3.49	1.98	1.90	2.47	0.08	0.54	0.41	0.02	92.71
Basalt B	Citric	52.47	13.68	3.69	3.93	2.42	2.39	2.95	0.12	0.66	0.15	0.02	82.48
Basalt B	Oxalic	24.26	6.00	14.63	4.30	7.43	0.26	2.47	0.19	1.15	0.28	0.02	60.99
Basalt B	Acetic	51.51	17.86	9.21	9.05	4.79	0.54	4.03	0.11	1.31	0.25	0.02	98.68

Appendix J: Tables of Calculations of Molar Oxide Ratios of
Unweathered and Weathered Granodiorite and Basalt

*Calculations determined from XRF data

EXPERIMENT 1: COLUMN STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	SiO2/Al2O3	SiO2/R2O3	Al2O3/Fe2O3	Bases:Alumina	Bases:Silica
GrDio.A	Citric	6.87	5.72	5.00	1.40	0.20
GrDio.A	Oxalic	6.75	5.68	5.33	1.44	0.21
GrDio.A	Acetic	6.56	5.53	5.33	1.44	0.22
GrDio.A	HCl	6.06	5.15	5.67	1.35	0.22
GrDio.A	HOH	6.12	5.20	5.67	1.29	0.21
Basalt A	Citric	5.44	3.95	2.67	2.31	0.42
Basalt A	Oxalic	5.31	3.70	2.67	2.50	0.47
Basalt A	Acetic	5.60	3.82	2.14	2.60	0.46
Basalt A	HCl	5.53	3.82	2.14	2.67	0.48
Basalt A	HOH	5.60	3.82	2.14	2.73	0.49

EXPERIMENT 2: BATCH STUDY- 4 WEEKS

PARENT MATERIAL	TREATMENT	SiO2/Al2O3	SiO2/R2O3	Al2O3/Fe2O3	Bases:Alumina	Bases:Silica
GrDio.A	Citric	6.18	5.25	5.67	1.29	0.21
GrDio.A	Oxalic	6.50	5.47	5.33	1.44	0.21
GrDio.A	Acetic	6.47	5.50	5.67	1.35	0.21
GrDio.A	HCl	6.69	5.63	5.33	1.44	0.21
GrDio.A	HOH	6.63	5.58	5.33	1.38	0.21
Basalt A	Citric	5.44	3.78	2.29	2.56	0.47
Basalt A	Oxalic	5.40	3.68	2.14	2.73	0.51
Basalt A	Acetic	5.25	3.65	2.29	2.50	0.48
Basalt A	HCl	5.47	3.73	2.14	2.60	0.48
Basalt A	HOH	5.67	3.86	2.14	2.83	0.48

EXPERIMENT 3: COLUMN STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	SiO2/Al2O3	SiO2/R2O3	Al2O3/Fe2O3	Bases:Alumina	Bases:Silica
GrDio.A	Citric	6.75	5.68	5.33	1.31	0.19
GrDio.A	Oxalic	6.75	6.00	8.00	1.25	0.18
GrDio.A	Acetic	6.63	5.58	5.33	1.37	0.21
GrDio.A	HCl	6.63	5.58	5.33	1.44	0.22
GrDio.A	HOH	6.56	5.53	5.33	1.50	0.23
Basalt A	Citric	5.00	4.09	4.50	1.89	0.38
Basalt A	Oxalic	5.36	3.75	2.33	2.50	0.47
Basalt A	Acetic	5.53	3.77	2.14	2.67	0.48
Basalt A	HCl	5.67	3.86	2.14	2.73	0.48
Basalt A	HOH	5.53	3.77	2.14	2.80	0.51

EXPERIMENT 4: BATCH- 11 WEEKS

PARENT MATERIAL	TREATMENT	SiO2/Al2O3	SiO2/R2O3	Al2O3/Fe2O3	Bases:Alumina	Bases:Silica
GrDio.A	Citric	6.63	5.58	5.33	1.37	0.21
GrDio.A	Oxalic	6.87	6.06	7.50	1.33	0.19
GrDio.A	Acetic	6.63	5.58	5.33	1.37	0.21
GrDio.A	HCl	6.29	5.35	5.67	1.29	0.21
GrDio.A	HOH	6.69	5.63	5.33	1.37	0.21
Basalt A	Citric	5.06	3.96	3.60	3.50	0.38
Basalt A	Oxalic	5.36	3.57	2.00	2.79	0.52
Basalt A	Acetic	5.67	3.86	2.14	2.73	0.48
Basalt A	HCl	5.79	3.86	2.00	2.79	0.48
Basalt A	HOH	5.60	3.65	1.88	2.80	0.50

EXPERIMENT 5: BATCH STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	SiO2/Al2O3	SiO2/R2O3	Al2O3/Fe2O3	Bases:Alumina	Bases:Silica
Gr.Dio. B	Citric	7.43	6.12	4.67	1.79	0.24
Gr.Dio. B	Oxalic	7.69	5.56	2.60	1.54	0.20
Gr.Dio. B	Acetic	7.07	5.58	3.75	1.53	0.22
Basalt B	Citric	5.31	4.05	3.20	2.31	0.43
Basalt B	Oxalic	5.43	3.70	2.00	2.44	0.51
Basalt B	Acetic	5.54	3.57	2.00	2.71	0.51
Hawaiin	Citric	6.21	3.95	1.75	3.29	0.53
Hawaiin	Oxalic	7.06	4.28	1.75	4.09	0.58

EXPERIMENT 6: CRUST ANALYSES
    BATCH EXPERIMENT-11 WEEKS

PARENT MATERIAL	TREATMENT	SiO2/Al2O3	SiO2/R2O3	Al2O3/Fe2O3	Bases:Alumina	Bases:Silica
Gr.Dio. A	Citric	6.09	4.47	2.75	1.90	0.31
Gr.Dio. A	Oxalic	6.89	3.26	0.90	2.11	0.31
Gr.Dio. A	Acetic	6.18	5.25	5.66	1.35	0.22
Gr.Dio. A	HCl	6.12	5.20	5.66	1.35	0.22
Gr.Dio. A	HOH	6.63	5.58	5.33	1.37	0.21
Basalt A	Citric	5.00	4.05	4.25	2.00	0.40
Basalt A	Oxalic	x	x	x	x	x
Basalt A	Acetic	5.25	3.65	2.29	2.31	0.44
Basalt A	HCl	5.25	3.65	2.29	2.31	0.44
Basalt A	HOH	x	x	x	x	x
Gr.Dio. B	Citric	5.75	4.31	3.00	2.25	0.39
Gr.Dio. B	Oxalic	7.25	2.76	0.62	1.87	0.26
Gr.Dio. B	Acetic	6.50	2.89	0.80	1.42	0.22
					1.62	0.24
Basalt B	Citric	6.69	5.80	6.50	5.00	0.70
Basalt B	Oxalic	6.67	2.66	0.67	1.89	0.40
Basalt B	Acetic	4.78	3.58	3.00	3.55	0.53
Hawaiin	Citric	6.64	4.29	1.83		

Appendix K$_1$:   Tables of Data from XRD Analyses of Unweathered
and Weathered Granodiorite and Basalt.

X-RAY DIFFRACTION ANALYSES

GRANODIORITE- COLUMN EXPERIMENT

MINERAL	ANGLE 2θ	D-SPACE	INTENSITY UNWEATHERED	CITRIC ACID		OXALIC ACID		ACETIC ACID		HCl		HOH	
				WKS-4	WKS-11	WKS-4	WKS-11	WKS-4	WKS-11	WKS-4	WKS-11	WKS-4	WKS-11
Micas	8.885	9.5220	598	62	115	64	143	116	109	107	129	105	159
Hornblende	10.557	8.3794	121	57	N.D.	73	104	60	69	N.D.	N.D.	61	68
K-Spar	20.973	4.2356	220	167	155	170	194	176	140	175	199	129	148
Plagioclase	22.071	4.0272	92	155	180	156	155	136	157	149	168	178	149
K-Spar	22.943	3.8761	108	55	65	77	N.D.	79	N.D.	66	66	73	N.D.
Ilmenite	23.798	3.7388	59	125	106	106	111	119	136	131	96	104	143
Plagioclase	24.445	3.6413	94	117	111	138	139	107	112	119	105	154	120
Quartz/ Micas	26.711	3.3373	1340	1222	1222	1026	1186	1254	768	1240	1158	776	1272
Plagioclase	28.061	3.1758	1194	407	598	760	1027	1130	591	748	818	540	467
Hornblende	28.365	3.1463	118	137	206	N.D.	N.D.	151	141	N.D.	175	120	132
Pyroxene/Magnetite	29.788	2.9992	57	67	92	101	80	103	116	84	137	93	61
Pyroxene	30.537	2.9273	112	129	133	160	137	130	134	140	143	132	148
Fe- silicate	31.605	2.8308	55	136	77	86	106	120	103	97	87	90	108
Biotite	33.951	2.6404	72	67	59	61	61	N.D.	N.D.	65	N.D.	58	N.D.
Magnetite/Hematite	35.692	2.5155	126	115	116	115	108	103	204	108	122	104	100
Quartz	36.702	2.4485	91	104	137	100	110	114	130	76	108	100	65
Titanite/ Hematite	39.586	2.2766	62	98	126	125	142	100	111	71	106	92	96
Periclase	42.513	2.1263	128	104	68	97	123	78	99	73	88	71	114
Micas	45.084	2.0109	93	47	N.D.	54	55	68	N.D.	57	N.D.	N.D.	N.D.
Quartz	50.283	1.8145	248	140	176	82	203	169	83	168	124	89	118
Fe- silicate	51.525	1.7736	128	90	73	55	68	66	81	69	74	81	66
Magnetite/Hematite	54.944	1.6711	73	58	66	60	73	62	62	N.D.	67	63	N.D.

GRANODIORITE- BATCH EXPERIMENT

MINERAL	ANGLE 2θ	D-SPACE	INTENSITY UNWEATHERED	CITRIC ACID		OXALIC ACID		ACETIC ACID		HCl		HOH	
				WKS- 4	WKS- 11	WKS- 4	WKS- 11	WKS- 4	WKS- 11	WKS- 4	WKS- 11	WKS- 4	WKS -11
Micas	8.885	9.5220	598	105 105	147	N.D.	N.D.	162	126	161	150	85	166
Hornblende	10.557	8.3794	121	55	65	N.D.	N.D.	79	61	81	60	76	48
K-Spar	20.973	4.2356	220	220	167	114	121	159	226	182	174	167	167
Plagioclase	22.071	4.0272	92	150	157	81	99	158	133	158	133	145	127
K-Spar	22.943	3.8761	108	92	66	N.D.	N.D.	83	55	81	55	62	N.D.
Ilmenite	23.798	3.7388	59	145	117	65	64	98	198	94	57	108	148
Plagioclase	24.445	3.6413	94	154	160	57	62	118	124	123	110	120	119
Quartz/ Micas	26.711	3.3373	1340	1189	999	611	616	1061	1295	1524	1295	869	887
Plagioclase	28.061	3.1758	1194	563	813	488	496	587	688	710	687	521	1013
Hornblende	28.365	3.1463	118	96	166	81	79	161	203	107	101	84	154
Proxene/ Magnetite	29.788	2.9992	57	78	88	68	72	94	78	92	78	72	100
Pyroxene	30.537	2.9273	112	144	124	107	60	153	135	170	135	133	187
Fe- silicate	31.605	2.8308	55	97	117	60	N.D	90	92	67	92	77	80
Biotite	33.951	2.6404	72	77	58	66	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Magnetite/Hematite	35.692	2.5155	126	114	125	79	61	97	99	101	99	131	92
Quartz	36.702	2.4485	91	87	127	89	63	98	220	175	150	109	95
Titanite/ Hematite	39.586	2.2766	62	89	113	96	61	89	104	69	98	95	105
Periclase	42.513	2.1263	128	67	113	69	87	69	118	83	67	107	52
Micas	45.084	2.0109	93	N.D.	N.D.	N.D.	N.D.	54	N.D.	80	56	N.D.	N.D.
Quartz	50.283	1.8145	248	92	117	110	76	145	237	166	116	167	119
Fe- silicate	51.525	1.7736	128	75	83	72	N.D.	51	83	79	98	60	92
Magnetite/Hematite	54.944	1.6711	73	39	62	50	52	66	56	68	70	N.D	N.D.

BASALT- COLUMN EXPERIMENT

MINERAL	ANGLE 2θ	D-SPACE	INTENSITY UNWEATHERED	CITRIC ACID		OXALIC ACID		ACETIC ACID		HCl		HOH	
				WKS- 4	WKS- 11	WKS- 4	WKS- 11	WKS- 4	WKS- 11	WKS- 4	WKS- 11	WKS- 4	WKS -11
Ox-Precipitate	18.290	4.8503	N.D.	N.D.	N.D.	N.D.	132	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Plagioclase	22.120	4.0184	151	190	157	143	129	152	133	161	138	155	163
Forsterite	22.952	3.8746	69	65	62	72	96	94	74	60	121	56	63
Plagioclase	23.770	3.7431	227	376	310	220	189	166	172	178	189	173	220
a) Plagioclase	24.562	3.6242	116	139	115	123	113	116	101	112	133	118	96
b) Fayalite	"	"	"	"	"	"	"	"	"	"	"	"	"
Micas/ Quartz	26.554	3.3567	72	92	76	82	N.D.	66	N.D.	67	N.D.	60	72
a) Plagioclase	27.908	3.1968	425	645	298	433	507	425	342	421	337	254	470
b) Hypersthene	"	"	"	"	"	"	"	"	"	"	"	"	"
Hornblende	28.508	3.1309	164	126	69	150	168	157	140	121	116	N.D.	N.D.
Pyroxene	29.858	2.9923	161	197	139	168	162	194	133	191	163	150	176
Pyroxene	30.440	2.9364	161	165	158	150	142	140	152	156	167	119	150
Hypersthene	30.827	2.9004	73	64	62	70	N.D.	54	79	77	107	68	64
Fayalite	31.602	2.8310	94	91	88	90	70	79	74	74	98	69	100
Hornblende	32.199	2.7799	N.D.	N.D.	N.D.	82	N.D.	80	59	59	N.D.	121	110
a) Ilmenite	35.008	2.5630	61	71	66	90	81	73	61	61	69	63	75
b) Fayalite	"	"	"	"	"	"	"	"	"	"	"	"	"
a) Magnetite	35.659	2.5177	175	165	144	170	133	167	158	170	173	233	156
b) Fayalite	"	"	"	"	"	"	"	"	"	"	"	"	"
c) Hematite	"	"	"	"	"	"	"	"	"	"	"	"	"
Quartz	36.448	2.4650	N.D.	57	34	79	96	160	89	84	62	87	112
Periclase	42.376	2.1329	87	125	76	81	102	99	77	78	80	77	71
Ox-Precipitate	44.840	2.0213	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D
Hematite	49.828	1.8300	N.D.	75	66	73	62	69	68	63	68	67	68
Fayalite	51.608	1.7710	150	86	61	N.D.	58	57	73	61	66	N.D.	84
Ilmenite	52.286	1.7496	60	53	47	54	89	59	74	73	64	81	76

BASALT- BATCH EXPERIMENT

MINERAL	ANGLE 2θ	D-SPACE	INTENSITY UNWEATHERED	CITRIC ACID		OXALIC ACID		ACETIC ACID		HCl		HOH	
				WKS- 4	WKS- 11	WKS- 4	WKS- 11	WKS- 4	WKS- 11	WKS- 4	WKS- 11	WKS- 4	WKS -11
Ox-Precipitate	18.290	4.8503	N.D.	N.D.	N.D.	N.D.	117	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Plagioclase	22.120	4.0184	151	185	152	116	199	160	141	157	168	127	129
Forsterite	22.952	3.8746	69	70	71	73	55	68	62	69	52	70	52
Plagioclase	23.770	3.7431	227	238	186	230	144	225	223	179	212	172	153
a) Plagioclase	24.562	3.6242	116	158	116	112	154	150	146	107	130	107	96
b) Fayalite	"	"	"	"	"	"	"	"	"	"	"	"	"
Micas/ Quartz	26.554	3.3567	72	75	65	75	77	76	86	78	75	60	71
a) Plagioclase	27.908	3.1968	425	406	295	380	300	411	354	308	465	345	435
b) Hypersthene	"	"	"	"	"	"	"		"	"	"	"	"
Hornblende	28.508	3.1309	164	160	59	98	N.D.	123	86	116	129	90	55
Pyroxene	29.858	2.9923	161	217	124	196	172	159	150	161	207	126	150
Pyroxene	30.440	2.9364	161	140	146	136	143	164	173	161	126	168	139
Hypersthene	30.827	2.9004	73	64	N.D.	70	57	N.D.	N.D.	N.D.	N.D.	N.D.	66
Fayalite	31.602	2.8310	94	84	56	90	63	97	104	79	85	88	81
Hornblende	32.199	2.7799	N.D.	61	N.D.	N.D.	N.D.	N.D.	N.D.	93	87	83	60
a) Ilmenite	35.008	2.5630	61	68	56	71	76	72	78	65	83	88	53
b) Fayalite	"	"	"	"	"	"	"	"	"	"	"	"	"
a) Magnetite	35.659	2.5177	175	188	161	223	123	181	181	222	179	157	219
b) Fayalite	"	"	"	"	"	"	"	"	"	"	"	"	"
c) Hematite	"	"	"	"	"	"	"	"	"	"	"	"	"
Quartz	36.448	2.4650	N.D.	95	N.D.	87	64	70	66	77	69	97	92
Periclase	42.376	2.1329	87	87	82	85	81	89	99	78	97	79	149
Ox- Precipitate	44.840	2.0213	N.D.	N.D.	N.D.	N.D.	83	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Hematite	49.828	1.8300	N.D.	76	72	N.D.	79	81	100	57	64	59	58
Fayalite	51.608	1.7710	150	64	N.D.	60	N.D.	103	86	64	89	N.D.	83
Ilmenite	52.286	1.7496	60	56	N.D.	94	67	60	59	64	50	62	107

Appendix K$_2$:   Tables of Data from XRD Analyses of Granodiorite
and Basaltic "crust".

Angle 2θ	D-Spacing	Intensity	Mineral
18.616	4.7661	195	Fe (II) Oxalate Dihydrate
21.037	4.2229	55	Quartz
22.127	4.0173	60	a) Plagioclase b) Fe (II) Oxalate
23.055	3.8575	83	Oxalic Acid
23.907	3.7220	62	a) K-Feldspar b) Plagioclase
24.563	3.6241	82	Plagioclase
26.734	3.3345	367	a) Micas b) Quartz
28.051	3.1808	229	Plagioclase
28.385	3.1442	71	a) Plagioclase b) Hornblende
29.677	3.0102	83	a) Plagioclase b) Pyroxene
30.498	2.9310	63	a) Pyroxene b) K-oxalate
31.594	2.8317	85	a) Ca-oxalate hydrate b) Na-oxalate
34.502	2.5994	82	Mica
35.618	2.5205	53	K-oxalate per hydrate
36.803	2.4421	54	a) oxalic Acid b) K-oxalate
39.610	2.2752	58	a) Hematite b) K-oxalate
50.308	1.8136	86	Quartz

Table: Identification of XRD peaks for Granodiorite/Oxalic Acid Crust.

Source: Batch experiment - 11 week weathering study.

Angle 2θ	D-Spacing	Intensity	Mineral
22.120	4.0184	196	Plagioclase
22.945	3.8758	77	Forsterite
23.824	3.7347	257	a) Plagioclase
			b) Ilmenite
24.577	3.6221	140	Fayalite
25.744	3.4604	66	a) Titanium Oxide
			b) K, Al, Silicate hydrate
26.577	3.3538	95	a) Quartz
			b) Mica
27.912	3.1964	586	Plagioclase
29.832	2.9949	135	a) Pyroxene (Augite)
			a) Plagioclase
			b) Pyroxene
			b) Plagioclase
30.801	2.9028	81	Pyroxene (Pigeonite)
31.671	2.8250	100	Fayalite
32.749	2.7345	60	a) Ilmenite
			b) $Ca_2 SiO_4$
			c) $K_2 Mg Si O_4$
33.912	2.6433	65	Hematite
35.112	2.5557	64	a) Magnetite
			b) Ilmenite
35.735	2.5125	190	Hematite
42.312	2.1360	105	a) Periclase
			b) Quartz
48.570	1.8744	80	Titanium Oxide
49.873	1.8284	66	a) Quartz
			b) Hematite
51.628	1.7703	83	Fayalite/Forsterite
52.300	1.7491	55	Ilmenite

Table: Identification of XRD peaks for Basalt/Citric Acid Crust.

Source: Batch experiment - 11 week weathering study.

Angle 2θ	D-Spacing	Intensity	Mineral
8.719	10.1411	117	Mica
20.856	4.2592	91	a) K-Feldspar b) Quartz
21.954	4.0486	112	Plagioclase
23.724	3.7503	74	a) Feldspar b) Ilmenite
24.299	3.6628	76	Plagioclase
26.563	3.3555	422	Quartz and Mica
27.869	3.2013	195	Plagioclase
29.697	3.0082	64	a) K-Feldspar b) Plagioclase
30.346	2.9454	108	a) Plagioclase b) K-Feldspar c) Pyroxene
33.997	2.6369	131	Hematite
35.432	2.5333	73	Magnetite
36.003	2.4945	58	a) Fe-silicate b) Hematite
36.640	2.4526	103	Quartz
39.403	2.2867	72	a) Nutile/Anatase
41.305	2.1857	74	Hematite
45.003	2.0143	61	Mica
49.825	1.8301	54	Quartz
51.391	1.7779	82	a) Ilmenite b) Fe-silicate
54.622	1.6801	54	a) Hematite b) Magnetite

Table: Identification of XRD peaks for Granodiorite/Citric Acid Crust.

Source: Batch experiment - 11 week weathering study.

Angle 20	D-Spacing	Intensity	Mineral
18.336	4.8382	822	a) Mg – oxalate hydrate b) Fe – oxalate hydrate c) Na-Fe (II) Oxalate Nona Hydrate
23.226	3.89295	130	a) Oxalic acid b) Fayalite
23.849	3.7310	76	Albite
28.404	3.1421	356	a) Ca-Oxalate b) Pyroxene
34.946	2.5674	153	Fayalite
37.969	2.3697	93	a) Ca-oxalate b) Mg – oxalate hydrate
43.178	2.0951	124	Unidentified
44.724	2.0262	179	a) Mg-oxalate hydrate b) Fe-oxalate hydrate
48.794	1.8663	109	a) Ca-oxalate b) Fe-Oxalate hydrate

Table   Identification of XRD peaks for Basalt/Oxalic Acid Crust

Source: Batch Experiment – 11 week weathering study.

Appendix L: Tables of Data from CEC and Surface Area
              Analyses of Unweathered and Weathered and
              Unweathered Granodiorite and Basalt.

GRANODIORITE AND BASALT UNWEATHERED AND WEATHERED RESIDUES: CEC. SPECIFIC SURFACE AND SURFACE CHARGE DENSITY

PARENT MATERIALS UNWEATHERED	CEC (me/100g)	SPECIFIC SURFACE (m²/g)	CHARGE DENSITY (T) (me/m²)) x 10⁻³
Granodiorite A	0.6	2.0	3.2
Granodiorite ite B	1.1	2.8	3.9
Basalt A	0.7	1.5	4.9
Basalt B	1.1	1.9	5.5
Hawaiin Basalt	0.3	2.0	1.7

*A:.1mm-.5mm
*B:<.1mm

EXPERIMENT 1: COLUMN STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	CEC (me/100g)	SPECIFIC SURFACE (m²/g)	CHARGE DENSITY (T) (me/m²)) x 10⁻³
GrDio. A	Citric	1.0	3.1	3.2
GrDio. A	Oxalic	1.5	4.5	3.2
GrDio. A	Acetic	1.0	3.1	3.2
GrDio. A	HCL	1.0	5.2	1.8
GrDio. A	HOH	1.9	14.1	1.3
Basalt A	Citric	1.8	3.9	4.7
Basalt A	Oxalic	3.9	5.2	7.4
Basalt A	Acetic	2.2	3.5	6.3
Basalt A	HCL	1.2	4.2	3.0
Basalt A	HOH	1.1	2.1	5.2

EXPERIMENT 2: BATCH STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	CEC (me/100g)	SPECIFIC SURFACE (m²/g)	CHARGE DENSITY (T) (me/m²)) x 10⁻³
GrDio. A	Citric	2.2	5.2	4.3
GrDio. A	Oxalic	2.7	4.6	5.9
GrDio. A	Acetic	1.8	4.3	4.3
GrDio. A	HCL	0.8	4.9	1.7
GrDio. A	HOH	0.9	12.9	1.0
Basalt A	Citric	3.5	9.8	3.6
Basalt A	Oxalic	2.3	8.1	2.8
Basalt A	Acetic	1.4	3.5	4.0
Basalt A	HCL	1.0	4.5	2.3.
Basalt A	HOH	1.9	7.3	2.6

EXPERIMENT 3: COLUMN STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	CEC (me/100g)	SPECIFIC SURFACE (m^2/g)	CHARGE DENSITY (T) (me/m^2) x 10^{-3}
GrDio. A	Citric	2.6	8.0	3.2
GrDio. A	Oxalic	2.8	8.5	3.3
GrDio. A	Acetic	1.0	2.8	3.5
GrDio. A	HCL	1.0	3.5	3.0
GrDio. A	HOH	1.8	5.9	3.0
Basalt A	Citric	3.9	6.5	6.0
Basalt A	Oxalic	2.9	4.6	6.3
Basalt A	Acetic	5.0	9.0	5.5
Basalt A	HCL	7.9	11.5	6.6
Basalt A	HOH	2.7	6.0	4.5

EXPERIMENT 4:BATCH-11 WEEKS

PARENT MATERIAL	TREATMENT	CEC (me/100g)	SPECIFIC SURFACE (m^2/g)	CHARGE DENSITY (T) (me/m^2) x 10^{-3}
GrDio. A	Citric	1.1	4.2	2.6
GrDio. A	Oxalic	4.1	9.8	4.2
GrDio. A	Acetic	2.7	8.0	3.4
GrDio. A	HCL	1.9	7.8	2.4
GrDio. A	HOH	2.0	6.9	2.9
Basalt A	Citric	3.9	6.2	6.3
Basalt A	Oxalic	3.1	6.0	5.2
Basalt A	Acetic	4.0	9.1	4.5
Basalt A	HCL	3.5	4.2	8.4
Basalt A	HOH	3.2	7.6	4.2

EXPERIMENT 5: BATCH-11 WEEKS

PARENT MATERIAL	TREATMENT	CEC (me/100g)	SPECIFIC SURFACE (m^2/g)	CHARGE DENSITY (T) (me/m^2) , 10^{-3}
GrDio. B	Citric	2.3	11.2	2.1
GrDio. B	Oxalic	2.4	12.1	2.0
GrDio. B	Acetic	1.7	10.3	1.6
Basalt B	Citric	3.9	7.8	4.9
Basalt B	Oxalic	3.6	13.1	2.8
Basalt B	Acetic	2.1	3.1	6.7
Hawaiin B	Citric	1.0	4.0	2.5
Hawaiin B	Oxalic	2.5	10.9	2.3

Appendix M: Tables of Data from Exchangeable Bases
               Analyses of Unweathered and Weathered
               Analyses.

EXCHANGEABLE BASES OF UNWEATHERED AND WEATHERED RESIDUES (meq/100g)

PARENT MATERIALS	EXCHANGEABLE BASES (meq/100g)			
	Calcium	Magnesium	Sodium	Potassium
Granodiorite A	0.53	0.03	0.11	0.25
Granodiorite B	0.70	0.09	0.18	0.20
Basalt A	0.24	0.11	0.12	0.10
Basalt B	0.39	0.27	0.20	0.09
Hawaiin Basalt	0.14	0.06	0.04	0.03

*A: .1-.5mm
*B: <.1mm

EXPERIMENT 1: COLUMN STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	EXCHANGEABLE BASES (meq/100g)			
		Calcium	Magnesium	Sodium	Potassium
Gr.Dio. A	Citric	0.06	0.44	0.04	0.14
Gr.Dio. A	Oxalic	0.24	0.25	0.08	0.22
Gr.Dio. A	Acetic	0.36	0.02	0.04	0.12
Gr.Dio. A	HCL	0.37	0.03	0.06	0.11
Gr.Dio. A	HOH	0.54	0.28	0.05	0.11
Basalt A	Citric	0.05	1.14	0.63	0.16
Basalt A	Oxalic	0.49	1.16	0.03	0.05
Basalt A	Acetic	0.10	0.04	0.03	0.04
Basalt A	HCL	0.22	0.51	0.06	0.05
Basalt A	HOH	0.36	0.12	0.04	0.04

EXPERIMENT 2: BATCH STUDY-4 WEEKS

PARENT MATERIAL	TREATMENT	EXCHANGEABLE BASES (meq/100g)			
		Calcium	Magnesium	Sodium	Potassium
Gr.Dio. A	Citric	0.10	0.40	0.04	0.13
Gr.Dio. A	Oxalic	0.22	0.59	0.05	0.23
Gr.Dio. A	Acetic	0.23	0.07	0.07	0.15
Gr.Dio. A	HCL	0.56	0.12	0.07	0.17
Gr.Dio. A	HOH	0.61	0.08	0.09	0.18
Basalt A	Citric	0.06	0.07	0.02	0.03
Basalt A	Oxalic	0.44	1.18	0.04	0.06
Basalt A	Acetic	0.14	0.07	0.06	0.06
Basalt A	HCL	0.34	0.17	0.08	0.09
Basalt A	HOH	0.29	0.18	0.08	0.06

EXPERIMENT 3: COLUMN STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	Calcium	EXCHANGEABLE BASES Magnesium	(meq/100g) Sodium	Potassium
Gr.Dio. A	Citric	0.03	0.62	0.06	0.25
Gr.Dio. A	Oxalic	0.07	1.02	0.07	0.59
Gr.Dio. A	Acetic	0.17	0.13	0.05	0.06
Gr.Dio. A	HCL	0.13	0.14	0.04	0.07
Gr.Dio. A	HOH	0.58	0.05	0.06	0.26
Basalt A	Citric	0.02	1.16	0.10	0.20
Basalt A	Oxalic	0.29	1.41	0.15	0.10
Basalt A	Acetic	0.09	0.27	0.09	0.08
Basalt A	HCL	0.08	0.19	0.10	0.08
Basalt A	HOH	0.32	0.14	0.06	0.08

EXPERIMENT 4: BATCH STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	Calcium	EXCHANGEABLE BASES Magnesium	(meq/100g) Sodium	Potassium
Gr.Dio. A	Citric	0.03	0.87	0.06	0.39
Gr.Dio. A	Oxalic	0.14	0.98	0.06	0.58
Gr.Dio. A	Acetic	0.23	0.12	0.04	0.10
Gr.Dio. A	HCL	0.19	0.09	0.04	0.33
Gr.Dio. A	HOH	0.42	0.14	0.05	0.12
Basalt A	Citric	0.00	6.46	0.05	0.05
Basalt A	Oxalic	0.27	10.13	0.05	0.15
Basalt A	Acetic	0.09	0.12	0.05	0.67
Basalt A	HCL	0.10	0.07	0.05	0.29
Basalt A	HOH	0.35	0.16	0.05	0.93

EXPERIMENT 5: BATCH STUDY-11 WEEKS

PARENT MATERIAL	TREATMENT	Calcium	EXCHANGEABLE BASES Magnesium	(meq/100g) Sodium	Potassium
Gr.Dio. B	Citric	0.19	1.18	0.14	0.35
Gr.Dio. B	Oxalic	0.11	0.95	0.14	0.51
Gr.Dio. B	Acetic	0.43	0.13	0.05	0.11
Basalt B	Citric	0.02	1.10	0.09	0.50
Basalt B	Oxalic	0.45	1.36	0.15	0.07
Basalt B	Acetic	0.06	0.19	0.09	0.77
Hawaiin	Citric	0.06	1.22	0.07	0.08
Hawaiin	Oxalic	0.20	0.88	0.16	0.23

Appendix N: Mass Balance Calculations

Note: The values may be used only for the basis of
          approimate comparisons for the following
          reasons:

1.   Colloidal material may overestimate values
     from solution and extractable Fe, Al, and
     Si analyses.
2.   Values for extractable Fe, Al, and Si are
     not additive but in fact overlap.
3.   Concentrations of ions in solutions may
     later form precipitates and contribute to
     both solid and solution analyses.
4.   Values for extractable Al and Si are less
     accurate than for extractable Fe.

MASS BALANCE CALCULATIONS BATCH AND COLUMN EXPERIMENT

Ca^{2+}, Mg^{2+}, Na^+, K^+
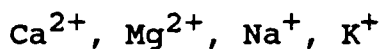
I. GRANODIORITE - % CaO

TREATMENT	A	B_{BCH}	C_{BCH}	D_{COL}	E_{COL}
Citric	4.93	0.77	20.20	0.51	10.30
Oxalic	4.93	0.37	7.45	0.24	4.92
Acetic	4.93	0.19	3.89	0.27	5.55
HCL	4.93	0.14	2.80	0.34	6.83
HOH	4.93	0.03	0.63	0.02	0.44

II. BASALT - % CaO

Citric	8.41	0.43	5.15	0.46	5.46
Oxalic	8.41	0.13	1.60	0.13	1.57
Acetic	8.41	0.12	1.49	0.15	1.84
HCL	8.41	0.17	2.07	0.18	2.20
HOH	8.41	0.01	0.15	0.00	0.00

I. GRANODIORITE - % MgO

Citric	2.15	0.40	18.76	0.20	9.20
Oxalic	2.15	0.61	28.57	0.45	20.93
Acetic	2.15	0.03	1.61	0.03	1.62
HCL	2.15	0.04	1.66	0.06	2.86
HOH	2.15	0.01	0.57	0.00	0.00

II. BASALT - % MgO

Citric	9.04	3.83	42.36	2.98	32.93
Oxalic	9.04	0.51	5.62	1.07	11.80
Acetic	9.04	0.03	0.29	0.06	0.69
HCL	9.04	0.04	0.39	0.06	0.69
HOH	9.04	0.00	0.00	0.00	0.00

A = % Oxide in unweathered material
B_{BCH} = Total % oxide in 11 wks batch leachate
C_{BCH} = % B of A
D_{COL} = Total % oxide in 11 wks batch leachate
E_{COL} = % D of A

MASS BALANCE CALCULATIONS BATCH & COLUMN EXPERIMENT

I. GRANODIORITE - % Na_2O

TREATMENT	A	B_{BCH}	C_{BCH}	D_{COL}	E_{COL}
Citric	3.77	0.05	1.33	0.03	0.77
Oxalic	3.77	0.06	1.70	0.05	1.28
Acetic	3.77	0.02	0.56	0.01	0.35
HCL	3.77	0.02	0.42	0.01	0.39
HOH	3.77	0.01	0.31	0.01	0.16

II. BASALT - % Na_2O

Citric	3.38	0.03	0.97	0.03	0.70
Oxalic	3.38	0.04	1.14	0.04	1.40
Acetic	3.38	0.03	0.87	0.01	0.17
HCL	3.38	0.03	0.93	0.02	0.59
HOH	3.38	0.01	0.34	0.00	0.00

I. GRANODIORITE - % K_2O

Citric	2.31	0.51	21.98	0.29	12.76
Oxalic	2.31	1.16	50.19	0.90	39.04
Acetic	2.31	0.13	5.45	0.06	2.50
HCL	2.31	0.10	4.30	0.07	3.10
HOH	2.31	0.04	1.74	0.01	0.58

II. BASALT - % K_2O

Citric	0.54	0.01	1.61	0.01	1.50
Oxalic	0.54	0.01	1.03	<0.01	1.00
Acetic	0.54	0.01	1.64	0.00	0.00
HCL	0.54	0.01	1.68	0.00	0.00
HOH	0.54	0.00	0.00	0.00	0.00

A = % Oxide in unweathered material
B_{BCH} = Total % oxide in 11 wks Batch leachate
C_{BCH} = % B of A
D_{COL} = Total % oxide in 11 wks Batch leachate
E_{COL} = % D of A

MASS BALANCE CALCULATIONS COLUMN EXPERIMENT

I. GRANODIORITE % Fe_2O_3

TREATMENT	A	B	C	D	E	F	G	H
Citric	5.21	1.17	0.20	1.52	3.66	22.48	70.26	92.74
Oxalic	5.21	3.17	6.92	2.23	1.00	60.85	19.21	80.06
Acetic	5.21	0.13	0.06	2.34	1.00	2.49	19.21	21.70
HCL	5.21	0.19	0.03	1.83	0.86	3.61	16.47	20.08
HOH	5.21	0.00	0.03	1.37	0.86	0.00	16.50	16.50

II BASALT - % Fe_2O_3

	A	B	C	D	E	F	G	H
Citric	12.46	9.51	0.34	1.66	0.43	76.30	3.44	79.74
Oxalic	12.46	2.85	18.59	3.00	6.95	22.83	55.78	78.61
Acetic	12.46	0.32	1.29	3.98	1.14	2.60	9.18	11.78
HCL	12.46	0.35	0.03	3.86	1.09	2.80	8.72	11.52
HOH	12.46	0.00	0.00	4.46	1.00	0.00	8.03	8.03

A = % Oxide in unweathered material
B = Total % oxide in 11 wks leachate
C = Pyrophoshate extractable % oxide
D = Ammonium Oxalate extractable % oxide
E = CBD extractable % oxide
F = % B of A
G = % E of A

MASS BALANCE CALCULATIONS COLUMN EXPERIMENT

I. GRANODIORITE % Al_2O_3

	A	B	C	D	E	F	G	H
Citric	16.61	0.82	0.11	0.26	0.23	4.91	1.37	6.28
Oxalic	16.61	2.19	0.08	0.15	0.30	13.19	1.82	15.01
Acetic	16.61	0.10	0.04	0.45	0.30	0.60	1.82	2.42
HCL	16.61	0.12	0.04	0.45	0.26	0.71	1.59	2.30
HOH	16.61	0.00	0.00	0.38	0.26	0.00	1.59	1.59

II. BASALT % Al_2O_3

	A	B	C	D	E	F	G	H
Citric	15.17	0.12	0.00	0.30	0.08	0.82	0.53	1.35
Oxalic	15.17	0.29	0.04	0.00	0.04	1.88	0.25	2.13
Acetic	15.17	0.07	0.04	0.30	0.15	0.48	1.00	1.48
HCL	15.17	0.05	0.00	0.30	0.19	0.35	1.25	1.60
HOH	15.17	0.00	0.00	0.38	0.15	0.00	1.00	1.00

A = % Oxide in unweathered material
B = Total % oxide in 11 wks leachate
C = Pyrophoshate extractable % oxide
D = Ammonium Oxalate extractable % oxide
E = CBD extractable % oxide
F = % B of A
G = % E of A
H = % total oxide removed (F + G)

MASS BALANCE CALCULATIONS COLUMN EXPERIMENT

1. GRANODIORITE % SiO_2

	A	B	C	D	E	F	G	H
Citric	63.80	0.56	0.38	0.00	0.38	0.88	0.60	1.40
Oxalic	63.80	1.42	0.79	0.00	0.21	2.24	0.34	2.58
Acetic	63.80	0.02	0.09	0.00	0.21	0.03	0.34	0.37
HCL	63.80	0.01	0.00	0.00	0.17	0.02	0.27	0.29
HOH	63.80	0.00	0.00	0.00	0.17	0.00	0.27	0.27

II. BASALT - % SiO_2

	A	B	C	D	E	F	G	H
Citric	49.96	4.26	1.01	0.00	0.38	8.52	0.60	9.12
Oxalic	49.96	4.26	0.96	0.00	0.43	8.52	0.86	9.38
Acetic	49.96	0.10	0.13	1.11	0.28	0.20	0.56	0.76
HCL	49.96	0.09	0.09	1.11	0.28	0.18	0.56	0.74
HOH	49.96	0.00	0.00	1.28	0.28	0.00	0.56	0.56

A = % Oxide in unweathered material
B = Total % oxide in 11 wks leachate
C = Pyrophoshate extractable % oxide
D = Ammonium Oxalate extractable % oxide
E = CBD extractable % oxide
F = % B of A
G = % E of A
H = % total oxide removed (F + G)

MASS BALANCE CALCULATIONS BATCH EXPERIMENT

I. GRANODIORITE - % Fe_2O_3

TREATMENT	A	B	C	D	E	F	G	H
Citric	5.21	2.37	0.37	1.43	0.72	45.49	13.81	59.70
Oxalic	5.21	4.68	5.72	2.43	2.86	89.83	54.89	144.70
Acetic	5.21	0.57	0.11	2.06	0.94	10.94	18.04	28.98
HCL	5.21	0.34	0.14	1.83	0.94	6.52	18.04	24.56
HOH	5.21	0.11	0.31	2.00	0.72	2.11	13.82	15.93

II. BASALT % Fe_2O_3

TREATMENT	A	B	C	D	E	F	G	H
Citric	12.46	4.40	0.57	1.89	0.54	35.31	4.33	39.64
Oxalic	12.46	1.69	13.44	1.89	0.72	13.56	5.78	19.34
Acetic	12.46	0.15	0.06	4.58	1.00	1.21	8.02	9.22
HCL	12.46	0.30	0.13	3.15	1.00	2.40	8.02	10.42
HOH	12.46	0.04	0.03	4.58	1.07	0.32	8.59	8.91

A = % Oxide in unweathered material
B = Total % oxide in 11 wks leachate
C = Pyrophoshate extractable (% oxide)
D = Ammonium Oxalate extractable (% oxide)
E = CBD extractable (% oxide)
F = % B of A
G = % E of A
H = % total removed (F + G)

MASS BALANCE CALCULATIONS BATCH EXPERIMENT

I. GRANODIORITE % Al_2O_3

TREATMENT	A	B	C	D	E	F	G	H
Citric	16.61	1.26	0.18	0.30	0.24	7.58	1.44	8.02
Oxalic	16.61	2.63	0.05	0.20	0.20	15.83	1.20	16.03
Acetic	16.61	0.17	0.06	0.48	0.27	1.02	1.62	2.64
HCL	16.61	0.06	0.06	0.48	0.27	0.36	1.62	1.98
HOH	16.61	0.05	0.00	0.48	0.27	0.30	1.62	1.92

II. BASALT % Al_2O_3

TREATMENT	A	B	C	D	E	F	G	H
Citric	15.17	0.16	0.00	0.00				1.18
Oxalic	15.17	0.22	0.00	0.09	0.02	1.47	0.13	1.60
Acetic	15.17	0.15	0.00	0.09	0.03	0.99	0.20	1.19
HCL	15.17	0.14	0.00	0.06	0.03	0.92	0.20	1.12
HOH	15.17	0.04	0.00	0.10	0.04	0.26	0.26	0.52

A = % Oxide in unweathered material
B = Total % oxide in 11 wks leachate
C = Pyrophoshate extractable % oxide
D = Ammonium Oxalate extractable % oxide
E = CBD extractable % oxide
F = % B of A
G = % E of A
H = % total oxide removed (F + G)

MASS BALANCE CALCULATIONS BATCH EXPERIMENT

I.   GRANODIORITE - % SiO_2

TREATMENT	A % SiO_2	B	C	D	E	F	G	H
Citric	63.80	0.97	0.38	0.00	0.32	1.52	0.50	2.02
Oxalic	63.80	1.83	0.62	0.00	0.48	2.86	0.75	3.61
Acetic	63.80	0.16	0.00	0.00	0.16	1.56	0.25	1.81
HCL	63.80	0.05	0.00	0.00	0.16	0.08	0.25	0.33
HOH	63.80	0.03	0.00	0.00	0.11	0.05	0.17	0.22

II.   BASALT - % SiO_2

	A	B	C	D	E	F	G	H
Citric	49.96	5.80	0.75	0.26	0.43	11.62	0.86	12.48
Oxalic	49.96	3.79	0.75	0.43	0.60	7.59	1.20	8.79
Acetic	49.96	0.18	0	1.63	0.54	0.37	1.08	1.45
HCL	49.96	0.15	0	0.94	0.21	0.30	0.43	0.73
HOH	49.96	0.04	0	1.63	0.54	0.08	1.08	1.16

A = % Oxide in unweathered material
B = Total % oxide in 11 wks leachate
C = Pyrophoshate extractable (% oxide)
D = Ammonium Oxalate extractable (% oxide)
E = CBD extractable (% oxide)
F = % B of A
G = % E of A
H = % total removed (F + G)