THE NATURE OF CALCIUM - ORGANIC COMPLEXES IN NATURAL SOLUTIONS AND ITS IMPLICATIONS ON MINERAL EQUILIBRIA

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This is to certify that the

# thesis entitled

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James I. Hoffman

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### ABSTRACT

# THE NATURE OF CALCIUM - ORGANIC COMPLEXES IN NATURAL SOLUTIONS AND ITS IMPLICATIONS ON MINERAL EQUILIBRIA

By

James I. Hoffman

Dissolved organic complexes are demonstrated to play such an important role in many natural aqueous environments that present, purely inorganic models must be severely modified. In many environments, especially in sediment pore waters, organic complexes probably act as the controlling factor for solution or precipitation of minerals. Crganic complexes cause cation activities to behave as complicated functions of Eh, pH, and the mass budget of dissolved organic matter. Presence of these complexing agents can cause solution of minerals whose cation's concentration is at a level of saturation.

Natural samples, containing the entire spectrum of available organic and inorganic components, were investigated to determine the role of dissolved organic matter in mineral equilibria. The magnitude and the effects of organic complexes on calcium ion activities were evaluated for surface waters and sediment pore waters from central Michigan lakes and streams, and marine and brackish waters of coastal North Carolina. Strong organic complexes were found to occur in significant proportions in many of these environments with as much as 50% of the total calcium existing in a complexed state. The nature of organic complexes was investigated by monitoring calcium activities with a calcium activity electrode and comparing results with the total concentration obtained by atomic absorption spectrophotometry and observations of pH, while various artificial perturbations were performed on natural fresh water samples.

Within samples, relationships between micro-organisms, atmospheric oxidation, and dissolved organic matter caused increases in pH and calcium activity with time. Thus, natural samples must be analyzed immediately or valuable information will be lost.

Additions of excess amounts of smaller divalent and trivalent cations caused ion exchange reactions between the calcium-organic complexes and added cations. Exchange preferences were not entirely in accordance with predictions based on present theories. The role of organic complexes in weathering takes on new implications, because slightly soluble cations such as iron and copper can now be effectively solubilized and transported as organic complexes.

Artificial additions of acid caused release of bound calcium ions. Interactions of added hydronium ions with dissolved organic matter produced strong pH buffering reactions between pH 7.6 and 6.6. These processes were irreversible.

Slight increases in the oxidation potential created new complexes which lowered calcium activity; but strong oxidation destroyed organic matter and released bound cations.

A new aqueous geochemical model, needed to characterize the

effects of dissolved organic material, was constructed from observations of a sample environment. The descriptions of ion activities were quasi-linear; those for pH variations were reciprocally linear. Future, universal generally acceptable models will have to be empirically determined from natural samples, whereas the current inorganic models are derived from synthetic systems. Gathering empirical data must involve determination of rates of influx and concentrations of natural acids, organic acids, dissolved organic matter, oxidizing and reducing agents, and the roles of geochemically active micro-organisms. Collection of these data will pose a formidable task, and interdisciplinary efforts will be needed for precise development of this ultimate model.

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James I. Hoffman

# A THESIS

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# INTRODUCTION

The earth's surface has been undergoing evolutionary changes for billions of years. Much of the change has been geochemical in nature, resulting from interactions between the low temperature aqueous surficial environment and materials formed under different equilibrium conditions (many characterized by high temperatures and pressures) and brought to the surface by various modes of crustal dynamics. Also, owing to the dynamics of the earth as a planet and its relative position in the solar system, environmental conditions on the continental surfaces do not remain constant for great lengths of time. Thus, materials that reach chemical equilibrium under surficial conditions at a given time, may be out of equilibrium at a later time.

Water serves three important functions in chemical processes in a natural environment: (1) it is a chemically reactive substance in its own right; (2) it serves to dilute or concentrate other reactants and products; and (3) it is a medium for other reactants and products.

One of the major goals of low temperature aqueous geochemistry is to determine the chemical reaction sets which constitute the systems of weathering, solution, and deposition in order to delineate their critical controlling parameters. More specifically, aqueous geochemistry aims to define ion stabilities and mineral equilibria to explain

and predict their behavior in the natural environments.

Chemists have long known that certain parameters tend to moderate aqueous reactions. Changes in the hydronium ion content (pH) resulting in acid-base type reactions, and trends resulting in the gain or loss of electrons which dictate the oxidation potential (Eh) are very important. A third variable, ionic strength, influences individual ion activity<sup>\*</sup> which directly affects the quantity of a particular ionic species in solution. These three factors form the basis for current geochemical models.

Current research in low temperature aqueous geochemistry has been primarily concerned with the behavior of simple inorganic analogues of natural systems. That is, the nature of the interactions of a relatively small number of ions under various conditions of Eh and pH have been studied in synthetic solutions. This simplified synthetic approach, summarized by Garrels and Christ, (1965), has been deemed necessary due to the inherent complexity of the natural system.

Results of this approach are not adequate to entirely explain either the nature or magnitude of observed weathering, transport, and precipitation phenomena or those inferred from the nature of products in the geologic record. For instance, conditions needed to explain Precambrian iron formations require the simultaneous transport and

<sup>\*</sup>activity - is the thermodynamic concentration, which is usually less than the total concentration in surface environments. It is the portion of the total concentration which is free to participate in chemical reactions.

precipitation of large amounts of iron and silica. Since, in terms of standard mineral equilibria theory, iron is most mobile under pH conditions that are unsuitable for concomitant transport of silica, current theory results in either a seeming paradox or an acceptance that current geochemical models are seriously incomplete.

The failures of the current model may be due to incomplete evaluation of all possible factors influencing ion solubility and transport. A factor which has not been much evaluated is the role dissolved organic substances play in aqueous environments. Because living organisms, both plant and animal, need elements in ionic form for survival, living matter has effectively increased weathering and solution reaction rates many fold over similar inorganic reactions. In addition to solubilization in response to nutrient needs, the earth's surface is bathed in organic metabolic wastes and the degradation products of dead organisms. It is surprising in this light that organic-inorganic interactions have not been more widely studied.

A few investigators over the past fifty years have indicated the relevance of dissolved organic substances in geochemical models. Important among them is the work of Gruner, (1922), who recognized the transport problems inherent in the nature of siliceous iron formations. He demonstrated that relatively large amounts of iron and silica could be transported in organic rich bog waters. Strengthening his case, Birge and Juday, (1934), showed that large amounts of dissolved organic matter were commonly present in fresh waters.

In general, current research concerning soluble organic matter has been directed along three approaches: (1) qualitative observations of natural systems; (2) observations of <u>in vitro</u> reactions between minerals and known organic species present in natural waters; and (3) precise identification of the dissolved organic species present in natural waters.

Baas Becking, et al, (1960) corroborated earlier more qualitative works in terms of Eh and pH limitations of natural environments, and showed that organic substances are present over a much broader range of Eh and pH than was previously expected. This type of work on general characteristics of natural waters is cruder than <u>in vitro</u> laboratory experiments, but has direct relevance to understanding the workings of natural aqueous systems.

Other researchers have demonstrated the effectiveness of reactions between soluble organic matter and common minerals. Evans, (1964), showed that quartz, carbonates, clay minerals, and ferromagnesian silicates could be rapidly solubilized by ATP, an organic complexing agent found in cell tissue. Bailey, (1967), showed that oxalic acid would effectively weather ferromagnesian minerals in a short time. Hem, (1965), showed that manganese was complexed and transported by gallic acids. Shapiro, (1964), and Christman, (1967), have shown that yellow organic acids can complex and transport a variety of cations. These studies have shown the importance of specific organic substances in specific reactions, but the reagent strengths used

experimentally and the simplicity of their systems are geologically unreasonable. All of these researchers designed their experiments to avoid the complexity and potential interactions which occur in natural environments; therefore, little information was gained concerning the relationships between Eh, pH, and dissolved organic substances.

Many workers have documented the presence of particular dissolved organic species in natural waters. Several hundred organic compounds have been identified; common among them are the dicarboxylic acids (such as oxalic and citric acid) which are effective complexing agents. Many of these soluble organic species and the experimental techniques used in identification are summarized by Breger, (1963), and Colombo and Hobson, (1964). Such data are helpful, but two factors combine to limit their usefulness: (1) species are identified without relative percentages and absolute concentrations; and (2) the analytical procedures so greatly modify the natural sample that in many cases the compound identified probably is a degradation product created by the separation procedures used prior to identification.

This study, modeled in spirit after Gruner's, (1922), is an attempt to understand the role of dissolved organic substances in mineral equilibria by observations of the nature of cation-soluble organic reactions in natural samples. The great variety of dissolved organic matter, with its wide spectrum of chemical properties, presents an enormous number of potential interactions with the inorganic portion of the geochemical environment. This study is designed to illuminate the

nature of the sum effect of the organic species, and their interactions on solution equilibria. Thus, for purposes of this study, the dissolved organic system has been observed and manipulated.

Several aspects of the role of organic complexes in mineral equilibria must be evaluated: (1) the quantitative importance of soluble organic complexes in aqueous environments; (2) the stability of these complexes; and (3) what effect interactions between soluble organic matter, Eh, pH, and cation composition has on the solution, transport, and deposition of minerals.

To solve these problems, this study has used natural samples in order to evaluate the interactions between dissolved organics and inorganic components and parameters. Analysis has been made on complete natural samples to characterize the role of organic complexes in the aqueous environment, rather than relying on systems containing only a few components in a less than real analogue. It is the combined behavior of the entire aqueous melange which is geologically significant.

### EXPERIMENTAL DESIGN

#### Introduction

The purpose of an experimental design is to plan the logic of an investigation to insure sufficient investigational coverage for solution of the problem. This presumes a subsequently derived clear formulation of the problem. The design insures, in an experimental sense, that the previously determined scope and relevance of the problem not be compromised. It provides an estimate of the magnitude of the task needed to solve the problem; and allows the investigator to plan for optimal efficiency of the research with regard to time and resources.

The first step in this study was to define the problem and evaluate its relevance to major geologic problems. This was done by consideration of the general role of organic substances; evaluation of the ideas of past workers; and by conducting a preliminary experiment to determine if, in fact, organic complexes of common cations existed in significant enough quantities to be observed with adequate precision with the means at hand. The first two points were evaluated and discussed in the Introduction.

#### Preliminary Experiment

The preliminary experiment was undertaken to discover whether the effect was of such a nature that it could be evaluated with our analytical resources. It was important that the experiment yield some qualitative measure of the magnitude of the complexing effect, in order to estimate its importance in aqueous geochemical environments. The experimental technique was designed to investigate the presence of natural organic complexes by placing them in competition for calcium ions with a synthetic complexing agent, EDTA.

This technique involves the removal of divalent calcium and magnesium ions from solution by binding them to the EDTA molecule. This process, called chelation (Martell and Calvin, 1952, pp. 9-15) results when complexes are formed between the polydentate ligand and the cation. EDTA is an extremely effective synthetic chelating agent for divalent cations. Eriochrome Black T, the colored indicator, is a weaker chelating agent, which displays a red color when it sequestors calcium and magnesium ions, and a blue color in the uncomplexed state. In the analysis, as EDTA is added during titrations, it first extracts all free calcium and magnesium from solution. Next it depletes those cations weakly bound to possible natural organic complexes; and finally the EDTA robs the indicator of its cations. In response, the Eriochrome Black T changes to a blue color. If complexing or chelating agents stronger than the indicator are present,

the EDTA will not have depleted them of their bound ions when the indicator turns blue. Thus some complexed calcium and magnesium in solution would escape detection. Since inorganic solutions contain no complexes which can compete with Eriochrome Black T, any such bound portion escaping detection must be in combination with dissolved organic matter. This conclusion is strengthened if that bound fraction can be released by destruction of the organic complexing agents.

A sample was taken from the Red Cedar River, (site B, Figure 1) and split into six 50 milliliter (ml.) aliquots which were analyzed by the colorimetric EDTA - Eriochrome Black T technique for total calcium and magnesium (Martell and Calvin, 1952, pp. 482 -490).

Three of six aliquots of sample were analyzed by this method for total calcium and magnesium. The other three aliquots were first evaporated to dryness; 10 ml. of concentrated nitric acid was then added to each residue to oxidize and degrade any organic matter present; and the resultant was slowly evaporated to dryness. After the second drying, the dried residue was dissolved in dilute hydrochloric acid and the solution was brought to its original aliquot volume with distilled water. These aliquots were then analyzed for total calcium and magnesium.

Results (Appendix A) indicated that the total calcium and magnesium present in the untreated samples was about 112 parts per million (ppm) whereas in the oxidized samples, the total for these ions was



Figure / CENTRAL MICHIGAN SAMPLING SITES

about 165 ppm. Since no calcium or magnesium was added in the course of the analysis, one must conclude that the presence of a significant proportion (about 30% in this case) of these cations was chemically masked in the untreated samples. Further it must be concluded that the aforementioned cations are strongly bound to an oxidizable host, because no known inorganic model can explain such results.

These results, along with previous preliminary concepts help define the nature of the ensuing investigation. Factors such as the interactions between dissolved organic complexing agents, oxidizing agents, and hydronium ions are of primary interest. These interactions were investigated by monitoring cation activities with changes in the Eh and pH of the samples. Secondly, variations of magnitudes of organic complexification of the common cations were investigated in both free waters and pore waters in fresh water and marine environments to determine the ubiquity of the effect.

Finally, the current model for aqueous geochemical systems has been modified to take into account the role dissolved organic matter plays in mineral equilibria in these environments. This involved expressing conclusions in a manner suitable for use in geochemical calculations.

A variety of geochemical environments are necessary to investigate this problem. Fresh waters in central Michigan (Figure 1) were chosen as the primary sampling sites and research efforts were concentrated here, because the ionic strength is low enough that no

inorganic complexing occurs to confuse the data. Since these samples may be treated as thermodynamically ideal solutions, any variations in cation activities in undersaturated solutions with changes in the important geochemical parameters must have been due to their interactions with dissolved organic complexes.

A reconnaissance study was made of several Mid-Michigan lakes in order to choose sampling sites which would exhibit a diversity of chemical compositions and environments. Data for concentrations of geologically important ionic species were collected at the sampling site using a Hach Chemical Company Direct Reading Engineer's Laboratory in accordance with their standard experimental techniques (Table 1). After reviewing these data, Holt Lake was excluded as a sampling site because of its chemical similarity to the Red Cedar River.

The Red Cedar River became the primary sampling site because it was known to have artificially enhanced organic levels (pollution), and because the preliminary experiment indicated that there was a significant interaction between dissolved organic matter and calcium and magnesium ions.

Several shallow lakes proximal to the laboratory were chosen representing a range of fresh water environments. Burke Lake is a small ground water fed system with little inflow of surface water and no man-made organic pollutants. Three environments within this lake were investigated: (1) pore waters from the upper five centimeters of

		Concentra	tions in parts pe	r million		
	Red Cedar River	Synthetic Red Cedar	Holt Lake	Burke Lake	Lake Lansing	Rose Lake
		River				
hd	8.31	7.80	8.10	7.80	8.40	7.70
Ca	103.00	100.00	94.00	58.00	33.00	80.00
Mg	35.00	35.00	23.00	31.00	17.00	32.00
Fe	0.68	1	0.35	0.00	0.04	3.40
Si	11.00	!	9.00	13.00	4.00	9.20
Cu	0.00	:	;	0.05	0.08	!
HCO <sub>3</sub>	255.00	211.00	260.00	225.00	110.00	209.00
co <sub>3</sub>	10.00	;	10.00	10.00	0.00	8 1
SO4	130.00	130.00	120.00	28.00	22.00	1
บี	45.00	83.00	40.00	20.00	32.00	1 1
Ionic	ſ			,	¢	
Strength	1.78 × 10 <sup>-2</sup>	$1.44 \times 10^{-2}$	$1.5 \times 10^{-2}$	$1.2 \times 10^{-2}$	6.9 × 10 <sup>-3</sup>	1
Ca	0.60	0.62	0, 60	0.65	0.70	
HCO <sub>3</sub>	0.90	0.90	0.90	0.90	0.90	
с0 <u>3</u>	0.60	0.62	0.60	0.65	0.68	
Values rep Uncertainti Ionic stren	resent the mean ( es are between 5 <sup>0</sup>	of three replicates % and 10% of conc	entration shown.			

Activity coefficients were interpolated from Garrels and Christ, (1965, p. 63, p. 104).

Ionic strengths were calculated from the data.

Table l

Major Ionic Species in Central Michigan Sampling Sites

sediments; (2) free waters proximal to the sediment - water interface; and (3) free surface lake waters.

Surface waters of two other lakes were investigated because they showed degrees of eutrophication different from Burke Lake. Rose Lake is in a more advanced state of eutrophication than Burke Lake, with only small amounts of artificial organic enhancement. Lake Lansing is a system with higher levels of both naturally and artificially enhanced dissolved organic matter than is found in Burke Lake; but lower levels than were found in the Red Cedar River during this experiment.

To test the generality of the fresh water observations, complementary, but more limited investigations of marine and brackish water environments were carried out in the vicinity of Topsail Island, North Carolina (Figure 2). Free water and sediment pore water samples were taken over a five day period in April, 1969, from both intrabarrier island marsh and from lagoonal environments.

# Instrumental Design

Analytical techniques used in the preliminary experiment yielded only relative proportions of bound or complexed cations to free cations. To gain further information, activities of individual cations were monitored and related to changes in the important geochemical parameters.



Because of interferences between chemically similar cations, analytical techniques are rare that allow measurement of an individual ion's activity in solution. Fortunately, the recent introduction of calcium specific ion electrodes allows reasonably accurate measurements of calcium ion activities free from interferences of other cations. Calcium is geologically important and is the most common divalent cation in fresh waters. Using the calcium ion electrode, changes in calcium activity were monitored for a variety of changes in pH, Eh, and ionic strength induced in natural samples. In addition, changes in activity against time were also monitored. This method measures only free divalent calcium; total calcium present in solution was determined by another method.

Atomic Absorption spectrophotometry (A. A.) is an excellent technique for measurement of total calcium in solution. This method involves vaporization of water samples in an air-acetylene flame. A. A. is based on the fact that atoms absorb radiation at specific wavelengths which are characteristic for each particular element. Energy at that wavelength, provided by a hollow cathode lamp, is passed through the flame in which the water samples have been vaporized. The instrument isolates the resonance wavelength, 4227 angstroms for calcium, with a grating monochromator. The intensity of the radiation remaining after passage through the flame is compared with that emitted by the source, giving a direct measure of all the calcium, both free and complexed, present in solution. This method gives an



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accurate and precise measure of the total calcium present, free from interferences of other elements.

Combining these two essentially different analytical techniques enables one to calculate by difference the proportion of free to complexed calcium, as well as to monitor changes in the calcium ion activity. One must suspect, however, that calcium results obtained from these two different analytical methods might not be directly comparable.

To evaluate the extent of differential responses and the instrumental precision, a factorial analysis of variance was performed using synthetic inorganic solutions prepared for standardization of the calcium specific ion electrode (for exact method of standardization, see Instrumental Methods).

Results of this analysis (Table 2) indicate that there is a significant interaction between these two instrumental techniques and the concentration of calcium in solution (Figure 3). At low calcium concentrations, A. A. reads slightly higher values than does the calcium activity electrode; while at high calcium concentrations the electrode reads higher values than does A. A. Thus at approximately 100 ppm. total calcium, the calcium ion electrode will indicate the presence of about 5 ppm more calcium than does the A. A.

Standard deviations were calculated for these two instrumental techniques using the data in Table 1 corresponding to the higher calcium concentrations. These corresponded to calcium concentrations

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Table	

# Instrumental Analysis of Variance

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Instrument	Calcium Ion				Replicate	1		I
Lested	Concentrations	П	7	Ś	4	'n	9	2
<b>Calcium Specific</b>	High	89.3	87.7	89.3	89.3	85.6	85.6	87.7
Ion Electrode	Low	18.3	18.3	18.3	18.3	17.8	18.3	17.3
Atomic Absorption	High	85.0	84.0	84.0	83.4	82.8	84.0	84.0
Ca - Mg Tube	Low	19.2	19.2	19.2	21.0	19.2	19.1	18.3

# Analysis of Variance Table

rce of D iation F is centrations	egrees of `reedom 6 1	Mean Square 1.667 31550.0	F Distribution  44964.7***
	1	12.49	17.814**
	1	47.60	67.857 <sup>**</sup>
r	18	0.70167	!
	27	5 1 1	   
ype I error ype I error	0.01 0.0001		



Variation in ppm from known Calcium Ion Concentration

known to exist in the Michigan sampling sites. The standard deviation for A.A. was 0.69 ppm calcium, and for the calcium activity electrode this was 1.66 ppm. These values were then used to determine the requisite sample size.

Determination of the sample size needed to insure the statistical validity of the results is perhaps the most important part of experimental design. The number of replications per sample is related to the size of real difference one wishes to be able to detect as significant. It was decided that if 10% of the total calcium in a sample was organically bound, then this would represent a geologically significant portion, and variations of about 10% were of interest. This amounts to from 3 - 10 ppm in the fresh water samples (Table 1).

Owen, (1967, p. 44), gives the relationship between requisite sample replication needed to see a critical difference in a normal distribution with the probability of rejecting a true hypothesis (Type I error) of 0.05 and specifying the probability of accepting a false hypothesis (Type II error).

Using the standard deviations determined from data generated for the factorial analysis of variance, and choosing a critical difference of 5 ppm, a sample size involving three replications assured a Type II error of less than 0.01 for A.A., and between 0.05 and 0.20 for the calcium specific ion electrode. Review of Table 2 indicates that the average difference seen by each method is over 15 ppm calcium for the Red Cedar River. With a number this large, Owen's

charts indicate the chances of committing a Type II error with the calcium electrode fall to less than 0.01.

In summary, the experimental design has isolated the problem and planned the attack. The preliminary experiment indicated the importance of organic complexes in fresh water. The sampling plan was formulated to test the ubiquity of organic complexes in a variety of environments and to investigate their relationships to important aqueous geochemical parameters. The instrumental methods of analysis needed to solve the problem were compared and contrasted by a factorial analysis of variance. Standard deviations were calculated for instrumental precision and for determination of the requisite sample size used in data collection.

# INSTRUMENTAL METHODS

Having formulated the experimental design, the following standard routine for sample analysis was established. The samples were: (1) collected in polyethylene containers; (2) filtered for all particles greater than five microns in diameter; and (3) split into aliquots for analysis by A.A., specific ion electrodes, and pH.

All water samples were collected in 500 ml. or 1000 ml. polyethylene bottles, care being taken to fill and cap the bottles so that as little air as possible was introduced with the sample. This precaution was to postpone any large scale atmospheric mixing until opened in the laboratory for filtration.

Samples were filtered through a variety of Whatman filter papers. A preliminary filtration took place through Whatman # 5 filter paper, primarily to remove floating and coarse suspended matter. A second filtration through Whatman # 42 or # 44 filter paper was effective for all particles five microns in diameter or greater. Filters were mounted in glass funnels.

Sediment samples taken from Burke Lake and Topsail Island were collected in 250 ml. wide mouthed, thick walled, polyethylene containers with special tight sealing lids. This material was returned to the laboratory, and the interstitial and associated water was

extracted by vacuum filtration through a Bückner funnel containing 2 - 5 micron teflon filters. The extraction process was aided by applying external pressure to the top of the sediment during filtration.

The purpose of filtration was to remove all suspended matter, especially clays, since certain clays undergo cation exchange reactions with most of the dominant cations. To insure that the filtration was effective in removal of clays, an aliquot of Red Cedar River water was evaporated to dryness, and a portion of the residue was subjected to an infrared absorption analysis, by Mr. A. Bailey. The resulting spectra (Figure 4) indicates that no clay minerals were present; but it does indicate a strong concentration of carbonate and the presence of a variety of organic compounds.

Following filtration, each sample was split into several aliquots. A 250 ml. aliquot was acidified with concentrated HCl to a pH between 2 and 3, and then analyzed by A.A. for calcium. The acidification insured that the calcium would remain in solution and it aided in the maintenance of proper flow through the burner, insuring a more accurate and precise analysis according to the procedures of Bentley, and Lee, (1967).

A Perkin Elmer Model #303 Atomic Absorption Spectrophotometer, with a Perkin Elmer Ca - Mg Lamp was used in the analysis. The insturmental techniques described in the Perkin Elmer manual were followed for machine operation. Standard solutions were prepared in accordance with the above instrumental techniques from analytical


Figure 4: Infrared Spectra of Red Cedar River Residue

grade  $CaCO_3$ , dilute HCl, and deionized water. Working curves were drawn plotting absorption versus calcium concentration over the ranges from 0 - 1 ppm calcium, in accordance with techniques described in the manual.

The acidified samples were diluted 10 to 20 times with deionized water using pipets and volumetric flasks. Water used in dilution of samples and preparation of standard solutions was first distilled and then passed through a Barnstead Bantum Demineralizer utilizing a mixed bed ion exchange column.

Prior to sample analysis, at least five standard 10 ppm and 0 ppm calcium solutions were run to insure the instrument was properly "warmed up", and giving stable repeatable absorption values on these solutions. Samples were then analyzed in groups of three, with 10 ppm standard solutions run for reference after every third sample analysis. Absorption values were converted to ppm calcium by reference to the working curve, and multiplied by the proper dilution factor for the total calcium concentration. This concentration has been termed total, because the absorption process evaluates all the calcium present as previously explained.

At least three non-acidified aliquots were analyzed for both free calcium ion and pH. Determination of calcium ion activity was made with an Orion Calcium Activity Electrode, model #92-90, in conjunction with a Beckman calomel reference electrode and an Orion model #401 Specific Ion Meter. Basic instrumental procedures were followed in accordance with those recommended in the Orion Instruction Manuals.

A  $1 \ge 10^{-1}$  M CaCl<sub>2</sub> standard solution was prepared from analytical grade CaCl<sub>2</sub> and deionized water. This was diluted as required to make  $1 \ge 10^{-3}$  and  $1 \ge 10^{-2}$  M CaCl<sub>2</sub> standard solutions, which were then used to standardize the specific ion electrodes.

Standardization was complicated by the fact that individual ion activity is seldom equal to the total concentration of that ion in solution due to the effect of the activity coefficient. The activity coefficient, which is a function of the ionic strength of the solution, affects ion activity according to the relationship:

From calculations of the ionic strengths of the sampling areas (Table 1), the calcium activity coefficients for these waters were extrapolated from a graph formulated by Garrels and Christ, (1965, p. 63). The calcium activity coefficient is always less than unity in the sampled sites, which means that the calcium activity will always be less than the total concentration. Since the ionic strength of a particular sample environment is essentially constant, the activity coefficients for that environment can be treated as a constant. Thus, in an inorganic solution, where no other interactions with calcium ion are possible, simple subtraction of the effect of the activity coefficient should make the calcium ion activity readings equal to the total concentration, all other factors being equal. This subtraction was incorporated into the standardization of the calcium activity electrode, so that its readings of calcium ion activity should be equal to the calcium concentrations given by A. A. for an inorganic standard solution.

Awareness of this inorganic activity coefficient was most important, because reactions of dissolved organics which would complex calcium ions would also result in calcium activity reductions. By removing the reduction caused by the inorganic activity coefficient, any calcium activity variations caused by interactions between organic complexes and this ion became readily apparent.

Analysis of the 1 x 10<sup>-3</sup> M CaCl<sub>2</sub> standard solution by A. A. gave a total calcium concentration of 36 ppm. To remove the effect of the activity coefficient, the calcium ion electrode was standardized so that the reading obtained for this standard solution was equal to an activity of 36 ppm. This activity corresponded to a reading of 0.00 millivolts (mv.) on the expanded mv. scale of the Orion Specific Ion Meter. Using the 0.00 mv. setting and various strengths of known standard solutions, a working curve was drawn by plotting mv. versus calcium concentration. A reference chart which directly converted mv. to ppm calcium was calculated from this curve for intervals of 0.25 mv. over the ranges expected for calcium concentrations in fresh water environments (Appendix B).

Samples were analyzed in either 100 ml. or 250 ml. beakers, depending on the size of the aliquot. Samples were stirred for at least fifteen seconds with a teflon stirring rod after insertion of the electrodes. A waiting period of at least two minutes was required for equilibrium to be achieved between the sample and the activity electrode.

The operating characteristics of the calcium electrode were extremely troublesome. The presence of small air bubbles on the electrode membrane caused erratic and unpredictable behavior. This was manifested as rapid fluctuations in the meter readings. These bubbles were difficult to dislodge and often the only recourse was to extract all moisture from the outer surface of the membrane with absorbent toweling. This, in turn, would require restandardization.

Further problems yielding erratic readings were caused by the slow and unpredictable decay of the liquid ion exchanger within the electrode body. This decay always led to high values for the calcium activity. This problem was detected when the values given by the calcium electrode exceeded those given by A. A. by more than that predicted by the analysis of variance. Those experimental values of calcium activity which exceeded the total concentration by more than 5 ppm were invalidated. Errors caused by this decay were usually between 10 and 30 percent before detection. Experience showed that this part of the calcium ion electrode operated properly for as long as four months, and as short as one month.

Other analytical problems were created by particle contamination of the membrane. This would set up wild fluctuations in the meter readings, often sending the needle off scale. This problem was rectified by replacement of the membrane.

Prior to sample analysis, the activity electrode was checked for proper standardization using the  $1 \times 10^{-3}$  M CaCl<sub>2</sub> and  $1 \times 10^{-2}$ M CaCl<sub>2</sub> standard solutions. The electrode was also checked with the  $1 \times 10^{-3}$  M CaCl<sub>2</sub> solution after every three sample analyses. Between each analysis the bodies of the activity electrode and calomel electrode were wiped dry with absorbent toweling to prevent contamination of the following analysis.

The Orion model #92-32 divalent cation activity electrode was standardized following the procedures described for the calcium activity electrode. The divalent electrode differs in that it responds to the combined activities of all divalent cations in solution; however, this response is not uniform for all divalent cations. Since the activity coefficients for all of the divalent cations present could not be determined, and the electrode response was variable, the divalent activity electrode was not used as a precise measure of absolute proportions of complexes divalent cations present. Instead, the electrode was used to monitor variations in activity, since the response variations and activity coefficients could be treated as a constant in a given sample. The same analytical problems which plagued the calcium ion electrode also affected this electrode. Concomitant with determination of activity, the pH of the sample was measured using a Photovolt Digicord pH Meter, and their pH and calomel electrodes in accordance with the Digicord instruction manual. The Digicord was standardized in Beckman pH 7.00 buffer solution at room temperature prior to each period of sample analysis. Drift from the standardized pH over a time period of four hours was negligible, thus restandardization after every three sample analyses was not necessary. The pH values were read when the digital readout stabilized to variations of + 0.02 pH units.

Since the nature of organic - inorganic interactions has not been previously investigated, there was a lack of information on sample deterioration with respect to degradation of the dissolved organic matter by atmospheric oxidation or other destructive processes. An experiment was run to examine degradation processes as reflected by release of calcium ions from organic complexes with time from sampling. The results of this experiment (Table 3) indicated that little calcium was released in the first 24 hours, but after this time calcium is released in large quantities. The geochemical implications of this time degradation are discussed in the next chapter. Analytically it means that natural samples have to be analyzed within 24 hours of collection, or valuable information might be lost. The fact that calcium is released with time presented another means of sample analysis to obtain proportions of complexed ions to free ions.

# Table 3

# Time Decay Experiment

# Red Cedar River Sample

Hours	Calcium Concentration in ppm
0.0	77.5
0.5	77.5
1.0	77.5
1.5	77.5
2.0	77.5
4.0	77.5
6.0	77.5
10.0	79.0
24.0	81.0
34.0	85.0
48.0	89.0
72.0	97.5
96.0	104.0
120.0	106.5
148.0	104.0

Total calcium concentration by A.A. = 106.8 ppm.

Analysis of marine and brackish water environments presented some special problems. High ionic strengths cause large depressions in the calcium ion activity (Garrels and Christ, 1965, p. 63). In addition, high magnesium ion concentrations (at least three times calcium concentrations) cause interferences with calcium activity readings with the calcium ion electrode. Furthermore, extensive ion pairs and possibly other unknown inorganic complexes were certainly present to confuse the data (Garrels and Christ, 1965, pp. 106 - 108). Thus precise results analogous to fresh water data were impossible to obtain.

Fortunately, the characteristics of the complexes observed in previous fresh water studies supplied a means of investigation. Complexes are unstable with respect to time, releasing their bound calcium during degradation. Thus, by monitoring the changes in calcium ion activity within a sample for at least 100 hours, a good estimate can be made of the amount of organic complexification. In this way problems involved with magnesium interferences, inorganic complexes, ion pairs, and ionic strength could all be treated as a constant, because these features of non-ideal inorganic solutions are not time dependent.

A standard solution<sup>\*</sup> was prepared for the calcium ion activity electrode which approximated marine and brackish water ionic strengths. The total calcium concentration was determined by A.A. to be equal to

<sup>\*</sup>standard solution: prepared by dissolving: 7.00 grams of NaCl, 0.50 grams of MgSO4 $\cdot$ 7 H20, and 0.25 grams of KCl in 56 ml. of  $1 \times 10^{-2}$  M CaCl<sub>2</sub> standard solution and bringing the volume to 500 ml. with deionized water.

333 ppm. This corresponded to a reading of +24.5 mv. on the specific ion meter; thus, for these experiments the calcium electrode was standardized at +24.5 mv. being equal to 333 ppm calcium.

Utilizing the described instrumental techniques, measurement of the important geochemical parameters and their interaction with calcium ion activity was carried out. By perturbing the samples through addition of acids, bases, oxidizing agents, and other cations, the effects of these disturbances on calcium ion activity were investigated. All sample analyses were made within thirty-six hours of collection to minimize loss of complexed calcium caused by time degradation of the dissolved organic matter.

### RESULTS

### Introduction

Results indicate that, in general, the presence of organic complexes of calcium causes the calcium ion activity coefficients to behave as a complex function of pH, Eh, and ionic strength. These results show that organic complexes play a significant role in many aqueous geochemical systems, and that the precise nature of this role is not <u>a priori</u> predictable. The results in the following sections present a number of different, but related aspects and conclusions concerning the relative and absolute magnitude of organic complexification of calcium ion; and the nature of the interactions between dissolved organic complexes and the inorganic aqueous geochemical system.

# Relative and Absolute Magnitudes of Organic Complexification

# Fresh Water Environments:

Relative proportions and absolute amounts of complexed calcium were determined over a six month period for fresh water environments in central Michigan (Figure 1), with pH readings concurrently taken. Results of this investigation (Table 4) indicate that amounts of Table 4

Magnitude of Calcium Complexification in Fresh Waters

Sample Location	Date	Total Calcium Ion in ppm	Calcium Ion Activity in ppm	Difference in ppm	<b>Percent</b> <b>Complexed</b>	Hq
Red Cedar River	9/4/68	85	61	24	28%	1
	9/16/68	106	74	32	30%	8.36
	9/30/68	110	74	36	33%	8.30
	10/2/68	110	78	32	2 9%	8.38
	10/8/68	107	82	25	23%	8.38
	10/8/68	107	78	29	2 7%	8.38
	10/9/68	101	77	24	24%	8.37
	10/17/68	103	74	29	28%	8.38
Artificial Red Cedar	10/18/68	66	98	1	:	7.10
Red Cedar River	11/12/68	103	89	14	13%	8.29
	11/19/68	95	83	12	13%	8.31
	11/20/68	103	61	12	12%	8.19
	1/21/69	60	57	ę	5%	7.80
	1/23/69	62	52	10	16%	7.73
	1/27/69	67	52	15	22%	7.81
	1/29/69	77	63	14	18%	1
	2/1/69	52	48	4	8%	8.07
	2/3/69	59	53	9	10%	7.86
	2/18/69	73	57	16	23%	8.06
	2/19/69	96	57	39	25%	8.09
	2 /20 /69	93	59	34	36%	7.99
	2 /20 /69	100	71	39	3 9%	8.20



Sample Location		Date	Total Calcium Ion in ppm	Calcium Ion Activity in ppm	Difference in ppm	Percent Complexed	Hq
Red Cedar River		2 /25 /69	87	63	24	2.8%	8.08
		2/27/69	67	65	32	33%	8.31
Lake Lansing		7/19/68	33	29	4	12%	8.40
)	Г	12/4/68	38	33	ъ	13%	8.14
	2	12/4/68	37	34	°	8%	7.54
	ŝ	12/4/68	39	33	9	15%	8.15
	4	12/4/68	40	34	6	15%	7.97
	S	12/4/68	36	32	4	11%	8.14
Burke Lake	A	12/4/68	63	63	0	1	7.66
	В	12/4/68	83	75	8	9%6	7.69
	U	12/4/68	65	64	1	:	7.67
	р	12/4/68	65	63	2	1	7.60
	មា	12/4/68	65	63	2	!	7.67
Water extracted							
ITOM		:			1		\ 
Burke Lake Muds	1	2/8/69	94	56	38	40%	7.64
	2	2/8/69	85	37	48	56%	8.13
	č	2/8/69	82	52	30	3 7%	7.46
	4	2/8/69	87	46	41	4 7%	7.68
	ъ	2/8/69	77	45	32	42%	7.73
	9	2/8/69	84	39	45	53%	8.10

Table 4 (cont'd.)

complexed calcium varied widely, both between different sampling sites and between samples taken at the same sampling site on different dates.

Proportions of complexed and total calcium in the Red Cedar River varied from 5% to 40%, and concomitantly the amount of complexed calcium varied from a minimum of 1 ppm to a maximum of 39 ppm. The low values represent samples collected in January during a winter thaw, when the river was at flood stage. High values occurred in September, 1968, and February, 1969, when the river was at a low stage. These variations were probably influenced primarily by the rate of discharge; that is, low values probably represent dilution of a relatively constant amount of organic complexes.

Surface waters in Lake Lansing exhibited much lower levels of complexed calcium (8% - 15%), compared to the Red Cedar River. These values reflect much lower total calcium concentrations, about 38 ppm, and a smaller quantity of organic matter, thus leading to lower amounts of complexed calcium, only 3 to 6 ppm.

In comparison to the Red Cedar River and Lake Lansing, surface waters in Burke Lake exhibited virtually no complexed calcium. The water in Burke Lake is primarily derived from lake bottom springs which probably contain little organic matter. This factor plus significant rates of influx and outflow, and the relative youth of the lake (an old gravel pit) is reflected by the early stage of eutrophication that presently exists. This is probably why little

or no organic complexing was observed in these surface waters.

Interstitial waters from dark colored organic rich sediments exhibited enhanced levels of calcium complexification. About 45% of the total calcium was complexed in pore waters extracted from the upper five centimeters of Burke Lake sediments. Total calcium ranged from 77 to 94 ppm, with from 30 to 48 ppm calcium existing in a complexed state. In comparison, the free surface waters in Burke Lake ranged from 63 to 83 ppm total calcium with only 0 to 8 ppm bound in complexes. Thus even when organic complexification plays only a slight role in overlying waters, it is an extremely important factor in underlying sediment interstices, a geologically important environment.

Organic complexes in pore waters can act as agents for solution or precipitation. Cations may be sequestered by complexing agents in sediment pores, causing solution of available minerals, even when activity is at saturation. Reactions involving the complexing agent and calcium ion can cause mobilization or precipitation of calcium ion under circumstances regarded as inimical by the inorganic model. Thus sediment pores can serve as a continuous source of cations as long as a supply of complexing agents is available.

### Marine and Brackish Water Environments:

The aforementioned results indicate the importance and widespread occurrence of dissolved calcium complexes in fresh water environments. To determine whether this was strictly a fresh water phenomenon or instead was a general effect, a reconnaissance study on free and sediment pore waters from marine and brackish water environments was undertaken near Topsail Island, North Carolina (Figure 2).

The North Carolina results (Table 5) show significant increases in calcium ion activity between initial readings taken at the time of sampling and determinations after five days. The difference between these two readings, or the amount of calcium released, is here taken to represent complexed calcium. The proportion of complexed calcium is calculated by dividing the amount released by the total amount, which is assumed to be equivalent to the amount present after five days.

Marsh water samples from Topsail Island had a normal marine ionic strength. Total calcium present was 420 ppm, of which 60 ppm initially were complexed, or about 14% of the total calcium.

A surface water sample taken near Thomas Landing, was from a brackish lagoon, which had a distinctly yellow - brown color. Shapiro (1964) found that yellow - brown coloring matter in natural waters was a good complexing agent for iron and other metals. The results of this

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# Magnitude of Calcium Complexification in Marine and Brackish Waters

Sample Location	Initial alcium Ion Activity	Calcium Ion Activity After 5 Days	Calcium Ion Complexed in ppm	Percent Complexed
A Topsail Island Marsh Water	360	420	60	14%
B Thomas Landing Lagoon Water	173	198	28	13%
C Topsail Island Lagoon Sediment & Water	168	208	40	15%
D Thomas Landing Lagoon Sediment & Water	182	210	28	1 3%
E Thomas Landing Lagoon Sediment & Water	182	206	24	12%
F Thomas Landing Lagoon Sediment & Water	182	238	44	24%

study tend to confirm his findings because 28 of the 198 ppm calcium were found to be complexed in these colored waters.

As in fresh waters, the largest amount of complexed calcium was found in pore waters which, in this instance, were extracted from black, organic rich, sediment from the vicinity of Thomas Landing. This sample contained 238 ppm total calcium, of which 44 ppm or 24% was initially complexed.

Generally, these results indicate that marine and brackish pore waters associated with dark - colored, organic rich sediments were enriched two or three times in complexed calcium with respect to the overlying free waters. The magnitude of organic complexes of calcium, precisely determined in fresh water, is shown to be present in the same relative proportion in similar marine environments. We must conclude that although the increased ionic strengths of marine and brackish waters makes them chemically different in some respects to fresh water, this is not a major factor in controlling the presence of organic complexes. The presence of excess amounts of cations other than calcium in marine waters probably is responsible for the slightly lower proportions of observed complexed calcium. If this is so, then according to results described in Cation Exchange, total amounts of organically complexed cations might be equal to or greater than in fresh waters.

# Time Degradation

Having determined absolute and relative magnitudes of calcium complexification in a range of natural environments, the nature of the complexing agent was deduced by observations and interpretations of changes in the calcium activity and pH in controlled experiments. Since it was shown (Table 3) that calcium activity in samples was variable with time, a more thorough examination of time - organic matter interactions served as a starting point.

Figure 5 shows the change in calcium ion activity with time expressed as change in the proportion of initially bound calcium released versus time in hours. In the first ten hours after collection no breakdown of calcium complexes was observed. This could represent a period in which less stable, non-complexing dissolved organic matter is being broken down; or it could represent a time period in which the sample does not degrade. Between ten and one hundred hours, the degradation process proceeds in a linear manner.

Degradation probably results from actions of two factors, bacterial action or atmospheric oxidation, either singly or in combination. Although the present investigation cannot clearly determine the degradation mechanism, the linear nature of the curve in Figure 5 does indicate that the rate of degradation is more or less constant.

The last 5% to 10% of the bound calcium was released more slowly than the previous portion as evidenced by a change in slope.



Figure 5: Time Degradation Effects on Complexed Calcium Ions

A reason for this might be the presence of a group of complexing agents which are distinctly more difficult to degrade; or that the general degradation process floods the micro-environment with products that retard further degradation.

The results of this experiment have important geologic implications. No currently known aqueous geochemical model can explain the time degradation trend. Explanation of these results must lie in considering the active presence of dissolved organic complexing material. In addition the calcium ion activity increase in time indicates that the calcium is bound to an organic host that is relatively easily degradable. Since these organic complexes are unstable, they must represent a significantly different type of chemical species than the well-known, highly stable, porphyrin complexes such as chlorophyll.

Another time degradation experiment was performed in which pH was monitored concomitantly with calcium ion activity (Table 6). These data indicated that the pH increased with time. Figure 6 was plotted to examine the nature of the relationship between calcium release and changes in pH. This plot indicates that the increase in pH occurs very quickly compared to calcium release, and is essentially completed before the majority of the calcium complexes break down. These pH changes are apparently due to a set of reactions independent of organic complex degradation. It is interesting to note that the major increase in pH occurs in the early portion of the calcium - organic

# Table 6

Time in Hours	Calcium Activity in ppm	Total Calcium by A. A.	Complexed Calcium	рН
0	65	97	32	8.32
2	68	97	29	8.39
6	68	97	29	8.52
24	75	97	22	8.64
48	89	97	8	8.55

### Time Degradation of a Red Cedar River Sample

complex degradation curve. This means that these pH trends might be related to breakdown of other less stable, non-complexing types of dissolved organic matter. The unstable organic matter may be high molecular weight molecules which are easily broken down by a variety of processes, and it is not uncommon that this decay removes hydronium ions from solution by hydrolysis (Degens, 1965, pp. 207, 209, 226). This degradation might in fact provide a reservoir of new complexing agents which would retard calcium ion activity increases.

# Perturbation Experiments

### Introduction:

Because ionic strength, pH, and Eh are important parameters for all geochemical models, natural samples were perturbed in a controlled manner to evaluate the response of organically complexed calcium to changes in concentrations of other cations, pH, and Eh.



Figure 6: Release of Complexed Calcium vs. pH with Time

### Cation Exchange:

Detailed studies of synthetic organic complexing agents has shown that such molecules have definite orders of preference for types of cations with which to complex (Martell and Calvin, 1952). This preference is a function of the size, charge, and shape of the candidate cation. If cations are introduced into a system containing a complexing agent which has previously bonded to a less desirable cation, an ion exchange reaction will take place in which the more preferred cation will be sequestered and the previously bonded cation released. The kinetics of the ion exchange are increased if the new cation is introduced in excess.

To test whether or not calcium was the most stably complexed cation, excess amounts of  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Ba^{2+}$ were added to separate aliquots of Red Cedar River samples. With the exception of  $Ba^{2+}$ , all of these cations caused release of bound calcium ion. The results of these exchange experiments are shown in Figure 7 (data in Appendix C). The greater relative size of the barium ion is probably the reason it did not effect calcium release. The  $Fe^{2+}$ effected more calcium release than  $Fe^{3+*}$ , which is in accordance with ligand field theory predictions.

<sup>\*</sup>Organic complexes of iron are especially important because this element is geologically common and the geologic record attests to its mobility in the past; yet it is almost insoluble inorganically in most common natural water. Thus, organic complexes supply a possible mechanism for the transport of iron in neutral to alkaline solutions.





Addition of copper caused the greatest calcium release. This high release is apparently not predicted by considerations of size and charge, because Fe<sup>3+</sup> should be more acceptable due to its smaller size and greater positive charge. Thus, the greater acceptability of copper must be due to highly specific steric preferences, characteristic of these complexing agents, which is predicted by considerations based on ligand field theory. The low values of exchange for Ni<sup>2+</sup> are not in accordance with predictions based on this theory. Reasons for this lack of exchange merit future investigation.

Perhaps most important was the result showing that excess magnesium ion is preferentially complexed over calcium. In marine environments where magnesium ions have a 3 to 1 ratio over calcium ions, the amount of complexed magnesium should exceed that of complexed calcium. Results of the North Carolina study indicated that about 15% of the magnesium ions may be complexed in those environments. This could have important ramifications on carbonate equilibria in marine and brackish water environments where large amounts of magnesium ions may exist in organic complexes, especially in sediment pore waters. Release of this bound magnesium, with lesser amounts of calcium when the complex degraded could cause precipitation of carbonate cement, and possibly act as another mechanism for dolomitization.

Summarizing these results, it appears that ion complexification is a function of the availability of an individual cation at the time of complex formation, and the concentration of that cation with respect to others in solution. The fact that exchange took place shows that those divalent cations smaller than calcium are transported in a complexed state. The role of organic complexes in weathering takes on new implications, because slightly soluble cations such as iron and copper can now be effectively solubilized and transported as organic complexes.

### pH Perturbations:

The previous experiments have shown that the amount of ion exchange increased as calcium complexes were presented with progressively smaller cations. Carrying this experimental approach one step further, various concentrations of hydronium ions (H<sup>+</sup>) were added to various samples, and the reactions monitored for changes in the calcium ion activity, divalent ion activity, and pH.

As a preliminary experiment, samples taken from Rose Lake and Lake Lansing were titrated with  $2 \times 10^{-2}$  M HCl and monitored for resulting pH. A region of extensive buffering was observed between pH 7.6 and 6.0 (Figure 8). Because buffering in the inorganic model is almost entirely attributed to bicarbonate ion, a synthetic inorganic Rose Lake solution<sup>\*</sup> was prepared and similarly perturbed to evaluate magnitudes of purely inorganic buffering. Samples of this synthetic

<sup>\*</sup>Synthetic Rose Lake solution contained sodium bicarbonate, calcium chloride, and magnesium sulfate in concentrations closely approximating those observed in natural samples (Table 1).



Rose Lake solution were titrated with  $2 \ge 10^{-2}$  M HCl in the same way as the natural samples.

Results (Figure 8) indicate that the buffering effect present in the synthetic Rose Lake was infinitessimal compared to natural samples. The observed buffering effect must have been due to the presence of dissolved organic matter. The degree of eutrophication in Rose Lake is much greater than that in Lake Lansing, and thus the larger quantity of organic matter in Rose Lake probably accounts for the greater degree of buffering observed in these samples.

The preliminary experiment indicated that dissolved organic matter acted as a buffer to increases in hydronium ion content. A detailed series of experiments was run on Red Cedar River samples, by perturbing the natural pH by additions of  $2 \times 10^{-2}$  M HCl and/or  $2 \times 10^{-2}$  M KOH, and monitoring the resulting pH, calcium activities, and divalent ion activities. Results of these experiments are tabulated in Appendix D.

Figure 9 is a typical plot of the pH data from these experiments. This plot is an example of one of several runs made with great precision to unequivocably characterize the buffering effect.

The buffered region appears at about pH 7.6 and terminates at about pH 6.6, essentially the same pH range as noted in the preliminary Lake Lansing and Rose Lake titrations. Associated with the addition of hydronium ions, there was a release of bound calcium ions causing an increase in the calcium activity. Possibly this could be an



exchange reaction between hydronium ions and organic complexes similar to that commonly observed with artificial complexing agents such as EDTA, and oxalic acid.

A synthetic Red Cedar River solution<sup>\*</sup> was prepared to test if the calcium ion activity increase upon addition of hydronium ion was due to the presence of inorganic complexes. This solution was then titrated with  $2 \times 10^{-2}$  M HCl following procedures identical to those used with natural samples. The acid titrations of the synthetic Red Cedar River sample caused no changes in the calcium ion activity (ppm); and as in preliminary experiment, no buffering region was observed (Figure 9). Thus, increases in calcium activity in the natural sample must be due to interactions between added hydronium ions and organic complexes of calcium ions. The additions of base  $(2 \times 10^{-2}$  M KOH) caused a slight lowering of calcium ion activity due to dilution until the pH increased to the point where carbonate precipitation began, which resulted in more substantial calcium activity decreases.

Part of the reason for calcium release upon addition of  $H^+$  is probably due to ion exchange between the very small  $H^+$  ions and previously bound Ca<sup>2+</sup> ions. Because the exchange process is based on charge balance theory, two  $H^+$  ions would have to be complexed for

 <sup>\*</sup>Synthetic Red Cedar River solution was prepared by dissolving
0.37 grams of MgSO<sub>4</sub>· 7H<sub>2</sub>O; 0.25 grams CaCO<sub>3</sub>; 0.083 grams of NaHCO<sub>3</sub> in a liter of deionized water.

every  $Ca^{2+}$  ion released. Calculations based on data in Appendix D indicate that approximately 3.5 to 5.0 H<sup>+</sup> ions were added for each  $Ca^{2+}$  ion released to pH 6.7, because further additions of hydronium ions caused little or no calcium release below this pH.

Because more than enough  $H^+$  ions were added to account for the observed amount of calcium released and pH changes, it must be concluded that many of the added  $H^+$  ions are playing another role. This fact was implied in discussions of the time effect on pH and calcium ion activity in a previous section. The majority of the added  $H^+$ ions were probably involved in degradation processes (hydrolysis) with the dissolved organic matter. The need for, and role of,  $H^+$  ions in hydrolysis of organic matter is well-known (Degens, 1965, pp. 209, 226, 254).

An important aspect of the cation exchange processes is reversibility. To test for reversibility a number of experiments were conducted in which a Red Cedar River sample was first subjected to an acid titration, then a base titration was performed, then re-acidification. The results of this are tabulated in Appendix D and summarized by Figure 10. The results indicate that the interaction between hydronium ions and the organic complexes is not a simple exchange process, for no reversibility was achieved. Additions of acid brought increases in the calcium ion activity until all complexed calcium was released. Intermediate addition of base caused no change in the calcium ion activity.



Generally, these results indicate that organic complexes are quite sensitive to additions of hydronium ions. Acidification of an environment will be buffered by the presence of organic matter. Part of the buffering effect is probably due to preferential release of calcium ions for hydronium ions in the complexes, and the other part is probably due to hydrolysis of high molecular weight organic matter. These results indicate that a large portion of the complexes are involved in degradation processes as well as cation exchanges, because acidification irreversibly alters part of the dissolved organic spectrum.

# Oxidation Perturbation:

Previous experiments investigated interactions between organic complexes of calcium ions and time, variations in concentrations of other cations, and variations in hydronium ion content. The following experiments use similar techniques to investigate the effect on organic complexes of oxidation potential changes.

The previously cited time decay study indicated that there is probably an oxidation effect on the organic complexes. To test the effect directly, six aliquots of Red Cedar River water were divided into two groups of three aliquots each. To one group enough 30%hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was added to result in a 2% concentration of peroxide in the aliquots. No peroxide was added to the other group. Calcium ion activity and pH was monitored in these groups for two days.

The results (Appendix E) of this experiment show an important difference between the behavior of the treated and untreated sample with respect to calcium ion activity (Figure 11). Results indicate that this slightly enhanced oxidation potential has actually created new complexes which lowered the calcium ion activity. This oxidation may be breaking down high molecular weight organic material and creating some relatively simple, dicarboxylic acid - like molecules which are doing the complexing. Conditions causing general complex degradation took hold in both treated and untreated groups within ten hours, and the previously observed linear degradation trends were produced. However, those samples treated with peroxide always contained relatively more complexed calcium at a given time.

It appears from these results that weak oxidation processes, such as atmospheric oxidation, actually create complexing species from available organic material. This may mean that when environments change from reducing to oxidizing, additional organic complexes are created which can act on the available cations. The effects of weak oxidation are constructive, whereas the effects of strong oxidation (Chapter 2) were shown to be destructive with respect to cation complexes. Since addition of peroxide, a strong oxidizing agent, caused decreases rather than increases in calcium release, one must conclude that the controlling degradation factor is something other than simple oxidation.

The observed pH variations in this experiment, involving rapid


Figure 11: Calcium Activity - Eh Relationships

increases in pH with time, were similar to those previously reported, both in peroxide treated and untreated samples. Slight depression of pH in the peroxide treated sample was due to the fact that Eh is not completely independent of pH. Increase in Eh will cause decreases in the pH, and vice versa (Garrels and Christ, 1965, p. 137).

The previously discussed experiment investigated the relationship between increased oxidation potentials and the resulting changes in calcium ion activities and pH. An experiment was especially designed to test for Eh - pH interactions; that is, if induced changes in these two parameters resulted in calcium ion activity levels that were not simply additive. The following table summarized this design. Samples in Table 7 were analyzed over a two day period, and results are summarized in Appendix E.

## Table 7

## Eh - pH Interaction Design

	No HCl*	2% HC1*	5% HCl*	10% HC1*
	added	by volume	by volume	by volume
No H2O2 <sup>**</sup>	3	3	3	3
added	replicates	replicates	replicates	replicates
2% H2O2 <sup>**</sup>	3	3	3	3
by volume	replicates	replicates	replicates	replicates

\* HCl =  $2 \times 10^{-2}$  M HCl \*\*H<sub>2</sub>O<sub>2</sub> = 30% H<sub>2</sub>O<sub>2</sub> The results of this experiment indicate that no interaction was present between additions of acid and peroxide. This lack of interaction is shown in Figure 12 which plots calcium activity against time. This graph shows that additions of acid did not alter the basic shape of the peroxide degradation curve with respect to the non - peroxide treated curves. The acid additions simply acted in an additive fashion increasing calcium ion activity at any given time. In all samples treated with peroxide, the calcium activity was lowered with respect to untreated samples.

Another clear result is the observed presence of a pH limit between 8.5 and 8.7, over time in the Red Cedar River (Figure 13). These observed pH limits are probably related to the quantity of hydronium ions needed for hydrolysis reactions with available organic matter, coupled with any use of hydronium ions in other types of degradation processes such as bacterial metabolic reactions. Since additions of peroxide did not affect observed pH, it appears that those reactions causing changes in observed pH are not the result of simple oxidation.

In summary, this experiment showed that no interaction existed between concomitant additions of peroxide and acid in natural samples. That is, that calcium ion activity in samples treated with peroxide displayed lower levels than untreated ones over the entire recorded span. Additions of acid uniformly raised the curve. In no sense was a relationship observed where combinations of peroxide and acid levels



Eh-pH EFFECTS ON CALCIUM ACTIVITY

Figure 12



produced abnormally low or high calcium activity results indicative of interaction. The previously reported lowering of calcium activities by increased oxidation potentials, and increases in calcium activity upon addition of acid were both evident in this experiment. Degradation of dissolved organic matter causes increases in observed pH. The degradation process probably consists largely of hydrolysis reactions, the limits of which may be controlled by the micro-biological ecology of the environments. Limiting pH values are probably a function of the total quantity and molecular types of available dissolved organic matter.

## Role of Organic Complexes in Calcite Equilibria in Burke Lake

Previous discussions have demonstrated the effectiveness of organic complexes as solubilizing agents, but they have not considered the role of complexes in precipitation reactions. To be an important factor in mineral precipitates, the amount of cation released upon complex degradation must cause supersaturation of that ion to initiate its precipitation. Many aqueous environments are near saturation, or indeed are saturated, as Burke Lake waters are with respect to calcium, and further cation additions should cause precipitation.

Since a large portion of the total calcium in Burke Lake sediment pore waters is bound in complexes, this environment provided an ideal situation for a theoretical examination of the role of organic complexes in calcite equilibria.

Relevant equations defining the inorganic relationships are as follows (Garrels and Christ, 1965, p. 76):

$$K_{calcite} = \frac{(Ca^{2+}) (CO_3^{2-})}{CaCO_3 calcite} = 10^{-8.3}$$

$$K_{H_2CO_3} = \frac{(H^+) (HCO_3^-)}{H_2CO_3} = 10^{-6.4}$$

$$K_{HCO_3^-} = \frac{(H^+) (CO_3^{2-})}{HCO_3^-} = 10^{-10.3}$$

$$K_{H_2O} = \frac{(H^+) (OH^-)}{H_2O} = 10^{-14.0}$$

$$K_{CO_2} = \frac{(H_2CO_3)}{P_{CO_2 gas}} = 10^{-1.47}$$

An equilibrium line expressing the solution or deposition of calcite can be drawn by solving the following equations and plotting the results as log  $Ca^{2+}$  versus pH. First a theoretical  $M_{CO_3^2-}$  can be obtained from

$$M_{CO_3^2-} = \frac{(10^{-10.3}) (\aleph_{HCO_3^2}) (M_{HCO_3^2})}{(\alpha_{H^+}) (\gamma_{CO_3^2^2})}$$

and when calculated for the pH range 7.5 to 8.5, and using the experimentally determined  $HCO_3^-$  (Table 8), for pH = 7.5,  $H^+ = 10^{-7.5}$ 

$$M_{CO_3}^2 - = \frac{(10^{-10.3}) (10^{-0.05}) (10^{-2.43})}{(10^{-7.5}) (10^{-0.19})} = 10^{-5.09}$$

## Table 8

## Calcite Equilibria Data for Burke Lake

			Total	Calcium
		pН	Calcium	Activity
Water Extracted from				(
Burke Lake Sediments	#1	7.64	10-2.63	10-2.86
	#2	8.13	10-2.68	10-3.03
	#3	7.46	10-2.70	10-2.84
	#4	7.68	10-2.66	10-2.94
	#5	7.73	10-2.72	10 <b>-2.</b> 95
	#6	8.10	10-2.68	10-3.00
Burke Lake Surface				
Waters	А	7.66	10 <b>-2.</b> 80	10-2.80
	В	7.69	10-2.70	10-2.73
	С	7.67	10-2.79	10-2.80
	D	7,60	10-2.79	10-2.80
	- Э	7.67	10-2.79	10-2.80

Ionic Strength =  $1.2 \times 10^{-2} M$   $M_{HCO_3}$  =  $225 \text{ ppm} = 10^{-2.43}$   $\gamma_{HCO_3}$  =  $10^{-0.05}$   $\gamma_{CO_3}^2$  =  $10^{-0.19}$   $\gamma_{Ca}^2$  =  $10^{-0.19}$  $P_{CO_2}$  =  $10^{-3.5}$  Then for  $H^+ = 10^{-8.5}$ ,  $CO_3^2 = 10^{-4.09}$ .

Calculation of theoretical  $M_{Ca}^{2+}$  at equilibrium with a given pH involves:

$$M_{Ca^{2+}} = \frac{10^{-8.3}}{(M_{CO_3^{2-}}) (\gamma_{CO_3^{2-}}) (\gamma_{Ca^{2+}})}$$

at pH = 7.5 this expression yields:

$$M_{Ca^{2+}} = \frac{10^{-8.3}}{(10^{-5.09})(10^{-0.19})(10^{-0.19})} = 10^{-2.83}$$

and at pH = 8.0 this yields  $M_{Ca}^{2+} = 10^{-3.33}$ . This result is plotted in Figure 14 as calcite equilibrium line A.

This equilibrium line can also be calculated by assuming that atmospheric  $P_{CO_2}$  is fixed. Garrels and Christ (1965, p. 53) find that  $10^{-3.4}$  moles of Ca<sup>2+</sup> are in equilibrium with calcite at pH 8.4, assuming the calcium activity coefficient equal to one. Since the calcium activity coefficient in Burke Lake is equal to  $10^{-0.19}$ , this equilibrium concentration becomes  $10^{-3.59}$ , at pH 8.4 and Line B is its expression in Figure 14. These two methods give theoretical limits as to the position of the calcium ion - calcite equilibrium line.

Table 8 lists the relevant experimental data for Burke Lake, and the data are plotted in Figure 14. The open circles are plots of Burke Lake surface waters, which indicate that the lake water is saturated with respect to calcite. The lower points of the vertical lines are the calcium ion activities taken from the specific ion electrodes for the pore waters. The tops represent the total calcium concentration



measured by A.A. The length of the line indicates the amount of calcium contained in organic complexes.

Organic complexes are playing an important role in this environment by acting as reservoirs for large amounts of calcium ions. The complexes can play two important parts. One, a sudden degradation of these complexes would flood these waters with great excesses of calcium ions, which should cause immediate precipitation of calcite, probably as a cement. The other role these complexes may play is as an intermediate stage in degradation of organic matter where they represent new complexes being created by oxidation processes. These new complexes may dissolve calcium from the sediment and act as a transport mechanism to the surface. The potential solution of calcium could actually create porosity within these recent sediments. These considerations leave no doubt that organic complexes play an important role in the carbonate equilibria in this environment. An important role for dissolved organic matter must be acknowledged if aqueous geochemical models are to be meaningful dynamic representatives of the natural system.

## NEW AQUEOUS GEOCHEMICAL MODEL

#### Introduction

A geochemical model is a set of factors that when integrated simulate the geochemical environment. This model can be used to predict geochemical behavior or infer genetic processes from geochemical products.

Although any sort of listing of properties constitutes a model, the essence of a model is best expressed in mathematical terms. Results of this research identify a number of new factors that must be included in aqueous geochemical models. The presently accepted inorganic model expresses characteristics of the geochemical system as succinct ratios or equations, and therefore additional factors should be expressed in a similar manner, if only for comparative purposes.

All aqueous geochemical models are centered around the concept of ion activity. In currently accepted models, ion activities are almost entirely independent of the other geochemical parameters, except at equilibrium. Relationships between ion activities and these parameters are summarized in equilibrium constants<sup>\*</sup>. Equilibrium

<sup>\*</sup>Equilibrium constant (K), for a reaction aA + bB = cC + dD, is  $K = \frac{C^{c} + D^{d}}{A^{a} + B^{b}}.$ 

constants are simple ratios describing ion activities at the point of equilibrium between solution or precipitation of the solid phase. Variations in the important inorganic parameters, pH or Eh, will alter equilibrium relationships causing either solution or precipitation. When similar changes occur at other than the equilibrium point, they do not cause alterations in ion activity. Assuming that inorganic effects are paramount, the equilibrium constant is sufficient to adequately describe aqueous geochemical systems.

Use of the present inorganic model results in significant overestimates of some cation activities, and grossly underrates the capability of natural waters to dissolve and transport ionic species. These insufficiencies are due to the previous assumptions that the ionic strength is the only control on ion activity except at equilibrium where it is controlled by solution or precipitation of its solid phase. In addition, equilibrium constants yield information on reaction direction, but give little information of rates or ion activities when conditions are other than at equilibrium. It is probably due to this factor that mass balance estimates have so often yielded values bearing little resemblance to those predicted by observed products.

Results of this investigation have shown that inorganic models are not correct. In addition to ion competitions existing at equilibrium between cation and solid, there is competition with other species in solution. The effect of organic complexing agents is very important in fresh waters, and compares well with effects of inorganic

competitions, such as ion pairs, in marine waters. In fact, it can be demonstrated that under conditions of saturation or supersaturation (predicted by the inorganic model), solution of the solid phase could occur.

Results given in earlier sections indicated that calcium ion activity varies with increases in Eh and decreases in pH. Indeed, without perturbation, activity increased with time within a single sample. These variations were ascribed to interactions between calcium ions and degradable organic complexing agents.

#### Example of the New Model

Limitations of the data available herein make it impossible to formulate a general universally sufficient empirical model, but one can examine the nature of interrelationships of data from this study in terms of relative magnitudes, rates, and functional types. As an example of the characteristics of such a model, general functional relationships are presented for the Red Cedar River, utilizing the data in Appendix E. These expressions predict calcium activities as a function of acid additions and time from sampling. Although not explicitly reflected, it must be kept in mind that the presence of organic complexing agents is implicitly necessary for validity of the following relationships:

Equations (1) to (3) express calcium ion activities as a function of time (T) with various amounts of acid added.

(1)  $\mathcal{A}_{Ca^{2+}} = 65 + 0.42 \text{ T} --$  no acid added (2)  $\mathcal{A}_{Ca^{2+}} = 77 + 0.36 \text{ T} -- 5\%$  by volume 2 x 10<sup>-2</sup> M HCl (3)  $\mathcal{A}_{Ca^{2+}} = 83 + 0.36 \text{ T} -- 10\%$  by volume 2 x 10<sup>-2</sup> M HCl

where  $\alpha_{Ca^{2+}}$  represents calcium ion activity in moles per liter, and T represents time in hours after sample collection.

Equation (4) expresses changes in calcium activity as a function of acid additions where "x" is acid in percent by volume.

(4) 
$$a_{Ca^{2+}} = 65 + 1.9x$$

Combining these four equations (assuming slopes in (1), (2), and (3) are approximately identical) into a single expression gives

(5) 
$$\mathcal{A}_{Ca^{2+}} = 65 + 1.9 x + 0.38 T.$$

Equation (5) represents a first attempt at a new model which takes into account variations in activity due to effects of organic complexing agents.

Figure 15 illustrates the effects of equations (1), (2), and (3), as functions of calcium ion activity versus time. Solid dots are observed values. Open circles represent theoretical values calculated from equation (5). The linear nature of calcium ion activity increases can be clearly seen in this graph. The effects of acid addition do not appreciably alter either the linear nature or slopes of the calcium organic complex degradation curves. The only effect of acid addition is one of increasing the amount of calcium released at a given time by a constant; that is, the amount of complexed calcium remaining is





lowered by a constant directly proportional to the volume of acid added.

Another example of the type of supplement needed in the current model is expressed by the following set of equations derived from values taken from Figure 13, relating the effects of time on pH:

(6) pH =  $(0.120 - 0.0001328 \text{ T})^{-1}$  for untreated sample (7) pH =  $(0.013 - 0.0000461 \text{ T})^{-1}$  for 5% by volume  $2 \times 10^{-2} \text{ M HCl}$ (8) pH =  $(0.0122 - 0.000063 \text{ T})^{-1}$  for 10% by volume  $2 \times 10^{-2} \text{ M HCl}$ 

Equation (9) expresses changes in pH as a function of acid additions where "x" is acid in percent by volume.

(9) pH = 8.33 - 0.209 x

The reciprocal linear equations (6), (7), and (8), in combination with equation (9) represent another example of the type of functional relationships needed to augment the present inorganic model. The geochemical meaning of the pH functions was previously discussed.

In conclusion, the effects of organic complexing agents on cation activity in synthetic solutions is not a new concept (Martell and Calvin, 1952); but prior to now determination of the relative importance of organic complexes on mineral equilibria was non-existent. The empirically derived models presented herein are only a first step toward generation of a much larger, general model for aqueous environments.

It is encouraging that supplements to the inorganic model will

be of a simple mathematical form with relationships being quasilinear or reciprocally linear. It is also obvious, that opposed to the functional simplicity of these effects, universal, generally acceptable models will have to be empirically determined from natural samples. This is in contrast to the inorganic model which was derived from and is universally correct for synthetic systems.

Collection of these empirical data must involve determination of rates of influx and concentrations of mineral acids and bases, organic complexing agents, dissolved organic matter, and oxidizing and reducing agents. Added to this will be characterizations of the geochemical role of the micro-biologic community. This formidable task will require interdisciplinary unions of thought involving geologists, ecologists, micro-biologists, and men of other scientific fields, to fully structure a relevant dynamic model of aqueous environments.

#### SUMMARY AND CONCLUSIONS

Organic complexes occur in significant amounts in many aqueous environments. These complexes often play an important role in mineral equilibria, especially in sediment pore waters. Rates of influx and degradation of dissolved organic matter certainly influence and probably control solution and precipitation of minerals in many aqueous systems. Organic complexes cause cation activities to behave as complicated functions of Eh, pH, and the mass budget of dissolved organic matter.

Interactions between dissolved organic matter, and degradation processes within samples caused increases in pH and calcium ion activities with time. The pH increases occurred quickly in the first few hours after sampling, whereas calcium ion activity increases occurred at a much slower, linear, rate over several days. Hydrolysis reactions affecting sample pH may have created products which tended to retard degradation of calcium - organic complexes.

Artificial perturbations of natural complexes revealed aspects of the nature of the organic complexing agents. Ion exchange reactions were observed when smaller divalent and trivalent cations were added in excess. Preferences were in accordance with predictions by

current ligand field theory except for the anomalously low exchange with nickel ion. The observed exchanges were probably controlled by steric factors of the complexing agents.

Artificial additions of acid caused release of complexed calcium, but additions of base caused no change in calcium ion activities. Interactions between added hydronium ions and calcium - organic complexes is irreversible. Additions of acid caused hydrolysis reactions which produced a strong pH buffering between pH 6.6 and 7.6.

Slight increases in oxidation potential probably created new complexes which lowered calcium ion activities; but strong oxidation tended to destroy organic matter, releasing complexed cations. Observed oxidation interactions with organic complexes were different than observed time degradation reactions, indicating that degradation processes were controlled by other factors.

Concomitant increases in Eh and decreases in pH created no apparent interactions. All observations indicated that decreases in pH caused increases in calcium ion activity, whereas the increases in Eh caused decreases in calcium activity. There were no anomalous differences observed in the variously treated samples.

The significance of interactions between dissolved organic matter and the inorganic system suggests a modification of the present aqueous geochemical model.

To demonstrate the nature of the inorganic - organic interactions, an empirical model was developed for the Red Cedar River from

observed data. This new model characterized calcium ion activities as a function of the magnitude of the complexed portion, changes in pH, and organic complex degradation rates with time from sampling.

It is encouraging that this supplement to inorganic models will be of a mathematically simple form with relationships being quasi - linear or reciprocally linear. It is also obvious that opposed to the functional simplicity of these effects, universal generally acceptable models will have to be empirically determined from natural samples. This concept is in opposition to the inorganic model which was derived from and is universally correct for synthetic systems.

Gathering empirical data must involve determination of rates of influx and concentrations of mineral acids and bases, organic acids, dissolved organic matter, oxidizing and reducing agents, and the roles of geochemically active micro-organisms. This formidable task should be the central effort of low temperature aqueous geochemistry. Interdisciplinary efforts will be required to precisely develop this new model.

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APPENDICES

#### APPENDIX A

## Preliminary Experiment

Sample taken from Red Cedar River, split into six aliquots

Total Calcium + Magnesium concentration measured by EDTA - Eriochrome Black T technique

Aliquots: A 113.5 ppm B 113.5 ppm C 110.0 ppm

The following treatments were carried out on the other three aliquots.

- 1. Evaporation to dryness
- 2. Addition of 10 ml. of concentrated HNO<sub>3</sub>
- 3. Evaporation to dryness
- 4. Solution with dilute HC1
- 5. Analysis for total calcium + magnesium concentration by above EDTA method

Aliquots: A' 168 ppm B' 160 ppm C' 166 ppm

Difference of x' - x = % of complexed calcium and magnesium

Thus: A' - A = 54.5 = 32% complexed B' - B = 46.5 = 29% complexed C' - C = 56.0 = 34% complexed

#### APPENDIX B

Calcium Ion Activity in Parts Per Million

Valid for 3 x  $10^{-2}$  M ionic strength solutions 1 x  $10^{-3}$  M CaCl<sub>2</sub> = 0.00 mv. = 36 ppm

mv. =	= ppm	mv. =	ppm	mv. =	• ppm	mv. =	ррш
+15.00	139	+8.75	79	+2.50	45	<b>-3.</b> 75	26
+14.75	136	+8.50	77.5	+2.25	44	-4.00	25.5
+14.50	133	+8.25	75.5	+2.00	43.5	-4.25	25
+14.25	130	+8.00	74	+1.75	42.5	-4.50	24.5
+14.00	127	+7.75	72.5	+1.50	41.5	-4.75	24
+13.75	124.5	+7.50	71	+1.25	41	-5.00	23.5
+13.50	122	+7.25	69.5	+1.00	40	-5.25	23
+13.25	119.5	+7.00	68	+0.75	39	-5.50	22.5
+13.00	117	+6.75	66.5	+0.50	38	-5.75	22
+12.75	114	+6.50	65	+0.25	37	-6.00	21.5
+12.50	111	+6.25	63.5	0.00	36	-6.25	21
+12.25	109	+6.00	62	-0.25	35	-6.50	20.5
+12.00	106.5	+5.75	60.5	-0.50	34	-6.75	20
+11.75	104	+5.50	59	-0.75	33.5	-7.00	19.5
+11.50	10 <b>2</b>	+5.25	58	-1.00	33	-7.25	19.0
+11.25	99.5	+5.00	56.5	-1.25	32	-7.50	18.75
+11.00	97.5	+4.75	55	-1.50	31	-7.75	18.5
+10.75	95	+4.50	54	-1.75	30.5	-8.00	18.25
+10.50	93	+4.25	53	-2.00	30	-8.25	17.75
+10.25	91	+4.00	52	-2.25	29.5	-8.50	17.5
+10.00	89	+3.75	51	-2.50	29	-8.75	17.25
+ 9.75	87	+3.50	49.5	<b>-2.</b> 75	28.5	-9.00	17
+ 9.50	85	+3.25	48	-3.00	28	-9.25	16.75
+ 9.25	83	+3.00	47	-3.25	27	-9.50	16.50
+ 9.00	81	<b>+2.</b> 75	46	-3.50	26.5	-9.75	16.25

## APPENDIX C

# Ion Exchange Experiments

# Variations in calcium activities upon additions of other cations

# Experiment #1: Reconnaissance

$MgCl_2 \cdot 7H_2O$	$Ca^{2+}$	MgCl <sub>2</sub> · 7H <sub>2</sub> O	$Ca^{2+}$
in grams	in ppm	in grams	in ppm
0.00	57	0.00	58
0.01	58	0.01	59
0.01	59	0.02	68
BaCl2	$Ca^{2+}$	FeCl <sub>3</sub> • xH <sub>2</sub> O	Ca <sup>2+</sup>
in grams	in ppm	in grams	in ppm
0.00	56	0.00	57
0.01	54	0.01	57
0.01	53	0.01	57
	C 2+	NiCla	$Ca^{2+}$
CuCl <sub>2</sub>	Ca 	ingrams	in ppm
in grams	in ppm	in grams	
0.00	57	0.00	57 57
0.01	59	0.01	50
0.02	63	0.01	59
0.01	63	0.01	59

Experiment #2: Divalent Magnesium Ions

MgCl <sub>2</sub> added	А	В	С
in grams	in ppm	in ppm	in ppm
0.00	52	52	52
0.01	59	57	55
0.01	52	62	55
0.01	57	62	62
0.01	68	65	62
0.02	74	74	74

Experiment #3: Divalent Iron

FeCl <sub>2</sub> · 4H <sub>2</sub> O in grams		A in ppm	B in ppm	C in ppm
8			• •	
0.00		56.5	56.5	56.5
0.01		56.5	62.0	60.5
0.01		56.5	60.5	58.0
0.01	ppt.	68.0	68.0	68.0
0.01	ppt.	68.0	68.0	68.0
0.01	ppt.	74.0	68.0	68.0

Experiment #4: Divalent Barium

BaCl <sub>2</sub> · 2H <sub>2</sub> O in grams		A Ca <sup>2+</sup> in ppm	B Ca <sup>2+</sup> in ppm	C Ca <sup>2+</sup> in ppm
0.00		62	62	62
0.01		59	57	62
0.01		57	55	57
0.01		57	57	57
0.01		57	57	62
0.01	ppt.	61	58	62

FeCl <sub>3</sub> · 6H <sub>2</sub> O in grams		A Ca <sup>2+</sup> in ppm	B Ca <sup>2+</sup> in ppm	C Ca <sup>2+</sup> in ppm
0.00				PP
0.00		68	68	68
0.01		70	70	70
0.01	ppt.	62	70	68
0.01	ppt.	76	74	74
0.01	ppt.	74	74	74
0.01	ppt.	74	74	74

# Experiment #5: Trivalent Iron

# Experiment #6: Divalent Nickel

NiCl <sub>2</sub> · 6H <sub>2</sub> O	A Ca <sup>2+</sup>	B Ca <sup>2+</sup>	$Ca^{2+}$
in grams	in ppm	in ppm	in ppm
0.00	56.5	56.5	56.5
0.01	56.5	55.0	55.0
0.01	56.5	55.0	56.5
0.01	56.5	59.0	56.5
0.01	52.0	52.0	47.0*
0.01	47.0*	47.0 <sup>*</sup>	47.0 <sup>*</sup>

\* Ionic strength effect

# Experiment 7: Divalent Copper

CuCl <sub>2</sub> · 2H <sub>2</sub> O in grams		A Ca <sup>2+</sup> in ppm	B Ca <sup>2+</sup> in ppm	C Ca <sup>2+</sup> in ppm
0 00		52.0	52.0	52.0
0.03		60.5	63.5	62.0
0.03		68.0	68.0	68.0
0.03	ppt.	52.0	54.0	52.0

Calcium electrode started a strong negative drift with precipitate.

## APPENDIX D

## pH Perturbations

# Experiment #1: Acid titration of two aliquots of Red Cedar River Aliquot B analyzed four hours later than A

Aliquot A: 100 ml.

Aliquot B: 100 ml.

pН	HC1	Ca <sup>2+</sup>	pН	HC1	$Ca^{2+}$
_	in ml.	Activity		in ml.	Activity
8.38	0.0	$1.62 \times 10^{-3} M$	8.45	0.0	$1.62 \times 10^{-3} M$
8.32	0.2	$1.62 \times 10^{-3} M$	8.34	0.2	$1.64 \times 10^{-3} M$
8.24	0.2	$1.63 \times 10^{-3} M$	8.27	0.2	$1.66 \times 10^{-3} M$
8.15	0.2	1.66 x 10 <sup>-3</sup> M	8.18	0.2	$1.68 \times 10^{-3} M$
8.07	0.2	$1.68 \ge 10^{-3} M$	8.09	0.2	$1.68 \times 10^{-3}$ M
7.98	0.2	$1.70 \times 10^{-3} M$	8.01	0.2	$1.69 \times 10^{-3} M$
7.90	0.2	$1.70 \times 10^{-3} M$	7.92	0.2	$1.71 \times 10^{-3} M$
7.84	0.2	1.71 x 10 <sup>-3</sup> M	7.85	0.2	$1.72 \times 10^{-3} M$
7.78	0.2	$1.72 \times 10^{-3} M$	7.78	0.2	$1.73 \times 10^{-3} M$
7.71	0.2	$1.72 \times 10^{-3} M$	7.76	0.2	$1.75 \times 10^{-3} M$
7.67	0.2	$1.74 \times 10^{-3} M$	7.69	0.2	$1.76 \times 10^{-3} M$
7.62	0.2	$1.76 \times 10^{-3} M$	7.65	0.2	$1.78 \times 10^{-3} M$
7.56	0.2	1.78 x 10 <sup>-3</sup> M	7.61	0.2	$1.78 \times 10^{-3} M$
7.52	0.2	$1.78 \times 10^{-3} M$	7.58	0.2	$1.79 \times 10^{-3} M$
7.49	0.2	$1.79 \times 10^{-3} M$	7.54	0.2	$1.80 \times 10^{-3} M$
7.46	0.2	$1.79 \times 10^{-3} M$	7.52	0.2	$1.80 \times 10^{-5} M$
7.44	0.2	$1.80 \times 10^{-3} M$	7.49	0.2	$1.80 \times 10^{-3} M$
7.43	0.2	$1.80 \times 10^{-3} M$	7.47	0.2	$1.80 \times 10^{-5} M$
7 41	0.2	$1.80 \times 10^{-3} M$	7.44	0.2	$1.81 \times 10^{-3} M$
7 40	0.2	$1.80 \times 10^{-3} M$	7.46	0.2	$1.81 \times 10^{-3} M$
	0.2		7.44	0.2	$1.82 \times 10^{-3} M$
			7.43	0.2	$1.82 \times 10^{-3} M$
Experiment #2A: Acid titration of 75 ml. Red Cedar River sample with  $2 \times 10^{-2}$  M HCl

pН	HC1	$Ca^{2+}$	pH	HC1	$Ca^{2+}$
	added	in ppm	-	added	in ppm
	in ml.			in ml.	
8.36	0.0	75.5	7, 23	0.1	97.5
8.36	0.1	75.5	7.21	0.1	97.5
8.26	0.1	77.5	7.16	0.1	97.5
8.17	0.1	77.5	7.20	0.1	97.5
8.08	0.1	79.0	7.20	0.1	97.5
8.04	0.1	81.0	7.14	0.1	97.5
7.94	0.1	81.0	7.19	0.1	97.5
7.86	0.1	81.0	7.11	0.2	97.5
7.81	0.1	81.0	7.10	0.2	97.5
7.80	0.1	81.0	7.04	0.2	97.5
7.76	0.1	83.0	7.01	0.2	97.5
7.73	0.1	85.0	6.96	0.2	97.5
7.66	0.1	85.0	6.98	0.2	97.5
7.62	0.1	89.0	6.90	0.2	97.5
7.58	0.1	89.0	6.90	0.2	97.5
7.58	0.1	89.0	6.88	0.2	97.5
7.55	0.1	89.0	6.85	0.2	97.5
7.50	0.1	89.0	6.77	0.2	97.5
7.49	0.1	89.0	6.87	0.2	97.5
7.50	0.1	91.0	6.75	0.2	97.5
7.44	0.1	91.0	6.70	0.2	97.5
7.46	0.1	91.0	6.68	0.2	97.5
7.45	0.1	91.0	6.58	0.2	97.5
7.39	0.1	93.0	6.58	0.2	97.5
7.35	0.1	93.0	6.57	0.2	97.5
7.38	0.1	91.0	6.55	0.2	97.5
7.38	0.1	91.0	6.52	0.2	97.5
7.34	0.1	93.0	6.46	0.2	97.5
7.34	0.1	93.0	6.48	0.2	97.5
7.33	0.1	93.0	6.44	0.2	97.5
7.32	0.1	93.0	6.37	0.2	97.5
7.33	0.1	97.5	6.32	0.2	97.5
7.27	0.1	97.5	6.26	0.2	97.5
7.28	0.1	95.0	6.18	0.2	71.J 07 5
7.32	0.1	97.5	6.11	0.2	97.5
7.23	0.1	97.5	6.04	0.2	97.5
7.27	0.1	97.5	5.98	0.2	71.5

Experiment #2B: Base titration of 75 ml. aliquot of Red Cedar River sample, with  $2 \times 10^{-2}$  M KOH (continuation of #2A)

pН	КОН	Ca <sup>2+</sup>	pН	КОН	$Ca^{2+}$	pН	КОН	$Ca^{2+}$
	in ml.	in		in ml.	in		in ml.	in
		ppm			ppm			ppm
8.38	0.0	74.0	9.25	0.1	45.0	9.69	0.1	31.0
8.35	0.1	74.0	9.27	0.1	43.5	9.70	0.1	31.0
8.42	0.1	74.0	9.28	0.1	43.5	9.72	0.1	31.0
8.45	0.1	72.5	9.30	0.1	43.5	9.73	0.1	31.0
8.49	0.1	71.0	9.31	0.1	43.5	9.74	0.1	30.0
8.53	0.1	68.0	9.34	0.1	42.5	9.75	0.1	30.0
8.61	0.1	68.0	9.34	0.1	42.5	9.76	0.1	30.0
8.62	0.1	68.0	9.35	0.1	42.5	9.77	0.1	30.0
8.67	0.1	65.0	9.37	0.1	41.5	9.78	0.1	30.0
8.73	0.1	63.5	9.39	0.1	41.5	9.79	0.1	29.5
8.75	0.1	62.0	9.39	0.1	41.0	9.82	0.1	29.0
8.80	0.1	62.0	9.41	0.1	40.0	9.82	0.1	29.0
8.83	0.1	59.0	9.42	0.1	40.0	9.82	0.1	29.0
8.86	0.1	59.0	9.44	0.1	40.0	9.83	0.1	28.5
8.88	0.1	56.5	9.45	0.1	40.0	9.84	0.1	28.5
8.90	0.1	56.5	9.47	0.1	40.0	9.86	0.1	28.0
8.95	0.1	56.5	9.47	0.1	38.0	9.87	0.1	28.0
8.86	0.1	56.5	9.49	0.1	38.0	9.88	0.1	28.0
8.98	0.1	54.0	9.50	0.1	38.0	9.89	0.1	28.0
9.00	0.1	54.0	9.52	0.1	38.0	9.90	0.1	28.0
ppt. nc	w clearly	visible	9.53	0.1	36.0	9.91	0.1	28.0
9.03	0.1	53.0	9.54	0.1	36.0	9.9 <b>2</b>	0.1	26.5
9.06	0.1	53.0	9.56	0.1	36.0	9.93	0.1	26.5
9.06	0.1	52.0	9.57	0.1	36.0	9.94	0.1	26.5
9.08	0.1	52.0	9.58	0.1	36.0	9.95	0.1	26.5
9.11	0.1	52.0	9.59	0.1	36.0	9.98	0.1	25.5
9.13	0.1	49.5	9.61	0.1	34.0	9.99	0.1	25.5
9.14	0.1	48.0	9.61	0.1	33.0	9.99	0.1	25.5
9.16	0.1	48.0	9.62	0.1	33.0	9.99	0.1	25.5
9.18	0.1	47.0	9.64	0.1	33.0	10.02	0.1	25.5
9.20	0.1	47.0	9.65	0.1	33.0	10.03	0.1	25.0
9.21	0.1	47.0	9.66	0.1	33.0	10.03	0.1	24.5
9.23	0.1	46.0	9.68	0.1	33.0	10.03	0.1	24.5
9.24	0.1	45.0	9.68	0.1	31.0	10.05	0.1	23.5

Drop in calcium activity due in part to dilution, and later to precipitation.

Experiment #3:	Titration of a Red Cedar River 100 ml.	sample
	using 2 x 10 <sup>-2</sup> M HCl or KOH	•

рH	КОН	Ca <sup>2+</sup>
	added	activity
	in ml.	
8.38	0.0	$1.78 \times 10^{-3} M$
8.43	0.2	$1.75 \times 10^{-3} M$
8.53	0.2	$1.72 \times 10^{-3} M$
8.57	0.2	1.71 x 10 <sup>-3</sup> M
8.63	0.2	$1.70 \times 10^{-3} M$
8.68	0.2	$1.68 \times 10^{-3} M$
8.73	0.2	1.68 x 10 <sup>-3</sup> M
8.77	0.2	$1.63 \times 10^{-3} M$
8.82	0.2	$1.62 \times 10^{-3} M$
8.86	0.2	$1.60 \times 10^{-3} M$
8.90	0.2	$1.60 \times 10^{-3} M$
8.94	0.2	$1.60 \times 10^{-3} M$
8.97	0.2	$1.56 \times 10^{-3} M$
9.00	0.5	$1.55 \times 10^{-3} M$
9.07	0.5	$1.50 \times 10^{-3} M$
9.20	0.5	$1.48 \times 10^{-3} M$
9.26	0.5	$1.43 \times 10^{-3} M$
9.31	0.5	$1.41 \times 10^{-3} M$
9.35	0.5	$1.38 \times 10^{-5} M$
9.39	0.5	$1.35 \times 10^{-3} M$
9.44	0.5	$1.32 \times 10^{-3} M$
9.49	0.5	$1.30 \times 10^{-5} M$

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#### Experiment #3: (cont'd.)

pН	HCl	$Ca^{2+}$	pН	HC1	$Ca^{2+}$
	added	activity		added	activity
	in ml.			in ml.	
		2			
8.38	0.0	$1.78 \times 10^{-3} M$	7.12	0.2	$1.89 \times 10^{-3} M$
8.36	0.1	1.75 x 10 <sup>-3</sup> M	7.11	0.2	$1.90 \times 10^{-3} M$
8.33	0.1	1.78 x 10 <sup>-3</sup> M	7.08	0.2	$1.90 \times 10^{-3} M$
8.30	0.1	$1.77 \times 10^{-3} M$	7.07	0.2	$1.90 \times 10^{-3} M$
8.25	0.1	$1.78 \times 10^{-3} M$	7.05	0.2	$1.90 \times 10^{-3} M$
8.21	0.1	$1.79 \times 10^{-3} M$	7.03	0.2	$1.90 \times 10^{-3} M$
8.16	0.1	$1.80 \times 10^{-3} M$	7.01	0.2	$1.90 \times 10^{-3} M$
8.11	0.1	1.79 x 10 <sup>-3</sup> M	6.99	0.2	$1.90 \times 10^{-3} M$
8.07	0.1	1.79 x 10 <sup>-3</sup> M	6.98	0.2	$1.90 \times 10^{-3} M$
8.02	0.1	$1.79 \times 10^{-3} M$	6.96	0.2	$1.90 \times 10^{-3} M$
7.98	0.1	$1.85 \times 10^{-3} M$	6.94	0.2	$1.90 \times 10^{-3} M$
7.93	0.1	$1.82 \times 10^{-3} M$	6.93	0.2	$1.90 \times 10^{-3} M$
7.89	0.1	$1.83 \times 10^{-3} M$	6.92	0.2	$1.90 \times 10^{-3} M$
7.86	0.1	$1.84 \times 10^{-3} M$	6.92	0.2	$1.90 \times 10^{-3} M$
7.81	0.1	1.83 x 10 <sup>-3</sup> M	6.90	0.2	$1.91 \times 10^{-3} M$
7.77	0.1	1.82 x 10- <sup>3</sup> M	6.88	0.2	$1.91 \times 10^{-3} M$
7.74	0.1	$1.83 \times 10^{-3} M$	6.87	0.2	$1.92 \times 10^{-3} M$
7.70	0.1	1.85 x 10 <sup>-3</sup> M	6.85	0.2	$1.92 \times 10^{-3} M$
7.67	0.1	1.85 x 10 <sup>-3</sup> M	6.85	0.2	$1.93 \times 10^{-3} M$
7.64	0.1	$1.85 \times 10^{-3} M$	6.83	0.2	$1.93 \times 10^{-3} M$
7.58	0.2	$1.85 \times 10^{-3} M$	6.82	0.2	$1.93 \times 10^{-3} M$
7.54	0.2	$1.85 \times 10^{-3} M$	6.81	0.2	$1.91 \times 10^{-5} M$
7.49	0.2	$1.85 \times 10^{-3} M$	6.80	0.2	$1.92 \times 10^{-3} M$
7.43	0.2	1.85 x 10 <sup>-3</sup> M	6.79	0.2	$1.93 \times 10^{-5} M$
7.40	0.2	1.88 x 10 <sup>-3</sup> M	6.76	0.5	$1.93 \times 10^{-3} M$
7.35	0.2	1.88 x 10 <sup>-3</sup> M	6.71	0.5	$1.93 \times 10^{-3} M$
7.33	0.2	$1.88 \times 10^{-3} M$	6.67	0.5	$1.93 \times 10^{-5} M$
7.29	0.2	1.89 x 10 <sup>-3</sup> M	6.62	0.5	$1.93 \times 10^{-3} M$
7.25	0.2	1.89 x 10 <sup>-3</sup> M	6.58	0.5	$1.93 \times 10^{-3} M$
7.23	0.2	1.89 x 10 <sup>-3</sup> M	6.55	0.5	$1.93 \times 10^{-3} M$
7.20	0.2	$1.89 \times 10^{-3} M$	6.50	0.5	$1.93 \times 10^{-3} M$
7.18	0.2	$1.89 \times 10^{-3} M$	6.46	1.0	$1.93 \times 10^{-5} M$
7.15	0.2	$1.89 \times 10^{-3} M$			

Experiment #4:	Reversible titration of Red Cedar River, 100 ml.
	sample, with $2 \times 10^{-2}$ M HCl and $2 \times 10^{-2}$ M KOH

pH	HC1	Divalent	pН	КОН	Divalent
	added	ppm	-	added	ppm
	in ml.			in ml.	
8.38	0.0	130	6.49	0.5	153
8.32	0.2	133	6.56	0.5	153
8.24	0.2	133	6.65	0.5	153
8.14	0.2	130	6.73	0.5	153
8.06	0.2	137	6.83	0.5	153
7.96	0.2	135	6.91	0.5	154
7.87	0.2	135	7.04	0.5	154
7.79	0.2	138	7.16	0.5	154
7.72	0.2	140	7.35	0.5	154
7.65	0.2	141	7.58	0.5	155
7.60	0.2	143	7.87	0.5	155
7.53	0.2	141	8.11	0.5	155
7.49	0.2	138	8.36	0.5	155
7.44	0.2	139	8.56	0.5	155
7.40	0.2	140	8.71	0.5	155
7.36	0.2	140	8.83	0.5	155
7.27	0.5	141	8.94	0.5	155
7.20	0.5	142	9.01	0.5	155
7.11	0.5	140	9.09	0.5	155
7.06	0.5	142	9.14	0.5	153
6.99	0.5	140	9.19	0.5	153
6.95	0.5	142	9.24	0.5	151
6.93	0.5	143	9.29	0.5	149
6.90	0.5	146	9.33	0.5	149
6.84	0.5	146	9.37	0.5	147
6.79	0.5	146			
6.75	0.5	146			
6.70	0.5	148			
6.66	0.5	148			
6.61	0.5	151			
6.58	0.5	151			
6.55	0.5	153			
6.50	0.5	152			
6.47	0.5	153			
6.43	0.5	153			
6.39	0.5	153			

A Reality and the second

Experiment #5: Reversible titration of three 100 ml. aliquots of Red Cedar River sample with  $2 \ge 10^{-2}$  M HCl and  $2 \ge 10^{-2}$  M KOH

Additions		А		В		С
in ml.	pН	$Ca^{2+}$	pH	Ca <sup>2+</sup>	pH	$Ca^{2+}$
		in ppm		in ppm		in ppm
HC1						
0.0	8.27	89.0	8.29	89.0	8.29	89.0
0.5	8.07	89.0	8.11	89.0	8.03	89.0
0.5	7.82	93.0	7.90	93.0	7.85	91.0
0.5	7.70	97.5	7.70	95 <b>.</b> 0	7.68	97.5
0.5	7.54	97.5	7.56	97.5	7.56	97.5
0.5	7.45	97.5	7.46	97.5	7.46	97.5
0.5	7.34	97.5	7.35	97.5	7.35	97.5
1.0	7.19	97.5	7.19	97.5	7.17	97.5
1.0	7.06	97.5	7.08	97.5	7.05	97.5
2.0	6.83	97.5	6.85	97.5	6.84	97.5
2.0	6.66	97.5	6.68	97.5	6.68	99.5
2.0	6.53	97.5	6.53	97.5	6.54	97.5
КОН						
1.0	6.71	97.5	6.72	97.5	6.71	97.5
1.0	6.89	97.5	6.89	97.5	6.89	97.5
1.0	7.08	95.0	7.07	95.0	7.11	97.5
2.0	7.93	93.0	7.91	93.0	8.06	91.0
2.0	8.75	81.0*	8.82	81.0*	8.87	81.0*
HC1						
2.0	7.87	89.0	7.94	89.0	8.04	89.0
2.0	7.21	91.0	7.24	91.0	7.25	91.0
2.0	6.88	93.0	6.90	93.0	6.88	93.0

\*precipitate

Experiment	<u>#6:</u> Revo Red 2 x 1	ersible titr Cedar Riv 10 <sup>-2</sup> M KO	ation of the er sample H	ree 50 ml. with 2 x 10	aliquots c - <sup>2</sup> M HCl	of and
Additions in ml.	pН	A Ca <sup>2+</sup> in ppm	pH	B Ca <sup>2+</sup> in ppm	pH	C Ca <sup>2+</sup> in ppm
HC1		••				
0.0	8.29	83.5	8.31	83.5	8.32	81.5
0.5	7.96	83.5	7.91	85.5	7.93	85.5
0.25	7.81	87.5	7.77	89.0	7.78	87.5
0.25	7.64	89.0	7.63	89.0	7.65	89.0
0.25	7.48	89.0	7.42	89.0	7.50	91.5

0.25	1.01	0 /. 0	•••			
0.25	7.48	89.0	7.42	89.0	7.50	91.5
кон						
	7 70	80.0	7 70	89 0	7.61	89.0
0.25	1.19	07.0	1.10	07.0	7 02	00.0
0.25	8.12	89.0	8.01	89.0	7.93	89.0
0.25	8.41	89.0	8.32	89.0	8.25	89.0
HCI						
0.25	0 10	0 15	8 10	91.5	8.04	89.0
0.25	8.10	9.15	0.10	04.0	7 91	96 0
0.25	7.96	91.5		94.0	7.01	90.0
0 25	7 75	97 5	7.69	96.0	7.63	97.5
0.25	7.15	77.5	7 54	07 5	7 52	97.5
0.25	7.58	91.5	1.50	71.5	1.56	, <b></b> .

Experiment #7:	Reversible titration Red Cedar River wi 2 x 10 <sup>-2</sup> M KOH	of 100 ml. aliquot of synthetic th $2 \times 10^{-2}$ M HCl and
рН	Additions in ml.	Ca <sup>2+</sup> in ppm
8.08 4.77	HC1 0.00 0.50	97.5 pH too low for reading
5.54 5.85 6.44 6.70 7.05 7.17 8.10 8.66 9.01	KOH 0.05 0.05 0.05 0.05 0.05 0.05 0.10 0.10	pH too low for reading pH too low for reading 89.0 97.5 99.5 99.5 99.5 99.5 99.5 99.5 97.5
8.50 7.21 7.03 6.58	HC1 0.10 0.10 0.10 0.20 KOH 0.30	97.5 99.5 95.0 97.5 95.0

Experiment #8:	Reversible titration of 75 r Red Cedar River using $2 \times 2 \times 10^{-2}$ M KOH	nl. sample of synthetic (10-2 M HCl and
Hα	Additions	$Ca^{2+}$
I	in ml.	in ppm
	HC1	
7.86	0.00	97.5
7.20	0.05	97.5
6.45	0.05	99.5
5.78	0.05	99.5
	КОН	
6.03	0.05	99.5
6.38	0.05	99 <b>. 5</b>
6,66	0.05	99.5
6.88	0.05	99.5
7.35	0.05	99.5
7, 96	0.05	99.5
8, 50	0.05	99.5
8 87	0.05	99.5
9,12	0.05	99.5
9.37	0.10	97.5
9.54	0.10	97.5
9.62	0.10	97.5
9.84	0.20	97.5
9,96	0.20	97.5
10.06	0.20	97.5
10.12	0.20	97.5
10.45	0.50	95.0 ppt.
10.55	0.50	91.0 ppt.
10.00		

Experiment #8: eversible titration of 75 ml sample of synthetic р.

#### APPENDIX E

## Eh - pH Perturbation Experiment

# Treatments with 30% $H_2O_2$ and 2 x 10<sup>-2</sup> M HCl 50 ml. aliquots of Red Cedar River Three replicates per block

## Calcium Activity Results

Time	No HCl	2% HCl/vol.	5% HCl/vol.	10% HC1/vol.
1 /2 hour 2% H <sub>2</sub> O <sub>2</sub> No H <sub>2</sub> O2	65, 65, 65 65, 65, 65	65, 65, 65 64, 64, 64	68, 67, 67 74, 79, 78	71, 71, 71 83, 83, 83
2 hours 2% H <sub>2</sub> O <sub>2</sub> No H <sub>2</sub> O <sub>2</sub>	64, 64, 64 68, 68, 68	66, 66, 66 71, 69, 71	67, 67, 67 78, 78, 79	71, 71, 72 84, 84, 84
6 hours 2% H <sub>2</sub> O <sub>2</sub> No H2O <sub>2</sub>	64, 64, 64 68, 68, 68	69, 69, 69 71, 71, 72	70, 70, 68 79, 79, 79	77, 77, 77 87, 87, 87
24 hours 2% H <sub>2</sub> O <sub>2</sub> No H <sub>2</sub> O <sub>2</sub>	71, 70, 71 75, 75, 75	73, 73, 73 78, 78, 78	73, 74, 74 80, 80, 82	85, 85, 85 95, 93, 93
48 hours 2% H <sub>2</sub> O <sub>2</sub> No H <sub>2</sub> O2	77, 77, 77, 88, 89, 89	78, 78, 78 94, 94, 96	84, 86, 84 94, 94, 94	95, 93, 95 99, 99,101

Time	No HCI		2% I	ICI		ß	% HC1		10	% HCI	
1/2 hour 2% H <sub>2</sub> O2/vol. No H <sub>2</sub> O <sub>2</sub> /vol.	8.07, 8.11, 8. 8.33, 8.33, 8.	10 7 30 7	. 55, 7	.56,7 .70,7	. 57	6.98, 7.08,	7.05, 7.12,	7.06 7.12	6.66, 6.64,	6.61, 6.63,	6. 71 6. 62
2 hours 2% H <sub>2</sub> O2/vol. No H <sub>2</sub> O2/vol.	8.08, 8.17, 8. 8.39, 8.39, 8.	16 7 36 7	. 70, 7 . 89, 7	. 77, 7 . 93, 7	. 75 . 89	7.26, 7.30,	7.28, 7.36,	7.29 7.31	6.89, 6.83,	6.83, 6.81,	6.90 6.83
6 hours 2% H <sub>2</sub> O <sub>2</sub> /vol. No H <sub>2</sub> O <sub>2</sub> /vol.	8.32, 8.35, 8. 8.51, 8.52, 8.	26 53 8	8.12,8 3.23,8	.10,8 .29,8	\$.18 \$.24	7.76, 7.79,	7.83, 7.90,	7.80 7.90	7.50, 7.51,	7.39, 7.46,	7.45 7.36
24 hours 2% H <sub>2</sub> O <sub>2</sub> /vol. No H <sub>2</sub> O <sub>2</sub> /vol.	8.56, 8.54, 8 8.61, 8.66, 8	. 48 . 64 8	3.52,8 3.56,8	. 52, 8	3.55 3.57	8.42, 8.48,	8.46, 8.51,	8.46 8.50	8.38, 8.39,	8.34, 8.37,	8.36 8.36
48 hours 2% H <sub>2</sub> O <sub>2</sub> /vol. No H <sub>2</sub> O <sub>2</sub> /vol.	8.67, 8.66, 8 8.55, 8.55, 8	. 63 . 53	3.68,8 3.64,8	. 68, 8	3.68 3.63	8.61, 8.65,	8.63, 8.66,	8.64 8.66	8.52, 8.57,	8.49, 8.57,	8.52 8.56

pH Results

