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A Kinetic Approach to the Inactivation of Zinc by Various Soil Constituents

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A KINETIC APPROACH TO THE INACTIVATION OF ZINC BY VARIOUS SOIL CONSTITUENTS

by

Shingara S. Sandhu

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Soil Chemistry

Approved:

UTAH STATE UNIVERSITY
Logan, Utah

1970

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Shingara S. Sandhu

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ABSTRACT

A Kinetic Approach to the Inactivation of Zinc by Various Soil Constituents

by

Singara S. Sandhu, Doctor of Philosophy

Utah State University, 1970

Major Professor: Dr. R. L. Smith
Department: Soils and Meteorology

The adsorption reaction of zinc onto prochlorite, pyroxene, and biotite minerals, from dilute solution (water) was studied under isothermal conditions by agitated nonflow experiment method. The equilibrium concentration of zinc in the solution was determined both by radioactive tracer technique and adsorption spectrophotometer methods. The data were collected at three temperatures.

The data were treated by the equation:

$$\frac{\partial\theta}{\partial t} = k_1(1-\theta)C - k_{-1}\theta$$

where θ is the fraction of total surface coverage and C is the equilibrium concentration of zinc in solution, k_1 and k_{-1} are the rate constants for the adsorption and reverse process and t is the time of reaction.

The specific rate constant for the adsorption reaction (k_1) depends on the nature of the mineral and mineral particle fraction. The k_1 increases with rise in temperature. The values for the desorption rate constant (k_{-1}) are small, indicating that zinc ions

are preferentially adsorbed over other exchangeable ions in the system.

The activation energy for the sorption process lay between 3 to 6 kcals/mole, eliminating chemical adsorption. The activation energy indicates the physical process of diffusion as the mechanism controlling step in the present study. The positive standard entropy of activation ($\Delta S^{\ddagger}$) is related to the change in the volume of activation complex ($\theta^{\ddagger}$) during the course of reaction.

The monolayer capacities for the three minerals and mineral fractions were evaluated. The percent of the surface area occupied by the adsorbed zinc ion was about 50 percent, 65 percent and 66 percent for prochlorite, pyroxene and biotite, respectively. This suggests that zinc is adsorbed on certain specific sites. The monolayer capacities increase as the temperature increases.

The change in the standard free energy of adsorption, $-\Delta^{\circ}G$, with the increased fraction of surface coverage allows speculation that:

1. The sites are energetically heterogenous.
2. There is mutual repulsion of adsorbed zinc ions at higher surface coverage.

The data show that zinc adsorption onto the minerals used in the present study is exchange adsorption. The initial adsorption plateau in the case of prochlorite and pyroxene is described as a result of exchange of solution zinc for weakly adsorbed sodium. The change in the nature of the curve beyond this region is speculated to the progressive exchange of other cations. The data for biotite are not conclusive and need further study. It appears that exchange adsorption is a step wise process and more than one plateau may be obtained if the

system is allowed to reach its ultimate equilibrium where all the exchange sites are completely saturated by the adsorbate. The small differential heat of adsorption ($\Delta^{\circ}H$) confirms the contention that the process is simply an exchange adsorption in the systems studied.

(97 pages)

INTRODUCTION

Zinc (Zn) is one of the essential nutrients for plant growth. Unlike the major nutrient elements, Zn is required in only infinitesimal amounts. Zinc deficiency, in most of the cases, is related to Zn supplying power of soil rather than the actual lack of element in the soil, since most mineral soils contain 80 to 300 ppm of total Zn. However, exchangeable Zn is usually less than one part per million; the remainder is fixed in unavailable form. Fixation may be defined as the process whereby a readily soluble plant nutrient is changed to less-soluble forms by reaction with inorganic or organic components of the soil, with the result that the element becomes restricted in its mobility in the soil and suffers a decrease in its availability to the plant.

Fixed Zn is often difficult to release in forms available to plants. Fixation mechanisms which have been postulated as contributing to Zn deficiency include organic complexes, precipitation of insoluble inorganic salts, and strong zinc-soil mineral interaction (adsorption).

Prochlorite, biotite, and pyroxene are silicate minerals which occur extensively in soils. They are widely apart from each other in their structural and chemical composition and are the representatives of sheet and chain silicates. Despite the widespread occurrence of these minerals in the soil system, relatively little data exist which specifically isolate the interaction between cations in solutions and the solid phase of these minerals.

The minerals and the crystalline solids found in the soil when dispersed in solution inherently posses an adsorptive potential because of the unsaturated forces which exist at the solid-liquid interfaces. The adsorptive potential found at the interfaces depends on the nature of the solid crystal and surface area exposed to the reaction. Because the clay size mineral fraction exposes a large surface area for adsorption reaction, it has been generally used as an adsorbent for adsorptive studies. However, the coarse mineral fraction can also be used for such purpose.

The adsorption reaction of Zn in the soil differs from other cations due to certain properties of Zn which are inherent to its position in the periodic table. The zinc ion possesses an 18 electron outer shell, a small ionic radius, and a relatively large charge density. The coupling of these properties produces a cation with strong polarizability; consideration of the polarization phenomena in the chemistry of soil Zn helps explain the strong adsorption of Zn on minerals and also its tendency to form numerous complexes.

Relatively little is known regarding the chemistry and kinetics of Zn adsorption on mineral surfaces. The present study was undertaken to investigate the chemical nature of Zn interaction on some common soil-forming minerals which are widely different from each other in their structural and chemical composition. This involves the evaluation of (a) the thermodynamic functions of Zn adsorption on various mineral surfaces, (b) the relationship between the specific rate constants and various factors, such as temperature and surface area of the minerals exposed to the reaction mechanism, and (c) the activation energy, the standard free energy of activation, $\Delta G^{\circ\ddagger}$, the standard enthalpy of activation, $\Delta H^{\circ\ddagger}$, and the standard entropy of activation, $\Delta S^{\circ\ddagger}$, in an attempt to postulate a reaction mechanism of Zn adsorption on the surfaces of various mineral fractions.

REVIEW OF LITERATURE

Fixation of Zn by inorganic colloids

The adsorption reaction of Zn in the soil differs from those of other cations. Jones et al. (1936) showed that small concentrations of Zn replace calcium (Ca) quantitatively from the soil. However, a part of the adsorbed Zn was not replaceable by neutral salts solutions. Hibbard (1940) and Brown (1950) showed that a part of Zn added to the soil could not be extracted by solutions of neutral salts. They also gave evidence that this strongly bound Zn was associated with the mineral fraction of the soil rather than with the organic matter. The Aiken clay loam soil used by Brown (1950) contained primarily kaolinite clay and had a distinct adsorption curve for Zn not shown by other soils studied. He found that in this case 24 hours shaking was necessary for complete adsorption of Zn, whereas in most of the other soils the equilibrium was reached within two hours. When the soil was saturated with different cations, the release of the adsorbed cations by Zn was in the order of $Na^{+} > Ca^{++} > K^{+} > Mg^{++}$. Equilibrium was reached in a much shorter time (eight hours) when the organic matter was removed. Acid extractants were more effective in removing adsorbed Zn than were the neutral salts.

Elgabaly and Jenny (1943) studied the cation and anion adsorption in various systems of Zn salts and Zn saturated clays. They found that the uptake of Zn by clays from zinc chloride (ZnCl) system involved Zn^{2+}, $ZnCl^{+}$, and $Zn(OH)^{+}$. Some of the Zn adsorbed by clays was non-replaceable. Later, Elgabaly (1950) reported that Zn could be fixed in the odd-third octahedral position in montmorillonite clays not filled by aluminium. In magnesium (Mg) minerals, Zn could replace Mg, but Mg could not replace all the Zn adsorbed. The amount of Zn fixed was correlated with the loss in exchange capacity of the clays which was in contrast to the work of Brown (1950).

Nelson and Melstead (1955) studied the reaction of Zn with certain soils and clay minerals and found that part of the Zn combined in a form that was extractable by acid but not ammonium acetate. This acid-extractable form increased with pH and time. They concluded that sorption of acid-soluble Zn had no effect on the cation exchange capacity of the clays. DeMumbrum and Jackson (1956) also have demonstrated the sorption of Copper (Cu) and Zn by montmorillonite from dilute solutions of Cu and Zn containing 0.5N calcium acetate ($Ca(OAc)_2$).

The possibility that lime minerals may constitute a potential adsorptive phase for certain cations was recognized by Leeper (1952), who postulated that in calcareous soils calcium carbonate may be an important adsorbent of heavy metals. Jurinak and Bauer (1956) found that Zn was adsorbed on the surface of calcite, while with dolamite and magnesite, Zn appears to penetrate into the crystal lattice and occupy vacant Mg sites. Seatz and Jurinak (1957) suggested that Zn may be adsorbed in a non-exchangeable form on commonly occurring lime minerals.

Teller and Hodgson (1960) studied the adsorption of Zn by layer silicates in dilute mineral suspensions. Detailed studies on montmorillonite and to a lesser extent on vermiculite, muscovite, and biotite, revealed the presence of at least two forms of specifically sorbed Zn, one of which was exchangeable by certain ions and the other, occurring in much smaller amounts, which was not exchangeable. The latter form was considered to result from lattice penetration; the former was associated with surface groups. They also noted that the total amount and the relative portion of these forms of sorbed Zn depended on the pH of the system, the time of reaction, the mineral species used, and the amount of Zn added. Equilibrium was not readily attained but tended to approach a slow steady state after several days.

Mangaroo, Himes, and McLean (1965) found that soils formed under neutral or slightly acid conditions adsorbed greater amounts of Zn than soils formed under very acid conditions. The stability constant for soil-zinc system after displacement of Zn by KCl and $Cu(OAc)_2$ was also higher for the near neutral soils. The organic matter content did not explain the difference in the amounts of Zn adsorbed and retained.

Bower and Truog (1940) showed that Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+} and Th^{4+} were retained by montmorillonite and Miami soil in quantities greater than the exchange capacity. The H^+, Na^+, K^+ and Ba^{2+} gave closely agreeing values. It was concluded that hydroxy ions such as $Mg(OH)^+$, $Ba(OH)^+$, and $Fe(OH)^{2+}$ were in competition with the normal ions for exchange sites.

Kinetics of adsorption from solution-systems

Adsorption phenomena is usually divided into two catagories: physical adsorption and chemisorption. The forces associated with physical adsorption are generally considered to be of the Van der Waal type. They include forces associated with dipole orientation, adsorbate polarization, and the dispersion effect. Although energetically weak in comparison to chemical reactions, Van der Waal's forces make a contribution to all interfacial attraction phenomena and are dominant in physical adsorption.

Chemisorption, as its name implies, describes the surface reaction whose forces are of the same type as those associated with chemical reaction, i.e., forces associated with electron sharing, electron rearrangement as in ionic and covalent bonding, and surface radical formation. This concept was strongly emphasized by Langmuir (1916). The heats of adsorption which accompany chemisorption are usually of a magnitude which suggest chemical reactions, and values of 20 to 100 K calories per mole of adsorbate are not uncommon. By contrast, the heat evolved in physical or Van der Waal adsorption are usually less than 10 K cals per mole of adsorbate.

An important consequence of the concept of chemisorption is that after a surface has become covered with a single layer of adsorbed molecules, it is essentially saturated; additional adsorption (multilayer formation) can occur only on the layer already formed. Langmuir (1918), Paneth and Vorwerk (1922) and Roberts (1935) have shown that a definite adsorption limit occurs, beyond which further molecules cannot be adsorbed readily. When the surface area is known, the limit is found to correspond to the existence of a unimolecular layer. This result is good evidence for the theory that chemical forces are involved in chemisorption.

It was suggested by Taylor (1931) that chemisorption is frequently associated with an appreciable activation energy and may, therefore, be a relatively slow process; for this reason it is frequently referred to as activated adsorption. The energies of activation are often of the order of 20 K cals per mole, and consequently the adsorption is extremely slow at low temperatures. Under these conditions, Van der Waal's adsorption, which requires little activation energy, will predominate.

In most of the adsorption studies it has been assumed that all surfaces are energetically homogeneous and that adsorbed molecules are arranged in simple layers, but in reality the surfaces are never homogeneous (Laidler, 1965) from the molecular standpoint. Some surface sites will be more active than others and chemical processes will occur predominately on the most active sites, which Taylor (1931) referred to as active centers. The active centers may actually correspond to certain types of lattice defects.

The complication that exists in connection with chemisorption is that there are interactions, usually of a repulsive nature, between atoms or molecules adsorbed side by side on a surface. The first evidence for this was obtained by Roberts (1935). He measured heats of adsorption of hydrogen on tungsten surface that was considered to be quite homogeneous. The heat was found to fall from about 45 K cals per mole for a bare surface to 15 K cals per mole for what was believed to be a fully covered surface. Later, Rideal and Trapnell (1950) and Trapnell (1951) indicated that the surface was only 70 percent covered and that the heats of adsorption became close to zero when the surface is actually fully covered. If the surface is really homogeneous, this change in heat of adsorption must be due to repulsive interaction between the adsorbed molecules; when the surface is sparsley covered, the molecules are sufficiently far apart not to interact with each other, but the repulsive interactions become important as the coverage increases. Additional evidence for repulsive interaction has been obtained by Emmert and Kummer (1950) using an isotope method and by Weber and Laidler (1950) on the basis of measurements of rates of adsorption.

Research on adsorption pehnomena has generally been concerned with equilibrium isotherm analysis. It has been established that the amount of adsorbate forming a monolayer on the adsorbent surface, after equilibrium is established, depends on various factors, including the nature of the adsorbent and the adsorbate, the temperature, and the concentration of the adsorbate solution. A number of adsorption isotherms equations have been suggested, some being empirical and others obtained theoretically. Of the theoretical equations the simplest type is that of Langmuir (1916). This applies to the ideal case of adsorption on a perfectly homogeneous surface with no interactions between adsorbed molecules.

Mechanisms of surface reactions are regarded as involving five consecutive steps (Laidler, 1965) as follows:

1. Diffusion of the reacting molecules to the surface.
2. Adsorption of the molecules on the surface.
3. Reaction on the surface.
4. Desorption of the products.
5. Diffusion of the desorbed products into the main body of the system.

If a large enough surface is used and the concentration of the adsorbent solution is realtively small, steps four and five in the above scheme of reaction mechanisms are negligibly small and one of the initial 3 steps then becomes the rate determination step. Diffusion in a liquid, like many other physical processes, has an activation energy, but the magnitude of this is usually not greater than 5 K cals per mole (Frost and Pearson, 1961). The systems with an activation energy greater than this will usually have steps 2 and 3 as the rate determining process. Many of the reactions between solids and solutions involve diffusion as the slow step (Laidler, 1965).

Eley (1953) derived a kinetic equation for unimolecular processes occurring in condensed phases which includes adsorption. The ultimate equation derived was

$$\log x - \frac{\gamma}{2.3RTx} = -At + \text{constant}$$

where $x = C_{(t)} - C_{(eq)}$; $C_{(t)}$ is the concentration of the reactants at time t; $C_{(eq)}$ is the concentration of the reactants at equilibrium; R is the universal gas constant and T is the temperature. The factor A incorporates the specific rate constant k.

Haque et al. (1968) used a slightly different form of the above equation in a kinetic study of the sorption of 2,4-D on clays. The equation used by Haque was

$$\ln(1-\theta) - \frac{\gamma(1-\theta)}{RT} - A't + \text{constant.}$$

When C_o, $C_{(\infty)}$ and $C_{(t)}$ respectively, where the concentrations of 2,4-D at the beginning, at equilibrium and at arbitrary time t, and γ is a constant, then

$$\theta = \frac{C_o - C_{(t)}}{C_o - C_{(\infty)}}$$

where θ was defined as the fraction of surface covered. Their data appeared to fit the equation for 2,4-D adsorption by illite, kaolinite and montmorillonite. Rate constants, activation energies, free energies of activation, heats of activation and entropies of activation were calculated for the sorption process.

The overall sorption process was explained in the light of the molecular structure of 2,4-D and the clay aggregates. The rate constants depended on the nature of the clay and fell between 2 and 22 x 10^{-7} seconds^{-1}. The rate constants decreased with an increase in surface area. The amount of 2,4-D sorbed per gram of clay was in the order of illite > montmorillonite > kaolinite. The temperature was found to have little effect on the amount of 2,4-D sorbed per gram of the clays. The activation energy was between 3 and 5 K cals per mole, indicating that diffusion was the rate controlling step in the reaction mechanism. It was found that clays with the larger surface area gave the higher activation energy.

Weber and Rumer (1965) indicated that the rate-limiting step for removal of organic solutes from dilute aqueous solutions by porous active carbon in an agitated non-flow system is one of intraparticle transport of the solute in the pores and capillaries of the adsorbent. Crank (1965) postulated that for a system in which intraparticle transport is a rate limiting step, the data for uptake of solute from solution should give a linear plot as a function of the square root of time, from the time the adsorbent was introduced to the system. Accordingly, Weber and Gould (1966) obtained the rate constants from the square of the slope of the straight line obtained from the plot of the amount of solute in milligrams removed from the solution per gram of carbon as a function of the square root of time. The rate constants for the adsorption of the various organic pesticides on the 273-micron carbon were found to be similar. They found that the ultimate capacity (monolayer capacity, Xm) was independent of the type of organic pesticides tested by them, but it was found to decrease with increasing temperature, showing that adsorption was an exothermic process.

Comparison of the values of activation energy (Ea) for the various pesticides and the neutral and anionic species indicated that much higher activation energy is associated with adsorption of neutral molecules than with the adsorption of anions. Weber and Gould (1965) used the equation

$$\Delta H = \frac{RT_1T_2}{T_2 - T_1}(\ln x_{m_1} - \ln x_{m_2})$$

for the evaluation of the differential heats of adsorption. The values obtained by them were about 4 K cals per mole. They postulated that since water had to be readsorbed during the adsorption process from aqueous solution, the ΔH values obtained were small.

Peterson and Kwei (1961) studied the kinetics of adsorption of polyvinyl acetate (PVAC) from dilute benzene solution onto the surface of chrome plate by radioactive tracer method, using the C^{14} labelled polymer. The value of θ, the fraction of surface covered, was considered as directly proportional to the amount of PVAC adsorbed. They found the initial rate of adsorption to be rapid. This early stage of the adsorption from dilute solutions was represented by a kinetic equation of the Langmuir type. The monolayer capacity was reported to be a function of PVAC concentration, and as the concentration of solutions was increased beyond 1.15×10^{-4} mole per liter, the plateau region became less well defined. They concluded that the initial adsorption of PVAC from dilute solution is two dimensional rather than three dimensional, with little or no interaction between adsorbed molecules up to a fairly high surface coverage. The adsorption from concentrated solutions was, however, thought to be predominantly three dimensional.

MATERIALS AND METHODS

Characteristics of minerals

The minerals used for the present adsorption studies were procured from Ward's Natural Science establishment. They were the American Petroleum Institute (API) research project 49's reference minerals. They were crushed in an iron mortar, pounded in a porcelain mortar and then fractioned by dry seiving using U. S. Standard Seive number 100, 200 and 300 mesh with diameter openings, in millimeters, as 0.149, 0.074, and 0.049, respectively. The fraction passing through 100 but not through 200 mesh was the coarse material. The fraction that passed through 200 but not through 300 mesh was the medium fraction and the one that passed through 300 mesh was the fine fraction.

The surface area of the various mineral fractions was determined by the ethylene gycol method of Bower and Goertzen (1958). The cation exchange capacity and exchangeable cations were determined by the method of Bower, Reitmeier and Fireman (1952). The cation exchange capacity (CEC) expressed as net change Meq x $10^{-6}/cm^2$ and exchangeable cations expressed as meq/100 grams of mineral fractions, along with some other mineral characteristics, are shown in Table 1. The minerals were found not to possess any exchangeable or soluble cations of iron and aluminium. Magnesium predominated in the exchange complex of prochlorite, whereas in biotite, Ca was the dominating exchangeable cation. In addition to Ca, pyroxene (augite) contained a considerable amount of exchangeable Na. The alkali characteristics of true micas are conspicuously absent in prochlorite.

Table 1. Characteristics of the minerals used[1] in adsorption studies

Determinations	Prochlorite[2]			Biotite			Pyroxene		
	Fine[3]	Medium[3]	Coarse[3]	Fine	Medium	Coarse	Fine	Medium	Coarse
pH	8.2	8.2	8.3	9.3	9.4	9.5	9.5	9.6	9.7
EMF (Mv/g)	0.22	0.24	0.25	0.50	0.56	0.65	0.60	0.64	0.65
Surface area (cm^2 x 10^4/g)	7.9	4.3	3.2	28.2	15.8	9.6	16.3	6.3	4.9
Net charge (meq 10^{-6}/cm^2)	2.9	2.8	2.5	2.0	2.2	2.7	3.31	3.03	3.58
Exch cations (meq/100 g)									
Ca	3.74	2.18	1.76	40.2	25.6	21.0	32.5	22.7	22.5
Mg	14.04	7.12	5.94	8.66	5.34	2.78	0.32	0.36	0.00
Na	2.95	1.69	1.62	0.86	0.64	0.41	17.22	5.65	4.50
K	0.49	0.13	0.33	1.91	0.96	0.59	11.36		

Table 1. Continued

Determinations	Prochlorite[2]			Biotite			Pyroxene		
	Fine[3]	Medium[3]	Coarse[3]	Fine	Medium	Coarse	Fine	Medium	Coarse
Soluble cations (mg/100 g)									
Ca	1.44	0.63	0.52	2.09	2.01	1.97	8.86	4.9	5.0
Mg	3.10	1.44	1.14	8.70	5.98	5.80	3.56	3.6	3.6
Na	1.5	0.80	0.72	16.66	10.82	10.74	8.35	2.47	2.18
K	1.76	0.86	0.49	30.0	20.0	20.17	13.90	5.25	3.40

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[1] Prochlorite was API Project 49, No. 1, Vermont, $(MgFe^{+3}Fe^{+2}Al)_6(SiAl)_4O_{10}(OH)_8$; Biotite was API Project 49, No. 3, Canada, $H_4K_2(MgFe)_6Al_2Si_6O_{24}$; Pyroxene was API Project 49, No. 6, Mexico, $CaMg(SiO_3)_2(MgFe)_2SiO_6$.

[2] Shirozu (1958) performed the analysis and the results have been quoted by Deer, Howie and Zussman (1962b) Table 25, Anal 27, p. 143. The composition is $(Mg_{3.26}Fe^{+3}_{0.84}Fe^{+2}_{0.64}Al_{1.09})Si_{2.86}Al_{1.18}O_{10}(OH)_8$.

[3] Fraction size.

X-ray diffractometry

X-ray diffraction data were obtained with seimens X-ray defraction equipment, using a copper target as a source of X-rays. Random orientations of the fine fraction of each mineral were prepared by seiving the sample powder directly onto the glass slides coated with a thin veneer of petroleum jelly. After allowing a few minutes for sufficient adhesion, the slides were inverted and the excess powder removed by tapping lightly on the side of the mount. The samples thus prepared were analyzed by X-ray diffraction. All diffractograms were obtained with goniometer scanning speeds of one degree two-theta per minute.

The data obtained for prochlorite were found to compare very closely with the American Society for Testing Materials (ASTM) index card No. 2.0028 and Shirozu's 1958 data of powder X-ray patterns for the prochlorite mineral (Deer, Howie and Zussman, 1962a). The X-ray data for biotite were found to be similar to the one reported in ASTM 1/1 index card No. 2.0045. The data for pyroxene compared favorably well with the ASTM index card No. 3.0623 and 3.0624. The X-ray data indicated that the minerals used in the present investigation are quite pure and free from contamination of other minerals. These data lead to the approximate molecular formulas shown in Table 1.

Description of minerals

Prochlorite: 2:1:1(2:2). It belongs to the chlorite group and occurs extensively in soils, mainly inherited from mafic and other rocks. The basic features of the atomic structure of chlorites were described by Pauling (1930). The detail investigation by McMurchy (1936) and Engelhardt (1942) established firmly that the structure is one of regularly

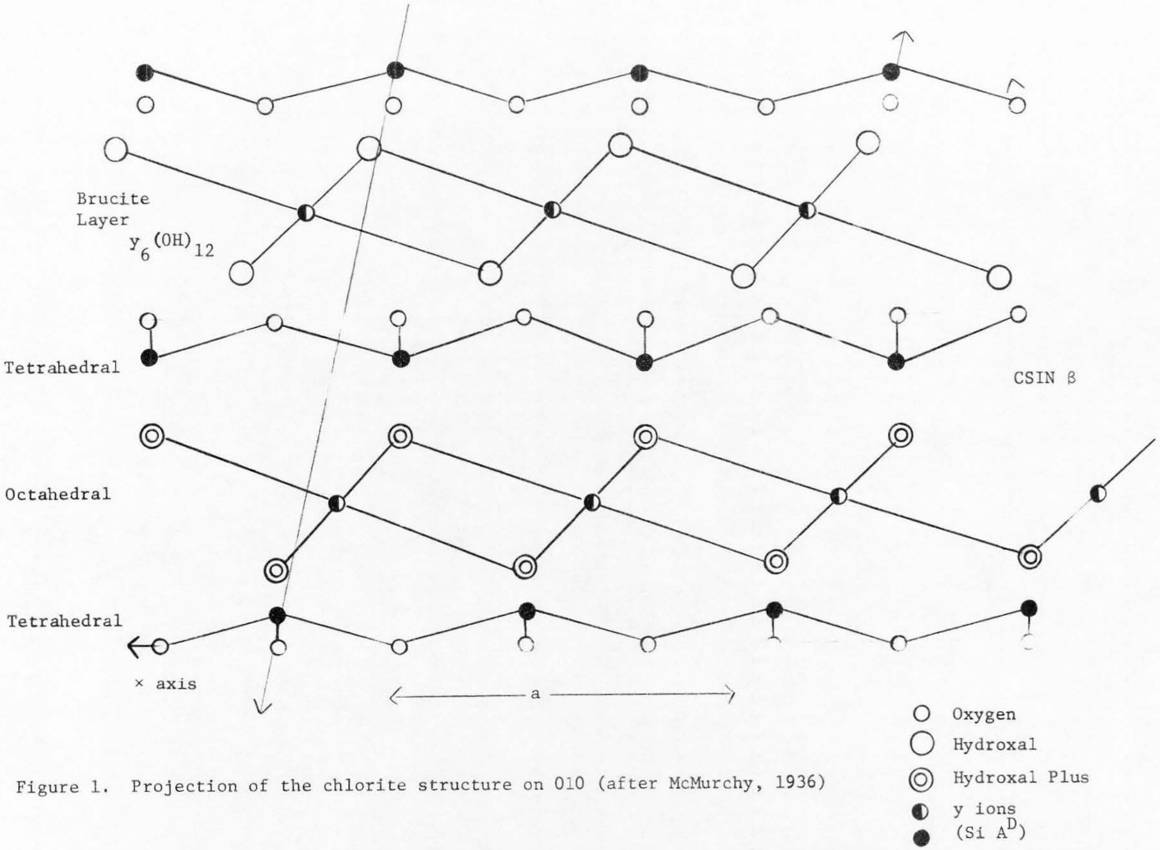


Figure 1. Projection of the chlorite structure on 010 (after McMurchy, 1936)

alternating talc-like $Y_6Z_8O_{20}(OH)_4$ and brucite-like $Y_6(OH)_{12}$ sheets. The pseudo-hexagonal networks of these components have a parameter approximately 5.3 Å, and the cell which results from their super-position has a = 5.3, b = 9.2, c = 14.3 Å, and β = 97°.

The b and c cell dimensions in prochlorite depend on the extent of substitution in the tetrahedral and octahedral sheets and can be calculated by the equations from Hey (1954)

$$b = (9.202 + 0.014\ Fe^{+3} + Fe^{+2}) + 0.023\ Mn^{+2}$$

$$c = 13.925 + 0.15(Si^{-4}) - 0.025\ Fe^{+3} + 0.25\ Mn^{+2}$$

The hydroxide interlayers, brucite, are sandwiched between the negatively charged mica-like layers as a replacement of K_2 in mica structure. The Si-O tetrahedron rotates about the X-axis, perpendicular to the layers, which aids in fitting tetrahedral and octahedral parts of the mica layer. The occupation of the tetrahedral sites by Si and Al and occupation of the octahedral sites by Fe, Mg and Al is non-random. The substitution of Al for Mg takes place in the brucite layer, giving rise to the positive charge which is symmetrically distributed between the hydroxide interlayer and the mica sheet itself, balancing the negative charge of the tetrahedral layer to some extent but not changing the nature of the negative charge distribution in the mica octahedral sheet. The change of mica-like mineral to prochlorite slightly increases the CEC.

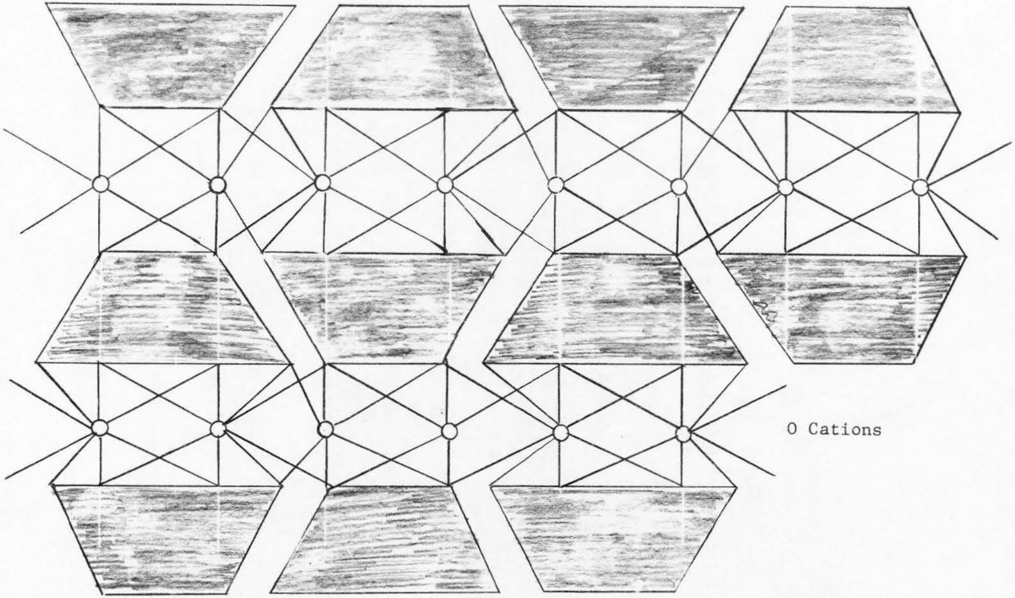
Biotite: 2:1. This is an iron rich trioctahedral mica which occurs extensively in soils. This mineral may be formed in soil during the weathering process or may be directly inherited from the soil forming rocks. In biotite the octahedral cation sites of the mica structure, ideally, are completely filled. Hendricks and Jefferson (1939) gave the following cell parameters for biotite similar to the one used in the present study: for 2M,

$$a = 5.3\ \mathring{A},\ b = 9.2\ \mathring{A},\ c = 10.1\ \mathring{A},\ \beta = 95°.$$

The chemical composition for the biotite used in the present study can be represented approximately by $H_4K_2(MgFe)_6Al_2Si_6O_{24}$, showing substitutions in the tetrahedral and octahedral sheets. Magnesium in the trioctahedral configuration is substituted by Fe^{+2} and also by trivalent ions (Fe^{+3} and Al^{+3}) and Al replaces Si in tetrahedral sites, usually in the ratio of Al:Si = 2:6, and thus the net negative charge develops in the tetrahedral layer. The net negative charge is balanced by K, which is chemically bound between the two adjacent silica tetrahedrons. Biotite binds K sufficiently to eliminate any water expansion characteristics.

Pyroxene (augite). The structure was described by Warren and Brog (1928). The augite is a ferromagnesium mineral, the structure of which consists of long chains of linked silica tetrahedra. It consists of a single chain in which 2 oxygens are shared in each tetrahedron. The pyroxene chains are linked laterally by cations like Ca, Mg, Fe, etc., in the manner shown in Figure 2.

The Mg and Fe are in octahedral coordination by oxygens which themselves are linked to only one silicon, while the larger cations are surrounded by eight oxygens, two of which are shared by neighboring tetrahedron in the chains. The cation to oxygen linkage, as shown in Table 2, is weaker than the silicon to oxygen linkage; as a result, these minerals have good cleavage and are fibrous.



End view of augite structure

Figure 2. Idealized structure of augite (drawn from Miller, 1965, p. 11)

The repeat distance along the length of the chain is approximately 5.25 Å and this defines the parameter of the c axis. The b axis calculated from Brown (1960) has been found to be about 8.91 Å,

$$b = 8.890 + 0.00256(\mathrm{Fe})\ \text{Å}.$$

The cell dimensions are:

$$a = 9.73,\ b = 8.91,\ c = 5.25\ \text{Å}.$$

Table 2. Molar energies of formation of cation to oxygen bonds in silicate minerals and glasses (reproduced from Miller, 1965, p. 71)

Cation	Bond energies	Cation	Bond energies
	cals		cals
Ca^{+2}	839	H^+ (in OH)	515
Mg^{+2}	912	Ti^{+4}	2,882
Fe^{+2}	919	Al^{+3}	1,878
Na^+	322	Si^{+4}	3,100
K^+	299		

The approximate unit cell formula derived from the chemical composition is given in Table 1. The substitution of Al for Si in the tetrahedral configuration seems to be the source of the net negative charge where two Si have been substituted for by Al and the mineral has a high net charge per square cm.

Adsorbate solution

Zinc is amphoteric in nature and a change in the pH of the system will affect its chemical activity. The minerals used for the adsorption reactions had an alkaline pH. It was thought desirable to use the adsorbate solution of the same pH as that of the adsorbent. It was also thought proper to eliminate the possibility of Zn precipitation, as zinc hydroxide ($Zn(OH)_2$), in the system due to changes in pH of the solution when treated with the minerals of high pH. In order to achieve this, the Zn solution, which was 0.001M with respect to stable Zn, was mixed with 0.2 mc of tracer Zn and was pretreated with 0.01N NaOH to bring the pH of the Zn solution to that of an aqueous suspension of the respective minerals. The treated solutions were cured at 70 C for 2 hours, cooled and filtered through Whatman No. 40 filter paper. The concentration of Zn in the filtrate was determined and is given in Table 3.

Table 3. The Zn concentration at the respective pH of the aqueous suspensions of three minerals

Mineral	pH	Zn moles/L x 10^{-5} C_1	K_{sp}
Prochlorite	8.2	1.25	43.7×10^{-15}
Biotite	9.3	1.76	44.2×10^{-15}
Pyroxene	9.5	1.78	17.8×10^{-15}

A pH of 8.8 has been reported in the literature to be zero point charge (ZPC) for the Zn ion. This should also coincide with the minimum solubility of Zn in an alkali system. Fulton and Swinehart (1954) reported the solubility of Zn to be minimum at approximately 1 x 10^{-3}M of dilute NaOH solutions.

The K_{sp} values calculated here seem to be in good agreement with 22.1 x 10^{-17} reported by Jurinak and Inouye (1962) for a pH of 9.3. The K_{sp} values in the pH range of 8.2 are not available from the literature, but the data reported here seem to be reasonably good when compared with the K_{sp} values of 9.1 x 10^{-18} and 7 x 10^{-18} reported by Jurinak and Inouye (1962) and Fulton and Swinehart (1954) for pH values around neutrality.

Method and procedure

Agitated non-flow experiments were used to investigate both the kinetics and equilibria of adsorption. The adsorbate solution was prepared in bulk and then diluted to the required concentrations of C_1, $C_{1/2}$, and $C_{1/4}$. The solutions were placed in a constant temperature room overnight to allow them to attain the desired temperature. Fifty mg of the fine and 200 mg of the coarse mineral fractions in each case were transferred to a 50 ml polyethelene centrifuge tube. The reaction vessel (polyethylene tube) was also placed in the constant temperature room overnight before 40 ml of Zn solution was transferred to it with an automatic burette. The tube was covered with a polyethylene film, and the mixture was agitated under isothermal conditions (in a constant temperature room, ± 1 C) on a shaker for the specified time. It has been reported by Weber and Morris (1963) that the rate of adsorption is independent of the stirring rate and agitation. At predetermined time intervals of 2, 4, 6, and 8 hours, the shaking was briefly interrupted, and the tubes were removed and centrifuged for 15 minutes at 3000 RPM. The supernatant liquid was transferred to 50 ml pyrex glass tubes and analyzed for An on a Perkin-Elmer model 303 atomic adsorption spectrophotometer using a digital readout attachment for a direct ppm reading. An aliquot of the supernatant solution was analyzed for tracer Zn in a scintillation well counter, Nuclear Chicago, model 183. For each study three blanks were also run.

The Langmuir equation used in the kinetic studies is based in principal on the formation of a monolayer capacity of adsorbate on the adsorbent surface. From this equation the fraction of surface covered, θ, is derived. The adsorbate concentration in the solution in the kinetic study was so low that it did not warrant a calculation of the monolayer adsorption capacity; therefore an attempt was made to use higher concentrations of Zn solution varying from 0.5 mg/L to 20 mg/L without treating the solution with NaOH before the adsorption studies. In so doing it was postulated that potential energy of the surface is greater than the free energy change generated, due to a rise in pH of the system when the Zn solution was equilibrated with the mineral fraction. Therefore, Zn from the solution should not precipitate as zinc hydroxide as long as there are adsorption sites available on the adsorbent surface and until the monolayer adsorption capacity has been satisfied.

THEORY

Langmuir isotherm adsorption equations

The relationship between the equilibrium concentration of a solute and the amount adsorbed at constant temperature defines the adsorption isotherm. The Langmuir adsorption equation is used in this study to describe the adsorption process. The assumptions used in its derivation are (a) that the surface is energetically homogeneous, (b) the energy of adsorption is constant, and (c) the adsorbate molecules are localized on specific sites without adsorbate interaction.

The adsorption and desorption process may then be represented as

$$C + S \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} \theta \qquad (1)$$

where C is the concentration of the adsorbate in solution, S is the activity of the vacant sites, and θ is the fraction of surface covered by the adsorbate molecules.

The Langmuir (1918) equation relating to this situation is as follows:

$$X/m = \frac{Xm\ b\ C_{eq}}{1 + b\ C_{eq}} \qquad (2)$$

in which X/m represents the mg of solute adsorbed per gram of mineral at equilibrium concentration, C_{eq}; Xm is the amount of adsorbate in mg adsorbed per gram of mineral to form a complete monolayer; and b denotes a constant (equilibrium constant, K_{eq}) related to energy of adsorption.

The linear form of equation (2) is

$$\frac{C_{eq}}{X/m} = \frac{1}{bXm} + \frac{C_{eq}}{Xm} \qquad (3)$$

and is used to evaluate Xm. The reciprocal of the slope of the straight line obtained by plotting $C_{eq}/X/m$ as a function of C_{eq} gives the monolayer capacity, or adsorption maximum, for the various mineral surfaces and the Y intercept gives the value of b.

Kinetic derivations

In the present treatment it is assumed that the data for the adsorption of Zn by the mineral surface can be represented by kinetic equations of the Langmuir type (Peterson and Kwei, 1961):

$$d\theta/dt = k_1(1 - \theta)C - k_{-1}\theta \qquad (4)$$

where θ is the fraction of total surface coverage and C is the equilibrium concentration of Zn in solution, k_1 and k_{-1} are the rate constants for the adsorption and the reverse process, and t is the time of reaction. The value of θ is considered to be directly proportional to the X_m, the monolayer capacity. θ is defined as:

$$\theta = \frac{X/m}{X_m} \qquad (5)$$

From equation (4) when the $d\theta/dt$ is zero, it follows that

$$\theta/(1 - \theta)C = k_1/k_{-1} = Keq \qquad (6)$$

The equations (2) and (6) are similar if b of equation (2) is substituted for K_{eq} in equation (6) and θ is defined as in equation (5). Then equation (6) becomes:

$$\frac{X/m}{Xm - X/m} = bC_{eq} \tag{7}$$

$$X/m(1 + bC_{eq}) = XmbC_{eq} \tag{8}$$

$$X/m = \frac{XmbC_{eq}}{1 + bC_{eq}} \tag{9}$$

An invariant equilibrium constant is obtained from systems approaching ideality. However, the equilibrium function of $\theta/(1 - \theta)C$ in its departure from constancy often indicates the nature of the factor responsible for non-ideality. The rearrangement of equation (6) gives:

$$C/\theta = C + \frac{k_{-1}}{k_1} \tag{10}$$

A plot of C/θ as a function C should give a straight line and the Y intercept of the plot gives a value for k_{-1}/k_1.

The rate equation (4) when integrated, gives:

$$-\ln\left(1 - \left(1 + \frac{k_{-1}}{k_1C}\right)\theta\right) = k_1C\ t \tag{11}$$

A plot of $-\log [1 - (1 + \frac{k_{-1}}{k_{1C}})\theta]$ vs t should give a straight line with a slope of $k_1C/2.303$ from which k_1, the rate constant for the forward reaction, can be calculated.

Energy of activation

Hood (1878) found empirically that the rate constant k_1 of a reaction varies with the absolute temperature T by the law

$$\log k_1 = B - \frac{A'}{T} \tag{12}$$

where B and A' are the constants. Van't Hoff (1884) gave theoretical significance to the law on the basis of the effect of temperature on equilibrium constant. Arrhenius (1889) extended this idea and showed that the variation of the equilibrium constant K_C (in concentration units) obeys the law:

$$\frac{d\ln K_C}{dT} = \frac{\Delta E}{RT^2} \tag{13}$$

where ΔE is the internal energy change for the reaction. The equilibrium condition for reaction in equation (1) can be formulated by equating two opposing reactions $k_1[S][C] = k_{-1}[\theta]$ where k and k_{-1} are the rate constants for the forward and reverse reactions, respectively. The equilibrium constant is, therefore, equal to k_1/k_{-1} and we have

$$\theta/[S][C] = \frac{k_1}{k_{-1}} = K_{eq} \text{ or } Kc \tag{14}$$

At low concentrations the reaction isochore equation (13) may therefore be written as

$$\frac{d\ln k_1}{dT} - \frac{d\ln k_{-1}}{dT} = \frac{\Delta E}{RT^2} \qquad (15)$$

which may be split in two equations

$$\frac{d\ln k_1}{dT} = \frac{E_1}{RT^2} + N \qquad (16)$$

and

$$\frac{d\ln k_{-1}}{dT} = \frac{E_{-1}}{RT^2} + N \qquad (17)$$

where $E_1 - E_{-1} = \Delta E$. Experimentally, it has been found that N can be set equal to zero (Laidler, 1965). The rate constant therefore is related to the temperature by equation of the form (Arrhenius equation)

$$\frac{d\ln k_1}{dT} = \frac{E_1}{RT^2} \qquad (18)$$

The equations (17) and (18) are interpreted to mean that when the reaction occurs between S and C (equation 1), there exists an equilibrium between S + C on the one hand, and the collision complex ($\theta^{\#}$) on the other. The $\theta^{\#}$ is known as the activated complex. The energy E_1 or Ea that is required for the system to pass from the state S + C to the activated state $\theta^{\#}$ is known as the energy of activation. There may be many collision complexes ($\theta^{\#}$) in existence at a given time in the reaction system, but only those with the energy Ea are capable of forming surface products directly and it is only these that are referred to as activated complexes.

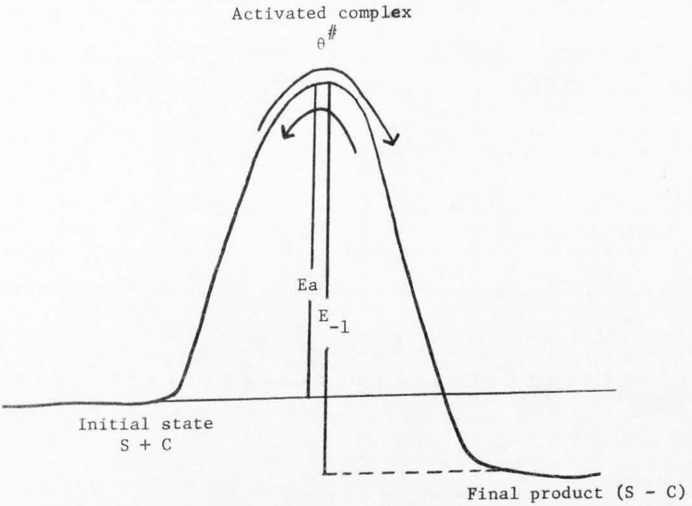


Figure 3. Energy-barrier diagram, showing the flow of activated complex in two directions

The rate equation (18) integrates to

$$\ln k_1 = -\frac{Ea}{RT} + \text{Constant}$$

where Ea is the energy of activation and is assumed to be independent of temperature over the temperature range studied.

This equation may be re-written with the constant equal to ln A.

$$k_1 = Ae^{-Ea/RT} = pZ_{sc}e^{-Ea/RT} \tag{19}$$

where A is a constant known as the frequency factor, and has the same units as the rate constant. A is equal to pZ where p is the stearic factor and Z is the collision number expressed as cc mole^{-1} sec^{-1} for a bimolecular reaction. Equation (19) can be tested by plotting log k_1 against the reciprocal of the absolute temperature and a straight line should be obtained with the slope = Ea/4.57.

Thermodynamic of adsorption

According to the absolute rate theory (Laidler, 1965), the equilibrium between reactants and the activated complex may be expressed in terms of thermodynamical functions as well as partition functions. Consider reactants A and B forming the activated complex $X^{\ddagger}$.

$$A + B = X^{\ddagger}$$

We can write

$$K^{\ddagger} = \left(\frac{[X^{\ddagger}]}{[A][B]}\right)_{eq} = \frac{F^{\ddagger}}{F_A F_B} e^{-E_A/RT} \tag{20}$$

where $F^{\ddagger}$, F_A, and F_B are the appropriate partition functions and $K^{\ddagger}$ is regarded as a modified equilibrium constant between the reactants and the activated states.

The process shown by equation (1) can be written

$$K^{\ddagger} = \left(\frac{[\theta^{\ddagger}]}{[S][C]}\right)_{eq} = \frac{F^{\ddagger}}{F_c F_s} e^{-Ea/RT} \tag{21}$$

The rate constant for the reaction shown by equation (20) is expressed (Laidler, 1965):

$$k_1 = \frac{kT}{h}\,\frac{F^{\mp}}{F_A F_B}\,e^{-E_A/RT} \tag{22}$$

where k is Boltzman's constant and h is Planck's constant. Comparison of (22) and (21) gives:

$$k_1 = \left(\frac{kT}{h}\right)k^{\mp} \tag{23}$$

assuming the transmission coefficient equals one. If we follow the thermodynamic analogy a step farther, $K^{\mp}$ can be expressed in terms of $\Delta G^{\circ\mp}$.

$$\Delta G^{\circ\mp} = -\,RT\ln K^{\mp} \tag{24}$$

where $\Delta G^{\circ\mp}$ is the difference between the free energy of the activated complex and the reactants, when all are in their standard states (usually unit concentration).

Substituting equation (23) we get:

$$k_1 = \frac{kT}{h}\,e\,-\,\frac{\Delta G^{\circ\mp}}{RT} \tag{25}$$

If k_1 is expressed in liters $\text{mole}^{-1}\ \text{sec}^{-1}$, the standard state for the free energy, enthalpy, and entropy, of activation is one mole per liter.

Gibb's standard free energy of activation is related to standard enthalpy and entropy of activation by:

$$\Delta G^{\circ\mp} = \Delta H^{\circ\mp} - T\Delta S^{\circ\mp} \tag{26}$$

and equation (25) can be written as

$$k_1 = \frac{kT}{h} e - \frac{\Delta H^{\circ\ddagger}}{RT} e \frac{\Delta S^{\circ\ddagger}}{R} \qquad (27)$$

Frost and Pearson (1961), starting from equation (23), related $\Delta H^{\circ\ddagger}$ to Ea in solutions in the liquid state

$$\Delta H^{\circ\ddagger} = RT^2 \frac{d\ln K^{\ddagger}}{dT} \qquad (28)$$

$$= RT^2 \frac{d\ln k_1}{dT} - RT \qquad (29)$$

$$\Delta H^{\circ\ddagger} = E_a - RT \qquad (30)$$

where Ea is the experimental energy of activation in the Arrhenius equation. Comparison of equations (19) and (27) gives:

$$Ae^{-E_a/RT} = \frac{kT}{h} e - \frac{\Delta H^{\circ\ddagger}}{RT} e \frac{\Delta S^{\circ\ddagger}}{R} \qquad (31)$$

Substituting for $\Delta H^{\circ\ddagger}$ in equation (31) we obtain:

$$Ae^{-E_a/RT} = pZ_{sc}{}^{-E_a/RT} = \frac{kT}{h} e^{-E_a/RT} e + \frac{RT}{RT} e \frac{\Delta S^{\circ\ddagger}}{R}$$

thus

$$\frac{kT}{h} e \frac{\Delta S^{\circ\ddagger}}{R} e = pZ_{sc} = A \qquad (32)$$

For the reactions at atomic or molecular levels, Z_{sc} is of the same magnitude as (k T/h); thus $\Delta S^{\circ\ddagger}$ is associated with the stearic hinderance. In any event $\Delta S^{\circ\ddagger}$ is expected to become more negative for a reaction between two poly-atomic molecules than for a reaction between two atoms.

Differential heat or adsorption and Gibbs free energy of adsorption

The differential heat of adsorption, defined for this study, is the difference in the amount of heat (energy) involved during the formation of monolayers measured at two temperatures. If a solid with X grams of adsorbate adsorbs ΔX grams of additional adsorbate with the evolution of ΔQ calories of heat, ΔQ is known as the differential heat of adsorption (Gregg, 1961). The differential heat of adsorption, though of limited significance, still indicates whether the reaction is exothermic or endothermic.

The differential heat of adsorption for monolayer coverage may be calculated from maximum levels of adsorption at two or more different temperatures by the Van't Hoff equation in the form (Weber and Gould, 1966)

$$\Delta H = \frac{RT_1T_2}{T_2 - T_1}(\ln Xm_1 - \ln Xm_2) \qquad (33)$$

where Xm_1 and Xm_2 are the monolayer capacities at temperature T_1 and T_2, respectively. Other terms have their usual meaning.

The Gibb's standard free energy for the monolayer capacity is calculated from

$$-\Delta G^\circ = RT\ln K \qquad (34)$$

where K, the equilibrium constant, corresponds to b in the linear form of the Langmuir equation (3). The Y intercept gives this value for K.

RESULTS AND DISCUSSION

Ionic form(s) of zinc

The literature does not present a clear picture about the structural composition of Zn in aqua and alkali solutions. Emeleus and Anderson (1938) reported that Scholdar isolated sodium zincate from concentrated solutions of sodium hydroxide. The formulas were determined as $An(OH)_3Na_3H_2O$ and $Zn(OH)_4Na_22H_2O$. Jurinak and Thorne (1955) hypothesized zincate formation in a zinc-bentonite system with an octahedral composition. But the choice of structures for Zn^{2+} appears to be between the tetrahedral and the outer orbital octahedral complexes. The electronic ground configuration of An is $(Ar)^{18}(3d)^{10}(4s)^2$. In acquiring an oxidative stage of Zn^{2+}, it loses 2 electrons from the 4s shell and achieves a pseudo-inert gas type configuration. Hence, the 3d orbital is not available for bond formation, and only the S and p orbitals can be used for the formation of tetrahedral complexes. The ionic or outer octahedral complexes can be attained by the formation of bond in the empty 4d shell, but this will not be possible for the charged or large ligands because of ligand-ligand repulsion. The water has considerable orientation power because of its high dipole moment and is a comparatively large ligand. Therefore water and hydroxal groups, theoretically, may be predicted to form Zn tetrahedral configurations rather than Zn outer orbital octahedral structures.

Stachelberg and Freghold (1940) used the polarographic research method to determine the composition of the Zn complex. These authors found a relationship between the wave potential of Zn reduction and concentration of sodium hydroxide in solution varying from 0.1N to 4.0N. The coordination number of Zn complex anion was found to be 4, and the stability constant was reported to be 1.3×10^{-17}. Korshunov and Khrulkova (1966) also investigated the coordinated structure of Zn^{2+} by polarographic studies and concluded that Zn^{2+} forms a tetrahedron. They reported that in the alkaline range of 0.2N to 2N sodium hydroxide, Zn^{2+} existed as a complex anion with hydroxal coordination number of 3 and 4. They further commented that it is quite possible for Zn^{2+} to form complexes with a smaller percentage of hydroxal coordination in solutions that are poor by hydroxal ions.

The ZPC for the zinc hydroxyl complex has been reported in literature to be at pH 8.8. Kolthoff and Kameda (1931) estimated that in a neutral solution the ratio of Zn^{2+} to $Zn(OH)^{+}$ concentration is 1000 to 1. The solubility of zinc hydroxide in dilute alkali (Fulton and Swinehart, 1954) has a minimum at approximately 1×10^{-3}M sodium hydroxide which approximates to the ZPC. The pH of the mineral-zinc solution systems used in this study, though variable (data not reported here), was not more than 8.8. Accordingly, it is safe to presume that in the present investigations Zn existed in tetrahedral coordination primarily as $Zn(H_2O)_4{}^{2+}$, though some may also be present as $[Zn(H_2O)_3(OH)]^{+}$. Elgabaly and Jenny (1943) reported the uptake of Zn^{2+} by clays from ZnCl systems in the form of Zn^{2+}, $Zn(OH)^{+}$, and $(ZnCl)^{+}$. The substitution of one water molecule by a hydroxyl group in the tetrahedral complex will not bring any major change in the cross sectional area of the Zn complex molecule because the radii of OH^{-} and H_2O are similar. Therefore, to avoid complications, only $[Zn(H_2O)_4]^{2+}$ will be used for evaluation of the fraction of surface covered.

The area of zinc tetrahedral complex ion

The tumbling water molecule in bulk liquid occupies a volume of a complete sphere. The water molecules in coordination with Zn, though oriented, still possess the vibrational degree of freedom but for the sake of evaluation of the radius of the water molecule we assume water to be a complete sphere. According to Pauling (1960), the covalent radius of the H in water is 0.30 Å and that of oxygen in single bond is 0.66 Å. After correction for electronegativity, this radius of oxygen increases to 0.74 Å. The O-H distance has been found to be 1.01 Å by the neutron diffraction method. The angle of configuration of two H atoms has been reported to be 104.5°. From these data the radius of a water molecule sphere has been evaluated to be 1.357 Å, whereas the radius obtained from the cross sectional area of a water molecule, in the vapor phase, resting on the absorbent surface, is about 1.85 Å (Gregg, 1961, p. 51).

Assuming that coordination of water with Zn^{2+} ion forming a zinc tetrahedron does not bring distortion of any considerable extent and that each of the four water molecules still has 1.357 Å as its radius, then the radius of zinc tetrahedron (presumed to be a sphere) can be calculated to be 3.104 Å. This gives the cross sectional area of the Zn complex molecule about 29.34 sq Å.

Mode of adsorption reaction

Each of the minerals used in the present study have a considerable cation exchange capacity. The total exchangeable cations for the fine fractions of prochlorite, pyroxene and biotite are 21.22, 61.40, and 51.53 meq/100 g, respectively (Table 1). Table 4 shows the meq/100 g of Zn retained by these minerals as calculated from the monolayer capacity.

Table 4. Zinc adsorption data on prochlorite, pyroxene, and biotite

Mineral fraction	Temp	Values pertaining to monolayer capacity					Values pertaining to low coverage			Area/ adsorbed Zn^{++}	Area/ adsorbed Zn^{++} at X_m
				b^*	$\Delta H°$	$-\Delta G°$		K	$-\Delta G°$		
	°C	mg/g	meq/100 g	$\frac{L}{M}$	$\frac{K\ cal}{M}$	$\frac{K\ cal}{M}$	θ	$\frac{L}{M}x10^4$	$\frac{K\ cal}{M}$	Å	%
Prochlorite	10	1.42	4.34				.300			60.3	48.6
Fine	20	1.48	4.53	2.84	0.332	2.42	.310	3.4	2.83	57.9	50.6
	30	1.60	4.89		0.706		.320			53.6	54.7
Coarse	10	0.57	1.74			1.45	.200		1.60	61.5	48.7
	20	0.58	1.77	1.87	0.159		.225	2.0		60.3	48.6
	30	0.6	1.83		0.301		.230			58.5	50.1
Pyroxene	10	3.74	11.43				.160			47.28	62.0
Fine	20	4.00	12.23	1.25	0.554	0.52	.260	1.69	1.22	44.20	66.3
	30	4.38	13.39		1.226		.208			40.38	72.6
Coarse	10	1.10	3.36				.119			47.7	61.5
	20	1.24	3.79	1.02	0.487	0.048	.166	1.18	0.39	42.36	69.2
	30	1.36	4.16		0.612		.170			38.64	75.9
Biotite	10	6.78	20.73							45.2	64.9
	20	7.09	21.68	0.727	0.513	0.554				43.2	67.9
	30	7.61	23.27		0.10	0.615				40.3	73.3

*Mean of 3 temperatures.

The Zn retained represents about 20%, 19%, and 40% of the total exchangeable cations for these minerals.

Mukherjee and Mitra (1946) have shown that a single cation may be held by a clay mineral with a wide range of bonding energies, and this is fundamentally related to the position on the silica-alumina packet at which the cation is sorbed. Accordingly, there are numerous types of energetically heterogeneous sites on these minerals. It is reasonable to think that some of the weakly held exchangeable cations are likely to be replaced first from their exchange sites to establish an equilibrium with the Zn ions in the solution, and thus the reaction on the mineral surface may be hypothesized as an exchange adsorption. A similar idea was put forward by Elgabaly and Jenny (1943).

Kelley (1948) pointed out that the replacing power of cations increases qualitatively with atomic number of ions. Brown (1950) reported that the release of the adsorbed cations by Zn from an Aiken clay loam was in the order of $Na^+ > Ca^{++} > K^+ > Mg^{++} > H^+$. In the present study, the calculated monolayer capacity of Zn adsorbed by prochlorite is close to the amount of exchangeable sodium (about $^{-3}$ meq/100 g).

The measured initial adsorption plateau (Figures 4 and 5) is assumed to be a result of the exchange of solution Zn for weakly adsorbed Na. The increase in Zn adsorption beyond the initial plateau is ascribed to the progressive exchange of other adsorbed cations on the silicate mineral surface. The data for both prochlorite and pyroxene can be explained on the basis of the selective exchange of Na by Zn at a low equilibrium concentration of Zn ion.

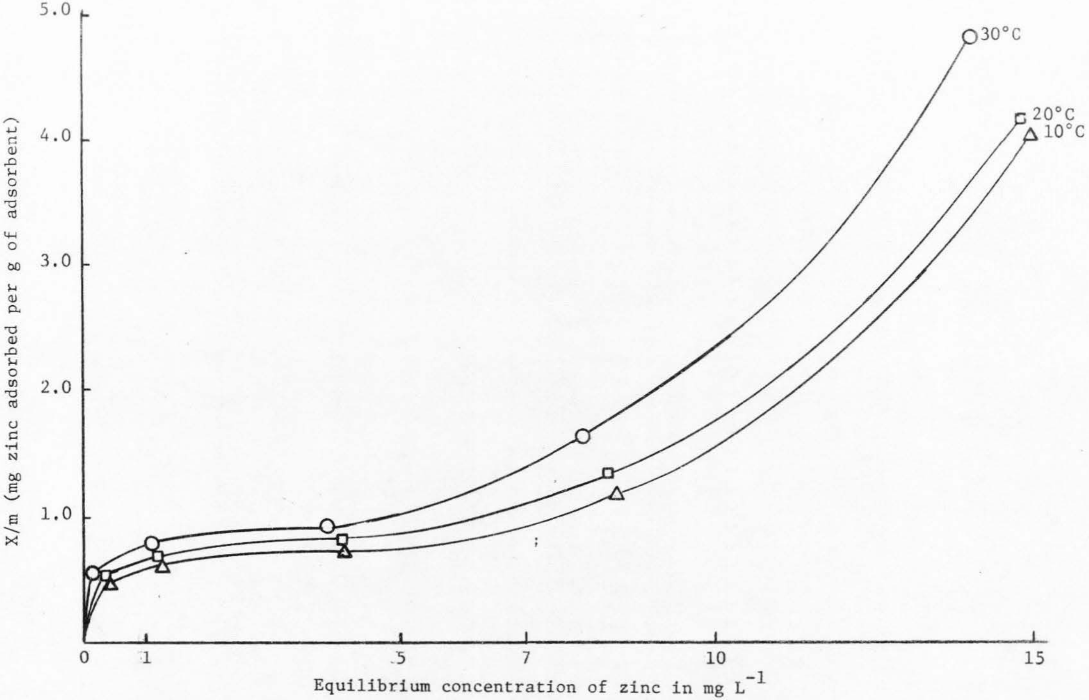


Figure 4. The effect of temperature on the adsorption of zinc by fine fraction of prochlorite.

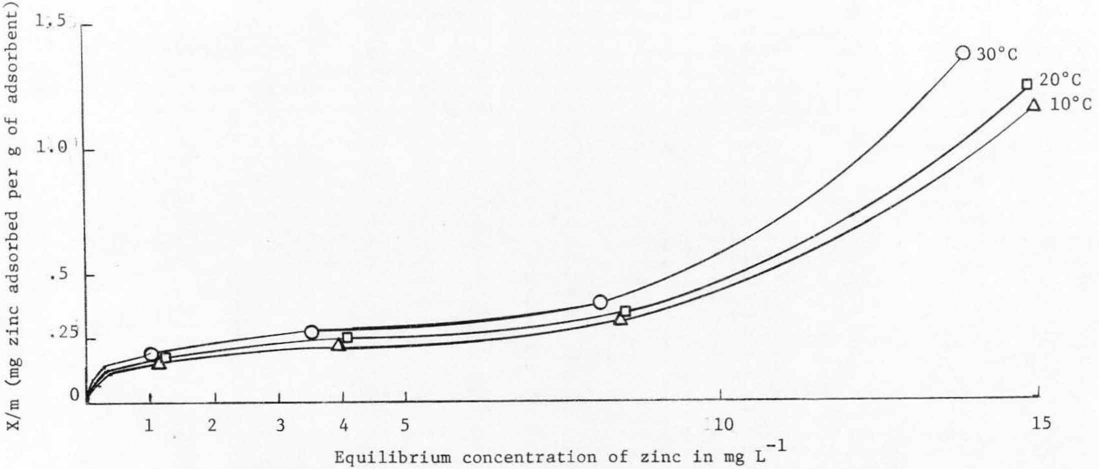


Figure 5. The effect of temperature on the adsorption of zinc by coarse fraction of prochlorite.

In the case of Zn adsorption by the fine fraction of biotite (Figure 6), which is essentially a Ca-saturated mineral, both the exchangeable Na and K are low; hence, the exchange between Zn and the monovalent cations cannot account for the apparent adsorption plateau noted in this case. The exchange mechanism is not apparent, but the subsequent data to be discussed do suggest that exchange adsorption is operative. We may agree with Marshall (1949) and assume that bonding energy of Ca is not uniform and only the weakly held exchangeable Ca is initially replaced by the adsorption of Zn. The data on the biotite are not conclusive and need additional study.

Ion exchange is a diffusion process (Grim, 1968) and its rate depends on the mobility of the ions in solution. The magnitude of the activation energy, Ea, (Table 5) shows that the diffusion in solution is the rate controlling step. These data support the concept of exchange adsorption by the minerals studied.

The differential heat of adsorption, $\Delta H°$, (Table 4) for the reaction is quite small, supporting the hypothesis of exchange adsorption. The heat involved in the course of an ion exchange reaction is usually small, about 2/K cal/mole (Grim, 1968), unless ion exchange is followed by some secondary reaction such as neutralization.

The monolayer capacities for the various minerals are temperature sensitivive, and the monolayer adsorption reactions are endothermic in nature. It can be perceived that with a rise in temperature, the number of successful collisions between Zn and the exchange sites should increase and more of the exchangeable cations can be replaced by Zn during the reaction.

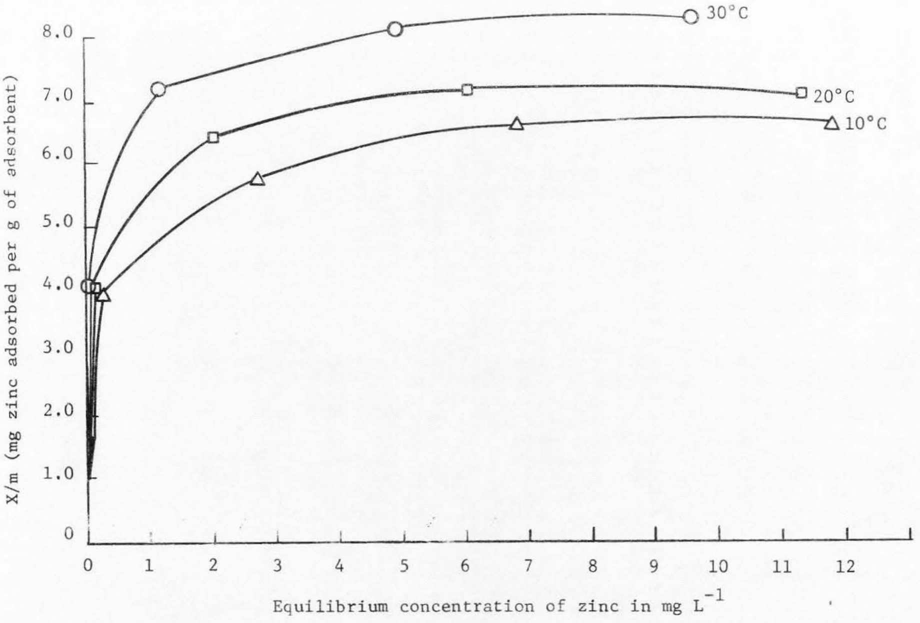


Figure 6. The effect of temperature on the adsorption of zinc by biotite.

Table 5. Rate parameters for the adsorption of zinc molecules on minerals

Mineral fraction	Temperature	k_{-1}/k_1	k_1	k_{-1}	Ea	$\Delta H^{\mp}$	$\Delta G^{\mp}$	$\Delta S^{\mp}$
		$M\ L^{-1} \times 10^{-5}$	$Sec^{-1}\ M\ L^{-1}$	$Sec^{-1} \times 10^{-4}$	k cals M^{-1}			ESU
Prochlorite								
Fine	10		8.55	2.52				
	20	2.95	12.81	3.78	6.18	5.60	2.31	2.16
	30		17.09	4.16				
Coarse	10		14.33	6.87				
	20	4.80	18.33	8.79	3.78			
	30		21.50	10.32				
Pyroxene								
Fine	10		3.25	2.07				
	20	5.95	5.06	3.22	6.37	5.67	0.156	19.23
	30		7.58	4.83				
Coarse	10		3.81	2.24				
	20	8.45	6.64	3.89	4.87			
	30		10.46	6.24				

Isotherms and monolayer formation

The isotherms based on equation (2) for the adsorption of Zn by fine and coarse fractions of prochlorite, pyroxene and biotite minerals are presented in Figures 4, 5, 6, 7, and 8 (see Appendix, Tables 8, 9, and 10). The isotherms approach a limiting value of adsorption with increasing concentration of adsorbate in solution. As the adsorbate concentration was increased to a relatively high level, a secondary adsorption occurred in the prochlorite and pyroxene systems but did not occur in the biotite system. The monolayer sorption of added Zn is apparently complete up to an equilibrium concentration of about 1.54 x 10^{-5} moles L^{-1} for prochlorite and 2.31 x 10^{-5} moles L^{-1} for pyroxene. In the case of biotite, the monolayer adsorption seems to be completed at a higher equilibrium concentration.

Since the multilayer adsorption at a solid-liquid interface is quite rare (DeBoer, 1953), the increase in adsorption beyond the monolayer may be attributed partly to the precipitation of Zn as $Zn(OH)_2$. Jurinak (1956), studying Zn adsorption in calcite, hypothesized the increased adsorption beyond the monolayer region was due to a second type of adsorption sites at the interface which become important as the concentration of Zn ion exceeds the saturation of type one sites. Only the monolayer region of adsorption will be considered in this study.

Figures 9, 10, 11, 12, and 13 show the linear plot for equation (3) for the isotherms discussed previously. The monolayer capacities of the Langmuir adsorption maximum (Xm) obtained from the slope of the lines along with the constant b, related to the energy of adsorption, at monolayer formation is given in Table 4. Table 4 also shows the values for $\Delta H°$ and $\Delta G°$ for adsorption for monolayer formation, obtained by the

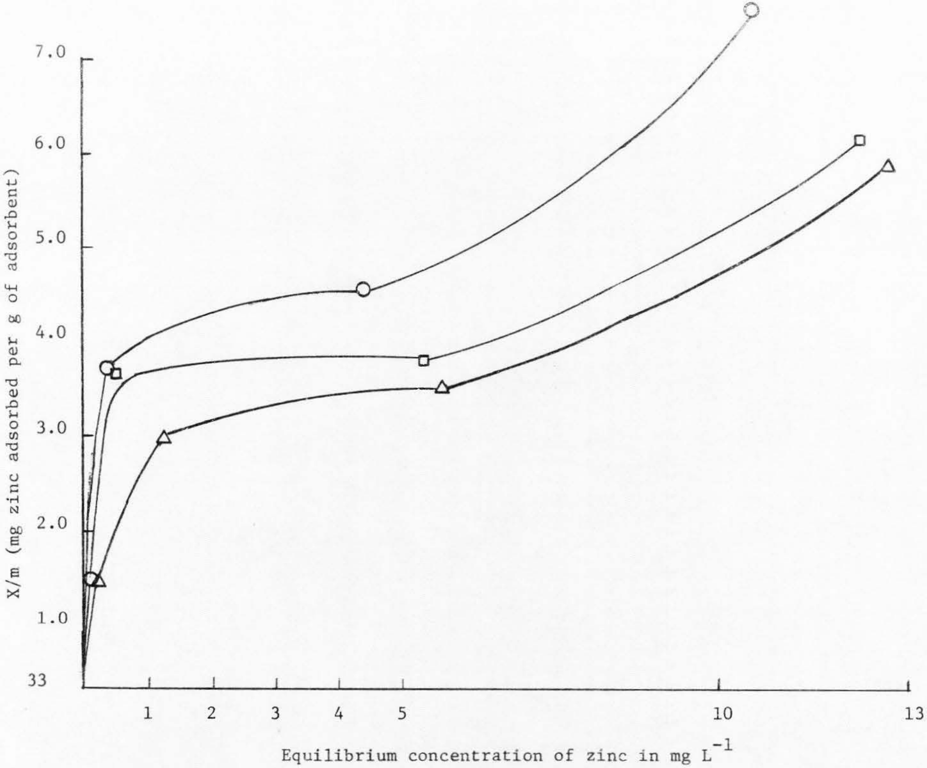


Figure 7. The effect of temperature on the adsorption of zinc by fine fraction of pyroxene.

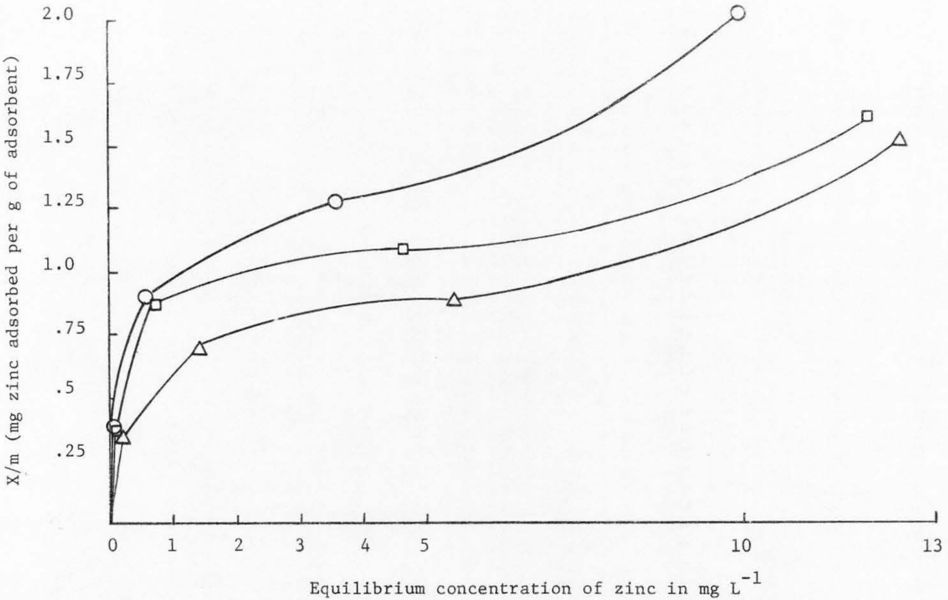


Figure 8. The effect of temperature on the adsorption of zinc by coarse fraction of pyroxene.

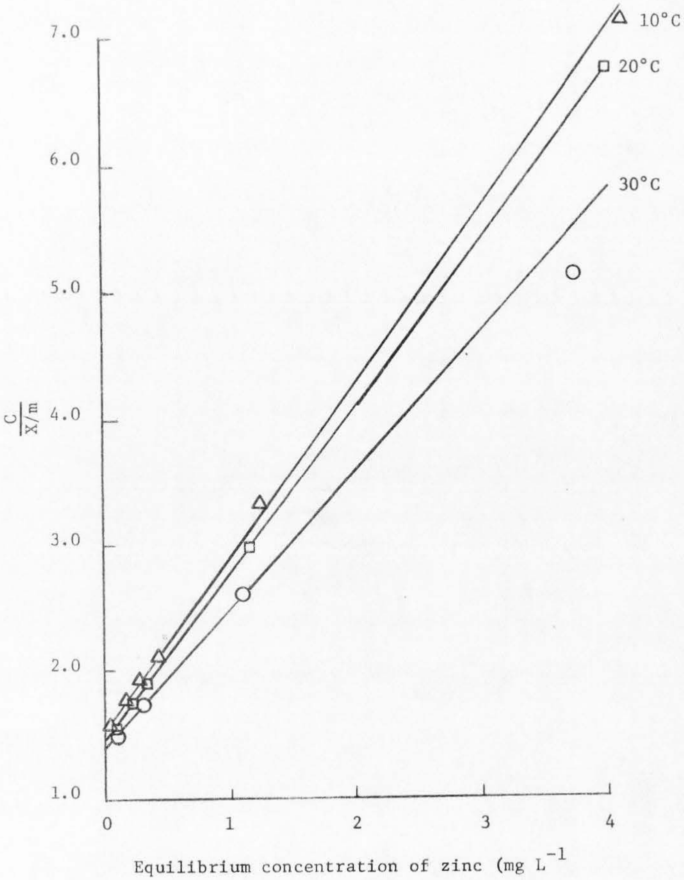


Figure 9. Linear plot (equation (3)) for the adsorption of zinc by fine fraction of prochlorite.

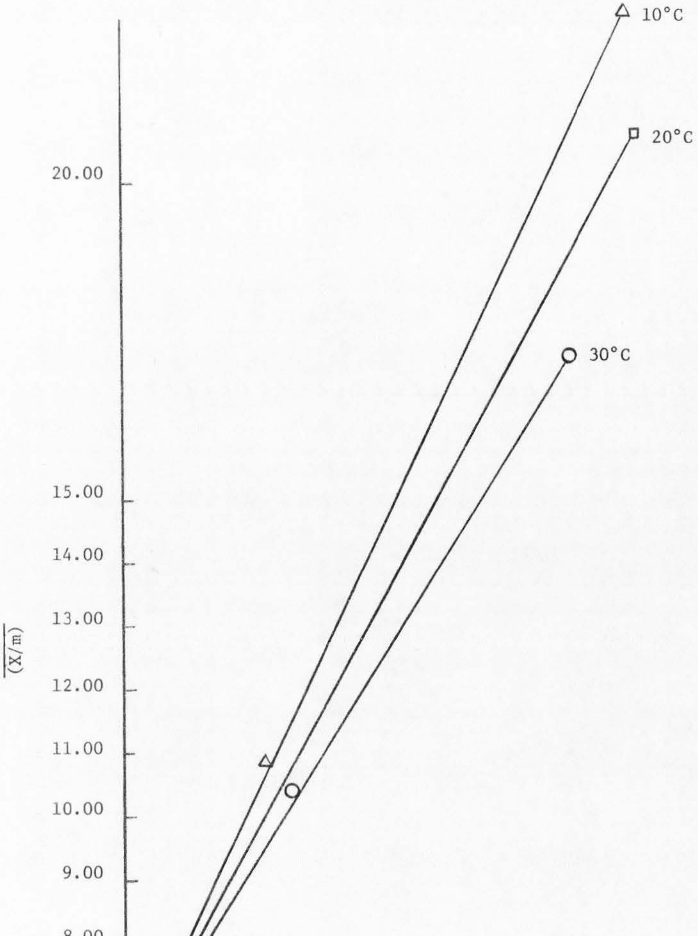


Figure 10. Linear plot (equation (3)) for the adsorption of zinc by coarse fraction of prochlorite.

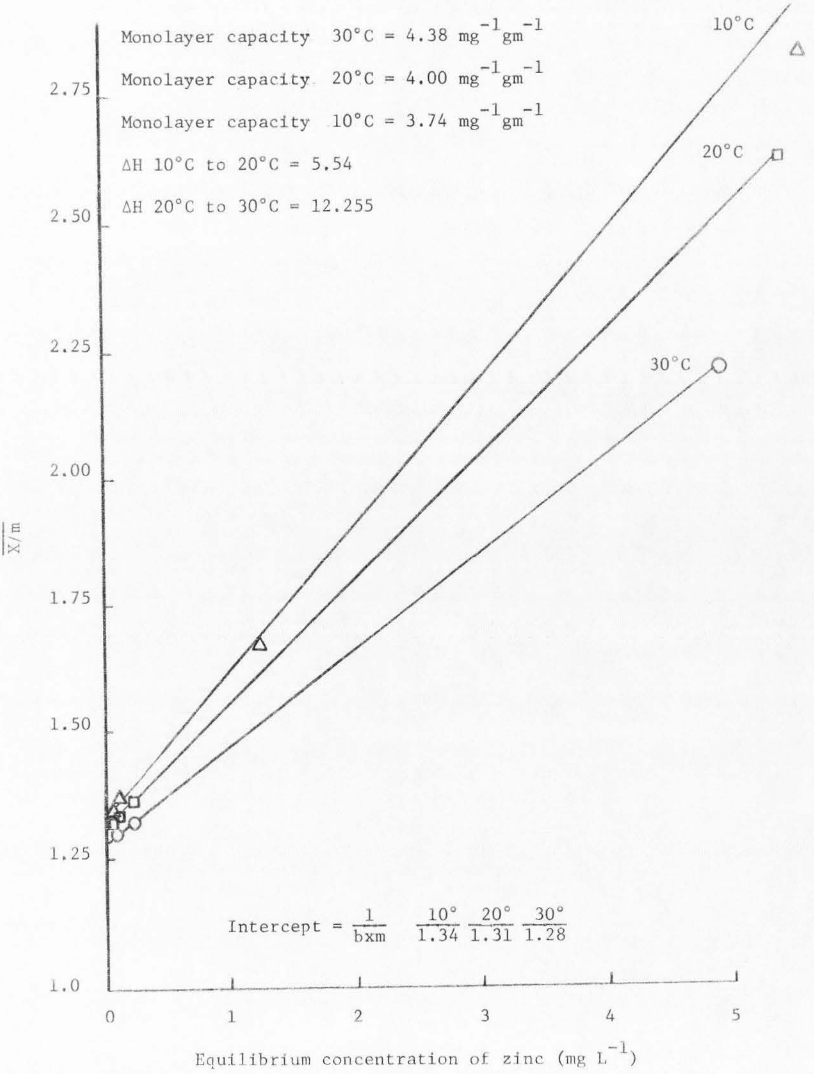


Figure 11. Linear plot (equation (3)) for the adsorption of zinc by fine fraction of pyroxene.

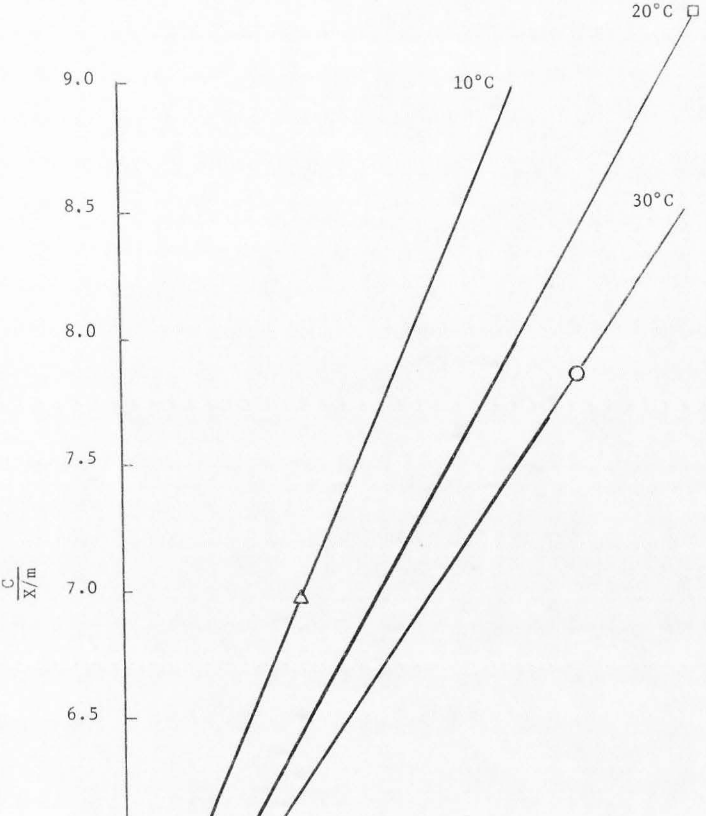


Figure 12. Linear plot (equation (3)) for the adsorption of zinc by coarse fraction of pyroxene.

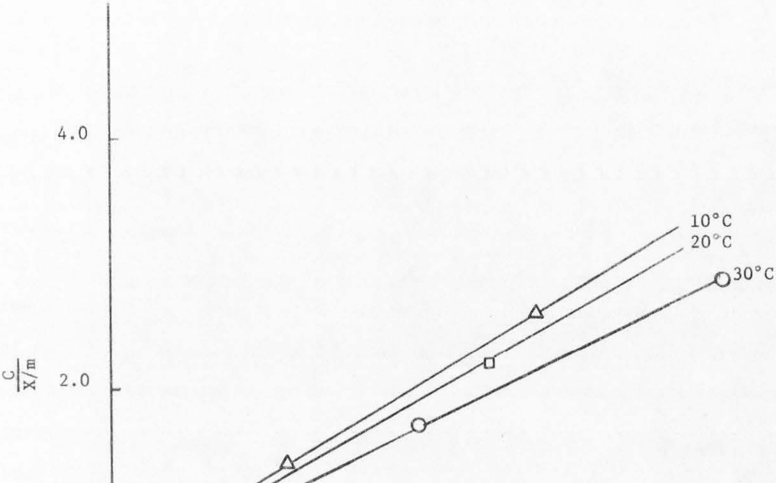


Figure 13. Linear plot (equation (3)) for the adsorption of zinc by biotite.

relation expressed in equations (33) and (34). The monolayer capacities are slightly temperature dependent and increase with increasing temperature, reflecting the endothermic nature of the adsorption reactions.

The adsorption is usually described as an exothermic process; accordingly the monolayer capacity (Xm) should decrease with increasing temperature. However, Haque et al. (1968) reported that temperature has little effect on the amount of 2,4-D adsorbed by clay minerals. Jurinak (1956) reported that the retention of Zn by dolomite and calcium-magnesite is endothermic, whereas the calcite showed an exothermic reaction with adsorbate Zn solution. Reyes and Jurinak (1967), studying molybdate adsorption in iron oxide, found an increase in the Langmuir adsorption maximum (Xm) with a rise in temperature. They postulated the formation of new active sites to justify this reaction and in support of this reported a slight increase in surface area.

The variation in the -ΔG° of adsorption, with the progressive increase in the fraction of surface covered by adsorbate molecules, has been used to define the adsorbate-adsorbate interaction at higher coverages or to characterize the nature of site change with increased adsorption. McMillan (1947) and Zettlemoyer and Walker (1948), in an attempt to reason out the decrease in free energy of adsorption, hypothesized two kinds of adsorption sites which were mathematically treated by an equation of the Langmuir type.

$$\theta = \frac{\alpha b_1 C_{eq}}{1 + b_1 C_{eq}} + \frac{(1 - \alpha)\ b_2 C_{eq}}{1 + b_2 C_{eq}}$$

in which b_1 and b_2 are the equilibrium constants for stronger and weaker sites, respectively, and α is the fraction of the total surface occupied by stronger sites. The rest of the terms have their usual meanings.

The variation in $-\Delta G^\circ$ of adsorption values (Table 4) with the change in the fraction of surface area covered is very small in the case of prochlorite, whereas it is quite pronounced in the case of pyroxene. It is difficult to resolve from the present data the factor responsible for the change in $-\Delta G^\circ$, but it may be speculated that the following factors are involved.

1. The sites are energetically heterogeneous.
2. The mutual repulsion of adsorbed Zn ions at higher surface coverage.
3. The distance of the initial adsorption reaction from equilibrium.

It seems resonable to assume that the potential active sites on the adsorbent surface may be slightly temperature dependent and new sites may become actively involved in adsorption with a rise in temperature. One type of active center can be more active (Laidler, (1965) for the adsorption of one species and the other type of sites more active for the adsorption of other species. Further, temperature may also affect the ionic species of the adsorbate. Korshunov and Khrulkova (1966) reported that instability constants of co-ordination compounds of Zn are temperature dependent. It appears that the ratio of $[Zn(H_2O)_4]^{2+}$ to $[Zn(OH)(H_2O)_3]^+$ will be low at low temperature (10 C), i.e., at a higher temperature the number of $[Zn(H_2O)_4]^{2+}$ ions will be greater than at the lower temperature which might account for some of the increase in adsorption that is noted with increasing temperature.

The monolayer capacities calculated on a per gram basis of minerals is in the order of biotite > pyroxene > prochlorite. A clearer picture of Zn adsorption can be realized if the results are regarded on the basis of area occupied by a single hydrated Zn ion on each of these minerals.

At monolayer capacity, the fraction of available surface area covered by prochlorite is approximately 48 to 55 percent, pyroxene 62 to 72 percent, and biotite 65 to 73 percent, which indicates a loose adsorbate film (Table 4). The zinc-water tetrahedron can be visualized as sitting flat with its major axis perpendicular to the surface. Since molecules are not closely packed, it implies that probably adsorption takes place on specific sites at the surface. DeBoer et al. (1962) postulated hydroxyl and oxygen atoms in alumina monohydrate to be the probable sites of adsorption.

The cell structure of all three silicate minerals is such as to give a b axis dimension of approximately 9 Å (prochlorite 9.2 Å, biotite 9.2 Å, pyroxene 8.9 Å) having six oxygen, or hydroxyl and oxygen, atoms located within this distance. This gives an atom to atom distance approximately equal to 1.78 Å within the mineral structure. The radius of the Zn tetrahedron, by hypothesizing a spherical model, has been calculated to be 3.10 Å, indicating that one Zn molecule will cover almost two sides to give an open packing as indicated in Figure 14.

Kinetics and thermodynamics of Zn adsorption

It has been shown in the preceding discussions that at low coverage ($\theta < 0.4$) there is no interaction between the adsorbed Zn molecules,

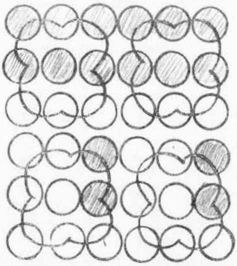


Figure 14. The adsorption of zinc tetrahedron molecule (thick lines) on prochlorite (schematic) along b and c direction. The shaded circles represent OH ions.

and as such each adsorbed molecule would occupy the same fraction of the total adsorbent surface. The value of θ can be considered as directly proportional to Xm, the monolayer capacity. The equilibrium values of θ for three different solution concentrations calculated from equation (5) along with C/θ for two mineral fractions are presented in Tables 6 and 7.

C/θ as a function of C, equation (10), for various mineral fractions is plotted in Figures 15, 16, and 17. The slope of the lines in each case is approximately one, and the y intercept gives the value of k_{-1}/k_1. These data are presented in Table 5. The reciprocal of k_{-1}/k_1 has been interpreted as the value of k_{eq} and used for the evaluation of $\Delta G°$ of adsorption at low coverage. The ratio of k_{-1}/k_1 is constant, irrespective of temperature and concentration, but is determined by the nature of the adsorbent and the fraction of surface

Table 6. Equilibrium adsorption data for prochlorite

Concentration	10 C		20 C		30 C	
	θ	C/θ	θ	C/θ	θ	C/θ
mole L^{-1} x 10^{-5}		mole L^{-1} x 10^{-5}		mole L^{-1} x 10^{-5}		mole L^{-1} x 10^{-5}
		Fine Fraction				
1.247	0.300	4.156	0.308	4.048	0.310	4.022
0.616	0.180	3.420	0.173	3.560	0.175	3.520
0.308	0.099	3.110	0.093	3.310	0.095	3.240
		Coarse Fraction				
1.247	0.200	6.230	0.220	5.670	0.210	5.930
0.616	0.112	5.500	0.110	5.500	0.110	5.500
0.308	0.060	5.130	0.059	5.220	0.600	5.130

Table 7. Equilibrium adsorption data for pyroxene at 10 C

Concentration	Fine Fraction		Coarse Fraction	
	θ	C/θ	θ	C/θ
mole L^{-1} x 10^{-5}		mole L^{-1} x 10^{-5}		mole L^{-1} x 10^{-5}
1.770	0.160	11.060	0.119	14.900
0.893	0.116	7.700	0.088	10.140
0.308	0.630	6.840	0.054	9.400

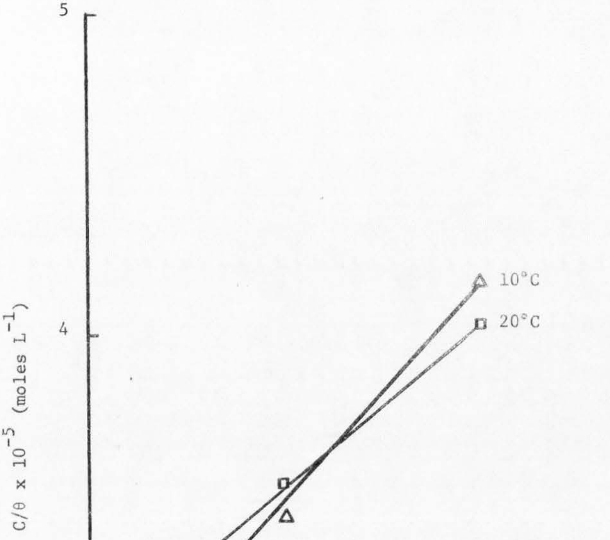


Figure 15. Plot of equilibrium data (equation (10)) for fine fraction of prochlorite.

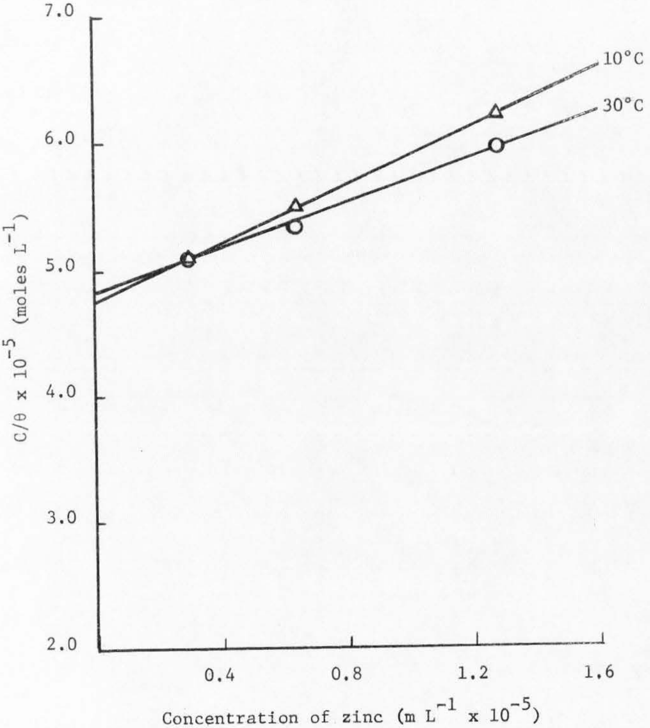


Figure 16. Plot of equilibrium data (equation (10)) for coarse fraction of prochlorite.

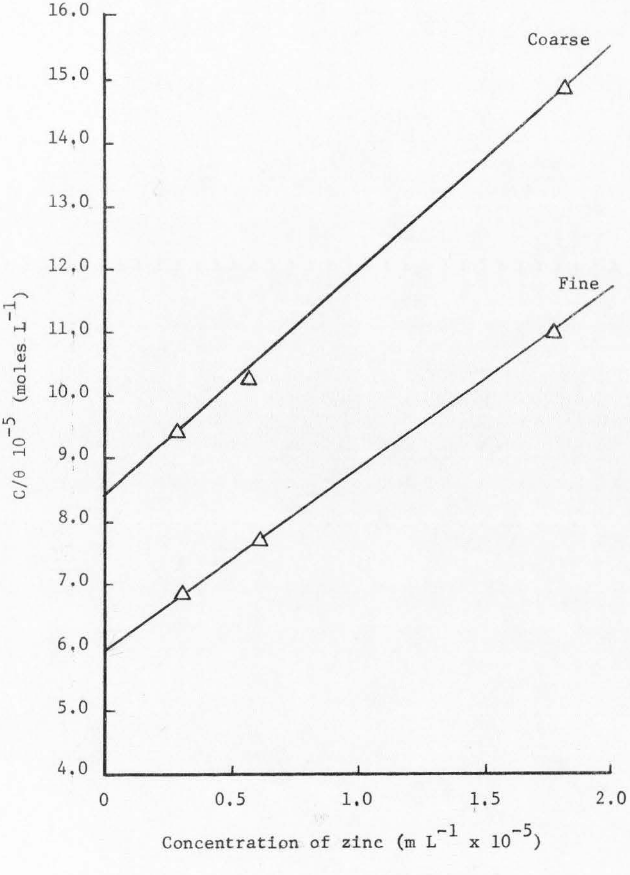


Figure 17. Plot of equilibrium data (equation (10)) for pyroxene.

covered (See Figures 15 and 16).

The value of k_{-1}/k_1 was substituted into the integrated rate equation (11) and the kinetic data plotted as a function of t (time), in Figures 18, 19, 20, and 21. A reasonably straight line was obtained in each case with a slope of $k_1c/2.303$. The values of k_1 and k_{-1} are listed in Table 5.

As is indicated by the data, the uptake of the solute by the adsorbent was rapid, and a considerable amount of Zn was inactivated at zero hour. The adsorption from the Zn solution onto the minerals was almost complete in 4 hours. Although a considerable amount of adsorbent surface was still available ($\theta < 0.4$) for reaction at the low concentration of Zn in solution, the diffusion of Zn in solution appears to be the rate limiting step.

The rate constants reported by Haque et al. (1968) for the adsorption of 2,4-D on the clay minerals were of the order of 10^{-7} sec^{-1}, whereas the value reported for the adsorption of PAVS on chrome plate by Peterson and Kwei (1961) is in the order of 191 sec^{-1}. Weber and Gould (1966) reported k_1 values of 51.8 sec^{-1} for the adsorption of 2,4-D on active carbon but this was found to be dependent on the concentration of the adsorbate solution. The values of rate constants obtained here are quite high. It has been postulated in the previous discussion that Zn is adsorbed as $Zn\ (H_2O)_4^{2+}$ or $Zn\ (OH)(H_2O)_3^{+}$ ion. The rate constants for the various mineral fractions indicate that diffusion is accelerated by electrostatic forces. The rate constants are somewhat dependent on the nature of the adsorbent surface and the surface areas. Rate constants are higher for prochlorite than pyroxene, although the surface exposed for adsorption is higher in the latter. The rate

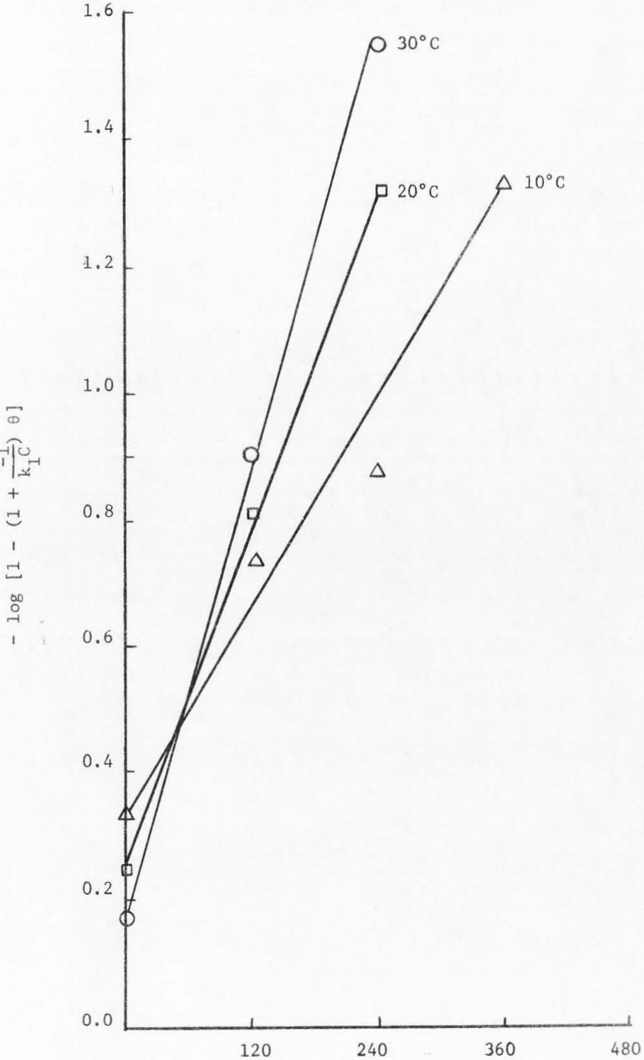


Figure 18. Plot of the kinetic data according to equation (11) for fine fraction of prochlorite.

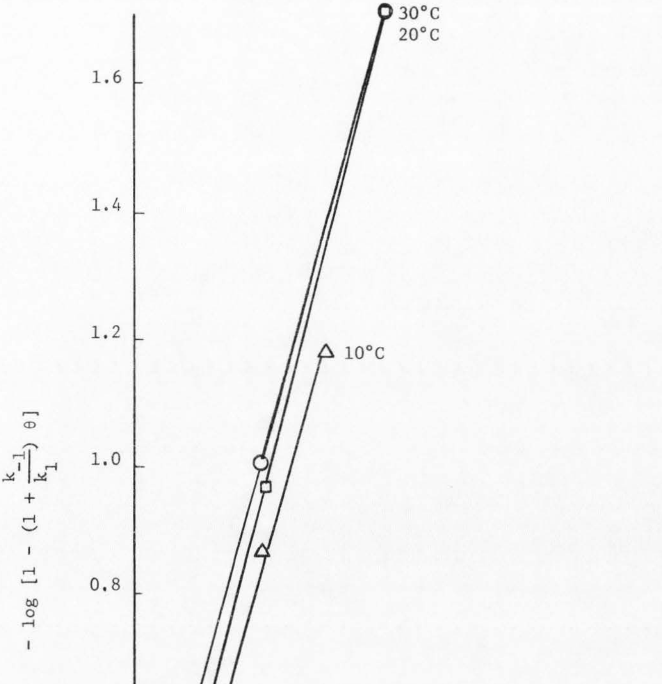


Figure 19. Plot of kinetic data according to equation (11) for coarse fraction of prochlorite.

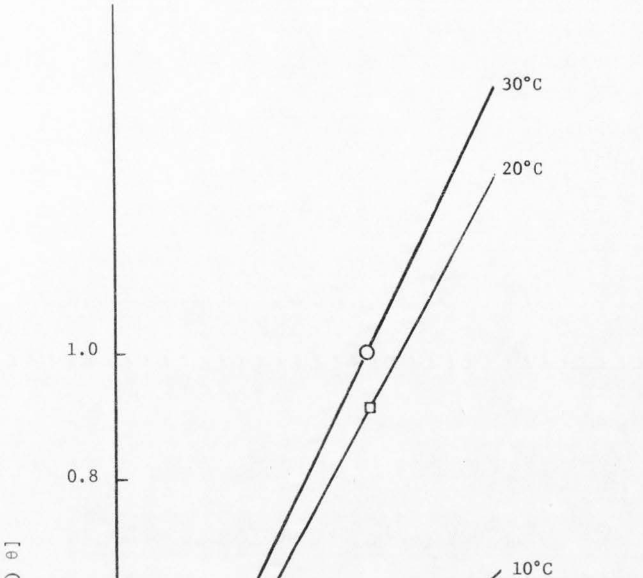


Figure 20. Plot of kinetic data according to equation (11) for fine fraction of pyroxene.

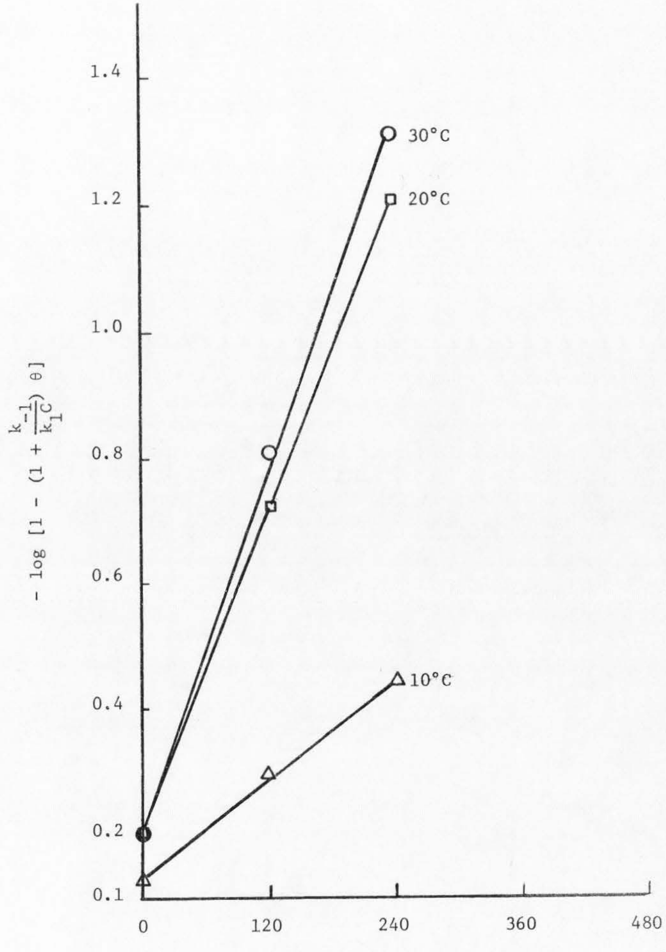


Figure 21. Plot of kinetic data according to equation (11) for coarse fraction of pyroxene.

constants seem to be associated with the $-\Delta G°$ of adsorption for the minerals. It is higher for prochlorite than for pyroxene (Table 4). The prochlorite is 2:2, hard and perfectly crystalline mineral. The negative charge that comes from the mica-like sheet is much higher than the positive charge that has its origin in the brucite-like sheet, sandwiched between two mica-like sheets. Pyroxene is a chain silicate, soft and fibrous, where most of the negative charge comes from substitution in the silica tetrahedral configuration.

The source of the origin in the net negative charge will influence the type of flocculation and particle aggregation. The flocculation may be expected to be more regular in prochlorite than in pyroxene. When Zn molecules come in contact with the mineral, it can adsorb on the surface and also diffuse in the aggregate. The rate of adsorption will be faster than the rate of diffusion. In the present study, the reaction rate is represented as the rate of sorption which includes sorption as well as diffusion.

The rate constants are temperature dependent and increase with increasing temperature, suggesting that inter-particle diffusion can be the reaction limiting process.

The k_{-1} values have been calculated and are of the order of 10^{-4} sec^{-1}. The values of k_{-1} as compared to k_1 are very small, showing that desorption is negligible. This is reasonable if one considers the magnitude of the surface areas involved and the low concentration of adsorbate. Because of the low k_{-1} values, it appears that Zn is preferentially adsorbed as compared with any ions that it replaces.

The assumption made by Haque et al. (1968), that the desorption reaction is small enough to be neglected when a large surface is exposed and the concentration of adsorbate is small, does not appear to be justified in their case because they reported high values of k_{-1}.

The Arrhenius law (equation 19) was tested by plotting log k_1 vs the reciprocal of the absolute temperature as shown in Figures 22 and 23. A straight line with a slope of Ea/4.56 was obtained. The activation energy, Ea, calculated by this reaction, is presented in Table 5.

The mechanisms of surface reactions for bimolecular process are regarded as involving five consecutive steps (Laidler, 1965) as follows:

1. Diffusion of the reacting molecule to the surface.
2. Adsorption of the molecules on the surface.
3. Reaction on the surface.
4. Desorption of the products.
5. Diffusion of the adsorbed products.

The values for the reversal of the adsorption constant k_{-1} have been found to be negligibly small (Table 5); therefore steps 4 and 5, in the above scheme, as the reaction rate controlling process are ruled out and one of the initial three steps becomes the rate determining mechanism.

The over-all process can be schematically depicted as

$$\underset{\text{(i)}}{\begin{array}{c}\text{Zn ion}\\ \text{in solution}\end{array}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(ii)}}{\begin{array}{l}\text{Zn ion on the}\\ \text{surface with a}\\ \text{small surface}\\ \text{contact}\end{array}} \xrightarrow{k_2} \underset{\text{(iii)}}{\begin{array}{l}\text{Adsorbed Zn ion}\\ \text{with Zn mole-}\\ \text{cule fully flat-}\\ \text{tened}\end{array}}$$

A somewhat similar conclusion was reached by Peterson and Kwei (1961) for the PVAS adsorption on the solid surface. The Zn ion reorientation on the surface is likely to be kinetically fast following the successful collision of the Zn ion with the solid surface. Step

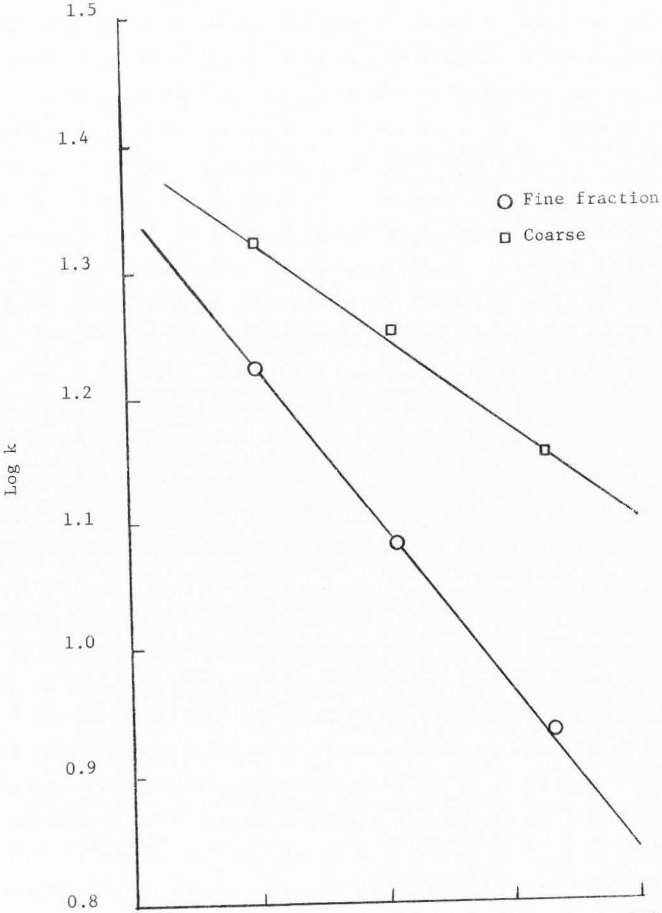


Figure 22. Arrhenius plot of rate constant vs temperature for prochlorite.

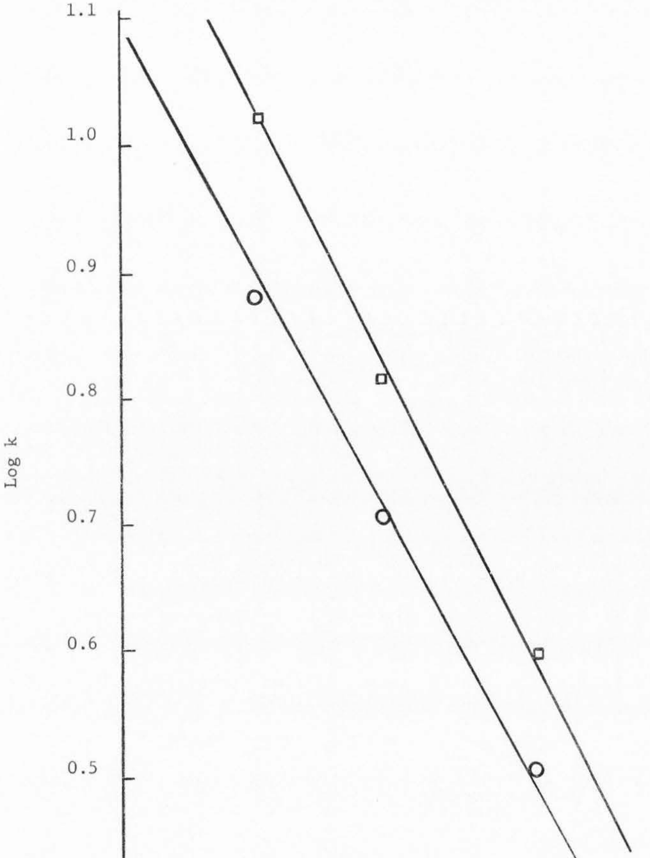


Figure 23. Arrhenius plot or rate constants vs temperature for pyroxene.

two, adsorption of Zn ion on the surface, is known to be a fast process. Accordingly, diffusion (step one) seems to be the rate-mechanism controlling process in the systems studied. Diffusion, being an endothermic process, infers that the rate of uptake of Zn by mineral should increase with a rise in temperature, which is supported by the rate constants reported in Table 5. In accord with the expectations for intraparticle transport by diffusion as the rate-limiting mechanism, the experimental activation energy values reported in Table 5 are all positive. Diffusion in a liquid (Laidler, 1965), like many other physical processes, has an activation energy, but the magnitude of this is generally around 5 K cals per mole. The activation energy values (Table 5) vary from about 3 K cals per mole to 6 K cals per mole, confirming the view that diffusion is the rate controlling mechanism.

Comparison of the values of Ea for the mineral fractions indicates that it is related to the surface area and structural composition of the minerals. The Ea is higher for prochlorite than for pyroxene when calculated on unit surface areas based and decreased with increasing particle size.

The thermodynamic constants, heat of activation ($\Delta H^{o\ddagger}$), Gibbs free energy of activation ($\Delta G^{o\ddagger}$), and entropy of activation ($\Delta S^{o\ddagger}$) for the activated complex $\theta^{\ddagger}$, calculated from equations (30), (25) and (26), respectively, are presented in Table 5. The $\Delta S^{o\ddagger}$ values for the activation reactions are positive, supporting the contention in this study that the adsorption reactions process is not the rate limiting step. The entropy of activation for pyroxene is greater than for prochlorite.

The hydrophylic nature of soil forming minerals has been explained by Van Olphen (1963). In the present system the adsorbent and adsorbate both are present in a highly hydrated form but pyroxene, because of its fibrous soft nature and the presence of easily hydrated cations (Na^+), is considered to be more hydrated than prochlorite.

The larger entropy of activation in the case of pyroxene is explained on the basis of change in the volume of activation. Evans and Polany (1935) pointed out that there may be change in the volume of the reactants as they pass into the activated state and also the volume change may result from reorganization of the solvent molecules. Studies of a variety of reactions (Buchanan and Hamann, 1955) had lead to the conclusion that for reactions in which ions or fairly strong dipoles are concerned, the solvent effects are generally more important than the structural ones. If the electric field is weakened (Laidler, 1965) when the activated complex is formed (as where two bodies of opposite signs come together), there will be some release of bond solvent molecules and the volumes and entropies of activation will be positive.

SUMMARY AND CONCLUSIONS

The studies reported here represent an attempt to apply the kinetic equation

$$\frac{\partial\theta}{\partial t} = k_1(1 - \theta)C - k_{-1}\theta \quad \text{(equation 4, theory)}$$

to the adsorption of Zn from solution (water) onto mineral surfaces. The adsorption reaction of Zn from dilute solution was studies for prochlorite, pyroxene and biotite minerals, under isothermal conditions. Agitated nonflow experiments were used to investigate both the kinetics and equilibrium of Zn adsorption by these minerals. The equilibrium concentration of Zn in the solution was determined both by radioactive tracer techniques and adsorption spectrophotometer methods. The data were collected at three temperatures.

The data obtained were described fairly well by the above kinetic equation. The specific rate constant for the forward reaction depends on the nature of the mineral and the mineral particle fraction. The specific rate constant (k_1) is temperature sensitive and increases with rise in temperature.

The values for the desorption rate constant are very small, proving that the Zn ions are preferentially adsorbed over other desorbed exchangeable ions in the system.

The activation energy for the sorption process lay between 3 to 6 K cals per mole, thus eliminating chemical adsorption. The activation energy indicates the physical process of diffusion as the mechanism controlling step in the present study. The standard free energy of activation, $\Delta G^{o\ddagger}$, enthalpy of activation, $\Delta H^{o\ddagger}$, and entropy of activation, $\Delta S^{o\ddagger}$, were also evaluated for these reactions. The positive $\Delta S^{o\ddagger}$ shows a change in the volume of activation complex during the course of reaction.

The monolayer capacities for the three minerals and mineral fractions were evaluated. The percent of the surface area occupied by adsorbed Zn ion was about 50 percent, 65 percent, and 66 percent for prochlorite, pyroxene, and biotite, respectively. This suggests that Zn is adsorbed on certain specific sites. The monolayer capacities increased as the temperature increased. The decrease in $-\Delta G^{o}$ with increased fraction of surface coverage allows speculation that:

1. The sites are energetically heterogeneous.
2. There is mutual repulsion of adsorbed Zn ions at higher surface coverage.

The data show that Zn adsorption onto the minerals used in the present study is exchange adsorption. The initial adsorption plateau in the case of prochlorite and pyroxene is described as a result of exchange of solution Zn for weakly adsorbed Na. The change in the nature of the curve beyond this region is speculated to be due to the progressive exchange of other cations. The data for the biotite are not conclusive and need further study. The present studies show that the exchange adsorption (ion exchange) is a step wise process and more than one plateau may be obtained if the system is allowed to reach its ultimate equilibrium where all the exchange sites are completely saturated by the adsorbate.

The differential heat of adsorption, $\Delta \overset{\circ}{H}$, for the adsorption reaction is small. This supports the contention that exchange adsorption takes place in the systems studied.

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APPENDIX

Table 8. Isotherm data for zinc adsorption on prochlorite at three temperatures

	Fine fraction				Coarse fraction		
Temp.	C	C eq	(X/m)	$C/X/_{m}$	C eq	(X/m)	$C/X/_{m}$
±1 K	mg/l	mg/l	mg/g		mg/l	mg/g	
303	0.5	0.083	0.334	1.500	0.087	0.083	6.053
	0.1	0.280	0.576	1.725	0.273	0.145	6.877
	2.0	1.070	0.744	2.675	1.080	0.184	10.860
	5.0	3.761	0.976	5.125	3.557	0.289	17.301
	10.0	7.970	1.624		8.103	0.379	
	20.0	14.060	4.712		13.967	1.347	
293	0.5	0.127	0.302	1.655	0.103	0.079	6.313
	0.1	0.343	0.526	1.901	0.360	0.128	7.813
	2.1	1.163	0.670	2.985	1.180	0.174	11.494
	5.0	4.073	0.741	6.747	4.097	0.241	20.746
	10.0	8.290	1.368		8.403	0.339	
	20.0	14.800	4.160		14.907	1.480	
283	0.5	0.133	0.293	1.706	0.120	0.076	6.579
	1.0	0.420	0.464	2.150	0.400	0.120	8.333
	2.0	1.260	0.592	3.378	1.140	0.172	11.628
	5.0	4.127	0.698	7.163	3.970	0.220	22.727
	10.0	8.427	1.211		8.377	0.320	
	20.0	14.923	4.667		14.943	1.134	

Table 9. Isotherm data for zinc adsorption on pyroxene at three temperatures

	Fine fraction				Coarse fraction		
Temp.	C	C eq	(X/m)	$C/X/_m$	C eq	(X/m)	$C/X/_m$
±1 K	mg/l	mg/l	mg/g		mg/l	mg/g	
303	0.5	0.013	0.390	1.280	0.017	0.097	5.141
	1.0	0.030	0.776	1.289	0.043	0.192	5.206
	2.0	0.053	1.540	1.298	0.090	0.382	5.241
	5.0	0.287	3.770	1.326	0.570	0.886	5.644
	10.0	4.347	4.522	2.211	3.620	1.276	7.837
	20.0	10.483	7.614		9.963	2.007	
293	0.5	0.030	0.376	1.325	0.023	0.097	0.143
	1.0	0.060	0.752	1.330	0.043	0.192	5.208
	2.0	0.130	1.496	1.335	0.100	0.380	5.263
	5.0	0.383	3.694	1.354	0.650	0.870	5.747
	10.0	5.293	3.766	2.655	4.600	1.080	9.259
	20.0	12.200	6.240		11.953	1.609	
283	0.5	0.033	0.374	1.336	0.040	0.092	5.435
	1.0	0.070	0.744	1.344	0.083	0.183	5.452
	2.0	0.177	1.458	1.377	0.170	0.366	5.474
	5.0	1.237	3.010	1.661	1.420	0.716	6.983
	10.0	5.600	3.520	2.841	5.443	0.911	10.977
	20.0	12.601	5.919		12.453	1.519	

Table 10. Isotherm data for zinc adsorption on biotite at three temperatures

Temp.	C	C eq	X/m	$(C/X/_{m})$
±1 K	mg/l	mg/l	mg/g	
303	2	0.017	1.586	
	5	0.027	3.978	1.257
	10	1.053	7.158	1.297
	15	4.870	8.104	1.851
	20	9.617	8.306	2.408
293	2	0.020	1.584	
	5	0.043	3.966	1.261
	10	1.957	6.434	1.554
	15	6.003	7.198	2.084
	20	11.250	7.000	2.857
283	2	0.037	1.570	
	5	0.180	3.857	1.970
	10	2.710	5.832	1.715
	15	6.767	6.586	2.278
	20	11.810	6.552	3.053

Table 11. Equilibrium isotherm data for zinc adsorption on minerals

	Fine fraction			Coarse fraction	
Temp.	C	C eq	X/M	C eq	X/M
±1 K	mg/l	mg/l	mg/g	mg/l	
		Prochlorite			
303	0.81	0.17	0.469	0.180	0.126
	0.40	0.05	0.280	0.060	0.068
	0.21	0.03	0.141	0.023	0.035
293	0.81	0.24	0.308		
	0.40	0.08	0.256		
	0.21	0.03	0.137		
283	0.81	0.28	0.300	0.240	0.114
	0.40	0.08	0.256	0.080	0.064
	0.21	0.03	0.141	0.030	0.034
		Pyroxene			
283	1.15	0.40	0.600	0.550	0.123
	0.58	0.035	0.436	0.024	0.111
	0.30	0.010	0.232	0.020	0.056

Table 12. Isothermal adsorption of zinc at three temperatures as influenced by time

	Fine fraction						Coarse fraction					
	10 C		20 C		30 C		10 C		20 C		30 C	
Time	C eq	X/M	C eq	X/M	C eq	X/M	C eq	X/M	C eq	X/M	C eq	X/M
hours	mg/ml	mg/g	mg/l	mg/g	mg/l	mg/g	mg/l	mg/g	mg/l	mg/g	mg/l	mg/g
					Prochlorite: C = 0.81 mg/l							
0	.60	.168	.58	.184	.47	.272	.66	.03	.61	.04	.53	.056
2	.39	.336	.30	.408	.32	.392	.30	.102	.28	.116	.24	.114
4	.30	.408	.24	.456	.24	.456	.26	.110	.20	.122	.18	.126
6	.28	.425	.22	.472	.18	.504	.24	.114	.18	.126	.16	.130
					Pyroxene: C = 1.15 mg/l							
0	.847	.202	.78	.296	.73	.336	.893	.051	.71	.088	.65	.10
2	.663	.390	.26	.712	.14	.808	.700	.096	.27	.176	.12	.206
4	.418	.586	.14	.808	.09	.848	.553	.119	.14	.202	.05	.224
6	.410	.594	.12	.824	.06	.872	.545	.121	.11	.208	.03	.232

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