# THE EFFECT OF SELECTED PRETREATMENTS ON THE PLASTICITY OF TWO CLAY SEDIMENTS

by

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# ABSTRACT

## The Effect of Selected Pretreatments on the Plasticity of Two Clay Sediments

The effects of a number of selected pretreatments on the plasticity properties of two clay sediments, one derived by weathering from the Queenston Shale of Southern Ontario and the other a sample of the Champlain Sea Clay or "Leda Clay" from eastern Canada, are discussed. The variations in the plasticity limits, as a result of the pretreatments, are considered with regard to the effect of the extraction of various soil constituents and with regard to other changes affecting the interaction among particles or aggregates of particles during the plasticity determinations.

The conclusions suggest that the role of natural peptizing agents has been underestimated in recent geotechnical research.

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# RESUME

## L'Effet de quelques prétraitements sélectionnés sur la plasticité de deux sédiments argileux

Nous discutons les effets d'un nombre de prétraitements sélectionnés sur la qualité de la plasticité de deux sédiments argileux, l'un qui a été altéré du "Queenston Shale" de l'Ontario du sud et l'autre qui est typique de l'argile de la Mer Champlain, ou l'argile de Leda, de l'est du Canada. Les variations dans leurs limites de plasticité, qui résultent de l'application des prétraitements, sont examinées à l'égard d'autres changements qui se produisent au cours de la détermination de la plasticité dans l'interaction entre les particules ou entre les agglomérations des particules.

Les conclusions suggèrent que le rôle des agents peptisants naturels a été sous-estimé dans les recherches géotechniques jusqu'à ce jour.

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# Chapter One:

# INTRODUCTION

The development of landforms on clay sediments has remained a relatively poorly understood process. Unlike coarse-grained material, in which the predominant force acting between particles is friction, the behaviour of clay material depends on a large number of factors related to the nature of the clay-sized particles and on the interstitial water. Clay-sized particles, less than two microns equivalent spherical diameter, possess large values of specific surface area and, therefore, interactions between particles are strongly affected by the attractive and repulsive forces which develop on these surfaces. The physical structure of the clay-sized material, the amount of surface area, and the nature of the surface, combined with the chemistry of the pore fluid, will dominate the gross physical properties of the soil and control the physical processes related to landform development on clay soils.

Plasticity measurements are a common part of any geotechnical investigation, since they yield important data on a number of the properties of the material. The range of water content over which the soil[1] maintains the plastic state, the plasticity index[2], can be used to obtain the "activity"[3] of the clay-sized fraction. Clays with low activities (less than 1),

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[1] The term "soil" is used here in both the pedological and engineering senses.

[2] The plasticity index is defined on p. 9.

[3] Activity is defined by Skempton [1953a] as the plasticity index divided by the percentage of clay-sized material.

such as kaolinitic clays, can be distinguished from material of medium activity (1-2), for example illitic or chloritic clays, and from the very active (greater than 4) montmorillonitic clays [Sowers and Sowers 1970, p. 28]. In addition, plasticity measurements can be used to identify soils containing large quantities of allophane by the peculiar plasticity properties of this material [Warkentin and Maeda 1974].

In addition, plasticity has been demonstrated to correlate very strongly with various strength parameters of soils. Skempton [1953a] indicated a strong correlation between the activity of normally consolidated clays and that proportion of their drained shearing strength originating from true cohesion. Grim [1962, p. 235] has shown that the plasticity index is related to the true angle of internal friction, and Voight [1973] collated data for a wide variety of sediments to show a correlation between the plasticity index and the residual angle of shearing resistance.

Researchers interested in the mechanism of mass movement have realized the importance of the liquidity index[4] as a determinant of the mode of a slope failure. Failures of cohesive material with a liquidity index of greater than unity often occur as flows, since the water content is greater than the liquid limit. Slope failures of material with a liquidity index of less than unity are more likely to occur as slides, because at this water content the slope material behaves plastically, rather than as a viscous fluid.

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[4] The liquidity index is defined as $\frac{w - PL}{LL - PL}$ in which w is the natural water content in the field, PL is the plastic limit and LL is the liquid limit.

Plasticity is not a time-independent attribute of a clay material. Moum [1968] and Moum and Rosenqvist [1957], for example, have shown that in situ changes in plasticity values can result from subaerial weathering of the clay material. In the case of the sensitive post-glacial clays of Scandinavia, the development of a stiff crust has been partially attributed to the increase in the liquid limit as a result of the alteration of mineralogy and oxidation of iron compounds. The stiff crust permits the development of these areas of sensitive clay for human occupation. In situ changes in the opposite direction, that is, to a lower liquid limit, in these same clay deposits at depth, have been postulated to be responsible for the dramatic flowslides which occur, causing extensive property damage and loss of life. Although the cause of the high sensitivity and the resulting flowslides is a topic of current debate, some researchers believe that they result, at least in part, from a change in the pore water chemistry which has resulted in a decrease in the net interactive energy among the particles [Rosenqvist 1966, Soderblom 1966]. Such changes have been indicated by decreases in the plasticity of the clay material. Other aspects of weathering on plasticity, particularly the irreversible collapse of interlayer space and the cementing of interparticle spaces associated with dessication, together with the concomitant decrease in specific surface area and liquid limit, have been discussed by Lambe [1960].

In some cases the plasticity of a clay soil can be manipulated to the betterment of mankind. The use of salt injection to stabilize clays and the use of flocculants or dispersants to change the properties of clays, either during or after construction, is a common engineering practice

[Sowers and Sowers 1970, p. 240, Ingles 1968]. The effectiveness of these treatments can often be determined prior to their application by the use of plasticity measurements.

For all of the reasons mentioned above, the factors affecting the plasticity of cohesive sediments and soils are important, to the theoretical geomorphologist, to the applied geomorphologist, and to the soils engineer. This study was concerned with some of these factors. Before describing its aims, however, a very brief review of the constituents of clays is in order here.

Clay-sized material in soils and sediments can be divided into four major groups: 1. Rock flour, primary minerals which have undergone extensive physical weathering; 2. Clay minerals; 3. Amorphous inorganic material, which consists of silica, metallic oxides, hydroxides and silicates, but which lacks the long-range order and repetition of unit cells found in crystalline material; and 4. Organic material in various states of decomposition. Each of these groups of material possess different properties and behaves differently under weathering conditions. Primary rock-forming minerals of clay-size vary widely in their stability in a moist oxidizing environment. Quartz will persist almost indefinitely under these conditions due to its low solubility, while the ferromagnesian minerals such as amphibole, pyroxene and biotite mica can be expected to weather rather readily, releasing their component ions into the pore fluid [Sangrey 1972]. The clay minerals are a common weathering product of the chemical breakdown of primary silicate minerals; the species of clay minerals found in a sediment or soil will depend primarily on the availability of metallic ions and silica in the pore fluid [Jackson 1968]. Amorphous inorganic material has been found in varying quantities in almost all soils. The relationship of this material to the crystalline soil components has been speculated to be a metastable stage between the breakdown of easily weathered, unstable minerals, and the formation of stable components such as the clay minerals or crystalline metallic oxides or hydroxides [De Villiers 1969]. Polymerization of the amorphous phase on the surfaces of clay minerals may be part of the mechanism of clay mineral growth in natural soil environments [Birkeland 1974, p. 91]. Amorphous organic material in soils consists primarily of vegetal litter and its decomposition products such as humus compounds and various soluble organic acids; in addition, soils derived from sediments can contain biogenetic material, including silica and carbonates from the exoskeletons of aquatic species.

The interaction of three or four of these components in a clay material will greatly complicate the understanding of the physical behaviour of the material. <u>In situ</u> changes in the mineralogy of the soil components, combined with changes in the physical nature or positional arrangement of the amorphous organic and inorganic phases with respect to the crystalline material, can result in changes in the consistency and strength of the soil. From either a geomorphic or an engineering point of view, these geochemical changes may be of great significance in explaining the spatial variation of soils strength and stability, an essential part of the understanding of the landscape. Much of the previous work on sediment and soil plasticity has focussed on the effect of particle size, mineralogy and the chemistry of the pore water; little research has been directed specifically towards the study of the effect of amorphous components on plasticity.

This inattention to the role of amorphous components on plasticity is all the more surprising in view of its documented importance in pedology. Numerous researchers have examined the effect of amorphous material on cation exchange capacity, specific surface area, and the aggregation of soil particles [Aguilera and Jackson 1953, Mehra and Jackson 1960, Follett _et al._ 1965 , Mitchell _et al._ 1968, Deshpande, Greenland and Quirk 1964 and 1968, Arca and Weed 1966]. The results of these separate studies indicate that there is a great variation in the effect that the amorphous constituents have on the soil, due to variations in the clay and non-clay components of the particular soil under consideration. These results will be discussed at greater length in Chapter Three.

The purpose of this research was therefore to investigate this topic as fully as possible for two sediments known to contain significant amounts of iron compounds. One means of investigating the role of this material is to apply the theory of selective chemical dissolution to the problem. Several approaches are possible. Leaching of undisturbed samples with selected chemicals will result in the selective dissolution of material along the pores of the material. Another approach is to work with disturbed samples, with the aim of removing as much of the amorphous phase as possible, regardless of its positional relationship. The latter course of action was chosen for the present investigation to determine the changes in plasticity which result from the extraction of a portion of the clay sediments with selective chemical dissolution pretreatments. No chemical dissolution techniques are available which will quantitatively remove amorphous material without any effect on the crystalline material, thus the techniques used in this study were chosen for their ability to remove certain portions of the soil material with a minimum of damage to the crystalline component. In addition to the examination of the plasticity of the material before and after treatment, additional tests were performed which would yield information about the causes of the changes in plasticity, as well as tests to monitor any changes in the mineralogy of the material.

The next two chapters discuss the theory and available experimental data relating to soil plasticity and to selective dissolution techniques respectively. The procedures and results of the present work are presented in the following three chapters and compared in the final chapter.

# Chapter Two:

# PLASTICITY LIMITS: THEIR MEANING AND CONTROLLING FACTORS.

## 2.1 Definitions.

The concept of the upper and lower limits of plasticity was first introduced by Atterberg in 1911 [Grim 1962, p. 205], for which reason these limits are often termed "Atterberg limits". They are used with reference to fine earth material (less than 420 microns) in a fully disturbed (remoulded) state. At low water contents, inadequate bonding exists among the fine earth particles and aggregates of a remoulded mass to prevent crumbling under pressure, and the material behaves as a semi-solid. At slightly higher water contents, however, cohesion among the constituents of the mass is increased, and the material behaves plastically, i.e., it will deform en masse under pressure, but retain its new shape after removal of the pressure. At very high water contents, this cohesion is reduced and the material will deform as a fluid. The plastic limit is interpreted as a measure of the water content on the boundary between the semi-solid and plastic states; the liquid limit is regarded as the moisture content at the upper limit of the range of plasticity, i.e., between the plastic and liquid states. The technique for determining the plastic limit was conceived by Allen [1942], and the apparatus and technique for determining the liquid limit were developed by Casagrande [1932]. Since then, these limits have been standardized, and as presented by the A.S.T.M. [1964] are defined as follows:

> "The plastic limit of a soil is the water content, expressed as a percentage of the weight of oven-dried soil, at the boundary between the plastic and semi-solid states. The boundary is arbitrarily defined as the lowest water content at which the soil can be rolled into threads 1/8 in. in diameter without the threads breaking into pieces." (p. 85)

and,

> "The liquid limit of a soil is the water content, expressed as a percentage of the weight of the oven-dried soil, at the boundary between the liquid and plastic states. The water content is arbitrarily defined as the water content at which two halves of a soil cake will flow together for a distance of 1/2 in. along the bottom of the groove separating the two halves, when the cup is dropped 25 times for a distance of 1 cm (0.3937 in.) at the rate of two drops per second." (p. 109)

The plasticity index is simply the difference in water content between the liquid and plastic limits. When the liquid limit is less than the plastic limit, the plasticity index is recorded as being zero.

It should be recognized that the term 'water content', throughout soil engineering practice, refers to moisture removed by heating the soil at 105-110°C [Gardner 1965]. Unfortunately, however, this temperature has no special significance in relation to the type of moisture extracted from the soil. Grim [1968, p. 235] makes a distinction between water lost at low temperatures (100-150°C) and high temperatures (>300°C). The former includes "the water in pores, on the surfaces, and around the edges of the discrete particles of minerals" as well as interlayer water in the case of swelling clay minerals; the latter refers to lattice water. In this context, soils containing allophane will loose structural water when heated to ~105°C, which in part explains their peculiar plasticity limit values. The inferred 'plateau' in dehydration curves from 100°C to 300°C is a relative feature only, however, and, more important in this relation, there is no sharp break in dehydration curves at 105°C. Cardner [1965] adds that, on the basis of such curves, a temperature of 165°C-175°C would be more appropriate for most soils, ensuring that all interlayer and adsorbed water is removed. He adds [Gardner 1965, p. 86], "However, excessive oxidation and decomposition of soil organic matter in this high temperature range would prevent its general adoption." For this reason, a temperature of 105°C-110°C is taken as a compromise.

## 2.2 Theoretical Aspects of the Plasticity Limits

At the plastic limit the water content is sufficient to wet the surfaces of all the particles and to fill the pores between the particles, and in the case of porous particles, such as diatomaceous sediment, to fill the pores within the particles; in addition, sufficient water is present to impart bonding among the constituents of the sediments, but insufficient to provide excessive lubrication. The water contained in a soil at the liquid limit includes the same water as at the plastic limit, plus additional water to provide the increased lubrication necessary for the material to flow when tapped. Warkentin and Maeda [1974] have shown for certain allophane soils that the amount of water held at the liquid limit state correlates quite closely with the water-holding capacity of these soils at a suction of 15 bars. However, the liquid limit is essentially a dynamic property of a sediment and is perhaps best interpreted in the context of the shear resistance of a saturated remoulded mass. Skempton [1953b], for example, has stated that the liquid limit is, in fact, a measure of the water content of the remoulded material at a shear strength of approximately 0.1 psi. The water content at the liquid limit can thus be viewed as the amount of water necessary to reduce the interaction among soil particles to lower the shear resistance to this value. Any treatment which changes the resistance to shear of an unconsolidated remoulded sediment, without a change in water content, thus implies a corresponding change (in the same direction) in the liquid limit of the sediment. This premise is used throughout the discussion below.

In order to understand the behaviour of cohesive material at the plastic and liquid limits, the nature of the interactions between particles must be considered. The water adsorbed on the clay particles, the forces generated by the electrostatic nature of the particles, the behaviour of the diffuse double layer, and the resulting particle interactions, as influenced by the soil mineralogy and the chemistry of the soil solution, will be discussed with reference to the behaviour of cohesive soils at the plastic and liquid limits.

### 2.2a Adsorbed Water on Clay.

The water within a few Angstroms of the clay surface has been shown to differ physically from "free" water, in that it is strongly bonded to the surface of the clay particles [Martin 1962, Rosenqvist 1962, Grim 1968, Mortland et al. 1963]. Although the exact nature of the water adjacent to a clay surface is not clear, various models have been proposed. Martin [1962] has analysed much of the data available at that time and arrives at the conclusion that two of the models fit most of the data; these are that the water adsorbed on the clay is 1) a solid-like substance, or 2) a two-dimensional fluid.

Rosenqvist [1962] and Ingles [1968] point out the importance of hydrogen and hydroxyl bonding between the liquid phase and the clay surfaces. Mortland et al. [1963] present evidence from experiments with the adsorption of $NH_3$ onto clay in a vacuum which indicates that water molecules adsorbed next to the clay surface are highly dissociated, indicating a relatively strong bonding mechanism between the water and the clay surface. Water molecules exhibit dipole properties, which has led some researchers to conclude that the water adjacent to the clay forms an ordered net similar to a crystal structure. Grim [1968, Chapter 8], who presents an excellent review of various theories on adsorbed water on clays, discounts this theory as being unlikely; earlier [Grim 1962, p. 219-221], however, he utilizes the hypothesis extensively in his own discussion of plasticity limits, specifically:

> "... the plastic limit is a measure of the water content which the particle surfaces can adsorb just slightly in excess of that which can be fixed in a highly rigid condition and which does not separate the particles too much to greatly reduce the attractive forces between them. In addition to the oriented water directly adsorbed in the surfaces, there would be some pore water in a liquid or semiliquid condition enclosed in pores in such manner that had little lubricating effect. It is difficult to estimate the thickness of the water layers and the amount of pore water at the plastic limit, because the amount of adsorbing surface cannot be determined. However, the amount of oriented water is probably of the order of 5 to 10 molecular layers, and the pore water probably ranges from about 20 per cent of the plastic limit value in the case of montmorillonite to a major part for some kaolinite clays."
> (p. 220)

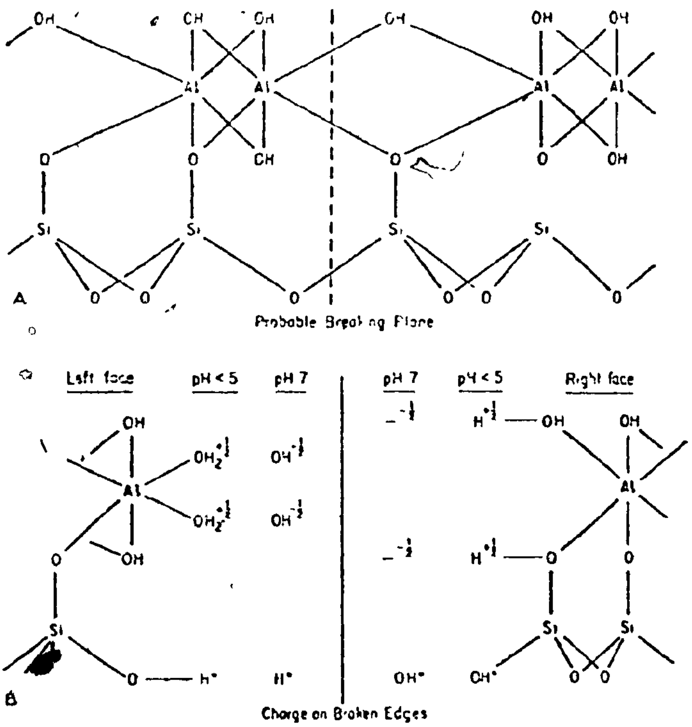
The theory which has gained most favour from researchers who are attempting to explain the interactions of clay material in suspension, in sediments and in soils, postulates that immediately adjacent to the clay particle surface, there is a very strongly adsorbed layer of water of at least one layer, but more likely several layers, thick [Ingles 1968, Yong and Warkentin 1975]. This layer of water is bonded to the surface of the clay by hydrogen bonding, and possesses much greater shear strength than normal water [Rosenqvist 1968]. At low water contents, this adsorbed water may be responsible for much of the strength of a clay material as these water films begin to merge. This concept of particle interaction is not accepted by some workers, however, for example Michaels [1959], who maintains "... interparticle-adhesion in clays occurs in spite of, rather than because of, the presence of water." At higher water contents, in contrast, the decreased viscosity of water at larger distances from the clay surface, together with reduced attractive forces among the particles due to their increased separation (see below, 2.2b), lowers this strength, it is believed, until ultimately the liquid limit state is reached.

### 2.2b Attractive and Repulsive Forces Acting Between Particles.

The interaction forces between particles will depend on the relative importance of the attractive Van der Waals force and electrostatic attractive and repulsive forces, as influenced by the physical nature and chemistry of the fluid phase. The Van der Waals forces are generated internally in every atom, through a mechanism related to the motion of the electrons about their nucleus [Fyfe 1964, p. 86]. The forces are electrical in nature, and diminish very rapidly with distance (inversely as the seventh power of the separation distance) for molecules but more slowly (as the third or fourth power) for plates [Ingles 1968]. Related to the other electrical forces on the clay particles, the Van der Waals force is strong. The rapid decrease in effect with distance is of great importance in the behaviour of the clay particles, both in terms of soil microstructure and plastic properties. This force is always attractive [Rosenqvist 1968].

In the absence of all other forces, these electromagnetic forces would pull all particles in a suspension together; however, clay minerals exhibit net negative charges on the crystal faces and, as a consequence, repulsive forces act to counter this attraction (see below, 2.2c). A major source of this negative charge is isomorphous substitution of lower valence cations within the crystal structure. The substitution may occur in the silica tetrahedral layer, for example, trivalent Al for tetravalent Si; or in the octahedral layer, divalent Ca, Mg or Fe for trivalent Al. In either case, the electroneutrality of the crystal is disturbed. In addition, because the structure of a clay mineral is theoretically infinite in two dimensions, where the crystal ends there will be unsatisfied valence bonds which can add to the electrical charge on the particle. In the case of kaolinite, these edge charges are of particular importance since there is very little isomorphous substitution within the crystal and the edge surface constitutes a high proportion of the total surface area. The edge charge on a clay mineral has been shown to vary with the pH of the solution (Figure 2.1). For kaolinite, at pH less than five, the edge bonds are positive; at pH seven and above, the charge becomes negative [Schofield and Samson 1954]. As a result, the electrostatic interaction between particles in soils will depend on the pH of the fluid phase. This variable pH-dependent charge can be expected to influence the behaviour of not only the 1:1 clay minerals such as kaolinite, but also the 2:1 and 2:1:1 clay minerals, some clay-size non-clay minerals and amorphous inorganic material [Van Olphen 1963, p. 18-20 and p. 90-93].

FIGURE 2.1



Kaolinite structure showing probable breaking plane and mechanism for edge charge by picking up hydrogen or hydroxyl from solution to give positive charge at low pH and negative charge at higher pH. [Yong and Warkentin 1975, p. 51]

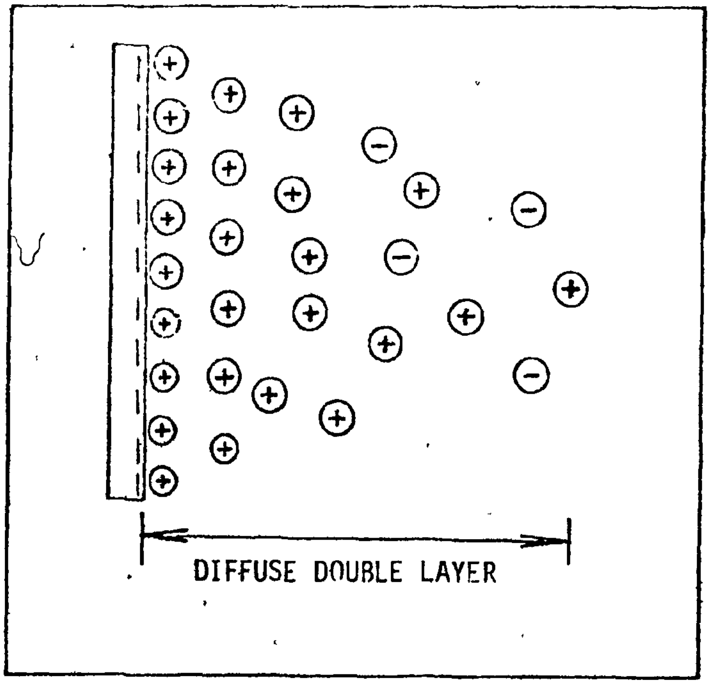
The existence of both attractive and repulsive forces among colloidal particles controls, to a great extent, the behaviour of suspensions subject to Brownian motion. In suspensions of very dilute electrolyte concentrations, the <u>net</u> interaction energy shows a repulsive barrier at a spacing of about 15-500 Å [Ingles 1968, p. 18], hindering flocculation by kinetic motion. At higher salt concentrations, however, circumstances are quite different, as outlined below (2.2c).

### 2.2d Diffuse Double Layer Theory.

In saline suspensions, the net negative charge on the clay mineral surface will result in the attraction of positively charged cations from the solution. According to kinetic theory, the cations will not be held firmly to the surface, but rather will form a diffuse field of cations, most densely packed at the surface, becoming more widely spaced as the distance from the surface increases (Figure 2.2). The distribution of the cations in the double layer can be expressed as a mathematical function of the charge at the surface, the valence of the cations and the concentrations of cations

FIGURE 2.2

The Diffuse Double Layer.

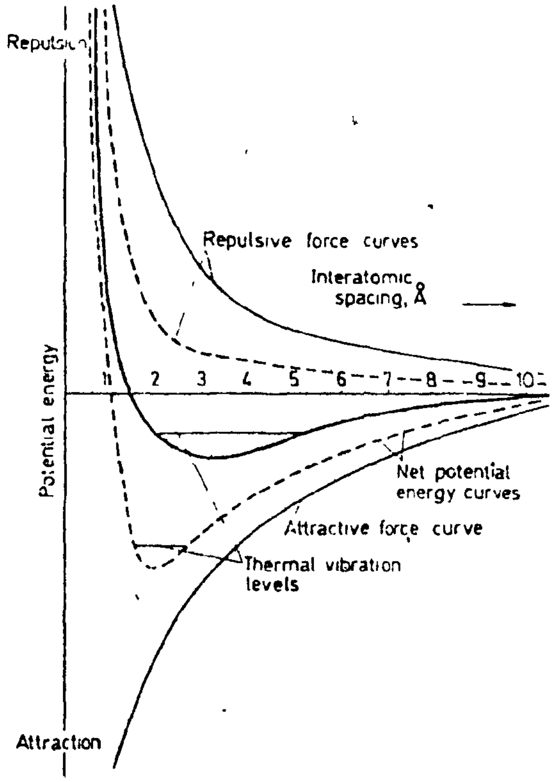


in solution [Rosenqvist 1968, Yong and Warkentin 1975]. Increasing the electrolyte concentration of the "free" solution (outside of the double layer) reduces the tendency of cations to diffuse towards it and thus depresses the thickness of the layer. Similarly, substituting divalent cations for monovalent cations in the solution will decrease the thickness of the layer, since fewer cations will be required to satisfy the electrical charge on the particles.

The Gouy-Chapman theory of the diffuse double layer can be used in an explanation of many aspects of the interaction of clay particles in soils as influenced by the cation concentration and valence. Increasing the salt concentration of the pore fluid, or the valence of the cations in solution, will decrease the thickness of the double layer as just indicated. The effect of this can be viewed in two ways, both reflecting the decreased repulsion in the inter-granular space (see Figure 2.3). Firstly, the strength of the <u>net</u> energy barrier at about 15-500 Å spacing is reduced, thus, in the case of suspensions, increasing the probability of flocculation arising from thermal movement across the barrier. Secondly, in a sediment (with no thermal movement) there is an increase in net attraction among particles because of the reduced repulsive energy. From either standpoint, this would be expected to increase the liquid limit of the sediment (on the basis of our initial premise) and experimental data confirm this in certain situations (discussed below, 2.3c).

Low [1959] and Rosenqvist [1962] point out that two of the basic assumptions of the double layer theory are questionable: "These assumptions were:

FIGURE 2.3



Potential energy curves for ionic and atomic interaction [Ingles 1968]

1) the potential energy of the exchangeable cations is influenced only by the electrical field of the clay particles; and 2) the clay surface itself does not attract water." [Rosenqvist 1962, p. 19] It is known that the exchangeable cations are affected by the water due to hydration shells and that the clay does indeed attract water molecules. Despite these limitations the theory is used, mainly because it works when applied to the interaction of clay particles, as demonstrated below.

## 2.3 Plasticity: Experimental Data

### 2.3a The Effect of Particle Size.

The plasticity of different clay minerals is partially a function of the difference in the size, and therefore the specific surface area, of the clay minerals of a specific species. Table 2.1 presents data from White [1949] which clearly demonstrate that the plasticity is a function of particle size as well as of the species of clay mineral. The proof that the size of particles is not the only factor is observable from the differences between the Atterberg limits of the fraction less than 1.0 micron in size of the different minerals. This increase in plasticity with decreasing size is precisely what would be expected from the previous discussion of adsorbed water. As the specific surface area increases, the amount of water necessary to coat the surface increases and, hence, the amount of water needed to attain plastic limit state is also increased. The liquid limit also increases with decreased particle size: at a fixed water content, a larger proportion of this water is "bound" to one or more particle surfaces, increasing the resistance to shear and, accordingly, producing a higher liquid limit. The greater increase

TABLE 2.1

The Effect of Particle Size on Atterberg Limits.

| Clay Mineral | Particle Size: Microns | Plastic Limit | Liquid Limit | Plasticity Index |
|---|---|---|---|---|
| Illite | | | | |
| Grundy Co., Illinois | whole | 35.70 | 61.20 | 25.50 |
| | <1.0 | 35.59 | 83.00 | 43.41 |
| | 0.5 | 52.27 | 103.65 | 51.38 |
| LaSalle Co., Illinois | whole | 24.75 | 35.90 | 11.15 |
| | <1.0 | 46.21 | 85.55 | 39.34 |
| | 0.5 | 52.98 | 111.25 | 58.27 |
| Kaolinite | | | | |
| Union Co., Illinois | whole | 36.29 | 58.35 | 22.06 |
| | <1.0 | 37.14 | 64.20 | 27.06 |
| | 0.5 | 39.29 | 71.60 | 32.31 |
| Montmorillonite | | | | |
| Pontotoc, Mississippi | whole | 81.41 | 117.48 | 36.07 |
| | <1.0 | 109.48 | 175.55 | 66.07 |

[From White 1949]

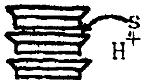
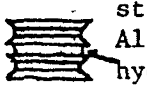
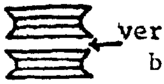
in the liquid limit than the plastic limit presumably reflects the larger number of molecular layers of adsorbed water held by the additional surface at the liquid limit than at the plastic limit condition.

### 2.3b The Effect of Mineralogy.

The plasticity of a clay material will also vary with the type of clay mineral and with the type of non-clay minerals found in the clay-size fraction. Table 2.2, after Soderman and Quigley [1965], summarizes some of the properties of the most common clay minerals.

## TABLE 2.2

Summarized Properties of Clay Mineral Groups

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Clay Type | * Symbol | Negative Charge per Unit Cell | ** Cation Exchange Capacity m.eq./100 gm | Glycol Retention mg/gm | Liquid Limit | Plasticity Index |
| **Kaolinite** |  strong $H^+$ bond | -0.01 | 3 | 20 | 29<br>to<br>73 | 1<br>to<br>37 |
| **Illite** |  strong $K^+$ bond | -1.0 | 25 | 80 | 59<br>to<br>100 | 25<br>to<br>58 |
| **Chlorite** |  strong bond Al, Mg or Fe hydroxide sheet | -0.5<br>to<br>-1.0 | 10-40 | 30 | Probably like illite | |
| **Vermiculite** |  weak Mg bond | -0.5<br>to<br>-0.7 | 150 | 150 | Probably between illite and montmorillonite | |
| **Montmorillonite** |  very weak bond | -0.3 | 100 | 260 | 123<br>to<br>700 | 65<br>to<br>600 |

* ▭ silica sheet, ▭ hydroxide sheet
**m.eq./100 gram = milliequivalents/100 grams of dry soil

[Columns 1-4 from Soderman and Quigley 1965, Columns 5 & 6 from Grim 1962]

Kaolinite, illite and chlorite are all non-swelling minerals. Water and exchangeable cations do not penetrate between the crystal platelets. Thus the water content at the plastic and liquid limits is, to a large extent, controlled by the amount of water adsorbed on the external surface of the minerals. The values presented for glycol retention are a measure of the specific surface area of the material (specific surface area in $m^2/g$ clay = mg glycol/g clay X 3.2 approx.) [Mortland and Kemper 1965]. In addition to differences in plasticity stemming from the different specific surface area of different minerals, as previously mentioned, other factors, such as the cation and anion exchange capacities, plus the differences in the shape of the particles, will result in higher plasticity indices for illitic than for kaolinitic soils; chlorite (for which plasticity data are scarce) is thought [Soderman and Quigley 1965] to resemble illite in this respect.

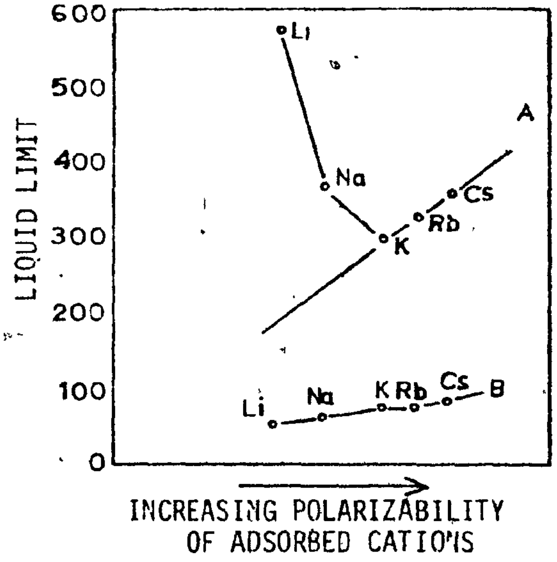
Vermiculite exhibits partial swelling properties, depending on the exchangeable cation and the actual charge per unit cell of the material in question. Very little information is available regarding the plasticity indices of vermiculite, but it seems likely that the material does not swell to the extent that a large quantity of water would be able to penetrate the layers during the determination of the Atterberg limits. For this reason, the material is more likely to have properties more similar to illite than to montmorillonite. The surface area, as indicated by glycol retention, is relatively high since the glycol would form a monolayer on the internal, as well as the external, surfaces.

Montmorillonite, and other related higher-swelling clay minerals, can adsorb water and cations between the platelets of the crystal; thus the water content at the plasticity limits will be related to the amount of dispersion of the clay platelets. The plasticity index is very large, corresponding to the large specific surface area (glycol retention; Table 2.2), which includes both internal and external surfaces. The dispersion of the crystal plates will, however, depend on the ability of the cations in the pore water to penetrate the interlayer space while retaining their hydration shells, as discussed further below.

### 2.3c The Effect of the Chemistry of the Pore Fluid.

Moum and Rosenqvist [1961] present data on the effect of different monovalent cations on the water content of illite and montmorillonite clays at the liquid limit. The results emphasize the marked difference in response to varying cation species between these two types of minerals. For illite, the liquid limit value increases with decreasing size of the hydrated cation. The smaller cations (with the larger hydrated radii) Li and Na, cause greater separation at the particle contacts, and therefore the strength of the material is less at a given water content than with the larger monovalent cations (with the smaller hydrated radii) Rb and Cs. Thus the amount of water that the clay can retain, at the theoretical 0.1 psi strength at the liquid limit, increases in the order Li, Na, K, Rb, Cs. For montmorillonite, the situation is significantly different. As Figure 2.4 shows, the water content at the liquid limit is high for Li, then drops with decreasing size of the hydrated cation for Na and then K; as the size of the hydrated cation continues to decrease, the liquid limit now increases from K to Rb and from Rb to Cs. This pattern can be explained by the different effect of the cations on the water

FIGURE 2.4



Relation between liquid limit of montmorillonitic and illitic clays and the polarizability of exchangeable cations: A. Montmorillonite B. Approximately 40% illite. [After Rosenqvist 1962]

content between particles (intercrystalline) and in interlayer positions (intracrystalline). The trend of increasing water content at the liquid limit, for intercrystalline water, is the same as for the illite, for the same reason. The difference between the two minerals lies in the behaviour of the intracrystalline water. The Li and Na cations are able to penetrate the interlayer positions while maintaining their hydration shells; thus the liquid limit is higher for Li than Na, since the former is more highly hydrated. The monovalent cations K, Rb and Cs all lose their hydration shells when they take up interlayer positions; thus the water content in the interlayers is small and the liquid limit values change as for illite.

Similarly, the effect of changed salt concentration, or changed cation valence, varies according to whether or not the clay minerals allow penetration of water into interlayer (intracrystalline) positions. Warkentin [1961] and Yong and Warkentin [1975] make the comparison between montmorillonite and kaolinite. For the former mineral, a decrease in valence and decreasing salt concentration both increase the liquid limit. This is consistent with the diffuse double layer theory: both changes produce a thicker diffuse layer, and therefore a transfer of water from intercrystalline to intracrystalline spaces. This arises directly from the high proportion of the surface area of montmorillonite which is intracrystalline. As a consequence of this transfer, at an unchanged water content, the amount of intercrystalline water is decreased, resistance to shear is increased, and therefore the liquid limit is also.

For non-swelling clay minerals the pattern is not quite so simple. Data for illite from Grim [1962], shown in Table 2.3, indicate that substitution of monovalent Na or Li for divalent Ca or Mg decreases the liquid limit. Again, this would be expected from the diffuse double layer theory; the effects are opposite to the changes in montmorillonite, because with illite only intercrystalline water is involved. The decreased valence increases the thickness of the diffuse layer and thus reduces intercrystalline bonding, and the liquid limit, for reasons given previously (2.2c). Similar changes, associated with decreasing the salt concentration, have been described by Rosenqvist [1955] for natural illitic-rich sediments in Norway. A sample of the clay was deposited under conditions of high salt content and subsequently divided into two samples; one was leached for five months with distilled wa-

TABLE 2.3

Atterberg Limit Values

| CLAY | | Ca$^{++}$ | | Mg$^{++}$ | | K$^{+}$ | | Na$^{+}$ | | Li$^{+}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Pw | Lw | Pw | Lw | Pw | Lw | Pw | Lw | Pw | Lw |
| Montmorillonite | (1) | 65 | 166 | 59 | 158 | 57 | 161 | 93 | 344 | 80 | 638 |
| | (2) | 65 | 155 | 51 | 199 | 57 | 125 | 89 | 443 | 59 | 565 |
| | (3) | 63 | 177 | 53 | 162 | 60 | 297 | 97 | 700 | 60 | 600 |
| | (4) | 79 | 123 | 73 | 138 | 76 | 108 | 86 | 280 | 82 | 292 |
| Illite | (1) | 40 | 90 | 39 | 83 | 43 | 81 | 34 | 61 | 41 | 68 |
| | (2) | 36 | 69 | 35 | 71 | 40 | 72 | 34 | 59 | 38 | 63 |
| | (3) | 42 | 100 | 43 | 98 | 41 | 72 | 41 | 75 | 40 | 89 |
| Kaolinite | (1) | 36 | 73 | 30 | 60 | 38 | 69 | 26 | 52 | 33 | 67 |
| | (2) | 26 | 34 | 28 | 39 | 28 | 35 | 28 | 29 | 28 | 37 |

Pw is plastic limit and Lw is liquid limit.

[After Grim 1962]

ter and the other was used as a control. The leached sample had a sensitivity of 90 at the end of the experiment, as compared to the control sample, which had a sensitivity of only 6.4. The plasticity values of the two samples, as shown in Table 2.4, indicate a large decrease in the liquid limit of the leached clay as compared to the unleached sample. Similar experiments by Pusch and Arnold [1969] with pure illitic material failed to produce a reduction in the liquid limit; their test procedures were somewhat controversial, however [Torrance 1970], and further discussion is deferred until Chapter 6.

TABLE 2.4

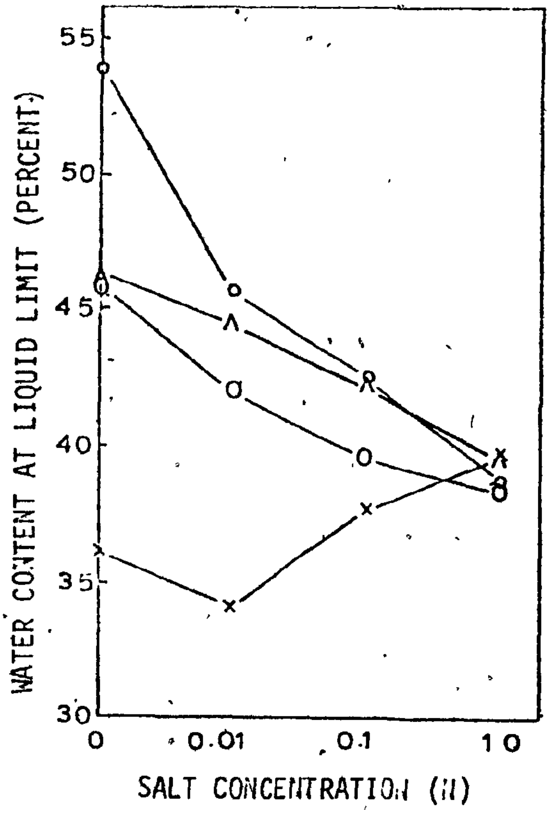
The effect of salt concentration on Atterberg limits
of a natural clay sample from Norway.

| Sample | Salt Concentration g/l | Plastic Limit | Liquid Limit | Plasticity Index |
|---|---|---|---|---|
| Leached | 1.0 | 18.0 | 27.4 | 9.4 |
| Unleached | 39.0 | 19.5 | 43.4 | 23.9 |

(After Rosenqvist 1955)

Often kaolinite is grouped with illite and other non-swelling clay minerals, but the unusually high proportion of edge charges of the former render its behaviour anomalous. The natural fabric of remoulded kaolinite in pure water is edge-to-face (EF) [Schofield and Sampson 1954] because of electrostatic attraction between negatively-charged face surfaces and positively-charged edges. As pH increases, the fixation of edge $H^+$ ions is considerably

FIGURE 2.5



Influence of salt concentration on liquid-limit of kaolinite clay at different pH and with different exchangeable cations:
o, natural kaolinite (pH 4) + calcium chloride; ʌ, sodium kaolinite (pH 6.5) + sodium chloride; O, calcium kaolinite (pH 6) + calcium chloride; x, sodium kaolinite (pH 10) + sodium chloride. [After Warkentin 1961]

weakened, and eventually disappears, so that edges also acquire a negative charge. The effect is a transformation of the fabric to a face-to-face (FF) pattern, with, therefore, fewer "contact zones", a decreased resistance at an uncharged water content, and thus a decrease in liquid limit as indicated in Figure 2.5. This same transformation in fabric from EF to FF also occurs as the salt concentration is increased [Schofield and Sampson 1954] because of the increased separation between the (thinner) oppositely-charged diffuse layers in contact areas. This is consistent with the decrease in liquid limit with increasing salt concentration (unlike illite). The exception in Figure 2.5 (for pH 10) represents the case in which all fixed positive edge charges have been removed; in this case the completely negatively-charged kaolinite is now comparable with illite, and shows an increase in liquid limit with increasing salt concentration, though unable to attain the very high liquid limit values of dilute, low pH solutions.

### 2.3d The Effect of Amorphous Inorganic Material on Plasticity.

Due to the paucity of experimental evidence, no general conclusions can be reached as to the effect of amorphous inorganic material on plasticity, although certain specific observations can be made.

Considerable research has been done on volcanic ash soils containing allophane, and reviewed by Wada and Harward [1974] and by Warkentin and Maeda [1974]. This particular amorphous material has the effect of greatly increasing the water content of the soil at both the plastic and liquid limits, but only if the determinations are performed on material which has not been dried. When allophane is dried, the material dehydrates irreversibly with a resultant drop in the Atterberg limits. For soils which possess large quantities of allophane, the material becomes non-plastic on oven drying at 110°C [Warkentin and Maeda 1974].

Moum [1968] has performed experiments to study the effect of adding amorphous iron compounds on the plasticity of a natural illitic clay from Norway. The results show that the amorphous iron increased the liquid limit and the strength of the remoulded clay. Moum [1968, p. 126] explains this as follows: "The iron gels thus introduced ($FeCl_2$, $FeCl_3$ and $Fe[OH]_3$) are believed to have positive charges and being adsorbed to the mineral surfaces as clusters which could build bridges between the grains." Another experiment by the same author indicated that oxidation of the natural post-glacial marine clay results in a similar increase in the liquid limit.

The effect of amorphous inorganic material on plasticity might be expected to depend on: 1) The water-holding capacity of the amorphous material as compared to the crystalline soil material, which will be a function of a. its specific surface area, and b. its surface chemistry (e.g., cation and anion exchange capacities); 2) The positional or structural arrangement of the material, which could be: a. discrete particles, b. coatings around individual particles, c. coatings around aggregates of particles, or d. cementing agents at the points of contact between particles.

Much more detailed study is required to elucidate the effect that amorphous components have on the physical behaviour of material, and on the physical and chemical nature of this material. The present study is intended as a contribution to that end.

# Chapter Three:

# CHEMICAL DISSOLUTION TECHNIQUES FOR THE EXTRACTION OF AMORPHOUS IRON, ALUMINUM AND SILICON COMPOUNDS IN SOILS AND SEDIMENTS.

## 3.1 Definition of Amorphous Material.

The definition of amorphous material in soils, as presented by Wada and Greenland [1974] and used here, is material of less than 2 micron equivalent diameter, which lacks order, as compared to crystalline material, which is well-ordered. Included in this term amorphous is material which has short-range order only (due to atomic packing and covalent bonding) or has long-range order in only one dimension, as opposed to crystalline material, which has long-range order and repetition of unit cells, usually in three dimensions, but in some cases (for example, single flakes of montmorillonite and randomly interstratified clay minerals) only in two. The degree of order in the mineralogy of soils is a continuum, such that the boundary between amorphous and crystalline is arbitrary. Due to the difference in the degree of order, the techniques used for the identification of crystalline soil components are not always applicable to the identification of amorphous material. Indeed, many works use the term amorphous specifically with reference to a particular method of identification, such as "X-ray amorphous material".

## 3.2 Methods of Identifying Amorphous Compounds.

The clay-sized compounds in soils and sediments are identified by two methods: 1) Physical examination of the material as it exists in the soil; and 2) Chemical dissolution of the components by selective chemical procedures.

Crystalline clay compounds can be identified by X-ray diffraction, electron diffraction, differential thermal analysis, and infra-red spectroscopy. In addition, electron microscopy can be of assistance in recognizing crystalline materials visually. Amorphous material does not possess long-range order and hence is not indicated directly on X-ray diffractograms, although its presence may be suspected from the strength of background noise in such traces. In some cases short-range order can be observed by electron diffraction. Differential thermal analysis and infra-red spectroscopy can be used to a limited extent to identify amorphous material, but in most cases the variable composition and the small amounts of this material make positive identification impossible. Electron microscopy has been used to show the occurrence of amorphous material in soils (without identifying it), and with the use of shadowing techniques, even electron-transparent amorphous gels have been identified [Jones and Uehara 1973]. Due to the difficulties associated with the identification of amorphous soil material by physical means, chemical dissolution of this material is the most common method of its determination.

## 3.3 Chemical Dissolution Techniques as a Determinant of Amorphous Material.

Because amorphous soil components are characterized by a lack of well-ordered structure, the component atoms are less well bonded to one another than in a crystalline material. Chemical dissolution techniques make use of this property to differentiate between crystalline and amorphous soil material. Extraction procedures, in general, are performed with chemical reagents that are of sufficient strength to remove the amorphous phase, while doing the minimum of damage to the crystalline component. Since the rate of reaction is more rapid with the amorphous material than with the crystalline material, the time of the reaction is often limited to minimize the destruction of crystalline materials. It has previously been mentioned that there is a continuum in the range of crystallinity of the inorganic soil material; the effectiveness of a chemical dissolution procedure in extracting amorphous material from a soil will depend on how closely the material extracted corresponds to material which does not possess long-range order.

## 3.4 Purpose of Chemical Dissolution Techniques.

In addition to identification, scientists are interested in the extraction and analysis of amorphous compounds from soils for a number of other reasons:

1) Pretreatment for mineralogical analysis; amorphous coatings on crystalline minerals makes identification by means of X-ray diffraction and differential thermal analysis difficult due to aggregation of particles, the masking of significant peaks by 'noise' and dilution of the crystalline components [Brewer 1964, Jackson 1956, Kittrick and Hope 1963].

2) Pedogenetic studies of such processes as podzolization and gleying require a quantitative measure of translocated sesquioxides in different horizons of the soil profile [Blume and Schwertmann 1969, McKeague and Day 1966, Mitchell et al. 1968, Sneddon, Lavkulich and Farstad 1972].

3) Evaluation of the effect of amorphous material on the physical pro-

perties of soils; this can best be accomplished by the comparison of physical properties before and after dissolution of the amorphous component [Follett et al. 1965 a & b]. The present study falls into this category.

The requirement for all of the above purposes is a chemical dissolution technique which effectively removes amorphous material while causing the least amount of disturbance to the crystalline component in the soil. If the chemical dissolution treatment is successful, then accurate measurement of the extracted material and analysis of the residual crystalline material will give a quantitative assessment of the soil composition. This is not to say that the same treatment will be ideally suited to all of the above purposes; the requirements are somewhat different for each, particularly for research on pedological processes which require differentiation of a number of forms of sesquioxides in the soil.

## 3.5 The Physical Form of Amorphous Iron, Aluminum and Silicon Compounds in Soils.

Amorphous compounds in soils have been interpreted physically in various ways by different workers: as coatings around single-mineral fragments; as coatings around aggregates of mineral fragments; as "bridges" between fragments, thus forming aggregates; as interlayer material in phyllosilicates; and as a separate particulate phase.

Follett et al. [1965b] performed chemical dissolution procedures in conjunction with measurements of physical properties of a soil. An increase in specific surface area following dissolution of the amorphous material was interpreted as an improvement in dispersion resulting from the removal of coatings on the clay minerals, or aggregates of clay minerals. Jones and Uehara [1973] used the electron microscope to examine samples of soil clay deposited on mounts with a holey substrate, which indicated that the particles were surrounded with "gelatinous material". In a separate phase of their study, in which iron oxide samples were shadowed with platinum, it was demonstrated that these particles are coated with electron-transparent material, presumably an iron oxyhydroxide gel. Further evidence of surface coatings on individual clay particle surfaces was presented by Greenland and Wilkinson [1969] who studied carbon replicas of clay particles before and after extraction of dithionite and alkali-soluble material. The authors concluded on the basis of the effect of different treatments on surface morphology that the surface coating was "composed of disordered silica and alumina rather than iron and aluminum hydroxide".

Jackson _et_ _al_. [1973], using a scanning electron microscope, identified hydrous metal oxide crusts, varying in thickness from 1-15 microns, intercalated between sequences of hundreds of vermiculite flakes. These packets contained predominantly 14 Angstrom crystallographic layers. Thus iron and aluminum oxyhydroxide compounds can form crusts within these large particles, as well as surface coatings. Following extraction with Na-citrate-bicarbonate-dithionite, the vermiculite pseudomorphs, weathered _in_ _situ_ from biotite, dispersed, producing a large number of thin phyllosilicate flakes. Dissolution of this "interlayer" oxyhydroxide material is another process which would result in an increase in specific surface area. In a previous paper, Jackson [1964] refers to "chloritization" of 2:1 clay minerals in which the interlayer positions are occupied by iron or aluminum oxyhydroxides. In this case, the material is assumed to form a single octahedral layer which results in the 14 Angstrom basal spacing of chlorite. In addition, these interlayers may be complete, in that they occupy all of the interlayer position, or they may form islands a few Angstroms in diameter, thus producing a weaker bond between layers, resulting in the "swelling chlorites" found in some soils.

Amorphous material also exists as a separate particulate phase of high specific area. Allophane, commonly developed in soils derived from volcanic ash, is characterized by high specific surface area, a high value of pH dependent cation exchange capacity and Al-O-Si bonding. Allophane exists as a polymer of silica and alumina over a range of $SiO_2/Al_2O_3$ ratios of about 1.3 to 2.0 [Wada and Harward 1974]. Hisingerite is an amorphous or "very finely crystalline" iron silicate with molar ratios of $SiO_2/(Fe_2O_3 + FeO)$ of between 1.4 and 3.2. The very weak X-ray diffraction pattern of hisingerite is similar to nontronite, an iron-rich smectite, and may be related to it either structurally or genetically [Lindqvist and Jansson 1962, Whelan and Goldich 1961].

In addition to the fact that the less well-ordered material is more readily soluble, due to the weaker bonding between atoms or molecules, there are two additional factors which make the amorphous material more susceptible to dissolution than the crystalline material: 1) If the amorphous phase is a surface coating, then this material will be attacked before the underlying crystalline material is exposed to the chemical reagents; and 2) If the amorphous phase is finely particulate material, then dissolution will take place preferentially, since there is more surface area exposed for the chemicals to attack.

## 3.6 Types of Chemical Dissolution Techniques:

All of the chemical dissolution techniques for the dissolution of amorphous compounds consisting of Si, Al and/or Fe are based on increasing the solubility of these compounds by chemical means. At neutral pH, all of these compounds are relatively insoluble in oxidized distilled water.

A number of approaches are available. The pH of the system can be adjusted such that these compounds become much more soluble; for example, a high pH will markedly increase the solubility of both Si and Al compounds, while under very acid conditions both Al and Fe compounds increase in solubility. Another approach available for increasing the solubility of Fe compounds is the use of a powerful reducing agent, such as dithionite, since ferrous iron has a much higher solubility than ferric iron. The third approach is to employ organic compounds, such as oxalate and citrate, capable of forming soluble organo-metallic complexes with trivalent metallic cations.

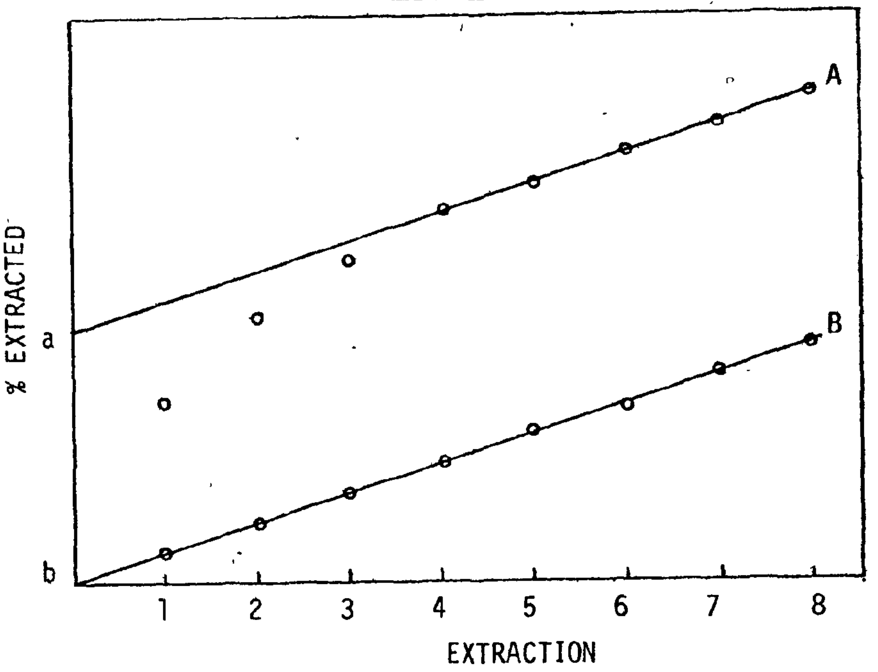
These techniques are discussed below with specific reference to the advantages and disadvantages of the different procedures and to their effects on different soil constituents.

### 3.6a pH-Dependent Dissolution Techniques.

The solubility of Si, Al and Fe compounds is relatively low at neutral pH. Using chemical extractants of very low or very high pH increases the solubility of Fe and Al compounds in the first case and Al and Si compounds in the latter. Jackson [1956, p. 72] suggested the use of 2% $NaCO_3$ to dissolve silicic cement and thus aid in the dispersion of clay particles prior to X-ray analysis. Hashimoto and Jackson [1960] employed a procedure which included a 2 1/2-minute treatment with boiling 0.5 N NaOH to dissolve silica and alumina, including allophane. Follett et al. [1965a] performed a comparative study of Hashimoto and Jackson's NaOH treatment and treatment with 5% $Na_2CO_3$, in which the sample was shaken for 16 hours, three or four times, at room temperature and subsequently treated three times on a steam bath for two hours each time. The results of the study indicated that the much shorter treatment with NaOH is less destructive to the crystalline material and more effective in removing amorphous material [De Villiers 1971]. Segalen [1968], in his study of tropical soils containing relatively large amounts of sesquioxides and silica, employed alternate acid and base treatments: 8 N HCl at room temperature for 30 minutes, to dissolve Fe and Al amorphous compounds; and 0.5 N NaOH in a boiling water bath for 5 minutes, to remove Al and Si compounds. The procedure is repeated until the amount of iron, aluminum and silicon in the extracts is low and relatively constant, usually 8 extractions. Up to 15% of these samples of tropical soils was dissolved by this treatment. Schwertmann [1973] has pointed out that Segalen's procedure is a much stronger extractant than treatments normally applied to the soils of temperate regions, although it has recently been applied to samples of post-glacial marine sediments in Eastern Canada [McKyes, Sethi and Yong 1974].

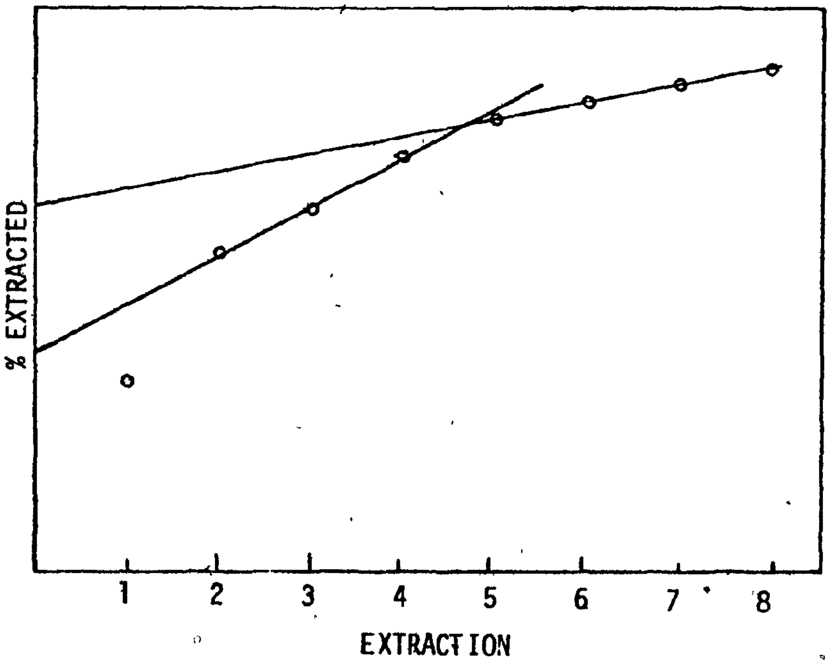
In all of the above procedures, the extraction of amorphous material is accomplished by increases in solubility resulting from extremes of pH. From the work of Follett et al. [1965a] and Wada and Greenland [1970], it can be concluded that the treatment in 0.5 N NaOH is effective in dissolving amorphous silica in soils without causing significant damage to the crystalline phyllosilicate clay minerals. Segalen's [1968] technique is not intended as a pretreatment for mineralogical analysis, but rather as a means of determining the amount of amorphous material in soils. Segalen [1968] points out that mineralogical analysis following treatment indicates that, although illite and kaolinite were little affected, montmorillonite was attacked by the treatment, possibly because of the very small particle size and high specific surface of this mineral. The data presented by Segalen indicate that the dissolution of the amorphous phase is considerably more rapid than the dissolution of most crystalline material, and thus the amount of amorphous material can be interpreted from the dissolution curve (Figure 3.1). A number of the dissolution curves show that there are more than two degrees of solubility, and hence crystallinity, in some soil samples (Figure 3.2). Compound curves such as these could potentially yield increased information on the variations in crystallinity of the soil material as it related to mineralogy. This field of study requires further attention, and perhaps refinement of the chemical treatments, to achieve this end.

FIGURE 3.1



Idealized dissolution curves: A. soil containing both crystalline and amorphous material (intercept a indicates amorphous material content) B. soil containing only crystalline material (intercept b indicates no amorphous material).
[After Segalen 1968]

FIGURE 3.2



**Dissolution curve exhibiting more than one degree of solubility of the soil components.**
**[After Segalen 1968]**

### 3.6b Reducing Agents for the Removal of Iron Compounds.

Two methods involving the use of reducing agents for the extraction of iron from soils are used in Canada at present. The technique of Mitchell and Mackenzie [1954] and Mackenzie [1954] uses an extractant composed of sodium dithionite and weak sodium hydroxide at pH 5.8 to 6.0 to create a reducing environment in which ferric iron compounds are converted to the more soluble ferrous form. The dithionite treatment is followed by a 0.05 N HCl washing to remove the reduced iron. The procedure is then repeated. This technique is still employed by some laboratories since the inorganic nature of the extractants allows for simpler determination of iron in the extracts [Stonehouse and St. Arnaud 1971].

The procedure of Aguilera and Jackson [1953], as modified by Mehra and Jackson [1960], employs sodium dithionite in conjunction with the complexing agent sodium citrate. This procedure is discussed in the next section with the other procedures employing complexing agents.

### 3.6c Extraction by Complexing Reactions - Amorphous Iron and Aluminum Compounds.

The complexing procedures make use of the property of some organic anions to form compounds preferentially with trivalent metallic cations. These anions form a number of bonds with the metallic cation such that the trivalent cations become enclosed within the organic molecule.

Three techniques for the dissolution of different portions of the amorphous iron and aluminum oxides, hydroxides and silicates are commonly being employed: Pyrophosphate preferentially extracts organic complexed iron and aluminum compounds [McKeague et al. 1971]; acid oxalate extracts organic and inorganic complexed iron and aluminum compounds but does not attack crystalline forms such as hematite, goethite or gibbsite [McKeague and Day 1966]; the Na-citrate-bicarbonate-dithionite (CBD) treatment of Aguilera and Jackson [1953], as modified by Mehra and Jackson [1960], has been used extensively to extract iron oxides and hydroxides from soils. Hematite and goethite are partially dissolved by the CBD treatment, depending on the degree of order in the structure and the size of the particles. McKeague and Day [1966] and Gorbunov, Dzyadevich and Tunik [1961] found that two extractions with CBD did not completely dissolve finely-ground samples of hematite and goethite, although Mehra and Jackson [1960] report that these compounds were completely dissolved in three treatments. Although considerable amounts of aluminum and silica are removed by the CBD treatment, crystalline gibbsite is little affected; allophane also appears to be resistant to CBD [Hashimoto and Jackson 1960].

Several workers have performed studies of these treatments on different soil minerals in order to determine which soil components are being affected. The work of McKeague and Day [1966] provides a comparison of the effect of oxalate and CBD on crystalline and amorphous iron and aluminum oxides (Tables 3.1 and 3.2).

TABLE 3.1

Effect of particle size on dissolution of hematite and goethite by dithionite and by oxalate extraction.

| | | Hematite | Goethite |
|---|---|---|---|
| Particle Size | Extractant | Fe extracted (%) | |
| 100 mesh | Dithionite | 28.8 | 17.9 |
| | Oxalate | 0.08 | 0.12 |
| 300 mesh | Dithionite | 39.6 | 28.8 |
| | Oxalate | 0.16 | 0.58 |

[From McKeague and Day 1966]

TABLE 3.2

Fe and Al % dissolved from various substances (100 mesh) by dithionite and by oxalate.

| | Dithionite | | Oxalate | |
|---|---|---|---|---|
| Mineral | Fe | Al | Fe | Al |
| Gibbsite | - | tr. | - | 0.1 |
| Feldspar | tr. | tr. | - | - |
| Hornblende | 0.3 | 0.1 | 0.5 | 0.2 |
| Muscovite | tr. | 0.2 | - | - |
| Olivine | 0.7 | tr. | 1.3 | tr. |
| Kaolinite | tr. | tr. | tr. | tr. |
| Montmorillonite | 0.4 | 0.1 | 0.2 | 0.1 |
| Illite | 0.3 | 0.1 | 0.2 | 0.1 |
| Amorphous Al-silicate* | - | 4.8 | - | 7.0 |
| Amorphous Fe-silicate** | 14.6 | - | 10.6 | - |

* Total value - Al 7.2%, Si 24.8%.
** Total value - Fe 14.7%, Si 24.0%.

[From McKeague and Day 1966]

From the data presented above, it can be concluded that neither oxalate nor dithionite (CBD) attacks to any significant extent the crystalline iron and aluminum silicates; dithionite is a stronger extractant of iron from iron oxides and amorphous Fe-silicate than oxalate, while for aluminum compounds the reverse is true. McKeague, Brydon and Miles [1971] present data on the effect of pyrophosphate, oxalate and dithionite (CBD) on various synthetic hydrated oxides and iron oxide minerals (Table 3.3).

TABLE 3.3

Total and extracted Fe contents of synthetic hydrated oxides and iron oxide minerals.

| | Total Fe * | $Fe_p$ | $Fe_o$ | $Fe_d$ |
|---|---|---|---|---|
| | | %** | | |
| Fe oxide sol | 16.4 mg Fe/ml | 4.0 | 100 | 100 |
| Amorphous Fe oxide | 54% | 0.5 | 100 | 100 |
| Goethite (100 mesh) | 63% | 0.0 | 0.2 | 28 |
| Hematite (100 mesh) | 70% | 0.0 | 0.1 | 41 |
| Magnetite (100 mesh) | 72% | 0.0 | 8.8 | 2.4 |

* Total Fe values for the Fe minerals were calculated.
** Fe extracted as % of the total Fe.

[From McKeague, Brydon and Miles 1971]

Pyrophosphate ($Fe_p$) does not attack crystalline or amorphous iron oxides; oxalate ($Fe_o$) and dithionite ($Fe_d$) are equally capable of extracting the iron from the Fe oxide sol and the amorphous Fe oxide; oxalate removes significantly less Fe from the well-crystallized iron oxide minerals hematite and goethite, but more from magnetite, than does dithionite. The laboratory analysis of the effects of the three dissolution techniques thus indicates that there is some validity in using them to differentiate between the various forms of iron and aluminum organic compounds, amorphous oxides and hydroxides and finely-crystalline components in the soil. It would be a mistake to assume that these three techniques can be used to differentiate precisely between the various forms of iron compounds in soils [Schwertmann 1973, Arshad et al. 1972, Pawluk 1972]; nonetheless, a reasonable separation of well-crystallized iron from completely amorphous forms of iron can be obtained from the use of complexing techniques.

Table 3.4 presents a compilation of data on the effect of a number of chemical dissolution procedures on some crystalline and amorphous compounds from the work of recent authors.

## 3.7 Treatment Sequence Effect.

In many instances, it is desirable to extract as much of the amorphous material from a soil sample as possible. Since the extraction procedures are usually specific to iron/aluminum or silicon/aluminum, as has already been discussed, combinations of treatments are commonly employed. When it is desirable to perform the minimum number of extractions to a sample, i.e., minimizing destruction of crystalline species, the order in which the procedures are performed becomes of some importance. The structural position or arrangement of the amorphous compounds, as well as the possible effects of one treatment on the material left in the soil by that treatment, requires some consideration. If, for example, silica forms a coating around the amorphous iron compounds, extraction of the silica will increase the extractability of the iron, but if the iron and silica are both equally exposed, then the alkali, the treatment normally used to remove silica, may cause partial crystallization of the amorphous iron compounds, thus de-

## TABLE 3.4

The Effect of chemical dissolution techniques on some crystalline and amorphous compounds.

| | CBD$^a$ | OXALATE$^b$ | PYRO-PHOSPHATE$^c$ | NaOH$^d$ | NaOH-CBD$^d$ | KOH-OXALATE$^e$ |
|---|---|---|---|---|---|---|
| CRYSTALLINE | | | | | | |
| Kaolinite | $1^b$ | $1^b$ | $1^c$ | $2^d$ | (2) | (1-2) |
| Illite | $1^b$ | $1^b$ | (1) | (1-2) | $2^e$ | (1-2) |
| Mica | | | | | $3^e$ | $2^e$ |
| Chlorite | (1-2) | (1) | (1) | (2) | $2^e$ | (1-2) |
| Montmorill. | $1^b$ | $1^b$ | $1^c$ | (1-2) | $2^e$ | (1-2) |
| Nontronite | $2^d$ | | (1) | | $4^e$ | $3^e$ |
| Magnetite | $2^b$ | $2^b$ | $1^c$ | (1) | (2) | (2) |
| Goethite | $3^b$ | $1^b$ | $1^c$ | (1) | (3) | (1) |
| Hematite | $3^b$ | $1^b$ | $1^c$ | (1) | (3) | (1) |
| Gibbsite | $1^b$ | $1^b$ | $1^c$ | $5^d$ | (5) | (5) |
| AMORPHOUS | | | | | | |
| Al-Silicate | $4^b$ | $5^b$ | | $5^d$ | (5) | (5) |
| Fe-Silicate | $5^b$ | $4^b$ | $1^c$ | | (5) | (5) |
| Fe Oxide Sol | $5^c$ | $5^b$ | $2^c$ | | (5) | (5) |
| Fe Oxide | $5^c$ | $5^b$ | $1^c$ | (1) | (5) | (5) |
| Allophane | $2^d$ | | (1) | $5^d$ | $5^e$ | $5^e$ |

**Effect on soil components:**

1 - Unaffected, less than 1% dissolved.
2 - 1-10% dissolved.
3 - 10-50% dissolved.
4 - 50-90% dissolved.
5 - More than 90% dissolved.

Parentheses indicate best estimate of effect by author.

**Legend:**

a) Mehra and Jackson, 1960.
b) McKeague and Day, 1966.
c) McKeague, Brydon and Miles, 1971.
d) Hashimoto and Jackson, 1960.
e) Dudas and Harward, 1971.

creasing their solubility. The following is a brief summary of the available literature on this aspect of dissolution of amorphous compounds.

Hashimoto and Jackson [1960] demonstrated that amorphous $Al_2O_3$, $SiO_2$ and aluminosilicates such as allophane were dissolved by 0.5 N NaOH followed by extraction with CBD. The authors indicated that the strong alkali removed alumina and silica, while the CBD removed primarily iron oxides and hydroxides but also alumina from the soil. The NaOH treatment does not extract iron from the soil sample due to the very low solubility at high pH. The dithionite treatment following the NaOH treatment is therefore necessary to prevent the deposition of the iron released from the alkali-soluble fraction. Weaver, Syers and Jackson [1968] developed a simple technique for the determination of silica in CBD extracts and indicate that considerable amounts of silica are released by this treatment, even after treatment with 0.5 N NaOH.

Follett <u>et al</u>. [1965b] used 5% $Na_2CO_3$ followed by the dithionite/acid treatment of Mitchell and Mackenzie [1954] to remove amorphous coatings from the crystalline minerals of two soil profiles, a podzol and a gley. More iron was released from the samples by the dithionite treatment if the samples were pretreated with alkali. The authors attributed this increase to two factors: 1) The increased dispersion that occurs with the $Na_2CO_3$ treatment, and 2) the close association of the iron oxides with the silica and alumina.

Wada and Greenland [1971] used chemical dissolution techniques, in conjunction with infrared analysis of the residue, in order to determine the effect of the treatments on the soil material. They did not follow the same sequence of treatments as Follett et al. [1965b]; the dithionite treatment (CBD [Mehra and Jackson 1960]) preceded the extraction with alkali. Both the 0.5 N NaOH treatment [Hashimoto and Jackson 1960] and the 2% $Na_2CO_3$ treatment [Jackson 1956, p. 72] were employed. It was found that the treatments effectively removed the amorphous material and no evidence of reprecipitated iron hydroxides was found. The treatment with $Na_2CO_3$ removed smaller amounts of well-ordered material than NaOH, while the latter was effective in extracting allophane and gibbsite.

Johnson and Ching-Hwan [1974] studied the effect of the order of treatments on the amount of material extracted from a number of soil profiles. Identical samples were treated; in one case the NaOH treatment [Hashimoto and Jackson 1960] preceded the extraction with CBD [Mehra and Jackson 1960], while in the other case the treatment sequence was reversed. Results showed that, in almost every case, the total amount of iron oxide, silica and alumina was greater when the CBD treatment was performed first. These results are directly opposite to the results of Follett et al. [1965b]. Johnson and Ching-Hwan proposed a number of reasons why the CBD extraction might remove more amorphous material if performed before the NaOH extraction: 1) CBD-soluble material was coating the alumina and silica, thus protecting it from attack by NaOH; 2) Iron atoms incorporated into the amorphous phase reduce the solubility of the silica and alumina; and 3) Treatment with boiling NaOH causes the order of amorphous iron oxides to increase, rendering them less soluble to CBD. The contradiction between the results of Follett et al. [1965b] and Johnson and Ching-Hwan [1974] can perhaps be explained by the differences in the extraction procedures used by the researchers. Follett et al. employed 5% $Na_2CO_3$ to remove the silica and alumina, and dithionite/acid (HCl) to remove iron compounds, while Johnson and Ching-Hwan used boiling 0.5 N NaOH and CBD. The other possibility is that the soil samples used by the different workers contained amorphous material in which the positional or structural relationship between the dithionite and alkali-soluble fractions was different.

Dudas and Harward [1971] performed sequential dissolution treatments on a number of standard and soil clays. The treatments used consisted of extraction with CBD [Mehra and Jackson 1960] followed by extraction with boiling 0.5 N base, then a second CBD and boiling base extraction, followed by a further CBD extraction. Duplicate treatments were performed using NaOH and KOH, so that the different effects of the two treatments could be assessed. The five extractions on each sample would result in greater destruction of the crystalline phase than the two or three treatments normally employed [Hashimoto and Jackson 1960]. The results of the study are a useful indication of the amount of damage that dissolution with hot base and CBD have on phyllosilicates. Nontronite, an iron-rich smectite species, was severely attacked by the extraction procedure, exhibiting a weight loss of 79% with NaOH and 60% with KOH. Biotite and interstratified vermiculite-mica samples showed weight losses of 13 and 7% respectively, as well as minor vermiculitization with NaOH, as a result of Na substitution in interlayer positions. Montmorillonite, chlorite, kaolinite and interstratified mica-chlorite did not appear to be appreciably affected by either of the dissolution treatments.

Chemical dissolution using 0.5 N NaOH and CBD is an effective means of removing amorphous compounds of Fe, Si and Al, as well as some forms of crystalline iron and aluminum oxides. The damage done to the phyllosilicate clay minerals depends on the mineralogy, but in general will be slight for most species. If the mineralogy is such that damage is likely to occur, then treatment by oxalate in conjunction with a hot base is probably a better procedure [Dudas and Harward 1971]. If the extended treatment of Dudas and Harward is to be avoided so that damage caused to the clay minerals is minimized, then it is important to know whether the sample is to be extracted with hot base or CBD first. If the CBD treatment is performed first, then iron oxyhydroxides released by NaOH are likely to be deposited on the surface of the soil minerals. To avoid this, a final CBD extraction is required. The decision as to the order of treatments can be made on the basis of the amount of iron extracted with and without prior extraction with NaOH, the procedure which results in the largest amount of iron in the CBD extract being the most effective.

## 3.8 Conclusions:

Chemical dissolution techniques are available which will extract the amorphous material from soil samples without doing extensive damage to crystalline clay minerals. Differentiation between different forms of amorphous and finely-crystalline minerals can be made, with an acceptable degree of error. Certain limitations are inherent in the procedures, particularly for soils containing very poorly crystalline or iron-rich phyllosilicates.

Further research into the structure and chemistry of the amorphous phase is necessary before chemical analysis of dissolution extracts can be used to quantitatively define the nature of the amorphous material. Differences in extraction techniques and the order of the treatments significantly change the chemistry of the extracts, casting great doubt on the validity of statements about the chemical composition of amorphous material based on such results.

# Chapter Four:

# PROCEDURES

## 4.1 Introduction.

For the purpose of the investigation, two samples containing a high proportion of clay-sized material were selected. The sample referred to as Queenston Shale Clay was chosen because of its strong red colour, inherent from the parent material from which it had weathered, which indicated that it contained an appreciable amount of ferric iron compounds. The other sample, referred to as Champlain Sea Clay, sampled from the Gatineau region, was expected to contain amorphous material on the basis of the study by McKyes, Sethi and Yong [1974]. A complete discussion of these samples will be presented in the appropriate chapters (Chapters 5 and 6 respectively) on the results of their treatments.

The procedures used throughout are standard techniques for soil analysis selected for their applicability to the experiment. This was done for a number of reasons: 1. in order that the results be more readily comparable to the results of previous researchers, 2. to avoid controversy regarding the effects of the treatments on the material, and 3. to allow other researchers to apply the techniques to their own research without becoming involved with long procedural investigations.

The experiment was conducted in two phases; the first involved the selection of techniques from those used in past research, and the testing of these techniques on small (usually 5 g) samples. Following these tests, each of the samples was examined to determine the effect of the extraction procedure on the mineralogy, and the extracts were analysed for chemical composition. The results of Phase I were used to choose the treatments to be used on the 200 g samples of Phase II. In this second phase, the treated samples and an untreated sample for each of the two clays were tested for their physical properties. These tests included the determination of the Atterberg limits, as well as other tests to assess the changes in the mineralogical and physical properties of the material. This chapter will outline the procedures used in both Phase I and Phase II of the experiments. The results of Phase I, on which the treatments used in Phase II were selected, are also presented here; the results of Phase II will be presented in Chapter 5 for the Queenston Shale Clay, and in Chapter 6 for the Champlain Sea Clay samples.

## 4.2 Collection and Preliminary Sample Preparation.

The material used in the experiments was sampled in the field and stored in air-tight containers for transportation to the laboratory. During the collection, transportation and preliminary preparation, the water content of the material was maintained at a level equalling or exceeding the minimum water content that the material could have attained in the field, thus preventing any irreversible dehydration of the suspected amorphous material.

Since Atterberg limits were to be determined on the samples, it was decided that the material greater than the 40 mesh sieve (420 microns), the maximum size of material used in the plasticity determinations [A.S.T.M.

1964], should be removed prior to the start of the actual experiment. The Queenston Shale Clay, which possessed some material greater than 420 microns in size, was diluted with deionized, distilled water and passed through the 40 mesh sieve as a slurry. The material was then dehydrated at 50°C with regular stirring, until the water content reached approximately 100 percent. The Champlain Sea Clay did not require sieving; the water content was raised to approximately 100 percent in order that the material could be homogenized. Both samples were mixed thoroughly and divided into sufficient 200 g samples for use in the subsequent tests. Each of these samples contained the equivalent of 200 g oven-dried soil, calculated on the basis of the water content at the time the homogenized samples were divided; the samples were never dried at any stage of the preparation, treatment or subsequent testing. These samples were stored in polyethelene containers at approximately 100 percent water content.

## 4.3 Phase I: Evaluation of Test Procedures on Small Samples.

In Phase I of the Experiment, the techniques used had to meet two basic requirements, in addition to being effective in removing the soil component they were designed to extract. These requirements were: 1. The sample had to remain flocculated at all times since the samples contained material too fine to sediment in reasonable time in the dispersed state, and 2. The volume of the extractant had to be such that when applied to the 200 g samples, the volume of the extractant would be manageable. As a result of the latter restriction, the procedures used were altered, wherever necessary, so that the extractions could be performed in four-litre pyrex beakers, or, in the case of the extraction with boiling base, in an eight-litre stainless steel beaker. This aspect will be discussed more fully in the description of the individual treatments which follows.

Phase I also included a series of treatments in which the order of the treatments was varied so that the treatment sequence effect could be assessed. The prime consideration in this regard was the order of treatments which would remove the largest amounts of material from the samples. The procedure used in this part of the experiment is discussed in Section 4.4c.

### 4.3a Extraction of Soluble Salts.

Soluble salts were extracted from the samples by the same procedure as is used to remove excess salts following homoionization procedures for X-ray analysis [Whittig 1965]. This procedure involves one washing with 50 percent methanol, one washing with 95 percent methanol, and two washings with 95 percent acetone. (A detailed outline of all of the extraction procedures used in this experiment is contained in the Appendix.) The procedure has the advantages of: 1. preventing deflocculation of the sample during the treatment, and 2. preventing possible hydrolysis and alumination of the soil components which might result from attempting to wash samples with distilled water.

### 4.3b Homoionization: NaCl.

Since the plasticity of clays is, in part, dependent on the cation adsorbed on the exchange complex, each sample was homoionized following each extraction. Sodium chloride was selected as the standard for homoionization since most of the extraction procedures employed reagents containing sodium, and thus the number of salt washings necessary to achieve homoionization could be reduced. As a basis for all of the determinations of physical properties, including the determination of plasticity, one sample of each of the two clays was homoionized with NaCl, without any prior treatment. The procedure adopted is similar to the standard homoionization procedures for soils [Whittig 1965]. The only difference was that only three NaCl washings were employed. Although three washings do not ensure complete homoionization, the number of washings was limited to decrease the risk of alteration to the clay minerals in the samples. The excess salt was washed from the samples as in Section 4.3a.

### 4.3c Extraction of Carbonate Material: Sodium Acetate Buffer Solution (SAB).

Preliminary analysis indicated that both of the samples contained some form of carbonate material, therefore it was deemed necessary to include in the extraction sequence a treatment for the removal of carbonates. Two procedures are commonly used for the extraction of carbonates from soil samples as part of a pretreatment procedure. These treatments are: 1. hydrochloric acid (2 N HCl) [Piper 1942], and 2. sodium acetate buffered at pH 5.0 [Brewer 1964]. Due to the suspected presence of amorphous iron compounds in the samples, the use of HCl was avoided, since amorphous iron is highly soluble in this medium.

The procedure adopted for the experiment is from Jackson [1958], as modified by Brewer [1964]. The samples were extracted twice with the sodium acetate buffer solution, once on a near-boiling water bath (90-95$^{o}$C) and once at room temperature. Following these extractions, the samples were homoionized with NaCl (Section 4.3b) and the excess salt removed (Section 4.3a) as has been outlined previously.

### 4.3d Extraction of Organic Matter.

Two methods for the extraction of organic matter were tested in Phase I of this experiment. The first method, as outlined below, is the method of Hutton [1950] employing hydrogen peroxide as the oxidizing agent, while the second is the procedure of Anderson [1963], as modified by Brewer [1964], employing sodium hypochlorite at pH 9.5 as the oxidizing agent. Both of these procedures were tested, for two reasons: 1. Both techniques have their disadvantages, the first because of the effect of the hydrogen peroxide separating the clay-mineral flakes, and the second because the high pH is likely to cause significant dissolution of silica from the samples; and 2. An effective treatment for the removal of organic matter is often necessary for the preparation of reproducible X-ray diffraction slides.

#### (i) Hydrogen Peroxide.

The hydrogen peroxide treatment employed was taken from Kunze [1965]. The only adaptation necessary was the increase in the amounts of hydrogen peroxide used; the ratio of hydrogen peroxide to the soil was not altered. This treatment is known to cause the formation of insoluble metallic oxalates if there is carbonate or other easily soluble material present in the soil [Farmer and Mitchell 1963]. For this reason, the samples were treated with the sodium acetate buffer solution as outlined in Section 4.3c prior to the peroxide treatment. Following the oxidation of the organic matter, the samples were homoionized and washed free of excess salt.

(ii) Sodium Hypochlorite.

The sodium hypochlorite treatment as adapted by Brewer [1964] consists of three treatments, each comprising a 30-minute extraction with sodium hypochlorite in a boiling water bath, followed by three washings with 1 N NaCl. The advantage of this procedure is that the samples do not need to be treated to remove the carbonates prior to the oxidation of organic matter. Following the hypochlorite treatment, the material was homoionized and washed free of excess salt.

### 4.3e Extraction of Iron and Aluminum Compounds: CBD Treatment.

Several techniques are available for the extraction of iron and aluminum compounds from soils as reviewed in Chapter 3. Of these techniques, the sodium citrate-bicarbonate-dithionite (CBD) procedure of Mehra and Jackson [1960] is probably the most widely applied. This procedure does not seriously alter any of the well-crystallized clay minerals found in weathered soils, with the possible exception of nontronite, an iron-rich variety of montmorillonite. In addition, it extracts iron from crystalline oxides and hydroxides in soils, since the size of these particles in soils is usually quite small. Amorphous oxides, hydroxides and silicates of iron and aluminum are also extracted. This treatment was selected because the Queenston Shale Clay, with its red stain, contained the crystalline iron compound hematite, identified on a random XRD trace (in Chapter 5). The soil:extractant ratio was within the limits as stated by Mehra and Jackson.

The CBD treatment was employed in two separate parts of Phase I. One aspect was the production of a treatment-dissolution curve, by extracting one sample eight times in succession, while the other aspect was the study of the treatment sequence effect, as outlined in more detail in Sections 4.4b and 4.4c respectively.

### 4.3f Extraction of Silicon and Aluminum Compounds: NaOH.

The final treatment tested in Phase I was the boiling NaOH extraction procedure of Hashimoto and Jackson [1960]. In order that this procedure be used, the ratio of alkali:soil had to be altered significantly. As employed by Hashimoto and Jackson, the procedure specified that 100 mg of clay be extracted with 100 ml of alkali. In order to extract the required 200 g samples at this alkali:soil ratio, 200 litres of extractant would be required. Fortunately the saturation levels for Al and Si in the base had been determined as being on the order of 600 ppm, thus one of the aims of Phase I, in regard to the alkali extraction, was to determine whether the saturation levels would be reached when the alkali:soil ratio was altered to an acceptable figure.

## 4.4 Results of Phase I.

Chemical analysis of the treatment extracts was performed using atomic absorption spectroscopy (AAS) on Jarrell-Ash, Dual Atom equipment for Ca, Mg, Na, K and Mn. Fe and Al were also determined by AAS; interference was suppressed by the addition of 2000 ppm Na to those samples and standards which did not already contain Na equal to or exceeding this level, according to the procedure of Webber et al. [1974]. Si was determined colorimetrically by the molybdate blue method of Weaver, Syers and Jackson [1968].

X-ray diffraction analysis (XRD) was performed following the procedures of Whittig [1965] on oriented aggregate slides prepared by placing 2 ml of 2% clay suspension on a 34 X 37 mm glass slide and allowing it to evaporate at room temperature. Random powder samples were prepared by sifting air-dried samples through a 70 micron sieve onto a glass slide coated with a thin film of vaseline. The slides were analysed on a Siemens Kristalloflex II diffractometer employing Ni-filtered Cu Kα radiation generated at 30 kV, 20 mA with slit widths of 0.6 and 0.4 mm.

The oriented samples were analysed under the following conditions: Mg-saturated in the air-dried and ethylene-glycol-saturated states; and K-saturated at room temperature and after heating to 300°C and 550°C. The addition of the 300°C heating stage, not included in the procedure of Whittig, is to ensure the collapse of the vermiculite [Raman and Ghosh 1974], while the heat treatment to 550°C [Raman and Ghosh 1974] rather than 500°C [Whittig 1965] was employed to ensure that the kaolinite, if present, was destroyed. In order to determine whether either of the clay samples contained kaolinite, the samples were heated for 1 hour in 1 N HCl. This treatment destroys chlorite, but does not affect the kaolinite, thus positive identification of chlorite is possible [Raman and Ghosh 1974].

### 4.4a Preliminary Treatments.

The results on the chemistry of the extracts of the treatments to remove soluble salts, to homoionize the sample and to extract carbonates and organic matter are presented in Table 4.1.

The soluble salts extracted from the two clay samples were predominantly Na and Ca for the Queenston Shale Clay and Na for the Champlain Sea Clay. The large amount of Ca which was removed from the Queenston Shale Clay by the homoionization procedure is partially the result of the replacement of Ca by Na on the exchange complex and may be partially due to dissolution of a portion of the carbonate material. The Champlain Sea Clay, on the other hand, released primarily Ca, with smaller amounts of Mg and K, during homoionization, which is due in part to the marine origin of this clay, and perhaps in part to _in situ_ weathering of primary minerals and carbonates.

The extraction of carbonate material resulted in relatively uniform amounts of Ca, Mg and Fe for the Champlain Sea Clay, indicating that there is present in the sample crystalline or amorphous carbonate compounds of these metallic cations. The Queenston Shale Clay, on the other hand, released primarily Ca, indicating the dominance of calcium carbonate in this sample. X-ray diffraction analysis (XRD) did not indicate the presence of crystalline carbonate compounds in either of the clay samples, although calcite was identified by XRD in a shale fragment of the Queenston Shale Clay removed by sieving during the initial preparation of the material.

Inorganic C was determined on the samples by the method of Bundy and Bremner [1972] before and after extraction with the sodium acetate buffer solution, which indicated that prior to treatment the samples contained 11.2

## TABLE 4.1

Results of Treatments on 5 g Samples.
(Data expressed in mg/g air-dried sample)

| | Ca | Mg | K | Na | Fe | Mn | Si |
|---|---|---|---|---|---|---|---|
| Queenston Shale Clay Treatment | | | | | | | |
| Removal of Soluble Salts | .12 | .005 | .01 | .14 | .04 | 0 | .01 |
| Homoionization | 4.3 | .10 | .42 | - | .10 | 0 | .02 |
| SAB | 33.6 | .57 | .84 | - | .36 | .78 | .17 |
| SAB + Hydrogen Peroxide | 31.2 | .39 | .68 | - | .31 | .68 | .17 |
| Sodium Hypochlorite | .57 | .05 | .76 | - | .29 | .10 | .07 |
| Champlain Sea Clay Treatment | | | | | | | |
| Removal of Soluble Salts | .06 | .05 | .02 | .10 | .06 | 0 | .02 |
| Homoionization | 2.4 | 1.10 | 1.0 | - | .10 | 0 | .05 |
| SAB | 3.3 | 2.25 | 1.1 | - | 1.85 | .14 | .34 |
| SAB + Hydrogen Peroxide | 3.1 | 2.12 | 1.5 | - | 1.45 | .14 | .33 |
| Sodium Hypochlorite | .60 | .39 | 1.8 | - | .20 | 0 | .13 |
| Analytical Error | ±10% | ±5% | ±10% | ±5% | ±5% | ±5% | ±5% |

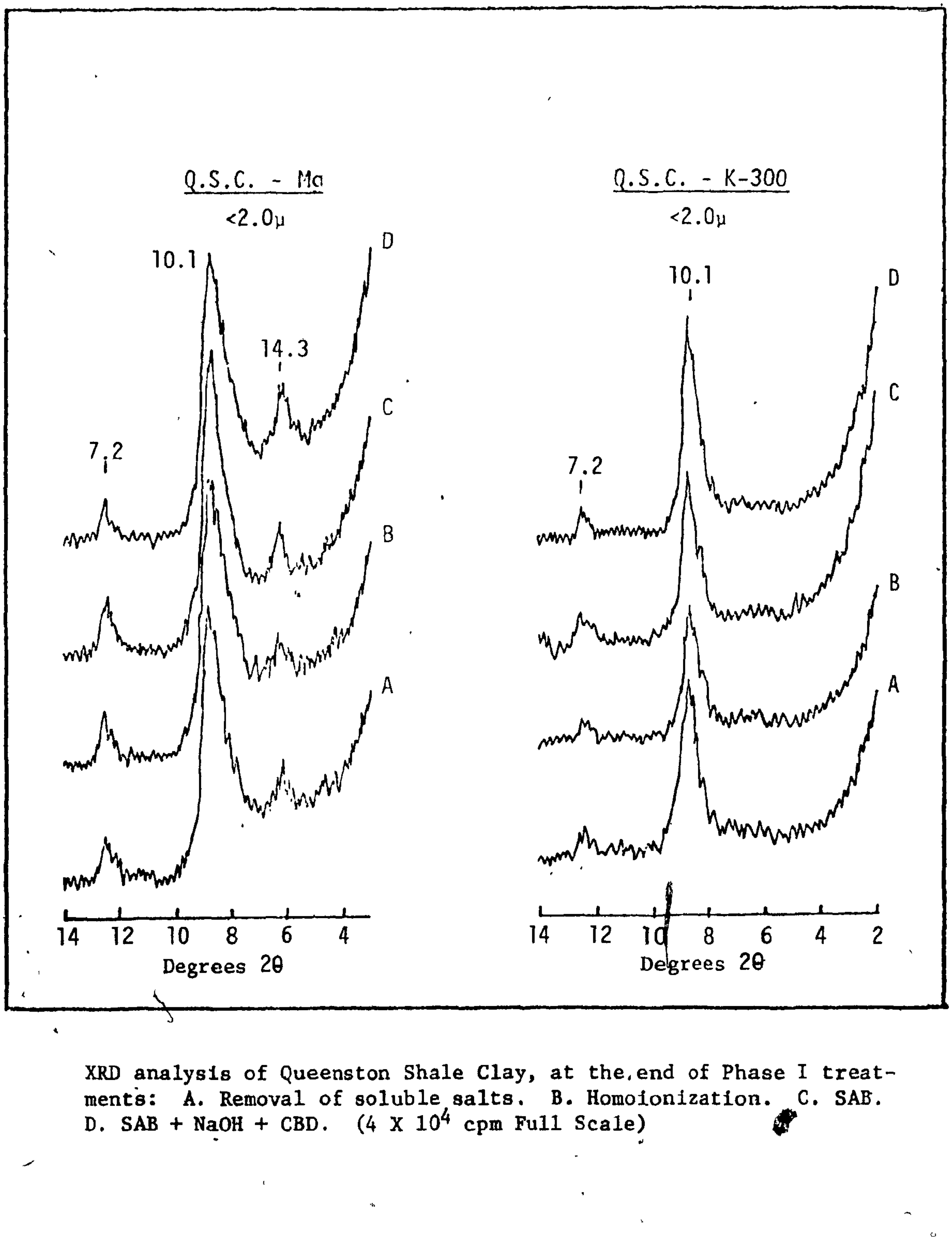
and .84 mg/g (inorganic C) for the Queenston Shale Clay and the Champlain Sea Clay respectively; the corresponding values following the extraction were .05 and .1 mg/g. The data for the samples treated sequentially to remove the carbonate and organic matter (using hydrogen peroxide) resulted in a significant drop (compared to the sole SAB treatment) in the amounts of Ca, Mg and Fe extracted from both of the samples. Although the procedure described by Brewer [1964] (which involved one washing with cold sodium acetate buffer solution and one washing with NaCl, following the initial treatment to dissolve the carbonates, and prior to the oxidation with hydrogen peroxide) was followed, the data indicate that insoluble metallic oxalates were formed in the sample. These data confirm the work of Farmer and Mitchell [1963] which indicated this disadvantage of using the technique. The data on the material removed by the sodium hypochlorite treatment are also confusing; for both samples, less Ca and Mg were removed by this treatment than by the homoionization procedure, thus indicating the formation of some insoluble compound containing these cations. The explanation for this has not been mentioned in the literature and no satisfactory explanation can be given here. For this reason, and because of the small amounts of organic C determined in the clays by the procedure of Tinsley [1950] (.006 mg/g for the QSC and .038 mg/g for the CSC), it was decided to eliminate treatment to remove organic matter from subsequent experiments.

XRD analysis of the treated samples of Phase I was performed to determine the effect of the treatments on the mineralogy of the clay-size fraction. In order to identify the changes in physical properties associated with removal of amorphous constituents, an important aspect of Phase I was to select treatments which would cause a minimum of alteration to the crystalline clay minerals. Low-angle XRD traces of the treated samples in the Mg-saturated (air-dried) and K-saturated (heated to 300$^{o}$C) states are included here (Figure 4.1 for the QSC and Figure 4.2 for the CSC). A more complete discussion of the mineralogy and a complete set of XRD traces are presented in Chapters 5 and 6.

The Queenston Shale Clay possesses an abundant 10.1 Angstrom mineral, as indicated in both traces of Figure 4.1; the 14.3 Angstrom peak on the Mg-saturated, air-dried trace virtually disappears in the K-saturated, 300$^{o}$C trace, in favour of the 10.1 Angstrom peak, indicating the presence of vermiculite. Although the 14.3 Angstrom peak virtually disappears on the K-saturated, 300$^{o}$C trace, the 7.2 Angstrom peak in both traces is interpreted as the second-order peak of chlorite, rather than a kaolinite peak, as evidenced by the elimination of this peak following a 1-hour treatment in hot 1 N HCl [Raman and Ghosh 1974]. The removal of soluble salts, the homoionization procedure and the SAB treatment (Traces A, B, and C of Figure 4.1) produce no significant alteration to the mineralogy. Variations in peak height, from one trace to another, are not positive identification of variations in mineralogy, since the slides were prepared without removal of organic matter which resulted in moderate variation in the surface smoothness of the slides.

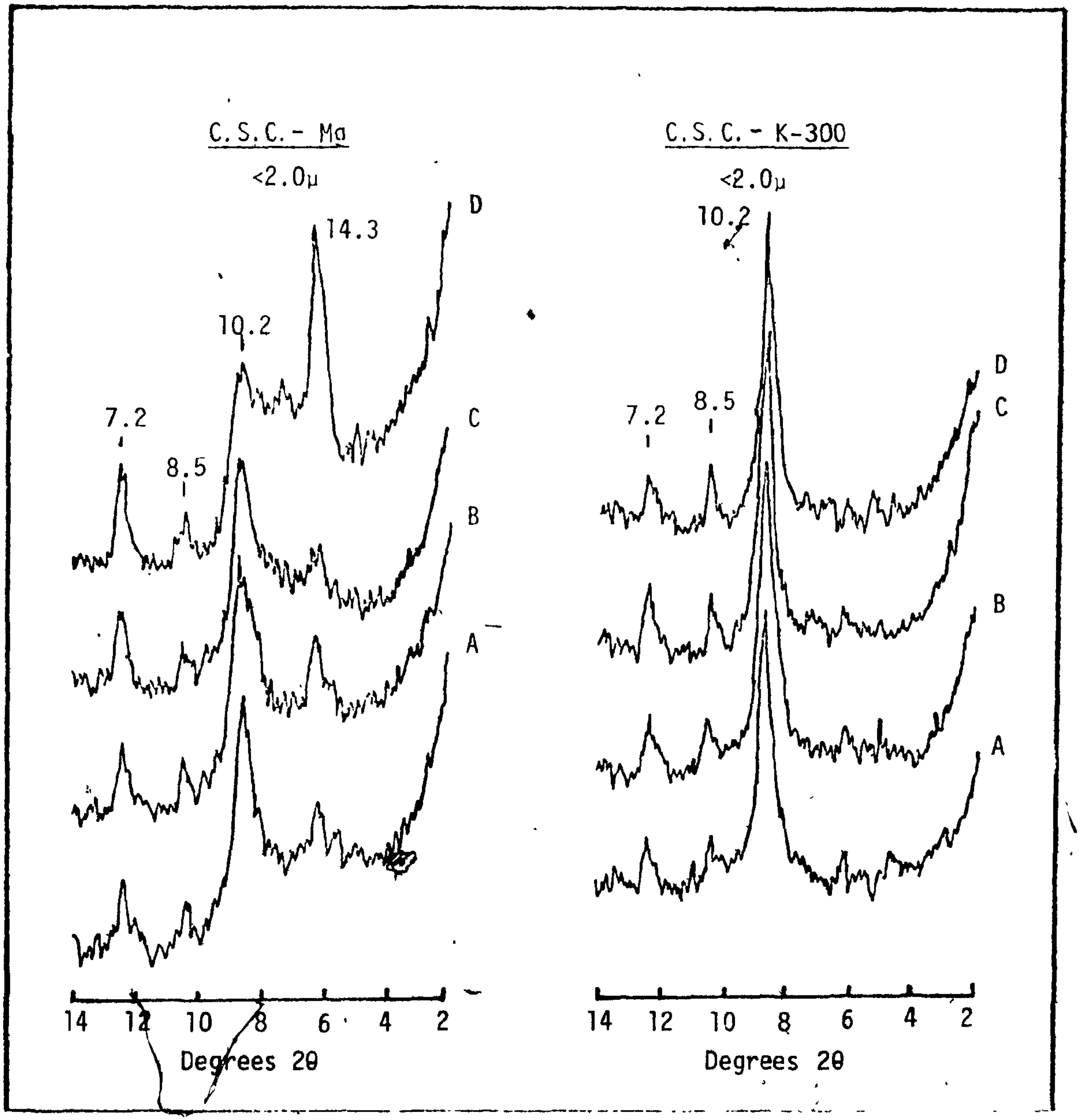
The diffractograms for the Champlain Sea Clay (Figure 4.2) indicate the presence of a 10.2 Angstrom mineral, and a 14.3 Angstrom mineral which collapses to 10.2 Angstrom on K-saturation and heating to 300$^{o}$C. As with the 14.3 Angstrom peak of the Queenston Shale Clay, the persistence of the 7.2

FIGURE 4.1



XRD analysis of Queenston Shale Clay, at the end of Phase I treatments: A. Removal of soluble salts. B. Homoionization. C. SAB. D. SAB + NaOH + CBD. (4 X $10^4$ cpm Full Scale)

FIGURE 4.2



XRD analysis of Champlain Sea Clay, at the end of Phase I treatments: A. Removal of soluble salts. B. Homoionization. C. SAB. D. SAB + NaOH + CBD. (2 X $10^4$ cpm Full Scale)

Angstrom peak on the K-saturated, 300°C trace indicates the presence of chlorite, not kaolinite. The 8.5 Angstrom peak, which does not change, is identified as amphibole. The mineralogy is not changed significantly by the first three treatments, as is indicated by Traces A, B and C on Figure 4.2.

### 4.4b Eight CBD Extractions.

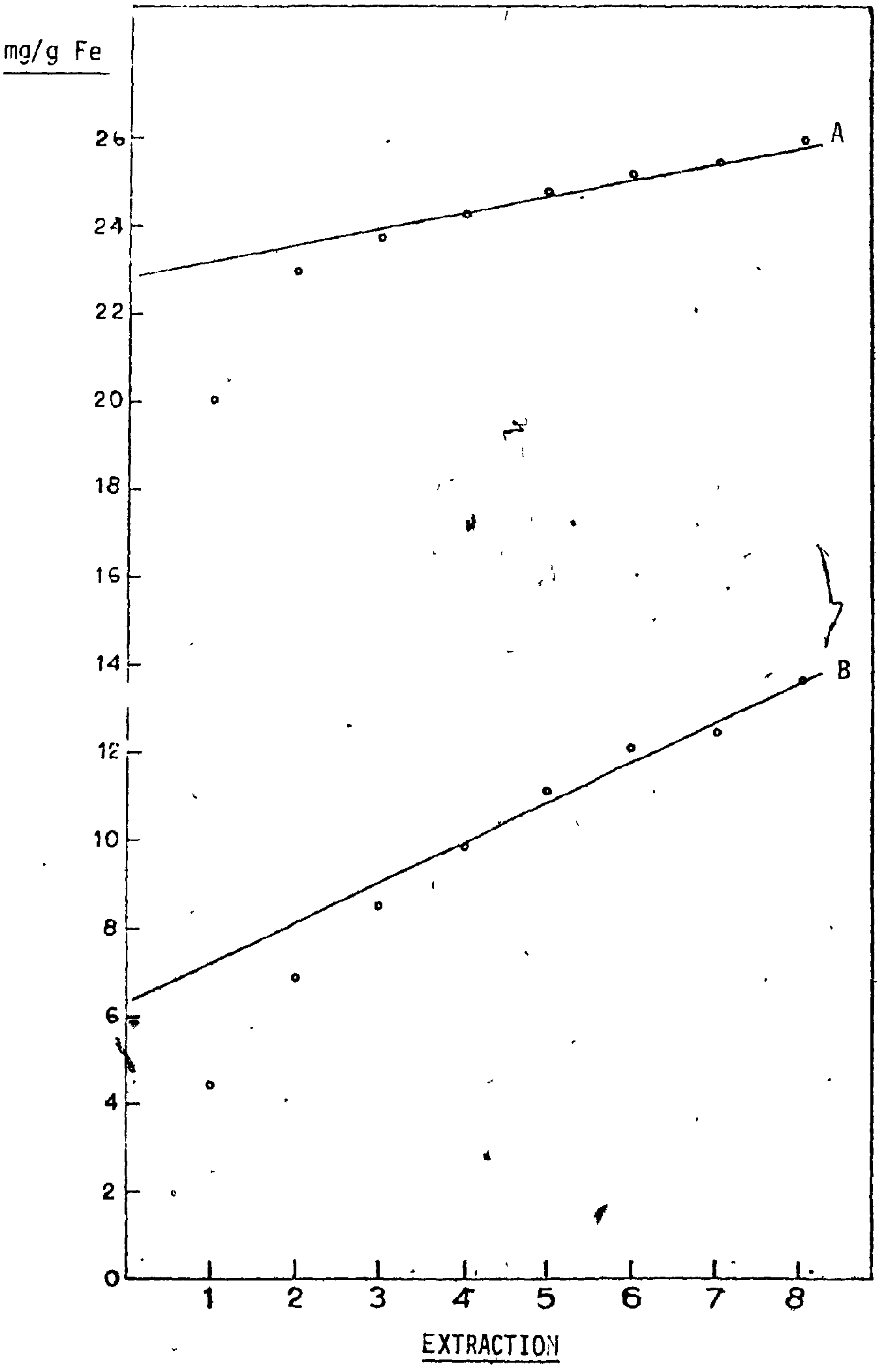
The chemical analyses of eight CBD treatment extracts are given in Table 4.2. In addition, Figure 4.3 shows the relationship between the number of treatments and the cumulative amount of iron removed. The rate at which different cations were removed varies considerably for the two clay sediments. Examining the results for the Queenston Shale Clay first, it is apparent that the calcium carbonate is not destroyed by the CBD treatment until six or seven extractions have been performed, at which time the amount of Ca in the extract drops significantly; the amounts of Mg, Mn and Si in the extracts decrease as the number of treatments increases; K is removed rapidly during the first two extractions and then reaches a low but uniform value; Fe, on the other hand, is extracted very strongly by the initial treatment and then reaches a low but uniform value for the last four extractions. This last aspect indicates that the iron in the sample is either amorphous or very poorly crystalline, or, alternatively, is composed of extremely fine crystalline particles which dissolve readily in the first CBD extractions. This conclusion is supported by the identification of hematite in the random powder XRD traces presented and discussed in Section 5.2a. The amount of iron released appears to be independent of the amounts of Si removed from clay, supporting the conclusion that the iron compounds are predominantly iron oxides or hydroxides, rather than amorphous or crystalline iron silicates.

## TABLE 4.2

Chemical Analysis of Eight CBD Extracts.
(Data expressed as mg/g of air-dried sample)

| | | Ca | Mg | K | Fe | Mn | Si |
|---|---|---|---|---|---|---|---|
| Queenston Shale Clay | | | | | | | |
| Extraction: | 1 | 5.34 | .12 | .36 | 12.14 | .50 | .37 |
| | 2 | 7.70 | .15 | .18 | 1.82 | .21 | .24 |
| | 3 | 4.67 | .11 | .12 | .42 | .14 | .21 |
| | 4 | 3.52 | .09 | .12 | .42 | .08 | .30 |
| | 5 | 3.03 | .09 | .12 | .24 | .07 | .27 |
| | 6 | 1.52 | .09 | .12 | .24 | .07 | .27 |
| | 7 | .18 | .04 | .12 | .24 | .05 | .18 |
| | 8 | 0 | .03 | .12 | .24 | .02 | .15 |
| Champlain Sea Clay | | | | | | | |
| Extraction: | 1 | .80 | 1.35 | .85 | 2.19 | .09 | .65 |
| | 2 | .02 | .30 | .55 | 1.25 | .03 | .67 |
| | 3 | .01 | .20 | .85 | .80 | .01 | .60 |
| | 4 | 0 | .16 | .90 | .65 | .01 | .65 |
| | 5 | 0 | .16 | .85 | .65 | 0 | .72 |
| | 6 | 0 | .14 | .85 | .50 | 0 | .65 |
| | 7 | 0 | .08 | .85 | .10 | 0 | .40 |
| | 8 | 0 | .10 | .85 | .50 | 0 | .55 |
| Analytical Error | | ±10% | ±5% | ±10% | ±5% | ±5% | ±5% |

FIGURE 4.3



Cumulative extraction curve of iron for eight CBD extractions:
A. Queenston Shale Clay, B. Champlain Sea Clay.

The Champlain Sea Clay sample exhibited significantly different response to the extraction procedure (Table 4.2, Figure 4.3). The amounts of Ca and Mn dropped off to zero after three and four extractions respectively, whereas the K and Si levels remained relatively constant throughout the eight extractions. The initial extraction of iron from the Champlain Sea Clay was appreciably less than that extracted from the Queenston Shale Clay sample. The amount extracted decreased gradually during the first four extractions, and thereafter varied in a manner corresponding to the increases and decreases of the Si, as do the amounts of Mg. In addition, in the later extractions, the amount of iron released was approximately twice that of the Queenston Shale Clay, indicating that there probably exists an iron-rich silicate, such as biotite, which is being both dissolved and degraded, as indicated by the high but uniform amounts of K in the extracts (seven times the amount extracted from Queenston Shale Clay).

For both clay samples, two CBD extractions appear to be effective in removing the readily soluble portion of the iron compounds present in the sample. Since the eight extractions employed in this portion of the study are greatly in excess of the number to be used on the 200 g samples, the residue was not analysed by XRD.

### 4.4c Treatment Sequence Effect.

Initial experiments substantiated the findings of Follett et al. [1965b] that iron extraction was increased if the alkali treatment preceded the CBD treatment (Table 4.3). Subsequent publication by Johnson and Ching-Hwan [1974], after completion of Phase I of the present work, indicated that the total amount of amorphous iron, aluminum and silicon compounds is increased further if the alkali extraction followed the CBD extraction. The present study has no data on the amounts of Si, Al and Fe extracted by CBD then NaOH procedure, but the data contained in Table 4.3, which indicate that more iron is extracted after the NaOH treatment, plus the data of Table 4.4, and subsequent data in Phase II which indicate that iron is virtually insoluble in the NaOH treatment, suggest that their findings are inapplicable with regard to these clay sediments.

### TABLE 4.3

The amount of iron in CBD extracts of carbonate-free samples with and without prior NaOH treatment.
(Data expressed as mg/g air-dried soil)

| TREATMENT | QSC | CSC |
|---|---|---|
| SAB and CBD | 14.2 | 4.6 |
| SAB and NaOH and CBD | 17.6 | 7.7 |

Analytical error = ±5%

The experiments summarized in Table 4.4, undertaken to discover the optimum position of the SAB extraction in the sequence, were tested by extractions in the following orders: A) SAB, NaOH, CBD; B) NaOH, CBD, SAB; and C) NaOH, SAB, CBD. The results, presented in Table 4.4, indicate that Sequence A is the best in terms of its ability ~~to extract~~ iron with the least amount of silica. The data indicate that treatment Sequence B extracts less K from the sample, and therefore is presumably less destructive of the illitic or micaceous material in the Champlain Sea Clay sample. Examination of Mg-saturated

## TABLE 4.4

Results of investigation of treatment sequence effect.
(Data expressed as cumulative amount extracted in mg/g air-dried soil.)

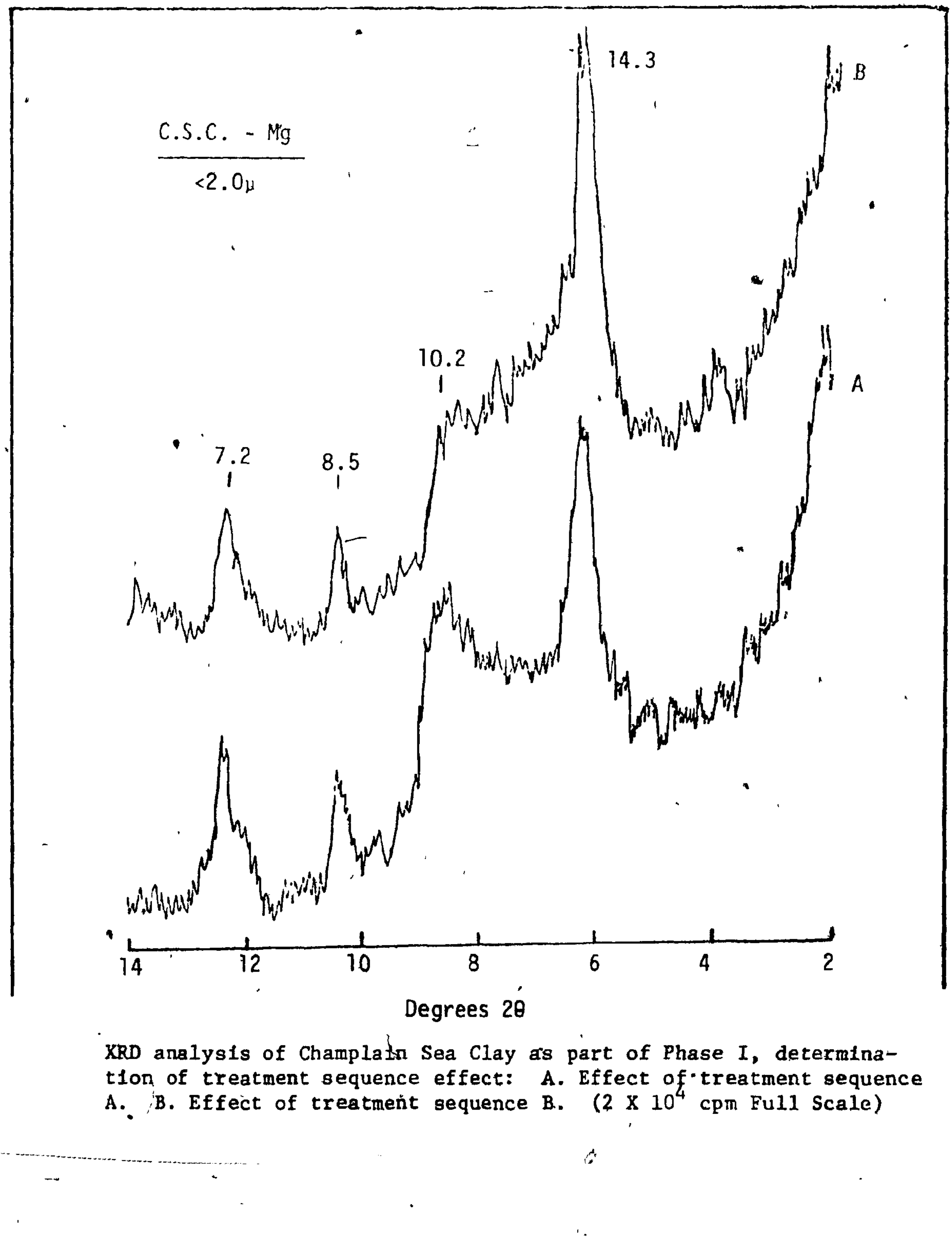
| | | Ca | Mg | K | Fe | Si | Al |
|---|---|---|---|---|---|---|---|
| QUEENSTON SHALE CLAY | | | | | | | |
| Treatment | | | | | | | |
| A | SAB | 27.0 | .42 | .5 | .1 | .11 | .8 |
| | SAB + NaOH | 27.0 | .42 | .8 | .35 | 2.7 | 2.2 |
| | SAB + NaOH +CBD | 27.2 | .51 | 1.1 | 18.0 | 3.4 | 2.8 |
| B | NaOH | 0 | 0 | .5 | .2 | 1.7 | 1.4 |
| | NaOH + CBD | 19.5 | .24 | .9 | 14.4 | 5.1 | 1.9 |
| | NaOH + CBD + SAB | 31.5 | .47 | 1.3 | 14.7 | 5.2 | 2.4 |
| C | NaOH | 0 | 0 | .50 | .2 | 1.6 | 1.2 |
| | NaOH + SAB | 27.0 | .48 | .80 | .45 | 1.8 | 1.3 |
| | NaOH + SAB + NaOH | 27.6 | .56 | 1.1 | 17.0 | 5.4 | 2.4 |
| CHAMPLAIN SEA CLAY | | | | | | | |
| Treatment | | | | | | | |
| A | SAB | 2.8 | .86 | 2.1 | .3 | .25 | 1.4 |
| | SAB + NaOH | 2.8 | .86 | 3.1 | .6 | 5.3 | 4.0 |
| | SAB + NaOH + CBD | 2.8 | .35 | 4.3 | 8.3 | 10.5 | 5.5 |
| B | NaOH | 0 | 0 | 1.2 | .2 | 5.7 | 2.5 |
| | NaOH + CBD | .6 | .84 | 2.6 | 7.2 | 11.3 | 4.3 |
| | NaOH + CBD + SAB | 2.5 | 1.3 | 2.9 | 7.7 | 11.6 | 4.6 |
| C | NaOH | 0 | 0 | 1.2 | .2 | 5.8 | 3.2 |
| | NaOH + SAB | 1.4 | .86 | 3.2 | .7 | 6.1 | 3.5 |
| | NaOH + SAB + CBD | 1.4 | 1.3 | 4.5 | 8.4 | 12.7 | 5.6 |
| Analytical Error | | ±10% | ±5% | ±10% | ±5% | ±5% | ±10% |

samples of this clay sediment using XRD indicate that in fact Sequence B produced a larger degradation of the 10 Angstrom mineral than did Sequence A, despite the greater amount of K extracted by the latter (Figure 4.4).

The amounts of Si and Al in the extracts from the 0.5 N NaOH treatment were less than 300 ppm for Si and less than 200 ppm for Al; thus the extractants removed only about half of the saturation capacity of the extractant. Therefore the soil:extractant ratio employed in Phase I could be applied to Phase II of the study.

XRD traces D in Figures 4.1 and 4.2 refer to the residue at the end of the Sequence A extraction. Examination of the Mg-saturated air-dried XRD trace for the Queenston Shale Clay (Figure 4.1), which had undergone SAB, NaOH, and CBD extractions, reveals a slight increase in the 14.3 Angstrom peak at the expense of the 10.1 Angstrom peak, indicating that slight degradation or vermiculization of the sample has occurred, as a result of the removal of interlayer K from the 10.1 Angstrom mineral. The asymmetry of the 10.1 Angstrom peak, tailing off in the direction of low 2θ angles, indicates that the vermiculization is a result of random interstratification of the illite/vermiculite material, rather than the production of a separate vermiculite phase. For the Champlain Sea Clay, this degradation is quite severe (Trace D, Figure 4.2), in keeping with the large value of K removal from the sample by the extraction procedure (Table 4.4). It has been shown that the ease with which interlayer K can be extracted is a function of the mineralogy of the micaceous material [Rousseau et al. 1972 and 1973]. The much greater degradation of the 10.2 Angstrom mineral in the Champlain Sea Clay favours

FIGURE 4.4



XRD analysis of Champlain Sea Clay as part of Phase I, determination of treatment sequence effect: A. Effect of treatment sequence A. B. Effect of treatment sequence B. (2 X $10^4$ cpm Full Scale) the interpretation that this mineral is a trioctahedral mica such as biotite, rather than a dioctahedral soil illite. To avoid this alteration in mineralogy, an additional treatment was performed on a 200 g sample of the Champlain Sea Clay, employing KOH in place of the NaOH, and acid ammonium oxalate in place of the CBD [Dudas and Harward 1971]. This latter treatment, with the substitution of potassium and ammonium cations in place of sodium for the latter part of the extraction procedure, prevents the replacement of interlayer K, and thus prevents the extreme vermiculization of the 10 Angstrom mineral. Chemical and XRD data for this treatment are presented in Chapter 6.

## 4.5 Phase II: Procedures Employed with 200 g Samples.

Based on the chemical analyses and X-ray diffraction analyses of Phase I, the following 200 g samples of each of the two clays were prepared for plasticity analysis: 1. untreated; 2. soluble salts extracted with sequential washings in 50% methanol, 95% methanol, 95% acetone, 95% acetone; 3. homoionized with NaCl; 4. carbonate material extracted with sodium acetate buffer solution (SAB); 5. alkali-soluble material, amorphous silica and aluminum compounds following extraction of carbonate material (SAB + NaOH); 6. iron and aluminum compounds extracted with two treatments of the sodium citrate-bicarbonate-dithionite reagent following extraction of carbonates and alkali-soluble material (SAB + NaOH + CBD). In addition a sample of the Champlain Sea Clay was prepared by the following procedure: 7. iron and aluminum compounds extracted with acid ammonium oxalate, following the extraction of the carbonates with SAB and the extraction of alkali-soluble silica and aluminum compounds using KOH in place of the NaOH (SAB + KOH + Oxalate). A complete outline of the laboratory extraction techniques is contained in the Appendix.

Chemical analysis was performed on the extracts from each of the treatments according to the procedures outlined in Section 4.4, with the replacement of the determination of Al colorimetrically by the xylenol orange procedure of Hesse [1971], since the chart recorder necessary for the analysis of Al using AAS was no longer available. Both techniques gave the same results, although the sensitivity of the colorimetric technique was higher.

Variations in the measurement of the amounts of material removed in Phase I as opposed to Phase II may have arisen for two reasons: 1. the 200 g samples were treated, and the suspended sediment allowed to settle for 48 hours prior to decantation, while the small samples of Phase I were centrifuged immediately, and decanted, and 2. the analyses of the extracts for the small samples were combined prior to the analytical determination, while the 200 g extracts were analysed individually. Therefore, the chemical analyses for the Phase II extracts are more precise, whereas the possible reprecipitation of the material solubilized by the extraction is more likely to have occurred with these larger samples. On the other hand, the longer treatment times with the 200 g samples may have increased the amount of material brought into solution.

X-ray analysis was performed on oriented aggregate slides of the 2.0-0.2 micron and <0.2 micron fractions separated by centrifuge sedimentation, in the Na-saturated air-dried and Na-saturated glycolated states. The decision to analyse the clay in the sodium-saturated state was made so that the behaviour of the clay, in the same state as during the Atterberg limit determinations, could be assessed.

The plasticity measurements were made according to the procedures set forth by the A.S.T.M. [1964]: plastic limit and plasticity index of soils (D 424-59) and liquid limit of soils (D 423-61T); three determinations were made of the plastic limit, and five values of water content at between 15 and 50 blows of the liquid limit device were used in the construction of the flow-curve to determine the liquid limit.

Particle size analysis was performed on the material smaller than 63 microns according to the procedure of Folk [1968], using sodium metaphasphate as a dispersant in a concentration of 2 g/l and 4 g/l for the Queenston Shale Clay and the Champlain Sea Clay samples respectively. The sedimentation times were calculated according to the procedure of Tanner and Jackson [1947], in order to determine the equivalent spherical diameter of the particles by Stokes law.

Specific surface area was determined by equilibrating air-dried samples over ethylene-glycol-saturated calcium chloride, according to the procedure of Mortland and Kemper [1965].

Cation exchange capacity (CEC) was determined by saturating the cation exchange sites with Na using sodium acetate buffered at pH 8.2 and then, following washing with ethanol to remove excess salt, exchanging the Na with $NH_4$

(ammonium acetate pH 7.0) according to the procedure of Hesse [1971]. The sodium content of the extracts was determined by AAS.

The pH of the soil was measured to 0.1 pH unit on a soil-water paste at twice the content at the liquid limit, using a Fisher Accumet pH meter.

# Chapter Five:

# QUEENSTON SHALE CLAY

## 5.1 Origin of Queenston Shale Clay.

The material from which the Queenston Shale Clay sample is derived was originally deposited in alluvial fans or deltas, as a result of outwash from highlands in the Appalachian geosyncline to the east during the late Ordevician approximately 450 million years ago. At this time the mineralogy of the material resembled a mixture of the sedimentary, metamorphic and igneous rocks of the Appalachian mountain system. According to Bradly and Dean [1966] the quartz and feldspars found in the coarse fraction of the Queenston Shale are a remnant of the primary mineralogy of this detrital material.

At the time of deposition this material underwent weathering, which probably resembled alteration processes described by Walker [1967] in red desert sediments. Walker studied red beds associated with bedded evaporite deposits, and red muds of intertidal and shallow subtidal origin in which the detrital grains are stained red due to the in situ alteration of iron-bearing detrital material, particularly the iron silicates hornblende and biotite. In an oxidized leaching environment, silica will be preferentially removed as the weathering of ferromagnesian minerals progresses, since the solubility of Si is much greater than ferric iron under these conditions. The accumulated iron causes the red stain apparent in red desert soils and sediment similar to the Queenston Shale. The crystallization of hematite in these conditions can be considered a three-step process involving: 1. dissolution of goethite or amorphous ferric hydroxide; 2. formation of hematite nuclei; and 3. growth of hematite crystals. This is similar to the process proposed by Schwertmann and Taylor [1973] for the formation of goethite. According to Walker [1967], the formation of hematite rather than goethite as the stable component is favoured under oxidizing conditions, even below the water table, a conclusion supported by the experimental work of Langmuir [1970]. Studies of red beds of varying ages indicate that the crystallization of hematite is an extremely slow process, since it is controlled by the solubility of ferric iron, and that red beds younger than about 10 million years are more likely to contain goethite than hematite. During the weathering process, the less stable trioctahedral micas would be expected to be replaced by dioctahedral soil illite and chlorite observed in the Queenston Shale, although the latter may also be the remnant of primary chlorite related to the Appalachian geosyncline.

Following the deposition and *in situ* weathering of the material, the region was submerged and during the Silurian, extensive beds of limestone, dolomite and sandstone were deposited over top of the red beds, which resulted in the consolidation and induration of the material to produce the Queenston Shale.

The sample of Queenston Shale Clay analysed in this study was collected from regolith of a steep valley-side slope of the Bronte Creek (Sheet 30 M/5 West, G.R. 972074) draining into Lake Ontario. The regolith comprised a poorly-sorted mixture of shale fragments and silty-clay material overlying flat-bedded parent shale at a depth of about 1 m. The presence of incompletely weathered shale debris in the regolith, which is typical of undercut slopes in the Bronte Creek and neighbouring streams incised into the shale, emphasizes the immaturity of the weathered product.

## 5.2 Results of Treatments on the Properties of the Queenston Shale Clay.

The changes in physical and physico-chemical properties of this clay following each treatment will be discussed by treatment, rather than by property, because of the obvious interaction among the different properties. The particular changes in plasticity will then be summarized in Section 5.3. The extraction procedures employed with the 200 g samples, as outlined in Section 4.5, are referred to here as follows:

| | |
|---|---|
| Q1: | Untreated |
| Q2: | Soluble salts extracted |
| Q3: | Homoionized with NaCl |
| Q4: | SAB |
| Q5: | SAB + NaOH |
| Q6: | SAB + NaOH + CBD |

### 5.2a Untreated Sample (Q1).

The chemical analysis of the soluble salts removed from the Q2 sample (Table 5.1) indicates that the salt concentration of the Q1 sample, calculated on the basis of the chlorides of the major cations, is about 1.6 g/l, consisting primarily of Na and Ca salts.

Un-oriented, random XRD analysis was performed on the 2.0-0.2 micron fraction of this sample, i.e., on about 20% of the total size range. The XRD trace, presented in Figure 5.1, indicates the presence of primary minerals in

## TABLE 5.1

Chemical analysis of Phase II extracts for the Queenston Shale Clay.
(Data expressed as mg/g air-dried sample)

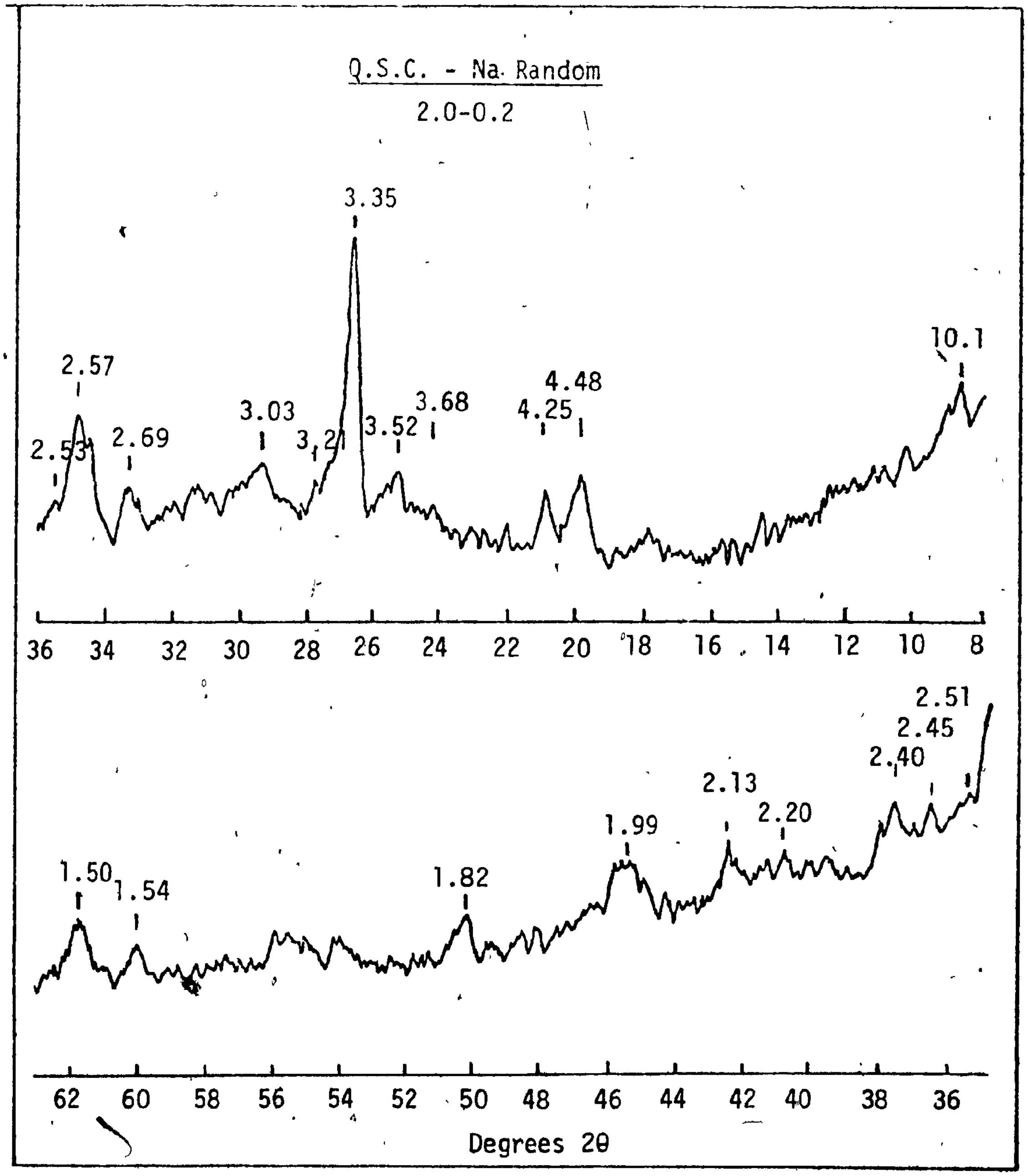
| | Ca | Mg | K | Fe | Mn | Si | Al |
|---|---|---|---|---|---|---|---|
| Q2 | .15 | .01 | .01 | .01 | .003 | .01 | 0 |
| Q3 | 2.83 | .07 | .32 | .08 | .08 | .03 | .09 |
| Q4 | 33.78 | .58 | .42 | 1.80 | .53 | .20 | .09 |
| Q5 | 37.1 | .47 | .98 | 1.13 | .40 | 1.22 | 1.1 |
| Q6 | 37.7 | .54 | 1.19 | 14.7 | .56 | 2.17 | 2.2 |
| Analytical Error | ±5% | ±5% | ±5% | ±5% | ±5% | ±5% | ±10% |

## TABLE 5.2

Summary of physical properties for Queenston Shale Clay.

| | % sand >63μ | % silt 63-2.0μ | % clay <2.0μ | % fine clay <0.24μ | SSA $m^2/g$ | CEC m.e./100 g | pH soil paste | Pw | Lw | PI |
|---|---|---|---|---|---|---|---|---|---|---|
| Q1 | 5.0 | 53.2 | 41.8 | 20.0 | 78 | 14.3 | 7.2 | 24.3 | 43.0 | 18.7 |
| Q2 | 4.4 | 52.9 | 42.7 | 21.5 | 90 | 13.6 | 7.5 | 24.5 | 42.1 | 17.6 |
| Q3 | 3.9 | 51.1 | 45.1 | 23.7 | 95 | 14.0 | 8.4 | 21.9 | 31.4 | 9.5 |
| Q4 | 3.4 | 50.5 | 46.1 | 23.1 | 81 | 18.0 | 7.3 | 22.3 | 35.1 | 12.8 |
| Q5 | 2.6 | 51.4 | 46.0 | 20.0 | 94 | 15.5 | 7.7 | 23.0 | 35.6 | 12.6 |
| Q6 | 1.5 | 50.8 | 47.7 | 26.1 | 75 | 14.1 | 8.9 | 21.9 | 32.8 | 10.9 |
| Analytical Error | ±.5 | ±.5 | ±.5 | ±.5 | ±6 | ±5% | ±.1 | ±.2 | ±.2 | ±.4 |

FIGURE 5.1



XRD analysis of random sample of untreated Queenston Shale Clay: (2 X $10^4$ Full Scale).

the clay-sized fraction. Quartz is identified by the weak 4.25 Angstrom peak and the strong 3.35 Angstrom peak, although this latter peak also includes the third-order (003) peak of the 10 Angstrom mineral. Minor amounts of feldspar are indicated by the 3.21 and 3.03 Angstrom peaks. Hematite is also identified by the peaks at 2.69, 2.51 and 2.20 Angstrom. The phyllosilicate clay minerals can also be identified by their hkl diffraction spacings: dioctahedral illite is identified by the strong peak at 4.48 Angstrom and the (060) peak at 1.50 Angstrom. The peak at 1.54 Angstrom is attributed to chlorite, although it is difficult to be certain that this peak is not due to trioctahedral mica or to quartz [Grim 1968]. The eight CBD extractions, discussed in detail in Section 4.4b, revealed that K is not easily displaced from interlayer positions. This additional information substantiates the view that the 10 Angstrom mineral is dioctahedral, rather than trioctahedral, illite. Since the vermiculite phase is interstratified with the illite, the hkl diffraction spacings will be the same as for the illite, since the structure of the octahedral layer is probably not affected by this interstratification. Discussion of the oriented XRD samples which were pretreated to remove soluble salts is deferred until discussion of the Q2 sample.

The physical properties of the untreated sample are outlined in Table 5.2. The particle size analysis reveals that the material is primarily composed of silt-sized material, while almost 50% of the clay-sized material is less than 0.24 microns in size. The pH of the soil, determined on a soil water paste at twice the water content of the liquid limit, is very close to neutral, at pH 7.2. The CEC value of 14.3 m.eq./100 g is a little high considering that the soil contains only 42% clay-sized material and that according to Grim [1968], illite in the 1.0-0.1 micron size range possesses a CEC of 13-20 m.eq./100 g, indicating that the silt-sized material may be responsible for some of the CEC, supporting the conclusion developed below that the silt consists of cemented aggregates of clay size. This view is supported by the relatively high value of SSA (78 $m^2/g$) which for an illitic material of only 42% clay size indicates that either the silt-sized material is contributing to the SSA values, or that there is material of very high specific surface area in the sample.

The plasticity values (plastic limit = 24.3 and liquid limit = 34.0) are in the range expected for material of this grain size and mineralogy. The activity (PI relative to the % clay-sized material present) is 0.45, which is slightly lower than might be expected (c 0.6) for illite according to Skempton [1953a] and Soderman and Quigley [1965]. Thus, even though the silt fraction is suspected to contribute to the specific surface area and cation exchange capacity of the material, it does not appear to contribute to its plasticity. This would be expected if the silt particles comprised porous aggregates of cemented clay-sized materials.

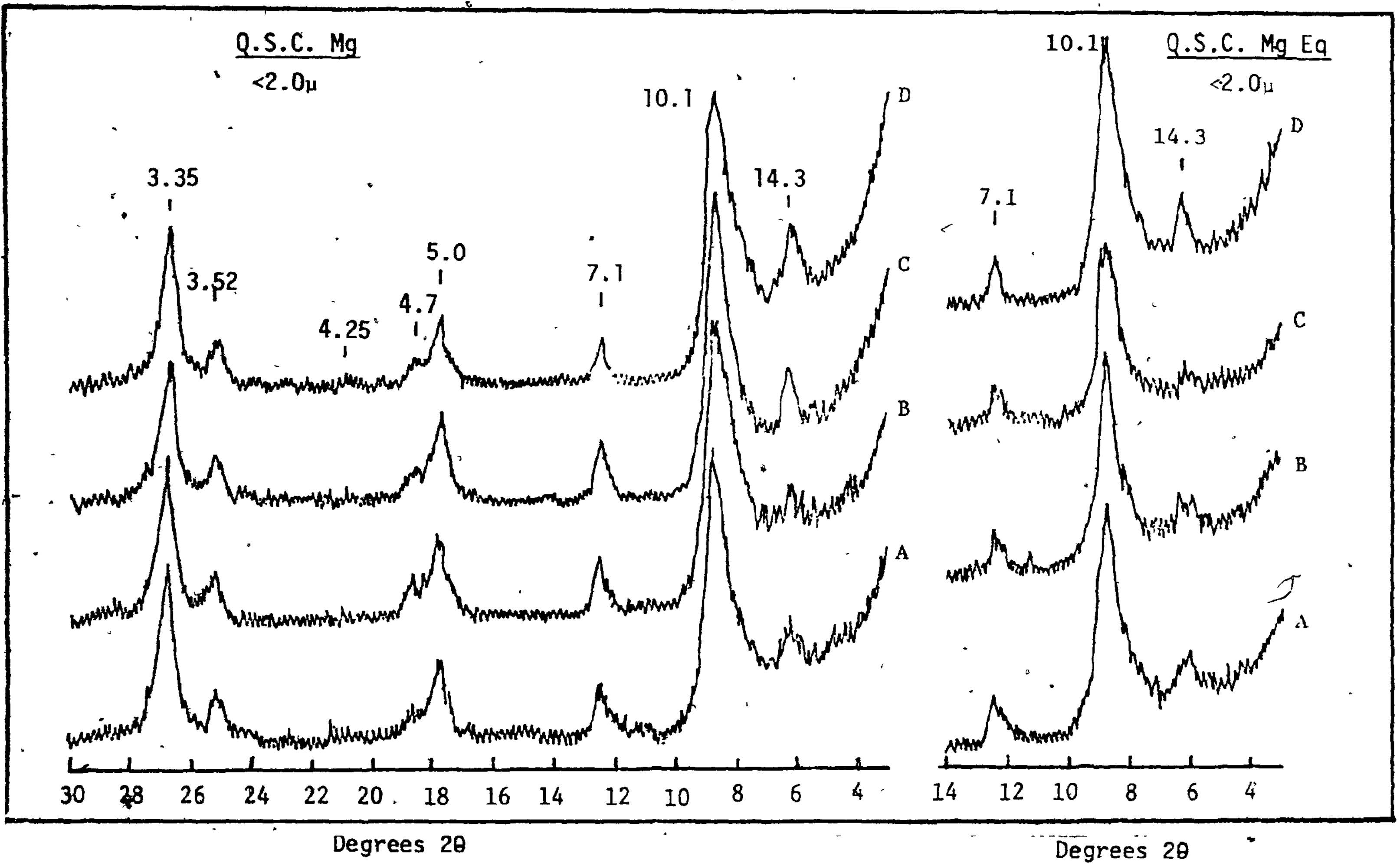
### 5.2b Treated to Remove Soluble Salts (Q2).

The data presented in Table 5.1 indicate that the chemistry of the soluble salts extracted compares quite well with the values obtained on the samples in Phase I (Table 4.1). Na was not, unfortunately, determined in the Phase II extracts but, on the basis of Phase I, is assumed to share the position with Ca as the dominant cation in the free solution.

The dominant clay mineral in the clay-sized fraction is the 10.1 Angstrom mineral, identified as dioctahedral illite; the 10.1 Angstrom peak is present in all of the XRD traces for the Queenston Shale. The traces of the fraction less than 0.2 micron in size indicates that the 10.1 Angstrom mineral completely dominates the clay mineral composition of this fraction. Vermiculite is present as interstratified illite/vermiculite as indicated by the shift of the low 2θ limb of the 10 Angstrom peak towards 12.6 Angstrom in the Mg-saturated, air-dried trace (Figure 5.2), compared with the K-saturated traces (Figures 5.3 and 5.4). The 14.3 Angstrom peak on the Mg-saturated trace collapses on K-saturation, air-dried and K-saturation, 300°C traces, and is indicative of an interstratified illite/vermiculite phase rather than chlorite. The probable existence of a chlorite peak at 14.3 Angstrom (marked on the Mg-trace) becomes quite poorly defined in the K-saturated, 300°C trace, although the second-order chlorite peak at 7.2 Angstrom remains. In order to determine whether the 7.2 Angstrom peak was chlorite or kaolinite, an untreated sample of the clay-sized material was treated with hot 1 N HCl for 1 hour, to destroy the chlorite. The absence of a 7.2 Angstrom peak following this treatment indicates that it is not due to kaolinite [Raman and Ghosh 1974]. The K-saturated 550°C treatment results in the elimination of the 7.2 and 14.3 Angstrom peaks of chlorite, indicating that this was a "soil chlorite" rather than a primary chlorite [Grim 1968, Raman and Ghosh 1974].

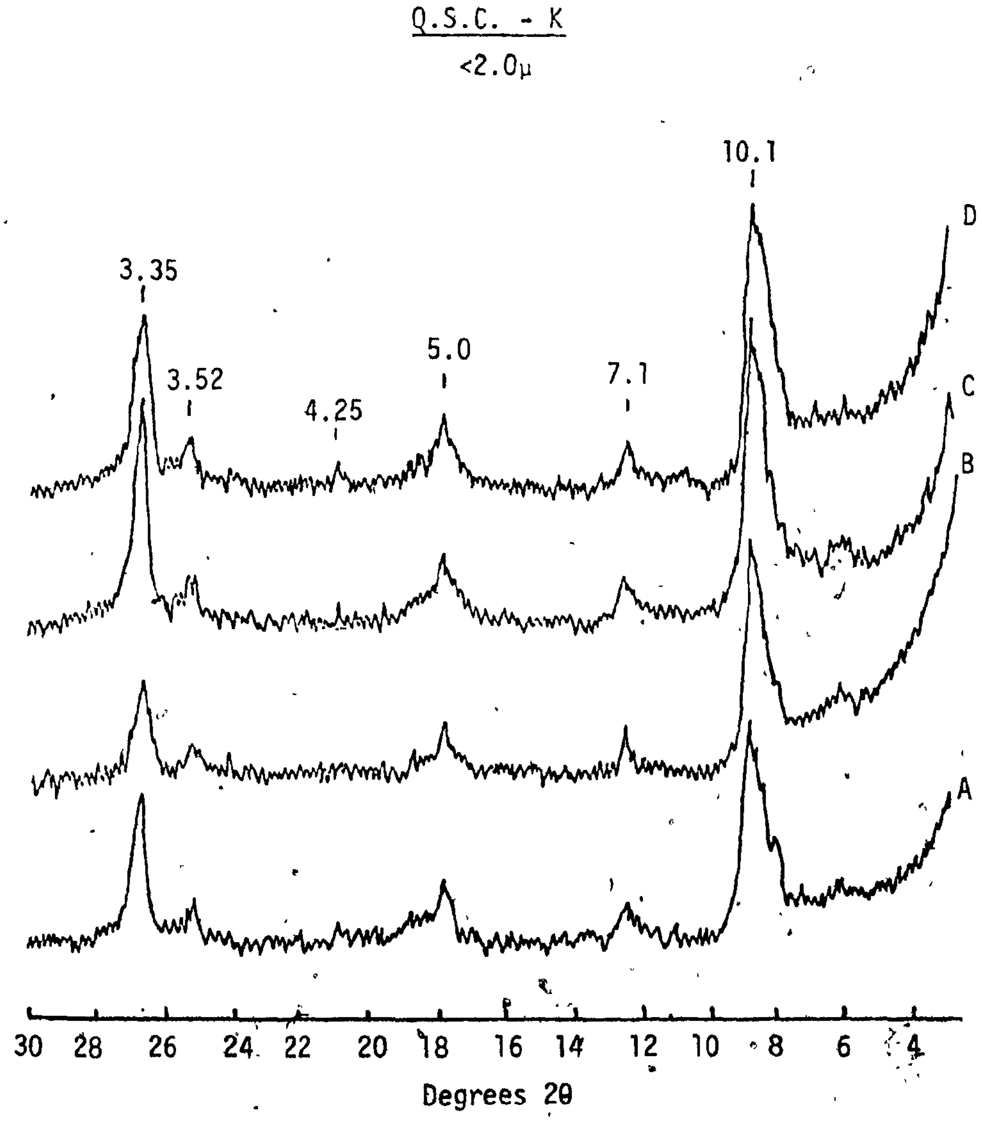
The particle-size analysis reveals that the treatment caused a decrease in the amount of sand- and silt-sized material and an increase in the amount of clay and fine clay, compared to the untreated (Q1) sample. This change is reflected in an increase in specific surface area. In view of the earlier

FIGURE 5.2



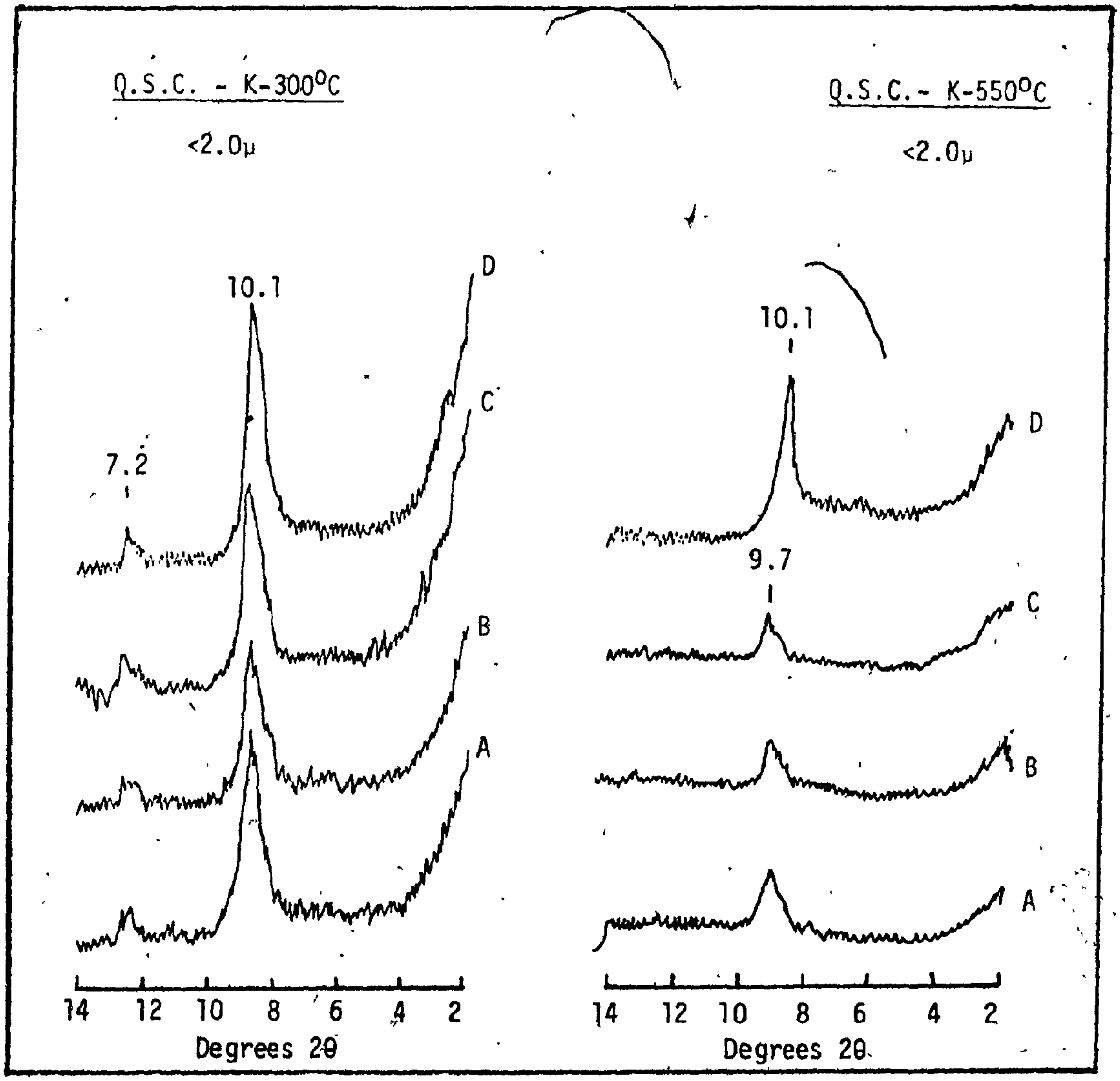
XRD analysis of Queenston Shale Clay at the end of Phase I treatments: A. Removal of soluble salts.. B. Homoionization. C. SAB. D. SAB + NaOH + CBD. ($4 \times 10^4$ Full Scale)

FIGURE 5.3



XRD analysis of Queenston Shale Clay at the end of Phase I treatments: A. Removal of soluble salts. B. Homoionization. C. SAB. D. SAB + NaOH + CBD. (4 X $10^4$ Full Scale).

FIGURE 5.4



XRD analysis of Queenston Shale Clay at the end of Phase I treatments: A. Removal of soluble salts. B. Homoionization. C. SAB. D. SAB + NaOH + CBD. (4 X $10^4$ Full Scale) interpretation of the silt- and sand-sized classes as cemented aggregates and the nature of this pretreatment, those changes are interpreted as a dispersion of some of those aggregates by the mixing process.

There is no significant (i.e., beyond experimental error) change in cation exchange capacity as a result of the treatment. On the assumption that dispersion of the original porous aggregates occurred as a result of mechanical breakdown, rather than dissolution of cement (which might be neutralizing exchange sites), no significant change in CEC would be expected.

The insignificant increase in the plastic limit, together with a small decrease in the liquid limit, resulted in a small decrease in plasticity; the change is consistent with the findings and theory (described in Chapter 2) dealing with decreasing salt concentration of pore fluid for muds comprising illitic minerals. This drop may have been partially offset by the increase in clay content and specific surface area.

### 5.2b Na-Homoionized Sample (Q3).

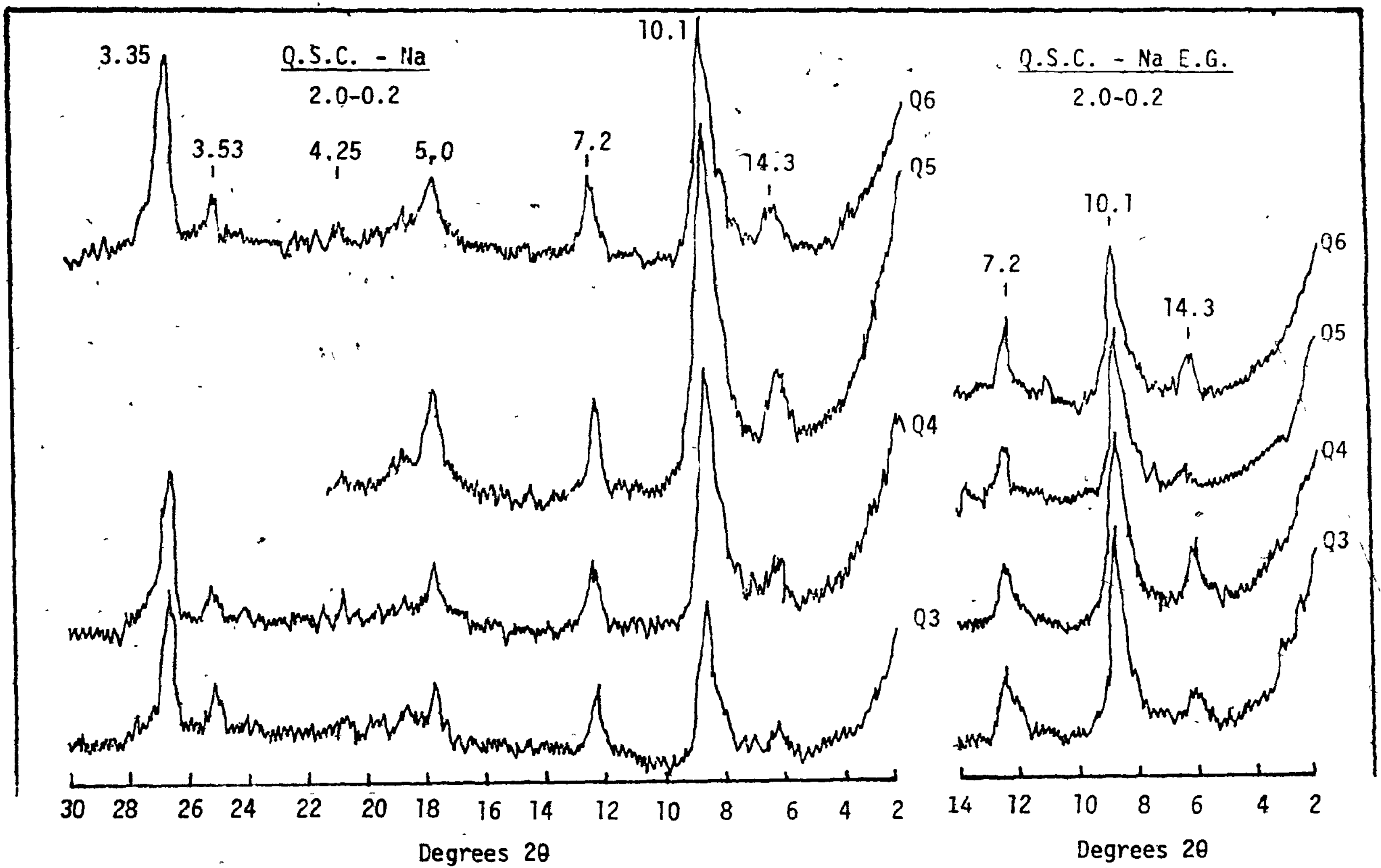
The Na-homoionization procedure of Phase II resulted primarily in the removal of calcium (Table 5.1), although considerably less than was indicated in Phase I of the study (Figure 4.1). The summation of the m.eq./100 g of soil is now very close to the calculated CEC value of 14.0, indicating that any dissolution of calcium carbonate during the homoionization procedure was insignificant.

XRD analysis of Mg- and K-saturated samples following homoionization reveals that no significant alteration occurs as a result of this treatment (Figures 5.2 to 5.4). Na-saturated slides of Q3 were prepared for the 2.0-0.2 micron fraction and the <0.2 micron fraction; traces are presented here (Traces A, Figures 5.5 and 5.6). In the Na-saturated trace of the 2.0-0.2 fraction, the illite is identified by the peak at 10.1 Angstrom and the chlorite by the peaks at 14.3 and 7.2 Angstrom. The vermiculite phase is evidenced by the slight broadening of the 10.1 Angstrom peak in the direction of low 2θ angles. The only change apparent on this sample, due to the ethylene-glycol saturation, is the decrease in the peak heights as a result of the disturbance of the orientation. The <0.2 micron fraction contains primarily illite, as indicated by the dominance of the 10.1 Angstrom peak; this size fraction does not appear to contain a swelling mineral component, as indicated by the effect of the ethylene-glycol saturation treatment.

Disaggregation of the sample by the increased number of treatments on Q3, compared with Q2, resulted in further decreases in the silt- and sand-sized fractions, and corresponding increases in the clay and fine clay fractions. In the discussion of Q2 it was indicated that this dispersion might be expected to produce a concomitant increase in specific surface area but not necessarily a change in CEC of the sample. In the treatment on Q3, neither property, in fact, showed a change in excess of the analytical error.

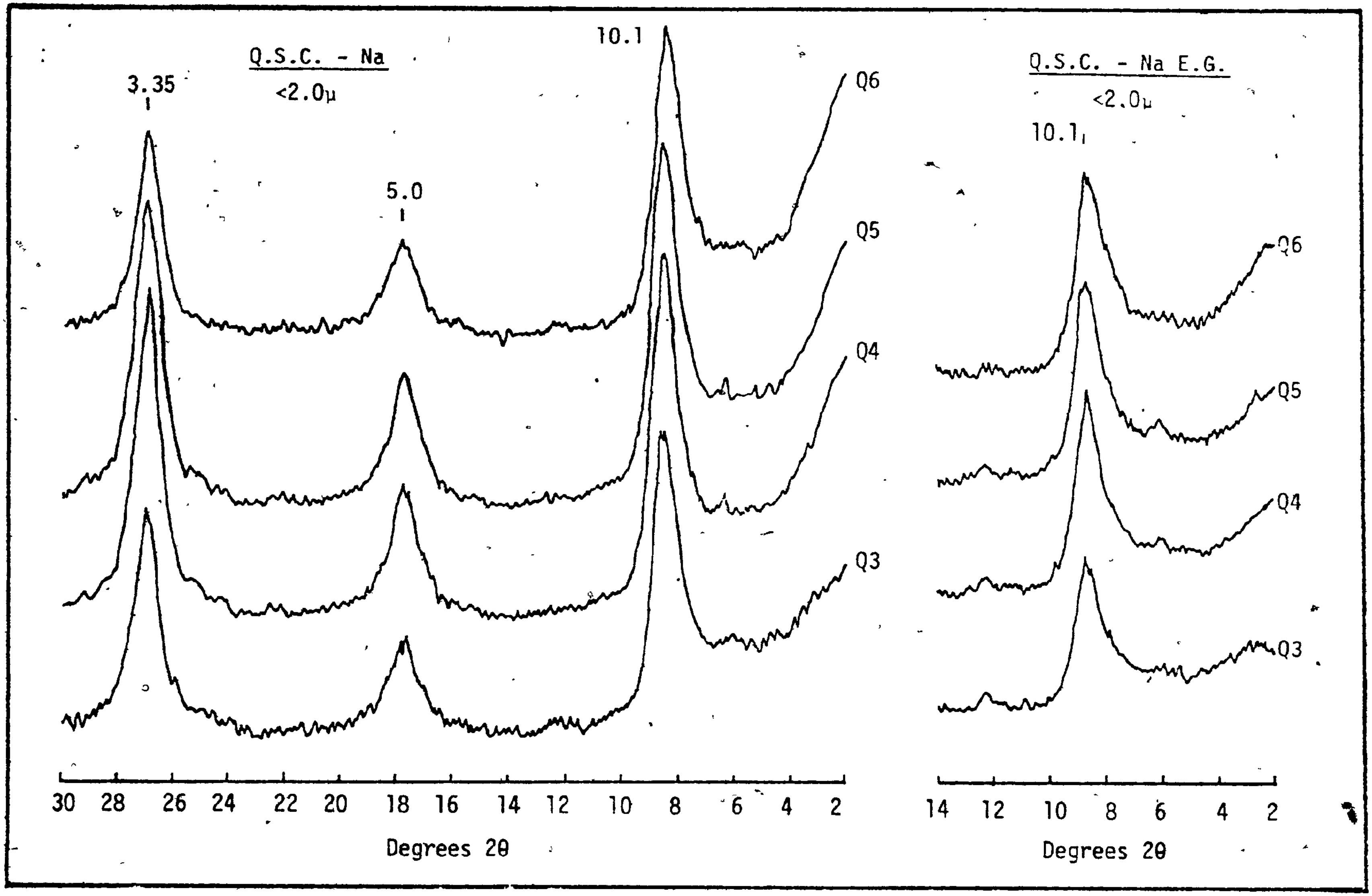
The significant decrease in both the plastic and liquid limits, particularly the latter, would be expected from the substitution of Na for Ca in the double layer of illitic minerals, as discussed extensively in Chapter Two. The marked rise in pH to 8.4 in this sample may also be significant; as discussed in Chapter 2, as the pH is increased, an increasing proportion of the

FIGURE 5.5



XRD analysis of Queenston Shale Clay at the end of Phase II treatments: Q3. Homoionization. Q4. SAB. Q5. SAB + NaOH. Q6. SAB + NaOH + CBD. (2 X $10^4$ Full Scale)

FIGURE 5.6



XRD analysis of Queenston Shale Clay at the end of Phase II treatments: Q3. Homoionization. Q4. SAB. Q5. SAB + NaOH. Q6. SAB + NaOH + CBD. (2 X $10^4$ Full Scale) charge on the clay minerals, and perhaps of the charges on the iron oxide compounds, will become negative, resulting in a less flocculated structure, and hence a lower liquid limit. This increase in negative charge would not be apparent from the CEC value, as this is determined at a constant pH 8.2.

The reason for the rise in pH in Q3 has not been established, but it could reflect the formation of a very dilute solution of sodium carbonate, as a result of the substitution of Na for Ca in the pore solution.

### 5.2d Treated to Remove Carbonates (Q4).

The chemical analyses of the Q4 extracts resulted in the removal of a large amount of Ca, believed to be due to the dissolution of calcium carbonate, which would correspond to about 9% of the soil by weight. The relatively high amount of Fe extracted, and the related increase in Mn extracted, may indicate dissolution of an iron (and Mn) carbonate, or it may be the result of the dissolution of iron oxide and/or hydroxide compounds in the SAB reagent. The Mg extracted probably originates from impurities in the calcium carbonate. The extraction of K by the SAB treatment alone (i.e., in excess of Q3) is quite small (0.1 mg/g), but may indicate some removal of interlayer K from the illite. Examination of the XRD traces for the SAB-treated sample, in the Mg- and K-saturated states (Figures 5.2 to 5.4) and the Na-saturated state of the 2.0-0.2 micron and <0.2 micron fractions, however, indicates no significant change in the mineralogy of the clay-sized material.

Particle-size analysis reveals a further drop in the sand and silt fractions, arising from dissolution, but more probably disaggregation, of this material by the SAB treatment. The clay size fraction increases accordingly, although the fine clay fraction decreases slightly, perhaps due to the dissolution of very small colloidal carbonate material. The significant drop in the specific surface area from 95 $m^2/g$ (Q3) to 81 $m^2/g$ for Q4 implies that the removal of material of relatively high specific surface area which may in fact consist of amorphous or very poorly crystalline calcium carbonate. It also implies that the major part of this colloidal carbonate material was not attached to other particle surfaces; if this were the case, exposure of previously blocked surface area would compensate for loss of area with dissolution of the carbonate. Thus, although $CaCO_3$ may have existed as a cement in the silt fraction, the major part of the carbonate is believed to have existed as a separate colloidal phase.

This removal of colloidal carbonate would account for the observed marked increase in CEC. According to Krauskopf [1967, p. 157], colloidal carbonate is usually positively charged, and in solutions of low electrolyte concentration this would neutralize negative charges on clay plates, even without physical blockage of the exchange site [Sumner and Davidtz 1965]. Removal of this material would thus be expected to raise the CEC of the residue.

This increase in plasticity following the SAB treatment cannot be attributed conclusively to any of the other changes observed, although it would be consistent with the return of the soil pH to a more neutral level. The effect of a change in CEC on the plasticity of a material dominated by non-swelling minerals of a constant size is not fully understood, but the increased repulsion might be expected to lower the liquid limit. The variations in soil fabric which result from variations in pH and CEC will be of considerable importance in determining the liquid limit of the material, although this aspect has not been adequately researched in the past.

### 5.2e Successive Treatments to Remove Carbonates and Si and Al Compounds (Q5).

In regard to the chemical analysis of the Q5 extracts compared to the Q4 extracts (Table 5.1), the decrease (in Q5) in the amounts of Mg, Fe and Mn extracted is of particular importance. The analysis of the extracts from each step of the Q5 procedure indicates that the NaOH treatment caused the precipitation of compounds involving these cations after previous compounds had been dissolved by the SAB treatment; presumably this precipitation involved the formation of insoluble metallic hydroxides. The increased Ca released by the Q5 sample is related to the SAB rather than the NaOH treatment, indicating that the 200 g samples were not identical in size and/or calcium carbonate content.

In addition to the effects mentioned above, the NaOH treatment extracted 1.2 mg/g Si and 1.1 mg/g Al; this material may represent dissolution of either amorphous or crystalline material in the soil. The significant increase in the amount of K extracted is presumably due to the removal of interlayer K from the illite; in view of the Si and Al extracted by this treatment, the possibility that the illite particles, particularly those of ≤0.2 microns, are being attacked by this treatment cannot be ruled out. This possibility was not verified, however, by XRD analysis of the residues.

The XRD analysis of the Na-saturated samples indicates that the mineralogy of the sample was not altered by the NaOH extraction. The increased peak height of Q5 on Figure 5.5 for the 2.0-0.2 micron fraction is due to slightly different preparation techniques employed with this sample; repeated attempts to prepare the slide by evaporation at room temperature failed to produce a slide without the clay peeling, and the slide was therefore warmed at low temperature on a hot plate during evaporation, which produced a satisfactory slide, although the XRD trace indicates that the orientation was somewhat better than that achieved with room temperature evaporation. Ethylene-glycol saturation has apparently disturbed the orientation slightly, since the peak heights for Q5 on Figure 5.6 are not significantly different from those for Q4.

Particle size analysis shows that further loss of sand-sized material is balanced by an increase in the silt fraction, rather than by the clay fraction as occurred during previous treatments. In addition, there is a shift in the composition of the clay fraction with a marked decrease in the fine clay. Both changes are interpreted as a consequence of recementing of fine material due to the precipitation of metallic hydroxides. The increased specific surface area emphasizes the fineness of this precipitation and suggests that little clogging of the original surface area in Q4 occurred, even though cemented aggregates developed. The decrease in the CEC is interpreted as neutralization or blockage of negatively-charged sites by the positively-charged metallic hydroxides.

The small, but significant, increases in both the liquid and plastic limit, but not the plasticity index, from Q4 to Q5 may be taken to indicate that the precipitated material is acting as a cementing agent between particles and as such increasing the amount of pore space at both of the plasticity limits. The cement presumably produces aggregates which are stable mechanically and thus increase the amount of pore water. The lack of any increase in the plasticity index would seem to indicate, however, no development of inter-aggregate bonding, as might be expected in electrostatic grounds. This increase in the limits would not have been expected from the increased pH of the soil, and the values obtained for the limits are therefore probably lower than would have been achieved had the precipitation of the hydroxide material occurred without a pH change.

### 5.2f <u>Treated to Remove Carbonates, Si, Al and Fe Compounds (Q6)</u>.

As for the previous sample (Q5), the increased amount of Ca extracted (compared to Q4) is the result of the SAB treatment rather than the NaOH or CBD extractions. The large amount of Fe (14.7 mg/g) extracted by the CBD treatment occurred primarily (79%) during the first of the two CBD treatments. The Fe, believed to have been extracted from hematite and perhaps amorphous iron compounds, would as $Fe_2O_3$ account for about 2% of the soil by weight. The CBD extraction completely removed the red pigmentation from the sample, leaving it grey in colour. The amounts of Al and Si removed by the CBD treatments are similar in magnitude to the amounts removed by the prior NaOH treatment. In addition, the CBD treatment results in much more Al being released during the NaCl homoionization than was released during homoionization following the NaOH treatment.

XRD analyses performed for the sample treated with SAB, NaOH and CBD show that there are some minor changes resulting from the extraction procedure. Figure 5.2 shows that the 10.1 and 14.3 Angstrom peaks of illite and chlorite, plus vermiculite, respectively, are better defined than for a sam~~ple~~ treated with SAB alone; this figure also demonstrates that there is no swelling clay mineral present in the sample. K-saturation (Figure 5.3) shows the collapse of the 14.3 Angstrom peak, due to vermiculite; at this stage, the chlorite peak is apparently hidden by the background noise, although the 7.1 Angstrom peak is still strong. The heat treatment further collapses the vermiculite and causes the 10.1 Angstrom peak to assume a much more symmetrical form. Heating to 550°C (Figure 5.4) eliminates the 7.1 peak entirely, as a result of the destruction of the "soil chlorite", although the 10.1 Angstrom peak is much less affected than for the other samples (Traces A, B, and C, Figure 5.4); this is indicated by the greater size of the 10.1 Angstrom peak and the fact that it has not shifted to 9.7 Angstrom as have the others.

The Na-saturated sample of Q6, for the 2.0-0.2 micron and the <0.2 micron fractions, also indicates that the mineralogy has not been changed significantly by the treatment as compared to the Q3, Q4 or Q5 traces on Figure 5.5 and 5.6. The ethylene-glycol treatment apparently disturbs the orientation of the clay particles, but does not show any evidence of a swelling component in the samples.

As with all the previously-mentioned samples, the treatment on Q6 resulted in a decrease in the amount of sand-sized material. The amount of silt in Q6 is less than in Q5, but not significantly different from the Q4 sample. The amounts of clay-sized and, particularly, fine clay-sized material were both increased significantly. In light of these particle-size data, the decrease in specific surface area appears anomalous; these changes, however, are very similar to those occurring after the treatments on Q4 and can, perhaps, be explained in a similar way. They are believed to reflect the removal of compounds of high specific surface area which were binding together the other soil components; in this case the compounds were predominantly iron ones. Support for this view is provided by Deshpande, Greenland and Quirk [1968], who indicated that, based on weight loss and change in specific surface area resulting from the deferration of red soils, iron compounds in their samples had values of specific surface area ranging from 100 to 400 $m^2/g$. Similar calculations for Q6 (assuming that the Fe compounds accounted for about 2% of the weight as indicated previously) would indicate a specific surface area of about 200 $m^2/g$ for the material extracted in Q6, quite consistent with the figures above, even allowing for analytical error.

The decrease in CEC as a result of the extraction procedures to a value well below that of Q4 and slightly less than Q5 is not, however, entirely in keeping with the hypothesis that iron compounds, bonded to the clay particles, have been removed. The positively-charged iron oxide compounds would be expected to result in neutralized negative charges on the surfaces of the clay minerals, and their removal should, therefore, increase the CEC of the sample. The decrease can only be explained by the removal of iron oxide compounds of high specific surface area, which possessed a significant amount of negative charge. The determination of CEC using sodium acetate at pH 8.2 may have caused the iron oxide compounds to develop negative surface charges similar to those developed on the edges of clay particles [Schofield 1949].

The existence of negative charges in ferric hydroxide sols in alkaline solutions, in contrast to the positive charge in acid solutions, was noted by Krauskopf [1967, p. 158]. The similar pH-dependence of the charge on aluminum hydroxide colloids has been discovered by Van Olphen [1963, p. 20]. This may well have contributed to the high CEC value of Q4, while removal of the fine iron and aluminum compounds would produce a decrease in CEC for the Q6 sample.

The drop in the plastic limit, the liquid limit and the plasticity index to lower values than obtained for Q4 or Q5, may be partially attributed to the removal of the iron compounds, binding together the soil particles. In addition, the decrease may well have been considerably enhanced by the conversion of the positively-charged edge sites to negatively-charged sites, thus causing the deflocculation of the sample during the plasticity determinations. The cause of this high pH is not well understood; the CBD extraction was buffered at pH 7.3; therefore the change in pH is due to subsequent alteration in the H-OH balance. Adsorption of the bicarbonate radical on positively-charged sites during the CBD extraction may have led to the later separation and dissociation to produce OH in the soil solution.

Another factor which may be of very great importance in explaining the decrease in plasticity for Q6 is the adsorption of the organic citrate ion onto the edge sites. This would produce a very similar effect to that of a high pH, namely a system in which all of the exposed surfaces were negatively charged; hence, dispersion would occur and the plasticity would be greatly reduced.

## 5.3 Summary of the Factors Affecting the Plasticity of the Queenston Shale Clay.

Taking all six samples together, no single variable offers a good correlation with the plasticity index. In view of the fact that several factors affect plasticity, this is hardly surprising. Considering the three variables, specific surface area, cation exchange capacity and soil pH, the latter, however, gives by far the best correlation. In addition, the discrepancies from this relationship can be accounted for by the more obvious other factors: Q1 and Q2, with pH value comparable to Q4 and Q5 respectively, have significantly higher plasticity indices. This is consistent with the fact that these two samples (Q1 and Q2) are essentially Ca-saturated, whereas all subsequent treatments created Na-saturated specimens. For illitic-rich soils, the former should have higher PI values. It is recognized, however, that with only six samples the statistical limitations of such conclusions are severe. Finally, for the four Na-saturated samples, the amount of variation in plasticity is extremely limited in view of the magnitude of the extractions.

# Chapter Six:

# CHAMPLAIN SEA CLAY

## 6.1 Origin and Properties of the Champlain Sea Clay

It is generally accepted that the sediments making up the Champlain Sea Clay are the result of glacial erosion of the igneous and metamorphic rocks of the Canadian Shield [Brydon and Patry 1961, Gillott 1971]. That this material is generally unweathered is borne out by the fact that amphiboles and pyroxenes have been identified in the clay-sized fraction of the sediment, despite the fact that these minerals are very easily weathered (as indicated by Jackson's [1968] weathering sequence). The material, often referred to as 'Leda Clay', was deposited in the offshore waters of the Champlain Sea, which encroached into the St. Lawrence, Ottawa and Lake Champlain basins immediately after the retreat of the Wisconsin glacier. The sediment was thus deposited under conditions of salinity, which varied both geographically and with time.

This deposition of rock flour in a saline environment has long been thought to be of major significance in the production of the "quick", or highly sensitive, deposits of eastern Canada and Scandinavia. Inasmuch as sensitivity is strongly correlated with liquidity index in these clays, and the development of sensitivity may be due to the decrease in liquid limit, any discussion of changes in plasticity (as in this thesis) must have implications in the context of sensitivity also. Rosenqvist [1955], Bjerrum and Rosenqvist [1956], and Torrance [1974] have produced sensitive clays by the leaching of natural Norwegian clay, by sedimenting the material in saline water, and subsequently leaching of the salt; the development of this sensitivity coincided with a decreased liquid limit and increased liquidity index. Pusch and Arnold [1969], in contrast, failed to produce a sensitive clay using illite by similar means. In these latter tests, however, organic matter had been removed using hydrogen peroxide, and, as Torrance [1970] has pointed out, the failure to produce a sensitive clay may have been due to the oxidation, rather than due to the fact that a pure illite had been used. Cabrera and Smalley [1973] emphasize a very different point, that the production of these highly sensitive clays is a result of the mineralogy of these post-glacial marine deposits, and is not strictly a function of the leaching of salt from the pore fluid. Considering that the material is composed primarily of rock flour, rather than the weathered clay minerals found in most clay deposits, the comments of Cabrera and Smalley are perhaps of some importance, although this will be discussed further in Section 6.3.

Although Rosenqvist [1955] maintained the importance of leaching in changing the nature of interparticle forces, he [Rosenqvist 1966] emphasizes that the primary consideration in the formation of quick-clays is the development of repulsive forces (or the decrease in net attractive forces) caused by alteration of the pore fluid, whether they be caused by leaching or some other factor. In support of this concept, Soderblom [1966] discusses the effect of dispersants on the sensitivity of marine clays from Sweden. Naturally-occurring dispersants, such as some organic acids, soluble silicates, and some soluble carbonates, could produce the sensitivity observed in the post-glacial clays. Similar conclusions were made by Penner [1964] in relation to the Champlain Sea Clays; samples of natural Champlain clay show a poor correlation between sensitivity and salt concentration, but a strong positive correlation between sensitivity and electro-kinetic potential, a phenomenon completely consistent with Rosenqvist's [1966] more general thesis. The findings of the present research are also relevant in this context as discussed later in this chapter.

McKyes, Sethi and Yong [1974] have suggested that the Champlain Sea sediments contain an appreciable amount (c 10%) of amorphous material, consisting primarily of iron and silicon compounds. The presence of this material in the sediments must be considered of some importance in relation to its physico-chemical and geotechnical properties. One obvious effect of the presence of amorphous cementing material would be an increased strength of the sample in an undisturbed state, and indeed Conlon [1966] and Kenney, Moum and Berre [1967], almost a decade ago, attributed the high undisturbed strength and apparent overconsolidation of Champlain Clay to cementation by iron compounds. The existence of such a cement might also account for the high void ratio (and thus high liquidity index) of Champlain Clay. Finally, such amorphous material might be expected to affect the liquidity index through the liquid limit, the topic of this research.

Although the origin of the amorphous phase is not yet known, the work of Loring and Nota [1968] and Brewer, Macauley and Sundby [1974] on the nature of present-day sedimentation occurring in the Gulf of St. Lawrence indicates that iron and, to a lesser degree, manganese oxides are being precipitated as coatings around particles and/or as a result of flocculation of iron compounds near the junction of the fresh and saline Gulf water. Considering the high content of iron in the amorphous phase, as discussed by McKyes, Sethi and Yong, the possibility that this amorphous material was deposited on the material prior to deposition may be of great importance when considering the observed open flocculated structure of the undisturbed Champlain Sea Clay [Gillott 1970].

Although laboratory studies, such as the leaching experiments mentioned previously, have resulted in alteration of the physical properties of the material, they cannot be expected to simulate the development of very high sensitivity values by processes directly comparable with those occurring in Nature. Several thousands of years of natural leaching may have produced changes not only in the pore fluid but also in the mineralogy of the material itself. For example, the sensitive clays have been shown [Soderman and Quigley 1965] to contain a small, but perhaps very important, portion of swelling clay mineral; this material is presumably due to <u>in situ</u> alteration, since it is not part of the Canadian Shield mineral assemblage from which the rock-flour has originated.

The sample of Champlain Sea Clay used in this study was taken from the Gatineau region, about six miles north of Ottawa (Sheet 31 G/12 E, GR 496404), from the side of a fresh (about 2 years old) road cut, sampled at a depth of 1 m, although this is in fact about 10 m from the original ground surface.

## 6.2 Results of the Treatments on the Properties of the Champlain Sea Clay.

As was done for the Queenston Shale Clay, the results of each treatment on the properties of the Champlain Sea Clay will be discussed individually. The samples will be referred to as follows:

C1: Untreated
C2: Soluble salts removed
C3: Homoionized with NaCl
C4: SAB
C5: SAB + NaOH
C6: SAB + NaOH + CBD
C7: SAB + KOH + Oxalate

### 6.2a Untreated Sample (C1).

The chemical analysis of the extracts from C2 (Table 6.1 and the Na concentration determined in Phase I) indicate the salt concentration of the sample C1 to be about 1.3 g/l, based on the calculation of the chlorides of the major cations. Bearing in mind that the sample was taken from well below the surface, extensive leaching might seem surprising, although this would in any case depend on the detailed stratigraphic variation in the juxtaposition of permeable sand and less permeable clay strata, for which no information is available.

In the untreated state, the particle size analysis (Table 6.2) revealed that the material was predominantly clay-size, of which almost one-half (44%) was <0.24 microns equivalent spherical diameter. The other 26.3 percent of the material was silt, while the amount of sand-sized material was below the range of accurate detection.

## TABLE 6.1

Chemical analysis of Phase II extracts for the Champlain Sea Clay.
(Data expressed as mg/g air-dried sample)

| | Ca | Mg | K | Fe | Mn | Si | Al |
|---|---|---|---|---|---|---|---|
| C2 | .08 | .03 | .03 | .02 | .003 | .009 | .05 |
| C3 | 1.28 | .71 | .62 | .04 | .010 | .05 | .09 |
| C4 | 2.06 | 1.58 | .81 | 1.54 | .15 | .31 | .20 |
| C5 | 2.1 | 1.7 | 2.6 | 1.01 | .12 | 6.8 | 3.9 |
| C6 | 2.1 | 2.0 | 2.9 | 5.7 | .17 | 9.8 | 5.1 |
| C7 | 2.9 | 3.3 | nd | 9.2 | .20 | 9.6 | 1.6 |
| Analytical Error | ±5% | ±5% | ±5% | ±5% | ±5% | ±5% | ±10% |

## TABLE 6.2

Summary of physical properties for Champlain Sea Clay.

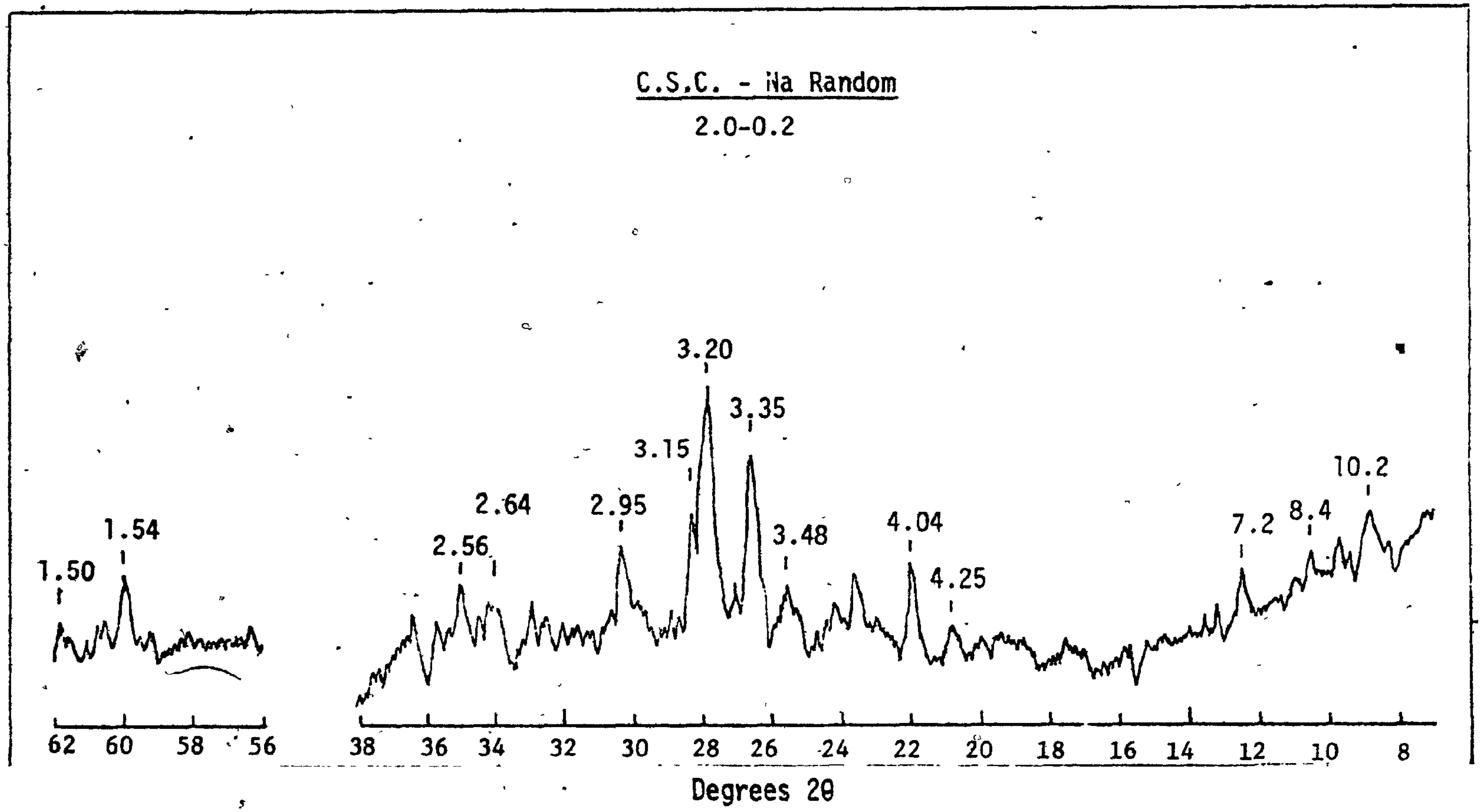
| | % sand >63μ | % silt 63-2.0μ | % clay <2.0μ | % fine clay <0.24μ | SSA m²/g | CEC m.e./100 g | pH soil paste | Pw | Lw | PI |
|---|---|---|---|---|---|---|---|---|---|---|
| C1 | <.01 | 26.3 | 73.7 | 32.3 | 90 | 16.3 | 7.9 | 30.3 | 55.4 | 25.1 |
| C2 | <.01 | 22.6 | 77.4 | 33.2 | 98 | 16.5 | 7.7 | 28.9 | 59.3 | 30.4 |
| C3 | <.01 | 24.2 | 75.8 | 33.0 | 94 | 17.7 | 7.8 | 28.2 | 58.0 | 29.8 |
| C4 | <.01 | 26.3 | 73.7 | 30.4 | 82 | 22.2 | 7.4 | 27.9 | 50.2 | 22.3 |
| C5 | <.01 | 25.6 | 74.4 | 30.3 | 78 | 23.0 | 7.4 | 27.5 | 54.6 | 27.1 |
| C6 | <.01 | 25.5 | 74.5 | 30.2 | 80 | 17.0 | 8.5 | 24.6 | 42.9 | 18.3 |
| C7 | <.01 | 24.0 | 76.0 | 33.5 | 85 | 14.6 | 7.1 | 22.1 | 32.9 | 10.8 |
| Analytical Error | | ±.5 | ±.5 | ±.5 | ±6 | ±5% | ±.05 | ±0.2 | ±0.2 | ±0.4 |

In order to determine the mineralogy of the Champlain Sea Clay, a random mount was prepared so that the primary minerals and phyllosilicates could be identified. Quartz is identified by the small peak at 4.25 and the much stronger peak at 3.35 Angstrom, although this latter also coincides with the third-order peak of the 10 Angstrom mineral; feldspar is identified by the peaks at 4.04, 3.20, 3.15 and 2.95 Angstrom. The amphibole, at 8.4 Angstrom, shows up clearly on the oriented traces, i.e., Figure 6.2, but is only present as a weak peak in Figure 6.1, indicating that this material is probably composed of cleavage fragments, such that the 8.4 Angstrom peak is enhanced by orientation of these particles.

The random XRD trace allows for the identification of both illite, a dioctahedral 10 Angstrom mineral, and biotite, a trioctahedral 10 Angstrom mineral. The illite is distinguished, on the basis of peaks at 2.56 and 1.50 Angstrom, from the biotite which has similar peaks at 2.64 and 1.54 Angstrom [Grim 1968]. Although chlorite is also a trioctahedral mineral, it does not possess strong peaks at either of these Angstrom spacings, although the chlorite is identified, on the random trace, by the strong but broad peak at 3.48.

Considering the high proportion of clay- and fine clay-sized material, the specific surface area of 90 $m^2/g$ is rather low. This perhaps reflects the unusual shape of the clay-sized materials in the sample. For a constant "equivalent spherical diameter", it might be expected that the specific surface area would correlate inversely with the actual form, or degree of equidimensionality, of the particles. Inversely, clay minerals have high specific surface

FIGURE 6.1



XRD analysis of random sample of untreated Champlain Sea Clay (2 X $10^4$ Full Scale).

area not only because of their small size but also because of their blade shapes. In contrast, rock flour, though angular, is believed to comprise particles of more equant shape and, hence, lower specific surface area. An exception to this appears to be quartz [Moon 1973, Smalley and Cabrera 1973] which, on grinding, may attain plate shapes. Quantitative XRD analysis of other Champlain Sea Clay samples [McKyes, Sethi and Yong 1974] indicates, however, that quartz is a minor (c 10%) constituent of the crystalline components of the sediment. The relatively low CEC value of 16.3 m.e./100 g is also indicative of the presence of non-clay minerals in the clay-sized fraction..

The values obtained for the plasticity limits of C1 are 30.3, 55.4 and 25.1 for the plastic limit, liquid limit and plasticity index respectively, values which are considered low, in comparison to material with a similar percent clay from the Ottawa area [Sangrey and Paul 1971].

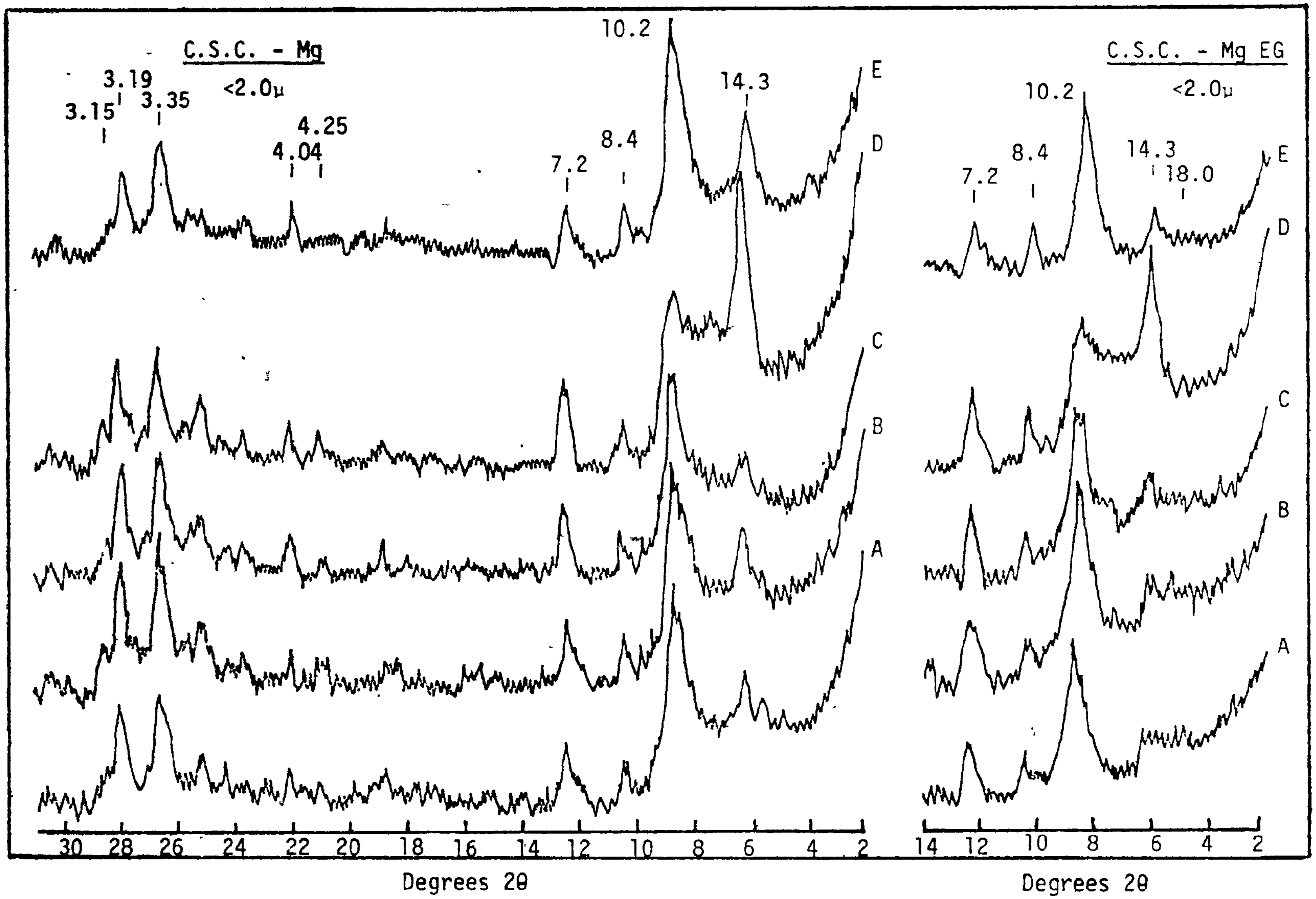
### 6.2b Treated to Remove Soluble Salts (C2).

The chemical analysis of the treatment extracts are presented in Table 6.1; as with the extracts for the Queenston Shale Clay sample, Na was not determined on the C1 extracts. The value obtained for Na from Phase I, 0.10 mg/g, is slightly higher than the value for Ca in Phase II; the concentrations of other cations are significantly lower than those of Ca. The value obtained for Al extracted appears to be quite high; this is not readily explained in light of the mild nature of the extractant.

XRD analysis on an oriented sample of the fraction less than 2.0 micron in size, as part of the Phase I study, allows for the identification of the mineralogy. Quartz is identified in Figure 6.2 by peaks at 4.25 Angstrom and 3.35 Angstrom, while the peaks at 4.04, 3.19 and 3.13 Angstrom are diagnostic of feldspar. The 8.4 Angstrom peak has been identified as amphibole by some authors, for example, McKyes, Sethi and Yong [1974] and others, and as a regularly interstratified clay mineral by others [Soderman and Quigley 1965]. The persistence of this 8.4 Angstrom peak in the K-saturated, 550°C diffractogram (Figure 6.4) favours the interpretation that this peak is due to amphibole.

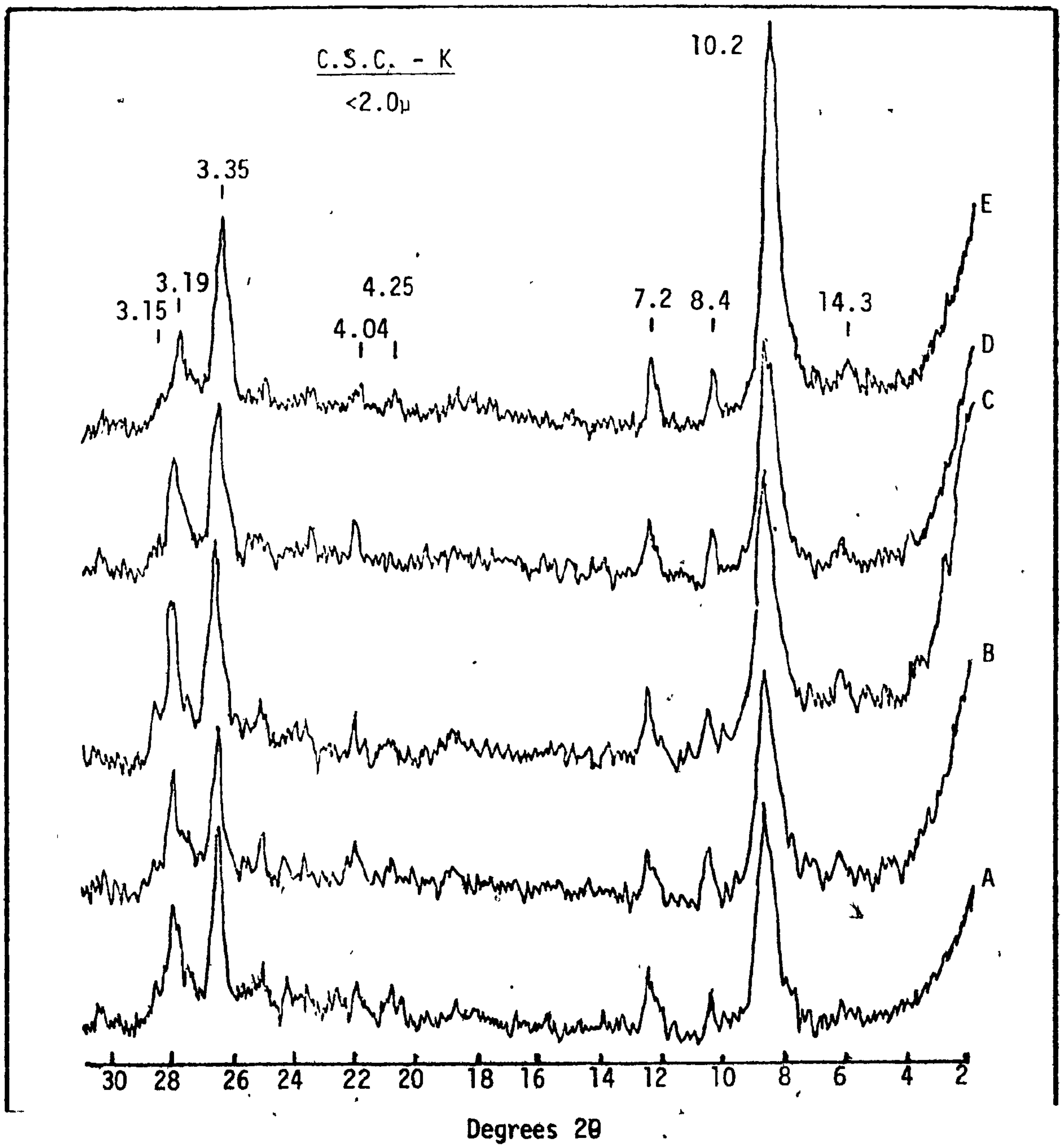
The clay-sized fraction also contains phyllosilicates. The peak at 10.2 Angstrom in Figure 6.2 indicates the presence of illite and, as demonstrated by the random XRD trace (Figure 6.1), biotite. Vermiculite, or degraded mica, is indicated by the asymmetrical 10.2 Angstrom peak and the peak at 14.3 Angstrom in the Mg-saturated, air-dried trace, which collapses to 10.2 Angstrom in the K-saturated, air-dried, and heated to 300°C traces (Figures 6.3 and 6.4). Chlorite is identified by the persistence of the very small 14.3 and 7.2 Angstrom peaks in the K-saturated 300°C trace, which disappear on heating to 550°C (Figure 6.4). Soderman and Quigley [1965] identify this mineral as an iron-rich chlorite, which therefore explains the lack of a well-defined 14 Angstrom peak and the presence of a much stronger, second-order 7.2 Angstrom peak. The presence of a swelling clay mineral in C2 is indicated on the Mg, ethylene-glycol trace by the rise in background noise between the 14 Angstrom peak and lower 2θ angles, which virtually "fills-in" the trough, visible in the Mg, air-dried trace (Figure 6.2). Montmorillonite has a 12.4 to 12.8 Angstrom peak in the K-saturated, air-dried state; the very low

FIGURE 6.2



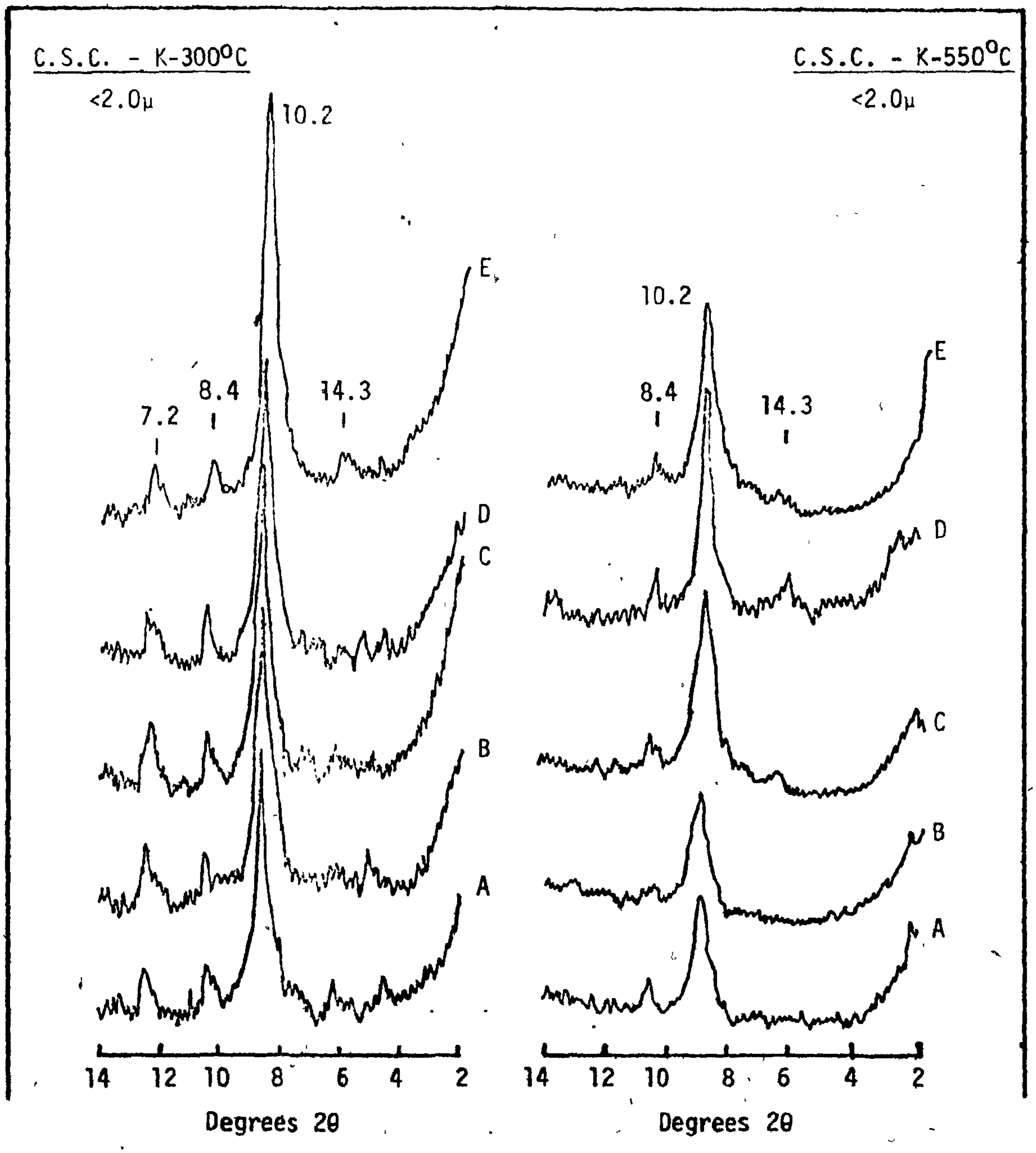
XRD analysis of the Champlian Sea Clay sample treatments: A. Removal of soluble salts. B. Homoionization. C. SAB. D. SAB + NaOH + CBD. E. SAB + KOH + oxalate. (2 X $10^4$ Full Scale)

FIGURE 6.3



XRD analysis of Champlain Sea Clay treatment: A. Removal of soluble salts. B. Homoionization. C. SAB. D. SAB + NaOH + CBD. E. SAB + KOH + oxalate. (2 X $10^4$ Full Scale)

FIGURE 6.4



XRD analysis of the Champlain Sea Clay sample treatments: A. Removal of soluble salt. B. Homoionization. C. SAB. D. SAB + NaOH + CBD. E. SAB-KOH-oxalate. (2 X $10^4$ Full Scale) level of background in this region ($7^{\circ}2\theta$) in Figure 6.3 does not lend itself to the interpretation of the swelling mineral as montmorillonite, although it could be a swelling chlorite, or perhaps a portion of the mixed mineral, illite/vermiculite, which has had some of the net negative charge, satisfied by the adsorption of amorphous iron compounds, as indicated by Soderman and Quigley [1965]. This last aspect will be discussed at greater length in relation to the extraction of iron and silicon compounds.

The treatment, with its mixing steps, has caused noticeable disaggregation of the silt, with a corresponding increase in the amount of clay-sized material, and a much smaller increase in the fine clay fraction (Table 6.2). The increase in specific surface area, from 90 (C1) to 98 (C2) mirrors this disaggregation although the change is within the degree of analytical error inherent in the technique. The slight increase in CEC is not significant, in relation to the analytical error.

The increase in plasticity as a result of the removal of the salt is the opposite of that expected by the leaching theory for illitic-rich material. The reasons for this increase are not known. In part it may reflect the disaggregation of some of the silt into clay-sized materials, but in view of the increase in activity (0.34 to 0.39), this is unlikely to be the major cause. It may reflect the existence of swelling minerals in the materials. A third possibility is that minor oxidation of iron compounds occurred during the treatment, a factor known to increase plasticity [Moum and Rosenqvist 1957].

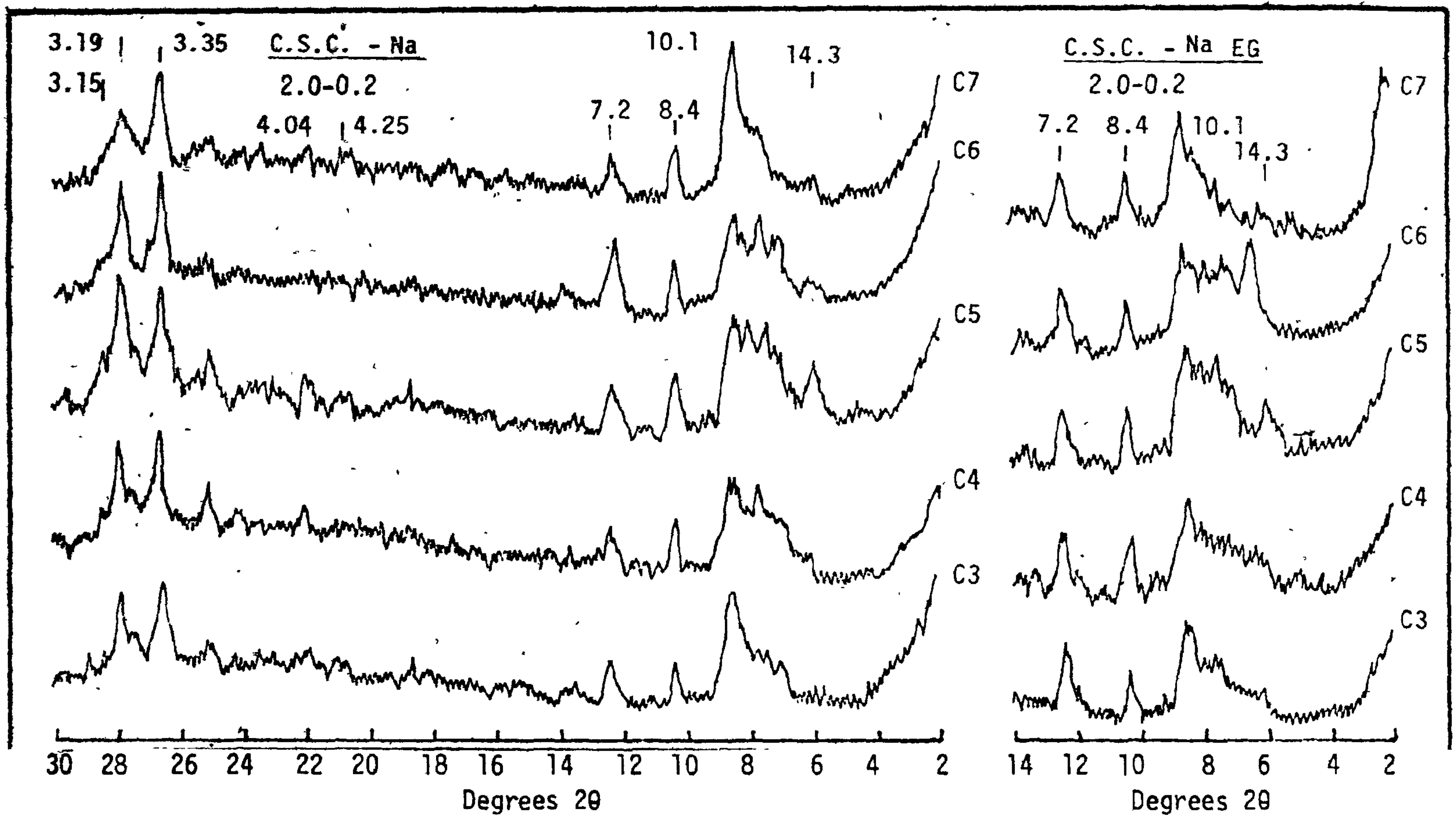
### 6.2c Na-Homoionized Sample (C3).

The homoionization procedure resulted in the extraction of a considerable proportion of Ca from the sample (1.28 mg/g) and lesser amounts of Mg and K (Table 6.1). The amounts of the divalent cations Ca and Mg form a larger proportion of the exchangeable cations than the monovalent cations, since the amount of Na originally on the exchange sites cannot be determined from the NaCl homoionization extracts; this calculation was based on the CEC and the m.eq./100 g of the divalent cations exchanged during the homoionization procedure. This is in keeping with the preferential adsorption of these divalent cations by clay minerals [Yong and Warkentin 1975].

The XRD traces (B) presented in Figures 6.2 to 6.4 indicate that the homoionization procedure does not affect the mineralogy, although for some unexplained reason, the 8.4 Angstrom peak of amphibole is virtually absent from the K-saturated 550°C trace (Trace B, Figure 6.4). The Na-saturated traces, Figures 6.5 and 6.6 for the 2.0-0.2 and <0.2 fractions, indicate the dominance of the 10 Angstrom mineral and the broad shoulder in the region of 12.5 Angstrom indicates the presence of the vermiculite portion of the mixed-layer mineral. The chlorite peak at 14.3 Angstrom is not defined, although the presence of this mineral in the 2.0-0.2 micron fraction is indicated by the 7.2 Angstrom peak. The <0.2 micron fraction produces a trace with relatively poor definition of any of the clay minerals, confirming the amorphous (to XRD) nature of this material.

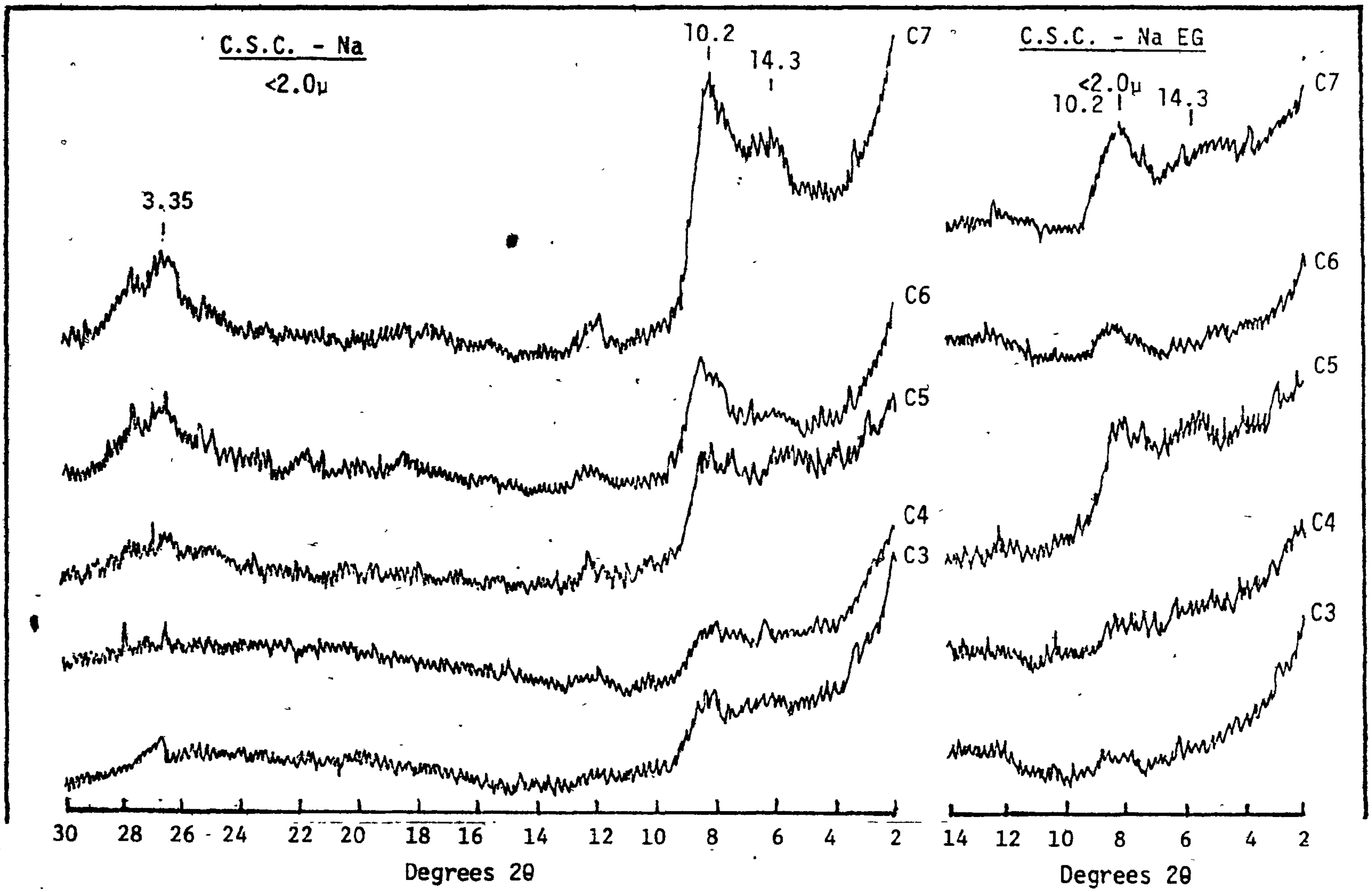
The particle size analysis data reveals a surprising increase in the amount of silt-sized material, indicating that perhaps aggregation of the

FIGURE 6.5



XRD analysis of the Champlain Sea Clay sample treatments: C3. Homoionization. C4. SAB. C5. SAB + NaOH. C6. SAB + NaOH + CBD. C7. SAB + KOH + oxalate. (2 X $10^4$ Full Scale)

FIGURE 6.6



XRD analysis of Champlain Sea Clay sample treatments: C3. Homoionization. C4. SAB. C5. SAB + NaOH. C6. SAB + NaOH + CBD. C7. SAB + KOH + oxalate. (2 X $10^4$ Full Scale) clay particles has taken place, since the amount of material extracted is insufficient to account for the relative drop in the amount of clay-sized material. The other possibility is that the sample was not completely homogeneous and the increase in the amount of silt is independent of the treatment. Despite the change in the grain size analysis, the specific surface area does not differ significantly from C1 and C2. The increase in CEC to a value of 17.7 compared to 16.3 (C1) and 16.5 (C2) is likewise not in excess of the analytical error.

There is a small decrease in plasticity as a result of homoionization, but this may merely reflect the decrease in the clay-size fraction; the activity (0.39) remains unchanged. The actual decrease in both of the limits is mildly surprising in view of the possible aggregation of clay particles into silt aggregates, but in any case is not a major change. The minor extent to which Na-homoionization affects the plasticity is somewhat surprising in view of the predominance of divalent cations on the original exchange complex.

### 6.2d Treated to Remove Carbonates (C4).

The SAB extraction, performed on C4, resulted in the extraction of a significant portion of iron and lesser amounts (relative to the homoionized sample Q3) of Ca and Mg. This may be due to the removal of iron carbonates, or it could be due to the production of soluble iron acetate from the most readily soluble iron compounds in the sample. The amounts of Mn, Si and Al are also greatly in excess of the amount removed by the homoionization procedure, which may indicate either chemical or structural association between the carbonate and Fe, Mn, Si and Al compounds in the material. The SAB treatment is considered to be too mild to dissolve the crystalline silicates; thus the material extracted is most probably amorphous.

The XRD analysis of the <2.0 micron fraction reinforces the conclusion that no significant alteration in the mineralogy of the phyllosilicates has occurred, although the slight broadening of the 10.1 Angstrom peak in Figure 6.2 does indicate that the removal of interlayer K has resulted in slight vermiculitization of the illite/vermiculite mixed mineral. This vermiculitization is also observed in the Na-saturated (2.0-0.2μ) trace (Figure 6.5), whereas the Na-saturated (<0.2μ) trace (Figure 6.6) indicates that the SAB treatment has not enhanced the clay mineral peaks; in fact, they are less well-defined than for C3, although this could merely be a function of slide preparation.

The amount of silt has again increased at the expense of the clay-sized fraction, while much of this decrease (in clay) is apparently due to the removal of material from the <0.2 micron fraction. Quantitative analysis of the extracts and assumptions regarding the cation:anion weight balance, indicates that dissolution could account for a weight loss of about 2 percent; if this occurred primarily within the clay-sized fraction it would easily account for the observed relative increase in silt. The drop in specific surface area is also in keeping with the removal of very fine material of high specific surface area. The CEC value increased significantly, indicating that the removal of this fine material has exposed a significantly large number of negatively-charged exchange sites. As with the Queenston Shale sample, this increase is consistent with the removal of colloidal carbonate material [Krauskopf 1967].

There is no significant change in the plastic limit following the SAB treatment, but the liquid limit, and hence plasticity, decreases markedly. Although this decrease coincides with a sharp decrease (2.1%) in the clay-sized fraction, as noted, there is also an appreciable fall in the activity from 0.39 to 0.30. This drop can be explained, perhaps, by the removal of positively-charged colloidal carbonate compounds from among negatively-charged clay particles, thus decreasing the remoulded strength of the material.

### 6.2e Successive Treatments to Remove Carbonates and Si and Al Compounds (C5).

The NaOH treatment, following the SAB treatment, resulted in the reprecipitation of Fe compounds (and to a much larger extent Mn compounds) which were not entirely removed from the sample by the SAB treatments. The large increase in the pH of the soil solution on the addition of the 0.5 N NaOH presumably caused the formation of insoluble iron hydroxides, which were not removed by the subsequent NaCl washings. The increase in the amounts of Mg, K, Si and Al removed may be partially due to dissolution of the trioctahedral mica; this is consistent with the decrease in silt-sized material and the lack of increase in the fine clay fraction (<0.24 microns). Additional data, not presented, on the <0.12 micron fraction, indicates that there was in fact an increase of 3 percent in the amount of this very fine material. This latter data, therefore, does not indicate the dissolution of fine mineral grains.

The XRD analysis of the Na-saturated samples indicates a significant change as a result of this extraction procedure. On the 2.0-0.2 trace (Figure 6.5) the 10.1 Angstrom peak is broadened considerably in the direction of low 2θ angles, although the absolute magnitude of the 10.1 Angstrom peak is not diminished compared to the C4 sample, indicating a degradation or vermiculitization of the mica fraction. The emergence of a strong 14.7 Angstrom peak indicates that deposition of iron hydroxides in interlayer positions has caused the production of a new chlorite phase; this is also supported by the increased size of the 7.1 Angstrom peak. The lack of significant change between the Na-saturated and Na-saturated, ethylene-glycol traces for this sample indicates that the swelling-mineral portion of the clay material has been stabilized by the precipitation of the iron hydroxides. The XRD of the fine clay fraction (Figure 6.6) indicates that the 10.1 Angstrom mineral, although severely degraded (as indicated by the broad plateau from 10.1 Angstrom to low 2θ angles) is emerging in this size fraction.

The decrease in specific surface area is not significant, nor is the increase in CEC. Presumably the CEC would have increased still further had the NaOH treatment not caused the reprecipitation of iron hydroxides on the mineral surfaces.

The insignificant decrease in the plastic limit is accompanied by a significant increase in the liquid limit and hence plasticity. The only significant changes observed in comparing C4 and C5 are, firstly, the precipitation of the iron oxides, and, secondly, the large increase in fine colloidal materials, believed to be 'dispersed' biotite. Those changes would provide opposite effects in terms of electrostatic surface charges; hence, perhaps, the lack of a significant change in CEC. The increase in abundance of both positive and negative electrostatic charges would be expected, however, to augment resistance to shear and hence increase the liquid limit. In addition, the chloritization of the vermiculite, and the stabilization of the swelling mineral, would act to decrease the liquid limit by reducing the amount of intracrystalline water during the plasticity determinations.

### 6.2f Treated to Remove Carbonates, Si, Al and Fe Compounds [NaOH-CBD] (C6).

The data on the chemical analysis of the C6 extracts are presented in Table 6.1. The most significant effect of the treatment is the removal of a large amount of Fe and lesser amounts of Si and Al. The relatively small increase in the amount of K extracted can be considered to support the conclusion that the CBD treatment has not greatly attacked the phyllosilicate minerals, although an alternative explanation is that the treatment dissolved the phyllosilicate flakes dispersed by the NaOH treatment, since if the proportion of (Mg,Fe):Al:Si is considered the composition can be seen to be relatively close to that of a (trioctahedral) biotite mica. The dissolution versus the extraction curve presented in Chapter 4 (Figure 4.3) indicates that the iron removed initially is much more readily extracted than the iron in the later extractions; thus the CBD treatment is felt to remove a significant proportion of amorphous material, although the NaOH-CBD treatment has been shown to have an adverse effect on the biotite mica [Dudas and Harward 1971].

The XRD analysis of Mg-and K-saturated o[illegible]ed slides indicates that the mineralogy has been somewhat transformed by the NaOH-CBD treatment. Figure 6.2, Trace D, for the sample in the Mg-saturated, air-dried state indicates that the mica has been largely transformed into vermiculite. The 14.3 Angstrom peak is larger than the 10.1 Angstrom peak; that this 14.3 Angstrom material is largely vermiculite is demonstrated by the strong 10.1 Angstrom peak following K-saturation (Figures 6.3 and 6.4). The 7.1 and 14.3 Angstrom peaks on the K-saturated 300°C and 550°C traces indicate that the chlorite is not severely affected by this treatment.

The diffractogram of the Na-saturated samples for the 2.0-0.2 micron fraction shows strong 10.1 and 12.3 Angstrom peaks indicating the vermiculitization of the material as mentioned above. Glycol saturation of this sample results in a shift of the 12.3 peak to 13.6 as a result of some minor swelling of the vermiculite, but no change in the intensity of the background in the region of 18 Angstroms. Soderman and Quigley [1965] have observed a similar change in a sample of "Leda Clay" of very similar mineralogy to the Champlain Sea Clay sample studied here. They attributed the elimination of the swelling mineral, listed as montmorillonite [Soderman and Quigley 1965, p. 182], to the removal of interlayer Al and Fe hydroxide compounds, which had acted to reduce the net charge per unit cell, and hence allowed the unextracted material to swell to 18 Angstroms on ethylene-glycol-saturation. Jackson [1968] terms this type of mineral swelling chlorite, a distinction that seems appropriate here, in light of the rock-flour origin of the sediment.

The particle size analysis indicates that no significant changes have taken place in the particle size analysis, indicating that the material has been removed relatively uniformly from all size fractions, or, more likely, that the material has been extracted primarily from the clay size fraction and the particle size distribution has been adjusted by means of disaggregation of the larger particles, due to the removal of cements, to produce the same distribution.

The specific surface area has not changed significantly from the value obtained in C4; on the other hand, the decrease in CEC is quite significant. This decrease is similar to the change observed in the Queenston Shale Clay as a result of the CBD treatment; and may similarly be attributed to the removal of material with a high negative charge. In this regard, Herbillon and Tran Vinh An [1969] have discussed the form of "silicon-iron mixed hydroxides" which, if present in the Champlain Sea Clay samples, as proposed by McKyes, Sethi and Yong [1974] would possess a large negative charge. The data for the amount of silicon extracted by the CBD treatment, which was not removed by the alkali dissolution procedure, would seem to favour the interpretation that there exists a mixed silicon-iron phase which, on the basis of its ease of extraction, might well be amorphous.

The plasticity of the C6 sample is considerably less than that of C4 or C5; a number of possible explanations for this are available: The removal of material with a high CEC, such as the amorphous iron-silicon hydroxides suggested by the work of Herbillon and Tran Vinh An [1969] would decrease the electrostatic forces acting between particles, and thereby reduce the strength of the material. The increased pH and the concomitant increase in negatively-charged edges, as indicated for kaolinite by Schofield and Samson [1954] would cause the sample to deflocculate. In addition, as mentioned for sample Q6 in Chapter 5, the adsorption or fixation of the citrate ion on edge sites would have the same effect as an increase in the pH, namely the dispersion of the material. In this context, the successive change in sedimentation volumes (in 1 N NaCl) after each treatment from C3 to C6 (discussed in Section 6.3) supports this conclusion that the drop in liquid limit arises from a marked deflocculation of the sediment.

Quigley [1972], in a discussion of the possible effects of the CBD treatment (and an EDTA treatment, which is also a complexing technique for the removal of iron and aluminum compounds) on the resistance of a remoulded Champlain Sea Clay (and by inference on its liquid limit) interpreted a decrease in strength, at constant water content, as a result of conversion of the swelling clay minerals present to vermiculite; the reduced interlayer water would produce an increase in intercrystalline water and thus a decrease in resistance (and also liquid limit). Such a change should also produce an increase in CEC, as a result of the removal of the iron and aluminum hydroxides from negatively-charged sites; this did not occur in sample C6, and fails to substantiate this view.

### 6.2g Treated to Remove Carbonates, Si, Al and Fe Compounds [KOH-Oxalate] (C7).

The increase in the amount of Ca removed by the C7 treatment is not due to the effect of the KOH-oxalate, but rather represents an increase in the amount of Ca extracted by the initial SAB treatment. The discrepancy with the other SAB-treated samples is thought to be due primarily to inhomogeneity among the samples. Significantly more Mg and Fe were removed by this treatment although Dudas and Harward [1971] found that the KOH-oxalate treatment was less destructive to the phyllosilicates, particularly in regard to biotite, than the NaOH-CBD treatment. Some of the difference is probably due to the more rapid treatment of this sample in which a centrifuge was employed to sediment the material, avoiding the prolonged gravity sedimentation. The amounts of Si and Al are less than the amounts removed by the NaOH-CBD treatment, which supports the conclusion that less of the phyllosilicate clay minerals were destroyed. In particular the amount of Al at 1.6 mg/g removed is less than the values of 3.9 mg/g (C5) and 5.1 mg/g (C6), although McKeague and Day [1966] present evidence that the oxalate is a stronger extractant of Al than is the CBD.

The XRD analysis indicates that the 10.1 Angstrom mineral was not seriously degraded by the KOH-oxalate treatment; the increased intensity of the 10.1 Angstrom peak (Trace E) in the Mg-saturated state, over the homoionized and SAB extracted samples (Traces B and C in Figure 6.2) is believed to be primarily a consequence of removal of amorphous material rather than K-fixation of vermiculite. The Mg-saturated, ethylene-glycol trace in Figure 6.2 indicates that the swelling mineral was not drastically affected by the treatment, so that the original mineralogy is largely unaffected by this extraction procedure. The Na-saturated trace of the 2.0-0.2 micron fraction confirms this for the material in the Na-saturated state (Figure 6.5), although the swelling component is not readily identifiable. The fine clay fraction possesses a much stronger clay mineral peak in the region of 10-14 Angstrom, although this material shows the largely interstratified nature of the illite/vermiculite clay mineral assemblage of this small size fraction. Of the treatments capable of removing the amorphous iron, aluminum and silicon compounds, this treatment apparently causes the least amount of degradation of the clay minerals, as indicated earlier by Dudas and Harward [1971].

The increase in the amount of clay-sized material is in keeping with the hypothesis that the material removed in excess of that removed in C6 was present as coatings on the clay particles. The increase in the SSA is less than the analytical error, but there is a large drop in the CEC following the treatment, which is attributed to the removal of negatively-charged particles from the material, as was the drop from C5 to C6.

As a result of the KOH-oxalate extraction, the plastic and, particularly, the liquid limit values decreased; the plasticity index in fact decreased to a very low value (10.8), equivalent to an activity of 0.14, both considerably less than the control sample (C3). As with the C5 sample, this decrease may be due to the removal of the amorphous material which contributes significantly to the CEC value and to the electrostatic interaction between grains; or, on the other hand, it may be due to the dispersant action of the oxalate ion, becoming very strongly bonded onto the edge sites of the octahedral layer and resisting exchange for Cl during the NaCl homoionization washings. Schofield and Samson [1954] have previously emphasized the ability of oxalate adsorption on edge sites to neutralize positive edge charges on kaolinite, and hence cause deflocculation of these suspensions, and the same mechanism is probably of more general applicability in creating dispersed fabrics and low liquid limits than reported in geotechnical literature.

## 6.3 Summary of the Factors Affecting the Plasticity of the Champlain Sea Clay.

In an examination of the various factors affecting the plasticity of the seven Champlain Sea Clay samples, the most obvious correlation is the decrease in plasticity which occurs on removal of Fe. Whether any conceptual significance can be attached in this is, however, dubious in view of possible differences in the chemistry and physical character of Fe compounds extracted in each treatment. For the last four treatments, the changes in plasticity are strongly correlated with changes (in the same direction) in CEC. However, bearing in mind that CEC was determined at pH 8.2, that pH values of the soil paste after treatments ranged from 7.1 to 8.5; and that CEC is a function of pH, it would be dangerous to draw conclusions from this pattern.

In looking at the seven samples as a whole, the C7 sample is distinctive in the extent of the decrease in its liquid limit and the fact that this occurred at neutral pH; it is suggested here that specific adsorption of the peptizing oxalate ion is the major reason for this. The other six samples show a reasonable inverse correlation between plasticity index and pH, but C4 and C5 fall somewhat below the "best fit line". This dependence on pH again suggests that suppression of positive edge charges and consequent deflocculation appears to be an important mechanism in lowering the liquid limit. Sedimentation volumes (after the final washing with 1 N NaCl), which are available for Q3 to Q6, agree with this interpretation. The changes in volume (875 ml; 700 ml; 950 ml; 775 ml) follow the changes in liquid limit (58; 50; 55; 43) and the pattern is consistent with the view that dispersion (i.e., deflocculation) and plasticity are inversely related, whatever the reasons for the change in dispersion might be.

## Chapter Seven:

## CONCLUSIONS

The application of selective dissolution techniques to the study of the role of various soil constituents has produced data open to a number of interpretations. The treatments applied to the Queenston Shale Clay sample, which contained primary and secondary minerals of a type found in weathered soils, did not result in any unexpected alteration of the mineralogy. This is not surprising, since the techniques used in the study were developed for the pretreatment and analysis of "soils" (used here in the pedological sense). The effect of some of the treatments on the Champlain Sea Clay sample produced severe alteration of the mineralogy. In particular the treatment sequences using SAB + NaOH and SAB + NaOH + CBD resulted in the vermiculitization of the biotite mica, as indicated by XRD analysis and by the amount of K extracted by the treatments. The use of KOH in place of the NaOH and acidified ammonium oxalate in place of the sodium citrate-bicarbonate-dithionite reagents alleviates this problem; although the possibility that naturally degraded, or vermiculitized mica, will "fix" potassium or ammonium in interlayer positions with this treatment cannot be ruled out. The mineralogy of the Champlain Sea Clay is very readily altered by <u>any</u> pretreatment capable of removing iron and aluminum hydroxide material, since it is apparent that these metallic compounds are in some way responsible for the production of the swelling clay mineral components.

As originally conceived, the purpose of the study was to determine the effect of the amorphous soil constituents on the plasticity of the two clay soils, one for which there are virtually no geotechnical problems, and the other for which the geotechnical problems are severe. Although the treatments used in this study were found to be effective in extracting the amorphous components with limited alteration of the mineralogy, as discussed above, examination of the experimental results does not allow for a simple interpretation of the role of the amorphous phase. The variations in properties not related to the amorphous material appear to be of equal, if not greater, importance in determining the plasticity of the material.

The role of the amorphous phase (disregarding for the moment the other changes which have resulted from the treatments of the material) can be seen as one of a "binding" agent between the particles, thus forming stable aggregates. This "binding" can occur in two distinct ways: 1) as cement between particles, or 2) as material which contributes significantly to the electrochemical interactions among particles. The first has the effect of forming stable pores within aggregates, thus increasing the plastic and liquid limits by approximately equal amounts, while the second increases the "activity" of the clay-sized material in the sense proposed by Skempton [1953a], in that it causes the material to behave in a more "active" manner. This higher activity of the original untreated material is indicated by both its higher plastic and liquid limits, particularly the latter, thereby accounting for the higher plasticity index.

Of the other changes in properties caused by the treatments, the effect of increased pH and the adsorption of organic anions on edge sites of the clay minerals are considered to be of the greatest importance. The resulting neutralization and perhaps reversal [Van Olphen 1963] of the positive edge charge has the effect of peptizing, or deflocculating, the sediment. This mechanism has been demonstrated for kaolinite by Schofield and Samson [1954], and the effect of pH alone on the plasticity of kaolinite was discussed by Warkentin [1964]. The effect of deflocculation of non-swelling clay on the liquid limit, in particular, is significant. The elimination of the edge-to-face bond as the dominant fabric interaction, in a soil being tested for plasticity, results in a decreased resistance to shear at an unchanged water content and hence a concomitant decrease in liquid limit and plasticity.

The significance of peptizing agents on the sensitivity of naturally-occurring illitic clays from Sweden has been recognized by Soderblom [1959 and 1966]. Since the sensitivity is largely a result of a high liquidity index, any alteration in the chemistry of the pore fluid, which affects the net interaction forces among clay particles and results in a reduction of the liquid limit without changing the water content, will increase the sensitivity of the material. The presence of minor amounts of organic material in much of the post-glacial clays may be of more significance than it has been accorded, since some organic acids are noted for their peptizing ability. Other peptizing agents, such as Mg and Na carbonates and some soluble silicates, can be expected to be found in trace quantities in these post-glacial sensitive clays.

Although the peptizing agents can account for the post-depositional decrease in liquid limit, the presence of amorphous material acting as cementing agents during the deposition and consolidation of the sensitive clay from eastern Canada must be taken into consideration in order to account for the high undisturbed strength and the very limited decrease in void ratio during consolidation. As mentioned in the introduction to Chapter 6, evidence is available to support the theory that iron compounds are sedimented with the detrital material; thus the origin of the amorphous material can be explained on these grounds, although the possibility exists that in situ weathering results in the release of iron, aluminum and silicon which subsequently polymerizes into the amorphous state.

The inability to distinguish between the roles of the introduced peptizing agents and the extracted material is attributed to the lack of proper control samples. The effect of pH, and hence the effect of deflocculation, could have been investigated, as could the role of a peptizing agent on samples not treated to remove the amorphous material. There was no reason to expect that the final pH would be anything but 7.0; perhaps the variations indicate inadequate washing during the homoionization of the samples. In addition, chemical dissolution techniques which do not contain the organic complexing agents could have been used; however, it should be emphasized that those techniques employed were chosen precisely because of the limited extent to which they were known to affect crystalline silicates; alternative dissolution techniques may have avoided the problem of peptization but created new ones of mineralogical damage. In this context it is perhaps significant that not only did the treatments used here extract considerably less Fe, Al and Si compounds than the treatment employed by McKyes, Sethi and Yong [1974] (c 10% compared to c 3.8%), but that the balance between peaks of primary and clay minerals on XRD traces was unchanged in this study, in contrast to the marked enhancement of the primary mineral peaks in HCl-NaOH treatment, on a similar sample, by those authors. This latter change could have been due to the much harsher extraction procedure [Schwertmann 1973] and a consequent enrichment of primary minerals, relative to clay minerals, in the residues analyzed by these workers. The choice of dissolution techniques used in the present study was made precisely to avoid this possible development.

Time limitations in the execution of this research, combined with a failure to anticipate the possible importance of "edge charges" on the plasticity of these materials, have led to the situation in which a number of interpretations are possible from the experimental data. Subsequent work will hopefully clarify this ambiguity.

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# APPENDIX

## Part 1. TREATMENTS USED IN PHASE I

### Preliminary Treatments:

Treatment 1. Washing out soluble salts.

1.1) 5 g sample placed in a 50 ml centrifuge tube with 25 ml of 50% methanol; mix, centrifuge and decant.

1.2) Add 25 ml of 95% methanol, mix, centrifuge and decant.

1.3) Add 25 ml of 95% acetone, mix, centrifuge and decant.

1.4) Repeat step (1.3).

Treatment 2. Homoionization with NaCl.

2.1) 5 g sample placed in 50 ml centrifuge tube with 25 ml of 1 N NaCl; mix, centrifuge and decant.

2.2) Add 25 ml of 1 N NaCl, mix, centrifuge and decant.

2.3) Repeat step (2.2).

2.4) Wash out excess salt as in (1.1) to (1.4).

Treatment 3. Removal of Carbonate Material.

3.1) 5 g sample placed in 50 ml centrifuge tube with 30 ml of 1 N Sodium Acetate buffer solution pH 5.0; mix and place in a 90°C water bath for 30 minutes, cool, centrifuge and decant.

3.2) Wash with 30 ml of sodium acetate buffer solution, centrifuge and decant.

3.3) Add 25 ml of 1 N NaCl, mix, centrifuge and decant.

3.4) Repeat step (3.3).

3.5) Wash out excess salts as in (1.1) to (1.4).

Treatment 4. Removal of Carbonate and Organic Material.

4.1) Proceed as for (3.1) to (3.3).

4.2) Add 10 ml of 30% hydrogen peroxide and place in a 65°C water bath; add 5 ml aliquots of hydrogen peroxide until reaction slows down (total hydrogen peroxide employed was 20 ml), add 25 ml of 1 N NaCl; mix, centrifuge and decant.

4.3) Add 25 ml of 1 N NaCl, mix, centrifuge and decant.

4.4) Repeat step (4.3).

4.5) Wash out excess salt as in (1.1) to (1.4).

## APPENDIX - TREATMENTS

Treatments Used in Phase I (cont'd)

Treatment 5. Removal of Organic Material.

5.1) Place 5 g sample in 50 ml centrifuge tube with 10 ml of sodium hypochlorite buffered at pH 9.5; mix, place in a boiling water bath for 30 minutes, cool, centrifuge and decant.

5.2) Add 10 ml of 1 N NaCl, mix, centrifuge and decant.

5.3) Repeat step (5.2) twice.

5.4) Repeat steps (5.1) to (5.3) twice.

5.5) Wash out excess salt as in (1.1) to (1.4).

Eight CBD Extractions:

Treatment 6. Removal of Iron Oxide and Hydroxides.

6.1) 2 g sample placed in 50 ml centrifuge tube with 20 ml of 0.3 M sodium citrate, 2.5 ml of 1 M sodium bicarbonate; place in 80°C water bath, when solution has reached 80°C, add .5 g of sodium dithionite, stir constantly for 1 minute and occasionally for 15 minutes; cool, centrifuge and decant.

6.2) Repeat (6.1) seven times.

6.3) Add 10 ml of 1 N NaCl, mix, centrifuge and decant.

6.4) Repeat step (6.3).

6.5) Wash out excess salt as in (1.1) to (1.4).

## Part 2. TREATMENTS FOR THE SEQUENCE TREATMENT EFFECT EXPERIMENT

Treatment A. Removal of Carbonates.

A.1) 0.5 g sample of homoionized sample placed in 50 ml centrifuge tube with 3 ml of 1 N sodium acetate buffer solution pH 5.0; place in a 90°C water bath for 30 minutes, cool, centrifuge and decant.

A.2) Add 5 ml of sodium acetate buffer solution, mix, centrifuge and decant.

A.3) Add 10 ml of 1 N NaCl, mix, centrifuge and decant.

A.4) Add 10 ml of 50% methanol, mix, centrifuge and decant.

Treatment B. Removal of Silica and Alumina.

B.1) Place 0.5 g of homoionized sample in a 50 ml centrifuge tube with 15 ml of 0.5 N NaOH; place in a 90°C water bath for 15 minutes, cool, centrifuge and decant.

## APPENDIX - TREATMENTS

Treatments for the Sequence Treatment Effect Experiment (cont'd)

B.2) Add 10 ml of 1 N NaCl, mix, centrifuge and decant.

B.3) Add 10 ml of 50% methanol, mix, centrifuge and decant.

Treatment C. Removal of Iron Oxides and Hydroxides.

C.1) Place 0.5 g of homoionized sample in a 50 ml centrifuge tube with 5 ml of 0.3 M sodium citrate, .6 ml of sodium bicarbonate; heat to 80°C in a water bath and add .125 g of sodium dithionite, stir constantly for 1 minute, and occasionally for 15 minutes, cool, centrifuge and decant.

C.2) Add 10 ml of 1 N NaCl, mix, centrifuge and decant.

C.3) Repeat steps (C.1) and (C.2).

C.4) Add 10 ml of 50% methanol, mix, centrifuge and decant.

## Part 3. TREATMENTS USED IN PHASE II

Sample 1. Untreated.

Treatment 2. Washing Out Soluble Salts.

2.1) Place 200 g sample in 4-1 beaker, add 1 litre distilled water and 1 litre methanol; mix, settle 48 hours, decant.

2.2) Add 1 litre 95% methanol, mix, settle 48 hours and decant.

2.3) Add 1 litre 95% acetone, mix, settle 48 hours, and decant.

2.4) Add 1 litre 95% acetone, mix, settle 48 hours and decant. Evaporate excess acetone at air temperature adding enough water to prevent sample from becoming dry.

Treatment 3. Homoionization with NaCl.

3.1) Place 200 g sample in 4-1 beaker, add 2 litres of N NaCl solution; mix, settle 48 hours and decant.

3.2) Add 1 litre N NaCl solution, mix, settle 48 hours and decant.

3.3) Add 1 litre N NaCl solution, mix, settle 48 hours and decant.

3.4)
to
3.7) Wash out soluble salt as per (2.1) to (2.4).

APPENDIX - TREATMENTS

Treatments Used in Phase II (cont'd)

Treatment 4. Removal of Carbonate Material.

4.1) Place 200 g sample in 4-1 beaker, add 1 litre sodium acetate buffer solution (pH 5.0), digest for 30 minutes in a 90°C water bath, settle 48 hours and decant (2-1 used for Queenston Shale Clay).

4.2) Add 1 litre of sodium acetate buffer solution, mix, settle 48 hours and decant.

4.3) Add 1 litre N NaCl solution, mix, settle 48 hours and decant.

4.4) Add 1 litre N NaCl solution, mix, settle 48 hours and decant.

4.5) to 4.8) Wash out soluble salts as per (2.1) to (2.4).

Treatment 5. Extraction of Silicon and Aluminum Compounds.

5.1) and 5.2) As per (4.1) and (4.2).

5.3) Transfer to 8-litre stainless steel beaker with 5 litres of water; heat to boiling, add 120 g solid NaOH dissolved in 1 litre water, boil 2½ mins., place in a cold water bath, settle 24 hours and decant.

5.4) Add 1 litre N NaCl solution, adjust pH to 7.0, settle 48 hours and decant.

5.5) Add 1 litre N NaCl solution, settle 48 hours and decant.

5.6) Add 1 litre N NaCl solution, settle 48 hours and decant.

5.7) Add 1 litre N NaCl solution, settle 48 hours and decant.

5.8) to 5.11) Wash out soluble salt as per (2.1) to (2.4).

Treatment 6. Extraction of Silicon, Aluminum and Iron Compounds.

6.1) to 6.4) As per (5.1) to (5.4).

6.5) Add 2 litres of .03 M Na-citrate and 250 ml of 1 N Na-bicarbonate, heat to 85°C in a water bath, add 50 g Na-dithionite, stir constantly for 1 minute and occasionally for 15 minutes, place in a cold water bath, settle 24 hours and decant.

6.6) Add 1 litre N NaCl solution, settle 48 hours and decant.

6.7) Repeat (6.5).

6.8) Add 1 litre N NaCl solution, settle 48 hours and decant.

## APPENDIX - TREATMENTS

Treatments Used in Phase II (cont'd)

6.9) Add 1 litre N NaCl solution, settle 48 hours and decant.

6.10) Add 1 litre N NaCl solution, settle 48 hours and decant.

6.11) to 6.14) Wash out soluble salt as per (2.1) to (2.4).

### Treatment 7. Extraction of Silicon, Aluminum and Iron Compounds.

7.1) Place 200 g sample in a 3-l beaker, add 1 litre of sodium acetate buffer; place in 90°C water bath for 1 hour, cool, centrifuge and decant.

7.2) Add 1 litre sodium acetate buffer, mix, centrifuge and decant.

7.3) Transfer to a 8-l stainless steel beaker with 5 litres of $H_2O$ and heat to boiling; add 1 litre of KOH (with 168.3 g KOH), boil for 2.5 minutes and immediately place in a cold water bath; settle 1 hour, centrifuge and decant.

7.4) Add 1 litre N NaCl solution, mix, centrifuge and decant.

7.5) Add 2 litres 0.2 M ammonium oxalate (pH 3.0) and shake for 4 hours in darkness; centrifuge and decant.

7.6) Add 1 litre N NaCl solution, shake, centrifuge and decant.

7.7) Add 1 litre N NaCl solution, shake, centrifuge and decant.

7.8) Add 1 litre N NaCl solution, shake, centrifuge and decant.

7.9) Add 1 litre 50% methanol, shake, centrifuge and decant.

7.10) Add 1 litre 95% methanol, shake, centrifuge and decant.

7.11) Add 1 litre 95% acetone, shake, centrifuge and decant.

7.12) Add 1 litre 95% acetone, shake, centrifuge and decant.