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CHEMICAL PROPERTIES OF CHAMPLAIN SEA SEDIMENTS

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ABSTRACT

Measurements of soluble components, and characterization of the charge on the mineral surfaces, are reported for five samples of the Champlain Sea sediments. Large amounts of magnesium, beyond the amount of dolomite present, were slowly released in solution from the broken surfaces of the minerals. Amorphous aluminosilicates made up less than 6% of the sample weight, and their removal did not improve the X-ray diffraction patterns or alter significantly the chemical properties of the sediments. Of the cation exchange capacity of 20 to 30 meq/100 g at pH 7, from 50 to 75% was found to be due to pH-dependent charge, which leads to preferential adsorption of monovalent ions. In equilibrium with artificial seawater, the samples had from 50 to 25% exchangeable sodium.

INTRODUCTION

The Champlain Sea sediments were deposited in an inland sea in late glacial times about 10 000 years ago (Karrow 1961). They are the parent materials for the productive soils of the St. Lawrence Lowlands, and form the subsoils for roads and engineering structures in urban areas and along rivers.

Brydon and Patry (1961) and Karrow (1961) considered the main source of the deposits to be igneous and metamorphic rocks of the Canadian Shield. The sediments are composed of ground-up primary minerals; mica and chlorite predominate, with smaller amounts of amphibole, quartz, and feldspar. The clay fraction usually contains small amounts of montmorillonite or interstratified illite–montmorillonite (Karrow 1961; Brydon and Patry 1961; Allen and Johns 1960).

The sediments were deposited in brackish water having a variable salt concentration, and the particles in this flocculated suspension settled out with a random particle arrangement, having a high porosity and consequently a high water content. When the sediment is disturbed, the random particle arrangement collapses because there is little interparticle bonding. The porosity then tends to decrease, the excess water becomes free, and the strength is greatly reduced. This sensitivity, and the large shrinkage on drying, cause problems in using the soils as foundation. While these unusual physical properties have stimulated many geotechnical studies, only limited information is available on geochemical properties. The primary minerals would be expected to have chemical properties, especially cation exchange characteristics, which would be different from those of other soils.

This paper presents measurements of soluble and amorphous mineral components and cation exchange characteristics of the Champlain Sea sediments.

EXPERIMENTAL

Five samples of the Champlain Sea sediments in the Ottawa Valley were chosen to provide a range in depth (Table I). In all samples, the air-dry soil

TABLE I

Description and properties of samples of marine sediments

Sample	Depth, ft.	Location	Description	Particle size analysis: % clay (<2 μ)	Particle size analysis: % silt (2–20 μ)	Particle size analysis: % sand (>20 μ)	Organic matter, %	pH: In H_2O	pH: In 0.01 M $CaCl_2$	Carbonates: Calcite, %	Carbonates: Dolomite, %
61-60	4	Macdonald College	Light grey clay with yellowish brown mottling	72	24	4	0.43	7.0	6.3	0	0
62-1	6	"	Light grey clay with pale yellow mottling	73	22	5	0.37	7.3	6.4	0	0
62-2	20	"	Light grey clay	71	23	2	0.74	8.2	7.6	3.4	1.9
61-62	26	Ottawa	Grey silty clay	62	30	2	0.89	7.9	7.7	0.8	0.5
61-61	45	"	Light grey sandy clay with white fossil remains	29	17	47	0.40	7.9	7.6	2.6	4.7

of less than 2 mm particle
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61-62	26	Ottawa	Grey silty clay	62	30	2	0.89	7.9	7.7	0.8	0.5
61-61	45	"	Light grey sandy clay with white fossil remains	29	17	47	0.40	7.9	7.6	2.6	4.7

of less than 2 mm particle size was used unless otherwise specified. Particle size was analyzed by the pipette method, dispersion with "Calgon", and stirring. Organic matter was measured by dichromate oxidation (Jackson 1958), the pH in 0.01 *M* $CaCl_2$ by the method of Schofield and Taylor (1955), and carbonates by the manometric procedure of Skinner *et al.* (1959). Incomplete analyses are reported for 61-62 because of an insufficient quantity of sample.

Soluble cations, exchangeable cations, and cation-exchange capacity of the soil were determined by the method of Yaalon *et al.* (1962). Calcium and magnesium were determined by complexometric titration with ethylenediamine tetraacetic acid (EDTA); calcium with calcein as the indicator (Van Schouwenburg 1961), and magnesium after separation of calcium with sodium tungstate, and using ammonium molybdate to suppress a possible phosphate interference (Middleton 1961). Lithium was determined at 673 mμ using a Beckman Model DU flame spectrophotometer. Chloride was determined by $Hg(NO_3)_2$–diphenylcarbazone complexometric titration (Clarke 1950). Xylene cyanole FF was added to the diphenylcarbazone – bromophenol blue mixed indicator.

Calcium and magnesium soluble in 0.1 *N* HCl and in 1 *N* NH_4OAc were determined as follows. A 0.500 g air-dry sample was placed in a 50 ml centrifuge tube with 40 cc of one solution and shaken for 1 hour. After the solution was centrifuged, the supernatant was removed. A further 40 cc of solution was added to the soil cake and shaken, and after 24 hours the supernatant was again removed. This operation was repeated for 11 more periods up to 1 632 h for HCl, and for 8 periods up to 1 152 h for NH_4OAc. The supernatant from the HCl extraction was treated with sodium diethyldithiocarbamate and isoamyl alcohol to remove interfering ions (Cheng *et al.* 1953), and Ca and Mg determined by complexometric titration with EDTA, using Eriochrome black T and Cal-red indicators (Patton and Reeder 1956).

Amorphous silica, alumina, and iron contents of the oven-dry, $<2\ \mu$, clay fractions were determined by the method of Hashimoto and Jackson (1960). X-Ray diffraction patterns were obtained for oriented films of clay dried onto glass slides. Total surface area was determined by the equilibrium ethylene glycol method of Bower and Goertzen (1959). Cation-exchange capacities of the $<2\ \mu$ fraction were determined by the micromethod of Mackenzie (1951).

The amount of permanent charge due to isomorphous substitution was taken as the milliequivalents of hydrogen present in a clay saturated with hydrogen. This was based on the assumption that only permanent charge (Schofield 1949) would be present at this low pH, below pH 4, and that this permanent charge would be balanced entirely by H ions. The clay was saturated with H by batch exchange with IR-120 exchange resin, and used immediately to prevent accumulation of aluminium and magnesium. Water and NaCl were added to give a 0.5% H-clay suspension in 0.5 *N* NaCl. It was assumed that the Na replaced all the H, and that the measured pH of this suspension gave the concentration of H present. This was calculated as meq of H/100 g soil. No correction from activity to concentration was attempted. This procedure was checked with three bentonite samples. The measured permanent charge varied from 76 to 89% of the total charge at pH 7. This agrees with the value of around 80% commonly assumed for bentonites.

The samples used for studies of cation equilibrium in artificial seawater were treated with 0.1 *N* HCl to remove carbonates, then neutralized with NaOH, and washed with NaCl. The excess salt was removed by ultrafiltration. The artificial seawater was made up from the formula of Whitehouse and McCarter (1958), using only those salts present in concentrations exceeding 30 mg/l. Technical grade NaCl was used. This contained about 1% KCl, which made the K concentration in the seawater too high.

A 4 g sample of soil and 33 cc of artificial seawater were shaken overnight and centrifuged, and the supernatant removed by decantation. Four more aliquots of seawater were added and shaken for 15 minutes and centrifuged, and the supernatant removed. The solution decanted after the last centrifuging was analyzed as a check on the cation concentration in the seawater. The weight of seawater occluded in the soil cake was calculated from the known weights of oven-dry soil and centrifuge tube.

The soil cake with occluded seawater was washed three times with NH_4OAc by the centrifuge procedure, and the amounts of Ca, Mg, K, and Na in the washings were determined after destruction of the acetate. From the concentrations of these cations in seawater, and the calculated volume of the occluded seawater, the amounts of these ions in the NH_4OAc extracts attributable to seawater were known. The differences were the amounts of exchangeable Na, K, Ca, and Mg held by the soil.

DISCUSSION OF RESULTS

Soluble Components

Preliminary experiments had indicated that it was impossible to prepare homoionic clay, that is, a sample with only one species of exchangeable cation, because magnesium and, to a lesser extent calcium, became soluble in the extracting solutions and gradually replaced other cations. The nature of this cation release from the sediments was, therefore, studied first.

The calcite and dolomite contents of the samples agree with the more extensive analyses by Brydon and Patry (1961). The total carbonate and the proportion of dolomite to calcite increase with depth (Table I). Samples 62-2 and 61-61 were separated into different size-fractions by sedimentation and decantation, and total carbonate of some of the fractions was determined. The clay fraction contains about 1% CO_2 while the sand and silt fractions contain from 4 to 8% CO_2 (Table II). The larger proportion of the carbonate in the soil is in the sand and silt fractions, even where these fractions are a smaller part of the total sample.

Removal of carbonates by treatment for ½ h with acid did not remove all of the soluble cations. Samples extracted for longer periods in ammonium acetate and HCl continued to release magnesium (Table III). Most of the calcium released is accounted for by the calcite and dolomite present, but large additional amounts of magnesium are released in both extracting solutions.

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TABLE II

Distribution of carbonate in size fractions

Sample	Fraction	Carbonate, % CO_2	% of total carbonate
62-2	Whole soil	2.2	100
	clay (<2 μ),	1.2	39
	sand, and silt (calcd. by difference)	5.4	61
61-61	Whole soil	3.4	100
	clay (<2 μ),	0.9	8
	sand (>20 μ),	3.8	52
	silt (calcd. by difference)	8.1	40

TABLE III

Calcium and magnesium released in 1 *N* NH_4OAc and 0.1 *N* HCl, corrected for soluble and exchangeable Ca and Mg

	Ca and Mg present in carbonate, meq/100 g		Ca and Mg released in 1 *N* NH_4OAc, meq/100 g				Ca and Mg released in 0.1 *N* HCl, meq/100 g			
			8 hours		48 days		1 hour		70 days	
Sample	Ca	Mg	Ca	Mg	Ca	Mg	Ca	Mg	Ca	Mg
61-60	0	0	0	0	16	65	N.d.	N.d.	N.d.	N.d.
62-2	87	20	N.d.*	N.d.	N.d.	N.d.	71	41	83	355
61-62	21	5	N.d.	1	N.d.	106	38	17	42	337
61-61	102	51	10	5	31	47	128	59	139	267

*Not determined.

This release of magnesium was still continuing after the periods shown in the table.

The release of magnesium in 0.1 *N* HCl is plotted in Fig. 1 as the amount

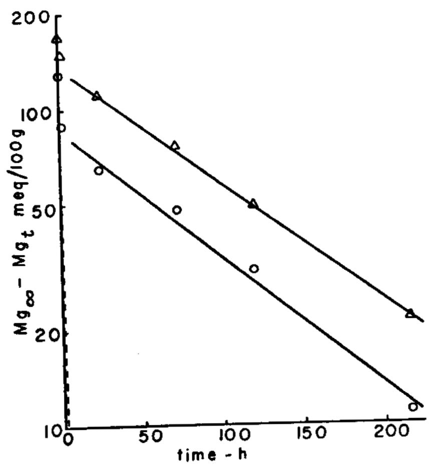

FIG. 1. Rate of release of Mg in 0.1 *N* HCl from Champlain Sea sediments. △, samples 62-2 and 61-62; ○, sample 61-61; - - -, release of Ca for these samples plotted on same scale.

of magnesium remaining vs. time. After the initial rapid release, which can be attributed to dissolution of dolomite, the logarithm of the amount of magnesium remaining vs. time is a straight line. This result, characteristic of a first-order reaction, can be interpreted as meaning that the magnesium is coming from one source. This interpretation is also indicated by the observation that the slopes of the two lines are approximately the same, even though different amounts of magnesium are released. The release of calcium, plotted on the same scale, shows that there is no comparable component which releases calcium slowly. The rapid solution of calcite is shown by the almost vertical line.

The magnesium probably comes from the surfaces of magnesium-bearing minerals such as amphibole and chlorite. It has been shown frequently that ions are released from the surfaces of minerals freshly ground in the laboratory. These sediments, which were ground by the ice and deposited in water with little subsequent weathering, would be expected to show a similar release of cations. This release accounts for the persistence of a large proportion of exchangeable magnesium, even in surface soils from which all of the carbonates have been leached.

Amorphous Material

These sediments exhibit properties which could be due to the presence of significant amounts of amorphous aluminosilicates. The X-ray diffraction pattern from oriented films of clay-size particles is weak. Samples in suspension show partial flocculation at intermediate salt concentrations, and in sodium silicate solution. Part of the material is flocculated and part remains in suspension. The same minerals were found in each fraction, but the peaks of the X-ray diffraction patterns of the suspended fraction were weaker. This could result from lesser crystallinity or smaller size of the suspended material. Samples at a water content in the plastic range also show a marked increase in stiffness on addition of NaOH, which could result from reaction of the hydroxide with free silicate.

The clay fraction of the samples examined contained only small amounts of amorphous aluminosilicates soluble in boiling NaOH (Table IV). The molar

TABLE IV

Amorphous material dissolved from the clay fraction by rapid NaOH boiling and free-iron removal treatments

Sample	Materials removed, %			Molar ratios	
	SiO_2	Al_2O_3	Fe_2O_3	SiO_2/Al_2O_3	SiO_2/R_2O_3
61-60	4.31	1.59	2.50	4.51	2.29
62-1	4.27	1.49	2.39	4.76	2.36
62-2	3.32	1.24	1.39	4.55	2.68
61-61	3.48	1.21	1.34	4.88	2.85

ratios of SiO_2/Al_2O_3 are fairly constant and within the range of the molar ratios of 4.1 to 5.4 for the total soil reported by Talvenheimo (1948), Schalin (1951),

and Burn* for samples of th
of the samples used in this
(SiO_2/R_2O_3) ratios increase
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Characterization of Charge

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*Personal communication, K. N
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Molar ratios	
SiO_2/Al_2O_3	SiO_2/R_2O_3
4.51	2.29
4.76	2.36
4.55	2.68
4.88	2.85

the range of the molar ratio s
heimo (1948), Schalin (1951),

and Burn* for samples of the Champlain Sea sediments. The total composition of the samples used in this study was not determined. The silica–sesquioxide (SiO_2/R_2O_3) ratios increase slightly with depth and are lower than the ratios of 2.9 to 4.0 found for the whole soil (see references above). This is due to the larger proportion of iron in the amorphous material. A larger amount of free iron near the surface is expected.

Removal of this amorphous material had little effect on the X-ray diffraction patterns. The peak intensity was enhanced slightly in some samples, probably as a result of more parallel orientation of particles on the slide. The exchange capacity and surface area were decreased slightly in two samples and unchanged in the other two. It appears that the component dissolved out as amorphous material is poorly crystalline material of the same composition, and with approximately the same properties, as the rest of the soil. The weak X-ray diffraction patterns are due to small crystal size and possibly shape, rather than to the presence of amorphous material coating a crystalline component.

Characterization of Charge

The source of the electrical charge on soil particles, whether from isomorphous substitution or broken bonds, influences the ratios of exchangeable cations. The Champlain Sea sediments were initially in equilibrium with salt or brackish water. Subsequent deposition of calcareous materials supplied calcium, which exchanged for some of the other cations. An understanding of the geochemistry of the sediments requires a knowledge of the exchangeable cations present.

The exchangeable cations of the sediments in the natural state are dominantly calcium and magnesium, with the proportion of magnesium highest for the surface samples (Table V). This results from magnesium being released, as discussed above, after the carbonates which supply calcium are leached from the upper layers. The total exchange capacity of the $<2\ \mu$ clay fraction is 33 meq/100 g for the two surface samples, and about 20 for the lower three samples. These values cover the range of about 20 determinations which have been made on clay fractions from soils developed on the Champlain Sea sediments.

The H-saturated clay fractions in 0.5 N NaCl had pH values of about 3.5. This hydrogen ion concentration was considered a measure of permanent charge that was due to isomorphous substitution, and the cation exchange capacity at pH 7 as total charge. The difference between the two is pH-dependent charge. On this basis, from one-half to three-quarters of the total charge at pH 7 is pH dependent (Table V). These values for pH-dependent charge are high when compared with values reported in the literature for soils. But, because these sediments contain only small amounts of clay minerals, most of the charge must be associated with broken surfaces of primary minerals, and this would be expected to be pH dependent.

*Personal communication, K. N. Burn, Division of Building Research, National Research Council, Ottawa.

TABLE V

Cation exchange capacity and exchangeable cations

Sample	Soluble cations, meq/100 g		Exchangeable cations, meq/100 g		Cation exchange capacity, (meq/100 g)	C.E.C. of clay fraction, (meq/100 g)	Measured permanent charge for clay fraction, (meq/100 g)	% pH dependent charge	Surface area, m^2/g
	Ca	Mg	Ca	Mg					
61-60	—	—	10.6	9.2	20.1	33	8	76	170
62-1	—	—	11.0	11.2	22.3	33	8	76	210
62-2	0.3	0.1	11.2	4.9	16.1	22	8	64	130
61-62	N.d.	N.d.	N.d.	N.d.	11.9	19	N.d.	—	N.d.
61-61	1.5	1.0	4.7	1.9	6.5	18	9	50	100

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Exchangeable cations in equilibri

Sample	Sum of exchangeable Ca, Mg, Na, and K, meq/100 g
61-60	19.5
62-1	18.3
62-2	13.5
61-61	4.5

The proportion of exchan
VI) is summarized in the Ga
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The higher exchange capacity and higher proportion of pH-dependent charge in the surface samples probably results from the distribution of particle sizes. There is a larger proportion of $<0.2\ \mu$ material in the clay fraction in the surface samples. These smaller particles would have a higher proportion of surface area in broken surfaces, and hence, a higher exchange capacity. The measurements of total surface area by glycol retention (Table V) bear out this explanation.

The charge on soil particles can be characterized by the relative adsorption of different cations. A preliminary study was made of the cation ratios for these sediments by measuring the proportion of different cations in equilibrium with seawater.

TABLE VI

Exchangeable cations in equilibrium with seawater and calculated Gapon exchange constants

Sample	Sum of exchangeable Ca, Mg, Na, and K, meq/100 g	Exchangeable cations (amount expressed as % of exchange capacity)				Gapon exchange constant $(\text{liter/mole})^{1/2}$
		Na	K	Ca	Mg	
61-60	19.5	50	18	2	30	1.01
62-1	18.3	45	23	2	30	1.00
62-2	13.5	40	23	2	36	0.78
61-61	4.5	26	24	9	40	0.48

The proportion of exchangeable cations in equilibrium with seawater (Table VI) is summarized in the Gapon exchange constant (e.g. Bolt 1955) calculated from the equation:

$$(\text{Na} + \text{K})_e/(\text{Ca} + \text{Mg})_e = G(\text{Na} + \text{K})_0/\sqrt{(\text{Ca} + \text{Mg})_0}$$

where $(\ )_e$ are the amounts of exchangeable Na, K, Ca, and Mg, expressed as meq/100 g, and $(\ )_0$ are the amounts in the artificial seawater expressed in moles/liter. The exchange constant, G, then has the units of $(\text{liter/mole})^{1/2}$.

The exchangeable cations are dominantly sodium and magnesium, with appreciable amounts of potassium. The potassium is higher than would be obtained in natural seawater because the NaCl used contained potassium. With decreasing charge and decreasing proportion of pH-dependent charge, the proportion of magnesium to sodium increases and the Gapon exchange constant decreases from 1 to 0.5. Exchange sites due to permanent charge have a higher bonding energy and divalent ions are preferentially adsorbed at these sites (Marshall 1954).

The value of the exchange constant, G, for ratios of sodium to calcium on illite (Bolt 1955) and montmorillonite (Bower 1959) is about 0.4. To make the exchange constants in seawater more closely comparable with sodium–calcium exchange, they can be recalculated to exclude potassium. The G values then range from 0.8 to 0.3. The samples with highest pH-dependent charge still adsorb relatively more sodium ions, but the other samples have exchange constants comparable with those of the minerals illite and montmorillonite.

If the cations in equilibrium with seawater are taken as the original exchangeable cations, leaching out of the free salt has been accompanied by a net loss of sodium replaced largely by calcium ions.

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INFLUENCES OF ABS
BARRIERS

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A review is presented of t
there is an absolute hydrolog
of pump test results are stre
equilibrium flow in the pres
limitations. It is concluded
reflected in any discernible v
tests, or, if it is reflected, ma

One widely accepted theore
tion and location of hydrologi
on the behavior of pumping
models permitting applicatio
common practice to use the
in conjunction with this meth
of image well and barrier sys
A critical review of this conce
give rise to misinterpretation
The method of images may
hydrologic barrier exists, sepa
ties within the same horizonta
is well known in electrical field
geophysical problems. The no
and in this paper the only ca
storage coefficient to the tran
equal, to a reasonable degre
in the light of the difficulties
of test results influenced by
that the presence of a partial
of pump test data alone. The
of the drawdown–time curves,
may not be reflected in any d

2. CONE OF I

In 1935, Theis suggested the
around a well producing at a
aquifer of constant storage c