

4959

GEOCHEMISTRY OF THE WEATHERED ZONE OF A FRACTURED

CLAYEY DEPOSIT

IN SOUTHWESTERN ONTARIO

by

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presented to the University of Waterloo
in fulfillment of the
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Master of Science
in
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ABSTRACT

The Sarnia till plain, which covers Lambton County in Southwestern Ontario, is a 25 to 50 m thick silty clay till deposited in late Wisconsinan time. Although the current water table is within one to two m of ground surface, a dry climatic period which occurred between 11,500 and 6,000 B.P. resulted in the oxidation of the uppermost 3 to 5 m. At the onset of weathering, oxidation of detrital sulfide derived from the black shale bedrock during glacial erosion caused calcite and dolomite dissolution. Na^+ was displaced from the exchange sites by Ca^{2+} and Mg^{2+} . Fractures, formed as a result of dessication, commonly occur to 5 m depth, and often contain secondary precipitates of iron and manganese, carbonates, or clayey alteration products. Gypsum in fractures is common but not ubiquitous. At 8 of the 12 sites, which are situated on or near the Black Shale till in the Southwestern corner of Lambton County, high major ion concentrations persist to depths of 8 to 12 m below ground surface. These profiles can be accounted for using a one-dimensional model which uses effective diffusion coefficients of 2.45 to $4 \times 10^{-7} \text{ cm}^2/\text{s}$, to simulate 10,000 years of diffusion starting at the point of maximum ion generation. At the LGS2 site a downwards velocity of 0.15 cm/a is superimposed on diffusion. These simulations are subject to uncertainties related to the starting depth used. The presence of secondary gypsum, and the continuing influence of exchange reactions confirms that groundwater flushing has not been extensive at these sites. One of the sites is at a particularly early stage of weathering, as indicated by a shallow oxidized zone, shallow penetration

of major ions, and little carbonate leaching. Relative to these 8 sites, the other four sites, located mainly to the north and east of the former sites on the St. Joseph till, are distinguished by low major ion concentrations, lack of gypsum, and SO_4^{2-} profiles which do not follow classical diffusion profiles. This suggests that the latter sites have been subjected to more groundwater flushing or less pyrite oxidation. Variations in the chemistry of the weathered zone across Lambton County are probably the result of small variations in topography or original till composition, with resulting variations in drainage and redox history.

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INTRODUCTION

Southwestern Ontario has several plains of clay-rich sediments deposited in late Wisconsinan time. The largest of these is the St. Clair clay plain, which covers Lambton County in the Sarnia area. These clay rich deposits are 35 to 45 m thick in much of the area. The present-day water table in the Sarnia area is generally within 1 to 2 m of ground surface, with yearly and seasonal fluctuation less than about 0.5 m (Desaulniers, 1986). The uppermost 3 to 5 m of the Sarnia till have been altered by oxidation which began during early Holocene time.

There are many visual indications that weathering has occurred. The weathered till is a brown color, in contrast to the gray color of the lower unweathered zone. Fractures are commonly found between 1 and 5.5 m depth (D'Astous et al., 1987) and have been observed locally to depths of up to 10 m (Hanna, 1986). Many of the fractures contain root channels in which much of the plant carbon has disappeared. Many of the fractures also show oxidation products, clay mineral alteration, coatings of iron and manganese, secondary carbonates, or gypsum.

Below the weathered zone, evidence from naturally occurring stable isotopes, including ^2H , ^{18}O , and ^{14}C , and ^{37}Cl , suggests that solute transport in the unweathered clay is dominated by diffusion rather than advection (Desaulniers et al., 1981; Desaulniers, 1986). In the weathered zone, however, tracer tests, tritium profiles, and hydraulic-head profiles indicate that groundwater flow occurs, mainly through

fractures and root holes (D'Astous et al., 1987).

Investigations by previous researchers indicate that several characteristics of the weathered zone are spatially variable. Whereas test pits at the Tricil site filled up at the rate of several hundred litres per day, similar test pits at the Lambton site remained dry for several days (D'Astous et al, 1987). Gypsum crystals, a common feature in fractures at the Lambton site, were not observed at the Tricil site.

Relative to the groundwater in the unweathered zone, the groundwater in the weathered zone generally has much higher concentrations of all major ions except Cl^- . These high major-ion concentrations in the weathered zone have been observed at numerous locations by previous investigators, such as Desaulniers et al. (1981), Heystee et al. (1982), Ash (1983), and Richards et al. (1984). Desaulniers (1986) noted that the depth to the bottom of the weathered zone based on visual features was much shallower than the depth of high major-ion concentrations, but he did not provide a quantitative assessment and explanation of this anomaly.

Abbott (1987) has determined on the basis of isotopic analysis and mass balance calculations that oxidation of pyritic sulfur has been the major source of sulfate in both the groundwater and gypsum in the weathered zone. The present investigation incorporates this finding into the development of a conceptual model for the genesis of all major

ions in the weathered zone.

The goals of this study are to determine the influence of mineral dissolution, precipitation and cation exchange on the major ion chemistry of groundwater in the weathered zone, and to relate the elevated major-ion concentrations in the unweathered zone immediately beneath the weathered zone to factors such as flow, diffusion, and duration of the period of geochemical weathering. The determination of how and when the major ion profiles developed will contribute to the understanding of the origin and character of the fractures and secondary minerals in the weathered clayey deposits, and to the determination of the thickness of the zone of active groundwater flow

The major-ion chemistry of groundwater was examined from detailed vertically-nested piezometers extending from 1 to 30 m below the surface at twelve sites in Lambton County. Major-ion analyses of water samples from piezometers were supplemented with major-ion analyses on waters squeezed from cores. Weathering features were observed in cores from 10 of the sites, as well as in a trench at the Lambton Generating Site.

STRATIGRAPHY AND GEOLOGIC HISTORY OF THE SARNIA TILL

The study sites in this investigation are situated in Lambton County, near the southern tip of Lake Huron. Six sites were located within the property of the Ontario Hydro Lambton Generating Station (LGS), with six additional sites distributed across the Sarnia clay plain (Figure 1).

The following description of the stratigraphy of Lambton County is based on Fitzgerald et al. (1979). The bedrock in Lambton County consists of the Devonian age bituminous black shale of the Kettle Point Formation. The slightly younger gray shales and limestones of the Port Lambton Group underly a triangular area in the vicinity of the LGS.

The overburden in Lambton County consists of a 35 to 50 metre thick deposit of clay-rich glacial till, overlain by a thin veneer of glaciolacustrine clay. The LGS sites and CIL are situated on the Black Shale till, a 30 to 35 m thick deposit which is at least 16,000 years old. The RP site is situated on deep water glaciolacustrine silt and clay. The other sites are situated on the St. Joseph Till, which lies stratigraphically above the Black Shale Till, separated from it by lacustrine sandy silt to clay. The St. Joseph Till is a 10 to 15 m thick deposit, the base of which has been dated at 13,100 years B.P.

Appendix IV(iii). Water Content
as weight percent of bulk wet weight

LGS1			LGS3		
Depth (mbgs)	Total %	Squeezed %	Depth (mbgs)	Total %	Squeezed %
-0.15	16.50	8.53	-0.06	18.47	11.52
-0.25	16.69	5.36	-0.18	18.48	11.02
-0.35	13.84	5.47	-0.23	17.79	6.32
-0.45	12.59	1.91	-0.36	16.32	11.95
-0.55	15.43	8.73	-0.47	17.20	14.33
-0.65	16.74	14.37	-0.55	17.29	14.17
-0.75	17.27	14.79	-0.65	18.20	15.64
-0.90	18.14	16.34	-0.73	18.73	15.24
-1.03	17.45	12.60	-0.83	18.87	15.67
-1.17	17.65	12.26	-0.91	19.20	18.14
-1.27	18.66	15.39	-1.01	18.90	15.39
-1.39	19.28	16.25	-1.09	18.13	12.66
-1.48	19.95	15.39	-1.17	17.78	12.00
-1.57	17.96	16.33	-1.36	17.61	11.56
-1.69	17.95	16.53	-1.59	19.01	15.02
-1.79	18.11	16.86	-1.67	18.72	16.27
-1.95	18.28	17.92	-1.78	17.34	16.36
-2.05	18.17	15.50	-1.87	17.76	13.63
-2.18	17.34	14.53	-1.98	17.85	15.49
-2.28	17.87	16.88	-2.07	18.21	15.06
-2.40	17.97	13.87	-2.19	16.27	15.04
-2.50	18.36	15.62	-2.28	17.19	15.31
-2.62	18.73	15.23	-2.38	16.70	10.90
-2.72	17.97	16.83	-2.47	17.86	15.55
-2.84	18.22	16.70	-2.57	18.99	19.03
-2.93	19.29	18.52	-2.66	16.85	14.11
-3.01	19.32	18.07	-2.78	19.31	17.60
-3.11	19.42	11.03	-2.87	20.97	20.13
-3.19	18.18	10.95	-2.98	22.44	24.45
-3.28	18.45	9.51	-3.21	20.99	16.05
-3.37	19.19	10.83	-3.29	19.92	15.90
-3.50	17.45	20.05	-3.39	19.97	20.01
-3.60	14.71	13.40	-3.47	20.50	18.37
-3.73	19.53	21.42	-3.71	18.58	16.69
-3.81	19.29	21.38	-3.79	20.37	23.22
-3.95	19.53	22.68	-3.97	21.59	24.28

Both the Black Shale and St. Joseph Till are composed of silty clay with an approximate composition of 40 to 60 % clay, 30 to 40 % silt, 5 to 10 % sand, and usually less than 5 % gravel (Hanna, 1966; Soderman and Kim, 1970). A mineralogical analysis of the unweathered till in the Sarnia area showed it to contain 14% illite, 10% chlorite, 40% quartz and feldspar, 35% carbonates, and 2% smectite (Ogunbadajo and Quigley, 1973). The St. Joseph Till contains less than 5% shale clasts, while the Black Shale till contains a much higher percentage (Fitzgerald et al., 1979).

The till deposits in much of the Sarnia area have been modified by a series of glacial lakes which formed during glacial retreat in late Wisconsinan time. This series of lakes formed and drained between 13,000 and 12,000 years B.P. (Dreimanis, 1964). Site ESS is located in an area which exhibits the influence of the near-shore sand and silt deposit of Glacial Lake Lundy. The crest of the Wyoming moraine, which was constructed of St. Joseph Till during the retreat of Lake Whittlesey (Chapman & Putnam, 1966) is situated on a line which roughly follows Highway 4 (Figure 1).

Based on the isotopic composition of water used by terrestrial plants, Edwards and Fritz (1987) have documented that 3 major climatic events occurred between the end of the Wisconsinan stage and the present. Conditions were colder and drier than at present between 11,500 and 7,400 years B.P., followed by a warm and dry period between

7,400 and 6,000 years B.P., which changed to a warm and moist climate from 6,000 to 1,000 years B.P. This evidence for the occurrence of a dry period in early Holocene time is corroborated by evidence of lower lake levels, beginning about 12,000 years B.P., in Lakes Erie, Huron and St. Clair (Dreimanis, 1970). Lake St. Clair exhibits a weathered surface up to 4.6 m below the current lake level (Dreimanis, 1970).

Weathering of the upper 3 to 5 m of the clayey till in Lambton County began during this dry period. In addition to the oxidation of iron sulfides and the formation of fractures, weathering also resulted in the oxidation of illite and chlorite, to produce up to 15% swelling clays in the shallow zone (Quigley and Ogunbadejo, 1976). Carbonate minerals have been leached from the upper 0.5 to 1.5 m, to be reprecipitated between 1.5 and 5 m depth (Ogunbadejo and Quigley, 1974).

METHODS OF INVESTIGATION

Piezometer Installation

All of the piezometer nests were installed by previous investigators. Desaulniers (1986) installed piezometers between 1 and 30 metres depth at 4 locations at the Lambton Generating Station (LGS) site in 1980 (LGS1, LGS2, LGS3 and LGS4). Harding (1986) installed 4 detailed piezometer nests between 1 and 10 metres depth at the LGS site in 1984 (LGS1a, LGS3a, LGS6a and LGS7a). The LGS1 and LGS3 sites were therefore each represented by 2 piezometer nests. Ross et al. (1986) installed nests between 1 and 16 metres depth at 10 locations elsewhere in Lambton County in 1985. These are referred to as the LIS nests.

The LGS piezometer nests are referred to as "augered hole piezometers" by D'Astous et al., (1987). Hollow-stem augers were used to drill holes at depths of 1 to 30 metres below the surface. Piezometers were constructed of 3.8 cm inner diameter PVC pipe with a 61 cm slotted tip wrapped with fiberglass cloth. Coarse silica sand was placed around the piezometer tip, followed by a 1 m bentonite seal. The hole was backfilled with a dry mixture of bentonite and drill cuttings. Details on piezometer construction can be found in Desaulniers (1986).

In contrast to the LGS nests, the LGSa and LIS nests, referred to as "Shelby hole piezometers" in D'Astous et al (1987), were installed

without sandpacks. A 70 mm diameter thin-walled shelby tube was pushed 0.41 to 0.5 m below the lowest auger hole, to the target depth. Tips were made of 5.1 cm inner diameter PVC pipe with a 50 cm long slotted tip wrapped with polyester geotextile. A flexible rubber stopper was placed above the tip. The holes were sealed with bentonite and backfilled to the surface with a mixture of bentonite and drill cuttings. Details on the installation of the LGSa and LIS piezometers can be found in Harding (1986) and Ross et al. (1986) respectively.

Coring and Trenching

For the purposes of visual observation and the laboratory removal of water, cores were collected from 7 of the sites, and a trench was dug on the LGS property. Cores from sites LGS6a and LGS7a were previously collected by Harding (1986), while core from the LGS2 site was collected by Desaulniers (1986).

At the LIS sites the shelby tube samples removed from the depth of piezometer tips were wrapped in saran wrap upon collection. They were re-wrapped tightly in several layers of saran wrap and transferred to a cold-room that was maintained at 7 °C within approximately one week of their collection. Cores were stored at 7°C in order to slow the rate of sediment aging (Lessard & Mitchell, 1985).

During the summer of 1985 cores were drilled at the LGS1 and LGS3 sites. Each core consisted of four successive 5.8 cm diameter

by 1.5 m long segments, representing a record from the surface to a depth of 6 m. These cores were recovered nearly 100% intact, and in good condition. Before drilling for each segment a hollow plexiglass cylinder was fitted inside a CME continuous tube sampler. Upon recovery, tightly fitting plastic caps were put on each end of the cylinders and sealed with tape. The plexiglass cylinders protected the cores from any impurities on the split spoon sampler, and prevented the cores from drying out during storage. The cores were transported back to the laboratory in coolers with ice, and stored in a cold room whose temperature was accurately maintained at 7°C.

During the summer of 1985 a back-hoe was used to dig a trench on the LGS site. The trench was approximately 3 m long, 1.5 m wide and 3.3 m deep. The major purpose of the trench was for visual observation of the till on a large scale. Samples were also collected, well-wrapped in saran wrap, and transported back to the laboratory on ice. Upon arrival at the laboratory, they were waxed and stored at 4 ° C until the removal of water was begun.

Water Sampling at Piezometers

Following the installation of piezometers in the Sarnia clay, water levels take several months to reach equilibrium; following the removal of water by pumping, water levels take several days or weeks to recover. Therefore, piezometers were pumped only during sample collection. The LIS nests were sampled in October 1985, 4 months after they were

installed. The LGS nests were sampled by previous investigators in 1982. The LGS1, LGS3 and LGS4 nests were sampled again in June, July and October of 1985. The LGSa nests were first sampled on June 3, 1985, approximately one year after installation; the LGS6a and LGS7a nests were resampled on June 7, 1985.

Piezometers at depths shallower than 10 metres were sampled using a peristaltic pump, while those below 10 metres were sampled using a one-way valve at the end of the tube, operated by a manual jerking motion. The water from each piezometer was sampled through tygon tubing that was cleaned between wells. The first 50 ml from each piezometer was discarded in order to further rinse the interior of the tubing. The water was filtered in-line through 0.45 micron Sartorius filters, before being collected in 125 ml high density polyethylene sample bottles. Two 125 ml samples were taken from each piezometer. One sample was acidified immediately with approximately 0.5 ml of Baker analyzed reagent grade nitric acid and used for cation analysis, while the other sample was left unacidified and used for anion analysis. Water samples were transported back to the laboratory in coolers with ice, and then kept refrigerated at 7°C until they were analyzed. pH, alkalinity, and temperature were measured in the field on separate samples.

Water Collection by Squeezing

In addition to the water samples that were collected from

piezometers, waters were squeezed in the laboratory from core and trench samples. The major-ion chemistry obtained using this method was compared to that obtained using piezometers. Appendix I provides a description of the procedure, as well as an analysis of the factors which affect the accuracy and reproducibility of squeezing.

At least one sample from each segment of the five discontinuous cores was squeezed. The entire cores from LGS1 and LGS3 were squeezed, in approximately seven cm long samples. Water contents were measured on each sample that was squeezed.

pH was measured on a separate sample, using a digital read-out Metrohm 632 pH meter. Because the amount of water produced from a clay sample (a maximum of about 30 ml) was never enough for an alkalinity titration, carbon was measured as total inorganic carbon (TIC) when analyses for the other major ions were done.

Water and Sediment Analyses

All water analyses were performed at the geochemistry laboratory of the University of Waterloo. Cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Sr^{2+}) were analyzed using a Varian 1475 flame type atomic absorption spectrophotometer. Anions (Cl^- , SO_4^{2-} , NO_3^- , Br^- , and NO_2^-) were analyzed using liquid ion exchange chromatography, with a Dionex System 12 Ion Chromatograph, which detects conductivity.

Total inorganic carbon was measured on squeezed and piezometer samples using a Beckman Model 915 Total Carbon Analyzer, which has an infra-red detector. Alkalinity expressed as bicarbonate was measured on piezometer samples by doing an acid titration with a standard H_2SO_4 solution to a pH of 4.3.

Calcite and dolomite percentages were determined using the gas evolution method of Dreimanis (1962). Complete sections were done on four cores, while one test at 15 m was done on two other cores. Duplicate analyses were done on each sample. Samples were crushed with a mortar and pestle, sieved to 200 mesh (-0.074 millimeters) and dried at 105 degrees celcius before analysis.

RESULTS

Visual Observation in Cores and Trench

A close examination of the weathered zone was undertaken by digging a 3.4 m deep trench on the LGS site. Features observed in this trench were similar to those observed in a similar trench dug on the LGS site by Harding (1986). Observations from these trenches are compared to observations made at 3 similar trenches dug on the Tricil site (Figure 1) by D'Astous et al. (1987). The till in both trenches was a brown in the oxidized zone, turning gradually to gray between 3 and 5 m depth. The brown was often mottled with light gray, suggesting that redox conditions varied spatially on a small scale.

At both sites, abundant vertical fractures were seen in the weathered zone to depths of 5 m, and often showed oxidation and gray fine-grained alteration coatings. While finely crystalline gypsum was common in the fractures at the LGS trenches, gypsum was not observed at the Tricil trench (D'Astous et al, 1987). Rather, these fractures contained iron and manganese coatings, and possibly secondary carbonates. Between the depths of 3 and 5 m, fractures at both sites were surrounded by oxidation haloes up to 5 cm in diameter. Rootlets and/or their remnant carbon traces were found along many fracture surfaces at all depths.

Observations at the Tricil site showed that fracture spacing was 1

fracture every 3 cm at 1 m depth, decreasing to 1 fracture every m at 5 m depth (D'Astous et al, 1987). At the Tricil site, water flow was observed from some fractures below the water table and the pits filled with water at rates of 30 to 90 litres per hour (D'Astous et al, 1987). At the LGS site, although one fracture at 3 m depth was visibly wetter than the surrounding matrix, no water was observed trickling into the trench.

Observations in trenches were supplemented with examination of cores from all sites except LGS4 and AL. The major features found by visual observation of cores are illustrated in Figures 2A to 2H, and documented in Appendix III. The dashed line on the figures marks the approximate division between the upper brown and lower gray zones. Seven of the 8 cores examined were oxidized to depths of 3 to 5 m. The CIL core was oxidized to only about 2 m, while cores from PC and ESS were grayish-brown to 12 m depth. The only fracture found below 5 m depth was one at 9 m at the RP site. Gypsum was found in cores from the LGS sites, RP, and CIL, but not at sites UC, PC, or ESS. At LGS1 and LGS3 large gypsum crystals up to 4 cm across occurred in the matrix between the depths of 1 and 4.5 m. These crystals were also found in the trench at the LGS site. They often occurred in clusters, which were sometimes associated with fractures.

A 5 mm by 5 mm lense of medium to fine-grained calcite crystals occurred at 1.2 m depth at LGS-1. Many of the near near-surface

fissures in all cores were filled with a white fine-grained precipitate. Whitish fine-grained flecks also occurred in the matrix, mainly in the oxidized zone. Although some of this material may have been gypsum, the majority was probably calcite, as indicated by its reaction with 10% hydrochloric acid. Occasional horizontal sandy or silty layers were found at various depths in most cores. At sites RP, CIL, and UC, small horizontal and vertical partings, up to 2 cm long and less than 5 mm thick were found between 4 and 12 m. These structures were filled with reddish brown or black silt, which is believed to be iron or manganese precipitates.

Below the weathered zone the till was a relatively uniform blue-gray plastic silty clay, with pebbles of black shale and carbonate derived from the underlying Kettle Point Formation scattered throughout.

The amount of calcite in the till, as weight percent of bulk dry soil, as determined at several depths from 4 sites, was mostly in the range of 10 to 18% in the upper 15 m. At LGS1, where calcite determinations were made to 24.5 m depth, it is apparent that calcite increased gradually with depth, from approximately 12% at 3 m to 25% at 22m.

At LGS1 and CIL, which are situated on the Black Shale till, dolomite ranged from 6 to 9% in the upper 24 m. At PC, dolomite ranged from 21 to 27% above 10 m, and decreased abruptly to 11% below 10 m.

This large percentage of dolomite above 10 m probably reflects the fact that PC occurs on the St. Joseph till, which is 10 to 15 m thick in the area. Similarly at RP, which lies on modified St. Joseph till, the upper 3 m is characterized by over 20% dolomite.

Description of Ground Water Chemistry

Results of the chemical analyses of the ground water are listed in Appendix II and illustrated in Figures 2a to 2h.

A comparison of results from the LGS1 nest between 1983 and three sampling intervals during 1985 indicates that the results are very similar over successive sampling dates. High reproducibility was also obtained during repeated sampling of the LGS4 and LGSa nests. Results agreed closely between the LGS1 and LGS1a sites with the exception of Na^+ . Anomalously high and erratically fluctuating Na^+ at the LGSa and LIS nests are attributed to the exchange of Na^+ for Ca^{2+} and Mg^{2+} on the bentonite seals.

A final check on the reliability of results was obtained by comparing the chemistry of waters obtained by squeezing with water from piezometers. Results were very similar at the LGS1, LGS3, RP and CIL sites. Although storage procedures for cores from sites PC, UC and ESS were similar to those of CIL and RP, a combination of lower concentrations and slightly later squeezing dates resulted in more

significant chemical changes during storage. At these sites sulfide oxidation during storage apparently caused increased concentrations of SO_4^{2-} , Ca^{2+} , Mg^{2+} and Na^+ . Appendix I provides further details on comparisons between core water and piezometer water.

In this paper, interpretation focuses on data sets which exhibited evidence of neither Na^+ contamination from bentonite nor core aging. Geochemical speciation and transport modelling was limited to data sets from piezometer nests LGS1, LGS2, LGS3, LGS4, UC, AL, and LGS3 below 6 m depth, and squeezed waters RP, CIL, and LGS3 above 6 m depth.

All twelve sites investigated exhibited major ion concentrations that were higher in the shallow weathered zone than in the lower unweathered zone. Sulphate exhibited the highest concentrations in the weathered zone, with lesser quantities of Mg^{2+} , Ca^{2+} , Na^+ , and HCO_3^{2-} , and slight increases in K^+ . pH, which was almost always within the range of 6.5 to 7.2, tended to be lowest near the water table, and increased gradually with depth.

Tables 1 and 2 summarize maximum major-ion concentrations attained in the weathered zone, as well as the depth at which they occur. The six LGS sites, as well as RP and CIL, were characterized by SO_4^{2-} concentrations which ranged from 2000 to 9600 mg/l and Mg^{2+} concentrations which ranged from 250 to 2000 mg/L. The latter ions reached maximum concentrations either within the visually weathered zone or less than 1 m below it. Major ion maxima occurred at slightly

shallower depths at the CIL site, while at LGS2, SO_4^{2-} and Mg^{2+} have peak concentrations at 12 to 15 m, which is 9 to 12 m below the depth of visual oxidation. With the exception of CIL, Na^+ reached maximum concentrations at 0.5 to 1.0 m below Mg^{2+} and SO_4^{2-} . Ca^{2+} exhibited a broad flat peak, with concentrations remaining relatively constant at 400 to 500 mg/L for depth intervals generally ranging from near surface to 6 to 10 m below ground surface. This depth was only 2.5 m at CIL, and 15.5 m at LGS2. At these eight sites elevated major ion concentrations, defined as greater than 1500 mg/l SO_4^{2-} , greater than 100 mg/l Mg^{2+} , and greater than 200 mg/l Ca^{2+} , generally persisted to depths of 8 to 12.5 metres below ground surface. This depth, however, ranged from 4.5 metres at CIL to 18 metres at LGS2.

The other four sites, PC, UC, ESS and ALLEN, were characterized by less than 1500 mg/L SO_4^{2-} , and lower concentrations of Mg^{2+} , Ca^{2+} , Na^+ , and HCO_3^- . According to the divisions mapped by Fitzgerald et al. (1979), the sites with high SO_4^{2-} are located on or near the Black Shale till, while the sites with low SO_4^{2-} , including Tricil, are located mainly on the St. Joseph till (Figure 1). According to till units mapped by Cooper et al. (1979), the AL site is located on an unnamed silty clay till.

In contrast to the other ions, which are thought to be produced in the weathered zone during geochemical reactions, Cl^- exhibits only low concentrations in the weathered zone, and a continuous and gradual

increase with depth. Desaulniers (1986) attributed this increase to upward diffusion from a source in the bedrock. At the 8 sites with high SO_4^{2-} , Na^+ exhibits a concentration maxima in the weathered zone, as well as a gradual increase with depth below the weathered zone.

Saturation indices were calculated using the geochemical mass transfer model PHREEQE developed by Parkhurst et al. (1980). In this program, the saturation index (SI) for a mineral is equal to $\log(\text{ion activity product}/\text{equilibrium constant})$. In the calculation of SI, complexing is taken into account. Consistent with the presence of gypsum in cores, speciation calculations indicate that gypsum saturation is attained in the weathered zone at the LGS sites, RP, and CIL with the maximum saturation index being approximately 0.3 (Figure 3). These sites are hereafter termed the gypsum-saturated sites. Gypsum saturation persists to depths ranging from 4 m at CIL to greater than 16 m at LGS2, but most generally persists to depths of about 10 m, which is well below the bottom of the weathered zone. At the four sites with low SO_4^{2-} , consistent with the lack of gypsum in cores, gypsum saturation was not achieved in the weathered zone (Figure 3), and these sites will thus be referred to as gypsum-unsaturated sites.

Saturation indices calculated using PHREEQE indicate that the majority of the sites are saturated or nearly saturated with respect to calcite and dolomite in the weathered zone, apparently becoming undersaturated at approximately 8 to 12 m below ground surface (Figures 4 and 5). At CIL, UC, and AL, dolomite saturation occurs only in the

upper 2.5 m, reflecting the shallow depth of major ion peaks at these sites. As a result of the high Mg^{2+} concentration at LGS1, that site is slightly supersaturated with respect to dolomite to a depth of 6.3 m. At LGS2 the water appears to be slightly supersaturated with calcite and dolomite in the upper 15 m, reflecting the relatively high pH at these sites.

As the water at depth is at least several thousand years old (Desaulniers, et al., 1981; Desaulniers, 1986) the apparent undersaturation with respect to carbonate minerals at depth must reflect uncertainties in the measurement of parameters involved in the carbonate system, probably pH. Although conditions of undersaturation at depth were characteristic of all sites analyzed in 1985, higher pH values were obtained by Desaulniers (1982) at the LGS1 and LGS2 sites. Desaulniers (1982) used a flow-through cell for pH measurements, whereas the current investigation did not. Speciations indicate that the former water chemistry is at equilibrium with respect to calcite at all depths, while dolomite exhibits slight undersaturation below 16 m. Therefore, the undersaturation at depth obtained during the current investigation is probably the result of erroneously low pH measurements.

DISCUSSION

Weathering Reactions at Sites which are Saturated with Gypsum

Abbott (1987) and Hendry et al. (1986) concluded on the basis of isotopic evidence that the oxidation of sulphide which was incorporated into the till from bedrock during glaciation was the major contributor to SO_4^{2-} in the weathered tills of Lambton County and southern Alberta, respectively. The source of the sulphide in southwestern Ontario is thought to be pyrite enclosed in black shale fragments (Abbott, 1987), while 80% of the SO_4^{2-} in Alberta is believed to be derived from the oxidation of organic sulphur. Relative to the tills in southwestern Ontario, the larger contribution of organic sulphur in the Alberta tills is probably the result of the lower pyrite content of the latter deposit. The majority of the SO_4^{2-} that was produced now exists as gypsum (Abbott, 1987; Hendry et al., 1986). Abbott (1987) concluded that pyrite oxidation was the sulphide source for all gypsum-saturated sites investigated, namely LGS1, RP, and CIL. The source of SO_4^{2-} at the gypsum-unsaturated sites was unknown (Abbott, 1987).

The oxygen necessary for pyrite oxidation entered the till as dissolved oxygen in recharging groundwater and as gaseous oxygen. Based on mass balance calculations, Hendry et al. (1986) concluded that

dissolved oxygen could not have produced the observed amount of SO_4^{2-} in the weathered till, and therefore that the majority of sulphide was oxidized by gaseous oxygen in a partially saturated zone above the water table, during periods of lower water table. In the Sarnia till, the majority of sulphide oxidation probably also occurred above the water table, which as explained above, increased from a level which was lower than at present at approximately 12,000 years B.P., to a level higher than at present between 6,000 and 1,000 years B.P.. Currently the water table fluctuates seasonally within 1 to 2 m of ground surface.

As mentioned previously, vertical fractures are abundant near the surface, and commonly occur to depths of 5 m. Several fracturing mechanisms have contributed to fracture formation in the weathered zone in Lambton county. Minor fracture sets are probably the results of volumetric shrinkage due to dessication (Vorauer et al., 1986). This implies that the fractures were formed during the period of lower water levels in early Holocene time, and that they were open at this time. Fractures allowed penetration of oxygen into the till. Evidence of this is the common occurrence of secondary oxides of iron and manganese, and the brown oxidation haloes observed around fractures below about 3 m. In addition, Hanna (1966) found that swelling clay minerals tend to be more abundant in fractures than in the matrix, as the plasticity index increased from 21.3% twelve inches from a fracture to 25.8% on the fracture surface. Carbonate-mineral dissolution has probably been more extensive along fractures, because oxygen availability was greatest at the fracture surface. After calcite dissolved to saturation, changes in

redox conditions or CO_2 levels apparently caused calcite to precipitate in some fractures. The presence of both calcite and iron and manganese precipitates implies two stages in the formation of fracture coatings, as would be expected for a deposit with a fluctuating water table.

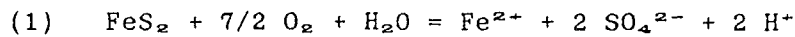
When the water table was deeper, a contributing factor to gypsum precipitation may have been evapotranspiration along root channels just above the water table (Adams, 1970). The $\delta^{18}\text{O}$ value of hydration water of gypsum in the weathered zone indicates that it precipitated in equilibrium with water which was isotopically heavier than modern water, and thus that it formed in water which was warmer than at present (Abbott, 1987). Although conditions were much colder and drier than at present from 11,500 to 7,400 years B.P., conditions were warmer and dryer than at present between 7,400 and 6,000 years B.P. (Edwards and Fritz, 1987).

At the eight gypsum-saturated sites, the major controls on the chemistry of the weathered zone are pyrite oxidation, carbonate dissolution, and gypsum precipitation, with a lesser influence of cation exchange.

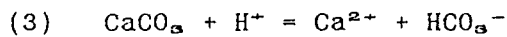
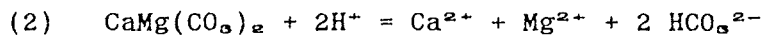
The H^+ produced by the oxidation of organic sulphur or sulfide minerals, as well as the oxidation of organic matter and root respiration caused the dissolution of carbonate minerals in the till. Pyrite oxidation and carbonate-mineral dissolution caused Ca^{2+} and SO_4^{2-}

concentrations to rise until saturation with respect to gypsum was attained. These processes can be summarized as follows:

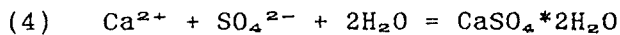
pyrite oxidation:



calcite and dolomite dissolution:



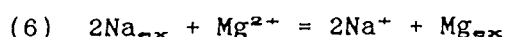
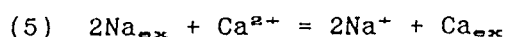
gypsum precipitation:



In addition to the above mineralogic controls, cation exchange reactions also exert an influence on the chemistry of the weathered zone. The oxidation of Fe^{2+} to Fe^{3+} is believed to result in the conversion of chlorite to smectite in the weathered zone of the till in southwestern Ontario (Fanning and Jackson, 1966). In a study of the weathered zone clay at a location 7 km east of Sarnia, Quigley and Ogunbadejo (1973) found that smectite increased from 2% at 4.5 m to 15% at 1.5 m. Cation exchange capacity on the minus 2 micrometre sized fraction was found to reflect this smectite production, increasing from 12 milliequivalents per 100 grams (meq/100 g) in the unweathered zone at 6 m to 42 meq/100 g at 1.5 m.

When the chemistry of a system changes as the result of mineralogic reactions, cation-exchange reactions will occur until the sorbed site population attains equilibrium with the new groundwater

chemistry (Reardon, 1981). Cation-exchange reactions in the Sarnia till would be expected to occur as follows. Before weathering Na^+ was the dominant pore-water cation, as indicated by its dominance in the groundwater at depth below the oxidized zone. Thus, it would also dominate the exchange sites. However, the normal order of preference for adsorption by clays is: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ (Stumm and Morgan, 1981). Laboratory determinations indicate that Ca^{2+} is greatly preferred on the exchange sites over Na^+ in the Sarnia till (Goodall and Quigley, 1977). Therefore, as Ca^{2+} and Mg^{2+} enter solution during carbonate dissolution in the weathered zone, equilibration would be expected to occur as Ca^{2+} and Mg^{2+} replace Na^+ on the exchange sites. Once all Na^+ has been displaced, Ca^{2+} , being more preferred than Mg^{2+} , would begin to replace Mg^{2+} . K^+ generally becomes fixed in a non-exchangeable position between the basal surfaces of illite (Grim, 1968). Equations representing exchange reactions in the Sarnia till are as follows:



As explained by Reardon (1981), displaced cations will go through a maximum at each point along the flow path with time before, ultimately, a steady state chemical evolutionary profile is attained which is dictated by mineral reactions. Once such a state of equilibrium is reached, exchange reactions will no longer exert an influence on groundwater chemistry. Depending on the exchange capacity, exchange site population and the chemistry of recharging pore-water, a considerable number of pore volumes of input groundwater may be required

before a steady-state chemical evolutionary profile is attained (Reardon, 1981).

Na⁺ profiles in the Sarnia till are the result of a combination of downward diffusion from the weathered zone and upward diffusion from the bedrock. Eventually, a steady-state profile will be reached, in which Na⁺ concentrations are approximately equal at all depths. At the gypsum-saturated sites, the presence of Na⁺ peaks in the weathered zone indicates that exchange reactions which occur in response to weathering are still exerting an influence on groundwater chemistry, which in turn suggests that groundwater flushing has not been extensive since weathering began. The fact that Na⁺ reaches maximum concentrations at 0.5 to 1 m below Mg²⁺, SO₄²⁻, and HCO₃⁻ is consistent with the fact that Na⁺ was displaced from the exchange sites earlier.

At the LGS sites and RP, the groundwater exhibits fewer mmols of Ca²⁺ than Mg²⁺ in the upper 9 m, while at CIL this deficiency is restricted to the upper 2.5 m (Figure 6). Figure 7 illustrates minimum Ca²⁺/Mg²⁺ ratios versus maximum SO₄²⁻ concentrations at several sites. Ca²⁺/Mg²⁺ molar ratios decrease as SO₄²⁻ concentrations increase, both with depth and across Lambton County; the minimum Ca²⁺/Mg²⁺ ratio observed was 0.1 at LGS1. As the dissolution of pure dolomite produces Ca²⁺/Mg²⁺ ratios of 1.0, lower ratios indicate that Ca²⁺ is being removed from the system. Three major processes which may potentially have produced this depletion of Ca²⁺ are gypsum precipitation, Ca²⁺

adsorption, or incongruent dolomite dissolution.

Ca^{2+} concentrations remain stable at 400 to 500 mg/L in the upper 9 m. As gypsum is at saturation over roughly the same depth range (Figure 3), this invariability in Ca^{2+} concentrations, and the fact that it occurs at lower concentrations than Mg^{2+} , is probably caused by the solubility control of gypsum.

Quantitative information regarding exchangeable cation populations was not obtained. However, an estimate of exchangeable Na^+ in solution was used to estimate the maximum contribution of Ca^{2+} adsorption to the depletion of Ca^{2+} with respect to Mg^{2+} . Using the assumption that the mmoles of bedrock-derived Na^+ in solution are approximately equal to the total mmoles of Cl^- in solution, a comparison of Na^+ and Cl^- on a per mole basis gives an indication of the amount of monovalent-divalent exchange that has occurred. With the exception of the LGS3 and AL sites, the excess of Na^+ over Cl^- ranges from over 15 mmoles/L at LGS1 to less than 2.5 mmoles/L at UC (Figure 8). At the LGS3 and AL sites, Cl^- occurs in greater concentrations than Na^+ . However, the relatively high K^+ and Cl^- concentrations at these sites, of over 350 mg/L, suggests that these ions may be the result of contamination from sources such as industrial waste or road salt.

The displacement of 15 mmoles/L of Na^+ would allow for the adsorption of a maximum of 7.5 mmoles/L of Ca^{2+} . The maximum excess of Mg^{2+} over Ca^{2+} is 70 mmoles/L at LGS1. This suggests that Ca^{2+}

adsorption could not contribute significantly to the depletion of Ca^{2+} . However, the large amounts of Mg^{2+} in the weathered zone at LGS1, which causes an apparent supersaturation with respect to dolomite, may be the result of the displacement of Mg^{2+} from the exchange sites by Ca^{2+} .

It is also possible that incongruent dolomite dissolution has contributed to the low $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios. This is the process in which calcite precipitation accompanies dolomite dissolution. The relative rates of dissolution of calcite and dolomite depend on factors such as the sequential distribution of the two minerals, effective dissolution rates, CO_2 partial pressure, temperature, and other factors (Palmer and Cherry, 1984). The temperature of the till in southwestern Ontario is about 10 °C, a temperature at which the solubility product of calcite is approximately twice as great as that of dolomite (Freeze and Cherry, 1979, p. 259). The percentages of calcite and dolomite (Appendix III) are high enough so that the availability of calcite and dolomite is not a limiting factor in carbonate dissolution.

As carbonate minerals can only dissolve until saturation is achieved, significant amounts of incongruent dolomite dissolution would require significant H^+ production. However, in the zone of pyrite oxidation, the precipitation of gypsum would tend to increase calcite dissolution (Palmer and Cherry, 1984; Shepherd et al., 1984). Therefore, it is unlikely that incongruent dolomite dissolution is a significant process in the weathered zone.

However, carbonate mineral analyses indicate that calcite may be precipitating in the weathered zone and immediately below it. At a site located 7 km east of Sarnia, Ogunbadejo and Quigley (1974) found that carbonates had been leached from the upper 1.5 m, to be deposited between 1.5 and 5 m depth, producing a carbonate content of 40 to 50%, compared with 31% for the underlying gray clay till. Although Lambton I and CIL exhibited a narrower range of carbonate content than the above site, they did exhibit high percentages of calcite between 0.5 and 1 m depth, before decreasing and then increasing gradually between 1.5 and 3.5 m (Figure 9). The larger and more gradual increase in calcite and dolomite below 18 m at LGS1 is probably a trend inherited from the original till.

As water infiltrates through the soil zone, it acquires acidity not only from pyrite oxidation, but also from CO_2 produced during root and microbial respiration, and the oxidation of organic matter. If there are lower CO_2 partial pressures deeper in the unsaturated zone, the infiltrating water will lose CO_2 to the soil air. This results in an increase in pH, and can cause calcite precipitation (Freeze and Cherry, 1979). Sr^{2+} at the gypsum-saturated sites, which ranges from 5 to 13 mg/L (Appendix II), may reflect incongruent dolomite dissolution, as Sr^{2+} tends to be incorporated in dolomite to a greater extent than in calcite. Sites with high Sr^{2+} tend to have low $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios. However, Sr^{2+} maxima occur a few metres below Mg^{2+} maxima. As Sr^{2+} is more preferred on the exchange sites than Mg^{2+} (Stumm and Morgan, 1979)

differences in mobility cannot account for this discrepancy.

Although the total range in pH with depth was generally only about 6.5 to 7.0, minimum values generally occurred at 4 to 6 m depth. The precipitation of calcite can cause slight pH decreases, as the removal of CO_3^{2-} leads to increased dissociation of HCO_3^- (Palmer and Cherry, 1984).

Weathering Reactions at Sites that are not saturated with gypsum

Four of the 12 sites--PC, ESS, UC and AL--have substantially lower concentrations of SO_4^{2-} , Mg^{2+} , Ca^{2+} , and Na^+ than the 6 sites discussed previously. Consistent with the lack of gypsum in these cores, gypsum saturation is not attained (Figure 3) and Ca^{2+} occurs at higher concentrations than Mg^{2+} on a per mole basis (Figure 6). In addition, these sites contain very little exchangeable Na^+ in the weathered zone, and all major ions reach maximum concentrations at the same depth in the weathered zone. This indicates that exchange reactions exert less of an influence on groundwater chemistry than at the gypsum-saturated sites.

The low major ion concentrations and lack of gypsum at the gypsum-unsaturated sites may be the result of either less pyrite oxidation, or more active groundwater flushing. The source of pyritic sulfur for

oxidation is thought to be the detrital black shale clasts (Abbott, 1987). These clasts are much more numerous in the Black Shale Till, where the gypsum-saturated sites are located, than in the St. Joseph Till, where the gypsum-unsaturated sites are located. Thus the latter sites may have lacked a sulphide source.

In addition to differences in original till composition, variations in major-ion concentrations across Lambton County are probably caused by differences in redox history, related to variations in topography. Adams (1970) noted that areas with a shallow oxidized crust were characterized by shallow-rooted vegetation, and hypothesized that shallow-crust areas occur in micro-depressions with poor drainage. The CIL site is located in a bog. Indications that weathering has been less extensive at CIL, relative to the other sites, is as follows: (1) the depth of the contact between oxidized and reduced zones is less; large fractures were not found, and unoxidized clayey laminae were preserved at 0.9 m. (2) depths of major ion maxima were less; gypsum saturation and low $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios persisted to lesser depths (3) carbonate mineral content was more uniform with depth (4) the maximum Na^+ concentration was not displaced from those of the other ions, possibly because Na^+ was displaced relatively recently, and has not yet moved below the other ions.

In contrast to the CIL site, calcite profiles at the gypsum-unsaturated sites suggest that they have been more extensively weathered. An indication of carbonate mineral content was obtained by

applying a small amount of 10% hydrochloric acid (HCL) to a fresh surface of till sample. Lack of reaction indicates that the sample does not contain substantial amounts of calcite. The four gypsum-saturated sites which were examined exhibited a reaction with 10% HCL at 90 cm depth (the shallowest sample available). At PC and ESS however, the samples at 90 cm did not react, while at UC porous brown patches which reacted were interspersed with gray clayey patches that did not react.

These results are consistent with the percentages of calcite and dolomite determined using the gas evolution method. Whereas calcite at PC increased from 4.8 to 12.8 % between one and two m depth, LGS1 and CIL contained at least 10% calcite in the shallow zone, and exhibited only slight increases with depth (Figure 9). In other words, groundwater flushing may have resulted in a greater removal of carbonate at the gypsum-unsaturated sites. The low major ion concentrations and relative lack of exchangeable Na^+ at these sites may also be related to lateral groundwater movement. At sites PC and ESS, core descriptions made during drilling (Ross et al., 1986) and core descriptions made during the current investigation (Appendix III) indicate that the color change from grayish-brown to gray did not occur until depths of 12 m. Thus deep fractures may cut through these sites.

Geochemical Simulations of the Weathered Zone

The geochemical mass transfer model PHREEQE was used to verify that

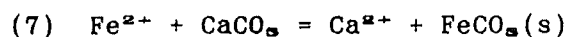
pyrite oxidation, accompanied by carbonate mineral dissolution, gypsum precipitation, and cation exchange, could have produced the chemistry observed in the weathered zone, given the starting material observed in the unweathered zone. The water chemistry from piezometer LGS1 at 21 m depth was used to represent the groundwater chemistry in the weathered till prior to oxidation. This invokes the assumption that before weathering the chemistry of the groundwater was homogeneous with depth. The water chemistry from piezometer LGS1 at 3 m was used to represent the groundwater chemistry of the weathered zone. The LGS1 site was chosen because information on the sulphide content of the solids was available (Abbott, 1987).

The oxidized till at LGS1 contains approximately 0.4% less sulfides by dry weight of till than the unoxidized till (Abbott, 1987). Assuming that the percent sulphides in the unoxidized zone represents the amount originally present in the unweathered till, this difference in percent sulfide represents the depletion of sulfide compounds through oxidative processes (Abbott, 1987). Using the fact that the dry bulk density and porosity of the till at LGS1 are 1.56 g/cm³ and 0.43 respectively (Heystee et al., 1982) 0.4% sulphides is equivalent to 226 mmol FeS₂ per litre of water. From equation (1), the oxidation of 226 mmol of pyrite consumes 791 mmol of oxygen, and produces 452 mmol of SO₄²⁻ per litre of water.

As the amount of iron in solution is less than 0.2 mmol/L (Table

1) the simulations must include a mechanism for the removal of aqueous iron. Some of this iron will probably be adsorbed on the exchange sites. Depending on the availability of oxygen, the remaining iron will either be oxidized to Fe^{3+} and precipitated as amorphous iron hydroxide, or it will be precipitated in the reduced state as siderite. Simulations using PHREEQE showed that the oxidation of pyrite produced supersaturation with respect to hematite and siderite, and undersaturation with respect to amorphous iron hydroxide. In considering the precipitation of a ferric oxide, the equilibrium constant for amorphous iron hydroxide rather than hematite is used, because the initial precipitate would probably be amorphous (Drever, 1982). Therefore, siderite equilibrium was maintained during pyrite oxidation.

Dubrovsky et al. (1984) investigated the migration of a plume derived from uranium tailings. They found that the Fe^{2+} produced during pyrite oxidation was precipitated as siderite at neutral pH's, and that the siderite did not precipitate directly, but replaced calcite:



In contrast to other possible reactions, the removal of Fe^{2+} through this mechanism does not produce additional acidity (Dubrovsky et al., 1984).

In simulating pyrite oxidation, PHREEQE handled Fe^{2+} using reaction (7). 791 mmoles of oxygen per litre of water were added to the water chemistry of the unweathered till at LGS1, while equilibrium was

maintained with respect to pyrite, calcite, dolomite, gypsum, and siderite. It was assumed that the removal of H^+ by moving groundwater is slow with respect to carbonate dissolution, so that all H^+ was consumed by calcite and dolomite dissolution. This assumption is supported by the conclusion of Ranch and White (1977) that carbonate minerals reach saturation within days. Because partially saturated conditions existed in the weathered till during oxidation, the weathered till was considered to be an open system with respect to PCO_2 . Calcite, dolomite, gypsum, and PCO_2 were maintained at the saturation levels calculated for the present groundwater at LGS1 at 3 m. It was assumed that mmoles of non-exchangeable Na^+ at 3 m was approximately equal to mmoles of Cl^- at that depth. The amount that Na^+ occurs in excess of Cl^- was accounted for by letting Ca^{2+} displace it from the exchange sites. Mg^{2+} - Na^+ exchange was not incorporated in the solution, as the PHREEQE computer code is limited to one exchange reaction. As Mg^{2+} is the dominant cation in the weathered zone at LGS1, neglect of this exchange reaction may be a significant limitation of these simulations.

Results of the simulations are shown in Table 3. From equation (1), the oxidation of 226 mmoles of pyrite consumes 791 mmoles of oxygen, and produces 452 mmoles of SO_4^{2-} and 452 mmoles of H^+ . This caused the dissolution of 295 mmoles of calcite and 81.4 mmoles of dolomite, to consume all 452 mmoles H^+ , according to equations (2) and (3). As 452 mmoles SO_4^{2-} were produced, and 94 mmoles SO_4^{2-} are now present in solution, 358 mmoles of gypsum must have precipitated. This

leaves 18 mmol of Ca^{2+} in solution. According to equation (5), the exchange of 15.1 mmol of Na^+ removes 7.56 mmol of Ca^{2+} , leaving 10.5 mmol of Ca^{2+} in solution. The calculated concentrations of dissolved ions and pH in the groundwater of the weathered till (Table 3) are in good agreement with the measured amount in the weathered zone at LGS1. The precipitation of Fe^{2+} as siderite produced the measured amount of HCO_3^- in solution. As percentages by dry weight of soil, the simulations showed that 1.7% gypsum precipitated, while 0.81% calcite and 0.41% dolomite dissolved. The exchange of 15.1 meq/L of Na^+ corresponds to 0.416 meq/100 g, which is well within the measured cation exchange capacity of the weathered zone. As the degree of exchange reactions invoked in the simulations was relatively minor, the limitation imposed by neglecting Mg^{2+} exchange may also be relatively minor.

A unique prediction of the chemical evolution of the weathered zone would require quantitative information on the history of CO_2 levels and exchange reactions. However, these simulations identify a set of reactions which can account for the chemistry observed in the weathered zone. Other mechanisms of Fe^{2+} removal would have caused more H^+ production, with a resultant greater mass transfer of gypsum, calcite, and dolomite. However, other mechanisms of Fe^{2+} removal would not have produced the measured $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratios. A more accurate simulation of the evolution of the weathered zone would require a physicochemical flow model to simulate diffusion along with geochemical reactions.

Downward migration of weathering products into the unweathered zone

Following their production in the weathered zone, major ions migrated downwards into the unweathered zone by diffusion and advection. Advection is predominantly downward in the unweathered zone at all of the study sites in Lambton County (Desaulniers, 1986; D'Astous et al, 1987).

Simulations of the downward migration of major ions below the weathered zone was carried out based on the earlier work of Desaulniers (1981, 1986) who simulated the migration of ^{18}O , ^3H and Cl in the till in Southwestern Ontario. Desaulniers (1981, 1986) concluded that the isotopic shift in ^{18}O with depth was the result of downward diffusion of ^{18}O from the weathered zone through the unweathered zone. He concluded that downward ^{18}O diffusion began about 10,000 to 12,000 years B.P. when deglaciation occurred. Desaulniers (1986) simulated the shift using the one-dimensional advection dispersion equation for non-retarded solutes in saturated porous media (Bear, 1972):

$$D = (d^2C/dx^2) - V(dC/dx) = dC/dt$$

where D = coefficient of dispersion = $D_m + D_e$

where D_m = coefficient of mechanical dispersion

D_e = effective diffusion coefficient

V = average linear ground water velocity

C = concentration

x = vertical distance travelled

t = time

At the velocities which occur in the unweathered zone of the Sarnia till, D_m is negligible compared to D_e , and therefore, the D is essentially equal to D_e (Desaulniers, 1986).

Oxidation of the shallow part of the Sarnia till probably began sometime around the beginning of the dry Hypsithermal Period 11,500 B.P. (Edwards and Fritz, 1986). In order to test the assumption that major ions have been diffusing down from the weathered zone since that time, simulated profiles of major ion transport downward from the bottom of the weathered zone into the unweathered zone were generated using the Ogata (1970) solution to the advection-dispersion equation, and compared to the field profiles. The effective diffusion coefficients for adsorbed species in porous media (D_e 's) were adjusted to obtain fits between observed profiles and theoretical profiles generated for times of 10,000 years.

The Ogata (1970) solution assumes that the clay is a saturated semi-infinite medium which is homogeneous with respect to porosity, hydraulic conductivity and effective diffusion coefficients, and that the hydraulic gradient has been constant throughout the Holocene (Desaulniers, 1986).

The starting point for matching each major ion profile to a

theoretical transport profile was the depth at which the ion reached its maximum concentration, which was generally a short distance below the visually weathered zone. Ca^{2+} at LGS1 and LGS3 persisted at maximum concentrations for significant depths in and below the weathered zone. For these cases transport simulations were started at the point where Ca^{2+} concentrations began to decrease significantly (Figure 10A). Major ion concentrations do not fall to zero at depth, but to a measurable background level. These background concentrations were subtracted from all data points. The simulations did not take into account geochemical reactions which affect major-ion concentrations, such as adsorption, precipitation, or dissolution.

The results of profile matching for Mg^{2+} , SO_4^{2-} , Ca^{2+} , and K^+ are shown in Figures 10 to 13. At all sites except CIL, UC and ALLAN, best fits were obtained using De^* 's of 2.45 to $4 \times 10^{-7} \text{ cm}^2/\text{s}$, with a slightly higher De^* of $6.7 \times 10^{-7} \text{ cm}^2/\text{s}$ for SO_4^{2-} at LGS3. Estimated diffusion coefficients were lower at CIL, UC and AL, ranging from 0.7 to $1.0 \times 10^{-7} \text{ cm}^2/\text{s}$. SO_4^{2-} at the latter two sites did not follow classical diffusion curves.

As Na^+ profiles are a combination of upward diffusion from the bedrock and downward diffusion from the weathered zone, Na^+ was not adjusted to a zero background value. As initial Na^+ concentrations at the bedrock were not available, the upward diffusion of Na^+ was not simulated. At all sites except LGS1 upward Na^+ diffusion has obscured downward diffusion (Figure 14). At LGS1 Na^+ follows a fairly well-

developed downward diffusion profile above 17 m, with a De^* of 1.3 to $1.6 \times 10^{-6} \text{ cm}^2/\text{s}$.

At all sites except LGS2, best fits for diffusion profiles were obtained using an average linear ground water velocity of 0 cm/a. At LGS2 a match to theoretical diffusion profiles required the incorporation of a velocity of 0.1 to 0.15 cm/a. Desaulniers (1986) used Darcy's Law and measured values of hydraulic conductivity, porosity and hydraulic gradient to calculate vertical groundwater velocities at LGS1 and LGS2. These were 0.37 and 0.91 cm/a, respectively. However, in the simulation of field profiles of ^{222}Rn and Cl migration, Desaulniers (1986) obtained best fit velocities similar to those obtained during the current investigation: 0 cm/a at LGS1 and 0.25 cm/a at LGS2.

The lower velocity obtained during field simulations may indicate that a threshold gradient is operative in the Sarnia till (Desaulniers, 1986). In detailed laboratory studies Law and Li (1981) found that a certain threshold gradient (0.1 to 0.29 in the clayey deposits studied) was necessary before advection would occur. The magnitude of the threshold gradient will vary with clay type (Desaulniers, 1986). Hydraulic gradients were less than 0.2 at all sites except CIL (0.26), ESS (0.27), LGS3 (0.48), and LGS2 (0.40) (D'Astous et al., 1987).

The effective diffusion coefficient for adsorbed species in porous media, De^* , is related to De by the relation

$De^* = De/R = De/(1 + p/n) \cdot K_d$ where

R = retardation factor

p = bulk density of soil n = porosity of soil

K_d = distribution coefficient

= mass of solute on solid phase per unit solid
phase/concentration of solute in solution

(Gillham et al., 1984).

This equation, along with measured values of bulk density, porosity, and tortuosity, was used to estimate K_d values for the ions (Table 4). As expected, K^+ is most highly retarded, followed by Ca^{2+} and then Mg^{2+} .

The effective diffusion coefficients obtained during the current investigation are lower than those obtained during other investigations of clayey till in the Sarnia area (Table 4). This is probably related to the fact that the current investigations used a slug input, rendering it necessary to begin simulations at the depth of maximum ion concentration. A more accurate simulation of major ion diffusion would require a variable input function, to more closely simulate the actual time over which major ions entered the groundwater. It is difficult to obtain quantitative results without using a physicochemical model to simulate geochemical processes along with diffusion.

At sites LGS2, LGS4, UC and AL, slightly greater diffusion

times were needed for the deep data points than for the shallow ones. This poor quality of fit may also be related to inaccuracies in the starting depths used for simulations. The poorness of fit for the lowermost two data points at LGS4 may be the result of contamination, as the latter points contain high levels of tritium (Abbott, 1987).

CONCLUSIONS

Conclusions about the Lambton County till drawn from this investigation are as follows:

(1) All twelve sites investigated exhibited SO_4^{2-} , Mg^{2+} , Ca^{2+} , Na^+ , and HCO_3^- concentrations that were higher in the weathered fractured zone than in the lower unweathered zone. At 8 of the 12 sites, located on or near the Black Shale till in the southwestern corner of Lambton County, maximum SO_4^{2-} concentrations ranged from 2200 to 9600 mg/L and maximum Mg^{2+} ranged from 250 to 2000 mg/L. Ca^{2+} occurred at lower concentrations than Mg^{2+} on a per mmole basis, and ranged from 400 to 500 mg/L for several metres in and below the weathered zone. Gypsum crystals, concentrated mainly in fractures, were found between the depths of 1 and 5 metres. The weathered zones at four of the sites, located mainly on the St. Joseph till to the north and east of the other sites, were characterized by less than 1500 mg/L SO_4^{2-} , lower concentrations of other major-ions, and lacked gypsum.

(2) Geochemical evidence supports the hypothesis initially derived from isotope data (Abbott, 1987) that SO_4^{2-} is the product of pyrite oxidation. Sulfuric acid produced during pyrite oxidation caused dissolution of calcite and dolomite to release Ca^{2+} , Mg^{2+} , and HCO_3^- to the water. At sites which exhibit gypsum saturation, Ca^{2+} concentrations are mainly controlled by gypsum precipitation, with the

lesser influence of Ca^{2+} exchange for Na^+ , and possibly incongruent dolomite dissolution. The presence of gypsum and the continuing influence of exchange reactions indicate that groundwater flushing has not been extensive at these sites.

(3) Following their release by weathering in the shallow zone, major ions diffuse downwards. At the sites which exhibit gypsum saturation, high concentrations of SO_4^{2-} , Mg^{2+} , and Ca^{2+} generally persist to depths of 8 to 12.5 m below ground surface, and these profiles are well-represented using one-dimensional models for saturated homogeneous media based entirely on Fick's Second Law of diffusion. Using diffusion coefficients of 2.45 to $4 \times 10^{-7} \text{ cm}^2/\text{s}$, with diffusion originating at the depth of maximum ion concentration, about 2 to 3 m below ground surface, the model simulates that major-ion profiles evolved during 10,000 years of diffusion. At the LGS2 site a downward advection of 0.15 cm/a in addition to diffusion was necessary for a good simulation. SO_4^{2-} profiles at sites with less than $2000 \text{ mg/l SO}_4^{2-}$ do not approximate diffusion curves.

(4) Following the retreat of the glacier that deposited the uppermost clayey till in the Sarnia area, about 13,000 years ago, shallow meltwater lakes occupied the area until about 12,000 years ago. The landscape was then exposed to weathering influences. A dry period, which occurred in southwestern Ontario between about 1150 and 7400 B.P., caused a lowering of the water table, which resulted in the weathering of the till to depths generally ranging from 3 to 5 metres.

Fracturing, pyrite oxidation, and carbonate dissolution probably began soon after this dry period began, and in areas where there is little lateral groundwater circulation, gypsum precipitation occurred in response to these processes.

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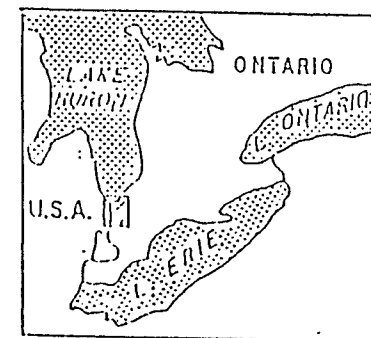
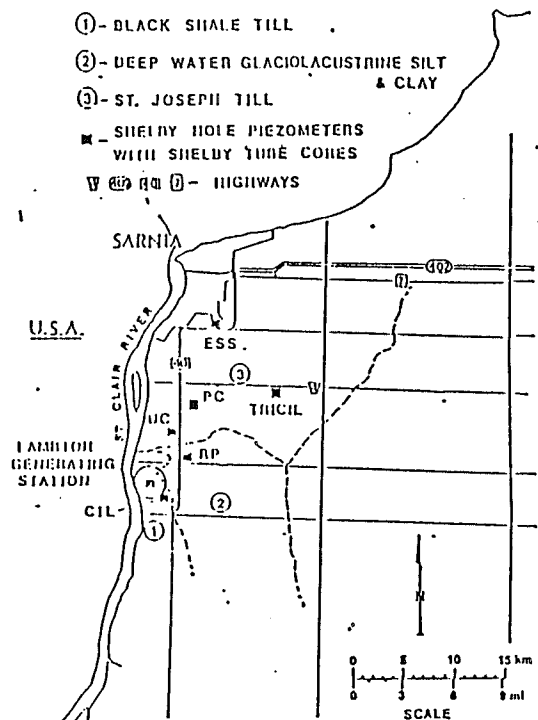
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STUDY SITES IN LAMBTON COUNTY



STUDY SITES AT THE LAMBTON GENERATING STATION

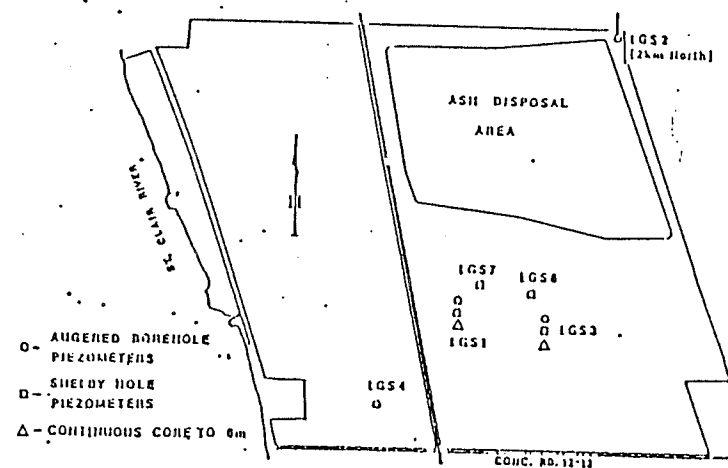


Figure 1: Study Sites in Lambton County

Legend for Figures 2a to 2h

G: gypsum crystals

F: large fracture

f: small fracture (usually less than 1 cm long)

S: large sand lense or layer

s: small sand lense

----- : contact between oxidized and reduced zone

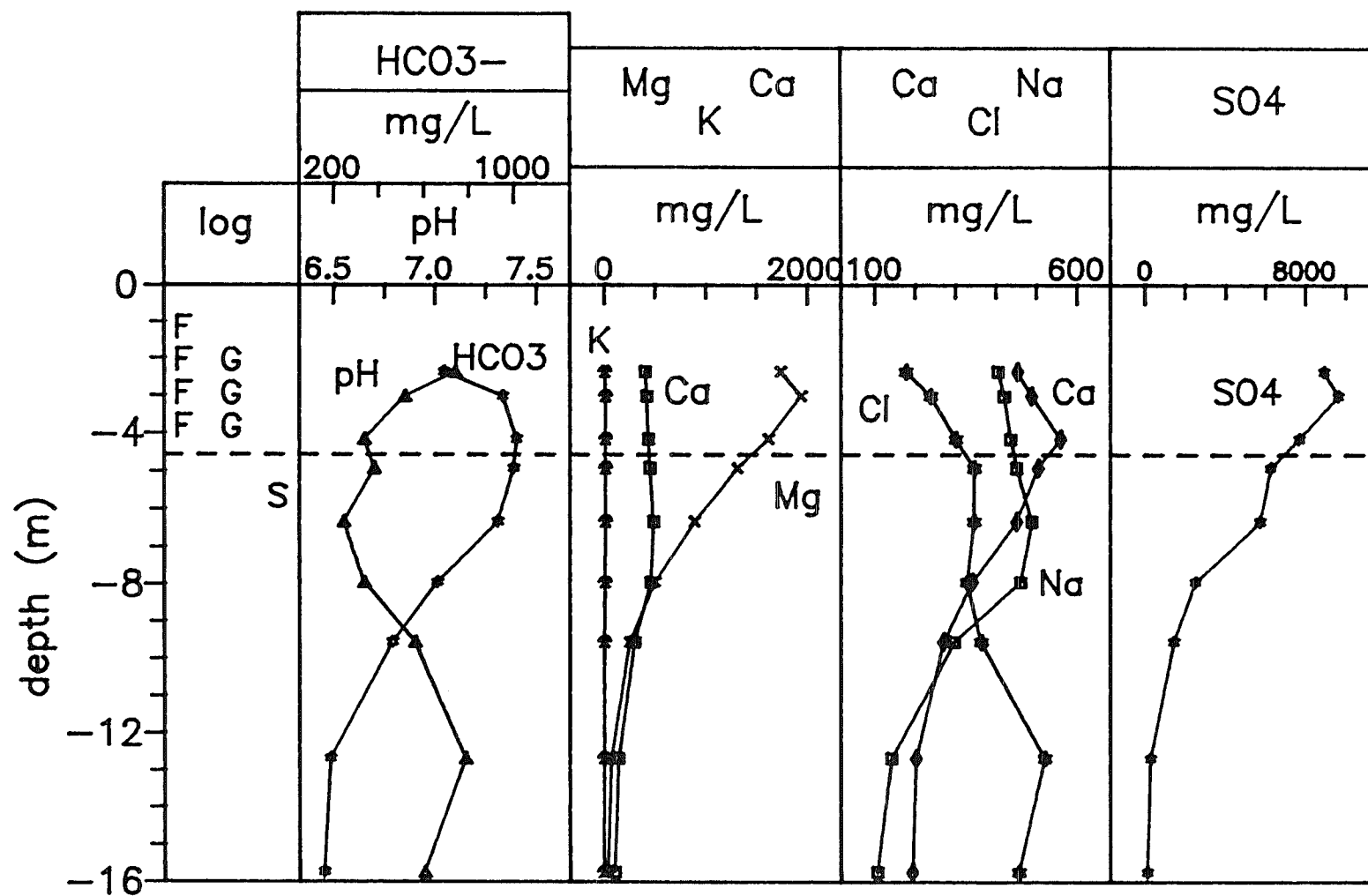


Figure 2a: Major-Ion Profiles at LGS1

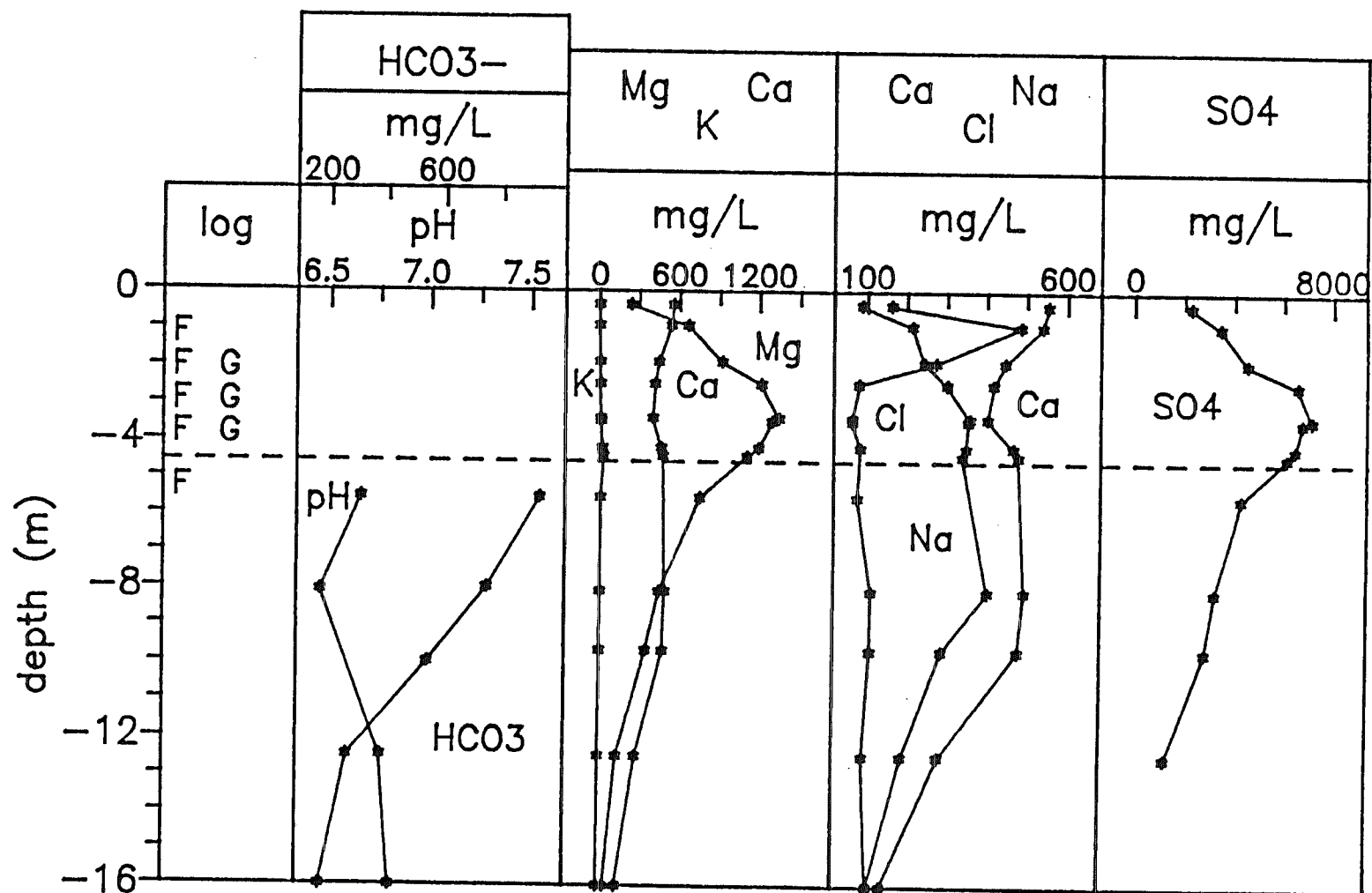


Figure 2b: Major-Ion Profiles at LGS3

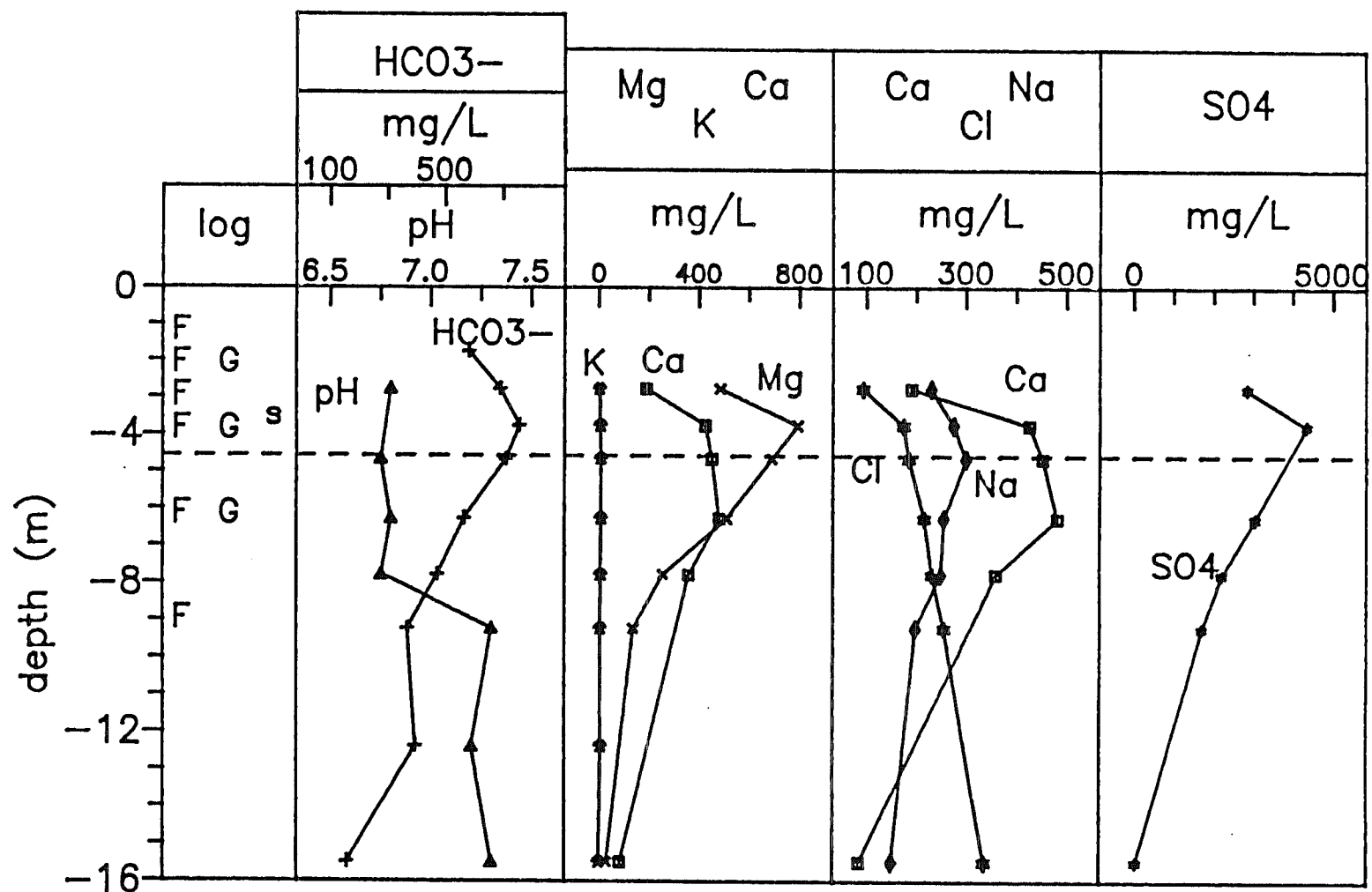


Figure 2c: Major-Ion Profiles at RP

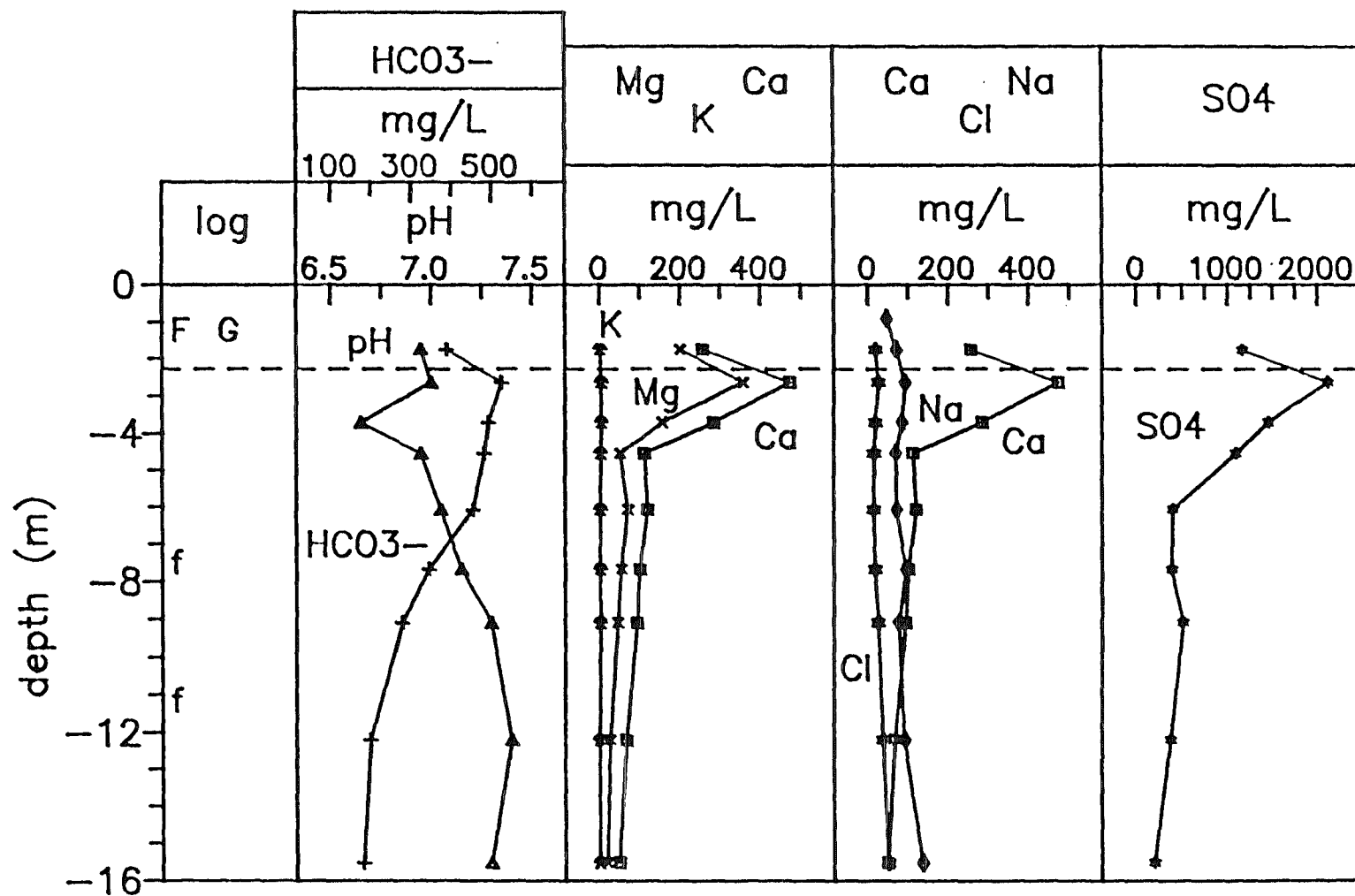


Figure 2d: Major-Ion Profiles at CIL

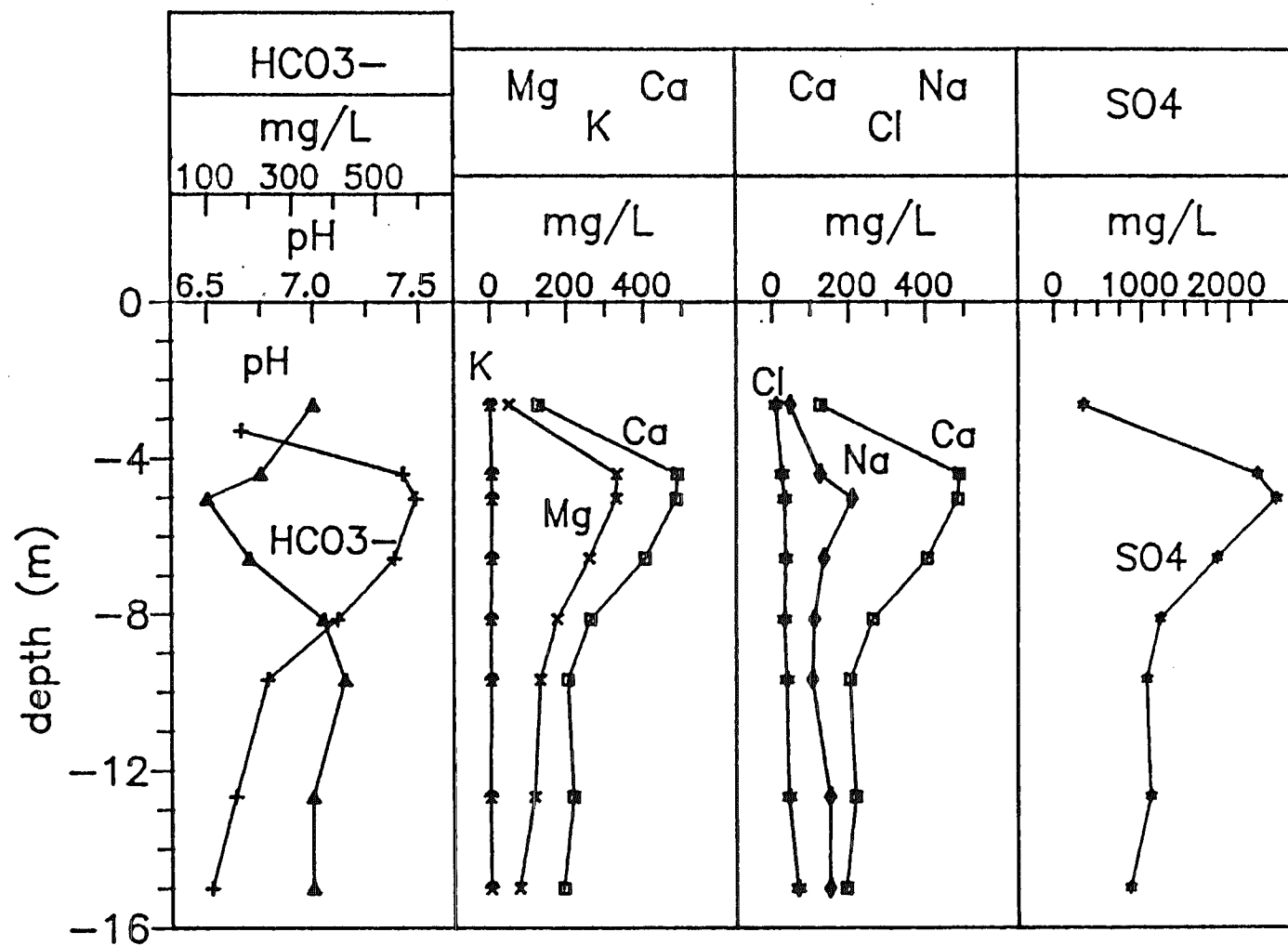


Figure 2e: Major-Ion Profiles at LGS4

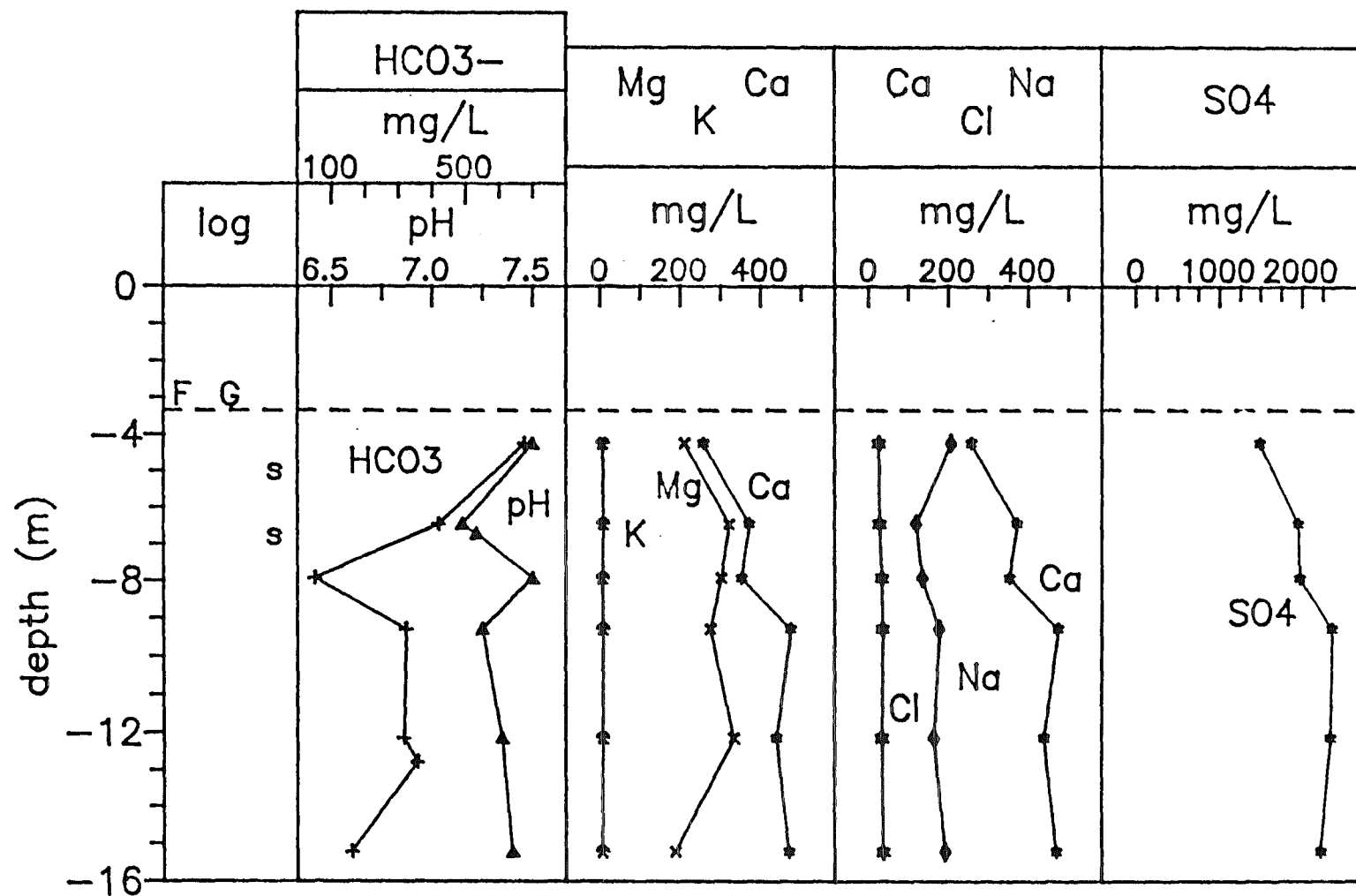


Figure 2f: Major-Ion Profiles at LGS2

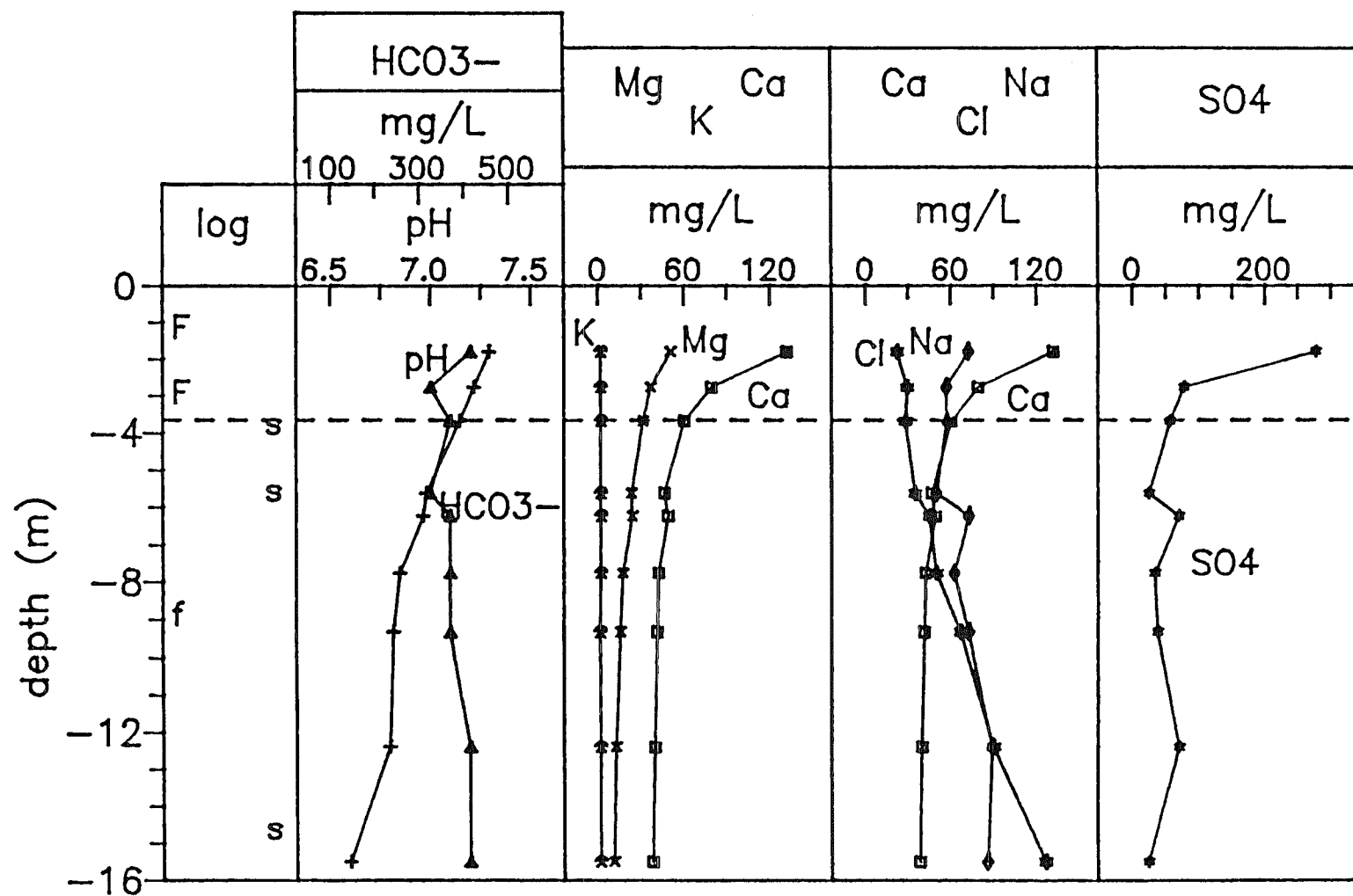


Figure 2g: Major-Ion Profiles at UC

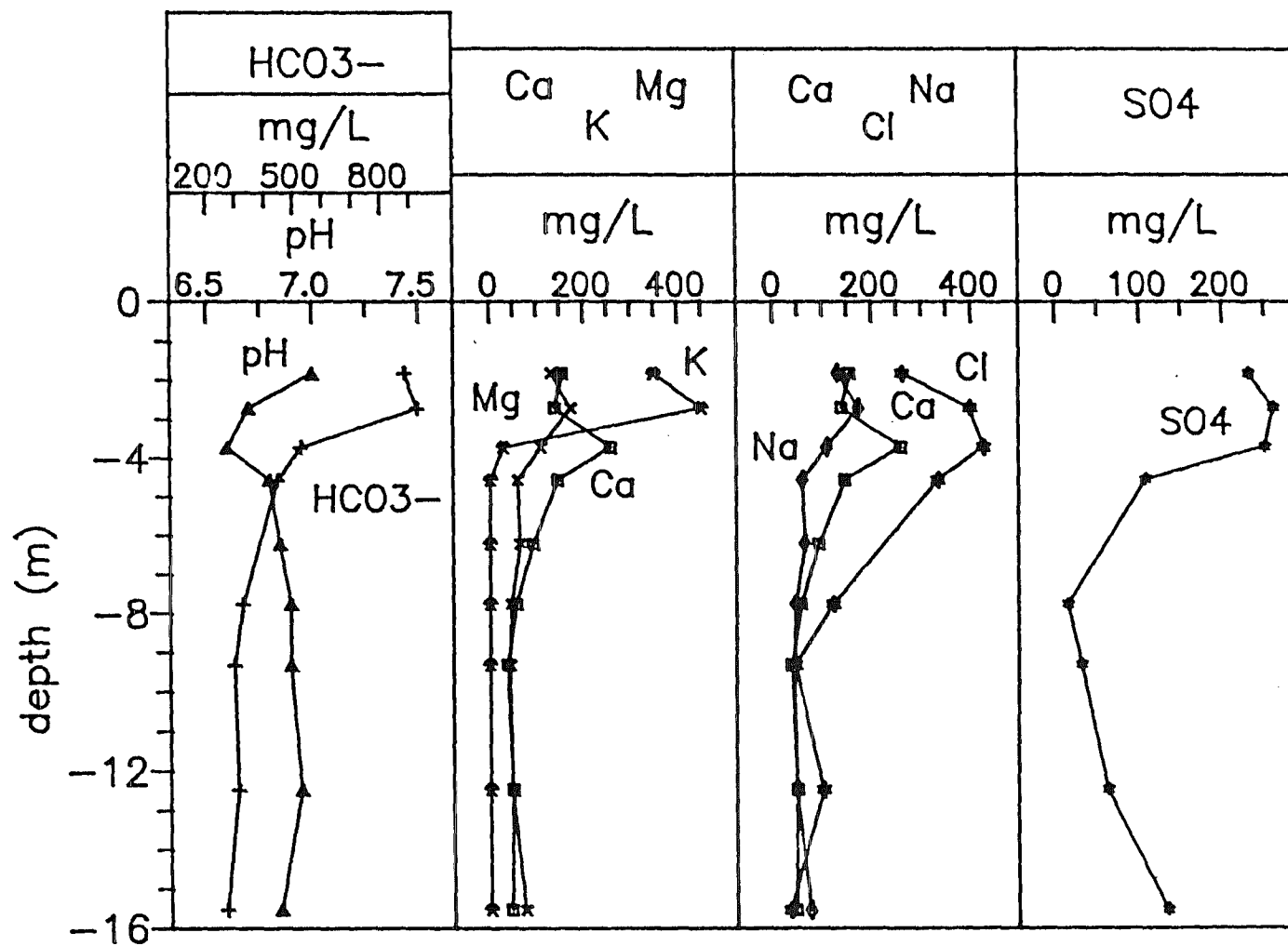


Figure 2h: Major-Ion Profiles at AL

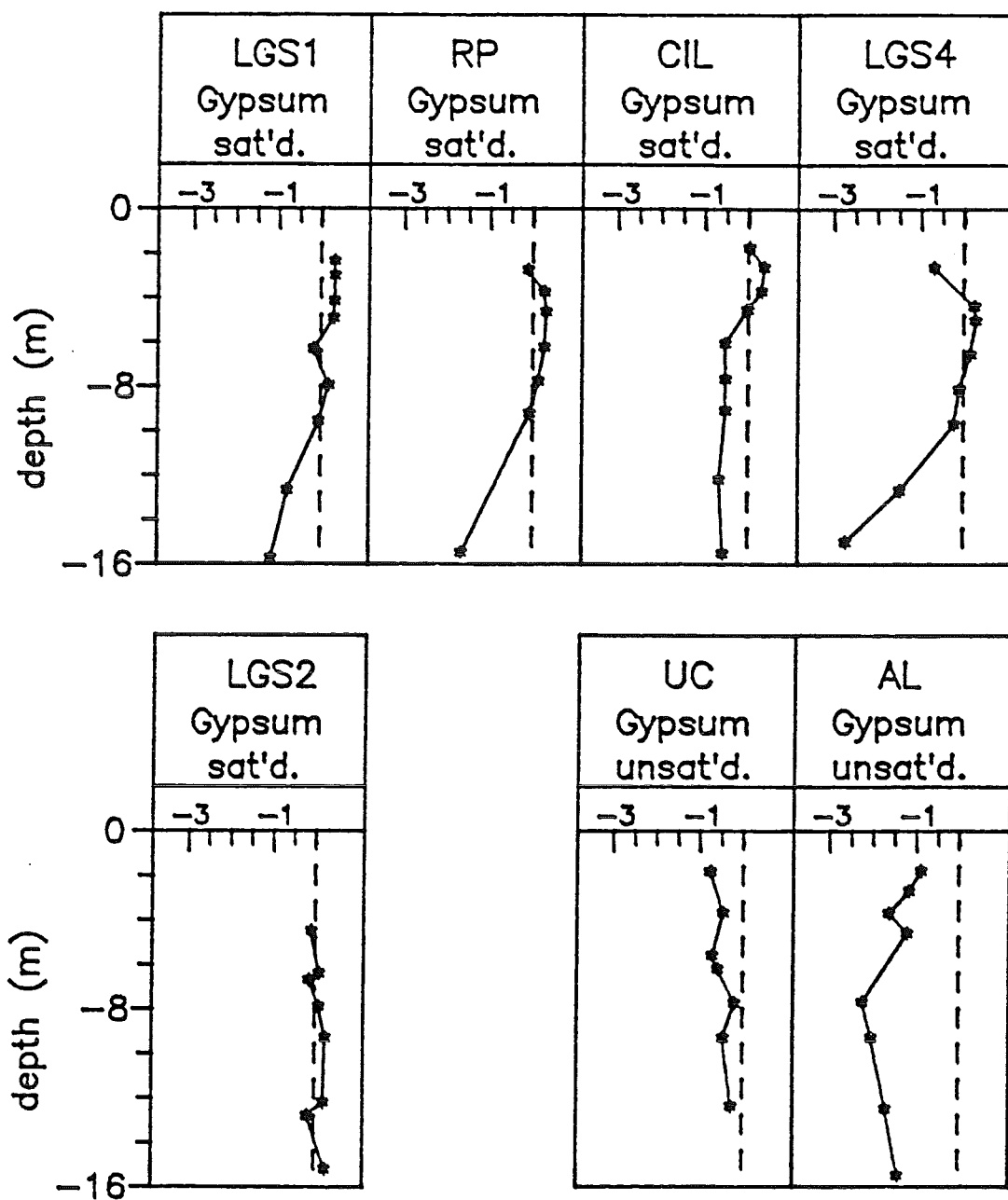


Figure 3: Gypsum Saturation Indices as $\log(iap/Keq)$

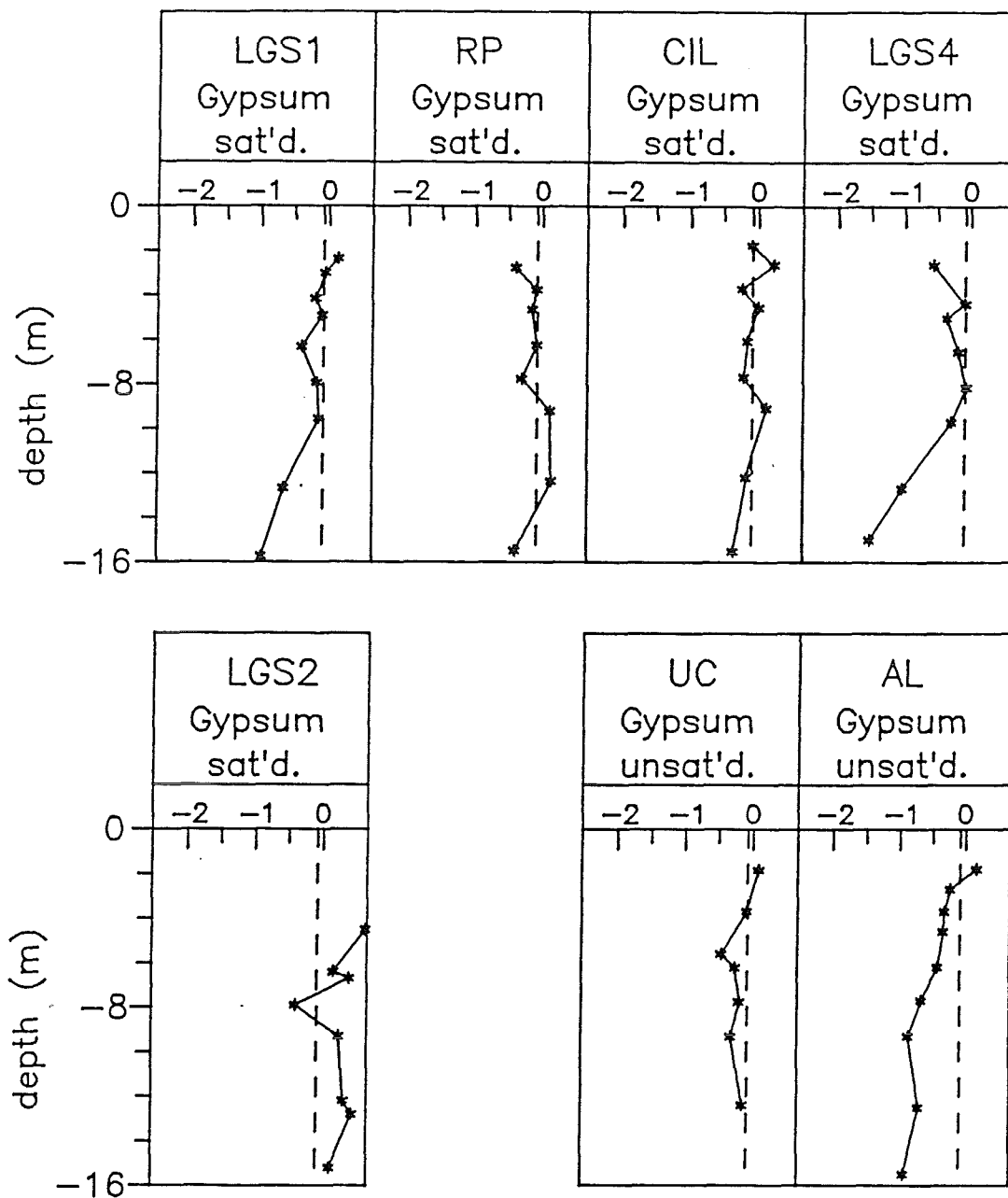


Figure 4: Calcite Saturation Indices as $\log(iap/Keq)$

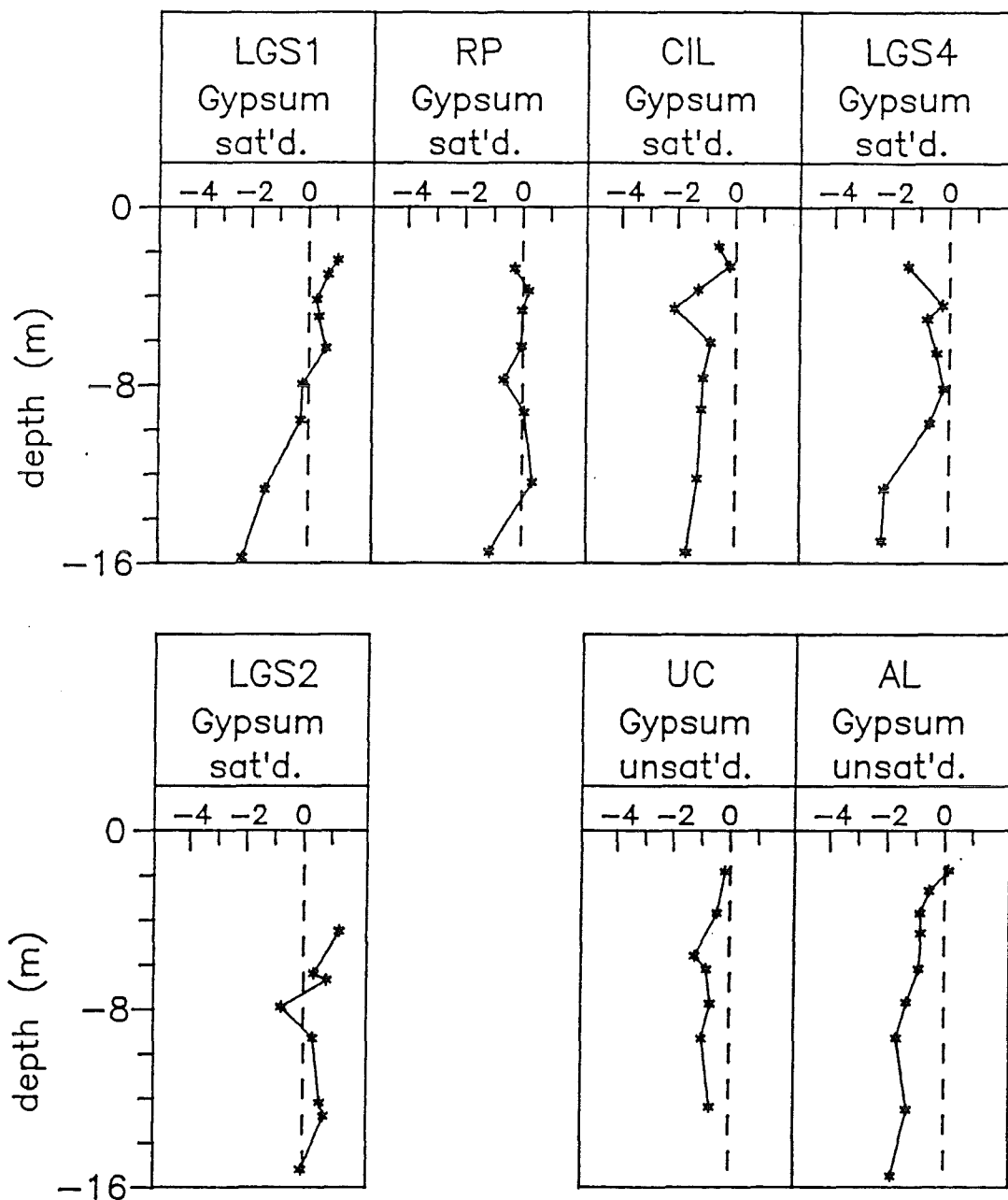


Figure 5: Dolomite Saturation Indices as $\log(iap/Keq)$

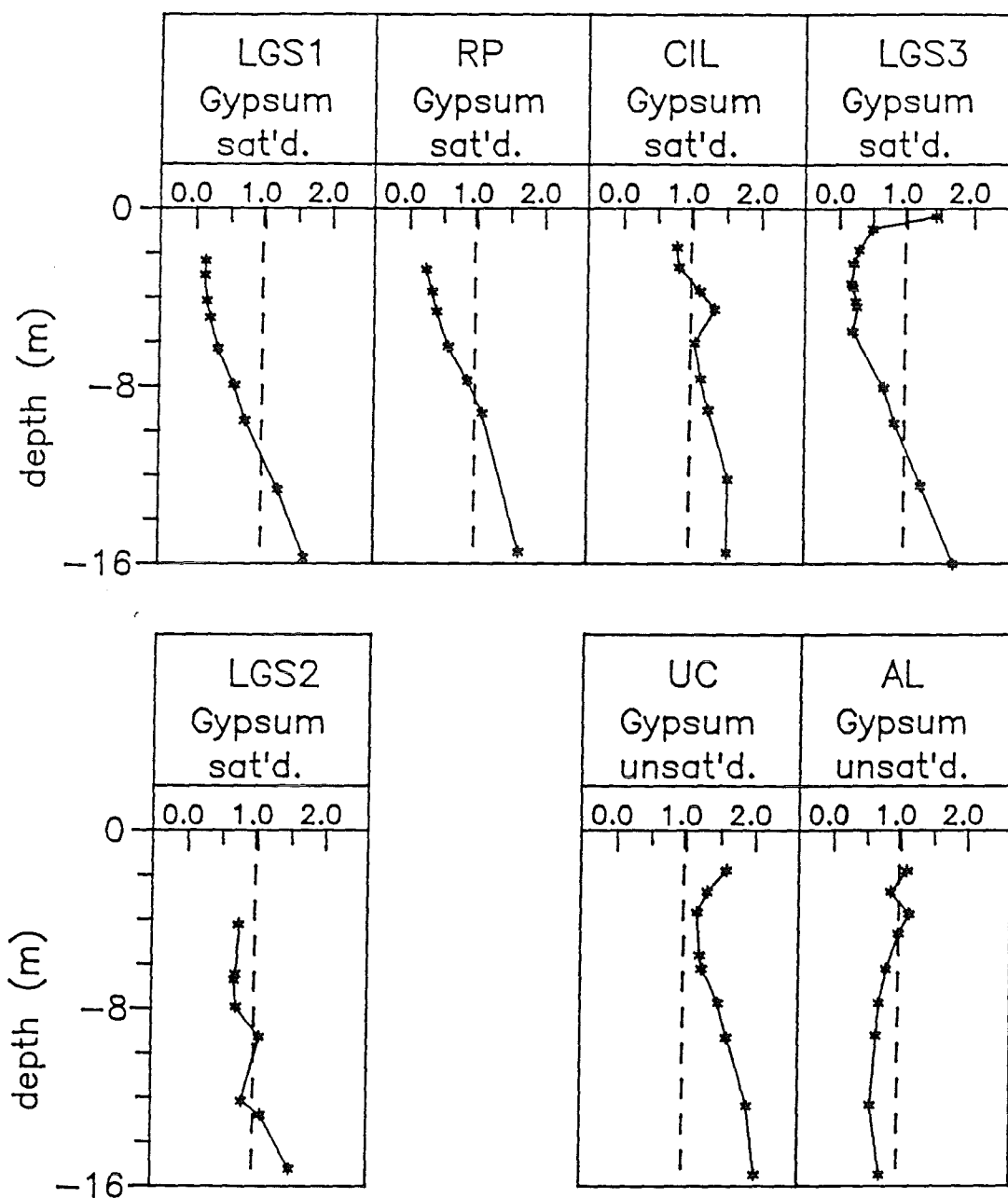


Figure 6: Ca^{2+} to Mg^{2+} Molar Ratios

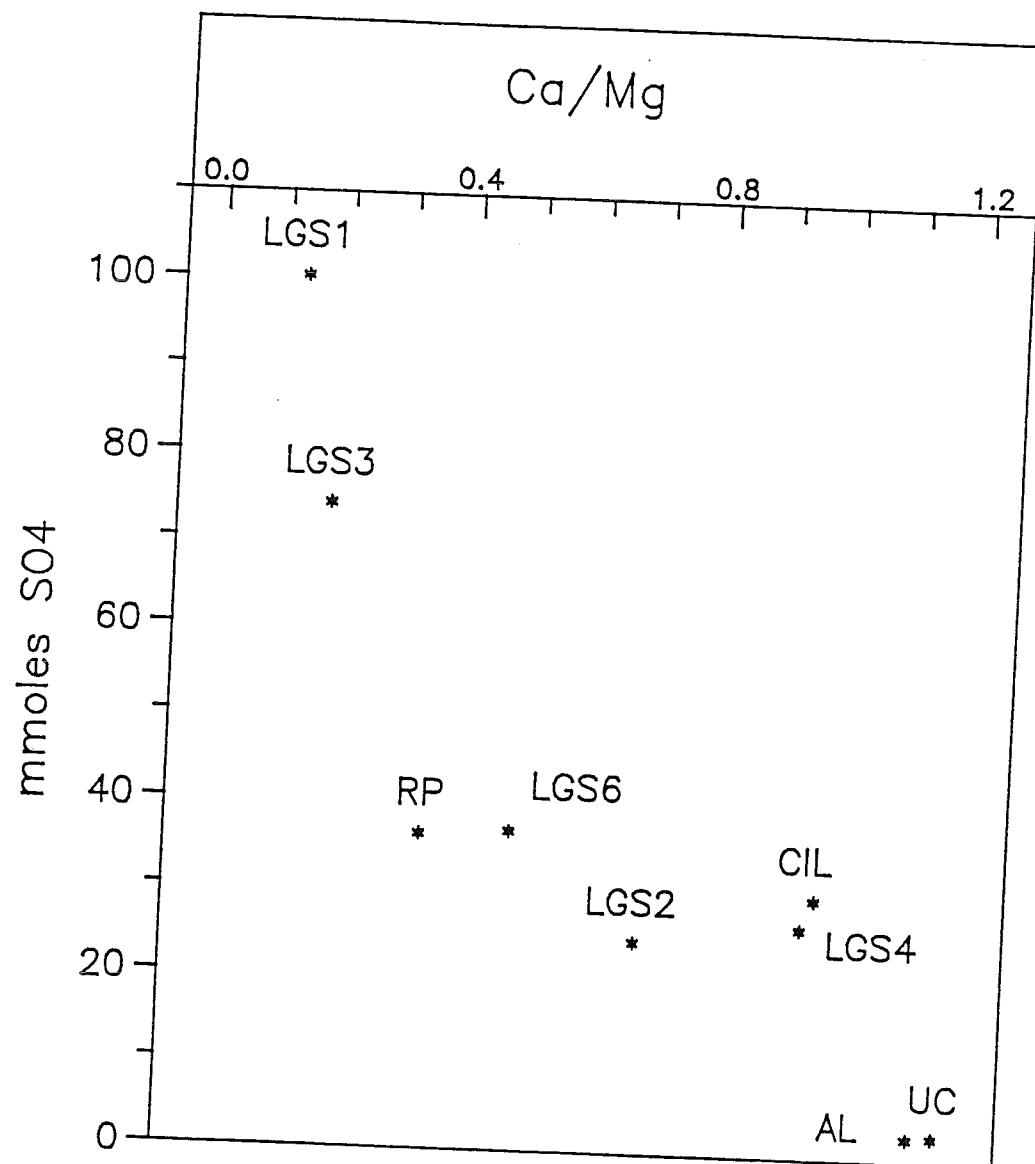


Figure 7: Ca/Mg Molar Ratios Versus SO4

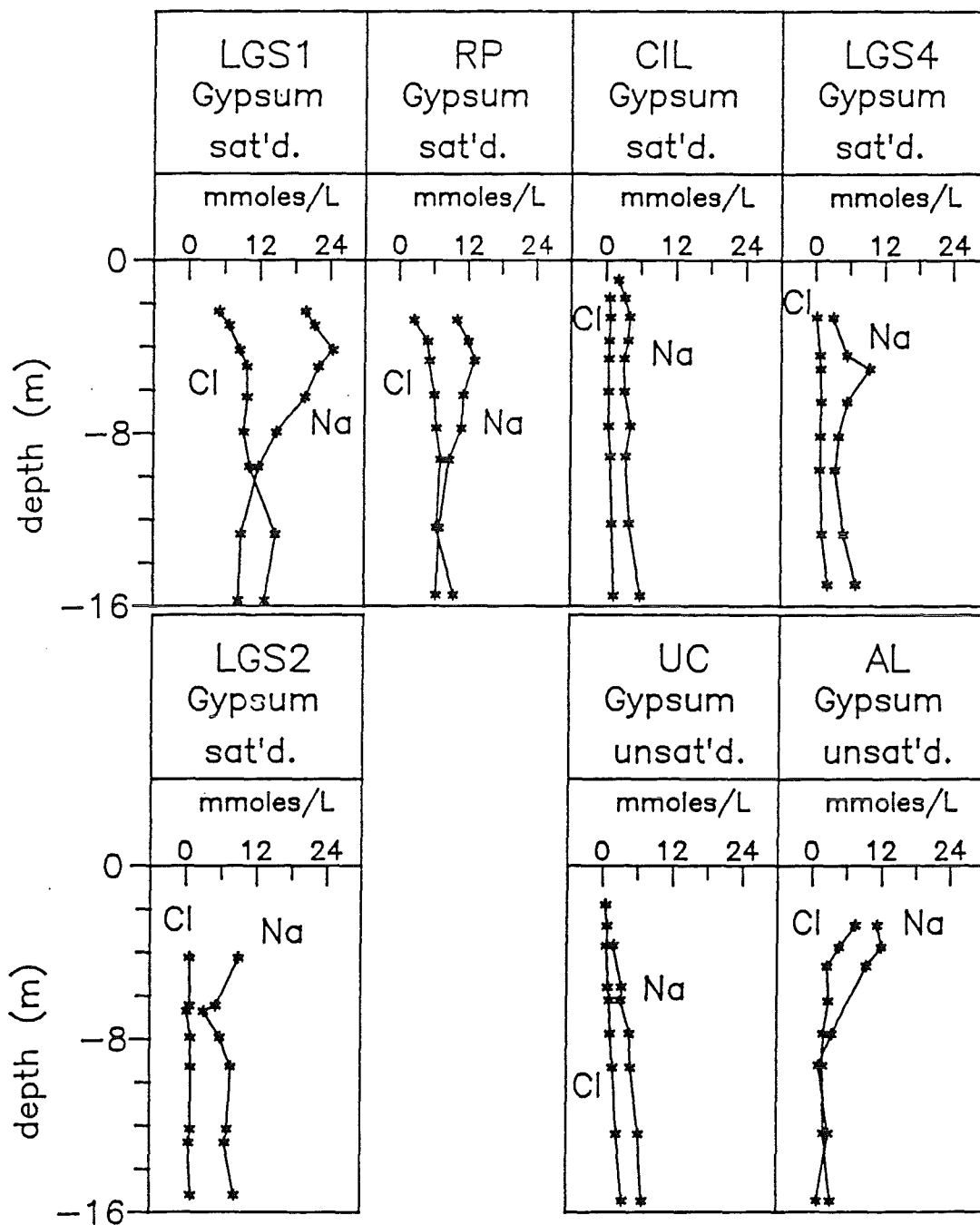


Figure 8: mmol/L of Na and Cl

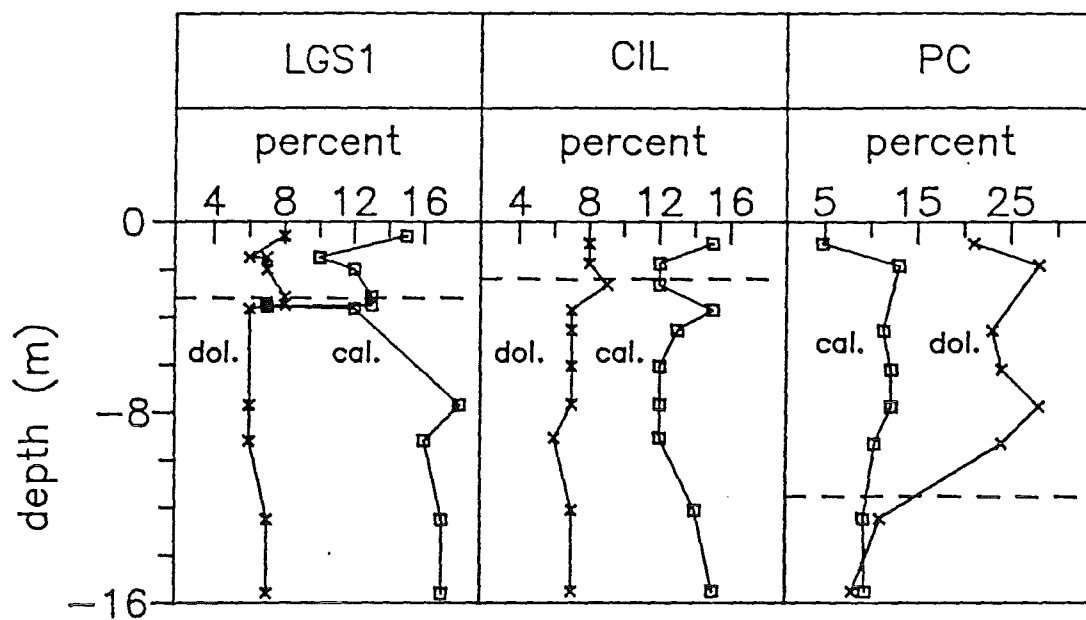


Figure 9a: Calcite and Dolomite Percentages

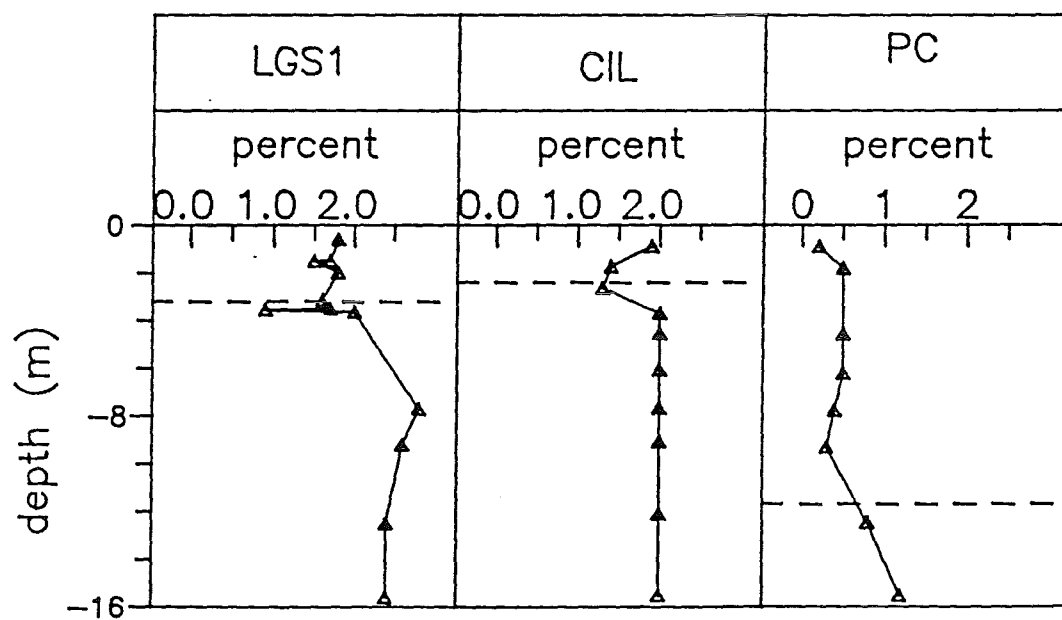


Figure 9b: Calcite/Dolomite

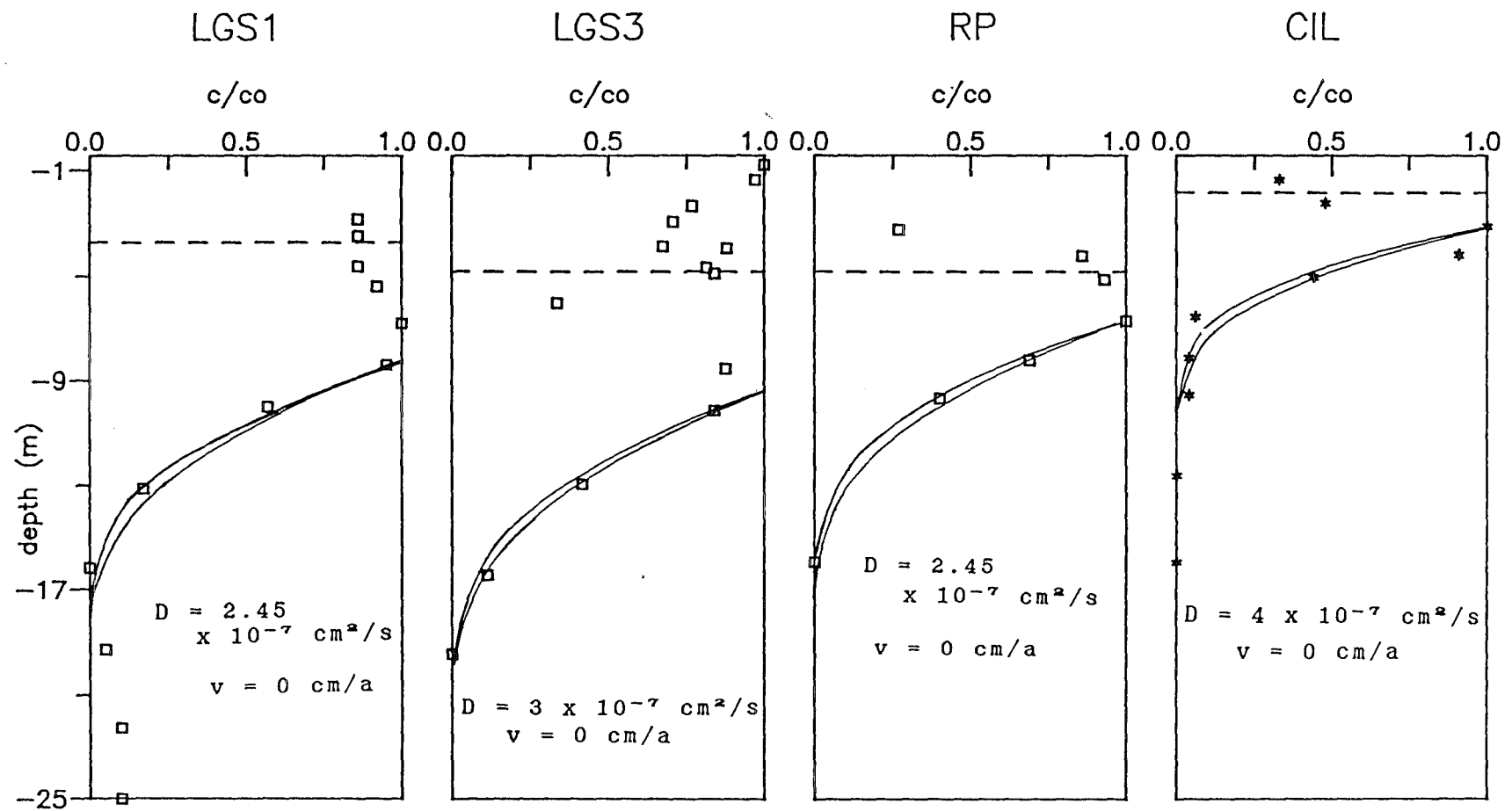


Figure 10a: Comparison between simulated and observed Ca^{2+} Profiles at the LGS1, LGS3, RP and CIL sites for time = 8,000 to 10,000 a.

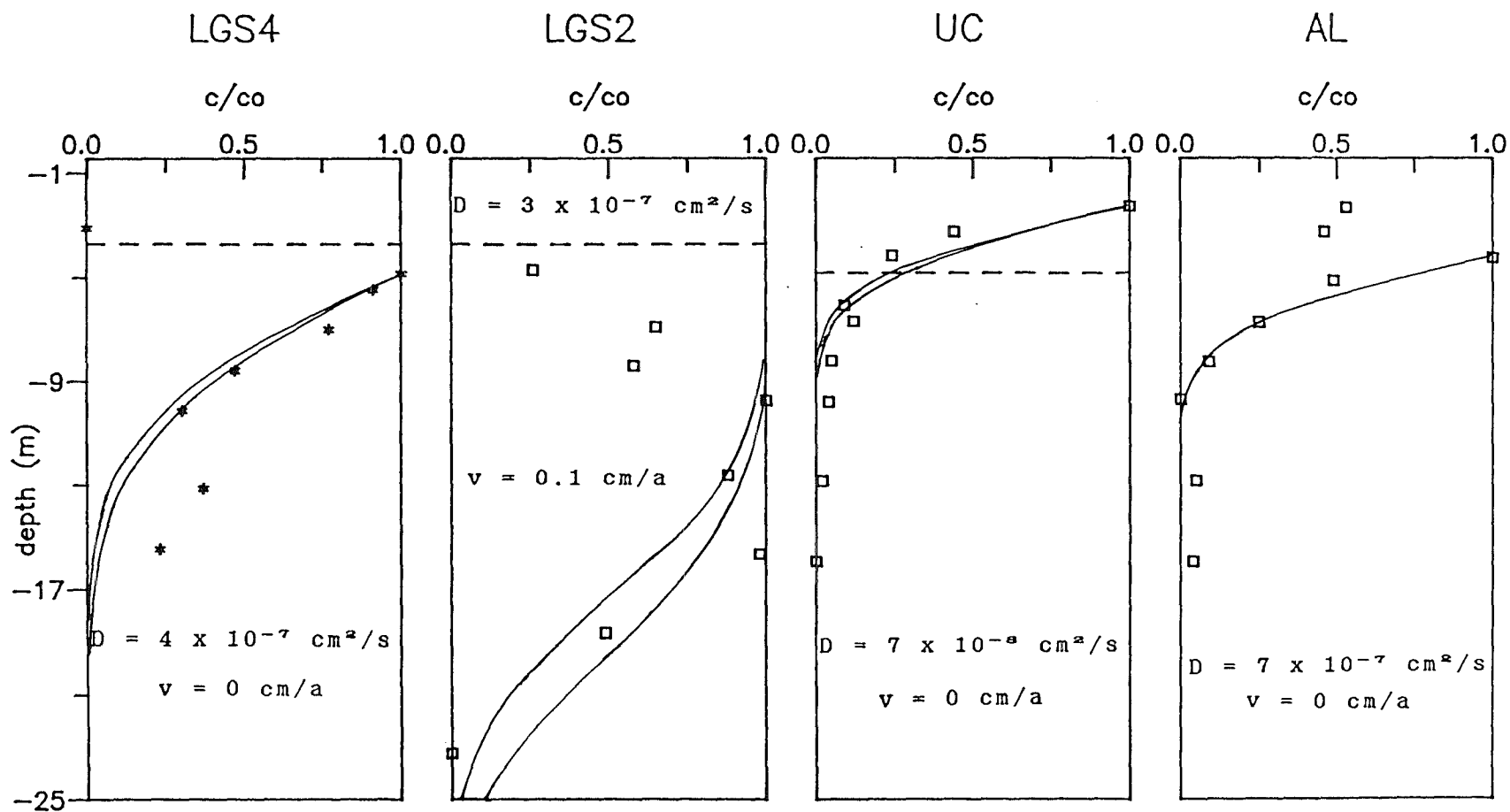


Figure 10b: Comparison between simulated and observed Ca^{2+} Profiles at the LGS4, LGS2, UC and AL sites for time = 8,000 to 10,000 a.

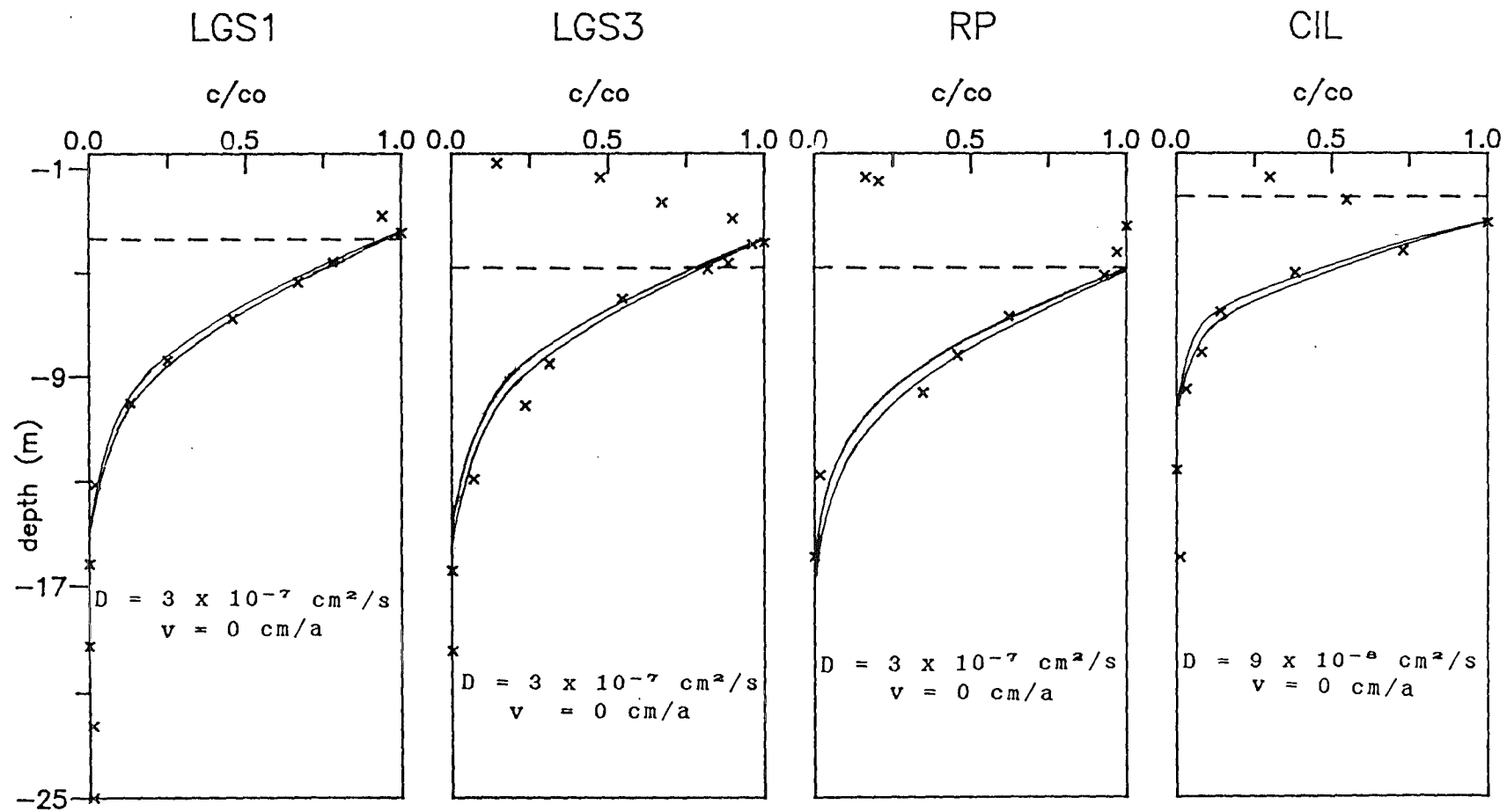


Figure 11a: Comparison between simulated and observed Mg^{2+} Profiles at the LGS1, LGS3, RP and CIL sites, for time = 8,000 to 10,000 a.

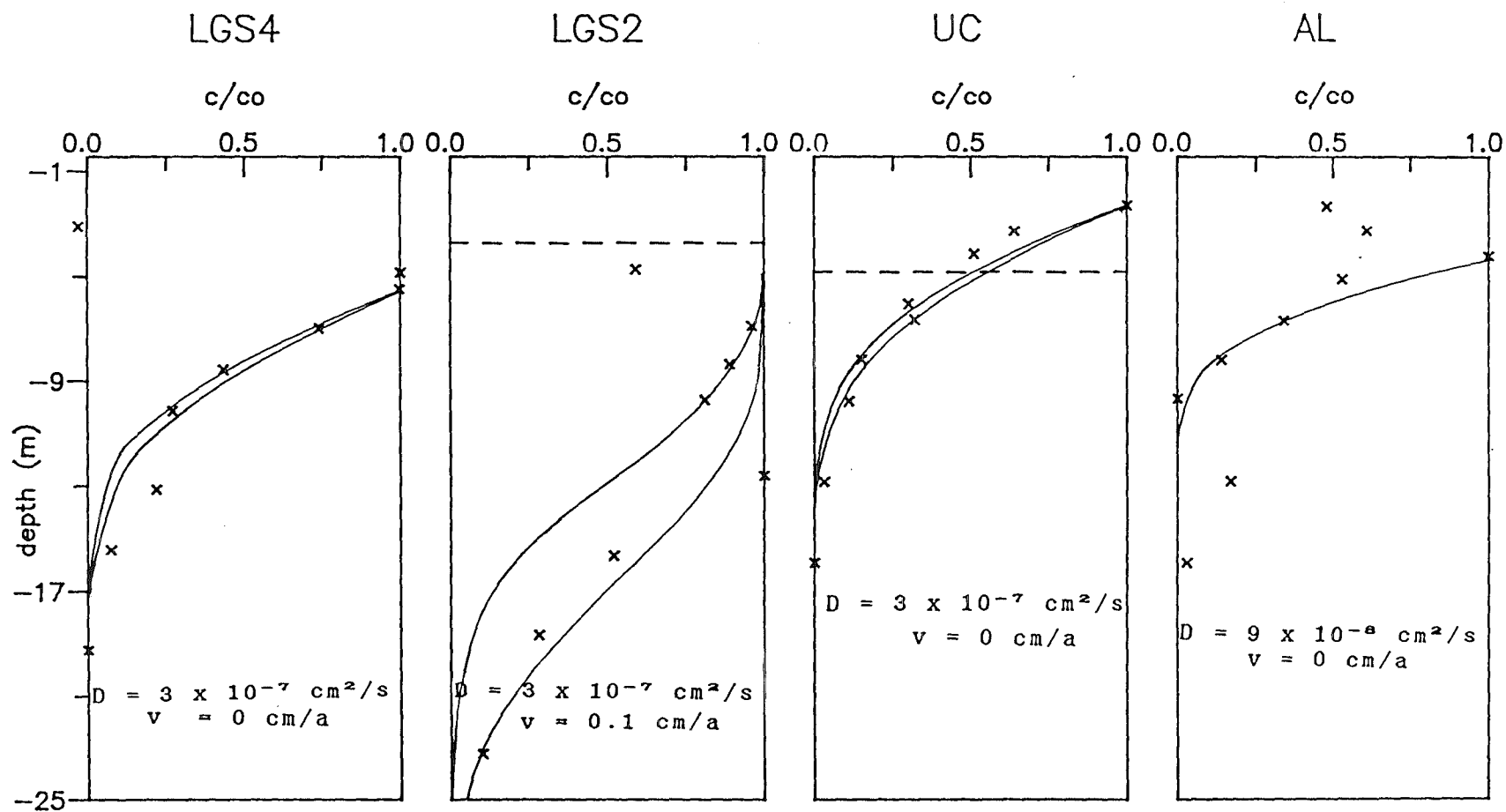


Figure 11b: Comparison between simulated and observed Mg^{2+} Profiles at the LGS4, LGS2, UC and AL sites for time = 8,000 to 10,000 a.

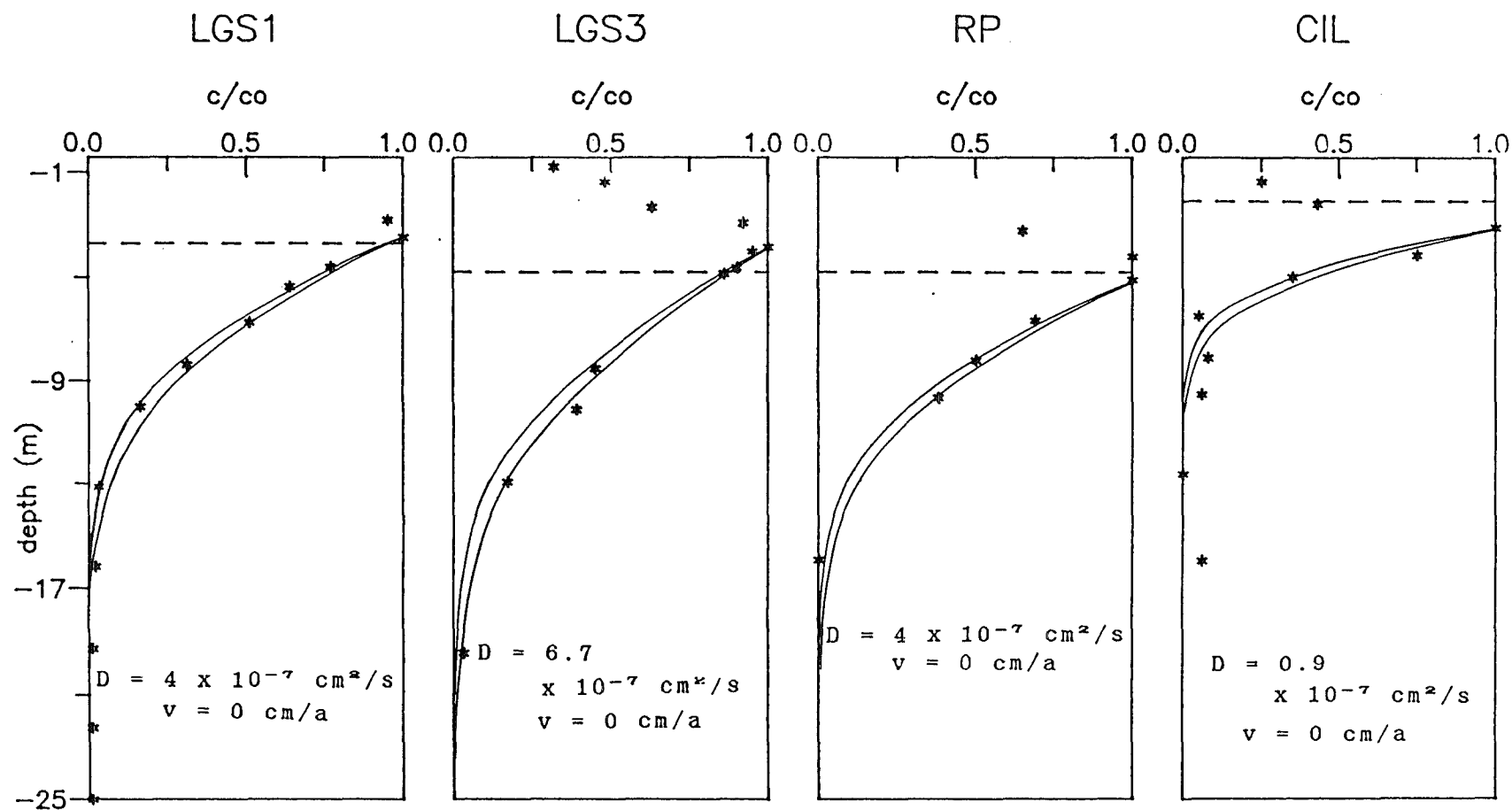


Figure 12a: Comparison between simulated and observed SO_4 Profiles at the LGS1, LGS3, RP and CIL sites for time = 8,000 to 10,000 a.

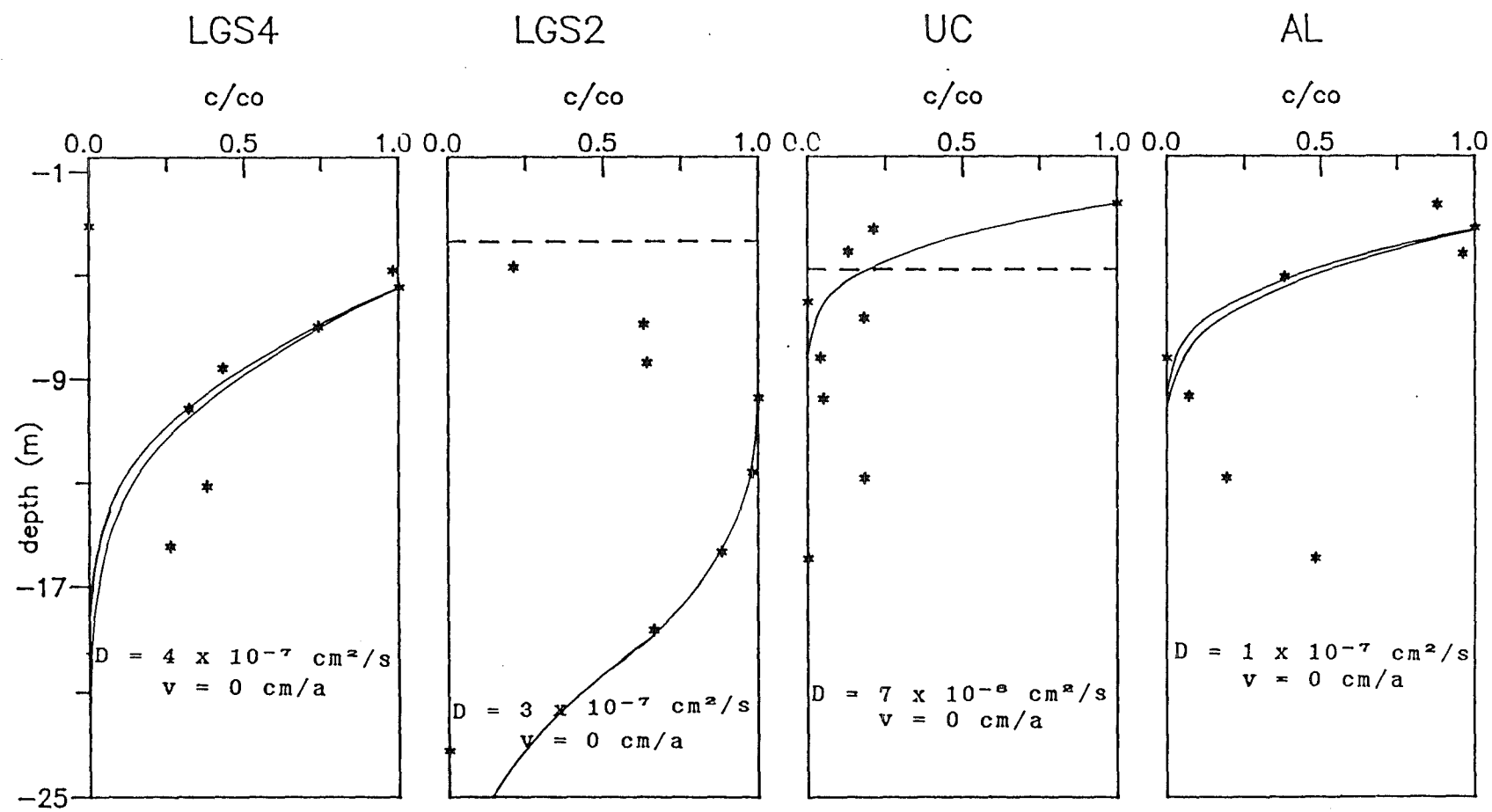


Figure 12b: Comparison between simulated and observed SO₄ Profiles at the LGS4, LGS2, UC and AL sites for time = 8,000 to 10,000 a.

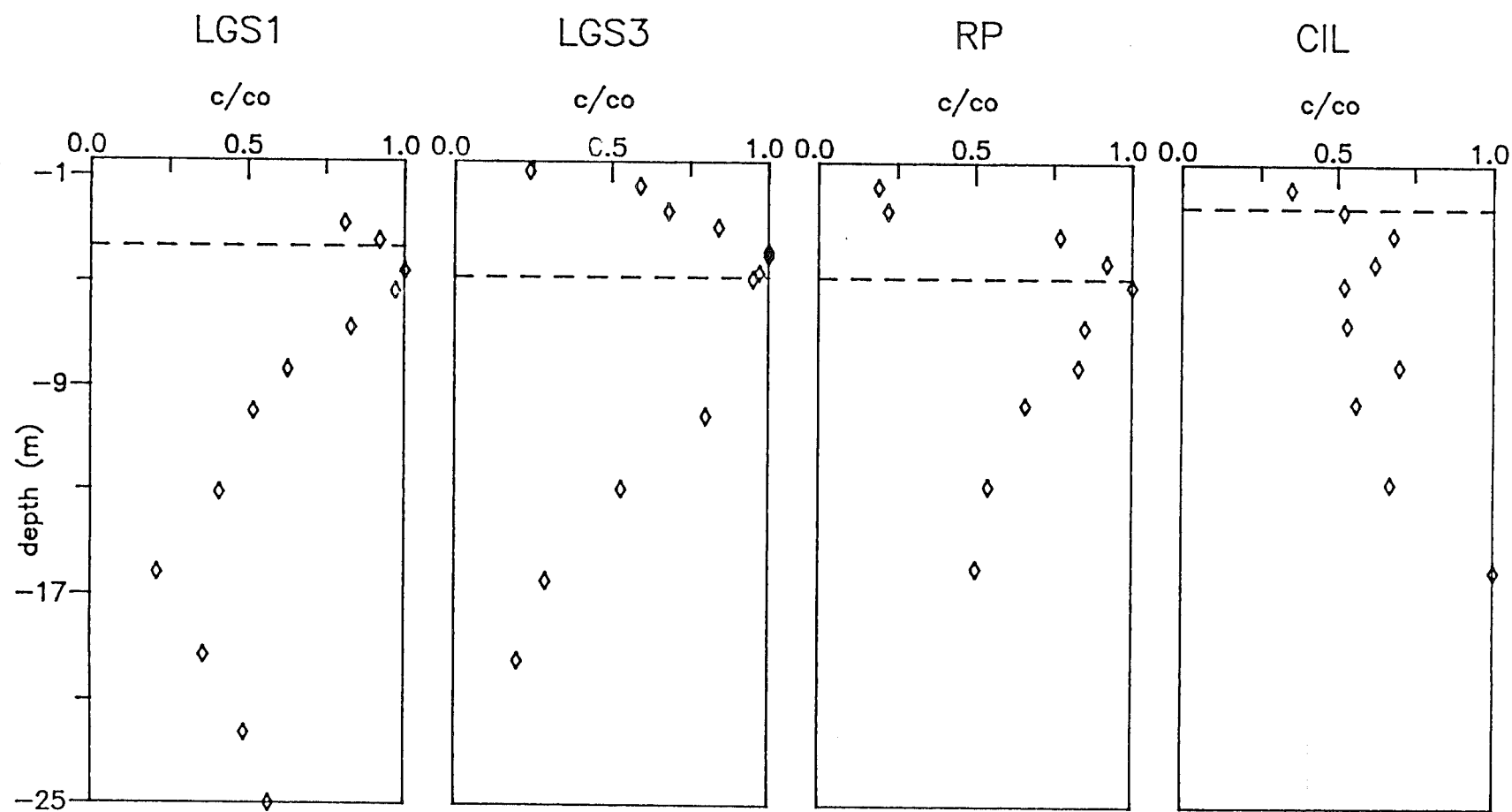


Figure 13a: Comparison between simulated and observed Na Profiles at the LGS1, LGS3, RP and CIL sites for time = 8,000 to 10,000 a.

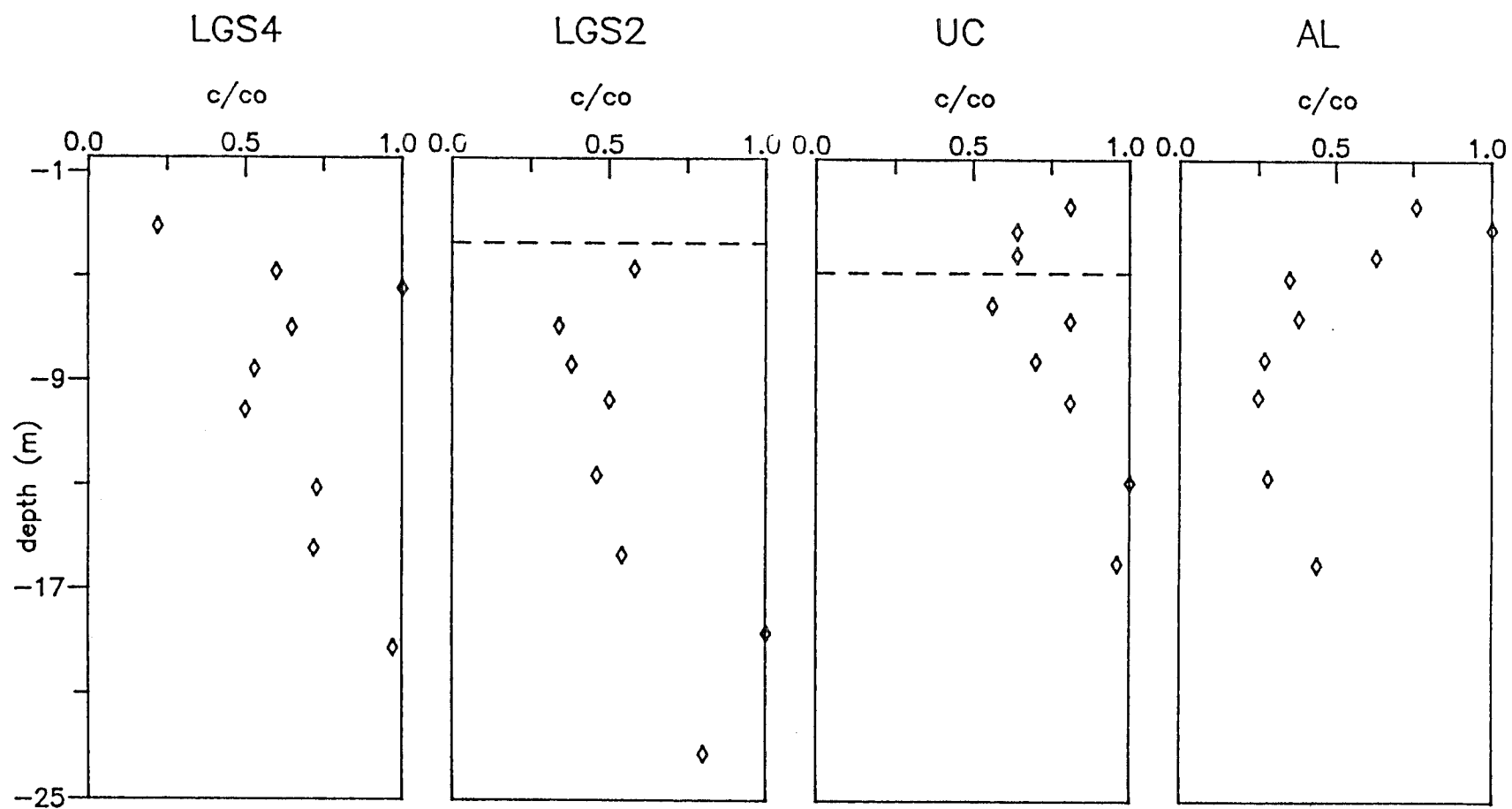


Figure 13b: Comparison between simulated and observed Na Profiles
at the LGS4, LGS2, UC and AL sites for time = 8,000 to 10,000 a.

Table 1: Maximum Concentrations Achieved in the Weathered Zone

SITE	SO4	Mg	Ca	Na	K	HCO3	pH
mg/L							
LGS1	9623	1940	488	560	14.8	1017	6.55
LGS3	7800	1440	552	365	25	---	----
*LGS6	3305	596	502	?	9.7	684	6.05
RP	3487	547	568	300	11.3	758	6.75
CIL	2870	272	588	93	10.4	525	6.65
LGS4	2344	327	507	215	6.7	583	6.65
LGS2	2227	334	470	355	9.3	676	7.15
*LGS7	2195	259.5	497	?	7.01	620	6.45
UC	278	51	132	72.4	2.7	457	7.0
AL	232	140	259	174	451	927	6.6
* PC	505	52.5	113	?	3.01	457	7.0
* ESS	876	67.3	193	?	3.77	488	7.1

* approximate concentrations only
Chemistry affected by bentonite seals

Table 2: Depths at which Maximum Concentrations Occur

SITE	Depth to reduced zone	SO4	Mg	Ca	Na	K	HCO3	pH
(metres below ground surface)								
LGS1	3.3	3.0	3.0	8.0	4.2	4.9	4.2	6.3
LGS3	4.5	3.4	3.4	9.7	8.0	4.4	---	---
LGS6	5.1	3.5	3.0	10.0	?	3.6	3.6	5.1
RP	4.5	4.6	3.8	6.2	4.6	4.6	3.8	4.6
CIL	1.75	2.6	2.6	2.6	2.6	3.7	2.6	3.7
LGS4	no core	5.0	4.4	4.4	5.0	5.0	5.0	6.5
LGS2	3.3	15.2	12.2	15.2	18.2	9.3	4.3	6.4
LGS7	5	5.0	5.0	5.0	?	5.0	3.8	5.0
UC	4	1.8	1.8	1.8	1.8	6.2	1.8	2.8
AL	no core	2.7	3.7	3.7	2.7	6.2	1.8	2.8
PC	12	2.7	2.7	2.7	?	2.7	4.6	1.8
ESS	12	1.8	1.8	1.8	?	2.9	3.7	4.7

Table 3: Results of Simulations of the Chemical Evolution of Weathered Zone

Parameter	Initial Conc. mmoles/L	Final Conc. measured mmoles/L	Final Concentration Simulated as % of dry sediment mmoles/L
pH	7	6.55	6.8
Ca	2.72	10.45	11.4
Mg	1.84	83.09	83.3
Na	7.28	22.4	24.1
SO ₄	1.07	99.94	94.5
TIC as CO ₃	1.91	15.58	14.8
pyrite oxidation			226
calcite dissolution			295 (0.81%)
dolomite dissolution			81.4 (0.41%)
gypsum precipitation			358 (1.7%)
Ca - Na exchange			7.56 (0.42 meq/100)

note: Saturation indices used were:
 calcite -.05
 dolomite 0.65
 gypsum 0.32
 PCO₂ -1.25

Table 4: Diffusion Coefficients

Source	Na	K	Ca	Mg	Cl	SO4
De* x 10 ⁻⁶ cm ² /s						
Lambton County Natural Field Conditions (This Study)	1.5	0.2	0.3	0.3		0.4
Lambton County Landfill Conditions (Quigley et al., 1987)	2.28	0.35	5.71	3.65	6.47	
Lambton County Laboratory Model Studies (Rowe et al., 1985)	3.01				5.7	
Northeastern Ontario Natural Field Conditions (Desaulniers, 1986)			2	2		
Marine Clay, Sweden (Sjoberg et al., 1983)			3 to 53	to 5		
*estimated Kd	0.91	8.64	5.67	5.67		4.18

Notes:

$$*K_d = (De/De^* - 1)/(p/n)$$

where

De = De of Cl (assumes Cl is conservative)

De* = De* obtained during the current simulations

p = bulk density = 1.56 g/cm³ (Heystee et al., 1982)

n = porosity = 0.43

Kd = distribution coefficient

= concentration adsorbed/concentration in solution

APPENDIX I.

THE SQUEEZING METHOD

ABSTRACT

The major ion chemistry of water which was pumped from two types of piezometers was compared to a laboratory method which involved squeezing the pore-water from core samples. The influence of pressure changes and sediment storage on the results obtained during squeezing was investigated. Pressure application caused an insignificant lowering of major ion concentrations, with K^+ exhibiting the largest effect. In spite of the small volumes of water generally obtained during squeezing, sample contamination was kept to a minimum. pH and total inorganic carbon must be measured as soon as possible after water collection, on samples which have not been exposed to the atmosphere. Sediment samples must be squeezed very soon after they are collected, as oxidation of sediments prior to squeezing results in large increases in the concentration of all major ions except Cl^- . The bentonite seals in shelby-hole piezometers caused cation exchange effects. Otherwise, shelby-hole and augered-hole piezometers gave inorganic chemistry results which were reproducible over successive sampling intervals, and were similar to one another and to non-aged squeezed samples. Squeezing is a viable method for sampling groundwater for the purposes of inorganic chemical analyses, and is advantageous over piezometer sampling in clays when samples are required quickly, when accurate stratigraphic control is required, or when the unsaturated zone is being sampled.

INTRODUCTION

As a result of their low permeability and reactive nature, clayey deposits present some unique problems for the collection of geochemically intact water samples.

Following pumping, it often takes weeks or months for water levels to recover in low permeability deposits. Thus the usual recommendation that 4 to 6 well-volumes be flushed from piezometers before sampling (Wilson and Rouse, 1983) is often disregarded. The most commonly used seals, bentonite or cement grout, have the potential to react chemically with the groundwater. Borehole smear which occurs during drilling may retard the entrance of water into the piezometer.

An alternative technique for collecting water samples from clays involves the application of pressure in order to squeeze the pore-water from a sample. This technique has been used to sample pore-waters mainly from clayey sediments (see for example, Siever et al., 1962; Manheim, 1966, 1974; Kalil and Goldhaber, 1973; Patterson et al., 1978; Murray et al., 1978; Frape and Patterson, 1981; Crooks and Quigley, 1984). Several sources of potential error involved in the method have been identified. These include pressure effects (Manheim, 1974; Morgenstern & Balasubramanian, 1980; Manheim, 1974) sample contamination, and storage effects, the latter of which encompass temperature fluctuations (Bischoff et al., 1970; Manheim, 1974) exposure to oxygen (Bray et al., 1973; Lessard and Mitchell, 1985), and

evaporation (Lessard and Mitchell, 1985).

The purpose of this investigation is to evaluate groundwater sampling techniques in low permeability clayey deposits. The major ion chemistry of water samples obtained from piezometers is compared to that of water obtained using the squeezing method. Factors with the potential to affect the chemistry of squeezed waters, including sediment storage, and pressure application, were also investigated.

A comparison of squeezed and piezometer waters was carried out at 7 sites in Lambton County. Five cores, extending from 1 to 15 m below ground surface, consisted of the shelby tube samples collected during the installation of the LIS piezometers. These sites were: RP, CIL, PC, UC and ESS (Figure 1). Two cores extended continuously from the surface to 6 m depth, at sites LGS1 and LGS3 (Figure 1). These 7 cores, as well as samples from 2 additional cores in Lambton County, were used in the laboratory investigation of pressure and storage effects.

METHODS OF INVESTIGATION

Procedures for the installation of piezometers, as well as the collection and storage of cores, is given in the main body of the paper.

In order to squeeze the water from clay samples in the laboratory, pressure was applied using both a hydraulic oil press and compressed nitrogen to operate a gas powered squeezing apparatus. The hydraulic oil method is illustrated in Figure A1. Pressure was applied to the stainless steel squeezer using an Enerpac P-39 pump. The amount of pressure being applied to the sample was detected using a voltmeter calibrated with a pressure transducer in line with the pressure guage.

The second squeezing method relied on 9 stainless steel squeezers connected in-line to a tank of compressed nitrogen (Figure A2). In this case the amount of pressure applied was measured directly from a pressure guage in the nitrogen line. In addition to the fact that 9 samples could be squeezed at one time, the gas squeezers also had the advantage that the amount of pressure applied was kept constant with an automatic pressure transducer. The hydraulic oil squeezer lacked such a device, and thus the applied pressure had to be continuously increased as the sample was compressed. This usually resulted in a small but significant pressure pumping action.

As squeezing produces small volumes of water, and potential sources of contamination are numerous, extreme care must be taken during

squeezer assembly. Between squeezing runs, all squeezer parts, including o-rings, were thoroughly washed and dried to remove clay and grease. All parts of the squeezers that were to come into contact with the clay sample or the extruded water were thoroughly rinsed with de-ionized water. These squeezer parts were touched only with disposable surgical gloves which had been previously rinsed with de-ionized water. Once rinsed, squeezer parts were allowed to air dry before assembly.

As each gas squeezer was individually made, all squeezer parts are labelled with a number from 1 to 9, and parts with the same number must be kept together. These squeezers were assembled as follows. Squeezer tops were placed upside down in a line supported between two 3 cm by 3 cm lathes to prevent the air ports from being crushed, and the pistons were placed on the tops. O-rings were greased with an inert silicone lubricant (Dow Corning high vacuum grease) before being put on the o-ring grooves. A disk of teflon with the same diameter as the piston was placed between the piston and the clay to help keep the upper parts of the squeezers clean. Squeezer barrels were then fitted over the tops and pistons.

Samples to be squeezed were then unwrapped and cut into 6 1/2 cm lengths for squeezing. The outer edges were quickly trimmed from each sample to remove parts which may have become contaminated as a result of handling or exposure to the atmosphere. Samples were then described, weighed and placed on the teflon inside the barrels. In later runs,

samples were placed inside polyethylene bags which had previously been rinsed with de-ionized water and air-dried. This reduced squeezer cleaning time, and protected the squeezers from damage resulting from the abrasion caused by pebbles during squeezing. Tests in which de-ionized water was placed inside the bags for 3 days showed that a negligible quantity of major ions were released from the bags.

Two Whatman 40 filter papers, followed by 2 stainless-steel wire mesh screens, were placed over the clay. Finally, the base was fitted over the barrel and the squeezers were bolted together.

The squeezer used in the hydraulic oil set-up was a standard squeezer design similar to that described by Siever (1962), Manheim (1966), Patterson et al. (1978) and Frape and Patterson (1981). The assembly of this squeezer was similar to that for the gas squeezers except that the procedure was from the bottom to the top.

All squeezing was carried out in a cold room at 7 °C. Pressure was applied in the following psi increments: 200, 450, 750. Pressure was stepped-up when water flow slowed down, which, for the clays investigated, usually occurred within 3 to 4 hours. In order to further reduce the potential for contamination, the first ml of expelled water was discarded.

During the initial squeezing runs water flowed from the access port in the squeezer base into 10 ml capacity gas-impermeable glass syringes.

Light-weight teflon caps, or parafilm stretched around the top of the syringe prevented the collecting water from exposure to the atmosphere. Later, the technique for collecting water was modified so that a length of polyethylene tubing ran from the access port directly into a 30 ml high-density polyethylene sample bottle. This arrangement greatly increased the efficiency of the sample collection operation. The assembled gas squeezers are illustrated in Plate A1.

The initial expelled water was collected in 0.5 ml vials and immediately measured for pH, using a Metrohm 632 digital readout pH meter with an AG 9100 Herisau electrode. As the volume of water produced was never enough to perform an alkalinity titration, total inorganic carbon (TIC) was measured in the laboratory at the time of other major-ion determinations, using a Beckman Model 915 Total Carbon Analyzer with an infra-red detector.

The procedure for water collection for major-ion analyses was the same as for piezometer samples. Two water samples were collected from each squeezed sample; following filtration, one sample was acidified immediately to a pH of less than 2 with reagent-grade Baker-analyzed nitric acid and used for cation analyses, while the other sample was left unacidified and used for anion analyses.

Squeezing was usually completed within 30 hours. Upon extrusion from the squeezers, clay samples were re-weighed. Approximately one

third of the sample (of a known weight) was then dried at 105 °C for 48 hours and re-weighed. In this way the total water content, as well as the proportion lost during squeezing, was determined.

RESULTS AND DISCUSSION

Laboratory Investigations

Water Sample Size

The amount of water removed during squeezing is a function of the total water content by weight, as shown in Figure A4. For the clays investigated, the water removed ranged from less than one tenth to almost one half of the total water in a sample. Water removal was less efficient for samples with low water contents.

Pressure Effects

When pressure is applied to clays they tend to act as filters, allowing water to pass, but retaining ions on the high pressure side of the membrane. This process is known alternately as hyperfiltration, reverse chemical osmosis, or anion exclusion. The property of clay minerals which is responsible for hyperfiltration is the Diffuse Double Layer (DDL), which is composed of the negatively charged clay surface and its associated layer of cations (Bohn et al., 1985).

As explained by Bolt (1976), the extent of the DDL corresponds to the width of the zone where ionic concentrations differ significantly from the bulk solution. Any factor which increases the tendency for cations to diffuse away from the clay surface increases the extent of

the DDL, and thus increases its influence. The thickness of the DDL varies inversely with the square root of bulk solution concentration and increases with increasing surface charge density of the clay (Bohn et al., 1985). The thickness of the DDL also varies inversely with the square root of the charge of the cations, as highly charged cations sit closer to the clay surface (Bohn et al., 1985). Therefore, the thickness of the DDL will increase as the surface charge density of the clay increases, as the electrolyte level decreases, and as the field strength (charge/surface area) of the cation decreases. Thus DDL theory predicts that the degree of hyperfiltration should increase with increasing montmorillonite content of the clay and decreasing electrolyte levels. Moreover, large monovalent cations should be more affected by hyperfiltration than small divalent cations.

Another geochemical process which results from the application of pressure to clay soil is a decrease in total cation exchange capacity as expanded layers are compressed (Weaver and Beck, 1971). For compaction pressures up to 20,000 psi, divalent cations are released to a greater extent than monovalent cations (Hanshaw, 1963; Weaver and Beck, 1971).

Results of previous investigations into the magnitude of chemical changes caused by the application of pressure are summarized in Table A1. These results indicate that pressures up to at least 700 psi cause negligible chemical changes to extruded water.

A series of tests were conducted to quantify the degree of hyperfiltration during squeezing exhibited by clay tills from southwestern Ontario. The 38 samples investigated may be subdivided into three groups. Group 1 samples were from depths of 24 to 30 m, while Group 2 samples were from depths of 1 to 12.5 m. Samples in Group 3 were homogenized in a milk-shake machine prior to being squeezed, in order to destroy their oriented fabric. For these 38 samples, two or more successive water samples, s1, s2 ... sn, were collected. For each major-ion in each till sample a filtration ratio (FR) was calculated as $FR = \text{concentration of ion in s1} / \text{minimum concentration of ion in subsequent samples}$.

Thus the larger the FR, the higher the degree of hyperfiltration.

Table A2 lists the FR's for each sample investigated, as well as the FR per ion obtained by averaging over samples from groups 1 and 2. Average FR's per ion were as follows:

$$K^+ > SO_4^{2-} > Na^+ > Ca^{2+} > Mg^{2+} = Cl^-.$$

$$1.3 > 1.09 > 1.05 > 1.04 > 1.01 = 1.01.$$

These FR's indicate that, as expected, concentrations tended to decrease slightly as squeezing proceeded. However, consistent with the findings of previous researchers summarized in Table A1, these changes are very small. For the 30 samples investigated, the maximum change in concentration between initial and subsequent water samples was a factor of 1.72, and FR's were generally much lower than this. This amount of fluctuation is within the analytical error of major-ion analyses, and is

insignificant for practical purposes.

The relative FR per ion indicates that small monovalent ions were retarded more than large divalent cations, consistent with DDL theory (Bolt, 1976). A similar sequence was found in shales by Kharaka and Berry (1973). The latter sequence was, in going from most retained to least retained:

$\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$.

The "TMS" model which is sometimes used to predict the movement of ions through clay membranes, predicts that the concentration of anions in extruded solutions should increase rather than decrease (Kharaka and Berry, 1973). However, this model is deficient in that it neglects the effect of complexing and the interaction of the diffusion of ions in and out of the membrane (Kharaka and Berry, 1973). The experimental results of the current investigation, and those of Kharaka and Berry (1973) show that anions as well as cations are lower in solutions extruded under pressure.

Average FR's for samples from Group 3 were less than 1, indicating that no net hyperfiltration occurred (Table A2). While a loss of cation exchange capacity, or possibly the dissolution of minor amounts of calcite, may be responsible for a small part of the increase in concentration, this degree of fluctuation is probably largely the result of experimental and analytical error. These tests are consistent with

the earlier finding of Benzel and Graf (1984) that clays with oriented structures are more efficient hyperfiltrators than clays with dispersed structures. The DDL is more effective for oriented structures than for dispersed structures (Bolt, 1976).

Relative to samples from Group 2, samples from Group 1 exhibited larger average FR's for all ions (Table A2). Samples at depth below the weathered zone (Group 1) contain lower major-ion concentrations and a larger proportion of Na^+ than samples from shallower depths (Group 2) (Rodvang, 1987). Thus the fact that Group 1 samples exhibit a higher FR is consistent with the DDL theory and the earlier findings of Hanshaw and Coplen (1973), that hyperfiltration increases as solution concentration decreases and the percentage of monovalent cations increases.

In controlled laboratory experiments, Kharaka and Berry (1976) found that the Filtration Ratio (FR), defined as concentration in input solution / concentration in effluent solution, increased as the compaction pressure applied to the membrane increased. In the current investigation, as the input concentration was unknown, FR was defined as the ratio between the initial sample s_1 , and successive samples s_2 , s_3 , amount of water extruded, a value denoted as "filtration efficiency" (FE) was calculated as the percentage decrease in concentration per ml of extruded water. That is, FE equals the decrease in concentration of the ion i between two successive water samples s , expressed as a

percentage of the average concentration of i in t .

FE = % decrease in concentration per ml water

$$= (i(s_{n-1}) - i(s_n)) * 100 / w(i, t) / (\text{ml between } s_{n-1} \text{ and } s_n)$$

FE values determined in this way for 38 till samples are listed in Table A3. Consistent with the observations of Kharaka & Berry (1976), FE tended to increase in going from s_1/s_2 to s_1/s_3 , s_1/s_4 et cetera. However, even though compaction pressures were usually greater on later samples, FR was almost always substantially higher for s_1/s_2 than for s_2/s_3 , s_3/s_4 et cetera. Sample 23, with an initial pressure application of 2000 psi, showed a smaller FR than a split of the same sample, number 22, with an initial pressure application of 750 psi. Thus in the current investigation, for pressures in the range of 200 to 2000 psi, the magnitude of the pressure applied did not appear to affect the magnitude of hyperfiltration. Moreover, the largest degree of hyperfiltration tended to occur during the initial application of pressure.

The effect of pressure fluctuations may be more significant. Two samples from Group 1 (15 and 25) retained more K^+ than the other samples (Table A2). These samples were subjected to a unique sequence of pressure increments. Whereas the sequence of pressure increments applied to the majority of samples was: 200, 450, 750, the pressure sequence applied to samples 15 and 25 was 750, 0 750. Although this test was applied to a limited number of samples, it implies that

pressure fluctuations decrease the reproducibility of successive water samples. A comparison of results between samples tested with the energpac system to those tested with the gas system supports this hypothesis. Reproducibility tended to be higher in the gas system, which made use of an automatic pressure regulating system, than in the energpac system, which lacked such a device. For example, sample RP40B in Table A3 was squeezed in the energpac system. Although the attempt was made to keep a constant pressure on the energpac piston, pressure fluctuations were unavoidable.

While pressure effects were not found to be a significant source of error in the squeezing method, sediment aging during storage was found to be detrimental. Lessard & Mitchell (1985) conducted a detailed investigation of the effects of sediment storage on the pore-water chemistry of quick clays. Even when water content remained practically unchanged, pore-water concentrations of Ca^{2+} , Mg^{2+} , and SO_4^{2-} increased by several fold. This effect was thought to be caused mainly by the oxidation of iron sulphide, which resulted in the formation of iron hydroxide and sulfuric acid. Carbonic acid was also thought to be produced by the oxidation of organic matter. Carbonic and sulfuric acid would cause the dissolution of calcium carbonate. One final effect was the increase in pore-water Na^+ and K^+ as exchange site equilibration occurred in response to the influx of divalent cations (Lessard and Mitchell, 1985).

Lessard and Mitchell (1985) found that exposure to air was the most

important factor in the aging process. Storage at 4 °C hindered the oxidation of organic matter and waxing in several layers of paraffin slowed aging. A sample which was left in the original shelby tube, waxed at both ends, showed no aging over 14 months. Presumably, storage in a waxed shelby tube provides the best barrier to the atmosphere.

In the current investigation, core samples that were not needed in the first squeeze were re-wrapped in several layers of plastic wrap and stored at 4 °C, to be squeezed at later dates. In some cases a core was split vertically down the middle, and the 2 halves were squeezed at different times.

In 8 of the 9 samples tested concentrations of all major ions consistently increased with time (Table A4a). In some cases drying may have been partly responsible for the increase in major ion concentrations with time; however, in 5 of the 9 samples water contents remained practically unchanged (Table A4). Therefore, the oxidation of iron sulfide, with resultant carbonate dissolution and exchange site equilibration (Lessard and Mitchell, 1985) is probably responsible for the change in pore-water chemistry with time.

An investigation into the effects of warming is also reported in Table A4, on samples with the prefix w. These results confirm those of Lessard and Mitchell (1985) and Fanning and Pilson (1971) that samples must be stored at insitu temperatures.

Field Results

Comparison of Squeezing and Piezometer Data

A comparison of a range of typical results obtained from squeezing to those obtained from piezometers is illustrated in Figures A5 to A10. A comparison of absolute concentrations is given in Appendix II, while Table A5 lists ratios of squeezed to piezometer results. The augered-hole and shelby-hole piezometers gave very similar chemical results provided that contamination from bentonite seals did not occur.

The uniformity of concentrations in the AHP-type piezometer nest at the LGS-1 site over 3 sampling periods (Table A5) suggests that this piezometer nest gave reliable results. In the SHP-type nest, Na^+ fluctuated erratically, and exhibited a concentration up to 4.2 times higher than in the adjacent AHP nest. Highly fluctuating results for Na^+ were also evident at the other SHP nests (Figures A5 to A10). Na^+ results from the AHP nests were much more similar to those from squeezing. The differences between Na^+ in SHP nests and squeezing were much too large to be accounted for with hyperfiltration. For example, Na^+ at LGS1 is up to 102% higher than in squeezing, whereas the average amount of Na^+ hyperfiltration was only 0.14%.

Sodium contamination in the SHP nests is probably related to the use of bentonite seals. To swell most effectively, bentonite should be saturated with Na^+ . When the seal encounters ground water, exchange

site equilibration will occur, as adsorbed Na^+ is replaced by the more preferred Ca^{2+} and Mg^{2+} . This exchange site equilibration can explain why the SHP nest exhibits water with higher Na^{2+} but lower Mg^{2+} , relative to water from the AHP nest at the LGS1 site (Table A5). Although bentonite seals were also used in the AHP piezometers, the use of a sandpack appears to have hindered their contaminating effect.

Major ion concentrations in squeezed waters were similar to those in piezometer waters provided that the cores did not age significantly prior to squeezing. As mentioned previously (Rodvang, 1987), storage procedures prior to the initial squeezing were as follows. The LGS cores (LGS1 and LGS3) were stored in plexiglass cylinders at 4 °C and squeezed within one to 7 months after their collection (Table A6). The LIS cores (RP, CIL, PC, UC and ESS) were stored at 4 °C in several layers of plastic wrap. Squeezing was completed within 5 months after sample collection. During the initial week following their collection, however, these cores were wrapped in only one layer of saran wrap, and stored at room temperature.

At the LGS sites an SHP and an AHP-type piezometer nest were located within one metre of the squeezed cores, while the LIS core samples were removed from the location at which SHP piezometer screens were subsequently installed. Although the major ion chemistry of groundwater in Lambton County is spatially variable on a small scale (Heystee et al., 1982; Ash, 1983; Rodvang, 1987) the closeness of the

spacing of these water samples minimized natural spatial variability.

Squeezed and piezometer results are very similar at sites LGS1, RP, and CIL, with the maximum difference in concentration being a factor of 1.7, 1.7 and 3.2, respectively (Figures A5 to A10; Table A5). At the LGS1 site squeezed results agree with piezometer results very closely except between the depths of 4.5 and 5.5 m, where Ca^{2+} and K^{+} are 1.5 to 2.5 times higher than in piezometers at those depths. These results can be related to pressure leaks which developed in the squeezers soon after the run began. As a result, samples sat in the squeezers for approximately 3 days while pressure valves were fixed. Apparently, the samples were exposed to enough air to undergo significant aging during this time.

The results agree less closely at sites PC, UC and ESS. Although in most cases the differences in absolute concentrations are no greater than at the other sites, the lower initial concentrations render these absolute differences more significant.

The discrepancy between major ion concentrations in squeezed and SHP-type piezometers is probably mainly the result of the combined influence of sediment aging and bentonite seals. The former would tend to cause increased total dissolved solids (TDS) in squeezed waters, while the latter would tend to decrease TDS in piezometer waters.

The Carbonate System

During squeezing, carbon dioxide (CO_2) is lost to the atmosphere, causing a considerable rise in pH, and possible CaCO_3 precipitation (Garrels and Christ, 1965; Brooks et al., 1968; Berner et al., 1970). Degassing of CO_2 has no net effect on alkalinity, but causes a decrease in total inorganic carbon (TIC), while calcite precipitation will cause a decrease in both TIC and alkalinity (Stumm and Morgan, 1979). During the current investigation the application of pressure caused the expulsion of a gas phase, evident as it filled syringes, followed by the expulsion of water. However, this gas phase was probably mainly air entrapped between the squeezer walls and the sample, rather than air from the sample itself. The expelled gas was evident as it filled syringes.

A comparison of TIC in squeezed waters (converted to equivalent concentration of HCO_3^-) to HCO_3^- in piezometer waters (Figure A13) suggests that degassing of CO_2 during squeezing caused a substantial decrease in TIC. The conversion of TIC to equivalent HCO_3^- concentration is valid, since all pH's were in the range of 6.4 to 10. In this pH range, TIC is essentially equivalent to HCO_3^- (Stumm and Morgan, 1979, p. 176). A continuous rise in the pH of water as it was extruded also occurred, to values up to one pH unit greater than those of piezometer waters.

It is unlikely that the discrepancy between squeezed and piezometer

results for TIC was caused by erroneously high CO_2 in piezometers. Exposure to air inside piezometers may have resulted in the oxidation of organic matter and the production of CO_2 , according to the reaction $\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$ (Stumm & Morgan, 1979). However, the following factors suggest that TIC/ HCO_3^- measured in piezometer samples are representative of insitu values: (1) concentrations remained stable over successive sampling rounds, whereas TIC values in squeezed samples exhibited relatively large fluctuations in successive water samples collected from the same sediment sample. (2) HCO_3^- in piezometers followed trends similar to those of Ca^{2+} and Mg^{2+} , as would be expected for a system in which Ca^{2+} , Mg^{2+} and HCO_3^- are produced during carbonate mineral dissolution in the weathered zone (Rodvang, 1987).

The precipitation of calcite from squeezed water may have contributed to the lowering of TIC. The addition of nitric acid prevented calcite precipitation in the sample on which Ca^{2+} and Mg^{2+} determinations were made. However, TIC determinations were carried out on the unacidified sample, sometimes up to several months after the water was collected. Berner et al., (1970) found that it was essential to perform alkalinity titrations within one day of squeezing.

Some authors (eg. Berner et al., 1970; Patterson et al., 1978; Emerson et al., 1980) have overcome the problem of CO_2 degassing by doing total alkalinity titrations immediately after water was extruded. In the current investigation, the amount of water obtained during squeezing was never enough to perform an alkalinity titration;

therefore, the amount of carbon in solution was measured as TIC on the non-acidified sample.

The accuracy of pH measurements may be improved by inserting a sturdy pH electrode directly into the sediment (eg. Brooks, et al, 1968; Weiler, 1973; Patterson et al., 1978). Siever et al. (1961) found that the pH by direct insertion was 7.4 to 7.8, versus 8.1 to 8.2 for expressed sea waters. pH measurements on waters expressed under nitrogen were very similar to those obtained by direct insertion. Gorham (1960) found that the pH measured on an expressed solution was up to 1.3 units higher than that obtained by direct insertion. However, Frape (1979) found that the 2 methods gave results which agreed within 0.06 pH units for a comparison of 15 samples of lake bottom sediments. This investigation also showed that processing the cores in a nitrogen atmosphere made little difference to the pH for the sediments analyzed. Fanning and Pilson (1971) obtained highly reproducible pH measurements by completely isolating the extruded pore-water from air before measurements were made.

Determinations of alkalinity, rather than TIC, will avoid the problem of CO₂ degassing. It is suggested that analyses of TIC or alkalinity, and pH, be carried out as soon as possible, on water which has never been exposed to the atmosphere.

Other Aspects for Comparison

From the preceeding discussion it is evident that squeezing can provide a viable alternative to piezometer sampling in the attainment of geochemically intact water samples. The question of which method is preferable depends largely on the situation.

As water can be squeezed from cores on the same day as drilling is carried out, this method is preferable if samples are required quickly. Squeezing can also provide detailed stratigraphic control. Whereas piezometer tips sample water from relativley large, poorly defined areas, the use of squeezing can obtain water samples from very restricted stratigraphic sections, and from sediment volumes as small as 100 cubic centimeters. Squeezing is especially useful when water samples from the unsaturated zone are required.

Piezometers have an advantage over squeezing for the purposes of long-term ground water monitoring, as drilling and piezometer installation need only be done once. When large volumes of water are required, such as for the determination of ^{18}O , or ^3H , piezometers are also preferable.

Squeezing can be quite labor intensive. It is recommended that the system allow for the squeezing of several samples simultaneously, in order to improve the efficiency of the operation.

The total cost per frame of the gas squeezers used in this

investigation, in 1984 prices, was approximately \$433. The squeezer used with the hydraulic oil set-up cost \$418., with an additional \$711. for the Enerpac, including pump, frame, hose and shut-off valve. The pressure transducer, pressure gage, reducing adaptor, hex nipple and gage adaptor added an additional \$718. to the cost of the hydraulic oil set up.

CONCLUSIONS

- (1) Shelby-hole piezometers suffered from contamination due to bentonite seals, involving the exchange of monovalent cations for divalent cations. Otherwise, water samples pumped from augered-hole and shelby-hole piezometers showed high reproducibility over duplicate and triplicate sampling intervals. Similar results were obtained from the two piezometer types when they were installed at the same site.
- (2) The inorganic chemistry of water which was squeezed from cores in the laboratory was similar to that of both augered-hole and shelby-hole piezometers, provided that bentonite seals did not cause significant contamination, and cores did not undergo aging prior to being squeezed. Sediment samples must be maintained at insitu temperatures, isolated from oxygen, and squeezed as quickly as possible after collection, to prevent aging. Aging causes increased concentrations of all major ions except Cl^- , and occurs very quickly after sample collection.
- (3) The maximum reduction in concentration caused by the application of pressures ranging from 200 to 2000 psi was a factor of 1.72. K^+ suffered more hyperfiltration than the other ions. Fluctuations in pressure lower the reproducibility of results.
- (4) pH and total inorganic carbon must be measured as soon as possible after water collection, on water which has been isolated from the atmosphere.

(5) For the purposes of inorganic chemical investigations, squeezing provides an advantage over piezometer sampling if samples are required quickly, if accurate stratigraphic control is required, or if samples from the unsaturated zone are required.

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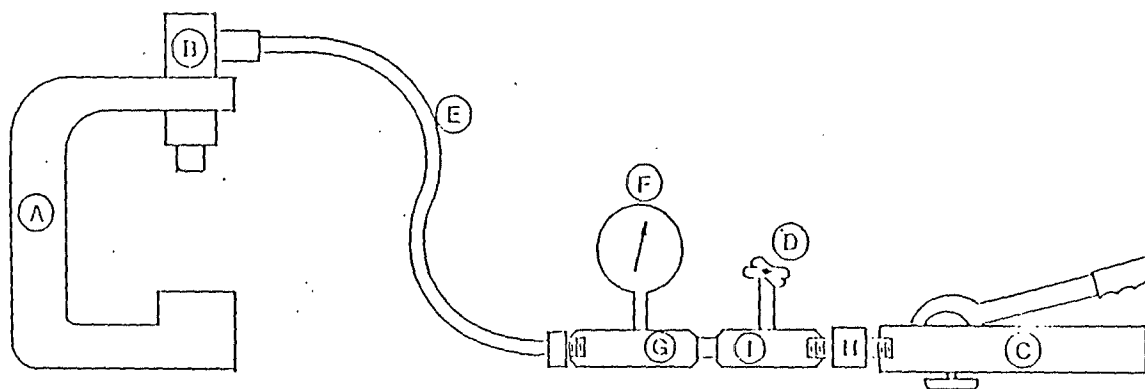
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ARBOR FRAME SETUP



- | | |
|--------------------------|-------------------------------|
| (A) - ENERPAC FRAME | (E) - HOSE |
| (B) - HYDRAULIC CYLINDER | (F) - PRESSURE GAGE |
| (C) - ENERPAC PUMP | (G) - MANIFOLD (GAGE ADAPTOR) |
| (D) - SHUT-OFF VALVE | (H) - HEX REDUCING NIPPLE |
| | (I) - REDUCING ADAPTOR |

Figure A1: Enerpac/Arbor Frame Setup

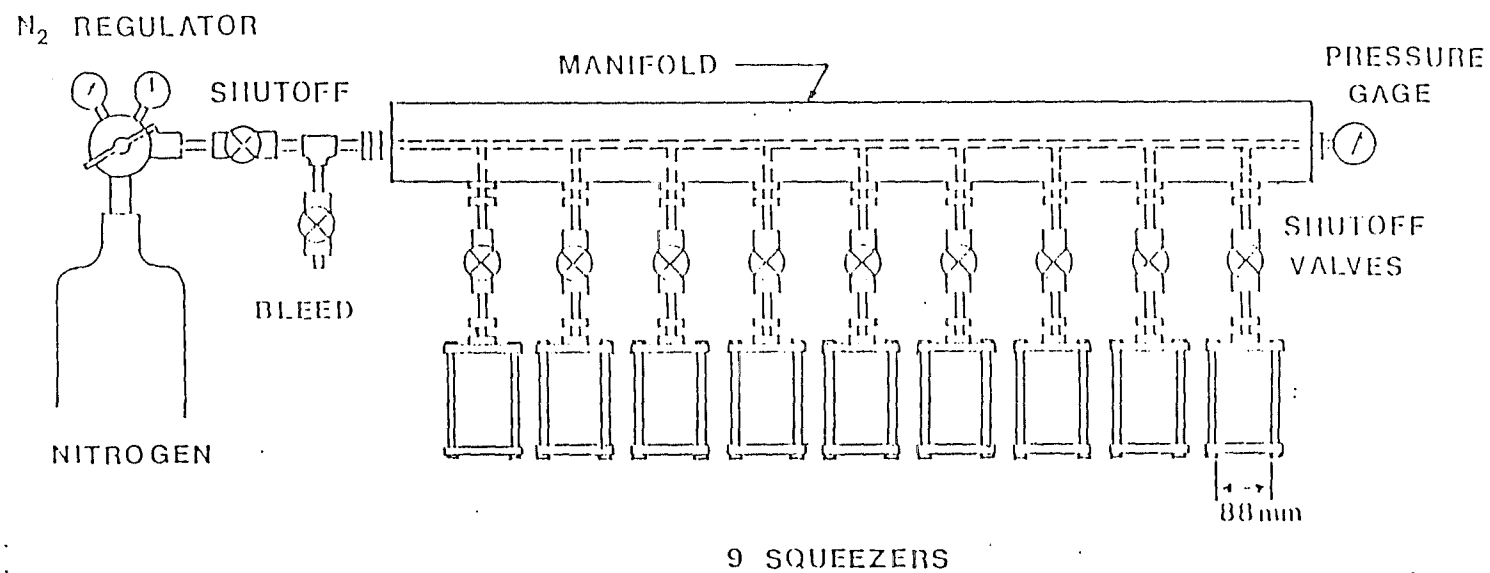
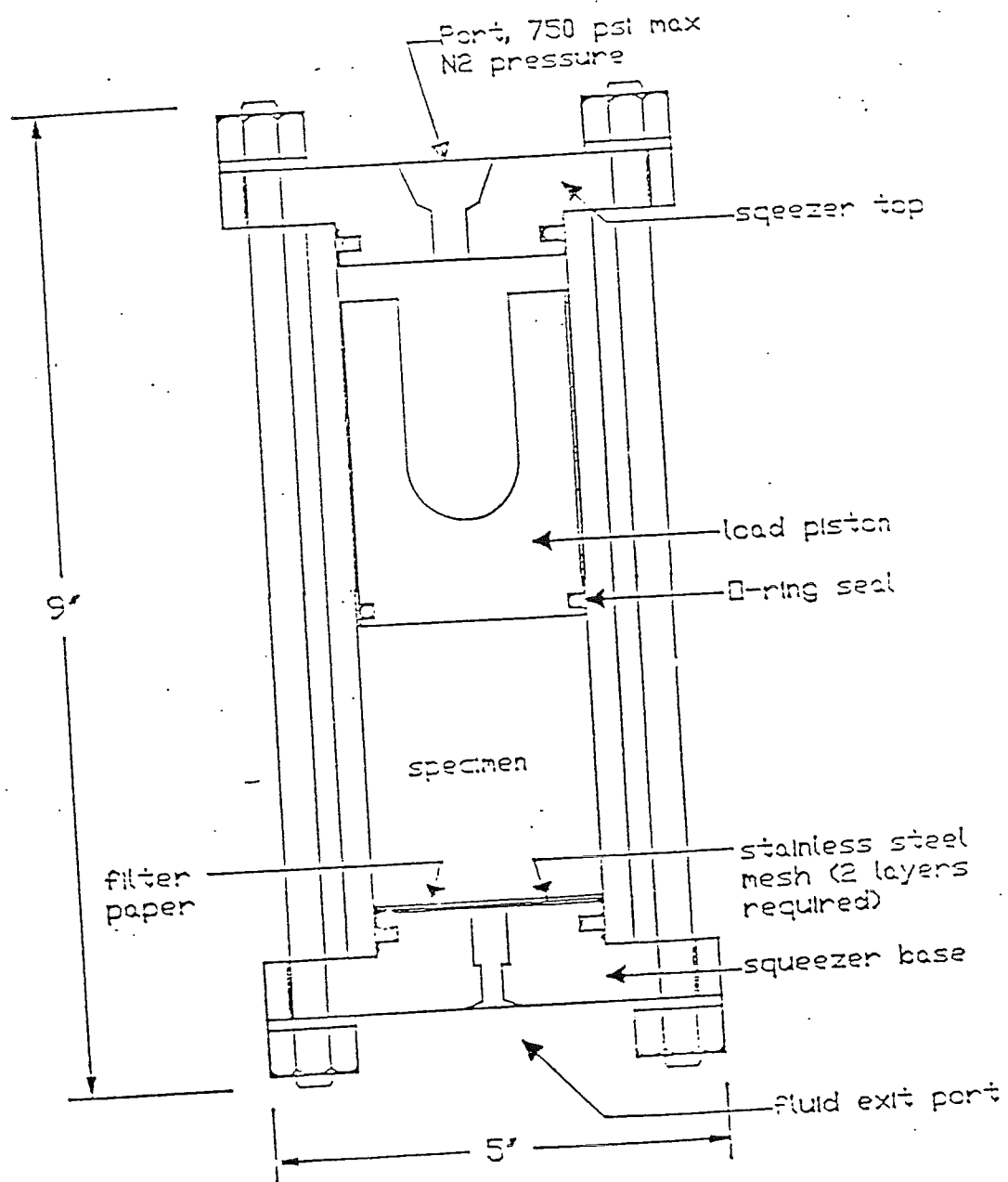


Figure A2: Pressure-Regulated Gas Squeezers



Pore Fluid Extractor

Design J. Bailechta
CAG M. Jones

Figure A3: Detailed View of Gas Squeezer

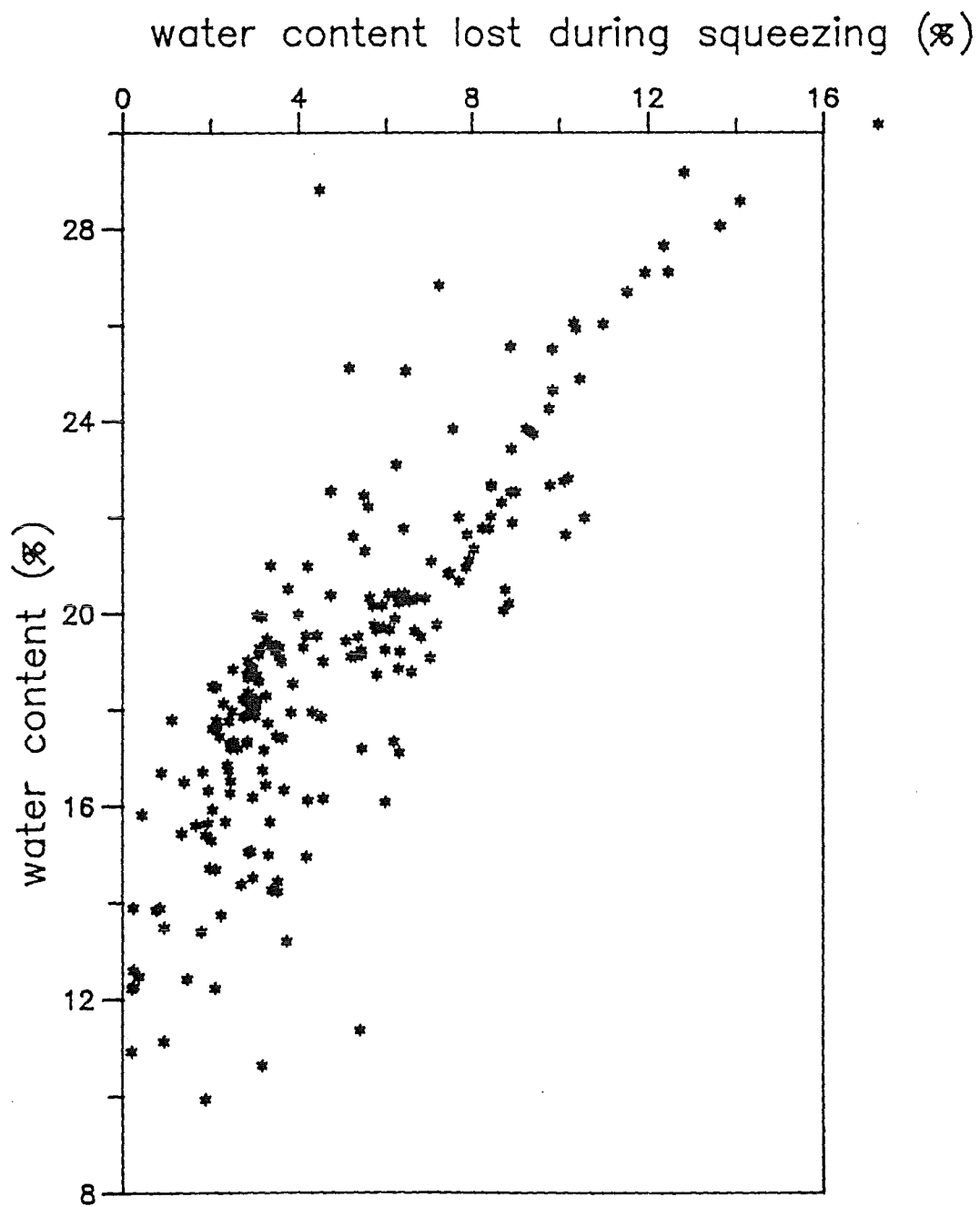


Figure A4: Water Content Lost During Squeezing Versus Water Content

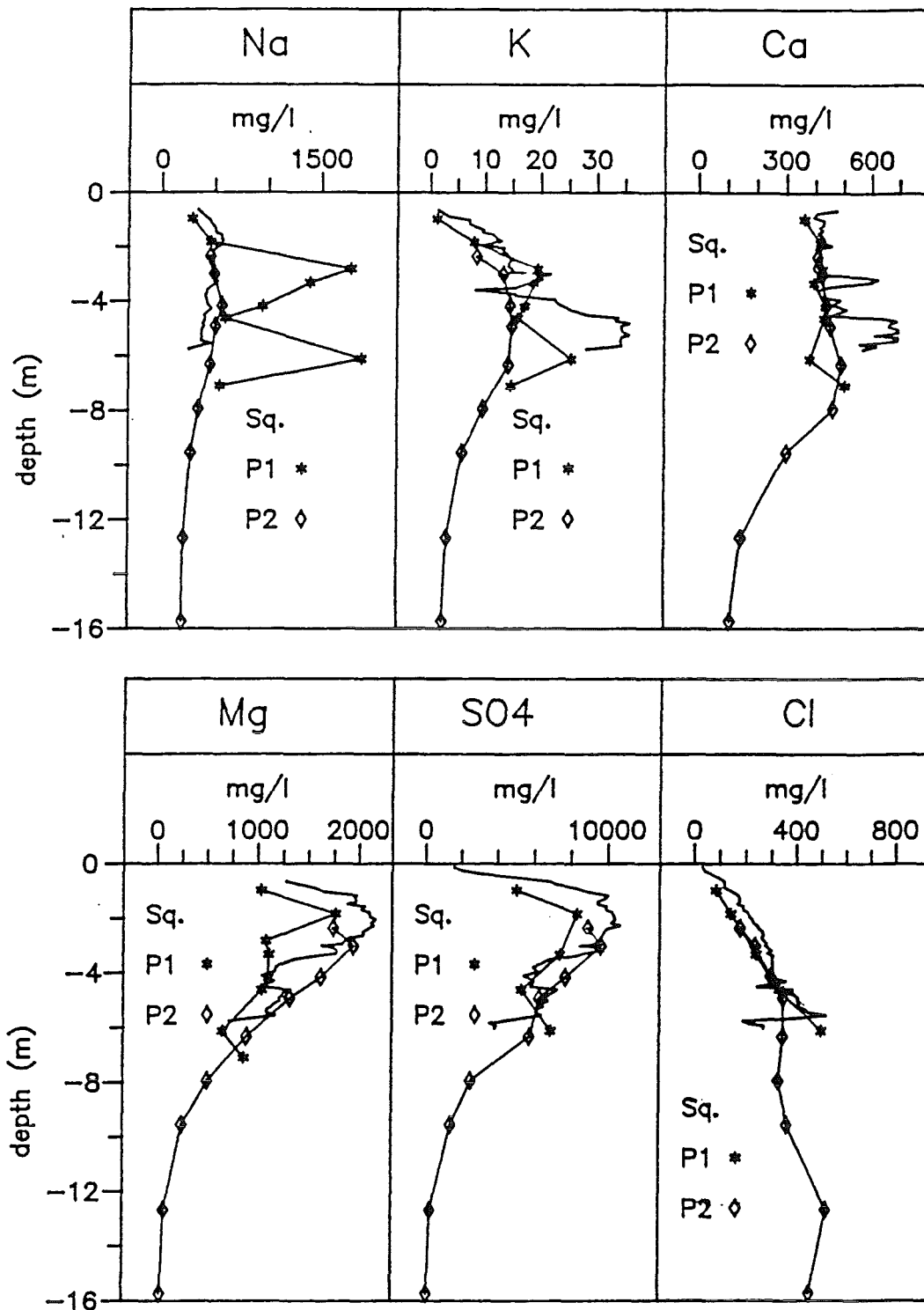


Figure A5: Major-Ion Profiles at LGS1
Comparison of Squeezed & Piezometer Results

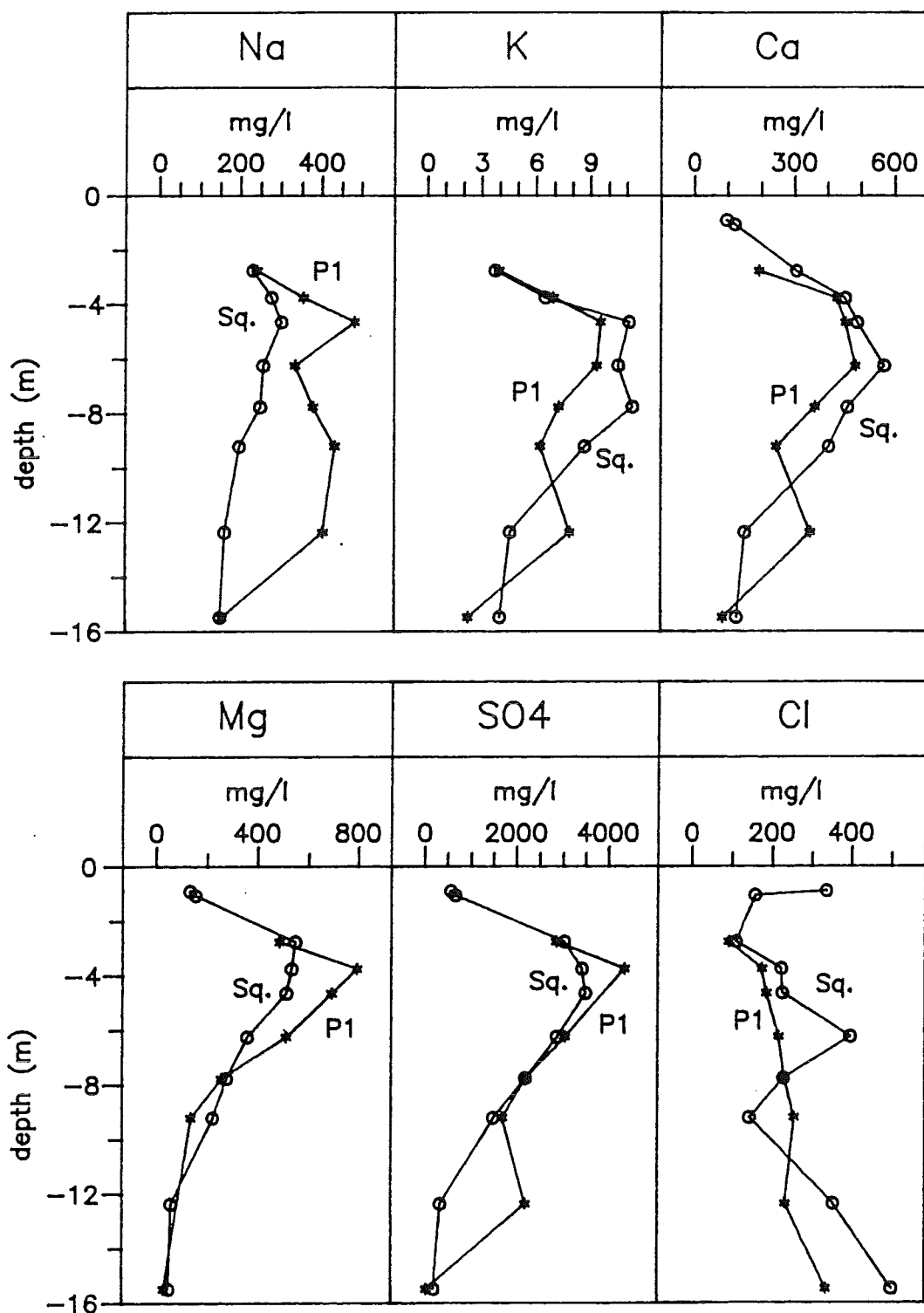


Figure A6: Major-Ion Profiles at RP

Comparison of Squeezed & Piezometer Results

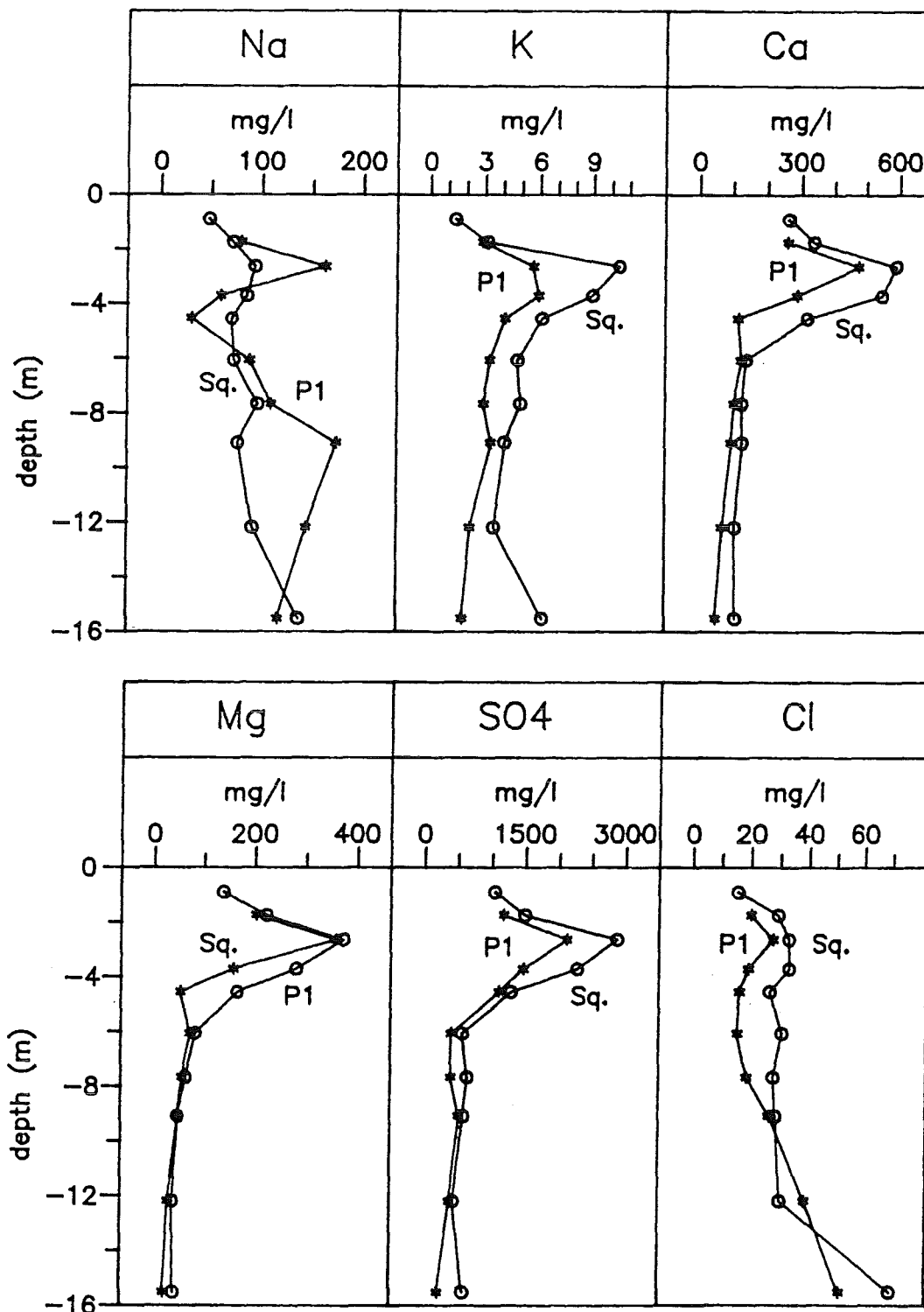


Figure A7: Major-Ion Profiles at CIL

Comparison of Squeezed & Piezometer Results

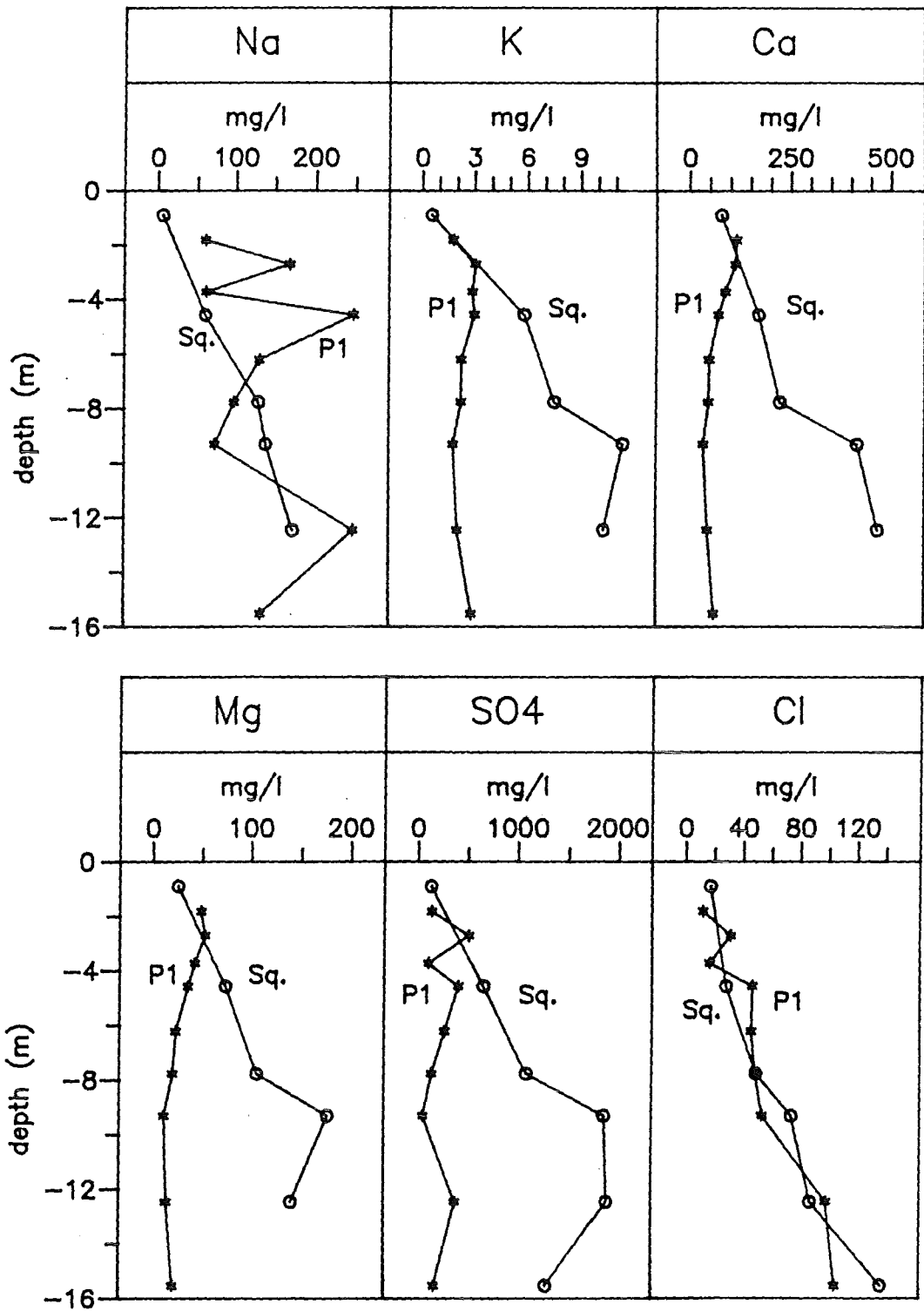


Figure A8: Major-Ion Profiles at PC

Comparison of Squeezed & Piezometer Results

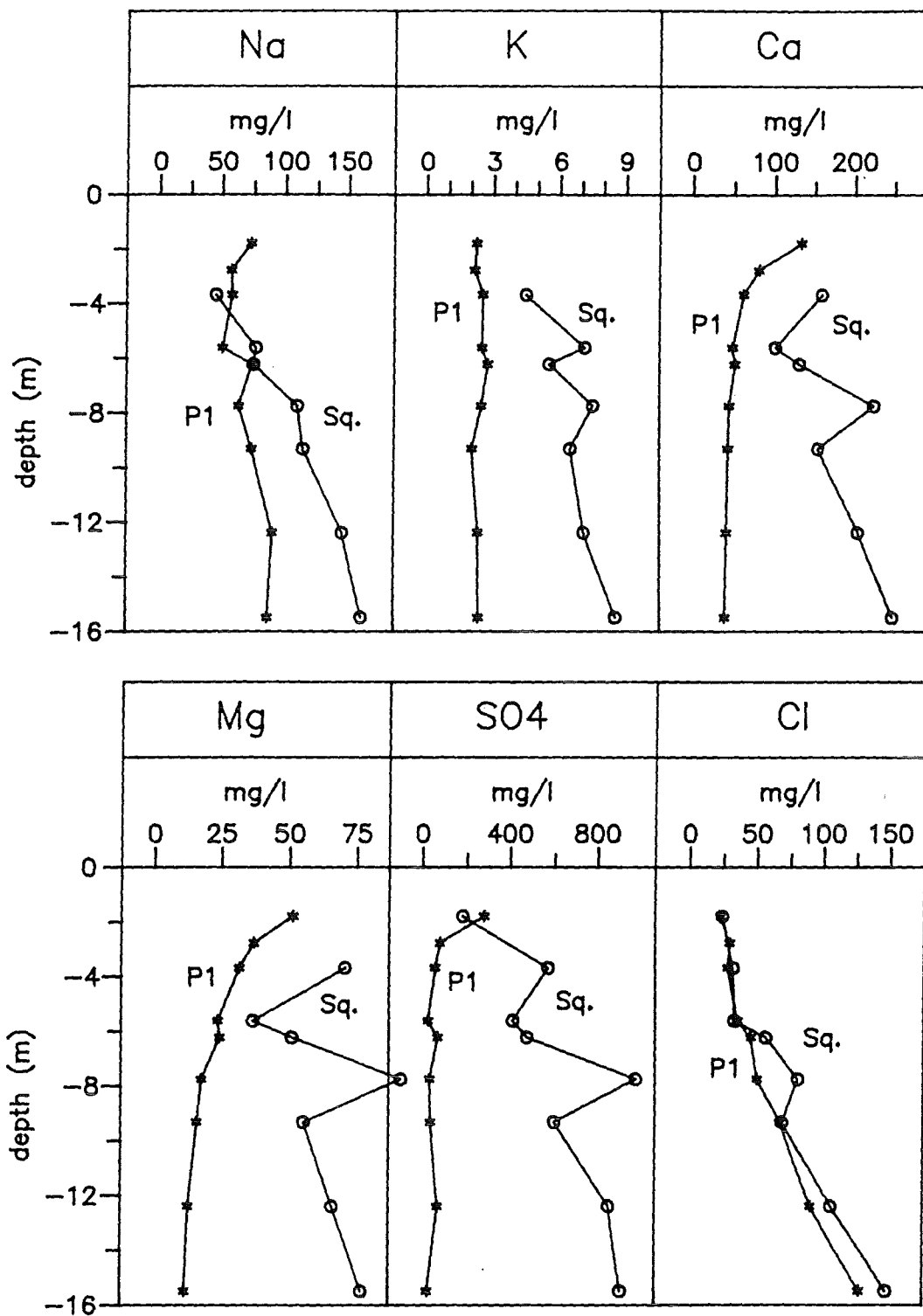


Figure A9: Major-Ion Profiles at UC

Comparison of Squeezed & Piezometer Results

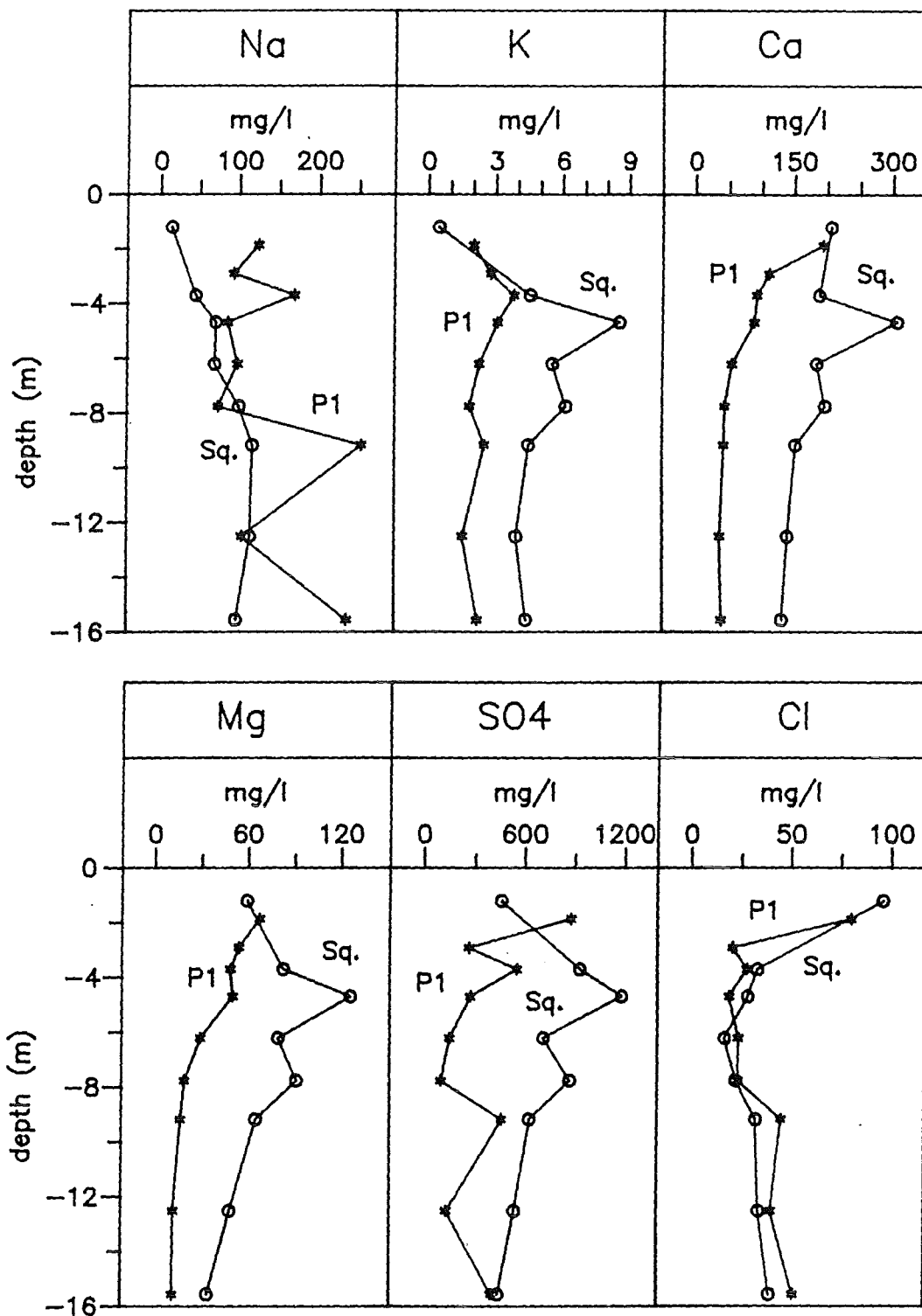


Figure A10: Major-Ion Profiles at ESS
Comparison of Squeezed & Piezometer Results

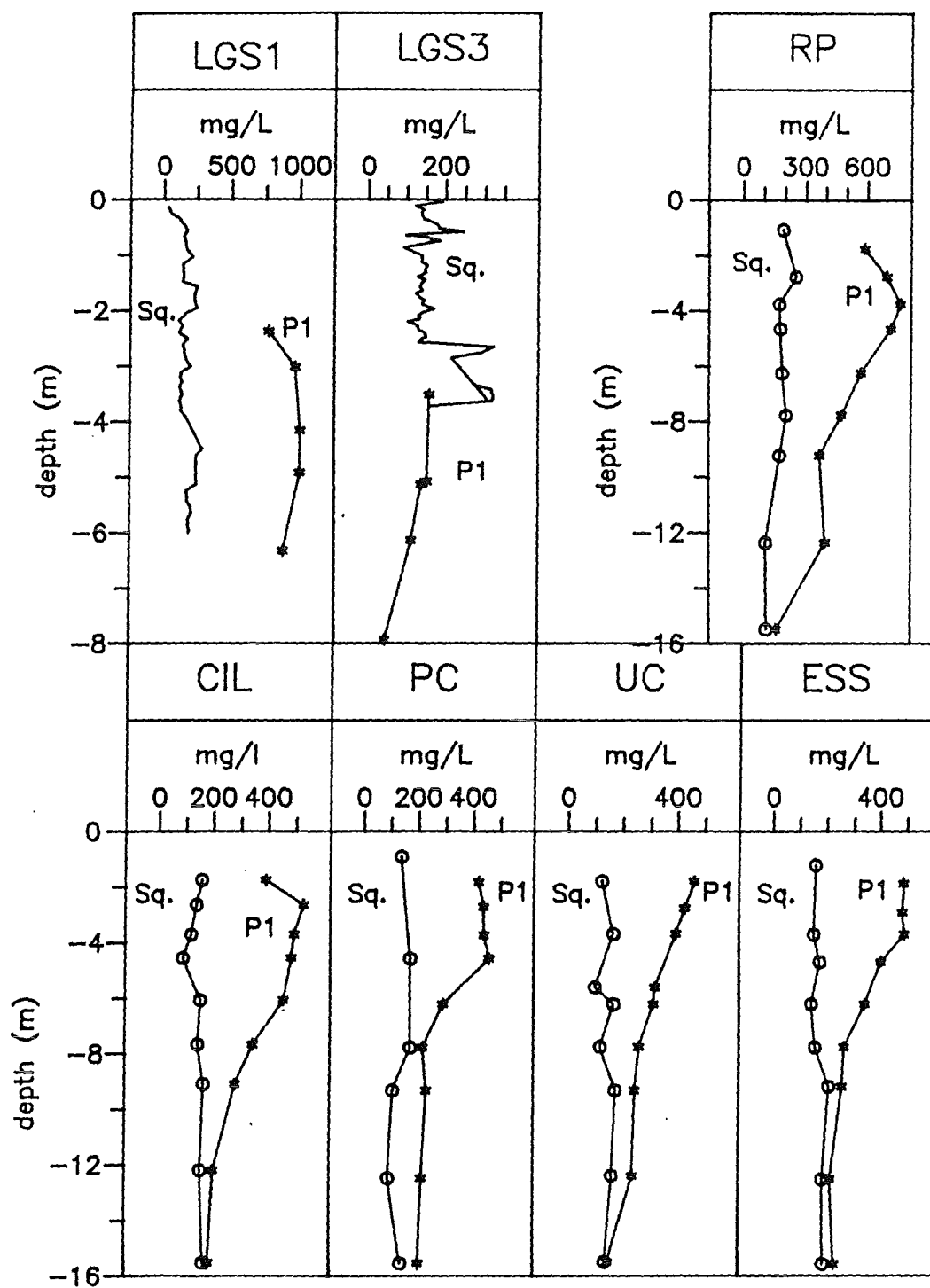


Figure A11: Comparison of Squeezed and Piezometer Results for Bicarbonate

Table A1: Pressure Effects During Squeezing
(Literature Review)

Author	Sediment	Pressure at which Concentration Decrease was Noted (PSI)
Burgess, 1921	California soils, mostly sandy	no effect up to 15,000
Von Engelhardt and Gaica, 1963	Kaolinite, from pure water to 2.4 N NaCl	no effect up to 44,000
Siever et al., 1965	Sodium illite (1 N NaCl)	no effect up to 150
Manheim, 1966	Deep-sea sediments	Chloride varied less than one percent between 580 and 12,000
Kriukov and Komarova, 1966 (In Manheim, 1974)	Sodium Bentonite (0.1 N NaCl) Sodium Bentonite (0.86 N NaCl)	8,500 for chloride 20,000 for chloride
Manheim and Sayles, 1974	Deep-sea sediments up to the ionic strength of sea-water	no effect up to 19,000
Patterson et al., 1978	Lake and river-bottom sediments	no effect up to 711.
Morgenstern and Balasubramanian, 1980	Bearpaw Shale	Total concentration constant up to 3,000 PSI

Table A2: Filtration Ratios

Sample Group	Sample Name	Pressure	Water Content	Na/ Ca+Mg	Na	K	Ca	Mg	Cl	SO4
Filtration Ratio										
Group 1										
1	BH27A	200-750	23.7	1.86	1.06	1.61	1.04	0.97	0.77	1.07
2	BH27B	200-750	23.4	1.87	1.07	1.46	1.03	0.97	0.97	1.07
3	BH27C	200-750	22.5	1.87	1.03	1.28	1.04	1.01	1.11	1.04
4	BH27D	200-750	22.5	1.85	0.95	1.39	1.05	0.94	0.82	1.03
5	BH30A	200-750	24.9	2.77	1.11	1.19	1.20	1.15	1.24	1.12
6	BH30B	200-750	25.5	2.39	1.09	1.41	1.15	1.07	1.00	1.12
7	BH24A	200-750	22.3	3.20	1.12	1.39	0.90	1.05	1.03	1.13
8	BH24B	200-750	22.6	2.54	1.16	1.63	1.23	1.20	1.31	1.47
9	BH24C	200-750	25.5	3.38	1.06	1.45	1.12	0.98	1.30	1.14
10	BH24D	200-750	26	2.90	1.08	1.55	1.12	1.08	1.17	1.16
11	BH24E	200-750	23.8	2.82	1.11	1.54	1.19	1.10	1.21	1.11
12	BH24F	200-750	32.5	3.27	1.09	1.51	1.13	1.09	1.24	0.84
AVE (Group 1)					1.08	1.45	1.10	1.05	1.10	1.11
Group 2										
13	BH3.5	450-750	15.4	0.31	1.03	1.00	1.02	1.02		
14	ESS3	200-750	10.6	0.08	1.01	1.09	1.02	0.99		
15	ESS20	750-0-750	14.4	0.33	1.09	1.39	0.98	0.95	1.08	1.03
16	RP40A	400-2000	22	0.76	1.07	0.98	1.06	1.06	1.00	1.02
17	RP40B	250-2250	21.6	0.79	0.86	0.89	0.58	0.84	0.92	1.13
18	CIL20-A	200-750	20.4	0.24	0.96	1.09	0.96	0.95	0.84	1.03
19	CIL20-B	200-750	19.7	0.24	1.03	1.11	1.02	1.01	0.87	1.05
20	CIL25-A	200-750	20.2	0.24	0.93	1.13	1.02	1.01	0.54	1.05
21	CIL25-B	200-750	16.1	0.28	1.09	1.15	1.11	0.89	0.63	1.31
22	UC20-A	750-2000	20.1	0.49	1.19	1.72	1.08	1.09	1.04	1.24
23	UC20-B	2000	20.5	0.50	1.10	1.28	0.93	0.92		
24	UC30-A	200-750	26.8	0.62	1.00	1.32	0.96	0.97	0.95	1.04
25	UC30-B	750-0-750	21.1	0.64	1.16	1.47	1.07	1.03	1.08	1.00
26	UC50	200-750	17.2	0.73	1.02	1.27	1.03	0.99	1.08	1.08
27	L318.6	200-750	22.6	0.28	0.97	1.02	0.98	1.02		
28	ST5P	200-750	11.3	0.31	0.97	1.24	0.95	0.95	1.13	1.01
29	BN-0	200-750	35.5	0.34	1.02	1.17	1.03	0.93	1.08	1.00
30	BN-12	200-750	26	0.85	1.02	1.21	1.05	0.96	1.00	1.23
AVE (Group 2)					1.03	1.20	0.99	0.98	1.01	1.09
AVE (samples 1 to 30)					1.05	1.30	1.04	1.01	1.01	1.09

Table A2 (Continued)

Group 3

31	LN1	200-750	26.7	1.65	1.02	0.97	0.95	1.06	1.12	1.05
32	LN2	200-750	25.9	1.67	0.90	0.92	0.89	0.93	0.97	1.07
33	LW1	200-750	29.2	1.64	1.09	1.11	1.03	1.05	1.10	1.04
34	LW2	200-750	27.1	1.63	0.93	0.93	0.95	0.94	0.95	0.93
35	HN1	200-750	28.6	1.19	0.88	0.88	0.93	1.86	0.95	0.90
36	HN2	200-750	27.1	1.19	0.90	0.89	0.90	0.91	0.89	0.96
37	HW1	200-750	28.1	1.19	0.90	0.97	0.96	1.03	1.01	1.03
38	HW2	200-750	27.6	1.16	0.95	1.13	0.93	0.96	0.95	0.97
AVE					0.95	0.98	0.94	1.09	0.99	0.99

Table A3: Filtration Efficiencies

Decrease in conc. per ml of extruded water
Expressed as % of total conc.

Sample	Na	K	Ca	Mg	Cl	SO4
BH14A	0.11	2.20	0.19	-0.70	-0.39	-0.56
	0.47	4.65	0.09	0.06	-0.94	0.71
	0.14	-0.13	0.22	0.10	-3.11	-0.13
	0.06	0.74	0.1	0.09		
AVE	0.20	1.87	0.15	-0.11	-1.48	0.01
BH14B	0.46	-0.31	-0.38	-0.05	0.00	0.00
	0.26	7.02	0.32	-0.32	-0.33	0.75
	0.06	-0.11	0.00	-0.06	0.09	-0.34
	0.30	-0.95	0.08	0.28		
AVE	0.27	1.41	0.01	-0.04	-0.08	0.14
BH14C	0.00	2.20	0.31	0.04	1.16	0.48
	0.27	1.90	0.12	0.17	0.37	0.14
	0.00	0.14	0.24	0.00	0.38	0.09
	0.10	0.04	0.00	-0.05	-0.33	-0.31
AVE	0.09	1.07	0.17	0.04	0.40	0.10
BH14D	1.02	4.67	0.50	-0.90	-0.36	-0.84
	0.00	1.36	-0.55	-0.33	-3.03	0.91
	0.55	0.54	0.60	0.12	2.29	0.08
	0.52	2.19	0.18	-0.37	-0.37	0.05
ESS-3	0.10	1.28	0.26	-0.22		
ESS-20	0.70	2.75	-0.03	-0.41		
RP40-A	0.04	1.08	-0.11	-0.14		
	0.67	0.00	1.20	1.20		
	0.31	-0.13	0.40	0.15		
	0.34	0.32	0.50	0.40		
RP40-B	-1.50	1.01	-0.83	-0.98	0.48	-0.52
	-0.17	0.00	-0.32	-0.62	-0.85	0.35
	0.08	-0.62	-0.18	-0.62	0.62	1.62
	-0.30	-0.05	-0.16	-0.74	-0.58	-1.72
	0.38	0.49	0.24	0.80	0.44	0.14
	-2.80	-3.35	-2.44	-0.72	-2.08	
	0.50	0.35	0.34	0.00		
	-0.62	-1.60	-1.15	-0.67		
	-0.55	-0.47	-0.56	-0.44	-0.33	-0.02

Table A3 (Continued): Filtration Efficiencies

Decrease in conc. per ml of extruded water
Expressed as % of total conc.

Sample	Pressure	Na	K	Ca	Mg	Cl	SO ₄
BH-27-C	200-200	0.00	2.20	0.31	0.04	1.16	0.48
	200-400	0.27	1.90	0.12	0.17	0.37	0.14
	400-600	0	0.14	0.24	0	0.38	0.09
	600-600	0.1	0.04	0	-0.05	-0.33	-0.31
	AVE	0.09	1.07	0.17	0.04	0.40	0.10
BH-27-D	200-200	1.02	4.67	0.5	-0.9	-0.36	-0.84
	200-400	0	1.36	-0.55	-0.33	-3.03	0.91
	400-600	0.55	0.54	0.6	0.12	2.29	0.08
	AVE	0.52	2.19	0.18	-0.37	-0.37	0.05
L3-18.6	200-200	-0.47	0.03	0.65	0.35	0.09	0.14
	200-600	0.26	0.38	0.61	-0.22		
	600-600	-0.33	0.66	0.00	0.00		
	AVE	-0.18	0.36	0.42	0.04	0.09	0.14
ST5P	200-450	0.50	3.50	-0.52	0.03	1.66	0.21
	450-750	-0.75	-1.43	-0.39	-1.05	0.45	0.00
	AVE	-0.13	1.04	-0.46	-0.51	1.06	0.11
BN-0	200-450	0.16	1.25	0.00	-0.60	0.69	0.00
	450-750	0.00	0.08	0.16	0.06	0.11	0.00
	AVE	0.08	0.67	0.08	-0.27	0.40	0.00
BN-12	200-450	0.26	1.26	0.00	-0.61	0.18	2.86
	450-750	0.04	0.67	0.35	0.04	0	0.58
	AVE	0.15	0.97	0.18	-0.29	0.09	1.72
ESS-3	450-750	0.1	1.28	0.26	-0.22		
ESS-20	750-0-750	0.7	2.75	-0.03	-0.41		
RP-40-A	400-750	0.04	1.08	-0.11	-0.14		
	750-1000	0.67	0	1.2	1.2		
	1000-2000	0.31	-0.13	0.4	0.15		
	AVE	0.34	0.32	0.5	0.4		
RP-40-B	250-250	-1.5	1.01	-0.83	-0.98	0.48	-0.52
	250-400	-0.17	0	-0.32	-0.62	-0.85	0.35
	400-600	0.08	-0.62	-0.18	-0.62	0.62	1.62
	600-600	-0.3	-0.05	-0.16	-0.74	-0.58	-1.72
	600-750	0.38	0.49	0.24	0.8	0.44	0.14
	750-900	-2.8	-3.35	-2.44	-0.72	-2.08	
	900-1300	0.5	0.35	0.34	0		
	1300-1700	-0.62	-1.6	-1.15	-0.67		
	AVE	-0.55	-0.47	-0.56	-0.44	-0.33	-0.02

Table A3 (Continued): Filtration Efficiencies

Decrease in conc. per ml of extruded water
Expressed as % of total conc.

Sample	Pressure	Na	K	Ca	Mg	Cl	SO ₄
CIL20-A	200-400	0.95	0.69	-0.60	-1.10	0.19	0.00
	400-600	0.00	1.08	-0.23	-0.42	-3.81	0.61
	600-600	0.44	-0.18	0.23	0.32		
	AVE	0.46	0.53	-0.20	-0.40	-1.81	0.31
CIL20-B	200-400	0.80	1.55	0.37	0.20	2.34	0.59
	400-600	0.22	0.77	-0.24	0.11	-0.44	0.43
	AVE	0.51	1.16	0.07	0.16	0.95	0.51
CIL25-A	200-200	0.23	1.25	0.06	-0.33	2.70	-0.47
	200-400	0.58	1.19	0.10	0.13	-1.34	0.17
	400-600	-0.50	0.12	0.11	-0.05	-6.70	0.32
	AVE	0.10	0.85	0.09	-0.08	-1.80	0.01
CIL25-B	200-400	-2.30	3.40	-2.80	-2.90	5.40	0.18
	400-600	0.30	0.37	0.05	-0.15	-9.60	0.29
	600-600	0.58	-0.92	0.71	0.58	0.27	-0.18
	AVE	-0.47	0.95	-0.68	-0.82	-1.49	0.10
UC20-A	750-750	1.10	3.20	-0.75	-0.89	0.00	0.00
	750-750	0.44	2.02	0.43	0.43	0.11	0.81
	750-1500	0.45	1.14	0.20	0.27	0.31	-3.71
	1500-2000	-0.24	0.15	0.22	-0.03	0.15	0.39
	2000-2000	1.72	0.34	-1.50	1.00		
	AVE	0.69	1.37	-0.28	0.16	0.14	-0.63
UC20-B	2000-2000	0.84	0.83	0.22	-0.25	0.38	0.12
	2000-2000	-0.07	1.55	-0.75	-0.6		
	AVE	0.38	1.19	-0.26	-0.42		
UC30-A	200-450	0.00	2.58	-0.42	-0.07	0.23	0.35
	450-750	0.00	0.44	0.23	-0.24	-0.46	0.15
	AVE	0.00	1.51	-0.09	-0.15	-0.12	0.25
UC30-B	750-750	0.78	1.47	0.36	0.13	0.26	0.00
	750-0-750	0.48	1.98	0.23	0.10	0.41	0.00
	AVE	0.63	1.73	0.30	0.12	0.34	0.00
UC50	200-450	0.04	1.15	0.17	-0.05	0.09	0.14
	450-750	0.09	0.47	-0.03	0.02	0.45	0.42
	AVE	0.07	0.81	0.07	-0.02	0.27	0.28

Table A3 (Continued): Filtration Efficiencies

Decrease in conc. per ml of extruded water
Expressed as % of total conc.

Sample	Pressure	Na	K	Ca	Mg	Cl	SO4
LN1	200-200	0.14	-0.30	0.22	0.88	0.41	0.32
	200-200	-0.70	-0.26	-0.47	-0.89	0.21	-0.06
	200-400	0.00	-0.10	0.15	0.00	1.30	-0.72
	400-600	0.78	0.54	0.61	0.80	0.33	0.62
	600-750	-0.08	0.00	-0.79	0.00		
AVE		0.03	-0.02	-0.06	0.16	0.56	0.04
LN2	200-200	-1.46	-1.69	-1.25	-0.65	0.25	0.33
	200-200	0.20	0.25	-0.09	0.21	-0.43	0.42
	200-400	0.41	0.33	0.14	0.34	0.50	-0.03
	400-600	0.00	-0.13	-0.26	0.00	-0.45	0.10
	600-750	-1.74	0.11	-0.27	-1.72		
AVE		-0.52	-0.23	-0.35	-0.36	-0.03	0.21
LW1	200-200	0.10	0.24	0.13	-0.05	0.21	-0.19
	200-450	-0.06	-0.03	-0.06	-0.04	0.16	0.10
	450-600	0.15	0.33	0.05	0.36	0.41	0.34
	600-750	0.48	0.38	0.12	0.15	0.12	0.02
AVE		0.17	0.23	0.06	0.11	0.23	0.07
LW2	200-200	0.28	0.45	0.26	0.19	-0.25	-0.05
	200-450	-0.06	-0.13	-0.02	-0.08	0.35	-0.07
	450-600	-0.77	-0.62	-0.62	-0.65	-0.76	-0.39
	600-750	0.06	0.32	0.18	0.00	-0.24	-0.41
AVE		-0.12	0.01	-0.05	-0.14	-0.23	-0.23
HN1	200-200	-0.66	-1.02	-0.67	0.00	-0.37	-0.37
	200-450	0.54	0.22	0.27	0.37	-0.11	-0.07
	450-600	1.29	1.68	0.04	1.05	-0.65	-3.35
	600-750	-2.95	-2.96	-2.96	-2.82	0.22	1.52
AVE		-0.45	-0.52	-0.83	-0.35	-0.23	-0.57
HN2	200-200	-0.78	-1.26	-1.14	0.22	1.08	0.40
	200-450	0.17	0.13	0.09	-0.05	-1.41	-0.49
	450-600	-0.85	-0.66	0.15	-1.17	-0.72	-0.40
	600-750	-0.62	-0.28	-1.13	-0.72		
AVE		-0.52	-0.52	-0.51	-0.43	-0.35	-0.16

Table A3 (Continued): Filtration Efficiencies

HW1	200-200	-1.28	-0.25	-0.41	0.03	0.00	-0.21
	200-450	0.61	0.02	0.03	-0.12	-0.07	-0.02
	450-600	0.18	0.10	0.12	0.24	0.05	-0.02
	600-750	0.00	0.00	-0.19	0.00	0.08	0.27
AVE		-0.12	-0.03	-0.11	0.04	0.02	0.01
HW2	200-200	-0.33	-0.20	-0.31	-0.06	0.00	0.05
	200-450	0.08	-0.05	-0.07	-0.02	-0.37	-0.13
	450-600	-0.37	-0.10	-0.31	-0.37	-0.03	-0.39
	600-750	0.17	0.20	-0.03	0.21		
AVE		-0.11	-0.04	-0.18	-0.06	-0.13	-0.16

Table A4: Documentation of Sediment Aging
(a): Absolute Concentrations

Sample	Squeezing Date	Na	K	Ca mg/l	Mg	Cl	S04
RP-40	85/12/11	161	4.55	150	58.3	354.5	343.5
	86/03/18	196	8.36	273	107	347	-----
	86/03/31	199	8.59	262	109	373	800
CIL-9	85/10/29	93.2	10.4	589	372	32.9	2870
	86/17/03	111	9.54	615	426	29.3	2817
CIL-20	85/10/29	73.9	5.07	136	82	30.4	500
	86/06/24 (s1)	101	12.1	384	209	31.2	1977
	86/06/24 (s2)	104	12.1	394	211	33.4	1985
CIL-25	85/10/29	95.7	5.19	124	62.1	27.5	632
	86/06/24 (s1)	104	12.1	394	211	33.4	1985
	86/06/24 (s2)	95.8	9.23	369	136	37.6	1495
UC-20	85/11/25	74.9	5.64	130	51.1	54.4	469
	86/03/11 (s1)	88.7	7.04	186	78.5	45.9	711
	86/03/15 (s2)	85.5	7.8	196	63.4	44.5	647
UC-30	85/11/25	113.5	6.44	153.5	55.2	33.8	69
	86/03/17	121	5.69	210	77.5	71	791
	86/04/01	138	10.7	235	87	69.6	902
UC-50	85/11/25	160	8.7	247	77.3	144	899
	86/03/17	153	7.1	239	76.1	144	898
ESS-3	85/11/17	13.6	0.455	206	59.2	95.6	456
	86/03/17	15.9	0.648	237	70.6	-----	-----
ESS-20	85/11/17	68.1	5.49	183	79.3	16.7	710
	86/04/01	106	11.59	320	142	28.7	1255
Number of Days at room temperature		Na	K	Ca	Mg	Cl	S04
*W13A (S1)	0	183	1.81	63.2	22.16	36.4	565
*W13A (S2)	10	191	2.24	84	28.6	50	476
*W13B (S1)	0	175	1.62	57	20.2	33.5	399
*W13B (S2)	8	176	2.02	69.1	22.3	35.9	394
*W16A (S1)	0	163	1.98	64.3	23.2	34.11	538
*W16A (S2)	14	174	1.83	77.2	30.18	43.1	577

* these samples were all squeezed on the same day

NOTE: s1 and s2 refer to splits of the sample sample

Table A4: Documentation of Sediment Aging
(b): Ratios of Subsequent to Initial Concentrations

Sample	Squeezing Date	Na	K	Ca	Mg	Cl	SO4
Concentration Increase (Ratio)							
RP-40	85/12/11						
	86/03/18	1.2	1.8	1.8	1.8	1.0	-----
	86/03/31	1.2	1.9	1.7	1.9	1.1	2.3
CIL-9	85/10/29						
	86/17/03	1.2	0.9	1.0	1.1	0.9	1.0
CIL-20	85/10/29						
	86/06/24 (s1)	1.4	2.4	2.8	2.5	1.0	3.9
	86/06/24 (s2)	1.4	2.4	2.9	2.6	1.1	4.0
CIL-25	85/10/29						
	86/06/24 (s1)	1.1	2.3	3.2	3.4	1.2	3.1
	86/06/24 (s2)	1.0	1.8	3.0	2.2	1.4	2.4
UC-20	85/11/25						
	86/03/11 (s1)	1.2	1.2	1.4	1.5	0.8	1.5
	86/03/15 (s2)	1.1	1.4	1.5	1.2	0.8	1.4
UC-30	85/11/25						
	86/03/17	1.1	0.9	1.4	1.4	2.1	11.5
	86/04/01	1.2	1.7	1.5	1.6	2.1	13.1
UC-50	85/11/25						
	86/03/17	0.9	0.8	1.0	1.0	1.0	1.0
ESS-3	85/11/17						
	86/03/17	1.2	1.4	1.2	1.2	-----	-----
ESS-20	85/11/17						
	86/04/01	1.6	2.1	1.7	1.8	1.7	1.7
Number of Days at room temperature		Na	K	Ca	Mg	Cl	SO4
*W13A (S1/S2)	0/10	1.0	1.2	1.3	1.3	1.4	0.8
*W13B (S1/S2)	0/8	1.0	1.2	1.2	1.1	1.1	1.0
*W16A (S1/S2)	0/14	1.1	0.9	1.2	1.3	1.3	1.1

Note: s1 and s2 refer to splits of the same sample

Table A5: Ratios of Squeezed to Piezometer Results
(1): LGS1

Squeezed/AHP-Piezometer Results							
Depth (m) Squeezed	Depth (m) P2	Na	K	Ca (Ratio)	Mg	Cl	SO4
2.40	2.37	1.1	1.7	1.0	1.2	1.4	1.1
3.11	3.02	1.0	1.5	1.4	0.9	1.2	1.0
4.11	4.16	0.8	1.6	1.1	0.6	0.9	0.7
4.92	4.92	0.8	2.3	1.5	0.9	1.2	1.0

Squeezed/SHP-Piezometer Results							
Depth Squeezed	Depth P1	Na	K	Ca (Ratio)	Mg	Cl	SO4
1.03	0.98	1.6	6.4	1.2	1.6	1.7	1.8
1.79	1.84	1.3	1.6	1.0	1.2	1.5	1.2
2.4	2.83	0.3	0.7	1.0	1.9	-----	-----
3.11	3.33	0.4	1.0	1.5	1.6	1.2	1.3
4.11	4.19	0.4	1.3	1.1	0.9	-----	-----
4.92	4.62	0.7	2.2	1.5	1.2	1.2	1.2

SHP-Type/AHP-Type Piezometer Results							
Depth (m) P1	Depth (m) P2	Na	K	Ca (Ratio)	Mg	Cl	SO4
2.83	2.37	3.9	2.3	1.0	0.6	-----	-----
3.33	3.02	2.8	1.4	0.9	0.6	1.0	0.8
4.19	4.16	1.7	1.2	1.0	0.7	-----	-----
4.62	4.92	1.2	1.1	1.0	0.8	1.0	0.8
6.13	6.33	4.2	1.8	0.8	0.7	1.4	1.2
7.11	7.95	1.6	1.5	1.1	1.7	-----	-----

Table A5: Ratios of Piezometer Results
on Different Dates
(1): LGS1 (Continued)

AHP-Type Piezometer Results						
Depth (m)	Na	K (85/06/18 to 85/07/11)	Ca	Mg	Cl	SO4
2.37	1.1	0.7	0.9	1.0	-----	
3.02	1.0	0.9	1.0	1.0	1.1	1.1
4.16	1.1	0.9	1.0	1.1	1.1	1.1
4.92	1.0	0.9	1.0	1.0	1.1	1.0
6.33	1.0	1.3	1.0	1.0	1.0	1.2
7.95	1.0	1.5	1.0	1.0	0.9	0.8

AHP-Type Piezometer Results						
Depth (m)	Na	K (85/07/11 to 85/10/17)	Ca	Mg	Cl	SO4
2.37	1.0	1.0	1.1	1.0	-----	
3.02	0.9	0.9	1.0	0.9	0.8	0.9
4.16	1.0	1.0	1.0	0.9	0.8	1.0
4.92	1.0	1.1	1.0	1.0	0.9	1.0
6.33	0.9	0.7	1.0	0.9	0.9	1.0
7.95	0.9	0.6	1.0	1.0	0.9	1.0

Table A5: Ratios of Squeezed to Piezometer Results
(ii): RP

Squeezed Results/SHP-Piezometer Results							
Depth	Na	K	Ca	Mg	Cl	SO4	HCO3
-0.91							
-1.07							
-2.06							
-2.77	1.0	0.9	1.6	1.1	1.2	1.1	0.4
-3.76	0.8	0.9	1.1	0.7	1.3	0.8	0.2
-4.65	0.6	1.2	1.1	0.7	1.2	0.8	0.2
-6.25	0.8	1.1	1.2	0.7	1.8	0.9	0.3
-7.77	0.7	1.6	1.3	1.1	1.0	1.0	0.4
-9.22	0.5	1.4	1.7	1.6	0.6	0.9	0.5
-12.37	0.4	0.6	0.4	0.2	1.5	0.2	0.3
-15.49	1.0	1.8	1.5	1.6	1.5	4.4	0.7

Table A5: Ratios of Squeezed to Piezometer Results
(iii): CIL

Squeezed Results/SHP-Piezometer Results								
Depth (m)	Na	K	Ca	Mg	Cl	SO4	HCO3	water
-0.91								19.0
-1.75	0.9	1.1	1.3	1.1	1.5	1.3	0.4	19.1
-2.64	0.6	1.9	1.2	1.0	1.2	1.4	0.3	17.8
-3.71	1.4	1.5	1.9	1.8	1.7	1.6	0.2	19.1
-4.55	2.3	1.5	2.8	3.2	1.7	1.2	0.2	20.4
-6.07	0.8	1.5	1.1	1.1	2.0	1.4	0.3	20.3
-7.67	0.9	1.7	1.2	1.1	1.5	1.6	0.4	19.9
-9.09	0.4	1.2	1.3	1.0	1.1	1.1	0.6	20.3
-12.19	0.6	1.6	1.5	1.3	0.8	1.1	0.8	20.9
-15.52	1.2	3.5	2.2	2.0	1.4	2.8	0.9	22.0

Table A5: Ratios of Squeezed to Piezometer Results
(iv): PC

Squeezed Results/SHP-Piezometer Results							
Depth	Na	K	Ca	Mg	Cl	SO4	HCO3
-4.57	0.2	2.0	2.4	2.1	0.6	1.6	0.4
-7.77	1.3	3.4	5.0	5.3	1.0	7.9	0.8
-9.32	1.9	6.5	12.7	15.6	1.4	35.5	0.5
-12.47	0.7	5.2	10.8	10.1	0.9	5.1	0.4

Table A5: Ratios of Squeezed to Piezometer Results
(v): UC

Squeezed Results/Piezometer Results							
Depth	Na	K	Ca	Mg	Cl	SO4	HCO3
-3.68	0.8	1.8	2.6	2.2	1.1	10.0	0.4
-5.61	1.5	2.9	2.1	1.6	0.9	16.5	0.3
-6.22	1.0	2.0	2.6	2.1	1.2	6.8	0.5
-7.75	1.7	3.1	5.2	5.2	1.6	28.4	0.5
-9.32	1.6	3.2	3.7	3.5	1.0	15.7	0.7
-12.39	1.6	3.1	5.1	5.1	1.2	12.0	0.7
-15.49	1.9	3.7	6.4	6.6	1.2	35.1	0.9

Table A5: Ratios of Squeezed to Piezometer Results
(vi): ESS

Squeezed Results/SHP-Piezometer Results							
Depth (m)	Na	K	Ca	Mg	Cl	SO4	HCO3
-3.71	0.3	1.2	2.0	1.7	1.2	1.7	0.3
-4.7	0.8	2.8	3.5	2.5	1.5	4.3	0.4
-6.22	0.7	2.5	3.4	2.7	0.7	4.8	0.4
-7.77	1.4	3.4	4.6	4.8	1.0	9.0	0.6
-9.19	0.5	1.8	3.7	3.9	0.7	1.4	0.8
-12.52	1.1	2.6	3.9	4.0	0.8	4.1	0.9
-15.57	0.4	2.0	3.4	2.9	0.8	1.1	0.8

Table A6: Dates of Squeezing and Core Collection

Samples	Date of First Squeezing	Date of Core Collection
L1-0 to L1-95	85/11/30	
L1-112 to L1-190	85/12/08	
L1-200 to L1-297	85/12/12	
L1-307 to L1-332	86/01/27	LGS 1 Core
L1-346 to L1-390	85/12/26	Collected
L1-404	85/07/25	85/06/25
L1-419	85/07/25	
L1-442	85/08/14	
L1-457 to L1-551	85/12/20	
L1-560 to L1-598	85/12/26	
L3-0 to L3-87	85/12/31	
L3-97 to L3-202	86/01/10	
L3-215 to L3-305	86/01/14	
L3-317 to L3-401	86/01/19	LGS 3 Core
L3-411	85/09/05	Collected
L3-427	86/01/27	85/06/25
L3-411 to L3-564	85/09/10	
L3-579	85/07/19	
L3-597	85/07/02	
RP-3 & RP-50	85/10/15	
Remaining RP	85/11/12	85/06/28
CIL-50	85/10/30	
Remaining CIL	85/10/29	85/06/26
ESS	85/11/17	85/07/05
PC	85/11/21	85/07/04
UC	85/11/25	85/07/03

APPENDIX II.
WATER CHEMISTRY DATA

Table A7 (i): LGS1; June 18, 1985

DEPTH	Na	K	Ca	Mg	Cl	SO4	Sr	TIC	HCO3	Alk. as mg/L CaCO3	pH
	mg/L										
-2.37	453.5	8.415	405.5	1740	178	8912	5.265	162	779.48	452	7.1
-3.02	488.5	13.21	420.3	1940	238	9623	6.403	207	979.97	672	6.85
-4.16	560	14.42	436.8	1620	301	7695	6.483	228	1017.4	664	6.65
-4.92	504	14.81	451.2	1315	347	6259	6.625	215	1014.9	716	6.7
-6.33	451	14.17	488.6	891	346	5737	7.503	212	894.04	608	6.55
-7.95	341.5	9.605	460.7	501	329	2513	9.013	141	574.74	488	6.65
-9.56	269.8	5.76	297.6	250	364	1451	8.745	89	435.16	312	6.9
-12.68	202.8	2.963	142.6	71.5	522	299	5.335	31	186.48	152	7.15
-15.74	193.8	2.232	107.4	40.8	457	132	4.205	19	127.55	100	6.95
-18.82	230.5	2.198	101.1	36.8	523	97	4.24	18	106.75	108	7.05
-21.81	253	2.202	105.8	39.25	623	87.1	4.553	17	106.75	100	6.95
-24.56	297.5	2.654	105.4	34.6	783	57.2	2.853	17.5	115.76	88	6.9
-26.74	167.5	2.332	82.48	33.45	313	36.3	1.953	9	66.79	88	6.85

Table A7 (ii): LGS1; July 11, 1985

Actual Depth (mbgs)	Na	K	Ca	Mg	Sr	Cl	SO4	HCO3	TIC
					(mg/L)				
-2.37	425	11.31	427.8	1770	6.030				
-3.02	483	14.69	427.9	1883	6.790	217	9053	954.45	216
-4.16	527	15.61	427.0	1475	6.705	281	7315	1016.10	250
-4.92	513	16.7	450.2	1280	6.725	327	6259	1010.20	248
-6.33	437	10.53	484.2	887.5	7.035	362	4816	909.51	224
-7.95	334	6.58	463.2	496	9.480	362	2988	639.43	148
-9.56	276	1.6	304.7	259.5	9.605	364	1581	458.80	92
-12.68	215	3.695	139.1	69.7	5.325	457	292	180.38	23
-15.74	111	2.38	68.2	24.95	2.228	457	149	152.31	15
-18.82	187	2.895	88.4	29.55	3.016	440	85.5	111.55	17
-21.81	257	3.448	108.4	38.55	4.576	708	73.7	116.11	18
-24.56	301	3.448	109.5	35.3	3.401	757	57.7	119.28	

Table A7 (iii): LGS1; October 17, 1985

Actual Depth (mbgs)	Na	K	Ca	Mg	Sr	Cl	SO4	Br	NO3	HCO3	Alk. as CaCO3	pH
					(mg/L)							
-2.37	425	11.3	403	1830	6.03	168	9138	<5	<5	689.5	548	
-3.02	515	15.6	419	2020	6.78	258	9600	<5	<5	950.7	536	6.75
-4.16	524	15.5	420	1580	6.72	334	7403	<5	<5	1012.0	724	6.55
-4.92	492	15.9	440	1300	6.9	374	6185	<5	<5	999.6	728	6.60
-6.33	463	14.5	468	1000	7.18	390	4892	<1	<1	929.1	644	6.60
-7.95	384	10.3	449	518	9.19	384	3004	<1	<1	660.0	496	6.65
-9.56	291	6.37	296	283	9.69	383	1575	<1	<1	460.3	372	6.80
-12.68	178	3.25	140	74.9	5.56	509	287	<1	<1	185.0	136	6.95
-15.74	192	2.53	110	45	3.73	462	152	<1	<1	157.0	112	7.00
-18.82	223	2.31	101	37.6	3.56	584	79.4	<1	<1	134.4	92	7.20
-21.81	268	2.43	109	44.8	4.04	645	103	<5	<5	116.7	88	7.00
-24.56	327	2.75	114	39.6	3.56	765	63.4	<5	<5	122.9	88	7.15
-26.74						421		<5	<5			

Table A7 (iv): LGS1a; June 3, 1985

Actual Depth (mbgs)	Na	K	Ca	Mg mg/L	TIC	HCO3	NO3	pH	Alk. as CaCO3
-0.98	278.5	1.093	357.9	1033	90	454	3.04	6.70	364
-1.84	457.0	7.855	415.5	1765	134	650	39.6	6.45	516
-2.83	1774.0	19.25	421.6	1077				6.65	782
-3.33	1384.0	18.51	392.3	1108	209	993	40.2	6.70	796
-4.02								6.65	1090
-4.19	942.0	16.99	433.3	1104				6.65	852
-4.62	595.5	15.87	430.1	1040	243	1133	6.09	6.75	888
-6.13	1875.0	25.26	378.4	651	223	1140	66.7	7.05	780
-7.11	541.5	14.64	502.0	867				6.95	756

Table A7 (v): LGS1; Squeezed, 1985

Depth	Na	K	Ca	Mg	Cl (mg/L)	SO4	Br	NO3	TIC	pH
-0.15					28	1576	<5	6	6.0	7.32
-0.25					36	2060	<5	<5	10.0	
-0.35					62	2855	<5	ND	22.0	
-0.55					100	5454	<5	<5	34.0	8.19
-0.65	331	1.3	471	1280	117	6858	<5	<5	29.0	8.15
-0.75	358	2.1	401	1380	113	7131	<5	<5	31.0	8.14
-0.90	393	3.2	392	1560	121	8241	<5	<5	33.0	8.13
-1.03	442	7.0	426	1640	150	8872	<5	<5	42.0	7.89
-1.17	459	7.0	425	1970	171	10000	<2	<2	27.0	7.87
-1.27	482	8.0	413	1960	177	9890	<2	<2	28.0	8.02
-1.39	507	9.7	424	1970	176	9445	<2	<2	28.5	8.00
-1.48	502	9.4	409	1880	169	9445	<2	<2	26.5	8.01
-1.57	557	11.3	420	2050	191	9920	<2	<2	48.0	8.05
-1.69	565	12.0	428	2020	191	9920	<2	<2	45.0	8.04
-1.79	574	12.8	413	2100	208	10235	<2	<2	44.0	8.09
-1.95	554	9.6	453	2110	217	10340	<2	<2	47.3	8.32
-2.05	512	13.4	400	2160	227	10395	<2	<2	32.0	8.04
-2.18	483	13.3	415	2120	233	10185	<2	<2	22.0	7.97
-2.28	483	13.8	414	2140	247	10660	<2	<2	26.5	8.01
-2.40	481	14.3	408	2080	254	9920	<2	<2	22.0	7.98
-2.50	480	14.7	401	2040	268	9815	<2	<2	34.0	8.06
-2.62	485	14.1	397	2040	269	9710	<2	<2	27.5	8.07
-2.72	461	14.2	392	1900	263	9594	<2	<2	29.5	8.08

Table A7 (v): (Continued) LGS1; Squeezed

-2.84	472	14.9	393	1850	273	9485	<2	<2	31.0	8.07
-2.93	466	14.5	405	1830	281	9202	<2	<2	34.5	8.08
-3.01	482	21.5	426	1620	279	8468	<2	<2	39.0	8.25
-3.11	490	19.3	569	1740	288	9599	<2	<2	25.3	
-3.19	499	20.2	617	1770	300	9540	<2	<2	24.0	
-3.28	517	19.4	597	1770	287	8662	<2	<2	26.0	
-3.37	500	17.1	521	1600	309	8311	<2	<2	23.0	
-3.50	446	15.6	422	1360	306	6810	<5	<5	26.5	
-3.60	421	8.1	410	1280	306	6550	<5	<5	23.0	
-3.73	417	15.3	412	1200	306	6125	<5	<5	25.0	
-3.81	402	15.4	415	1180	306	5942	<5	<5	25.0	
-3.95	417	22.3	484	1170	306	6198	<5	<5	34.0	
-4.11	422	22.9	460	1043	280	5466	<1.5	<1.5		
-4.30	462	25.0	508	1158	358	5978	<1.5	<1.5		
-4.50	398	28.1	453	1030	249	5818	<1.5	<1.5	56.0	
-4.61	403	33.7	635	1290	385	7234	<5	<5	47.5	
-4.72	400	33.2	686	1250	365	7020	<5	<5	47.5	
-4.81	381	35.6	664	1240	394	6787	<5	<5	47.0	
-4.92	393	34.2	657	1210	406	6543	<5	<5	47.0	
-5.03	375	34.3	692	1210	408	6755	<5	<5	47.0	
-5.13	367	34.6	693	1160	412	6436	<5	<5	48.0	
-5.24	367	35.6	609	1130	408	6490	<5	<5	34.0	
-5.33	371	34.3	690	1090	432	6170	<5	<5	34.5	
-5.44	363	34.1	688	1080	448	6064	<5	<5	35.0	
-5.55	448	44.4	557	1170	518	6383	<5	<5	40.0	
-5.64	360	34.2	614	985	418	5532	<5	<5	41.0	
-5.76	252	28.1	567	713	190	4310	<5	<5	35.5	
-5.84					209	3564	<5	<5	36.0	
-5.94					270	3936	<5	<5	37.0	
-6.02					270	3830	<5	<5	37.0	

Table A8: LGS2; 1982

depth (mbgs)	Na	K	Ca	Mg	Cl	SO4	HCO3	PH	Temp. Deg. C.
(mg/L)									
-4.25	207	7.5	258	212	26.4	1492	676	7.50	9
-6.45	119	9.2	372	322	28.4	1955	420	7.15	9
*-6.72	73	4.98	274	245	12.4	1167	667	7.22	9
-7.93	134	7.6	352	302	33.2	1972	50	7.50	9
-9.28	177	9.3	475	276	35.7	2362	323	7.25	9
-12.16	164	9	440	334	34.2	2345	317	7.35	9
** -12.79	155	3.69	230	130	23.8	1113	357	7.57	9
-15.22	192	7.5	470	190	37.1	2227	162	7.40	9
-18.2	355	5.7	326	119	43.5	1994	131	7.30	9
-22.8	285	3.95	181	66	51.9	1236	123	7.60	9
-26.1	255	3.5	101	36.2	73.3	825	95	8.00	9

* screened interval = 110 cm long (standard length = 60-80 cm)

**screened interval = 375 cm long

Table A9 (i): LGS3; June 18, 1985

Depth (mbgs)	Na	K	Ca	Mg	Sr	Cl	SO4	TIC	HCO3	Alk. as CaCO3	pH	Temp Deg. C
	(mg/L)											
-8	370.5	11.18	483.6	645.0	8.638	110	4060	152	743.36	143	6.85	16
-10	286.3	7.390	476.9	351.5	10.06	108	2800	112	537.30	103	7.05	16
-12.5	188.5	4.885	280.3	139.0	7.278	91.1	1224	45	257.11	52	6.75	17
-16	105.1	3.040	138.5	49.00	1.903	104		27	164.83		6.8	
-19	72.87	2.192	86.5	50.20	1.090	46.7	200	21	116.02			

Table A9 (ii): LGS3a; June 3, 1985

depth (mbgs)	Na	K	Ca	Mg	Cl	SO4	TIC	Alk. as CaCO3	PH
	(mg/L)								
-5.55	279.8	12.39	243	752	74.4	4200	157	464	6.65
-8.09	401.5	9.64	493.5	451.5	110	3195	137	448	6.45
-10.21	303	6.35	397.2	246.5	119	2170	87	356	6.75

Table A9 (iii): LGS3; Squeezed, 1985

Depth	Na	K	Ca (mg/L)	Mg	Cl	SO4	Br	NO3	TIC	pH
-0.06	0				113	1465	<2	<2	37.0	7.90
-0.18					77.5	1530	<2	<2	24.0	8.15
-0.28	0				134	2209	<2	<2	27.8	
-0.36	86	0.42	552	236	161	2270	<2	<2	27.0	0.00
-0.47	133	0.51	524	336	276	2305	<2	<2	27.3	8.16
-0.55	150	0.68	523	389	314	2567	<2	<2	28.0	8.21
-0.65	175	0.81	528	482	425	2787	<2	<2	33.0	8.23
-0.73	181	0.90	530	545	439	3006	<2	<2	35.0	8.26
-0.83	185	0.96	545	587	462	3281	<5	<5	36.0	8.32
-0.91	212	1.77	538	663	484	3420	<5	<5	48.0	8.46
-1.01	198	1.57	523	706	488	3740	<5	<5	19.0	7.82
-1.09	203	1.98	505	746	478	3783	<5	<5	31.0	8.06
-1.17	204	2.29	493	762	472	3850	<5	<5	36.0	8.07
-1.36	227	3.20	532	860	488	4630	<5	<5	18.0	7.97
-1.59	224	3.24	442	858	379	4390	<5	<5	27.0	8.00
-1.67	226	3.49	447	870	358	4570	<5	<5	27.0	7.99
-1.78	234	4.30	443	908	285	4570	<5	<5	27.0	8.05
-1.87	242	5.63	444	918	272	4510	<5	<5	29.5	8.04
-1.98	244	6.49	428	970	212	5027	<5	<5	28.5	8.05
-2.07	250	5.58	420	990	189	4880	<5	<5	29.0	7.90
-2.19	285	6.84	431	1120	121	5910	<2	<2	24.8	7.73
-2.28	270	35.60	493	1040	140	5330	<2	2.14	28.5	8.45
-2.38	288	8.46	416	1150	92.7	6587	<2	<2	26.5	8.01
-2.47	299	8.02	416	1210	77.8	6541	<2	<2	26.0	7.93
-2.57	297	8.88	405	1200	73.2	6321	<2	<2	27.0	7.94
-2.66	337	10.00	432	1350	72.8	7461	<2	<2	24.0	7.90
-2.78	352	10.20	447	1440	59.1	7803	<2	<2	26.0	7.91

Table A9 (iii) (Continued): LGS3; Squeezed. 1985

-2.87	338	10.60	411	1390	57.5	7803	<2	<2	28.0	7.91
-2.98	297	9.91	386	1210	47.3	6541	<2	<2	27.0	7.91
-3.10	341	10.70	393	1350	59.7	6943	<2	<2	33.0	7.98
-3.21	363	12.00	407	1380	62.6	7230	<2	3.13	27.3	7.85
-3.29	356	28.70	494	1370	68.4	7115	<2	6.25	25.0	7.93
-3.39	357	11.70	401	1340	61.5	7115	<2	6.25	26.0	7.98
-3.47	358	11.70	412	1320	61.9	6885	<2	3.13	20.0	7.97
-3.60	358	12.30	422	1290	62.6	6770	<2	<2	25.0	7.98
-3.71	363	14.10	414	1290	65.5	6736	<2	<2	25.5	8.01
-3.79	365	14.90	511	1360	64.8	7140	<2	<2	28.5	7.97
-3.89	353	14.30	496	1290	63.3	6731	<2	<2	29.0	7.96
-3.97	339	12.70	415	1140	62.6	6040	<2	<2	26.5	8.02
-4.05	356	15.70	547	1260	61.2	6810	<2	<2	25.3	7.95
-4.19	348	23.82	465	1191	82.5	6431	ND	ND	63.0	8.00
-4.34					103.5	6180	<5	<5	57.5	
-4.50	339	31.63	478	1106	131.5	6115	<5	<5	42.0	7.80
-5.65	290	23.93	410	899	98.3	4938	<5	<5	59.5	8.22
-5.26	544	40.03	455	1500	212	7843	<5	<5	54.0	8.01
-5.41	258	26.40	347	668	223	3922	<5	<5	62.0	8.34
-5.57	217	22.51	350	550	114	3295	<5	<5	63.0	8.26
-5.72	288	24.23	490	774	103.9	4738	<5	<5	62.5	8.24
-5.87	294	19.92	499	719	101	4068	<3	14.03	31.8	
-6.00	287	17.49	484	701	85.5	3978	<1.5			

Table A10 (i): LGS4; July 12, 1985

DEPTH	Na	K	Ca	Mg	Cl	SO4	Sr	TIC	HCO3	pH	Temp. Deg. C.
				(mg/L)							
-3.3	69.3	6.45	27.97	8.175	6.44	165	0.189	28.0	178		18
-4.39	123.5	5.84	507.6	327	24.5	2294	5.67	111.0	553	6.75	
-5.03	215	6.66	465	295	30	2344	6.155	137.0	583	6.85	
-6.55	124.3	5.863	397.2	135.5	31.6	1776	7.19	115.0	533	6.65	16
-8.14	90.5	4.478	251.5	155	28.8	1095	7.355	73.0	401	6.95	16
-9.69	77.55	4.225	174.1	101.8	26.3	858	6.005	41.0	238	7.00	16
-12.68	113.2	3.915	207.6	101.8	40.1	986	7.58	26.0	165	7.00	17
-15	162.3	3.273	140.2	51.2	76.4	740	4.835	16.0	110	7.00	15

Table A10 (ii): LGS4; October 1985

DEPTH	Na	K	Ca	Mg	Cl	SO4	Sr	Fe	TIC as CO3	pH
(mg/L)										
-2.65	46.2	1.78	126	49.5	10.4	334	0.428	0.21	177.7	7
-4.39	125	5.86	488	331	25.7	2326	0.55	6.98	554.6	6.75
-5.03	209	6.58	485	330	32.5	2541	6.41	3.09	684.5	6.5
-6.55	135	5.41	405	260	34.7	1873	8.17	6.63	574.6	6.7
-8.14	110	3.91	263	176	31.6	1217	7.98	7.11	364.7	7.05
-9.69	105	4.06	204	131	37.5	1061	6.99	1.07	204.8	7.15
-12.68	152	2.78	219	117	44.2	1113	8.54	0.57	129.9	6.55
-15	151	4.07	194	77.3	68	876	6.77	0.66		
-18.8	202	2.83	152	57.3	94.8	742	5.67	0.32	79.9	6.35

Table A11 (i): LGS6; June 3, 1985

Depth (mbgs)	Na	K	Ca	Mg	Sr	Cl	SO4	HCO3	NO3	TIC	Alk. as CaCO3	Ph
					(mg/L)							
-1.88	200.3	1.364	324.8	251	1.502	53.2	1890	372	18.6	73	300	6.0
-3.02	222.5	5.13	429.4	543		95.8	3250	469	5.33	89	376	6.3
-3.59	576.5	9.93	405.0	491		124	3630	684	28.9	134	536	6.4
-4.53	358.0	9.7	480.0	576	7.203	167	3450	660	57.2	136	496	6.6
-5.09	228.3	9.37	472.3	511		168	3025	632	7.61	126	540	6.4
-5.54	252.8	8.35	519.1	479	8.613	191	2970	623	97.4	133	508	6.3
-6.16	349	9.385	521.2	405	8.74	199	2900	646	<3	132	552	6.
-7.07	287.8	8.39	511.1	352	9.548	207	2610	612	<3	127	500	6.4
-7.97	265.5	8.835	519.5	312	10.070	221	2350	616	<3	130	524	6.5
-9.18	208.5	5.973	418.0	233	9.970	214	1800	650	<3	116	452	6.5
-10.02	318.5	5.633	371.9	193	10.070	236	1680	494	3.35	102	300	6.5

Table A11 (ii): LGS6; June 7, 1985

Depth (mbgs)	Na	K	Ca	Mg	Sr	Cl	S04	HCO3	NO3	TIC	Alk. as CaCO3	Ph
				(mg/L)								
-1.09	39.6	0.295	209.4	107.3	0.41	27.2	730		<3	57	280	6.50
-1.88	193.5	1.333	332.4	267.5	1.55	54.4	1980	372	28.9	70	300	6.95
-3.02	242.0	5.703	472.9	596	3.40	97.8	3540	469	<3	107	404	6.30
-3.47	354.5	8.53	444.4	560	3.66	123	3805	684	<3	113	456	6.25
-3.59	434.5	9.725	433.8	526	4.27	124	3630	660				
-4.53	309.0	9.46	467.7	558	7.31	167	3450	632				
-5.09	265.3	8.205	499.2	541	8.14	181	3350	623	6.7	152	540	6.05
-5.54	280.5	8.695	502.6	449	8.81	181	3210	646	<3	139	504	6.35
-7.07	251.8	7.565	439.9	301	8.71	207	2610	612	3.04		452	6.15
-7.97	351.5	8.015	495.6	294.5	9.72	217	2570	616	<3	135	524	6.35
-9.18	237.0	5.958	407.0	229	9.85	210	2010	650	<3	109	452	7.05
-10.02	332.5	5.93	372.0	199	9.70	220	1790	494	3.04	113	416	7.05

Table A12: LGS76 June 7, 1985

Depth m	Na	K	Ca	Mg	Sr	Cl	SO4	TIC	Alk. as CaCO3	PH	Temp. Deg. C.
				(mg/L)							
-1.95	50.75	2.853	185.9	102.3	0.643						16
-3.84	199.5	5.94	201.6	93.75	0.922	68.7	910	122	460	6.75	16
-4.56	121	6.715	389.1	191.8	2.005	25.5	1445	116	404	6.8	12
-4.97	139.3	7.01	497	259.5	2.728	70.2	2195	107	412	6.45	12
-6.09	154.6	6.365	400.8	237	3.849	130	1852	102	380	6.55	12
-8.08	90.6	2.77	157.8	97	2.662	53.2	1285	82	368	5.85	13

Table A13 (1) : RP: Squeezed, 1985

Depth (m)	Na	K	Ca	Mg	Cl	SO ₄	TIC	pH
-0.91	57.4	0.478	94.8	131	152	336	565	
-1.07	66.3	0.798	119	152	157	664	37	8.15
-2.06								
-2.77	230	3.71	304.4	547	111	3018	49	8.18
-3.76	275	6.46	451	532	222	3414	33.5	8.13
-4.65	300	11.1	488	512	225	3487	34.5	8.05
-6.25	255	10.5	568	359	397	2859	26	8.3
-7.77	248	11.3	459	277	228	2188	40	8.03
-9.22	197	8.65	402	222	144	1497	34	8.17
-12.37	161	4.55	150	58.3	354.5	343.5	21	8.21
-15.49	150	4	126	50	500	200	22	8.09

Table A13 (ii): RP; SHP-Piezometers, October, 1986

Depth (m)	Na	K	Ca (mg/L)	Mg	Sr	Cl	SO4	pH	HCO3
-1.07	148	1.59	82.3	209	1.47	41.7	692	----	583
-2.77	239	3.92	191	485	3.18	92.9	2845	6.8	692
-3.76	353	6.88	426	793	5.49	174	4341	----	758
-4.65	480	9.51	453	691	6.47	185	4360	6.75	711
-6.25	333	9.31	482	511	7.29	216	3029	6.8	566
-7.77	377	7.2	359	257	6.5	231	2188	6.75	472
-9.22	431	6.2	243	136	4.93	255	1696	7.3	368
-12.37	402	7.82	346	329	5.38	233	2190	7.2	396
-15.49	155	2.23	84.8	31.6	2.67	336	45.4	7.3	159

Table A14 (i): CIL; Squeezed, 1985

Depth (mbgs)	Na	K	Ca (mg/L)	Mg	Cl	SO4	TIC
-0.91	47.6	1.35	262	137	15.4	1037	
-1.75	71.5	3.08	336	221	29	1486	31
-2.64	93.2	10.4	588	372	32.9	2870	27
-3.71	85.3	8.91	544	280.5	32.9	2268	23
-4.55	70.6	6.1	316	165.5	26.3	1288	17
-6.07	72.6	4.75	136	82.1	30.4	563	30
-7.67	95.9	4.91	123	62.1	27.5	632	28
-9.09	77.4	4.09	126	47	28.3	578	32
-12.19	91.7	3.5	105	36.6	29.9	437	30
-15.52	136.8	6.17	108	39.6	69	584	32

Table A14 (ii): CIL; SHP-Piezometers, October, 1986

Depth (mbgs)	Na	K	Ca (mg/L)	Mg	Cl	SO4	pH	Alk. as CaCO3	HCO3
-0.91									
-1.75	79.7	2.83	258	202	19.8	1170	6.95	384	389
-2.64	162	5.62	474	358	27.3	2117	7.00	368	525
-3.71	59	5.89	285	157	18.9	1462	6.65	380	492
-4.55	30.7	4.08	113	52.5	15.9	1102	6.95	180	482
-6.07	88	3.23	121	71.5	15.2	403	7.05	376	454
-7.67	109	2.89	101	54.9	18.4	395	7.15	272	344
-9.09	173	3.32	94	46.2	26.2	518	7.30	220	278
-12.19	144	2.18	68	27.2	38.5	381	7.40	204	199
-15.52	117	1.78	49.4	19.8	51	208	7.30	200	181

Table A15 (i): PC; Squeezed, 1985

Depth (mbgs)	Na	K	Ca (mg/L)	Mg	Cl	SO4	TIC
-0.91	5.71	0.52	76.5	25.1	16.8	129	27
-1.83							
-2.72							
-3.73							
-4.57	60.3	5.79	168	73.7	27.9	653	33.5
-6.22							
-7.77	128	7.49	222	105	48.6	1078	33.5
-9.32	137	11.4	415	176	73.4	1855	21
-12.47	171	10.3	467	140	86.8	1883	18
-15.54					136	1278	27

Table A15 (ii): PC; SHP-Piezometers, October, 1986

Depth (mbgs)	Na	K	Ca (mg/L)	Mg	Cl	SO4	pH	HCO3
-0.91								
-1.83	60.3	1.73	113	48.7	11.7	136	6.95	418
-2.72	167	3.01	110	52.5	30.8	505	7.15	437
-3.73	61.3	2.85	85.3	42.1	16.3	103	7.2	438
-4.57	246	2.95	69.3	35.2	46.2	400	7.25	457
-6.22	129	2.2	46.6	23	45.5	265	7.1	289
-7.77	97.1	2.19	44.8	19.8	48.3	136	7.3	215
-9.32	72.4	1.75	32.7	11.3	53	52.2	7.1	228
-12.47	246	2	43.1	13.8	97.8	372	7.5	212
-15.54	131	2.81	58.5	20.5	104	165	7.3	201

Table A16 (i): UC; Squeezed, 1985

Depth (mbgs)	Na	K	Ca (mg/L)	Mg	Cl	SO4	TIC
-1.8					23.9	181	24
-2.77							
-3.68	44.7	4.44	158	70.4	31.9	571	32.2
-5.61	76.15	7.09	99.4	36.6	33.3	412	19.2
-6.22	74.3	5.48	129.5	50.8	56.5	477	32.5
-7.75	109	7.46	223	91.8	80.9	973	23
-9.32	113.5	6.44	153.5	55.2	69	602.7	33.8
-12.39	144.5	7.07	203.5	65.8	106	852.5	31.5
-15.49	160	8.52	247	77.1	147.3	906	26.7

Table A16 (ii): UC; SHP-Piezometers, October 1986

Depth (mbgs)	Na	K	Ca (mg/L)	Mg	Cl	SO4	pH	Alk. as HCO3 CaCO3	
-1.8	72.4	2.21	132	51	22.5	278	7.2	308	457
-2.77	57	2.14	79.3	36.9	29.5	78.1	7.0	400	423
-3.68	57.5	2.49	60.5	31.6	28.3	57	7.1	320	391
-5.61	50	2.45	46.8	23.6	35.2	25	7.0	280	316
-6.22	72.9	2.71	49.5	24.4	45.4	70	7.1	268	310
-7.75	62.7	2.42	42.7	17.6	50.1	34.3	7.1	232	257
-9.32	72.8	2.02	41.7	15.9	67.3	53.3	7.1	196	242
-12.39	89.6	2.29	39.9	12.8	90.4	71.3	7.2	168	234
-15.49	86	2.32	38.4	11.6	127	25.8	7.2	176	146

Table A17 (i); ESS; Squeezed, 1985

Depth (mbgs)	Na	K	Ca (mg/L)	Mg	Cl	SO4	TIC
-1.22	13.6	0.455	206	59.2	95.6	456	39.9
-1.88							
-2.92							
-3.71	44	4.5	187	82.6	33	930	29.5
-4.7	69.2	8.53	305	126	28.2	1182	34
-6.22	68.1	5.49	183	79.3	16.7	710	28
-7.77	99	6.09	196	91	22.2	871	31
-9.19	116	4.43	151	65.1	32.3	626	41
-12.52	113	3.89	139	48.5	34	539	36.5
-15.57	96.2	4.35	131	34.3	39.5	444	37

Table A17 (ii): ESS; SHP-Piezometers, October, 1986

Depth (mbgs)	Na	K	Ca (mg/L)	Mg	Cl	SO4	pH	Alk. as HCO3 CaCO3	
-1.22									
-1.88	123	1.98	193	67.3	79.9	876	7.2	456	485
-2.92	92.1	2.73	110	54	20.5	263	7.2	440	481
-3.71	168	3.77	91.3	48.5	27.6	551	7.2	412	488
-4.7	84.7	3.04	87.3	50.1	18.9	272	7.1	338	401
-6.22	96.9	2.22	53.5	29.2	23.4	148	7.3	296	341
-7.77	72.4	1.79	42.2	19.1	23.3	96.6	7.3	228	264
-9.19	252	2.45	41.3	16.5	45.1	460	7.5	220	256
-12.52	103	1.5	35.9	12.1	40.1	132	7.5	184	213
-15.57	234	2.17	38.9	11.9	51.1	401	7.5		230

Table A18: AL; SHP-Piezometers, October, 1986

Depth (m)	Na	K	Ca	Mg	Cl	SO4	pH	HCO3
	(mg/L)							
-1.83	132	350	156	86.5	262	232	7	884
-2.77	174	451	140	100	399	261	6.7	927
-3.76	110	30.9	259	140	426	251	6.6	527
-4.65	61.2	3.46	147	91.5	334	109	6.8	446
-6.25	66.1	2.74	91	72.4			6.85	
-7.77	46.8	2.33	58	52.1	123	16.1	6.9	327
-9.22	43.9	2.15	39.2	37.2	46.2	32.6	6.9	297
-12.37	49.3	2.68	50.4	54.5	103	63.5	6.95	309
-15.49	76.1	2.36	47	40.4	35.7	134	6.85	269

APPENDIX III.

SATURATION INDICES AT SELECTED SITES

Table A19 (i): LGS1; 1982

DEPTH	pH	Epm Bal.	PCO2	Saturation Indices		
				Cal.	Dol.	Gyp.
-2.37	6.98	1.64	-1.52	-0.18	0.48	0.24
-3.02	7.40	1.25	-1.78	0.43	1.64	0.29
-4.16	7.00	-2.52	-1.29	0.19	1.05	0.33
-4.92	7.03	-0.26	-1.33	0.25	1.09	0.31
-6.33	7.05	-0.7	-1.36	0.32	1.06	0.3
-7.95	7.10	0.64	-1.57	0.29	0.74	0.25
-9.56	7.40	-1.29	-1.97	0.38	0.84	0.01
-12.68	7.60	-2.4	-2.45	0.2	0.17	-0.66
-15.74	7.60	-0.14	-2.5	0.11	-0.14	-0.97
-18.82	7.70	-30.1	-2.73	-0.11	-0.56	-0.51
-21.81	7.45	-2.43	-2.59	-0.32	-0.99	-1.36
-24.56	7.70	-3.51	-2.78	0.03	-0.34	-1.33

Table A19 (ii): LGS1; June 18, 1985

DEPTH	pH	EPM BALANCE	PCO2	Saturation Indices		
				Cal.	Dol.	Gyp.
				(input TIC)		
-2.37	7.10	-5.18	-1.5	0.13	1.01	0.31
-3.02	6.85	-4.93	-1.1	-0.06	0.67	0.32
-4.16	6.65	-1.53	-1.0	-0.20	0.29	0.30
-4.92	6.70	-1.21	-1.0	-0.11	0.36	0.29
-6.33	6.55	-10.02	-1.1	-0.40	0.61	-0.19
-7.95	6.65	5.51	-1.1	-0.13	-0.21	0.17
-9.56	6.90	-0.33	-1.5	-0.15	-0.27	-0.07
-12.68	7.15	-4.60	-2.3	-0.66	-1.52	-0.79
-15.74	6.95	-1.51	-2.2	-0.98	-2.30	-1.17
-18.82	7.05	-1.00	-2.3	-0.91	-2.16	-1.33
-21.81	6.95	-3.85	-2.2	-1.00	-2.35	-1.37
-24.56	6.90	-8.77	-2.5	-1.30	-3.10	-1.57
-26.74	6.85	14.19	-1.9	-0.93	-2.20	-1.79

Table A19 (iii): LGS1; October 17, 1986

DEPTH	pH	Epm	Saturation Indices			
		Balance	PCO2	Cal.	Dol.	Gyp.
-2.37	6.75	-4.26	-1.27	-0.38	0.03	0.3
-3.02	6.55	-2.97	-0.99	-0.49	-0.17	0.31
-4.16	6.60	-1.7	-0.99	-0.34	0.01	0.28
-4.92	6.60	-1.63	-0.99	-0.29	0.01	0.27
-6.33	6.65	-0.77	-1.05	-0.18	0.07	0.27
-7.95	6.80	-1.33	-1.28	-0.06	0.04	0.2
-9.56	----	-0.26	-1.46	-0.23	-0.37	-0.08
-12.68	6.95	-5.4	-1.91	-0.62	-1.41	-0.82
-15.74	----	-3.2	-2.01	-0.69	-1.67	-1.12
-18.82	7.20	-6.38	-2.25	-0.55	-1.43	-1.42
-21.81	7.00	-3.27	-2.14	-0.82	-1.94	-1.3
-24.56	7.15	-3.48	-2.25	-0.61	-1.59	-1.5

Table A20: LGS2; 1982

depth (mbgs)	pH	PCO2	Cal.	Dol.	Gyp.
			Saturation input TIC	Indices	
-4.25	7.5	-1.82	0.66	1.34	-0.11
-6.45	7.15	-1.68	0.22	0.49	0.08
*-6.72	7.22	-1.54	0.44	0.93	-0.16
-7.93	7.5	-2.96	-0.37	-0.69	0.07
-9.28	7.25	-1.9	0.28	0.44	0.23
-12.16	7.35	-2.01	0.34	0.68	0.19
*-12.79	7.57	-2.15	0.47	0.78	-0.19
-15.22	7.4	-2.34	0.14	0.01	0.24
-18.2	7.3	-2.32	0.19	-0.7	0.09
-22.8	7.6	-2.64	-0.09	-0.51	-0.22
-26.1	8	-3.14	0.02	-0.31	-0.53

Table A21: LGS4; October 17, 1985

Depth (m)	pH	PCO2	Cal. Saturation Indices	Dol.	Gyp.
-3.3	6.75	-1.94	-0.57	-1.46	-0.71
-4.39	6.85	-1.3	-0.09	-0.25	0.21
-5.03	6.65	-1.04	-0.37	-0.79	0.24
-6.55	6.95	-1.24	-0.19	-0.47	0.12
-8.14	7.00	-1.7	-0.07	-0.22	-0.13
-9.69	7.00	-2.03	-0.29	-0.67	-0.24
-12.68	-----	-1.78	-1.04	-2.27	-1.49
-15	7.00	-1.9	-1.52	-2.35	-2.74
-18	7.10	-2.01	-1.79	-3.92	-3.77

Table A22: RP; SHP-Piezometers, October 1986

Depth (m)	pH	PCO2	Cal. Saturation Indices	Dol.	Gyp.
-1.07	-----				
-2.77	6.80	-1.25	-0.40	-0.29	-0.13
-3.76	-----	-1.23	-0.09	0.20	0.24
-4.65	6.75	-1.22	-0.16	-0.02	0.28
-6.25	6.80	-1.34	-0.09	-0.04	0.24
-7.77	6.75	-1.37	-0.31	-0.65	0.10
-9.22	7.30	-1.92	-0.10	0.06	-0.09
-12.37	7.20	-1.82	0.13	0.36	0.06
-15.49	7.30	-2.25	-0.39	-1.13	-1.70

Table A23: CIL; SHP-Piezometers, October 1986

Depth (mbgs)	pH	PCO2	Cal.	Dcl.	Gyp.
-1.75	6.95	-1.70	-0.29	-0.58	-0.15
-2.64	7	-1.80	-0.10	-0.22	0.18
-3.71	6.65	-1.40	-0.58	-1.32	-0.03
-4.55	6.95	-2.00	-0.95	-2.14	-0.40
-6.07	7.05	-1.80	-0.37	-0.88	-0.69
-7.67	7.15	-2.00	-0.48	-1.14	-0.75
-9.09	7.3	-2.30	-0.49	-1.18	-0.69
-12.19	7.4	-2.40	-0.51	-1.34	-0.88
-15.52	7.3	-2.30	-0.69	-1.71	-1.19

Table A24: UC; SHP-Piezometers, October 1986

Depth (m)	pH	PCO2	Cal.	Dol.	Gyp.
			Saturation Indices		
-1.8	7.20	-1.71	0.08	-0.17	-0.78
-2.77	7.00	-1.57	-0.33	-0.91	-1.43
-3.68	7.10	-1.68	-0.34	-0.89	-1.64
-5.61	7.00	-1.69	-0.63	-1.48	-2.06
-6.22	7.10	-1.78	-0.53	-1.28	-1.62
-7.75	7.10	-1.86	-0.64	-1.59	-1.95
-9.32	7.10	-1.88	-0.68	-1.70	-1.91
-12.39	7.20	-1.98	-0.62	-1.65	-1.68
-15.49	7.20	-2.18	-0.81	-2.06	-2.1

Table A25: AL; SHP-Piezometers, October 1986

Depth (m)	pH	PCO2	Cal. Saturation Indices	Dol.	Gyp.
-1.83	7	-1.26	0.157	0.143	-0.906
-2.77	6.7	-1.02	-0.239	-0.539	-1.18
-3.76	6.9	-1.21	-0.333	-0.846	-1.64
-4.65	6.3	-1.4	-0.35	-0.819	-1.22
-6.25	6.85	-1.45	-0.43	-0.89	----
-7.77	6.9	-1.6	-0.674	-1.31	-2.24
-9.22	6.9	-1.63	-0.863	-1.66	-2.04
-12.37	6.95	-1.66	-0.71	-1.3	-1.71
-15.49	6.85	-1.64	-0.935	-1.85	-1.42

APPENDIX IV.

SEDIMENT CHARACTERISTICS

Appendix IV (1). Chittick Results

Table A26: Chittick Results at LGS1

Depth (m)	% CALCITE		% DOLOMITE		AVERAGE VALUES			
	(1)	(2)	(1)	(2)	% CAL.	% DOL.	TOTAL CAL./DOL.	
-0.60	14.6	14.4	6.2	7.8	14.5	7.0	21.5	2.1
-1.55	10.3	10.2	6.4	6.0	10.3	6.2	16.5	1.7
-1.55	9.8	10.0	6.0	6.5	9.9	6.3	16.2	1.6
-2.00	12.0	12.0	7.0	6.5	12.0	6.8	18.8	1.8
-3.15	12.0	13.8	7.0	8.4	12.9	7.7	20.6	1.7
-3.50	12.6	13.8	8.2	7.2	13.2	7.7	20.9	1.7
-3.65	11.4	11.9	6.0	5.6	11.7	5.8	17.5	2.0
-7.70	17.6	17.8	6.4	6.4	17.7	6.4	24.1	2.8
-9.20	16.4	16.3	6.0	6.4	16.4	6.2	22.6	2.6
-12.50	16.8	16.8	7.0	7.3	16.8	7.2	24.0	2.3
-15.60	16.6	16.6	7.0	7.0	16.6	7.0	23.6	2.4
-18.85	16.0	15.8	7.6	8.2	15.9	7.9	23.8	2.0
-21.80	25.4	25.9	8.4	8.4	25.7	8.4	34.1	3.1
-24.50	22.2	24.0	8.2	7.0	23.1	7.6	30.7	3.0

Table A27: Chittick Results at CIL

Depth (m)	% CALCITE		% DOLOMITE		AVERAGE VALUES			
	(1)	(2)	(1)	(2)	% CAL.	% DOL.	TOTAL CAL./DOL.	
-0.9	15.2	14.2	7.5	8.2	14.7	7.9	22.6	1.9
-1.8	11.6	12.0	8.5	8.3	11.8	8.4	20.2	1.4
-2.6	12.2	12.1	9.8	8.8	12.2	9.3	21.5	1.3
-3.7	14.5	14.6	7.1	6.7	14.6	6.9	21.5	2.1
-4.6	13.2	13.2	7.6	6.8	13.2	7.2	20.4	1.8
-6.1	12.4	12.0	6.8	7.2	12.2	7.0	19.2	1.7
-7.7	12.8	12.0	6.6	6.6	12.4	6.6	19.0	1.9
-9.1	11.8	11.6	6.4	6.4	11.7	6.4	18.1	1.8
-12.1	13.5	13.8	7.6	7.0	13.7	7.3	21.0	1.9
-15.5	15.0	15.4	7.6	7.4	15.2	7.5	22.7	2.0

Table A28: Chittick Results at RP

Depth (m)	% CALCITE		% DOLOMITE		AVERAGE VALUES			
	(1)	(2)	(1)	(2)	% CAL.	% DOL.	TOTAL	CAL./DOL.
-2.1	18.6	17.6	24.0	24.5	18.1	24.3	42.4	0.7
-2.8	18.5	18.0	47.6	46.6	18.3	47.1	65.4	0.4
-3.8	13.0	11.2	12.4	12.4	12.1	12.4	24.5	1.0
-4.7	9.6	9.9	5.2	6.0	9.8	5.6	15.4	1.7
-6.2	10.8	11.2	4.8	4.5	11.0	4.7	15.7	2.4
-7.8	11.4	13.8	6.8	6.1	12.6	6.5	19.1	2.0
-9.2	12.0	12.8	8.2	7.0	12.4	7.6	20.0	1.6
-12.4	13.0	12.0	7.2	8.5	12.5	7.9	20.4	1.6
-15.5	8.8	9.5	9.5	8.6	9.2	9.1	18.2	1.0

Table A29: Chittick Results at PC

DEPTH (m)	% CALCITE		% DOLOMITE		AVERAGE VALUES			
	(1)	(2)	(1)	(2)	CALCITE (%)	DOLOMITE (%)	TOTAL (%)	CAL/DOL
-0.91	4.8	4.8	21.4	21.4	5	21	26	0.2
-1.83	13.0	12.6	27.3	27.6	13	28	40	0.5
-4.57	11.4	11.6	23.2	22.0	11	23	34	0.5
-6.22	12.2	11.4	23.4	23.8	12	24	35	0.5
-7.77	12.2	10.2	26.8	26.6	11	28	39	0.4
-9.32	10.4	10.4	24.2	24.4	10	24	35	0.3
-12.47	9.2	8.8	10.8	10.8	9	11	20	0.8
-15.54	9.4	9.0	7.9	7.8	9	8	17	1.2

Appendix IV (ii). Core Descriptions

General notes:

1. fragments = coarse sand and gravel sized particles of black shale or limestone.
2. all fractures are gray-surfaced and vertical unless otherwise noted. Their presence is emphasized by underlining.
3. * denotes core descriptions made by Harding (1986) during piezometer installation.
4. "flecks" are fine to coarse sand-sized powdery patches scattered in the matrix. They are a whitish to yellowish color unless otherwise noted. Their composition is probably either gypsum or limestone.

LGS1

- | | |
|-----------|--|
| 0 - 0.6 | rusty-brown. crumbly, silty, dry. rootlets and organic carbon. abundant hairline-thick <u>fractures</u> . small flecks. |
| 0.6 - 1.1 | yellowish-brown mottled with gray. silty. faint remnant banding. rootlets. <u>fracture</u> from 0.6 to 1.1 m, filled with gray silty material, with gypsum fill beginning below 0.8 m. small flecks. |
| 1.1 - 2.5 | yellowish-brown mottled with gray, becoming slightly darker at 2.2 m. extremely abundant narrow <u>fractures</u> , often containing rootlets and minor or abundant sand-sized gypsum; abundant shale frags. abundant fine-grained gypsum, usually following root channels, but also as lenses in matrix. <u>fracture</u> extending from 1.3 to 1.4 m ends in a lense of well-crystallized gypsum 3 x 1 cm; similar lense of gypsum at 1.2 m. |
| 2.5 - 3.1 | fairly uniform medium-gray with a yellowish tinge. no roots or organic carbon seen. fewer fragments. abundant short <u>fractures</u> , filled discontinuously with gypsum. occasional lenses filled with coarse-grained gypsum. |
| 3.1 - 3.5 | brownish-gray with a yellowish-gray <u>fracture</u> halo down one side. remnant carbon. abundant fragments. abundant small flecks. plastic. |

- 3.5 - 4.0 light gray. fracture, 40 cm long and 1 cm diameter filled with coarse gypsum, ends in a lense of gypsum crystals. also a few short thin gypsum-filled fractures.
- 4.0 - 4.6 uniform brownish-gray. some shale fragments. minor scattered flecks. minor organic carbon traces. fractures not noted below 4 m.
- 4.6 - 5.7 uniform medium gray. homogeneous and plastic. no fractures. some shale fragments.
- 5.7 - 6.0 uniform dark gray clay with several stringers of coarse sand.

LGS3

- 0 - 0.5 crumbly, sandy, dry.
- 0.6 - 1.0 yellowish-brown mottled with gray. abundant fractures.
- 1.0 - 1.5 rusty-brown, stiff, silty. faint remnant banding between yellowish-brown and gray. abundant fractures. rootlets. some shale fragments. gypsum seen in fractures beginning at 1.3 m.
- 1.5 - 2.5 mottled rusty-brown and gray, changing to mottled yellowish-brown and gray at 2.0 m. gradually more gray with depth. distinct cm scale layering of yellowish-brown and gray. plastic. abundant fractures surrounded by gray haloes. occasional gypsum around roots and as small flecks in matrix.
- 2.7 - 3.0 prominent layering of yellowish-brown and gray. plastic. very abundant gypsum as flecks and lenses in the matrix. abundant shale fragments. fractures surrounded by gray haloes. some short horizontal and vertical partings filled with rust-colored silt.
- 3.0 - 3.7 uniform slightly rusty brown. stiff. very large fracture filled with gypsum and gray clayey material, ending in a 7 x 7 cm lense of coarse gypsum crystals and sandy layers, extending from 3 to 3.5 m. remnant black layering, with abundant organic carbon.

- 3.7 - 4.4 uniform brown. gray gypsum-filled fracture with large gray halo extends the length of the sample. faint remnant layering of yellowish-brown and brown. very few gypsum flecks. minor shale fragments and organic carbon traces.
- 4.4 - 4.7 uniform gray. plastic. minor shale fragments. no gypsum noted.
- 4.7 - 6.0 uniform gray. brown fracture halo, significantly more moist than surrounding matrix, up to 8 cm in diameter, extends from 4.7 to 5.1 m. small fractures within the halo. minor black shale fragments. minor small flecks in matrix. scattered lenses of gray silty clay. fractures not noted below 5.1 m.

***LGS6**

- 1.0 heavily oxidized, brownish-gray. silty, stiff. rootlets and organic carbon common. minor fragments.
- 3.5 grayish-brown. silty, stiff. fine dark laminations.

***LGS7**

- 2.0 grayish-brown. silty, stiff. abundant fractures. minor white powder. mm scale light and dark laminations at base.
- 3.0 dark brown. silty, stiff. 1 to 2 mm thick laminations of light and dark. fragments.
- 4.0 yellowish-brown mottled with dark brown. fine laminations of brown silt cross-cutting gray fractures.
- 4.5 to 6.0 dark gray. silty, plastic. fragments.

LGS2

3.0 to 3.3	uniform brown. stiff. long <u>fracture</u> filled with large gypsum crystals. large limestone pebbles.
3.3 to 3.6	uniform gray. plastic. abundant small flecks. some greenish-brown mottling.
3.6 to 4.6	uniform gray, becoming slightly darker with depth. plastic. some reddish or greenish flecks. rare fragments. some small black sandy patches.
4.6 to 8.1	uniform gray. plastic. occasional small flecks. some discontinuous horizontal partings filled with rust-colored fine sand.
8.1 to 9.5	brownish-gray. stiff. horizontal or high angle dark gray <u>laminae</u> which look more porous than the surrounding matrix. large fragments.
21.0	uniform gray. plastic.

RP

0.91	mottled light and dark rusty-brown. silty. highly <u>fractured</u> . abundant flecks of matrix gypsum.
2.06	uniform gray. plastic. highly <u>fractured</u> . abundant flecks.
2.77	rusty brown mottled with some gray. stiff. highly <u>fractured</u> .
3.7	rusty-brown. stiff. large <u>fractures</u> with roots and rare small gypsum crystals. lenses of red or black sand. lenses of white powdery material.
4.7	dark gray faintly mottled with brownish gray. stiff. lenses of red and black sand. lenses of crystallized gypsum.
6.3	uniform gray. long <u>fracture</u> with 4 cm dia. halo, filled with black or red silt and rare gypsum. abundant black shale fragments.

- 7.8 uniform gray. minor shale fragments. minor flecks.
- 9.2 uniform gray. long fracture with brown halo.
- 12.4 dark gray with a horizontal break to lighter gray. plastic. some shale fragments.
- 15.5 uniform gray with minor black laminae. plastic. horizontal partings filled with rust-colored silt. some shale fragments.

CIL

- 0.9 gray clayey areas mottled with yellowish brown silty patches. stiff. abundant gypsum flecks in matrix. abundant traces of organic carbon and horizontal laminae of organic matter. abundant shale fragments. fractured.
- 1.7 yellowish-brown sandy clay layered with more fine-grained gray clay. stiff. abundant shale frags. gypsum flecks in silty laminae. fractured.
- 2.7 & 3.7 uniform gray. silty, stiff. shale fragments. minor gypsum flecks.
- 4.5 to 15.5 gray. plastic. minor lenses of fine black sand at 6, 7.6, and 12 m. short vertical fractures filled with rust colored fine sand at 7.6 and 12 m.

PC

- 0.9 reddish brown mottled with light gray. silty. highly fractured. large lense of dark gray clay. abundant flecks.
- 1.8 & 2.1 yellowish brown mottled with brown. abundant flecks. fractured.
- 4.6 to 12.5 uniform grayish brown. lense of white flakey clay at 6 m. minor small flecks of red and yellow scattered throughout. vertical sand-filled parting with no color

change at 9 m. reddish sandy layer 1 cm thick at 7.8 m.
sandy at 9 m.

12.2 & 15.5 uniform gray. minor scattered flecks of orange and
white. horizontal laminae of reddish clay at 12.2 m.

UC

0.9 to 2.8 rusty-brown mottled with gray. abundant roots. silty
and aggregated. fractured. scattered flecks.

3.7 & 5.6 uniform gray. silty. fractured. brownish-red sandy
lenses noted at 3.7 and 5.6 m.

6.2 to 9.3 uniform gray, becoming gradually darker with depth.
abundant flecks. abundant shale frags and short rusty-
brown fractures at 9.3.

12.4 to 15.5 uniform dark gray. some large shale frags. minor flecks.
minor lenses or layers up to 5 mm thick, filled with
black or reddish fine sand.

ESS

1.2 bright brownish-red mottled with light and dark gray.
silty. stiff. fragments, sand lenses, fractures.
abundant flecks.

3.7 to 5.0 grayish-brown. silty. stiff. long fracture with brown
halo at least 6 cm dia., without gypsum.

6.2 to 12.2 grayish-pinkish brown. silty, stiff. abundant pebbles.
some flecks.

15.6 gray. minor flecks.

Appendix IV (iii). Water Content Data
as weight percent of bulk wet weight

RP			CIL		
Depth (mbgs)	Total %	Squeezed %	Depth (mbgs)	Total %	Squeezed %
-0.91	16.43	19.81	-0.91	19.00	23.99
-1.07	16.18	38.85	-1.75	19.08	18.74
-2.06	13.48	6.96	-2.64	17.84	25.26
-2.77	16.33	22.56	-3.71	19.14	28.42
-3.76	17.71	18.71	-4.55	20.40	31.53
-4.65	18.53	20.91	-6.07	20.30	33.99
-6.25	17.40	20.93	-7.67	19.88	31.16
-7.77	14.94	28.07	-9.09	20.31	33.06
-9.22	17.94	24.15	-12.19	20.95	37.52
-12.37	21.75	38.60	-15.52	22.00	38.36
-15.49	21.98	37.23			

PC			UC		
Depth (mbgs)	Total %	Squeezed %	Depth (mbgs)	Total %	Squeezed %
-0.91	17.30	16.42	-0.94	13.89	1.73
-1.83	10.92	1.85	-1.80	13.88	6.13
-2.72	12.26	2.03	-2.77	12.47	2.86
-4.57	15.04	19.07	-3.68	14.37	18.85
-6.22	12.22	1.75	-5.61	19.70	30.17
-7.77	12.22	17.18	-6.22	20.25	32.24
-9.32	14.68	14.37	-7.75	17.22	14.24
-12.39	15.60	10.71	-9.32	20.82	35.71
-15.49	15.92	12.80	-12.39	19.24	31.06
			-15.49	21.75	29.44

Appendix IV(iii). Water Content
as weight percent of bulk wet weight

LGS1			LGS3		
Depth (mbgs)	Total %	Squeezed %	Depth (mbgs)	Total %	Squeezed %
-4.11	18.73		-4.05	21.29	25.89
-4.30			-4.19	20.20	43.82
-4.50			-4.34	19.42	25.03
-4.61	19.10	27.19	-4.50	19.76	
-4.72			-4.65	22.74	44.46
-4.81	19.65	29.36	-4.80	22.80	44.75
-4.92			-4.96	19.09	27.64
-5.08	19.75	28.99	-5.11	16.74	19.05
-5.13			-5.26	19.63	33.91
-5.24	20.39	29.74	-5.41	21.10	37.60
-5.33	19.51	27.43	-5.57	21.87	40.82
-5.44	20.15	28.24	-5.72	22.65	43.23
-5.55	20.19	29.33			
-5.64	18.85	33.31			
-5.76	14.22	24.85			
-5.84	11.12	8.44			
-5.94	13.39	13.33			
-6.02	12.41	11.79			

ESS		
Depth (mbgs)	Total %	Squeezed %
-1.22	19.23	28.19
-3.71	15.06	19.38
-4.70	9.93	18.93
-6.22	14.25	23.83
-7.77	13.73	16.35
-9.19	14.51	20.47
-12.52	15.67	21.48
-15.57	17.16	18.85