EXPERIMENTAL INVESTIGATION OF CATION EXCHANGE BETWEEN FORMATION WATERS AND SANDSTONES AND SHALES, PHALEN COLLIERY, CAPE BRETON

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ABSTRACT

The Phalen Colliery mines coal from the Phalen seam in the Upper Carboniferous Sydney Mines Formation. Flooding events in the colliery since 1992 warrant an investigation of the origin and chemical history of the inflow water. Formation waters, sourced from brines and with salinities up to five times seawater, drip into the mine from overlying roof rocks. Formation water chemistry shows a trend of increasing Na/Ca ratio with decreasing salinity which may result from Na-Ca cation exchange with pore-filling clays. This experiment was designed to test the exchange hypothesis.

Kaolinite, illite, and chlorite group clays fill or rim sample pore spaces. Clay fractions from six sandstone and three shale samples across the colliery were equilibrated with Na-Ca-Cl solutions (concentration = 4000 to 5400 mmol/L, $[Na]/\sqrt{[Ca]} = 70$ to 120, pH = 5.6) modelled after Phalen formation water chemistry. Solution cations exchanged with clay cations. A 0.25M $Ba(NO_3)_2$ solution extracted exchangeable Na and Ca from the clay and cation exchange capacity (CEC) was measured.

Measured CEC's range from 0.07 to 0.93 meq/100g (0.21 meq/100g mean). Direct relationships between sample clay percent and 1) cation exchange capacity, 2) exchangeable sodium, and 3) exchangeable calcium, are evidence of cation exchange. CEC depends more on pore clay-filling than sample porosity alone.

This experiment suggests that Na-Ca cation exchange between formation waters and in situ clays is a feasible mechanism to explain the formation water Na/Ca ratio trend. Formation water dilution causes an enrichment in Na upon exchange with clays. Literature CEC's are higher than CEC's reported here for the same clay species. CEC's from this study may be underestimated due to experimental constraints, or may have changed over time due to clay burial diagenesis.

Key Words: Phalen Colliery, clay, formation water, brine, sodium, calcium, cation exchange, cation exchange capacity, salinity

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TABLE OF ABBREVIATIONS

Br	Bromide
Ca	Calcium
CaX	Exchangeable calcium
CBDC	Cape Breton Development Corporation
CEC	Cation exchange capacity
Cl	Chloride
ESR	Exchangeable sodium ratio
ESP	Exchangeable sodium percentage
HCO_3^-	Bicarbonate
K	Potassium
Mg	Magnesium
Na	Sodium
NaX	Exchangeable sodium
NH_4OAc	Ammonium acetate
SAR	Sodium adsorption ratio
SO_4	Sulphate
Sr	Strontium
TDS	Total dissolved solids

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CHAPTER 1: INTRODUCTION

1.1 Objective and Thesis Statement

The objective of this study is to experimentally quantify cation exchange capacities of sandstones and shales in the Phalen Colliery, Cape Breton. Hypotheses tested include: Did cation exchange occur between formation waters and sediments in the Phalen Colliery, and to what extent? Were the original formation water chemical compositions modified by cation exchange, and are trends in formation water geochemistry the result of exchange? Which minerals hosts exchange sites, and to what extent does mineralogy affect the degree of cation exchange? Is cation exchange capacity influenced by sample porosity and pore clay-filling? Is the degree of cation exchange influenced by the concentration and composition of the formation waters? Does formation water chemistry vary spatially in the Phalen Colliery, and do the spatial trends correlate? Do trends in formation water chemistry correlate with exchange trends? How do experimental cation exchange capacities compare with values quoted in literature? Can a model for cation exchange in the Phalen Colliery be proposed?

Cation exchange is the replacement of one cation for another at the exchange sites of solid matter (Appelo and Postma, 1996). Cation exchange between rocks and fluids is invoked to explain variations in groundwater chemistry. Ion exchange processes are studied in fields of soil chemistry, water purification, retardation and removal of environmentally hazardous groundwater pollutants, treatment of nuclear waste, and the development of synthetic resins.

This study is part of the larger Carboniferous Hydrogeology Project, which is analyzing the geochemical and hydrogeological evolution of Phalen Colliery waters. The present experiment is significant because there are no previous studies of the role of cation exchange in water-rock reactions in the Phalen Colliery, nor in the Sydney Coalfield. The Carboniferous Hydrogeology Project will use cation exchange capacity values to better understand Phalen mine waters. Quantitative knowledge of water-rock reactions in the Phalen Colliery will aid in understanding water flow between the overlying flooded Lingan Colliery and the underlying Phalen Colliery.

1.2 Scope

The scope of this experiment is limited to six sandstone and three shale samples in the Phalen Colliery. The reliability of extrapolating results to other samples, rock types, or mines in the Sydney Coalfield is unknown. Sandstone and shale samples are from cores drilled in the Phalen Colliery, and are limited to borehole locations chosen by the Cape Breton Development Corporation.

The experimental variables in this study attempt to approximate reality. Rock powder is from actual mine samples. Na/Ca ratios in the experimental solutions mimic the end member ratios calculated for formation waters. However, the experimental solution chemistries are simpler than Phalen formation water chemistries. Sodium and calcium are the most common cations in the Phalen waters. Exchange of other cations and anions may occur, but this experiment is limited to the study of Na-Ca exchange dynamics. In this experiment, cation exchange takes place in a laboratory and not in nature. This distinction must be accounted for when interpreting results.

1.3 Phalen Colliery

The Phalen Colliery is operated by the Cape Breton Development Corporation (CBDC). CBDC has extracted coal from the Phalen coal seam since 1984, and the Phalen Colliery has operated under flooded workings since 1992. Roof control problems and water inflows up to 15 L/s have economical and safety impacts on mining operations (CBDC, 1994a). Such substantial water volumes warrant a geochemical investigation of the origin and history of the inflow water.

Formation waters exist in the pores of sandstones and shales before mining, and are not modified through mining activity. Phalen Colliery formation water is the focus of this study. Formation water samples were collected at braced roadways in the mine before mining in the area. At braced roadways, the overlying roof sandstone is intersected by boreholes or tunneling, and formation water drips from the borehole. Formation water samples were also collected as drips from the sandstone roof (Fig 1.1).

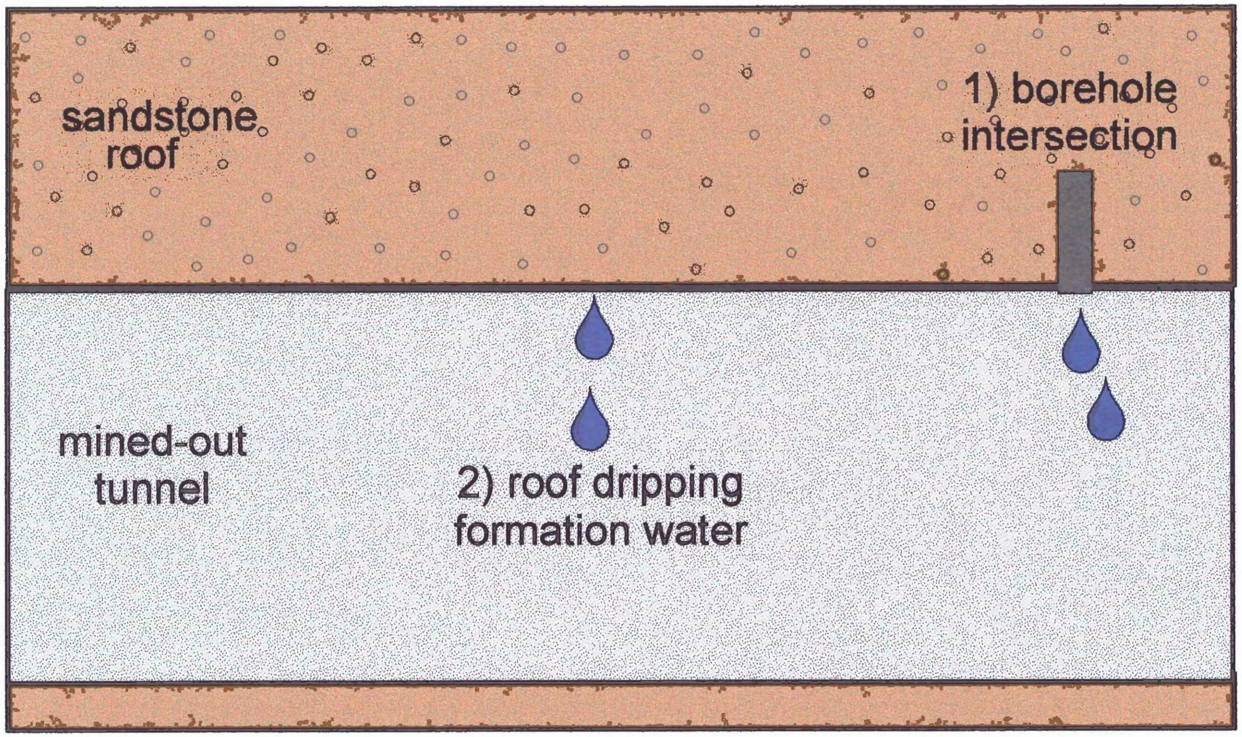

Fig. 1.1 Diagram showing Phalen formation waters dripping from boreholes and from the sandstone roof (after Kennedy, 1997). Phalen formation waters were sampled by CBDC and the Carboniferous Hydrogeology Project. Waters were collected where 1) boreholes or tunneling intersect the sandstone roof, or 2) the roof drips formation water.

1.4 Geology of Study Area

1.4.1 Sydney Basin and Sydney Coalfield

The Phalen Colliery is located in the central part of the Sydney Coalfield. The Sydney Coalfield is situated on the northeast coastline of Cape Breton Island, Nova Scotia (Fig. 1.2). The Coalfield is in the Carboniferous Sydney Basin, which extends 450 km eastward under the Atlantic Ocean (Gibling and Bird, 1994). The Sydney Basin comprises an onshore portion 520 km^2 in area and an offshore portion 36,000 km^2 in area (Hacquebard, 1983).

The Sydney Basin is fault-bounded, by the Mountain Fault to the northwest and by the Mira River-Bateson Fault to the southeast (Gibling et al., 1987). Strata dip toward the center of the basin from all directions, creating a bowl-shaped basin structure (Gibling and Bird, 1994). The coalfield is tectonically stable, with folds plunging gently below the Atlantic Ocean (Gibling and Bird, 1994).

1.4.2 Stratigraphy

The Phalen Colliery is located on the Phalen coal seam, near the base of the Sydney Mines Formation (CBDC, 1994a) (Fig. 1.3). The Sydney Mines Formation and the underlying South Bar Formation and Waddens Cove Formation comprise the Morien Group (Gibling and Bird, 1994). The Morien Group is approximately two km thick onshore, and is Upper Carboniferous, Westphalian to Stephanian, in age (Rust et al.,

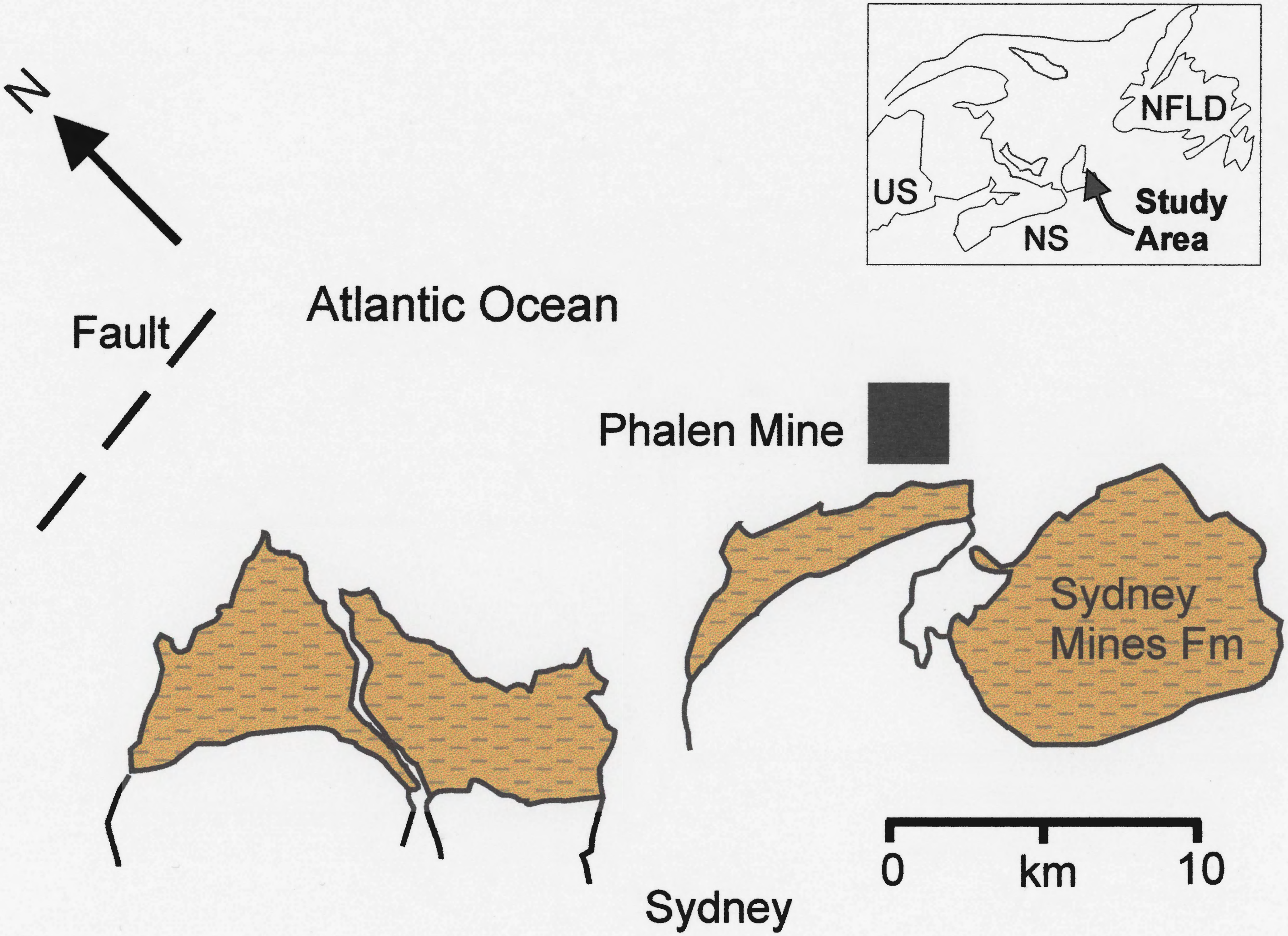

Fig. 1.2 Location map of the Phalen Colliery (after Gibling and Bird, 1994). The Colliery is located off the northeastern coastline of Cape Breton Island, Nova Scotia. Sandstones and shales belong to the Sydney Mines Formation.

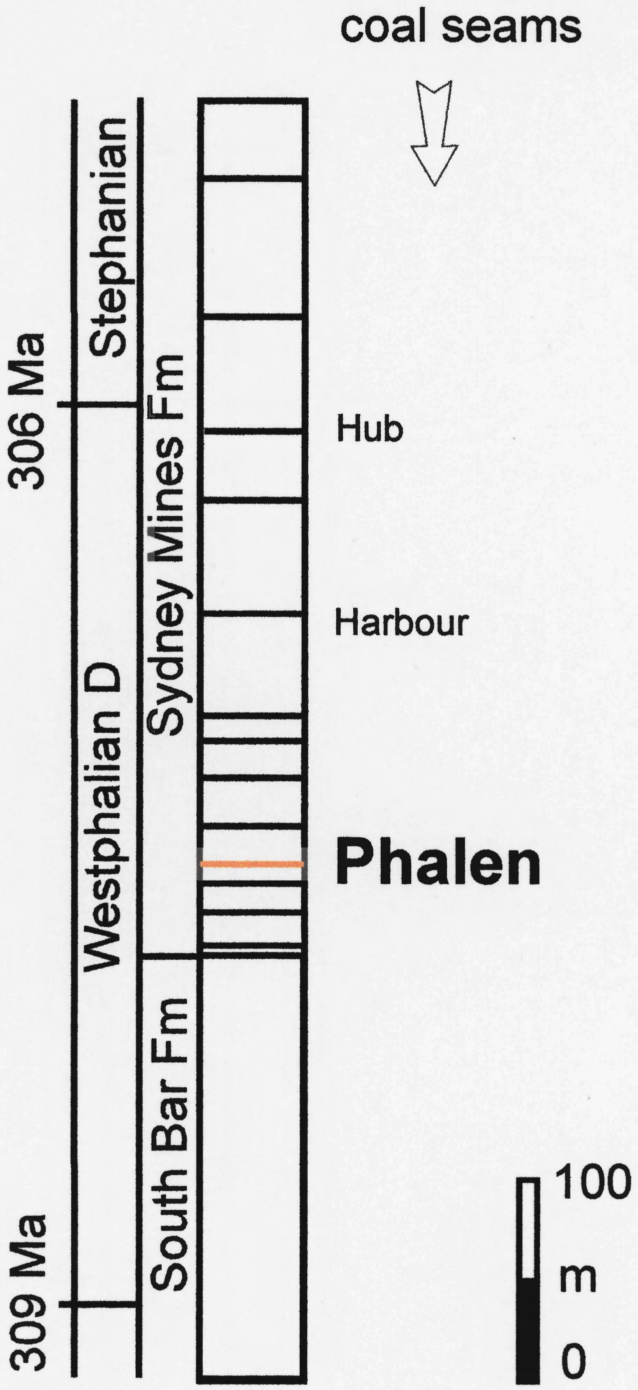

Fig. 1.3 Stratigraphic location of the Phalen coal seam, in the Sydney Mines Formation (after Gibling and Bird, 1994).

1987). A package of Lower Carboniferous rocks, including the Windsor Group, unconformably underlies the Morien Group (Fig. 1.4) (Boehner and Giles, 1986).

The Sydney Mines Formation is Westphalian D to Stephanian in age (~295 Ma) (Rust et al., 1987). Rock types in the Sydney Mines Formation include sandstone, mudstone, coal, and carbonaceous limestone and shale (Gibling and Bird, 1994). Channel sandstones are up to 15 m thick and laterally extensive (Rust et al. 1987). Sandstones are fine- to medium-grained, and well to poorly cemented. Rust et al. (1987) interpreted the Sydney Mines Formation as a predominantly fluvial deposit. Facies represented include fluvial channels and finer-grained bay-fill and floodplain deposits (Gibling and Bird, 1994).

Windsor Group marine evaporites, limestones, dolomites, and clastics are Visean (~340Ma) in age (Boehner, 1986). The Windsor Group is part of a Lower Carboniferous package of rocks upon which the Sydney Mines Formation rests with angular unconformity (Boehner and Giles, 1986). Other groups in the Carboniferous package, the Mabou and Horton Groups, are predominantly siliciclastic rock units that show evaporite occurrences and salt casts (Boehner, 1986).

1.4.3 Brine Origin of Formation Waters

Formation waters are waters in the pores of a deeply buried rock (Drever, 1988). Phalen Colliery sandstones contain formation waters believed to have been isolated from mixing with mine-generated fluids (Martel and Gibling, in prep.). The origin of the in situ formation waters can be determined geochemically.

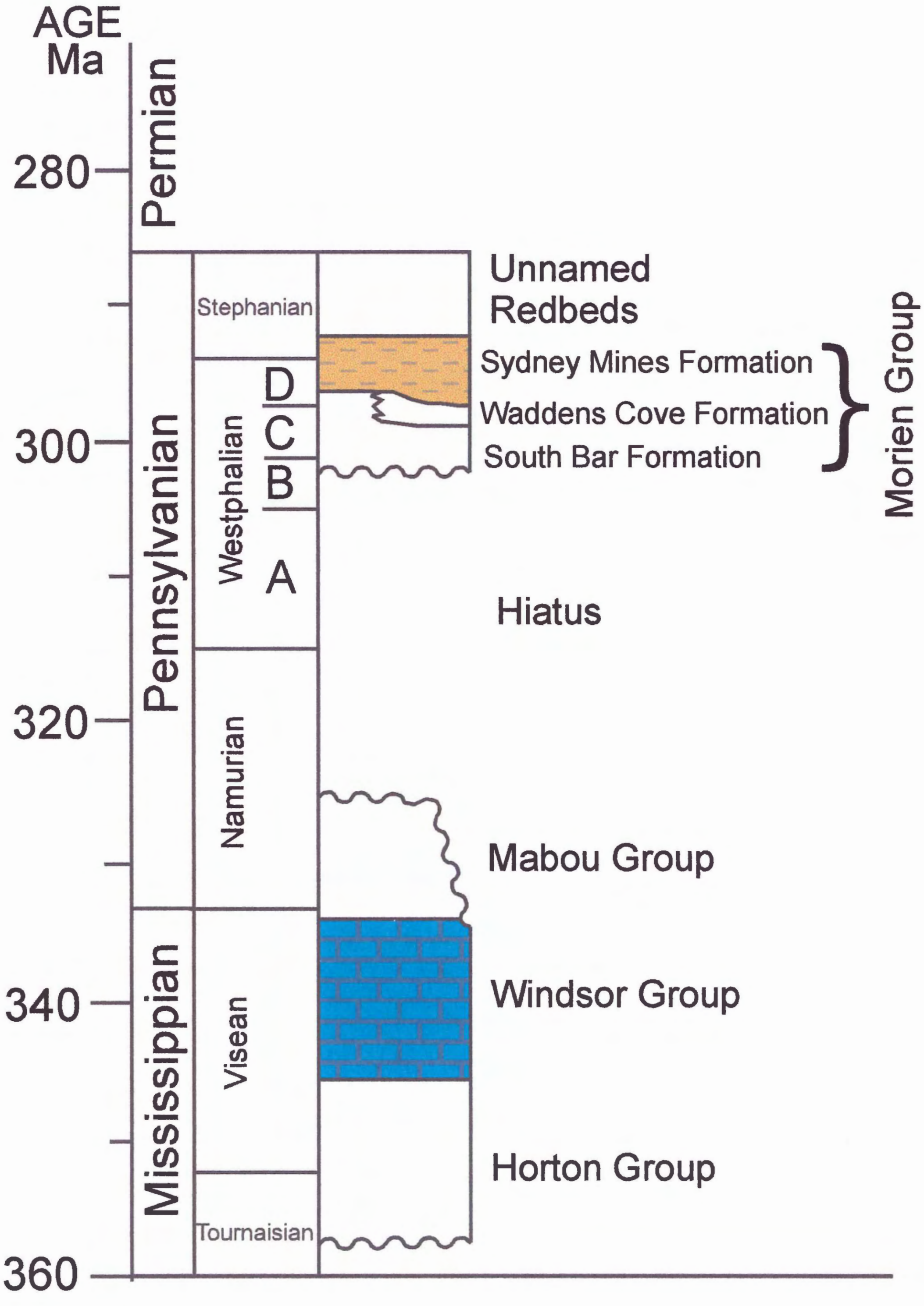

Fig. 1.4 Stratigraphic column showing the Carboniferous Morien and Windsor Groups (after Gibling et al., 1987).

The Windsor Group evaporites lie approximately two km below the Sydney Mines Formation (Rust et al., 1987). Martel and Gibling (in prep.) infer that Phalen formation waters are the evaporative residues remaining after Windsor Group salt precipitation in the Visean (~340 Ma). The waters have high bromide concentrations, and bromide is enriched relative to chloride. This chemistry suggests the waters are evaporative residues (Martel and Gibling, in prep.). The concentrations of total dissolved solids in Phalen formation waters are up to five times greater than the value for seawater. An evaporation factor of 30 - 32 times for Phalen waters is calculated based on the conservative Br/Cl ratio (Martel and Gibling, in prep.).

If the Windsor brines are implicated as the major source of Phalen formation waters, brines were emplaced after deposition of the Sydney Mines Formation. The brines probably moved upward in the Mid- to Late Carboniferous or later, along fault planes penetrating the Carboniferous section of the offshore Sydney Basin (Martel and Gibling, in prep.). During deep burial of the Windsor Group, or during Mesozoic basin inversion associated with mid-Atlantic rifting, compaction and diagenesis of clays would have expelled water (Martel and Gibling, in prep.). The fluids would have escaped along fault planes and pushed the heavy brines upward. Phalen formation waters are saline and have been stagnant and isolated from mixing since their emplacement (Martel and Gibling, in prep).

1.4.4 Modification of Brine Chemistry

There is strong evidence that Phalen formation waters originated from seawater evaporation. However, formation water chemistry differs from the chemistry of evaporated seawater. Martel and Gibling (in prep.) suggest that the brines were modified chemically by water-rock reactions.

Relative to the chemistry of evaporated seawater, Phalen formation waters are enriched in Ca, Sr, and Br, and depleted in Na, K, Mg and SO_4 (Martel and Gibling, in prep.). Calcite dissolution, and dolomite and gypsum precipitation, could have removed Mg and SO_4 from the water and added Ca and Sr (Martel and Gibling, in prep.). Minor calcite dissolution is documented in Phalen sandstones as the localized removal of cements, leaving unusually high pore spaces (Gibling, pers. comm.). Potassium could be depleted during aluminosilicate formation (Martel and Gibling, in prep.). Sodium could be depleted during albite and clay formation. Sodium loss in Phalen sandstones is documented in albite formation in potassium feldspar (Gibling, pers. comm.). Halite precipitation could enrich the seawater residue in bromide (Martel and Gibling, in prep.). Concentrations of Na and Ca in the brine waters may have been modified by cation exchange between waters and clays in sandstones and shales.

Whereas the above chemical reactions may have modified the chemical composition of the original brines, water chemistry trends (explained in further detail in Chapter 4) favour sodium-calcium cation exchange. This study focuses on clay reactions and examines sodium-calcium cation exchange as a means of modifying formation water chemistry.

1.5 Thesis Organization

This introduction has outlined the objectives and scope of the study, the geological history of the Sydney Coalfield, and the mining and water inflow history of the Phalen Colliery. Chapter 2 is a review of ion exchange processes, and defines many geochemical processes and terms described in this study. Chapter 3 describes the design and procedure of the cation exchange capacity experiment. It addresses previous work in experimental determinations of cation exchange capacity and compares several procedures. It also details the sample choice and preparation, modelled conditions, and calculations of this cation exchange capacity experiment. Geochemical, mineralogical, and mathematical results are presented in Chapter 4. Results are discussed, multiple working hypotheses are examined, and a model for cation exchange in the Phalen Colliery is presented in Chapter 5. Chapter 6 offers conclusions and recommendations for future work.

CHAPTER 2: ION EXCHANGE

2.1 Introduction

Cation exchange is examined as a possible water-rock chemical reaction of sandstones and shales with formation waters in the Phalen Colliery. This chapter introduces the phases, reaction equations, and effects of ion exchange. Ion exchange terms used hereafter in this thesis are defined.

2.2 Ion Exchange Definitions

2.2.1 Ion Exchange

Ion exchange is the replacement of one ion for another at the surface of solid matter (Appelo and Postma, 1996). Figure 2.1 illustrates the ion exchange process at the surface of a clay mineral. Simple ion exchange involves two exchanging ions (such as Na and Ca) and two exchanger phases (such as solution and clay). Upon exchange, the charged ions redistribute between the two phases without forming new types of chemical bonds and without distorting the solid lattice (Lehto and Harjula, 1996). Ion exchange is a stoichiometric process; the solution and clay phases maintain electroneutrality (Townsend, 1993). For exchange of cations of different valence, exchange occurs on an

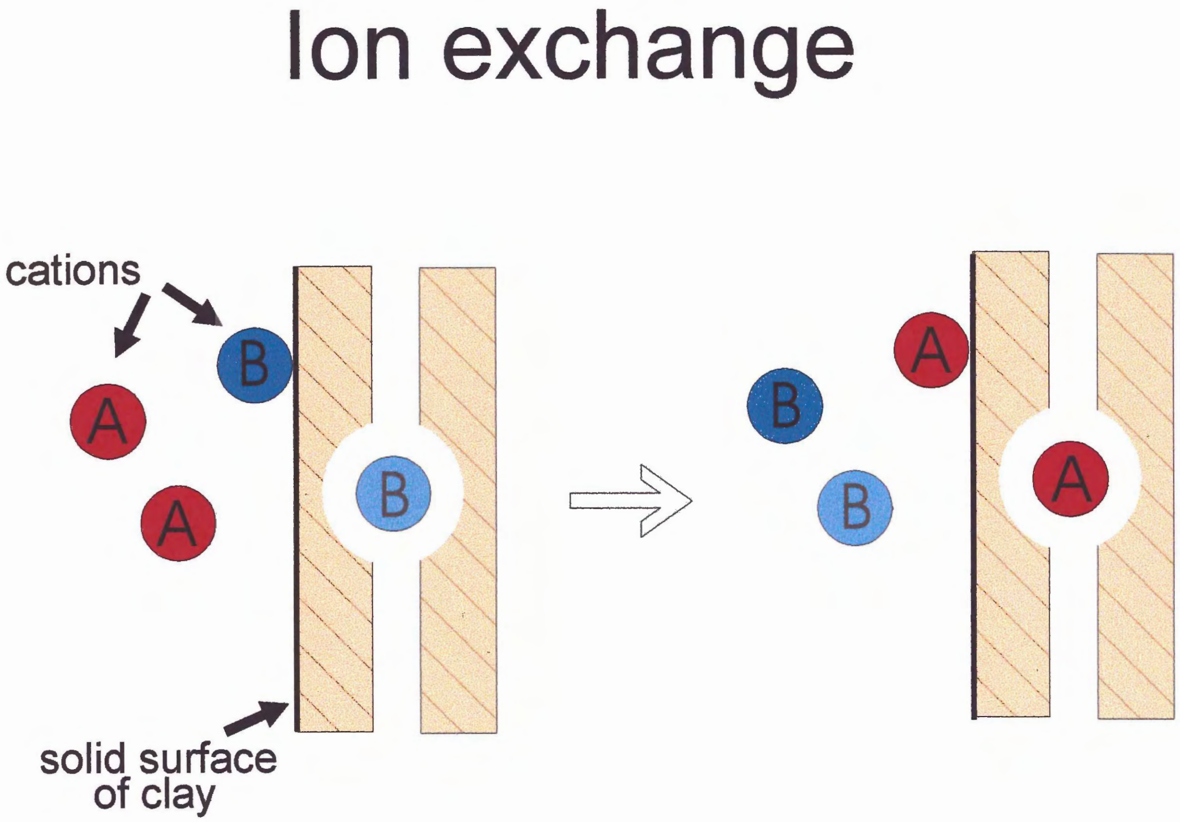

Fig. 2.1 Diagram showing ion exchange between a solution and clay phase (after Appelo and Postma, 1996). On the left, cation A is free in solution and cation B is adsorbed onto, and in the interlayer position of, the clay. Upon ion exchange, cation A is adsorbed onto, and in the interlayer position of, the clay. Cation B is displaced into solution. Cations A and B are referred to as exchangeable cations.

equivalent charge basis, which maintains electroneutrality during exchange (Townsend, 1993).

2.2.2 Ion Exchanger

An ion exchanger is defined by the International Union of Pure and Applied Chemistry as "a solid or liquid, inorganic or organic, containing ions, exchangeable with others of the same sign of charge present in a solution in which the exchanger is considered to be insoluble" (Harjula and Lehto, 1995). In this study, the two exchanger phases are clay and solution.

2.2.3 Ion Exchange Capacity

The ion exchange capacity of a material is the total amount of ions that can be adsorbed, or the milliequivalents of exchange sites per gram (Lehto and Harjula, 1996). The ion exchange capacity of a solid constrains the degree of exchange reaction (Appelo and Postma, 1996). Ion exchange capacity is partitioned into cation exchange capacity and anion exchange capacity. Cation exchange capacity, where solution cations exchange with cations in clay exchange sites, is the focus of this study.

2.3 Clay Minerals as Exchangers

2.3.1 Introduction to Clay Minerals

Clay minerals are fine-grained, crystalline, hydrous, phyllosilicates with layered lattice structures (Drever, 1988). Clay minerals are composed of tetrahedral and octahedral sheets of atoms, and interlayer cations and anions (Weaver, 1989). Clay minerals are characterized by different combinations and arrangements of sheets and ions. Clays have a very small particle size and a large surface area per volume (Drever, 1988). The surface area allows more ion adsorption, making clay minerals effective ion exchangers (Appelo and Postma, 1996). The structures of some clay minerals are described below and illustrated in Figure 2.2.

2.3.2 Kaolinite Group

The formula of kaolinite group clay minerals is $Al_2Si_2O_5(OH)_4$ (Weaver, 1989). The 1:1 kaolinite crystal lattice structure consists of an octahedral sheet and a tetrahedral sheet in each repeating layer (Weaver, 1989). O^{2-} and OH^- ions coordinate with Al^{3-} and Si^{4+}. The layers in the kaolinite structure bond by weak van der Waals forces (Drever, 1988). Dickite is a polymorph of kaolinite with a different vacant cation site (Weaver, 1989). Halloysite is a highly disordered form of kaolinite with mismatched octahedral and tetrahedral layers, resulting in a cylindrical structure (Weaver, 1989).

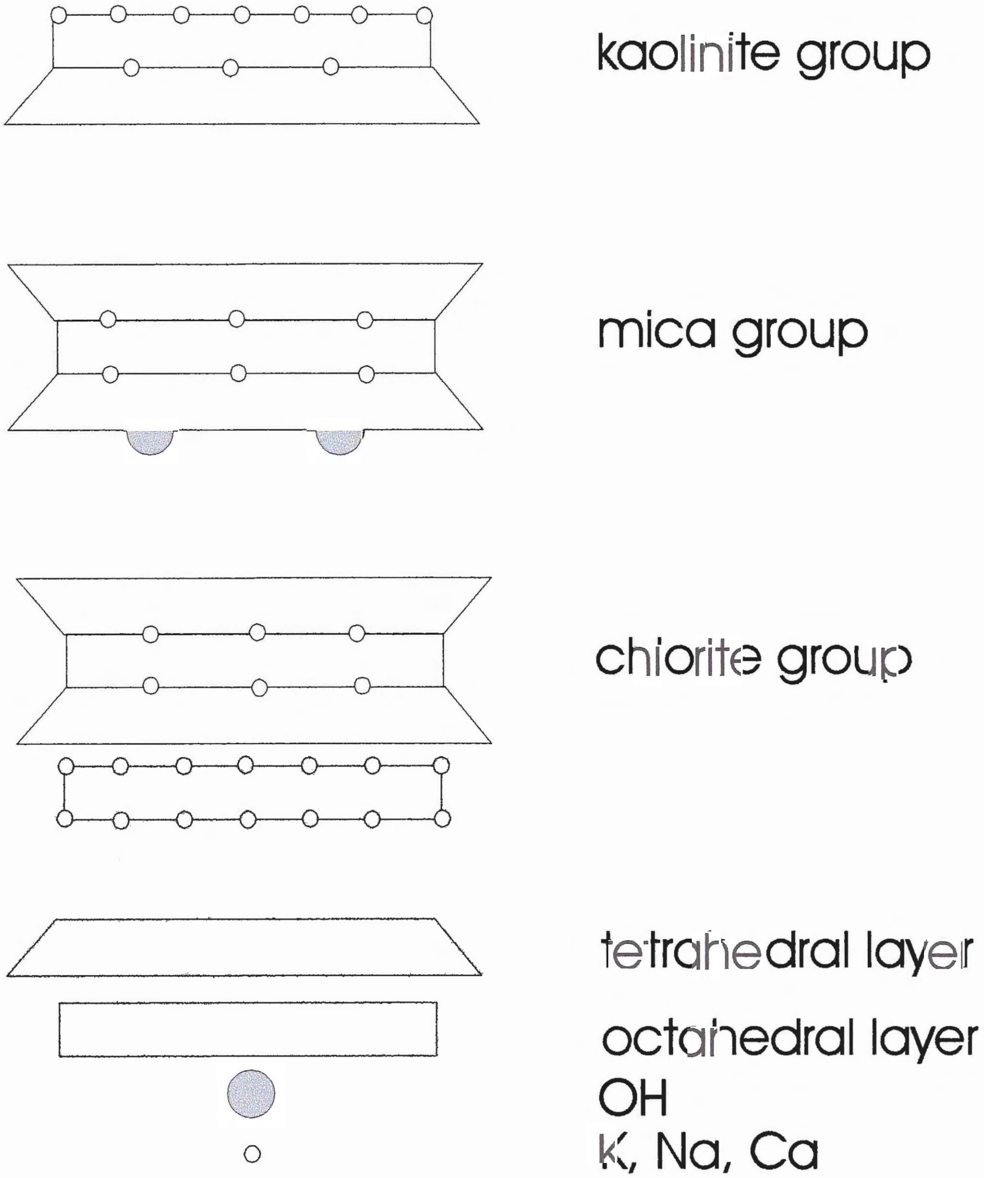

Fig. 2.2 Structure of kaolinite, mica (illite), and chlorite group clays (after Weaver, 1989). Stacking of sheets and positions of interlayer cations are shown.

2.3.3 Mica Group

Muscovite ($KAl_2(AlSi_3O_{10})OH_2$), biotite ($K_2(Mg, Fe)_3AlSi_3O_{10}(OH, O, F)_2$), lepidolite ($K(Li, Al)_3(Si, Al)_4O_{10}(F, OH)_2$), phlogopite ($K_2Mg_3AlSi_3O_{10}(OH,F)_2$), and illite ($K_2(Si_8Al_2)Al_4O_{20}(OH)_4$) are mica group minerals (Weaver, 1989). Mica group minerals have a 2:1 crystal lattice structure. In the three-sheet structure, the middle octahedral sheet is surrounded by two tetrahedral sheets (Weaver, 1989). Potassium occupies the interlayer position, neutralizing the charge and bonding the layers (Weaver, 1989). The illite structure has less interlayer K^+, less Al^{3+}, and more Si^{4+} than muscovite, and may have Fe^{2+} and Mg^{2+} (Drever, 1988).

2.3.4 Chlorite Group

The chemical formula of chlorite is $(Mg, Fe, Al)_6(Si, Al)_4O_{10}(OH)_8$ (Drever, 1988). Chlorite has a 2:1 crystal lattice structure, with a tetrahedral-octahedral-tetrahedral sheet arrangement (Weaver, 1989). Mg^{2+}, Fe^{2+}, and OH^- occupy the interlayer space in the crystal lattice (Weaver, 1989). Layers in the chlorite structure bond by electrostatic and hydrogen bonding (Weaver, 1989).

2.3.5 Smectite and Mixed Layer Clays

The general chemical formula of smectite is $Al_{1.67}Mg_{0.33}Si_4O_{10}(OH)_2$ (Weaver, 1989) Smectite occurs in a mixed-layer illite/smectite form where layers of illite and smectite are regularly or randomly interstratified (Weaver, 1989). Smectite has a 2:1

crystal lattice structure, and is composed of expandable layers (Weaver, 1989). Interlayer positions host the exchangeable cations (Weaver, 1989).

2.3.6 Surface Chemistry of Clays

Adsorption is the process by which charged ions are attached to the oppositely charged surface of a clay mineral (Appelo and Postma, 1996). Ions may be removed from, or exchanged at, the clay surface (Appelo and Postma, 1996). On an atomic scale, the clay surface is not smooth, but is heterogeneous. Adsorption of ions onto the irregular solid surface occurs rapidly and requires little energy (Laidler and Meiser, 1995). Positively charged ions from the solution are attracted to the negatively charged solid. The ions form a fixed layer, called the Stern layer, at the surface of the solid (Laidler and Meiser, 1995; Drever, 1988). Oppositely charged mobile ions form a diffuse layer, called the Guoy layer, in the solution (Drever, 1988). Figure 2.3 shows the Stern and Guoy layers. The ion exchange properties of clays vary with the layer in which exchange takes place. Cations in the diffuse Guoy layer exchange more rapidly, and with less required energy, than cations in the fixed Stern layer (Drever, 1988).

2.3.7 Cation Exchange Capacities of Various Clays

Table 2.1 lists the cation exchange capacities, measured in meq/100g, of some clay minerals. Smectites have a high number of expandable layers, and a high cation exchange capacity (Hower and Mowatt, 1966). As the amount of expandable layers

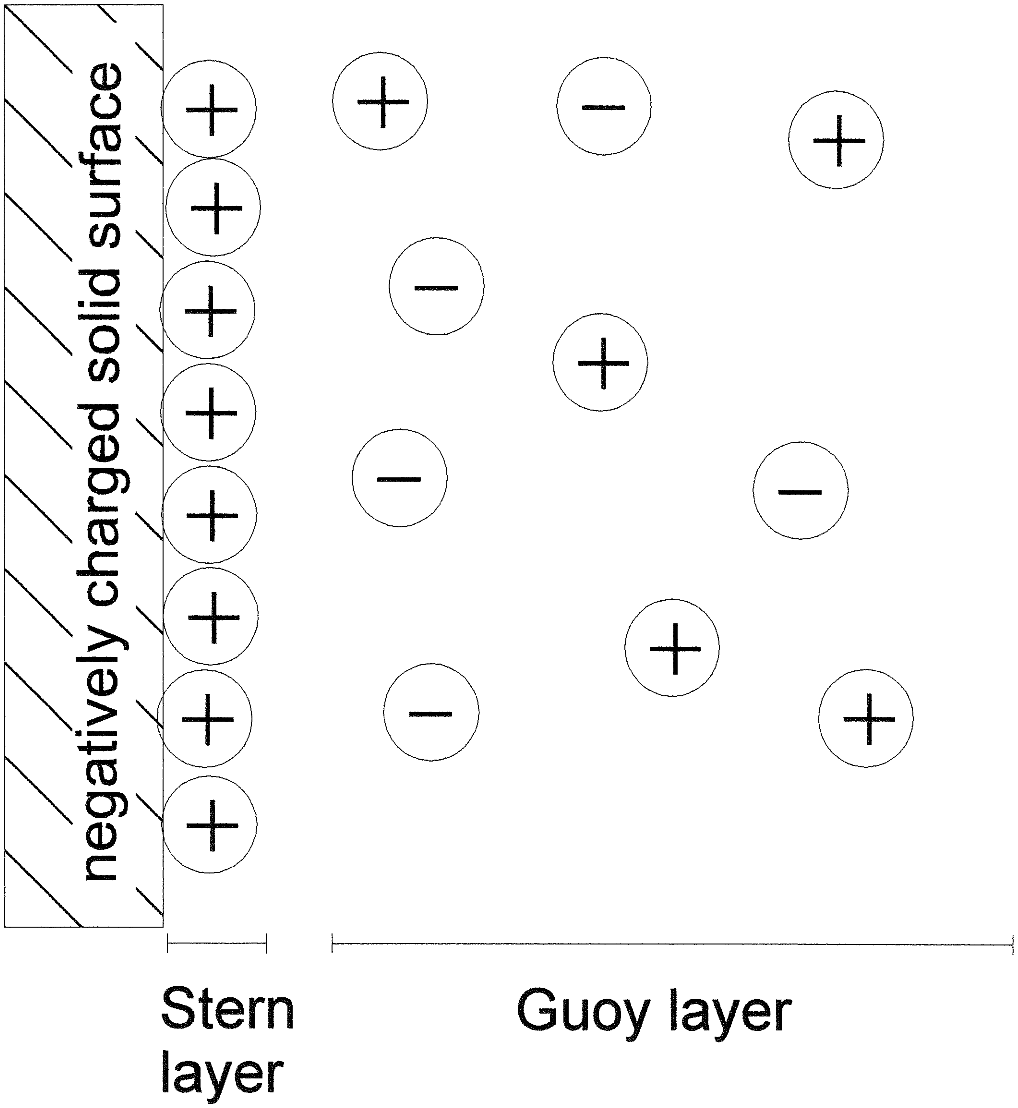

Fig. 2.3 Diagram showing the fixed Stern and diffuse Guoy layers (after Drever, 1988). Cation exchange in the Guoy layer requires less energy than cation exchange in the Stern layer.

Clay Mineral	Cation exchange capacity (meq/100g)
smectite	60-130
illite	10 - 40
kaolinite	3-15
chlorite	<10

Table 2.1 Cation exchange capacities of clay minerals. Values are from Drever (1988) and Appelo and Postma (1996), and are calculated for soil and sediment constituents.

decreases from smectite to illite, the cation exchange capacity decreases (Hower and Mowatt, 1966). Kaolinite and chlorite group clays have low cation exchange capacities (Drever, 1988).

2.4 General Exchange Reactions

2.4.1 Heterovalent Exchange Reactions

Ion exchange takes place between homovalent ions, such as Na^+ and K^+, or between heterovalent ions, such as Na^+ and Ca^{2+}. This study examines the heterovalent exchange between monovalent sodium and divalent calcium. Continental, fresh water, environment clays contain predominantly calcium in the exchange sites (Appelo and Postma, 1996). Sodium and chloride are the major ions in saline Na-Cl brines (Drever, 1988). When a Na-Cl brine reacts with a continental clay, Na^+ in the brine substitutes for exchangeable Ca^{2+} in the clay. The clay exchange site takes up Na^+ and releases Ca^{2+} into the water (Appelo and Postma, 1996). The mass balance equation is:

$$Na^+ + Ca_{0.5}X \rightarrow NaX + \tfrac{1}{2}\, Ca^{2+} \qquad (2.1)$$

where NaX and CaX are exchangeable sodium and exchangeable calcium (Dzombak and Hudson, 1995).

The heterovalent exchange reaction has an equilibrium constant that is the selectivity coefficient for sodium-calcium exchange (Amrhein and Suarez, 1991):

$$K_{Na\text{-}Ca} = \frac{[NaX]\,[Ca^{2+}]^{0.5}}{[Ca_{0.5}X]\,[Na^+]} \qquad (2.2)$$

2.4.2 Exchange Values

The exchangeable sodium ratio (ESR), or exchangeable sodium percentage (ESP), calculates the ratio of adsorbed sodium and calcium ions in the clay. The ESR is the ratio of exchangeable sodium (NaX) to exchangeable calcium (CaX), and is defined by Amrhein and Suarez (1990) as

$$\mathrm{ESR} = \mathrm{NaX} / \mathrm{CaX} \tag{2.3}$$

or $$\mathrm{ESP} = (\mathrm{NaX} / \mathrm{CaX}) \times 100\%. \tag{2.4}$$

The sodium adsorption ratio (SAR) quantifies the tendency of sodium to be adsorbed at exchange sites instead of other cations (Amrhein and Suarez, 1991). The sodium adsorption ratio is the relationship of sodium to calcium and magnesium concentrations in the solution phase, defined by Amrhein and Suarez (1991) as:

$$\mathrm{Na}^+ / (\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})^{0.5}. \tag{2.5}$$

For studies of simple Na-Ca exchange, where Mg is not considered, the sodium adsorption ratio is defined as:

$$\mathrm{Na}^+ / (\mathrm{Ca}^{2+})^{0.5}. \tag{2.6}$$

Cation exchange capacity (CEC) is defined by Amrhein and Suarez (1990) as the sum of exchangeable sodium (NaX) and exchangeable calcium (CaX) such that

$$\mathrm{CEC} = \mathrm{NaX} + \mathrm{CaX}. \tag{2.7}$$

Cation exchange capacity is measured in meq/100g of solid clay.

2.4.3 Selectivity in Concentrated vs. Dilute Solutions

Divalent cations are preferred over monovalent cations in clay exchange sites (Appelo and Postma, 1996). In the heterovalent exchange of sodium and calcium between a clay and solution, the clay prefers Ca^{2+}. Dilution of that solution causes more Ca^{2+} adsorption onto the clay, and less Ca^{2+} released into solution (Appelo and Postma, 1996).

An enrichment in clay calcium with dilution is the result of the valence difference between sodium and calcium in Equation 2.2 (Sayles and Mangelsdorf, 1977; Appelo and Postma, 1996). The sodium ion is monovalent, calcium is divalent. In Equation 2.2, K is an equilibrium constant which is, by definition as a constant, the same for all degrees of dilution (Drever, 1988). The numerator in Equation 2.2 is the amount of exchangeable sodium (NaX) in the clay and the concentration of calcium in the solution ([Ca]). The denominator in Equation 2.2 is the amount of exchangeable calcium in the clay (CaX) and the concentration of sodium in the solution ([Na]). Upon dilution of the solution, [Ca] and [Na] both decrease as the concentration of the water decreases. The [Na] term is squared to account for the difference in valence between Na^{+} and Ca^{2+}. Because the [Na] term is squared, its value decreases more than [Ca] decreases upon dilution of the water. The value of the equilibrium constant must be maintained. An adjustment of NaX and CaX is necessary, as [Na] and [Ca] decrease, to keep K constant. CaX increases to account for the fact that [Na] has decreased more than [Ca]. NaX decreases, and K remains constant. As CaX increases, more exchangeable calcium is taken up into the clay exchange sites.

Thus, upon dilution, cations of higher charge are selectively taken up into the clay over cations of lower charge (Sayles and Mangelsdorf, 1977). The higher valence cation, Ca^{2+}, displaces the lower valence cation, Na^{+}, to a greater degree with increasing dilution of a solution (Drever, 1988). In sodium-calcium exchange, dilution causes an enrichment of sodium in the solution, and an enrichment of calcium in the clay. As described in Chapter 4, Phalen formation waters vary in the degree of dilution spatially throughout the Colliery. The effects of dilution on sodium-calcium cation exchange between Phalen formation waters and sandstones and shales must be examined.

2.4.4 Piper Plots

Piper plots are used in this study to plot the cation and anion chemistries of different waters. A general Piper plot is illustrated and explained in Figure 2.4. When cation exchange is the major chemical reaction, the water chemical analyses plot in a straight line parallel to the side of the diamond (Appelo and Postma, 1996). In cation exchange reactions, the relative proportions of cations change with increasing exchange. However, the relative proportions of anions are unaffected. If anion chemistry changed, the trend on the Piper plot would be diagonal, and not parallel to the side of the diamond.

When saline Na-Cl brines exchange with continental Ca-rich clays, the brines become enriched in Ca^{2+} displaced from the exchange sites of the clay (Appelo and Willemsen, 1987). The exchange trend on the Piper plot is from high sodium to high calcium. Upon dilution, the water becomes enriched in Na^{+} and the exchange trend on the Piper plot is from high calcium to high sodium (Appelo and Postma, 1996).

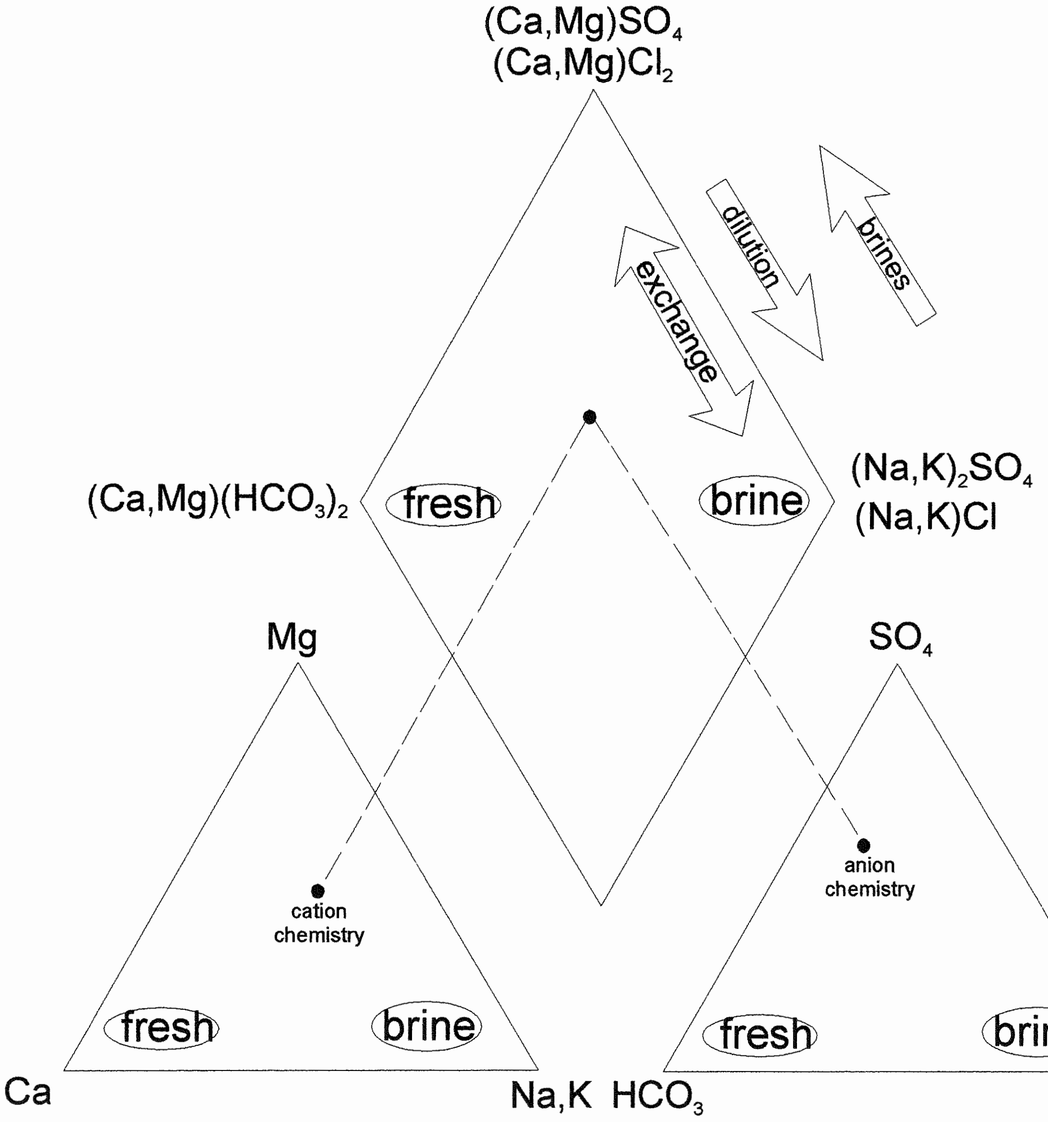

Fig. 2.4 Diagram showing the method of plotting analyses on a Piper plot (after Appelo and Postma, 1996). A Piper plot is a chemical diagram on which cation and anion percentages plot on two separate lower triangles. On a diamond central field, the points on the two lower triangles are combined into one representative data point. A cation exchange trend is a line parallel to the edge of the diamond field. Upon reaction of Na-Cl brines with Ca-rich clays, waters enrich in calcium and the exchange trend is toward high Ca. Upon dilution, the exchange trend is toward high Ca.

CHAPTER 3: METHODS

3.1 Background

3.1.1 Significance of Experiment

A cation exchange capacity (CEC) experiment with Phalen Colliery rocks and waters is significant as there have been no previous studies of cation exchange in water-rock reactions in the Sydney Coalfield. Quantitative cation exchange values will aid in understanding formation water history and in modelling the chemical reactions associated with water movement between the Lingan and Phalen Collieries.

3.1.2 Previous CEC Experiments

3.1.2.1 Experimental solutions

Cation exchange capacity experiments involve two steps and employ two types of solutions: equilibrating solutions and extracting solutions. Equilibrating solutions invoke cation exchange with the clay. The equilibrating solution equilibrates with the clay through repeated shaking and centrifuging (Amrhein and Suarez, 1990). During equilibration, exchangeable solution cations exchange with exchangeable clay cations. After equilibration, the extracting solution removes from the clay any cations that have been exchanged. The extracting solution reacts with the clay, and exchangeable cations in the extracting solution exchange with exchangeable cations in the clay (Amrhein and

Suarez, 1990). The exchangeable cations gained by the extracting solution reflect the cation exchange capacity of a clay (Amrhein and Suarez, 1990).

3.1.2.2 Previous experimental work

Cation exchange capacity experiments have existed since the 1930's (eg. Mehlich, 1938). Traditional procedures involve saturating a soil or rock exchanger with a cation-containing solution. The solution is eliminated by washing, and cations in the exchanger are measured (Polemio and Rhoades, 1977). Different procedures employ different exchangers, and different equilibrating, extracting, and washing solutions. CEC is non-conservative, and different methods yield different results (Polemio and Rhoades, 1977).

Older CEC experimental procedures have certain disadvantages. Equilibrating solutions may be removed with an alcohol and water wash before applying the extracting solution. Washing removes soluble ions and fine clay particles, and introduces foreign ions into the experiment (Polemio and Rhoades, 1977). Methods using radioactive tracers to measure CEC require extensive precautions and equipment to handle radioisotopes (Amrhein and Suarez, 1991; Wild and Keay, 1964).

Older procedures employ NH_4OAc as an extracting solution. However, calcite and gypsum are extremely soluble in NH_4OAc, and resulting calculated exchangeable calcium values are inaccurate (Amrhein and Suarez, 1990). In calcareous soils, calcite dissolution affects the equilibrating and extracting solution compositions. Cations from the mineral dissolution occupy exchange sites, preventing saturation of the sites with sodium (Amrhein and Suarez, 1991). As a result, cation exchange capacity is underestimated (Polemio and Rhoades, 1977). The reader is referred to Thomas (1982) and Rhoades (1982) for a comprehensive analysis of errors associated with older cation exchange capacity experiments. The method used in this experiment is described in Section 3.3.

3.2 Samples

3.2.1 Sample Location

Sample locations in this study were limited to previously drilled Phalen boreholes where porosity, permeability, and Na/Na+Ca data were available. Figure 3.1 shows the location of samples. This study employed nine samples: six sandstone and three shale samples. Sandstone samples are PH 50-3, PH 53-5, PH 59-1, PH 102-6, PH 104-5, and PH 105-6. Shale samples are PH 53-12, PH 100-11, and PH 251-14.

3.2.2 Sample Preparation

The sandstone and shale samples were crushed into powder in the rock crushing room at Dalhousie University. Whole rock portions from each sample were stored in capped Nalgene bottles. Some whole rock powder from each sample was sieved through a 250-micrometer hand sieve to enrich the clay-sized portion. The portion less than, and the portion greater than, 250 micrometers were stored in capped Nalgene bottles.

3.2.3 Sample Identification

Eighteen samples were prepared for X-ray diffraction study: nine whole rock samples and nine clay-enriched samples. Powdered samples were hand ground with

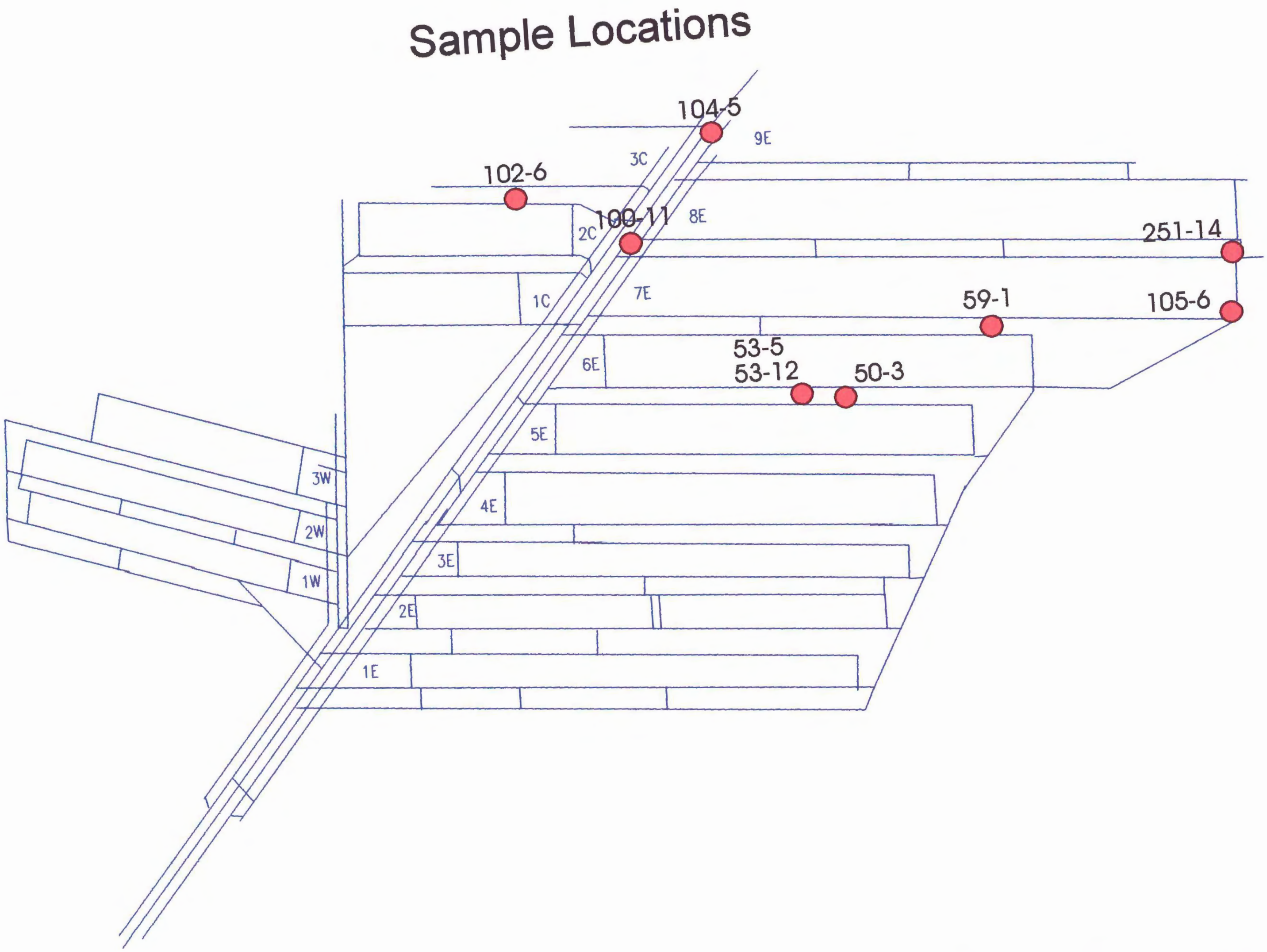

Fig. 3.1 Map of approximate locations of sampled boreholes in the Phalen Colliery. Blue labels indicate mine panels.

acetone and applied to frosted glass slides. Each sample ran for one hour and five minutes in the X-ray diffractor, using a copper tube anode (Cu Kα X-rays) on a continuous scan from four to 82°. Minerals were identified using the automatic phase identification in the PC-APD diffraction software program. Traces were checked visually to confirm the identification of all significant peaks, and unreasonable phases were eliminated. Sample mineralogy is described in Chapter 4, and mineral peak graphs are shown in Appendix A.

Although X-ray diffraction analysis yielded the sample clay mineralogy, it was also necessary to understand the relationships of the clay minerals with other mineral grains and with the porosity. Thin sections of the six sandstone samples were examined under the petrographic microscope to estimate porosity, to identify the location of clay minerals, and to analyze the relationships between porosity and pore-filling clays. Results of petrographic analysis are presented in Chapter 4.

3.3 Experimental Procedure

3.3.1 Experimental Design

This CEC experimental method is based on the procedure of Amrhein and Suarez (1990), and modified to suit this study. The Amrhein and Suarez (1990) procedure is advantageous because it can be modified to suit a desired experiment. Cation exchange capacity can be measured for any solution composition, concentration, and pH. The Amrhein and Suarez (1990) procedure employs small sample sizes; exchangeable sodium, exchangeable calcium, and cation exchange capacity are measured simultaneously from one gram of clay. In older methods, a fresh clay sample is needed for each calculation.

The Amrhein and Suarez method makes the following assumptions about elements in the extracting solution. Calcium is from the clay exchanger or from mineral dissolution. Sodium is distributed in exchanger and solution phases. Chloride is the only anion in the equilibrating solution. Bicarbonate is from solution and dissolved mineral phases.

3.3.2 Preparation of Experimental Solutions

The equilibrating solution concentrations in the Amrhein and Suarez (1990) procedure range from 25 to 1000 mmol/L, the sodium adsorption ratios (SAR's) range from five to 50. This approach employed solutions of higher concentration and SAR than suggested in literature, in order to represent Phalen formation waters. Phalen formation water concentrations range from 4000 to 5400 mmol/L, and SAR's range from 70 to 120.

The extracting solution in the Amrhein and Suarez (1990) procedure is 0.25 M $Mg(NO_3)_2$. Since Phalen waters contain significant concentrations of magnesium, $Mg(NO_3)_2$ was not an appropriate extracting solution. This study employed 0.25 M $Ba(NO_3)_2$ as the extracting solution, based on the low barium concentrations in formation waters and on the use of barium in other literature procedures (e.g. Hendershot and Duquette, 1986). Since higher valence cations are preferred in clay exchange sites, Ba^{2+}

will replace any exchangeable Na^+ in the clay and extract it for measurement (Appelo and Postma, 1996). Between homovalent cations, the ion with the larger ionic radius is preferred in the clay exchange sites (Appelo and Postma, 1996). Ba^{2+} will replace any Ca^{2+} in the clay and extract it for measurement. Thus Ba^{2+} is an appropriate cation to extract both Na^+ and Ca^{2+} ions from clay.

Experimental equilibrating solutions were modelled after Phalen formation waters. Phalen formation waters were collected by CBDC and analyzed at the Environmental Services Laboratory at the University College of Cape Breton. Formation water chemistry is discussed in Chapter 4. Four different equilibrating solutions were made according to the chemistry listed in Table 3.1. The four solutions encompass the range in total electrolyte concentration and sodium adsorption ratio of Phalen formation waters (Fig. 3.2). The solutions are pH 5.6, the average pH of formation waters. The formation water sodium adsorption ratios (SAR) range from 70 to 120. The SAR is a measure of the amount of Na relative to Ca in the formation water. Phalen formation waters are saline; the Na concentration exceeds the Ca concentration in all waters. Total electrolyte concentration in Phalen waters ranges from 4000 to 5400 mmol/L. Total concentration is divided evenly between cations and anions. The concentrations of Na and Ca in each equilibrating solution were calculated from the SAR and the total concentration, as in Amrhein and Suarez (1990).

Tables 3.2 and 3.3 list the chemicals used in the preparation of the equilibrating and extrcting solutions. The experiment required approximately two litres of equilibrating solution. For ease of mixing, the solutions were prepared in one litre increments. NaCl and $CaCl_2$ were mixed in distilled water in masses listed in Table 3.2.

Solution	SAR	Concentration (mmol/L)
1	70	4000
2	70	5400
3	120	4000
4	120	5400

Table 3.1 Concentrations and sodium adsorption ratios of the four experimental equilibrating solutions.

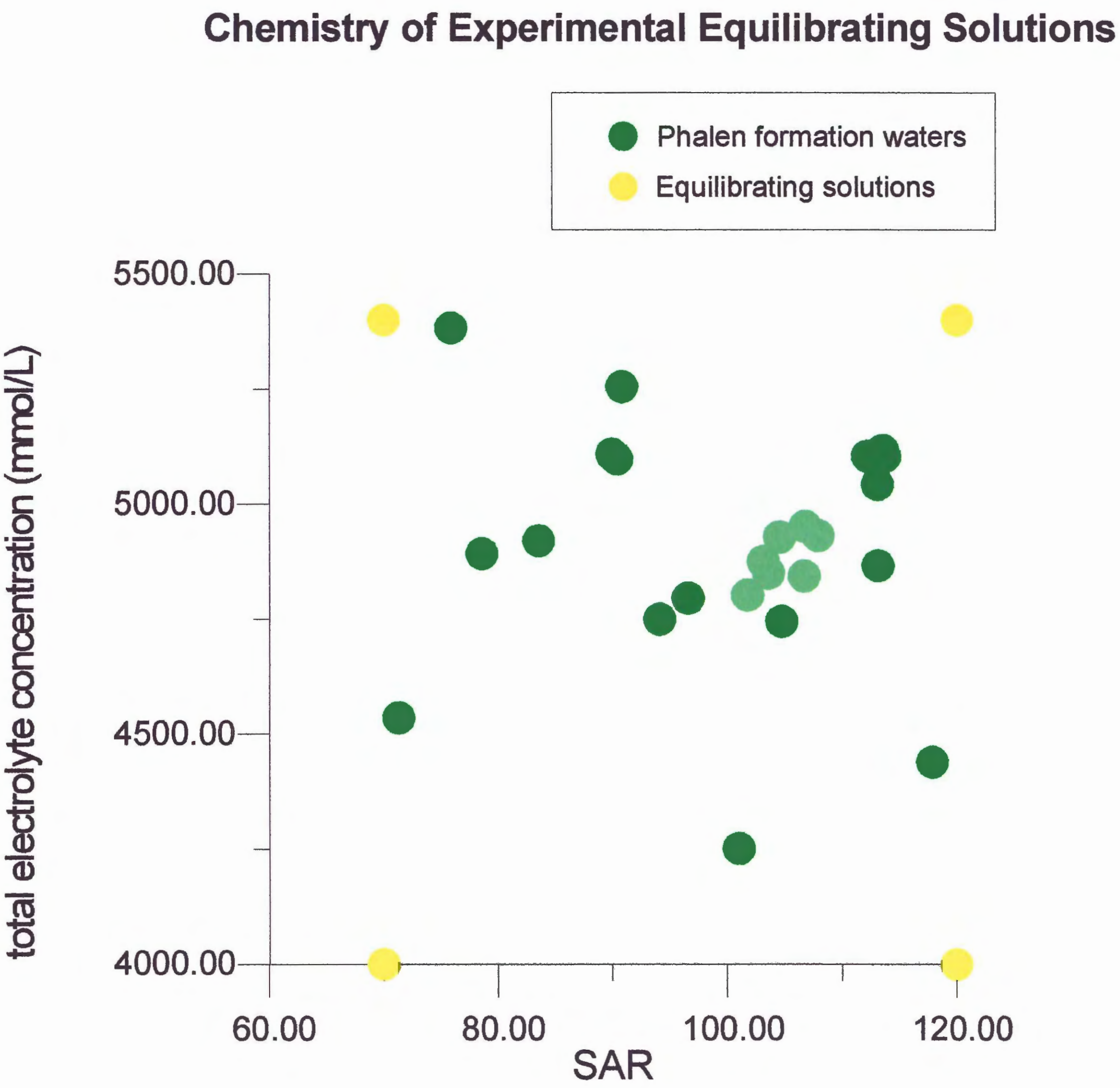

Fig. 3.2 Graph showing the chemistry of Phalen formation waters and the four experimental equilibrating solutions. The equilibrating solutions encompass the range of total electrolyte concentration and sodium adsorption ratios of Phalen waters, and are meant to be representative.

Solution	Volume (L)	Mass NaCl (g)	Mass $CaCl_2$ (g)
1	1.0	89.11	35.89
1	1.0	89.18	35.94
2	1.0	113.16	57.79
2	1.0	113.14	57.80
3	1.0	104.03	16.63
3	1.0	104.02	16.63
4	1.0	130.76	28.35
4	1.0	130.63	28.30

Table 3.2 Masses of NaCl and $CaCl_2$ dissolved in 1 L increments of distilled water to make 2 L of each of the four equilibrating solutions.

Volume of extracting solution (L)	**Mass of $Ba(NO_3)_2$ (g)**
1.0	65.35
1.0	65.36
1.0	65.36
1.0	65.34
1.0	65.34

Table 3.3 Mass of barium nitrate dissolved in each 1 L increments to make 5 L of extracting solution.

The equilibrating solutions were stored in capped Nalgene bottles. The experiment required approximately five litres of $Ba(NO_3)_2$ extracting solution. For ease of mixing, the solution was prepared in one litre increments. The masses of barium nitrate dissolved in distilled water are listed in Table 3.3. The extracting solution was stored in capped Nalgene bottles.

3.3.3 Procedure

Masses of NaCl and $CaCl_2$ for the equilibrating solutions were measured on an electronic balance. The chemicals were dissolved in distilled water by manual mixing and magnetic stirring. Solution pH was brought to 5.6 by dropwise addition of HCl and NaOH. The solutions were stored in capped Nalgene bottles.

Approximately one gram of clay from each sample was reacted with each of the four equilibrating solutions. The masses of clay were measured on an electronic balance, and the clay was poured into tared 50 ml centrifuge tubes. The mass of clay from each sample is listed in Table 3.4.

Each equilibrating solution was measured into 30 ml aliquots and poured into the centrifuge tubes containing the clay samples. The solution and clay were equilibrated by shaking in a New Brunswick Scientific G-53 shaker for one hour at 220 rpm. After shaking, the test tubes were centrifuged four at a time for two minutes at 2500 rpm. The decantate was poured off and discarded. The equilibration steps were repeated three additional times to allow adequate exchange. After the fourth centrifugation, the final decantates for each sample were saved in Nalgene bottles.

Sample	Mass of Clay (g)	Sample	Mass of Clay (g)
PH50-3-1	1.00	PH104-5-3	1.02
PH50-3-2	1.01	PH104-5-4	1.00
PH50-3-3	1.01	PH105-6-1	1.01
PH50-3-4	1.00	PH105-6-2	1.00
PH53-5-1	1.01	PH105-6-3	1.01
PH53-5-2	0.99	PH105-6-4	1.01
PH53-5-3	1.01	PH53-12-1	1.00
PH53-5-4	1.01	PH53-12-2	1.00
PH59-1-1	1.01	PH53-12-3	1.00
PH59-1-2	1.01	PH53-12-4	1.01
PH59-1-3	1.01	PH100-11-1	1.00
PH59-1-4	1.00	PH100-11-2	1.00
PH102-6-1	1.00	PH100-11-3	1.01
PH102-6-2	1.02	PH100-11-4	1.02
PH102-6-3	1.01	PH251-14-1	1.02
PH102-6-4	1.02	PH251-14-2	1.01
PH104-5-1	1.02	PH251-14-3	1.00
PH104-5-2	1.00	PH251-14-4	1.00

Table 3.4 Each equilibrating solution was reacted with one gram of clay from each rock sample. The exact mass of clay reacted with each solution is listed. The table also shows the sample numbering scheme used hereafter in this thesis. For example, sample PH 50-3-1 is the clay-sized portion from borehole 50-3, reacted with equilibrating solution 1.

After equilibration, the clay samples were treated with the $Ba(NO_3)_2$ extracting solution to remove the exchanged cations. The solution was measured into 33 ml aliquots and poured into the centrifuge tubes containing the clay. The clay and solution were mixed and centrifuged for two minutes at 2500 rpm. The decantate was poured off. The extraction procedure was repeated twice, so 100ml of extracting solution decantate was obtained. Nalgene bottles were capped and stored in a refrigerator until analysis.

3.4 Calculations

Exchangeable calcium, exchangeable sodium, exchangeable sodium ratio, and cation exchange capacity are calculated from analysis of the extracting and equilibrating solutions. Calculations were modified from Amrhein and Suarez (1990) and performed in milliequivalent units to account for the heterovalent exchange between sodium and calcium (see Section 2.2.1).

Table 3.5 defines values used in the following calculation equations. The parameters are defined as in Amrhein and Suarez (1990). Exchangeable sodium (NaX) is calculated as:

$$NaX = T_{Na} - T_{Cl} E_{Na} \quad \text{(mmol/kg).} \tag{3.1}$$

Exchangeable calcium (CaX) is calculated as:

$$CaX = T_{Ca} - T_{Cl} E_{ca} \quad \text{(mmol/kg).} \tag{3.2}$$

Exchangeable sodium ratio (ESR) is calculated as:

$$ESR = NaX / CaX. \tag{3.3}$$

Cation exchange capacity is calculated as:

$$CEC = NaX + CaX. \tag{3.4}$$

Term	Definition
NaX	exchangeable sodium ions associated with the exchanger clay phase (meq/100g)
CaX	exchangeable calcium ions associated with the exchanger clay phase (meq/100g)
T_{Na}	total sodium ions found in the extracting solution (meq/100g)
T_{Cl}	total chloride ions found in the extracting solution (meq/100g)
T_{Ca}	total calcium ions found in the extracting solution (meq/100g)
[Na]	concentration of sodium in the equilibrating solution final decantate (mmol/L)
[Ca]	concentration of calcium in the equilibrating solution final decantate (mmol/L)
E_{Na}	equivalent fraction of sodium ion in the equilibrating solution E_{Na}= [Na] / [Na] + [Ca]
E_{Ca}	equivalent fraction of calcium ion in the equilibrating solution E_{Ca}= [Ca] / [Na] + [Ca]
ESR	exchangeable sodium ratio
CEC	cation exchange capacity (meq/100g)

Table 3.5 Explanation of terms used in calculation equations. Definitions are from Amrhein and Suarez (1990).

CHAPTER 4: RESULTS

4.1 Water Chemistry

4.1.1 Phalen Formation Water Chemistry

The equilibrating solutions in this study are modelled after the chemistry of Phalen formation waters. Chemical analyses of Phalen formation waters were provided by the Cape Breton Development Corporation and are listed in Table 4.1. Chemical data were examined so trends in formation water chemistry could be related to cation exchange.

4.1.2 Original Waters and Waters Equilibrated with Calcite

Phalen formation waters are interpreted as the evaporative residues from Windsor Group salt precipitation (Sect. 1.4.3). The original chemical composition of the water was modified through water-rock reactions, possibly cation exchange. The Carboniferous Hydrogeology Project has attempted to geochemically model the hypothetical evolution of the original Windsor brine waters to the Phalen formation waters. Prior to emplacement as Phalen formation waters, the original brines moved through calcite-rich rocks and may have equilibrated with calcite (Sect. 1.4.4) (Martel and Gibling, in prep.). The chemical compositions of the original brine waters and the waters equilibrated with calcite were modelled by Martel in the PHREEQCI geochemical modelling program. Table 4.2 gives the modelled chemistry of the original brine waters and the brines after equilibration with

Site	Geology	pH	TDS	Na	K	Mg	Ca	Sr	Mn	Fe	NH4	Ba	Zn	Cu
6	CBDC-648	5.8	153871	40000	191	2600	13000	1210	3.4	5.2	49.6			
3S	Dal PH 3S	5.1	155983	41200	199	2690	12000	2030		27.2	48.1			
3WWF	CBDC-589	5.3	176153	40200	160	4400	21300		18.1	22.4	60		0.03	0.01
6 ET	CBDC-645	5.9	150010	32750	200	3800	16000	1080	5.2	3	49.66	323	0.2	0.22
6 ET	CBDC-646	5.8	170332	43000	240	4200	17000	860	6.28	24	52.31	421	1.42	0.28
6 EB	CBDC-648	5.8	153894	40000	191	2600	13000	1210	3.4	5.2	49.6	860	0.02	0.02
3 S	CBDC-663	5.7	151054	40600	213.5	2370	11400	844		27.8	52.2			
2 CB	CBDC-664	5.4	160033	38000	178.5	3220	15700	882		46.4	59.2			
2 CB	CBDC-665	6	165156	41050	195	3390	15800	794		33.4	57.95			
9 ET	PH-2835	5.5	160077	45800		2550	12450	2025		35.6	53.6	0.05	0.01	0.01
9 ET	PH-2841	5.9	159860	46700		2630	12800			32.8	57.1			
9 ET	PH-2847	5.5	160474	46450		2630	12700			29.8	49.3			
3 S	PH-2850	4.8	155511	43450		2725	12300			24.8	48.9			
3 S	PH-2621	4.9	138754	40400		2110	8910			80.4	52.4			
3 S	PH-2606	5.4	133784	37450		2070	10425			36.6	35.6			
8 ET	PH-2264	5.8	158719	43000	209	2650	12300	2080		26.2	47.1	975	0.01	0.01
9 ET	PH-1611	5.3	155208	41950	216	2515	12550	840		33.8	51.4			
9 ET	PH-1612	5.6	160943	46450	246	2460	13000	862		32.2	50.5			
7 ET	PH-1229	6.1	164510	41000	224	2780	15600	1082		6.66	50.55			
8 EB	PH-1200	6	154550	41900	204	2540	11700	1305		35.8	53.09			
8 ET	PH-976	5.9	152894	41150	224.5	2360	12400	818		24	53.7			
3 S	PH-697	5.7	156862	42100	225	2490	12300	724		28.8	47.82			
6 ET	PH-407	5.9	160053	37300	210	3570	17100	1000		8	55.26			
2 CB	PH-441	5.5	152328	40150	212	2825	13800	1006	5.8	30	46.89	475	1.63	0.22
9EB	Dal PH 9EBN	6.2	152621	44800	194	2660	11900	41	11	41	50		<.5	<.2

Table 4.1 Chemical analyses of Phalen formation waters, from CBDC and the Carboniferous Hydrogeology Project. All analyses are in mg/L.

Site	Geology	Ni	Cl	Br	SO4	HCO3	Al	B
6	CBDC-648		96814		1			0.02
3S	Dal PH 3S		97780	935.2	1	7.8		
3WWF	CBDC-589		110000		11			
6 ET	CBDC-645	0.02	96126		1	0	0.3	0.02
6 ET	CBDC-646	0.04	104955		1	0	0.42	0.02
6 EB	CBDC-648	0.02	96814		1	23.26	0.27	0.02
3 S	CBDC-663		95525		1.7	20.25		0.02
2 CB	CBDC-664		101945		1	0.53		0.06
2 CB	CBDC-665		103834		1	0.43		0.05
9 ET	PH-2835	0.01	97135		2.7	25.02	0.01	0.85
9 ET	PH-2841		97605		6.42	28.99		
9 ET	PH-2847		98546		1	68.3		
3 S	PH-2850		96956		5.7	0.4		
3 S	PH-2621		87200		1	0.4		
3 S	PH-2606		83746		1	19.6		
8 ET	PH-2264	0.01	98362		1	43.3	0.61	0.45
9 ET	PH-1611		97050		1	0.4		0.02
9 ET	PH-1612		97828		1	13.1		0.02
7 ET	PH-1229		103716		1	49.85		0.02
8 EB	PH-1200		96754		1.9	56.58		0.02
8 ET	PH-976		95828		8.9	26.7		0.02
3 S	PH-697		98919		1	26.87		0.06
6 ET	PH-407		100788		1	20.84		0.02
2 CB	PH-441	0.04	94257		1	0	4	0.02
9EB	Dal PH 9EBN	<.2	92900	950	<2	35	<1	<.5

Table 4.1 continued

Water	Cl	Br	SO_4	Mg	Ca	K	Na	Sr
original	5896	25.1	542.5	1634	0	310	3473	5.3
equilibrated with calcite	5896	25.6	3.6	283	812	310	3473	5.3

Table 4.2 From geochemical modelling, the chemistry of the original Windsor brine waters and the waters equilibrated with calcite. All units are mmol/L.

calcite. The model shows that the original Windsor brines had high Na and Cl concentrations, fairly high Mg and SO_4 concentrations, and no Ca. Equilibration of the original brine waters with involves some calcite dissolution and some gypsum precipitation. This enriched the waters in Ca, and depleted the waters in Mg and SO_4.

4.1.3 Formation Water Trends

The chemical analyses of Phalen formation waters, original brine waters, and waters equilibrated with calcite were plotted on a Piper plot in the Hydrowin program (Fig. 4.1). Features of Piper plots are described in Section 2.5.2. Figure 4.1 shows several chemical trends. 1) Phalen formation waters plot on a straight line parallel to the edge of the diamond field. This trend is characteristic of cation exchange between Ca and Na (Appelo and Postma, 1996). 2) The amount of HCO_3^- in the formation waters is a constant value of almost zero. Constant HCO_3^- suggests that precipitation or dissolution of calcite did not substantially modify formation water chemistry. 3) As Phalen formation waters evolved from the original Windsor brine waters, the chemistry changed. Brine waters equilibrated with calcite plot with Phalen formation waters on the Piper plot. The relative proportions of Na and Ca in the waters equilibrated with calcite resemble the relative proportions in the formation waters. Despite this resemblance, the salinities of the waters equilibrated with calcite are much higher than the salinities of the formation waters. 4) The Phalen formation water trend in the cation triangle is irrespective of the anion chemistry. From the formation water chemistry listed in Table 4.1, concentrations of ions can be related to formation water salinity. Phalen formation waters increase in Na

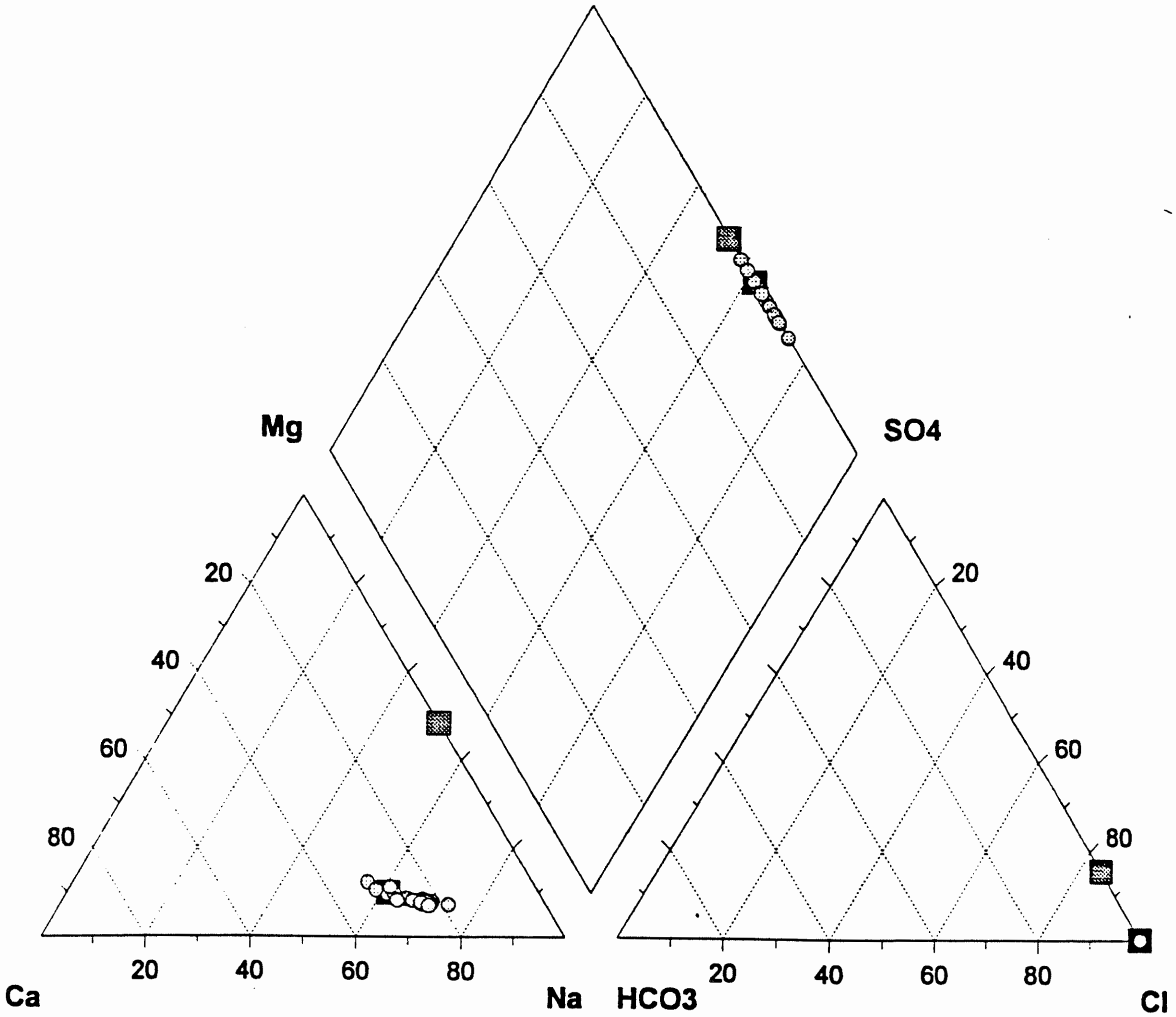

Fig 4.1 Chemical analyses of Phalen formation waters, original Windsor brine waters, and brine waters equilibrated with calcite, plotted on a Piper plot. Windsor brine waters are shown by the light square. Waters equilibrated with calcite are shown by the dark square. Phalen formation waters are shown by the circles. Phalen formational water chemistry displays a straight line trend from Ca to Na. The straight line trend along the border of the upper diamond field is characteristic of an exchange reaction.

concentration with decreasing salinity. Phalen formation waters increase in Ca and Mg concentrations with increasing salinity.

4.2 Sample Mineralogy

4.2.1 X-Ray Diffraction

Whole rock and clay mineralogies of the nine samples were determined by X-ray diffraction analysis. Table 4.3 lists the whole rock mineralogy of each sample. The sandstone samples (PH 50-3, 53-5, 59-1, 102-6, 104-5, and 105-6) have quartz, feldspar, mica, clay, and carbonate mineralogies. The shale samples (PH 53-12, 100-11, and 251-14) have quartz, mica, and clay mineralogies. Table 4.4 lists the clay portion mineralogy for each sample. Chlorite, mica (illite), and kaolinite group clays are represented in the clay samples. These groups are low cation exchange capacity clays (Sect. 2.3.7). X-ray diffraction mineral peak graphs for each sample are shown in Appendix A.

4.2.2 Sample Petrography

Stained thin sections of the six sandstone samples were described petrographically. The abundance and filling of pore spaces, and the percentage of clay in each sample, were related to the measured cation exchange capacity. Photomicrographs of the six sandstone samples are shown in Appendix B. Table 4.5 gives the visual estimates of the sample clay percentages and describes the pore spaces. Visual estimates of sandstone porosity range

Sample	**Whole Rock Mineralogy**
PH 50-3	quartz, chaoite, illite, baileychlore, albite, neotocite, calcite, nimite, clinochlore, muscovite, kaolinite, tychite, phlogopite
PH 53-5	quartz, halite, sergeevite, clinochlore, baileychlore, neotocite, kaolinite, clinochlore
PH 53-12 (shale)	quartz, pyrite, illite, muscovite, chaoite, baileychlore, muscovite, kaolinite
PH 59-1	quartz, neotocite, graphite, gaspeite, dolomite
PH 100-11 (shale)	quartz, muscovite, chaoite, clinochlore, illite, phlogopite, kaolinite
PH 102-6	quartz, nimite, albite, fraipontite, baileychlore, chamosite
PH 104-5	quartz, neotocite, baileychlore, pennantite, kaolinite, nepheline
PH 105-6	quartz, fraipontite, neotocite, nimite, baileychlore, kaolinite, illite, muscovite
PH 251-14 (shale)	quartz, illite, muscovite, nimite

Table 4.3 Whole rock mineralogy for each sample from X-ray diffraction analysis. See Appendix A for peak graphs.

Sample	Clay Mineralogy
PH 50-3	chlorite, baileychlore, clinochlore
PH 53-5	phlogopite, baileychlore, clinochlore, muscovite
PH 53-12 (shale)	muscovite, illite, kaolinite, baileychlore, phlogopite
PH 59-1	illite, kaolinite, biotite, muscovite, baileychlore, phlogopite
PH 100-11 (shale)	muscovite, illite, clinochlore, nimite, cookeite, chamosite
PH 102-6	muscovite, baileychlore, phlogopite
PH 104-5	illite, kaolinite, muscovite, nimite, clinochlore, baileychlore, biotite
PH 105-6	kaolinite, clinochlore, illite, baileychlore, phlogopite, biotite, chamosite, muscovite
PH 251-14 (shale)	illite, muscovite, baileychlore, clinochlore, nimite

Table 4.4 Clay-sized portion mineralogy for each sample from X-ray diffraction analysis. Clay groups represented are predominantly kaolinite, chlorite, and mica (illite) groups. See Appendix A for peak graphs.

Sandstone Sample	**Avg CEC meq/100g**	**Clay %**	**Porosity %**	**Permeability (md)**	**Grain size, pore size and shape**	**Pore filling**
PH 50-3	0.26	13	5	0.17	grain size: fine-grained pore size: ~ grain size pore shape: irregular, angular	most pores clay-filled
PH 104-5	0.25	12	1	1.83	grain size: fine-grained pore size: ~1/2 avg grain size pore shape: round to sub-round	most pores clay-filled
PH 105-6	0.23	10	2	0.16	grain size: very fine-grained pore size: less than avg grain size pore shape: rounded to elongate	most pores clay-filled
PH 102-6	0.19	8	20	0.11	grain size: very fine-grained pore size: 1/2 to full grain size pore shape: regular, sub-round	most pores small, unfilled, some filled with vfg clay
PH 59-1	0.14	6	25	42.5	grain size: fine-grained pore size: up to 5 times grain size pore shape: angular and irregular	most pores unfilled
PH 53-5	0.13	8	3	0.12	grain size: fine-grained pore size: less than avg grain size pore shape: sub-round to irregular	most pores unfilled, with occasional clay rims

Table 4.5 Summary of sandstone sample petrographic descriptions. Relationships between porosity, clay filling, and cation exchange capacity are emphasized. See Appendix B for photomicrographs of the six sandstone samples.

from 1 to 25%. Sandstone grain size ranges from very fine-grained to fine-grained. Sandstone pore size ranges from less than to five times the average sample grain size. Pore filling varies among the sandstone samples. Pores are filled with, or rimmed by, clay, or are unfilled.

4.3 CEC Experiment Results

4.3.1 Laboratory Analysis of Experimental Solutions

The equilibrating and extracting solution decantates were analyzed at Philip Analytical Services in Halifax. Thirty-six samples were analyzed for Na^+, Ca^{2+}, Cl^-, and HCO_3^-. Laboratory analysis procedures are described in Appendix C. The chemical analyses for all samples are listed in Table 4.6.

4.3.2 Calculated Exchange Values

The extracting and equilibrating solution chemical analyses were used in the Amrhein and Suarez (1990) equations (Sect. 3.5) to calculate several exchange values. The calculations were modified from units of millimoles to units of milliequivalents. Conversion to equivalent units accounts for the cation valence difference in the heterovalent exchange of Na^+ and Ca^{2+}. In the equilibrating solutions, Na^+ and Ca^{2+} are associated with one or two Cl^- ions, respectively. In exchange reactions, Na^+ and Ca^{2+} substitute on an equivalent-for-equivalent basis (Sect. 2.2.1) (Dzombak and Hudson,

Sample	Na mg/L extracting solution	Ca mg/L extracting solution	Cl mg/L extracting solution	HCO3 mg/L extracting solution	Na mg/L equilibrating solution	Ca mg/L equilibrating solution	Cl mg/L equilibrating solution	HCO3 mg/L equilibrating solution
PH 50-3-1	293	74.1	463	<100	36600	9160	64600	<100
PH 50-3-2	403	124	747	<100	46500	15300	91200	<100
PH 50-3-3	335	36.8	491	<100	41300	4190	62300	<100
PH 50-3-4	429	63	687	<100	50100	7030	80800	<100
PH 53-5-1	285	69.4	526	<100	34000	8690	59900	<100
PH 53-5-2	401	128	792	<100	43700	14700	8380	<100
PH 53-5-3	389	41.6	602	<100	44600	4550	68200	<100
PH 53-5-4	462	65.9	802	<100	52400	7340	84900	<100
PH 53-12-1	275	69	480	<100	32600	8300	57000	<100
PH 53-12-2	419	130	793	<100	41800	14000	76800	<100
PH 53-12-3	419	44.9	644	<100	42700	4360	64600	<100
PH 53-12-4	530	72.7	866	<100	53200	7600	86000	<100
PH 59-1-1	321	81.4	555	<100	36900	9120	63300	<100
PH 59-1-2	361	112	729	<100	44300	14700	84000	<100
PH 59-1-3	335	36.3	529	<100	42200	4220	63500	<100
PH 59-1-4	406	57.9	691	<100	51400	7360	82700	<100
PH 100-11-1	239	63.2	428	<100	36700	9120	63300	<100
PH 100-11-2	374	116	703	<100	45200	14900	86400	<100
PH 100-11-3	258	29.8	358	<100	41300	4170	62200	<100
PH 100-11-4	464	69.1	735	<100	52300	7480	84100	<100
PH 102-6-1	313	78.8	521	<100	36800	9420	64100	<100
PH 102-6-2	400	127	793	<100	45200	14900	88800	<100
PH 102-6-3	406	58.8	672	<100	43700	4420	66000	<100
PH 102-6-4	424	61.5	687	<100	50200	7130	81700	<100

Table 4.6 Laboratory analysis of equilibrating and extracting solutions, given in mg/L. Nine rock samples were reacted with four equilibrating solutions, yielding 36 samples. In all samples bicarbonate was below detection limit.

Sample	Na mg/L extracting solution	Ca mg/L extracting solution	Cl mg/L extracting solution	HCO3 mg/L extracting solution	Na mg/L equilibrating solution	Ca mg/L equilibrating solution	Cl mg/L equilibrating solution	HCO3 mg/L equilibrating solution
PH 104-5-1	286	72.2	465	<100	37700	9380	65100	<100
PH 104-5-2	373	116	704	<100	45800	15500	87200	<100
PH 104-5-3	346	36.1	499	<100	42400	4180	63100	<100
PH 104-5-4	453	64.8	713	<100	50400	6980	80900	<100
PH 105-6-1	299	72.8	514	<100	34700	8810	60700	<100
PH 105-6-2	420	131	814	<100	45500	14800	85300	<100
PH 105-6-3	505	75.1	810	<100	46200	4540	70700	<100
PH 105-6-4	465	66.9	732	<100	53200	7460	84800	<100
PH 251-14-1	324	78.6	534	<100	36200	9140	63400	<100
PH 251-14-2	396	121	716	<100	44700	14600	84800	<100
PH 251-14-3	366	37.7	516	<100	41800	3980	62600	<100
PH 251-14-4	479	69	516	<100	50100	6830	79900	<100

Table 4.6 continued

1995). Converting concentrations to milliequivalent units accounts for the charge difference between Na^+ and Ca^{2+}; this difference would not be accounted for if calculations were performed in molar units.

Table 4.7 lists the calculated values of exchangeable sodium (NaX), exchangeable calcium (CaX), equivalent fractions of sodium and calcium in the solution phase (E_{Na}, E_{Ca}), exchangeable sodium ratio (ESR), and cation exchange capacity (CEC), for each sample (see Section 3.4 for definition of terms). NaX ranges from 0.058 to 0.786 meq/100g, with a 0.167 meq/100g mean. CaX ranges from 0.008 to 0.141 meq/100g, with a 0.036 meq/100g mean. ESR, the ratio of exchangeable Na to exchangeable Ca, ranges from 0.702 to 10.9, with a 4.72 mean. CEC ranges from 0.073 to 0.927 meq/100g with a 0.209 meq/100g mean.

4.4 Trends in Sandstones and Shales

4.4.1 Clay % and CEC

Cation exchange capacity is related to the amount and type of clay in a sample, and whether the pores are empty or filled with clay. Figure 4.2 shows a direct relationship between the clay percentage in each sandstone sample and the measured cation exchange capacity of that sandstone sample. The direct relationship can be extrapolated to include the shale samples, which are essentially 100% clay, with the highest CEC's. In sandstone, clay minerals host the exchange sites (Weaver, 1989). A sandstone with a high clay percentage has more exchange sites, and as a consequence, a higher cation exchange

Sample	TNa meq/L	TNa meq/100g	TCl meq/L	TCl meq/100g	[Na] meq/L equilibrating solution	[Ca] meq/L equilibrating solution
PH 50-3-1	12.74	1.21	13.06	1.24	1592	457
PH 50-3-2	17.53	1.67	21.07	2.01	2023	764
PH 50-3-3	14.57	1.39	13.85	1.32	1796	209
PH 50-3-4	18.66	1.78	19.38	1.85	2179	351
PH 53-5-1	12.40	1.18	14.84	1.41	1479	434
PH 53-5-2	17.44	1.66	22.34	2.13	1901	734
PH 53-5-3	16.92	1.61	16.98	1.62	1940	227
PH 53-5-4	20.10	1.92	22.62	2.16	2279	366
PH 53-12-1	11.96	1.14	13.54	1.29	1418	414
PH 53-12-2	18.23	1.74	22.37	2.13	1818	699
PH 53-12-3	18.23	1.74	18.17	1.73	1857	218
PH 53-12-4	23.05	2.20	24.43	2.33	2314	379
PH 59-1-1	13.96	1.33	15.65	1.49	1605	455
PH 59-1-2	15.70	1.50	20.56	1.96	1927	734
PH 59-1-3	14.57	1.39	14.92	1.42	1836	211
PH 59-1-4	17.66	1.68	19.49	1.86	2236	367
PH 100-11-1	10.40	0.99	12.07	1.15	1596	455
PH 100-11-2	16.27	1.55	19.83	1.89	1966	744
PH 100-11-3	11.22	1.07	10.10	0.96	1796	208
PH 100-11-4	20.18	1.92	20.73	1.98	2275	373
PH 102-6-1	13.61	1.30	14.70	1.40	1601	470
PH 102-6-2	17.40	1.66	22.37	2.13	1966	744
PH 102-6-3	17.66	1.68	18.95	1.81	1901	221
PH 102-6-4	18.44	1.76	19.38	1.85	2184	356
PH 104-5-1	12.44	1.19	13.12	1.25	1640	468
PH 104-5-2	16.22	1.55	19.86	1.89	1992	773
PH 104-5-3	15.05	1.43	14.08	1.34	1844	209
PH 104-5-4	19.70	1.88	20.11	1.92	2192	348
PH 105-6-1	13.01	1.24	14.50	1.38	1509	440
PH 105-6-2	18.27	1.74	22.96	2.19	1979	739
PH 105-6-3	21.97	2.09	22.85	2.18	2010	227
PH 105-6-4	20.23	1.93	20.65	1.97	2314	372
PH 251-14-1	14.09	1.34	15.06	1.44	1575	456
PH 251-14-2	17.23	1.64	20.20	1.93	1944	729
PH 251-14-3	15.92	1.52	14.55	1.39	1818	199
PH 251-14-4	20.84	1.99	14.55	1.39	2179	341

Table 4.7 Table of calculated exchange values. Calculations are according to Section 3.4, and values are defined in Table 3.5. Values referred to hereafter include NaX (exchangeable sodium), CaX (exchangeable calcium), ESR (exchangeable sodium ratio) and CEC (cation exchange capacity). Shale samples are PH 53-12, PH 100-11, and PH 251-14.

Sample	ENa	ECa	TCa	TCa	NaX	CaX	ESR	CEC
	meq/l	meq/L	meq/L	meq/100g	meq/100g	meq/100g		meq/100g
PH 50-3-1	0.777	0.223	3.70	0.353	0.248	0.075	3.31	0.322
PH 50-3-2	0.726	0.274	6.19	0.590	0.213	0.039	5.40	0.252
PH 50-3-3	0.896	0.104	1.84	0.175	0.206	0.037	5.52	0.244
PH 50-3-4	0.861	0.139	3.14	0.300	0.188	0.044	4.31	0.231
PH 53-5-1	0.773	0.227	3.46	0.330	0.088	0.009	9.32	0.098
PH 53-5-2	0.722	0.278	6.39	0.609	0.126	0.016	7.93	0.142
PH 53-5-3	0.895	0.105	2.08	0.198	0.164	0.028	5.79	0.192
PH 53-5-4	0.862	0.138	3.29	0.313	0.058	0.015	3.87	0.073
PH 53-12-1	0.774	0.226	3.44	0.328	0.141	0.036	3.88	0.178
PH 53-12-2	0.722	0.278	6.49	0.618	0.197	0.027	7.42	0.224
PH 53-12-3	0.895	0.105	2.24	0.214	0.187	0.032	5.85	0.219
PH 53-12-4	0.859	0.141	3.63	0.346	0.197	0.018	10.98	0.215
PH 59-1-1	0.779	0.221	4.06	0.387	0.168	0.058	2.93	0.226
PH 59-1-2	0.724	0.276	5.59	0.533	0.077	0.008	10.06	0.085
PH 59-1-3	0.897	0.103	1.81	0.173	0.113	0.026	4.30	0.139
PH 59-1-4	0.859	0.141	2.89	0.275	0.088	0.013	6.60	0.101
PH 100-11-1	0.778	0.222	3.15	0.301	0.095	0.045	2.11	0.141
PH 100-11-2	0.726	0.274	5.79	0.552	0.179	0.033	5.41	0.212
PH 100-11-3	0.896	0.104	1.49	0.142	0.207	0.042	4.95	0.249
PH 100-11-4	0.859	0.141	3.45	0.329	0.226	0.050	4.51	0.276
PH 102-6-1	0.773	0.227	3.93	0.375	0.215	0.057	3.78	0.272
PH 102-6-2	0.726	0.274	6.34	0.604	0.111	0.019	5.85	0.130
PH 102-6-3	0.896	0.104	2.93	0.280	0.064	0.092	0.70	0.156
PH 102-6-4	0.860	0.140	3.07	0.293	0.170	0.034	5.03	0.203
PH 104-5-1	0.778	0.222	3.60	0.343	0.213	0.066	3.24	0.279
PH 104-5-2	0.720	0.280	5.79	0.552	0.183	0.022	8.17	0.206
PH 104-5-3	0.898	0.102	1.80	0.172	0.229	0.035	6.48	0.265
PH 104-5-4	0.863	0.137	3.23	0.308	0.224	0.045	4.93	0.269
PH 105-6-1	0.774	0.226	3.63	0.346	0.169	0.035	4.90	0.204
PH 105-6-2	0.728	0.272	6.54	0.623	0.148	0.028	5.20	0.176
PH 105-6-3	0.899	0.101	3.75	0.357	0.137	0.137	1.00	0.273
PH 105-6-4	0.861	0.139	3.34	0.318	0.233	0.045	5.11	0.278
PH 251-14-1	0.775	0.225	3.92	0.374	0.230	0.051	4.48	0.282
PH 251-14-2	0.727	0.273	6.04	0.576	0.242	0.051	4.75	0.292
PH 251-14-3	0.902	0.098	1.88	0.179	0.267	0.043	6.25	0.310
PH 251-14-4	0.865	0.135	3.44	0.328	0.786	0.141	5.59	0.927

Table 4.7 continued

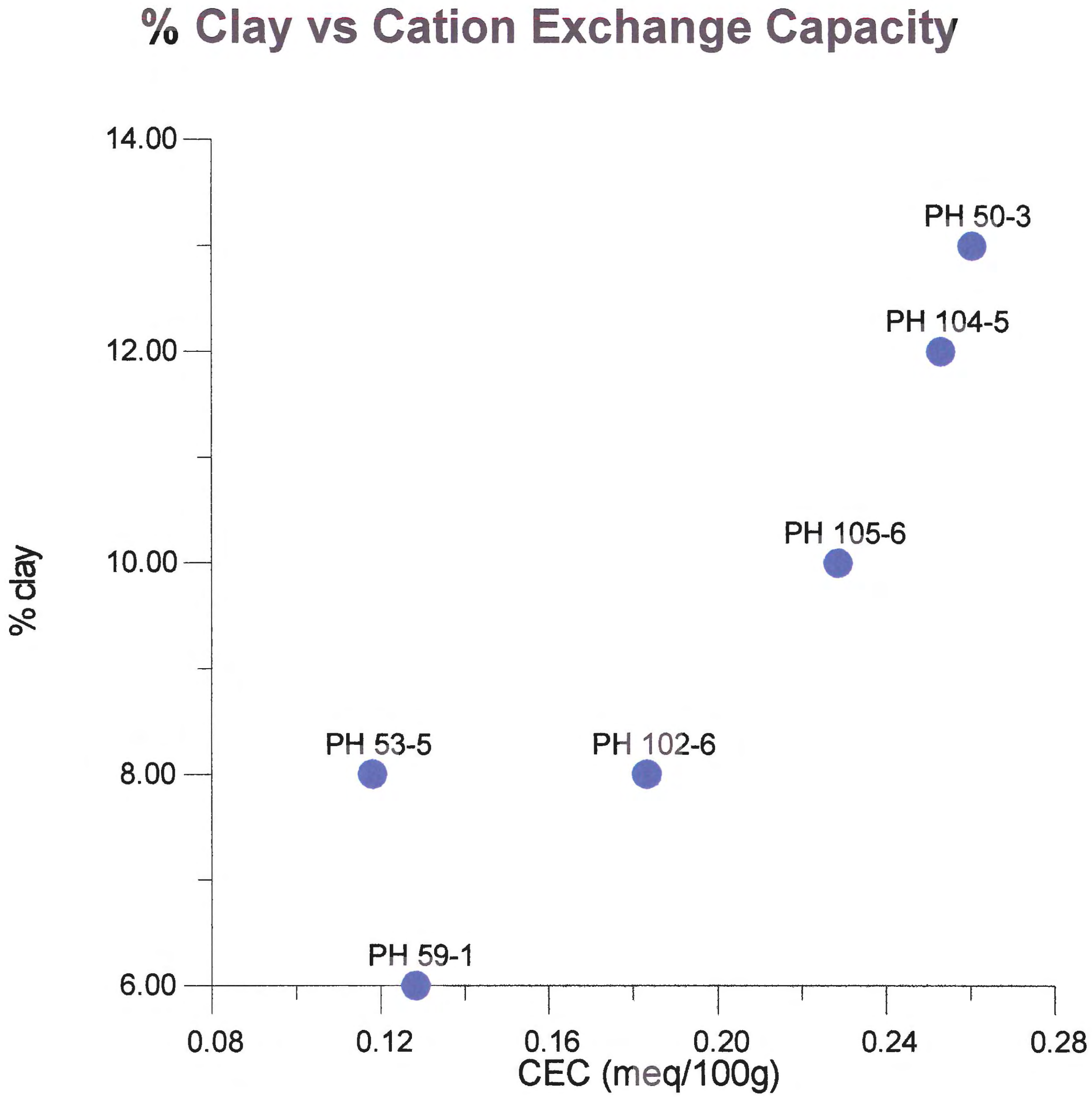

Fig. 4.2 Graph of estimated % clay versus calculated cation exchange capacity for the six sandstone samples. In a direct relationship, samples with the highest clay percentage have the highest cation exchange capacity.

capacity.

4.4.2 Clay % and Exchangeable Cations

There is a direct relationship between the clay percentage in each sandstone sample and the measured exchangeable sodium (NaX) and exchangeable calcium (CaX) values for the sample (Fig. 4.3; Fig. 4.4). Exchangeable sodium and calcium are held in the exchange sites of clay minerals (Weaver 1989). The samples with the highest clay percentage have the highest measured NaX and CaX. Cation exchange capacity is the sum of exchangeable cations (Amrhein and Suarez, 1990). As expected, the samples with the highest NaX and CaX have the highest CEC's. As sample clay content increases, the number of exchange sites increases, and consequently the amount of exchangeable sodium, exchangeable calcium, and the cation exchange capacity increases.

4.4.3 Porosity/Permeability and CEC

When porosity and permeability are plotted against CEC, NaX, and CaX, there is no clear relationship (Fig. 4.5; Fig. 4.6). The sandstone cation exchange capacity does not seem to be a simple function of the porosity or permeability, but depends on the relationship between porosity and clay distribution. Sandstone PH 59-1 has the highest porosity but one of the lowest CEC's (Fig 4.7). Sandstone PH 104-5 has the second highest CEC, but the lowest porosity. The sandstones with the highest CEC have the highest % clay. Most pore spaces are filled with, or rimmed by, clay. The sandstones

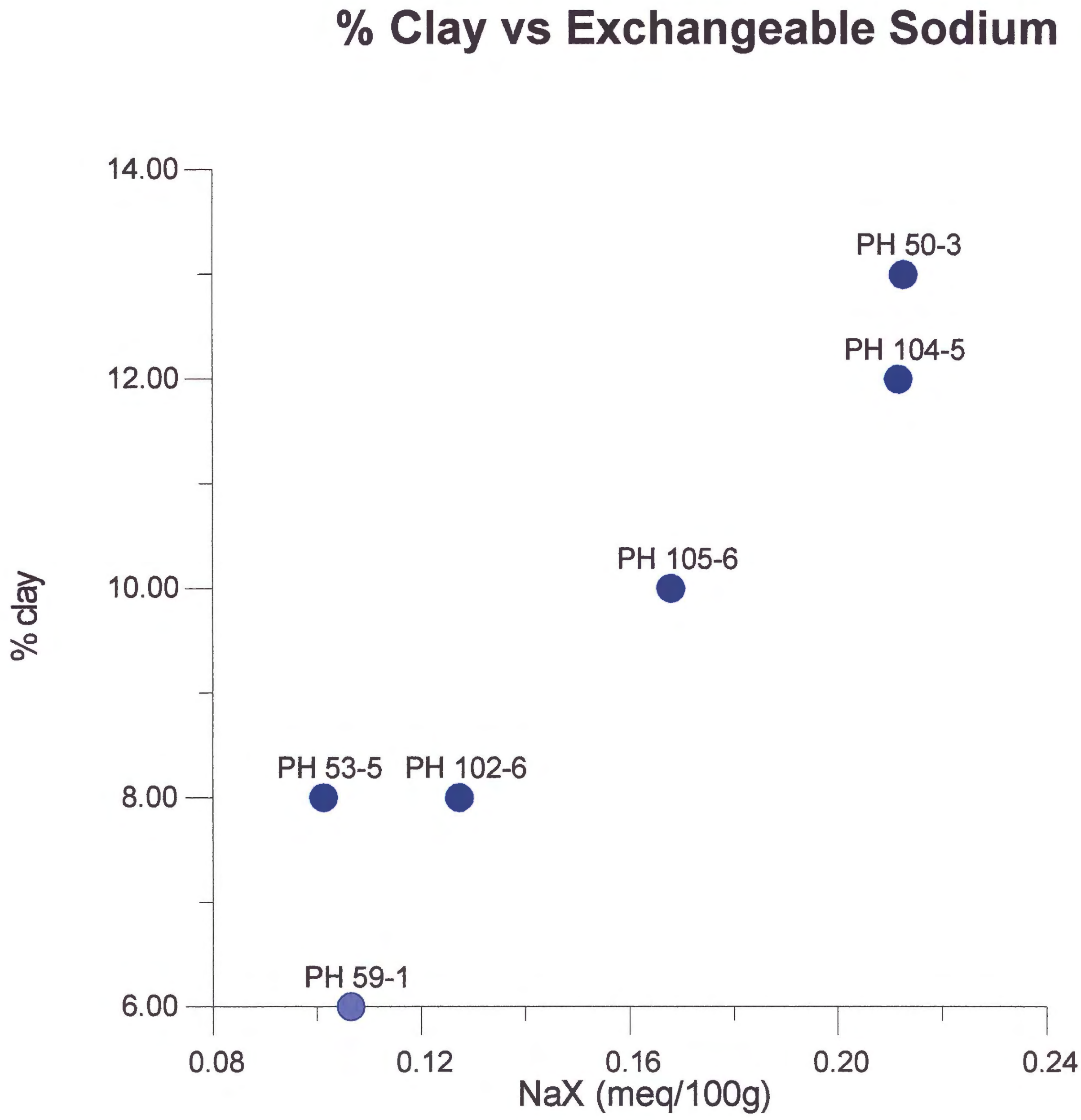

Fig. 4.3 Graph of estimated % clay versus calculated exchangeable sodium for the six sandstone samples. The direct relationship correlates with the trend of increasing CEC with increasing clay % (Fig. 4.2).

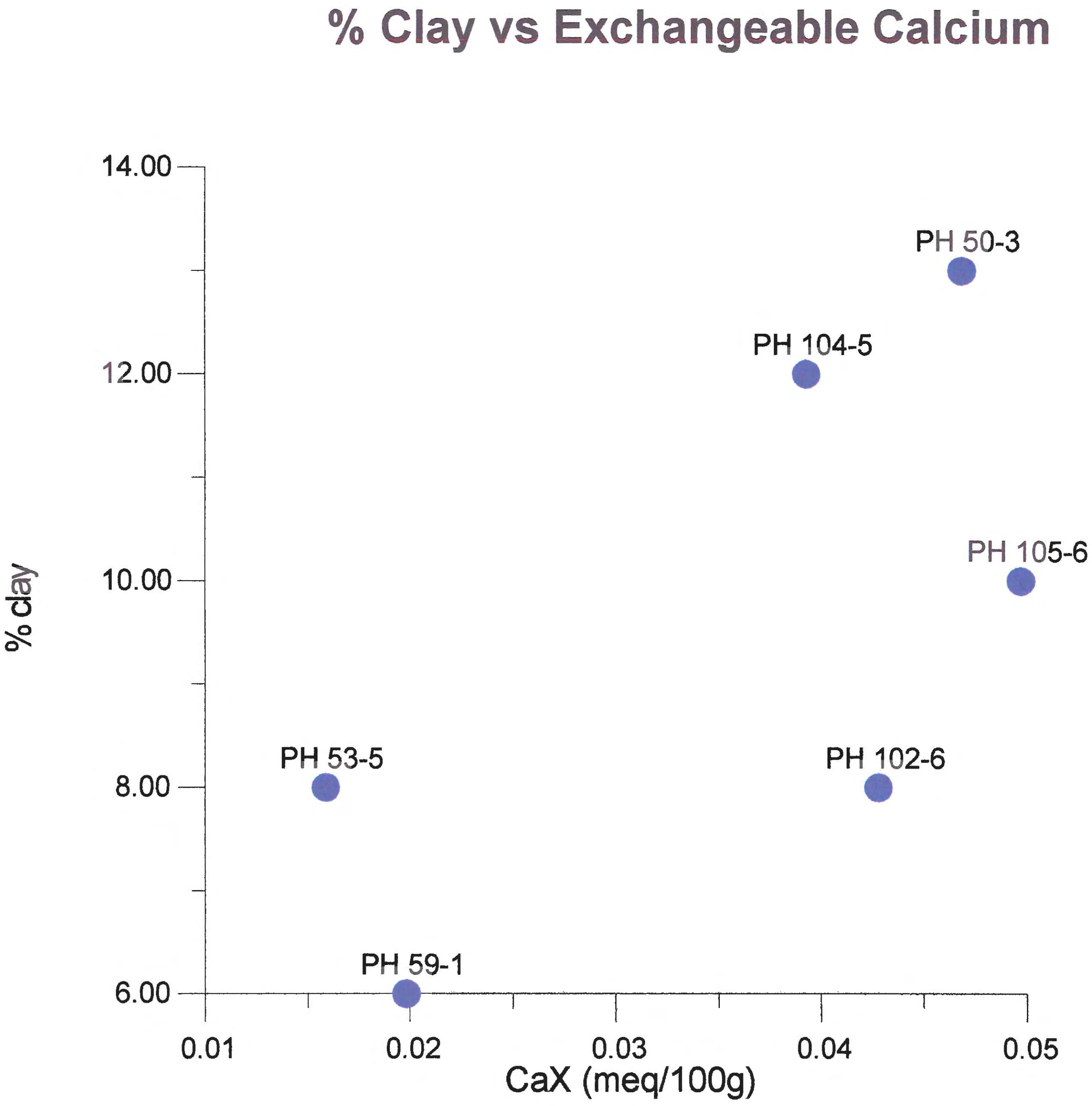

Fig. 4.4 Graph of estimated % clay versus calculated exchangeable calcium for the six sandstone samples. The direct relationship correlates with the trend of increasing CEC with increasing clay % (Fig. 4.2).

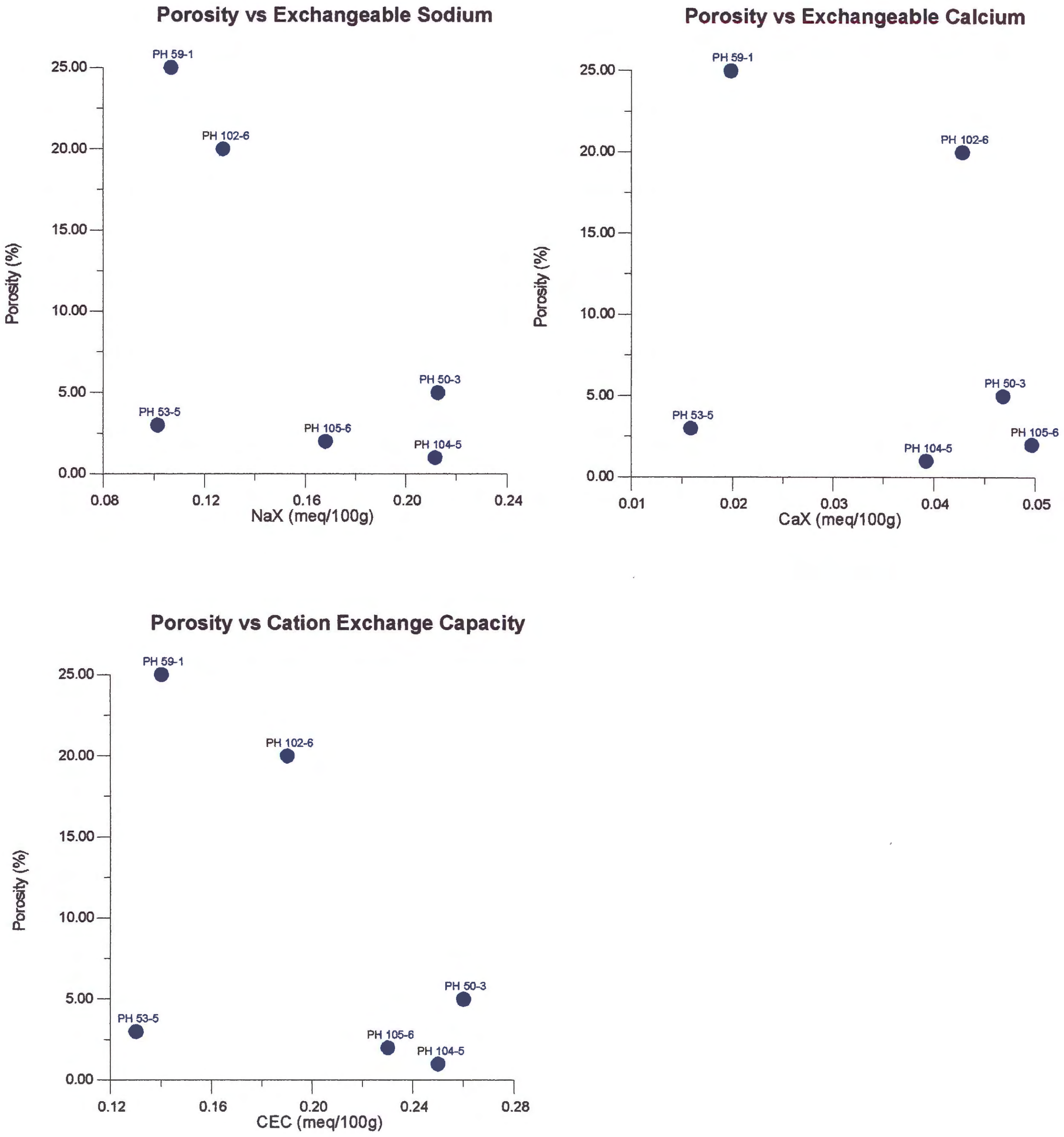

Fig. 4.5 Graphs of sandstone porosity against average exchangeable sodium, exchangeable calcium, and cation exchange capacity. No clear relationship is evident.

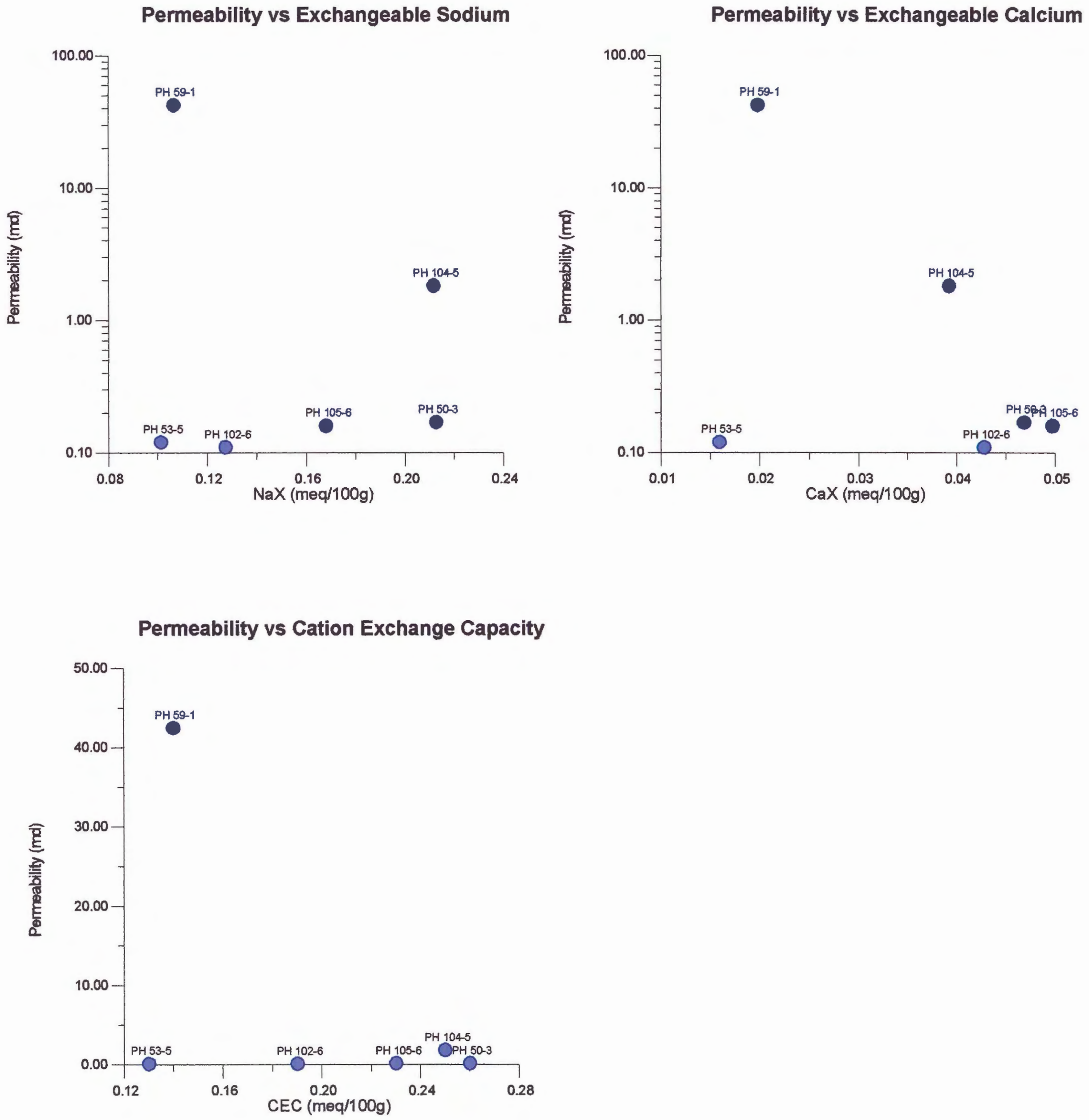

Fig. 4.6 Graphs of sandstone permeability against average exchangeable sodium, exchangeable calcium, and cation exchange capacity. No clear relationship is evident.

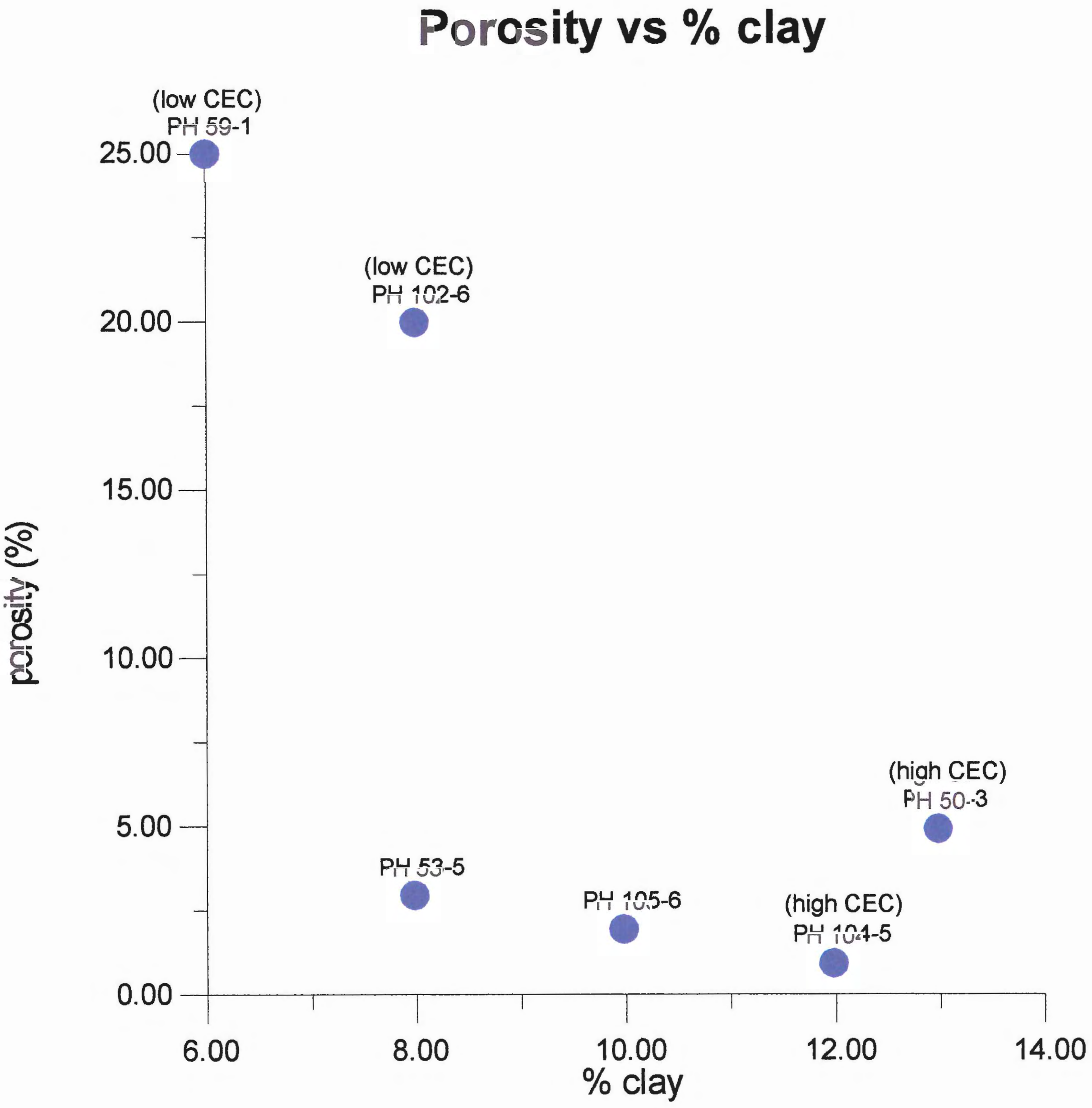

Fig. 4.7 Graph of sample porosity versus % clay for the six sandstone samples. Pores of the highest porosity samples are empty. Pores of the lowest porosity samples are filled with or rimmed by clay. The lowest porosity samples have the highest clay % and the highest CEC. CEC is more dependent on whether pores are clay-filled than the actual sample porosity.

with the lowest CEC have the lowest % clay. Most pore spaces are empty, even though porosity and permeability are high. Thus, cation exchange capacity depends more on whether the pores are filled with clay than the actual porosity of the sample.

4.5 Trends in Formation Water Chemistry

Contour maps of the spatial variation in the formation water chemistry across the Phalen Colliery were constructed. Spatial trends in formation water Na/Ca ratio and salinity were constructed in the Surfer contouring software package.

4.5.1 Salinity Trend

Formation water salinity is plotted spatially in Figure 4.8 and the mine plan is overlain. There is a trend in salinity across the Phalen Colliery. The water sample collected at 4 west wall face (4WWF) is located to the west in the mine, and the sample collected at 3 slope (3S) is located deeper and further to the east in the mine. Formation waters at 4WWF are the highest salinity waters, whereas formation waters at 3S are the lowest salinity waters. The spatial trend in salinity shows that Phalen formation waters are more dilute deeper, and further east, in the mine.

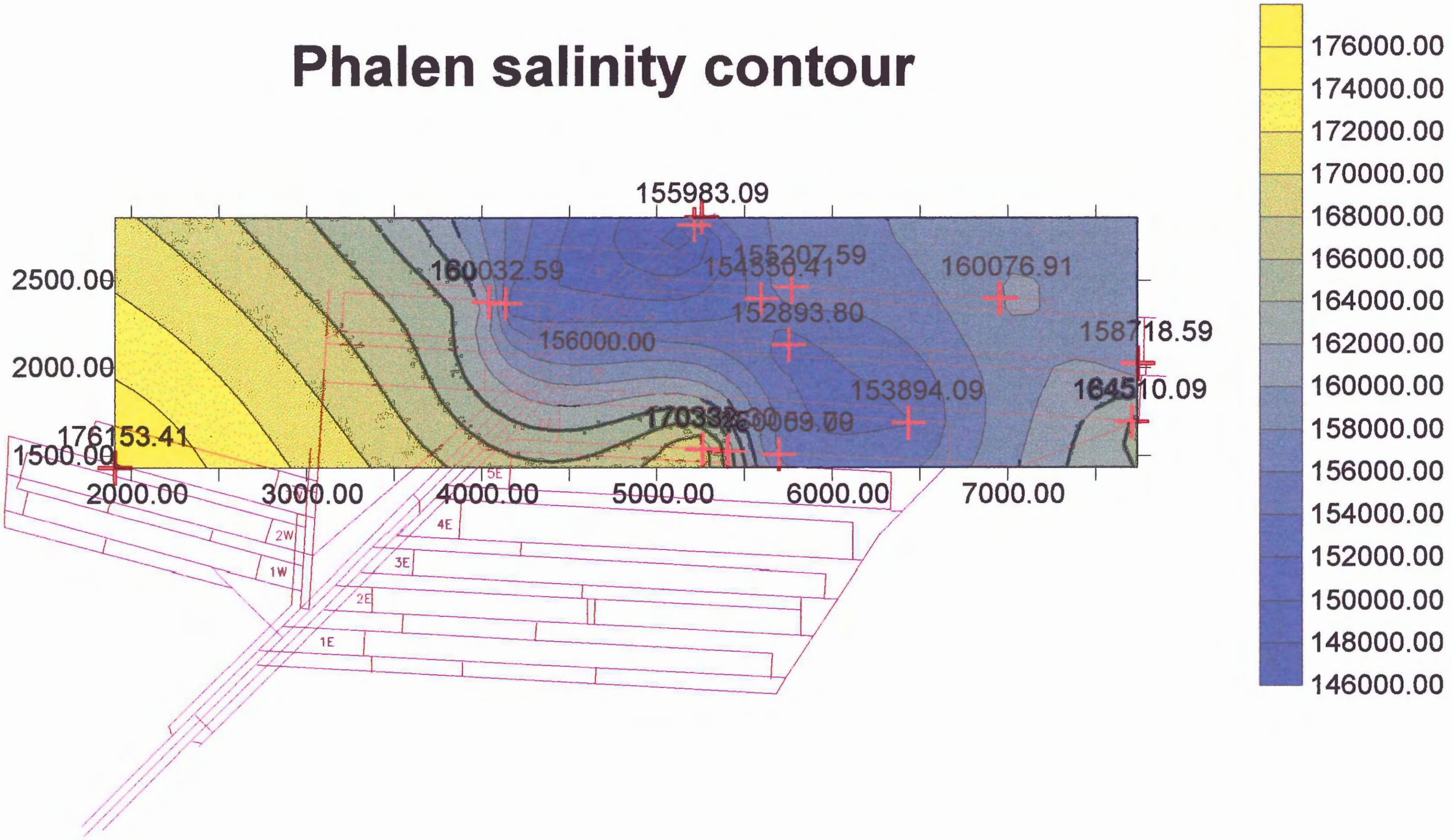

Fig. 4.8 Salinity, measured in total dissolved solids (mg/L), of formation warers is plotted spatially in the Phalen Colliery. Yellow indicates a high formation water salinity; blue indicates a more dilute water. Salinity varies spatially in the Phalen Colliery. At 4WWF, on the bottom left of the figure, formation waters are very saline. Toward 3S, in the upper middle of the figure, the waters are more dilute. X and Y coordinates of the mine (in metres) are shown along the axes of the contour map. Red crosses indicate the locations of formation water samples, and the numbers above the crosses are salinities in mg/L.

4.5.2 Na/Ca Ratio

The ratio of Na/Ca in Phalen formation waters is plotted spatially in Figure 4.9. There is a trend in the Na/Ca ratio across the Phalen Colliery that correlates with the spatial salinity trend. Sodium is more concentrated in dilute waters and calcium is more concentrated in saline waters. The spatial trend shows that the relative amounts of sodium and calcium vary spatially in the mine. The change in Na/Ca ratio could be the result of Na-Ca cation exchange. This possibility is discussed in Chapter 5.

4.6 Effects of Solution Concentration and SAR on Exchange

4.6.1 Representative Equilibrating Solutions

The four experimental equilibrating solutions were made to reflect Phalen formation waters, encompassing the range in formation water concentration and sodium adsorption ratios (Table 3.1). Solution 1 reflects low concentration, high calcium (low SAR) waters. Solution 2 reflects high concentration, high calcium (low SAR) waters. Solution 3 reflects low concentration, high sodium (high SAR) waters. Solution 4 reflects high concentration, high sodium (high SAR) waters. In this experiment, equilibrating solutions were reacted with clay samples to invoke cation exchange between solution cations and clay cations. The effects of solution concentration and SAR on measured exchange values were examined.

Table 4.8 lists the average measured exchangeable calcium, exchangeable sodium,

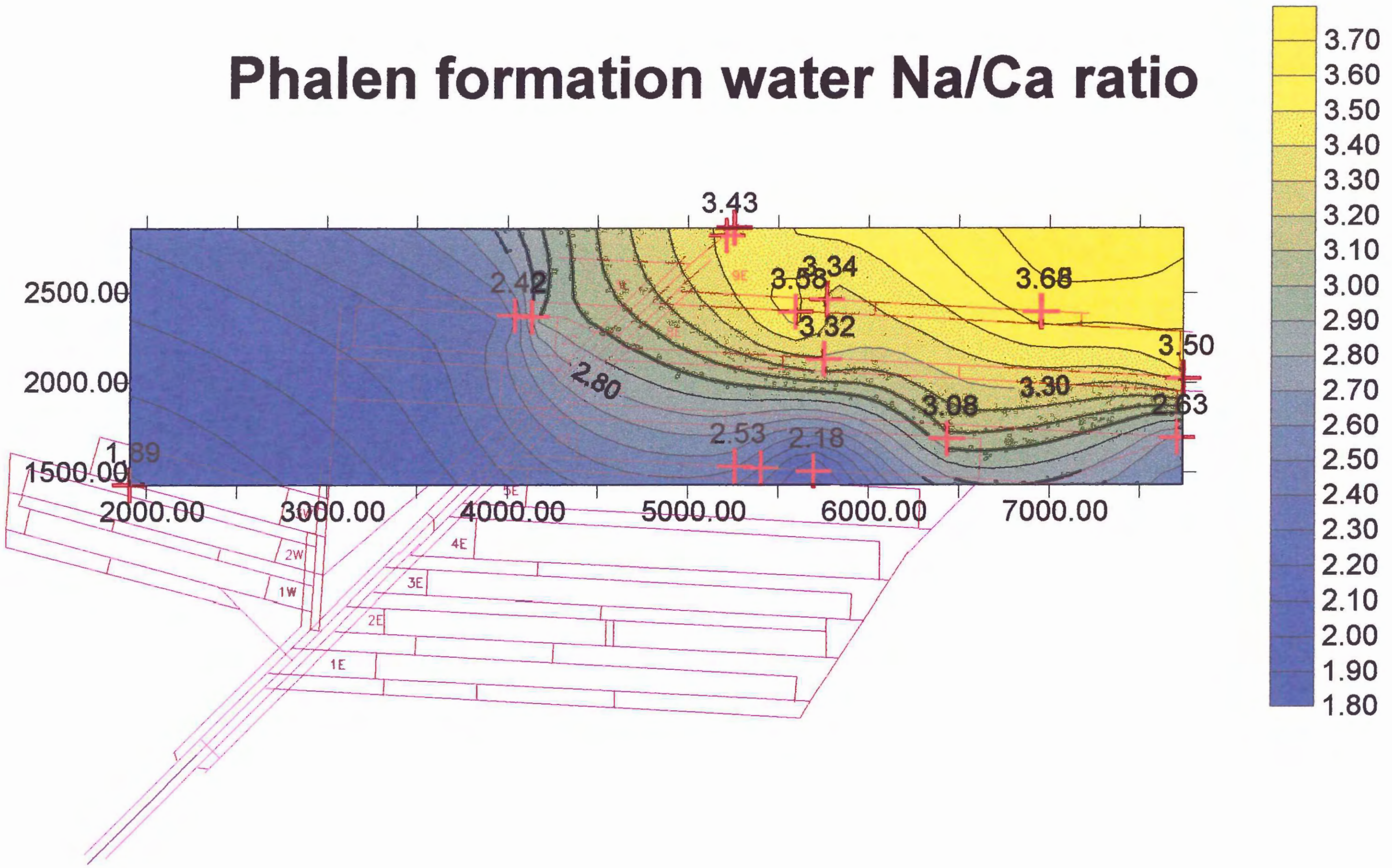

Fig. 4.9 The ratio of Na/Ca in formation waters is plotted spatially in the Phalen mine. X and Y coordinates (in metres) of the mine are shown along the axes of the contour map. Yellow indicates an enrichment in Na in the water; blue indicates an enrichment in Ca in the water. There is a spatial trend in the Na/Ca ratio across the mine which correlates with the spatial trend in salinity (Fig. 4.8). With decreasing salinity and increasing dilution, formation waters are enriched in Na and depleted in Ca.

Average Exchange Value	**Equilibrating Sol 1 4000 mmol/L, SAR 70**	**Equilibrating Sol 2 5400 mmol/L, SAR 70**	**Equilibrating Sol 3 4000 mmol/L, SAR 120**	**Equilibrating Sol 4 5400 mmol/L, SAR 120**
CaX sandstone	0.0498	0.0221	0.0593	0.0327
CaX shale	0.0444	0.0368	0.0388	0.0696
CaX all samples	0.048	0.027	0.0525	0.0450
NaX sandstone	0.184	0.143	0.152	0.160
NaX shale	0.155	0.206	0.22	0.403
NaX all samples	0.174	0.164	0.175	0.241
CEC sandstone	0.233	0.165	0.212	0.193
CEC shale	0.2	0.243	0.259	0.473
CEC all samples	0.222	0.191	0.227	0.286

Table 4.8 Summary table of investigation of the effects of varying equilibrating solution concentrations and SAR's. All values are given in units of meq/100g. An avergage exchange value for sandstones, for shales, and for all samples, is listed for each equilibrating solution.

and cation exchange capacity values for samples reacted with each equilibrating solution. Histograms of calculated exchange values of samples reacted with each equilibrating solution are presented in Figure 4.10, Figure 4.11, and Figure 4.12.

4.6.2 Effects of Concentration on Exchange

To examine the effects of equilibrating solution concentration on exchange, solutions of constant SAR and different concentrations were compared (solutions 1 and 2, and solutions 3 and 4). At constant SAR, measured exchangeable sodium and calcium varied at differing solution concentrations.

Measured exchange values for the nine samples reacted with equilibrating solutions 1 and 2 (SAR 70) were compared. In five samples, the lower concentration solution (#1) yielded higher measured NaX values. In eight samples, the lower concentration solution yielded higher CaX values. In five samples, the lower concentration solution yielded higher CEC values. Generally, at a constant SAR of 70, lower concentration equilibrating solutions yielded the highest exchange values.

Measured exchange values for the nine samples reacted with solutions 3 and 4 (SAR 120) were compared. In four samples, the lower concentration solution (#3) yielded higher measured NaX values. In five samples, the lower concentration solution yielded higher CaX values. In four samples, the lower concentration solution yielded higher CEC values.

Comparisons of equilibrating solutions of constant SAR's were combined to obtain the general effects of solution concentration on measured exchange values. Low

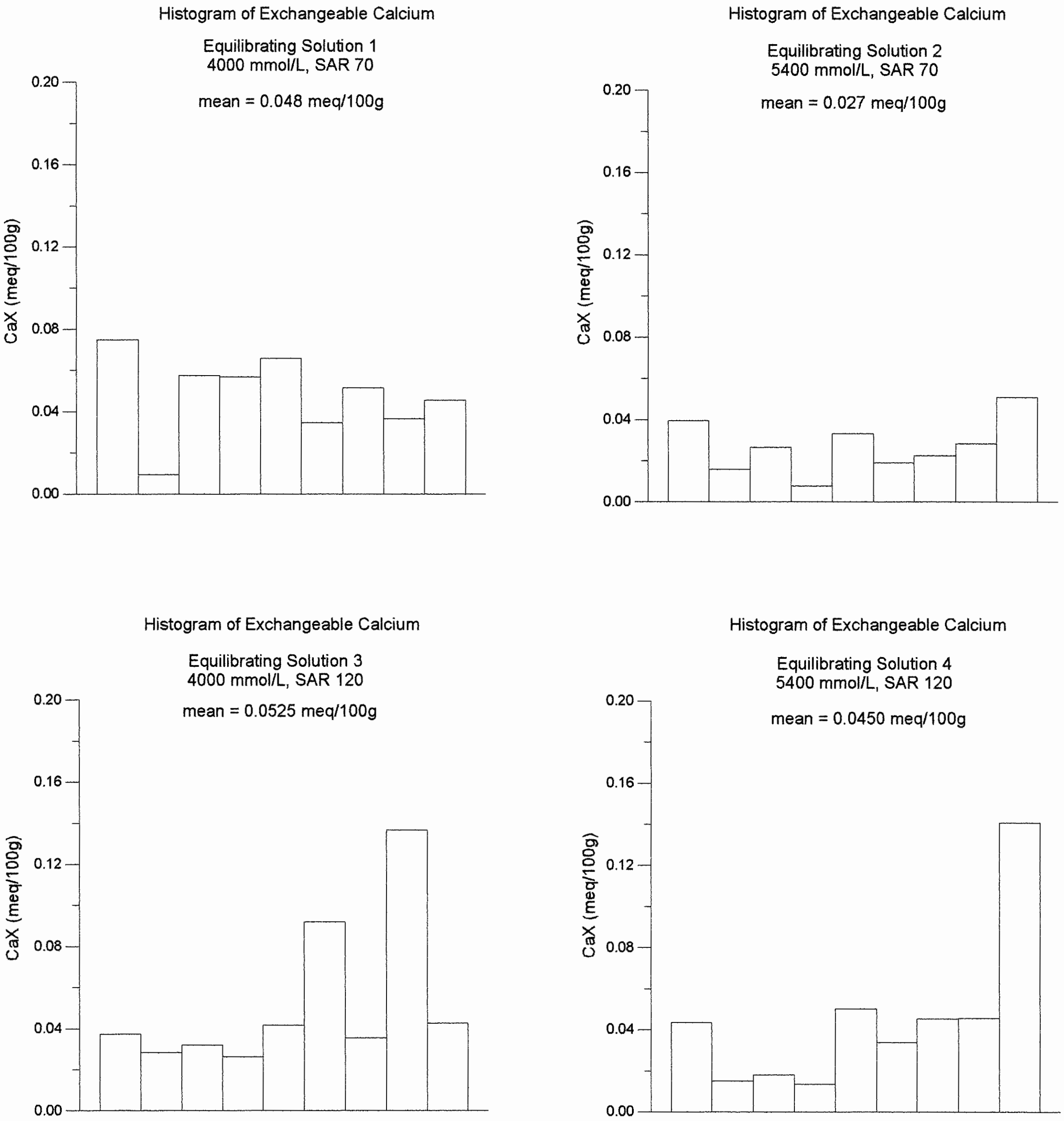

Fig. 4.10 Histograms of calculated exchangeable calcium from the reactions of sandstone and shale samples with the four different equilibrating solutions.

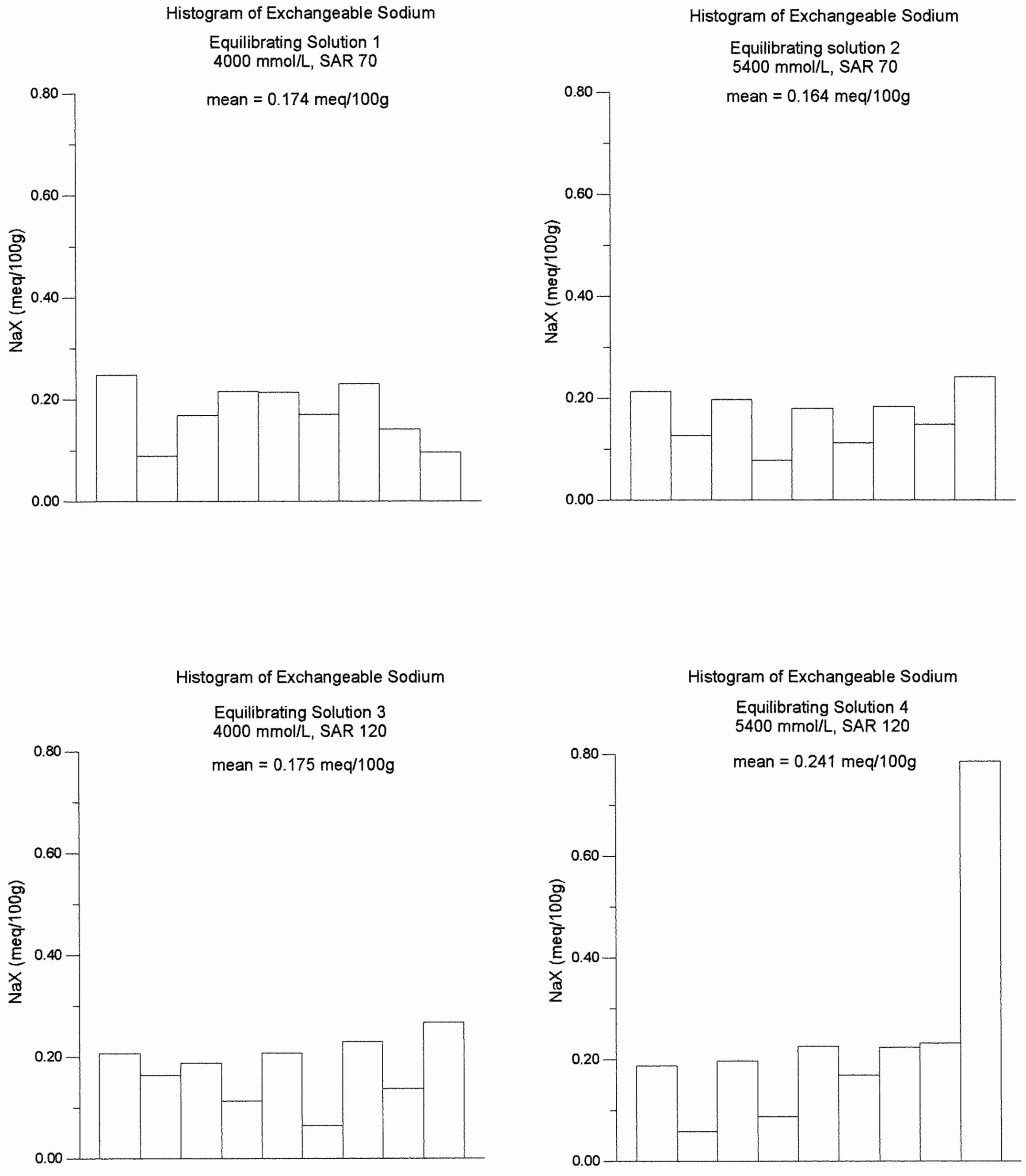

Fig. 4.11 Histograms of calculated exchangeable sodium from the reactions of sandstone and shale samples with the four different equilibrating solutions.

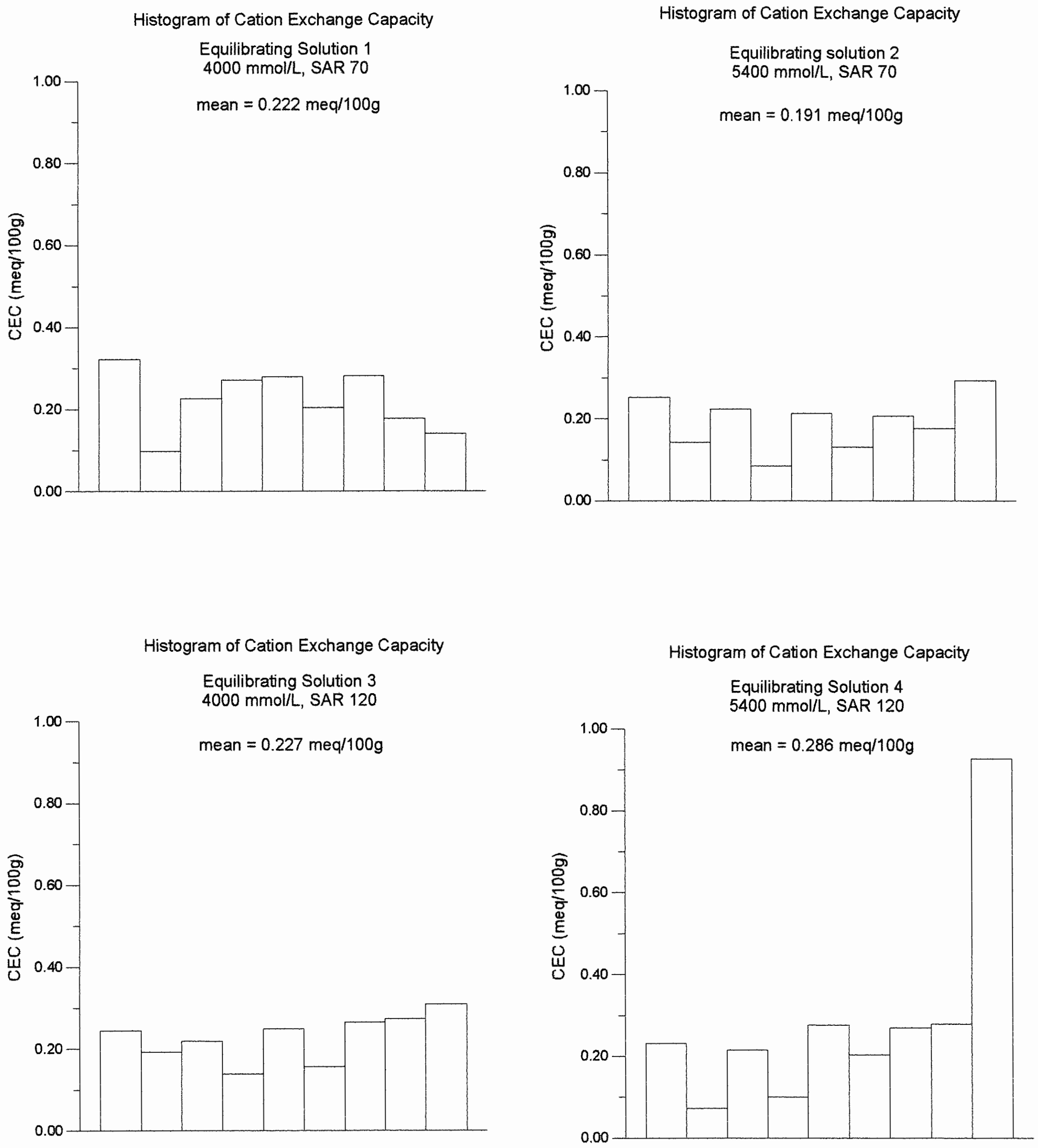

Fig. 4.12 Histograms of calculated cation exchange capacity from the reactions of sandstone and shale samples with the four different equilibrating solutions.

concentration solutions yielded high measured CaX for 72% of samples, high NaX for 50% of samples, and high CEC for 50% of samples. Generally, the highest exchange values are obtained from reacting clays with lower concentration equilibrating solutions.

Amrhein and Suarez (1990) and Curtin et al. (1995) report no variation in CaX, NaX, or CEC with changing concentration. Higher exchange values at lower concentrations in this study may be a reflection of the ability of this experimental procedure to measure exchange at high salinities (see Chapter 5 for further discussion).

4.6.3 Effects of Sodium Adsorption Ratio on Exchange

To examine the effects of equilibrating solution sodium adsorption ratio (SAR) on exchange, solutions of constant concentration and different SAR's were compared (solutions 1 and 3, and solutions 2 and 4). At constant concentration, measured exchangeable sodium and calcium varied at different solution SAR's.

Measured exchange values for the nine samples reacted with equilibrating solutions 1 and 3 (concentration 4000 mmol/L) were compared. In five samples, the high SAR solution (#3) yielded higher measured NaX values. In six samples, the low SAR solution (#1) yielded higher CaX values. In five samples, the high SAR solution yielded higher CEC values.

Measured exchange values for the nine samples reacted with equilibrating solutions 2 and 4 (concentration 5400 mmol/L) were compared. In seven samples, the high SAR solution (#4) yielded higher measured NaX values. In seven samples, the high SAR solution yielded higher CaX values. In seven samples, the high SAR solution yielded higher CEC values.

Comparisons of equilibrating solutions at constant concentration were combined to obtain the general effects of changing solution SAR on exchange values. High SAR equilibrating solutions yielded high CaX for 56% of samples, high NaX for 67% of samples, and high CEC for 67% of samples. Generally, the highest calculated exchange values are obtained from reacting clays with higher SAR equilibrating solutions.

4.6.4 Effects of Equilibrating Solution Chemistry on Individual Samples

Possible effects of equilibrating solution chemistry on the measured exchange values of individual samples were examined. The nine clay samples were reacted with four equilibrating solutions. The exchanger (clay) remained constant while the solution varied, and four values of NaX, CaX, and CEC are measured for each sample. Table 4.9 identifies the solution that yielded the highest and lowest exchange values for each sample. Graphs of the four values of NaX, CaX, and CEC for each sample are plotted in Figure 4.13, Figure 4.14, and Figure 4.15. Generally, all the NaX data points fall within a fairly small range, as do all the CaX and CEC data points.

Effects of equilibrating solution chemistry on measured exchange values are not evident. In eight of nine samples, one equilibrating solution yielded the highest values for both NaX and CEC. However, the actual solution differed among the samples. In five of nine samples, one equilibrating solution yielded the highest values for NaX, CaX, and CEC. Overall, the highest exchange values were not obtained from reaction with any one particular equilibrating solution.

Sample	Value	Highest	2nd highest	2nd lowest	Lowest
PH 50-3	NaX	1	2	3	4
	CaX	1	4	2	3
	CEC	1	2	3	4
PH 53-5	NaX	3	2	1	4
	CaX	3	2	4	1
	CEC	3	2	1	4
PH 59-1	NaX	1	3	4	2
	CaX	1	3	4	2
	CEC	1	3	4	2
PH 102-6	NaX	1	4	2	3
	CaX	3	1	4	2
	CEC	1	4	3	3
PH 104-5	NaX	3	4	1	2
	CaX	1	4	3	2
	CEC	4	3	1	2
PH 105-6	NaX	4	1	2	3
	CaX	3	4	1	2
	CEC	4	3	1	2
PH 251-14	NaX	4	3	2	1
(shale)	CaX	4	1	2	3
	CEC	4	3	2	1
PH 53-12	NaX	2	4	3	1
(shale)	CaX	1	3	2	4
	CEC	2	3	4	1
PH 100-11	NaX	4	3	2	1
(shale)	CaX	4	1	3	2
	CEC	4	3	2	1

Table 4.9 Table showing which equilibrating solution (1, 2, 3, or 4) yielded the highest and lowest exchange values upon reaction with each sample.

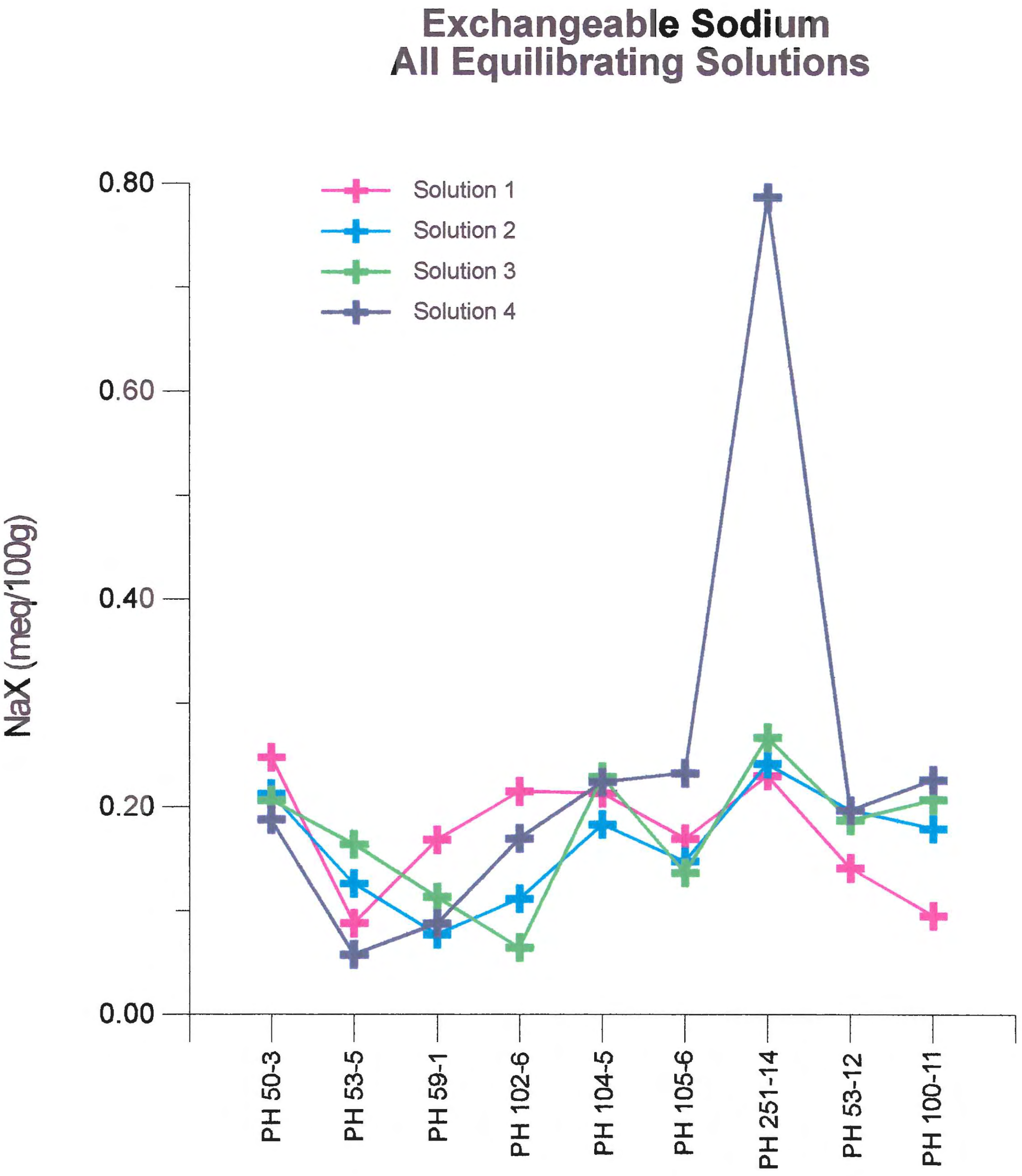

Fig. 4.13 Distribution of exchangeable sodium, by equilibrating solution, for each sample.

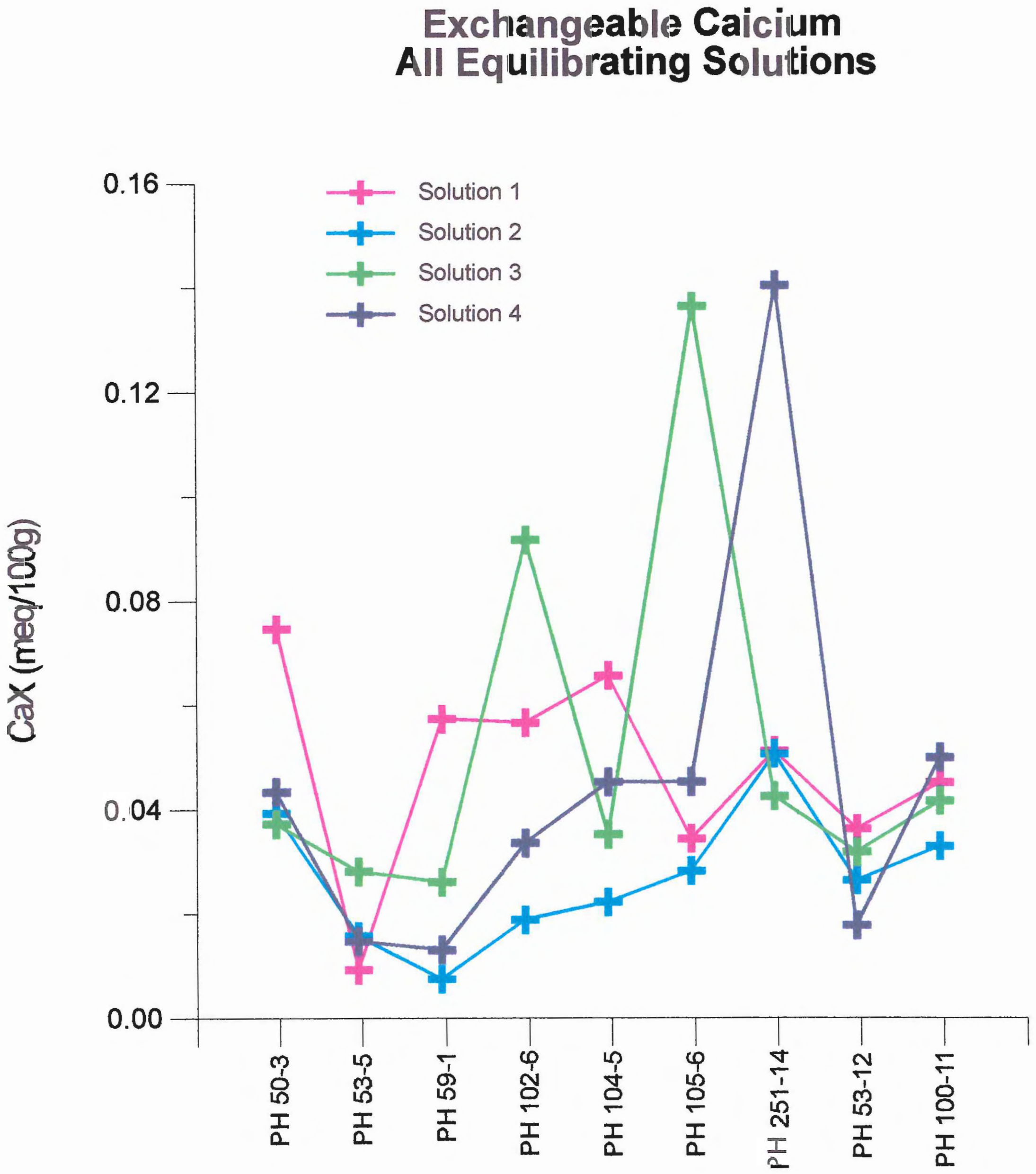

Fig. 4.14 Distribution of exchangeable calcium, by equilibrating solution, for each sample.

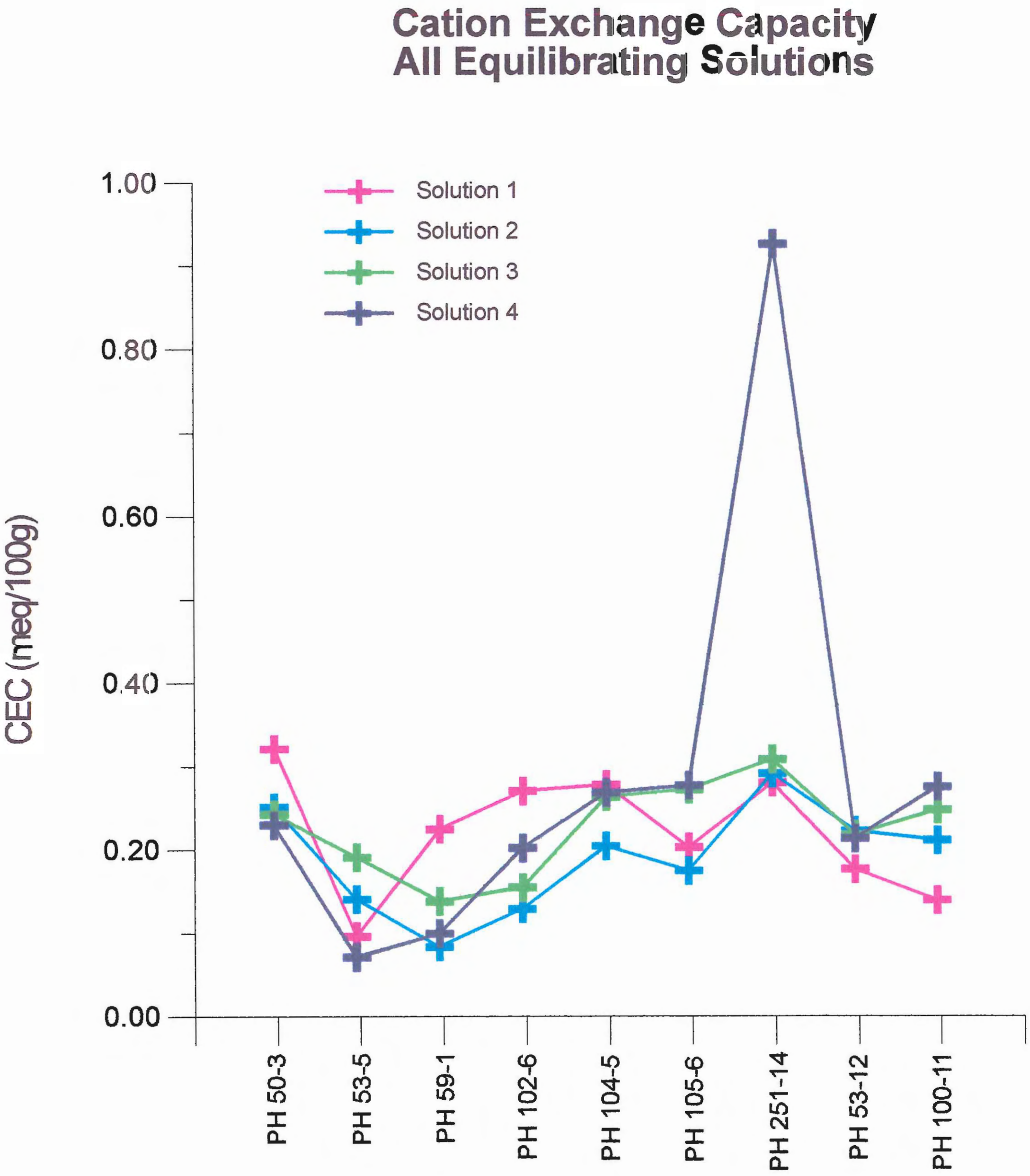

Fig. 4.15 Distribution of cation exchange capacity, by equilibrating solution, for each sample.

CHAPTER 5: DISCUSSION

5.1 Introduction

This chapter offers a discussion of the results presented in Chapter 4. Trends in Phalen formation water chemistry, and in rock cation exchange capacities, suggest the possibility of sodium-calcium cation exchange. This chapter examines the evidence of cation exchange between rocks and waters in the Phalen Colliery, and the extent and feasibility of cation exchange as a modifier of formation water chemistry. A model for cation exchange in the Phalen Colliery is offered. Other processes that may have modified the formation water chemistry are evaluated.

5.2 Evidence for a Single Water Population

Windsor brines probably ascended along fault planes to be emplaced as formation waters in the Sydney Mines Formation (Section 1.4.3). Some dilution probably occurred as the formation waters displaced the connate waters present in the Sydney Mines Formation sandstones and shales. The interpretations in this chapter are based on an assumption that Phalen formation waters are a single water population, and have been relatively immobile since emplacement.

Evidence exists that Phalen formation waters are a single water population.

Formation water trends show both chemical (Fig. 4.1) and spatial (Fig. 4.8, Fig. 4.9) continua. Continuous trends suggest that the formation waters are one population. Spatial plots of formation waters of multiple sources and histories would likely show local highs and lows, and chemical trends would be scattered and irregular.

Evidence exists that Phalen formation waters have been fairly immobile since emplacement. The formation waters presently occupy very low permeability sandstones with a high degree of calcite cementation locally (M. Gibling, pers. comm.). The low permeability and strong cementation would have impeded further movement of formation waters after emplacement. Ongoing work by Gibling, including the identification of sphalerite crystals in deep ankerite cements, suggests the brines have been in the sandstones since the period of deepest burial (M. Gibling, pers. comm.).

If Phalen formation waters are assumed to be one population and immobile, modifications to water chemistry should have occurred in situ. Thus, processes modifying the formation water chemistry are limited to interactions between the waters and the sandstones and shales into which they have been emplaced.

5.3 Evidence for Cation Exchange

5.3.1 Evidence from Formation Water Chemistry

Evidence from formation water chemistry supports the hypothesis of sodium-calcium cation exchange between formation waters and sandstones and shales in the

Phalen Colliery. Formation water chemical analyses plot in a straight line trend between Ca and Na on a Piper plot (Fig. 4.1). The variation in the relative proportions of sodium and calcium is not accompanied by a variation in anion proportions. Variation in only the relative proportions of sodium and calcium suggests exchange between the two cations. The spatial trend in formation water Na/Ca ratio (Fig. 4.9) corresponds to the Piper plot trend. The spatial trend in salinity (Fig. 4.8) correlates with the spatial trend in Na/Ca ratio.

5.3.2 Experimental Evidence

Evidence from this experiment supports the hypothesis of sodium-calcium cation exchange between formation waters and sandstones and shales in the Phalen Colliery. Exchangeable sodium and exchangeable calcium values were measured for all samples reacted with all equilibrating solutions. Had there been no exchange, all exchange values would have been measured as zero. Samples were Phalen Colliery sandstones and shales, and equilibrating solutions were modelled from Phalen formation water chemistry. Thus, the experimental procedure should simulate cation exchange between Phalen rocks and formation waters.

The most clay-rich sandstone samples have the highest measured exchangeable sodium and exchangeable calcium values. The most clay-rich samples also have the highest measured cation exchange capacity values. These trends are in accord with exchange theory. A rock with a higher clay mineral percentage has more exchange sites, more exchangeable sodium and calcium in the sites, and a higher cation exchange capacity.

5.3.3 *Model for Cation Exchange in the Phalen Colliery*

Phalen formation water salinity shows a gradual dilution trend from very saline 4WWF waters to more dilute 3S waters (Fig. 4.8). The spatial trend in salinity correlates with the spatial trend in formation water Na/Ca ratio (Fig. 4.9). Where Phalen formation waters are more dilute, the ratio of sodium to calcium in the water is higher. As salinity decreases, the formation water Na/Ca ratio increases, and the water is enriched in Na relative to Ca. Thus, formation water dilution affects sodium-calcium cation exchange.

Phalen formation waters are heterovalent solutions containing Na and Ca. Dilution of Phalen formation waters would have caused the clay exchange sites to selectively take up higher valence cations (Ca^{2+}) relative to lower valence cations (Na^{+}) (see Section 2.4.4 for the theory of dilution and exchange). The selective uptake of Ca^{2+} into clay exchange sites enriches the formation water in Na^{+}.

Figure 5.1 shows the interaction between formation waters and sandstones and shales at various formation water salinities. At first contact between rocks and formation waters, the waters are very saline and sodic, and the continental clays are calcic. At 4WWF, where the formation waters are very saline, some Na in the water substitutes for some Ca in the clay exchange sites. As a result, the water is enriched in Ca and the clay is enriched in Na. However, the enrichment pattern changes with increasing formation waters dilution. With evolution of formation waters from the saline 4WWF waters to the more dilute 3S waters there is a relative gain in Na. As the waters are diluted, the clays

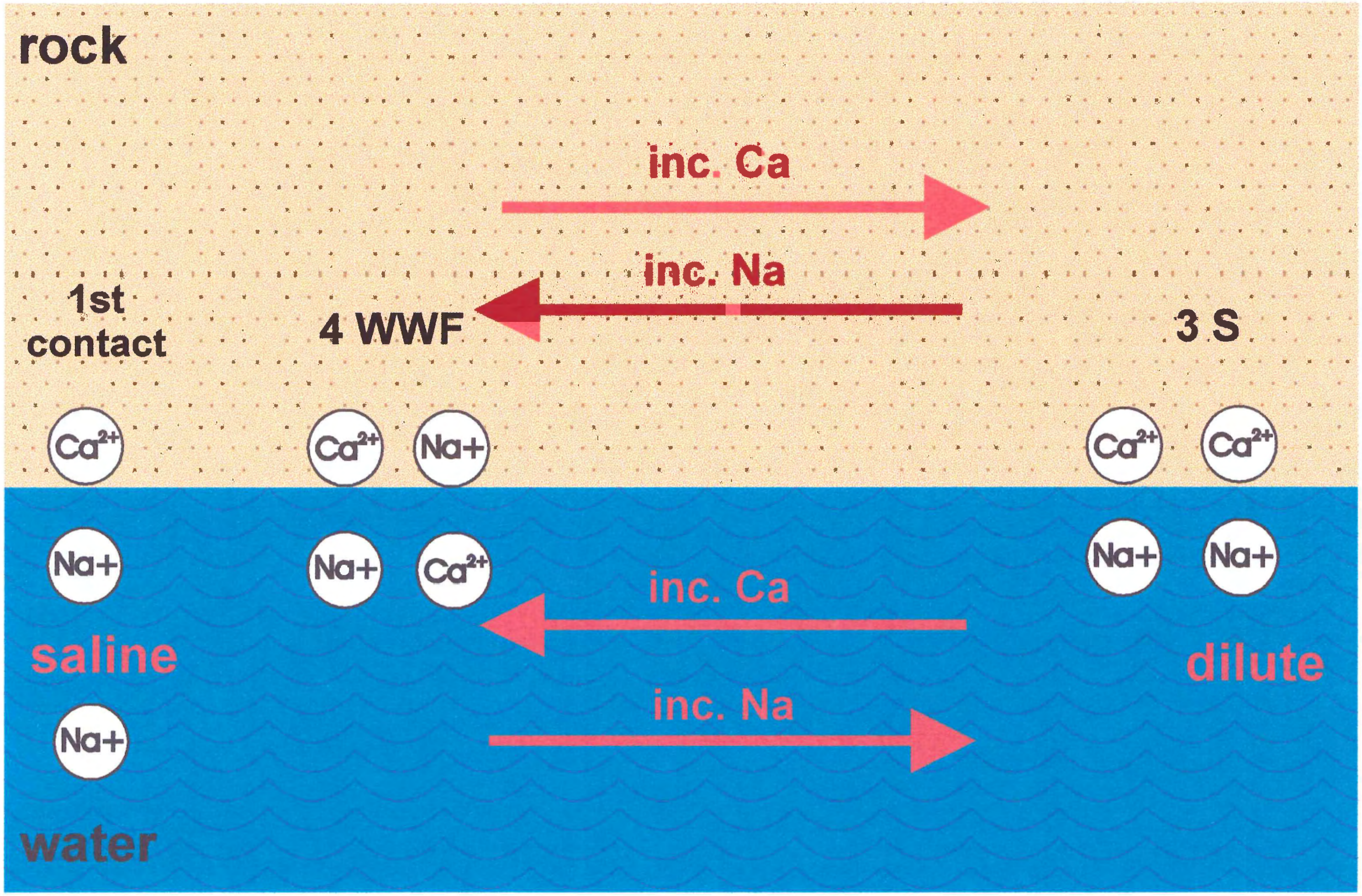

Fig. 5.1 Diagram showing the interaction between Phalen formation waters and rocks at varying formation water salinities. Red arrows indicate chemical trends. At first contact, formation waters are saline and sodic, and clays are continental and calcic. At 4WWF, Na in the water exchanges with Ca in the clay, and the water is enriched in Ca. With increasing dilution, the clay selectively uptakes the higher valence cation (Ca) into the exchange sites. As a consequence, the water is enriched in Na.

selectively take up the higher valence Ca^{2+} from the formation waters into the exchange sites. The calcium substitutes for exchangeable sodium in the exchange sites, and the sodium is released into the formation water. Increasing dilution causes increased Ca uptake into the clay, and increased Na input into the water. With dilution, formation waters become enriched in sodium. The trend of increasing sodium and decreasing calcium in diluted formation waters corresponds to the Piper plot trend (Fig. 4.1).

5.4 Exchange Feasibility

5.4.1 Experimental vs Literature CEC's

Despite evidence for sodium-calcium cation exchange in the Phalen Colliery, the experimentally determined cation exchange capacities from this study are significantly lower than literature values for the same clay groups. According to literature, CEC's for the sample mineralogy are between 3 and 40 meq/100g (Drever, 1988; Amrhein and Suarez, 1991; Appelo and Postma, 1996) (Table 2.1). All values calculated in this study are less than 1 meq/100g (Table 4.7). The maximum experimentally measured sandstone CEC is 0.322 meq/100g, the minimum sandstone CEC is 0.072 meq/100g, and the mean sandstone CEC is 0.186 meq/100g. The maximum experimentally measured shale CEC is 0.927 meq/100g, the minimum shale CEC is 0.141 meq/100g, and the mean shale CEC is 0.259 meq/100g.

The difference between experimental and literature CEC's may reflect the experimental procedure. Most literature CEC experiments are conducted on soil clays, not sandstone or shale clays. The clays in this experiment have undergone more compaction than soil clays. Greater compaction would decrease the clay surface area available for reaction with formation waters. Thus, higher literature CEC values for the sample mineralogy may result from using soil samples in experiments.

The difference between experimental and literature CEC's may reflect the experimental unsuitability. This procedure may be inapplicable to a study of Phalen rocks and formation waters. The experiment attempted to realistically model the very saline Phalen formation waters. As a result, the equilibrating solution concentrations in this study were up to two orders of magnitude higher than concentrations in the Amrhein and Suarez (1990) procedure. Extremely high salinities and concentrations may restrict the effectiveness of this procedure. The concentrated equilibrating solutions may require longer equilibration or extraction steps or a more concentrated extracting solution. In Section 4.6.2, the exchange values measured at different equilibrating solution concentrations were compared. Lower concentration solutions yielded higher exchange values. This experimental procedure may be more effective at lower concentrations, and at higher concentrations, the ability to exchange may be hindered.

Cation exchange capacity experiments, both in this study and in literature methods, are invoked under laboratory conditions and not in nature. Experiments may not accurately simulate cation exchange between rocks and waters. The procedures attempt to approximate reality, but there are certain differences. These differences must be taken into account when interpreting experimentally determined CEC's. Experiments are conducted on crushed clay-sized samples, so the surface area exposed for reaction is greater than in nature. The duration of exchange is much less than in nature. Equilibration of clays and solutions is accelerated by shaking and centrifuging, an agitation that does not occur in nature. Modern flow-through experimental procedures may be more realistic than the traditional batch experiments used here. In flow-through procedures, the ratio of clay to solution is small (Curtin et al., 1995). The clay is stationary throughout the experiment, while a mobile solution is passed through the clay. These conditions more closely approximate exchange in nature, where mobile formation waters react with pore-filling clays in a stationary rock.

The experimentally determined CEC's are low, but not zero, and so the procedure is at least somewhat effective in measuring exchange. It is possible that, because of the differences in the chemistries of Phalen formation waters and literature solutions, the exchange reactions did not go to completion and the full cation exchange capacity was not measured.

5.4.2 Required Rock Volumes

The measured exchange values for Phalen sandstones and shales are lower than the values for those clay minerals given in the literature. To examine if exchange between formation waters and present-day rocks is feasible, the rock volumes required to produce the formation water chemistry through exchange were calculated. An assumption is made that the formation waters have been relatively stationary since emplacement and that waters were diluted during emplacement (Sect. 5.2). Calculations of required rock volumes depend on the assumption that any cation exchange modifying the formation water chemistry occurred in situ.

Rock volumes required for exchange were calculated as follows. Phalen formation water sample PH-2606, from the 3S mine panel, is the most dilute water. The Cl ion acts conservatively, so the Cl ratios of each formation water sample relative to PH-2606 can be used as a dilution factor. The Na and Ca concentrations of each formation water were multiplied by the dilution factor to calculate diluted concentrations. If the dilution trend is associated with cation exchange, the difference between the Na concentration of PH-2606 and the Na concentration of another diluted water represents exchanged Na. The difference between the Ca concentration of PH-2606 and the Ca concentration of another diluted water represents exchanged Ca. Using the values for exchanged cations and the CEC, the amount of clay required for exchange with a litre of formation water was calculated for each sample (Table 5.1). Several CEC's were employed in the calculations: the minimum, maximum, and mean experimental sandstone and shale CEC's, the minimum and maximum literature illite CEC, and the minimum and maximum literature kaolinite CEC (Table 5.1).

The lowest experimental sandstone CEC requires a mean of 135 kg clay to exchange Na and 45 kg of clay to exchange Ca. The highest sandstone CEC requires a mean of 30 kg of clay to exchange Na and 10 kg of clay to exchange Ca. The mean sandstone CEC requires a mean of 52 kg of clay to exchange Na and 17 kg of clay to exchange Ca. The lowest experimental shale CEC requires a mean of 69 kg to exchange Na and 23 kg to exchange Ca. The highest shale CEC requires a mean of 10.5 kg of clay

Site	Geology	Na	Mg	Ca	Cl	Cl ratio	dil. to 3S Na	dil. to 3S Ca	3S-sample mg/L Ca	3S-sample meq/L Na	3S-sample meq/L Ca	kg clay Na exch. min ss CEC	kg clay Na exch. max ss CEC	kg clay Na exch. mean ss CEC
6	CBDC-648	40000	2600	13000	96814	0.865	34601	11245	820.25	123.93	40.93	172.1	38.5	66.6
3S	Dal PH 3S	41200	2690	12000	97780	0.856	35287	10278	147.32	94.10	7.35	130.7	29.2	50.6
3WWF	CBDC-589	40200	4400	21300	110000	0.761	30605	16216	5791.27	297.73	289.00	413.5	92.5	160.1
6 ET	CBDC-645	32750	3800	16000	96126	0.871	28532	13939	3514.37	387.91	175.38	538.8	120.5	208.6
6 ET	CBDC-646	43000	4200	17000	104955	0.798	34311	13565	3139.69	136.55	156.68	189.7	42.4	73.4
6 EB	CBDC-648	40000	2600	13000	96814	0.865	34601	11245	820.25	123.93	40.93	172.1	38.5	66.6
3 S	CBDC-663	40600	2370	11400	95525	0.877	35594	9994	430.71	80.74	21.49	112.1	25.1	43.4
2 CB	CBDC-664	38000	3220	15700	101945	0.821	31216	12897	2472.27	271.15	123.37	376.6	84.2	145.8
2 CB	CBDC-665	41050	3390	15800	103834	0.807	33108	12743	2318.29	188.85	115.69	262.3	58.6	101.5
9 ET	PH-2835	45800	2550	12450	97135	0.862	39487	10734	308.90	88.60	15.42	123.1	27.5	47.6
9 ET	PH-2841	46700	2630	12800	97605	0.858	40069	10983	557.52	113.92	27.82	158.2	35.4	61.2
9 ET	PH-2847	46450	2630	12700	98546	0.850	39474	10793	367.67	88.04	18.35	122.3	27.3	47.3
3 S	PH-2850	43450	2725	12300	96956	0.864	37530	10624	199.16	3.48	9.94	4.8	1.1	1.9
3 S	PH-2621	40400	2110	8910	87200	0.960	38800	8557	1867.93	58.71	93.21	81.5	18.2	31.6
3 S	PH-2606	37450	2070	10425	83746	1.000	37450	10425						
8 ET	PH-2264	43000	2650	12300	98362	0.851	36610	10472	47.29	36.52	2.36	50.7	11.3	19.6
9 ET	PH-1611	41950	2515	12550	97050	0.863	36199	10830	404.60	54.40	20.19	75.6	16.9	29.2
9 ET	PH-1612	46450	2460	13000	97828	0.856	39764	11129	703.70	100.64	35.12	139.8	31.3	54.1
7 ET	PH-1229	41000	2780	15600	103716	0.807	33106	12596	2171.30	188.97	108.35	262.5	58.7	101.6
8 EB	PH-1200	41900	2540	11700	96754	0.866	36267	10127	298.00	51.47	14.87	71.5	16.0	27.7
8 ET	PH-976	41150	2360	12400	95828	0.874	35962	10837	411.61	64.73	20.54	89.9	20.1	34.8
3 S	PH-697	42100	2490	12300	98919	0.847	35642	10413	11.67	78.63	0.58	109.2	24.4	42.3
6 ET	PH-407	37300	3570	17100	100788	0.831	30993	14209	3783.60	280.86	188.81	390.1	87.2	151.0
2 CB	PH-441	40150	2825	13800	94257	0.888	35673	12261	1836.10	77.31	91.63	107.4	24.0	41.6
9EB	Dal PH 9EBN	44800	2660	11900	92900	0.901	40386	10727	302.42	127.69	15.09	177.3	39.7	68.7
											max:	538.76	120.47	208.55
											min:	4.836	1.081	1.872
											mean:	134.59	30.09	52.10

Table 5.1 Calculations of the amount of clay required for exchange to produce the formation water chemistry. Water sodium and calcium concentrations are multiplied by a dilution factor, and several CEC's are used to calculate the required amounts of clay, in kg. Maximum, minimum, and mean amounts of required clay are listed at the bottom.

Site	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay
	Na exch.	Na exch.	Na exch.	Na exch.	Na exch.	Na exch.	Na exch.	Na exch.	Na exch.	Ca exch.	Ca exch.	Ca exch.	Ca exch.
	min sh	max sh	mean sh	min illite	max illite	min kaol	max kaol	min chl	max chl	min ss	max ss	mean ss	min sh
	CEC	CEC	CEC	CEC	CEC	CEC	CEC	CEC	CEC	CEC	CEC	CEC	CEC
6	87.9	13.4	47.9	1.24	0.31	4.13	0.83	12.39	1.24	56.85	12.71	22.01	29.03
3S	66.7	10.2	36.3	0.94	0.24	3.14	0.63	9.41	0.94	10.21	2.28	3.95	5.21
3WWF	211.2	32.1	115.0	2.98	0.74	9.92	1.98	29.77	2.98	401.39	89.75	155.38	204.96
6 ET	275.1	41.8	149.8	3.88	0.97	12.93	2.59	38.79	3.88	243.58	54.46	94.29	124.38
6 ET	96.8	14.7	52.7	1.37	0.34	4.55	0.91	13.66	1.37	217.61	48.66	84.24	111.12
6 EB	87.9	13.4	47.9	1.24	0.31	4.13	0.83	12.39	1.24	56.85	12.71	22.01	29.03
3 S	57.3	8.7	31.2	0.81	0.20	2.69	0.54	8.07	0.81	29.85	6.68	11.56	15.24
2 CB	192.3	29.3	104.7	2.71	0.68	9.04	1.81	27.12	2.71	171.35	38.31	66.33	87.50
2 CB	133.9	20.4	72.9	1.89	0.47	6.30	1.26	18.89	1.89	160.68	35.93	62.20	82.05
9 ET	62.8	9.6	34.2	0.89	0.22	2.95	0.59	8.86	0.89	21.41	4.79	8.29	10.93
9 ET	80.8	12.3	44.0	1.14	0.28	3.80	0.76	11.39	1.14	38.64	8.64	14.96	19.73
9 ET	62.4	9.5	34.0	0.88	0.22	2.93	0.59	8.80	0.88	25.48	5.70	9.86	13.01
3 S	2.5	0.4	1.3	0.03	0.01	0.12	0.02	0.35	0.03	13.80	3.09	5.34	7.05
3 S	41.6	6.3	22.7	0.59	0.15	1.96	0.39	5.87	0.59	129.46	28.95	50.12	66.11
3 S													
8 ET	25.9	3.9	14.1	0.37	0.09	1.22	0.24	3.65	0.37	3.28	0.73	1.27	1.67
9 ET	38.6	5.9	21.0	0.54	0.14	1.81	0.36	5.44	0.54	28.04	6.27	10.86	14.32
9 ET	71.4	10.9	38.9	1.01	0.25	3.35	0.67	10.06	1.01	48.77	10.91	18.88	24.91
7 ET	134.0	20.4	73.0	1.89	0.47	6.30	1.26	18.90	1.89	150.49	33.65	58.25	76.85
8 EB	36.5	5.6	19.9	0.51	0.13	1.72	0.34	5.15	0.51	20.65	4.62	8.00	10.55
8 ET	45.9	7.0	25.0	0.65	0.16	2.16	0.43	6.47	0.65	28.53	6.38	11.04	14.57
3 S	55.8	8.5	30.4	0.79	0.20	2.62	0.52	7.86	0.79	0.81	0.18	0.31	0.41
6 ET	199.2	30.3	108.4	2.81	0.70	9.36	1.87	28.09	2.81	262.24	58.64	101.51	133.91
2 CB	54.8	8.3	29.8	0.77	0.19	2.58	0.52	7.73	0.77	127.26	28.46	49.26	64.98
9EB	90.6	13.8	49.3	1.28	0.32	4.26	0.85	12.77	1.28	20.96	4.69	8.11	10.70
max:	275.11	41.85	149.77	3.88	0.97	12.93	2.59	38.79	3.88	401.39	89.75	155.38	204.96
min:	2.470	0.376	1.344	0.035	0.009	0.116	0.023	0.348	0.035	0.809	0.181	0.313	0.413
mean:	68.72	10.45	37.41	0.97	0.24	3.23	0.65	9.69	0.97	45.05	10.07	17.44	23.01

Table 5.1 continued

Site	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay	kg clay
	Ca exch.	Ca exch.	Ca exch.	Ca exch.	Ca exch.	Ca exch.	Ca exch.	Ca exch.
	max sh	mean sh	min illite	max illite	min kaol	max kaol	min chl	max chl
	CEC	CEC	CEC	CEC	CEC	CEC	CEC	CEC
6	4.42	15.80	0.409	0.102	1.36	0.27	4.09	0.41
3S	0.79	2.84	0.074	0.018	0.25	0.05	0.74	0.07
3WWF	31.18	111.58	2.890	0.722	9.63	1.93	28.90	2.89
6 ET	18.92	67.71	1.754	0.438	5.85	1.17	17.54	1.75
6 ET	16.90	60.49	1.567	0.392	5.22	1.04	15.67	1.57
6 EB	4.42	15.80	0.409	0.102	1.36	0.27	4.09	0.41
3 S	2.32	8.30	0.215	0.054	0.72	0.14	2.15	0.21
2 CB	13.31	47.63	1.234	0.308	4.11	0.82	12.34	1.23
2 CB	12.48	44.67	1.157	0.289	3.86	0.77	11.57	1.16
9 ET	1.66	5.95	0.154	0.039	0.51	0.10	1.54	0.15
9 ET	3.00	10.74	0.278	0.070	0.93	0.19	2.78	0.28
9 ET	1.98	7.08	0.183	0.046	0.61	0.12	1.83	0.18
3 S	1.07	3.84	0.099	0.025	0.33	0.07	0.99	0.10
3 S	10.06	35.99	0.932	0.233	3.11	0.62	9.32	0.93
3 S								
8 ET	0.25	0.91	0.024	0.006	0.08	0.02	0.24	0.02
9 ET	2.18	7.80	0.202	0.050	0.67	0.13	2.02	0.20
9 ET	3.79	13.56	0.351	0.088	1.17	0.23	3.51	0.35
7 ET	11.69	41.84	1.084	0.271	3.61	0.72	10.84	1.08
8 EB	1.60	5.74	0.149	0.037	0.50	0.10	1.49	0.15
8 ET	2.22	7.93	0.205	0.051	0.68	0.14	2.05	0.21
3 S	0.06	0.22	0.006	0.001	0.02	0.00	0.06	0.01
6 ET	20.37	72.90	1.888	0.472	6.29	1.26	18.88	1.89
2 CB	9.88	35.38	0.916	0.229	3.05	0.61	9.16	0.92
	1.63	5.83	0.151	0.038	0.50	0.10	1.51	0.15
max:	31.18	111.58	2.89	0.72	9.63	1.93	28.90	2.89
min:	0.063	0.225	0.006	0.001	0.019	0.004	0.058	0.006
mean:	3.50	12.52	0.32	0.08	1.08	0.22	3.24	0.32

Table 5.1 continued

to exchange Na and 3.5 kg of clay to exchange Ca. The mean shale CEC requires a mean of 37 kg of clay to exchange Na and 12.5 kg of clay to exchange Ca.

Sample porosity must be accounted for when interpreting exchange feasibility. Formation waters occupy the pore spaces of sandstones and shales (Drever, 1988). Cation exchange occurs between the formation waters and the clays that fill or rim the pores. In a sandstone sample of 10% porosity, only 10% of the calculated rock volume is available for exchange between formation water and clays. Phalen samples generally have a higher percent clay than percent pore spaces, thus a higher volume of clay is available for reaction with a smaller volume of water (T. Martel, pers. comm.). Phalen shales have a higher porosity than sandstones, and a much higher percent clay. The density of clay is over two times the density of water (Weaver, 1989). Therefore, if a sandstone contains 10% clay and 10% porosity (the space occupied by formation water), twice as much clay is required in order to have the same volume as the water.

Literature CEC values for the Phalen sample clays are higher than experimental CEC's. For comparison, the calculations of rock volumes required for exchange were performed using literature CEC's for kaolinite and illite, the most common and the highest CEC clays in the Phalen samples. The minimum literature illite CEC requires a mean of 0.97 kg of clay to exchange Na and 0.32 kg to exchange Ca. The maximum literature illite CEC requires a mean of 0.24 kg of clay to exchange Na and 0.08 kg to exchange Ca. The minimum literature kaolinite CEC requires a mean of 3.2 kg of clay to exchange Na and 1.1 kg to exchange Ca. The maximum literature kaolinite CEC requires a mean of 0.65 kg of clay to exchange Na and 0.22 kg of clay to exchange Ca.

Using literature CEC's for the clay minerals present in the Phalen samples, the rock volumes required to exchange sodium and calcium are less than the rock volumes required using the experimental CEC's. Despite the discrepancy between the experimental and literature CEC's, for the reasons discussed above, clays in the Phalen sandstones and shales could have adequately exchanged sodium and calcium with formation waters and modified the water chemistry to the degree observed.

5.5 Possible explanations for the Na/Ca Trend With Dilution

Formation waters vary in Na/Ca ratio spatially across the Phalen Colliery (Fig. 4.9). The spatial Na/Ca ratio trend correlates with a spatial salinity trend (Fig. 4.8). More dilute formation waters are enriched in sodium (Sect. 5.3.3). Several hypotheses are presented to explain the observed formation water chemical trends: cation exchange with Phalen sandstones and shales with present mineralogies, historic exchange with Sydney Mines Formation and Windsor Group smectite, and other chemical reactions.

5.5.1 Cation Exchange with Sydney Mines Formation Kaolinite and Illite

5.5.1.1 Cation exchange at experimental CEC's

The experimentally determined CEC's of Sydney Mines Formation clays in the Phalen Colliery are lower than literature values for kaolinite and illite. Despite the discrepancy, cation exchange between formation waters and sandstones and shales may be a feasible process for modifying formation water chemistry. Figure 5.2 is a proposed

Proposed Exchange Timeline

340 Ma	295 Ma	Mid Carboniferous to Triassic	Post-Carboniferous
Windsor brines form ⇨	Sydney Mines Formation deposited (Phalen shales and sandstones) ⇨	Brines move Brines emplaced as Phalen formation waters ⇨	Formation waters exchange with Phalen clays

Fig. 5.2 Timeline of the events of brine formation and movement, Sydney Mines Formation deposition, and sodium-calcium cation exchange. Dates are from Boehner (1986), Rust et al. (1987), and Martel and Gibling (in prep.).

timeline of the generation, movement, and emplacement of brines as formation waters, and of exchange between formation waters and Phalen clays.

This experiment was conducted on six sandstone and three shale samples from the Phalen Colliery. This small sampling may not represent the large channel sandstones in the Colliery. CEC's may be higher or lower in other sandstone samples. This study has identified a direct relationship between sample clay percentage and CEC. Phalen sandstones with higher clay percentages may have higher cation exchange capacities than the samples tested in this study. Cation exchange with formation waters in shales may have played a more important role. Formation waters may have interacted with larger than expected rock volumes before dilution.

5.5.1.2 Cation exchange at literature CEC's

Sydney Mines Formation kaolinite and illite may have higher CEC's than those recorded in this experiment. If the clays have the CEC's cited in literature, cation exchange could account for the amounts of exchanged sodium and calcium in the formation waters. The discrepancy between literature and experimental CEC's may reflect the suitability of the experiment (as discussed in Sect. 5.4.1). Also, it is possible that at the time of exchange with formation waters, the kaolinite and illite CEC's resembled the literature CEC's and have since decreased. Sediment compaction after exchange would have reduced the clay surface area exposed for reaction with formation water. The capacity of the clay to exchange sodium and calcium could have decreased, perhaps to the experimental values.

5.5.2 Historic Exchange with Smectite

5.5.2.1 Cation exchange with Sydney Mines Formation smectite

Phalen formation water chemistry may have been modified early in the water history. There is evidence from vertisol-type paleosols in the Sydney Mines Formation that smectite was present in the clay mineralogy (Tandon and Gibling, 1994). Smectite is a high CEC clay which converts to illite upon burial (Hower et al., 1976).

Phalen formation water chemistry may have been affected by exchange with smectite which has since converted to illite. Windsor Group brines were generated at ~340 Ma (Boehner, 1986). The Sydney Mines Formation was deposited at ~295 Ma (Rust et al., 1987). Windsor brines are inferred to have moved upwards along fault planes in the Mid-Carboniferous or later, and were emplaced in the Sydney Mines Formation to become formation waters. The formation waters could have exchanged with smectite in the pore spaces. At ~280 Ma, up to four km of sediments buried the Sydney Mines Formation (Ryan and Zentilli, 1993). Burial may have invoked the smectite-illite transition, and the waters could have undergone subsequent exchange with illite. If formation water chemistry reflects a historic exchange event with smectite, the exchange cannot be experimentally recreated with the present mineralogy.

Ongoing work by Gibling suggests that the brines entered the Sydney Mines Formation during deep burial, when smectite may already have been converted to illite (M. Gibling, pers. comm.). If this is the case, exchange between brines and large volumes of Sydney Mines Formation smectite is unlikely. The hypothesis of exchange with Phalen Sydney Mines Formation smectite is not favoured.

5.5.2.2 Cation Exchange with Windsor Group smectite

Brines may have exchanged with smectite or other clays in the Windsor Group before smectite converted to illite (M. Gibling, pers. comm.). Exchange with smectite may have occurred before or as the brines migrated. An exchange episode prior to the deposition of the Sydney Mines Formation does not accord with the evidence that formation waters are one population, and that the chemical modification occurred in situ in the Phalen sandstones and shales (Sect. 5.2). The hypothesis of exchange between formation waters and Windsor Group clays is not favoured.

5.5.3 Other Chemical Reactions

Other chemical reactions may have acted independently, or in conjunction with cation exchange, to modify the formation water chemistry. Precipitation of calcite could decrease, and dissolution of calcite could increase, the amount of calcium in the formation waters. However, geochemical modelling has shown that calcite, gypsum, and dolomite are undersaturated in the Phalen Colliery (T. Martel, pers. comm.). Formation water HCO_3^- concentration is constant as Na and Ca concentrations vary with decreasing salinity (Fig. 4.1). This evidence suggests that chemical reactions involving calcite, gypsum, and dolomite are unlikely. The hypothesis of other chemical reactions modifying formation water chemistry is not favoured.

5.5.4 Summary of Possibilities

Phalen formation water chemistry has been modified from the original Windsor brine water chemistry. Figure 5.3 shows the possible chemical water-rock reactions and exchange events which may have, separately or in some combination, modified the formation water chemistry. Formation water chemistry may have been modified by 1) cation exchange with Sydney Mines Formation kaolinite and illite at experimentally measured cation exchange capacities, 2) cation exchange with Sydney Mines Formation kaolinite and illite at cation exchange capacities cited in the literature, 3) calcite precipitation, dissolution, and diagenetic reactions, 4) early cation exchange with Sydney Mines Formation smectite, or 4) early cation exchange with Windsor Group smectite during brine reflux and migration. This study has concentrated on the role of cation exchange with present-day Sydney Mines Formation clays. The favoured hypothesis is that cation exchange between Phalen formation waters and kaolinites and illites in the sandstones and shales modified the formation water chemistry. The sodium-calcium cation exchange accounts for the Piper plot chemical trend, and for the variation in formation water Na/Ca ratio with dilution.

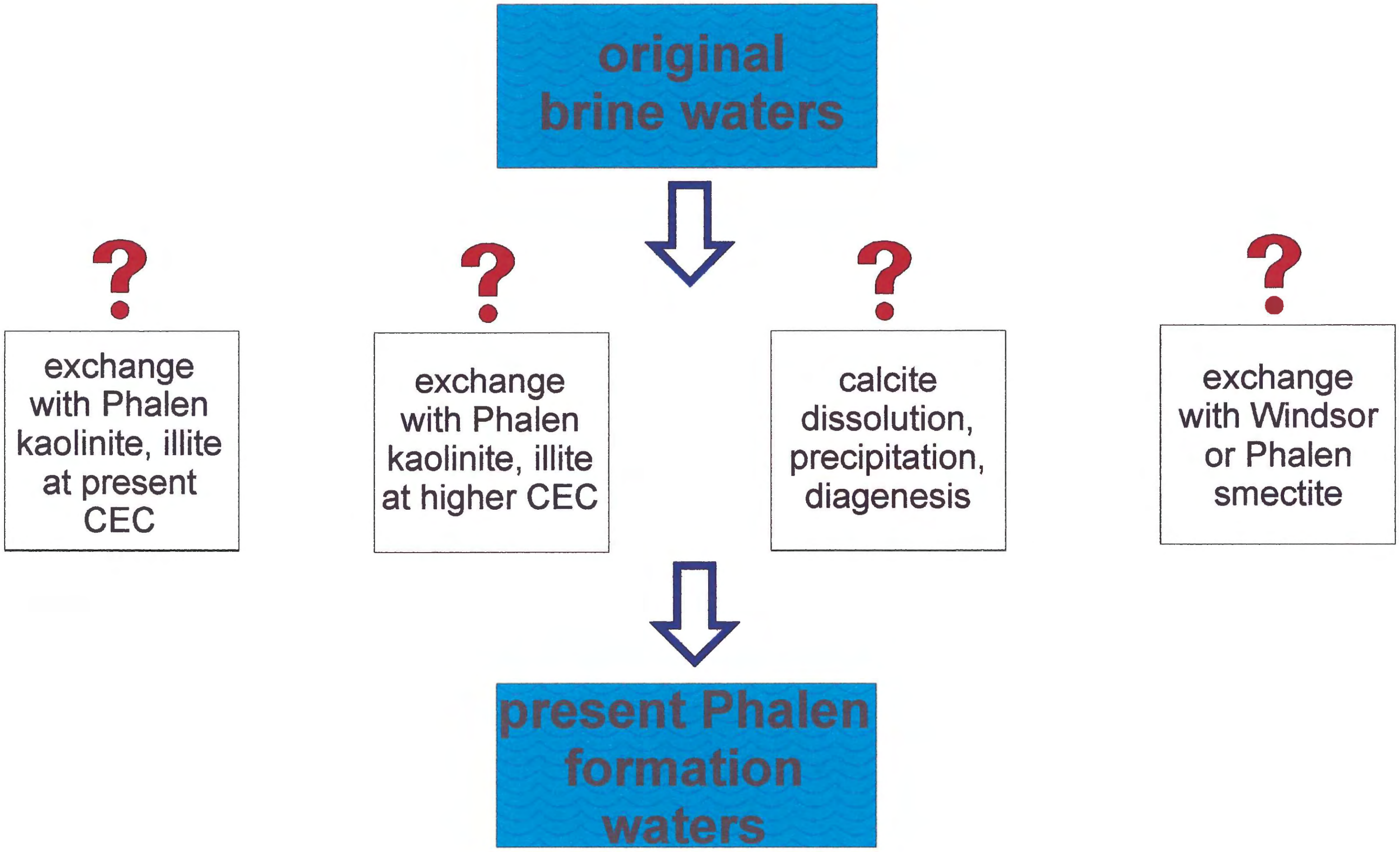

Fig. 5.3 Summary of possible processes which may have modified the chemical composition of the original brine waters to the chemistry of the present Phalen formation waters. The favoured hypothesis is cation exchange between formation waters and clays in Phalen sandstones and shales.

CHAPTER 6: CONCLUSIONS

6.1 Conclusions

This study tested the hypothesis of cation exchange between sandstones and shales and formation waters in the Phalen Colliery as a process modifying formation water chemistry. Mineralogy, porosity, and pore-filling of sample sandstones and shales were identified. Chemical trends in formation waters were examined. This experiment simulated cation exchange between Phalen formation waters and sandstones and shales, and measured cation exchange capacities for each rock sample. Formation water chemistry trends were related to cation exchange trends.

Analysis of sandstones and shales in the Phalen Colliery gives the following conclusions:

1. Porosity ranges from 1 to 25% in the sandstone samples studied.
2. Clay mineralogy is predominantly chlorite, kaolinite, and illite.
3. Clay percentage ranges from 6 to 13% in the sandstone samples studied. Most clay is pore-filling.

Analysis of Phalen formation water chemistry gives the following conclusions:

1. Formation water chemistry has been modified from an original evaporative residue chemistry.
2. On a Piper plot, Phalen formation water chemical analyses show a straight line trend between calcium and sodium. The trend suggests sodium-calcium cation

exchange.

3. Formation water Na/Ca ratio varies spatially across the Phalen Colliery, with higher Na/Ca ratios in the northeast portion of the mine and lower Na/Ca ratios in the southwest portion of the mine.
4. Formation water salinity varies spatially across the Phalen Colliery, with higher salinities west in the mine and lower salinities east in the mine.
5. The spatial trend in formation water Na/Ca ratio correlates with the spatial trend in salinity. Formation waters with high Na/Ca ratios are low salinity, formation waters with low Na/Ca ratios are high salinity. Dilution of formation waters causes an enrichment of Na in the water.
6. Continuous trends in salinity and Na-Ca chemistry, and the low permeability of Phalen sandstones and shales, imply that Phalen formation waters are a single population.

The experiment to determine cation exchange capacity of sandstones and shales in the Phalen Colliery gives the following conclusions:

1. Cation exchange capacity ranges from 0.07 to 0.93 meq/100g. Exchangeable sodium ranges from 0.06 to 0.79 meq/100g. Exchangeable calcium ranges from 0.008 to 0.14 meq/100g.
2. There is a positive relationship between sample clay percentage and 1) cation exchange capacity, 2) exchangeable sodium, and 3) exchangeable calcium.
3. Cation exchange capacity is more dependent on the abundance of clay-filled pores than on actual sample porosity.

4. The favoured explanation for the formation water Na/Ca trend with dilution is cation exchange between formation waters and in situ clays. Sodium-calcium cation exchange likely occurred after emplacement of formation waters in Phalen sandstones and shales. Experimental CEC values may be underestimated, or may have changed over time.

6.2 Recommendations for Future Work

Further research for this project should involve the following aspects:

- Experiments on a greater number of Phalen sandstone and shale samples to determine variability and spatial trends in cation exchange capacity.
- Detailed mapping of clay distribution in the Phalen Colliery.
- Research into the effects of high solution salinities on cation exchange capacity experiments.
- Experimental runs using a more concentrated, or a different composition, extracting solution. Runs with longer equilibration and extraction steps.
- Experimental runs using equilibrating solution concentrations modelled after the original Windsor brine chemical composition to simulate the first exchange event.
- Experimental runs using flow-through methods, and comparison of results with batch method results.

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APPENDIX A

X-Ray Diffraction Peak Graphs

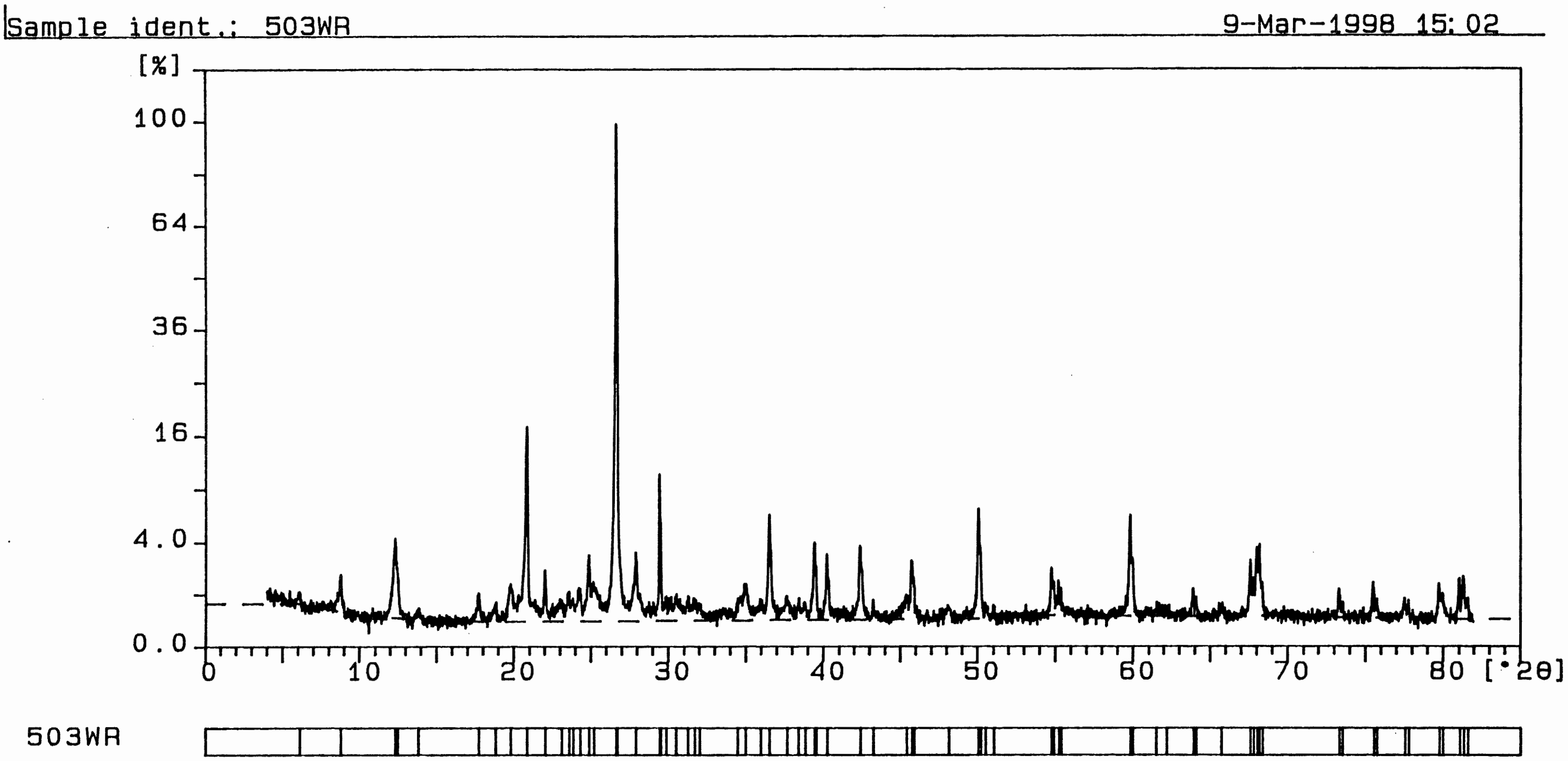

Fig A1 X-ray diffraction mineral peak graph for the whole-rock portion of sandstone sample PH 50-3.

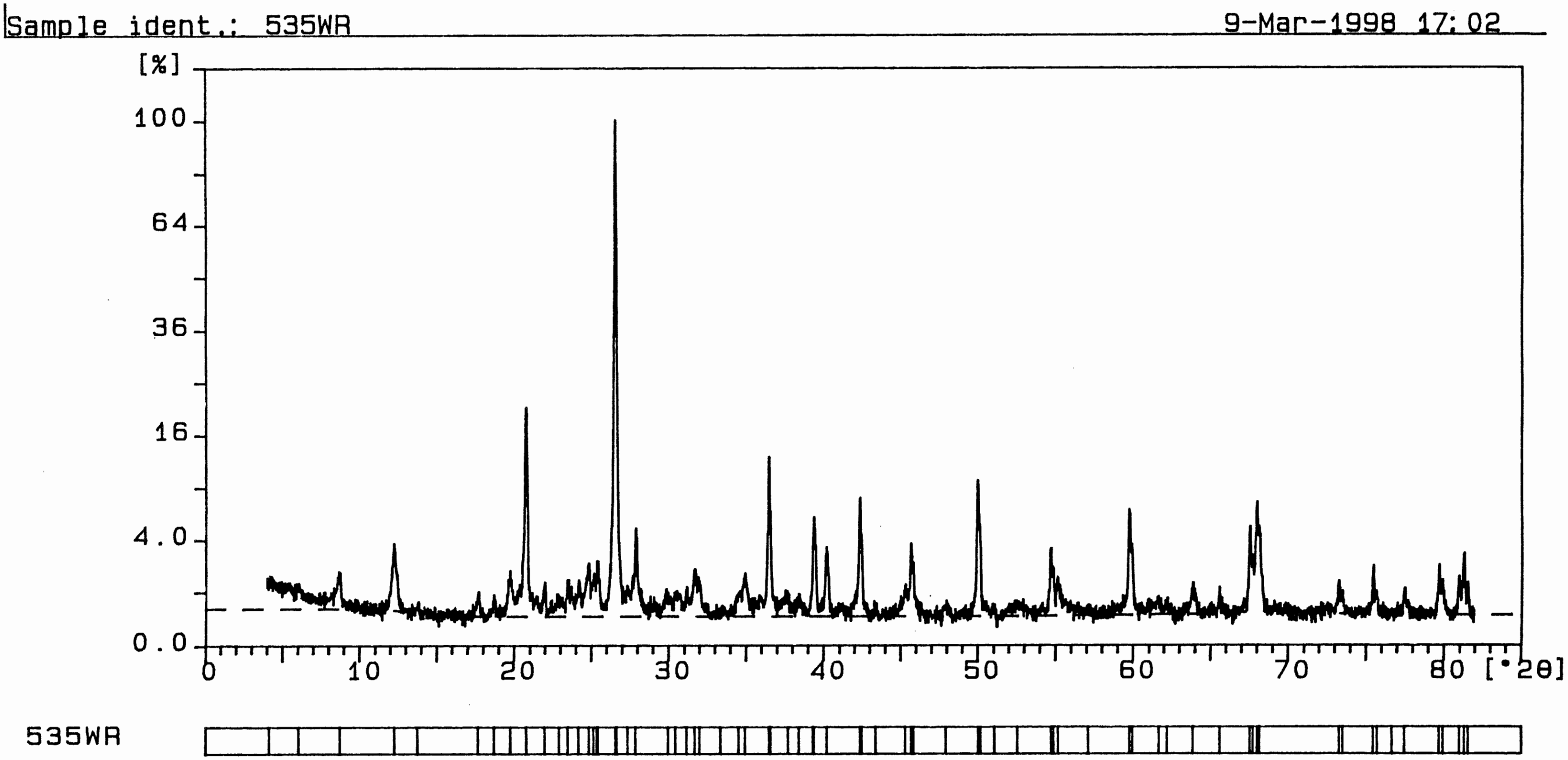

Fig A2 X-ray diffraction mineral peak graph for the whole-rock portion of sandstone sample PH 53-5.

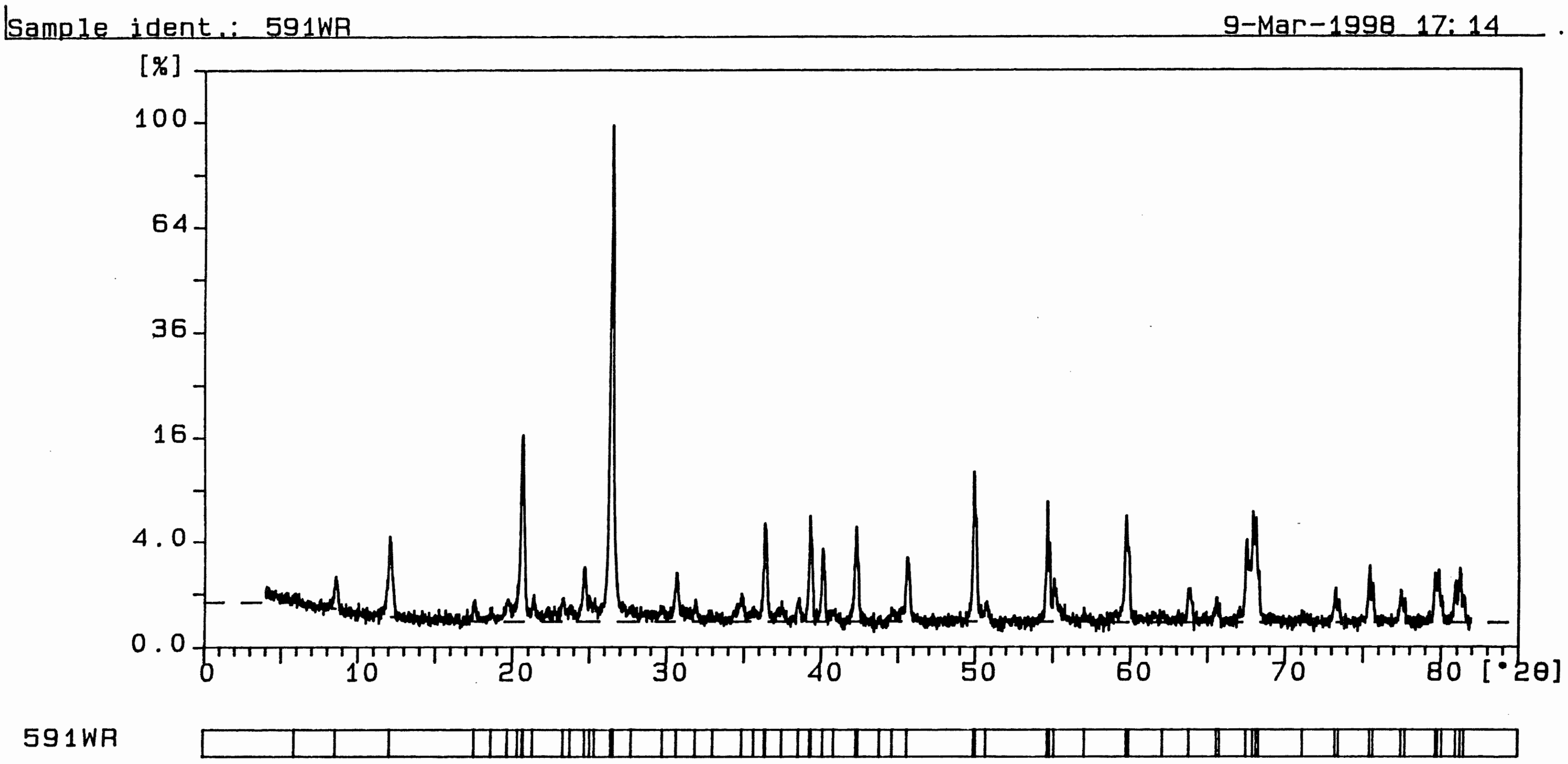

Fig A3 X-ray diffraction mineral peak graph for the whole-rock portion of sandstone sample PH 59-1.

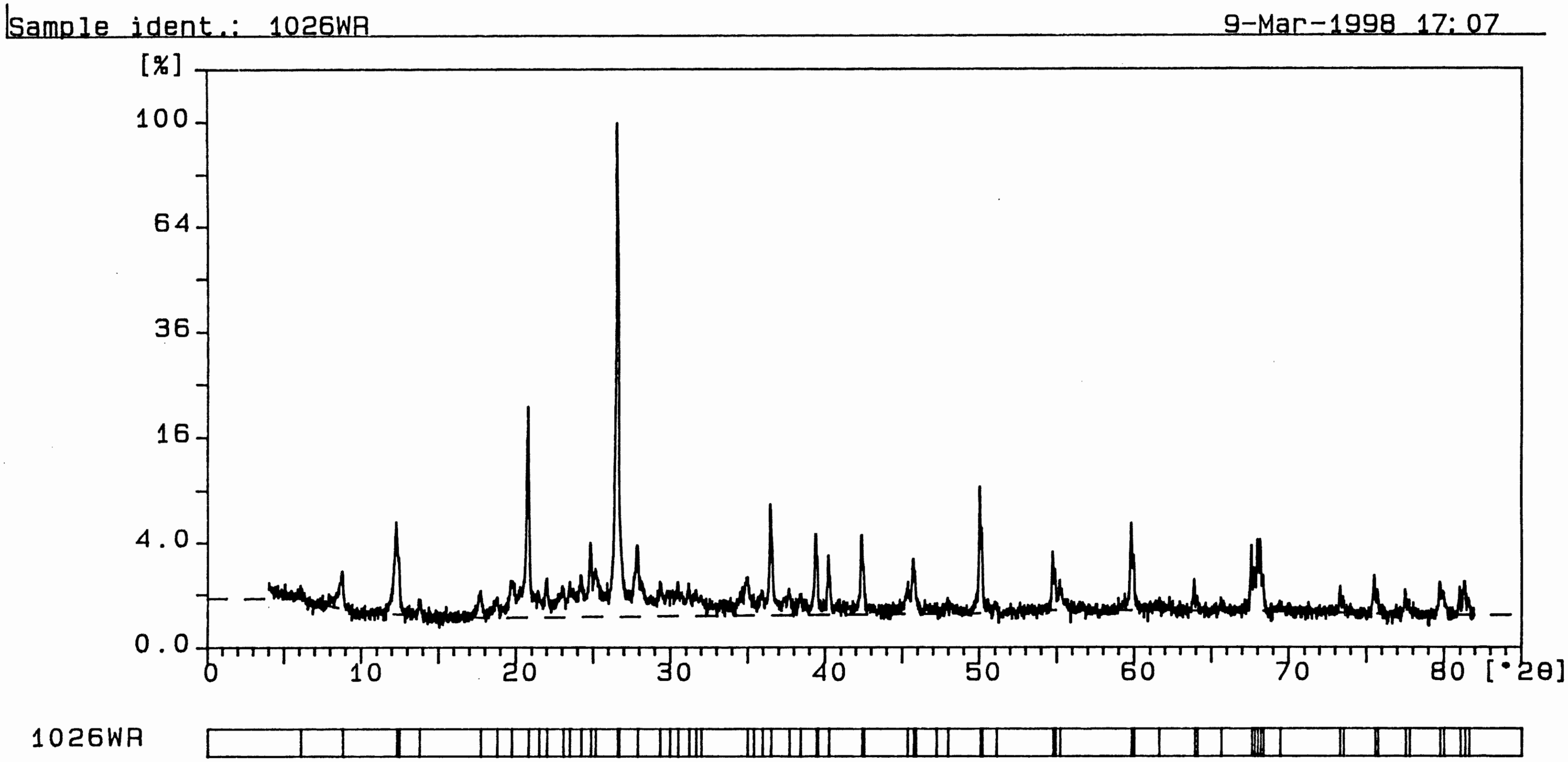

Fig A4 X-ray diffraction mineral peak graph for the whole-rock portion of sandstone sample PH 102-6.

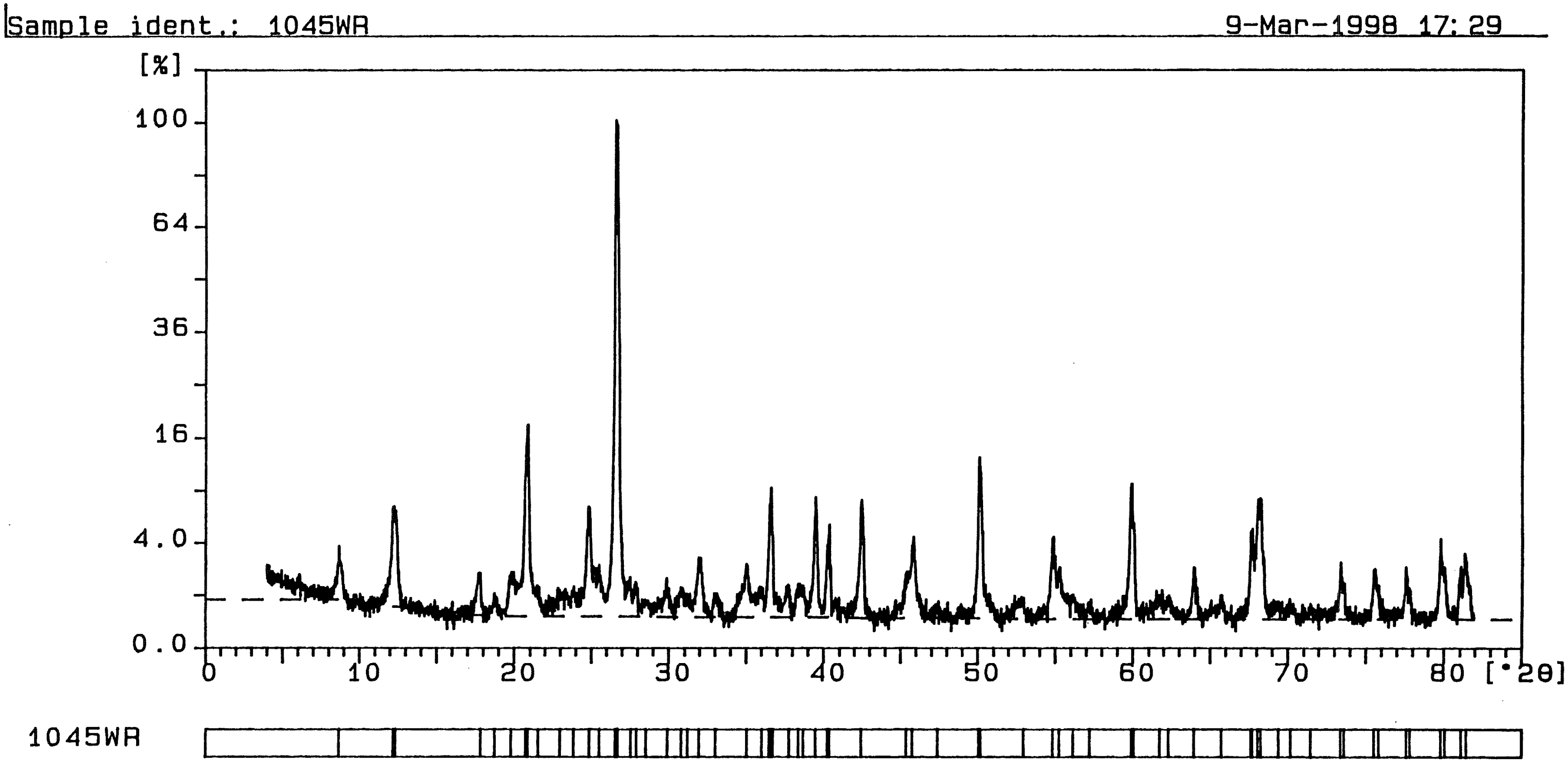

Fig A5 X-ray diffraction mineral peak graph for the whole-rock portion of sandstone sample PH 104-5.

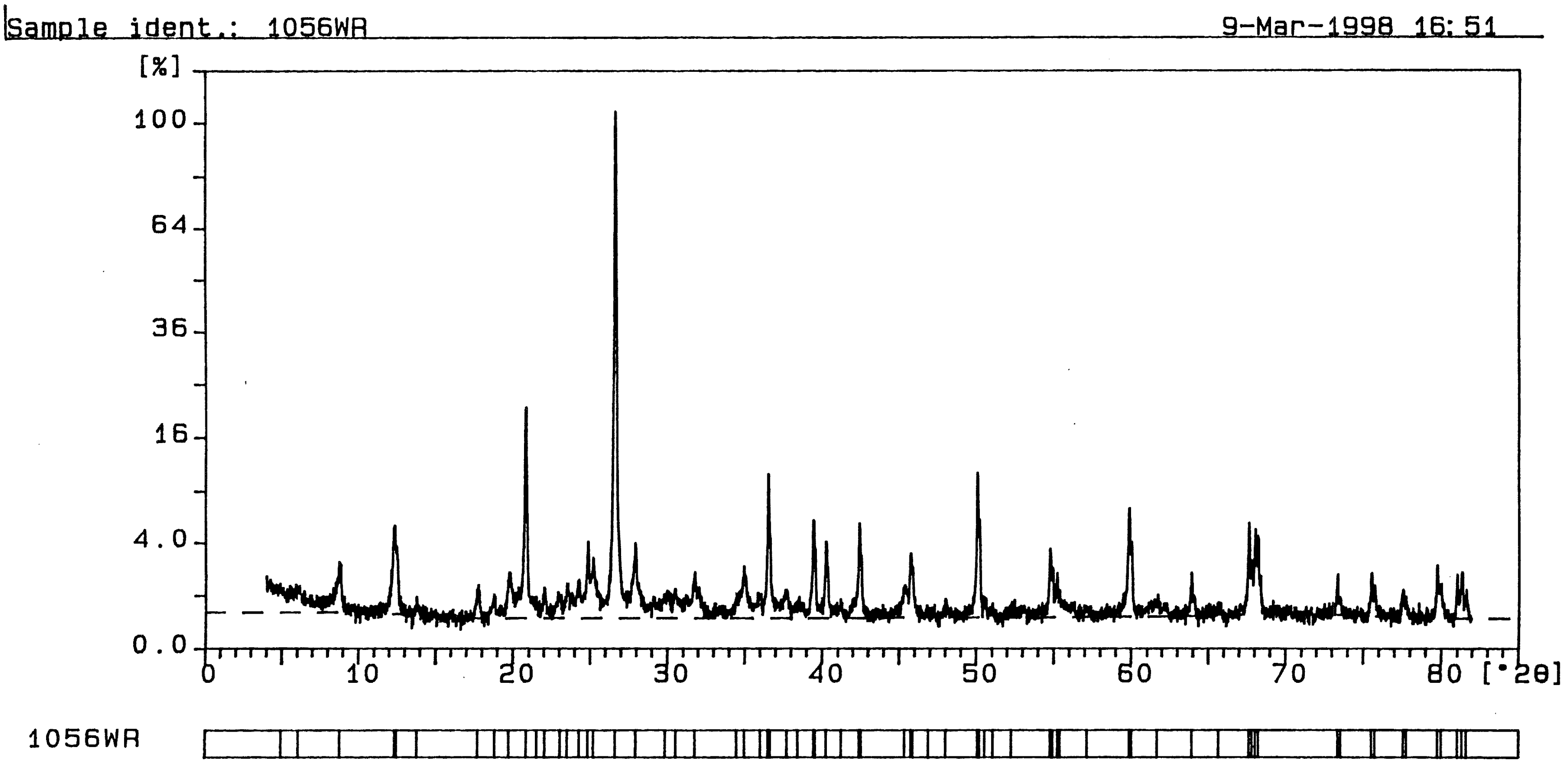

Fig A6 X-ray diffraction mineral peak graph for the whole-rock portion of sandstone sample PH 105-6.

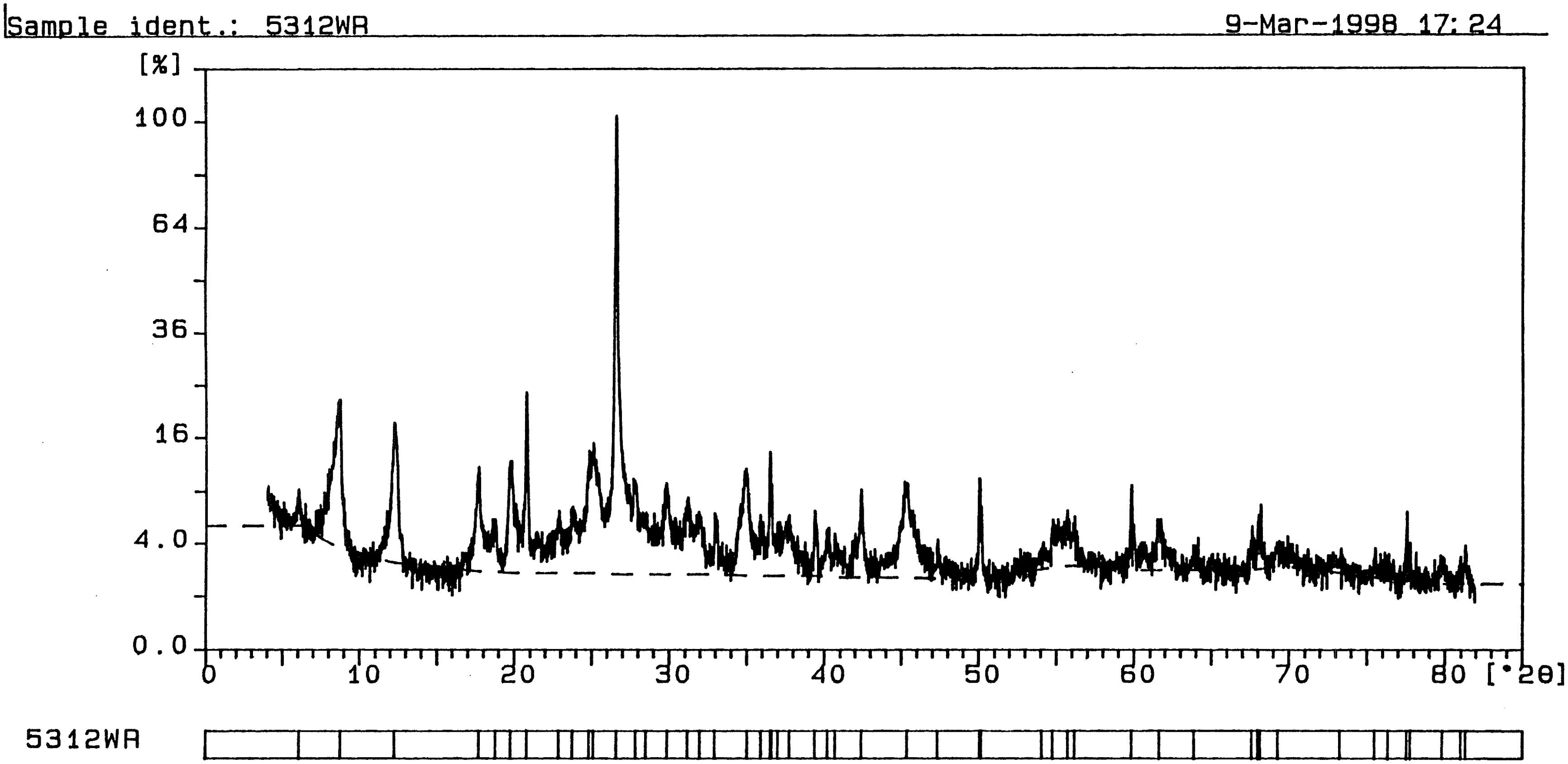

Fig A7 X-ray diffraction mineral peak graph for the whole-rock portion of shale sample PH 53-12.

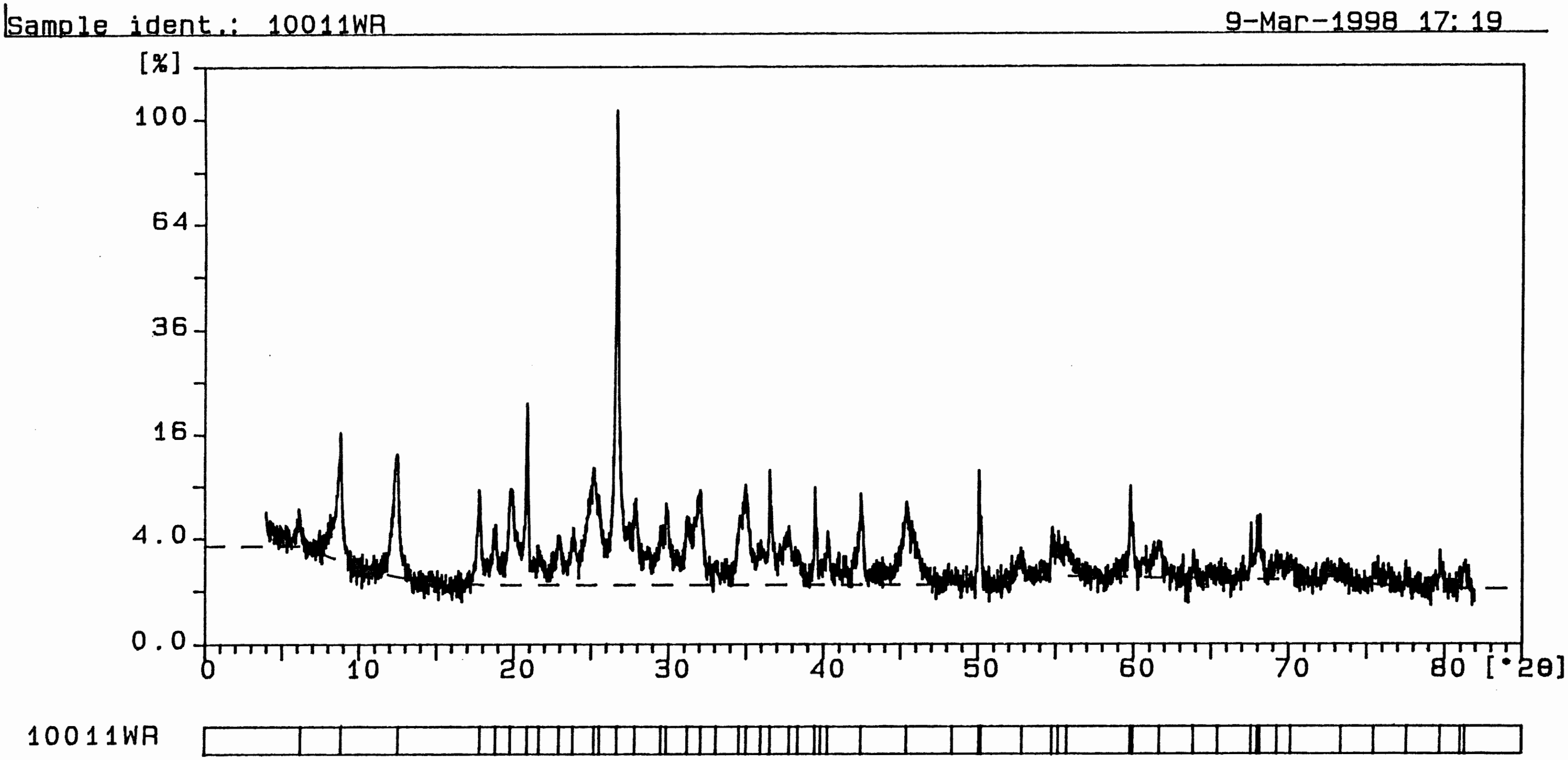

Fig A8 X-ray diffraction mineral peak graph for the whole-rock portion of shale sample PH 100-11.

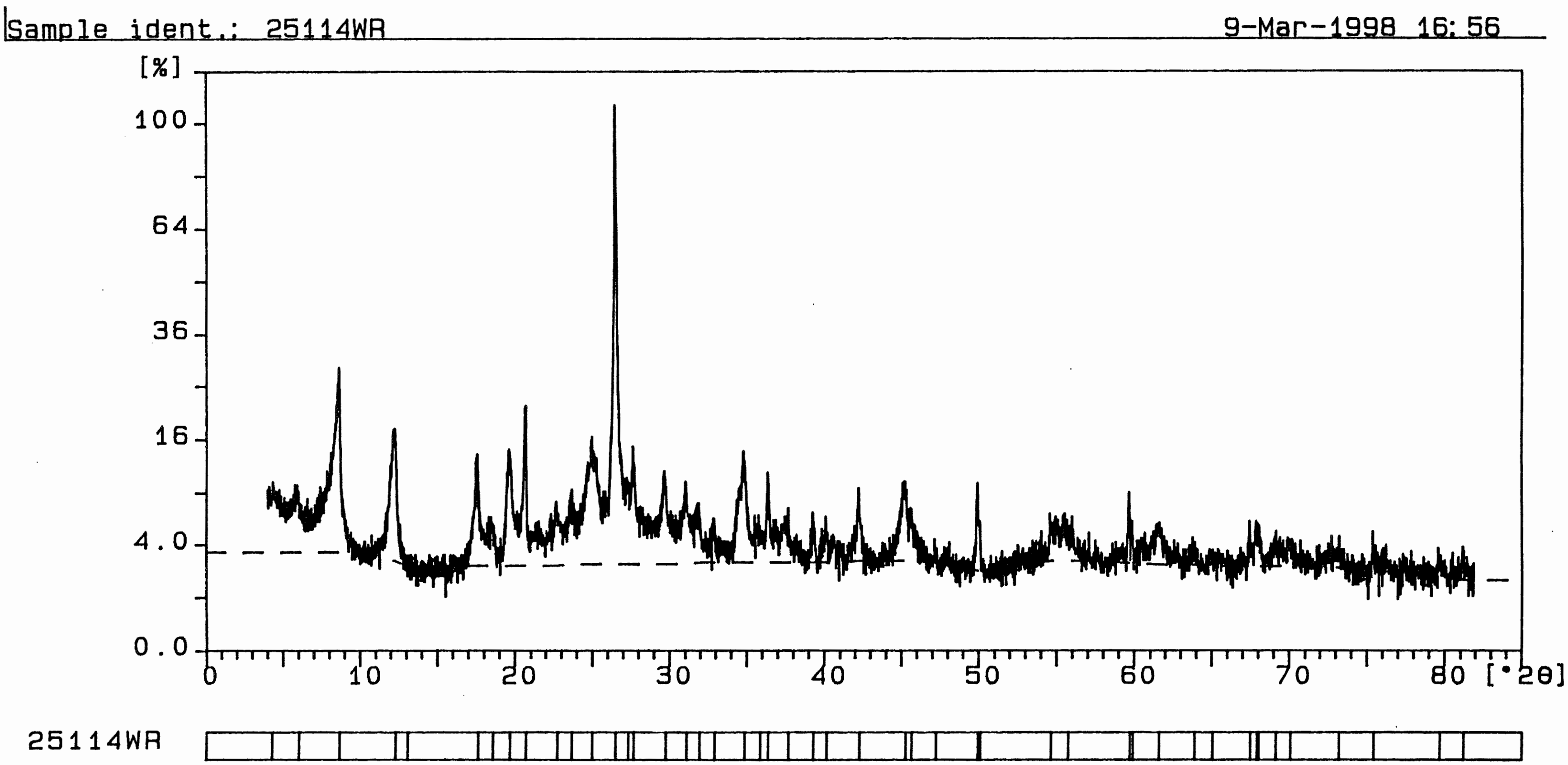

Fig A9 X-ray diffraction mineral peak graph for the whole-rock portion of shale sample PH 251-14.

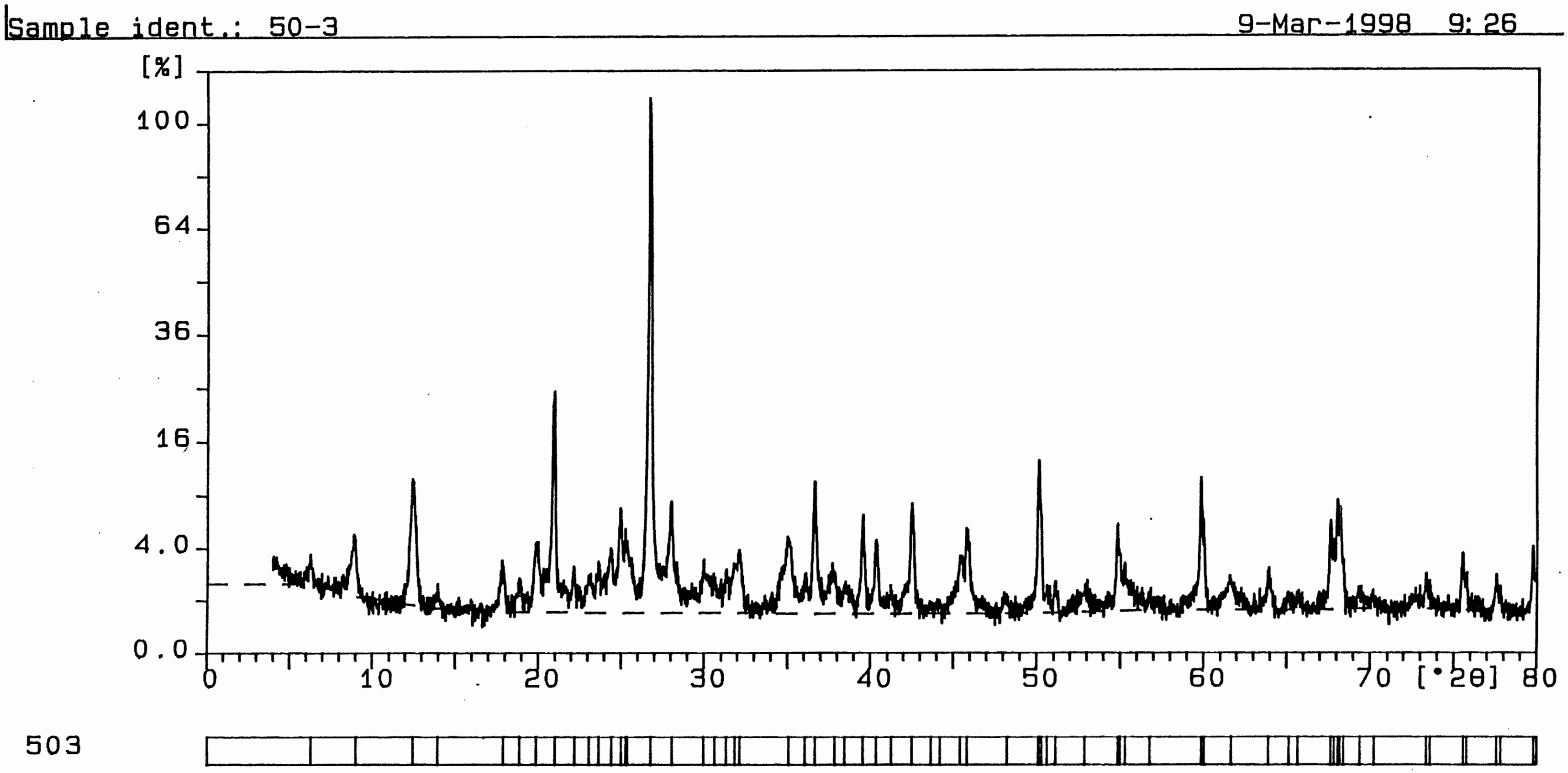

Fig A10 X-ray diffraction mineral peak graph for the clay-sized portion of sandstone sample PH 50-3.

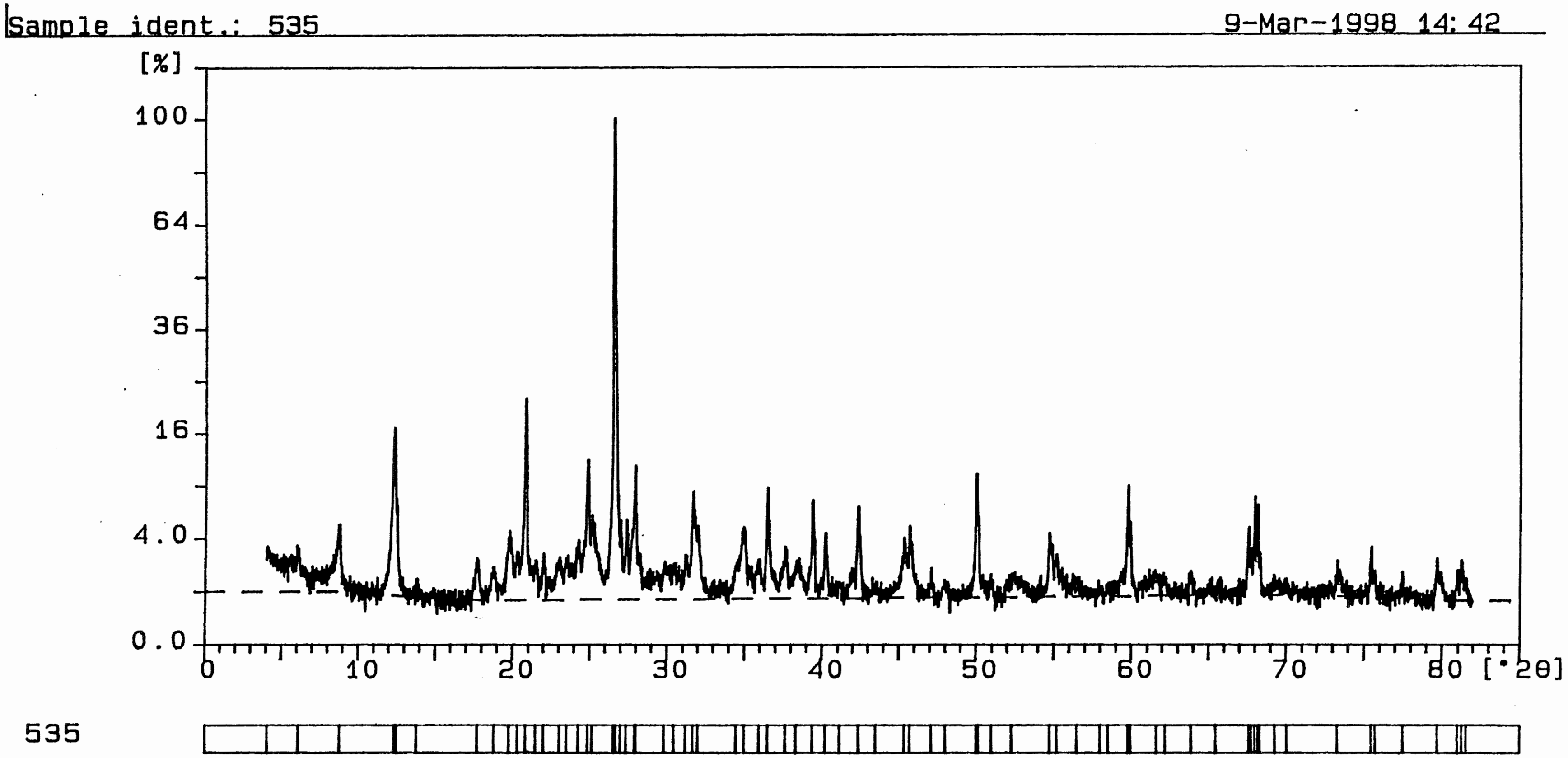

Fig A11 X-ray diffraction mineral peak graph for the clay-sized portion of sandstone sample PH 53-5.

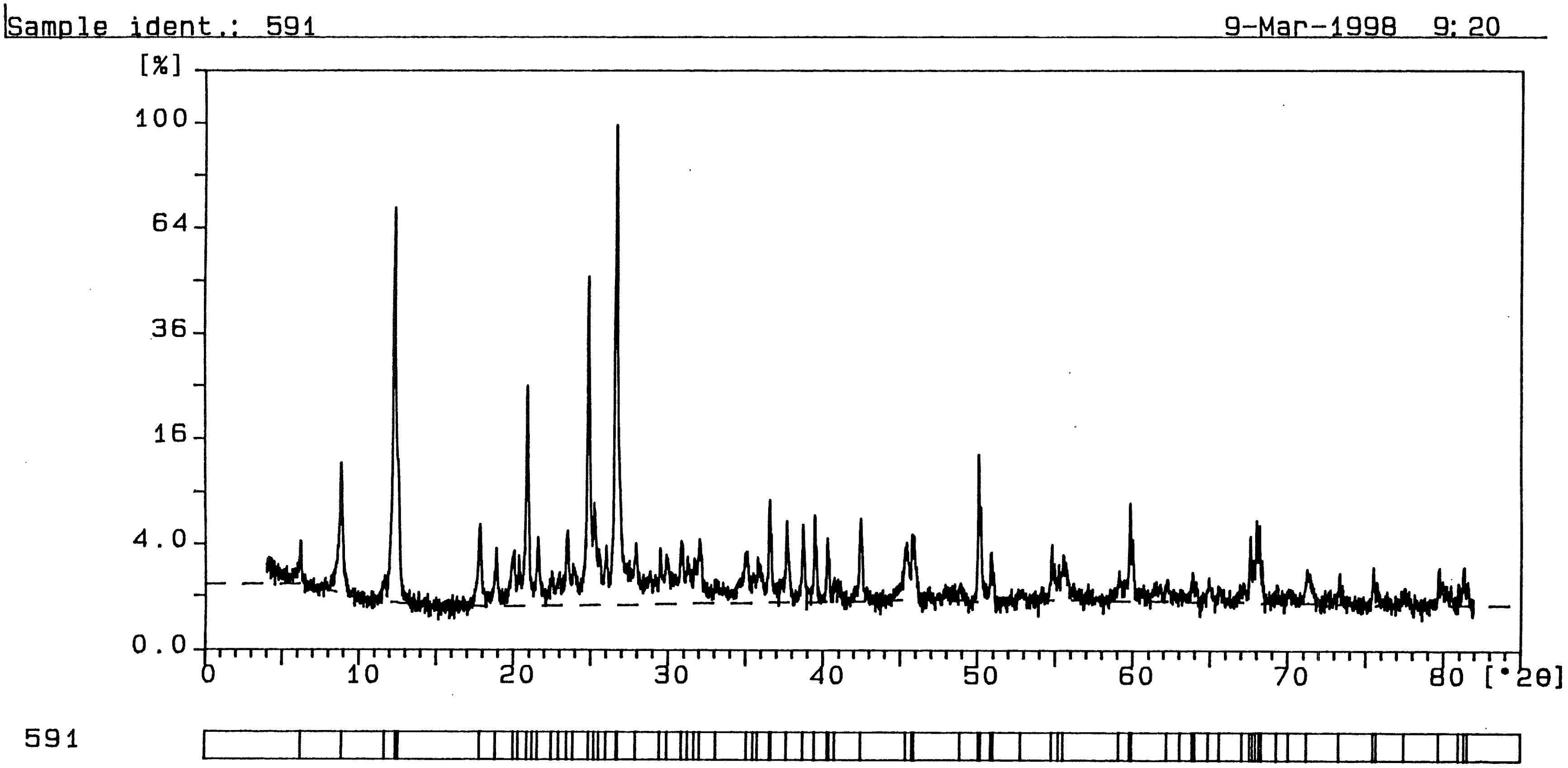

Fig A12 X-ray diffraction mineral peak graph for the clay-sized portion of sandstone sample PH 59-1.

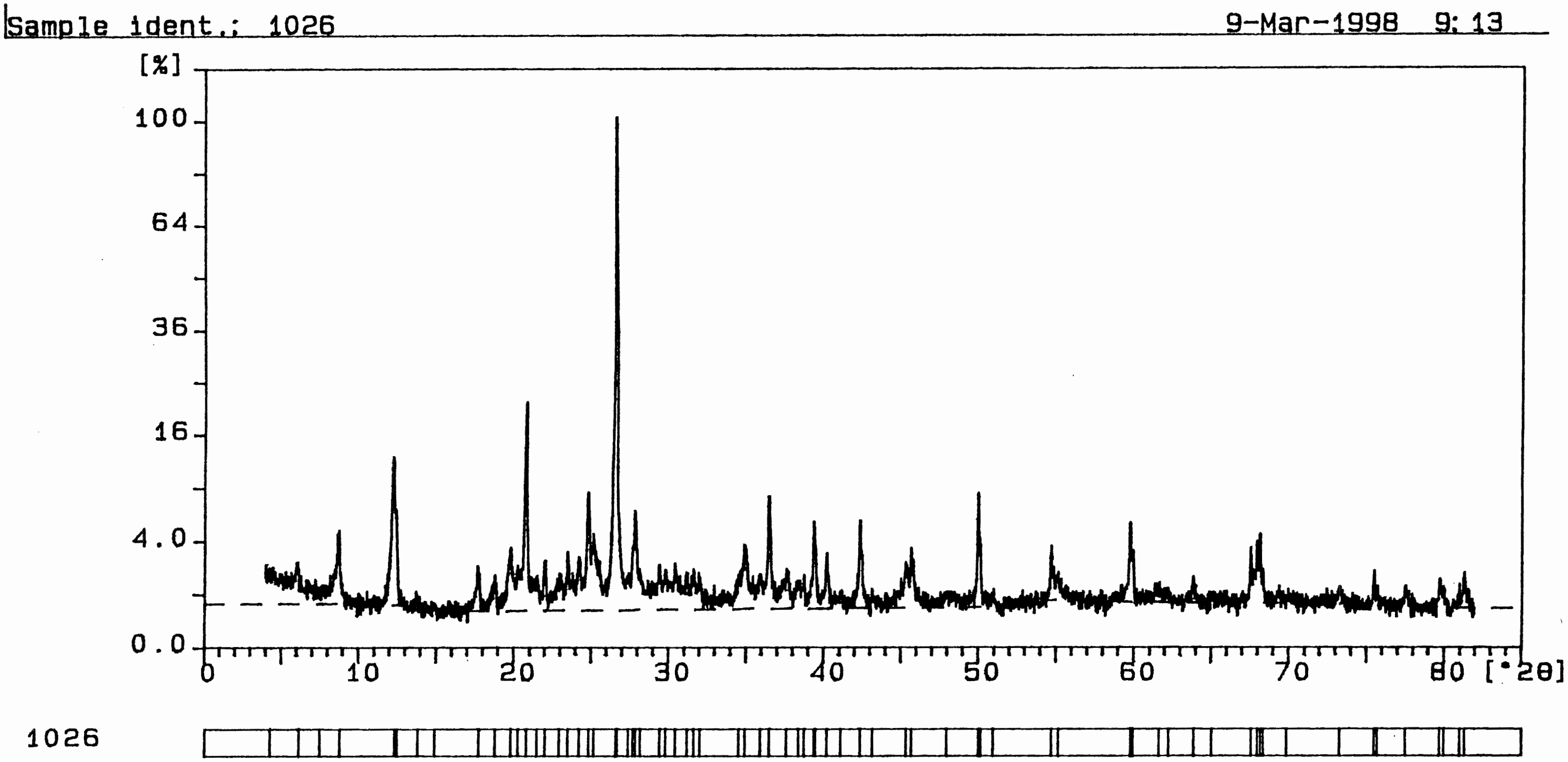

Fig A13 X-ray diffraction mineral peak graph for the clay-sized portion of sandstone sample PH 102-6.

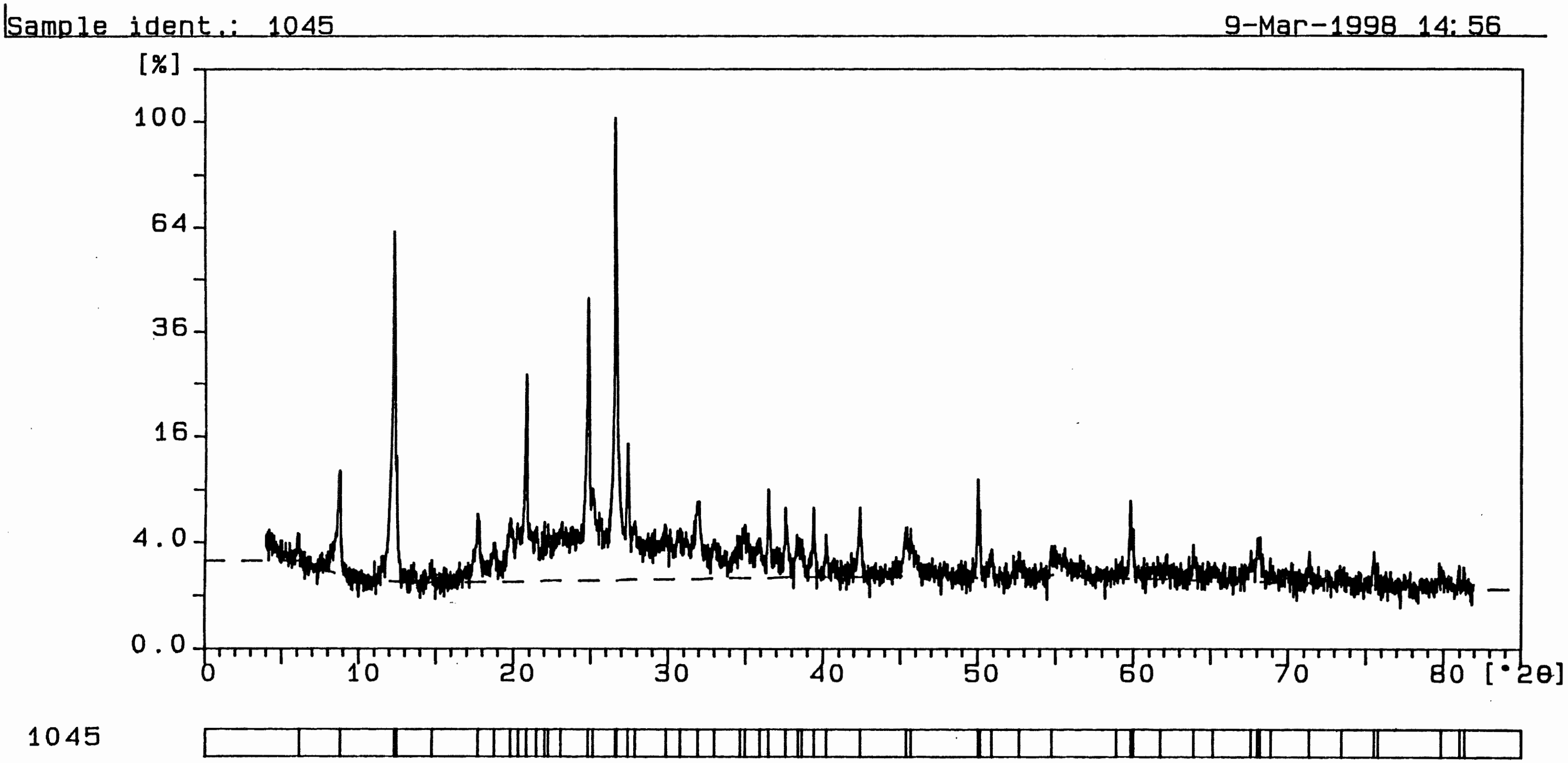

Fig A14 X-ray diffraction mineral peak graph for the clay-sized portion of sandstone sample PH 104-5.

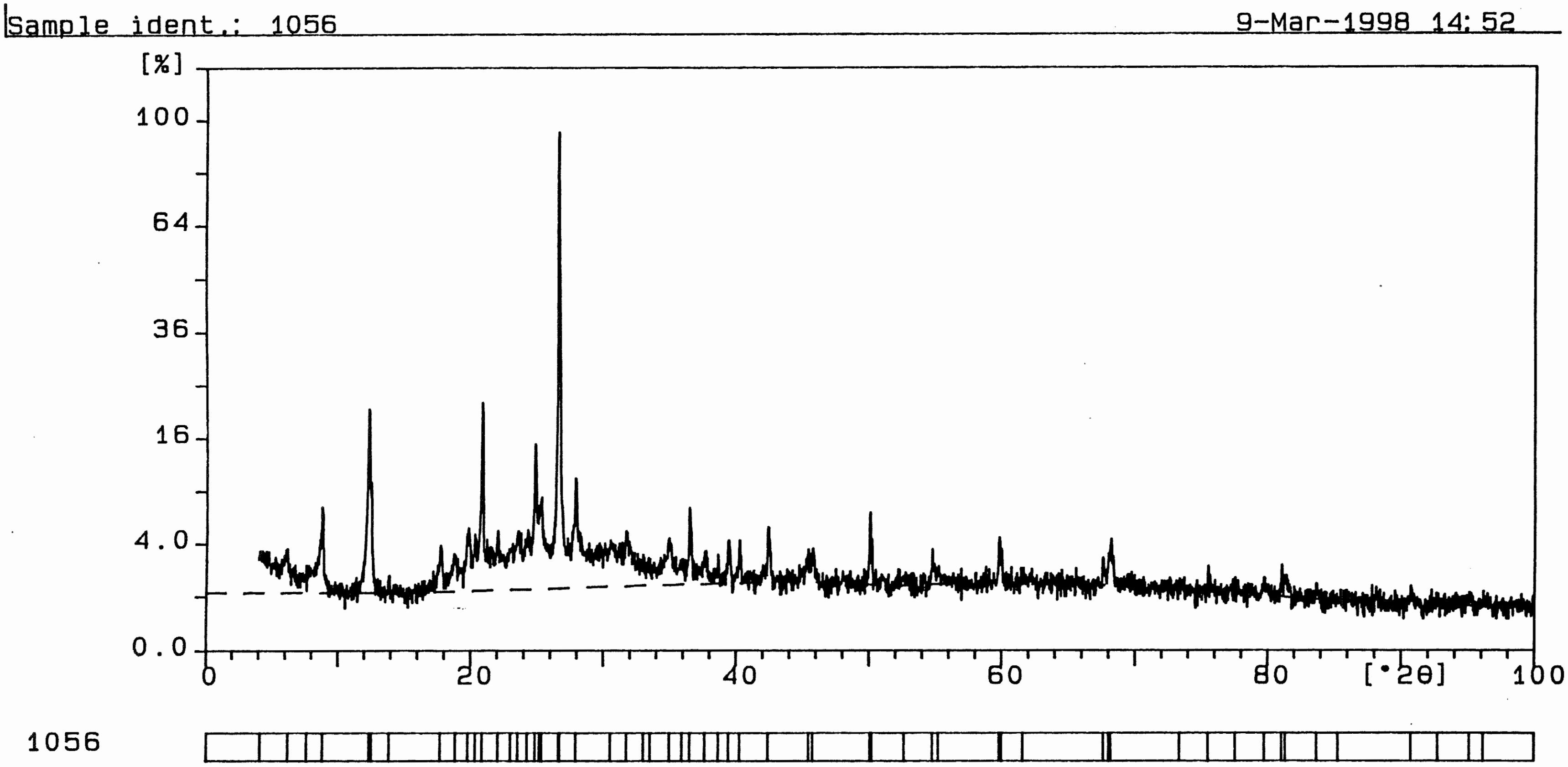

Fig A15 X-ray diffraction mineral peak graph for the clay-sized portion of sandstone sample PH 105-6.

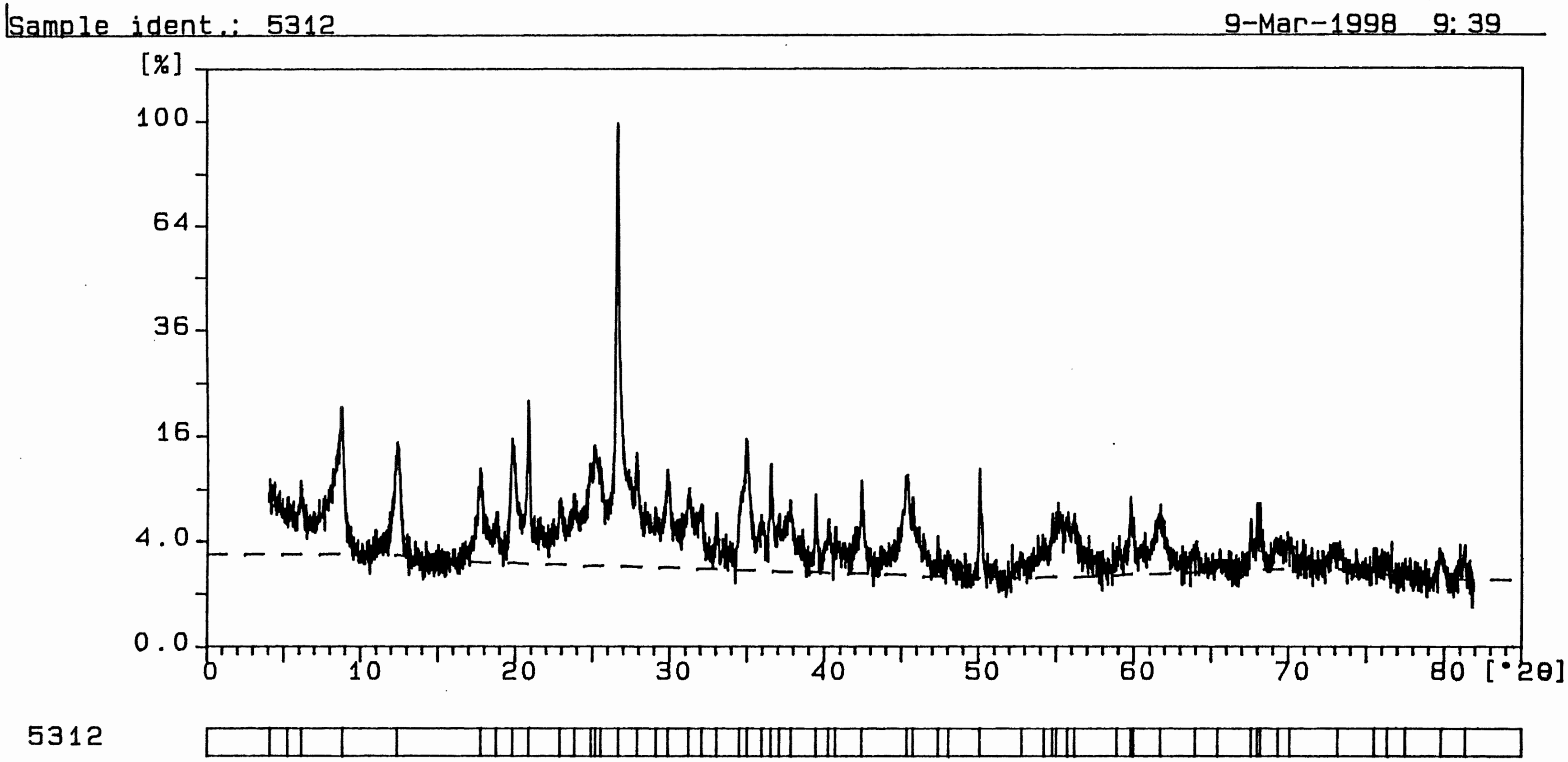

Fig A16 X-ray diffraction mineral peak graph for the clay-sized portion of shale sample PH 53-12.

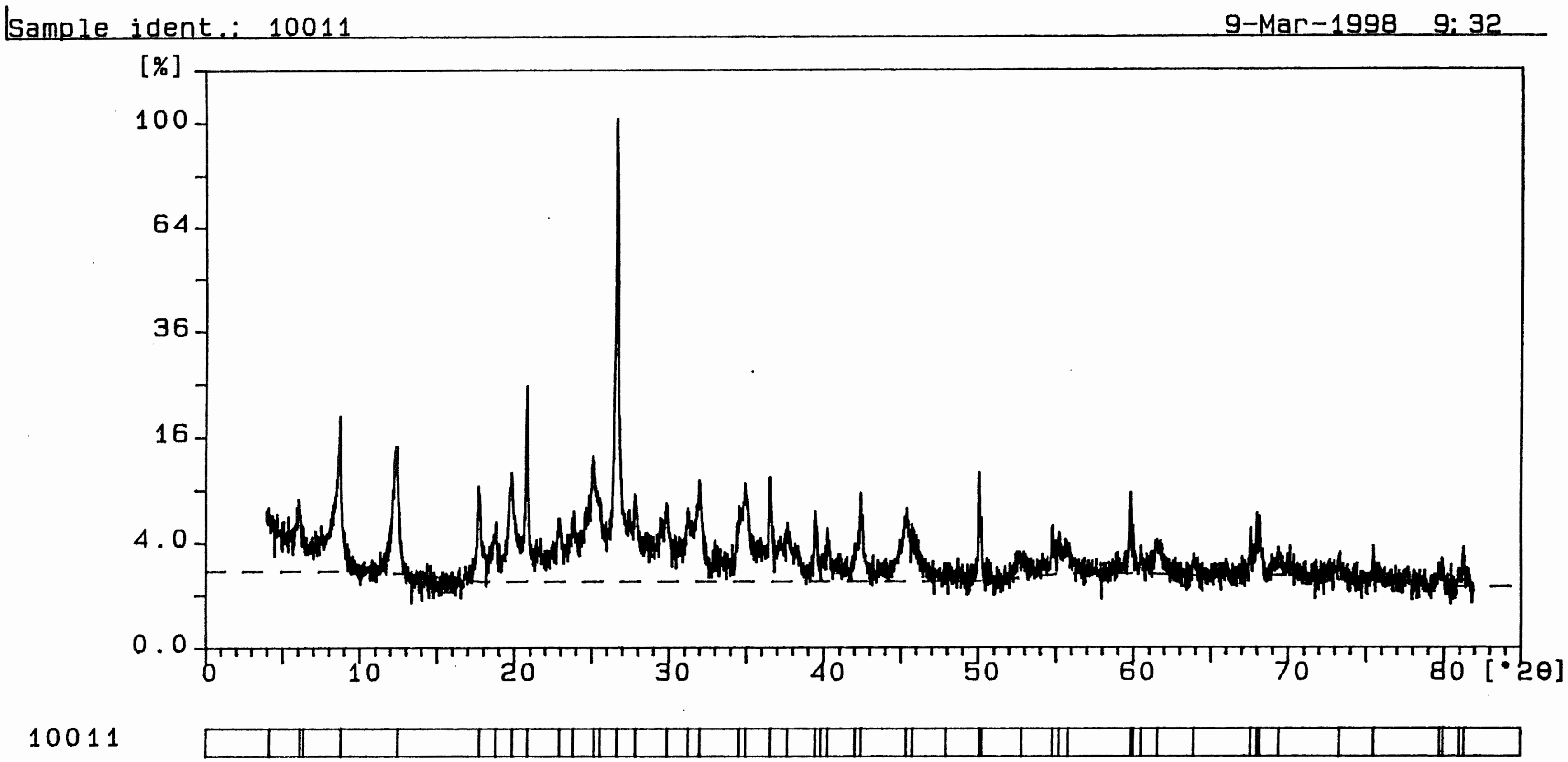

Fig A17 X-ray diffraction mineral peak graph for the clay-sized portion of shale sample PH 100-11.

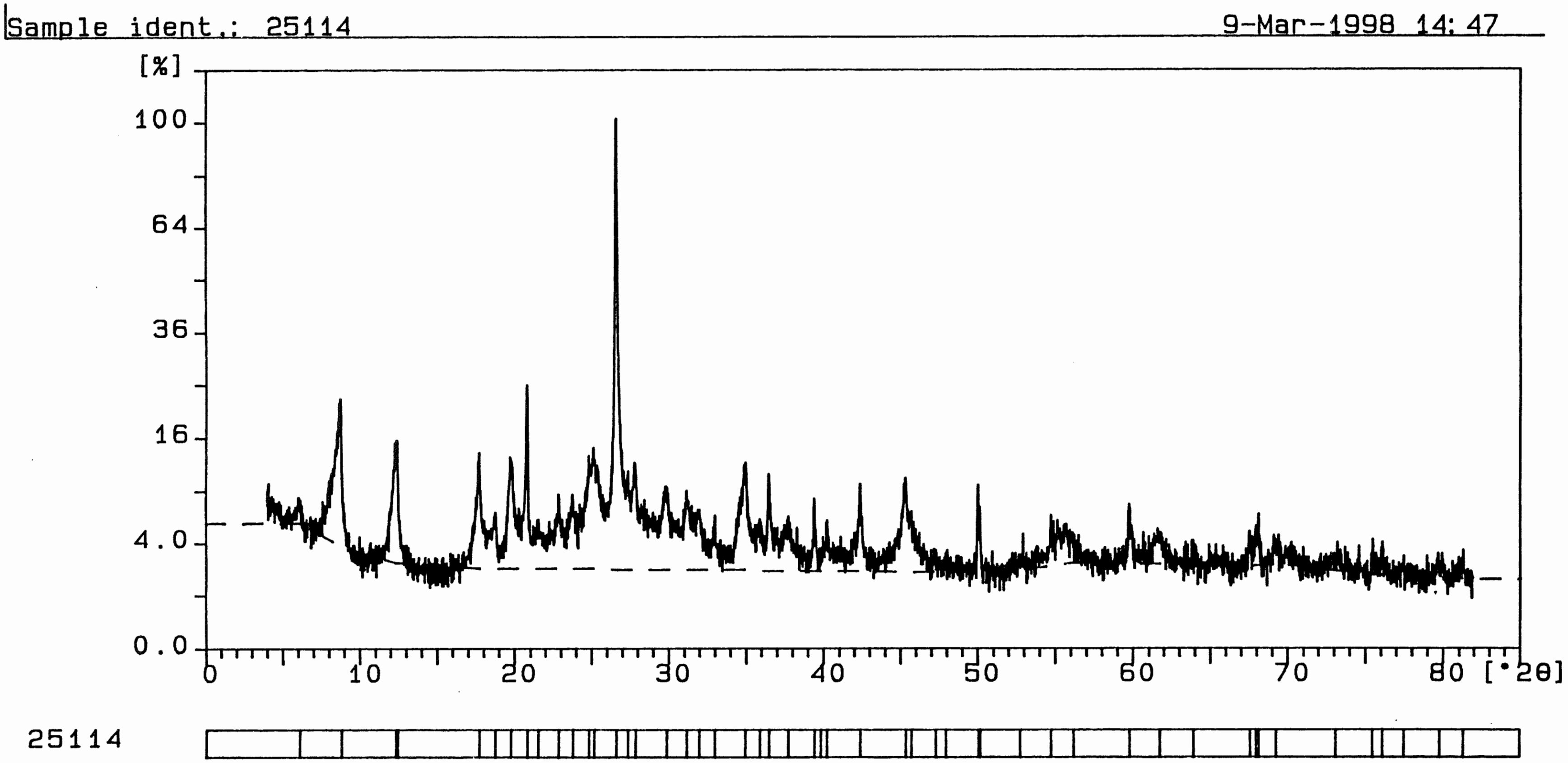

Fig A18 X-ray diffraction mineral peak graph for the clay-sized portion of shale sample PH 251-14.

APPENDIX B

Sandstone Photomicrographs

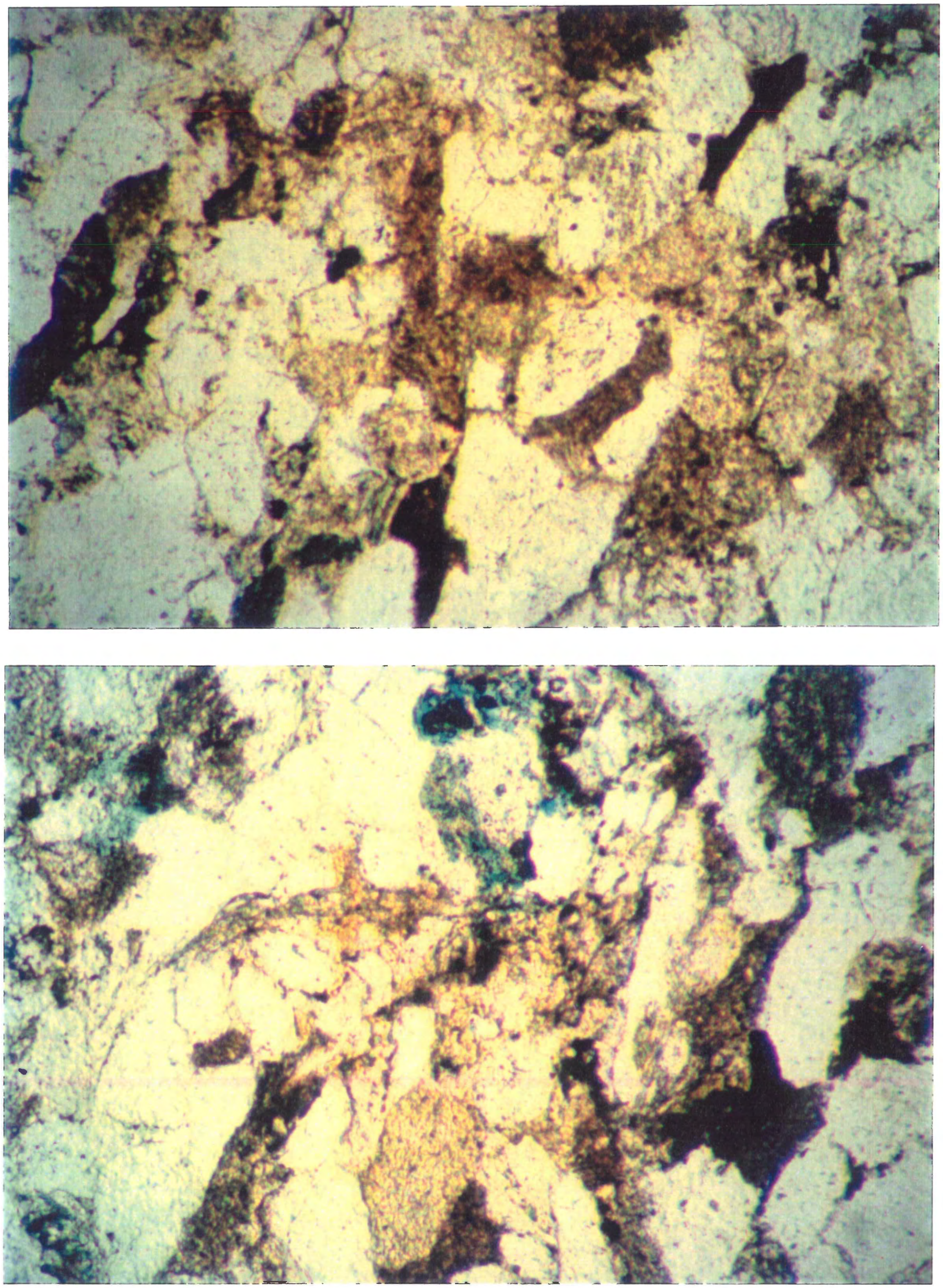

Fig. B1 Photomicrographs of sandstone PH 50-3. Magnification is 32 times actual size, field of view is 0.5 mm by 1.0 mm. Most pores in the low porosity sandstone are filled with, or rimmed by, clay. PH 50-3 has the highest CEC of the sandstone samples.

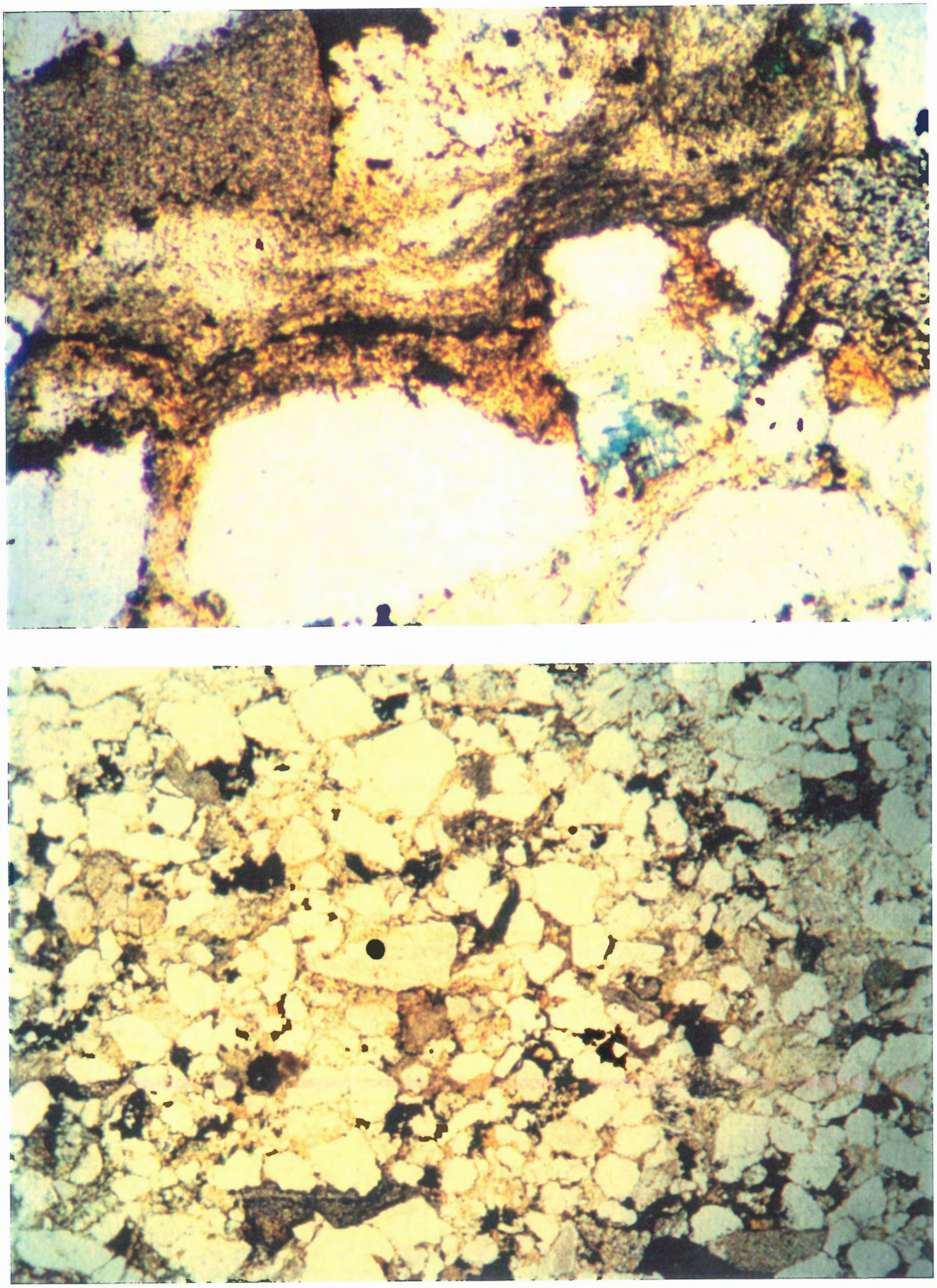

Fig. B2 Photomicrographs of sandstone PH 104-5. Magnification is 32 times actual size, field of view 0.5 mm by 1.0 mm (upper) and 6.3 times, field of view 4 by 6 mm (lower).

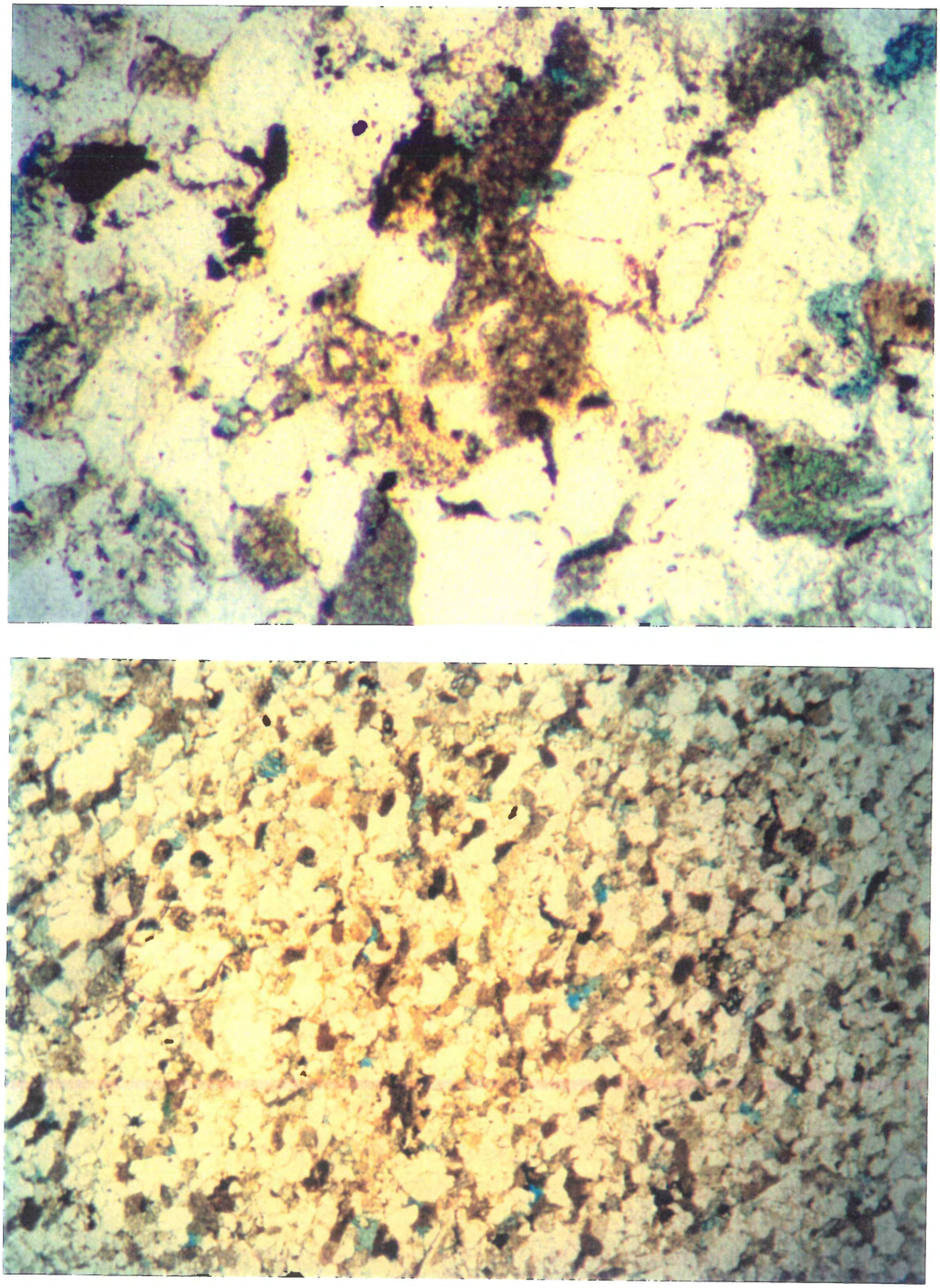

Fig. B3 Photomicrographs of sandstone PH 105-6. Magnification is 32 times actual size, field of view 0.5 mm by 1.0 mm (upper) and 6.3 times, field of view 4 by 6 mm (lower).

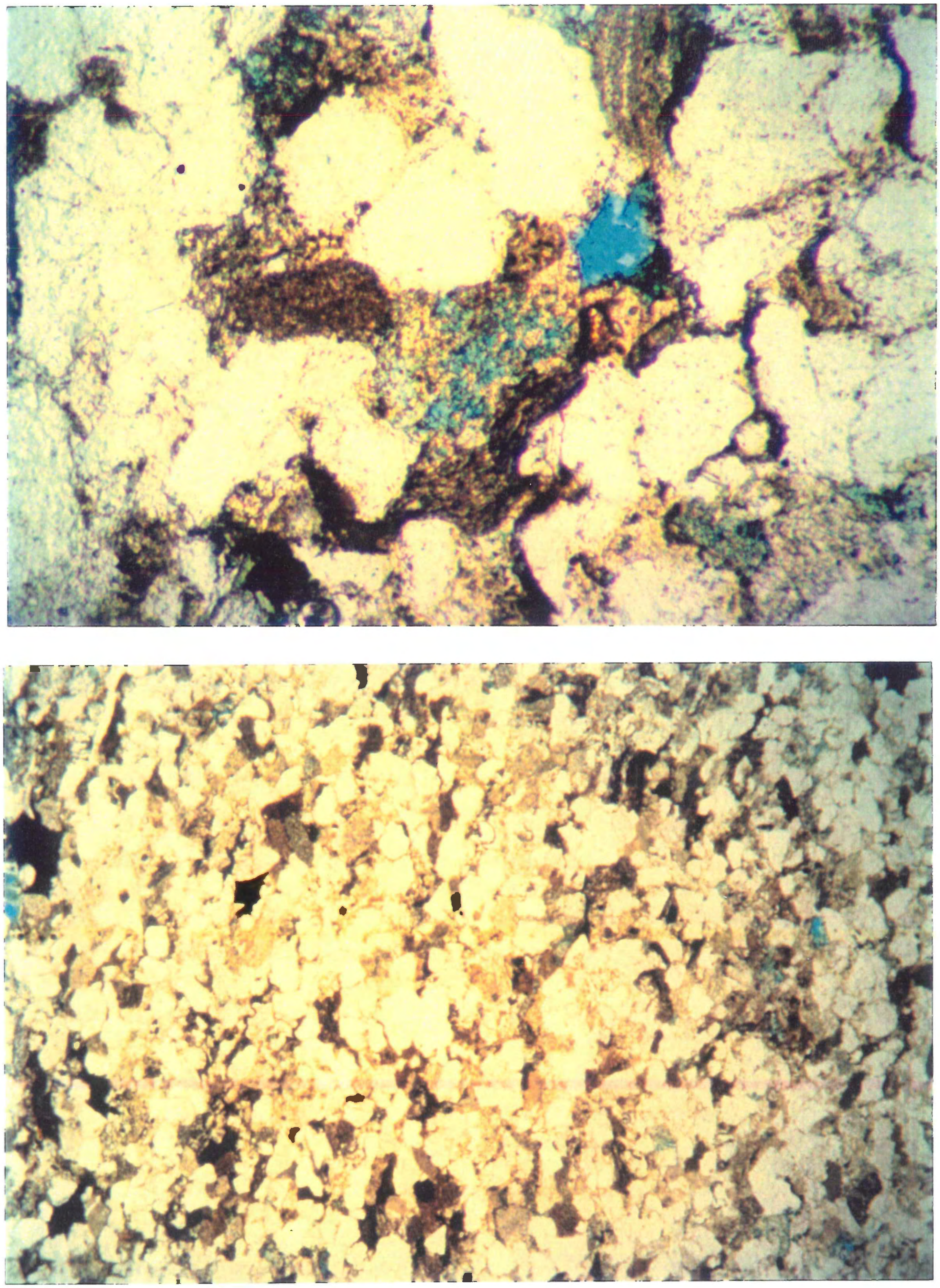

Fig. B4 Photomicrographs of sandstone PH 53-5. Magnification is 32 times actual size, field of view is 0.5 mm by 1.0 mm (upper) and 6.3 times, field of view 4 by 6 mm (lower).

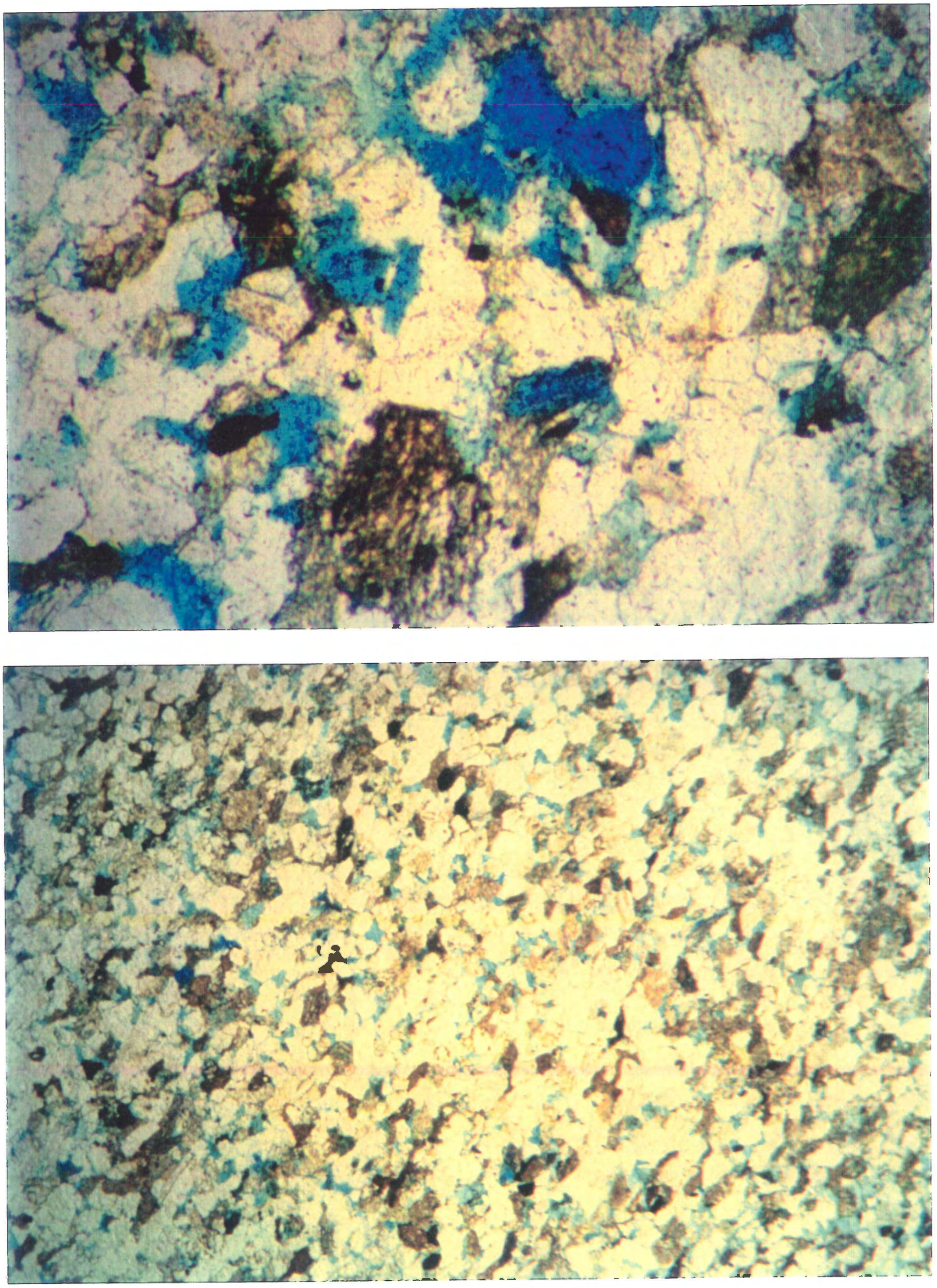

Fig. B5 Photomicrographs of sandstone PH 102-6. Magnification is 32 times actual size, field of view 0.5 mm by 1.0 mm (upper) and 6.3 times, field of view 4 by 6 mm (lower).

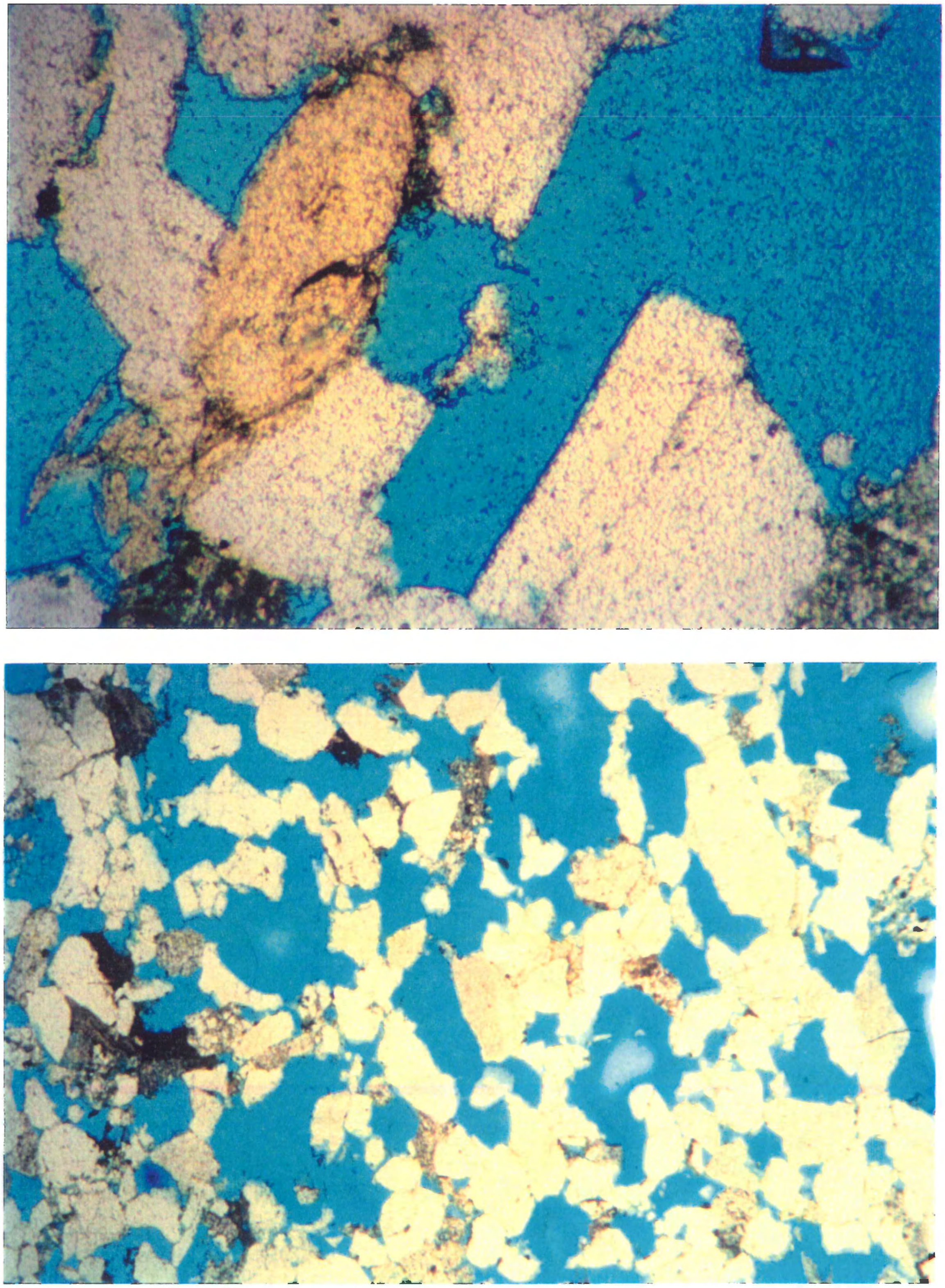

Fig. B6 Photomicrographs of sample PH 59-1. Magnification is 32 times actual size, field of view 0.5 mm by 1.0 mm (upper) and 6.3 times, field of view 4 by 6 mm (lower). Porosity is high but most pores are empty. PH 59-1 has the lowest CEC.

APPENDIX C

Philip Analytical Service Laboratory Procedures

Philip Analytical Services Method Summaries:

Analysis of Chloride in Water/Seawater:

Reference: USEPA Method #325.1

1. Scope and Application

This method can be applied to natural waters and wastewaters with a chloride content in the range of 1.0 to 500 mg/L. Higher concentrations can be brought within this range by proper dilution.

2. Summary

This method is based on the displacement of thiocyanate ion from mercuric thiocyanate by chloride ion and the subsequent reaction of the liberated thiocyanate ion with ferric ion to form the coloured ferric thiocyanate complex. This complex is proportional to the original chloride concentration and is measured at 480 nm using an automated colorimeter (Cobas/Fara or Hitachi 911).

3. Quality Assurance

Reagent blanks, internal reference materials, and method spikes are analyzed in the same manner as mentioned above for the samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate samples are also analyzed at a frequency of 10%.

Analysis of Alkalinity in Water/Seawater

Reference: USEPA Method #310.2

1. Scope and Application

This method is applicable to the determination of alkalinity in surface, ground or sea water, as well as industrial wastes. The samples must be free of turbidity and high colour, as only clear samples can be analyzed. Samples with suspended or particulate matter that can be centrifuged or filtered out are acceptable. The limit of quantitation is 1mg/L as $CaCO_3$.

2. Summary

Using a Centrifugal analyzer (Cobas/Fara or Hitachi 911), samples are combined with a methyl orange reagent. Methyl orange is used as an indicator because its pH range is the same as the equivalence point for total alkalinity. The methyl orange has been mixed with a weak buffer to maintain a pH of 3.1, just below the equivalence point. Any alkalinity due to the sample when mixed with the methyl orange will cause a decrease in colour which is measured at 550 nm.

3. Quality Assurance

Reagent blanks, internal reference materials, and method spikes are analyzed in the same manner as mentioned above for the samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%.

Major Metals in Aqueous Samples by ICP-OES

Reference: USEPA Method #200.7

1. Scope and Application

This method is applicable to a variety of metals in drinking, surface, seawater, domestic and industrial waste waters. The LOQs are as follows:

Analyte	**LOQ (mg/L)**
Sodium	0.1
Potassium	0.1
Calcium	0.1
Magnesium	0.1
Iron	0.02
Manganese	0.01
Copper	0.01
Zinc	0.01
Phosphorous	0.1

2. Summary of Method

In direct aspiration optical emission spectroscopy, a sample is aspirated and atomized in an argon plasma. The atomized sample is then ionized causing the individual ions to emit characteristic wavelengths upon returning to stable conditions. The wavelengths emitted are split via a polychrometer and the focused signals are measured using a charged coupled segmented array detector. The raw signals are converted to concentrations by comparison to the emission strengths of calibration standards.

3. Quality Assurance

Quality control effort includes the analysis of certified reference materials, method spikes, matrix spikes, duplicates, and method blanks. A minimum QC effort of 10% is maintained.