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# Fluid evolution and diagenesis of a Carboniferous channel sandstone in the Prince Colliery, Nova Scotia, Canada

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## ABSTRACT

The subsea Prince Colliery of the Sydney Basin extracts coal at depths up to 330 m below sea level from beneath the Prince Sandstone, a channel body and local aquifer. The sandstone has up to 42.5 md permeability and 19.5% porosity, mainly secondary porosity generated from near-complete dissolution of early formed calcite cement, remnants of which are present locally. Some pores are partially filled with quartz overgrowths on framework grains and aggregates of kaolinite, quartz, siderite, and minor illite. Formation waters within the Prince Sandstone are Na-Ca-Cl fluids with total dissolved solids (TDS) from 7,950 to 47,840 mg/L, increasing downdip, and high Br:Cl ratios. Salinity estimates using geophysical logs on wells drilled prior to mining agree well with the TDS values, confirming that the fluid samples are relatively pristine. The saline component originated as residual evaporative brines derived from the underlying Windsor Group, and probably entered the sandstone along faults during deep Permo-Triassic burial.

The saline formation waters have been diluted by fresh surficial fluids that, based on isotopic data, were warmer than present precipitation, suggesting interglacial or preglacial sources. These surficial fluids entered the Prince Sandstone aquifer along the nearby Mountain Fault and/or from the surface, and dilution may have taken place at any time since the mid-Mesozoic, when basin inversion brought the strata to a near-surface position. The dilute fluids may have promoted generation of secondary porosity within the sandstone, probably long after maturation of the coals, as there is little evidence in the coalfield that fluids released during maturation generated high porosity levels.

## RÉSUMÉ

La mine de charbon Prince, située sous la mer, du bassin de Sydney extrait du charbon d'une profondeur allant jusqu'à 330 m sous le niveau de la mer, à partir du dessous du Grès de Prince, une masse de chenal et un aquifère local. Le grès montre jusqu'à 42,5 md de perméabilité et 19,5% de porosité, surtout une porosité secondaire générée à partir de la dissolution quasi complète d'un ciment de calcite précoce, pour lequel on retrouve des restes localement. Quelques pores sont partiellement remplis d'excroissances de quartz sur la fraction principale des grains de quartz et d'agrégats de kaolinite, de quartz, de sidérite et d'illite en quantité mineure. Les eaux de formation à l'intérieur du Grès de Prince sont des fluides à Na-Ca-Cl montrant des solides dissous totaux (SDT) allant de 7 950 à 47 840 mg/l, s'accroissant en aval-pendage, et des hauts rapport Br:Cl. Les estimations de salinité faites en utilisant les diagrammes géophysiques de puits forés avant la mine, concordent bien avec les valeurs de SDT, confirmant que les échantillons de fluides sont relativement de première origine. Les composantes salines ont pour origine les saumures évaporatives résiduelles dérivées du Groupe de Windsor sous-jacent, qui ont probablement pénétrées dans le grès en longeant des failles durant l'enfouissement profond du Permo-Trias.

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Les eaux salines de formation ont été diluées par des fluides d'eaux douces de surface qui, en se basant sur les données isotopiques, étaient plus chauds que la précipitation présente, ce qui suggère des sources interglaciaires ou préglaciaires. Ces fluides de surface ont pénétré l'aquifère du Grès de Prince le long de la Faille Mountain adjacente et/ou à partir de la surface, et une dilution a pu prendre place à tout moment depuis le milieu du Mésozoïque, quand l'inversion du bassin a amené les strates près de la surface. Les fluides dilués ont possiblement favorisé la génération de la porosité secondaire à l'intérieur du grès, probablement longtemps après la maturation des charbons car il y a peu d'évidence dans ce champ de charbon que les fluides relâchés durant la maturation aient généré de hauts niveaux de porosité.

Traduit par Lynn Gagnon

## INTRODUCTION

The Sydney Basin of Cape Breton Island, Nova Scotia, has been the major source of coal in Atlantic Canada since mining commenced in the early 1700s. Sydney coal is currently mined principally from the subsea Prince and Phalen mines operated by the Cape Breton Development Corporation (CBDC). The Prince Mine, the subject of this study, extracts coal by retreat longwall mining from the Hub seam of the Upper Carboniferous Sydney Mines Formation, which crops out close to the Atlantic coast and dips towards the ocean (Fig. 1). The deepest workings presently lie about 4 km offshore and 330 m below sea level.

Water inflows have occasionally been a problem during subsurface mining in the coalfield (Haites, 1951). Sudden, large inflows of variably saline water into the subsea Phalen Mine in 1992 prompted investigation of the regional groundwater system, in view of pumping costs and potential hazard to miners and equipment (Cape Breton Development Corporation, 1994). Concern was expressed that some water might have originated from the overlying ocean. More than 3000 water analyses have been obtained to date from the Phalen and Prince mines, and some samples represent formation water (water within the pores of deeply buried rocks: Drever, 1988) that drips from exposures and boreholes in the working roof at depths up to nearly 700 m below sea level. These samples are unusually reliable, with minimal risk of contamination by drilling fluids or mixing of waters from different levels — a common problem in oilfield and aquifer samples. The most saline waters are Na-Ca-Cl brines with

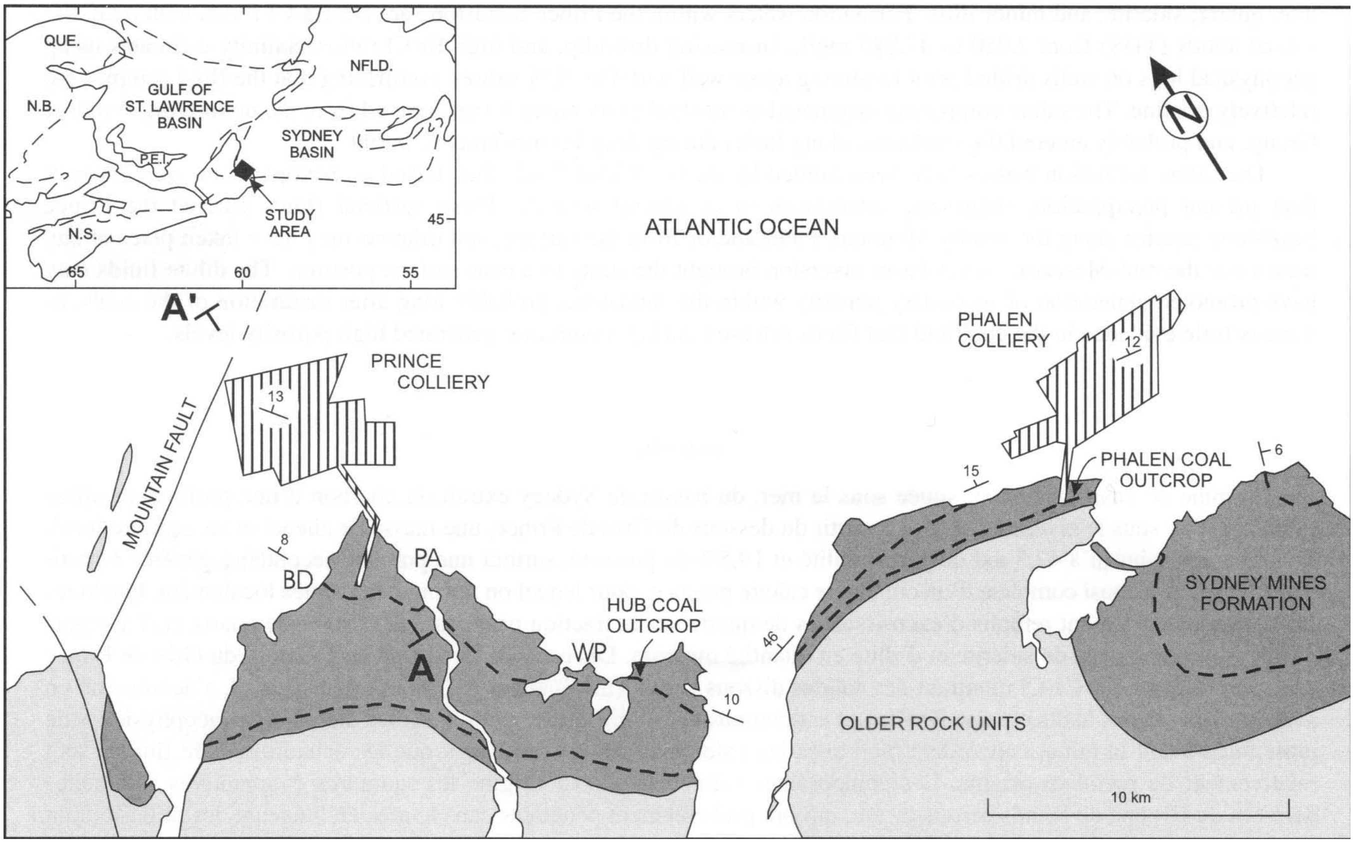

**Fig. 1.** Geological map to show partial distribution of the Sydney Mines Formation in the Sydney Basin (see inset) and the subsea Prince and Phalen Collieries which work the seaward-dipping Hub Coal and Phalen Coal, respectively. Coastal outcrops are Bras d'Or (BD), Point Aconi (PA) and Wetneck Point (WP). A-A' indicates line of cross-section shown in Figure 3.

salinity more than five times that of sea water (up to 176,094 mg/L). They are interpreted as formation brines derived originally from evaporative basins associated with the Lower Carboniferous Windsor Group (Martel *et al.*, *in press*). Fractures above the Phalen longwall have intersected the overlying, drowned Lingan Mine, allowing periodic large inflows to invade the lower workings (Cape Breton Development Corporation, 1994).

This paper outlines the geological and hydrogeological setting of the Prince Mine. This mine has experienced few inflow problems, as overlying flooded workings are absent. Although relatively few water samples are available, they are important because they provide information about the hydrogeology of strata in a shallow subsea setting (<350 m) for which reliable information is rarely available. We draw upon several sources of information: stratigraphic and sedimentological data from wells, mine workings and nearby outcrops; petrographic information and porosity and permeability measurements from core samples; porosity and salinity estimates from geophysical logs; and chemical analysis of waters sampled in the mine. We use this suite of information to investigate the evolution of formational fluids sampled in the mine and the diagenetic history of the sandstone bodies that contain them. Key observations to be explained include 1) the unusually high permeability and porosity, mainly of secondary origin, of roof sandstones in the Prince Mine compared with sandstones in the Phalen Mine and elsewhere in the Sydney Coalfield, and 2) the presence of high-salinity formation waters that increase progressively in salinity downdip under the ocean and possibly away from the nearby Mountain Fault. We explore the hypothesis that porosity generation in the sandstone reflects groundwater recharge downdip in a homoclinal structural setting, and/or along the fault, during the Mesozoic–Cenozoic when the Carboniferous strata were close to the surface.

Natural gas and locally liquid hydrocarbons are present in sandstone bodies in the Sydney Mines Formation, and occasionally emerge violently in the mines (Aston *et al.*, 1990), at faults (Haites, 1951) and at the seafloor (Courtney, 1996). Gas shows have also been identified at the level of the Sydney Mines Formation in offshore petroleum wells (Murphy Oil Company, 1974). The timing of porosity generation with respect to maturation is an important question in reservoir evaluation in Atlantic Canada.

## GEOLOGICAL SETTING

### STRATIGRAPHY AND STRUCTURE

The Sydney Basin is located in northeastern Nova Scotia (Cape Breton Island) and under the adjacent Atlantic Ocean (Fig. 1). The basin developed following the Middle Devonian Acadian Orogeny and subsided episodically until latest Carboniferous or Early Permian time (Fig. 2). The Lower Carboniferous Horton Group is mainly conglomeratic and >800 m thick onshore, and occupies a series of half-grabens with south-dipping master faults (Gibling *et al.*, 1999c). The Windsor Group rests conformably on the Horton Group and is about 1000 m thick at Sydney, including hundreds of metres of marine halite, gypsum and anhydrite, with minor potash salts (Boehner, 1986). The conformably overlying Mabou Group is about 200 m thick and comprises lacustrine mudstones, sandstones and limestones. Windsor strata extend across the master faults to rest directly on Precambrian to Devonian basement rocks, implying that Windsor and Mabou strata were deposited during a phase of thermal subsidence (Gibling *et al.*, 1999c). The Upper Carboniferous Morien Group rests with angular unconformity on Lower Carboniferous rocks (Fig. 2), commencing with the South Bar Formation, a braided-fluvial sandstone unit about 1000 m thick.

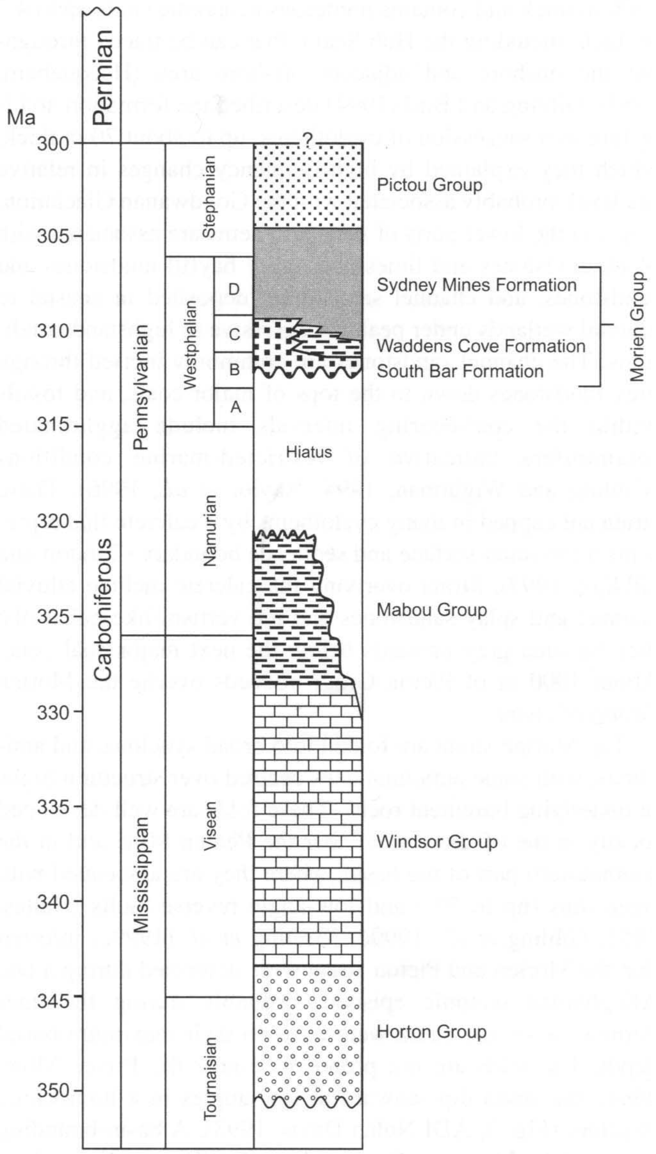

**Fig. 2.** Generalised stratigraphic column for the Carboniferous fill of the Sydney Basin onshore. Radiometric ages from Okulitch (1995). Modified from Gibling *et al.* (1987).

The Sydney Mines Formation (Westphalian D to Stephanian), of particular importance for this study, is about

1000 m thick and contains numerous economic coals up to 4.3 m thick, including the Hub Seam, that can be traced throughout the onshore and adjacent offshore area (Hacquebard, 1983). Gibling and Bird (1994) described the formation architecture as a succession of cyclothems, up to about 70 m thick, which they explained by high-frequency changes in relative sea level, probably associated with the Gondwanan Glaciation. Coals in the lower parts of the cyclothems are associated with black mudstones and limestones, grey bayfill mudstones and sandstones, and channel sandstones, deposited in coastal to alluvial wetlands under peak transgressive to highstand conditions. The channel sandstones are commonly incised through grey mudstones down to the tops of major coals, and fossils within the coal-bearing intervals include agglutinated foraminifera indicative of restricted-marine conditions (Gibling and Wightman, 1994; Naylor *et al.*, 1996). These strata are capped in many cyclothems by a calcrete that represents a lowstand surface and sequence boundary (Tandon and Gibling, 1997). Strata overlying the calcrete include alluvial channel and splay sandstones and red vertisol-like paleosols; they become grey upwards below the next major coal zone. About 1000 m of Pictou Group redbeds overlie the Morien Group offshore.

The Morien strata are folded into broad synclines and anticlines, with some anticlinal axes centred over structural highs in underlying basement rocks. These folds are well developed locally in the offshore area, near the Phalen Mine and in the southeastern part of the basin, where they are associated with steep dips (up to 50°) and low-angle reverse faults (Haites, 1951; Gibling *et al.*, 1999c). Gibling *et al.* (1999c) inferred that the Morien and Pictou strata were deformed during a late Alleghanian tectonic episode, probably during the later Permian when the strata were close to their maximum burial depth. The folds are not pronounced near the Prince Mine, where the strata dip seaward at low angles in a homoclinal structure (Fig. 3; ADI Nolan Davis, 1993). A basin-bounding strand of the Mountain Fault with a NE-SW trend lies a short distance north of the Prince Mine (Fig. 1). The fault offsets the coal measures, and has probably reactivated a Horton master fault. Structural contours for the Hub Seam in the mine rise towards the fault which has brought the South Bar Formation to surface on its northwestern side (Fig. 3). Although the subsea location precludes a detailed analysis of the fault, the Windsor Group and Sydney Mines Formation may lie in close proximity across the fault (Fig. 3).

The Sydney Mines Formation outcrop belt has probably been close to the surface since the Mesozoic. Fission-track analysis indicates that exhumation was underway by the Late Triassic (Grist *et al.*, 1995), and Lower Cretaceous strata rest upon Carboniferous rocks in central Cape Breton Island (Dickie, 1987) and in the eastern offshore part of the Sydney Basin (Bell and Howie, 1990), where they include marine beds. Water depth over the Prince Mine workings is about 25-40 m, and the bedrock is covered by a thin Quaternary sediment blanket with bedrock ridges exposed locally (Courtney, 1996). The coastal cliffs are undergoing rapid retreat, and the mine site was probably subaerial until geologically recent times, although late Quaternary highstands of sea-level may have covered the area.

## THE HUB CYCLOTHEM

Saunders (1995) described the Hub Cyclothem, an interval about 50 m thick from the Hub to the Bonar Coal, and identified three assemblages that can be traced for >30 km across the basin, as far as outcrops extend. The three sections closest to the Prince Mine are shown in Figure 4. Assemblage 1 is 28-45 m thick, and contains channel bodies of pebbly coarse to fine sandstone, up to 15 m thick and with multiple storeys and lateral accretion sets. Calcite cement is lacking in most outcrops. Associated strata include thin sheet-like sandstones and siltstones, grey laminated and rooted mudstones, dark carbonaceous mudstone, and coal. The Hub Coal is locally >2 m thick and highly split; thinner coals are less common above. Saunders (1995) inferred that the assemblage formed in coastal wetlands traversed by meandering rivers, probably part of a distributary channel network. Marine influence is indicated

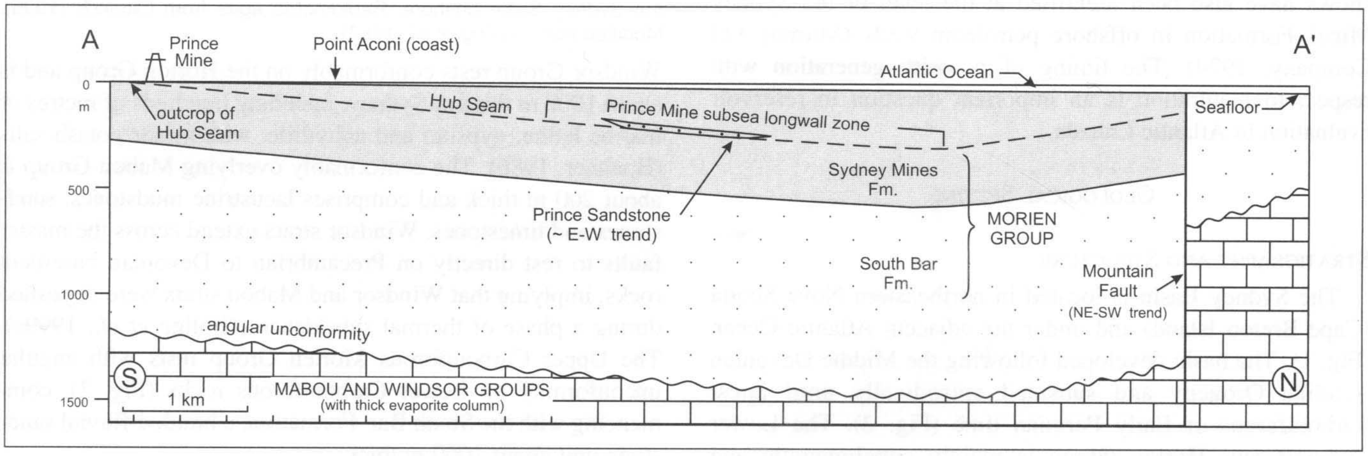

**Fig. 3.** Cross-section through the Prince Mine area along A-A' (Fig. 1). Geological data from Boehner and Giles (1986) and Cape Breton Development Corporation (1994) Prince Mine plans. Thickness estimates for groups and formations are derived from well studied parts of the basin.

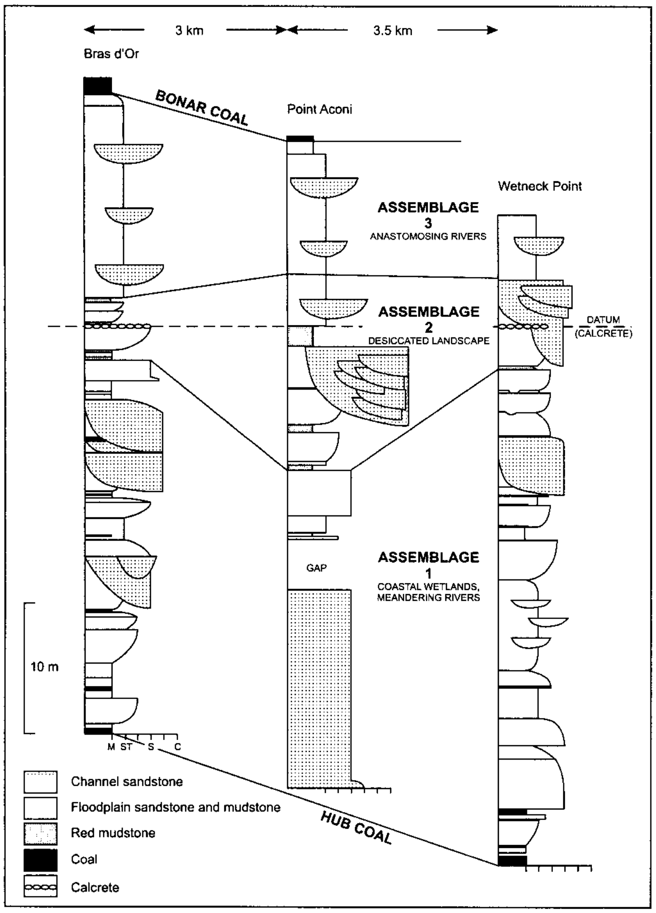

**Fig. 4.** Stratigraphic columns for the Hub Cyclothem in coastal sections closest to the offshore Prince Mine (located in Fig. 1). Line of section is approximately along depositional strike. Modified from Saunders (1995).

by the high sulphur content of the coal (up to 4.5%) and the presence of agglutinated foraminifera in mudstones (Wightman *et al.*, 1994).

Assemblage 2 is 5-11 m thick, and comprises laminated to poorly stratified red and grey mudstones (paleosols of vertisol type), sandstone and siltstone sheets, and narrow channel bodies commonly >5 m thick. A single calcrete up to 1 m thick is present in most outcrops. The assemblage formed on a desiccated land surface with incised channels and dryland paleosols. Assemblage 3 is 13-22 m thick, and comprises grey siltstone sheets, minor red siltstone, and narrow channel bodies <2.5 m thick. The sandstones are strongly cemented with calcite. The assemblage formed on a dryland, anastomosing river plain, probably under conditions of rising base level that culminated in accumulation of peats (the Bonar Coal).

### General Hydrogeological Implications

The channel bodies of Assemblage 1, shortly above the Hub Coal (Fig. 4), are likely to provide the best aquifers. They are relatively thick, especially where they contain amalgamated storeys, coarse grained and moderately cemented, as well as being partially to completely isolated within mudstone-dominated successions which probably form important aquitards. In contrast, most strata of Assemblages 2 and 3 are likely to exhibit a relatively low permeability, as they include mudstones, dense calcrete, and channel sandstones that are relatively fine grained and well cemented. The homoclinal, seaward dip of the strata should have promoted downdip recharge of shallow groundwater following Mesozoic uplift to the near-surface zone, and the proximity of the mine site to the Mountain Fault (Fig. 3) allows the possibility that basinal fluids have invaded the aquifers during deep burial and subsequent exhumation. Some of these inferences are tested for the Prince mine site in the following sections.

Competent sandstone bodies at outcrop in the Sydney Mines Formation are well fractured by orthogonal joint systems, which control groundwater flow in shallow settings (Baechler, 1986), and hydraulic conductivities for sandstone units within 30 m of the subcrop surface range from $10^{-3}$ to $10^{-5}$ cm/sec (F. Baechler, unpublished data). However, fracture systems probably contribute little to flow below 75 m depth (ADI Nolan Davis, 1993).

## The Prince Sandstone

### Stratigraphy

Strata in the Prince Mine are known from the P6 and H12 holes drilled from the surface prior to mining, from many short cores drilled upwards from the mine galleries, and from limited observation in mine tunnels. The short cores extend less than 20 m above the coal, and are correlated with, but do not completely penetrate, strata equivalent to Assemblage 1 onshore.

The Hub Coal is about 2.3 m thick in the mine area, and is overlain by up to 4 m of grey mudstone, siltstone and thin sandstone, with plant fragments and siderite nodules. The overlying channel sandstone (hereafter termed the *Prince Sandstone*) is up to 13 m thick, and cuts through the mudstone to rest locally upon the Hub Coal in a zone about 400 m wide (Fig. 5). The curvilinear low depicted in Figure 5 includes basal conglomerate lags and probably represents in part the thalweg of a sinuous channel flowing to the east and northeast (Calder *et al.*, 1987). The base of the sandstone rises progressively to the north and south, where it overlies mudstones above the coal.

The sandstone in the P6 well shows a blocky profile on the gamma-ray log and is divided into three storeys (Fig. 6). The basal storey is 3 m thick, fine grained, well sorted and cross laminated to massive. A grey mudstone 24 cm thick forms the topmost stratum. Storey 2 is 8 m thick and is medium- to coarse-grained in its lower part, grading to fine-grained sandstone above. A thin pebbly sandstone with extrabasinal clasts up to 1 cm in diameter is present near the storey base, where plant fragments and fine carbonaceous material are especially common. Storey 3 comprises a thin layer with mudstone intraclasts (up to 5 cm), overlain by grey-brown laminated siltstone and grey mudstone. Higher strata are grey mudstones

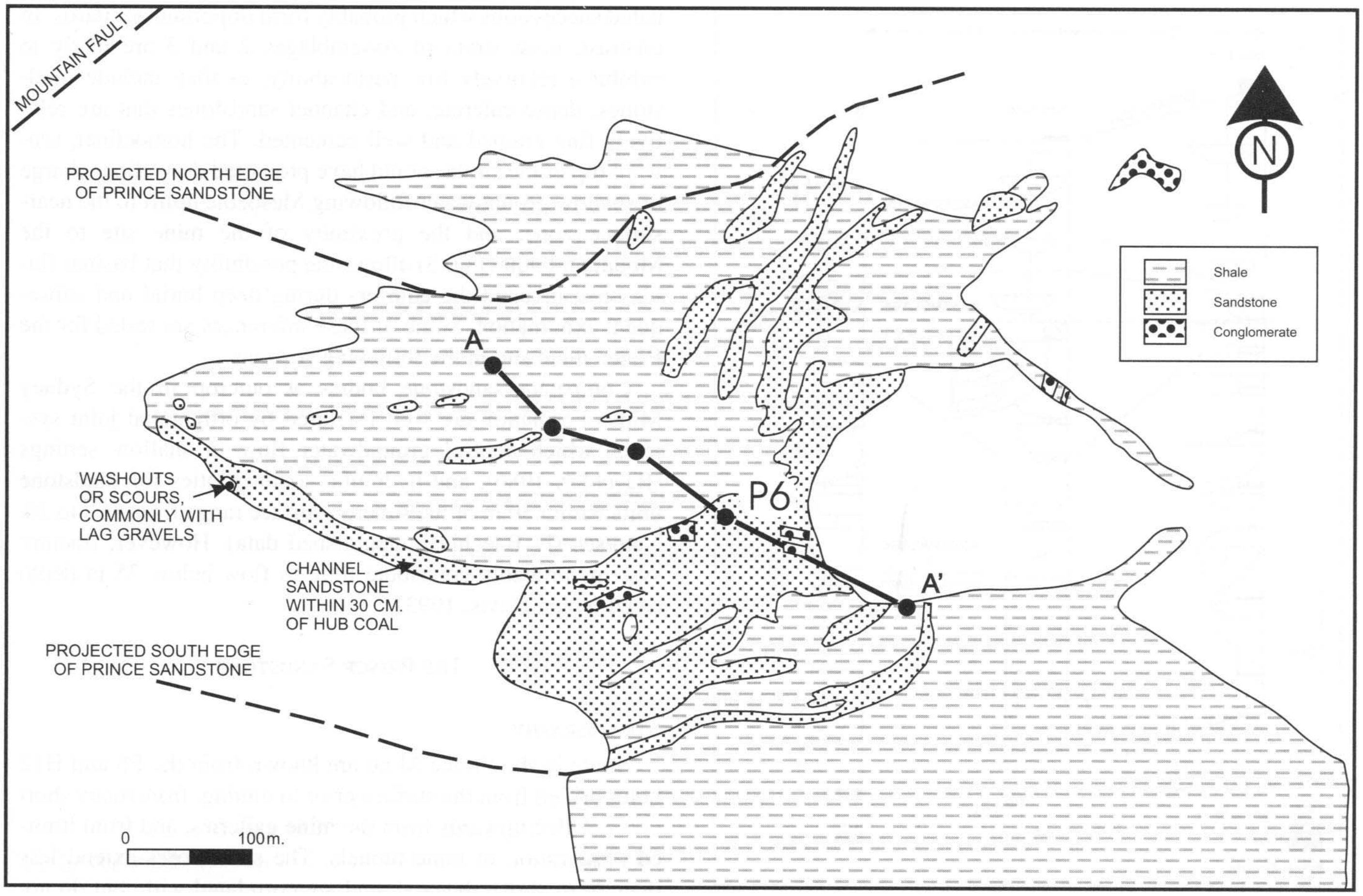

**Fig. 5.** Roof rocks overlying the Hub Coal. The Prince Sandstone rests directly on the coal in the vicinity of P6, where it forms a curvilinear channel body. Projected edges mark the limits of the zone where the sandstone is within 30 cm of the top of the coal. Locations of boreholes used in the cross-section of Figure 7 are shown. Simplified from 1994 Prince Mine plans. Mapped area covers most of the mine workings shown in Figure 12, with the exception of the two northernmost mining panels.

and siltstones, with thin beds of fine-grained sandstone, coal, and carbonaceous mudstone. The lateral continuity of the storeys and their bounding surfaces is difficult to ascertain, but the storeys may extend across the width of the channel body (Fig. 7).

### Porosity and Permeability

Porosity and permeability data (Figs. 6, 8) were obtained commercially from 12 samples from core P6, using a helium porosimeter and a nitrogen permeameter. Sandstones in Storey 1 have permeability values of 0.2-1.33 millidarcy (md) and 11.4-13.9% porosity. Sandstones in Storey 2 have higher values, with 0.41-20.9 md permeability and 12.3-16.9% porosity. No data are available for Storey 3 and mudrocks. One sample from core PM59 had 19.5% porosity and 42.5 md permeability. Porosity and permeability show a positive correlation, with a considerable spread of data (Fig. 8).

Effective porosity values were calculated from the wireline log of the P6 well using standard methods that include correction for clay content of the rock matrix (Crain, 1986; Schlumberger, 1996). Calculated values match closely with those measured in the core (Fig. 9). Sandstones overlying the Hub Coal are exceptionally porous compared with sandstones at higher stratigraphic levels, but porosity is enhanced at depths <100 m (Fig. 9).

### Petrography and Diagenetic History

Nine Prince Sandstone samples (cores P6, PM59 and PM65) were examined using thin sections, the electron microprobe and the scanning electron microscope. Of six samples from the P6 core, five represent Storey 2 and one represents Storey 1. The major grain types are mono- and polycrystalline quartz, with sand-sized clay aggregates composed principally of kaolinite and illite. Although the latter may include bedrock mudstone clasts, the majority are probably mud fragments released into Late Carboniferous rivers from adjacent floodplains, as inferred from abundant evidence that they have undergone compaction between more rigid quartz grains. Metamorphic rock fragments and chert are minor framework constituents, and muscovite, biotite, tourmaline, and zircon are accessory minerals. Coarse-grained, pebbly lags include siderite and chert clasts, probably derived from adjacent paleosols and/or eroded bayfill muds.

Poikilotopic calcite cement is widespread in Morien Group sandstones (based on 146 thin sections studied by Gibling and Nguyen, 1999) but is present only as small, ragged patches in

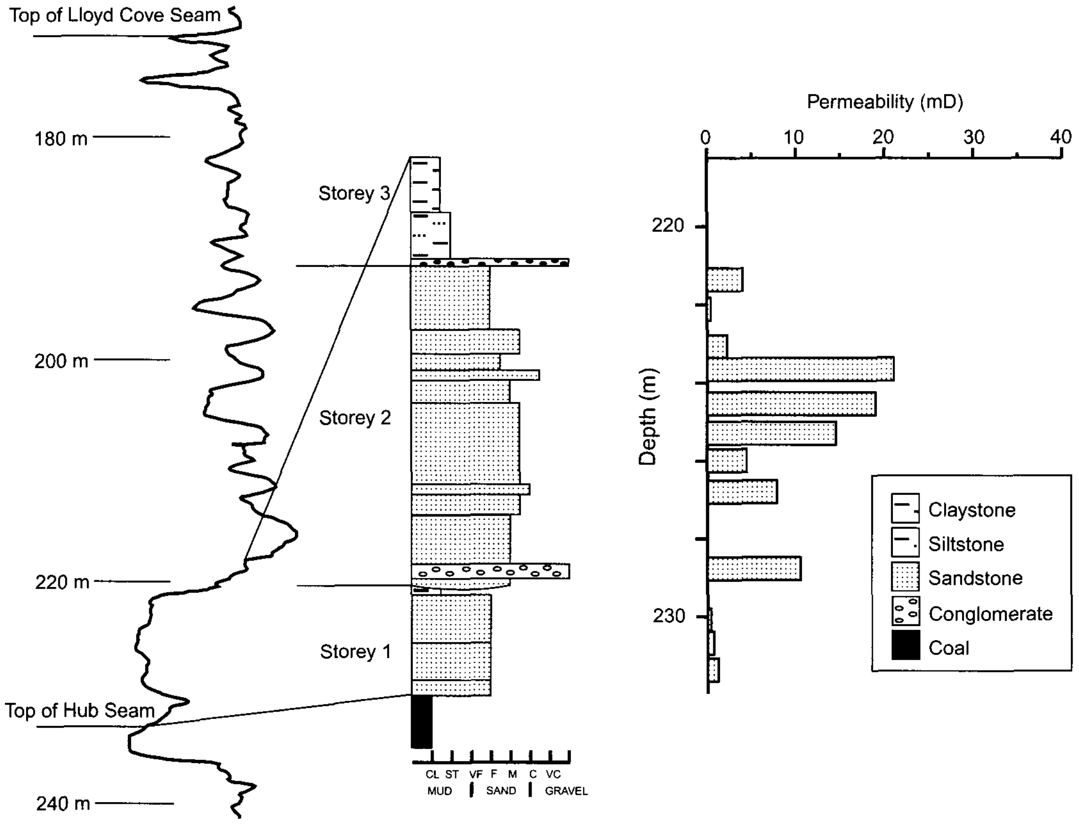

**Fig. 6.** Lithological and gamma-ray logs for the P6 well in the Hub Coal roof. Permeability measurements are shown alongside the lithological column, which is subdivided into three storeys.

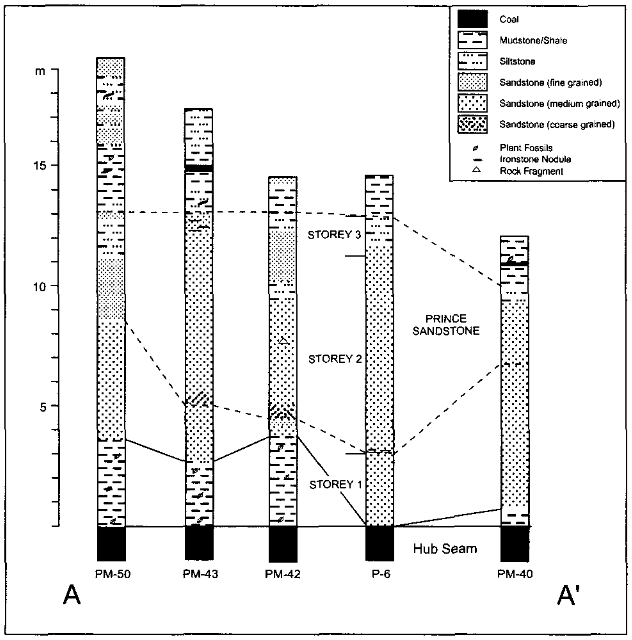

**Fig. 7.** Correlation of borehole logs from the Prince Mine roof. Line of cross section is A-A' in Figure 5.

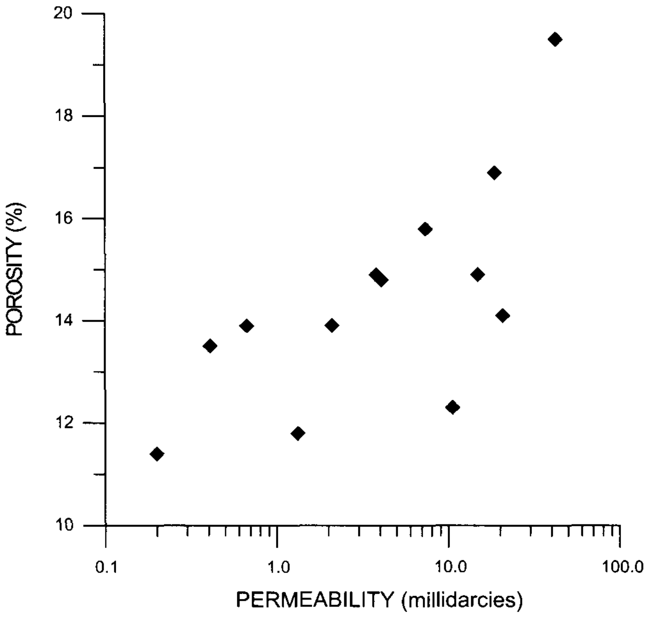

**Fig. 8.** Plot of porosity and permeability for samples from the Prince Sandstone.

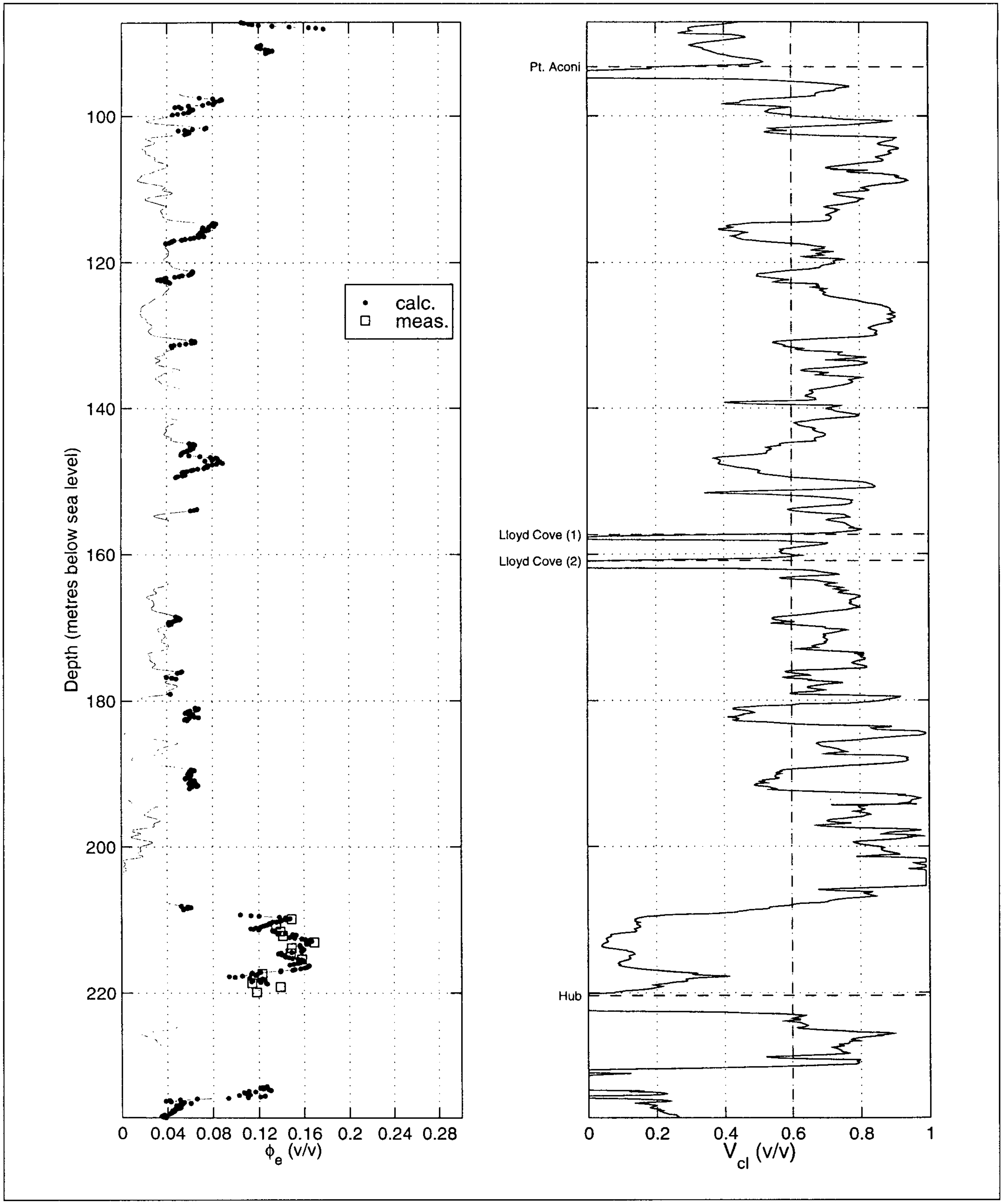

**Fig. 9.** Depth in P6 well plotted against effective porosity ($\phi_e$) and volumetric proportion of clay minerals within rock matrix ($V_{cl}$), both estimated on a volume for volume (v/v) basis. In the lefthand plot, the light line shows effective porosity smoothed using a 0.5 m Savitzky-Golay filter; dots are plotted intervals where $V_{cl}$ is less than 60% and coal is not present. Measured porosity values were obtained from core using conventional methods. In the righthand plot, the stratigraphic positions of the Hub, Lloyd Cove (two leaves) and Point Aconi Seams are shown.

the sample suite. Where present, the cement contains framework grains (including undeformed mud fragments) that apparently "float" in the cement, indicating early cementation prior to significant compaction of the sand. Early pyrite euhedra and siderite crystals rim some grains.

Pore space was estimated for three samples using 500 points in thin sections and 2400-3000 automatically scanned points under the electron microprobe, with pores assessed as unclassified points. Porosity estimates ranged from 10.6 - 17.8%, with good agreement between the two methods and commercially obtained estimates for the same samples. Large (>1 mm in diameter) and irregular pores are prominent, and the presence of calcite-cemented patches suggests that many pores originated by cement dissolution. The pores are bordered by quartz framework grains that exhibit well developed overgrowths, and siderite crystals rest upon the overgrowths or are intergrown with them (Figs. 10, 11A). The pores contain kaolinite "books" intergrown locally with illite fibres, with abundant micropores (Fig. 11B), and small quartz crystals also contribute to some pore fills. The pore-filling clays postdate the siderite and most of the quartz. A few pores are blocky in shape, with partial kaolinite fills, and may represent alkali feldspar or perthite grains that were dissolved during burial (good evidence for this is seen in Phalen Mine sandstones).

Although samples from the Prince Sandstone are presently highly porous, we infer that porosity was originally substantially occluded during shallow burial, as a result of calcite

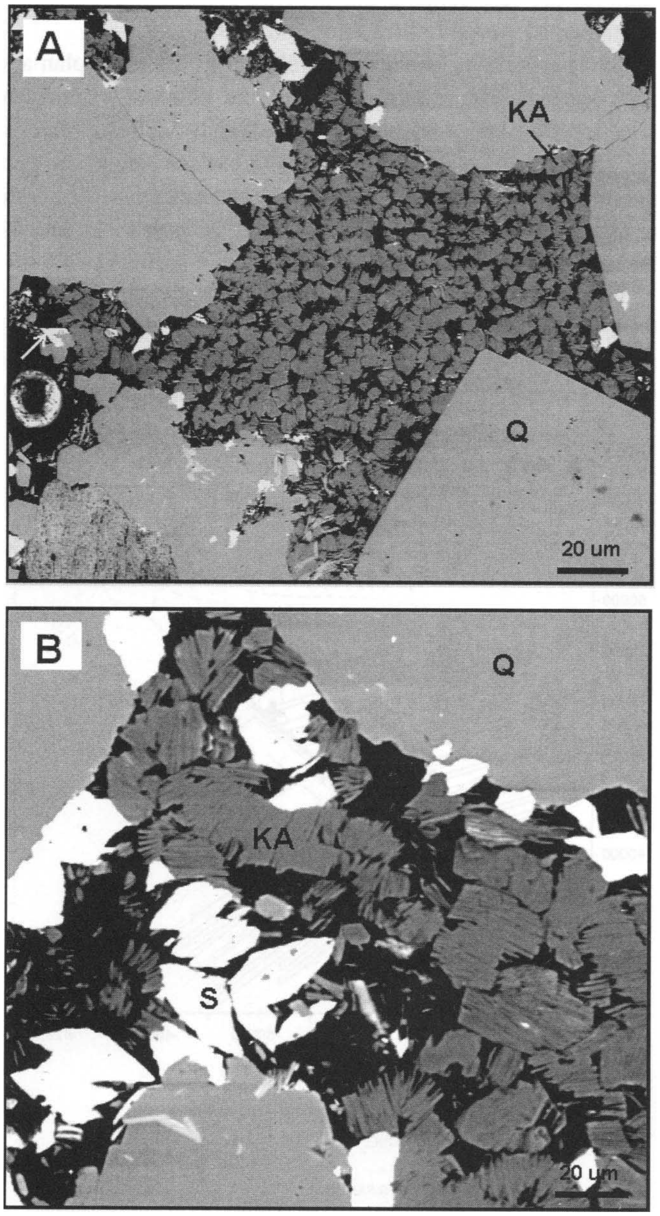

**Fig. 10.** Pores and partial fills in Prince Sandstone as seen in backscattered electron microprobe images of sample P6-5. A. Pore ~150 μ in diameter, bordered by quartz grains (Q) with well developed euhedral overgrowths. A clay aggregate is present at lower left. The pore contains well formed "books" of authigenic kaolinite (KA), euhedra of siderite and quartz, locally intergrown with siderite (arrowed). Large circle at lower left is an artefact. B. Pore fill of kaolinite (KA) and siderite (S), between framework quartz grains (Q).

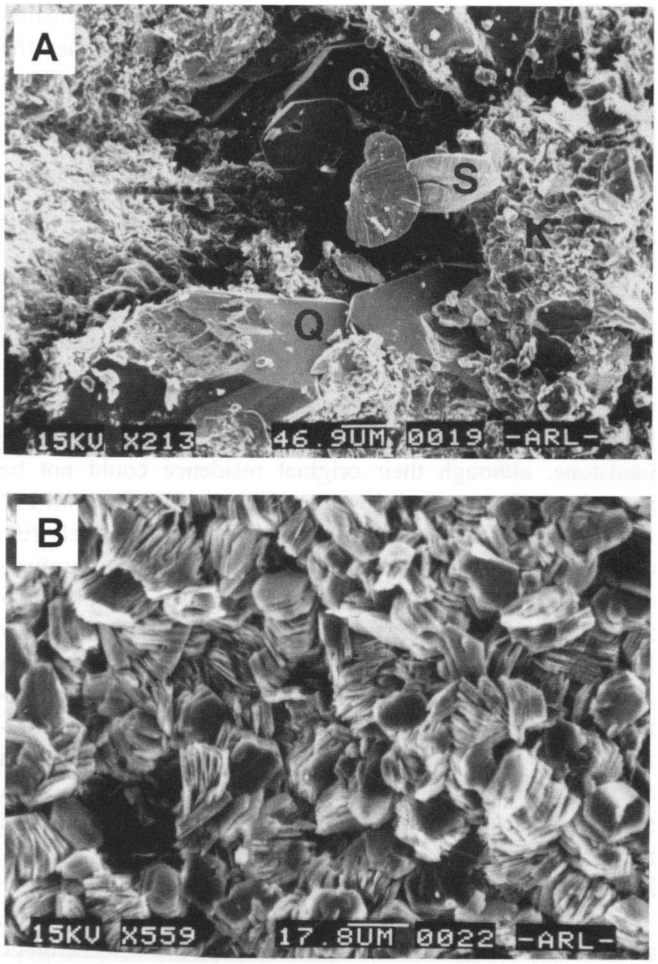

**Fig. 11.** Pores in Prince Sandstone as seen under the scanning electron microscope. A. View into pore about 0.5 mm in diameter, partially filled with euhedral overgrowths on framework quartz grains (Q), siderite (S) and kaolinite (K). B. Closeup of kaolinite books about 20 μ in diameter and intercrystalline porosity.

cementation and compaction of mud fragments and matrix. This is inferred from the presence of ragged patches of calcite cement with floating framework grains, coupled with the abundance of calcite cement in sandstones throughout the Morien Group (Gibling and Nguyen, 1999). It is not know if the cement was originally pervasive or present as irregular patches. At a later time, we infer that secondary pores were generated by dissolution of calcite cement and, probably, feldspar grains, causing partial collapse of the rock framework. These pores were later partly filled by quartz overgrowths, calcite, siderite, and authigenic clays.

All thin sections examined showed similar grain types and diagenetic trends. However, the sample from Storey 1 is fine grained, and has abundant deformed mud fragments and matrix, as well as local calcite-cemented patches; it appears considerably less porous than samples from Storey 2. Porosity varies from effective (large, interconnected pores between a collapsed framework) to non-effective (isolated dissolved grains and micropores between clays). The rocks have undergone only minor deformation, and fractures were not observed in the available samples. Thus, fluid connection is probably maintained through pores of the type observed under the microscope, although fractures may be more common than available evidence suggests.

## WATER CHEMISTRY

### SAMPLING AND ANALYSIS

*Formation waters* were collected from braced drivages (roadway tunnels) within the mine prior to significant coal extraction, when fracturing in the surrounding rock had been minimal. Drips emanating from roof sandstone or from boreholes intersecting sandstone were sampled. The fluids probably occupied pore space within the basal portion of the Prince Sandstone, although their original residence could not be determined. Eight samples were collected at depths from 192 to 331 m below sea level. Although we report relatively few samples, we stress that these samples have been carefully selected in consultation with CBDC scientists as representative of waters in the mine area prior to longwall mining. They thus represent an unusually reliable subsurface suite that has undergone minimal contamination as a result of mine operations. Samples collected by mine geologists prior to the initiation of this study were no longer available, and formation water samples among this suite could not be duplicated, because the sandstones at the collection points have drained out during subsequent mining. Thus, a full data set, especially for Br and isotopic analysis, is not available for all samples.

*Gob waters* are samples from collection points that drain mined-out areas (gobs). Drivages encompass a reserve block and coal is extracted progressively toward the main slope by retreat longwall mining beneath movable roof supports. As the supports move forward, the roof collapses, allowing waters to drain through fractures into the gob. The gobs are exposed to varying degrees of aeration, and waters may represent mixtures from panels mined at different times. They have undergone chemical reactions with mine rock that the formation waters have not, and may contain formation waters from several strata levels mixed with the products of mine-rock reactions and fluids from operating machinery. Swath bathymetry studies of the sea floor over the Prince Mine show that subsidence associated with collapse of the mined-out panels has reached the sea floor (Forrester *et al.*, 1996), suggesting that the rock body above the mine may be extensively fractured. The twelve gob samples are less reliable but provide confirmatory evidence for trends observed in formation samples.

Sample location is shown in relation to the mine plan and position of the Prince Sandstone in Figure 12. Most waters were obtained from areas where the Prince Sandstone rests on, or is less than 30 cm above, the Hub Coal. Four samples (three gob; one formation) came from areas where the sandstone is at higher levels, up to 4 m above the coal, and the host rocks may be "wings" of the Prince Sandstone or separate sediment bodies.

Prince Mine waters have been sampled routinely by CBDC, and additional samples were collected during this study. The latter were filtered through 0.45μ filters and stored in Nalgene polypropylene bottles. Temperature was measured

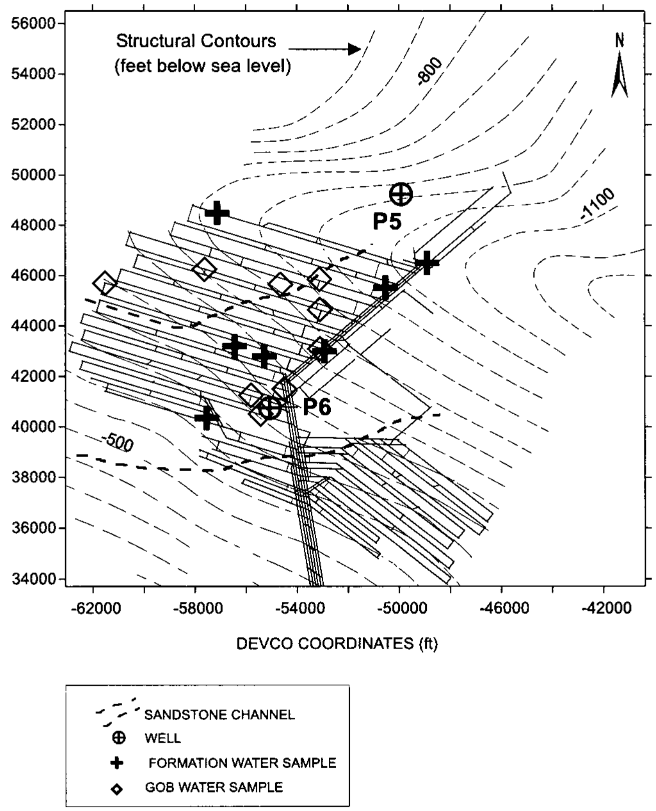

**Fig. 12.** Simplified mine plan of the Prince Mine. Structural contours are shown for the Hub Seam with the onshore outcrop designated as zero. Also shown are the approximate northern and southern edges of the sandstone channel body (Fig. 5), termed here the Prince Sandstone. Water sample locations are indicated; three gob sample points represent two water samples each; one formation water sample is not shown on the plot as coordinates are not known.

at all locations using a standard thermometer. Eh and pH could not be measured within the mine due to restrictions on the use of equipment underground, but were measured at the surface immediately after collection. Major and trace element analysis was conducted at Environmental Services Laboratory, Sydney, a CAEL accredited laboratory, using standard methods (American Water Works Association, 1989). Samples were split, filtered, acidified and analysed within two days of collection. The concentration of total dissolved solids (TDS, in mg/L) was calculated as the ionic sum of major and minor constituents (Na, K, Ca, Mg, Fe, Sr, Cl, $SO_4$ and 0.6 alkalinity), not including trace elements. Bromine was measured by Philips Analytical Services Corporation, Halifax, Nova Scotia, using ICP-MS (Long and Martin, 1991). Samples were preserved to pH<2 with nitric acid, and bromine was monitored at 79 and 81 amu, both of which are relatively free from interferences in a nitric acid matrix. Precision was 0.0033 mg/L and the detection limit was 0.05 mg/L.

Oxygen and hydrogen isotope ratios were measured at the Environmental Isotope Laboratory, University of Waterloo, Ontario. Oxygen isotope ratios were determined using $CO_2$ equilibration (Epstein and Mayeda, 1953; Fritz *et al.*, 1986), and D isotopic values were determined using zinc reduction (Coleman *et al.*, 1982). Both methods employed conventional gas-source mass spectrometry, and results are reported with respect to the SMOW standard (Craig, 1961). Precision was 3 per mil for D and 0.2 per mil for $^{18}O$ in water.

In view of the highly variable salinity of the waters, we use the term "brine" for saline fluids without specific concentration limits (see discussions in Carpenter, 1978, and Hanor, 1994), although some samples are less concentrated than seawater. We emphasize here chemical components, especially Cl, Br, Na, and O and H isotopes, that are especially important for evaluating the origins of water and solutes; Martel *et al.* (*in press*) discuss other components in Prince and Phalen samples.

Salinity was estimated within the Prince Sandstone directly above the Hub Seam using wireline data from two exploration holes, P5 and P6. These wells were drilled prior to mining activity, and responses recorded in the logs should represent relatively pristine formation fluids. The mine has subsequently encroached on the position of P6, allowing a close comparison of measured and log-derived salinity. Well P5 lies beyond the mined area but, due to the local structure, lies within the depth range of the water samples (Fig. 12). First, appropriate corrections for borehole conditions and for the effects of clay minerals were applied, and porosity was calculated using density and neutron porosity logs (Schlumberger, 1996). Given accurate porosity estimates, formation water resistivity may be estimated using the Archie Equations (Archie, 1942) with wireline measurements from a deep-reading resistivity tool (Kwader, 1986; Gran *et al.*, 1992; Lindner-Lunsford and Breton, 1995; Schnoebelen *et al.*, 1995; Jorgensen, 1996). Since aquifers in the study area contain significant clay mineral fractions, a modified form of the Archie Equations (Poupon and Leveaux, 1971) was used (Appendix 1). Finally, conversion of formation water resistivity to salinity was accomplished using the empirical relationship given by Bateman and Konen (1977) and was verified with water chemistry data from numerous samples within the study area.

### Major Element Analysis

*Formation water samples* have total dissolved solid (TDS) values from 7,950 to 47,840 mg/L (Table 1). The samples are Na-Ca-Cl brines. Major cations are Na and Ca, with lesser Mg, Sr, K, Fe and $NH_4$. The major anion is Cl, with minor amounts of $HCO_3$ and $SO_4$. The pH varies from 6.7 - 8.1. Br:Cl ratios are relatively high, and plot above the seawater evaporation curve defined by Fontes and Matray (1993a) (Fig. 13). Values of TDS increase progressively with depth (Fig.14), and chloride contours are subparallel to structural contours (compare Figs. 12 and 15). Figure 14 shows that log-derived salinity estimates are in good agreement with TDS values at comparable depths, confirming that the formation water samples are representative of pre-mining fluids. Na:Cl ratio decreases from 0.87 to 0.61 with depth (Fig. 16).

*Gob water samples* in all parts of the mine are relatively saline (TDS 24,473 to 46,561 mg/L) and the samples are also Na-Ca-Cl brines. Br:Cl ratios resemble those of formation waters (Fig. 13). Fe and $SO_4$ concentrations are up to 712 and

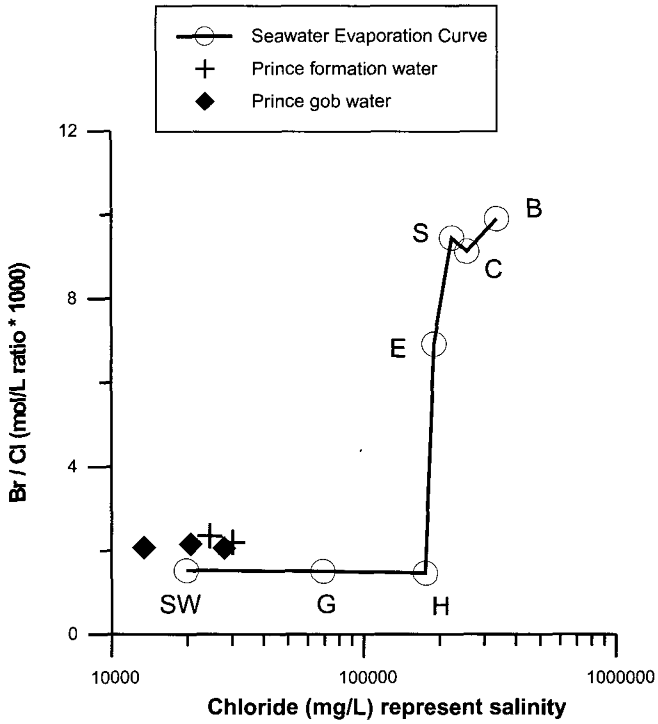

**Fig. 13.** Br/Cl ratios for Prince waters plotted against Cl, which represents Salinity. Evaporative seawater curve is derived from data in Fontes and Matray (1993a): SW = sea water composition; G, H, E, S, C and B refer to point of precipitation of gypsum, halite, epsomite, sylvite, carnallite and bischofite, respectively. See text for explanation of formation and gob waters. The relative Br enrichment of the Prince samples (positioned above the curve) is indicative of an origin from evaporated seawater, rather than from local seawater. Note that, although the plot is based on a small number of available Br analyses for Prince Mine waters (see text and Table 1), the larger data set for Phalen Mine waters shows a similar pattern (Martel *et al.*, in press).

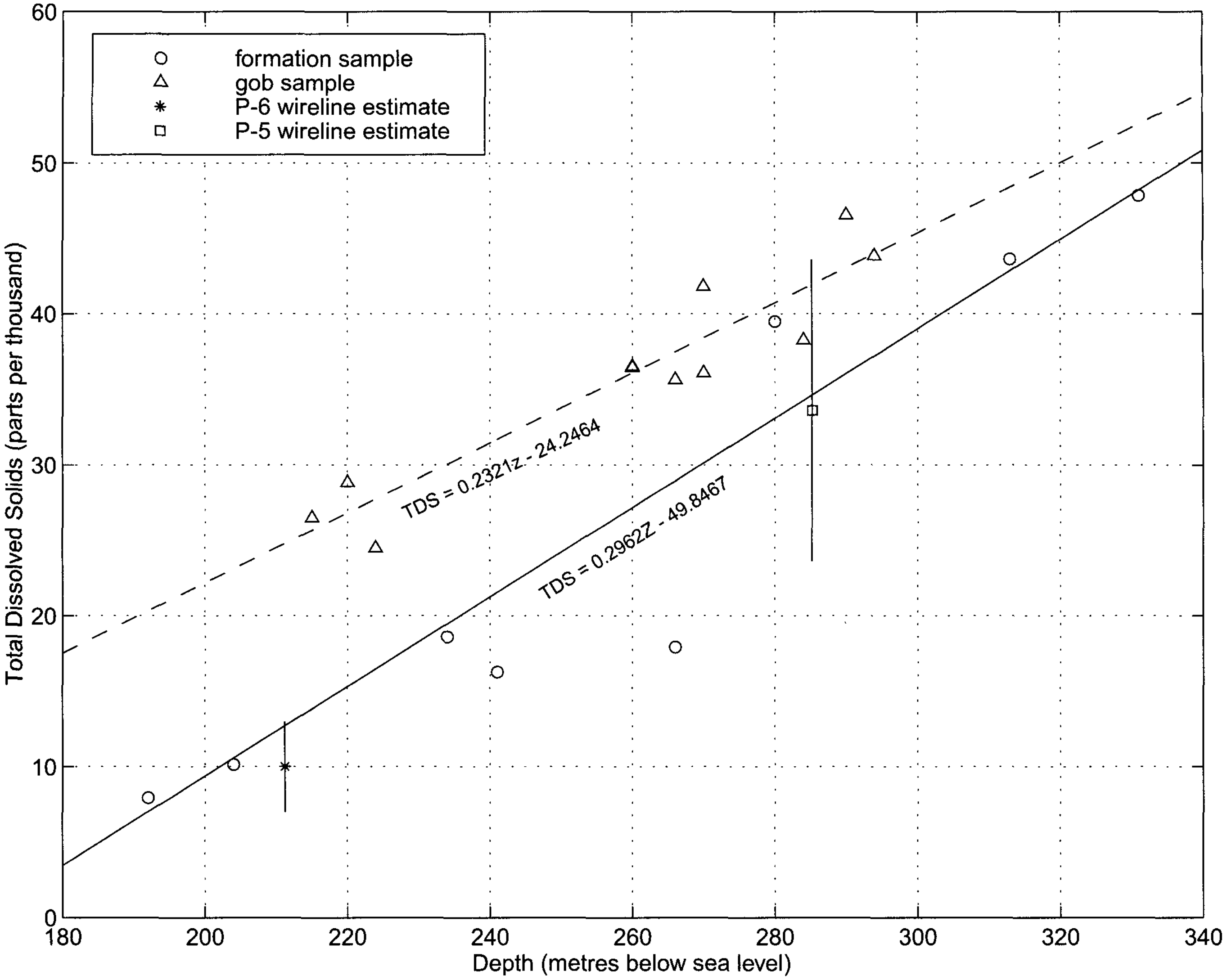

**Fig. 14.** Plot of salinity (TDS in ‰) against depth for Prince Mine waters. Data include water chemistry analyses and geophysical estimates from wireline data in wells P5 and P6, which were drilled before mining occurred. The dashed line is the Bisquare Regression Estimate (Mosteller and Tukey, 1977) based on gob samples only. The solid line is the Bisquare Regression Estimate based on the formation samples and the wireline data. Empirical error estimates of +/-20% are indicated for the wireline data.

2313 mg/L, respectively — much greater than the maximum values of 7.5 and 12 mg/L recorded for formation waters (Table 1). Their alkalinity is also much lower, as is pH which ranges from 2.6 to 5.9. Gob water salinity increases downdip at a rate broadly comparable to that of formation water samples, but most gob samples have higher salinity than formation waters at a similar depth (Fig. 14). Na:Cl ratios for gob waters are less than 0.7 and show no systematic trend with depth, although the ratios are generally similar to or lower than formation water samples at similar depth (Fig. 16). Reasons for the poor correlation with depth are explored below.

### Isotopic Analysis

Figure 17 shows a hydrogen/oxygen isotope plot for Prince samples and other waters, with TDS values beside each sample. The single sample of Prince formation water plots close to the Global Mean Water Line (GMWL) but distant from both local rainwater and local seawater. The sample also plots close to two Phalen samples of much higher salinity. The five gob samples plot near the formation water sample, defining a near-linear trend that runs obliquely to and straddles the GMWL. The gob samples show no apparent isotopic trend with salinity.

## Discussion

### Origin of Brines

The origin of brines in the Phalen and Prince mines was discussed in detail by Martel *et al.* (*in press*). Similar trends are apparent in formation waters from both areas, and key lines of geochemical interpretation are briefly set out here.

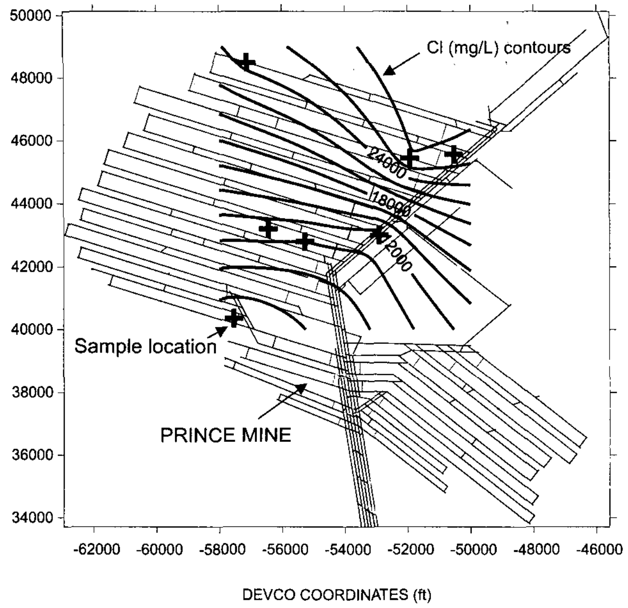

**Fig. 15.** Contour map of chloride concentration in formation waters from the Prince Mine. Sample locations are marked by crosses (see Fig. 12 for locations). Comparison with Figure 12 shows that Cl contours are subparallel to structural contours, as depth to coal increases generally to the northeast. The mine grid system is oriented north-south and is in feet. Note the general increase of salinity downdip and locally away from the Mountain Fault (to northwest of the mine: Fig. 5).

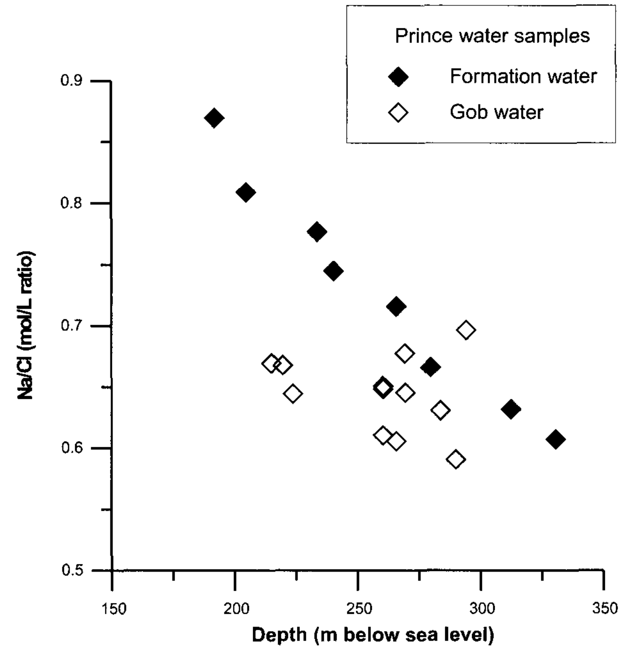

**Fig. 16.** Na/Cl ratio against depth for Prince waters. Both formation and gob waters show decreasing ratios downdip. Gob samples have generally lower ratios than formation samples at corresponding depths.

Formation water solute content exceeds sea-water concentration in both mines, and exceeds 176,000 mg/L in Phalen formation waters. Br:Cl ratios greater than those of evaporated sea water (Fig. 13) have been widely used to infer that an original seawater source evaporated past the point of halite precipitation, resulting in a Br-enriched residual brine (Rittenhouse, 1967; Egeberg and Aagaard, 1989; Fontes and Matray, 1993a; Nativ, 1996). Similar reasoning is used to explain Na:Cl ratios that are considerably lower than those of seawater (Fig. 16; *e.g.* Nativ, 1996). Dilution of brines by low-salinity waters lowers the concentrations but does not affect solute ratios. The Br:Cl ratio can be used to estimate the degree of evaporation needed to generate the parent brines, by comparison with the seawater evaporation curve (Egeberg and

**Table 1**. Geochemical analysis of groundwater samples from the Prince Mine. Concentrations are in mg/L, apart from pH values. Isotope ratios are expressed in δ (‰) as per mille differences relative to Standard Mean Oceanic Water (SMOW). Mine section indicates location within longwall mining panels. Depth is in metres below sea level. See text for explanation of formation and gob waters.

| Sample # | Mine Section | Depth | Na | K | Mg | Ca | Sr | Fe | $NH_3$ (N) | Cl | $SO_4$ | Br | Alkalinity | TDS | pH | δ18O | δD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FORMATION WATER** | | | | | | | | | | | | | | | | | |
| CBDC-518 | 4 WWF | 192 | 2650 | 52 | 93 | 345 | | 0.0 | 1.4 | 4700 | 2.4 | | 177.0 | 7950 | 7.9 | | |
| CBDC-559 | 4 Decline | 266 | 5200 | 81 | 294 | 1030 | | 0.9 | 3.9 | 11200 | 12.0 | | 160.0 | 17918 | 8.1 | | |
| CBDC-43 | 8 WT | 205 | 3200 | 64 | 175 | 463 | | 6.8 | 1.9 | 6100 | 2.0 | | 210.0 | 10139 | 7.7 | | |
| CBDC-594 | 9 WWF | 234 | 5590 | 90 | 402 | 1370 | | 2.5 | 2.9 | 11100 | 3.0 | | 76.0 | 18606 | 7.5 | | |
| CBDC-602 | 9 WWF | 241 | 4830 | 72 | 302 | 991 | | 0.4 | 3.1 | 10000 | 2.0 | | 140.0 | 16285 | 7.6 | | |
| CBDC-676 | 14 WB | 313 | 11100 | 93 | 1135 | 4090 | 62.6 | 5.1 | 5.8 | 27105 | 3.6 | | 44.9 | 43627 | 6.7 | | |
| Dal Pr 4D | 4 Decline | 331 | 11900 | 108 | 1145 | 4345 | 82.3 | 4.5 | 6.1 | 30230 | <1 | 150 | 31.5 | 47840 | 7.9 | -5.48 | -31.31 |
| PR 3 | 15 WBL | 280 | 10580 | | 958 | 3320 | 54.6 | 7.5 | 0.7 | 24500 | 3.7 | 130 | 105.0 | 39488 | 7.3 | | |
| **GOB WATER** | | | | | | | | | | | | | | | | | |
| CBDC-571 | 5 WB | 215 | 6770 | 104 | 660 | 1900 | | 32.0 | 3.1 | 15600 | 1420.0 | | 1.0 | 26490 | 2.7 | | |
| CBDC-570 | 6 WWF | 220 | 7230 | 112 | 830 | 1900 | | 197.0 | 3.7 | 16700 | 1870.0 | | 1.0 | 28843 | 2.9 | | |
| DAL Pr 7WB | 7 WB | 224 | 5615 | 67 | 871 | 2025 | 30.3 | 187.0 | 3.0 | 13440 | 2235.0 | 63 | 0.4 | 24473 | 2.6 | -6.99 | -42.38 |
| DAL Pr 10WB | 10 WB | 266 | 8070 | 126 | 1290 | 2535 | 42.5 | 712.0 | 4.0 | 20550 | 2313.0 | 100 | 0.4 | 35643 | 4.0 | -6.9 | -42.41 |
| Dal Pr 12 WB | 12 WB | 290 | 10700 | 153 | 1625 | 4280 | 65.9 | 149.0 | 4.8 | 27950 | 1633.0 | 130 | 0.4 | 46561 | 4.4 | -5.71 | -36.57 |
| CBDC-673 | 13 WT x-cut # 3 | 260 | 9000 | 180 | 1120 | 2800 | 40.2 | 19.8 | 3.8 | 21330 | 1978.7 | | 0.4 | 36473 | 5.2 | | |
| CBDC-674 | 13 WT x-cut # 3 | 260 | 8640 | 163 | 1060 | 2675 | 61.6 | 28.4 | 3.5 | 21830 | 1983.5 | | 3.5 | 36447 | 5.6 | -4.42 | -29.42 |
| CBDC-677 | 12 WWF | 284 | 9170 | 140 | 1305 | 3535 | 48.8 | 43.2 | 4.3 | 22425 | 1584.6 | | 0.4 | 38256 | 4.5 | | |
| CBDC-679 | 13 WT x-cut # 2 | 270 | 10175 | 174 | 1473 | 3470 | 46.2 | 95.4 | 5.4 | 24318 | 2063.7 | | 0.4 | 41821 | 3.1 | | |
| CBDC-680 | 13 WT x-cut # 3 | 260 | 9000 | 159 | 1163 | 3018 | 37.4 | 39.4 | 2.6 | 21410 | 1678.8 | | 23.1 | 36522 | 5.9 | -4.33 | -30.27 |
| CBDC-681 | 13 WT x-cut # 2 | 270 | 9145 | 164 | 1265 | 2760 | 40.0 | 79.4 | 2.2 | 20815 | 1810.0 | | 0.4 | 36081 | 5.2 | | |
| CBDC-684 | 14 WT x-cut #1 | 294 | 11400 | 141 | 1470 | 3210 | 451.0 | 24.6 | 4.7 | 25242 | 1914.8 | | 0.0 | 43858 | 4.9 | | |

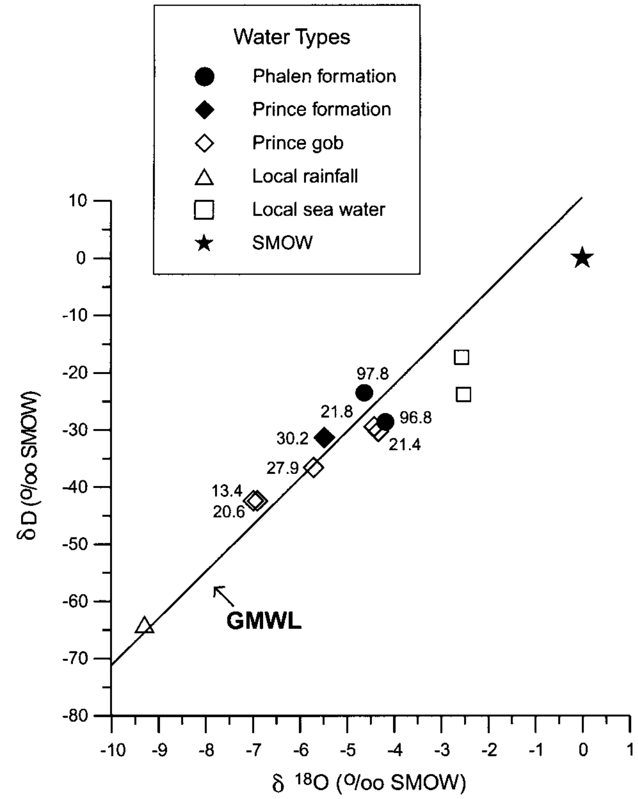

**Fig. 17.** Oxygen - hydrogen isotope plot for Prince and related water samples. Cl values in thousands of mg/L are shown beside data points. Global Meteoric Water Line (GMWL) and composition of Standard Mean Oceanic Water (SMOW) from Drever (1988).

Aagaard, 1989). We estimate that the degree of evaporation experienced by the original Prince brines prior to dilution was 15-18 times. Evaporation initially enriches the remaining water in heavy isotopes ($^{18}O$, $^{2}H$), so that evaporated seawater generally plots to the right of the GMWL (Sofer and Gat, 1975). This is not the case for the Prince brines (Fig. 17), probably due to the high degree of dilution of the original brines.

Parameters for Na deficit and Ca excess (as defined by Davisson and Criss, 1996) show a linear correlation for Sydney brines, suggesting that the brines have been modified through albitization of plagioclase during their residence in the basin fill (Martel *et al.*, *in press*). Other water/rock reactions are also indicated from geochemical evidence (Martel *et al.*, *in press*). Gob samples also show high Br:Cl and low Na:Cl ratios, and are inferred to contain a major component of parent brine; however, their high Fe and $SO_4$ contents indicate modification by water/rock reactions, especially with pyrite in coal, mudstone, and sandstone fragments within the gob.

Halite dissolution and hyperfiltration cannot be ruled out as minor contributors to the Sydney brines (Martel *et al.*, *in press*). Halite dissolution has been inferred to explain saline groundwater (*e.g.* Banner *et al.*, 1989; Fontes and Matray, 1993b; Hanor, 1987, 1994), but this explanation is improbable for the Prince waters, based on the strong geochemical contrast between the mine waters and salt springs in Atlantic Canada (Cole, 1930), which show low Br:Cl and high Na:Cl ratios typical of evaporite dissolution. Hyperfiltration can concentrate solutes during the passage of fluid through a semi-permeable membrane such as a mudstone under a high hydrostatic pressure differential (Graf, 1982). This mechanism has been invoked to explain brines in basins that contain overpressured zones or that lack evaporites, but neither condition applies to the Sydney Basin. Many workers have questioned the ability of this mechanism to produce significant brines in natural settings (Schwartz and Muehlenbachs, 1979; Egeberg and Aagaard, 1989; Hanor, 1994). However, Nolan Davis and Associates (1992) presented data supporting the possible localized presence of such a process onland in the Point Aconi area near the Prince Mine. Bromine is preferentially concentrated by some plants (Edmunds, 1996) and Br associated with organic matter in the Morien Group could have contributed to the fluids, although this would not explain the high Cl concentrations.

We suggest that the brines originated during precipitation of Windsor Group evaporites, which underlie the Sydney coal measures (Fig. 2). Saline deposits are only minor components of other Paleozoic formations in the region, and Triassic evaporites are present below the Atlantic margin, but are not known in the Sydney Basin. Additional circumstantial evidence favours a Windsor source: highly saline fluid inclusions are present in mineral deposits in Atlantic Canada that, at least in some cases, have been dated as mid-Carboniferous (Ravenhurst *et al.*,1989; Armstrong *et al.*, 1993; Pan *et al.*, 1993).

### BRINE DILUTION

Although Windsor evaporative brines probably supplied the bulk of the solutes in the Prince waters, many water samples presently have salinities below that of seawater, suggesting that the brines have been highly diluted. The progressive increase in salinity with depth (Figs. 14, 15) strongly implies that the dilute fluids entered the sandstones from surficial sources, while the Prince Sandstone was close to the present land surface. What were these fluids, and when did they enter the sandstone?

Isotopic values for Prince waters lie close to the GMWL (Fig. 17), which might suggest mixing with relatively young surficial waters. However, the isotopic data do not correspond with modern rainwater (Fig. 17), and meteoric addition during earlier geological periods is most reasonable, for example during the Cenozoic when glacial and interglacial conditions affected the area. The relatively high hydrogen isotopic ratios indicate that the diluting fluids were warmer than present-day local rainfall, suggesting mixing during a previous interglacial period or during preglacial times (cf. Siegel, 1991; Steuber and Walter, 1994). One problem with such an explanation is the similar isotopic composition of the relatively dilute Prince waters (up to 48,000 mg/L) and the relatively saline Phalen waters (up to 176,000 mg/L), as shown in Figure 17: isotopic differences would be expected between these sample groups in view of the variable degree of dilution. Other, more complex, explanations include isotopic effects during the original evaporative cycle and equilibration with methane or hydrogen sulphide gas during residence in the sandstones (Martel *et al.*, *in press*).

The two gob samples containing ~21,000 mg/L of Cl might have been diluted by seawater as they lie on a possible mixing line between formation water and local seawater (Fig. 17). Br values are not available for these samples, so that the definitive Br:Cl ratio is unknown. However, both samples have among the lowest Na:Cl ratios of the suite (0.65 and 0.61), which does not support a modern ocean source. There is no geochemical evidence that fracturing of the rock body during longwall retreat has allowed sea water penetration to 200 m below sea level — the upper limit of the present sample suite. Shallower formation water samples (35-70 m below sea level) from the subsea Point Aconi Tunnel, south of the Prince Mine, show evidence of a young seawater component (Gibling *et al.*, 1999b).

The simplest explanation for fluid evolution in the Prince Sandstone involves a single brine and a single dilute component. However, the high solute contents of the original brines would have overwhelmed the solute contribution from other possible components, for which isotopic data provide the most telling evidence. The brines themselves could have represented mixing of several components during recharge and subsequent migration to their present site.

Brines with isotopic values that plot close to the GMWL were also recorded by Nativ (1996) from Oak Ridge, Tennessee, where brines with up to ~200,000 mg/L TDS are present at shallow depth. The presence in the brines of detectable tritium and a high percentage of $^{14}C$ to >268 m depth led Nativ to suggest that surficial waters have penetrated deeply, probably along fractures, and mixed with old formation waters.

### Fluid Evolution in the Prince Sandstone

A possible scenario for fluid evolution within the Prince Sandstone is shown in Figure 18, which draws also on data from the Phalen Mine and elsewhere in the basin. The initial, connate fluids of strata above the Hub Coal may have been marine to brackish, based on the high sulphur content of the coal and the presence of foraminifera in Assemblage 1 of the Hub Cyclothem. However, the Prince Sandstone is a channel body and initial fluids may have been fresh, continental water. Additionally, Assemblages 2 and 3 are alluvial plain deposits, and marine waters could have been flushed by fresh groundwaters during the lowstand, regressive period indicated by Assemblage 2. Porosity was reduced by calcite cementation prior to significant compaction, as indicated by remnant carbonate cements in the Prince Sandstone and by well preserved cements in the Phalen sandstones. The calcite could have been emplaced from relatively shallow groundwaters, as nodular and groundwater calcretes are present at many levels in the Sydney Mines Formation (Tandon and Gibling, 1997) and sandstones of alluvial Assemblages 2 and 3 are well cemented by calcite (Saunders, 1995). Cementation at greater burial depth is also possible. Compaction of mud fragments and matrix in uncemented sandstone further reduced porosity.

The Hub Coal is bituminous, and vitrinite reflectance levels for the coal in some Sydney wells range from 0.9 to 1.0% Ro (Hacquebard, 1984), implying that the coal underwent considerable thermal maturation during burial. Fission-track analysis indicates that the coal measures began to cool below ~125°C during or prior to the Late Triassic (Grist *et al.*, 1995) and that cooling continued through the later Mesozoic. This cooling phase is documented regionally, and probably signals the onset of Atlantic extensional rifting with associated basin inversion and flank uplift (Keen and Beaumont, 1990). Thus, coalification, which is linked with peak thermal conditions, would have been essentially complete by the Late Triassic, possibly much earlier.

We speculate that residual Windsor brines entered the Morien Group during deep burial, probably in the Permian to early Triassic (Fig. 19A). Circumstantial evidence for this inference comes from the Phalen Mine, where the brines occupy sandstones with much lower porosity and permeability than the Prince Sandstone (6% and 0.2 md average, respectively, from 146 samples: Gibling *et al.*, 1999a). This suggests that the brines entered the sandstones early and have been retained in a near-immobile condition. The brines probably moved upward along faults which displace the coal measures and were probably active during late Alleghanian tectonism in the Permian. The Mountain Fault which cuts the Prince Sandstone (Fig. 5) was probably one such conduit, especially as the Windsor Group is elevated on its northwestern side (Fig. 3). The brines may have been at original strength, or may have been partially diluted prior to or during emplacement through mixing with connate and shallow burial fluids. Hydrocarbons generated during burial maturation may have occupied the Prince Sandstone by this time.

The Morien Group was progressively exhumed during the Mesozoic, and may have reached surface by the Early Cretaceous (Fig. 19B), as strata of this age overlie Carboniferous rocks elsewhere in Cape Breton and mainland Nova Scotia. The Prince Sandstone may have been within range of surficial fluids, including continental and marine waters, since the mid- to late Mesozoic. The increase of salinity with depth in the mine (Fig. 15) suggests that the brines have been diluted with surface-derived fluids. We speculate that these fluids also dissolved calcite cement and feldspars to create the secondary porosity observed in the Prince Sandstone. The age of these fluids is not known, and they can only be linked to waters warmer than present meteoric fluids, but the exhumation history suggests that they entered the sandstone during the Mesozoic and/or Cenozoic. The presence of a variety of pore-filling cements suggests that dissolution was a geologically old event, as considerable time would be required for their formation.

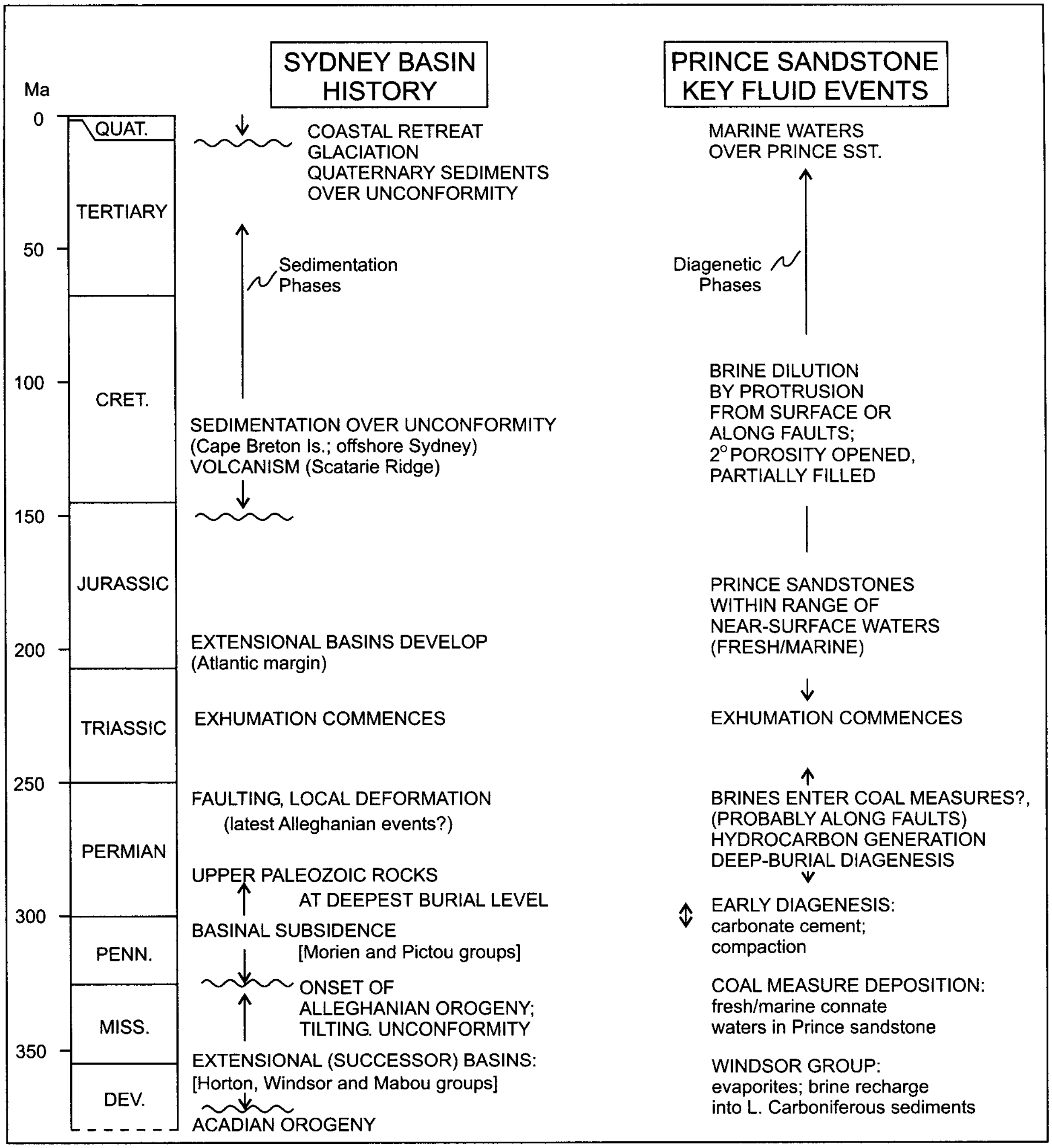

**Fig. 18.** Possible relative chronology of geological and hydrogeological events that affected the Prince Sandstone, offshore Sydney Basin.

Salinity contours (Fig. 15) are based on a small number of samples but suggest, in addition to a downslope increase, a salinity decrease northwestward towards the Mountain Fault. This raises the possibility that some diluting fluids entered the sandstone along the fault, rather than more generally from the surface. Figure 9 provides some support for this hypothesis as sandstones at higher levels in the Hub Cyclothem are less porous than the Prince Sandstone, suggesting that the porosity increase is not entirely a near-surface phenomenon.

Secondary porosity at depth in sedimentary basins has been

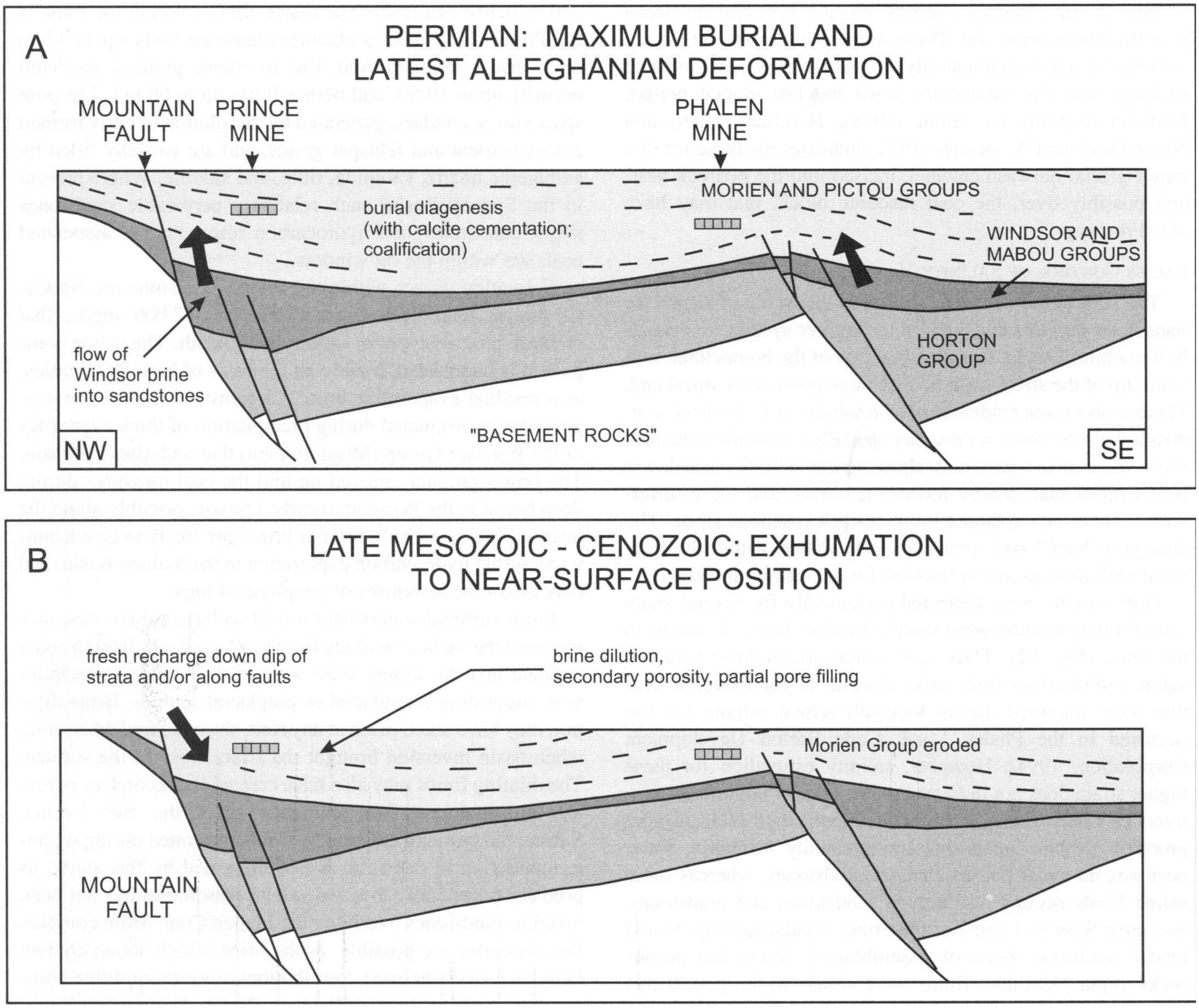

**Fig. 19.** Schematic diagrams to show major events inferred for the burial history and fluid evolution of the Prince Sandstone. Section line runs NW-SE across the Mountain Fault and through the Prince and Phalen Mine areas (Fig. 1).

linked to the generation of organic acids and acid anions through organic maturation during burial (Schmidt and Macdonald, 1979; Surdam *et al.*, 1989, 1993; Shebl and Surdam, 1996). These components are inferred to take part in chemical reactions that dissolve carbonate cements and framework grains, including feldspars. Many factors probably govern the degree to which porosity is enhanced by this process, including the composition of organic and inorganic phases, the initial porosity and permeability characteristics of the host rocks, the timing of reactions, the availability of a fluid flux, and the development of migration pathways (Surdam *et al.*, 1984). The activity of burial fluids provides an attractive explanation for secondary porosity generation in the Prince Sandstone, especially in view of its position directly above a thick, mature coal. However, such an explanation is not supported by evidence elsewhere in the Sydney Basin. Sandstones in the Phalen Mine, which also overlie a major coal, average only 6% porosity, predominantly within corroded feldpars, and the sandstones are pervasively cemented with calcite, which shows no indication of dissolution (Gibling and Nguyen, 1999). Porosity estimates from well logs through the Sydney Mines Formation and the upper South Bar Formation indicate that the elevated porosity levels observed in well P6 are exceptional and that median porosities for sandstones do not exceed 7% in any of the studied wells (Shimeld, 1999). However, Shimeld noted enhanced porosity at shallow depth (<100 m) in several wells. This regional assessment of porosity suggests that burial fluids have not generated substantial secondary porosity in Sydney Mines sandstones as a result of carbonate dissolution.

Late in the Cenozoic, coastal erosion brought the ocean over the Prince mine site. The coal measures strata are locally covered by a low-permeability till, which may have reduced recharge into the sandstones since the last glacial period. Surficial mapping by Grant (1988), Baechler (1986) and Nolan Davis and Associates (1992) indicates the presence of a major glacial outwash channel, incised into the bedrock near, and possibly over, the coal resource block, that may have aided recharge.

### FACIES CONTROL OF SALINITY VARIATION

The persistence of basinal brines in the near-surface Prince Sandstone suggests that parts of the aquifer system are virtually immobile. This is, in part, a function of the homoclinal, seaward dip of the strata, with no discharge point at the distal end. There is also some evidence that the salinity and chemical composition of formation waters vary spatially within the mine roof rocks. Gob waters generally show higher salinities and lower Na:Cl ratios than nearby formation waters, and these differences cannot be explained by mine-rock reactions alone. The change in Na:Cl ratio precludes evaporation within the fractured rock mass as an explanation for the salinity increase.

Gob samples were collected periodically for several years after formation water were sampled and at similar locations in the mine (Fig. 12). Thus, gob waters might have received saline contributions from rocks at some height above the coal that were fractured during longwall retreat mining (as has occurred in the Phalen Mine: Cape Breton Development Corporation, 1994). However, salinity estimation for these higher strata does not indicate the presence of strata with relatively elevated salinity (J. Shimeld, unpublished data). A more probable explanation is that lower salinity formation water occupies the most porous channel sandstones, whereas more saline fluids occupy less porous sandstones and mudstones, including Storeys 1 and 3 of the Prince Sandstone (Fig. 6) and bayfill sandstone sheets of Assemblage 1. These less porous rocks might yield their fluids more slowly to the gob. If this hypothesis is correct, less porous sandstones and mudstones have locally retained immobile brines while dilute, surficial waters have protruded preferentially into more porous parts of the Prince Sandstone. Aquifer compartments may be separated, for example, by mudstones at storey boundaries (Figs. 6, 7). Plumes or protrusions of water are known to move preferentially through high-conductivity conduits, including fractures and highly permeable layers, and may isolate less conductive parts of the rock body (Schwartz and Muehlenbachs, 1979; Domenico and Robbins, 1985; Smalley *et al.*, 1988; Siegel, 1991; Steuber and Walter, 1994; Nativ, 1996). Similarly, low permeability zones within hydrocarbon reservoirs can act as baffles to oil movement, leading to reservoir heterogeneity (Hohn *et al.*, 1997).

## CONCLUSIONS

The subsea Prince Mine of the Sydney Basin extracts coal from the Upper Carboniferous Hub Seam at depths of up to 330 m below sea level. The major aquifer within the mine is the Prince Sandstone, a channel-sandstone body up to 13 m thick that is multistoreyed, fine to coarse grained, and with porosity up to 19.5% and permeability up to 60 md. The pore spaces are secondary, generated by dissolution of early formed calcite cement and feldspar grains, and are partially filled by authigenic quartz, kaolinite, illite, and siderite. Where present in the Sydney Basin, such relatively permeable sandstones might constitute good hydrocarbon reservoirs, as associated coals are within the oil window.

Formation waters within the Prince Sandstone are Na-Ca-Cl brines, with TDS from <8000 to >47,000 mg/L, that increase progressively in salinity with depth. The saline component is interpreted, mainly on the basis of high Br:Cl ratios, as a residual evaporative brine. Circumstantial evidence suggests that it originated during precipitation of thick evaporites of the Windsor Group (Mississippian) that underlies the basin. The brines probably moved up into the coal measures during deep burial in the Permian to early Triassic, possibly along the nearby Mountain Fault. Similar brines are likely to be encountered during hydrocarbon exploration in the Sydney Basin, and may affect the responses of geophysical logs.

Fresh surficial waters later mixed with the brines, descending from the surface or along the Mountain Fault. Isotopic data indicate that the waters were warmer than present precipitation, suggesting interglacial or preglacial sources. Brine dilution may have taken place at any time since the mid-Mesozoic, when basin inversion brought the strata close to the surface. The diluting fluids may also have created the secondary porosity, although no firm evidence links the two events. Substantial porosity creation by fluids generated during organic maturation in the basin is not supported by this study, as porosity is generally low and calcite dissolution has not been noted in sandstones overlying the Phalen Coal. More complex fluid histories are possible, as the brine's high solute content may have overwhelmed contributions from more dilute components, making them difficult to detect. The persistence of brines within these near-surface rocks suggests that near-immobile zones are present, and protrusion of dilute fluids may have followed more porous zones within the channel sandstone, bypassing saline zones in less porous rocks.

The present study indicates that the saline fluids in the Prince Sandstone are primarily basinal brines, and concern that mine-induced fracturing has allowed seawater to penetrate into the subsea mine appears unfounded.

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## APPENDIX 1: GEOPHYSICAL ESTIMATES OF SALINITY

Because of the presence of clay minerals in the Prince Sandstone, we used a modified form of the Archie Equations (Archie, 1942) developed by Poupon and Leveaux (1971) to estimate formation water resistivity:

$$\sqrt{\frac{1}{R_O}} = \sqrt{\frac{\phi^m}{aR_w}} + V_{cl}^{(1-0.5Vcl)}\sqrt{\frac{1}{R_{cl}}} \qquad (1)$$

where $V_{cl}$ is the volumetric proportion of clay minerals in the rock matrix, and $R_{cl}$ is the bulk resistivity of the clay minerals. Equation 1 was developed empirically for use in Indonesia (hence it is known as the Indonesia Formula) where comparatively fresh formation waters and high clay mineral contents invalidate the use of the Archie Equations (see Worthington, 1985, for a review of reservoir evaluation in clay-rich sands). Since similar conditions are present within the study area, Equation 1 was chosen as the best available empirical model for calculation of $R_w$.

**Table 2:** Results of nonlinear regression applied to Equation 1.

| Well | $R_{cl}$ (ohmm) | $R_w$@24°C (ohmm) | NaCl equivalent salinity (part per thousand) |
|---|---|---|---|
| P-5 | 11.5 | 0.186 | 33.6 |
| P-6 | 28.4 | 0.565 | 10.0 |

In the application of Equation 1, the following assumptions were made:

1. The sandstone unit is 100% saturated with water. This is reasonable as hydrocarbons were not detected during drilling of P5 or P6, and there are no obvious hydrocarbon indicators on the wireline logs.
2. The tortuosity factor, *a*, is equal to one, which is a commonly accepted value of *a* in granular rocks. Also, as pointed out by Bussian (1983) and supported by Berg (1995), *a* is really a parameter introduced from pragmatic attempts to apply the Archie Equations to sandstones containing significant clay mineral fractions. From more theoretical considerations, *a* is not a meaningful parameter (Bussian, 1983).
3. The cementation factor, *m*, is equal to 2.0. This is a common value for *m* in tightly cemented sandstones (Asquith and Gibson, 1982) and, in the absence of laboratory measurements, is the best estimate possible.

A Levenberg-Marquardt nonlinear regression algorithm (Press *et al.*, 1995) was used to estimate $R_w$ and $R_{cl}$ within the sandstone unit at P5 and P6. Results of the nonlinear regression are listed in Table 2 and plotted on Figure 14. Rough confirmation of the results is provided by the fact that regression estimates for $R_{cl}$ fall within the range of deep induction values (8-30 ohmm) measured within the most clay-rich intervals at P5 and P6.

Estimates of the error associated with the results listed in Table 2 are difficult to quantify because of the nonlinear nature of Equation 1 and the many potential sources of error. However, recent attempts to estimate salinity using wireline data indicate that, given sufficient care, serviceable results can be expected. For instance, in comparison with laboratory-derived salinities from sandstone aquifers, Jorgensen (1996) reported average errors of less than 25%. Better results were obtained by Schnoebelen *et al.* (1995) for calcareous aquifers, where errors ranged between 0.07% and 28% with a mean of 9.9%. The methodology of both these studies is based on the Archie Equations, and corrections for the presence of clay minerals were not applied. Relative to the Jorgensen (1996) study, higher accuracy was achieved in the Schnoebelen *et al.* (1995) study, possibly because of the negligible effect of clay minerals in calcareous aquifers. Given careful consideration of clay mineral effects, as in the present study, it appears reasonable to expect errors of 10-20%, which is sufficient for many applications.

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