

THE ORIGIN OF WATER LEAKS
IN SASKATCHEWAN POTASH MINES

A Thesis Presented to the College
of Graduate Studies and Research
in Partial Fulfillment of the
Requirements for the degree
of Master of Science in Geology

Mark B. Wittrup
University of Saskatchewan
1988

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This thesis is dedicated to my
wife Susan for all her support
and understanding throughout
this project.

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Head of the Department of Geological Sciences

University of Saskatchewan

Saskatoon, Saskatchewan

Canada S7N 0W0

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ABSTRACT

Recent mine-level floods at some Saskatchewan potash mines have demonstrated the need to identify accurately the source(s) of water leaks so as to assist in remedial or preventative action. Chemical compositions of the waters are inadequate tracers of these leaks because the concentrations of most of the elements change during the migration of the fluids. In marked contrast to most of the chemical constituents dissolved in the water, the stable isotopes of oxygen and hydrogen are conservative elements of water. Within the Elk Point Basin, δD and $\delta^{18}O$ values of basinal waters normally increase with depth because of mixing between trapped formation waters, which have isotopic compositions near those of seawater, and local surface waters, which have much lower δD and $\delta^{18}O$ values. Thus, the water in each aquifer within the basin generally has a unique isotopic composition in any given vertical section. This unique value, when compared to the flood or leak waters, allows an assessment to be made as to the origin of the flood waters. This comparison can be made irrespective of the changes that occur in the chemical composition during migration of the fluid.

Flood waters in the potash mines of Saskatchewan have chemical and stable isotopic compositions that indicate three different origins for mine level fluids. These are, 1) "normal", halite and sylvite saturated, basinal brines from Devonian formations directly above the deposits, which are a combination of meteoric waters and connate waters mixing within the basin, 2) "short circuited", undersaturated waters of predominantly meteoric

origin, from stratigraphically higher aquifers such as the Cretaceous Mannville Group, and 3) Ca-rich brines that may represent ancient fluids associated with recrystallization of the evaporites. Short circuiting probably occurs when relatively "fresh" formation waters are directed to lower stratigraphic units through a collapse structure or related feature. Mining may reactivate the structures through which these "short circuited" waters flow.

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INTRODUCTION

Problems with water inflows have been encountered since the beginning of potash mining in Saskatchewan. Initially, problems were encountered during the sinking of shafts through the Cretaceous Mannville Group aquifer (Fuzesy, 1982). Water problems associated with the Mannville Group aquifer escalated until a severe leak ultimately forced the abandonment of a potash mine at Unity, Saskatchewan (Fuzesy, 1982). The Mannville aquifer was the source of a major flood in 1970 at the Cominco mine, Vanscoy, Saskatchewan, which took two years to correct (Prugger, 1979), and has been blamed as the source for the recent flooding at the Potash Corporation of America (PCA) mine at Patience Lake, Saskatchewan (Star-Phoenix, 87/01/31). The recent flooding at the PCA mine, which reached 26,550 l/min, has forced its closure for at least two years.

In addition to leaks into the PCA and Cominco mines, several other mines have recently experienced severe mine-level flooding problems. These mines are the Potash Corporation of Saskatchewan (PCS) mine at Rocanville and the International Minerals and Chemical Corporation (IMC) K-2 mine at Esterhazy. The flood at the Rocanville mine has ceased but water flows of up to 32,000 litres per minute have been reported at the IMC mine (Star-Phoenix, 87/01/10). The recent closure of the PCA mine in January 1987, and the loss of some 400 jobs, due to flooding is a reflection of the ultimate severity of the water leak problem in all potash deposits. Water leaks into potash mines always have been of concern because of the soluble nature of the evaporite minerals. Leaks in potash mines are especially noticeable because of the normally dry conditions which exist in them.

Knowledge of the source of the leaks is of great assistance in planning preventative or remedial action, such as in undertaking a cement-grouting program to stop water inflow. Past attempts to determine the origin of the water inflows have relied on the use of the chemical compositions of the waters. However, no substantial study exists which compares waters from various formations with mine-level inflows, except for compilations by Sproule Associates Limited in 1980 and 1981. They compiled data on the chemical compositions of water collected from wells in the potash mining districts and compared them with analyses from mine level waters. These comparisons relied upon a wide variety of data sources, with little documentation about the collection or analytical techniques. It is probable that a large number of the formation water analyses were contaminated by drilling fluids.

Comparison of the chemical compositions of mine-level waters with formation waters is of limited use in tracing the origin of mine-level leaks because the water increases its load of dissolved solids as it passes through the highly-soluble evaporites of the Prairie Formation. Chemical compositions of waters also would be expected to change as the water passes through various formations on their way to the mine level. As a result, no single ion is believed to behave conservatively. Certainly there is well-documented evidence for subsurface dissolution in sedimentary basins, an example being the large portions of the Prairie Formation which have been removed (i.e.: Holter, 1969). For this reason, the stable isotopes of oxygen and hydrogen have been used as a means to identify the source of waters leaking into potash mines, because stable isotope compositions change little during the dissolution of salts (Kyser, 1987), and as a

result are not subject to the same problems of interpretation encountered with chemical data.

This study uses oxygen and hydrogen isotopes, and chemical compositions to compare fluids collected from PCS mines at Cory, Allan, Lanigan and Rocanville, Saskatchewan (Figure 1). Samples were collected from all accessible leaks in the mine shafts except Lanigan's which is leak-free because of a welded steel lining, and from all leaks in the mining levels (sample descriptions are found in Appendix I). Chemical and stable isotopic compositions (Appendices II and III, respectively) from the shaft samples are compared with the mine level samples in order to determine the source of the mine-level waters.

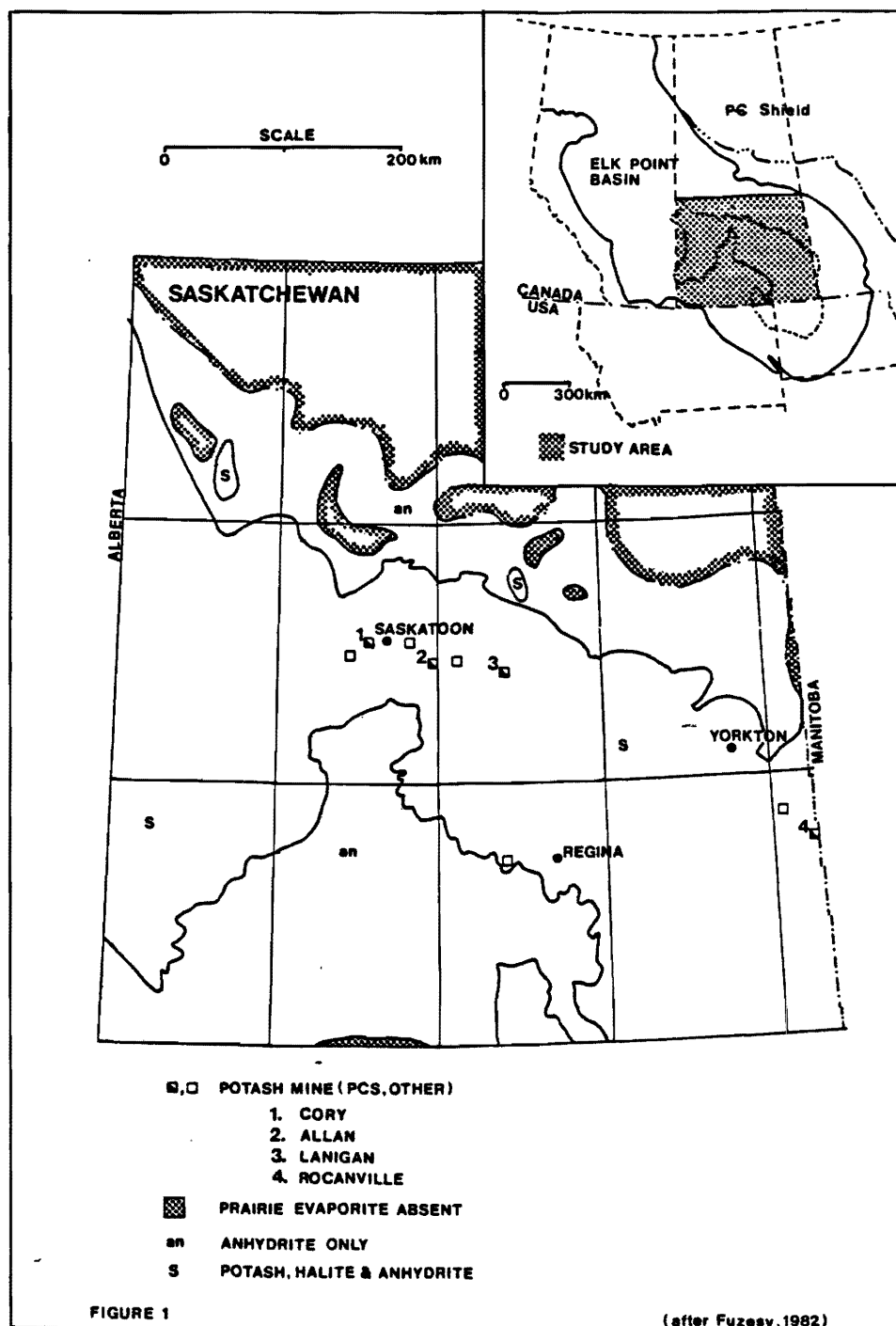


FIGURE 1: Location map showing the position of the four Potash Corporation of Saskatchewan (PCS) potash mines in relation to the edge of the potash bearing portion (S) of the Prairie Formation. Modified after Fuzesy (1982).

GEOLOGY

GENERAL STATEMENT

A concise synthesis of the stratigraphy of the four PCS potash mines did not exist before this study. Geological data from the four mines were therefore compiled from a variety of sources, including PCS Mining files for the four mines (e.g. Danyluk and Watkins, 1978), Geological Survey of Canada reports for Cory (Price and Ball, 1970), Lanigan and Allan (Price, 1971) and Rocarville (Price, 1970), and for the Prairie Formation (Phillips, 1982) (Figure 2).

A uniform nomenclature was devised using the formation names of Kent and Simpson (1973) because the existing nomenclature was extremely varied. The Blairmore Formation has been named the Mannville Group in this study because of the general usage of that name within the Williston Basin (Maycock, 1967). The Nisku Formation has not been renamed the Birdbear Formation as recommended by Christopher (1961). For the Prairie Formation the stratigraphic nomenclature used is that of Phillips (1982). The Prairie Formation is used in this study to describe the Prairie Evaporite Formation because of its general usage by PCS.

The general geology of the Elk Point Basin has been described by Kent and Simpson (1973) and by Nelson (1970). The geology and petrology of the Prairie Formation has been described by Holter (1969), Worsely and Fuzesy (1979), Fuzesy (1983) and Langford et al (1986). This chapter summarizes the results from these reports and describes the geological relation between the Prairie Formation and the Elk Point Basin.

FIGURE 2: The four main potash-bearing members of the Prairie Formation, the Patience Lake Member (PLM), the Belle Plaine Member (BPM), the White Bear Member (WBM) and the Esterhazy Member (EM), are shown in relation to the general geology and stratigraphy at the Cory, Allan, Lanigan and Rocanville mines. Sample locations are shown as dots where only a single sample was collected and as a square where multiple samples were collected. Formation use is also shown.

Prairie Formation

Potash deposits mined in Saskatchewan are found within the upper 70 metres of the Middle Devonian Prairie Formation (or the Prairie Evaporite Formation) of the Elk Point Group at depths of approximately 1000 metres below the surface. Within the Prairie Formation the four main potash bearing members, in descending stratigraphic order are: Patience Lake, Belle Plaine, White Bear and Esterhazy Members (Figure 3). The Patience Lake Member is mined at the Cory, Allan and Ianigan mines, and the Esterhazy member is mined at Rocarville.

The Prairie Formation was deposited from the hypersaline waters of a stagnant body of water which may have received periodic influxes of seawater from the northwest portion of the Elk Point Basin (Gorrell and Alderman, 1968). The Middle Devonian climate was hot and arid, and water movement within the basin was restricted because of the Winnipegosis reefs and reef-like mound structures (Fuzesy, 1983).

Within the Elk Point Basin, the Prairie Formation varies from 0 to 200 metres thick. The thickest portion of the formation is within the potash mining-district in the Saskatoon area while, in the Rocarville area, the thickness is approximately 140 metres. The Prairie Formation has three main divisions (Figure 3), (1) the lower Whitkow Salt, which is largely halite with minor anhydrite, (2) the Shell Lake Gypsum, which has the dolomitic Quill Lake Member and (3) the upper Loeftard Salt, which is predominantly halite, but also has the four main potash-bearing members.

The potash members are composed of halite (NaCl), sylvite (KCl), sylvinite (a mixture of halite and sylvite crystals) and carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) (Fuzesy, 1983). Carnallite is not common in the mining

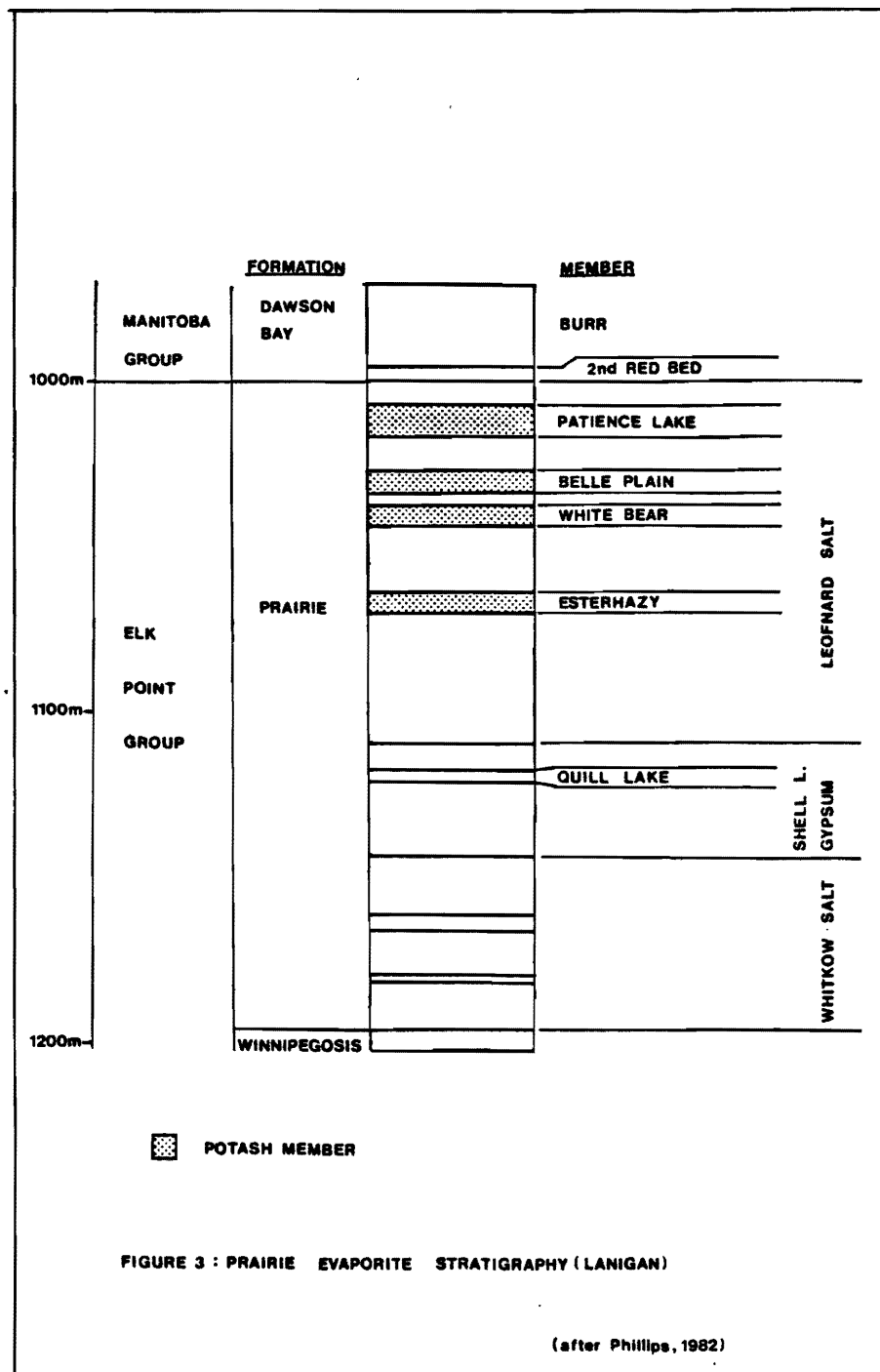


FIGURE 3: A typical cross-section through the Prairie Formation, in this case the Lanigan Mine, with the four main potash-bearing horizons shaded (after Phillips, 1982).

level at the Cory or Allan mines. There is a variable percentage of insoluble clay minerals, anhydrite, dolomite, quartz and magnetite in the potash. The clay minerals, which may occur as long continuous seams, are mainly chlorite and illite, of probable detrital origin, and septechnorite, montmorillonite and sepiolite of probable authigenic origin (Mossman et al, 1982; and Boys et al, 1986). From the petrologic relations and distribution of bromine in evaporite minerals of the Prairie Formation, Schwerdtner (1964) and Wardlaw and Watson (1966) postulated that there was a series of recrystallization events because of the movement of hypersaline solutions through the formation. Holter (1969) suggests that these recrystallization events are responsible for the concentration of sylvite (potash) by the breakdown and dewatering of carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{Cl}^- + 6\text{H}_2\text{O} + \text{KCl}$). The dewatering reactions left sylvite and produced a MgCl_2 -rich brine which migrated to other areas of the Prairie Formation to form thick carnallite deposits. Some authors (e.g.: Fuzesy, 1983) do not believe that enough magnesium was available from the breakdown of carnallite deposits to generate the MgCl_2 -rich brines in the Prairie Formation. Consequently Fuzesy suggests that Mg-rich dolomitizing fluids from the Winnipegosis Formation and, possibly fluid reactions with clay minerals supplied a large portion of the magnesium for the MgCl_2 -rich fluids.

Recrystallization events may have taken place during the major tectonic activity which occurred at the end of the Cretaceous Period. Wardlaw (1968), however, notes that, based on potassium-argon radiometric dating, recrystallization probably was not associated with major salt-solution events, but was earlier during deposition of the Prairie Formation. Baadsgaard (1986), using Rb-Sr and K-Ca isotope data, suggests

that major recrystallization occurred during the late Cretaceous and post-Cretaceous periods, coincident with uplift of the Rocky Mountains and a major movement of fluids.

Large portions of the Prairie Formation have been partially, or completely, removed by dissolution of the salt (Holter, 1969). These dissolution events are believed to have been almost immediately after deposition of the evaporites and to have continued intermittently through Devonian and Cretaceous periods (Gorrell and Alderman, 1968). Baadsgaard (1986) further suggests that dissolution may even have continued to the present. Solution of the salt edge is responsible for the shape of the present edge of the Prairie Formation and is believed to be responsible for the formation of collapse structures and a variety of structural features such as the Hummingbird structure (Bishop, 1974). Bishop (1974) argues that, rather than multiple stages of salt dissolution, a large number of the observed features could be due to a large, single event such as that postulated by Baadsgaard (1986) for the Cretaceous and post-Cretaceous periods.

Regional Geology

The Prairie Formation unconformably overlies the Winnipegosis Formation which has an irregular topography created by reefs and reef-like mound structures that extend locally up to 100 metres into the Prairie Formation (Jones, 1965). The boundary between the two formations is gradational and Jones (1965) places the boundary at the first appearance of primary carbonate-anhydrite laminations or the first primary anhydrite and halite beds.

The Winnipegosis Formation is predominantly carbonates which have undergone local dolomitization. The Winnipegosis Formation generally is porous but tends to be salt plugged in areas overlain by evaporites (Gorrell and Alderman, 1968). The movement of solutions through the Winnipegosis is considered to govern the location of salt solution features within the Prairie Formation (Gendzwill, 1978). How these fluids move through the Winnipegosis is not well understood, but probably is due to the upwards deflection of horizontally-moving fluids when they come in contact with a Winnipegosis reef or reef-like mound structure (Gendzwill, 1978; Gendzwill and Wilson, 1987).

The Winnipegosis Formation, in turn, is underlain by, in descending stratigraphic order, the carbonaceous shales of the Devonian Ashern Formation, the dolomites of the Silurian Interlake Formation, Upper Ordovician dolomites (with minor halite layers) and by the lower Ordovician-Cambrian "basal clastic division" (Kent and Simpson, 1973). The basal clastic division consists of the Middle Ordovician Winnipeg and the Upper Cambrian Deadwood formations which lie unconformably on the Precambrian Basement Complex. This clastic basal division is composed largely of coarse grained sands grading upwards into calcareous siltstones and coarse shales. The basal Cambrian-Ordovician group is a major aquifer system within the Elk Point Basin (Downey, 1984a,b) and the Deadwood Formation is also an important target aquifer for the disposal of brines produced from the processing of ore at some potash mines (Simpson and Dennison, 1975).

The Precambrian Basement Complex has not been well described because of its depth from the surface, but probably consists of a series of

gneisses derived from Proterozoic metasediments, metavolcanics and granites similar to those described in northern Saskatchewan (i.e.: Lewry and Sibbald, 1980).

The Prairie Formation is overlain by dolomitic mudstone of the Second Red Bed Member of the Dawson Bay Formation and marks the beginning of a series of Upper Devonian cyclic deposits of limestone, dolomite and evaporites which, in ascending stratigraphic order, includes the Dawson Bay, Souris River, Duperow and Nisku Formations. These sequences are unconformably overlain by the Lower Cretaceous Mannville Group which is, in turn, overlain by a thick sequence of Cretaceous shales (Kent and Simpson, 1973).

In the Rocanville area, between the Upper Devonian Nisku Formation and the Cretaceous rocks, there is an additional sequence of Upper Devonian and Mississippian rocks. The Mississippian Madison Group may be an important source of fluids in the Rocanville area as this unit is identified by Downey (1984a & 1984b) as a major aquifer within the Elk Point Basin. Jurassic rocks also are present between the Nisku and Mannville Formations in the Allan and Lanigan areas.

The Mannville Group is the basal series of Cretaceous rocks in Saskatchewan. It is composed largely of poorly consolidated sandstones, and is an aquifer with a large fluid-volume and a high fluid pressure. Christopher (1980) notes that the Mannville Group may be recharged in western Saskatchewan near the Rocanville area, and possibly, throughout Saskatchewan by fluids from the underlying Paleozoic rocks.

Overlying the Cretaceous is a series of Quaternary to recent sediments largely of glacial and fluvioglacial origin. A very complex aquifer system

is found within Quaternary strata (i.e.: Van der Kamp, 1986, and McMonagle, 1987).

Collapse Structures

Collapse structures are relatively common in the Elk Point Basin (figure 4). They occur where the Prairie Formation has undergone complete or partial dissolution, causing a subsequent collapse of the overlying strata. Collapse structures commonly are filled by breccia of collapsed material derived from the overlying strata and matrix deposited by subsequent fluids (e.g.: Parker, 1967). The level to which collapse structures disrupt the stratigraphy is generally regarded as representing a minimum age for their formation.

Dissolution of the Prairie Formation is believed to be due largely to the upward movement of fluids from the Winnipegosis Formation within porous reefs and reef-like mound structures (e.g.: Gendzwill, 1978). Enough of the lower portion of the Prairie Formation is removed in this way to result in the development of vertical cracks. It is through these cracks that fresher waters subsequently flow driven by a brine density-flow mechanism such as that described by Anderson and Kirkland (1980). Hitchon (1969a) notes that drawdown from the South Saskatchewan River may be an example of a recent solutioning mechanism responsible for the large Saskatoon salt solution area.

Once collapse structures form, they may become conduits for the vertical movement of fluids under brine density-flow conditions or due to fluid pressures from an intersected aquifer. Collapse structures could have variable porosity because of the breccia infill and variability of the

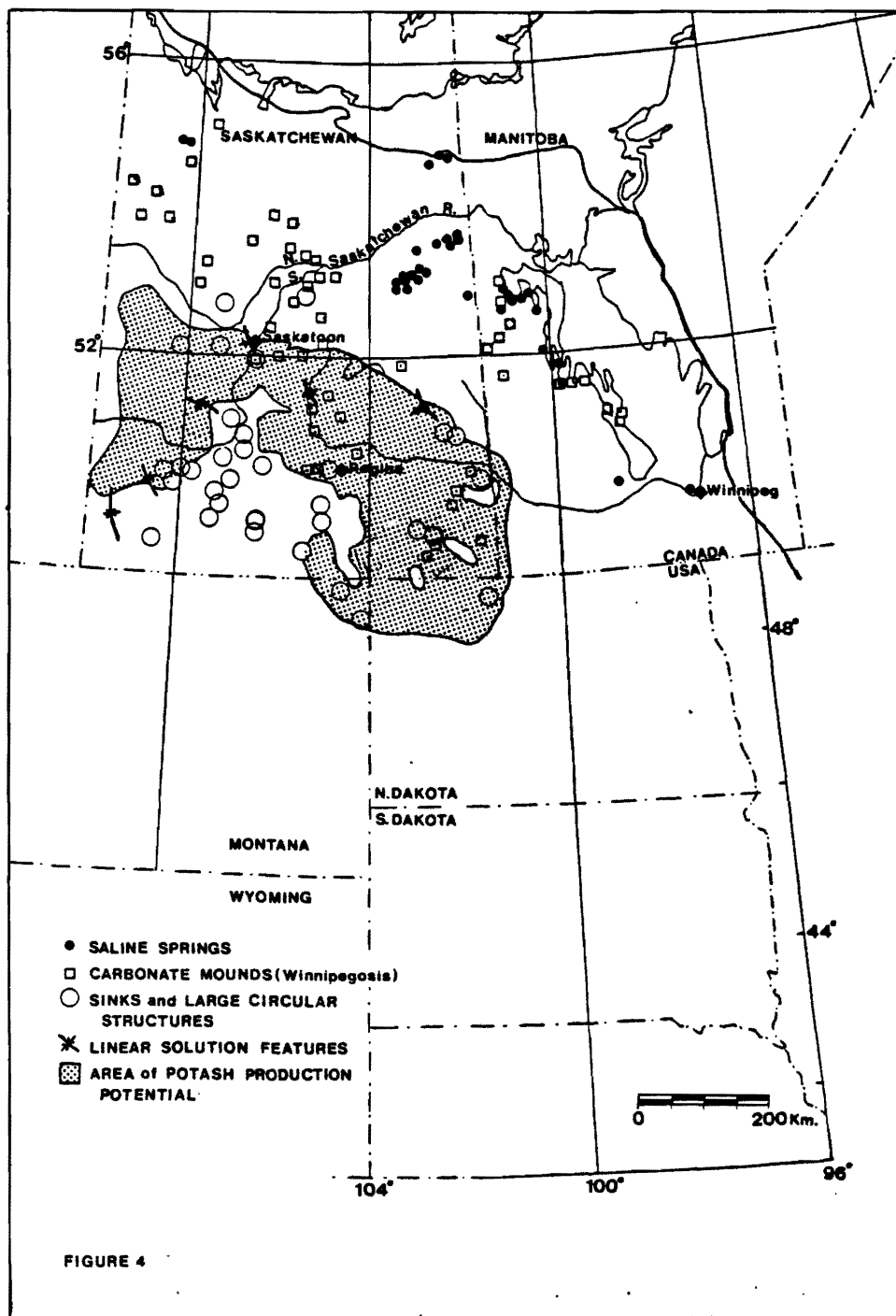


FIGURE 4: A map showing the location of carbonate (Winnipegosis) mounds, solution features, and saline springs in relation to the edge of the potash bearing portion of the Prairie Formation. Data is from Christopher et al, 1971, Fuzesy, 1982, and Kent and Simpson, 1973.

composition of the matrix material. It is probable, therefore, that collapse structures and related vertical structures within the basin are conduits for the vertical movement of fluids, such as the movement of waters to a lower stratigraphic horizon. That collapse structures cause stratigraphic disruptions and that they will respond to overpressuring has been described in the Howe Lake hydrodynamic blowout structure (Christiansen et al, 1982). Mining, through removal of the potash members, may create areas of lower pressure by opening up voids in the structure thereby allowing fluid movement. Where recognized collapse structures are avoided within the potash mines because of their water-bearing potential (Baar, 1972) and their general lack of ore material. Collapse structures have been described in detail by De Mille et al (1964), Christiansen (1967 and 1971), Christiansen et al (1982), Parker (1967), Baar (1972 and 1973), Bishop (1974), Gendzwill (1978), Gorrell and Alderman (1978), and MacKintosh and McVittie (1983).

Hydrogeology

Hydrodynamics within the Williston and Elk Point basins generally are not well known within the area of the potash mines. This lack of information is due largely to the paucity of oil well drill data, especially for the deep aquifers. In a report to the potash companies Sproule Associates Limited (1980) summarized the available data and noted the paucity of data, especially in the potash mining district. The hydrology described in this chapter is a synthesis of data from the earlier theoretical work of Toth (1962 and 1963), the early work on the Alberta Basin by van Everdingen (1968), Hitchon (1969a and 1969b), Hitchon and

Friedman (1969), Billings et al (1969), and the more recent work on the Elk Point Basin (Williston Basin) by Sproule Associates Limited (1980), Downey (1984a and 1984b) and Betcher (1986). Other authors are included as noted.

Fluid flow within the Elk Point Basin has its origins in the southern and southwestern recharge zones of the central Montana uplift, the Rocky Mountains and the Cypress Hills (Figure 5). Flow within the Elk Point Basin trends north to northeasterly at approximately right angles to the axis of the basin and generally points towards the area of saline spring discharge in east-central Saskatchewan and west-central Manitoba (Figure 5). Hitchon (1969a,b) notes that, in general, fluid flow in the western sedimentary basin mimics the topography and is modified locally by variations in the topography and geology.

Downey (1984a) notes that there is an additional recharge area in the Manitoba escarpment. However, the net fluid movement from this recharge area is also to the northeast. The extent of down dip penetration from the Manitoba Escarpment recharge area is unknown, but it may extend towards the Manitoba-Saskatchewan border (Betcher, 1986 unpub.). How this affects fluid flow in the Rocanville area is unclear. Fuzesy (1987, personal communications) has indicated from recent work in the Rocanville-Esterhazy area, that he has been unable to detect a distinct flow direction in the Devonian aquifers. Betcher (1986) notes a northerly deviation from the normal easterly flow, in the Ordovician Winnipeg Formation around Brandon, Manitoba, which may be due to recharge from the Manitoba Escarpment.

Meteoric water enters exposed Phanerozoic formations in the recharge zones and moves laterally along these formations. These fluids generally stay within the bounds of the formations they enter. The presence of salt

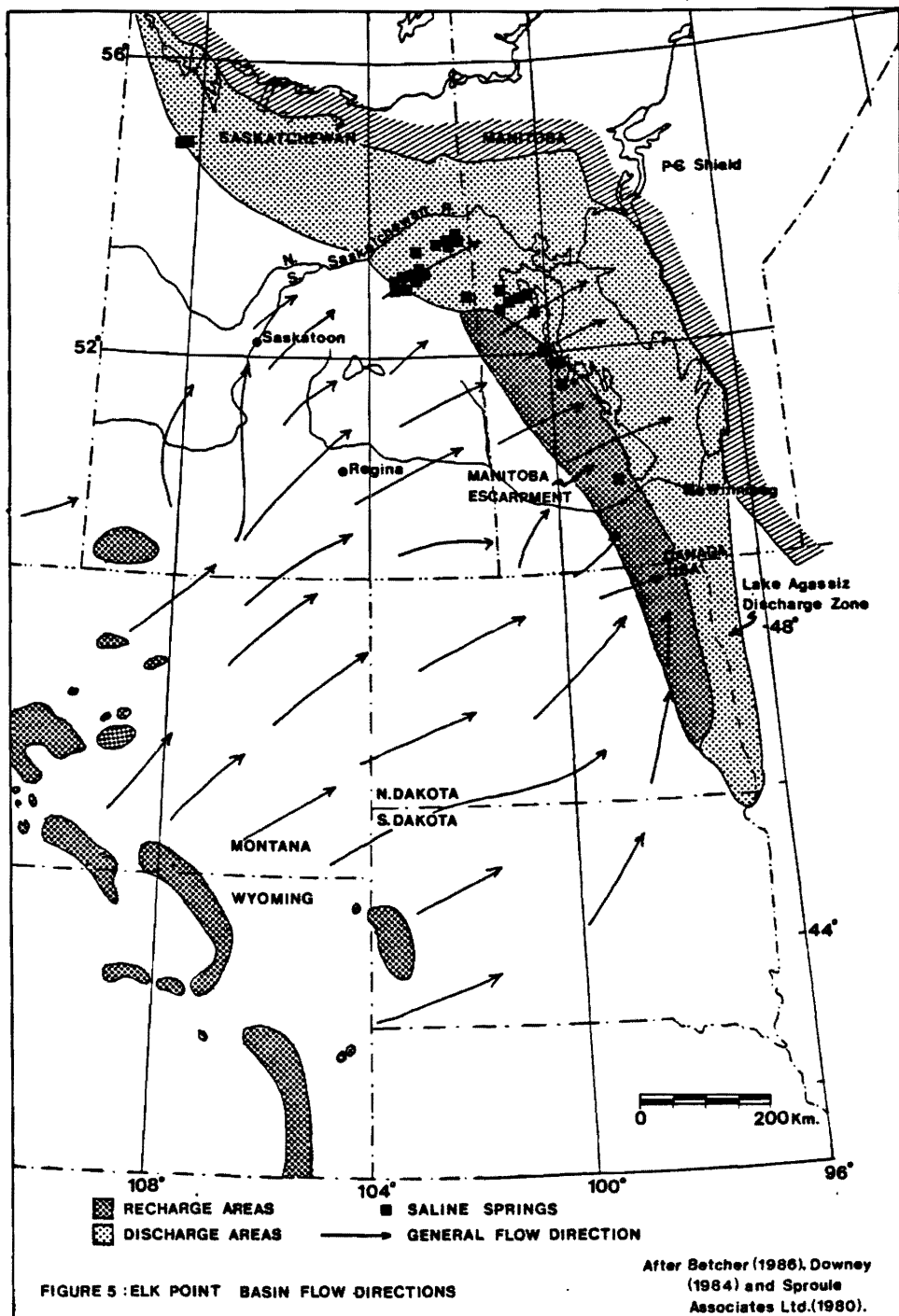


FIGURE 5: Compilation of fluid flow directions within the Elk Point Basin from the postulated recharge areas in the Central Montana Uplift through to the areas of discharge where formations subcrop or abut against the Canadian Shield (PC Shield). An additional area of recharge is located along the western edge of the discharge area and is associated with the Manitoba Escarpment. Data is from Betcher, 1986, Downey, 1984a,b, and Sproule Associates Ltd., 1980 and 1981.

solution features and saline springs is evidence that the fluid system is not static.

Downey (1984b) identifies the Cambrian-Ordovician clastics (the basal clastic division), the Mississippian Madison aquifer in the Rocanville area only and the Mannville basal-Cretaceous aquifer as the main aquifers in the Elk Point Basin affecting the mine areas with the Precambrian basement, the Devonian chemical sediment sequence and the Cretaceous shales as confining horizons. A fourth aquifer system resides in the Quaternary deposits which overlie the Cretaceous formations.

This study supports the findings of a great number of other authors (previously noted, see Chemical Composition Chapter) who have reported that brines within a basin become progressively more saline with depth. The salinity is greatest where fluids are in contact with the Prairie Formations indicating that salt solutioning is, or has been, effective. In general, the salinity of fluids within a given aquifer increases with distance from the recharge zones depending on the flow rate and geology.

For purposes of this study, the Prairie Formation is considered to be the lower confining layer to fluids in this study due to the impermeability of evaporites to saturated solutions. The upper confining layer is considered to be the Cretaceous shales because of their relative impermeability. Therefore, the rock between the Dawson Bay and the Mannville Group may be considered to be one large aquifer system. Dunn (1982) and Sproule Associates Ltd. (1980) note the similarity among the fluid flow patterns within this interval and take this as evidence that there is vertical communication between the formations. Christopher (1980) suggests that an area of high head pressures within the Mannville Group in

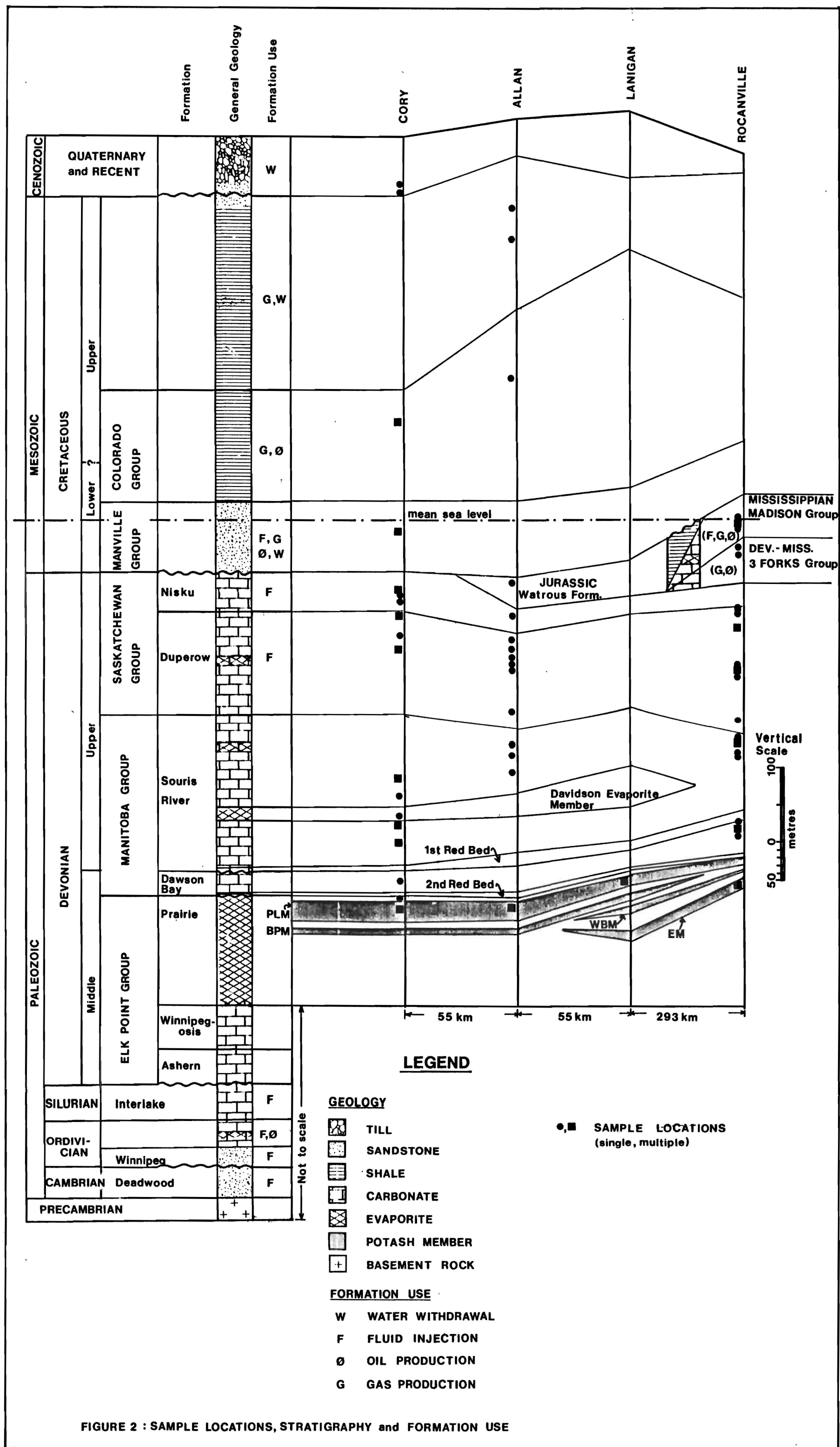


FIGURE 2 : SAMPLE LOCATIONS, STRATIGRAPHY and FORMATION USE

the Rocanville area is due to the inflow of fluids from the underlying Devonian sequences, although evidence in this thesis suggests this is not the case.

In general, little is known about the detailed effects of collapse structures and major salt-solution features on the flow regimes within the mining areas. Dunn (1982) notes that in the Saskatoon potash mining district fluid flow in the Dawson Bay Formation is to the northeast, and that the contact between the 2nd Red Bed Member and the Prairie Formation is a conduit for fluids. It is probable that the Dawson Bay is, at least locally, a major aquifer.

CHEMICAL COMPOSITIONS

SAMPLE COLLECTION

Water samples were collected wherever an inflow could be detected within the mine shafts and in the mining levels. Samples were collected in plastic sample bottles and sealed tightly. Where possible, the temperature and pH of the waters were measured at the collection site. Inflows within the shaft linings are generally small trickles coming from small holes within the concrete lining. They are easily spotted because of the wet patches they produce in shafts and by the salt deposits they commonly leave. Inflows in the shafts are assumed to come from the formation directly behind the concrete lining. It is unlikely that fluids flow vertically to the shaft inflow points because of the tightness of the concrete shaft lining against the formations and because of the consistency in the increase of the isotopic compositions with depth. Inflows on the mining levels were sampled wherever they occurred. The inherent dryness of the potash mining horizons makes inflows easy to recognize as they produce wet patches, and, on the mining levels, often spectacular groupings of salt stalagmites and stalactites are found at inflow sites. The source of these mine level inflows was determined through comparison of the mine level chemical and stable isotopic compositions with those waters collected from the mine shafts.

ANALYTICAL TECHNIQUES

Chloride

Chloride was determined using the Mohr method of titrating a buffered solution with silver nitrate in the presence of potassium chromate indicator. The end point occurs with the first permanent appearance of a buff colour, indicating that all of the chloride has reacted with the silver and that the excess silver is reacting to form the bright red compound, silver chromate. This technique yields an error of $\pm 2\%$ on the most concentrated samples. Determination of Cl using an Orion ion-specific electrode method was tried and the results agreed with those obtained by titration to within $\pm 10\%$ on all mine shaft samples. However, the ion-specific electrode method gave erratic results on mine-level samples, even on diluted samples. For this reason, the titration data were used because they provided a consistent data set.

Sodium, Magnesium, Potassium and Calcium

The four major cations, Na, Mg, K, and Ca, were determined by the use of atomic absorption spectrophotometry. A 10 ml sample was diluted with deionized water. Samples were centrifuged before dilution in order to remove any suspended solids. One percent lanthanum oxide was added to the solutions to act as an ionic stabilizer. All of the samples were run on a Perkins Elmer 2380 atomic absorption spectrophotometer using an air-acetylene flame, and calibrated against commercial and prepared standards. Replicate analyses suggest that the errors are $\pm 3\%$.

Fluoride, Bromide and Iodide

The concentrations of F, Br, and I were determined with single element ion-selective electrodes. Undiluted samples were used in most cases due to the generally low concentrations of these halides. In some samples bromide was found in concentrations higher than expected necessitating dilution with de-ionized water. At first, it was thought that an interference problem existed because no literature reference could be found to explain such high Br values. However, serial dilutions produced the same results to within $\pm 10\%$.

Density and Total Dissolved Solids

Density was determined by weighing ten millilitres of sample in small teflon cups which had been air-dried for at least 24 hours. Most samples were centrifuged in order to remove any suspended solids which might affect the density. The average error from a series of multiple measurements from one sample was ± 0.001 g/l. A value for the total dissolved solids (TDS) was derived by subtracting the measured density of the fluid from the density of water. This produced a value for the TDS in the sample in grams per litre.

Alkalinity

Bicarbonate and carbonate were determined using a standard analytical procedure (ASTM, 1984) involving the microtitration of a given amount of the original sample (usually 10 ml) with 0.1 N hydrochloric acid. The amount of acid needed to change the pH to values of 4.5 and 8.1 indicating the amounts of HCO_3^- , CO_3^{2-} and OH^- based on their stoichiometric

relationship. HCO_3^- was detected in all but three samples, two of which contained CO_3^{2-} (samples 1-19 and 3-11) and one which contained OH^- (sample 3-19).

pH

Where possible, the pH was measured in the field using commercially available colourimetric pH test strips. These strips are considered accurate, by the manufacturer, to ± 0.1 pH units. Where the pH could not be determined in the field, measurements were made in the laboratory using a combination pH electrode which yielded an accuracy of ± 0.1 pH units.

Sulphate

Twenty-seven samples (Appendix I, part III) were analyzed for sulphate at the Potash Corporation of Saskatchewan analytical laboratory using x-ray fluorescence spectrophotometry. PCS reports that the values generally are accurate to $\pm 2\%$ for water samples with a high TDS load. Values obtained for sulphate from these water samples are similar to those values reported in the literature for fluids from the Dawson Bay Formation and the mining levels (Dunn, 1982; and Sproule Associates Ltd., 1980).

Analysis of Chemical Data

Chemical compositions were initially examined using a number of binary combinations. The binary approach was unsatisfactory because it allowed only a limited comparison between the various components so that a multivariate data analysis technique, correspondence analysis (Lebart et

al., 1984, and Greenacre, 1984) was used. Correspondence analysis is a multivariate factor-analysis method which examines several different variables simultaneously, allowing for a more encompassing analysis of the data set. This technique calculates new variables, called factors, which are more useful for describing the system being studied than the measured variables. The rest of the variables are then compared to the two chosen variables so that in a ten variable system, only 3 or 4 factors may be sufficient to describe all of the variation in the system. The advantage of the correspondence analysis technique is that the variations displayed usually reflect the natural processes of the system being studied. The factor plots selected show each factor in a multivariate relationship to both the initial variables and the samples studied. A practical example of the use of correspondence analysis is described by Mellinger (1986).

Correspondence analysis involves choosing two factors which are believed to be of importance in the system under study. The remaining factors are included only if they are believed to help with the understanding of the system. All samples included have been measured for the variables considered to be included in the analysis. For this study, 77 samples were used, and Na, K, Ca, Mg, Br, δD , $\delta^{18}O$, pH, TDS, and depth from surface were considered as variables. Factors were calculated using the variables Cl, Na, K, Ca, Mg and Br, with the other variables δD , $\delta^{18}O$, pH, TDS, and depth being displayed only in the calculated factors. A few of the variables such as δD , $\delta^{18}O$, TDS and depth were divided into smaller groups in order to better understand their relation to the factors.

Equilibrium thermodynamics was used to determine whether variations in the chemical composition of the waters are responding to variations in

lithology. This technique is described in Appendix IV. Thermodynamics for systems with high ionic strengths are tenuous because experimental data for salt systems are available for ionic strengths of less than six. Virtually all of the samples examined in this study had high ionic strengths, some as high as 14. Wood (1975 and 1976), Pitzer (1987) and Weare (1987) have discussed the complexity of these systems in detail and the difficulty of predicting the results from thermodynamic data, even in controlled settings.

RESULTS

Total Dissolved Solids and Chloride

The quantity of total dissolved solids (TDS) and concentrations of chloride in water samples from potash mines and shafts increase with depth, in a relatively uniform manner reaching a maximum in the mining-level samples (Figure 6). The only deviation from this trend occurs in samples from the shaft of the Rocarville mine which have higher TDS within the Devonian sequence relative to water samples from the shafts of the other mines. In samples from the Souris River Formation, the TDS contents of waters from the Rocarville mine are similar to those of samples from the other mines. The Cory mine-level samples, and some samples from the Lanigan mine, have the highest TDS with an average value of 350 g/l. This is significantly higher than the 250 g/l of the other mine level samples.

TDS contents vary directly with the amount of chloride present in the sample. In general, all of the major constituents of the waters studied, except sulphate, increase with depth reaching maximum concentrations in mining level waters.

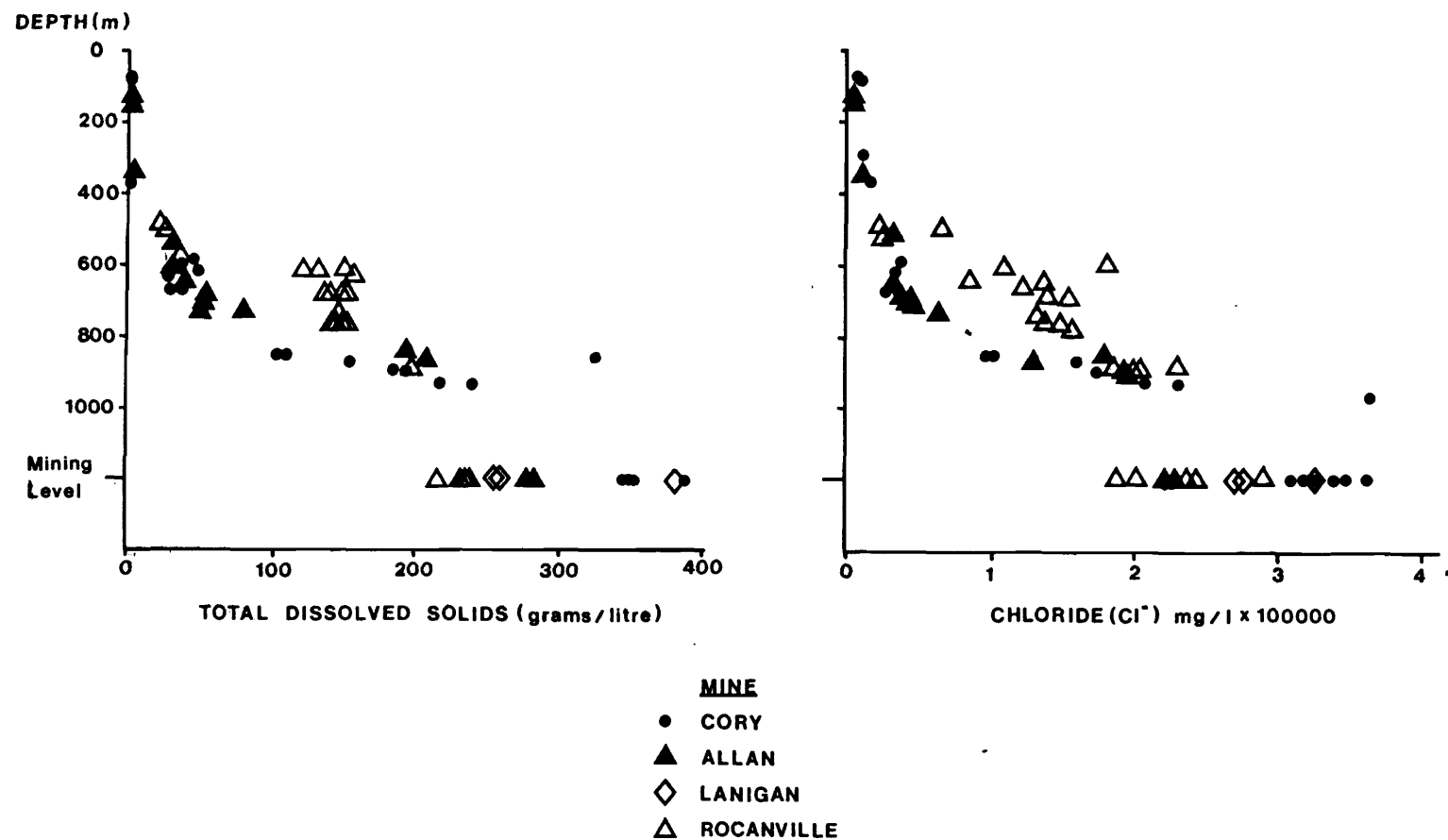


FIGURE 6: Relation between total dissolved solids and depth, and chloride and depth. Mine level samples have been plotted on a single horizon.

FIGURE 6

Sodium, Potassium, Calcium and Magnesium

The concentrations of Na, K, Ca, and Mg increase with depth, but in a less uniform manner than do TDS and Cl contents (Figures 7 and 8). In water samples taken from Cretaceous aquifers, the concentration of these ions is relatively low, rarely exceeding 10,000 mg/l. Water samples from the Devonian sequence exhibit an increase in these cations with depth. For example, Na increases in concentration with depth from approximately 34,000 mg/l immediately below the Mannville Formation to 104,500 mg/l at the base of the Souris River Formation. Unlike K, Ca, and Mg, Na concentrations are lower in waters from the Dawson Bay Formation than those from the overlying Souris River Formation. The Na concentration from mine-shaft samples varies inversely with Ca, that is, an increase in Na is coincident with a decrease in the amount of Ca in the sample. This indicates that the water composition is probably responding to changes in the lithology; Na contents increase as a result of the dissolution of halite bearing-evaporites, and Ca and Mg contents increase due to the dissolution of carbonates or anhydrite.

In contrast to the irregular, but consistent, increase in the concentration of these ions with depth, is the large degree of variability in their concentrations in mining level waters. Large shifts in the concentrations of these ions are probably a function of the type of salt available for solutioning and the composition of the original fluid. Several water samples with high Ca concentrations (>131,000 mg/l) are found at the Cory and Lanigan mines and represent a group of distinct Ca-rich waters. A group with anomalously high Mg concentrations (83,900 to 93,300

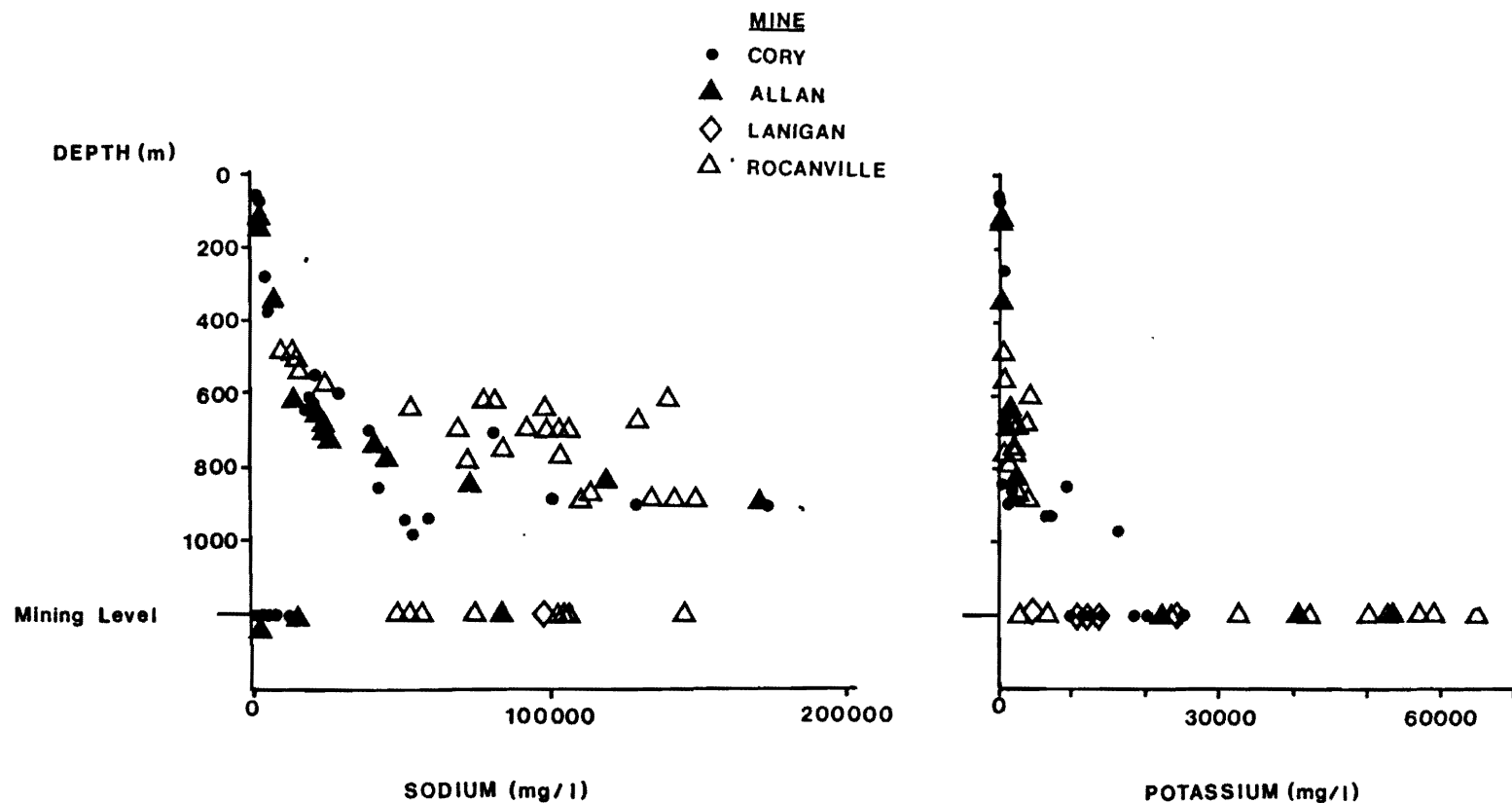


FIGURE 7: Sodium and potassium values of the waters are plotted with respect to depth. Sodium concentrations increase and vary dramatically within the Devonian sequence (i.e. below 500m) due to the presence of halite-bearing horizons. Potassium concentrations increase with depth in a gradual manner with large increases in mine-level waters.

FIGURE 7

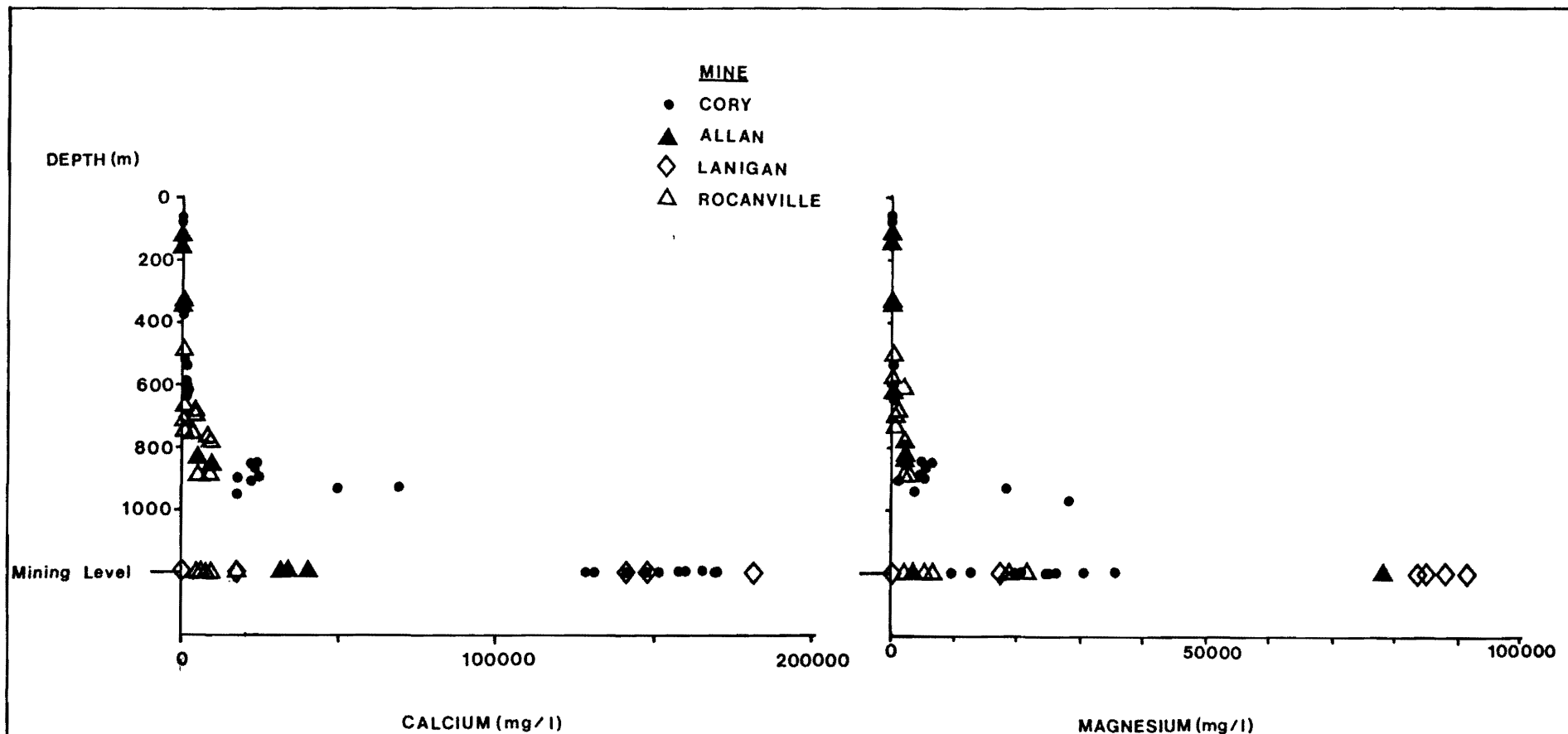


FIGURE 8: Calcium and magnesium values are plotted with respect to depth. Calcium and magnesium contents both gradually increase in concentration with depth and exhibit a large degree of variability in mining-level waters. Very high concentrations of calcium are found in waters from the Cory and Lanigan mines, and very high concentrations of magnesium are found in several samples from the Lanigan mine and one sample from the Allan mine.

FIGURE 8

mg/l) is present at the Lanigan mine. However, only in one example (sample 2-15) does this correspond to a sample with a high Ca concentration. All of the Ca-rich waters from the Cory mine have low Na concentrations ranging from 1,680 to 7,770 mg/l.

Bromide, Iodide and Fluoride

Br and I contents increase in concentration with depth and both show great variability in their concentrations in waters from the mining levels (Figure 9). F (not graphed) is present in all samples in very low concentrations, with a maximum of 0.2 mg/l (sample 1-16). In general, F shows little variation with depth and is virtually absent in all mining level samples at values of 0.002 to 0.004 mg/l, very close to the detection level.

Br contents increase gradually with depth, from concentrations of 4.0 mg/l (sample 1-13) in near surface water samples to a maximum of 21,747 mg/l (sample 1-5) in waters collected from the Dawson Bay Formation. Br in the mining level waters varies from 56 mg/l (sample 4-16) to a maximum of 28,479 mg/l (sample 2-5). Within the mine-water samples, two distinct groups of Br concentrations are present. The first group represents all the mine-level samples from the Cory mine and has concentrations of 16,397 mg/l to 22,438 mg/l. The second group represents mine-level water samples from the remaining mines with bromide concentrations of less than 10,000 mg/l. The Lanigan mine is the one exception to this distribution of bromide, with samples present from both groups. The very high values of Br concentrations found at the Cory and Lanigan mines are in waters that are also Ca-rich.

Iodide follows a similar pattern to Br, increasing gradually with

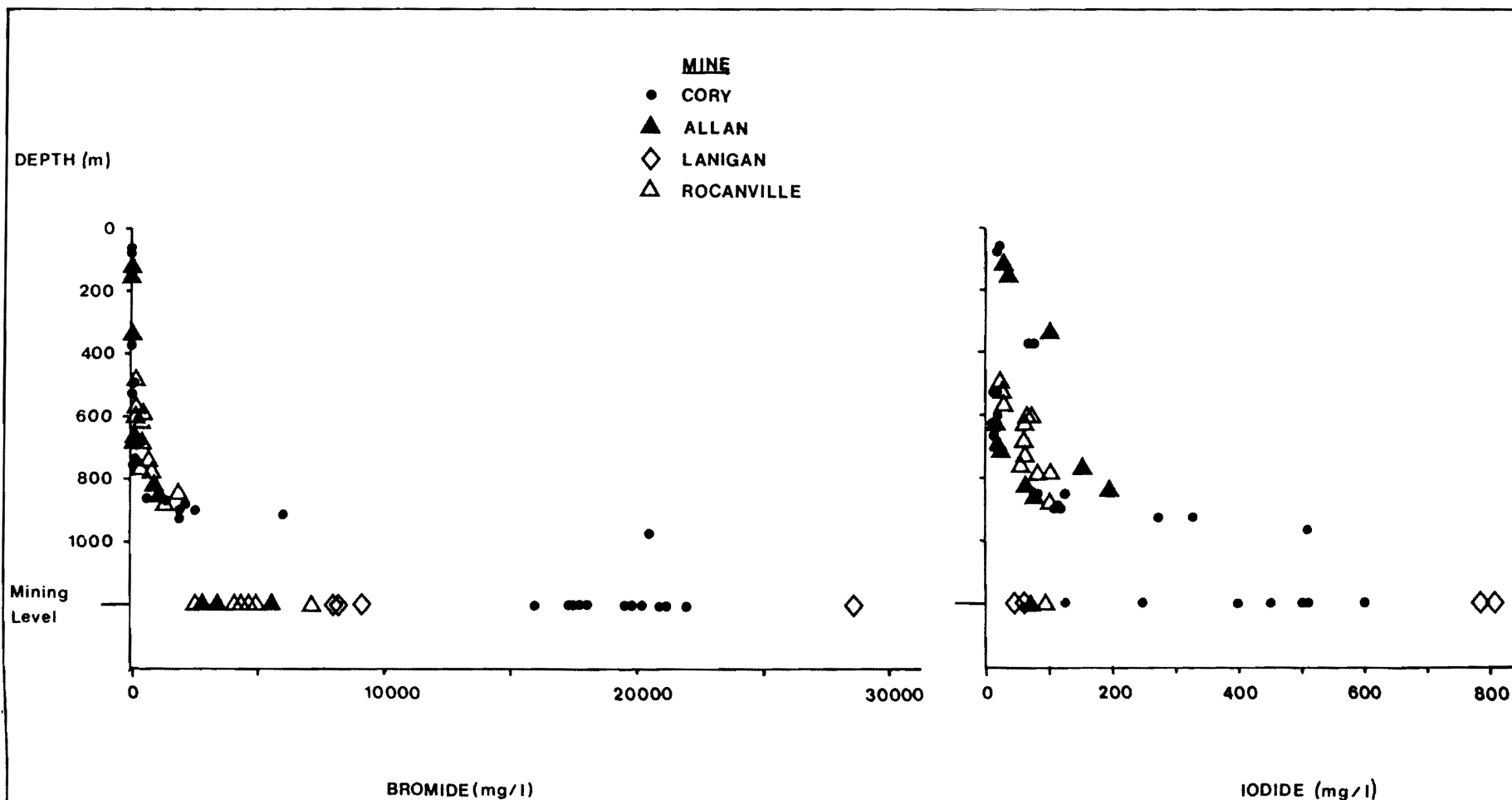


FIGURE 9: Bromide and iodide values of the waters are plotted with respect to depth. Both bromide and iodide concentrations gradually increase with depth, although the iodide profile is a little more irregular. Again, a great deal of variability is seen in the concentrations from mine-level waters. Waters with bromide contents greater than 15000 mg/l may be indicative of fluids which are residual to the recrystallization of evaporites under conditions of low temperature and low water/rock ratios.

FIGURE 9

depth from near-surface values of <20 mg/l to maximum values of 330 mg/l just above the mining level. The variability in concentration is marked in samples from the mining levels, ranging from 46 mg/l to 806 mg/l. In general, the high iodide contents (i.e.: >300 mg/l) correspond to the Ca-rich waters of the Cory mine and to the Mg-rich waters of the Lanigan mine. Two Ca-rich samples have iodide contents of 121 and 248 mg/l which are similar to concentrations found in other mine level samples.

pH and Alkalinity

In waters collected from the mine shafts pH values fall within a restricted range, from slightly basic to slightly acid (Figure 10). On the mining level, with one exception, pH is distinctly acidic, with values <6.0. The Ca-rich fluids have distinctly low pH values within the range of 4.0 to 4.7 pH units.

Alkalinity varies considerably with depth, ranging from 0 to 1,464 mg/l. Variations in HCO_3^- contents do not correlate well with any of the other dissolved ions. The high variability in results may stem from the analytical technique, that is, the insensitivity of the pH metering in relation to the extremely small size of the sample that had to be used. Alkalinity values were not plotted but are included in Appendix II.

Sulphate

A small number of samples were analyzed for sulphate content (Appendix II, Part III). The results show that high sulphate contents exist in samples collected from Devonian strata above the mining levels, with values ranging from 1200 mg/l in the Souris River Formation to 18332 mg/l in the

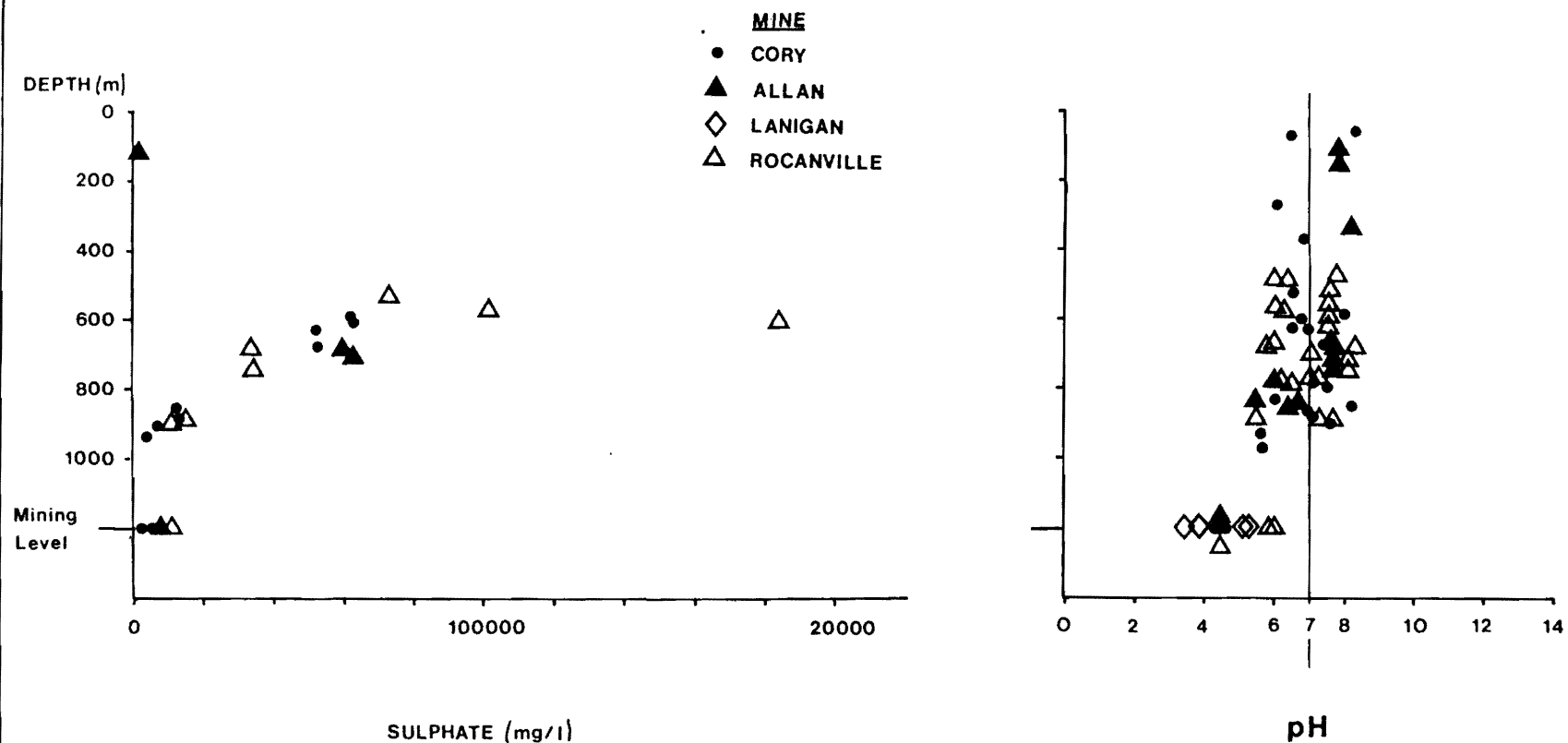


FIGURE 10: Sulphate contents and pH values of the waters are plotted with respect to depth. Sulphate is the only constituent of the waters to decrease in concentration with depth. High sulphate contents within waters are probably due to the dissolution of anhydrite. The pH of waters from mine shaft samples is weakly acidic to weakly basic throughout the profile whereas mine-level waters have a much lower pH.

FIGURE 10

Duperow Formation (Figure 10). Sulphate is the only ion to show a decrease in concentration with depth. High sulphate contents are probably due to the dissolution of anhydrite. Thermodynamic calculations indicate that all of the samples are theoretically oversaturated with anhydrite and gypsum.

Mine-level samples have relatively low sulphate contents, probably reflecting the small amount of anhydrite present within the mine-level evaporites. The sulphate that is present may be due to water flow from the Dawson Bay Formation. Similarly, the one sample from the Cretaceous has a very low sulphate content, probably due to the absence of anhydrite layers.

STABLE ISOTOPE GEOCHEMISTRY

INTRODUCTION

Water is composed of hydrogen and oxygen which have two and three naturally occurring stable isotopes, respectively (Table 1).

Table 1: Stable Isotopes of Hydrogen and Oxygen

<u>Element</u>	<u>Stable Isotope</u>	<u>Global Abundance(%)</u>
Hydrogen	^1H	99.985
	^2H or D (Deuterium)	0.015
Oxygen	^{16}O	99.756
	^{17}O	0.039
	^{18}O	0.205

Water molecules hence have different masses depending on the isotopic composition of the oxygen and hydrogen atoms. A water molecule of H_2^{16}O has a mass number of 18 and a water molecule of D_2^{18}O has a mass number of 22. The vapour pressure of water varies inversely to the mass number, that is, the lower the mass number the higher the vapour pressure, because water molecules with lower mass numbers are more stable in the vapour phase than water molecules with heavier mass numbers. This difference in mass results in the separation of waters of different isotopic composition as water goes through repeated evaporation and precipitation within the meteoric water cycle. Water vapour, therefore, is depleted in the heavier isotopes with respect to the starting composition of the water, and the precipitation resulting from the condensation of the vapour is enriched in the heavier isotopes. Thus, due to the retention of heavy isotopes in the originating

waters and the concentration of the heavy isotopes in precipitation, the light isotope content of water vapour increases with distance from its source.

The isotopic composition of water is reported as the D/H or $^{18}\text{O}/^{16}\text{O}$ ratio in the sample relative to these ratios in standard mean ocean water (SMOW). These variations are normally small and are reported as delta values (δ) in units of per mil using the following formula:

$$\delta^{18}\text{O} = \left| \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} - 1 \right| \times 1000$$

The partitioning of the stable isotopes of water among various phases is dependent on temperature and, as a result, the isotopic composition of precipitation becomes a function of latitude, altitude and climatic conditions. In addition, water is removed during cooling of a cloud as the cloud passes from the oceans to the continents. The water remaining in the cloud becomes increasingly depleted in the heavy isotopes as the precipitation proceeds.

Because the isotopic composition of meteoric water during condensation and evaporation processes is determined by the difference between the mass of the H and D atoms as well as the difference between the ^{18}O and ^{16}O atoms, D/H and $^{18}\text{O}/^{16}\text{O}$ ratios of meteoric waters are usually proportional. This proportional trend forms the meteoric water line (MWL), where

$$\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$$

and along which most surface waters cluster.

Meteoric water in Saskatchewan is very depleted in ^{18}O and D relative to SMOW because of its latitude, cool climate and distance from the ocean

(Figure 11). The median values for meteoric waters in Saskatchewan are -150 for δD and -20 for $\delta^{18}O$ with a wide range of values due to seasonal variations typical of the extremes found in continental climates (McMonagle, 1987).

The isotopic compositions of meteoric water in Saskatchewan, and possibly throughout the recharge area for the Elk Point Basin, have probably not changed greatly since glacial times because there have been no major changes in elevation or climate. When meteoric water enters the ground, δD and $\delta^{18}O$ values change because of mixing of meteoric water with pre-existing formation waters and because of isotope exchange reactions with the surrounding rocks. Therefore, near surface groundwaters, because of more rapid flushing, largely reflect the isotopic composition of meteoric waters, whereas deeper formation waters, more distant from their source and not as rapidly flushed, usually become relatively enriched in the heavier isotopes because of exchange reactions with host rocks. Exchange of isotopes between water and minerals normally affects $\delta^{18}O$ values more than δD values of the water because of the large oxygen and small hydrogen contents in most minerals.

The main mechanism by which δD and $\delta^{18}O$ values increase with depth in most sedimentary basins is by the mixing of meteoric waters having, for example values near $\delta D = -150$ and $\delta^{18}O = -20$ with trapped formation waters which have values near $\delta D = -30$ and $\delta^{18}O = -1$ (Hitchon and Friedman, 1969). The formation waters may be true connate water or water which has resided long enough in the basin to become ^{18}O rich as a result of the exchange reactions between the water and rock. For recent waters, such exchange reactions between water and rock are negligible due to the slow rate of

FIGURE 11: The isotopic evolution of meteoric water from its source in the ocean to the interior plains is diagrammed. Ocean water has a δD value and a $\delta^{18}O$ value of zero. With distance from the ocean, increased altitude, increased latitude and decreased temperature, meteoric water is progressively depleted in the heavier isotopes of oxygen and hydrogen. Thus, precipitation on the interior plain has low δD and $\delta^{18}O$ concentrations, relative to ocean water, as shown by the average value for Saskatchewan surface waters ($\delta D = -150$ and $\delta^{18}O = -20$). This average isotopic composition of the surface waters is taken to be the average value for waters entering the groundwater system in the recharge areas of the interior plains.

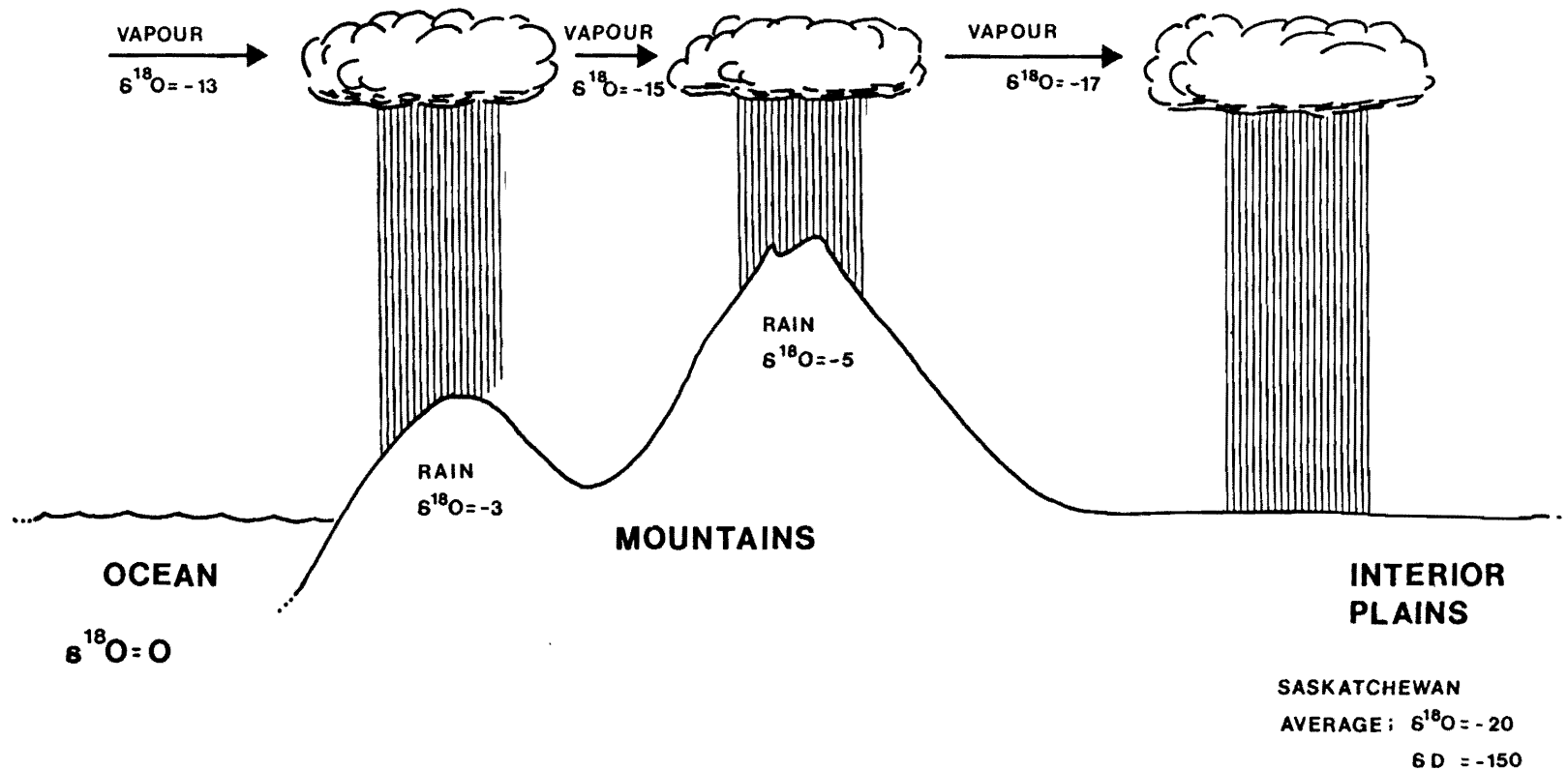


FIGURE 11

exchange of hydrogen with clays and oxygen with carbonates and silicates.

Waters presently in the Alberta Basin are dominantly recent meteoric waters that have either displaced or mixed with pre-existing basin waters (Clayton et al, 1966). The Alberta Basin is interconnected with the Elk Point Basin and it is not unreasonable to assume that the same mechanisms operate in both basins. δD and $\delta^{18}O$ values within a basin increase with depth in a uniform manner and each basin develops a unique δD vs $\delta^{18}O$ trend with depth (Hitchon and Friedman, 1969). Because δD and $\delta^{18}O$ values in a given aquifer increase with distance from the recharge areas, Schwartz et al (1981) proposed that the increase in δD and $\delta^{18}O$ with distance from the source means that the basinal trend also could be constructed by stacking the data from individual aquifers. They further note that variations in D and ^{18}O contents also could be accounted for by variations in the flushing rates of individual formations by meteoric waters. In a vertical section, δD and $\delta^{18}O$ values may deviate from the general enrichment trend with depth in a basin by having slightly lower D/H and $^{18}O/^{16}O$ ratios in formations that are flushed more thoroughly, or by having slightly higher ratios where fluid flow is more restricted.

Waters which differ in their stable isotopic compositions from waters in surrounding formations either represent waters with very different flushing rates or they represent waters which have been transferred from a higher, or lower, formation through some conduit. Such waters are "short-circuited", that is, while they represent mixtures of pre-existing formation water and meteoric water, their isotopic compositions suggest that these fluids are out of place with respect to the isotopic compositions of fluids in the surrounding formations. An example of short-

circuiting would be the presence of waters with values for $\delta D = -110$ and $\delta^{18}O = -10$ in the mining levels where normal isotopic contents are $\delta D = -50$ and $\delta^{18}O = -1$. Because of this difference in isotopic compositions, the source of waters of low isotopic composition found on a mining level (shortcircuited waters) should be identifiable by comparing its isotopic composition with those of overlying formations.

Analytical Techniques

δD values (Appendix III) were determined using the uranium method of producing hydrogen gas from water described by Friedman (1953). The resultant hydrogen gas was analyzed in an isotope ratio mass spectrometer (VG 602C) and duplicate analyses suggest a reproducibility of ± 3 per mil.

$\delta^{18}O$ values were determined by equilibrating 10 ml of degassed sample with a carbon dioxide of known isotopic composition in a process similar to that of Epstein and Mayeda (1953). The isotopic composition of equilibrated CO_2 gas was analyzed on a mass spectrometer and duplicate analyses suggest a reproducibility of ± 0.1 per mil. The $^{18}O/^{16}O$ ratio is reported with respect to SMOW in units of per mil. Samples were equilibrated for periods of up to three days in order to assure the complete equilibration of the sample. This time period was chosen after considering problems noted by Sofer and Gat (1972) in equilibrating CO_2 with concentrated brines.

The correction factors of Sofer and Gat (1972) for the effects of high ionic strengths in brines on the apparent $\delta^{18}O$ values were tested with respect to the spectrum of chemical compositions. These corrections take into account the effects of Mg, Ca, and K on the activity of ^{18}O . Na has a

negligible effect on the activity of ^{18}O . The corrections are small for near surface samples, however, it shifted some of the mine level $\delta^{18}\text{O}$ values by as much as +5 per mil. This large shift in the $\delta^{18}\text{O}$ values is largely due to the high concentrations of Mg, which have the largest effect on the activity of the ^{18}O in the samples. Because the overall basinal trend was not shifted appreciably, the effect proposed by Sofer and Gat (1972) may not be significant (Kyser, 1987). Since the conclusions of the study were not affected significantly, the corrected values were not used for this study. No correction factor was used for the hydrogen data because it was obtained from a distilled sample.

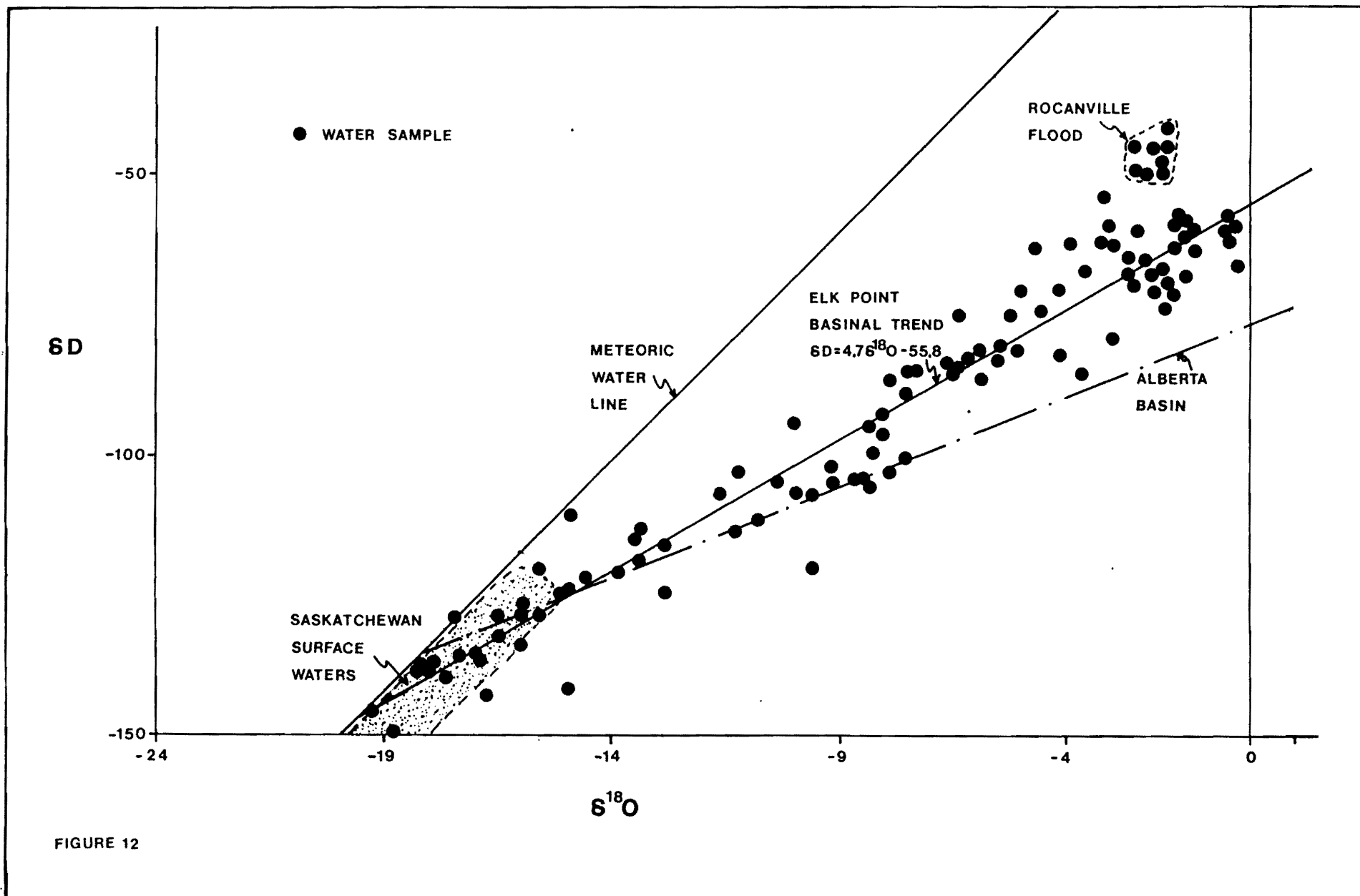
Results

δD and $\delta^{18}\text{O}$ values of both mine-shaft and mine-level samples plotted in Figure 12 illustrate a trend with depth similar to that of the Alberta Basin (Hitchon and Friedman, 1969). This trend shows the expected enrichment in the δD and $\delta^{18}\text{O}$ values with depth. A line of best-fit was calculated for the isotope data (Figure 12) using the least squares method. The best-fit line, excluding samples from the Rocanville flood which were not included because they appear to represent a distinct, and separate, group, has the following equation:

$$\delta\text{D} = 4.7 \times \delta^{18}\text{O} - 55.8$$

Within a given aquifer, there can be substantial variations in the isotopic compositions of the water (Figure 13). An example of this is the Duperow Formation which has a median value for δD and $\delta^{18}\text{O}$ of -135 and -17 respectively, in the Cory area and -83 and -6 respectively in the Rocanville area. Such large variations in the isotopic composition of

FIGURE 12: δD and $\delta^{18}O$ values for all of the water samples analysed in this study (Appendix III). The isotopic compositions for near surface samples plot near the field for Saskatchewan surface waters (shaded area). With increasing depth the waters become increasingly enriched in the heavier isotopes along a line defined by $\delta D = 4.7 \times \delta^{18}O - 55.8$ (the Elk Point Basinal Trend). The trend for the Alberta Basin (Hitchon and Friedman, 1969) has been included for comparison, as these fluids are from another portion of the Western Interior Basin of which the Elk Point Basin is part. The small cluster of samples for the Rocanville flood were not included in calculating the trend of the basinal waters because of their unique position on the plot.



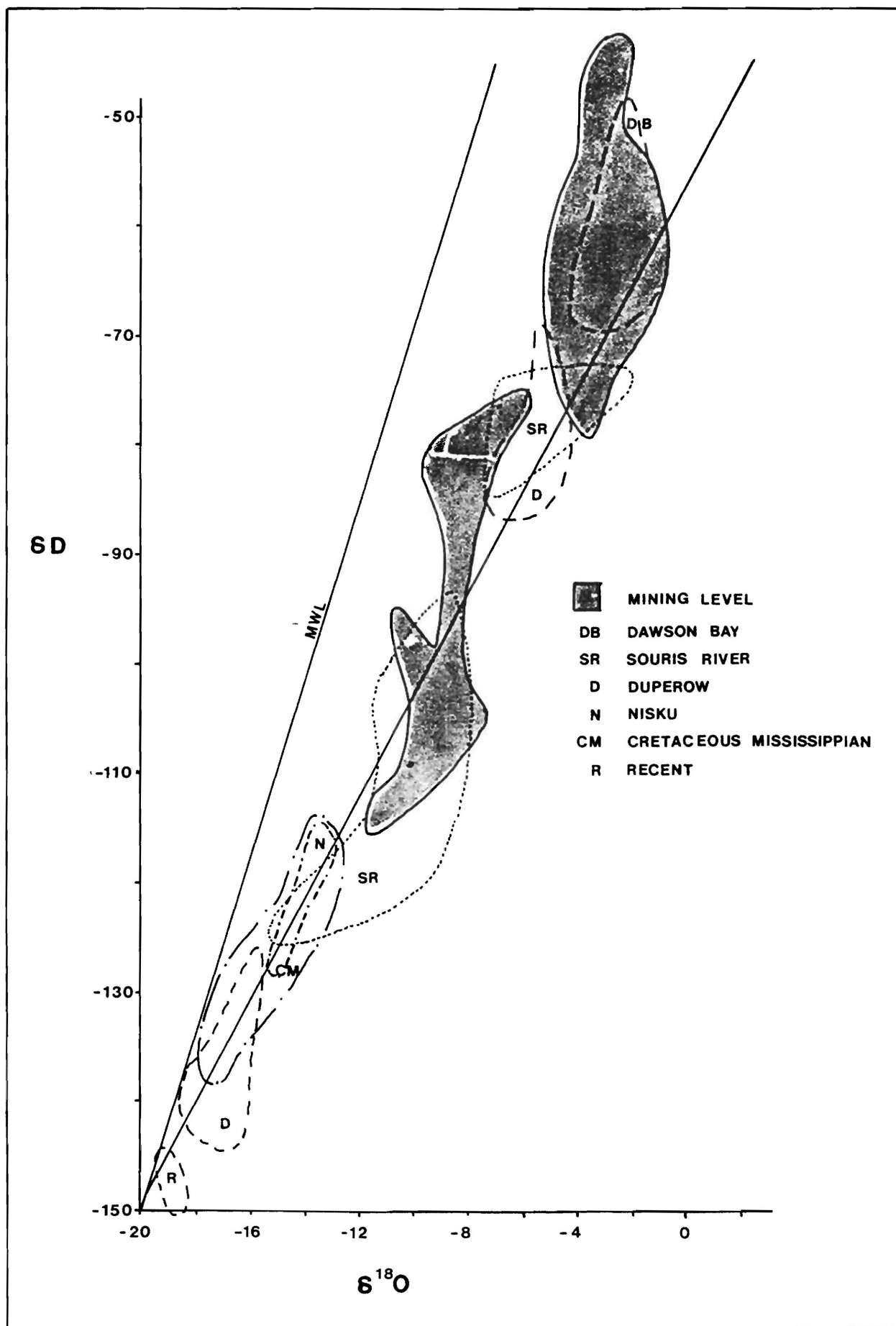


FIGURE 13: The stable isotope data for the whole project is grouped by formation. All of the data points shown in Figure 12 are included in this diagram. Mine-level samples fall within the shaded areas.

waters from the same formation falls along the basinal trend and indicate that, regardless of the path the waters have taken, they are the result of mixing between meteoric and formation waters.

Cory Mine

Isotopic compositions of the waters from the Dawson Bay and Prairie Formations are similar suggesting that they have closely related fluid systems (Figure 14). The Dawson Bay and the Prairie Formation fluids have isotopic concentrations which are distinct from the isotopic concentrations of other Cory water samples. With the exception of some samples from Cretaceous formations, there is the expected increase in the isotopic values of waters from the Cory mine with depth. Recent waters plot very close to the meteoric water line indicating a high component of modern meteoric water. Variations in the isotopic compositions with depth fall very close to the trend of the Elk Point and other basins indicating that these waters are the result of mixing between meteoric waters and pre-existing formation waters. Stable isotope compositions for the samples from Cretaceous formations lie between those of the stratigraphically lower Nisku and Duperow water samples and this may indicate that the Cretaceous aquifers in this area are isolated from the other aquifers and have no apparent connection with other formations.

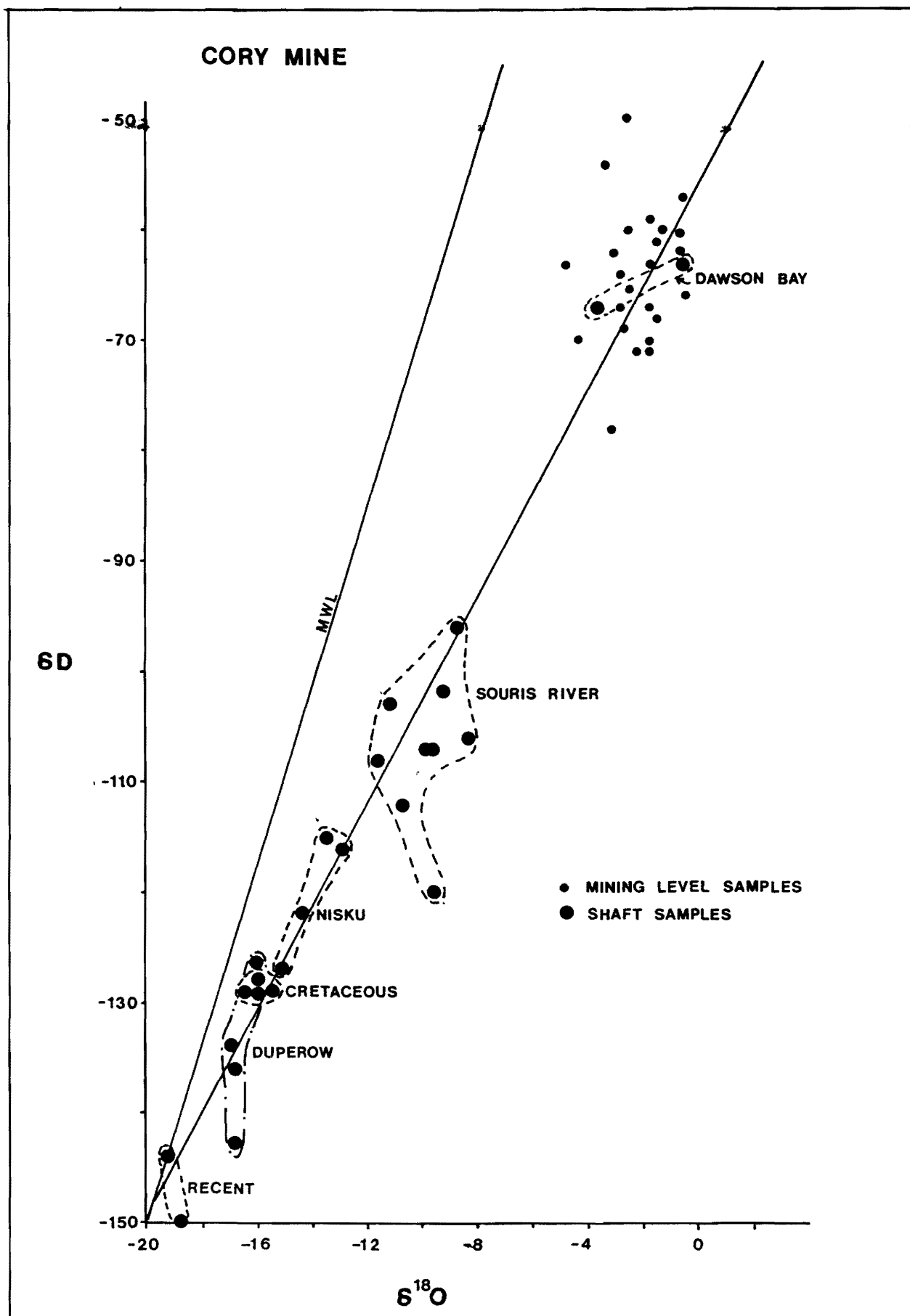


FIGURE 14: δD vs $\delta^{18}O$ values for the Cory Mine are plotted in relation to the meteoric water line (MWL) and the Elk Point basinal trend. Mine-shaft samples are grouped by formation and the mine-level samples are represented by the small dots.

Allan Mine

δD and $\delta^{18}O$ values for the Allan mine waters are shown in Figure 15 and they also show the expected increase in the concentration of heavy isotopes with depth. As at the Cory mine, there is a large gap between the Souris River Formation water samples and those from the Prairie Formation at the mining level, indicating that the two aquifer systems are probably isolated from each other. No samples from the Dawson Bay Formation are available to compare with the mining level samples. The proximity of some isotopic compositions to the MWL indicate a large meteoric component in the Devonian and Cretaceous sequences in the Allan area.

Lanigan Mine

Unfortunately, no samples are available from the shaft of the Lanigan mine because of its welded steel shaft lining. The one bin area water sample has a similar isotopic composition to mine-level water samples from the Cory and Allan mines (Figure 15). The remaining mine-level samples, when compared to the isotopic compositions of formation waters from the two closest mines, Cory and Allan, have values which are between the Souris River and Dawson Bay Formation waters. This would indicate that, for at least some of the mine-level waters at the Lanigan mine, there is a meteoric water component.

Rocanville Mine

In general, samples of water from the shaft and mine at Rocanville (Figure 16) become increasingly enriched in D and ^{18}O with depth. Three main differences between the Rocanville data and those from the other mines

ALLAN and LANIGAN MINES

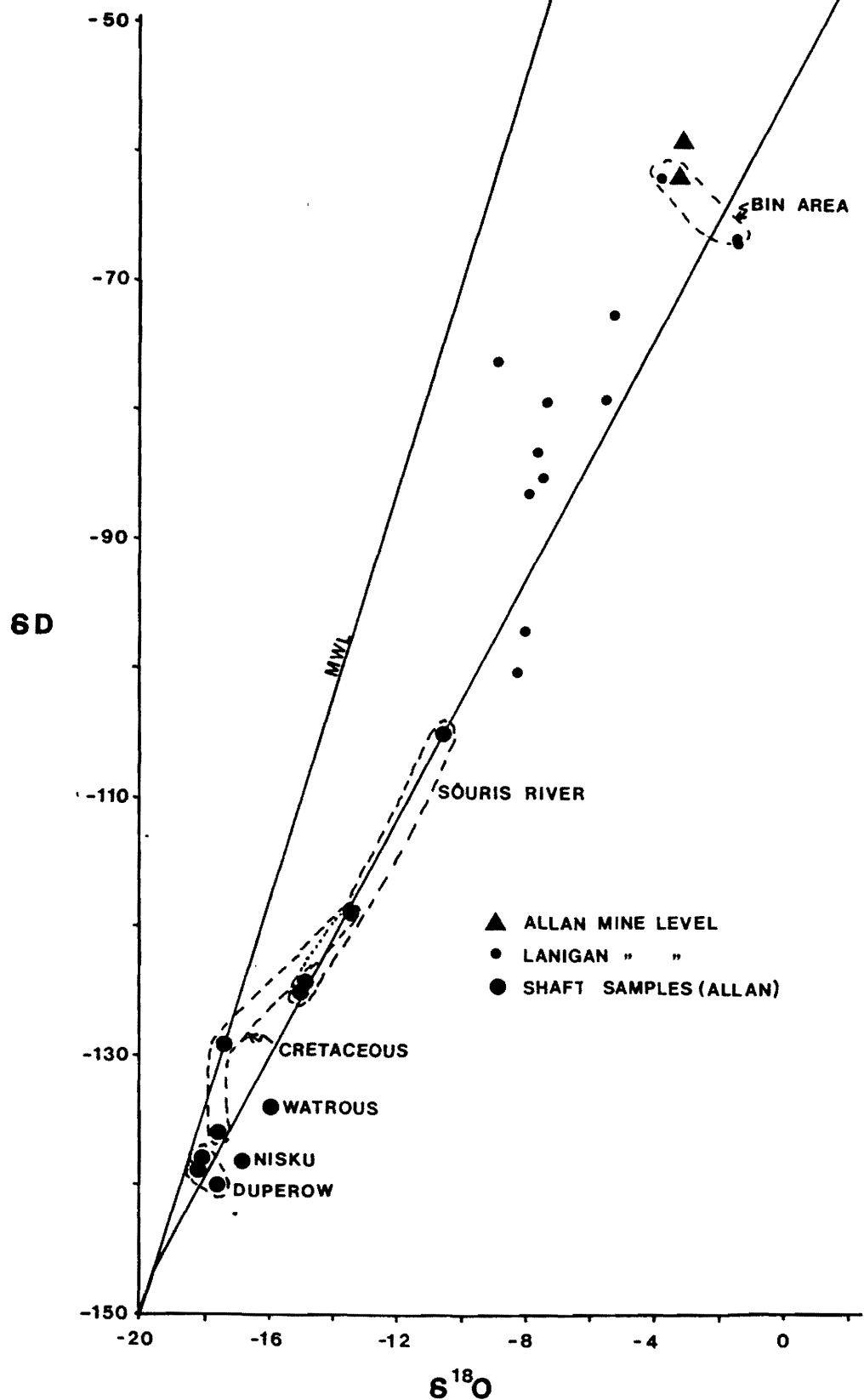


FIGURE 15: δD and δ¹⁸O values for water samples from the Allan and Lanigan mines are plotted in relation to the MWL and the Elk Point basinal trend.

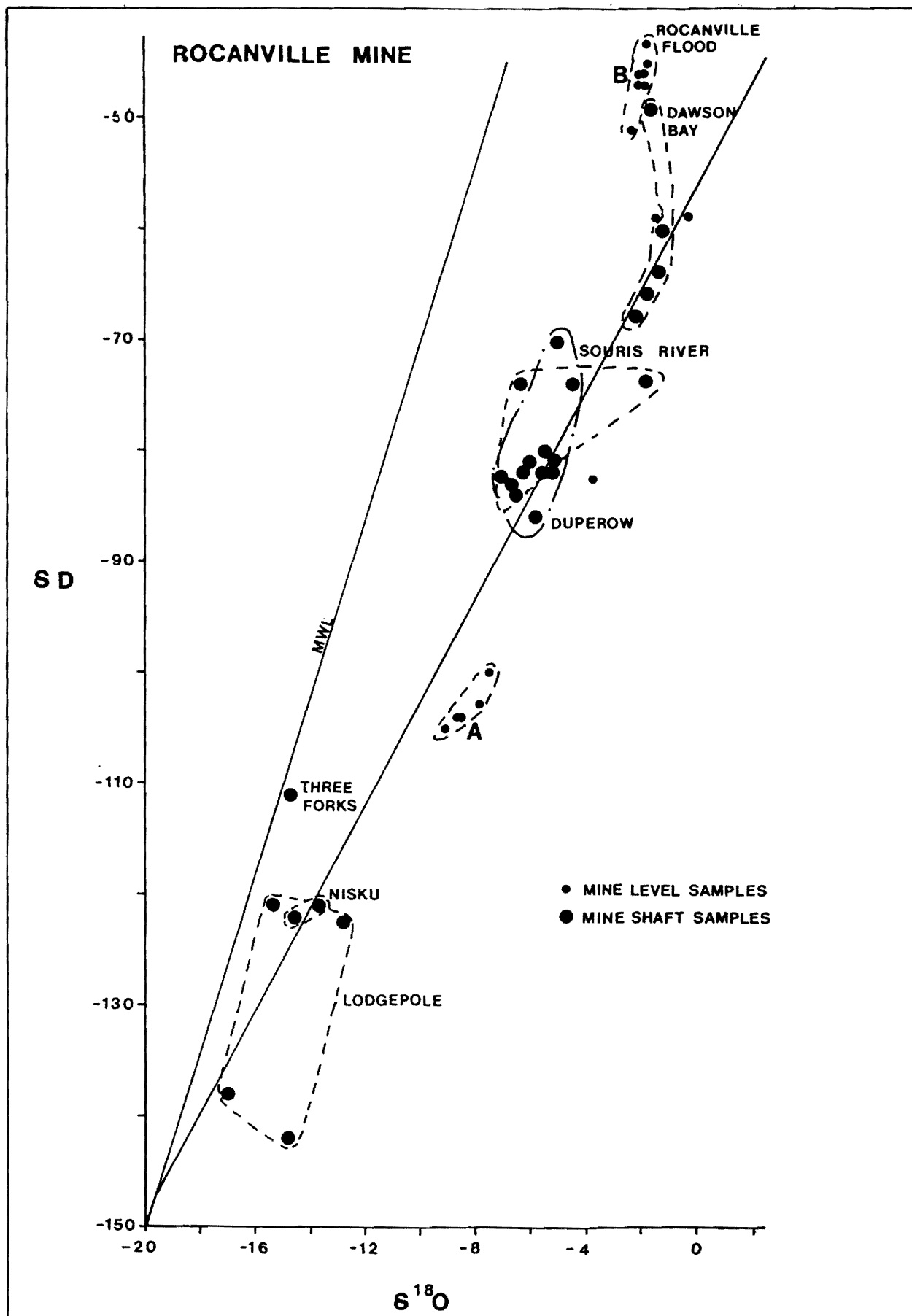


FIGURE 16: δD and $\delta^{18}O$ values for water samples from the Rocanville Mine are plotted with respect to the meteoric water line (MWL) and the Elk Point basalinal trend.

include: 1) a cluster of mine level samples which have lower isotopic values in relation to the other mine level samples (Group A, Figure 16), 2) there is a large difference in the isotopic compositions of the Nisku and the Duperow formation waters, whereas at the other mines a large difference existed between the Souris River and the Dawson Bay formations, and, 3) a group of mine level samples, which represent waters from the Rocanville flood, have distinct δD values which lie off the main basinal trend (Group B, Figure 16).

The group A mine-level samples (Figure 16) probably represent a group of samples which have a significant input of meteoric water. Group A samples do not have isotopic compositions that directly correspond to any other group of samples analyzed from the Rocanville area. Group A waters have isotopic compositions ($\delta D \approx -104$ and $\delta^{18}O \approx -8$) which are intermediate to those of the Nisku-Lodgepole and the mine level-Souris River samples indicating that the inflow waters may be a combination of these two waters or a mixture of mine level waters with a very high proportion of meteoric water. The Group A waters, therefore, represent waters with a large component of meteoric water which have moved from a higher stratigraphic level to the mining level, probably with some mixing with pre-existing formation waters. The origin of these waters may be the large aquifer system represented by the Nisku, Three Forks and the Lodgepole formations.

The large difference between the isotopic compositions of the Lodgepole-Nisku waters and the Souris River-Dawson Bay waters may indicate that these aquifer systems are isolated from each other. Clustering of the Lodgepole and Nisku formation waters near the MWL indicates a large component of relatively modern meteoric water. Additionally, the

overlapping of the values from the Lodgepole and Nisku Formations indicates that they are part of the same aquifer system, or, that they represent two separate formations with similar flushing rates. The similarity in the isotopic compositions of the Souris River and Duperow formation waters indicates that these two formations either are part of the same aquifer system or that these two formations have similar flushing rates.

Rocarville mine-level and Dawson Bay Formation waters have similar isotopic compositions indicating that they are the same aquifer system. This overlap in isotopic compositions exists for both the "normal" mine waters and the Rocarville flood waters (Group B, Figure 16). The Group B waters have distinct isotopic compositions ($\delta D \approx -47$ and $\delta^{18}O \approx -2$) compared to all mine-level waters. Group B isotopic compositions reflect an enrichment of approximately 12 per mil in deuterium with respect to the other mine-level water samples.

DISCUSSION

It is a common feature of sedimentary basins that the salinities of formation waters increase with depth (White, 1965; Dickey, 1969; Dingman and Angino, 1969; and Graf, 1982). A number of mechanisms have been suggested for this increase in salinity including membrane filtration (e.g. Bredehoeft et al, 1963; White, 1965; Berry, 1968; van Everdingen, 1968; Hitchon et al, 1971; and Graf, 1982), brine density flow (Anderson and Kirkland, 1980) and the dissolution of evaporite units (Hitchon et al, 1971).

Membrane filtration allows for the selective movement of certain molecules or ions in a fluid under pressure through a semi-permeable membrane. Pressure is created in a confined aquifer by basinal loading, tectonic pressures, or osmotic pressure. Water easily moves through the semi-permeable layers which, in the basinal setting, are normally represented by shale or clay layers. The ease of movement of ions is controlled by their charges and radii, together with temperature and pressure. Through the process of membrane filtration, upward-moving water becomes progressively less saline as dissolved solids are removed, and as a result, water at depth becomes increasingly more saline due to the increase of residual dissolved solids. In general, where membrane filtration is a factor, there is a general increase in Mg, Ca, Na, Cl and Ca+Mg/Na with depth (van Everdingen, 1968).

Brine density separation occurs when two fluids, one with a larger amount of dissolved solids, interact, resulting in the denser brine sinking

relative to less dense brines. Although this mechanism may be too simplistic for generating concentrated brines at depth, the movement of these denser brines can create flow within a basin through the mechanism of brine density flow (Anderson and Kirkland, 1980). Such flow may be important in the salt solutioning process as it may allow for the circulation of undersaturated fluids.

The dissolution of evaporites is another major source of saline solutions at depth. Hitchon et al (1971) suggest that dissolved minerals are largely responsible for the high salinities of formation waters within the Western Canada sedimentary basin. They further state that these formation waters are due to a mixing of trapped sea water (connate water) and meteoric water, combined with the dissolution of evaporites.

It is likely that the high salinities at depth within the Western Canada sedimentary basins are caused by a combination of these three concentrating mechanisms. Certainly, membrane filtration has been invoked as a mechanism for increasing the salinities (Hitchon et al, 1971). However, it has been noted that Na and Cl increase with distance from the recharge zone (Schwartz et al, 1981) and, therefore, a more complex mechanism is probably in operation. This is especially true as fluids do not appear to be strongly confined within the basin, a necessary step in building up the pressures required for membrane filtration. Recent work on the stable isotopic compositions of fluid inclusions in evaporite minerals by Knauth and Beeunas (1986) suggests that basinal waters, especially in basins with large evaporite sequences, may have evolved through the mixing of meteoric waters with ancient evaporite brines. This mixing of saline waters with meteoric waters easily could explain the gradual increase in

total dissolved solids with depth. Fritz and Frape (1980) suggest that high salinities may be derived by the interaction of connate water from a sedimentary basin circulating through Precambrian basement rocks.

Concentrations of the major cations associated with evaporite minerals in the basin on a Janecke ternary plot (Figure 17) indicate that all of the mine-shaft samples are in the stability field for halite + solution, whereas the mine-level samples lie within the stability fields for sylvite or carnallite + solution. This is probably determined by the local geology inasmuch as mine-shaft waters are likely to have been in contact with halite-dominated evaporites and carbonates, whereas the mine-level waters are likely to have been in contact with sylvite and carnallite as well as halite. Sodium contents are lower than would be expected in mine-level waters when compared to the amount of halite available for dissolution in relation to sylvite and carnallite. This is because halite is the least soluble of the three main salt minerals found in the potash horizons and the concentrations of the other ions in solution probably limit its solubility. Therefore, higher Na concentrations relative to K would be expected in mine-shaft samples and the opposite in mine-level waters.

The activity of an ion is a measure of its effective concentration (Appendix IV). The mine level samples either straddle the halite-sylvite equilibrium line or they lie within the sylvite plus solution stability field (Figure 18). This diagram confirms that, for samples from the mine shafts, the dissolution of halite controls the Na and K values, and, in the mining levels, the dissolution of sylvinite (halite plus sylvite) and sylvite control the Na and K concentrations of the waters. The dissolution of carnallite may provide some of the dissolved K where high Mg contents

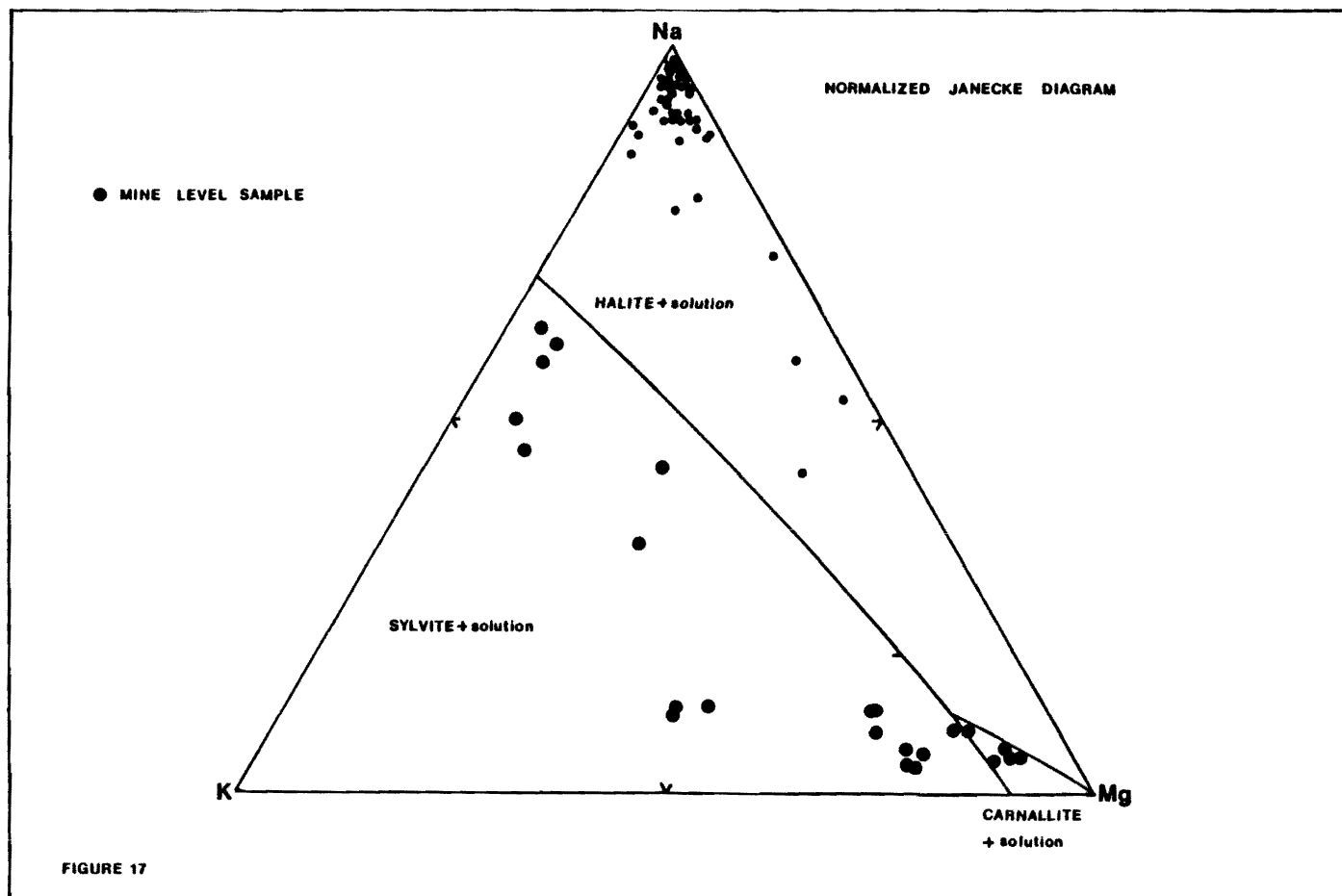


FIGURE 17

FIGURE 17: All the mine-shaft and mine-level samples are shown plotted on a Na-K-Mg Normalized Janecke Diagram. The stability fields for halite, sylvite and carnallite in contact with a solution are shown.

are also found in the same mine level water sample.

Clays and feldspars appear to have no direct bearing on the Na-K concentrations on samples collected from both the shafts and the mine levels. This is illustrated in Figure 18 where the muscovite-paragonite and the potassium feldspar-albite equilibrium lines have been plotted. The distance the data plots from the equilibrium lines indicates that these phases have little influence on the Na-K contents of the waters except for three water samples from Cretaceous formations whose data points plot close to the albite-K-feldspar line. All waters are theoretically in equilibrium with potassium feldspars since all of the data plot within the stability field of potassium feldspar plus solution.

Correspondence analysis factors (Figure 19) indicate that with increasing depth, the system becomes less dominated by halite. That is, with respect to the other major cations, the relative concentration of Na decreases, and other chlorides have a larger input. The correspondence analysis shows that all of the shaft samples plot within the area defined by the Na and Cl-TDS factors, indicating that the dissolution of halite is the main source of dissolved solids. The concentration of potassium, while behaving relatively independently with respect to the other major cations, has its strongest correlation with the mine-level samples indicating that the largest source of potassium in the waters is from the dissolution of sylvite and carnallite. For "normal" mine-level samples the correspondence analysis indicates that Mg and K, and to a lesser extent Ca and Br, are the dominant cations. The correspondence analysis shows that the Rocarville mine flood samples plot within the same region as the mine-shaft samples, the region in which halite has the dominant control on the TDS load. This

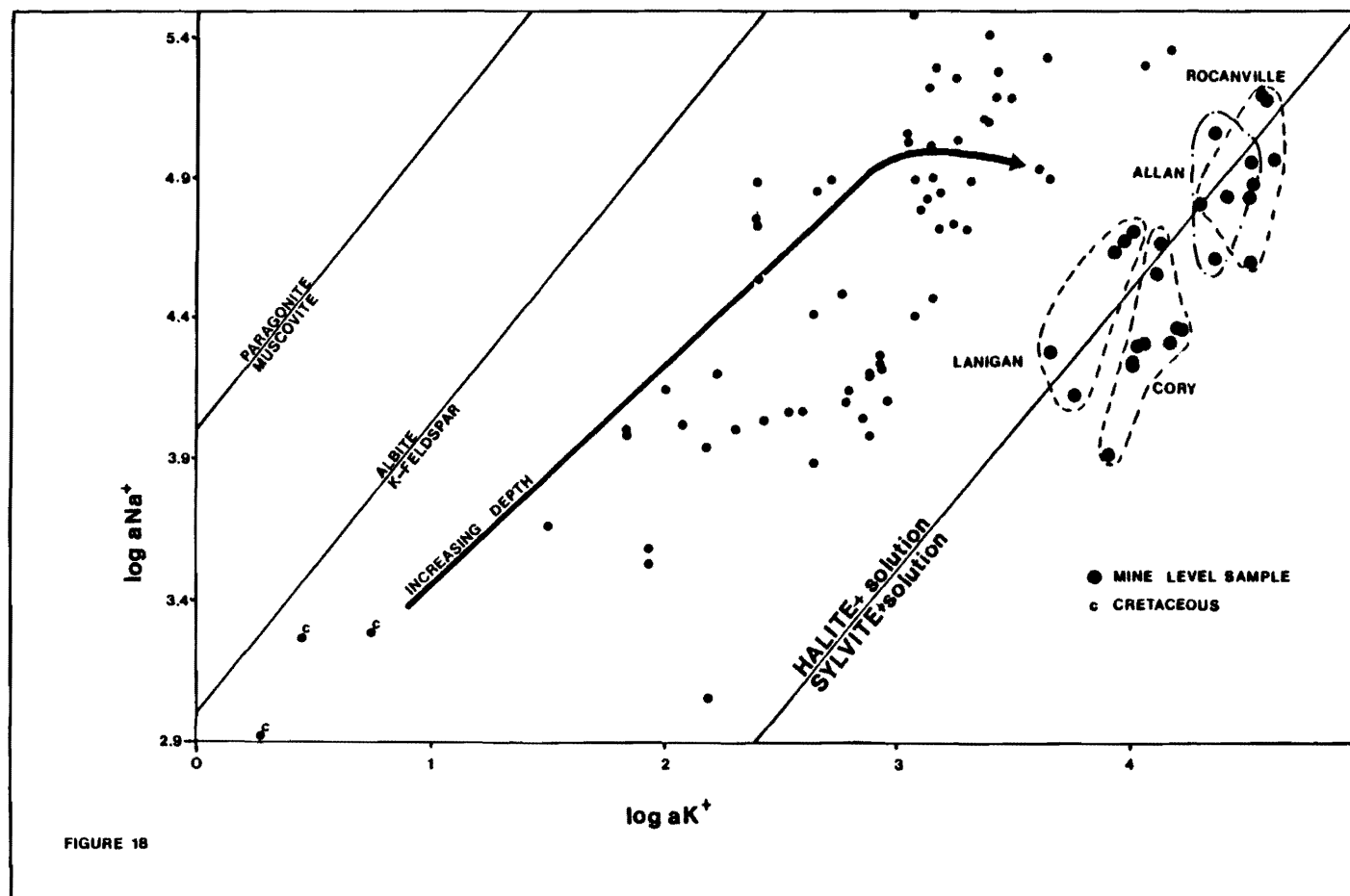


FIGURE 18

FIGURE 18: The activities of Na and K for mine-shaft samples (small dots) and mine-level samples are plotted in relation to the theoretical stability fields of halite, sylvite, and some common Na-K clay minerals.

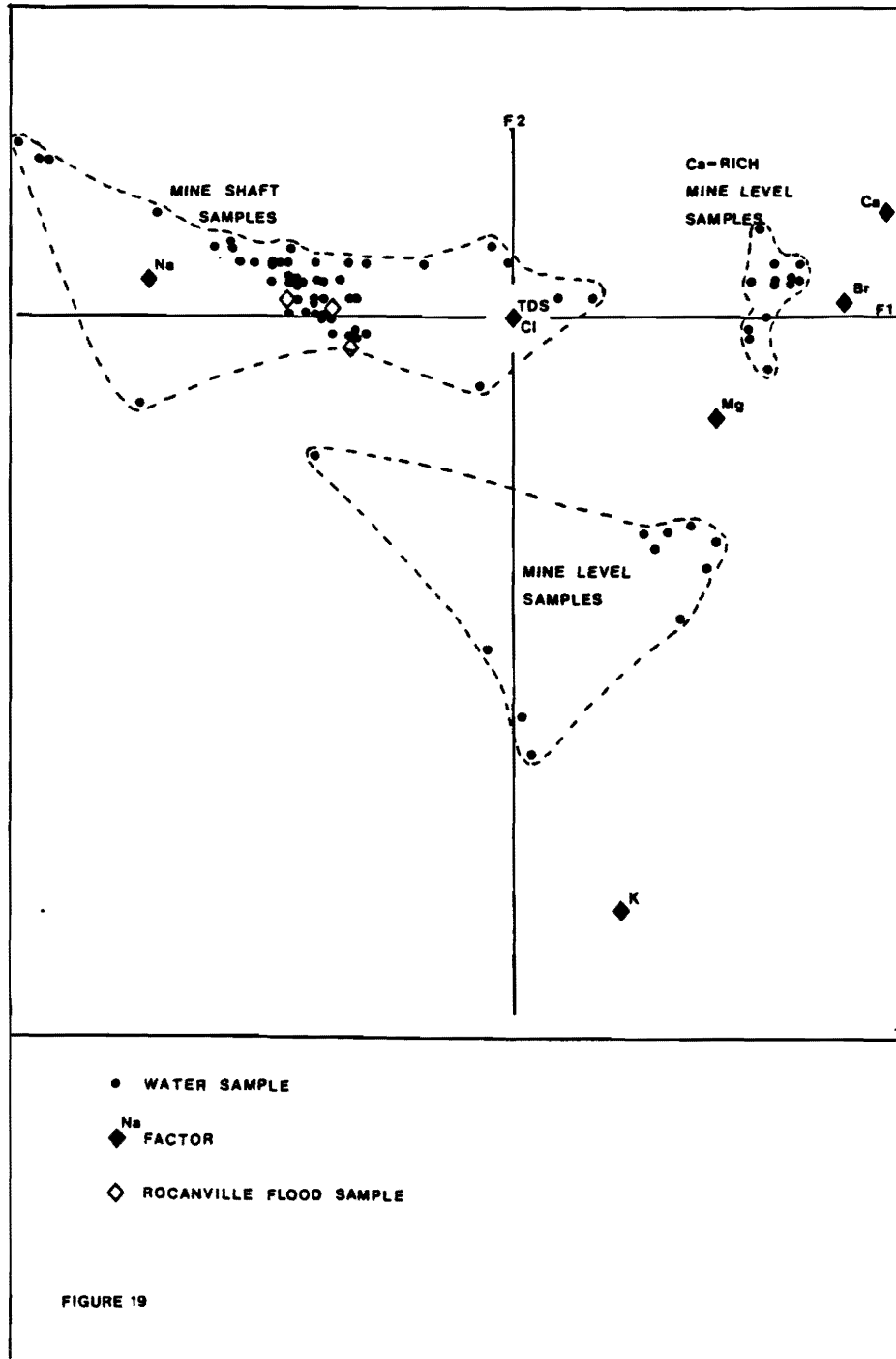


FIGURE 19: This correspondence analysis plot illustrates the relationship of the main chemical components of the waters (TDS, Cl, Na, K, Mg, Ca, and Br) to one another. Although this is a three-dimensional technique all of the data in this study plotted in the two dimensions illustrated (F1 and F2).

suggests that, until the time of flooding, the Rocarville flood waters did not migrate through the mining levels.

Calcium and magnesium correlate with each other (Figure 19) and these two cations dominate the calcium-rich mine-level samples. Correspondence analysis also shows that the Ca and Mg have a high negative correlation with respect to Na. From thermodynamic data (Figures 20 and 21), it is most likely that the Ca and Mg contents of the waters are theoretically controlled by reaction with carbonates. The activities of Ca and Mg indicate that all of the water samples fall within the theoretical dolomite plus solution stability field (Figure 20). This theoretical equilibrium with dolomite is maintained even when the activity of CO_2 is varied (Figure 21). For activities of CO_2 of $10^{-3.5}$, the activity of CO_2 in water in equilibrium with the atmosphere, some samples fall within the solution stability field, but all of these are mine-level samples.

The apparent equilibrium between carbonates and the waters does not explain adequately the high Mg and high Ca contents in some of the mine-level samples. It is probable that the dissolution of carnallite is partially responsible for some of the high Mg concentrations. At the Lanigan mine, carnallite has been observed precipitating from the brines (T. Danyluk, pers. comm.). The Ca-rich brines range in concentration of Ca from 141,000 to 170,200 mg/l and have very low Na contents. Although these samples have high Mg contents, they are not those with the highest Mg concentrations. The origin of these Ca-rich brines is not well understood but they may represent connate brines which have undergone membrane filtration, a process which greatly increases the Ca+Mg/Na ratio (Graf, 1982), or they may be brines residual to the process of dolomitization.

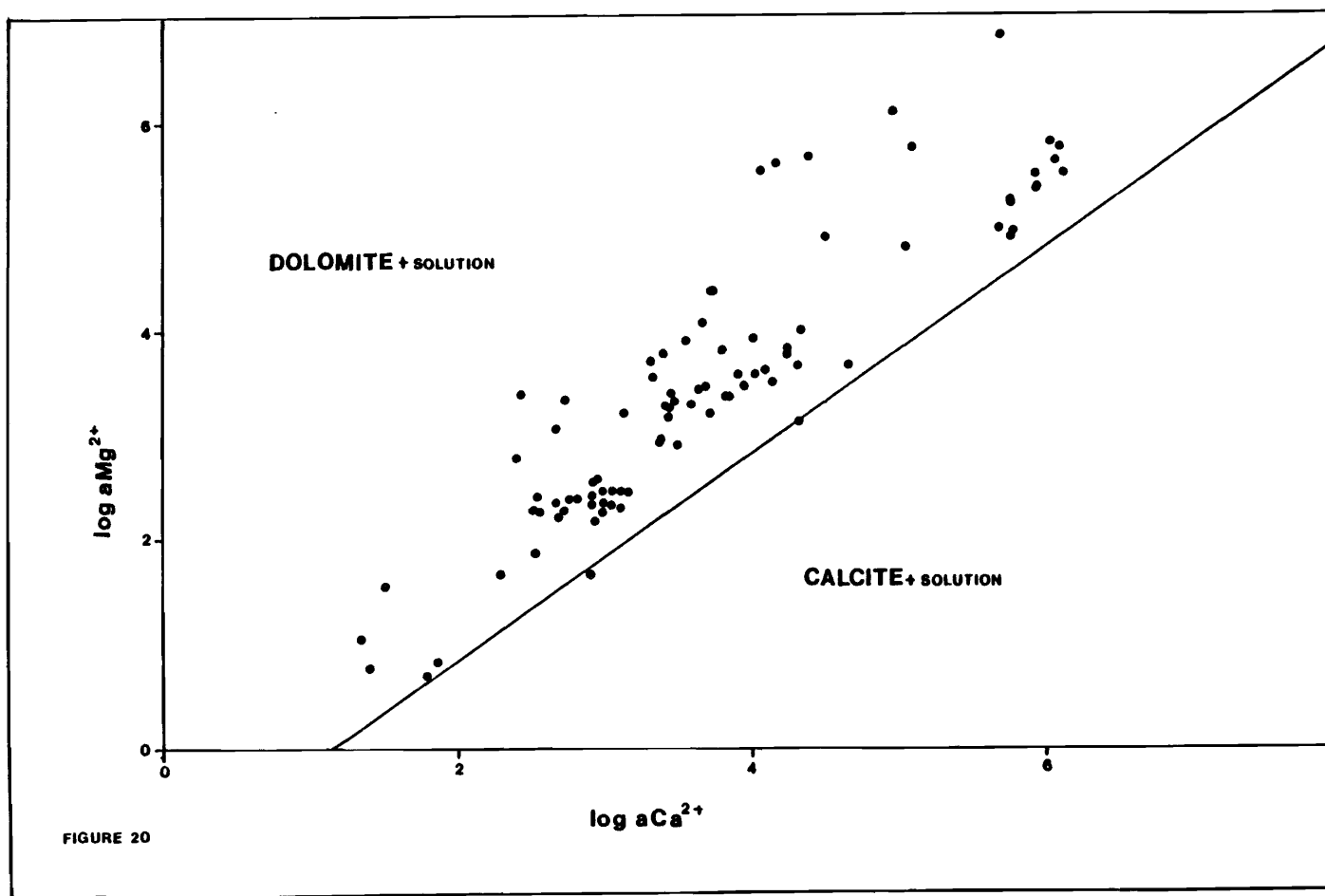


FIGURE 20

FIGURE 20: The activities of Ca and Mg for all the water samples have been plotted with respect to the theoretical stability fields for dolomite and calcite in contact with a solution.

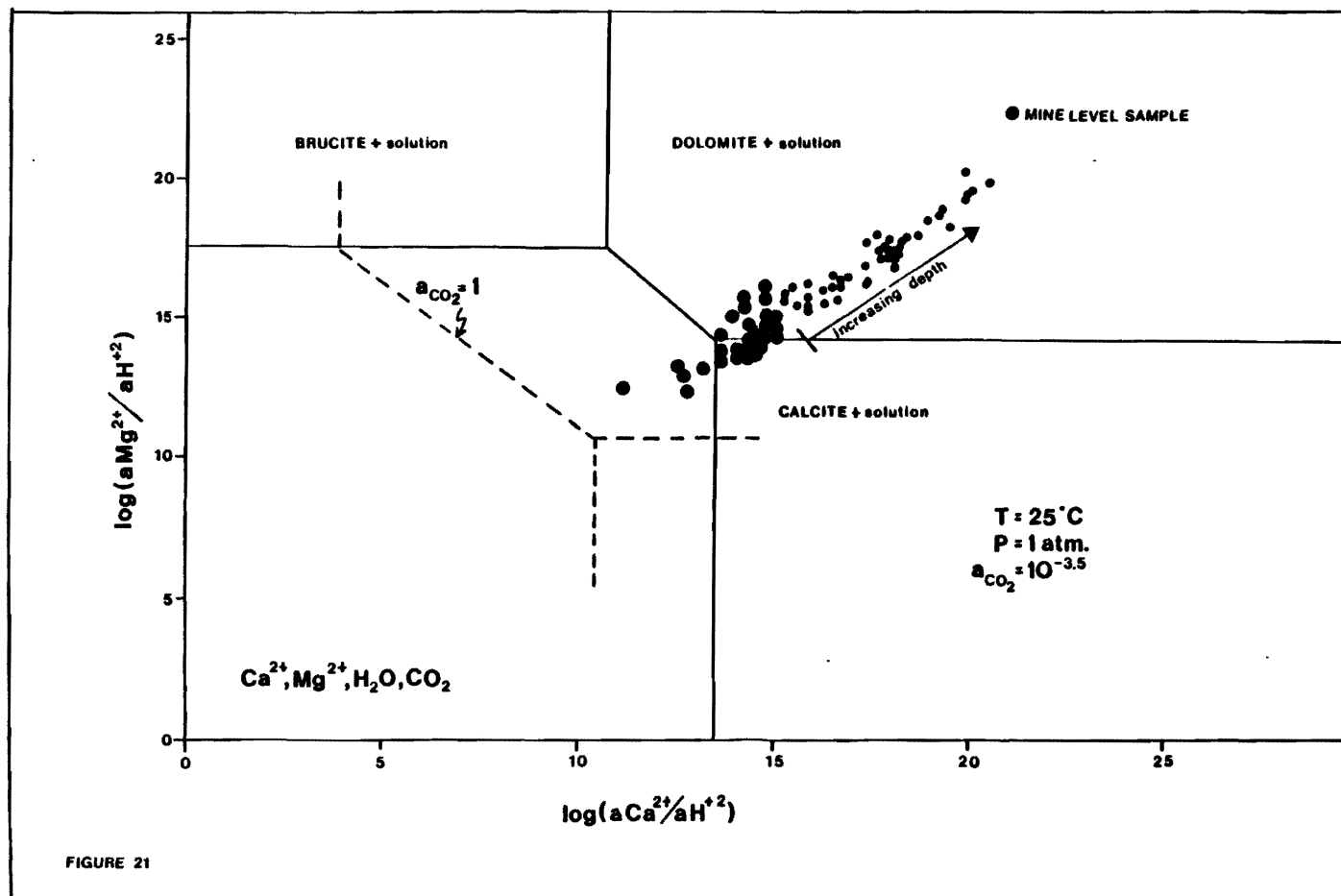


FIGURE 21: The activities of Ca and Mg are plotted with respect to the system Ca, Mg, H₂O and CO₂. The theoretical stability fields for brucite, dolomite and calcite with respect to a solution are shown.

Both processes could explain the low Na, and the relatively high Ca and Mg values. These Ca-rich brines also are characterized by high Br concentrations of from 16397 to 28479 mg/l (Figure 9) which indicates that, regardless of their ultimate origin, they are residual to at least one phase of evaporite recrystallization. The close association between Mg, Ca and Br is shown by the clustering of the Ca-rich samples in the correspondence analysis (Figure 16), however, Br is only a supplementary factor and as such has little or no influence on the positioning of the major factor points.

Kendall (1987) offers an alternative method for producing Ca-rich brines. For the removal of sulphate from concentrated seawater in the Elk Point Basin, Kendall suggests that calcium chloride brines originating within Winnipegosis Formation reefs were vented, via springs, into the concentrated seawater of the Elk Point Basin where the calcium reacted with the sulphate to form gypsum (now preserved as anhydrite). These Ca-rich brines could now be represented by the calcium brines found in the Cory mine. This implies that some of the mine level brines may have their origin from below the Prairie Formation, specifically, from the Winnipegosis Formation and would be further evidence that these calcium rich brines may be residual to the dolomitization process.

Various combinations of the molar ratios of the major ions were examined to see if chemical compositions could be used to determine the source of mine level-leaks. A wide variety of combinations were tried, and two combinations were found to have some potential, these are 1) Ca+Mg/Na molar ratios versus depth (Figure 22), and 2) Na+K/Cl molar ratios versus depth (Figure 23). It is only through comparison with the stable isotope

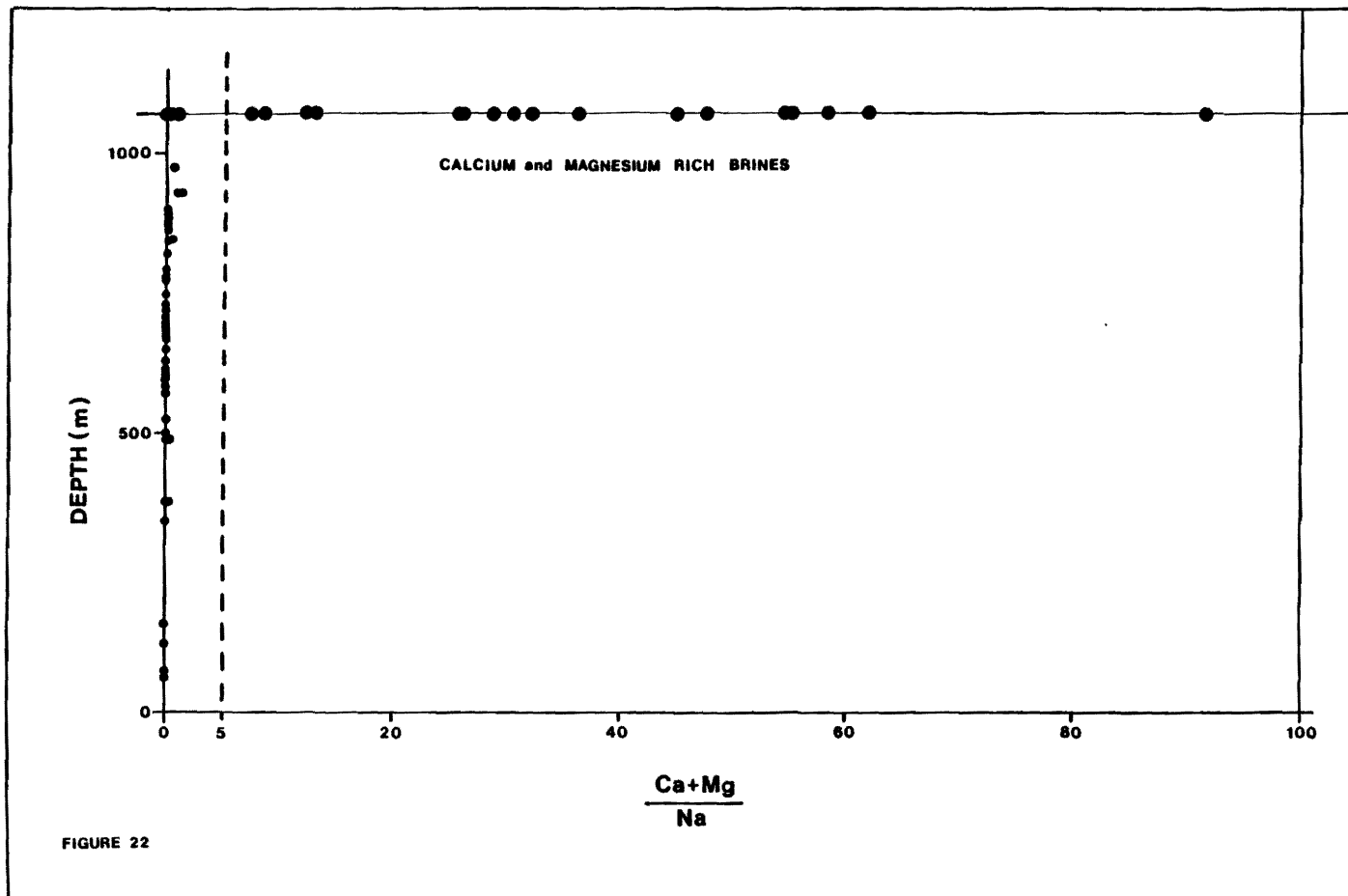


FIGURE 22: Ca+Mg/Na molar ratios are plotted with respect to depth. Mine-shaft samples are represented by small dots and mine-level samples by large dots. Ca- and Mg-rich samples are characterized by Ca+Mg/Na molar ratios of >5 . All other waters in this study had a Ca+Mg/Na molar ratios of < 5 .

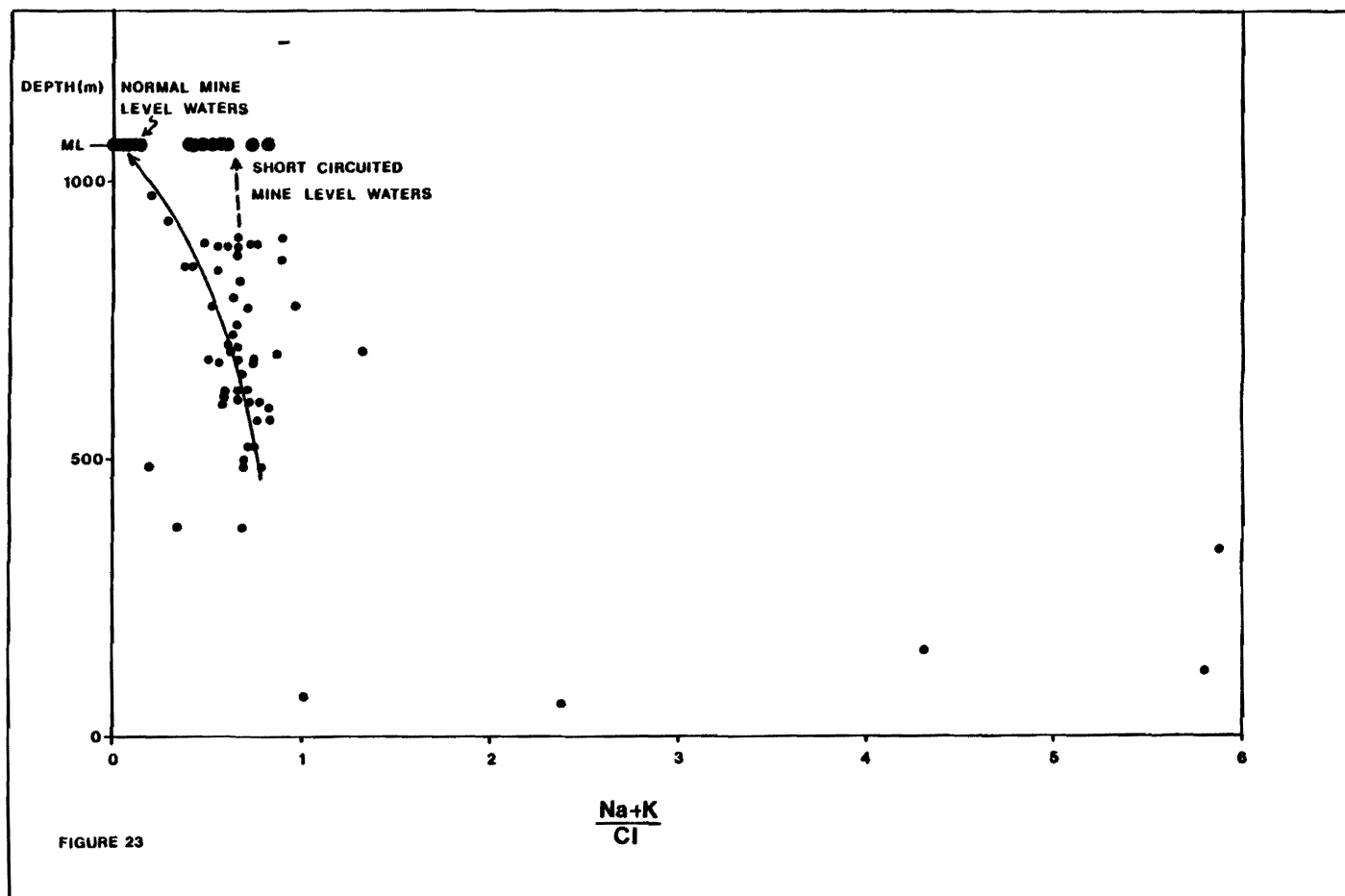


FIGURE 23: All of the mine-level samples (large dots) in this study, on the basis of stable isotope data, can be divided into two groups based on their $\frac{Na+K}{Cl}$ molar ratios; 1) "normal" mine-level waters, and 2) "shortcircuited" mine-level waters. All mine-shaft waters, except the Dawson Bay Formation waters, trend towards the shortcircuited waters group indicating the affinity of shortcircuited waters with formational waters.

data that these ratios were identified as being useful.

Mine-level brines can be divided into two populations on the basis of their Ca+Mg/Na molar ratios (Figure 22). The first population is that with high Ca+Mg/Na molar ratios (>5) and the second population is defined by those points with a Ca+Mg/Na molar ratios of <5 . The Ca+Mg/Na molar ratios of >5 correspond to the high Ca- and Mg-rich brines and probably represent fluids residual to the dissolution and precipitation of evaporites. This may explain the high Br contents in some of the mine-level waters because Br is concentrated within the fluid phase during precipitation leading to high Br concentrations in residual fluids. Mine-level brines with Ca+Mg/Na molar ratios of <5 represent both the "normally" evolved basinal brines and the "short-circuited" brines of formational affinity.

Figure 23 shows that mine level waters can be divided into two groups based on their Na+K/Cl molar ratios. The group which represents "normal" mine level waters (from stable isotope evidence) is comprised of samples with Na+K/Cl molar ratios of < 0.2 . "Short-circuited" samples (i.e. those with stable isotopic compositions indicative of a significant meteoric water component) have Na+K/Cl molar ratios of > 0.2 which are similar to those of waters from the mine-shafts collected from formations above the Dawson Bay Formation.

The variability of Br concentrations may reflect whether the waters have dissolved primary evaporites. Bromine is trapped in primary halite but is released during recrystallization (Wardlaw and Watson, 1966). Stoessel and Carpenter (1986) demonstrated that high concentrations of bromine are indicative of fluids residual to the recrystallization of sylvite and halite. The range of values they give closely match those derived for

mine-level brines in the present study, except for the high Ca-brines found at the Cory and Lanigan mines.

Stoessel and Carpenter (1986) show that to obtain high Br concentrations in brines, the fluid must be residual from the recrystallization of halite under conditions of low temperature and low water to rock ratios, a process during which bromide is selectively removed from the halite. From Stoessel and Carpenter's (1986) data, the distribution coefficient for Br between halite and solution is 0.047 to 0.053 for brines in contact with halite with approximately 125 ppm Br, the average Br content of halite from the mine-levels of the Prairie Formation (Fuzesy, 1983). Br concentrations in residual brines in equilibrium with this halite would be 2,500-3,500 mg/l which are similar to those in waters from the mine-levels, except for the Ca- and Mg-rich brines.

The high Br concentrations found in the Ca- and Mg-rich brines is more problematic. If a distribution coefficient of 0.049 is used (an average of the values noted above), the high Br brines could be generated by having a fluid in equilibrium with halites containing 575-920 ppm Br. Halite Br contents of this range have not been reported from the Prairie Formation. Thus, the high Br concentrations in the waters may be residual from multiple recrystallization of halites in a closed system which did not allow for the subsequent removal of excess bromine. Both sylvite and carnallite contain bromine in concentrations up to 1,300 and 1,400 ppm respectively (Fuzesy, 1983), however, their contribution to the system is not known.

The absence of sulphate minerals in the Upper Prairie Formation is problematic because late stage precipitates should be dominantly Mg-

sulphates during evaporation of seawater (Harvie and Weare, 1980). Sulphate must have been removed from the system prior to the deposition of the Prairie Formation. Kendall (1987) suggests that calcium chloride rich fluids entered the Elk Point Basin through springs in the Winnipegosis Formation and reacted with the sulphate in the concentrated seawater brines forming gypsum (now preserved as anhydrite). This process removed the sulphate from the system allowing for the formation of the present potash horizons. This early precipitation of sulphate possibly is represented by the anhydrites of the Lower Whitkow Salt and Shell Lake Gypsum members of the Prairie Formation. The synchronous deposition of anhydrite at the margins of the basin and halite (plus potash) in the central portion of the basin due to variations in seawater concentrations may also account for the lack of anhydrite, or Mg-sulphate minerals, in the Upper Prairie Formation (Schrieber, 1981).

SUMMARY

Stable isotopic compositions indicate that formation waters within the potash mining districts of Saskatchewan consist of two end members, meteoric water and connate water trapped in the Prairie and Dawson Bay Formations, with all other waters being a mixture between the two. Meteoric water enters the groundwater system in the major recharge areas of the central Montana uplift and mixes with the pre-existing formation water. The proportion of meteoric water decreases within an aquifer with distance from the recharge area and with depth. The basinal trend developed from the isotope data, as well as the increase in total dissolved solids with depth, confirm this mixing model.

From chemical compositions of the waters, it is apparent that, regardless of the path that the waters flow, they increase in TDS with depth. Even in the short distance from the Dawson Bay Formation to the mining levels there is a marked increase in the amount of TDS, indicating that any waters passing through the Prairie Formation increase its load of dissolved solids. Even though we can make some generalizations about the origins of the brines using chemical compositions (ie: Figures 22 and 23) these only have been possible because of the correlation with the isotopic data. The stable isotopes behave conservatively whereas the dissolved components do not.

The chemical data indicate that waters in the basin respond to the composition of the rocks through which they have moved. Calcium and magnesium concentrations are controlled by the dolomites, and the sodium

and potassium values are controlled by the dissolution of evaporites.

From the stable isotope results, it is clear that basinal waters are the result of mixing of fresher meteoric waters with pre-existing saline formation waters. While the exact method of deriving concentrated saline waters is not clear, it is likely due, in large part, to the dissolution of evaporites. Br concentrations indicates these fluids have recrystallized evaporites under conditions of low temperature and low water-to-rock ratios. Locally, the dissolution or recrystallization of carnallite may have added large amounts of Br to the system. The high Ca and Mg concentrations of some waters indicate that some of these brines are residual from dolomitization within the basin, the breakdown of carnallite to sylvite, or, both, although all of the fluids are theoretically in equilibrium with dolomites. The fluids entering the mine-level have either been derived from fluids interstitial to the evaporites, or they have entered the mine-level through collapse structures or fracturing from younger formations.

Waters that have shared a mutual aquifer system are evident from similarities in their hydrogen and oxygen isotopic compositions. In the Cory and Allan areas two distinct aquifer systems appear to be present. The uppermost aquifer system spans the range from Quaternary/recent waters to those of the Souris River Formation. This upper aquifer system is characterized by a large input of meteoric water, but it still exhibits the trend of isotope enrichment and an increased TDS load with depth. The lower aquifer system is composed of the Dawson Bay Formation waters and waters from the mining levels. While the upper aquifer system behaves essentially like a small basin composed of a number of closely related aquifers,

samples from the lower aquifer system have identical isotopic compositions indicating that it is a single, and isolated, aquifer.

In the Rocarville area, there are three distinct aquifer systems evident from the stable isotope data. These are: 1) the upper aquifer system composed of the Nisku Formation and all of the formations above it, 2) the middle aquifer system which is comprised of the Duperow and Souris River Formations, and 3) the lower aquifer system which is composed of the mining level waters and those from the Dawson Bay Formation. All three of these aquifer systems at Rocarville fall into very tight, but distinct, groupings of isotopic compositions.

From the stable isotope data there can be little doubt that the Dawson Bay waters are closely associated with most mine-level waters. Dawson Bay waters even show great similarities in chemical composition to the mine level waters. It is likely that most, but not all, of the mine waters are due to the direct leakage of Dawson Bay waters into the mining levels. This is good evidence that the Dawson Bay is a wide spread aquifer system which is largely isolated from the formations above and, in turn, isolates the mining levels from fluids from above. Fractures and other structural disruptions, could provide the conduits for Dawson Bay fluids to leak into the mining level, and for the fluids from stratigraphically higher formations to pass through the Dawson Bay Formation to the mining-level.

At the Rocarville mine, two anomalous fluid groups exist; the Rocarville flood waters, and the Group A brines which, from the stable isotope evidence, are believed to represent waters from the upper aquifer system. The Rocarville flood waters represent fluids which probably were isolated from the basinal flow pattern by collection in a structural trap.

That this trapped water was related to Dawson Bay waters is demonstrated by similarities in stable isotope values and chemical composition data. It is also probable, from the position of these waters on the factor plot, that the flood waters may never have migrated through the Prairie Formation prior to the flooding event.

The Group A waters represent water which may have been directed downwards to the mining level from an aquifer with a larger component of meteoric water. A model which can be used to explain this is the movement of isotopically distinct water moving down through a confining horizon in a collapse structure, or related structural feature. As an example, Figure 24 shows water from a stratigraphically higher position moving downwards through a collapse structure and entering the mining level. This water, with an isotopic composition which differs greatly from the "normal" mining level samples, may be called "short-circuited" water. Such short-circuited waters are undersaturated in salts and, therefore, have the potential to do a great deal of erosional damage to the potash.

The conduit for short-circuited Rocarville water is problematic as there are no major collapse structures nearby. It is probable, therefore, that this water has its origin at some distance from the mine. The water intersected the Dawson Bay formation and through this aquifer migrated into the vicinity of the Rocarville mine where it leaks into the mine. There is some indication that waters with low δD and $\delta^{18}O$ values are entering the Ianigan mining level as well, although, without shaft samples, it is possible only to say that there is a component of meteoric water in one group of mine waters.

Christopher's (1980, and reiterated in Dunn, 1982) contention that

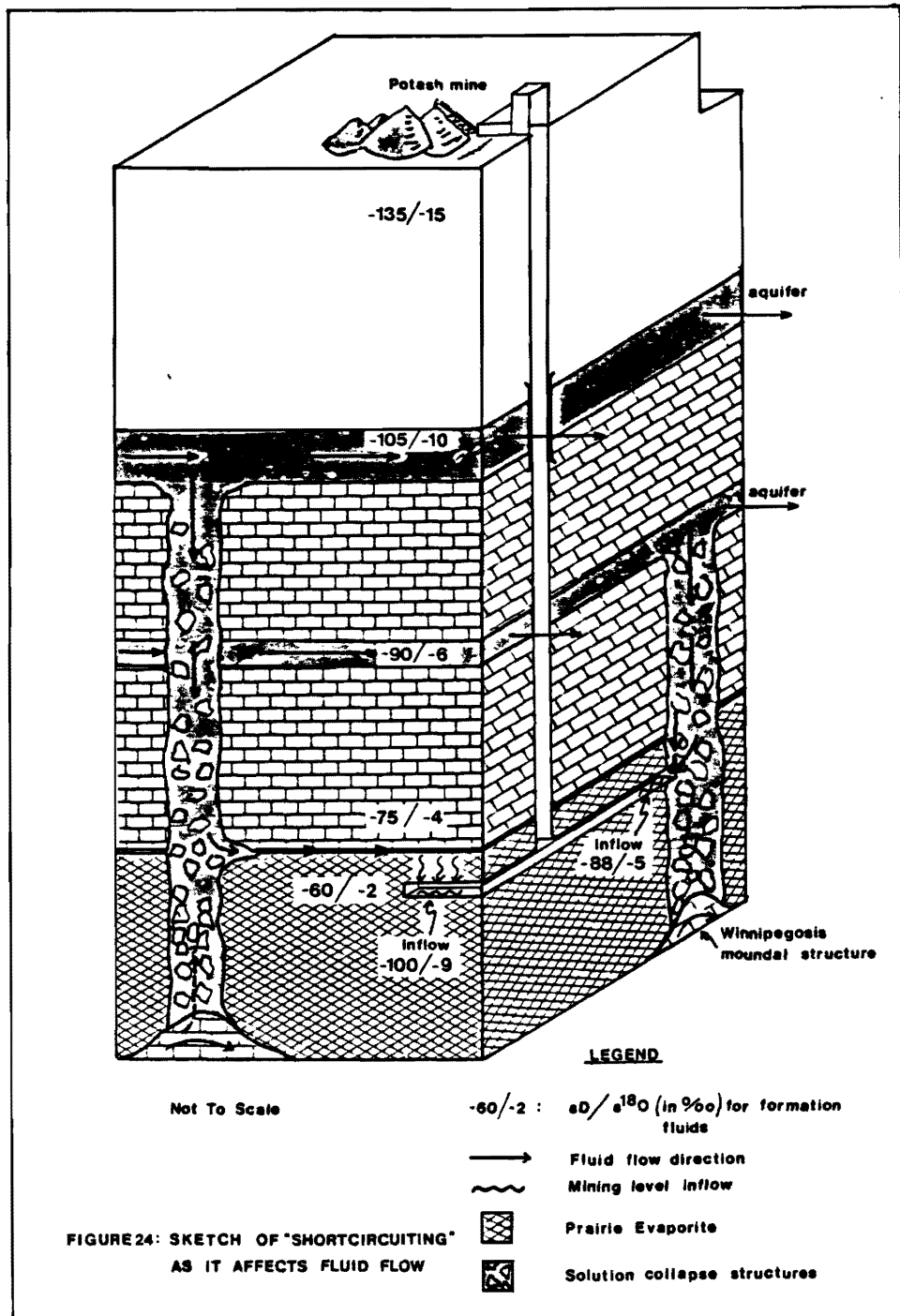


FIGURE 24: Sketch of "shortcircuiting" as it affects fluid flow. This diagram illustrates mechanisms by which water depleted in the heavy isotopes from a stratigraphically higher formation can be channeled downwards to the mining levels. The danger from this type of water is that it may be relatively unsaturated, and can create a great deal of damage, through solutioning, on the mining horizons.

Mannville Group waters are being recharged by overpressured waters from the Devonian sequence is supported neither by the stable isotope nor the solution chemistry detailed in this study, neither in the Saskatoon nor the Rocarville-Esterhazy mining districts. For Devonian waters to be present in the Mannville Group, isotopic evidence of waters with a small component of meteoric water and anomalously high TDS would be expected within the Mannville aquifer. These have not been found in this study and the stable isotope evidence from Rocarville mining level waters suggests that the Mannville Group waters have received a very high recharge of meteoric water, either as a result of a high flushing rate from a distant recharge area, or through close contact with local recharge areas.

CONCLUSIONS

In conclusion the following points can be made:

1) The stable isotopes of hydrogen and oxygen, because of their conservative behaviour, are a very powerful tool capable of detailing the flow regimes in a basinal setting. The waters leaking into the Rocarville mine, and possibly the Ianigan mine, can only be detected reliably using stable isotope geochemistry.

2) Chemical compositions of the brines are not useful in determining their source because of the non-conservative behaviour of dissolved constituents. This is because of the large amount of soluble material that the waters must pass through before reaching the mining levels. There is evidence, however, that the chemical composition of the brines, using various ratios of the dissolved species (ie: Figures 22 and 23), are useful in drawing preliminary conclusions about the origin of the waters. 3)

The waters in the Dawson Bay Formation and the mining levels are chemically and isotopically similar indicating that they are from the same aquifer system. This aquifer system appears to be isolated from the overlying aquifers. The Dawson Bay Formation may be a much more extensive aquifer than previously recognized. Most mine level waters probably have their origin in the Dawson Bay Formation and migrate to the mining levels through structural conduits perhaps reactivated by the mining process.

4) At the Rocarville mine, and possibly at the Ianigan mine, waters having isotopic compositions indicative of an origin in Mississippian and

Upper Devonian aquifers have entered the mining-levels. Collapse structures, and related features, are believed to be the conduits for these "short-circuited" fluids.

5) Water within the basin is composed of a mixture of meteoric water and pre-existing formation water. Chemical compositions of the water is controlled by the lithology: Na and K by the dissolution of evaporites, and Ca and Mg by equilibration with dolomites. Br concentrations in the mining-level water samples indicate that mine-level fluids (not short-circuited waters) are residual from the recrystallization of evaporites at low temperatures and at low water to rock ratios. It is possible that these fluids are the origin of the fluids in the Dawson Bay Formation.

6) Ca- and Mg-rich brines found at the Cory and Lanigan mines may be fluids residual from low temperature, low water-to-rock recrystallization of evaporites, breakdown of carnallite to sylvite, and dolomitization within the basin. These brines may have their origin in the Winnipegosis Formation.

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APPENDIX I
SAMPLE DESCRIPTIONS

APPENDIX I: SAMPLE DESCRIPTIONS

<u>SAMPLE</u>	<u>DEPTH(m)*</u>	<u>SAMPLE DESCRIPTION</u>
<u>CORY MINE</u>		
1-1	61	Recent/glacial drift
1-2	593	U.Devonian Nisku Fm.
1-3	610	as above
1-4	866	U.Devonian Souris River Fm.
1-5	975	M.Devonian Dawson Bay Fm.
1-6	378	Cretaceous, 2nd White Speck.
1-7	524	Cretaceous Mannville Group
1-8	627	U.Devonian Duperow Fm.
1-9	674	as above
1-10	847	M.Devonian Souris River Fm.
1-11	900	as above
1-12	930	as above
1-13	73	Recent/glacial drift
1-14	378	Cretaceous, 2nd White Speck.
1-15	524	Cretaceous Mannville Group
1-16	600	U.Devonian Nisku Fm.
1-17	626	U.Devonian Duperow Fm.
1-18	673	as above
1-19	647	M.Devonian Souris River Fm.
1-20	890	as above:Davidson Evaporite
1-21	900	M.Devonian Souris River Fm.
1-22	930	as above
1-23	Mine level	B-324,entry 3200
1-24	Mine level	P-6-12X,entry 6200
1-25	Mine level	B-407,entry 4300
1-26	Mine level	Entry 200
1-27	Mine level	P-6-12X,entry 3200
1-28	Mine level	B-324,entry 3200
1-29	Mine level	B-407,entry 4300
1-30	Mine level	P-6-12X,entry 6300
1-31	Mine level	B-699,entry 6000
1-32	Mine level	B-695,entry 6100
1-33	Mine level	B-694,entry 6200
1-34	Mine level	B-324,05/1982
1-35	Mine level	Entry 3200,11/1982
1-36	Mine level	Entry 3200,06/1983
1-37	Mine level	B-408,entry 4300,05/1982
1-38	Mine level	as above,11/1982
1-39	Mine level	as above,05/1983
1-40	Mine level	B-06,entry200,11/1982
1-41	Mine level	as above,06/1983

* Below Surface

<u>SAMPLE</u>	<u>DEPTH</u>	<u>DESCRIPTION</u>
<u>CORY MINE (continued)</u>		
1-42	Mine level	P-6-12X, entry 6300, 11/1982
1-43	Mine level	as above, 06/1983
1-44	914	U. Devonian Souris River Fm.
1-45	663	U. Devonian Duperow Fm.
1-46	594	U. Devonian Nisku Fm.
1-47	1006	M. Devonian Dawson Bay Fm.
1-48	Mine level	Entry 4300, 06/1983
1-49	Mine level	Entry 200
1-50	Mine level	P-6-12X, entry 6200, 06/1983
1-51	Mine level	Entry 3200, 06/1983
<u>LANIGAN MINE</u>		
2-1	Mine level	Branch 6
2-2	Mine level	Branch 7, S.E. Sump
2-3	Mine level	Branch 7
2-4	Mine level	Bin area under a salt back
2-5	Mine level	Bin under the Dawson Bay Fm.
2-6	Mine level	BO-379
2-7	Mine level	Branch 6/1900', 05/1984
2-8	Mine level	Branch 6/2550'SE, 05/1984
2-9	Mine level	Branch 6/1850'SE, 05/1984
2-10	Mine level	10/01/1984
2-11	Mine level	3/01/1984
2-12	Mine level	Bin area under a salt back
2-13	Mine level	Bin under the Dawson Bay Fm.
2-14	Mine level	Branch 2/end, 06/1983
2-15	Mine level	Drill hole, 01/1987
<u>ROCANVILLE MINE</u>		
3-1	500	Mississippian Lodgepole Fm.
3-2	524	U. Devonian 3 Forks Group
3-3	610	U. Devonian Duperow Fm.
3-4	744	as above
3-5	878	M. Devonian Dawson Bay Fm.
3-6	890	as above
3-7	486	Mississippian Lodgepole Fm.
3-8	572	U. Devonian Nisku Fm.
3-9	604	U. Devonian Duperow Fm.
3-10	625	as above
3-11	680	as above
3-12	692	as above
3-13	777	U. Devonian Souris River Fm.
3-14	792	as above
3-15	884	M. Devonian Dawson Bay Fm.

<u>SAMPLE</u>	<u>DEPTH</u>	<u>DESCRIPTION</u>
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ROCANVILLE MINE (continued)

3-16	Mine level	Panel 408, Room 10
3-17	Mine level	Panel 408, Room 7
3-18	Mine level	Panel 405, Extension 0023
3-19	Mine level	Draining level valves
3-20	Mine level	408-00-07, 1986
3-21	Mine level	408-00-01, 1986
3-22	Mine level	405-00-23, 1986
3-23	486	Mississippian Lodgepole Fm.
3-24	572	U. Devonian Nisku Fm.
3-25	625	U. Devonian Duperow Fm.
3-26	680	as above
3-27	777	U. Devonian Souris River Fm.
3-28	884	M. Devonian Dawson Bay Fm.
3-29	Mine level	306-00-13, 20/11/1984, RF
3-30	Mine level	306-00-13, 27/11/1984, RF
3-31	Mine level	Face brine, 7/12/1984, RF
3-32	Mine level	Parvis#5, 12/12/1984, RF
3-33	Mine level	Room 13/800', 20/12/1984, RF
3-34	Mine level	Leak, 21/12/1984, RF
3-35	Mine level	Leak, 27/12/1984, RF
3-36	Mine level	Room 13, 8/01/1985, RF
3-37	Mine level	Brine inflow, 19/01/1985, RF
3-38	Mine level	306-00-13, 20/11/1984, RF
3-39	Mine level	306-00-13, 27/11/1984, RF
3-40	Mine level	306-00-03, 10/04/1984
3-41	695	U. Devonian Duperow Fm.
3-42	774	U. Devonian Souris River Fm.
3-43	604	U. Devonian Duperow Fm.
3-44	887	M. Devonian Dawson Bay Fm.
3-45	486	Mississippian Lodgepole Fm.
3-46	Mine level	405-00-24 Ext., 06/1983
3-47	Mine level	408-00-07 Ext., 06/1983
3-48	672	U. Devonian Duperow Fm.

ALLAN MINE

4-1	122	Cretaceous Lea Park Fm.
4-2	158	as above
4-3	341	Cretaceous 2nd White Speck.
4-4	655	U. Devonian Nisku Fm.
4-5	707	U. Devonian Duperow Fm.
4-6	713	as above
4-7	774	as above
4-8	841	U. Devonian Souris River Fm.
4-9	860	as above
4-10	610	Jurassic Watrous Fm.

<u>SAMPLE</u>	<u>DEPTH</u>	<u>DESCRIPTION</u>
<u>ALLAN MINE (continued)</u>		
4-11	683	U.Devonian Duperow Fm.
4-12	701	as above
4-13	726	as above
4-14	823	U.Devonian Souris River Fm.
4-15	Mine level	Surface water contaminated
4-16	Mine level	10/06/1986
4-17	Mine level	09/1986

APPENDIX II
CHEMICAL COMPOSITIONS

APPENDIX II: CHEMICAL COMPOSITIONS (Sample Descriptions are in Appendix I)**CORY MINE**

	<u>Cl (mg/l)</u>	<u>Na (mg/l)</u>	<u>K (mg/l)</u>	<u>Ca (mg/l)</u>	<u>Mg (mg/l)</u>
1-1	709	1520	166	30	7
1-2	35600	28000	1360	1964	870
1-3	33800	21000	1010	3180	640
1-4	160000	103500	2220	21740	5650
1-5	355000	54870	16300	18200	28400
1-6	14790	4907	128	771	368
1-7	N/A	20720	1188	2341	450
1-8	29600	17000	430	2202	670
1-9	33800	18300	630	2183	620
1-10	101000	42000	940	24500	4800
1-11	199000	130000	2290	22640	1500
1-12	228000	60000	6300	68500	18300
1-13	1067	1080	2	26	13
1-14	7800	5240	121	58	65
1-15	28500	19500	955	1841	470
1-16	32000	17300	1143	1917	760
1-17	29200	17000	430	1954	820
1-18	24900	18000	540	2010	830
1-19	96400	36000	710	22180	6600
1-20	171000	81000	1890	25300	4750
1-21	194000	173000	1510	18950	4770
1-22	207000	51000	7100	50720	3700
1-23	320000	7770	14400	170200	30800
1-24	308000	3350	11900	165600	19900
1-25	326000	6370	14300	169900	25700
1-26	363000	1680	10000	134700	19600
1-27	319000	4020	13300	160700	20500
1-28	342000	3710	12400	152400	24500
1-29	340000	3250	11800	151500	25800
1-30	342000	4120	18500	147000	9400
1-31	362400	4540	20500	141000	10400
1-32	346900	7060	25800	149000	36000
1-33	346500	5000	20000	131000	12700

IANIGAN MINE

2-1	271000	11000	12300	8470	88000
2-2	273000	10200	11200	4510	83900
2-3	277000	11980	13400	5340	84900
2-4	325000	2750	7100	141000	782
2-5	367000	3200	5100	180600	17800
2-15	290300	9800	25800	149000	93300

Cl (mg/l) Na (mg/l) K (mg/l) Ca (mg/l) Mg (mg/l)

ROCANVILLE MINE

3-1	21300	14600	108	713	411
3-2	21000	15600	108	1123	362
3-3	110000	76400	400	763	301
3-4	130000	84000	2020	5320	1180
3-5	186000	118000	2890	6550	1590
3-6	199000	143000	2160	7620	2000
3-7	19600	13300	238	1177	515
3-8	28500	21700	161	1248	420
3-9	110000	79900	392	2330	313
3-10	138700	97000	720	1014	350
3-11	139000	90000	2160	4040	1170
3-12	153500	93000	2450	3920	1250
3-13	136000	130000	1760	3840	2260
3-14	157000	99000	840	7940	1980
3-15	227000	135000	2810	7840	1920
3-16	187000	57000	32300	6080	21967
3-17	229000	109000	59700	9940	6100
3-18	222000	105200	57700	9570	2900
3-19	205000	145000	23500	3790	6200
3-20	229600	74400	65000	7210	5790
3-21	238200	45900	50000	5930	19700
3-22	242200	55400	53200	18900	5700
3-23	64715	11970	717	1260	488
3-24	29600	24700	272	1090	257
3-25	81400	52400	410	574	120
3-26	142400	69700	3190	3560	710
3-27	142400	72100	2800	4080	810
3-28	201500	108000	3930	5410	1050
3-29	N/A	102800	42000	709	133
3-32	196000	139500	4200	5100	2450
3-33	197800	98800	6500	4000	2350
3-35	181000	96200	3300	4000	2170
3-36	186700	133000	4900	12000	3400
3-41	148000	193000	3910	3150	2070
3-42	144900	102000	2280	4170	1870
3-43	182000	138000	3750	340	2460
3-44	200600	150000	4300	5540	2490
3-45	20400	16000	188	1010	470
3-48	120800	105000	400	632	370

ALLAN MINE

4-1	354	2050	3	73	6
4-2	530	2280	6	85	8
4-3	1020	6250	45	362	84
4-4	31000	19800	1465	2216	330

	<u>Cl (mg/l)</u>	<u>Na (mg/l)</u>	<u>K (mg/l)</u>	<u>Ca (mg/l)</u>	<u>Mg (mg/l)</u>
<u>ALLAN MINE(continued)</u>					
4-5	42700	24900	1250	2007	330
4-6	44500	27000	1370	2245	510
4-7	N/A	46600	2280	2770	650
4-8	136000	73000	2410	2370	2400
4-9	196000	173000	1810	8160	2810
4-10	26700	15500	320	1848	100
4-11	33800	24200	1240	2098	530
4-12	40900	25700	1390	2059	520
4-13	65000	39300	1930	2355	610
4-14	180000	120000	1740	5109	2060
4-15	238200	83800	53000	2499	3130
4-16	303650	8510	41000	33600	78200
4-17	282400	15300	21600	40300	148000

APPENDIX II: PART II.

	<u>Br(mg/l)</u>	<u>I(mg/l)</u>	<u>F(mg/l)</u>	<u>pH</u>	<u>DENSITY</u>	<u>HCO3 (mg/l)</u>
<u>CORY MINE</u>						
1-1	9	20	0.041	8.3	0.99887	317
1-2	196	17	0.19	8.0	1.04459	195
1-3	186	16	0.15	7.5	1.04769	110
1-4	1720	101	0.005	6.9	1.15552	104
1-5	21747	508	0.002	5.7*	N/A	N/A
1-6	91	70	0.04	6.0*	N/A	N/A
1-7	200	23	0.05	6.5*	N/A	N/A
1-8	12945	12	0.1	6.5*	N/A	N/A
1-9	173	14	0.04	7.4	1.03617	104
1-10	863	127	0.05	8.2	1.11247	1464
1-11	2804	108	0.03	7.6	1.19881	183
1-12	5956	330	0.002	5.6	1.23988	110
1-13	4	17	0.1	6.5*	0.9947	305
1-14	77	76	0.13	6.8*	0.998	N/A
1-15	160	16	0.12	6.5*	1.03098	N/A
1-16	162	17	0.2	6.8*	1.03775	122
1-17	155	15	0.11	7.0*	1.02696	268
1-18	168	18	0.04	7.5*	1.02846	256
1-19	906	80	0.004	8.0*	1.10472	61
1-20	2157	114	0.004	7.2*	1.18555	207
1-21	2460	118	0.003	7.5*	1.19338	244
1-22	2206	273	0.002	6.0*	1.21739	146
1-23	22438	457	0.002	4.4	1.39194	0
1-24	21143	121	0.002	4.5	1.34889	290
1-25	16397	508	0.002	4.4	1.3471	232
1-26	19849	248	0.002	4.7	1.34182	165
1-27	19676	400	0.002	4.5*	1.34111	122
1-28	20172	508	0.002	4.3*	1.35443	158
1-29	21575	603	0.002	4.5*	1.3536	0
1-30	18800	N/A	N/A	4.4	1.3483	N/A
1-31	17800	N/A	N/A	4.3	1.3511	N/A
1-32	17500	N/A	N/A	4.4	1.34213	N/A
1-33	17800	N/A	N/A	4.4	1.34353	N/A

LANIGAN MINE

2-1	8630	46	0.002	3.4	1.25575	0
2-2	8803	83	0.002	5.1	1.26383	0
2-3	9320	67	0.002	5.3	1.25999	73
2-4	20539	782	0.002	4.4	1.38649	0
2-5	28479	806	0.002	4	N/A	0
2-15	5600	N/A	N/A	4.5	N/A	N/A

* pH measured using paper strips

	<u>Br(mg/l)</u>	<u>I(mg/l)</u>	<u>F(mg/l)</u>	<u>pH</u>	<u>DENSITY</u>	<u>HCO3 (mg/l)</u>
<u>ROCANVILLE MINE</u>						
3-1	125	22	0.3	7.6*	1.02749	271
3-2	110	26	0.07	7.6*	1.03022	6
3-3	673	66	0.06	7.6*	1.12157	77
3-4	992	62	0.006	8.2*	1.14621	100
3-5	2114	98	0.002	7.3*	1.19394	34
3-6	2200	101	0.003	7.1*	1.19622	48
3-7	119	22	0.12	7.8	1.03455	N/A
3-8	154	21	0.1	7.6	1.03584	24
3-9	647	70	0.06	7.5	1.1341	79
3-10	880	64	0.01	7.6	1.15765	N/A
3-11	828	60	0.01	8.3	1.14978	37
3-12	906	59	0.007	7.0*	N/A	N/A
3-13	880	53	0.006	7.3	1.15106	49
3-14	1121	82	0.007	6.5*	1.2079	N/A
3-15	2157	100	0.003	7.7	1.19512	85
3-16	5005	77	0.002	5.9	1.22977	N/A
3-17	4228	92	0.003	5.8	N/A	152
3-18	5005	71	0.004	6.0	1.2412	37
3-19	2589	89	0.18	11.4	1.2155	0
3-20	4400	N/A	N/A	4.7	1.2282	N/A
3-21	4700	N/A	N/A	4.4	1.2358	N/A
3-22	6600	N/A	N/A	4.3	1.2387	N/A
3-23	88	N/A	N/A	6.3	1.0328	N/A
3-24	108	N/A	N/A	6.3	1.0415	N/A
3-25	510	N/A	N/A	6.0	1.1342	N/A
3-26	720	N/A	N/A	8.3	1.1434	N/A
3-27	720	N/A	N/A	7.0	1.1415	N/A
3-28	1190	N/A	N/A	7.0	1.1998	N/A
3-32	2650	N/A	N/A	5.2	1.1919	N/A
3-33	2150	N/A	N/A	5.1	1.1917	N/A
3-35	1950	N/A	N/A	5.1	1.1827	N/A
3-36	1900	N/A	N/A	5.2	1.1782	N/A
3-41	780	N/A	N/A	5.7	1.1518	N/A
3-42	750	N/A	N/A	6.2	1.1478	N/A
3-43	840	N/A	N/A	6.2	1.1522	N/A
3-44	2000	N/A	N/A	5.5	1.1993	N/A
3-45	64	N/A	N/A	6.0	1.0211	N/A
3-48	500	N/A	N/A	6.0	1.1423	N/A

ALLAN MINE

4-1	32	25	0.03	7.8*	0.99742	134
4-2	32	35	0.02	7.8*	0.99956	189
4-3	76	99	0.01	8.2*	1.0082	130
4-4	160	15	0.06	7.6*	1.03852	176
4-5	211	18	0.13	6.7*	1.05402	73

* pH measured using paper strips

	<u>Br (mg/l)</u>	<u>I (mg/l)</u>	<u>F (mg/l)</u>	<u>pH</u>	<u>DENSITY</u>	<u>HCO3 (mg/l)</u>
4-6	211	21	0.06	7.6*	1.04741	73
4-7	318	155	0.04	6.0*	N/A	N/A
4-8	1174	192	0.005	6.7*	1.1782	N/A
4-9	2028	76	0.04	6.4*	1.20803	18
4-10	148	15	0.04	7.6*	1.02987	28
4-11	207	18	0.06	7.6*	1.05328	110
4-12	208	18	0.07	7.6*	1.0496	152
4-13	323	20	0.04	7.6*	1.08019	85
4-14	1812	67	0.03	5.5	1.1948	N/A
4-15	3322	71	0.05	4.7	1.2765	109
4-16	2635	N/A	0.002	4.3	1.2836	N/A
4-17	5500	N/A	N/A	4.3	1.2753	N/A

APPENDIX II: PART III

<u>SAMPLE</u>	<u>SO₄ (mg/l)</u>
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CORY MINE

1-2	6222
1-3	6233
1-9	5193
1-17	5118
1-19	1200
1-20	1285
1-21	644
1-22	363
1-24	185
1-29	459

LANIGAN MINE

2-1	223
2-2	433
2-3	394

ROCANVILLE MINE

3-2	7356
3-4	3338
3-5	1417
3-6	1478
3-8	10337
3-9	18332
3-11	3280
3-17	1064

ALLAN MINE

4-1	53
4-5	6160
4-9	1366
4-11	6060
4-16	326

Sample	Depth(m)	Sample description	δD	δ18O	Cl,mg/l	Na,mg/l	K,mg/l	Ca,mg/l	Mg,mg/l	I,mg/l	F,mg/l	Br,mg/l	SO4mg/l	pH	HCO3,mg/l	DENSITY g/cc	TDS g/l
4-2	158	as above	-136	-17	530	2280	6	85	8	35	.02	32		7.8	189	.99956	0
4-3	341	Allan,Cret.2nd White Speckled Fm.	-119	-13.4	1070	6250	45	362	84	99	.01	76		8.2	130	1.0082	8.2
4-10	610	Allan,L.Jurassic Watrous Fm.	-134	-16	26700	15500	320	1848	100	15	.04	148		7.6	28	1.02987	29.9
4-4	655	Allan,U.Dev.Nisku Fm.	-136	-17.4	31000	19800	1465	2216	330	15	.06	160		7.6	176	1.03852	38.5
4-11	683	Allan,U.Dev.Duperow Fm.	-139	-18	33800	24200	1240	2098	530	18	.06	207	5753	7.6	110	1.05328	23.5
4-12	701	as above	-138	-18.1	40900	25700	1390	2059	520	18	.07	208		7.6	152	1.0496	49.6
4-5	707	Allan,U.Dev.Duperow Fm.	-139	-18.3	42700	24900	1250	2007	330	18	.13	211	5844	6.7	73	1.05402	54
4-6	713	as above	-140	-17.6	44500	27000	1370	2245	510	21	.06	211		7.6	73	1.04741	47.4
4-13	725	as above	-137	-16.9	65000	39300	1930	2355	610	20	.04	323		7.6	85	1.08019	80.2
4-7	774	as above	-138	-18		46600	2280	2770	650	155	.04	318		6			
4-14	823	Allan,M.Dev.Souris R.Fm.	-124	-14.9	180000	120000	1740	5109	2060	67	.03	1812		5.5		1.1948	194.8
4-8	841	Allan,M.Dev.Souris R.Fm.,Hatfield Mbr.	-105	-10.4	136000	73000	2410	2370	2400	192	.005	1174		6.7		1.1549	154.9
4-9	860	Allan,M.Dev.Souris R.Fm.,Harris Mbr.	-125	-15.1	196000	173000	1810	8160	2810	76	.004	2028	1131	6.43	18	1.20805	208.1
4-15	1082	Allan,mine level,surface water contaminated	-113	-13.3	238100	83800	53000	2499	3130	71	.05	3322		4.7	109		
4-16	1082	Allan,mine level,10/01/86,	-62	-3.2	303655	8510	41000	33600	78200		.002	2635	254	4.3		1.2836	283.6
4-17	1082	Allan,mine level	-59	-3.1	282400	15300	21600	40300	148000			5500		4.3		1.2753	275.3

NOTE: Complete stable isotope data set is found in Appendix III.

Sample	Depth(m)	Sample description	SD	δ18O	Cl,mg/l	Na,mg/l	K,mg/l	Ca,mg/l	Mg,mg/l	I,mg/l	F,mg/l	Br,mg/l	SO4mg/l	pH	HCO3,mg/l	DENSITY g/cc	TDS g/l
2-15	1052	Lan.,mine level,drill hole,01/87	-96		290300	98000	25000	15500	93300			5600		4.5			
ROCANVILLE MINE																	
3-7	486	Rocn.,Lodgepole Fm.	-125	-12.9	19600	13300	238	1177	515	22	.12	119		7.8		1.03455	34.6
3-23	486	Rocn.,Mississippian Lodgepole Fm.	-121	-15.6	64700	11970	718	1260	4880			88		6.3		1.0328	32.8
3-45	486	Rocn., Lodgepole Fm.9/06/83	-138	-17	20400	16000	188	1010	470			64		6			
3-1	500	Rocn.,Mississippian Lodgepole Fm.	-142	-14.9	21300	14600	108	713	411	22	.06	125		7.6	271	1.02749	27.5
3-2	524	Rocn.,U.Dev.Three Forks Fm.	-111	-14.9	21000	15600	108	1123	362	26	.07	110	7140	7.6	6	1.03022	30.2
3-8	571	Rocn.,Nisku Fm.	-121	-13.8	28500	21700	161	1248	420	21	.1	154	9980	7.6	24	1.03584	35.8
3-24	572	Rocn.,U.Dev.Nisku Fm.	-122	-14.5	29600	24700	272	1090	2520			108		6.3		1.03754	37.5
3-9	603	Rocn.,Duperow Fm.	-74	-4.6	110000	79900	392	2330	313	70	.06	647	16165	7.5	79	1.1341	134.1
3-43	604	Rocn., Duperow Fm.,9/06/83	-81	-6	182000	138000	3750	340	2460			840		6.2			
3-3	610	Rocn.,U.Dev.Duperow Fm.	-82	-4.2	110000	76400	400	763	301	66	.06	673		7.6	77	1.12157	121.6
3-10	625	Rocn.,Duperow Fm.	-81	-5.1	138700	97000	720	1014	350	64	.01	880		7.6		1.15765	157.6
3-25	625	Rocn.,U.Dev.Duperow Fm.	-70	-5	81400	52400	410	574	1200			510		6		1.1342	134.2
3-26	680	as above	-84	-6.4	142400	69700	3190	3560	7100			720		8.3		1.1434	143.4
3-11	680	Rocn.,Duperow Fm.	-82	-6.2	139000	90000	2160	4040	1170	60	.01	828	2853	8.3	37	1.14978	149.8
3-48	689	Rocn., Duperow Fm.,9/06/83	-83	-6.7	120800	105000	400	630	370			500		6			
3-12	692	Rocn.,Duperow Fm.	-82	-5.5	153500	93000	2450	3920	1250	59	.007	906		7			
3-41	695	Rocn., Duperow Fm.,9/06/83	-85	-6.5	148600	193000	3910	3150	2070			780		5.7			
3-4	744	as above	-86	-5.9	130000	84000	2020	5320	1180	62	.006	992	2912	8.2	100	1.14621	146.2
3-42	774	Rocn., Souris River Fm.,9/06/83	-84	-6.6	144900	102000	2280	4170	1870			750		6.2			
3-27	777	Rocn.,M.Dev.Souris R. Fm.	-74	-6.4	142400	72100	2800	4060	8100			720		7		1.14147	141.5
3-13	777	Rocn.,Souris R.Fm.	-80	-5.5	136000	130000	1790	3840	2260	53	.006	880		7.3	49	1.15106	151.1
3-14	792	Rocn.,Souris R.Fm.	-74	-1.9	157000	99000	840	7940	1980	82	.007	1121		6.5		1.20794	207.9
3-5	878	Rocn.,M.Dev.Dawson Bay Fm.	-68	-2.1	186000	118000	2890	6550	1590	98	.002	2114	1187	7.3	37	1.19394	193.9
3-44	887	Rocn., Dawson Bay Fm.,9/06/83	-66	-1.9	200600	150000	4300	5540	2490			2000		5.5			
3-15	884	Rocn.,Dawson Bay Fm.	-60	-1.4	227000	135000	2810	7840	1920	100	.003	2157		7.7	85	1.19512	195.1
3-28	884	Rocn.,M.Dev.Dawson Bay Fm.	-49	-1.9	201500	108100	3930	5410	10500			1190		7		1.1998	199.8
3-6	890	as above	-59	-1.4	199000	143000	2160	7620	2000	101	.003	2200	1236	7.1	48	1.19622	196.2
3-29	1067	Rocn., mine level,306-00-13,20/11/84	-46	-2.1		102800	42200	709	132								
3-16	1067	Rocn.,mine level,panel408,room10	-103	-7.9	187000	57000	32300	6080	21967	77	.002	5005		5.9		1.22977	229.8
3-17	1067	Rocn.,mine level,panel408,room07	-105	-9.1	229000	109000	59700	9940	6100	92	.003	4228	862	5.8	152		
3-18	1067	Rocn.,mine level,panel405,ext.0023	-104	-8.6	222000	105200	57700	9570	2900	71	.004	5005		6	37	1.2412	241.2
3-19	1067	Rocn.,mine level,draining level,valves	-59	-.3	205000	145000	23500	3790	6200	89	.18	2589		11.4	0	1.2155	215.5
3-20	1067	Rocn.,mine level,408-00-07,1986	-100	-7.5	229600	74400	65000	7210	5760			4400		4.7		1.2282	228.2
3-21	1067	Rocn.,mine level,408-00-01,1986	-104	-8.5	238200	45900	50000	5930	19700			4700		4.4		1.2358	235.8
3-22	1067	Rocn.,mine level,405-00-23,1986	-85	-3.7	242200	55400	53400	18900	5700			6600		4.3		1.2387	238.7
3-32	1067	Rocn.,mine level,parviz#5,12/12/84	-47	-2.1	196000	139500	4200	5100	2450			2650		5.2		1.1919	191.9
3-33	1067	Rocn.,mine level,leak,Rm.13-800',20/12/84	-46	-1.8	197800	98800	6500	4000	2350			2150		5.1		1.1917	191.7
3-35	1067	Rocn.,mine level,brine leak,27/12/84	-47	-1.8	181200	96200	3300	4000	2170			1950		5.1		1.1827	182.7
3-36	1067	Rocn.,mine level,Rm.13 8/01/85	-43	-1.8	186800	133000	4900	12000	3400			1900		5.2		1.1782	178.2
ALLAN MINE																	
4-1	122	Allan,U.Cret.Lea Park Fm.	-129	-17.5	354	2050	3	73	6	25	.03	32	53	7.8	134	.99742	0

APPENDIX II: PART IV, DATA SUMMARY

Sample Depth(m) Sample description

			SD	δ18O	Cl, mg/l	Na, mg/l	K, mg/l	Ca, mg/l	Mg, mg/l	I, mg/l	F, mg/l	Br, mg/l	SO4mg/l	pH	HCO3, mg/l	DENSITY g/cc	TDS g/l
CORY MINE																	
1-1	61	Cory, Recent/Quaternary	-150	-18.8	709	1520	166	30	7	20	.041	9		8.3	317	.99887	0
1-13	73	Cory, Recent/Quaternary	-144	-19.3	1067	1080	2	26	13	17	.1	4		6.5	305	.9947	0
1-6	378	Cory, Cret. 2nd White Speckled Fm.	-129	-16.5	14800	4907	128	771	368	70	.04	91		6			
1-14	378	Cory, Cret. 2nd White Speckled Fm.	-129	-16	7800	5240	121	58	65	76	.13	77		6.8		.998	0
1-15	524	Cory, Cret. Blairmore Fm.	-128	-16	28500	19500	955	1841	470	16	.12	160		6.5		1.03098	31
1-7	524	Cory, Cret. Blairmore Fm.	-129	-15.5		20720	1188	2341	450	23	.05	200		5.7			
1-2	593	Cory, U. Dev. Nisku Fm.	-115	-13.5	35600	28000	1360	1964	870	17	.19	196	5956	8	195	1.04459	44.6
1-16	600	Cory, U. Dev. Nisku Fm.	-122	-14.4	32000	17300	1143	1917	760	17	.2	162		6.8	122	1.03775	37.8
1-3	610	as above	-116	-12.8	33800	21000	1010	3180	640	16	.15	186	5949	7.5	110	1.04769	47.7
1-8	625	Cory, U. Dev. Duperow Fm.	-127	-16	29600	17000	430	2202	670	12	.1	12945		6.5			
1-17	626	Cory, U. Dev. Duperow Fm.	-143	-16.8	29200	17000	430	1954	820	16	.11	155	4984	7	268	1.02696	27
1-18	673	as above	-134	-17	24900	18000	540	2010	830	18	.04	168		7.5	256	1.02846	28.5
1-9	674	as above	-133	-16.5	33800	18300	630	2183	620	14	.04	173	5012	7.4	104	1.03617	36.2
1-10	847	Cory, M. Dev. Souris R. Fm.	-103	-11.2	101000	42000	940	24500	4800	127	.05	863		8.2	1464	1.11247	112.5
1-19	847	Cory, M. Dev. Souris R. Fm.	-120	-9.6	96400	36000	710	22180	6600	80	.004	906	1086	8	61	1.10472	104.7
1-4	866	Cory, U. Dev. Souris R. Fm.	-106	-8.3	160000	103500	2220	21740	5650	101	.005	1720		6.9	104	1.15552	155.5
1-20	890	as above, Davidson Evaporite Mbr.	-112	-10.8	171000	81000	1890	25300	4750	114	.004	2157	1084	7.2	207	1.18555	185.6
1-11	899	as above	-107	-9.6	199000	130000	2290	22640	1500	108	.03	2804		7.6	183	1.19881	198.8
1-21	899	Cory, M. Dev. Souris R. Fm.	-107	-9.9	194000	173000	1510	18950	4770	118	.003	2460	540	7.5	244	1.19338	193.4
1-22	929	as above	-102	-9.2	207000	51000	7100	50270	3700	273	.002	2206	298	6	146	1.21739	217.4
1-12	930	as above	-94	-8.4	228000	60000	6300	68500	18300	330	.002	5956		5.6	110	1.23988	239.9
1-5	975	Cory, M. Dev. Dawson Bay Fm.	-67	-3.6	355000	54870	16300	18200	28400	508	.002	21747		5.7			
1-23	1036	Cory, mine level, B-324, entry 3200	-65	-2.3	320000	7770	14400	170200	30800	457	.002	22438		4.4	0	1.36194	361.9
1-24	1036	Cory, mine level, P-6-12X, entry 6200	-58	-1.4	308000	3350	11900	165600	19900	121	.002	21143	137	4.5	290	1.34889	348.9
1-25	1036	Cory, mine level, B-407, entry 4300	-70	-4.2	326000	6370	14300	169900	25700	508	.002	16397		4.4	232	1.3471	347.1
1-26	1036	Cory, mine level, entry 200	-62	-2.9	363000	1680	10000	134700	19600	248	.002	19849		4.7	165	1.34182	341.8
1-27	1036	Cory, mine level, Pane 6-12X, entry 6200, trip 2	-66	-.3	319000	4020	13300	160700	20500	400	.002	19676		4.5	122	1.34111	341.1
1-28	1036	Cory, mine level, B-324, entry 3200	-62	-.5	342000	3710	12400	152400	24500	508	.002	20172		4.3	158	1.35443	354.4
1-29	1036	Cory, mine level, B-407, entry 4300	-57	-.5	340000	3250	11800	151500	25800	603	.002	21575	339	4.5	0	1.3536	353.6
1-30	1036	Cory, mine level, entry 6300, Panel 6-12X	-61	-1.4	340200	4270	18500	146000	9400			18800		4.4		1.3463	348.3
1-31	1036	Cory, mine level, entry 6000, B699	-59	-1.6	362400	4720	20500	142000	10500			17800		4.3		1.3511	351.1
1-32	1036	Cory, mine level, entry 6100, B695	-54	-3.2	346900	7060	25800	149000	36000			17500		4.4		1.34213	342.1
1-33	1036	Cory, mine level, entry 6200, B694	-71	-2.1	346500	5010	19800	132000	12800			17800		4.4		1.34353	342.5
LANIGAN MINE																	
2-1	1052	Lan., mine level, Branch 6	-93	-8	271000	11000	12300	8470	88000	46	.002	8630	178	3.4	0	1.25575	255.7
2-2	1052	Lan., mine level, Branch 7, S.E. Sump	-86	-7.9	273000	10200	11200	4510	83900	83	.002	8803	343	5.1	0	1.26383	263.8
2-3	1052	Lan., mine level, Branch 7	-85	-7.5	277000	11980	13400	5340	84900	67	.002	9320	313	5.3	73	1.25999	260
2-4	1052	Lan., mine level, Bin under salt back	-62	-3.9	325000	2750	7100	141000	19600	782	.002	20539		4.4	0	1.38649	386.5
2-5	1052	Lan., mine level, Bin under Dawson Bay	-75	-5.3	367000	3200	5100	180600	17800	806	.002	28479		4	0		

APPENDIX III
STABLE ISOTOPE DATA

APPENDIX III: STABLE ISOTOPE DATA (Sample Descriptions are in Appendix I)

<u>SAMPLE</u>	δD	$\delta^{18}O$
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CORY MINE

1-1	-150	-18.8
1-2	-115	-13.5
1-3	-116	-12.8
1-4	-106	-8.3
1-5	-67	-3.6
1-6	-129	-16.5
1-7	-129	-15.5
1-8	-127	-16
1-9	-133	-16.5
1-10	-103	-11.2
1-11	-107	-9.6
1-12	-94	-8.4
1-13	-144	-19.3
1-14	-129	-16
1-15	-128	-16
1-16	-122	-14.4
1-17	-143	-16.8
1-18	-134	-17
1-19	-120	-9.6
1-20	-112	-10.8
1-21	-107	-9.9
1-22	-102	-9.2
1-23	-65	-2.3
1-24	-58	-1.4
1-25	-70	-4.2
1-26	-62	-2.9
1-27	-66	-0.3
1-28	-62	-0.5
1-29	-57	-0.5
1-30	-61	-1.4
1-31	-59	-1.6
1-32	-54	-3.2
1-33	-71	-2.1
1-34	-78	-3.0
1-35	-60	-2.5
1-36	-67	-2.7
1-37	-69	-2.6
1-38	-64	-2.7
1-39	-60	-0.6
1-40	-50	-2.5
1-41	-71	-1.7
1-42	-63	-1.7
1-43	-63	-4.7

SAMPLE δD $\delta^{18}O$

CORY MINE (CONTINUED)

1-44	-108	-11.6
1-45	-136	-16.8
1-46	-135	-16.8
1-47	-63	-0.5
1-48	-60	-0.6
1-49	-70	-1.7
1-50	-63	-1.2
1-51	-63	-1.7

IANIGAN MINE

2-1	-93	-8.0
2-2	-86	-7.9
2-3	-85	-7.5
2-4	-62	-3.9
2-5	-75	-5.3
2-6	-81	-8.8
2-7	-100	-8.2
2-8	-88	-7.6
2-9	-84	-7.3
2-10	-96	-8.4
2-11	-97	-8.0
2-12	-67	-1.4
2-13	-67	-1.4
2-14	-84	-5.5

ROCANVILLE MINE

3-1	-142	-14.9
3-2	-111	-14.9
3-3	-82	-4.2
3-4	-86	-5.9
3-5	-68	-2.1
3-6	-59	-1.4
3-7	-125	-12.9
3-8	-121	-13.8
3-9	-74	-4.6
3-10	-81	-5.1
3-11	-82	-6.2
3-12	-82	-5.5
3-13	-80	-5.5
3-14	-74	-1.9
3-15	-60	-1.4
3-16	-103	-7.9
3-17	-105	-9.1

SAMPLE δD $\delta^{18}O$

ROCANVILLE MINE (CONTINUED)

3-18	-104	-8.6
3-19	-59	-0.3
3-20	-100	-7.5
3-21	-104	-8.5
3-22	-85	-3.7
3-23	-121	-15.6
3-24	-122	-14.6
3-25	-70	-5.0
3-26	-84	-6.4
3-27	-74	-6.4
3-28	-49	-1.9
3-29	-46	-2.1
3-30	-51	-2.3
3-31	-46	-2.1
3-32	-47	-2.1
3-33	-46	-1.8
3-34	-45	-1.8
3-35	-47	-1.8
3-36	-43	-1.8
3-37	-46	-2.0
3-38	-46	-2.1
3-39	-51	-2.3
3-40	-59	-1.6
3-41	-85	-6.5
3-42	-84	-6.6
3-43	-81	-6.0
3-44	-66	-1.9
3-45	-138	-17.0
3-46	-114	-11.2
3-47	-96	-10.1
3-48	-83	-6.7

ALLAN MINE

4-1	-129	-17.5
4-2	-136	-17.4
4-3	-119	-13.4
4-4	-136	-17.4
4-5	-139	-18.3
4-6	-140	-17.6
4-7	-138	-18.0
4-8	-105	-10.4
4-9	-125	-15.1
4-10	-134	-16.0
4-11	-139	-18.0
4-12	-138	-18.1

ALLAN MINE (cont.)

4-13	-137	-16.9
4-14	-124	-14.9
4-15	-113	-13.3
4-16	-62	-3.2
4-17	-59	-3.1

APPENDIX IV
THERMODYNAMIC CALCULATIONS

APPENDIX IV: THERMODYNAMIC CALCULATIONS

To determine the activity, or effective concentration, of the major dissolved components of the waters it was necessary to choose a series of equations which best describe the system under study in thermodynamic terms. The activity of a given solute in the brine is derived from the following equation;

$$a = \gamma m \quad (1)$$

where a is the activity, γ is the activity coefficient and m is the molality. The activity of an ion is a measure of the effective concentration of that ion in relation to the ionic strength of the solution in which that ion is present. The molality (moles/kg solvent) is derived from direct measurement. The activity coefficient is that value which describes the non-ideal behaviour of a component in the water (i.e. differences between the measured concentration and the effective concentration).

Most formulae for calculating the activity coefficient are valid only at low ionic strengths, that is, ionic strengths of <1. Examples of this are the Guntelberg and Davies equations (Stumm and Morgan, 1981, page 135) which are not recommended above ionic strengths of 0.1 and 0.5 respectively. These formulae are of no use in this study because of the high ionic strengths of the waters, some of the mine waters having ionic strengths >14.

Pitzer's equations are recommended by Pytkowicz (1979a) as being valid to high ionic strengths. Tables of coefficients calculated using Pitzer's

equation are found in Pytkowicz (1979a) and show activity coefficients for NaCl, KCl, CaCl₂, and MgCl₂.

Ionic strengths (I) (Table 3) were calculated using the following formula;

$$I = \frac{1}{2} \sum m_i v_i^2 \quad (2)$$

where m is the molality of component i and v is the charge of component i .

Activity coefficients were derived by plotting the activity coefficient data from Pytkowicz (1979a) after interpolation at the ionic strength of a given sample (Figure 25). Since

$$\gamma_{\text{NaCl}} = \gamma_{\text{Na}^+} = \gamma_{\text{Cl}^-} \quad (3)$$

(Pytkowicz, 1979a) it is then possible to derive the activity coefficients for Na⁺, K⁺, Ca⁺⁺, and Mg⁺⁺. A graph which illustrates the activity coefficients calculated using Pitzer's equation is shown with lines for both the Guntelberg and Davies equations for comparison in Figure 25. Experimental data supports the use of the Pitzer equation up to ionic strengths of 6 (Pytkowicz, 1979a). These activity coefficients only represent a good estimation of the system since they were derived for single salt systems using formulae derived mainly from seawater evaporation studies. No reliable system presently exists for describing multiple salt systems at high ionic strengths.

The calculated activities can be used to examine the possible minerals

that are controlling the chemical compositions of the solutions. The activity of solutes are determined by dissolution and precipitation of minerals and are governed by reactions such as $AB = A^+ + B^-$. The equilibrium constant (K) for these reactions are expressed as:

$$\log K = \log \left| \frac{a_{\text{products}}}{a_{\text{reactants}}} \right| \quad (4)$$

In order to derive log K, the free energy (ΔG°_r) of the reaction must be derived from the following equation;

$$\Delta G^\circ_r = \Delta G^\circ_{\text{products}} - \Delta G^\circ_{\text{reactants}} \quad (5)$$

Values of ΔG°_f (free energy of formation for the elements) for the products and reactants were taken from tables in Drever (1982). The calculated ΔG°_r value is related to K by:

$$\Delta G^\circ_f = -2.303RT \log K \quad (6)$$

where $-2.303RT = 1363.7 \text{ cal mol}^{-1}$ at 25°C . The stability of the mineral phase A may be expressed in terms of the activities of the solutes as listed in Table 2 and shown in Figures 18, 20 and 21. Once the relative fields of stability of minerals have been derived, the activities calculated from the actual data can be substituted into the log K equation in order to determine which minerals in the solutions are saturated and, hence, which minerals control the chemical compositions of the solutions.

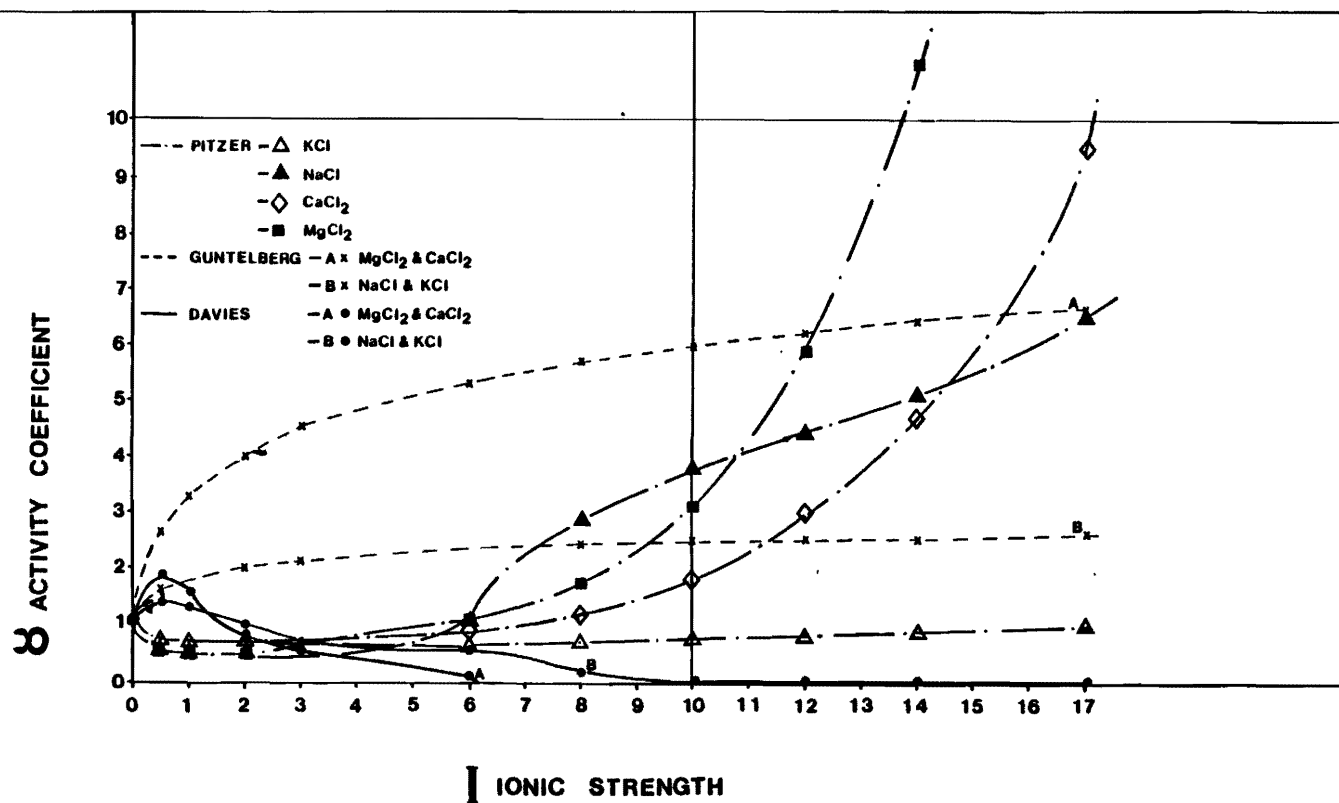


FIGURE 25

FIGURE 25: This diagram compares theoretically derived activity coefficients with ionic strength for a number of common salts.

TABLE 2: Reactions used in determining Figures 18, 20 and 21.

Figure 18: Na, K, Cl system ($\log a_{\text{Na}}$ vs $\log a_{\text{K}}$)

	$\log K$
$\text{NaCl} = \text{Na}^+ + \text{Cl}^-$	0.8
$\text{KCl} = \text{K}^+ + \text{Cl}^-$	0.45
$\text{NaCl} + \text{K}^+ = \text{KCl} + \text{Na}^+$	0.6
$\text{Na}^+ + \text{KAlSi}_3\text{O}_8 = \text{K}^+ + \text{NaAlSi}_3\text{O}_8$	-3.0
$\text{Na}^+ + \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 = \text{K}^+ + \text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	-3.9

Figure 20: Ca, Mg, CO_3 , Cl system ($\log a_{\text{Mg}}$ vs $\log a_{\text{Ca}}$)

	$\log K$
$\text{Ca}^{++} + \text{Mg,Ca}(\text{CO}_3)_2 = \text{Mg}^{++} + 2\text{CaCO}_3$	1.1
$\text{Ca}^{++} + 2\text{MgCO}_3 = \text{Mg}^{++} + \text{Mg,Ca}(\text{CO}_3)_2$	2.2
$\text{MgCl}_2 + \text{Ca}^{++} = \text{CaCl}_2 + \text{Mg}^{++}$	10.1

Figure 21: Mg, Ca, CO_2 , CO_3 , H_2O , H system. ($\log a_{\text{Mg}}/a_{\text{H}^2}$ vs $\log a_{\text{Ca}}/a_{\text{H}^2}$)

	$\log K$
$\text{Mg,Ca}(\text{CO}_3)_2 + 2\text{H}^+ = \text{Mg}(\text{OH})_2 + \text{Ca}^{++} + 2\text{CO}_2$	3.7
$\text{Ca,Mg}(\text{CO}_3)_2 + 2\text{H}^+ = \text{CaCO}_3 + \text{Mg}^{++} + \text{H}_2\text{O} + \text{CO}_2$	9.9
$\text{Mg}(\text{OH})_2 + 2\text{H}^+ = \text{Mg}^{++} + 2\text{H}_2\text{O}$	16.1
$\text{CaCO}_3 + 2\text{H}^+ = \text{Ca}^{++} + \text{CO}_2 + \text{H}_2\text{O}$	9.9

TABLE 3: Ionic Strengths (I).

Sample	(I)	Sample	(I)
Cory Mine		Rocarville Mine	
1-1	0.05	3-1	0.66
1-2	1.30	3-2	0.70
1-3	1.16	3-3	3.28
1-4	5.73	3-4	4.05
1-9	1.02	3-5	5.70
1-10	3.62	3-6	6.43
1-11	6.91	3-7	0.64
1-12	8.30	3-8	0.95
1-13	0.04	3-9	3.43
1-14	0.23	3-11	4.26
1-15	0.98	3-13	5.05
1-16	1.0	3-14	4.81
1-17	0.91	3-15	6.71
1-18	0.88	3-16	6.24
1-19	3.29	3-17	9.91
1-20	5.56	3-18	9.58
1-21	7.54	3-19	7.74
1-22	6.99	Allan Mine	
1-23	14.09	4-1	0.05
1-24	13.44	4-2	0.06
1-25	14.13	4-3	0.17
1-26	12.52	4-4	1.07
1-27	3.46	4-5	1.32
1-28	13.30	4-6	1.41
1-29	13.18	4-7	3.78
Ianigan Mine		4-9	7.05
2-1	5.27	4-10	0.83
2-2	5.01	4-11	1.19
2-3	5.29	4-12	1.33
2-4	12.13	4-13	2.01
2-5	14.58	4-14	5.51
		4-16	8.79