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THE GEOCHEMISTRY AND SOURCE FOR SOLUTES IN GROUND WATER FROM THE PENNSYLVANIAN BEDROCK SEQUENCE IN THE MICHIGAN BASIN

By

Bruce David Meissner

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ABSTRACT

THE GEOCHEMISTRY AND SOURCE OF SOLUTES FOR GROUND WATER FROM THE PENNSYLVANIAN BEDROCK SEQUENCE IN THE MICHIGAN BASIN

By

Bruce David Meissner

Ground water form the Grand River-Saginaw aquifer and Parma-Bayport aquifer contain dissolved solids concentrations up to 92,000 and 240,000 mg/L, respectively. Analysis of geochemical data from the Grand River-Saginaw aquifer (550 geochemical and 150 stable-isotope samples) indicates that (1) the dominant hydrochemical facies in decreasing areal distribution, are Ca-HCO_3, Na-Cl, and Ca-SO_4; (2) Na-Cl facies are present in all units within the Saginaw Bay Area, a regional ground-water-discharge area; (3) cation ternary diagrams indicate the principle process affecting water chemistry in the aquifers is mixing of Ca- and Na-rich solutions; (4) isotopic ratios indicate that the water in the aquifers is meteoric; (5) ratios of selected ions to Br and Cl as well as Carpenter Function:Cl ratios suggest that the solutes in the aquifers have resulted, in part, from dilution of a marine derived brine from the Parma-Bayport aquifer. Solute concentrations of other less concentrated waters in the aquifers (TDS < 750 mg/L) have originated through rock-water interaction that has occurred in the overlying glacial-drift material prior to recharge into underlying bedrock aquifers. Brine in the Parma-Bayport aquifer appears to have been derived through the evapo-concentration of seawater concentrated to near halite precipitation and enriched in Ca and depleted in SO_4, Mg, and K with respect to equivalently evaporated seawater.

ACKNOWLEDGMENTS

I would like to dedicate this thesis to my wife and fellow geologist Jolene Meissner. Her support throughout this graduate school ordeal was nothing short of fantastic. I would like to thank my parents for providing continued support and encouragement throughout my college career and never asking the most aggravating question a geologist is confronted with: "What the hell are you going to do with Geology?"

A special thanks to my mentor Tim Flood, his love of geology and genuine concern and confidence in his students provided the impetus to pursue my own interests in Geology. I would like to thank my advisor Dave Long for much needed help and many discussions providing guidance in this work as well as my committee members Duncan Sibley and Graham Larson. The U.S Geological Survey-WRD funded this research and Norm G. Grannemann provided invaluable help and complete support throughout this work, "Thank You Norm". Others at the U.S Geological Survey I would like to thank include Craig E. Oberst for patiently answering many questions about sampling procedures, D. B. Westjohn for many critical reviews of my work and helpful discussions, and other past members of the RASA project.

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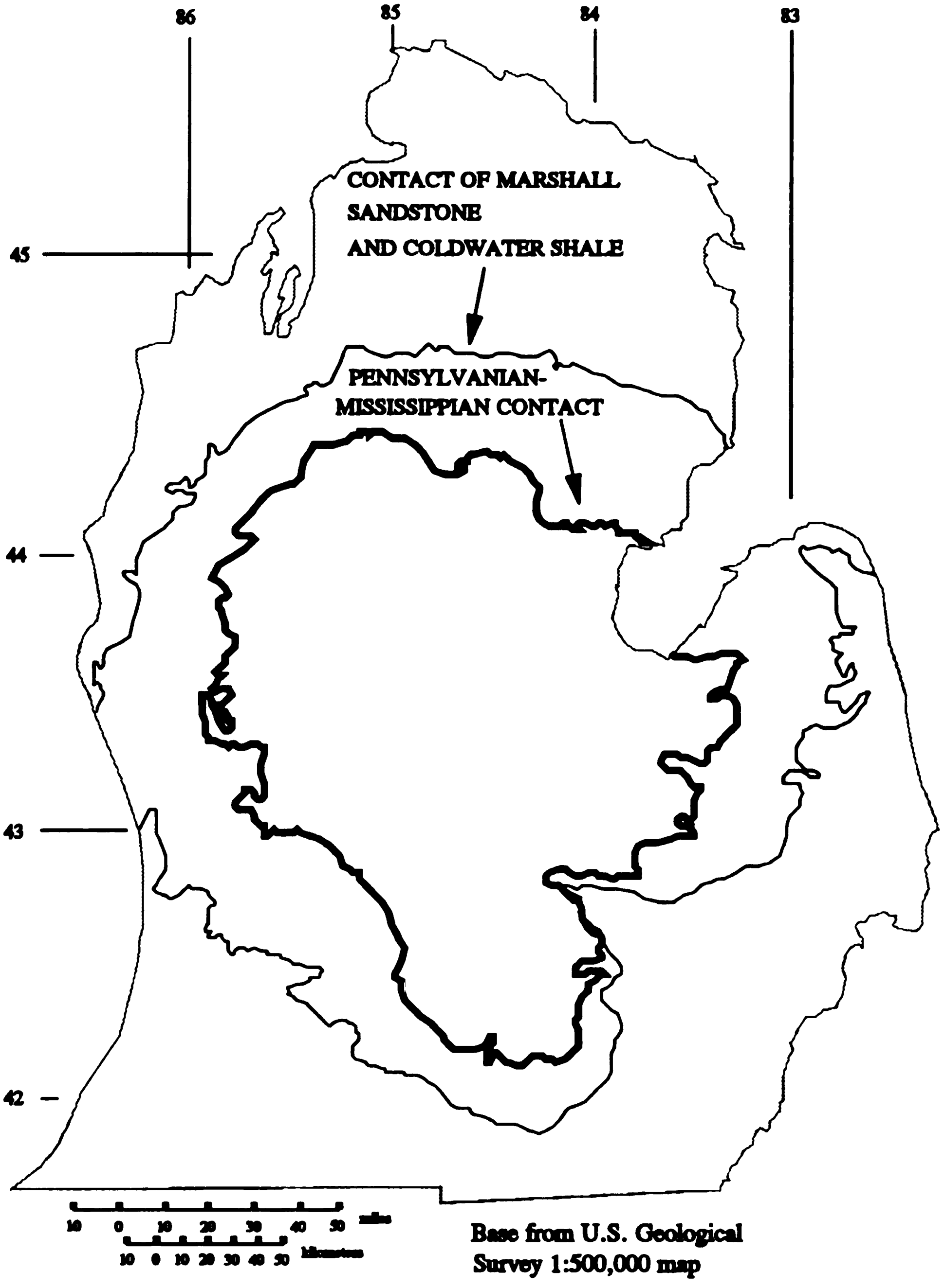
CHAPTER 1: INTRODUCTION

PURPOSE AND SCOPE

The purpose of this thesis is to describe the geochemistry and source for solutes in ground water from the Pennsylvanian and a portion of the Mississippian bedrock sequence in the Michigan basin. The principle aquifers being studied include the Pennsylvanian age Grand River-Saginaw and Pennsylvanian-Mississippian age Parma-Bayport aquifers (referred to collectively in this thesis as the Pennsylvanian aquifers). This thesis encompasses two of four aquifers presently being studied in the U.S. Geological Survey-Water Resource Division, Michigan Regional Aquifers System Analysis (RASA) project. The RASA study area is bounded by the contact between the Coldwater Shale and the Marshall Sandstone, and the study area for this thesis is defined by the Pennsylvanian-Mississippian contact in the Michigan basin. Figure 1 displays the RASA study area as well as the study area for this thesis. The goal of the RASA project is to study the geology, geochemistry, and the hydrology of aquifers in Mississippian and younger units in the central part of the Lower Peninsula of Michigan. The aquifers studied in the RASA project include the Mississippian age Marshall aquifer, the Parma-Bayport and Grand River-Saginaw aquifers as well as Quaternary age Glacial-Drift aquifers (Figure 2).

Presently water ranging from fresh to brine exists in near surface bedrock aquifers (Mississippian and younger) in the Michigan basin. Brine in the Mississippian-age Marshall sandstone has been related to evapo-concentrated seawater (Long et al., 1993; Meissner et al., 1992).

Water in the Pennsylvanian aquifers shows a variety of concentrations ranging from fresh water to brine. Ground water data indicates fresh water and saline water exist in the Grand River-Saginaw aquifer and water ranging from fresh to brine is present in the Parma-Bayport aquifer. Brine and saline ground water in the Pennsylvanian aquifers have



Base from U.S. Geological Survey 1:500,000 map

Figure 1. RASA study area bounded by the Marshall Sandstone-Coldwater Shale contact. Also included is the Pennsylvanian-Mississippian contact bounding the study area of this thesis.

Era	Period	Epoch	Stratigraphic Unit		Hydrogeologic Unit
Cenozoic	Quaternary	Pleistocene Holocene			Glacial-drift aquifers
					Glacial till-red beds confining unit
Mesozoic	Jurassic	Late	Unnamed red beds		
Paleozoic	Pennsylvanian	Middle	Grand River Formation		Grand River-Saginaw aquifer
		Early	Saginaw Formation		
					Saginaw confining unit
				Parma Sandstone	Parma-Bayport aquifer
	Mississippian	Late	Grand Rapids Group: Bayport Limestone		
			Grand Rapids Group: Michigan Formation		Michigan confining unit
				Stray Sandstone	Marshall aquifer
		Early	Marshall Sandstone	Napoleon Sandstone	
			Coldwater Shale		Coldwater confining unit

Figure 2. Stratigraphic column and hydrogeologic units in the study area (Modified from Mandle and Westjohn, 1989; stratigraphic column modified from Michigan Geological Survey, 1964, Chart 1).

been documented by several investigators, Houghton (1838), Winchell (1861), Lane (1899), Cooper (1905), Leverett and others, (1906), Cook (1913), Twenter (1966), Western Michigan University (1981) Long et al., (1988), Westjohn (1989), Mandle and Westjohn, (1989), and Meissner et al., (1992).

Recently Westjohn, (1989) delineated the existence of brine in the Pennsylvanian strata through the application and interpretation of electric (resistivity) and porosity logs. Westjohn (1989) defined the top of the shallowest brine-bearing sandstone in the Pennsylvanian bedrock sequence, and this distribution of brine is shown on Figure 3. Brine in the Pennsylvanian units exists where in direct contact with the Michigan Formation, along the perimeter of the contoured area. In the center of the basin Pennsylvanian units contain brine as much as 150 meters above the Michigan Formation (Westjohn, 1989). The Parma Sandstone is the shallowest brine reservoir in the basin with brine found at distances as small as 10 miles down regional dip from areas containing freshwater (Westjohn personal commun., 1992). The Parma Sandstone does contain fresh water where it subcrops and is in direct contact with the glacial drift.

The impact of geologic control on the distribution of brine in the Pennsylvanian aquifers is an important issue to present and must be considered when making basin wide interpretations of the controls on ground water chemistry and origin of brine conclusions. In general, the Pennsylvanian rock sequence is brine bearing where it is confined and isolated, such as when it is capped by shale or where it is overlain by Jurassic deposits (Westjohn, personal commun., 1992). The extent of brine and saline water in the Pennsylvanian aquifers is extensive and unfortunately few chemical analyses are available for the more concentrated waters in the aquifers, however enough data is available to provide a general evaluation of the geochemistry.

Wilson and Long, (1986 and 1993) found Michigan basin Devonian and Ordovician formation brines to have originated from the evaporation of seawater. Brine in the Mississippian age Marshall Sandstone has been to be geochemically and isotopically

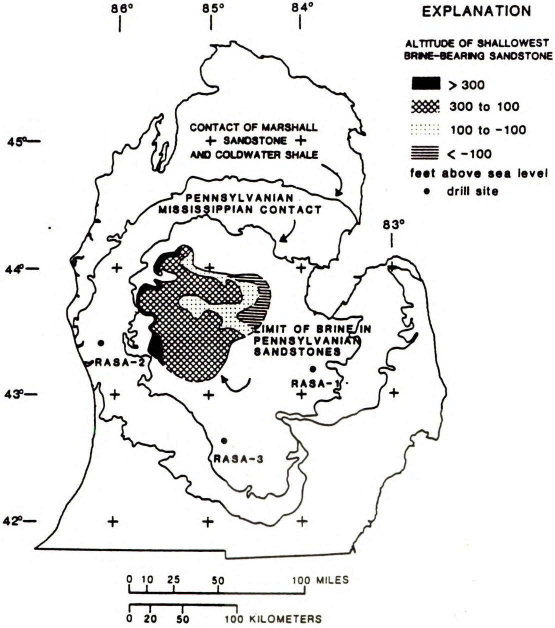


Figure 3. Contour map showing the altitude of the top of the shallowest brine-bearing sandstone in the Pennsylvanian rock sequence (Modified from Westjohn, 1989, figure 18).

similar to the Devonian brine (Meissner et al., 1992). One of the hypotheses for this thesis is that brine in the Pennsylvanian/Mississippian age Parma-Bayport aquifer is similar to the Marshall and Devonian brines. In this study the Parma-Bayport brine chemistry is compared to the chemistry of brine from the Marshall Sandstone and Devonian-aged Traverse Group to make interpretations on the origin and evolution of the Parma-Bayport brine. The understanding of the concentrated waters in the Parma-Bayport aquifer may lend insight into the source of concentrated fluids present in the Grand River-Saginaw aquifer. The Parma-Bayport brine is compared to ground water from the Grand River-Saginaw aquifer to investigate the hypothesis that brine, possibly the Parma-Bayport brine, is the source of solutes for many waters in the Grand River-Saginaw aquifer. The existence of a relationship between brine in the Michigan basin and the chemistry of waters in the Grand River-Saginaw aquifer may have implications on regional ground water flow in the basin.

APPROACH

The origin and evolution of waters in sedimentary basins has been the focus of many studies in recent years (Clayton et al., 1966; Graf et al., 1966; Hitchon, 1969, 1971; Nesbitt, 1985; Wilson and Long, 1986 and 1993; Egeberg and Aagaard, 1989; Wilson, 1989). Within these studies chemical and isotopic data from groundwater samples were used to determine the main processes controlling the chemistry of the water. Analysis of chemical and isotope data for waters in sedimentary basins commonly deals with the question: how has this particular body of water evolved through time? The methodology used in answering this question entails separating the water samples into two phases, the solvent and the solutes. The solvent is the water molecule itself whereas the solutes are the dissolved chemical species in the ground water sample. The source of the solvent and the solutes in a water mass can be independently identified through data reduction techniques involving chemical and isotope data from the aquifer. The isotope data, particularly the stable isotopes of oxygen and hydrogen, are used to determine the source of the water molecules in the system, identify water masses and interpret mixing relations among various water masses (Long et al., 1986). The chemical data is used to evaluate the source of the solutes relating their source to be the result of rock-water interaction, mixing of water masses or brine evolution processes (Carpenter, 1978; Bath and Edmunds, 1981; Land, 1987; Long et al., 1988; Egeberg and Aagaard, 1989; Banner et al., 1989; Steuber and Walter, 1991).

Major processes affecting groundwater chemistry include concentrating and modifying processes (Wilson, 1989). Concentrating processes include evaporation, evaporite dissolution, and shale membrane filtration (Hitchon, 1969). Modifying processes include the alteration of water chemistry through rock - water interaction, biologic activity, and through the mixing of water masses of different composition (Wilson, 1989). Early studies in geochemistry of natural ground waters dealt with geochemical processes as being the only control on the composition and concentration of ground water (Domenico and Schwartz, 1990). However, mass transport processes, particularly mixing often play a major role in controlling ground water chemistry (Hitchon et al., 1969; Desauliniers et al., 1981; Siegel and Mandle, 1984; Long et al., 1988). Frape et al., (1984) states that the unraveling of the geochemical evolution of ground water with different chemistries in a given rock mass involves addressing geochemical reactions and/or mixing. The role of advection and dispersion on solute concentrations and stable isotope values is important to consider as a control on ground water chemistry in Michigan basin sediments.

The impact of geological change in the Michigan basin must have had a great impact on ground water chemistry evidenced presently by the existence of many different water masses with different chemistries within the basin's aquifers (Twenter, 1966; Western Michigan University, 1981; Long et al., 1988; Westjohn, 1989). Changes related to depositional episodes, structural processes (uplift and deformation) as well as periods of glaciation may have had an impact on ground water chemistry. Potential changes could result from the displacement of water from aquifers through uplift or compaction, the emplacement of water whether from present day recharge to the aquifers or from water emplaced that is associated with the deposition of marine sediments. Difficulty arises in deciphering the impact and magnitude that various geologic events could have had on ground water chemistry. The geologic history of the Michigan basin with past emplacement and displacement of water combined with present day regional hydrology develops a complex origin and evolution of ground water presently occupying the aquifers.

GEOHYDROLOGIC FRAMEWORK

The Michigan basin is a nearly circular basin in which an extensive accumulation of sedimentary rocks underlies the Lower Peninsula of Michigan, parts of Michigan's Upper Peninsula, Illinois, Ohio, Indiana, Wisconsin, and Ontario, Canada (Figure 4). Sedimentary rock, which ranges in age from Precambrian through Jurassic, exceeds 17,500 ft. in thickness near the center of the basin and overlies Precambrian crystalline rocks (Lillienthal, 1978). The sedimentary rocks are mantled by glacial deposits, the result of glaciation during late Wisconsinan time (Mandle and Westjohn, 1988).

AQUIFERS

There are four major aquifers of concern in the framework of this thesis, a Glacial-drift aquifer and three bedrock aquifers separated by confining units (Figure 2). The bedrock aquifers, in ascending order, are the Marshall, Parma-Bayport, and Grand River-Saginaw aquifers. The Coldwater shale that ranges from 500 to 1,100 ft in thickness, forms the base of the aquifer system. This thesis concentrates on the Grand River-Saginaw and Parma-Bayport aquifers, however chemistry of waters in the overlying Glacial Drift

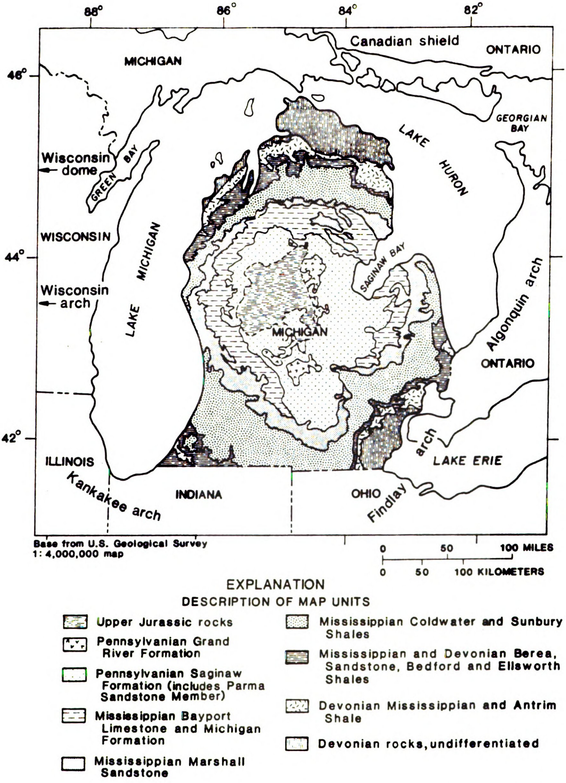


Figure 4. Geologic map of the Lower Peninsula of Michigan (Modified from H.M Martin, 1955, fig. 11).

aquifer and especially the underlying Marshall aquifer is important to the discussion in the thesis and therefore is referred to in comparison of chemical similarities and differences.

The Marshall aquifer is the basal aquifer in the RASA study area. It includes sandstones that overlie the Coldwater confining unit as well as sandstones that form the lower part of the Michigan Formation (Fig. 2). The Marshall aquifer consists of two or more permeable sandstones in the central part of the basin, but, toward the subcrop regions, the aquifer consists of one permeable sandstone. In areas where more than one sandstone is present, intercalated carbonate, shale, siltstone, and/or evaporite separate permeable sandstones. The composite thickness of permeable sandstone ranges from approximately 75 to 225 ft (D.B. Westjohn, personal commun., 1992). Separating the Marshall and overlying bedrock aquifer is the Michigan confining unit.

The Michigan confining unit is an intercalated sequence of thin bedded limestone, dolomite, shale, gypsum, anhydrite, and lenses of sandstone. The unit ranges from 100 ft in thickness near the fringes of the subcrop area to about 400 ft over the central part of the study area. (D.B. Westjohn, personal commun., 1992).

Cohee (1965) reports that the Bayport Limestone overlies the Michigan Formation and consists of limestone, cherty or sandy limestone, as well as intercalated sandstone and limestone. The Bayport Limestone is thin or absent in the central part of the basin. In areas where the Bayport is absent the Parma Sandstone is present and overlies the Michigan confining unit. Recent geophysical studies indicate that the Bayport consists predominantly of permeable limestone and sandstone (D.B., Westjohn, written communication, 1991). The Parma Sandstone and Bayport Limestone are combined to form the Parma-Bayport aquifer because they form a hydraulically connected and stratigraphically continuous permeable unit over most of the basin. The thickness of the Parma-Bayport aquifer ranges from 75 to 150 ft. Over most of the study area, the aquifer is overlain by shale that comprises the Saginaw confining unit.

Overlying the Saginaw confining unit is the Grand River-Saginaw aquifer. Pennsylvanian rocks have been subdivided into the Saginaw (Early Pennsylvanian) and Grand River Formations (Late Pennsylvanian). The stratigraphic column published by the State (Michigan Department of Conservation, 1964) shows the Grand River and Saginaw Formations separated by a major erosional unconformity. This interpretation is based primarily on the work of Kelly (1936), who suggested rock units exposed near Grand Ledge, Michigan, are younger than the Saginaw Formation. Kelly (1936) noted the presence of a basal conglomerate associated with proposed younger Pennsylvanian rocks, and suggested the name Grand River Group. The nomenclature proposed by Kelly (1936) was modified slightly in the stratigraphic column published for the State, but rather than indicate "Group" status, this stratigraphic column assigns rocks suggested to be Late Pennsylvanian to the Grand River Formation. The bedrock geological map recently published by the State (Milstein, 1987) shows a 350 mi^2 area where glacial deposits are underlain by the Grand River Formation, and delineation of the formation is based entirely on nomenclature recorded on geological logs of hydrocarbon exploration boreholes, or holes drilled for water wells. There are no known stratigraphic horizons of regional extent that separate Grand River and Saginaw Formations, and in general it is not possible to assign formational nomenclature based on geological descriptions. Pennsylvanian sandstones are stratigraphically discontinuous, only locally constitute the dominant lithology, with shale, siltstone, limestone, and coal as minor contributors to the total thickness of the Pennsylvanian rock sequence. For purposes of characterizing the hydrogeological framework of the Michigan basin aquifer system, the composite thickness of the Pennsylvanian sandstones is grouped to form the Grand River-Saginaw aquifer (D.B. Westjohn, personal commun., 1992). The Grand River-Saginaw aquifer is considered as a single layer for modeling purposes. The composite thickness of sandstones ranges from 300 to 400 ft in the east-central part of the basin, where Pennsylvanian rocks are the thickest (600 to 700 ft). However, over most of the basin the composite thickness of the sandstones that comprise the Grand River-Saginaw aquifer is less than 200 ft (D.B. Westjohn, personal commun., 1992).

Transmissivity values for 47 aquifer tests performed on the Grand River-Saginaw aquifer range from 975 to 43,333 ft^2/d. Horizontal hydraulic conductivity is estimated to range from 1 to 100 ft/d (Vanlier et. al., 1973; Michigan Department of Public Health, Engineering Division, written communication, 1987; Michigan Department of Natural Resources, Geological Survey Division, written communication, 1987).

Mineralogic information on aquifer matrix is limited as unfortunately little literature on the geology of the Pennsylvanian bedrock sequence in Michigan exists (Figure 2). The Saginaw Formation sands are predominantly fine grained litharenites. The aquifer is generally not cemented but does contain small amounts of quartz and calcium-carbonate cement (Wood, 1969). Preliminary solid-phase data from the RASA project indicates that the sandstone aquifer that now contains freshwater may have previously contained brine (Kramer and Westjohn, 1993). Also the mineral paragenetic sequence and carbonate phases are similar in Pennsylvanian and Mississippian sandstones and isotopic compositions of authegenic mineral phases have the same range of values in Pennsylvanian and Mississippian sandstones (Kramer and Westjohn, 1993). The solid phase work suggests that basin wide evolution of brine resulted in a suite of authegenic mineral phases common to all Carboniferous sandstones (Kramer and Westjohn, 1993).

During the Mesozoic and early Cenozoic an eroded bedrock surface developed. Sediments accumulated briefly during the Late Jurassic and Late Cenozoic Eras. Red Beds of Jurassic age overlie the Grand River and Saginaw Formations in the west-central part of the study area. The red beds are composed of red mud, poorly consolidated red shale, gypsum, and minor amounts of sandstone. The red beds together with the fine-grained glacial deposits form the subregional glacial till-red beds confining layer (Mandle and Westjohn, 1989).

The Glacial-drift aquifer is composed of deposits ranging from fine-grained lacustrine clay, glacial till, and glaciofluvial deposits (Mandle and Westjohn, 1989). Glacial deposits range from 10 to 1000 feet thick throughout Michigan (Western Michigan University, 1981). Where coarse-texture deposits predominate, as in the northern and northwestern parts of the study area, they are productive aquifers. In low-lying areas, such as the Saginaw Lowland area where proglacial lake beds predominate, the Quaternary deposits are a confining unit for more permeable, underlying unconsolidated deposits and sedimentary rock. None of these deposits is regionally continuous; they are aquifers or confining units in relatively small areas. The alluvium and outwash, or other coarse-grained Quaternary deposits are grouped to form the Glacial-Drift aquifer.

GROUND-WATER FLOW DIRECTIONS

Physical flow information for the Pennsylvanian aquifers is not available, however regional hydrology is proposed. Preliminary computer simulations of freshwater head distributions for the Grand River-Saginaw aquifer indicate that ground water flows from the upland areas toward the regional discharge area in and around the Saginaw Bay Area (Figure 5) (Mandle and Westjohn, 1989; G. Barton, personal commun., 1993). Vugrinovich, (1986) noted a similar distribution in hydraulic heads, which were not corrected for reference density. Vugrinovich concluded that hydraulic head in the Marshall and Grand River-Saginaw aquifers were generally in equilibrium with present-day land-surface elevations. Larson (1979) found tritium concentrations in the Tri-county region that indicated direct recharge to the Saginaw Formation and therefore to the Grand River-Saginaw aquifer is taking place. Ground-water flow information available for the southern portion of the study area indicates that the flow of the area is controlled by the local surface topography and not by movement in other formations (Wood, 1976; VanLier, et al., 1973).

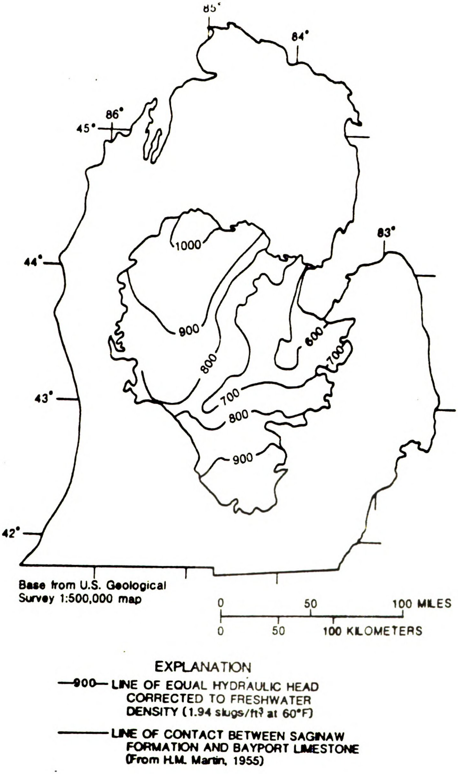


Figure 5. Map showing simulated pre-development equivalent freshwater head in the Grand River-Saginaw aquifer (Mandle and Westjohn, 1989, fig. 9).

PREVIOUS STUDIES ON GEOCHEMISTRY OF THE SYSTEM

The only work done on the geochemistry of ground water in the Pennsylvanian aquifers has focused on the Grand River-Saginaw aquifer (Wood, 1969, and 1976; VanLier et al., 1973; Slayton, 1982; Long et al., 1986, and 1988; Badalamenti, 1992). Previous studies performed on the geochemistry of the Grand River-Saginaw aquifer have focused on portions of the aquifer, no basin wide study has been done. Two main areas of the aquifer have been studied, the southern part (Wood, 1969, and 1976; VanLier et al., 1973; Slayton, 1982) and the central part, specifically near Saginaw Bay (Long et al., 1986, and 1988; Badalamenti, 1992).

Wood (1969), studied the distribution, source and mineral equilibria of major chemical constituents in ground water from the Saginaw Formation within the context of the geology and flow system of the aquifer in the Upper Grand River-Basin, Michigan (Figure 6). The main source of solutes is from rock-water interactions in the overlying glacial drift, which is hydraulically connected with the Saginaw Formation. Mixing with lower formations in the southern part the Pennsylvanian subcrop area is limited as the underlying Bayport limestone is allowing only small amounts of water to pass into the overlying aquifer. Leaching experiments on soil-glacial material and Saginaw Formation sandstone to determine source of dissolved-solids supported this interpretation. Water obtained from leaching the glacial material was found to be very similar to water found in the Glacial-Drift and Grand River-Saginaw aquifers. Leaching experiments also indicated that the sandstones from the Saginaw Formation yield very small amounts of dissolved solids.

Wood (1976) summarized five features that are of importance in the evaluation of water quality of the southern part of the Grand River-Saginaw aquifer system: 1) There was considerable variation in the concentration of several chemical parameters over very short horizontal distances, 2) Water quality does not appear to be related to the depth of the well, 3) Water in wells in the overlying glacial material yielded water of poorer quality

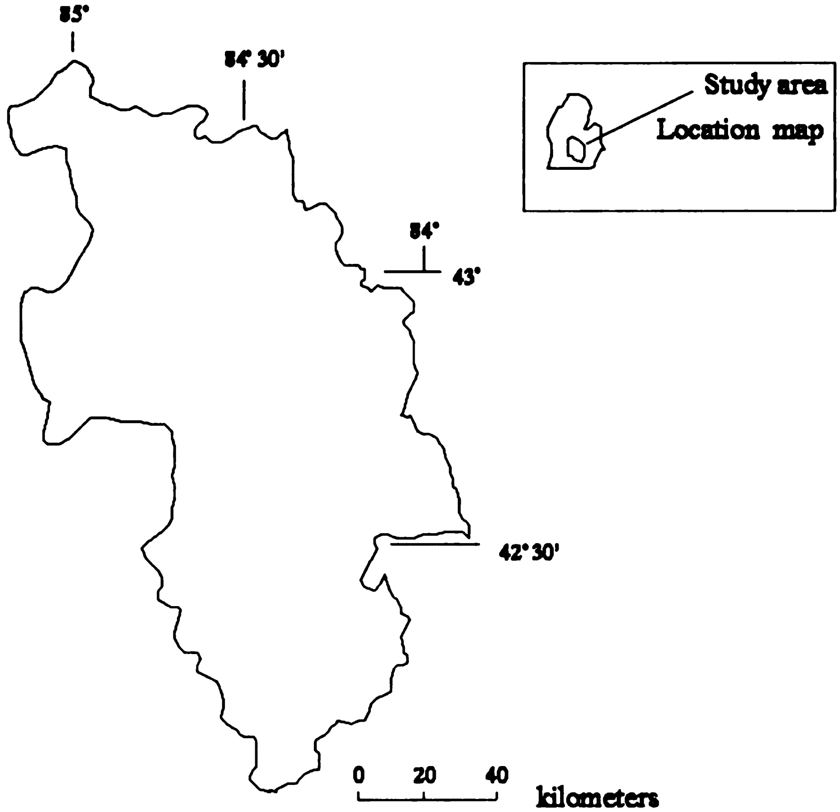


Figure 6. Study area for Wood (1969) Ph.D dissertation in the upper Grand River basin.

than water from wells completed in the Saginaw Formation, 4) Water quality in some wells completed in the Saginaw Formation experienced a sudden deterioration, although the wells had yielded water of good quality for many years, and 5) Base flow of unpolluted streams appears to contain more dissolved-solids than water from wells in the Saginaw Formation (Wood, 1976). These five features of the Saginaw Formation led to Wood (1976) to present a model for ion filtration (reverse osmosis) impacting water chemistry of the aquifer. Wood's model for ion filtration described two types of water found in the Saginaw Formation. The first type of water derived its dissolved-solids from dissolution of minerals in the overlying glacial drift and moved along flow path into the Saginaw Formation, the chemistry of this water type is identical to that found in the overlying glacial drift material. The second type of water also derived its dissolved solids from the overlying glacial drift, however the flow line for this water intersected a clay or shale bed with membrane properties. This water while passing through the filter will have the dissolved solids concentrations reduced creating anomalous water chemistry observed relative to water above in the drift.

Slayton (1982) revisited the work of Wood (1969 and 1976) and performed a study investigating field evidence for shale membrane filtration (reverse osmosis) of ground water primarily in areas of Eaton and Ingham counties. In this study Slayton found that in areas of the Saginaw Formation where shale is present shale membrane filtration is a process that controls groundwater geochemistry. Water samples in areas of the Saginaw Formation had dissolved-solids concentrations greater than those found in the overlying drift. Slayton provided two explanations for the dissolved-solids distributions 1) direct recharge to the Saginaw Formation in areas supported by high tritium concentrations (Larson, 1979) and 2) areas where shale is present in the Saginaw Formation low tritium concentrations prevail and are believed to be impacted by shale-membrane filtration. Slayton concluded that shale membrane filtration and direct recharge were occurring within the study area.

Long et al., (1986 and 1988) studied 100 ground water samples from the Grand River-Saginaw aquifer in Bay county MI (Figure 7). The chemical and isotope database generated was used to determine the chemical controls on ground water in selected townships in Bay county. Saline water was found in the Grand River-Saginaw aquifer and was attributed to upward advection or diffusion of brine. Isotopically light meteoric water was found in the study area and was attributed to ground water recharge to the aquifer when the climate was cooler, such as during recent glaciation. Sulfate reduction was shown to be occurring in the aquifer affecting SO_4 and HCO_3 concentrations as well as $\delta^{34}S$ and $\delta^{13}C$ values.

Badalamenti, (1992) studied 55 samples from the Grand River-Saginaw aquifer within the Saginaw Lowland incorporating the study area of Long et al., (1986) (Figure 8). She found that the Saginaw Lowland Area was a transition zone between 1) modern meteoric water and brine compositions and 2) the occurrence or lack of sulfate reduction in the system. She concluded that the regional ground water system is influenced by meteoric water and brine end-members. The brine end-member is most dominant in Bay county.

The work of Long et al., (1986 and 1988) and Badalementi 1992) indicate the mixing of brine and meteoric water as a source for chemical trends observed in the Saginaw Bay Area and east-central part of the basin. With additional data from the Grand River-Saginaw and especially data from the Parma-Bayport brine and deeper formations the relationship between brine and less concentrated water in the overlying aquifers can be better analyzed.

METHODS OF DATA COLLECTION AND ANALYSIS

Ground-water sample locations for the Michigan RASA project were selected based on well location, depth, open interval, pumping equipment, aquifer type, and lithology (Dannemiller, 1990). The majority of the samples were taken from municipal and

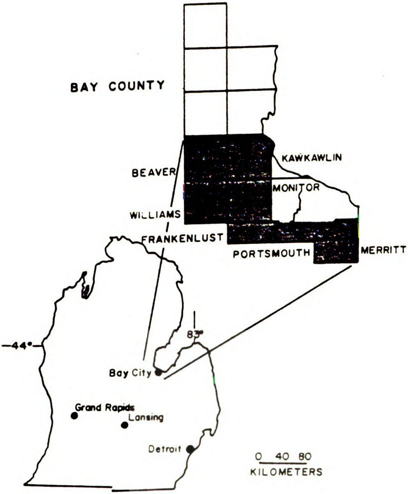


Figure 7. Study area for Long et al., (1986, 1988) Geochemistry of ground waters in Bay county MI. (modified from Long et al., 1986, fig. 1.1)

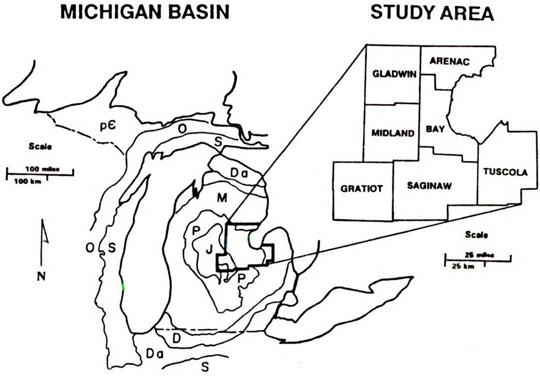


Figure 8. Study area for Badalameni (1992) M.S. thesis The Geochemistry and isotopic chemistry of saline ground water derived from near-surface deposits of the Saginaw Lowland, Michigan basin (Modified from Badalamenti, 1992, fig. 1.2).

domestic wells from which drillers logs were available. The samples were collected from the wells once sufficient pumping yielded constant temperature and specific conductance. Analysis of the samples included measurements of parameters used for geochemical modeling. At each well site samples were taken and were field tested for specific conductance, pH, and temperature, also on-site concentrations of dissolved oxygen, alkalinity as $CaCO_3$, sulfide as S, total iron, and ferrous iron were determined on the majority of samples, see Table 1 for the methods used in the determination of these concentrations.

Further analysis of the samples included lab analysis for dissolved organic carbon (DOC), sulfate, sulfide, Mn, Mg, Fe, total dissolved solids as Residue on evaporation (ROE), Sr, Br, Al, Li, Ca, Na, K, Cl, B, As, Zn, and F. Stable isotope analysis was performed on many samples also. Isotopic ratios of $^{18}O/^{16}O$, $^{2}H/^{1}H$, $^{34}S/^{32}S$, and $^{13}C/^{12}C$ were measured along with percent ^{14}C and Tritium (^{3}H) analysis on selected samples. In preparation for chemical analysis of the water samples they were filtered through a membrane with a pore size of .45 um (micrometer). During this process the water filtered was supplied through a continuous flow line to minimize exposure of the sample to the atmosphere. The water samples were preserved according to methods described in Brown and others (1970) and Skougstad and others (1978), (Dannemiller and Baltusis, 1990). The samples were then analyzed by the U.S. Geological Survey National Water Quality Laboratory in Arvada, Co.

This thesis encompasses all above study areas, and a database that includes 550 chemical and 150 isotopic (O and D) analyses. Thirty-one chemical and isotopic analyses have been derived from Long et al., (1986) and 240 chemical analyses from Wood (1969). This thesis also adds 165 chemical and isotopic analyses from RASA sampling efforts (Dannemiller and Baltusis, 1990), 106 chemical analyses from the Department of Health (Mark Breithart, 1992), 20 chemical analyses from the USGS WATSTORE database (1974-1987), 6 chemical analyses from the Department of Natural Resources

Table 1: Methods of measuring and analyzing ground water at well site (modified from Dannemiller and Baltusis, 1990).

Property of constituent	**Measurement**
Temperature, in degrees Celsius	Recorded during specific-conductance measurement by use of thermistor in specific-conductance probe. Probe calibrated with a certified mercury thermometer (Wood, 1976, p. 10).
Specific conductance in microsiemens at 25° Celsius.	Specific-conductance meter calibrated with standards obtained from U.S.G.S. National Water Quality Laboratory. Results were temperature corrected by use of the following correction factor, where temperature (T) is measured in degrees Celsius: $\text{correction factor} = 1 / 1 + [0.2(T-25)]$
pH	pH meter calibrated with two standard solutions (pH 4.00 and 7.00). Sample water kept at its original temperature during measurement by means of a water bath.
Alkalinity (bicarbonate) in milligrams per liter	Potentiometric titration with 0.01639N H_2SO_4 through end inflection points. Centroid of the inflection point was graphically determined (Stumm and Morgan, 1981). Sample water kept at original temperature with water bath.
Dissolved oxygen in milligrams per liter	Azide modification of Winkler method used (Hach Chemical Co., 1987). Sample kept from exposure to atmosphere during collection. The sample bottle was filled in oxygen free atmosphere.
Ferrous iron, (Fe^{2+}) in micrograms per liter	1, 10 phenanthroline method used (Hach Chemical Co., 1987). Sample was prevented from exposure to the atmosphere during sampling.
Total iron (Fe), in micrograms per liter	Ferrozine method used (Hach Chemical Co., 1987)
Sulfide (S^{2-}), in milligrams per liter	Methylene blue method used (Hach Chemical Co., 1987). Sample kept isolated from atmosphere during sampling.

(written commun., 1987) and 10 isotope analyses sampled summer 1991, (unpublished data, USGS WATSTORE database). Figure 9 shows the study area and distribution of sample locations where chemical analyses are available for the Grand River-Saginaw aquifer. The majority of chemical and isotope data for the Grand River-Saginaw aquifer exists in the area outside the brine bearing region defined by Westjohn, (1989). No chemical or isotope data exists in the northwest part of the aquifer due to thick glacial deposits that serve as the regions major source of ground water (Baltusis, 1992). Data for the Parma-Bayport includes 5 chemical and 6 isotope samples from the RASA database, 1 chemical analysis from Wood, (1969) and 5 chemical analyses from the Department of Natural Resources (written commun., 1987). Figure 10 shows the study area of Parma-Bayport aquifer and displays sample locations with chemical and isotopic analyses available.

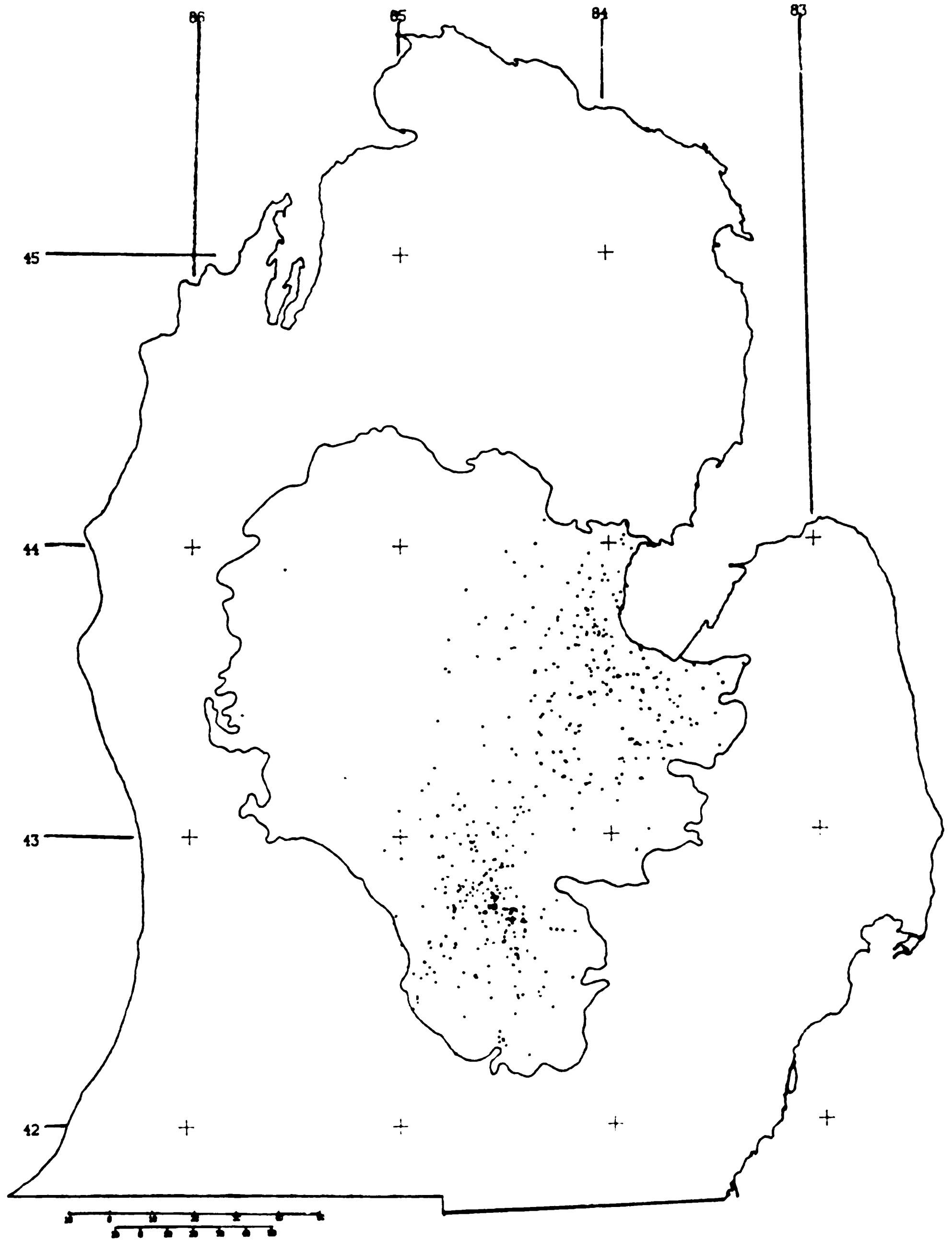


Figure 9. Sample locations where chemical analyses are available for ground water from the Grand River-Saginaw aquifer.

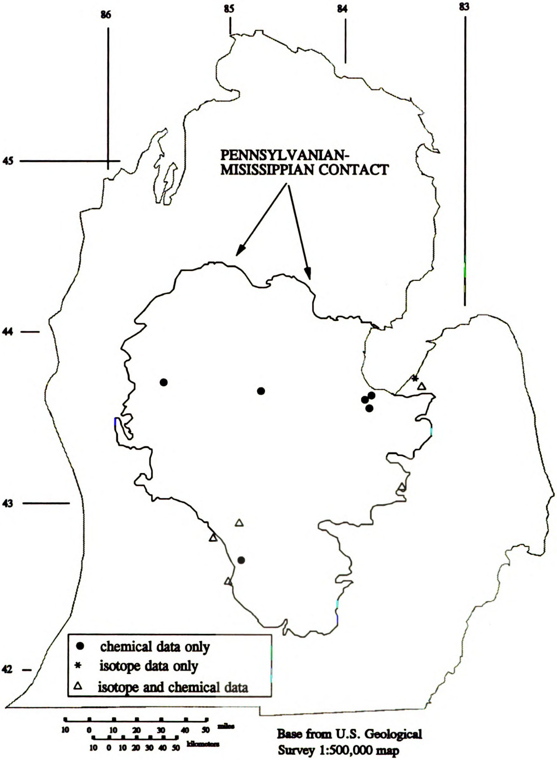
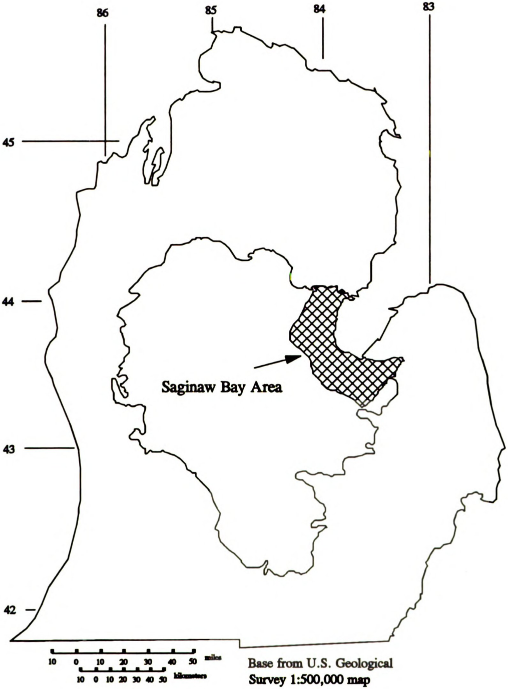


Figure 10. Sample locations where chemical analyses are available for ground water from the Parma-Bayport aquifer.

CHAPTER 2: GEOCHEMICAL DISTRIBUTION MAPS

INTRODUCTION

The following maps and discussion describe the areal variations of chemical properties of ground water from Grand River-Saginaw and Parma-Bayport aquifers. Maps of dissolved solids, dissolved chloride, dissolved sulfate and hydrochemical facies are discussed. The purpose of these maps is to provide a general distribution and discussion of patterns of parameters chosen. Constituents used for map preparation were chosen based on importance in describing chemical properties and trends of ground water in the aquifer. Dissolved-solids and dissolved chloride were chosen as the encroachment of saline water in the basin is a concern in some parts of the aquifer specifically in the Saginaw Bay Area. For the purposes of this thesis the Saginaw Bay Area is defined as the east-central portion of the Michigan basin bounded by the outermost moraine of the Port Huron Morainic system (Figure 11). Dissolved sulfate is depicted to investigate the potential impact of gypsum dissolution in Jurassic deposits and the effect on water chemistry (Cohee et al., 1951) as well as the impact of sulfate reduction in the Saginaw Bay Area (Long et al., 1988). Hydrochemical facies are used as a common tool of classifying the water chemistry of the aquifer and portrayal of regions of the aquifer with similar chemical characteristics. Data used in the preparation of the maps was derived from a variety of well depths and therefore represent general distribution patterns only. Although databases used to compile these maps provide sufficient data to prepare maps for the Grand River-Saginaw aquifer, insufficient data are available for ground water in the Parma-Bayport aquifer. However, general statements about dissolved solids, dissolved chloride, dissolved sulfate and hydrochemical facies are made and can be found at the end of this section.



Base from U.S. Geological
Survey 1:500,000 map

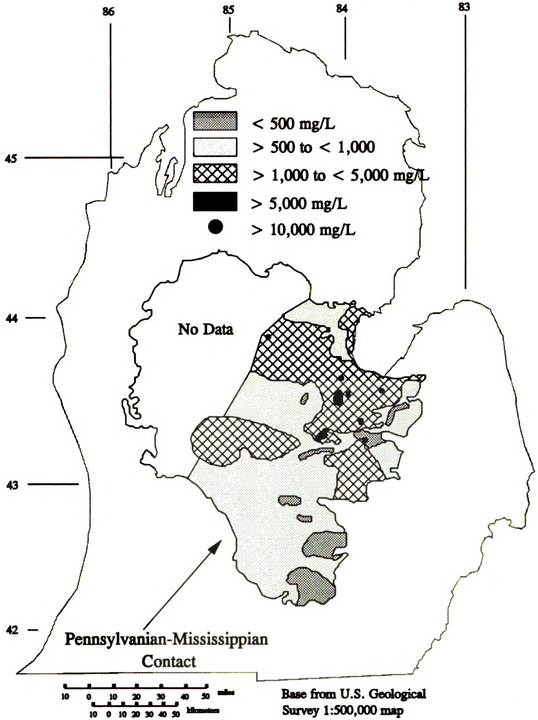
Figure 11. Location of the Saginaw Bay Area (Modified from Wayne and Zomberge, 1965).

DISSOLVED SOLIDS

A map of dissolved-solids concentrations was prepared for water from the Grand River-Saginaw aquifer (Figure 12). The concentrations were determined by summing the major cation and anion species from analysis of each sample. Dissolved-solids concentrations range from 41 to 92,352 mg/L within the aquifer with a geometric mean of 832 mg/L. In the southern part of the aquifer and around much of the fringe area, where data has been collected, dissolved-solids concentrations are generally less than 1,000 mg/L and suitable for human consumption, with most of the water sampled containing dissolved solids concentrations less than 750 mg/L. Water from the east-central part of the aquifer and part of the Saginaw Bay Area commonly contains dissolved-solids concentrations that exceed 1,000 mg/L and, locally, exceed 10,000 mg/L. An increase in dissolved-solids concentrations is noted from the southern part of the aquifer to the Saginaw Bay Area. The sources of dissolved solids may be due to the addition of solutes through water-rock interaction (Hem, 1989), through the mixing of meteoric water and brine from the Parma-Bayport aquifer and from water derived from the overlying Glacial-Drift aquifer in the southern part of the aquifer. Dissolved solids concentrations in the Glacial drift aquifer mimic the concentrations in the Grand River-Saginaw aquifer in the southern and southeast edge of the aquifer. These concentration trends in recharge areas of the aquifer may indicate solutes derived in the Glacial drift aquifer as the source of solutes in recharge areas of the Grand River-Saginaw aquifer. No trend of increasing dissolved-solids concentrations with depth is noted in the southern part of the aquifer.

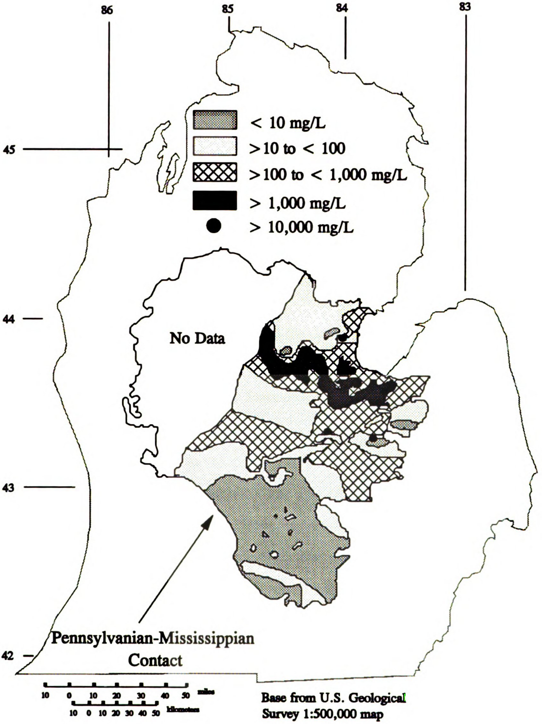
DISSOLVED CHLORIDE

Dissolved chloride concentrations in water from the Grand River-Saginaw aquifer are shown on Figure 13. Chloride concentrations vary from 0.7 to 55,000 mg/L with a



Base from U.S. Geological Survey 1:500,000 map

Figure 12. Dissolved-solids concentration distribution map for ground water from the Grand River-Saginaw aquifer.



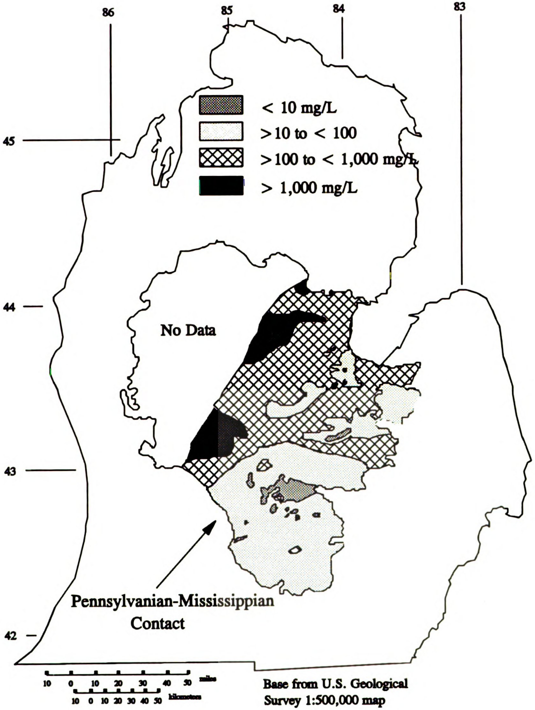
Base from U.S. Geological Survey 1:500,000 map

Figure 13. Dissolved chloride comcentration distribution map for ground water from the Grand River-Saginaw aquifer.

geometric mean of 28.5 mg/L. Water from about the southern one third of the aquifer has a chloride concentration of less than 10 mg/L. Only in a few small areas of the northern and eastern parts does the aquifer yield water with concentrations this low. Concentrations greater than 1,000 mg/L occur in water in part of the Saginaw Bay Area and form a band that extends to the north-central part of the aquifer. Chloride concentrations in water from about one half of the areal extent of the aquifer and range from 10 to 1,000 mg/L. Sources of chloride for water in the Grand River-Saginaw aquifer may be from dissolution of halite (NaCl), probably incorporated in the glacial drift (Wood, 1969) or from mixing with brine from the Parma-Bayport aquifer.

DISSOLVED SULFATE

Concentrations of dissolved sulfate from the Grand River-Saginaw aquifer range from 0.2 to 3,500 mg/L with a geometric mean of 56.0 mg/L. Sulfate concentrations do not exhibit concentration trends similar to those observed for dissolved-solids and dissolved chloride distributions (Figures 12 and 13). Water from the southern part of the aquifer generally has a dissolved sulfate concentration less than 100 mg/L and, locally, less than 10 mg/L (Figure 14). Concentrations of less than 100 mg/L also occur in water from an area within the Saginaw Bay Area and from the eastern edge of the aquifer toward the basin center as well as an area in the basin center. The area of low sulfate concentration in the Saginaw Bay Area may be due to sulfate reduction shown to be a process taking place in the Saginaw Bay Area based on the interpretation of stable isotope ratios of carbon and sulfur from ground water (Long, and others, 1988). Sulfate concentrations greater than 1,000 mg/L occur in water from parts of the west-central portion of the aquifer. The distribution of high sulfate concentrations in the southwest part of the aquifer coincides with the location of Jurassic deposits that contain gypsum ($CaSO_4 \bullet 2H_2O$) (Cohee, 1965), that may dissolve to provide sulfate to ground water. High sulfate concentrations in the



Base from U.S. Geological Survey 1:500,000 map

Figure 14. Dissolved sulfate concentration distribution map for ground water from the Grand River-Saginaw aquifer.

north-central part of the aquifer may be influenced by Jurassic deposits located directly to the west (Cohee, 1965). Gypsum ($CaSO_4 \bullet 2H_2O$) and anhydrite ($CaSO_4$) is believed to be unevenly distributed in the overlying glacial deposits and dissolution of these minerals may be providing an additional source of sulfate to the Grand River-Saginaw aquifer (Wood, 1969).

HYDROCHEMICAL FACIES AND PIPER PLOTS

The concept of hydrochemical facies is a means of describing the diagnostic chemical character of water (Back, 1961). Piper (1944) developed a diagram, commonly referred to as a Piper plot, that enables the classification of waters using six chemical components that allows easy visual chemical comparisons of the chemistry of water samples, identification of water having different characteristics, evaluation of mixing among water having different characteristics, and determination of the chemical evolution of ground water. The chemical components used consist of three cationic Ca, Mg, and Na+K and three anionic Cl, HCO_3+CO_3, and SO_4 species or groups of species as these ions account for the electrical balance in most natural waters (Hem, 1989). Construction of the diagram entails converting cation and anion concentrations to units of milliequivalents per liter and then calculating relative percentages of the cation and anion species or groups of species. The cations and anions each sum to 100%. Each sample is plotted on respective cation and anion ternary diagrams and on a central diamond-shaped diagram (Figure 15a). The sample location on the diamond diagram is determined by the intersection of projections from its position in the cation and anion ternary diagrams. The projections are made along lines that are parallel to Na+K and HCO_3+CO_3 axes. The intersection of the projections represents the composition of the water concerning six chemical components and is the basis for identifying the hydrochemical facies of a ground-

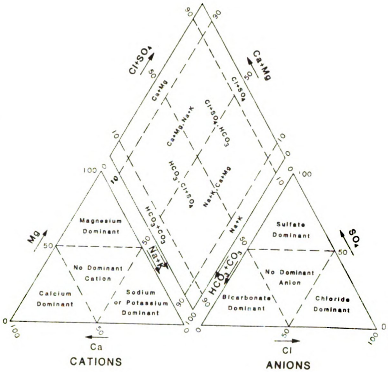


Figure 15(a).--Modified Piper plot depicting the classification scheme for hydrochemical facies (Piper, 1944).

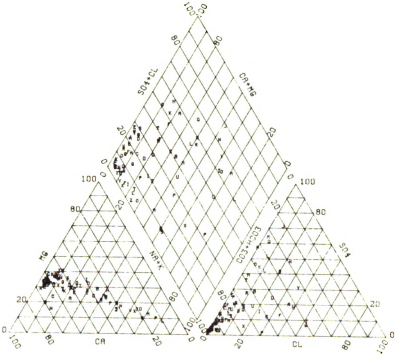


Figure 15(b).--Piper plot for ground water in the Grand River-Saginaw aquifer with dissolved-solids concentrations less than or equal to 750 mg/L.

water sample (Figure 15a). Hydrochemical facies are used to classify the chemical composition of ground water in terms of the dominant cation and anion.

The dominance criteria is based on percentage of milliequivalents of major cations (Ca, Mg, and Na + K) and major anions (Cl, SO_4, and HCO_3 +CO_3) within the sample. For example, in water dominated by sodium and chloride (Na-Cl facies), the sodium and chloride ions would be greater than 50 percent of the total cations and anions, respectively. A water sample that has no cation or anion that exceeds 50 percent of the total cations or anions is grouped as a no dominant cation or no dominant anion facies.

The data used to construct the Piper plot for the Grand River-Saginaw aquifer consists of 237 water samples with less than 10% charge imbalance. A major limitation in making interpretations from Piper plots is that water samples with very different dissolved-solids concentrations, but with the same relative proportions of cation and anion species will plot at the same position on the diagram. This limitation can be handled in many ways (Hem, 1989). In this report we chose to handle this limitation by constructing three Piper plots (Figures 15b to 15d) in which the samples are grouped as a function of dissolved solids. The ranges of dissolved solids are less than 750 mg/L, 753 to 2,000 mg/L, and greater than 2,000 mg/L.

At all ranges of dissolved solids, water samples in the cation ternary diagram plot along a line with very little scatter from the Ca-dominant area to the Na-dominant area. Samples are weighted to Ca dominant at low dissolved solids (Figure 15b) and Na dominant at high dissolved-solids (Figure 15d). Water samples in the anion ternary diagram plot between HCO_3 + CO_3 - SO_4 dominant at low dissolved solids (Figure 15b), among HCO_3 + CO_3 - Cl - SO_4 dominant at intermediate dissolved solids (Figure 15c) and Cl - SO_4 dominant at high dissolved solids (Figure 15d). Distribution in Figures 15b and 15c show more concentrated waters in each interval plotting closer to the SO_4-Cl dominant area. The change in the distribution pattern of the data in the diamond area as a

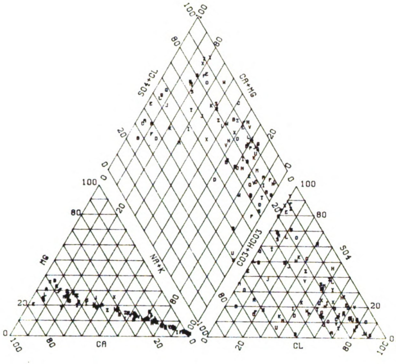


Figure 15(c).--Piper plot for groundwater in the Grand River-Saginaw aquifer with dissolved solids concentrations from 751 to 2,000 mg/L.

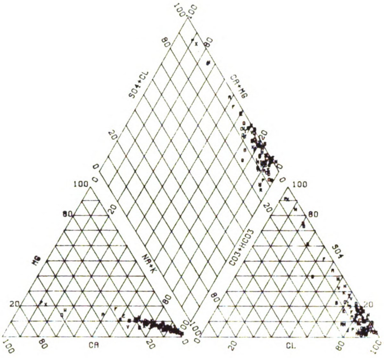


Figure 15(d).--Piper plot for ground water in the Grand River-Saginaw aquifer with dissolved-solids concentrations greater than 2,000 mg/L.

function of increasing dissolved solids reflects those changes in the cation and anion ternary diagrams.

The pattern changes in the ternary and diamond diagrams are consistent with the hypothesis in which waters with different compositions are mixing. At low dissolved solids concentrations, meteoric water frequently evolves from a Na or Ca - SO_4 dominant rain solution to a Ca - HCO_3 dominant ground water solution (Berner and Berner 1987). Such an evolutionary pathway could explain the trends on Figure 15b. At high dissolved-solids concentrations, ground water masses that are Na - Cl and Ca - SO_4 dominant are frequently found because of the dissolution of halite (NaCl), gypsum ($CaSO_4 \bullet 2H_2O$), and anhydrite ($CaSO_4$); or the presence of formation brine (Na - Ca - Cl rich solutions). Mixing among such water could explain the trends (Figure 15d). The trends at intermediate dissolved-solids concentrations (Figure 15c) are most likely the result of mixing of water masses of low dissolved-solids concentrations (Figure 15b) and high dissolved solids concentrations (Figure 15d).

A hydrochemical facies map for Grand River-Saginaw aquifer (Figure 16) was prepared to show the areal distribution of significant chemical aspects of the facies as classified on the Piper plot (Figures 15b to 15d). There are three dominant hydrochemical facies observed in ground water from the Grand River-Saginaw aquifer; Ca-HCO_3, Ca-SO_4, and Na-Cl. Locally, Na-HCO_3 as well as Na-SO_4 facies are present. Ground water in the southern part of the Grand River Saginaw aquifer is dominated by Ca-HCO_3 facies. Calcium-bicarbonate facies are typical of water recently recharged. (Back, 1961; Berner and Berner, 1987). The distribution of Ca-HCO_3 facies in the Grand River-Saginaw aquifer mimics the distribution with that found in the overlying Glacial-Drift aquifer (Wahrer, 1993). Calcium-sulfate facies are found in the west-central and northeastern regions of the aquifer and, in part of the Saginaw Bay Area extending out into the basin center, sodium-chloride facies are mainly present. Calcium-sulfate facies are most likely influenced by Jurassic deposits overlaying parts of the aquifer in the southwest and

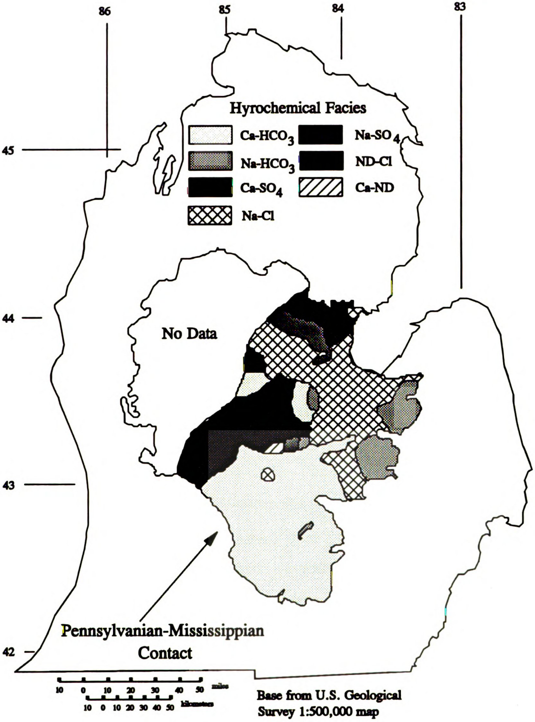


Figure 16. Hydrochemical facies map for ground water from the Grand River-Saginaw aquifer.

upgradient in the north-central parts. Sodium-chloride facies present in and around the Saginaw Bay Area could be the result of halite dissolution in the overlying glacial deposits or from mixing with upwelling brine in that area. Separating Ca-SO_4 and Na-Cl facies in the north-central part of the aquifer is an area of Na-SO_4 facies. The Na-SO_4 facies are believed to be the result of a mixture of sodium-chloride and calcium-sulfate facies in that part of the aquifer. Sodium-bicarbonate facies are found along the eastern edge of the aquifer and are believed to be derived from mixing between sodium-chloride facies and calcium-bicarbonate facies.

PARMA-BAYPORT AQUIFER

Limited chemical data are available for ground water from the Parma-Bayport aquifer (11 chemical and 6 isotope samples). Figure 10 shows sample locations for the Parma-Bayport aquifer. The distribution of hydrochemical facies for water from the Parma-Bayport aquifer is similar to the distribution in the Grand River-Saginaw aquifer. However, distributions of chloride, dissolved solids and sulfate differ from the trends observed in the Grand River-Saginaw aquifer. Chloride concentrations exceed 100,000 mg/L in the Saginaw Bay Area and west-central parts of the aquifer. Dissolved-solids concentrations are more than 200,000 mg/L in the Saginaw Bay Area and west-central part of the aquifer. Sulfate concentrations are similar to those of the Grand River-Saginaw aquifer in the south, but are more concentrated in the Saginaw Bay Area, with values as high as 3,796 mg/L.

SUMMARY

Geochemical distribution maps based on chemical analyses of ground water from the Grand River-Saginaw aquifer were prepared. The maps show spatial distributions of dissolved-solids, dissolved chloride, dissolved sulfate, and hydrochemical facies.

Concentrations of dissolved-solids and chloride in the Grand River-Saginaw aquifer show an increasing trend toward the Saginaw Bay Area from the fringes of the study area. Source of solutes for dissolved solids in the south and southeastern parts of the aquifer may be derived from rock-water interaction in the Grand River-Saginaw aquifer or from rock water interaction occurring in the overlying glacial deposits prior to recharge into the Grand River-Saginaw aquifer. Solutes also may be derived from mixing or dilution of underlying brine in the Parma-Bayport aquifer. Chloride sources may also be related to a brine source or from dissolution of halite probably incorporated in overlying glacial drift (Wood, 1969).

Dissolved sulfate concentrations throughout the basin show no apparent trends. Low concentrations of sulfate in the Saginaw Bay Area may be due to sulfate reduction shown to be a process proven to be taking place through interpretation of stable isotope ratios of C and S from groundwater in that region (Long and others, 1988). High concentrations of sulfate may be due to dissolution of gypsum in Jurassic deposits (Cohee and others, 1951) or from gypsum and anhydrite unevenly distributed in the overlying glacial deposits (Wood, 1969).

Distribution of data on Piper plots (Figures 15b to d) show a cation trend from Ca dominant at low dissolved solids to Na dominant at high dissolved solids, and also an anion trend from HCO_3+CO_3-SO_4 dominant at low dissolved solids to HCO_3+CO_3-SO_4-Cl at intermediate dissolved solids to Cl-SO_4 dominant at high dissolved solids. These three trends indicate a mixing of water masses of various compositions. Three main facies are present in the Grand River-Saginaw aquifer: Ca-HCO_3, Ca-SO_4, and Na-Cl.

Calcium-bicarbonate facies are found mainly in the south consistent with waters recently recharged (Back, 1961; Berner and Berner, 1987). Calcium-sulfate facies are mainly located in the west-central and northeastern areas and sodium-chloride facies are found in the Saginaw Bay Area.

The overall distribution of data on the dissolved-solids, dissolved chloride and hydrochemical facies maps indicates mixing as a possible mechanism to explain distribution patterns observed for waters in the central part of the study area. However, chemical processes must also be considered as factors affecting the solute concentrations of dilute waters in the system. The scatter of data on the Piper diagrams, specifically for the waters of low concentrations (< 750 mg/L), may indicate chemical processes as well as physical processes are impacting water chemistry. Also the chemistry of the dilute samples in the Pennsylvanian aquifers, specifically in the south, is most likely to be controlled by water derived from the Glacial-Drift aquifer that are controlled by chemical processes as indicated by Wood (1969). The chemistry of more concentrated samples, such as in the center of the study area and in the Saginaw Bay Area are shown to be impacted by physical processes (Long et al, 1988). The following sections analyze chemical data from the Parma-Bayport and Grand River-Saginaw aquifers to examine the extent of chemical and physical processes affecting their water chemistry.

CHAPTER 3: GRAPHICAL DATA REDUCTION AND RESULTS

INTRODUCTION

Determining the source for solutes in ground water from the Pennsylvanian aquifers involves not only addressing the origin and evolution of brine in the Parma-Bayport aquifer but also investigating the impact of brine from the Parma-Bayport on water chemistry of the Grand River-Saginaw aquifer. A brine source for solutes for many waters in the Grand River-Saginaw aquifer is proposed and data reduction techniques will focus on this idea. Specifically, analysis of Cl/Br ratios for ground water in the Pennsylvanian aquifers will be used to evaluate the source of Cl in the aquifers.

Another type of data reduction implemented in this study involves plotting log ion (Ca, Mg, SO_4 etc.) versus log Br and log Cl to investigate the origin of brine in the system and decipher the impact of brine affecting the chemistry of water found in the Grand River-Saginaw aquifer. Brine is known to exist in the Pennsylvanian bedrock sequence as shown in Figure 3 and formation brine is also present in the underlying Mississippian and Devonian formations. Wilson and Long, (1993) determined the origin of brine in the Devonian Formations from evapo-concentrated seawater and brine in the Marshall aquifer has been shown to have originated through the evaporative concentration of seawater (Meissner, et al., 1992). By analogy to conclusion of brine origin in the Devonian Formations and Marshall aquifer a similar origin for brine in the Parma-Bayport is suggested. Chemical data from the Devonian-age Traverse Group and the Marshall aquifer will be used to compare to brine chemistry in the Parma-Bayport to help in the interpretation of the origin and evolution of the Parma-Bayport brine. Also the brine chemistry of the Parma-Bayport will be compared with concentrated water (> 750 TDS) in the Grand River-Saginaw aquifer to aid in the interpretation of the source for solutes of these waters.

CL/BR RATIO ANALYSIS

Chloride/bromide ratios are useful in the determination of the source of Cl for a given water chemistry. A solution derived through the dissolution of halite would have a Cl/Br ratio of around 3025 (Wilson and Long, 1984), whereas brine in the Michigan basin has Cl/Br ratios ranging from 400 to 600 (Wilson, 1989). The great difference in Cl/Br ratios that a result from different sources of Cl enables the identification of the major source of Cl for a water sample.

Figure 17 is a frequency histogram of data from Grand River-Saginaw aquifer, with values ranging from 7.5 to 1500, with a mean of 367. Distributions of data on the histogram show a strong correlation to Michigan basin brine ion ratios. Many samples plot within brine Cl/Br ratio zone indicating water in the Grand River-Saginaw aquifer is genetically related to formation brine in the Michigan basin. Limited Br data from the most concentrated Parma-Bayport samples prohibits detailed discussion. The data plotting to the left of the Michigan basin brine ratios may indicate fresher water mixing with brine causing dilution of the Cl/Br ratio below 400 expected for brine. Other data plotting to the right of the brine ratio show some dissolution of halite may affect water chemistry. Halite is known to be heterogeneously distributed in the overlying glacial drift (Wood, 1969). Few data exhibit high Cl/Br ratios expected for halite dissolution indicating halite dissolution is only occurring in isolated areas of the aquifer possibly related to road salt contamination of ground water.

BRINE/SALINE WATER SOURCE ANALYSIS

Analysis of Cl/Br ratios indicate the major source of Cl for waters in the Grand River-Saginaw aquifer to be from brine. This next section analyzes water in the Pennsylvanian

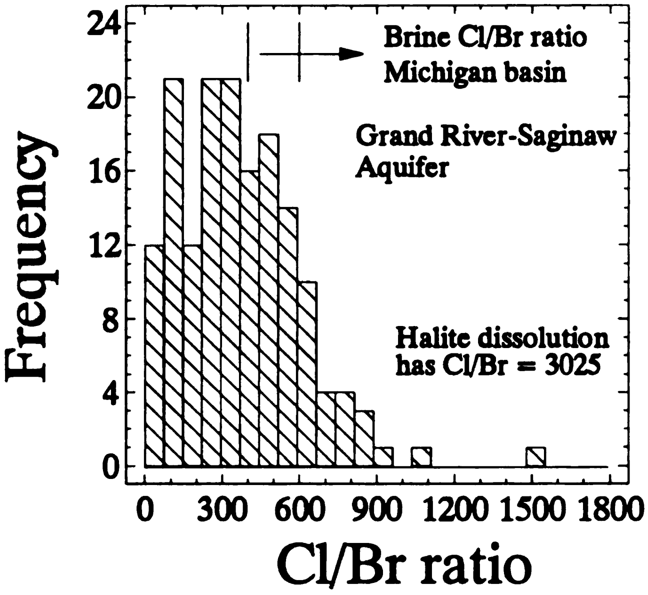


Figure 17a. Frequency histogram of Cl/Br ratios for ground water sampled from the Grand River-Saginaw aquifer.

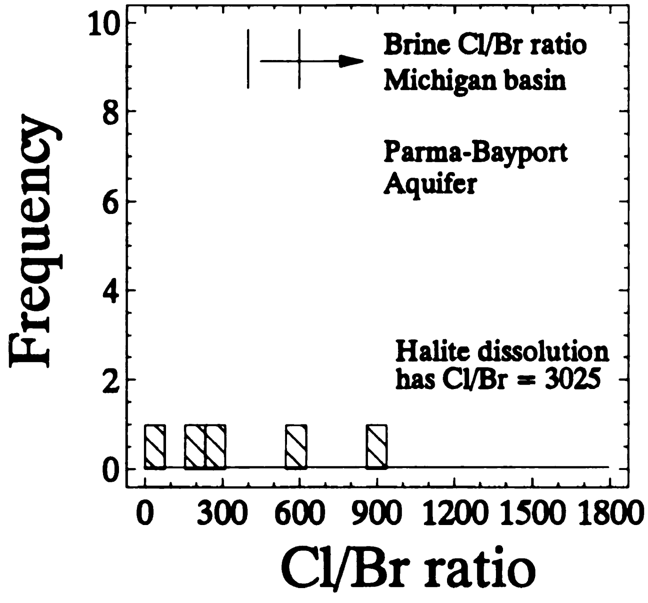


Figure 17b. Frequency histogram of Cl/Br ratios for ground water sampled from the Parma-Bayport aquifer.

aquifers to determine the origin and evolution of Parma-Bayport brine and to determine if the source for solutes for water in the Grand River-Saginaw aquifer are linked to formation brine in the Michigan basin.

Further investigation of the source for solutes for water in the Pennsylvanian aquifers applies the concepts developed by Carpenter (1978). Carpenter (1978) demonstrated how formation water chemistry can be compared with evaporating seawater to make interpretations as to possible origins and evolutions of brine chemistry. The ideas of Carpenter, (1978) will be applied first to determine the origin of brine and saline water in the Pennsylvanian bedrock system and second to compare concentrated water in the Pennsylvanian units to deeper formation brine on the basin. Making the comparison of formation water compositions with the evaporation trends of seawater is justified because the composition of seawater has remained reasonably constant since Cambrian time (Holland, 1978).

The method proposed by Carpenter (1978) is based on the premise that brines produced by the evaporation of sea-water will be moved from their point of origin as a result of sediment compaction, tectonic deformation, and other processes. The result of this in the case of the Michigan basin is the potential, certainly in the past and possibly today, for interaction between brine and meteoric water. This mixing between brine and less concentrated waters in the Michigan basin may be an explanation for the occurrence of concentrated waters found in the Pennsylvanian bedrock sequence and in the overlying Glacial-Drift aquifer.

During the evaporative concentration of seawater the ratios of ions within a solution remain constant until the onset of mineral precipitation. The constant relationship between ions is expressed as $B/A=k$ or $B=kA$, where A and B are ions and k is a constant. The logarithmic form of this equation is: $\log B = \log A + \log k$ and a plot of $\log_{10}A$ versus $\log_{10}B$ produce a straight line with a 1:1 slope regardless of the value of k; therefore any ion that deviates from this relationship is affected by processes other than removal of water molecules from solution (Carpenter, 1978). To investigate the chemical history of brine derived from seawater the use of one or more conservative constituents are required. A conservative constituent may neither precipitate/dissolve nor participate in diagenetic reactions with subsequent mineralogical environments (Carpenter, 1978). Hence, a plot of a conservative ion concentration versus the degree of evaporation would be a straight line. During the initial evaporation of seawater, both Cl and Br behave conservatively and increase in concentration, however the Cl/Br ratio remains constant at its normal seawater value (Carpenter, 1978; McCaffrey et al., 1987). Figure 18 shows that if solutes in water were derived from the dissolution of halite Cl/Br ratios would plot near region A whereas solutions plotting near regions B and C are representative of water derived through the evapo-concentration of seawater (Long, personal commun., 1992). In addition, log ion:log Br and log ion:log Cl plots can indicate if a brine has been affected by dilution with seawater or freshwater (Carpenter, 1978). In the following comparisons Br and Cl are used as conservative indicators for the degree of evaporation reached by seawater from some of the concentrated waters aquifers and also as an indicator of rock-water interaction that may have taken place. Chloride was also used as a conservative indicator as few samples are concentrated beyond halite saturation. Ion:Br and ion:Cl plots will be used to evaluate similarities between brine in the Parma-Bayport aquifer and Mississippian and Devonian brine of the Michigan basin and evaluate hypothesized mixing between brine and meteoric water in the Pennsylvanian aquifers.

Land and Prezbindowski, (1981) suggest caution must be applied in making the above interpretations. Land and Prezbindowski, (1981) state if a dissolution reaction was a reversible chemical reaction and the partitioning coefficient still determined the Cl/Br ratio in the solid and solution the solution at equilibrium with halite would have a much lower Cl/Br ratio than suggested above. The result of this is waters formed by halite dissolution may plot along seawater evaporation trajectory causing erroneous and ambiguous interpretations. Considering the nature and rates of reactions, brine from a reservoir

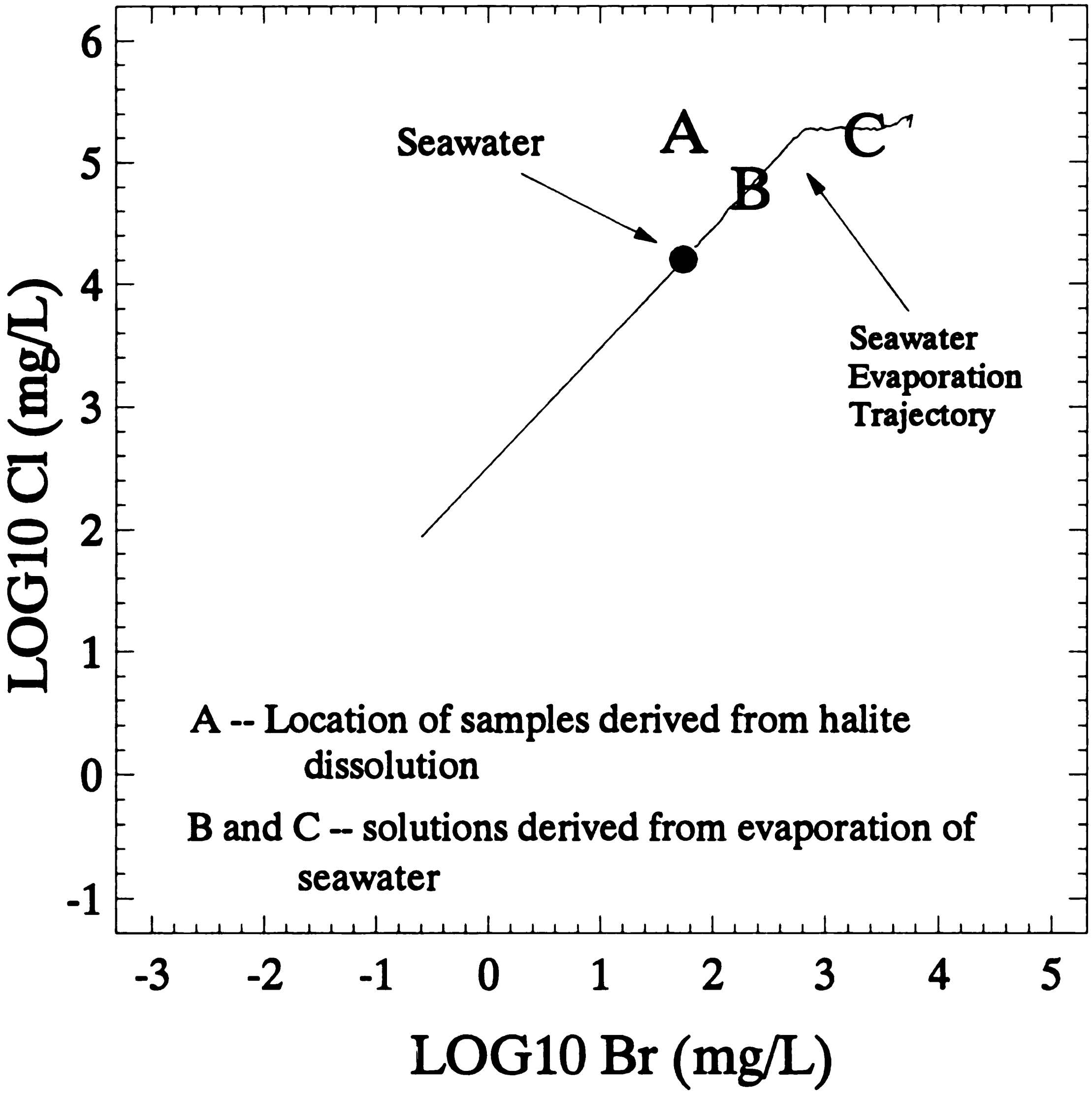


Figure 18. Interpretation of brine origin from location around seawater evaporation trajectory.

formed through halite dissolution that plot as a cluster on the seawater evaporation trajectory will be expected to be rare (Wilson and Long, 1984). Also Cl/Br ratios acquired through subaerial evaporation or subsurface interactions with evaporite deposits, are subsequently preserved for interpretation because these anions generally do not participate in diagenetic reactions with other minerals (Stuebber and Walter, 1991) making interpretations of processes affecting brine chemistry based on ion ratio plots is justified.

Origin of brine

Figure 19 depicts the relationship between the water chemistry of the Traverse Group, Marshall aquifer, Parma-Bayport and Grand River-Saginaw aquifers that is consistent with a model in which freshwater is mixing with formation brine (Long et al, 1993). The more concentrated waters show a close correspondence with the seawater evaporation trajectory indicating a source from evaporated seawater as plausible for Parma-Bayport brine. Lesser concentrated waters extend along a concentration continuum indicating dilution below seawater composition. Data distribution shows a scattering of dilute waters from the Pennsylvanian and Mississippian aquifers indicating a freshwater end-member with variable Cl and Br concentration exists. This dilute end-member appears to be mostly unaffected by mixing with more concentrated waters indicating that other source of solutes exists for the dilute waters in the system.

Sodium-chloride relations are shown on Figures 20 and 21 and provide better evaluation of the mixing relationships described above from Cl-Br relations as more data exists. Overall distribution of Figure 20 and 21 shows a similarity between Parma-Bayport brine with less concentrated Mississippian brine on this diagram as they plot along the evaporation of trajectory just short of halite saturation. A decreasing degree of concentration is noted from the Traverse > Marshall > Parma-Bayport > Grand River-Saginaw aquifer from data distribution on both Figures 20 and 21. As in the previous

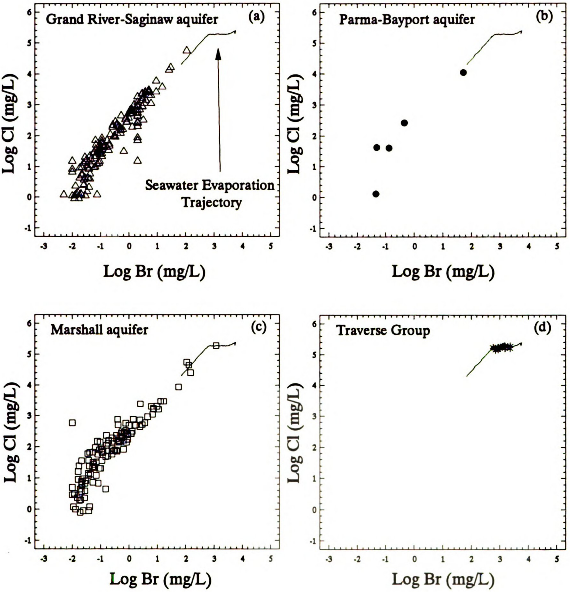


Figure 19. Cl-Br relations of ground water from the Grand River-Saginaw (a), Parma-Bayport (b), and Marshall (c) aquifers and Traverse Group (d) waters with the evaporation of seawater trajectory (McCaffery et al., 1987).

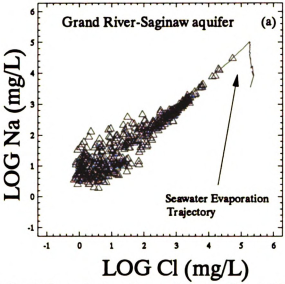


Figure 20a. Na-Cl relations of ground water from the Grand River-Saginaw aquifer with evaporation of seawater trajectory (McCaffery et al., 1987).

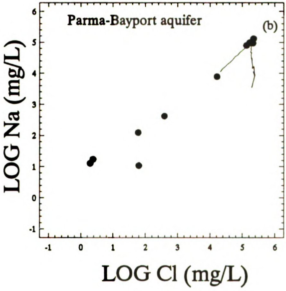


Figure 20b. Na-Cl relations of ground water from the Parma-Bayport aquifer with evaporation of seawater trajectory (McCaffery et al., 1987).

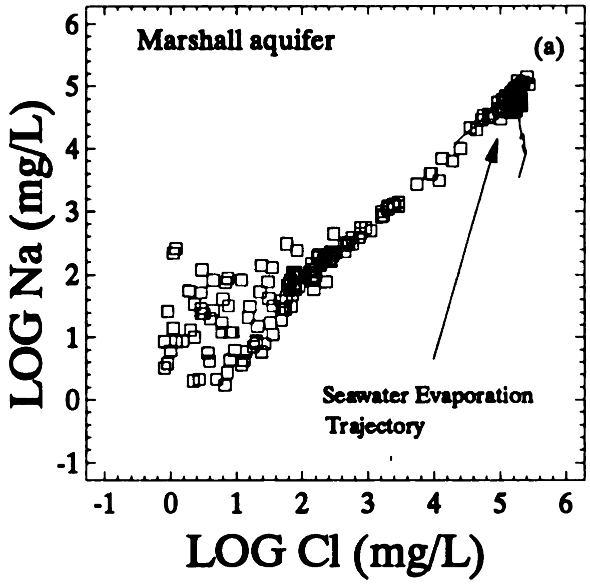


Figure 21a. Na-Cl relations of ground water from the Marshall aquifer with evaporation of seawater trajectory (McCaffery et al., 1987).

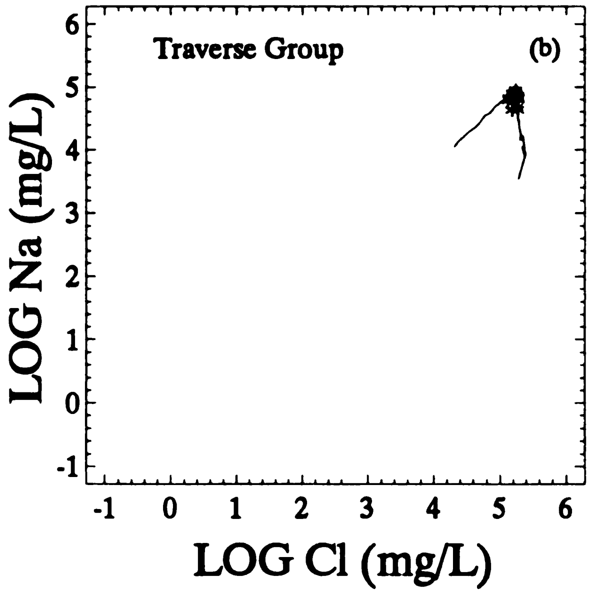


Figure 21b. Na-Cl relations of ground water from the Traverse Group with evaporation of seawater trajectory (McCaffery et al., 1987).

figure a dilute end-member water mass exists that is mostly unaffected by brine chemistry. Good evidence is provided for a mixing relationship between Pennsylvanian brine with more dilute Pennsylvanian waters similar to Stueber and Walter, (1991) who showed dilution of Silurian and Devonian brine by meteoric waters in the Illinois basin.

Chemical Changes in the Subsurface

Departure from an ion:Br or ion:Cl seawater evaporation trajectory indicates changes in chemical composition of evaporated seawater that has occurred as a result of diagenetic reactions in the subsurface (Steuber and Walters, 1991). As shown above Na corresponds well to the seawater evaporation trajectory indicating little impact of rock-water interaction impacting Na concentrations of more concentrated water.

Potassium-bromide and potassium-chloride relations are shown on Figure 22 and 23 respectively. Data distribution indicates K depletion with respect to the seawater evaporation trajectory. Carpenter, (1978) suggests a depletion of K from a brine is due to reactions with low K clay minerals such as kaolinite to produce K rich clays such as illite, as well as authigenic K-feldspar. Wilson, (1989) attributed alumino-silicate reactions as the cause for depletion of K in Devonian brine.

Calcium-bromide and calcium-chloride relations are shown on Figures 24 and 25 respectively. Relations between Ca-Cl and Ca-Br reveal Ca enrichment relative to the seawater evaporation trajectory and a dilution trend extends downward from the most concentrated samples. Magnesium-bromide and magnesium-chloride relations on Figures 26 and 27 show a complementary depletion in magnesium concentration relative to the seawater evaporation trajectory. A mechanism to elevate Ca and deplete Mg concentration is dolomitization of limestone (Carpenter, 1978). Wilson, (1989) in a study of Devonian and Silurian formation brine of the Michigan basin found dolomitization to be a major diagenetic reaction controlling Ca and Mg concentrations. In this study Wilson

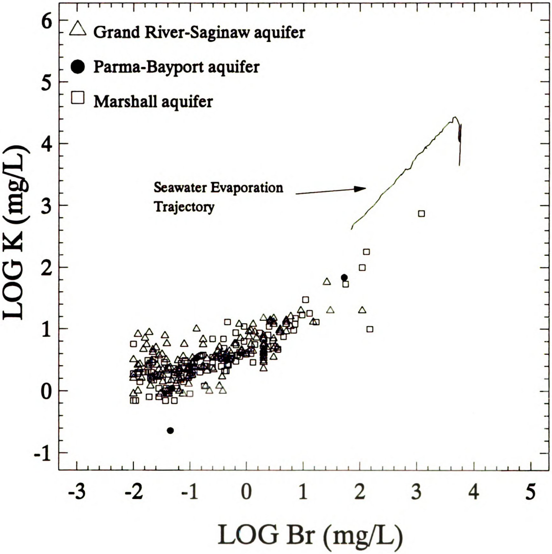


Figure 22. K-Br relations of ground water from Grand River-Saginaw, Parma-Bayport, and Marshall aquifers with evaporation of seawater trajectory (McCaffery et al., 1987).

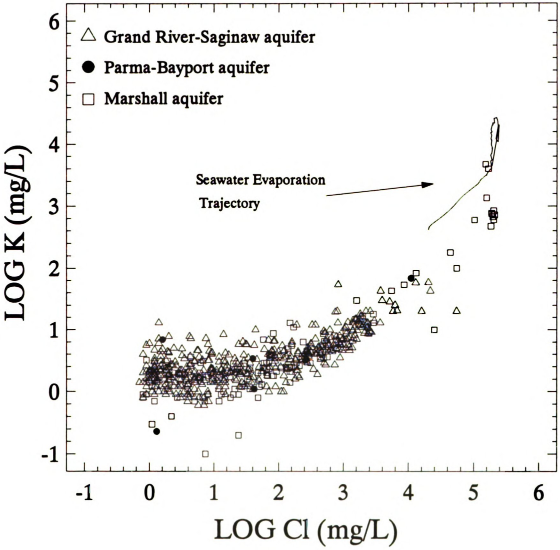


Figure 23. K-Cl relations of ground water from Grand River-Saginaw, Parma-Bayport, and Marshall aquifers with evaporation of seawater trajectory (McCaffery et al., 1987).

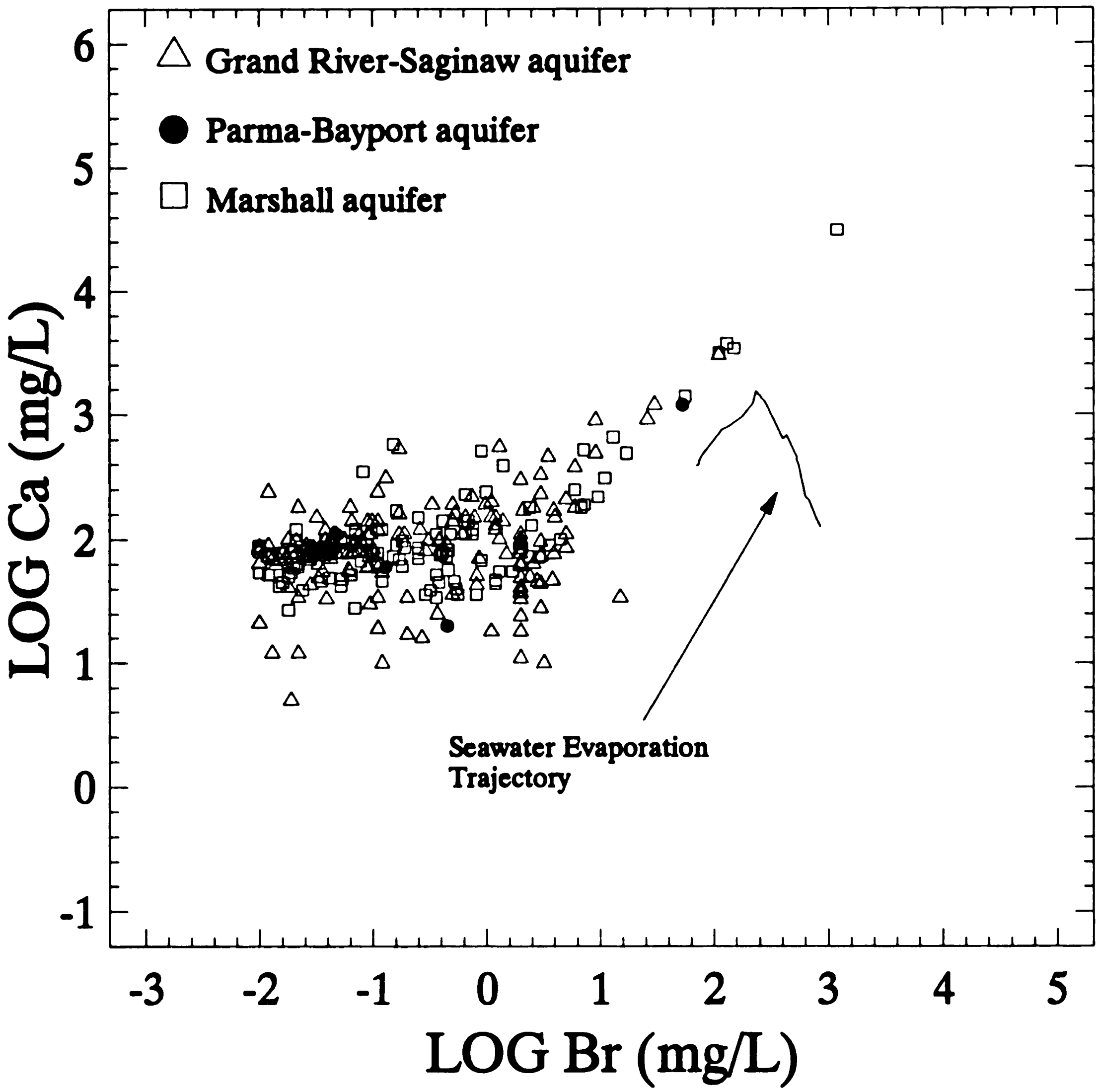


Figure 24. Ca-Br relations of ground water from Grand River-Saginaw, Parma-Bayport, and Marshall aquifers with evaporation of seawater trajectory (McCaffery et al., 1987).

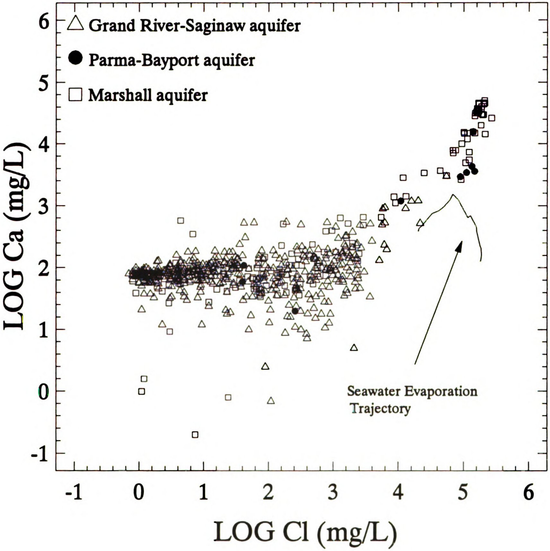


Figure 25. Ca-Cl relations of ground water from the Grand River-Saginaw, Parma-Bayport, and Marshall aquifers with evaporation of seawater trajectory (McCaffery et al., 1987).

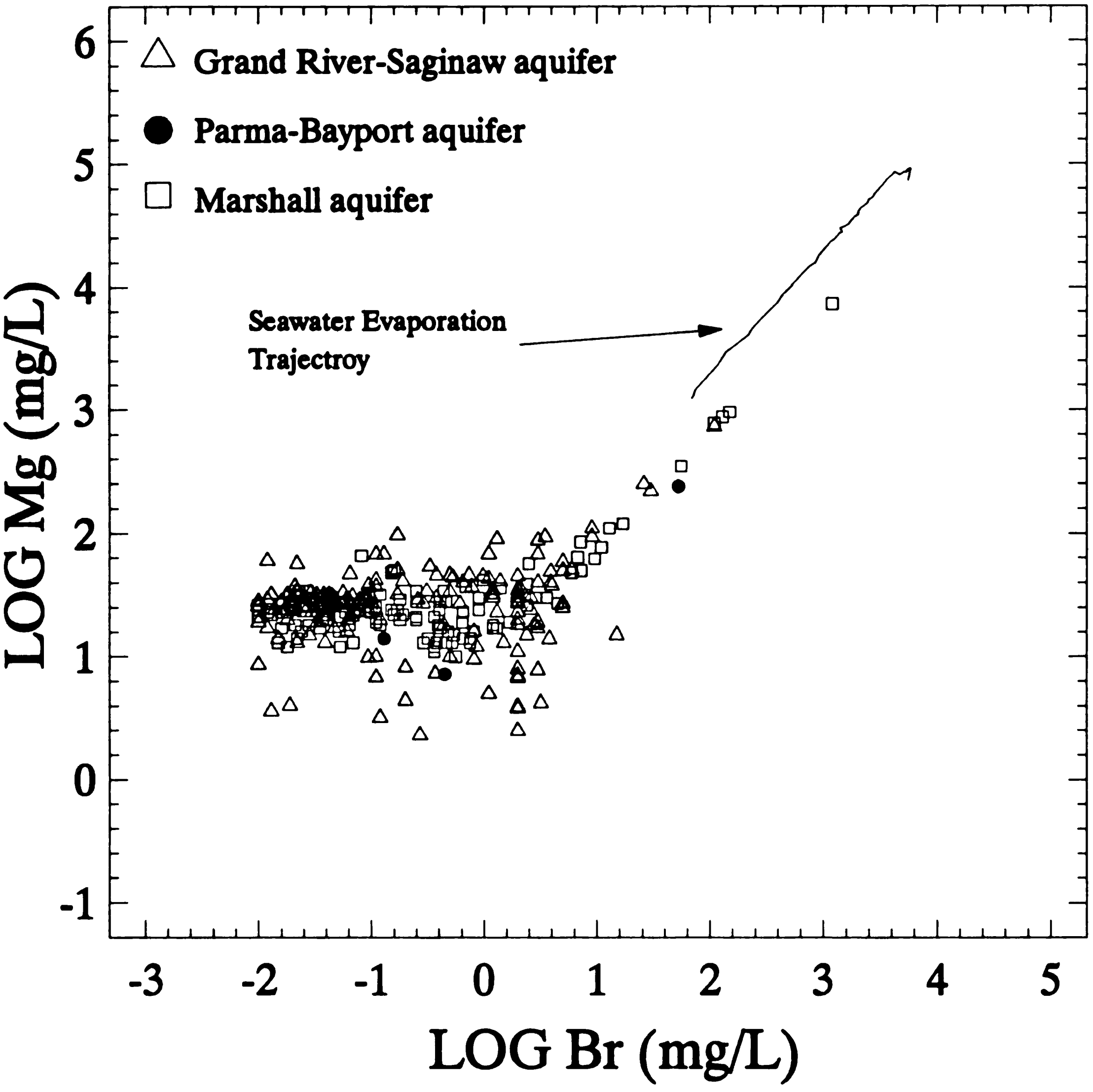


Figure 26. Mg-Br relations of ground water from Grand River-Saginaw, Parma-Bayport, and Marshall aquifers with evaporation of seawater trajectory (McCaffery et al., 1987).

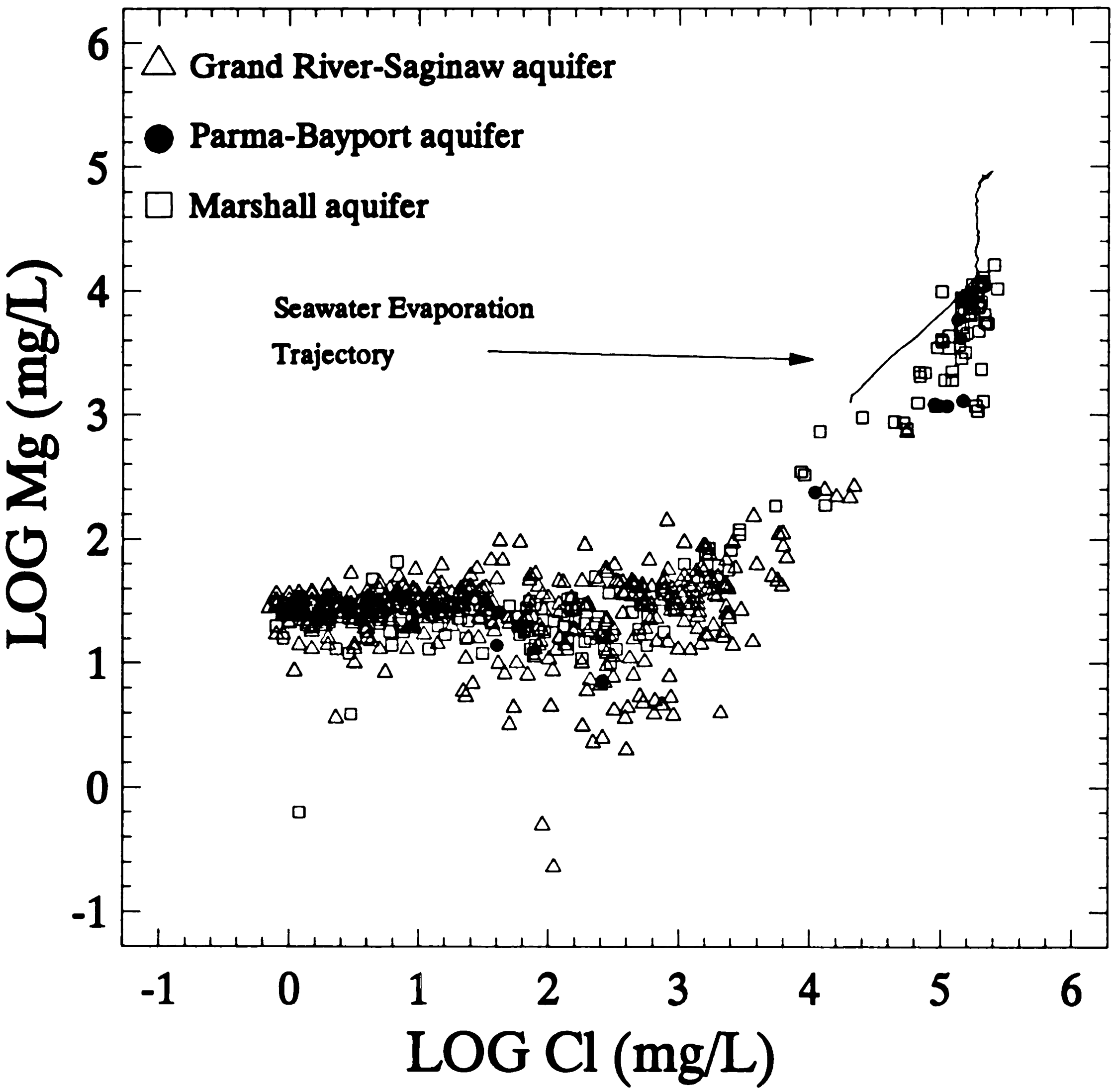


Figure 27. Mg-Cl relations of ground water from Grand River-Saginaw, Parma-Bayport, and Marshall aquifers with evaporation of seawater trajectory (McCaffery et al., 1987).

used the 1:1 relationship of Ca enrichment to Mg depletion through the dolomitization reaction to test his data. The difference in Mg in each sample and equivalently concentrated seawater was calculated based on measured Br in each sample. This Mg deficiency was assumed to result only from dolomitization and so was converted to a predicted Ca concentration based on a 1 for 1 mole replacement. Wilson then adjusted the predicted Ca for $CaSO_4$ dissolution and then compared Ca to Mg. Similar enrichment and depletion behavior in Ca and Mg concentrations are noted in Parma-Bayport waters, however the degree of enrichment and depletion is not 1:1 as Wilson found for Devonian brines. Specifically, 2 data points, one from the western region of the study area and one from the center of the study area are more Ca enriched than Mg depleted indicating an additional control on Ca concentration than dolomitization. The added Ca could be the result of gypsum dissolution known to exist in Jurassic deposits in that part of the study area. Unfortunately, no sulfate data exists for the two westernmost samples to investigate this hypothesis. Three data points in Saginaw Bay Area indicate an even Mg depletion and Ca enrichment similar to Marshall and Devonian brine. Similar to previous Figures, Ca and Mg relations relative to Cl and Br indicate a dilute end-member water not related to brine chemistry.

Sulfate-bromide and sulfate-chloride relations are shown on Figure 28 and 29. In all three aquifers sulfate depletion is noted with respect to the seawater evaporation trajectory. Wilson, (1991) noted sulfate reduction as a process causing depletion of sulfate in Devonian and Silurian formation brine. A similar data distribution exists for the Marshall and Parma-Bayport aquifer brine implying a similar process is impacting or has impacted these waters. The distribution of Parma-Bayport brine data on Figure 29 appears to bridge the gap between Marshall brine samples and concentrated waters from the Grand River-Saginaw aquifer. This distribution does not appear top be a artifact of sampling from the Marshall aquifer as analysis of Cl and SO_4 distribution maps for the Marshall aquifer indicate that no waters exists in the aquifer with Cl and SO_4

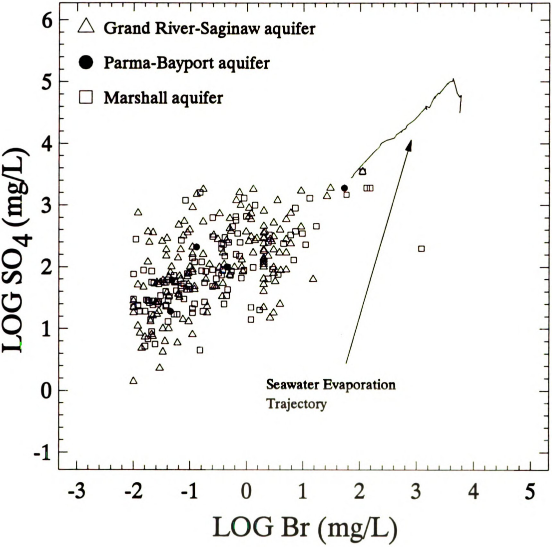


Figure 28. SO_4-Br relations of ground water from Grand River-Saginaw, Parma-Bayport, and Marshall aquifers with evaporation of seawater trajectory (McCaffery et al., 1987).

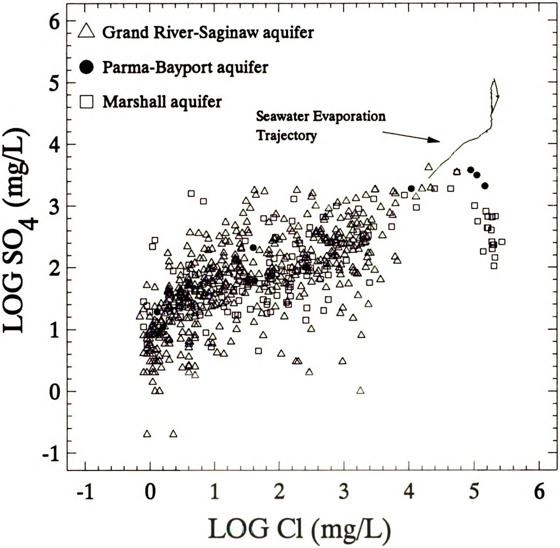


Figure 29. SO_4-Cl relations of ground water from Grand River-Saginaw, Parma-Bayport, and Marshall aquifers with evaporation of seawater trajectory (McCaffery et al., 1987).

concentrations necessary to plot in that region of Figure 29. This may indicate that the Marshall brine is mostly isolated from mixing with fluids in overlying aquifers and that the major source for solutes for the more concentrated waters in the Grand River-Saginaw aquifer are derived primarily from the Parma-Bayport brine.

Carpenter Function Analysis

A further test to link the chemistry of Michigan basin brine with the chemistry of Pennsylvanian groundwaters relies on Carpenter's, (1978) approach to account for diagenetic reactions involving divalent cations and carbonate and sulfate minerals to deduce whether a brine originated from evaporation of seawater followed by such reactions or if the brine had a more complex origin. Added complexities might include diagenetic reactions involving monovalent cations, silicate minerals or halite. The quantity of divalent cations charge balanced by only Cl was defined by:

$$CF = Ca + Mg + Sr - HCO_3 - SO_4$$

This approach is defined as the Carpenter Function (CF). Plot CF versus Br, and evaporating seawater defines a trajectory unaffected by dolomitization, recrystallization or precipitation of $CaCO_3$ or $CaSO_4$ precipitation (Carpenter,1978). Plots of CF versus Br and Cl versus CF were prepared to further correlate water chemistry of concentrated waters in the Pennsylvanian units to that of underlying brine. The CF values for brine samples were calculated using the formula:

$$CF = Ca + Mg - SO_4$$

because HCO_3 concentrations are low.

Figure 30 indicates a trend of the more concentrated samples toward the seawater evaporation trajectory for limited Pennsylvanian water samples. This distribution of data

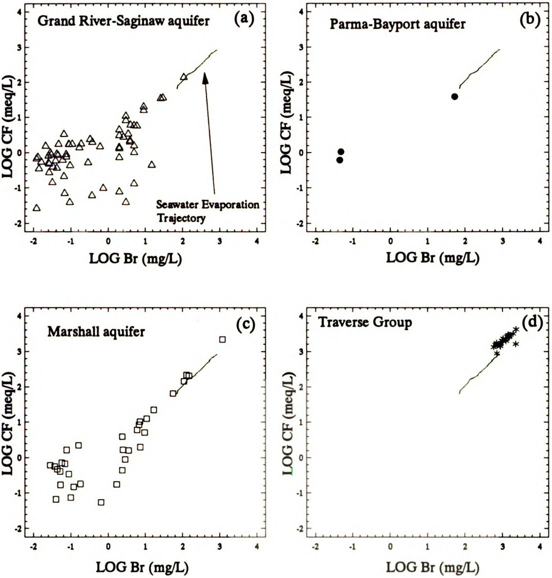


Figure 30. Carpenter Function (CF)-Br relations of ground water from the Grand River-Sagianw (a), Parma-Bayport (b), and Marshall aquifers (c), and Traverse Group (d) waters with evaporation of seawater trajectory (McCaffery et al., 1987).

compliments Cl:Br (Figure 19) and Na:Cl (Figures 20 and 21) plots by indicating a mixing of waters in the Michigan basin. A similar distribution is recognized for Marshall and Traverse samples that plot to the left of the seawater evaporation trajectory line. The Cl:CF (Figure 31) plot is also similar to the Cl:Br and Na:Cl plots in matching the seawater trend, however the Cl:CF plot apparently reflects higher degrees of evapo-concentration than are predicted by other plots. The overall data distribution on Figure 31 shows an excellent decreasing degree of concentration from Devonian to Marshall which plot beyond halite precipitation to Parma-Bayport and then to Grand River-Saginaw samples plotting above and near to seawater composition. A dilution trend is apparent for concentrated Mississippian and Pennsylvanian waters extending downward from seawater composition. This concentration continuum implies a common origin for solutes for water >750 mg/L in the system. One interesting trend noted on Figure 31 is 1 sample from the Grand River-Saginaw and 3 samples from the Parma-Bayport plot to the left of the seawater evaporation trajectory whereas all data but 1 sample analyzed from the Marshall and 1 from the Traverse-Dundee plot to the right of the line. This Cl enrichment indicated by a few Pennsylvanian waters poses an interesting problem not presented in other figures thus far. This problem may be explained one of three ways: 1) This data although hardly representative of the entire Parma-Bayport brine may indicate that it is not entirely similar to the deeper formation brine present in the basin and does not share a similar evolutionary history; 2) even though previous plots indicate chemical similarities with limited data from the Parma-Bayport one cannot completely exclude the possibility that the Parma-Bayport brine was not affected by other diagenetic alterations than those of deeper formation brine in the basin ; 3) analytical error associated with sampling a brine may skew these data as the quality of the Parma-Bayport brine data must be considered. The third explanation provided above seems the most likely choice.

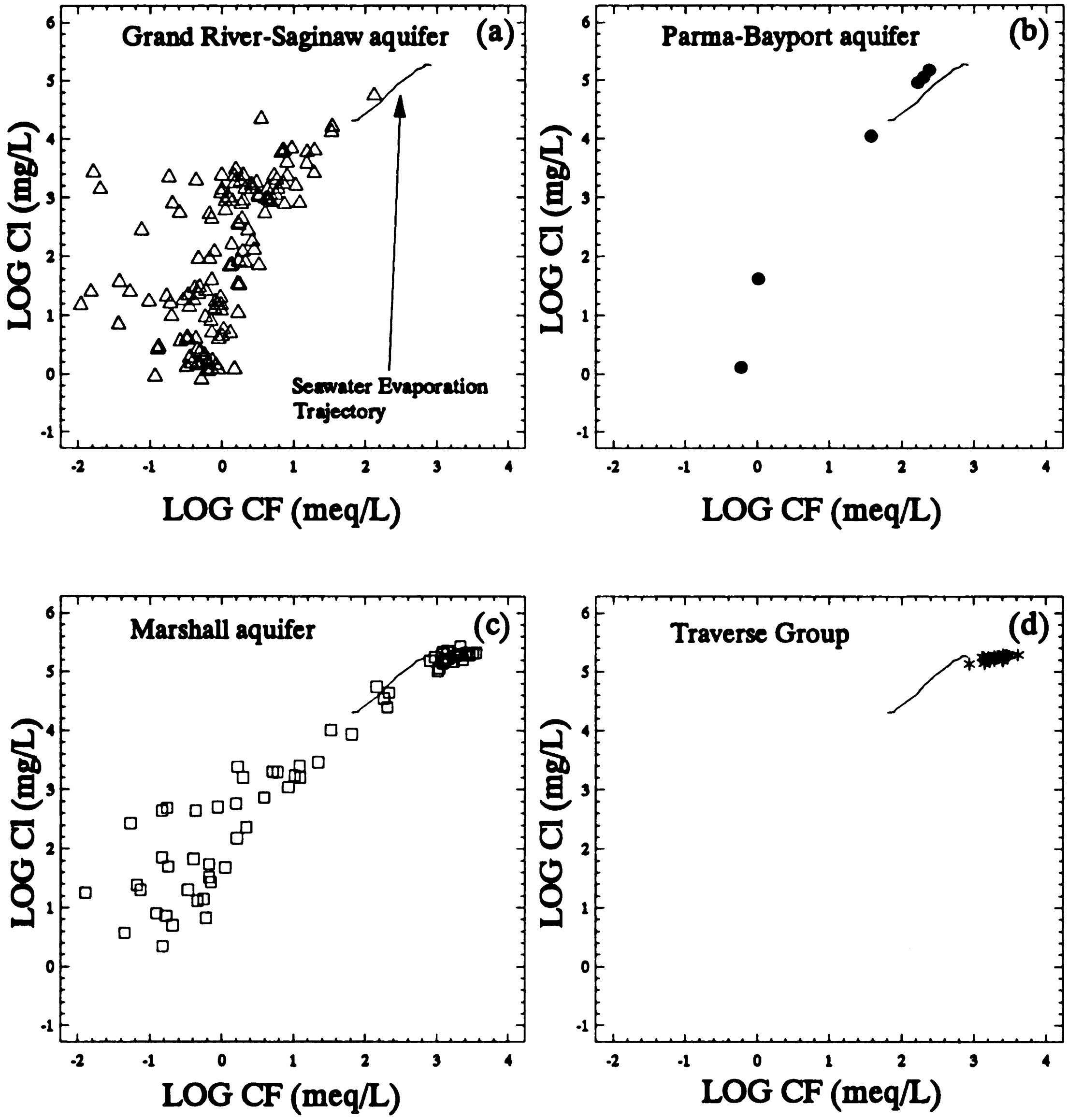


Figure 31. CF (Carpenter Function)-Cl relations of ground water from the Grand River-Saginaw (a), Parma-Bayport (b), and Marshall aquifers (c) and Traverse Group water (d) with evaporation of seawater trajectory (McCaffery et al., 1987).

SUMMARY

Frequency histograms of Cl/Br ratios of water from Grand River-Saginaw and Parma-Bayport aquifers indicate the major source of Cl is more likely from a brine source than from the dissolution of halite. This points to the importance of the Parma-Bayport brine as a source of solutes to concentrated waters of the Grand River-Saginaw aquifer.

It appears that Cl:Br (Figure 19) and Na:Cl (Figures 20 and 21) relations imply that the origin of brine in the Parma-Bayport aquifer is from evaporative concentrated seawater just short of halite saturation and K:Br and K:Cl (Figures 22 and 23), Ca:Br and Cl (Figures 24 and 25), Mg:Br and Cl (Figures 26 and 27), and SO_4:Br and Cl (Figures 28 and 29) show the more concentrated waters may be affected by alumino-silicate reactions, some degree of dolomitization, and sulfate reduction, and possibly affected by gypsum dissolution. Without more data from the aquifer a definitive origin of the brine cannot be reached. Data from brine in the Parma-Bayport was found to be geochemically similar to brine found in the Marshall Sandstone and Traverse Group albeit not as concentrated, lending credibility to its implied origin, even though a slight deviation is noted from CF:Cl plot (Figure 31).

Ion:Br and ion:Cl relations (Figures 19-31) indicate a link between the Parma-Bayport brine and concentrated waters from the Grand River-Saginaw aquifer. The Parma-Bayport brine appears to provide the source for solutes for much of the Grand River-Saginaw aquifer. A concentration continuum observed on Figures 19 to 31 imply a common origin for solutes of more concentrated waters in the system. Also the ion:Br and ion:Cl relations show that not only a Cl-rich end-member water mass (Parma-Bayport brine) exists but also a dilute end-member water mass is important in explaining the geochemistry of all waters in the Pennsylvanian aquifers. The Cl-rich end-member is shown to be impacting the water chemistry of ground water in the Grand River-Saginaw aquifer indicated by the mixing trend downward from the seawater evaporation trajectory on ion:Br and ion:Cl plots. The scatter of data associated with the dilute end-member indicates that these samples are mostly isolated from interaction with brine as a source of solutes and therefore the solutes are derived from a different source, i.e., rock-water interaction. Figure 32 summarizes location of water masses discussed on the previous diagrams.

It is important to note the location of the dilute and more concentrated water masses of the Grand River-Saginaw aquifer discussed. In general the more concentrated water is mainly found in and around the Saginaw Bay Area as well as the east-center part of the study area. Dilute water in the system is typically located in the southern part of the aquifer as well as around the fringes of the aquifer. These generalized distributions are not an artifact of sampling for what they do indicate is that different processes are operating in different parts of the aquifer controlling ground water chemistry.

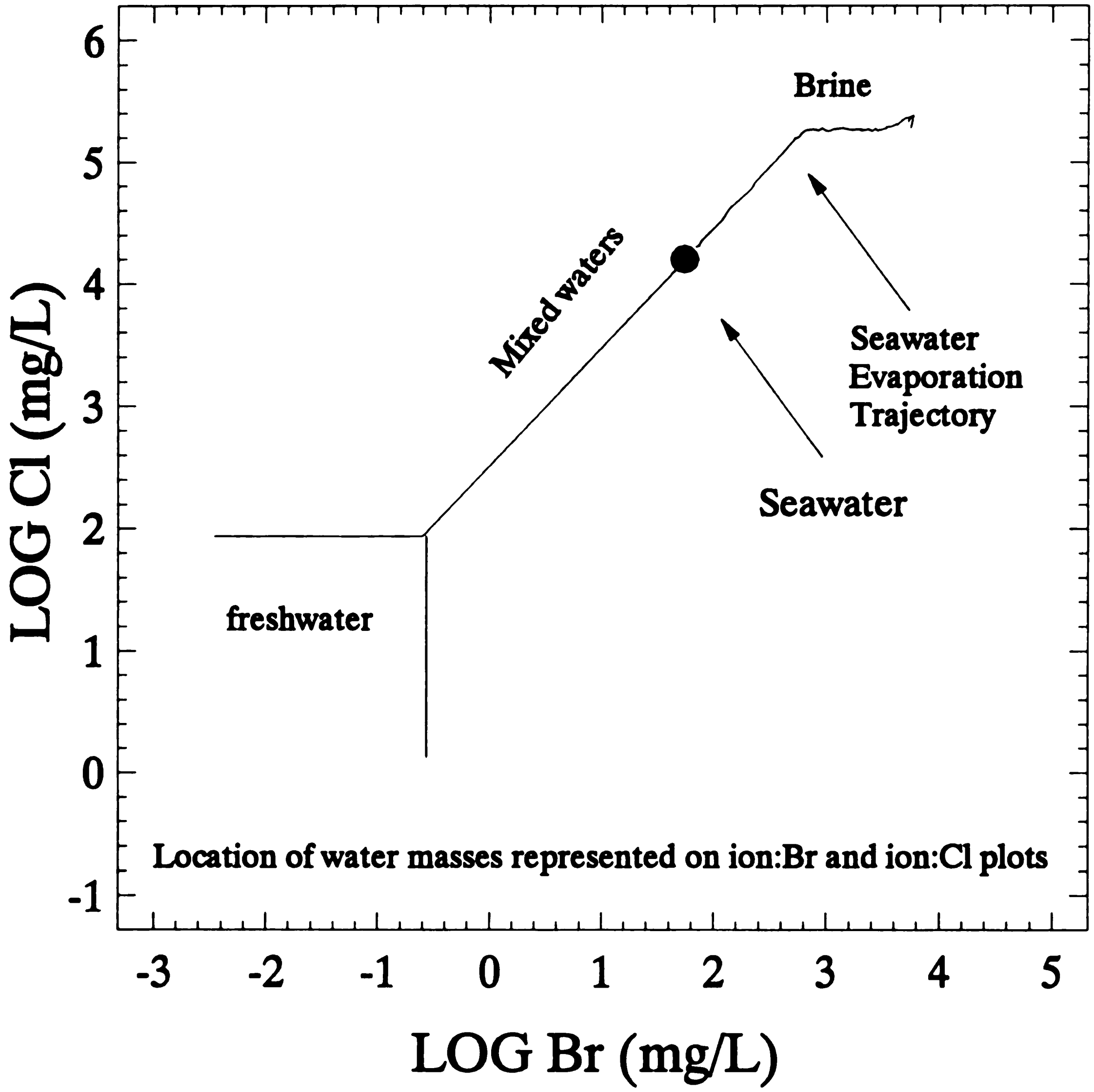


Figure 32. Cl-Br relations with evaporation of seawater trajectory presenting the location of water masses portrayed on a generalized Cl:Br plot. Designated locations on the figure are based on trends portrayed on previous diagrams (figures 19 to 31).

CHAPTER 4: CHEMICAL MODELING

INTRODUCTION

An additional technique used to determine controls on the chemistry of natural waters involves the use of geochemical models. The chemistry of groundwaters may be greatly influenced by rock-water interactions and a geochemical model, such as WATEQ4F, can be used to determine which dissolution precipitation and oxidation-reduction reactions may be proceeding in the aquifer. As indicated earlier a source of solutes for more concentrated water in the Pennsylvanian aquifers appears to be from brine present in the deeper Pennsylvanian system and in the Mississippian and Devonian bedrock sequences. The dilute end-member (dissolved solids <750) present in many of the diagrams above seems mostly unimpacted by the brine chemistry and therefore the solutes in these less concentrated waters must be supplied from a different source, i.e. rock water interaction or from solutes derived from the Glacial-Drift aquifer. Wood, (1969) indicated in the southern portion of the Pennsylvanian subcrop that water in the overlying Glacial-Drift aquifer was more concentrated than the water in the Grand River-Saginaw aquifer indicating a source of solutes to the Grand River-Saginaw aquifer from the Glacial-Drift aquifer and the potentiometric surface indicates a hydraulic connection between the drift and Grand River-Saginaw aquifer.

WATEQ4F, a chemical speciation code for natural waters was used to model water from the Grand River-Saginaw aquifer. The model uses field measurements of temperature, pH, Eh, dissolved oxygen, alkalinity, the chemical analysis of a water sample and calculated density of each sample as input and calculates the distribution of aqueous species, ion activities and mineral saturation indices that indicate the tendency of a water to precipitate or dissolve a set of minerals (Ball et al, 1991). WATEQ4F achieves this by relying on the concepts of thermodynamic equilibrium, the Debye-Huckel/ B dot equation for activity coefficients and experimental equilibrium and speciation constants and by iteratively solving a series of simultaneous equations that determine equilibrium constants and mass balance equations for each component in the system. The calculation provides saturation indices (SI) of minerals that may be reacting in the system. The SI of a particular mineral is defined as:

$$SI = \log \frac{IAP}{K_t}$$

where IAP is the ion activity product of the mineral water reaction and K_t is the thermodynamic equilibrium constant adjusted to the temperature of the given sample. The SI is approximately equal to 0 when a water sample is at equilibrium with a particular mineral phase. When the SI is greater than 0 the water is supersaturated with respect to that mineral and the precipitation of that mineral would be possible. An SI less than 0 indicates undersaturation with respect to the mineral phase and suggests the mineral will undergo dissolution. Speciation calculations show the reliable results up to the ionic strength of seawater (ionic strength=.72) (Ball and Nordstrom, 1991). Only one sample exceeded this degree of concentration in the Grand River-Saginaw aquifer, all other data fall within the limits of the model. The success of the model is dependent upon high quality data and accurate and internally consistent thermodynamic data base. Data with only less than 10 percent difference in charge balance were modeled and the most complete thermodynamic data set available for solubility product constants and ion association constants including data from Nordstrom et al., (1990) was used. Table 2 includes equilibrium constants used in modeling.

The chemical model WATEQ4F was implemented to analyze the degree in which mineral components of the aquifers may be reacting with groundwater. Three mineral systems will be investigated: the carbonate system (calcite, dolomite and aragonite),

Table 2. Selected Thermodynamic data used in WATEQ4F calculations of saturation indices.

MINERAL NAME	LOG K	REFERENCE
Anhydrite	-4.36	Nordstrom et al., (1990)
Aragonite	-8.336	Plummer and Busenberg, (1982)
Calcite	-8.48	Plummer and Busenberg, (1982)
Chalcedony	-3.55	Nordstrom et al., (1990)
Dolomite	-16.54	Nordstrom et al., (1990)
Gypsum	-4.58	Nordstrom et al., (1990)
Halite	1.582	Robie and Waldbaum, (1968)
Quartz	-3.98	Nordstrom et al., (1990)

evaporite minerals (gypsum, anhydrite, and halite), and silicate and alumino-silicate minerals (quartz and chalcedony). The mineral phases chosen are a reflection of aquifer matrix and aquifer cements (carbonate minerals and silica), evaporites were chosen due to presence in overlying Glacial-Drift aquifer and Jurassic deposits. The output from the model pertaining to these minerals will be used in evaluating their impact on water chemistry in the Grand River-Saginaw aquifer. Frequency histograms and discussion of the distribution of mineral saturation index values from selected compounds are one result of chemical modeling. Also activity-activity or mineral stability diagrams are useful in interpreting chemical modeling data.

Density Determination

The density of each water was used as input for the model and therefore needed to be calculated. The density of water varies with temperature and salinity and it is possible to calculate the density of a water sample by using a series of equations described by Gudramovics, (1981). At constant temperature, the relationship between density and salinity is linear. Salinity was estimated from the chloride concentration by equation (1) (Schopf, 1980):

$$\text{(1) Salinity (‰)} = 1.80655 * (\text{Cl (‰)})$$

To calculate the density of water at the measured temperature in the well, the value of the y-intercept and slope must be calculated. The y-intercept refers to the density of pure water at a specified temperature and is determined through equation (2) (Weast, 1979):

$$\text{(2) y-intercept} = (999.83952 + 16.945176 * T - 7.9870401 * 10^{-3}\,T^{2} - 46.170461 * 10^{-6}\,T^{3} + 105.56302 * 10^{-9}\,T^{4} - 280.54253$$

$$* 10^{-12} T^5) / (1 + 16.87985 * 10^{-3} * T) * 1000$$

The slope for the specified temperature is calculated by equation (3) (Horne, 1969):

$$(3)\ \text{Slope} = 8.300245 * 10^{-4} - 2.2274915 * 10^{-5} * \ln T$$

Once the salinity, y-intercept and slope were calculated at the temperature of the sample, the density was calculated by equation (4):

$$(4)\ \text{Density} = (\text{Salinity} * \text{Slope}) + \text{y-intercept}$$

RESULTS AND DISCUSSION

Carbonate Minerals

Figures 33, 34 and 35 show distribution of saturation indices for calcite, aragonite, and dolomite. Average calcite saturation index of .054 indicates that calcite is near equilibrium with waters throughout most of the aquifer. Calcite SI distribution shows some supersaturation with respect to calcite in the southern portion of the study area that may be a reflection of water in this recharge area being influenced by the removal of CO_2 from solution enhancing the aggressiveness of the water in dissolving solids, such as calcite (Domineco and Schwartz, 1990). Calcite SI values in and around Saginaw Bay Area are undersaturated with respect to calcite. This may indicate the mixing of two fluids as the mixing of two solutions at equilibrium with calcite can result in a solution undersaturated or supersaturated with respect to calcite (Langmuir, 1971). This is due to the non-linear relationship between the concentration of Ca and the partial pressure of CO_2 in equilibrium with calcite (Drever, 1988). Also the Saginaw Bay Area may be lacking in

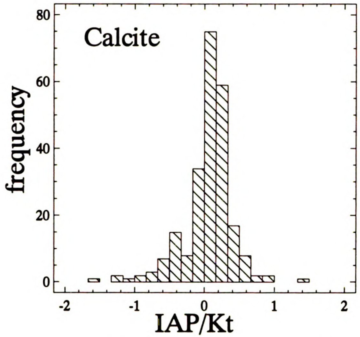


Figure 33. Frequency histogram for calcite saturation index values for ground water from the Grand River-Saginaw aquifer.

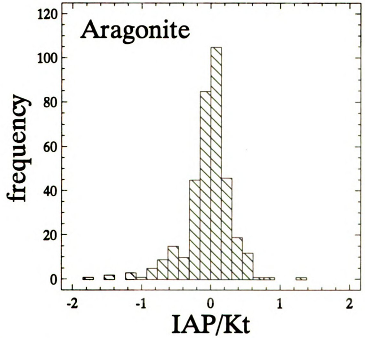


Figure 34. Frequency histogram for aragonite saturation index values for ground water from the Grand River-Saginaw aquifer.

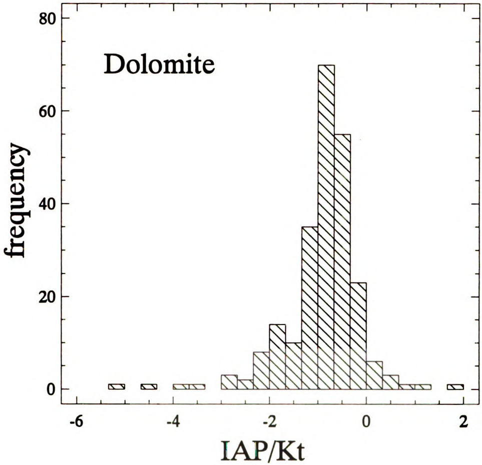


Figure 35. Frequency histogram of dolomite saturation index values for ground water from the Grand River-Saginaw aquifer.

carbonate material and therefore carbonate equilibrium is not a control in the Saginaw Bay Area (Long et al., 1988). The average SI of dolomite and aragonite of -.9014 and -.0993 respectively suggest that waters are slightly undersaturated with respect to these minerals throughout the aquifer. No major trend in SI distribution is noted with either dolomite or aragonite within the study area, a fairly consistent distribution of data is observed. Similar SI values for calcite, aragonite and dolomite are noted in the Glacial-drift aquifer in the southern and fringe areas of the aquifer.

Evaporite minerals

Figures 36, 37 and 38 show distribution of SIs for halite, gypsum, and anhydrite from Pennsylvanian waters. Waters are undersaturated with respect to halite and gypsum throughout the study area. The average SI of gypsum is -1.6718, and halite with an average SI of -6.2300 appears to be highly undersaturated with respect to halite.

Alumino-Silicate and Silicate minerals

The controls on the solubility of Si and Al are more difficult to address than carbonate or evaporite minerals. In this study Si was studied directly from modeling output, however Al was studied though indirect ways.

Figures 39 and 40 presents frequency histograms portraying the distribution of quartz and chalcedony SIs. The average quartz SI of .3835 suggests waters are slightly supersaturated with respect to the mineral. Chalcedony SI average value of -.0970 indicates near equilibrium for most waters. Consistent trends of SIs for quartz and chalcedony are noted throughout the study area.

The technique most relied upon for an easy portrayal of stability relations between silicates and aqueous solutions are on activity-activity or mineral stability diagrams

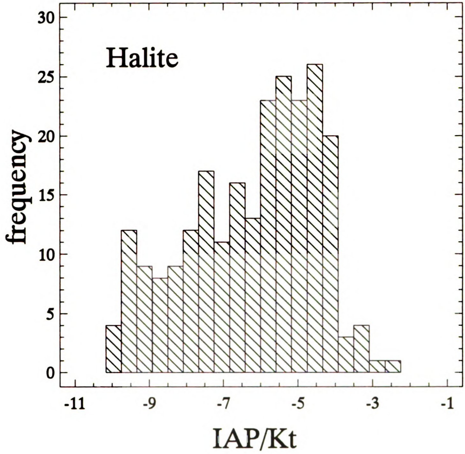


Figure 36. Frequency histogram of halite saturation index values for ground water from the Grand River-Saginaw aquifer.

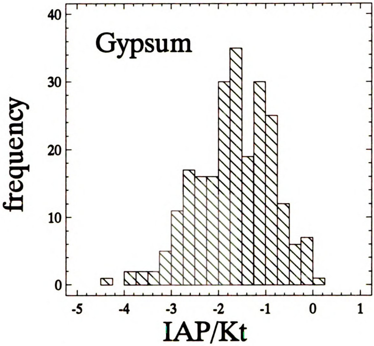


Figure 37. Frequency histogram for gypsum saturation index values for ground water from the Grand River-Saginaw aquifer.

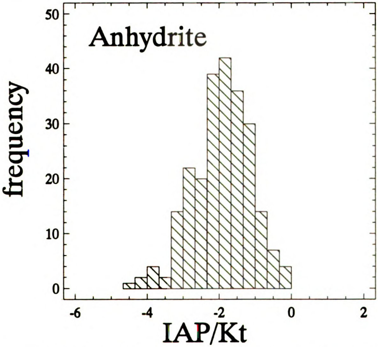


Figure 38. Frequency histogram for anhydrite saturation index values for ground water from the Grand River-Saginaw aquifer.

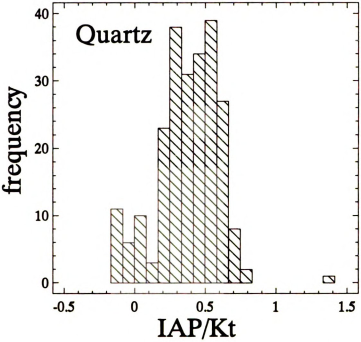


Figure 39. Frequency histogram for quartz saturation index values for ground water from the Grand River-Saginaw aquifer.

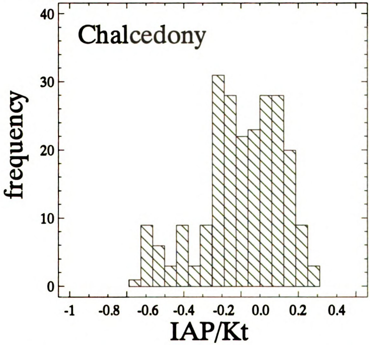


Figure 40. Frequency histogram for chalcedony saturation index values for ground water from the Grand River-Saginaw aquifer.

(Garrels and Christ, 1965). These diagrams are based on activities calculated with chemical modeling and on thermodynamic stability fields. This graphical technique uses the assumption that all of the Al in the system is retained in solid phases, an assumption that should be valid based on the low solubility of Al minerals (Long et al., 1986). Based on this assumption the stability fields of Al bearing minerals can be described in terms of the activities of the other dissolved species of the rock/water system (Long et al., 1986).

Using the results of the chemical modeling on the ground water data an activity-activity diagram was created for Na-aluminosilicate minerals presented as Figure 41. The mineral stability presented on Figure 41 are based on Drever (1988). The ground-water sample data plot within the kaolinite stability field. This indicates the potential for equilibrium of the ground water with respect to kaolinite.

Using the results of the chemical modeling on the ground water data an activity-activity diagram of K-aluminosilicate minerals is presented on Figure 42. The stability fields in the diagram are taken from Drever (1988). The ground water data plot within the kaolinite and muscovite fields.

SUMMARY

The results from WATEQ4F modeling indicate water-rock interaction is impacting the solute concentrations of water from the Grand River-Saginaw aquifer. The magnitude of rock-water interaction affecting ground water chemistry is difficult to quantify however within the Grand River-Saginaw aquifer it is believed to be minimal as SIs are at or close to equilibrium with respect to calcite as well as quartz and chalcedony. The impact of water-rock interactions affecting solute concentrations of more concentrated water in the system is small, as shown earlier the magnitude of solutes for these waters are derived through mixing with brine. The more dilute waters in the system especially in the southern part of the aquifer water-rock interactions are believed to be the dominant control on the

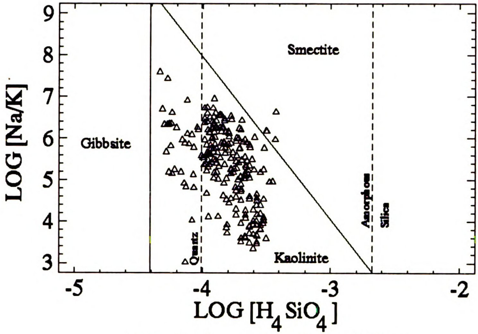


Figure 41. Mineral stability diagram of sodium aluminosilicate minerals.

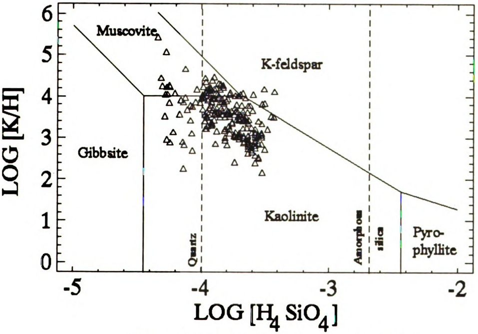


Figure 42. Mineral stability diagram of potassium aluminosilicate minerals.

chemical character of ground water in the Grand River-Saginaw aquifer. However active rock-water interaction is not likely to be occurring in the aquifer as shown by Wood (1969). This leads to the interpretation that the source of solute concentrations observed in the more dilute waters in the system are derived through rock-water interaction that has occurred in the overlying glacial-drift deposits prior to recharge into the bedrock aquifers. This is in accordance with similar SI values, facies and dissolved solids distributions observed in the Glacial-Drift aquifer waters (Wahrer personal commun., 1992). This points to the importance of infiltrating water from the Glacial drift aquifer as a source of solutes for less concentrated waters in the Pennsylvanian aquifers.

CHAPTER 5: ISOTOPE DATA REDUCTION AND RESULTS

INTRODUCTION

Isotopic compositions of elements having low atomic numbers are variable due to isotopic fractionation in the course of certain chemical and physical processes occurring in nature. Fractionation is due to variations in physical and chemical properties of the isotopes (Faure, 1986). Some of the most important elements in which variations of isotopic composition have been noted are hydrogen, oxygen, sulfur and carbon. The use of stable isotopes of H, O, S and C in ground water studies has been widespread (Clayton et al., 1966) (Graf et al., 1966) (Hitchon, 1969) (Desauliniers, 1981) (Siegel and Mandle, 1984) (Bradbury, 1984) (Long, et al., 1988) (Plummer at al., 1990) and (Long et al., 1993). Ground water studies related to these elements specifically involve D and ^{18}O, ^{13}C and ^{34}S (Domenico and Schwartz, 1990). The stable isotope ratios of O, H, S, and C were measured in selected goundwater samples from the Grand River-Saginaw Aquifers as a part of the RASA project (Dannemiller and Baltusis, 1990) (RASA, 1992) and Bay County Project (Long et al., 1986). Only H and O stable isotope data exist for the Parma-Bayport aquifer (Dannemiller and Baltusis, 1990). These data will be used to determine the evolution of ground water chemistry, detect the presence of different ground water masses, the mixing relationships between ground water masses, and the impact of microbiological processes on water chemistry. Analyzing the isotopic composition of water masses provides an independent check on controls on water chemistry as previously discussed from interpretation of chemical data. The best model for the geochemistry of an aquifer is obtained when the results of isotopic analysis are combined with the results from the chemical data reduction techniques (Long et al., 1986).

OXYGEN AND DEUTERIUM ISOTOPES

Oxygen and Deuterium isotopes are useful in the identification of water masses, mixing relations between water masses and potential relative ages of water masses. The isotopic composition of O and D is reported in terms of the difference of the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios relative to a standard called SMOW (Standard Mean Ocean Water). The isotope ratio is reported as a $\delta^{18}O$ and δD value, where the δ values are expressed as a per mil (‰) deviation from SMOW:

$$\delta = [\, R_x - R_{std} \,] / R_{std} * 10^3$$

where R_x is the isotopic ratio in the samples and R_{std} is the isotopic ratio in the standard. Negative δ values correspond to samples relatively depleted (i.e. light) in the heavy isotope species relative to the standard (Faure, 1986). Because the differences between the standard and the sample are often small the δ value is multiplied by 1000.

Figure 43 shows δD and $\delta^{18}O$ relations for ground water from the Pennsylvanian aquifers. These data are compared to the global meteoric water line of Craig (1961) and a local meteoric water line from Simcoe, Ontario, Canada (Desauliniers et al., 1981). The Simcoe data were collected precipitation approximately 120 miles east of the study area. The equation for the Craig line is $\delta D = 8*\delta^{18}O + 10$ and that of the Simcoe line is $\delta D = 7.5*\delta^{18}O + 12.6$. The distribution of data is in close agreement with both the Craig and Simcoe meteoric water lines indicating the water is of meteoric origin, that is water is assumed to have originated from the atmosphere and is unaffected by other isotopic processes. Figure 43 also shows a wide range of isotopic signatures of meteoric water exists in the Pennsylvanian aquifer. This large range does not reflect seasonal isotopic

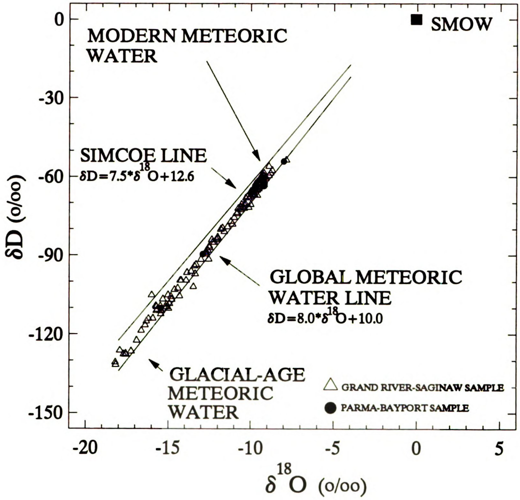


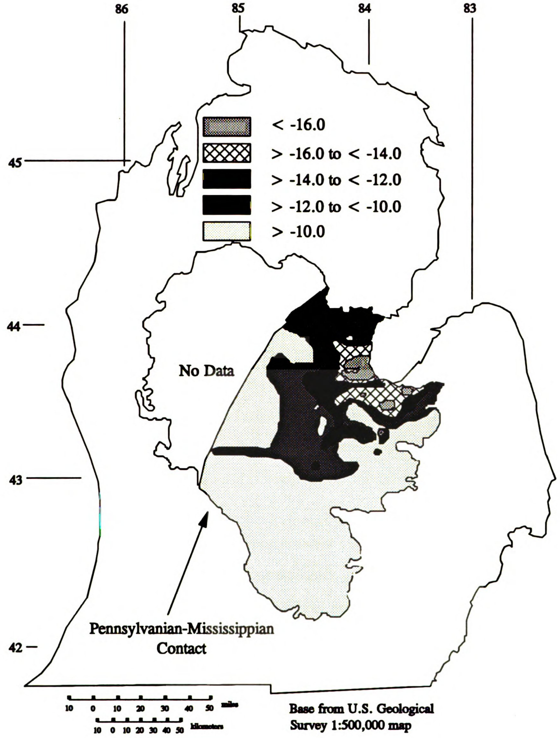
Figure 43. δD versus $\delta^{18}O$ for ground water from Grand River-Saginaw and Parma-Bayport aqiufers.

variability in recharge water because ground water typically homogenizes this variability into a yearly average (Lloyd and Heathcote, 1985), (Long, et al., 1988). Isotopic signatures of δD and $\delta^{18}O$ range from -53.5 ‰ and -7.85 ‰ to -131.5 ‰ and -18.19 ‰ respectively. The heaviest (least negative values) isotopic signatures observed, ranging from around -8.00 ‰ to -12.00 ‰ are interpreted to represent modern meteoric ground water in the aquifers. The heaviest signatures will be referred to as modern (post glacial) meteoric water. Isotopically light signatures (< -16.0 ‰), found in ground water in the Pennsylvanian units, as low as -18.19 ‰, are significantly lighter than expected from modern recharge. Thus the very light values are anomalous and indicate that ground water recharged the system when the climate was cooler. This interpretation is similar to findings of other investigators who have discovered very light $\delta^{18}O$ values in ground water (Desauliniers et al., 1981) (Siegel and Mandle, 1984) (Bradbury, 1984) and (Long et al, 1988). For example, Desauliniers suggests that ground water in glacial clays of the Erie lowland in southwestern Ontario originated from a cooler climate and is a mixture of late Pleistocene and modern ground water. $\delta^{18}O$ values as light as -17 ‰ were found and ^{14}C dates on water with light isotope signatures showed an age of >8,000 years before present. Long et al., (1988) on the basis of Desauliniers work concluded that ground water in Bay county in the eastern portion of the Saginaw Bay Area to be >8,000 years old. This would suggest that during periods of glacial ice advances in Michigan ground water recharge by glacial meltwater, depleted in ^{18}O, would have occurred in the basin. This water is referred to as glacial meteoric water.

Distribution on Figure 43 indicates that modern and glacial meteoric water have mixed causing a continuum of plotted values to be present. Interpretation of the data distribution on Figure 43 indicates three water masses are present: (1) modern meteoric water (-8.00 ‰ to -12.00 ‰) (2) glacial age meteoric water (< -16.0 ‰) and (3) mixture of glacial age meteoric and modern meteoric water (-12.10 ‰ to -15.90 ‰) . Unfortunately, isotope data for Parma-Bayport brine does not exist, therefore a fourth water mass known to exist in the system is not represented on Figure 43.

Analysis of the areal distribution of $\delta^{18}O$ in Figure 44 reveals an interesting pattern of data exists. δD signatures have the same general trends as $\delta^{18}O$ and therefore a distribution map of δD is not included. The distribution of $\delta^{18}O$ shows a pattern of decreasing values from > -10.00 ‰ in the south and west-central regions to values < -16.00 ‰ present in the Saginaw Bay Area. This distribution follows data distribution of Figure 43 that indicated mixing occurring between modern meteoric water (mostly in the south and central part of the aquifer) and glacial age meteoric water (found exclusively in the Saginaw Bay Area). The existence of thick relatively impermeable deposits mapped as lake sediments in the Saginaw Bay Area may be limiting the vertical movement of modern recharge in the area preventing mixing with isotopically light water (Farrand and Bell, 1984). Along with the region being identified as a regional discharge location these waters are able to retain the isotopically light signature due to slow flushing of the system inhibited by overlying relatively impermeable sediments (Long et al., 1988) (Mandle and Westjohn, 1989). The southern region of the study area is dominated by water with modern meteoric signatures, this is in agreement with a hypothesized recharge area for the aquifer based on previous discussion of hydrochemical facies, and dissolved solids concentration distribution maps (Figures 12 and 16).

The mixing relationship described between modern meteoric and glacial age meteoric does not represent the only mixing proposed to be taking place in the system. Previous interpretations of elemental constituent plots (Figures 19 to 31) indicate meteoric water mixing to some degree with brine as a source for solutes for much of the water in the Grand River-Saginaw aquifer. Specifically, it is interesting to reference the distribution of dissolved-solids and Cl on Figures 12 and 13 that show some of the more concentrated waters in the system coincide with the distribution of isotopically light ground water in the Saginaw Bay Area. Further the source of Cl and dissolved-solids can be attributed to



Base from U.S. Geological Survey 1:500,000 map

Figure 44. δ^{18}O distribution for ground water sampled from the Grand River-Saginaw aquifer.

mixing with brine from previous discussion. A question develops concerning the relationship between brine and glacial-age meteoric water in the system, providing solutes to the isotopically light water. In order to explain the scenario proposed by the isotope data and chemical data a three end-member mixing relationship between modern meteoric water, glacial-meteoric water and brine must exist.

Mixing of water masses

Figure 45 is a plot of $\delta^{18}O$ versus Cl for ground water in the Pennsylvanian aquifers. The data distribution indicates at low Cl concentrations (<100 mg/L) $\delta^{18}O$ values are between - 10.0 and -8.0 ‰. As Cl concentrations increase (>200 mg/L) $\delta^{18}O$ values exhibit a variety of signatures from - 18.0 to - 8.0 ‰. Chloride concentrations as high as 5,000 to 7,000 mg/L have associated isotopic values as low as -18.0 ‰. The most concentrated samples represented on the plot with Cl concentrations > 10,000 mg/L are associated with the most isotopically heavy water sampled from the Pennsylvanian aquifers. Interpreting this plot to explain a mixing relationship between water masses that can explain both the chemical data and isotopic data is difficult as no data from the Parma-Bayport brine end-member exists.

In order to better investigate this mixing problem it is necessary to focus on a study by Long et al., (1993). Long et al., (1993) performed a study encompassing all waters within the RASA study and were able to define the mixing relationship between brine, modern meteoric and glacial meteoric water based on the premise that only a small amount of the Cl content of a brine would be required to produce the observed Cl content in the mixed waters and therefore not having a great impact on the isotopic signature. Using data from the Glacial Drift aquifer as well as the Grand River-Saginaw, Parma-Bayport, and Marshall aquifers a $\delta^{18}O$ versus Cl diagram was created (Figure 46). Isotope data from Marshall brine is the only available brine end-member data (Clayton et al., 1966). Due to

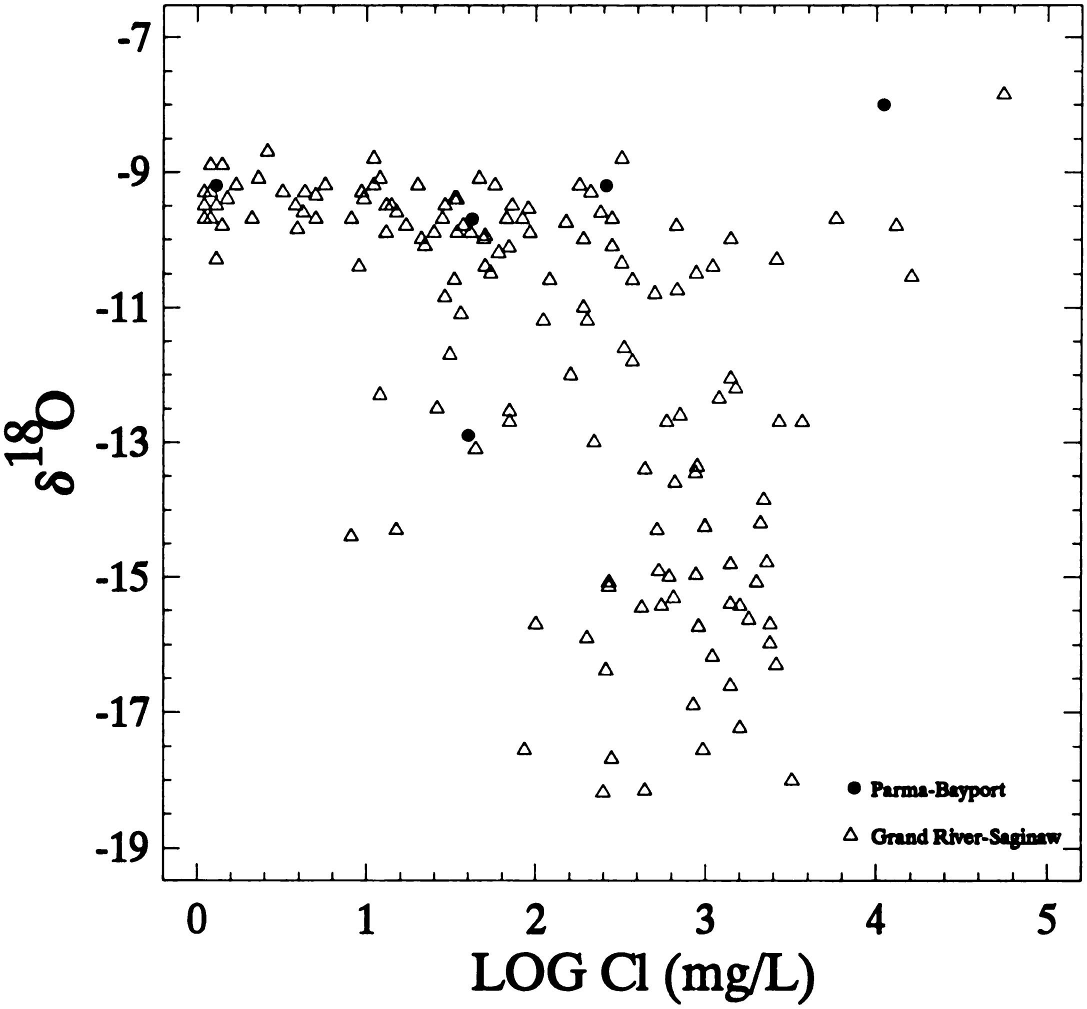


Figure 45. $\delta^{18}O$ versus Cl for ground water from Grand River-Saginaw and Parma-Bayport aquifers.

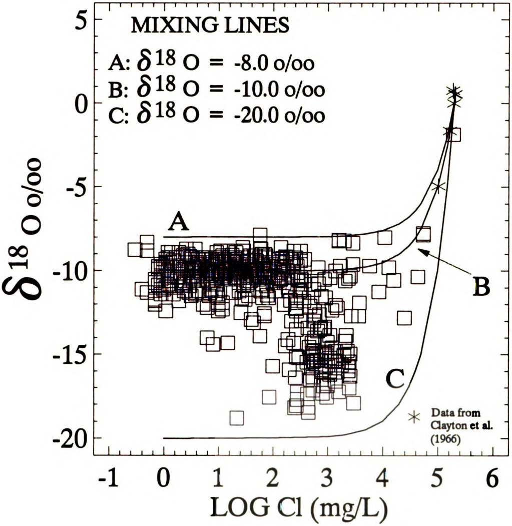


Figure 46. $\delta^{18}O$ versus Cl for ground waters sampled from the Glacial-Drift, Grand River-Saginaw, Parma-Bayport and Marshall aquifers (Modified from Long et al., 1993).

chemical similarities previously shown between the Parma-Bayport brine and brine in the Marshall Formation an assumption is made for this thesis that the two brines are also isotopically similar. With this assumption the same method of Long et al., (1993) can be applied specifically to the Pennsylvanian waters.

Figure 46 is a plot of $\delta^{18}O$ versus Cl concentration of groundwater samples from the entire RASA study in an effort to link mixing relations observed from chemical data (Figures 19 to 31) with that of isotope data (Figure 43). Long et al., (1993) investigated mixing on the isotopic signature of water, a fresh water and a brine were theoretically mixed in various proportions and the resultant $\delta^{18}O$ values and Cl concentrations were calculated. The fresh water end-member was assigned a Cl concentration of 1.00 mg/L and three isotopic signatures -8.00 ‰, the heaviest modern meteoric water, -10.00 ‰, the average modern meteoric water, and -20.00 ‰, isotopically light glacial age meteoric water. The brine end-member was assigned a Cl concentration of 200,000 mg/L and a $\delta^{18}O$ signature of 0 ‰, based on data from Clayton et al., (1966). Chloride concentrations were calculated by weight averaging the end-members and the $\delta^{18}O$ value of the mixed waters was calculated using the following equations:

$$\delta^{18}O_{MIXTURE} = F * X * \delta^{18}O_{BRINE} + (X - 1) * \delta^{18}O_{FRESH}$$

$$Cl_{MIXTURE} = X * Cl_{BRINE} + (X - 1) * Cl_{METEORIC}$$

Where F is the ratio of the water weight in brine to the weight in pure water and X is the fraction of brine mixed. A value of .70 was used for F in the calculations (Wilson and Long, 1993). Results of calculations on Figure 46 show all data fall within a mixing envelope defined by -8.00 ‰, -10.00 ‰, and -20.00 ‰ $\delta^{18}O$ values. It is interesting to note the $\delta^{18}O$ values of the mixtures remain relatively constant over the range of most of the data. The $\delta^{18}O$ values do not change significantly in the mixtures until Cl concentrations exceed 10,000 mg/L that can be simulated if the fresh water end-member mixed with 5% brine. Therefore, Long et al., (1993) showed mixing fresh water (recent and glacial) with various amounts of brine can account for the observed Cl and $\delta^{18}O$ values of groundwater in the study area. This same mechanism is believed to be operating in the Pennsylvanian bedrock system as mixing with brine in the Parma-Bayport as the source of solutes for the more concentrated samples in the Grand River-Saginaw aquifer. Therefore it is hypothesized that mixing of Parma-Bayport brine with modern meteoric and glacial meteoric waters from the Grand River-Saginaw is providing the solute concentrations observed, without impacting $\delta^{18}O$ signatures of the glacial meteoric water as shown by Long et al., (1993). Without isotope data from the Parma-Bayport brine a more definitive conclusion is prohibited.

Summary

Analysis of $\delta^{18}O$ and δD from Pennsylvanian waters indicate three water masses are present; (1) modern meteoric (post-glacial) and (2) glacial age meteoric a third water mass exists in the Pennsylvanian bedrock sequence, the Parma-Bayport brine which is not represented due to lack of isotope data. Modern meteoric values are mainly found in the south and periphery of the basin and glacial age water is restricted to a portion Saginaw Bay Area with mixed water present separating the modern and glacial waters. A model can be formulated to explain mixing with a brine as a source of solutes while preserving the isotopically light signatures. This is most useful in correlating the chemical data and isotope data of isotopically light waters with high Cl concentrations in the Saginaw Bay Area. This model may be used to explain the mixing between Parma-Bayport brine and Grand River-Saginaw waters and explain solute and solvent geochemistry.

SULFUR AND CARBON ISOTOPES

The stable isotopes of C and S are typically used in carbonate and sulfate-sulfide systems. These systems are very complex in the subsurface and C and S isotopes are used best at process identification (Domineco and Schwartz, 1990)

Sulfur Isotopes

Sulfur isotopes signatures can be used to identify the processes contributing to the evolution of S chemistry. In ground water sulfate may be derived from dissolution of calcium-sulfates and through the oxidation of iron-sulfides. Specifically, the ratio of ^{34}S to ^{32}S is of concern in sulfur isotope studies. The isotopic composition is expressed in terms of $\delta^{34}S$ that is defined as: (Bowen, 1988)

$$\delta^{34}S = [R_x - R_{std}] / R_{std} * 10^3$$

where R_x is the isotopic ratio in the samples and R_{std} is the isotopic ratio in the standard. Negative δ values correspond to samples relatively depleted (i.e. light) in the heavy isotope species relative to the standard (Faure, 1986). The standard is the S in troilite (FeS) of the iron meteorite Canyon Diablo whose $^{32}S/^{34}S$ ratio is 22.22 ‰.

Dissolution of solids containing S in a ground water system can change the $\delta^{34}S$ value or SO_4 concentration of ground water depending upon the source of sulfate, i.e., gypsum, organic matter (peat or coal), or from oxidation of sulfide minerals such as pyrite or possibly a combination of all of these (Domenico and Schwartz, 1990). An important fractionation reaction involving S that operates in ground water systems is sulfate reduction that takes the general form:

$$2\,H + SO_4 + 2\,[CH_2O] = 2\,H_2O + H_2S + CO_2$$

The result of this process is depletion in sulfate concentrations and enrichment in $\delta^{34}S$ value. The isotopic fractionation associated with this reaction appears to be due to the bond strength with ^{34}S forming stronger bonds than ^{32}S (Long et al., 1986). The degree to which fractionation occurs is a function of the temperature, availability of nutrients, pH, type of organic material utilized, and type of bacteria present (Kaplan, 1983). In inorganic systems however, the extent of isotopic fractionation that occurs is due to different rates at which S-O bonds are broken (Faure, 1986).

The bacteria identified to be of primary importance in the reduction of sulfate is *Desulfovibrio desulfuricans* an anaerobic bacteria which splits oxygen from sulfate and excretes H_2S that is enriched in ^{32}S relative to sulfate, and the sulfate in pore water becomes isotopically heavier. Therefore the expected trend for sulfate reduction is decreasing sulfate concentrations accompanied by increasing $\delta^{34}S$ values.

Long et al., (1986), performed a study on groundwater in Bay County, MI. from the Glacial Drift and Grand River-Saginaw aquifers. Through the use of C and S isotopes they were able to delineate sources of sulfate for groundwater samples analyzed. Control on sulfate concentrations could not be entirely linked to only the dissolution of gypsum and oxidation of pyrite. Another control on sulfate concentrations mainly a biochemical process was indicated. Long concluded based on analysis of S as well as C isotopic signatures that sulfate reduction was occurring in aquifers in Bay County.

Data used in this thesis are from RASA sampling from 1986-88 (Dannemiller and Baltusis, 1990) and 1991 (WATSTORE, 1992) which include 18 S isotopic analyses and data from Long et al., (1986) adding 14 S analyses. Figure 47 is a frequency histogram of S isotopic data from the Grand River-Saginaw aquifer. Values range from -2.9 ‰ to 67.44 ‰ with an average of 21.04 ‰. Most data fall within a 12 ‰ to 32 ‰ range, however due to only 32 samples available the distribution of data may not actually reflect

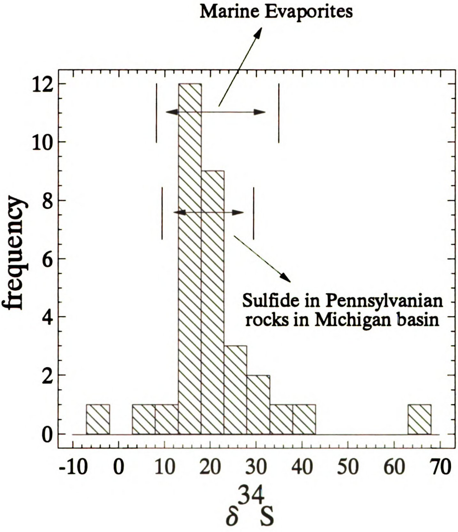


Figure 47. Frequency histogram for $\delta^{34}S$ in dissolved sulfates for ground water from the Grand River-Saginaw aquifer. Ranges shown represent $\delta^{34}S$ values for marine evaporites (Anderson and Arthur, 1983) and sulfide in Pennsylvanian rocks in the Michigan basin.

true sulfur isotope distribution in groundwaters throughout the Grand River-Saginaw aquifer.

Sources of sulfate to waters in the Grand River-Saginaw aquifer have been stated as being from dissolution of gypsum and oxidation of iron sulfides (Long et al., 1986), (Wood, 1969). These minerals will have different $\delta^{34}S$ signatures, therefore the signature of groundwater could reflect the source of sulfate. One problem exists in that the $\delta^{34}S$ values for gypsum do not exist for this system and therefore must be estimated. $\delta^{34}S$ values for pyrite in the Pennsylvanian units of the Michigan basin range from 9.6 to 29.3 and a values for ancient sulfates in marine-evaporites have signatures from 8 to 35 ‰ with Pennsylvanian age sulfates ranging from 15 to 22 ‰ (Anderson and Arthur, 1983) Isotope data available on Figure 47 show 2 samples are < 10 ‰ and 1 is greater than 45 ‰. Nearly all data fall within the isotopic signature of associated with gypsum and pyrite making it difficult to differentiate a single source of sulfate. Few samples plot outside the ranges used for pyrite and gypsum leading to the interpretation that bacterial processes are causing the high S isotope values observed. To further investigate this $\delta^{34}S$ is plotted versus sulfate for Grand River-Saginaw waters.

Figure 48 plots $\delta^{34}S$ versus sulfate concentration and shows higher sulfate concentrations (> 300 mg/L) are associated with $\delta^{34}S$ values < 20 ‰ and lower sulfate concentrations (< 300 mg/L) are associated with $\delta^{34}S$ values as high as 67.44 ‰. The depletion of sulfate as $\delta^{34}S$ signature becomes heavier is what is expected if the microbiological reduction of sulfate is occurring in the system (Long et al, 1986). The distribution observed on Figure 48 shows some data form an increasing $\delta^{34}S$ signature as sulfate concentration decreases. Not all data, even some from Bay county, adhere to this trend indicating sulfate reduction may be occurring albeit in isolated areas. This is consistent with the conclusion of Long et al., (1988) as sulfate reduction was shown to be taking place in various parts of the aquifer for different lengths of time, therefore explaining uneven degrees of isotope enrichment and sulfate depletion present.

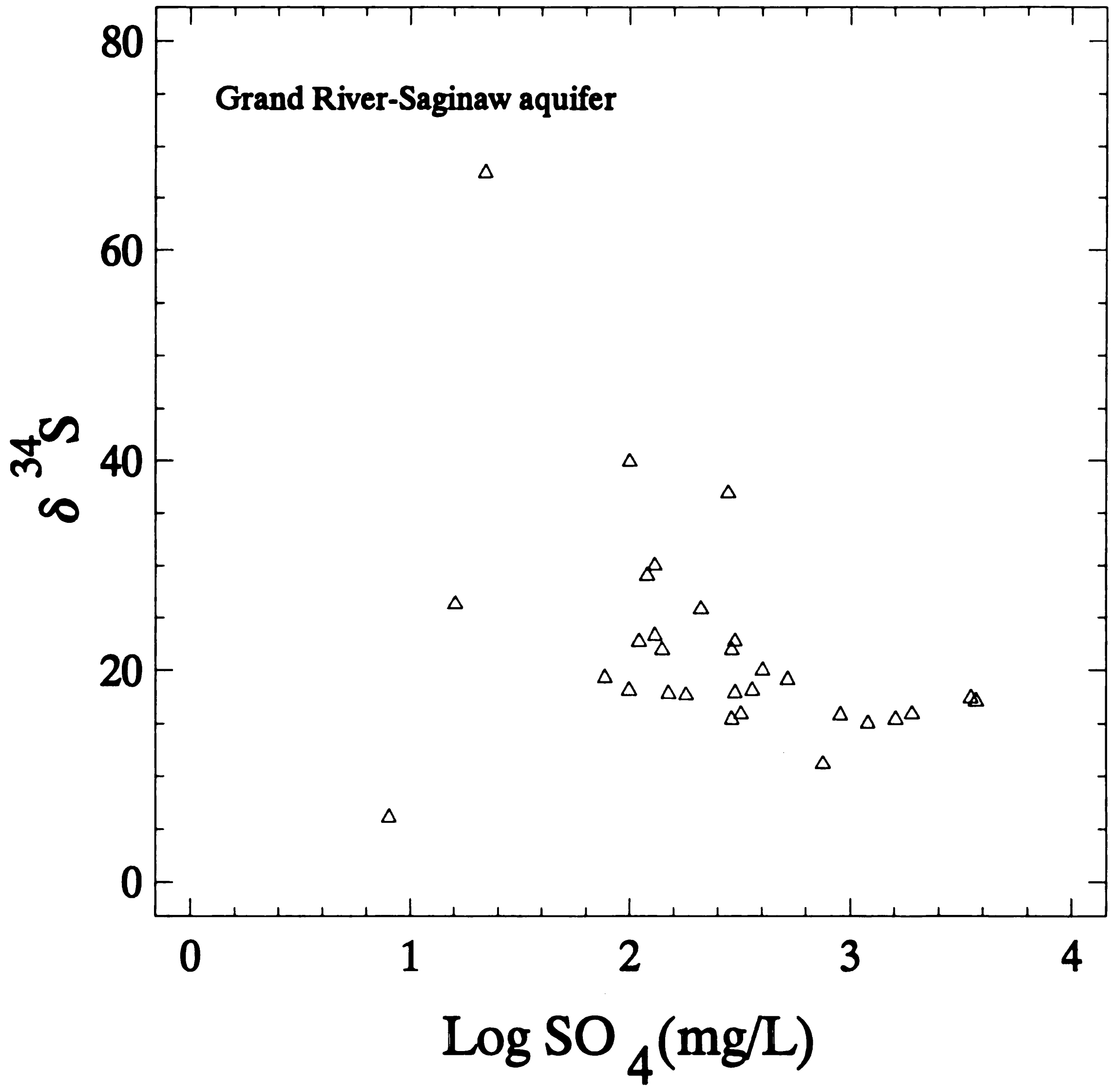


Figure 48. $\delta^{34}S$ versus SO_4 for ground water from the Grand River-Saginaw aquifer.

Carbon Isotopes

The concentration of stable carbon isotopes in ground water is used to indicate the origin and evolution of ground water and determine the source of dissolved inorganic carbon (DIC) in an aquifer. Dissolved inorganic carbon species (H_2CO_3, HCO_3, CO_3, and CO_2) are important components in ground water as they buffer pH, produce alkalinity, complex other dissolved species and affect the solubility of many minerals common in aquifers (Long et al, 1986). The isotopic composition is expressed in terms of $\delta^{13}C$ which is defined as:

$$\delta^{13}C = [R_x - R_{std}] / R_{std} * 10^3$$

where R_x is the isotopic ratio in the samples and R_{std} is the isotopic ratio in the standard. Negative δ values correspond to samples relatively depleted (i.e. light) in the heavy isotope species relative to the standard (Faure, 1986). The carbon isotopic signature obtained from a ground water sample is the result of exchange of ground water with various sources of carbon (coal, CO_2 gas in soil zones, carbonate minerals, other carbon bearing minerals, methane gas, and plant material) each of which has a distinct range of δ ^{13}C values that is the basis of being able to differentiate sources of carbon in an aquifer. Marine carbonates including aragonite, calcite, and dolomite commonly have $\delta^{13}C$ values from -2.0 ‰ to +2.0 ‰. Atmospheric CO_2 has values from-5.0 ‰ to -7.0 ‰. Land plants found in temperate and colder climates have $\delta^{13}C$ values from -30.0 ‰ to -20.0 ‰. It is important to note that DIC is likely to be the result of many carbon sources (Long et al, 1986).

Carbon isotopes available for this thesis include 50 analyses obtained from Long et al, (1986) and 43 analyses obtained from RASA sampling (Dannemiller and Baltusis, 1990), (WATSTORE database, 1991). $\delta^{13}C$ values range from -21.36 ‰ to -6.16 ‰ with an average of -13.34 ‰ (Figure 49). Long et al, (1988) indicated that organic matter was a more important source for carbon than carbon derived from carbonate minerals in the Bay county area. This was based on 57% of the $\delta^{13}C$ values were < -15.0 ‰. A $\delta^{13}C$ value of -15.0 ‰ is the lower limit generally expected for a mixed carbonate mineral-organic source (Long et al., 1986). Sources for organic carbon in Bay county area could be from lignite, organic-rich shales, and organic rich "fire-clay" in many cases associated with coal. Also Long et al, (1988) also found an uneven distribution of $\delta^{13}C$ values to be indicative of microbiologic activity, principally sulfate reduction, however no direct relationship was found between decreasing $\delta^{13}C$ values and increasing HCO_3, a by-product of sulfate reduction. This lead to the conclusion that sulfate reduction is occurring in Grand River-Saginaw aquifer in Bay county, however it is heterogeneously distributed with some areas having higher reduction rates than others.

Data located outside Bay county indicate that carbonate minerals may be having more of an impact on the source of carbon combined with an organic source as values are typically -15.0 ‰ to -12.5 ‰. This is shown by Thorstensen and Fisher, (1979), in which a combined source of carbon consisting of lignitic material (-25.0 ‰) and carbonate minerals (0.0 ‰) result in an actual average value of $\delta^{13}C$ in ground water of -12.1 ‰. This interpretation is consistent with the presence of coal deposits in the Saginaw Formation (Wanless and Shideler, 1975) and ubiquitous presence of carbonate cements in the Grand River-Saginaw aquifer (D. Sibley personal commun., 1992).

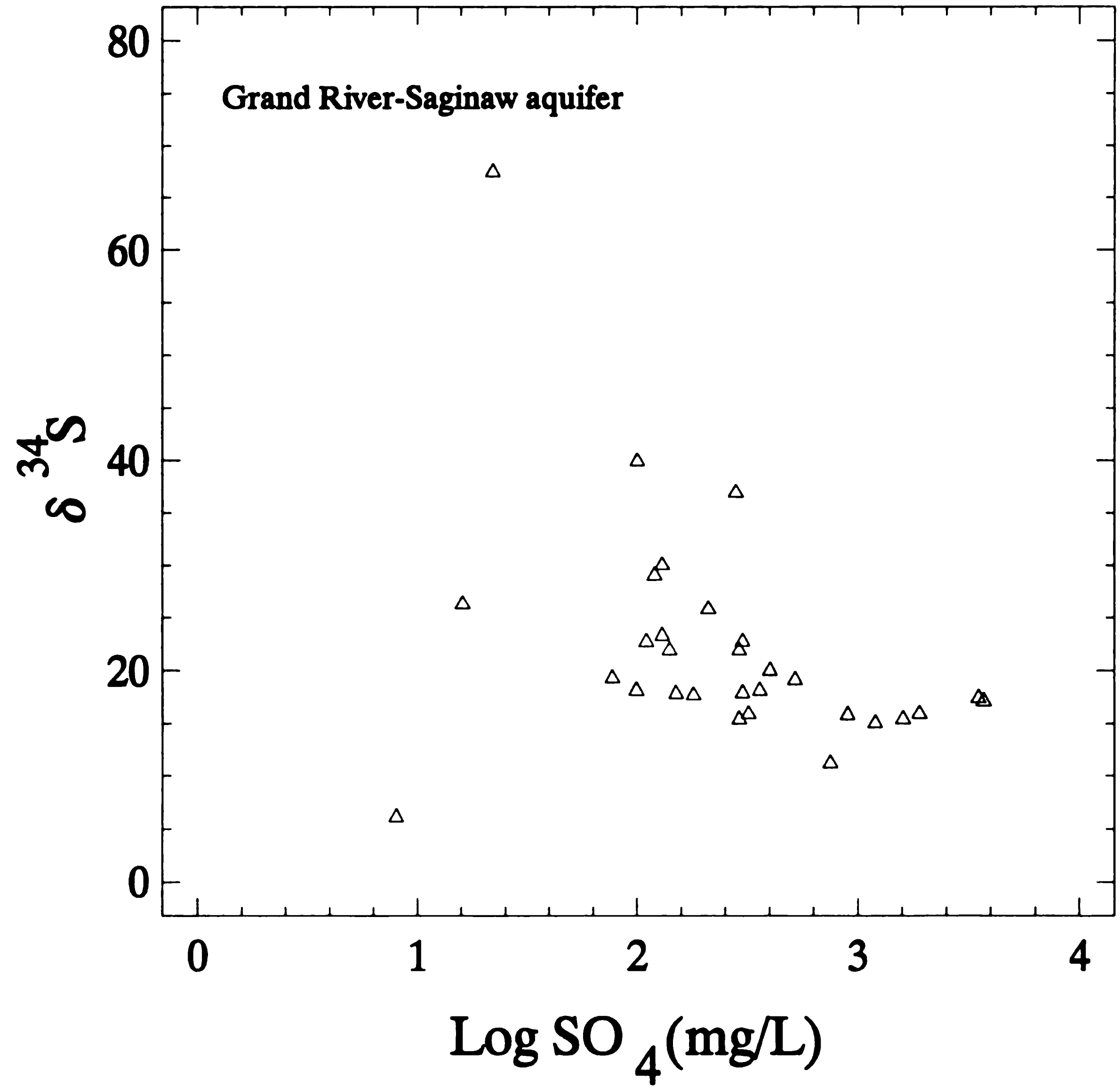


Figure 48. $\delta^{34}S$ versus SO_4 for ground water from the Grand River-Saginaw aquifer.

Summary

Sulfur and carbon isotope data are more difficult to interpret than oxygen and deuterium as these need a systematic site-specific characterization of important reactions in terms of sources and sinks of carbon and sulfur. The scale of this thesis does not allow this interpretation and lack of important S and C source solid-phase information precludes anything more than speculation of sources of S and C from limited isotope database available.

In accordance with the work of Long, et al, 1986 sulfate reduction is occurring in portions of the Saginaw Bay Area, however many samples show no evidence of it occurring in the rest of the system. Sulfur isotope data show the influence of gypsum dissolution and pyrite oxidation as a source of sulfate to the system, although it is not possible to differentiate which has a greater impact on sulfate concentrations. The impact of mixing with brine cannot be overlooked in analyzing the sulfur isotope data. Addition of sulfate to the system from a brine source has also been shown to be important and is to be considered as a more significant source than dissolution of gypsum and oxidation of pyrite.

In the Bay county area organic matter appears to be a more important source of carbon than carbon from carbonate minerals. Also, consistent with sulfur isotope data sulfate reduction is occurring albeit heterogeneously distributed throughout the Bay county region. Carbon isotope data from outside Bay county indicate the source of carbon is equally impacted by carbon from organic matter and carbon from carbonate minerals.

CHAPTER 6: SUMMARY AND CONCLUSION:

SUMMARY

The geochemical distribution maps indicate high concentrations of dissolved solids and chloride exist in the central part of the aquifer and in the Saginaw Bay Area. Low concentrations are mainly found in the south and southeastern parts of the aquifer consistent with areas designated as recharge areas to the aquifer. The low dissolved solids concentrations show a similar distribution to those found in water sampled from the overlying glacial drift aquifer. Low concentrations of sulfate exist in the Saginaw Bay Area and high concentrations are present where the aquifer is overlain by or near Jurassic deposits. Piper plots show a linear trend on the cation ternary diagram between dilute Ca-rich water (< 750 mg/L) and more concentrated (>2,000 mg/L) Na-rich water end-members with a mixing trend separating them. Water in the anion ternary plot between $HCO_3 + CO_3 - SO_4$ dominant at low dissolved solids, among $HCO_3 + CO_3 - Cl - SO_4$ dominant at intermediate dissolved solids and $Cl - SO_4$ dominant at high dissolved solids. Distributions on anion ternary diagrams show more concentrated waters in each interval plotting closer to the SO_4-Cl dominant area. The change in the distribution pattern of the data in the diamond area as a function of increasing dissolved solids reflects those changes in the cation and anion ternary diagrams. The pattern changes in the ternary and diamond diagrams are consistent with the hypothesis in which water masses with various compositions are mixing. Main hydrochemical facies in the Pennsylvanian aquifers are Ca-HCO_3, Na-Cl, and Ca-SO_4. With Ca-HCO_3 facies predominantly in the south and Na-Cl facies mainly in the east-central part of the aquifer.

Analysis of Cl/Br ratios provide evidence that waters in the Pennsylvanian aquifers are genetically related to formation brine and the source of Cl is not related to halite dissolution.

Brine in the Michigan basin Traverse Group and Marshall aquifer is proposed to have formed from the evapo-concentration of seawater. Brine in the Parma-Bayport was hypothesized to have formed through the same process therefore chemical analyses were compared to evaporation of seawater trajectories according to the method proposed by Carpenter, (1978). Chloride:bromide and sodium:chloride diagrams allowed the preliminary interpretation that the Parma-Bayport brine had originated from evapo-concentrated seawater and that solutes of less concentrated saline water in the Grand River-Saginaw aquifer plotted along a dilution trend from brine concentration. This relationship show a link between brine and other concentrated waters in the system. Interpretation of ion:Br and ion:Cl diagrams showed the Grand River-Saginaw aquifers saline water as being genetically related to Parma-Bayport brine as well as further indicating the similarity of the Parma-Bayport brine and Marshall brine and Traverse Group brine. The Parma-Bayport brine showed diagenetic alterations from dolomitization, some degree of sulfate reduction and possibly alumino-silicate reactions.

The dilute water end-member (< 750 mg/L), located mostly in the southern and southeastern parts of the aquifer, can be explained through rock-water interaction occurring in the glacial drift deposits causing the concentrations observed. Minor mixing with brine is also believed to serve as an additional albeit minor source of solutes. Geochemical modeling shows that a source of solutes derived from rock-water interaction taking place in the Grand River-Saginaw aquifer is likely. Solutes of less concentrated waters of the Grand River-Saginaw aquifer are derived mostly through rock water interaction occurring as the water moves through the overlying glacial drift aquifer and eventually recharges the Grand River-Saginaw aquifer. In these areas where less concentrated waters are present, dissolved solids concentrations and hydrochemical facies distributions mimic those found in the overlying Glacial-Drift aquifer supporting this conclusion. The chemical similarity between water in the Grand River-Saginaw and Glacial-Drift aquifers especially in the southern part of the aquifer is in accordance with a hydraulic potential for water to move from the drift to the Grand River-Saginaw aquifer in the southern portion of the aquifer (Wood, 1969).

Stable isotopes of O and D indicate three meteoric water masses are present in the aquifer: (1) modern meteoric water, (2) glacial age meteoric with a third water mass, the Parma-Bayport brine not represented by O and D data on the diagram. A mixing model was applied to explain high solute concentrations (>3,000 mg/L dissolved-solids) associated with water with a glacial meteoric water signature based on requiring only a small percentage of brine to cause solute concentrations observed without and having no effect on the isotopic signature of the water sample. This model links mixing interpretations made independently from analysis of chemical and isotope data. The model explains mixing relationships between brine, modern meteoric water and glacial meteoric water causing solute concentrations and isotopic signatures for the majority of samples.

Stable isotopes of C and S indicate, in accordance with Long et al., (1988), that sulfate reduction is occurring in the Saginaw Bay Area. The source of sulfate could not be unequivocally decided based on sulfur isotopic signatures. Gypsum dissolution and pyrite oxidation are implicated as sources of sulfate, however lack of data for the aquifer (32 samples) and the overriding importance of brine, previously pointed out, as a source of solutes for Grand River-Saginaw water must be considered in the interpretation of sulfur isotope data. Carbon isotope data also supported the interpretation of Long et al., (1988) that sulfate reduction was occurring in Saginaw Bay Area. Sources of carbon in the aquifer system also could not be concluded with organic carbon and carbon from carbonate minerals as important sources.

CONCLUSIONS

1) Three water masses are identified in the Pennsylvanian aquifers:

   (1) Modern meteoric water

   (2) Glacial meteoric water

   (3) Parma-Bayport brine

2) Water chemistry in the southern part of the Grand River-Saginaw aquifer is mainly controlled by recharge water which acquires solutes through rock-water interaction that occurs in the overlying Glacial-Drift deposits. In parts shale membrane filtration (reverse osmosis) may be occurring causing the lower dissolved-solids concentrations in the Grand River-Saginaw aquifer than in overlying Glacial-Drift aquifer.

3) Ground water with higher dissolved solids concentrations in the Grand River-Saginaw aquifer, particularly in the east-central part of the study area, are mostly influenced by mixing with brine in the Parma-Bayport aquifer. Mixing is occurring closer to Saginaw Bay as this area is identified as a regional discharge area for the aquifer system. The mixing relationships between all water masses does exist and is identified in the Pennsylvanian aquifers through linking isotope and chemical data by analogy to Long et al., (1993).

4) The origin of the Parma-Bayport brine can be implied even with limited data available. It appears that the origin of brine in the Parma-Bayport aquifer is from evaporative concentrated seawater just short of halite saturation and the brine has been impacted by aluminosilicate reactions causing K depletion, some degree of dolomitization affecting Ca and Mg concentrations, and sulfate reduction lowering sulfate concentrations, and possibly impacted by gypsum dissolution. Without more data from the aquifer a definitive origin of the brine cannot be reached. Data from brine in the Parma-Bayport was found to be

hydraulic potential for water to move from the drift to the Grand River-Saginaw aquifer in the southern portion of the aquifer (Wood, 1969).

Stable isotopes of O and D indicate three meteoric water masses are present in the aquifer: (1) modern meteoric water, (2) glacial age meteoric with a third water mass, the Parma-Bayport brine not represented by O and D data on the diagram. A mixing model was applied to explain high solute concentrations (>3,000 mg/L dissolved-solids) associated with water with a glacial meteoric water signature based on requiring only a small percentage of brine to cause solute concentrations observed without and having no effect on the isotopic signature of the water sample. This model links mixing interpretations made independently from analysis of chemical and isotope data. The model explains mixing relationships between brine, modern meteoric water and glacial meteoric water causing solute concentrations and isotopic signatures for the majority of samples.

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