CHEMISTRY AND ORIGIN OF OIL AND GAS WELL BRINES IN WESTERN PENNSYLVANIA

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AND NATURAL RESOURCES

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PREFACE

This paper was originally written in 1985 and submitted to the Pennsylvania Geological Survey for publication soon after. To our regret, a combination of circumstances at the Survey in the intervening years prevented it from being published. Now, in 2010, interest in the report has been renewed because of the brines and related problems being encountered in drilling and production of gas from the Marcellus shale. Recent analyses of flowback water from Marcellus wells indicate that late-emerging portions of the flowback water have compositions similar to the oil and gas brines from the other stratigraphic units discussed in this report. The data and concepts contained herein also should be useful in understanding the effects of injecting brines and waste waters into the deep subsurface. Indeed, the very high radium contents indicate that caution should be used in handling these brines.

Because of this new interest, the manuscript was brought out from storage, and with some attention to what still needed to be done, the report is ready for a belated release. There was no attempt to update the manuscript, with the exception of Figure 1. The latest version of this map easily replaced the previous version. It should also be noted that out-of-date information is contained in Table 1, the most obvious being that two Pennsylvanian units, the Allegheny and Pottsville, are now considered to be formations rather than groups. For more recent information concerning the geologic units, refer to Shultz, 1999. A short version of this report can be found in Rose and Dresel, 1990.

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CHEMISTRY AND ORIGIN OF OIL AND GAS WELL BRINES IN WESTERN PENNSYLVANIA

by

P. Evan Dresel[1] and Arthur W. Rose[2]

ABSTRACT

Brines having moderate to high salt content (up to 343 grams per liter [g/L]) occupy most pore spaces in rocks below a depth of a few thousand feet in Pennsylvania and are brought to the surface during oil and gas operations. Forty analyses of brines from a range of geologic environments in western Pennsylvania are reported here, accompanied by brief descriptions of analytical methods required to obtain valid and accurate data, especially for unstable parameters such as pH and oxidation state. The brines are dominated by Na-Ca-Cl. Maximum concentrations, in milligrams per liter (mg/L), are as follows: Na, 83,300; Ca, 41,600; Cl, 207,000; Mg, 4,150; K, 4,860; Fe, 494; Sr, 13,100; Ba, 4,370; Li, 315; Br, 2,240; I, 56; SO_4^{2-}, 850; Cu, 0.13; Pb, 0.04; and Zn, 1.3. Density reaches a maximum of 1.201 grams per cubic centimeter and electrical conductivity a maximum of 211,000 microSiemens per centimeter. The pH is 5.5 to 7.3 but becomes more acid upon oxidation of Fe^{2+}. The oxidation state is ambiguous but relatively reducing, probably defined by coexistence with iron-bearing carbonates, pyrite, methane, and carbon dioxide. The content of hydrogen sulfide is very low, less than 1 mg/L. Samples having high Ba and Sr have low SO_4^{2-} (<20 mg/L) and are approximately saturated with barite and celestine or strontianite. Very high contents of Ra (up to 5,300 picocuries per liter) occur in some samples that have high Ba and low SO_4^{2-}, judging from six analyzed samples. Alkalinity is relatively low (<200 mg/L as HCO_3^-) and appears to include some organic anions. The concentrations of Na, Cl, Br, Ca, and Mg and the density and electrical conductivity are closely correlated. Plots allow prediction of electrical conductivity, density, total dissolved solids, Cl, or Na from any of the other variables in this group.

The Na-Cl-Br composition of the most concentrated brines from oil and gas reservoirs in Upper Devonian rocks is close to the composition of seawater evaporated to the stage of halite precipitation. In the total group of samples, the contents of Na, Ca, Mg, Cl, and Br are largely explainable by mixing of this evaporated seawater with varying amounts of freshwater or seawater. The concentrated end member is interpreted as a residual pore fluid expelled from the Silurian Salina evaporite formation or a similar saline formation. Brines from the Medina Group in northwestern Pennsylvania appear to have had a slightly more concentrated end member, evaporated to near the state of magnesium salt precipitation, and brines from the Ridgeley Sandstone in south-central Pennsylvania have slightly higher Cl:Br ratios than the main group of brines in the Upper Devonian rocks. The degree of uniformity of the brines over large regions and their presence in rocks many thousands of feet above the evaporites suggest major migration of the brines since their original formation. Nearly all brines from oil wells producing from the Upper Devonian have less than 130 g/L total dissolved solids, whereas brines from gas wells commonly have more than 150 g/L total dissolved solids. Some brines from Mississippian and Pennsylvanian rocks, though exhibiting the same dilution trends, have less than 50 g/L dissolved solids. The dilution with freshwater/seawater could have occurred at any time since the Devonian, though a small suite of δD and $\delta^{18}O$ determinations does not suggest an input of Pleistocene water.

The inferred evaporite origin of a major component of the brines suggests that no major flushing of these rocks with meteoric waters has occurred since the Silurian, and that the brines have been more or less stagnant over geologic time periods. The brines can be sources of Ba, Ra, and Fe contamination in some areas. Iron could have been derived largely by corrosion of steel casing, though further study would be required to support such a conclusion.

The Ca:Mg ratio is explainable by dolomitization, probably mainly during early diagenesis but continuing to relatively recent times, based on a correlation of the Ca:Mg ratio with present-day reservoir temperature. Potassium contents are evidently affected by feldspar-clay reactions and do not follow dilution trends.

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INTRODUCTION

Most oil and gas wells produce a saline solution, or brine, in addition to the desired oil and gas (Collins, 1975). The wells of western Pennsylvania are no exception. Previous analyses (Poth, 1962) indicated that these brines have moderate to high salinities (5,000 to 270,000 mg/L [milligrams per liter] dissolved solids) and that the major solutes are sodium and calcium chlorides, which are accompanied by a wide range of other solutes at lower concentrations. However, major questions remain concerning the geographic and geologic distribution of salinities and the pH, oxidation state, and chemistry of the brines at depth. There are also questions concerning the origin, history, and present hydrology of the brines and the content and geographic distribution of trace elements contained in them. The purposes of this study are to report new results bearing on these questions and to summarize prior and new data on brines in Pennsylvania.

A number of recent developments require better data on the brines. Gas drilling and production has been accompanied by claims of water pollution possibly caused by the brines produced with the gas. Economic oil and gas development and production requires an understanding of brine chemistry to evaluate porosity, oil and gas content of reservoirs, and corrosion and precipitation effects during production. Safe disposal of the brines requires information on their composition and inferred reactions with materials at disposal sites. Similar brines probably occur at depth in most sedimentary rocks of the state. Proposals for injection of wastes into deep aquifers will require knowledge of the brine composition. The distribution and nature of oil and gas may be related to brine chemistry. The brines could be the source of valuable chemicals. Finally, the chemistry of these brines could be analogous to that of past fluids that formed ores in this and other regions.

The chemical analysis of brines is more demanding than the analysis of dilute solutions. A number of new analytical methods were tested by Dresel (1985) and used on the new analyses reported here. Some of these methods may be useful to other analysts faced with similar problems.

Strictly speaking, the term "brine" means water with more than 35,000 mg/L (about 3.5 percent) total dissolved solids (Hem, 1985, p. 157). In this report, however, the terms "oil-field brine," "oil-and-gas-field brine," "sedimentary-basin brine," and "saline formation water" are used interchangeably to mean the chloride-rich waters found in sedimentary environments and commonly brought to the surface during oil and gas production. Thus, several samples that

have less than 35,000 mg/L dissolved solids will be discussed with the more concentrated samples.

The 40 new analyses completed by Dresel (presented in both his 1985 report and in this paper) add significantly to the relatively small number of previously published analyses. Barb (1931) reported analyses for some major constituents in brines from 45 oil wells in Pennsylvania. Poth (1962) provided major- and trace-element data for 51 samples from Cambrian through Pennsylvanian aquifers. Kelley and others (1973) made available a compilation of brine analyses that included Poth's values, those from Barb, and analyses submitted by oil and gas companies. The sampling and analytical methods for these analyses and the quality of the results are highly variable. Waite and others (1983) reported a number of brine analyses. Of the published analyses, those of Poth, in which 20 elements were reported, are the most complete. However, most of his samples were from the area north and west of Pittsburgh, he did not attempt to evaluate the oxidation state, his pH values probably do not represent conditions at depth, and he gives no data for lead. The analyses of Dresel fill some of these gaps in the previous data. After presentation of the new analyses, the Dresel and Poth data are discussed and interpreted.

HISTORY

Brine seeps in Pennsylvania and surrounding areas have been used as a source of salts since prehistoric times. Brine was utilized by the white settlers from the second half of the eighteenth century on. The history of the brine industry is discussed in greater detail by Bownocker (1906), Stout and others (1932), and Price and others (1937). In the early 1800s, wells were dug and later drilled for brine production. In 1815, a brine well in West Virginia first started to exploit natural gas. The gas was used in the brine evaporators. In 1868, the first commercial production of bromine from brine in Ohio was started. Calcium chloride recovery began a few years later. In 1884, there were 16 salt-making establishments in Pennsylvania (Harris and others, 1908).

Technology developed for the brine industry was used by Col. Edwin Drake when he drilled the first oil well in Titusville in 1859. Since the demise of the brine industry, brine has continued to be produced as a by-product of the oil and gas industries. Shallow oil wells in Pennsylvania produce, on the average, about 1 to 2 bbl (barrels) (160 to 320 L) of brine per day, whereas shallow gas wells produce 0 to 2 bbl (0 to 320 L) and deep gas wells produce 0 to 4 bbl (0 to 640 L) per day. Waite and others (1983), who col-

lected these statistics, suggested that the brine may be an important source of local pollution. Presently, the brine is disposed of in a number of ways. A few disposal wells are in operation. More commonly, the brine is discharged to the land surface after treatment to separate the water fraction from the oil or gas. Brine, in some instances, is discharged to streams after special pretreatment or through municipal sewage treatment plants. Some counties spread brine on roads for dust and ice control. Waite and others (1983) discussed brine disposal in detail.

GEOLOGY OF OIL AND GAS PRODUCTION IN PENNSYLVANIA

Production of oil and gas in Pennsylvania, usually accompanied by brine, is almost completely restricted to the Appalachian Plateau in the western half of the state (Figure 1). The generalized stratigraphy of this region is shown in Table 1. Oil pools are located mainly in the northwestern part of the state, and most of the oil-producing areas are in Warren, McKean, Venango, Forest, and Elk Counties. Oil is produced from Upper Devonian strata, although some oil is also produced from Lower Silurian, Mississippian, and Pennsylvanian rocks. Hydrocarbon production is divided arbitrarily into "shallow" and "deep" groupings, which refer to the stratigraphic position of the producing zone rather than the well depth. The Upper Devonian, Mississippian, and Pennsylvanian "shallow gas" is the most extensively exploited and is found in a broad band from Potter and McKean Counties in the north to Greene, Fayette, and Somerset Counties in the south. "Deep gas" is defined as being from Middle Devonian and older rocks. The Lower Devonian Ridgeley Formation is an important gas producer in the eastern part of the hydrocarbon region, mainly in Somerset, Cambria, Clearfield, Clinton, and Potter Counties. The Silurian Medina Group is a gas and oil producer in the extreme northwestern part of the state, including Erie, Crawford, Warren, Venango, and Mercer Counties. The Tuscarora Formation (stratigraphically equivalent to the Medina) is a minor gas producer in central Pennsylvania. There is also minor oil and gas production outside these main accumulations, as shown in Figure 1.

The Appalachian Plateau in western Pennsylvania encompasses a large area of shallowly dipping sedimentary rocks. The near-surface upper Paleozoic sedimentary rocks are broadly folded. Fold axes are generally parallel to the Allegheny Front. At depth, especially near the Allegheny Front, the rocks are thought to be deformed by the stresses that formed the "Eastern Overthrust belt" (Pohn and Purdy, 1979; Berg and others, 1980; Harper and Laughrey, 1982). The deformation consists of long bedding-plane thrusts and associated low-angle thrusts. Normal faults, high-angle reverse faults, and strike-slip faults are associated with the major décollements. The folds and faults may form important hydrocarbon traps in some areas, particularly in fields producing from the Ridgeley Formation.

CHARACTER OF OIL AND GAS RESERVOIRS

The nature of the reservoir rocks, especially their mineralogy, is important in limiting certain chemical characteristics of the brines, as discussed later. In the following sections, the characteristics of the most important reservoirs, especially those sampled by Dresel (1985), are summarized.

Upper Devonian Sandstones

Both oil and gas are produced from Upper Devonian rocks in Pennsylvania. The Upper Devonian sandstones are discontinuous and form stratigraphic traps. Most are known only from well logs and are called by local, informal names. Thus, the sandstones at a given stratigraphic position may have different names in different areas. The oil-bearing sandstones are found in the Bradford and Venango Groups (Table 1).

The lower Bradford Group sandstones range from light gray to dark brown and are of highly variable grain size. Krynine (1940) described the Third Bradford sand in drill core from the Bradford and Kane areas as a medium- to fine-grained graywacke containing siltstone and sandstone layers. The sandstone consists of 60 to 65 percent quartz grains, 30 percent rock fragments, and 3 to 4 percent biotite, plus muscovite and very little feldspar. Chlorite may be detrital or may be formed from biotite. Krynine (1940) reported calcite cement, ankerite/siderite, and some authigenic sericite or illite. He found dolomite present as small idiomorphic rhombs. Gypsum and anhydrite occur rarely. Some of the clay fraction is possibly montmorillonite. Other authigenic minerals include anatase, apatite, barite, and rare fluorite. One of Krynine's specimens contained galena. Pyrite is abundant and is associated with organic material. A small amount of hematite and limonite after siderite was found. Tourmaline, zircon, and apatite are the most common heavy minerals. Wolfe's (1963) description of the Bradford sands from the subsurface in Armstrong, Indiana, Clarion, and Jefferson Counties
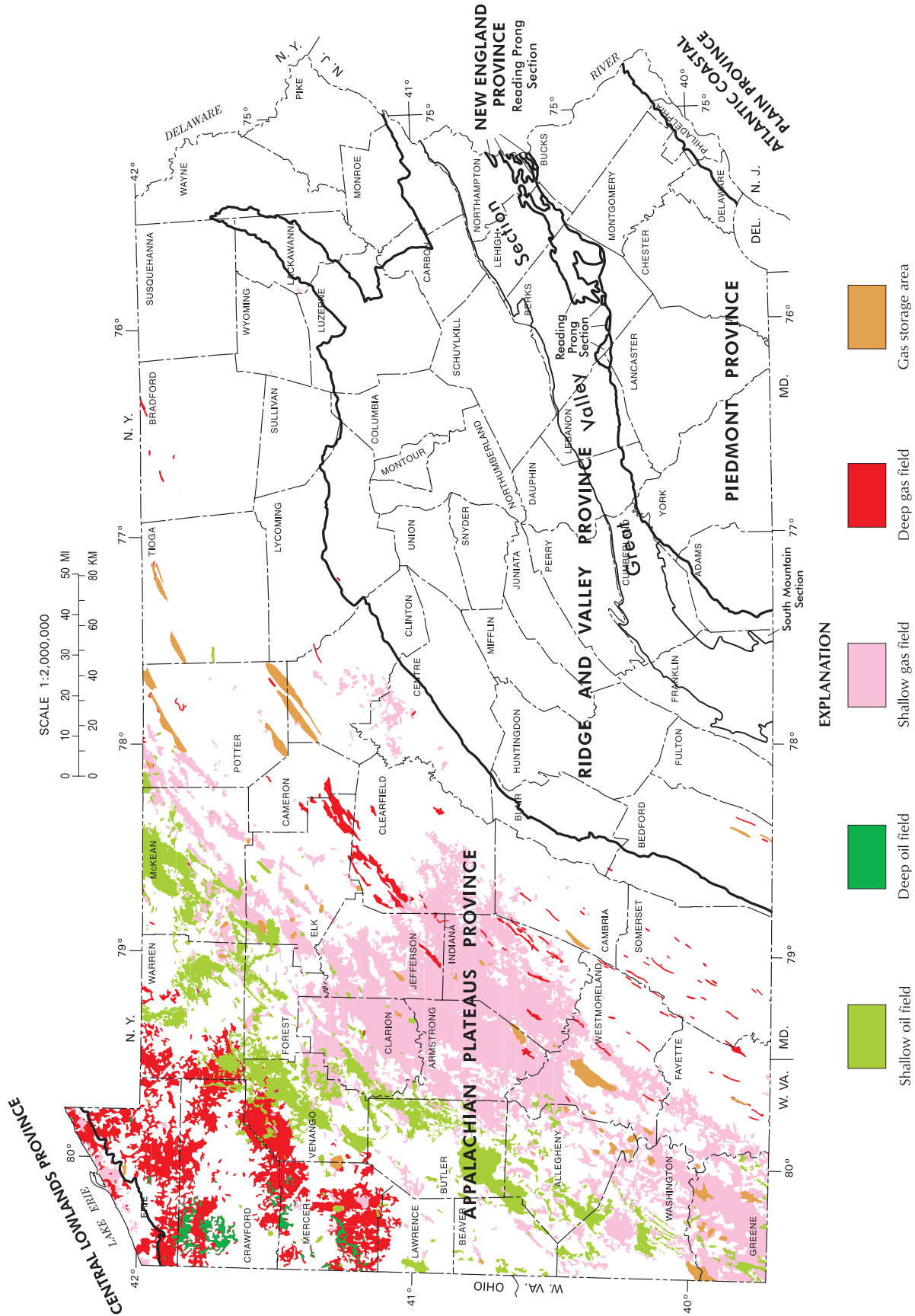
Figure 1.   Map showing the locations of oil and gas fields and physiographic province boundaries in Pennsylvania (modified from McCoy and Schmitt, 2007).

Table 1. *Generalized Stratigraphy of Western Pennsylvania*

(After Berg and others, 1983)

Systems	Geologic units	
	West	South-central/central
Permian	Dunkard Group	
	Greene Fm.	
	Washington Fm.	
	Waynesburg Fm.	
Pennsylvanian	Monongahela Group	
	Uniontown Fm.	
	Pittsburgh Fm.	
	Conemaugh Group	
	Casselman Fm.	
	Glenshaw Fm.	
	Allegheny Group	Allegheny Group
	Freeport Fm.	
	Kittanning Fm.	
	Clarion Fm.	
	Pottsville Group	Pottsville Group
	Homewood Fm.	
	Mercer Fm.	
	Connoquenessing Fm.	
	Sharon Fm.	
	Olean Cgl.	
Mississippian	*Unconformity*	*Unconformity*
	Mauch Chunk Fm.	Mauch Chunk Fm.
	Greenbrier Fm.	
	Loyalhanna Fm.	Loyalhanna Fm.
	Unconformity	
	Burgoon Ss.	Pocono Fm.
	Shenango Fm.	
	Cuyahoga Group	
	"Murrysville Sand"	
	Berea Ss./Corry Ss.	Rockwell Fm.
	Bedford Sh.	
	Cussewago Ss.	
Devonian		
Upper	Riceville Fm./Oswayo Fm.	Rockwell Fm.
	Venango Group	Catskill Fm.
	Chadakoin Fm.	
	Bradford Group	
	Elk Group	Lock Haven Fm.
	West Falls Fm.	
	Sonyea Fm.	Brallier Fm.
	Genesee Fm.	Harrell Sh.
Middle	Tully Ls.	Hamilton Group
	Hamilton Group	Tully Ls.
		Mahantango Fm.
	Marcellus Fm.	Marcellus Fm.
	Onondaga Fm.	Onondaga Fm./
		Selinsgrove Ls.

Table 1. *(Continued)*

Systems	Geologic units	
	West	South-central/central
Devonian		
Lower	Bois Blanc Fm.	Needmore Sh.
	Oriskany Ss.	
	Unconformity	*Unconformity*
		Ridgeley Ss.
		Licking Creek Ls.
		Shriver Fm.
		Mandata Sh.
		Corriganville Ls.
		New Creek Ls.
Silurian		
Upper	Keyser Fm./	Keyser Fm.
	Bass Islands Dol./	
	Akron Dol./Bertie Dol.	
	Salina Group	Tonoloway Fm.
		Wills Creek Fm.
		Bloomsburg Fm.
	Lockport Dol.	Mifflintown Fm.
Lower	Clinton Group	Rose Hill Fm.
	Medina Group	Tuscarora Fm.
Ordovician		
Upper	Queenston Sh./	Juniata Fm.
	Juniata Fm.	
		Bald Eagle Fm./
		Oswego Fm.
	Reedsville Sh.	Reedsville Sh.
	Antes Sh.	Antes Sh.
	Coburn Fm.	Coburn Fm.
	Salona Fm.	Salona Fm.
	Nealmont Fm.	Nealmont Fm.
	Benner Fm.	Benner Fm./
		Linden Hall Fm.
	Snyder Fm.	Snyder Fm.
	Hatter Fm.	Hatter Fm.
Middle/Lower	Loysburg Fm.	Loysburg Fm.
	Beekmantown Group	Beekmantown Group
	Bellefonte Fm.	Bellefonte Fm.
		Axemann Fm.
	Nittany Fm.	Nittany Fm.
	Larke Fm.	Larke Fm.
Cambrian		
Upper	Gatesburg Fm.	Gatesburg Fm.
	Warrior Fm.	Warrior Fm.
	Potsdam Ss.	

is similar to Krynine's. Wolfe also noted clastic dolomite and dolomite cement. Glohi (1984) described the petrography of Bradford Group sandstones in Indiana County. He found 42 to 51 percent quartz grains, 3 to 9 percent feldspar, 10 to 25 percent rock fragments containing up to 3 percent mica, up to 1 percent heavy minerals, and traces of carbonate and chert grains. The cement included quartz overgrowths, dolomite, clay minerals, and some traces of calcite and siderite. One sample included 24 percent iron oxide pore fillings.

The Upper Devonian Venango Group includes the drillers' Venango sands and the Red Valley sand. The group generally consists of gray sandstone interbedded with gray shale, although red shale is common in the middle part of the group.

Modarresi (1963) performed a detailed study of the First Venango sand from drill core from Warren County. This is a tightly cemented, fine-grained sandstone containing common shale partings. The sandstone consists of 45 to 50 percent detrital quartz grains, 16 percent rock fragments, 3 to 4 percent mica, 10 to 14 percent matrix clay, 16 to 17 percent silica cement, 1 to 2 percent carbonate cement, and 1 to 2 percent feldspar. The matrix clay fraction is mainly kaolinite, and the carbonate cement was reported to be ankerite.

Laughrey and Harper (1984) described the Venango Group as being made up of interbedded conglomerates, sandstones, siltstones, and shales. The sandstones are fine to coarse grained, in many places conglomeratic, and poorly to moderately well sorted. In the sandstone, they found 65 to 90 percent quartz, trace to 10 percent sericitized feldspar (plagioclase > orthoclase > microcline) and less than 1 to 15 percent rock fragments. Accessory minerals include mica (unspecified species), zircon, tourmaline, and magnetite. The principal cements are up to 10 percent silica, 5 percent calcite and dolomite, and smectite plus vermicular chlorite.

The Bradford Group is interpreted as marine, whereas the Venango Group is deltaic to marine (Modarresi, 1963; Kelley, 1967; Laughrey and Harper, 1984 and personal communication).

Ridgeley and Oriskany Sandstones

In Pennsylvania, the rocks formerly termed Oriskany Sandstone have been divided into two units. The Ridgeley Sandstone is present in the subsurface of the south-central and central parts of the state and crops out in the Ridge and Valley province. The Oriskany Sandstone, at approximately the same horizon in the northwest, is separated from the Ridgeley Sandstone by a no-sand area caused by either erosion or nondeposition (Abel and Heyman, 1981). The Oriskany occurrence in the northwest is discontinuous and may include the Bois Blanc Formation sandstone. Gas production from the Ridgeley Sandstone is generally from structural traps. Abel and Heyman (1981) defined the Ridgeley in the subsurface of Pennsylvania from a gamma-ray log format (a parastratigraphic rock unit defined by characteristic log deflections). This format cuts facies boundaries and includes sandstone underlain by limestone and interbedded limestone and sandstone.

The Ridgeley Sandstone is generally a gray, medium-grained quartz arenite (Rosenfeld, 1953). It is light orange to buff in outcrop. Most of the Ridgeley is silica cemented, but there are highly calcareous areas (Krynine, 1941). Welsh (1984) included silica-cemented quartz arenite, sandy biosparite, carbonate-cemented quartz wacke, and coquinoid carbonate-cemented quartz arenite in the Ridgeley Sandstone. Conglomeratic areas were reported by Willard and others (1939). Rosenfeld (1953) reported a mean effective porosity of 7.6 percent and a mode of 4.0 percent. The average composition reported by Rosenfeld for Ridgeley quartz sandstone is as follows: detrital silicates, 77.7 percent; authigenic silica, 9.5 percent; clastic carbonate, 7.1 percent; fixed crystalline carbonate, 3.8 percent; other clastics, 1.4 percent; and other cements and matrices, 0.5 percent. Detrital silicates reported by Rosenfeld include about 1 percent feldspar and 0.2 percent heavy minerals. The authigenic silica is mainly clear quartz overgrowths, but locally consists of microcrystalline quartz or quartz having flamboyant radiating extinction. The clastic carbonates are fossil fragments, whereas the fixed crystalline carbonate includes sparry calcite, small rhombs of dolomite, and small rhombs of siderite or ankerite. R. Borkowski (personal communication) reported relatively iron-rich ankerite rims on top of less iron-rich dolomite cores of crystals, based on staining of thin sections. Welsh (1984) reported fractures healed by calcite, whereas Basilone and others (1984) noted quartz and ferroan calcite fracture fillings. Other clastics include phosphate pellets and rock fragments containing rare biotite and chlorite and a few flakes of muscovite. Interstitial limonite is commonly present, and one section had barite or celestine cement. Hodgson (1970) reported, from the Oriskany in New York, zircon, magnetite, muscovite, authigenic pyrite, and limonite pseudomorphs after pyrite. Stow (1938) reported zircon, tourmaline, rutile, leucoxene, chlorite, and limonite as the Oriskany heavy minerals in Pennsylvania. His samples were taken from outcrop. The Oriskany and Ridgeley are generally thought of as shallow-marine deposits.

Medina Group and Tuscarora Formation

The stratigraphy of the Lower Silurian Medina Group and Tuscarora Formation in Pennsylvania has been described by Cate (1961, 1965), Piotrowski (1981), and Laughrey (1984). The Medina Group is considered to be the northwestward extension of central Pennsylvania's Tuscarora Formation. Unlike the Upper Devonian sandstones and the Ridgeley Formation, the Medina is stratigraphically below the evaporites of the Upper Silurian Salina Group.

The Medina Group is divided into three formations in Pennsylvania. The lowermost is the Whirlpool Sandstone, which is a light-gray quartzose to subarkosic sandstone containing subordinate mudrock. It lies disconformably on the Queenston Shale. The middle Cabot Head Shale is a dark- to medium-dark-gray marine shale that includes some lenticular quartzose sandstone laminations and local lenticular sandstone bodies or beds. The major part of the Medina Group is made up of the Grimsby Sandstone tongue. This grades upward from the Cabot Head Shale and consists of medium- to very fine grained, light-gray to red sandstone and siltstone interbedded with silty shale and clayey shale. It thickens to the southeast, where it becomes the Tuscarora Formation. The red part generally comprises the upper two-thirds of the unit and may be more porous and permeable than the white part.

In a thorough study of Medina core, Laughrey (1984) reported zircon, epidote, tourmaline, hornblende, ilmenite, magnetite, and sphene as detrital accessory minerals. He recognized eight diagenetic events that are reflected by the following paragenesis:

(1) Feldspar overgrowths consisting of intermediate alkali feldspar on detrital potassium feldspar.
(2) Nodular anhydrite, calcite, and siderite cementation. The anhydrite was interpreted as being due to the presence of hypersaline pore waters during or just after deposition. The calcite is a minor component of the cement, but some could have been lost through dolomitization. The siderite, found in the upper Grimsby Sandstone, represents anoxic conditions associated with biologic activity and organic matter during burial.
(3) Authigenic clay minerals including pore linings of illite, iron-rich chlorite, mixed-layer chlorite/illite and chlorite/smectite. The illite and mixed-layer clays also replace feldspars.
(4) Silica cementation. Silica forms quartz overgrowths and engulfs earlier calcite cement.
(5) Authigenic leucoxene formed from the alteration of rutile and ilmenite.

(6) Compaction and pressure solution.
(7) Dolomitization. Dolomite cement replaces the cements mentioned above and is thus interpreted as forming late in the burial history.
(8) Hematite cementation. Late diagenetic hematite is indicated by its presence as fracture fillings that crosscut other cements, replacement of previous cements, and hematite filling of secondary voids. Laughrey interpreted the hematite as being formed from oxidizing fluids entering through vertical fractures.

Piotrowski (1981) reported approximately 3 percent porosity in the Tuscarora Formation and 6 to 9 percent in the Medina Group. Laughrey (1984) demonstrated that the facies of the Medina Group in the subsurface of Crawford County are compatible with Martini's (1971) model of deposition as a shelf/longshore-bar/tidal-flat/deltaic complex.

OCCURRENCE OF HALITE

As discussed later in this report, the present brines are believed to have been derived in large part from evaporation of seawater to the stage of halite precipitation. The distribution of evaporites, specifically halite, in the region is therefore of interest. Major halite beds are known to occur in the Salina Group of Silurian age (Cate, 1961, 1965; Fergusson and Prather, 1968), as shown in Figure 2. The halite beds are thickest in north-central Pennsylvania and adjacent New York, but they extend throughout most of western Pennsylvania.

COLLECTION AND ANALYSIS OF NEW SAMPLES

HORIZONS AND AREAS SAMPLED

The new sampling and analyses reported here are of a reconnaissance nature. The intent was to survey a variety of localities and types of wells in order to gain a general view of results obtained using up-to-date analytical methods and to compare those results with older analyses. No attempt was made to obtain detailed sampling in any one area. Both oil and gas wells were sampled, as were a variety of producing horizons ranging from Lower Silurian to Upper Devonian. In general, the samples were located along a northwest-trending strip from Somerset and Indiana Counties, near the eastern edge of the Appalachian Plateau, to Crawford County, near the Ohio border in northwestern Pennsylvania. A total of 40 samples were analyzed. Additional samples covering
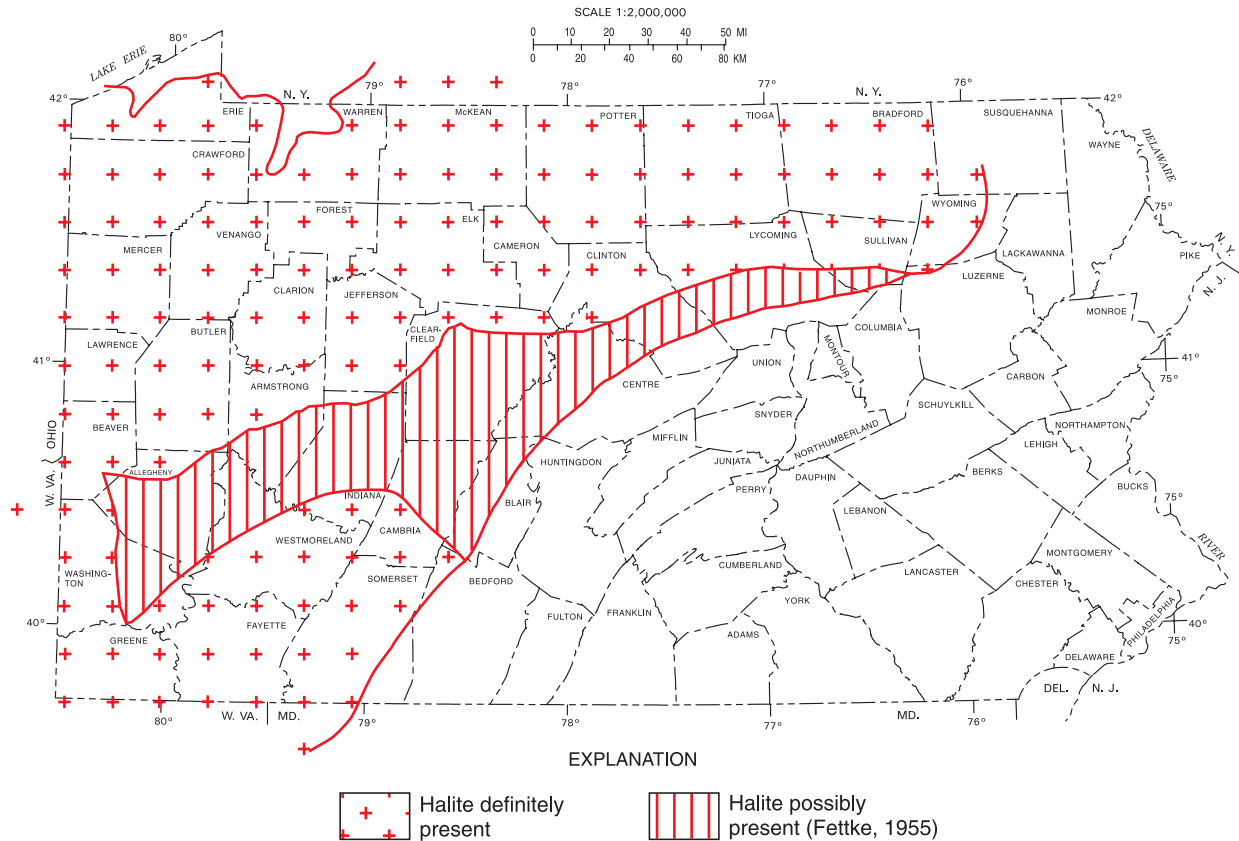
Figure 2. Map showing the distribution of halite in the Silurian Salina Group, based on maps of Fergusson and Prather (1968) and Fettke (1955).

a wider areal and stratigraphic range, especially those of Poth (1962), are included in the interpretation and discussion.

The foremost consideration in choosing wells for sampling was the availability of a significant amount of brine that could be considered representative of brine at depth. Many oil and gas wells produce too little brine to obtain a sample. From some wells, fresh samples were obtained but the quantities were too small to perform a complete set of analyses. Areas that had been subjected to water flooding were avoided. In nearly all cases, the wells had been in production for a year or more, so contamination by drilling and completion fluids was unlikely.

The samples were collected between July and December 1982. Well locations and descriptions are given in Table 2. The locations are plotted on Figure 3. Fourteen oil wells and 26 gas wells were sampled. Twenty-five of these, including all of the oil well samples, are from the Upper Devonian. Ten of the gas well samples are from the Medina Group, one is from the Tuscarora, and four are from the Ridgeley. The perforation depths range from less than 590 ft to more than 10,830 ft.

SAMPLING TECHNIQUES

Brine samples were collected as close to the wellhead as possible, with the assistance of personnel from operating companies. Freshly produced samples were favored. Where fresh samples were unavailable or where insufficient water was produced (samples ED–82–14, 19, 21, 22, 32, 33, 34, and 35), samples were taken from brine holding tanks (Table 2).

The freshly produced samples from oil wells were collected from the pipe before the oil-water separator. The oil was pumped from the well, and when water started to be produced it was collected in a 5-liter glass sample bottle. Residual oil was allowed to separate in the sample jug, and the water was drawn off through a bottom spigot.

Samples from the Medina Group gas wells were collected from gauge fittings at the wellhead. When the well was opened to the atmosphere, water rose with the escaping gas, producing fine droplets. With this method of production, it was difficult to collect an adequate amount of sample. Thus, for freshly produced Medina samples, only sample ED–82–27 has

Table 2. Stratigraphic Data, Locations, and Depths of Brine Samples

(From Dresel, 1985)

| Sample	Horizon	Type	County	Township	Quadrangle (7.5-minute)	Latitude (N)	Longitude (W)	Collar elevation (feet above sea level)	Perforation depth below ground surface		Date drilled	Sample point
									Upper (feet)	Lower (feet)		
ED–82–01	Upper Devonian	Gas	Indiana	East Mahoning	Marion Center	40°47'17"	79°03'54"	1,300	2,540	3,500	1978	Wellhead
–02	do.	Gas	do.	Rayne	Clymer	40°44'09"	79°02'49"	1,218	2,144	2,999	1977	do.
–03	do.	Gas	do.	do.	do.	40°44'09"	79°02'49"	1,300	2,144	2,999	1977	Separator
–04	do.	Gas	Jefferson	Henderson	McGees Mills	40°59'15"	78°49'45"	1,480	2,583	3,390	1978	Wellhead
–05	do.	Gas	Indiana	Banks	Burnside	40°51'53"	78°50'57"	1,625	—	—	—	do.
–06	do.	Gas	do.	do.	do.	40°51'53"	78°50'57"	1,625	—	—	—	do.
–07	do.	Gas	do.	do.	do.	40°50'28"	78°48'35"	1,518	2,264	3,339	1978	do.
–08	do.	Gas	do.	White	Indiana	40°36'16"	79°09'53"	1,284	2,050	3,628	1981	do.
–09	do.	Gas	do.	South Mahoning	Plumville	40°46'39"	79°08'16"	1,360	2,837	3,488	1973	do.
–10	do.	Gas	do.	Canoe	Punxsutawney	40°53'06"	78°56'42"	1,578	2,712	3,562	1976	do.
–11	do.	Gas	do.	Grant	Rochester Mills	40°46'40"	78°58'43"	1,881	2,790	3,582	1974	do.
–12	Red Valley	Oil	Venango	President	President	41°27'53"	79°33'59"	1,400	573	590	1981	Brine tank
–13	Venango Second	Oil	do.	Allegheny	Pleasantville	41°32'29"	79°32'03"	1,640	755	765	1980	Wellhead
–14	Glade	Oil	Forest	Hickory	Kellettville	41°34'19"	79°21'38"	1,757	640	650	1981	Brine tank
–15	Venango First and Third	Oil	Warren	Southwest	Grand Valley	41°41'30"	79°33'38"	1,450	—	—	—	Wellhead
–16	Glade	Oil	do.	Pleasant	Warren	41°49'18"	79°12'11"	1,640	1,116	1,171	1979	do.
–17	do.	Oil	do.	do.	do.	41°48'57"	79°12'39"	1,400	926	996	1979	do.
–18	do.	Oil	do.	do.	do.	41°48'34"	79°12'32"	1,730	1,146	1,200	1977	do.
–19	Cooper	Oil	do.	Sheffield	Ludlow	41°38'21"	78°57'41"	1,852	1,937	1,959	1968	Brine tank
–20	Kane	Oil	Elk	Highland	Russell City	41°34'26"	78°53'57"	1,880	2,300	—	—	Wellhead
–21	Cooper	Oil	Warren	Sheffield	Ludlow	~41°38'00"	~78°58'00"	1,800	1,900	1,930	1980	Brine tank
–22	Medina	Gas	Crawford	Summit	Harmonsburg	41°39'43"	80°19'49"	1,100	4,047	4,174	1981	do.
–23	Venango Second and Third	Oil	Venango	Sandy Creek	Kennerdell	41°21'41"	79°48'01"	1,450	900	1,100	1981	Wellhead
–24	do.	Oil	do.	do.	do.	41°21'48"	79°48'01"	1,410	900	1,100	1981	do.
–25	do.	Oil	do.	do.	do.	41°21'48"	79°48'01"	1,410	900	1,100	1981	do.
–26	do.	Oil	do.	do.	do.	41°21'48"	79°48'01"	1,410	900	1,100	1981	do.
–27	Medina	Gas	Crawford	Fairfield	Hadley	41°29'23"	80°08'13"	1,410	5,025	5,280	1981	do.
–28	do.	Gas	do.	do.	Geneva	41°30'22"	80°08'20"	1,395	5,024	5,127	1982	do.
–29	do.	Gas	do.	Union	do.	41°33'06"	80°09'49"	1,320	4,790	4,894	1981	do.
–30	do.	Gas	do.	Fairfield	Cochranton	41°31'36"	80°06'29"	1,160	4,784	4,964	1980	do.
–31	do.	Gas	do.	East Mead	do.	41°35'34"	80°04'27"	1,400	4,810	4,990	1982	do.
–32	do.	Gas	do.	Fairfield	New Lebanon	41°29'40"	80°03'51"	1,390	5,100	5,350	1981	Brine tank
–33	do.	Gas	do.	do.	Cochranton	41°30'23"	80°03'53"	1,260	5,035	5,120	1981	do.
–34	do.	Gas	do.	do.	do.	41°30'02"	80°03'14"	1,450	5,234	5,340	1981	do.
–35	do.	Gas	do.	do.	New Lebanon	41°29'31"	80°03'19"	1,315	5,172	5,276	1981	do.
–36	Tuscarora	Gas	Centre	Boggs	Snow Shoe SE	41°00'01"	77°50'35"	1,680	10,941	10,974	1977	Separator
–37	Ridgeley	Gas	Somerset	Black	Murdock	39°58'17"	79°05'29"	2,120	8,839	8,946	1979	do.
–38	do.	Gas	do.	do.	do.	39°56'28"	79°07'10"	1,870	8,778	8,843	1979	do.
–39	do.	Gas	do.	do.	do.	39°56'01"	79°06'38"	2,105	8,850	8,954	1979	do.
–40	do.	Gas	do.	Stonycreek	Stoystown	40°02'30"	78°55'00"	2,357	8,544	8,620	1973	do.
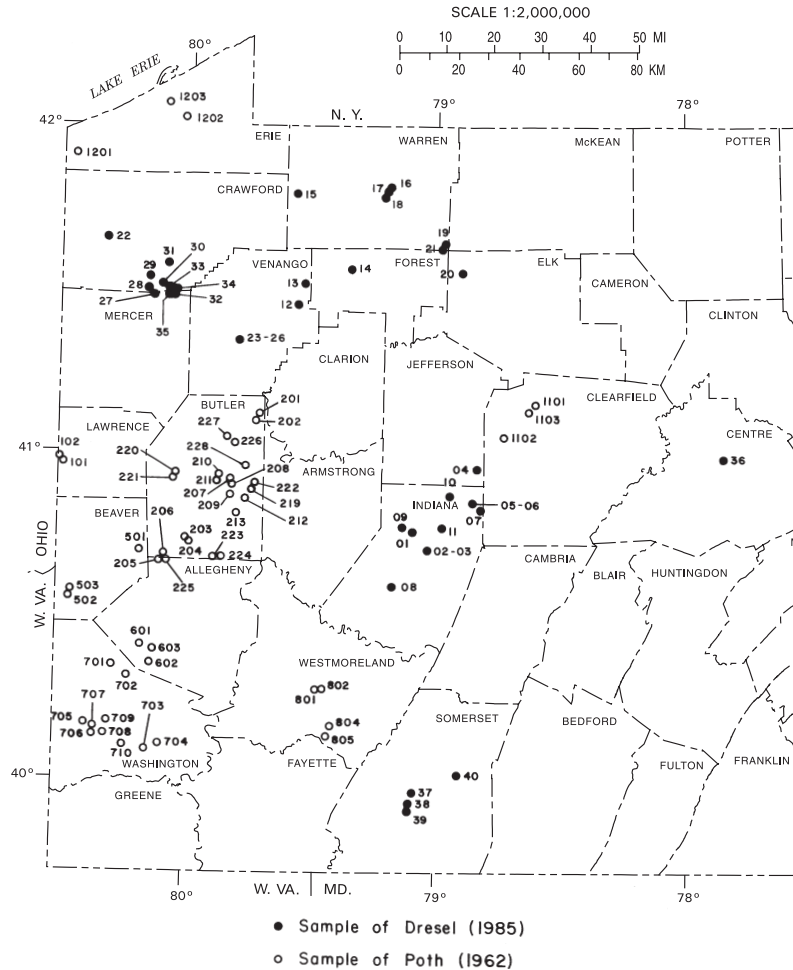
Figure 3. Map showing the locations of samples of Dresel (1985) and Poth (1962).

a complete set of analyses. Sample ED–82–30 is only missing an alkalinity titration. Samples ED–82–28, 29, and 31 were of insufficient volume to obtain complete analyses.

The samples from the Ridgeley and Tuscarora gas wells were obtained from gas-water separators located near the wellhead.

Upper Devonian gas wells were sampled in several ways. The well from which sample ED–82–01 was obtained produced large amounts of brine, which were pumped to the surface. The well that produced sample ED–82–11 had sufficient gas pressure to be sampled by opening the well to the atmosphere and blowing off the brine, which was sampled from a valved fitting on the wellhead. In order to sample most Upper Devonian wells (ED–82–02 through ED–82–10), however, approximately 25 mL of soap was dropped down the wells, and the wells were opened to the atmosphere. The samples then came to the surface as foam after a period of 1 to 15 minutes

and flowed brine briefly. A sample of the soap showed a pH of 7 and very low alkalinity, so it does not act as a significant buffer. It does not appear that the soap had an appreciable effect on the water chemistry. Most samples were collected from valves immediately beyond the main valve stem while the major gas flow was directed through a larger pipe into a separator.

In general, these methods are adequate for the collection of samples for major cations and anions but are not necessarily adequate for volatile species (dissolved carbonate, hydrogen sulfide) and oxidation-sensitive species (Fe^{2+}), as discussed later. Valid samples for these constituents would require sampling at depth into a sealable container and appropriate measurements in a manner to prevent loss or interaction with air. For trace cations that are constituents of the casing, well bore, and valves, additional precautions might be needed. Thus, all brine data must be carefully evaluated for accuracy.

SAMPLE PRESERVATION

Brine samples collected for laboratory analysis were stored in polyethylene bottles. Samples were filtered at the well site through 0.45-μm Millipore or Metricel filters using nitrogen pressure. A polyethylene-lined or stainless steel filter holder was used. For some of the oil well samples, it was necessary to prefilter the sample through glass wool to prevent clogging by oil droplets. Several of the samples (ED–82–03, 07, 08, 22, 27, 28, 29, and 31) proved difficult to filter, apparently because of paraffin precipitates. In those cases, samples were allowed to settle or were filtered only through glass wool, and only a small amount of filtered sample was collected.

Approximately 1 L of filtered, nonacidified sample was collected when possible. A second 500-mL or smaller filtered sample was acidified with 2 mL of ultrapure (Baker Ultrex) nitric acid. This treatment reduced the pH to about 1 and served to keep iron and other elements in solution. Nonfiltered samples were left nonacidified.

The samples underwent notable changes after collection. Immediately after collection, the water was colorless or tinged greenish gray. Within one-half hour, the water had a yellowish cast in all but the most dilute samples. Nonacidified samples turned bright orange as iron hydroxide precipitated, reducing the pH in the sample bottle by several units. Some orange iron hydroxide was commonly left on the filters, suggesting some oxidation before this step. Acidified samples turned bright yellow, presumably due to the formation of ferric chloride upon oxidation. Samples ED–82–01 and ED–82–02 precipitated a small amount of white material in the acidified samples. A portion of the precipitate from

Table 3. *Results of*

(From

Sample	Temper-ature (°C)	Conduc-tivity (μS/cm)	Total dissolved solids, measured (g/L)	Total dissolved solids, calculated (g/L)	Density (g/ml)	Eh (V)	pH (units)	Li (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Sr (mg/L)	Ba (mg/L)	Mn (mg/L)
ED–82–01	13	190,000	213	202	1.134	0.150	6.2	38.1	56,700	190	2,520	18,000	691	171	17.7
–02	19	192,000	—	207	1.142	.110	6.6	46.3	58,300	192	2,500	18,800	1,490	843	16.6
–03	24	188,000	223	207	1.142	.150	6.45	45.5	58,500	193	2,520	19,000	1,470	815	15.8
–04	15	183,000	259	186	1.129	.133	6.5	35.1	52,100	130	2,410	17,100	1,290	1,020	21.1
–05	14	204,000	259	248	1.163	.134	6.45	47.3	63,500	190	2,880	24,700	2,340	1,840	26.7
–06	16	199,000	—	253	1.168	.100	6.5	47.8	63,700	200	2,850	25,100	2,420	2,010	27.7
–07	14	204,000	—	299	1.201	.021	6.2	61.3	71,900	352	3,140	34,400	6,080	698	68.2
–08	11	128,000	—	116	1.093	−.001	6.8	20.2	30,600	290	1,650	11,000	404	174	25.5
–09	14	196,000	—	244	1.159	.180	6.3	43.3	61,900	200	2,970	24,500	1,420	7.1	18.6
–10	14	167,000	—	172	1.115	.010	6.8	23.4	47,400	126	2,150	14,900	578	623	15.3
–11	15	185,000	222	205	1.138	.095	6.5	47.2	58,900	180	2,600	17,700	936	668	13.3
–12	13	195,000	—	12	1.006	.055	7.3	.3	3,400	44	195	1,580	22	17.0	1.1
–13	16	114,000	—	93	1.068	.055	6.9	2.1	25,000	177	1,570	8,150	129	2.4	3.3
–14	24	144,000	—	132	1.089	.089	6.4	6.1	35,000	189	2,110	12,700	117	.8	10.9
–15	13	75,000	—	57	1.037	.129	6.5	2.0	15,200	51	910	3,930	124	355	4.1
–16	11	134,000	128	109	1.079	.055	6.9	7.2	30,000	85	2,050	11,800	152	2.8	11.7
–17	13	112,000	100	91	1.062	.033	7.1	4.3	24,000	64	1,510	8,680	141	ND	7.5
–18	15	138,000	129	116	1.083	.044	6.8	6.2	31,000	83	2,180	12,600	151	ND	11.1
–19	—	18,100	—	10	1.004	.372	6.75	.4	3,000	49	100	920	5	6.8	2.2
–20	10	93,000	73	72	1.047	−.001	6.6	.6	19,800	41	1,150	5,780	191	ND	4.5
–21	19	87,900	68	67	1.043	.072	6.6	1.4	17,400	73	1,040	6,110	39	ND	4.5
–22	22	157,000	—	152	1.106	.095	6.2	19.1	37,600	948	2,050	16,600	477	ND	43.3
–23	22	102,000	88	82	1.052	.117	6.7	1.2	21,800	66	1,400	6,490	137	51.7	.7
–24	—	99,700	—	—	—	—	—	—	—	—	—	—	—	—	—
–25	—	128,000	—	—	—	—	—	—	—	—	—	—	—	—	—
–26	—	101,000	—	—	—	—	—	—	—	—	—	—	—	—	—
–27	13	195,000	—	257	1.179	.055	6.3	86.8	42,400	4,860	4,150	41,600	1,610	ND	49.4
–28	13	201,000	—	246	1.175	.010	5.9	63.2	59,900	1,650	2,750	26,900	1,030	3.8	64.9
–29	14	—	—	310	1.212	—	—	71.5	78,900	1,730	3,790	36,300	1,430	3.5	80.0
–30	10	185,000	217	210	1.135	.078	6.5	52.2	51,100	1,400	2,160	22,000	893	3.2	44.9
–31	8	205,000	—	263	—	.033	6.46	63.8	65,300	1,580	3,120	30,100	1,160	3.9	71.1
–32	—	188,000	—	—	—	—	—	—	—	—	—	—	—	—	—
–33	—	188,000	—	—	—	—	—	—	—	—	—	—	—	—	—
–34	—	191,000	—	—	—	—	—	—	—	—	—	—	—	—	—
–35	—	154,000	—	—	—	—	—	—	—	—	—	—	—	—	—
–36	15	208,000	286	259	1.181	.218	5.49	157	70,700	2,360	1,370	25,500	3,810	919	96.5
–37	28	118,000	106	101	1.067	—	5.63	105	24,400	978	797	8,930	4,400	1,510	6.2
–38	23	196,000	245	230	1.154	.141	6.14	277	61,300	2,580	1,580	17,600	8,930	3,890	5.6
–39	26	211,000	—	302	1.212	.177	5.65	315	79,900	3,180	2,050	23,800	13,100	4,370	5.7
–40	27	211,000	354	343	1.222	.205	5.53	315	83,300	3,890	2,390	28,400	12,800	3,680	5.8

[1]ND, not detected.
[2]Tr, trace.

sample ED–82–02 was examined by X-ray diffraction and analyzed by emission spectrograph. The precipitate was made up of barite and a minor amount of halite. The halite could have been formed during filtering and drying of the precipitate. The cause of the barite precipitation is unclear. It is possible that a small amount of sulfide in solution oxidized to sulfate; however, no sulfide was detected in either sample, and no odor of hydrogen sulfide was noted in this sample or any other. Other possible explanations include temperature changes and mixing of waters from more than one aquifer.

ANALYSIS

The chemical analyses included field analyses and laboratory analyses. Field analyses were used for parameters that might change rapidly upon exposure to surface conditions, and included pH, temperature, alkalinity, Eh, dissolved O_2, and sulfide. The field analyses, including filtering, took approximately one hour per site. Laboratory analyses included major cations (Na, Ca, Mg, K, Fe, Mn, Ba, Sr), anions (Cl, Br, I, SO_4), trace elements (Li, Cu, Pb, Zn), and, for some samples, Si, Al, B, ^{226}Ra, and sulfur, oxygen, and hydrogen isotopes. The physical parameters of conductivity, density, and, in some instances, total dissolved solids were also measured in the laboratory. The analytical results are given in Tables 3, 5, 6, and 7. The analytical methods are summarized in Table 4. For details, see Dresel (1985).

Some comments on the analytical data of Table 3 are necessary. The measured temperature does not represent reservoir temperature, owing to gas expansion, cooling during flow to the surface, and other factors; the listed temperature is mainly useful to in-

Analyses of Brines

Dresel, 1985)

Fe (mg/L)	Cu (mg/L)	Zn (mg/L)	Pb (mg/L)	Dissolved oxygen (mg/L)	Alkalinity as HCO_3^- (mg/L)	Sulfide (mg/L)	SO_4^{2-} (mg/L)	F (mg/L)	Cl (mg/L)	Br (mg/L)	I (mg/L)	Charge balance (percent)	^{226}Ra (pCi/L)	Sample
141	0.03	0.06	0.04	ND[1]	73	ND	3.7	ND	122,000	1,170	56	2.1	—	ED–82–01
117	.02	.03	.02	—	114	ND	1.0	ND	123,000	1,180	46	3.6	—	–02
90	—	—	—	—	90	—	ND	ND	123,000	1,100	44	3.8	—	–03
118	.02	.03	.02	1.0	66	ND	7.6	ND	111,000	1,070	39	3.5	—	–04
125	.03	.04	.01	2.5	60	—	1.8	ND	151,000	1,340	39	.6	—	–05
122	.01	.04	.04	—	—	—	11	ND	155,000	1,350	42	−.3	1,900	–06
344	.08	.15	.03	.5	163	0.2	18	ND	181,000	1,250	11	1.5	—	–07
245	—	—	—	.5	127	.9	4.5	—	70,600	622	35	1.1	—	–08
117	.08	.06	.01	.2	43	.5	140	ND	151,000	1,210	39	−.8	200	–09
164	.13	.32	.02	ND	64	.5	50	ND	105,000	983	37	.7	—	–10
101	.01	.10	.01	.5	70	.2	1.0	ND	123,000	1,190	53	3.1	—	–11
ND	ND	.04	ND	—	258	ND	2.0	ND	6,780	94	1	10.0	—	–12
48	.02	.08	.01	—	ND	ND	270	ND	57,400	586	20	.2	—	–13
74	.01	.02	ND	4.0	927	—	570	ND	80,500	800	30	1.3	—	–14
116	ND	.04	ND	4.0	ND	.1	7.5	ND	35,400	365	11	−4.4	—	–15
75	.01	.06	ND	.2	ND	.2	390	ND	63,200	792	29	7.2	—	–16
18	.01	.07	.01	.3	ND	ND	350	ND	55,800	609	22	.8	0	–17
20	.02	.04	.01	1.0	ND	ND	850	ND	67,800	835	31	5.9	—	–18
41	ND	.02	ND	2.5	—	—	3.9	ND	5,760	99	3	6.8	—	–19
194	.01	.02	ND	.1	ND	.2	14	ND	44,000	436	16	.4	—	–20
98	.02	.04	ND	1.5	ND	ND	310	ND	41,200	437	13	−.6	—	–21
392	.04	.61	.04	.2	ND	1.0	400	—	93,000	943	12	1.0	—	–22
18	ND	.04	ND	1.2	185	ND	17	ND	50,000	472	14	−2.9	—	–23
—	—	—	—	—	—	—	8.0	—	49,300	429	16	—	—	–24
—	—	—	—	—	—	—	260	—	69,300	638	19	—	—	–25
—	—	—	—	—	—	—	160	—	48,800	478	14	—	—	–26
432	.07	.63	ND	2.0	ND	.6	280	—	159,000	2,240	17	−.6	500	–27
488	—	—	—	.6	ND	ND	360	—	151,000	1,860	24	−.1	—	–28
464	.06	1.12	.02	—	—	—	270	—	187,000	—	—	3.6	—	–29
177	.01	.51	.02	—	—	.1	260	ND	130,000	1,490	15	−1.6	—	–30
494	—	—	—	—	—	—	300	—	159,000	1,990	26	2.0	—	–31
—	—	—	—	—	—	—	270	—	128,000	1,560	19	—	—	–32
—	—	—	—	—	—	—	280	—	132,000	1,630	22	—	—	–33
—	—	—	—	—	—	—	200	—	135,000	1,720	22	—	—	–34
—	—	—	—	—	—	—	270	—	92,000	1,140	14	—	—	–35
310	.01	.22	ND	1.0	39	.4	2.5	3	152,000	1,540	26	4.0	5,300	–36
458	.01	.05	ND	.5	ND	2.5	2.2	Tr[2]	58,900	349	16	2.7	—	–37
240	.01	.03	ND	.5	194	.9	ND	Tr	133,000	763	35	3.8	—	–38
207	.01	.41	ND	.2	122	.2	1.0	Tr	174,000	1,010	52	4.1	5,000	–39
225	.05	1.26	.02	1.5	99	.1	ND	Tr	207,000	1,130	44	−.9	—	–40

Table 4.　*Field and Laboratory Analytical Methods*

(See Dresel, 1985, for details)

Parameter	Method	Accuracy	Detection limit	Comments and problems
		FIELD ANALYSES		
Temperature	Mercury thermometer	±0.5° C	—	Surface temperature; no correction for gas expansion, cooling from reservoir to surface; several wells have heaters at surface.
pH	Corning Model 4 meter, calomel combination electrode	±0.2 units	—	Possible problems of differing temperatures of buffers and sample, high ionic strength, Br poisoning, loss of CO_2, iron-oxide precipitation.
Eh	Corning Model 4 meter, Pt electrode, calomel reference	?	—	Probably approximates $Fe^{2+}-Fe(OH)_3$ equilibrium caused by sample oxidation.
Dissolved O_2	YSI Model 51 oxygen meter and YSI 5739 probe	±0.05 ppm	0.05 ppm	Possibly affected by O_2 access from air.
Sulfide	Orion sulfide-selective electrode, double-junction Ag/AgCl reference; Orion Model 407 or Corning Model 4 meter, calibrated using sulfide standards (Orion Research, Inc., 1979)	—	0.1 mg/L	Milky white precipitate formed; many measurements unstable.
Alkalinity	Titration with 0.05N H_2SO_4 (Lico and others, 1982), using pH meter as above, to pH 4.5 or inflection point	±0.3 mg/L	—	Many samples appear to contain organic anions. Some also contain bicarbonate.
		LABORATORY ANALYSES		
Conductivity	Beckman Model RC–16C conductivity bridge, probe with cell constant 1	—	—	Precipitation of iron oxides before measurement.
Density	Weigh 25 ml of filtered, non-acidified sample at 25°C	±0.001 g/ml	—	—
Total dissolved solids	Dry 50 ml of filtered brine from well at 180°C for 1 hour	Poor	—	Problems of spattering and incomplete water loss.
Chloride	Aminco-Cotlove Cl titrator; dilution by 1,000 required	±7 percent	—	Includes Br and I.
Bromide and iodide	Hypochlorite oxidation (Br and I) and bromine oxidation (I) by titration (Lico and others, 1982)	±0.5 percent	—	—
Fluoride	Orion F electrode and Orion Model 701A mV meter (Orion Research, Inc., 1976)	—	—	Considerable drift. Not quantitative below 1 mg/L.
Radium-226	^{222}Rn content at equilibrium (Rose and Korner, 1979)	—	—	—
Sulfate	Pretreatment by passing 100 ml through alumina column, elution with ammonia (Lico and others, 1982), then passing through cation-exchange column (Dowex 50–X8); determination by turbidimetry (U.S. Environmental Protection Agency, 1979)	±0.3 mg/L (<5 mg/L) ±3 mg/L (5 to 50 mg/L)	—	—
Na, Ca, Mg, K, Fe, Mn, Ba, and Sr	Spectraspan III argon plasma emission spectrometer after dilution by 400 or 2,000; matrix correction for Na enhancement	—	—	—
Li	Perkin-Elmer Model 703 atomic absorption spectrometer after dilution by 400	—	—	—
Cu, Pb, Zn	APDC-MIBK extraction, back extraction into HNO_3, and atomic-absorption determination	—	<0.01 mg/L Cu 0.1 mg/L Pb <0.02 mg/L Zn	—
Si, Mn, Al, Cu, B, and others included in Table 5	Emission spectrography of dried residues	±50 percent?	—	Analyses by N. H. Suhr, Pennsylvania State University.
Sulfur isotopes	Thode and others (1961)	—	—	Low yield.

Table 5.   *Emission Spectrographic Semiquantitative Analyses[1]*

(Quantities are in milligrams per liter)

Sample[2]	SiO_2	Mn	Fe	Al	Cu	Ag	Ba	B
ED–82–01	4	20	100	<2	<0.2	<0.2	200	<4
–04	4	40	100	<2	<.2	<.2	800	<4
–11	8	40	200	8	.2	<.2	800	<4
–16	5	20	100	4	.4	.1	500	7
–20	3	20	200	2	<.08	<.08	8	6
–23	2	2	4	<.9	.09	<.09	20	<2
–30	4	90	400	<2	.2	<.2	40	7
–36	6	100	600	<3	<.3	<.3	1,000	20
–40	7	10	200	<4	<.4	<.4	1,000	20

[1]Analyses by N. H. Suhr, Mineral Constitution Laboratory, Pennsylvania State University.
[2]No samples had detectable As, Be, Bi, Co, Cr, Ge, In, Mo, Ni, Pb, Sb, Sn, V, Y, Zn, or Zr.

Table 6.   *Sample Alkalinities Measured to the Most Negative Slope of the Titration Curve, to pH 4.5, and to pH 3.5*

(Quantities are in milliequivalents per liter)

Sample	Endpoint pH[1]	Alkalinity to the endpoint pH	Alkalinity to pH 4.5	Alkalinity to pH 3.5
ED–82–01	3.6	1.20	0.946	1.23
–02	4.0	1.87	1.75	2.07
–03	3.9	1.48	1.37	1.61
–04	4.0	1.09	1.06	1.31
–05	4.0	.99	.90	1.11
–06	—	—	—	—
–07	3.4	2.68	2.22	2.66
–08	4.3	2.08	2.03	2.48
–09	4.3	.70	.65	.86
–10	4.8	1.06	1.21	1.64
–11	4.2	1.15	1.05	1.36
–12	4.2	4.23	3.99	4.55
–13	ND	—	1.97	4.55
–14	—	—	—	—
–15	4.3	15.2	14.89	15.89
–16	ND	—	2.09	3.10
–17	ND	—	2.07	3.50
–18	ND	—	6.14	1.36
–19	—	—	—	—
–20	ND	—	1.92	3.16
–21	ND	—	1.76	3.10
–22	ND	—	2.17	4.84
–23	4.0	3.04	2.86	3.38
–27	ND	—	3.32	4.15
–28	ND	—	3.47	4.88
–29	—	—	—	—
–30	—	—	—	—
–31	—	—	—	—
–36	3.8	.64	.48	.66
–37	ND	—	1.69	3.24
–38	3.6	3.18	2.72	3.23
–39	3.6	2.00	1.73	2.03
–40	3.5	1.63	1.37	1.65

[1]ND, endpoint not detected.

Table 7.   *Sulfate Sulfur, Oxygen, and Deuterium Isotope Analyses*

(Quantities are in parts per thousand)

Sulfate sulfur isotope analyses[1]	
Sample	$\delta^{34}S$
ED–82–09	−15.45
–10	−9.21
–18	−18.57
–30	−6.10

Oxygen and deuterium isotope analyses[2]		
Sample	$\delta^{18}O(SMOW^3)$	$\delta D(SMOW)$
ED–82–01	−2.5	−39
–07	−.8	—
–09	−1.9	−35
–10	−3.0	−39
–11	−2.0	−39
–18	−4.4	−41
–23	−5.6	−39
–29	−3.1	−38
–30	−3.6	−39
–36	−2.3	−40
–37	−.5	−41
–38	−1.7	−51
–40	+2.0	−42

[1]Analyses by L. D. Hoy under the direction of Hiroshi Ohmoto, Pennsylvania State University.
[2]Values for $\delta^{18}O$ determined by C. H. Gammons under the direction of Hiroshi Ohmoto, Pennsylvania State University. Values for δD by Geochron Laboratories, Cambridge, Mass.
[3]SMOW, Standard Mean Ocean Water.

dicate the temperature of field analyses. The pH can be affected by differences of up to 5°C between the temperature of the standardizing buffers and the sample, and by effects of high ionic strength. However, the pH of most previous samples seems to have been measured in the laboratory after appreciable iron

precipitation had lowered the pH as much as 4 units, whereas the results reported for the samples collected in this study are probably accurate to a few tenths of a pH unit. The Eh and dissolved O_2 measurements probably represent a maximum oxidation state caused by exposure to the air, as discussed later. The measured sulfide is near the useful detection limit of the method and should be taken as a maximum value. None of the samples smelled of hydrogen sulfide, and the quantity of that gas is below detection in all gas analyses from Pennsylvania available to the writers.

ALKALINITY

The alkalinity was determined by titration with standard acid while monitoring pH. In most natural waters, HCO_3^- and CO_3^{2-} are the major components of alkalinity and show an inflection, or "endpoint" (rapid pH change with only small added volumes of acid), at pH 4.5. Most Pennsylvania brines showed either no inflection or had a poorly defined inflection of pH 3.5 to 4. Examples are illustrated in Figure 4, as are theoretical titration curves for bicarbonate and acetate ions for comparison. This behavior suggests that alkalinity in the brines is due to a mixture of bases, and that HCO_3^- is not the major source of alkalinity. The presence of a range of organic anions (Carothers and Kharaka, 1978; Willey and others, 1975) is the most likely cause of the observed behavior. These anions are minor compared to chloride but are important in defining the behavior of the brines on acidification and other chemical changes, and also lead to uncertainty in the determination of the true concentration of HCO_3^-, with resulting uncertainty as to saturation in calcite and other carbonates. More specific analyses are highly desirable.

CHARGE BALANCE

The charge balance of the samples agrees within 10 percent for all samples for which there are complete analyses of major ions (Table 3). The charge balance is computed as follows:

$$\text{Charge balance (\%)} = \frac{\Sigma m_i z_i}{\Sigma m_i |z_i|} \times 100 \qquad (1)$$

where m_i is the molality of ion i and z_i is its charge. Hem (1985) suggested that the charge balance for dilute waters (250 to 1,000 mg/L) should be within 1 to 2 percent. The samples that have a charge balance greater than 5 percent are all fairly dilute oil well samples, and all have an excess of cations. This pattern may indicate that the analytical techniques were inappropriate for this type of sample or these concentrations. Errors in sodium, calcium, and chlorine are the most likely cause of significant difficulties in the determination of charge balance, because other elements generally do not constitute a high enough proportion of dissolved solids to affect charge balance. Possibly an unrecognized matrix enhancement increased the analytical values for sodium and led to the positive charge balance values.

RELATIONSHIPS OF TOTAL DISSOLVED SOLIDS TO CONDUCTIVITY, CHLORIDE, AND DENSITY

Figure 5 illustrates the relationships among conductivity, density, chloride, and total dissolved solids. The content of total dissolved solids is calculated from the total of dissolved species. As indicated by the figure, these parameters are all closely related. The agreement indicates a lack of major analytical problems. Given one of these parameters, the other parameters can be estimated using these graphs.

RESERVOIR CONDITIONS FOR NEW SAMPLES

CHANGES DURING PRODUCTION AND SAMPLING

The analyses define the compositions of the brines at the time they were sampled at the surface. However, the brines can undergo a number of changes during accumulation in the well bore, travel to the surface, and sampling. The most obvious of these are pressure and temperature changes, which may, in turn, affect the gases dissolved in the brine. Loss of carbon dioxide, hydrogen sulfide, and other volatiles will change the pH, sulfur content, and oxidation state. Dissolved oxygen can increase through atmospheric contamination. Barite, carbonate, or other solids can precipitate to form well scale. The brine can react with steel tubing and other material in the well bore and wellhead. Water can condense out of the gas phase to dilute the brine. Mixing of brine from several reservoirs, or mixing with shallow groundwater owing to faulty well construction, can affect a few samples. As discussed in the following section, considerable interpretation is required to infer the composition of the brine at depth in the reservoir rocks.

Logically, the volatile, trace, and minor constituents of the brine are the most susceptible to
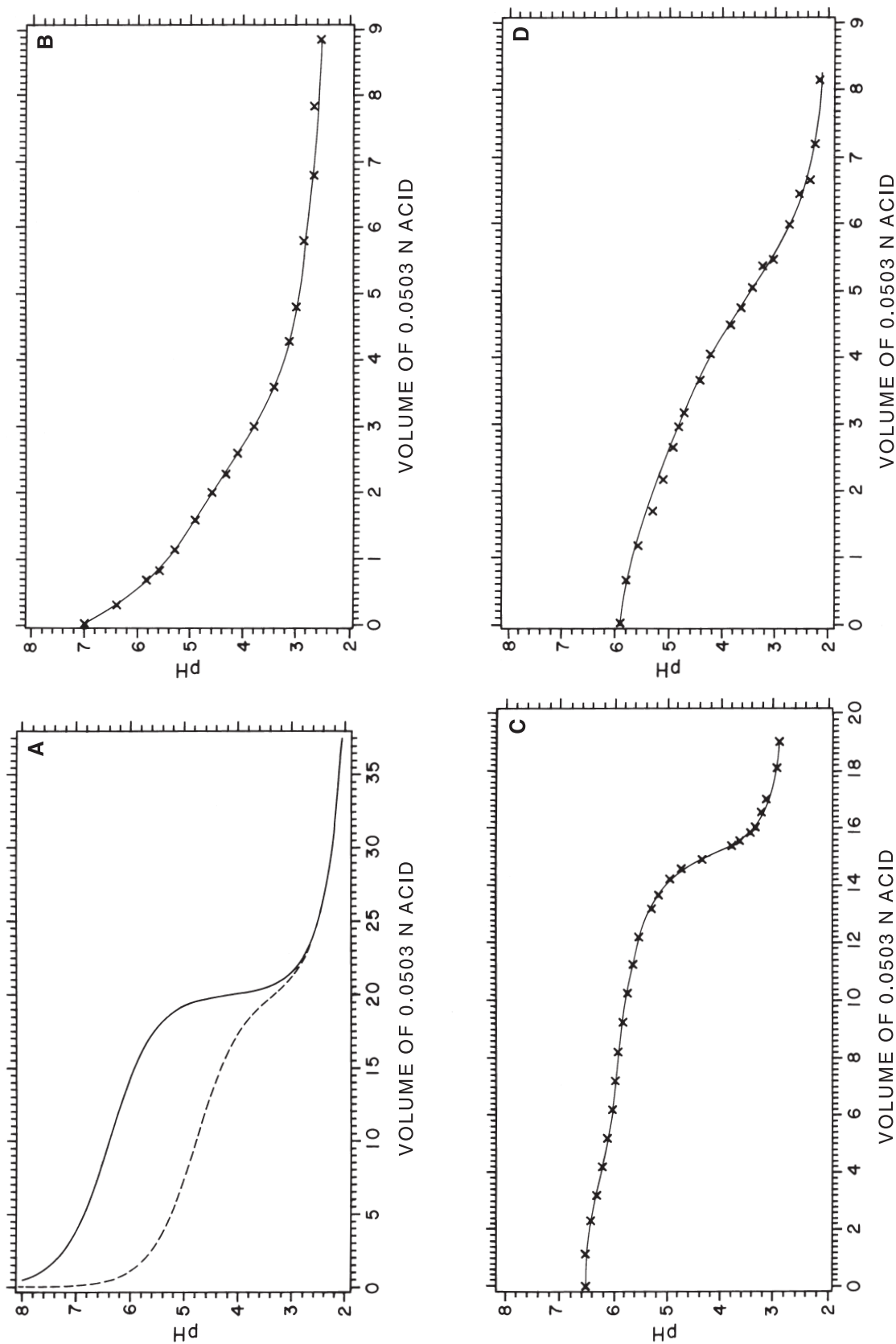
Figure 4.   Alkalinity titration curves. A. Theoretical curves for 0.02M bicarbonate (solid) and 0.02M acetate (dashed); B. Sample ED–82–17, showing concave upward curve with no inflection point; C. Sample ED–82–15 showing strong inflection near pH 4, plus minor deviation near pH 6; D. Sample ED–82–28, showing very gradual change with no clear endpoint.
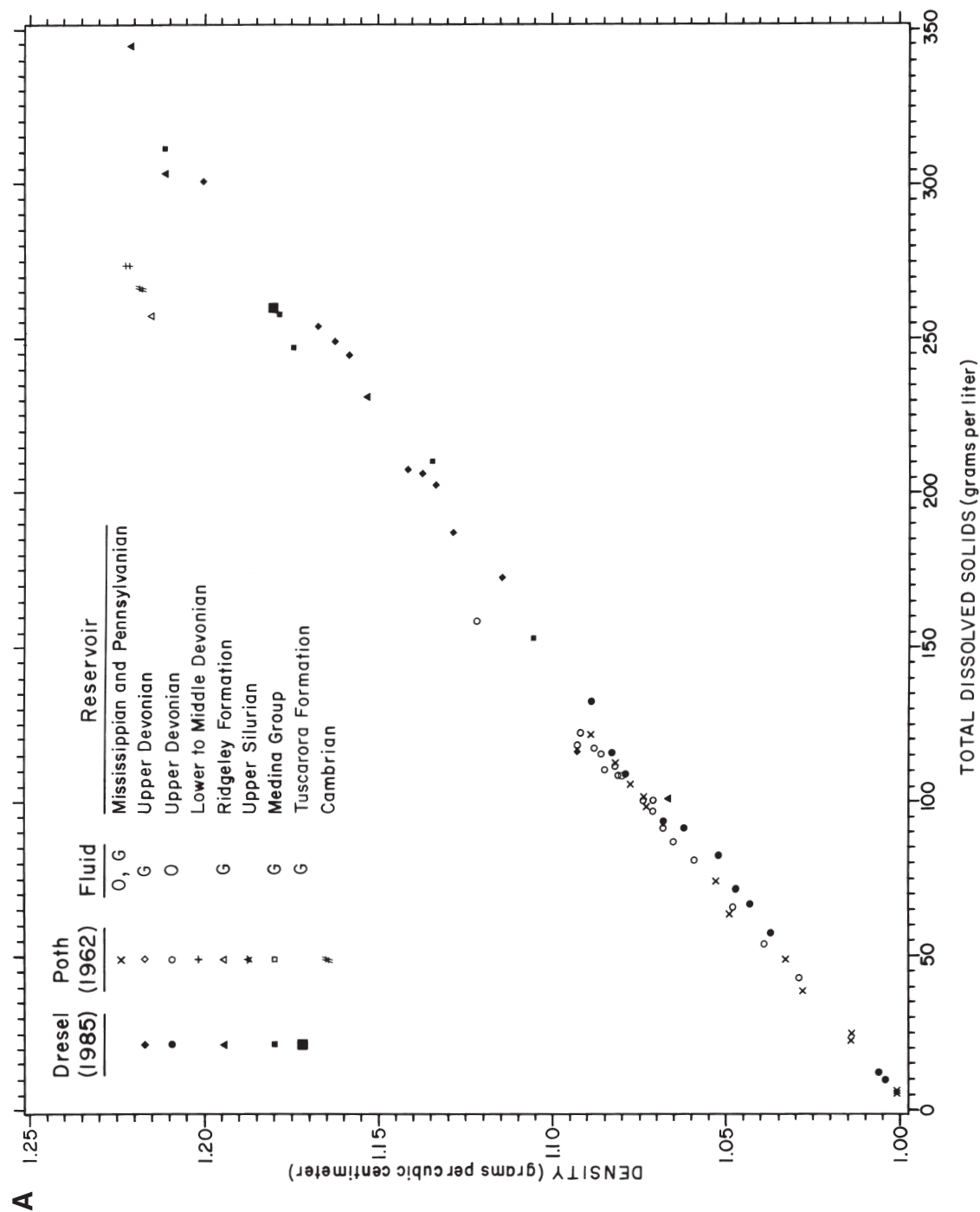
Figure 5.   Plots of relations among density, total dissolved solids, chloride, and conductivity for samples of Dresel (1985) and Poth (1962). Refer to the explanation in Figure 5A for Figures 5B–5F. O, oil; G, gas. A. Total dissolved solids vs. density; B. total dissolved solids vs. conductivity; C. total dissolved solids vs. chloride; D. conductivity vs. chloride; E. conductivity vs. density; F. density vs. chloride.

Figure 5. (Continued).

Figure 5.   (Continued).

Figure 5. (Continued).

Figure 5.   (Continued).

Figure 5. (Continued).

CHLORIDE (milligrams per liter)

DENSITY (grams per cubic centimeter)

See Figure 5A for explanation

F
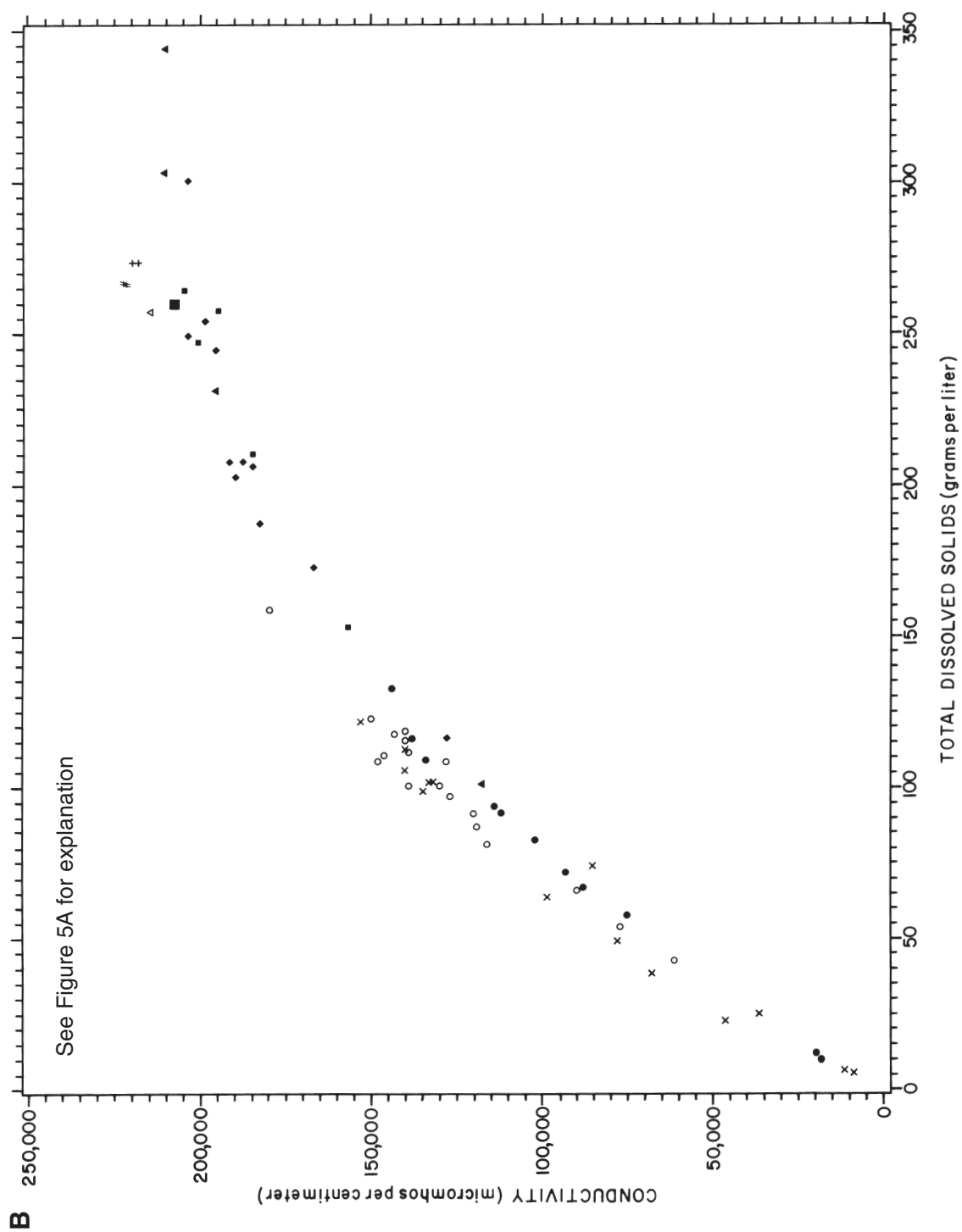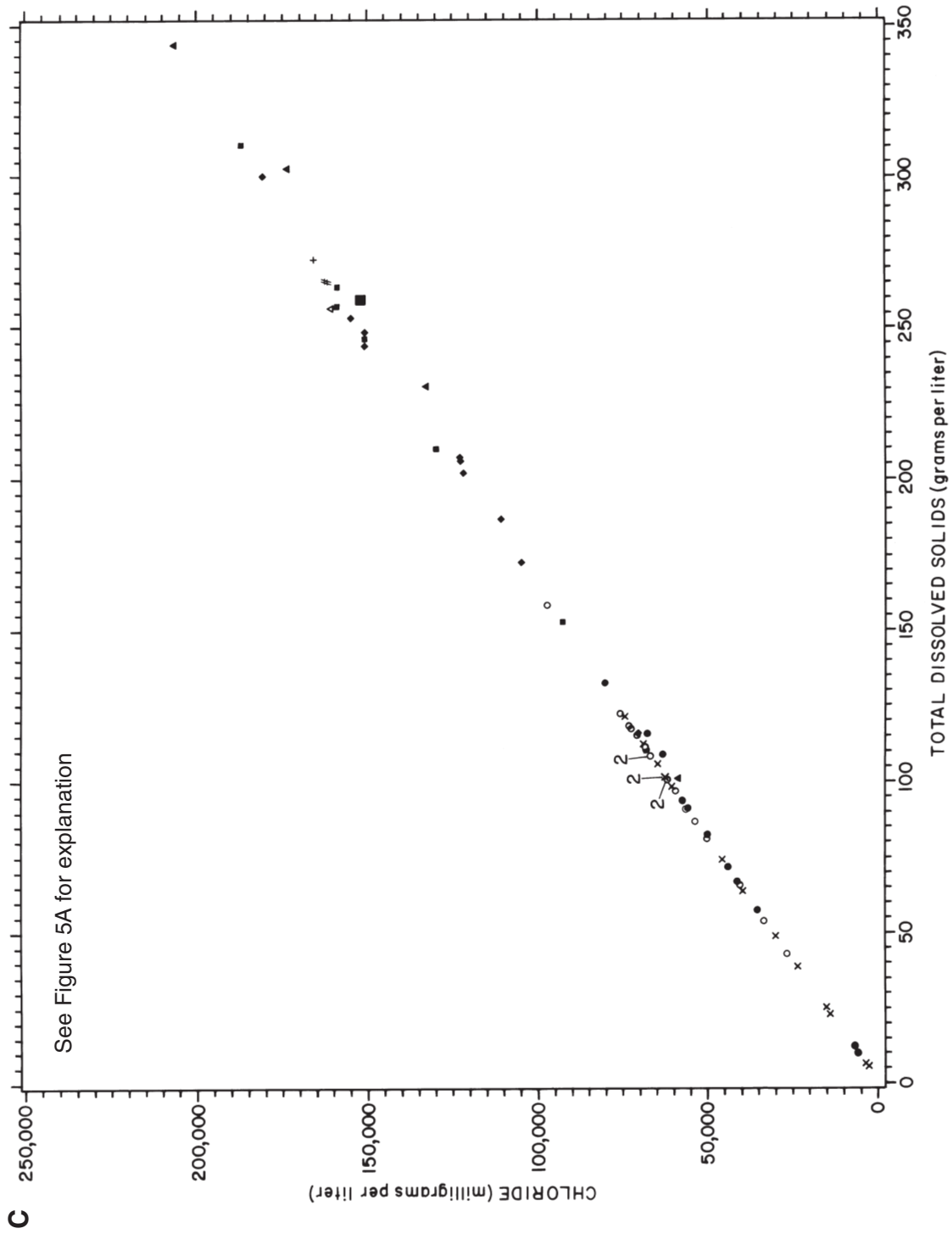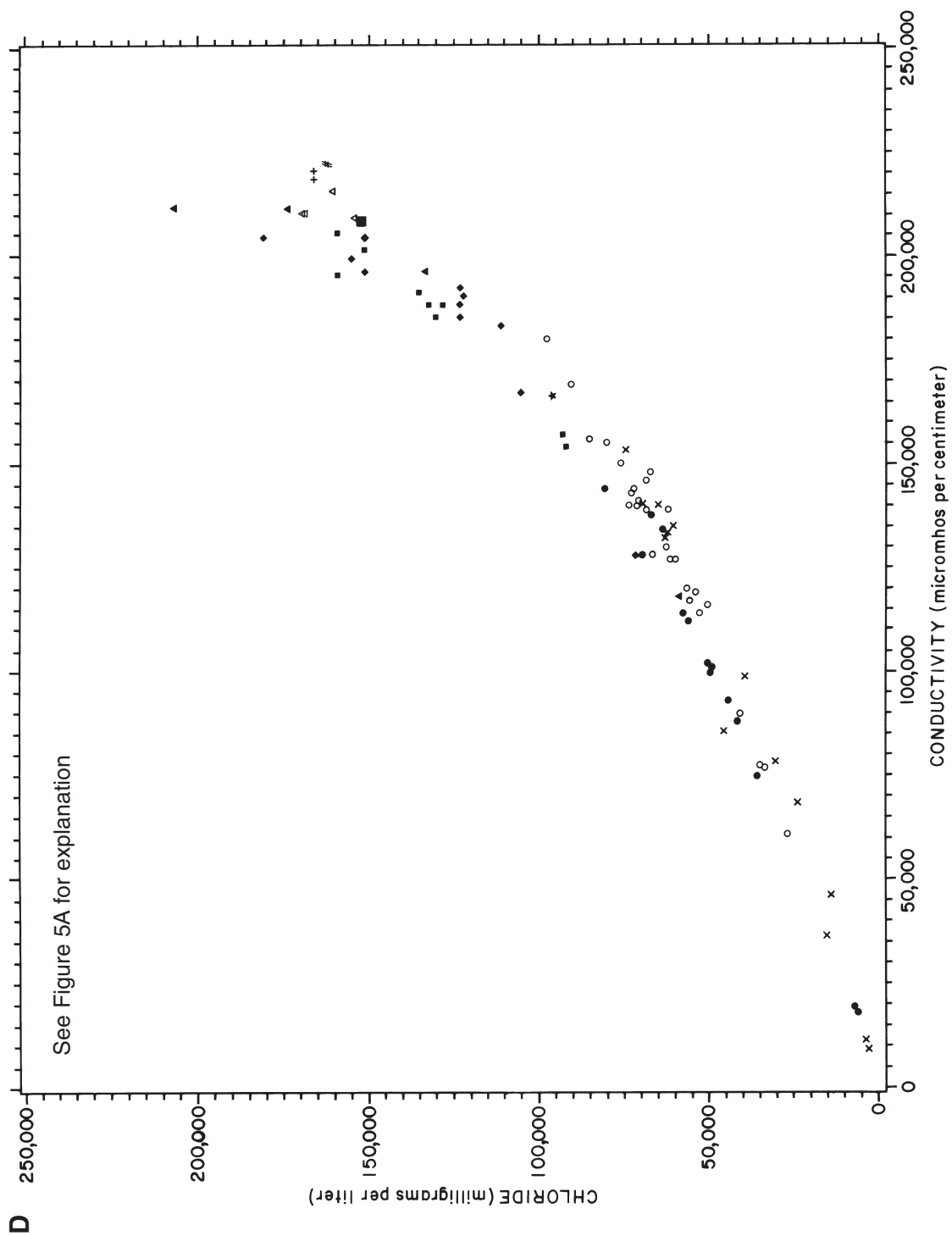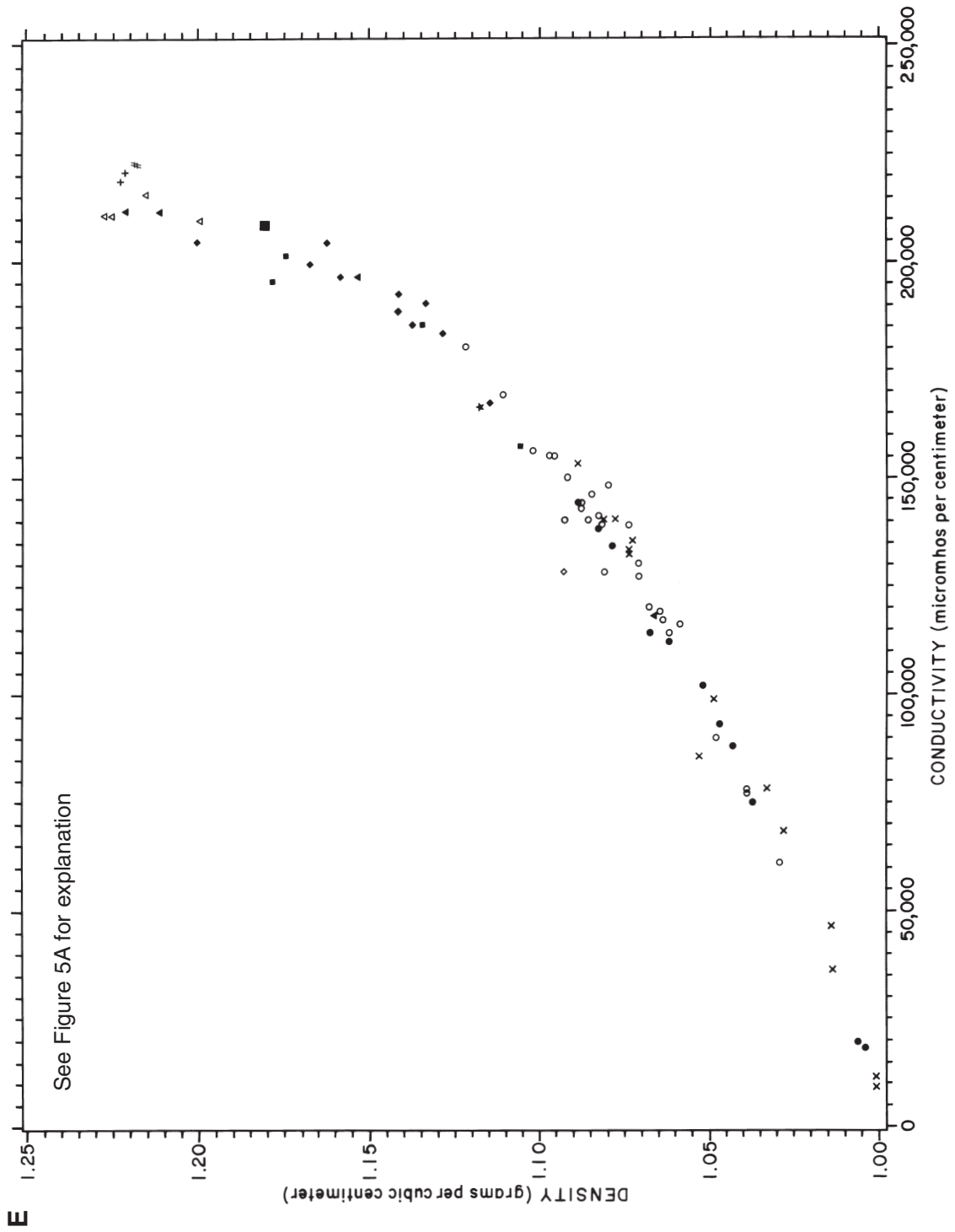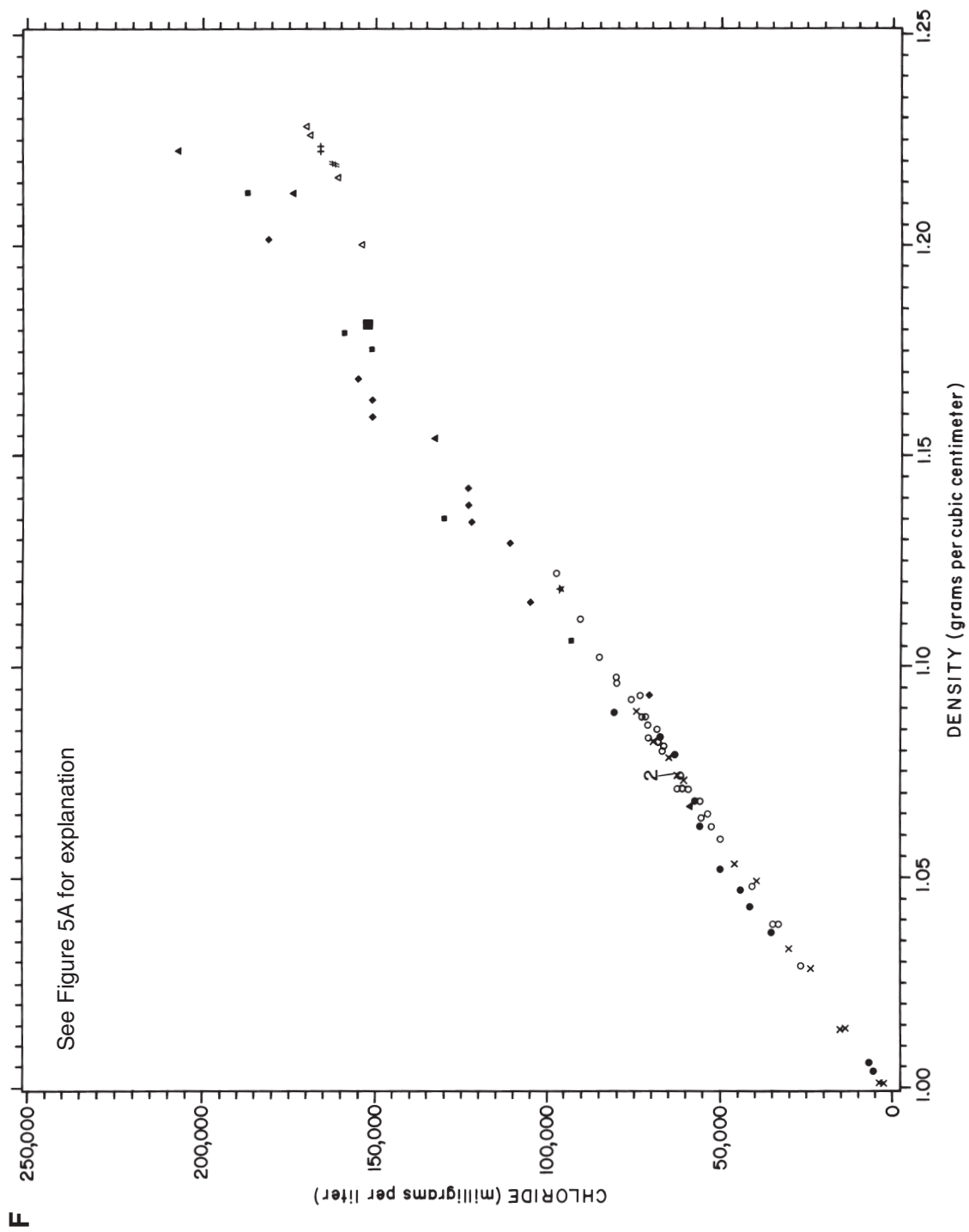
change, and the major constituents are the least likely to be changed. Therefore, the contents of Na, Ca, Mg, K, and Cl are considered to be well defined by the chemical analyses, except for the possible effects of dilution or condensation, which would affect all of them proportionally. Also, the brine coexists with large amounts of a gas phase composed of methane, accompanied by minor to trace amounts of other gases. Contents of minor species, such as barium and strontium, can be considered minimal, possibly affected by precipitation. Elements present in the steel and valves of the well, such as iron and manganese, are possible contaminants. On the following pages, a discussion and interpretation of the nature and magnitude of these effects are presented, and the composition of the brine at depth before it entered the wells is inferred.

TEMPERATURE

The temperatures listed in Table 3 were measured at the surface in the brine collection bottle and may not reflect the temperatures in the producing formation. Grisafi and others (1974) indicated that the temperatures obtained at the bottom of the holes from electric logs on newly drilled wells may also not be the temperature of the rocks in the undisturbed formation because of thermal perturbation during drilling. Therefore, temperatures at depth were calculated from well depth and a generalized geothermal gradient for the region (Maurath and Eckstein, 1981). A geothermal gradient of 25°C/km and a surface temperature of 12°C were used in the calculations. The results are given in Table 8 and are used in the following sections. The calculated temperatures range between 16°C and 94°C.

CONDENSATION AND SEPARATION OF VOLATILES

During the production of natural gas, some methane will exsolve from the aqueous phase when pressure drops. However, the loss will have negligible effect on either the gas or liquid phases, particularly for brines having high ionic strength (Byrne and Stoessel, 1982; Stoessel and Byrne, 1982).

Adiabatic cooling during sampling can cause dilution of brine samples by condensate. This effect has been reported for geopressured geothermal waters by Kharaka and others (1977), who found some "brines" in the Gulf Coast area to be composed dominantly of condensate. Condensation is most significant in wells that have a high pressure at depth and

low production of brine. High temperature at depth increases the water content of the gas so there will be greater potential for dilution.

Kharaka and others (1977) used deviations from expected cation ratios and silica contents at measured bottom-hole temperatures to estimate the amount of dilution. They indicated that the empirical Na-K-Ca geothermometer of Fournier and Truesdell (1973) is the most effective for use in studying geopressured Gulf Coast brines. Subsurface temperatures estimated from samples diluted by condensed water were significantly different from the measured temperatures. The diluted waters usually gave depressed Na-K-Ca geothermometer readings.

The low temperatures of the Pennsylvania brine aquifers make the use of the Na-K-Ca geothermometer of questionable value. Also, the Na-K-Ca temperatures may be dependent on lithology. For example, of the Ridgeley samples, those that have the highest volume of produced water and the highest dissolved solids, and that are therefore the least sensitive to dilution, give geothermometer readings above 200°C. Ridgeley sample ED–82–37, however, is notable for its low concentrations compared to other deep gas samples. It is from a well that produces little water (less than 1 barrel per day, or 300 liters per day). In this situation, dilution in the well bore cannot be ruled out. Dilution effects in other Ridgeley samples from similar depths would be masked by the greater brine production. In the following discussion, condensation is assumed to be insignificant in oil and shallow gas wells. The high salinity of most deep wells indicates that condensation from expanding gas has, at most, a secondary effect on the composition.

pH

The transport of brine from the reservoir rocks to the surface could result in an increase in pH through changes in the carbonate equilibria. In general, the pressure of carbon dioxide in the gas will be reduced through the lowering of the total pressure. This will cause reaction (2), below, to go to the right:

$$H^+ + HCO_3^- = CO_2(aq) + H_2O(liq) = CO_2(g) + H_2O(liq) \qquad (2)$$
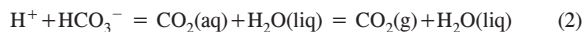
The result is an increase in pH if this is not buffered by other reactions. Reaction (2) will not change the alkalinity because the changes in molality of H^+ and HCO_3^- will cancel each other. At constant known carbonate, the redistribution of pH-sensitive species with changing pressure of carbon dioxide can be calculated but because other sources of alkalinity are significant in the Pennsylvania brines, this approach is not feasible.

Table 8. *Subsurface Temperatures Calculated From the Geothermal Gradient[1]*

Sample	Depth (meters)	Temperature (°C)
ED–82–01	920	35
–02	784	32
–03	784	32
–04	910	35
–05	—	[2]35
–06	—	[2]35
–07	854	33
–08	865	34
–09	964	36
–10	956	36
–11	971	36
–12	177	16
–13	232	18
–14	197	17
–15	—	[2]17
–16	349	21
–17	293	19
–18	358	21
–19	594	27
–20	701	30
–21	584	27
–22	—	[2]51
–23	—	[2]20
–24	—	[2]20
–25	—	[2]20
–26	—	[2]20
–27	1,570	51
–28	1,547	51
–29	1,476	49
–30	1,486	49
–31	1,494	49
–32	1,593	52
–33	1,548	51
–34	1,611	52
–35	1,592	52
–36	3,294	94
–37	2,710	80
–38	2,685	79
–39	2,713	80
–40	2,616	77

[1]Geothermal gradient 25°C/km; surface temperature 12°C.
[2]Estimated temperature.

If the water is saturated with calcite, carbon dioxide loss will cause calcite precipitation according to the following reaction:

$$Ca^{2+} + 2HCO_3^- = CaCO_3(s) + H_2O(liq) + CO_2(g) \qquad (3)$$
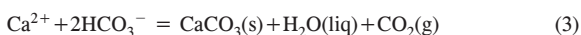
This reaction decreases the alkalinity, and the pH will not increase as much during loss of carbon dioxide as it would if no precipitation had occurred. The calculation of pH in equilibrium with calcite is not affected by errors in measurement of pH and alkalinity, which is an advantage because of the low values and ambiguous source of alkalinities for most Pennsylvania samples. Equilibrium with calcite is indicated by limestone horizons and variable but significant amounts of carbonate cement and crystalline calcite reported in most petrographic descriptions of the sandstones, as discussed previously. Also, most samples are at or near calcite saturation using measured pH values (Dresel, 1985).

The pH in the $Ca\text{-}Cl\text{-}CO_3^{2-}-H_2O$ system is fixed at constant temperature, carbon dioxide fugacity, and calcium activity when in equilibrium with calcite, as discussed by Garrels and Christ (1965). The reaction is simply expressed as follows:

$$CaCO_3 + 2H^+ = CO_2(g) + H_2O(liq) + Ca^{2+} \qquad (4)$$
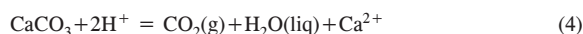
The equilibrium expression for this reaction can be rearranged and solved for temperature (Dresel, 1985) to yield

$$pH = (7.187 - 796.4/T - \log a_{Ca^{2+}} - \log f_{CO_2})/2 \qquad (5)$$

where a is chemical activity, f is fugacity, and T is temperature in kelvins.

Formula (5) can be used to estimate the subsurface pH if the contents of calcium and other major elements in the brine are known and the carbon dioxide content and total pressure of associated gas are available (Dresel, 1985). Several gas analyses and total pressures are available for Ridgeley and Medina wells (Table 9). These gas analyses and the activities of calcium calculated from the calcium concentrations have been used to estimate in situ pH (Table 10).

The computed pH for each horizon varies only within a range of 0.5 unit, reflecting the fact that the calculations are not highly sensitive to variations in calcium content. The calculated pH values differ from the measured values by a maximum of 0.5 unit and fall in the range 5.3 to 6.3. In view of the relatively small differences between calculated and measured pH, the measured pH values are used in subsequent calculations where gas analyses are not available. Evidently, the brines contain very little dissolved carbonate, so little pH change occurs on release of pressure and loss of CO_2.

In some previous publications, pH values much lower than those measured or calculated here were recorded (Poth, 1962; Kelley and others, 1973). These acid pH values were apparently caused by iron oxide precipitation after oxidation at the surface, as was observed for the samples of this study when pH was measured days or weeks later.

OXIDATION STATE

The oxidation state of the brines is important in understanding the abundance and behavior of iron, manganese, sulfur, carbon, and other elements that

Table 9.   *Gas Analyses for Wells in the Medina Group, Tuscarora Formation, and Ridgeley Sandstone*

Horizon	CH_4 (mole percent)	CO_2 (mole percent)	Pressure (atm)	Source
Medina	91.35	0.12	45.9	Cabot Oil and Gas Corp., Meadville, Pa.
do.	91.65	.01	—	do.
do.	91.14	.02	47.6	do.
do.	91.25	.01	46.25	do.
Tuscarora	76.48	.04	—	Amoco Production Co., Somerset, Pa.
Ridgeley	97.98	.33	—	do.
do.	98.16	.25	—	do.
do.	—	—	169	do.
do.	—	—	136	do.
do.	—	—	84	do.

Values used in calculation					
Horizon	x_{CH_4}[1]	x_{CO_2}	Pressure (atm)	X_{CO_2}[2]	f_{CO_2}[3]
Medina	0.91	0.0002	46.2	0.80	0.0074
Tuscarora	.76	.0004	136	.68	.037
Ridgeley	.98	.003	136	.60	.24

[1]x, mole fraction in gas phase.
[2]X, fugacity coefficient.
[3]f, fugacity.

have multiple oxidation states in nature. Therefore, an attempt has been made to define the oxidation state of the brines.

The presence of abundant methane and measurable carbon dioxide in gases of the region defines a relatively reduced oxidation state for the gases. In view of the coexistence of the gas with the brines and with reservoir rocks for geologic time periods, it is reasonable to assume that most, if not all, species involved in redox reactions in the brine are at least ap-

Table 10.   *Values for pH Estimated From f_{CO_2} Assuming Equilibrium with Calcite by Equation 5*

Sample	Temperature[1] (K)	$a_{Ca^{2+}}$[2]	f_{CO_2}	Calculated pH	Measured pH
ED–82–27	324	0.345	0.0074	6.1	6.3
–28	324	.230	.0074	6.2	5.9
–29	322	.448	.0074	6.1	—
–30	322	.165	.0074	6.3	6.5
–31	322	.358	.0074	6.1	6.5
–36	367	.116	.037	5.9	5.5
–37	353	.028	.24	5.8	5.6
–38	352	.087	.24	5.6	6.1
–39	353	.164	.24	5.4	5.6
–40	350	.364	.24	5.3	5.5

[1]Temperature calculated from the geothermal gradient.
[2]Calcium activity calculated by the Pitzer method.

proximately in equilibrium with the gas and mineral phases. Sulfate is a probable exception, as discussed later.

The oxidation state defined by methane and carbon dioxide can be expressed as follows:

$$CO_2(g) + 8H^+ + 8e^- = CH_4(g) + 2H_2O(liq) \qquad (6)$$
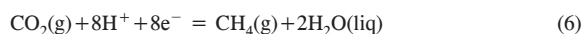
A variety of other measures of oxidation state in the brine can be calculated, as summarized in Table 11. These calculations are based on the known or possible presence of pyrite and organic matter (petroleum, estimated by graphite) in the reservoir, plus analyses of SO_4^{2-}, H_2S, CO_2, and CH_4 in gases and aqueous solutions, and the presence of iron oxide filtered from many waters. If the various redox systems of dissolved species in the brines were in equilibrium internally (reactions A and G, Table 11) and with the

Table 11.   *Reactions Used for Calculation of Oxidation State*

Equation	Reaction	E^O(25°C)[1] (volts)	ΔH_r^O(25°C)[2] (kilocalories)
A	$CO_2(g) + 8H^+(liq) + 8e^- = CH_4(g) + 2H_2O(liq)$	0.169	−60.46
B	$C(graphite) + 4H^+ + 4e^- = CH_4(g)$	.132	−17.88
C	$Fe_2O_3(hematite) + 6H^+ + 2e^- = 2Fe^{2+} + 3H_2O(liq)$	.656	−50.46
D	$FeOOH(goethite) + 3H^+ + e^- = Fe^{2+} + 2H_2O(liq)$	.645	−23.66
E	$Fe(OH)_3(amorphous) + 3H^+ + e^- = Fe^{2+} + 3H_2O(liq)$	.972	−29.54
F	$Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- = FeS_2(pyrite) + 8H_2O(liq)$	.362	−131.58
G	$SO_4^{2-} + 10H^+ + 8e^- = H_2S(aq) + 4H_2O(liq)$	.301	−65.44

[1]E^O, standard electrode potential calculated using thermodynamic data from Wagman and others (1968, 1969) and other sources listed by Dresel (1985).
[2]ΔH_r^O, standard enthalpy change of the reaction using data from Wagman and others (1968) and other sources quoted by Dresel (1985).

minerals involved (reactions B through F), the Eh calculated for all reactions should be equal within the error of the analytical and thermodynamic data, using the analytical data for Fe, H_2S, and SO_4^{2-}, appropriately converted to activities. However, the results of such calculations show a complete lack of agreement, as illustrated in Figure 6A for sample ED–82–39.

The relatively high values of measured Eh and calculated Eh for $Fe^{2+}/Fe(OH)_3$ compared to other values (Figure 6A) probably result from oxidation of the sample during collection and measurement. Therefore, these values are not considered meaning-

ful. The relatively high Eh values determined from SO_4^{2-}/FeS_2 and SO_4^{2-}/H_2S may reflect the extremely slow rate of reaction between SO_4^{2-} and H_2S at low temperatures. For example, at pH 4 to 7, the reaction of H_2S and SO_4^{2-} to 90 percent of their equilibrium ratio requires 9×10^9 years at 50°C and 2×10^8 years at 100°C (Ohmoto and Lasaga, 1982). In addition, the amounts of SO_4^{2-} and H_2S are very low, and the analytical data are open to some question, especially for H_2S.

The remaining Eh values, those calculated from CO_2/CH_4, C/CH_4, Fe_2O_3/Fe_2^+, and $FeOOH/Fe^{2+}$, have the additional problem of falling in the field of
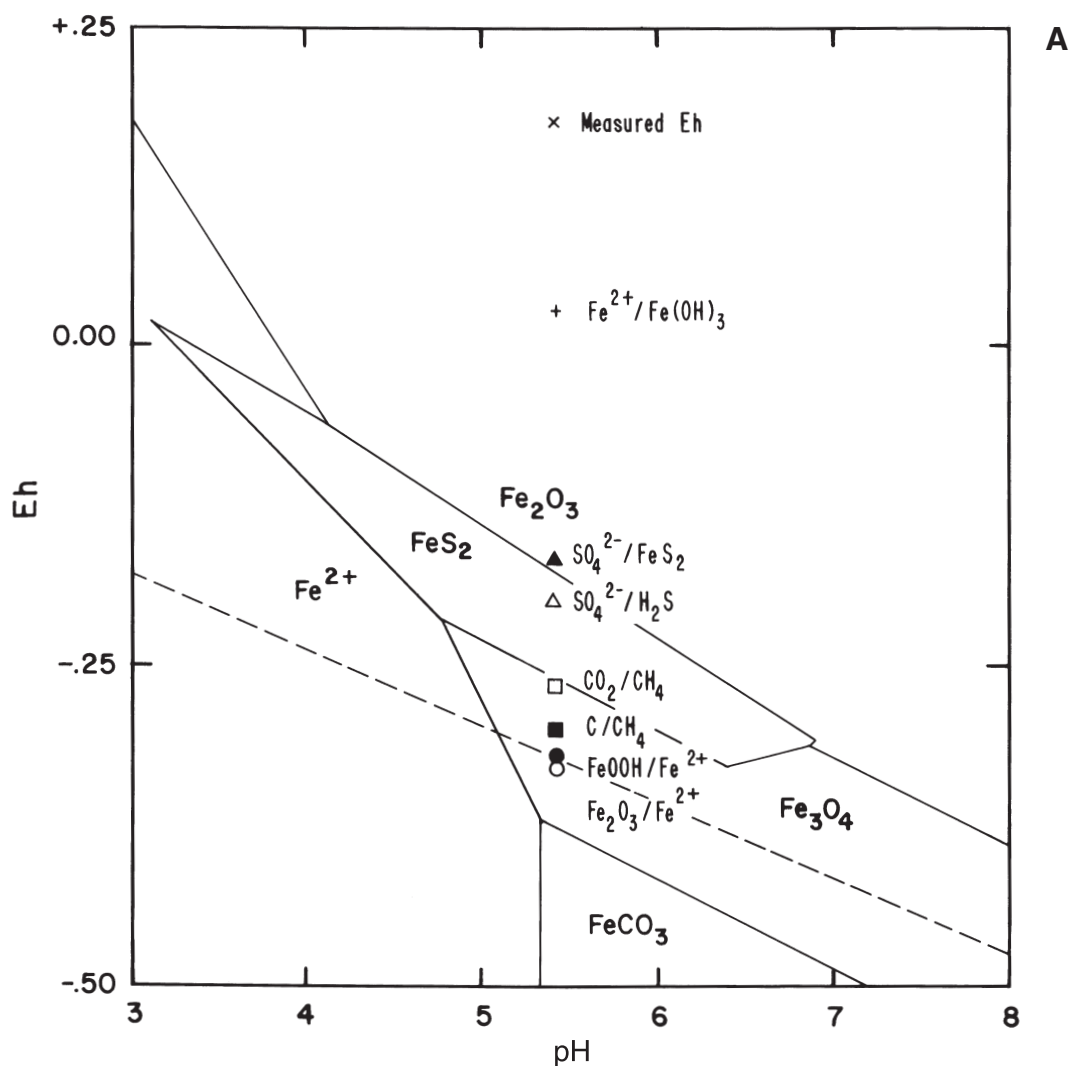
Figure 6. Eh-pH plots for sample ED–82–39. Dashed line is H_2O lower stability limit. A. Stability for activity total Fe = 5.6×10^{-4}, activity total S = 9×10^{-8}, fugacity of CO_2 = 0.24 atm, for reactions of Table 11 at 80°C. B. Stability for inferred true conditions with activity total Fe = 3.8×10^{-5}, activity total S = 1.6×10^{-7}, activity of siderite = 0.1, T = 80°C. Square in Figure 6B indicates Eh/pH for CO_2/CH_4 of gas from area.
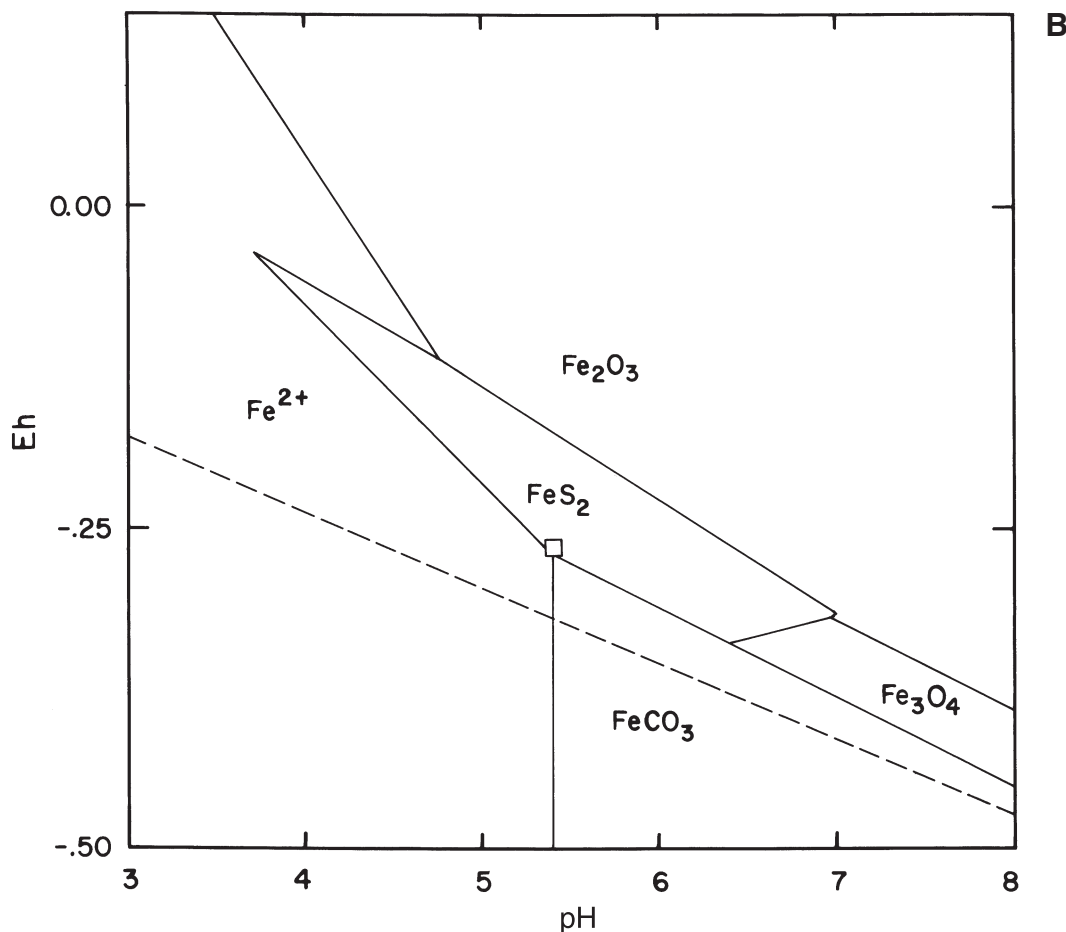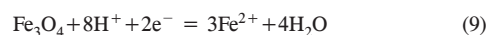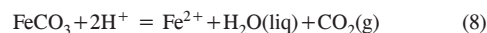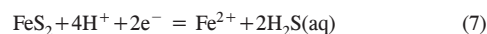
Figure 6. *(Continued)*.

magnetite stability on the Eh-pH diagram. This condition is unlikely because pyrite is an observed iron mineral in most horizons, although hematite does occur in red beds in parts of the Upper Devonian section and as a late authigenic cement in the Red Medina (drillers' term) and some sandstones of the Upper Devonian units. Calculations using the measured iron contents result in supersaturation values of 10^3 to 10^{10} for magnetite and pyrite. This extreme supersaturation may be caused by contamination of the brine with iron from the steel in the well bore, especially in view of the known corrosion of tubing and other steel in wells (C. D. Stahl, personal communication). This apparent excess in dissolved iron content and the general lack of iron oxides in the reservoir rocks indicate that the Eh values calculated from $FeOOH/Fe^{2+}$ are not applicable in most areas.

Another evaluation of the oxidation state and content of hydrogen sulfide and iron in the reservoir can be calculated from the following assumptions:

(1) The pH is defined by calcite saturation plus the calcium content and the fugacity of carbon dioxide, as previously described (equations 4 and 5).

(2) The Eh is defined by CO_2/CH_4 equilibrium (equation 6).

(3) The fluids are in equilibrium with pyrite and with an iron-bearing carbonate (siderite, or dolomite or calcite containing iron in solid solution), but not with magnetite, as defined by the following reactions:

$$FeS_2 + 4H^+ + 2e^- = Fe^{2+} + 2H_2S(aq) \qquad (7)$$

$$FeCO_3 + 2H^+ = Fe^{2+} + H_2O(liq) + CO_2(g) \qquad (8)$$

$$Fe_3O_4 + 8H^+ + 2e^- = 3Fe^{2+} + 4H_2O \qquad (9)$$

Given the values of pH, Eh, and f_{CO_2} defined above, three unknowns remain: the content of iron in the brine; the content of hydrogen sulfide in the brine; and a_{FeCO_3}, the activity or purity of the iron carbonate component in siderite, ankerite, or calcite. Given that magnetite is *not* present, a unique solution is not possible, but the boundary condition at which magnetite just becomes unstable relative to pyrite and an

iron-bearing carbonate can be evaluated. This condition corresponds to the situation at which the Fe_3O_4 field on Figure 6A forms an infinitely thin sliver between the FeS_2 and $FeCO_3$ fields (Figure 6B). According to equation 9 and calculations by Dresel (1985), the iron concentration under these conditions is about 2 mg/L. The H_2S content is then calculated from equation 7 to be about 0.01 mg/L and the a_{FeCO_3} to be 0.09. The value of a_{FeCO_3} of 0.09 is equivalent to about 10 percent siderite end member in calcite or ankeritic dolomite. In view of the fact that magnetite is assumed to be barely stable but is actually never found, the Fe^{2+} value is almost certainly lower, resulting in somewhat higher H_2S and lower a_{FeCO_3}. The above calculations provide an upper limit to iron in solution under the inferred reservoir conditions.

This calculation is very approximate, but it is consistent with the presence of ferran dolomite, ferroan calcite, and impure siderite, as observed in the reservoir rocks. Measurements of the composition of this carbonate are highly desirable, but the agreement is good enough to lend support to the above calculated iron and hydrogen sulfide contents.

The low calculated hydrogen sulfide content is consistent with the lack of detectable hydrogen sulfide in gas analyses. The hydrogen sulfide content may be sufficient to limit the content of copper, lead, zinc, and other sulfide-forming metals in the brines. The low calculated iron content in the brine suggests that the much higher observed iron contents probably arise by dissolution of casing and other well parts. An analysis of brine before it contacts steel in the well would be desirable to confirm the low iron content. If the iron content is actually this low, some of the undesirable properties of the brines, such as precipitation of iron oxides and acidity, could be decreased by procedures to minimize corrosion.

ORIGIN OF THE BRINES

The chemistry of oil field brines is determined by a wide variety of physical processes and chemical reactions. The physical processes can include evaporation of fresh or ocean water, dilution with freshwater, mixing with other saline waters, and membrane filtration (reverse osmosis). Possible chemical reactions include precipitation or dissolution of salts, dehydration of hydrous minerals, and alteration of minerals in the enclosing rocks. Redox reactions within the fluid and reactions with a gas or oil phase can also modify the chemistry of the brine.

An understanding of the origin of these brines should allow prediction of the range in composition of future brine samples from the region. It may also allow an understanding of cementation and other mineralogical changes in concealed rocks, and of the past flow of fluids in the subsurface.

Most brines have an origin that is related in some way to seawater. The composition of seawater during its concentration by evaporation is affected by the precipitation of evaporite minerals as well as the removal of water. The sequence of formation of evaporite minerals at 25°C and the change in composition of seawater during evaporation are shown in Table 12. During the precipitation of evaporite minerals, bromine is largely conserved in the fluid phase.

Table 12. *Change in Chemical Composition During Seawater Evaporation[1]*

(Quantities are in milligrams per liter)

Stage of evaporation	Ca	Mg	Na	K	SO$_4$	Cl	Br
Black Sea water	233	679	5,820	193	1,460	10,340	35
Nomal seawater[2]	420	1,330	11,060	410	2,790	19,890	69
Gypsum precipitation begins[3]	1,700	5,200	44,000	1,460	11,000	80,000	269
Gypsum visible	1,040	7,590	59,700	2,220	13,300	107,800	396
Halite precipitation begins[3]	600	10,200	99,000	3,300	18,000	180,000	617
Halite visible	307	19,600	94,300	5,600	27,700	183,300	1,010
Halite	—	50,500	55,200	15,800	76,200	187,900	2,670
MgSO$_4$ precipitation begins	—	56,100	48,200	17,700	82,200	190,500	2,970
Potassium-salt precipitation begins	—	72,900	22,100	25,900	56,100	224,000	4,770
Potassium salts	—	92,600	8,960	18,800	54,200	254,000	6,060

[1]After Carpenter (1978).
[2]After Holland (1978) at density 1.028 g/cm^3.
[3]Determined graphically.

Bromine does not form any minerals of its own in evaporite sequences (Braitsch, 1971) and substitutes only to a limited extent in other evaporite minerals. The first halite to crystallize contains only about 68 ppm bromide, compared to 617 mg/L in solution, and the halite crystallized at the stage of sylvite saturation contains only about 260 ppm bromide (Rittenhouse, 1967). The concentration of bromide is thus an index of evaporation. Plots of other dissolved species versus bromide during the evaporation of seawater are, in effect, plots of concentration versus degree of evaporation. Analytical data from brine samples plotted on the same diagrams will indicate how the brines are related to seawater evaporation.

Carpenter (1978) used the quantity "MCl_2" as another conservative quantity during the evaporation of seawater to the point of precipitation of carnallite ($KMgCl_3 \cdot 6H_2O$). MCl_2, in milliequivalents per liter (meq/L), is derived as follows:

$$MCl_2 = Ca^{2+} + Mg^{2+} + Sr^{2+} + Ba^{2+} - SO_4^{2-} - CO_3^{2-} \qquad (10)$$

MCl_2 is essentially the amount of alkaline earths charge-balanced by chloride. Carpenter did not include barium, but it has been included here because of its relatively high abundance in these samples. Precipitation or dissolution of carbonates, sulfates, and halite does not change MCl_2. Plots of species concentration versus MCl_2 can be interpreted in a similar manner to plots of species concentration versus bromide.

The relationship of MCl_2 (meq/L) to bromide (mg/L) during seawater evaporation is represented by the following formula:

$$\log MCl_2 = \log m_{Br^-} + 0.011 \qquad (11)$$

A plot of MCl_2 versus bromide for the new brine samples and the samples of Poth (1962) is shown in Figure 7. Most of the samples for both sets of data fall near the line expected for evaporated seawater, although the Ridgeley samples and a few others show either an elevated MCl_2 or a decreased bromide level. This relation indicates that the two conservative quantities are affected by the same processes and suggests that the waters were originally seawater modified by evaporation and/or dilution.

Plots of chloride versus bromide and MCl_2, and corresponding seawater evaporation lines, are shown in Figure 8. These plots show that the samples do not follow the evaporation curves but form approximately linear trends that intersect the evaporation line beyond the point of halite saturation, near point A. The bromide:chloride ratio for nearly all brines is greater than that for seawater. Once again, the Ridgeley samples show a relative bromide depletion, and the Medina samples show a relative bromide enrichment. Similar trends hold for sodium, as shown in Figure 9.

MIXING EFFECTS

The observed trends in brine concentrations can be explained by the mixing of dilute water, probably either freshwater or trapped seawater, with seawater evaporated past the point of halite saturation (composition approximately at point A on Figure 8). Most samples cluster along the line calculated for the dilution of brine with freshwater, but for some brines a component of seawater is suggested. The samples containing the highest sodium and chloride fall near the seawater evaporation line, indicating an evaporated seawater source. Many of the brines, especially those from the oil wells, represent mixtures of 70 to 90 percent dilute water and only 10 to 30 percent evaporated water. The compositions of brines from different units suggest slightly different saline end members, and a few samples fall well off the main trend, suggesting more complex mixing or other processes.

The plots of chloride and sodium versus bromide show more scatter than the plots of those components versus MCl_2. However, for individual horizons, mixing lines are apparent for the different elements. Thus, there appears to be some other process, perhaps dissolution of low-bromide halite or mixing with waters that have dissolved halite, causing minor changes in the concentration of bromide. Dilution is the major cause of variation in sodium, bromide, and chloride contents of the samples and has an apparent effect on most other elements.

The nature of the diluting water is not completely defined, but it appears to be mainly freshwater for most samples, based on the deuterium data (Table 7). The δD value for present groundwaters of the region is about -40 to -55 ppt (parts per thousand) (Peter Deines, personal communication), and the δD of seawater is 0 ppt. The nearly constant δD of -40 ± 5 ppt suggests mixing of freshwater (δD approximately -40 ppt) with brine of composition A, also having δD of about -40 ppt. However, data for additional samples could show a seawater component in some. The experiments on evaporation of seawater by Sofer and Gat (1975) and Gutsalo (1980) show that seawater can be evaporated to brines having $\delta D = -40$ ppt. The low δD of the proposed end-member brine is consistent with surficial evaporation
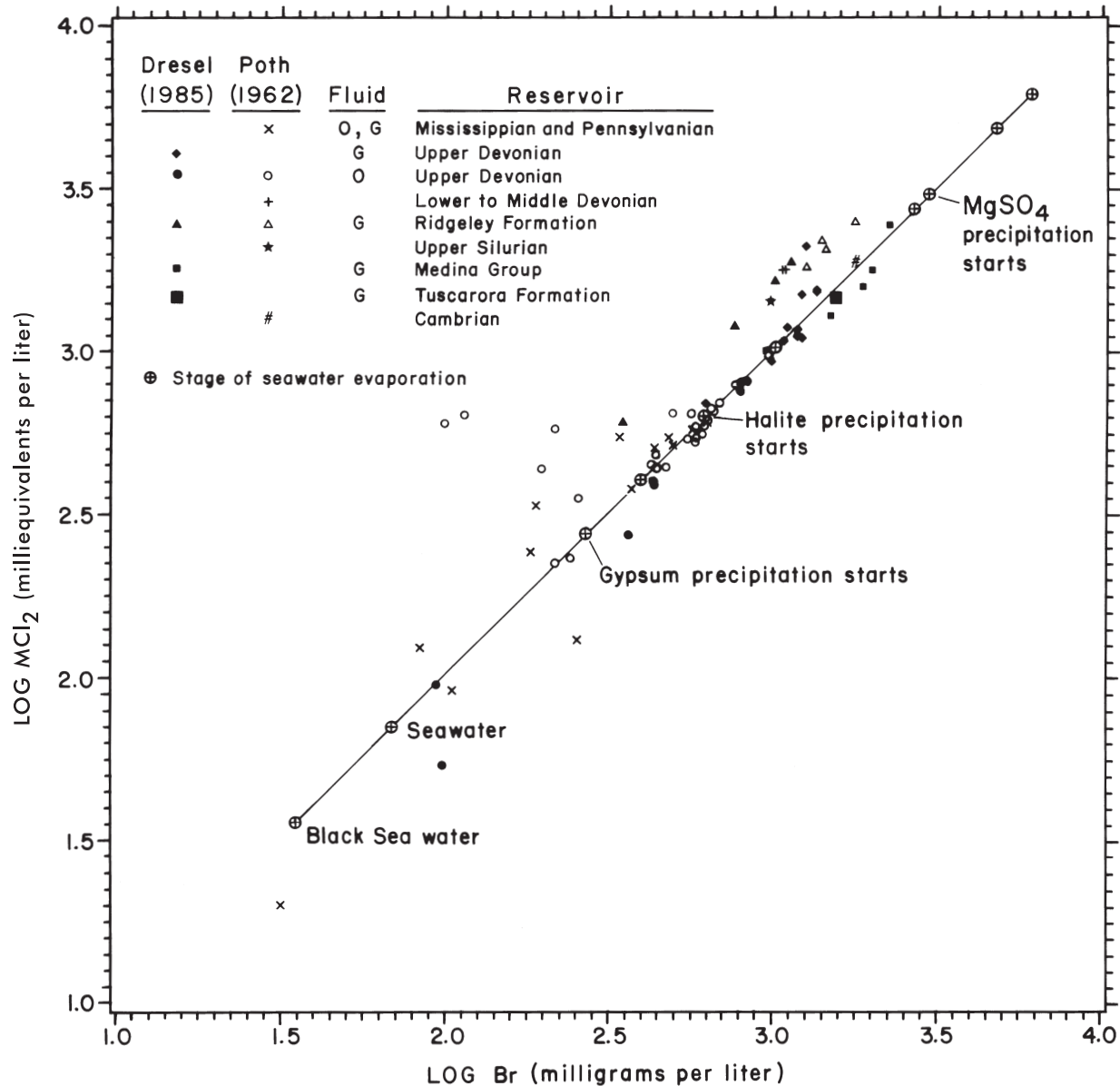
Figure 7. Plot of log MCl₂ versus log Br for samples of Dresel (1985) and Poth (1962). The line is a plot of these components during the evaporation of Black Sea water.

of seawater under slightly humid conditions (Dresel and others, 1985; Knauth and Beeunas, 1986).

Halite was widely deposited in the Upper Silurian Salina Group (Figure 2). The brines generated during this evaporite-forming epoch are a possible source for residual brine of composition A. The migration of these concentrated brines into Upper Devonian strata and other units might have resulted in mixing with varying amounts of freshwater or connate seawater already occupying the pores of the sedi-

ments. Recent mixing of freshwater is also likely. The existence of local goethite and hematite on fractures and pervading some zones (Laughrey, 1984) is also indicative of penetration of the reservoirs by surface waters.

Other workers have suggested flow through semipermeable shale units as a means to create brines of varying salinity (Graf and others, 1966; Hitchon and others, 1971; Kharaka and Berry, 1973; Kharaka and Smalley, 1976), but this process does
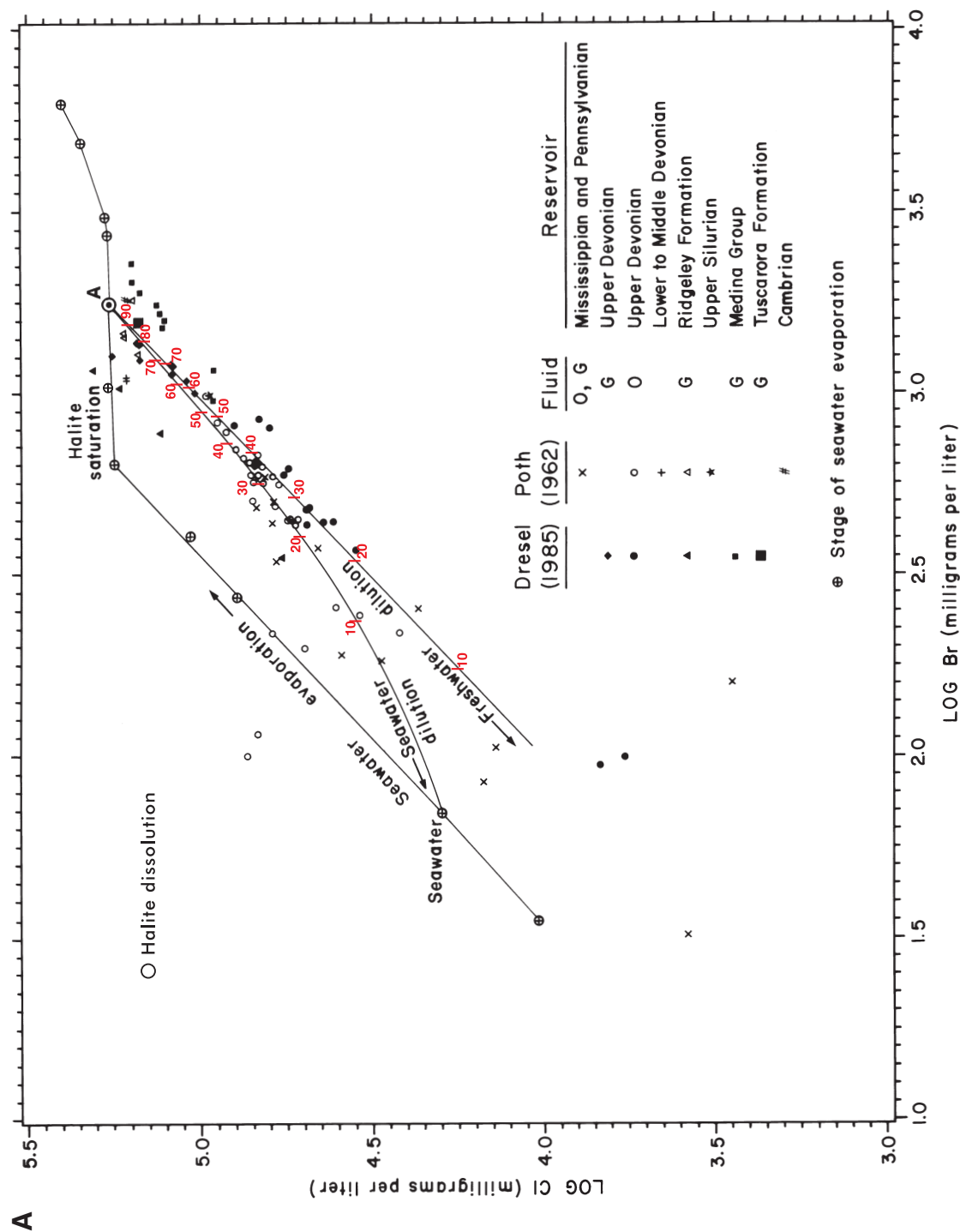
Figure 8.   Plots of log Cl versus log Br and log MCl$_2$ (see text for definition) for samples of Dresel (1985) and Poth (1962). Lines are plots of these components for seawater evaporation and for dilution of composition A with freshwater and seawater. The red numbers on these curves are percent of A, which has the following composition: Cl = 177,830 mg/L, Br = 1,700, Na = 78,500, Ca = 31,600, Mg = 3,390, and K = 320; MCl$_2$ = 1,800 meq/L. A. Plot of log Cl versus log Br. The point labeled "halite dissolution" is the Br:Cl ratio resulting from post-depositional dissolution of halite in low-salinity water. B. Similar plot for log Cl versus log MCl$_2$.
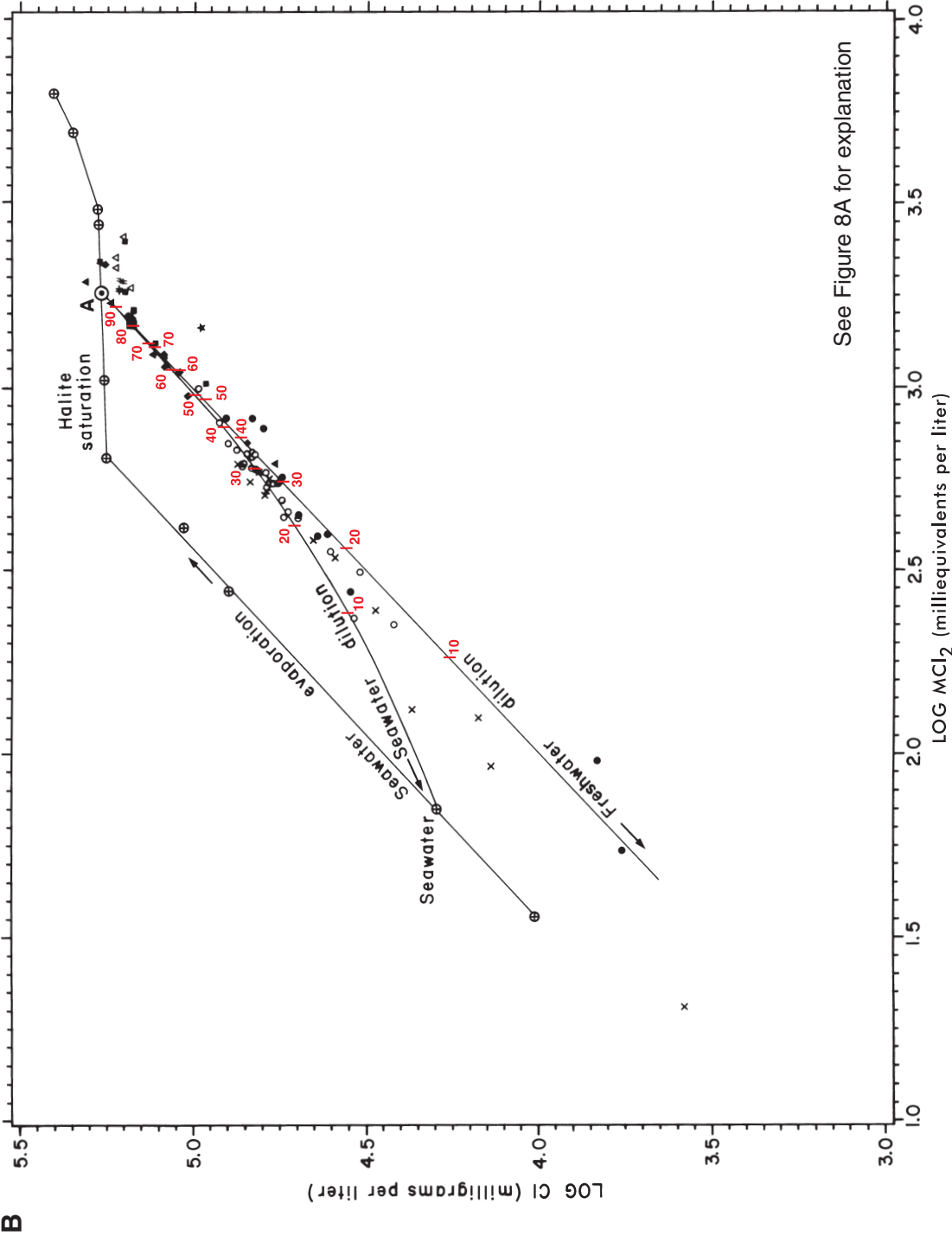
Figure 8. (Continued).
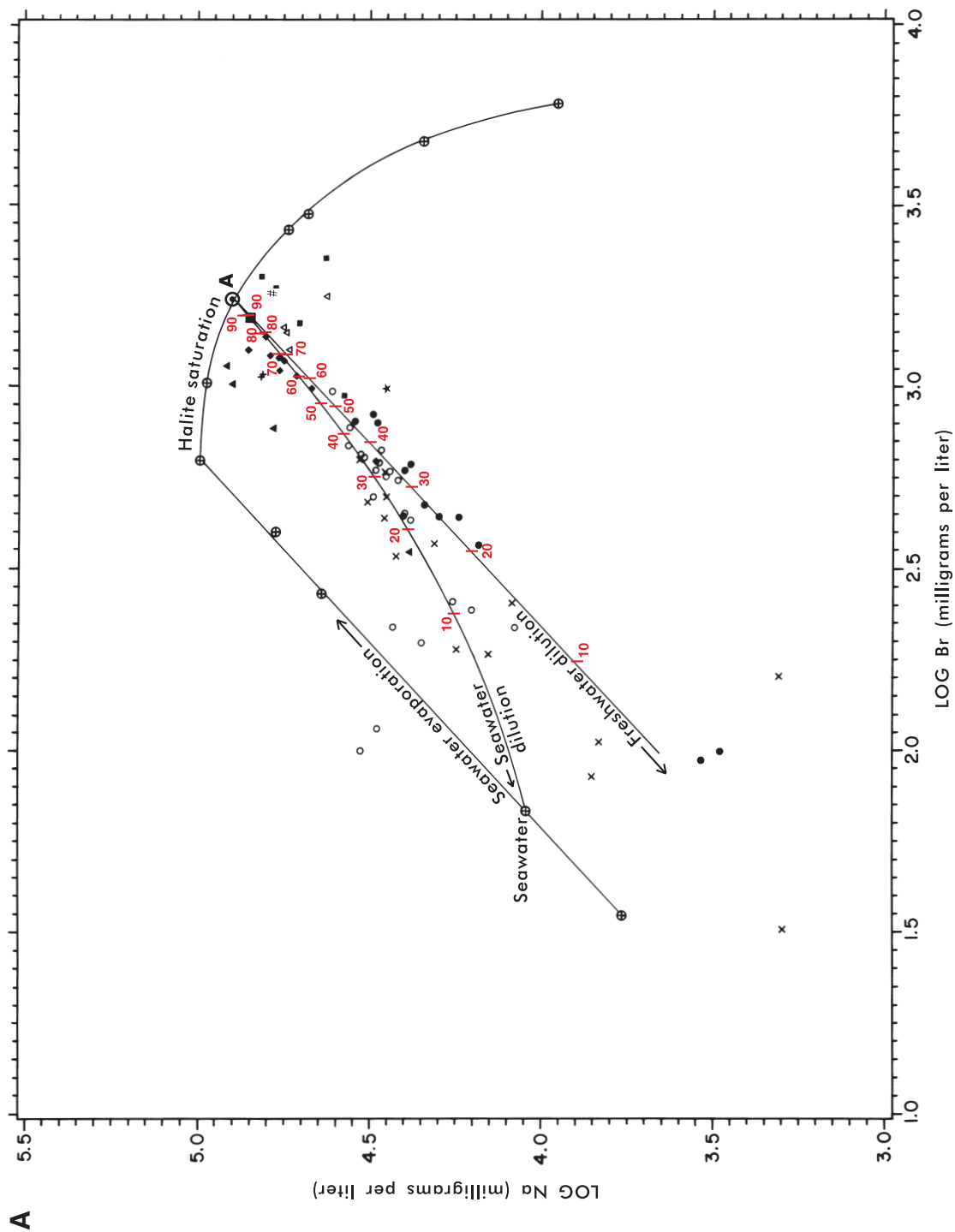
Figure 9.   Plots of log Na versus log Br and log MCl_2. See Figure 8A for explanation of lines and symbols. A. Plot of log Na versus log Br; B. plot of log Na versus log MCl_2.
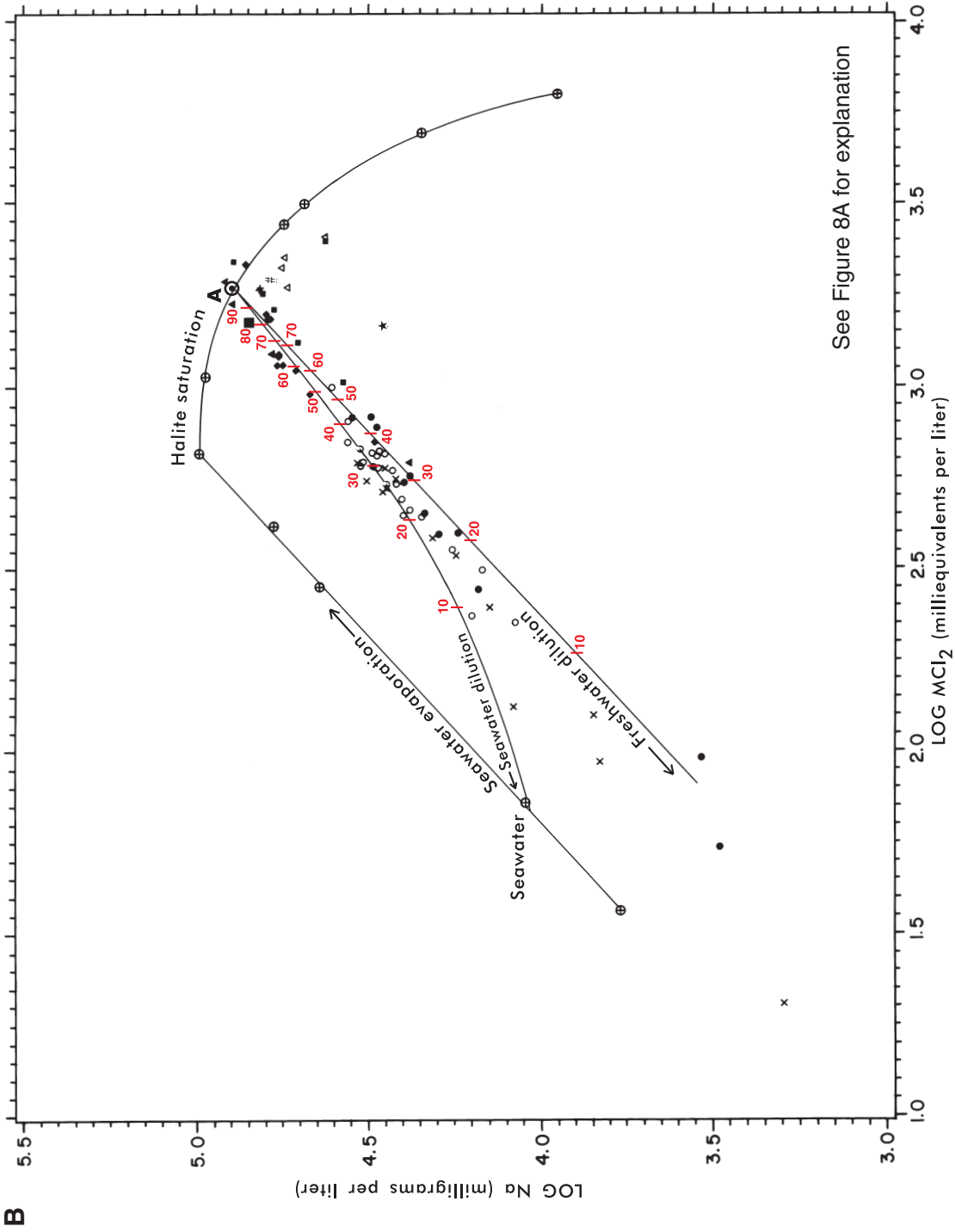
Figure 9. (Continued).

not seem to explain the Pennsylvania data satisfactorily. The ratio of calcium to sodium, measured in milligrams per liter, remains about 3 in all of the Pennsylvania brines (Figure 10), whereas waters claimed to have been formed by the membrane filtration process typically show a marked increase in the ratio of calcium to sodium with increasing salinity, as well as other changes in ratios of elements. Experiments also show a selective degree of retention by the membrane effect. The lack of changes in ratios involving calcium, sodium, chlorine, bromine, and other major elements argues against membrane filtration as a cause for the varying salinity. The position of saline end members along the evaporation curve, and the seawater ratio of bromide to MCl_2 (Figure 7), suggest an evaporated seawater for the concentrated end member, rather than a membrane-filtered water.

DOLOMITIZATION

Calcium and magnesium do not show the same close relationship to the seawater evaporation line as do sodium and chloride. Figure 11 shows that the calcium values lie above the seawater evaporation line, and Figure 12 shows that the magnesium values lie below the evaporation line. The plots suggest that most of the variability in calcium and magnesium can be explained by the mixing of a concentrated brine with freshwater and/or seawater. The most likely explanation of the calcium and magnesium content of the concentrated end member is the exchange of calcium and magnesium during dolomitization.

Sufficient magnesium is present in evaporated seawater to produce the excess of calcium in most Pennsylvania brines by the following dolomitization reaction:

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+} \qquad (12)$$
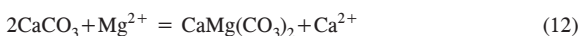
Calculations by Dresel (1985), assuming conservation of bromide during seawater evaporation, show that consumption of magnesium by this reaction releases as much or more calcium than is observed in most of the brines. For the Medina brines, some additional magnesium loss is indicated. The trend of Medina brines extends toward the position for magnesium-salt precipitation. Possibly these brines are mixtures of a brine more evaporated than that of composition A with brines diluted from composition A. Reactions involving chlorite are also possible.

Support for dolomitization as a significant process is also provided by calculations showing that the ratios of calcium to magnesium in the brines approximate equilibrium between calcite and dolomite. Dolo-

mite is approximately saturated in the brines (Dresel, 1985), and the activity ratio of magnesium to calcium decreases with increasing reservoir temperature, as is expected for equilibrium between calcite and dolomite, although the ratios lie above the equilibrium curve (Figure 13). Uncertainties in the solubility of dolomite or equilibrium with disordered dolomite (Stoessel and Moore, 1983) could affect the location of the stability boundaries and explain the deviations from the equilibrium curve.

Dolomite is abundant in the Salina Group (Cate, 1961, 1965), so dolomitization probably began and was most active during and shortly after the trapping of the brine in the sediment. A near-equilibrium condition apparently was maintained through changes in temperature until the brines approached their present temperatures. Based on this model, at least some dolomitization in the deeper reservoir rocks occurred long after burial, while the rocks were at temperatures at least as high as those presently existing. This is consistent with the observation of late diagenetic dolomite in the Medina Group (Laughrey, 1984).

OTHER INTERACTIONS

Water-rock interactions other than dolomitization may control the concentration of many of the minor constituents. Table 13 shows the concentrations of minor and trace elements in seawater, and the maximum concentration of each that would be obtained by concentrating a seawater source 64 times, based on the highest bromide concentration. Comparison with the maximum measured values shows that lithium, barium, strontium, iron, manganese, copper, zinc, and lead reach concentrations in brine that are higher than possible through seawater evaporation. Table 13 and Figure 14 show that potassium is depleted relative to seawater, even in the samples that are very close to the seawater evaporation line for sodium and chloride. The values do not seem to fall along a mixing line. Recent interaction with the reservoir rocks must provide sources and sinks for potassium and many other minor and trace constituents and control their concentrations. The high values of radium in some brines indicate interaction of brine with reservoir rock over the past few thousand years, based on the 1,600-yr half-life of radium.

BARIUM AND STRONTIUM

Although barium and strontium form similar minerals, the barium and strontium in solution could have originated from different rock types. Table 13 shows that the typical strontium content for limestone
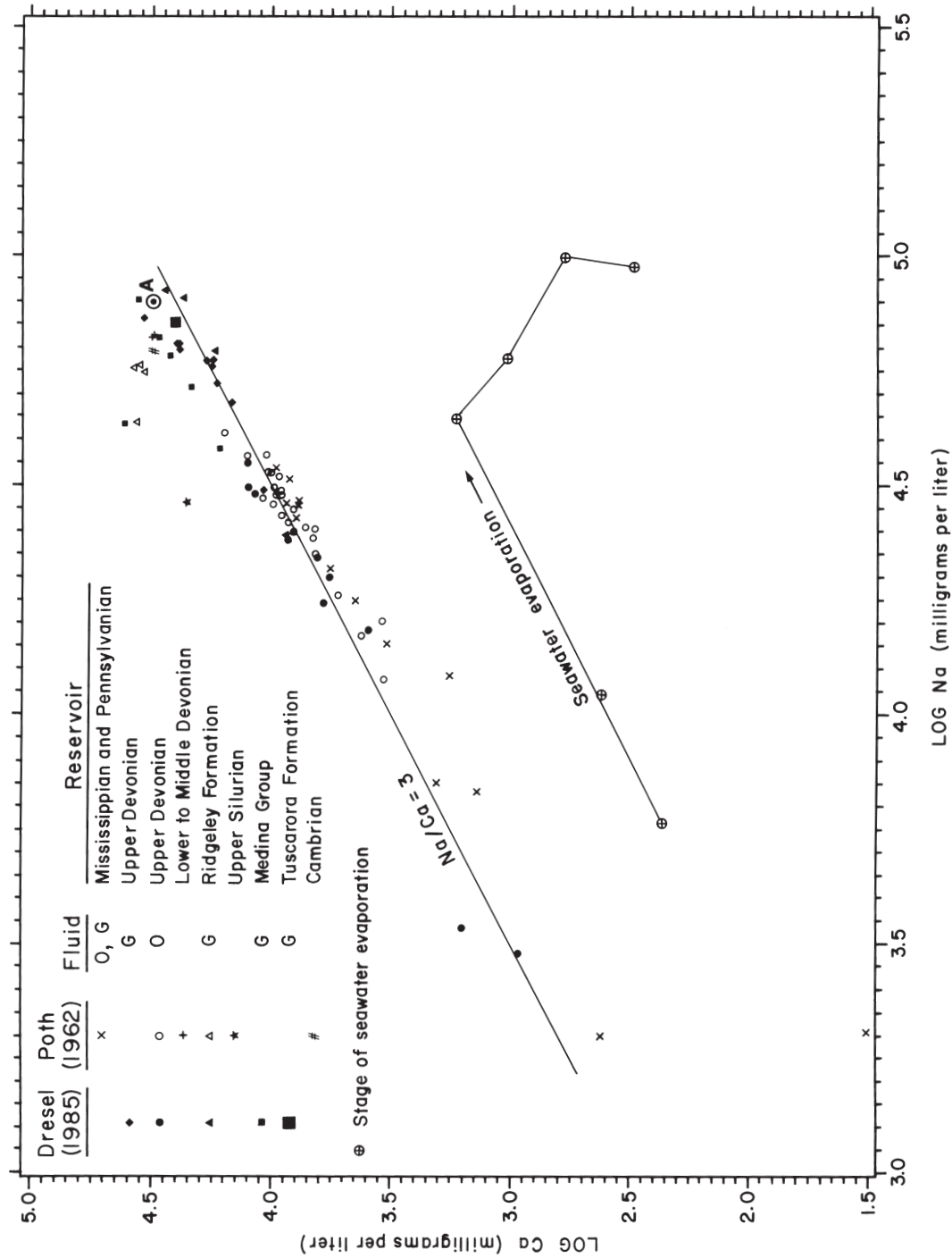
Figure 10.   Plot of log Ca versus log Na. Lines show seawater evaporation path and the sodium to calcium ratio of 3. The latter shows that there is only a minor change in the sodium to calcium ratio with salinity in samples from Pennsylvania.
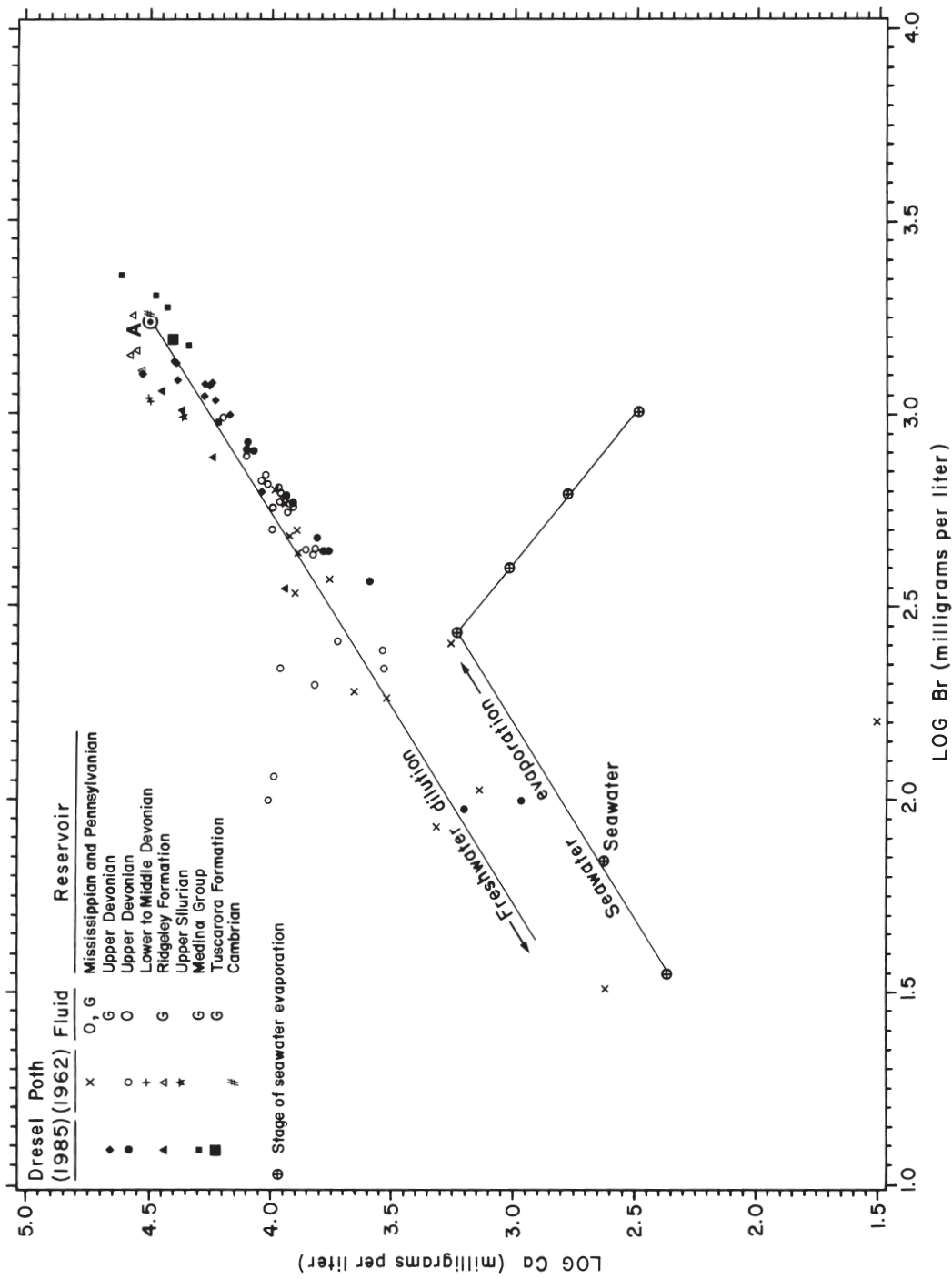
Figure 11.   Plot of log Ca versus log Br. Lines show seawater evaporation path and dilution of composition A by freshwater.
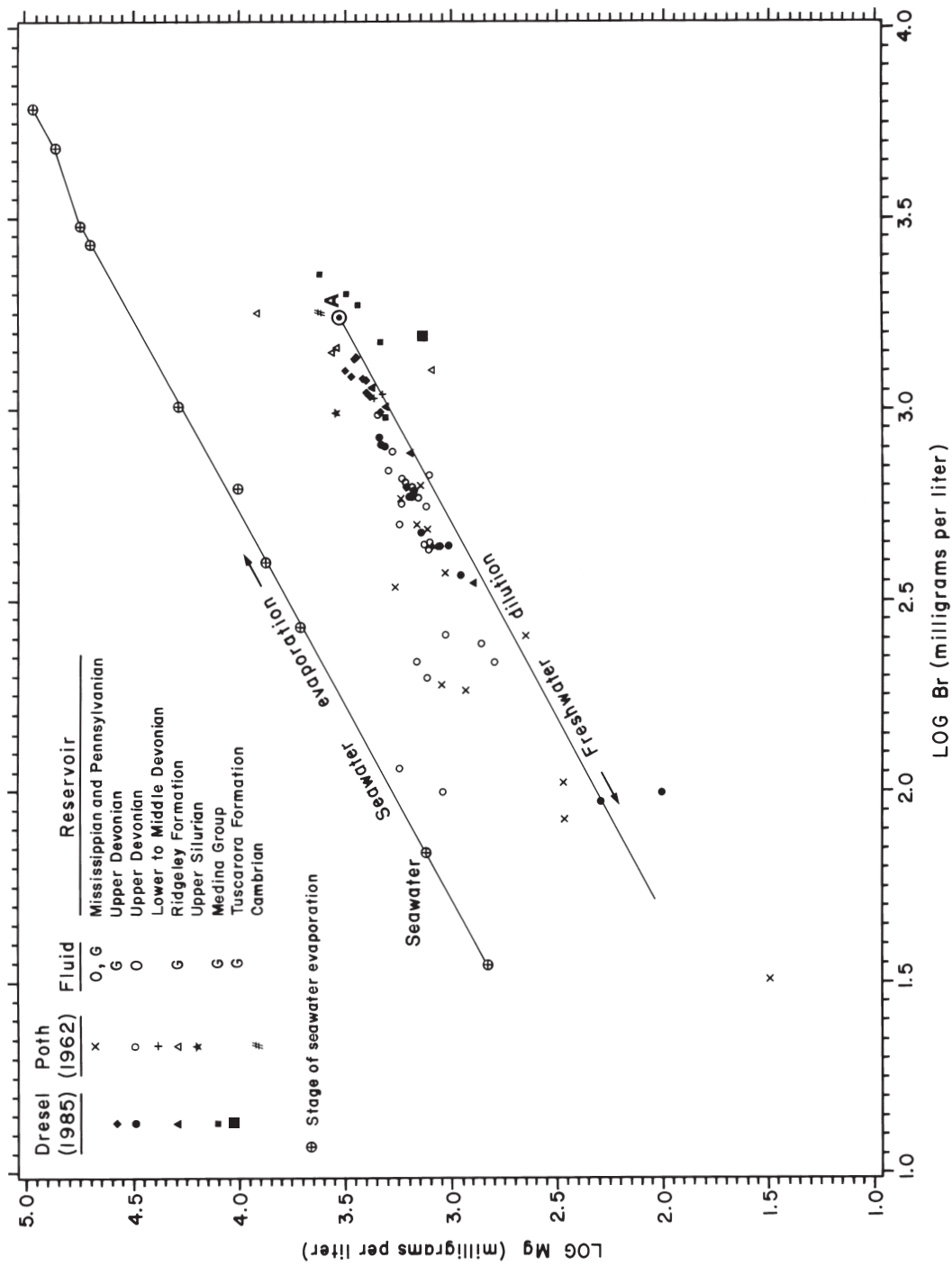
Figure 12. Plot of log Mg versus log Br. Lines show seawater evaporation path and dilution of composition A by freshwater.
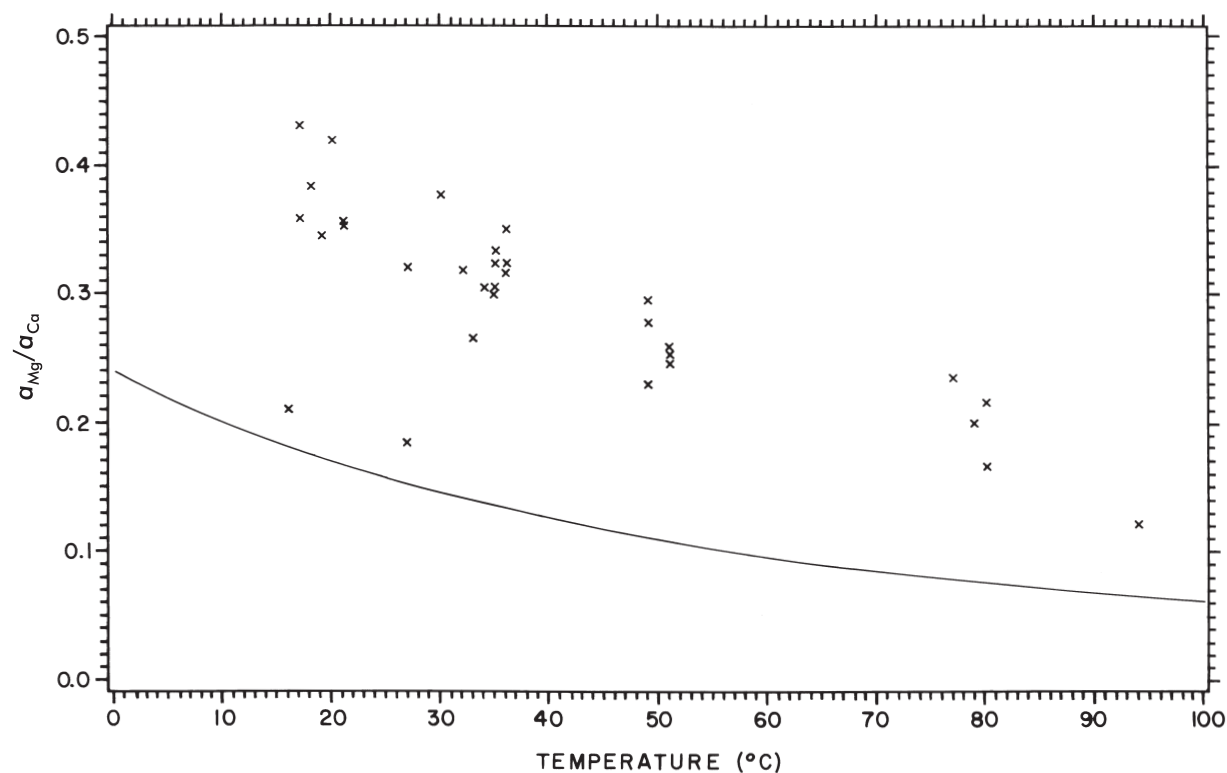
Figure 13.   Plot of Mg:Ca activity ratio versus inferred temperature of reservoir for samples of Dresel (1985), showing a tendency toward the relation that would be expected for equilibrium with calcite-dolomite (curved line) but offset in the direction for disordered dolomite.

Table 13.   *Minor-Element Concentrations in Seawater, Pennsylvania Brines, and Typical Rocks*

Element	Seawater[1] (mg/L)	Concentrated seawater[2] (mg/L)	Pennsylvania brines[3] (mg/L)	Limestone[4] (mg/kg)	Sandstone (mg/kg)	Shale (mg/kg)
Li	0.17	11	315	5	15	66
K	392	25,100	4,860	31	148	245
Sr	8.1	520	13,100	600	20	300
Ba	.021	1.3	4,370	10	—	580
Mn	.004	.03	96	1,100	50	850
Fe	.0034	.22	494	30	180	490
Cu	.0009	.06	.13	4	2	45
Zn	.005	.32	1.26	20	16	95
Pb	.00003	.002	.04	9	7	20

[1]Seawater composition from Turekian (1969).
[2]Maximum quantities in a brine produced by concentrating seawater 64 times.
[3]Maximum quantities in Pennsylvania brines.
[4]Compositions of typical rocks from Drever (1982), except K and Fe, which are from Wedepohl (1970).
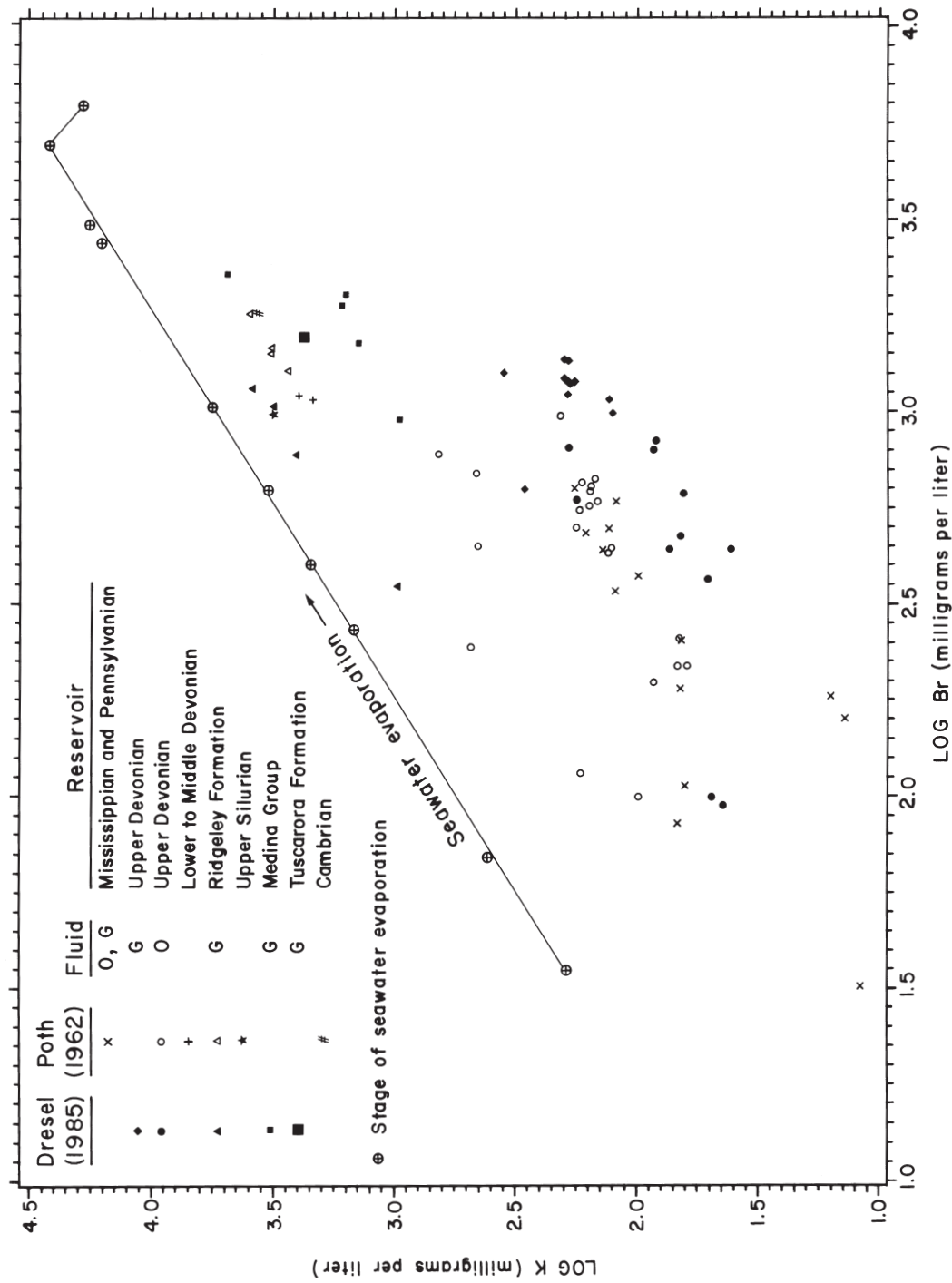
Figure 14. Plot of log K versus log Br and seawater evaporation path.

(about 600 ppm) is much higher than its concentrations in clastic sediments (20 to 300 ppm). Barium, on the other hand, has low concentrations in limestone (10 ppm) and a much higher content in shale (up to 580 ppm). Although strontium could be released during dolomitization, barium is more likely derived by silicate alteration. Barium concentration is probably limited by barite precipitation and strontium by strontianite or celestine precipitation, because the samples are near saturation for these minerals (Dresel, 1985). The incorporation of barium and strontium is thus dependent upon the development of a low concentration of sulfate and carbonate as well as a source of barium and strontium.

It might be thought that barium is contributed from dissolution of barite used in drilling mud. This process would result in equimolar amounts of barium and SO_4^{2-}. The lack of SO_4^{2-} in most samples shows that this is not the source of barium. The high strontium values also require a natural source.

POTASSIUM AND LITHIUM

Potassium is depleted relative to the seawater evaporation line, but lithium is enriched, probably because of reactions with the rock minerals. Both lithium and potassium are found in silicate minerals such as feldspars and clays. The potassium concentrations are probably related to silicate alteration, such as the feldspar-mica-clay reactions that were described by Laughrey (1984). Lithium, which tends to be concentrated in the same areas in which magnesium is concentrated in silicates, could be related to chlorite formation and alteration. Neither element follows simple mixing lines when plotted against bromide (Figures 14 and 15), although dilution could affect the concentration within the Oriskany and Medina horizons.

Figure 16 shows the relationship between lithium and potassium. A break in lithium values between the oil and gas wells and a break in potassium values between the shallow and deep gas wells are suggested.

DISCUSSION

The newer analyses of Dresel (1985), in combination with the previous analyses of Poth (1962) and others, show that Na-Ca-Cl brines more concentrated than seawater are produced by more than 95 percent of the Pennsylvania oil and gas wells sampled to date. In general, saline water is found at depths of a few thousand feet or less in most parts of western Pennsylvania (Shuster, 1979). The interpretations of this study indicate that the ratios of major ions and the probable origin of the ions are similar for all these concentrated brines, covering most of western Pennsylvania and including waters from the early Silurian Tuscarora-Medina Group, the lower Devonian Ridgeley Sandstone, and the various Upper Devonian reservoirs. Thus, although relatively few samples have been analyzed, the results can be generalized with reasonable assurance to samples that might be taken from other wells.

The data for chlorine, bromine, sodium, and MCl_2 show that most brines are closely approximated as mixtures of two end members. The concentrated end member (composition A, Figure 8A) is inferred to be seawater that was evaporated beyond the point of halite precipitation. The composition of end member A is about 185,700 mg/L Cl, 1,700 mg/L Br, 70,500 mg/L Na, 31,600 mg/L Ca, and 3,400 mg/L Mg. The more dilute end member is inferred to be freshwater for most samples, though a range of compositions representing seawater/freshwater mixtures is likely for some samples. The most concentrated brines are composed of 80 to 90 percent of composition A, but many waters, especially from oil wells, contain only 10 to 30 percent of composition A and 70 to 90 percent freshwater or a similar fluid. Given a value for Cl, Br, Na, Ca, Mg, total dissolved solids, density, or conductivity, the remainder of these parameters can be estimated using Figures 5 and 8 through 12.

The new data show that some chemical parameters determined in previous analyses are not representative of the brines at depth. In particular, the in situ pH is generally 6.2 ± 1, rather than the more acid values reported in many previous determinations. The cause of the low pH values previously measured was oxidation and precipitation of Fe^{2+} to form $Fe(OH)_3$ during the extended period between sampling and measurement in the laboratory. A second parameter not representing in situ conditions is iron. The concentrations of tens to hundreds of milligrams per liter of this constituent in most analyses are apparently due to corrosion. The concentrations in the pore water outside the drill hole are calculated to be only a few milligrams per liter.

Most of the brines from the Ridgeley Sandstone and the Upper Devonian gas wells, as well as a few other samples, have low SO_4^{2-} and very high barium and strontium. The SO_4^{2-} in the original seawater has apparently been depleted by precipitation of anhydrite and by sulfidation of iron minerals to form pyrite. The resulting low SO_4^{2-} has allowed dissolution of barium and strontium during interactions of
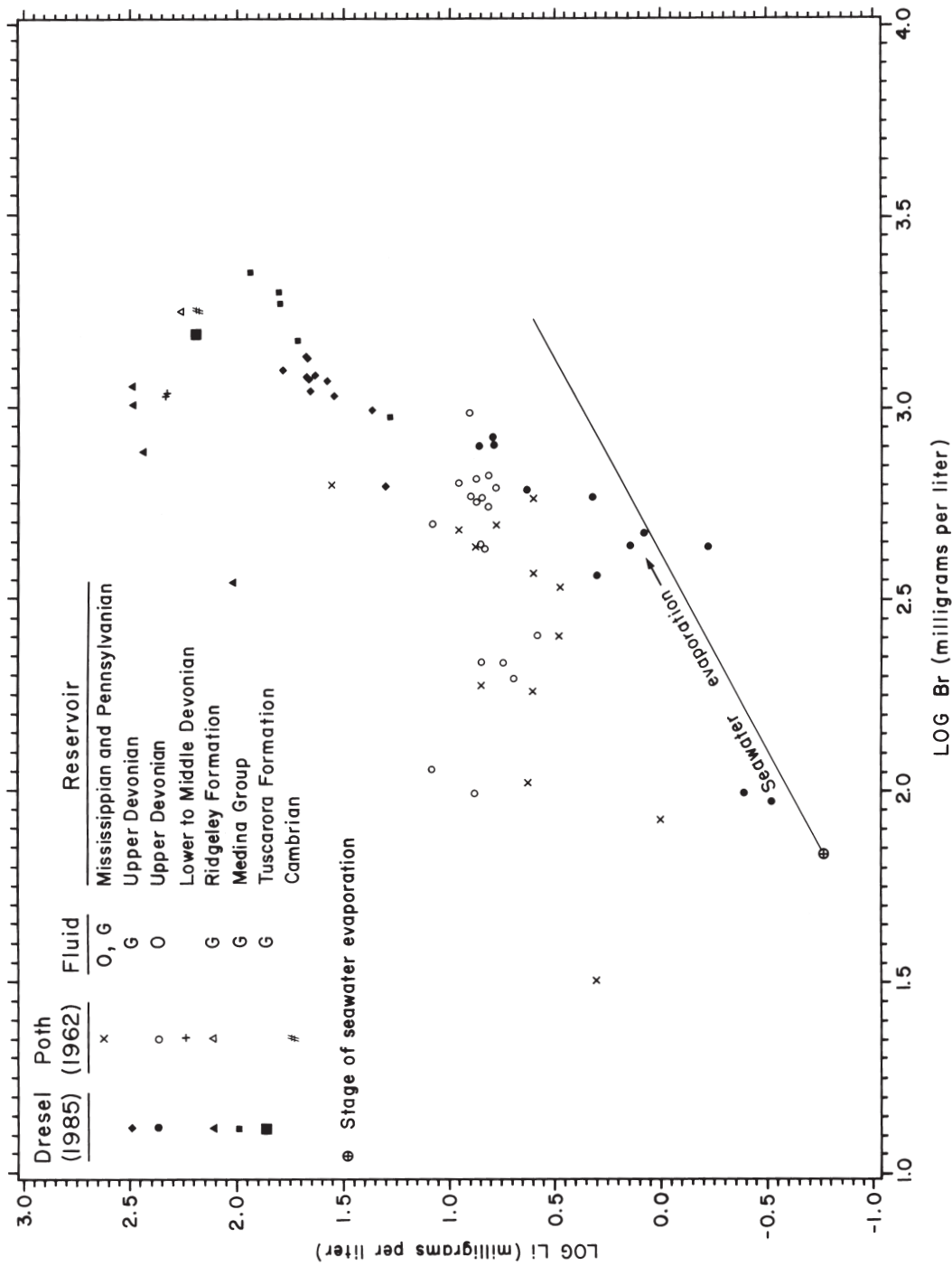
Figure 15. Plot of log Li versus log Br and seawater evaporation path.
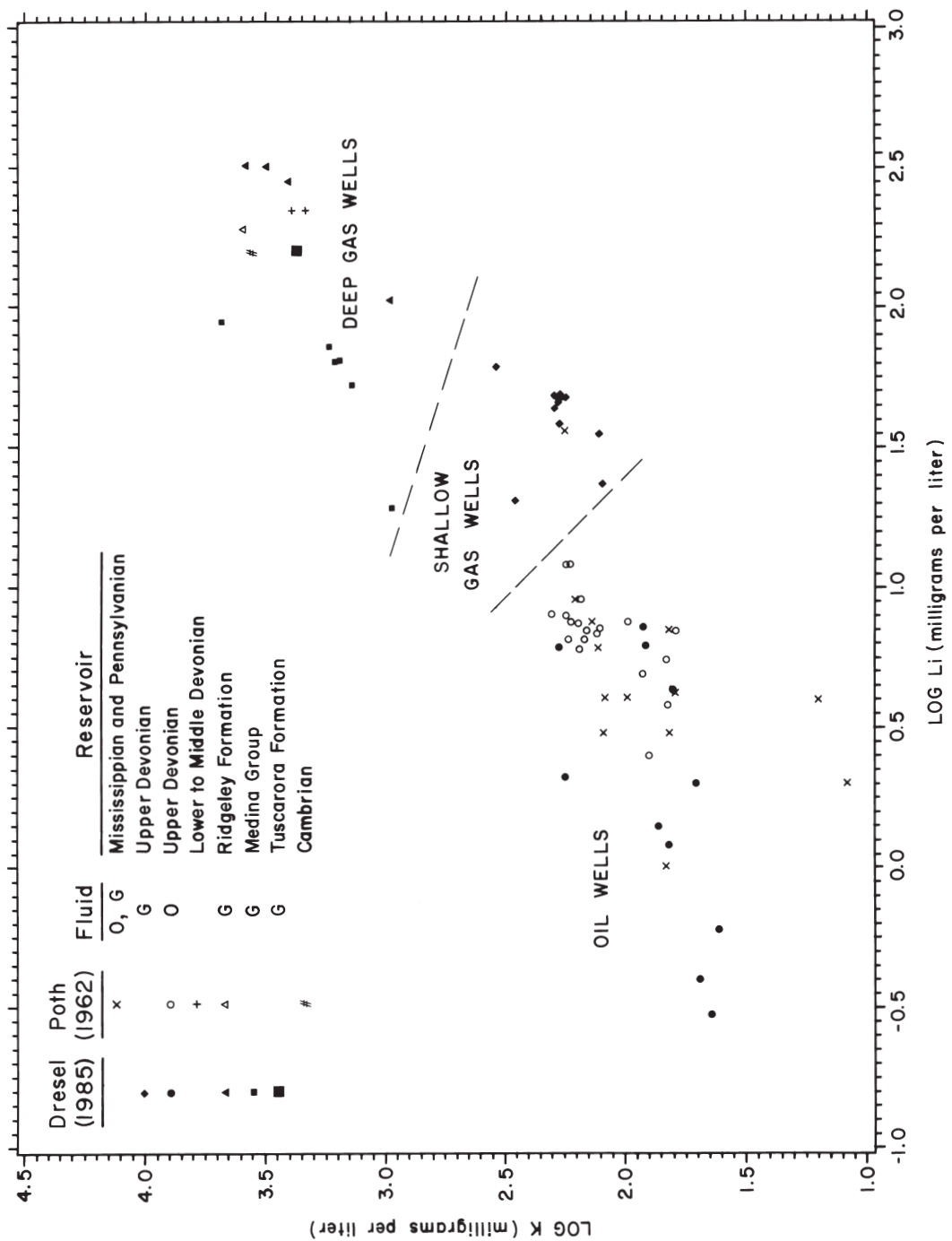
Figure 16. Plot of log K versus log Li showing relation to type and depth of well.

the brine with silicates and carbonates. Barium values of a hundred to a few thousand milligrams per liter are common in the brines. Contamination by these high-barium brines is very likely the source of barium contents exceeding the drinking-water limits in some private wells and small municipal water supplies in western Pennsylvania (Richard Wardrop, personal communication). The high barium values also would furnish deposits of $BaSO_4$ (barite) if the brines were mixed with seawater or other SO_4^{2-}-bearing waters. Related brines may have formed the barite and celestine, in part associated with lead and zinc sulfides in carbonate rocks of central Pennsylvania (Smith, 1977; Howe, 1981). The content of lead, zinc, and copper in the brines is very low, typically less than 0.1 mg/L, though a few samples contain about 1 mg/L Zn.

Based on the six samples analyzed, radium shows a general correlation with barium and strontium and an inverse correlation with SO_4^{2-}, though the correlation is not perfect. The radium values are high enough that a possible radiation hazard exists, especially where radium could be adsorbed on iron oxides and accumulate in brine tanks.

The alkalinity titration curves indicate that low contents of organic anions are present in the brines, but the exact nature of these anions is uncertain. Further study of this question is desirable.

The brines are believed to have originated as the residual pore fluid in halite evaporites, probably the salts of the Silurian Salina Group, which are present in most of western Pennsylvania. A likely origin involves mobilization of these residual brines out of the salt during compaction by overlying beds and during late Paleozoic deformation. The relatively permeable Ridgeley Sandstone is only a few hundred feet above the Salina Group in much of the region. This aquifer may have allowed the brine to flow laterally over the region. Sufficient fracturing to allow the cross-formational flow appears to be present in the region. Because these brines are much more dense than seawater, they would tend to displace the normal connate water from the underlying marine and nonmarine sediments as well. The great decrease in porosity caused by deep burial of the lower and middle Paleozoic sediments probably was adequate to cause gross flow of pore fluids in them. Because the remaining porosity of these sediments is very low, the volume of residual brine from the salt beds probably is adequate to fill all of the present pores in the Devonian and older sedimentary rocks, especially if dilution is considered.

Surface waters have mixed with the brines at some time since they formed by evaporation. This mixing probably occurred during Tertiary or Quaternary time, though it could have been as early as Devonian, in which case it would have been related to nonmarine Catskill sedimentation farther to the east. Some brines appear to include a seawater component, probably the normal connate seawater of Paleozoic marine sediments. The interaction of halite-unsaturated freshwater or seawater and halite beds, followed by mixing with the residual brine, may have contributed to the salt content in the Ridgeley samples.

Some trends between composition and stratigraphic unit or geographic location appear to exist. In general, the brines in the Ridgeley and older units (Medina, Tuscarora, and Cambrian rocks) have relatively high salinity (generally greater than 250 g/L total dissolved solids), though a few exceptions exist. The ratio of bromide to chloride of the Medina brines in Crawford County is slightly higher (0.0125) than that of the main group of samples in the Devonian (0.0091), which, in turn, is higher than that of the Ridgeley brines in Somerset County (0.0057). However, the Ridgeley brines from Clearfield County that were analyzed by Poth (1962) have a bromide-to-chloride ratio that is about equal to that of the main group of Devonian brines. The high bromide-to-chloride ratio of the Medina brines suggests that they could have originated from a more highly evaporated seawater than that represented by composition A.

Within the main group of Devonian brines, the brines from oil wells nearly always have less than 130 g/L total dissolved solids, and the gas wells usually have values greater than 150 g/L, though a few exceptions exist. These differences indicate that the brines associated with oil generally have undergone more dilution than those with gas. Some brines from Mississippian and Pennsylvanian rocks (Poth, 1962) have low total dissolved solids (<50 g/L) and have undergone major dilution by freshwater.

The basic chemistry of the brines appears to have been established by the evaporation and mixing processes described above, but some interaction with the enclosing rocks appears to have followed the migration into the present environment, as indicated by the correlation of ratios of magnesium to calcium with inferred present-day temperatures, and by the diversity of potassium and lithium values. Dolomitization and mica-clay-chlorite alteration, as observed by Laughery (1984; personal communication), probably are responsible for these modifications in the brine.

The preservation of brines interpreted to have been formed in mid-Paleozoic time indicates that these brines form a stable "layer" having a density appreciably higher than that of surface water. This density stratification has enabled the brines to persist since Paleozoic time.

CONCLUSIONS

Highly saline brines occupy pore spaces in sedimentary rocks at depth throughout western Pennsylvania. Brines are likely to be present at depth in other parts of the state, in view of the apparently stable gravity-stratification that has allowed brines to persist since Paleozoic time. The composition of brines in other parts of the state remains to be determined. The properties of these brines are important to a wide variety of questions, including some that pertain to oil and gas exploration and production, water pollution, deep waste disposal, cementation of sedimentary rocks, and the genesis of ore deposits.

The content of Na, Ca, Mg, Br, and total dissolved solids, and the density and electrical conductivity are closely correlated in these brines and can be predicted from a knowledge of any one of these constituents. Sulfate and carbonate contents are generally low but somewhat variable. Contents of barium and strontium are limited by the solubility of sulfates and carbonates but can be relatively high, so that admixture of even small amounts of the brine with near-surface freshwater can produce barium levels above current limits established by the U.S. Environmental Protection Agency for drinking water. The level of radium in brines and in brine-holding tanks deserves further investigation in view of possible radiation hazards. Iron content in the brines appears to be largely a function of corrosion of steel in the oil and gas wells. The oxidation of this iron is responsible for very acid pH values previously measured.

The brines appear to have formed mainly by dilution of highly evaporated seawater with freshwater, possibly during migration of the highly evaporated seawater away from the salt beds that were its source. Slightly different parent brines are suggested for different areas and reservoir rocks, and the dissolution of halite beds could have contributed to the formation of some brines.

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