MAJOR GEOCHEMICAL PROCESSES RELATED TO THE HYDROLOGY OF THE MADISON AQUIFER SYSTEM AND ASSOCIATED ROCKS IN PARTS OF MONTANA, SOUTH DAKOTA, AND WYOMING

By John F. Busby, Roger W. Lee, and Bruce B. Hanshaw

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ABSTRACT

Concentrations of fluoride and gross alpha and gross beta particle activity exceeded limits established by the National Interim Primary Drinking Water Regulations for public water supplies in a number of wells in the project area. Analysis and interpretation of the chemical and isotopic data, supported by the equilibrium-state computer model WATEQF, led to the following conclusions: (1) The Madison aquifer system is, and has been, an active hydrologic system that contains no connate water; (2) the major geochemical control on the system is the dedolomitization reaction caused by the dissolution of gypsum or anhydrite and dolomite, which causes the precipitation of calcite; (3) in some areas, notably flow path 3 in the Central Montana trough, sulfate reduction and cation exchange are important reactions that control observed water chemistry; (4) the Central Montana trough, because of the great thickness of bedded evaporites, is geochemically dissimilar to the rest of the area; (5) the most significant recharge to the system occurs in the areas of uplift, where the Madison aquifer system is exposed at the surface; and (6) the potential for the outgassing of carbon dioxide, from wells having temperatures greater than 40 degrees Celsius, and the concomitant precipitation of calcite is in agreement with the carbon dioxide pressure (P_{CO_2}) values greater than atmospheric.

INTRODUCTION

An estimated 40 percent of the low-sulfur coal reserves in the United States occur at shallow depth in the 500,000 square-kilometer area known as the northern Great Plains. Within this large area, much of the estimated coal reserves is found within the Powder River basin. Large-scale development of this coal will place an extensive demand on the limited water resources of the area. It has been estimated that as much as 250 cubic hectometers of water per year eventually will be needed to fully develop the coal resources. Surface water, however, is distributed unevenly in time and space, and most sources of ground and surface water have been appropriated throughout much of the area. This may necessitate development of available unappropriated ground-water resources.

Several of the sedimentary rock formations that underlie the coal-bearing formations, particularly the Mississippian Madison Limestone and its equivalents and associated rocks, which collectively are called the Madison aquifer system in this report, are thought to have significant water-supply potential; however, little was known about this potential when a U.S. Geological Survey study was begun during 1976. The overall purpose of this study was twofold: (1) To determine where greatest yielding wells at shallowest depths would produce water of suitable quality for municipal and industrial supplies; and (2) to determine regional effects of additional water development on the hydrologic system.

The principal objectives of the geochemical part of the overall study were: (1) To describe chemical character (quality) of the ground water; (2) to delineate spatial distribution of the solutes (these two objectives commonly are described as the hydrochemical facies of the aquifer system); (3) to determine mineralogic controls on chemistry of the ground water; (4) to describe and define chemical reactions that control the chemistry; and (5) to examine a variety of chemical data to provide insight into the hydrologic system.

Mesozoic and Paleozoic sedimentary rocks underlie younger coal-bearing formations that are primarily of Tertiary age; several of these pre-Tertiary formations have significant ground-water potential. The most promising is the Madison aquifer system. This aquifer system is comprised of varying amounts of limestone, dolomite, and gypsum or anhydrite. The aquifer crops out in the western part of the Northern Great Plains and in the center of the study area around the Black Hills. Within the study area, the top of the aquifer is as much as 5,000 meters below land surface. Because of the great depths of this aquifer in many parts of the area, little was known about its water-supply potential and geochemistry when the study began. Available information indicates that well yields range from as little as 1 liter per second to almost 600 liters per second; most wells yield less than 60 liters per second.

The Madison aquifer system currently (1981) supplies water for domestic, stock, municipal, industrial, and oil-field water-flood uses, but the total production is relatively small. However, large-scale withdrawals could result in hydrologic and economic problems, such as decline in potentiometric surface, depletion of flow of streams and springs, or deterioration of water quality from existing wells. Ground-water withdrawals during the past 15 years have caused large declines in the potentiometric surface in the center of the Powder River structural basin. The Madison study area, shown in figure 1, includes eastern Montana, western North Dakota, western South Dakota, a small part of northwestern Nebraska, and northeastern Wyoming. Western North Dakota was excluded from this geochemical study for the following reasons:
(1) Ground-water quality deteriorates rapidly eastward from eastern Montana and northeastward from South Dakota toward the Williston basin in North Dakota; (2) extreme salinity of the water produced from massive salt deposits would not be helpful in defining geochemistry of the larger freshwater part of the area; and (3) general water-quality characteristics are described in numerous articles that deal with the oil-field brines of the Williston basin such as that by Anderson and Swinehart (1979).

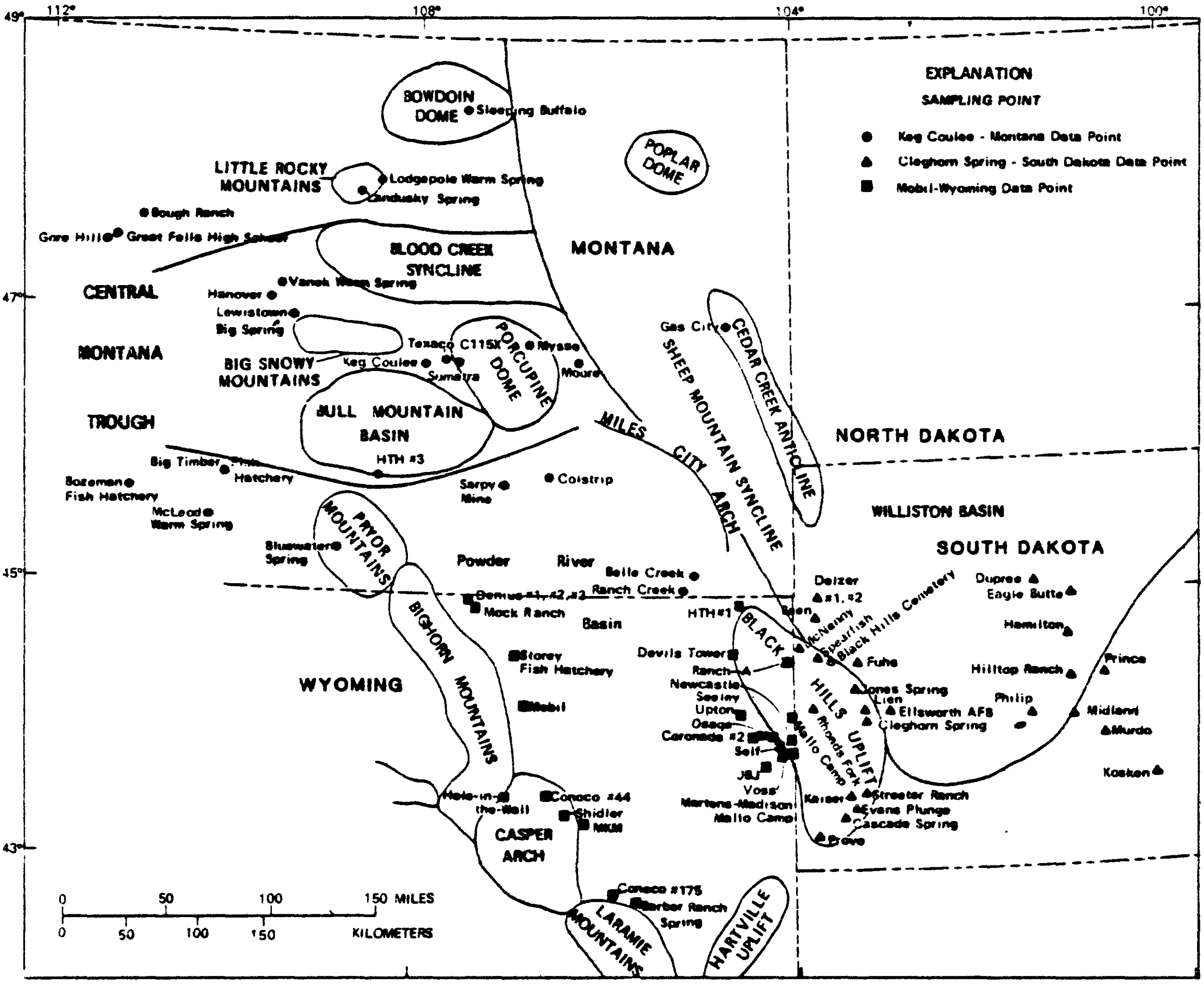

Figure 1.--Geologic structure associated with the Madison aquifer system and sample locations.

Data used in the description and discussion of the geochemistry of the Madison aquifer system were obtained from water wells, many of which originally were drilled as oil tests, and from springs. Although a great number of oil-test wells have been drilled into the Madison aquifer, most did not completely penetrate the aquifer. Most of these wells were drilled to develop oil fields or to explore known geologic structures; they are, therefore, concentrated in select localities, leaving large areas nearly devoid of any stratigraphic, structural, or geochemical information. Few data were collected by the drillers for geochemical purposes during these oil tests; typically, data were obtained that were useful in defining geologic framework and mineralogy. Some data, such as water-temperature measurements, aquifer porosity, and water-level measurements were obtained during oil-field tests. Information virtually is nonexistent for determination of regional values for recharge, discharge, transmissivity, storage, vertical leakage, water use, water quality, and potentiometric surface. Information on these hydrologic properties is necessary to evaluate the water-supply potential of the Madison aquifer; these features have been discussed in other reports in the Madison Limestone series.

A survey was made of existing wells and springs in eastern Montana, western South Dakota, and northeastern Wyoming to determine the most suitable sampling points for the geochemical study. Initially, about 200 wells or springs were screened for proper completion and availability. As a result of this screening, 75 wells and springs were chosen for sampling. Sites that were not sampled generally were not possible to sample; however, some sites were not sampled because other nearby sites that were selected would nearly duplicate the information. The 75 sites sampled represent nearly all available water-quality information throughout the freshwater part of the study area. Samples were analyzed for major and minor chemical constituents, dissolved gases, gross alpha and gross beta particle activity, and stable and radioactive isotopes. The pH, alkalinity, water temperature, and specific conductance were determined at the sampling sites and in the laboratory as well. The data set thus acquired provided a network of carefully screened geochemical information that could be used as a standard for the comparison of geochemical information from other sources, such as oil-test records within the study area.

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SUMMARY OF REGIONAL GEOLOGY IN THE STUDY AREA

During Mississippian time, the study area was part of the Cordilleran platform. This platform was bordered on the west by the Cordilleran miogeosyncline, oriented approximately north-south in Idaho and western Montana. The miogeosynclinal trough received both shelf-carbonate and deep-water terrigenous detritus (Rose, 1976; Sando, 1976a). Much of the thick detrital sedimentation came from the Antler Orogenic belt, which was probably an island arc system that underwent intermittent tectonism during Mississippian time, and lay to the west of the miogeosyncline. The Transcontinental arch, east of the study area, was low lying and sporadically contributed minor amounts of detritus that spread thinly across the platform. Thus, the Cordilleran platform was a shallow-water depositional shelf on which predominantly carbonate and evaporite sediments were deposited during much of Mississippian time.

The study area was entirely within the Cordilleran platform environment during Mississippian time. The Black Hills uplift was not a regionally significant tectonic element until Late Cretaceous time (Agnew and Tychsen, 1965) and had little effect during Paleozoic time; although during Silurian and Devonian time, the area was elevated. During all of the Mississippian period, the study area was a classic shallow-sea because, although it was generally under water during much of Mississippian time, the seas were probably less than a few meters deep (Sando, 1976a). As summarized recently by Hanshaw and Back (1979), the seas were warm, under such shallow conditions, and therefore they were conducive to prolific biologic productivity and accumulation and preservation of limy body parts. Although modern, warm, shallow ocean water is oversaturated with respect to calcite, aragonite, dolomite, and magnesite, the magnesium-ion hydration barrier is thought to prevent effectively both organic or inorganic formation of dolomite and magnesite. Therefore, throughout geologic history, plants and animals that use carbonate minerals in their life processes have apparently only produced the calcium-rich phases, calcite and aragonite, in hard parts of their bodies. Under generally shallow-water conditions that prevailed in the study area, shoaling conditions and reef building were probably common; the modern-day counterpart is the Bahama Islands and the surrounding shallow-sea environment. During Mississippian time, the study area likely would have been a difficult area in which to negotiate a boat, even a shallow-draft vessel. At various times, there was probably a large number of reefs continually changing and shifting in time and space, and many oolite- and crinoid-bank shoals and lagoons. The lagoonal areas probably were evaporating basins in which gypsum crystals sometimes formed and became incorporated into the limy sediments. This theory would explain the widespread occurrence of gypsum, which is an important control on the geochemistry of present-day ground water. Seawater needs to be evaporated to only about 80 percent of original volume to precipitate gypsum, whereas it must be evaporated to about 10 percent of the original volume to precipitate halite (Clarke, 1924). Thus, in a lagoonal environment that frequently received influxes of seawater, gypsum commonly could precipitate, whereas evaporation seldom would proceed to the point of halite precipitation. Evidence of areas with more restricted circulation or a greater evaporation rate is provided by the significant accumulations of bedded evaporites that occurred in the Williston basin and Central Montana trough during the Late Mississippian. Where circulation briefly was restricted, gypsum should have precipitated and remained as a minor accessory mineral; however, where circulation was restricted for longer times, gypsum (and even halite) should be found in bedded sequences.

The Madison aquifer system in the project area consists of a sequence of marine carbonates and evaporites deposited during Mississippian time. Depositional environments grade both laterally and vertically from subaerial exposure to shallow marine carbonates and evaporite facies. The Madison Group consists of, from oldest to youngest, the Lodgepole Limestone, Mission Canyon Limestone, and Charles Formation or their stratigraphic equivalents.

The Lodgepole Limestone is predominantly a cyclic carbonate sequence, consisting largely of fossiliferous to micritic dolomite and limestone, argillaceous and thin-bedded over most of the study area (Smith, 1972). The unit ranges from 0 to more than 300 meters thick and averages about 100 meters in the study area (Andrichuck, 1955).

The Mission Canyon Limestone consists of a coarsely crystalline limestone at its base, grading upward to finer crystalline rocks and evaporite minerals (Miller, 1976). It is a massive dolomitic limestone deposit containing one evaporite cycle, and sharing a second evaporite cycle with the lower part of the Charles Formation (Andrichuck, 1955). Bedded evaporite minerals are absent throughout most of Wyoming and South Dakota, although bedded evaporites occur in southeastern Montana and northwestern North Dakota, and gradually thicken from central Montana toward their maximum thicknesses in the Williston basin (Andrichuck, 1955). The Mission Canyon ranges from 0 to 200 meters thick, and averages about 100 meters in the study area. Even where bedded evaporite deposits are absent, gypsum or anhydrite may be disseminated throughout the aquifer. This is important because the calcium-sulfate minerals, which are ubiquitous, provide the major driving force in the geochemical system, and their presence is mainly responsible for the geochemical reactions that occur within the aquifer system.

The Charles Formation generally is a marine evaporite sequence consisting of anhydrite and halite with interbedded dolomite, limestone, and argillaceous material. The Charles ranges from 0 to more than 100 meters thick, with an average value of about 80 meters within the study area (Andrichuk, 1955). Pre-Jurassic erosion removed most of the Charles Formation in the western and southern parts of the study area.

The structure of the Madison Group may be explained, at least in part, by a wrench-fault tectonic model, which suggests that deposition was penecontemporaneous with tectonic movement (Brown, 1978; Brown and others, 1982). Recurring faulting of basement blocks in response to shear forces may have controlled deposition and diagenesis of the Madison Limestone. Facies boundaries of depositional sequences commonly coincide with major structural features, which act as either hydraulic barriers or conduits to fluid movement in the Madison aquifer.

During and after deposition of the Mississippian sequence, the rocks were locally subjected to subaerial exposure and erosion and developed a regional karst surface. Solution brecciation also occurred after deposition wherever subaerial exposure occurred. Whether solution brecciation and karst development occurred simultaneously before deposition of Pennsylvanian rocks (McCaleb and Wayhan, 1969; Sando, 1976b), or whether karst development occurred during Chesterian time, with solution brecciation taking place in one or more episodes (Roberts, 1966; Brown, 1978), has yet to be resolved. As a result of karstification and solution brecciation, areas of significant porosity and permeability occur in the Black Hills area and throughout the upper part of the Mission Canyon Limestone, and perhaps the Charles Formation in the Williston basin. These zones are capable of storing and transmitting large volumes of ground water.

During Late Cretaceous and Tertiary time and into the present, the Madison and its equivalents have been exposed by uplift in many parts of the study area; these are major recharge areas to the aquifer today. For example, recharge occurs where the Madison is exposed around the edge of the Black Hills of South Dakota and Wyoming, the Bighorn Mountains of Wyoming, the Beartooth

Mountains, the Big Snowy Mountains, and the Little Belt Mountains of Montana. Although the Madison is exposed in the Little Rocky Mountains in north-central Montana, recharge is localized; in this area, both local recharge and regional discharge occurs, as will be demonstrated later from interpretation of the geochemical data. This concept further is substantiated by the freshwater-head data from Miller and Strausz (1980), shown on plate 1 (in pocket).

ORIGIN OF CARBONATE AQUIFERS--A GEOCHEMICAL PERSPECTIVE

Recent studies by carbonate petrologists and geochemists have provided hydrologists with new insights into the origin and explanation of many aquifer characteristics and hydrologic phenomena of carbonate aquifer systems. Knowledge of the chemistry, mineralogy, depositional environments, and diagenesis of carbonate rocks is important to hydrologists to understand the ability of the rock fabric to develop porosity and permeability, through geochemical, tectonic, and hydrologic processes that develop the aquifer. This section discusses the geochemical nature and processes involved in the origin and development of a carbonate aquifer such as the Mississippian Madison aquifer system.

Carbonate rocks are among the most productive aquifers, although permeability and porosity may vary greatly from the time of deposition until their functioning as an aquifer after burial. These variations are related to the depositional environment, chemical reactivity of aquifer minerals, and post-depositional tectonics. Carbonates and associated minerals are susceptible to geochemically caused changes from their biological-chemical origins to, and continuing with, their functioning as aquifers in the subsurface. To understand porosity relationships in carbonate rocks, it is necessary to understand geochemistry of the origin and diagenesis of carbonate rocks.

Although some modern carbonate sediments are deposited in the deep sea, most carbonate deposition occurs in warm, shallow seas (less than 12 meters deep). The final site of accumulation and initial lithification is typically in the intertidal to supratidal zone, which has been called the knee-deep environment. This discussion is limited to carbonates from typical shallow marine environments, because the Madison Group in the study area was deposited in such an environment.

Most shallow or near-surface ocean water is supersaturated with respect to magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$), calcite ($CaCO_3$), and aragonite ($CaCO_3$). Increasing temperature, decreasing pressure, and outgassing of carbon dioxide (CO_2) lead to increases in saturation levels. Despite ocean-water saturation with respect to magnesite and dolomite, these minerals are unknown as primary precipitates in marine environments. This apparently is due to the interaction of magnesium ions with water molecules, leading to hydrated magnesium ions with very strongly bound water molecules in aqueous solution. To be incorporated into a crystal structure such as dolomite or magnesite, the magnesium ion must be dehydrated, a process requiring almost twice the energy necessary for the dehydration of the calcium ion (Lippmann, 1973); this phenomenon commonly is called the magnesium-hydration barrier. Modern marine carbonate accumulations are initially one or the other mineralogic forms of calcium carbonate: either aragonite or calcite. Thermodynamically, calcite should precipitate directly from seawater; however, it has been shown both by experiments and field observations that only aragonite precipitates inorganically. It is well-documented experimentally, that with molar magnesium to calcium ratios greater than about 2, even with small dissolved-solids concentrations, aragonite precipitates rather than calcite. Thus, because the magnesium-to-calcium ratio of ocean water is 5.3, only aragonite is precipitated inorganically, although not in large quantities. Most current investigators agree that organisms are overwhelmingly responsible for the formation of almost all calcium carbonate in present-day oceans. The vast majority of Madison rocks show biogenic origins (Blatt and others, 1972).

At near-surface conditions, most oceanic water is supersaturated with respect to the calcium carbonate minerals, calcite and aragonite, whereas deep-ocean waters generally are undersaturated; the majority of the biogenic or inorganic calcium carbonate minerals that form near the surface dissolve in the deep ocean, as they sink through the water column. Thus, the calcium carbonate minerals that eventually incorporate into the geologic record are formed and preserved in shallow warm-water environments. Various estimates of biogenic production of calcium carbonate sediment in the shallow marine environment range from hundreds to thousands of grams per square meter per year; the average rate in biogenically productive areas is probably between 500 and 1,000 grams per square meter per year.

Although they are volumetrically insignificant in modern and (apparently also) ancient areas of carbonate accumulation, including the Madison Group, reefs are the most spectacular form of calcium carbonate mineral accumulation. Typically, reef structures preserved in the rock fabric are productive aquifers or oil reservoirs, because of initial large values of porosity and permeability, and updip proximity to petroleum-source beds. The landward side of a typical reef development is an area of restricted circulation in which evaporites may develop by evaporative concentration. Gypsum and, less commonly, halite, are precipitated in such an environment. This type of environment was very common throughout many parts of the study area at various times during the Mississippian.

Brown (1978) states that in a shallow-shelf area, such as existed in the Mississippian seas, subtle vertical adjustments on the basement block may have drastically affected the sedimentation pattern. He indicates that it is common for these structural elements to control the sites of bioherms and reef buildups, and also the accumulation of evaporites, either directly or by sea-level adjustments. It is our premise, based on geochemical studies, that this type of minor restricted circulation in the back-reef environments was common throughout the entire area, and accounts for the occurrence of gypsum or, today, anhydrite, ubiquitous in the Madison aquifer system.

Carbonate-sand accumulations are volumetrically less important than carbonate muds, both in areas of modern marine carbonate deposition, and in the ancient rock record; yet, these sands are commonly prolific aquifers. Sand-size carbonate grains tend to accumulate near their site of origin in higher energy areas than carbonate muds, which typically develop in lower energy environments. Sands typically accumulate as linear features, such as bars, beaches, and beach ridges. The clay-size content generally is small in carbonate sands, because of the winnowing action of higher energy environments in which sands evolve and accumulate.

The origins of most carbonate sands may be conveniently divided into two categories: (1) Inorganic oolites; and (2) skeletal remains of calcareous invertebrates. It is now widely agreed that oolites result from the direct precipitation of aragonite in a high-energy environment subjected to strong bottom currents. Oolites that are smooth, oblate-to-prolate spheroids with concentric rings of carbonate, typically are well-sorted and several millimeters in diameter. Recent work indicates that larger pisolites may form primarily in the vadose zone after emergence and not in the marine environment.

The second source of sand-sized carbonate particles is skeletal remains of marine invertebrates. Many organisms have sand-size shells; some larger shells readily disintegrate into sand-size particles. For example, most calcitic shells are coarse-grained and readily disintegrate into sand-size material, whereas aragonitic shells typically disintegrate into clay-size particles. Other, larger organisms are broken into sand-size particles by either physical or biological processes. During diagenesis in the subsurface, aragonitic oolite converts to calcite containing little magnesium, producing areally extensive cementation. Cementation that occurs in the vadose zone is usually minor; alteration under phreatic conditions results in more extensive cementation. Because oolites originate in a high-energy environment, finer particles are winnowed out; wind erosion and dune accumulation further enhance sorting. In general, sparingly cemented oolitic rocks have extremely large values of porosity and permeability, and commonly are very productive aquifers.

Modern carbonate sediments have a strongly developed bimodal distribution of grain size and consist of sand- and clay-size carbonate particles. Mud consisting of clay-size particles is predominant, and is composed of needle-shaped aragonite particles averaging about 3 micrometers long by 0.5 micrometer wide. When these carbonate muds lithify to micrites or calcilutite, individual crystals are approximately 5 micrometers in diameter from recrystallization during lithification.

Carbonate muds have several origins, the most important of which is biological. Calcareous green algae are prolific producers of aragonite needles that precipitate around threads of living cells. After plant death, aragonite needles are released to incorporate into carbonate mud, accumulating in a bottom environment markedly devoid of land-derived sediment. Many other organisms contribute directly to carbonate mud accumulation by decomposition after death. Larger organisms yield materials that disintegrate to mud as a result of wind and wave action, burrowing, boring, grazing, and biological abrasion. The latter process may be divided into two parts: (1) Mechanical, as when a fish takes a bite of coral and spits out the crushed carbonate skeleton; and (2) digestive, when carbonate material passes through the digestive system and is abraded and partly dissolved internally, before being excreted as fine particles.

Recrystallization of metastable calcium carbonates to calcite creates greater permeability in some carbonate sediments. Upon initial emergence from shallow marine environments, most carbonate sand bodies and reefs are already aquifers; however, the clay-sized carbonate material initially has significant porosity, but little permeability. Without early fracture development in response to effects of tectonic activity, these calcilutites would be relatively unproductive aquifers. As a result of selective solution and inversion of the metastable aragonite to calcite and recrystallization, the porosity is redistributed into larger void spaces that may not change the overall pore volume of the rock, but that greatly increase permeability.

Another major process that redistributes porosity and permeability in carbonates is dolomitization, which occurs in a variety of environments. These environments include those associated with prelithification, such as in the back-reef environment where reflux dolomites may form, and in sabkha flats. These types of dolomites are early diagenetic and typically associated with evaporite minerals, especially gypsum or anhydrite. However, these early diagenetic dolomitization processes cannot account for most of the regionally extensive dolomites in the geologic record.

The major environment of regional dolomitization, which is largely responsible for dolomite in the Madison aquifer, is in the subsurface mixing zone (zone of dispersion) of freshwater and seawater, where profound changes in mineralogy and redistribution of porosity and permeability begin at the time of early emergence and continue through the time when the rocks are well-developed aquifers (Hanshaw and others, 1971; Hanshaw and Back, 1979).

When parts of mature carbonate rocks are exposed subaerially, karstification occurs. Spectacular features, such as large caverns and solution brecciation, are major porosity developments that result from leaching of soluble evaporite minerals from the carbonate host rock by percolating meteoric waters (McCaleb and Wayhan, 1969; Sando, 1976a).

Another important control on permeability distribution in a mature aquifer system is the process known as dedolomitization. Without this process, which is driven irreversibly by dissolution of the evaporite mineral gypsum, carbonate aquifers would, for the most part, quickly become geochemically static. The process of dedolomitization represents the major, modern-day geochemical process in the Madison aquifer system.

As a result of this study, it has been found that geochemical processes in the Madison aquifer are similar to those in other carbonate aquifers described by Hanshaw and Back (1979). The processes that control the chemistry of water in the Madison are basically simple. Water in the recharge areas has large carbon dioxide concentrations and relatively small dissolved-solids concentrations. As water moves through the aquifer, it immediately begins to dissolve calcite, dolomite, and gypsum from the aquifer. This results in an increase in the total carbon dioxide concentration, with increases in many of the other chemical constituents, particularly sulfate, calcium, and magnesium ions. Eventually, equilibrium with respect to calcite dissolution is obtained, and no more calcite is dissolved from the aquifer; however, the ground water still is undersaturated with respect to dolomite and gypsum, and it continues to dissolve both of these minerals. During this continuing dissolution, dolomite contributes calcium, magnesium, and carbonate species to the water, and gypsum contributes both calcium and sulfate. The common calcium ion from the two sources and carbonate from the dolomite in solution, combine to further precipitate calcite. This process of dolomite dissolution and calcite precipitation is termed dedolomitization. As a result of these processes, the total dissolved inorganic carbon decreases slightly, while the other constituents continue to increase. The entire chemical system will continue to operate in this manner until equilibrium with gypsum or anhydrite is obtained or until all gypsum and anhydrite are dissolved. Within the geochemical study area, equilibrium with gypsum or anhydrite seldom is obtained, although the parts of the aquifer system containing water with excessive chloride and dissolved-solids concentrations have not been studied thoroughly, especially in eastern Montana and in North Dakota.

HYDROLOGY

The following discussion of geohydrology is based largely on the results of the geohydrologic study conducted for the Madison project by Downey (1982).

Freshwater Heads

The freshwater-head map, plate 1 (in pocket), indicates that the highlands are the main recharge area. Flow is controlled largely by fracture permeability induced by structural control (Joe S. Downey, U.S. Geological Survey, written commun., 1981). Flow in Montana is generally to the north into Canada and east into North Dakota. In Wyoming, plate 1 indicates a steep gradient from the western edge of the Black Hills toward the center of the Powder River basin, with a potential for the flow to move to the north and east around the northern end of the Black Hills, and to the south-southeast toward South Dakota and Nebraska. A component of flow is indicated to the north-by-northeast from the Laramie range. This interpretation is not supported by the geochemical maps or vector flow plots; (see sections on distribution of chemical and physical parameters and trilinear diagrams and the subsequent discussion of evolution of ground-water chemistry by flow path). Rather, it appears that the recharge from the southern end of the Powder River basin is diverted toward the center of the Powder River structural basin, where a large cone of depression is observed. Flow from the Bighorn Mountains appears to follow a steep gradient toward the east and northeast. In the southern part of the Bighorn Mountains, the flow is toward the potentiometric low near Midwest, Wyoming. North of this area, the freshwater-head map indicates that flow is down an extremely steep gradient to the northeast. Other data (see sections on evolugion of ground-water chemistry by flow path, distribution of chemical and physical parameters, and trilinear diagrams) indicate that the major flow is to the north along the front of the Bighorn Mountains, controlled by a fault zone, and moves to the east past the northern end of the Black Hills, where it joins the component flow moving to the north from the Black Hills.

In South Dakota, the major recharge is from the Black Hills, with the water moving down a gentle gradient to the east with a slightly steeper gradient to the northeast.

Flow Paths

The flow paths considered in this report were selected using two sets of criteria:

1. The path reflected a significant amount of flow, determined from a vector-flow map.
2. The amount of data existing along that flow path was sufficient to permit some analysis of the geochemistry.

The vector-flow map, developed by Joe S. Downey of the U.S. Geological Survey, was based on the solution of Darcy's law at each node of a three-dimensional digital model prepared for this project by Joe S. Downey (U.S. Geological Survey, written commun., 1982). The solution then was posted to the map as a vector giving the relative magnitude and direction of the flow at that node. A map showing general flow directions based on the vector-flow map is shown in figure 2.

Using the two criteria given above, the flow paths to be used were generated by connecting the vectors having the largest magnitude along a smoothly trending direction. Because it was recognized that flow lines are an abstraction of a more general direction of flow, an area of arbitrary size encompassing the flow line was selected for subsequent analyses. Generalized flow paths constructed from the vector-flow map and used for analysis of the Madison aquifer system are shown in figure 3.

EVOLUTION OF GROUND-WATER CHEMISTRY IN CARBONATE AQUIFER SYSTEMS

The distribution of chemical species in water from carbonate aquifers is not random; it is controlled by: (1) All the processes and reactions of diagenesis, including recrystallization, dolomitization, and cementation; (2) geologic activity; (3) dissolution and reprecipitation of minerals during ground-water movement; and (4) mass transfer of chemical species. Physical manifestations of this interplay of hydrology, sedimentology, mineralogy, and water chemistry are seen in landscape modification, karst features, porosity and permeability distribution, and in establishment and functioning of local and regional flow systems. The observed chemical character of water in carbonate aquifers is both a control on the physical properties of the system and a response to them. The chemistry of ground water is a result of the relationship between mineralogy and flow regime, because these determine the occurrence, sequence, rates, and progress of reactions. The mineralogy of an aquifer and its water geochemistry are reflected in each other and change in a systematic and generally predictable manner; this interrelationship is readily seen on a trilinear diagram for the data from specified flow paths.

Data in figure 4 (Hanshaw and Back, 1979) provide a conceptual model that depicts the changes in water chemistry of carbonate aquifers from the time of deposition in the shallow marine environment through their development as aquifer systems. When carbonate sediments first emerge from the marine

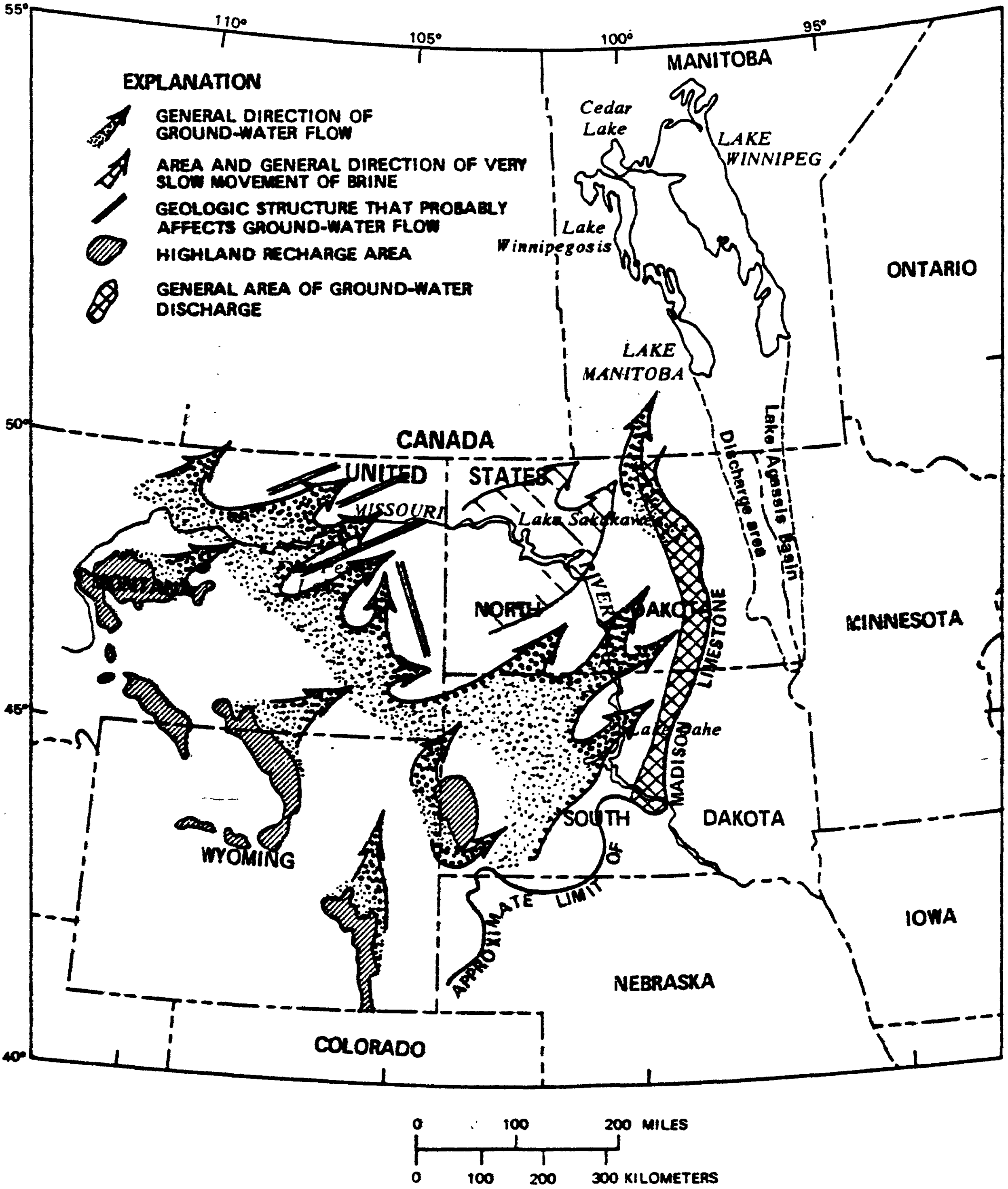


Figure 2.--Generalized directions of ground-water flow in the Madison aquifer in the Northern Great Plains.

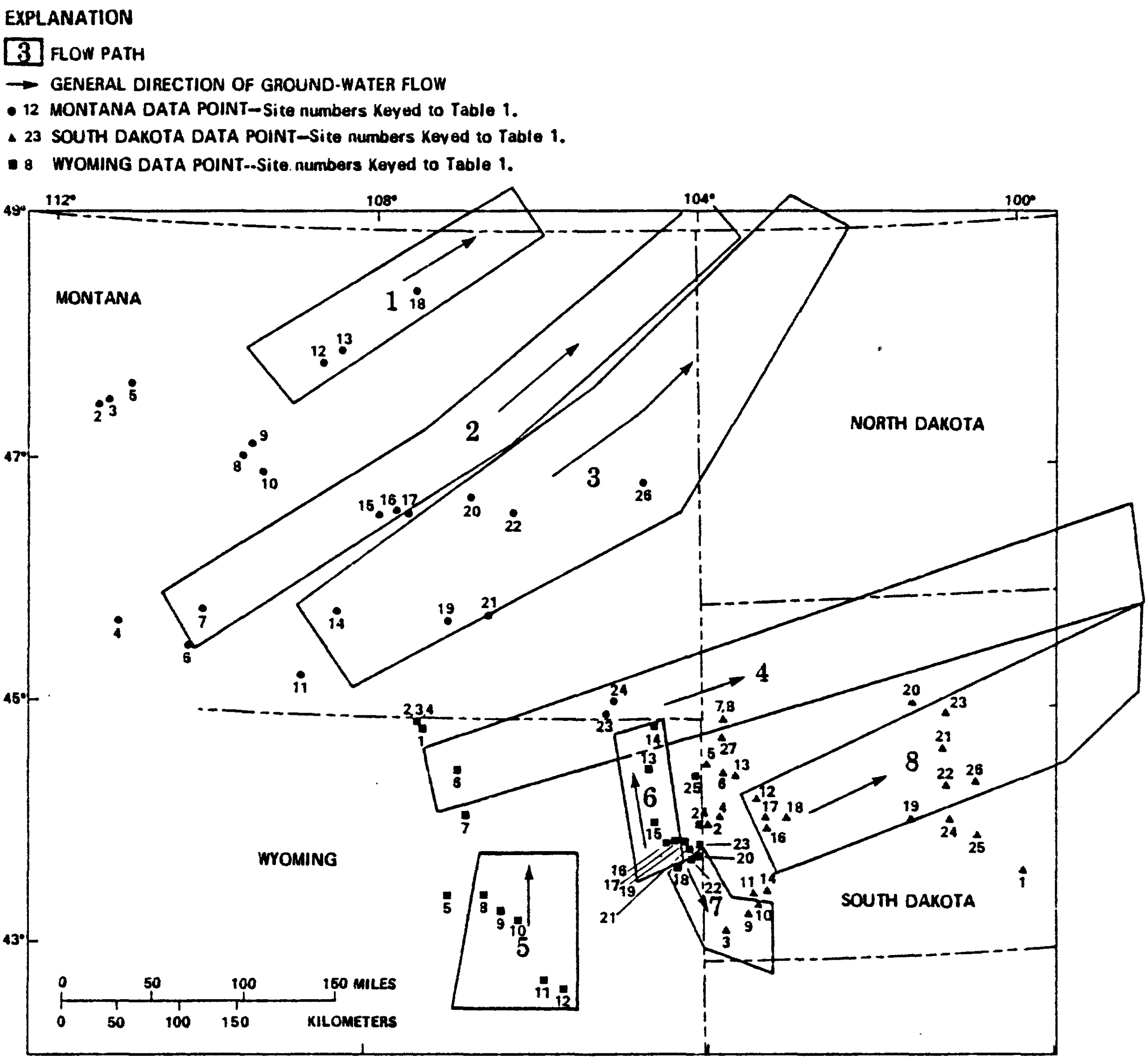
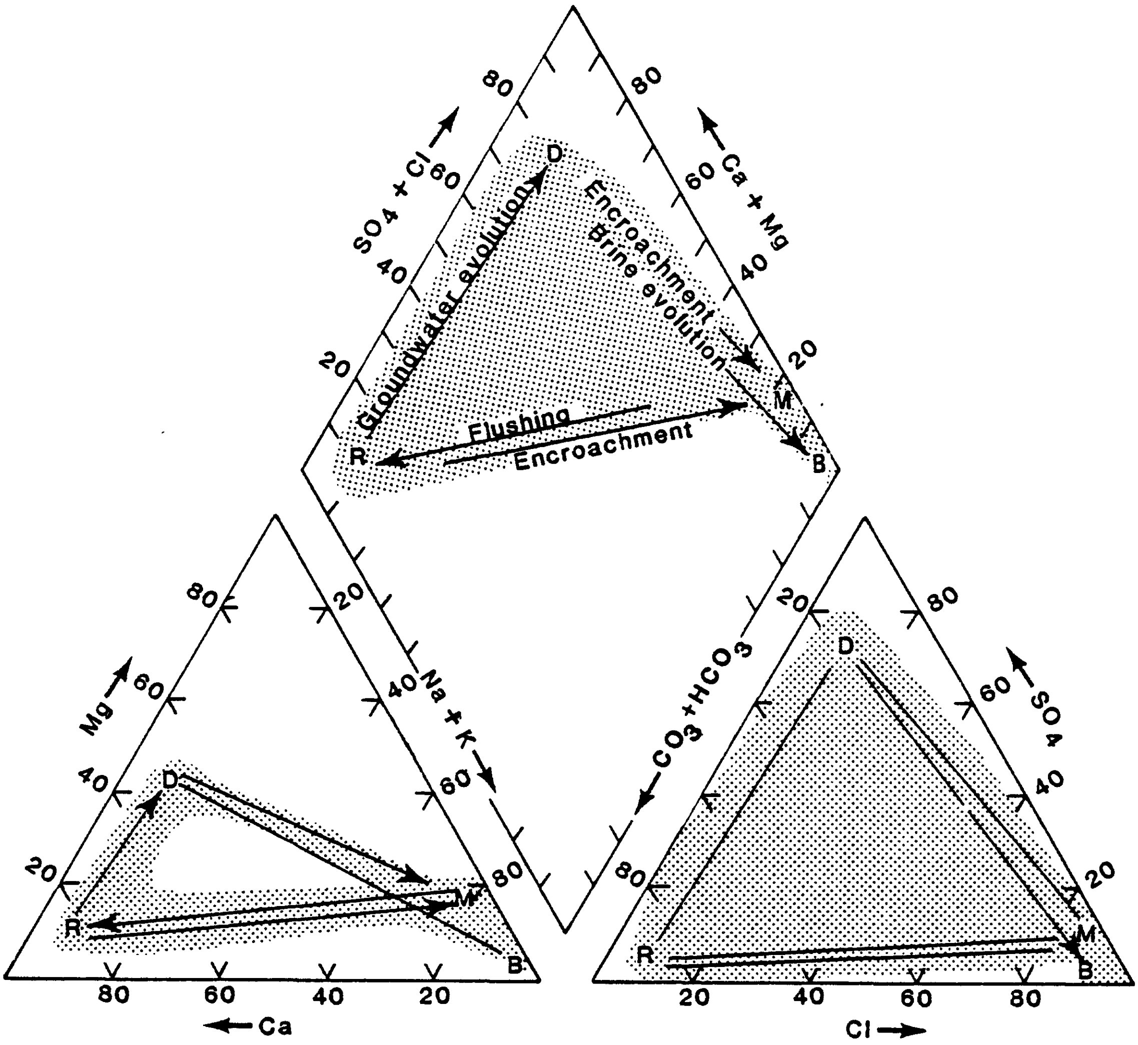


Figure 3.--Flow paths used in analysis of the geochemical data of the Madison aquifer system.



EXPLANATION

Stippling indicates area into which analysis may plot
Lines indicate direction of evolutionary process

WATER CLASSIFICATION

M	Marine water
R	Recharge water
D	Downgradient water
B	Brine

REACTION PATHS

M → R	Recrystallization of aragonite to calcite; selective dissolution of aragonite; inversion of calcite with decrease in magnesium; and cementation
R	Solution of calcite
R → M	Simple mixing; dissolution in dispersion zone
R → D	Dissolution of dolomite and gypsum; dedolomitization
D → M	Dolomitization
D → B	Dissolution of halite (Brine Evolution)

Figure 4.--Reaction paths showing evolution of water chemistry in carbonate aquifers.

environment, they undergo flushing of ocean water by freshwater. During this process, some of the most widespread mineralogic and petrologic transformations occur. Some of these reaction paths are shown by the marine to recharge (M→R) pathway (fig. 4). Concisely, the dissolved-solids concentration decreases; major ions change from predominantly sodium, chloride, magnesium, and sulfate to calcium and bicarbonate; and sediments are recrystallized, selectively dissolved, cemented, and perhaps dolomitized.

After the initially uncemented calcium carbonate sediments have been transformed into a rock aquifer, many additional chemical changes occur both in ground water and in aquifer mineralogy. In recharge areas (R) in figure 4, ground water is typically a calcium bicarbonate type. During the downgradient movement of ground water, recharge to discharge (R→D) pathway in figure 4, magnesium increases owing to dissolution of dolomite and magnesium enriched calcite; calcium remains relatively constant; sulfate increases as gypsum dissolves; and bicarbonate generally decreases slightly. As the parts of the Madison aquifer system containing more saline water are approached, such as in the Central Montana trough and especially toward the Williston basin, the change is from discharge (D) in figure 4 toward the discharge-brine evolution (D→B) pathway, which is the pathway for brine evolution resulting from halite dissolution.

DATA PRESENTATION AND INTERPRETATION

Well Depths and Intervals Sampled

The state (location), arbitrary well number, well depth, and concentration of dissolved solids for each well considered in this study are shown in the tables in the supplementary data section at the end of the report. Well depths were obtained from well schedules furnished by the District Offices of the Water Resources Division (U.S. Geological Survey) in Montana, South Dakota, and Wyoming.

Major Cation and Anion Species

Data for major cations and anions are shown in the tables at the end of the report. Waters having a temperature equal to or less than 15 degrees

Celsius were classified as recharge waters. Fifteen degrees Celsius is the mean annual air temperature in the elevated areas. In recharge samples, calcium concentrations ranged from 32 to 530 milligrams per liter. Typically, magnesium concentrations were less than 30 milligrams per liter in the recharge samples, although these concentrations were large compared to concentrations in water from the Floridan aquifer presented by Hanshaw and others (1971). Water from the Floridan aquifer system was found to have a magnesium-to-calcium ratio as small as 0.05 in recharge areas; the ratio increased downgradient to maximum values of about 1. The magnesium to calcium ratio will be discussed later in this section.

Throughout the study area, sodium varied greatly, and it is related to the solution of chloride minerals. Waters in the recharge areas are characterized by sodium and potassium concentrations that generally were less than 5 milligrams per liter. Typically, as the chloride concentrations increased, potassium concentrations increased correspondingly; see the tables in the supplementary data section at the end of the report. This probably is due to the substitution of potassium for sodium in halite (NaCl). However, there are many instances where potassium concentrations were much greater than would be expected, simply from the dissolution of potassium chloride incorporated into halite crystals. A possible source of excess potassium comes from the dissolution of authigenic clays or the dissolution of potassium feldspars.

Gas Samples

Gas samples were obtained in the manner described in the supplementary data section at the end of the report. Although these samples were obtained primarily for the use of another research project not associated with the Madison study, they contain interesting information regarding the Madison aquifer system. The data, reported by Donald Fisher of the U.S. Geological Survey, are presented in table 1. In this table, and in those in the following sections, the data are listed by State so that they may be readily located for use. The data indicate that argon and helium, both rare gases, were present in all samples, but concentrations generally were less than 1 milligram per

Table 1.--*Gas analyses from selected sites, in milligrams per liter*

Site	Temperature (degrees Celsius)	Argon	Helium	Methane	Nitrogen	Oxygen	Carbon dioxide	Hydrogen	Other
Sumatra, Mont.	84.1	0.22	0.075	0.87	6.0	[3]<0.10	1.7	0.37	[1]0.13 [1] .11
Moore, Mont.	86.9	.12	.024	.47	2.5	[3] <.01	107	Trace	[2]18 [1] .16
Colstrip, Mont.	97.5	.59	.034	.45	12	[3] <.01	66	[3]<.0005	[2]2.2
HTH #3, Mont.	51.8	.91	.028	.34	23	[3] <.01	17	.0004	[1] .1
Sleeping Buffalo, Mont.	40.9	.65	.013	.02	19	.12	21	[3]<.0001	----
Cascade Spring, S. Dak.	20.0	.86	.011	[3]<.03	19.9	1.95	46	[3]<.0005	----
Midland, S. Dak.	71.0	.97	.011	[3]<.03	24.7	[3]<.013	40	[3]<.0005	----
Philip, S. Dak.	68.0	.68	.003	[3]<.08	14.5	.012	40	.0002	----
HTH #1, Wyo.	46.2	.99	.025	[3]<.01	27.9	[3]<.02	18	.060	----
Hole-in-the-Wall, Wyo.	8.2	.89	[3]<.0005	[3]<.02	23.0	9.7	14	------	----
Conoco #44, Wyo.	32.2	1.37	.38	.22	35.0	[3]<.03	7.7	------	----
Ranch Creek, Wyo.	52.7	.72	.012	[3]<.03	17.0	.17	39	[3]<.0005	----

[1] Ethane.

[2] Hydrogen sulfide.

[3] Implies that the gas was not detected at the specified detection limit; for example, <.0005 implies that the hydrogen concentration is less than .0005 mg/L and, therefore, not detected.

liter. Methane also was present in all samples, although concentrations were less than 1 milligram per liter. Nitrogen gas also was present in all samples, although the concentrations varied greatly from one location to another. Surprisingly, oxygen concentrations varied considerably; possibly some of the larger concentrations of oxygen are indicative of atmospheric contamination, although Donald Fisher (U.S. Geological Survey, oral commun., 1980) does not believe this to be true for these analyses. From the standpoint of this study, the most important gas analyzed was carbon dioxide, because it is possible to calculate the total inorganic carbon concentration that should be present in the water at the points where these gas samples were collected, and to predict the possibility of outgassing.

Minor Elements

Concentrations of strontium, lithium, boron, and vanadium in the samples were anomalously large throughout much of the study area, meriting further discussion of these elements. The general approach used in describing the variations of these elements was:

1. The dissolved-solids, water-temperature, and freshwater-head maps were used to associate a sample with a particular recharge area.
2. Correlation matrices were used for each recharge area to show the strength of relationships between variables.
3. Results of the correlation matrices and regression relations were used to select the most likely sources of a particular ion in solution.

Correlation matrices for each recharge area are contained in tables 2 through 5. Within the correlation matrix, the upper number (the correlation coefficient) gives the strength of the relationship between the two variables. The upper number in the table rows (the correlation coefficient) has a maximum value of +1 and a minimum value of -1. For the purposes of this paper, a correlation coefficient greater than +0.8 (direct relationship) or less than -0.8 (inverse relationship) is considered to be a strong relationship between the variables. The middle number (tables 2 and 3) or the lower number (tables 4 and 5) is the result of a test of the null hypothesis that the correlation is equal to zero, that is, no significant correlation.

Table 2.--*Correlation matrix for strontium, lithium, boron, and vanadium in water from the Madison aquifer system associated with recharge from the Bighorn Mountains*

[Upper number is correlation coefficient (see text); middle number is significance level (see text); lower number is number of samples]

	pH	Water temperature	Dissolved solids	Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Sulfate	Chloride
	-0.48987	0.50726	0.52538	0.52048	0.24669	0.53490	0.52282	-0.44006	0.49399	0.53176
Strontium	0.1060	0.0923	0.0794	0.0828	0.4396	0.0731	0.0812	0.1523	0.1026	0.0752
	12	12	12	12	12	12	12	12	12	12
	-0.73046	0.94413	0.96789	0.90219	0.66117	0.98282	0.99592	-0.65224	0.89185	0.99232
Lithium	0.0070	0.0001	0.0001	0.0001	0.0192	0.0001	0.0001	0.0215	0.0001	0.0001
	12	12	12	12	12	12	12	12	12	12
	-0.70103	0.93189	0.93902	0.88019	0.61574	0.95448	0.96980	-0.64621	0.86414	0.96410
Boron	0.0111	0.0001	0.0001	0.0002	0.0330	0.0001	0.0001	0.0232	0.0003	0.0001
	12	12	12	12	12	12	12	12	12	12
	0.09053	0.07035	0.14885	0.14242	0.11807	0.15452	0.15609	0.38549	0.06589	0.18507
Vanadium	0.7796	0.8280	0.6443	0.6588	0.7148	0.6316	0.6281	0.2159	0.8388	0.5647
	12	12	12	12	12	12	12	12	12	12

	Copper	Molybdenum	Gross alpha	Gross beta	Silica	Strontium	Lithium	Boron	Vanadium
	0.60099	0.06473	0.09889	0.24291	0.47675	1.00000	0.52779	0.47566	-0.07417
Strontium	0.0388	0.8416	0.8158	0.5621	0.1171	0.0000	0.0778	0.1181	0.8188
	12	12	8	8	12	12	12	12	12
	-0.27870	0.25913	0.05032	0.20942	0.97059	0.52779	1.00000	0.97129	0.17479
Lithium	0.3804	0.4161	0.9058	0.6187	0.0001	0.0778	0.0000	0.0001	0.5869
	12	12	8	8	12	12	12	12	12
	-0.33818	0.28133	0.04039	0.19949	0.93732	0.47566	0.97129	1.00000	0.10900
Boron	0.2823	0.3757	0.9243	0.6358	0.0001	0.1181	0.0001	0.0000	0.7360
	12	12	8	8	12	12	12	12	12
	-0.24715	-0.22877	-0.29239	-0.16019	0.12430	-0.07417	0.17479	0.10900	1.00000
Vanadium	0.4387	0.4745	0.4822	0.7047	0.7003	0.8188	0.5869	0.7360	0.0000
	12	12	8	8	12	12	12	12	12

Table 3.--*Correlation matrix for strontium, lithium, boron, and vanadium in water from the Madison aquifer system associated with recharge from the Black Hills*

[Upper number is correlation coefficient (see text); middle number is significance level (see text); lower number is number of samples]

	pH	Water temper-ature	Dissolved solids	Calcium	Magnesium	Sodium	Potassium	Bicar-bonate	Sulfate	Chloride
Strontium	-0.59788 0.0001 38	0.62403 0.0001 38	0.94128 0.0001 38	0.91366 0.0001 38	0.88465 0.0001 38	0.49541 0.0016 38	0.83134 0.0001 38	-0.73340 0.0001 38	0.93428 0.0001 38	0.46637 0.0032 38
Lithium	-0.57366 0.0018 27	0.62990 0.0004 27	0.78969 0.0001 27	0.72214 0.0001 27	0.68215 0.0001 27	0.96265 0.0001 27	0.87063 0.0001 27	-0.64067 0.0003 27	0.76227 0.0001 27	0.89480 0.0001 27
Boron	-0.46323 0.0172 26	0.56145 0.0029 26	0.78589 0.0001 26	0.71923 0.0001 26	0.71547 0.0001 26	0.89414 0.0001 26	0.91389 0.0001 26	-0.53313 0.0051 26	0.75425 0.0001 26	0.74393 0.0001 26
Vanadium	0.14353 0.4842 26	0.05150 0.8027 26	-0.28591 0.1568 26	-0.27679 0.1710 26	-0.25898 0.2014 26	-0.16550 0.4191 26	-0.26979 0.1826 26	0.20800 0.3079 26	-0.27251 0.1780 26	-0.13387 0.5144 26

	Copper	Molybdenum	Gross alpha	Gross beta	Silica	Strontium	Lithium	Boron	Vanadium
Strontium	-0.24567 0.2472 24	0.18970 0.3746 24	0.25771 0.2727 20	0.37476 0.1035 20	0.65155 0.0001 38	1.00000 0.0000 38	0.78480 0.0001 24	0.80249 0.0001 23	-0.21422 0.3263 23
Lithium	-0.27681 0.1622 27	-0.03000 0.8819 27	0.54138 0.0137 20	0.64500 0.0021 20	0.69977 0.0001 27	0.78480 0.0001 24	1.00000 0.0000 27	0.90296 0.0001 24	-0.25281 0.2128 26
Boron	-0.25617 0.2269 24	-0.08944 0.6777 24	0.17148 0.4963 18	0.27825 0.2636 18	0.58637 0.0017 26	0.80249 0.0001 23	0.90296 0.0001 24	1.00000 0.0000 26	-0.19052 0.3725 24
Vanadium	-0.00393 0.9848 26	0.21440 0.2929 26	-0.15667 0.5095 20	-0.20008 0.3977 20	0.09438 0.6465 26	-0.21422 0.3263 23	-0.25281 0.2128 26	-0.19052 0.3725 24	1.00000 0.0000 26

Table 4.--*Correlation matrix for strontium, lithium, boron, and vanadium in water from the Madison aquifer system associated with recharge from the Big Snowy Mountains*

[Upper number is correlation coefficient (see text); lower number is significance level (see text)]

	pH	Water temperature	Dissolved solids	Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Sulfate	Chloride
Strontium	-0.79399	0.47259	0.98012	0.95539	0.97099	0.76377	0.89789	0.15037	0.99231	0.53329
	0.0186	0.2370	0.0001	0.0002	0.0001	0.0274	0.0025	0.7223	0.0001	0.1735
Lithium	-0.80290	-0.00917	0.76951	0.58064	0.72161	0.97944	0.89364	0.80869	0.66169	0.93246
	0.0164	0.9828	0.0256	0.1312	0.0424	0.0001	0.0028	0.0151	0.0739	0.0007
Boron	-0.91015	0.32554	0.73441	0.66951	0.60392	0.88373	0.84117	0.65308	0.63669	0.97473
	0.0017	0.4314	0.0380	0.0694	0.1129	0.0036	0.0089	0.0791	0.0896	0.0001
Vanadium	-0.17813	0.22562	0.01983	0.29886	-0.02643	-0.14990	-0.00965	-0.18697	0.10901	-0.04650
	0.6730	0.5911	0.9628	0.4721	0.9505	0.7231	0.9819	0.6575	0.7972	0.9129

	Copper	Molybdenum	Gross alpha	Gross beta	Silica	Strontium	Lithium	Boron	Vanadium
Strontium	-0.81284	-0.61067	0.73627	0.90002	0.38610	1.00000	0.65024	0.62566	0.06643
	0.0142	0.1078	0.0373	0.0023	0.3448	0.0000	0.0809	0.0971	0.8758
Lithium	-0.77090	-0.86097	0.61532	0.88033	0.15045	0.65024	1.00000	0.88397	-0.13802
	0.0251	0.0060	0.1044	0.0039	0.7221	0.0809	0.0000	0.0036	0.7445
Boron	-0.89088	-0.71481	0.30820	0.73360	0.50095	0.62566	0.88397	1.00000	0.10838
	0.0030	0.0463	0.4577	0.0383	0.2060	0.0971	0.0036	0.0000	0.7984
Vanadium	-0.39450	0.15656	-0.12930	-0.11032	0.21435	0.06643	-0.13802	0.10838	1.00000
	0.3335	0.7112	0.7603	0.7948	0.6102	0.8758	0.7445	0.7984	0.0000

Table 5.--*Correlation matrix for strontium, lithium, boron, and vanadium in water from the Madison aquifer system associated with recharge from the Beartooth Mountains*

[Upper number is correlation coefficient (see text); lower number is significance level (see text)]

	pH	Water temper- ature	Dissolved solids	Calcium	Magnesium	Sodium	Potassium	Bicar- bonate	Sulfate	Chloride
Strontium	-0.73208	0.84512	0.88011	0.64239	0.51474	0.74393	0.84371	0.34373	0.76335	0.71774
	0.0029	0.0001	0.0001	0.0132	0.0596	0.0023	0.0001	0.2289	0.0015	0.0038
Lithium	-0.22185	0.58561	0.86087	0.14690	0.05330	0.92205	0.92027	0.49093	0.37459	0.88998
	0.4459	0.0278	0.0001	0.6163	0.8564	0.0001	0.0001	0.0747	0.1870	0.0001
Boron	-0.22075	0.58767	0.87482	0.15030	0.04512	0.94030	0.91016	0.54504	0.36468	0.91140
	0.4482	0.0271	0.0001	0.6080	0.8783	0.0001	0.0001	0.0438	0.1998	0.0001
Vanadium	-0.15925	0.47879	0.66221	0.09325	-0.03846	0.72460	0.68886	0.69282	0.20919	0.71023
	0.5866	0.0833	0.0099	0.7512	0.8961	0.0034	0.0064	0.0060	0.4729	0.0044

	Copper	Molybdenum	Gross alpha	Gross beta	Silica	Strontium	Lithium	Boron	Vanadium
Strontium	-0.71229	-0.42186	0.52368	0.88606	0.64011	1.00000	0.65984	0.67781	0.52179
	0.0043	0.1330	0.0546	0.0001	0.0137	0.0000	0.0102	0.0077	0.0557
Lithium	-0.46897	-0.36369	0.17616	0.82423	0.35839	0.65984	1.00000	0.97347	0.69548
	0.0907	0.2012	0.5469	0.0003	0.2083	0.0102	0.0000	0.0001	0.0057
Boron	-0.45879	-0.35135	0.17115	0.79573	0.37102	0.67781	0.97347	1.00000	0.81697
	0.0989	0.2180	0.5585	0.0007	0.1915	0.0077	0.0001	0.0000	0.0004
Vanadium	-0.30100	-0.21803	0.14173	0.55222	0.44879	0.52179	0.69548	0.81697	1.00000
	0.2957	0.4540	0.6289	0.0406	0.1075	0.0557	0.0057	0.0004	0.0000

For example, the correlation between sodium and lithium in waters associated with the Bighorn Mountains recharge area is 0.9828, at a significance level of 0.0001. This means that there is a strong direct relationship between sodium and lithium, and there is 1 chance in 10,000 that the true correlation coefficient is equal to zero. For the purposes of this paper, a value of the lower number less than or equal to 0.05 indicates that the correlation is significantly different from zero, and therefore, the relationship is meaningful. A large and significant value for the same correlation coefficient indicates the existence of a relationship; these values do not imply cause and effect. The concentrations of the dissolved minor cations and anions are shown in the tables in the supplementary data section at the end of the report.

The mean, standard deviation, and concentration range of strontium, lithium, boron, and vanadium, as well as the concentration of water from the aquifer with respect to seawater (column 7, Enrichment of water) are shown in table 6. The line labeled, Maximum enrichment of element, tabulates the ratio of the concentration of an element in the sampled water to its concentration in seawater. The row labeled, Sodium chloride brine, lists the average concentration of the element in a sodium chloride brine (White and others, 1963). The dissolved solids of even the most concentrated waters in the system (table 6) are quite dilute with respect to seawater, supporting the concept that the Madison aquifer system has been and is being flushed by fresher waters, and does not contain connate waters within the area studied. The lack of connate water is substantiated further by the del deuterium and del oxygen-18 data for the study area; it is discussed in more detail in the section on isotopic data.

Strontium, atomic number 38, is a member of group IIA of the periodic table, and chemically is similar to calcium and barium. Like calcium and barium, strontium can form carbonate minerals such as strontianite, and sulfate minerals such as celestite, although these phases have not been identified in rock samples from the Madison aquifer system. Strontium can occur in solid solution with the orthorhombic calcium carbonate, aragonite,

Table 6.--*Mean, standard deviation, and concentration range of strontium, lithium, boron, and vanadium in water from the Madison aquifer system*

[Mean, standard deviation, concentration range, sodium chloride brine, and area average values in micrograms per liter]

Recharge area	Parameter	Elements				Enrichment of water
		Strontium	Lithium	Boron	Vanadium	
Bighorn Mountains:	Mean------------------	2,195	150	183	5.08	
	Standard deviation----	2,970	268	270	5.88	
	Range-----------------	500-9,100	0-870	7-890	0-18	
	Maximum enrichment of element----------	.7	5.12	.04	16,933	0.06
Black Hills Mountains:	Mean------------------	3,730	40.63	81.38	1.77	
	Standard deviation----	3.800	52.95	107.42	2.77	
	Range-----------------	7-1,200	0-230	0.0-490	0.0-11.00	
	Maximum enrichment of element----------	.09	1.35	.02	5.9×10^6	.07
Big Snowy Mountains:	Mean------------------	3,560	121	208	1.038	
	Standard deviation----	2,650	126	187	1.051	
	Range-----------------	980-8,600	20-330	30-510	0.0-3.4	
	Maximum enrichment of element----------	.66	1.94	.05	3.46×10^6	.01
Beartooth Mountains:	Mean------------------	8,780	1,192	2,139	13.54	
	Standard deviation----	5,420	1,466	2,662	23.02	
	Range-----------------	140-1,500	2.0-4,400	10-7,900	0.0-68.0	
	Maximum enrichment of element----------	.12	25.88	.47	4.51×10^7	.13
	Sodium chloride brine[1/]	---	7.050	30,000	---	
Area average----------------------------------		4,377	322.95	572.69	4.94	

[1/] Data from White and others (1963).

but is found in only very limited amounts in the rhombohedral form, calcite. Strontium also substitutes readily in dolomites and even more readily in gypsum. Because there is no aragonite in the Madison aquifer system, strontium in the ground water may be related to its release from dolomite and gypsum (or anhydrite) during dissolution, or minerals, such as celestite, disseminated throughout the aquifer with the other evaporites.

That disseminated evaporites are a possible source of strontium is demonstrated in figure 5, which is a plot of sulfate versus strontium from Madison ground-water samples. There is a distinct linear relationship, and the line passes through the origin; this provides evidence that the strontium in Madison ground water comes primarily from dissolution of disseminated evaporites. Minor amounts of strontium also may come from dolomite dissolution and possibly release from clay minerals.

In the areas associated with recharge from the Beartooth Mountains, Big Snowy Mountains, and the Black Hills, the highest and most significant correlation of strontium is with sulfate, a finding consistent with figure 5. The weaker and less significant correlation with pH in each of these areas could indicate a partial control of strontium by its carbonate phase, strontianite. However, because of the low and insignificant correlation between strontium and bicarbonate, and the fact that the system is saturated with strontianite, it is unlikely that strontianite is a significant source of strontium in these recharge areas.

The waters associated with recharge from the Bighorn Mountains show no significant correlation with any of the parameters, which indicates that, for this area, arguments of strontium control by gypsum or celestite do not apply, and that strontium probably is originating from a variety of sources.

Lithium, atomic number 3, is a member of group IA of the periodic table, but is chemically more like the elements in group IIA than its congeners in group IA. Lithium is a common constituent of brines in closed basins of the arid west (Vine, 1975a), and the element also is concentrated in clay minerals, especially illite and hectorite, a lithium-rich montmorillonite.

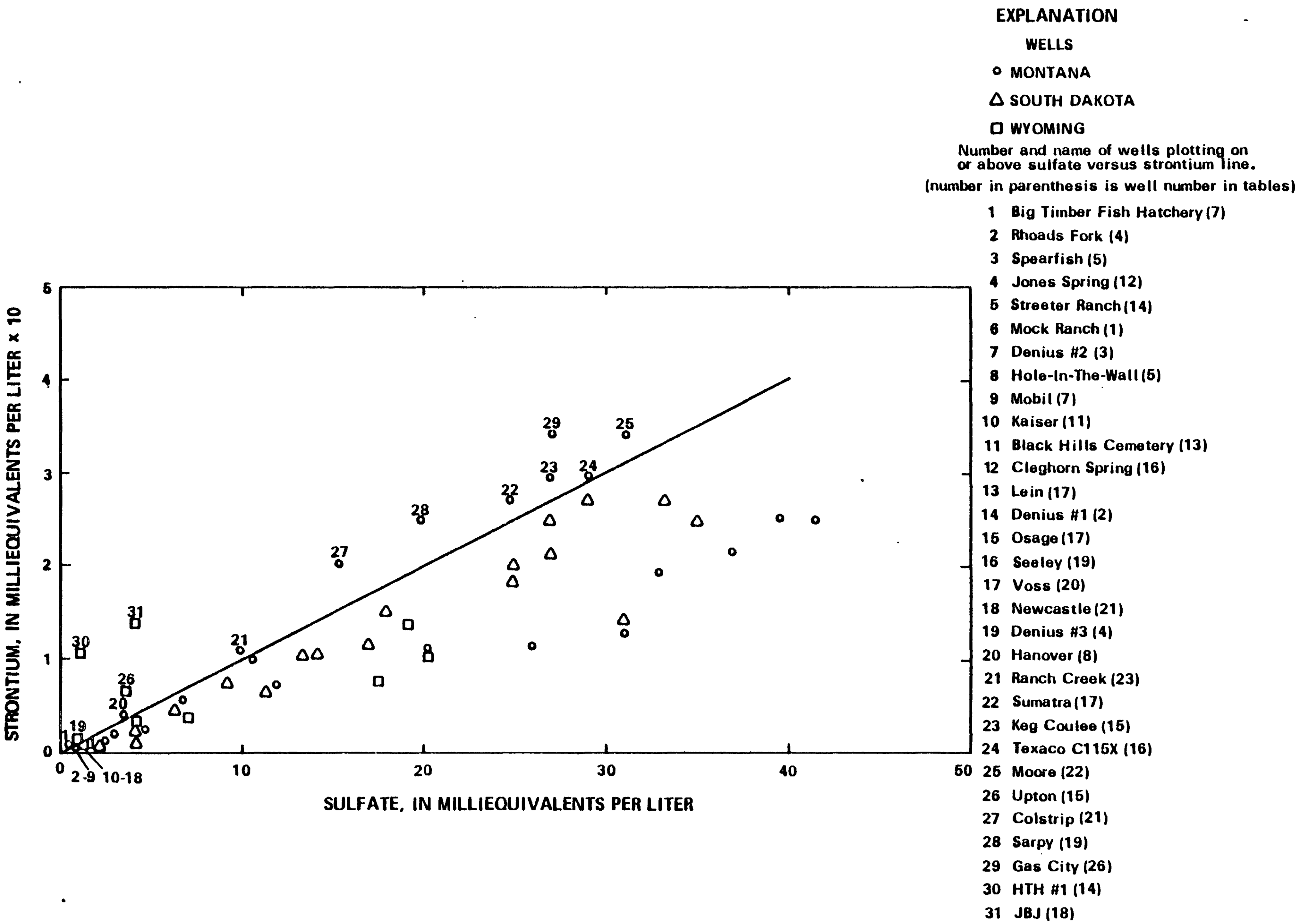


Figure 5.--Relationship between sulfate and strontium.

The average concentration of lithium in seawater is 0.17 milligram per liter (Horne, 1969), while the average lithium concentration of sodium chloride type brines is 7.05 milligrams per liter (White and others, 1963). Concentrations of lithium found in the study area are enriched between 1.35 and 25.88 times the values associated with seawater. Because lithium is more concentrated than would be expected from an average sodium chloride brine, and because the waters are more dilute than seawater, Carpenter and Miller (1969) point out that lithium is not concentrated in marine evaporites, but normally is concentrated in the clay phases. During diagenesis, lithium generated by alteration of lithium-rich micas in the pegmatites distributes itself between the clays and dolomite lattice. Lithium not incorporated into clays or dolomites will remain in the residual waters where it may be concentrated by evaporation.

Data in table 6 show the concentration of lithium to be greatest in waters originating as recharge from the Beartooth Mountains. Lithium concentrations in waters associated with other recharge areas decrease in the following order: Bighorn Mountains, Big Snowy Mountains, and Black Hills.

Waters affected by recharge from the Bighorn Mountains or the Black Hills show a very good correlation between lithium and the cations: calcium, magnesium, sodium, and potassium; and between lithium and the anions: sulfate, chloride, and silica. This finding is consistent with the above discussion on geochemical controls on lithium. Data for the Big Snowy recharge area show no relationship among lithium, calcium, and silica, but significant correlations among lithium and magnesium, chloride, and bicarbonate, indicating that the dissolution of dolomite and disseminated evaporites is a potential source in this area. A more surprising result is obtained for waters related to the Beartooth Mountains; here, there is some degree of correlation between lithium concentrations and those of sodium and potassium, and chloride, but no correlation at all to the concentrations of calcium, magnesium, sulfate, or bicarbonate. At this point in the flow system, calcite, dolomite, gypsum, and anhydrite have reached a phase boundary, and lithium is derived from the evaporite minerals.

Boron, atomic number 5, is a member of group IIIA of the periodic table; it would be expected to show metallic properties analogous to those of the aluminum group. However, like lithium, boron is characterized by the diagonal relationship, and its chemistry more nearly resembles the metalloids of group IVA, the carbon group. Boron occurs in most natural waters as the undissociated boric acid, and the borate system is second only to the carbonate system in its effectiveness as a buffer in natural aquatic systems (Hem, 1970).

Boron is concentrated in marine sediments, having its largest concentration in the illites, glauconites, montmorillonites, and halloysites at concentrations of 435 ± 127 parts per million (Reynolds, 1964). Boron is common in petroleum, with concentrations ranging from a trace to 100 milligrams per liter (Collins, 1975). With the exception of waters associated with the Big Snowy Mountains recharge area, concentrations of boron are dilute with respect to seawater.

The positive correlations, in the waters associated with recharge from the Bighorn Mountains, between boron and calcium, lithium, sodium, potassium, chloride, sulfate, and silica, when considered with the negative correlation between boron and pH indicate that there are two major controls on the concentration of boron: (1) Dissolution of dissolved evaporites; and (2) diagenesis of clay minerals (notably illite or montmorillonite) (Reynolds, 1964).

Correlation matrices for the Black Hills and Beartooth Mountains recharge areas show no relationship (at the levels of correlation coefficient and significance specified in this paper) between boron and pH or silica. The inverse relationship between pH and boron observed in waters associated with recharge from the Big Snowy Mountains probably is due to the effect of the boron itself on pH, as no other pH-controlling anions appear to be significant. From these observations, the inference is that the boron in all three areas originates from the dissolution of evaporite minerals along the flow path.

Vanadium, atomic number 23, is a member of group VB of the periodic table and is one of the d block (transition) elements. Because of its electron configuration (which is responsible for its position in the periodic table), vanadium forms independent minerals in sedimentary rocks, the most notable being carnotite, $K_2(UO_2)_2(VO_4)_2 \cdot H_2O$, tyuyamunite, $Ca[UO_2]_2[VO_4] \cdot 5\text{-}8H_2O$, both members of the carnotite group of elements, and vanadinite, $Pb_5(VO_4)_3Cl$.

Vanadium rarely occurs in carbonate minerals, but is concentrated in iron-bearing silicates. Vanadium is concentrated by many plants; relatively large concentrations of vanadium (0.3 to 280 parts per million) associated with petroleum are probably from plants (Hunt, 1980).

Vanadium is enriched tenfold in the project area waters compared to seawater. Lack of correlations between vanadium and any other cation or anion in the Big Snowy, Bighorn, and Black Hills recharge areas indicates that vanadium may be derived from the organic phase for which there are no analytical data available. However, data from the correlation matrix from the Beartooth recharge area indicate that vanadium correlates well with potassium, chloride, sodium, and sulfate, and likely is associated with the evaporite minerals.

Radioactive Isotopes

The radiochemical parameters, gross alpha and gross beta particle activity, were measured during the Madison study to provide data on distribution of radioactive isotopes in the Madison Limestone.

Gross alpha and gross beta particle activity is a measure of the concentration of alpha particles (helium nuclei) and beta particles (electrons) generated by one or more of the three radioactive decay series: Uranium-238 (uranium series), uranium-235 (actinium series), and thorium-232 (thorium series). These parent isotopes decay with the emission of alpha particles, beta particles, and gamma radiation, through a series of radioactive daughter products: Uranium-238 to lead-206, uranium-235 to lead-207, and thorium-232 to lead-208.

Gross alpha particle activity is expressed in terms of picocuries of natural uranium per liter of water. A factor of 0.68 picocurie per microgram of natural uranium is used to convert values in micrograms per liter to values in picocuries per liter. Gross beta particle activity is expressed in terms of picocuries per liter, using cesium-137 as a calibration isotope. The range of gross alpha and beta values determined in the waters associated with each recharge area is presented in table 7.

Regression analyses were used to examine relationships between water temperature, silica, pH, and bicarbonate and the radiochemical indicators, gross alpha and gross beta particle activity. Although uranium is known to migrate as the carbonate complex, no significant regression relationship was found between pH or bicarbonate and gross alpha or gross beta particle activity. Regression analysis is a technique in which a best-fitting line is calculated by minimizing the sum of the squares of the deviations or variances from the mean value of the sample. That line has the form:

$$y = \hat{\beta}_o + \hat{\beta}_1 X_i ,$$

where y is the dependent variable, the variable being estimated from the data.

In the following examples, the dependent variable is the logarithm to the base 10 (log 10) of the concentration of gross alpha or gross beta particle activity measured in picocuries per liter; $\hat{\beta}_o$ is an estimate of the population parameter $\hat{\beta}_o^{(o)}$ and represents the intercept of the line; $\hat{\beta}_1$ is an estimate of the population parameter $\hat{\beta}_1^{(o)}$ and represents the slope of the line; and X_i is the *ith* value of the independent variable; in these examples, the water temperature (in degrees Celsius) and the log of concentration of silica (in milligrams per liter) were used as independent variables. The general linear-models procedure found in the statistical program package SAS-79 was used to perform the regression analysis.

The summary of the regression analysis (table 8) was created using SAS-79; the table is divided into three parts labeled: (1) Analysis of variance; (2) miscellaneous statistics; and (3) report of parameter estimates. The analysis of the variance part of the table contains the following

Table 7.--*Concentration of dissolved gross alpha and dissolved gross beta particle activity, in picocuries per liter, in water from the Madison aquifer system*

(MN = Montana; SD = South Dakota; WY = Wyoming; DEG C = degrees Celsuis; MG/L = milligrams per liter; PC/L = picocuries per liter)

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	DISSOLVED SOLVIDS (MG/L)	GROSS ALPHA (PC/L)	GROSS BETA (PC/L)
2	GORE HILL 20N 03E 28CDAD	MN	7.13	14.0	1250	19	18
3	GREAT FALLS HIGH SCHOOL 20N 04E 07BDAC	MN	7.40	13.1	551	12	4.8
4	BOZEMAN FISH HATCHERY 01S 06E 34BCDA	MN	7.84	8.6	204	2.4	1.1
5	BOUGH RANCH 22N 06E 09DDAB	MN	7.06	17.9	2490	52	34
6	MCLEOD WARM SPRING 03S 13E 34ABAB	MN	7.40	24.6	320	5.0	1.2
7	BIG TIMBER FISH HATCHERY 01N 14E 15DAAA	MN	7.64	10.7	240	2.6	3.9
8	HANOVER 16N 16E 22DCCC	MN	7.63	20.4	398	6.7	2.5
9	VANEK WARM SPRING 17N 18E 19DBCA	MN	7.40	19.6	614	18	1.9
10	LEWISTOWN BIG SPRING 14N 19E 05ABCC	MN	7.58	10.6	348	4.0	2.5
11	BLUEWATER SPRING 06S 24E 09BCAA	MN	7.29	14.3	2290	53	38
12	LANDUSKY SPRING 25N 24E 32DABC	MN	7.24	20.4	1360	23	12
13	LODGEPOLE WARM SPRING 26N 25E 24BCDB	MN	7.08	31.6	1640	21	14
14	HTH #3 02N 27E 35AAB01	MN	6.80	51.8	2680	170	63
15	KEG COULEE 11N 30E 35ADAA	MN	6.50	61.7	5500	180	150
16	TEXACO C115X 11N 32E 15ABAC	MN	7.10	84.0	6000	180	180

Table 7.--*Concentration of dissolved gross alpha and dissolved gross beta particle activity, in picocuries per liter, in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	DISSOLVED SOLVIDS (MG/L)	GROSS ALPHA (PC/L)	GROSS BETA (PC/L)
17	SUMATRA 11N 32E 24ADCD	MN	7.51	84.1	5730	58	160
18	SLEEPING BUFFALO 32N 32E 35CDBD	MN	7.00	40.9	3250	150	61
19	SARPY MINE 01N 37E 26BDDD	MN	6.70	83.3	1583	130	77
20	MYSSE FLOWING 12N 39E 09AACA	MN	6.66	63.8	4120	560	170
21	COLSTRIP 02N 41E 34BADA	MN	6.52	97.2	1444	640	110
22	MOORE 10N 43E 21CDCA	MN	6.81	86.9	6380	300	220
23	RANCH CREEK 09S 53E 22ABAC	MN	6.94	52.7	955	63	15
24	BELLE CREEK 08S 54E 21ADAD	MN	7.01	56.2	1000	38	12
26	GAS CITY 14N 55E 27CDDB	MN	6.61	91.5	5390	410	150
6	FUHS 05N 03E 12DCCB	SD	7.21	10.7	544	4.4	3.6
7	DELZER #1 12N 03E 28BACBB	SD	7.51	55.6	2410	81	38
8	DELZER #2 12N 03E 32ACBC	SD	6.77	55.6	2630	200	39
11	KAISER 06S 05E 24BAAA	SD	7.40	15.0	224	4.0	3.6
13	BLACK HILLS CEMETERY 05N 05E 25ABD	SD	7.28	12.4	239	18	3.2
14	STREETER RANCH 06S 06E 15AACC	SD	7.61	19.4	183	14	4.6
17	LIEN 02N 07E 18BCA	SD	7.41	11.9	222	7.7	3.0

Table 7.--*Concentration of dissolved gross alpha and dissolved gross beta particle activity, in picocuries per liter, in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	DISSOLVED SOLVIDS (MG/L)	GROSS ALPHA (PC/L)	GROSS BETA (PC/L)
20	DUPREE 13N 21E 31BDDA	SD	6.82	56.5	2330	410	82
21	HAMILTON 08N 23W 26ACDA	SD	6.92	58.2	2030	150	27
22	HILLTOP RANCH 05N 24E 30CA	SD	6.70	61.8	1980	4000	440
23	EAGLE BUTTE 12N 24E 17CBBD	SD	7.00	55.5	2200	110	44
25	MURDO 01S 26E 36ACA	SD	6.68	59.1	1550	230	68
26	PRINCE 05N 27E 22CD	SD	6.89	57.0	2010	370	93
27	BEAN 09N 03E 20CDD	SD	7.10	41.5	820	18	8.7
1	MOCK RANCH 57N 87W 21DBC01	WY	7.50	10.8	214	0.4	3.0
5	HOLE-IN-THE-WALL 41N 84W 20BAC	WY	7.25	8.2	210	4.2	0.3
7	MOBIL 49N 83W 27DDA	WY	7.31	7.1	164	3.0	1.5
8	CONOCO #44 41N 81W 09CDA	WY	7.17	32.2	2180	350	68
9	SHIDLER 40N 79W 31BCA	WY	7.55	72.6	2570	270	69
10	MKM 39N 78W 26CDC	WY	6.71	88.1	3430	190	93
11	CONOCO #175 33N 75W 20AAC	WY	7.30	30.1	718	1900	350
12	BARBER RANCH SPRING 32N 74W 03CBD	WY	7.46	15.7	259	18	4.1
14	HTH #1 57N 65W 15DA	WY	6.99	46.2	930	15	8.9

Table 7.--*Concentration of dissolved gross alpha and dissolved gross beta particle activity, in picocuries per liter, in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	DISSOLVED SOLVIDS (MG/L)	GROSS ALPHA (PC/L)	GROSS BETA (PC/L)
19	SEELEY 46N 62W 18BDC	WY	7.30	13.0	273	5.6	2.1
22	SELF 45N 61W 33AB01	WY	7.30	29.8	351	20	5.4
25	RANCH A 52N 60W 18C	WY	7.26	12.2	505	8.1	3.4

Table 8.--*Summary of regression analysis for water temperature and gross alpha particle activity*

General linear models procedure

(Dependent variable: log gross alpha particle activity)

Analysis and variance				Miscellaneous statistics			
Source	DF	Sum of squares	Mean square	F value	PR > F	R^2	C.V.
Model	1	19.85526824	19.85526824	55.00	0.0001	0.534003	37.3348
Error	48	17.32667401	0.36097238	---	STD DEV	---	Log alpha mean
Corrected total	49	37.18194225	---	---	0.60080977	---	1.60924924

Report of parameter estimates

Parameter	Estimate	T for H_0: parameter=0	PR > $\|T\|$	STD error of estimate
Intercept	0.68332883	4.52	0.0001	0.15101602
Temp	0.02331941	7.42	0.0001	0.00314425

columns: Source, for the source of variability; DF, for the number of degrees of freedom associated with a particular variability source; Sum of squares, for reporting the sum of squares for each source of variability; and Mean square, the result of dividing the sum of squares for a particular component of the variance by the number of degrees of freedom. The mean-square column is used to generate the value of the F statistic shown under miscellaneous statistics.

The miscellaneous statistics part of the table gives the value F calculated by dividing the mean square associated with the regression model by the mean square for error. The larger the value of F, the less likely it is to be exceeded and the more likely the regression model is valid. The value of PR>F gives the probability that a greater value of F can occur. The small value of probability F (0.0001) shown in table 8 indicates that the data fit the linear regression model. The R^2 value, the coefficient of association, is calculated as the ratio of the sum of squares model to the sum of squares total; R^2 ranges from 0 to 1. The larger the value of R^2, the better the fit of the data to the regression model. The square root of R^2 is the value of the correlation coefficient; it measures the degree of the association between the two variables. In the example shown in table 8, the R^2 value is 0.534 and the value of R would be 0.731.

The CV value is the coefficient of variation, a dimensionless measure of the variability of the population. The standard deviation about the mean, another measure of variability, and the mean of the dependent variable, a measure of the central tendency of the population, also are reported in this section.

The final part of the table, the Report of parameter estimates, is the most significant. The parameter column contains the statistical parameter whose values are reported in the rest of the row. The row value labeled Intercept is the $\hat{\beta}_o$ of the regression equation, while the row labeled Temp represents $\hat{\beta}_1$, the slope of the regression line. The Estimate column reports the values of $\hat{\beta}_o$ and $\hat{\beta}_1$, while the column headed T for H_o: parameter = 0 is the value of the t statistic calculated under the null hypothesis that the values for the intercept, $\hat{\beta}_o$, and slope, $\hat{\beta}_1$, are equal to zero. The column headed, PR>|T|, reports the probability of a greater value of T, the test statistic. The less the probability of a greater value of T, the less likely the null hypothesis is true, that is, the true value of the parameter is equal to zero. The value of a probability greater than the test statistic shown in table 8 means that both the slope, $\hat{\beta}_1$, and intercept, $\hat{\beta}_o$, of the regression line are significant. The last column in the table, STD error of estimate, is a measure of the component random error in the estimated parameter.

A plot of the regression line for water temperature, in degrees Celsius, versus log gross alpha particle activity, in picocuries per liter, is shown in figure 6. The probability of a greater F for the model shown in table 8 indicates that the linear regression model is appropriate, while the PR>|T| column shows that both the values of $\hat{\beta}_o$ and $\hat{\beta}_1$ are significantly different from zero. The R^2 value of 0.534003 shows that the line is a reasonably good fit to the data. The lines above and below the mean line are the upper and lower 95-percent confidence intervals about the mean and indicate the range of values within which the population mean may be expected to fall.

Results for regression of water temperature and log gross beta particle activity are shown in table 9 and figure 7. These results indicate that a linear model is appropriate, and that both the slope and intercept are significantly different from zero. The R^2 value of 0.607650 indicates that the data fit the model.

In a similar manner, tables 10 and 11, coupled with figures 8 and 9, show that the relationships between silica and gross alpha and gross beta particle activity are well-fit by a linear-regression model. The relationship between gross alpha and gross beta and silica (figs. 8 and 9) indicates a dependence of the gross alpha and gross beta concentrations on the concentration of silica in the solution phase. Since the solubility of silica increases with temperature (see figures at end of report), it makes sense that

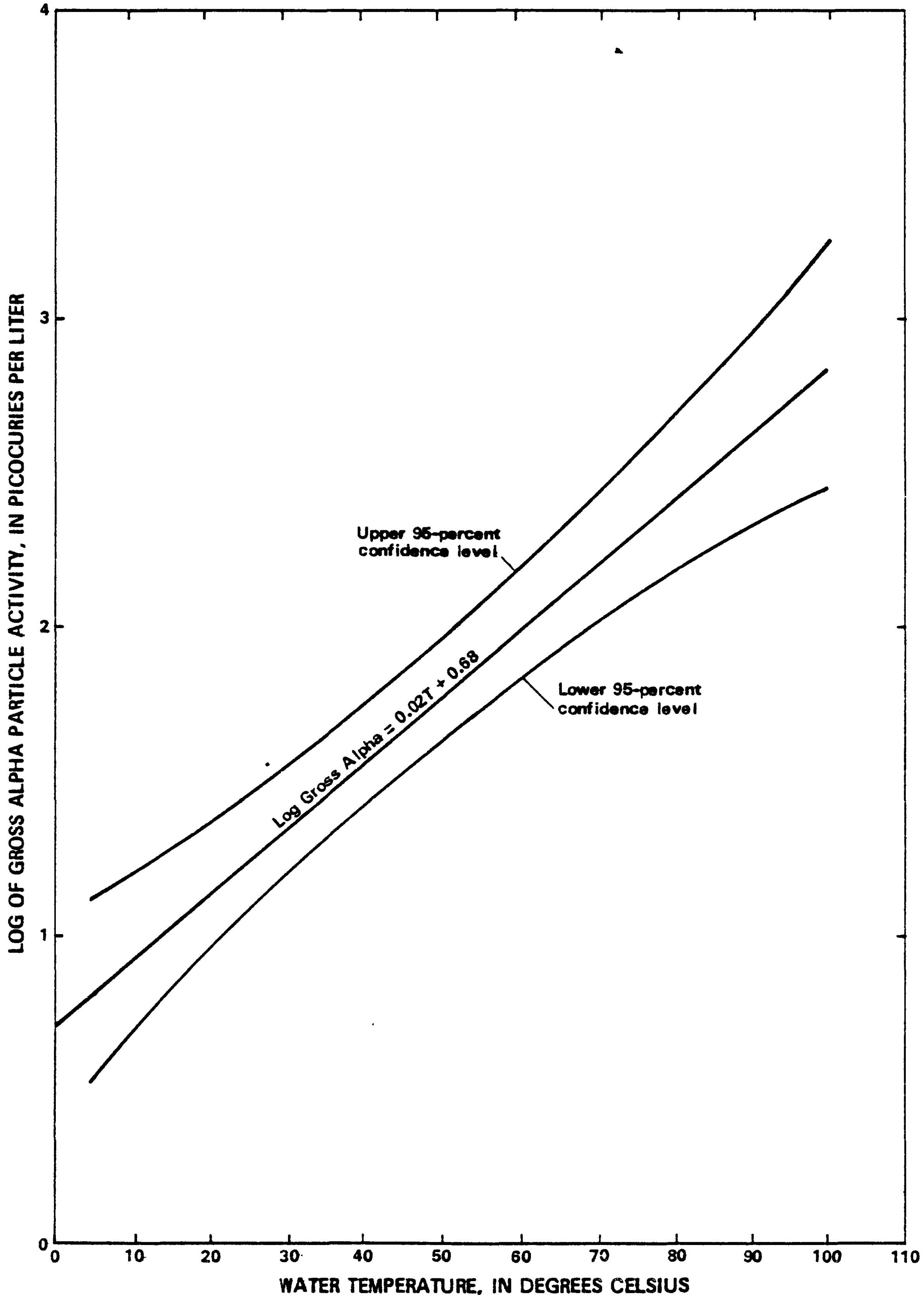


Figure 6.--Relationship between water temperature and gross alpha particle activity.

Table 9.--*Summary of regression analysis for water temperature and gross beta particle activity*

General linear models procedure

(Dependent variable: log gross beta particle activity)

Analysis and variance				Miscellaneous statistics			
Source	DF	Sum of squares	Mean square	F value	PR > F	R^2	C.V.
Model	1	18.09025227	18.09025227	74.34	0.0001	0.607650	39.7982
Error	48	11.68056663	0.24334514	---	STD DEV	---	Log beta mean
Corrected total	49	29.77081890	---	---	0.49330025	---	1.23950431

Report of parameter estimates

Parameter	Estimate	T for H_0: parameter=0	PR > $\|T\|$	STD error of estimate
Intercept	0.35569598	2.87	0.0061	0.12399306
Temp	0.02225881	8.62	0.0001	0.00258161

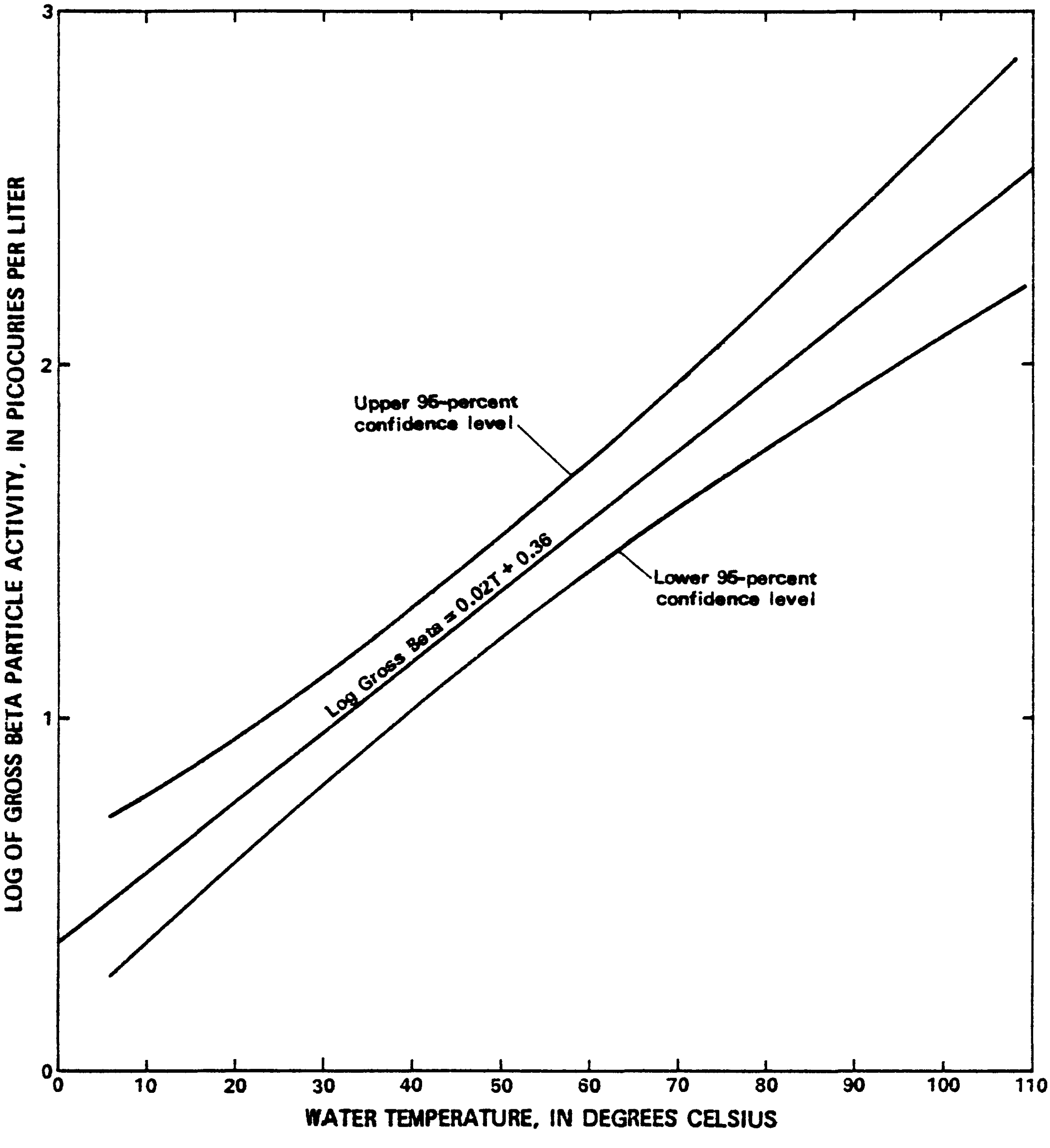


Figure 7.--Relationship between water temperature and gross beta particle activity.

Table 10.—*Summary of regression analysis for silica and gross alpha particle activity*

General linear models procedure

(Dependent variable: log gross alpha particle activity)

Analysis and variance				Miscellaneous statistics			
Source	DF	Sum of squares	Mean square	F value	PR > F	R^2	C.V.
Model	1	20.48061305	20.48061305	58.86	0.0001	0.550821	36.6549
Error	48	16.70132919	0.34794436	---	STD DEV	---	Log alpha mean
Corrected total	49	37.18194225	---	---	0.58986809	---	1.60924924

Report of parameter estimates

Parameter	Estimate	T for H_o: parameter=0	PR > $\|T\|$	STD error of estimate
Intercept	-1.05563309	-2.96	0.0048	0.35722215
Log S102	2.12453155	7.67	0.0001	0.27691508

Table 11.--*Summary of regression analysis for silica and gross beta particle activity*

General linear models procedure (Dependent variable: log gross beta particle activity)							
Analysis and variance				Miscellaneous statistics			
Source	DF	Sum of squares	Mean square	F value	PR > F	R^2	C.V.
Model	1	15.73810560	15.73810560	53.83	0.0001	0.528642	43.6217
Error	48	14.03271330	0.29234819	---	STD DEV	---	Log alpha mean
Corrected total	49	29.77081890	---	---	0.54069233	---	1.23950431

Report of parameter estimates

Parameter	Estimate	T for H_0: parameter=0	PR > $\|T\|$	STD error of estimate
Intercept	-1.09654921	-3.35	0.0016	0.32744147
Log S102	1.86237845	7.34	0.0001	0.25382940

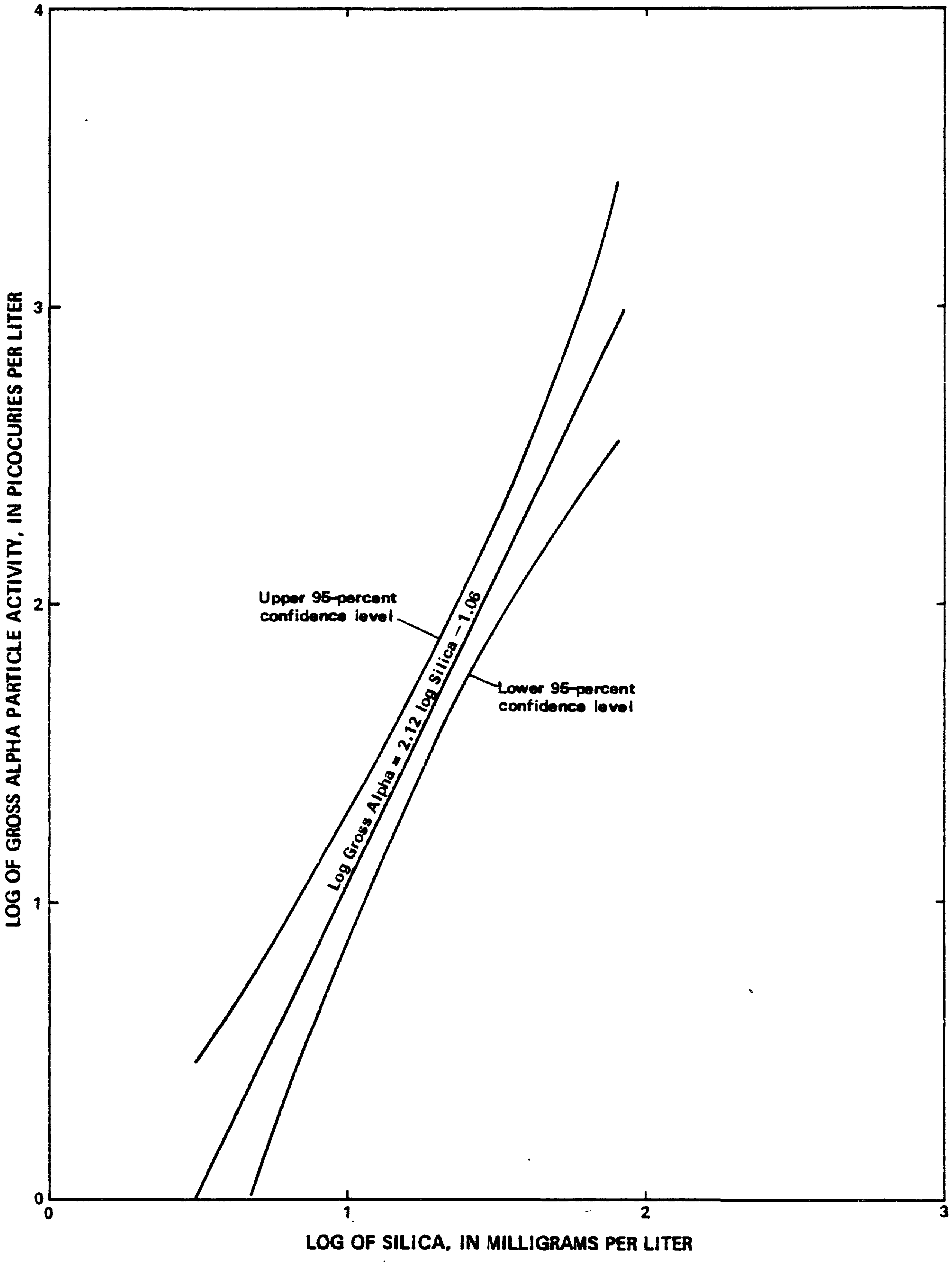


Figure 8.--Relationship between silica and gross alpha particle activity.

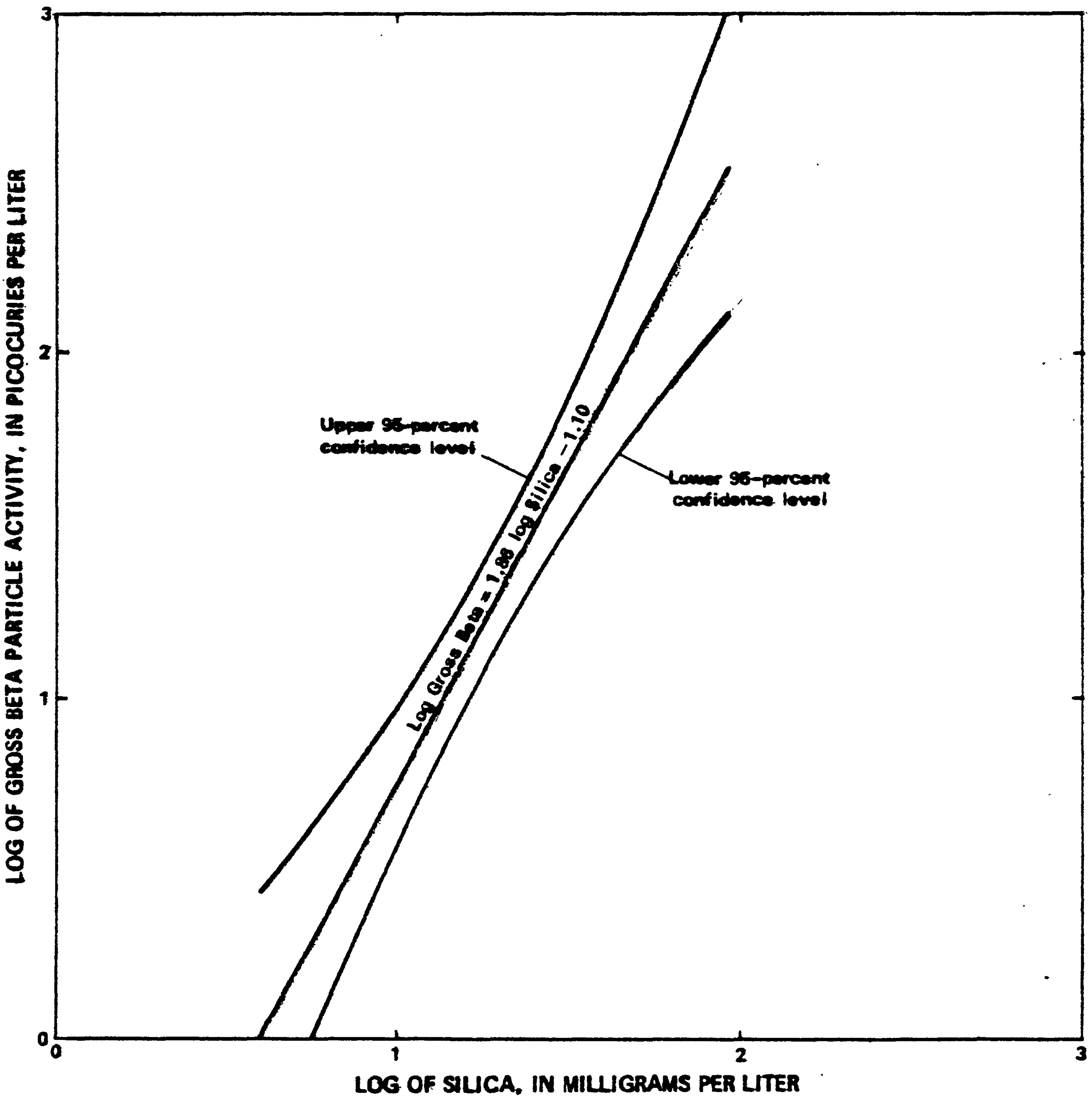


Figure 9 .--Relationship between silica and gross beta particle activity.

the concentrations of gross alpha and gross beta particle activity also increase with temperature (figs. 6 and 7). The inference drawn from this set of internally consistent relationships is that the source of the gross alpha and gross beta particle activity is in some way associated with a silicate phase, such as the clay minerals, shales, or detrital feldspars.

Behavior of Selected Chemical Parameters by Flow Paths

Dissolved Solids

Dissolved solids increased steadily from the recharge areas downgradient to deeper wells (pl. 2, in pocket). Dissolved solids range from 164 milligrams per liter in the Bighorn Mountains to 6,380 milligrams per liter in the Central Montana trough. Of the eight flow paths studied, flow path 5 showed a reversal in this trend. Analysis of the chemical data indicate that well number 7, assigned to flow path number 5 on the basis of the vector-flow maps, should be associated with flow path 4. The probable assignment of well number 7 to flow path 4 and the steepness of the dissolved solids gradient coming off of the Big Horn Mountains indicates the presence of structural discontinuities. The existence of these discontinuities is confirmed by the information on figure 1.

Temperature

If well 7 is considered to be on flow path 4 rather than its assigned flow path, flow path number 5, temperatures increase downgradient of recharge areas over much of the study area, with the exception of flow path 8, where there is a slight cooling trend in the easternmost part of the path near the area of subcrop of the Madison Limestone. Madison sediments nearer land surface might contain cooler waters as a result of lower temperatures of the rocks themselves; mixing with shallower and cooler waters also might produce lower temperatures in this area.

Chloride

Dissolved chloride (pl. 3, in pocket) shows strong similarities to the dissolved-solids map (pl. 2), indicating that much of the dissolved solids increase occurring throughout the system is caused by dissolution of halite (NaCl). Chloride ranges from low values in the major recharge areas (0.3 milligrams per liter in the Bighorn Mountains) to much greater values downgradient (2,400 milligrams per liter in the Central Montana trough). Chloride gradients are lower in ground waters from the Black Hills recharge area, especially eastward toward the subcrop, indicating less halite in the aquifer. Anomously low value of chloride concentration occurs on flow path 3 at point 20 in Montana. The value at this point and the lower than normal value at point 26 are indicative of mixing of Madison waters with waters containing lower concentration of chloride originating from some other source.

Sulfate

The distribution of dissolved sulfate (pl. 4, in pocket) follows trends similar to those indicated by dissolved solids and chloride. The concentrations range is from 1.8 milligrams per liter in the Black Hills to 1,900 milligrams per liter in the Central Montana trough. All the flow paths except flow path 5 (see previous section on hydrology) indicate downgradient increases in sulfate concentrations. Steep gradients in sulfate concentration are observed near recharge areas in all five areas, indicating that waters in contact with sediments contain larger proportions of sulfate minerals, such as gypsum or anhydrite.

Magnesium to Calcium Ratio

The equivalent ratios of magnesium to calcium (pl. 5, in pocket), equivalents Mg/equivalents Ca, appear to decrease downgradient throughout most of the study area. Ratios range from 0.91 in the Bighorn Mountains to 0.13 in the Central Montana trough.

Bicarbonate to Sulfate Ratio

Ratios of the equivalents of bicarbonate to sulfate (pl. 6, in pocket) (equivalents HCO_3/equivalents SO_4) show significant decreases downgradient from the recharge areas. Values range from 0.07 in the Central Montana trough and northwestern South Dakota to 167 in the Black Hills. Flow paths 2 and 3 show anomalous behavior.

The anomalous behavior along flow path 2 at wells 16 and 17 is most likely due to an erroneous value of bicarbonate discussed later in this section. Flow path 3 shows a complete reversal in trend due to either leakage from other aquifers or a change of lithofacies.

pH

The pH is observed to decrease downgradient throughout most of the study areas (pl. 7, in pocket). The pH values range from 7.69 in the Bighorn Mountains to 6.50 in the Central Montana trough. The flow paths reflect the trend of downgradient decreases in pH in the ground water with exceptions in flow paths 2, 5, and 8. Flow path 2 shows a reversal in the trend of pH values. This trend reversal may be due to a change in lithofacies or mixing of waters, but is most likely due to inaccuracies in the measurement of pH at these points. The suspected inaccuracies are due to the high temperatures of these wells (temperature is 84.0 degrees Celsius at well 16 in Montana and 84.1 degrees Celsius at well 17 in Montana), and the influence of an indeterminate corrosion-preventive compound being added immediately prior to sampling at well number 17. Flow path 5 shows the same flow path discontinuity evident in the other maps. Flow path 8 shows a trend reversal that may be related to a change in lithofacies or mixing.

Partial Pressure of Carbon Dioxide

The negative logarithm of the partial pressure of CO_2 (pl. 8, in pocket) in atmospheres (-Log P_{CO_2}) was calculated by using values of onsite measurement of pH and field bicarbonate, and temperature and analytical data for the major ions at the well head or spring outlet as input to the computer code WATEQF (Plummer and others, 1978). Values of -Log P_{CO_2} range from 2.60 in the Beartooth Mountains to 0.87 in the Central Montana trough. The flow paths generally show this trend of increasing P_{CO_2} downgradient except for flow paths 2 and 8. Results for flow path 2 in the Central Montana trough probably is due to poor field data for pH and bicarbonate. Well 17 is a water-supply well in an oil-field operation that is injected continuously with corrosion inhibiting chemicals, which probably affected the pH and bicarbonate measurements. Laboratory values for pH and bicarbonate were taken for well 16, which undoubtedly changed the equilibrium of the solution producing an erroneous value.

The values of -log P_{CO_2} show a slight but general decrease from the recharge area toward the subcrop indicating a general downgradient increase in P_{CO_2}. The observed increase in the partial pressure of carbon dioxide (decrease in -log P_{CO_2}), in the face of increasing dissolved solids and temperature, indicates that the CO_2 in the Mississippian ground waters is from a source other than recharge.

Total Inorganic Carbon

Total inorganic carbon (C_T) in Madison ground water as calculated (in millimoles per liter) using the computer code WATEQF (pl. 9, in pocket) generally had the largest values upgradient in the recharge areas followed by a downgradient decrease throughout most of the area; the major exception to this trend was the Central Montana trough. Values over the area range from highs of 7.91 millimoles per liter in the Central Montana trough to as low as 2.04 millimoles per liter in the center of the Powder River structural basin. In the recharge areas, the C_T is greatest (about 5.20 millimoles per liter) in the Black Hills, decreasing to about 4.5 millimoles per liter in the Bighorn Mountains, to about 4.0 millimoles per liter in the Beartooth Mountains and finally to about 3.5 millimoles per liter in the Big Snowy Mountains. Flow paths 2, 3, and 5 demonstrate trend reversals. Flow path 5 is the same apparent hydraulic discontinuity previously described.

Flow paths 2 and 3 both initially decrease in C_T, but dramatically increase to C_T values 50 percent larger than recharge waters. This indicates a substantial influx to the system of inorganic carbon from some source. Well 17, Montana and well 7, South Dakota are likely the result of poor data as discussed in the section on pH.

Sodium Plus Potassium

Chemical data over most of the study area show some sodium plus potassium in milliequivalents per liter in excess of chloride in milliequivalents per liter. This indicates a source of sodium plus potassium in addition to the dissolution of halite (NaCl) and sylvite (KCl).

The relationship of the excess sodium plus potassium to the other major cations, calcium and magnesium, is shown in figure 10. This graph furnishes a criterion against which to test the feasibility of cation exchange occurring in the system as the waters move downgradient.

The data indicate that along most flow paths, if cation exchange is occurring, it is not the only process, and, in most situations, not a primary process. Sodium may be released during the diagenesis occurring in the aquifer from non-stoichiometric minerals or hydrolysis of sodium silicate minerals. A regression of log (Meq NA + Meq K) against log (Meq Ca + Meq Mg) follows a straight line as predicted by the linearized form of the mass action expression, indicating a strong likelihood that calcium or magnesium or both are being exchanged for sodium in the system.

DATA AND INTERPRETATION FOR HYDROLOGICALLY SIGNIFICANT ISOTOPES

Stable and radioactive isotopes supply information on the mineralogic source of the water, estimation of flow velocities, and identification of areas of recharge and leakage. The hydrologically significant isotopes considered in the report are shown in table 12. A more complete discussion of the uses of stable and radioactive isotopes in the hydrologic system may be found in Hoefs (1973) and Fritz and Fontes (1980).

All stable isotopes are reported in δ (del) notation typically written as δD, δ^{13}C, δ^{18}O, and δ^{34}S, where D is the heavy isotope of hydrogen (deuterium) and ^{13}C, is the heavy isotope of carbon; 18_{0} is the heavy isotope of oxygen; and 34_{S} is the heavy isotope of sulfur. The definition of δ measured in per mille (parts per thousand, ^{0}/00), is given by the equation:

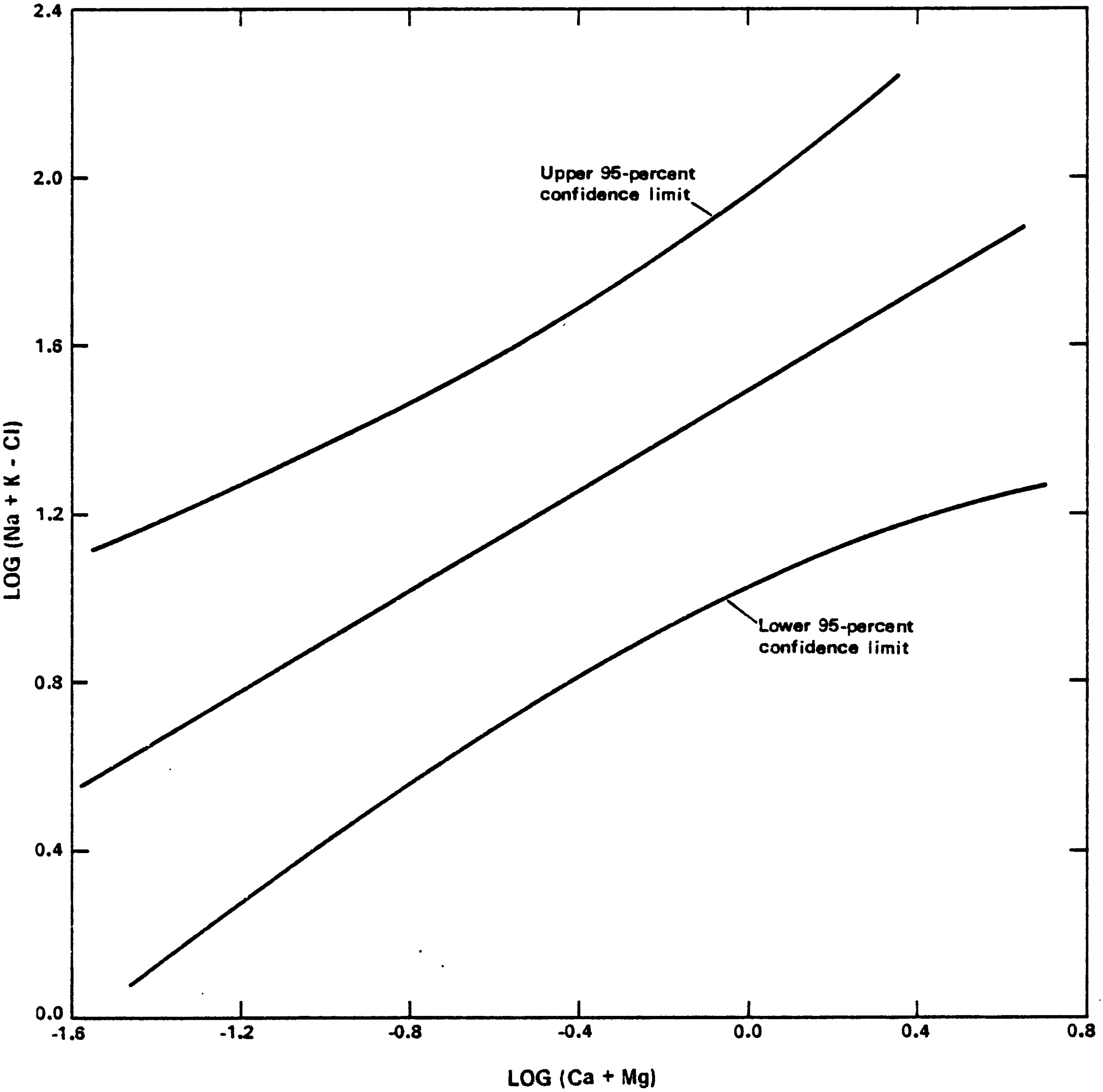


Figure 10.--Relationship between sodium plus potassium minus chloride (in milliequivalents per liter) and calcium plus magnesium (in milliequivalents per liter).

Table 12.--*Hydrologically significant isotope data for water from the Madison aquifer system*

[$\delta^{13}C$ = Del carbon-13 (here referenced to Peedee belemnite, in column 3); ^{14}C = Carbon-14 (here in percent modern in column 4); δD_{SMOW} = Del deuterium referenced to Vienna standard mean ocean water (in column 5); $\delta^{18}O_{SMOW}$ = Del oxygen-18 referenced to Vienna standard mean ocean water (in column 6); $\delta^{34}S_{CD}$ = Del sulfur-34 referenced to Canyon Diablo troilite (in column 7); TU = Tritium, expressed in tritium units (in column 8)]

Site number on plates	Well or spring name	$\delta^{13}C$	$^{14}C_{MDN}$	δD_{SMOW}	$\delta^{18}O_{SMOW}$	$\delta^{34}S_{CD}$	TU
			Montana				
2	Gore Hill	-3.18	3.6±0.2	-148.75	-19.35	22.91	1.0±0.9
3	Great Falls High School	-7.20	24.2±0.2	-146.2	-19.00	7.71	16.1±1.2
4	Bozeman Fish Hatchery	-8.98	84.1±0.5	-143.7	-18.90	3.34	115. ±5
5	Bough Ranch	-3.80	1.3±0.5	-141.25	-18.15	20.87	-0.1±0.8
6	McLeod Warm Spring	-7.57	52.5±0.5	-140.7	-18.50	17.95	45.5±2.4
7	Big Timber Fish Hatchery	-14.11	103.9±0.6	-142.65	-18.60	-4.46	124. ±6
8	Hanover	-5.32	25.4±0.3	-140.45	-18.25	17.48	-0.0±0.8
9	Vanek Warm Spring	-5.18	29.3±0.3	-139.65	-18.35	17.78	5.3±0.5
10	Lewiston Big Spring	-4.97	35.8±0.4	-139.2	-18.25	14.93	0.8±0.9
11	Bluewater Spring	-9.51	---	-146.9	-19.35	---	0.5±0.9
12	Landusky Spring	-7.46	Sample too small.	-138.75	-18.25	21.33	21.9±1.4
13	Lodgepole Warm Spring	-7.04	28.0±0.4	-134.75	-17.8	23.86	31.8±1.8
14	HTH #3	-3.68	---	---	---	---	0.1±0.2
15	Keg Coulee	-1.68	1.0±0.2	-136.40	-16.80	17.75	---
17	Sumatra	-3.61	---	-136.15	-16.90	18.16	---
18	Sleeping Buffalo	-3.22	4.2±0.4	-138.35	-18.40	22.40	---
19	Sarpy Mine	-2.33	3.3±0.2	-151.4	-19.80	17.21	---
20	Mysse	-2.34	0.8±0.5	-141.5	-18.25	17.24	---
21	Colstrip	-2.67	---	-146.05	-19.05	14.67	---
22	Moore	-2.40	1.6±0.2	-141.75	-18.00	17.50	---
23	Ranch Creek	-6.17	10.0±0.2	-137.6	-18.10	11.75	---
24	Belle Creek	-6.02	9.5±0.2	-137.9	-18.25	11.71	---

Table 12.--*Hydrologically significant isotope data for water from the Madison aquifer system*--Continued

Site number on plates	Well or spring name	$\delta^{13}C$	$^{14}C_{MDN}$	δD_{SMOW}	$\delta^{18}O_{SMOW}$	$\delta^{34}S_{CD}$	TU
			South Dakota				
1	Kosken	-6.20	7.8±0.4	-126.6	-16.75	13.5	0.1±0.7
2	McNenney	-11.5	79.6	-127	-17.43	11.36	114 ±6
3	Provo	-9.4	7.3	-131	-17.09	10.89	---
4	Rhoads Fork	-11.0	92.9	-125	-17.22	6.22	62 ±2
5	Spearfish	-10.7	74.3	-126	-17.06	3.19	87 ±5
6	Fuhs	-8.89	53.8±0.4	---	-16.13	4.50	65.6±3.0
7	Delzer #1	-4.60	4.6±0.7	---	-19.66	15.20	0 ±0.6
8	Delzer #2	-2.61	2.8±0.2	---	-18.13	15.50	0 ±0.6
9	Cascade Spring	-9.1	19.4	-118	-15.48	12.50	---
10	Evans Plunge	-9.7	28.5	-121	-16.71	---	---
11	Kaiser	-9.46	81.1±0.6	---	-12.13	9.00	27.7±1.4
12	Jones Spring	-11.6	100.0	-110	-14.61	6.67	276.0±10
13	Black Hills Cemetery	-9.88	69.1±5	---	-15.04	-5.10	---
14	Streeter Ranch	-6.65	52.2±0.4	-88.40	-12.05	---	10.6±0.8
16	Cleghorn Spring	-9.6	91.6	-103	-13.23	5.75	182.0±8
17	Lien	-8.03	68.5±0.5	---	-14.19	-3.20	16.6±0.9
18	Ellsworth AFB	-9.1	5.8	-107	-14.13	---	---
19	Philip	-7.2	2.8	-125	-17.55	14.52	---
20	Dupree	-2.04	2.8±0.4	-143.65	-19.00	16.61	10.2±0.8
21	Hamilton	-3.50	2.4±0.2	---	-17.74	15.50	---
22	Hilltop Ranch	-6.63	4.6±	-132.4	-17.60	14.71	0.0±0.6
23	Eagle Butte	-2.40	2.2±0.4	-137.1	-18.25	15.99	0.6±0.6
24	Midland	-6.2	2.4	-128	-17.62	14.96	---
25	Murdo	-5.55	3.2±0.8	-131.45	-17.35	14.19	1.3±0.7
26	Prince	-4.72	4.0±0.3	---	-17.87	15.30	---
27	Bean	-6.23	3.3	---	-17.80	11.50	---

Table 12.--*Hydrologically significant isotope data for water from the Madison aquifer system*--Continued

Site number on plates	Well or spring name	$\delta^{13}C$	$^{14}C_{MDN}$	δD_{SMOW}	$\delta^{18}O_{SMOW}$	$\delta^{34}S_{CD}$	TU
			Wyoming				
1	Mock Ranch	-7.10	57.7±0.6	-138	-18.35	---	35.4±1.4
2	Denius #1	-6.88	8.4±0.3	-137.85	-18.50	9.73	19.8±1.1
5	Hole-in-the-Wall	-10.77	87.4±0.6	-139.1	-18.30	---	0.5±0.6
6	Storey Fish Hatchery	-7.87	88.8±0.5	-138.95	-18.35	---	107 ±4
7	Mobil	-9.75	62.2±0.9	-132	-17.45	11.51	56.7±2.7
8	Conoco #44	-5.14	<1.8	-154.05	-20.10	8.40	-0.5±0.6
9	Shidler	-4.04	6.2±0.7	-153.65	-20.15	8.09	1.2±0.8
10	MKM	-4.66	2.6±0.3	-152.05	-19.70	8.52	0.2±0.8
11	Conoco #175	-6.23	13.9±1.8	-145.5	-19.25	11.18	0.8±0.5
12	Barber Ranch Spring	-11.74	83.7±0.6	-137.65	-18.20	7.75	53.0±2.5
13	Devils Tower	-6.80	59.0±0.5	-139.95	-17.85	11.68	1.5±0.6
14	HTH #1	-6.632	12.7	---	---	11.60	5.4±
15	Upton	-8.2	14.7	-133	-18.18	12.16	---
16	Coronado #2	-7.51	36.0±0.4	-133.30	-17.60	---	0.0±0.6
17	Osage	-10.0	54.7	-135	-18.15	10.44	0.5±0.2
18	JBJ	-4.24	4.8±0.3	-130.65	-17.95	11.68	0.3±0.5
19	Seeley	-7.82	61.4±0.5	-133.5	-17.75	9.94	0.8±0.6
20	Voss	-7.26	44.5±0.5	-130.65	-17.4	10.09	2.3±0.5
21	Newcastle	-10.4	46.2	-130.0	-17.66	9.84	0.1±0.2
22	Self	-6.60	31.2±4	-131.80	-17.60	10.49	-0.1±0.4
23	Martens Madison	-9.56	61.9±0.6	-130.95	-17.45	---	---
24	Mallo Camp	-8.00	92.9±0.7	---	---	---	---
25	Ranch A	-10.81	74.4±0.6	---	-17.49	11.2	41.6±2.0

$$\delta = \left(\frac{\text{R sample}}{\text{R standard}} -1\right) 1{,}000,$$

where R is the ratio of the isotopic species under consideration. For example:

$$\delta D = \left(\frac{\text{D/H sample}}{\text{D/H standard}} -1\right) 1{,}000,$$

where R, in this case, would be equal to the D/H ratio. Notice that the D/H ratio in a sample is not determined directly, but rather is compared to a standard in a mass spectrometer. In a manner similar to this, one can define the δ terms for carbon-13, oxygen-18, and sulfur-34. The standard for del carbon-13 is the Peedee belemnite. The standard for del deuterium and del oxygen-18 is standard mean ocean water, abbreviated SMOW. In recent years, a new standard called V-SMOW has been used. This abbreviation stands for Vienna Standard Mean Ocean Water; the word Vienna refers to the city in Austria where the International Atomic Energy Agency (IAEA) is permanently housed. The IAEA is a clearing house for V-SMOW. The standard for del sulfur-34 is the Canyon Diablo troilite.

Any chemical, physical, or biological process that a liquid, gas, or solid phase undergoes will cause the isotopic ratios of the elements that comprise that phase to change. For example, when liquid water evaporates to form water vapor, lighter isotopes tend to be enriched preferentially in the more mobile phase, in this case, the vapor. During the process of evaporation, the remaining liquid water becomes enriched isotopically in the heavier isotopes of hydrogen (deuterium) and oxygen (oxygen-18). In general, the lighter isotopes of any element prefer the less dense, more mobile phase; isotopic gases are lighter than liquids, and liquids are in turn, lighter than solids.

Hydrogen is actually a mixture of three isotopes, the most common of which is normal hydrogen, sometimes called protium; the nucleus of protium contains one proton and no neutron. The much less abundant, heavy isotope of hydrogen is called deuterium, which contains one proton and one neutron in the nucleus. The atomic mass of deuterium is 2, and of normal hydrogen, 1. Tritium is the third isotope of hydrogen, and is comprised of one proton and two neutrons in the nucleus of the atom; it has an atomic mass of 3. This configuration is metastable; tritium decays by beta emission and has a half life of 12.26 years.

Oxygen has no naturally occurring radioactive isotopes. The most abundant isotope is oxygen-16; oxygen-18 is next in abundance. A third isotope, much less prevalent, has an atomic weight of 17.

Although there are many permutations in which the isotopes of hydrogen and oxygen can be put together to form a water molecule, there are only three common forms: $HH^{16}O$, $HD^{16}O$, and $HH^{18}O$. Each of these isotopically different forms of water has a vapor pressure different from the others and is constant at any given temperature and pressure. The vapor pressure ratio of $HD^{16}O$ to $HH^{16}O$ compared to $HH^{18}O$ to $HH^{16}O$ is 8. Therefore, the isotopes of hydrogen and oxygen occur in meteoric waters, on a world-wide basis, with a simple relationship defined by the equation $\delta D = 8\delta^{18}O + 10$. If del deuterium versus del oxygen-18 for meteoric waters were plotted, the relationship would be a line with a slope of 8 (which comes from the ratio of vapor pressures), and an intercept of 10 on the deuterium axis; this intercept often is referred to as deuterium excess. In various parts of the world, deuterium excess is not 10; for example, in the Mediterranean, deuterium excess is 22.

Evaporation from the ocean causes a water-vapor cloud to become isotopically lighter than the ocean from which it came. As this cloud approaches land and rises in elevation, rain that comes out of the water vapor will be heavier isotopically than the water vapor that remains in the cloud; thus, the isotopic composition of precipitation varies with elevation. More dramatically, there is a large variation in the del deuterium and del oxygen-18 of precipitation with latitude; the ratio becomes larger with increasing temperature. In general, the greater the temperature difference between the site of evaporation and the site of eventual precipitation, the greater the isotopic effect. Also, because of the temperature effect, snow generally is isotopically much lighter than rain at the same location. Furthermore, different storm paths typically have strikingly varied isotopic compositions.

For example, storms from the west generally are lighter isotopically than storms that come from the south out of the Gulf of Mexico and up the Mississippi Valley; this is because western storms have gone over higher elevations and usually are associated with cooler temperatures. Paleoclimatic changes over North America since the last ice age (10,000 years before present) may have caused shifts in the dominant sources of storm tracks (Bryson and others, 1970) more recently producing Gulf-storm dominance east of the Black Hills (less than 5,000 years before present).

Deuterium and Oxygen-18

Del deuterium and del oxygen-18 values relative to V-SMOW for all of the sample points from the Madison study area that are shown in figure 11 were obtained from the data in table 12. A clustering of points occurs at about -20 to -16 per mille in figure 11. Furthermore, there is no discernable regional pattern to the isotopic composition of the ground water, with the exception of the isotopic composition of oilfield waters from Keg Coulee and Sumatra in the Central Montana trough. The rest of the isotopic data for Montana and much of Wyoming shows little variation. The average del oxygen-18 is approximately -18 per mille ± 1 per mille, and there does not seem to be any consistent pattern between age of the water and its isotopic composition. This was the subject of a recent paper by Hanshaw and others (1978b), who used these data for interpretations of the paleoclimate. One of the important conclusions that comes from the study of the isotopic composition of the water in the Madison is that all the water is of meteoric origin; none of it possibly can be fossil or connate water left in the aquifer from a previous geological time. This conclusion also is substantiated by the carbon-14 data from ground-water samples given later in this report.

A group of data points in figure 10 have an isotopic composition heavier than -16 per mille for del oxygen-16. All of these sample points are from the east side of the Black Hills uplift and relatively close to the Black Hills. These anomalous data are apparently the result of a difference in storm tracks that affect the east and west sides of the Black Hills uplift. The west side of the Black Hills is isotopically similar to most of the rest

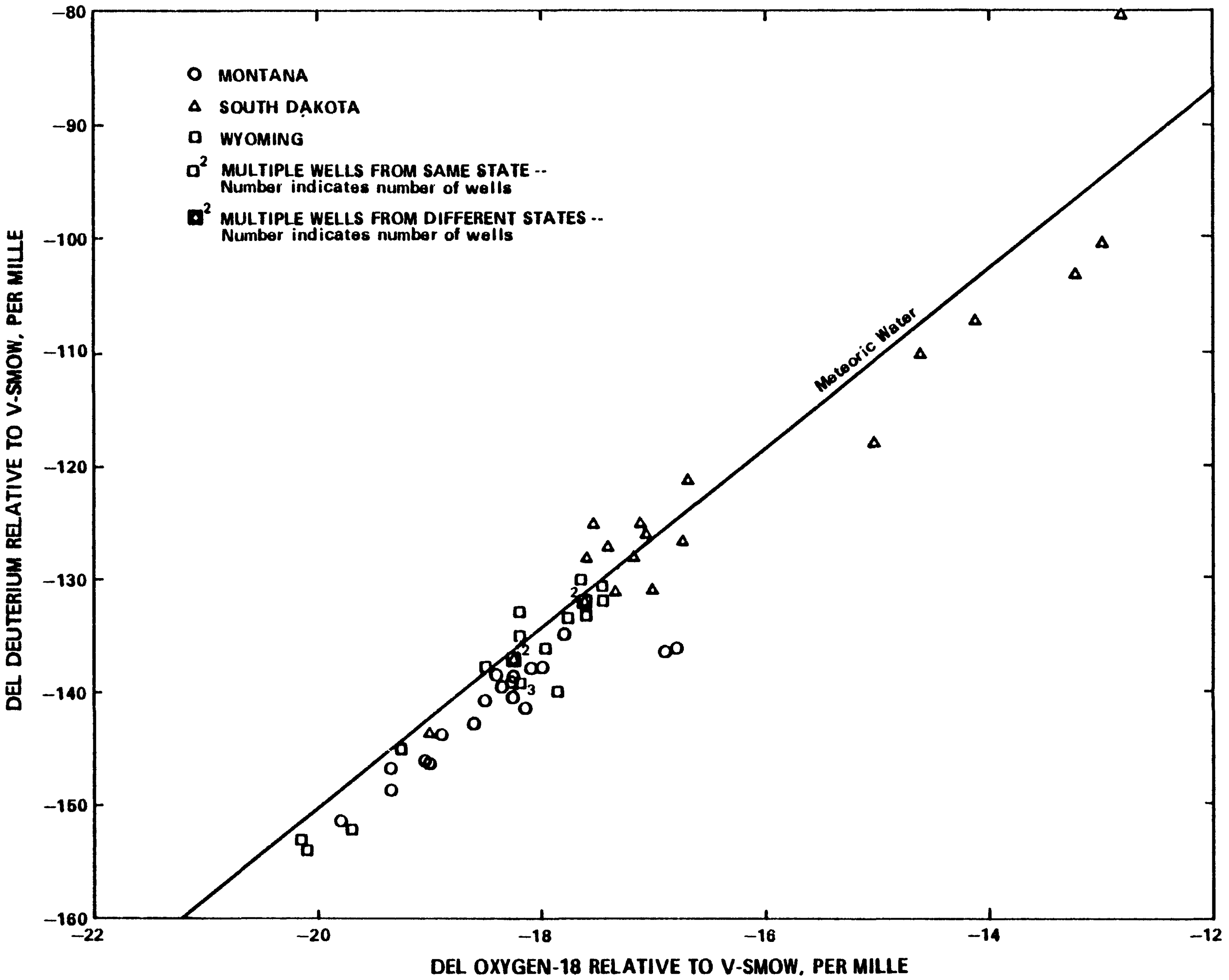


Figure 11.--Plot of del oxygen-18 versus del deuterium, referenced to meteoric water line.

of the data in Wyoming and Montana and is affected primarily by storms from the west and northwest. Storm tracks from the Gulf of Mexico apparently bring isotopically heavier water only to the east side of the Black Hills uplift, where subsequent recharge causes isotopically heavier ground water on that side of the uplift. However, it is important to note that the isotopically heavy water is not present far downgradient east of the Black Hills. Based on isotopic data, ground water in the central part of South Dakota is derived primarily from recharge on the western and southwestern sides of the Black Hills, rather than recharge from the east side. This also indicates that the predominant recharge to the Madison aquifer in most of South Dakota is from the south and west side of the Black Hills, and that recharge on the eastern side is relatively insignificant and does not extend far downgradient.

It has been suggested that the Madison aquifer system in North Dakota was recharged by glacial melt water during the Pleistocene glaciation (Downey, 1973). Joe S. Downey of the U.S. Geological Survey (oral commun., 1980) more recently suggested that a signal characteristic of the glacial waters might be observed in the D/H or $^{18}O/^{16}O$ ratios of the present-day waters.

If the waters of the Madison aquifer system were heavily affected by glacial melt water, the del oxygen-18 values would be expected to approach del oxygen-18 values characteristic of ice, -28 to -40 per mille (Faure, 1977). In the study area, values of del oxygen-18 ranged from -20.15 to -12.05 per mille (table 12), a result inconsistent with recharge by glacial melt waters but consistent with recharge by meteoric waters. In addition to the results of this study, Hanshaw points out that such a signal has never been observed in the contiguous United States (Hanshaw and others, 1978a).

Tritium

Natural tritium generated by the reaction:

$$N_7^{14} + n \rightarrow T + C_6^{12}$$

was at levels between 4 and 25 picocuries per liter prior to the onset of the atmospheric testing of thermonuclear weapons in 1952. Since the 1952 bomb testing, atmospheric levels greater than 2,000 picocuries per liter have been observed, permitting the use of bomb-induced tritium as a ground-water tracer.

As expected, higher values of tritium were observed in the recharge area, with values on the eastern side of the Black Hills being somewhat higher than those observed on the western side of the Black Hills; these higher values on the eastern side are consistent with the previously expressed concept that most of the recharge in the Black Hills originates during summer gulf coast storm tracks (Gat, 1980).

In Montana, McLeod, Lodgepole, and Landusky Springs show significant amounts of tritium, indicating that, although these springs originate from the Madison aquifer system, they are mixed with waters of recent recharge as they approach the surface. The higher tritium values associated with these springs also indicate that carbon-14 ages calculated from these waters will be younger than expected due to contamination with atmospheric carbon-14.

Sulfur-34

Isotopic ratios in the dissolved sulfate ($\delta^{34}S_{SO_4}$) exhibit lighter values in the recharge areas to heavier values downgradient, with very little variation in values in the downgradient areas (pl. 10, in pocket). Values range from -5.1 per mille in the Black Hills to 23.86 per mille in the Little Rocky Mountains. The negative $\delta^{34}S_{SO_4}$ values may be localized effects, not necessarily representative of recharge waters as a whole. Probably the 3 to 6 per mille values are more representative of recharge waters.

Flow path 1 shows little change, but this area has the heaviest values. Flow paths 2 and 3 show the downgradient consistency of the values. Site 6, a spring in Montana, has an anomalously high $\delta^{34}S_{SO_4}$, similar to values found in the Central Montana trough. This may be a local effect for the site, but the number may represent more closely $\delta^{34}S_{SO_4}$ values from gypsum or anhydrite indigenous to the Madison sediments, and the lower values near the recharge areas may represent some other sulfate sources.

Flow path 5 shows a decrease downgradient to the Midwest, Wyoming area, then the expected increase, which is probably in another flow regime. This decrease in $\delta^{34}S_{SO_4}$ could indicate a leakage or secondary source of sulfate minerals with a different $\delta^{34}S_{SO_4}$ than sulfate minerals in Madison sediments. A $\delta^{34}S_{SO_4}$ anomaly near Great Falls, Montana also indicates that well 3 may produce water from an aquifer other than the Madison. Likewise, a steep gradient at the southern end of the Black Hills is consistent with leakage, a change in lithofacies, or a structural control diverting the water and preventing its normal evolution.

A study of the sulfur isotopic composition of dissolved sulfate species should help determine the origin of the sulfate. A plot of del sulfur-34 for the dissolved sulfate against the sulfate concentration of the water is shown in figure 12. Several facts are indicated: There is an approximately linear correlation, with an intercept at approximately 9 per mille at 0 sulfate, going up to approximately 22 per mille at 2,000 milligrams per liter sulfate. Several data points plot above the trend; these are all from south-central Montana and may represent sulfate reduction. Two points labeled Bear Butte and Cascade Spring from South Dakota are mixed waters; that is, both the well at Bear Butte and Cascade Spring are producing a mixture of dissolved sulfates from both Permian evaporites and Mississippian evaporites; the Bear Butte well was uncased from the Permian to its depth in the Mississippian. Cascade Spring issues from Permian rocks although it is thought that part of the water comes from a Mississippian source.

For comparison purposes, water from one known well in the Minnelusa Formation (identified on the far right of figure 14) was plotted; its position plots within the band for Permian evaporites and correlates with its production from Permian rocks. Although its total sulfate is approximately 1,900 milligrams per liter, it is isotopically very much lighter than water from similarly known Mississippian wells with large sulfate concentrations.

One geochemical finding of this study concerns the three wells at Midwest, Wyoming, which plot below the band for the Permian evaporites (fig. 12). Water from all three wells (Shidler, MKM, Conoco-44) has a sulfate concentration

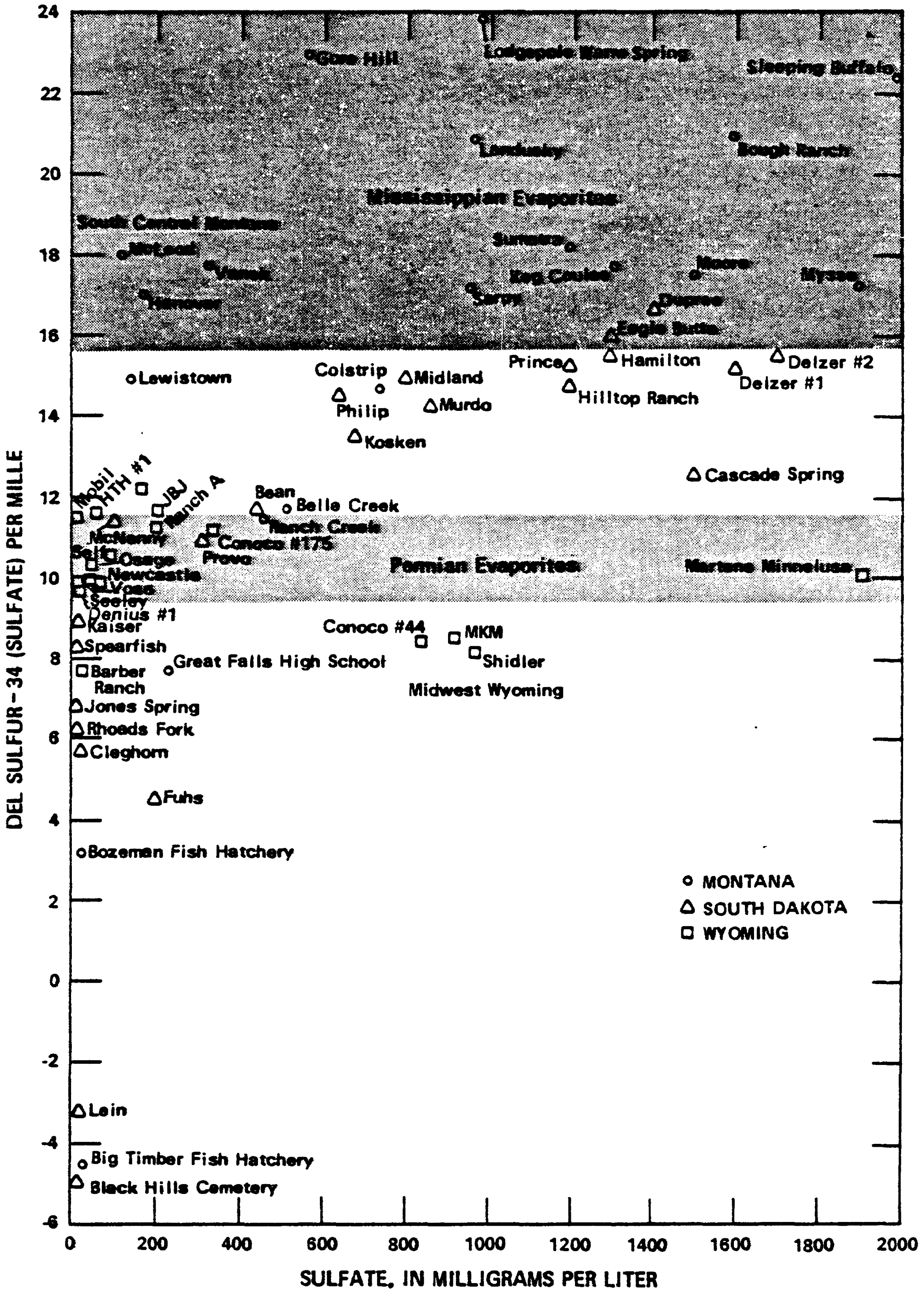


Figure 12.--Del sulfur-34 versus sulfate for water from the Madison aquifer system.

between 800 and 1,000 milligrams per liter, and all are isotopically much lighter than Mississippian-age sulfate. In this area, drawdown has been extensive as a result of intensive pumping over several decades. The isotopic composition of water from all three wells is nearly identical at about 8 per mille. According to figure 12, however, water with a sulfate concentration of 800 to 1,000 milligrams per liter should have an isotopic composition of approximately 16 per mille, if the sulfate were of Mississippian age. The lighter isotopic composition indicates that water from these three wells may not be produced solely from the Mississippian rocks, but rather from the cross-formational dewatering of Permian rocks. This is hydrologically significant, because Konikow (1976) used this cone of depression in calculating the regional transmissivity of the Madison aquifer. If these three wells are withdrawing significant quantities of water, not from the Mississippian, but cross-formationally from the Permian, then leakage may be an important factor in the hydrologic analysis of that particular cone of depression, and transmissivity values for Mississippian sediments in this region require re-evaluation.

These data for Midwest, Wyoming are of further significance when it is considered that the large dissolved-solids concentrations in the Madison (pl. 2) that are predicted for the center of the Powder River basin are predicated on data from these wells in the Midwest region. If waters from these wells have dissolved-solids concentrations from Permian sediments, then water in the entire Powder River basin may have different dissolved-solids concentrations, which are possibly smaller than the extrapolation of the data on plate 2 would indicate.

Carbon-13

Isotopic ratios of carbon-13 (del carbon-13 in per mille) are relatively light in the recharge areas and become heavier downgradient (pl. 11), indicating fairly significant carbon-13 sources in the aquifer. The del carbon-13 values range from -16.56 per mille in the Bighorn Mountains to +0.55 per mille in eastern South Dakota. Flow paths generally reflect the decrease with trend reversals in 5 and 8. Flow path 5 has anomalous data in the north end indicating the previously discussed hydraulic discontinuity. A minor reversal from well 9 to well 8 may indicate that the direction of flow is reversed; that is, 8 to 9 could be the more general flow direction. Flow path 8 shows a trend reversal in central South Dakota near the subcrop. This could indicate leakage from an aquifer whose inorganic carbon is lighter in del carbon-13.

The principal reason for obtaining samples for del carbon-13 analysis was to adjust carbon-14 data for dilution by dissolution of dead (zero) content of carbon-14 limestone, or for any reactions that may occur, including dissolution and precipitation, along flow paths that affect the isotopic composition of the carbon. Presently, only unadjusted ages are reported. Some of the isotopic variations of carbon will be discussed in this section. Because the standard for isotopic analysis for carbon is a marine fossil (the Peedee belemnite), most limestones plot close to zero percent in isotopic composition. Land plants, on the other hand, plot in two categories, both of which are isotopically very light compared to marine limestones. The more common type of plant has an isotopic composition of about -25 per mille; another type of plant (typical of grasses and tropical plants, such as corn and tomatoes) has an isotopic composition of about -15 per mille because of a different metabolic pathway. The important reservoir of carbon dioxide from which the ground-water system is recharged is the soil zone, not the atmosphere.

Unlike the atmosphere, which contains about 20 percent oxygen and 0.3 percent carbon dioxide, the soil zone typically contains 1 to 2 percent carbon dioxide generated by decay of organic material and plant respiration. When rainfall infiltrates this zone, it absorbs large quantities of isotopically light carbon dioxide.

Carbon-14

The unadjusted carbon-14 ages were calculated from the known half-life of carbon-14 of 5,730 years and the decay equation:

$$t_{\frac{1}{2}} = \frac{5{,}730}{\log 2} \log \frac{A_{\text{initial}}}{A_{\text{measured}}} ,$$

where

$t_{\frac{1}{2}}$ = half-life,

$A_{initial}$ = 100 percent modern use for soil zone and atmospheric carbon dioxide, and

$A_{measured}$ = carbon-14 measured in percent modern.

Unadjusted carbon-14 ages for ground waters of the Madison aquifer system are shown in table 13. These values contain no corrections for dilution of initial recharge carbon-14 to carbon-12 ratios with dead carbon from dissolution of aquifer materials, nor changes in recent recharge waters containing greater than 100 percent modern carbon-14 from modern-day atmospheric thermonuclear testing.

EVOLUTION OF GROUND-WATER CHEMISTRY BY FLOW PATH

Using the generalized regional flow paths discussed in the section on hydrology and the concept of well-defined geochemical evolutionary paths in carbonate aquifer systems as discussed in the section on geochemical evolution, it should be possible to identify the particular evolutionary path taken by a water as it moves along a flow path.

The trilinear diagrams for each flow path were prepared using the computer code 'Trilin' developed by Ruth Seidel and Joe S. Downey (U.S. Geological Survey, written commun., 1979).

Flow Path 1

The trilinear diagram for flow path 1, comprised of a cation triangle, anion triangle, and quadrilinear section containing a summary of information from the two triangular fields, is shown in figure 13. The uniformity of the data shown on the anion triangle is consistent with: (1) The identification of the Little Rocky Mountains as an area of local recharge and discharge; and (2) a system controlled by dissolution of a sulfate phase. The decrease in magnesium and calcium coupled with the increase in sodium suggests cation exchange may be important. The possible controlling mechanism is dissolution of gypsum to the gypsum phase boundary, with minor dissolution of halite accompanying a modest amount of cation exchange.

Table 13.--*Unadjusted carbon-14 ages of ground water from the Madison aquifer system (in years before present)*

Site number on plates	Well or spring name	Carbon-14 (modern)	Unadjusted carbon-14 age (years before present)
	Montana		
2	Gore Hill	3.6 ± 0.2	27,500
3	Great Falls High School	24.2 ± 0.2	11,700
4	Bozeman Fish Hatchery	84.1 ± 0.5	1,400
5	Bough Ranch	1.3 ± 0.5	35,900
6	McLeod Warm Spring	52.5 ± 0.5	5,300
7	Big Timber Fish Hatchery	103.9 ± 0.6	Recent
8	Hanover	25.4 ± 0.3	11,329
9	Vanek Warm Spring	29.3 ± 0.3	10,100
10	Lewiston Big Spring	35.8 ± 0.4	8,500
11	Bluewater Spring	-----	------
12	Landusky Spring	Sample too small.	------
13	Lodgepole Warm Spring	28.0 ± 0.4	10,500
14	HTH #3	-----	------
15	Keg Coulee	1.0 ± 0.2	38,100
17	Sumatra	-----	------
18	Sleeping Buffalo	4.2 ± 0.4	26,200
19	Sarpy Mine	3.3 ± 0.2	28,200
20	Mysse	0.8 ± 0.5	39,900
21	Colstrip	-----	------
22	Moore	1.6 ± 0.2	34,200
23	Ranch Creek	10.0 ± 0.2	19,000
24	Belle Creek	9.5 ± 0.2	19,500

Table 13.--*Unadjusted carbon-14 ages of ground water from the Madison aquifer system (in years before present)*--Continued

Site number on plates	Well or spring name	Carbon-14 (modern)	Unadjusted carbon-14 age (years before present)
	South Dakota		
1	Kosken	7.8 ± 0.4	21,100
2	McNenney	79.6	1,900
3	Provo	7.3	21,600
4	Rhoads Fork	92.9	600
5	Spearfish	74.3	2,500
6	Fuhs	53.8 ± 0.4	5,100
7	Delzer #1	4.6 ± 0.7	25,500
8	Delzer #2	2.8 ± 0.2	29,600
9	Cascade Spring	19.4	13,600
10	Evans Plunge	28.5	10,400
11	Kaiser	81.1 ± 0.6	1,700
12	Jones Spring	100.0	Recent
13	Black Hills Cemetery	69.1 ± 5	3,100
14	Streeter Ranch	52.2 ± 0.4	5,400
16	Cleghorn Spring	91.6	700
17	Lien	68.5 ± 0.5	3,100
18	Ellsworth Air Force Base	5.8	23,500
19	Philip	2.8	29,600
20	Dupree	2.8 ± 0.4	29,600
21	Hamilton	2.4 ± 0.2	29,900
22	Hilltop Ranch	4.6	25,500
23	Eagle Butte	2.2 ± 0.4	31,600
24	Midland	2.4	30,800
25	Murdo	3.2 ± 0.8	27,500
26	Prince	4.0 ± 0.3	26,600
27	Bean	3.3	28,200

Table 13.--*Unadjusted carbon-14 ages of ground water from the Madison aquifer system (in years before present)*--Continued

Site number on plates	Well or spring name	Carbon-14 (modern)	Unadjusted carbon-14 age (years before present)
	Wyoming		
1	Mock Ranch	57.7 ± 0.6	4,500
2	Denius #1	8.4 ± 0.3	20,500
5	Hole-in-the-Wall	87.4 ± 0.6	1,100
6	Storey Fish Hatchery	88.8 ± 0.5	1,000
7	Mobil	62.2 ± 0.9	3,900
8	Conoco #44	<1.8	33,200
9	Shidler	6.2 ± 0.7	23,000
10	MKM	2.6 ± 0.3	22,900
11	Conoco #175	13.9 ± 1.8	16,300
12	Barber Ranch Spring	83.7 ± 0.6	1,500
13	Devils Tower	59.0 ± 0.5	4,400
14	HTH #1	12.7	17,100
15	Upton	14.7	15,800
16	Coronado #2	36.0 ± 0.4	8,400
17	Osage	54.7	5,000
18	JBJ	4.8 ± 0.3	25,100
19	Seeley	61.4 ± 0.5	4,000
20	Voss	44.5 ± 0.5	6,700
21	Newcastle	46.2	6,400
22	Self	31.2 ± 4	9,600
23	Martens Madison	61.9 ± 0.6	4,000
24	Mallo Camp	92.9 ± 0.7	600
25	Ranch A	74.4 ± 0.6	2,400

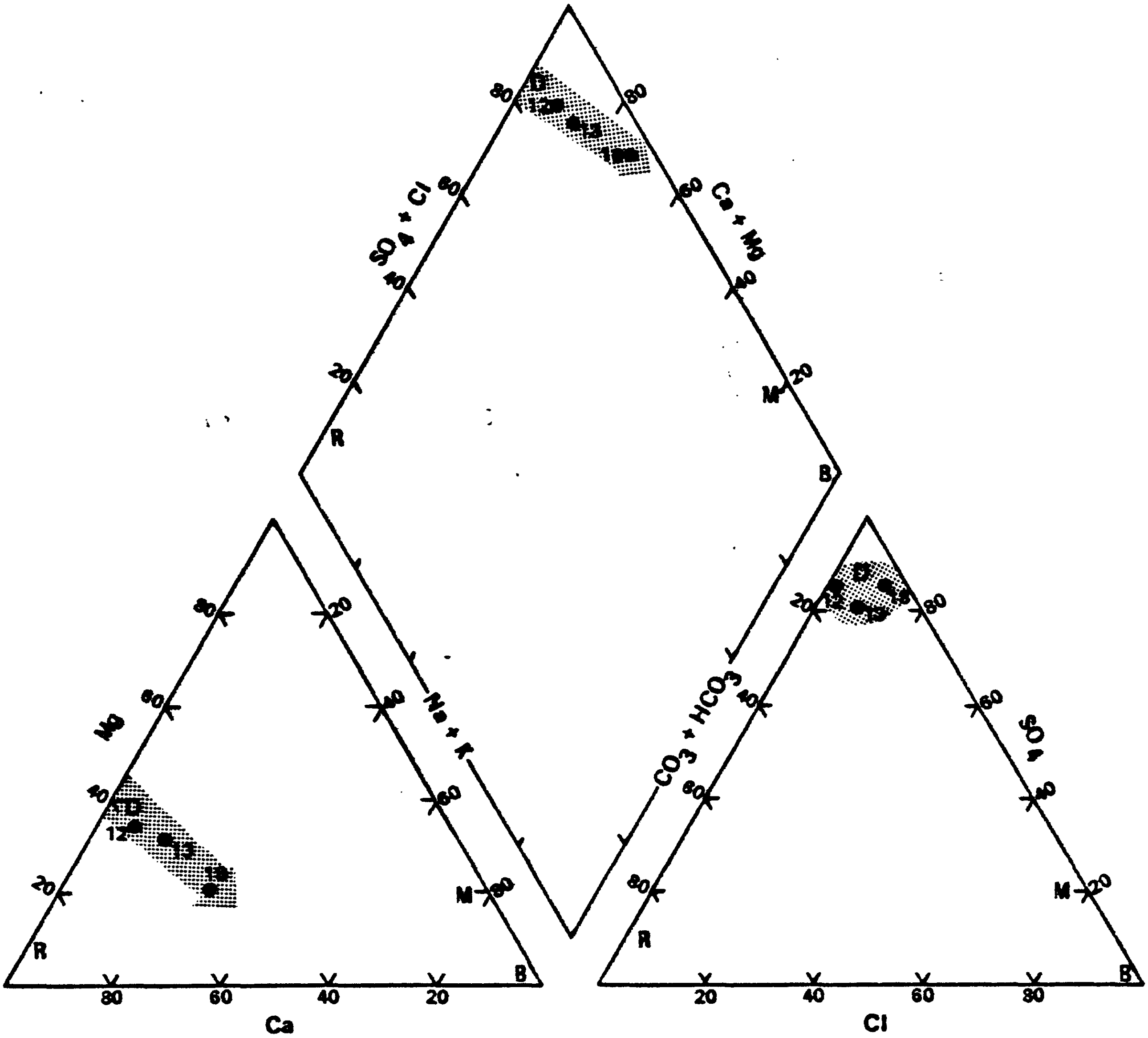


Figure 13.--Evolution of ground-water geochemistry downgradient along generalized regional flow path 1.

EXPLANATION FOR FIGURE 13

Well Identification and Dissolved Solids

Well number	Latitude	Longitude	Dissolved Solids (mg/L)
12	47.875	108.684	1,360
13	47.996	108.460	1,640
18	48.491	107.527	3,250

Percentage of Cations

Calcium	Magnesium	Sodium	Potassium
58	34	7.4	1.0
55	31	13	1.2
51	20	27	1.3

Percentage of Anions

Bicarbonate	Carbonate	Sulfate	Chloride
14	0	83.5	2.2
13	0	80.0	7.3
5	0	84.2	11

Symbols

● Montana

➡ Dominant pathway

Water Classification

R	Recharge water	M	Marine water
D	Discharge water	B	Brine water

Flow Path 2

The trilinear diagram for flow path 2 is shown in figure 14. This diagram shows water evolving from a recharge-type water to a mixed sodium chloride-sulfate. The relative concentrations of calcium and magnesium decrease along the flow path, while the relative concentration of sodium plus potassium increases downgradient. The evolution of water, as shown on the quadrilinear diagram, follows the R→M of figure 4, which represents the alteration of the water from a discharge-type of water to a sodium chloride-sulfate type of water downgradient. The relative constancy of the concentration of dissolved solids along this flow path, coupled with the observed pattern, indicate that possible mechanisms explaining this flow path are: (1) Leakage from the underlying Cambrian-Ordovician aquifer system; and (2) dissolution of dolomite, gypsum, and halite with precipitation and cation exchange.

Flow Path 3

The trilinear diagram, figure 15, displays the geochemical evolution of ground water along flow path number 3. Along this flow path, the water is evolving from a recharge type of water into water with composition associated with salt-water encroachment; marine on figure 4, as shown by comparison with the quadrilinear diagram (fig. 4). Along this flow path, the cation triangle indicates a relative decrease in magnesium and calcium, with a significant increase in sodium plus potassium.

The anion triangle shows a transition from a sulfate to chloride-dominated water. The quadrilinear diagram shows a change from a calcium magnesium sulfate type of water to a sodium chloride-sulfate water.
The trilinear diagram for flow path 3 is consistent with the following mechanisms:

1. Dissolution of halite, gypsum, and dolomite accompanying calcite precipitation.
2. Mixing with sodium chloride-type brines downgradient.

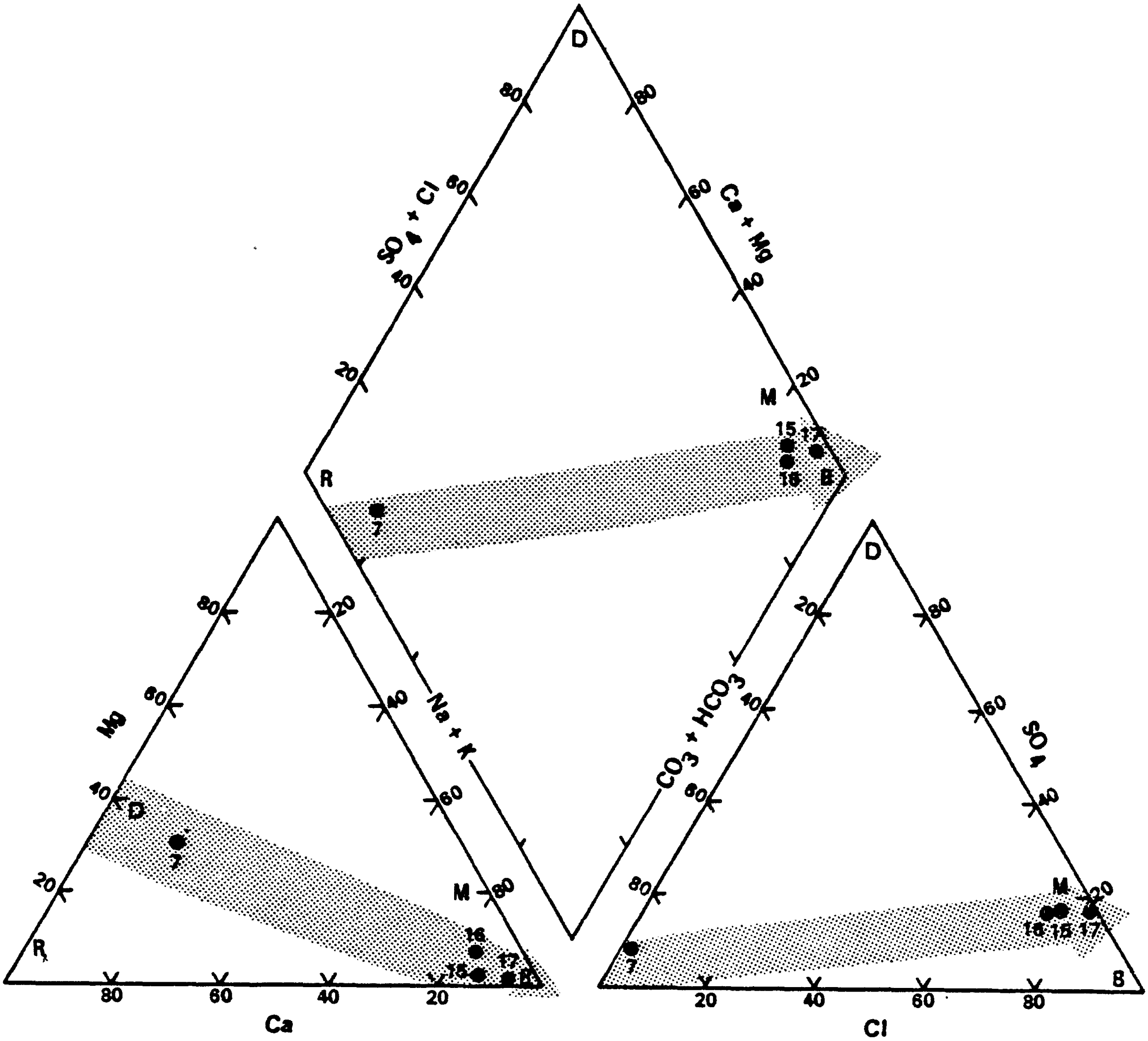


Figure 14.--Evolution of ground-water geochemistry downgradient along generalized regional flow path 2.

EXPLANATION FOR FIGURE 14

Well Identification and Dissolved Solids

Well number	Latitude	Longitude	Dissolved Solids (mg/L)
7	45.833	109.964	1,240
15	46.682	107.905	5,500
16	46.714	107.674	6,000
17	46.694	107.631	5,730

Percentage of Cations

Calcium	Magnesium	Sodium	Potassium
53	27	17	3.2
11	2.8	82	3.9
9.1	2.4	84	4.4
6.2	1.6	88	3.8

Percentage of Anions

Bicarbonate	Carbonate	Sulfate	Chloride
91	0	6.8	1.9
7	0	17.9	74
9	0	18.0	73
2	0	15.9	82

Symbols

● Montana

➡ Dominant pathway

Water Classification

R	Recharge water	M	Marine water
D	Discharge water	B	Brine water

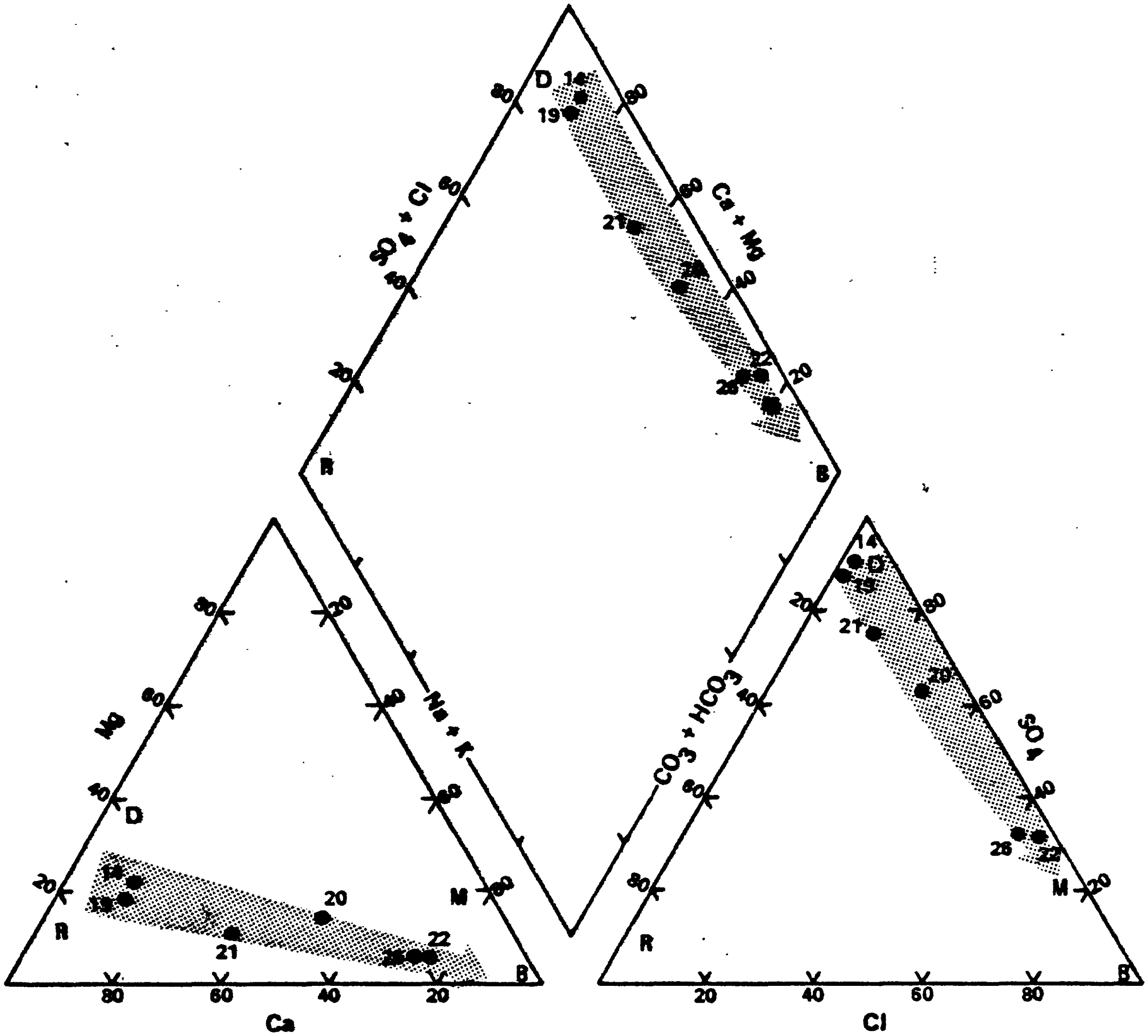


Figure 15.--Evolution of ground-water geochemistry downgradient along generalized regional flow path 3.

EXPLANATION FOR FIGURE 15

Well Identification and Dissolved Solids

Well number	Latitude	Longitude	Dissolved Solids (mg/L)
14	45.873	108.329	2,680
19	45.802	107.083	1,583
21	45.885	106.623	1,444
20	46.817	106.817	4,120
22	46.686	106.321	6,380
26	46.936	104.746	5,390

Percentage of Cations

Calcium	Magnesium	Sodium	Potassium
65	22	11	2.6
68	18	8.9	5.3
52	11	29	8.1
34	14	48	3.8
19	5.5	73	3.3
21	5.8	70	3.2

Percentage of Anions

Bicarbonate	Carbonate	Sulfate	Chloride
6	0	91.0	2.7
10	0	87.4	2.6
11	0	75.5	13
9	0	62.9	28
5	0	30.1	65
7	0	31.1	62

Symbols		Water Classification			
●	Montana	R	Recharge water	M	Marine water
⇨	Dominant pathway	D	Discharge water	B	Brine water

Flow Path 4

The trilinear diagram for flow path 4 is shown in figure 16. The cation triangle for flow path 4 shows little change in the relative proportions of cations. The anion triangle shows a dramatic change from a bicarbonate type of water to a sulfate type of water, and the quadrilinear diagram shows an evolution characterized by a change from a high calcium-magnesium bicarbonate water to a calcium-magnesium sulfate water (pathway R→D, fig. 4). The behavior shown along the evolutionary pathway for flow path 4 is consistent with the mechanisms of calcite precipitation driven by dissolution of gypsum and dolomite.

Flow Path 5

The trilinear diagram shown in figure 17 represents the geochemical evolution of ground water down flow path number 5. From the evidence furnished by maps of chemical constituents, well number 7 on the diagram should not be considered as part of this flow path. Along flow path 5, the cation triangle shows decreases in calcium and magnesium with increasing sodium. The anion triangle shows a substantial decrease in bicarbonate down the flow path with significant increases in sulfate and chloride. The behavior of sulfate is variable, showing an increase of approximately 60 percent followed by a 30-percent downgradient decrease. The quadrilinear diagram is consistent with an evolution from a recharge to a discharge type of water followed by development of a brine.

When the indications along the flow path are considered in conjunction with the geology, the possible mechanisms are:

1. Dissolution of gypsum, halite, and dolomite with precipitation of calcite.
2. A change in facies from a dolomite to an evaporite as water moves downgradient toward Midwest, Wyoming.
3. Leakage from the overlying or underlying unit.

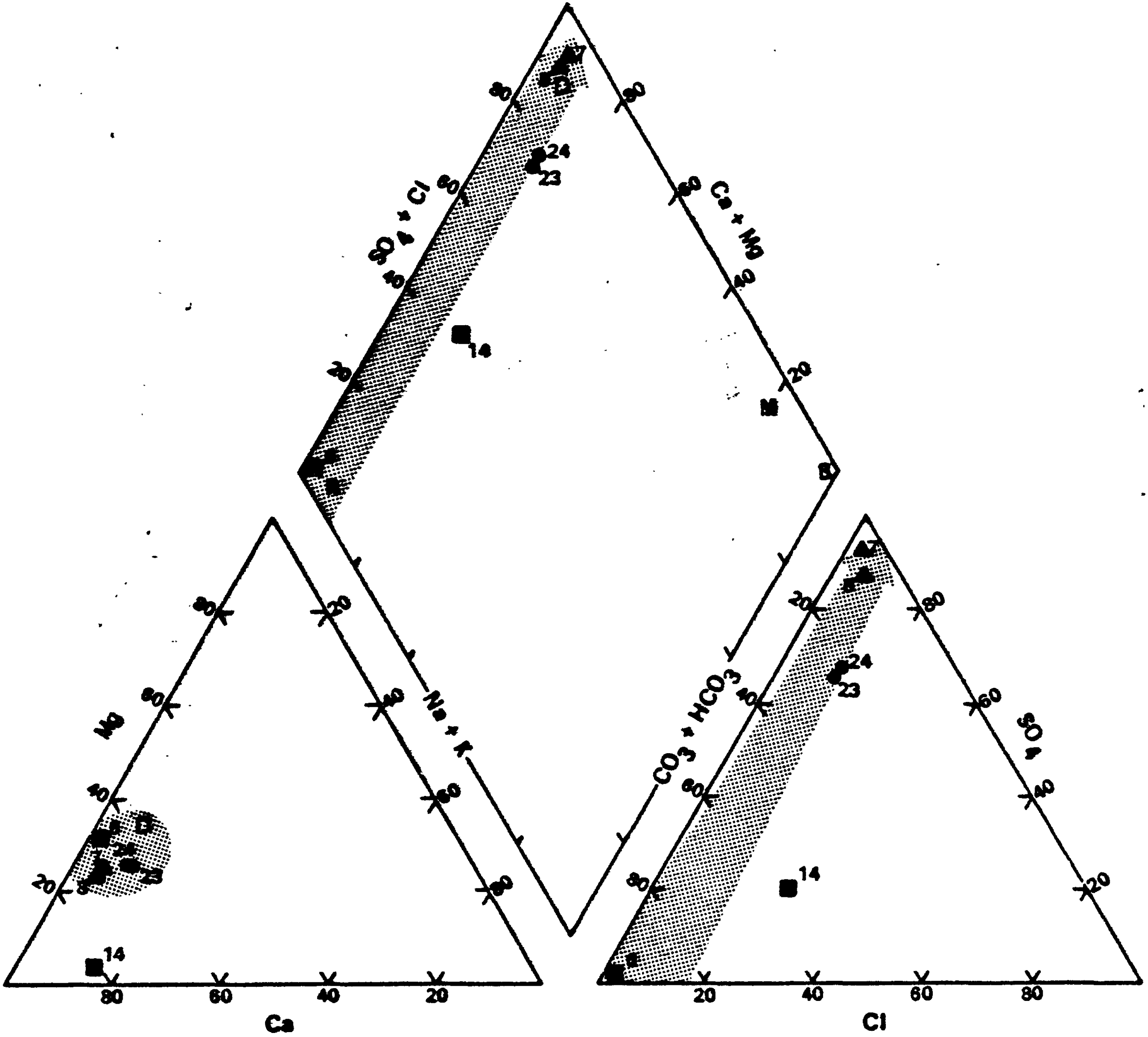


Figure 16.--Evolution of ground-water geochemistry downgradient along generalized regional flow path 4.

EXPLANATION FOR FIGURE 16

Well Identification and Dissolved Solids

Well number	Latitude	Longitude	Dissolved Solids (mg/L)
6	44.575	106.893	191
23	45.047	105.206	955
24	45.131	105.099	1,000
14	44.932	104.559	930
8	44.964	103.775	2,630
7	44.982	103.750	2,410

Percentage of Cations

Calcium	Magnesium	Sodium	Potassium
66	32	1.6	0.3
63	25	11	1.4
63	25	10	1.3
81	3.0	14	1.8
71	23	5.0	0.8
69	24	4.2	2.4

Percentage of Anions

Bicarbonate	Carbonate	Sulfate	Chloride
97	0	1.79	1.1
23	0	66.6	10
22	0	68.2	10
55	0	20.1	24
8	0	87.6	4.7
5	0	93	2.0

Symbols

● Montana
▲ South Dakota
■ Wyoming
➡ Dominant pathway

Water Classification

R Recharge water
D Discharge water
M Marine water
B Brine water

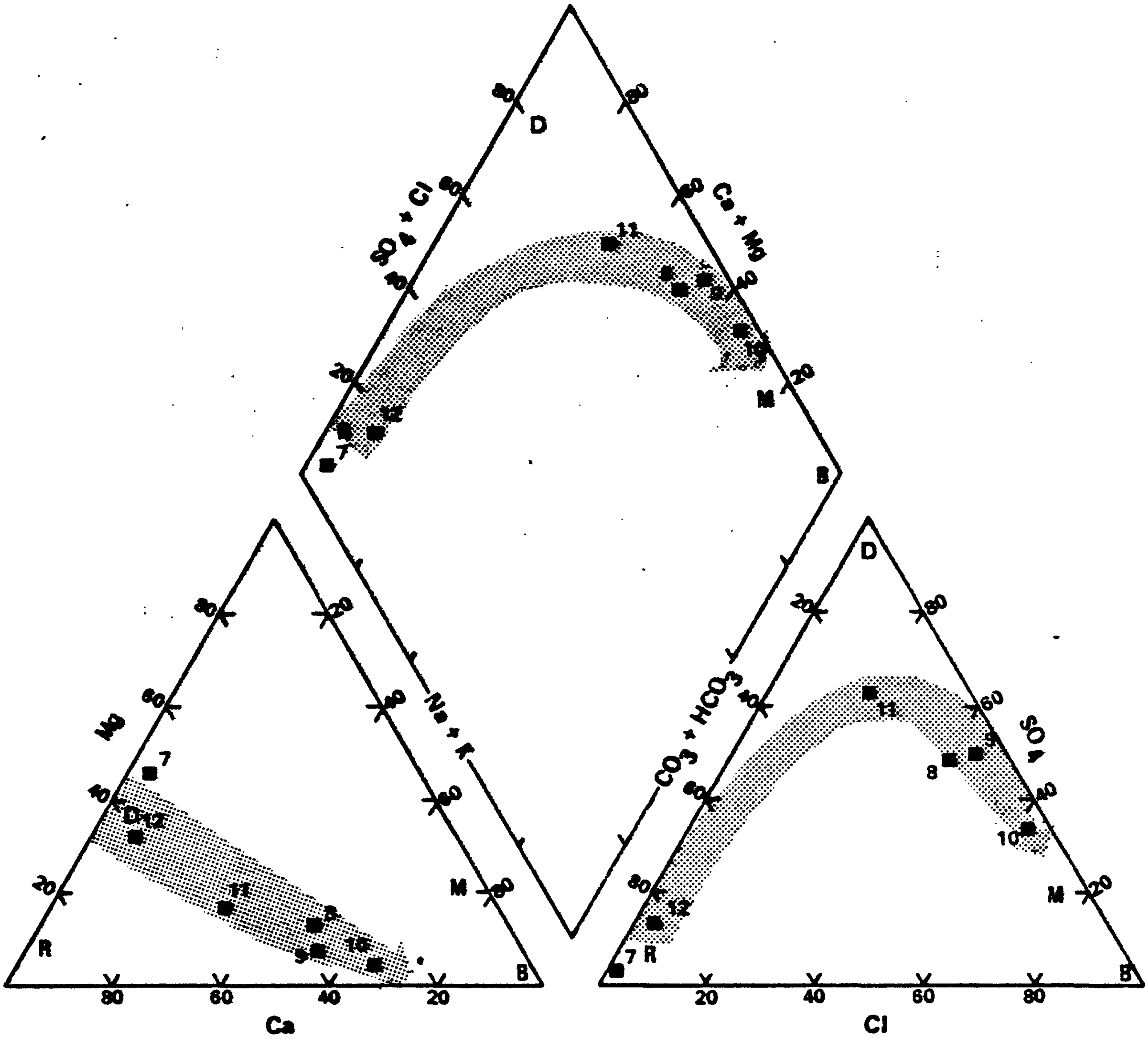


Figure 17.--Evolution of ground-water geochemistry downgradient along generalized regional flow path 5.

EXPLANATION FOR FIGURE 17

Well Identification and Dissolved Solids

Well number	Latitude	Longitude	Dissolved Solids (mg/L)
12	42.764	105.689	259
11	42.809	105.873	718
10	43.317	106.186	3,430
9	43.393	106.385	2,570
8	43.535	106.591	2,180
7	44.186	106.829	164

Percentage of Cations

Calcium	Magnesium	Sodium	Potassium
58	33	7.5	1.6
49	18	30	2.3
27	6.4	63	3.4
36	9.8	52	2.2
35	15	48	1.9
49	48	2.9	0.8

Percentage of Anions

Bicarbonate	Carbonate	Sulfate	Chloride
82	0	15.4	2.7
18	0	64.0	18
4	0	34.7	61
5	0	50.9	44
10	0	50.1	40
94	0	4.86	0.8

Symbols

■ Wyoming

⇨ Dominant pathway

Water Classification

R Recharge water

M Marine water

D Discharge water

B Brine water

Flow Path 6

The geochemical evolution of the water along flow path number 6 is shown in figure 18. Along this flow path, wells numbered 14 and 18 in Wyoming plot off the line expected for a smooth evolutionary trend. These minor deficiencies are explained easily by the presence of the numerous faults and variable lithologies in the immediate vicinity of the Black Hills.

Since the concentrations of dissolved solids along flow path 6 are all less than 1,000 milligrams per liter, the anomalous position of well number 18 must be explained in terms of the highly variable lithologies observed in the vicinity of the Black Hills, or the mixing of waters via movement along the numerous faults in the Black Hills.

The cation triangle shows no clear evolutionary trend. All wells along this flow path have a chemistry consistent with the dissolution of dolomite and calcite. The anion triangle shows a decrease in bicarbonate and an increase in sulfate down the flow path with chloride remaining relatively constant.

The quadrilinear diagram shows the evolution of a ground water along the R→D pathway of figure 4. These evolutionary paths are consistent with congruent dissolution of dolomite and gypsum in a gypsum-dominated system accompanying calcite precipitation.

Flow Path 7

Along flow path number 7 (fig. 19), wells 20 and 23 in Wyoming are at virtually the same location, and their reversal in position on the trilinear diagram may be explained by the natural variability of the system. Well number 11 in South Dakota is too far downgradient on the presumed flow path to be associated with flow path number 7. The evolutionary path discussed below consists of flow from wells 20, 21, 22, and 23, treated as a group, downgradient through wells 18 → 10 → 3.

The cation triangle along flow path number 7 shows increases in sodium with decreases in calcium and magnesium as the waters flow downgradient.

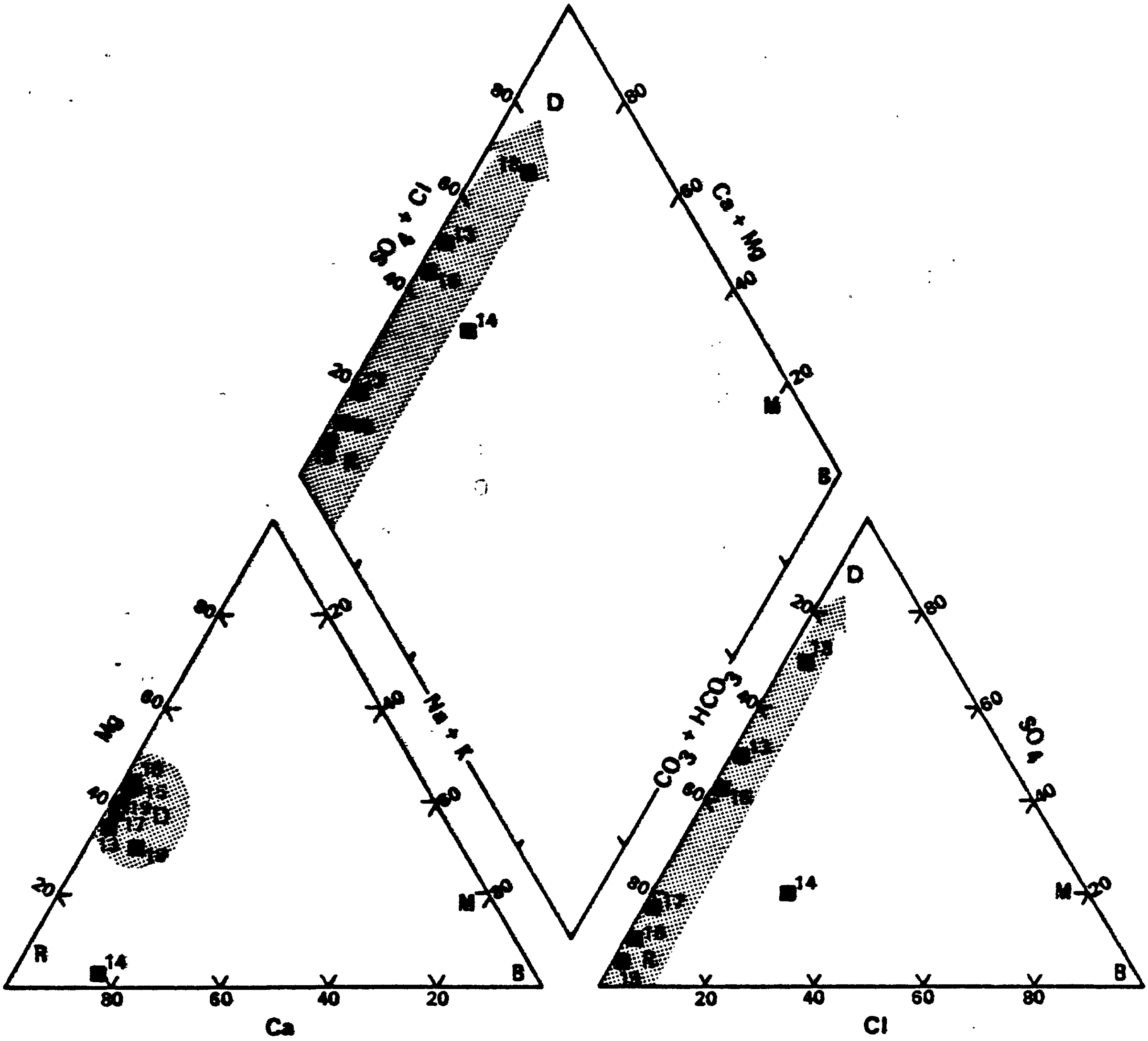


Figure 18.--Evolution of ground-water geochemistry downgradient along generalized regional flow path 6.

EXPLANATION FOR FIGURE 18

Well Identification and Dissolved Solids

Well number	Latitude	Longitude	Dissolved Solids (mg/L)
18	43.793	104.385	374
19	43.968	104.353	273
17	43.968	104.412	311
16	43.964	104.496	267
15	44.121	104.640	456
13	44.574	104.697	512
14	44.932	104.559	930

Percentage of Cations

Calcium	Magnesium	Sodium	Potassium
60	30	7.9	2.1
59	40	1.0	0.5
60	38	1.6	0.4
54	43	1.5	1.0
55	42	1.4	0.6
62	35	1.8	0.6
81	3.0	14.1	1.8

Percentage of Anions

Bicarbonate	Carbonate	Sulfate	Chloride
27	0	69.2	3.6
93	0	6.69	0.4
82	0	17.4	0.3
88	0	11	0.4
56	0	43.4	0.3
50	0	49.3	0.8
55	0	20.1	24

Symbols

■ Wyoming

⇨ Dominant pathway

Water Classification

R	Recharge water	M	Marine water
D	Discharge water	B	Brine water

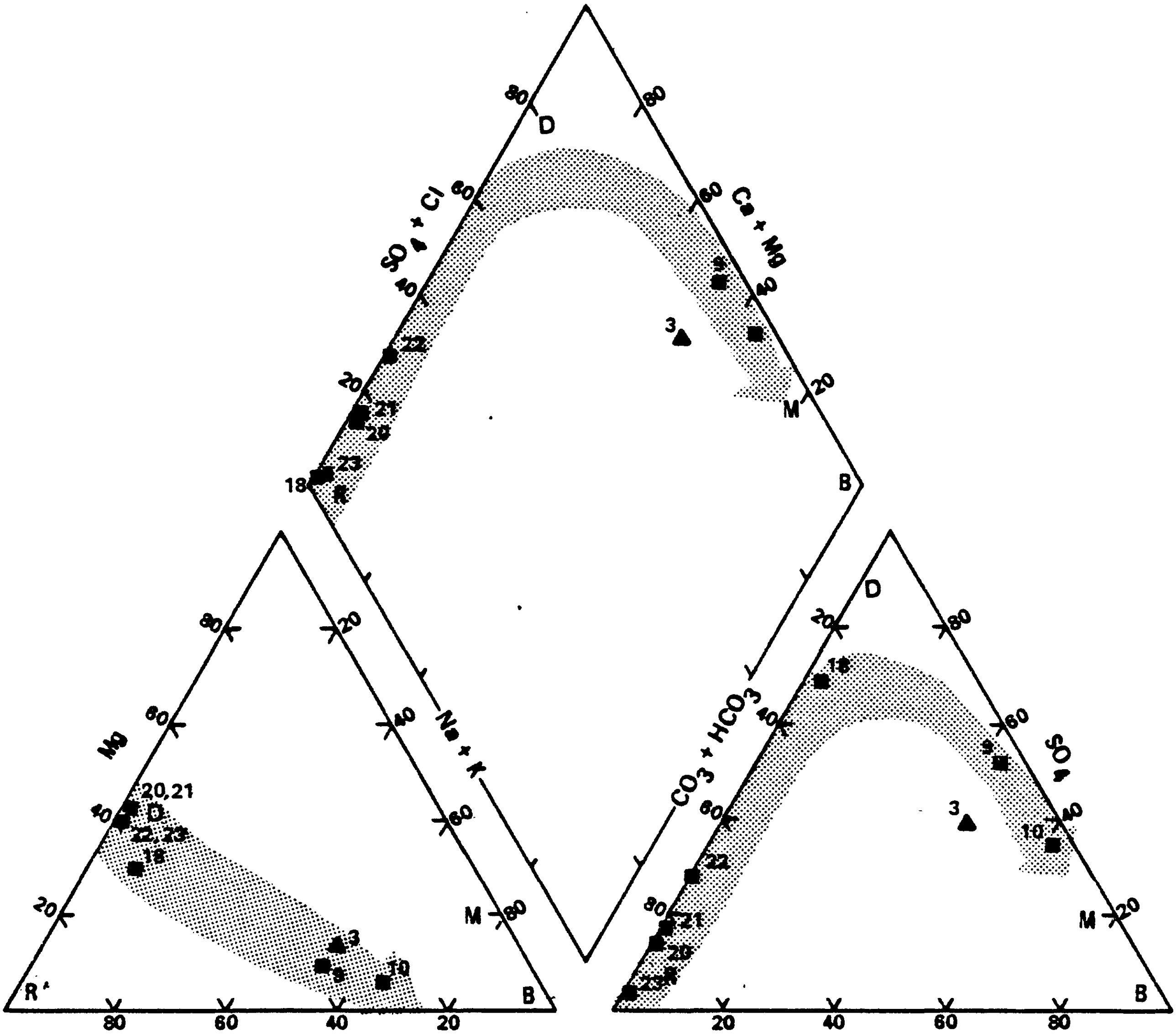


Figure 19.--Evolution of ground-water geochemistry downgradient along generalized regional flow path 7.

EXPLANATION FOR FIGURE 19

Well Identification and Dissolved Solids

Well number	Latitude	Longitude	Dissolved Solids (mg/L)
20	43.861	104.186	309
23	43.886	104.108	268
21	43.861	104.194	302
22	43.841	104.186	351
18	43.793	104.385	374
3	43.234	103.861	1,070
10	43.317	106.186	1,140
9	43.393	106.385	2,280

Percentage of Cations

Calcium	Magnesium	Sodium	Potassium
55	42	2.0	0.9
57	40	2.2	1.0
56	42	2.0	.9
57	40	1.7	.8
60	30	7.9	2.1
32	14	51	2.7
27	6.4	63	3.4
36	9.8	52	2.2

Percentage of Anions

Bicarbonate	Carbonate	Sulfate	Chloride
84	0	14.9	0.8
95	0	4.28	0.7
82	0	17.0	0.6
71	0	27.8	0.9
27	0	69.2	3.6
17	0	37.9	45
4	0	34.7	61
5	0	50.9	44

Symbols

▲ South Dakota

■ Wyoming

⇨ Dominant pathway

Water Classification

R Recharge water

D Discharge water

M Marine water

B Brine water

The anion triangle shows a change from a bicarbonate-rich water to one relatively enhanced in sulfate followed by an enrichment in chloride.

The quadrilinear diagram is consistent with water that evolves from a recharge to discharge-type water, followed by brine evolution (fig. 4). The mechanisms consistent with data presented in figure 21 are:

1. Dissolution of dolomite, gypsum, and halite with precipitation of calcite.
2. Leakage of a Na-Mg-Cl-SO_4 brine into the system.

Flow Path 8

The trilinear diagram for wells along flow path 8 are shown in figure 20. The evolution along this flow path matches the pathway recharge to discharge in figure 4. The cation diagram for this flow path indicates no clear trend, with virtually all of the wells plotting in the field of dominantly magnesium and calcium water. The anion diagram shows more variability; the waters evolve from dominantly bicarbonate to dominantly sulfate with a small increase in chloride.

The quadrilinear part of the trilinear diagram (fig. 20) shows a general evolution from a recharge type of water to a discharge water (fig. 4).

The evolutionary path shown in figure 22 is consistent with the mechanisms:

1. Dedolomitization, that is dissolution of gypsum and dolomite, with precipitation of calcite.
2. Water that originated in a dolomitic- to low-magnesium calcite facies moving into contact with an evaporite facies.
3. Leakage from an overlying or underlying unit.

Examples of Use

As an example of the use of chemical data and the trilinear diagram, consider the polygon bounded by the wells numbered 8, 9, 10, 11, and 12 in Wyoming. The data for these wells are shown in table 14. Table 14 was

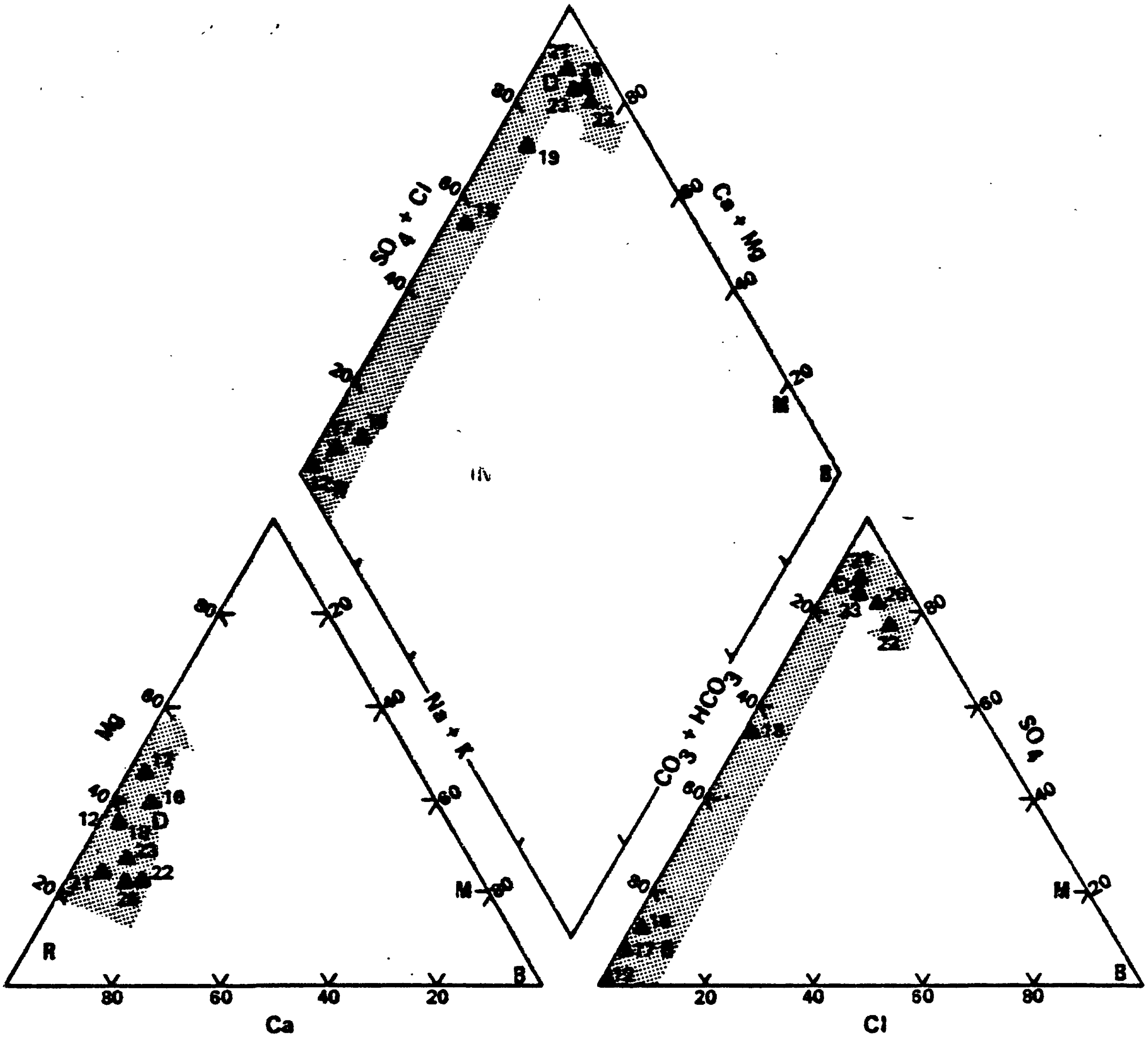


Figure 20.--Evolution of ground-water geochemistry downgradient along generalized regional flow path 8.

EXPLANATION FOR FIGURE 20

Well Identification and Dissolved Solids

Well number	Latitude	Longitude	Dissolved Solids (mg/L)
12	44.285	103.484	269
17	44.135	103.329	222
16	44.059	103.302	
18	44.150	103.079	461
19	44.089	101.650	1,080
22	44.361	101.277	1,980
21	44.623	101.302	2,030
23	45.000	101.238	2,200
26	44.373	100.849	2,010

Percentage of Cations

Calcium	Magnesium	Sodium	Potassium
60	39	1.1	0.3
51	46	2.3	1.1
53	40	5.4	1.9
60	36	2.8	1.4
62	27	8.9	2
63	22	13	1.2
69	24	4.9	1.3
61	28	8.2	2.2
66	22	10	1.6

Percentage of Anions

Bicarbonate	Carbonate	Sulfate	Chloride
98	0	2.20	0.3
92	0	6.83	1.0
86	0	12.6	1.6
44	0	55.7	.4
26	0	67.3	6.3
8	0	78.2	14
8	0	87.2	4.4
9	0	85.1	5.6
8	0	82.2	10.2

Symbols	Water Classification		
▲ South Dakota	R Recharge water	M Marine water	
⇨ Dominant pathway	D Discharge water	B Brine water	

Table 14.--*Concentrations of selected chemical constituents from selected wells in Wyoming, in milligrams per liter*

Well number on plates	Well name	Calcium	Magnesium	Sodium	Chloride	Sulfate	Bicarbonate	Dissolved solids
12	Barber Ranch Spring	56	19	8.3	4.4	34	230	259
11	Conoco-175	110	25	77	70	340	123	718
10	MKM	290	41	760	1,200	920	130	3,430
9	Shidler	300	49	490	620	970	120	2,570
8	Conoco-44	250	61	380	490	840	220	2,180

extracted directly from the tables in the supplementary data section at the end of the report; it shows identification information, concentrations of major constituents, and dissolved solids.

The trilinear diagram for flow path number 5 (fig. 17) shows that the waters along this flow path are following an evolutionary trend from recharge to discharge. Furthermore, from table 14, one sees that the recharge area (wells 11 and 12, Wyoming) is typified by water containing less than 100 milligrams per liter of chloride, from 34 to 340 milligrams per liter of sulfate, and a dissolved-solids concentration ranging from 259 to 718 milligrams per liter. The downgradient wells have dissolved-solids concentrations from 2,180 to 3,430 milligrams per liter, and sulfate concentrations ranging from 840 to 970 milligrams per liter. From the reaction path in figure 17 and the data in table 14, the general chemistry within the quadrilateral outlined by these wells can be predicted. Waters from a well drilled inside that area should have sulfate concentrations at least as large or larger than those in the recharge area, but probably no greater than 900 milligrams per liter; chloride concentrations should range from about 70 to 1,000 milligrams per liter. The actual concentration of observed chloride would depend on proximity of the sample point to the brines observed in the vicinity of Midwest, Wyoming. Using logic analogous to that outlined in the preceding paragraphs in addition to the data contained in table 14, the freshwater-head map (pl. 1), and the appropriate trilinear diagram, one can predict the expected composition of water that would be obtained from wells in large parts of the study area.

ENVIRONMENTAL GEOCHEMISTRY

A summary of environmentally significant constituents and their concentrations in the Madison aquifer system is shown in table 15. The constituents gross alpha, gross beta, and fluoride were observed to exceed the limits recommended by the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 1976, 1976 [1978], and 1977).

Table 15.--*Statistical summary for concentrations of selected environmentally significant constituents in water from the Madison aquifer system*

[µg/L = micrograms per liter; pCi/L = picocuries per liter]

Recharge area	Parameter	Elements										
		Arsenic (µg/L)	Barium (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Lead (µg/L)	Mercury (µg/L)	Selenium (µg/L)	Fluoride (µg/L)	Zinc (µg/L)	Gross alpha (pCi/L)	Gross beta (pCi/L)
Bighorn Mountains:	Mean----------------	4.5	41.7	---	1.7	1.0	---	1.0	1,210	31.67	342.2	73.6
	Standard deviation--	7.6	66.86	---	4.0	1.5	---	1.0	1,530	39.27	644.2	117.84
	Range---------------	0.0-25.0	0.0-200	---	0.0-10.0	0-5.0	---	0.0-4.0	100-4,400	0.0-140	2.4-1,900	0.3-350
Black Hills:	Mean----------------	2.0	6.2	2.6	4.0	2.0	0.018	1.74	1,440	132.11	288.3	45.22
	Standard deviation--	2.1	8.4	6.6	7.0	6.0	.062	2.43	1,300	204.47	882.09	97.05
	Range---------------	0.0-11.0	0.0-300	0.0-3.0	0.0-20.0	0.0-29.0	0.0-0.3	0.0-8.0	0.0-3,700	0-840	4.0-4,000	2.1-440.0
Big Snowy Mountains:	Mean----------------	4.0	0.0	0.0	0.0	1.62	.038	.50	1,725	15.88	17.10	11.21
	Standard deviation--	5.01	0.0	0.0	0.0	1.06	.106	.534	740	22.64	15.98	11.04
	Range---------------	0.0-14.0	0.0	0.0	0.0	0.0-3.0	0.0-0.30	0.0-1.0	900-3,200	0.0-70	2.1-52.0	1.9-34
Beartooth Mountains:	Mean----------------	2.54	84.62	0.0	2.31	1.846	.115	.693	3,120	9.62	214.08	94.25
	Standard deviation--	2.84	98.71	0.0	4.38	.689	.331	1.03	2,130	12.05	208.46	74.39
	Range---------------	0.0-8.0	0.0-200	0.0	0.0-10.0	0.0-3.0	0.0-1.20	0.0-3.0	200-5,400	0.0-40.0	2.4-640	1.1-220
	Limits for public water supplies	1/ 50	1/ 1,000	1/ 10	1/ 50	1/ 50	1/ 2.0	1/ 10.0	3/	2/ 5,000	1/ 15	1/ 50

1/ U.S. Environmental Protection Agency, 1976 [1978]. Limits for fluoride based on annual average of the maximum daily air temperatures for the location in which the community water system is situated (see page 5 of reference). Concentration of gross beta particle activity based on the statement: "If the gross beta particle activity exceeds 50 pCi/L, an analysis of the sample must be performed to identify major radioactive constituents present and the appropriate organ and total body doses shall be calculated. . . ."

2/ U.S. Environmental Protection Agency, 1977.

3/ National Interim Primary Drinking Water Regulations, Public Law 93-523, Federal Register, August 27, 1980, Section 141.11. Fluoride limit for public water supplies for Montana and Wyoming is 2,000 µg/L and for North Dakota and South Dakota 2,400 µg/L.

Wells in which gross alpha particle activity exceeds the U.S. Environmental Protection Agency recommended limit of 15 picocuries per liter and those wells that may exceed the recommended limit of 50 picocuries per liter for gross beta particle activity are shown in table 16. The 50 picocurie per liter limit applies when the activity of strontium-90 exceeds 8 picocuries per liter and the activity of tritium is less than 20,000 picocuries per liter. The qualifier "may" is used because the levels of strontium-90 were not measured. A listing of the wells that exceed the recommended limits for fluoride is shown in table 17.

EQUILIBRIUM MODELS

Introduction

Knowing whether a water is undersaturated, supersaturated, or at equilibrium with a particular solid phase is an invaluable aid in deducing the controlling chemical mechanism in an aqueous system. Whether a water is undersaturated, supersaturated, or at equilibrium with a particular solid phase depends on the magnitude of the saturation index. The saturation index (SI) is defined as the ratio of the ion activity product (IAP) to the equilibrium constant, corrected for temperature (K_T), and is expressed by:

$$SI = \log \frac{(IAP)}{K_T} \quad .$$

If the SI is positive, the solution is supersaturated with respect to the considered solid phase, and the potential exists for precipitation of the solid phase. If the SI is negative, the system is undersaturated with respect to the solid phase, and the potential exists for dissolution of the solid phase. If the SI is zero, the aqueous system is in equilibrium with the solid phase.

The IAP for a solid phase has the form of the equilibrium constant for the dissociation of the solid phases. Using the dissolution of calcite ($CaCO_3 = Ca^{+2} + CO_3^{-2}$) as an example:

$$IAP = a_{Ca^{+2}} \, a_{CO_3^{-2}}$$

Table 16.--*Listing of wells and springs where water contained excessive concentrations of gross alpha particle activity, gross beta particle activity, or both*

[Underlined value exceeds limits established by U.S. Environmental Protection Agency, 1976 (1978)]

State	Well or spring name	Picocuries per liter	
		Gross alpha	Gross beta
Montana:	Gore Hill	19	18
	Bough Ranch	52	34
	Vanek Warm Spring	18	1.9
	Bluewater Spring	53	38
	Landusky Spring	23	12
	HTH #3	170	63
	Keg Coulee	180	150
	Texaco C115X	180	180
	Sumatra	58	160
	Sleeping Buffalo	150	61
	Sarpy Mine	130	77
	Mysse	560	170
	Colstrip	640	110
	Moore	300	220
	Ranch Creek	63	15
	Belle Creek	38	12
	Gas City	410	150
South Dakota:	Delzer #1	81	38
	Delzer #2	200	39
	Black Hills Cemetery	18	3.2
	Dupree	410	82
	Hamilton	150	27
	Hilltop Ranch	4,000	440
	Eagle Butte	110	44
	Murdo	230	68
	Prince	370	93
	Bean	18	8.7
Wyoming:	Conoco #44	350	68
	Shidler	270	69
	MKM	190	93
	Conoco #175	1,900	350
	Barber Ranch Spring	18	4.1
	Self	20	5.4

Table 17.--*Listing of wells and springs where water contained excessive concentrations of fluoride*

[Values exceed those listed in the National Interim Primary Drinking Water Regulations, Public Law 93-523, Federal Register, August 27, 1980, Section 141.11]

State	Well or spring name	Well or spring number	Fluoride (milligrams per liter)	Standard
Montana	Gore Hill	2	2.4	2.0
	Bough Ranch	5	3.2	
	Keg Coulee	15	5.2	
	Texaco C115X	16	5.4	
	Sumatra	17	4.9	
	Sleeping Buffalo	18	3.3	
	Sarpy Mine	19	4.5	
	Mysse	20	4.2	
	Colstrip	21	4.7	
	Moore	22	5.4	
	Ranch Creek	23	3.3	
	Belle Creek	24	3.6	
	Gas City	26	4.7	
South Dakota	Delzer #2	8	3.6	2.4
	Hamilton	21	3.4	
	Hilltop	22	2.9	
	Eagle Butte	23	3.7	
	Midland	24	2.8	
	Murdo	25	2.6	
	Prince	26	3.4	
Wyoming	Conoco #44	8	3.0	2.0
	Shidler	9	3.5	
	MKM	10	4.4	
	HTH #1	14	2.8	

where a is the activity (effective concentration) of the species considered, in this case the calcium ion (Ca^{+2}), and the carbonate ion (CO_3^{-2}).

The activity is calculated from

$$a_i = \gamma_i M_i$$

where:

γ_i is the activity coefficient of species i, and

$[M_i]$ represents the molality of the species i corrected for ion pairing and complexation.

The calculation of saturation indices for the species considered in this paper were made using the computer code WATEQF developed by Plummer and others, (1978). The WATEQF computer code is a FORTRAN IV version of the original PL-1 code written by Truesdell and Jones (1974). An overview of the steps in WATEQF is shown in table 18.

Thermodynamic Data

The thermodynamic data used in the calculation of the saturation indices are shown in table 19. Table 19 does not represent the complete WATEQF data base; it contains the reactions supported by the analytical data obtained from the water samples collected during the course of the project.

As indicated in table 18, the value of K must be adjusted from the reference temperature to the measured temperature prior to the calculation of the saturation index. The equation used by WATEQF to perform this adjustment is:

$$\mathrm{Log}K_T = A + BT + C/T^2 + DT^2 + E/T^2$$

where $\log K_T$ is the value of equilibrium constant at T, the measured temperature, and A, B, C, D, and E are the fitted coefficients to experimental data. The phases and constituents available with WATEQF are shown in table 20. For cases where sufficient data were not available to fit a temperature dependent expression for $\log K_T$, WATEQF uses the vant'Hoff equation to adjust the equilibrium constant to a new temperature.

Table 18.--*Overview of steps in WATEQF*

Step	Summary of activity
1. Input analytical data.	
2. Convert analytical data to molality.	
3. Initialize.	Starting values of the concentrations of the free ions are estimated.
4. Calculate ionic strength (I.S.).	
5. Calculate activity coefficients.	Activities are calculated for each species considered on basis of extended Debye-Hückel equation ($I.S.<0.1m$) or the Davie's equation ($I.S.<0.5m$).
6. Solve set of simultaneous equations.	Equations of mass action are solved to obtain speciation.
7. Adjust molalities.	Molalities of the free ions are computed from the total concentration in analyzed total concentration and the computed ion pairing and complexation.
8. Iterate to specified tolerance.	Check for mass balance between computed and analyzed total molalities of elements. Return to step 4 if calculations do not meet specified tolerance.
9. Calculate ion activity products (IAP) and saturation indices.	Use appropriate activities and $\log K_T$ to determine saturation state of aqueous solution with respect to various solid phases.
10. Output data.	

Table 19.--*Thermodynamic data used in calculation of saturation indices*

[I = the reaction number assigned for use within the WATEQF code; ΔH^{o}_{r} = the value of the thermodynamic variable 'heat of reaction' or 'enthalpy'; $\log K_{TO}$ = the measured equilibrium constant at 25 degrees Celsius (298.15°K)]

I number	Mineral names	Mineral or species abbreviations	ΔH^{o}_{r} ($\mathrm{KcalMol}^{-1}$)	$\mathrm{Log}K_{TO}$	Reaction
12	Dolomite	DOLOMITE	-8.2900	-17.0200	$CaMg(CO_3)_2 = Ca^{+2} + Mg^{+2} + 2CO_3^{-2}$
13	Calcite	CALCITE	-3.1900	-8.4100	$CaCO_3 = Ca^{+2} + CO_3^{-2}$
18	Anhydrite	ANHYDRIT	-3.7690	-4.5480	$CaSO_4 = Ca^{+2} + SO_4^{-2}$
19	Gypsum	GYPSUM	0.2610	-4.7590	$CaSO_4 \cdot 2H_2O = Ca^{+2} + SO_4^{-2} + 2H_2O$
143	Strontianite	STRONT	2.3610	-9.2520	$SrCO_3 = Sr^{+2} + CO_3^{-2}$
144	Celestite	CELEST	-1.0540	-6.4660	$SrSO_4 = Sr^{+2} + SO_4^{-2}$

Table 20.--*Coefficients used in the adjustment of logK for temperature*

$[\mathrm{LogK}_T = A + BT + C/T + DT^2 + E/T^2]$

Reaction number	Phase species	Coefficients				
		A	B	C	D	E
13	Calcite	13.453	-0.0401	-3,000	0.0	0.0
15	H_2SiO_4(aq)	39.478	-.065927	-12,355.1	.0	.0
25	$MgOH^+$(aq)	0.684	.0051295	0.0	.0	.0
36	H_2CO_3(aq)	-14.83435	.032786	3,404.71	.0	.0
69	HCO_3^-(aq)	-6.498	.02379	2,902.39	.0	.0
73	KSO_4^-(aq)	3.1046	.0	-673.6	.0	.0
74	$MgCO_3^o$(aq)	.991	.00667	.0	.0	.0
75	$MgHCO_3^+$(aq)	2.319	-.11056	.0	.000029812	.0
78	$CaHCO_3^+$(aq)	-2.95	.0133	.0	.0	.0
79	$CaCO_3^o$(aq)	-27.393	.05617	-4,114.0	.0	.0
90	HSO_4^-(aq)	-5.35065	.0183412	557.2461	.0	.0
92	H_2S(aq)	11.17	.02386	-3,279.0	.0	.0

The expression for the vant'Hoff equation is:

$$\mathrm{LogK}_{T} = \mathrm{LogK}_{To} - \frac{\Delta H^{o}_{r}}{2.303R} \left(\frac{298.15 - T}{(298.15)\ T} \right)$$

where:

LogK_{To} = Log K at 298.15^{o}K

R = gas constant = 1.98719 x 10^{-3} KCaLK^{-1} Mol^{-1}

ΔH^{o}_{r} = standard entholpy of reaction in KCaL Mol^{-1}

T is the temperature at which the reaction is expressed, in degrees Kelvin (K^{-}).

The saturation indices for selected phases that appear to be potentially important in the geochemical interpretation of the system are shown in table 21.

Analysis of Saturation Indices Maps

General trends in the saturation indices are shown as follows: (1) Calcite (pl. 12 in pocket), dolomite (pl. 13 in pocket), strontianite (pl. 14 in pocket), gypsum (pl. 15 in pocket), anhydrite (pl. 16 in pocket), and celestite (pl. 17 in pocket) are shown on the contour maps of saturation indices (pls. 12-17 in pocket); (2) carbonate species along each flow path are shown in table 21; and (3) sulfate species are shown in table 22.

The trends along flow path 1 are indicative of control by the dissolution of gypsum, while those along flow paths 2, 4, 5, 7, and 8 show waters that are saturated with respect to calcite, undersaturated, but approaching saturation with respect to dolomite, and undersaturated with gypsum, a set of conditions consistent with a dedolomitization reaction.

Waters along flow path 3 are oversaturated with calcite, saturated to supersaturated with respect to dolomite, and saturated with respect to gypsum in the recharge area. These saturation indices suggest that dedolomitization is not active along flow path 3. The decrease in saturation with respect to gypsum is indicative of sulfate reduction. These indications are consistent with the dissolution of gypsum and sulfate reduction.

Table 21.--*General behavior of saturation indices down flow paths--carbonates*

Flow path	Calcite	Dolomite	Strontianite
1	All values above saturation. About constant down flow path.	Just above saturation in outcrop (0.19) decreasing downgradient.	Undersaturated along flow path. Saturation state decreases downgradient.
2	All values above saturation. Increase downgradient to supersaturated values.	Undersaturated near recharge area. Values increase downgradient achieving supersaturation.	Undersaturated all along flow path. Increase downgradient.
3	All values above saturation. Increase to values above saturation downgradient.	A general downgradient increase from values near saturation to values showing slight supersaturation.	All values are undersaturated at about SI = -1.15.
4	Undersaturated in recharge area. Increases to and above the phase boundary downgradient.	Increase downgradient from values showing undersaturation in recharge areas to supersaturated values downgradient.	Undersaturated all along flow path. Begins at -2.56 and increases to -0.65.
5	Values near recharge area are near saturation and increase to values just above saturation.	Undersaturated values near recharge area. Increase downgradient to values just above saturation (+0.16).	All values undersaturated. Decreases downgradient from -1.65 to -8.14.

Table 21.--*General behavior of saturation indices down flow path--carbonates*--Continued

Flow path	Calcite	Dolomite	Strontianite
6	Variable--Enters system near saturation. Increases downgradient.	Variable--Oscillates around saturation.	Undersaturated--Increases downgradient (-1.65 to -8.14).
7	Variable but with a general downgradient increase. Stays near phase boundary (-0.107 to 0.18).	Variable--Stays just on low side of phase boundary.	Undersaturated--Shows a downgradient (-1.65 to -8.14).
8	Variable--Oscillates about the phase boundary.	Undersaturated near recharge area. Approaches phase boundary.	All undersaturated--A slight decrease downgradient.

Table 22.--*General behavior of saturation indices down flow paths--sulfates*

Flow path	Gypsum	Anhydrite	Celestite
1	Increases from undersaturated to values representative of saturation.	Undersaturated along flow path. Decreases downgradient.	Slightly undersaturated in recharge area. Increases to phase boundary. Undersaturated--Approaches saturation downgradient.
2	Undersaturated--Increases toward phase gypsum downgradient.	Undersaturated--A downgradient increase.	Undersaturated--Approaches saturation downgradient.
3	Variable--Saturated in recharge area. Increases downgradient.	Values near saturation (0.05 to 0.12). Slight decrease downgradient.	Near saturation along flow path. Slight decrease downgradient.
4	General downgradient increase from undersaturation to saturation.	General downgradient increase from undersaturation to saturation.	General downgradient increase from undersaturated to saturated.
5	Variable and undersaturated. Shows a downgradient increase.	All undersaturated. Saturation index shows downgradient increase.	Undersaturated--Increases downgradient but does not reach saturation.
6	Variable and undersaturated. Shows a downgradient increase.	All undersaturated with a general downgradient increase.	All undersaturated--Goes from undersaturated to saturation down the flow path.

Table 22.--*General behavior of saturation indices down flow paths--sulfates*--Continued

Flow path	Gypsum	Anhydrite	Celestite
7	Downgradient increase from undersaturation to phase boundary.	All undersaturated--Saturation index increases downgradient.	Undersaturated--Approaches saturation (-0.09) down flow path.
8	Undersaturated--A downgradient increase toward saturation.	Undersaturated--Increases downgradient approaching phase boundary.	Undersaturated--Increases downgradient toward phase boundary.

The saturation indices along flow path 6 show the system to be above saturation with respect to calcite and dolomite, but undersaturated with respect to gypsum. These saturation indices are consistent with control of the system by dissolution of gypsum.

DATA SUMMARY

A summary of the observed behavior for the parameters pH ($-\log a_{H+}$), partial pressure of carbon dioxide (P_{CO_2}), magnesium to calcium ratio (Mg/Ca), bicarbonate to sulfate ratio (HCO_3/SO_4), saturation index for calcite (calcite SI), saturation index for dolomite (dolomite SI), saturation index of gypsum (gypsum SI), del carbon-13, and $\delta^{34}S_{SO_4}$ down each flow path is shown in table 23. The observed trend of each parameter is represented by an arrow with ↑ signifying an increasing trend down a flow path and ↓ a decreasing downgradient trend. The arrows show only the trend of a particular parameter downgradient and contain no indication of the magnitude of the trend nor the scatter in the data.

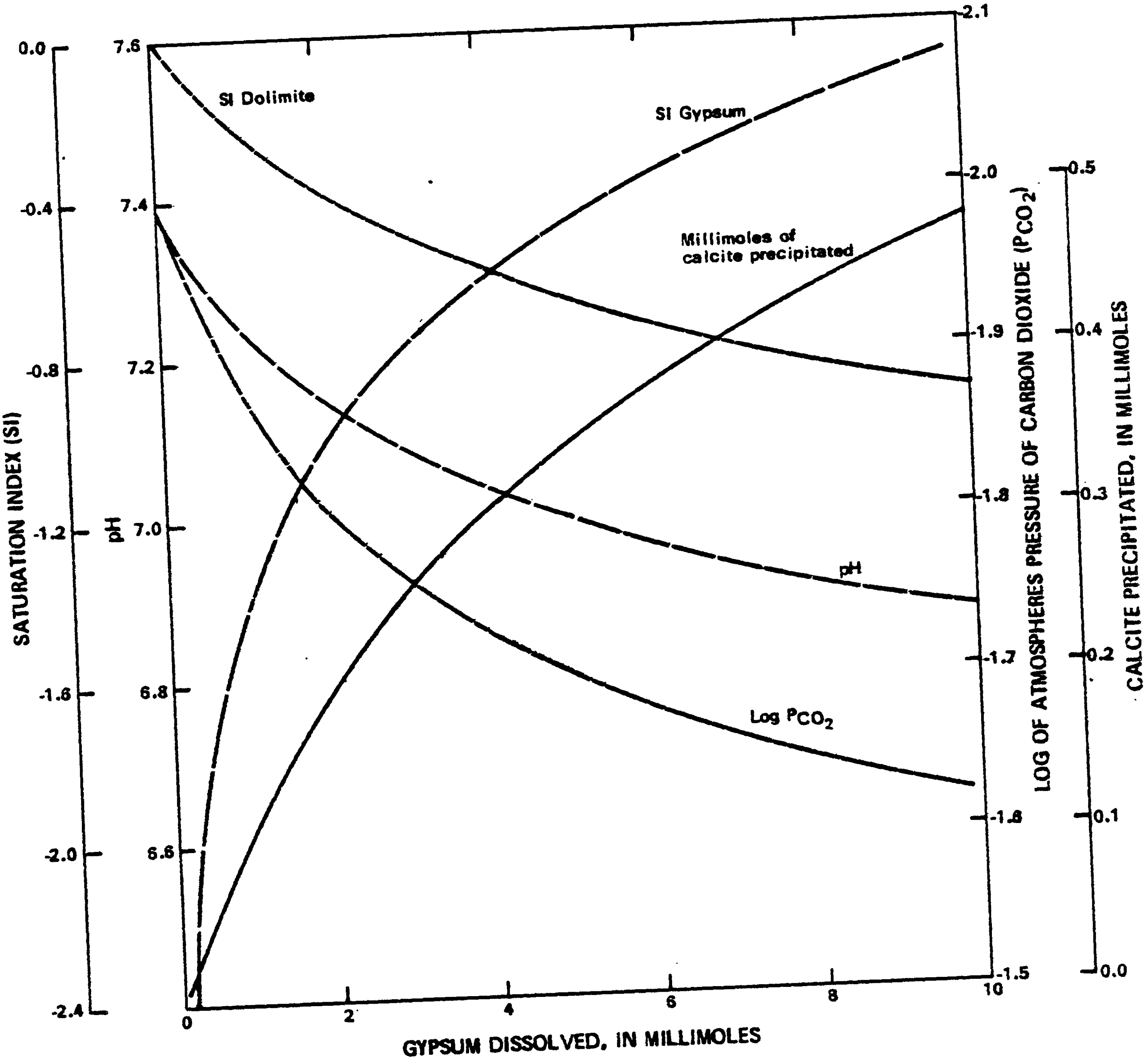
The trends of all parameters along flow paths 4, 6, 7, and 8 are identical (table 23), except for the trend in del carbon-13 along flow path 6, which decreases downgradient as opposed to downgradient increases along flow paths 4, 7, and 8.

The increase in P_{CO_2} and decreases in pH and total inorganic carbon (C_T), and increase in the saturation index of gypsum follow the trends shown in figure 21, which represents the closed system dissolution of gypsum into a water initially saturated with calcite and dolomite (L. N. Plummer, U.S. Geological Survey, written commun., 1981). As gypsum dissolves, calcite is precipitated and the water becomes increasingly undersaturated with dolomite, as shown in figure 21. Therefore, if both dolomite and gypsum are present, as in the Madison system, both dolomite and gypsum would dissolve causing precipitation of calcite. This reaction results in a decrease in pH and an increase in P_{CO_2} (pressure of carbon dioxide) along the flow path.

Table 23.--*Summary of observed behavior of parameters for each flow path*

[c = values that are constant within analytical error]

Parameter	Flow path							
	1	2	3	4	5	6	7	8
pH	↓	↓	↓	↓	↓	↓	↓	↓
P_{CO_2}	↑	↑	↑	↑	↑	↑	↑	↑
C_T	↓	↑	↑	↓	↑	↓	↓	↓
Mg/Ca	↓	↓	↓	↓	↓	↓	↓	↓
HCO_3/SO_4	↓	↓	↑	↓	↓	↓	↓	↓
Calcite SI	↑	↑	↑	↑	↑	↑	c	↑
Dolomite SI	↓	↑	↑	↑	↑	↑	↑	↑
Gypsum SI	↑	↑	↓	↑	↑	↑	↑	↑
$\delta^{13}C$	↑	↑	↑	↑	↓	↓	↑	↑
$\delta^{34}S_{SO_4}$	↑	↑	c	↑	↓	↑	↑(c)	↑



EXPLANATION

Initial solution is calcite and dolomite saturated with CO_2 at $10^{-2.0}$ Atm at 25° Celsius

Gypsum is then allowed to dissolve in equilibrium with calcite in a system closed to CO_2

Figure 21.--Theoretical evolution of a water initially saturated with calcite and dolomite as gypsum dissolves and calcite is allowed to precipitate.

Information from trends in the trilinear diagrams and saturation indices (table 24) for flow paths 4, 6, 7, and 8 also are consistent with the incongruent dissolution of dolomite caused by the dissolution of gypsum. The first in the series of reactions would be the dissolution of gypsum, calcite, and dolomite in the presence of normal soil CO_2 (10^{-3} - 10^{-1} bar) (Freeze and Cherry, 1979) resulting in approximate initial pH values of 8.3. As the recharge water moves downgradient, dissolution of gypsum causes calcite precipitation, lowering the pH. As the pH decreases in a closed system, P_{CO_2} will increase via the redistribution of the equilibrium concentration of HCO_3^-. If the five-phase (calcite, dolomite, gypsum, solution, and gas) five-component (CaO, MgO, CO_2, H_2SO_4, and H_2O) system were in equilibrium at a fixed pressure and temperature, the composition of the system would be constant, a behavior pattern generally approached near the terminus of each flow path. The fact that gypsum reaches the phase boundary on only two flow paths (1 and 4), and the fact that the magnesium to calcium ratio is continually decreasing downgradient indicates that the system does not reach the five-phase equilibrium condition described above.

Because the solid phases comprising the Madison aquifer system were deposited in a shallow marine environment, the del carbon-13 values of the solid phase should be between approximately zero and 2 per mille compared to del carbon-13 values ranging between -12 and -17 parts per thousand for soil CO_2 in semiarid regions (Mook, 1980). As the conditions in the aquifer change downgradient from those of an open system to a closed system, the del carbon-13 values resulting from dissolution of a carbonate would be expected to increase as observed for all flow paths except 5 and 6. The observed decrease in del carbon-13 along flow paths 5 and 6 has not been explained satisfactorily yet. Because both flow paths include areas of petroleum production, a mechanism involving CO_2 evolution via decarboxylation during the maturation of petroleum is logical but has not been demonstrated.

The graph of log (Meq Na + Meq K) against log (Meq Ca + Meq Mg) (fig. 10) and downgradient decrease in pH indicates that cation exchange is not a significant control of the water chemistry down flow paths 4, 6, 7,

Table 24.--*Mechanistic evidence from trilinear diagrams and saturation indices*

Flow path	Trilinear diagrams	Saturation indices
1	Dissolution of gypsum and halite to gypsum phase boundary, with cation exchange.	Calcite saturation probably maintained by calcite precipitation. Dolomite saturation maintained by dissolution of dolomite saturated solutions. Gypsum dissolution is undersaturated solution.
2	Dissolution of gypsum to phase boundary, accompanying dolomite dissolution and calcite precipitation.	Dissolution of dolomite and gypsum and calcite precipitation.
	Leakage.	
3	Dissolution of halite, gypsum, and dolomite with calcite precipitation.	Incongruent dissolution of gypsum, calcite, and dolomite in the presence of sulfate reduction and cation exchange.
	Mixing.	
4	Dissolution of gypsum and dolomite with calcite precipitation.	Dissolution of calcite, dolomite, and gypsum becoming incongruent to calcite downgradient.

Table 24.--*Mechanistic evidence from trilinear diagrams and saturation indices*--Continued

Flow path	Trilinear diagrams	Saturation indices
5	Dissolution of gypsum, halite, and dolomite with calcite precipitation. A facies change from a dolomitic to an evaporitic facies. Leakage.	Dissolution of dolomite and gypsum with calcite saturation maintained by precipitation.
6	Dissolution of dolomite and gypsum accompanying calcite precipitation.	Dissolution of dolomite and gypsum with calcite saturation maintained by precipitation.
7	Dissolution of dolomite, gypsum, and halite with calcite precipitation. Leakage.	Dissolution of dolomite and gypsum with calcite saturation maintained by precipitation.
8	Dolomite and gypsum dissolution with calcite precipitation. Facies change. Leakage.	Dissolution of dolomite and gypsum with calcite saturation maintained by precipitation.

and 8. If the dissolution of a carbonate phase is driven by the cation exchange, the pH should increase by the carbonate added to the system.

Decreasing ratios of bicarbonate to sulfate along flow paths 4, 6, 7, and 8, increasing values of $\delta^{34}S_{SO_4}$, and increasing saturation indices of gypsum downgradient indicate that sulfate reduction is not a significant mechanism along these flow paths.

Flow path 1, associated with the Little Rocky Mountains, has components of local recharge, local discharge, and some regional recharge and does not appear to be of major regional significance. Waters along this flow path appear to be controlled by precipitation of calcite in the presence of a dissolving gypsum and contained in a closed system as evidenced by the decrease in pH and C_T and increase in P_{CO_2}.

While the trilinear diagram supports cation exchange as a viable mechanism, the mechanism is not supported by the excess sodium graph (fig. 10), the increasing saturation indices for gypsum and calcite, nor the decreasing pH, as previously discussed in the section on flow paths 4, 6, 7, and 8. Sulfate reduction is ruled out as a major mechanism along flow path 1 by the decreasing bicarbonate to sulfate ratio, the downgradient increase in the saturation index of gypsum, the increase in del carbon-13, and the trilinear diagram that shows an evolutionary path inconsistent with sulfate reduction. Since the evolutionary trends of the waters in this area are not consistent with the mechanism of sulfate reduction, and since the area is an area of local recharge superimposed on a regional flow system, the most reasonable mechanism for flow path 1 would be one tied to the mixing of waters from the two sources of water: local and regional flow.

The trends along flow path 2 are identical to those of flow path 4 except for the increase in total inorganic carbon. The similarity in trends eliminates sulfate reduction and cation exchange as significant mechanisms along this flow path. The pH and P_{CO_2} trends are consistent with the incongruent dissolution of a carbonate phase in a closed system; the increase in total inorganic carbon is indicative of carbon input from another source.

The source of carbon, as yet undetermined, is most likely coming from within the system because of the presumed closed system conditions.

The trends in pH, P_{CO_2}, calcite SI, and dolomite SI along flow path 3 are consistent with the incongruent dissolution of a carbonate phase under closed system conditions; the downgradient increase in total inorganic carbon is indicative of carbon input from another source such as sulfate reduction, methaneogensis, coalification, or leakage.

The action of sulfate reduction as a controlling mechanism is supported by the increases in C_T and the bicarbonate to sulfate ratio, the decrease in the saturation index of gypsum, and the presence of faculative thermophilic sulfate reducing bacteria in HTH #3 at a depth of 1,750 meters and a temperature of 70 degrees Celsius (Greg Olsen, U.S. Geological Survey, written commun., 1980).

The presence of cation exchange is supported by the excess sodium graph, figure 10, and the trilinear diagram, figure 15, but not by the pH trend. Contributions by leakage through confining beds and changes in lithofacies again cannot be ruled out as possible controls.

The chemical signals associated with flow path 5 are consistent with the dedolomitization hypothesis except for the isotope ratios of del carbon-13 and del sulfur-34. Analysis of the trilinear diagram for flow path 5 supports a change in lithofacies or leakage, as well as the incongruent dissolution of dolomite in the presence of gypsum. That leakage is occurring along the northern end of flow path 5 is supported further by presence of Permian type sulfates in waters from the Mississippian aquifer.

HYPOTHESES

In the absence of mass-transfer modeling of the major system components and isotopes, and in the absence of data on sulfur-34 ratios for the sulfide phase, the following hypotheses are offered regarding the behavior of the Madison aquifer system:

1. The Madison aquifer system is active hydraulically. All uncorrected carbon-14 ages are less than 40,000 years before present. Preliminary calculations using a numeric solution to the mass-transfer equations developed by Wigley and Plummer (1978) indicate a corrected age of less than 20,000 years for these waters (Roger Lee, U.S. Geological Survey, written commun., 1982). Additional mass-transfer modeling of the system is underway to validate the results.
2. Recharge to the Madison aquifer system is from the mountainous areas. The most significant recharge on the eastern side of the Black Hills occurs during the spring of the year from storms that are on a Gulf Coast storm track.
3. The dominant control on water chemistry in the Madison aquifer system is the incongruent dissolution of dolomite (forming calcite) accompanying dissolution of gypsum.
4. Only flow path 3 associated with the Central Montana trough shows appreciable evidence of cation exchange and sulfate reduction.
5. The $\delta^{34}S_{SO_4}$ data for wells in the Powder River basin near Midwest, Wyoming indicate leakage from the overlying Permian.
6. The trilinear diagrams are consistent with leakage in several areas.
7. Along several of the flow paths, notably number 3 in Montana and number 7 in Wyoming, the discontinuous nature of the water chemistry downgradient is consistent with either a change in the dominant mineralogy contacting the waters or the mixing of waters originating from two or more sources.
8. Because of the relatively high values of P_{CO_2} in the system, the possibility of outgassing of carbon dioxide with the concomitant precipitation of calcite is likely in the higher temperature (greater than 40 degrees Celsius) wells.
9. Although the waters studied generally have a dissolved-solids concentration less than 5,000 milligrams per liter, they are not without potential environmental problems (table 25).

Table 25.--*Percentage of wells sampled, by State, exceeding National Interim Primary Drinking Water Regulations*

[Number in parentheses is number of samples taken]

State	Parameter					
	Gross alpha particle activity		Gross beta particle activity		Fluoride	
Montana	70.83	(25)	41.67	(25)	54.20	(25)
South Dakota	38.46	(27)	11.54	(27)	26.90	(27)
Wyoming	24.00	(25)	16.00	(25)	16.00	(25)

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SUPPLEMENTARY DATA

Sample Collection and Laboratory Analysis

It is an axiom of geochemical investigations that valid interpretations cannot be made with inaccurate chemical data; interpretations and modeling using inaccurate data are worse than wrong--they are misleading. Therefore, caution was applied in the selection of sampling points and in the collection of these samples. Records of wells and springs were examined to determine those wells and springs that yielded water only from the Madison aquifer system; the 75 sampling sites used in this study were the result of this screening. Because of the depth of wells and salinity of the ground water in North Dakota, no samples were obtained for geochemical studies. Because the Madison is virtually nonexistent in Nebraska, no work was done in that State.

Sampling Conditions

Samples from springs were collected as close as possible to the orifice, and wells were pumped for as long as possible before sampling to insure that the samples collected were representative of the water in the aquifer. Typically, wells were pumped until at least three or more casing volumes of water had been discharged. Where this was not possible because of the large diameter casing of the wells or because the owners did not allow the wells to be pumped for a sufficient time, the wells were pumped until the values of pH, water temperature, alkalinity, and specific conductance were stable for three consecutive sets of measurements made during a 30-minute interval.

Water Temperature

Water temperature measured at the well head must be considered as an approximation of the formation-water temperature. The difference between the temperature of the surrounding rocks and ground water and the temperature of the formation water depends on: (1) Thermal conductivity of the casing material; (2) thermal conductivity of rocks surrounding the casing; (3) difference between formation-water temperature and the temperature of overlying rocks and ground water; (4) rate of discharge; and (5) length of time the well was permitted to flow. If the temperature measured at the well head does not change significantly during the sampling period (typically 2 to 3 hours), the temperature at the well head was considered a good approximation of the temperature at depth. Temperature was measured using a set of class 1 mercury-in-glass thermometers, each of which spans a 20 degrees Celsius temperature range. The temperature was recorded to the nearest 0.1 degree Celsius.

Because it was recognized that temperatures measured at the well head are only an approximation of bottom-hole temperatures, reliability of the data was tested by comparing values measured at the well head to those predicted from the silica geothermometer. The silica geothermometer is based on the fact that solubilities of the two controlling forms of silica, quartz and chalcedony, are well known as a function of temperature (Fournier and Rowe, 1966).

A plot of the temperature as a function of silica concentration and temperature defines the field in which a particular silica concentration should plot at a specified temperature (fig. 22). If the surface temperatures were plotted outside the stability field of the silicates, the bottom-hole temperature, where available, was used; otherwise, the temperature at the surface was used.

pH

The pH of a ground-water system is a major control of the solubility of trace cations such as iron, aluminum, and mercury that form hydroxy complexes, and of the minerals that contain weak-acid anions in their structure, such as carbonates, phosphates, and silicates. For geochemical interpretation, it is extremely important to obtain accurate pH measurements. The pH of a sample measured in the laboratory may increase or decrease by as much as 1 pH unit from the pH measured at the sampling site; in this report, only onsite pH measurements have been used. The pH was measured at the sampling site using an Orion* Model 407-pH meter and a Markson combination electrode; measurements were recorded to the nearest 0.01 pH unit. The meter and electrodes were

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*Any use of trade names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

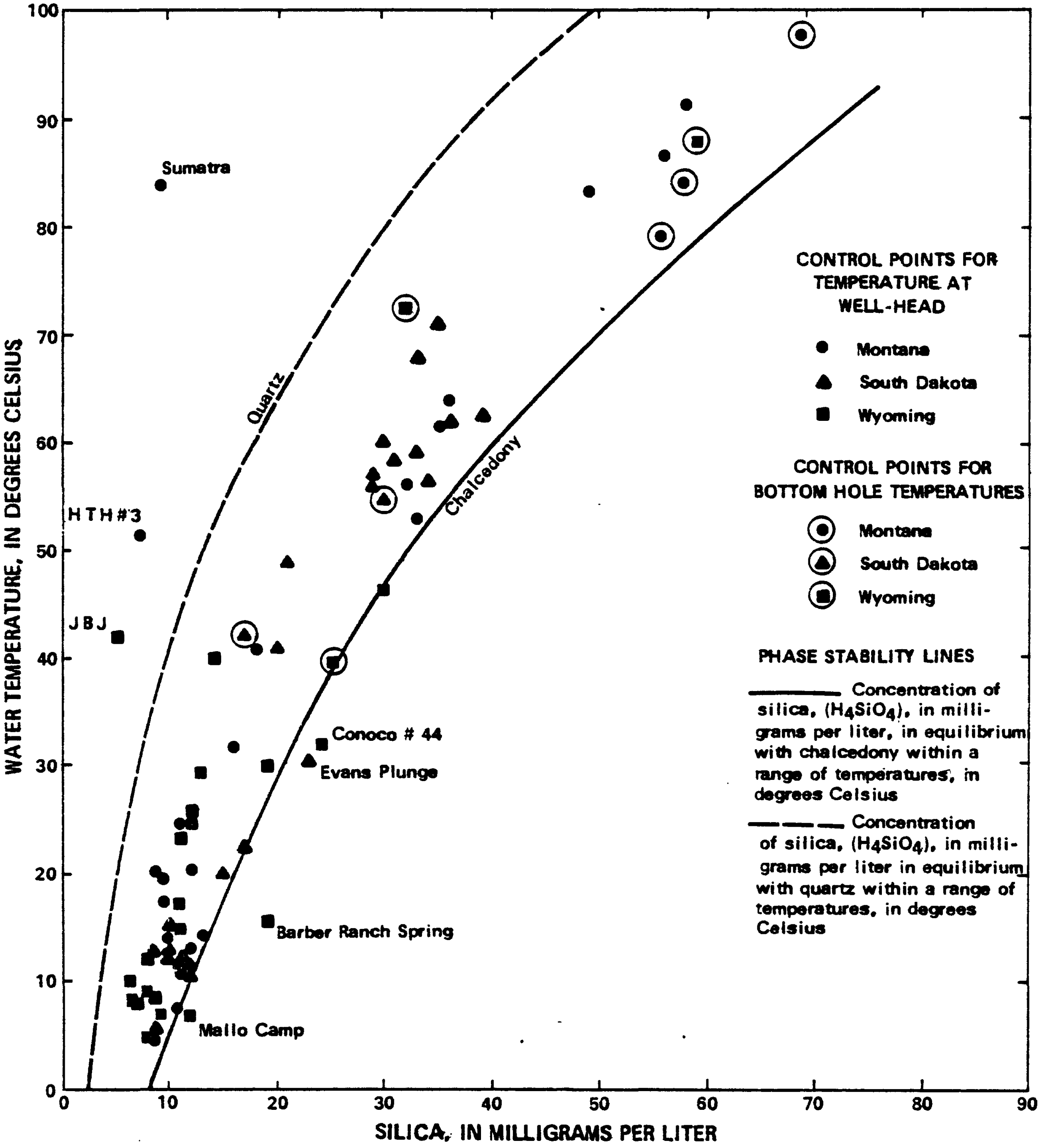

Figure 22.--Stability fields of quartz and chalcedony (silica geothermometer) with well-head and bottom-hole water temperatures superposed.

standardized using a double buffer check that bracketed the expected pH of the sample, with the buffers in thermal equilibrium with the water to be sampled.

Alkalinity

Alkalinity, a measure of the acid-neutralizing capacity of a solution, also was measured at the sampling site. Although all weak-acid anions contribute to alkalinity of a sample, the anions of the carbonate-bicarbonate acid-base system dominate in limestones, and the alkalinity is used as a measure of the total inorganic carbon in the ground-water system. Alkalinity was determined by potentiometric titration against a 0.01639 normal sulfuric acid. The end point of that titration was obtained from the second derivative titration curve (Wood, 1976).

Specific Conductance

Specific conductance (electrical conductivity) of a solution is a measure of the ability of that solution to transport current via the ions in solution. Because the amount of current transported is proportional to the number of charge carriers (ions), specific conductance may be used as an estimate of the concentration of dissolved solids (Hem, 1970). Specific conductance is used at the sampling site to help the geochemist decide how sampling should proceed. Specific conductance, at 25 degrees Celsius, was measured using a Beckman RB-3 conductivity meter and dip cell.

Sampling Prior to Laboratory Analysis

The chemical constituents selected for use in this study were chosen for three reasons: (1) To aid in geochemical interpretation of the flow system and chemical reactions controlling geochemistry of the water (constituents used in this interpretation were the major cation and anion species, stable isotopes, tritium, and carbon-14); (2) to provide information for future work in environmental geochemistry; and (3) to support other research projects (constituents determined for this purpose were trace elements, radiochemical data, and dissolved gases).

Samples for major- and trace-constituent determinations were collected and preserved according to the methods of Brown and others (1970). Samples for radiochemicals were collected, preserved, and analyzed according to procedures set forth by Thatcher and others (1977).

Analyses for all constituents, except dissolved gases, stable isotopes, and the radioactive isotopes, carbon-14 and hydrogen-3 (tritium), were performed by the U.S. Geological Survey's water-quality laboratory in Denver, Colorado, using the methods outlined in Skougstad and others (1979). Members of the U.S. Geological Survey performed these other analyses: Donald W. Fisher, dissolved gases; Tyler B. Coplen, isotopes of hydrogen and oxygen; R. O. Rye, sulfur isotopes, after concentration by Joseph Chemerys; and F. J. Pearson, carbon isotopes.

Dissolved Gases

Dissolved gases were collected to support studies on the geochemical cycle and behavior of dissolved gases in natural aqueous systems. The samples were collected at the sample source using the sampling device shown in figure 23 (Hobba and others, 1977). A vacuum was created in the side arm of the flask in the laboratory prior to being shipped to the sampling sites. Tygon plastic tubing attached at point A was inserted as far into the water stream as possible, with the stopcocks (B and C) in the flowthrough position. After at least three sample volumes had flowed through the sample container to ensure removal of adsorbed gases, the upper stopcock (C) was closed, followed by the closing of the lower stopcock (B). The sampler then was removed from the water stream and both stopcocks were opened to the side arm. All samples were analyzed for argon, carbon dioxide, helium, hydrogen, methane, nitrogen, and oxygen. Selected samples from Montana were analyzed for ethane and hydrogen sulfide.

Isotope Sampling

Samples were obtained for the radiochemical indicators, gross alpha and beta particle activity, using the methods detailed in Thatcher and others (1977). The results of the radiochemical sampling is discussed in the section,

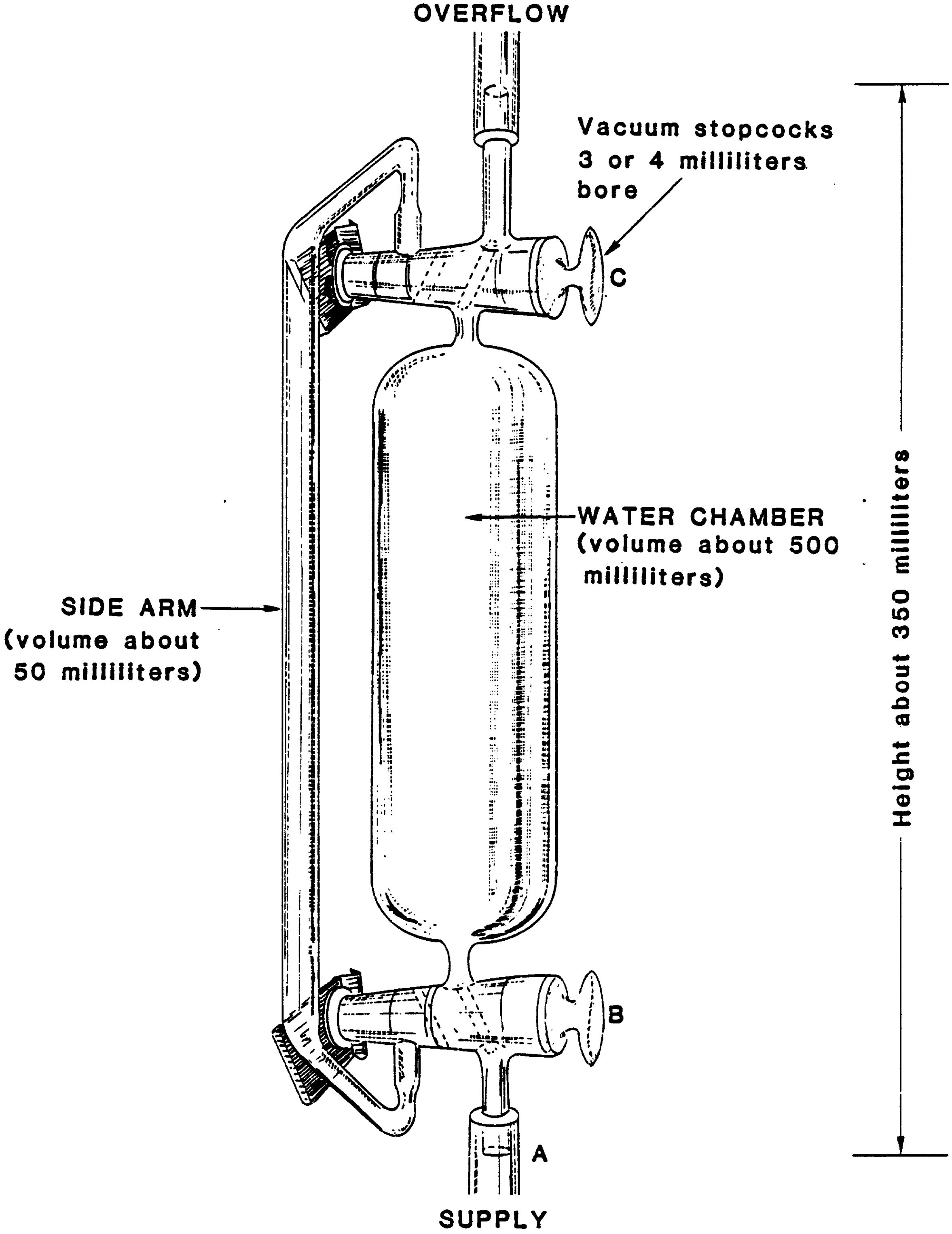

Figure 23.--Sampling device for dissolved gases in water.

Radioactive Isotopes. In addition, samples were obtained for the determination of the stable isotopes of hydrogen, oxygen, carbon, and sulfur, as well as the radioactive isotopes, carbon-14 and tritium. The following procedures were used in collecting samples for:

1. Hydrogen-2 (deuterium) and oxygen-18: Water samples were collected in 118.30-milliliter (4-ounce) glass bottles with polyseal caps. The bottles were rinsed twice, filled to the brim, and sealed. The caps were tightened twice at several hour intervals; then the bottles were inverted to the neck in melted paraffin to prevent any evaporation.

2. Hydrogen-3 (tritium): Water samples were collected in two 500-milliliter glass bottles with polyseal caps. The bottles were rinsed twice, filled to the brim, and sealed. The caps were tightened twice and sealed with paraffin (as above).

3. Carbon-13: The reagent for this collection was prepared in the following manner: 454 grams of strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$) were added to a 2-liter bottle of reagent-grade ammonium hydroxide. The carbon dioxide that commonly is absorbed into any strong solution of hydroxide settles out as a fine white precipitate of strontium carbonate. The clear supernatant liquid was decanted into 1-liter bottles for use at the sampling sites.

   Samples were collected in 1-liter sample bottles, rinsed twice with ground water, and filled to the brim. About 50 milliliters then were poured out and replaced by the ammonium hydroxide reagent, which contains strontium chloride, until the bottle was brimfull. The caps were tightened twice and sealed with paraffin (as above).

4. Carbon-14: The preparation of a water sample for carbon-14 analysis consisted of precipitation of all dissolved inorganic carbonate species from a water sample in a large funnel-like apparatus of 100-liter capacity. The procedure was straightforward, but required attention to detail, particularly to minimize exposure to air. A

2-liter polyethylene container was attached to the bottom of the funnel and the water sample added through a hose; the water was added to the funnel with care to prevent splashing that would entrain atmospheric carbon dioxide into the sample. When the funnel was about 90 percent full, 500 milliliters of sodium hydroxide solution (solution 1, below), then 500 milliliters of strontium chloride (solution 2, below), were added. Then a few grams of a wetting agent, ferrous ammonium sulfate, ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) was dissolved in a beaker of the ground water and added to the water in the funnel. When the funnel was full, the hose was removed and the funnel was sealed from the atmosphere by emplacing a plastic top. In a short time, a coarse, usually colored, agglomerate of the sulfates and carbonates of strontium precipitated into a plastic bottle that was attached to the bottom of the collection apparatus. The reaction and settling generally was complete in 1 or 2 hours. In a few instances (generally very saline waters and those waters with large concentrations of magnesium, sulfate, or aluminum), more precipitate formed than would fit into the 2-liter bottle. When this happened, the flap valve at the bottom of the funnel was closed, the first bottle was removed and capped, and a second bottle (filled with untreated sample water) was placed on the apparatus. The flap valve was again opened and the second bottle was allowed to fill with precipitate. In some instances, this had to be done three times to collect all the precipitate; however, the general situation only required one sample container.

Solution 1: All sodium hydroxide (even that advertised as being carbon dioxide free) in pelletized or solution form, contains some carbonate species that must be removed. This reagent is prepared by dissolving 150 grams of sodium hydroxide per 600 grams of distilled water. Fifteen milliliters of clear strontium chloride solution (solution 2, below) is added to remove all carbonate species and the solution is allowed to stand overnight to enable the strontium carbonate to settle out. The clear supernate is decanted and stored in airtight glass bottles.

Solution 2: 454 grams of strontium chloride hexahydrate are dissolved in 1 liter of distilled water. One milliliter of sodium hydroxide solution (solution 1) is added and the solution allowed to stand overnight to settle out any precipitate. The clear supernate is decanted and stored in airtight glass bottles.

5. Del sulfur-34: Sulphur isotopic ratios of both dissolved sulfate ion and sulfide were determined by collecting a large volume water sample (generally 10 to 20 liters). The sulfide ion was precipitated from solution by the addition of zinc acetate and sodium hydroxide. The precipitate was pumped with nitrogen and collected on a 0.1-micrometer filter. The precipitate was analyzed directly by mass spectroscopy. Sulfate ion was stripped from the filtrate by adsorption on anion exchange resins. Concentrated sulfate was removed from the column with dilute nitric acid and the eluate concentrated by evaporation. The sulfate was precipitated from the solution as barium sulfate.

Because of some, as yet, undetermined problem, the field procedure for the collection of sulfide did not yield a sufficient amount of zinc sulfide to enable determination of $\delta^{34}S$ on the samples collected. Three possible causes of the deficiency of sulfide are plausible:

1. Coprecipitation of the carbonate phase with sulfide resulting in an extreme dilution of the sulfide phase in the sample.
2. Oxidation of the collected sulfide to sulfate by oxygen contained in the water adsorbed on the sample.
3. Oxidation of the collected sulfide to sulfate by oxygen remaining in the sample bottle, the result of inadequate flushing of the sample bottle with nitrogen.

Four possible modifications of the sampling procedure could alleviate this difficulty:

1. Onsite, collect full, 30-liter containers of water in glass containers. Add a nitrogen blanket above the water, seal tightly. After a period of several hours, retighten, tape, and paraffin to prevent diffusion of oxygen in the sample. The sulfide and sulfate isotopes then would be separated in the laboratory.
2. Collect a large (30 liters) container of water and buffer the water to a pH of 7. Nitrogen pump the gases into a second container that has a solution of distilled water (pH adjusted to 14) with sodium hydroxide and 0.1 molar with respect to zinc ion. The water from the second container would be nitrogen pumped onto the 0.1-micron filter to collect the sulfide for subsequent analysis.
3. Apply the procedure previously described in this report, but add a step of drying the sample under nitrogen for 2 hours, followed by putting the sample in a glass container flushed with nitrogen, taped, and sealed.
4. Precipitate the samples directly in the field, without adjustment of pH, using cadmium chloride as the precipitant.

Table 26.--*Concentrations of dissolved major cations in water from the Madison aquifer system*

(MN = Montana; SD = South Dakota; WY = Wyoming; DEG C = degrees Celsius; MG/L = milligrams per liter; MEQ/L = milliequivalents per liter)

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	DEPTH*	INTERVAL SAMPLED*	PH (UNITS)	TEMPER-ATURE (DEG C)	DISSOLVED SOLIDS (SUM-MG/L)	CALCIUM (MG/L) (MEQ/L)	MAGNESIUM (MG/L) (MEQ/L)	STRONTIUM (MG/L) (MEQ/L)	SODIUM (MG/L) (MEQ/L)	POTASSIUM (MG/L) (MEQ/L)
2	GORE HILL 20N 03E 28CDAD	MN	--	--	7.13	14.0	1250	170 8.48	76 6.25	3.2 0.07	130 5.65	13 0.33
3	GREAT FALLS HIGH SCHOOL 20N 04E 07BDAC	MN	--	--	7.40	13.1	551	96 4.79	37 3.04	1.1 0.03	32 1.39	3.9 0.10
4	BOZEMAN FISH HATCHERY 01S 06E 34BCDA	MN	0	--	7.84	8.6	204	50 2.49	17 1.40	0.14 0.00	1.0 0.04	0.6 0.02
5	BOUGH RANCH 22N 06E 09DDAB	MN	1,300	--	7.06	17.9	2490	320 15.97	200 16.45	8.6 0.20	150 6.52	20 0.51
6	MCLEOD WARM SPRING 03S 13E 34ABAB	MN	0	--	7.40	24.6	320	71 3.54	23 1.89	0.49 0.01	1.5 0.07	1.4 0.03
7	BIG TIMBER FISH HATCHERY 01N 14E 15DAAA	MN	0	--	7.64	10.7	240	51 2.54	16 1.32	0.4 0.01	9.2 0.40	2.9 0.08
8	HANOVER 16N 16E 22DCCC	MN	750	--	7.63	20.4	398	84 4.19	29 2.39	1.1 0.04	2.8 0.12	1.2 0.03
9	VANEK WARM SPRING 17N 18E 19DBCA	MN	0	--	7.40	19.6	614	130 6.49	40 3.29	2.5 0.06	3.6 0.16	1.3 0.03
10	LEWISTOWN BIG SPRING 14N 19E 05ABCC	MN	0	--	7.58	10.6	348	75 3.74	28 2.30	0.98 0.02	2.4 0.10	0.9 0.02
11	BLUEWATER SPRING 06S 24E 09BCAA	MN	0	--	7.29	14.3	2290	530 26.45	67 5.51	5.6 0.13	71 3.09	2.7 0.08
12	LANDUSKY SPRING 25N 24E 32DABC	MN	7,175	--	7.24	20.4	1360	280 13.97	99 8.14	4.9 0.11	41 1.78	9.2 0.24
13	LODGEPOLE WARM SPRING 26N 25E 24BCDB	MN	0	--	7.08	31.6	1640	260 13.97	96 7.90	5.6 0.13	79 3.44	12 0.31
14	HTH #3 02N 27E 35AAB01	MN	7,175	--	6.80	51.8	2680	490 24.45	100 8.23	9.5 0.22	95 4.13	39 1.00
15	KEG COULEE 11N 30E 35ADAA	MN	--	6,456- 6,515	6.50	61.7	5500	350 17.46	53 4.36	13 0.30	1500 65.25	120 3.07
16	TEXACO C115X 11N 32E 15ABAC	MN	6,770	--	7.10	84.0	6000	320 15.97	52 4.28	13 0.30	1700 73.95	150 3.84

Table 26.--*Concentrations of dissolved major cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	DEPTH*	INTERVAL SAMPLED*	PH (UNITS)	TEMPER-ATURE (DEG C)	DISSOLVED SOLIDS (SUM-MG/L)	CALCIUM (MG/L) (MEQ/L)	MAGNESIUM (MG/L) (MEQ/L)	STRONTIUM (MG/L) (MEQ/L)	SODIUM (MG/L) (MEQ/L)	POTASSIUM (MG/L) (MEQ/L)
17	SUMATRA 11N 32E 24ADCD	MN	--	6,453 6,833	7.51	84.1	5730	220 10.98	34 2.80	12 0.27	1800 78.30	130 3.32
18	SLEEPING BUFFALO 32N 32E 35CDBD	MN	--	3,116- 3,180	7.00	40.9	3250	510 25.4	120 9.87	11 0.25	310 13.48	26 0.66
19	SARPY MINE 01N 37E 26BDDD	MN	--	--	6.70	83.3	1580	320 15.9	51 4.20	11 0.25	48 2.09	49 1.25
20	MYSSE FLOWING 12N 39E 09AACA	MN	5,103	--	6.66	63.8	4120	450 22.45	110 9.05	11 0.25	730 31.75	99 2.53
21	COLSTRIP 02N 41E 34BADA	MN	9,336	--	6.52	97.2	1440	220 10.98	28 2.30	9.0 0.21	140 6.09	67 1.71
22	MOORE 10N 43E 21CDCA	MN	0	--	6.81	86.9	6380	380 18.96	68 5.59	15 0.34	1700 73.95	130 3.32
23	RANCH CREEK 09S 53E 22ABAC	MN	--	4,460- 4,578	6.94	52.7	955	190 9.48	46 3.78	4.8 0.11	38 1.65	8.0 0.20
24	BELLE CREEK 08S 54E 21ADAD	MN	8,000	--	7.01	56.2	1000	200 9.98	48 3.95	4.7 0.11	38 1.65	8.0 0.20
26	GAS CITY 14N 55E 27CDDB	MN	7,800	--	6.61	91.5	5390	370 18.46	61 5.02	15 0.34	1400 60.90	110 2.81
1	KOSKEN 42N 26W 34ABCD	SD	--	2,660- 2,935	6.70	63.5	1190	240 11.98	48 3.95	4.6 0.11	27 1.17	11 0.28
2	MCNENNEY 02N 01E 21BBC	SD	220	--	7.18	11.5	362	87 4.34	24 1.97	0.89 0.02	2.1 0.09	1.4 0.03
3	PROVO 10S 02E 03	SD	3,846	--	6.97	60.0	1070	110 5.49	30 2.47	2.2 0.05	200 8.70	18 0.46
4	RHOADS FORK 02N 02E 15	SD	0	--	7.35	5.7	256	66 3.29	23 1.89	0.07 0.00	0.90 0.04	0.60 0.02
5	SPEARFISH 06N 02E 10D	SD	578	--	7.39	13.2	283	52 2.59	23 1.89	0.15 0.00	2.1 0.09	1.1 0.03
6	FUHS 05N 03E 12DCCB	SD	550	--	7.21	10.7	544	88 4.39	63 5.18	0.50 0.01	5.8 0.25	3.6 0.09
7	DELZER #1 12N 03E 28BACBB	SD	4,558	--	7.51	55.6	2410	510 25.45	110 9.05	12 0.27	36 1.57	35 0.89

Table 26.--*Concentrations of dissolved major cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	DEPTH*	INTERVAL SAMPLED*	PH (UNITS)	TEMPER-ATURE (DEG C)	DISSOLVED SOLIDS (SUM-MG/L)	CALCIUM (MG/L) (MEQ/L)	MAGNESIUM (MG/L) (MEQ/L)	STRONTIUM (MG/L) (MEQ/L)	SODIUM (MG/L) (MEQ/L)	POTASSIUM (MG/L) (MEQ/L)
8	DELZER #2 12N 03E 32ACBC	SD	5,453	--	6.77	55.6	2630	550 27.44	110 9.05	11 0.25	45 1.96	12 0.31
9	CASCADE SPRING 08S 05E 20	SD	0	--	6.89	20.0	2280	540 26.95	83 6.83	6.2 0.14	27 1.17	5.2 0.13
10	EVANS PLUNGE 07S 05E 13BCCC	SD	0	--	6.90	30.5	1140	210 10.48	41 3.37	2.9 0.07	86 3.74	11 0.28
11	KAISER 06S 05E 24BAAA	SD	--	690- 780	7.40	15.0	224	47 2.35	18 1.48	0.24 0.01	9.7 0.42	2.9 0.0
12	JONES SPRING 04N 05E 23	SD	0	--	7.20	12.9	269	71 3.54	22 2.30	0.12 0.00	1.5 0.07	0.60 0.02
13	BLACK HILLS CEMETERY 05N 05E 25ABD	SD	--	--	7.28	12.4	239	55 2.74	23 1.89	0.33 0.01	2.3 0.10	1.3 0.03
14	STREETER RANCH 06S 06E 15AACC	SD	--	929- 939	7.61	19.4	183	40 2.00	15 1.23	0.28 0.01	9.2 0.40	2.3 0.05
16	CLEGHORN SPRING 01N 07E 08	SD	0	--	7.41	11.6	203	42 2.10	19 1.56	0.10 0.00	4.9 0.21	2.7 0.08
17	LIEN 02N 07E 18BCA	SD	0	--	7.41	11.9	222	46 2.30	25 2.06	0.14 0.00	2.4 0.10	1.8 0.05
18	ELLSWORTH AFB 02N 08E 13BDC	SD	4,436	--	7.01	49.0	461	91 4.54	33 2.71	0.94 0.02	4.9 0.21	3.7 0.10
19	PHILIP 01N 20E 01ACDD	SD	4,010	--	6.78	68.0	1080	220 10.98	58 4.77	4.5 0.10	18 0.78	7.3 0.18
20	DUPREE 13N 21E 31BDDA	SD	4,500	--	6.82	56.5	2330	390 19.46	94 7.73	12 0.27	110 4.78	49 1.25
21	HAMILTON 08N 23W 26ACDA	SD	3,760	--	6.92	58.2	2030	420 20.96	90 7.40	9.2 0.21	34 1.48	15 0.38
22	HILLTOP RANCH 05N 24E 30CA	SD	--	3,380- 4,110	6.70	61.8	1980	360 17.96	77 6.33	8.0 0.18	85 3.70	13 0.33
23	EAGLE BUTTE 12N 24E 17CBBD	SD	4,325	--	7.00	55.5	2200	390 19.46	110 9.05	11 0.25	60 2.61	28 0.72
24	MIDLAND 01N 25E 06CAA	SD	3,320	--	6.69	71.0	1310	270 13.47	66 5.43	5.5 0.13	25 1.09	9.7 0.26

Table 26.--*Concentrations of dissolved major cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	DEPTH*	INTERVAL SAMPLED*	PH (UNITS)	TEMPER-ATURE (DEG C)	DISSOLVED SOLIDS (SUM-MG/L)	CALCIUM (MG/L) (MEQ/L)	MAGNESIUM (MG/L) (MEQ/L)	STRONTIUM (MG/L) (MEQ/L)	SODIUM (MG/L) (MEQ/L)	POTASSIUM (MG/L) (MEQ/L)
25	MURDO 01S 26E 36ACA	SD	3,313	--	6.68	59.1	1550	300 14.97	65 5.35	6.6 0.15	46 2.00	13 0.33
26	PRINCE 05N 27E 22CD	SD	2,475	--	6.89	57.0	2010	410 20.46	83 6.83	9.0 0.21	72 3.13	20 0.51
27	BEAN 09N 03E 20CDD	SD	3,511	--	7.10	41.5	820	160 7.98	51 4.20	3.3 0.08	14 0.87	5.0 0.13
1	MOCK RANCH 57N 87W 21DBC01	WY	1,596	--	7.50	10.8	214	56 2.79	20 1.65	0.20 0.00	0.40 0.02	0.60 0.02
2	DENIUS #1 58N 87W 32BA	WY	--	--	7.60	9.0	219	40 2.00	29 2.39	0.17 0.00	0.60 0.03	1.1 0.03
3	DENIUS #2 58N 87W 32BAB	WY	--	940- 1,176	7.55	8.3	199	55 2.74	16 1.32	0.11 0.00	0.60 0.03	0.50 0.01
4	DENIUS #3 58N 87W 32BB	WY	--	--	7.69	8.5	315	74 3.69	30 2.47	0.55 0.01	1.9 0.08	<0.01 0.00
5	HOLE-IN-THE-WALL 41N 84W 20BAC	WY	424	--	7.25	8.2	210	35 1.75	32 2.63	0.10 0.00	1.6 0.07	0.60 0.02
6	STOREY FISH HATCHERY 53N 84W 13BDC	WY	765	--	7.30	8.0	191	52 2.59	15 1.23	0.07 0.21	1.4 0.06	0.50 0.01
7	MOBIL 49N 83W 27DDA	WY	1,111	--	7.31	7.1	164	32 1.60	19 1.56	0.09 0.00	2.2 0.10	1.0 0.03
8	CONOCO #44 41N 81W 09CDA	WY	--	2,682- 2,882	7.17	32.2	2180	240 11.98	61 5.02	3.4 0.08	380 16.53	25 0.64
9	SHIDLER 40N 79W 31BCA	WY	6,155	--	7.55	72.6	2570	300 14.97	49 4.03	4.6 0.11	490 21.31	35 0.89
10	MKM 39N 78W 26CDC	WY	--	6,931- 7,180	6.71	88.1	3430	290 14.47	41 3.37	6.0 0.14	760 33.06	69 1.76
11	CONOCO #175 33N 75W 20AAC	WY	--	8,844- 9,154	7.30	30.1	718	110 5.49	25 2.06	1.6 0.04	77 3.35	9.8 0.26
12	BARBER RANCH SPRING 32N 74W 03CBD	WY	1,465	--	7.46	15.7	259	56 2.79	19 1.56	0.36 0.01	8.3 0.36	2.6 0.08
13	DEVILS TOWER 53N 65W 18BBD	WY	--	448- 468	7.20	17.1	512	110 5.49	38 3.13	NS NS	3.7 0.16	1.5 0.05

Table 26.--*Concentrations of dissolved major cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	DEPTH*	INTERVAL SAMPLED*	PH (UNITS)	TEMPER- ATURE (DEG C)	DISSOLVED SOLIDS (SUM-MG/L)	CALCIUM (MG/L) (MEQ/L)	MAGNESIUM (MG/L) (MEQ/L)	STRONTIUM (MG/L) (MEQ/L)	SODIUM (MG/L) (MEQ/L)	POTASSIUM (MG/L) (MEQ/L)
14	HTH #1 57N 65W 15DA	WY	4,355	--	6.99	46.2	930	180 8.98	44 3.62	4.5 0.10	36 1.57	7.6 0.20
15	UPTON 48N 65W 25CC	WY	3,161	--	7.12	25.7	456	88 4.39	41 3.37	2.9 0.07	2.6 0.11	2.2 0.05
16	CORONADO #2 46N 64W 13CCA	WY	4,522	--	7.16	39.8	267	56 2.79	27 2.22	0.38 0.01	1.8 0.08	1.7 0.05
17	OSAGE 46N 63W 15BD	WY	372	--	7.20	23.4	311	70 3.49	27 2.22	0.32 0.01	2.1 0.09	1.4 0.03
18	JBJ 44N 63W 26CAC	WY	6,881	--	6.70	45.1	374	73 3.64	22 1.81	6.0 0.14	11 0.48	4.8 0.13
19	SEELEY 46N 62W 18BDC	WY	2,677	--	7.30	13.0	273	66 3.29	27 2.22	0.25 0.01	1.3 0.06	1.2 0.03
20	VOSS 45N 61W 28AB	WY	--	2,468- 2,738	7.30	26.1	309	63 3.14	29 2.39	0.39 0.01	2.6 0.11	1.7 0.05
21	NEWCASTLE 45N 61W 20DCA	WY	--	2,618- 2,638	7.20	25.0	302	64 3.19	29 2.39	0.38 0.01	2.6 0.11	1.7 0.05
22	SELF 45N 61W 33AB01	WY	--	3,169- 3,596	7.30	29.8	351	73 3.64	31 2.55	0.61 0.01	2.5 0.11	2.1 0.05
23	MARTENS MADISON 45N 60W 07CA	WY	--	640- 720	7.50	15.6	268	61 3.04	26 2.14	NS NS	2.7 0.12	2.0 0.05
24	MALLO CAMP 47N 60W 04BDA	WY	--	230- 380	7.60	7.7	245	57 2.84	24 1.97	NS NS	1.3 0.06	0.70 0.02
25	RANCH A 52N 60W 18C	WY	--	--	7.26	12.2	505	120 5.99	30 2.47	1.1 0.03	2.6 0.11	1.4 0.03

*Feet below land surface; an entry of 0 depth represents a spring; -- represents missing data

NOTE: NS means parameter of interest not sampled.
NC means value not calcuated.

Table 27.--*Concentrations of dissolved major anions and silica in water from the Madison aquifer system*

(MN = Montana; SD = South Dakota; WY = Wyoming; DEG C = degrees Celsius; MG/L = milligrams per liter; MEQ/L = milliequivalents per liter)

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	BICAR-BONATE (MG/L) (MEQ/L)	CHLORIDE (MG/L) (MEQ/L)	FLUORIDE (MG/L) (MEQ/L)	SULFATE (MG/L) (MEQ/L)	BROMIDE (MG/L) (MEQ/L)	SILICA (MG/L)
2	GORE HILL 20N 03E 28CDAD	MN	7.13	14.0	340 5.57	110 3.10	2.4 0.13	570 11.87	0.7 0.01	15 NC
3	GREAT FALLS HIGH SCHOOL 20N 04E 07BDAC	MN	7.40	13.1	260 4.26	14 0.39	0.9 0.05	230 4.79	0.10 0.00	12 NC
4	BOZEMAN FISH HATCHERY 01S 06E 34BCDA	MN	7.84	8.6	220 3.61	1.1 0.03	0.2 0.01	23 0.48	<0.001 NC	4.8 NC
5	BOUGH RANCH 22N 06E 09DDAB	MN	7.06	17.9	260 4.26	64 1.81	3.2 0.17	1600 33.31	0.3 0.00	9.7 NC
6	MCLEOD WARM SPRING 03S 13E 34ABAB	MN	7.40	24.6	190 3.11	1.1 0.03	0.6 0.03	120 2.50	<0.001 NC	11 NC
7	BIG TIMBER FISH HATCHERY 01N 14E 15DAAA	MN	7.64	10.7	230 3.77	2.8 0.08	0.3 0.02	27 0.56	<0.001 NC	16 NC
8	HANOVER 16N 16E 22DCCC	MN	7.63	20.4	200 3.28	1.5 0.04	1.4 0.07	170 3.54	<0.001 NC	8.9 NC
9	VANEK WARM SPRING 17N 18E 19DBCA	MN	7.40	19.6	200 3.28	2.4 0.07	1.5 0.08	330 6.87	<0.001 NC	9.3 NC
10	LEWISTOWN BIG SPRING 14N 19E 05ABCC	MN	7.58	10.6	190 3.11	1.8 0.05	1.1 0.06	140 2.91	<0.001 NC	6.7 NC
11	BLUEWATER SPRING 06S 24E 09BCAA	MN	7.29	14.3	220 3.61	2.4 0.07	1.4 0.07	1500 31.23	0.01 0.00	13 NC
12	LANDUSKY SPRING 25N 24E 32DABC	MN	7.24	20.4	210 3.44	19 0.54	1.6 0.08	970 20.20	0.1 0.00	17 NC
13	LODGEPOLE WARM SPRING 26N 25E 24BCDB	MN	7.08	31.6	200 3.28	67 1.89	1.7 0.09	990 20.61	0.2 0.00	16 NC
14	HTH #3 02N 27E 35AAB01	MN	6.80	51.8	160 2.62	39 1.10	0.7 0.04	1800 37.48	0.5 0.01	7.0 NC
15	KEG COULEE 11N 30E 35ADAA	MN	6.50	61.7	340 5.57	2000 56.42	5.2 0.27	1300 27.07	11 0.14	55 NC
16	TEXACO C115X 11N 32E 15ABAC	MN	7.10	84.0	440 7.21	2100 59.24	5.4 0.28	1400 29.15	12 0.15	58 NC

Table 27.--*Concentrations of dissolved major anions and silica in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER- ATURE (DEG C)	BICAR- BONATE (MG/L) (MEQ/L)	CHLORIDE (MG/L) (MEQ/L)	FLUORIDE (MG/L) (MEQ/L)	SULFATE (MG/L) (MEQ/L)	BROMIDE (MG/L) (MEQ/L)	SILICA (MG/L)
17	SUMATRA 11N 32E 24ADCD	MN	7.51	84.1	80 1.30	2300 64.88	4.9 0.26	1200 24.98	12 0.15	9.1 NC
18	SLEEPING BUFFALO 32N 32E 35CDBD	MN	7.00	40.9	150 2.46	190 5.36	3.3 0.17	2000 41.64	0.60 0.01	18 NC
19	SARPY MINE 01N 37E 26BDDD	MN	6.70	83.3	140 2.29	21 0.59	4.5 0.24	960 19.99	0.10 0.00	49 NC
20	MYSSE FLOWING 12N 39E 09AACA	MN	6.66	63.8	340 5.57	630 17.77	4.2 0.22	1900 39.56	2.4 0.03	36 NC
21	COLSTRIP 02N 41E 34BADA	MN	6.52	97.2	140 2.29	96 2.71	4.7 0.25	740 15.41	0.60 0.01	69 NC
22	MOORE 10N 43E 21CDCA	MN	6.81	86.9	300 4.92	2400 67.70	5.4 0.28	1500 31.23	6.90 0.09	56 NC
23	RANCH CREEK 09S 53E 22ABAC	MN	6.94	52.7	210 3.44	56 1.58	3.3 0.17	480 9.99	0.10 0.00	33 NC
24	BELLE CREEK 08S 54E 21ADAD	MN	7.01	56.2	210 3.44	57 1.61	3.6 0.19	520 10.83	0.20 0.00	32 NC
26	GAS CITY 14N 55E 27CDDB	MN	6.61	91.5	390 6.39	1900 53.60	4.7 0.25	1300 27.07	0.10 0.00	58 NC
1	KOSKEN 42N 26W 34ABCD	SD	6.70	63.5	140 2.29	40 1.13	1.7 0.09	680 14.16	0.200 0.000	39 NC
2	MCNENNEY 02N 01E 21BBC	SD	7.18	11.5	260 4.26	0.6 0.02	0.3 0.02	100 2.08	NS NC	12 NC
3	PROVO 10S 02E 03	SD	6.97	60.0	180 2.95	270 7.62	1.3 0.07	310 6.45	NS NC	30 NC
4	RHOADS FORK 02N 02E 15	SD	7.35	5.7	310 5.08	0.4 0.01	0.1 0.01	3.1 0.06	NS NC	8.8 NC
5	SPEARFISH 06N 02E 10D	SD	7.39	13.2	270 4.43	0.6 0.02	0.2 0.01	8.2 0.17	NS NC	10 NC
6	FUHS 05N 03E 12DCCB	SD	7.21	10.7	340 5.57	3.9 0.11	0.2 0.01	200 4.16	<0.001 NC	12 NC
7	DELZER #1 12N 03E 28BACBB	SD	7.51	55.6	110 1.80	25 0.71	3.1 0.16	1600 33.31	0.10 0.00	17 NC

Table 27.--*Concentrations of dissolved major anions and silica in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER- ATURE (DEG C)	BICAR- BONATE (MG/L) (MEQ/L)	CHLORIDE (MG/L) (MEQ/L)	FLUORIDE (MG/L) (MEQ/L)	SULFATE (MG/L) (MEQ/L)	BROMIDE (MG/L) (MEQ/L)	SILICA (MG/L)
8	DELZER #2 12N 03E 32ACBC	SD	6.77	55.6	190 3.11	67 1.89	3.6 0.19	1700 35.39	0.20 0.00	29 NC
9	CASCADE SPRING 08S 05E 20	SD	6.89	20.0	240 3.93	31 0.87	1.6 0.08	1500 31. 3	NS NC	15 NC
10	EVANS PLUNGE 07S 05E 13BCCC	SD	6.90	30.5	230 3.77	110 3.10	1.1 0.06	550 11.45	NS NC	23 NC
11	KAISER 06S 05E 24BAAA	SD	7.40	15.0	230 3.77	3.7 0.10	0.5 0.03	14 0.29	0.10 0.00	15 NC
12	JONES SPRING 04N 05E 23	SD	7.20	12.9	330 5.37	0.5 0.01	0.1 0.01	5.8 0.12	NS NC	8.4 NC
13	BLACK HILLS CEMETARY 05N 05E 25ABD	SD	7.28	12.4	270 4.43	1.8 0.05	0.3 0.02	11 0.23	<0.001 NC	10 NC
14	STREETER RANCH 06S 06E 15AACC	SD	7.61	19.4	200 3.28	2.5 0.07	0.4 0.02	9.4 0.20	<0.001 NC	17 NC
16	CLEGHORN SPRING 01N 07E 08	SD	7.41	11.6	200 3.26	2.2 0.06	<0.1 NC	23 0.48	NS NC	11 NC
17	LIEN 02N 07E 18BCA	SD	7.41	11.9	240 3.93	1.5 0.04	0.2 0.01	14 0.29	0.10 0.00	11 NC
18	ELLSWORTH AFB 02N 08E 13BDC	SD	7.01	49.0	200 3.28	1.0 0.03	0.6 0.03	200 4.16	NS NC	21 NC
19	PHILIP 01N 20E 01ACDD	SD	6.78	68.0	160 2.62	22 0.62	2.6 0.14	640 13.32	NS NC	33 NC
20	DUFREE 13N 21E 31BDDA	SD	6.82	56.5	160 2.62	120 3.39	3.6 0.19	1400 29.15	0.40 0.01	34 NC
21	HAMILTON 08N 23W 26ACDA	SD	6.92	58.2	160 2.62	48 1.35	3.4 0.18	1300 27.07	0.20 0.00	31 NC
22	HILLTOP RANCH 05N 24E 30CA	SD	6.70	61.8	150 2.46	160 4.51	2.9 0.15	1200 24.98	4.20 0.05	36 NC
23	EAGLE BUTTE 12N 24E 17CBBD	SD	7.00	55.5	180 2.95	63 1.78	3.7 0.19	1300 27.07	0.20 0.00	30 NC
24	MIDLAND 01N 25E 06CAA	SD	6.69	71.0	150 2.46	28 0.79	2.8 0.15	800 16.66	NS NC	35 NC

Table 27.--*Concentrations of dissolved major anions and silica in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	BICAR-BONATE (MG/L) (MEQ/L)	CHLORIDE (MG/L) (MEQ/L)	FLUORIDE (MG/L) (MEQ/L)	SULFATE (MG/L) (MEQ/L)	BROMIDE (MG/L) (MEQ/L)	SILICA (MG/L)
25	MURDO 01S 26E 36ACA	SD	6.68	59.1	150 2.46	61 1.72	2.6 0.14	860 17.91	0.30 0.00	33 NC
26	PRINCE 05N 27E 22CD	SD	6.89	57.0	140 2.29	110 3.10	3.4 0.18	1200 24.98	0.50 0.01	29 NC
27	BEAN 09N 03E 20CDD	SD	7.10	41.5	190 3.09	17 0.48	1.7 0.09	450 9.37	0.40 0.01	20 NC
1	MOCK RANCH 57N 87W 21DBC01	WY	7.50	10.8	250 4.10	0.5 0.01	0.2 0.01	8.1 0.17	<0.001 NC	6.3 NC
2	DENIUS #1 58N 87W 32BA	WY	7.60	9.0	240 3.93	0.7 0.02	0.7 0.04	22 0.46	<0.001 NC	7.8 NC
3	DENIUS #2 58N 87W 32BAB	WY	7.55	8.3	240 3.93	0.3 0.01	0.2 0.01	2.8 0.06	<0.001 NC	5.2 NC
4	DENIUS #3 58N 87W 32BB	WY	7.69	8.5	310 5.08	0.6 0.02	0.3 0.02	43 0.90	<0.001 NC	8.9 NC
5	HOLE-IN-THE-WALL 41N 84W 20BAC	WY	7.25	8.2	260 4.26	1.3 0.04	0.2 0.01	6.2 0.13	<0.001 NC	6.7 NC
6	STOREY FISH HATCHERY 53N 84W 13BDC	WY	7.30	8.0	220 3.61	1.4 0.04	0.1 0.01	3.2 0.07	NS NC	6.8 NC
7	MOBIL 49N 83W 27DDA	WY	7.31	7.1	190 3.11	0.9 0.03	0.2 0.01	7.7 0.16	<0.001 NC	9.3 NC
8	CONOCO #44 41N 81W 09CDA	WY	7.17	32.2	220 3.61	490 13.82	3.0 0.16	840 17.49	4.3 0.05	24 NC
9	SHIDLER 40N 79W 31BCA	WY	7.55	72.6	120 1.97	620 17.49	3.5 0.18	970 20.20	1.9 0.02	32 NC
10	MKM 39N 78W 26CDC	WY	6.71	88.1	130 2.13	1200 33.85	4.4 0.23	920 19.15	3.5 0.04	59 NC
11	CONOCO #175 33N 75W 20AAC	WY	7.30	30.1	12 1.95	70 1.97	1.4 0.07	340 7.08	0.40 0.01	19 NC
12	BARBER RANCH SPRING 32N 74W 03CBD	WY	7.46	15.7	230 3.77	4.4 0.12	0.3 0.02	34 0.71	0.10 0.00	19 NC
13	DEVILS TOWER 53N 65W 18BBD	WY	7.20	17.1	270 4.43	2.6 0.07	0.5 0.03	210 4.37	NS NC	11 NC

Table 27.--*Concentrations of dissolved major anions and silica in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPERATURE (DEG C)	BICARBONATE (MG/L) (MEQ/L)	CHLORIDE (MG/L) (MEQ/L)	FLUORIDE (MG/L) (MEQ/L)	SULFATE (MG/L) (MEQ/L)	BROMIDE (MG/L) (MEQ/L)	SILICA (MG/L)
14	HTH #1 57N 65W 15DA	WY	6.99	46.2	210 3.44	54 1.52	2.8 0.15	60 1.25	0.20 0.00	30 NC
15	UPTON 48N 65W 25CC	WY	7.12	25.7	280 4.59	0.8 0.02	1.2 0.06	170 3.54	NS NC	12 NC
16	CORONADO #2 46N 64W 13CCA	WY	7.16	39.8	280 4.59	0.8 0.02	0.2 0.01	28 0.58	NS NC	14 NC
17	OSAGE 46N 63W 15BD	WY	7.20	23.4	300 4.92	0.7 0.02	0.4 0.02	50 1.04	NS NC	11 NC
18	JBJ 44N 63W 26CAC	WY	6.70	45.1	100 1.64	7.6 0.21	1.4 0.07	200 4.16	NS NC	4.5 NC
19	SEELEY 46N 62W 18BDC	WY	7.30	13.0	300 4.92	0.8 0.02	0.3 0.02	17 0.35	<0.001 NC	12 NC
20	VOSS 45N 61W 28AB	WY	7.30	26.1	310 5.08	1.7 0.05	0.3 0.02	43 0.90	NS NC	12 NC
21	NEWCASTLE 45N 61W 20DCA	WY	7.20	25.0	290 4.75	1.2 0.03	0.3 0.02	47 0.98	NS NC	12 NC
22	SELF 45N 61W 33AB01	WY	7.30	29.8	280 4.59	2.1 0.06	0.6 0.03	86 1.79	<0.001 NC	13 NC
23	MARTENS MADISON 45N 60W 07CA	WY	7.50	15.6	310 5.08	1.4 0.04	0.3 0.02	11 0.23	<0.001 NC	11 NC
24	MALLO CAMP 47N 60W 04BDA	WY	7.60	7.7	300 4.92	1.0 0.03	0.1 0.01	1.8 0.04	NS NC	12 NC
25	RANCH A 52N 60W 18C	WY	7.26	12.2	280 4.56	1.4 0.04	0.3 0.02	200 4.16	0.10 NC	8.0 NC

NC - Value was not calculated.
NS - A sample was not obtained for the parameter in question.

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*

(MN = Montana; SD = South Dakota; WY = Wyoming; DEG C = degrees Celsuis;
UG/L = micrograms per liter; NS = parameter not sampled)

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	ALUM-INUM (AL) (UG/L)	ANTI-MONY (SB) (UG/L)	ARSENIC (AS) (UG/L)	BARIUM (BA) (UG/L)	BERYL-LIUM (BE) (UG/L)	CADMIUM (CD) (UG/L)	CHROMIUM (CR) (UG/L)
2	GORE HILL 20N 03E 28CDAD	MN	7.13	14.0	10	NS	14	<100	NS	<1	<1
3	GREAT FALLS HIGH SCHOOL 20N 04E 07BDAC	MN	7.40	13.1	10	NS	<1	<100	NS	<1	<1
4	BOZEMAN FISH HATCHERY 01S 06E 34BCDA	MN	7.84	8.6	10	NS	1	<100	NS	<1	<1
5	BOUGH RANCH 22N 06E 09DDAB	MN	7.06	17.9	<10	NS	<1	<100	NS	<1	<1
6	MCLEOD WARM SPRING 03S 13E 34ABAB	MN	7.40	24.6	10	NS	7	<100	NS	<1	<1
7	BIG TIMBER FISH HATCHERY 01N 14E 15DAAA	MN	7.64	10.7	10	NS	2	<100	NS	<1	<1
8	HANOVER 16N 16E 22DCCC	MN	7.63	20.4	10	NS	3	<100	NS	<1	<1
9	VANEK WARM SPRING 17N 18E 19DBCA	MN	7.40	19.6	10	NS	3	<100	NS	<1	<1
10	LEWISTOWN BIG SPRING 14N 19E 05ABCC	MN	7.58	10.6	40	NS	<1	<100	NS	<1	<1
11	BLUEWATER SPRING 06S 24E 09BCAA	MN	7.29	14.3	<10	NS	1	200	NS	<1	10
12	LANDUSKY SPRING 25N 24E 32DABC	MN	7.24	20.4	20	NS	9	<100	NS	<1	<1
13	LODGEPOLE WARM SPRING 26N 25E 24BCDB	MN	7.08	31.6	10	NS	3	<100	NS	<1	<1
14	HTH #3 02N 27E 35AAB01	MN	6.80	51.8	10	NS	<1	<100	NS	<1	<1
15	KEG COULEE 11N 30E 35ADAA	MN	6.50	61.7	10	NS	<1	100	NS	<1	<1
16	TEXACO C115X 11N 32E 15ABAC	MN	7.10	84.0	20	NS	3	<100	NS	<1	<1

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	COBALT (CO) (UG/L)	COPPER (CU) (UG/L)	IRON (FE) (UG/L)	LEAD (PB) (UG/L)	LITH-IUM (LI) (UG/L)	MANG-ANESE (MN) (UG/L)	MERCURY (HG) (UG/L)
2	GORE HILL. 20N 03E 28CDAD	MN	7.13	14.0	<10	<1	980	2	330	20	<0.1
3	GREAT FALLS HIGH SCHOOL 20N 04E 07BDAC	MN	7.40	13.1	NS	1	80	<1	60	20	<0.1
4	BOZEMAN FISH HATCHERY 01S 06E 34BCDA	MN	7.84	8.6	NS	1	100	2	<10	<1	<0.1
5	BOUGH RANCH 22N 06E 09DDAB	MN	7.06	17.9	NS	<1	180	<1	300	20	0.3
6	MCLEOD WARM SPRING 03S 13E 34ABAB	MN	7.40	24.6	NS	1	<10	2	<10	<1	<0.1
7	BIG TIMBER FISH HATCHERY 01N 14E 15DAAA	MN	7.64	10.7	NS	<1	10	2	<10	<1	<0.1
8	HANOVER 16N 16E 22DCCC	MN	7.63	20.4	<10	1	10	2	20	<1	<0.1
9	VANEK WARM SPRING 17N 18E 19DBCA	MN	7.40	19.6	NS	1	30	2	20	<1	<0.1
10	LEWISTOWN BIG SPRING 14N 19E 05ABCC	MN	7.58	10.6	NS	1	40	3	20	<1	<0.1
11	BLUEWATER SPRING 06S 24E 09BCAA	MN	7.29	14.3	NS	1	10	1	50	10	<0.1
12	LANDUSKY SPRING 25N 24E 32DABC	MN	7.24	20.4	NS	<1	30	2	80	<1	<0.1
13	LODGEPOLE WARM SPRING 26N 25E 24BCDB	MN	7.08	31.6	NS	<1	20	2	140	10	<0.1
14	HTH #3 02N 27E 35AAB01	MN	6.80	51.8	NS	<1	970	<1	400	460	<0.1
15	KEG COULEE 11N 30E 35ADAA	MN	6.50	61.7	NS	<1	390	2	3500	80	<0.1
16	TEXACO C115X 11N 32E 15ABAC	MN	7.10	84.0	NS	<1	50	2	4400	50	<0.1

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	MOLYB-DENUM (MO) (UG/L)	NICKEL (NI) (UG/L)	SELE-NIUM (SE) (UG/L)	SILVER (AG) (UG/L)	TIN (SN) (UG/L)	VANA-DIUM (V) (UG/L)	ZINC (ZN) (UG/L)
2	GORE HILL 20N 03E 28CDAD	MN	7.13	14.0	<1	NS	1	NS	NS	1.2	<10
3	GREAT FALLS HIGH SCHOOL 20N 04E 07BDAC	MN	7.40	13.1	1	NS	<1	NS	NS	0.1	70
4	BOZEMAN FISH HATCHERY 01S 06E 34BCDA	MN	7.84	8.6	1	NS	<1	NS	NS	0.5	<10
5	BOUGH RANCH 22N 06E 09DDAB	MN	7.06	17.9	<1	NS	<1	NS	NS	<0.1	<10
6	MCLEOD WARM SPRING 03S 13E 34ABAB	MN	7.40	24.6	1	NS	<1	NS	NS	0.9	<10
7	BIG TIMBER FISH HATCHERY 01N 14E 15DAAA	MN	7.64	10.7	1	NS	1	NS	NS	2.2	<10
8	HANOVER 16N 16E 22DCCC	MN	7.63	20.4	1	NS	1	NS	NS	0.9	<10
9	VANEK WARM SPRING 17N 18E 19DBCA	MN	7.40	19.6	1	NS	<1	NS	NS	0.7	10
10	LEWISTOWN BIG SPRING 14N 19E 05ABCC	MN	7.58	10.6	2	NS	1	NS	NS	0.9	<10
11	BLUEWATER SPRING 06S 24E 09BCAA	MN	7.29	14.3	6	NS	2	NS	NS	3.4	10
12	LANDUSKY SPRING 25N 24E 32DABC	MN	7.24	20.4	1	NS	1	NS	NS	3.4	20
13	LODGEPOLE WARM SPRING 26N 25E 24BCDB	MN	7.08	31.6	1	NS	<1	NS	NS	1.1	10
14	HTH #3 02N 27E 35AAB01	MN	6.80	51.8	<1	NS	<1	NS	NS	<0.1	30
15	KEG COULEE 11N 30E 35ADAA	MN	6.50	61.7	<1	NS	<1	NS	NS	22	8
16	TEXACO C115X 11N 32E 15ABAC	MN	7.10	84.0	<1	NS	1	NS	NS	68	10

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	ALUM-INUM (AL) (UG/L)	ANTI-MONY (SB) (UG/L)	ARSENIC (AS) (UG/L)	BARIUM (BA) (UG/L)	BERYL-LIUM (BE) (UG/L)	CADMIUM (CD) (UG/L)	CHROMIUM (CR) (UG/L)
17	SUMATRA 11N 32E 24ADCD	MN	7.51	84.1	30	NS	1	100	NS	<1	15
18	SLEEPING BUFFALO 32N 32E 35CDBD	MN	7.00	40.9	10	NS	1	<100	NS	<1	<1
19	SARPY MINE 01N 37E 26BDDD	MN	6.70	83.3	10	NS	<1	200	NS	<1	10
20	MYSSE FLOWING 12N 39E 09AACA	MN	6.66	63.8	<10	NS	4	200	NS	<1	<1
21	COLSTRIP 02N 41E 34BADA	MN	6.52	97.2	10	NS	8	<100	NS	<1	<1
22	MOORE 10N 43E 21CDCA	MN	6.81	86.9	10	NS	6	200	NS	<1	<1
23	RANCH CREEK 09S 53E 22ABAC	MN	6.94	52.7	10	NS	2	<100	NS	<1	<1
24	BELLE CREEK 08S 54E 21ADAD	MN	7.01	56.2	<10	NS	3	200	NS	<1	<1
26	GAS CITY 14N 55E 27CDDB	MN	6.61	91.5	80	NS	<1	200	NS	<1	10
6	FUHS 05N 03E 12DCCB	SD	7.21	10.7	20	NS	1	<100	NS	3	<1
7	DELZER #1 12N 03E 28BACBB	SD	7.51	55.6	<10	NS	2	100	NS	<1	10
8	DELZER #2 12N 03E 32ACBC	SD	6.77	55.6	10	NS	1	100	NS	1	10
11	KAISER 06S 05E 24BAAA	SD	7.40	15.0	20	NS	1	100	NS	<1	10
13	BLACK HILLS CEMETERY 05N 05E 25ABD	SD	7.28	12.4	<10	NS	2	300	NS	1	<1
14	STREETER RANCH 06S 06E 15AACC	SD	7.61	19.4	10	NS	11	<100	NS	<1	<1
17	LIEN 02N 07E 18BCA	SD	7.41	11.9	20	NS	3	100	NS	<1	<1

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	COBALT (CO) (UG/L)	COPPER (CU) (UG/L)	IRON (FE) (UG/L)	LEAD (PB) (UG/L)	LITH-IUM (LI) (UG/L)	MANG-ANESE (MN) (UG/L)	MERCURY (HG) (UG/L)
17	SUMATRA 11N 32E 24ADCD	MN	7.51	84.1	NS	<1	20	2	3800	140	0.6
18	SLEEPING BUFFALO 32N 32E 35CDBD	MN	7.00	40.9	NS	<1	440	2	340	20	<0.1
19	SARPY MINE 01N 37E 26BDDD	MN	6.70	83.3	NS	<1	560	2	330	20	0.2
20	MYSSE FLOWING 12N 39E 09AACA	MN	6.66	63.8	NS	<1	20	2	2100	10	<0.1
21	COLSTRIP 02N 41E 34BADA	MN	6.52	97.2	NS	<1	340	2	570	8	<0.1
22	MOORE 10N 43E 21CDCA	MN	6.81	86.9	NS	<1	20	2.2	2300	8	<0.1
23	RANCH CREEK 09S 53E 22ABAC	MN	6.94	52.7	NS	<1	20	2	40	20	<0.1
24	BELLE CREEK 08S 54E 21ADAD	MN	7.01	56.2	NS	<1	50	2	40	8	<0.1
26	GAS CITY 14N 55E 27CDDB	MN	6.61	91.5	NS	<1	100	3	1500	20	1.2
6	FUHS 05N 03E 12DCCB	SD	7.21	10.7	NS	<1	10	29	<10	3	<0.1
7	DELZER #1 12N 03E 28BACBB	SD	7.51	55.6	NS	<1	7900	<1	90	150	0.1
8	DELZER #2 12N 03E 32ACBC	SD	6.77	55.6	NS	<1	5700	4	60	60	<0.1
11	KAISER 06S 05E 24BAAA	SD	7.40	15.0	NS	<1	80	<1	10	30	<0.1
13	BLACK HILLS CEMETERY 05N 05E 25ABD	SD	7.28	12.4	NS	2	20	3	<10	5	0.3
14	STREETER RANCH 06S 06E 15AACC	SD	7.61	19.4	NS	<1	20	2	10	4	<0.1
17	LIEN 02N 07E 18BCA	SD	7.41	11.9	NS	6	10	2	<10	<1	<0.1

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	MOLYB-DENUM (MO) (UG/L)	NICKEL (NI) (UG/L)	SELE-NIUM (SE) (UG/L)	SILVER (AG) (UG/L)	TIN (SN) (UG/L)	VANA-DIUM (V) (UG/L)	ZINC (ZN) (UG/L)
17	SUMATRA 11N 32E 24ADCD	MN	7.51	84.1	<1	NS	1	NS	NS	25	<10
18	SLEEPING BUFFALO 32N 32E 35CDBD	MN	7.00	40.9	<1	NS	<1	NS	NS	1.9	40
19	SARPY MINE 01N 37E 26BDDD	MN	6.70	83.3	<1	NS	3	NS	NS	<0.0	<10
20	MYSSE FLOWING 12N 39E 09AACA	MN	6.66	63.8	<1	NS	<1	NS	NS	6.5	<10
21	COLSTRIP 02N 41E 34BADA	MN	6.52	97.2	<1	NS	<1	NS	NS	0.6	<10
22	MOORE 10N 43E 21CDCA	MN	6.81	86.9	<1	NS	<1	NS	NS	7.0	<10
23	RANCH CREEK 09S 53E 22ABAC	MN	6.94	52.7	24	NS	5	NS	NS	11	20
24	BELLE CREEK 08S 54E 21ADAD	MN	7.01	56.2	23	NS	<1	NS	NS	6.7	20
26	GAS CITY 14N 55E 27CDDB	MN	6.61	91.5	<1	NS	2	NS	NS	59	10
6	FUHS 05N 03E 12DCCB	SD	7.21	10.7	1	NS	1	NS	NS	<0.1	590
7	DELZER #1 12N 03E 28BACBB	SD	7.51	55.6	34	NS	<1	NS	NS	<0.1	840
8	DELZER #2 12N 03E 32ACBC	SD	6.77	55.6	7	NS	<1	NS	NS	<0.1	190
11	KAISER 06S 05E 24BAAA	SD	7.40	15.0	2	NS	1	NS	NS	<0.1	<10
13	BLACK HILLS CEMETERY 05N 05E 25ABD	SD	7.28	12.4	7	NS	3	NS	NS	0.7	20
14	STREETER RANCH 06S 06E 15AACC	SD	7.61	19.4	1	NS	2	NS	NS	3.9	<10
17	LIEN 02N 07E 18BCA	SD	7.41	11.9	<1	NS	1	NS	NS	<0.1	230

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	ALUM-INUM (AL) (UG/L)	ANTI-MONY (SB) (UG/L)	ARSENIC (AS) (UG/L)	BARIUM (BA) (UG/L)	BERYL-LIUM (BE) (UG/L)	CADMIUM (CD) (UG/L)	CHROMIUM (CR) (UG/L)
20	DUPREE 13N 21E 31BDDA	SD	6.82	56.5	20	NS	<1	<100	NS	<1	20
21	HAMILTON 08N 23W 26ACDA	SD	6.92	58.2	<10	NS	<1	<100	NS	<1	10
22	HILLTOP RANCH 05N 24E 30CA	SD	6.70	61.8	10	NS	3	<100	NS	<1	20
23	EAGLE BUTTE 12N 24E 17CBBD	SD	7.00	55.5	10	NS	1	<100	NS	<1	20
25	MURDO 01S 26E 36ACA	SD	6.68	59.1	10	NS	4	<100	NS	<1	10
26	PRINCE 05N 27E 22CD	SD	6.89	57.0	<10	NS	<1	200	NS	<1	<1
27	BEAN 09N 03E 20CDD	SD	7.10	41.5	<10	NS	3	NS	NS	<1	<1
1	MOCK RANCH 57N 87W 21DBC01	WY	7.50	10.8	<10	NS	1	200	NS	<1	<1
2	DENIUS #1 58N 87W 32BA	WY	7.60	9.0	10	NS	<1	<100	NS	<1	<1
3	DENIUS #2 58N 87W 32BAB	WY	7.55	8.3	30	NS	<1	<100	NS	<1	<1
4	DENIUS #3 58N 87W 32BB	WY	7.69	8.5	30	NS	<1	<100	NS	<1	<1
5	HOLE-IN-THE-WALL 41N 84W 20BAC	WY	7.25	8.2	30	NS	3	<100	NS	<1	<1
6	STOREY FISH HATCHERY 53N 84W 13BDC	WY	7.30	8.0	10	NS	1	<100	<10	<1	<1
7	MOBIL 49N 83W 27DDA	WY	7.31	7.1	10	NS	1	<100	NS	<1	<1
8	CONOCO #44 41N 81W 09CDA	WY	7.17	32.2	<10	NS	<1	100	NS	<1	10
9	SHIDLER 40N 79W 31BCA	WY	7.55	72.6	10	NS	2	<100	NS	<1	10

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	COBALT (CO) (UG/L)	COPPER (CU) (UG/L)	IRON (FE) (UG/L)	LEAD (PB) (UG/L)	LITH-IUM (LI) (UG/L)	MANG-ANESE (MN) (UG/L)	MERCURY (HG) (UG/L)
20	DUFREE 13N 21E 31BDDA	SD	6.82	56.5	NS	<1	300	<1	230	40	<0.1
21	HAMILTON 08N 23W 26ACDA	SD	6.92	58.2	NS	<1	3000	<1	20	50	<0.1
22	HILLTOP RANCH 05N 24E 30CA	SD	6.70	61.8	NS	<1	860	<1	170	110	<0.1
23	EAGLE BUTTE 12N 24E 17CBBD	SD	7.00	55.5	NS	4	3000	<1	110	90	<0.1
25	MURDO 01S 26E 36ACA	SD	6.68	59.1	NS	<1	1400	2	70	50	<0.1
26	PRINCE 05N 27E 22CD	SD	6.89	57.0	NS	<1	420	<1	120	20	<0.1
27	BEAN 09N 03E 20CDD	SD	7.10	41.5	NS	2	40	4	20	<1	0.1
1	MOCK RANCH 57N 87W 21DBC01	WY	7.50	10.8	NS	<1	20	<1	<10	<1	<0.1
2	DENIUS #1 58N 87W 32BA	WY	7.60	9.0	NS	5	90	<1	<10	20	<0.1
3	DENIUS #2 58N 87W 32BAB	WY	7.55	8.3	NS	1	10	1	<10	<1	<0.1
4	DENIUS #3 58N 87W 32BB	WY	7.69	8.5	NS	1	10	1	10	20	<0.1
5	HOLE-IN-THE-WALL 41N 84W 20BAC	WY	7.25	8.2	NS	5	30	1	10	<1	<0.1
6	STOREY FISH HATCHERY 53N 84W 13BDC	WY	7.30	8.0	<10	20	NS	1	10	5	<0.1
7	MOBIL 49N 83W 27DDA	WY	7.31	7.1	NS	1	90	5	<10	70	<0.1
8	CONOCO #44 41N 81W 09CDA	WY	7.17	32.2	NS	1	870	<1	360	20	10
9	SHIDLER 40N 79W 31BCA	WY	7.55	72.6	NS	<1	2400	<1	390	240	<0.1

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	MOLYB-DENUM (MO) (UG/L)	NICKEL (NI) (UG/L)	SELE-NIUM (SE) (UG/L)	SILVER (AG) (UG/L)	TIN (SN) (UG/L)	VANA-DIUM (V) (UG/L)	ZINC (ZN) (UG/L)
20	DUPREE 13N 21E 31BDDA	SD	6.82	56.5	<1	NS	<1	NS	NS	<0.1	<10
21	HAMILTON 08N 23W 26ACDA	SD	6.92	58.2	<1	NS	<1	NS	NS	<0.1	20
22	HILLTOP RANCH 05N 24E 30CA	SD	6.70	61.8	4	NS	<1	NS	NS	0.1	180
23	EAGLE BUTTE 12N 24E 17CBBD	SD	7.00	55.5	<1	NS	<1	NS	NS	<0.1	60
25	MURDO 01S 26E 36ACA	SD	6.68	59.1	<1	NS	<1	NS	NS	<0.1	400
26	PRINCE 05N 27E 22CD	SD	6.89	57.0	<1	NS	<1	NS	NS	<0.1	10
27	BEAN 09N 03E 20CDD	SD	7.10	41.5	17	NS	8	NS	NS	5	150
1	MOCK RANCH 57N 87W 21DBC01	WY	7.50	10.8	2	NS	4	NS	NS	1.5	30
2	DENIUS #1 58N 87W 32BA	WY	7.60	9.0	1	NS	3	NS	NS	0.5	10
3	DENIUS #2 58N 87W 32BAB	WY	7.55	8.3	2	NS	1	NS	NS	14	<10
4	DENIUS #3 58N 87W 32BB	WY	7.69	8.5	1	NS	1	NS	NS	18	10
5	HOLE-IN-THE-WALL 41N 84W 20BAC	WY	7.25	8.2	<1	NS	1	NS	NS	2.9	70
6	STOREY FISH HATCHERY 53N 84W 13BDC	WY	7.30	8.0	1	<1	<1	<1	NS	1.4	10
7	MOBIL 49N 83W 27DDA	WY	7.31	7.1	4	NS	1	<1	NS	0.7	20
8	CONOCO #44 41N 81W 09CDA	WY	7.17	32.2	2	NS	<1	<1	NS	6.5	<10
9	SHIDLER 40N 79W 31BCA	WY	7.55	72.6	5	NS	<1	<1	NS	2.4	20

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPERATURE (DEG C)	ALUMINUM (AL) (UG/L)	ANTIMONY (SB) (UG/L)	ARSENIC (AS) (UG/L)	BARIUM (BA) (UG/L)	BERYLLIUM (BE) (UG/L)	CADMIUM (CD) (UG/L)	CHROMIUM (CR) (UG/L)
10	MKM 39N 78W 26CDC	WY	6.71	88.1	NS	NS	12	100	NS	<1	<1
11	CONOCO #175 33N 75W 20AAC	WY	7.30	30.1	10	NS	25	100	NS	<1	<1
12	BARBER RANCH SPRING 32N 74W 03CBD	WY	7.46	15.7	<10	NS	5	<100	NS	<1	<1
13	DEVILS TOWER 53N 65W 18BBD	WY	7.20	17.1	<10	<10	3	40	NS	<1	<1
14	HTH #1 57N 65W 15DA	WY	6.99	46.2	10	NS	1	200	NS	<1	<1
15	UPTON 48N 65W 25CC	WY	7.12	25.7	20	NS	1	<100	NS	<1	<1
16	CORONADO #2 46N 64W 13CCA	WY	7.16	39.8	10	NS	2	<100	<10	1	<1
18	JBJ 44N 63W 26CAC	WY	6.70	45.1	20	NS	2	<100	<10	<1	<1
19	SEELEY 46N 62W 18BDC	WY	7.30	13.0	10	NS	3	<100	NS	<1	<1
20	VOSS 45N 61W 28AB	WY	7.30	26.1	10	NS	4	<100	<10	<1	<1
22	SELF 45N 61W 33AB01	WY	7.30	29.8	10	NS	3	<100	NS	<1	<1
23	MARTENS MADISON 45N 60W 07CA	WY	7.50	15.6	<10	<10	1	NS	<10	<1	<1
24	MALLO CAMP 47N 60W 04BDA	WY	7.60	7.7	<10	<10	1	NS	<10	<1	10
25	RANCH A 52N 60W 18C	WY	7.26	12.2	20	NS	1	<100	NS	<1	<1

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	COBALT (CO) (UG/L)	COPPER (CU) (UG/L)	IRON (FE) (UG/L)	LEAD (PB) (UG/L)	LITH-IUM (LI) (UG/L)	MANG-ANESE (MN) (UG/L)	MERCURY (HG) (UG/L)
10	MKM 39N 78W 26CDC	WY	6.71	88.1	NS	<1	6900	<1	870	150	<0.1
11	CONOCO #175 33N 75W 20AAC	WY	7.30	30.1	NS	<1	2400	<1	150	300	<0.1
12	BARBER RANCH SPRING 32N 74W 03CBD	WY	7.46	15.7	NS	1	20	3	10	10	<0.1
13	DEVILS TOWER 53N 65W 18BBD	WY	7.20	17.1	NS	5	30	1	10	<1	<0.1
14	HTH #1 57N 65W 15DA	WY	6.99	46.2	NS	<1	5800	<1	40	160	<0.1
15	UPTON 48N 65W 25CC	WY	7.12	25.7	<10	11	NS	1	<10	<1	<0.1
16	CORONADO #2 46N 64W 13CCA	WY	7.16	39.8	<10	3	NS	<1	<10	<1	<0.1
18	JBJ 44N 63W 26CAC	WY	6.70	45.1	<10	<1	NS	<1	30	200	<0.1
19	SEELEY 46N 62W 18BDC	WY	7.30	13.0	NS	1	20	<1	<10	<1	<0.1
20	VOSS 45N 61W 28AB	WY	7.30	26.1	<10	1	NS	<1	<10	<1	<0.1
22	SELF 45N 61W 33AB01	WY	7.30	29.8	NS	2	20	<1	10	20	<0.1
23	MARTENS MADISON 45N 60W 07CA	WY	7.50	15.6	NS	1	<10	<1	<10	10	<0.1
24	MALLO CAMP 47N 60W 04BDA	WY	7.60	7.7	NS	20	<10	1	<10	<1	<0.1
25	RANCH A 52N 60W 18C	WY	7.26	12.2	NS	<1	10	1	<10	<1	<0.1

Table 28.--*Concentrations of dissolved minor cations in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	MOLYB-DENUM (MO) (UG/L)	NICKEL (NI) (UG/L)	SELE-NIUM (SE) (UG/L)	SILVER (AG) (UG/L)	TIN (SN) (UG/L)	VANA-DIUM (V) (UG/L)	ZINC (ZN) (UG/L)
10	MKM 39N 78W 26CDC	WY	6.71	88.1	8	NS	<1	<1	NS	10	140
11	CONOCO #175 33N 75W 20AAC	WY	7.30	30.1	27	NS	<1	NS	NS	<0.1	30
12	BARBER RANCH SPRING 32N 74W 03CBD	WY	7.46	15.7	<1	NS	1	NS	NS	3.1	40
13	DEVILS TOWER 53N 65W 18BBD	WY	7.20	17.1	13	3	1	NS	NS	1.8	240
14	HTH #1 57N 65W 15DA	WY	6.99	46.2	17	NS	8	NS	NS	<0.1	<10
15	UPTON 48N 65W 25CC	WY	7.12	25.7	8	1	6	<1	NS	NS	<10
16	CORONADO #2 46N 64W 13CCA	WY	7.16	39.8	2	<1	1	<1	NS	1.3	<10
18	JBJ 44N 63W 26CAC	WY	6.70	45.1	50	<1	<1	<1	NS	<0.1	<10
19	SEELEY 46N 62W 18BDC	WY	7.30	13.0	2	NS	1	NS	NS	1.6	20
20	VOSS 45N 61W 28AB	WY	7.30	26.1	3	<1	3	<1	NS	1.9	<10
22	SELF 45N 61W 33AB01	WY	7.30	29.8	4	NS	4	NS	NS	2.8	<10
23	MARTENS MADISON 45N 60W 07CA	WY	7.50	15.6	2	2	1	NS	NS	6.6	10
24	MALLO CAMP 47N 60W 04BDA	WY	7.60	7.7	1	<1	<1	NS	NS	2.2	180
25	RANCH A 52N 60W 18C	WY	7.26	12.2	8	NS	1	NS	NS	0.5	370

Table 29.--*Concentration of dissolved minor anions in water from the Madison aquifer system*

(MN = Montana; SD = South Dakota; WY = Wyoming; DEG C = degrees Celsuis;
UG/L = micrograms per liter; MG/L = milligrams per liter)

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	BORON (UG/L)	IODIDE (MG/L)	NITROGEN KJELDAHL (MG/L)	SULFIDE (MG/L)	PHOSPHATE (MG/L)
2	GORE HILL 20N 03E 28CDAD	MN	7.13	14.0	510	0.03	0.3	0.9	<0.02
3	GREAT FALLS HIGH SCHOOL 20N 04E 07BDAC	MN	7.40	13.1	90	0.02	<0.01	NS	<0.01
4	BOZEMAN FISH HATCHERY 01S 06E 34BCDA	MN	7.84	8.6	10	<0.001	<0.01	NS	<0.01
5	BOUGH RANCH 22N 06E 09DDAB	MN	7.06	17.9	330	0.06	0.56	NS	<0.01
6	MCLEOD WARM SPRING 03S 13E 34ABAB	MN	7.40	24.6	10	<0.001	0.16	NS	<0.01
7	BIG TIMBER FISH HATCHERY 01N 14E 15DAAA	MN	7.64	10.7	40	<0.001	0.19	NS	<0.01
8	HANOVER 16N 16E 12DCCC	MN	7.63	20.4	30	<0.001	<0.01	NS	<0.01
9	VANEK WARM SPRING 17N 18E 19DBCA	MN	7.40	19.6	60	<0.001	<0.01	NS	<0.01
10	LEWISTOWN BIG SPRING 14N 19E 05ABCC	MN	7.58	10.6	30	<0.001	<0.01	NS	<0.01
11	BLUEWATER SPRING 06S 24E 09BCAA	MN	7.29	14.3	170	0.01	0.01	NS	<0.01
12	LANDUSKY SPRING 25N 24E 32DABC	MN	7.24	20.4	210	<0.001	<0.01	NS	<0.01
13	LODGEPOLE WARM SPRING 26N 25E 24BCDB	MN	7.08	31.6	410	0.01	<0.01	NS	<0.01
14	HTH #3 02N 27E 35AAB01	MN	6.80	51.8	370	0.01	0.70	4.5	0.01
15	KEG COULEE 11N 30E 35ADAA	MN	6.50	61.7	6100	0.15	1.90	57	<.01
16	TEXACO C115X 11N 32E 15ABAC	MN	7.10	84.0	7900	0.19	2.40	130	0.01

Table 29.--*Concentration of dissolved minor anions in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	BORON (UG/L)	IODIDE (MG/L)	NITROGEN KJELDAHL (MG/L)	SULFIDE (MG/L)	PHOSPHATE (MG/L)
17	SUMATRA 11N 32E 24ADCD	MN	7.51	84.1	6800	0.24	2.50	NS	<.01
18	SLEEPING BUFFALO 32N 32E 35CDBD	MN	7.00	40.9	1000	0.06	0.91	0.3	<.01
19	SARPY MINE 01N 37E 26BDDD	MN	6.70	83.3	340	0.01	0.33	2.9	0.03
20	MYSSE FLOWING 12N 39E 09AACA	MN	6.66	63.8	3200	0.12	1.50	NS	<.01
21	COLSTRIP 02N 41E 34BADA	MN	6.52	97.2	670	0.02	0.43	4.0	<.01
22	MOORE 10N 43E 21CDCA	MN	6.81	86.9	3300	0.16	2.10	19	<.01
23	RANCH CREEK 09S 53E 22ABAC	MN	6.94	52.7	90	<.001	<.01	NS	0.09
24	BELLE CREEK 08S 54E 21ADAD	MN	7.01	56.2	90	<.001	0.07	NS	<.01
26	GAS CITY 14N 55E 27CDDB	MN	6.61	91.5	4700	0.41	9.50	54	0.06
1	KOSKEN 42N 26W 34ABCD	SD	6.70	63.5	2	NS	NS	0.7	NS
6	FUHS 05N 03E 12DCCB	SD	7.21	10.7	20	<.001	0.17	0.5	<.01
7	DELZER #1 12N 03E 28BACBB	SD	7.51	55.6	140	0.01	0.11	NS	<.01
8	DELZER #2 12N 03E 32ACBC	SD	6.77	55.6	170	<.001	0.19	0.2	<.01
10	EVANS PLUNGE 07S 05E 13BCCC	SD	6.90	30.5	NS	NS	NS	0.3	NS
11	KAISER 06S 05E 24BAAA	SD	7.40	15.0	30	<.001	NS	0.1	<.01
12	JONES SPRING 04N 05E 23	SD	7.20	12.9	30	<.001	0.10	NS	NS

Table 29.--*Concentration of dissolved minor anions in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER- ATURE (DEG C)	BORON (UG/L)	IODIDE (MG/L)	NITROGEN KJELDAHL (MG/L)	SULFIDE (MG/L)	PHOSPHATE (MG/L)
13	BLACK HILLS CEMETERY 05N 05E 25ABD	SD	7.28	12.4	10	NS	0.08	0.2	0.03
14	STREETER RANCH 06S 06E 15AACC	SD	7.61	19.4	NS	NS	<.01	0.3	NS
17	LIEN 02N 07E 18BCA	SD	7.41	11.9	<100	<.001	0.19	NS	<.01
19	PHILIP 01N 20E 01ACDD	SD	6.78	68.0	NS	NS	NS	0.3	NS
20	DUPREE 13N 21E 31BDDA	SD	6.82	56.5	490	0.01	0.90	19	NS
21	HAMILTON 08N 23W 26ACDA	SD	6.92	58.2	130	<.001	0.26	0.7	0.03
22	HILLTOP RANCH 05N 24E 30CA	SD	6.70	61.8	140	NS	12	0.9	NS
23	EAGLE BUTTE 12N 24E 17CBBD	SD	7.00	55.5	250	NS	.76	0.2	NS
24	MIDLAND 01N 25E 06CAA	SD	6.69	71.0	NS	NS	NS	0.3	NS
25	MURDO 01S 26E 36ACA	SD	6.68	59.1	100	NS	0.41	0.7	NS
26	PRINCE 05N 27E 22CD	SD	6.89	57.0	180	0.01	0.47	0.6	<.01
27	BEAN 09N 03E 20CDD	SD	7.10	41.5	<100	NS	0.05	0.2	NS
1	MOCK RANCH 57N 87W 21DBC01	WY	7.50	10.8	230	<.001	<.01	NS	<.01
2	DENIUS #1 58N 87W 32BA	WY	7.60	9.0	<100	<.001	<.01	NS	<.01
3	DENIUS #2 58N 87W 32BAB	WY	7.55	8.3	<100	<.001	0.02	NS	NS
4	DENIUS #3 58N 87W 32BB	WY	7.69	8.5	<100	<.001	<.01	NS	<.01

Table 29.--*Concentration of dissolved minor anions in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	BORON (UG/L)	IODIDE (MG/L)	NITROGEN KJELDAHL (MG/L)	SULFIDE (MG/L)	PHOSPHATE (MG/L)
5	HOLE-IN-THE-WALL 41N 84W 20BAC	WY	7.25	8.2	<100	<.001	NS	NS	0.03
6	STOREY FISH HATCHERY 53D 84W 13BDC	WY	7.30	8.0	<100	NS	NS	NS	0.03
7	MOBIL 49N 83W 27DDA	WY	7.31	7.1	<100	<.001	NS	NS	<.01
8	CONOCO #44 41N 81W 09CDA	WY	7.17	32.2	360	0.03	0.76	NS	0.03
9	SHIDLER 40N 79W 31BCA	WY	7.55	72.6	430	0.03	0.32	NS	<.01
10	MKM 39N 78W 26CDC	WY	6.71	88.1	890	0.02	0.11	NS	<.01
11	CONOCO #175 33N 75W 20AAC	WY	7.30	30.1	200	0.01	<.01	NS	<.01
12	BARBER RANCH SPRING 32N 74W 03CBD	WY	7.46	15.7	<100	0.01	0.20	NS	0.06
13	DEVILS TOWER 53N 65W 18BBD	WY	7.20	17.1	<100	NS	0.12	NS	0.06
14	HTH #1 57N 65W 15DA	WY	6.99	46.2	<100	<.001	0.54	NS	0.03
16	CORONADO #2 46N 64W 13CCA	WY	7.16	39.8	<100	NS	0.01	NS	0.02
18	JBJ 44N 63W 26CAC	WY	6.70	45.1	<100	NS	0.15	NS	<.01
19	SEELEY 46N 62W 18BDC	WY	7.30	13.0	<100	0.01	0.17	NS	0.03
20	VOSS 45N 61W 28AB	WY	7.30	26.1	<100	NS	0.01	NS	0.06
22	SELF 45N 61W 33AB01	WY	7.30	29.8	<100	0.01	0.10	NS	<.01
23	MARTENS MADISON 45N 60W 07CA	WY	7.50	15.6	<100	<.001	<.01	NS	<.01

Table 29.--*Concentration of dissolved minor anions in water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	PH (UNITS)	TEMPER-ATURE (DEG C)	BORON (UG/L)	IODIDE (MG/L)	NITROGEN KJELDAHL (MG/L)	SULFIDE (MG/L)	PHOSPHATE (MG/L)
24	MALLO CAMP 47N 60W 04BDA	WY	7.60	7.7	<100	NS	0.16	NS	<.01
25	RANCH A 52N 60W 18C	WY	7.26	12.2	<100	<.001	0.34	NS	<.01

NOTE: NS means parameter of interest not sampled.

Table 30.--*Selected saturation indices and related data for water from the Madison aquifer system*

(MN = Montana; SD = South Dakota; WY = Wyoming; log (PCO2) = negative log of partial pressure of carbon dioxide; MMOLES/L = millimoles per liter)

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	LOG (PCO2)	TOTAL INORGANIC CARBON (MMOLES/L)	ARAGONITE	CALCITE	DOLOMITE	STRONTIANITE	GYPSUM	ANHYDRITE	CELESTITE
2	GORE HILL 20N 03E 28CDAD	MN	1.70	6.54	-0.25	0.04	-0.08	-1.02	-0.58	-0.90	-0.87
3	GREAT FALLS HIGH SCHOOL 20N 04E 07BDAC	MN	2.09	4.58	-0.24	0.05	-0.15	-1.26	-1.02	-1.36	-1.57
4	BOZEMAN FISH HATCHERY 01S 06E 34BCDA	MN	2.60	3.68	-0.13	0.19	-0.02	-1.74	-2.11	-2.49	-3.33
5	BOUGH RANCH 22N 06E 09DDAB	MN	1.78	4.74	-0.28	0.00	0.05	-0.89	-0.10	-0.39	-0.16
6	MCLEOD WARM SPRING 03S 13E 34ABAB	MN	2.15	3.28	-0.25	0.01	-0.18	-1.66	-1.36	-1.57	-2.10
7	BIG TIMBER FISH HATCHERY 01N 14E 15DAAA	MN	2.36	4.05	-0.25	0.06	-0.28	-1.44	-2.04	-2.40	-2.81
8	HANOVER 16N 16E 22DCCC	MN	2.37	3.49	-0.01	0.26	0.31	-0.91	-1.17	-1.43	-1.48
9	VANEK WARM SPRING 17N 18E 19DBCA	MN	2.17	3.50	-0.14	0.13	0.00	-1.00	-0.80	-1.06	-1.08
10	LEWISTOWN BIG SPRING 14N 19E 05ABCC	MN	2.40	3.34	-0.29	0.10	-0.28	-1.23	-1.26	-1.62	-1.78
11	BLUEWATER SPRING 06S 24E 09BCAA	MN	2.08	3.98	0.08	0.37	0.06	-0.89	0.12	-0.20	-0.37
12	LANDUSKY SPRING 25N 24E 32DABC	MN	2.00	3.85	-0.08	0.18	0.19	-0.94	-0.25	-0.50	-0.51
13	LODGEPOLE WARM SPRING 26N 25E 24BCDB	MN	1.81	3.68	-0.12	0.14	0.16	-1.05	-0.28	-0.43	-0.44
14	HTH #3 02N 27E 35AAB01	MN	1.58	2.94	-0.12	0.20	-0.03	-1.25	0.01	0.05	-0.04
15	KEG COULEE 11N 30E 35ADAA	MN	0.87	7.67	-0.25	0.14	0.66	-1.34	-0.56	-0.44	-0.44
16	TEXACO C115X 11N 32E 15ABAC	MN	1.21	7.91	0.47	0.98	1.16	-0.66	-0.46	-0.24	-0.20

Table 30.--*Selected saturation indices and related data for water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	LOG (PCO2)	TOTAL INORGANIC CARBON (MMOLES/L)	ARAGONITE	CALCITE	DOLOMITE	STRONTIANITE	GYPSUM	ANHYDRITE	CELESTITE
17	SUMATRA 11N 32E 24ADCD	MN	2.34	1.26	0.00	0.60	0.20	-1.10	-0.65	-0.37	-0.27
18	SLEEPING BUFFALO 32N 32E 35CDBD	MN	1.82	2.80	-0.09	0.19	0.08	-1.06	0.06	0.00	0.01
19	SARPY MINE 01N 37E 26BDDD	MN	1.22	3.03	-0.24	0.36	-0.29	-1.45	-0.36	-0.08	-0.11
20	MYSSE FLOWING 12N 39E 09AACA	MN	0.98	7.04	0.02	0.43	0.38	-1.15	-0.12	0.01	-0.06
21	COLSTRIP 02N 41E 34BADA	MN	0.90	3.81	-0.53	0.24	-0.94	-1.29	-0.60	-0.23	-0.24
22	MOORE 10N 43E 21CDCA	MN	1.05	5.58	0.06	0.70	0.41	-1.18	-4.27	-0.11	-0.14
23	RANCH CREEK 09S 53E 22ABAC	MN	1.48	4.08	-0.06	0.27	0.19	-1.18	-0.66	-0.62	-0.68
24	BELLE CREEK 08S 54E 21ADAD	MN	1.54	3.85	0.03	0.38	-0.38	-1.14	-0.63	-0.56	-0.67
26	GAS CITY 14N 55E 27CDDB	MN	0.91	4.98	-0.22	0.48	-0.18	-1.49	-0.45	-0.12	-0.16
1	KOSKEN 42N 26W 34ABCD	SD	1.35	2.97	-0.36	0.05	-0.46	-1.67	-0.49	-0.36	-0.58
2	MCNENNEY 02N 01E 21BBC	SD	1.84	5.04	-0.45	-0.26	-0.73	-0.11	-2.61	-1.68	-2.46
3	PROVO 10S 02E 03	SD	1.51	3.45	-0.24	-0.03	-0.06	.	-1.00	-0.90	-1.64
4	RHOADS FORK 02N 02E 15	SD	1.97	5.71	-0.40	-0.22	-0.58	.	-2.89	-3.31	-5.06
5	SPEARFISH 06N 02E 10D	SD	2.03	4.93	-0.36	-0.17	-0.34	.	-2.56	-2.90	-4.26
6	FUHS 05N 03E 12DCCB	SD	1.79	6.37	-0.40	-0.10	-0.21	-1.70	-1.13	-1.49	-2.00
7	DELZER #1 12N 03E 28BACBB	SD	2.38	1.82	.45	.80	1.16	-0.65	-0.02	0.05	0.00

Table 30.--*Selected saturation indices and related data for water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	LOG (PCO2)	TOTAL INORGANIC CARBON (MMOLES/L)	ARAGONITE	CALCITE	DOLOMITE	STRONTIANITE	GYPSUM	ANHYDRITE	CELESTITE
8	DELZER #2 12N 03E 32ACBC	SD	1.38	3.84	-0.02	0.33	0.19	-1.18	0.02	0.08	-0.02
9	CASCADE SPRING 08S 05E 20	SD	1.60	4.98	-0.17	0.10	-0.33	-0.93	0.09	-5.19	-0.09
10	EVANS PLUNGE 07S 05E 13BCCC	SD	1.53	4.68	-0.26	-0.07	-0.38	.	-0.52	-0.68	-1.38
11	KAISER 06S 05E 24BAAA	SD	2.11	4.08	-0.44	-0.16	-0.55	-1.89	-2.36	-2.67	-3.30
12	JONES SPRING 04N 05E 23	SD	1.77	6.13	-0.36	-0.17	-0.50	-0.11	-2.61	-2.94	-4.53
13	BLACK HILLS CEMETERY 05N 05E 25ABD	SD	1.93	4.99	-0.48	-0.19	-0.61	-1.82	-2.42	-2.76	-3.30
14	STREETER RANCH 06S 06E 15AACC	SD	2.35	3.44	-0.27	0.00	-0.19	-2.61	-2.58	-2.85	-4.35
16	CLEGHORN SPRING 01N 07E 08	SD	2.19	3.56	-0.60	-0.41	-0.81	-0.06	-2.18	-2.53	-3.85
17	LIEN 02N 07E 18BCA	SD	2.11	4.35	-0.48	-0.18	-0.50	-2.11	-2.38	-2.72	-3.56
18	ELLSWORTH AFB 02N 08E 13BDC	SD	1.56	3.88	-0.23	-0.02	-0.03	.	-1.14	-1.13	-2.11
19	PHILIP 01N 20E 01ACDD	SD	1.33	3.33	-0.21	0.01	0.03	.	-0.53	-0.37	-1.08
20	DUPREE 13N 21E 31BDDA	SD	1.54	2.80	-0.20	0.15	-0.09	-1.20	-0.15	-0.08	-0.01
21	HAMILTON 08N 23W 26ACDA	SD	1.58	3.04	0.01	0.38	0.29	-1.16	-0.14	-0.05	-0.15
22	HILLTOP RANCH 05N 24E 30CA	SD	1.35	3.16	-0.27	0.12	-0.26	-1.47	-0.28	-0.11	-0.22
23	EAGLE BUTTE 12N 24E 17CBBD	SD	1.63	3.31	-0.06	0.22	0.22	-0.25	-0.22	-0.19	-0.09
24	MIDLAND 01N 25E 06CAA	SD	1.25	3.19	-0.28	-0.06	-0.12	.	-0.42	-0.23	-0.94

Table 30.--*Selected saturation indices and related data for water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	LOG (PCO2)	TOTAL INORGANIC CARBON (MMOLES/L)	ARAGONITE	CALCITE	DOLOMITE	STRONTIANITE	GYPSUM	ANHYDRITE	CELESTITE
25	MURDO 01S 26E 36ACA	SD	1.36	3.17	-0.32	0.05	-0.37	-1.53	-0.35	-0.26	-0.39
26	PRINCE 05N 27E 22CD	SD	1.61	2.69	-0.08	0.28	0.07	-1.25	-0.16	-0.09	-0.19
27	BEAN 09N 03E 20CDD	SD	1.77	3.43	-0.12	0.16	0.15	-1.20	-0.70	-0.75	-0.85
1	MOCK RANCH 57N 87W 21DBC01	WY	2.20	4.35	-0.32	-0.02	-0.36	-1.96	-2.53	-2.88	-3.74
2	DENIUS #1 58N 87W 32BA	WY	2.32	4.13	-0.42	-0.11	-0.28	-1.86	-2.24	-2.61	-3.28
3	DENIUS #2 58N 87W 32BAB	WY	2.27	4.23	-0.33	-0.01	-0.49	-2.09	-2.98	-3.36	-4.36
4	DENIUS #3 58N 87W 32BB	WY	2.30	5.40	0.01	-5.41	0.33	-1.17	-1.75	-2.13	-2.54
5	HOLE-IN-THE-WALL 41N 84W 20BAC	WY	1.94	4.82	-0.81	-0.49	-0.95	-2.41	-2.83	-3.22	-4.06
6	STOREY FISH HATCHERY 53N 84W 13BDC	WY	2.05	4.16	-0.63	-0.32	-1.11	-2.56	-2.93	-3.32	-4.48
7	MOBIL 49N 83W 27DDA	WY	2.14	3.45	-0.92	-0.60	-1.38	-2.52	-2.73	-3.13	-3.97
8	CONOCO #44 41N 81W 09CDA	WY	1.86	3.90	-0.05	0.21	0.16	-1.17	-0.42	-0.56	-0.76
9	SHIDLER 40N 79W 31BCA	WY	2.20	2.07	0.05	0.33	0.21	-1.14	-0.33	-0.38	-0.60
10	MKM 39N 78W 26CDC	WY	1.50	2.72	-0.48	-0.16	-0.89	-1.68	-0.44	-0.40	-0.56
11	CONOCO #175 33N 75W 20AAC	WY	2.22	2.18	-0.37	-0.11	-0.53	-1.48	-0.87	-1.03	-1.24
12	BARBER RANCH SPRING 32N 74W 03CBD	WY	2.16	4.10	-0.30	-0.02	-0.33	-1.65	-1.93	-2.23	-2.76
13	DEVILS TOWER 53N 65W 18BBD	WY	1.84	5.09	-0.28	0.00	-0.25	.	-1.01	-1.30	.

Table 30.--*Selected saturation indices and related data for water from the Madison aquifer system*--Continued

SITE NUMBER ON PLATES	WELL OR SPRING NAME LEGAL DESCRIPTION	STATE	LOG (PCO2)	TOTAL INORGANIC CARBON (MMOLES/L)	ARAGONITE	CALCITE	DOLOMITE	STRONTIANITE	GYPSUM	ANHYDRITE	CELESTITE
14	HTH #1 57N 65W 15DA	WY	1.59	3.98	-0.09	0.21	0.12	-1.41	-0.67	-0.68	-0.73
15	UPTON 48N 65W 25CC	WY	1.70	5.18	-0.28	-0.08	-0.08	.	-1.19	-1.39	-1.74
16	CORONADO #2 46N 64W 13CCA	WY	1.64	5.09	-0.18	0.09	0.21	-1.88	-2.09	-2.16	-2.89
17	OSAGE 46N 63W 15BD	WY	1.75	5.50	-0.24	-0.04	-0.10	.	-1.72	-1.95	-3.18
18	JBJ 44N 63W 26CAC	WY	1.58	2.22	-0.97	-0.68	-1.55	.	-1.20	-1.22	.
19	SEELEY 46N 62W 18BDC	WY	1.91	5.49	-0.34	-0.05	-0.34	-1.89	-2.18	-2.51	-3.26
20	VOSS 45N 61W 28AB	WY	1.82	5.60	-0.14	0.12	0.20	-1.63	-1.84	-2.04	-2.65
21	NEWCASTLE 45N 61W 20DCA	WY	1.75	5.34	-0.26	-0.07	-0.07	.	-1.79	-2.00	-3.12
22	SELF 45N 61W 33AB01	WY	1.84	5.07	-0.08	0.18	0.30	-1.48	-1.52	-1.69	-2.17
23	MARTENS MADISON 45N 60W 07CA	WY	1.58	6.23	-0.62	-0.34	-0.86	.	-4.08	-4.39	.
24	MALLO CAMP 47N 60W 04BDA	WY	2.23	5.23	-0.20	0.12	-0.07	.	-3.18	-3.57	.
25	RANCH A 52N 60W 18C	WY	1.92	5.06	-0.26	0.03	-0.39	-1.37	-0.98	-1.32	-1.64