

METHODS USED AND DATA SETS CONSIDERED

Most of the data used in this study were collected as part of the U.S. Geological Survey Regional Aquifer System Analysis Program (Busby and others, 1983, 1991) or the Black Hills Hydrology Study, using applicable methods and protocols. Data sets considered primarily include samples collected prior to the end of water year 1998, when data collection for the Black Hills Hydrology Study was completed. However, several isotope samples collected during water year 2000 also are considered. Additional chemical data for precipitation in Newcastle, Wyoming, were obtained from the National Atmospheric Deposition Program/National Trends Network (1999).

For geochemical analyses involving major ions, a cation/anion balance within 10 percent was used as a general sample selection criterion. For some selected single constituents, all applicable data were used. For geochemical analyses based on pH or results of speciation calculations, only samples collected specifically for the Black Hills Hydrology Study were used because these samples were collected using a closed-system device, thereby avoiding reaction with the atmosphere during sampling. Field measurement of pH values included temperature compensation to correct for the effect of temperature on electrode response.

For some samples used in speciation calculations, an estimated temperature was calculated from a linear regression of temperature with distance from outcrop area. The geochemical program PHREEQC (Parkhurst and Appelo, 1999) was used for speciation calculations and for conducting forward geochemical modeling to illustrate relations among chemical parameters that would be expected for certain chemical reactions.

Selected site information for all samples considered in this report is presented in table 7 in the Supplemental Information section at the end of this report. The same site numbers are used consistently throughout the report.

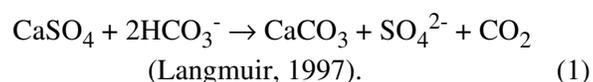
GEOCHEMISTRY OF MADISON AND MINNELUSA AQUIFERS

The major-ion and isotope chemistry of the Madison and Minnelusa aquifers are discussed in the following sections. The discussion of major-ion chemistry includes information regarding distribution of major ions, saturation state, and evolutionary

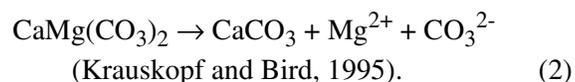
processes. Stable isotopes of oxygen and hydrogen are used to evaluate ground-water recharge areas and flow-paths. Tritium, which is an unstable hydrogen isotope, is used for analysis of ground-water ages.

Major-Ion Chemistry

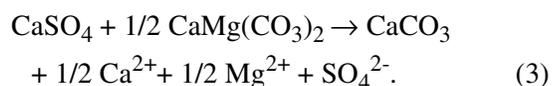
Major reactive minerals in the Madison and Minnelusa aquifers are calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and anhydrite (CaSO_4). The interactions of these minerals with water and dissolved gases, to a large extent, defines the chemical composition of ground water in the two aquifers. An important consequence of the presence of both calcite and anhydrite in the Madison and Minnelusa aquifers is the potential for precipitation of calcite by the common-ion effect, which can be represented as



In partially dolomitized limestone, dolomite dissolution also can lead to precipitation of calcite:



The term “dedolomite” was originally used to describe the replacement of dolomite by calcite during near-surface chemical weathering (von Morlot, 1847). Strictly speaking, “dedolomitization” describes the formation of the mineral phase dedolomite, which is calcite pseudomorphous after dolomite. In this report, “dedolomitization” is used to describe a combination of the above two reactions (eqs. 1 and 2), in which the irreversible dissolution of anhydrite in waters saturated with calcite and dolomite drives additional dissolution of dolomite and concurrent precipitation of calcite (Back and others, 1983). The dedolomitization reaction can be represented as:



The extent to which dedolomitization occurs in the Madison and Minnelusa aquifers can be illustrated through the major-ion chemistry and saturation indices of the ground water as well as through identification of trends in pH and calcium, magnesium, and sulfate concentrations.

Distribution of Major Ions

The major-ion chemistry of water in the Madison and Minnelusa aquifers can be illustrated with trilinear and Stiff (1951) diagrams, which show spatial variations and possible trends in the major-ion chemistry of the waters. In constructing Stiff diagrams, the average milliequivalent value was used where more than one sample existed for a site. For clarity, not all diagrams were plotted on the maps, but an effort was made to include diagrams representative of the water chemistry in a particular area.

A trilinear diagram showing percentages of major ions in the Madison aquifer is shown in figure 9, and the distribution of major-ion chemistry in the Madison aquifer throughout the study area is shown in figure 10. Figure 9 shows two main types of water in the Madison aquifer: calcium magnesium bicarbonate type and calcium sodium chloride sulfate type. Figure 10 shows that water in the Madison aquifer is dominated by calcium, magnesium, and bicarbonate ions throughout most of the study area. The high concentrations of chloride, sulfate, and sodium in the southwestern part of the study area relative to the rest of the study area probably reflect the presence of more evolved ground water and regional flow, or greater amounts of evaporite minerals available for

dissolution. Ion chemistry is somewhat anomalous for site 188 (Rapid City area), which has high chloride with calcium and magnesium, rather than sodium.

A trilinear diagram showing percentages of major ions in the Minnelusa aquifer is shown in figure 9, and Stiff diagrams representative of the major-ion chemistry in water from Minnelusa wells are shown in figure 11. Figure 9 illustrates three main types of water in the Minnelusa aquifer: calcium magnesium bicarbonate type, calcium magnesium sulfate type, and calcium magnesium bicarbonate sulfate chloride type. Figure 11 shows that water in the Minnelusa aquifer generally evolves downgradient from a calcium magnesium bicarbonate type to a calcium magnesium sulfate type due to dissolution of anhydrite. In the Hot Springs area, ground water in the Minnelusa aquifer is characterized by higher concentrations of sodium and chloride. Because chloride is conservative in water, it can be used to identify leakage between aquifers (Busby and others, 1995). The high chloride concentrations in this area in both the Madison and Minnelusa aquifers could reflect hydraulic connection between the aquifers. The dissolution of evaporite minerals and the presence of more evolved ground water contributed by regional flow also are possible explanations for the occurrence of this water type in the Minnelusa aquifer.

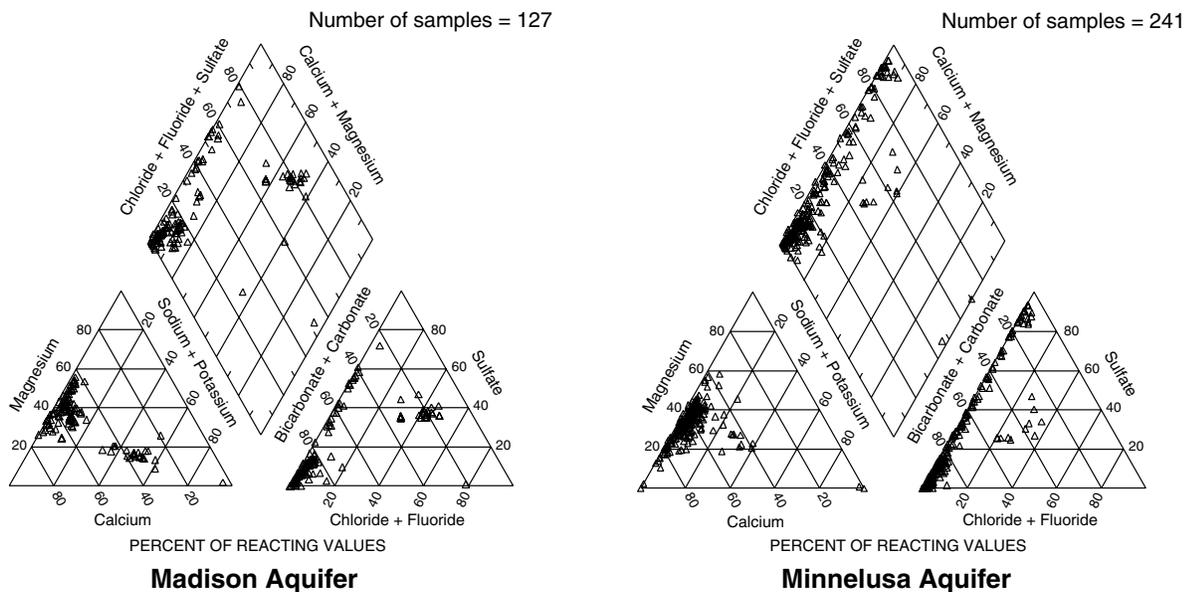


Figure 9. Trilinear diagrams showing proportional concentrations of major ions in the Madison and Minnelusa aquifers.

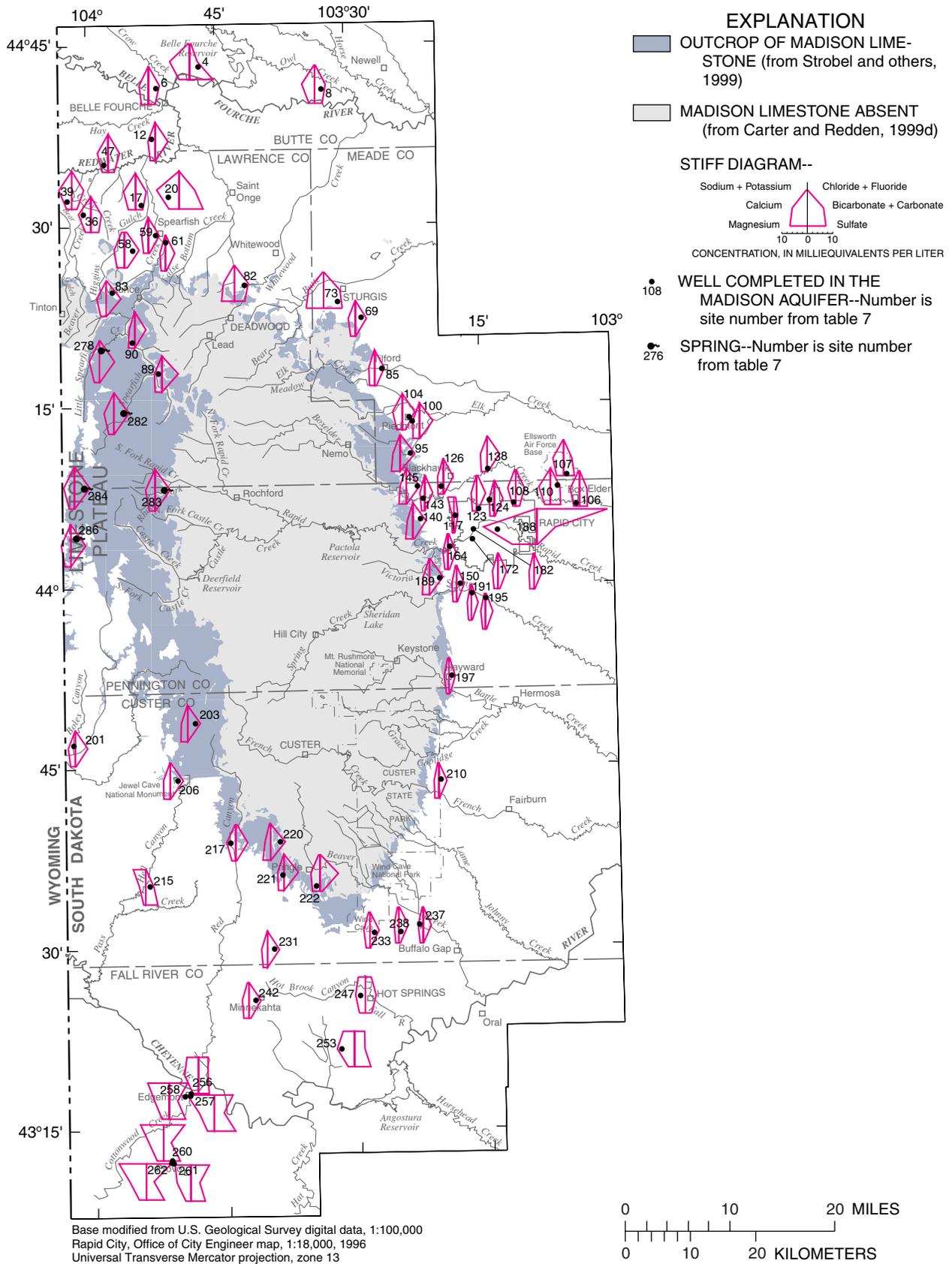


Figure 10. Selected Stiff diagrams showing the distribution of major-ion chemistry in the Madison aquifer.

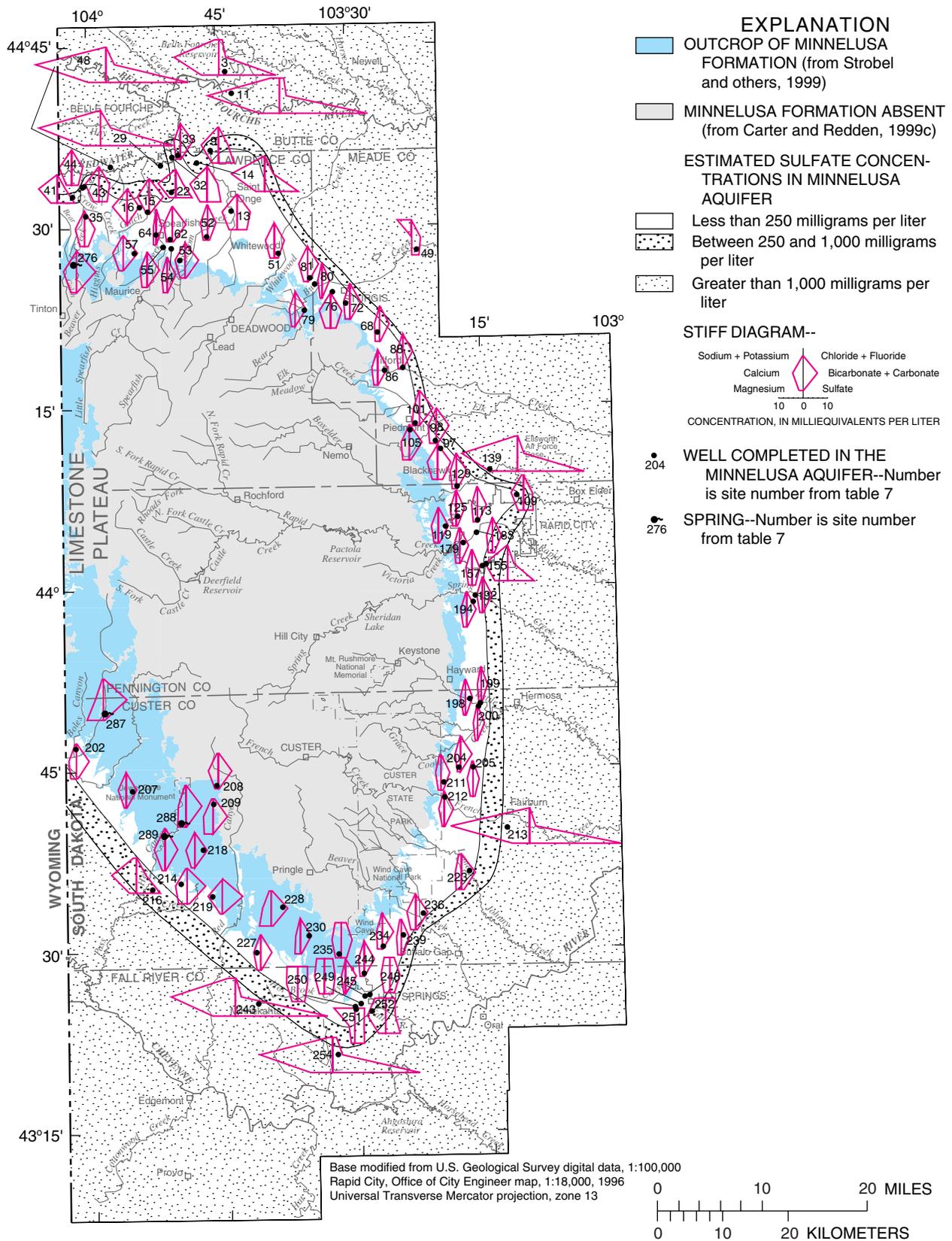


Figure 11. Selected Stiff diagrams showing the distribution of major-ion chemistry in the Minnelusa aquifer. Approximate location of anhydrite dissolution front showing transition between low and high sulfate concentrations also is shown.

Sulfate concentrations in the Madison aquifer generally are low and increase slightly with increasing distance from outcrop areas (fig. 10). In contrast, an extremely sharp gradation in sulfate concentrations occurs in the Minnelusa aquifer, such as near sites 22, 29, 32, and 33 in the northern part of the study area. Sulfate concentrations in the Minnelusa aquifer are dependent on the amount of anhydrite present in the Minnelusa Formation. Thick anhydrite beds were observed in cores from Minnelusa Formation drill holes in the southern Black Hills (Braddock and Bowles, 1963; Brobst and Epstein, 1963). These thick anhydrite deposits are mostly absent in and near outcrops because of earlier removal by dissolution in the subsurface (Epstein, 2000).

Where dissolution of anhydrite currently is taking place (Epstein, 2000), a transition zone from low to high sulfate concentrations is postulated, as shown in figure 11. Sulfate concentrations less than 250 mg/L delineate a zone in which anhydrite probably has been largely removed by dissolution. The zone in which sulfate concentrations are between 250 and 1,000 mg/L marks the position of the "anhydrite dissolution front," an area of active removal of anhydrite by dissolution. Downgradient from the anhydrite dissolution front, sulfate concentrations are greater than 1,000 mg/L, which delineates a zone in which thick anhydrite beds remain in the formation. A similar approach was presented by Klemp (1995), who used specific conductance of ground-water samples from the Minnelusa aquifer to identify a line of dissolution of anhydrite. Brobst and Epstein (1963), Gott and others (1974), Kyllonen and Peter (1987), and Epstein (2000) also presented models of this anhydrite dissolution front, wherein the Minnelusa Formation is thinner near the outcrop area because of removal of the anhydrite and thicker where the anhydrite still remains. Epstein (2000) proposed that sinkholes in overlying formations are caused by collapses in the Minnelusa Formation because of removal of anhydrite, and that the sinkholes mark the zone of active dissolution of anhydrite.

Dissolution of anhydrite cements could increase hydraulic conductivity and secondary porosity in the Minnelusa aquifer; thus, low sulfate concentrations may indicate areas of greater hydraulic conductivity and enhanced secondary porosity where anhydrite has been removed from the aquifer. The anhydrite dissolution front in the northern Black Hills generally is located farther from outcrop areas than in other locations, although basinward deflections of the front also

are apparent in the Rapid City area and along the southeastern flank of the uplift. In some areas, basinward deflections may correspond with structural features where enhanced hydraulic conductivity can occur; however, available data are insufficient for conclusive determinations.

Saturation State

Saturation indices measure departures from thermodynamic equilibrium and can be used to develop hypotheses related to the reactivity of minerals in an aquifer. The saturation index (SI) for a particular mineral generally indicates whether the ground water is undersaturated ($SI < 0$), at equilibrium ($SI = 0$), or supersaturated ($SI > 0$) with respect to that particular mineral. If ground water is undersaturated with respect to a mineral, as indicated by a negative SI, the ground water would theoretically dissolve the mineral if present. Conversely, if ground water is supersaturated with respect to a mineral, then the mineral would theoretically precipitate from the ground water. There is some uncertainty associated with the range in SI values that indicates equilibrium because of uncertainties in field-measured pH, laboratory-analyzed concentrations, and ionic strength and equilibrium constants involved in calculations of SI values (Langmuir, 1997).

The geochemical program PHREEQC (Parkhurst and Appelo, 1999) was used to calculate SI values for 41 samples (35 wells) from the Madison aquifer and 25 samples (24 wells) from the Minnelusa aquifer (table 1). The default thermodynamic database, phreeqc.dat (Parkhurst, 1995), provided the thermodynamic data for calculations. Although anhydrite is more common than gypsum in the Madison and Minnelusa aquifers, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the more stable phase. Therefore, SI_{gypsum} is used as an indicator for both anhydrite and gypsum throughout the remainder of this report.

Calculated SI values show that water in the Madison aquifer is greatly undersaturated with respect to halite (NaCl) and, to a lesser extent, with respect to gypsum. These minerals should, if present, continue to dissolve in the Madison aquifer. However, ground water in the Madison aquifer remains undersaturated with respect to gypsum even at the highest sulfate concentrations (fig. 12). Figure 13 shows that most waters in the Madison aquifer are in equilibrium with respect to calcite and are slightly undersaturated with respect to dolomite.

Table 1. Saturation indices for selected samples from wells completed in the Madison and Minnelusa aquifers

[SI_{calcite}, calcite saturation index; SI_{dolomite}, dolomite saturation index; SI_{gypsum}, gypsum saturation index; SI_{halite}, halite saturation index; e, estimated; --, no data]

Site number	Station identification number	Temperature (degrees Celsius)	pH (standard units)	SI _{calcite}	SI _{dolomite}	SI _{gypsum}	SI _{halite}
Madison Aquifer							
6	444129103514801	29.4	7.2	0.0	0.0	-1.6	-10.2
36	443100104002001	11.3	7.4	.1	-.3	-1.3	-10.3
58	442802103544601	11.3	7.3	.1	-.1	-1.8	-7.7
59	442919103511601	12.3	7.4	-.1	-.4	-2.3	-9.6
61	442842103505501	7.8	7.6	-.1	-.4	-2.4	-9.4
83	442435103571101	e10.9	7.2	.0	-.4	-3.1	-10.5
85	441759103261202	11.5	7.5	-.1	-.4	-2.1	-10.6
95	441055103230501	13.8	7.4	.1	.2	-3.2	-11.0
100	441337103225002	12.5	7.3	-.1	-.3	-2.7	-10.5
106	440629103040901	47.5	6.9	-.2	-.3	-1.5	-9.9
112	440519103160701	20.6	7.7	.1	.2	-2.8	-10.2
116	440526103173001	13.6	7.7	.0	-.1	-2.7	-9.7
116	440526103173001	13.2	7.6	.0	-.2	-2.6	-9.2
121	440500103193601	13.8	7.6	.0	-.1	-2.5	-9.4
123	440612103152001	15.3	7.5	-.2	-.4	-2.7	-10.1
123	440612103152001	15.2	7.5	-.1	-.3	-2.6	-8.9
124	440655103140501	20.0	7.5	-.1	-.1	-2.7	-9.4
138	440931103141401	20.3	7.3	-.1	.0	-2.7	-10.4
145	440811103222201	16.8	7.3	-.1	-.1	-3.0	-10.2
161	440205103172001	13.7	7.6	-.1	-.5	-2.4	-8.9
164	440308103184601	7.0	7.6	-.2	-.8	-2.3	-9.0
168	440300103173501	e12.7	7.0	-.7	-1.7	-2.4	-9.1
168	440300103173501	18.4	7.7	.1	.0	-2.3	-8.9
169	440220103164001	15.2	7.7	.0	-.2	-2.3	-9.2
169	440220103164001	16.0	7.6	-.1	-.4	-2.4	-9.1
172	440342103160701	16.5	7.6	-.1	-.2	-2.3	-9.1
172	440342103160701	17.8	7.7	.1	.1	-2.0	-9.4
176	440310103173802	14.8	7.7	-.1	-.2	-2.0	-9.2
178	440338103173302	12.0	7.7	.0	-.2	-2.3	-9.3
182	440430103160202	15.5	7.7	.0	.0	-2.5	-9.6
185	440443103161301	16.2	7.7	.1	.0	-2.7	-9.7
186	440446103161701	e16.3	7.4	-.3	-.6	-2.7	-10.2
186	440446103161701	16.4	7.7	.1	.0	-2.7	-10.4
188	440427103131701	26.4	6.1	-.3	-.8	-2.1	-6.9

Table 1. Saturation indices for selected samples from wells completed in the Madison and Minnelusa aquifers—Continued[SI_{calcite}, calcite saturation index; SI_{dolomite}, dolomite saturation index; SI_{gypsum}, gypsum saturation index; SI_{halite}, halite saturation index; e, estimated; --, no data]

Site number	Station identification number	Temperature (degrees Celsius)	pH (standard units)	SI _{calcite}	SI _{dolomite}	SI _{gypsum}	SI _{halite}
Madison Aquifer—Continued							
195	435851103143501	13.3	7.5	-0.3	-0.8	-2.4	-8.7
201	434700104021401	10.1	8.1	.6	1.0	-2.7	-9.8
210	434350103201901	14.5	7.9	.2	.3	-2.4	-9.6
215	433517103534201	14.5	8.3	.6	.6	-1.4	-7.9
238	433115103251401	17.2	7.7	.1	.0	-2.4	-8.6
242	432548103414801	21.0	7.5	.2	.3	-2.0	-8.7
253	432136103321001	21.3	7.3	.2	.0	-1.0	-6.5
Minnelusa Aquifer							
29	443515103513901	13.4	7.3	.4	.3	-.1	-9.8
35	443100104002002	10.4	7.4	.0	-.4	-1.7	-10.6
44	443320104004501	11.5	7.4	.1	-.2	-1.4	-10.3
48	443515103572501	18.3	7.1	.2	-.1	.0	-9.7
65	443100103543001	13.0	8.6	1.3	2.1	-2.5	-10.4
81	442545103343701	12.5	8.6	1.2	2.0	-2.2	-10.3
86	441759103261201	11.2	7.5	-.1	-.4	-2.7	-10.3
113	440528103155201	15.2	7.5	-.1	-.3	-2.4	-10.3
118	440544103180001	10.8	7.9	.2	.1	-2.3	-9.1
119	440516103194001	19.6	7.6	.2	.3	-2.4	-9.2
129	440818103180801	18.5	7.6	.2	.2	-2.5	-10.3
177	440310103173801	12.6	7.8	.1	.0	-2.3	-9.4
179	440338103173301	12.0	7.8	.2	.1	-2.4	-9.8
181	440414103164601	16.1	7.5	.1	.0	-1.6	-9.2
183	440430103160201	11.7	7.7	.0	-.2	-2.6	--
183	440430103160201	14.2	7.7	.1	.1	-2.2	-9.6
187	440452103155301	14.8	7.7	.1	.2	-2.2	--
192	435916103161802	12.4	7.2	-.4	-1.1	-2.5	-9.7
199	435018103155801	12.8	7.7	-.2	-.7	-2.7	-9.6
211	434350103201902	e11.5	7.7	.0	-.3	-2.1	-9.0
216	433517103534202	13.6	7.4	.3	.0	-.7	-8.7
227	433003103420701	13.8	7.5	.1	-.1	-2.5	-9.5
239	433115103251402	14.2	7.8	.1	.0	-2.3	-8.8
243	432548103414802	17.2	7.3	.2	.0	.0	-7.8
254	432127103325601	19.6	7.0	.2	.0	.0	-7.4

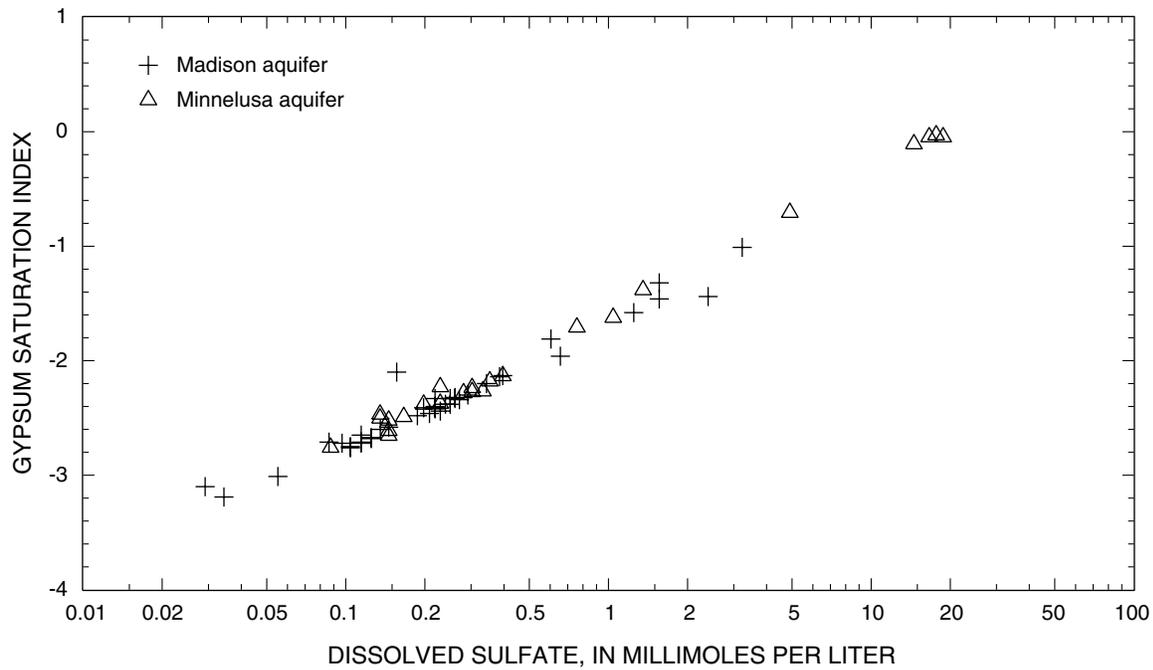


Figure 12. Relation between gypsum saturation index and dissolved sulfate in the Madison and Minnelusa aquifers.

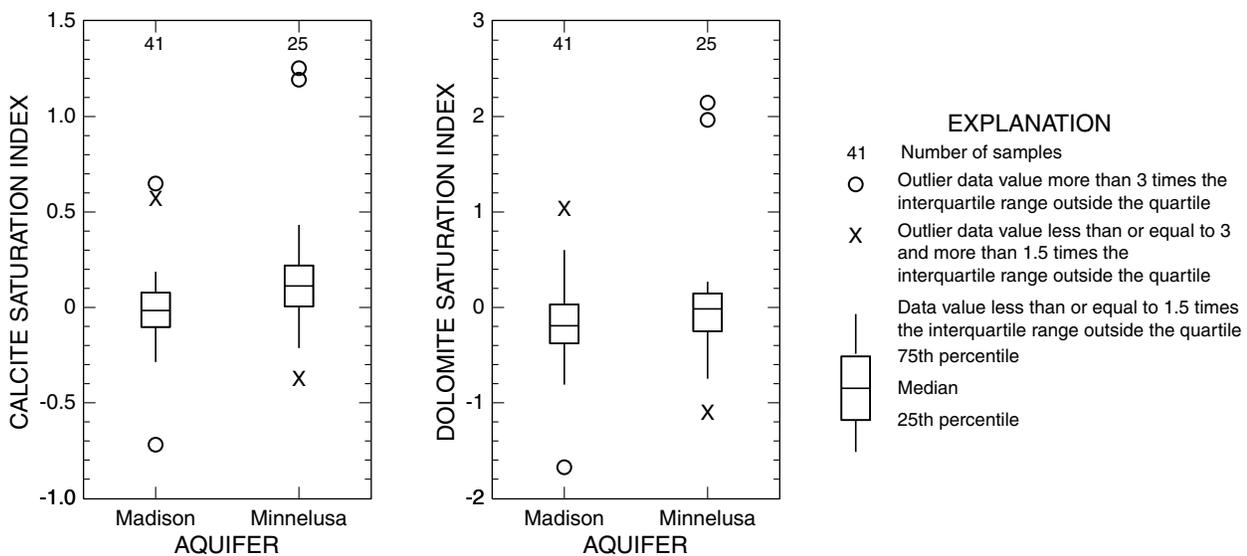


Figure 13. Boxplots showing calcite and dolomite saturation indices for selected samples from the Madison and Minnelusa aquifers.

All samples from the Minnelusa aquifer are undersaturated with respect to halite, and most are undersaturated with respect to gypsum. In some samples, SI values for gypsum approach zero, indicating near equilibrium with respect to gypsum at high sulfate concentrations (fig. 12). Most samples in the Minnelusa aquifer are near equilibrium to slightly supersaturated with respect to calcite and are saturated with respect to dolomite (fig. 13).

For most samples in both the Madison and Minnelusa aquifers, SI values for gypsum, calcite, and dolomite are indicative of the occurrence of dedolomitization. Busby and others (1983) noted that conditions consistent with the dedolomitization process generally include waters that are in equilibrium with respect to calcite, undersaturated but approaching saturation with respect to dolomite, and undersaturated with respect to gypsum. Samples that are undersaturated with respect to gypsum, calcite, or dolomite may be indicative of large hydraulic conductivity, especially in the Madison aquifer, where fast flow velocities and short ground-water residence times in karst conduits may limit the extent of mineral dissolution. Undersaturation with respect to these minerals also could result from the influence of streamflow recharge for samples collected near loss zones in outcrops of the Madison Limestone and Minnelusa Formation. The contribution of calcium from anhydrite dissolution could cause slight supersaturation with respect to calcite or dolomite due to the common-ion effect. Samples with high SI values for calcite and dolomite may reflect errors in pH measurements, which are not uncommon primarily because of instrumentation problems. All of the positive outlier values in figure 13 are associated with pH values greater than 8 (table 1), which may be of questionable validity.

The saturation state with respect to gypsum of water in the Madison and Minnelusa aquifers may provide insight into mechanisms controlling hydraulic connection between the aquifers. Because water in the Madison aquifer remains undersaturated with respect to gypsum even at the highest sulfate concentrations (fig. 12), upward leakage could drive increased dissolution of anhydrite in the Minnelusa Formation, especially where Minnelusa aquifer water is nearly saturated with respect to gypsum.

Evolutionary Processes

As shown in figures 10 and 11, dissolved sulfate concentrations generally increase with distance from

outcrops in the Madison and Minnelusa aquifers, indicating that sulfate can be used as a measure of the reaction progress. Variations in pH and concentrations of calcium and magnesium as a function of dissolved sulfate can be used to evaluate chemical processes occurring in the aquifers.

Forward geochemical modeling was used in this study to illustrate trends in pH and calcium and magnesium concentrations with increasing dissolution of anhydrite. It is assumed in the modeling that the aquifer contains calcite, dolomite, and anhydrite and is recharged by rainwater. Hypothetical recharge water was created by defining water with a temperature of 15°C and a pH of 5.4, which was the average pH of rainwater at Newcastle, Wyoming, from August 1981 through December 1998 (National Atmospheric Deposition Program/National Trends Network, 1999). The recharge water was allowed to equilibrate with calcite and dolomite at a P_{CO_2} of 10^{-2} bar, typical of values in the soil zone (Freeze and Cherry, 1979). Conceptually, the recharge water then moved into a saturated zone containing calcite, dolomite, and anhydrite. The saturation index of dolomite was fixed at -0.2 to represent slight undersaturation with respect to dolomite, and the saturation index of calcite was fixed at 0 to represent equilibrium conditions. These values are consistent with the dedolomitization process and reflect median SI values in the Madison aquifer (fig. 13). Dissolution of anhydrite occurred incrementally and was limited not to exceed gypsum equilibrium. Reactions were carried out at a constant temperature of 15°C, which is representative of average temperatures in the Madison and Minnelusa aquifers in the study area (table 1).

For the simulated reactions occurring in the saturated zone, changes in modeled pH values and concentrations of calcium and magnesium, relative to increasing sulfate concentrations, are summarized in table 2 and figure 14. Table 2 shows the pH; molality of calcium ($m\text{Ca}$), magnesium ($m\text{Mg}$), and sulfate ($m\text{SO}_4$) in solution; number of moles of anhydrite ($\Delta m_{\text{anhydrite}}$), calcite ($\Delta m_{\text{calcite}}$), and dolomite ($\Delta m_{\text{dolomite}}$) dissolved or precipitated (negative values indicate precipitation); and saturation index for gypsum ($\text{SI}_{\text{gypsum}}$) for each reaction step. Figure 14 shows how the modeled pH, calcium molality, and magnesium molality change with reaction progress. Calcite precipitated while dolomite dissolved, pH decreased, and concentrations of dissolved magnesium and sulfate increased during reaction with anhydrite. In the ninth model reaction step, the solution reached saturation with respect to gypsum.

Table 2. Selected results of geochemical modeling

[°C, degrees Celsius; *m*Ca, calcium molality; *m*Mg, magnesium molality; *m*SO₄, sulfate molality; Δ*m*_{anhydrite}, number of moles of anhydrite dissolved or precipitated (negative values indicate precipitation); Δ*m*_{calcite}, number of moles of calcite dissolved or precipitated (negative values indicate precipitation); Δ*m*_{dolomite}, number of moles of dolomite dissolved or precipitated (negative values indicate precipitation); SI_{gypsum}, gypsum saturation index]

Temperature (°C)	pH (standard units)	<i>m</i> Ca	<i>m</i> Mg	<i>m</i> SO ₄	Δ <i>m</i> _{anhydrite}	Δ <i>m</i> _{calcite}	Δ <i>m</i> _{dolomite}	SI _{gypsum}
15	7.20	0.0029	0.0019	0.0025	0.0025	-0.0010	0.0006	-1.1316
15	7.11	.0044	.0028	.0050	.0050	-.0030	.0015	-.7708
15	7.05	.0059	.0038	.0075	.0075	-.0050	.0025	-.5555
15	7.01	.0074	.0047	.0100	.0100	-.0070	.0034	-.4020
15	6.98	.0089	.0057	.0125	.0125	-.0090	.0044	-.2830
15	6.95	.0104	.0066	.0150	.0150	-.0110	.0053	-.1859
15	6.92	.0119	.0076	.0175	.0175	-.0130	.0063	-.1041
15	6.90	.0135	.0085	.0200	.0200	-.0150	.0073	-.0334
15	6.89	.0143	.0090	.0213	.0225	-.0160	.0078	.0000
15	6.89	.0143	.0090	.0213	.0250	-.0160	.0078	.0000

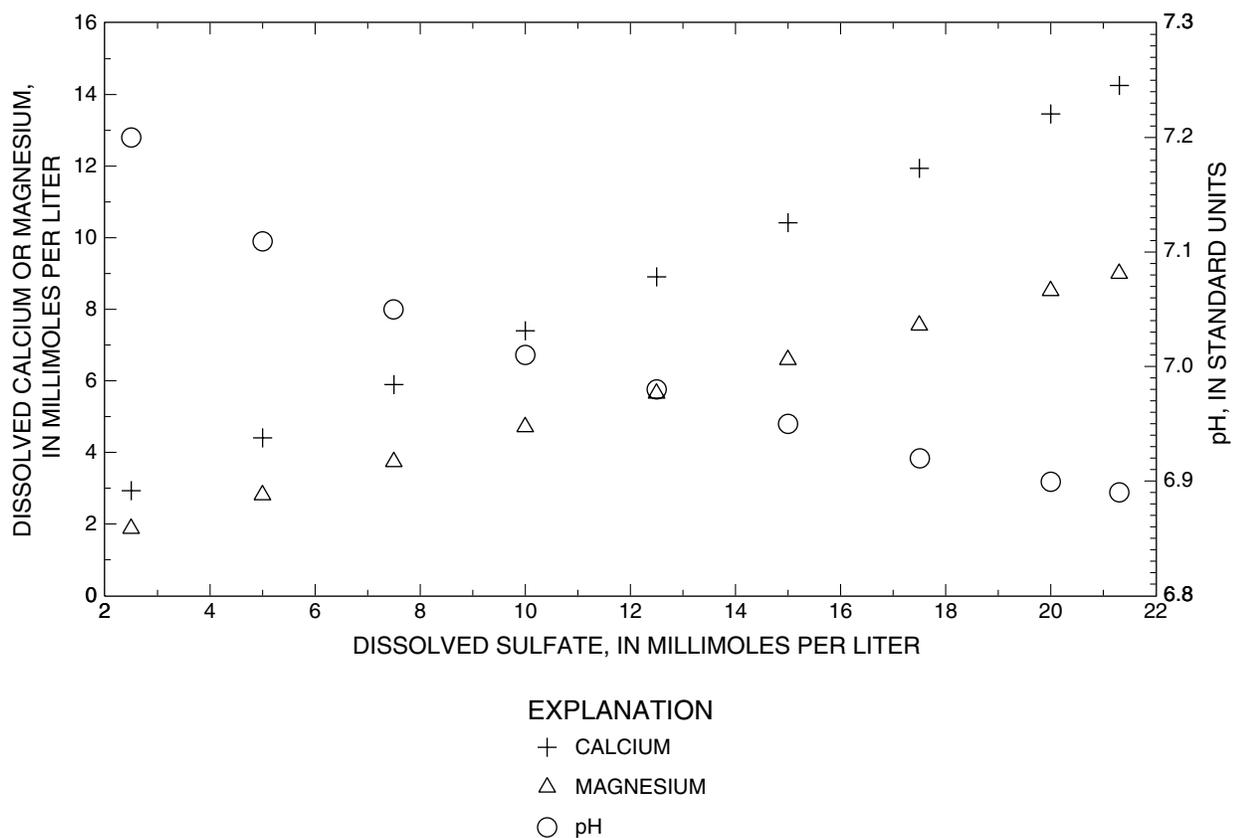


Figure 14. Modeled relations between calcium and magnesium concentrations, pH, and dissolved sulfate.

The forward modeling results indicate that the incongruent dissolution of dolomite occurring in conjunction with anhydrite dissolution should result in increases in calcium and magnesium concentrations and a decrease in pH. Figure 15 shows the relation between dissolved calcium and magnesium concentrations and dissolved sulfate in the Madison and Minnelusa aquifers. To show only data reflecting significant reaction progress, only samples with sulfate concentrations greater than 1 millimole per liter are included. The variations of dissolved calcium and magnesium concentrations with dissolved sulfate shown in figure 15 for the Madison and Minnelusa aquifers are similar to those resulting from the geochemical modeling shown in figure 14 in that both calcium and magnesium concentrations increase with increasing sulfate concentrations, with calcium increasing at a greater rate. However, the modeled calcium/magnesium ratio is lower than observed in the Madison and Minnelusa aquifers. The relative rates of increase of calcium and magnesium concentrations are affected by the equilibrium constants (K) as well as temperature. Comparison of actual calcium and magnesium concentrations to model results indicates that if dedolomitization is occurring in both the Madison and Minnelusa aquifers, conditions in the aquifers (temperature, K_{dolomite}) are similar but not identical to those that were modeled.

Figure 16 shows the relation between pH and dissolved sulfate in the Madison and Minnelusa aquifers. In the Minnelusa aquifer, pH generally is lower at high sulfate concentrations, which supports the occurrence of dedolomitization. In the Madison aquifer, the data are consistent with dedolomitization, but pH trends are limited by the extent of anhydrite dissolution.

Other processes that could cause a decrease in pH along a flowpath include nitrate reduction, denitrification, and sulfate reduction. These reactions become important in environments in which the oxygen introduced by ground-water recharge has been depleted (Langmuir, 1997). Oxygen is supplied to ground water by the movement of air through unsaturated material above the water table as well as by recharge (Hem, 1992). This oxygen is consumed by reaction with organic materials and reduced inorganic minerals such as pyrite and siderite. Well-oxygenated ground water may persist for long distances along a flowpath if little reactive material is available. In both the Madison and Minnelusa aquifers, most samples have dissolved oxygen concentrations greater than 2 mg/L (fig. 17), which indicates that the aquifers are

well oxygenated, even at considerable distances from the outcrops. Much of the recharge to the aquifers is from streamflow losses or through outcrop areas with limited soil development. Thus, recharge has limited interaction with organic materials in the soil horizon and consumption of oxygen is incomplete. Reduction of sulfate, nitrate, and ferric iron minerals, methane fermentation, and anaerobic decay of organic matter, therefore, are not likely in the Madison and Minnelusa aquifers in the study area.

Isotope Chemistry

This section presents information regarding the isotope chemistry of the Madison and Minnelusa aquifers in the Black Hills area. Stable isotopes of oxygen (^{18}O and ^{16}O) and hydrogen (^2H , deuterium; and ^1H) are used to evaluate ground-water flowpaths, recharge areas, and mixing conditions. The radioisotope tritium (^3H) provides additional information for evaluation of mixing conditions and ground-water ages.

Isotope data for selected sampling sites are presented in tables 7 and 8 in the Supplemental Information section. The majority of sampling sites are ground-water sites, including wells (or caves) and springs. Spring samples are categorized as either headwater springs (generally located upgradient of streamflow loss zones) or downgradient springs (within or downgradient of loss zones). Two of the downgradient springs (sites 291 and 299) are perched springs that are located along stream channels where streamflow losses occur. The remainder of the downgradient springs are located downgradient of loss zones and are presumed to be artesian springs. Data also are included for 14 surface-water sites, all of which are located immediately upgradient from loss zones where recharge occurs to the Madison or Minnelusa aquifers. Data for three meteorological sites also are provided.

Background Information and Isotopic Composition of Recharge Water

This section provides background information regarding stable isotopes and tritium. Because of spatial variations in isotopic signatures for precipitation in the Black Hills area, stable isotopes can be used for identification of potential recharge areas and evaluation of ground-water flowpaths. Tritium is useful for evaluation of ground-water ages because large temporal variations of concentrations in precipitation have resulted from atmospheric testing of thermonuclear bombs during the 1950's and 1960's.

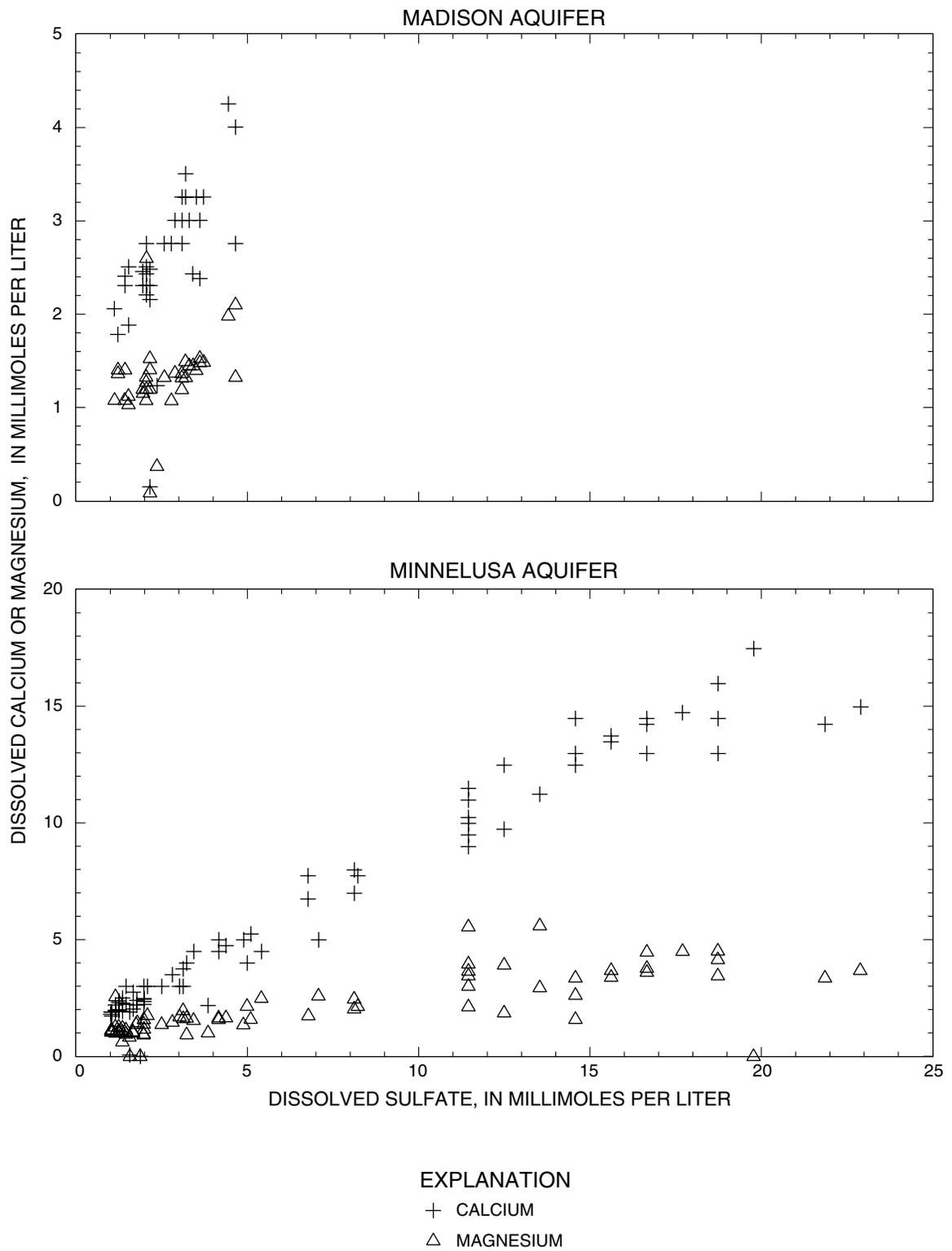


Figure 15. Relations between dissolved calcium and magnesium concentrations and dissolved sulfate in the Madison and Minnelusa aquifers.

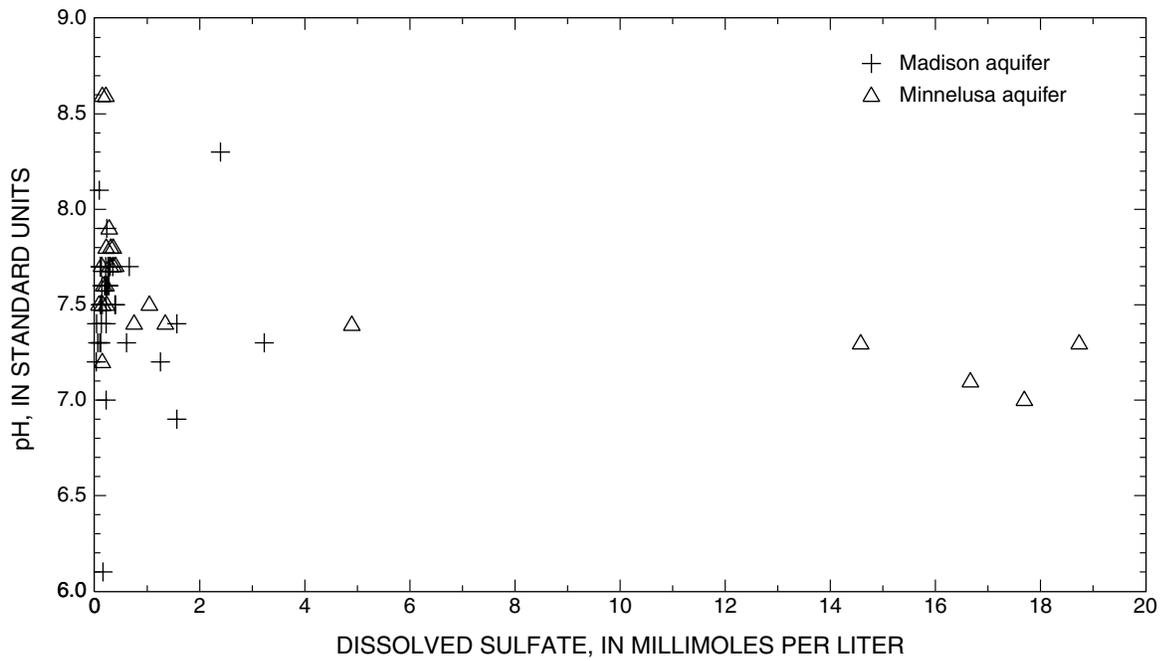


Figure 16. Relation between pH and dissolved sulfate in the Madison and Minnelusa aquifers.

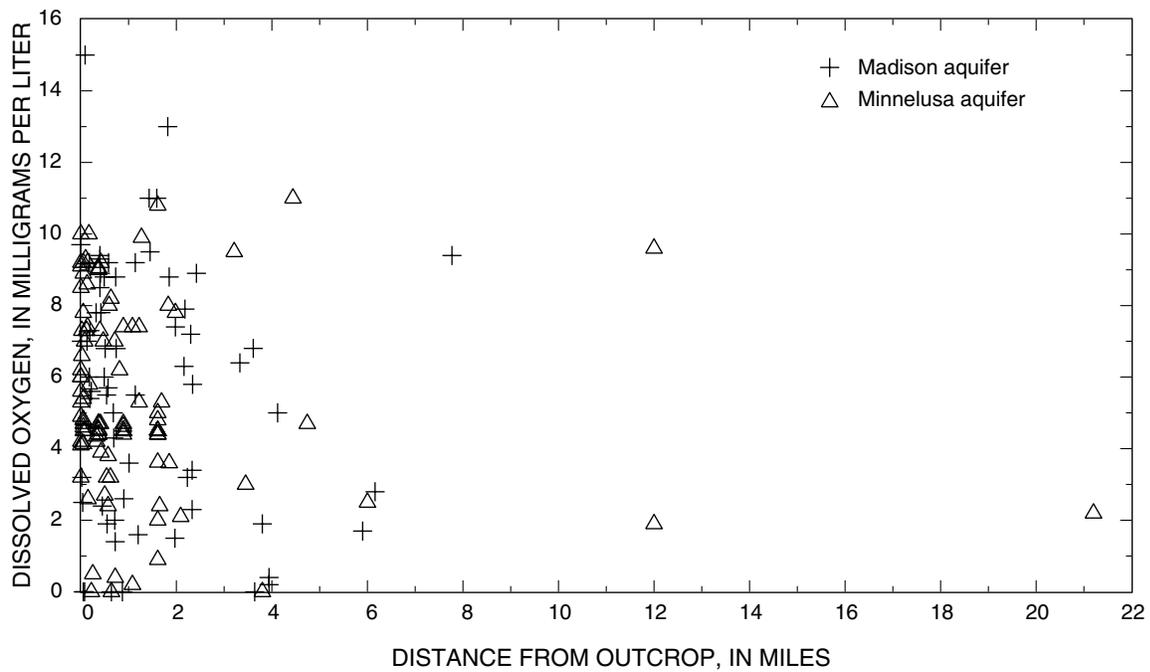


Figure 17. Relation between dissolved oxygen and distance from outcrop in the Madison and Minnelusa aquifers.