

Prepared in cooperation with the
South Dakota Department of Environment and Natural Resources
and the West Dakota Water Development District

Episodic Sediment-Discharge Events in Cascade Springs, Southern Black Hills, South Dakota

Water-Resources Investigations Report 99-4168



Cover photograph: Shows Cascade Springs. Photograph by J.S. Clark

U.S. Department of the Interior
U.S. Geological Survey

Episodic Sediment-Discharge Events in Cascade Springs, Southern Black Hills, South Dakota

By Timothy S. Hayes

Water-Resources Investigations Report 99-4168

Prepared in cooperation with the South Dakota Department
of Environment and Natural Resources and the
West Dakota Water Development District

U.S. Department of the Interior

Bruce Babbitt, Secretary

U.S. Geological Survey

Charles G. Groat, Director

The use of firm, trade, and brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Rapid City, South Dakota: 1999

For additional information write to:

**District Chief
U.S. Geological Survey
1608 Mt. View Road
Rapid City, SD 57702**

Copies of this report can be purchased from:

**U.S. Geological Survey
Information Services
Box 25286
Denver, CO 80225-0286**

CONTENTS

Abstract.....	1
Introduction	2
General Geohydrology and Possible Sediment Sources.....	6
Acknowledgments	8
Methods of Data Collection and Analyses	8
Evaluation of Possible Sediment Sources.....	9
Mineralogy of Suspended Sediment and Possible Sediment Sources.....	9
Examination of Lower Hell Canyon and Breccias	13
Geologic Examination	13
Mineralogic Analysis of Minnekahta Limestone Breccia	15
Grain-Size Analyses of Upper Minnelusa Formation Breccia Pipes and Wall Rocks	15
Geochemical Evolution of Cascade Springs Water	16
Previous Modeling Efforts.....	18
New Modeling Efforts	18
Input Data Sets.....	18
Chemical Composition of Ground Water	18
Stoichiometries of Aquifer Minerals	18
Isotopic Values for Aquifer Minerals and Ground Water.....	20
Model Results	20
Implications for the Role of Artesian Springs in Regional Geohydrology	22
Summary and Conclusions	23
References Cited.....	24
Appendices	27

ILLUSTRATIONS

1. Location map showing Cascade Springs, other nearby springs, wells, and miscellaneous rock and ground-water sampling sites.....	3
2. Map showing geology in the vicinity of Cascade Springs	5
3. Hydrograph for Cascade Springs (station number 06400497) for February 20 through March 10, 1992.....	6
4. Graph showing X-ray diffraction pattern of the unseparated suspended sediment collected from Cascade Springs on February 28, 1992.....	10
5-7. Graphs showing comparison of X-ray diffraction patterns for:	
5. The unseparated 1992 suspended sediment and its clay fraction	11
6. The heated and unheated clay fractions of the 1992 suspended sediment	11
7. The clay fractions of the 1992 suspended sediment and eight possible source units stratigraphically below the spring-discharge points	12
8. Photograph showing small breccia pipe hosted in the upper Minnelusa Formation in lower Hell Canyon.....	14
9-12. Graphs showing comparison of:	
9. X-ray diffraction patterns of clay fractions of the 1992 suspended sediment from Cascade Springs and red matrix from a breccia in the Minnekahta Limestone	15
10. Grain-size distributions for Minnelusa Formation wall rock (Pm-6) and breccia mass (Pm-7).....	16
11. Grain-size distributions for Minnelusa Formation wall rock (Pm-8) and breccia mass (Pm-9).....	17
12. Grain-size distributions for Minnelusa Formation wall rock (Pm-10) and breccia mass (Pm-11) with white, bedding plane exposure	17
13. Schematic showing potential processes enhancing hydraulic conductivity in Minnelusa Formation, resulting from upward leakage from Madison aquifer	23

TABLES

1. Generalized stratigraphic sequence in the southern Black Hills area.....	4
2. Physical properties, inorganic-constituent concentrations, and isotope ratios in ground water from Hot Brook Spring and Cascade Springs used in NETPATH modeling.....	19

APPENDICES

1. Additional discussion of NETPATH modeling.....	29
2. NETPATH output.....	30

Episodic Sediment-Discharge Events in Cascade Springs, Southern Black Hills, South Dakota

By Timothy S. Hayes

ABSTRACT

Cascade Springs is a group of artesian springs in the southern Black Hills, South Dakota, with collective flow of about 19.6 cubic feet per second. Beginning on February 28, 1992, a large discharge of red suspended sediment was observed from two of the six known discharge points. Similar events during 1906-07 and 1969 were documented by local residents and newspaper accounts. Mineralogic and grain-size analyses were performed to identify probable subsurface sources of the sediment. Geochemical modeling was performed to evaluate the geochemical evolution of water discharged from Cascade Springs. Interpretations of results provide a perspective on the role of artesian springs in the regional geohydrologic framework.

X-ray diffraction mineralogic analyses of the clay fraction of the suspended sediment were compared to analyses of clay-fraction samples taken from nine geologic units at and stratigraphically below the spring-discharge points. Ongoing development of a subsurface breccia pipe(s) in the upper Minnelusa Formation and/or Opeche Shale was identified as a likely source of the suspended sediment; thus, exposed breccia pipes in lower Hell Canyon were examined. Upper Minnelusa Formation breccia pipes in lower Hell Canyon occur in clusters similar to the discrete discharge points of Cascade Springs. Grain-size analyses showed that breccia masses lack clay fractions and

have coarser distributions than the wall rocks, which indicates that the red, fine-grained fractions have been carried out as suspended sediment. These findings support the hypothesis that many breccia pipes were formed as throats of abandoned artesian springs.

Geochemical modeling was used to test whether geochemical evolution of ground water is consistent with this hypothesis. The evolution of water at Cascade Springs could not be suitably simulated using only upgradient water from the Minnelusa aquifer. A suitable model involved dissolution of anhydrite accompanied by dedolomitization in the upper Minnelusa Formation, which is caused by upward leakage of relatively fresh water from the Madison aquifer. The anhydrite dissolution and dedolomitization account for the net removal of minerals that would lead to breccia pipe formation by gravitational collapse. Breccia pipes in the lower Minnelusa Formation are uncommon; however, networks of interconnected breccia layers and breccia dikes are common. These networks, along with vertical fractures and faults, are likely pathways for transmitting upward leakage from the Madison aquifer.

It is concluded that suspended sediment discharged at Cascade Springs probably results from episodic collapse brecciation that is caused by subsurface dissolution of anhydrite beds and cements of the upper Minnelusa Formation, accompanied by replacement of dolomite by

calcite. It is further concluded that many breccia pipes probably are the throats of artesian springs that have been abandoned and exposed by erosion. The locations of artesian spring-discharge points probably have been shifting outwards from the center of the Black Hills uplift, essentially keeping pace with regional erosion over geologic time. Thus, artesian springflow probably is a factor in controlling water levels in the Madison and Minnelusa aquifers, with hydraulic head declining over geologic time, in response to development of new discharge points.

Development of breccia pipes as throats of artesian springs would greatly enhance vertical hydraulic conductivity in the immediate vicinity of spring-discharge points. Horizontal hydraulic conductivity in the Minnelusa Formation also may be enhanced by dissolution processes related to upward leakage from the Madison aquifer. Potential processes could include dissolution resulting from leakage in the vicinity of breccia pipes that are abandoned spring throats, active spring discharge, development of subsurface breccias with no visible surface expression or spring discharge, as well as general areal leakage from the Madison aquifer into the Minnelusa Formation.

INTRODUCTION

Cascade Springs is a group of artesian springs in Fall River County, South Dakota, that contributes the majority of flow to Cascade Creek (fig. 1). Numerous other artesian springs occur within or near the outcrop belt of the Spearfish Formation (confining beds), between the outcrop belts of the Minnelusa Formation and the Inyan Kara Group (fig. 1) on the margins of the Black Hills uplift (Rahn and Gries, 1973). Most are believed to discharge ground water originating from the Madison and/or Minnelusa aquifers (Rahn and Gries, 1973; Back and others, 1983; Whalen, 1994; Klemp, 1995). A generalized stratigraphic sequence for the southern Black Hills area is presented in table 1.

Artesian springs have been studied extensively as part of the Black Hills Hydrology Study, which was initiated in 1990 to assess the quantity and quality of surface water and ground water in the Black Hills area.

This long-term study is a cooperative effort between the U.S. Geological Survey (USGS), the South Dakota Department of Environment and Natural Resources, and the West Dakota Water Development District, which represents various local and county cooperators, including Fall River County.

The flow of Cascade Springs has been measured by the USGS at streamflow-gaging station 06400497 (fig. 2) since 1976. Flow during water years¹ 1976-93 averaged 19.6 cubic feet per second, with very little variability (Miller and Driscoll, 1998).

Water from Cascade Springs normally is quite clear; however, a large discharge of red, suspended sediment from two of six known discharge points (fig. 2) was reported by a local resident on the morning of February 28, 1992. USGS personnel responded by collecting suspended sediment samples and making various field measurements during the next several days. Sediment discharge from Cascade Springs slowed, and essentially ceased, over the course of the following week. Springflow during February 20 to March 10, 1992, was nearly constant, as shown in the hydrograph for station 06400497 (fig. 3).

The discharge of sediment generated considerable interest among various local residents, who aided in documenting at least two other similar events. One event occurred sometime around September 1969 (Charles "Bus" Halls, Marie Hill, and Dave Nelson, oral commun., March through June 1992). Marie Hill provided a whole-water sample (water and sediment) collected in a quart jar during the 1969 event. Another event that occurred between December 14, 1906, and January 11, 1907, is described in the book "Early Hot Springs" (Twomey and Magee, 1983), which contains the following quote from the local newspaper at that time:

Cascade Runs Red

The big geyser at Cascade got stirred up somehow Tuesday night and belched up red gypsum and all sorts of hot looking stuff, turning Cascade Creek to blood red. It continued throwing out red stuff all Wednesday morning, up to the time of this writing, and we believe also is throwing out more water than usual.

¹In U.S. Geological Survey reports, water year is the 12-month period, October 1 through September 30. The water year is designated by the calendar year in which it ends; thus, the water year ending September 30, 1993, is called the "1993 water year."

Table 1. Generalized stratigraphic sequence in the southern Black Hills area

[Modified from Gott and others, 1974, and Anderson and others, 1999]

Erathem	System	Series	Geologic unit	Hydrogeologic unit
Cenozoic	Quaternary		Alluvial deposits	Alluvial aquifer
	Tertiary	Pleistocene and Pliocene (?)	Gravel deposits	Locally used as aquifer in study area; deposits generally unconsolidated
		Pliocene (?) to Oligocene	White River Group	Locally used as aquifer in study area; composition variable, ranging from unconsolidated gravels to confining beds
Mesozoic	Cretaceous	Upper	Carlile Shale	Confining beds
			Greenhorn Formation	
			Belle Fourche Shale	
		Lower	Mowry Shale	
			Newcastle Sandstone	
			Skull Creek Shale	
	Inyan Kara Group	Fall River Formation	Inyan Kara aquifer	
		Lakota Formation		
	Jurassic	Upper	Morrison Formation	Confining beds
			Unkpapa Sandstone	
Middle		Sundance Formation		
Triassic		Spearfish Formation		
Paleozoic	Permian		Minnekahta Limestone	Confining bed
			Opeche Shale	
	Pennsylvanian		Minnelusa Formation	Minnelusa aquifer
				Confining bed
	Mississippian		Madison Limestone	Madison aquifer
	Devonian		Englewood Formation	Confining bed
Cambrian		Deadwood Formation	Deadwood aquifer	
Precambrian			Quartzite, schists, and granite	Confining bed

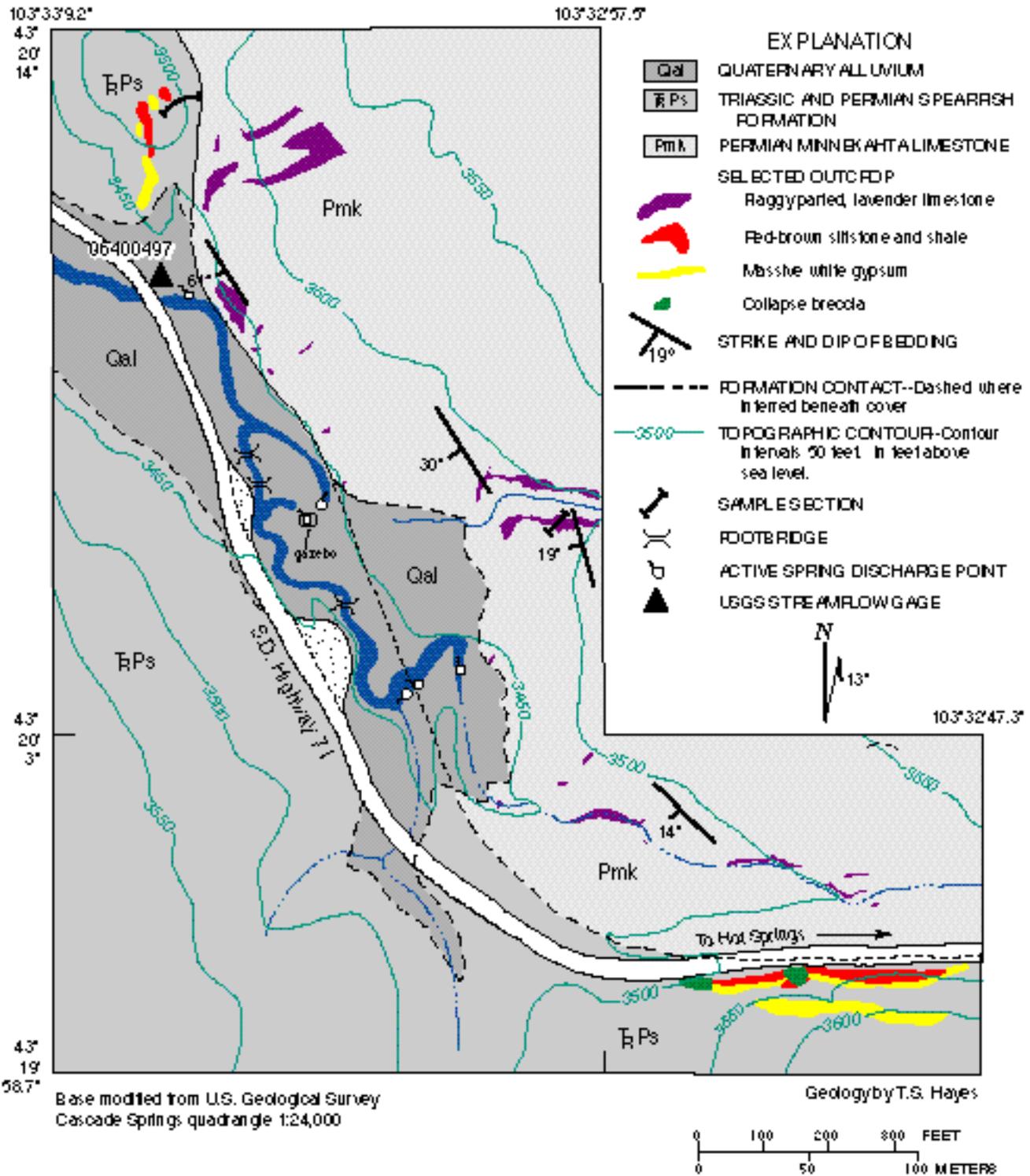


Figure 2. Geology in the vicinity of Cascade Springs. Sediment discharge occurred from the two spring vents nearest the gazebo.

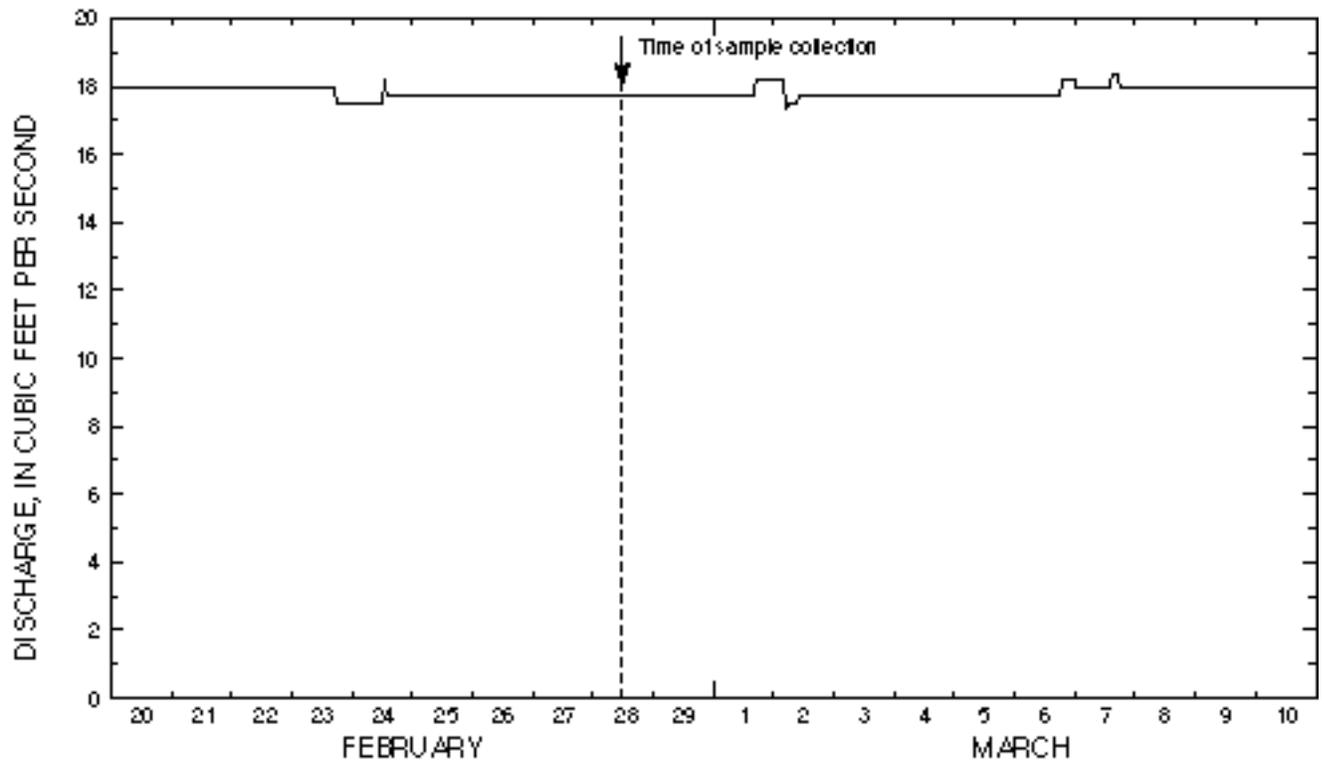


Figure 3. Hydrograph for Cascade Springs (station number 06400497) for February 20 through March 10, 1992.

The sediment samples collected during 1969 and 1992 presented a unique and timely opportunity to investigate various geohydrologic processes at Cascade Springs. This study first sought to identify the source of the suspended sediment. X-ray diffraction mineralogic analyses of sediment samples were performed and compared to analyses of samples taken from various geologic units at and stratigraphically below the discharge points. Once the source of the sediments was identified as the underlying upper Minnelusa Formation and/or Opeche Shale, additional field investigations, X-ray diffraction comparisons, and grain-size analyses of breccia pipes within the upper part of the Minnelusa Formation were conducted. That work tested the emerging hypothesis that exposed breccia pipes within the upper Minnelusa Formation are the subsurface throats of earlier artesian springs. Finally, geochemical modeling was used to test whether geochemical evolution of ground water is consistent with this hypothesis. The results indicate that ongoing subsurface dissolution of anhydrite and dolomite in the upper Minnelusa Formation, which causes episodic collapse brecciation, is the probable cause of the release of sediment. Relatively fresh water from the Madison aquifer is the probable agent of dissolution. The

purpose of this report is to present the results of this study.

General Geohydrology and Possible Sediment Sources

There are six known discrete discharge points at Cascade Springs (fig. 2). The three most upstream discharge points are within a flat-bottomed upper spring basin. Farther downstream are the two “gazebo” discharge points where the suspended sediment was discharged. These are located within a middle area of hummocky relief where depressions may indicate other abandoned discharge points. The most downstream discharge point is located about 90 feet upstream from the USGS streamflow-gaging station (fig. 2).

The six discharge points occur within Quaternary-age alluvial deposits (fig. 2) in a narrow valley along the contact between the Spearfish Formation and the underlying Minnekahta Limestone, near the crest of the strongly asymmetric Cascade Anticline (Post, 1967). The beds of these two formations dip between 15° and 60° (generally about 30°) to the southwest on the western flank of the south-plunging anticline (fig. 1).

Rahn and Gries (1973) described the contact between the Spearfish Formation and Minnekahta Limestone as a typical location for large springs that discharge from aquifers in the Madison Limestone and Minnelusa Formation. Leakage between the Madison and Minnelusa aquifers is common, but highly variable (Peter, 1985; Greene, 1993). The general direction of ground-water flow in the study area in both the Minnelusa and Madison aquifers is from north to south, but also may be from the northwest to southeast, or west to east (Whalen, 1994). The chemical evolution of water within the Madison aquifer in the Black Hills area has been studied at the regional scale by Back and others (1983), Plummer and others (1990), and Busby and others (1991). The water of Cascade Springs had been noted by Back and others (1983) to be a likely product of aquifer mixing, based on sulfur isotopes. Whalen (1994) concluded that the flow of Cascade Springs consists of a mix of approximately equal proportions of water from the Madison and Minnelusa aquifers.

The sediment discharged from Cascade Springs could have originated from any of three general sources. First, unlithified alluvial deposits near the discharge points could easily erode to produce a flush of sediment. A second possibility is collapse brecciation due to subsurface mineral dissolution in underlying bedrock units. Dissolution of anhydrite in the upper part of the Minnelusa Formation has been reported in earlier studies based on Minnelusa rock textures, mineralogy, and stratigraphy (Bowles and Braddock, 1963; Braddock and Bowles, 1963; Gott and others, 1974). A third possibility is erosion of cave fill from within the karstified Madison Limestone.

The subsurface sediment sources described above would require a zone of permeability through which to transport sediment to the surface with flow rates sufficient to keep silt continually in suspension. Breccia pipes (chimney-like features filled with angular clasts in a fine-grained matrix) are a likely possibility because confining layers of the Opeche Shale and within the Minnelusa Formation are not known to have undergone karstification, and no known faults exist in the immediate vicinity (Post, 1967; and fig. 2). A breccia pipe described by Post (1967) is located about 850 feet southeast of the upper spring basin (fig. 2). The beds around that breccia pipe dip about 15° southwesterly, but the breccia pipe has irregular, near-vertical boundaries probably indicating that it was superimposed on already tilted beds. A gypsum bed

within the Spearfish Formation drops about 1 to 5 feet as it crosses the top of the pipe outcrop, demonstrating that the pipe is a collapse breccia. The pipe is a pale greenish buff, cylindrical mass that is hosted in road-cut outcrops of red siltstones in the lower Spearfish Formation.

Seven distinct bedrock stratigraphic intervals from the Madison Limestone, which is the deepest likely source of water, up to the land surface, were considered as possible sources of the suspended sediment. The bedrock units considered are, from oldest to youngest, the Madison Limestone, three intervals (lower, middle, and upper) of the Minnelusa Formation, the Opeche Shale, the Minnekahta Limestone, and the lower part of the Spearfish Formation. Quaternary-age alluvium and cave fill from within the Madison Limestone also were considered as possible sources. Following are descriptions of these units, from oldest to youngest.

The Mississippian-age Madison Limestone, which consists primarily of buff-colored, massively bedded limestone, is exposed nearest to Cascade Springs to the north of the outcrop of the Minnelusa Formation near Onyx Cave (fig. 1). Caves within the Madison Limestone commonly contain partial fillings of red (terra rosa), fine, infiltrated sediment (Greene, 1993), with break-down fragments from the cave walls and ceiling and insoluble chert fragments.

The Pennsylvanian- and Permian-age Minnelusa Formation is over 700 feet thick in the area, and can be divided into three intervals. The lower Minnelusa Formation includes a basal, red, conglomeratic sandstone that is overlain by about 15 feet of pink, micritic limestone beds containing chert nodules and by about 70 feet of red mudstone beds with intercalated thin limestone beds. The middle interval of the Minnelusa Formation is over 300 feet thick and consists of dolostones, limestones, sandstones, and minor (black and red) shales or mudstones. The upper Minnelusa Formation, which is about 300 feet thick in outcrop in the area, lies above a red, mudstone-rich marker bed, locally known as the Red Marker.

The upper Minnelusa Formation, which is described by Bowles and Braddock (1963) and Gott and others (1974), consists of sandstone-in-sandstone breccia with sparse breccia clasts and contorted discontinuous beds of limestone and dolostone, along with other beds of sandstone that are not brecciated. The sandstones and breccias are varied bright colors of red, yellow, and white in the cliffs forming the canyon walls

above Hot Brook Spring (fig. 1). The upper Minnelusa Formation breccias are believed to result from solution collapse brecciation accompanied by dissolution of anhydrite beds and cements during weathering and recharge to shallow aquifers.

Basinward (down dip), the upper Minnelusa Formation is 150 feet thicker in the subsurface than in outcrop, with the difference being beds of anhydrite and sandstones cemented by anhydrite in the subsurface (Bowles and Braddock, 1963). Braddock and Bowles (1963) showed that the anhydrite dissolution was accompanied by conversion of dolostone beds to medium-crystalline limestone beds (dedolomitization).

The Permian-age Opeche Shale is about 65 feet thick near Cascade Springs and is composed primarily of red siltstones, shales, and fine-grained sandstones. The Permian-age Minnekahta Limestone is about 40 feet thick and composed of flaggy- to slabby-parting, purple-colored, very pure limestone. The Minnekahta Limestone is exposed just to the northeast from Cascade Springs (fig. 2). Near the spring-discharge points, only the lowermost 60 feet of the Triassic- and Permian-age Spearfish Formation are present. These rocks are principally orange-red siltstone and claystone, locally dolomite-cemented, with beds of massive, white gypsum (fig. 2).

The alluvium through which Cascade Springs discharge is locally derived from the lower Spearfish Formation and the Minnekahta Limestone. The alluvium is gravelly, with clasts of all lithologies from both bedrock formations. Finer grain-size portions of the alluvium are dominated by material from the red siltstones and claystones of the lower Spearfish Formation.

Acknowledgments

Numerous local residents, including Marc Lamphere, Dave Nelson, Charles "Bus" Halls, Russell Raby, and Marie Hill, provided information. Mrs. Hill provided a sample from the 1969 sediment discharge event. Mike Wiles of Jewel Cave National Monument provided samples of cave-fill sediment from Jewel Cave. The sample crushing, grain-size separations, grain-size distributions, and X-ray diffraction analyses were performed at the former Branch of Energy and Marine Geology of the U.S. Geological Survey in Denver, Colorado, where USGS colleagues Ken Esposito, Gene Whitney, and C. Gil Bowles provided help, references, data, and discussion.

METHODS OF DATA COLLECTION AND ANALYSES

Two samples of turbid water (approximately 20 liters total) were collected from Cascade Springs by the USGS on February 28, 1992. Additionally, a whole-water sample collected during the 1969 event by a local resident was provided to the USGS. The samples were filtered using a 0.45-micrometer Teflon filter membrane to recover the suspended sediment, which consisted of silt and finer grain sizes (<64 microns) and was brick red-orange in color.

Samples from each of the seven potential bedrock source intervals were collected at the nearest possible location of each interval to Cascade Springs. For each of the bedrock samples, a single chip of rock of about 1 inch in each dimension was collected from each 1-foot-thick stratigraphic interval while traversing up each section. The chips were composited, crushed, homogenized, and a sample split of about 2 pounds was pulverized for 1 minute in a miniature ball mill with steel balls.

The upper 100 feet of the Madison Limestone was sampled at and just north of the mouth of Onyx Cave (fig. 1). The lower Minnelusa Formation was sampled just south of the mouth of Onyx Cave. The uppermost 100 feet of the middle interval of the Minnelusa Formation was sampled in Hot Brook Canyon just above Hot Brook Spring. The upper Minnelusa Formation and the Opeche Shale also were sampled above Hot Brook Spring. The Minnekahta Limestone and the Spearfish Formation were sampled within 1,000 feet of Cascade Springs (fig. 2).

Samples of cave-fill sediments were collected from two caves in the Black Hills. One sample of muddy, orange, internal sediment was collected from Brooks Cave (which is located just west of Rapid City, about 20 miles north of the study area) and two samples of stratified and unstratified, red, muddy, internal sediments were obtained from Jewel Cave (fig. 1). Unlithified cave-fill sediments were not crushed, homogenized, or pulverized because they disaggregated in a horn-type ultrasonic device in water before wet sieving.

Mineralogic analyses of selected samples were performed by X-ray diffraction (XRD) by the author in the laboratory of the former Branch of Energy and Marine Geology of the USGS in Denver, Colorado. For all XRD determinations, a Phillips APD-3600 automated diffractometer was used with copper K-alpha radiation, run at 45 kilovolts and

30 milliAmps. XRD scans were from 2° to 64° two-theta, at 0.02° per step and one step per second. XRD peak positions then were determined by the APD-3600 2nd Derivative Peak Algorithm. For most XRD patterns, a peak matching program was run to match peaks to known minerals, but all mineralogic identifications reported here also have been confirmed by detailed examination of the patterns.

Grain-size separations for clay mineralogic analyses of the suspended sediment and of each potential source interval sample were made using combinations of standard wet sieving and differential-settling-rate techniques. Limestone and calcite-cemented sandstone samples were treated to remove all carbonates from the less-than-64-micron size separates using methods described in Jackson (1969) before the differential-settling-rate techniques were used to separate the clay fraction. For each sample, XRD slides were prepared for the less-than-2-micron fraction and the 2-to-10-micron fraction.

The less-than-2-micron fractions were mounted as oriented clay-mineral slides (Moore and Reynolds, 1989). These slides were run a second time by XRD after employing glycolation techniques described by Moore and Reynolds (1989) that allow quantification of the percent of smectite interlayers in any illite/smectite mixed-layer clays. Some of the oriented clay-mineral slides also were run a third time by XRD after heating to 550°C for one hour as described by Moore and Reynolds (1989). Because kaolinite is destroyed during heating, the comparison of XRD runs before and after heat treatment allows chlorite to be distinguished from kaolinite.

Outcropping breccia pipes were examined and sampled in Hell Canyon northwest of Hot Springs (the Pm samples shown in fig. 1). Samples of breccia pipes and their wall rocks were treated by the method described by Jackson (1969) to dissolve calcite cements. The disaggregated wall rock and breccia samples then were separated into grain-size fractions by wet sieving and differential-settling-rate techniques. Grain-size fractions were dried and weighed, and the data were plotted as cumulative grain-size distributions.

Geochemical modeling of the chemical evolution of Cascade Springs ground water was performed using the computer program NETPATH (Plummer and others, 1991; 1994). NETPATH calculates a balanced chemical reaction assumed to occur along a ground-water flow path between two sampling points, using minerals that are known or assumed to occur in the aquifer between the sampling points.

EVALUATION OF POSSIBLE SEDIMENT SOURCES

XRD mineralogical analyses were performed for samples from the alluvium, selected bedrock units, and cave fill from the Madison Limestone and compared to those of the suspended sediment samples collected from Cascade Springs water on February 28, 1992. Field examinations of upper Minnelusa Formation breccia pipes were performed when initial XRD mineralogical analyses indicated that the suspended sediment came from the upper Minnelusa Formation and/or the Opeche Shale.

Mineralogy of Suspended Sediment and Possible Sediment Sources

By weight, the suspended sediment collected during 1992 from Cascade Springs contained about 90 percent grain sizes between 4 to 64 microns and about 10 percent grain sizes less than 4 microns. The XRD pattern of the suspended sediment prior to separation into grain-size fractions is shown in figure 4. The sediment is composed principally of quartz, with its major peak at 26.7° two-theta; calcite, with its major peak at 29.4°; and dolomite, with its major peak at 31°. The red color of the sediment is due to hematite, which has a broad low peak near 33°. Peaks at 8.9° and 12.4° indicate at least two discrete phyllosilicate minerals are present: illite or muscovite, or both, at 8.9° and chlorite or kaolinite, or both, at 12.4°.

For this study, it was not important to distinguish whether the mineral with its peaks at 8.9°, 17.6°, 19.8°, 26.5°, and others was illite, muscovite, or some other mica (fig. 4). However, it was checked whether or not that mineral had any expandable smectite interlayers. Checks for expandable smectite interlayers were made in each sample that was compared with the suspended sediment. Because the suspended sediment did not have expandable smectite interlayers, the mineral was either pure illite or some other mica. The distinction wasn't important to this study and was not made; thus, that mineral will be referred to hereafter simply as mica. The possible source interval samples all additionally lacked any interlayered illite/smectite. The hkl indices (Moore and Reynolds, 1989) assigned to the peaks on XRD patterns then are assigned as if the mineral is muscovite, where the peak at 8.9° two-theta is its 001 peak (for the muscovite unit cell), not the 002 peak as in illite's unit cell.

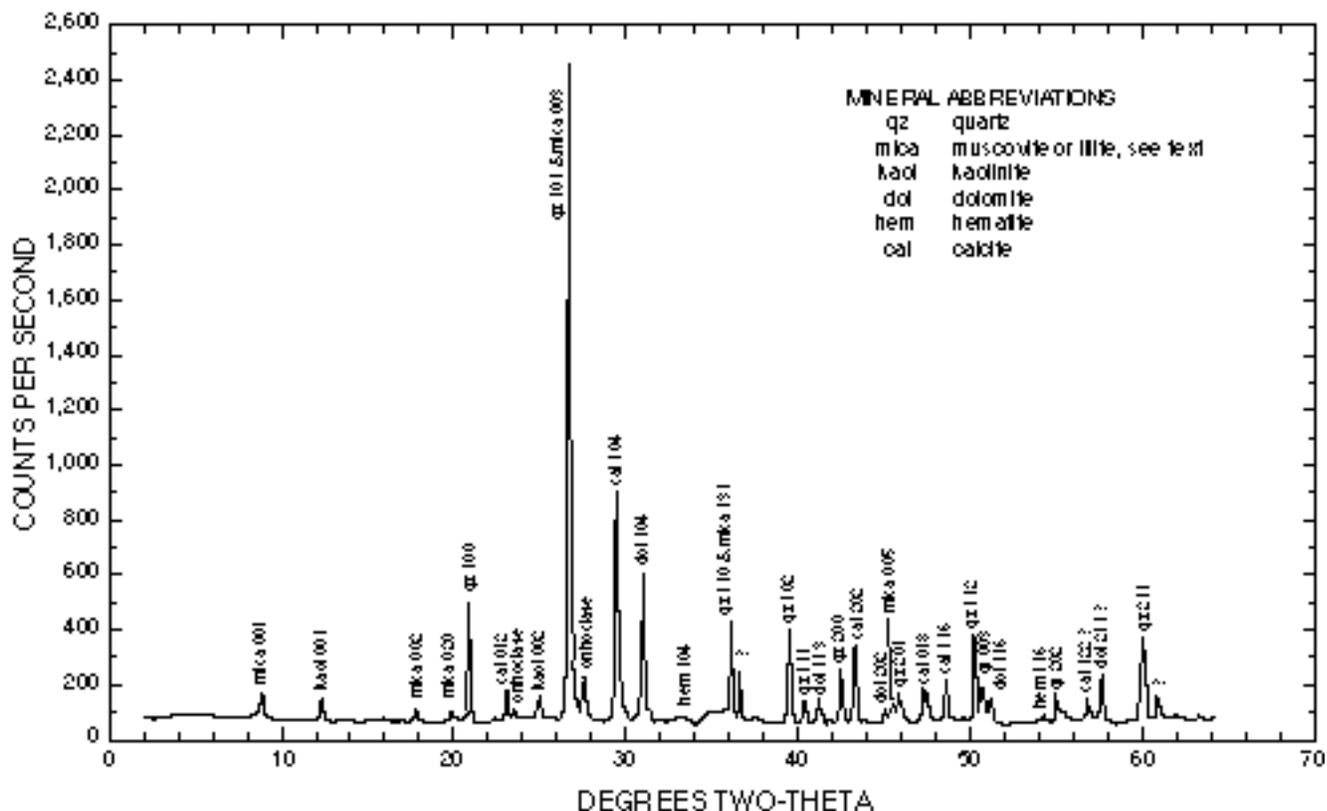


Figure 4. X-ray diffraction pattern of the unseparated suspended sediment collected from Cascade Springs on February 28, 1992. Each peak is identified by an abbreviation of the mineral or minerals that produced the peak and by the hkl index (Moore and Reynolds, 1989) of the peak.

The clay fraction (<2 microns) of the 1992 suspended sediment is compared with the unseparated suspended sediment mineralogy in figure 5. The highest intensity peaks from the clay fraction indicate the mica phase with peaks at 8.8°, 17.8°, 26.8°, and 45.4°. A second set of peaks is composed of those at 12.4°, 24.9°, and smaller peaks at higher two-theta. This set is due to chlorite or kaolinite, or both. The peak near 33° is from hematite and is more sharply defined in the clay fraction than in the unseparated sediment. Analyses of the sample collected during 1969 (not illustrated) had all of the same minerals as the 1992 event's samples, though peak intensities were notably different. In the 1969 sample, the silt fraction was perhaps dominated by calcite, and the clay fraction was very similar to the 1992 sediment.

Comparison of the glycolated and unglycolated clay fraction patterns of the 1992 suspended sediment (not illustrated) indicated no shift in the position of the 8.9° peak. This indicates that the potassium-bearing clay is essentially 100 percent illite with no smectite mixed layers, or it is muscovite.

The comparison of the clay fraction pattern of the 1992 suspended sediment before and after heating (to 550°C for 1 hour) is shown in figure 6. The peaks at 12.4°, 24.9°, 37.9°, and 38.6° two-theta disappeared after heating, which indicates that the second clay is kaolinite and that only a very small proportion of chlorite could be present.

The results of the XRD analyses and the weights of the size fractions indicate that the suspended sediment consisted principally of silt-sized quartz, calcite, and dolomite, in a mixture with clay-sized mica, kaolinite, and hematite. The XRD patterns for the clay fractions of each of seven possible bedrock sources and cave fill for the Madison Limestone are compared with the clay fraction of the 1992 suspended sediment in figure 7. The possible alluvial source is not shown in figure 7 because the alluvium had the same clay minerals as the lower Spearfish Formation. Because the clay fraction of all three cave-fill samples had the same minerals, only the unstratified sample from Jewel Cave is shown in figure 7.

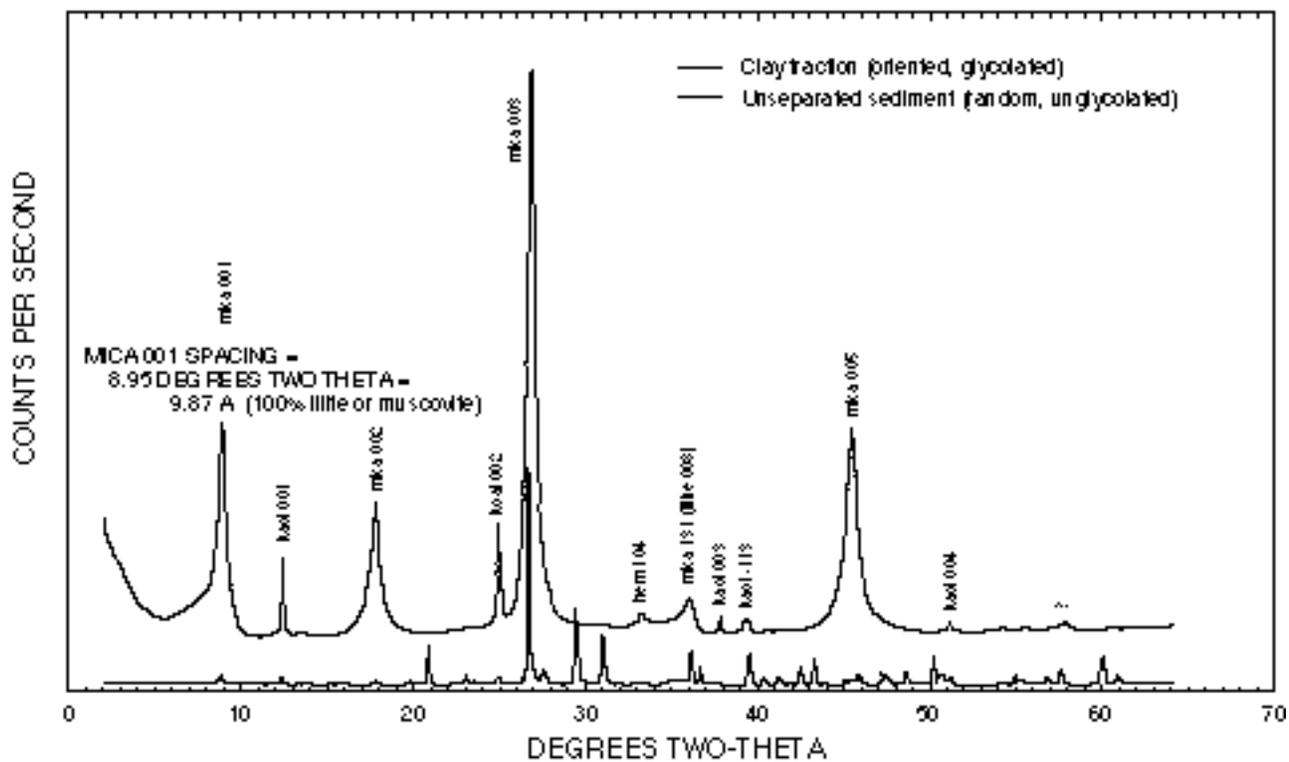


Figure 5. Comparison of X-ray diffraction patterns for the unseparated 1992 suspended sediment and its clay fraction. Mineral abbreviations and hkl indices are as in figure 4.

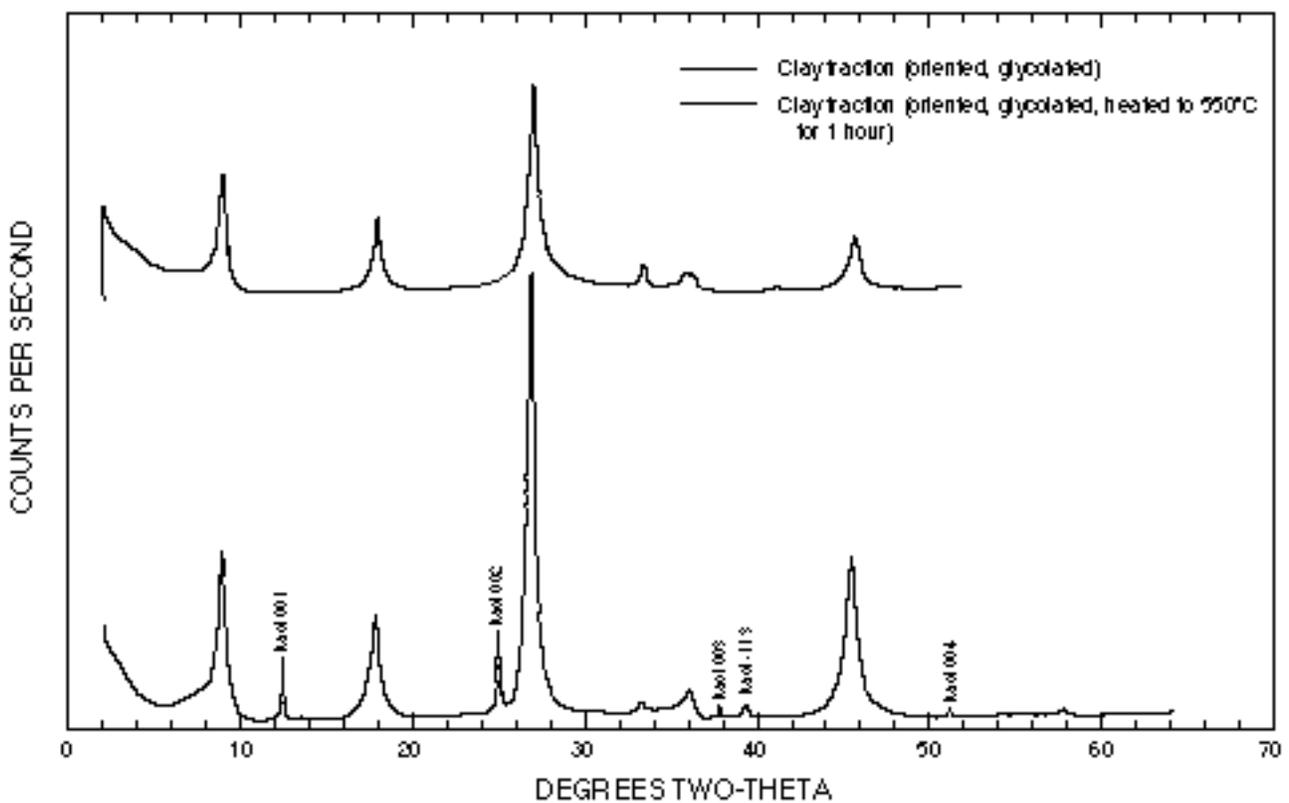


Figure 6. Comparison of X-ray diffraction patterns for the heated and unheated clay fractions of the 1992 suspended sediment. Mineral abbreviations and hkl indices are as in figure 4.

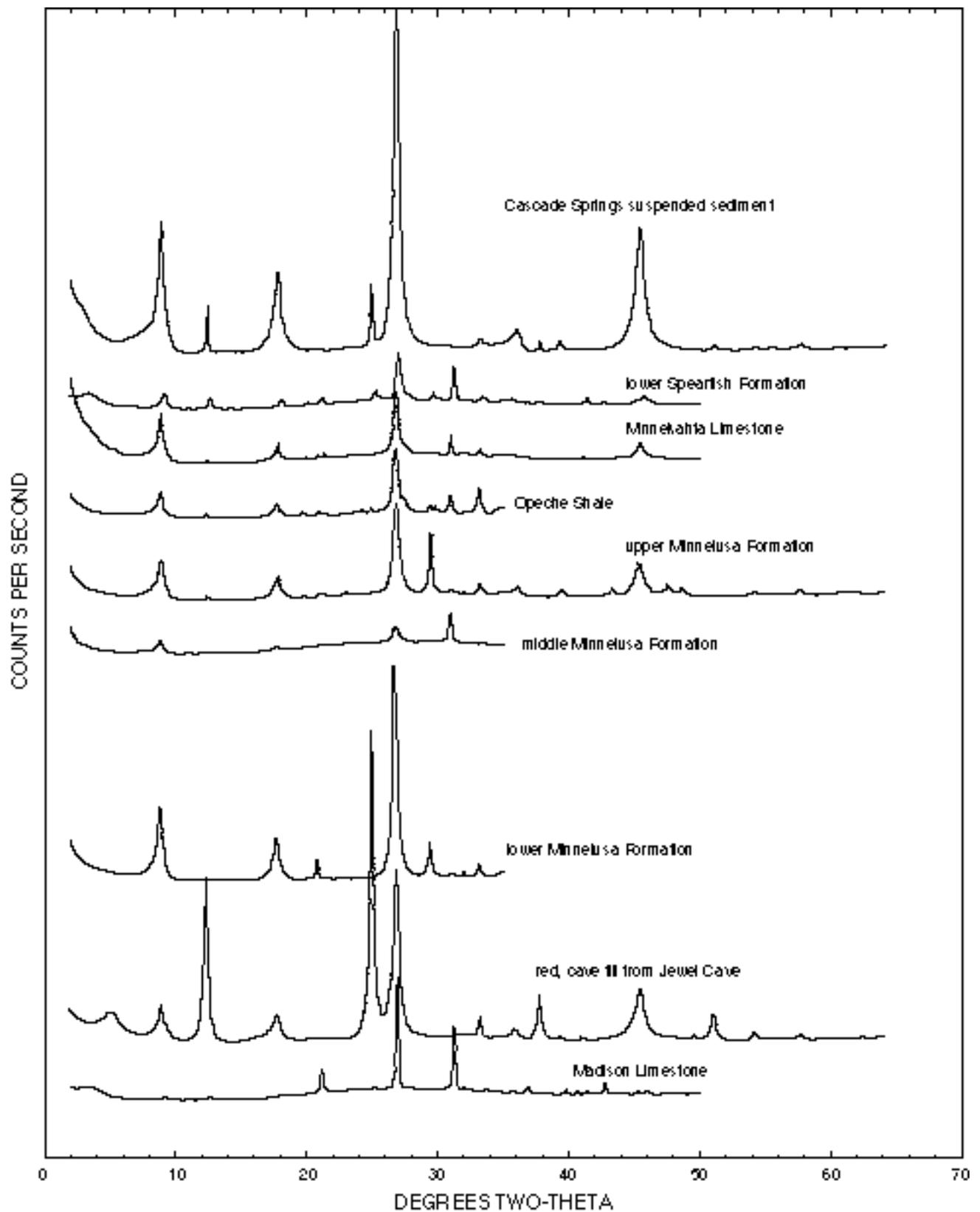


Figure 7. Comparison between the X-ray diffraction patterns for the clay fractions of the 1992 suspended sediment and eight possible source units stratigraphically below the spring-discharge points. Peaks as identified on figures 4 and 5; new additional peaks described in text.

The XRD patterns (fig. 7) show that possible matches to the clay fraction of the suspended sediment are the clay fractions of the upper Minnelusa Formation, the Opeche Shale, and the Minnekahta Limestone. Patterns from these three units match the peak positions of all minerals found in the suspended sediment, although peak intensities are different. Quartz is the major component of the clay-size fractions for samples from both the upper Minnelusa Formation and Opeche Shale, as indicated by the quartz 100 peak at 20.9° two-theta. The clay-sized quartz probably resulted from the artificial crushing and pulverizing processes that the suspended sediment did not undergo. However, the Minnekahta Limestone produced virtually no silt-sized acid-insoluble residues when subjected to dissolution by the method of Jackson (1969), so the Minnekahta Limestone could not have provided the quartz silt that volumetrically dominated the unseparated suspended sediment.

The clay-size fraction of the Madison Limestone (fig. 7) consists principally of quartz and dolomite, but it has a separate smectite clay peak near 3.9° that was absent from the pattern of the suspended sediment. The red unstratified cave fill from Jewel Cave has smectite clay that yielded a separate peak near 5°. The major clay of the cave-fill sample probably is kaolinite, not mica. The lower and middle Minnelusa Formation samples lack the kaolinite that was found in the suspended sediment.

The lower Spearfish Formation has a separated smectite clay peak at 3.8° that is not present in the suspended sediment (fig. 7). The clay fraction of Quaternary-age alluvium (not shown) matches all peaks of the lower Spearfish Formation clay including its smectite peak, so a near-surface source of the suspended sediment is not likely. Therefore, the probable source of the suspended sediment is the upper Minnelusa Formation and/or the Opeche Shale.

Examination of Lower Hell Canyon and Breccias

The results of the mineralogic analyses indicated that the suspended sediment probably came from the upper Minnelusa Formation and/or Opeche Shale. These stratigraphic intervals are known for their breccia pipes (Bowles and Braddock, 1963; Gott and others, 1974). There is a breccia pipe near Cascade Springs that cuts the lower part of the Spearfish Formation (Post, 1967, and fig. 2).

Based on the mineralogic results and the earlier studies of breccia pipes, it was hypothesized that upper Minnelusa Formation breccia pipes could be the former throats of abandoned artesian springs. The coarse-grained fraction in the breccia pipe may have remained after the fine-grained, red-colored silt and clay was washed upwards and out. This hypothesis was further tested with field examinations and laboratory work on breccia pipes. Grain-size analyses were performed to determine if the pipes contain less fine-fraction materials than their wall rocks. This would support the hypothesis that the pipes are formed by collapse accompanied by elutriation of the fine-grained red fraction.

Geologic Examination

Breccia pipes hosted in the upper Minnelusa Formation (Pm sites in fig. 1) were examined in Hell Canyon southwest of Jewel Cave. Hell Canyon was chosen because it offered the opportunity to relate spatially to the karstified Madison Limestone at Jewel Cave. Two USGS drillholes that each penetrated parts of the Minnelusa Formation (Bowles and Braddock, 1963) had been drilled earlier in lower Hell Canyon, so stratigraphy within the Minnelusa Formation was very well known there. Breccia pipes and brecciation are conspicuous in many places along lower Hell Canyon. In addition, there are numerous pale yellow to white, circular-shaped, bedding-surface outcrops of upper Minnelusa Formation sandstone away from the walls of lower Hell Canyon that probably represent breccia pipes not yet cut by erosion. Some, but not all, of these light-colored circular zones on bedding-surface outcrops no longer have discernible bedding and have visible breccia clasts within the pale yellow to white masses.

Breccia pipes of the upper Minnelusa Formation, where best exposed, are near-vertical, cylindrical, light-colored masses ranging from several feet to 65 feet in diameter. Single breccia pipes commonly are about 15 to 30 feet in diameter (fig. 8) at a stratigraphic level about 100 feet from the top of the Minnelusa Formation. Many breccia pipes occur in clusters, with individual pipes spaced from 2 to 300 feet apart. If there are similar breccia pipes beneath each modern discharge point of Cascade Springs, the pipes would form a similarly spaced array.

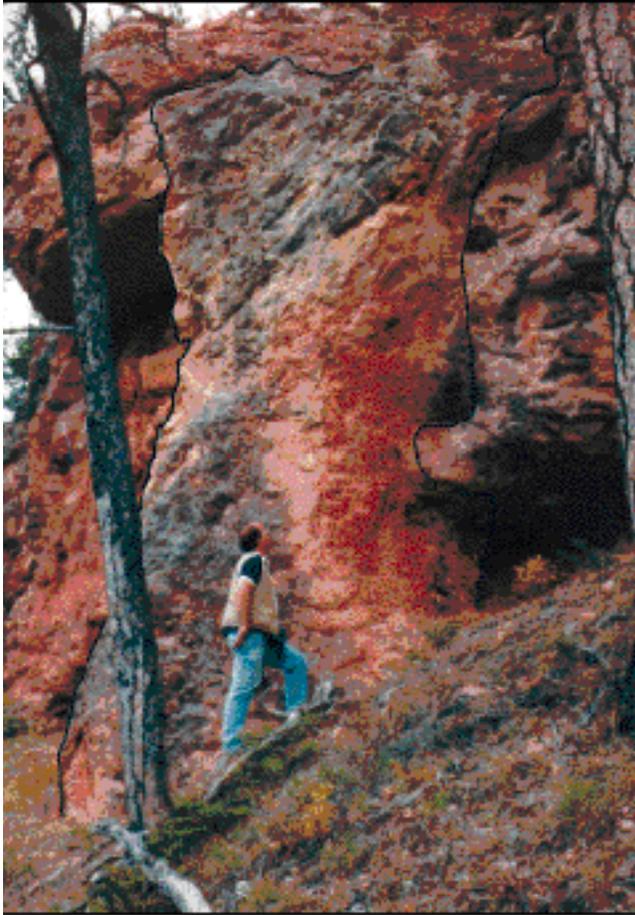


Figure 6. Small breccia pipe hosted in the upper Minnelusa Formation in lower Hell Canyon.

Both the red sandstone wall rocks that exhibit little distortion or brecciation, and the breccia pipe interiors, are loosely cemented with calcite. Most of the pale yellow interior mass of a typical pipe, which consists of laminated sandstone fragments apparently floating within unlaminated sandstone matrix, does not have discernible fragments of relict-bedded rock, which may indicate considerable fluidization within the pipes during formation. Where there are such fragments of beds, the bedding dip, fragment-to-fragment, is at chaotic angles. At the pipe edges, there are places where bedded fragments have fallen in toward the center (see also Bowles and Braddock, 1963, p. C94).

Other features related to the breccia pipes also were observed. Near one larger mass of bedding-surface exposure of white sandstone within red sand-

stone wall rocks, an 8-inch-amplitude fold within red sandstone wall rock was found. The small fold is overturned and faulted in its crest, with displacement of the overriding limb in the direction toward the center of the white mass. It is sandwiched within beds that are otherwise conformable with the regional dip. At another location the lower levels of a breccia pipe in the upper Minnelusa Formation are exposed below the cylindrical portion of the breccia pipe. The non-red sandstone cylinder tapers downward ending in a small, visibly unaltered fracture in red, fine-grained, calcite-cemented sandstone. The definable tapered light-colored mass ends about 90 feet vertically below the top of the pipe exposure and about 190 feet below the top of the formation.

Breccia pipes (vertical, cylindrical features) are conspicuously absent in the lower Minnelusa Formation; however, other breccia features are common. Numerous networks of connected breccia layers and short, vertical breccia dikes were observed in the lower Minnelusa Formation, and also have been described by Bowles and Braddock (1963). These networks typically consist of breccia layers along bedding planes that are connected by the breccia dikes.

Downward-displaced masses of Minnekahta Limestone are present in several locations southwest of the upper Minnelusa Formation exposures along Hell Canyon. Many of these simply may be blocks slumped from the outcrop rim of the Minnekahta Limestone; however, the Minnekahta Limestone-clast breccia in figure 1 is a breccia pipe that has been displaced downward by about 30 feet from the continuous outcrop rim of undisturbed Minnekahta Limestone. This breccia pipe contains conspicuous matrix sediments of two discrete generations. The first-generation, red, clayey matrix fills most of the space between angular, unbleached Minnekahta Limestone fragments. Druses of fine calcite crystals line remaining open spaces between masses of the red matrix sediment and the inter-clast remnant voids. Red matrix material in this breccia is not discernibly laminated. The second-generation breccia fill is composed of laminated purple clay that is nearly pure kaolinite and is found only in larger solution features that cut clasts and earlier matrix alike. The first-generation, red matrix was hypothesized to have originated as suspended sediment below the level of a former spring, because the color is very similar to the suspended sediment from Cascade Springs.

The breccia in the Minnekahta Limestone is at the margin of an interpreted larger depression in the Minnekahta Limestone bedding surface. The depression extends rim-to-rim of the canyon and contains several downward-displaced, locally brecciated Minnekahta Limestone blocks. The blocks are underlain by larger, but still separated masses of light-colored upper Minnelusa Formation, that mostly retain their original bedding.

Mineralogic Analysis of Minnekahta Limestone Breccia

A sample from the Minnekahta Limestone breccia was collected, and its red, first-generation matrix was separated by hand picking and was mineralogically analyzed using XRD techniques. The red matrix of the breccia, like the Cascade Springs suspended sediment, is rich in quartz silt. That result indicates that the source of the red matrix is not the Minnekahta Limestone, because the stratigraphic interval sample from the Minnekahta Limestone contained no silt-sized, acid-insoluble residue. The

XRD pattern of the clay fraction of the red breccia matrix matches all peak positions of the 1992 suspended sediment (fig. 9) and has no separated smectite clay peak, supporting the interpretation that it originated as suspended sediment in a former spring system. The clay fraction of the breccia matrix differs from the suspended sediment only in having minor quartz, marked principally by a quartz 100 peak at 20.9° two-theta.

Grain-Size Analyses of Upper Minnelusa Formation Breccia Pipes and Wall Rocks

If the red clayey sediments from Cascade Springs and the red matrix in the Minnekahta Limestone-clast breccia were sediments carried upward or out in suspension from developing breccia pipes in the upper Minnelusa Formation, then the breccia pipes in the Minnelusa Formation should contain less fine-fraction materials than their wall rocks. Therefore, the pipes should have coarser grain-size distributions and lesser clay and silt fractions than the wall rocks.

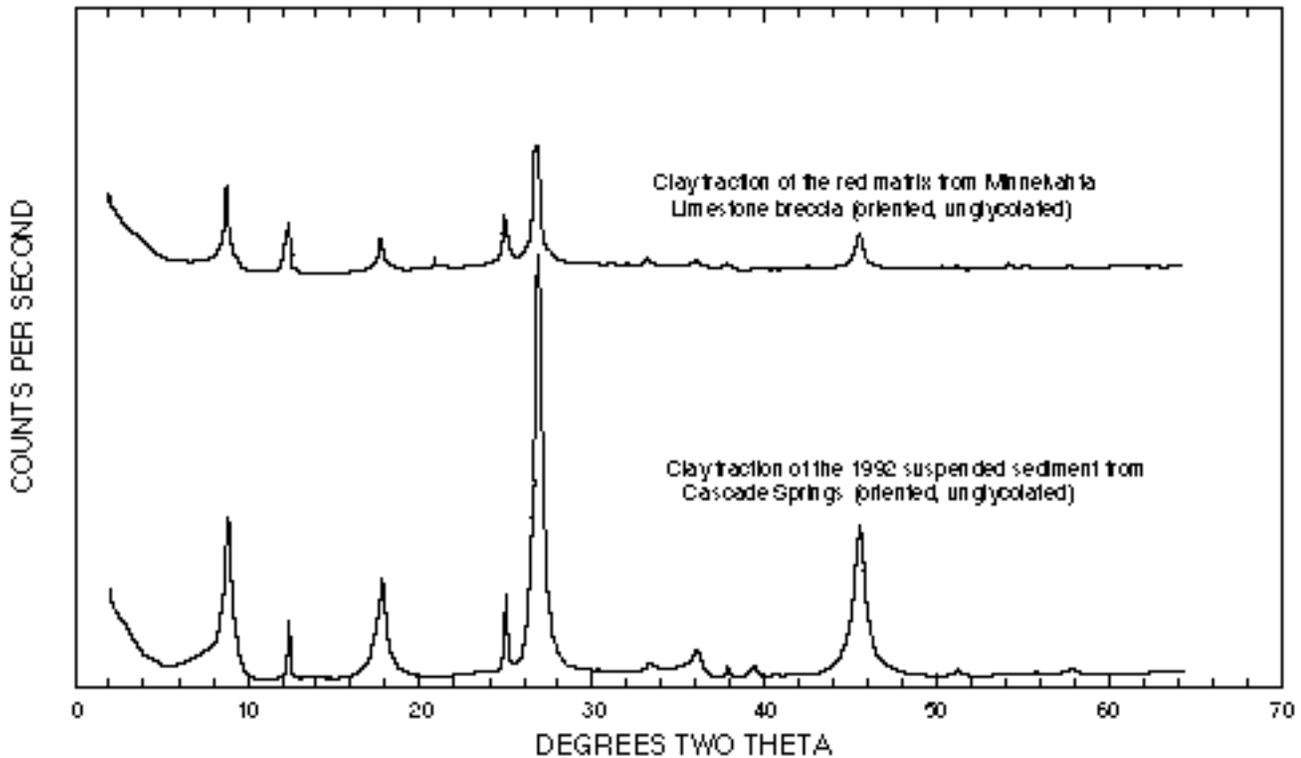


Figure 9. Comparison of X-ray diffraction patterns of clay fractions of the 1992 suspended sediment from Cascade Springs and red matrix from a breccia in the Minnekahta Limestone.

. Sample pairs were taken from three breccia masses and their adjacent wall rocks in the upper Minnelusa Formation in lower Hell Canyon (fig. 1). These were from two well-defined pipes (Pm-6/7 and Pm-8/9) and one area of white, bedding-plane exposure (Pm-10/11). After leaching calcite cements from the samples, the grain-size distributions of each sample were determined, and those of the breccia masses and wall rocks were compared (figs. 10-12). In all three samples, the breccia masses have coarser grain-size distributions than the wall rocks

Clay-fraction mineralogy of the three breccia pipes could not be compared to the clay fraction of the suspended sediment because the pipe samples contained no measurable clay. The clay mineralogy of all three wall rock samples (not illustrated) closely matched the clay mineralogy of the suspended sediment, containing mica as the major phase, kaolinite and hematite as minor phases, and no smectite.

GEOCHEMICAL EVOLUTION OF CASCADE SPRINGS WATER

Results from XRD mineralogy and grain-size analyses strongly indicate that the source of the

sediment discharged during 1969 and 1992 at Cascade Springs is a developing, subsurface breccia pipe within the upper Minnelusa Formation, similar to the pipes examined in lower Hell Canyon. Pipe development may entail dissolution of anhydrite and replacement of dolomite with calcite, leading to episodic collapse brecciation. The process could be caused by leakage of relatively “fresh” water from the Madison aquifer into the overlying Minnelusa Formation. With continued mineral dissolution and episodic collapses, the fine fraction of the Minnelusa Formation might be suspended and largely discharged in episodic suspended sediment discharge events.

The feasibility of these suggested processes was tested by modeling the geochemical evolution of ground water along several flowpaths using the computer program NETPATH (Plummer and others, 1991; 1994). Water samples from both the Madison and Minnelusa aquifers from various wells and other springs located to the north and northwest of Cascade Springs were tested as possible upgradient sources for water discharged at Cascade Springs. Preliminary results of this effort were reported by Whalen (1994).

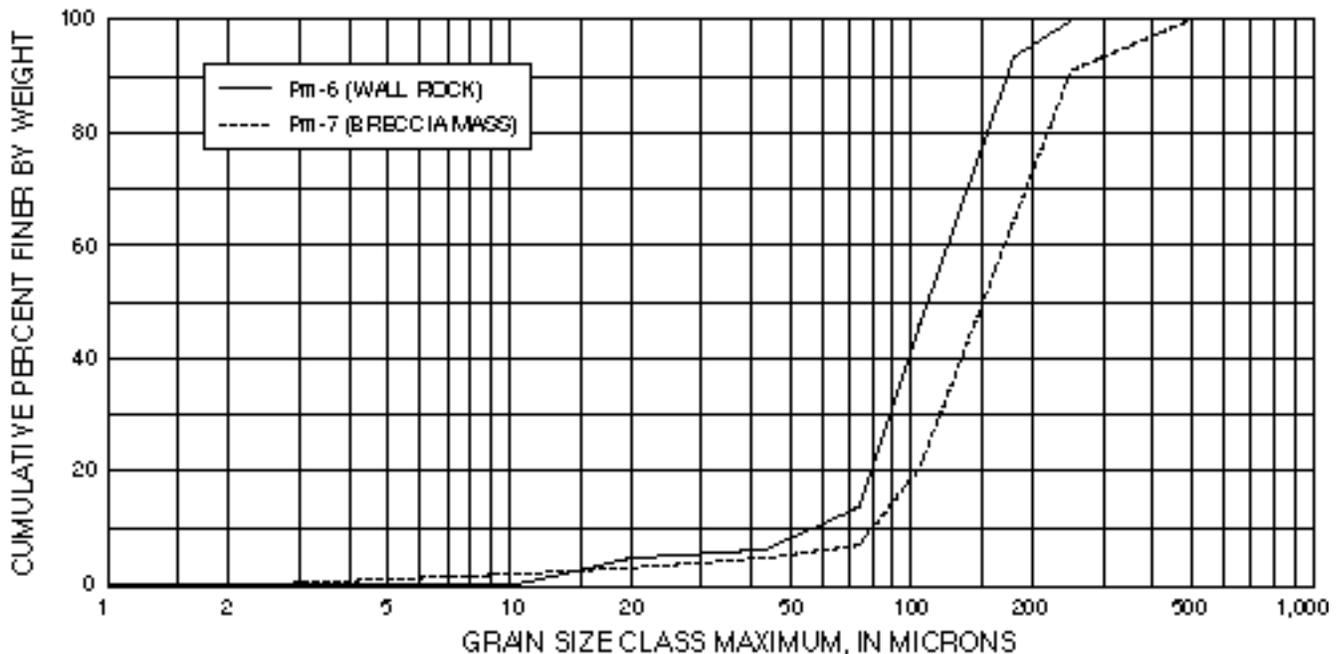


Figure 10. Comparison of grain-size distributions for Minnelusa Formation wall rock (Pm-6) and breccia mass (Pm-7).

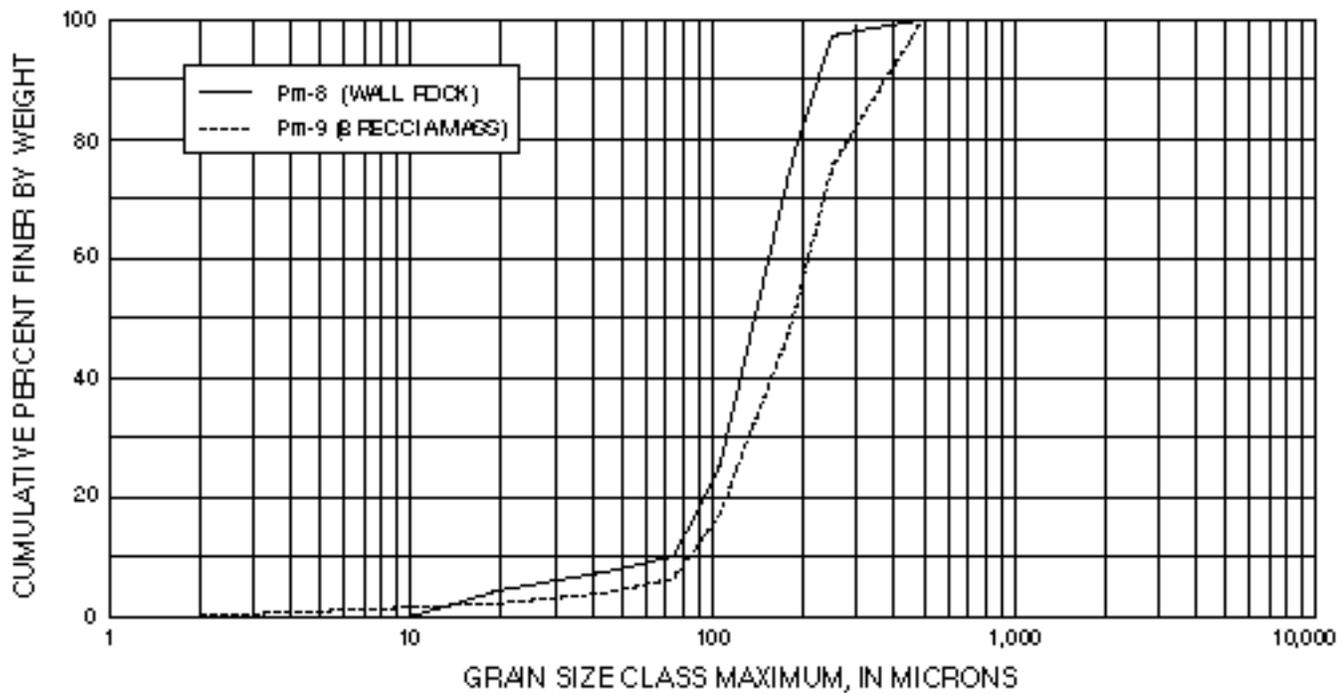


Figure 11. Comparison of grain-size distributions for Minnelusa Formation wall rock (Pm-8) and breccia mass (Pm-9).

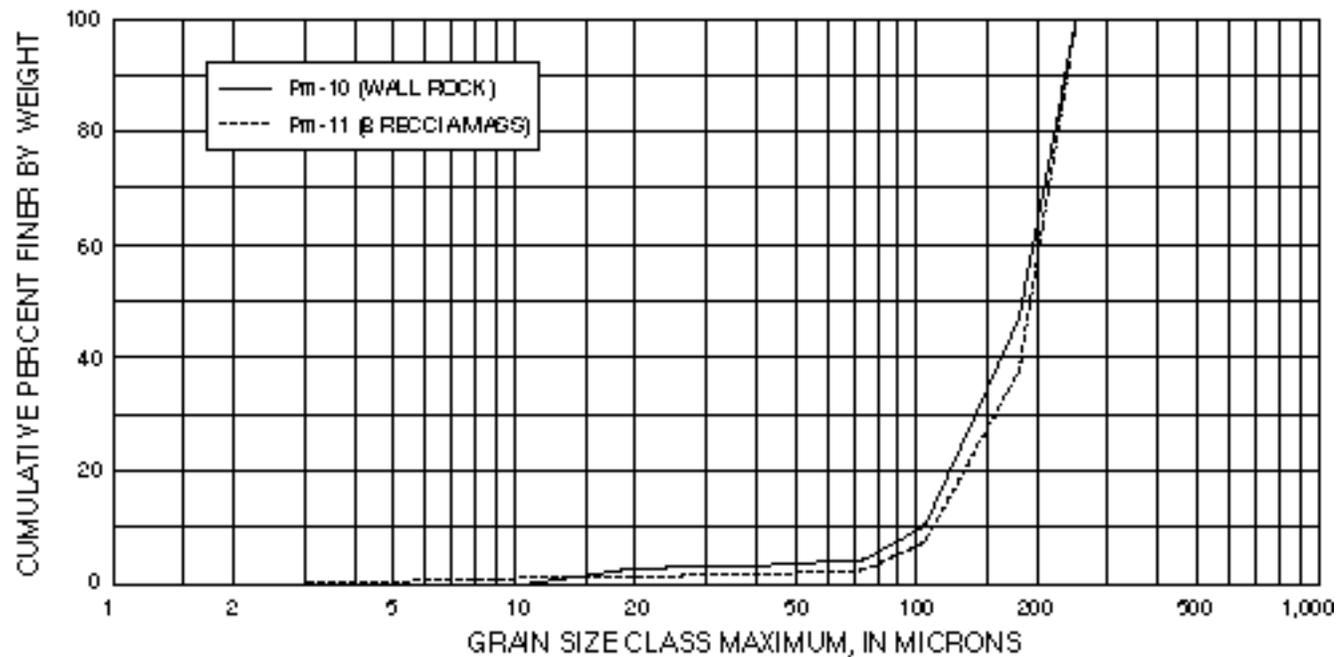


Figure 12. Comparison of grain-size distributions for Minnelusa Formation wall rock (Pm-10) and breccia mass (Pm-11) with white, bedding plane exposure.

Previous Modeling Efforts

Whalen (1994) found that water from the Minnelusa aquifer immediately upgradient from Cascade Springs is more saline than the water from Cascade Springs and, therefore, could not evolve by mineral dissolution to match the composition of Cascade Springs. Whalen (1994) also considered three samples from potential upgradient sources of water from the Madison aquifer. Samples were collected from an observation well at Minnekahta Junction, Hot Brook Spring, and the Russell-Fetter private well (fig. 1). Whalen (1994) concluded that of these three samples, only water similar to that from Hot Brook Spring could evolve to the same composition as water from Cascade Springs. The other two water samples had heavier carbon isotope values than the Cascade Springs water, which indicates that these two samples are more evolved than Cascade Springs.

Whalen (1994) found two geochemical models, each using the computer program NETPATH (Plummer and others, 1991, 1994), that suitably simulated evolution of the water from Hot Brook Spring to the composition at Cascade Springs. In both models, the water from Hot Brook Spring had to react extensively with dolomite and anhydrite that had isotopic compositions typical of Minnelusa aquifer minerals, rather than of the same minerals from the Madison aquifer. In the first model, water from Hot Brook Spring was reacted with minerals from the Minnelusa aquifer. In the second model, water from Hot Brook Spring was mixed with water from a Minnelusa aquifer well near Cascade Springs. In the second model, NETPATH calculated mixing proportions of 44 percent Madison aquifer (Hot Brook Spring water) and 56 percent Minnelusa aquifer. This mixing model also required dissolution of Minnelusa Formation anhydrite and dolomite and precipitation of calcite. Back and others (1983) had earlier suggested that dissolved sulfate concentrations in water from Cascade Springs are the product of aquifer mixing, based on sulfur isotopes in water samples.

New Modeling Efforts

A refinement of the first of Whalen's (1994) models, in which water from Hot Brook Spring is reacted with minerals from the Minnelusa aquifer, is presented in the following sections. An additional discussion of the NETPATH modeling is presented in

appendix 1, and output from the NETPATH-based model (Plummer and others, 1991, 1994) is presented in appendix 2.

Input Data Sets

Three sets of input data are utilized by NETPATH: (1) chemical composition of upgradient and downgradient ground water, (2) stoichiometries of probable minerals in the aquifer, and (3) isotopic composition of selected elements (carbon, sulfur, and strontium) in both ground water and aquifer minerals. These input data sets are described in the following sections.

Chemical Composition of Ground Water

The first set of NETPATH input is the measured chemical concentration of various constituents in the upgradient and downgradient ground-water samples, which, for this model, are from Hot Brook Spring and Cascade Springs, respectively. Measured concentrations of nine constituents—calcium, magnesium, sodium, potassium, carbon, sulfur, chloride, silica, and strontium—were used in this model (table 2). Only the carbon from the measured dissolved carbonate species of each sample was used, and no oxidation-reduction reactions were tested. For other situations, however, NETPATH can incorporate measurements of organic carbon species and can test oxidation-reduction of carbon and sulfur components, as discussed in appendix 1. Sampling methods and laboratory analytical methods were described by Whalen (1994). Within the NETPATH program, concentrations are converted to chemical activities by applying activity coefficients calculated for the ionic strength and temperature of each water sample. These chemical activities are the constraints in NETPATH modeling.

Stoichiometries of Aquifer Minerals

The second set of NETPATH input is the stoichiometry of aquifer minerals. Minerals available for reaction with the upgradient ground water are those observed or assumed to be present in the aquifer(s) along the flowpath(s) to the downgradient water sample location. NETPATH constructs a set of linear mass-balance equations, one for each of the nine measured constituents. The equations are solved simultaneously by iteration, with the designated aquifer minerals acting as sources or sinks of ions. This calculation requires at least nine minerals or gases ("phases") containing at least one each of the constituents measured.

Table 2. Physical properties, inorganic-constituent concentrations, and isotope ratios in ground water from Hot Brook Spring and Cascade Springs used in NETPATH modeling

[mg/L, milligrams per liter; µg/L, micrograms per liter; deg C, degrees Celsius; IT, incremental titration]

Station number	Local identifier	Date	pH, field (standard units) (00400)	Temperature, water (deg C) (00010)	Oxygen, dissolved (mg/L) (00300)	Calcium, dissolved (mg/L as Ca) (00915)	Magnesium, dissolved (mg/L as Mg) (00925)	Sodium, dissolved (mg/L as Na) (00930)	Potassium, dissolved (mg/L as K) (00935)
432703103302801	Hot Brook Spring	10-03-94	7.55	23.6	6.10	66	26	39	5.6
06400497	Cascade Springs	(¹)	6.89	20.0	1.95	540	83	27	5.2

Local identifier	Bicarbonate, dissolved, IT, field (mg/L as HCO ₃) (00453)	Sulfate, dissolved (mg/L as SO ₄) (00945)	Chloride, dissolved (mg/L as Cl) (00940)	Silica, dissolved (mg/L as SiO ₂) (00955)	Strontium, dissolved (µg/L as Sr) (01080)	C-13/C-12 stable isotope ratio (per mil) (82081)	S-34/S-32 stable isotope ratio (per mil) (82086)	Sr-87/Sr-86 isotope ratio
Hot Brook Spring	257	73	48	19	² 849	-9.2	10.7	² 0.71478
Cascade Springs	240	1,500	31	15	² 6,577	-9.1	12.5	² 0.70877

¹From Busby and others, 1991.

²Zell Peterman, U.S. Geological Survey, written commun., 1994.

Work by Back and others (1983), Plummer and others (1990), and Busby and others (1991) indicated that the major water/rock reactions in the Madison aquifer in the downgradient direction are dissolution of anhydrite and dolomite and precipitation of calcite. Field geologic observations support these proposed reactions. In the upper levels of Brooks Cave (located about 20 miles north of the study area), which has walls almost completely lined with sheets of “dogtooth” (scalenohedral) spar calcite crystals, shelf-like deposits of laminated calcite are present, forming over the top of the spar crystal sheets. These are interpreted to indicate formerly stable water levels of calcite-precipitating ground water. Similar calcite “shelves” are widespread within Wind Cave (Ford and others, 1993), and calcite “shelves” and “rafts” are present at the surface of “Windy City Lake,” which is the present-day ground-water level in Wind Cave.

At lower elevations, Brooks Cave contains dolostone wall rocks. At these lower levels, many of the calcite crystal sheets have parted from their walls. The exposed dolostone walls have subhorizontal flutes, grooves, and rills of up to a few tenths of inches of local relief etched into them. The flutes, grooves, and rills

are evidence of dolomite dissolution, as is the fact that the calcite crystal sheets have parted from only the dolostone walls. Anhydrite in the Madison aquifer in the Black Hills area has not been described; however, proposed intertidal depositional environments of the rocks are consistent with the presence of minor amounts of anhydrite (Hardie, 1977; Peterson, 1984).

Braddock and Bowles (1963) suggested from stratigraphic and petrographic studies that mineral reactions in the downgradient direction in the Minnelusa aquifer were dissolution of anhydrite and replacement of dolomite by calcite (dedolomitization). Consistent with these observations, the aquifer minerals used in the NETPATH model calculations included calcite, dolomite, carbon dioxide (gas), and gypsum. Celestite (SrSO₄), halite, quartz, albite, illite, and potassium feldspar were included to account for observed changes in the entire suite of analyzed constituents. A user-created celestian anhydrite solid solution was added, as a phase, along with NETPATH’s celestite and gypsum. All three of the phases, summed together, represent anhydrite in the aquifer minerals (see discussion of NETPATH modeling in appendix 1).

Isotopic Values for Aquifer Minerals and Ground Water

The third major input to NETPATH consists of isotopic values for carbon, sulfur, and strontium from both aquifer minerals and ground-water samples. Isotopic mineral values can be measured directly in mineral samples, abstracted from literature values for the formations involved, or estimated from published data for the evolution of isotopic composition of sea water and marine precipitates through geologic time. Temporal variations in isotopic composition of marine precipitates have been published by Vezier (1983) for carbonate carbon, Claypool and others (1980) for sulfate sulfur, and Smalley and others (1994) for sea-water strontium. The ground-water isotope values used in this report were measured directly (table 2).

The mineral isotope values used in preliminary NETPATH runs were based on measured values for minerals in the Madison and Minnelusa aquifers. After preliminary runs confirmed a general anhydrite dissolution and dedolomitization reaction, and that measured mineral isotopic values were close to the values required for convergence of observed and model-calculated isotope ratios in the downgradient water, the mineral isotope values were modified by trial and error to produce convergence with the measured Cascade Springs isotopic values. The convergent-model input values then were evaluated for their feasibility in terms of known isotopic fractionation effects, especially kinetic isotope fractionation effects.

An inherent NETPATH assumption is that the downgradient water is truly evolutionary from the upgradient water. If NETPATH is run without isotopic constraints and with only a few measured chemical concentrations, the program commonly generates a large number of different balanced chemical reactions that potentially might explain the chemical evolution between the upgradient and downgradient water. If more measured chemical concentrations are added, and the complete suite of major reactive aquifer minerals are known, NETPATH generally generates only a few plausible reactions. In the model described here, only one reaction was generated. When measured ground-water and mineral isotopic values are added, the remaining plausible solutions become even more constrained, because use of each measured isotopic ratio actually yields the mathematical equivalent of two additional mass-balance equations (one for each isotope of the measured ratio).

Model Results

NETPATH related the chemistry of water from upgradient Hot Brook Spring to downgradient Cascade Springs by a chemical reaction equation that can be summarized as:

{ Hot Brook Spring water + dissolving dolomite, CO₂ gas, celestian anhydrite, quartz, and potassium feldspar = Cascade Springs water + precipitating calcite, albite, illite, and halite }

The specific model equation is:

$$4.4273 \text{ HCO}_3^- + 0.7603 \text{ SO}_4^{2-} + 1.6476 \text{ Ca}^{2+} + 1.0700 \text{ Mg}^{2+} + 1.6973 \text{ Na}^+ + 0.1433 \text{ K}^+ + 1.3546 \text{ Cl}^- + 0.3164 \text{ H}_4\text{SiO}_4 + 0.0097 \text{ Sr}^{2+} + 2.37313 \text{ dolomite} [\text{CaMg}(\text{CO}_3)_2] + 1.04178 \text{ CO}_2(\text{gas}) + 14.89302 \text{ celestian anhydrite} [\text{Ca}_{0.9956}\text{Sr}_{0.0044}\text{SO}_4] + 0.23100 \text{ quartz} [\text{SiO}_2] + 0.03995 \text{ potassium-feldspar} [\text{KAlSi}_3\text{O}_8] = 4.8733 \text{ HCO}_3^- + 15.6534 \text{ SO}_4^{2-} + 13.5062 \text{ Ca}^{2+} + 3.4223 \text{ Mg}^{2+} + 1.1773 \text{ Na}^+ + 0.1333 \text{ K}^+ + 0.8766 \text{ Cl}^- + 0.2503 \text{ H}_4\text{SiO}_4 + 0.0753 \text{ Sr}^{2+} + 5.34202 \text{ calcite} [\text{CaCO}_3] + 0.04191 \text{ albite} [\text{NaAlSi}_3\text{O}_8] + 0.08321 \text{ illite} [\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2] + 0.47809 \text{ halite} [\text{NaCl}]$$

In the model equation above, the major ionic species measured in the two waters have been converted from milligrams per liter (as measured and listed in table 2) to moles per kilogram of water (molal concentrations) of the proper ionic species for the measured pH and temperature of each sample. The measured ionic species have been balanced by dissolution of anhydrite containing strontium as the mineral celestite in solid solution in a molar proportion typical for anhydrite (Palache and others, 1951, p. 426), and by dissolution of dolomite, quartz, and potassium feldspar. The precipitation of calcite, albite, illite, and halite balance the equation. The coefficients of the mineral phases and of gaseous carbon dioxide (dissolving) were calculated by NETPATH.

The model equation is the only mass-balance solution that is suitable, given the combination of chemical, mineralogic, and isotopic data that was input. In this equation, other possible choices may exist for the minerals that are in lesser concentrations in the waters, but any other choices for the minerals of calcium, magnesium, sulfur, and carbon are unlikely to produce a near-convergence between the model-calculated and measured isotopic composition of Cascade Springs. Measured isotope values in the two water samples and chosen isotope values for the minerals then can add information based on the

nearness to convergence of the calculated and measured isotopic ratios in the downgradient water.

Isotopic values typically are reported as $\delta^{13}\text{C}$ for carbon-isotope ratios and $\delta^{34}\text{S}$ for sulfur-isotope ratios in units of per mil (‰) relative to a reference standard. The strontium isotope ratios are not converted to per mil values. A positive δ -value indicates that the sample is enriched in the heavy isotope relative to the standard, and a negative δ -value indicates depletion in the heavy isotope.

Given the calculated proportions of anhydrite and dolomite dissolving and calcite precipitating from the NETPATH-modeled reaction to produce the chemical composition of Cascade Springs, the only isotopic input mineral values that permit matches to the measured sulfur, carbon, and strontium isotope values in Cascade Springs are a $\delta^{13}\text{C}$ for dolomite carbon of -4.6‰, a $\delta^{34}\text{S}$ for anhydrite sulfur of +12.5‰, and a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for anhydrite of 0.70877.

The $\delta^{13}\text{C}$ value for dolomite of -4.6‰ is closer to measured mineral values for the Minnelusa Formation, which range from -0.4 to -1.4‰ (Clayton and others, 1992), than to dolomite values from Mississippian-age rocks (representative of values for dolomite within the Madison Limestone), which range from +2.35 to +3.9‰ (Meyers, 1988; Bhattacharyya and Seely, 1994). The $\delta^{34}\text{S}$ value for dissolving anhydrite of +12.5‰ is closer to the average value for Minnelusa Formation anhydrite than it is to typical values for Madison Limestone anhydrite. The average value for Minnelusa Formation anhydrite is taken to be +13.18‰. This value comes by thickness-weighting and averaging more than 50 unpublished anhydrite $\delta^{34}\text{S}$ values from Minnelusa Formation cores from the Pass Creek No. 2 well in lower Hell Canyon (fig. 1) (C.G. Bowles, retired from U.S. Geological Survey, written commun., 1994).

Madison Limestone anhydrite $\delta^{34}\text{S}$ values have not been measured directly, but they have been calculated to range from +12.8‰ to +22.6‰ (Busby and others, 1991, p. F38), with most values toward the higher end of that range. Dissolving dolomite with a $\delta^{13}\text{C}$ of -4.6‰ and anhydrite with a $\delta^{34}\text{S}$ of +12.5‰, lighter even than the probable Minnelusa Formation average mineral values, is plausible because kinetic isotope fractionation effects from laboratory experiments also have given isotopically lighter carbon and isotopically lighter sulfur in the water than equilibrium-predicted values whenever equilibrium was not attained (R.O. Rye, U.S. Geological Survey, oral

commun., 1984). Thus, the Minnelusa mineral values for $\delta^{13}\text{C}$ in dolomite and $\delta^{34}\text{S}$ in anhydrite are much more reasonable as sources for Cascade Springs carbon and sulfur than the isotopically heavier Madison Limestone dolomite and anhydrite.

Strontium-isotope ratios on the sea-water evolution curve of Smalley and others (1994) range from 0.70788 to 0.70835 (range center of 0.70812) for Mississippian time (Madison Limestone), and range from 0.70760 to 0.70843 (range center of 0.70802) for early Permian time (upper Minnelusa Formation). These sea-water evolution curves were derived mainly from carbonate minerals in fossils, assuming that there is no fractionation of the strontium isotopes between the sea water and the mineral, as has been observed for modern shells and other organic tests (Faure, 1977). The convergent-model $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70877 for the celestian anhydrite is more radiogenic than either range, but this high value indicates a Minnelusa Formation source because the high-end values of the upper Minnelusa Formation-age range are closest to the modeled value. Also, the Minnelusa Formation has a siliciclastic detrital component that could provide radiogenic strontium whereas the Madison Limestone does not. However, no strontium isotope data are available for any strontium-bearing minerals from either the Madison Limestone or Minnelusa Formation.

Additional evidence indicates that the majority of strontium in ground water from the flanks of the Black Hills is from (celestian) anhydrite in the Minnelusa Formation. Strontium is present only in relatively low concentrations (generally 100 to 800 micrograms per liter) (Whalen, 1994; Klemp, 1995) in samples from the Madison aquifer, but strontium is found locally in high concentrations (6,000 to 11,000 micrograms per liter) (Whalen, 1994; Klemp, 1995) in some samples from the Minnelusa aquifer. The samples from the Minnelusa aquifer with high strontium concentrations are relatively far from Minnelusa Formation outcrops where anhydrite beds and cements are present in the subsurface (Bowles and Braddock, 1963). Dissolved strontium concentrations directly vary with dissolved calcium and sulfate concentrations in water from Minnelusa aquifer wells, which indicates that anhydrite in the Minnelusa Formation is the source of all three ions.

The suitable NETPATH-based model indicates input of fresh water from the Madison aquifer while dissolving Minnelusa Formation minerals or mixing with water from the Minnelusa aquifer. As found by

Whalen (1994) and previously stated, however, the chemical and isotopic compositions of Cascade Springs cannot be modeled from any nearby Minnelusa aquifer water alone. Isotopic composition of Cascade Springs also is more consistent with dissolution of minerals from the Minnelusa Formation rather than minerals from the Madison Limestone.

The suitable NETPATH-based chemical model describes a net dissolution of upper Minnelusa Formation minerals, anhydrite, and dolomite. Such dissolution is consistent with accompanying gravity-driven collapse, elutriation of fine-grained minerals, and production of a coarse-grained brecciated residue (breccia pipe) within the upper Minnelusa Formation.

IMPLICATIONS FOR THE ROLE OF ARTESIAN SPRINGS IN REGIONAL GEOHYDROLOGY

Field, laboratory, and geochemical modeling observations provide an integrated understanding of suspended sediment discharged at Cascade Springs. The suspended sediment probably results from episodic collapse brecciation that is caused by ongoing subsurface dissolution of anhydrite beds and cements of the upper Minnelusa Formation, accompanied by replacement of dolomite by calcite. The dissolving agent probably is relatively fresh water from the Madison aquifer that is leaking upwards through the Minnelusa Formation and discharging at the springs.

Breccia pipes commonly occur in the upper Minnelusa Formation, but very few have been observed in the lower part of the formation, near the contact with the Madison Limestone. Numerous networks of interbedded breccia layers and short, vertical breccia dikes do occur in the lower Minnelusa Formation, however. These breccia networks, along with vertical fractures and faults, are likely pathways for transmitting water from the Madison aquifer to the upper Minnelusa Formation, where collapse breccia pipes typically occur (fig. 13).

Many exposed breccia pipes of the upper Minnelusa Formation and the Minnekahta Limestone probably are the throats of abandoned artesian springs. Abandonment of upgradient spring-discharge points and occupation of new ones, in the downgradient direction, probably has kept pace with erosion over geologic time. Overall, the locations of artesian spring-discharge points within or near outcrops of the Spearfish Formation probably have been shifting

outward from the center of the Black Hills uplift, essentially matching rates with regional erosion. For example, the breccia pipe southeast of Cascade Springs that was described by Post (1967) is at a higher elevation than but in northwesterly alignment with the current spring-discharge points (fig. 2). In response to erosion and development of new discharge points at lower elevations, hydraulic head in the Madison and Minnelusa aquifers also would decline over geologic time. Thus, artesian springflow probably is a factor in controlling water levels in the Madison and Minnelusa aquifers.

Evidence exists that hydraulic head in the Madison aquifer has dropped relative to the tilted layers of sedimentary rocks within the recent geologic past. Ford and others (1993) measured uranium-series isotopic ages of calcite shelves from many different elevation and stratigraphic levels of Wind Cave, which showed that the water levels in the Madison Limestone have dropped more than 300 feet during the last 350,000 years. This is consistent with the concept that locations of artesian springs are shifting outwards from the Black Hills uplift, as outcrop belts shift outwards as a result of erosion.

Ground water discharging from the Madison aquifer at artesian springs was referred to as “rejected recharge” by Huntoon (1985). Huntoon hypothesized that recharge is rejected from the Madison aquifer as transmissivity decreases with distance from upgradient recharge areas. Interactions with the overlying Minnelusa Formation may be an important factor in this process. Upwelling water from the Madison aquifer (rejected recharge) at locations like Cascade Springs is shown to be a likely process by which breccia pipes are formed through dissolution in the Minnelusa Formation and other overlying bedrock units. Under this hypothesis, vertical hydraulic conductivity would be greatly enhanced within breccia pipes. Furthermore, horizontal hydraulic conductivity also may be enhanced in the Minnelusa Formation by dissolution processes related to upward leakage from the Madison aquifer. Potential processes could include dissolution resulting from leakage in the vicinity of breccia pipes that are abandoned spring throats, active spring discharge, and development of subsurface breccias with no visible surface expression or spring discharge, as well as general areal leakage from the Madison aquifer into the Minnelusa Formation. These potential processes are schematically illustrated in figure 13.

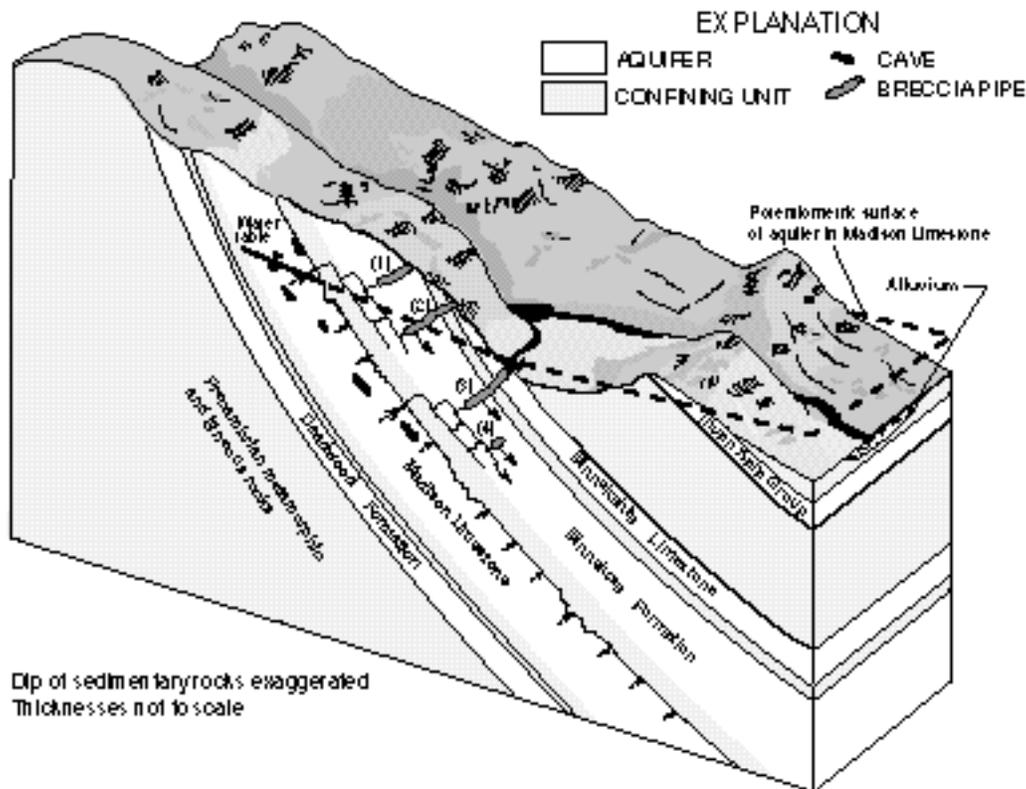


Figure 13. Schematic showing potential processes enhancing hydraulic conductivity in Minnelusa Formation, resulting from upward leakage from Madison aquifer. Breccia pipes occur primarily in the upper Minnelusa Formation; however, faults, fractures, and networks of interbedded breccia layers connected with short, vertical breccia dikes may be mechanisms for transmitting upward leakage. Vertical hydraulic conductivity is enhanced in breccia pipes and horizontal hydraulic conductivity also may be enhanced. The schematic shows: (1) exposed breccia pipe above hydraulic head in Madison aquifer; (2) exposed breccia pipe with hydraulic head below land surface; (3) breccia pipe at active spring-discharge point; and (4) developing breccia pipe. Arrows show general areal leakage and focused leakage at breccia pipes.

SUMMARY AND CONCLUSIONS

Cascade Springs is a group of artesian springs in the southern Black Hills, South Dakota, with collective flow of about 19.6 cubic feet per second. On February 28, 1992, a large discharge of red, suspended sediment was observed from two of the six known discharge points. Sediment discharge ceased within about a week. Similar events during 1906-07 and 1969 were documented by local residents and newspaper accounts.

Mineralogic and grain-size analyses indicate that the probable cause of the episodic sediment discharge is ongoing, subsurface development of a breccia pipe(s) within the upper Minnelusa Formation. Geochemical modeling indicates that upward leakage from the Madison aquifer causes dissolution of

anhydrite and dolomite within the upper Minnelusa Formation, leading to formation of solution-collapse breccia pipes. It is concluded that many exposed breccia pipes probably are throats of abandoned artesian springs resulting from outward shifting of spring sites from the center of the Black Hills uplift. This response to erosion provides a mechanism for controlling hydraulic head in the Madison and Minnelusa aquifers over geologic time.

X-ray diffraction mineralogic analyses of the suspended sediment were performed and compared to analyses of samples taken from nine geologic units at and stratigraphically below the spring-discharge points. The suspended sediment discharged in 1992 was about 90 percent silt and 10 percent clay, and consisted primarily of silt-sized quartz, calcite, and dolomite mixed with clay-sized mica, kaolinite, and

hematite. The upper Minnelusa Formation and/or Opeche Shale were identified as the probable sources for the suspended sediment, based on matches between clay mineralogies. Other stratigraphic intervals with differing clay mineralogy were eliminated as possible sources of the suspended sediment.

Ongoing development of a subsurface breccia pipe(s) in the upper Minnelusa Formation was identified as a likely source of the suspended sediment; thus, exposed breccia pipes in lower Hell Canyon were examined. Breccia pipes hosted in the upper Minnelusa Formation generally are pale yellow relative to their red wall rocks. Many occur in clusters similar to the discrete discharge points of Cascade Springs. Grain-size analyses showed that breccia masses lack clay fractions and have coarser distributions than the wall rocks, which indicates that the red, fine-grained fractions have been carried out as suspended sediment. The clay mineralogy of red matrix from a collapse breccia in the Minnekahta Limestone was matched to that of the upper Minnelusa Formation and suspended sediment from Cascade Springs. This further supports the hypothesis that many breccia pipes are formed as throats of abandoned artesian springs.

Geochemical modeling was used to test whether geochemical evolution of ground water is consistent with this hypothesis. The evolution of water at Cascade Springs could not be satisfactorily simulated using only upgradient water from the Minnelusa aquifer, which is more saline than Cascade Springs. A suitable model involved dissolution of anhydrite accompanied by dedolomitization in the upper Minnelusa Formation, which is caused by upward leakage of relatively fresh water from the Madison aquifer. The anhydrite dissolution and dedolomitization account for the net removal of minerals that would lead to breccia pipe formation by gravitational collapse. Breccia pipes in the lower Minnelusa Formation are uncommon; however, networks of interconnected breccia layers and breccia dikes are common. These networks, along with vertical fractures and faults, are likely pathways for transmitting upward leakage from the Madison aquifer.

The combination of evidence indicates that suspended sediment discharged at Cascade Springs probably results from episodic collapse brecciation that is caused by subsurface dissolution of anhydrite beds and cements of the upper Minnelusa Formation, accompanied by replacement of dolomite by calcite. The dissolving agent probably is relatively fresh water from

the Madison aquifer that is leaking upwards through the Minnelusa Formation.

It is further concluded that many exposed breccia pipes in the Minnelusa Formation, and other overlying bedrock units, probably are the throats of artesian springs that have been abandoned and exposed by erosion. The locations of artesian spring-discharge points probably have been shifting outwards from the center of the Black Hills uplift, essentially keeping pace with regional erosion over geologic time. Thus, artesian springflow probably is a factor in controlling water levels in the Madison and Minnelusa aquifers, with hydraulic head declining over geologic time in response to development of new discharge points.

Development of breccia pipes as throats of artesian springs would greatly enhance vertical hydraulic conductivity in the immediate vicinity of spring-discharge points. Horizontal hydraulic conductivity in the Minnelusa Formation also may be enhanced by dissolution processes related to upward leakage from the Madison aquifer. Potential processes could include dissolution resulting from leakage in the vicinity of breccia pipes that are abandoned spring throats, active spring discharge, development of subsurface breccias with no visible surface expression or spring discharge, as well as general areal leakage from the Madison aquifer into the Minnelusa Formation.

REFERENCES CITED

- Anderson, M.T., Driscoll, D.G., and Williamson, J.E., 1999, Ground-water and surface-water interactions along Rapid Creek near Rapid City, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 98-4214, 99 p.
- Back, W., Hanshaw, B.B., Plummer, L.N., Rahn, P.H., Rightmire, C.T., and Rubin, M., 1983, Process and rate of dedolomitization: Mass transfer and ^{14}C dating in a regional carbonate aquifer: Geological Society of America Bulletin, v. 94, p. 1415-1429.
- Bhattacharyya, D.P., and Seely, M.R., 1994, Multiple dolomitization of the Warsaw and Salem Formations (Middle Mississippian), western flank of the Illinois Basin; textural, trace elemental, and isotopic signatures of four types of dolomite; a case study: Developments in Sedimentology, v. 51, p. 238-308.
- Bowles, C.G., and Braddock, W.A., 1963, Solution breccias of the Minnelusa Formation in the Black Hills, South Dakota and Wyoming, *in* Short papers in geology and hydrology, Articles 60-121: U.S. Geological Survey Professional Paper 475-C, p. C91-C95.

- Braddock, W.A., and Bowles, C.G., 1963, Calcitization of dolomite by calcium sulfate solutions in the Minnelusa Formation, Black Hills, South Dakota and Wyoming, *in* Short papers in geology and hydrology, Articles 60-121: U.S. Geological Survey Professional Paper 475-C, p. C96-C99.
- Busby, J.F., Plummer, L.N., Lee, R.W., and Hanshaw, B.B., 1991, Geochemical evolution of water in the Madison aquifer in parts of Montana, Nebraska, North Dakota, South Dakota, and Wyoming: U.S. Geological Survey Professional Paper 1273-F, 89 p.
- Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: *Chemical Geology*, v. 28, p. 199-260.
- Clayton, J.L., Warden, A., Daws, T.A., Lillis, P.G., Michael, G.E., and Dawson, M., 1992, Organic geochemistry of black shales, marlstones, and oils of Middle Pennsylvanian rocks from the northern Denver and southeastern Powder River Basins, Wyoming, Nebraska, and Colorado: U.S. Geological Survey Bulletin 1917-K, 44 p.
- DeWitt, E., Redden, J.A., Buscher, D., and Wilson, A.B., 1989, Geologic map of the Black Hills area, South Dakota and Wyoming: U.S. Geological Survey Miscellaneous Investigations Map I-1910.
- Faure, G., 1977, *Principals of isotope geology*: New York, John Wiley and Sons, 589 p.
- Ford, D.C., Lundberg, J., Palmer, A.N., Palmer, M.V., Dreybrodt, W., and Schwarcz, H.P., 1993, Uranium-series dating of the draining of an aquifer—the example of Wind Cave, Black Hills, South Dakota: *Geological Society of America Bulletin*, v. 105, p. 241-250.
- Gott, G.B., Wolcott, D.E., and Bowles, C.G., 1974, Stratigraphy of the Inyan Kara Group and localization of uranium deposits, southern Black Hills, South Dakota and Wyoming: U.S. Geological Survey Professional Paper 763, 57 p.
- Greene, E.A., 1993, Hydraulic properties of the Madison aquifer system from analysis of aquifer tests in the western Rapid City area, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 93-4008, 77 p.
- Hardie, L.A., ed., 1977, *Sedimentation on the modern carbonate tidal flats of northwest Andros Island, Bahamas*: Baltimore, Johns Hopkins University Press, 202 p.
- Huntoon, P.W., 1985, Rejection of recharge water from Madison aquifer along eastern perimeter of Bighorn Artesian Basin, Wyoming: *Ground Water*, v. 23, no. 3, p. 345-353.
- Jackson, M.L., 1969, *Soil chemical analysis—Advanced course (2d ed.)*: Madison, Wis., published by the author, 895 p.
- Klemp, J.A., 1995, Source aquifers for large springs in northwestern Lawrence County, South Dakota: Unpublished M.S. Thesis, South Dakota School of Mines and Technology, Rapid City, S. Dak., 175 p.
- Meyers, W.J., 1988, Paleokarstic features in Mississippian limestones, New Mexico, *in* James, N.P., and Choquette, P.W., eds., *Paleokarst*: New York, Springer-Verlag, p. 306-328.
- Miller, L.D., and Driscoll, D.G., 1998, Streamflow characteristics for the Black Hills of South Dakota, through water year 1993: U.S. Geological Survey Water-Resources Investigations Report 97-4288, 322 p.
- Moore, D.M., and Reynolds, R.C., 1989, *X-ray diffraction and the identification and analysis of clay minerals*: New York, Oxford University Press, 332 p.
- Palache, C., Berman, H., and Frondel, C., 1951, *The system of mineralogy of James Dwight Dana and Edward Salisbury Dana, v. 2, Halides, nitrates, borates, carbonates, sulfates, phosphates, arsenates, tungstates, molybdates, etcetera*: New York, John Wiley and Sons, 1,124 p.
- Peter, K.D., 1985, Availability and quality of water from the bedrock aquifers in the Rapid City area, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 85-4022, 34 p.
- Peterson, J.A., 1984, Stratigraphy and sedimentary facies of the Madison Limestone and associated rocks in parts of Montana, Nebraska, North Dakota, South Dakota, and Wyoming: U.S. Geological Survey Professional Paper 1273-A, 34 p.
- Plummer, L.N., Busby, J.F., Lee, R.W., and Hanshaw, B.B., 1990, Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota: *Water Resources Research*, v. 26, p. 1981-2014.
- Plummer, L.N., Prestemon, E.C., and Parkurst, D.L., 1991, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH: U.S. Geological Survey Water-Resources Investigations Report 91-4078, 227 p.
- 1994, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH version 2.0: U.S. Geological Survey Water-Resources Investigations Report 94-4169, 130 p.
- Post, E.V., 1967, Geology of the Cascade Springs quadrangle, Fall River County, South Dakota: U.S. Geological Survey Bulletin 1063-L, 61 p.
- Rahn, P.H., and Gries, J.P., 1973, Large springs in the Black Hills, South Dakota and Wyoming: *South Dakota Geological Survey Report of Investigations 107*, 46 p.
- Smalley, P.C., Higgins, A.C., Howarth, R.J., Nicholson, H., Jones, C.E., Swinburne, N.H.M., and Bessa, J., 1994, Seawater Sr isotope variation through time; a procedure for constructing a reference curve to date and correlate marine sedimentary rocks: *Geology*, v. 22, p. 431-434.

- Turner, P., 1980, Continental red beds: New York, Elsevier, 562 p.
- Twomey, K., and Magee, H., eds., and Mueller, D., and Petty, N., compilers, 1983, Early Hot Springs: Hot Springs, S. Dak., Star Publishers, 117 p.
- Veziar, J., 1983, Trace elements and isotopes in sedimentary carbonates, in Reeder, R.J., ed., Reviews in Mineralogy, v. 11, Carbonates: Chelsea, Mich., Mineralogical Society of America, p. 265-299.
- Whalen, P. J., 1994, Source aquifers for Cascade Springs, Hot Springs, and Beaver Creek Springs in the southern Black Hills of South Dakota: Unpublished M.S. Thesis, South Dakota School of Mines and Technology, Rapid City, S. Dak., 299 p.
- Wolcott, D.E., 1967, Geology of the Hot Springs quadrangle, Fall River and Custer Counties, South Dakota: U.S. Geological Survey Bulletin 1063-K, 16 p.

APPENDICES

Appendix 1: Additional discussion of NETPATH modeling

The objective in modeling the evolution of Hot Brook Spring water into Cascade Springs water, was to determine the simplest water/mineral reaction that would explain the concentrations of all the major dissolved ions. Redox calculations were avoided because the measurements of dissolved oxygen were not considered to be reliable.

However, it is possible that redox reactions involving sulfur, iron, and dissolved and suspended organic carbon species may yield a better match to the isotopic data. Evidence suggesting oxidation/reduction processes includes: (1) the alteration of hematite iron to an unidentified ferrous iron mineral in bleached, finely porous, dolomitized Minnekahta Limestone outcrop adjacent to modern Cascade Springs' upper spring basin on the east (fig. 2); (2) the existence of coatings of unidentified, amorphous, soft, dark-brown, organic material (dead oil) on rounded gypsum clasts within the breccia pipe described by Post (1967); and (3) the low dissolved oxygen concentration of Cascade Springs water and its very large difference from the dissolved oxygen concentration of Hot Brook Spring (table 2). These features probably indicate reduction of ferric iron and sulfate sulfur from the rock coupled with oxidation of solution-borne organic(?) carbon species to produce the dead oil. Reduction of the rock sulfate could produce H_2S , a species widely suspected to be involved in the "bleaching" of red beds (Turner, 1980), although H_2S is not present in high concentrations in the current Cascade Springs water. These mineralogic alteration features may date from earlier times and different Cascade Springs water compositions, however. The above serves as a disclaimer to any possible inference from the text that the calculated reaction is the "only" reaction that explains Cascade Springs composition.

Application of NETPATH was otherwise nearly straightforward as prescribed in Plummer and others (1994), with the concentrations of bicarbonate, sulfate, silicic acid, chloride, calcium, magnesium, potassium, sodium, strontium, $\delta^{13}C$, and $\delta^{34}S$ of each analyzed water as constraints, and using Hot Brook Spring as the initial water and Cascade Springs as the final water (table 2). The only nonstandard use of NETPATH was that the 11 "constraints" above required 11 "phases" to also be input, notably including a strontium phase. The direct variation of strontium with calcium and sulfate in Minnelusa aquifer water in the Black Hills (discussed in the text) indicated that the source of the high strontium concentrations in Cascade Springs water was upper Minnelusa Formation anhydrite. However, to have a number of mineral and gas phases equal the number of chemical and isotopic "constraints," anhydrite (gypsum) was kept as a phase, pure celestite was used as another, and a new mineral, celestian anhydrite solid solution (celss) with 4 mole-percent celestite in an anhydrite solid solution was added.

The standard NETPATH output for this run is presented in appendix 2. Standard NETPATH outputs are described in Plummer and others (1994).

In the text presentation of this output, a standard chemical equation was written within which the celestian anhydrite solid solution, the anhydrite (gypsum), and the celestite were combined and expressed in terms of total moles of sulfate, calcium, and strontium in a single dissolving phase. That "additive" phase has proper molar proportions of celestite and anhydrite to balance the text equation.

Appendix 2: NETPATH output

Initial Well : hotbrook
 Final Well : cascade

	Final	Initial
C	4.8733	4.4273
S	15.6534	.7603
CA	13.5062	1.6476
MG	3.4223	1.0700
NA	1.1773	1.6973
K	.1333	.1433
CL	.8766	1.3546
SI	.2503	.3164
SR	.0753	.0097
I1	-44.3471	-40.7311
I3	195.6670	8.1356

CALCITE	CA	1.0000	C	1.0000	RS	4.0000	I1	-6.7000	I2	50.0000
DOLOMITE	CA	1.0000	MG	1.0000	C	2.0000	RS	8.0000	I1	-9.2000
			I2	.0000						
CO2 GAS	C	1.0000	RS	4.0000	I1	-16.8700	I2	100.0000		
GYPSUM	CA	1.0000	S	1.0000	RS	6.0000	I3	12.5400		
CELESTIT	SR	1.0000	S	1.0000	RS	6.0000	I4	.7088	I3	12.5400
celss	S	1.0000	CA	.9600	SR	.0400	I3	12.5000	I4	.0284
NaCl	NA	1.0000	CL	1.0000						
ALBITE	NA	1.0000	AL	1.0000	SI	3.0000				
SiO2	SI	1.0000								
K-SPAR	K	1.0000	AL	1.0000	SI	3.0000				
ILLITE	K	.6000	MG	.2500	AL	2.3000	SI	3.5000		

1 model checked
 1 model found

MODEL 1

CALCITE	-5.34202
DOLOMITE	2.37313
CO2 GAS	1.04178
GYPSUM	33.37685
CELESTIT	.83845
celss	-19.32228
NaCl	-.47809
ALBITE	-.04191
SiO2	.23100
K-SPAR	.03995
ILLITE	-.08321

	Computed	Observed
Carbon-13	-9.1328	-9.1000
C-14 (% mod)	28.6974*	19.4000
Sulfur-34	12.5382	12.5000
Strontium-87	.708770	.708770
Nitrogen-15	Insufficient data	

 Adjusted C-14 age in years: 3237.* * = based on Original Data

Model (for initial A0)	A0 (initial)	Computed (no decay)	Observed	age (final)
Original Data	55.60	28.70	19.40	3237.
Mass Balance	55.79	28.75	19.40	3252.
Vogel	85.00	37.11	19.40	5362.
Tamers	52.70	27.87	19.40	2994.
Ingerson and Pearson	36.80	23.32	19.40	1521.
Fontes and Garnier	36.22	23.15	19.40	1462.
Eichinger	33.42	22.35	19.40	1171.
User-defined	100.00	41.40	19.40	6266.

Data used for Carbon-13

Initial Value: -9.2000 Modeled Final Value: -9.1328

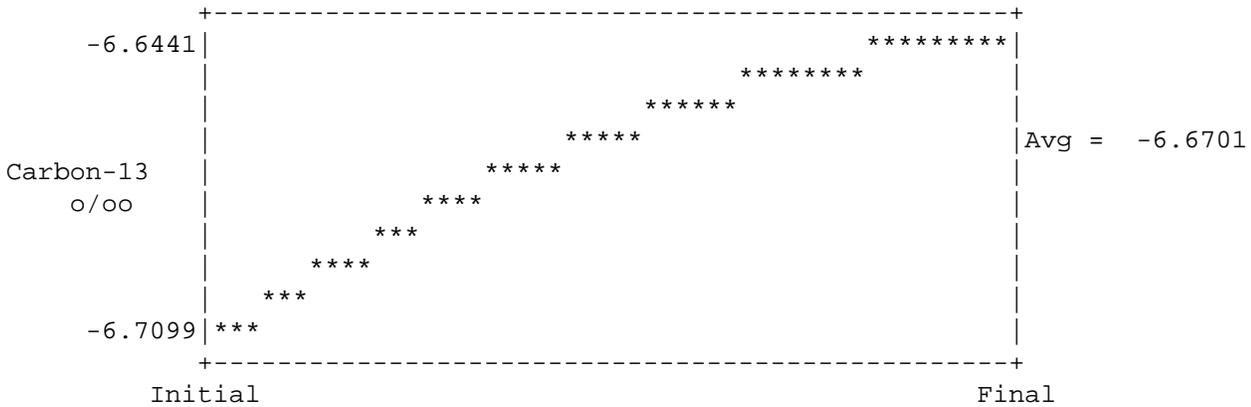
2 dissolving phases:

Phase	Delta C	Isotopic composition (o/oo)
DOLOMITE	4.74627	-4.6000
CO2 GAS	1.04178	-16.8700

1 precipitating phases:

Phase	Delta C	Fractionation factor	Average Isotopic composition (o/oo)
CALCITE	-5.34202	2.5119	-6.6701

Isotopic composition of precipitating CALCITE



Data used for C-14 (% mod)

Initial Value: 55.6000 Modeled Final Value: 28.6974

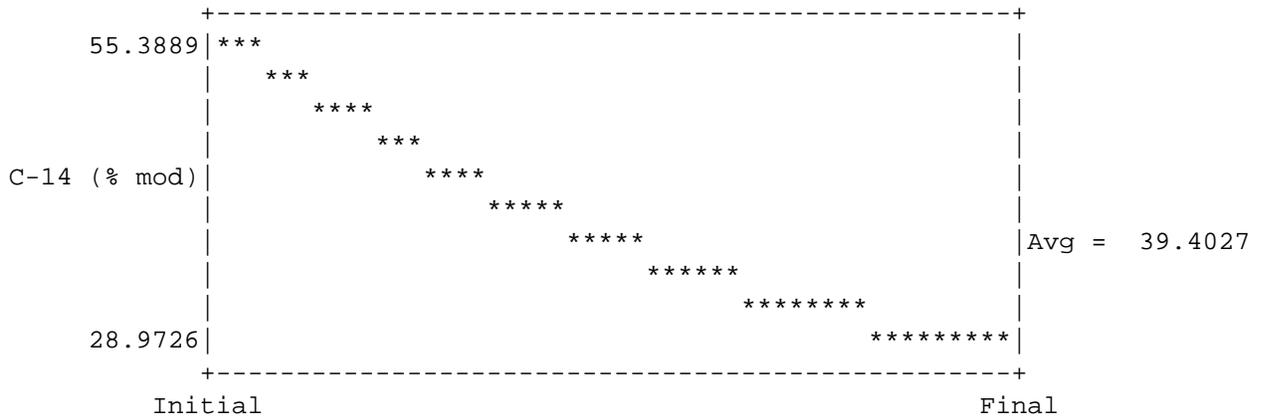
2 dissolving phases:

Phase	Delta C	Isotopic composition (% modern)
DOLOMITE	4.74627	.0000
CO2 GAS	1.04178	100.0000

1 precipitating phases:

Phase	Delta C	Fractionation factor	Average Isotopic composition (% modern)
CALCITE	-5.34202	5.0239	39.4027

Isotopic composition of precipitating CALCITE



Data used for Sulfur-34

Initial Value: 10.7000 Modeled Final Value: 12.5382

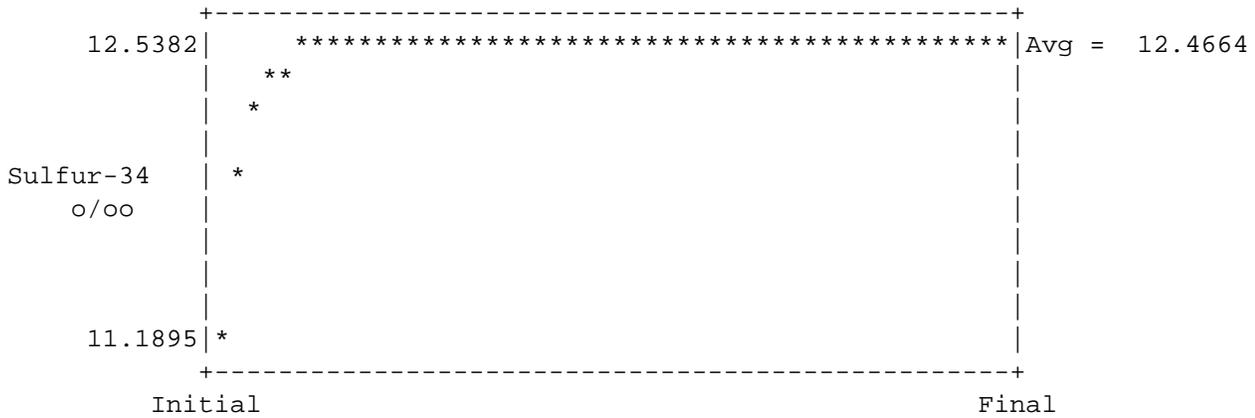
2 dissolving phases:

Phase	Delta S	Isotopic composition (o/oo)
GYPSUM	33.37685	12.5400
CELESTIT	.83845	12.5400

1 precipitating phases:

Phase	Delta S	Fractionation factor	Average Isotopic composition (o/oo)
celss	-19.32228	.0000	12.4664

Isotopic composition of precipitating celss



Data used for Strontium-87

Initial Value: .7148 Modeled Final Value: .7088

1 dissolving phases:

Phase	Delta SR	Isotopic composition (o/oo)
CELESTIT	.83845	.7088

1 precipitating phases:

Phase	Delta SR	Fractionation factor	Average Isotopic composition (o/oo)
celss	-.77289	.0000	.7089

Isotopic composition of precipitating celss



Data used for Nitrogen-15
Insufficient data