

WATER-QUALITY DATA FOR DOUGHTY SPRINGS, DELTA COUNTY, COLORADO,  
1903-1994, WITH EMPHASIS ON SULFUR REDOX SPECIES

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U.S. GEOLOGICAL SURVEY

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Denver, Colorado

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U.S. GEOLOGICAL SURVEY

Open-File Report 96-619



DEPARTMENT OF THE INTERIOR

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## EXPLANATION OF ABBREVIATIONS

g/L (grams per liter)	psi (pounds per square inch)
kw (kilowatts)	V (volts)
L/min (liters per minute)	µg (microgram)
m (meters)	µL (microliter)
meq/L (milliequivalent per liter)	µS/cm (microSiemen per centimeter)
mg/L (milligrams per liter)	nm (nanometer)
ml (milliliter)	ppm (parts per million)
mM (millimoles per liter)	ppb (parts per billion)
M (moles per liter)	
µM (micromoles per liter)	

δ<sup>2</sup>H (<sup>2</sup>H/<sup>1</sup>H ratio referenced to the VSMOW standard)

δ<sup>18</sup>O (<sup>18</sup>O/<sup>16</sup>O ratio referenced to the VSMOW standard)

D.O. (Dissolved Oxygen)

D.O.C. (Dissolved Organic Carbon)

Spec. Cond. (Specific Conductance)

VSMOW (Vienna Standard Mean Ocean Water)

CHEM (undifferentiated chemical analysis)

COLOR (colorimetry)

COND (conductance)

DCP (direct-current plasma atomic-emission spectrometry)

EC (electrochemical method)

EDTA (ethylenediamine tetraacetic acid)

FAAS (flame atomic-absorption spectrometry)

GR (gravimetry)

IC (ion chromatography)

ICP (inductively-coupled plasma atomic-emission spectrometry)

MHZ (megahertz)

RF (radio frequency)

SPEC (semiquantitative spectrographic analysis)

TITR (titrimetry)

ZGFAAS (graphite-furnace atomic-absorption spectrometry with Zeeman correction)

na (not available)

nd (not determined)

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ABSTRACT

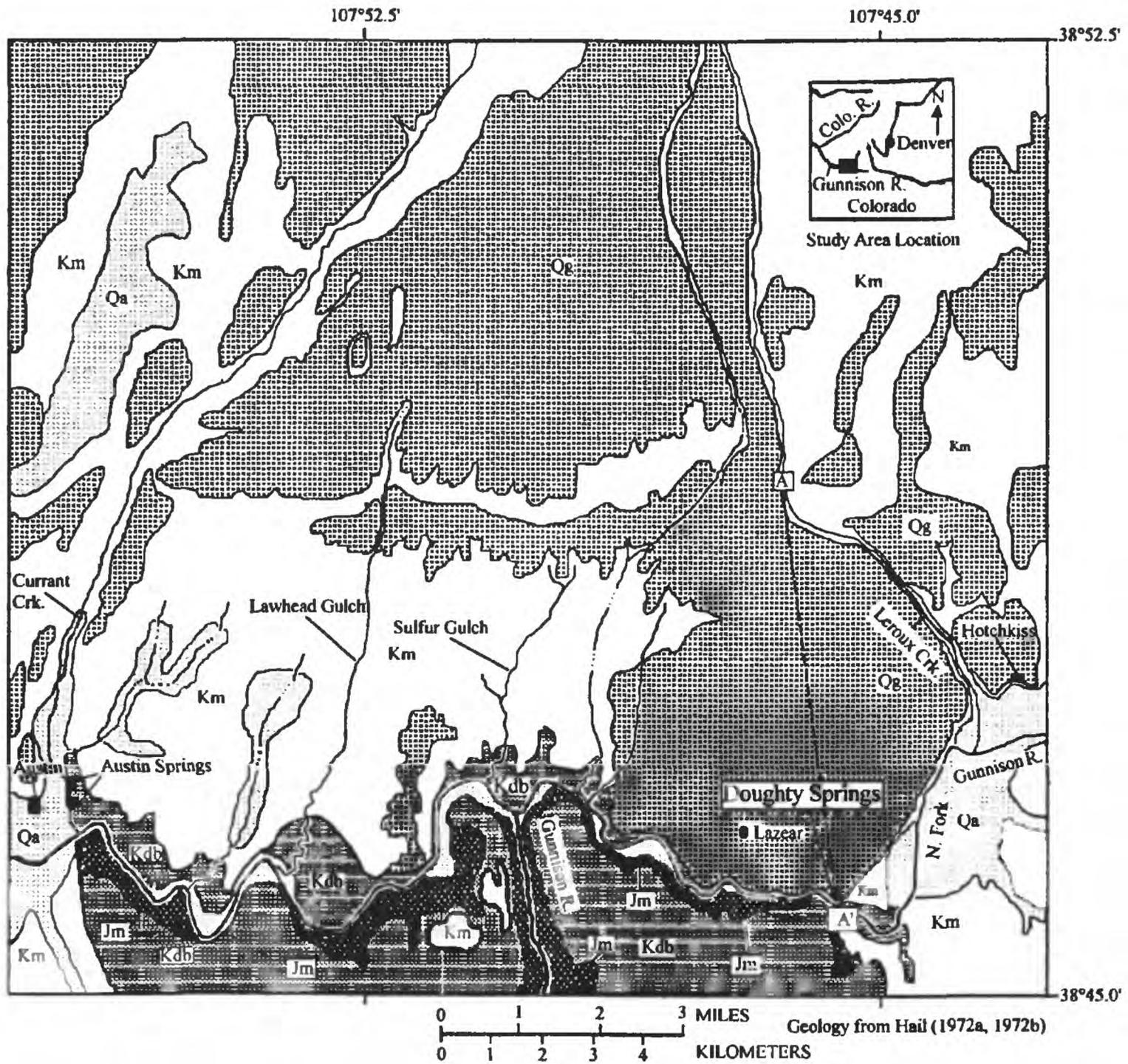
Doughty Springs are a series of radioactive springs of unusual chemical character that issue near the base of the Dakota Sandstone along the North Fork of the Gunnison River in western Colorado. These springs contain high concentrations of hydrogen sulfide, carbon dioxide, and barium. A large terrace of calcite and barite has formed from the spring waters along the banks of the river. This report summarizes the geological knowledge about the area around Doughty Springs, discusses the methods used to analyze springs samples, and compiles available water-quality data from 1903 to 1994.

## INTRODUCTION

Nearly a century ago, Headden (1905a,b,c) described a group of unusual radioactive springs on the Doughty property in Delta County, Colorado, from which he had collected and analyzed water samples during 1903-05. These springs actively precipitate calcite, barite, and elemental sulfur, forming a large terrace along the north bank of the North Fork of the Gunnison River near the town of Lazear (figs. 1 and 2). American Indians used the springs for therapeutic purposes before the arrival of white settlers who continued the practice.

In 1911, more samples of Doughty Springs were collected, analyzed, and reported by the Colorado Geological Survey (George and others, 1920). We are unaware of any further studies until those of Cadigan (1982) and Cadigan and others (1976, 1977, 1979, 1982) of the U.S. Geological Survey who documented the distribution of natural radioactivity in reconnaissance studies of various springs and their precipitates, including Doughty Springs, for the Atomic Energy Commission.

Our field work on Doughty Springs began in 1980 as part of a study to look at the occurrence of hydrated aluminum hydroxysulfate minerals, especially the mineral doughtyite reported by Headden (1905c). The scope of research broadened to consider the rates and mechanisms of precipitation of calcite and barite, the rate of H<sub>2</sub>S oxidation, the speciation of dissolved sulfur upon H<sub>2</sub>S oxidation, and the applicability of chemical models to these processes as well as to the water-rock interactions occurring in the aquifer. The site also became a useful



EXPLANATION

- |   |   |                              |
|---|---|------------------------------|
| <b>Qa</b> Alluvium                                      | <b>Km</b> Mancos Shale                              | <b>Jm</b> Morrison Formation |
| <b>Qg</b> Terrace Gravels                               | <b>Kdb</b> Dakota Sandstone/ Burro Canyon Formation |                              |
| A - A' Trace of hydrogeologic section shown in figure 3 |   |                              |

Figure 1. Generalized geology of the North Fork, Gunnison River mineral springs area.

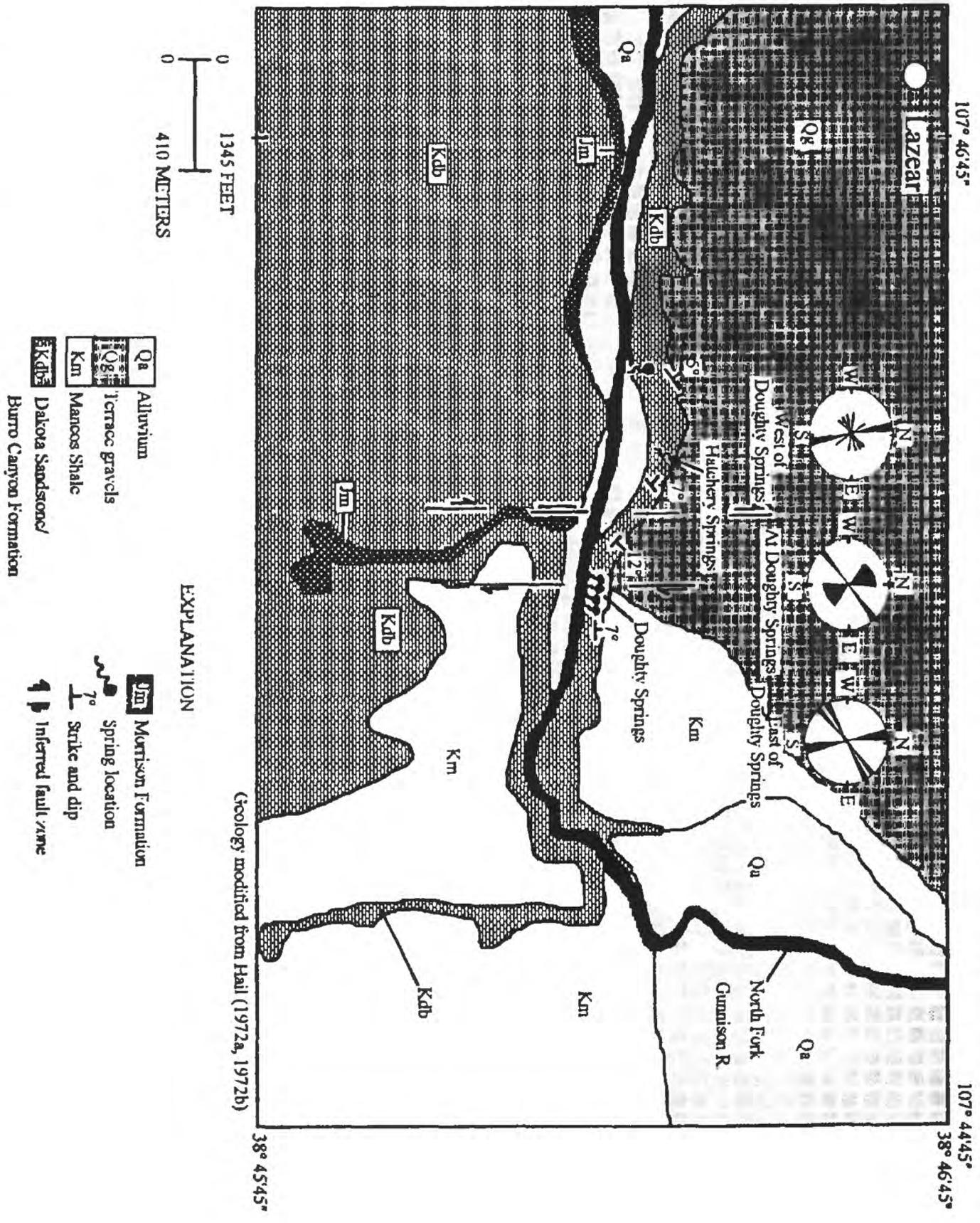


Figure 2. Detailed geology and location of Doughty Springs.

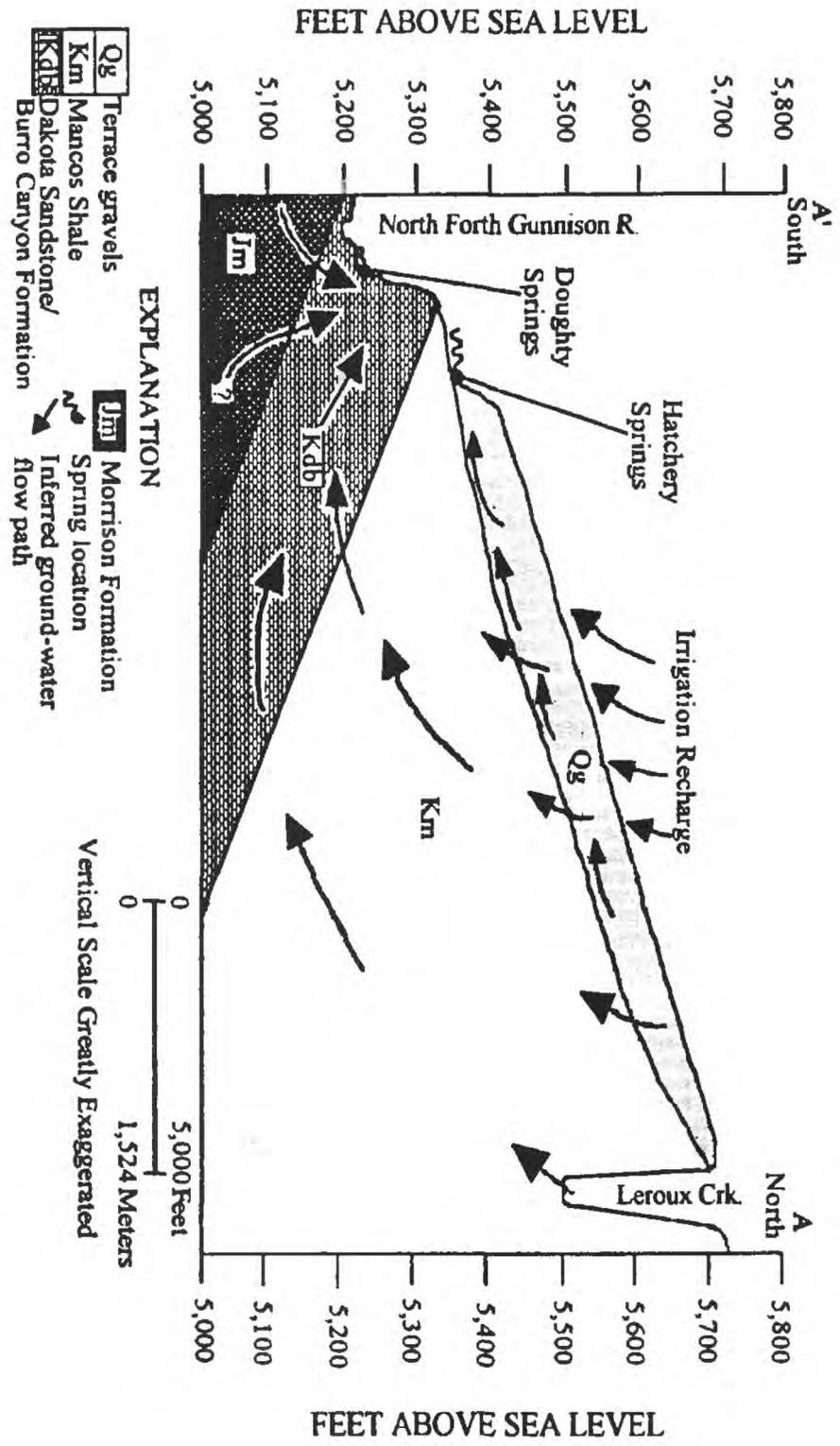


Figure 3. Schematic hydrogeologic-section indicating possible routes of ground-water flow. Trace of section shown on Figure 1.

location to test and develop field sampling procedures for unstable dissolved species. Field methods, with a mobile laboratory truck for on-site analyses, were compared and contrasted with standard preservation techniques for analyses that were performed days to weeks later in a chemical laboratory.

### Purpose and scope

The purpose of this report is to compile water-quality data on Doughty Springs and to comment on problems related to the preservation of unstable species such as  $\text{H}_2\text{S}$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{Ba}^{2+}$ . For waters in which  $\text{H}_2\text{S}$  is oxidizing and barite is precipitating,  $\text{SO}_4^{2-}$  also is unstable in the sense that its concentration may increase or decrease (or both) upon storage, unless appropriate precautions are taken.

## HYDROGEOLOGY

### Geologic setting

The consolidated rocks exposed in the suspected recharge area of the springs range in age from Jurassic to upper Cretaceous. The geology of the region is complex, owing to the intrusion of Tertiary volcanic rocks that comprise the San Juan Mountains to the south of the study area and the West Elk Mountains to the east of the study area. These volcanic rocks are not present

in the immediate vicinity of the mineral springs area but may exist at relatively shallow depths as evidenced by sulfide-rich, 40-50°C water in the C.R. Chinn well in the North Fork Gunnison River valley (Cadigan and others, 1976). The following geological descriptions were taken from Meeks (1950), Williams (1964), Lohman (1965), Craig (1971), Hanson (1971), Tweto and others (1976), Schwochow (1978), Steven and Hail (1989), and Cole and Young (1991). The generalized geologic map of the North Fork Gunnison River mineral springs area is shown in figure 1.

The Morrison Formation is Jurassic age, and the oldest formation exposed in the study area. The Morrison is composed of a 500- to 900-ft thick assemblage of colorful beds of siltstone, mudstone, sandstone, conglomerate, limestone, bentonite, and reworked volcanic ash (Williams, 1964). Rapid facies changes are common and few beds consist of the same material for any great distance. Uranium and vanadium ore deposits occur in the Morrison Formation on the western side of the Uncompahgre Plateau.

The Burro Canyon Formation of Early Cretaceous age overlies the Morrison Formation and consists of 50 to 120 ft of sandstone, shale or siltstone, conglomerate (containing chert pebbles), and thin lenticular limestone. An erosional unconformity separates the Burro Canyon from the overlying Dakota Sandstone which consists of conglomeratic sandstone, carbonaceous and lignitic shale, lignite coal, and buff-colored sandstone and is approximately 80- to 200-ft thick. The gradational contact of the Dakota Sandstone with the overlying Mancos Shale is difficult to determine and in some locations the two formations intertongue. The intertonguing

suggests a transgression of the Cretaceous sea and development of an organic-rich marine environment for shale deposition.

The Mancos Shale of Late Cretaceous age outcrops in many areas throughout western Colorado and Utah. The formation ranges from 2,000- to 3,000-ft thick and is composed of massive, fossiliferous marine shale with interbedded sandstone, siltstone, and volcanic ash layers. The Mancos Shale is the lateral equivalent of the Niobrara Formation, Cody Shale, and Pierre Shale in Montana, Nebraska, South Dakota, and Wyoming. The Mancos Shale is a regressive prodelta-plume complex genetically related to the deltaic systems active along the western interior seaway of Cretaceous age, and is divided into the lower shale member, the Ferron Sandstone member (or the Juana Lopez member), the Mancos B member, and the Buck Tongue member (Cashion, 1973; Gill and Hail, 1975; Cole and Young, 1991). The lower shale member contains massive and laminated silty-mudstone and sandy-siltstone parasequences that contain disseminated pyrite, lenticular kerogen and coal, and pyrite mineralization associated with ash beds. The Mancos B is characterized by lenticular, cyclic, upward parasequences that range in thickness from 6 to 90 ft, and is composed of five main lithofacies: silty claystone, sandstone claystone, sandy siltstone, bioturbated muddy sandstone, and sandy dolomite (as beds and concretions). Volcanic ash layers occur as interbeds throughout the Mancos Shale and range from less than 1-in. to 2-ft thick. The ash layers in the study area may have originated from the Sevier Orogeny in central Utah (Young, R.G., oral commun., 1992); however, no published information is available on the ash layers.

Quaternary terrace gravels on the northern side of the North Fork Gunnison River valley (figs. 1 and 2) are composed of glacial outwash from erosion of the basalt-capped Grand Mesa located north of the Doughty Springs area. These deposits range from 5- to 60-ft thick and are comprised of poorly sorted materials consisting of fine rock flour, sand, gravel, cobbles, and boulders. The parent material of the terrace deposits generally consists of basalt mixed with weathered and transported detritus from the Mancos Shale and sedimentary units of Tertiary age that underlie the Grand Mesa. Alluvium occurs along the North Fork Gunnison River (figs. 1 and 2) and consists of recent alluvial detritus of Holocene age weathered from the upper North Fork Gunnison River valley and the mountains to the east of the study area. Alluvial deposits on Mancos Shale terrane are frequently a combination of fluvial sediments and mudflows of Mancos Shale residuum.

The deep canyons and gorges of the Gunnison River and the North Fork of the Gunnison River, and related geomorphological features of the Doughty Springs region, were formed by erosion of structural weaknesses caused by the Gunnison uplift. The Gunnison uplift occurred during the Laramide orogeny, the last major uplift of the Rocky Mountains, and is related to the middle Tertiary volcanism of the West Elk Mountains to the east and the San Juan volcanic field to the southeast. Figure 2 shows the geology and orientation of major and complementary joint sets in the vicinity of Doughty Springs. In the immediate vicinity of Doughty Springs, the variability of major joints (northwest-southeast trending), plus the changes in strike through the area, indicate the occurrence of a fault zone at Doughty Springs. This fault zone and the fault zone at Austin Springs cut across the strike of the rocks (called cross-strike faults).

Mineral resources of the North Fork Gunnison River mineral springs area are limited to sulfur in isolated outcrops of Mancos Shale, coal in the Dakota Sandstone, and bentonitic clay and "alum" deposits (Headden, 1905c) in the Morrison Formation. Selenium also occurs as a trace element in pyrite of the Mancos Shale, and is present in high concentrations in irrigation drainwater from crop land on Mancos Shale terrain.

### Ground-Water Flow

Ground-water flow in the North Fork Gunnison mineral springs area occurs as a combination of shallow percolation through terrace gravels (recharged by irrigation) and deep ground-water flow along faults. Large springs occur at the contact of the terrace gravels and the Mancos Shale near the North Fork Gunnison River. Several fish hatcheries use water from these terrace deposit springs. Smaller mineralized springs occur at cross-strike faults (Austin Springs, Lawhead Gulch, Sulphur Gulch, and Doughty Springs, fig. 1) where ground-water moves upward from deep sources. Cross-strike faults also may function as conduits for downward percolation of ground-water from shallow irrigation recharge and from perennial streams that traverse a length of a cross-strike fault (for instance, Currant Creek and Leroux Creek, fig. 1). Figure 3 shows a hydrogeologic section of ground-water flow in the Doughty Springs area. Following the trace of section A-A' shown in figure 1, the trend of joints at Doughty Springs is consistent with stream drainage patterns in the upper part of Leroux Creek. The 300-ft gradient between Leroux Creek and Doughty Springs (fig. 3) is sufficient to drive ground-water flow downward along the cross-strike fault through the Mancos Shale. Geothermal ground water from wells is present in

the area (Cadigan and others, 1976), and the shallow ground water may be mixing with geothermally-heated ground water, which then resurges at the mineralized springs.

## METHODS OF DETERMINING SULFUR SPECIES AND OTHER CONSTITUENTS

### Pre-1980 sample collection

The three studies of Doughty Springs prior to 1980 (Headden, 1905a,b,c; George and others, 1920; Cadigan and others, 1976) contain little information about sample collection and preservation methods. No information at all is available in Headden (1905a,b), except that samples were "too old" for labile sulfidic species to be determined. R.D. George and others (1920) report no details of sampling and sample preservation, except to state that most chemical constituents were analyzed several months after sample collection. Cadigan and others (1976) also give no information on sample collection and preservation procedures. Conversation with one of the authors (R.A. Cadigan, oral commun., 1995), however, verified that samples were neither filtered nor acidified.

### Post-1980 sample collection

Sample collection and preservation for the post-1980 samples listed in this report depended upon the constituent and the method of the analysis, and changed somewhat (especially for sulfur species) over the 14-year period of data collection. Therefore, some details of the

sample collection and preservation are discussed in the next section on specific analytical methods. Descriptions of methods that did not change over the 1980-1994 time period follow immediately.

Samples were filtered if they were to be analyzed for major cations, trace metals, Fe(II)/Fe(III), major anions, alkalinity, density, and dissolved organic carbon (D.O.C.). Samples were pumped from the source through medical-grade silicone tubing with a portable peristaltic pump. Samples for DOC were filtered through a 0.2-micrometer silver filter membrane in a stainless-steel filter holder (Malcolm and McKinley, 1972). Other samples were pumped through a 142-mm diameter all-plastic pre-cleaned filter holder (Kennedy and others, 1976) containing a 0.1-micrometer Millipore<sup>1</sup> filter membrane. Samples for cations and trace metals analysis were stored in polyethylene or fluorinated polymer bottles previously rinsed with 10% nitric acid. At least 500 ml (milliliters), and more commonly 1 L (liter), of sample was pumped through the filter before taking the trace metal sample. Samples for anions, alkalinity, and density were collected in polyethylene bottles that had been rinsed in doubly-distilled water.

Samples were not filtered if they were to be analyzed for pH, Eh (oxidation/reduction potential), dissolved gases (including dissolved oxygen), temperature, specific conductance, <sup>2</sup>H, and <sup>18</sup>O. Samples for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotope determinations were collected directly from the source into amber glass bottles, leaving no head space, and sent to the USGS isotope laboratory in Reston, Virginia. Temperature, pH, Eh, and specific conductance were measured on samples pumped directly from the source into a cylindrical plexiglass chamber containing ports for the

desired electrode and for calibrating solutions.

Samples collected during 1980-81 for major cation, and trace metal determinations were stabilized by adding 2 ml of low trace metal-grade nitric acid to every 250 ml of filtered sample, and samples for Fe(II)/Fe(III) determinations were stabilized by adding 2 ml of redistilled or low trace metal-grade concentrated HCl to every 250 ml of filtered sample, followed by chilling in an ice chest or refrigerator until analysis. All other samples were stabilized only by chilling. The same procedures were followed after 1981, except that samples for major cation and trace metal determinations were acidified with HCl.

### Analytical Methods

A variety of different analytical methods were used from 1903-94, and these are summarized in the Appendix (tables 14-18). Since most analytical procedures were of an established, routine nature, the method corresponding to each descriptor in tables 14 and 15 is described briefly in tables 16 and 17. In the following paragraphs, only general conditions or variants of standard procedures are discussed.

All reagents used were of the maximum purity practicably obtainable, at least to the reagent-grade standards of the American Chemical Society. Doubly-distilled de-ionized water and redistilled or low trace metal-grade acids were used in all preparations. For direct-current plasma, inductively-coupled plasma (ICP), flame atomic-absorption, and graphite-furnace atomic-absorption spectrometric analyses, external standards, blanks, sample dilutions, and spiking

solutions were made with commercial ICP elemental standard solutions or standard solutions composed of elements or their compounds of the highest commercially-available purity. USGS were used as independent standards for checking accuracy.

Samples were diluted as necessary to bring the analyte concentration within the optimal range of the method. In elemental analyses, several dilutions of each sample, with the extremes of the range differing by factors of 2 to 100, were analyzed to check for concentration effects on the analytical method.

Calibration curves were determined by the use of several standards, measured at regular intervals within each batch of samples. If there was evidence for the presence of matrix effects, spike-recovery and standard-addition measurements were performed. USGS Standard Reference Waters T-117, T-115, and T-111, and M-102 and M-72 were used as independent checks of the analytical methods for major and trace metals and major anions, respectively, in some analyses. Standard Reference Water data appear in table 18. Estimates of detection limits were obtained from calculations of  $3\sigma_{\text{blank}}$ , where  $\sigma_{\text{blank}}$  is the standard deviation of several dozen measurements of the constituent in a blank solution, and are reported in table 17. Also listed in table 17 are typical values of reproducibility of samples where the analyte concentration is at least ten times the detection limit.

### Barium determination

Low and poorly reproducible Ba concentrations were encountered in the ICP and

ZGFAAS analyses of Doughty Springs samples, especially Drinking Spring. This problem apparently was caused by (1) the high Ba, H<sub>2</sub>S, and SO<sub>4</sub><sup>2-</sup> concentrations in Doughty Springs samples, (2) the slow oxidation of H<sub>2</sub>S relative to the on-site filtering process, and (3) the formation of microcrystalline barite (BaSO<sub>4</sub>) precipitate during storage, even in 0.06 N HCl. Part of the barite precipitate appears to have adhered to the surface of the plastic sample containers and was not included when aliquots of sample were removed for dilution. Sonicating the sample for approximately 1 minute before subsampling resulted in much higher barium concentrations and better reproducibility for 1993-1994 samples compared with those measured with no treatment except acid addition. Similar increases in Ba concentration were obtained by adding 10% (v/v) of 0.1M Na<sub>2</sub>EDTA to the sample in the field immediately after filtration to complex the Ba (1994 samples). For both treatments, barium concentrations 3-4 times greater and with better reproducibility were observed. The comparison of barium recoveries for the different sample treatments is shown in figure 4 for the 1993 and 1994 Drinking Spring data. Samples from Drinking Spring were the only ones that were subjected to the EDTA or sonication treatment. A recent study (Putnis and others, 1995) suggests that diethylene triamine pentaacetic acid (DTPA) is a better reagent than EDTA for maintaining Ba in solution in the presence of sulfate.

BA CONCENTRATION IN MILLIGRAMS PER LITER

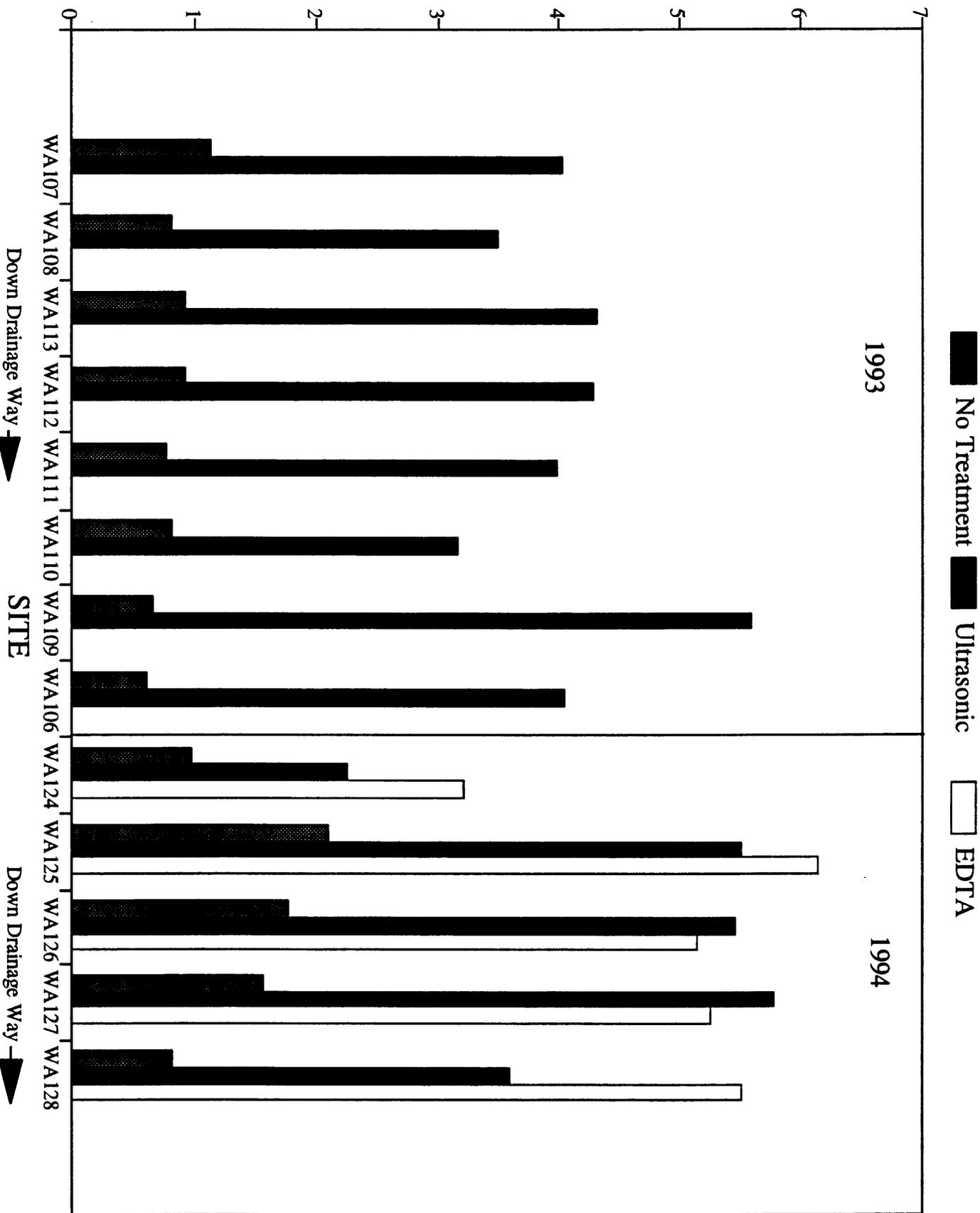


Figure 4. Barium concentration as a function of sample treatment.

## Thiosulfate determination

The distribution of sulfur species during oxidation of H<sub>2</sub>S by oxygen will change rapidly with time according to the rates of several competing reactions. Based on the works of Chen and Morris (1972), O'Brien and Birkner (1977), and Zhang and Millero (1994), the following reactions may occur:

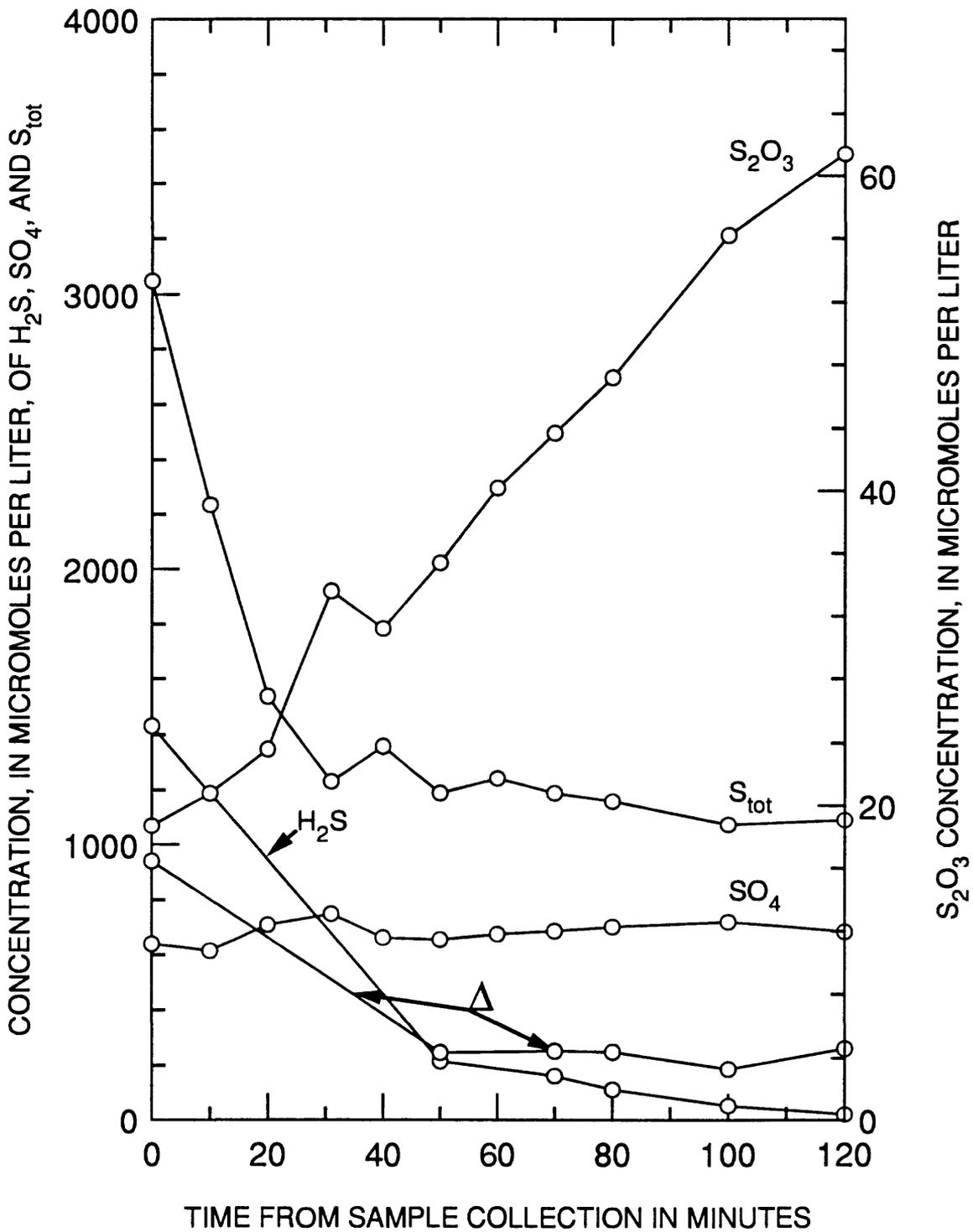
Reaction number	Reaction	Conditions where reaction is important
1	$\text{HS}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{S} \rightarrow \text{H}_2\text{S}\uparrow$	pH ≤ 7
2	$\text{HS}^- + 2 \text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+$	6 ≤ pH ≤ 8.5, [HS <sup>-</sup> ]:[O <sub>2</sub> ] low
3	$2\text{HS}^- + 2 \text{O}_2 \rightarrow \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O}$	pH ≥ 6, [HS <sup>-</sup> ]:[O <sub>2</sub> ] low
4	$\text{HS}^- + 3/2 \text{O}_2 \rightarrow \text{SO}_3^{2-} + \text{H}^+$	pH ≥ 7, [HS <sup>-</sup> ]:[O <sub>2</sub> ] low
5	$\text{HS}^- + 1/2 \text{O}_2 + \text{H}^+ \rightarrow \text{S} + \text{H}_2\text{O}$	6 ≤ pH ≤ 8.5, [HS <sup>-</sup> ]:[O <sub>2</sub> ] high
6	$n\text{S} + \text{HS}^- \rightleftharpoons \text{S}_n^{2-} \text{ (n = 4,5)} + \text{H}^+$	6 ≤ pH ≤ 8, [HS <sup>-</sup> ]:[O <sub>2</sub> ] high
7	$\text{S}_n^{2-} + 3/2 \text{O}_2 \rightarrow \text{SO}_3^{2-} + \text{H}^+ + n\text{S}$	6 ≤ pH ≤ 8, [HS <sup>-</sup> ]:[O <sub>2</sub> ] high
8	$\text{S}_n^{2-} + 2 \text{O}_2 \rightarrow \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} + n\text{S}$	6 ≤ pH ≤ 8, [HS <sup>-</sup> ]:[O <sub>2</sub> ] high
9	$\text{SO}_3^{2-} + 1/2 \text{O}_2 \rightarrow \text{SO}_4^{2-}$	All pH
10	$\text{S} + \text{SO}_3^{2-} \rightleftharpoons \text{S}_2\text{O}_3^{2-}$	7 ≤ pH ≤ 8

Since the oxidation of thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) to sulfate (SO<sub>4</sub><sup>2-</sup>) takes place at a negligible rate (Rolla and Chakrabarti, 1982) under the conditions present in Doughty Springs samples, this reaction was omitted.

The neutral pH and high initial [HS<sup>-</sup>]:[O<sub>2</sub>] ratio (~10:1) of Doughty Springs waters, combined with the reaction rate data for reactions (2)-(9) in Chen and Morris (1972) and O'Brien

and Birkner (1977) suggest that thiosulfate, elemental sulfur, sulfite, and polysulfides are the most likely products of oxidation, other than sulfate, after samples are collected. The evolution of sulfur species in a Doughty Springs water is illustrated in figure 5, which shows the results of a batch experiment conducted in 1993 on a filtered sample from the Boiling Spring source. The sample was stirred and aerated on-site immediately after collection. During the reaction, sulfate, sulfide, thiosulfate, and total sulfur ( $S_{tot}$ , as sulfate, after the addition of hydrogen peroxide) were measured. The presence of elemental sulfur was indicated by the cloudy appearance of the solution, but sulfur concentration was not quantified. The residuum represented by  $\Delta$  in figure 5 and defined as  $S_{tot} - ([H_2S] + 2[S_2O_3^{2-}] + [SO_4^{2-}])$  is consistent with the presence of elemental sulfur, sulfite, and polysulfides. However, sulfite was analyzed for by IC, but not found in Doughty Springs samples, and polysulfides were not found by direct spectrophotometry (Schwarzenbach and Fisher, 1960) in samples that were sealed on-site and analyzed later at the State University of New York-Stony Brook (SUNY-Stony Brook). Therefore, we conclude that S is the major component of  $\Delta$  in figure 5.

In samples for  $S_2O_3^{2-}$  analysis, sulfide was removed from the dissolved phase to prevent over-estimation of in-situ  $S_2O_3^{2-}$  caused by the slow oxidation of sulfide to  $S_2O_3^{2-}$ . In 1992, the sample was drawn into a plastic syringe through a filter, then transferred quickly on ice to the mobile laboratory for analysis. However, it was observed that under these conditions sulfide in the sample oxidized to  $S_2O_3^{2-}$  with a half-life of about 1 hour, leading to reported  $S_2O_3^{2-}$  concentrations that are likely to be over-estimates.



**Figure 5.** Evolution of sulfur species in a Boiling Spring sample during a batch aeration experiment.

During the 1993-94 sample collection, analytical problems arising from sulfide oxidation were minimized by drawing unfiltered sample into a 60 ml syringe containing 1 ml of 1M ZnCl<sub>2</sub> to precipitate ZnS and prevent the oxidation of sulfide to S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. The sample was then pressure-filtered directly into the ion chromatograph on-site (mobile laboratory) or the sample was stored on ice and analyzed a few days to weeks later in either Boulder, Colo. or SUNY-Stony Brook. In 1994, the same procedure was used except that 1 ml of 1 M Cd acetate was substituted for the ZnCl<sub>2</sub>, because the smaller solubility product constant of CdS ( $K = 10^{-27.0}$ ) compared with the solubility product constant for ZnS ( $K = 10^{-22.5}$ ) (Smith and Martell, 1976) might result in the better preservation of the sulfide. However, more recent work (Xu and Schoonen, 1995; Xu, Schoonen, and Strongin, *Geochim. Cosmochim. Acta*, in press) has established that semiconductors such as pyrite (FeS<sub>2</sub>) or CdS can catalyze the oxidation of thiosulfate by oxygen. The catalytic effect depends on the free energies of the conduction and valence bands of the semiconductor relative to the free energy levels of the S<sub>2</sub>O<sub>3</sub><sup>2-</sup>/SO<sub>4</sub><sup>2-</sup> redox couple in solution. By contrast, the valence and conduction band energies of ZnS cannot facilitate the thiosulfate oxidation reaction. Therefore, we authors believe that thiosulfate in water samples needs to be stabilized by adding 1 ml of 1M ZnCl<sub>2</sub> to 60 ml of sample, stored on ice, and analyzed as quickly as possible.

### Sulfate determination

The sulfide oxidation reactions that affect thiosulfate and barium determination also affect sulfate determination. Even after filtration at the sampling site, Doughty Springs samples

contained a  $\text{BaSO}_4$  ion activity product close to or exceeding the solubility product constant of barite ( $K = 10^{-10.02}$  from Nordstrom and Munoz, 1994), and an  $\text{H}_2\text{S}/\text{SO}_4^{2-}$  molar ratio ranging from 0.5 to 2.5 at the spring sources (see next section for data). If sulfide is not removed during sample collection and filtration, it continues to oxidize, and the sulfate concentration may rise, keeping the solution supersaturated with respect to barite. The measurable sulfate concentration should decrease, then increase again as the supply of aqueous barium is exhausted by precipitation while the sulfide oxidation continues. Some evidence for this mechanism may be observable in the sulfate data in figure 5.

Therefore, to avoid large errors in  $\text{SO}_4^{2-}$  concentration (on the order of a factor of two for Drinking Spring, Boiling Spring, and Bird's Nest Spring waters), it was necessary to do ion chromatography for sulfate on samples in which sulfide had been preserved upon collection by Cd or Zn addition and chilling. The Cd, Zn preservation procedure was used only for 1987-1994 samples. Consequently, measured sulfate concentrations in 1980 (see table 1) and 1981 contain a component derived from sulfide oxidation that does not exceed  $[\text{H}_2\text{S}] \text{ (mg/L)} \times 2.8$ .

## WATER CHEMISTRY, GAS, AND ISOTOPE DATA

Water analyses for Doughty Springs are shown in tables 1-11. They are organized first by spring, then by sampling site, then by chronological order. Blank spaces in the tables indicate that the parameter was not measured. In these tables, "source" samples were collected at the origin of the spring, and "drainage way" samples were collected at various flow distances from the source of those springs with a well-defined discharge. Data in the tables collected before

1980 retain the significant figures reported by the investigator. For data sets that contained the concentrations of major anions, major cations, alkalinity, and specific conductance, the WATEQ4F program (Ball and Nordstrom, 1991) was used to calculate ion sums, charge balances, and calculated specific conductance. Those data sets having charge and/or specific conductance balances exceeding 10 percent are footnoted if an explanation for the problem could be determined.

The results of gas and isotope analyses are listed in tables 12 and 13. Methods used in these analyses are listed in table 17.

Table 1. Site data and water analyses for Drinking Spring at source

Reference	Headden(1905a)	George and others(1920)	Cadigan and others(1976)
Sample Code No.	No. VI	73	DEL6
Date Collected	1903-1905	1911	9/12/73
Temperature (°C)		16.67	15
Density (g/ml)	1.00377		
pH (field/lab)			6.5/--
Spec. Cond. (µS/cm) (field/lab)			5000/--
Dissolved Solids (mg/L)	3353		3420
Eh (V)			
D.O. (mg/L)			
Alkalinity (mg/L HCO <sub>3</sub> )	1475 <sup>2</sup>	1785	2150
CO <sub>2</sub> (mg/L)			
Sum Cations (meq/L)	54.4	52.05	57.4
Sum Anions (meq/L)	54.4	52.04	56.3
Charge Balance %	0	0.03	1
<u>Constituent (mg/L)<sup>1</sup></u>			
Ca	105.7	59.2	110
Mg	39.4	44.7	43
Na	1057.1	952.5	1100
K	61.7	205	47
SO <sub>4</sub>	625.4	229.6	94
S <sub>2</sub> O <sub>3</sub>			
H <sub>2</sub> S	47.1	61	
F			2.5
Cl	700.5	682.6	720
Br	5.2		
I			
SiO <sub>2</sub>	21	17.0	17
NO <sub>2</sub>			
NO <sub>3</sub>			0.01
NH <sub>4</sub>	1.2		
Al	0.5		0.075
Fe (total)	0.7		<0.010
Fe(II)			
B	1.9		5.3
PO <sub>4</sub>		none	0.12
Li	3.1	"Trace"	3.4
Sr	6.6		3.6
Ba	13.2		3.5
Rb			
Mn	1.6	none	0.66
Zn	"Trace"		<0.022
Pb			<0.003
Be			0.002
Mo			<0.0005
V			<0.020
Tl			
Cr			<0.001
Co			<0.003
Ni			<0.005
Cu			<0.010
Cd			<0.010
As (total)			<0.046
As(III)			
As(V)			

<sup>1</sup> Significant figures as they appear in the original article

<sup>2</sup> Estimated as that alkalinity needed to give zero charge imbalance and assuming pH=6.2

Table 1. Site data and water analyses for Drinking Spring at source (cont.)

Reference	This study	This study	This study	This study	This study	This study
Sample Code No.	80WA129	81WA110	87WA106	92WA107	93WA107	94WA124
Date Collected	5/8/80	4/8/81	7/28/87	10/22/92	6/17/93	6/17/94
Temperature (°C)	15.65	16.0	15.0	15.9	14	14.4
Density (g/ml)	1.00113			1.00110		1.00127
pH (field/lab)	6.00/--	6.22/--	6.30/8.35	6.10/--	6.31/8.67	6.28/8.53
Spec. Cond. (µS/cm) (field/lab)	5500/--	5700/--	4650/--	4700/--	5000/--	--/4500
Dissolved Solids (mg/L)						
Eh (V)	-0.085	-0.049	-0.067			
D.O. (mg/L)	<0.03			0.5	1.1	0.25
Alkalinity (mg/L HCO <sub>3</sub> )	2080	2170	1770	1860	2250	2040
CO <sub>2</sub> (mg/L)	1400 <sup>1</sup>				1160	
Sum Cations (meq/L)	57.7	64.1	57.4	52.5	53.1	52.6
Sum Anions (meq/L)	62.6	56.1	49.3	48.3	56.9	53.4
Charge Balance %	-8.1	13.2 <sup>2</sup>	15.2 <sup>3</sup>	8.3	-6.9	-1.5
<u>Constituent (mg/L)</u>						
Ca	121	122	106	99	109	110
Mg	48.4	46	48.8	51	49	51.1
Na	1050	1230	1090	989	995	985
K	46.4	48.5	45.7	45	42	45.3
SO <sub>4</sub>	280	84	29.0	124	90.5	163
S <sub>2</sub> O <sub>3</sub>				0.0	0	0
H <sub>2</sub> S	53.2	59.9	25.0	26.5	44	45.4
F	2.1	2.4	1.7	2.3	1.80	1.9
Cl	790	710	729	583	684	640
Br	3.0	3.4		3.27	3.44	2.7
I	0.18					
SiO <sub>2</sub>	19	17	13	25	24	28
NO <sub>2</sub>	0.061					
NO <sub>3</sub>	0.37	0.22		0.22	1.00	
NH <sub>4</sub>	0.88			0.677	1.5	
Al	0.08	0.04		0.1	0.07	<1.5
Fe (total)	0.016	<0.02	0.013	0.031	0.025	<1.1
Fe(II)	0.016		0.013	0.031	0.025	
B	3.3	3.2	3.9	2.6	3.4	3.3
PO <sub>4</sub>	0.008					
Li	2.7	4.7	2.3	2.8	2.5	2.3
Sr	3.2	3.8	2.9	2.5	2.9	3.0
Ba	4.4	6.1	0.39	0.7	4.0	3.2
Rb	0.13	0.16	0.22			
Mn	0.92	0.96	0.95	0.82	0.95	0.91
Zn	<0.005	<0.006	0.11	<0.09	<0.04	<0.035
Pb	<0.020	0.051		<0.48	<0.8	<0.53
Be	0.002	0.003		<0.006	<0.004	<0.007
Mo	<0.003	<0.003		<0.01		
V	0.012	0.018		<0.09	<0.3	<0.07
Tl	0.005	0.012		<3.0		
Cr	<0.002	<0.003		<0.14	<0.04	<0.32
Co	<0.005	<0.005		<0.06	<0.03	<0.14
Ni	<0.004	<0.004		<0.14	<0.03	<0.14
Cu	<0.003	<0.003		<0.7	<0.2	<0.49
Cd	<0.001	<0.010		<0.17	<0.02	<0.14
As (total)		<0.36		<3.8	<1.2	<1.2
As(III)	0.030					
As(V)	<0.001					

1 Corrected for difference between source temperature and measurement temperature 2 Na probably too high 3 Alkalinity probably too low and Na too high

Table 2. Site data and water analyses for Drinking Spring drainage way, 1992

Reference	This study	This study	This study	This study
Sample Code No.	92WA107	92WA108	92WA109	92WA110
Date Collected	10/21/92	10/21/92	10/21/92	10/21/92
Flow Distance from Source(m)	0	3.0	5.5	10.1
Temperature (°C)	15.9	16.8	17.0	17.3
Density (g/ml)	1.00110	1.00078	1.00101	1.00125
pH (field/lab)	6.10/--	6.40/--	6.53/--	6.92/--
Spec. Cond. (µS/cm) (field/lab)	4700/--	4920/--	4960/--	4880/--
Dissolved Solids (mg/L)				
Eh (V)				
D.O. (mg/L)	0.5	3.6	3.8	4.1
Alkalinity (mg/L HCO <sub>3</sub> )	1860	1990	2080	2030
CO <sub>2</sub> (mg/L)				
Sum Cations (meq/L)	52.5	55.8	55.5	57.2
Sum Anions (meq/L)	48.3	52.0	54.1	53.5
Charge Balance %	8.3	7.1	2.6	6.9
D.O.C. (mg/L)	2.8	2.3	2.1	3.1
<u>Constituent (mg/L)</u>				
Ca	99	102	103	110
Mg	51	50	51	52
Na	989	1060	1050	1080
K	45	47	49	50
SO <sub>4</sub>	124	95.4	84.7	104
S <sub>2</sub> O <sub>3</sub>	0.0	0.26	0.47	0.89
H <sub>2</sub> S	27	26	20	10
F	2.3	2.7	2.7	2.7
Cl	583	659	690	680
Br	3.3	3.5	3.7	4.2
I				
SiO <sub>2</sub>	25	18	19	21
NO <sub>2</sub>				
NO <sub>3</sub>	0.22	0.95		0.10
NH <sub>4</sub>	0.68	0.98	1.13	1.05
Al	0.1	0.1	0.1	0.11
Fe (total)	0.031	0.029	0.041	0.092
Fe(II)	0.031	0.029	0.041	0.089
B	2.6	3.0	2.9	3.1
PO <sub>4</sub>				
Li	2.8	3.0	3.2	3.2
Sr	2.5	2.7	2.5	2.8
Ba	0.7	2.3	0.79	0.86
Rb				
Mn	0.82	0.89	0.91	0.93
Zn	<0.09	0.08	<0.13	<0.05
Pb	<0.48	<1.6	<0.55	<0.35
Be	<0.006	<0.014	<0.01	<0.012
Mo				
V	<0.09	<0.07	<0.1	<0.054
Tl	<3.0	<1.5	<0.3	<0.6
Cr	<0.14	0.08	<0.5	<0.26
Co	<0.06	<0.08	<0.10	<0.04
Ni	<0.14	<0.12	<0.015	<0.021
Cu	<0.7	<0.04	0.18	<0.35
Cd	<0.17	<0.04	<0.15	<0.03
As (total)	<3.8	1.9	<1.7	<0.84
As(III)				
As(V)				

Table 2. Site data and water analyses for Drinking Spring drainage way, 1992 (cont.)

Reference	This study	This study	This study
Sample Code No.	92WA111	92WA112	92WA113
Date Collected	10/21/92	10/21/92	10/21/92
Flow Distance from Source(m)	14.6	19.2	24.1
Temperature (°C)	16.8	17.0	19.0
Density (g/ml)	1.00123	1.00104	1.00125
pH (field/lab)	7.10/--	7.36/--	7.69/--
Spec. Cond. (µS/cm) (field/lab)	4870/--	4920/--	4820/--
Dissolved Solids (mg/L)			
Eh (V)			
D.O. (mg/L)	3.6	3.4	5.5
Alkalinity (mg/L HCO <sub>3</sub> )	2030	2010	2030
CO <sub>2</sub> (mg/L)			
Sum Cations (meq/L)	58.0	57.6	56.2
Sum Anions (meq/L)	53.4	53.0	53.5
Charge Balance %	8.3	8.4	5.0
D.O.C. (mg/L)	2.1	2.3	2.4
<u>Constituent (mg/L)</u>			
Ca	107	107	106
Mg	55	56	51
Na	1100	1090	1070
K	49	47	50
SO <sub>4</sub>	99.7	98.9	106
S <sub>2</sub> O <sub>3</sub>	1.42	1.84	1.42
H <sub>2</sub> S	4.3	1.8	0.3
F	2.6	2.5	2.4
Cl	686	686	690
Br	3.5	3.5	3.2
I			
SiO <sub>2</sub>	13	20	15
NO <sub>2</sub>			
NO <sub>3</sub>	0.10	0.22	0.71
NH <sub>4</sub>	0.77	0.97	0.85
Al	0.13	0.08	0.09
Fe (total)		0.038	0.041
Fe(II)	0.039	0.038	0.041
B	3.0	2.5	3.2
PO <sub>4</sub>			
Li	3.0	3.0	3.0
Sr	2.7	2.7	2.8
Ba	0.56	0.70	0.85
Rb			
Mn	0.86	1.02	0.87
Zn	<0.03	<0.01	<0.09
Pb	<0.32	<0.43	<0.31
Be	<0.01	<0.01	<0.01
Mo			
V	<0.13	<0.06	<0.075
Tl	<2.8	<0.28	<0.42
Cr	<0.34	<0.35	<0.24
Co	<0.04	<0.013	<0.017
Ni	<0.05	<0.12	<0.003
Cu	<1.3	<0.11	<0.15
Cd	---	<0.005	<0.15
As (total)	<5.0	<0.9	<0.34
As(III)			
As(V)			

Table 3. Site data and water analyses for Drinking Spring drainage way, 1993

Reference	This study	This study	This study	This study
Sample Code No.	93WA107	93WA108	93WA113	93WA112
Date Collected	6/17/93	6/17/93	6/17/93	6/18/93
Flow Distance from Source(m)	0	3.0	5.5	10.1
Temperature (°C)	~14	14.9	16.5	19.6-19.9
Density (g/ml)				
pH (field/lab)	6.31/8.67	6.64/--	6.77/--	6.91/--
Spec. Cond. (µS/cm) (field/lab)	5000/--	4460/--	4570/--	4510/--
Dissolved Solids (mg/L)				
Eh (V)	0.037	0.077	0.008	-0.003
D.O. (mg/L)	1.1	4.0	2.9	3.6
Alkalinity (mg/L HCO <sub>3</sub> )	2250	2260	2290	2310
CO <sub>2</sub> (mg/L)				
Sum Cations (meq/L)	53.1	55.3	55.8	56.0
Sum Anions (meq/L)	56.9	57.1	57.9	58.2
Charge Balance %	-6.9	-3.2	-3.7	-3.9
D.O.C. (mg/L)				
<u>Constituent (mg/L)</u>				
Ca	109	109	110	107
Mg	49	47	46	46
Na	995	1050	1060	1070
K	42	42	43	43
SO <sub>4</sub>	90.5	82.3	62.6	64.7
S <sub>2</sub> O <sub>3</sub>	0	0.3	0	0.47
H <sub>2</sub> S	44	24	20	11
F	1.8	1.9	2.0	2.0
Cl	684	692	720	717
Br	3.4	3.5	3.7	3.6
I				
SiO <sub>2</sub>	24	25	22	22
NO <sub>2</sub>				
NO <sub>3</sub>	1.00	0.42	0.47	0.24
NH <sub>4</sub>	1.5	1.0	1.4	1.3
Al	0.07	0.09	0.10	0.09
Fe (total)	0.025	0.021	0.026	0.025
Fe(II)	0.025	0.021	0.026	0.025
B	3.4	3.3	3.6	3.3
PO <sub>4</sub>				
Li	2.5	2.6	2.7	2.6
Sr	2.9	3.0	3.0	2.8
Ba	4.0	3.5	4.3	4.3
Rb				
Mn	0.95	0.94	1.02	0.95
Zn	<0.04	<0.04	<0.04	<0.04
Pb	<0.8	<0.8	<0.8	<0.8
Be	<0.004	<0.004	<0.004	<0.004
Mo				
V	<0.3	<0.3	<0.3	<0.3
Tl				
Cr	<0.04	<0.04	<0.04	<0.04
Co	<0.03	<0.04	<0.03	<0.04
Ni	<0.03	<0.012	<0.05	<0.012
Cu	<.2	<.2	<.2	<.2
Cd	<0.02	<0.03	<0.02	<0.02
As (total)	<0.12	<0.12	<0.12	<0.12
As(III)				
As(V)				

Table 3. Site data and water analyses for Drinking Spring drainage way, 1993 (cont.)

Reference	This study	This study	This study	This study
Sample Code No.	93WA111	93WA110	93WA109	93WA106
Date Collected	6/18/93	6/18/93	6/18/93	6/17/93
Flow Distance from Source (m)	14.6	19.2	24.1	~27
Temperature (°C)	21.6-22.0	23.1-23.3	23.4-24.9	~17
Density (g/ml)				
pH (field/lab)	7.09/9.15	7.30/8.98	7.70/9.14	7.81/9.20
Spec. Cond. (µS/cm) (field/lab)	4480/--	4520/--	4510/--	5050/--
Dissolved Solids (mg/L)				
Eh (V)	-0.019	-0.019	0.063	.277
D.O. (mg/L)	2.1-2.3	1.9-2.0	4.4	6.6
Alkalinity (mg/L HCO <sub>3</sub> )	2310	2290	2290	2230
CO <sub>2</sub> (mg/L)		169		
Sum Cations (meq/L)	55.9	55.0	54.9	56.0
Sum Anions (meq/L)	58.2	57.8	57.9	54.9
Charge Balance %	-4.0	-5.0	-5.3	2.0
D.O.C. (mg/L)				
<u>Constituent (mg/L)</u>				
Ca	107	107	108	106
Mg	46	46	47	48
Na	1070	1050	1050	1070
K	43	43	43.0	43
SO <sub>4</sub>	68.9	84.4	80.1	80.1
S <sub>2</sub> O <sub>3</sub>	0.63	0.90	0.95	1.60
H <sub>2</sub> S	6.7	1.0	0.5	1.2
F	1.9	1.9	2.0	1.8
Cl	717	705	718	687
Br	3.6	3.6	3.6	3.4
I				
SiO <sub>2</sub>	21	22	21	21
NO <sub>2</sub>				
NO <sub>3</sub>	0.52	0.55	0.42	0.98
NH <sub>4</sub>	1.3	1.3	1.0	1.0
Al	0.078	0.082	0.078	0.072
Fe (total)	0.025	0.034	0.029	0.035
Fe(II)	0.025	0.034	0.029	0.035
B	3.4	3.3	3.1	3.5
PO <sub>4</sub>				
Li	2.6	2.6	2.7	2.7
Sr	2.8	2.8	2.9	3.0
Ba	4.0	3.2	5.6	4.0
Rb				
Mn	0.93	0.93	0.86	0.98
Zn	<0.04	<0.04	<0.04	<0.04
Pb	<0.8	<0.8	<0.8	<0.8
Be	<0.004	<0.004	<0.004	<0.004
Mo				
V	<0.3	<0.3	<0.3	<0.3
Tl				
Cr	<0.04	<0.05	<0.08	<0.04
Co	<0.04	0.03	<0.008	0.03
Ni	<0.04	<0.012	<0.012	<0.012
Cu	<.2	<.2	<.2	<.2
Cd	<0.02			
As (total)	<0.12	<0.12	<0.12	<0.12
As(III)				
As(V)				

Table 4. Site data and water analyses for Drinking Spring drainage way, 1994

Reference	This study	This study	This study	This study
Sample Code No.	94WA124	Site 2	Site 3	Site 4
Date Collected	6/17/94	6/17/94	6/17/94	6/17/94
Flow Distance(m)/Travel Time(sec)	0	0.36/1	0.76/3	1.17/5
Temperature (°C)	14.4	14.5	14.7	14.9
Density (g/ml)	1.00127			
pH (field/lab)	6.28/8.53	6.31/--	6.37/--	6.42/--
Spec. Cond. (µS/cm) (field/lab)	--/4500			
Dissolved Solids (mg/L)				
Eh (V)				
D.O. (mg/L)	0.25	0.8	1.4	1.6
Alkalinity (mg/L HCO <sub>3</sub> )	2040	2100	2110	2150
CO <sub>2</sub> (mg/L)				
Sum Cations (meq/L)	52.6			
Sum Anions (meq/L)	53.4			
Charge Balance %	-1.5			
D.O.C. (mg/L)				
<u>Constituent (mg/L)</u>				
Ca	110			
Mg	51.1			
Na	985			
K	45			
SO <sub>4</sub>	71.6	55.5	41.7	37.1
S <sub>2</sub> O <sub>3</sub>	0	0	0	0
H <sub>2</sub> S	45	43	38	34
F	1.8			
Cl	636			
Br	2.7			
I				
SiO <sub>2</sub>	28			
NO <sub>2</sub>				
NO <sub>3</sub>				
NH <sub>4</sub>				
Al	0.064			
Fe (total)	<0.11			
Fe(II)				
B	3.3			
PO <sub>4</sub>				
Li	2.3			
Sr	3.0			
Ba	3.2			
Rb				
Mn	0.91			
Zn	<0.035			
Pb	<0.53			
Be	<0.007			
Mo				
V	<0.07			
Tl				
Cr	<0.32			
Co	<0.14			
Ni	<0.14			
Cu	<0.49			
Cd	<0.14			
As (total)	<1.19			
As(III)				
As(V)				

Table 4. Site data and water analyses for Drinking Spring drainage way, 1994 (cont.)

Reference	This study					
Sample Code No.	94WA125	Site 6	Site 7	94WA126	Site 9	Site 10
Date Collected	6/17/94	6/17/94	6/17/94	6/17/94	6/17/94	6/17/94
Flow Distance(m)/Travel Time (sec)	1.59/6	2.13/9	2.74/13	3.20/18	3.73/23	4.22/28
Temperature (°C)	15.3	15.5	16.1	16.3	17.2	17.3
Density (g/ml)	1.00123					
pH (field/lab)	6.47/8.46	6.56/---	6.67/---	6.71/--	6.79/--	6.87/--
Spec. Cond. (µS/cm) (field/lab)	--/4870					
Dissolved Solids (mg/L)						
Eh (V)						
D.O. (mg/L)	2.7	3.2	3.5	4.1	3.9	4.0
Alkalinity (mg/L HCO <sub>3</sub> )	2160	2130	2160	2160	2160	2170
CO <sub>2</sub> (mg/L)						
Sum Cations (meq/L)	55.6					
Sum Anions (meq/L)	55.2					
Charge Balance %	0.7					
D.O.C. (mg/L)						
<u>Constituent (mg/L)</u>						
Ca	107			108		
Mg	43.3			44.7		
Na	1060			1060		
K	45.9			48.5		
SO <sub>4</sub>	28.7	37.1	31.9	40.6	43.1	42.7
S <sub>2</sub> O <sub>3</sub>	0	0.12	0.12	0.12	0.12	0.26
H <sub>2</sub> S	30	26	20	17	17	13
F	2.1					
Cl	717					
Br	2.6					
I						
SiO <sub>2</sub>	21			19		
NO <sub>2</sub>						
NO <sub>3</sub>						
NH <sub>4</sub>						
Al	0.08			0.08		
Fe (total)	<0.11			<0.11		
Fe(II)						
B	2.9			3.3		
PO <sub>4</sub>						
Li	2.7			2.6		
Sr	2.9			3.0		
Ba	6.1			5.2		
Rb						
Mn	0.92			0.92		
Zn	<0.035			<0.035		
Pb	<0.53			<0.53		
Be	<0.007			<0.007		
Mo						
V	<0.07			<0.07		
Tl						
Cr	<0.32			<0.32		
Co	<0.14			<0.14		
Ni	<0.14			<0.14		
Cu	<0.49			<0.49		
Cd	<0.14			<0.14		
As (total)	<1.19			<1.19		
As(III)						
As(V)						

Table 4. Site data and water analyses for Drinking Spring drainage way, 1994 (cont.)

Reference	This study				
Sample Code No.	94WA130	Site 12	Site 13	94WA127	Site 15
Date Collected	6/17/94	6/17/94	6/17/94	6/17/94	6/17/94
Flow Distance(m)/Travel Time (sec)	4.88/32	5.61/44	6.15/51	6.65/56	7.39/64
Temperature (°C)	17.1	17.5	17.7	17.8	18.1
Density (g/ml)	1.00137	1.00148	1.00135	1.00144	1.00139
pH (field/lab)	6.95/8.61	6.92/8.40	7.00/8.68	6.99/8.76	7.01/8.71
Spec. Cond. (µS/cm) (field/lab)	--/4780	--/4820	--/4820	--/4810	--/4800
Dissolved Solids (mg/L)					
Eh (V)					
D.O. (mg/L)	4.1	3.1	3.1	2.5	2.6
Alkalinity (mg/L HCO <sub>3</sub> )	2180	2180	2190	2180	2200
CO <sub>2</sub> (mg/L)					
Sum Cations (meq/L)	55.3			56.6	
Sum Anions (meq/L)	54.8			55.6	
Charge Balance %	0.8			1.8	
D.O.C. (mg/L)					
<u>Constituent (mg/L)</u>					
Ca	109			110	
Mg	45.1			44.7	
Na	1060			1080	
K	45.3			47.6	
SO <sub>4</sub>	44.1	41.7	41.3	45.0	43.6
S <sub>2</sub> O <sub>3</sub>	0.92	0.49	0.54	1.45	0.64
H <sub>2</sub> S	10	11	10	7.5	7.6
F	2.7	1.9	1.9	1.9	2.0
Cl	684	711	703	717	719
Br	2.6	2.6	2.7	3.0	3.0
I					
SiO <sub>2</sub>	20			20	
NO <sub>2</sub>					
NO <sub>3</sub>					
NH <sub>4</sub>					
Al	0.08			0.09	
Fe (total)	<0.15			<0.11	
Fe(II)					
B	3.3			3.3	
PO <sub>4</sub>					
Li				2.6	
Sr	3.0			3.0	
Ba	5.1			5.3	
Rb					
Mn	0.91			1.1	
Zn	<0.05			<0.035	
Pb	<0.75			<0.53	
Be	<0.01			<0.008	
Mo					
V	<0.1			<0.07	
Tl					
Cr	<0.45			<0.32	
Co	<0.2			<0.14	
Ni	<0.2			<0.14	
Cu	<0.7			<0.49	
Cd	<0.2			<0.14	
As (total)	<1.7			<1.2	
As(III)					
As(V)					

Table 4. Site data and water analyses for Drinking Spring drainage way, 1994 (cont.)

Reference	This study				
Sample Code No.	Site 16	94WA128	94WA129	Site 19	Site 20
Date Collected	6/17/94	6/17/94	6/17/94	6/17/94	6/17/94
Flow Distance(m)/Travel Time (sec)	8.05/68	8.61/73	---/---	---/---	---/---
Temperature (°C)	18.7	18.8	19.9		
Density (g/ml)	1.00139				
pH (field/lab)	7.05/8.73	7.05/--	7.80/--	7.61/--	7.75/--
Spec. Cond. (µS/cm) (field/lab)	--/4780				
Dissolved Solids (mg/L)					
Eh (V)					
D.O. (mg/L)	2.0	1.4			
Alkalinity (mg/L HCO <sub>3</sub> )	2170	2160			
CO <sub>2</sub> (mg/L)					
Sum Cations (meq/L)		66.6			
Sum Anions (meq/L)		63.5			
Charge Balance %		4.7			
D.O.C. (mg/L)					
<u>Constituent (mg/L)</u>					
Ca		108	47.9		
Mg		44.6	39.9		
Na		1080	140		
K		48.2	14.2		
SO <sub>4</sub>	46.9	60.4			
S <sub>2</sub> O <sub>3</sub>	0.60	3.1			
H <sub>2</sub> S	5.7	0.7			
F	1.5				
Cl	722				
Br	2.4				
I					
SiO <sub>2</sub>		23	61		
NO <sub>2</sub>					
NO <sub>3</sub>					
NH <sub>4</sub>					
Al		0.09	0.004		
Fe (total)		<0.11	<0.11		
Fe(II)					
B		3.1	<0.63		
PO <sub>4</sub>					
Li		2.7	0.03		
Sr		2.9	0.5		
Ba		5.5	<0.14		
Rb					
Mn		0.8	<0.42		
Zn		<0.035	<0.035		
Pb		<0.53	<0.53		
Be		<0.007	<0.007		
Mo					
V		<0.07	<0.07		
Tl					
Cr		<0.32	<0.32		
Co		<0.14	<0.14		
Ni		<0.14	<0.14		
Cu		<0.49	<0.49		
Cd		<0.14	<0.14		
As (total)		<1.2	<1.2		
As(III)					
As(V)					

Table 5. Site data and water analyses for Bathtub Spring

Reference	Headden(1905a) <sup>1</sup>	This study	This study	This study	This study
Sample Code No.	No. V	80WA128	81WA109	87WA107	87WA108
Date Collected	1903-1905	5/8/80	4/8/81	7/28/87	7/28/87
Temperature (°C)		~23.0	~24.5	22.0	22.8
Density (g/ml)	1.00378				
pH (field/lab)		7.15/--	7.20/--	5.65/8.62	6.25/8.65
Spec. Cond. (µS/cm) (field/lab)		5200/--	5150/--	5200/--	5050/--
Dissolved Solids (mg/L)	3446				
Eh (V)		0.056	0.0145	0.0377	
Alkalinity (mg/L HCO <sub>3</sub> )	1913	2120	2150	1850	1870
CO <sub>2</sub> (mg/L)		148 <sup>2</sup>			
Sum Cations (meq/L)		58.5	61.3	55.9	56.9
Sum Anions (meq/L)		54.7	55.7	54.1	53.3
Charge Balance %		6.8	9.5	3.2	6.5
D.O.C. (mg/L)					
<u>Constituent (mg/L)</u>					
Ca	118.2	119	119	76.3	66.1
Mg	64.8	47.7	48	52.6	52.6
Na	1163.9	1110	1170	1080	1120
K	59.4	46.5	49.6	50.3	51.9
SO <sub>4</sub>	478.6	57	91	75	84
H <sub>2</sub> S		0.17	0.02		
F		2.0	2.3	1.6	1.9
Cl	774.9	710	710	825	777
Br		2.8	3.3		
I		0.18			
SiO <sub>2</sub>	21	18	18	12	10
NO <sub>2</sub>		0.02			
NO <sub>3</sub>		1.0	0.4		
NH <sub>4</sub>	0.5	1.2			
Al	0.7	0.07	0.04		
Fe (total)	0.5	0.044	<0.02	0.008	0.008
Fe(II)		0.043		0.008	0.008
B		3.4	3.1	4.0	4.2
PO <sub>4</sub>		<0.0002			
Li	3.4	2.8	4.7	2.3	2.4
Sr	2.9	3.1	3.7	2.6	2.5
Ba	"Trace"	2.8	3.6	0.17	0.18
Rb		0.127	0.16	0.23	0.23
Mn	1.3	0.91	0.88	0.53	0.29
Zn	"Trace"	<0.005	<0.006	0.10	0.11
Pb		0.029	0.048		
Be		<0.002	0.002		
Mo		<0.003	<0.003		
V		0.013	0.016		
Tl		0.006	0.012		
Cr		<0.002	<0.003		
Co		<0.005	<0.005		
Ni		<0.004	<0.004	0.08	0.11
Cu		<0.003	<0.003		
Cd		<0.001	<0.01		
As (total)			<0.36		
As(III)		0.030			
As(V)		<0.001			

<sup>1</sup> Significant figures as they appear in the original <sup>2</sup> Corrected for difference between source and measurement temperature

Table 6. Site data and water analyses for Boiling Spring at source

Reference	Headden(1905a)	George and others(1920)	George and others(1920)	Cadigan and others(1976)
Sample Code No.	No. III <sup>1</sup>	74 <sup>2</sup>	75 <sup>3</sup>	DEL7(1)
Date Collected	1903-1905	1911	1911	9/12/73
Temperature (°C)		17.8	18.0	
Density (g/ml)	1.00393			
pH (field/lab)				
Spec. Cond. (µS/cm) (field/lab)				
Dissolved Solids (mg/L)	3632	3712	3936	
Eh (V)				
D.O. (mg/L)				
Alkalinity (mg/L HCO <sub>3</sub> )	2279	1251	1761	
CO <sub>2</sub> (mg/L)				
Sum Cations (meq/L)				
Sum Anions (meq/L)				
Charge Balance %				
D.O.C. (mg/L)				
<u>Constituent (mg/L)<sup>4</sup></u>				
Ca	120.4	161	183	
Mg	55.2	100.2	91.8	
Na	1200.2	917	997.5	
K	63.2	210	210	
SO <sub>4</sub>	200.4	1053	791	
S <sub>2</sub> O <sub>3</sub>				
H <sub>2</sub> S	38.5	51	59	
F				
Cl	820	684	738.7	
Br	4.2			
SiO <sub>2</sub>	15.6	24.5	58.7	
NO <sub>3</sub>				
NH <sub>4</sub>	1.1			
Al	0.4			0.1
Fe (total)	3.5			<0.01
Fe(II)				
B	2.53			5.1
PO <sub>4</sub>		"none"	"Trace"	
Li	6.8	"Trace"	"Trace"	3.1
Sr	3.3			3.0
Ba	"Trace"			0.34
Rb				
Mn	2.3	"none"	"Trace"	0.85
Zn	"Trace"			<0.022
Pb				<0.003
Be				0.003
Mo				<0.0005
V				<0.022
Tl				
Cr				0.002
Co				<0.003
Ni				<0.005
Cu				<0.011
Cd				<0.010

<sup>1</sup> The site designations are somewhat uncertain

<sup>2</sup> Identified as "...between Bird's Nest and Bath Tub Spring.." -- probably part of the Boiling Spring complex

<sup>3</sup> Identified as "...between Bird's Nest Spring and No. 74.." -- probably part of the Boiling Spring complex

<sup>4</sup> Significant figures as they appear in the original

Table 6. Site data and water analyses for Boiling Spring at source (cont.)

Reference	This study	This study	This study
Sample Code No.	81WA108	87WA101	93WA101
Date Collected	4/8/81	7/28/87	6/15/93
Temperature (°C)	17.0	16.8	15.3
Density (g/ml)			
pH (field/lab)	6.30/--	4.8/8.74	6.28/8.72
Spec. Cond. (µS/cm) (field/lab)	6100/--	6300/--	5590/--
Dissolved Solids (mg/L)			
Eh (V)	-0.0765	-0.111	-.038
D.O. (mg/L)			0.3
Alkalinity (mg/L HCO <sub>3</sub> )	2330	1810	2350
CO <sub>2</sub> (mg/L)			1180
Sum Cations (meq/L)	59.8	61.6	61.1
Sum Anions (meq/L)	62.0	53.3	62.1
Charge Balance %	-3.6	14.5 <sup>1</sup>	-1.7
D.O.C. (mg/L)			
<u>Constituent (mg/L)</u>			
Ca	132	112	116
Mg	51	54.4	49.6
Na	1130	1150	1170
K	51	49.7	45
SO <sub>4</sub>	100	95.0	93.5
S <sub>2</sub> O <sub>3</sub>			1.7
H <sub>2</sub> S	54	34	44
F	2.4	1.8	1.8
Cl	820	808	813
Br	4.9		4.2
I			
SiO <sub>2</sub>	15	14	17
NO <sub>2</sub>			
NO <sub>3</sub>	<0.05		0.99
NH <sub>4</sub>			1.4
Al	0.03		0.12
Fe (total)	<0.02	0.019	0.038
Fe(II)		0.019	0.038
B	3.6	4.7	3.6
PO <sub>4</sub>			
Li		2.5	3.1
Sr	3.7	3.0	2.9
Ba	0.65	0.25	0.46
Rb	0.16	0.22	
Mn	1.0	1.03	0.97
Zn	<0.006	1.1	<0.04
Pb	0.053		<0.8
Be	0.004		<0.004
Mo	<0.003		
V	0.017		<0.3
Tl	0.018		
Cr	<0.003		<0.04
Co	<0.005		<0.008
Ni	<0.004	0.063	<0.012
Cu	<0.003		<0.2
Cd	<0.01		<0.02
As (total)	<0.36		<1.5
As(III)			
As(V)			

<sup>1</sup> Alkalinity probably too low

Table 7. Site data and water analyses for Boiling Spring drainage way, 1987

Reference	This study	This study	This study	This study	This study
Sample Code No.	87WA101	87WA102	87WA103	87WA104	87WA105 <sup>1</sup>
Date Collected	7/28/87	7/28/87	7/28/87	7/28/87	7/28/87
Flow Distance from Source (m)	0	5	7	14	14
Temperature (°C)	16.8	22.0	22.5	24.5	24.5
Density (g/ml)					
pH (field/lab)	4.8/8.74	4.75/8.64	5.27-5.35	5.4/8.41	5.4/8.55
Spec. Cond. (µS/cm) (field/lab)	6300/--	5280/--	5400/--	6560/--	
Dissolved Solids (mg/L)					
Eh (V)	-0.111	-0.067	-0.073	-0.030	
D.O. (mg/L)					
Alkalinity (mg/L HCO <sub>3</sub> )	1810	1870		1907	1900
CO <sub>2</sub> (mg/L)					
Sum Cations (meq/L)	60.6	60.5		61.0	61.2
Sum Anions (meq/L)	53.2	52.9		54.0	53.7
Charge Balance %	12.9 <sup>2</sup>	13.4 <sup>2</sup>		12.3 <sup>2</sup>	13.0 <sup>2</sup>
D.O.C. (mg/L)					
<u>Constituent (mg/L)</u>					
Ca	112	110		111	116
Mg	54.4	53.5		59.9	54.8
Na	1150	1150		1150	1160
K	49.7	48.2		48.1	47.8
SO <sub>4</sub>	95	47		79	69
S <sub>2</sub> O <sub>3</sub>					
H <sub>2</sub> S	34	7.9			
F	1.8	1.8		1.8	2.0
Cl	808	793		793	793
Br					
I					
SiO <sub>2</sub>	14	13		14	14
NO <sub>2</sub>					
NO <sub>3</sub>					
NH <sub>4</sub>					
Al					
Fe (total)	0.019	0.013		0.005	0.003
Fe(II)	0.019	0.013		0.005	0.003
B	4.7	4.5		4.6	4.1
PO <sub>4</sub>					
Li	2.5	2.5		2.5	2.5
Sr	3.0	3.0		4.0	3.0
Ba	0.25	0.22		0.17	0.17
Rb	0.22	0.22		0.23	0.23
Mn	1.0	0.99		0.96	0.96
Zn	1.1	1.2		0.68	0.70
Pb					
Be					
Mo					
V					
Tl					
Cr					
Co					
Ni	0.063	0.070		0.150	0.023
Cu					
Cd					
As (total)					
As(III)					
As(V)					

<sup>1</sup> Unfiltered sample    <sup>2</sup> Alkalinity probably too low

Table 8. Site data and water analyses for Boiling Spring drainage way, 1992

Reference	This study					
Sample Code No.	92WA101	92WA102	92WA103	92WA104	92WA105	92WA106
Date Collected	10/21/92	10/21/92	10/21/92	10/21/92	10/21/92	10/21/92
Flow Distance from Source (m)	0	0	1.5	3.4	5.3	8.3
Temperature (°C)	16.6	16.9	17.0	17.3	17.5	17.8
Density (g/ml)	1.00166	1.00150	1.00190	1.00167	1.00176	1.00139
pH (field/lab)	6.48/--	6.48/--	6.57/--	6.59/--	6.64/--	6.72/--
Spec. Cond. (µS/cm) (field/lab)	5650/--	5560/--	5560/--	5420/--	5530/--	5530/--
Dissolved Solids (mg/L)						
Eh (V)	-0.050	-0.050	-0.045	-0.035	-0.035	-0.018
D.O. (mg/L)	1.4	2.1	2.4	2.8	3.4	3.9
Alkalinity (mg/L HCO <sub>3</sub> )	2340	2310	2300	2300	2310	2300
CO <sub>2</sub> (mg/L)						
Sum Cations (meq/L)	66.6	65.7	65.0	63.2	60.1	61.3
Sum Anions (meq/L)	63.5	61.9	61.4	61.5	61.5	61.9
Charge Balance %	4.7	5.9	5.7	2.9	-2.3	-1.0
D.O.C. (mg/L)	2.1	2.4	2.3	1.4	1.6	1.8
<u>Constituent (mg/L)</u>						
Ca	111	110	108	107	96	98
Mg	57	55	52	54	47	46
Na	1290	1270	1260	1220	1170	1200
K	51	50	50	48	50	47
SO <sub>4</sub>	140	96.3	77.1	80.5	82.6	86.8
S <sub>2</sub> O <sub>3</sub>	*****	*****	*****	*****	*****	*****
H <sub>2</sub> S	33	29	35	23	23	
F	2.7	2.7	3.5	2.7	2.7	3.1
Cl	849	835	834	834	822	841
Br	3.9	3.7	4.0	4.4	4.8	4.6
I						
SiO <sub>2</sub>	16	16	14	15	14	15
NO <sub>2</sub>						
NO <sub>3</sub>	0.59	0.46	0.89	<0.09	0.34	0.71
NH <sub>4</sub>	1.1	1.0	1.1	1.0	1.1	0.73
Al	0.64	0.37	2.0	0.09	0.11	0.10
Fe (total)			0.73			0.016
Fe(II)	0.212	0.117	0.73	0.186	0.015	0.016
B	3.4	3.3	3.5	3.3	3.1	3.2
PO <sub>4</sub>						
Li	3.9	3.7	3.8	3.8	3.8	3.7
Sr	2.7	2.8	2.7	2.7	2.4	2.6
Ba	1.1	2.2	1.0	0.74	0.51	0.53
Rb						
Mn	1.1	1.0	1.1	1.1	1.0	0.95
Zn	<0.01	<0.02	0.08	<0.38	<0.01	<0.01
Pb	<0.4	<0.32	<0.2	<0.2	<0.07	<0.2
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mo						
V	<0.09	<0.09	<0.10	<0.06	<0.16	<0.09
Tl	<2.0	<1.3	<1.3		<1.4	<0.5
Cr	<0.21	<0.18	<0.16	<0.21	<0.16	<0.36
Co	<0.06	<0.07	<0.11	<0.009	<0.04	<0.08
Ni	<0.1	<0.14	<0.09	<0.11	<0.003	<0.014
Cu	<0.11	<0.11	<0.6	<0.18	<0.9	<0.13
Cd	<0.04	<0.005	<0.005	<0.005	<0.013	<0.10
As (total)	<0.6	0.4	<1.0	<0.38	<0.8	<1.5
As(III)						
As(V)						

\*\*\*\*\* Detectable, but not reliable due to measurement difficulties in the field

Table 9. Site data and water analyses for Bird's Nest Spring

Reference	Headden(1905) <sup>1</sup>	This study	This study
Sample Code No.	No. II	80WA127	81WA107
Date Collected	1903-1905	5/8/80	4/8/81
Temperature (°C)		17.6	17.5
Density (g/ml)	1.00393		
pH (field/lab)		6.38/--	6.35/--
Spec. Cond. (µS/cm) (field/lab)		6000/--	6400/--
Dissolved Solids (mg/L)	3744		
Eh (V)		-0.082	-0.077
D.O. (mg/L)		0.02	
Alkalinity (mg/L HCO <sub>3</sub> )	2433	2450	2400
CO <sub>2</sub> (mg/L)		1300 <sup>2</sup>	
Sum Cations (meq/L)		71.2	67.0
Sum Anions (meq/L)		66.4	66.1
Charge Balance %		7.0	1.3
D.O.C. (mg/L)			
<u>Constituent (mg/L)</u>			
Ca	118.6	131	131
Mg	54.3	60.7	58
Na	1273.6	1320	1270
K	66.1	50.1	53.5
SO <sub>4</sub>	141.7	87	160
S <sub>2</sub> O <sub>3</sub>			
H <sub>2</sub> S	39	50	42
F		2.2	2.4
Cl	861.5	850	890
Br	9.5	4.3	4.8
I		0.20	
SiO <sub>2</sub>	17	15	14
NO <sub>2</sub>		0.081	
NO <sub>3</sub>		0.44	<0.05
NH <sub>4</sub>	1.7	1.2	
Al	0.5	0.08	0.05
Fe (total)	0.3	0.081	0.12
Fe(II)		0.076	
B	2.0	4.2	3.8
PO <sub>4</sub>		<0.0002	
Li	4.9	3.4	5.9
Sr	3.5	3.0	3.5
Ba	"Trace"	0.17	0.16
Rb		0.16	0.16
Mn	2.2	1.1	1.0
Zn	"Trace"	<0.005	<0.006
Pb		<0.02	0.053
Be		0.005	0.005
Mo		<0.003	<0.003
V		0.015	0.016
Tl		0.004	0.014
Cr		<0.002	<0.003
Co		<0.005	<0.005
Ni		<0.004	<0.004
Cu		<0.003	<0.003
Cd		<0.001	<0.01
As (total)			<0.36
As(III)		<0.009	
As(V)		0.001	

<sup>1</sup> Significant figures as they appear in the original

<sup>2</sup> Corrected for difference between source and measurement temperature

Table 10. Site data and water analyses for Alum and Black Springs

Site Reference	Alum Spring Cadigan and others(1976)	Alum Spring This study	Alum+Black This study	Black Spring <sup>1</sup> Headden(1905)	Black Spring This study
Sample Code No.	DEL9	80WA130	81WA106	No. I	80WA126
Date Collected	9/12/73	5/8/80	4/8/81	1903-1905	5/8/80
Temperature (°C)	14	20.65	21.0	17.5	18.75
Density (g/ml)		1.0028		1.00400	1.00054
pH (field/lab)	2.9/--	2.75/--	5.70/--		6.20/--
Spec. Cond. (µS/cm) (field/lab)	2600	2900/--	2670/--		6300/--
Dissolved Solids (mg/L)	2120			3683	
Eh (V)		0.236	0.031		-0.09
D.O. (mg/L)		0.02			0.02
Alkalinity (mg/L HCO <sub>3</sub> )	0	0	121	2160	1980
CO <sub>2</sub> (mg/L)		860 <sup>2</sup>			1500 <sup>2</sup>
Sum Cations (meq/L)	21.1	25.0	25.8	63.0	66.7
Sum Anions (meq/L)	24.8	27.9	24.8	61.9	63
Charge Balance %	-16.1 <sup>3</sup>	-10.9 <sup>3</sup>	4.1	1.9	5.8
D.O.C. (mg/L)					
<u>Constituent (mg/L)</u>					
Ca	170	167	156	126.1	131
Mg	98	102	105	60.9	69.3
Na	180	218	308	1197.8	1200
K	22	19.4	24	58.9	50.6
SO <sub>4</sub>	1500	1670	1200	273.1	500
S <sub>2</sub> O <sub>3</sub>				11	
H <sub>2</sub> S		4.8	7.2	49	50
F	0.7	0.66	0.7		
Cl	25	92	130	815.7	700
Br		0.4	0.9	15	3
I		0.09			0.19
SiO <sub>2</sub>	60	70	57	19	19
NO <sub>2</sub>		0.21			0.055
NO <sub>3</sub>	0.48	0.17	0.44		0.81
NH <sub>4</sub>		0.5		1.3	1.4
Al	10	25	2.3	4.6	0.65
Fe (total)	47	48.3		1.2	0.88
Fe(II)		48	29.3		0.88
B	0.33	0.38	0.68	0.03	3.8
PO <sub>4</sub>	0.18	0.0092			0.0009
Li	0.19	0.26	<0.1	1.6	3.1
Sr	0.90	1.3	1.4	3.5	2.8
Ba	0.037	0.14	0.033		0.13
Rb		<0.03	<0.03		0.136
Mn	1.2	1.1	0.87	4.0	1.0
Zn	0.51	0.013	0.006	"Trace"	0.009
Pb	0.01	<0.02	<0.015		<0.02
Be	0.012	0.006	0.002		0.002
Mo	0.0007	<0.003	<0.003		<0.003
V	<0.013	0.023	0.007		0.013
Tl		<0.004	0.012		0.006
Cr	0.026	<0.002	<0.003		<0.002
Co	<0.022	<0.005	<0.005		<0.005
Ni	0.015	<0.004	<0.004		<0.004
Cu	0.04	<0.003	<0.003		<0.003
Cd	<.01	<0.001	<0.01		<0.001
As (total)	<0.046		<0.36		
As(III)		0.006			<0.009
As(V)		<0.001			<0.001

<sup>1</sup> Significant figures as they appear in the original <sup>2</sup> Corrected for difference between source and measurement temperature

<sup>3</sup> Anion concentrations (probably sulfate) are too high

Table 11. Site data and water analyses for Carl James' well and Carl James' field

Site	C.J. well	C.J. well	C.J. field #1	C.J. field #2
Reference	This study	This study	This study	This study
Sample Code No.	92WA114	93WA102	92WA115	93WA103
Date Collected	10/23/92	6/16/93	10/23/92	6/16/93
Temperature (°C)	15.2	14.6,14.2	9.0-9.2	19.1
Density (g/ml)	0.99914		0.99903	
pH (field/lab)	7.40/--	7.67/8.56	7.38/--	8.05/8.62
Spec. Cond. (µS/cm) (field/lab)	1350/--	1110/--	1110/--	1470/--
Dissolved Solids (mg/L)				
Eh (V)				
D.O. (mg/L)		1.3		6.0
Alkalinity (mg/L HCO <sub>3</sub> )	560	520	610	810
CO <sub>2</sub> (mg/L)				
Sum Cations (meq/L)	14.6	11.6	12.2	17.4
Sum Anions (meq/L)	13.6	13.6	10.8	19.8
Charge Balance %	6.4	-17.4 <sup>1</sup>	12.3	-12.6 <sup>1</sup>
D.O.C. (mg/L)	4.2			
<u>Constituents (mg/L)</u>				
Ca	57	51	86	98
Mg	56	40	71	92
Na	179	144	54	160
K	17	13.5	11	16
SO <sub>4</sub>	259	278	61.5	344
S <sub>2</sub> O <sub>3</sub>		<0.09		<0.09
H <sub>2</sub> S				
F	0.86	0.60	0.68	0.75
Cl	6.7	8.2	2.7	33.9
Br	<0.11	0.12	<0.11	0.35
I				
SiO <sub>2</sub>	56	62	40	55
NO <sub>2</sub>				
NO <sub>3</sub>	1.7	0.85	<0.09	46
NH <sub>4</sub>				
Al	0.004	0.007	0.08	0.005
Fe (total)	0.105	0.007	0.184	0.034
Fe(II)	0.004	0.007	0.150	0.033
B	0.3	<0.04	<0.9	<0.04
PO <sub>4</sub>				
Li	0.05	0.023	0.06	0.045
Sr	0.62	0.57	0.98	1.3
Ba	0.04	0.037	0.10	0.089
Rb				
Mn	<0.11	<0.04	0.29	<0.04
Zn	0.04	<0.02	<0.053	<0.02
Pb	<0.33	<0.4	<1.0	<0.4
Be	<0.01	<0.002	<0.01	<0.011
Mo				
V	<0.12	<0.15	<0.10	<0.15
Tl	<0.36			
Cr	<0.10	<0.02	<0.27	<0.02
Co	<0.03	<0.02	<0.26	0.008
Ni	<0.08	<0.006	<0.092	<0.006
Cu	<0.17	<0.1	<0.05	<0.1
Cd	<0.05	<0.01	<0.032	<0.01
As (total)	<1.5	<0.6	<2.9	<0.6
As(III)				
As(V)				

<sup>1</sup> Anion concentrations (probably sulfate) are too high.

Table 12. Gas and isotope analysis: various spring waters

Reference Sample No.	Drinking Spring at source	Drinking Spring at source	Drinking Spring on drainage way	Drinking Spring on drainage way	Drinking Spring, on drainage way			
	This study	This study	This study	This study	This study	This study	This study	This study
80WA129	92WA107	92WA108	92WA109	92WA110	92WA111	92WA112		
<u>Gas</u>								
N <sub>2</sub> (mg/L)	0.73							
Ar (mg/L)	0.04							
CH <sub>4</sub> (mg/L)	<0.02							
He (mg/L)	<0.002							
CO (mg/L)								
CS <sub>2</sub> (mg/L)								
<u>Isotope</u>								
$\delta^2\text{H}^*$	-119.4	-115.7	-119.9	-119.8	-119.5	-119.5	-118.5	
$\delta^{18}\text{O}^*$	-15.65	-15.02	-15.64	-15.82	-15.74	-15.67		
$\delta^{13}\text{C}^{***}$								
Tritium (T.U.)***								
Reference Sample No.	92WA113	93WA107	93WA106	93WA108	93WA109	93WA110	93WA111	93WA111
<u>Gas</u>								
N <sub>2</sub>								
Ar		0.01847						
CH <sub>4</sub>								
He		0.00292						
CO		0.01847						
CS <sub>2</sub>								
<u>Isotope</u>								
$\delta^2\text{H}^*$	-119.1	-120	-119	-120.2	-119.6	-119.8	-119.9	-119.9
$\delta^{18}\text{O}^*$	-15.59	-15.83	-15.48	-15.79	-15.56	-15.81	-15.8	-15.8
$\delta^{13}\text{C}^{***}$								
Tritium (T.U.)***		4.33						

\* Per mil relative to Vienna Standard Mean Ocean Water \*\* Per mil relative to Pee Dee Belemnite \*\*\* Corrected to collection date



Table 12. Gas and isotope analysis: various spring waters (cont.)

	Carl James' well	Carl James' field #2
Reference	This study	This study
Sample Code No.	93WA102	93WA103
<u>Gas</u>		
N <sub>2</sub>		
Ar		
CH <sub>4</sub>		
He		
CO		
CS <sub>2</sub>		
δ <sup>3</sup> H*	-113.9	-110
δ <sup>18</sup> O*	-15.63	-15.16
δ <sup>13</sup> C**		
Tritium (T.U.)***	3.62	30

\*Per mil relative to Vienna Standard Mean Ocean Water

\*\*Per mil relative to PeeDee Belemnite

\*\*\*Corrected to collection date

Table 13. Gas and sulfur isotope analysis on precipitates and sinters.

Sample No.	δ <sup>34</sup> S(per mil)*
92WA129-BaSO <sub>4</sub>	-6.8
93WA107-S	+20.8
93WA107-BaSO <sub>4</sub>	+21.4
93WA124-AgS	+21.2
93WA107-sint.	+12.7

\*Relative to Vienna Canyon Diablo Troilite Reference Standard

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## APPENDIX

Analytical methods reported or otherwise known for all the Doughty Springs investigations are summarized in tables 14-15, wherein the analytical method is indicated by a descriptor, for example ICP1 represents inductively-coupled plasma spectroscopic method #1. Tables 16 and 17 contain explanations of descriptors used in tables 14-15 corresponding to the analytical methods referred to in Headden (1905a,b), George and others (1920), and Cadigan and others (1976), and the methods used in this study. The majority of the analyses before 1980 were done by undescribed methods, or by methods for which details are not available. An example of the analytical methods used on spring water samples at the time of publication of Headden's paper may be found in Haywood and Smith (1905).

Table 18 contains the results of post-1980 analyses of USGS Standard Reference Waters performed concurrently with samples and the comparison of these results with the known concentration of the species in the reference water.

Table 14. Methods of analysis for samples collected during 1905-76

Investigator	Headden	George	Cadigan
Sample collection date	1903-1905	1911	1973
Parameter or constituent	Method of analysis		
Specific conductance	nd	nd	na
Dissolved solids	na	GR1	nd
Alkalinity	na	TITR1	na
CO <sub>2</sub>	na	nd	nd
D.O.C.	nd	TITR2	nd
Ca	na	GR6	CHEM1
Mg	na	GR7	CHEM1
Na	na	GR10	CHEM1
K	na	GR8	CHEM1
SO <sub>4</sub>	na	GR4	COLOR1
H <sub>2</sub> S	na	TITR3	nd
F	nd	nd	CHEM1
Cl	na	TITR4	COLOR1
Br	na	nd	nd
I	na	nd	nd
SiO <sub>2</sub>	na	GR2	CHEM1
NO <sub>3</sub>	nd	nd	CHEM1
NH <sub>4</sub>	na	nd	nd
Al	na	GR3	SPEC1
Fe (total)	na	TITR5	SPEC1
B	na	nd	SPEC1
PO <sub>4</sub>	nd	GR5	CHEM1
Li	na	GR9	SPEC1
Sr	na	nd	SPEC1
Ba	na	nd	SPEC1
Mn	na	nd	SPEC1
Zn	na	nd	SPEC1
Pb	nd	nd	SPEC1
Be	nd	nd	SPEC1
Mo	nd	nd	SPEC1
V	nd	nd	SPEC1
Cr	nd	nd	SPEC1
Co	nd	nd	SPEC1
Ni	nd	nd	SPEC1
Cu	nd	nd	SPEC1
Cd	nd	nd	SPEC1
As (total)	nd	nd	SPEC1
δ <sup>13</sup> C			ISOT1

Table 15. Methods of analysis for samples collected during 1980-94

Investigator	Nordstrom	Nordstrom	Nordstrom
Sample collection date	5/8/80	4/8/81	7/28/87
Parameter or constituent	Method of analysis		
Specific conductance	CONDI	CONDI	CONDI
Dissolved solids	nd	nd	nd
Eh	nd	EC4	EC4
pH	PH1	PH1	PH2
Dissolved Oxygen	GC1	nd	nd
Alkalinity	TI1	TI1	TI1
CO <sub>2</sub>	GC1	nd	nd
D.O.C.	nd	nd	nd
Ca	DCP	DCP	ICP1
Mg	DCP	DCP	ICP1
Na	DCP	DCP	ICP1
K	DCP	DCP	ICP1
SO <sub>4</sub> , SO <sub>3</sub>	IC1	IC1	IC2
S <sub>2</sub> O <sub>3</sub>	nd	nd	nd
H <sub>2</sub> S	EC1	EC1	EC1
F	IC1,EC2	IC1	IC2
Cl, Br	IC1	IC1	IC2
SiO <sub>2</sub>	DCP	DCP	ICP1
NO <sub>2</sub>	IC1	nd	nd
NO <sub>3</sub>	IC1	IC1	nd
NH <sub>4</sub>	EC3	nd	nd
Al	DCP,FAAS1	DCP	nd
Fe (total)	C1	DCP	C1
Fe(II)	C1	nd	C1
B	DCP	DCP	ICP1
PO <sub>4</sub>	C2	nd	nd
Li	DCP,FAAS2	DCP	ICP1
Sr	DCP	DCP	ICP1
Ba	DCP	DCP	ICP1
Rb	DCP	DCP	ICP1
Mn, Zn, Pb, Be	DCP	DCP	ICP1
Mo	DCP	DCP	nd
V	DCP	DCP	ICP1
Tl	DCP	DCP	nd
Cr, Co, Ni, Cu, Cd	DCP	DCP	ICP1
As (total)	DCP	DCP	nd
As(III)	C2	nd	nd
As(V)	C2	nd	nd
N <sub>2</sub>	GC1	nd	nd
Ar	GC1	nd	nd
CH <sub>4</sub>	GC1	nd	nd
He	GC1	nd	nd

Table 15. Methods of analysis for samples collected during 1980-94 (Cont.)

Investigator	Nordstrom	Nordstrom	Nordstrom
Sample collection date	10/22/92	7/17/93	6/17/94
Parameter or constituent	Method of analysis		
Specific conductance	COND2	COND2	COND2
Eh	EC4	EC4	nd
pH	PH2	PH2	PH2
Dissolved Oxygen	EC5	EC5	EC5
Alkalinity	TITR1	TITR1	nd
D.O.C.	DOC1	nd	nd
Ca	ICP2,FAAS3	ICP2,FAAS3	ICP2
Mg	ICP2,FAAS3	ICP2,FAAS3	ICP2
Na	ICP2,FAAS3	ICP2,FAAS3	ICP2,FAAS4
K	ICP2,FAAS3	ICP2,FAAS4	ICP2,FAAS4
SO <sub>4</sub> , SO <sub>3</sub>	IC2	IC2	IC2
S <sub>2</sub> O <sub>3</sub>	IC3	IC3	IC3
H <sub>2</sub> S	EC1	C3	C3
F	IC2	IC2	nd
Cl	IC2	IC2	IC2
Br	IC2	IC2	IC2
I	nd	nd	nd
SiO <sub>2</sub>	ICP2	ICP2	ICP2
NO <sub>2</sub>	nd	nd	nd
NO <sub>3</sub>	IC2	IC2	IC2
NH <sub>4</sub>	C4	nd	nd
Al	ZGFAAS1	ZGFAAS1	ICP2
Fe (total)	C1	C1	ICP2
Fe(II)	C1	C1	nd
B	ICP2	ICP2	ICP2
Li	FAAS3	FAAS3	FAAS3
Sr	ICP2	ICP2	ICP2
Ba	ICP2,ZGFAAS2	ICP2,ZGFAAS2	ICP2
Mn	ICP2	ICP2	ICP2
Zn	ICP2	ICP2	ICP2
Pb	ICP2	ICP2	ICP2
Be	ICP2	ICP2	ICP2
Mo	ICP2	nd	nd
V	ICP2	ICP2	ICP2
Tl	nd	nd	nd
Cr	ICP2	ICP2	ICP2
Co	ICP2	ICP2	ICP2
Ni	ICP2	ICP2	ICP2
Cu	ICP2	ICP2	ICP2
Cd	ICP2	ICP2	ICP2
As (total)	ICP2	ICP2	ICP2
CH <sub>4</sub>	nd	GC2	nd
CO	nd	GC2	nd
CS <sub>2</sub>	nd	GC2	nd
δ <sup>2</sup> H	ISOT2	ISOT2	nd
δ <sup>18</sup> O	ISOT3	ISOT3	nd
δ <sup>34</sup> S	nd	ISOT4	ISOT4
Tritium	nd	ISOT5	nd

Table 16. Explanation of analytical methods for samples collected during 1905-76

Method descriptor	Description of method
GR1	100 ml of sample were evaporated in a Pt dish over a water bath, then dried at 120°C.
GR2	Untreated sample was filtered, evaporated, treated with HCl to remove carbonates, evaporated to dryness again, taken up in 1:1 HCl, filtered, and the residue ignited and weighed as silica.
GR3	Filtrate from GR2 was treated with ammonium hydroxide to precipitate Al and Fe. The total mixed oxide was determined, then Fe (see TITR5), and the Al by difference.
GR4	Filtrate from GR2 was treated with BaCl <sub>2</sub> to determine sulfate as the Ba salt.
GR5	Filtrate from GR2 was analyzed for ammonium phosphomolybdate by precipitation with ammonium molybdate.
GR6	Filtrate from GR3 was made more alkaline with ammonia, oxalate added, and the Ca precipitated as the oxalate salt, ignited, and weighed as CaO.
GR7	Filtrate from GR6 was heated to dryness, redissolved in ammonium hydroxide, precipitated as ammonium magnesium phosphate, ignited, and determined as Mg pyrophosphate.
GR8	Filtrate from GR7 was analyzed for total alkali chlorides and then for K by precipitation as the chloroplatinic acid complex.
GR9	Filtrate from GR7 was evaporated to alkali chloride salts, the LiCl was dissolved in amyl alcohol, and precipitated as the sulfate.
GR10	Na determined by difference between total alkali chloride salts and analyses of Li and K.
TITR1	Samples were titrated with 0.05N HCl to a phenolphthalein endpoint to determine carbonates and to a methyl orange endpoint to determine bicarbonates.
TITR2	Sample acidified with sulfuric acid was boiled in the presence of potassium permanganate and the excess permanganate titrated with oxalate.
TITR3	Sample was titrated in the field with 0.1N iodine solution to a starch endpoint.
TITR4	Sample with carbonates removed by titration with sulfuric acid was titrated with silver nitrate with potassium chromate as indicator.
TITR5	Filtrate from GR2 was evaporated, ignited, redissolved in sulfuric acid, the Fe reduced by sheet aluminum, and the Fe determined by titration with potassium permanganate.
CHEM1	Described as "chemical analysis"--no other information available
SPEC1	Arc-spark semi-quantitative spectrographic analysis on dried aqueous samples--a variant of the method of Myers and others (1961)
COLOR1	Described as "colorimetric analysis"--no other information available
ISOT1	<sup>13</sup> C measurement, no other information available

Table 17. Explanation of analytical methods for samples collected during 1980-94  
[rsd, relative standard deviation]

Designator	Species determined	Analyst(s)	Equipment used	Reference(s) or comments	rsd, detection limit, mg/L
PH1	[H <sup>+</sup> ]	Nordstrom, Ball	Beckman $\phi$ 21 meter, Leeds and Northrup comb. electrode	Two buffer calibration at sample temp. using 7.00, and 4.01 or 9.18 pH buffers	<b>0.02 pH units</b>
PH2	[H <sup>+</sup> ]	Nordstrom, Ball, Cunningham	Orion Research SA 250 meter, Orion Ross comb. electrode	Two buffer calibration at sample temp. using 7.00, and 4.01 or 9.18 pH buffers	<b>0.02 pH units</b>
COND1	Conductance	Nordstrom, Ball	Lab-Line Mho-Meter, model MC-1	Manual temperature correction, conductance check with 0.0100N KCl	
COND2	Conductance	Authors	Orion Research, model 126	Automatic temperature correction, conductance check with 0.0100N KCl	<b>≤0.5%</b>
TI1	Alkalinity(mg/L HCO <sub>3</sub> )	Ball	Manual titration, or Orion Research model 960/940 autotitrator, potentiometric detection	Fishman and Friedman (1989)	<b>2%, 0.4 mg/L</b>
EC1	S <sup>2-</sup>	Nordstrom, Ball	Orion Research model 94-16A Ag/Ag <sub>2</sub> S electrode	Baumann (1974)	<b>0.005 mg/L</b>
EC2	F	Nordstrom	Orion Research model 96-09 comb. F. electrode	Barnard and Nordstrom (1980)	<b>~3%</b>
EC3	NH <sub>4</sub>	Nordstrom, Ball	Orion Research model 95-10 NH <sub>3</sub> electrode		<b>~4%</b>
EC4	Eh	Nordstrom, Ball	Orion Research model 96-78-00 Pt electrode	Electrode checked using Zobell's solution (Zobell, 1946), at the sample temperature	
EC5	[O <sub>2</sub> ] <sub>dis.</sub>	Authors	Orion Research model 840 DO meter and probe	Automatic sample temperature and barometric pressure correction	<b>1%</b>
DOC1	Dissolved organic carbon	G.R. Aiken (USGS, Boulder)	Oceanography International model 700 carbon analyzer	Some samples were diluted to reduce interference from Cl <sup>-</sup> (Aiken, 1992)	<b>~10%, 0.2 mg/L</b>

Table 17. Explanation of analytical methods for samples collected during 1980-94 (Cont.)

Designator	Species determined	Analyst(s)	Equipment used	Reference(s) or comments	<i>rsd, detection limit, mg/L</i>
GCI	Dissolved N <sub>2</sub> , Ar, CH <sub>4</sub> , O <sub>2</sub> , and He	D.W. Fisher (USGS, Reston VA)		Samples collected as per Pearson and others(1978) and temperature-corrected as per Weiss(1974)	O <sub>2</sub> : 0.030 CH <sub>4</sub> : 0.005 H <sub>2</sub> S: 0.600
GC2	Dissolved CO, CH <sub>4</sub> , and CS <sub>2</sub>	C.G. Patterson (Univ. Colo. at Boulder, Dept. of Geol. Sciences)		Samples collected unfiltered in brown bottles, avoiding head space. General method: Patterson and Runnells(1992)	
DCP	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Sr, V, and Zn	Ball	SpectraSpan IIIA simultaneous multi-element direct-current plasma spectrometer with two cassettes. Inter-element interferences were corrected with MEGACRUNCH software (J.W. Ball, personal communication).	Ball and Nordstrom(1994). 2.5% (w/v) of Li <sup>+</sup> or Cs <sup>+</sup> was added as ionization buffer	<b>~2% for all elements</b> Al: 0.010 As: 0.400 B : 0.020 Ba: 0.005 Be: 0.002 Ca: 0.200 Cd: 0.010 Co: 0.005 Cr: 0.003 Cu: 0.003 Fe: 0.015 K : 0.300 Mg: 0.020 Mn: 0.010 Na: 0.200 Ni: 0.004 Pb: 0.020 Si: 0.200 Sr: 0.005 V : 0.005 Zn: 0.006

Table 17. Explanation of analytical methods for samples collected during 1980-94 (Cont.)

Designator	Species determined	Analyst(s)	Equipment used	Reference(s) or comments	<i>rsd detection limit, mg/L</i>
ICP1	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Sr, V, and Zn	Ball	Leeman Labs Plasma-Spec III, simultaneous, multi-element, inductively coupled plasma spectrometer. Inter-element interferences were corrected with MEGACRUNCH software (J.W. Ball, personal communication).	Ball and Nordstrom (1989)	~2% for all elements Al: 0.500 As: 0.300 B : 0.200 Ba: 0.005 Be: 0.001 Ca: 0.050 Cd: 0.005 Co: 0.002 Cr: 0.010 Cu: 0.050 Fe: 0.100 K : 0.300 Mg: 0.500 Mn: 0.020 Na: 0.200 Ni: 0.003 Pb: 0.200 Si: 0.500 Sr: 0.002 V : 0.075 Zn: 0.010

Table 17. Explanation of analytical methods for samples collected during 1980-94 (Cont.)

Designator	Species determined	Analyst(s)	Equipment used	Reference(s) or comments	rsd, detection limit, mg/L.
ICP2	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Sr, Ti, V, and Zn	Cunningham	Leeman Labs Plasma-Spec III, simultaneous, multi-element, inductively coupled plasma spectrometer. Inter-element interferences were corrected with MEGACRUNCH software (J.W. Ball, personal communication).	Same conditions as ICP1, except that analytical wavelengths for Al, As, Cu, V, and Zn were different, and detection limits were estimated from a large number of blank determinations.	~2% for all elements Al: 0.220 As: 0.170 B : 0.090 Ba: 0.020 Be: 0.001 Ca: 0.050 Cd: 0.020 Co: 0.020 Cr: 0.045 Cu: 0.070 Fe: 0.150 K : 0.870 Mg: 0.090 Mn: 0.060 Na: 0.400 Ni: 0.020 Pb: 0.075 Sr: 1.02 Ti: 0.500 V : 0.010 Zn: 0.005

Table 17. Explanation of analytical methods for samples collected during 1980-94 (Cont.)

Designator	Species determined	Analys(s)	Equipment used	Reference(s) or comments	<i>rsd, detection limit, mg/L.</i>
FAAS1	Al	Ball	Perkin-Elmer model 306 flame atomic absorption spectrometer, with N <sub>2</sub> /acetylene flame, in absorption mode	8-hydroxyquinoline/MIBK extraction method of Barnes (1975)	~2%, 0.005
FAAS2	Li	Ball	Perkin-Elmer model 306 flame atomic absorption spectrometer, with air/acetylene flame, in absorption mode	2500 mg/L Na ionization buffer	~2%, 0.005
FAAS3	Na, K, Ca, Mg, and Li	Cunningham	Perkin-Elmer model 5000 flame atomic absorption spectrometer, with air/acetylene flame, in absorption mode	1000 mg/L K or Cs ionization buffer	~2% Na: 0.005 K : 0.025 Ca: 0.030 Mg: 0.030 Li: 0.003
FAAS4	Na, K	Cunningham	Perkin-Elmer model 5000 flame atomic absorption spectrometer, with air/acetylene flame, in emission mode	1000 mg/L Cs ionization buffer	~2% Na: 0.040 K : 0.007

Table 17. Explanation of analytical methods for samples collected during 1980-94 (Cont.)

Designator	Species determined	Analyst(s)	Equipment used	Reference(s) or comments	<i>rsd, detection limit, mg/L.</i>
ZGFAAS1	Al	Cunningham	Perkin-Elmer model 5000 graphite furnace atomic absorption spectrometer with an AS-40 autosampler and platform atomization	Mg nitrate as matrix modifier	0.005
ZGFAAS2	Ba	Cunningham	Perkin-Elmer model 5000 graphite furnace atomic absorption spectrometer with an AS-40 autosampler and wall atomization		0.001
C1	Fe(II) and Fe <sub>ox</sub>	Ball	Bausch and Lomb Spectronic 710 UV-Vis spectrometer (1980-1987) and a Hewlett-Packard 8452A diode array spectrometer (1992-1994) with 1 and 5 cm cells	Ferrozine method of Stookey (1970)	3%, 0.005
C2	As(III), As(V), and PO <sub>4</sub>	Ball	Bausch and Lomb Spectronic 710 UV-Vis spectrometer with 1 and 5 cm cells	Strickland and Parsons(1968); Johnson(1971); Stauffer(1980)	3% As(III,V): 0.004 PO <sub>4</sub> : 0.0002
C3	H <sub>2</sub> S	Cunningham	Hach Co. DR-2000 UV-Vis absorption spectrometer and Hach method # 8131 reagents	Method based on ALPHA(1975)	0.005
C4	NH <sub>4</sub>	R.C. Antweiler, USGS, Boulder CO	Alpkem model RFA-300 flow injection analyzer	Method based on Solorzano(1969)	3% 0.012
IC1	F, Cl, SO <sub>4</sub> <sup>2-</sup> , Br, NO <sub>2</sub> , and NO <sub>3</sub>	Ball	Dionex Corp., model 16 ion chromatograph with guard, separator and suppressor columns	NaHCO <sub>3</sub> /Na <sub>2</sub> CO <sub>3</sub> eluent	3%

Table 17. Explanation of analytical methods for samples collected during 1980-94 (Cont.)

Designator	Species determined	Analyst(s)	Equipment used	Reference(s) or comments	<i>rsd, detection limit, mg/L.</i>
IC2	F, Cl, SO <sub>4</sub> <sup>2-</sup> , SO <sub>3</sub> <sup>2-</sup> , NO <sub>3</sub> and Br <sup>-</sup>	Schoonen, Xu, Cunningham	Dionex Corp., model 2010i/2000i ion chromatograph with AG4A guard and AS4A separator columns and an Anion Micromembrane Suppressor-II column	NaHCO <sub>3</sub> /Na <sub>2</sub> CO <sub>3</sub> eluent	2-3%, F=.03 Cl=.05, Br=.11, NO <sub>3</sub> =.09, S <sub>2</sub> O <sub>3</sub> =.09, SO <sub>3</sub> =.15 SO <sub>4</sub> =.15
IC3	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	Schoonen, Xu	Dionex Corp., model 2010i/2000i ion chromatograph with two AG4A guard columns and AS4A separator column and an Anion Micromembrane Suppressor-II column	NaHCO <sub>3</sub> /Na <sub>2</sub> CO <sub>3</sub> eluent, see text for discussion of method	2-3%
ISOT2	$\delta^2\text{H}$	T.B. Coplen and J.A. Hopple, USGS, Reston VA	V.G. Micromass model 602 mass spectrometer	Coplen and others(1991). Standardization against VSMOW <sup>1</sup> ( $\delta^2\text{H} = 0$ ) and SLAP <sup>2</sup> ( $\delta^2\text{H} = -428$ per mil)	1.5 per mil
ISOT3	$\delta^{18}\text{O}$	T.B. Coplen and J.A. Hopple, USGS, Reston VA	DuPont model 21-491 mass spectrometer	Epstein and Mayeda(1953) Standardization against VSMOW <sup>1</sup> ( $\delta^{18}\text{O} = 0$ ) and SLAP <sup>2</sup> ( $\delta^{18}\text{O} = -55.5$ per mil)	0.1 per mil
ISOT4	$\delta^{34}\text{S}$	R.W. Carmody, USGS, Reston VA	Finnigan MAT model 251 mass spectrometer	Canfield and others(1986) Robinson and Kusakabe(1975) Coleman and Moore(1978). Standardization against VCDT <sup>3</sup>	
ISOT5	tritium	R.L. Michel, USGS, Reston VA	Packard Tri-Carb scintillation counter. Electrolytic <sup>3</sup> H enrichment.	Thatcher and others(1977)	

1 Vienna Standard Mean Ocean Water 2 Standard Light Antarctic Precipitation 3 Vienna Canyon Diablo Trolite

Table 18. Measurements of Standard Reference Waters

Constituent	Combined 1992 data			Combined 1993 data		
	Anal. method	SRW <sup>1</sup>	Observed concn./Ref. concn. <sup>2</sup>	Anal. method	SRW	Observed concn./Ref. concn.
Ca	ICP	T1111	21.0 [0.51, 20.3 [0.3]	ICP	T1115	47.9 [2.01, 50.9 [2.0]
Mg	ICP	T1111	6.70 [0.11, 5.97 [0.07]	ICP	T1115	29.4 [1.3], 27.6 [1.0]
Na	FAAS	T1111	61.2 [1.0], 53.8 [0.5]	FAAS	T1115	141, 140 [5]
K	FAAS	T1111	2.59 [0.06], 2.67 [0.07]	FAAS	T1115	5.29, 5.41 [0.32]
SO <sub>4</sub>						
F						
Cl						
Br						
SiO <sub>2</sub>	ICP	T1111	10.5 [0.2], 9.82 [0.14]	ICP	T1115	10.5 [1.0], 9.9 [0.5]
NO <sub>3</sub>						
NH <sub>4</sub>						
Al	GFAAS	T1111	0.0819 [0.0004], 0.083 [0.009]	GFAAS	T1117	0.079, 0.0790 [0.0194]
Fe (total)	ICP	T1111	<0.20, 0.054 [0.003]	ICP	T1115	1.21 [0.05], 1.175 [0.060]
B	FAAS	T1115	0.136 [0.002], 0.132 [0.012]	ICP	T1115	<0.22, 0.099 [0.011]
Li	ICP	T1111	0.156 [0.004], 0.162 [0.005]	FAAS	T1115	0.126, 0.132 [0.012]
Sr	ICP	T1111	0.026 [0.006], 0.0270 [0.0015]	ICP	T1115	0.67 [0.03], 0.672 [0.026]
Ba	ICP	T1111	0.76 [0.10], 0.619 [0.013]	ICP	T1115	0.249 [0.012], 0.250 [0.012]
Mn	ICP	T1111	0.360 [0.020], 0.320 [0.005]	ICP	T1115	0.454 [0.018], 0.455 [0.021]
Zn	ICP	T1111	<0.20, 0.0188 [0.0014]	ICP	T1115	0.380 [0.017], 0.381 [0.021]
Pb	ICP	T1111	0.009 [0.001], 0.0077 [0.0003]	ICP	T1115	<0.22, 0.0134 [0.0024]
Be	ICP	T1111	<0.075, 0.0270 [0.0017]	ICP	T1115	0.053 [0.004], 0.0535 [0.0030]
V	ICP	T1111	0.026 [0.005], 0.0258 [0.0010]	ICP	T1115	<0.083, 0.0177 [0.0028]
Cr	ICP	T1111	0.009 [0.002], 0.0090 [0.0005]	ICP	T1115	0.037 [0.007], 0.0357 [0.0039]
Co	ICP	T1111	0.016 [0.004], 0.0155 [0.0001]	ICP	T1115	0.018 [0.004], 0.0154 [0.0029]
Ni	ICP	T1111	<0.050, 0.0109 [0.0005]	ICP	T1115	0.020 [0.002], 0.0174 [0.0027]
Cu	ICP	T1111	0.029 [0.001], 0.0230 [0.0005]	ICP	T1115	<0.055, 0.017 [0.0036]
Cd	ICP	T1111	<0.30, 0.0033 [0.0003]	ICP	T1115	0.015 [0.002], 0.0140 [0.0015]
As (total)	ICP	T1111				<0.33, 0.014 [0.002]
As(III)						
As(V)						

<sup>1</sup> USGS Standard Reference Water

<sup>2</sup> [ ] = standard deviation

Table 18. Measurements of Standard Reference Waters (Cont.)  
Combined 1994 data

Constituent	Anal. method	SRW <sup>1</sup>	Observed concn./Ref. concn. <sup>2</sup>
Ca	ICP	T117	21.3 [0.4], 20.9 [1.2]
Mg	ICP	T117	10.3 [0.2], 10.05 [0.44]
Na	ICP	T117	20.7 [0.2], 20.00 [1.26]
K	ICP	T117	2.03 [0.23], 2.11 [0.19]
SO <sub>4</sub>			
S <sub>2</sub> O <sub>3</sub>			
F			
Cl			
Br			
SiO <sub>2</sub>	ICP	T117	12.2 [0.8], 11.85 [0.64]
NO <sub>3</sub>			
NH <sub>4</sub>			
Al	GFAAS	T115	0.0300 [0.0009], 0.040 [0.020]
Fe (total)			
B	ICP	T117	<0.16, 0.151 [0.028]
PO <sub>4</sub>			
Li			
Sr	ICP	T117	0.268 [0.004], 0.2650 [0.0111]
Ba	ICP	T117	0.093 [0.009], 0.0985 [0.0063]
Rb			
Mn	ICP	T117	0.217 [0.003], 0.2200 [0.0149]
Zn	ICP	T117	0.177 [0.002], 0.1760 [0.0093]
Pb	ICP	T117	<0.113, 0.0050 [0.0013]
Be	ICP	T117	0.004 [0.001], 0.0048 [0.0004]
V	ICP	T117	<0.015, 0.0047 [0.0018]
Cr	ICP	T117	<0.068, 0.0103 [0.0016]
Co	ICP	T117	<0.030, 0.0043 [0.0007]
Ni	ICP	T117	<0.030, 0.0100 [0.0025]
Cu	ICP	T117	<0.105, 0.0060 [0.0018]
Cd	ICP	T117	<0.030, 0.0022 [0.0004]
As (total)	ICP	T117	<0.26, 0.0069 [0.0014]
As(III)			
As(V)			

<sup>1</sup> USGS Standard Reference Water  
<sup>2</sup> [ ] = standard deviation