# Saratoga: The Bubbles of Reputation and their Implications for an Embryonic Rift System in the Upper Hudson River Valley

A thesis presented to the Faculty
of the State University of New York
at Albany
in partial fulfillment of the requirements
for the degree of
Master of Science

Department of Geological Sciences

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# ABSTRACT

Carbonated, alkaline, saline waters occur over a wide area in the upper Hudson River Valley approaching 1,000 square miles. Through the sampling (spring and fall) of 39 locations, half of which were hitherto unsamples, the waters are shown to be a complexly mixed system with at least five major components.

They are:

1) a gaseous phase consisting primarily of $CO_2$;
2) a fluid (containing the dissolved $CO_2$) possibly analogous to a metamorphic brine whose major chemistry is $HCO_3$>Na>Cl;
3) formational waters of variably low salinities which may be the end products of progressive dilution of Paleozoic connate brines by meteoric waters; major chemistry Cl>Na>$HCO_3$;
4) constituents added by reactions of the carbonated waters with the wall rocks of the Proterozoic basement and the Paleozoic aquifer;
5) normal surface ground waters of meteoric origin which seasonably dilute the deeper carbonated waters while also capping and "damping" the system.

Several segregated water types comprised largely of components #2, 3, and 5 above can also be recognized.

Through the use of stable isotopes of C, O, and H, the $CO_2$ is conclusively demonstrated to be of thermal origin. $C^{13/12}$ values of -2 to -8 per mil distinguish the carbon to be of juvenile or, more probably, of mantle origin. This in turn raises new tectonic questions when conjoined

with the structural evidence presented showing the upper Hudson Valley lowlands to be fault controlled. The combination of the two imply that the lowlands represent a proto or embryonic rift system.

# Acknowledgements

My appreciation for unstinted help throughout this project is particularly expressed to Dr. George W. Putman of the SUNYA faculty and Dr. James R. Dunn of Dunn Geoscience Corporation. Without their aid and advice this investigation could well have been impossible.

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# 1.0 Introduction

## 1.1 Location and Physiographic Setting

The city of Saratoga Springs is located in eastern upstate New York just beneath the foothills of the Adirondack Mountains (Figure 1.1). It is serviced by a number of excellent highways including the Adirondack Northway (I-87) which passes only a mile east of the city.

To the north and northwest the lower Adirondacks jut out to form a small peninsula from the main mountain mass. The remainder of the area is covered by variable depths of glacial debris passing into the Mohawk Valley lowlands to the south and west and the Hudson Valley lowlands to the east. A few small lakes dot the region; most notable are Saratoga Lake 3 kilometers east of the city and the curious Round Lake 6 kilometers to the southeast. Relief is commonly low to moderate in these areas, varying up to 70 meters in the form of glacial kames and drumlins interspersed with many sharp fault scarps usually less than 30 meters in height. The adjacent Adirondacks have a relief of only about 30 meters in the immediate vicinity of the city but increase gradually to 250 meters a few kilometers north. They form a sharp boundary with the Hudson lowlands to the east in the form of the McGregor Fault scarp which juxtaposes Precambrian metamorphic rocks of the Adirondacks against the lower Paleozoic shales and carbonates of the lowlands. This scarp loses relief at Saratoga Springs while increasing in relief and apparent vertical displacement to the north (Isachsen, 1979).

Figure 1.1 Location map

Sketch map of New York State. Area of interest outlined by dotted line.

## 1.2 Regional Geologic Setting

Saratoga Springs is seated at the confluence of contrasting geologic provinces. Northwest are the structurally complex medium to high grade Precambrian metamorphic rocks of the Adirondacks. These are generally considered to be a continuation of the Grenville province of the Canadian shield of Quebec since both areas yield Grenvillian metamorphic ages of 1.0 to 0.9 b.y. Many of the rocks may ultimately in fact be early to middle Proterozoic in age, but reliable age dating is as yet uncertain and incomplete from this environment. Ages of detrital zircons from presumed Proterozoic sandstones have yielded dates exceeding 1.5 b.y. as a possible minimum age for the metasedimentary rocks.

Beginning only a mile to the north of the city of Saratoga Springs on the western, upthrown side of the Saratoga Fault outcrops a series of unmetamorphosed Lower Ordovician dolostones and limestones. These extend to the west throughout the Mohawk Valley, broken into many small blocks by an extensive set of high angle, normal faults. Regional dips in these carbonates are on the order of $4^{\circ}$ to the south (Fisher and Hanson, 1951).

To the south and east these dolostones are unconformably overlain by a series of upper Ordovician shales and siltstones. Equivalent to the Utica Shale in the central and western areas of the state, this sequence is variably termed the Schenectady, Snake Hill, Normanskill, or Austin Glen formations within the area of study. It is poorly understood because of look-alike lithologies, extensive glacial cover, and sparse drillhole data. Although probably broken by many faults like the westerly carbonates and overlain to the east by several deformed allochthonous sheets of Normanskill shale (Figure 1.2), these rocks can nonetheless be treated as structurally "simple" in that portion of the study area west of the Hudson River.

Of particular interest is the Hudson River Valley itself, a prominent north-south linear feature that is highly visible on ERTS imagery. From the city of Hudson Falls the river courses due south virtually in a straight line for nearly 300 kilometers to terminate in the Triassic aulacogen at New York City. North of the river's westerly right angle bend into the southern Adirondacks at Hudson Falls the same linear continues to the Canadian St. Lawrence River Valley in the form of the grabens of Lake George and Lake Champlain (Figure 1.2). The northern portion of the greater lowlands, then, is demonstrably structrually controlled. The direct course of the river in the south and several parallel fault systems (i.e. the Ramopo fault) strongly suggest the southern portion is structurally controlled as well. Together they form a linear structure nearly 700 kilometers long terminating in probable failed rift arms at either end.

Also of note is the Taconic sequence, a series of dominantly clastic and pelitic Cambrian and Ordovician rocks that in New York State extend about 250 kilometers from the

LEGEND

▨ Precambrian
☐ Ordovician Shale
(undeformed)
⬚ Devonian Seds.

Taconic Slices

1. Giddings Brook
2. Bird Mountain
3. Chatham
4. Rensselaer Plat.
5. Dorset Mtn.-
Everett

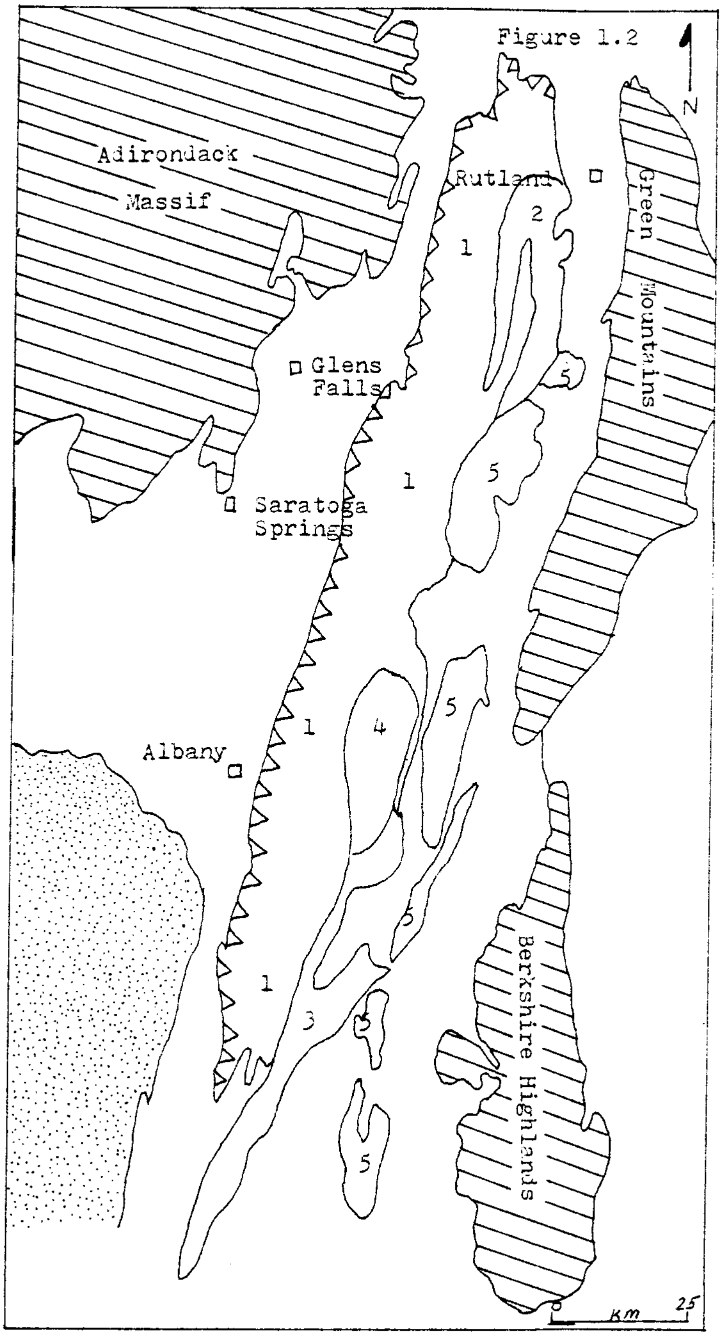


Figure 1.2

southern part of Lake Champlain through the southern end of Dutchess County (Figure 1.2). A complexly deformed structural series, the Taconics are the subject of one of the oldest controversies in North American geology and present two distinct problems. The first, due partially to look-alike lithologies, involves the stratigraphic correlation of the lithostratigraphic units present and the composition, sequence, and relationships of the faunas. The second problem is concerned with the types of major structures present and whether the Taconic sequence is allochthonous, autochthonous, or parautochthonous in nature, or in what proportions if mixed (Theokritoff, 1964).

Recent work by Zen (1967) has disclosed six or seven discrete structural slices overlapping eastward with the structurally highest slice, the Dorset Mountain or Everett Slice, present in western Massachustts. He also separates the Taconics into high and low sequences based on topography, relative structural position, and stratigraphy. The Everett Slice comprises the high Taconics while the Giddings Brook, Chatham, and Rensselaer Plateau slices form the low Taconics. Traditionally interpreted to have been emplaced as soupy, soft sediment slides, evidence has recently been presented that suggests these rocks could have been thrust into their present position as coherent imbricate tectonic slices (Rowley and Kidd, 1979). Whichever interpretation is correct, the allochthonous nature of the slices has been clearly established. Still open is the autochthonous or parautochthonous nature of the coeval rocks of the Champlain Valley and the Vermont Valley sequences directly underlying or surrounding the allochthon.

Separating the low Taconics from the relatively undeformed rocks to the west is the famous Emmon's or Logan's line. It is a wildflyschlike material containing fossiferous and nonfossiliferous fragments of the allochthon occasionally reaching a mile across strike (E-W). Zen (1967) and others have cited this unit as singular evidence of gravity gliding of at least the Giddings Brook slice in the Middle Ordovician. This feature is of interest to this study because it hosts Reid's Mineral Spring and lies immediately east of several other occurrences of carbonated water near the town of Melrose.

## 1.3 Glacial Geology

Glacial geology is an important factor in the area of study since most of the bedrock is obscured by various types of glacial deposits. It will be discussed only briefly herein because it is not generally germane to the problem at hand.

Most of the area from Albany north to Glens Falls was once the site of deglacial Lake Albany and several smaller successors. These have all left beach strand lines at the following elevations: Lake Albany, 355'; Lake Quaker Springs, 310'; Lake Coveville, 210'. Broad sandy flats, exposed at the lake shore as the lake levels dropped, supplied large quantities of Lake Albany sediments. Winds, eroding these newly exposed shore areas, created large wedges of fine sediment extending into the lake and aeolian dunes on the flats. The lake and dune sand may extend to over 50 meters in thickness in portions of the study area (Dineen and Rogers, 1979).

Other than the lake sediments major deltas are also an important contributor to the glacial depoaits. Saratoga Springs is largely situated on just such a delta from a large tributary stream flowing into the former lake along the preglacial Ballston bedrock channel (now the site of Ballston Lake). Other major streams flowed along the Colonie, Mohawk, and the Hudson-Battenskill channels. The deltaic sedimentary deposits left behind become thicker and coarsen northward due to the progressive northward retreat of the ice margin (Dineen and Rogers, 1979).

### 1.4 History of the Springs

The story of the springs, their commercial exploitation, and the eventual development of the city into one of America's most famous resorts is a fascinating tale that has been recounted elsewhere in many forms. Scientific purposes do not permit a full treatment herein, yet no study can entirely ignore their history since they are the source of all that Saratoga has become today; a pastoral setting hosting some of the finest recreational and cultural facilities in New York State, a town of grand Empire and Victorian architecture, and a center for the racing of some of this country's finest thoroughbred horses. All this has sprung from the springs.

The discovery of the carbonated mineral seeps of Saratoga can be unquestionably credited to the Indians who drank from the "Big Medicine Spring" for many years to cure all and sundry afflictions. It was they who reportedly brought the first white man to the spring (now known as the High Rock) in 1767 for treatment; Governor William Johnston, who was suffering from an acute case of gout common to many people of that and this time who have generous table habits and sedentary liver action. While many later accounts credit the good statesman with the springs' discovery, this is certainly not the case. Excavations performed in the mid-1800's under the site of the High Rock cone of tufa (formerly the orifice through which the spring flowed) found various layers of tufa, leaf mold, etc.; and, at a depth of 17 feet, the charred remains of a fire. At the base of the cone was found a square framework of logs laid about the spring. Apparently the Indians' interest in balneology predated even the Roman baths.

The original High Rock Spring has since been replaced by a drilled well in the same position at the northern end of the Saratoga Fault scarp within the city (Plate 3). The earliest written accounts mention this to be the largest of seven naturally flowing springs all located in the "Valley of the Springs". This figurative name describes the village brook which courses northeasterly beneath the Saratoga Fault scarp to the vicinity of the Red Spring from whence it flows more easterly, terminating just beyond the Eureka Spring in a marsh locally known as the "Great Bear Swamp" (Plate 3). The springs were all discovered within this mile and one half section extending from the present day Congress Park to the swamp, beginning with the Congress Spring in 1792. Here carbonated water was found issuing from a "seam in the rock" later recognized to be the fault scarp. As with the ensuing springs, the area was excavated, the seams enlarged, and the pooling water contained by a plank box lined with clay.

Through the first half of the 19th century the supply of the mineral waters was limited to a total flow of about 120 gpm contained in the open enclosures throughout the village. This was more than sufficient to supply the local citizenry who came frequently to dip of the waters. As their fame spread hotels were erected to house the curiosity seekers and the ill who came in ever-increasing numbers to take the "cure". So numerous did they become that the amount of water and their modest enclosures became practically and fashionably inadequate for the growing resort. To meet the increasing demand, drilling into the rock was begun in the 1870's, the first wells drilled being the Geyser Spring, Hathorn North and South, Seltzer, Ainsworth, etc. By the turn of the century dozens of wells had been put down with even the most modest of inns touting its own uniquely curative mineral water well.

Julius Z. Fromel is credited with being the originator of the scheme for extracting $CO_2$ from the waters at the Seltzer Spring in the ensuing years: Geyser, 1892; Lincoln, 1894; New York Carbonic, 1895; and Natural Carbonic, 1905. Several hundreds of wells were drilled during this period to extract greater quantities of gas causing an increasing drop in the head of the mineral waters from 20 feet to 190 feet below the level of the ground (Sixth Annual Report of the Commissioner, 1905). Three stages of depletion were reached necessitating more drastic recovery methods each time to maintain gas production. Over this period these activities had a pronounced effect on the discharge of otherprivate and public sources from the Coesa Spring all the way north to the Red Spring. An illustration of this effect is seen in the decrease of $CO_2$ pressure at the Hathorn #1 Spring from 21 pounds in 1901 to zero in 1904.

At the instigation of a concerned "Citizen's Committee" of hotel owners, merchantmen, and concerned citizenry the "Anti-Pumping Law" was passed in 1908 which prohibited the pumping of any wells or springs which extended into the bedrock. Its constitutuionality was upheld after extensive litigation and the state established the Saratoga Springs Commission in 1909 to safeguard the "heritage of the mineral waters" for the people of New York State. Special funding was obtained through several acts passed in the State Legislature and the property of the Natural Carbonic Gas Company was acquired for the reservation on October 21, 1911. This was the last of the commercial gas enterprises to close its doors.

Over the course of the next 20 years interest in the springs was maintained largely because the city had now become a substantial resort with a new horse racing track, gambling casino, and the summer homes of America's oldest and wealthiest families. The Springs Commission consequently received adequate funding(interrupted only from 1916-1919 by the first world war) to acquire more land and upgrade the existing facilities. During this period the bathhouses, bottling plant, hotels, and attendant facilities were constucted on the expanded Springs Reservation. New wells were driven and the tubing, packing, and housing of the old sources were vastly upgraded. Several engineering and other scientific studies were also commissioned to study the waters which produced a large volume of data, much of which is still valuable and is used in this report.

Since 1930 interest in the curative properties of the peculiar waters has waned somewhat; their mystique largely tarnished by the advances of modern medicine. Few new wells have been drilled, the hotels have largely disappeared, and few still come to rest and take the "cure". The Saratoga Springs Reservation still exists, however, the major attractions are now the picnic grounds, golf course, and the Performing Arts Center. Baths can still be taken, now without reserving space ahead of time; something unheard of 50 years ago.

Breaking this long drought is a recent resurgence of interest which may highlight the waters once again. The rekindling has come from the recent fad for seltzer water and a persistent, increasing demand for bottled water. Lastly, the search for alternative energy has sparked new research into the origin of the $CO_2$ and the potential for an attendant useable geothermal system. It is the first stage of this research that is the topic of this thesis.

## 1.5 Previous Work

The naturally carbonated mineral springs of Saratoga have been the object of considerable interest ever since their discovery by colonists in the late eighteenth century. It was quite common to ascribe all sorts of beneficient medicinal properties to unusual waters in those times and Saratoga first received medical citations as early as 1770. During the 19th century testimonials proliferated and a major resort spa grew to flourish around the increasing number of mineral water wells drilled in and around the town of Saratoga. This activity naturally fostered many studies which were largely "pseudoscientific" in nature and mostly designed to tout the curative properties of the waters. Several early sets of analyses were also performed by reputable chemists of the time, notably Dr. John Steele (1840) and Professor Charles F. Chandler (1875) (Table 4, appendix). Their analytical work can be considered relatively accurate for many of the major dissolved constituents in the waters. The first interpretation of the system was attempted by Professor James F. Kemp(1912) who combined the prior analytical and other data with new sets of analyses by the U.S. Department of Agriculture to produce an exhaustive study of the waters (Table 5, appendix).

Kemp's work still remains as an outstanding example of scientific analysis even though it was performed over 65 years ago. Not only does he compile a complete historical/analytical sketch of the Saratoga area springs and wells, he cites other occurrences from Albany to Whitehall and links them into a unified interpretation. Among some of his noteworthy conclusions are these: 1) that "Faults furnish an upward passage for the gas and dissolved mineral matter..... but the tight cap of slates above the limestones act as a roof to prevent their escape, except in the springs and bore holes"; 2) the gas ($CO_2$) is one of the most important features of the water and is generally present in amounts between one to five volumes gas/volume solution; 3) the temperature of the waters averages between $50^{\circ}F$ and $53^{\circ}F$, $2^{\circ}F$ to $5^{\circ}F$ above the mean annual air temperature for Saratoga Springs; and 4) that the source of the gas was probably due to the action of silicic acid on limestone or expiring volcanic activity (citing the volcanic plug of Northumberland, Stark's Knob, as evidence) somewhere deep-seated in the "basin" to the east.

Cushing and Reudemann (1914) touched next upon the springs in their study of the geology of the Saratoga area. While they did not attempt an in-depth look, noting that such an effort would be redundant after Professor Kemp's work, their mapping supported the conclusion that the points of issuance of the water were fault controlled. They also found that Stark's Knob was allochthonously related to the Taconic thrust sequence (i.e. faulted in and could not have generated the $CO_2$); however, they still concurred with Kemp's major interpretation that a deep-seated igneous source for the gas and waters occurred in the easterly basin.

The last significant study of the waters was conducted by R.J. Colony for the specifically appointed Saratoga Springs Commission under the aegis of the State of New York in 1930. While the commission's primary concern was the well-being of the large health resort, considerable data was collected about the waters themselves. Among these were new sets of chemical analyses arranged in a table corresponding to a north-south well progression. These showed a somewhat inconsistent but general increase in total salinity and various separate salts from north to south. Bicarbonates were also plotted from well to well, the result showing that the rate of increase in chloride contents was greater than the rate of increase in bicarbonates from north to south.

Additional analytical information was determined by Lester W. Strock in 1940. By virtue of two early emission spectrographic analyses he determined that the Orenda and Geyser wells contained anomalous zirconium and beryllium.

The last published contribution to the Saratoga problem was by Lang (1959) who, on the basis of a single isotope analysis, concluded that the $C^{13/12}$ ratio for the $CO_2$ gas at Saratoga was compatible with a derivation from marine limestones.

## 1.6 Statement of the Problem

While Kemp initially proferred a thermal derivation for the $CO_2$ , most subsequent workers have either skirted or ignored the problem of a carbonation mechanism for primarily two reasons: the cool surface temperatures of the waters and the lack of known igneous activity in eastern North America since the Mesozoic (100 my ago). These facts have led to at least three other unpublished hypotheses of origin for the $CO_2$ being advanced from time to time:

1) the direct oxidation of carbonaceous beds (i.e.coal or peat) or by organic decomposition with the accompanying production of $CO_2$ or methane;
2) the reaction of the Gailor dolostones with $H_2SO_4$ produced from the near-surface oxidation of sulfide minerals and/or the decomposition of organic detritus producing humic acids; and,
3) the release of structurally entrapped, thermally

provoked $CO_2$ of Mesozoic age originally deep in the lowlands to the east now being released due to renewed tectonic activity and the accompanying easing of lithostatic pressure through erosion.

The primary purpose of this study, then, was to examine the proposition whether the waters and/or $CO_2$ gas were thermally derived or could be accounted for in another manner. Related problems considered were:

1) the areal extent and distribution of the carbonated waters;
2) the possible mixing of different water types, their identification and distribution;
3) the source of the $CO_2$;
4) the development of a plausible geologic model for the gas and water;
5) geologic structures in the immediate vicinity of Saratoga Springs and their relationship to the hydraulics of the carbonated waters and regional tectonics;
6) the implications for Neogene tectonics should the gas be thermally derived.

## 1.7 Scope of the Study

This study was designed around two preliminary, inexpensive techniques of geochemical exploration: 1) a geologic literature review, and 2) a regional sampling of the waters. The literature review has not only focussed on the geologic, hydrologic, and chemical data available for the greater Saratoga area, but was expanded into a study of worldwide geothermal systems. Particular attention was given to systems with free $CO_2$, since the modeling of this type of system; $CO_2$-$HCO_3$-Cl-Na-Ca-Mg; was thought to be similar to other systems worldwide.

While many sets of reliable analyses exist for some of the more famous wells in and around the city of Saratoga Springs, virtually no data later than 1930 is available for the less publicized occurrences. The sampling program was designed, therefore, to place more emphasis on other, new carbonated water localities in the upper Hudson River Valley to determine the areal extent of the waters. Furthermore, the sampling program was expanded to include uncarbonated saline waters to determine whether or not mixing of this component with another was taking place in the Saratoga waters and the proportions of each. Spring and fall rounds of sampling were performed to determine: 1) if seasonal chemical fluctuations were present, 2) the reliability of the spring analyses, and 3) the presence and extent of any surficial meteoric water dilution.

Several analytical techniques (post 1930) were also used to provide a better understanding of the waters and furnish possible clues to the derivation of the $CO_2$. These included gas analyses of 13 samples, stable isotope analyses of 5 representative waters, and plasma emission analyses of the elements zirconium and yttrium.

Limited geologic mapping of the Cambro-Ordovician aquifer sequence in the USGS 7.5" Saratoga Springs quadrangle was also done to supplement existing data and to integrate with mapping of the sequence performed around the remainder of the Adirondack periphery. This mapping was done in an effort to better understand the relationship of the structures found therein to the regional tectonic picture, Secondary purposes included a better understanding of the structure of the aquifer and the consequent flow patterns of the carbonated waters.

## 1.8 Methods of Investigation

The bulk of the work for this study was performed during 1978 and early 1979 while the author was employed by Dunn Geoscience Corporation of Latham, New York. The research was sponsored by the New York State Energy Research and Development Authority as part of an assessment of the geothermal energy potential of New York State. Minor field work was also performed during the summer of 1979 as a follow up of mapping done during the summers of 1974 and 1975.

Water samples collected from 39 springs and wells around the Saratoga lowlands were analysed by Health Research Inc., a division of the New York State Health Department. Of these, about half are from previously unsampled locations. The waters from the spring sampling series (36 locations) were analysed for F (free), N (nitrate, nitrite), Cl, $SO_4$, B, Be, Fe, K, Na, Zn, Ca, Li, Mg, $SiO_2$, Zr, Br, I, $PO_4$, Cd, Pb, Al, Ba, Sr, Sn, Cr, Mn, Y, pH (laboratory and field), alkalinity (to methyl orange) and total dissolved solids. Be, Zn, Cd, Pb, Cr, and Mn were omitted in the fall sample series of analyses and N(total), TOC (total organic carbon), and alkalinity (laboratory: pH 4.5) were substituted. Those trace metals deleted were insignificant in the spring sampling results while TOC was added to aid in carbon isotope interpretations. Three characteristic uncarbonated saline water wells were also added to the fall series to aid in determining the components added by wallrock reaction or dissolution.

Due to an anticipated lower water table, less meteoric dilution, and, therefore, greater brine-gas concentrations, systematic sampling for isotope analyses was conducted during the fall program. Analyses were performed for $C^{13/12}$ (water and gas) and $O^{18/16}$ (water and gas) on all wells and four surface bodies of water by Krueger Enterprises, Inc. $C^{13/12}$ measurements were also made on some typical samples of Paleozoic carbonate, Precambrian marbles, and graphite within the marbles, by the same firm. All of these analyses were received but proposed D/H measurements could not be made due to equipment problems. Because of a possible interlaboratory bias, precision problems with the oxygen isotope determinatons, and lack of D/H data, the interpretation of much of the water isotope data is uncertain at best and is not considered in this study.

During the summer six critical wells were selected for preliminary isotope analyses of the free gas and carbonate precipitate phases. These were performed at no expense by Dr. J.R. O'Neil of the U.S.Geological Survey, Menlo Park, California. Seven other qualitative gas isotope analyses were also performed on the mass spectrometer at SUNYA under the direction of Dr. J.S. Kim.

$Ra^{226}$, another known component of the Saratoga waters, was determined for many of the water wells by the radiological division of Health Research Inc. under the direction of Dr. John Matuzek. Those waters not included were the traditional wells of Satatoga Springs for which recent reliable data are already present.

## 1.9 Data Presentation

A systematic approach of data presentation is attempted throughout this report. Section 1-4 are confined as much as possible to an outlay and discussion of the data with only minor interpretation as necessary . The remainder deals primarily with interpretations with little additional data presented.

Each of the sampled waters has been given an index number and a grouping which is used systematically throughout this thesis. Two criteria of group selection have been used with some subjective intermixing:

1) similar chemical properties, and
2) spatial relationships

For the sake of clarity and conciseness the salient characteristics of the various water groupings have been summmarized in table 4.1 followed by discussions on a group basis. Most tables and the indiviual chemical parameters of the waters have been placed in an appendix to facilitate the reading of this report.

## 2.0 GEOLOGY

Because the principal thrust of this research centers around the chemistry and geochemistry of the carbonated Saratoga-type waters, the geology of the area is described here in more general terms than is usual. A detailed approach is taken primarily with those portions of the geologic framework that influence either the chemistry of the waters or their flow patterns. A second focal point includes those aspects which contribute to a better understanding of the regional tectonic picture.

As a consequence a good deal of the description below follows from the literature and from work performed by others with whom the author has had communication. Those portions which are original are primarily structural in nature, occasionally stratigraphic, and stem from geologic mapping of the carbonates around the southern Adirondack periphery during the summers of 1974 and 1975.

### 2.1.1 Precambrian Basement

Precambrian basement rocks outcrop in the north central portion of the Saratoga quadrangle and underlie the Paleozoic rocks of the entire upper Hudson Valley study area. Most of the basement rocks are believed to be from 1-2 billion years old, however, they have been extensively metamorphosed to the upper amphibolite to granulite facies during the Grenville event at .9 to 1.0 billion years ago. Geothermometry and geobarometric estimates place the peak of the Grenville metamorphism at 8-9 kilobars (24-36 km), an unusually deep episode of metamorphism for which a double continental thickness has been suggested (McClleland, 1979). Consequently, stratigraphic and structural relationships in these rocks are commonly extremely convoluted with some authors suggesting as many as 5 distinct episodes of folding (Turner, 1979) with little agreement about a recognizable stratigraphy.

The rocks consist of mixed metasediments and metaigneous rocks with iron and titanium-rich anorthosites and metagabbros forming an Adirondack core some 100 km north of Saratoga Springs. The metasediments outcrop immediately north of the city and consist of quartzites, locally highly graphitic schists, garnet-sillimanite gneisses (khondalite), thinly interbedded graphite-pyrite-sillimanite schists, and coarse calcitic marbles often containing graphite in large disseminated flakes. Granitic and syenitic rocks are very common (charnockites and mangerites) with the former frequently enriched in radioactive minerals with or without magnetite.

These rocks are important with respect to the carbonated waters in several ways. First, the postulated $NaHCO_3$ type basement fluid probably derives most of its $Na^+$ from plagioclase feldspar present as a major phase in the charnockites, mangerites, and many paragneisses (Turner, 1979).

K-spar is also present as a source of $K^+$, however, not in proportions approaching that of $Na^+$ under low temperature (<200°C) hydrothermal conditions (see Martin or Smith Experimental before analyses). The marbles, too, may be locally important though they are far less abundant than other rock types. $CO_{2(aq)}$ or a metamorphic brine rising through appreciable sections of marble can be expected to dissolve considerable amounts of $Ca\text{-}MgCO_3$ enlarging fissures and reducing effective pressures from lithostatic toward hydrostatic.

### 2.1.2 The Cambro-Ordovician Aquifer

#### 2.1.2.1 Potsdam Formation

Resting unconformably on the Precambrian basement, the Potsdam sandstone is a massive, heavily bedded orthoquartzite, well cemented by quartz itself. It is comprised of well rounded quartz grains, is generally not porous, and is highly insoluble in ground water, and presumably, in the carbonated mineral waters as well. While not porous, the beds are brittle and probably have some resevoir characteristics due to secondary fracture permeability.

Traditionally interpreted as a prograding beach sand, the bulk mineralogy is rather monotonous except in the basal portions where much of the sandstone is arkosic with stream channels in the lowermost 20 feet (Figure 2.1). Alkali feldspars and perthite derived from the underlying Precambrian basement comprise up to 20% of the lower beds decreasing to

Figure 2.1 Basal Potsdam formation unconformably resting on the Precambrian basement at Putnam Station, New York. Note the tight, "welded"appearance of the unconformity.

less than 5% as much as 200 feet upward in the formation as near Whitehall, New York. The stream channels and the basal 1 to 10 feet are true arkosic conglomerates which contain a large amount of heavy detrital minerals including allanite, uranothorite, magnetite, ilmenite, etc. These portions are also heavily chloritized and contain anomalous Cu and Zn in amounts from 50 to 200 ppm which strongly indicate the passage of mineralizing fluids at some time in the past. Figure 2.1 is a photograph of this basal portion near Putnam Station, New York, from which samples were analyzed with high values of Cu, Zn, U, and Th. Notice in particular the clean contact between the Precambrian and the basal Potsdam. Despite the indicated passage of former fluids, the unconformity almost appears "welded" together and certainly could not serve as a conduit for the current mineralized waters if it persists in this fashion near the Saratoga area.

Despite its generally poor resevoir capabilities, the Potsdam may contribute somewhat to the chemistry of the waters. Zr and Yt may come respectively from detrital zircon and allanite while some iron may be contributed by various phases including hematite often found high in the formation. $Ra^{226}$, present in anomalously high quantities primarily in the brine component of some waters, may also be added from the uranium present in the uranothorite and, possibly, deposited in small quantities as coffinite just above the unconformity.

The Potsdam surrounds and forms an on-lap facies to the Adirondack terrain, portions of which survived as islands during early Cambrian time (J.R. Dunn, pers. com.). The Potsdam may be up to several hundred feet thick, but because it was deposited on a highly irregular surface its detailed disposition and thicknesses are not predictable. In the immediate Saratoga area the formation outcrops to the west and northwest of the city and is believed to total about 100 ft., thickening rapidly to the east. To the author's knowledge there have been no drillholes driven through the Potsdam in this area so this figure should only be considered as an estimate.

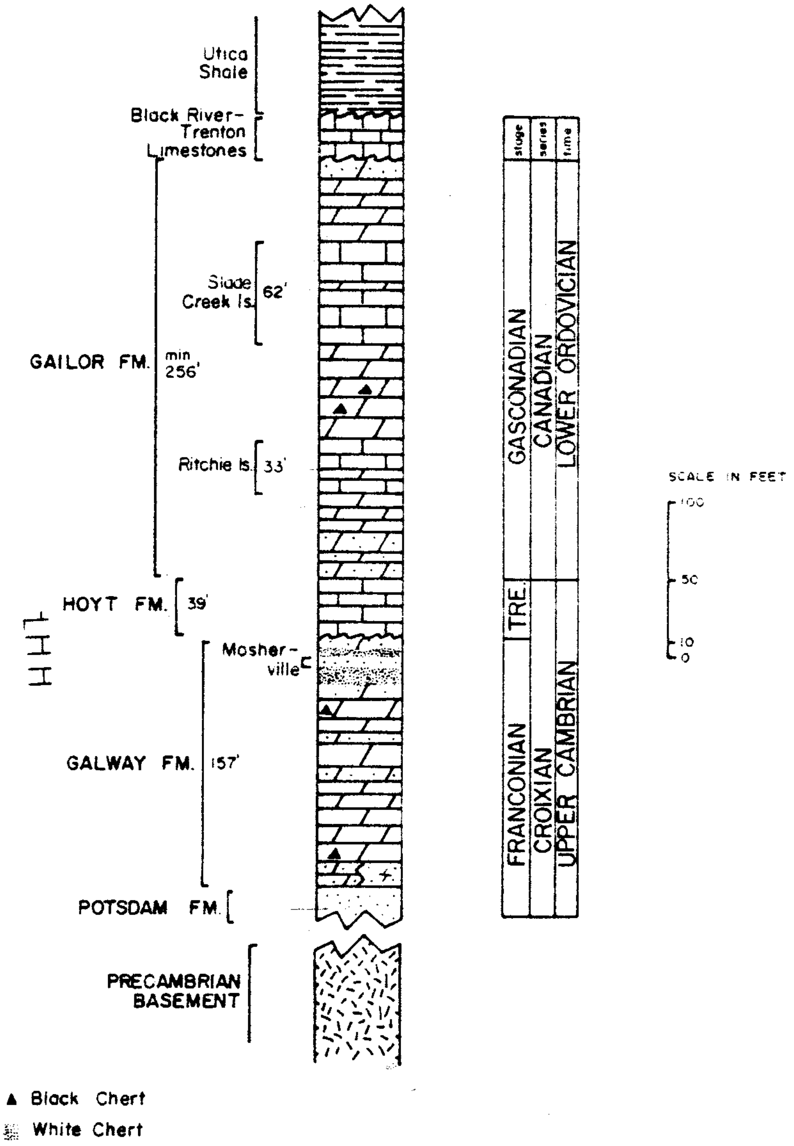
### 2.1.2.2 Galway Formation

The Potsdam sandstones are gradually replaced upwards by the quartzites, quartzose dolostones, and dolostones of the Galway formation without a distinct separating stratigraphic horizon. The Theresa "passage beds" of Colony (1930), this alternating transitional sequence has since been renamed because the type Theresa occurs north of Watertown and is not continuous through the subsurface. The type Theresa is Ordovician in age whereas that in the eastern Mohawk Valley is Cambrian, hence, the preferred name Galway (Fisher and Hanson, 1951; Rickard, 1973).

In the Saratoga area this formation averages about 160' thick but is known to increase fairly rapidly to the west to a possible maximum of about 300' (G. Banino, pers. com.) in the Galway area. The lowermost 60 feet has only been penetrated by a single reliable diamond drillhole in the Pallette Quarry 2 miles west of the city of Saratoga Springs. From this the lower portion is known to be an alternating series of orthoquartzites (remarkably similar to the upper Potsdam sands just below) and quartzose dolostones both averaging 5' to 10' in thickness. The quartz content of the dolostones and the thickness of the quartzites decrease upward in the formation. Dolomites in the lower section are medium to light gray, massive crystalline, fine to medium grained.

Upper portions of the Galway are a rather monotonous series of thinly bedded (one to four feet), fine grained, light to dark gray dolostones relieved only by a few thin (usually less than two feet thick) layers of sands and sandy dolostones. Apparently deposited as lime muds in a low energy supratidal to intertidal marine environment the formation has been extensively dolomitized wiping out most of the primary structures. Authigenic alkali feldspar (microcline) is known to be ubiquitous throughout the formation further to the west (Braun and Friedman, 1968) and probably is present in the Saratoga area as well. The top 16 feet of this formation consists of interbedded light gray, medium grained dolomite interspersed with dark to white chert locally comprising 20% or more of the rock. These chert horizons are commonly oolitic and occur at 2.7, (37 cm thick), 3.4 (12 cm), 4.6 (3.5 cm), and 6.6 (25 cm) meters below the top of the formation (Mazzullo et al., 1978). Further, the cherts are of the distinctive mottled white variety known as novaculite which furnishes a very useful marker horizon in the area. Because the cherts are more resistant to weathering, a local unconformity is discontinuously present in the Saratoga area. While Mazzullo et al (1978) did not discover this feature it is easily visible in the high northern face of the Pompa Quarry where the Hoyt formation rests unconformably on these upper cherts (Figure 2.2). Well developed paleokarsts are abundant beneath this horizon; several of them are also visible in the Pompa Quarry (Figure 2.3).

# GENERALIZED STRATIGRAPHY OF THE SARATOGA AREA



(Modified after Mazzullo etal. 1977)

FIGURE 2

Figure 2.3 Northern face of the Pompa quarry. Note small fault zone in the center of the picture obliquely projecting out of the face at app. N60°E. Displacement about 3 meters.

Figure 2.4 Paleokarst beneath Hoyt/Gailor unconformity. Note the large angular clasts in the blocks at the toe of the face.

At 16.7 and 27.3 meters below the top of the formation are three prominent zones of light gray, medium crystalline dolostone with abundant vugs commonly filled with sparry calcite or dolomite (Mazzullo et al., 1978). At 7.0 meters below the top is a very vuggy zone filled with the above two minerals and, in addition, well terminated clear quartz crystals. This zone may correspond to that one further west in the Tribes Hill formation filled with the famous doubly terminated clear quartz crystals known as "Herkimer diamonds". Dolomite and calcite inclusions (usually white but occasionally rose colored) are found throughout the formation but are more abundant in the above zones. Minor pyrite preferentially occurs in thin beds of dark, carbonaceous dolomite. Lesser sphalerite is also known to occur in the breciated and darker, more carbonaceous beds.

### 2.1.2.3 Mosherville Sandstone

The Mosherville was first described by Fisher (Fisher and Hanson, 1951) as an 8 to 10 feet thick bed of hard, white orthoquartzite occuring at the top of the Galway formation. Fisher further recommended its use as a marker bed throughout the region siting several occurrences other than the type locality of Mosherville. Mazzullo et al (1978) detected a 1 meter thick bed of hard , light cream, cross stratified dolomitic sandstone 5.5 meters below the top of the formation in drill core from the Pallette Quarry. They considered this to be the Mosherville but pointed out the existence of numerous similar beds in the area and questioned its usefulness as a stratigraphic marker.

The author notes that the presumed horizon of the Mosherville is exposed approximeately 1 km west of the Pallette Quarry in the high northern face of the Pompa Quarry, Nowhere is this sandstone unit or an equivalent bedvisible. With this in mind, the proviso of Mazzullo et al is all the more cogent; the usefulness of the Mosherville has been overstated in the past. It is the opinion of the author that the top of the Galway formation should be redefined as the highest layer of novaculite chert. This horizon is prevalent in outcrop throughout the region due to its resistance to weathering.

### 2.1.2.4 Hoyt Limestone

The Hoyt formation has sparked considerable interest in the past literature because of its large, well preserved specimens of Cryptozoon reefs (Figure 2.5). These are well exposed at Lester Park and the Petrified Gardens in the same general area west of Saratoga Springs near the Pompa Quarry. The Hoyt consists of approximately 40 feet of medium bedded, dark gray, fine to coarse textured limestone and subordinate dolostone with abundant stromatolites, crytalgalaminites, and oolites and contains a Trempealeaunan fauna according to Fisher and Hanson (1951) and Taylor and Halley (1974).

### 2.1.2.5 Gailor Formation

The Gailor formation consists of 256 plus feet of medium to thick bedded, light to medium gray, fine to medium crystalline, slightly cherty dolstone with two prominent limestones intercalated within the Saratoga area. Characteristically dark gray, both these limestones are also fine to coarsely crystalline calcilutites difficult to distinguish from one another in the field (Mazzullo et al.,1978). The lower limestone is thought to be the Ritchie member after the type section near the Pompa Quarry described by Fisher and Hanson (1951) and redescribed by Fisher and Mazzullo (1976). The upper limestone is 62 feet thick and is termed the Slade Creek. It has only been identified in core sections from the Pallette Quarry (Mazzullo et al., 1978), never in outcrop.

The remainder of the formation consists of light gray, medium to coarsely crystalline dolomites quite like those of the underlying Galway formation. Field identification of the two can sometimes be very difficult in areas of poor outcrop. Complicating this are rapid facies changes to dark gray, silty and sandy (quartzofeldspathic) medium crystalline dolostone in distances of only a few kilometers (Mazzullo et al., 1978). These two facts pose serious problems for the stratigrapher in this area.

The Gailor formation is the rock unit which is classically supposed to be the primary carrier of the carbonated waters. In this respect the intercalated limestones assume great significance because of their greater solubility in carbonic acid. The waters should be slowly enlarging the fractures and joints within these members to form cavities capable of storing larger quantities of the waters while adding dissolved $Ca^{++}$, $HCO_3^-$, and $Mg^{++}$(from the dolomites) to the waters.

### 2.1.2.6 Trenton and Black River Carbonates

Following deposition of these lower Ordovician carbonates most of the eastern North American shelf was uplifted and eroded to form the regional Knox unconformity. This feature is taken to be the upper limit of the Gailor formation (and its lateral equivalent, the Tribes Hill formation) throughout the Mohawk Valley. Extensive karsting has developed below the unconformity in the upper Gailor as is visible in the type Gailor section in the abandoned quarry in Saratoga Springs (Figure 2.3). Above this has been deposited the Amsterdam limestone, the basal bed of which is a thin, irregular conglomerate containing pebbles of the Gailor dolomites (Cushing and Reudemann, 1914) in the Saratoga area.

The Amsterdam is a thin to shaly bedded, dark gray colored, highly fossiliferous limestone highly reactive in dilute HCl. Its most distinctive features are its conglomeratic appearance and irregular lumpy bedding unlike any other limestones in the area. The Amsterdam averages from 35 to

40 feet thick in its limited exposures in the vicinity of Saratoga Springs.

Above the Amsterdam is an alternating series of shales and limestones some 40 feet thick. This unit is not exposed at the surface but is known from cuttings in the mineral wells drilled throughout the area. Reudemann (1914) has termed this limestone the Glens Falls limestone and assigned a Trenton age to it.

### 2.1.3 The Ordovician Shale "Caprock"

### 2.1.3.1 Canajoharie Shale

The Canajoharie shale is the surface rock in much of the Saratoga quadrangle extending north from Ballston Spa and east to the folded Snake Hill shales in the area of Saratoga Lake. The formation consists of soft black, carbonaceous, more or less calcareous, argillaceous shales quite distinct from those of the Normanskill-Snake Hill. The former weathers a characteristic light drab like the Utica Shale while the latter weathers grayish brown or spotted or whitish when somewhat siiceous (Cushing and Reudemann, 1914). Frequently intercalated among the soft shales are harder, bluish gray muds indurated by calcite which are mostly 3 to 6 inches thick but occasionally reach as much as 3 to 4 feet. These mud beds fracture conchoidally while the shale is fissile and splintery. Its uniform, carbonaceous, fissile character is the most distinguishing feature of the formation (Cushing and Reudemann, 1914).

Much of the shale contains abundant pyrite which oxidizes to fill the cleavage and bedding planes with rusty brown lmonite and is also probably responsible for the minor $H_2S$ and $SO_4^=$ in some of the mineral wells. The formation is also known to contain anomalous uranium scavenged by the carbonaceous matter in what was probably a reducing environment. It may ultimately be the source of the $Ra^{226}$ in the waters, though this is unlikely for reasons discussed in section 4. 10.

Because the shale is very soft its occurrence in outcrop is rare. For the most part it is covered by glacial debris, emerging only in roadcuts and in streams which have cut through the drift to expose the shales in their higher portions. The best exposures occur along the Kayderosseras Creek in Ballston Spa and along the Northway just north of exit 12. Estimates of its total thickness vary from 1000 feet (Reudemann, 1930) to 1100 feet (Cushing and Reudemann, 1914) based on inference from topographic relief.

### 2.1.3.2 The Schenectady Formation

The Schenectady formation overlies the Canajoharie shale on the surface in most of the study area west of the Taconic allochthonous front. They appear west of Saratoga in the town of Galway and thence extend in a broad belt southwest to the Helderberg Escarpment and eastward to Logan's Line.

In the lower Mohawk Valley the formation consists of about 2000 feet of light gray bluish to dark gray silstones, sandstones, and subgraywackes interbedded with silty dark gray shales forming a monotonous, uniformly alternating series. Resembling a turbidite sequence, these rocks were probably deposited in a relatively shallow water distal shelf or proximal slope environment. Abundant mud cracks in the shaly facies attest to this.

### 2.1.3.3 The Snake Hill Shale

First identified by Reudemann(1911), the Snake Hill shale outcrops in the easternmost portion of the Saratoga quadrangle in the area of Saratoga Lake, the type locality. The formation is comprised of medium dark gray, silty, micaceous shales with intervals of thin to thick bedded gray (weathering tan) siltstones and fine to medium textured sandstones (Fisher, 1977). The dark shales not infrequently containthin intercalations of sandy limestones and gray crystalline limestone reaching half a foot in thickness (Reudemann, 1930).

The Snake Hill is severely folded and, perhaps, faulted (thrust faulted) in all its exposures. This has made estimates of thickness difficult, however, Reudemann (1930) places a minimum value of 3000 feet on the formation. The rocks are depicted on the New York State geological map (1970) as allochthonous sheets forming a discontinuous zone from Glens Falls south through the Capital District.

## 2.2 Structure

The structure of the greater Saratoga area can be subdivided into several provinces. To the north are the complexly folded and faulted Precambrian rocks of the Adirondack massif. Their structure has been the topic of several recent studies in which some workers have suggested these rocks have undergone as many as 5 different episodes of folding (McClelland, 1970; Turner, 1979). Other studies have shown these rocks to also be literally "diced" by many high angle normal and reverse faults. Most of these are older faults that have been reactivated by the recent doming of the Adirondacks (see section 9.0). Their dominant trend is approximately N20E; consistent with the long axis of the elliptical dome or arch. A subordinate (possibly conjugate) NW trending set is also present. Both these fault sets manifest themselves in rather pronounced topographic scarps that are suggestive of true fault scarps, not merely fault line scarps.

The second areal province is considered to be that of the Taconic allochthon and its possible western outliers of Snake Hill shales which are prevalent in the Quaker Springs USGS 7.5" quadrangle. These rocks are also complexly folded and faulted, however, they have undergone only the mildest degree of metamorphism to slates (?) and phyllites in the southern portions of the allochthon, A well pronounced slaty cleavage with consistent easterly dips is diagnostic of these rocks. So too are a multiplicity of low angle easterly dipping thrust faults along which the pelitic rocks of the allochthon are postulated to have been moved tens (perhaps more than 100) of kilometers westward. Possibly situated above undeformed autochthonous shelf sediments, these rocks provide an added dimension to the caprock, probably making it extremely difficult for the carbonated waters to rise to the surface in these areas.

The third structural province is that of the relatively undeformed Paleozoic sediments west of the allochthonous front throughout most of the study area comprising the Cambro-Ordovician aquifer and caprock of plate 3. For the most part these rocks are nearly horizontal or have a very gentle dip south of only a few feet per mile. Only in the immediate vicinity of faults do the dips change significantly to as much as 20° or more. At first sight this description would seem to constitute the simplest of structural environments. The rocks, however, are broken by numerous high angle normal and reverse faults similar to the Precambrian rocks of the Adirondacks only to an even greater dgree. While complicating the picture to some extent, several valuable pieces of information can nonetheless be gained from a consideration of this faulting. Since the patterns present here have the largest bearing on the flow patterns of the waters in the aquifer and the regional tectonics, they will be discussed below in some detail.

### 2.2.1 Faulting in the Paleozoic Rocks- Dominant Trends

The dominant fault pattern in the flat-lying Paleozoic rocks around the southern periphery is the same as that through the Adirondacks- NNE. Several large through-going faults continue southward out of the Adirondack Highlands that decrease in throw away from the mountains. Like their more numerous northern counterparts, these faults are generally normal with their western sides upthrown at very high angles usually between 70° and 90°. Approximately 12 of these faults with measurable displacements over 100 feet extend southeasterly from the Adirondacks into the Mohawk Valley (Fisher, 1954). All decrease in throw to the south and tend to "hook" to the west at their southernmost limits (D. Fisher, pers. com.). Of these 4 are unusually large and deserve special mention:

(1) Little Falls Fault- The most westerly of the major step faults, the Mohawk River has carved out a large gorge in the upthrown block at Little Falls. Displacement is about 900 feet at the Mohawk River.

(2) Noses Fault- Perhaps the most visible fault of the group, the Noses Fault forms a very prominent easterly-facing fault scarp. The western, upthrown block is Precambrian basement with the Lower Ordovician beds outcropping at the summit. Displacement at the Mohawk River is approximately 850 feet.

(3) Hoffman's or Wolf Hollow Fault- This fault is

comprised of approximately 3 smaller faults 10-12 miles due west of Saratoga Springs. These combine to form a single large break crossing the Mohawk River at Rotterdam Junction. Fisher(1954) has estimated the displacement at the Mohawk River to be about 1600 feet. Work by the author further north, however, suggests 500 feet to be a more reasonable estimate.

(4) McGregor Fault- The McGregor Fault has been mentioned elsewhere in this report as the large fault in the Saratoga area juxtaposing the Precambrian Adirondack Highlands to the west with the easterly Paleozoics of the lowlands. This fault actually divides just north of the city where it breaks up into several lesser faults including the Ballston Lake-Saratoga Fault (Isachsen, 1978). Displacement immediately north of the city probably exceeds 1000 feet.

These are the large visible faults. Two more of similar magnitude may be inferred from linears to lie to the east of the McGregor Fault. One probably lies under the present Hudson River. This may be inferred from the strong linear aspect of the Hudson and its right angle bend to the northwest at Hudson Falls. The second may lie under the preglacial Hudson River channel that is now defined by lakes Saratoga and Round (Dineen, 1979). Should these linears define faults it is interesting to note the gradual shift in direction of these major faults. The Little Falls, Noses, and Hoffman's Faults strike approximately N20E. The latter three gradually strike more N-S: McGregor N10E, paleo-Hudson N5E, and the present day Hudson due north. This shift may indicate a basic difference in the stress regimes reactivating these older faults. This will be discussed further in section 9.0.

### 2.2.2 Faulting in the Paleozoic Rocks- Subordinate Trends

In addition to the major NNE faults there are several sets of smaller faults with lesser displacements in the Paleozoic cover around the southern Adirondack periphery. These can be most easily seen in the areas of carbonate outcrop which are literally diced by these normal faults. They are so numerous, in fact, that it is difficult to select a position from which to walk a half mile without crossing at least one fault. In the shale-covered areas this relationship probably holds as well, however, due to their greater plasticity or weakness faults do not tend to form traceable fault scarps as in the carbonates. This can be best seen in plate 3 in the outcropping dolomites west of Saratoga Springs which are literally a structural "hash". In the area of the city southward to Ballston Spa (shale covered) only a few linears can be traced in the topography which probably indicate throughgoing faults.

An examination of two areas around the periphery are sufficient to ascertain the fault patterns. The chosen areas are the Saratoga Springs USGS 7.4" quadrangle (Plate 3) and the Pattersonville 7.5" quadrangle (Figure 2.4) 20 miles further west and some 5 miles south. The Saratoga Springs quadrangle is mapped with most faults verified by field inspection and/or drillhole data. The Pattersonville area has been only cursorily mapped, however, the faults have been inspected in the field.

The first feature to be noticed when examining plate 3 is the large number of faults in the outcropping carbonates. The trend of the major set is from N60E to N40E while a far smaller conjugate set strikes between N40W and N15W. The evidence from field mapping and numerous drillholes in the area of the Pompa crushed stone quarry is compelling that the major fault set is comprised of normal faults with predominant vertical movement- not strike-slip movement. Development of these small horsts and grabens is characteristic of block faulted areas such as the much larger Basin and Range Province of the western United States, The classic interpretation of block faulted regions is that they have been extended perpendicular to the strike of the faults or subject to extensional strain. In this context it is important to note that perpendiculars drawn to the major fault set extend through the center of the Adirondacks.

Some degree of qualitative age dating of these faults can also be attempted in this area. Figure 2.2 is a photograph of the north face of the Pompa quarry. In it 3 separate faults parallel to the major N60E trend are visible

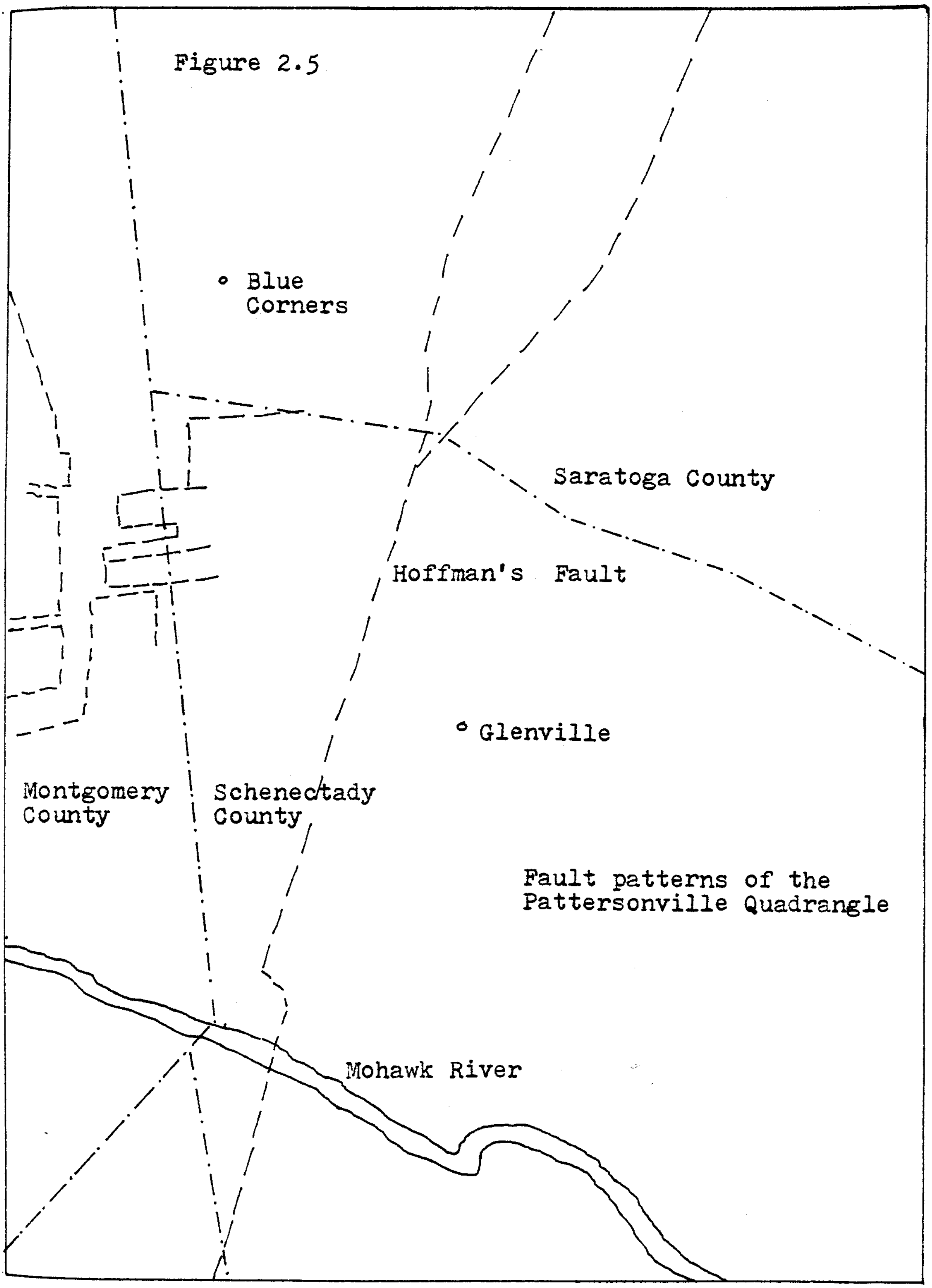


Figure 2.5

Fault patterns of the Pattersonville Quadrangle with total displacements of less than 5m apiece. The largest of these (~5m) may express itself on the surface by a slight depression in the topography, however, this is uncertain since the present erosion surface corresponds to an unconformity overlain by the Hoyt limestone (see section 2.1). Two major faults striking N60E through the Pompa quarry several hundred feet south of this face provide even better evidence. Drillhole data confirm the presence of a downdropped block between these two faults (see Plate 3) while the topography gives few clues as to their presence. Immediately east of the quarry across the Petrified Gardens road the faults have a topographic expression of about 100 feet. The western wall of this graben is another fault scarp with calcite-filled tension gashes visible at the toe of the scarp. The juvenile aspect of these scarps argue strongly for a recent reactivation of these portions of the two older faults. The presence of dolomite at the bottom of the graben argues against exhumation of a shale-covered paleo graben and the ENE strike of the graben argues against glacial ice gouging as a mechanism of formation. The only viable alternative would appear to be relatively recent activation. This follows from studies of erosion rates which indicate that features on the order of 100 feet should be completely beveled in approximately 200,000 years. Even more significant are the other small horsts and grabens in this area which have low scarps on the order of 20 to 50 feet with a similar amount of topographic expression. In fact, almost all topographic map linears in the carbonates are found to be fault scarps when inspected in the field.

In the Pattersonville quadrangle we find a similar pattern of numerous small block faulted topography only in the carbonates. Here, however, the strike of the principal set is E-W with a conjugate N-S group. Here, too, is a small graben complex (Crane's Hollow) striking N-S with E-W breaks along its length reminiscent of oceanic transform offsets. Perpendiculars to this set also pass through the center of the Adirondack uplift, however, here those perpendiculars are N-S in direction. The combination of these two data sets are compatible with tensional stress from the domical uplift as the cause of this block faulting pattern. No other explanation seems easily reconciled with the youthful aspect of these faults or their shift in direction along the periphery.

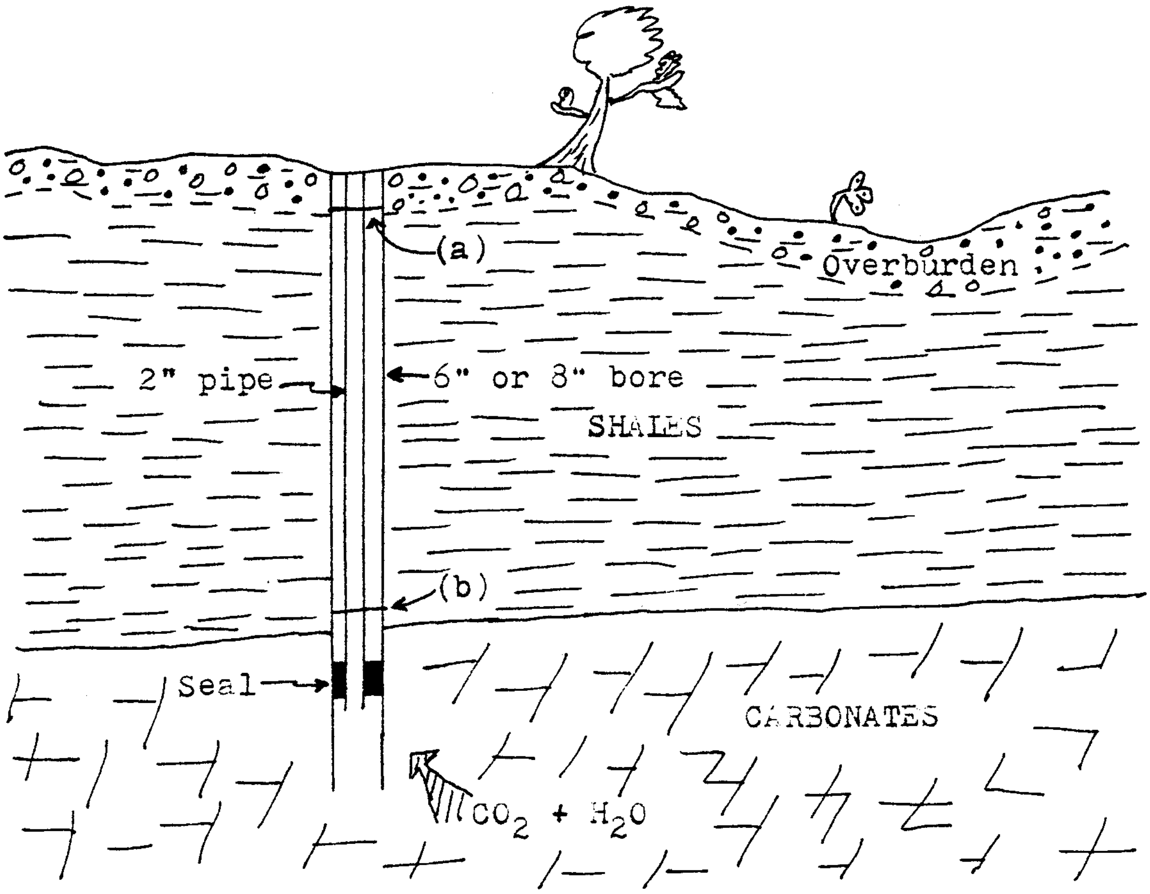
Another interesting characteristic of this faulting can only barely be discerned in the two maps of these areas and has been confirmed by other discussions (D. Fisher, per. com., 1979). That is that the magnitude and intensity of the block faulting decreases from Saratoga westward around the periphery. So, too, does the frequency. This relates well to the geomorphology of the uplift which indicates the eastern Adirondacks to be the area of greatest uplift ( the High Peaks region). It may also be related to the increase in displacement eastward of the 4 major step faults and their gradual shift to a more N-S direction.

A final point to consider about the subordinate faulting is its effect on the flow patterns of the carbonated waters. Because the carbonates are so broken throughout their range around the southern periphery it is reasonable to infer that they are also broken by numerous faults underneath the masking shale caprock. These breaks should have at least two counterbalancing effects. First, the large number of small breaks should tend to develop a maximum of fracture permeability. At the same time, larger breaks, particularly reverse faults, will tend to isolate aquifer subsystems such as the $NaHCO_3$ basemant fluid and saline waters of variable chlorinity. This should contribute to a heterogenous pattern of water mixing such as is presently observed among the wells of the Saratoga group.

# 3.0 THE WATERS

## 3.1 Some Physical Observations

As was mentioned earlier, all but a few "springs" are, in fact, driven wells puncturing a thin shale and/or hardpan cap to tap the carbonated mineral waters of the carbonate/ sandstone aquifer below. Records show that 27 mineral water wells have been drilled in Ballston Spa (B. Puckhaber, pers. com.) while over 150 have been drilled in and around the city of Saratoga Springs, many of which are shown on plate 3. Only a few are still active today and only a few (<10) have been drilled since 1950. These factors largely determined the sites sampled during this study.



Most of the newer wells employ submersible pumps to raise the water to the surface i.e. Rosemary and Big Red. The older sources, however, relied on an ingenious combination of devices utilizing the gas pressure as a motive force. This method is described for a typical well in figure 3.1.

When a "vein" or fracture controlled discharge of carbonated water was struck, drilling would terminate from 10' to 20' beyond this point. A seal made from leather, wood, or rubber would then be fitted with tubing (usually less than 2" diameter) and lowered to a level just above the producing zone. This would serve to segregate the upper meteoric waters while permitting the lower mineral waters to rise up the narrow tubing to the level of the hydrostatic head. In a typical well 170 feet in depth water flows into the bottom under a pressure of 70 pounds/square inch, which will, under ordinary circumstances, support a column of water approximately 160 feet in height- level (a). In an average well with a $p_{CO_2}$ of 2.5 atm. the gas will begin to exsolve at level (b) with the result that its specific gravity will continually decrease as it ascends the well. Assuming an average specific gravity of the frothy water as .5 that of the water below level (b) the hydrostatic pressure would then sustain a column of the gaseous water 75 feet beyond level (a) equal to the distance between (a) and (b). In other words it will eject the water from the mouth of the well with a pressure of 15 pounds/square inch- sufficient to throw it high in the air.

This principle applies in all wells with varying degrees of efficiency depending on the $p_{CO_2}$ and the height of the local water table. In most cases the effect is not as pronounced as in the hypothetical well above although a few wells have been this dramatic. The Champion #1 well, active in the late 1800's, continually spouted a dozen or so feet in the air and could be made to gush to heights of 80 feet or so by placing an iron plate over the mouth for several hours allowing the gas pressure to increase to 10+ atmospheres. In wells with an insufficient combination of factors to raise the water to the surface without a pump the desired result may still be achieved by tapering the final 10 to 40 feet of the tubing. This will also increase the effective $p_{CO_2}$ and force the water above the surface as in the Island Spouter well below:

Island Spouter well in Saratoga Springs Reservation along Geyser Brook.
Water is forced up the 2" pipe which tapers to ¾" over the top 30' to increase effective $pCO_2$

## 3.2 Distribution of Saratoga- Type Waters

Carbonated saline waters of the Saratoga type are found over an area of approximately 1000 square miles in the upper Hudson Valley region. The location of all sampled and several unsampled locations for which partial published analyses are available are shown on the plate 4. Inspection shows them to be bounded on the west by the Hoffman's and McGregor faults. To the south the boundary appears to approximate the Normanskill Creek since only uncarbonated saline waters are found south of this limit to the Helderberg Escarpment. While no carbonated wells were found in the city of Albany during this study, the occurrence of one drilled in 1827 on South Ferry Street is recorded in the literature (Kemp, 1912). The northernmost carbonated water site is also recorded by Kemp as the Adirondack Spring in the town of Whitehall. This is now defunct, however, a private saline water well with high bicarbonate content and no free gas (Davis well) was sampled in Smith's Basin only 20 miles south of Whitehall.

The carbonated waters from this study are confined to the undeformed rocks west of Logan's Line- the allochthonous front. Since this time, however, several private water wells with meteoric water, methane, and free $CO_2$ have been located in the Taconic thrust sheet in the towns of New Lebanon and Cambridge. The presence of $CO_2$ has been verified by a simple $Ca(HCO_3)_2$ precipitate. Analyses are not available at the time of this writing, however, the data is mentioned to illustrate the large area underlain by the gaseous waters.

Several intesting points occur with regard to the distribution of the waters:

1) The saline carbonated waters are only found west of Logan's Line in areas underlain by the undeformed shale caprock.
2) The melange sequence at the western edge of the allochthon hosts Reid's Mineral Spring (a natural spring) and several other occurrences further south near the town of Melrose.
3) All known occurrences of the carbonated waters (public and private) are situated along either known faults or prominent surface linears.

From this data it seems reasonable to conclude that faults and fracture systems are the principle upward conduits for the carbonated waters trapped beneath the shales as was suggested by Kemp (1912) and others. It also seems reasonable to assume that the waters may underlie the western margin of the allochthon, as is suggested by the many occurrences along the melange sequence and the few interior ones (apparently $CO_2$ gas in meteoric water) which further suggest the thicker allochthonous sequence may serve as an effective caprock.

## 3.3 Temperature

Temperature measurements were performed on each of the waters during sample collection (Plates 1 and 2) and are summarized in Table 4.1. In general these have not borne out the earlier conclusion that the carbonated waters of the Saratoga group are 2° to 4°C warmer than normal. Earlier measurements upon which this comparison is based were made in shallow gravel aquifer wells (Kemp, 1912; Heath, 1963). When juxtaposed against meteoric water wells of similar depths in the area there is, in fact, a trend for the meteoric waters to be from 1° to 2°C warmer than the carbonated waters

This distinction is reinforced by several comparative temperature measurements made at sites in the Saratoga Springs Reservation. The results are as follows:

| SAMPLE SITE | SPRING | FALL |
|---|---|---|
| Ferndell Spring<br>(free flowing hillside spring) | 6.2 | 14.1 |
| Geyser Brook | 7.1 | 13.5 |
| State Seal<br>(approximately 140' well into shale) | 6.1 | 15.5 |

Table 3.1 All measurements in °C.

While these measurements indicate that the carbonated wells are from 2° to 8°C warmer than shallow ground water in the spring, the measurements made of the water from the control wells of similar depths display far less variation. The deep ground water group, then, should be considered a more representative check than shallow well or surface water.

During the spring and fall samplings anomalously high temperatures are exhibited by the Red, Doster, Yezzi, and Bloodgood wells. The latter three are private residences with unusually large holding tanks in the cellars. Anomalous temperatures at these particular sites are probably due to incomplete flushing of the tanks despite long discharge periods prior to temperature measurement. The first member of this group, the Red Spring, is a free flowing well at the northern end of the Saratoga Fault in Saratoga Springs. Situated less than 1,000 feet north of the Peerless Spring, the Red is essentially a sodium bicarbonate type water in major chemistry and possesses a distinct excess of silica. The elevation in temperature is very slight, however, and does not justify an optimistic interpretation of thermal water at relatively shallow depths of less than a kilometer.

Close inspection of plates 1 and 2 shows another 1 to 2 degree negative temperature shift with increasing $HCO_3^-$, and, in most cases, free $CO_2$ among the waters of the Saratoga group. This further suggests that the exsolution of gaseous $CO_2$ as the waters rise up the wellpipe lowers their temperature. This effect has been quantified at the Kizildere geothermal field in southwestern Turkey where exsolution of a 1.5 to 2.0% content of dissolved $CO_2$ gas (by volume) traveling up a 500m borehole cools the fluids about $10^{\circ}C$ from an ambient temperature of $190^{\circ}C$ (James, 1975).

## 4.0 WATER CHEMISTRY

### 4.1 Thermal Waters

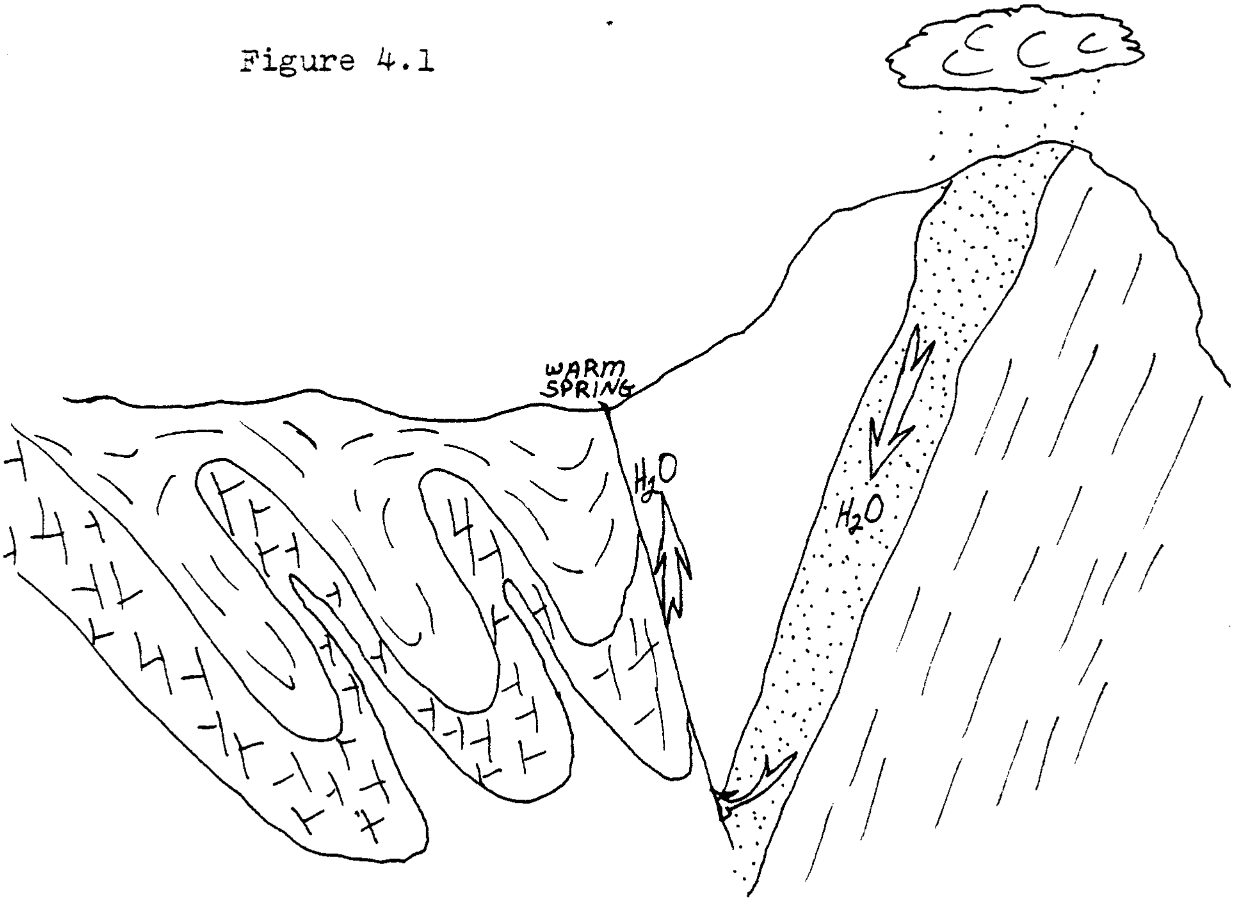
Thermal waters from the two presently known locations in the Northeast were sampled and designated as such in plates 1 and 2. The Lebanon Springs site consists of a single high flow spring (approximately 500 gpm) issuing from a bedrock fracture within a developed spring house excavated through thim glacial cover just west of a major thrust fault separating the Stockbridge limestone and the Walloomsac slate. However, at Williamstown, Massachusetts, about 15 miles north northeast, several thermal water wells are known, including Sand Springs which issues along the same fault system from Pleistocenc cover at a reported discharge rate of about 400 gpm at a fairly constant 74°F. A private residence approximately 100 meters distant with similar thermal water (residence of Fred George) was selected for sampling for logistical reasons.

The analyses indicate that these waters are very similar to each other and normal surface ground water in this area (Hobba, 1976, 1979). The slight relative enrichment of $Ca^{++}$, $Mg^{++}$, and $Sr^{++}$ in Lebanon Springs probably reflects leaching of the Stockbridge limestone while the minor sulfate may be a product of oxidation in the slates.

The low TDS values of these waters and their low contents of silica (9.1 & 10 mg/l in the spring and 15 & 16 mg/l fall) indicate that these waters have not been heated much above their present temperature; perhaps a maximum of 30° to 40°C (Hobba, pers. com.). In September 1979, a thermal gradient measurement was made by the author in an abandoned water well in the hamlet of Stephentown, New York, 5 miles north of Lebanon Springs. The well was drilled 503 feet into the Walloomsac slate and yielded a gradient of 14.9°C/km. This indicates that the Lebanon Springs water may have circulated as deeply as 2 km (assuming normal shallow ground water temperatures as 10°C and maximum heating to 40°C) to intersect the thrust fault.

Recent interest in alternative energy sources prompted examination of most of the Appalachian warm springs. From this research has evolved a deep circulation model common to all the southern occurrences that is diagrammed below:

Figure 4.1



The essential ingredients of this model are: 1) high angle faulting which serves as a rapid upward conduit for the waters and 2) steeply dipping rocks with high fracture permeability transmitting large amounts of surface water to unusually great depths. In this context it is interesting to note that topographic lineaments, of the type usually associated with high angle faults in the Taconics, occur in both Lebanon Springs and Williamstown. Similar, too, is the Stoackbridge limestone which possesses high fracture permeability as do the quartzite beds of the southern Appalachian warm springs.

Conversely, it is interesting to note that these two sites host the only known thermal springs north of Virginia. Their presence in the same area as free $CO_2$ discharges is a geologically suggestive and curious coincidence, nonetheless, the data indicate that this is what it is- a coincidence.

## 4.2 Meteoric Water Control Wells

A group of four wells tapping normal surficial ground water was selected as a control group in the immediate vicinity of Saratoga Springs. Two of these are driven into the Gailor formation west of the city (Pompa and Y.K. Greene) while the other two (Bloodgood and the Saratoga Veterinary Hospital) are located in the overlying shales east and north of Saratoga Springs.

Plate 2 shows these waters to subgroup according to lithology with wells in carbonate rocks having higher $HCO_3^-$,

$Cl^-$, $Ca^{++}$, and $Mg^{++}$ concentrations than non-carbonate rock wells. The molar ratios of tables 2s and 2f of the appendix also show a distinct separation of these waters from the other groups which can be used as a basis for interpretation. The only anomaly in the group appears to be the Pompa well which has a relatively high concentration of NaCl for normal ground water. Since this well is situated within 50 feet of a major east-west fault it seems very possible that it may contain a small component of Saratoga-type water transmitted along this conduit.

## 4.3 Southern Saline Waters

The southern saline waters group includes 6-7 wells (sampled spring and fall), 4 of which may be examples of diluted, yet chemically characteristic basinal brines or formational waters (White, 1965). As such, they are very important since they provide some means of gauging the proportions of elements added by carbonic acid leaching and thermal effects to form the Saratoga-type waters. The exceptions in this group are: the Figliomeni well, a neutralized high bicarbonate water; the Pattersonville well, a complex mixed type with some Saratoga components; and the Congly well which is situated in an area of known (unavailable for sampling) carbonated waters and which may also have mixed components- notably $K^+$.

The chemical parameters of the remaining four wells show some significant patterns as follows:

## WATER GROUP SUMMARY

|  | Saratoga Springs | North Central | Southern Brine | Thermal Waters | Control Wells | Sulfate Waters (Mixed Types) |
|---|---|---|---|---|---|---|
| Temperature |  |  |  |  |  |  |
| Spring | 9-12° C | 8-14° C | 9-16° C | 22-23° C | 11-13° C | 9-13° C |
| Fall | 10-14° C | 11-16° C | 11-14° C | 22-23° C | 11-16° C | 9-13° C |
| Carbonation | Free $CO_2$:1200-5000 mg/l $HCO_3$ | Free $CO_2$: 900-2750 mg/l $HCO_3$ | Uncarbonated: 250-400 mg/l $HCO_3$ | Uncarbonated: 100-160 mg/l $HCO_3$ | Uncarbonated: 2-360 mg/l $HCO_3$ | Carbonated and uncarbonated |
| Total Dissolved Solids | 2000-15,000 mg/l decreasing northward | 4000-1200 mg/l | 4500-1900 mg/l | 200-100 mg/l | 500-100 mg/l | 5500-2500 mg/l |
| Major Chemistry | $HCO_3 \geqslant Cl > Na$ | $HCO_3 > Na > Cl$ | $Cl > Na > HCO_3$ | Variable | Variable | $SO_4 > HCO_3 > Cl > Na$ |
| <u>Minor Chemistry</u> |  |  |  |  |  |  |
| Potassium | Large Excess 40-340 mg/l | Intermediate Excess 20-70 mg/l | Normal 7-11 mg/l | Normal 1 mg/l | Normal 0-3 mg/l | 8-50 mg/l Excess in carbonated wells |
| Silica |  |  |  |  |  |  |
| Spring | 7-46 mg/l | 8-15 mg/l | 5-11 mg/l | 9-10 mg/l | 6-7 mg/l | 9-14 mg/l |
| Fall | 12-70 mg/l | 13-22 mg/l | 10-17 mg/l | 15-16 mg/l | 11-12 mg/l | 15-22 mg/l |
| Zirconium | Anomalous | Anomalous | Not Detected | Not Detected | Not Detected | Anomalous in carbonated wells |
| <u>Molar Ratios (Spring)</u> |  |  |  |  |  |  |
| Na/Cl | .65-1.13 | 1.0-3.5 | .73-1.14 | .98-1.20 | 20-40 | Variable |
| Na/K | 11-26 | 22-92 | 140-170 | 9-40 | 63-83 | Variable |
| Cl/K | 11-28 | 12-45 | 80-180 | 8-40 | 1.5-3.0 | Variable |
| $\frac{Br \times 1000}{Cl}$ | 6-16 | 10-60 | 5-9 | 18 | 12-70 | Variable |
| Ca/Mg | .6-2.8<br>Variable | 1.0-3.1 | 2.2-2.7 | 1.1-1.5 | Variable | Variable |

1) High $Cl^-$, $Na^+$, $Br^-$, $I^-$, and $Sr^{++}$
2) Low $HCO_3^-$, $K^+$, and $SiO_2$
3) Undetectable $Zr^{++}$
4) Distinctive groupings of the following molar ratios: Na/Cl, Na/K, Cl/K, and Cl/Br

When compared with the chemistry of other basinal waters and brines in marine sedimentary basins (Table 6.4), the waters in this group appear to have very similar chemical patterns and may have a similar origin as well, (White, 1965). The only essential difference between these waters and the true basinal brines is their very dilute nature, consequently they are more properly termed saline waters.

Figures 6.1 and 6.2 best illustrate this distinction among water types. While the salinity of these waters as sampled peaks at about 5000 mg/l, a vector was drawn to indicate the expected composition trend without assuming this value of salinity as a limit. In fact, evidence of higher salinities exists in the three most saline Saratoga wells (Hathorn #3, Orenda, and Bischoff) which appear to have a larger saline water component. Past analyses, too, indicate values for TDS on the order of 20,000 ppm to have been fairly common in the now defunct Ballston Spa wells suggesting that "pristine" or original brine (corrected for $HCO_3^-$, etc.) may have been of 1% or more total salinity, (see section 6.2 for further discussion).

## 4.4 Saratoga Springs Group

The sampled wells of this group were selected on the basis of availability, representative chemistry and location. Many wells were not sampled due to redundancy and the presence of earlier analyses. However, enough were selected to establish trends by comparison with previous results. These are arranged from south to north on plates 1 and 2 (Old Iron through Gurn) and as numbers 1-14 on all tables in the appendix.

The primary and striking feature of these waters is, of course, the presence of large amounts of dissolved $HCO_3^-$ and $CO_2$. Field and laboratory alkalinity titrations were performed on these samples during the same day with close agreement. They show amounts of $HCO_3^-$ up to nearly 5,000 ppm (Titrated Alklinity in tables in the appendix) present in two of the wells with a mode of approximately half this value. pH measurements vary from 5.5 to 6.5 at the wellhead, yet values less than this are probable in the aquifer resevoir since the pH rises rapidly with the exsolution of gaseous $CO_2$. Indeed, measurements were found to be several tenths of a pH point higher when made in a beaker at the wellhead less than a minute after collection than when the probe was held directly in the discharge. While all pH measurements were made in this second fashion, the variation makes values of less than 5.0 in the resevoir seem reasonable.

Perhaps the second major feature of this group of waters is their obvious saline nature, NaCl or common salt being the primary constituent of most wells. If the uncarbonated southern waters can be considered representative of unaltered saline water, their molar Na/Cl ratios fall in the range .70 to unity (Table 4.1 and Tables 2s and 2f of the appendix). This tendency toward $Cl^-$ enrichment beyond stoichiometric NaCl is characteristic of most basinal brines (White, 1965), and is seen here in the more saline wells of the Saratoga group (Table 6.4). Tables 2s and 2f of the appendix show, however, that there is a general trend toward relative $Na^+$ enrichment from south to north within this group which correlates with a general decrease of total dissolved solids. This is particularly apparent in the anomalous Rosemary well which is truly a sodium bicarbonate water.

As can be seen in figure 4.1 the relative amounts of potassium contained in the Saratoga group waters is distinctly higher than that of other North American basinal brines or ordinary sea water. While most brines of younger basins contain far higher total dissolved solids (from 200,000 to 300,000 ppm or more) some, such as the Illinois Basin, contain less (from 5,000 to 8,000 ppm). In all cases the relative abundance of potassium is less than that of seawater-except for Saratoga-type waters. In fact, the discrepancy for the Saratoga group waters is even larger than illustrated, since the total dissolved solids in Saratoga waters includes appreciable amounts of bicarbonates not found in other basinal brines.

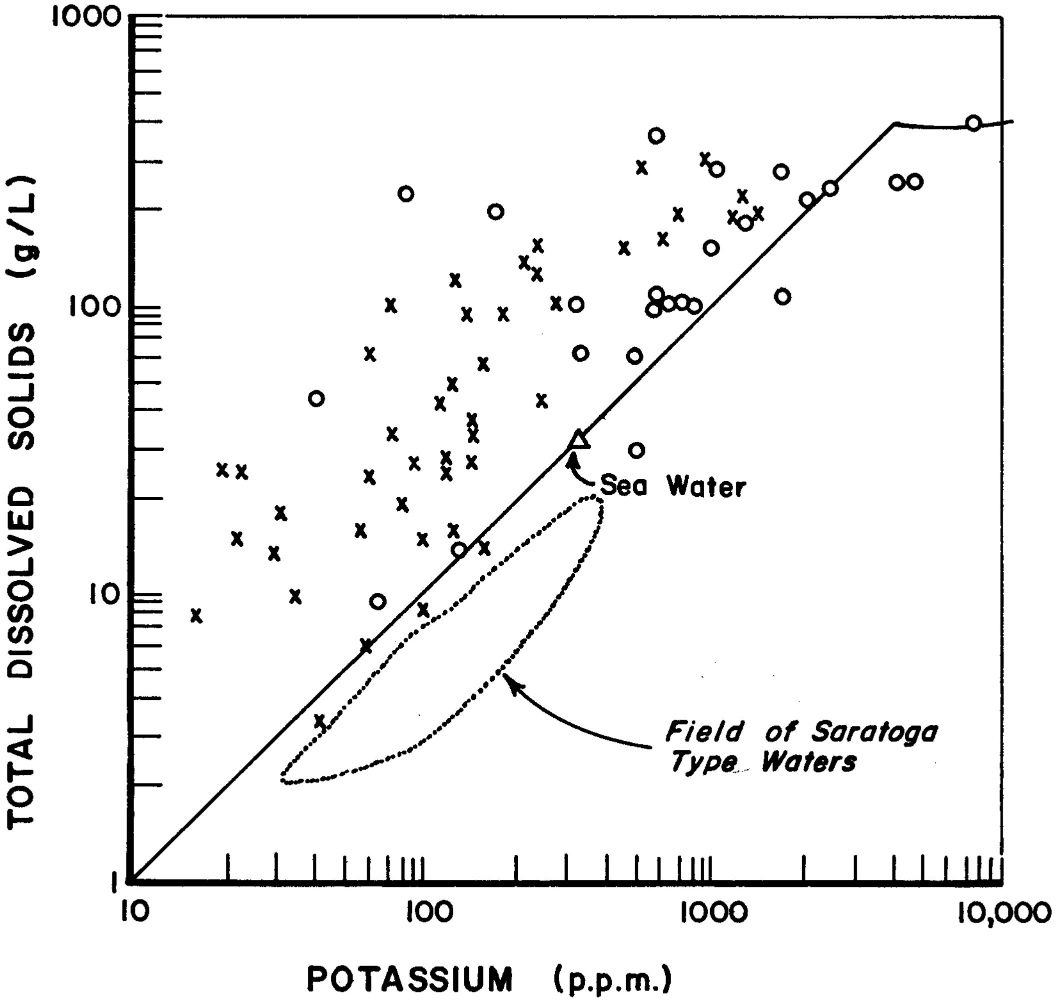


Figure 4.1 POTASSIUM CONTENTS vs. TOTAL DISSOLVED SOLIDS IN OIL FIELD BRINES AND SARATOGA WATERS

OIL FIELD WATERS FROM SANDSTONE (o) & CARBONATE (x) RESERVOIRS

*from Rittenhouse, G. et al. 1968*

Of the diverse suite of trace elements present in this group of waters, Br, I, Sr, Ba, and Li are considered important because they are usually diagnostic of basinal brines. While some proportion of these components may be derived by carbonic acid leaching of the Paleozoic carbonate aquifer and the underlying basement complex, the relatively high values of these elements varying in concert with the total dissolved solids content should be considered good evidence of incorporation from a saline water component. Further testimonial is provided by the similar correspondence of element contents in relation to TDS value among the southern saline waters group.

Among the trace elements, zirconium contents appear to be anomalously high. Analyses of over 2,800 samples of oil field brines provide a reliable data base which indicate normal $Zr^{++}$ contents of about 10 ppb in basinal brines. Both sets of analytical results here show zirconium to be sporadically distributed in distinctly anomalous amounts approaching 400 ppb. Normally this could be considered a clear indication of reactions at elevated temperatures since the mineral zircon (the primary source of zirconium) is extremely stable at temperatures of less than 200°C. Unfortunately this must be considered equivocal information in the case of Saratoga since information is lacking about the efficiency of carbonic acid leaching of zirconium and its transport in aqueous $CO_2$-bearing systems. Moreover, its presence in the north central group where a cooler subsurface temperature is indicated could mean that leaching is the preferred mechanism. For now this remains an open question.

Silica (as $SiO_2$) is present in distinctly anomalous amounts only in the Saratoga group of waters. Since this is considered the clearest indication of a subsurface thermal system it will be discussed separately under geothermometry.

## 4.5 North Central Carbonated Waters

This group includes five wells and springs located east and north of the city of Saratoga Springs as shown on plate 3. In the principal aspect of carbonation these wells are similar to the Saratoga group, but in most other respects they are quite different.

The essential characteristics of this group are perhaps best shown by the molar ratios in tables 2s and 2f of the appendix and the water group summary, table 4.1. Na/Cl and Cl/Br ratios indicate that most of these waters are sodium bicarbonate in nature like the Rosemary of the Saratoga group. Sodium is present in great excess in the Martin well in contrast to depletion in Cl and Ca.

The major chemistry of this fluid would seem to be essentially $HCO_3>Na>Cl>K$ in nature on the basis of the data for the wells of this group (Plates 1 and 2). This pattern may result from the addition of a carbonated Na-rich basement fluid component to the aquifer.

Another interesting aspect is the relatively low $SiO_2$ content in conjunction with intermediate proportions of $K^+$.

Both of these parameters would seem to indicate low subsurface temperatures ($<50^{\circ}C$) for this group of wells. It is also possible to infer from these relationships that in these waters $K^+$ may be a product of cool carbonic acid leaching of K-feldspar in rocks of the basement complex or Paleozoic section. Therefore $K^+$ or ratios (Na/K) may not be used alone as an indicator of subsurface temperatures in these waters.

## 4.6 Sulfate Waters and Middletown Springs

Four spatially unrelated locations (Vita Spring, Davis, Pitcher, and Sharon Springs) exhibit relatively high sulfate contents (>1,000 mg/l) in the water and have, therefore, been grouped together. These represent mixed water types with variable salt,carbonation, (Vita Spring, Davis) and a large component of contained shale water. Apart from sulfate content these waters have little in common and their molar proportions and ratios should be used only tentatively in comparing analyses of other waters.

Middletown Springs also seems to be unrelated. It was placed between the two groups of carbonated waters in the spring analyses because of its northern location and anomalous $HCO_3^-$ content (also reported in the literature; Peale, 1886). The presence of the latter was not borne out by the fall sampling and it has, therefore, been shifted to the surface water control group.

## 4.7 Vichy, France

Through a fortuitous set of circumstances, it was possible for the author to visit Vichy, France, during a trip to Europe on other business during the summer of 1978. This was thought to be relevant because Vichy possessed naturally carbonated springs that seemed as carbonated as Saratoga from the available literature (note the deliberate namesake, Saratoga Vichy). The thermal nature of the springs in a large graben near the Massif Centrale, an area of Quaternary vulcanism, also contributed to this decision.

From the data in plate 3 it can be seen that the two springs sampled at Vichy bear a striking resemblance to the postulated basement fluid component at Saratoga as represented by the north central group (particularly the Martin well) and the Rosemary well. They are simply sodium bicarbonate waters of higher surface discharge temperature than Saratoga without the reaction products added from the leaching of a carbonate host rock ($Ca^{++}$, $Mg^{++}$, etc.).

One of these springs, Hôpital, is clearly thermal (34°C) while the other appears to mix with a larger, cold component of surface water, discharging at a temperature of 19°C. Silica values are similar, however, and in both cases are less than in some Sartoga wells apparently with minimal dilution from a saline basinal water component.

## 4.8 Gas Analyses

**Five** gas analyses were performed concurrently with the isotope analyses by Dr. O'Neil. The results are tabulated below:

| | Hathorn #3 | Orenda | Big Red | Bennet | Martin |
|---|---|---|---|---|---|
| He | <0.01 | <0.01 | <0.01 | 0.05 | 0.27 |
| $H_2$ | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Ar | <0.02 | <0.02 | 0.04 | 0.09 | 0.57 |
| $O_2$ | 0.02 | 0.37 | 0.18 | 0.02 | 0.06 |
| $N_2$ | 0.14 | 1.37 | 1.80 | 4.06 | 45.25 |
| $CH_4$ | 0.50 | 0.42 | 2.26 | 6.30 | 13.39 |
| $CO_2$ | 99.08 | 97.52 | 95.77 | 89.64 | 40.73 |
| $C_2H_6$ | <0.01 | <0.01 | <0.01 | 0.01 | 0.01 |
| | 99.74 | 99.68 | 100.05 | 100.17 | 100.28 |

Table 4.2 Saratoga gas analyses

These analyses show several interesting trends, chief among them that the dominant gas is, not unexpectedly, $CO_2$. This is particularly true for the three Saratoga group wells, which top 95% $CO_2$ in all cases; the bulk of the remainder due primarily to methane and nitrogen.

The large relative excess of the methane, nitrogen, and argon components in the Martin and Bennet wells which are driven into shales can most easily be ascribed to these rocks; the methane, in particular. The large nitrogen component may be derived from atmosperic air trapped in meteoric shale water. The $O_2$ could have been used up by reaction with sulfides which are ubiquitous in shales, but the nonreactive argon simply varies with the nitrogen.

Thermal waters also commonly contain large excesses of radiogenic helium and argon which may be used as tracers in mixtures of deep heated thermal waters with near surface ground waters (Mazor, 1977). Unfortunately, the detection of radiogenic argon is complicated by the relatively large amounts of atmospheric argon-40 often dissolved in the water. This appears to be the case in the Martin and Bennet wells which may contain excess argon; but not to an extent visible through the atmospheric veil.

The analyses indicate an enrichment of He over that in the atmosphere by a factor of approximately $10^4$ in the Bennet well and $10^3$ in the Martin well- values far beyond possible analytical error. The source of the helium is not known. Possibly it may be the result of radioactive decay of elements in the shales.

## 4.9 Radium$^{226}$

The Saratoga waters have been known to contain anomalous amounts of radium since the early 1920's, only a few years after radioactivity was discovered. Unusual waters at resorts and spas were analysed for their radium content at this time and until the 1960's, constituted the vast majority of data available on the radioactivity of natural waters. Not until then were systematic radioactive measurements of ground waters done because of public concern over contamination emanating from atomic waste piles. Public health guidelines delineating preferred limits for Radium$^{226}$ in public water supplies were established then and are slowly being refined.

Three sets of analyses of Ra$^{226}$ in the waters of the classic Saratoga Springs-Ballston Spa wells were performed as an outgrowth of this concern during the 1960's and early 1970's. This data was kindly supplied by the Radiological Division of Health Research, Inc., consequently, most of the wells of this area were not remeasured for Ra$^{226}$ content during this program. The remainder of them were analysed, however, and the results appear in table 6 of the appendix.

Examination of this table shows that both the north central group of carbonated waters and the uncarbonated southern brine group have similar Ra$^{226}$ concentrations of from 5 to 15 pci/l. Only the Saratoga group contains higher amounts in levels that approach 400 pci/l (Hathorn #3) yet may drop as low as 6-10 pci/l (Congress). Inspection also shows that the majority of the Ra$^{226}$ contents of this group of waters vary sympathetically with the brine component with one possibly significant exception- the Big Red well.

Since the natural radioactivity of water is considered to be derived primarily from the rocks and minerals with which it has been in contact, the underlying rocks of this area would appear to be more uraniferous than in the remainder of the sampling area. At present, we may consider at least two mechanisms of transmission to the carbonated water from two possible source areas:

(1) Through the saline water component which has reached equilibrium with the more uraniferous Paleozoic sediments present only in this area;

(2) Through the basement $NaHCO_3$ component which may be leaching uranium-bearing minerals localized in faults in the Precambrian basement under the city of Saratoga Springs.

The first hypothesis is supported by the following observations: (a) the variation of $Ra^{226}$ levels fluctuating in concert with the saline water component in most of the waters; (b) the presence of a minor uranium province (pegmatitic) in the adjacent northwest Adirondacks, a possible source area for the Paleozoic sediments. The second is favored by: (a) the low levels of radium for the Big Red well, its apparently major saline water component; and, (b) the slightly favorable evidence (Ca/Mg ratios and isotopic values) at this time for local entry points of the carbonated basement fluid into the aquifer near the city of Saratoga Springs.

Resolution of this problem carries with it major information, since the first hypothesis implies the presence of a closed circulation environment; one probably induced by a fault with a major component of vertical offset east of Saratoga Springs. Further sampling and/or more direct geophysical information concerning basement structure should permit a distinction between these two mechanisms.

## 4.10 Seasonal Fluctuatuions

While minor variations exist between some of the wells from spring to fall, three major patterns seem to be noteworthy and, to some extent, interrelated.

First, there appears to be a general increase in the amount of gas present in the fall. pH measurements are lower and alkalinities are higher in many of the waters. These parameters are related to the gas content by the following simple equation:

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$

With $H^+$ (pH) increasing and the amount of $H_2O$ constant or decreasing there is clearly an increase of $CO_2$ indicated. The reason for this is uncertain, however, the simplest explanation would appear to be a lower water table and consequent less dilution from meteoric water. This should result from the normal seasonal runoff cycle and, possibly, extended pumping of the wells through the peak summer season.

Secondly, it is noteworthy that a corresponding increase in salt does not occur during the fall. Dissolved solids, the most reliable measurement, show a slight, though discernible decrease while $Cl^-$ and $Na^+$ contents generally do not fluctuate outside analytical error (Hathorn#3 and Red wells excepted). Should the gas be transported in solution in the saline waters within the aquifer further east a corresponding increase in discharge and/or salt content would also take place.

Finally, several of the trace elements show increases from spring to fall including: $Al^{+++}$, $Zr^{++}$, and $SiO_2$. $SiO_2$ is of singular significance (discussed under $SiO_2$ geothermometry), however, all three of these elements can most reasonably be inferred to derive from carbonic acid leaching and/or basement fluids rather than the saline water component. $Al^{+++}$, absent in connate waters, could be derived from the leaching of aluminosilicates in the basement. $Zr^{++}$ may be derived from high temperature thermal fluid leaching of zircon in the basement or by low temperature carbonic acid leaching of zircon in either the basement or the overlying Potsdam formation. In any case the proportions of these three elements should vary seasonally in the well discharges with the proportion of gas/fluid pumped through the system. Considered in conjunction with the minor decrease in dissolved solids, the marked increase in $CO_2$, $Al^{+++}$, $Zr^{++}$, and $SiO_2$ may suggest a local source for these components and a more widespread but ambient source for the saline waters. This interpretation is problematical without the other supporting data supplied in section 7.

# 5.0 GEOTHERMOMETRY

## 5.1 The Alkali Geothermometer

The impetus for this study was largely initiated by the $CO_2$ source problem for the Saratoga waters and the anomalous high subsurface temperatures indicated by the alkali geothermometer as applied to existing data (Figure 5.1). An empirical method of estimating the last temperature of water-rock interaction, the geothermometer is based upon molar Na, K, and Ca concentrations in waters with discharge temperatures ranging from 4° to 340°C (Fournier and Truesdell, 1972). The equation derived is:

$$\log K = \log (Na/K) + B \log (\sqrt{Ca}/Na)$$

where $K = 10^3/T$ or the reciprocal of absolute temperature; K, Na, and Ca are expressed as molality concentrations; and B is a constant whose value is 1/3 if $\log \sqrt{Ca}/Na$ is negative; 4/3 if $\log \sqrt{Ca}/Na$ is positive except when log K is $>100^\circ C$, then log K is recalculated using $B = 4/3$.

The authors point out several pitfalls that can be encountered when applying this method. One is the dilution of deep waters with shallow meteoric waters, while the presence of $CO_2$ and/or calcium-rich waters are another. $CO_2$-rich waters are often saturated with $Ca^{++}$ in the subsurface but tend to deposit calcium carbonate rapidly at the surface or near surface. Discharges are consequently often depleted in the $Ca^{++}$ ion and the geothermometer tends to yield values

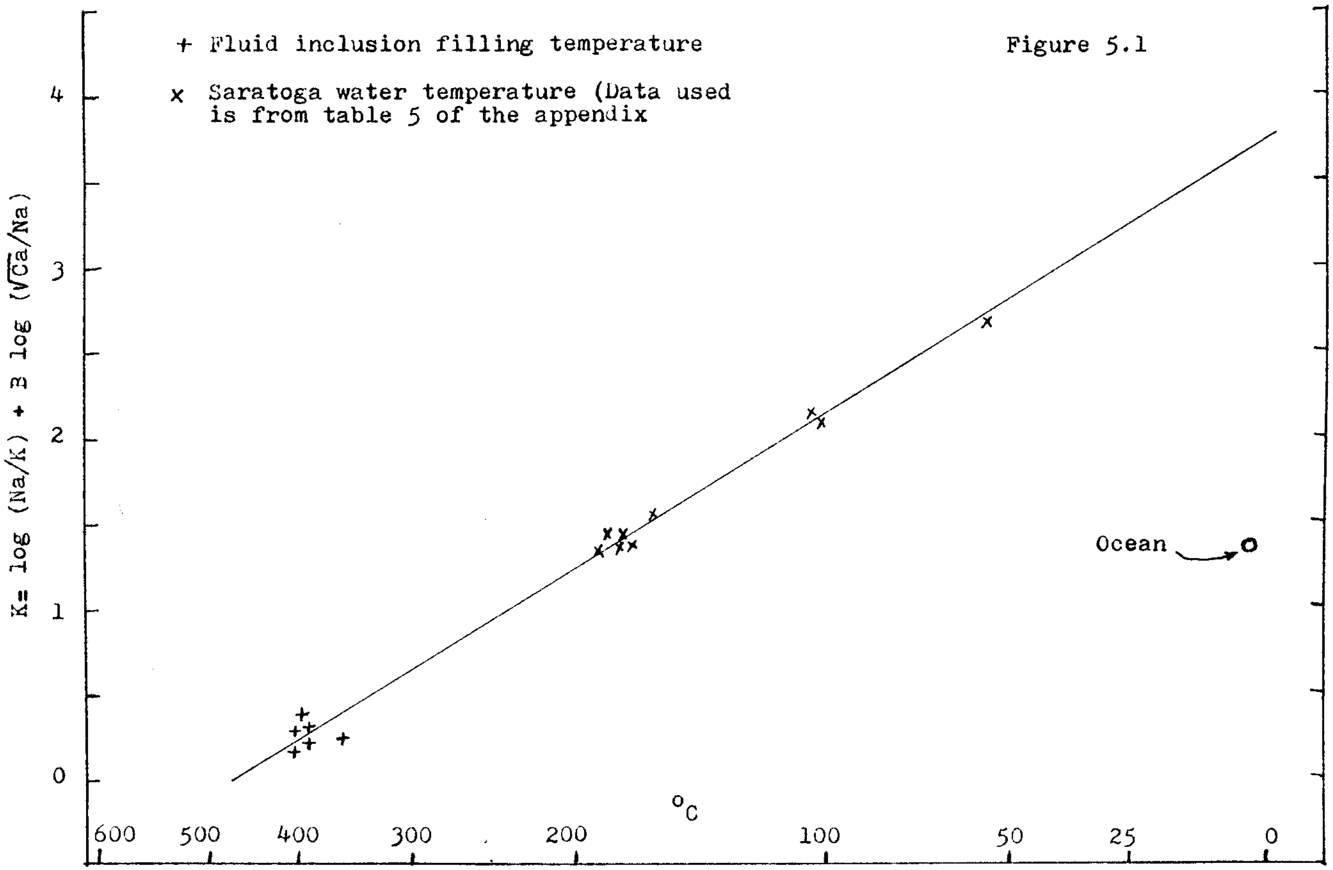


Figure 5.1
+ Fluid inclusion filling temperature
x Saratoga water temperature (Data used is from table 5 of the appendix
Ocean
K= log (Na/K) + B log (√Ca/Na)
4
3
2
1
0
°C
600
500
400
300
200
100
50
25
0

that are far too high. This proviso certainly applies to the Saratoga waters. So do two others:

(1) the presence of a variably dilute saline water contributing excess $Na^+$ to the waters and, therefore, indicating lower subsurface temperatures;

(2) carbonic acid leaching of:

   a. the Paleozoic aquifer: contributing not only excess $Ca^{++}$ and $Mg^{++}$, but $K^+$ from authigenic K-feldspar in the Hoyt limestone and the dolostones of the Galway and Gailor formations. Excess $K^+$ will indicate anomalously high aquifer temperatures;

   b. the Proterozoic basement: contributing excess $Na^+$, $K^+$, and perhaps sporadic $Ca^{++}$ because of the erratic distribution of calcitic marbles in the basement. $Na^+$ and $K^+$ may vary in the molar proportions contributed depending on the distribution of sodic and potassic feldspars in the basements rocks traversed by the fluids and the nature of the alteration reactions which leach alkalis.

Comparison of the analyses of the carbonated and uncarboanated waters shows that most, perhaps all, of these processes are operating. Below are listed the general chemical characteristics of each water group:

| | UNCARBONATED | CARBONATED |
|---|---|---|
| Ca | 7-27 mg/l | 82-770 mg/l |
| Cl | 800-2000 | 160-7500 |
| Alk | 210-283 | 984-4080 |
| Na | 280-110 | 160-4300 |
| K | 4-11 | 18-330 |

Table 5.1 General chemical characteristics. All values in mg/l.

While the data speaks largely for itself, some points bear discussion. $Na^+$ and $Cl^-$ contents overlap because of mixing but have a far greater range in the carbonated waters. Components of both basement leaching and formational fluids, it is virtually impossible to separate the contribution of each except in the possible cases of the Rosemary and Martin wells. $Ca^{++}$, $Na^+$, and $K^+$ also vary on a group basis, i.e. between the Saratoga and north central groups, however, there is no way to discriminate the effects of low temperature leaching from any possible higher temperature mineral breakdown and incorporation of these various elements.

Perhaps the best way to perceive this problem is to consider the Rosemary and Martin wells as the best examples of essentially basement derived and exchanged fluids mixed with a meteoric component. Certainly there is very little of an indigenous saline water component in these waters as is indicated by their similarity, low Ca/Mg ratios, high $HCO_3/Cl$ ratios and isotope data for the Martin well. If this is the case, it is interesting to note that the Rosemary yields the lowest log K for all the wells- equivalent to over 300°C.

This might seem consistent with a thermal interpretation, however, tables 3s and 3f of the appendix show anomalous alkali thermometer results for all of the high TDS wells, even the uncarbonated ones, largely due to the bias induced by the $K^+$ of typical Saratoga-type waters (Figure 4.1). With a strong dependence of the thermometer on $K^+$ content, and anomalous $K^+$ in Saratoga waters, anomalous results are expected from this alone.

The best that can be said of the alkali thermometer at this time is that it tends to reflect the pattern of apparent subsurface heating inferred from the $SiO_2$ data. In this respect it might be qualitatively accurate, however, it cannot in any way be relied upon quantitatively.

## 5.2 Silica Geothermometer

The quantitative silica geothermometer is based on the solubility of silica phases in water and has been widely used for over 10 years as the most generally reliable method of estimating subsurface temperatures in hot spring systems. Recent work by Swanberg (1979) and others has also shown a linear correlation of dissolved silica content in non-thermal waters with observed heat flow measurements throughout a large portion of the continental United States. In one case, the mineral quartz dominates dissolved silica contents which then may be used to quantitatively estimate subsurface resevoir temperatures. In a second case, several other silica species (chalcedony, cristobalite, or amorphous silica) may control dissolved silica (Fournier, 1975) leading to somewhat higher contents.

The equation relating the solubility, C, in mg $SiO_2$/ liter water to temperature in the range of 0-250°C for the pure silica mineral quartz is:

$$t^{o}C = \frac{1309}{5.19 - \log C} - 273.15$$

Insertion of the highest dissolved silica content into this equation (70 ppm from the Big Red well) gives a value of 119°C as the last temperature of equilibration in the last subsurface resevoir. This value is most likely to be a minimum because: (1) dilution obviously occurs, and (2) dissolved silica of this quantity at ambient temperatures is distinctly metastable and should precipitate out of solution fairly rapidly.

A second question which must be posed, however, is whether or not quartz is the controlling phase of the contained silica species. To this there is no definite answer at this time, however, several facts suggest that either quartz or chalcedony is the controlling dissolved silica phase in the Saratoga group waters. The best evidence appears in the regional pattern of silica values in the meteoric waters, saline waters, and other carbonated waters. All of these exhibit low silica contents consistent with regional ground water equilibrium values at low subsurface temperatures (9 to 15°C), and a controlling quartz phase. Should chalcedony be the dominant species, its equation of:

$$t^{o}C = \frac{1032}{4.69 - \log C} - 273.15$$

yields a subsurface temperature of 89°C for the preceding example.

Noting this possibility and the fact that the quartz geothermometer does not appear to be as accurate below resevoir equilibration temperatures of 150°C (Fournier, 1975), it seems prudent to suggest that the apparent minimum subsurface temperature range indicated at this time by the silica geothermometer is from appproximately 90° to 120°C.

If this temperature range is accurate, two general resevoir models can be considered, viz:

(1) the waters are heated anomalously, but slightly, in the subsurface aquifer, possibly in the vicinity of the discharge;

(2) a small component of deep superheated water or deep superheated fluid ($CO_2$ and $H_2O$) imperfectly mixes with a larger, cold upper component of diluted basinal brines and/or meteoric water.

Should the first case be true and the heating be taking place in the aquifer, it is difficult to understand the sharp areal pattern(s) in the distribution of the higher silica values. Relatively shallow heating of a single phase fluid to the degree directly indicated by the quantities of $SiO_2$ (90° to 120°C) should produce more uniformity among the wells, not disparity. Most of the wells of the Saratoga group are located in a rather small area where distances of

>300 m often separate chemically distinct wells (e.g. Rosemary and Lincoln) and/or wells with high and low silica values (e.g. Red and Peerless). Another point to consider is that the uncarbonated saline water component has uniformly low silica values (10-15 mg/l $SiO_2$). This also argues strongly for the addition of $SiO_2$ by basement fluids and against low temperature heating in the aquifer toward the center of the basin.

The data indicate the second mechanism to be the preferred choice in this instance. Considered in conjunction with the large amounts of free $CO_2$, and an association with excess $K^+$ relative to $Cl^-$, atypical of basinal brines; the $SiO_2$ values (to 70 mg/l) may indicate a zone of superheated fluid interaction in the basement. This is particularly true when the degree of mixing with dilute basinal brines and meteoric water (dilution of the original brines with meteoric water may be a continuing process independent of carbonation) under Saratoga is taken into account. The data show, for instance, that the Big Red well water with 70 mg/l $SiO_2$ also has a large saline water component. Taking only this factor into consideration, an amount of $SiO_2$ of at least 100 mg/l $SiO_2$ in the postulated basement fluid prior to dilution with basinal waters seems reasonable- possibly low.

The $SiO_2$ results from the spring and fall sampling have been contoured in figures 5.2 and 5.3 along numerical guidelines suggested by recent work in New Mexico (Swanberg, 1979).

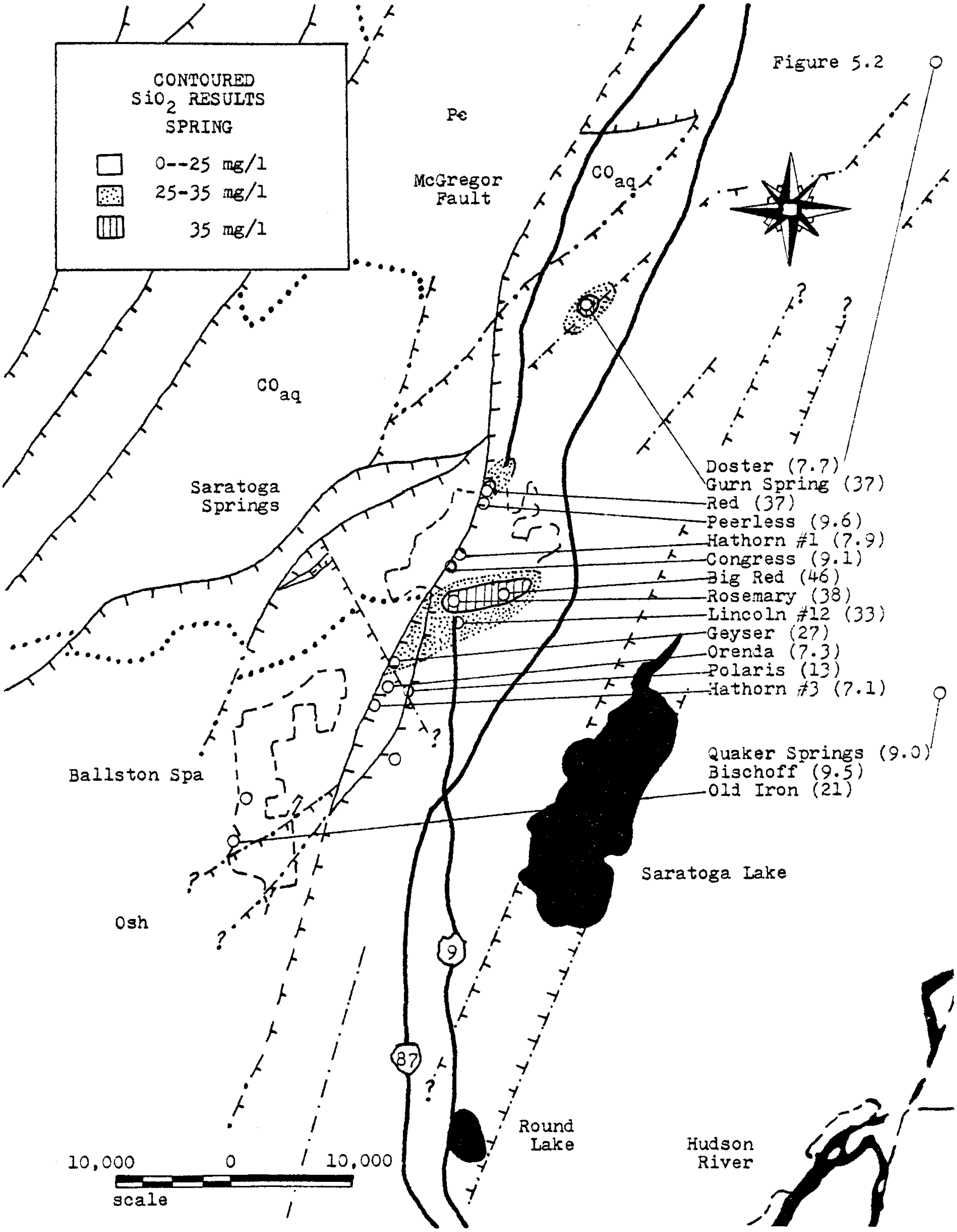
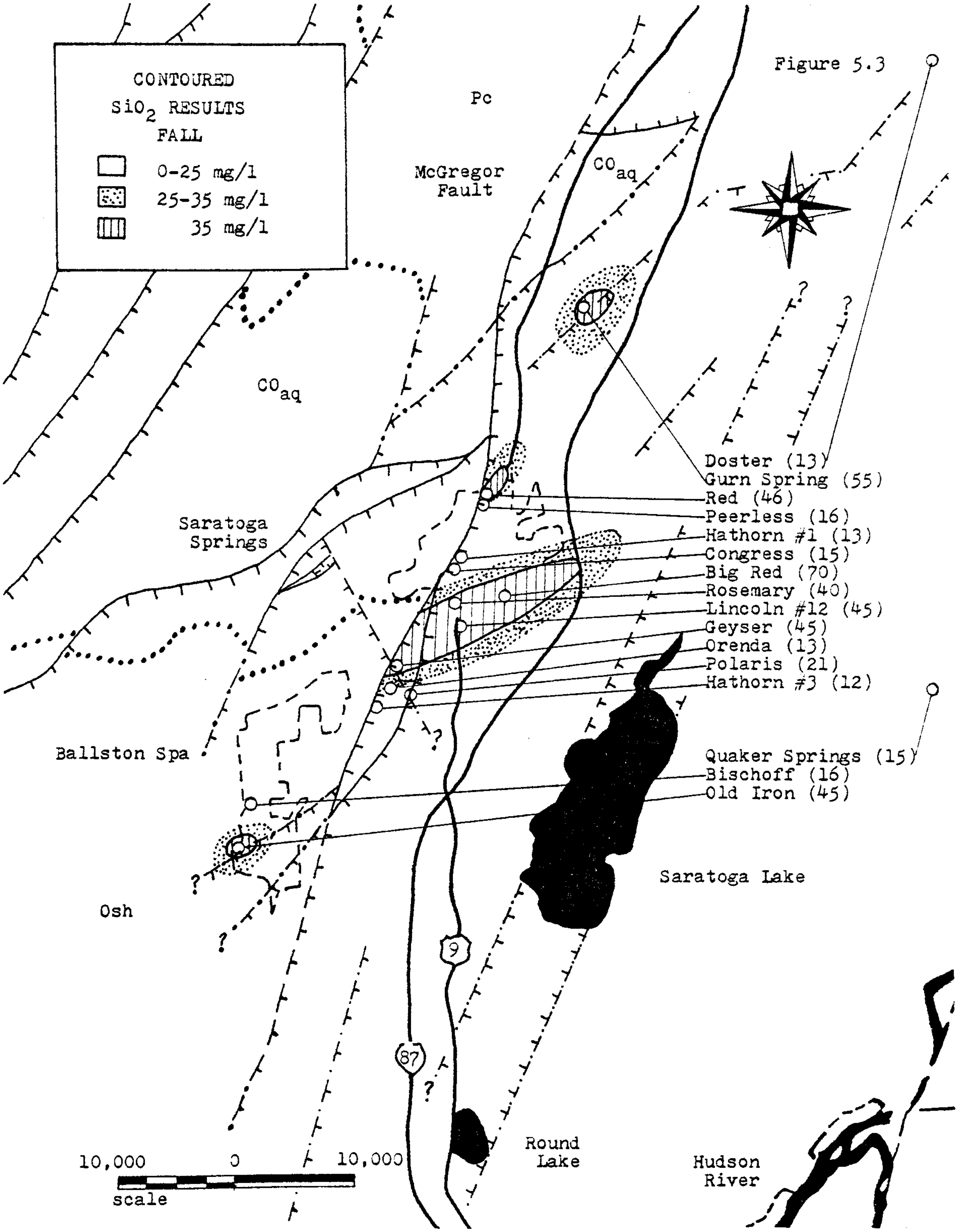


Figure 5.2
CONTOURED
$SiO_2$ RESULTS
SPRING
☐ 0--25 mg/l
▨ 25-35 mg/l
▥ 35 mg/l
Pє
McGregor Fault
$CO_{aq}$
$CO_{aq}$
Saratoga Springs
Ballston Spa
Osh
Doster (7.7)
Gurn Spring (37)
Red (37)
Peerless (9.6)
Hathorn #1 (7.9)
Congress (9.1)
Big Red (46)
Rosemary (38)
Lincoln #12 (33)
Geyser (27)
Orenda (7.3)
Polaris (13)
Hathorn #3 (7.1)
Quaker Springs (9.0)
Bischoff (9.5)
Old Iron (21)
Saratoga Lake
9
87
Round Lake
Hudson River
10,000
0
10,000
scale

Figure 5.3


CONTOURED
$SiO_2$ RESULTS
FALL
☐ 0-25 mg/l
▨ 25-35 mg/l
▥ 35 mg/l
Pc
McGregor Fault
$CO_{aq}$
$CO_{aq}$
Saratoga Springs
Ballston Spa
Osh
Doster (13)
Gurn Spring (55)
Red (46)
Peerless (16)
Hathorn #1 (13)
Congress (15)
Big Red (70)
Rosemary (40)
Lincoln #12 (45)
Geyser (45)
Orenda (13)
Polaris (21)
Hathorn #3 (12)
Quaker Springs (15)
Bischoff (16)
Old Iron (45)
Saratoga Lake
Round Lake
Hudson River
9
87
?
10,000
0
10,000
scale

They indicated several sets of anomalies extending approximately ten miles along the McGregor Fault system. The central anomaly may be the most interesting of the group because of: 1) its larger size; and 2) the increasing silica values from west to east.

This last datum encourages the interpretation that a primary zone of superheated fluids may lie eastward under the thicker shale cover. The spatial position of the anomalies, however, should be considered as only a qualitative indication of the location of a zone of heating- not as direct pathfinders. This is due to the fault-controlled nature of the water pathways and the limited number of sampling points.

## 5.3 $O^{18/16}$ Implications

The results of 5 stable isotope analyses are listed below:

| SAMPLE | $\delta D$ | $\delta^{18}O$ MEASURED | $\delta^{18}O$ CALCULATED |
|---|---|---|---|
| Hathorn #3 | -64.2 | -9.22 | -9.28 |
| Orenda | -63.6 | -10.39 | -9.20 |
| Big Red | -65.9 | -10.36 | -9.49 |
| Bennet | -79.0 | -12.10 | -11.13 |
| Martin | -90.4 | -13.26 | -12.55 |

Table 5.2 Stable isotope analyses

where:

$\delta$ = isotope fractionation ratio in <u>sample</u>;

expressed in parts per thousand (per mil)
difference relation to the standard
D= deuterium isotope of hydrogen
$^{18}O$= oxygen isotope mass 18

and presented graphically in figure 5.4. Two very significant implications emerge from this data.

First, waters in the immediate Saratoga system appear to be essentially of meteoric origin. This is calculated from the $^{18}O$ analysis of the Hudson River water by using the equation formulated by Craig (1961) for meteoric waters:

$$D = 8\delta^{18}O + 10$$

Given that the 3 most saline carbonated waters in table 5.2 have mostly meteoric $H_2O$ molecules, the derivation of the saline water component comes into question. The characteristics of this component are thoroughly discussed in section 6.2 but, suffice it to say that it clearly is not unmodified sea water or derived from the solution of evaporites. Most connate brines and saline oil field waters, even at total salinities comparable to Saratoga, (10,000-15,000 mg/l TDS, Illinois Basin waters, figure 5.3) however, are characterized by relatively high $\delta D$ and commonly appreciably higher $\delta^{18}O$ values as a result of isotopic exchange with the host rocks. A mixture of minor connate formational water of high salinity and new or old meteoric water could explain the data, at least with respect to saline components; so, too, could the ultrafiltration of only meteoric water as is discussed in section 6.2.

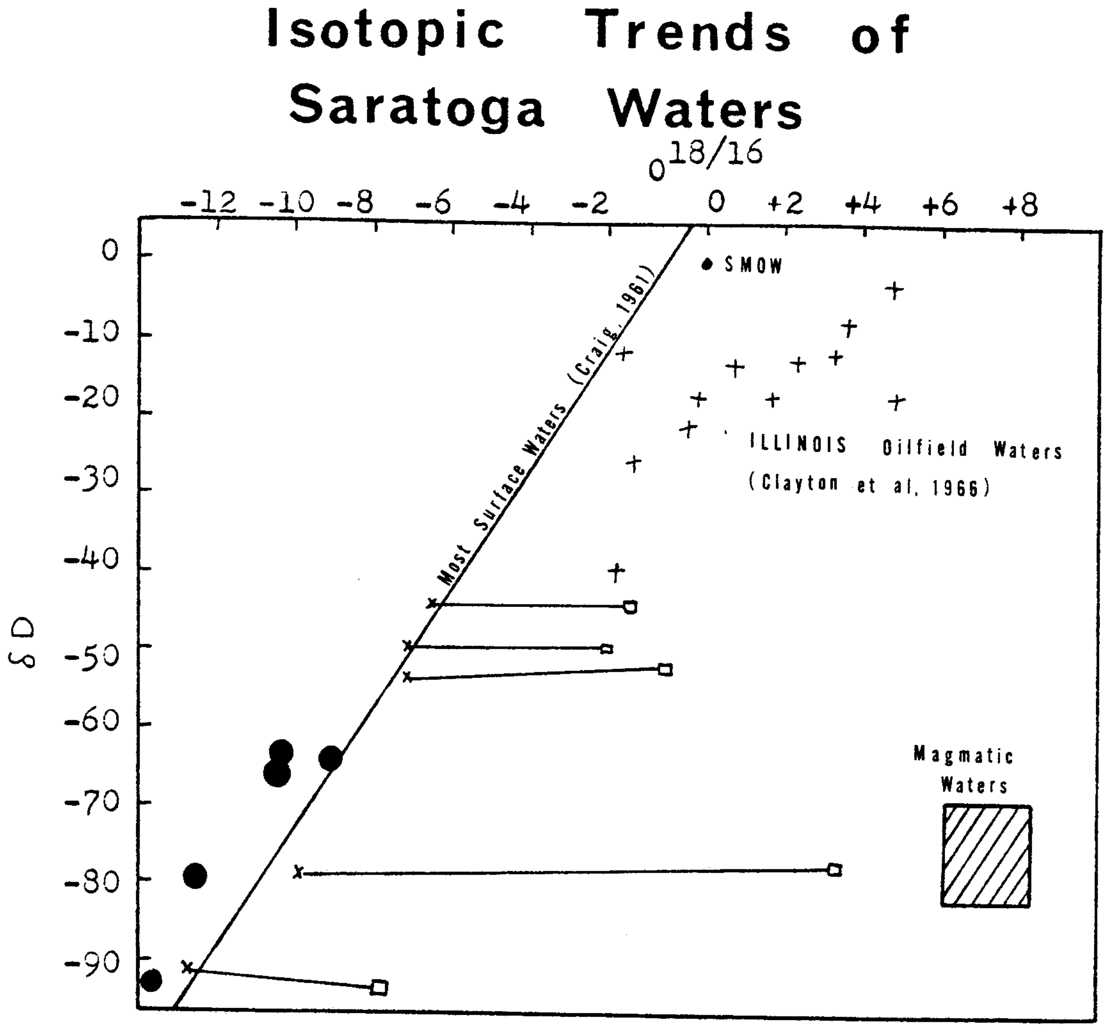


Figure 5.4 Isotopic composition of some thermal and mineral waters (modified after White, Barnes, and O'Neil, 1973). Saratoga waters indicated by closed circles while lines indicate the trends of studied hydrothermal systems showing limits of measured differences.

The remaining two wells, Bennet and Martin, are located some 20 miles north of Saratoga Springs (see Plate 4). $\delta D$ and $\delta^{18}O$ values for these waters are too low for current precipitation. They are consistent with values from subarctic water, however, and suggest a retention of ice age water in the northern portions of the Paleozoic aquifer.

Last, an oxygen isotope "shift" (-.8 up to -1 per mil) was found in the water of four of the five samples analysed; i.e. $\delta^{18}O$ values relative to $\delta D$ which are depleted (more negative) than meteoric water itself and opposite to the effects of mixing meteoric water with non-meteoric water (formational waters) as noted above. This type of oxygen isotope shift has been predicted for carbon dioxide water systems but until now has not actually been observed. The significance of the shift lies in the implications of prior higher temperatures for the $CO_2$.

Figure 5.5 is a plot of the fractionation effect of $CO_2$ gas in water vs. temperature. Exchange of the oxygen species occurs after the reaction

$$1/2\ CO_2{}^{16} + H_2O^{18} = 1/2\ CO_2{}^{18} + H_2O^{16}$$

with an increasing fractionation upon cooling. With an assumed initial temperature of 300°C the $CO_2$ (or $CO_2$ and $H_2O$) should be in equilibrium with the surrounding rocks with a $\delta^{18}O$ of approximately +6 per mil. The rising $CO_2$ (hot or cold) then contacts meteoric water at some point in its ascent and is cooled to approximately 10°C. Fractionation then demands that $^{18}O$ be stripped from the water to produce

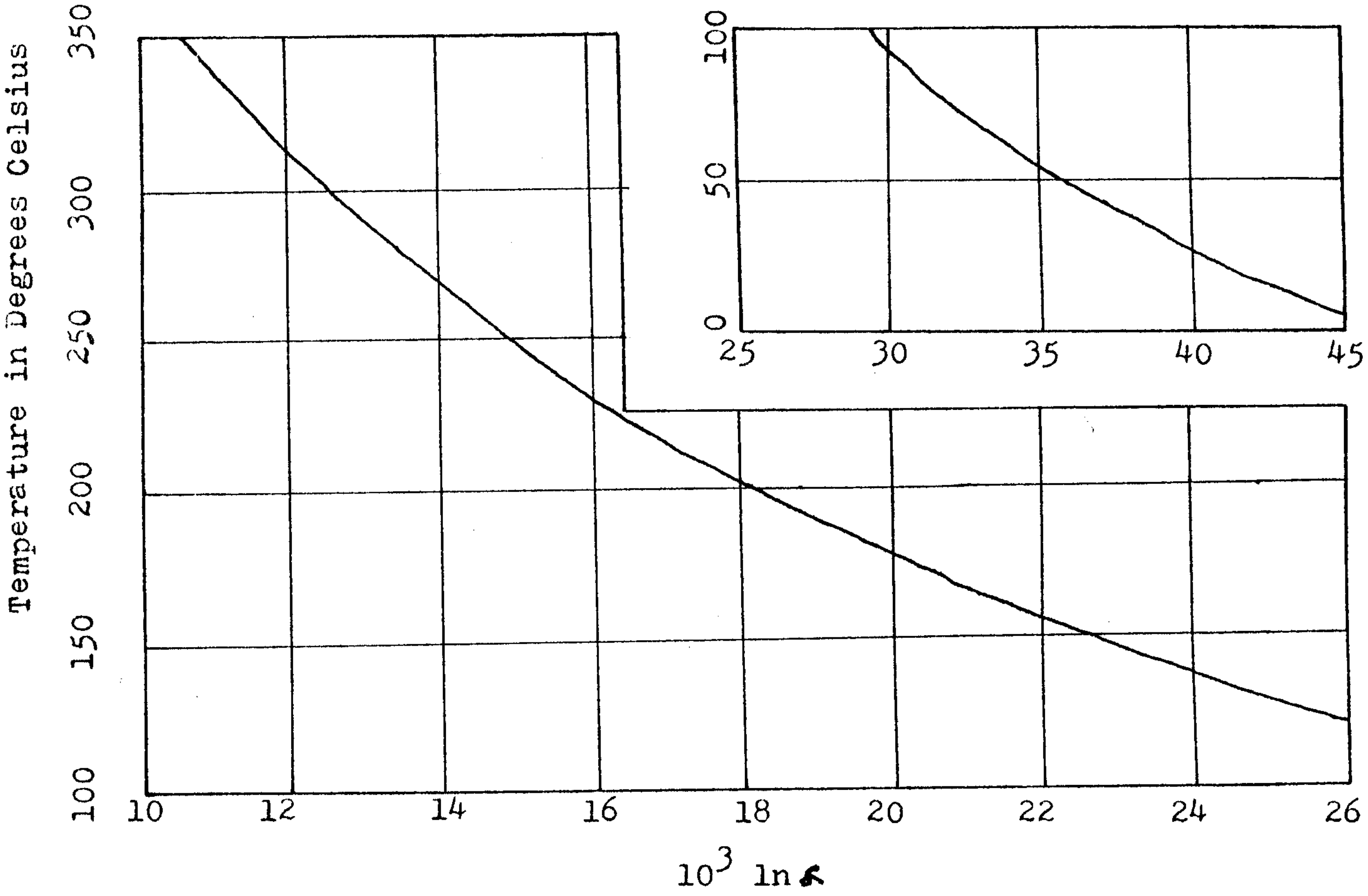


Figure 5.5 Fractionation of carbon dioxide and water

the obsrved -1 per mil shift because the $^{18}O$ in the $CO_2$ must rise to +25 to +30 per mil to satisfy equilibrium conditions. Since the $^{18}O$ of $CO_2$ must increase considerably to cause the shift, the $^{18}O$ of the $CO_2$ must begin life in the range of +5 to +10 per mil; the range of mantle $CO_2$ from a devolatizing magma. Were it derived from the Paleozoic carbonates or even the Precambrian marbles, $^{18}O$ in the resultant metamorphic $CO_2$ would have a $\delta^{18}O$ of +25 to +30 per mil and, hence, an isotope shift would not occur.

One final datum can be extracted from this information; the minimal amount of $CO_2$ needed to cause the observed shift. Below is a schematic diagram of the situation using the Big Red well data:

$CO_2$ (mantle or juvenile) $^{18}O = +6$
$CO_2 + H_2O$ (mixes with water) $^{18}O = -9.49$
cools to $10^\circ C$ $CO_2 + H_2O = +43$

$O_2$ in $H_2O$ (-9.49) -10.36 = .87
$O_2$ in $CO_2$ (+6) 32.64

Assuming the maximum possible fractionation effect of +43 per mil requires a positive shift of 32.64 for the $O_2$ in the $CO_2$ to accomodate the fractionation. The amount of $CO_2$ needed follows from:

$(1000\ g/H_2O)\ (8/9\ O) = 888\ gO/1\ H_2O$
$(.87)\ (888\ gO/\ 1\ H_2O) = 774$ per mil units of $^{18}O/1\ H_2O$
so that
$X\ gms.\ O_{CO_2} = \frac{774}{43}\ gO/1\ H_2O = 18\ gms.\ O/1\ H_2O$

$$\frac{(11 \text{ gms. } CO_2)}{(8 \text{ gms. } O)} \; (18 \text{ gms.} O) = 24.75 \text{ gms. } CO_2$$

approximately 25,000 mg/l of $CO_2$ are required. The significance of this lies in the fact that for the few $CO_2$ systems well described in the literature, 6,000 to 8,000 mg/l of $CO_2$ appear normal. Not only does Saratoga appear to contain more $CO_2$ gas than other systems, but the amount also implies that the system is effectively degassing. The gassiest waters sampled (Hathorn #3 and Orenda) only approach 1/2 this quantity of $CO_2$ in solution at the wellhead.

## 6.0 MIXING OF WATER TYPES

Part of the puzzling aspect presented by the Saratoga waters has been due to their mixed nature quite unlike any other waters described in the literature. This topic was partially addressed in section 4 and will be dealt with fully herein. It can be shown that the Saratoga-type waters represent a complexly mixed system with at least five major components. They are:

1) a gaseous phase consisting primarily of $CO_2$;
2) a fluid (containing the dissolved $CO_2$) possibly analogous to a metamorphic water whose major chemistry is $HCO_3^- > Na^+ > Cl^-$;
3) basinal brines of low salinities which may be the end products of progressive dilution of Paleozoic connate brines by meteoric waters; major chemistry $Cl^- > Na^+ > HCO_3^-$;
4) constituents added by reactions of the carbonated waters with wall rocks of two types: the Proterozoic basement and the Paleozoic aquifer;
5) normal surface ground waters of meteoric origin which seasonably dilute the deeper carbonated waters while also capping and "damping" the system.

Several segregated water types comprised largely of components #2, 3, and 5 above can also be recognized. In particular, the north central group of waters is similar yet chemically distinct from the Saratoga group, differing in critical ions such as $K^+$, $Cl^-$, and $Si^{4+}$. The principles of mixing also bear heavily on the hydraulics of the Saratoga group and proximity to basement feed zones for the $CO_2$ and/or carbonated fluid. These topics will be cursorily discussed herein and dealt with fully in the next section.

### 6.1 The $CO_2/NaHCO_3$ Basement Fluid

The existence of a $NaHCO_3$ basement fluid containing dissolved $CO_2$ was first postulated by the good Dr. Kemp as were so many other aspects of the Saratoga system. His evidence was based on the chemistry of the unique Smith Experimental well which was unfortunately drilled 3 years after his publication concerning the waters. A record of his unpublished reinterpretation stands in several later reports to the Saratoga Springs Commission (1915, 1916) and in trial transcripts where he acted as an expert witness (Carl Edwards, pers. com.). Multiple lines of evidence are now virtually conclusive that a $NaHCO_3/CO_2$ fluid is being injected into the Paleozoic aquifer containing variably dilute saline waters directly under the city of Saratoga Springs and elsewhere in the lowlands. Most of the data relevant to this point are discussed in the next section, however, for the sake of convenience here, a local injection mechanism will be assumed.

The peculiar Smith well was drilled in August, 1915, 1/4 mile west of the then postulated extension of the Saratoga Fault (Colony, 1930; see Plate 3). The water tapped was virtually pure $NaHCO_3$ with negligible chlorides (Table 6.1). Its strong similarity to the waters of Vichy, France, (see Plate 2) created quite a stir at the time (Report of the Commission, 1916) which in turn was fed into the publicity grist mill. In July, 1916, however, after 6 hours of strong pumping, the seals blew out and the water gushed out to a height of 6-10 feet until the drillers could arrive to cap it (Colony, 1930). A sample taken for analysis at this time showed a radical change in chemistry to a high TDS, NaCl carbonated water similar to many of the more saline carbonated waters on the reservation, particularly the Orenda (Tables 6.2 and 6.3).

SMITH EXPERIMENTAL WELL

| September 1915 | | July 1916 | |
|---|---|---|---|
| Ions and Radicles | Conc. | Ions and Radicles | Conc. |
| $SiO_2$ | 3.5 | $SiO_2$ | 32.00 |
| $SO_4$ | trace | $SO_4$ | trace |
| $HCO_3$ | 4616.0 | $HCO_3$ | 3303.6 |
| $NO_3$ | trace | $NO_3$ | trace |
| $NO_2$ | trace | $NO_2$ | trace |
| $PO_4$ | none | $PO_4$ | none |
| $PO_2$ | trace | $PO_2$ | trace |
| Cl | 108.68 | Cl | 3685.0 |
| Br | 10.74 | Br | 32.22 |
| I | 2.29 | I | 1.52 |
| Fe | 104.83 | Fe | 10.05 |
| Al | 32.48 | Al | 4.04 |
| Mn | none | Mn | none |
| Ca | 264.72 | Ca | 634.2 |
| Ba | 2.26 | Ba | 11.21 |
| Na | 1089.65 | Na | 2245.30 |
| Sr | trace | Sr | trace |
| Mg | 137.33 | Mg | 268.89 |
| K | 91.07 | K | 200.16 |
| Li | 9.01 | Li | 6.74 |
| TDS | 6533.3 | TDS | 10,419 |

Table 6.1 Analyses of Smith Experimental well- before and after.

The implied segregation of $NaHCO_3$ vs. NaCl water types in the Smith well can most easily be ascribed to an initial direct tapping of a $NaHCO_3$ type water-bearing fault or fracture-controlled conduit. Strong pumping undoubtedly increased the radius of the cone of depression, probably tapping an artesian saline water-bearing fracture zone. The segregation theory is supported by the present day Rosemary well sampled during this program. It, too, is a true $NaHCO_3$ water which stands amidst the other saline waters not unlike a lemon on a cherry tree. Ionic concentration of the Smith (before and after), the Rosemary, and the Orenda waters are compared in table 6.2 with striking results. It shows the Smith before water to be a stronger $NaHCO_3$ water than the Rosemary, yet containing similar concentrations of Ca, Mg,

Molal Concentrations of Selected Comparable Waters

| | Smith Sept. 1915 | Rosemary | Smith July 1916 | Orenda |
|---|---|---|---|---|
| $HCO_3$ | 75.68 | 39.17 | 54.16 | 65.55 |
| Na | 47.40 | 25.66 | 97.66 | 100.04 |
| Cl | 3.07 | 15.79 | 103.95 | 115.63 |
| Ca | 6.60 | 6.74 | 15.82 | 18.71 |
| Mg | 5.65 | 7.81 | 11.06 | 12.34 |
| $SiO_2$ | .53 | .67 | .06 | .22 |
| K | 2.33 | 2.23 | 5.12 | 5.88 |
| Br | .13 | .24 | .40 | .93 |
| Al | 1.20 | .03 | .15 | .01 |
| Li | .41 | .27 | .97 | 1.44 |
| TDS | 6533.3 | 3000 | 10,419 | 10,780 |

Table 6.2 Comparison of both phases of the Smith Experimental well with analogous waters sampled during this program. All values are expressed as molality x 1000 except TDS which is in units of mg/l.

K, Br, Li, and, particularly, anomalous $SiO_2$. The Smith after water can be bearly distinguished from the relatively high TDS Orenda water. Particular note is again made of the $SiO_2$ concentrations which drop from 32 mg/l to 3.5 mg/l in the Smith well analyses. This is contrasted to 40 mg/l in the Rosemary and 10 mg/l for the Orenda.

Selected Molar Ratios of Smith and Comparable Waters

| Ratio | Smith Sept. 1915 | Rosemary Oct. 1978 | Smith July 1916 | Orenda Oct. 1978 |
|---|---|---|---|---|
| Na/Cl | 15.44 | 1.62 | .94 | .87 |
| Ca/Mg | 1.17 | .86 | 1.43 | 1.52 |
| Na/K | 20.34 | 11.53 | 19.07 | 17.01 |
| Cl/K | 1.32 | 7.01 | 20.30 | 19.66 |

Table 6.2 Comparison of selected ratios of molal concentrations of waters in table 6.2.

The $NaHCO_3$ Smith water has been compared to the Rosemary water because of their relative proximity in an area of literally hundreds of saline carbonated waters. In fact, it is more similar to the waters of the Martin residence some 20 miles northeast in Fort Edward. Both lie on the same vector in figure 6.1 delineating the basement fluid. Both have relatively lower Ca and Mg contents which argue against a long term exposure of this fluid to the Paleozoic carbonate section.

## 6.2 Saline Waters

Most saline waters of marine sedimentary rocks may have been initially similar to present day ocean water. Compaction of the sediments and the escape of interstitial waters began at the time of deposition and probably continued for many millions of years. Such waters have commonly been referred to as connate or "fossil" in the past, a term that is defined by White (1957, p.1661) to mean:

> 'fossil' water that has been out of contact with the atmosphere for at least an appreciable part of a geologic period. It consists of the fossil interstitial water of unmetamorphosed sediments and extrusive volcanic rocks and water that has been driven from the rocks.

While the term is still in use, there is now sound experimental and field evidence which suggests that most of the $H_2O$ molecules of these waters are meteoric in origin in the few fields studied to date (McKelvey and Milne, 1962; Graf et al. 1966). This derives from ultrafiltration, a process first described by De Sitter (1947) whereby fine grained sediments behave as semipermeable membranes or "salt sieves", permitting a selective escape of water and concentrating the dissolved salts in water remaining behind the membrane (White, 1965). The dissolved salts, then, are probably original sea water ions concentrated by compaction and/or meteoric water flushing. Salinities of these formation waters tend to increase exponentially because the efficiency of ion rejection decreases with increased solution concentration (Kemper, 1961; Henshaw, 1962).

With this basic background it is now possible to examine the Saratoga system with respect to its saline waters. These are best represented by the southern saline waters group whose most reliable diagnostic members are the Yezzi, August Bohl, and Gorman wells. Total salinities of these waters are low (less than 1 g/l) compared to most other basinal formation waters which often reach 30 to 40 g/l or higher (White, 1965). Nonetheless, a few fields with low TDS waters do exist which provide some sort of comparative data base. A few analyses from these are listed in table 6.4.

The existence of an admixed formational water in the carbonated Saratoga type waters was first suggested by Cushing and Reudemann (1914) as their only difference with the earlier study of Kemp (1912). The existence of this component is no longer in doubt; the presence of uncarbonated saline waters around the periphery of the lowlands removing any lingering questions. What is in doubt are chemical interpretations concerning the nature of the deep seated $NaHCO_3$ fluids which might otherwise be made with more confidence were it not for the complicating formational water. This "extra filter" appears to be unique in the thermal literature; a dubious distinction of some possible note.

Figures 6.1 and 6.2 are plots of $HCO_3^-$ vs. $Cl^-$ ion concentrations for the fall and spring 1978 samplings. These parameters were chosen because of the well defined uncarbonated saline water vector and the minimal amounts of $Cl^-$ apparently present in the basement fluid. This latter vector is also well defined by the Martin (17), Rosemary (8), and Smith Experimental (before SB) wells, with meteoric water

Table 6.4

Typical Subsurface Saline Waters

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Type | Connate Na-Ca-Cl (?) | Connate NaCl (?) | Connate NaCl (?) | Meteoric NaCl |
| Field | Eldorado | Cymric | Cole Creek | Illinois Basin |
| Location | Saline Co. Illinois | Kern Co. | Natrona Co. Wyoming | DeWitt Co. Illinois |
| Lithology | Limestone | Sandstone | Sandstone | Sandstone |
| Age | Mississippian | Early Miocene | Late Cretaceous | Middle Ordovician |
| Producing Depth feet | 2,900 | 3,000 | 4,600 | 2,200 |
| $SiO_2$ | 6.9 | 52 | 20 | |
| Al | 1.5 | .9 | .6 | |
| Fe | 5.6 | 6.4 | 15 | |
| Mn | .2 | .3 | .05 | |
| Zn | | .06 | | |
| Ca | 10,100 | 325 | 57 | 37 |
| Mg | 1,920 | 123 | 23 | 17 |
| Sr | 279 | 21 | 9 | |
| Ba | 2 | 7.2 | 13 | |
| Na | 42,000 | 6,150 | 6,300 | 475 |
| K | 323 | 136 | 11 | 21 |
| Li | 26 | 4.9 | 1.0 | |
| $NH_4$ | 42 | 45 | 11 | |
| $HCO_3$ | 72 | 666 | 1,010 | 383 |
| $SO_4$ | 990 | 4.1 | 1.1 | 84 |
| Cl | 90,300 | 9,940 | 9,690 | 557 |
| Br | 341 | 35 | 128 | |
| I | 17 | 20 | 105 | |
| TDS | 157,000 | 17,100 | 17,000 | 1,570 |
| Ratios by Weight | | | | |
| Ca/Mg | 3.19 | 1.60 | 1.50 | 1.29 |
| Na/Cl | .47 | .62 | .65 | 1.25 |
| Na/K | 221.2 | 76.9 | 978.6 | 38.3 |
| Cl/K | 308.4 | 80.6 | 976.2 | 30.6 |

Table 6.4 (cont.)

Typical Subsurface Saline Waters

| | 5 | 6 | 7 |
|---|---|---|---|
| Type | Meteoric NaCl | Connate to Evaporites | Meteoric Na-Ca-Cl |
| Field | Illinois Basin | Potash oil Test | Illinois Basin |
| Location | Douglas Co. Illinois | Grand County Utah | Adams Co. Illinois |
| Lithology | limestone | anhydrite | dolomite |
| Age | Middle Ordovician | Pennsylvanian | Early Silurian |
| Producing Depth feet | 1,400 | 3,500 | 2,800 |
| $SiO_2$ | | 0 | |
| Al | | 66 | |
| Fe | | 750 | |
| Mn | | 260 | |
| Zn | | 60 | |
| Ca | 260 | 52,700 | 670 |
| Mg | 63 | 39,200 | 210 |
| Sr | | 2,000 | |
| Ba | | 8 | |
| Na | 1,980 | 5,990 | 3,520 |
| K | 75 | 18,800 | 30 |
| Li | | 66 | |
| $NH_4$ | | 849 | |
| $HCO_3$ | 152 | 1,010 | 306 |
| $SO_4$ | 473 | 4 | 8 |
| Cl | 2,600 | 241,000 | 7,270 |
| Br | | 3,080 | |
| I | | 42 | |
| TDS | 5,620 | 366,608 | 12,000 |
| Ratios by Weight | | | |
| Ca/Mg | 2.50 | .82 | 1.93 |
| Na/Cl | .92 | .025 | .77 |
| Na/K | 45.3 | .54 | 198.7 |
| Cl/K | 49.2 | 14.1 | 258.4 |

analyses 1, 2, 3, and 6 from White, 1965; 4, 5, and 7 from Graf, D.L. et al, 1966 control wells plotting near the origin. Subtraction of this basement vector from any point should yield the approximate amount of $Cl^-$ present in the formational water. It can be seen that the most saline uncarbonated water sample (Gorman) only has a concentration of $81^+$ millimoles $Cl^-$ while the Bischoff and Hathorn #3 waters contain almost 180 millimoles $Cl^-$. Combining this with enough $Na^+$ to obtain a Na/Cl ratio of .96 (the Gorman ratio) yields a formational water with 10,400 mg/l dissolved NaCl. Also taking into account the fact that several defunct carbonated wells exceeded 20,000 ppm total dissolved solids, it seems probable that the undiluted formational water averages 12,00 to 15,000 mg/l total dissolved solids, mostly NaCl, but including minor ions such as $Ca^{++}$, $Mg^{++}$, $Br^-$, etc.

Another interesting aspect of the formational water mixing problem derives from a close inspection of these figures with respect to the location of the wells. It can be seen that the total salinity and $HCO_3^-$ ion concentrations increase in a general way toward the south where the shale cap thickens. Wells from the Hathorn #3 south through the Ballston Spa group are $600^+$ feet in depth with the total dissolved solids values increasing from 16,000 in the Hathorn to a peak of 20,000 in Ballston Spa. This is less of a difference than is present in the northern wells. It is of particular interest because a depth of 750 feet is equal to the present best estimate of the minimum differential pressure needed (200 to 500 psi) for effective ultrafiltration to take place

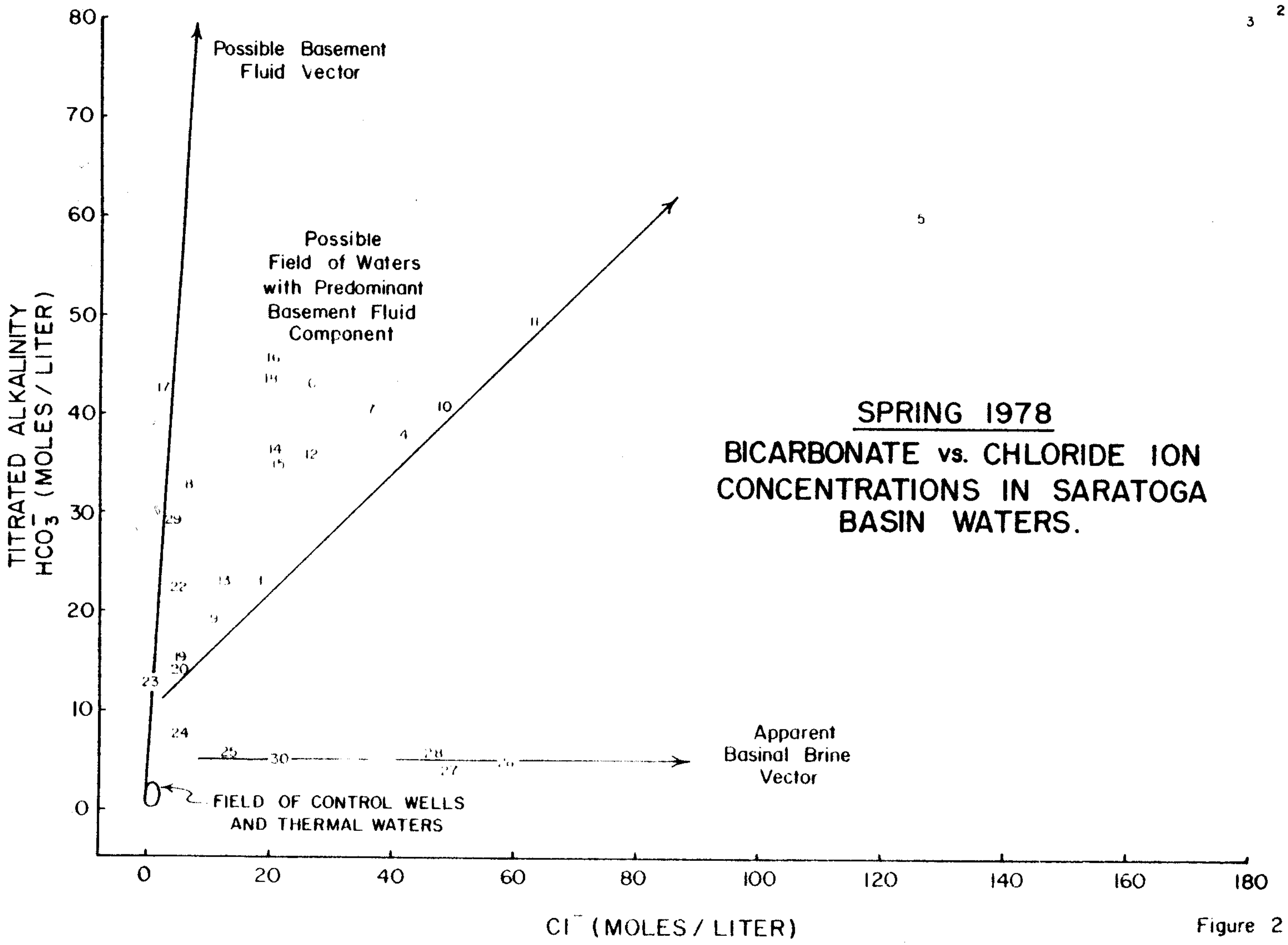
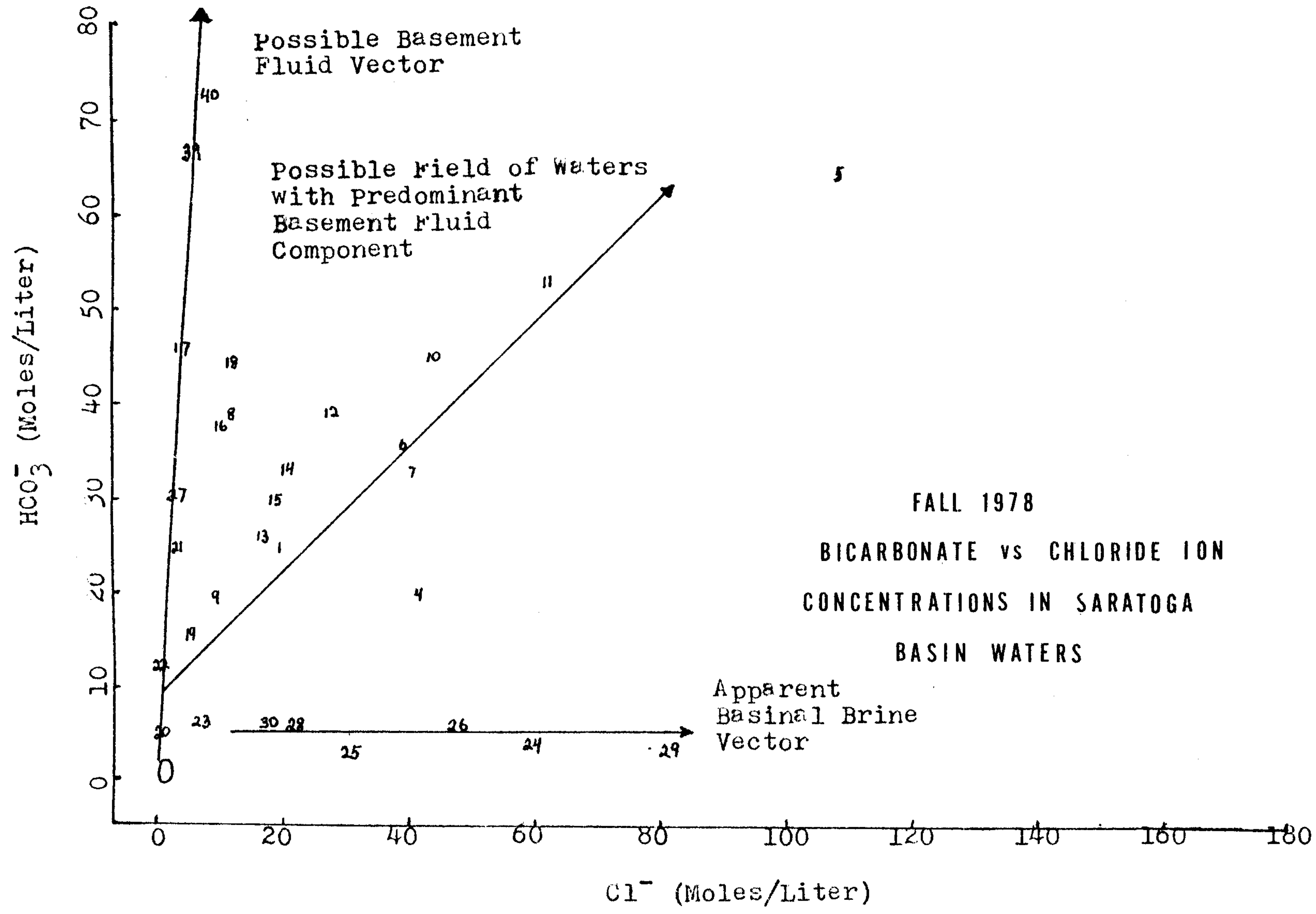

SPRING 1978
BICARBONATE vs. CHLORIDE ION CONCENTRATIONS IN SARATOGA BASIN WATERS.
TITRATED ALKALINITY
$HCO_3^-$ (MOLES / LITER)
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
$Cl^-$ (MOLES / LITER)
Possible Basement Fluid Vector
Possible Field of Waters with Predominant Basement Fluid Component
Apparent Basinal Brine Vector
FIELD OF CONTROL WELLS AND THERMAL WATERS
2
3
5
11
16
18
6
17
7
10
4
14
15
12
8
29
22
13
1
9
19
20
23
24
25
30
28
27
26

Figure 2



FALL 1978

BICARBONATE vs CHLORIDE ION CONCENTRATIONS IN SARATOGA BASIN WATERS

(Graf et al, 1966). These wells just approach this value accounting for their higher total dissolved solids, lower change of NaCl, and lower $SiO_2$. This may all be due to meteoric water dilution, of course, with all filtration taking place long ago.

While 15,000mg/l appears to be the upper limit of the salinity for the known samples, theory predicts an increase to possible contents of 100,000mg/l or more toward the center of the lowlands if the thickness of the shales were to exceed 2 km. Evidence for increasing salinity with depth has been well established by many case studies (Graf et al, 1966; Chebotarev, 1963, etc.). The tendency for waters near the periphery to peak near 20,000 mg/l salinity inplies a restricted circulation system unconnected with the deeper parts of the basin if higher salinities exist. More direct evidence for this suggestion is discussed in sections 4.5 and 6.3.

Some final obsevations on saline water mixing evolve from a review of the molar ratios, the most revealing of which may be the Cl/Br ratios, (Tables 2s and 2f of the appendix). The most reliable analyses of the southern saline waters group give ratios between 110 and 190, far below the 663 of sea water (Livingston, 1963; White et al, 1963). It is not known whether these waters could have derived their $Cl^-$, $Br^-$, and $Na^+$ components from an original ultrafiltration of meteoric water or whether filtration has thus modified original sea water. The near 1.0 Na/Cl ratios suggest sea water, while more certainly these ratios preclude leaching of halite as a source of NaCl since Cl/Br ratios higher than sea water would result.

Of equal importance are the patterns of Cl/Br ratios. The Martin and Smith (before) waters have ratios of 17 and 23, respectively, which are consistent with those of the meteoric water control group. The values also suggest that the basement fluids contribute a negligible quantity of these elements. The Saratoga group's ratios, however, span a range from 113 to 169 (excluding the Rosemary's 61) while the north central waters range from 46 to 96 (excluding the Martin well). The former are virtually identical to the southern group; the latter intermediate between saline water and meteoric water. This pattern of ratios shows the degree of saline water mixing as well as any other single ratio or chemical parameter.

## 6.3 The Meteoric Water "Cap"

The properties and function of the glacial-shale-hardpan cap above the Paleozoic carbonates in the immediate Saratoga Springs area was discussed in section 2 and illustrated in plate 3. It has long been known that this material hosts normal meteoric water suitable for domestic use with a variable water table averaging 10-25 feet in depth (Kemp, 1912; Colony, 1930). A representative analysis from a shallow spring (the Ferndell Spring), issuing from this strata and bottled for many years under the name of State Seal follows below:

| IONS AND RADICLES | CONTENT (PPM) |
|---|---|
| $SiO_2$ | 5.0 |
| $SO_4$ | 22 |
| $HCO_3$ | 104 |
| $NO_3$ | trace |
| $NO_2$ | trace |
| $PO_4$ | trace |
| $BO_2$ | 0.25 |
| Cl | 4.8 |
| Br | none |
| I | none |
| Fe | .40 |
| Al | .034 |
| Mn | .002 |
| Ca | 32.2 |
| Ba | .038 |
| Sr | .11 |
| Mg | 4.4 |
| K | .15 |
| Na | 2.0 |
| Li | .01 |
| $NH_4$ | trace |
| $Ra^{226}$ | 2.1 uuC/l |
| TDS | 175 |

Table 6.5 Analysis of the State Seal water. Analysis made in August 1959 by G.E. Hegger (chemist for the Saratoga Springs Reservation) from a sample taken from bottled water.

These data illustrate an interesting hydrologic property of the caprock system that has regional implications for the possible existence of a hidden geothermal system (section 10). Sulfates are uniformly present in these "Upper" ground waters (particularly those in shales) as shown by the results of the analysis quoted above but only the barest traces of sulfates are present in the carbonated or saline mineral waters (Plates 1 and 2). These sulfates are derived by oxidation of pyrite contained in the shales producing $H_2SO_4$. Excess bicarbonates, chlorides, anomalous trace elements, and, particularly, free $CO_2$ are found in these uppper waters. Minor infiltration of the mineral water can perhaps be seen in the slighly abnormal concentrations of $Ra^{226}$, a very mobile component.

All of this serves to indicate the extremely effective segregation properties of the shale cum hardpan cap while also acccounting for the paucity of natural carbonated seeps. The relative thinness of the cap (varying from a few feet near the Red Spring to only several hundred in the area of the reservation) emphasizes this effect. Further east, where the thickness of the caprock system is greater (perhaps as much as several thousand feet near the Taconic allochthon) meteoric water saturation of the shales could effectively damp out any deeper geothermal system. Its efficiency is demonstrated by: 1) the small number of carbonated wells in areas of shale cover; and 2) the presence of a sizable component of meteoric shale water- characterized by high contents of $SO_4^=$ in the few examples of carbonated waters in these areas, i.e. Davis, Vita Spring, Pitcher, and Pattersonville.

Another aspect of meteoric water mixing in the immediate Saratoga area may be deduced from the present data set. While the saturated shale cap effectively traps the lower carbonated waters, it does not appear to keep the meteoric water out. Evidence for this is discussed in section 4.10, on seasonal fluctuations in response to the hydraulic pressure of the ground water zone. An increase of $SiO_2$ and $HCO_3^-$ with lower pH values in the mineral waters strongly indicate less dilution of deep basement fluids during the fall. Since TDS and Cl contents do not change appreciably, a general seasonal saline water component dilution during the spring does not appear likely. The lower spring values then, may be most reasonably assigned to dilution of discharging wells by excess meteoric water entering the aquifer from the spring runoff. Further, section 7.1.3 concerning historical chemical changes indicates that long term meteoric water flushing of the aquifer is an ongoing process which is progressively diluting the saline waters under Saratoga Springs. The flushing effect tends to decrease in strength from the north to the south correlating with an increase in the thickness of the shale caprock. This is precisely the pattern to be anticipated from meteoric dilution.

## 7.0 FLUID ENTRY AND TRANSPORT IN THE AQUIFER

One of the classic intriguing questions posed by the Saratoga waters has been their source and possible direction of flow to the resevoir zones at the points of discharge. Corollaries of this problem are the mechanisms and efficiency of transport in the aquifer and the Precambrian basement. Most earlier workers have addressed these problems with varying success (Kemp, 1912; Cushing and Reudemann, 1914; Colony, 1930; Strock, 1941) defining most of the principal points among them. Combined with the additional data available from this study, it is now possible to answer most of the questions (at least in a limiting perspective) as they pertain to the immediate area of the city. It is also possible to partially answer these questions for the greater carbonated water system of the upper Hudson Valley.

### 7.1 Saratoga Springs Group

### 7.1.1 Major Ion Trends

Major ions are defined herein as $Cl^-$, $HCO_3^-$, and $Na^+$ without including $K^+$, $Mg^{++}$, $Ca^{++}$, and $Br^-$ as in other portions of this report (see appendix). Two significant patterns emerge from a review of this data:

1) $Cl^-$, $HCO_3^-$, and $Na^+$ ion concentrations decrease in a general, though somewhat erratic, way from south to north;
2) the <u>rate</u> of decrease from south to north is greater

for $Cl^-$ than $Na^+$ or $HCO_3^-$ which, in fact, become the dominant ions in the northerly wells.

These observations are not new, but were first recognized by Colony (1930) and presented in an elegant plot including the well logs for the individual water chemistry data points. The concentrations of these ions are also plotted from south to north for the fall 1978 sampling in figure 7.1. This shows a rapid decrease in concentrations as well as a general crossover point for the $Cl^-$ anion at the Geyser well. From this point north $HCO_3^-$ and $Na^+$ dominate the individual waters or, in other words, decrease at a lower rate than the $Cl^-$ anion.

What can be made of this? Colony interpreted these facts to indicate a south to north movement of the waters with attendant dilution by meteoric waters along the way. As corroboration he cited a pumping test conducted in the early 1900's among the closely spaced Lincoln wells. This revealed a general SE/NW movement of the waters in this area which he further interpreted as an indication of water flow through the primary conduit of the Saratoga Fault; this being thought to underly the Carbonic Acid Company's lands at the time.

Today these facts require reinterpretation because of new supportive data. The decrease in major ion content from south to north also coincides with the decreasing thickness of the shale caprock. These two parameters should vary sympathetically because of increasing dilution of the remnant

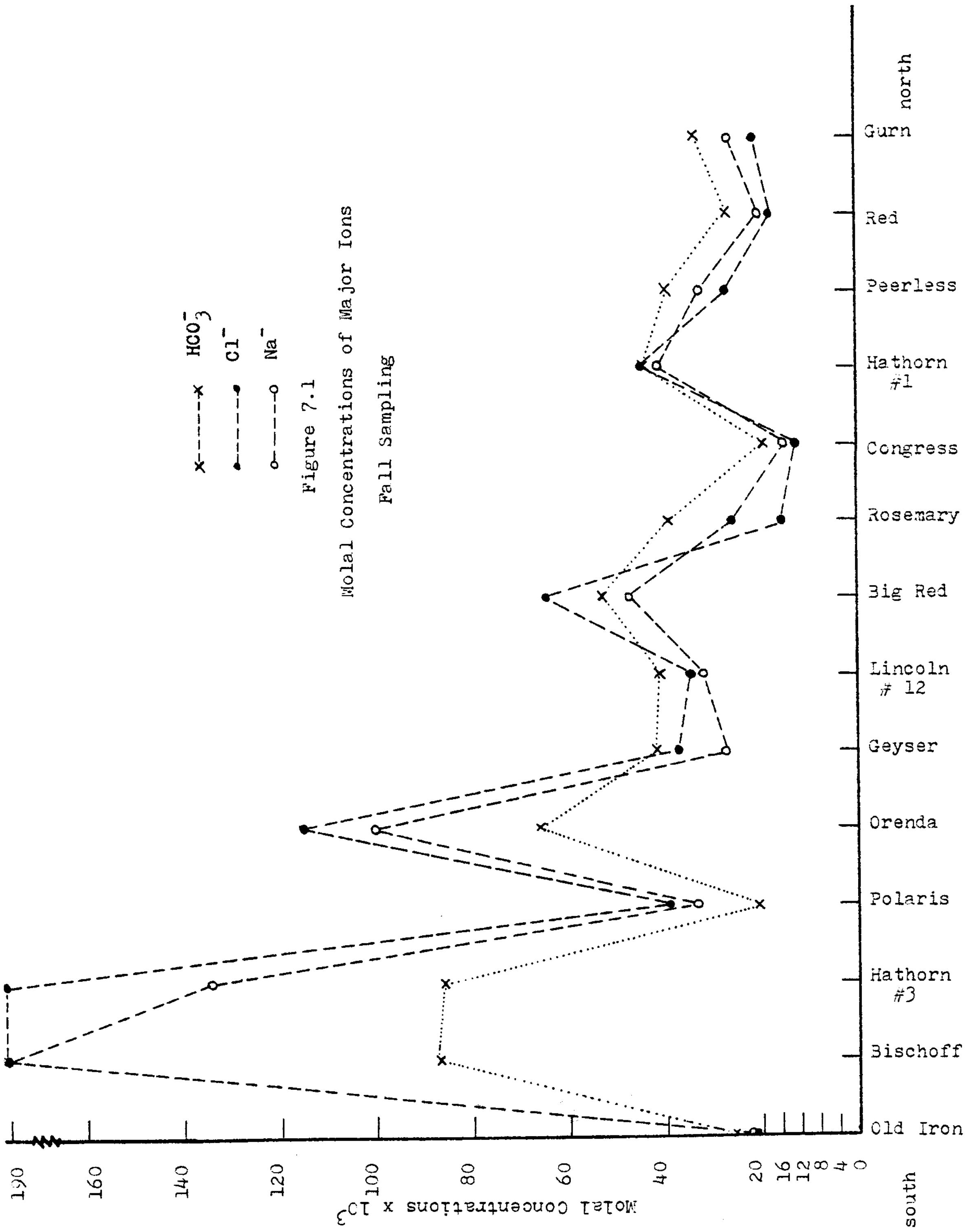


Figure 7.1

Molal Concentrations of Major Ions

Fall Sampling

brines by meteoric waters with decreasing cap thickness.

This explanation demands, of course, that the $NaHCO_3$ type basement fluid enters or is injected into the Paleozoic aquifer more or less continuously along the Saratoga Fault as well as others. The relative rate of increase of $Na^+$ and $HCO_3^-$ ions contents from south to north can also most easily be explained by this hypothesis. Selective dilution of only the $Cl^-$ ion (again, in a relative sense) is difficult to understand as a process applying to a single phase fluid moving north from Ballston Spa and, presumably, points south.

### 7.1.2 Historical Data Patterns - Chemical

Only rarely is it possible to examine water chemistry patterns over intervals of tens or even a few years. Saratoga provides one of the few pleasnt exceptions because of early interest in the purported therapeutic properties of the waters. A reliable record dates back at least to the Haywood and Smith analyses of 1905 and, probably, to the Chandler series of 1875 (see appendix). Still older less reliable analyses back to the 1840's also exist. From 1905 to the present a continuous, though sporadic, record exists because of New York State's establishment of the Saratoga Springs Reservation. This created a position for a chemist to monitor the chemistry of the waters on an annual basis. Some of this data is available (see appendix) and reveals several interesting trends when plotted systematically.

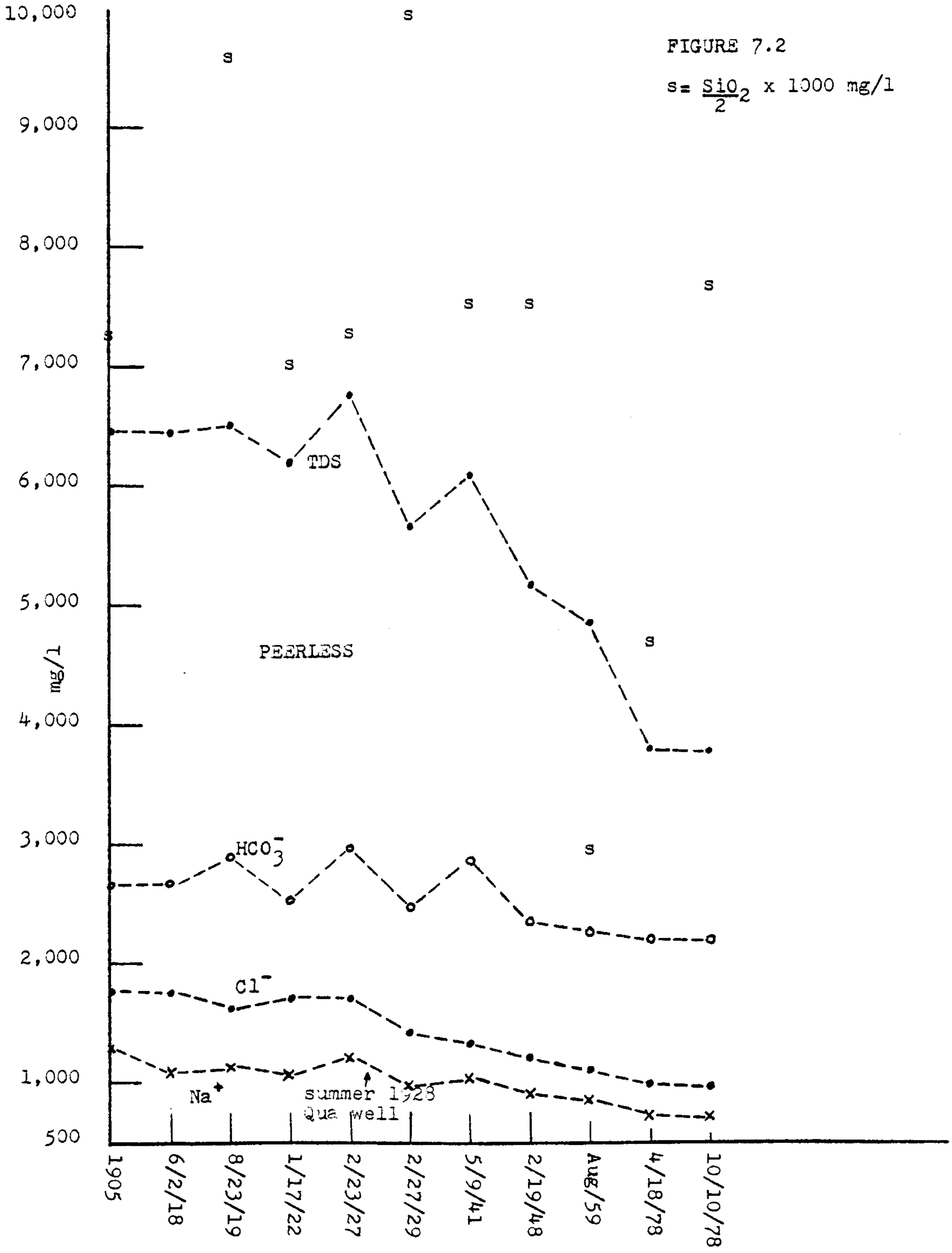


FIGURE 7.2

s= $\frac{SiO_2}{2}$ x 1000 mg/l

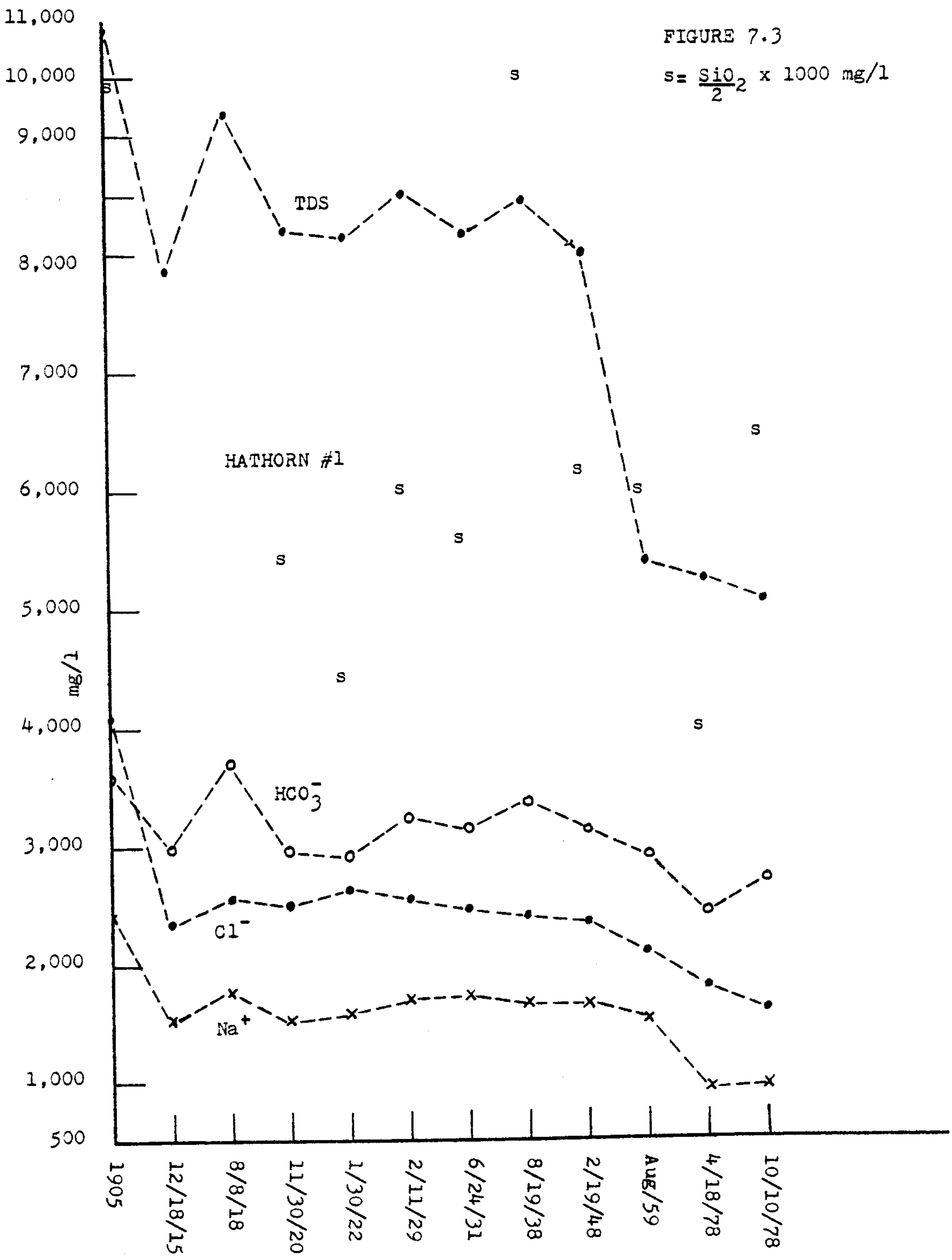


FIGURE 7.3

$s = \frac{SiO_2}{2} \times 1000$ mg/l

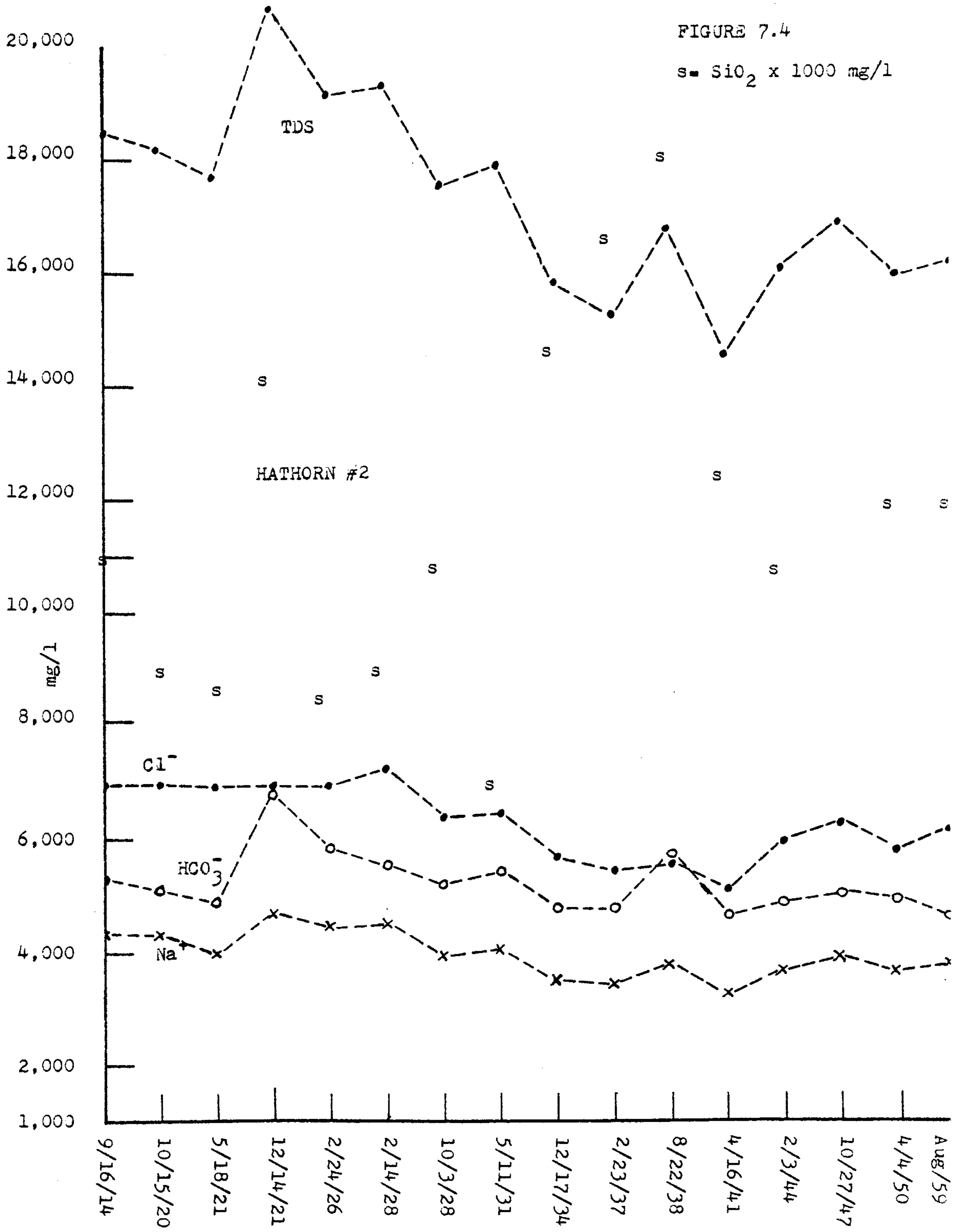
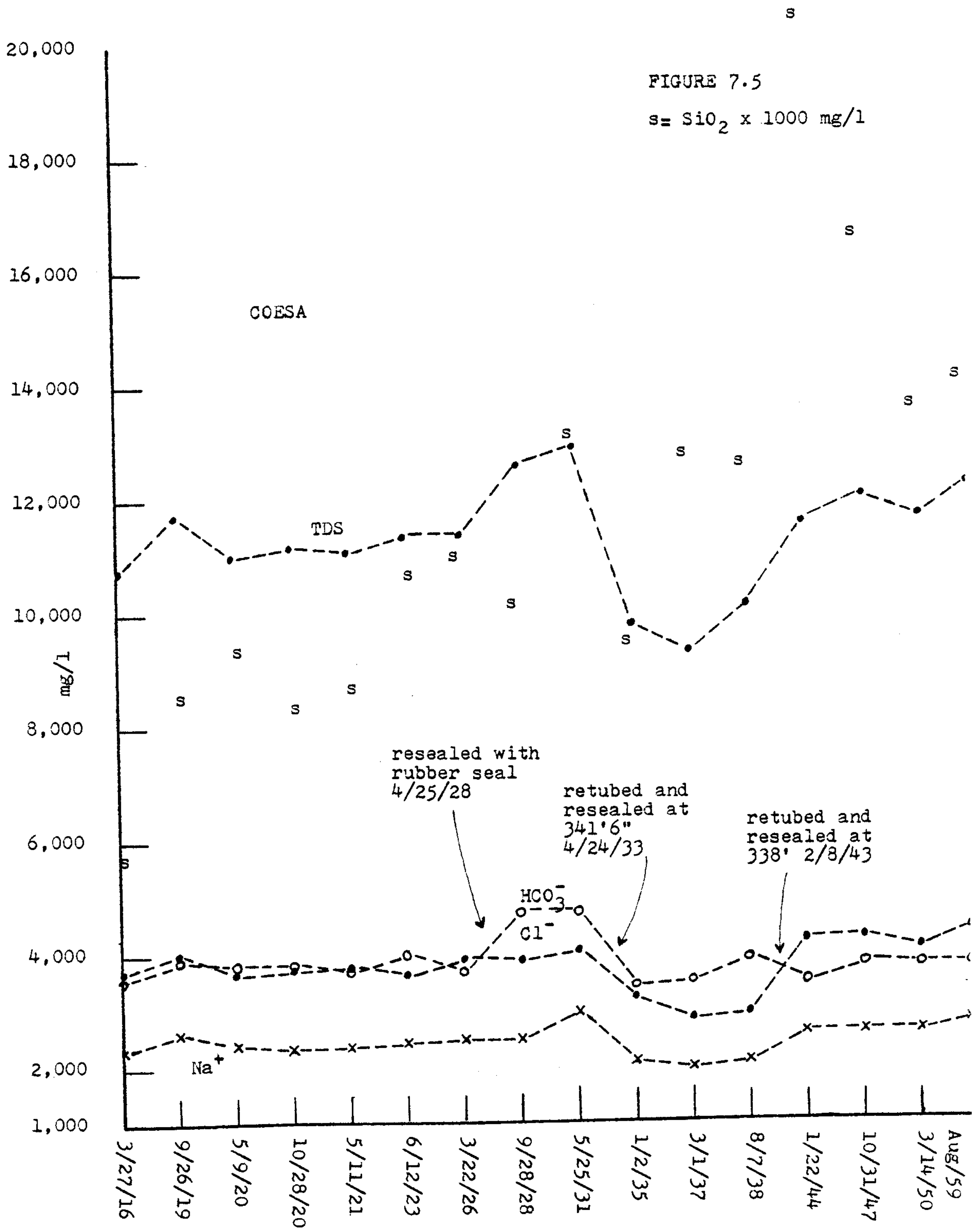


FIGURE 7.4

s= $SiO_2$ x 1000 mg/l

FIGURE 7.5

$s = SiO_2 \times 1000$ mg/l



resealed with rubber seal 4/25/28

retubed and resealed at 341'6" 4/24/33

retubed and resealed at 338' 2/8/43

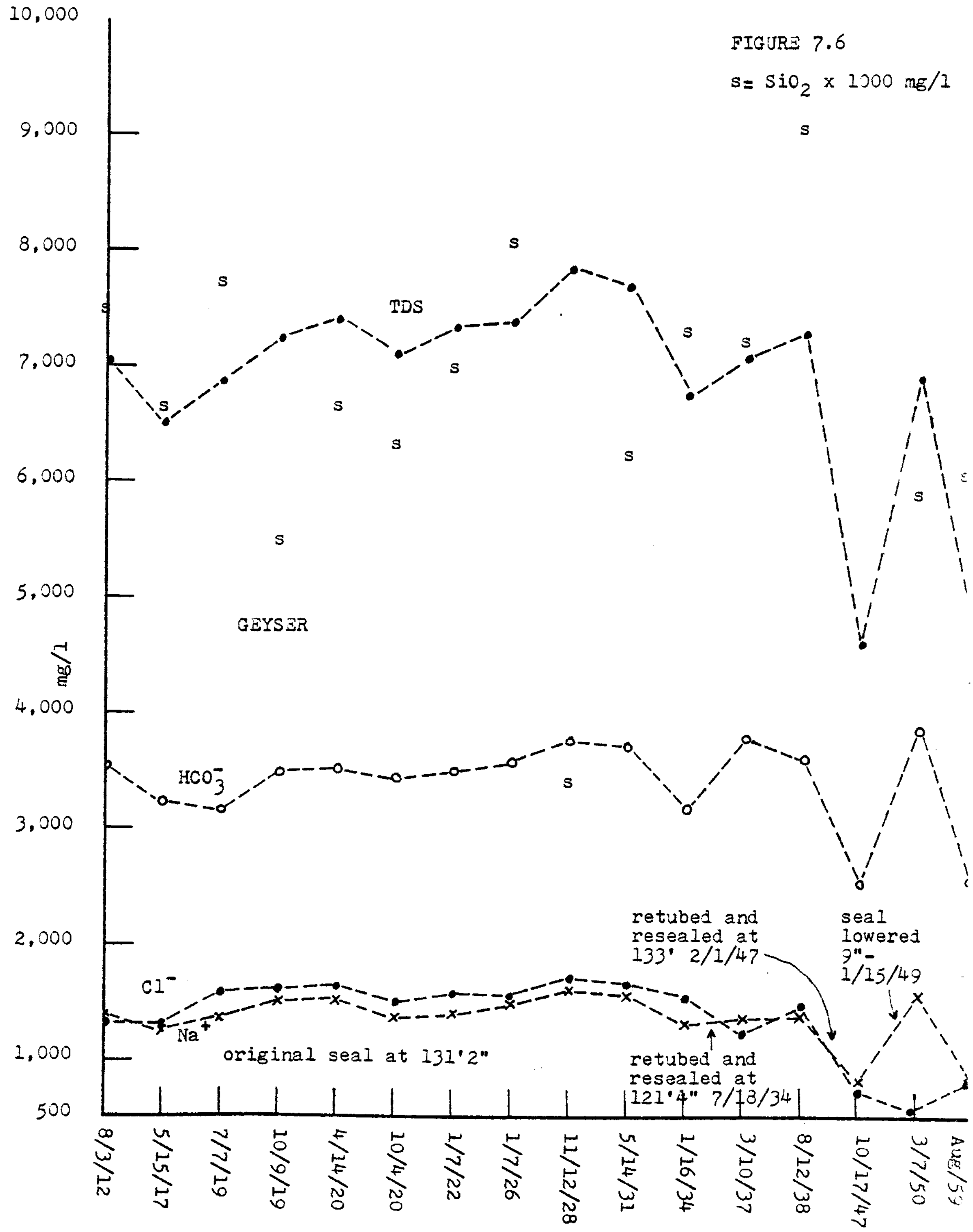


FIGURE 7.6

s= $SiO_2$ x 1000 mg/l

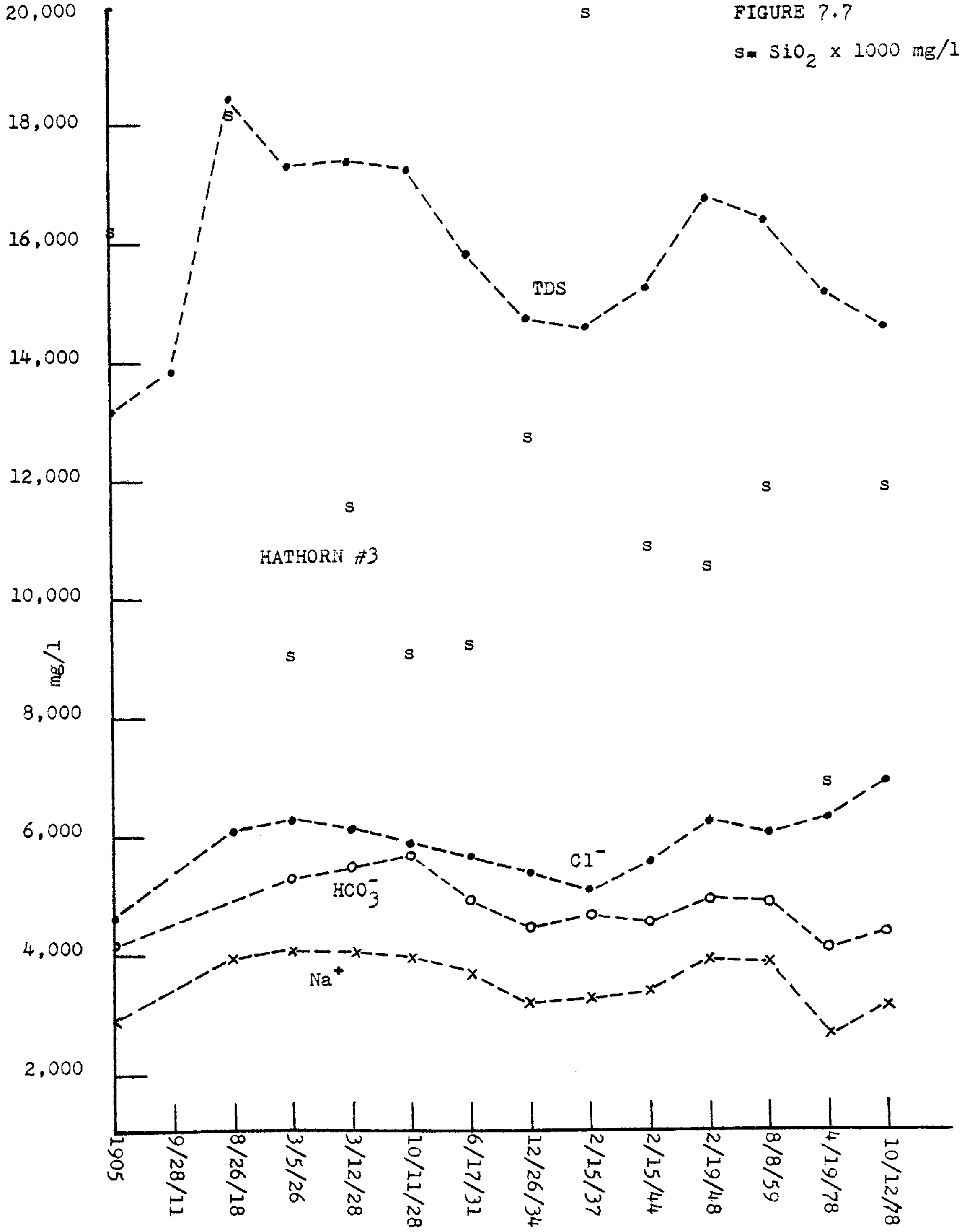


FIGURE 7.7

s= $SiO_2$ x 1000 mg/l
HATHORN #3
mg/l
20,000
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
TDS
$Cl^-$
$HCO_3^-$
$Na^+$
s
1905
9/28/11
8/26/18
3/5/26
3/12/28
10/11/28
6/17/31
12/26/34
2/15/37
2/15/44
2/19/48
8/8/59
4/19/78
10/12/78

Figures 7.2 through 7.7 are time vs. concentration plots of the six wells for which the most data is available (see appendix). The parameters included are TDS, $SiO_2$, $Na^+$, $HCO_3^-$, and $Cl^-$. While each graph discloses information about individual wells, some general correlations also emerge. They are discussed below in order of decreasing certitude and importance.

First there appears to be a general decreases in TDS, $Cl^-$, $Na^+$, and $HCO_3^-$ through the years in many of the wells. Figures 7.2 - 7.4, the Peerless, Hathorn #1, and Hathorn #2 wells offer the best evidence of this trend. In all of these waters there is a marked drop in the total salinity since the early 1900's. Close inspection also shows a generally greater decrease in the $Cl^-$ ion than with $Na^+$ or $HCO_3^-$ or, accordingly, with the remnant brine component rather than components of the basement fluid. This further implies that these wells are tapping a restricted "brine resevoir" with little or no loss of the $NaHCO_3$ - type fluid. Such a restricted circulation system is quite plausible if the block faulting immediately west of the city extends under the shale cap; and there is every reason to believe this so. Further implied is the direct injection of a $NaHCO_3$ - type carbonated fluid into the aquifer underneath the city in the vicinity of the wells.

Of the three other plots, one, the Geyser well, (figure 7.6) may exhibit this pattern. The more recent data, however, are too scattered to be certain of this interpretation.

The remaining two wells, Hathorn #3 and the Coesa show a small increase in TDS and $Cl^-$ content from the late 1940's to the present. While antithetical to the general pattern, these wells are in close proximity to one another (approximately 200 meters) and have similar water chemistry now as well as historically. They are considered anomalous at this time (for reasons discussed further below) because other wells with less reliable data also conform to the pattern of decresing salinity, i.e. the Lincoln wells (see appendix).

Another pattern of some import is best seen in the Geyser and Coesa wells, figures 7.5 and 7.6. Large variations in TDS and individual ion content in these waters are coincident with retubing and resealing operations as noted on the graphs. This obsevation is but another indication of the heterogeneity induced by ongoing water mixing in the Paleozoic aquifer under Saratoga Springs. It is all the more impressive that raising or lowering the seals less than 10 feet can create a different water type as in the Coesa well, 1938 to 1944, or in the Geyser, 1947 to 1950.

A third more tenuous correlation that appears for most of the six plotted wells is an inverse relation of $SiO_2$ with the $Cl^-$ ion. The uncertainty derives mostly from strong seasonal fluctuations of $SiO_2$ content due to increased meteoric dilution during the spring runoff, a principle prviously discussed in section 6.3. This trend is clearest in figures 7.4 and 7.5 for the Hathorn #2 and Coesa waters.

### 7.1.3 The $CO_2$ Gas

Another qualitative indicator of transport times and entry points of the carbonated $NaHCO_3$ - type fluid into the aquifer is provided simply by the presence of free $CO_2$ in the waters. More specifically, the dominant carbonate species of most of the carbonated waters is $H_2CO_3$ or dissolved $CO_{2(aqueous)}$ and $HCO_3^-$ ion. This follows from the ionization equation of $H_2CO_3$:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^=$$

which can be restated in terms of equilibrium concentrations and ionization constants as:

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_1 = 10^{-6.47} \text{ at } 10^\circ C$$

and $$\frac{[H^+][CO_3^=]}{[HCO_3^-]} = K_2 = 10^{-10.49} \text{ at } 10^\circ C$$

or slightly rearranged in the form

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{10^{-6.47}}{H^+}$$

and $$\frac{[CO_3^=]}{[HCO_3^-]} = \frac{10^{-10.49}}{H^+}$$

From these expressions it can be easily seen that the concentrations of the dissolved carbonate ion species equal unity when the pH equals 6.47 and 10.49, respectively. At pH values less than 6.47 the dominant carbonate species in the first equation is $H_2CO_3$. Commonly having pH values of 6.0 to 6.2 or less, most of the Saratoga waters are therefore moderately to markedly acidic.

The discharge of such acidic waters from dolostones and limestones containing highly reactive carbonate minerals is very significant in itself. The reaction

$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca^{++} + 2HCO_3^-$$

for example, is very rapid in the righthand direction. Should the waters have traveled any appreciable distance in the carbonate aquifer, say 5 miles or more, it would be expected that most or all of the $H_2CO_3$ would have reacted with the wall rocks to form $HCO_3^-$. That this is not the case is shown by the pH readings and demonstrated in section 7.1.4 by calculations showing an undersaturation of $Ca^{++}$ in most of the waters.

This relative limitation of $HCO_3^-$ can be shown in another way. Neutrality can be defined by two equations:

$$\frac{[H_2CO_3]}{p_{CO_{2(g)}}} = K_{CO_2} = 10^{-1.47}$$

and $$\frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = K_{H_2CO_3} = 10^{-6.47}$$

(constants from Garrels and Christ, 1965). Since the reaction of the acid/gas with the carbonate wall rocks will tend toward neutrality the potential amount of $HCO_3^-$ for this state can be calculated for any desired well by substituting $10^{-7.0}$ for $H^+$ and the calculated $p_{CO_2}$ values from tables 3s and 3f of the appendix. Insertion of these values shows the following results for a few of the waters:

| WELL | $HCO_3^-$ at NEUTRALIZATION |
|---|---|
| Orenda | 27,248 |
| Rosemary | 14,974 |
| Martin | 20,340 |

Table 7.1 Amounts of $HCO_3^-$ at neutralization of some of the carbonated waters.

This large relative departure of the actual $HCO_3^-$ values from the calculated limits can only mean that the waters have not traveled very far from their points of entry into the aquifer. Since the hydraulics as well as carbonate dissolution rates are not known, the actual distance may only be speculated, however, an upper limit of one to two miles would semm reasonable. Arguments developed in other portions of this chapter show that, for at least a few of the wells, i.e. Rosemary, the distance is considerably less than this figure.

### 7.1.4 $CaCO_3$ Equilibria

Most carbonated waters are known to deposit tufa or travertine ($CaCO_3$) at their points of issuance; Mammoth Springs in Yellowstone National Park being a classic example. The Saratoga "springs" also deposit tufa (figure 3.1) although not in the quantities one might expect from highly carbonated waters in contact with limestones and dolomites. Modest tufa mounds themselves suggest that the waters are undersaturated in the $Ca^{++}$ ion with respect to residence time in the aquifer. Equilibrium $Ca^{++}$ calculations for representative waters of Saratoga Springs and other water groups are done below modified after a method recommended by Garrels and Christ (1965).

Limestones and dolostones in contact with dissolved $CO_{2(aq)}$ will undergo the following general reaction:

$$CaCO_{3(s)} + H_2CO_{3(aq)} \rightleftharpoons Ca^{++} + 2HCO_3^-$$

Further dissociation of the carbonates and acid will occur as:

$$CaCO_3 \rightleftharpoons Ca^{++} + CO_3^= \qquad -\log K_{CaCO_3} = 10^{-8.15}$$

$$H_2CO_{3(aq)} \rightleftharpoons H^+ + HCO_3^- \qquad -\log K_{H_2CO_3} = 10^{-6.47}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad -\log K_{HCO_3} = 10^{-10.49}$$

where $H_2CO_3$ is dissolved $CO_2$ and K = equilibrium constant at 10°C and 1 atm. pressure (Garrels and Christ, 1965)

Since $H_2CO_3$ can be expressed in terms of $H^+$, $HCO_3^-$, and $CO_3^=$, only two equations are needed to define saturation as a function of carbonation:

$$(1) \quad \frac{[Ca^{++}]\,[CO_3^=]}{[CaCO_3]} = K_{CaCO_3} = 10^{-8.15}$$

$$(2) \quad \frac{[H^+]\,[CO_3^=]}{[HCO_3^-]} = K_{HCO_3} = 10^{-10.49}$$

Reexpressing and rearranging these equations in terms of molal concentrations and activity coefficients yields:

$$(1a) \quad m_{Ca^{++}}\, m_{CO_3^=} = \frac{10^{-8.15}}{y_{Ca^{++}}\, y_{CO_3^=}}$$

$$(2a) \quad \frac{a_{H^+}\, m_{CO_3^=}}{m_{HCO_3^-}} = \frac{10^{-10.49}\, y_{HCO_3^-}}{y_{CO_3^=}}$$

where $Ca^{++}$, $a_{H^+}$, and $m_{HCO_3^-}$ can be computed directly from the analyses and $y_{Ca^{++}}$, $y_{CO_3^=}$, and $y_{HCO_3^-}$ are the activity coefficients of the respective ionic species.

The activity coefficients of the individual waters are of concern because they are electrolytic solutions of variable strength whose dissolved substances are largely dissociated into charged particles. Because the nature of the interaction of the dissolved ions with each other and with the solvent changes in a complex way with concentration, activity coefficients must be individually calculated for each water based on its ionic strength. Ionic strength (I) is defined by

$$I = 1/2 \sum m_1 z_1^2$$

where $m_1$= molality of the given ionic species and

$z_1$= charge of the $i^{\underline{th}}$ ion in solution

Having determined I, the activity coefficients of $Ca^{++}$, $CO_3^=$, and $HCO_3^-$ can be calculated by the Debye-Hückel expression:

$$-\log y_i = \frac{A z_i^2 \ I}{1 + å_1 B \ I}$$

Here $z_1$ and I have the meanings previously ascribed in the definition of ionic strength, and A and B are constants characteristic of the solvent (water) at a specified temperature and pressure. Values of A= .4960 and B= .3258 x $10^{-8}$ are used herein for water at 10°C and a pressure of 1 atm. (Garrels and Christ, 1965). The symbol $å_1$ defines the "effective diameter" of the ion in solution and has been experimentally determined for many ions. Those used are $Ca^{++} = 6 \times 10^8$, $CO_3^= = 4.5 \times 10^8$, and $HCO_3^- = 4.5 \times 10^8$ (Garrels and Christ, 1965).

The equlibrium calculation for $Ca^{++}$ solubility is detailed below for the Rosemary well with antilogarithms used throughout for facility. Only major ions are considered in determining ionic strength of the individual waters; the effect of the minors should be negligible.

ROSEMARY (Fall 1978)

| Ion | Concentration (mg/l) | Molality (m) |
|---|---|---|
| $HCO_3^-$ | 2390 | .040 |
| $Cl^-$ | 560 | .016 |
| $Na^+$ | 590 | .0257 |
| $Ca^{++}$ | 270 | .0067 |
| $Mg^{++}$ | 190 | .0078 |
| $K^+$ | 87 | .0022 |

Taking the ions as they appear from top to bottom:

$$I = 1/2 \left[(.040 \times 1) - (.016 \times 1) - (.0257 \times 1) - (.0067 \times 4) - (.0078 \times 4) - (.0022 \times 1)\right]$$

$$= .045$$

$y_{Ca^{++}}$, $y_{HCO_3^-}$, and $y_{CO_3^=}$ are now calculable

$$-\log y_{Ca^{++}} = \frac{(.4960)\ (4)\ (\sqrt{.045})}{1 + (6 \times 10^8)\ (.3258 \times 10^{-8})\ (\sqrt{.045})}$$

$$= .298$$

$$-\log y_{HCO_3^-} = \frac{(.4960)\ (1)\ (\sqrt{.045})}{1 + (4.5 \times 10^8)\ (.3258 \times 10^{-8})\ (\sqrt{.045})}$$

$$= .080$$

$$-\log y_{CO_3^=} = \frac{(.4960)\ (4)\ (\sqrt{.045})}{1 + (4.5 \times 10^{8})\ (.3258 \times 10^{-8})\ (\sqrt{.045})}$$

$$= .321$$

Substituting $a_{H^+}$, $m_{HCO_3^-}$, and $y_{CO_3^=}$ in equation 2a

$$\frac{10^{-6.0}\ m_{CO_3^=}}{10^{-1.40}} = \frac{10^{-10.49}\ 10^{-.08}}{10^{-.32}}$$

$$m_{CO_3^=} = 10^{-5.65}$$

Using this value and $y_{Ca^{++}}$ and $y_{CO_3^=}$ in equation 1a

$$m_{Ca^{++}}\ 10^{-.30} = \frac{10^{-8.15}}{10^{-.32}\ 10^{-5.65}}$$

$$m_{Ca^{++}} = 10^{-1.88} \text{ or } .013m$$

Thus calculated, the equilibrium calcium content is $10^{-1.88}$ while the analysed calcium is $10^{-2.17}$, so the Rosemary water is undersaturated with respect to precipitation of calcium carbonate by a factor of approximately two according to these calculations. Equilibrium calculations for some of the representative waters are tabulated below:

| SAMPLE | DATE OF SAMPLING | I | CALCIUM EQUILIBRIUM<br>CALCULATED | <br>ANALYTICAL |
|---|---|---|---|---|
| Rosemary | fall 1978 | .045 | 521 mg/l | 270 mg/l |
| Big Red | spring 1978 | .135 | 621 | 340 |
| Peerless | spring 1978 | .08 | 853 | 420 |
| Red | spring 1978 | .091 | 586 | 260 |
| Orenda | spring 1978 | .186 | 364 | 510 |
| Bennet | spring 1978 | .071 | 365 | 250 |
| Martin | spring 1978 | .062 | 271 | 100 |
| Hathorn #1 | spring 1978 | .095 | 420 | 410 |
| Hathorn #3 | spring 1978 | .52 | 1183 | 680 |
| Doster | spring 1978 | .06 | 133 | 97 |
| August Bohl | spring 1978 | .0535 | 163 | 27 |

Table 7.2 Calculated $CaCO_3$ equilibria

These values are considered relatively accurate since the numbers used represent the best experimental data available. Uncertainties are most likely to occur with the individual activities calculated by the Debye-Hückel equation where I is greater than .05 (Garrels and Christ, 1965). Accordingly, activity coefficients for the three wells significantly above this figure (Big Red, Orenda, and Hathorn #3) were recalculated using the preferred mean salt method described by Garrels and Christ (1965). Of these only the Hathorn #3, the well with the highest ionic strength, differed significantly and the calculated value that appears in table 7.2 was obtained by this second method.

These calculations establish beyond doubt that most of the waters are undersaturated with respect to calcium. Reinforcement for this is provided by the Orenda well; the only water apparently saturated with $Ca^{++}$ it is also the only well with a large mound of tufa present. Since the dissolution of $Ca^{++}$ from the action of $H_2CO_3$ on $CaCO_3$ is a very rapid reaction these values indicate that the carbonated waters could not have traveled very far from their points of entry into the carbonate aquifer.

### 7.1.5 Silica Stability

Although $SiO_2$ was discussed at length in section 5.2 and is mentioned elsewhere, several nuances of interpretation remain that have a strong bearing on transport time in the aquifer and associated points of injection. Figure 7.8

is a plot of $SiO_2$ vs. time after smpling for water collected from the wellhead of a Hawaiian geothermal bore. While the data only encompass a short 4 day time span, it is sufficient to demonstrate the relatively rapid rate of $SiO_2$ decay in thermal waters cooled to ambient temperatures. Extrapolation of this curve to the Saratoga well contents of higher $SiO_2$ i.e. Big Red 70, Gurn 55, or Rosemary 40, indicates that the $SiO_2$ apparently would not remain in solution in these waters for more than a month at their surface discharge temperatures of approximately $10^oC$.

The only caveat that might be appended to this observation is contained in figure 7.9, a plot of $SiO_2$ in solution vs. pH of the solvent (water). It can be seen that acidic waters tend to hold slightly less $SiO_2$ in solution than basic waters. At the possible pH values of less than 6.0 in the aquifer (and perhaps even lower in the basement) this effect also suggests a short transport time in the aquifer. In other words it may be stated that the distinct metastability of excess $SiO_2$ in solution in these waters strongly suggests that the injection points of deeper basement fluids into the aquifer are not too far distant from the wells.

In section 5.2 it was noted that the overall pattern of $SiO_2$ levels is one of sharp differences in wells often separated by very short distances, i.e. Peerless and Red. Such a pattern is best understood if the irregular mixing of the deep $NaHCO_3$-type fluid with the dilute connate waters is occurring at multiple points under the city of Saratoga

Figure 7.8 $SiO_2$ Concentrations vs. Time After Sampling

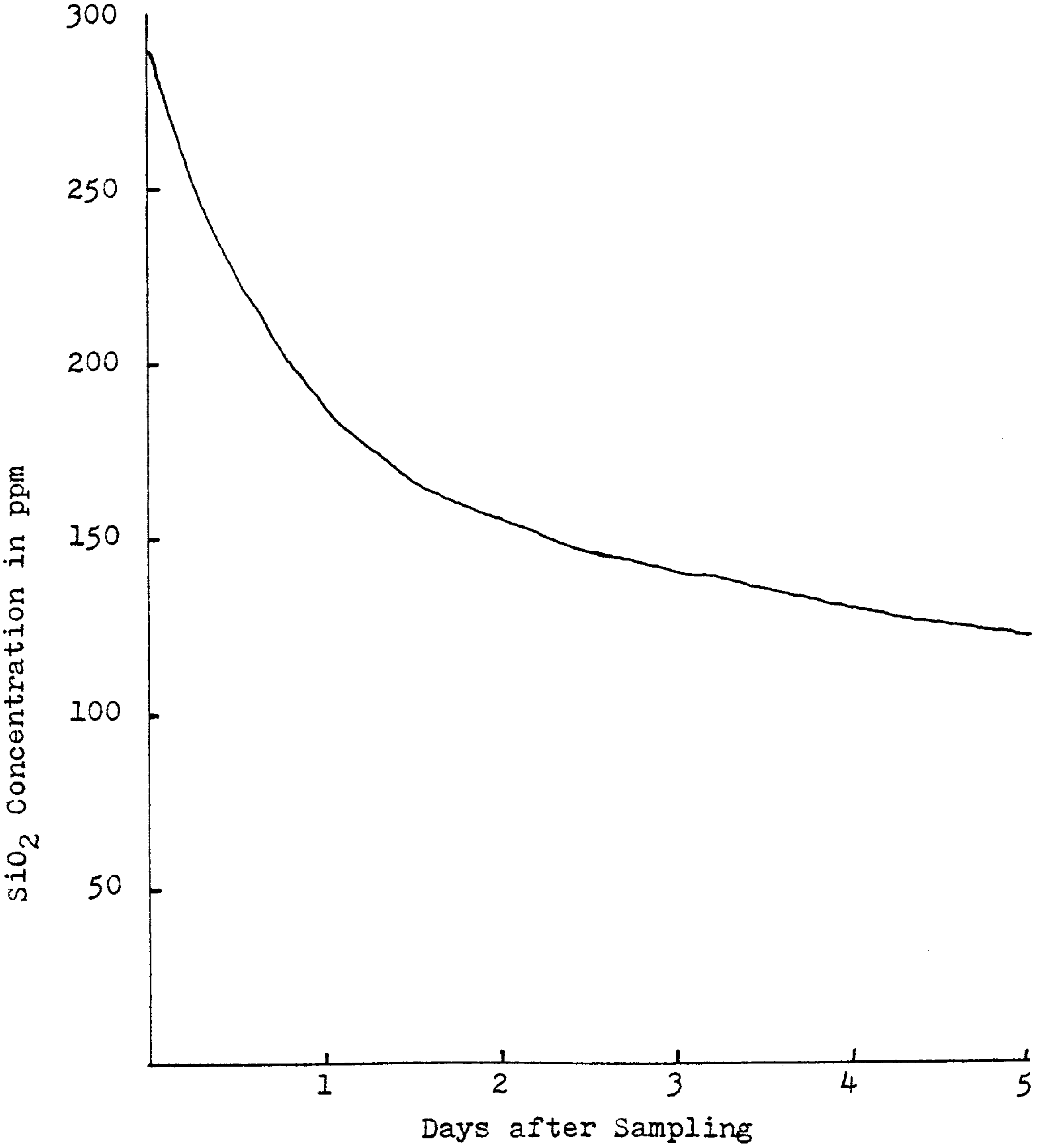
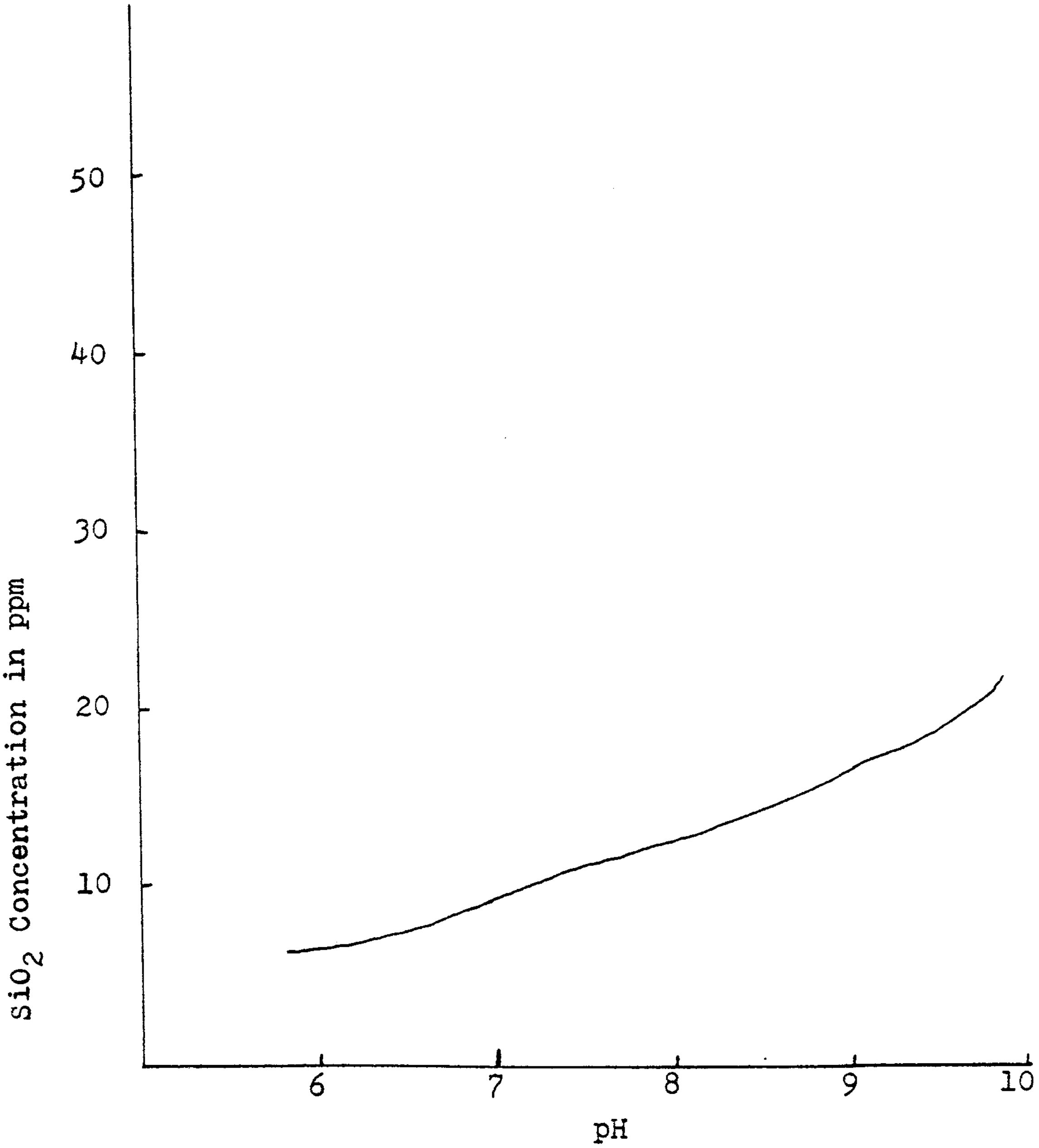


Figure7.9 $SiO_2$ Concentrations vs. pH of Solvent



Springs.

A close inspection of the $SiO_2$ levels from the spring and fall samplings discloses that of all the wells sampled only the Rosemary and the Yezzi sites exhibit virtually no change from spring to fall. In the case of the Yezzi well this behavior can be best explained by the location of a large holding tank in the basement near a wood stove. In the case of the Rosemary (outside fountain) the explanation appears to be linked with its $NaHCO_3$ character. In fact, the similar levels of $SiO_2$ provide a powerful argument that this well is indeed tapping in large part an example of the "pristine" basement fluid. It also suggests that the $SiO_2$ "base level" of the deep fluid coming up the McGregor Fault system is about 40 mg/l and that higher $SiO_2$ levels further east are due to mixing with a basement fluid of greater than 70 mg/l $SiO_2$.

### 7.1.6 Molar Ratios

In any of the literature of the chemistry of subsurface waters one of the first things that the reader notices is the profusion of molar ratios used to distinguish various water types and certain characteristics concerning them. Accordingly this study is no exception and in tables 2s and 2f of the appendix will be found tabulations of five different ratios calculated for each of the waters (Ca/Mg, Na/Cl, Cl/Br, Na/K, and Cl/K).

Most of these ratios are extremely useful in distinguishing water types. All except Ca/Mg group into distinct patterns which clearly separate the various waters: Saratoga group, north central waters, southern "brine" waters, and the meteoric control group. Ca/Mg values span a range from .50 to 4.0 without grouping according to a water type. Within the two carbonated water groups, however, there are some distinct and interesting correlations.

The meaning of the Ca/Mg ratios must first be considered. Both these constituents make up the cations of dolomite, $CaMg(CO_3)_2$, while $Ca^{++}$ alone derives from limestone and calcite, $CaCO_3$. The solubilities of both also increase at lower temperatures, both being minimal above 100°C. It is highly probable, then, that both ions are derived primarily from low temperature carbonic acid leaching of the carbonate aquifer wall rocks. As such, substantial differences among samples may reflect two sets of conditions:

(1) local variations in the chemical compositions of the enclosing aquifer rocks, and

(2) transit time in the aquifer- providing that it be of short duration relative to the rate of rock dissolution.

The second reason follows from the fact that the reaction of carbonic acid with $CaCO_3$ is a relatively rapid one, particularly within highly reactive limestones.

Table 2s of the appendix shows intriguing large scale variations in the Ca/Mg ratios from the spring sampling. While ratios from wells of the uncarbonated southern brine group show fairly uniform values from 2.2 to 2.7 (with the exception of Auguste Bohl- 1.09- possible analytical error) the waters of the Saratoga group vary from .57 (Big Red) to 2.76 (Lincoln #12). Some variation may be expected due to analytical error and lithologic differences, yet the outcropping cabonates west of Saratoga are relatively homogenous while these wells are concentrated in a relatively small area. Some apparent correlations with low Ca/Mg ratios are: (1) deep wells penetrating to the lower Galway formation (approximately 50% orthoquartzite) -Hathorn #3, (2) high yield wells along obvious linears- Orenda and Geyser, (3) $NaHCO_3$ waters with low Cl/Br ratios indicating a dominant basement fluid component- Rosemary, (4) high $SiO_2$ contents- Big Red, Rosemary, and Geyser.

Table 2f of the fall results shows far less variation among the ratios with values normatively falling between 1.5 and 2.0. This general tendency may be related to **the lower** table, however, this point is not entirely clear. The only distinctly anomalous Ca/Mg ratios in this set are the Rosemary and Big Red wells. This is very significant since these two waters possess the best evidence for proximal points of entry of the basement fluids. The Rosemary is a sodium bicarbonate water with consistent $SiO_2$ contents falling almost on the basement fluid vector in figure 6.1. The Big Red contains a highly anomalous $SiO_2$ content in the fall which should be metastable at these temperatures. Considered as a group, these correlations may indicate proximity to "feed zones" or sources of $CO_2$ and basement fluids.

## 7.2 North Central Group

Like the Saratoga group of carbonated waters, the north central group is also considered to have its entry points into the aquifer near the actual wells sampled. This follows from multiple lines of evidence similar to the reasoning detailed for the Saratoga group. Rather than reiterate the basic principles behind each chemical parameter, the reasons are listed below with brief explanations as required.

(1) The $NaHCO_3$ nature of the waters i.e. Quaker Spring, Bennet, Martin, and Doster.

Not only does this characteristic indicate minimal contamination by the saline waters, it also speaks for a basic difference between the two groups, and, by implication, differing points of entry. Past workers, i.e. Kemp (1912), Colony (1930), Strock (1941) thought the $NaHCO_3$ nature of these and other northern waters to be due to dilution of the water during its passage in the aquifer from an entry point south of Ballston Spa. This explanation is implausible because selective deletion of only the $Cl^-$ ion is extremely unlikely. As was mentioned for the internal major chemistry of the Saratoga group, this pattern can be most easily explained by the rising of the $NaHCO_3$ basement fluid directly into progressively weaker saline waters in the shallower portions of the lowlands.

(2) The presence of considerable free $CO_2$ in these waters in conjunction with low pH readings from 6.0

As was discussed earlier the presence of the unneutralized $CO_2$ gas (or $H_2CO_3$) is a good qualitative indicator of a short residence time in the carbonate aquifer. The high $H^+$ concentrations indicating the acidic character of the water serve to further the comparison.

(3) The far lower D/H values for the two northern waters sampled (Bennet and Martin, section 5.3, table 5.2) when compared with the three waters sampled from the Saratoga group.

As was discussed in section 5.3, the lower D/H values probably indicate a retention of ice age water in the northern portions of the lowlands. In any case, they clearly indicate the northern waters to be a separate system from the Saratoga group since they are up to 25 per mil lower than the range of meteoric water. The northerly migration cum dilution hypothesis cannot explain this data.

(4) Undersaturation of the Bennet and Martin waters with respect of the $Ca^{++}$ ion (table 7.2).

As was discussed in the previous section, $Ca^{++}$ undersaturation can most easily be attributed to a short residence time in the carbonate aquifer.

(5) Distinctive groupings of several molar ratios including Ca/Mg, Na/Cl, and Cl/Br (tables 2s and 2f of the appendix).

Again, these are diagnostic of not only different water groups but of other factors as well. The Ca/Mg ratios, for instance, are indicators of residence times in the aquifer. It is notable that only 3 wells have ratios of $<1$ in the fall; Rosemary, Big Red, and Martin. The first two are high $SiO_2$ waters of the Saratoga group while the Martin well has the lowest D/H and $C^{13/12}$ ratios as well as being the "purest" example of $NaHCO_3$. This is also reflected by the very high Na/Cl ratio which indicates a minimal addition of $Cl^-$ from saline waters.

The Cl/Br ratios are an excellent way to distinguish different subsurface water types and, in some cases, the derivation of the ions in solution. The calculated ratios show the north central waters to range from 17 to 88 while the Saratoga group ranges from 96 to 339 excepting the Rosemary; 61. Clearly the groups are different water types. Furthermore the ratios of the northern group are the same as those of the meteoric control group while those of the Saratoga group are similar to those of the uncarbonated "brine" wells.

Summarizing, the evidence clearly shows the two groups to be unconnected, that is chemically controlled by differing mixtures of water types emanating from different resevoirs or source areas. The evidence also points to proximal points of entry into the aquifer, paricularly in the case of the Martin well, although the data set is not as tightly constrained as with the more numerous wells of the Saratoga group.

## 7.3 The Greater Carbonated Water System - Summary

Having demonstrated that at least two principal water systems are separated and distinct (Saratoga and north central) and moreover, that the issuance of a $NaHCO_3$ basement fluid into the aquifer from entry points (probably faults and fractures) proximal to the actual discharge points is likely, some inference can now be made concerning the greater carbonated water system of the upper Hudson Valley.

Considered mostly from a geometrical viewpoint, the presence of unneutralized carbonated water under Albany and Schenectady indicates several more points of issuance in these areas. So, too, does the$CO_2$ in New Lebanon and Williamstown, Mass., since migration of $CO_2$ from the western flat-lying sediments under the allochthon and then up is an unlikely process. In short, the presence of $CO_2$ far south of Saratoga and Fort Edward indicates at least several more points of issuance in these areas since the lowlands have a far greater thickness of shale to the south near Albany. The migration of charged waters downdip and across many normal faults is extremely unlikely, therefore the waters also must rise in the south.

It thus appears likely that the demonstrable pattern of multiple points of entry near the city of Saratoga persists throughout the lowlands. That is, that $CO_2/NaHCO_3$ and, perhaps, other components undetected in the small, peripheral area of Saratoga Springs, are rising up many of the basement faults and fractures to mix with the saline waters in many separate places. It also seems quite possible that two of the principle lines of entry may be along the major inferred fault systems underlying the present and preglacial Hudson River channels much in the same manner as the McGregor Fault seems to act as a conduit for the $NaHCO_3$ along its length from Saratoga Springs to Ballston Spa, and, presumably, further southward.

## 8.0 $CO_2$ SOURCES

$CO_2$ discharges issue from almost every conceivable rock type worldwide but are generally thought to come from three different sources: (1) organic material, (2) marine carbonate rocks, and (3) the mantle or direct degassing from igneous melts (Barnes, I. et al., 1978). Organic material may include coal, graphite, fossilized wood, or petroleum and its relatives, i.e. asphalt, natural gas, etc. but commonly is depleted in $^{13}C$ with values between -20 to -30 per mil. Marine carbonates and their metamorphic equivalents commonly have $^{13}C$ isotope compositions near zero relative to the PDB (Peedee Belemnite) standard. Mantle or juvenile $CO_2$ isotope compositions are known from fluid inclusion work. Two studies have reported $^{13}C$ compositions of $-7.6 \pm .5$ per mil (Pineau et al, 1976)and -4.7 to -5.8 from inclusions in Pacific Ocean basalts (Moore et al., 1977). Thus mantle or juvenile $CO_2$ can be generally expected to range from -4.7 to -8.0 per mil (Barnes I. et al., 1978).

Listed below in table 8.1 are $C^{13/12}$ analyses of the gas and water of five representative waters as well as three typical rock types encountered in the area. The gas and water samples were collected concurrently in August 1978 with the D/H and $O^{18/16}$ samples and analysed by J.R. O'Neil of the U.S.G.S. in Menlo Park, California. The rock samples were analysed by Geochron Laboratories, Cambridge, Mass. The two Adirondack samples are grab samples from Precambrian dolomitic marbles collected in roadway outcrops in the Glen along Route 28. The Beekmantown sample is a composite ground from 6" core splits collected at 50' intervals in a 500' core traversing the entire carbonate section. The core was made available courtesy of Dunn Geoscience Corporation as part of a zinc exploration program conducted during the mid 1970's in the Paleozoic carbonates around the southern Adirondack periphery.

The samples reflect additions of $CO_2$ from two sources: (1) the basement fluid, and (2) dissolution reaction with the carbonate wall rock after the following equation:

$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca(HCO_3)_2$$

$C^{13/12}$ MEASUREMENTS

| SAMPLE | CARBONATE PPT. | $CO_2/g$ | ROCK |
|---|---|---|---|
| Hathorn | +.57 | -5.03 | --- |
| Orenda | +.60 | -5.15 | --- |
| Big Red | -3.92 | -6.84 | --- |
| Bennet | -4.35 | -7.55 | --- |
| Martin | -4.91 | ND | --- |
| Beekmantown | ----- | ----- | -1.5 |
| Adirondack Marble | ----- | ----- | +2.0 |
| Adirondack Marble with Graphite | ----- | ----- | -2.5 |

Table 8.1 $C^{13/12}$ measurements of water and gas samples from 5 wells done by J.R. O'Neil of the USGS, Menlo Park, California. Three comparative rock smples done by Geochron Laboratories, Cambridge, Mass.

The measured carbonate precipitate, $Sr(HCO_3)_2$, is equivalent to the dissolved $Ca(HCO_3)_2$ while the gas reflects a mixture of carbon isotopically derived from both wall rocks and the basement fluid. The gas values are variable but consistently less than those of the precipitate. This variability reflects a changing fractionation of carbon in the $H_2CO_3$ after

$$CO_{2(aq)} + H_2O \rightleftharpoons HCO_3^- + H^+$$
$$\Delta^{13}C \text{ from } +3 \text{ to } +5 \text{ per mil}$$

Consequently, the precise proportions of $^{13}C$ added from the two sources cannot be calculated; but qualitative data interpretation is possible. The two wells with positive carbon isotope ratios in the precipitate contain a large admixture of saline water and are thought to discharge some distance from the points of $CO_2$ entry into the aquifer on the basis of Ca/Mg ratios and $SiO_2$ data. As such they should have a greater propotion of wall rock carbon and a smaller one of deep $CO_2$. The other three wells contain proportionally less saline water and are believed to discharge nearer their points of entry of carbon dioxide. In this context it is interesting to note their increasingly negative $\delta^{13}C$ values indicating larger proportions of deep $CO_2$. Unfortunately the culmination of the trend, the Martin well, has no $^{13}C$ gas data, however, a projection from the nearby slightly saline Bennet well places the gas at about -8 per mil, the assumed lower limit of mantle $CO_2$.

In this general context the $C^{13/12}$ data of Saratoga are very powerful. Should Irwin, Barnes, and O'Neil (1978) be correct in their 3-fold classification of $CO_2$ sources, the deep Saratgan gas appears to be primarily derived from degassing of an igneous melt (juvenile $CO_2$) or from the mantle.

Since the values indicate a similar derivation for the gas of the Saratoga vicinity waters and the north central waters, a very large areal spread, the mantle seems the more likely of the two alternatives. Considering, too, the large mass flux of gas in relation to other carbonated systems again favors the mantle as the dominant source of the gas which emerges in the $NaHCO_3$-type basement fluid.

## 8.1 Global Analogies

In order to fully appreciate the anomalous character of the Saratoga system it is necessary to take a look at some of the other $CO_2$-bearing systems around the world. A map depicting the global distribution of carbon dioxide discharges and major zones of seismicity is presented as plate 5. It is only slightly modified from a map produced by Barnes et al (1978) as part of a USGS open-file report and is included in this report because of its direct bearing on the matter at hand. $CO_2$ discharges are defined as those of a gas containing more than 90% $CO_2$ by volume by chemical analysis, or as a water containing at least 1 gram per liter dissolved $CO_2$ or bicarbonate ($HCO_3^-$) with a pH less than 8.3. The cutoff point was placed at 1 g/l because this limit was found to depict the same general areas of occurrences as lesser values (Barnes et al, 1978).

A number of relationships appear from an inspection of this map. First, there appear to be two major concentrations of $CO_2$ discharges around the world. One is in the narrow circum-Pacific belt traditionally referred to as the "ring of fire". The second concentration is a broad area in central and southern Europe and Asia Minor. In both areas the correlation of the discharges with historical zones of seismicity and areas of active vulcanism is striking. They are, of course, active plate boundaries primarily involved with subduction in which $CO_2$ is generally being rleased from igneous intrusions or the metamorphism of carbonate-bearing rocks at depth. The metamorphism may be of two varieties: regional and local. Many of the occurrences in the Pacific "ring of fire" are probably local; derived either by direct magmatic degassing or by decarbonization contact metamorphism where an igneous intrusion encounters adjacent carbonate-bearing rock. The broad distribution of the $CO_2$ discharges in Europe, often in areas devoid of vulcanism, suggest that regional metamorphism at depth is taking place now in the affected areas.

Besides metamorphism and direct devolatilization, it has also been suggested that $CO_2$ may be discharged directly from the mantle. A prerequisite for this mechanism is the presence of fractures that extend to sufficient depth to tap the mantle gas. In this context it is interesting to note that the mantle has been suggested as a possible source of $CO_2$ springs in Northern California and in the Sierra Nevadas (Barnes et al, 1973). In the former case most of the springs are located along the San Andreas Fault system, a major transform which can easily be conceived to persist to the mantle. The Sierra Nevada discharges are located in the

Basin and Range province, a wide area of horst and graben development which may be due to a large, imperfect strike-slip regime between the Pacific and North American plates (Sengor and Burke, 1978). In this case it is more difficult to suppose unusually deep faulting because such a tectonic environment usually hosts listric faults. The $CO_2$ must, as a consequence, be present as a separate phase to at least as shallow a depth as the admixed meteoric water circulates (Barnes et al, 1978).

Equally as impressive is the general absence or scarcity of $CO_2$ discharges in Canada, Australia, and most of the other older cratonic regions of the world. Of the intraplate occurrences, most are concentrated in strike-slip regimes (i.e. Mongolia) and areas of nascent rifting (East African rift valley system). Those few systems unconnected with any obvious fundamental tectonic processes of current activity number only four. Of these Saratoga is by far and away the strongest and most dynamic of the group. It is all the more significant due to its position in the Appalachian chain, an old collision generated mountain belt now within the North American plate.

Other factors to consider in comparing Saratoga to other $CO_2$-bearing syatems are the size and strength of the discharges. The Saratoga system should really be considered as the greater upper Hudson Valley system which extends over 1000 square miles. This appears to be larger than any other single system reported in the literature, including Wairikei

New Zealand, and Niland in the Imperial Valley of California. The amount of gas from a number of individual discharges in the Saratoga system is also extremely high with $p_{CO_2}$ approaching 5 atm. in some wells. Very few individual discharges worldwide contain as much $CO_2$ as the Saratoga wells.

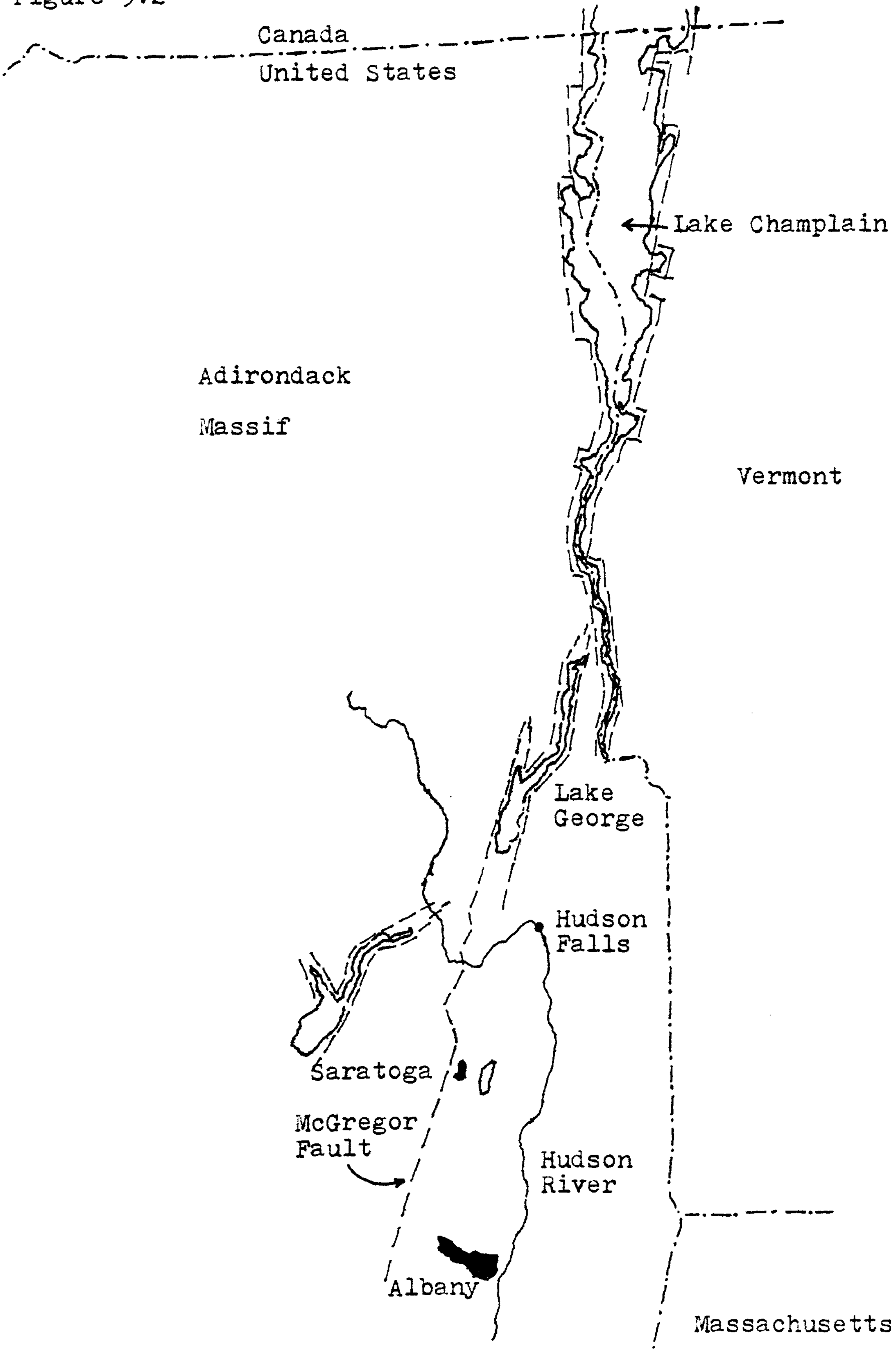
All this serves to emphasize the uniqueness of the Saratoga system. Its very magnitude places some limits on the possible source of the gas. Small intrusions, i.e. dykes cannot explain the amount and distribution of the $CO_2$ nor the $C^{13/12}$ isotope data. We are left, then, with only two alternatives, a large intrusion in the lower crust and degassing of the mantle. Either of these solutions may satisfy the existing data, however, both require unusually deep, active faulting as a mechanism for transporting the gas upward to the surface. This conclusion will be examined in the succeeding section.

## 9.0 REGIONAL STRUCTURE AND TECTONICS

Of the several regional structural elements to consider as possibly germane to the $CO_2$ discharges, perhaps the first should be the linear system of Lake Champlain, Lake George, and the Hudson River Valley. As was mentioned earlier in section 1.4, this topographic feature is an outstanding one on satellite imagery (ERTS). Not mentioned was the fact that Lakes Champlain and George have long been known to be normal fault bounded structures of the variety known as grabens. Together they form a long, narrow N-S valley or trough some 200 km long bisecting the Adirondack Mts. to the west and the Green Mts. to the east (figure 9.1). The structurally controlled depression that they represent is continued to the south in the form of the upper Hudson River Valley. This is bounded to the west by the large normal McGregor and Hoffmans Faults and may be bounded to the east by several reactivated thrusts. That this linear system is a structurally controlled one is a long held view with which most geologists would concur. What is open to question is the age of this system; it is that point which is addressed by this chapter.

Evidence for recent tectonic movement in the region is provided by five releveling lines over portions of the Adirondack massif, a dissected elongate dome having a north-northeast axis about 190 km long and an east-west dimension of about 140 km (Isachsen, 1975). The most informative of these releveled lines extends from Saratoga Springs north

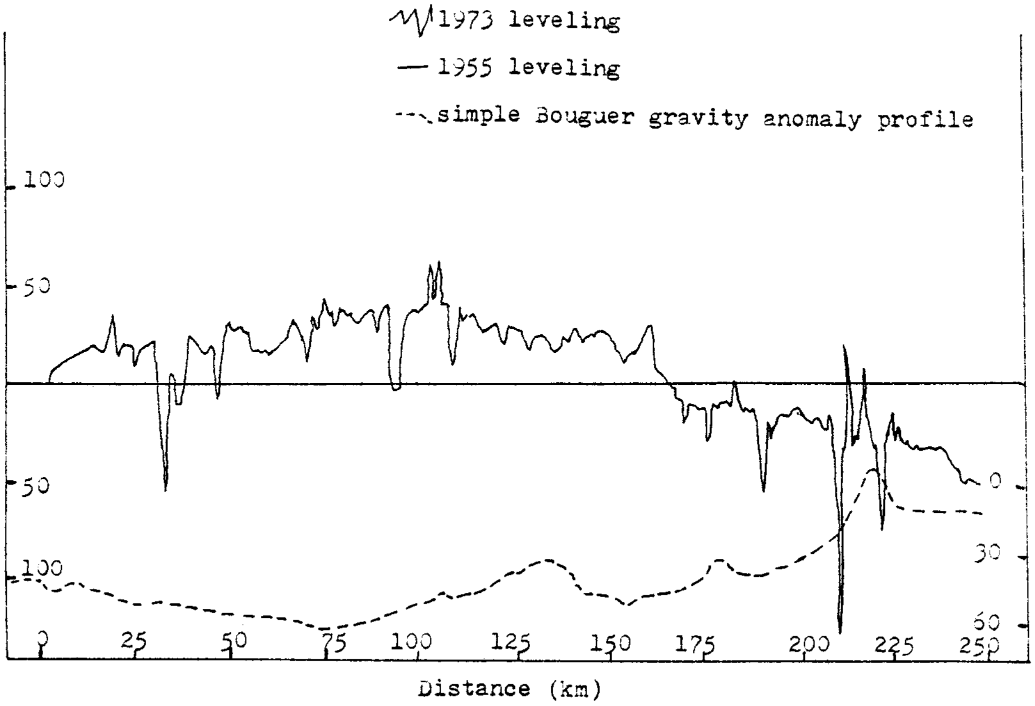
Figure 9.2


Canada
United States
Lake Champlain
Adirondack
Massif
Vermont
Lake
George
Hudson
Falls
Saratoga
McGregor
Fault
Hudson
River
Albany
Massachusetts

across the margin of the depression to Rouses Point, a distance of 245 km (see figure 9.1). It is reproduced in figure 9.2 after Isachsen (1975). The line shows an uplift of 4 cm along the central portion and a subsidence at the northern of 5 cm. The differential uplift with subsidence at the northern end argues strongly for a tectonic rather than a glacio-isostatic mechanism (Isachsen, 1975). Most interesting is the extremely rapid rate of doming indicated by this data, 2.2 to 2.8 mm/yr. Such a rate can account for the minimal uplift of 1600 meters of the highest part of the Adirondack dome in a period of only 600,000 years. The position of the releveling line in the depressed zone where it extends over the Proterozoic-Precambrian unconformity, demands closer inspection, however. Isachsen based his figure of 1600 meters for minimum amplitude of the dome on a reconstruction of the unconformity. With it situated in the trough, however, the area cannot have undergone this rate of uplift for even an appreciable fraction of the period of time that the High Peaks region has been undergoing uplift or the Paleozoic cover would be more fully eroded. This demands that the uplift today is episodic or oscillatory, an interpretation mentioned as probable by Isachsen (1975), and requires a displacement offset along the western margin of the trough.

If the geomorphology of the dome can be considered representative of fundamental tectonic processes (as appears to be the case) it cautions us to transcend political boundaries

Figure 9.2



Geodetic leveling profile showing magnitude of arching along eastern flank of the Adirondack dome during the period 1955-1973. After Isachsen (1975).

and ask "What of the Green Mountains?". Rising only a few miles east of the grabens in Vermont, the mountains reach heights comparable to the Adirondacks. Why are they up? It has been suggested that the Adirondacks present day topography could be entirely reduced by erosion to a peneplain in only $10^7$ years (K. Burke, pers. com.). By this logic neither the Adirondacks nor the Green Mts. can be older than this figure in terms of single uplift history. Furthermore, the adjacent character of the two uplands cautions us to ask whether or not related tectonic processes are responsible for both uplifts. It seems quite posssible that the intervening trough may be a downdropped section transecting a larger scale domical or irregular uplift which could well include not only the Green Mts., but extend over the present Appalachians of the eastern United States. In this regard, these features could well resemble present day high spots in Africa whose domes have "cracked" by rifts (Sengör and Burke, 1978). If this is true, the geomorphology of the region would be a better indicator of relatively long term tectonic processes than the releveling lines which can only describe processes that are instantaneous by comparison with geologic events.

Having considered the possibility of a larger uplift it is now time to examine one more piece of evidence, the small grabens around the periphery of the Adirondacks. It was noted in section 2.2.2 that these change orientation westward from Saratoga Springs so that perpendicular bisectors drawn through them still intersect roughly near the center of the Adirondack dome. Provided that these grabens are being formed by extensional stress from the uplift, their pattern indicates that only the Adirondack massif is involved in the doming. If these were only part of a larger uplift including the Green Mts. it could be anticipated that they would not take on a more northerly aspect.

This much seems true but, again, the grabens only date a certain small portion of the uplift. Their age can be estimated from their heights and a knowledge of erosion rates in carbonate terrain. The largest of the grabens is the Pompa structure. With an elevation of approximately 30 meters it should be entirely eroded within 200,00 years. The smaller grabens of Crane's Hollow and the attendant block faulting with scarp reliefs of 5-20 meters should erode in 30,000 to 125,000 years. For at least the past 200,000 years, then, it would appear that the Adirondack massif has been the focus of domical uplift. In periods prior to this time it is possible that it may have been part of a larger episode of arching which also raised the Green Mts. and the Appalachians.

By virtue of inverse logic it is also possible to state that many of the fault scarps in the area also appear to exhibit a youthful aspect simply because they have not been eroded. The McGregor Fault, for instance, has a moderate to large amount of relief with Paleozoic carbonates often found within several hundred feet of the toe of the scarp. While this was ascribed to differential glacial erosion in the past, it is more possible that the fault has seen recent reactivation. Even more convincing are the numerous small breaks in the carbonates with relief on the order of 3-10 meters. Since many strike roughly E-W, glacial gouging is not a satisfactory mechanism of formation. Holocene faulting is by far the most plausible explanation.

Given the evidence for recent doming of the Adirondacks and recent movemnt on many of the faults, it is time to examine the system with respect to Saratoga. This report has shown that the $CO_2/NaHCO_3$-type fluid is of thermal derivation, at least as far as the $CO_2$ is concerned, as well as being dynamic, that is, being produced today. While it is as yet too early to determine whether the source is the mantle or a large intrusion in the lower crust, the distinction makes no difference in tectonic terms. Both mechanisms require unusually deep, open faulting as a conduit to the surface. Both hypotheses are also expressions of the first igneous activity since the Mesozoic in the Northeast. When considered in conjunction with the regional Adirondack doming which has been suggested as being caused by a hot spot (K. Burke, pers. com.) and the large regional graben structures the presence of the $CO_2$ lends strong credence to the idea that a full scale continental rift may be beginning. This is not to say that the Lake Champlain, Lake George, upper Hudson Valley linear will become an active plate boundary; it is to say, however, that the combination of structural data and the $CO_2$

indicate the presence of a rift in its early or embryonic stages. Whether or not this protorift will ever fully develop extrusive vulcanism and/or into a full plate boundary permitting mantle upwelling is a matter for conjecture.

## 10.0 ECONOMIC GEOLOGY

It is hoped that this report has at least succeeded so far in demonstrating the relationship of the $CO_2/NaHCO_3$ basement fluid to thermally derived carbon dioxide beyond all reasonable doubt. With this done it next behooves us to ask the practical question, "Is there a geothermal system associated with the carbonated waters that might be tapped as a source of useable geothermal energy?". To this there can be no definite answer at this particular time because all of the evidence is as yet indirect and in large part is dependent upon the interpretation of $SiO_2$ thermometry. It will be the function of this section to assess this indirect data to produce a preliminary assessment of the potential.

Certainly the most favorable evidence for the existence of a useable system is the presence of a significant $SiO_2$ anomaly (as shown in figures 5.2 and 5.3) indicating possible subsurface resevoir temperatures as high as 90° to 120°C. This would appear to indicate that there is a heat exchange zone high in the crust or that the fluid retains its heat until it meets the colder waters contained in the carbonate aquifer. Moreover, it especially indicates that the postulated heated water has not traveled very far in the aquifer from its point of entry because $SiO_2$ at these levels cannot remain in solution very long in waters of 10° to 15°C (see section 5.2). This would all appear quite favorable.

A closer look at the anomaly, however, reveals several facts which would lead to a different interpretation. Most important is the constancy of silica values in the Rosemary water from spring (38 mg/l) to fall (40 mg/l). All other waters of the Saratoga and other groups show a noticeable change of $SiO_2$ between the two seasons indicating either a shallow derivation of the water (i.e. meteoric control group) or a small admixture of saline water. Since the Rosemary contains only a negligible amount of saline water, the constant levels not only imply a deep derivation of the $SiO_2$ but also suggest that these amounts are the essential limiting or base levels of the fluid in the immediate area of the city. In this regard it is critical to note the 40 mg/l is present in an example of basement fluid discharging at 10°C at the surface.

This should immediately make us question the validity of the supposed anomaly, for the Vichy, France, waters discharge at approximately 40°C carrying about 40 mg/l of dissolved $SiO_2$. Other $CO_2$-charged waters worldwide with silica in these amounts or even less are also thermal. This raises the possibility that the $SiO_2$ may be coming up with the $NaHCO_3$ as a metastable silica gel, or reflects equilibria with this silica phase.

On the positive side of the ledger is the fact that the silica anomaly increases in magnitude to the east of the city. This is principally based on the Big Red well which exhibits 70 mg/l of $SiO_2$ after dilution and, perhaps, 100 mg/l or more prior to dilution. On the negative side would appear to be the fact that this water too has an ambient discharge temperature. The water chemistry indicates, however, that this water also contains a large component of saline water which presumably could be enough to chill the warm or hot $NaHCO_3$ fluid entering the aquifer nearby. With silica possibly increasing to the east it is but a simple extrapolation to think that a suitable drill target may exist within 1 to 5 miles of the Big Red well along a major fault or fracture zone. With this in mind it becomes very tempting to speculate that the probable fault controlled preglacial Hudson River channel underlying Saratoga Lake may represent this conduit. Certainly exploration efforts should be concentrated in the area between the Big Red well and this inferred major structure.

As to the rest of the lowlands, predictability at this point is poor. The Canajoharie Shale and the other shales overlying it should be able to effectively contain almost any geothermal system. Only 3,000 feet of as yet unlithified clays conceal the $360^{\circ}C$ geothermal resevoir known as the Mesa anomaly in the Imperial Valley, California. Certainly the 1000+ feet of the soft, fissile shales of the Canajoharie formation should be able to trap small amounts of $40^{\circ}$ to $150^{\circ}C$ water anywhere in the lowlands. However, in this context the lack of anomalous silica contents in any wells should again be noted.

Another observation centers around the physiochemical properties of the gas/carbonic acid. As discussed in section 7.1.3 the dissolved $CO_2$ (aqueous) or $H_2CO_3$ issuing from the basement into the aquifer should be highly acidic with pH's certainly under 6.0 and, conceivably, lower than 5.0. When this acid contacts the carbonates $CaCO_3$ will surely be dissolved, enlarging the fractures and reducing the effective pressure from lithostatic toward hydrostatic. The lowering of pressure should cause the dissolved $CO_2$ to exsolve thereby cooling the waters considerably. This effect should occur whenever the waters come in contact with carbonates, whether in the basement or the aquifer, thereby having a pronounced role in the potential size, shape, and site of any geothermal resevoir.

For instance, if the conjugate effect of dilution with the saline waters of the aquifer is also considered, it seems rather difficult to picture a warm or hot resevoir persisting very far into the Paleozoic carbonates. Since the cold saline waters should also be contained in the underlying Potsdam sandstones the most likely drill target would appear to be basement fractures and faults at their juncture with the Paleozoic aquifer. This interpretation depends, of course, on there being only a small amount of $CO_2$-charged fluid coming up from the deeper basement- which is the most likely course of events.

The next question to be answered concerns the temperature of any possible system. While silica geothermometry predicts the last resevoir temperature to be aminimum of $90^{\circ}$ to $120^{\circ}C$, there are some good reasons to believe this figure is too high. These stem from the fact that, to the author's knowledge, there are no $CO_2$ springs worldwide with a discharge temperature greater than 75°C. Contrast this to hot springs (without $CO_2$) often found discharging at temperatures near boiling or even above. In fact, the vast majority of $CO_2$ springs discharge at temperatures less than 50°C, one of the exceptions being a spring of South Island, New Zealand, discharging at 55°C. The reason for this may be that gas exsolution chills these waters. In any event, this powerful analogy should lead one to predict that the most probable temperatures of the $CO_2/NaHCO_3$ fluid are from 40° to 80°C at depths from 1 to 3 kilometers.

While this range is hardly equal to that normally sought for power production (>180°C) in other parts of the world, it could be very significant in this area of the country. The Northeast is the most energy poor area of the country; it is the largest user and the smallest provider of raw materials. An indigenous source of energy here is worth far more than a similar source of energy in any other sector of the country. These conditions justify the taking of larger risks and incurring higher drilling costs. For instance, such a target would not even be considered as economical in the West where only potential power producing systems near population centers are of interest. In this area, however, even 40°C water at a depth of 2 kilometers with sufficient discharge would prove economic for direct heating of apartment complexes, greenhouses, and various industrial uses. Therefore the continued exploration for a geothermal system in this area is quite justified; it should be pursued until every possible lead is exhausted.

## Analytical Methodology

| Parameter | Analytical Procedure | Reference | Precision |
|---|---|---|---|
| Fluoride, Free | Activity of fluoride ion measured using Orion ion-selective electrode | 3 | ±6.2% at 1.29 mg/l |
| Nitrogen, Ammonia | Indophenol blue-Ammonia reaction with alkaline phenol, hypochloride and nitroprusside | 2 | ± 8.1% at 0.37 mg/l |
| Nitrogen, Nitrite | Automated diazotization with sulfanilimide and coupling with Azo dye | 2 | ± 5.8% at 14.9 ug/l |
| Nitrogen, Nitrate plus Nitrite | Copper cadmium reduction of nitrate to nitrite determined by diazotization as above | 2 | ± 4.7% at 2.6 mg/l |
| Chloride | Automated ferricthiocyanide | 2 | ± 5.8% at 39.6 mg/l |
| Sulfate as $SO_4$ | Automated reaction with $BaCl_2$ and methylthymol blue | 3 | ± 5.0% at 29 mg/l |
| Carbon, Organic | Purging of inorganic carbon, oxidation of organic | 6 | ±17.6% at 11.7 mg/l |

Analytical Methodology (cont.)

| Parameter | Analytical Procedure | Reference | Precision |
|---|---|---|---|
| TOC | carbon to $CO_2$. $CO_2$ detected by infrared spectroscopy | | |
| Boron | Reaction of boron with Curcumin to form red rosocyanine dye | 3 | ± 6.6% at 1.0 mg/l |
| Barium | Direct aspiration atomic absorption spectrometry; nitrous oxide acetylene flame | 2 | ± 5.9% at 1.4 mg/l |
| Iron | Direct aspiration atomic absorption spectrometry; air-acetylene flame | 2 | ± 4.8% at 0.97 mg/l |
| Potassium | " | 2 | ± 6.6% at 9.2 mg/l |
| Sodium | " | 2 | ± 2.6% at 44.9 mg/l |
| Zinc | " | 2 | ± 3.7% at 0.59 mg/l |
| Calcium | " | 2 | ± 5.4% at 50.7 mg/l |

Analytical Methodology (cont.)

| Parameter | Analytical Procedure | Reference | Precision |
|---|---|---|---|
| Lithium | " | 2 | NA |
| Magnesium | " | 2 | ± 7.7% at 16.6 mg/l |
| Strontium | " | 2 | NA |
| Bromide | Bromide oxidation followed by bromination of phenol Red D dye | 3 | ± 5.1% at 0.74 mg/l |
| Iodide | Iodide proportionately catalyzes the reduction of ceric ions by arsenious acid | 3 | ± 9.6% at 0.24 mg/l |
| Silica Reactive as $SiO_2$ | Ammonium molybdate reaction with silica to form heteropoly acids. Reduction to heteropolyine | 3 | NA |
| Nitrogen, Total Kjeldahl | Conversion to ammonia by $H_2SO_4$-$Na_2SO_4$ digestion. Ammonia determined by manual indophenol blue. | 1 | ± 8.9% at 0.67 mg/l |
| Phosphate, Total as P | Conversion to ortho-P by acid persulfate digestion. Ortho-P determined by manual indephenol blue | 2 | ± 5.4% at 0.24 mg/l |

Analytical Methodology (cont.)

| Parameter | Analytical Procedure | Reference | Precision |
|---|---|---|---|
| Solids, Dissolved | Filtration thru glass fiber filter. Evaporation, dried for 15 min. at 180°C | 3 | NA |
| Alkalinity, Electrometric | Titration to pH 4.5 with 0.02N $H_2SO_4$. Reported as "$CaCO_3$" | 3 | ± 7.5% at 44.0 mg/l |
| Aluminum | Flameless atomic absorption spectrometry using graphite furnace | 2,4 | ± 25.5% at 0.10 mg/l |
| Tin | " | 2,4 | NA |
| Yttrium | Plasma Emission | 5 | NA |
| Zirconium | " | 5 | NA |

References:

1. Adrat, D. and Canelli, E. New York State Department of Health Technical Memorandum, April, 1976.
2. EPA Manual of Methods for Chemical Analysis of Waters and Wastes
3. Standard Methods for the Examination of Water and Wastewater. 14th Edition. APHA, AWWA, WPCF (1976).
4. Perkin-Elmer Corporation, Analytical Methods for Atomic Absorption Spectrometry using the HGA Graphite Furnace.
5. Jarrel-Ash Corp., Waltham Mass, (These parameters analysed at Jarrel Ash by NYSDH personnel
6. Oceanographic Internation Corp., Instruction and Procedure Manual for the total carbon system Model 0524B.

## 1978 SAMPLING SITES - SOURCE DATA

| Sampling Site | Location | Owner | Description | Depth of Well | Yield(GPM) |
|---|---|---|---|---|---|
| Lebanon Springs | Lebanon Springs | Town of Lebanon Springs | Overflow pipe | Natural spring; Stockbridge Limestone | 75 or 500 GPM; both reported |
| Sand Spring | Williamstown, Massachusetts | Mr. Fred George | Pumped well; tap at top | 84' well in glacial mat. | 400 |
| Old Iron | Ballston Spa, New York | Town of Ballston Spa | Fre flowing well | 640' in Beekmantown dolomites | >10 |
| Bischoff | Ballston Spa New York | Mr. Louis Pastore | Intermittent free flowing well | ~900' in Beekmantown dolomites | unknown |
| Hathorn #3 | Saratoga Springs Reservation | State of New York | Free flowing well | 806' into Hoyt limestone | 3/4 |
| Polaris | Saratoga Springs Reservation | State of New York | Free flowing well | 209' into Amsterdam limestone | 2 |
| Orenda | Saratoga Springs Reservation | State of New York | Free flowing well | 344' into Trenton limestone | controlled at 10 to 12 |
| Geyser | Saratoga Springs Reservation | State of New York | Free flowing well | 138' into Amsterdam limestone | ~1 |
| Lincoln #12 | Saratoga Springs Reservation | State of New York | Free flowing well | 325' | 100 |

# 1978 SAMPLING SITES - SOURCE DATA (cont.)

| Sampling Site | Drilled | Tubing and Seal | Notes |
|---|---|---|---|
| Lebanon Springs | | | |
| Sand Spring | c. 1950 | | |
| Old Iron | unknown | rubber and wood seal at 384'<br>1 1/4" copper pipe | |
| Bischoff | 1926-1928 | unknown | pipe now broken ~5' below ground level; water issues from ground nearby intermittently as pressure builds up; flows 1-3 days at 2-3 week intervals |
| Hathorn #3 | 1905 | leather seal at 493'; 1 1/4" copper pipe | |
| Polaris | NA | NA | spouting well to height of app. 6' |
| Orenda | 1906 | sealed at 301' and 145' with perforationsbetween; retubed in 1938 with 326' of 1 1/4" copper pipe | originally drilled by Carbonic Acid Co., its natural flow was very large 45-50 GPM; ceased flow on 2/27/38 and retubed as described. Exploration in pushing down copper pipe showed first flow of 3 GPM at 279'. No flow below 312'. |
| Geyser | 1953 | unknown | water flowing from this fountain is at present piped from the Lincoln#7 well. |
| Lincoln #12 | 1944 | brass tubing to 111'<br>no seal | |

## 1978 SAMPLING SITES - SOURCE DATA (cont.)

| Sampling Site | Location | Owner | Desription | Depth of Well | Yield(GPM) |
|---|---|---|---|---|---|
| Rosemary | Grand Union Motel, Saratoga Springs, NY | Mr. James Benton | Pumped well | 425' into Beekmantown dolomites | ~5 |
| Congress #1 | Congress Park Saratoga Spgs. | City of Saratoga Springs | Free flowing well | Unknown | ~5 |
| Hathorn #1 | Saratoga Springs | City of Saratoga Spgs. | Pumped well | 1006' into Potsdam formation | 1 |
| Big Red | Saratoga Springs | Saratoga race track | Pumped well | ~1800' into carbonates | ~8 |
| Yezzi | Guilderland, New York | Mr. Daniel Yezzi | Basement tap | Unknown; TD in Ordovician shales | Unknown |
| Figliomeni | Parkers Corners, NY | Mr. Joseph Figliomeni | Basement tap | 345' into Ordovician shales | Unknown |
| Tudor Pines | Central Bridge New York | Tudor Pines Homes | Inside tap | 500' into Ordovician shales | Unknown |
| Gorman | Sloansville, New York | Mr. Gorman | Outside tap | Unknown | |
| Pattersonville | Pattersonville, New York | NYS Thruway Authority | Inside tap | ~100' into Ordovician shale | ~10 |
| Pompa | Milton, NY | Pompa Bros. Quarry | Outside tap | 90' into Beekmantown dolomites | >10 |
| Y.K. Greene | Wilton, NY | Mr. Y.Kittner Greene | Inside tap | 550' into Beekmantown dolomites | Unknown |

## 1978 SAMPLING SITES - SOURCE DATA (cont.)

| Sampling Site | Drilled | Tubing and Seal | Notes |
|---|---|---|---|
| Rosemary | c. 1965 | Unknown | |
| Congress #1 | Unknown | NA | At least 5 wells are driven within an area of 2 acres within the park; drill, tubing, and chemical data are available for all but comparisons cannot be made due to uncertainity in well numbering. |
| Hathorn #1 | 1914 (?) | 60' of $\frac{1}{2}$" copper pipe with downhole triplex pump | well originally free flowing (with seals) at 5 GPM in 1916; many problems with variable, diminished flow since then |
| Big Red | 1975 | tubing to 90' with submersible pump at this level | |
| Peerless | 1913 | Seal at 114'; retubed many times; presently 68' of $\frac{1}{2}$" copper pipe | Flow of this well was stopped or strongly diminished whenever Qua well (drilled 1927) was pumped. |
| Red | 1914 | 24" seal from 42-44' 42' of $1\frac{1}{4}$" copper tubing | In August 1931 the flow was noticed to decrease from 3 to 2 qts./min. whenever Qua well was pumped. |

## 1978 SAMPLING SITES- SOURCE DATA (cont.)

| Sampling Site | Location | Owner | Description | Depth of Well | Yield (GPM) |
|---|---|---|---|---|---|
| Bloodgood | Malta, NY | Judge Bloodgood | Outside tap | 125' into Ordovician shale | Unknown |
| Saratoga Veterinary Hospital | Wilton, NY | Saratoga Veterinary Hospital | Outside tap | 300' into Ordovician shale | Unknown |
| Wilson | Altamont, NY | Mr. Arthur Wilson | Inside tap | 180' into Ordovician shale (?) | Unknown |
| Middletown Springs | Middletown Springs, Vermont | Middletown Springs Historical Society | Natural spring | Reworked Pleistocene alluvium | 5 |
| Celestins | Vichy, France | Unknown | Natural spring | | |
| Hopital | Vichy, France | Unknown | Natural spring | | |
| Peerless | Saratoga Springs, NY | City of Saratoga Spgs. | Free flowing well | 151' | 1¼ |
| Red | Saratoga Springs, NY | City of Saratoga Spgs. | Free flowing well | 57' | 5 |
| Gurn Spring | Gurn Springs New York | Wilton Medical Center | Natural Spring | Issues from 8' of Pleistocene cover on Beekmantown | 5 |
| Quaker Spring | Quaker Springs New York | Quaker Spgs. Historical Society | Pump well | 400' into Snake Hill shale | Unknown |

## 1978 SAMPLING SITES - SOURCE DATA (cont.)

| Sampling Site | Location | Owner | Description | Depth of Well | Yield (GPM) |
|---|---|---|---|---|---|
| Bennet | Moreau, NY | Mr. Jeffrey Bennet | Outside tap | 140' into Ordovician shale | Unknown |
| Martin | Moreau, NY | Mr. Gerald Martin | Outside tap | 293' into Ordovician shale | <10 |
| McNeil | Argyle, NY | Mr. Harold McNeil | Outside tap | 80' into Pleistocene gravels | Unknown |
| Sharon Spring | Sharon Spring New York | Town of Sharon Springs | Overflow pipe | Natural spring in Silurian shale | Unknown |
| Vita Spring | Durkeetown, New York | Ms. Elizabeth Rozelle | Overflow | 248' into the Beekmantown | <10 |
| Davis | Smith's Basin New York | Mr. James Davis | Basement tap | 180' into Ordovician shale | Unknown |
| Pitcher | Dunnsville, New York | Mr. LeRoy Pitcher | Basement tap | 180' into Ordovician shale | Unknown |
| Congly | Melrose, NY | Ms. Dolores Congly | Bathroom tap | 330' into Ordovician shale | Unknown |
| Auguste Bohl | Bethlehem, New York | Auguste Bohl Equipment Corp. | Office tap | ~150' into Ordovician shale | Unknown |

## TABLE 1S

## Molar Concentrations x $10^3$ of Major Elements Spring Sampling

| Index Number | Location | Na | Cl | K | Mg | Ca | Br |
|---|---|---|---|---|---|---|---|
| 1. | Old Iron | 15.66 | 19.74 | 1.02 | 3.21 | 7.73 | .16 |
| 2. | Bischoff | 187.04 | 183.32 | 8.44 | 8.22 | 19.21 | .54 |
| 3. | Hathorn #3 | 113.09 | 177.68 | 8.18 | 17.27 | 16.97 | 1.13 |
| 4. | Polaris | 36.54 | 42.30 | 2.53 | 4.94 | 9.48 | .25 |
| 5. | Orenda | 82.64 | 126.91 | 6.14 | 11.10 | 12.72 | .76 |
| 6. | Geyser | 34.80 | 33.84 | 2.51 | 8.22 | 8.23 | .28 |
| 7. | Lincoln #12 | 31.32 | 39.48 | 2.56 | 3.7 | 10.23 | .30 |
| 8. | Rosemary | 12.18 | 7.90 | 1.84 | 6.58 | 5.99 | .14 |
| 9. | Congress #1 | 14.79 | 14.10 | 1.25 | 2.55 | 5.74 | .12 |
| 10. | Hathorn #1 | 40.45 | 50.78 | 2.40 | 4.11 | 10.23 | .34 |
| 11. | Big Red | 60.89 | 64.87 | 2.33 | 14.80 | 8.48 | .44 |
| 12. | Peerless | 31.75 | 28.20 | 2.38 | 4.11 | 10.48 | .25 |
| 13. | Red | 13.48 | 15.51 | .92 | 3.13 | 6.49 | .14 |
| 14. | Gurn Spring | 26.97 | 21.51 | 1.79 | 4.11 | 7.98 | .23 |
| 15. | Quaker | 42.63 | 21.15 | .46 | .86 | 2.05 | .20 |
| 16. | Bennet | 36.54 | 21.15 | 1.66 | 3.00 | 6.28 | .28 |
| 17. | Martin | 15.66 | 4.51 | .46 | 2.38 | 2.50 | .26 |
| 18. | Doster | 42.19 | 19.18 | .54 | 1.07 | 2.42 | .43 |
| 19. | McNeil | 8.26 | 7.05 | .74 | 1.44 | 4.49 | .08 |
| 20. | McNeil duplicated | 6.96 | 6.77 | .74 | 1.48 | 3.99 | .05 |
| 21. | Middletown Springs | .48 | .51 | .10 | .17 | .60 | .003 |
| 22. | Vita Spring | 13.92 | 6.20 | 1.33 | 5.35 | 9.73 | .15 |

TABLE 1S (cont.)

| Index Number | Location | Na | Cl | K | Mg | Ca | Br |
|---|---|---|---|---|---|---|---|
| 23. | Davis | 7.39 | .68 | .20 | 21.79 | 6.99 | .08 |
| 24. | Pitcher | 3.83 | 6.49 | .31 | 16.04 | 8.48 | .04 |
| 25. | Pattersonville | 10.44 | 16.92 | .10 | 1.44 | 3.74 | .02 |
| 26. | Congly | 43.50 | 59.23 | .72 | 1.40 | 1.40 | .35 |
| 27. | Auguste Bohl | 42.50 | 50.77 | .28 | .62 | .67 | .28 |
| 28. | Yezzi | 47.84 | 47.95 | .28 | .19 | .45 | .44 |
| 29. | Figliomeni | 32.62 | 4.79 | .23 | .07 | .18 | .15 |
| 30. | Tudor Pines | 25.66 | 22.56 | .18 | .08 | .18 | .001 |
| 31. | Pompa | .22 | .17 | .08 | 1.19 | 4.49 | .01 |
| 32. | YK Greene | 4.13 | .11 | .05 | .22 | .19 | .005 |
| 33. | Bloodgood | 1.91 | .08 | .05 | .02 | .16 | .003 |
| 34. | Saratoga Veterinary Hospital | 3.61 | .08 | .05 | .09 | .16 | .001 |
| 35. | Lebanon Springs | .27 | .23 | .03 | .58 | .85 | .004 |
| 36. | Fred George | .08 | .08 | .002 | .45 | .50 | .003 |

## TABLE 1F

### Molar Concentrations x $10^3$ of Major Elements
### Fall Sampling

| Index Number | Location | Na | Cl | K | Mg | Ca | Br |
|---|---|---|---|---|---|---|---|
| 1. | Old Iron | 22.62 | 21.15 | .87 | 3.25 | 7.98 | .23 |
| 2. | Bischoff | 191.38 | 194.60 | 7.67 | 19.33 | 23.10 | 1.63 |
| 3. | Hatnorn #3 | 134.84 | 194.60 | 8.18 | 16.86 | 23.70 | 1.25 |
| 4. | Polaris | 33.49 | 39.48 | 2.56 | 6.58 | 9.98 | .30 |
| 5. | Orenda | 100.04 | 115.63 | 5.88 | 12.34 | 18.71 | .93 |
| 6. | Geyser | 27.84 | 36.66 | 2.81 | 6.17 | 7.98 | .33 |
| 7. | Lincoln #12 | 32.19 | 33.84 | 2.81 | 7.81 | 8.48 | .43 |
| 8. | Rosemary | 25.66 | 15.79 | 2.23 | 7.81 | 6.74 | .24 |
| 9. | Congress | 14.79 | 12.69 | .98 | 2.63 | 4.99 | .13 |
| 9a. | Congress duplicated | 15.22 | 11.00 | .98 | 2.59 | 8.73 | .08 |
| 10. | Hathorn #1 | 41.32 | 45.13 | 3.32 | 6.58 | 10.23 | .36 |
| 11. | Big Red | 47.84 | 64.87 | 2.56 | 11.51 | 8.23 | .51 |
| 12. | Peerless | 32.19 | 27.64 | 2.30 | 4.93 | 10.48 | .28 |
| 13. | Red | 20.44 | 18.33 | .92 | 3.70 | 7.24 | .19 |
| 14. | Gurn Spring | 26.10 | 21.15 | 1.84 | 4.52 | 8.23 | .19 |
| 15. | Quaker | 38.28 | 19.74 | .31 | .74 | 1.40 | .16 |
| 16. | Bennet | 21.75 | 12.69 | 1.20 | 2.67 | 4.99 | .23 |
| 17. | Martin | 24.79 | 5.63 | .38 | 2.84 | 2.74 | .31 |
| 18. | Doster | 39.58 | 16.92 | .46 | 1.15 | 2.50 | .34 |
| 19. | McNeil | 10.44 | 7.33 | .74 | 1.69 | 4.24 | .09 |
| 20. | Sharon Spring | .65 | 1.44 | .04 | 3.00 | 9.98 | .008 |
| 20a. | Sharon Spring duplicate | .52 | 1.21 | .05 | 3.70 | 9.98 | .016 |

TABLE 1F (cont.)

| Index Number | Location | Na | Cl | K | Mg | Ca | Br |
|---|---|---|---|---|---|---|---|
| 21. | Vita Spring | 22.18 | 6.49 | 1.18 | 5.35 | 8.73 | .10 |
| 22. | Davis | 7.39 | .45 | .19 | 23.03 | 8.48 | .07 |
| 23. | Pitcher | 3.83 | 6.49 | .28 | 18.50 | 3.24 | .02 |
| 24. | Congly | 41.32 | 59.23 | .59 | 2.26 | 3.49 | .36 |
| 25. | Auguste Bohl | 23.05 | 28.20 | .16 | .41 | .50 | .18 |
| 26. | Yezzi | 29.14 | 47.95 | .25 | .23 | .40 | .44 |
| 27. | Figliomeni | 27.84 | 4.79 | .19 | .07 | .17 | .13 |
| 28. | Tudor Pines | 21.75 | 21.15 | .17 | .09 | .17 | .25 |
| 29. | Gorman | 78.29 | 81.23 | .51 | .78 | 1.87 | 1.63 |
| 30. | Pattersonville | 13.05 | 14.95 | .10 | 1.93 | 4.99 | .04 |
| 30a. | Pattersonville duplicated | 12.61 | 18.33 | .10 | 1.85 | 3.49 | .04 |
| 31. | Pompa | .13 | .48 | .10 | 1.69 | 3.24 | .02 |
| 32. | Y.K. Greene | 4.26 | .14 | .06 | .17 | .12 | .08 |
| 33. | Bloodgood | 1.57 | .08 | .02 | .02 | .05 | .007 |
| 34. | Saratoga Veterinary Hospital | 3.04 | .08 | .07 | .19 | .25 | .02 |
| 35. | Wilson | 1.87 | .56 | .13 | 1.32 | 1.42 | .06 |
| 36. | Middletown | .17 | .14 | .06 | .14 | .60 | .008 |
| 37. | Lebanon Spring | .34 | .20 | .04 | .62 | .85 | .01 |
| 38. | Fred George | .09 | .08 | .03 | .49 | .50 | .005 |
| 39. | Celestins | 30.45 | 6.77 | 2.15 | .37 | NA | .11 |
| 40. | Hopital | 31.32 | 9.87 | .90 | 1.85 | NA | .16 |

NA = Not Available

## TABLE 2S

### Selected Molar Ratios
### Spring Sampling

| Index Number | Location | Ca/Mg | Na/Cl | Cl/Br | Na/K | Cl/K |
|---|---|---|---|---|---|---|
| 1. | Old Iron | 2.41 | .79 | 123 | 15.35 | 19.35 |
| 2. | Bischoff | 2.34 | 1.02 | 339su | 22.16 | 21.72 |
| 3. | Hathorn #3 | .98 | .64 | 159 | 13.83 | 21.72 |
| 4. | Polaris | 1.92 | .86 | 169 | 14.44 | 16.72 |
| 5. | Orenda | 1.15 | .65 | 167 | 13.46 | 20.67 |
| 6. | Geyser | 1.00 | 1.03 | 125 | 13.86 | 13.48 |
| 7. | Lincoln #12 | 2.76 | .79 | 132 | 12.23 | 15.42 |
| 8. | Rosemary | .91 | 1.54 | 61 | 6.62 | 4.29 |
| 9. | Congress #1 | 2.25 | 1.05 | 118 | 11.83 | 11.28 |
| 10. | Hathorn #1 | 2.49 | .80 | 149 | 16.85 | 21.16 |
| 11. | Big Red | .57 | .94 | 151 | 26.13 | 27.34 |
| 12. | Peerless | 2.55 | 1.13 | 113 | 13.34 | 11.85 |
| 13. | Red | 2.08 | 1.13 | 119 | 14.65 | 16.86 |
| 14. | Gurn Spring | 1.94 | 1.27 | 96 | 15.07 | 12.02 |
| 15. | Quaker Spring | 2.37 | 2.02 | 106 | 92.67 | 45.98 |
| 16. | Bennet | 2.08 | 1.73 | 78 | 22.01 | 12.74 |
| 17. | Martin | 1.05 | 3.47 | 17 | 34.04 | 9.80 |
| 18. | Doster | 2.26 | 2.20 | 46 | 78.13 | 35.52 |
| 19. | McNeil | 3.12 | 1.17 | 88 | 11.16 | 9.53 |
| 20. | McNeil duplicated | 2.70 | 1.03 | 169su | 9.41 | 9.15 |
| 21. | Middletown | 3.47 | .94 | 167 | 4.8 | 5.1 |
| 22. | Vita Spring | 1.82 | 2.24 | 41 | 10.47 | 4.66 |
| 23. | Davis | .32 | 10.92 | 10 | 36.95 | 3.4 |

TABLE 2S (cont.)

| Index Number | Location | Ca/Mg | Na/Cl | Cl/Br | Na/K | Cl/K |
|---|---|---|---|---|---|---|
| 24. | Pitcher | .53 | .59 | 162 | 12.35 | 20.94 |
| 25. | Pattersonville | 2.60 | .62 | 1695 | 104.4 | 169.2 |
| 26. | Congly | 2.50 | .73 | 169 | 60.42 | 82.26 |
| 27. | Auguste Bohl | 1.09 | .86 | 188 | 155.36 | 181.32 |
| 28. | Yezzi | 2.43 | 1.00 | 111 | 170.86 | 171.25 |
| 29. | Figliomeni | 2.64 | 6.80 | 32 | 141.83 | 20.83 |
| 30. | Tudor Pines | 2.18 | 1.14 | 141 | 142.56 | 125.33 |
| 31. | Pompa | 3.77 | 1.29 | 15 | 2.75 | 2.13 |
| 32. | Y.K. Greene | .87 | 36.63 | 22 | 82.6 | 2.2 |
| 33. | Bloodgood | 3.19 | 22.62 | 27 | 63.67 | 2.67 |
| 34. | Saratoga Veterinary Hospital | 1.66 | 42.67 | 80 | 72.2 | 1.6 |
| 35. | Lebanon Springs | 1.47 | 1.20 | 55 | 9.0 | 7.67 |
| 36. | Fred George | 1.10 | .98 | NA | 40.0 | 40 |

NA Not Available

SU Suspect

## TABLE 2F

### Selected Molar Ratios
### Fall Sampling

| Index Number | Location | Ca/Mg | Na/Cl | Cl/Br | Na/K | Cl/K |
|---|---|---|---|---|---|---|
| 1. | Old Iron | 2.46 | 1.07 | 94 | 26.01 | 24.33 |
| 2. | Bischoff | 1.23 | .98 | 120 | 24.94 | 25.36 |
| 3. | Hathorn #3 | 1.41 | .69 | 141 | 16.46 | 23.78 |
| 4. | Polaris | 1.52 | .85 | 132 | 13.10 | 15.44 |
| 5. | Orenda | 1.52 | .87 | 125 | 17.01 | 19.66 |
| 6. | Geyser | 1.29 | .76 | 113 | 9.89 | 13.03 |
| 7. | Lincoln #12 | 1.09 | .95 | 79 | 11.44 | 12.03 |
| 8. | Rosemary | .86 | 1.62 | 67 | 11.53 | 7.10 |
| 9. | Congress | 1.90 | 1.17 | 102 | 14.83 | 12.72 |
| 9a. | Congress duplicated | 3.37 | 1.38 | 147 | 15.26 | 11.03 |
| 10. | Hathorn #1 | 1.55 | .92 | 125 | 12.43 | 13.57 |
| 11. | Big Red | .72 | .74 | 126 | 18.71 | 25.36 |
| 12. | Peerless | 2.12 | 1.16 | 101 | 13.98 | 12.01 |
| 13. | Red | 1.90 | 1.12 | 98 | 22.20 | 19.91 |
| 14. | Gurn Spring | 1.82 | 1.24 | 113 | 13.17 | 11.49 |
| 15. | Quaker Spring | 1.89 | 1.94 | 122 | 124.72 | 64.33 |
| 16. | Bennet | 1.87 | 1.71 | 56 | 18.09 | 10.56 |
| 17. | Martin | .97 | 4.63 | 17 | 64.63 | 13.97 |
| 18. | Doster | 2.16 | 2.34 | 50 | 85.98 | 36.76 |
| 19. | McNeil | 2.52 | 1.42 | 81 | 14.07 | 9.89 |
| 20. | Sharon Spring | 3.32 | .45 | 180 | 15.94 | 35.15 |
| 21. | Sharon Spring duplicated | 2.70 | .43 | 76 | 9.72 | 22.58 |

TABLE 2F (cont.)

| Index Number | Location | Ca/Mg | Na/Cl | Cl/Br | Na/K | Cl/K |
|---|---|---|---|---|---|---|
| 21. | Vita Spring | 1.66 | 3.42 | 63 | 18.86 | 5.51 |
| 22. | Davis | .37 | 16.39 | 7 | 39.60 | 2.42 |
| 23. | Pitcher | .18 | .59 | 405 | 13.61 | 23.06 |
| 24. | Congly | 1.54 | .70 | 164 | 70.24 | 100.69 |
| 25. | Auguste Bohl | 1.21 | .82 | 161 | 145.38 | 177.86 |
| 26. | Yezzi | 1.77 | .61 | 110 | 117.47 | 193.26 |
| 27. | Figliomeni | 2.46 | 5.86 | 38 | 145.12 | 25.00 |
| 28. | Tudor Pines | 1.90 | 1.03 | 86 | 128.84 | 125.31 |
| 29. | Gorman | 2.40 | .96 | 26 | 153.06 | 159.27 |
| 30. | Pattersonville | 1.89 | .69 | 448 | 129.79 | 188.63 |
| 30a. | Pattersonville duplicated | 2.58 | .87 | 365 | 130.82 | 149.86 |
| 31. | Pompa | 1.92 | .28 | 299 | 1.39 | 4.93 |
| 32. | Y.K. Greene | .70 | 30.23 | 181 | 69.44 | 2.30 |
| 33. | Bloodgood | 2.90 | 18.63 | 12 | 76.53 | 4.16 |
| 34. | Saratoga Veterinary Hospital | 1.29 | 36.23 | 467 | 42.52 | 1.18 |
| 35. | Wilson | 1.08 | 3.32 | 10 | 14.34 | 4.32 |
| 36. | Middletown | 4.41 | 1.20 | 18 | 2.88 | 2.40 |
| 37. | Lebanon Springs | 1.37 | 1.72 | 18 | 8.28 | 4.82 |
| 38. | Fred George | 1.01 | .98 | 28 | 32.31 | 3.31 |
| 39. | Celestins | NA | 4.50 | 63 | 14.16 | 3.15 |
| 40. | Hopital | NA | 3.17 | 61 | 34.80 | 10.97 |

## TABLE 3S

### Calculated Results
### Spring

| Index Number | Location | Calculated Alkalinity | Excess Alkalinity | Titrated Alkalinity | $P_{CO_2}$ |
|---|---|---|---|---|---|
| 1. | Old Iron | 18.784 | -4.083 | 23.778 | 1.280 |
| 2. | Bischoff | 10.232 | -52.834 | 81.526 | 4.389 |
| 3. | Hathorn #3 | 11.333 | -64.592 | 80.127 | 4.314 |
| 4. | Polaris | 25.334 | -5.768 | 37.965 | 2.044 |
| 5. | Orenda | 8.640 | -44.273 | 60.345 | 3.249 |
| 6. | Geyser | 36.026 | +0.952 | 42.761 | 2.302 |
| 7. | Lincoln #12 | 21.852 | -8.167 | 40.363 | 2.173 |
| 8. | Rosemary | 30.798 | +4.281 | 32.970 | 1.775 |
| 9. | Congress | 17.605 | +0.686 | 19.662 | 1.058 |
| 10. | Hathorn #1 | 20.356 | -10.315 | 39.764 | |
| 11. | Big Red | 44.314 | -3.973 | 49.155 | 2.646 |
| 12. | Peerless | 34.725 | +3.548 | 36.467 | 1.963 |
| 13. | Red | 19.040 | -2.028 | 22.979 | 1.237 |
| 14. | Gurn Spring | 31.448 | +5.815 | 36.766 | 1.979 |
| 15. | Quaker Spring | 27.640 | +21.472 | 36.167 | 1.947 |
| 16. | Bennet | 34.819 | +15.383 | 45.159 | 2.431 |
| 17. | Martin | 20.846 | +11.145 | 42.561 | 2.291 |
| 18. | Doster | 29.878 | +23.012 | 43.161 | .232 |
| 19. | McNeil | 13.649 | +1.213 | 14.586 | .785 |
| 20. | McNeil duplicated | 11.732 | +0.190 | 13.987 | .753 |
| 21. | Middletown | 1.365 | -0.029 | 12.288 | .066 |
| 22. | Vita Spring | 12.192 | +7.713 | 22.579 | 1.215 |
| 23. | Davis | 2.107 | +6.717 | 12.388 | .066 |

TABLE 2S (cont.)

| Index Number | Location | Calculated Alkalinity | Excess Alkalinity | Titrated Alkalinity | $P_{CO_2}$ |
|---|---|---|---|---|---|
| 24. | Pitcher | 3.059 | -2.659 | 7.293 | .561 |
| 25. | Patternson-ville | 2.998 | -6.483 | 5.295 | .040 |
| 26. | Congly | -4.986 | -15.731 | 4.196 | .322 |
| 27. | Auguste Bohl | -4.515 | -7.270 | 6.873 | .052 |
| 28. | Yezzi | 1.122 | -0.100 | 5.515 | .042 |
| 29. | Figliomeni | 28.264 | +27.826 | 29.833 | .160 |
| 30. | Tudor Pines | 3.791 | +3.099 | 5.654 | .004 |
| 31. | Pompa | 9.847 | +0.048 | 5.994 | .046 |
| 32. | Y.K. Greene | 4.740 | +4.019 | 5.095 | .003 |
| 33. | Bloodgood | 1.928 | +1.829 | 2.178 | .000 |
| 34. | Saratoga Veterinary Hospital | 4.039 | +3.525 | .043 | .000 |
| 35. | Lebanon Spring | 2.400 | +0.044 | 2.537 | .001 |
| 36. | Fred George | 1.713 | -0.001 | 1.838 | .000 |

All values expressed in moles x 1000/liter except apparent $P_{CO_2}$ which is in units of atmosperes.

Calculated Alkalinity $= [Na^+] + [K^+] + 2\,[Ca^{++}] + 2\,[Mg^{++}] - 2\,[SO_4^{--}] - [Cl^-]$

Excess Alkalinity $= [Na^+] - [Cl^-]$

Titrated Alkalinity $= 2\left(\frac{\text{Alkalinity}}{100.08}\right)$ where 100.08= m.wt. $CaCO_3$

$P_{CO_2}$ is defined by two equations:

1. $\frac{[H^+]\,[HCO_3^-]}{K_{H_2CO_3}} = [H_2CO_3]$ where $K_{H_2CO_3} = 10^{-6.47}$ at STP
2. $P_{CO_2} = \frac{[H_2CO_3]}{K_{CO_2}}$ where $K_{CO_2} = 10^{-1.26}$

## TABLE 3F

### Calculated Results
### Fall

| Index Number | Location | Calculated Alkalinity | Excess Alkalinity | Titrated Alkalinity | $P_{CO_2}$ |
|---|---|---|---|---|---|
| 1. | Old Iron | 24.80 | +1.47 | 25.58 | 1.096 |
| 2. | Bischoff | 89.31 | -3.22 | 86.73 | 1.862su |
| 3. | Hathorn #3 | 29.54 | -59.76 | 85.33 | 4.571 |
| 4. | Polaris | 29.69 | -5.99 | 20.98su | 3.548su |
| 5. | Orenda | 52.39 | -15.99 | 65.55 | 2.818 |
| 6. | Geyser | 22.29 | -8.82 | 41.97 | 1.413 |
| 7. | Lincoln #12 | 33.74 | -1.65 | 41.77 | 2.818 |
| 8. | Rosemary | 41.20 | +9.87 | 39.17 | 2.089 |
| 9. | Congress | 27.84 | +4.22 | 19.38 | 1.010 |
| 9a. | Congress duplicated | 18.32 | +2.10 | 19.18 | 1.007 |
| 10. | Hathorn #1 | 33.13 | -3.81 | 44.76 | 2.400 |
| 11. | Big Red | 25.01 | -17.01 | 53.16 | 3.631 |
| 12. | Peerless | 37.67 | +4.55 | 39.17 | 3.311 |
| 13. | Red | 24.91 | +2.11 | 26.78 | 1.148 |
| 14. | Gurn Spring | 32.19 | +4.95 | 33.41 | 1.413 |
| 15. | Quaker | 23.11 | +18.54 | 30.98 | 1.047 |
| 16. | Bennet | 25.58 | +9.06 | 38.57 | 1.202 |
| 17. | Martin | 31.70 | +19.16 | 46.76 | 1.995 |
| 18. | Doster | 30.42 | +22.16 | 44.96 | 3.890su |
| 19. | McNeil | 11.71 | +3.11 | 16.19 | 1.137su |
| 20. | Sharon Spring | -12.27 | -0.79 | 5.10 | |
| 21. | Sharon duplicated | -10.76 | -0.69 | 5.20 | |

TABLE 3F (cont.)

| Index Number | Location | Calculated Alkalinity | Excess Alkalinity | Titrated Alkalinity |
|---|---|---|---|---|
| 21. | Vita Spring | 45.03 | +15.69 | 24.38 |
| 22. | Davis | 70.15 | +6.94 | 12.79 |
| 23. | Pitcher | -8.89 | -2.66 | 7.59 |
| 24. | Congly | -5.82 | -17.91 | 4.40 |
| 25. | Auguste Bohl | -3.17 | -5.15 | 6.77 |
| 26. | Yezzi | -17.30 | -18.91 | 5.52 |
| 27. | Figliomeni | 23.72 | +23.05 | 30.30 |
| 28. | Tudor Pines | 1.29 | +0.60 | 5.68 |
| 29. | Gorman | 2.87 | -2.94 | 3.88 |
| 30. | Pattersonville | 11.04 | -1.90 | 6.59 |
| 30a. | Pattersonville duplicated | 4.81 | -5.72 | 6.59 |
| 31. | Pompa | 7.32 | +0.35 | 5.92 |
| 32. | Y.K. Green | 4.76 | +4.12 | 7.39 |
| 33. | Bloodgood | 1.65 | +1.49 | 2.32 |
| 34. | Saratoga Veterinary Hospital | 3.91 | +2.96 | 4.32 |
| 35. | Wilson | 3.59 | +1.31 | 5.40 |
| 36. | Middletown Springs | 1.27 | +0.03 | 1.18 |
| 37. | Lebanon Springs | 2.54 | +0.14 | 2.52 |
| 38. | Fred George | 1.83 | +0.01 | 1.84 |
| 39. | Celestins | NA | +23.68 | 67.65 |
| 40. | Hopital | NA | +21.45 | 73.74 |

NA Not Available

SU Suspect

## TABLE 4

### Analyses of Saratoga Waters by Dr. Charles F. Chandler (1860-1875)

| | Geyser Spouting | Hathorn #3 | Congress | Empire | High Rock | Crystal | Vichy | United States |
|---|---|---|---|---|---|---|---|---|
| Cl | 5997.6 | 5338.0 | 4195.6 | 5242.2 | 4097.3 | 3456.1 | 1441.8 | 1533.4 |
| Br | 28.9 | 20.4 | 112.9 | 1.9 | 9.7 | 5.5 | 13.0 | 11.2 |
| I | 3.6 | 2.7 | 2.0 | 8.7 | 1.2 | 0.9 | tr | 0.6 |
| $HCO_3$ | 5374.0 | 4993.2 | 4519.9 | 2189.4 | 2977.6 | 2618.0 | 2896.0 | 2398.1 |
| $SO_4$ | 3.0 | tr | 8.4 | 25.9 | 15.1 | 20.2 | tr | 0.2 |
| $PO_4$ | tr | 0.1 | 0.2 | 0.3 | tr | 0.1 | tr | 0.2 |
| $SiO_2$ | 11.9 | 21.4 | 14.3 | 24.8 | 38.4 | 54.6 | 12.8 | 54.1 |
| Na | 4267.0 | 3435.7 | 2759.1 | 3450.2 | 2774.7 | 2244.2 | 1249.7 | 973.4 |
| K | 221.0 | 85.0 | 78.2 | 59.5 | 92.1 | 90.6 | 125.8 | 76.7 |
| Li | 11.9 | 20.4 | 8.5 | 3.6 | 3.4 | 7.6 | 3.1 | 8.5 |
| Ca | 710.8 | 712.3 | 598.4 | 457.3 | 549.6 | 425.0 | 397.8 | 388.6 |
| Ba | 19.4 | 15.8 | 8.4 | 0.6 | 4.5 | 6.6 | 5.4 | 8.2 |
| Sr | 2.7 | tr | tr | tr | tr | tr | tr | 0.1 |
| Mg | 417.1 | 492.7 | 340.3 | 120.1 | 153.5 | 210.0 | 115.9 | 203.7 |
| Fe | 5.4 | 6.8 | 1.9 | 4.4 | 8.1 | 22.1 | 0.2 | 3.9 |
| Al | tr | 1.2 | tr | 3.8 | 11.1 | 2.8 | 4.1 | 0.8 |
| Total | 16856.0 | 15102.8 | 11915.0 | 11567.2 | 10718.5 | 9132.4 | 6244.5 | 5641.0 |

Source: The Mineral Springs of Saratoga, James F. Kemp, N.Y.S. Museum Bulletin159, 1912

## TABLE 5

### Analyses of Saratoga Waters by J.K. Haywood and B.H. Smith
United States Department of Agriculture
1905

| | Hathorn #3 | Lincoln | Hathorn #1 | Congress | Geyser | Peerless | High Rock | Hyde South |
|---|---|---|---|---|---|---|---|---|
| Cl | 4674.7 | 4068.4 | 3685.5 | 3327.9 | 1025.1 | 1773.1 | 483.3 | 7179.0 |
| Br | 47.1 | 76.0 | 26.9 | 26.8 | 11.8 | 16.8 | 6.7 | 60.0 |
| I | 1.7 | 1.9 | 1.5 | 0.8 | 1.0 | 1.0 | .2 | 2.3 |
| $HCO_3$ | 4147.1 | 4221.0 | 3585.6 | 3573.3 | 4353.2 | 2634.4 | 1141.0 | 6566.0 |
| $SO_4$ | 3.4 | 3.5 | 5.6 | 8.7 | 1.4 | 4.0 | 15.7 | 3.0 |
| $SiO_2$ | 16.2 | 32.7 | 19.6 | 19.8 | 20.8 | 14.8 | 33.4 | 27.6 |
| Na | 2951.8 | 2688.0 | 2430.7 | 2199.3 | 2010.9 | 1298.5 | 348.0 | 4833.0 |
| K | 197.8 | 243.7 | 197.2 | 192.0 | 29.0 | 94.7 | 84.3 | 346.0 |
| Li | 7.4 | 1.8 | 0.5 | 5.4 | 3.6 | 0.4 | 0.9 | 15.5 |
| Ca | 765.0 | 675.8 | 650.7 | 562.1 | 116.4 | 530.4 | 223.9 | 991.0 |
| Ba | 7.5 | 11.7 | 5.5 | 7.1 | 2.6 | 2.1 | 0.7 | 13.1 |
| Sr | --- | ---- | tr | --- | --- | --- | --- | --- |
| Mg | 328.0 | 325.9 | 228.8 | 278.2 | 60.6 | 90.9 | 60.6 | 469.0 |
| FeAl | 6.7 | 13.9 | 9.8 | 14.7 | 8.4 | 5.6 | 12.3 | 21.4 |
| $NO_3$ | tr | tr | --- | --- | tr | --- | --- | --- |
| $NO_2$ | tr | --- | --- | tr | --- | tr | --- | --- |
| Mn | --- | --- | --- | --- | --- | --- | --- | tr |
| $NH_4$ | 12.8 | 7.3 | 10.7 | 10.3 | 11.4 | 5.9 | 0.9 | 14.5 |
| Total | 13170.3 | 12371.6 | 10858.6 | 10232.7 | 7656.2 | 6472.6 | 2347.2 | 20542.6 |

Source: The Mineral Springs of Saratoga. J.F. Kemp, N.Y.S. Museum Bulletin 159, 1912

## TABLE 7

## $\mathrm{Ra}^{226}$ in Saratoga Waters

| Index Number | Location | Result | Sampling Date |
|---|---|---|---|
| 1. | Old Iron | 10.1 ± .81 | Fall, 1978 |
| 2. | Bischoff | 135 ± 5.4 | Fall, 1978 |
| 3. | Hathorn #3 | 430 ± 37 | Spring, 1971 |
| 4. | Polaris | 102 ± 8 | Spring, 1971 |
| 5. | Orenda | 232 ± 18 | Spring, 1971 |
| 6. | Geyser | 25 ± 2 | Spring, 1971 |
| 7. | Lincoln #12 | 32 ± 2.2 | Fall, 1978 |
| 8. | Rosemary | 12.2 ± .85 | Fall, 1978 |
| 9a. | Congress | 32 ± 1.0 | Spring, 1972 |
| 9b. | Congress | 6.0 ± .66 | Fall, 1978 |
| 9c. | Congress duplicate | 10.7 ± .86 | Fall, 1978 |
| 10. | Hathorn #1 | 220 ± 18 | Spring, 1971 |
| 11. | Big Red | 23 ± 3.2 | Fall, 1978 |
| 12. | Peerless | 82 ± 8 | Spring, 1971 |
| 13. | Red | 81 ± 7 | Spring, 1971 |
| 14. | Gurn Spring | 42 ± 1.3 | Fall, 1978 |
| 15. | Quaker Spring | 6.1 ± .43 | Fall, 1978 |
| 16. | Bennet | 1.6 ± .22 | Fall, 1978 |
| 17. | Martin | 13.1 ± 1.2 | Fall, 1978 |
| 18. | Doster | 8.6 ± .69 | Fall, 1978 |
| 19. | McNeil | 19.4 ± 1.2 | Fall, 1978 |
| 20a | Sharon Spring | .25 ± .08 | Fall, 1978 |
| 20b. | Sharon Spring duplicate | .19 ± .17 | Fall, 1978 |

TABLE 7 (cont.)

| Index Number | Location | Result | Sampling Date |
|---|---|---|---|
| 21. | Vita Spring | .5 ± .12 | Fall, 1978 |
| 22. | Davis | .15± .08 | Fall, 1978 |
| 23. | Pitcher | .12± .07 | Fall, 1978 |
| 24. | Congly | 7.6 ± .46 | Fall, 1978 |
| 25. | Auguste Bohl | 3.1 ± .40 | Fall, 1978 |
| 26. | Yezzi | 3.1 ± .29 | Fall, 1978 |
| 27. | Figliomeni | 1.5 ± .26 | Fall, 1978 |
| 28. | Tudor Pines | 1.1 ± .20 | Fall, 1978 |
| 29. | Gorman | 13.2 ± .8 | Fall, 1978 |
| 30. | Pattersonville | 1.3 ± .2 | Fall, 1978 |
| 30a. | Pattersonville duplicated | 2.8 ± .3 | Fall, 1978 |
| 31. | Pompa | 2.3 ± .3 | Fall, 1978 |
| 32. | Y.K. Greene | .14± .11 | Fall, 1978 |
| 33, | Bloodgood | .19 | Fall, 1978 |
| 34. | Saratoga Veterinary Hospital | NA | |
| 35. | Wilson | NA | |
| 36. | Middletown Springs | .08 | Fall, 1978 |
| 37. | Lebanon Springs | .26± .08 | Fall, 1978 |
| 37a. | Lebanon Springs | .28± .13 | Fall, 1978 |
| 38. | Fred George | .4 ± .18 | Fall, 1978 |
| 39. | Celestins | 25 ± 2 | Summer, 1971 |
| 40. | Hopital | NA | |

all values expressed in units of pico curies/liter

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# ANALYTICAL DATA

SPRING 1978 SAMPLING

| | Thermal Waters | | Saratoga Springs Area | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | LEBANON SPRINGS | FRED GEORGE | OLD IRON | BISCHOFF | HATHORN No 3 | POLARIS | ORENDA | GEYSER | LINCOLN No 12 | ROSEMARY | CONGRESS |
| Date and Time of Sampling | 5/26/11 | 4/28/10 | 4/18/10 | 5/04/10 | 4/19/14 | 4/19/10 | 4/09/11 | 4/09/11 | 5/04/12 | 4/18/14 | 5/04/14 |
| Water Temperature °C | 22.2 | 23.0 | 11.0 | 11.2 | 10.0 | 11.5 | 10.0 | 5.0 | 12.0 | 12.0 | 11.2 |
| Ph (Field) | 8.2 | 8.2 | 6.4 | 6.2 | 6.0 | 6.2 | 6.2 | 6.0 | 6.4 | 6.0 | 6.5 |
| Chloride | 8. | 3. | 700 | 6500 | 6300 | 1500 | 4500 | 1200 | 1400 | 280 | 500 |
| Sulfate ($SO_4$) | 2.5 | 9.0 | 5.0 | 22.0 | 4.0 | 7.0 | 23.0 | 11.0 | 12.0 | 20.0 | 40.0 |
| Alkalinity (Methyl Orange) | 127 | 92 | 1190 | 4080 | 4010 | 1900 | 3020 | 2140 | 2020 | 1650 | 984 |
| Sodium | 6.2 | 1.9 | 360 | 4300 | 2600 | 840 | 1900 | 800 | 720 | 280 | 340 |
| Potassium | 1.LT | .1LT | 40 | 330 | 320 | 99 | 240 | 98 | 100 | 72 | 49 |
| Calcium | 34 | 20 | 310 | 770 | 680 | 380 | 510 | 330 | 410 | 240 | 230 |
| Magnesium | 14 | 11 | 78 | 200 | 420 | 120 | 270 | 200 | 90 | 160 | 67 |
| Iron | .05 LT | .05 LT | 12.0 | 0.96 | 3.8 | 1.8 | 2.7 | 9.3 | 8.7 | 7.0 | 3.4 |
| Nitrate and Nitrite | 0.2 | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT |
| Nitrogen, Nitrite | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT |
| Ammonia | 0.007 | 0.005 LT | 3.7 | 21.0 | 18.0 | 5.5 | 12.0 | 6.0 | NA | 3.6 | 2.0 |
| Phosphate | 0.005 LT | 0.005 LT | 0.047 | 0.027 | 0.015 | 0.029 | 0.018 | 0.041 | 0.047 | 0.039 | 0.008 |
| Flouride (Free) | 0.024 | 0.1 LT | 0.72 | 0.1 LT | 0.58 | 0.82 | 0.78 | 0.78 | 0.22 | 0.56 | 0.16 |
| Bromide | 0.34 | 0.26 | 13.0 | 43.0 | 90.0 | 20.0 | 61.0 | 22.0 | 24.0 | 11.0 | 9.8 |
| Iodide | 0.004 | 0.004 | 0.42 | 4.0 | 3.6 | 0.62 | 2.5 | 0.56 | 0.79 | 0.12 | 0.27 |
| Beryllium | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT |
| Boron | 0.20 LT | 0.2 LT | 0.75 | 4.8 | 2.3 | 1.7 | 3.0 | 1.4 | 1.3 | 1.1 | 0.47 |
| Cadmium | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT |
| Chromium | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT |
| Aluminum | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 | 0.06 | 0.05 LT | 0.05 | 0.05 LT | 0.05 | 0.05 LT | 0.05 LT |
| Lead | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 |
| Lithium | 0.05 LT | 0.05 LT | 1.9 | 15.0 | 10.0 | 2.8 | 7.8 | 2.6 | 2.7 | 0.63 | 1.0 |
| Manganese | 0.03 LT | 0.03 LT | 0.30 | 0.03 | 0.14 | 0.15 | 0.14 | 0.17 | 0.19 | 0.14 | 0.13 |
| Silica | 9.1 | 0.100 | 21.0 | 9.5 | 7.1 | 13.0 | 7.3 | 27.0 | 33.0 | 38.0 | 9.1 |
| Strontium | 0.34 | 0.05 LT | 10.0 | 33.0 | 21.0 | 6.0 | 16.0 | 6.9 | 6.7 | 4.2 | 2.0 |
| Barium | 0.5 LT | 0.5 LT | 3.1 | 36.0 | 8.6 | 2.1 | 8.6 | 1.8 | 3.4 | 1.1 | 0.6 |
| Tin | 1.0 LT | 1.0 LT | 1.0 LT | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 LT | 1.0 LT | 1.0 LT |
| Zinc | 0.05 LT | 0.05 | 0.05 | 0.05 LT | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 LT | 0.05 | 0.05 LT |
| Yttrium | 0.01 LT | 0.01 | 0.02 | 0.06 | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 | 0.01 LT | 0.01 LT |
| Zirconium | 0.01 LT | 0.01 LT | 0.01 LT | 0.29 | 0.32 | 0.06 | 0.23 | 0.04 | 0.04 | 0.01 | 0.01 LT |
| Total Dissolved Solids | 167 | 120 | 2560 | 14820 | 15190 | 4290 | 10580 | 4280 | 4210 | 3220 | 1820 |

| | Saratoga Springs Area | | | | | North Central Carbonated Waters | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | HATHORN No 1 | BIG RED | PEERLESS | RED | GURN SPRING | QUAKER | BENNET | MARTIN | DOSTER | MC NEIL | MC NEIL (duplicated) | MIDDLETOWN SPRINGS |
| Date and Time of Sampling | 4/19/13 | 4/09/13 | 4/19/13 | 4/18/11 | 5/04/14 | 4/27/12 | 4/25/12 | 4/20/13 | 4/25/11 | 4/27/15 | 4/27/15 | 4/25/18 |
| Water Temperature °C | 11.9 | 11.0 | 11.0 | 12.0 | 8.5 | 8.2 | 12.0 | 10.5 | 13.5 | 11.2 | 11.2 | 4.5 |
| Ph (Field) | 6.2 | 6.0 | 6.0 | 6.3 | 6.3 | 6.5 | 6.3 | 6.3 | 7.0 | 6.4 | 6.4 | 7.3 |
| Chloride | 1800 | 2300 | 1000 | 550 | 750 | 750 | 750 | 160 | 680 | 250 | 246 | 18 |
| Sulfate ($SO_4$) | 11.0 | 28.0 | 11.0 | 6.0 | 9.0 | 10.0 | 36.0 | 21.0 | 25.0 | 6.0 | 7.0 | 12.0 |
| Alkalinity (Methyl Orange) | 1990 | 2460 | 1825 | 1150 | 1840 | 1810 | 2260 | 2130 | 2160 | 7300 | 7000 | 615.0 SU |
| Sodium | 930 | 1400 | 730 | 310 | 620 | 920 | 840 | 630 | 970 | 190 | 160 | 11 |
| Potassium | 94 | 91 | 93 | 36 | 70 | 18 | 65 | 18. | 21 | 29 | 29 | 4. |
| Calcium | 410 | 340 | 420 | 260 | 320 | 82 | 250 | 100 | 97 | 180 | 160 | 24 |
| Magnesium | 100 | 260 | 100 | 76 | 100 | 21 | 73 | 58 | 26 | 35 | 36 | 4.2 |
| Iron | 21 | 11.0 | 1.9 | 6.7 | 16.0 | 2.1 | 7.7 | 1.8 | .48 | .88 | .93 | .05 LT |
| Nitrate and Nitrite | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 3.3 |
| Nitrogen, Nitrite | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT |
| Ammonia | 7.0 | 11.0 | 4.6 | 4.0 | 5.0 | 2.3 | 11.0 | 7.0 | 12.0 | 0.6 | 0.6 | .015 |
| Phosphate | 0.015 | 0.050 | 0.036 | 0.030 | 0.11 | 0.007 | 0.005 | 0.012 | 0.006 | 0.008 | 0.005 | 0.008 |
| Flouride (Free) | 0.70 | 0.19 | 0.68 | 0.76 | 0.27 | 0.53 | 0.12 | 0.42 | 0.52 | 0.1 LT | 0.14 | 0.1 LT |
| Bromide | 2.7 | 3.5 | 2.0 | 11.0 | 18.0 | 16.0 | 22.0 | 2.1 | 3.4 | 6.4 | 3.9 | 0.24 |
| Iodide | 0.80 | 1.0 | 0.38 | 0.28 | 0.28 | 0.29 | 0.27 | 0.12 | 0.47 | 0.75 | 0.074 | 0.005 LT |
| Beryllium | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT |
| Boron | 1.6 | 2.0 | 1.1 | 0.79 | 1.0 | 1.6 | 2.7 | 2.0 | 3.5 | 0.67 | 0.74 | 0.20 LT |
| Cadmium | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT |
| Chromium | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT |
| Aluminum | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT | .33 | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT |
| Lead | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 | 0.01 | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT |
| Lithium | 3.8 | 4.9 | 2.4 | 0.83 | 2.0 | 3.7 | 2.6 | 1.1 | 5.3 | 0.44 | 0.47 | 0.05 LT |
| Manganese | 0.12 | 0.14 | 0.25 | 0.20 | 0.32 | 0.72 | 0.39 | 0.18 | 0.10 | 0.46 | 0.46 | 0.03 LT |
| Silica | 7.9 | 46.0 | 9.6 | 37.0 | 37.0 | 9.0 | 11.0 | 10.0 | 7.7 | 15.0 | 15.0 | 3.4 |
| Strontium | 6.7 | 18.0 | 4.2 | 5.2 | 2.8 | 13.0 | 14.0 | 7.9 | 13.0 | 1.7 | 2.2 | 0.1 |
| Barium | 3.2 | 5.0 | 1.1 | 1.1 | 3.5 | 1.2 | 1.2 | 1.5 | 4.7 | 1.1 | 0.7 | 0.05 |
| Tin | 1.0 | 1.0 | 1.0 LT | 1.0 LT | 1.0 LT | 1.0 | 1.0 LT | 1.0 LT | 1.0 LT | 1.0 | 1.0 LT | 1.0 LT |
| Zinc | 0.05 | 0.05 LT | 0.05 | 0.05 LT | 0.05 LT | 0.30 | 0.09 | 0.05 LT | 0.09 | 0.05 | 0.05 | 0.05 LT |
| Yttrium | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.03 | 0.04 | 0.01 LT | 0.01 LT | 0.03 | 0.02 | 0.02 |
| Zirconium | 0.10 | 0.04 | 0.08 | 0.01 LT | 0.01 LT | 0.05 | 0.23 | 0.12 | 0.10 | 0.01 LT | 0.01 LT | 0.01 LT |
| Total Dissolved Solids | 5250 | 7710 | 3820 | 2170 | 3080 | 3330 | 3790 | 2590 | 3510 | 1160 | 1180 | 648 |

| | Sulfate Waters | | | Southern Brine Waters | | | | | | Surface Water Control Wells | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | VITA SPRING | DAVIS | PITCHER | PATTERSONVILLE | CONSLY | AUGUST BOHL | YEZZI | FIGLIOMENI | TUDOR PINES | POMPA | Y.K. BRESKE | BLOODGOOD | SARATOGA VETERINARY HOSPITAL |
| Date and Time of Sampling | 4/20/11 | 4/25/15 | 5/02/13 | 5/02/15 | 4/27/15 | 4/28/11 | 5/02/11 | 5/02/13 | 5/25/10 | 5/23/10 | 5/23/10 | 5/23/10 | 5/25/10 |
| Water Temperature °C | 9.0 | 10.5 | 9.0 | 12.5 | 11.8 | 14.0 | 15.5 | 9.2 | 11.1 | 11.8 | 12.8 | 11.2 | 12.3 |
| Ph (Field) | 6.5 | 7.0 | 6.8 | 7.3 | 6.7 | 7.4 | 7.2 SU | 7.3 | 8.2 | 7.5 | 8.0 | 9.0 | 8.5 |
| Chloride | 220 | 24 | 230 | 600 | 2100 | 1800 | 1700 | 170 | 800 | 6. | 4. | 3 LT | 3 LT |
| Sulfate ($SO_4$) | 1300 | 3000 | 2100 | 48.0 | 2.0 | 2 LT | 2 LT | 10.0 | 20 | 80.0 | 8.0 | 3.0 | 3.0 |
| Alkalinity (Methyl Orange) | 1130.0 | 6200 | 3650 | 2650 | 210.0 | 3440 | 276.0 | 1493 | 283.0 | 3000 | 255.0 | 109.0 | 219.0 |
| Sodium | 320 | 170 | 88 | 240 | 1000 | 1000 | 1100 | 750 | 590 | 5.0 | 95 | 44 | 83 |
| Potassium | 52 | 8.0 | 12 | 4. | 28 | 11 | 11 | 9. | 7. | 3 | 7. | 1 LT | 2. |
| Calcium | 390 | 280 | 340 | 150 | 140 | 27 | 18 | 74 | 72 | 180 | 76 | 2.1 | 6.3 |
| Magnesium | 130 | 530 | 390 | 35 | 34 | 15 | 4.5 | 1.7 | 2.0 | 29 | 53 | 4 | 2.3 |
| Iron | 1.4 | 30.0 | .10 | 51 | .17 | 39 | .30 | .13 | 3.4 | 33 | 1.3 | .05 | .09 |
| Nitrate and Nitrite | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT | 0.2 LT |
| Nitrogen, Nitrite | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT |
| Ammonia | 5.0 | 5.5 | 0.95 | 0.26 | 7.5 | 2.3 | 38 | 2.3 | 45 | 0.16 | 2.4 | .28 | 1.5 |
| Phosphate | 0.005 LT | 0.005L | 0.005 LT | 0.005 | 0.005 LT | 0.065 | 0.008 | 0.009 | 0.008 | 0.005 LT | 0.018 | 0.063 | 0.015 |
| Flouride (Free) | 0.18 | 0.1 LT | 0.1 LT | 0.11 | 0.1 LT | .82 | 2.10 | 1.5 | 084 | 0.26 | 1.60 | 0.76 | 1.8 |
| Bromide | 12.0 | 6.0 | 3.5 | 1.4 | 2.8 | 22.0 | 35.0 | 12.0 | 13.0 | 0.88 | 0.46 | 0.27 | 0.10 LT |
| Iodide | 0.044 | 0.007 | 0.010 | 0.014 | 0.43 | 2.5 | 5.3 | 1.9 | 1.0 | 0.010 | 0.34 | 0.007 | 0.093 |
| Beryllium | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT | 0.02 LT |
| Boron | 1.4 | 0.37 | 0.3 | 0.2 | 0.89 | 0.7 | 0.9 | 1.0 | 0.93 | 0.20 | 0.81 | 0.20 | 0.64 |
| Cadmium | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT | 0.002 LT |
| Chromium | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT |
| Aluminum | 0.05 LT | 0.05 | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT | 0.05 LT | 0.94 | 0.05 LT | 0.05 LT |
| Lead | 0.01 LT | 0.01 | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT |
| Lithium | 0.84 | 0.19 | 0.18 | 0.05 | 2.0 | 4.2 | 4.4 | 2.8 | 2.0 | 0.05 | 0.18 | 0.05 LT | 0.25 |
| Manganese | 1.8 | 0.35 | 0.17 | 0.15 | 0.59 | 0.03 LT | 0.03 | 0.05 | 0.03 | 0.04 | 0.03 LT | 0.03 LT | 0.03 LT |
| Silica | 14.0 | 12.0 | 9.0 | 6.5 | 6.5 | 10.0 | 11.0 | 6.2 | 5.4 | 7.2 | 6.9 | 6.2 | 6.4 |
| Strontium | 9.3 | 7.0 | 6.0 | 1.0 | 2.8 | 9.2 | 6.7 | 2.5 | 1.4 | 1.4 | 1.2 | 0.1 | 1.0 |
| Barium | 0.5 | 0.5 | 0.5 | 0.5 | 2.0 | 0.5 | 0.9 | 0.5 | 0.5 LT | 0.5 LT | 0.5 LT | 0.5 LT | 0.5 |
| Tin | 1.0 LT | 1.0 LT | 1.0 LT | 1.0 LT | 1.0 | 1.0 LT | 1.0 | 1.0 LT | 1.0 LT | 1.0 LT | 1.0 LT | 1.0 LT | 1.0 LT |
| Zinc | 0.05 | 3.0 | 0.05 | 0.05 LT | 0.05 | 0.34 | 0.05 LT | 0.05 LT | 0.05 LT | 0.16 | 2.7 | 0.05 LT | 0.05 LT |
| Yttrium | 0.01 LT | 0.01 | 0.01 | 0.05 | 0.02 | 0.01 LT | 0.01 LT | 0.03 | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT |
| Zirconium | 0.04 | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT | 0.01 LT |
| Total Dissolved Solids | 3900 | 5490 | 4120 | 1470 | 4430 | 3190 | 3310 | 1970 | 1870 | 274 | 301 | 109 | 261 |

NOTE:
The units of all values are expressed in mg/l
except Nitrogen, Nitrite which is μmg/l.

LT = Less Than
NA = Not Available
SU = Suspect

# ANALYTICAL DATA

## FALL 1978 SAMPLING

| | Thermal Waters | | Saratoga Springs Area | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | LEBANON SPRINGS | FRED GEORGE | OLD IRON | BISCHOFF | HATHORN No. 3 | POLARIS | ORENDA | GEYSER | LINCOLN No. 12 | ROSEMARY | CONGRESS | CONGRESS (duplicated) | HATHORN No. 1 | BIG RED | PEERLESS | RED | GURN |
| Date and Time of Sampling | 10/25/06 | 10/25/10 | 10/10/02 | 10/16/10 | 10/12/12 | 10/13/10 | 10/13/09 | 10/13/12 | 10/18/10 | 10/5/12 | 10/12/12 | 10/12/12 | 10/10/13 | 10/10/11 | 10/10/10 | 10/10/11 | 10/5/02 |
| Water Temperature °C | 22.5 | 22.1 | 10.5 | 9.9 | 10.2 | 13.5 | 10.2 | 14.5 | 10.8 | 11.9 | 12.1 | 12.1 | 11.0 | 10.0 | 10.5 | 13.6 | 10.6 |
| pH (Field) | 8.1 | 8.2 | 6.2 | 6.4 | 6.0 | 5.5 | 6.1 | 5.9 | 6.5 | 6.0 | 6.3 | 6.3 | 6.0 | 5.9 | 5.8 | 6.1 | 6.4 |
| Chloride | 7 | 3 | 750 | 6900 | 6900 | 1400 | 4100 | 1300 | 1200 | 560 | 450 | 390 | 1600 | 2500 | 980 | 650 | 750 |
| Sulfate ($SO_4$) | 28 | 9 | INTERF | INTERF | INTERF | INTERF | INTERF | INTERF | INTERF | 19 | INTERF | 54 | INTERF | 9 | 4 | 4 | 5 |
| Alkalinity Electron pH 4.5 | 126 | 92 | 1280 | 4340 | 4270 | 1050SU | 3280 | 2100 | 2090 | 1960 | 960 | 970 | 2240 | 2660 | 1960 | 1340 | 1672 |
| Sodium | 7.8 | 2.0 | 520 | 4400 | 3100 | 770 | 2300 | 640 | 740 | 590 | 340 | 350 | 950 | 1100 | 740 | 470 | 600 |
| Potassium | 1.6 | 1.0 | 34 | 300 | 320 | 100 | 230 | 110 | 110 | 87 | 39 | 39 | 130 | 100 | 90 | 36 | 72 |
| Calcium | 34 | 20 | 320 | 950 | 950 | 400 | 750 | 320 | 340 | 270 | 200 | 140 | 410 | 330 | 420 | 290 | 330 |
| Magnesium | 15 | 12 | 79 | 470 | 410 | 160 | 300 | 150 | 190 | 190 | 64 | 63 | 160 | 280 | 120 | 90 | 110 |
| Iron | .05 | .05 LT | 10 | .07 | .08 | 1.6 | 2.3 | 2.7 | 6.2 | 6.2 | 2.3 | 2.4 | 1.6 | 81 | 1.7 | 6.0 | 29 |
| Nitrate and Nitrite | 2 | 2 LT | 2 LT | .2 | .2 LT | 2 LT | 2 LT | 2 LT | 2 LT | 2 LT | .2 LT | .2 LT | .2 LT | .2 LT | .2 LT | .2 LT | 2 LT |
| Nitrite | 5 LT | 5 LT | 12 | 5 | 5 | 5 | 15 | 8 | 7 | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 7 | 5 LT | 5 LT |
| Ammonia | .007 | .007 | 3.2 | 3.2 | 16 | 4.3 | 12 | 4.3 | 4.5 | 4.1 | .78 | 1.5 | 6.5 | 8.0 | 3.5 | 3.6 | 3.0 |
| Nitrogen Total | 3.8 | 2 LT | 3.6 | 26 | 21 | 6.1 | LA | 5.8 | 6.1 | 43 | 2.1 | 2.0 | 6.4 | 10 | 4.9 | 3.8 | LA |
| Carbon Organic (TOC) | 3.8 | 1.8 | 1.0 | 1.0 | 1.8 | 9.0 | 28 | 1.0 | 1.0 LT | 34 | 10 | 1.0 | 6.0 | 88 | 8.0 | 1.0 LT | 22 |
| Phosphate | .006 | .010 | .052 | .018 | .014 | .019 | .035 | .014 | .036 | .10 | .035 | .014 | .027 | .056 | .032 | .034 | .15 |
| Fluoride (Free) | .25 | .1 LT | .45 | .1 LT | .34 | .74 | .58 | .52 | .60 | .32 | .50 | .50 | .59 | .23 | .54 | .58 | .43 |
| Bromide | 95 | 44 | 18 | 130 | 110 | 24 | 74 | 26 | 34 | 19 | 10 | 6.0 | 29 | 41 | 22 | 15 | 15 |
| Iodide | .006 | .004 | .49 | 4.2 | 4.3 | .54 | 2.6 | .43 | .87 | .45 | .19 | .16 | .78 | .62 | .45 | .42 | .15 |
| Boron | 20 LT | .20 LT | .86 | 3.2 | 3.5 | 1.1 | 1.6 | .87 | 1.6 | 1.2 | .79 | .65 | 1.4 | 1.5 | .96 | .58 | 1.0 |
| Aluminum | .05 LT | .05 LT | .05 LT | .06 | .05 | .05 | .26 | .05 LT | .05 | .09 | .05 LT | .05 LT | .22 | .05 LT | .16 | .08 | .32 |
| Lithium | .01 LT | .01 LT | 2.0 | 14 | 12 | 2.8 | 10 | 2.8 | 2.7 | 1.9 | .80 | 7.9 | 3.8 | 4.8 | 2.6 | 1.2 | 2.0 |
| Silica | 15 | 16 | 45 | 16 | 12 | 21 | 13 | 45 | 45 | 40 | 15 | 16 | 13 | 70 | 16 | 46 | 55 |
| Strontium | .3 | .05 LT | 7.8 | 25 | 17 | 4.7 | 14 | 5.2 | 5.1 | 4.0 | 1.6 | 1.6 | 5.0 | 11 | 3.3 | 4.8 | 2.5 |
| Barium | .5 LT | .5 LT | 6.7 | 34 | 21 | 5.1 | 17 | 5.1 | 5.0 | 3.7 | .7 | .5 | 5.3 | 8.7 | 3.8 | 3.4 | 7.4 |
| Tin | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT |
| Yttrium | .003 | .002 LT | .003 | .002 LT | .002 LT | .002 LT | .010 | .002 LT | .007 | .002 LT | .002 LT | .004 | .006 | .002 LT | .008 | .004 | .007 |
| Zirconium | .003 LT | .003 LT | .010 | .123 | .025 | .100 | .237 | .053 | .048 | .045 | .015 | .009 | .120 | .016 | .090 | .016 | .003 LT |
| Total Dissolved Solids | 179 | 117 | 2610 | 17500 | 14610 | 4420 | 10780 | 4320 | 4240 | 3000 | 1710 | 1740 | 5080 | 6460 | 3820 | 2430 | 3230 |

| | North Central Carbonated Waters | | | | | Sulfate Waters | | | | | Southern Brine Waters | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | QUAKER | BENNET | MARTIN | DOSTER | MC NEIL | VITA SPRING | DAVIS | PITCHER | SHARON SPRINGS | SHARON SPRINGS (duplicated) | CONELY | AUGUST SOHL | YEZZI | PHILOMENA | TIOGA PINES | GORMAN | PATTERSON-VILLE (duplicated) | PATTERSON-VILLE |
| Date and Time of Sampling | 10/11/12 | 10/18/11 | 10/12/10 | 10/12/11 | 10/11/10 | 10/17/12 | 10/16/12 | 10/09/12 | 10/19/15 | 10/18/15 | 10/11/02 | 10/20/16 | 10/08/20 | 10/08/03 | 10/20/12 | 10/20/10 | 10/19/10 | 10/19/10 |
| Water Temperature °C | 11.6 | 12.5 | 11.2 | 15.8 | 11.8 | 9.9 | 10.2 | 12.5 | 8.9 | 8.9 | 12.5 | 13.8 | 14.2 | 13.1 | 10.8 | 10.6 | 12.5 | 12.5 |
| pH (Field) | 6.2 | 6.4 | 6.7 | 5.8 SU | 6.8 | 6.7 | 7.4 | 7.2 | 7.8 | 7.8 | 7.4 | 7.7 | 8.4 | 7.7 | 8.5 | 7.2 | 7.8 | 7.8 |
| Chloride | 700 | 450 | 190 | 600 | 260 | 230 | 16 | 230 | 51 | 43 | 2100 | 1000 | 1700 | 170 | 750 | 2880 | 650 | 530 |
| Sulfate ($SO_4$) | INTERF | 40 | INTERF | INTERF | INTERF | INTERF | INTERF | 2400 | 1800 | 1800 | INTERF | 2 LT | 2 | 9 | 2 LT | 2 | 60 | 54 |
| Alkalinity Electron pH 4.5 | 1550 | 1930 | 2340 | 2250 | 810 | 1220 | 640 | 380 | 290 | 260 | 220 | 339 | 276 | 1516 | 284 | 194 | 330 | 330 |
| Sodium | 880 | 500 | 570 | 910 | 240 | 510 | 170 | 88 | 15 | 12 | 950 | 530 | 670 | 640 | 500 | 1800 | 290 | 300 |
| Potassium | 12 | 47 | 15 | 18 | 29 | 46 | 73 | 11 | 1.6 | 2.1 | 23 | 6.2 | 9.7 | 7.5 | 6.6 | 20 | 3.8 | 3.9 |
| Calcium | 56 | 200 | 110 | 100 | 170 | 350 | 340 | 130 | 400 | 400 | 140 | 20 | 16 | 6.9 | 6.9 | 75 | 140 | 200 |
| Magnesium | 18 | 65 | 69 | 28 | 41 | 130 | 560 | 450 | 73 | 90 | 55 | 10 | 5.5 | 1.7 | 2.2 | 19 | 45 | 47 |
| Iron | .47 | 1.9 | 1.5 | 44 | 10 | 1.7 | .05 LT | .21 | .05 | .05 LT | 8 | 27 | .22 | .22 | 1.7 | .50 | .31 | .37 |
| Nitrate and Nitrite | .2 | 2 LT | 2 LT | 2 LT | 2 LT | .2 LT | 2 LT | .2 | 2 LT | .2 | 2 | 2 LT | 2 LT | .2 | .2 LT | .2 LT | .2 LT | .2 LT |
| Nitrite | 5 LT | 5 LT | 5 | 5 LT | 5 LT | 5 LT | 5 | 5 LT | 5 LT | 5 LT | 84 | 5 | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT |
| Ammonia | 3.3 | 8.0 | 6.0 | 9.5 | .59 | 5.5 | 3.4 | 1.1 | .23 | 25 | 75 | 80 | 3.5 | 2.3 | 3.4 | 13 | .29 | 24 |
| Nitrogen Total | 3.5 | 10 | 7.2 | LA | 1.3 | 5.9 | 4 | 1.0 | .5 | LA | LA | 64 | 5.3 | 3.0 | 5.3 | 17 | LA | .5 |
| Carbon Organic (TOC) | 3.4 | 1.0 LT | 20 | 1.4 | 1.0 | 2.4 | 6 | 1.0 LT | 1.0 LT | 1.0 LT | 1.0 | 1.0 LT | 4.2 | 3.8 | 2.4 | 1.0 LT | 1.0 LT | 1.0 LT |
| Phosphate | .027 | .031 | .022 | .014 | .008 | .008 | .043 | .002 LT | .005 LT | .005 LT | .002 | .041 | .020 | .017 | .005 | .007 | .005 | .007 |
| Fluoride (Free) | .34 | .29 | .20 | .58 | .20 | .19 | .11 | .14 | 1.18 | 1.15 | .11 | .1 LT | 2.3 | 1.6 | 1 LT | .19 | .18 | .20 |
| Bromide | 13 | 18 | 25 | 27 | 72 | 8.3 | 5.5 | 1.3 | 71 | 1.3 | 29 | 14 | 35 | 10 | 20 | 130 | 3.3 | 3.3 |
| Iodide | .37 | .16 | .17 | .60 | .094 | .040 | .005 LT | .011 | .009 | .008 | .27 | 1.3 | 4.7 | 1.1 | .89 | 3.5 | .028 | .027 |
| Boron | 1.1 | 2.0 | 2.0 | 2.8 | .68 | 1.2 | .28 | .37 | .20 | .26 | .40 | .57 | .69 | 1.0 | .96 | 1.0 | .29 | .50 |
| Aluminum | .06 | .16 | .05 LT | .05 LT | .05 LT | .22 | .05 LT | .05 LT | .05 LT | .05 LT | .06 | .05 LT | .05 | .22 | .05 | .05 LT | .05 LT | .05 LT |
| Lithium | 3.0 | 1.9 | 1.1 | 6.9 | .52 | .83 | .17 | .18 | .02 | .03 | 2.0 | 2.4 | 4.5 | 2.6 | 2.0 | 8.7 | .06 | .06 |
| Silica | 15 | 17 | 16 | 13 | 22 | 22 | 18 | 15 | 16 | 17 | 10 | 17 | 11 | 12 | 10 | 10 | 11 | 11 |
| Strontium | 8.8 | 8.6 | 7.7 | 11 | 2.1 | 12 | 11 | 8.6 | 11 | 9.3 | 21 | 3.6 | 5.4 | 2.0 | 1.6 | 34 | 9 | 1.0 |
| Barium | 2.6 | 2.8 | 7.9 | 16 | 3.0 | .5 LT | .5 LT | .5 LT | .5 | .5 LT | 9.1 | 2.8 | 2.4 | 9 | 5 | 12 | .5 LT | .7 |
| Tin | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | INTERF | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT |
| Yttrium | .004 | .005 | .002 LT | .004 | .007 | .005 | .002 LT | .012 | .002 LT | .003 | .003 | .002 LT | .004 | .005 | .006 | .002 LT | .002 LT | .003 |
| Zirconium | .066 | .228 | .210 | .170 | .009 | .050 | .003 LT | .003 LT | .003 LT | .003 LT | .003 LT | .003 LT | .003 LT | .025 | .003 LT | .003 LT | .003 LT | .003 LT |
| Total Dissolved Solids | 2650 | 2730 | 2600 | 3230 | 1270 | 3720 | 5460 | 4180 | 2400 | 2520 | 4300 | 2030 | 3335 | 2070 | 1910 | 6550 | 1420 | 1480 |

| | Surface Water Control Wells | | | | | | Vichy France | |
|---|---|---|---|---|---|---|---|---|
| | POMPA | T.K. GREENE | BLOODWOOD | SARATOGA VETERINARY HOSPITAL | WILSON | MIDDLETOWN SPRINGS | CELESTINS | HÔPITAL |
| Date and Time of Sampling | 10/6/10 | 10/18/13 | 10/06/23 | 10/06/11 | 10/18/17 | 10/26/09 | 07/14/10 | 07/14/09 |
| Water Temperature °C | 10.8 | 11.3 | 15.5 | 11.5 | 13.1 | 10.7 | 19.3 | 34.4 |
| pH (Field) | 7.5 | 8.6 | 9.2 | 8.5 | 7.3 | 7.6 | 6.7 | 6.8 |
| Chloride | 17 | 5 | 3 LT | 3 | 20 | 5 | 240 | 350 |
| Sulfate ($SO_4$) | 110 | 5 | 2 | 3 | 160 | 15 | 170 | 220 |
| Alkalinity Electron pH 4.5 | 296 | 370 | 116 | 216 | 270 | 59 | 3385 | 3690 |
| Sodium | 3.1 | 98 | 36 | 70 | 43 | 3.9 | 700 | 720 |
| Potassium | 3.8 | 2.4 | .8 | 2.8 | 5.1 | 2.3 | 84 | 35 |
| Calcium | 130 | 4.7 | 2.1 | 10 | 57 | 24 | LA | LA |
| Magnesium | 41 | 4.1 | .44 | 4.7 | 32 | 3.3 | 9.1 | 11 |
| Iron | .16 | .12 | .05 | .12 | .31 | .05 | .05 LT | .14 |
| Nitrate and Nitrite | .2 LT | .2 LT | 2 LT | 2 LT | .2 LT | 1.5 | .4 | .2 LT |
| Nitrite | 5 LT | 5 LT | 5 LT | 5 LT | 5 LT | 5 | 5 | 12 |
| Ammonia | 20 | 2.4 | .30 | 1.7 | 1.0 | .005 | .005 | .17 |
| Nitrogen Total | 2 LT | 2.6 | .6 | 19 | 2.0 | .2 | .1 | .6 |
| Carbon Organic (TOC) | 1.2 | 1.0 LT | 1.0 | 2.8 | 1.8 | 1.0 | 10 | 10 |
| Phosphate | .002 | .014 | .059 | .009 | .005 LT | .2 | .095 | .18 |
| Fluoride (Free) | 26 | 1.60 | 78 | 1.7 | .23 | .1 | 4.7 | 6.4 |
| Bromide | 1.3 | 6.3 | .56 | 1.5 | 4.4 | 68 | 6.6 | 13 |
| Iodide | .010 | .45 | .006 | .098 | .060 | .003 | .007 | .049 |
| Boron | .20 LT | .84 | 2 LT | .50 | .39 | .20 | 1.3 | 1.8 |
| Aluminum | .05 LT | .05 | .05 LT | .05 LT | .05 LT | .05 | .5 LT | .05 LT |
| Lithium | .01 | .25 | .02 | .19 | .10 | .01 | 3.6 | 5.0 |
| Silica | 12 | 11 | 11 | 11 | 15 | 5 | 37 | 44 |
| Strontium | 1.3 | .9 | .1 | 1.3 | 4.6 | .05 | 9 | 1.6 |
| Barium | .5 LT | .5 | .5 | .5 | .5 LT | .5 | 0.5 LT | 0.5 LT |
| Tin | .05 LT | .05 LT | .05 LT | .05 LT | .05 LT | .05 | 1.0 LT | 1.0 LT |
| Yttrium | .002 LT | .002 LT | .005 | .004 | .002 LT | .002 | NA | NA |
| Zirconium | .004 | .017 | .003 | .010 | .003 LT | .003 | NA | NA |
| Total Dissolved Solids | 436 | 290 | 140 | 230 | 454 | 102 | 3411 | 4566 |

NOTE

The units of all values are expressed in mg/l except Nitrogen, Nitrite which is μ mg/l

SU - Suspect
LT - Less Than
LA - Lab Accident
NA - Not Available
INTERF - Interference